

Reactive solvation and transport simulations of OH⁻ ions in aqueous environment: A multistate empirical valence bond (MS-EVB) approach

I.S. UFIMTSEV¹, A.G. KALINICHEV², T.J. MARTINEZ¹
AND R.J. KIRKPATRICK³

¹Department of Chemistry, Stanford University, Stanford, CA 94305 (*correspondence: ufimtsev@stanford.edu)

²Department of Chemistry, Department of Geological Sciences, Michigan State University, East Lansing, MI 48824 (*correspondence: kalinich@chemisry.msu.edu)

³College of Natural Science, Michigan State University, East Lansing, MI 48824

Proton exchange reactions involving hydronium (H₃O⁺) and hydroxide (OH⁻) ions in water are important geochemical and environmental process and significantly influence mineral dissolution and precipitation and the binding and transport of contaminants in soil and water. The abnormally high diffusion rate of these charge defects is attributed to the so-called Grotthus mechanism of successive proton exchange events between neighboring H₂O molecules rather than simple ion diffusion. Numerous theoretical and experimental investigations of H₃O⁺ diffusion in acidic solution provide a consistent picture of this process, in which the excess proton diffuses through successive interconversions between solvated H₃O⁺(H₂O)₃ and (H₂O···H···OH₂)⁺ structures, known as Eigen and Zundel ions, respectively. The diffusion of the OH⁻ ion in basic aqueous solutions was usually assumed to be simply a 'mirror representation' of the H₃O⁺ transport, with the OH⁻ ion having predominantly three H₂O molecules in the first solvation shell that donate hydrogen bonds to it. However, recent theoretical and experimental studies have called this mechanism into question. These studies have produced alternative mechanisms involving a different OH⁻ coordination scheme and a more complex solvent reorganization around the ion as the system approaches the transition state and the ion becomes capable of recombining with one of the nearest water molecule's protons to form a different stable OH⁻ ion.

We have developed a new multistate empirical valence bond model of OH⁻(aq) suitable for classical molecular simulations, which accurately captures the major structural, energetic, and dynamic aspects of the proton transfer reactions around the hydrated OH⁻ ion and is in good agreement with experimental data and the results of ab initio molecular dynamics simulations. The model predicts an approximately two-fold increase of the OH⁻ mobility due to proton exchange reactions.

Testing forcing mechanisms of deglaciation: Cosmogenic dating of Laurentide Ice Sheet retreat in Wisconsin and surface mass balance modeling

DAVID J. ULLMAN^{1*}, ANDERS E. CARLSON¹,
ALLEGRA N. LEGRANDE², FARON S. ANSLOW³,
MARC W. CAFFEE⁴, JOSEPH M. LICCIARDI⁵
AND KENT M. SYVERSON⁶

¹Dept. of Geoscience, Univ. of WI-Madison, Madison, WI (*correspondence: ullman@wisc.edu)

²NASA GISS & CCSR, Columbia Univ., New York, NY

³Earth and Ocean Sciences, Univ. of British Columbia, Vancouver, BC Canada

⁴Dept. of Physics, Purdue Univ., West Lafayette, IN

⁵Dept. of Earth Sciences, Univ. of NH, Durham, NH

⁶Dept. of Geology, Univ. of WI-Eau Claire, Eau Claire, WI

Determining the phasing of Northern Hemisphere (NH) ice sheets relative to changes in insolation, greenhouse gases, and climate is key to understanding the mechanisms that give rise to ice ages and ice-sheet retreat. Early retreat of NH ice sheets ~19-24 ka suggests boreal insolation as the ultimate driver of ice retreat [1]. Alternatively, tropical sea surface temperatures (SST) and atmospheric CO₂ may lead portions of ice-sheet retreat, implicating them as an alternative driver of deglaciation [2, 3]. Here, we present new ¹⁰Be cosmogenic exposure dates from boulders on the terminal moraines of three distinct lobes of the Laurentide Ice Sheet (LIS) in Wisconsin. Until present, the retreat onset of this region was poorly understood through limited radiocarbon dates. This new cosmogenic chronology provides an important constraint on the retreat of the LIS southern margin at the LGM.

To assess if boreal summer insolation could drive initial LIS retreat, we employ an energy moisture balance model to assess the LIS mass balance at the LGM with climate forcing from the Goddard Institute for Space Studies (GISS) ModelE-R. We compare the effects of alternate LIS topographies: the current standard ICE5-G [4] and an alternative reconstruction with lower topography over the Keewatin Dome [5]. We put these model results in the context of our new cosmogenic exposure dates and the existing retreat chronology for the LIS southern margin, testing the mechanisms controlling the onset of the last deglaciation.

[1] Clark *et al.* (2009) *Science* **325**, 710–714. [2] Lea *et al.* (2006) *Quat. Sci. Rev.* **25**, 1152–1167 [3] Stott *et al.* (2007) *Science* **318**, 435–438 [4] Peltier (2004) *ARES* **32**, 111–149 [5] Licciardi *et al.* (1998) *Quat. Sci. Rev.* **17**, 427–488.