

AMORPHIZATION AND D/H FRACTIONATION OF KEROGENS DURING EXPERIMENTAL ELECTRON IRRADIATION: COMPARISON WITH CHONDRITIC ORGANIC MATTER. C. Le Guillou^{1,2}, S. Bernard³, L. Remusat³, A. J. Brearley¹ and H. Leroux⁴. ¹Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque, NM 87106, USA (corentin.san@gmail.com). ²Institut für Geology, Mineralogy and Geophysics, Ruhr Universität Bochum, Bochum, Germany. LMCM, CNRS UMR 7202, MNHN, Paris, France. ⁴Unité Matériaux et Transformations, CNRS UMR 8207 - Université Lille 1, 59655 Villeneuve d'Ascq, France.

Introduction: Organic matter (OM) in chondrites is highly enriched in deuterium in comparison to the sun. This property is thought to result from ion-molecule reactions, possibly driven by UV irradiation in the interstellar media (ISM) or the proto-solar nebula (PSN) [1, 2]. Recently, [3] showed that electron irradiation of carbon-based polymers (epoxy and cyanoacrylate) in a TEM could produce significant δD increase (up to 1000 ‰). They thus speculated that some of the deuterium enrichment of chondritic OM particles in the ISM or the PSN could have been driven by similar irradiation processes. However, they did not thoroughly investigate the reaction mechanisms responsible for the fractionation and the kinetics of the process.

An improved understanding of electron irradiation mechanisms requires that the influences of parameters such as beam current, temperature and the nature of the organic precursor to be constrained more thoroughly. With such information, isotopic fractionations induced by electron irradiation may eventually be extrapolated with greater confidence to extraterrestrial environments.

We prepared focused ion beam (FIB) sections of terrestrial type I and III kerogens that were then irradiated in a TEM under various fluence rates at both room temperature and at 92K, a temperature closer to ISM and PSN environments, in order to constrain the irradiation-induced structural modifications and fractionation mechanisms. The molecular structure, chemical and isotopic evolution of the irradiated samples have been investigated using synchrotron-based Scanning Transmission X-ray Microscopy (STXM) at the carbon K-edge and NanoSIMS.

Experimental: Two well-known kerogens have been selected: a type I kerogen (Green River shale; H/C = 1.6; N/C = 0.025, $\delta D = -150$ ‰) and a type III kerogen (H/C = 0.7; O/C = 0.06; N/C = 0.016, $\delta D = -92$ ‰). The type I kerogen mainly consists of aliphatic chains with a significant contribution of olefinic carbons ($-C=C-$), while the type III kerogen, classified as mature one, is more aromatic. This type III kerogen has an elemental composition within the same range as

chondritic insoluble OM in type 1 and 2 carbonaceous chondrites [1].

Three different FIB sections were prepared with great care. Two FIB sections of the type I kerogen were irradiated in a TEM operated at 200 kV, respectively at 293 K and at cryogenic temperature (-181°C, 92K) using a cryogenic sample holder cooled by liquid nitrogen. A type III kerogen FIB section was also irradiated at room temperature. For each section, we used the low magnification mode of the TEM and the smallest condenser aperture to locate the sample. This low electron exposure at a fluence rate of about $10^{11} e^- \cdot cm^{-2} \cdot s^{-1}$ resulted in a total fluence of $6 \times 10^{12} e^- \cdot cm^{-2}$. After location of the sample, 1 micron diameter spots were irradiated in bright field mode at different beam currents (from 1 to 600 pA) for 30 minutes resulting in total fluences from 1.1×10^{18} to $6.7 \times 10^{20} e^- \cdot cm^{-2}$. The irradiated volume is a wide, thin cylinder ($\sim 1 \mu m$ in diameter x 100 nm thick).

Samples were analyzed by STXM at the Advanced Light Source (ALS, [4]) to obtain spectra for each region irradiated under different condition. Spectra were then normalized to the total carbon content and fitted with Gaussian bands [5] to obtain quantitative information about spectral evolution and to better compare spectra. NanoSIMS: the sample surface was rastered by a primary Cs^+ beam set to a beam current of 7 pA. Secondary ion images of $^1H^-$, $^2D^-$ and $^{12}C^-$ were recorded using the combined analysis mode.

Results: STXM shows that progressive amorphization is the main molecular evolution caused by irradiation with increasing current (Fig. 1): we observe a fading of distinguishable absorption peaks initially present in the kerogens (aromatics, aliphatics, ketones) and the development of a continuous absorption between 284 eV and 289 eV. Type I and III kerogen both tend toward amorphization, but type III kerogen reacts slower at the lowest fluences. At liquid nitrogen temperature, however, no significant molecular evolution is observed with increasing beam current.

NanoSIMS mapping shows that at room temperature, hydrogen loss occurs and is correlated with isotopic fractionation whose degree is related to the beam current or total fluence (Fig. 2). The highest

δD increase is of about 1000‰, as in [3]. Hydrogen loss is non-linearly related to the fluence. At liquid nitrogen temperature, the loss of hydrogen and the corresponding fractionation are much more limited.

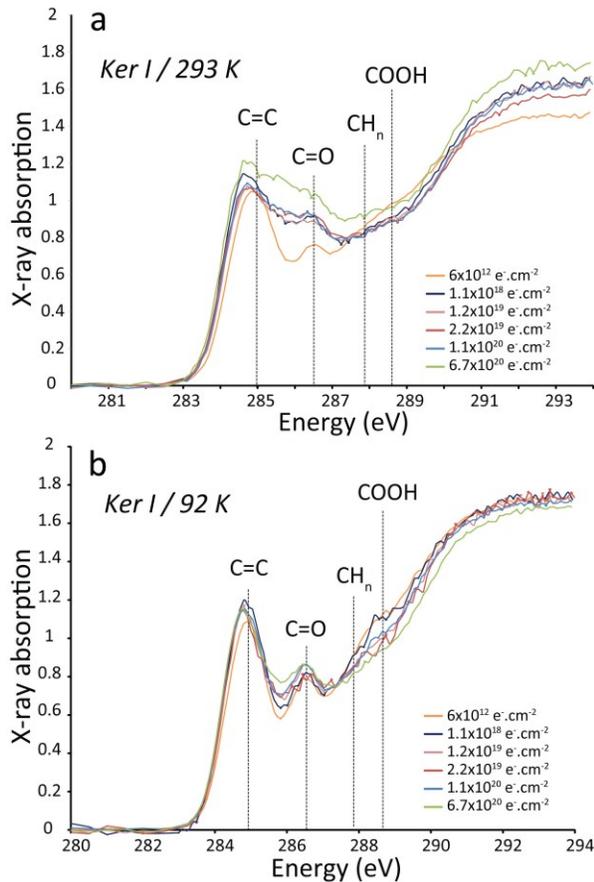


Figure 1: Normalized STXM spectra of the type I kerogen irradiated at 200kV and at different beam currents; a) at room temperature, progressive amorphization occurs; b) at liquid nitrogen temperature, no changes are observed.

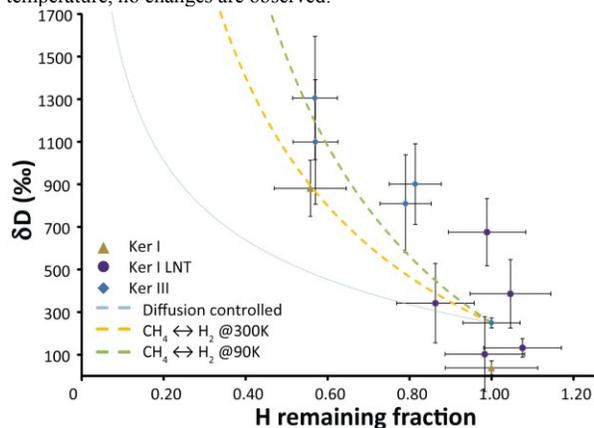


Figure 2: δD versus H remaining fraction of irradiated spots of the different FIB sections at various beam currents. The D/H fractionation is correlated to the decrease of the H/C ratio and seems to follow a Rayleigh distillation behavior.

Discussion: We suggest that amorphization and hydrogen loss are controlled by radiolysis (carbon-hydrogen bonds are broken and hydrogen is lost), coupled with recombination. The rate-limiting step is the defect diffusion which controls the recombination probability [6]. Indeed, at low temperature, radiolysis effects are the same since this mechanism only depends on the energy of the incoming electrons. However, recombination, i.e. the reconstruction of new covalent bonds between carbon and hydrogen is more favorable at lower temperature due to slower defect diffusion rates, and therefore limits the H loss. Since the system is open (the TEM column is under vacuum) and H loss and δD increase are correlated, we suggest that the fractionation is due to a Rayleigh distillation. The lighter H is lost (as gaseous species) more readily and the residue is progressively enriched in D. Fractionation due to differences in diffusion rates of H and D does not fit the data, whereas a model based on equilibrium reactions between CH_4 and H_2 better reproduces the apparent fractionation factor.

In chondrites, STXM spectra reported by several authors do not show such a high amorphization degree [7, 8, 9, 10], and the measured H/C ratio are much higher than those observed in our experimentally-irradiated spots. These observations indicate that organic matter particles in chondrites have not been exposed to irradiation processes of comparable intensity. Due to the very low fluence rate and temperature conditions in the interstellar medium, such an electron irradiation mechanism may be kinetically inhibited, and is unlikely to be responsible for the large deuterium excess found in extraterrestrial organics. In the PSN, temperature and fluence can vary, and evolutions are more difficult to assess.

The data reported here also show that STXM or NanoSIMS experiments should not be performed on organic samples that have already been investigated using TEM, even under soft irradiation conditions.

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References: [1] Robert F. and Epstein S. (1982) *GCA*, 81-95 [2] Remusat L. et al. (2010) *ApJ*, 1048 [3] De Gregorio B.T. (2010) *GCA*, 4454-4470 [4] Kylcoyne A. L. D. (2003) *J. of Synch. Rad.* 10, 125-136 [5] Bernard S. et al. (2010) *Carbon*, 2506-2516 [6] Hobbs L.W. (1987) *Intro. to analytical elec. microscopy* [7] Flynn G. J. et al. (2003) *GCA*, 4791-4806 [8] Keller L. P. (2004) *GCA* 68, 2577-258 [9] Herd C. D. K. et al. (2011) *Science* 332, 1304-1307 [10] Le Guillou C. and Brearley A. J. (2011) *LPSC XXXXII* (# 1996)