

# Computer modeling of carbonatefluorapatite structure

Kalinichenko E.A.<sup>1</sup>, Brik A.B.<sup>1</sup>, Radchuk V.V.<sup>2</sup>, Melaschenko A.O.<sup>3</sup>

<sup>1</sup> *Semenenko Institute of Geochemistry, Mineralogy and Ore Formation of NAS of Ukraine,  
34 Palladin ave., Kyiv, Ukraine*

<sup>2</sup> *Institute for Telecommunications and Global Information Space of NAS of Ukraine, 13 Chokolovsky blv., Kyiv, Ukraine*

<sup>3</sup> *Glushkov Institute of Cybernetic of NAS of Ukraine, 40 Glushkova ave., Kyiv, Ukraine*

kalinichenko@igmof.gov.ua, abrik@igmof.gov.ua, valentyn.radchuk@gmail.com,  
javatask@ukr.net

**Abstract.** *Computer modeling of structural defects (CO<sub>3</sub>-groups, excess F<sub>x</sub> atoms, Na atoms, Ca vacancies, OH-groups, fixed H<sub>2</sub>O<sub>fix</sub> molecules) in the crystal lattice of carbonatefluorapatite (CFAP) has been performed with GULP program using grid-techniques. The translated cell of 3\*3\*3 elementary cells [Ca<sub>252</sub>Na<sub>9</sub>□<sub>9</sub>]<sub>270</sub>[(PO<sub>4</sub>)<sub>140</sub>(CO<sub>3</sub>)<sub>15</sub>□<sub>7</sub>]<sub>162</sub>[F<sub>36</sub>OH<sub>16</sub>(CO<sub>3</sub>)<sub>1</sub>]<sub>54</sub>(F<sub>x</sub>)<sub>9</sub>·7H<sub>2</sub>O<sub>fix</sub> with the chemical composition near to the synthesized sample (2.7 wt % CO<sub>2</sub>, 3.3 wt % F) has been considered. There were optimizing of about 300 variants of CFAP structure (at even distributions of CO<sub>3</sub>-groups and PO<sub>4</sub>-vacancies and different distributions of atoms of F<sub>x</sub> and Na, Ca vacancies, OH-groups and H<sub>2</sub>O<sub>fix</sub> molecules), from that 35 variants have been optimized. The web-sites of uagrid.org.ua and grid.inpracom.kiev.ua. were used for calculations, all calculations were executed in the "GEOPARD" virtual organization. The structural defects of certain type in the most probable CFAP structure were found to be located approximately evenly, distanced from each other: H<sub>2</sub>O<sub>fix</sub> molecules - in PO<sub>4</sub>-vacancies, excess F<sub>x</sub> atoms - in O3\* vacancies in (CO<sub>3</sub>)<sub>B</sub>-groups in the AB cluster, distanced and nearly of H<sub>2</sub>O<sub>fix</sub> molecules, aside from H<sub>2</sub>O<sub>fix</sub>, OH- groups in channels – near CO<sub>3</sub>-groups. The Na (I) atoms (mainly, near the (CO<sub>3</sub>F<sub>x</sub>)<sub>B</sub>-clusters, in the direction of O1 and F<sub>x</sub>) and Ca(II) vacancies (mainly, near the CO<sub>3</sub>-groups with O3\* vacancies) are most distanced from each other and the AB cluster. Simulation data suggest the experimental results: OH-groups and F atoms are localized in two different structural sites that correspond to data of NMR <sup>1</sup>H and <sup>19</sup>F for the synthesized sample.*

## Keywords

Isomorphism, carbonatefluorapatite structure, carbonate substitutions, computer modeling, GULP.

## 1 Introduction

Apatites Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(F,Cl,OH)<sub>2</sub> exhibit large isomorphic variations in cationic and anionic (in particular, substitutions by CO<sub>3</sub><sup>2-</sup>-ions) sites [1 - 9]. Carbonateapatites, containing ions of F<sup>-</sup> - and OH<sup>-</sup>, are widespread in geological rocks, francolite (carbonatefluorapatite (CFAP) with F contain higher stoichiometrical) is characteristic for sedimentary phosphorus-bearing rocks [1 - 6]. The intensively investigations of carbonate and concomitant substitutions in fluorapatite Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>F<sub>2</sub> (FAP) are explained by the necessary of solving of mineralogical tasks and development of synthesis technologies of materials of the various applications, including biocompatible, on the basis of FAP [1 - 10].

## 2 Related works

Numerous researches of natural, biogenic and synthetic carbonateapatites showed that CO<sub>3</sub><sup>2-</sup>-ions can substitute for the F<sup>-</sup> (OH<sup>-</sup>) ions in the structural channels along the [001] axis (A-type substitution) and PO<sub>4</sub><sup>3-</sup>-ions (B-type), following appearance of concomitant structural defects and change of physical and chemical parameters [1 - 6]. Mechanisms of carbonate substitutions in carbonatehydroxylapatite (CHAP) and CFAP in largely analogical [2 - 6]. The F atoms in francolite occupy two structurally different sites, the excess F<sub>x</sub> atom lies in the outer wall of the apatite channel [2, 5, 6]. The fixed water molecules (H<sub>2</sub>O<sub>fix</sub>) stabilize an imperfect structure and localized mainly: near CO<sub>3</sub>-groups in CFAP and in OH vacancies in columns in CHAP [2 - 5].

A computer modeling complements experimental methods to solve of many tasks related to structural properties of solids [5, 8 - 11]. The apatite structure with different substitutions was computer modeled in some works [5, 8 - 10 etc].

### 3 Isomorphism in CFAP structure

The aim of this research was the study of distribution of admixture atoms and groups and concomitant structural defects in the structure of synthesized CFAP by the computer modeling.

#### 3.1 Methodology of computer modeling

The CFAP structure (2.7 wt % CO<sub>2</sub>, 3.3 wt % F, the elementary cell parameters:  $a = 9.3141 \text{ \AA}$ ,  $c = 6.8991 \text{ \AA}$  [3]) was modeled by the semiempiric method, using interatomic potential-based simulation techniques. The interactions of structure ions were approximated by interatomic potentials using to simulate substitutions in apatites, potentials for the molecules of H<sub>2</sub>O, fixed on the HAP surface [9, 10], were used for the H<sub>2</sub>O<sub>fix</sub> molecules in CFAP.

The crystallochemical formula of the synthesized CFAP sample was determined on data of chemical analysis and NMR [3]. The translated cell of 3\*3\*3 elementary cells with near chemical composition [Ca<sub>252</sub>Na<sub>9</sub>□<sub>9</sub>]<sub>270</sub> [(PO<sub>4</sub>)<sub>140</sub>(CO<sub>3</sub>)<sub>15</sub>□<sub>7</sub>]<sub>162</sub>[F<sub>36</sub>OH<sub>16</sub>(CO<sub>3</sub>)<sub>1</sub>](F<sub>x</sub>)<sub>9</sub>·7H<sub>2</sub>O<sub>fix</sub> (about 1100 atoms) was considered to model structure. There were considered approximately even distributions of (CO<sub>3</sub>)<sub>B</sub>-groups and PO<sub>4</sub> vacancies (□), mostly distanced from each other, 12 possible directions of O-H-bonds in H<sub>2</sub>O<sub>fix</sub> molecules in □(PO<sub>4</sub>), 12 distributions of excess F<sub>x</sub> atoms of, 9 and 8 - Na and □Ca in cationic sites of M (I) and M (II), accordingly (at Na(I) /□Ca(II) and □Ca(I) /Na(II)), 9 - O-H-bonds in channels and 4 - O-H-bonds near the (CO<sub>3</sub>)<sub>A</sub>-group. The crystallographic coordinates of ions in FAP, OH-group ions - in HAP [7], ions of CO<sub>3</sub>-groups in CFAP [6] and a few variants of structural sites of excess F<sub>x</sub> atoms [5, 6] were used

Structure variants at different distributions of structural defects had been optimized (the ion coordinates, when the internal energy  $U$  was minimum, had been determined) in the GULP program, and the Helmholtz free energy  $F$  of the optimized structure has been determined [8 - 11]. The most probable structure has the min( $F$ ).

#### 3.2 Using of grid-techniques for modeling

The GULP module must be compiled as the library added to ChemShell. After compiling of ChemShell with built-in GULP it can be started by ordinary (theory=gulp).

All calculations were conducted, using grid-infrastructure that accelerated calculations considerably (the optimization duration of one structure variant on the personal computer is about twenty-four hours). The administrator got data as files \*.gin. Programmatic package of GULP is not parallel, for its use in grid it is necessary to start many copies and process different structures simultaneously. Administrators divided all files into two cycles are treatment of these pair and odd names of files (all names of input files are index numbers) to parallel of task. The administrator sent structures to the separate grid-processor, on that the GULP package copy is started and obtained a file with expansion \*.gout on an exit. This file administrator directed back to the researcher.

The mean time of calculation was 1.38 hours of one task. For realization of calculations the web--sites of uagrid.org.ua and grid.inpracom.kiev.ua were used. All calculations were executed in the virtual organization "GEOPARD", organized by Glushkov Institute of Cybernetic of NAS of Ukraine, Semenenko Institute of Geochemistry, Mineralogy and Ore Formation of NAS of Ukraine and Subbotin Institute of Geophysics of NAS of Ukraine.

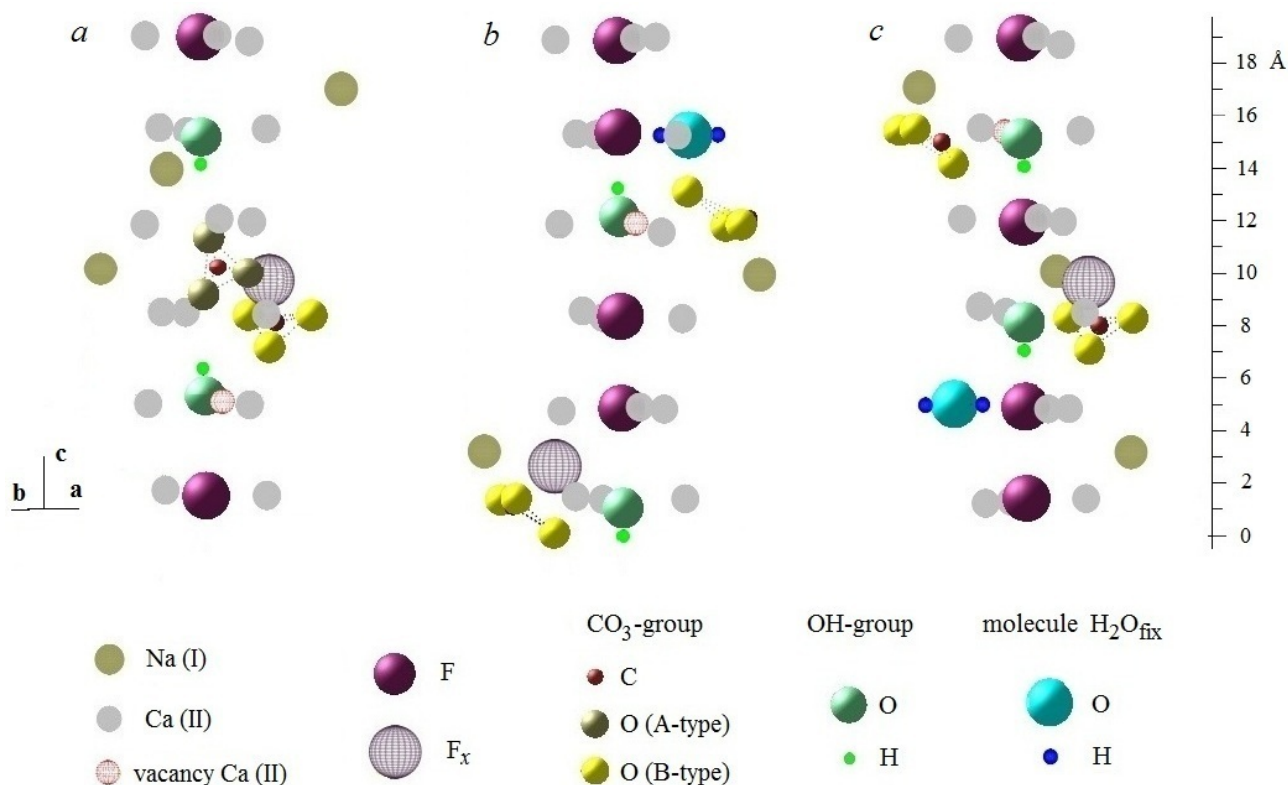
#### 3.3 The distribution of structural defects in CFAP

The optimization of about 300 variants of CFAP structure had been processed, 35 variants have been optimized. The accuracy of optimization substantially lower ( $\min(\text{Gnorm}) = \min |\text{grad}(U)| = 0,453$ ), than FAP structure optimized at the ion coordinates [7] and the used potential parameters [9, 10]:  $\text{Gnorm}(\text{FAP}) \approx 3 \cdot 10^{-5}$ . Presumably, it is due to complication of approximation of ion interactions in the structure with generous amount of structural defects. The Helmholtz free energies (to each elementary cell) of the optimized structures of CFAP (- 438.7 ÷ - 434.0 eV) and FAP (- 461.8 eV) are one order approximately.

The optimization accuracy of 10 variants of CFAP structure, for that  $\text{Gnorm} \leq 2$ , notably higher than others. For a few these variants the value of  $F = - 438.7 \div - 434.6 \text{ eV}$  (to each elementary cell), but the H<sub>2</sub>O<sub>fix</sub> molecules are substantially distorted: distances  $|\text{O} - \text{H}|_{\text{w}} = 1.6 - 3 \text{ \AA}$ ,  $|\text{H} - \text{H}|_{\text{w}} = 3 - 5 \text{ \AA}$ . The interaction of protons is neglected at such distances between them. At the same time, the duplicate line due to interaction of closely-spaced protons of H<sub>2</sub>O<sub>fix</sub> molecules is observed in the <sup>1</sup>H NMR spectrum of the synthesized sample [3]. Therefore the CFAP structure, in which of structures of H<sub>2</sub>O<sub>fix</sub> molecules are least distorted (distances  $|\text{O} - \text{H}|_{\text{w}} = 1.15 - 1.56 \text{ \AA}$  and  $|\text{H} - \text{H}|_{\text{w}} = 1.96 - 2.33 \text{ \AA}$  are

some higher, than in an H<sub>2</sub>O molecule - 0,958 and 1,58 Å, accordingly), with  $F = -434.0$  eV and sufficiently low  $G_{\text{norm}} = 0.818$  was supposed to be the most probable. Interaction of protons on such distances can cause a duplicate line in the <sup>1</sup>H NMR spectrum with the split of  $\Delta_{\text{H-H}} = \Delta_{\text{H-H}}^{\text{w}} \cdot (|\text{H} - \text{H}|_{\text{w}}^{\text{H}_2\text{O}} / |\text{H} - \text{H}|_{\text{w}}^{\text{CFAP}})^3 \sim 0.65 - 1.1$  mT, where  $\Delta_{\text{H-H}}^{\text{w}} = 2.1$  mT - the duplicate split of the fixed H<sub>2</sub>O molecules in <sup>1</sup>H NMR spectrum,  $|\text{H} - \text{H}|_{\text{w}}^{\text{H}_2\text{O}}$  - the distance between protons in an H<sub>2</sub>O molecule [12].

In the optimized CFAP structure there are most displacements of atoms of H and O in H<sub>2</sub>O<sub>fix</sub> molecules and OH-groups - up to 0.7 Å from initial sites ( $|\text{O} - \text{H}|_{\text{hydroxyl}} = 1.08$  Å, at initial coordinates 0.96 Å), displacements of C atoms - up to 0.3 Å and other ions - does not exceed 0.1 Å from initial sites (in FAP structure). The structural defects of certain type are located approximately evenly, mostly distanced from each other.



**Fig. 1.** The typical channel structures in the optimized CFAP structure: the AB cluster (1 channel) (a) and (CO<sub>3</sub>F<sub>x</sub>)<sub>B</sub> clusters (of 4 analogical channels) far from the H<sub>2</sub>O<sub>fix</sub> molecules (b) and near the H<sub>2</sub>O<sub>fix</sub> molecules, F<sub>x</sub> atom - aside from H<sub>2</sub>O<sub>fix</sub> (c). The Ca (II) atoms are at  $z = 1/4 + n/2$ , where  $n = 0 - 5$ . The atoms of Ca (I) and PO<sub>4</sub>-groups are not shown.

Figure 1 shows the typical structures of channels in the optimized CFAP structure. The H<sub>2</sub>O<sub>fix</sub> molecules occupy the PO<sub>4</sub>-vacancies: O atoms - in P sites, OH-bonds are directed to sites of O1 and O2. The excess F<sub>x</sub> atoms are in the O3\*-vacancies in (CO<sub>3</sub>)<sub>B</sub>-groups in the structural AB cluster (fig. 1, a), distanced and near the H<sub>2</sub>O<sub>fix</sub> molecules (fig. 1, b and c, accordingly). Hydroxyls in channels are near (CO<sub>3</sub>)<sub>B</sub>-groups, protons are directed toward the (CO<sub>3</sub>)<sub>B</sub>-group planes. The Na (I) atoms and Ca (II) vacancies are most distanced from each other and located, mainly: the Na (I) atoms are near the (CO<sub>3</sub>F<sub>x</sub>)<sub>B</sub> clusters (except the AB cluster), in the direction to O1 and F<sub>x</sub>, the Ca (II) vacancies are near the (CO<sub>3</sub>)<sub>B</sub>-groups with the O3\* vacancies in the same plane with the atoms of O8 and O9.

The obtained data correspond to experimental and literary data. In the optimized CFAP structure of CFAP the atoms of F and OH- groups are localized in two different structural sites, in accordance with <sup>1</sup>H and <sup>19</sup>F NMR data for synthesized CFAP [3]. By computer modeling data, the F atoms are both in channels and out of channels near (CO<sub>3</sub>)<sub>B</sub>-groups, excess F<sub>x</sub> atom localization is varied depending on chemical composition of CFAP [2, 5]. The presence of the excess F<sub>x</sub> atom with large electronegativity relatively not far from an OH-group ( $|\text{F}_x - \text{H}(\text{OH})| = 3.83$  Å) must result in the decrease of electron density on the hydroxyl proton. This can explain appearance of the second, more high-frequency, component in <sup>1</sup>H MAS NMR spectra of the synthesized CFAP samples when excess F<sub>x</sub> atoms are uptake in the structure [3]. The computer modeling of B-type substitutions in HAP was established the O-H-bond directs toward the (CO<sub>3</sub>)<sub>B</sub>-group plane [9].

## 4 Conclusion

The distribution of structural defects ( $\text{CO}_3$ -groups, excess  $\text{F}_x$  atoms, Na atoms, Ca vacancies, OH-groups, fixed  $\text{H}_2\text{O}_{\text{fix}}$  molecules) in synthesized CFAP (2.7 wt %  $\text{CO}_2$ , 3.3 wt % F) was studied by computer modeling in the GULP program, using grid-techniques. The next CFAP structure is found to be the most probable (structural defects of certain type are located approximately evenly, most distanced from each other): the  $\text{H}_2\text{O}_{\text{fix}}$  molecules are in the  $\text{PO}_4$  vacancies (O atoms – in P sites, OH-bonds are directed to sites of O1 and O2, distances  $|\text{O} - \text{H}|_{\text{w}} = 1.15 - 1.56 \text{ \AA}$ ,  $|\text{H} - \text{H}|_{\text{w}} = 1.96 - 2.33 \text{ \AA}$ ), the excess  $\text{F}_x$  atoms are in the  $\text{O}3^*$  vacancies in  $(\text{CO}_3)_{\text{B}}$ -groups in the structural AB cluster, distanced and near the  $\text{H}_2\text{O}_{\text{fix}}$  molecules, the OH-groups in channels are near  $(\text{CO}_3)_{\text{B}}$ -groups. The Na (I) atoms and Ca (II) vacancies are most distanced from each other and from the AB cluster and mainly located: the Na(I) atoms - near the  $(\text{CO}_3\text{F}_x)_{\text{B}}$  clusters, in the direction of O1 and  $\text{F}_x$ , the Ca(II) vacancies – near the  $(\text{CO}_3)_{\text{B}}$ -groups with the  $\text{O}3^*$  vacancies. The obtained data correspond to the results of experimental investigations of synthesized CFAP with different contains of  $\text{CO}_2$  and F.

## 5 Acknowledgments

The research has been fulfilled within the framework of Government scientific and technical program of introduction and application of grid-techniques in 2009 - 2013, project 38/13 "The application of grid- techniques for investigation of the radiation-stimulated processes, phase transformations and isomorphic substitutions in minerals in connection with solution of the applied tasks».

## References

- [1] Y. Pan, M.E. Fleet: Compositions of the Apatite-Group Minerals: Substitution Mechanisms and Controlling Factors. *Reviews in Mineralogy and Geochemistry*, 48 (1): 13-49, 2002.
- [2] H.E.Mason, F.M. McCubbin, A. Smirnov, B.L. Phillips: Solid-state NMR and IR spectroscopic investigation of the role of structural water and F in carbonate-rich fluorapatite. *American Mineralogist*, 94 (4): 507-516, 2009.
- [3] А.Б. Брик, О.В. Франк-Каменецкая, В.А. Дубок и др.: Особенности изоморфных замещений в синтетических карбонатфторапатитах по результатам исследования ЭПР и ЯМР. *Минералогический журнал*, 35 (2): 38 – 45, 2013.
- [4] O. Frank-Kamenetskaya, A. Kol'tsov, M. Kuz'mina et al.: Ion substitutions and non-stoichiometry of carbonated apatite-(CaOH) synthesized by precipitation and hydrothermal methods. *Journal of Molecular Structures*, 992: 9-18, 2011.
- [5] P. Regnier, A.C. Lasaga, R.A. Berner et al.: Mechanism of  $\text{CO}_3^{2-}$  substitution in carbonate-fluorapatite: Evidence from FTIR-spectroscopy,  $^{13}\text{C}$  NMR and quantum mechanical calculations // *American Mineralogist*, 79: 809-818, 1994.
- [6] M.E. Fleet, X. Liu: Accommodation of the carbonate ion in fluorapatite synthesized at high pressure *American Mineralogist*, 93 (12): 1460-1469, 2008.
- [7] J.M. Hughes, M. Cameron, K.D. Crowley: Structural variation in natural F-, OH- and Cl-apatites. *American Mineralogist*, 74 (7-8): 870-876, 1989.
- [8] C. Meis, J.D. Gale, L. Boyer et al.: Theoretical Study of Pu and Cs Incorporation in a Mono-silicate Neodymium Fluoroapatite  $\text{Ca}_9\text{Nd}(\text{SiO}_4)(\text{PO}_4)_3\text{F}_2$ . *Journal of Physical Chemistry A*, 104 (22): 5380-5387, 2000.
- [9] S. Peroos, Z. Du, N.H. de Leeuw: A computer modeling study of the uptake, structure and distribution of carbonate defects in hydroxy-apatite. *Biomaterials*, 27: 2150-2161, 2006.
- [10] N.H. de Leeuw: A computer modeling study of the uptake and segregation of fluoride ions at the hydrated hydroxyapatite (0001) surface: introducing a  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$  potential model. *Physical Chemistry Chemical Physics*, 6: 1860-1866, 2004.
- [11] J.D. Gale, A.L. Rohl: The General Utility Lattice Program (GULP). *Molecular Simulation*, 29 (5): 291-341, 2003.
- [12] А. Абрагам: Ядерный магнетизм. М.: ИЛ, 1963.