ESRF	**Experiment title:** Single crystal diffraction experiments on kaolinite:dimethylsulfoxide intercalate	**Experiment number:** CH315
Beamline: ID13	**Date of experiment:** from: October, 22 to: October, 26	**Date of report:** Feb. 23,1998
Shifts: 15	**Local contact(s):** M. Burghammer	*Received at ESRF':*

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Report:

The clay minerals and especially kaolinite can intercalate a number of small organic molecules, a process that could be used to temporarily store these chemicals in the the structure and shows promising catalytic properties. In oder to understand the catalytic properties it is importand to know the binding of the guest molecules to the kaolinite host structure. A powder refinement of the kaolinite:DMSO intercalate was not satisfactory. The current experiment was undertaken to obtain single crystal date for a structure refinement and for an analysis of disorder.

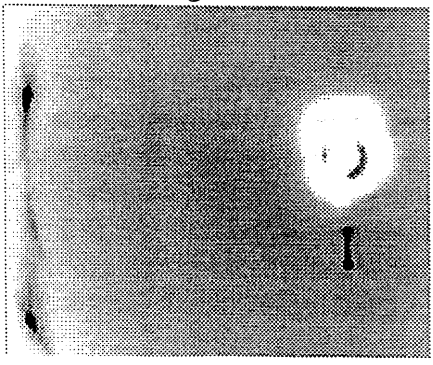
Preliminary experiments showed that the kaolinite:DMSO intercalate is not stable in a scanning electron microscope (SEM). The samples could therefore not be intercalated first and then mounted inside the SEM as had been done for previous experiments on micrometer sized single crystals of kaolinite (HC415, CH233). Instead several single crystals from various locations, representing different crystal qualities, were mounted onto thin glass fibers. The crystal volumes ranged from 15 to less than 1 μm^3. After the samples had been mounted the samples were exposed to the vapor of DMSO at 70°. A powder sample was intercalated under the identical conditions to verify the completeness of the intercalation. Since the individual single crystals are too small for laboratory experiments, no prior check of the

their intercalation was possible.

The data collections were carried out at the microfocus beamline ID 13. This beamline is the only beamline suited for diffraction experiments on crystals of such small sizes.
Several samples were screened to find a completely intercalated sample of good crystal quality. These checks revealed that all samples did not intercalate completely and that they decayed rapidly within some 10 minutes in the primary beam. Subsequent attempts to preform experiments at liquid nitrogen temperature with a cryogenic gas stream failed due to ice build up. The experimental background has to be reduced to the utmost minimum in order to record diffraction pattern form micrometer sized crystals. This requires a maxmimum free path of the X-ray through air of 7mm. For a successful1 repetition of the experiments we are currently investigating in collaboration with the beam line staff the options of microfocussing of a cryogenic gas stream.

Subsequent experiments on powders in the laboratory revealed that the kaolinite:DMSO intercalate decomposes already at temperatures as low as 70°, while previous reports suggested temperatures above 120°.

The X-ray induced thermal decomposition was followed during the current experiment by taking repeated exposures around the 001 reflection. We could show that at these low temperatures the diffusion of the DMSO is not a cooperative effect as it is at higher temperature. The final structure after thermal decpomposition above 160° resumes the original crystal quality. A lower temperatures still decomposes but a much more intensive diffuse scattering is observed in our single crystal diffraction pattern. Our preliminary interpretation is that many small islands of intercalated material remain in a matrix of collapsed kaolinite. This causes severe elastic deformation of the silicate sheet and in turn diffuse scattering.



The pattern shows the two maxima of the 001_{DMSO} and 001 with a broad abnd of diffuse scattering connecting them. The reflections to the left reveal diffuse scattering due to stacking faults as well.