

Clay and claystone sorption of (in)organic ions: Insights from diffraction, spectroscopy and DFT

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Clays and claystone are used for a variety of sealing applications such as waste confinement, radioactive waste- oil- and carbon- geological storage. Drawing on our own research, this presentation explores new theoretical contributions to debates on spatial and temporal contaminant mobilities, uncovers different mechanistic modes of mineral reactivity, and contributes to re-imagining mechanistic-based performance assessment of clay-carbonate- and sulfide-rich geo-engineering systems.

Clay edges and basal planes are known to complex a variety of toxics and radionuclides (RNs) but a combination of XRD, XAFS, NMR and molecular dynamics simulations has led to new insights on ternary surface complexes formed with organics (dissolved organic matter, anthropogenic molecules¹) shown to enhance the retention of some cations and RNs. On the other hand, neutron and X-Ray diffraction, XAFS spectroscopy, and DFT theoretical modeling have confirmed ion substitution as an important sorption process for both carbonate and sulfide minerals. DFT, diffraction and EXAFS results demonstrated that selenite substitutes at carbonate anion sites in calcite². Divalent metal cations substitute at Fe sites in mackinawite (FeS)³, an iron sulfide precursor of pyrite difficult to identify in natural medium due to the small size (≈ 5 nm) of its coherent domains. Such substitutions can impact the mineral stability and solubility, a phenomenon of importance for FeS since this mineral is often considered to be unstable, and thus neglected in long term geological repository thermodynamic calculations. DFT also allows to calculate the interfacial energy of various mineral faces, thus to evaluate the reactivity of their nanoparticulate counterparts as a function of environmental variables (e.g., partial pressure ratios of H_2S/H_2). Therefore a clever combination of computational, spectroscopic and diffraction methods leads to new insights into our “macroscopic” view of “sorption”, a phenomenon of such critical importance in risk assessment.

[1] Aristilde, et al. (2010). *Env. Sci. Technol.* 44, 7839-7845 [2] Aurelio et al. (2010) *Chemical Geology* 270, 249–256 [3] Kwon et al. (2015) *Am. Mineralogist* 100, 1509-1517