

# A hierarchical structure for apatite crystals

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Received: 1 June 2006 / Accepted: 19 September 2006  
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**Abstract** Based on the experimental results taken from the references, a reasonable hierarchical structure of apatite (both fluorapatite and hydroxyapatite) crystals has been proposed for the first time. The structure consists of four levels of the hierarchy: the smallest level is made of single unit-cells and/or Posner's clusters with the linear dimensions slightly below 1 nm, the second level comprises X-ray coherent scattering blocks of 50–80 nm in size, the third level is represented by dislocation blocks of 0.3–2.0  $\mu\text{m}$  in size and, finally, there are macroblocks of 35–50  $\mu\text{m}$  in size.

## Introduction

Calcium apatites (fluorapatite and hydroxyapatite) are known to be the main source of inorganic phosphorus in nature. For example, hydroxyapatite (in various ion-substituted and non-stoichiometric forms) appears to be the main inorganic part of animal and human bones and teeth [1, 2], while fluorapatite is the major component of many types of natural phosphate rock [2–4]. Therefore, natural apatites are widely used for the industrial production of various phosphorus-containing chemicals, elementary phosphorus and inorganic fertilizers [3], while the chemically pure apatites are used as a starting material to produce artificial bone grafts, as well as for the simulation of dental caries and bone mineralization [1, 2, 5]. Different properties of calcium apatites have been investigated as a result.

Mammalian bones turn out to have a complicated hierarchical structure [6]. After all organic and biological com-

pounds have been removed, the rest of bones consist of calcium apatite of biological origin [1, 2, 5]. Thus, it is reasonable to presume, that apatite might have a hierarchical structure as well. Seeking in the literature resulted in the conclusion that up to now nobody has ever tried to investigate this subject. Therefore, this communication appears to be the first attempt to create a hierarchical structure for apatite. Taking into the consideration a great similarity between the crystal structures of fluorapatite and hydroxyapatite [1–5], the experimental results for crystals of both natural fluorapatite and chemically pure hydroxyapatite have been taken from the references, analyzed, mutually compared and used for the creation of the hierarchical structure.

## Materials and methods

All experiments were performed with natural fluorapatite and chemically pure hydroxyapatite. The preparation techniques of hydroxyapatite are widely available in the scientific literature and, for example, were reviewed in Refs. [5, 7–9], while the preparation techniques of chemically pure fluorapatite are rather similar to those of hydroxyapatite but the synthesis must be performed in the presence of the necessary amount of  $\text{F}^-$  ions (usually, NaF or  $\text{NH}_4\text{F}$  is added) [5]. Crystals of various dimensions of both apatites were studied mainly by scanning electron microscopy (SEM) and X-ray diffraction techniques.

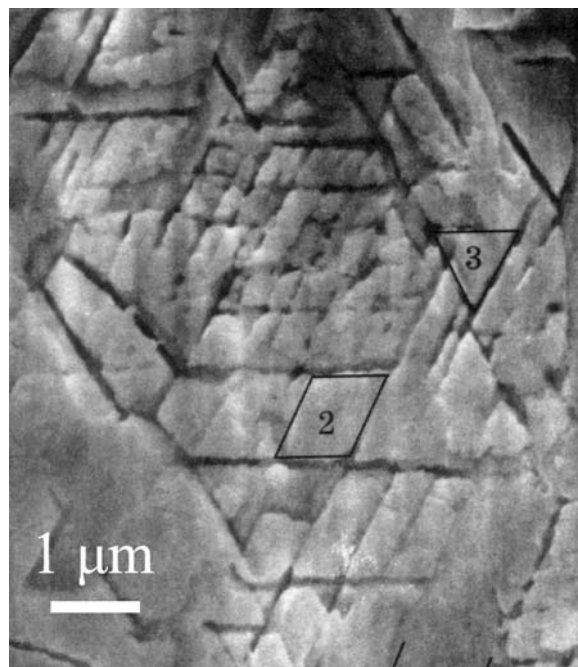
Seeking in various scientific databases (Medline, Science Direct, Ingenta Connect and ACS database) was the major method to collect necessary data. The following keywords: “fluorapatite”, “hydroxyapatite”, “calcium phosphates”, “block”, “block structure”, “hierarchy”, “hierarchical structure”, “cluster” were used for the search.

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## Results and discussion

Not many experimental data, related to the hierarchical structure of apatite, are available in the scientific literature. Structural imperfection of the single crystals of natural fluorapatite was investigated by both X-ray diffraction [10] and chemical etching in acidic solutions [11, 12]. The chemical analysis of the investigated crystals is given in Table 1. Initially, the surface of the single crystals of natural fluorapatite was polished; afterwards, the polished crystals were scratched by a pyramid-shaped diamond indenter with the angles of 136 degrees. The scratching rate was 0.1 cm/s, while the indenter was loaded by an external mass of 10–200 g [11, 12]. The scratched crystals were etched in either 2% aqueous solution of citric acid or 0.1 N aqueous solution of HCl for 15 min at ambient temperature. Afterwards, the etched surface was studied by scanning electron microscopy. Two structural levels of the irregularity were found as a result: coherent scattering blocks approximately of 50–60 nm in size were discovered by X-ray diffraction [10], while another type of blocks of rhombic shape with angles of 120 and 60 degrees and approximately of 0.3–2.0  $\mu\text{m}$  in size were found by the chemical etching (Fig. 1) [11, 12]. The larger blocks appeared due to the presence of dislocation networks and, therefore, were named as “dislocation blocks”. The authors noticed: “During chemical etching of fragments of fluorapatite single crystals, which had been previously plastically deformed by intending their surface, we revealed dislocation networks those formed blocks 0.3–2.0  $\mu\text{m}$  in size. The blocks have a shape of rhombi or parallelograms with angles characteristic for the fluorapatite unit cell.” [Ref. 12, p. 31].

The majority of the available experimental results is devoted to the smallest construction blocks of the apatite structure, frequently called as “Posner’s cluster” ( $\text{Ca}_9(\text{PO}_4)_6$ ) after the person, who predicted its existence [13]. For example, the crystal structure of hydroxyapatite was studied by high resolution transmission electron microscopy. Nanoparticles of apatite with the dimensions close to 1 nm were discovered as a result [14]. Another research group studied aqueous solutions of the simulated body fluid by means of intensity-enhanced dynamic light scattering technique and discovered the presence of a calcium phosphate cluster from 7 to 10  $\text{\AA}$  in



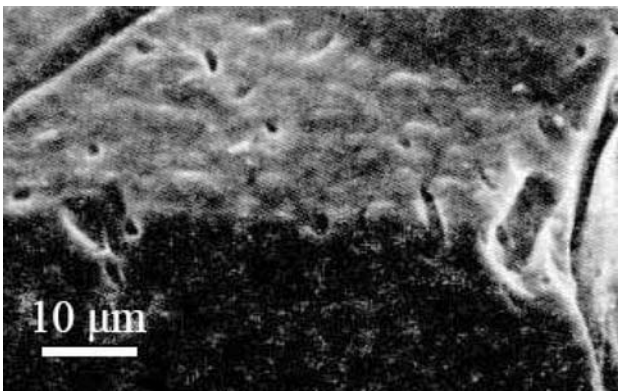
**Fig. 1** A SEM image of the scratched surface of natural fluorapatite after etching in 0.1 N aqueous solution of HCl for 15 min at ambient temperature. Dislocation blocks of 0.3–2  $\mu\text{m}$  in sizes are easily seen. Reproduced with permission from Ref. [9]

sizes, which they took to be the Posner’s cluster [15]. Combination of this finding with the previous results by the same researchers on hydroxyapatite *a*-face grow by step flow with a height of 0.8 or 1.6 nm obtained by atomic force microscopy technique [16] resulted in introducing a cluster growth model for hydroxyapatite that involved selective hexagonal packing of  $\text{Ca}_9(\text{PO}_4)_6$  clusters. According to the model, “hydroxyapatite contains two crystallographically distinct, but same size (8.15  $\text{\AA}$   $\times$  8.7  $\text{\AA}$ )  $\text{Ca}_9(\text{PO}_4)_6$  cluster units” [15]. Additional details on the Posner’s cluster, which might be considered to be roughly spherical with a diameter of about 9.5  $\text{\AA}$ , are available elsewhere [17–21]. The results of these investigations correlate well to each other and appeared to be close to the unit-cell dimensions of apatites ( $a = 9.391 \pm 0.001 \text{\AA}$ ,  $c = 6.878 \pm 0.002 \text{\AA}$ ) [1–5].

Investigations by scanning electron microscopy (SEM) in the secondary electron mode of partly dissolved crystals of apatites usually reveal etch pit formation on the crystal surface [22, 23]. The pits are known to be a result of the presence of dislocations inside the crystals. Sometimes, among the pits, etch hillocks might also be found on some faces of natural fluorapatite (Fig. 2). These hillocks were found on the surface of crystals etched in 7 N aqueous solutions of phosphoric acid for 30 seconds at ambient temperature. They had a smooth hexagonal shape and were about  $1.0 \pm 0.5 \mu\text{m}$  in size. Their height appeared to be 0.5–2.0  $\mu\text{m}$  above the average level of the crystal faces of fluorapatite [24, 25].

**Table 1** The chemical analysis of the single crystals of natural fluorapatite, mass. %. Taken from Ref. [11]

$\text{P}_2\text{O}_5$	41.24
CaO	54.54
F	2.32
$\text{SiO}_2$	0.36
$\text{Fe}_2\text{O}_3$	0.09
$\text{SO}_3$	1.12
$\text{CO}_2$	0.09
$\text{H}_2\text{O}$	0.4
Ca/P = 1.676	



**Fig. 2** A SEM image of natural fluorapatite after etching in 7 N aqueous solutions of phosphoric acid for 30 seconds at ambient temperature. Hillocks are seen on the upper part of the image

The dimensions of the hillocks appeared to be close to those of the aforementioned dislocation blocks [11, 12]. However it does not seem to be just a coincidence. The hillocks were found to become visible after the chemical etching of fluorapatite; moreover, the crystals of natural fluorapatite were discovered to dissolve with random microscopic fluctuations in crystal dimensions with the parameter equal to  $1.15 \pm 0.05 \mu\text{m}$  [25]. Therefore, during dissolution, the local surface areas of natural fluorapatite fluctuated with the parameter equal to the dimensions of the dislocation blocks. These blocks, most probably, reflected a relationship between the fluctuations in crystal sizes during

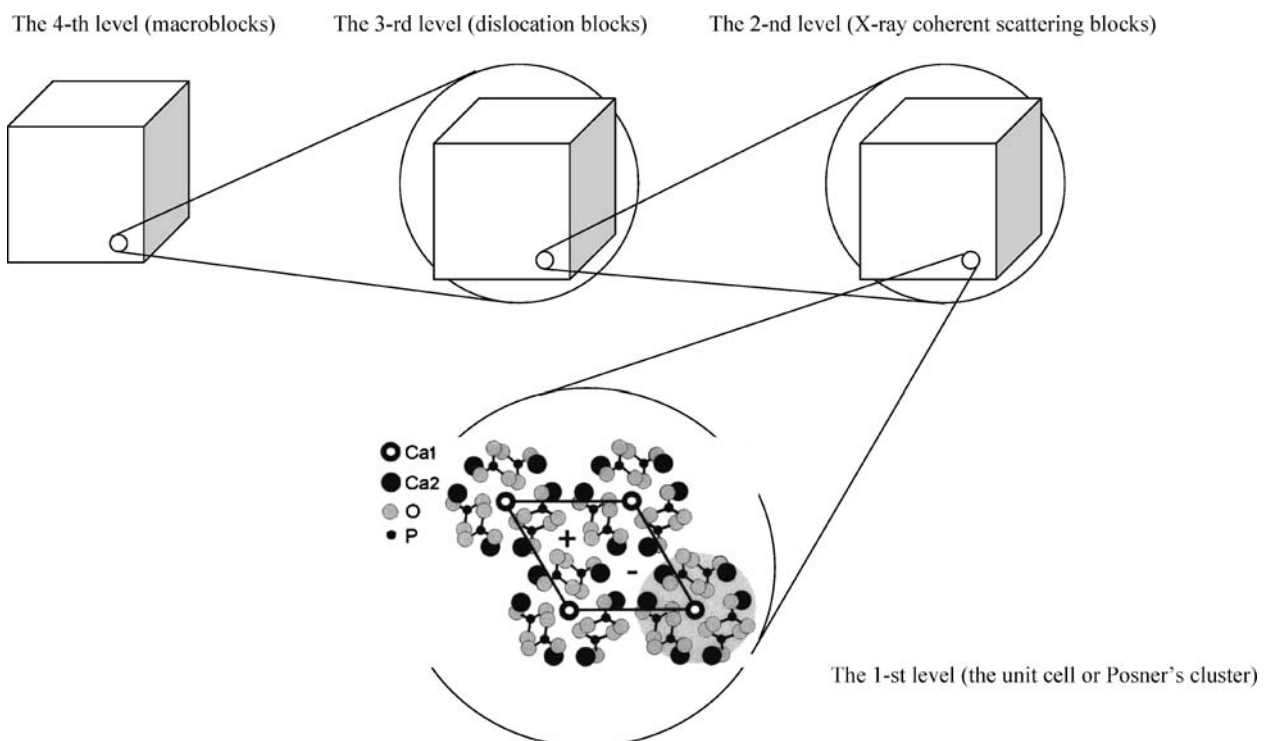
dissolution [25] and the micro-heterogeneity of natural fluorapatite [11, 12].

By means of the SEM investigations in the cathodoluminescent mode, natural fluorapatite was found to shine heterochromously from all crystal faces [26]. The emission spectra observed were due to local heterogeneities in the allocation of impurities inside the natural crystals. A size distribution of the spots with equal colours and similar brightness was measured. The spots were found to be different in dimensions, but their distribution by size had two maximums. One of them was about several square microns (or of  $1\text{--}2 \mu\text{m}$  in length) and the other one was about  $1000\text{--}2500 \mu\text{m}^2$  (or of  $35\text{--}50 \mu\text{m}$  in length) [26].

The first maximum in the size distribution of colour spots correlates well with the dimensions of both the dissolution hillocks [25] and the dislocation blocks [11, 12]. To the best of my knowledge, no information on any irregularities in the crystal structure of apatites equal to the second maximum ( $1000\text{--}2500 \mu\text{m}^2$ ) is available in the literature. Presumably, the latter represent yet not established either structural (for example, twin-type) or compositional macro-irregularities appeared during the formation of natural crystals.

[–18pc]

For the chemically pure hydroxyapatite, the evidence of the structural units similar to the aforementioned coherent scattering blocks of  $50\text{--}60 \text{ nm}$  in sizes found in fluorapatite [10] arises from the results of the conventional X-ray diffraction measurements. Based on the diffraction peak broad-



**Fig. 3** A graphical sketch of possible hierarchical structure of apatites. Note that the cubic shape is shown for the simplicity of drawing only

ening, unsintered (as precipitated) calcium orthophosphates with Ca/P molar ratio within 1.50–1.67 were found to consist of crystallites (other names: subgrains, blocks) with the linear dimensions ranging from 10 nm (for Ca/P = 1.50) to 27 nm (for Ca/P = 1.67), while similar sintered calcium orthophosphates appeared to consist of crystallites with the linear dimensions ranging from 49 nm (for  $\beta$ -tricalcium phosphate) to 78 nm (for hydroxyapatite) [27, 28].

## Conclusions

Thus, by means of the literature analysis, a reasonable hierarchical structure for apatite crystals (both fluorapatite and hydroxyapatite) might be created. The structure consists of four levels of hierarchy (Fig. 3). The first one is equal to either apatite unit-cells or Posner's clusters and has dimensions slightly lesser or almost equal to 1 nm. The second level corresponds to the X-ray coherent scattering blocks of 50–80 nm in size. A simple comparison of the dimensions suggests that each X-ray coherent scattering blocks should consist of 120,000–500,000 unit-cells and/or Posner's clusters. The third level corresponds to the dislocation blocks of 0.3–2.0  $\mu\text{m}$  in size. Each of them presumably consist of about 200–60,000 X-ray coherent scattering blocks. The fourth level corresponds to macroblocks of 35–50  $\mu\text{m}$  in size. Each of the latter is expected to consist of approximately 5,000–4,500,000 dislocation blocks.

It is clear that the third and fourth levels of the hierarchy might be discovered in relatively big single crystals only. Taking into the consideration that big single crystals of hydroxyapatite are almost unavailable, it is not surprising that up to now the largest levels of the hierarchy have been discovered in fluorapatite only.

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