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Interfacial structure and acidity of the orthoclase (001) surface: Understanding the effect of the surface metal cation

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Abstract

Surface acid chemistry is central to the interfacial properties of orthoclase. In this study, we report a first-principles molecular dynamics (FPMD) study of interfacial structures and acid constants (p*K*a) of orthoclase (001) with the presence of Na^+/K^+ cations on the surface. Detailed structural analyses demonstrate that Na^+ and K^+ have similar coordination structures on the surface, while the exchange of Na^+ for K^+ hardly changes the hydration structures of surface groups. The surface groups (i.e., ≡SiOH, ≡AlOH, and $\equiv AlOH_2$) have p*K*as of 11.5, 18.5, and 7.8 with K^+ and 5.5, 17.7, and 4.3 with Na^+, respectively. FPMD-derived p*K*as indicate that with K^+ on the surface, $\equiv AlOH_2$ is the only active group in the common pH range, while Na^+ decreases surface p*K*as of surface groups and makes $\equiv AlOH_2$ and ≡SiOH active. Based on the p*K*as, we derive a PZC (point of zero charge) of 9.7 and 4.9 for orthoclase (001) with surface K^+ and Na^+, respectively. This means that Na^+ significantly enhances surface acid reactivity. The implication for understanding the geochemical properties of orthoclase is discussed with a focus on the surface complexation of metal cations.

Keywords: First-principles molecular dynamics, orthoclase-water interface, microscopic structures, acid constant, adsorption sites