

Effects of surface heterogeneity on Rb⁺ sorption at the quartz (101)– water interface[†]

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Mineral–water interfacial reactions are central to geochemical processes that govern the fate and transport of nutrients and heavy metals. Many mineral surfaces possess heterogeneous structures such as defects, which affect their interfacial reactivity. In this work, we determined the effects of surface heterogeneity on Rb⁺ uptake at the quartz (101)–water interface from 10 mM RbCl solution at pH 9.8 using in-situ specular X-ray reflectivity (XR) measurements and density functional tight binding molecular dynamics (DFTB-MD) simulations. Two surface spots (designated as Spots A and B) with different surface structures were measured by XR to determine Rb⁺ sorption behavior. Spot A had a stoichiometric surface composition (i.e., with minimal defect density), where Rb⁺ adsorbed as an inner-sphere surface complex at $z = 1.43 \text{ \AA}$ (where z is the average height of the two terminal O atoms from the ideal surface). In contrast, Spot B showed a significantly higher defect density (i.e., ~50% topmost Si vacancies) and was covered by a ~3 Å-thick poorly crystalline SiO₂ layer at $z = 1.75 \text{ \AA}$. Rb⁺ adsorbed at Spot B as two species at $z = -0.9$ and 4.92 \AA , respectively, with ~7 times higher total coverage than at Spot A. The first species was an inner-sphere complex in the Si vacancy sites, which was confirmed by DFTB-MD simulations. The second species was interpreted mostly as adsorption on the poorly crystalline SiO₂ layer. These results unravel the molecular mechanisms of how surface heterogeneity controls the reactivity of mineral–water interfaces toward nutrients and metals.

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