On the temperature dependence of mineral surface protonation and ion adsorption reactions

DAVID J. WESOLOWSKI[1] MICHAEL L. MACHESKY[2], SERGUEI N. LVOV[3], MILAN PREDOTA[4], MOIRA K. RIDLEY[5] AND PETER T. CUMMINGS[6]

[1]Oak Ridge National Laboratory, Oak Ridge, TN 37831-6110, USA (wesolowskid@ornl.gov)
[2]University of Illinois, Champaign, IL 61820, USA
[3]The Pennsylvania State University, University Park, PA 16802, USA
[4]University of South Bohemia, 370 05 Ceske Budejovice, Czech Republic
[5]Texas Tech University, Lubbock, TX 79409, USA
[6]Vanderbilt University, Nashville, TN 37235, USA

The vast majority of mineral surface reaction studies have been conducted at room temperature. However, many processes of interest in the geosciences, materials and chemical sciences, electrical power generation, ore processing, chemical industries, etc., involve the interaction of aqueous solutions with mineral surfaces at elevated temperatures. Fortunately, recent advances in experimental, analytical, computational and theoretical approaches have greatly expanded our understanding of the temperature dependencies of surface protonation reactions and the resulting surface charge development. There is a smaller, but growing body of literature, including the extensive studies by this research team of rutile (alpha-TiO_2), on the changes in ion adsorption equilibria with increasing temperature, which are intimately related to surface protonation equilibria. We will review these studies and demonstrate broad generalities relatable to the properties of homogeneous hydrothermal solutions. Ion pairing equilibria and the acid-base properties of aqueous species change profoundly, and have profound effects on system behaviour, with increasing temperature. Similarly, we show that ion adsorption is greatly enhanced at elevated temperatures and surface protonation equilibria have become both readily measurable and predictable. It is no longer necessary or appropriate to ignore temperature effects on surface reactions, and this information is critically needed to make fundamental advances in our understanding of, for instance, heterogeneous reaction rates and mechanisms.

$$t_1 = \frac{m_{phyto}}{f_{Si}} = 500\,yrs \qquad t_2 = \frac{r^0}{\lambda k_r V_o} = 30\,yrs$$

This research team has been largely supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Geoscience Research Program through grants to Oak Ridge National Laborotory, which is managed for the U.S.D.O.E. by UT-Battelle, LLC under contract DE-AC05-00OR22725.

Dissecting the large-scale spatiotemporal variation in *Ricinus communis* (Castor Bean) seed oil δ^2H

J.B. WEST[1], H.W. KREUZER[2] AND J.R. EHLERINGER[3]

[1]Department of Ecosystem Science and Management, Texas A&M University (*correspondence: jbwest@tamu.edu)
[2]Pacific Northwest National Laboratory (helen.kreuzer@pnl.gov)
[3]Department of Biology, University of Utah (jim.ehleringer@utah.edu)

Plant lipid isotope ratios record important aspects of environmental variation. For example, along with composition, the isotope ratios of lipids in sedimentary records yield insights to past species distributions and climate conditions. Lipids also have the potential to be useful for forensic reconstructions. Correctly interpreting these records requires that we understand what controls isotopic variation and in cases where inferences are to be made about geographic origins, an emphasis must be placed on understanding the primary drivers of large-scale spatial and temporal variability. Potential sources of variation include the isotopic composition of soil moisture, fractionations associated with biophysical processes such as transpiration, and biochemical processes such as photosynthesis and fatty acid synthesis. As part of a comprehensive evaluation of the large-scale spatiotemporal variation of castor bean isotopic composition, we report here results of an analysis of the global-scale variation of castor oil hydrogen isotope ratios. Over 250 seeds from plants grown in key castor bean growing regions, including Brazil, China, India, and many locations in the USA, as well as other locations in Europe and Central America were analyzed. We observed a significant correlation between spatial variation of seed oil δ^2H and that of modeled global precipitation δ^2H. A large amount of the observed variation remained unexplained by this simple relationship. Comparisons were made between our observations and spatiotemporal variations in climate by using the monthly climate grids (University of East Anglia, CRU TS 3.0) that revealed a significant influence of climate on an inter-annual basis. Correlations were also observed between seed oil δ^2H and seed characteristics, perhaps suggesting a role of either plant stress or seed maturity on seed oil δ^2H. A revised model, driven by both long-term modeled precipitation δ^2H and inter-annual variations in climate yielded improved explanatory power. The extent to which plant stress could mediate the hydrogen isotopic composition of seed lipids remains unclear and will be key to refining our understanding and predictive capacity.