



**Experiment title:** Investigation of the mineral/sorbate interface structure of the (104) calcite surface with proline- and glucose- aqueous solution with GIXRD-techniques

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**Report:**

In continuation of our investigation of the structure of the (104) cleavage surface of calcite with GIXRD techniques, we measured specular and nonspecular crystal truncation rods (CTR) of the calcite surface in contact with aqueous solution of proline (Pro) and glucose.

In analogy to the previous measurement of the calcite/glycine solution interface we observed significant deviation from the hydrated calcite surface structure (fig. 1), but also no reconstruction of the surface or adsorbate layer. The analysis so far indicates the coverage of the topmost surface by an ordered water layer, followed by the proline molecules in a second ordered layer above the surface, similar to the glycine/calcite/water interface<sup>1</sup>. A model of the lateral orientation of the proline and glucose molecules was derived from forcefield simulations (fig. 2). It will be applied to the further analysis of the data using the software ROD<sup>2</sup>.

**Performance of the experiment**

The experiment was carried out at beamline ID32 at the ESRF. The incident X-ray beam was set to an energy of 18.6 keV (0.6666 Å wavelength). A well-defined calcite (104)-surface was obtained by cleavage of an optical quality island spar. The sample was then immediately mounted in an electrochemical cell, coupled to the six-circle-diffractometer of the beamline. A drop of the saturated aqueous solution of proline was put on the sample surface with a pipette and spread out to a film. The electrochemical cell was then closed with mylar foil, which was sucked in using a syringe. This reduced the drop of solution on the sample to a thin film, covering the whole surface.

The measurements of the CTRs were performed in vertical scattering geometry. The incoming beam was vertically and horizontally defined by slits to 0.02 mm and 0.4 mm, respectively. The incidence angle

between the horizontally mounted sample surface and the X-ray beam was selected to  $0.5^\circ$ . The scattered beam was defined by a pair of slits in front of the detector set to 3 mm x 3 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. Additionally L-scans along the measured CTR were performed. After background subtraction and correction they were used for the determination of contributions from the background in the rocking scan integration.

After the first part of the experiment the calcite sample was cleaned with ethanol in an ultrasonic. The sample was mounted again on the diffractometer after inspection of the surface with an optical microscope. The second solution of glucose was applied as described above and a data set of specular and nonspecular CTR was measured.

## Results

The results presented here are preliminary results, because of the timeconsuming analysis of the rocking scans and the accomplishment of the atomistic simulation. The integration of the Rocking scans in order to obtain the CTRs must be made very carefully, because due to instabilities of the beam position on the sample during the measurement the background in the scans had to be examined for every scan, comparing the intensity to the respective intensity in the L-scans of the respective CTR. Nevertheless, we obtained a set of 11 CTR (834 non-equivalent data points) for the proline/calcite interface (4 CTR are shown in fig. 1). The rocking scans of the glucose/calcite interface are not yet integrated and corrected, but will be analysed as soon as possible.

With this experiment we continued the investigation of the surface structure of the (104) calcite cleavage surface in contact with different organic molecules in solution, related to biomineralisation. We obtained from our data of the last experimental period a detailed picture of the mineral/surface structure on atomic scale of the calcite/glycine system: When the calcite surface is exposed to aqueous glycine solution, the interface is composed of a laterally ordered monolayer of water in a distance of  $1.9(1)$  Å from the surface with two water molecules per surface unit cell area. This hydration layer is followed by a second layer with one glycine and one water molecule per surface unit cell in a distance of  $3.1(1)$  Å, also with perfect lateral order. The surface of the calcite substrate is only slightly relaxed within the topmost 3 - 4 layers, as similar to what has already been observed for the water film. These results were published in Langmuir<sup>1</sup>.

The analysis of the data of the proline/calcite interface are in progress. So far a first calculation of the structure factors using the hydrated calcite surface as structure model was not able to match the experimental structure factors. Here the conformation and position of the simulation of proline on calcite (fig. 2) will be used in the further analysis.

## References

- [1] U. Magdans, X. Torrelles, K. Angermund, J. Rius, Langmuir, accepted 22.02.2007
- [2] E. Vlieg, J. Appl. Cryst. 33, 401-405 (2000)

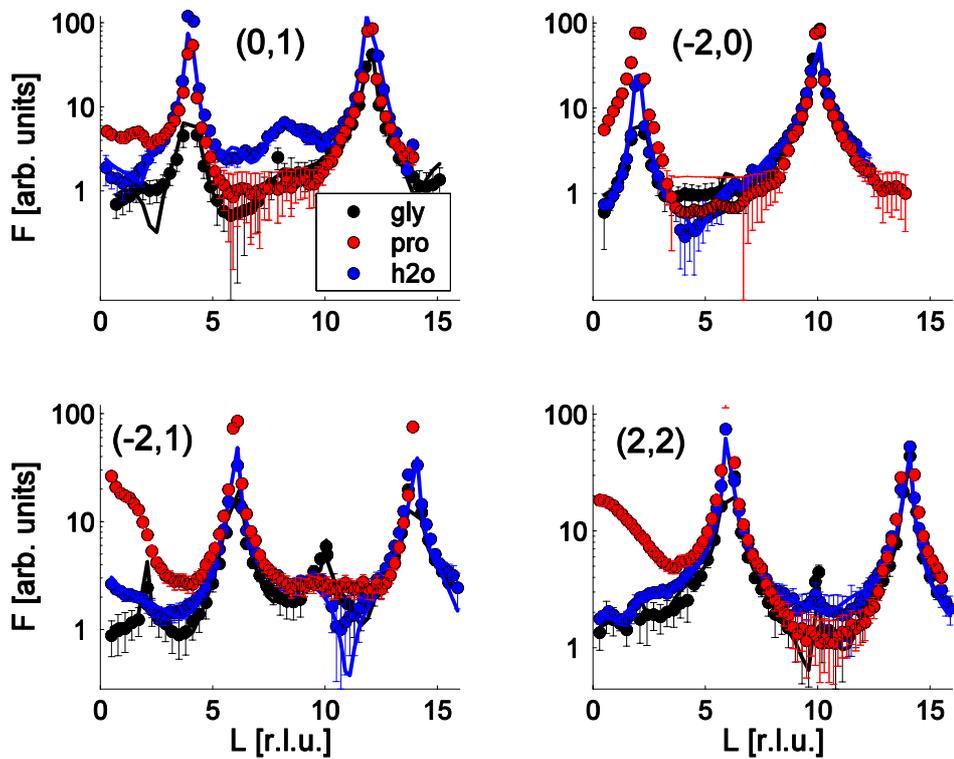


Fig. 1: CTR measured for the calcite surface in contact with pure water (blue), aqueous glycine solution (black) and aqueous proline solution. Lines indicate the fit of the experimental data from the structure model of the hydrated surface (blue line) and the glycine/calcite interface (black line). The analysis of the proline-data is in progress.

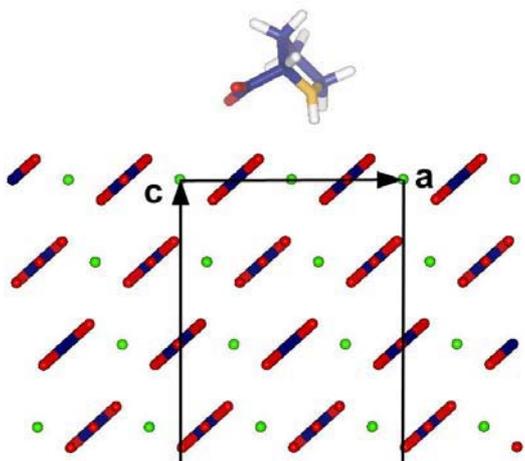


Fig. 2: Molecular modeling simulation of the docking of a proline anion to the calcite surface.