Experimental report

05/06/2020

Proposal: 7-04-161 **Council:** 4/2018

Title: Influence of calcium interlayer cations on confined water atomic vibrations in swelling clays with contrasted hydrophobic properties.

Research area: Other...

This proposal is a continuation of 7-04-147

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Samples: (Ca0.4.nH2O)(Mg5.2Li0.8)(Si8.0)O20(OH)4
(Ca0.4.nH2O)(Mg5.2Li0.8)(Si8.0)O20(F)4

Instrument	Requested days	Allocated days	From	To
IN1 LAG	5	5	06/07/2019	11/07/2019

Abstract:

Hectorite is a swelling clay mineral formed by two tetrahedral sheets sandwiching a central octahedral sheet. This last is constituted by magnesium atoms with a few substitutions by lithium atoms. Isomorphic substitutions generate a negative layer charge balanced by hydrated interlayer cations. Anionic substitutions with fluorine (F-Hect) replacing structural hydroxyl groups (OH-Hect) induce the reduction of water content in the interlayer space of F-Hect as confirmed by gravimetric, X-ray diffraction experiments and molecular simulations. Water organization is also affected, atomic vibrations signal indicates an isotropic environment of the confined water molecules in F-Hect in contrast with the known anisotropic character of confined water in OH-Hect. These results were restricted to samples with sodium as interlayer cations. To improve the F-Hect characterization, we now wish to study the same samples saturated with calcium, well known to impact the organization and dynamics of confined water. The impact of both cation and anionic field on the librational bands of interlayer water would thus be studied. Such experiment is estimated to 5 days of beam time on Lagrange.

Confinement strongly affects dynamical properties of liquids, water being one of the most important examples. Swelling clay minerals are a prime example of 2D water confinement, being layered alumino-silicates formed by two sheets of silica tetrahedra sandwiching a magnesium/lithium octahedral hydroxide sheet. Isomorphic substitutions in the hydroxide sheets induce a permanent negative layer charge compensated by the presence of hydrated cations in the interlayer space. Depending on water activity and cation nature, hydration of the structure results in the incorporation of 0, 1 or 2 planes of interlayer H_2O molecules, corresponding to the dehydrated, mono-hydrated and bi-hydrated states, respectively. For hectorite, a magnesium-rich member of the swelling clay minerals, hydroxyl groups from the magnesium/lithium hydroxide sheet can be easily replaced by fluorine. Fluorinated samples (hereafter referred to as fluorohectorite or Hectorite-F) represent ideal specimens to probe interlayer H_2O organization using neutron radiation owing to the absence of structural OH groups.

This experiment aimed at studying the anisotropy of H_2O molecule vibration modes in fluorinated and hydroxylated swelling clays samples prepared with Calcium as interlayer cation. For each sample, inelastic spectra were recorded parallel and perpendicular to the clay layers ($Q^{//}$ and $Q^{\perp}$ to the clay layers) at low temperature in order to decrease the Debye Waller factor for the dehydrated and bi-hydrated states (0W and 2W respectively). The Inelastic Neutron Scattering (INS) spectra shown in Figure 1 was measured at 5 K in the range of energy transfers from 8 to 4000 cm^{-1} with an energy resolution of $\Delta E/E \approx 2$ using LAGRANGE. In the present experiment the energy transfer was calculated by subtracting 4.5 meV, the energy of the PG crystals in the ellipsoid, from the energy of the incoming neutrons selected with a focusing Cu(220) single crystal and bent Si(111) and Si(311) reflections. The background spectrum from the cryostat and an empty sample holder was measured separately and then subtracted from the raw INS spectrum of the sample. Data sets were then normalized for monitor counts and corrected for empty cell.

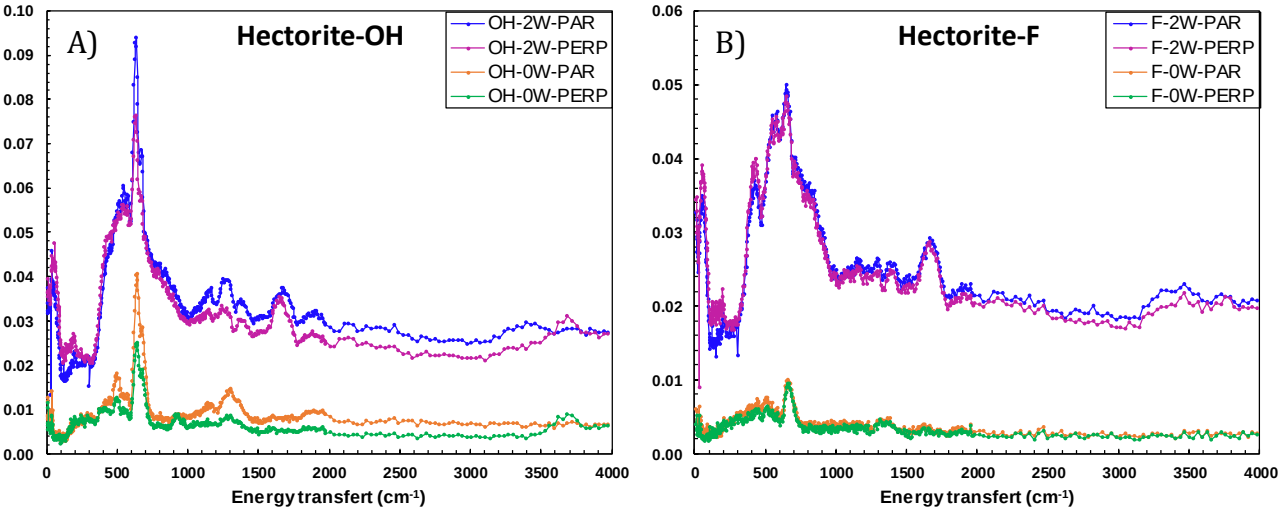

Figure 1. (a) INS spectra of hectorite OH with 0 and 2 layers of water and (b) INS spectra of hectorite F with 0 and 2 layers of water.

The experimental results were confronted to numerical predictions carried out by Ab-initio Molecular Dynamics (AIMD) simulations (Figure 2) calculated by using the CASTEP *ab-initio* simulation package in Materials Studio software. By comparing experimental INS spectra of dehydrated samples with calculated ones, it is possible to assign all the observed vibrational bands for dry hectorite, even those that are very weak in IR spectra. Such an agreement between calculated and experimental spectra validates the model.

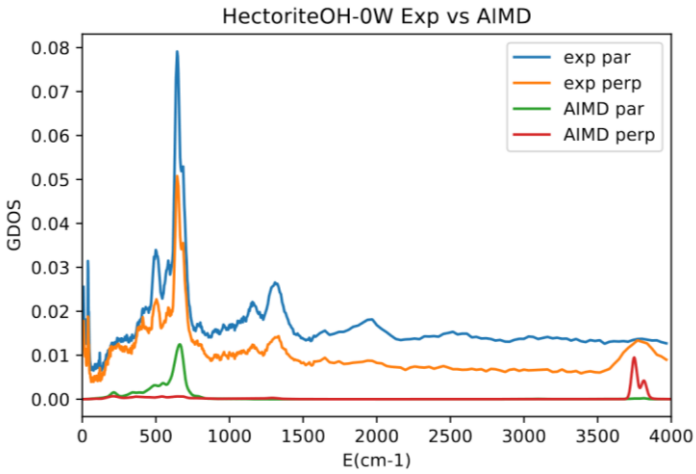

Figure 2 Comparison of the experimental and AIMD simulations INS spectra for dehydrated hectorite OH.

The density of states of hydrated hectorite currently being calculated by means of *ab-initio* Molecular Dynamics simulations. The velocities of the different atomic species will allow calculating the partial density of states and subsequently the INS spectra. Using such a strategy, different contributions to the GDOS can be computed in two directions: the parallel and the perpendicular one. This comparison will allow assessing the effect of the hydrophobicity of the framework on the librational bands of confined water.