LIGHT ELEMENT QUANTIFICATION BY TEM-EDS AND APPLICATION TO ORGANICS MAPPING IN ULTRA CARBONACEOUS ANTARCTIC MICROMETEORITES (UCAMMs).

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Introduction: The collection efficiency of light elements (C, N, O) by EDX spectroscopy in transmission electron microscopes (TEM) has made tremendous progresses recently thanks to the new generation of windowless silicon drift detectors.

Quantifying these elements was so far almost impossible because of low signal to noise ratio and poor reproducibility of the measurements. The other limitation is the strong absorption of these low energy X-rays within the samples, which has to be corrected and requires a good knowledge of the thickness and density of the sample. Here, we carefully determined the calibration factor (k-factors) of our detectors, we developed new ways of estimating the mass thickness (thickness*density) and quantified the uncertainties related to the absorption correction procedure. This development allows us to map and quantify -pixel by pixel- the composition of light elements-bearing materials, such as organics, water bearing phases, etc..

UCAMMs are ideal candidates [1, 2] to illustrate how such quantification can be precious to shed light on the nature and origin of organics at the nanometer scale.

Samples and Methods: We used a Titan Themis TEM operating at 300 kV and equipped with a super-X four quadrant detectors to acquire the EDX data. k-factors were obtained using wedge shaped samples of variable thickness (0 to 1 micrometer), prepared either by FIB or ultramicrotomy techniques.

We acquired an EDX spectrum-image of an UCAMM (DC06-07-18, hereafter DC18) with low beam current (200 pA) and short dwell time (2 μs). A high number of frames allows to reach a high signal to noise ratio. The dataset is then inspected frame by frame to monitor potential beam damage. None was observed in the present case.

Results: We acquired EDX spectrum-image of reference samples across regions of variable thicknesses. k-factors are obtained by extrapolating the elemental ratio (C/Si for instance for a silicon carbide standard sample) to an equivalent thickness of zero, i.e. where no absorption occurs. We used generally the Fe, Ca and Si total intensity as thickness proxy, because these elements are weakly absorbed. The extrapolation method of [3] was used to retrieve the k-factor. For oxygen, we used various silicates and obtained a k-factor mean value of 0.98 ($\sigma 1 = 0.02$). For nitrogen, we used a silicon nitride Si_3N_4 and obtained a k-factor value of 1.24.
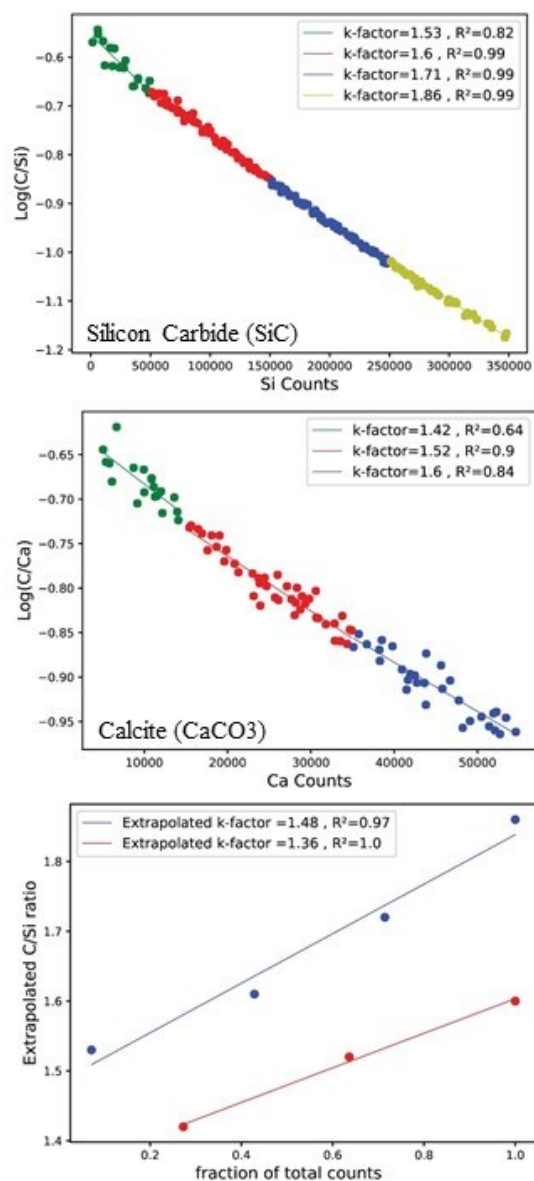

Fig.1: C/Si and C/Ca vs. Si and Ca intensity used as thickness proxy. Bottom, extrapolated k-factor values for different thickness ranges, expressed as the fraction of total counts of the peak used as thickness proxy.

For carbon, we used silicon carbide and calcite samples. The situation is more complex. The curve is not linear as expected and the extrapolated k-factor value seems to depend on the thickness range that is considered (Fig. 1). This might be due to over simplification related to the extrapolation method, but in the absence of alternative theories, we overcame this issue empirically. We first extracted k-factors values obtained for different thickness ranges and then extrapolated these values (Fig. 1c). The average C/Si k-factor, using silicon carbide and calcite, is found equal to 1.42 (±0.06).

In order to estimate the uncertainties of the quantification related to the absorption correction calculation, we ran an 'inverse' quantification of the mapped samples using the HyperSpy software [4]. We used various "synthetic" thickness maps and observed how the C/Si ratio varies. For instance, for a density of 1.5 (organics) and a thickness of 100 nm, a change of 15% on the mass thickness leads to a relative error on the C/Si lower than 5%.

Application to UCAMM: We analyzed a sub-area of the FIB section (Fig. 2) with a pixel size of 8 nm. It consists of an aggregate of GEMS-like particles surrounded by homogeneous smooth organic. It reveals a nitrogen a sodium-rich organic material and a zonation of these elements which are enriched towards the silicates. (N/C bulk atomic ratio = 0.33, up to 0.45 locally). Being able to evidence this kind of zonation will hopefully help us understanding the origin of these organic materials, possibly formed by irradiation of N-rich ices [5].

Conclusion: We showed that it is possible to precisely quantify light elements such as C, N and O using EDX spectroscopy. It has the advantage over EELS of allowing the measurements of all elements simultaneously. It opens new avenues for studying organic materials at the nanometer scale in various samples such as meteorites, soils, Archean rocks, etc.
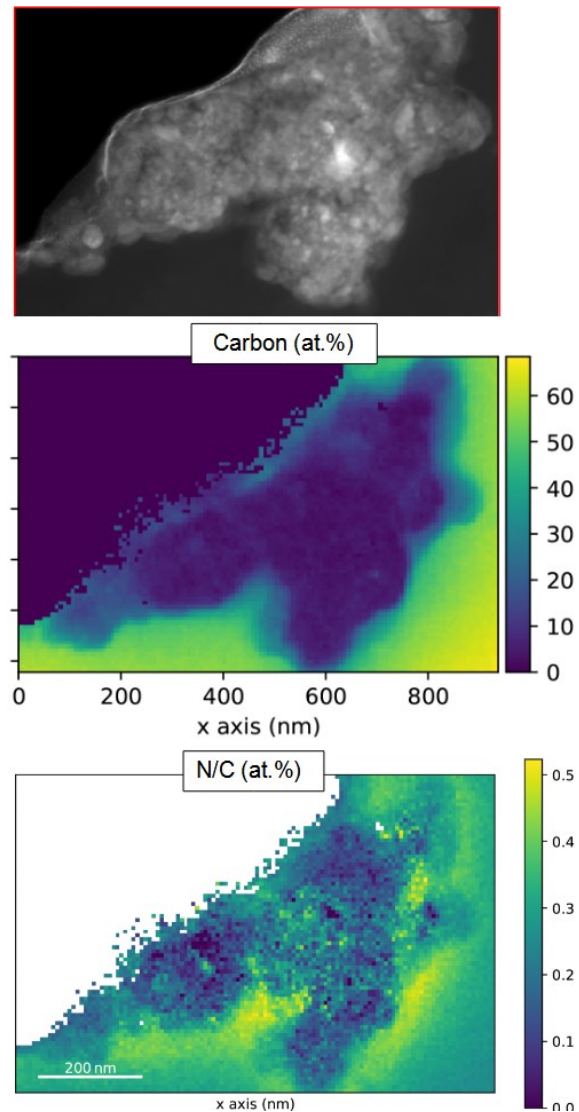

Fig.2: Top. High angle annular dark field image of the DC 18 UCAMM. Center. Quantified carbon map showing a carbon rich material surrounding a carbon poor central silicate region. Bottom. N/C (at.) map showing a very nitrogen rich organic material, with increasing N/C ratio towards the silicate area. The organics are also rich in Sodium and a similar zonation is observed.

References:
[1] Duprat J., et al. (2010) *Science* 328, 742-745. [2] Yabuta H., et al. (2017) *Geochim. Cosmochim. Acta* 214, 172-190. [3] Horita, Z., Sano, T., & Nemoto, M. (1987). *Ultramicroscopy*, *21*(3), 271-276. [4] De la Pena et al. https://doi.org/10.5281/zenodo.592838 [5] Dartois E., et al. (2013) *Icarus* 224, 243-252.