Equilibrium D/H fractionation of carbon-bound hydrogen

YING WANG AND ALEX L. SESSIONS

Department of Geological and Planetary Sciences, California Institute of Technology (ywjojo@gps.caltech.edu, als@gps.caltech.edu)

As sedimentary organic matter (SOM) thermally matures, δD values of individual hydrocarbons increase steadily while biosynthetic offsets between linear and isoprenoid lipids steadily disappear [1]. Both observations can potentially be explained by extensive H exchange, but this has been difficult to test because the equilibrium fractionations for organic H are not well known. To remedy this situation, we have experimentally measured equilibrium fractionation for select molecules, and used the results to calibrate ab initio computational estimates. Since most aliphatic H exchanges very slowly [2], we take advantage of keto-enol tautomerism that leads to fast equilibration of H adjacent to the carbonyl group (α-H). Seven ketones, including straight, branched and cyclic chains, were incubated individually with 7-9 waters of varying δD at 25°C, 50°C, or 70°C, until equilibrium was achieved. Fractionation factors (ε values) for α-H are then obtained by regressing δD of ketones vs. waters. Based on our experimental data, ε is on the level of -160‰, -120‰ and +10‰ for methyl, methylenic and tertiary α-H respectively.

Molecular vibrations for the same ketones were then computed using density functional theory (DFT; B3LYP/6-311g** basis set with solvation effect), and ε for all H positions in the ketones was calculated and calibrated using the experimental data for α-H positions. Based on these computations, the average ε over the range of 10°C to 90°C is -137‰, -75‰ and -3‰ for aliphatic methyl, methylenic and tertiary H respectively (fig. 1). The temperature dependence is observed to be positive for $\varepsilon < -110‰$ and negative for $\varepsilon > -110‰$. By summing the effects for individual positions, we predict ε values between -80‰ and -90‰ for *n*-alkanes (ε increases with chain length), ~-96‰ for pristane and ~-100‰ for phytane. These estimates agree well with field data for matured hydrocarbons (-80‰ to -110‰) [1].

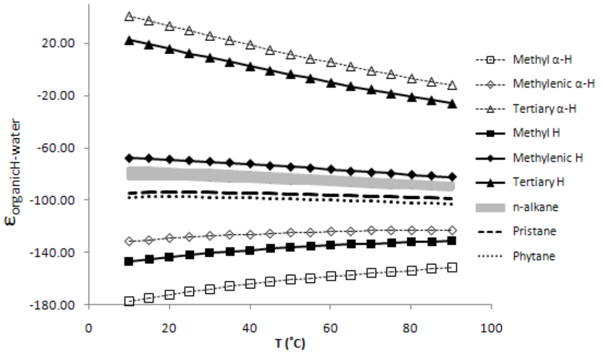

Figure 1: Predicted equilibrium fractionations between organic H and water from calibrated DFT calculations.

[1] Schimmelmann *et al.* (2006) *Annu. Rev. Earth. Planet. Sci.* **34**, 501-533. [2] Sessions *et al.* (2004) GCA, **68**, 1545-1559.

Impact of *S. oneidensis* MR-1 biofilm coatings on trace element partitioning at metal-oxide/water interfaces: A long period XSW-FY study

YINGGE WANG[1]*, A. GELABERT[1], J. HA[1], G. ONA-NGUEMA[1], J. GESCHER[2], C. CORDOVA-ARDY[2], J.R. BARGAR[3], J. ROGERS[3], P.J. ENG[4], S.K. GHOSE[4], A.M. SPORMANN[2] AND G.E. BROWN, JR.[1,3]

[1]Dept.of Geological and Environmental Sciences, Stanford University, Stanford, CA 94305, USA (*correspondence: ygwang@stanford.edu)
[2]Dept. of Civil and Environmental Engineering, Stanford University, Stanford, CA 94305, USA
[3]Stanford Synchrotron Radiation Laboratory, SLAC, Menlo Park, CA 94025, USA
[4]GSECARS, University of Chicago, Chicago, IL 60637, USA

The effects of the microbial biofilms on mineral reactivity and geochemical cycling of metal(loid) ions are poorly understood at a molecular level. In this study, long-period X-ray standing wave-florescence yield (XSW-FY) spectroscopy was used to measure *in situ* partitioning of trace metal(loid) ions at *S. oneidensis* MR-1 biofilm-coated α-alumina (0001), (1-102) and hematite (0001) single crystal surfaces. The competitive sorption effects between various metal(loid) ions were also probed by exposing biofilm/mineral interfaces to different trace elements simultaneously.

Aqueous Pb(II) and Zn(II) XSW-FY partitioning profiles at biofilm/mineral interfaces with concentrations ranging from 10^{-4} M to 10^{-7} M at pH 6 showed that at low concentrations The effects of the Pb(II) was preferentially sorbed at the mineral surfaces (10^{-7} M for α-alumina (1-102) surface), and partitioned more and more into biofilms at higher concentration. These observations confirm that biofilms do not block the reactive sites of mineral surfaces, and instead they provide more sorption sites for metal(loid) ions. Hematite (0001) was found to be the most reactive surface for metal ion sorption at these complex interfaces followed by α-alumina (1-102) and α-alumina (0001). Furthermore a competitive effect between Pb(II) and Zn(II) was observed at low metal concentrations ($\leq 10^{-6}$ M), longer exposure time, and in the presence of multiple cations: Pb(II) partitioned more into the biofilms, whereas Zn(II) partitioned more to the metal oxide surface.