ESRF	**Experiment title:** WAXS studies of the temperature dependence of orientational ordering in a nanolayered silicate	**Experiment number:** 01-02-678
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Scientific background – motivation for the study :

Natural clays have been widely studied from a structural and phenomenological point of view, in particular in the geo-sciences [1]. 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. We have been studying for several years the interaction between clay particles and the solvent in hydrated 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.

The synthetic swelling clay fluorohectorite is a very appropriate compound for such studies, as it exhibits a behavior identical to those of natural smectite clays, while presenting precisely defined chemical properties characteristic of synthetic compounds. The 1 nm thick meso-sheets of this 2:1 (smectite) clay possess a negative surface charge on their planar boundaries which allows them to stack like deck of cards by sharing charge-compensating intercalate cations. The latter cations can be exchanged so as to tune the electrostatic interactions between the stacks and/or the solvent.

In the WAXS experiments presently reported, we studied colloidal system of fluorohectorite particles in salt water. Clay particles are platelets consisting of stacks of about a hundred of meso-sheets [4] as mentioned above ($\sim$ 100 nm), with dimensions along the meso-sheets ranging from a few hundreds of nm up to a few μm. For colloidal systems consisting of such asymmetric particles, nematic phases can arise spontaneously (i.e, without shear of external field). Direct structural evidence of nematic ordering has been provided recently for colloidal systems of laponite [5], another synthetic smectite clay for which meso-sheets do not stack and present a very monodisperse size distribution. Our polydisperse fluorohectorite colloidal systems exhibit a spontaneous gravity-induced separation, where as many as 4 different phases may be observed in the same sample tube [2]; observation of phase-separated samples between cross-polarizers suggests nematic ordering for one of these phases [6].

A series of SAXS measurements was carried out at the DUBBLE beam line BM26B in June 2003.

This experiment showed that there is no correlation in the positions of the particles, but their relative orientations are correlated, the particles having their silica sheets vertical (on average). The presently reported WAXS experiments were carried out in order to test the isotropy of the particle orientation in the azimuthal plane, as well as to investigate the dependence of this ordering on temperature.

Experimental method:

The three types of samples studied consisted of fluorohectorite (X=Na, Ni and Fe) particles immersed in a silicone oil (viscosity 100 cSt). They were investigated by Wide Angle X-Ray Scattering, using a wavelength $\lambda = 0.71$ Å. The samples were prepared in tubes in which the different phases lie on top of each other. The sample holder could be translated in the three directions of space, and rotated. A specially designed temperature-control system was used.

Two-dimensional diffractograms were recorded at various vertical positions along the sample tubes (corresponding to various clay particle- and salt- concentrations). Firstly, a series of cylindrical sample tubes were used in order to test for the nature of the nematic phase: if no change is observed when rotating the tubes, it means that there is no unique macroscopic direction for ordering, but rather many directions, all of them horizontal but corresponding to different azimuthal angles. Secondly, centrifuge-settled samples were studied with respect to gravity-settled samples. Thirdly, different shapes (rectangular section, square section, circular section) made out of various materials (quartz glass, borosilicate glass, kapton) were used under the same conditions to investigate whether the interaction of the particles with the cell walls influence the bulk ordering of the suspensions, and how. Fourthly, vertical scans were carried out on cylindrical sample tubes for different temperatures.

The 6 shifts of beam time awarded were fully utilized. The quantity of data acquired is very large.

Results obtained:

For cylindrically-shaped quartz sample tubes, the ordered phase present in the scattering volume was found to give isotropic scattering with respect to the azimuthal angle, which means that there is no single nematic domain there. Either there are many small nematic domains with random orientations of the directions of these domains, or the phase is not nematic, but pseudo-nematic (isotropic distribution of the directors in the azimuthal plane). The geometry of the phase is related to the the causes for the ordering: steric effects responsible for a thermodynamically stable ordered phase in the first case, or, in the second case, possible ordering induced by the fluid flow during gel settling, in which case the phase could well be frozen in a meta-stable state. Collected data on the influence of the shape of and material force for the cell walls is in the process of being analyzed. The data on the temperature dependence of the phases is also currently being analyzed.

References

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