Apatite, competitive Sorption of small molecules on the (100)-surface

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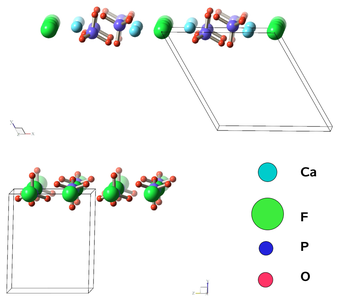
SURFACE DIFFRACTION EXPERIMENTS AND COLLAGEN-APATITE INTERACTION

Apatite:

In nature, large apatite crystals occur. The hexagonal-prismatic morphology shows large (100)-prism faces with surface flatness sufficient for GIXRD experiments. However, apatite crystals of gem-stone quality are only known from fluorapatite varieties and not of compositions related to biomineral apatite.

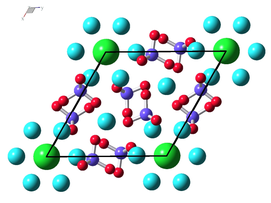


Structure plots of apatite:

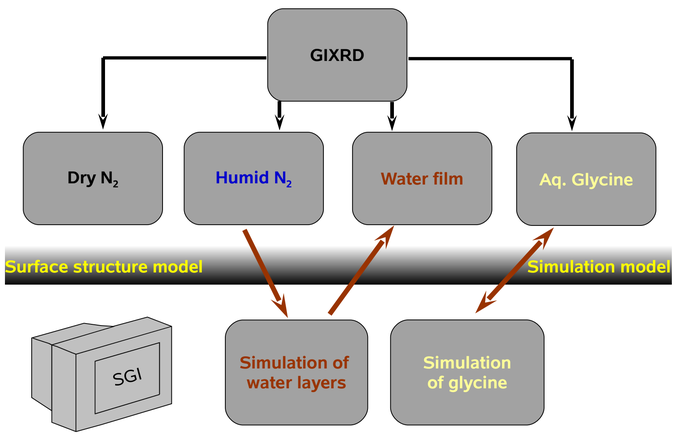
Right: projection // [001]

Above: (100) //[001]

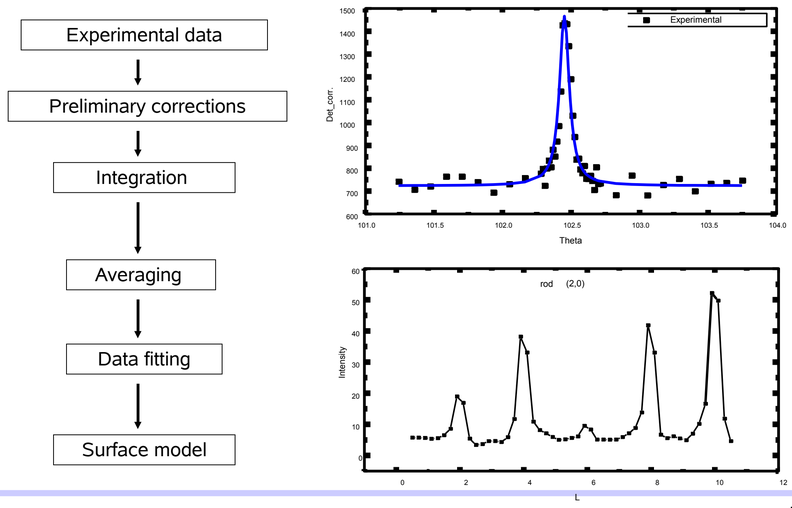
Left: (100) //[100]



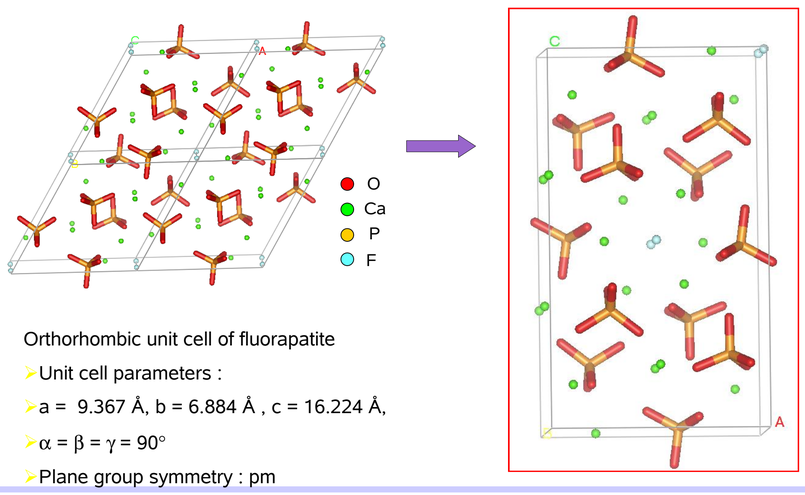
Work flow



Data Analysis



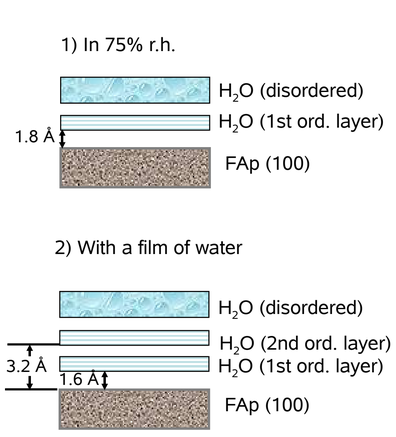
The apatite surface unit cell

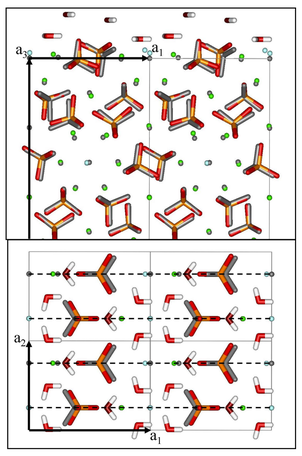


Orthorhombic unit cell of fluorapatite

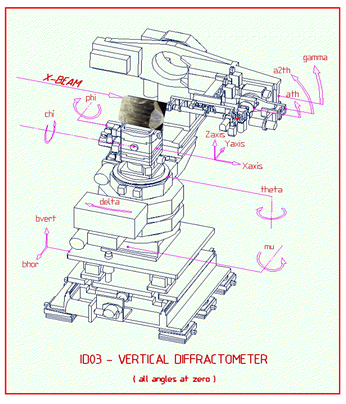
- Unit cell parameters :
- a = 9.367 Å, b = 6.884 Å , c = 16.224 Å,
- $\alpha = \beta = \gamma = 90°$
- Plane group symmetry : pm

Fluorapatite (100) surface with single adsorbate: water



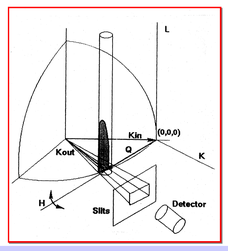


Sample and GIXRD experiment



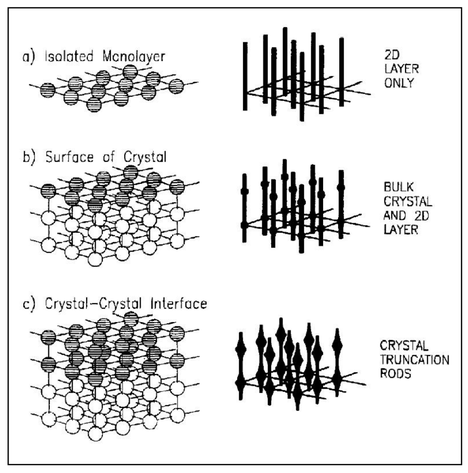
Schematic view of the 6-circle diffractometer at ID3, ESRF Sample was kept under controlled atmosphere in an electrochemical cell. Rel. humidity was controlled with an air stream running through water, liquid film was controlled with thin plastic foil on top of the sample.

- Sample: Durango Apatite of size 10x5 mm
- Fluorapatite
- Measured face: hexagonal (100) face
- Wavelength : 0.7205 Å
- Experiments in dry N_2, with relative humidity: ~ 75%, sample covered with water film, and samples covered with sat. glycine solution (isoelectric point).



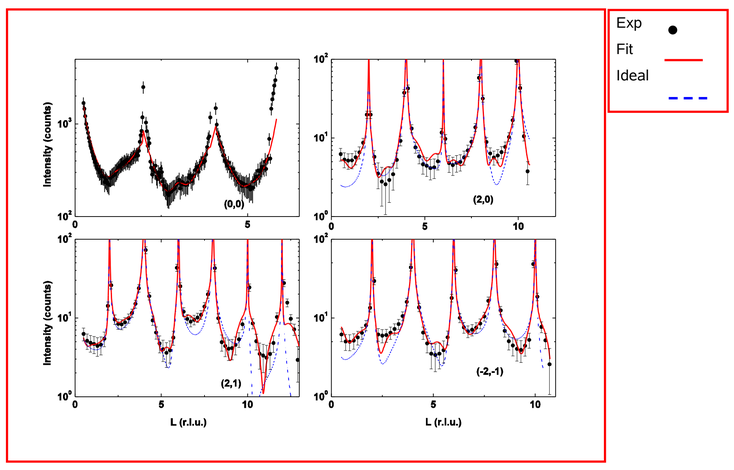
Crystal truncation rods along l-index are measured; in addition specular reflectivity of the (100) face is recorded and included in data analysis.

The Crystal Truncation Rod



For the incident X-ray beam sufficiently close to the critical angle the contribution of surface atoms in the scattered signal is substantial. An isolated monolayer yields a grid of diffraction rods. A sorbate ordered on a crystalline substrate yields crystal truncation rods as diffraction signal. Here, bulk diffraction intensity (Bragg peaks) and intensity from surface and surface near scatterers (rods) are detected free from signal overlap. This allows for a detailed geometrical analysis of the local bonding situation on and near the surface.

Refined crystal truncation rods (dry and humid ambient)



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Fluorapatite (100) surface in dry N_2 atmosphere

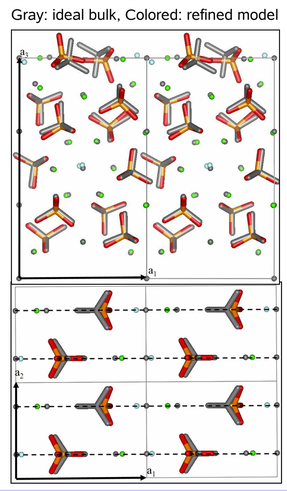
Refined parameters in ROD*:

- Translational shifts (in x, y, z directions)
- Rotations of rigid molecules (PO_4)
- Site occupation factors
- DW factors

FAp (100) surface in dry atmosphere shows:

- Ideal termination (F-Ca-PO_4)
- Sof ≅ 1 for surface atoms
- Relaxations in surface unit cell maximum in topmost layer →

Gray: ideal bulk, Colored: refined model



*E. Vlieg, J. Appl. Crystallogr. **33,** 401 (2000)

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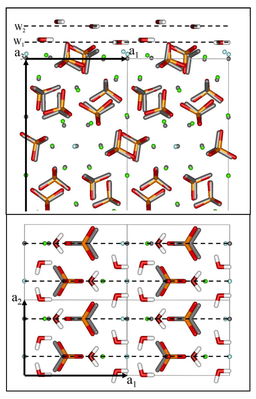
Water and aqueous soln. of glycine: A comparison

a) Water film



Distance	Water	Water + glycine
A_2 – surf.	3.2(1)	3.1(3)
A_1 – surf.	1.6(1)	1.6(2)
Ca^{2+} - W_1/O^{coo-}	2.28(4)	2.31(7)/ 2.45(2)

b) Aq. film of glycine