## In-situ AFM study of cationexchange reactions in phlogopite

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The ion-exchange in phyllosilicates is one of the most extensively studied geochemical processes due to its great importance in many different fields ranging from the chemical composition in a local environment to applications in technology and engineering. Ion-exchange reactions can further be used for the characterisation of 2:1 phyllosilicates. Here, we present new results about the mechanism and kinetics of ion-exchange reactions in phlogopite and show details about the interaction of micas with organic and inorganic ions in monolayer resolution.

The cation-exchange between  $K^+$  and guest ions (noctylammonium ions and Na<sup>+</sup>) caused a swelling of the phlogopite layers that can be detected by AFM (Fig. 1). The reaction initiates at cleavage steps on the mineral surface. The magnitude of swelling depends on the guest cation and on the number of layers reacting simultaneously. Inorganic and organic cations showed differed reaction rates. The propagation rate of the reaction front also depends on temperature. Furthermore, the propagation rate decreases with an increasing distance from the cleavage steps which clearly points towards a diffusion controlled mechanism.

The reverse exchange of the guest ions by potassium caused the reaction to reverse, i.e. the swollen areas are returning to the original morphological state. However, the kinetics of the reverse reaction was markedly different and the restoration remained incomplete. A few isolated regions with guest ions remained on the surface. The reverse exchange also caused the formation of a series of bulges and hillocks (height up to 50 nm) which are presumably caused by osmotic swelling.



Figure 1. a) cleavage steps on the pristine phlogopite surface; b) 41 min. later, the ion-exchange reaction between K<sup>+</sup> and noctylammonium ions causes interlayer swelling (scan field  $8.8 \times 8.8 \ \mu m^2$ ).