

Density functional theory simulation of acid hydrolysis of an SiOSi linkage on the (101) surface of α -quartz

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The phenomenon of silicate dissolution has been studied and modeled with quantum mechanical calculations for decades. However, due to computational limitations early calculations did not include solvation effects at the mineral-water interface nor the structure of the mineral. Advances in hardware and software have now made it possible to include the mineral structure and explicitly model the mineral-water interface on the scale of a few nanometers.

This work focuses on the common mineral and model system $\text{SiO}_2\text{-H}_2\text{O-HCl}$. Hydrolysis of Si-O-Si linkages are thought to control the dissolution of polymerized silicates, so focusing on this reaction has implications for weathering of a wide variety of rock types. The inclusion of a solution phase in these simulations will allow the results to be contrasted against previous studies where solvation was absent or limited. HCl was added to the system to simulate the effect of low pH on the dissolution which has been experimentally observed to increase rates dramatically. The fact that a Cl^- ion is used to charge balance the model system is used to explore the effects that counterions in the electrical double layer have on the structure and energetics of the H^+ -catalyzed hydrolysis reaction.

Structures of the α -quartz (101)-water model system calculated with periodic DFT molecular dynamics are consistent with experimental observation as a first test of the modeling methodology. The $\text{SiO}_2\text{-H}_2\text{O}$ model was then constrained to protonate an Si-O-Si linkage which lengthened the Si-O bonds at this site but raised the system energy unrealistically. Addition of HCl to the system lowered the energy to form the protonated Si-O-Si linkage significantly. A pathway to protonation of this linkage and subsequent hydrolysis based on formation of a H-bond from a nearby Si-OH group is predicted to have a relatively low-energy barrier of activation. The Cl^- was found to play a role in stabilizing the protonated Si-O-Si linkage by providing local charge balance within the electrical double layer. Using these DFT simulations to train and test a reactive force field for larger simulations will also be discussed.

Lunar space weathering via exposure to ultraviolet radiation

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We are currently investigating space weathering due to ultraviolet (UV) irradiation on the Moon. The Moon receives approximately 116 W/m^2 [1], but, to our knowledge, it has been considered negligible in its contribution to lunar space weathering. Our spectra (Figure 1) obtained before and after irradiating San Carlos olivine with UV in a vacuum demonstrate many of the same spectral features associated with space weathering by the solar wind and/or micrometeorite impacts. Olivine samples were exposed to UV irradiation from a Newport Solar Simulator with a power density of about 1223 W/m^2 through a quartz window for varying times up to 594 hours while under a vacuum of approx. 10^{-6} torr. The reflectance spectra obtained at RELAB demonstrate the distinct reddening and darkening of space-weathered olivine surfaces as well as the suppression of the spin-forbidden absorption bands at about 450 nm in the silicate structure. This form of space weathering appears to occur for even modest ultraviolet wavelengths with enough energy to break chemical bonds (e.g. a 100 nm photon carries 12.4 eV of energy while the Si-O bond in quartz is only 6.4 eV).

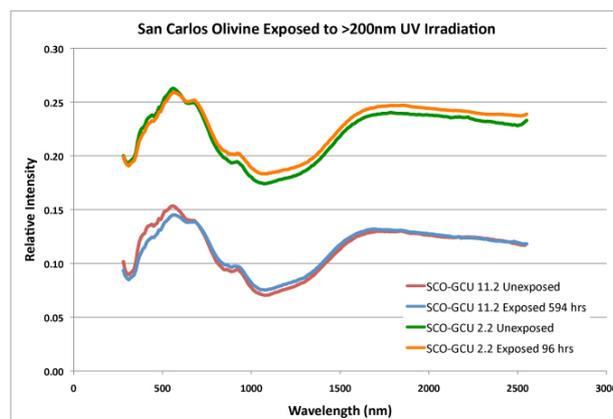


Figure 1. Before and after visible-NIR spectra of two San Carlos olivines. The spectra are offset by a relative intensity of 0.10 for clarity.

[1] Arvesen, J.C. *et al.* (1969) *Applied Optics* **8** 2215–2232.