The deuterium/hydrogen distribution in chondritic organic matter attests to early ionizing irradiation

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Primitive carbonaceous chondrites contain a large array of organic compounds dominated by insoluble organic matter (IOM). A striking feature of this IOM is the systematic enrichment in deuterium compared with the solar hydrogen reservoir. This enrichment has been taken as a sign of low-temperature ion-molecule or gas-grain reactions. However, the extent to which Solar System processes, especially ionizing radiation, can affect D/H ratios is largely unknown. Here, we report the effects of electron irradiation on the hydrogen isotopic composition of organic precursors containing different functional groups. From an initial terrestrial composition, overall D-enrichments and differential intramolecular fractionations comparable with those measured in the Orgueil meteorite were induced. Therefore, ionizing radiation can quantitatively explain the deuteration of organics in some carbonaceous chondrites. For these meteorites, the precursors of the IOM may have had the same isotopic composition as the main water reservoirs of the inner Solar System.
CARBONACEOUS CHONDRITES RESULT FROM THE ACCRETION OF MATERIALS FORMED DURING THE EARLY STAGES OF THE SOLAR SYSTEM’S HISTORY. THESE METEORITES TYPICALLY CONTAIN A LARGE AMOUNT (UP TO 4–6 wt%) OF ORGANIC MATTER, WHICH WAS FORMED BY ABIOTIC PROCESSES AND OCCURS AS SMALL GRAINS IN THE FINELY GRAINED MATRIX FROM A FEW HUNDRED NANO METRES TO A FEW MICROMETRES IN DIAMETER. THE INSOLUBLE ORGANIC MATTER (IOM) CONSISTS OF SMALL AROMATIC UNITS, WHICH ARE HIGHLY SUBSTITUTED AND ARE CONNECTED BY SHORT AND BRANCHED ALIPHATIC CHAINS. THE PRESENCE OF MONORADICALS AND DIRADICALS IS A MAJOR STRUCTURAL FEATURE OF EXTRATERRESTRIAL IOM, AND THEY ARE RARELY FOUND IN TERRESTRIAL PROGENY.

THE SOLAR HYDROGEN RESERVOIR AND THE JOVIAN ATMOSPHERE RESULT FROM THE ACCRETION OF CARBONACEOUS CHONDRITES. CARBONACEOUS CHONDRITES RESULT FROM THE ACCRETION OF MATERIALS FORMED DURING THE EARLY STAGES OF THE SOLAR SYSTEM’S HISTORY. THESE METEORITES TYPICALLY CONTAIN A LARGE AMOUNT (UP TO 4–6 wt%) OF ORGANIC MATTER, WHICH WAS FORMED BY ABIOTIC PROCESSES AND OCCURS AS SMALL GRAINS IN THE FINELY GRAINED MATRIX FROM A FEW HUNDRED NANO METRES TO A FEW MICROMETRES IN DIAMETER. THE INSOLUBLE ORGANIC MATTER (IOM) CONSISTS OF SMALL AROMATIC UNITS, WHICH ARE HIGHLY SUBSTITUTED AND ARE CONNECTED BY SHORT AND BRANCHED ALIPHATIC CHAINS. THE PRESENCE OF MONORADICALS AND DIRADICALS IS A MAJOR STRUCTURAL FEATURE OF EXTRATERRESTRIAL IOM, AND THEY ARE RARELY FOUND IN TERRESTRIAL PROGENY.

RESULTS

EXPERIMENTAL STRATEGY. DESPITE BEING STRUCTURALLY DISTINCT FROM THE IOM, POLYMERS ARE SUITABLE ANALOGUES. POLYMERS AND IOM SHARE THE SAME FUNCTIONAL GROUPS (FOR EXAMPLE, ALIPHATIC CHAINS AND AROMATIC CYCLES). YET, POLYMERS CONSIST OF LONG CHAINS COMPOSED OF MANY REPETITIVE UNITS (MONOMERS), WHEREAS THE IOM DOES NOT SHOW ANY SIGNIFICANT REPETITION OF THE unit. POLYMERS ARE TYPICALLY MANUFACTURED WITH TIGHTLY CONTROLLED STEREOCHEMISTRY, WHEREAS THE IOM IS HETEROGENEOUS AT THE MOLECULAR SCALE. POLYMERS ARE SAME FUNCTIONAL GROUPS TO DERIVE TYPICAL INTRAMOLECULAR FRACTIONATION FACTORS. ELECTRONS WERE SELECTED AS IONIZING RADIATION BECAUSE THEIR IONIZING EFFICIENCY AND THEIR PENETRATION DEPTH ARE BOTH HIGHER THAN OTHER CANDIDATES (ULTRAVIOLET PHOTONS AND PROTONS). CONSEQUENTLY, ELECTRON IRRADIATIONS ARE EASY TO CARRY OUT IN THE LABORATORY, IRRADIATED MATERIALS ARE EASIER TO CHARACTERISE BY CONVENTIONAL SPECTROSCOPIC AND ISOTOPIC METHODS, AND DERIVED PROPERTIES ARE BULK PROPERTIES RATHER THAN SURFACE PROPERTIES. FOR COMPARISON, WE HAVE ALSO PERFORMED SOME ULTRAVIOLET IRRADIATION EXPERIMENTS (SEE SUPPLEMENTARY NOTE 1 FOR DETAILS). THE RESULTS SUGGEST THAT THE NATURE OF THE IRRADIATION MAY NOT HAVE A DETERMINING EFFECT.

EFFECTS OF ELECTRON IRRADIATION. ELECTRON IRRADIATION OF THE THREE POLYMERS AFFECTS THEIR STRUCTURES IN A SIMILAR WAY. FIRST, FOR EACH POLYMER, THE INTENSITY OF THE INFRARED SIGNAL DECREASES RELATIVE TO ALL OF THE C–H GROUPS, NAME CH3 (1,465 cm-1), CH (2,890 cm-1) AND RING (3,030 cm-1), AT SIMILAR RATES (FIG. 1). THIS INDICATES THAT ALL C–H BONDS ARE SIMULTANEOUSLY AFFECTED BY IRRADIATION. HENCE, THE DECREASE OF THE SIGNAL OF THE FUNCTIONAL C–H GROUPS IS INDEPENDENT OF THE DISSOCIATION ENERGY OF INDIVIDUAL C–H BONDS. SECOND, THESE IRRADIATED FEATURES AND THE DECREASE OF THE H+/C−H2, MEASURED BY TOF-SIMS, FOLLOW A COMPARABLE TREND FOR THE THREE POLYMERS (FIG. 2). ALL OF THESE STRUCTURAL AND COMPOSITIONAL DATA CAN BE DESCRIBED BY A FIRST-ORDER RATE EQUATION. THE Dose constant (Kd) derived from this formalism describes the rate dependence of the structural evolution for each analogue versus energy deposition. FOR THE THREE POLYMERS, THE Kd VALUES ARE COMPARABLE (4 × 10−25 cm2 eV−1 for PE AND PET, 5 × 10−25 cm2 eV−1 for PS, ALSO SEE THE METHODS SECTION). THIS INDICATES THAT BOTH C–H
Figure 1 | Evolution of the infrared peak area of C–H functional groups.
All of the experiments were performed at 30 keV and 300 K. This evolution is documented for (a) polyethylene (PE), (b) polystyrene (PS) and (c) polyethylene terephthalate (PET). For each sample, the intensity of the infrared signal related to CH₂ (1,465 cm⁻¹), CH (2,890 cm⁻¹) and ring (3,030 cm⁻¹) are considered. The peak areas (namely A_CH₂, A_CH, A_Aring) are normalized to the peak area of non-irradiated starting materials. On the three panels, the blue region represents the plateau, whereas structural, compositional and isotopic changes are still functions of the electron dose in the grey area. The doses required to reach 90% of the structural plateau delimit the blue and grey regions of the plots.

Discussion
The three studied polymers have different D/H plateau values. The nature and the relative proportions of the different C–H groups present in the starting material.

Figure 2 | Structural and compositional evolution of the three polymers.
All of the experiments were performed at 30 keV and 300 K. A combination of ToF-SIMS (H⁺/C₂H₄⁺) and FTIR data (the peak areas A_CH₂, A_CH, A_Aring) are presented for (a) polyethylene (PE), (b) polystyrene (PS) and (c) polyethylene terephthalate (PET). Data are all normalized between 0 and 1, allowing a direct comparison of different physical quantities. All evolutions are relative to the properties of the non-irradiated precursor. The coefficient K_e is the electron dose constant obtained from a first-order rate equation (see the Methods section for details). On the three panels, the blue region represents the plateau, whereas structural, compositional and isotopic changes are still functions of the electron dose in the grey area. The doses required to reach 90% of the structural and chemical plateaus delimit the blue and grey regions of the plots. Data for PET are from ref. 22.
signature of Orgueil was shaped by irradiation, the bulk isotopic composition of the precursor of the IOM before irradiation was very similar to the composition of our starting material, being very close to SMOW. The composition of the water trapped in Orgueil is also commensurate with SMOW\textsuperscript{14}. Therefore, our result suggests that both the precursor of the IOM and the water in Orgueil may have had the same initial isotopic composition as most of the water of the inner bodies. More generally, this new fractionating process could explain the systematic D-enrichment measured in the IOM relative to the water present in all carbonaceous chondrites\textsuperscript{14}. Such a contrasting behaviour between water and organic matter would be consistent with the poor efficiency of the disk ionization in enhancing the D/H of the solar water reservoirs\textsuperscript{25}.

In the protoplanetary disk, other solar ionizing particles, such as energetic photons and protons, may also have contributed to shaping the structural and isotopic signature of the IOM. Preliminary results of the structural and isotopic evolutions of a PET film irradiated by ultraviolet radiation suggest that the nature of the incoming ionizing particle may not be the pivotal factor. For a given deposited energy, the D/H and the nature of the radicals formed are comparable for ultraviolet and electron irradiation (Fig. 3, Methods section and Supplementary Fig. 4). However, each particle has its own characteristic penetration depth and ionizing efficiency. In this respect, electrons appear to be relatively versatile and are able to modify the target over several micrometres in depth. Still, our results call for a detailed comparison of the effects of these different forms of ionizing radiation at the molecular scale. Such a comparison could help to better understand the molecular processes responsible for the deuteration of organic precursors. These mechanisms are not yet clearly identified and may either operate during the interaction with the incoming particles or during the rearrangement/recombination of the material. The fact that, for a given deposited energy, ultraviolet and electron irradiation induce comparable D-enrichments suggests that fractionation may be primarily produced during recombination rather than during the interactions between a given type of particle and the organic precursors. However, this assertion must be experimentally confirmed because it would lead, in turn, to a more comprehensive description of the D/H evolution in organic matter in the protoplanetary disk regions exposed to ionizing radiation from the protosun. Finally, a better understanding of the irradiation-driven fractionation of other light elements (such as nitrogen, carbon and oxygen) should also shed new light on the nature and evolution of the extraterrestrial IOM and water reservoirs, and it might even extend our findings to CR chondrites that show strong enrichments in both heavy nitrogen and deuterium.

**Methods**

**Sample preparation and irradiation.** The PS samples were prepared by spin-coating deposition on a silicon wafer. Spin-coating is a centrifugal force-driven method for the deposition of thin films on a flat substrate. The deposition was achieved by the rotation of the substrate, on which a small quantity of the solubilized film is spread. The PS was solubilized in toluene. For a speed of 2,000 r.p.m. and a concentration of 10 wt% PS in toluene, a final thickness of 1.3 μm was obtained. After the deposition, samples were stored under secondary vacuum conditions for several hours to ensure complete evaporation of toluene and polymerization of the film. The PET samples were derived from a 10-μm-thick film (GoodFellow Cambridge Limited) and were mounted to a brass sample holder using conductive copper tape. The PET consisted of a 900-nm-thick film that was biaxially oriented and semi-crystalline (from Good Fellow Co.), and it was deposited on a brass sample holder.

Electron irradiation experiments were carried out on a Hitachi S4700 field-emission gun scanning electron microscope at 30 keV (at the Electron Microscope Facility, Université Lille 1). Electron fluences were measured with a Faraday cup. The onset of the melting of PE is typically lower than 80°C. After irradiation, the film did not show any indication of thermal degradation. We can thus estimate the temperature of the samples under the electron beam to be between 20 and 80°C. After irradiation experiments and between the different analytical steps, all samples were stored under a flow of dry argon in the dark.

Ultraviolet irradiations were performed on PET films. They were performed with a polychromatic ultraviolet lamp (Hamamatsu irradiation system) equipped with a band-pass filter at 239 nm. At this wavelength, the coupling between ultraviolet and the PET film was especially efficient\textsuperscript{24}. The nominal energy of the lamp was 300 μW cm\textsuperscript{-2}. However, the filter absorbed 80% of the incident energy at 239 nm so that the actual energy of the lamp during these experiments was estimated to be 60 μW cm\textsuperscript{-2}.

**Determination of the energy deposited (electron and ultraviolet doses).** The modifications induced by electron irradiation are directly proportional to the energy deposited in the sample\textsuperscript{22}. The fluence (that is, the number of electrons per surface unit) is an important parameter in the determination of the energy

| Electrons/cm² | 1.0 × 10²⁵ | 2.0 × 10²⁵ |
|---------------|------------|------------|
| PET           | 6          | 12         |
| PS            | 4          | 8          |
| PE            | 2          | 4          |

This table provides experimental isotopic signatures for benzilic (δD(Benz)) and aromatic (δD(Arom)) C–H functional groups determined from the irradiated samples. Derived equilibrium fractionation factors between these groups are also reported (εBenz-Arom). Measurements on the Orgueil (CC) chondrite\textsuperscript{9} and results of the experimental exchange experiments\textsuperscript{24} are reproduced for comparison.
Sample analysis. The evolution of the molecular structure of samples during irradiation was studied by infrared spectroscopy (FTIR) using the imager spotlight 300 from Perkin-Elmer at UMET, University Lille 1. Transmission spectra were collected at a raster speed of the 750–4,000 cm⁻¹ range. A linear baseline correction was applied to each spectrum between 750 and 3,700 cm⁻¹. The peak areas were evaluated using Gaussian deconvolution (the commercial Peakfit software by Systat software, Inc. was used for this purpose). For the PS film, the infrared spectra were complicated by the presence of interference fringes. These fringes were removed from the spectrum by a 200–400 Hz band-pass filter. The spectra were further corrected for instrumental mass fractionation (performed at CRPG, Nancy) and was found to be 463 ± 3%. Concentrations of organic radicals were derived from electronic paramagnetic resonance (EPR). The EPR spectra were recorded with a Bruker Elexys E300 operating at 9 GHz at LASIR, University Lille 1. Amplitude modulation and microwave power were set to 2 G and 5 mW, respectively. For ultraviolet irradiation, the film of PET (6 × 6 mm²) size was directly irradiated inside the transmission mode high sensitivity (TMHS) cavity through optical windows. The spin concentration was determined using weak pitch with a double integration procedure. Typically, in this analytical configuration, the absolute error on the spin concentration is better than 5%.

Kinetic analysis of structural and isotopic changes. All of the structural, chemical and isotopic changes presented in this study share a common kinetics during irradiation. A first-order rate law successfully describes such changes. Typically, a first-order rate law relates the time derivative of the concentration of a given species to its instantaneous concentration through a time constant. As the electron dose E is a function of both the stopping power and the electron fluence equation (1), the evolution of a quantity A is described as:

\[ \frac{dA}{dt} = -k_d · |A| \]  

where \( k_d \) is the dose constant. The integration of this relation gives access to the evolution of the quantity A as a function of the electron dose:

\[ |A| = |A_0|e^{-k_d \cdot E} \]  

where \( |A_0| \) is the initial intensity of a given feature of the polymer over an increasing dose E. The different patterns of change can be compared because the dose constant is a direct proxy for the rate of molecular change through irradiation. For this purpose, we used normalized quantities (peak areas and ratios).

Based on this fitting procedure, we determined the electron dose required for each sample to reach 90% of the plateau value (Supplementary Table 2). These doses were, in turn, used as threshold values to determine the isotopic signature of each sample at the plateau. All experiments performed at higher doses were taken into account to calculate the characteristic isotopic signature on the plateau. Typically, two data points for each polymer were found to sit on the plateau. The isotopic plateau values for each polymer were determined as the mean of the isotopic data situated on the plateau. The error was taken as the 1σ standard deviation of such data set.

Determination of intramolecular fractionation factors. As for the structural evolution, the isotopic data set shows isotopic plateaus (Fig. 3). The isotopic signatures of irradiated materials at their respective plateaux (given relative to SMOW) are 463 ± 113%, 315 ± 30% and 272 ± 60% for PE, PS and PET, respectively. The isotopic signature of each C–H bond was then determined assuming local equilibrium under the electron beam. A simple mass balance was considered because the initial relative proportions of the C–H bonds are known, and all C–H groups are lost at a comparable rate during irradiation, as discussed above. Hence:

\[ \frac{D_{H\text{H}}}{D_{H\text{D}}} \]  

\[ \Delta D_{\text{H}, \text{D}} = 463 \pm 113\% \]

\[ \frac{D_{H\text{H}}}{D_{H\text{D}}} \]  

\[ \Delta D_{\text{H}, \text{D}} = 81 \pm 126\% \]

From these molecular 5D (relative to SMOW), the intramolecular fractionation compared the intensity ratio \( H/C\text{H}_4 \) for each irradiated spot with the surrounding uniradiated material. This choice of using a molecular fragment instead of a simple ion (C⁺) is related to the analytical mode used for ToF-SIMS analysis. This setup has two advantages. First, it provides information on the evolution of the carbon skeleton through irradiation (from H⁺ to C1−H3 masses). After irradiation, the light masses (corresponding to short fragments of irradiated matter) are more abundant than heavy molecular fragments (Supplementary Fig. 3). This is the direct result of the chain scission caused by irradiation. Second, this setup reduces the carbon-based (C⁺) contamination during surface analysis. For these reasons, C1−H3 moieties were chosen as the proxy for documenting the effects of ultraviolet and electron irradiation as a function of the energy deposition in the first few hundred nanometres, which is the typical thickness analysed by NanoSIMS for the D/H measurements. The energy deposited in the film directly depends on the electronic stopping power (that is, the linear rate of the energy transfer between the incoming particle and the target). Here, the characteristic electron path and the stopping power are taken from the ESTAR database (Supplementary Table 1). To take into account both the fluence and the stopping power, all of the isotopic and structural data are presented as a function of the dose (E):

\[ E = \alpha_E F \]  

where E is the electron dose (eV cm⁻²), \( \alpha_E \) is the electronic stopping power (MeV cm⁻¹) and F is the fluence (e⁻ cm⁻²).
Factors were easily determined:

\[ \frac{D_{\text{Enzyme/Aromatic}}}{{D_{\text{Aromatic}}}} = 2.03 \pm 0.29 \]  

\[ \frac{D_{\text{Aliphatic/Aromatic}}}{{D_{\text{Aromatic}}}} = 1.35 \pm 0.19 \]  

The errors of the ratios were propagated to the \( x \) values (quadratic sums), and the relative errors of the factors were found to be lower than 14%.

**Timescale for a similar irradiation in the disk.** In a protoplanetary context, the timescale required for the irradiation to reach a dose comparable to those studied here was determined from the measured present-day energy distribution of the quiescent solar flux\(^{16}\). This distribution follows a power law where low-energy electrons (from 1 to 10 keV) are much more abundant than high-energy ones (Supplementary Fig. 5). For the low-energy range (1–10 keV), the integrated flux and the associated electron dose rate were calculated (blue and red areas in Supplementary Fig. 5). The stellar activity of the protostars has been shown to be at least three orders of magnitude higher than today\(^{19,28}\). Thus, we considered an electron flux higher than the quiescent present-day solar flux by three orders of magnitude. In this context, only a few hundred years are needed to produce the same deposited energy that was experienced in our experimental irradiations (Supplementary Table 3).

Finally, protoplanetary environments are optically thick and cold. Therefore, direct electron (photon or ion) irradiation is essentially effective on a thin and warmer layer of the disk surface. Conversely, close to the midplane, the dust is not exposed to solar particles. This shield effect, however, poorly efficient because of the vertical motions predicted to occur in a turbulent disk\(^{23}\). Current models show that micrometre-sized dust from the disk might have spent up to 5% of its lifetime at altitudes where irradiation is efficient\(^{15}\). Therefore, the doses required to reach the plateau values are completely compatible with the typical lifetime of the disk.

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**Author contributions**

B.L. performed experiments and data analysis with feedback from M.R., L.R. and H.L. and benefitting from an original idea by M.R. and L.R. NanoSIMS, Infrared spectroscopy, EPR spectroscopy and ToF-SIMS analyses were performed by L.R., C.D., H.V. and N.N., respectively. H.L. and J.-M.L. provided expertise on the physics of electron irradiation and polymers, respectively. All co-authors discussed the results. M.R. wrote the manuscript, with important contributions from L.R., F.R. and B.L.

**Additional information**

Supplementary Information accompanies this paper at http://www.nature.com/naturecommunications

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