

## The effect of the sizes of alkali cations on structural variations in layered silicate materials

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Computational techniques were used to investigate the structures and stabilities of a series of solid solutions of the phyllosilicate material  $\text{Li}_{2(1-x)}\text{M}_{2x}\text{Si}_2\text{O}_5$  ( $M = \text{Na}, \text{K}, \text{Rb}, \text{Cs}$  and  $x = 0, 0.25, 0.5, 0.75, 1$ ) as well as solid solutions of the mixed alkali phyllosilicate  $\text{KLiSi}_2\text{O}_5$  with Na, K, Rb and Cs replacing the Li and K ions. To eliminate unnecessary duplication of calculations, a program based on symmetry arguments is employed to identify equivalent configurations. Even so, hundreds of calculations were still needed to sample the complete set of inequivalent configurations of a wide range of solid solutions.

Our simulations show that in the wide range of composition studied, solid solutions of the mixed  $\text{KLiSi}_2\text{O}_5$  phyllosilicate with Na, Rb and Cs, retain the basic features of the  $\text{KLiSi}_2\text{O}_5$  structure, e.g. a three-dimensional channel structure of six-membered rings made up of corner-sharing silica tetrahedral. However, the K ions rather than the Li ions are preferentially replaced by the guest ions, especially Rb and Cs. In the mono-cationic phyllosilicate  $\text{Li}_2\text{Si}_2\text{O}_5$ , the main features are a two-dimensional six-ring structure and symmetric chair-like conformation of the silicate groups. We found that this structure became significantly distorted when the bigger Rb and Cs cations replaced lithium ions. Although solid solutions of all guest ions in silicates are energetically feasible to some extent, only ion exchange of K ions for Na ions from aqueous solution is calculated to be an exothermic process.

## Molecular dynamics simulation of the water/ $\alpha$ -quartz interface

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Interaction of water with oxide surfaces affects both the surface reactivity and functionality and the structure and dynamics of the near-surface aqueous phase. Quantitative understanding of these interactions is of great interest in many geochemical and technological systems. Silica is very important in this regard, because of its natural abundance and ubiquitous practical applications.

To better understand the molecular-level structural and dynamical properties of water/ $\alpha$ -quartz (0001) interfaces under different protonation states, we have performed MD computer simulations using the recently developed CLAYFF force field (Cygan et al., 2004). The effect of pH on the interfacial properties was emulated by varying the degree of surface protonation for the simulated models. For a fully protonated quartz surface (low pH), about 50% of surface OH groups are oriented parallel to the surface, form H-bonds to other surface OHs, and accept H-bonds from  $\text{H}_2\text{O}$  molecules. The other 50% of OHs are oriented perpendicular to the surface and donate H-bonds to the interfacial  $\text{H}_2\text{O}$  molecules.

On average, all surface water molecules donate or accept H-bonds to/from the surface OH groups with equal probability, and together they form a well interconnected H-bonding network similar to the ones observed for hydroxide interfaces (Kalinichev and Kirkpatrick, 2002; Wang et al., 2004). The structure and composition of the quartz surface imposes significant positional and orientational ordering on the  $\text{H}_2\text{O}$  molecules nearest to the surface. This is qualitatively consistent with the results of recent sum-frequency vibrational spectroscopic measurements for the same system, where some observed spectral features were interpreted as being "ice-like" (Ostroverkhov et al., 2004).

### References

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