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# Investigation of atomic structure of fluorapatite (100) surface and apatite – organic interface by GIXRD technique

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## Introduction

Apatite ( $\text{Ca}_5[\text{X}](\text{PO}_4)_3$ , X= F, OH, Cl) is an important mineral which occurs in many types of igneous, metamorphic and sedimentary rocks. Its role as a biomineral in nature makes it interesting theme for research. Hydroxyapatites are important constituent of the endoskeleton (bones and teeth) in vertebrates including humans. The study of the interaction between apatite and inorganic species requires a profound understanding of the details of apatite surface structure and the interactions with biomolecules that take place at atomic scale. We investigated the structure of fluorapatite (100) surface in dry, humid and completely hydrated environments with Grazing Incidence X-ray Diffraction (GIXRD). Measurement of specular and non-specular crystal truncation rods (CTR) provided information about the surface structure of mineral and sites of adsorption on atomic scale. These studies were further followed by the apatite – glycine interface study in which aqueous solution of glycine was allowed to adsorb on the fluorapatite (100) surface. While, for such kind of atomic scale information usually simulation studies are more common (1), our studies for first time show the experimental evidences.

## Method of measurement

### Specular reflectivity scans :

- > L scan along surface normal
- > Sensitive to normal surface modifications only
- > Affected by structural contributions coming from disordered surface regions also

### Crystal truncation rod scans (Rocking scans) :

- > Detector is fixed and sample is rotated around its surface normal.
- > Intensity distribution is measured along each selected L value of the rod.
- > Sensitive to lateral surface modifications.

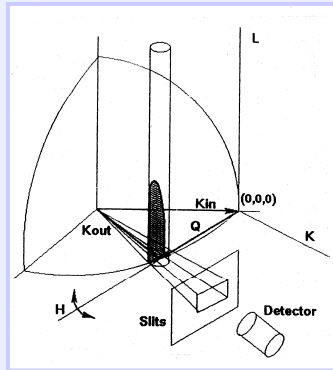


Fig. 1. Geometry of scans.

## Experimental details

- > Sample: Durango Apatite of size 10x5 mm
- > Measured face: hexagonal (100) face
- > Wavelength : 0.7205 Å
- > For humid atmosphere R. H. ~ 75% , for hydrated condition a film of water and for organic interface a film of aqueous glycine solution was used.

## Analysis of CTRs

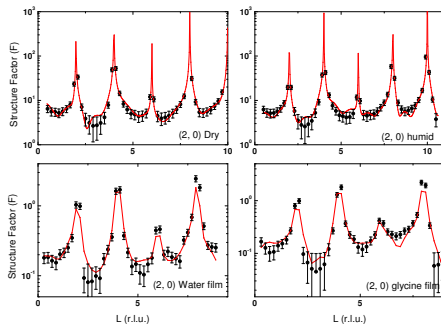


Fig. 2. Non specular crystal truncation rods of the fluorapatite (100) surface with (a) dry N2 (b) humid N2 (c) water film and (d) glycine film. Experimental structure factors are shown in black together with the calculated structure factors (red) in ROD program (2) from the respective structure models. The differences can be seen in between the Bragg peaks for different conditions. They show the surface features and allow to deduce the surface model.

## Model of the fluorapatite surface in dry N<sub>2</sub> environment

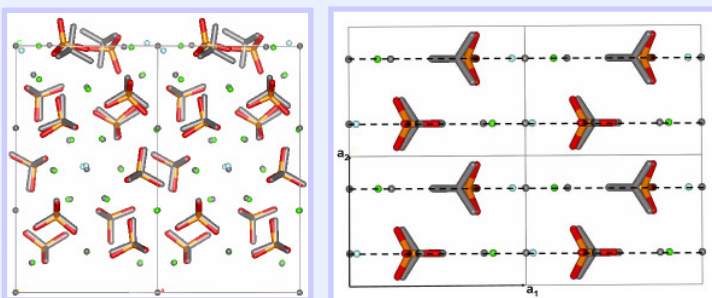


Fig. 3. The fluorapatite orthorhombic unit cell ( $a_1 = 9.367 \text{ \AA}$ ,  $a_2 = 6.884 \text{ \AA}$ ,  $a_3 = 16.224 \text{ \AA}$ ) is displayed (x-z projection). Bulk structure is colored in grey and the refined structure is displayed multicolored (Ca green,  $\text{PO}_4$  red-orange, F blue).

## Model of the fluorapatite surface in humid environment

Water molecules arrange themselves in one laterally ordered monolayer at about  $1.8 (\pm 0.1) \text{ \AA}$  above the relaxed fluorapatite surface.

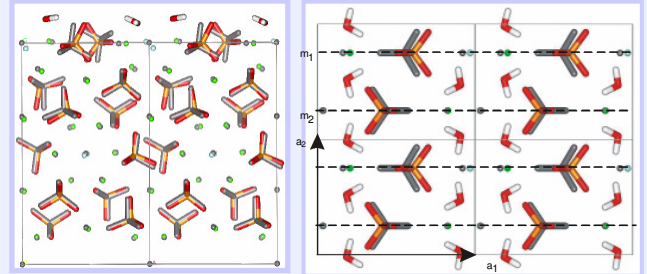


Fig. 4. The fluorapatite orthorhombic unit cell is displayed. Bulk structure is colored in grey and the refined structure is displayed multicolored (Ca green,  $\text{PO}_4$  red-orange, F blue,  $\text{H}_2\text{O}$  red-white).

## Model of the fluorapatite surface with water film

In presence of water film two laterally ordered water layers at about  $1.7 (\pm 0.1) \text{ \AA}$  and  $3.16 (\pm 0.1) \text{ \AA}$  above the relaxed fluorapatite surface.

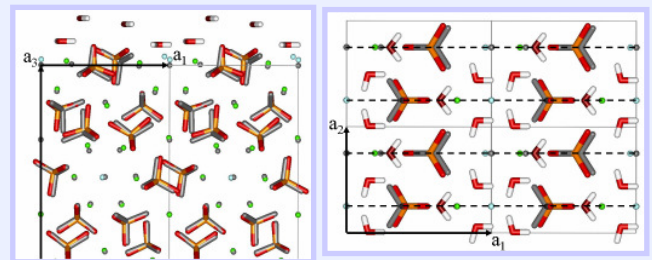


Fig. 5. The fluorapatite orthorhombic unit cell is displayed. First and second layer of water can be seen with 4 and 2 water molecules respectively. Color code is same as in previous figures.

## Model of the fluorapatite surface with film of glycine solution

In presence of aqueous glycine film the laterally ordered adsorbed layers are mixed with glycine and water molecules. Water molecules of first and second layer in above case share occupancies with glycine molecules.

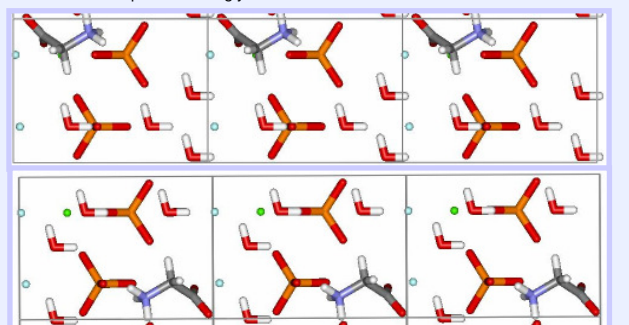


Fig. 6. The fluorapatite unit cell with lateral arrangement for glycine and water molecules. Two motifs of glycine and water molecules are considered corresponding to two mirror planes of surface unit cell symmetry. Color code is same as in previous figures.

## Summary

- > In dry atmosphere, strong relaxations of surface atoms were observed. The magnitude of these relaxations decreased successively in humid atmosphere and in hydrated conditions, which indicates stabilization of surface in presence of water.
- > In presence of humid atmosphere (r.h. ~75%), adsorption of water resulted in one laterally ordered monolayer at about  $1.8 (\pm 0.1) \text{ \AA}$  over relaxed fluorapatite surface. In hydrated condition a second laterally ordered water layer was observed at  $3.16 (\pm 0.1) \text{ \AA}$  above the relaxed mineral surface which was connected to the first water layer and surface  $[\text{PO}_4]$  by H bonding.
- > In presence of aqueous film of glycine, water – glycine arrangement in two layers is laterally ordered where the occupancies of water was shared by glycine.
- > These experimental evidences prove the presence of adsorption sites on the mineral surface and show the ordered arrangement of adsorbates.

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