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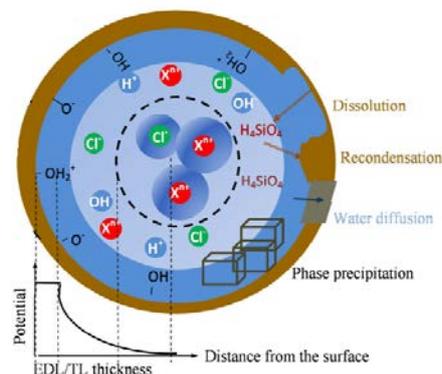
# ETUDE DE LA CHIMIE DE L'EAU EN PRESENCE D'IONS DANS DES SILICES NANOPOREUSES

## Chemistry of water in nanoconfined media in presence of different ions

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Prediction of material behaviors regarding their interactions with water is interesting for geochemistry and requires the use of modelling. Thermodynamic models and rate laws integrated in computer programs (PHREEQC, JChess...) used to predict materials dissolution kinetics and phase transformation integrate data obtained from experiments performed in diluted media. Due to the fact that most of the materials in these domains are nanoporous filled with water and ions (clay materials, secondary minerals formed from rocks, alteration layer of glasses...) and the validity of these models and rate laws are still not proven yet, thus, prediction can be defective.<sup>1</sup> The strong interaction between water and the surface in confined media are not considered in such calculations.



Furthermore, it is also expected that nanoconfined water molecules are strongly influenced by the presence of ions through sorption processes at the surface. The ions ability to be solvated also modify the electrostatic interactions in the system. These are really important since it strongly impacts the hydrolysis rate of materials<sup>2,3</sup>

The PhD can be divided in three main parts :

### 1. Validation of Double/Triple layer models within model samples

Due to the fact that chemical reactions in materials are controlled by an interfacial layer of few nm the first goal is to determine the pore size domain of validity of the conceptuel model such as the Electric Double / Triple layer.<sup>4,5</sup> Before adjusting the models in confined media having this critical size known to modify the properties of aqueous solution, 3 nm typically, we started to investigate the ions distributions at SiO<sub>2</sub> surface in 5 nm confined media. To reach this goal, we used a SiO<sub>2</sub> model system consisting in two parallel plane surfaces spaced of 5 nm (nanochannels) filled of electrolyte solution XCl<sub>2</sub> (X = Ba, Ca, Mg). To characterize the ion distribution we have used X-ray reflectivity (ESRF Grenoble BM32), technique particularly interesting since it allows the determination of electron density profiles perpendicular to the surface.

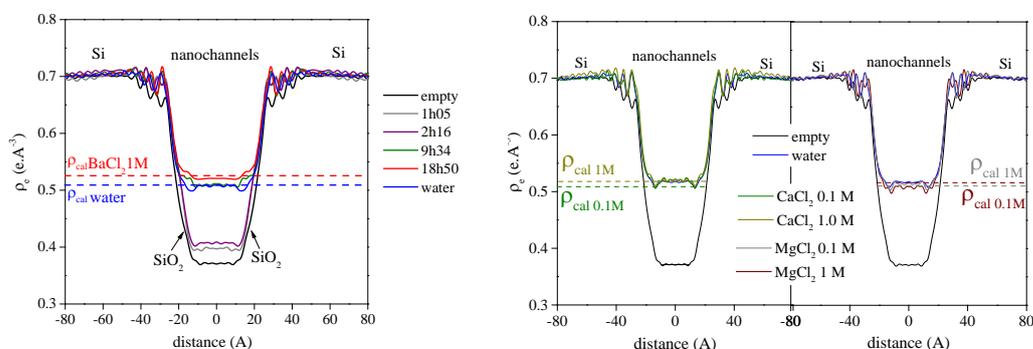


Figure 1 : Electron density profiles obtained from X-Ray Reflectivity measurements for XCl<sub>2</sub> solutions (X= Ba<sup>2+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>). The figures show the first results of X-Ray reflectivity measurements. After the filling process one can observe an increase of electron density at the silica surface perhaps due to adsorption of ions on to the surface.

## **2. Water reactivity and geochemistry**

The second part deals with the investigation of water reactivity inside two different confined media (MCM-41 and SBA-15). At first adsorption isothermes are accomplished in order to determine the concentration of ions inside the pores. These isothermes were made by analyzing the material and the different salt solution by ICP-AES and Ionic Chromatography. Furthermore SAXS measurements should give information about the material evolution depending certain parameters. Analyzing the Bragg-Peaks of the material one can predicate dissolution and recondensation rates under different conditions (varying concentration and species of salt solutions, time, temperature etc.)

## **3. Structure and dynamics of water**

The main focus in the last part of the PhD should be lied on the determination of water dynamics and the corresponding structure within the pores. Here especially the interaction of water with the surface molecules and the hydration behavior of water are interesting. The properties should then be investigated as a function of decreasing pore size. This can be done by grafting methyl groups inside the pores step-by-step. By using differential scanning calorimetry and thermal gravimetric analysis binding enthalpy between water molecules and surface groups can be measured. The dynamics of nanoconfined water is characterized using Quasi-Elastic neutron scattering (QENS) and NMR. Expecting strong interaction between the molecules and the surface in confined media we are estimating a slow down of water motion from the pico to the macro scale.<sup>2</sup> In a last step RAMAN and low-temperature RAMAN can give information about the hydration enviroment of water molecules and the arrangement between themselves. All these features should be influenced by different ion species.

All the obtained results in this PhD should help to better understand the evolution of nanoporous materials inside water and different ion solutions. Adjusting the dissolution kinetics and the electrostatic models at the surface should lead to an enhanced prediction of material evolution. This prediction is made with computer programs which use data from experiments in bulk solution up to now. Furthermore the obtained results should be compared with the theoretical modelling of the Laboratoire de Modélisation Mésooscopique et Chimie Théoretique at ICSM (LMCT).

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