Equilibrium D/H Fractionation of Organic Hydrogen

A.L. SESSIONS[1] AND Y. WANG[1]

[1] Department of Geological and Planetary Sciences, California Insitute of Technology; ywjojo@gps.caltech.edu; als@gps.caltech.edu

Interpretations of D/H data from ancient organic molecules must generally address the possibility of isotopic exchange with ambient water. A lack of systematic changes in δD of organic molecules with age is commonly used to infer the lack of exchange, as are large differences in the D/H ratios of organic molecule and water. Implicit in this argument is the assumption that organic molecules are far from isotopic equilibrium with environmental water. Yet there are currently no experimental data to buttress the assumption. The goal of our current study is to experimentally measure the relevant equilibrium fractionation factors in model organic compounds.

Rapid isomerization of keto and enol forms of ketones under acidic or basic catalysis produces rapid equilibration of alpha-H on timescales of days, facilitating experimental measurements. A cyclic ketone, cyclohexanone, was incubated with four waters of varying D/H ratio under acidic or basic conditions, at 25, 50, or 70°C, and for up to 3 weeks. Exchange was quantified by measuring substrate δD values by GC-IRMS at discrete time intervals. Isotopic equilibrium was confirmed via attainment of constant δD values, and was approached from both directions.

The equilibrium fractionation factor (α) for alpha-carbonyl H can be calculated from the slope of the correlation line between δD(substrate) and δD(water) at equilibrium. At 25°C and 50°C, α is found to be 0.832 ± 0.016 and 0.811 ± 0.015 respectively. The increase in fractionation with increasing temperature is unexpected, but also reproducible. Preliminary exchange experiments under acid catalysis show that the equilibrium fractionation is ~10‰ larger compared to base catalysis at the same temperature, while the exchange half-live is about two orders of magnitude longer when $[H^+]$ is equivalent to $[OH^-]$ in base-catalyzed experiments. The uncertainty in our estimate of fractionation factors is about one order of magnitude lower than previous estimates based on spectroscopic data.

The measured equilibrium fractionations are similar to the range of δD values observed in n-alkyl lipids of living organisms. If our results are representative of methylenic H, then most n-alkyl lipids are close to H-isotopic equilibrium with environmental waters. We suggest that the biosynthetic fractionation of hydrogen in n-alkyl lipids is probably affected by the rapid equilibration of ketonic α-H in the acetogenic pathway. Regardless, our results imply that constant δD values over time for these lipids cannot be used as *de facto* evidence for a lack of exchange.