Molecular mechanism of dissolution, growth and ion uptake at the clay mineral/water interface

René Schliemann[1]*, Inna Kurganskaya[2], Sergey V. Churakov[1,3]

[1] Institute of Geology – Univ. of Bern, Bern 3012, Switzerland (*corresp.: rene.schliemann@geo.unibe.ch)
[2] MARUM - University Bremen, Bremen 28359, Germany
[3] Laboratory for Waste Management - Paul Scherrer Institute, Villigen PSI, Switzerland

Clay minerals are widely used as backfill material at disposal sites to protect the environment from toxic waste. The interplay between adsorption and desorption, crystal growth, dissolution and changes in pore water chemistry is of key importance for the prediction of the pollutants' transport and their retention time. Atomistic simulations help to understand the underlying molecular reaction mechanisms and kinetics. While the cation exchange or the adsorption at the basal planes of clay minerals is well-understood[1], the ion sorption process on the edge sites remains a complex and challenging problem[2]. The ionic sorption is pH-dependent, due to the different protonation states of the surface oxygen sites correlating with their affinity towards adsorbed ions. In addition, the dissolution and growth of clay platelets modify the surface topography and the availability of sorption sites[3]. We investigated the molecular mechanisms of clay mineral dissolution by *ab initio* MD simulations using the Metadynamics (MtD) approach[4] to obtain activation energies for step-by-step detachment/attachment of structure building tetrahedral and octahedral edge sites. Simulations are performed for pyrophyllite (110) surface as the energetically most stable edge face.

The results of the simulation for pH neutral water show that detachment of the Si(t) and Al(o) ions proceeds through at least four reaction steps. These steps include breaking and forming oxygen bridges to neighbouring Si(t) and Al(o) forming bi- or monodentate structures, allowing for H_2O molecules to alter the remaining bonds of the detaching species. The mechanisms and activation energies obtained have extreme importance for the parametrisation of the kinetic Monte Carlo model developed on the basis of a previous approach[3]. This allows us to build a model of montmorillonite particle dissolution and growth as a function of saturation state.

[1] Rotenberg, B. et al. (2009) *Geochim. Cosmochim. Acta* **73**, 4034-4044. [2] Churakov, S. V. & Daehn, R. (2012) *Environ. Sci. Technol.* **46**, 5713−5719. [3] Kurganskaya, I. & Luttge, A. (2013) *Geochim. Cosmochim. Acta* **120**, 545-560. [4] Laio, A. & Parrinello, M. (2002) *Proc. Natl. Acad. Sci. U.S.A.* **99**, 12562-12566.