ESRF	**Experiment title:** Investigation of the interface structure of the (104) calcite surface with dipeptide ß-asp-gly in aqueous solution with GIXRD	**Experiment number**: SI-1443
Beamline: BM25B	**Date of experiment**: from: 26/01/2007 to: 30/01/2007	**Date of report**: 26/02/2008
Shifts: 12	**Local contact(s)**: Dr Juan RUBIO-ZUAZO	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Dr. Uta MAGDANS[a]*

Prof Dr. Hermann GIES[a]

Dr. Xavier TORRELLES[b]*

Aparna Pareek[a]*

[a] Dep. of Geology, Mineralogy and Geophysics, Ruhr-University Bochum, Germany

[b] Institut de Ciencia de Materials de Barcelona (CSIC), Spain

Report:

With a new preparation method of calcite surfaces described by Chada et al. [1] we investigated the adsorbate/surface layer structure of the dipeptide ß-asp-gly (CAS-no. 3790-52-1) on the calcite (104) surface. The surfaces of the calcite samples were prepared using the method of Chada et al. and checked with AFM before the experiment, showing surfaces with terraces of more than 10 µm width, separated by macrosteps (Fig. 1). This corresponded with the results obtained by Chada et al., but we observed a higher rms-roughness on the terraces of about 30-40 Å.

We measured the specular reflectivity and several non-specular CTRs of the prepared calcite (104) face, covered by a thin film of ß-asp-gly aqueous solution. The intensity of the measured CTRs was very weak. Despite of all efforts to enhance the signal/noise ratio (changing the sample, changing the energy of the incoming beam, optimizing the slits), most of the rocking scans were not analysable due to the bad signal/noise ratio. The flux of the incoming beam on BM25 (in 16 bunch-mode) was to weak to compensate the damping of the scattered intensity by the dipeptide solution. Also the mylar foil of the sample cell causes additional diffuse reflection, as we know from previous experiments, e.g. 25-02-603. So despite of our efforts we were not able to measure a analysable dataset and could not obtain information about the dipeptide/mineral surface structure on atomic scale.

Experiment details:

The experiment was carried out at the CRG beamline BM25, branch B, on the six-circle-diffractometer. The energy of the beam was 15.3 keV (0.8105 Å). The calcit samples were prepared by cleavage of calcite crystals with very high optical quality from MICAF, Brazil. The pieces of about 5x5x3 mm size were stored in pre-equilibrated saturated calcite solution for 24 h, dried and examined with AFM. Three samples with the best surface quality were brought to the ESRF.

The sample was mounted in air in an electrochemical cell attached to the diffractometer in vertical scattering geometry. In dry environment conditions the specular reflectivity (Fig. 2) as well as L-scans and rocking scans of some non-specular CTR were measured. Then a drop of the dipeptide solution was applied to the surface. The cell was closed with mylar foil (thickness 6µm) and the drop of solution on the surface was reduced to a film by generating a small depression in the cell using a syringe.
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 3 mm at the sample position. The incidence angle between the horizontally mounted sample surface and the X-ray beam was selected to 0.5°. 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.

We explored in this way three calcite samples, but we did not obtain an analysable data set with the dipeptide solution on the calcite surface. In dry conditions the specular and the measured nonspecular scans were about a factor 10 lower in intensity compared to data measured at ID03, but they still indicated a suitable surface, as expected by the AFM measurement. But with solution and mylar covering the surface, the scattered intensity decreased rapidly. Fig. 2 shows the specular reflectivity measured in dry conditions (empty circles) compared to the intensity loss of the surface signal with the dipeptide solution on top (filled circles). The background of the scans was subtracted and correction factors (polarization, Lorentz- and experimental factors) were applied. The signal of the rocking scans also completely vanishes in the background signal, only very near to the bragg peaks we obtain some weak intensity (not shown here). Thus the data set collected is not suitable to yield information about the interface structure of ß-asp-gly on the calcite surface.
There are probably several reasons for the low signal/noise ratio. From previous experiments we know that the adsorbate film and the mylar foil enhance the diffuse reflection and weaken the intensity of the diffracted beam. But due to the higher flux and brilliance e.g. at ID03 and ID32, the signal/noise ratio was high enough to obtain good data sets (e.g. experiments SI-1073, results published in [3], SI-1328, [4], [5]). BM25 is equipped for surface diffraction experiments, but the intensity of the beam provided is not high enough to perform experiments with very low photon yield.
The adsorption behaviour of the dipeptide in solution also influences the measured signal, depending on the formation of an ordered adsorbate layer or a reconstruction. It is possible that ß-asp-gly dipeptide molecules just accumulate on the surface with a statistical distribution, instead of forming a periodically ordered pattern, which would cause more diffuse scattering and reduce the measured intensity signal.

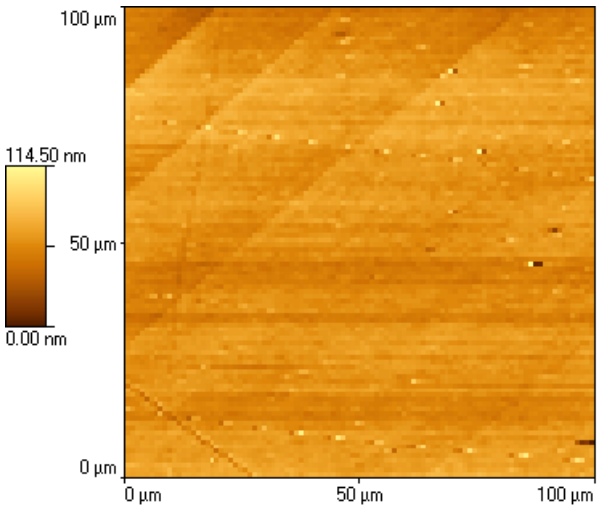

Fig. 1: AFM picture of the calcite surface terraces prepared according to Chada et al.[1]

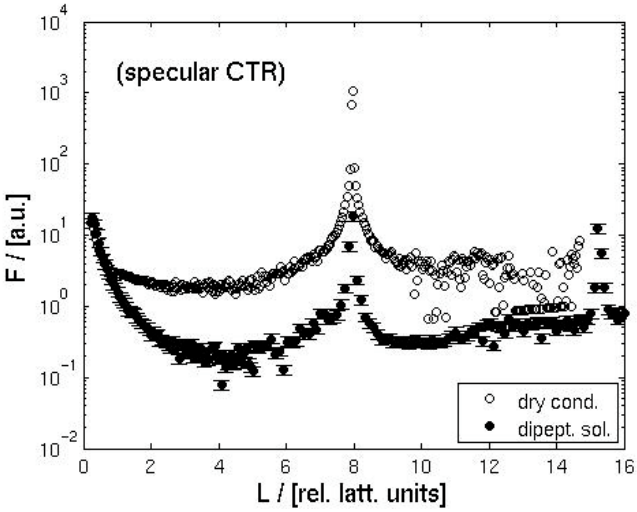

Fig. 2: Specular reflectivity of the calcite (104) surface in dry conditions and with the ß-asp-gly aqueous solution.

References:

[1] Chada V.G.R., Hausner, D.B., Strongin, D.R., Rouff, A.A., Reeder, R.J., *J., Coll. Interf. Science* **288**, 350-360 (2006)
[2] Vlieg E., *J. Appl. Crystallogr.* **30**, 532-543 (1997)
[3] Pareek, A., Torrelles, X., Rius, J., Magdans, U., Gies, H.: Role of water in the surface relaxation of the fluorapatite (100) surface by grazing incidence x-ray diffraction, *Phys. Rev. B* **75**, 035418 (2007)
[4] Magdans, U, Torrelles, X., Angermund, K., Gies, H., Rius, J. : Crystalline order of a water/glycine film coadsorbed on the (104) calcite surface, *Langmuir* **23**, 4999-5004 (2007)
[5] Pareek, A., Torrelles, X., Angermund, K., Rius, J., Magdans, U., Gies, H.: Structure of Interfacial Water on Fluorapatite (100) Surface, Langmuir; (Research Article); 2008 ; ASAP Article; DOI: 10.1021/la701929p