Ab initio atomistic thermodynamics of water vapor-pyrophyllite (010) surface

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The lateral edge surfaces of 2:1 phyllosilicates are important sites for metal sorption, but the surface structures and stability remain difficult to investigate experimentally. Density functional theory (DFT) atomistic thermodyanmics allows us to examine the stability of mineral-gas interfaces as a function of environmental variables. In this presentation, we show our DFT results for the stability of wate-pyrophyllite (010) surface as a function of temperature, surface coverage, and the vapor pressure of water.

The surface excess energy calculated at 0 K in vacuum space without vibrational contribution predicts that increased H_2O coverage lowers the energy, implying that hydration enhances stability. On the other hand, surface free energy calculations demonstrate that the surface stability varies with temperature, the chemical potential of water (μ), and the extent of the surface coverage (Figure 1). We have examined the structure and stability of a surface defect that was intitally proposed as alternative bulk structure by Edelman and Favjee [1] and also identified at the edge surface in classical molecular dynamics smulations [2]. This defect posseses an inverted Si tetrahedron such that the apical O points toward the interlayer (Figure 1). Possible roles of this defect in the edge surface reactivity will be discussed.

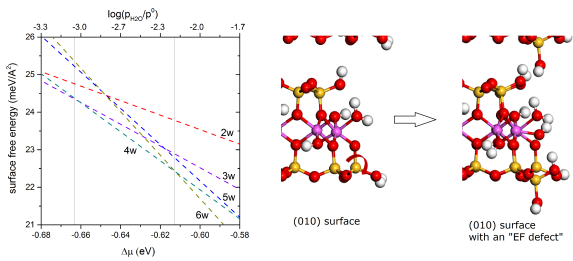

Figure 1: Surface free energy of hydrated pyrophyllite-1*Tc* (010) surface computed at 300 K where *N*w represensts a H_2O coverage (left). Surface with and without defect (right).

[1] C.H. Edelman and J.C.L. Favejee (1940) *Z. Krist.* **A*102***, 417. [2] A. Newton (2012) Ph.D. thesis, University of California at Berkeley.