DEUTERIUM-HYDROGEN EXCHANGE BETWEEN ORGANIC MATTER AND WATER: IMPLICATIONS FOR CHEMICAL EVOLUTION DURING ASTEROIDAL PROCESSING.

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Introduction: The high deuterium (D) enrichment in insoluble organic matter (IOM) in chondrites has largely been attributed to low temperature chemistry in the interstellar medium (ISM) or the early outer Solar System. Therefore, IOM is proposed to form in the icy mantles of interstellar dust grains through UV-induced photopolymerization of low molecular weight organic molecules [1]. Alternatively, a possible scenario of IOM formation has been proposed using interstellar formaldehyde (CH_2O) through the polymerization after planetesimal accretion, in the presence of liquid water [2]. Highly deuterated formaldehyde is observed in ISM, e.g., the $[CD_2O]/[CH_2O]$ abundant ratio in star forming region in ISM is 0.02-0.4 [3]. However, even among the highest D-enriched IOM has significantly lower (by a factor of ~2) D content compared with ISM molecules, e.g., a CR1 chondrite GRO95577 has a δD of 3303‰ [4]. While water in the solar system is much depleted in D, e.g., D/H ratio of water in comet 103P/Hartley 2 is 2.96×10^{-4} (close to the terrestrial water values) [5]. Thus, D-H exchange between D enriched IOM precursor and D depleted water could have occurred during and/or after the formation of IOM.

Here we report D-H exchange experiments between organic matter and water during and after IOM synthesis.

D-H exchange experiments: Our recent study revealed that IOM in primitive chondritic meteorites is predominantly derived from the polymerization of interstellar formaldehyde with incorporation of ammonia, evidenced by molecular spectroscopic characters [6]. We conducted two series of D-H exchange experiments based on the formaldehyde polymerization hypothesis; (1) D-H exchange between formaldehyde and water during formaldehyde polymer (FP) synthesis, and (2) D-H exchange between FP and water.

(1) D-H exchange between formaldehyde and water. The starting aqueous solution contained formaldehyde 2 mol/l and glycolaldehyde ($C_2H_4O_2$) 1 mol/l, $Ca(OH)_2$ 0.2 mol/1, NH_4OH 0.4 mol/l (N/C atomic ratio = 0.1). We prepared these solutions with (a) CD_2O (99 atom % D) and D_2O (D_2O/H_2O = 9/1, v/v), (b) CH_2O and D_2O, (c) CD_2O and H_2O, and (d) CH_2O and H_2O. The solutions were sealed in glass tubes and heated at 250ºC for 72 hours. After the heating, the supernatants were removed and the residues were washed with 2N HCl to remove bound calcium ions.

The FPs were then washed with deionized water and dried.

(2) D-H exchange between formaldehyde polymer (FP) and water. The most D-enriched FP $[CD_2O+D_2O]$ and the most D-depleted FP $[CH_2O+H_2O]$ which obtained from experiment #1 were selected as starting materials of D-H exchange experiments. The FP $[CD_2O+D_2O]$ was heated in H_2O, and the FP $[CH_2O+H_2O]$ was heated in D_2O (D_2O/H_2O = 9/1, v/v), at 150ºC, 200ºC and 250ºC for 1 hour up to 504 hours (21 days) in sealed glass tubes.
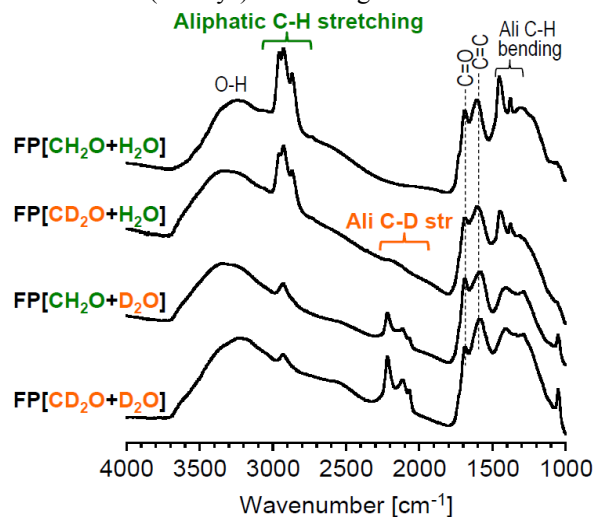

Fig.1: FTIR spectra of formaldehyde polymers (FPs).

Results and Discussion: *(1) D-H exchange between formaldehyde and water.* Fig. 1 shows Fourier transform infrared (FTIR) spectra of FPs. FPs synthesized with D_2O show large aliphatic C-D bands with small aliphatic C-H bands regardless of starting with CD_2O or CH_2O. FP with CD_2O and H_2O shows small aliphatic C-D bands and large aliphatic C-H bands. FP with CH_2O and H_2O shows aliphatic C-H bands and no C-D band was observed. The aliphatic C-D/C-H band area ratios obtained from IR spectra are shown in Fig. 2. These results indicate that most of the hydrogen in FPs is derived from water.

(2) D-H exchange between formaldehyde polymer (FP) and water. Fig. 2 shows the IR C-D/C-H band area ratio change with time. Three-dimensional diffusion was found to be the best fit for these D-H exchange profiles among the rate laws tested (fit curves are shown in Fig. 2).
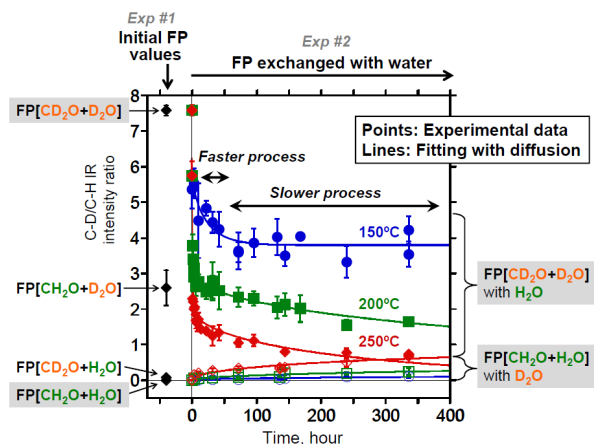
Fig. 2: The IR C-D/C-H band area ratios change with time. The C-D/C-H ratios of FPs obtained from experiment #1 are also shown.

For the D-poor FP exchanged with D_2O, the apparent reaction rate constants k were obtained by the fitting curves with the three-dimensional diffusion equation:

$$I_{D/H} = \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp(-n^2 kt), \quad k = \frac{D\pi^2}{a^2} \qquad (1)$$

where $I_{D/H}$ is the IR C-D/C-H band area ratio, t is the time, D is the diffusion coefficient, and a is the radius of the polymer particles. For the D-rich FP exchanged with H_2O, the apparent reaction rate constants k_1 (faster reaction) and k_2 (slower reaction) were obtained by the fitting curves with a combination of three-dimensional diffusion equations. Then the apparent activation energies E [kJ/mol] and the frequency factors A [s^{-1}] are obtained by the apparent rate constants k and the reaction temperatures T with the Arrhenius equation:

$$\ln k = \ln A - \frac{E}{RT} \qquad (2)$$

where R is the gas constant, and T is the temperature. The kinetic parameters were obtained as $E = 80 \pm 5$, $\ln A = 3.5 \pm 1.2$ for the D-poor FP exchanged with D_2O, and as $E_1 = 53 \pm 11$, $\ln A_1 = 5.3 \pm 2.8$ (faster reaction), $E_2 = 67 \pm 7$ and $\ln A_2 = 1.4 \pm 1.7$ (slower reaction) for the D-rich FP exchanged with H_2O.

Now that the relationship between time t, temperature T and C-D/C-H band ratio $I_{D/H}$, with the equations 1 and 2, is established. Using obtained kinetic expressions, D-H exchange profiles can be estimated for a certain time and temperature, as shown in Fig. 3, based on the assumption that the kinetic rate low is invariance. These diagrams indicate that D-H exchange of polymers with D-rich water is slower than with D-poor water.

For primitive carbonaceous chondrites, it is possible to assume that D/H ratio of IOM decreased by exchanging with D-depleted water. For example, starting from the value of GRO 95577 ($\delta D=3303‰$, D/H=0.00067 [4]) down to the value of Murchison ($\delta D=811‰$, D/H=0.00028 [4]), the time scales of alteration are estimated as 5 years at 100°C, 100 years at 50°C, and 10^4 years at 0°C using the obtained kinetic expression. For ordinary chondrites, D/H ratio of IOM might have increased by exchanging with D-rich water [4]. For example, starting from the values of Murchison up to the values of WSG 95300 ($\delta D=11850‰$, D/H=0.002 [4]), the time scales of alteration can be estimated as 6 months at 200°C, and 100 years at 100°C.
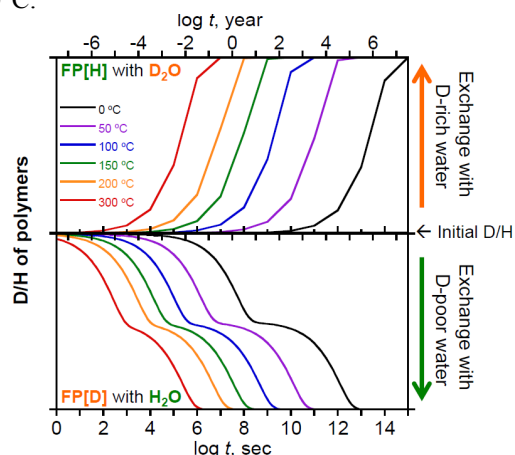

Fig. 3: D-H exchange profiles of polymers calculated by the experimental kinetic parameters.

Conclusions: Experimental simulations of D-H exchange between organic matter and water were conducted considering the following two processes; (1) IOM polymerization process starting with formaldehyde in the presence of water, and (2) D-H exchange between water and IOM. Most of the hydrogen in IOM might be derived from water during polymerization. The D-H exchange also occurs after polymerization. We obtained the kinetic expressions of D-H exchange between D-rich FP and D-poor water, and between D-poor FP and D-rich water. The estimated D-H exchange timescales between IOM and water may be determined experimentally.

References: [1] Greenberg J. M. et al. (1995) *ApJ, 455,* L177. [2] Cody G. D. et al. (2011) *PNAS, 108,* 19171-19176. [3] Loinard L. et al. (2002) *Planet. Space Sci., 50,* 1205-1213. [4] Alexander C. M. O'D. et al. (2010) *GCA, 74,* 4417-4437. [5] Hartogh P. et al. (2011) *Nature, 478,* 218-220. [6] Kebukawa et al. (2013) *ApJ, 771,* 19.