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D/H and microstructure of irradiated organic dust analogs

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Abstract

It is unknown how the widespread organic matter in primitive Solar System materials formed. In this study, we explore UV and X-ray irradiation as drivers in the formation of organics from simple ices. We compare microstructures and H isotopic compositions of samples produced under controlled irradiation experiments simulating environments in dense molecular clouds or the outer Solar Nebula with those of natural samples. The irradiation results in an increase of δD of up to ~1000‰ and the induction of some graphitic ordering at the molecular level.

1. Introduction

Organic matter is present in a wide range of primitive Solar System materials, and how it formed is a matter of debate [1]. Organic matter in primitive meteorites has much higher D/H and $^{15}N/^{14}N$ ratios than the Sun, and the process that formed organic matter likely contributed to these heavy isotopic compositions [1]. In this project, we evaluate irradiation of ices as a formation pathway for organic matter by comparing the H mass fractionation resulting from these processes with the H isotopic compositions of natural samples. In addition, we investigate the microstructure of the samples using scanning transmission electron microscopy (STEM).

Relatively complex organic molecules can be made in the laboratory by UV irradiation of simple ices under vacuum at temperatures of ~10–15 K. These ices are believed to be present in molecular clouds and the outer Solar Nebula. UV irradiation breaks chemical bonds and forms reactive ions and radicals which will recombine upon warm-up to form more complex molecules. Organic materials that formed from ices in this manner may have been irradiated further in the Solar Nebula, resulting in the alteration of their structure, chemical composition, and/or isotopic composition [2,3]. Electron irradiation of organic matter (epoxy, cyanoacrylate, terrestrial kerogens, and polymers) can induce D-enrichments of δD up to ~1000 ‰ [2,4]. UV irradiation results in similar D enrichments [4]. Consequently, it appears that the type of irradiation resulting in changes in H isotopic composition is not as important as the total energy deposited into the organics [4]. In this study, we investigate the microstructure and D/H ratios of organics produced from astrophysical ice analogs of different compositions, and how these D/H ratios vary when these organics are irradiated with different energies and doses of X-ray photons.

2. Methods

Samples were produced at the Astrochemistry Laboratory of NASA Ames following the methods in [5]. Four different starting ice mixtures were used: H_2O:CH_3OH:CO:NH_3 = 100:50:10:10 (B22, B18), and 100:50:20:10 (C3), H_2O:CH_3OH:CO:NH_3:$C_{10}H_8$ = 100:50:10:10:1 (B21, B23, B19) and 100:50:20:10:1 (C5). The most significant difference between the samples is that some contain naphthalene ($C_{10}H_8$) and some do not. The recovered samples were further irradiated with X-rays with different energies, broad band (80-450 eV) or C edge (293 eV), and durations at room temperature (RT) and under vacuum at the National Synchrotron Radiation Research Center (NSRRC) in Taiwan.

Irradiated and un-irradiated fractions of the samples were analyzed for H isotopic compositions using the Carnegie Cameca NanoSIMS 50L. For each sample, at least five particles were analyzed. Data is presented as permil deviations relative to SMOW (Fig.1). Some samples were also analyzed with the Nion UltraSTEM 200-X at NRL, Washington DC.

Annular dark field images and electron energy loss spectra were collected at 60 kV to assess structures and C bonding.

3. Results

The samples that were analyzed using STEM all appeared amorphous in the images. Electron energy loss (EELS) spectra indicate that the RT post-irradiation induces some degree of graphitic ordering on a molecular scale in all samples, but there were no indications of crystalline graphite. There are no obvious variations in the degree of graphitization with radiation energy or dose in the samples analyzed so far.

All X-ray irradiated samples were enriched in D compared to SMOW (Fig. 1). In the samples without naphthalene, enrichment of D relative to H appears to have occurred already during the formation of organics from ices under UV light, with δD between ~500 ‰ and 1200 ‰ (Fig. 1). The equivalent, not post-irradiated samples with naphthalene tend not to be enriched in D. Instead, D enrichment in the samples with naphthalene tends to occur during X-ray irradiation, probably due to the loss of H atoms as bonds break [4]. δD in the samples without naphthalene appears to decrease with increasing photon dose. This is harder to understand and indicates that processes induced by irradiation of these samples are more complex than previously thought.

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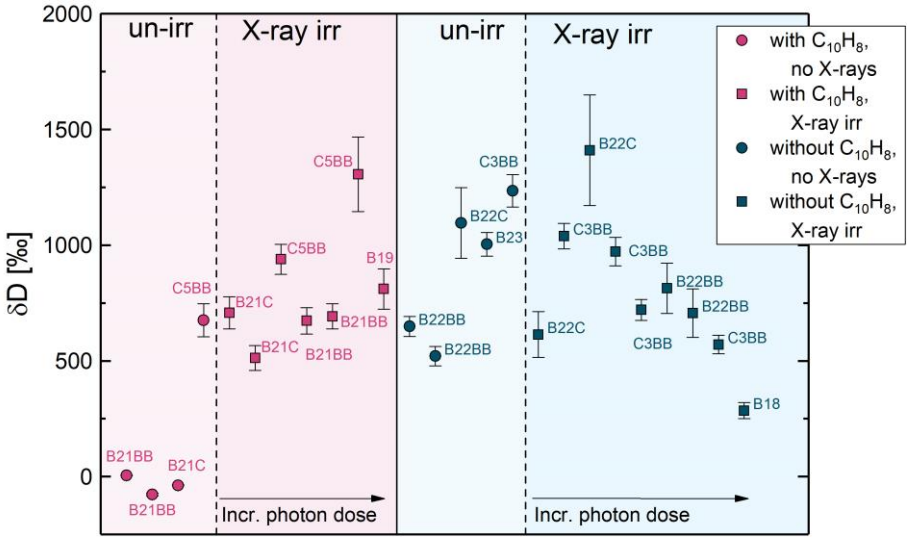

Figure 1. δD of the samples analyzed so far. The samples are divided into two groups: with (pink) and without (blue) naphthalene. The samples are ordered relatively to the increasing photon dose, but the photon dose is not to scale.