Structure and stability of pyrophyllite edge surfaces: Effect of temperature and water chemical potential

Kideok D. Kwon [*], Aric G. Newton

Department of Geology, Kangwon National University, Chuncheon 24341, Republic of Korea

Abstract

The surfaces of clay minerals, which are abundant in atmospheric mineral dust, serve as an important medium to catalyze ice nucleation. The lateral edge surface of 2:1 clay minerals is postulated to be a potential site for ice nucleation. However, experimental investigations of the edge surface structure itself have been limited compared to the basal planes of clay minerals. Density functional theory (DFT) computational studies have provided insights into the pyrophyllite edge surface. Pyrophyllite is an ideal surrogate mineral for the edge surfaces of 2:1 clay minerals as it possesses no or little structural charge. Of the two most-common hydrated edge surfaces, the AC edge, $(1\,1\,0)$ surface in the monoclinic polytype notation, is predicted to be more stable than the B edge, $(0\,1\,0)$ surface. These stabilities, however, were determined based on the total energies calculated at 0 K and did not consider environmental effects such as temperature and humidity. In this study, atomistic thermodynamics based on periodic DFT electronic calculations was applied to examine the effects of environmental variables on the structure and thermodynamic stability of the common edge surfaces in equilibrium with bulk pyrophyllite and water vapor. We demonstrate that the temperature-dependent vibrational energy of sorbed water molecules at the edge surface is a significant component of the surface free energy and cannot be neglected when determining the surface stability of pyrophyllite. The surface free energies were calculated as a function of temperature from 240 to 600 K and water chemical potential corresponding to conditions from ultrahigh vacuum to the saturation vapor pressure of water. We show that at lower water chemical potentials (dry conditions), the AC and B edge surfaces possessed similar stabilities; at higher chemical potentials (humid conditions) the AC edge surface was more stable than the B edge surface. At high temperatures, both surfaces showed similar stabilities regardless of the water chemical potential. The equilibrium morphology of pyrophyllite crystals is also expected to be dependent on these two environmental variables. Surface defects may impact the surface reactivity. We discuss the thermodynamic stability of a possible Si cation vacancy defect which provides additional hydroxyl group on the surface.
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1. INTRODUCTION

Clay minerals are abundant in atmospheric mineral dust which influences the formation and radiative properties of high altitude ice clouds through heterogeneous ice nucleation (Pruppacher and Klett, 1997; Forster et al., 2007; Jeong and Achterberg, 2014). In aerosol-climate modeling, measured data of ice nucleation efficiency for kaolinite, illite, or smectite are parameterized to represent the ice nucleation properties of mineral dust depending on the mineral composition (Hoose et al., 2008; Storelvmo et al., 2008; Hoose and Möhler, 2012). The estimation of ice nucleation properties of atmospheric mineral dusts may be improved through a mechanistic understanding of the ice formation process at clay mineral surface (Freedman, 2015; Tang et al., 2016). In particular, molecular-level characterization of ice nucleation sites and interactions of water

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vapor with the mineral surface can allow us to determine whether and why the ice nucleation efficiency differs among minerals. Kaolinite (1:1 clay mineral) studies have identified as possible ice nucleation sites hydroxyl groups of basal planes and surface defects in deposition mode nucleation, in which water vapor adsorbs first to the mineral surface and nucleates ice (Hu and Michaelides, 2007; Croteau et al., 2010; Cox et al., 2013; Welti et al., 2014). Edge surface may also play a role in the nucleation as the edge surface adsorbs water more strongly than the basal planes (Croteau et al., 2009) and initial ice on the mineral surface may not be crystalline but amorphous (Lamb and Verlinde, 2011). For smectite and illite (2:1 clay minerals), the lateral edge surface is postulated to be an important nucleation site (Freedman, 2015) mainly because the functional group of the exposed basal planes is hydrophobic siloxane. However, the detailed atomistic structure and thermodynamic properties of the clay mineral edge itself are not clearly characterized yet, in part due to the experimental difficulties in isolating the mineral edges and resolving the inherent disorder of the edge surfaces. The current study addresses the structure and thermodynamic stability of the edge surface.

Theoretical and molecular-level computational studies have provided insights into the structure of clay mineral edge surfaces, particularly for pyrophyllite, which primarily forms through low-grade metamorphic processes. Pyrophyllite is the prototypical 2:1 dioctahedral phyllosilicate comprising two Si tetrahedral sheets joined to an Al octahedral sheet. Because pyrophyllite lacks structural charge, the basal siloxane planes are relatively inert and the interlayer does not swell. Only the edge surfaces of pyrophyllite are reactive due to OH functional groups that protonate and deprotonate depending on pH. Thus, pyrophyllite is an ideal surrogate for the edge of 2:1 clay minerals (Keren and Sparks, 1995). The application of periodic bond chain (PBC) theory (Hartman, 1973) to 2:1 dioctahedral phyllosilicates identified three types of edge surfaces (White and Zelazny, 1988). Because two of these edges are symmetrically equivalent, discussion of the edge surface can be simplified to the two edge surfaces geometries. In the monoclinic polytype, the symmetrically equivalent edges correspond to the (1 1 0) surface, and the unique edge is the (0 1 0) surface. In the triclinic polytype, the former edge coincides with the (0 1 0) surface, and the latter edge is approximately coincident with the (−1 1 0) surface (Bickmore et al., 2003; Kremleva et al., 2012; Newton and Sposito, 2015). In the current study, we use the original edge designations of White and Zelazny (1988). The AC edge refers to the two symmetrically equivalent surfaces, and the B edge surface denotes the unique edge (Fig. 1). Geometry optimizations with density functional theory (DFT) have demonstrated how the atomistic structures of the edge surfaces differ from the bulk (Bickmore et al., 2003; Churakov, 2006). At the point of zero net proton charge (p.z.n.p.c.), each exposed tetrahedral–octahedral–tetrahedral unit of the hydrated edge surfaces possesses two silanol sites ($\equiv$Si—OH), an amphoteric site ($\equiv$Al—OH$_2$), and a singly- or doubly-coordinated aluminol site depending on the surface type ($\equiv$Al—OH or $\equiv$Al$_2$—OH) (White and Zelazny, 1988; Bleam et al., 1993; Bickmore et al.,

2003). The Al edge sites appear to have disorder in the coordination configuration, the degree of which differs depending on the edge type (Tazi et al., 2012; Liu et al., 2015; Newton and Sposito, 2015). Molecular dynamic simulations based on DFT also reported spontaneous proton transfers among the surface hydroxyls and adsorbed water molecules (Churakov, 2007; Suter et al., 2015).

Compared with the atomistic structure of surfaces, the surface stability at different temperature and humidity conditions has been little investigated, although the AC edge surface appears to be more stable than the B edge surface. The surface excess energies of hydrated pyrophyllite edges were reported in previous DFT studies (Churakov, 2006; Martins et al., 2014; Lavikainen et al., 2015). The calculated energies were relatively small and differed little among the surfaces considered, but the AC edge surface generally possessed a slightly lower surface energy than the B edge surface; equilibrium morphologies for pyrophyllite crystals were also predicted based on the calculated energies. Of note, the energies used in the previous studies were not free energies but total energies calculated at 0 K (i.e., surface excess energy) which did not include thermal vibrational energies. When the vibrational contribution is greater than the variations among the surface excess energies, the thermodynamic stability at ambient conditions cannot be assessed based on the excess energies calculated at 0 K. Moreover, the energy comparison in the previous studies required that surfaces be of the same stoichiometry; stability was determined at a given surface coverage but cannot be determined among surfaces at different surface coverage or water vapor pressures.

In the current study, we have examined the structure and thermodynamic stability of the AC and B edge surfaces as a function of temperature and water vapor pressure through application of DFT atomistic thermodynamics (Reuter and Scheffler, 2001; Sun et al., 2003). This method links the DFT total-energy electronic structure calculations and the thermodynamic and statistical mechanic concepts to obtain insights into the surface stability as a function of the environmental variables without adjustable parameters. When a surface is in thermodynamic equilibrium with the bulk structure and a gas phase, the atomistic thermodynamics method calculates the free energy of the surface by examining solid and gas phases separately within DFT and using the DFT results as an input in the thermodynamics (Rogal and Reuter, 2007). For the first time, we calculated surface free energies of the hydrated AC and B edge surfaces of pyrophyllite at different temperatures and water chemical potentials (i.e., water vapor pressures). We show how the stability of pyrophyllite edge surfaces and the equilibrium morphology vary under different environmental conditions. The surface atomistic structures are also presented with the adsorption energies for water molecules sorbed to the surface from the vapor phase.

We also investigated the stability of surface defects. Defects on the surface create additional heterogeneity in the ice nucleation sites with likely effects on the ice nucleation ability of clay minerals (Schuttlefield et al., 2007; Croteau et al., 2010; Freedman, 2015). Recent classical molecular dynamics simulations and DFT simulations