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Amorphization and D/H fractionation of kerogens during experimental electron irradiation: Comparison with chondritic organic matter

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ABSTRACT

Irradiation is common in the interstellar medium and the protosolar nebula. We have investigated the effects of electron irradiation on kerogens of type I and III in a 200 kV transmission electron microscope (TEM), at 293 K and 92 K, using various fluences. Using synchrotron-based scanning transmission X-ray microscopy (STXM) and NanoSIMS, we have demonstrated a progressive amorphization coupled with hydrogen loss and a significant deuterium to hydrogen ratio (D/H) fractionation, with δD increasing by up to 1000‰. Hydrogen loss is non-linearly related to the fluence. Irradiation under cryogenic conditions (92 K) hinders amorphization and D/H elevation. We suggest that these effects are controlled by radiolysis (carbon—hydrogen bonds are broken and hydrogen is lost), coupled with recombination. The amorphization and hydrogen loss are rate-limited by defect diffusion which controls the recombination probability. The D/H increase appears to follow a Rayleigh distillation law with an apparent fractionation factor similar to the equilibrium fractionation factor of the isotopic exchange reaction $CH_4 + HD \leftrightarrow CH_3D + H_2$.

This study represents a first step to estimate the kinetics and timescales of D/H fractionation under ionizing radiation. Extrapolatation of this fractionation behavior to natural environments remains difficult at this point because simultaneous irradiation by protons and other cosmic rays at various energies also occurs. However, the present results show that isotopic fractionation by electron irradiation at 200 kV alone might have been kinetically inhibited at the low temperatures of the interstellar medium and the outer region of the protosolar nebula. In addition, we show that STXM or NanoSIMS experiments should not be performed on organic samples that have already been investigated using TEM, even under low flux electron irradiation conditions.

1. Introduction

Carbonaceous chondrites contain complex refractory organic material (OM; Hayatsu and Anders, 1981). The reaction pathways that led to the formation of this extraterrestrial material are still debated. In chondrites, OM is finely distributed among other materials such as phyllosilicates, oxides and sulfides (Garvie and Buseck, 2007; Zega et al., 2010; Le Guillou et al., 2011). A component of this OM exhibits high D/H and $^{15}N/^{14}N$ ratios compared to the Sun or terrestrial materials (Robert and Epstein, 1982; Meibom et al., 2007; Charnley and Rodgers, 2008; Floss and Stadermann, 2009; Alexander et al., 2007; Aléon, 2010; Marty, 2012). Two environments have been proposed to explain where such deuterium enrichments could have been produced: the protosolar nebula (PSN) (Remusat et al., 2006, 2009, 2010; Willacy and Woods, 2009) and the interstellar medium (ISM), possibly during the dense molecular cloud phase (Robert and Epstein, 1982; Floss and Stadermann, 2009). In the ISM, ion–molecule or gas-grain reactions, in irradiated environments at very low temperature (<70 K), could have favored deuterium enrichment (Geiss and Reeves, 1981; Aikawa and Herbst, 1999; Sandford et al., 2001; Watanabe and Kouchi, 2008). In the outer region of the PSN, small molecules such as those present in comets could have also undergone cold chemistry in a similar way as in the ISM (Aikawa and Herbst, 1999). This OM is then accreted into asteroidal parent bodies, together with water ice and other more refractory materials, where it encounters aqueous and thermal processes (Huang et al., 2007; Garvie and Buseck, 2007; Remusat et al., 2008; Alexander et al., 2010; Cody et al., 2011; Le Guillou et al., 2012).

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Irradiation studies of both experimental and natural materials are crucial to understand the molecular and isotopic evolution of the OM and shed new light on its original state. Irradiation of OM in extraterrestrial environments by proton or other ions has been previously experimentally investigated (Strazzulla and Baratta, 1992; Cooper et al., 2001; Moroz et al., 2004; Gomis and Strazzulla, 2005; Muñoz Caro et al., 2006; Brunetto et al., 2009; Godard et al., 2011). These studies demonstrated that ion irradiation induces the formation of refractory carbons from smaller molecules (by gradual dehydrogenation and polymerization) or the progressive amorphization of soots. However, none of these studies have discussed the evolution of isotopic signatures during irradiation. UV irradiation is also widely studied since UV photolysis of OM is assumed to be an efficient source of energy for cryogenic organic chemistry (e.g., Bernstein et al., 1995, 1999; Sandford et al., 2000; Dartois et al., 2005; Muñoz Caro et al., 2006; Mennella, 2008). In addition to proton and UV, electron fluxes are known to occur in both the ISM and the PSN (Meyer et al., 1998; Padovani et al., 2009; Godard et al., 2011). Electron irradiation has been mostly studied with applications to material science (Hobbs, 1987; Banhart, 1999; Egerton and Rauf, 1999; Egerton et al., 2004; Ammar et al., 2010). These studies have provided a conceptual basis for electron-organics physico-chemical interactions like knock-on damage, radiolysis, amorphization, and mass loss.

Recently, De Gregorio et al. (2010) showed that electron irradiation of carbon-based polymers (epoxy and cyanoacrylate) in a TEM could produce significant δD increases (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 its kinetics. Understanding those mechanisms would be a first step to model isotopic fractionation induced by electrons in space.

An improved understanding of electron irradiation mechanisms requires better constraints on the influences of the main experimental parameters on given organic precursors. Such constraints may eventually allow the fractionations caused by electron irradiation to be extrapolated with greater confidence to extraterrestrial environments. In this work, we irradiated Focused Ion Beam-prepared (FIB) sections of terrestrial type I and III kerogens in a TEM under various fluence rates at both room temperature and at 92 K, in order to constrain more thoroughly the irradiation-induced structural modifications and isotopic fractionation mechanisms. Experiments at 92 K are relevant to investigate the impact of low temperature encountered in the dense molecular cloud and the outer region of the PSN (where temperatures could drop below 50 K – Aikawa and Herbst (1999) and Sandford et al. (2001)). The molecular structure, the chemical and the isotopic evolution of the irradiated samples have been investigated using synchrotron-based STXM at the carbon K-edge and NanoSIMS.

2. Sample and experimental conditions

2.1. Kerogens: description and relevance

Two reference kerogens have been selected for this study: a type I kerogen from the Green River shale formation (H/C = 1.6; O/C = 0.07; N/C = 0.025, δD = −150‰) and a type III kerogen from the Appalachians Eastern Coal Province (H/C = 0.7; O/C = 0.06; N/C = 0.016, δD = −92‰). These reference materials have been provided by IFP Energies Nouvelles. The investigated type I kerogen mainly consists of aliphatic chains with a significant contribution of olefinic carbons (C=C), while the investigated type III kerogen, classified as a mature one, is more aromatic (Vandenbroucke, 2003; Vandenbroucke and Largeau, 2007). Although its molecular composition is different from that of chondritic insoluble organic matter from type 1 and 2 carbonaceous chondrites (Cody et al., 2008a), this type III kerogen has an elemental composition within the same range (Alexander et al., 2007). In contrast to chondritic organic matter (Busemann et al., 2006; Remusat et al., 2009; Okumura and Mimura, 2011), the investigated type III kerogen exhibits a homogeneous isotopic composition at the submicrometer scale.

2.2. Focused Ion Beam sample preparation

Samples for TEM irradiation were prepared using the Focused Ion Beam (FIB) technique, with a FEI Quanta 3D FEGSEM/FIB instrument installed at the Department of Earth and Planetary Sciences, University of New Mexico. The FIB Ga ion milling was carried out at an ion beam voltage of 30 kV and beam currents from 3 nA down to 10 pA for the final thinning step. Ultrathin sections were lifted out *in situ* using an Omniprobe 200 micromanipulator and transferred to a Cu TEM half grid for final ion milling. The final FIB sections thickness was slightly larger than 100 nm. Detailed descriptions of the FIB extraction procedures can be found in Heaney et al. (2001) and Wirth (2004, 2009). FIB preparation may induce some modifications of the materials. A few nanometers of amorphized materials can form on each side of the section. Bernard et al. (2009) have shown that the FIB milling does not induce significant changes in the speciation of carbon in model polymers as measured by STXM-based C-XANES spectroscopy. The use of a dual beam FIB apparatus may also lead to the degradation of OM by SEM imaging, especially during the last steps of the preparation, but although significant for polymers, this effect remains very limited for kerogen-like materials (Bassim et al., 2012). To minimize this damage as much as possible, imaging of the sample was carried out at low voltage (5 kV) and low electron beam current (50 pA).

2.3. Irradiation conditions in the TEM

The TEM irradiation was carried out using a JEOL 2010F FEG-TEM/STEM in the Electron Microbeam Analysis Facility at the Department of Earth and Planetary Sciences and Institute of Meteoritics, University of New Mexico. The JEOL 2010F was operated at 200 kV. Three different FIB sections were prepared. Two FIB sections of the type I kerogen were irradiated, respectively, at 293 K and at cryogenic temperature (−181 °C, 92 K) using a GATAN cryogenic sample holder cooled by liquid nitrogen. Temperature was monitored by a thermocouple located at the tip of the holder. A type III kerogen FIB section was also irradiated at room temperature. For each section, we used the low magnification mode and the smallest condenser aperture to locate the sample. This low electron exposure at a fluence rate of about 10^{11} e^- cm^{-2} s^{-1} resulted in a total fluence of 6×10^{12} e^- cm^{-2}. After location of the sample, 1 micron diameter spots were irradiated in bright field mode at beam currents from 1 to 600 pA (measured by the probe recording the illumination of the screen) for 30 min duration (Table 1), resulting in fluence rates from 6×10^{14} to 4×10^{17} e^- cm^{-2} s^{-1} and total fluences from 1.1×10^{18} to 6.7×10^{20} e^- cm^{-2}. The irradiated volume is a wide and short cylinder (~1 μm in diameter × 100 nm thick; Fig. 1).

2.4. Analytical methods

2.4.1. Scanning transmission electron microscopy (STXM)

2.4.1.1. Data collection. Following Bernard et al. (2012a, 2012b), STXM experiments were done on beamline 5.3.2.2 (STXM Polymer beamline – Kilcoyne et al., 2003) at the Advanced Light Source