

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: Interaction of the (100) surface of fluorapatite with water and single amino acids gly and pro in solution.	Experiment number: 25-02-603
Beamline: BM25B	Date of experiment: from: 22.02.2006 to: 28.02.2006	Date of report: 23.03.2007
Shifts:	Local contact(s): Dr. German Rafael CASTRO	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Dr. Xavier TORRELLES^b * Ms. Aparna PAREEK^a * Prof Dr. Hermann GIES^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 two separate GIXRD experiments to investigate the structure of (i) the fluorapatite – water interface (completely hydrated) (ii) fluorapatite - glycine interface. This experiment is a continuation of our previous measurements on fluorapatite (100) surface in dry and humid atmosphere [see ESRF Report SI-1073].

Two large data sets comprising each 23 Crystal truncation rods were measured for water film and glycine solution film respectively, 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.

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 in completely hydrated conditions and with glycine solution, a drop of water/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 surface in completely hydrated conditions. The analysis of CTR data taken with film of glycine solution is in progress and would be reported later. For analysis, we use an orthorhombic fluorapatite unit cell, with cell parameters $a_1 = 9.367 \text{ \AA}$, $a_2 = 6.884 \text{ \AA}$, $a_3 = 16.224 \text{ \AA}$, 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 - water interface in completely hydrated condition:

The initial model used for solving the surface structures of the (100) fluorapatite surface in completely hydrated condition 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 experiment with fluorapatite (100) surface in humid (with 75% r.h.) N_2 -atmosphere, we obtained a surface model where crystal surface was covered with an ordered monolayer of water at a distance of about $1.8 (1) \text{ \AA}$ above the relaxed surface. This monolayer of water is formed by four water molecules per unit cell which are related by symmetry (pm) of the underlying surface. Furthermore, water layer on fluorapatite (100) surface is stabilized by small atomic relaxations in surface unit cell. These atomic relaxations in surface layers were observed to decrease with increasing depth [3, ESRF report SI-1073].

CTR analysis in completely hydrated conditions renders a surface model which shows the presence of two ordered water layers. The first water layer on the surface consists of four water molecules, which are coupled by pm symmetry as described above. The second water layer consists of two water molecules on the mirror planes ($a_2 = 0.25$, $a_2 = 0.75$) in between the first water layer and the surface phosphates. Hence, there is direct interaction of second layer water molecules with surface phosphates. These water molecules are further stabilised by hydrogen bonding with first water layer. Fig.1 shows two CTRs along with their calculated fits obtained in ROD.

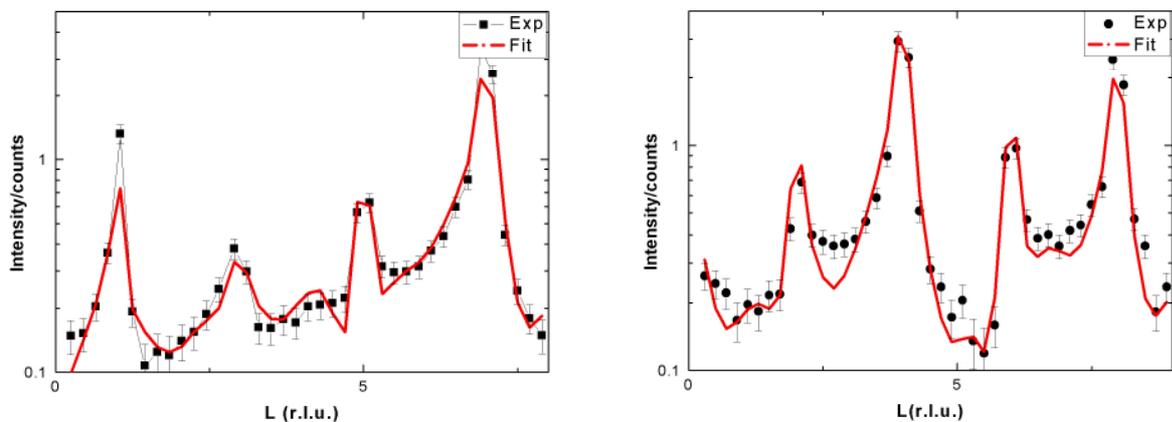


FIG.1. Two typical nonspecular crystal truncation rods of the hydrated fluorapatite (100) surface. Experimental structure factors are shown in black (error bars) together with the calculated structure factors (red) from the structure model displayed in FIG. 2.

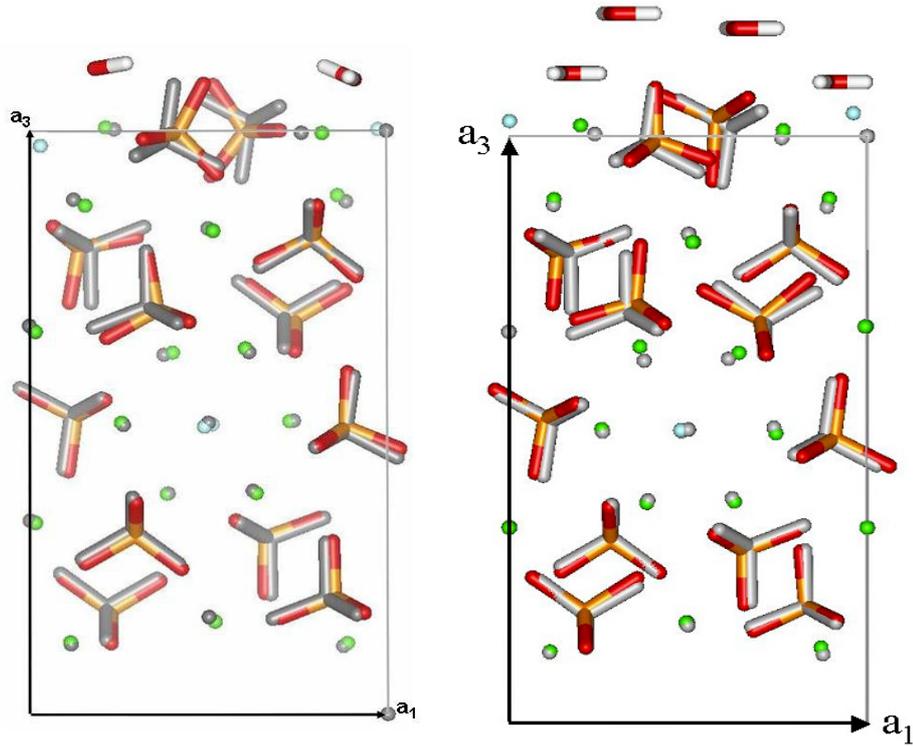


FIG. 2. Refined surface structure model of the orthorhombic unit cell of fluorapatite in humid (75% r.h.) N_2 ambient (left) and with water film (right). The ideal bulk structure is colored in grey and the refined structure is displayed multicolored (Ca green, PO_4 red-orange, F blue, H_2O red-white).

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)