

ORIGIN OF CHONDRITIC AND COMETARY REFRACTORY ORGANIC MATTER: RADIOLYTIC OR THERMAL CARBONIZATION? M. Faure¹, E. Quirico¹, A. Faure¹, D. Baklouti², P. Boduch³, H. Rothard³, E. Ballanzat³, E. Dartois², R. Brunetto², L. Bonal¹, P. Beck¹, B. Schmitt¹ ¹Institut de Planétologie et d'Astrophysique de Grenoble (IPAG); Université Grenoble Alpes/CNRS-INSU, UMR 5274, Grenoble F-38041, France, ma-thilde.faure@obs.ujf-grenoble.fr, ²Institut d'Astrophysique Spatiale, CNRS / Université Paris Sud, Bâtiment 121, 91405 Orsay, France, ³CIMAP-Ganil (CEA CNRS UMR6252, ENSICAEN, Univ. Caen Normandie) Caen France.

Introduction: Refractory organic matter (ROM) from primitive chondrites and interplanetary grains of asteroidal and cometary origins is a polyaromatic solid that resembles terrestrial kerogens. The place where ROM was formed and the nature of its formation process are still debated, and there is no scenario that fulfills the complete set of available constraints. It has recently been proposed that high-temperature conditions were necessary to account for the polyaromatic structure [1,2]. Also, it was outlined that irradiation processes may be involved, either to account for isotopic enrichments [3] or to account for high N abundance in rare C-rich Antarctic Micro-Meteorites [4].

Here we address the issue of the formation of ROM by ion irradiation, which might be an alternate process to heating. We present an experimental study of the formation of ROM through ion irradiation of a simple polymer polyethylene glycol 1450 (PEG1450). This polymer does not contain aromatic rings and its elemental content in C, H and O (O/C=0.5 and H/C=2) resembles that of Soluble Organic Matter (SOM), the methanol-extracted fraction from carbonaceous chondrites. It is therefore well suited to study the settlement of a polyaromatic structure in a simple and soluble material.

Experimental: 60 μ m films of PEG1450 were deposited on a ZnSe window. High energy irradiation experiments (carbon ions at 1 MeV/uma) were performed under vacuum (10^{-6} mbar) and at room temperature at the heavy ion accelerator facility GANIL. Infrared spectra were recorded at different projectile fluences. Five samples have been irradiated, with fluences up to 4.10^{14} ions/cm². In addition, Raman spectroscopy (514 nm) was performed at Laboratoire de Géologie de Lyon to characterize the polyaromatic structure of the samples. Both IR and Raman data allowed comparison with ROM extracted from primitive chondrites.

Results: Beyond a fluence of a few 10^{14} ions/cm², the overall sample turned brown with a tendency to crack. Infrared spectra of PEG1450 irradiated to 4.10^{14} ions/cm² are shown in figure 1 with the assignment of some vibrational bands in table 1. During irradiation, the composition is significantly modified. First, we can observe a large decrease of the band intensities around 2900 cm⁻¹ (assigned to CH₂) as well as in the 800-1500 cm⁻¹ range (assigned to the skeletal stretching mode and to CH₂). Hydroxyles (OH) start disappearing

above 5.10^{12} ions/cm². Two bands appear when the fluence exceeds 6.10^{13} ions/cm², one around 1720 cm⁻¹ assigned to carbonyl (C=O) and the other around 1600 cm⁻¹, assigned to olefin carbons C=C. These bands disappear at higher fluences (around 10^{14} ions/cm²). A small band appears at 2115 cm⁻¹ for a fluence higher than 10^{14} ions/cm², which is characteristic of the presence of alkynes (C \equiv C).

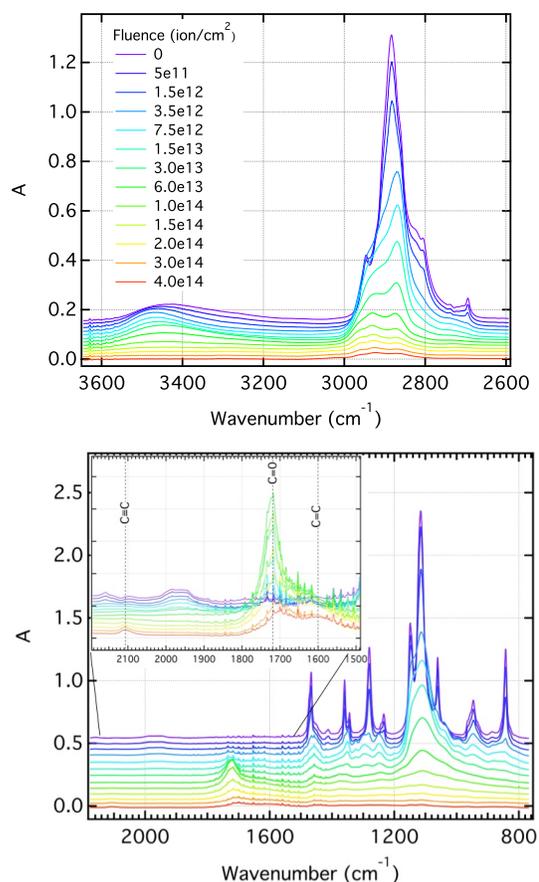


Fig. 1 : FTIR absorption spectra of irradiated PEG1450 at different fluences from no irradiation (purple) to a fluence of $4.0 \cdot 10^{14}$ ions.cm⁻² (red) in the range [2600 - 3600 cm⁻¹] (top), and [800 -2200 cm⁻¹] (bottom). A zoom on the [1500 -2200 cm⁻¹] range is presented in the insert.

514 nm Raman spectroscopy was finally performed on irradiated PEG1450 samples. However, the fluorescence signal was so high that no structure was observed in the range 1700-1100 cm⁻¹. Therefore the sp² structure could not be determined accurately.

Position (cm ⁻¹)	Vibrational mode	Evolution
3460	stretching O-H	↘
2947	stretching CH ₂	↘
2890 - 2895	stretching CH ₂	↘
2860 - 2825 - 2805	overtone or combination modes of twisting, bending and wagging mode of CH ₂	↘
2110	stretching C=C	↗
1700	stretching C=O	↗
1640	stretching C=C	↗
1450	bending CH ₂	↘
1360	wagging & twisting CH ₂	↘
1280	twisting & wagging CH ₂	↘
1150	stretching C-O-C & rocking CH ₂	↘
1120	stretching C-C & C-O	↘
1100	stretching C-O-C	↘
1060	stretching C-O-C & rocking CH ₂	↘
945	stretching C-O-C	↘
840	rocking CH ₂	↘

Tab. 1 : IR frequencies observed in PEG1450 [5]. Arrows indicate increasing (↗) and decreasing (↘) intensity of the bands during irradiation.

Discussion : The irradiation of PEG1450 leads to the formation of new chemical groups such as C=O, C=C, C≡C and -CH₃. The film thickness also decreases continuously, pointing to mass loss. The formation of C=O and -CH₃ reflects the loss of the polymeric structure. The appearance of C≡C and C=C corresponds to the loss of H and bond formation from neighbouring radicals. Overall, these chemical modifications are accompanied by cross-linking and disordering, which appears as band broadening. Nevertheless, there is no clear evidence of aromatic rings nor polyaromatic structure.

The comparison of irradiated PEG1450 (with fluence higher than 2.10^{14} ions/cm²) and ROM extracted from meteorites (named in this case IOM for Insoluble Organic Matter) is shown in figure 2. Before irradiation, the polymer is very different from the ROM. After irradiation, a large and not well structured absorbance appears between 800 cm⁻¹ and 1800 cm⁻¹ as observed in ROM. Looking closer at this range, we can observe four bands similar to ROM and assigned to C=O, C=C, CH₂ and CH₃. In the range 2800 cm⁻¹ to 3000 cm⁻¹, we also find strong similarities (in shape and relative intensities) with the four vibrational bands due to CH₂ and CH₃. However, the structural properties of irradiated PEG1450 do not fully match that of ROM. First, alkynes (C≡C) are formed during irradiation but they are not observed in the ROM. 514 nm Raman spectra of ROM also lead to the observation of bands D and G but in the case of irradiated PEG1450, only a strong fluorescence is observed. This suggests a strong difference in the structure of irradiated PEG1450 and ROM.

The evolution of composition and structure of PEG1450 has similarities with changes observed in the irradiation of other polymers, in particular disordering and cross-linking. However, the nature of the precursor

controls the nature of the irradiated samples [6]. While many precursors evolve towards an amorphous carbon [7], polymers containing aromatic rings in their initial structure may exhibit a polyaromatic structure [8]. In conclusion, while similarities between irradiated PEG1450 and ROM are observed, the formation of ROM without high temperature appears challenging. Precursor effects need to be investigated in more details before final conclusions can be drawn.

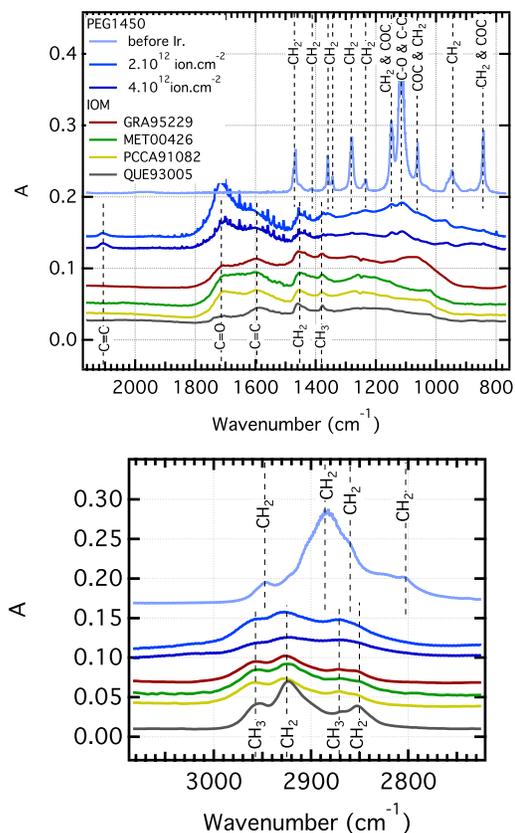


Fig 2. Infrared spectra of PEG1450 after two high fluences irradiation compared to non-irradiated PEG1450 and to IOM from four different meteorites in the range [800 -2200 cm⁻¹] (top), and [2600 - 3600 cm⁻¹] (bottom).

References: [1] Cody et al. (2011) *PNAS* [2] Quirico E. et al. (2014) *GCA* 136, 80–99. [3] Laurent et al. (2014) *GCA* 142, 522-534 [4] Dartois et al. (2013) *Icarus* 224, 243-252 [5] Miyazawa, T. et al. (1962) *J. Chem. Phys.*, 37, 2764–2776. [6] Reynaud et al. (2001) *Spec. Acta Part A* 57, 797-814 [7] Strazzulla G. et al. (2001) *Acta. A. Mol. Biomol. Spectrosc.*, 57, 825-842. [8] Costantini et al. (2002) *Nucl. Inst. Meth. Phys. Res. B* 194, 132-140