Electrolyte adsorption on chlorite: Cryogenic-XPS reveals competition between cations and anions

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Chlorites are a group of phyllosilicate minerals common in sedimentary rocks, low-grade pelitic metamorphites and soils. They are often present in the clay fraction in sandstones where they play an important role in the preservation of porosity [1] [2]. Understanding their behaviour and its change with solution composition is of fundamental importance for interpreting geochemical relationships in porous media.

We mixed hand ground Mg-rich chlorite with 1-50 mM solutions of NaCl and $CaCl_2$ and followed the change in the surface excess of ions. We used cryogenic X-ray photoelectron spectroscopy (cryo-XPS) because it probes only the topmost layers of the material [3] [4], in this case, the vitrified chlorite-solution interface.

Chlorite shows stronger preference for Ca^{2+} than Na^+, as predicted from the ionic charge density difference. However, the concentration of Cl^- close to the surface increases with decreasing bulk solution concentration compared to Na^+.This trend is not observed in $CaCl_2$ solutions (Fig 1.). Na^+-Cl^- surface competition shows interesting trends that disobey theoretical approximations [5]. Such information has important implications for understanding the behaviour of anionic organic molecules on clay mineral surfaces.

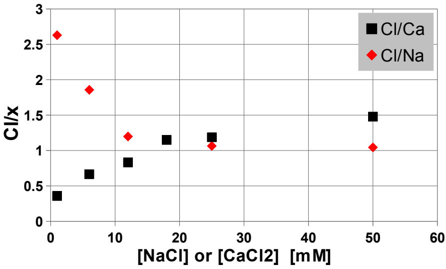

Figure 1 Ratio of Cl^- and cation close to the clay surface as a function of the bulk concentration

[1] Platt, J. D. (1993), *Clay Minerals*, **28**, 393-416 [2] Hillier, S. (1994), *Clay Minerals*, **29**, 665-680 [3] Shchukarev & Sjöberg (2005), *Surface Science*, **584**, 106-112 [4] Shchukarev et al. (2007), *Journal of Physical Chemistry C*, **111**, 18307-18316 [5] Laird, D. (2006), *Applied Clay Science*, **34**, 74-87