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D-H exchange kinetics between organic solids and water: Implications for D/H content in chondritic organic matter

D-H exchange kinetics between organic solids and water: Implications for D/H content in chondritic organic matter

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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 (<˜200 K) interstellar medium (ISM) [1]. A possible synthesis scenario of IOM formation has been proposed using highly deuterated interstellar formaldehyde [2]. However, even among the highest D enriched IOM has significantly lower (by a factor of ˜2) D content compared with ISM molecules [3]. While water in the solar system is much depleted in D [4]. 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.

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 [2,5]. In addition, montmorillonite (clay mineral) was shown to enhance the yield of the formaldehyde polymer. 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^{o}C, 200^{o}C and 250^{o}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. We use a peak area ratio of an aliphatic C-H stretching band at 2985-2835 cm^{-1} and an aliphatic C-D stretching band at 2250-2055 cm^{-1} as an indicator of D-H exchange.

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. The apparent reaction rate constants were obtained by the fitting curves with a combination of three-dimensional diffusion equations [6]. Then the apparent activation energy and the frequency factor are obtained by the apparent rate constants and the temperature with the Arrhenius equation.

Using obtained kinetic expressions, D-H exchange profiles can be estimated for a certain time and temperature, based on the assumption that the kinetic rate low is invariance. Compared with aliphatic C-H loss profiles which is obtained by Murchison IOM [7], D-H exchange occurs faster than aliphatic loss in lower temperature range (<˜200^{o}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.

The diffusion controlled D-H exchange is consistent with the fact that organic nano-globules have higher D/H values compared with fluffy IOM [8]. Because the D-H exchange rate depends on the grain size, therefore final D/H values depends on the grain size.

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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] Alexander C. M. O ’D. et al. (2010) GCA, 74, 4417-4437. [4] Hartogh P. et al. (2011) Nature, 478, 218-220. [5] Kebukawa Y. et al. (2010) Meteoritics & Planet. Sci., 45, A103. [6] Crank J. (1970) In Mathematics of Diffusion. [7] Kebukawa Y. et al. (2010) Meteoritics & Planet. Sci., 45, 99-113. [8] Nakamura-Messenger K. et al. (2006) Science, 314, 1439-1442.

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