

SCALE-DEPENDENT METHODS FOR NITROGEN ELEMENTAL QUANTIFICATION IN INSOLUBLE ORGANIC MATTER BY IMAGING WITH THE NANOSIMS .

A. Thomen and F. Robert Laboratoire de Minéralogie et de Cosmochimie du Muséum. E-mail : athomen@mnhn.fr

Introduction : Correlated microscopic variations between elemental and isotopic compositions of N in Insoluble Organic Matter of carbonaceous chondrites were tentatively search in recent studies [1,2]. At a micrometer scale, *i.e.* the typical size of a *hotspot* in the IOM, this topic is addressed by quantitative imaging with a NanoSIMS. We proposed here two methods of N elemental quantification with "improper" samples, (*i.e.* rough sample surface) the surfaces of which often mimics those of natural samples (IPDs or IOM).

Materials and method : The calibration of the N concentrations was done with: a charcoal , a type 3 kerogen , a type 1 kerogen and Murchison IOM, with increasing N/C from 2.2×10^{-3} to 3.27×10^{-2} respectively. Several $10 \times 10 \mu\text{m}^2$ images of CN, C and C_2 of 128^2 pixels of the standards were acquired by rastering the Cs^+ primary beam with $\sim 2\text{pA}$ and 200 nm diameter. Ion images are sequentially reconstructed. Steady-state equilibrium is achieved by implantation of a Cs^+ dose of $2 \times 10^{17} \text{cm}^{-2}$ prior to the analysis. Image files are processed with L'IMAGE software (L.Nittler copyright). The CN/C and CN/ C_2 ratios are extracted at two different spatial scales with the whole image defined by (i) one ROI and by (ii) ~ 300 ROIs (that is 6^2 pixels for each ROI). Each scale has its own drawbacks: (i) at the image scale, the artifacts of the chemical ion ratios linked to the topographic state of the samples, have a tendency to vanish, (ii) at a 6^2 pixels scale ($0.2 \mu\text{m}^2$), our calibration accounts for topographic effects and the possible chemical heterogeneities of the standard. On ideal standards, *i.e.* polished and chemically homogeneous standards, the two approaches should yield identical results.

Results : Whatever the scale, the precision and detection limit for the N content in IOM is better determined by the CN/ C_2 than by the CN/C ratios. At the scale (i): inversion of the 95% confidence interval for the mean CN/C ratios corresponds to a relative uncertainty of $\pm 60\%$ of the atomic N/C ratio. In the same way for CN/ C_2 , the relative uncertainty is $\pm 22\%$. At the scale (ii) we observe for the CN/C and CN/ C_2 distributions of each standards, pronounced tails with clear departures from gaussian distribution. These non-gaussian distribution strongly affect the correlation coefficient of least-square regression and thus the precisions of the calibrations. When transformed in log-normal distributions, the variance of the residues is nearly constant, illustrating the improvement of the regression quality.

At the scale (ii) prediction interval [3] is used to quantify the uncertainties on the N content measured at a micrometer scale: inversion of 95% level gives a relative uncertainty of $\pm 33\%$ for the calibration based on the CN/ C_2 but $\pm 100\%$ for CN/C (that is covering the whole range of natural variations in kerogens or IOM !). We will show several application of these methods for IOM of chondrites at the conference.

References: [1] Busemann H. et al. 2006. *Science* 312:728-730. [2] De Gregorio B.T. et al. 2011. *GCA* 15:4454-4470. [3] Draper N. & Smith H. , 2008, Applied Regression Analysis.