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ESRF

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application:**

http://193.49.43.2:8080/smis/servlet/UserUtils?start

Reports supporting requests for additional beam time

Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

· fill in a separate form for each project or series of measurements.

· type your report, in English.

· include the reference number of the proposal to which the report refers.

· make sure that the text, tables and figures fit into the space available.

· if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** X-Ray microscopy study of clay gels and clay/polysaccharide aggregates	**Experiment number**: SC774
Beamline: ID21	**Date of experiment**: from: 9 nov 2000 to: 14 nov 2000	**Date of report**: 12/02/2001
Shifts: 15	**Local contact(s)**: Barbara Fayard, Murielle Salomé, Jean Susini	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

One of the aims of our experiment carried out on ID21 beamline in November 2000 was the *in situ* characterization of the porous structure of aqueous clay gels. Indeed, X-Ray microscopy allows to investigate much larger scales than those probed by scattering techniques. A secondary aim was to get a better understanding of the role and status of calcium ions in controlling the aggregation behaviour of clay minerals and the fabric of clay-polysaccharide aggreggates.

First experiments carried out at the Ca K absorption edge were unsatisfactory mainly because of the ubiquituous presence of calcium impurities in all the polymer windows tested. We then shifted to lower energies, working at 2.5 keV in order to perform a mapping of silicon atoms, (main components of clay minerals) through their fluorescence yield. Despite some experimental difficulties associated with the use of secondary vacuum, high quality images of montmorillonite clay gels could be obtained using such set-up (Figures 1 and 2). Figure 1 shows the silicon fluorescence yield image obtained on a first montmorillonite gel. It has been rebuilt from 4 different scans (100µm by 100µm with a resolution of 1µm and a dwell time of 400ms) The most striking feature of this image is the presence of long range orientational order (= 200 µm) with aligned domains richer in silicon (3 to 8 µm wide) alternating with Si-poor zones (5 to 30 µm wide) corresponding to water domains. Some water pockets with a non-lamellar morphology can be observed in zones where different clay-rich lamellae end. The silicon-rich objects are at least two orders of magnitude

larger than the size of the elementary clay layers which are polydisperse between 0.1 and 0.8 µm. **This image therefore represents the first direct experimental evidence for the existence of a superstructure in montmorillonite gels**. It must be stressed out that this orientational order is not directly due to individual clay platelets but to “packs” of clay layers, the structure of which remains to be determined.

A second image (Figure 2) obtained on a second montmorillonite gel with the same concentration, using identical acquisition parameters as the previous image, reveals similar oriented domains of silicon-rich lamellae alternating with water domains. However, in this case, orientational defects can clearly be observed. Two main types of defects can be distinguished : (i) bundles of lamellae secant to other bundles with an angle of around 110° (arrows 1 and 2); (ii) kink-folded structures affecting silicon-rich lamellae (arrows 3 and 4) that are typical of sheared structures observed in sedimentary and metamorphic rocks.

Our X-ray microscopy study of montmorillonite gels unambiguously reveals for the first time, the existence of large-scale structures much larger than individual clay platelets. At the same time, it raises numerous questions about the fundamental physical mechanisms underlying the formation of such entities. Using the present set-up, much information can be extracted by fully exploring the phase diagram concentration/ionic strength for a given clay sample and by investigating the influence of particle morphology (size and anisotropy) and polydispersity on the existence and formation of superstructures in both natural and synthetic (laponite) clay samples.

A publication based on these measurements was submitted to Langmuir in January 2001. (Evidence for oriented mesostructures in clay gels by synchrotron-based X-ray fluorescence microscopy by I. Bihannic, L. J. Michot, B. S. Lartiges, D. Vantelon, J. Labille, F. Thomas, J. Susini, M. Salomé, B. Fayard)

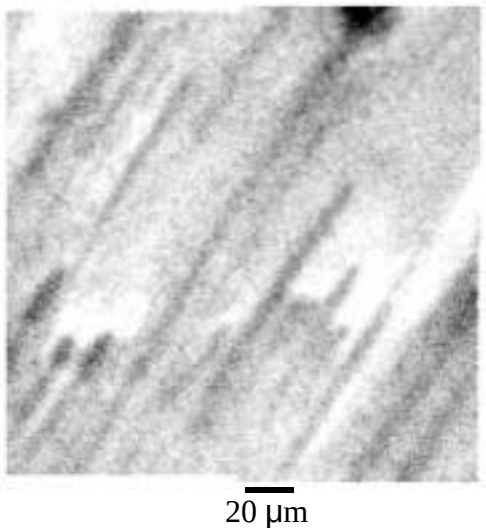

Figure 1. Silicon fluorescent yield mapping of a montmorillonite (Swy-2) clay gel at 50 g/l (resolution : 1 µm, dwell time : 400 msec).

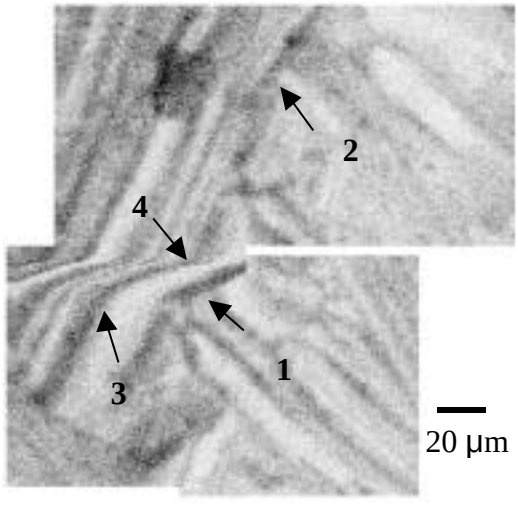

Figure 2. Silicon fluorescent yield mapping of a montmorillonite (Swy-2) clay gel at 50 g/l (resolution : 1 µm, dwell time : 400 msec. The arrows show the various types of orientational defects.