

# MODELING THE ROLE OF FLUORINE ON THE WETTABILITY OF CLAYS

The widespread use of clays in many fields of physicochemistry (formulation, catalysis, environment) is partly due to their retention properties on the mineral surface. Environmental applications range from water purification to deep geological storage of radioactive waste and carbon dioxide. Clay is a charged lamellar inorganic material with a wide range of pore sizes. The presence of counterions is what causes clays to swell: on contact with water, the cations hydrate and the water penetrates and swells even the smallest pores. Water plays a crucial role in retention properties, as it is the vector for potentially mobile species in the medium.

More specifically, we are concerned here with the significant differences in properties between fluorinated clays and their hydroxylated counterparts, in particular their swelling and wettability properties with respect to water, when the fluorine constituting the sheet is not in immediate contact with the fluid. Our aim is to study how fluorine influences its neighboring atoms to such an extent as to significantly modify interactions at the material surface and make fluorinated clays more hydrophobic.

Classical atomic simulations are the tool of choice for studying the fine mechanisms of interaction between water and the material surface. New, highly promising interatomic potentials, taking into account the polarizability of atoms, have been developed at PHENIX on the basis of ab initio simulations. Better than any other set of classical potentials, they enable us to recover the static and dynamic properties of many systems, including clays [1,3].

The aim here is to use this polarizable potential to model hydroxylated and fluorinated clays of varying charge (hectorites and micas) by classical molecular dynamics: 1) the differences in hydration free energies between these two types of clay will be calculated by thermodynamic integration (alchemical transformation from a hydroxylated clay to a fluorinated clay); 2) we will seek to understand how the enthalpic and entropic contributions obtained can be linked to the fluid arrangement at the interface (hydrogen bonds with the surface and between water molecules, location of counterions, etc.). ...).

More generally, this study will lead to a better understanding of the physicochemical phenomena responsible for the structural and dynamic behavior of fluid at the interface of inorganic materials. It should also enable the candidate to acquire a thorough grounding in the chemistry theoretical training in the physicochemistry of interfaces and porous media.

[1] Tazi,S., Molina,J.J., Rotenberg,B., Turq,P., Vuilleumier,R., Salanne,M., JCP, 2012, 136, 114507

[2] Tesson,S., Louisfrema,W., Salanne,M., Boutin,A., Rotenberg,B., Marry,V., JPCC, 2017, 121, 9833-9846

[3] Tesson,S., Louisfrema,W., Salanne,M., Boutin,A., Ferrage,E., Rotenberg,B., Marry,V., JPCC, 2018, 122, 24690-24704

[4] Lagardère,L. et al., Chem. Sci., 2018, 9, 956-972

**Internship period:** February – June 2024. Dates can be adapted around this period. This internship will take place in the PHENIX laboratory, located on the Pierre et Marie Curie Campus of Sorbonne Université.

*The internship will be adapted to the sanitary conditions and home working will be implemented if necessary.*

## Contact :

*Sorbonne University is a world-class, research-intensive university bringing together a broad range of arts, humanities, social sciences, natural sciences, engineering and medicine. The scientific Pierre and Marie Curie campus was completely refurbished in 2016.*

*PHENIX is a laboratory at the interface between Chemistry, Physics and Materials Science with a long-standing expertise of colloidal systems, electrolytes and fluids under confinement. Its strength lies in a combination of experimental and modelling activities (numerical simulations). Several international projects and networks are in place in PHENIX, providing a rich and multinational environment.*

