

DEUTERIUM-HYDROGEN EXCHANGE KINETICS: IMPLICATIONS FOR EARLY CHEMICAL EVOLUTION OF CHONDRITIC INSOLUBLE ORGANIC MATTER. Y. Kebukawa and G. D. Cody, Geophysical Laboratory, Carnegie Institution of Washington, 5251 Broad Branch Rd NW, Washington DC, 20015, USA (ykebukawa@ciw.edu).

Introduction: The high deuterium enrichment in insoluble organic matter (IOM) in chondrites has largely been attributed to small molecule chemistry prior to IOM, in the results of ion-molecule interactions at low temperature ($< \sim 200^{\circ}\text{K}$) interstellar medium (ISM) [1]. A possible synthesis scenario of IOM formation has been proposed using interstellar formaldehyde [2]. Highly deuterated formaldehyde is observed in ISM, e.g., the $[\text{HDCO}]/[\text{H}_2\text{CO}]$ abundance ratio in molecular clouds is 0.01-0.03 [3], and the $[\text{D}_2\text{CO}]/[\text{H}_2\text{CO}]$ abundant ratio in star forming region in ISM is 0.02-0.4 [4]. 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‰ [5]. 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) [6]. 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 kinetics obtained using laboratory synthesized organic polymers, in order to evaluate the D-H exchange between D enriched organic polymers and D depleted water.

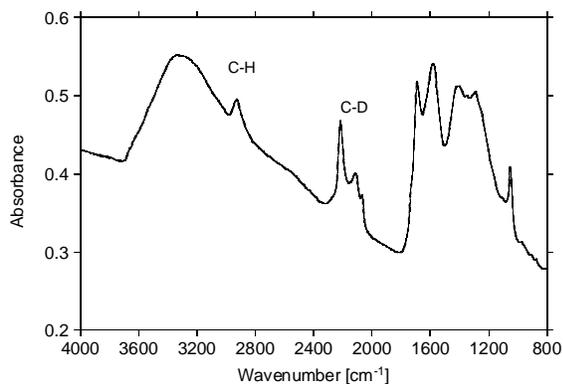


Fig. 1: An FTIR spectrum of D-FormPoly before starting exchange experiments.

D-H exchange experiments: Our recent study revealed that insoluble organic matter (IOM) in primitive chondritic meteorites is predominantly derived from the polymerization of interstellar formaldehyde with incorporation of ammonia, evidenced by molecular spectroscopic characters [2,7]. We used laboratory synthesized D enriched formaldehyde polymer (D-

FormPoly) as a starting material of D-H exchange experiments. The polymers were incubated in H_2O at 150°C , 200°C and 250°C for 1 hour up to 504 hours (21 days) in sealed glass tubes. Fourier transform infrared (FTIR) spectra of D-FormPoly were collected after the incubations. Fig. 1 shows an FTIR spectrum of D-FormPoly before starting exchange experiments. We use a peak area ratio of an aliphatic C-H stretching band at $2985\text{-}2835\text{ cm}^{-1}$ and an aliphatic C-D stretching band at $2250\text{-}2055\text{ cm}^{-1}$ as an indicator of D-H exchange.

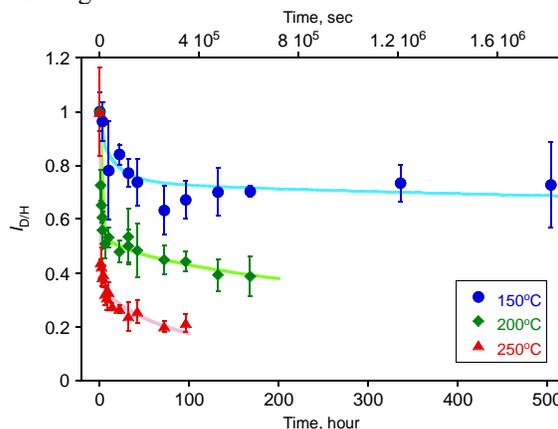


Fig. 2: Changes with time in C-D/C-H band area ratio, fitted by the three-dimensional diffusion rate law (solid curves). The C-D/C-H ratio $I_{D/H}$ is normalized by an initial D-FormPoly value.

Results and Discussion: Fig. 2 shows the IR C-D/C-H band area ratio ($I_{D/H}$) change with time. The D-H exchange rates were faster in the higher incubation temperatures. Several kinetic rate laws were considered for these D-H exchange profiles, e.g., n -order reaction and diffusion. Three-dimensional diffusion was found to be the best fit among the rate laws tested (fit curves are shown in Fig. 2). 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 [8]:

$$I_{D/H} = b \cdot \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-n^2 k_1 t) + (1-b) \cdot \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-n^2 k_2 t),$$

$$k_i = \frac{D_i \pi^2}{a^2} \quad (i = 1, 2) \quad (1)$$

where t is the time, D_i is the diffusion coefficient, a is the radius of the polymer particles, and b is the fraction of the faster reaction. Then the apparent activation energy E_i [kJ/mol] and the frequency factor A_i [s⁻¹] are obtained by the apparent rate constants k_i and the temperature T with the Arrhenius equation:

$$\ln k_i = \ln A_i - \frac{E_i}{RT} \quad (2)$$

where R is the gas constant, and T is the temperature. The kinetic parameters were obtained as $E_1 = 63 \pm 11$, $\ln A_1 = 7 \pm 3$, $E_2 = 104 \pm 11$ and $\ln A_2 = 10 \pm 3$.

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. Compared with aliphatic C-H loss profiles (dashed curves in Fig. 3) which is obtained by Murchison IOM [9], D-H exchange occurs faster than aliphatic loss in lower temperature range (<~200°C). This result suggests that D in highly D enriched IOM precursor could exchange with H in D depleted water without significant molecular structure change in low temperature aqueous alteration process.

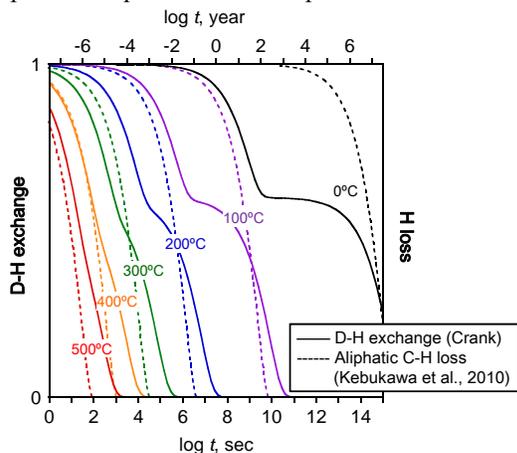


Fig. 3: D-H exchange profiles for several temperatures. Dashed curves are aliphatic C-H loss profiles obtained by Murchison IOM [9].

The diffusion controlled D-H exchange is consistent with the fact that organic nano-globules have higher δD values compared with fluffy IOM [10]. Because the D-H exchange rate k_i depends on the grain size a (see eq. 1), therefore final D/H values depends on the grain size as shown in Fig. 4.

Combined D-H exchange kinetics with polymer yield kinetics [11], we obtain D/H population histogram for a certain alteration time and temperature, e.g., 300,000 years and 0°C (Fig. 5). It shows the popula-

tion peak at low D/H and a tail towered to higher D/H with decreasing population, consistent with observed δD population of chondritic IOM [12].

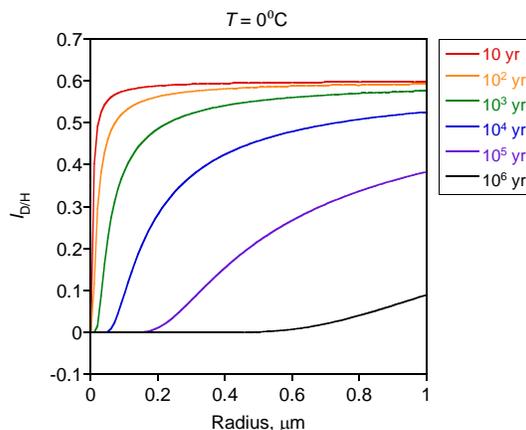


Fig. 4: D-H exchange profiles with the grain size at 0°C.

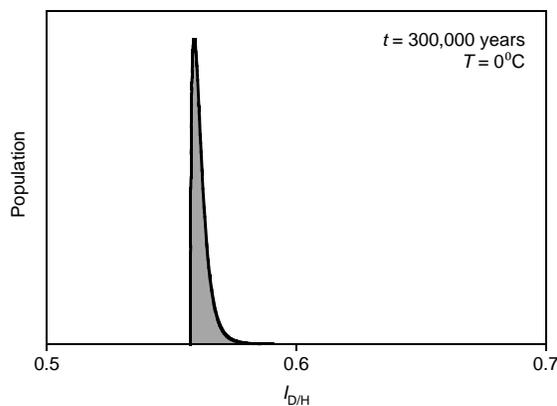


Fig. 5: D/H population histogram for the alteration of 300,000 years at 0°C.

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References: [1] Robert F. and Epstein S. (1982) *GCA*, 46, 81-95. [2] Cody G. D. et al. (2011) *PNAS*, 108, 19171-19176. [3] Loren R. B. and Wootten A. (1985) *APJ*, 299, 947-955. [4] Loinard L. et al. (2002) *Planet. Space Sci.*, 50, 1205-1213. [5] Alexander C. M. O'D. et al. (2010) *GCA*, 74, 4417-4437. [6] Hartogh P. et al. (2011) *Nature*, 478, 218-220. [7] Kebukawa Y. et al. (2010) *Meteoritics & Planet. Sci.*, 45, A103. [8] Crank J. (1970) In *Mathematics of Diffusion*. [9] Kebukawa Y. et al. (2010) *Meteoritics & Planet. Sci.*, 45, 99-113. [10] Nakamura-Messenger K. et al. (2006) *Science*, 314, 1439-1442. [11] Kebukawa Y. et al. in preparation. [12] Herd C. D. K. et al. (2011) *Science*, 332, 1304-1307.