Experimental report

09/02/2018

Proposal: 7-04-147 **Council:** 4/2016

Title: Influence of structural fluorine on the atomic vibrations of confinedwater in swelling clays

Research area: Other...

This proposal is a new proposal

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Samples: (Na0.8nH2O)(Mg5.2Li0.8)(Si8.0)O20(OH)
(Na0.8nH2O)(Mg5.2Li0.8)(Si8.0)O20(F)4

Instrument	Requested days	Allocated days	From	To
IN1	6	6	20/01/2017	26/01/2017

Abstract:

Swelling clay minerals (Hectorite) are layered alumino-silicates formed by two sheets of silica tetrahedra sandwiching a magnesium/lithium octahedral hydroxide sheet. In addition to isomorphic cation substitutions, hectorite layers may present anionic substitutions with fluorine replacing the structural hydroxyl groups resulting in the decrease of H2O molecules hydrating interlayer cations. This proposal aims at studying the anisotropy of the vibration modes of interlayer H2O molecules in both hydroxylated and fluorinated swelling clays. We propose to study the vibration modes of H2O molecules on the inelastic spectrometer Lagrange that will allow reaching the relevant excitation energies. The samples under investigation will be those previously studied by means of GCMC and X-ray diffraction experiments and which displayed a clear directional contrast. The time needed for such experiments 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 (hectorite) 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 (inset Fig. 2). 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, 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. In addition to isomorphic cation substitutions, hydroxyl groups from the magnesium/lithium hydroxide sheet can be 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 hydroxylated and fluorinated hectorites. 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, mono-hydrated and bi-hydrated states (0W, 1W and 2W respectively). The Inelastic Neutron Scattering (INS) spectra shown in Figure 2 was measured at 5 K in the range of energy transfers from 16 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.

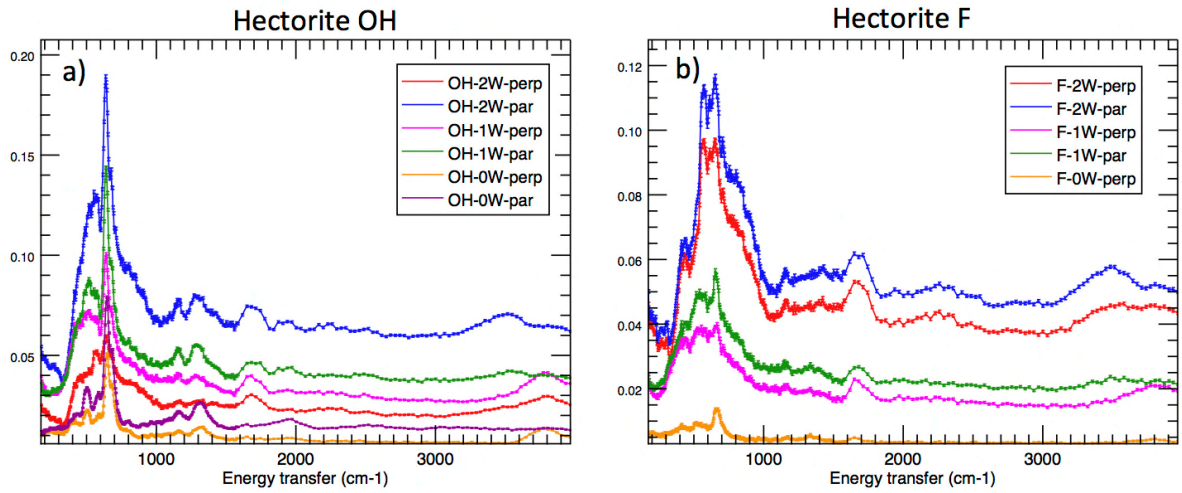

Figure 1. (a) INS spectra of hectorite OH with 0, 1 and 2 layers of water and (b) INS spectra of hectorite F with 0, 1 and 2 layers of water.

The experimental results were confronted to numerical predictions carried out by normal modes analysis (Figure 2). The theoretical VDOS (ω) was calculated using the

direct method on the basis of first-principles calculations. Calculations on the relaxed structure and the eigenmodes, obtained from the dynamical matrix, were calculated by using the DMol3 *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.

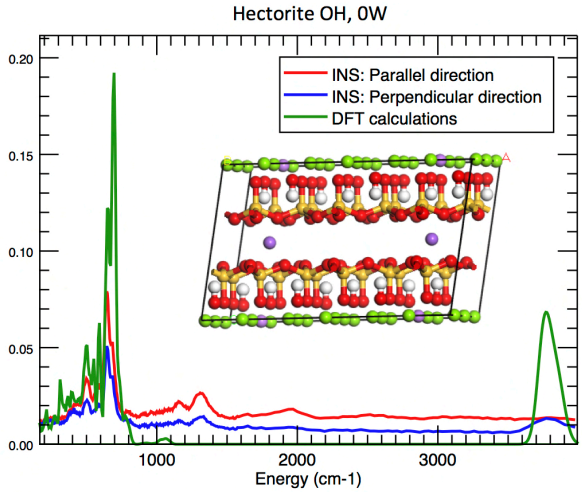

Figure 2 (a) Comparison of the experimental and DFT-calculated INS spectra for dehydrated hectorite OH. Inset shows the crystal structure. Key: Mg, green; light purple, Li; red, O; white, H; yellow, Si.

The density of states of hydrated hectorite are 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.