

Surface Hydrophobicity and Energetics at Mica-Water Interfaces

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Phyllosilicate-water interfaces are relevant to a variety of surface-mediated geochemical processes such as heterogeneous nucleation and subsurface reactive transport properties. The intrinsic chemical heterogeneity of phyllosilicates (i.e. cationic and anionic substitution) can give rise to diverse crystal structures and surface physicochemical properties such as hydrophobicity, which in turn determines the nature of interfacial reactions.

This study aims at examining the effects of fluorine/hydroxyl substitution on the hydrophobicity of the basal surface of phlogopite in the presence of various counterions (K^+ , Na^+ and Cs^+). The surface properties of phlogopite mica are closely related to minerals of the clay group: they share a two dimensional structure with interlayer cations and a wetting behavior dictated both by the presence of hydroxyl groups and hydrated cations. We employ a combination of computational and experimental methods. The energetics of surface hydration are calculated using classical molecular dynamics simulations while surface hydration processes are monitored in situ using near-ambient pressure X-ray photoelectron spectroscopy and interfacial water properties are probed by X-ray reflectivity. Results suggest that the surface hydrophobicity is particularly well manifested at or above 1 monolayer coverage of water for Na^+ -bearing phlogopite. At lower water coverage, on the other hand, entropic contribution to water adsorption is non-negligible and seems to reflect the type of counterions. This study overall provides molecular basis for surface hydrophobicity, applicable to the microscopic details, energetics and kinetics of various reactions occurring at the phyllosilicate-water interfaces.