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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.

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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:** Analysis of the interaction of water molecules with the calcite growth face (001)	**Experiment number**: SI-831
Beamline: ID03	**Date of experiment**: from: 12.09.2002 to: 17.09.2002	**Date of report**: 26.02.2003
Shifts: 12	**Local contact(s)**: Dr. Christopher Walker	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

We investigated the (104) calcite cleavage surface of calcite under dry and humid conditions with GIXRD techniques at beamline ID03 at the ESRF. We measured for the first time CTRs of the freshly cleaved calcite (104) face under dry and humid N2 gas (r.h. about 80 %), as well as the specular rod (00L) under both conditions.

The measurement of the originally proposed (001) surface of calcite was impossible to perform, because of the roughness of the (001) surfaces of our few natural geological samples was to high for surface diffraction measurements. The (001) surface expressed in the morphology of some geological calcites turned out to be a pseudo-face, consisting mostly of steps of monolayer height and with a high step-density. So we were forced to concentrate in our experiment on the (104) calcite surface, which is obtained by cleavage and therefore these surfaces are almost step-free with wide flat terraces with a roughness of about 2.8 A (from reflectivity experiments).

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 sagitally focusing Si(111) crystal monochromator and set to an energy of 17.2 keV (0.7205 A 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 in a PET chamber with 2 capton windows coupled to a six-circle diffractometer. 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 0.1 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 was carried out with the software ROD [1]. We used the orthorhombic calcite unit cell, with cell parameters $a_1 = 8.095$ A, $a_2 = 4.990$ A und $a_3 = 24.2864$ A [*], to model the bulk and the surface atom positions. Accordingly the (104) face of the hexagonal system equals the (001) face of the orthorhomic unit cell. The orthorhombic cell has the space 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. Refined parameters are the positions, site occupation factors (sofs) and Debye-Waller factors (DWF) of the atoms in the surface cell.

[*] unit cell parameters obtained from transformation of the hexagonal to the orthorhombic system

Calcite surface structure under dry conditions

The analysis of the CTRs of the calcite (104) surface under dry conditions yielded a bulk terminated surface structure with a relaxation of the topmost 3 layers of atoms in the surface cell. No surface reconstructions were detected for this surface under dry or humid conditions. The bulk and refined atom positions of the calcite surface cell are shown in fig. 1 a,b.

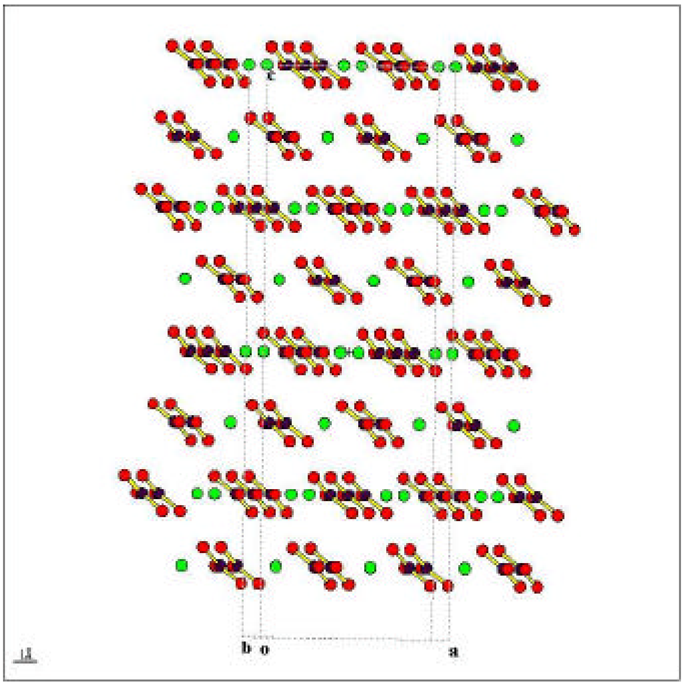

Fig 1.a: Bulk structure of the orthorhombic surface cell model of calcite.
(green = Ca, black = C, red = O).

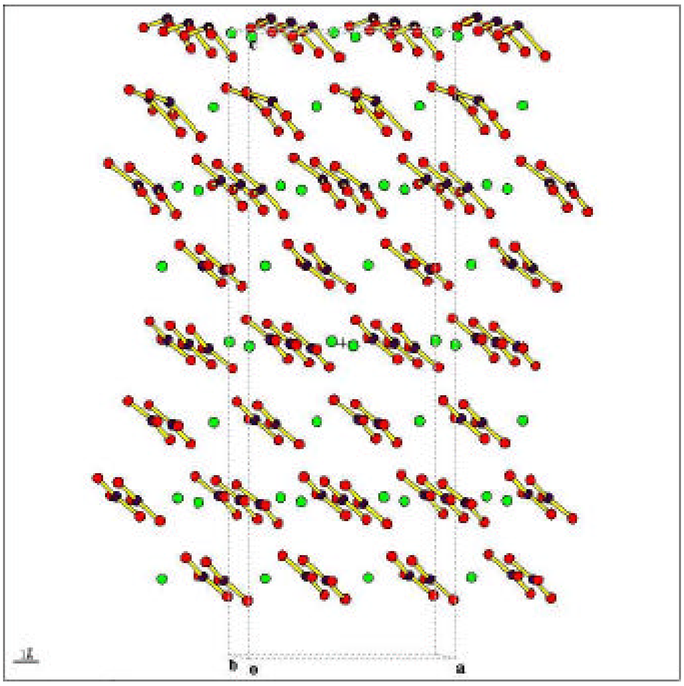

Fig 1.b: Refined structure of the orthorhombic surface cell model of calcite.
(green = Ca, black = C, red = O).

The analysis show a relaxation of the atoms in the first 3 layers of the surface cell. The protruding oxygen atoms of the topmost carbonate groups are shifted of -0.77 A in z-direction. The carbonate groups of the 1st and 2nd layer are distorted in a convex manner. The carbon atoms are shifted upwards in z-direction of about 0.34 A and 0.39 A in the 1st and 2nd layer, respectively. The movement of the calcium atoms is relatively small, the Ca´s of the topmost layer are moved downwards in z-direction of –0.16 A and upwards in the 2nd layer of 0.10A. These results agree in general with results of atomistic simulations of the relaxation in the anhydrous (104) calcite surface published by Wright et al. [2]. However, we do not observe a concav distortion of the 2nd layer carbonate groups and the shift of the calcium atoms obtained from our experiment is about a factor 5 smaller than the Ca-movement predicted in the simulation.

The probability of creating vacancies on the terraces in the cleavage process was also checked by refining the occupancy factors of the two topmost surface layers. The refinement of these parameters resulted in an occupation of 36% for all atoms in the 1st layer and 64% occupation for all atoms in the 2nd layer.

Fig. 2a shows the fit of the one of the six measured CTR's for the dry surface while Fig. 2b shows the differences between dry and wet surfaces.

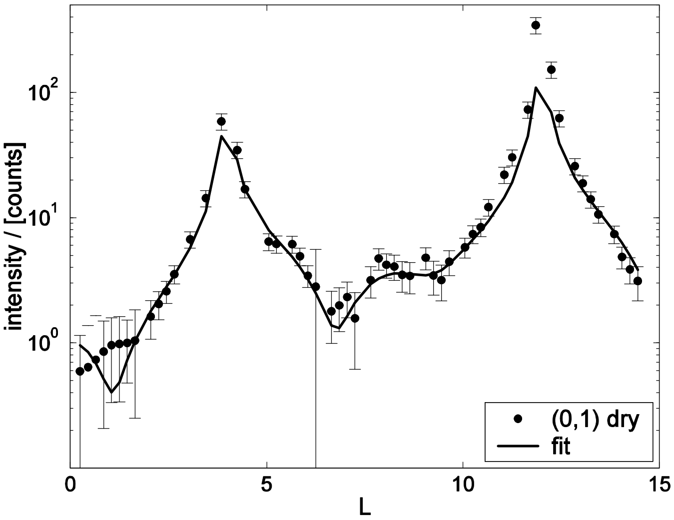

Fig. 2a: Intensity of the measured (0,1)-CTR of the dry (104) calcite surface plotted against L. The filled circles are the experimental data, the line indicate the respective fit.

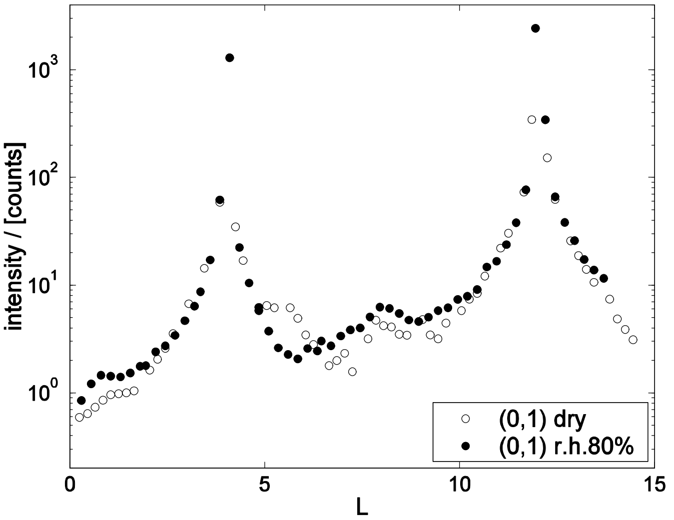

Fig. 2b: Measured (0,1)-CTR of the (104) calcite surface under dry (open circles) and humid (closed circles) conditions. The errorbars are not shown here for higher clarity of the differences between both curves.

Calcite surface structure under humid conditions

The analysis of the experimental data of the calcite surface under humid N_2-gas with a r.h. of 80% is still in progress. The comparison with the dry CTRs shows a clear difference in intensity variation between the Bragg peaks (fig. 2b).

References

[1] Elias Vlieg, Appl. Crystallogr. 33, 401 (2000).
[2] K. Wright, R.T. Cygan, B. Slater, Phys. Chem. Chem. Phys. 3, 839-844 (2001)