# Metadynamics simulations of Si-O bond hydrolysis using ReaxFF potential models

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Electronic structure calcuations are frequently employed to investigate the stability and hydrolysis of Si-O bonded interactions at silicate mineral surfaces. Due to the significant computational expense associated with these methods, cluster models are typically utilized that endeavor to approximate the properties of the mineral-water interface. However, owing to the limited inclusion of solvation effects, the adequacy of this approach is frequently questioned. Recent advances in the development of empirical reactive potentials (e.g. ReaxFF) promise to enable the simulation of Si-O hydrolysis on more extended representations of the mineral-water interface, but available parameter sets require further vetting.

This work aims to characterize the behavior of several ReaxFF potential models during Si-O hydrolysis; namely, the Ca/Si/O/H and Si/O/H models of Manzano [1] and Yeon [2], respectively. The Si/O/H interactions in the Manzano potential are identical to those in the original Si/O/H model of Fogarty et al. [3], while those in the Yeon potential are reparameterized to better reproduce potential energy barriers to hydroxylation. For each model, the free energy landscape for the hydrolysis of disiloxane is obtained from well-tempered metadynamics simulations at 200°C, using the minimum Si-water-oxygen and the maximum Si-bridging-oxygen distances as collective variables.

A preliminary analysis shows that under near neutral pH conditions, the Si-O hydrolysis mechanisms favored by each model are distinct. With the Manzano model, hydrolysis proceeds via dissociative water adsorption at a Si-centre, resulting in the formation of a pentacoordinated intermediate, and the transfer of a proton to the briging oxygen position prior to the ultimate dissociation of the Si-O bond. These findings are consistent with the results of several earlier electronic structure calculations. In contrast, with the Yeon model, dissociative water adsorption results in the transfer of a proton to the bulk solution, and the protonation of the bridging oxygen occurs during a subsequent reaction step.

[1] Manzano *et al.* (2012) *J. Am. Chem. Soc.* **134**, 2208-2215.
[2] Yeon and van Duin (2016) *J. Phys. Chem. C* **120**, 305-317. [3] Fogarty *et al.* (2010) *J. Chem. Phys.* **132**, 174704.