



	<b>Experiment title:</b> Phase transitions in complex materials – The effect of absorbed water on clay structure	<b>Experiment number:</b> 01-02-321
<b>Beamline:</b> BM01A	<b>Date of experiment:</b> from: 18/07/2001                      to: 22/07/2001	<b>Date of report:</b> 26/09/2003
<b>Shifts:</b> 12	<b>Local contact(s):</b> Dr. Jon Are Beukes	<i>Received at ESRF:</i>
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### Scientific background – motivation for the study :

Clay is a traditional material with a number of important geotechnical and industrial applications [1]. Natural clays have been widely studied from a structural and phenomenological point of view, in particular in the geo-sciences. However, little is known about the microscopical mechanisms that are responsible for complex physical phenomena (as liquid to non-liquid transitions) observed in clay systems. In particular, variations in water contents and salt concentration are responsible for the drastic (and often detrimental) phase transitions observed in clay layers in nature, which are still poorly understood. Hence, there is currently a growing scientific activity associated with synthetic clay materials. We have been studying for several years the interaction between clay particles and the solvent in clay systems [2, 3], trying to relate the changes in the internal microscopic structure to macroscopic behavior. High intensity X-rays have proved to be a most important tool in these studies, as it allows us to dynamically probe the nano-structure of the material, on a time-scale of a few minutes.

Dehydrated clays can be viewed as intercalation compounds within the general context of "nano sandwiches". All dehydrated clays are based on a layered silicate meso- structure. The so-called 2:1 clays (or smectites) thus consist of 1 nm thick and charged (negative surface charge and a smaller positive edge charge) meso sheets, which in the dehydrated state stack (like decks of cards) by sharing charge-compensating cations. The 1nm thick sheet maybe broken down into three atomic layers, i.e. generally one metal hydroxide layer sandwiched in between two identical silicone tetrahedral oxide layers. Into this structure, monolayers of water may be intercalated together with the charge compensating cations. In the experiment reported here we studied the synthetic clay X-fluorohectorite, where X is an exchangeable cation.

The purpose of the experiment was to investigate the dynamics of water intercalation into a synthetic fluorohectorite clay as measured by x-ray scattering by monitoring the "out of plane" Bragg peaks, which measures the clay silicate interlayer stacking distance, as it moved due to the intercalation of water molecules, mono-layer by mono-layer.

### Experimental method:

We collected 2D diffractograms at a wavelength  $\lambda = 0.8 \text{ \AA}$  from fluorohectorite,  $\text{Na}-(\text{Mg}_2\text{Li})\text{Si}_4\text{O}_{10}\text{F}_2$ . The measurements were performed as a function of time at different temperatures (between 0 and 130 °C) and with varying degree of relative humidity. The temperature and humidity were controlled by a specially designed portable setup that includes a small closed cell (with beryllium windows) containing the sample. This setup was brought to ESRF from Norway. The cell is supplied with tubing where air circulates via a chamber in which the humidity is controlled by means of a saturated salt solution. Heating and cooling are performed by means of a resistor film and a Peltier element, respectively. The cell was fit onto the space available in the sample area for the MAR image plate system, and heat shields were installed in order to avoid any accidental heating of the MAR goniometer base or slit system.

From initial studies on this system we knew that the structural changes related with water absorption would take up to a few hours at each temperature, and this was confirmed. We investigated Na-fluorohectorite samples at 2 different relative humidities (RH), near 0 % RH and near 100% RH. We thus studied the absorption process (time scale and structural changes) connected with water uptake in swelling clays, using fluorohectorite as an example.

### **Results obtained:**

The degree of water uptake influences drastically the physical properties of the initially dehydrated clay. We wanted to determine how this is connected to the destabilization of the interaction between the building blocks of the material. How does the internal structure of the material change with water uptake ? An interesting observation is the ability of Ni-fluorohectorite to uptake a maximum amount of 3 water mono-layers, in contrast to 2 layers for Na-fluorohectorite, as previously observed [3] and hereby confirmed . Earlier observations on the Na-fluorohectorite stacking distance as a function of temperature and humidity were confirmed, while similar results are in the process of being obtained for Ni-fluorohectorite. Of particular interest is the possibility of Hendricks-Teller like random intercalation in such systems; such transient peaks were observed during transition from one water layer configurations to two-water layer configurations. Little is known about positioning of intercalated water on and close to internal clay surfaces, and also little is known about whether presence of water molecules causes structural changes to take place internally in the 1 nm thick smectite clay platelets. We hope to get information about these and other questions, by focusing on the in plane Bragg peaks of our SNBL MAR data. Due to the very large number of two-dimensional plate data collected during this run, we are still in the process of analyzing the data. These analyzes address in particular a study of the in-plane peaks, which we hope will provide information on the distortion of the silicate sheets under the effect of the intercalation of water.

In terms of data collection the experimental run was a great success, even under the available conditions of single bunch mode at ESRF during our run. However, trying to resolve the width of the (001) peaks, we found out that the contribution of the instrument resolution to that width was of the same order of magnitude as the width itself, hence it was not possible to accurately determine the intrinsic width of the peak, relative to the diffraction by the sample. During the experiment we used a focused mean, and we think that using an unfocused beam would allow us to resolve the intrinsic width of the diffraction peaks, in the future. Such a study is being seriously considered. Nevertheless, this first experiment at SNBL has established the foundation for further applications from us for MAR SNBL experiments on the continuation of this project and on other related projects.

### **References:**

- [1] B. Velde. *Introduction to Clay Minerals*. Chapman and Hall, London, 1992.
- [2] J. O. Fossum. Physical phenomena in clays. *Physica A*, 270(1-2), 1999.
- [3] G. J. da Silva, J. O. Fossum, and E DiMasi et al. Synchrotron X-ray scattering studies of water intercalation in a layered synthetic silicate. *Phys. Rev. E*, 66(1):011303, 2002.