

X-ray Reflectivity of the Muscovite-Water Interface in CaCl_2 and BaCl_2 Solutions: Mechanism of Cation Sorption

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Introduction

The basal surface of micas and most clays carries a permanent negative charge due to isomorphous cation substitutions in the bulk mineral, and it is therefore an important site of cation sorption reactions in nature. Recent analyses of sorption on mica basal surfaces indicate that anions like Cl^- can cosorb with some cations.^{1,2} Evidence based on cation-exchange measurements suggests also that the same cosorption mechanisms occur on smectite clay.³ While much is known macroscopically about cation sorption on micas and clays, there is little direct information on the atomic-scale surface relaxation of the basal surface of these minerals and its effects on sorption mechanisms. Given the geochemical importance of the phyllosilicate-water interface, a full atomic-scale characterization of this interface is warranted.

Micas have the highest surface charge of all phyllosilicates. This charge is localized in the basal tetrahedral sheets rather than in both tetrahedral and octahedral sheets as in clays, and it is balanced by interlayer cations that bind layers together through electrostatic forces. These relatively weak electrostatic bonds can be easily truncated by cleaving, resulting in a large reactive surface whose structural properties can be determined by x-ray reflectivity. We report the first successful atomic-scale structural analysis of the interface between muscovite mica and solutions of CaCl_2 and BaCl_2 . The results provide insight on the extent of surface relaxation and cation sorption mechanisms.

Methods and Materials

ASTM V-1 grade muscovite ($\text{KA}_3\text{Si}_3\text{O}_{10}(\text{OH})_2$) sheets were freshly cleaved and immersed in 50 ml of 0.01 M CaCl_2 or 0.01 M BaCl_2 for at least 1 hour to ensure cation saturation of the surface. The sheets were mounted in a thin film cell,⁴ and x-ray reflectivity data were collected on the wet surfaces at the 12-BM station (BESSRC-CAT, Advanced Photon Source, Argonne National Laboratory) at an x-ray wavelength of 0.635 Å. Reflected x-ray intensity was measured by rocking-curve scans through the specular reflection condition followed by background subtraction and area integration of the rocking-curve peaks. Plots of reflected intensity between bulk Bragg peaks vs. momentum transfer Q [$=(4\pi/\lambda)\sin(\theta)$, where λ is the x-ray wavelength and θ is the angle of incidence with respect to the surface plane] were reproduced on different muscovite samples for both solutions. Changes in the reflected x-ray intensity were reproduced by reversibly changing the solution in contact with the muscovite surface. High resolution (~ 1.3 Å) reflectivity data were modeled using atomistic structural models that include surface relaxation, sorbate concentration and position, water structure, and surface roughness.

Results and Discussion

Muscovite in CaCl_2 . Preliminary fits assuming Ca^{2+} formed inner-sphere (IS) or outer-sphere (OS) complexes and disallowing

muscovite relaxation resulted in an overcompensation of the muscovite surface charge. A good charge balance was obtained with either IS or OS CaCl^+ surface complexes, in agreement with previous XPS analysis indicating the presence of some Cl^- at the surface.¹ Adding muscovite relaxation to the model (Fig. 1) improved the fits and showed that the overall relaxation may propagate as much as 50 Å into the bulk mineral, although individual layers contract by no more than 0.05 ± 0.02 Å. The IS CaCl^+ model resulted in nearly exact compensation of the surface charge.

Muscovite in BaCl_2 . The best fit model (Fig. 1) was obtained for IS Ba^{2+} . The modeled relaxation of mica layers matched the

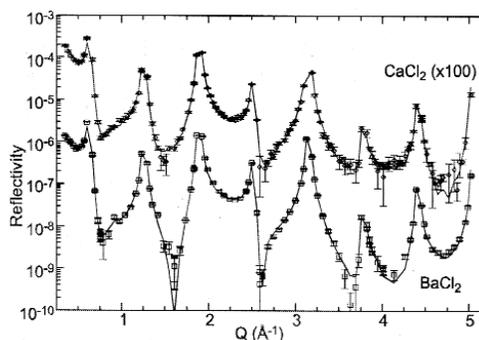


FIG. 1. Reflectivity data. Differences in relative intensity are clearly visible (e.g., near 4.2 and 4.8 Å⁻¹). Smaller but significant changes are found throughout the data.

pattern observed in CaCl_2 , with layer contraction $\leq 0.04 \pm 0.02$ Å and deep (~ 40 Å) propagation of the relaxation. This model agrees with previous XPS analyses² showing no evidence for cosorption of Cl^- with Ba^{2+} .

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