EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

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.

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.

ESRF	**Experiment title: Investigation of the mineral - adsorbate interface structure of the (100) surface of fluorapatite (FAp) with GIXRD**	**Experiment number**: SI-1414
Beamline: BM25B	**Date of experiment**: from: 31.01.07 to 06.02.07, 25.06.07 to 02.07.07	**Date of report**: 03.03.2008
Shifts:	Local contact(s)**: Dr. Juan RUBIO-ZUAZO**	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Prof. Dr. Hermann GIES[a]

Ms. Aparna PAREEK[a] *

Dr. Xavier TORRELLES[b]*

Dr. Uta Magdans [a]*

[a] **Fak. GMG Inst. f. Mineralogie/Kristallographie, Ruhr-University Bochum, Germany**

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

Report:

We performed the GIXRD experiments to investigate the structure of fluorapatite (100) - adsorbate interface with aqueous solution of adsorbates like glycine and glucose. This experiment was a continuation of our previous measurements on fluorapatite (100) surface with a drop of water [see ESRF Report 25-02-603].

For glycine, we measured a large data set of 23 Crystal truncation rods, where 10 CTRs were measured with l-step of 0.2 and rest 13 were measured with l-step of 0.4. The CTRs with l-step 0.4 were later interpolated by using the information from corresponding stationary L-scans. The CTR data set for glycine was measured during the experiment 25-02-603. To investigate the nature of fluorapatite (100) - adsorbate interface, the similar experiments were performed for glucose solution, too. However, due to the instability of the beamline, it was not possible to measure large data sets, therefore only few rods were measured in this case and analysis in progress.

Experimental:

The experiment was carried out at the surface diffraction beamline BM25B at the ESRF. The fluorapatite crystal used was a natural mineral obtained from Durango, Mexico, with a flat natural growth (100) surface of the size about 10 x 5 mm. The crystal was mounted in an electrochemical cell coupled to a six-circle diffractometer. For measurements with the glycine and glucose solution, a drop of solution was maintained as film on the crystal surface using a Mylar foil.
The measurements of the CTRs were performed in vertical scattering geometry. The incoming beam was focused about 0.5 mm and horizontally defined by slits to about 1.5 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 1 mm x 1 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.

Here we report the surface model of fluorapatite (100) surface with an aqueous film of glycine. For analysis, we use an orthorhombic fluorapatite unit cell, with cell parameters $a_1 = 9.367$ Å, $a_2 = 6.884$ Å, $a_3 = 16.224$ Å, to model the bulk and the surface atom positions. Accordingly the 100) face of the hexagonal system equals the (001) face of the orthorhombic unit cell. This surface has the plane group symmetry pm with two mirror planes at $a_2 = 0.25$ and $a_2 = 0.75$. The used surface cell consists of 6 layers of atoms (in z direction).

Structure of fluorapatite (100) – aqueous glycine interface:

The initial model used for solving the surface structures of the (100) fluorapatite surface with an aqueous film of glycine was the ideal apatite surface termination where atomic relaxations were permitted in the 6 topmost surface layers. The final coordinates were determined by least square (L.S.) fitting of the experimental and calculated intensities. The L.S. refinement was carried out with a modified version of ROD [1], that handles the phosphate groups as rigid bodies, thus reducing the number of parameters [2].

From the data analysis of previous experiments we experienced the nature of fluorapatite (100) surface in dry, humid and completely hydrated conditions [3, 4]. In the previous experiment with fluorapatite (100) – water interface, we obtained a surface model where crystal surface was covered with two laterally ordered layers of water at a distance of 1.6(1) and 3.2(1), above the relaxed surface [4, ESRF report 25-02-603]. First ordered layer of water is formed by four water molecules per unit cell which are related by symmetry (*pm*) of the underlying surface, while the second is formed of two water molecules per unit cell. CTR analysis with a film of aqueous glycine solution results in two laterally ordered mixed layers of water and glycine molecules which exist in site competition to each other. The surface model contains two domains each with Sof = 0.5, where one glycine and 4 water molecules per unit cell arrange themselves in two laterally ordered layers. Glycine molecules show direct contact with the fluorapatite (100) surface via surface Ca^{2+} cations [5].

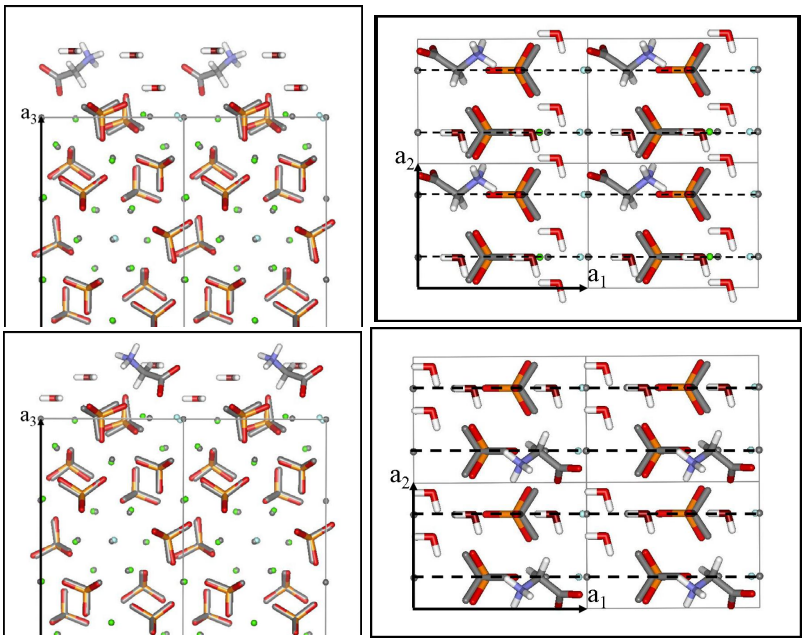

Fig. 1. Refined fluorapatite (100) surface structure model obtained using mixed adsorbate layers of water and the glycine molecules. ([PO4]-groups represented by tetrahedra; water in V-shape; Ca, F atoms by spheres, glycine molecule is shown in colored stick model). The experimentally refined structure is displayed multicolored (Ca atoms, green; [PO4]-groups, red-orange; F atoms, blue; water molecules, red-white). Broken lines show the presence of two mirror planes normal to $\mathbf{a_2}$. Top and vertical

view of the two structural domains are shown (above) structural domain 1, (below) structural domain 2. Each glycine molecule in one structural domain occurs with occupancy factor 0.5 and so the corresponding water molecules. Therefore, total sof of one structural domain is 0.5. Only one structural domain is possible out of two.

Structure of fluorapatite (100) – aqueous glucose interface:

The figure below shows a l-scan of fluorapatite (100) surface with an aqueous film of glucose, which shows differences with the l-scan of fluorapatite surface measured in dry atmosphere during the same beam conditions. It can be seen clearly from the scans the there are some distinct differences at the intensity minima, which can be considered due to the organic film on the fluorapatite (100) surface. Detailed analysis of crystal truncation rod data is in progress.

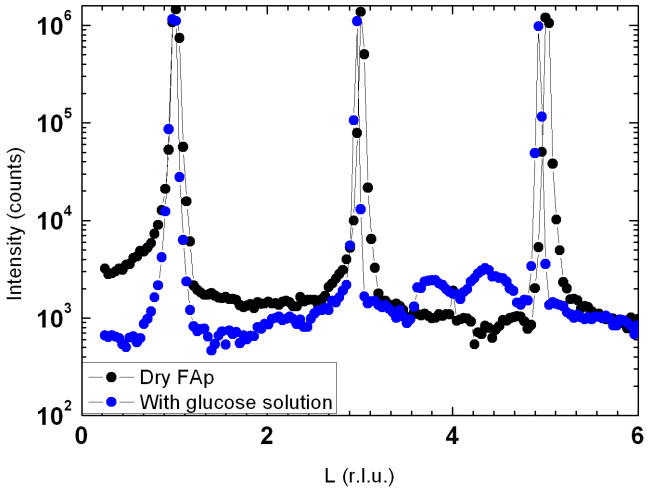

Fig. 2. Measured l-scans of fluorapatite (100) surface in dry atmosphere and with an aqueous film of glucose. Large differences at minimum values of L are quite evident from the figure.

References:

[1] Vlieg E., Appl.Crystallogr. 33, 401 (2000)
[2] X. Torrelles, E. Barrena, C. Munuera, J. Rius, S. Ferrer and C. Ocal, Langmuir 20**,** 9396 (2004).
[3] A.Pareek, X. Torrelles, J. Rius, U. Magdans and H. Gies, Phys. Rev. B, 75, 035418 (2007).
[4] A. Pareek, X. Torrelles, J. Rius, U. Magdans and H. Gies, Langmuir (2008) (in press).
[5] A. Pareek, X. Torrelles, J. Rius, U. Magdans and H. Gies (manuscript in preparation).