

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.



	Experiment title: Analysis of the interaction between organic adsorbates and the (104) calcite cleavage surface	Experiment number: SI-928
Beamline: ID03	Date of experiment: from: 04.12.2003 to: 09.12.2003	Date of report: 23.02.2004
Shifts: 15	Local contact(s): Dr. Hyojung KIM	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Prof. Dr. Hermann GIES ^a * PhD Uta MAGDANS ^a * Dr. Xavier TORRELLES ^b * ^a Fak. GMG, Inst. f. Mineralogie/Kristallographie, Ruhr-University Bochum, Germany ^b Institut de Ciencia de Materials de Barcelona (CSIC), Spain		

Report:

In continuation of our investigation of the structure of the (104) cleavage surface of calcite with GIXRD techniques, we measured in the first part of our beamtime for the first time CTRs of the completely hydrated calcite (10.4) surface. The experimental data show additional peaks between the Bragg peaks of calcite, caused by an ordered layer of water molecules on the surface.

In the second part of the experiment we measured CTRs of the freshly cleaved calcite (104) face covered by a thin film of benzoic acid solution, as well as the specular rod (00L). Here the intensity of the measured CTRs is very weak. Most of the rocking scans were not analysable because of the bad S/N ratio. The scattered intensity was damped by the film of the buffered solution and by the mylar foil of the sample cell, which caused additional diffuse reflection. We were not able to obtain information about the arrangement of the adsorbed benzoic acid molecules on the surface and their structure conformation.

Experimental

The experiment was carried out at the surface diffraction beamline ID03 at the ESRF. The incident X-ray beam, generated by an undulator, was monochromatized with a sagittally focusing Si(111) crystal monochromator and set to an energy of 17.2 keV (0.7205 Å wavelength). An optical-quality calcite single crystal was freshly cleaved in air into pieces of about 11 mm x 9 mm x 4 mm in size. A sample without optically visible steps and defects was selected and mounted under a continuous stream of N₂ in an X-ray transparent electrochemical cell coupled to a six-circle diffractometer. The cell was then closed with mylar foil and filled with solution (ultrapure water, buffered benzoic acid

solution) using a syringe. By generating an depression in the cell by the syringe the mylar foil was sucked in reducing the film thickness of solution between the sample surface and the foil.

The measurements of the CTRs were performed in vertical scattering geometry. The incoming beam was vertically focused to about 1 mm and horizontally defined by slits to about 0.2 mm at the sample position. The incidence angle between the horizontally mounted sample surface and the X-ray beam was selected to 0.3° , close to the critical angle of calcite. The scattered beam was defined by a pair of slits in front of the detector set to 2 mm x 2 mm along the surface normal (vertical) and surface plane (horizontal), respectively.

The integrated intensity of a given reflection was obtained by orienting the sample and detector to the respective diffraction condition and then collecting the detector signal in a rocking scan around the surface normal at both sides of the diffraction maximum. The intensity profiles were corrected for polarization, Lorentz- and experimental factors, fitted with a Lorentzian function and integrated after subtracting a linear background.

The analysis of the CTR data of the hydrated surface with the software ROD [1] is in progress. We use the orthorhombic calcite unit cell, with cell parameters $a_1 = 8.095 \text{ \AA}$, $a_2 = 4.990 \text{ \AA}$ und $a_3 = 24.2864 \text{ \AA}$, to model the bulk and the surface atom positions. Accordingly the (104) face of the hexagonal system equals the (001) face of the orthorhombic unit cell. The (001) surface of the orthorhombic cell has the plane group pg with a glide plane symmetry along a_1 -direction. The used surface cell consists of 8 layers of atoms (in z-direction), with 2 calcium and 2 carbonate groups, respectively. The 1st ordered layer of watermolecules (2 per surface cell) is positioned about 1 \AA above the topmost calcite layer. Additional layers of ordered watermolecules will be required to obtain a good fit of the experimental data. Refined model parameters are the atom positions, rotation and deformation of the carbonate groups, site occupation factors (sofs) and temperature factors of the atoms in the surface cell and the watermolecules.

Hydrated calcite surface structure

We present here only preliminary results of the analysis of our data because of the short time between experiment and report-deadline. The analysis of the Rocking scans in order to obtain the CTRs must be made very carefully and is therefore relatively timeconsuming.

With this experiment we have now completed the investigation of the surface structure of the (104) calcite cleavage surface as a function of different stages of hydration. We obtained from our data of the last experimental period for the first time a detailed picture of the mineral/surface structure on atomic scale of the calcite/water system with X-ray diffraction methods. Our results show an increasing relaxation of the topmost surface layers due to the influence of water. We observed a large rotation of the topmost carbonate groups and a small tilt of these groups towards the surface in contrast to the model proposed by Fenter et al. derived from the one-dimensional electron density profile of their X-ray reflectivity experiment [2]. We were able to obtain from our data also information about the lateral structure of the ordered layer of water molecules on the calcite surface. In agreement with theoretical simulations [3] the water molecules are positioned in about 2.2 \AA distance above the Ca-ions completing the octahedral coordination of Ca with O atoms. Because of the rotation of the topmost carbonate groups the Ca-O-octahedron on the surface is strongly distorted. With increasing depth this rotation decreases due to the decreasing relaxation of the structure. The bulk configuration is reached in the 4th layer of the orthorhombic calcite surface cell. A paper about these results is in preparation and will be published as soon as possible in the European Journal of Mineralogy (EJM). The present analyse of the data of the completely hydrated surface show a pronounced intensity between the Bragg peaks of calcite. Figure 1 shows the (2,1,L)-CTR of the calcite (104) surface as measured for the clean dry surface (red points), the surface in a humid environment with 80% r.h. (blue diamonds) and the surface covered with a thin film of liquid water (black squares). The large difference between the three curves indicates a change in the structure of both surface and ordered water layer. We have no detailed information so far, but the analysis is in progress.

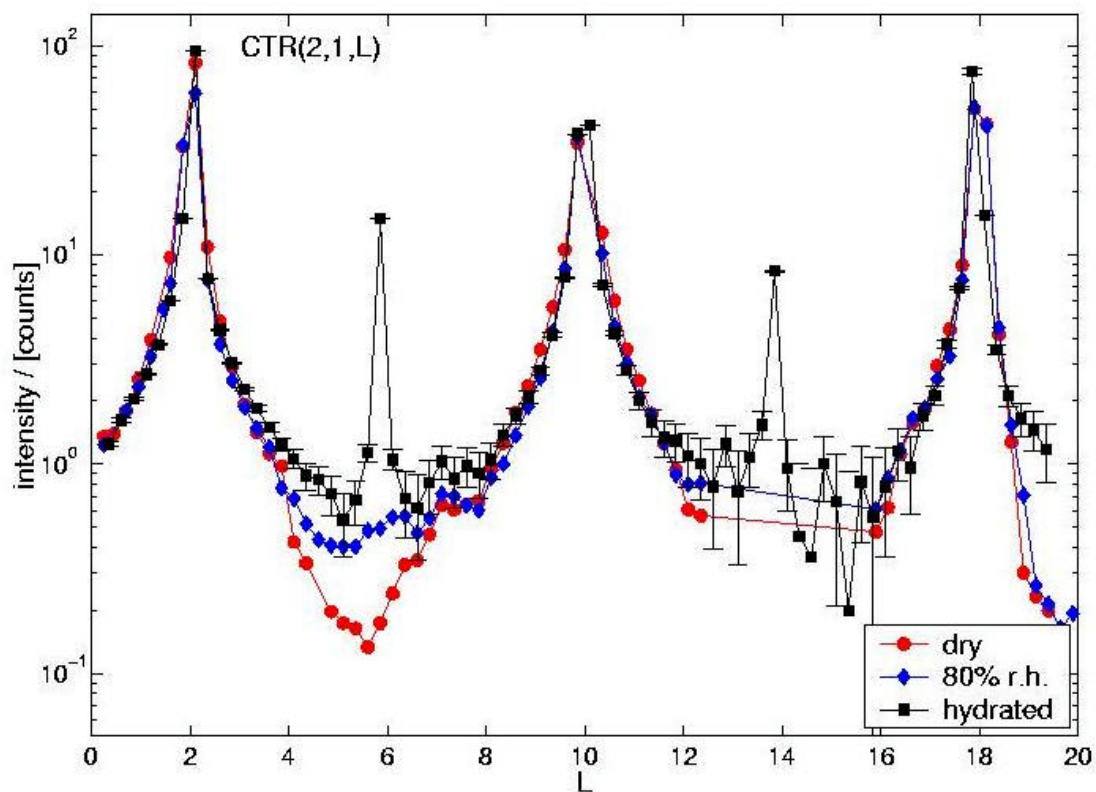


Fig. 1: Experimental data of the (2,1,L)-CTR of the (104) calcite surface under dry (red circles) and humid N_2 -atmosphere with 80% r.h. (blue diamonds) compared with the measured data of the completely hydrated surface (black squares). The errorbars are only shown here for the CTR of the hydrated surface for higher clarity.

References

- [1] Vlieg E., *Appl. Crystallogr.* **33**, 401 (2000)
- [2] Fenter P., Geissbühler P., DiMasi E., Srajer G., Sorensen L.B., Sturchio N.L., *Geochim. Cosmochim. Acta* **64**, 1221-1228 (2000)
- [3] de Leeuw N.H., Parker S.C., *J. Chem. Soc. Faraday. Trans.* **93**(3), 467-475 (1997)