

ISOTOPE IMAGING AND THE KINETICS OF DEUTERIUM-HYDROGEN EXCHANGE BETWEEN INSOLUBLE ORGANIC MATTER AND WATER. Y. Kebukawa^{*1}, S. Kobayashi², N. Kawasaki¹, G. D. Cody³, and H. Yurimoto^{1,2}, ¹Department of Natural History Sciences, Hokkaido University, N10 W8, Sapporo, 060-0810, Japan, ²Isotope Imaging Laboratory, Creative Research Institution Sousei, Hokkaido University, N21 W10, Sapporo, 001-0021, Japan, ³Geophysical Laboratory, Carnegie Institution of Washington, 5251 Broad Branch Rd NW, Washington DC, 20015, USA. *yoko@ep.sci.hokudai.ac.jp

Introduction: The high deuterium 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 [e.g. 1]. The IOM in carbonaceous chondrites has various D/H ratios that generally decrease with increasing alteration, while the IOM in ordinary chondrites has large D enrichments that increase with increasing metamorphism [2]. In either case, the differences in H isotopic compositions among chondrites are likely the result of kinetic isotopic exchange between IOM and water [2].

We have studied kinetics of D-H exchange between organic matter and water, using laboratory analog of IOM derived from the polymerization of formaldehyde with incorporation of ammonia [3,4]. We previously proposed the three-dimensional diffusion model to fit the experimental curves, since this model gave the best fit [5,6]. If the D-H exchange rates are controlled by diffusion, one expects to observe a classical diffusion profile into the organic grains. Here we report the results of isotope microscope analyses of the D-H exchanged IOM analog (Formaldehyde Polymers; FP).

Experimental: We conducted D-H exchange experiments between FP and water starting with D-enriched FP (FP-D) and the normal FP (FP-H). The FP-D was heated in H₂O, and the FP-H was heated in D₂O (D₂O/H₂O = 9/1, v/v), 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 FPs were collected in order to obtain the aliphatic C-D/C-H band area ratios (Fig. 1).

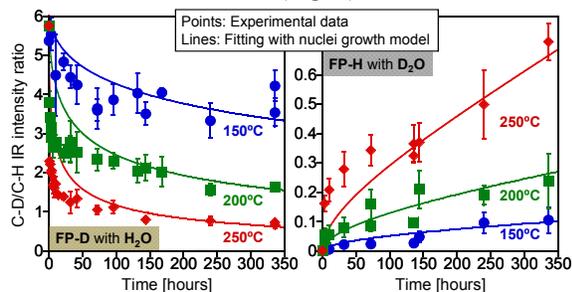


Fig. 1: The C-D/C-H ratios with time obtained by FTIR.

Hydrogen isotopes were measured on the D-H exchanged FP-D grains by in-situ quantitative isotope ratio imaging using HokuDai isotope microscope sys-

tem (Cameca ims-1270 equipped with Stacked CMOS-type Active Pixel Sensor; SCAPS [7]). The sample surface was homogeneously irradiated over a field area of $\sim 100 \times 100 \mu\text{m}^2$ using a rasterized Cs⁺ primary beam. The primary beam was set to 20 keV and 2–5 nA.

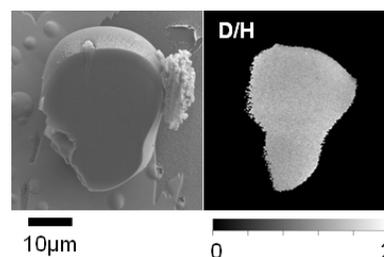


Fig. 2: (left) A SEM image of cross-sectioned FP-D grain exchanged with H₂O for 3h at 200°C. (right) An isotope image of D/H count ratios for the cross-sectioned grain surface.

Results and Discussion: Fig. 2 shows isotope image of D/H count ratios for a focused ion beam (FIB) milled cross-section surface of the FP-D grain exchanged with H₂O for 3h at 200°C. If the D-H exchange rates are controlled by diffusion into the particles as previously proposed [5,6], one expects a contoured D/H profile across the the FP-D grain; D/H ratio decreases from the center to the edge. However, D/H ratio of the cross-section surface of the grain is quite homogeneous. We also obtained the relationship between the grain size of FP-D and D/H ratios (Fig. 3). No relationship was observed between the FP grain sizes and D/H ratios. These results indicate that the D-H exchange between FP and water is *not* controlled by diffusion. Alternatively, after an attempt to fit with several kinetic rate laws, Avrami-Erofeev nuclei growth model was found to be the best fit for the experimental data sets of the D/H ratios of FP exchanged with water (Fig. 1). The nuclei growth model explains well the homogeneous D/H distributions in inter- and intra- grains, since this model considers the nucleation of products at active sites ($-\text{C}-\text{D}$ replaced by $-\text{C}-\text{H}$, and vice versa) and the rate at which the nucleated particles grow [8]. The active sites are expected to be homogeneously distributed in the FP grains and to be smaller than the spatial resolution of the isotope imaging.

The apparent reaction rate constants k were obtained by the fitting curves with the Avrami-Erofeev nuclei growth model:

$$kt = [-\ln(1 - \alpha)]^2 \quad (1)$$

where α ($0 \leq \alpha \leq 1$) is the degree of reaction progress defined by $\alpha = 1 - [D/(D+H)]/[D/(D+H)]_{t=0}$ for FP-D exchanged with H_2O , and $\alpha = [D/(D+H)]$ for FP-H exchanged with D_2O . The $D/(D+H)$ was obtained by the IR C-D/C-H band area ratio. The apparent activation energies E [kJ/mol] and frequency factors A [s^{-1}] are obtained by the apparent rate constants k and the reaction temperatures T with the Arrhenius equation:

$$\ln k = \ln A - E/RT \quad (2)$$

where R is the gas constant, and T is the temperature. The kinetic parameters were obtained as $E = 78 \pm 4$, $\ln A = 2.5 \pm 1.0$ for the FP-D exchanged with H_2O , and as $E = 56 \pm 3$, $\ln A = -1.3 \pm 0.8$ for the FP-H exchanged with D_2O .

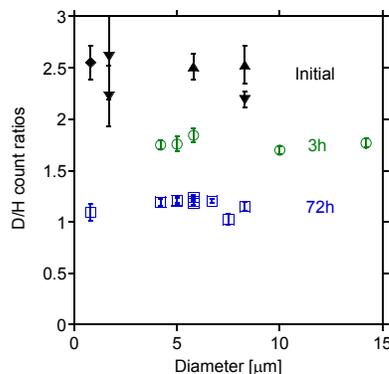


Fig. 3: The relationship between the D/H ratio and the grain size of FP-D exchanged with H_2O at $200^\circ C$ for 3 hours (green) and 72 hours (blue). Errors are one standard deviation.

Using obtained kinetic expressions, D-H exchange profiles can be estimated for any time and temperature, as shown in Fig. 4, based on the assumption that the kinetic rate law is invariant.

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 ($\delta D = 3303\%$ [2]) down to the value of Murchison ($\delta D = 811\%$ [2]), the time scales of alteration are estimated as 400 years at $100^\circ C$, 2×10^4 years at $50^\circ C$, and 4×10^6 years at $0^\circ C$ using the obtained kinetic expression. For ordinary chondrites, D/H ratio of IOM might have increased by exchanging with D-rich water [2]. For example, starting from the values of Murchison up to the values of WSG 95300 ($\delta D = 11850\%$ [2]), the time scales of alteration can be estimated as 10 years at $100^\circ C$, 200 years at $50^\circ C$, and 1×10^4 years at $0^\circ C$.

The variation of bulk IOM D/H ratios for each chondrite would be explained by the differences of alteration temperatures, time scales or isotopic compositions of fluid. However, δD hot spots [9,10] and var-

ious δD values observed in single meteorite [11] cannot be explained by the differences of alteration conditions, and indicating the differences in initial D/H composition of organic matter.

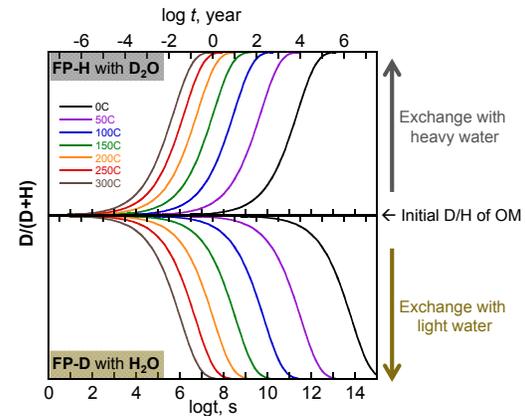


Fig. 4: D-H exchange profiles of organics calculated by obtained kinetic expressions.

Conclusions: We have conducted experimental simulations of D-H exchange between organic matter and water using FP as an analog of IOM. Our new isotope imaging data of the experimental products indicates that the D-H exchange is *not* controlled by diffusion as we previously proposed. Alternatively, Avrami-Erofeev nuclei growth model was found to be the best fit for the experimental data of the D-H exchange between FP and water, and explained well the homogeneous distribution of D/H ratio in the FP grains. 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. The homogeneous H isotope exchange indicates the difference in initial isotopic compositions for D-rich hot spot and organic nanoglobules.

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