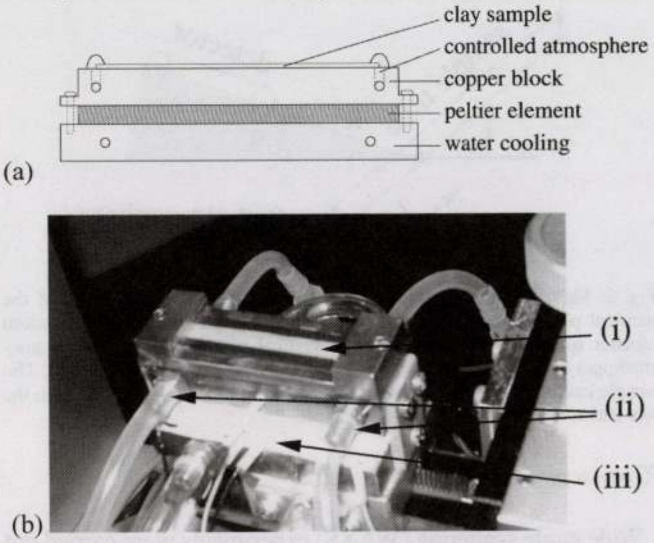

Fig. 3: (a) Side view of the sample holder, with copper block and Peltier element underneath - (b) Photo of the sample environment during an experiment carried out on a sedimented sample. The sedimented sample is isolated from the lab atmosphere by a thin kapton film glued on top of it.

a temperature of 24°C, with dry air circulating at both ends, long enough for all scatterers to be at equilibrium under a 1WL hydration state. Reference scattering spectra were then recorded. The spectrum labeled "1WL" in Fig. 4 is an example of such a graph. Temperature was then lowered down to 5°C. Half an hour later, thermal equilibrium was reached and we started circulating humid air at one end of the sample, imposing a humidity gradient across the length of the sample. This was defined as the initial time for water diffusion. Water penetrating the sample came in contact with particles in the 1WL state at a temperature where their equilibrium state is 2WL, hence triggering the displacement of an intercalation front in the sample, along with water diffusion.

Pressure was measured in the chambers at both ends of the samples prior to- and at the end of- the experiment. No significant pressure gradient was measured between the sample ends.

X-RAY DATA

Scattering from the nano-layered particles

The one-dimensional scattering spectra display sharp peaks for deviation angles 2θ corresponding to a Bragg reflection of some of the scatterers in the scattering volume. Apart from peaks from quartz impurities (denoted by "Q" in Fig. 4), these sharp peaks are mostly those characteristic of Bragg planes associated with the particle stacks. In Fig. 4, we show reference spectra for scattering volumes where the scatterers are in the 1WL and 2WL hydration states, and for the two types of samples. The various (00k) orders observed are indicated. Due to form factor effects, some of those orders are extinct. The spectra for the sedimented samples exhibited a large background caused by the silicon glue that we used to seal the top of the samples to the kapton. This was not observed for the powder samples, as they were inside capillary tubes.

The (001) peaks are very weak for the sedimented samples, this is due to some shadowing effect by the copper block at low angle as these samples are actually lying in a trench carved onto the top surface of the copper block. For that reason we had to treat higher order peaks when working with the sedimented samples, while for powder samples we could use the first order peaks, which are also the better resolved ones. For that reason we only present, in what follows, data obtained from the powder samples.

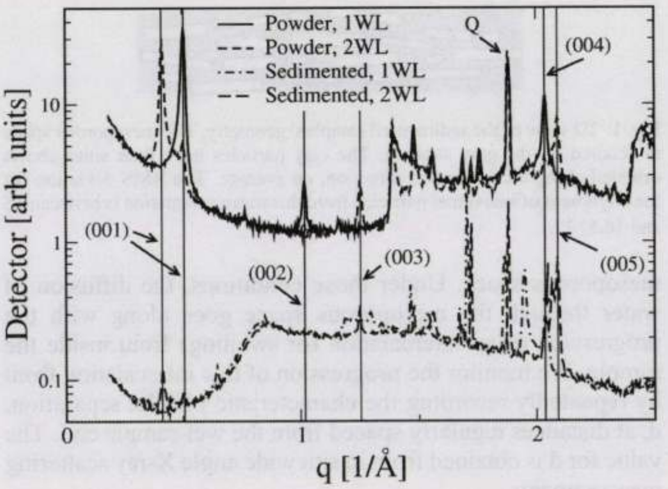

Fig. 4: Scattering spectra as a function of the momentum transfer q for powder (spectra at the top) and sedimented samples (spectra at the bottom). In each case, two spectra are shown: one recorded at a position in the sample where most of the scatterers are in the 1WL hydration state, the other at a position where most are in the 2WL state. The vertical scale is logarithmic, the spectra have been normalized arbitrarily for conveniency.

Hydration transition at a given position

Fig. 5(a) is a close view of the spectrum measured at a position l = 7.0 mm from the wet end of the sample, at different times after the diffusion process has started. The width of the beam was 3 mm. As water diffuses inside the sample, the relative humidity in the scattering volume increases. Consequently, water starts intercalating in some of the scattering particles. This is marked by a decrease in the intensity of the peak characteristic for the pure 1WL hydration state, and the appearance of an asymmetry in its shape. This asymmetry evolves into a broad and low intensity peak that appears between the 1WL and 2WL peaks. This is characteristic of the existence of scatterers in various coexisting mixed Hendricks-Teller intercalation states, with different proportions of 1WL and 2WL spacings inside scatterers[12]. These mixed states progressively blend into the shoulder of the pure 2WL peak that has started appearing after 7 hours. After ~ 17 h, only a pure 2WL peak is observed. We therefore consider that the intercalation front has penetrated in the scattering volume at t = 7.0 h, and left it 10±1 hours later.

From Fig. 5(a), we have plotted the evolution of the relative intensities for the pure 1WL and 2WL peaks as a function of time (see Fig. 5(b)). This was done by first subtracting the background from Fig. 5(a), and then normalizing the amplitudes by those observed when no random intercalation is present. From the intersection of the two curves, we infer that the time at which the mean front position is in the middle of the scattering volume is ~ 8.7±1 h, at l = 7±1 mm.