Exchange kinetics of monovalent cations at the muscovite (001) – water interface

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In-situ real-time observations of the sorption of ions at mineral surfaces are key to understanding the processes that control transport of the elements in nature. Here we present new results on the exchange dynamics between Rb^+ and Na^+ adsorbed at the muscovite (001) - water interface. These two cations are distinct in adsorption mode (Rb^+ adsorbs mostly as an inner-sphere (IS) complex, whereas Na^+ adsorbs as an outer-sphere (OS) complex) and adsorption strength (the adsorption constant of Rb^+ is ~40 times larger than Na^+) [1].

The sorption kinetics and changes in adsorbed ion speciation were monitored simultaneously using time-resolved resonant anomalous X-ray reflectivity (RAXR). The measured RAXR data were analyzed using the model-independent imaging technique [2] to quantify the changes in adsorbed ion coverage and partitioning among different adsorbed species as the system evolves.

The analyses indicate a path-dependency in reaction kinetics, showing an *apparently* slower rate (by a factor of ~2.5) for the desorption of Rb^+ (and presumed replacement by Na^+) compared to the reverse reaction. The measured data were compared to a simulation of a two-component exchange reaction to detemine the *intrinsic* adsorption and desorption rates for the individual components. The results suggest that the adsorption rate of Rb^+ is ~30 times faster than that of Na^+, whereas the desorption rate of Rb^+ is only slightly slower (by ~50%). The results also show a striking difference in the time-resolved speciation of adsorbed Rb^+ during the reactions. Most Rb^+ immediately forms an IS complex during adsorption (i.e., when Rb^+ presumably exchanges with Na^+). In contrast, IS Rb^+ transforms slowly to OS Rb^+ during its desorption (and presumed replacement by Na^+) over the timespan (~30 sec) observed. These results demonstrate that cation hydration and speciation play a central role in determining the adsorption dynamics of cations at the mineral-water interface.

[1] Lee *et al* (2013) *Geochim Cosmochim Acta*, **123**, 416-426.
[2] Park *et al* (2007) *J Appl Crystallogr*, **40**, 290-301.