# X-ray Reflectivity Study of the Water-Muscovite (001) Interface

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## Introduction

The interaction of water with phyllosilicate mineral surfaces is important in mineral surface geochemistry. One of the most frequently studied phyllosilicate mineral surfaces is the muscovite (001) surface. However, *in situ* structural studies of muscovite (001) single-crystal surfaces are still quite rare. We have performed an *in situ* x-ray reflectivity study of a water-muscovite (001) interface. X-ray reflectivity is a unique tool for *in situ* investigation of water-mineral interfaces because x-rays, which only weakly interact with matter, penetrate mm-thick solutions. Muscovite is an appropriate sample for x-ray reflectivity study because it can be obtained as a reasonably good single crystal and has a molecularly smooth surface.

## Experimental

The x-ray experiment was carried out at the BESSRC-CAT beamline12-BM. X-rays of 19 keV energy were incident on a muscovite sample sealed with an approximately 39-μm-thick water above the surface, held in place by a thin kapton window. The specular x-ray reflectivity at an incident angle $\theta$, $R(\theta)$, is the fraction of the incident x-ray flux that is reflected from the muscovite (001) surface; it is therefore sensitive to the electron density distribution in the surface-normal direction. This information reveals the structural relaxations of the muscovite surface in the aqueous environment, as well as the structure of water at the interface.

## Results

We have a few major observations from our results. First, we found that the muscovite (001) surface in water is molecularly flat in the dimension of the x-ray coherence length; this is consistent with atomic-force microscopy studies of mica (001), which showed perfect surfaces in substantially large areas. Second, by repeating reflectivity measurements at a selected number of scattering angles over time, we showed that the water-muscovite (001) interface was stable over the course of hours, without detectable x-ray beam damage in the form of surface chemical modifications. Third, the best-fit model to the reflectivity data showed that there was only very limited relaxation in the muscovite (001) surface. Specifically, all atom layers below those belonging to the top Si tetrahedral layer showed relaxation <0.04(2) Å. The relaxation of atoms within the top Si tetrahedra was small but significant. Finally, an adsorbed layer of water is specifically located at a height not very different from that of the ideal $K^+$, suggesting ionic exchange between surface $K^+$ and aqueous $H_3O^+$, or specific adsorption of $H_3O^+$. We also find that the water above the interface cannot be fitted with a random, featureless profile. Instead a water profile with noticeable density modulation above the interface was needed in order to obtain a good fit to the reflectivity data. This modulation includes both a moscuvite-surface first-hydration layer as well as smaller modulation of liquid water near the moscuvite-water interface.

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