

Silicic acid: An experimental and *ab initio* study of explicit solvation and reaction kinetics

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Ab initio quantum chemistry has become a powerful supplement to experimental studies of gas-phase systems in particular. However, while the application to species of geochemical interest such as silicic acid, H_4SiO_4 , is achievable, it is dramatically complicated by the presence of water. As both computer speed and the efficiency of quantum chemical algorithms progress, it is becoming increasingly feasible to go beyond simple continuum descriptions of the solvent to the inclusion of explicit solute-solvent interactions.

We have recently benchmarked the effects of explicit solvation in a theoretical study of a counter-intuitive reverse isotope shift observed in the vibrational spectra of aqueous H_4SiO_4 and D_4SiO_4 [1]. Upon deuteration, the antisymmetric ν (Si-O) stretching modes shifts to higher frequencies, in opposition to what is anticipated from reduced mass arguments. DFT/B3LYP/6-31+G (d)-based models are unable to describe this shift without the inclusion of explicit water molecules. Specific hydrogen bonding interactions, present only within an explicit solvation framework, are found to significantly stiffen and blueshift the δ (Si-O-H/D) bending modes. In D_4SiO_4 , these bends subsequently couple with the ν (Si-O) modes; resonance effects blueshift the stretching modes by a greater extent than the increased mass-induced red shift, leading to a net reverse-isotope shift. Similarly, the positions of δ (Si-O-H/D) modes in the IR and symmetric ν (Si-O) modes in the Raman, and peak widths and heights are also only reproduced with the inclusion of explicit solvation effects.

On the strength of these results, we have begun exploring the feasibility of deriving a kinetic model of silicate polymerization and hydrolysis almost entirely from first principles. We present preliminary results benchmarking transition state theory approximations and the roles of implicit and explicit solvation in modelling the kinetics of H_4SiO_4 dimerization. Early results suggest that this approach may provide a surprisingly good model of reaction kinetics and thermodynamics in pH- and temperature-dependent systems.

[1] McIntosh *et al.* (2011) *Phys. Chem. Chem. Phys.* **13**, 2314–2322.

How and where redox-sensitive trace metals can answer the question productivity or ventilation

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The enrichment of redox-sensitive trace metals such as Re and Mo is commonly used to infer changes in paleo redox conditions of marine sediments. Determining why redox conditions changed is trickier because both organic carbon flux (e.g. export productivity) and changes in bottom water oxygen (e.g. ventilation) can influence sedimentary redox. Which of these factors is the dominant control can be sorted out by analyzing Ag along with the redox-sensitive metals noted above. Unlike these other metals, Ag does not accumulate after sediment deposition. Rather it is scavenged from the water column by organic particles and transported to the sediment as part of the biogenic particle flux. Its accumulation in sediments is therefore related to productivity. Thus, high Ag in combination with high Re and/or Mo suggests that high productivity is controlling sedimentary redox while a combination of low Ag and high Re and/or Mo suggests a lack of ventilation. Some environments, however, don't lend themselves well to the use of redox-sensitive trace metals. Surface sediments from the OMZ on the Pakistan Margin, for example, are characterized by relatively low Re and Mo concentrations in comparison to oceanographically similar regions off Mexico and Peru. Silver concentrations are also anomalously low except near the base of the OMZ indicating post-depositional oxidation and loss of Ag. Together these trace metal data suggest that OMZ sediments on the Pakistan Margin are at best weakly suboxic despite their high organic carbon content and the low bottom water oxygen values.