CHEMICAL AND NITROGEN ISOTOPIC COMPOSITION OF THE *HOTSPOTS* IN ORGUEIL INSOLUBLE ORGANIC MATTER

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Introduction: The Insoluble Organic Matter (IOM) of Orgueil (CI) chondrite is a highly unequilibriated material. At the molecular scale, Orgueil IOM appears as a mixing between aromatic, benzilic, aliphatic and radical C-H bonds. Each of these components have a different δD from +550 to +100,000 , correlated with their bond energy [1, 2]. The radical bond, with a δD up to +100,000 [2, 3] is the carrier of the Hydrogen isotopic anomalies in Orgueil IOM. The enrichments in D of the IOM can be explained by simple isotopic exchange between a D-rich reservoir H_3^+, and the C-H bonds in the organic matter[2, 3]. The lack of correlation of the C/H with δD in the hotspots [4] confirm this hypothesis. However, the ^{15}N enrichments are not fully explained. Because of its low content, C-N bond Nitrogen isotopic heterogeneity is not yet measurable with conventional mass spectrometry technique [1]. Therefore, a analogous interpretation for the origin of δD isotopic heterogeneity is not yet or partially formulated for the ^{15}N enrichments [2, 5]. The origin of the ^{15}N enrichements could be a mechanism different than a simple nitrogen isotopic exchange between a ^{15}N-rich reservoir and CN bonds in IOM. A more precise determination of the nitrogen content of the ^{15}N *-hotspots* will help us to assess their origin. Here we used the NanoSIMS in quantitative imaging mode to measured the C and N isotopic and N/C elemental compositon of the IOM of Orgueil. The measured CN^-/C^- elemental ratio of micrometer area can be highly modified by topographic effect or non-equilibrium sputtering of the sample under ion bombardment. Here, we present preliminary results on N/C vs. $\delta^{15}N$ measurements with a better control of the systematic error on elemental ratio.

Method: We conducted quantitative imaging measurements of the IOM of Orgueil with the NanoSIMS. A type 1 kerogen of known isotopic and elemental compositions is used as a standard. We measured $^{12}C^-$, $^{12}C_2^-$,$^{13}C^{12}C^-$, $^{12}C^{14}N^-$,$^{12}C^{15}N^-$ masses on electrons multipliers in multicollecton mode. A normal-incidence 16keV Cs^+ of 1-1.9 pA is rastered on a $10x10\mu m^2$ area with a dwell time of 1,000 μs per pixel. Lateral resolution is estimated at about 150 nm. Isotopic and elemental ratio are extracted from images with L'IMAGE(L.R.Nittler) software. The vacuum in the analysis chamber was kept below 8×10^{-10} Torr in order to minimise the possible effect of the residual gas in the CN^- signal. A special care was applied to : (i) reach the steady-state sputtering equlibrium to ensure fluence-independant elemental ratio measurement, (ii) estimate the topographic effect on the elemental and isotopic ratio.

Steady-state fluence : The fluence to reach steady-state sputtering equilibrium was determined on Korapox resin and type 1 kerogen by recording the C_2^- counting rate. After Cs^+ bombardement reached a $>2\times10^{17}at.cm^{-2}$ fluence, the C_2^- couting rate varies within 2%. Given the sputering equilibrium is mainly controled by the Cs content of the sample surface, one reasonably assumed all ionised species reach steady-state sputtering at this fluence [6]. Therefore, the areas of interest are rastered with a 180 to 200pA Cs^+ beam on $12 \times 12\mu m^2$ during 300-600s.

Sample topography: chemically homogeneous but rough samples show heterogeneous ionic images as well as heterogeneous elemental CN^-/C^- and CN^-/C_2^- ratio images. This topographic effect on elemental ratio simulate a chemical contrast. Therefore, the identification of the true chemical heterogeneity is difficult. To quantify this effect, a rough sample of gold-coated Korapox resin was prepared : first polished untill we obtain a mirror surface, then depolished with alumina $0.3\mu m$ to create parallel ripples. The ripples create a relief of at most 0.3 μm in the beam trajectory. Secondary electrons images are recorded along with ion images to estimate the roughness of the sample.

Results: *Steady-state sputtering yield* : After a presputtering with a fluence of $>2\times10^{17}at.cm^{-2}$, the CN^-/C^- and CN^-/C_2^- of each cycle vary within 10%(1σ).

Topographic effect on elemental ratio : The figure 1 is the $CN-/C^-$ image of the depolished resin: the ripples appear perpendicular to the profil (solid line) shown by the figure 2. The $CN-/C^-$ and $CN-/C_2^-$ vary in this single image in the range of 20% and 15% respectively. Unfortunately, it is hard to related the "top" of the ripple to maximum count rate and the "valley" to the minimum. Even if the true N/C of the resin is un-
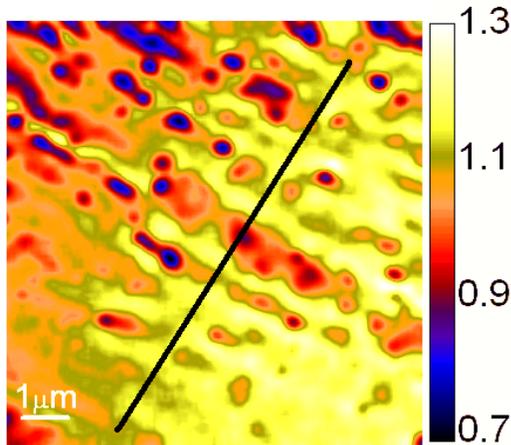
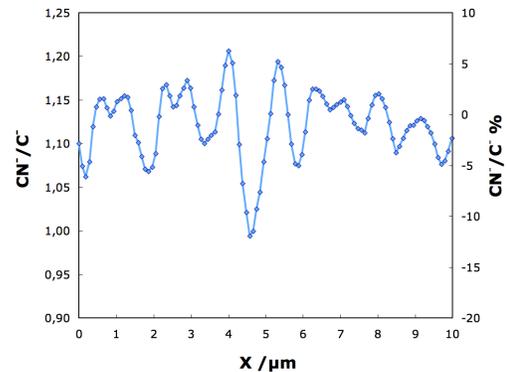Figure 1: CN^-/C^- image of the depolished Korapox resin.

Figure 2: CN^-/C^- and relative CN^-/C^- variation relative to the mean of the profile of the depolished resin in the black line in figure 1

known, relative variations of the CN^-/C^- anc CN^-/C_2^- ratio are used to estimate an uncertainty on the topographic effect.

Intra-image QSA effect on carbon isotopic ratio : inside an ionic image, the carbon isotopic composition is linearly correlated to the C_2^- dimer counting rate. $\delta^{13}C_2^-$ underwent an *intra*-image QSA effect. Inside a Orgueil IOM image, a variation of the C_2^- couting rate by a factor 6 accounts for 5‰ variation of the carbon isotopic ratio. In the same image, a variation of the CN^- counting rate by factor 5 accounts for about 1‰ variation of the $\delta^{15}N$.

The nitrogen isotopic compositon of the measured *hotspots* vary between +260 to +700‰, in the accordance with previous work [5].The bulk composition of the Orgueil IOM varies in the range of +29 to +34 ‰ in accordance with conventional mass-spectrometry study [7].

Nitrogen content of the hotspots : In this preliminary report, we used only the kerogen of type 1 to correct the CN^-/C^- and CN^-/C_2^-. The reproducibility on the CN^-/C^- and CN^-/C_2^- are respectively 11% and 10% (1σ) on 8 measurements of the type-1 kerogen . The CN^-/C^- and CN^-/C_2^- ratio of the ^{15}N-*hotspots* varies from 0.22 to 1.0 and from 0.22 to 0.59. The true N/C ratio of the ^{15}N-*hotspots* is in the range of 0.012 to 0.067.

Discussion: This preliminary work consists of the first attempt to evaluate the steady-state and topographic effect on the CN^-/C^- and CN^-/C_2^- ratio. Ulthough not negligible, these effects are small compared to the observed variation of CN^-/C^- and CN^-/C_2^- in these

measurements. An accurate N/C ratio calibration with CN^-/C^- and CN^-/C_2^- will be present at the meeting. The observed heterogeneity in the IOM for CN^-/C^- and CN^-/C_2^- ratio seems related to a real chemical heterogeneity and therefore illustrated structural variations at the molecular scale. This last point will be illustrated by recent example obtained in the IOM of the carbonaceous meteorites.

References: [1] L. Remusat, et al. (2006) *Earth and Planetary Science Letters* 243:15. [2] D. Gourier, et al. (2008) *Geochimica et Cosmochimica Acta* 72:1914. [3] L. Remusat, et al. (2009) *The Astrophysical Journal* 698(2):2087. [4] H. Busemann, et al. (2006) *Science* 312(5774):727. [5] A. Thomen, et al. (2009) *Meteoritics and Planetary Science Supplement* 72:5284. [6] H. Gnaser (1996) *Phys Rev B* 54(23):17141. [7] C. Alexander, et al. (2007) *Geochimica et Cosmochimica Acta* 71(17):4380 .