

Study of cations and charge distribution in swelling clay sheets by XPEEM

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Swelling clay minerals, such as montmorillonites, are lamellar aluminosilicates formed with two silica sheets sandwiching an aluminum or magnesium hydroxide sheet. Isomorphous substitutions by lower charge metal cations in the crystal lattice result in permanent negative charge that is compensated by electrostatically attracted cations (exchangeable). The lateral extension of individual layers ranges from 25 to 1000 nm while they are 10 Å thick. They exhibit a natural heterogeneity at different organization levels: substitutions in the crystalline network, size and shape of the sheets, structures resulting from sheets interactions, and macroscopic behavior (aggregation, rheology). Understanding these structures remains an open question as well as the links existing between them. As distribution of structural cations and charge is the lowest level of heterogeneity, it might control at least part of the other organization levels and macroscopic behavior. Our objective was then to investigate this level of organization at the individual layer scale taking advantage of the performances of the X-PEEM installed on the ELETTRA Nanospectroscopy beamline (Trieste, Italy). High resolution X-PEEM imaging using core level spectroscopy performed on clay monolayer deposits enabled us to single out the different clay sheets and to study their local composition and charge distribution. From the intensity variations of the photoemission core level spectra, one can deduce the local distribution of the relevant species. Meanwhile, their binding energy provides information on their electronic and chemical environment. Indeed, substituted cations in the layer influence the electronic environment of the neighboring atoms which results in variations in the core level binding energy (BE) of the atom of interest.

We studied two montmorillonites from different ore bodies, Wyoming and Milos. They exhibit different macroscopic properties (i.e. rheology, sol-gel transitions) and octahedral iron distributions (ordered in Wyoming, randomized in Milos) although their lattice formulae are very similar. X-PEEM measurements (Images, local XPS and XPS dispersive plane spectra) were performed recording the Si2p, Al2p and Mg2p core levels spectra from the clay sheets. A major result comes from the Si2p photoemission core level spectra which position shifts to the lower BE as substitutions in the silica layer, thus tetrahedral charge, increase. Our preliminary results clearly demonstrate that, for a given clay ore body, charge is not homogeneously distributed from one sheet to another. Furthermore, a large layer can exhibit two different silica environments and at least one of these two environments varies with the ore bodies. This last result is of peculiar interest as it may be a new clue to understand the variations in macroscopic behavior exhibited by different ore bodies.