Molecular Dynamics Simulation of the Structure, Dynamics, and Energetics of Water at Mineral Surfaces

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MD simulations of water at surfaces of several silicates (quartz, muscovite, and talc) and hydroxides (Mg-, Ca-, Al-, Ca/Al- and Mg/Al-hydroxides) were performed to provide new insight into the fundamental molecular-level relationships between the inorganic substrate structure and the properties of interfacial water at these surfaces. All the hydroxide surfaces (including a fully hydroxylated quartz surface) show very similar H_2O density profiles perpendicular to the interface due to the prevalent effects of the H-bonding network development across the substrate-water interfaces. However, the predominant orientations of the interfacial H_2O molecules and their detailed near-surface structure and dynamics are quite different reflecting the differences in the substrate structural charge distribution and the surface density and orientations of the substrate OH groups. The density profiles and other structural and dynamic characteristics of H_2O at the two siloxane surfaces are very different from each other and from the hydroxide surfaces, because the muscovite surface is negatively charged and hydrophilic, while the talc surface is neutral and hydrophobic. At hydrophilic neutral surfaces both donating and accepting H-bonds from the H_2O molecules are contributing to the development of the interfacial H-bond network, whereas at hydrophilic but charged surfaces only accepting or donating H-bonds with H_2O molecules are possible. The first water layer at all substrates is well ordered parallel to the surface, reflecting substrate crystal structures and indicating the reduced translational and orientational mobility of interfacial H_2O molecules. At longer time scale (100 ps) their dynamics can be decomposed into a slow, virtually frozen, regime due to the substrate-bound H_2O and a faster regime reflecting the molecular dynamics far from the surface. At shorter times (<10 ps) the two dynamical regimes are superimposed. The higher ordering of interfacial water compared to bulk liquid can not be adequately described as simply "ice-like", but rather as that of supercooled water.