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CHEMICAL AND STRUCTURAL CHARACTERIZATION OF NATURAL PHOSPHATE OF HAHOTOE (TOGO)

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ABSTRACT. Chemical and structural characterizations of natural phosphates of Hahotoe (Togo) have been performed. From chemical analysis and FTIR study, it can be concluded that the material is carbonated fluoroapatite with poor substitution of calcium by cadmium and manganese. From these results, the molecular formula proposed is:

$$Ca_{9.925}Cd_{0.004}Mn_{0.013}[(PO_4)_{5.886}(CO_3)_{0.113}]F_2.$$

Powder X-ray diffraction fitting results confirm that compound belongs to the apatite family crystallising in the hexagonal system, space group $P6_3/m$. The cell parameters are: a = 9.3547(5) Å; c = 6.8929(4) Å.

KEY WORDS: Natural phosphate, Fluoroapatite, Infrared, X-Ray diffraction, Rietveld structure refinement

INTRODUCTION

Geochemical studies have demonstrated the great capacity of apatitic mineral to retain a large variety of trace elements like heavy metals, rare-earth elements. This capacity is due to their particular crystalline structure that allows isomorphous substitutions. Carbonate fluoroapatite (francolite) is the main mineral phosphate present in sedimentary phosphorites. It is microcrystalline and differs from synthetic pure apatites because of complex substitutions in apatite structure. These substitutions result in tremendous variations in chemical reactivity and stability of carbonate fluoroapatites and concern particularly divalent cations like cadmium [1-4], lead [5, 6], and strontium [7, 8]. Other cations can also be exchanged (Mn^{2+}, Zn^{2+}, Mg^{2+}, Ba^{2+}, Cu^{2+}, Co^{2+}).

The aim of this study is therefore to determine chemical composition and crystal structure of sedimentary phosphorites of Togo for purification and commercial exploitation.

EXPERIMENTAL

Sample

The mineral apatite used in this study comes from the sedimentary phosphate rock of Hahotoe (Togo). The raw ore is a mixture of phosphate and clays grey rock. Treatment of ores allows the

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elimination of clays in the material. About 30 g of rock was crushed and introduced in 1 L of demineralized water. The mud was shacked for 1 h and centrifuged at 3000 rpm for 30 min. Filtrate containing clays was separated from the solid residue rich in phosphate. For the same sample, operation was repeated 10 times. The solid residue was dried at 100 °C for 24 h and calcined at 800 °C for 4 h. The final compound is call washed material in the following.

Characterzations

Chemical characterizations

Chemical composition of separate raw ore and solid obtained after washing has been carried out. One gram of the compound was calcinated at 600 °C for 12 h and dissolved in 2 mL concentreted HCl (36%) and resulting solution diluted and analyzed for Ca, Cd, Mn, K, Cu, Mg, Si and Fe by atomic absorption spectrometry. Phosphorus was measured colorimetrically by using a phosphomolybdate blue method. Carbon determination was performed using an EA100 CHNS instrument.

Physical analysis

Infrared measurement

Fourier transform infrared (FTIR) spectroscopy was performed on KBr pellets containing homogeneous mixture of 2 mg of compound and 300 mg KBr using Perkin Elmer 1600 series FTIR spectrometer. The IR scan was performed from 400 to 4000 cm^{-1}.

X-Ray measurement

Powder X-ray diffraction analysis for the natural phosphate was carried out using a Seifert XRD 3000 TT diffractometer equipped with a diffracted beam monochromator. Experimental details of data collection are reported in Table 1. The cell dimensions were calculated using DICVOL 91 [9, 10].

After indexation of the full pattern, the cell parameters have been refined with NBS*AIDS83 program [11]. Structure refinements were performed using the FULLPROF program [12].

Table 1. Experimental details of X-ray powder-profile data collection.

Radiation	Cu, $K\alpha_{1,2}$, $I(\lambda_1)/I(\lambda_2) = 0.5$
Divergence slits	3.00 mm -Soller-2.00 mm
Receiving slits	-Soller-0.10 mm
2θ Range (°)	8 – 160
Step scan	θ – θ
Step width (2θ)	0.02°
Counting time (s) [range (°2θ)	30 [8-60], 40 [60-100], 50 [100-160]
Sample	Powder (particle size < 90 μm) compressed in cylindrical sample holder of 24 mm diameter and 0.5 mm depth
Temperature	Room temperature (293 K)

RESULTS AND DISCUSSION

Chemical analysis of raw and washed material has been performed. Results reported in Table 2 show that treatment of crushed phosphate rock allows the separation of clays containing the majority of metal oxides from the calcium phosphate. Nevertheless, the final material contains traces of clays, silica and other metallic oxides (MgO, Al_2O_3, Fe_2O_3, etc.). But concentration of cadmium and manganese are varying as phosphates concentration indicates that they are included in the phosphate compound. Presence of fluoride and carbon in the material after calcination at 800 °C indicates that calcium phosphate contained in rock is a carbonated fluoroapatite.

Table 2. Chemical composition (in weight percentage) of raw and washed materials.

Parameters	Raw material	Washed material
%CaO	35.80	55.6
%P_2O_5	28.20	38.30
% SiO_2	12.5	2.10
% Fe_2O_3	7.2	0.03
%Al_2O_3	5.6	0.01
% MgO	3.8	0.01
%K_2O	2.6	0.02
% Na_2O	2.8	0.01
%CO_3^{2-}	0.75	0.68
% F	0.15	0.40
Cd (ppm)	49	58
Mn (ppm)	74	86
Zn (ppm)	35	3.5
Cu (ppm)	45	2.7

IR absorption spectra of raw and washed materials are represented in Figure 1. The two spectra are typical of carbonated fluoroapatite with carbonate vibration absorption bands observed at 1460 and 1465 cm^{-1} (stretching vibrations). Absorptions in the ranges 970 – 1100 cm^{-1} (stretching) and 560 – 620 cm^{-1} (bending) were attributed to PO_4^{3-} vibrations [9]. Water absorption bands can be observed at 3400 and 1650 cm^{-1}. On top of these apatite bands, raw material spectra revealed infrared absorption in 3500 – 3600 cm^{-1} and 600 – 800 cm^{-1} ranges, confirming the presence of other compounds.

X-Ray diffraction characterisation was performed on the washed compound. It reveals a pure crystalline fluoroapatite (FAP) phase containing about 5% of α quartz. The peaks in the diffraction patterns are relatively sharp and well resolved. All of them can be attributed to the hexagonal apatite type structure (SG: $P6_3/m$) and α quartz (SG: $P3_221$). Experimental a and c values are reported in Table 3 in comparison with synthetic stoichiometric [13], carbonated FAP [14], and natural carbonated FAP containing uranium [15] ones.

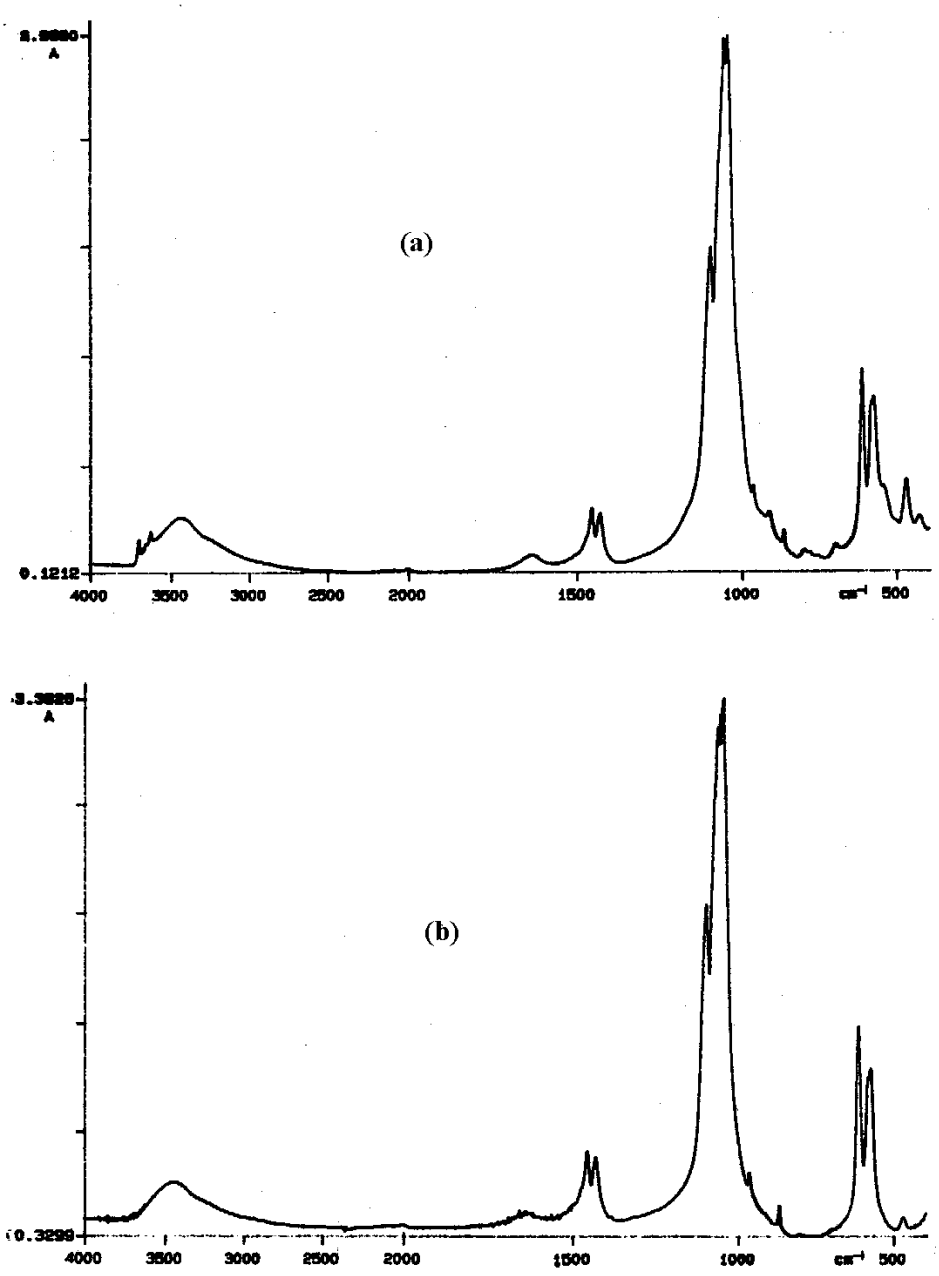

Figure 1. IR spectrum of raw material (a) and washed material (b).

Table 3. Comparison of experimental and references cell parameters.

Parameters	Washed material	Stoichiometric FAP [13]	Synthetic carbonated FAP [14]	Uranium carbonated FAP [15]
a (Å)	9.3547 (5)	9.372	9.3249(1)	9.364
C (Å)	6.8929(4)	6.886	6.9213(1)	9.899

Rietveld structure refinements are performed using the FULLPROF program. Atomic coordinates of carbonated hydroxyapatite (HAP) used as starting parameters, are those given by El Feki *et al*. [14] substituting OH by F. Occupancy factors of PO_4^{3-} and CO_3^{2-} are optimised according to a full occupancy of P or C 6h site.

The substitution of CO_3^{2-} by PO_4^{3-} infers a change of the negative charge which is counterbalanced by the formation of vacancies in the metal sites. A restraint was applied on the occupancy in order to take into account the electroneutrality.

Ca, Cd and Mn occupancy factors were refined but strong correlations occur. Therefore, values proportional to experimental results of the chemical analysis were introduced in the refinement. Parameters related to this final refinement are reported in Table 4.

Table 4. Parameters related to final refinements of natural carbonates FAP.

Parameters	Carbonated FAP
Formula	$Ca_{9.925}Cd_{0.004}Mn_{0.013}[(PO_4)_{5.886}(CO_3)_{0.113}]F_2$
Cell parameters	a = 9.3547(5) Å; c = 6.8929(4) Å
System	Hexagonal
Space group	$P6_3/m$
Final agreement factors	R_p= 0.149 ; R_{wp} = 0.173
	R_F = 0.0558 ; R_B = 0.079
Percentage	χ_2 = 0.0299
	FAP = 95.11%
	α quartz = 4.89%

The final fractional coordinates, thermal displacement parameters and occupation factors for compound are reported in Table 5. Selected interatomic distances are given in Table 6 together with those for carbonated HAP [14]. The observed and calculated profiles are shown in Figure 2.

Table 5. Final atomic parameters for natural apatite.

Atom	x	y	z	B(Å^2)
O1	0.329(2)	0.480(2)	1/4	2.9(5)
O2	0.587(3)	0.466(3)	1/4	3.5(5)
O3	0.335(2)	0.252(2)	0.071(2)	3.7(4)
P	0.397(1)	0.370(1)	1/4	2.4(2)
C	0.397(1)	0.370(1)	1/4	2.4(2)
CA1	1/3	2/3	0.002(2)	2.9(2)
Cd1	1/3	2/3	0.002(2)	2.9(2)
Mn1	1/3	2/3	0.002(2)	2.9(2)
CA2	0.2408(9)	-0.009(1)	1/4	2.3(1)
Cd2	0.2408(9)	-0.009(1)	1/4	2.3(1)
Mn2	0.2408(9)	-0.009(1)	1/4	2.3(1)
F	0	0	1/4	3.3(6)

Table 6. Interatomic distances (Å) for natural carbonated fluoroapatite (FAP) and synthetic carbonated hydroxyapatite (HAP) [14].

	Natural FAP	Synthetic HAP [14]
P-O(1)	1.45(3)	1.416(2)
P-O(2)	1.54(2)	1.445(1)
P-O(3) x2	1.56(2)	1.562(1)
Site M1		
Ca1-O(1) x3	2.43(2)	2.442(1)
Ca1-O(2)$_{i}$ x3	2.45(2)	2.441(1)
Ca1-O(3)$_{ii}$ x3	2.84(2)	2.772(1)
Site M2		
Ca2-O(3)$_{iii}$ x2	2.34(2)	2.314(1)
Ca2-O(3)$_{v}$ x2	2.47(2)	2.594(1)
Ca2-O(1)$_{vi}$	2.68(2)	2.604(1)
Ca2-O(2)$_{iv}$	2.38(2)	2.420 (1)
Ca2 - F$_{v}$	2.30 (1)	Ca2-OH$_{v}$ 2.47 (2)

Symmetry operators: (i) x - y, x, -0.5 + z; (ii) 1 - x, 1 - y, -z; (iii) y, 1 - x + y, 0.5 + z; (iv) 1-y, 1 + x – y, z; (v) x, 1 + y, z, (vi) –x + y, 1 – x, z.

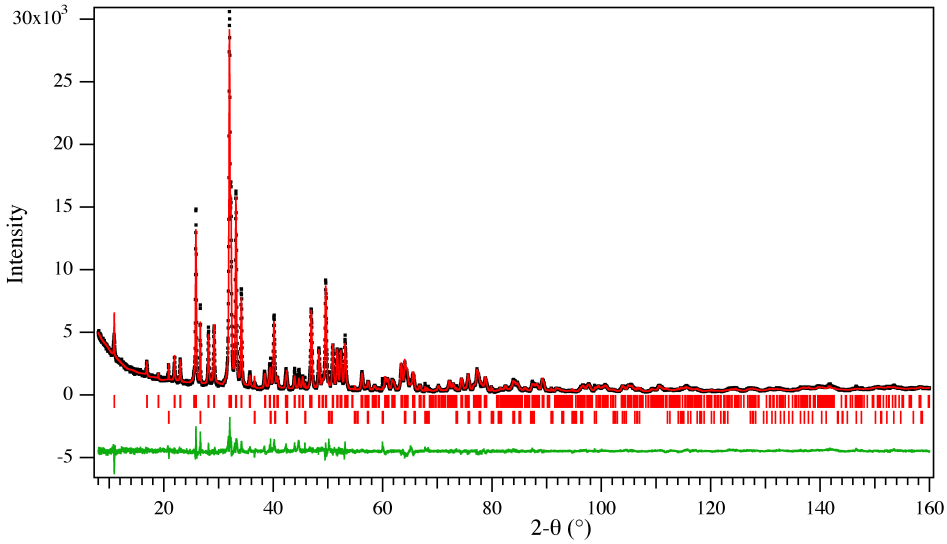

Figure 2. Comparison between experimental and calculated X-ray patterns of natural carbonated fluoroapatite (2θ range 20 – 160°).

Chemical analysis (Table 1) and IR absorption spectra (Figure 1) allow us to consider the washed material as a carbonated fluorapatite (FAP) containing traces of clays. Increased amounts of cadmium and manganese content during cleaning treatment show that both elements can not be separated from the apatite by this physical treatment. We can conclude, as reported in many works [16-20], to the probable presence of cadmium and manganese in calcium sites. From chemical results and assuming a partial substitution of PO_4^{3-} by CO_3^{2-} the chemical formula is:

$$Ca_{9.925}Cd_{0.004}Mn_{0.013}[(PO_4)_{5.886}(CO_3)_{0.113}]F_2$$

This formula is in good agreement with electroneutrality. X-Ray diffraction patterns refinement was performed considering these cationic and anionic substitutions.

Substituting a carbonate (CO_3^{2-}) for phosphate (PO_4^{3-}) infers a lack of one oxygen atom. This oxygen can be distributed over every oxygen site. Some authors [21-23] showed that, in this case, CO_3^{2-} is situated on faces O1–O2-O3 or O1–O2–O3vii of the PO_4^{3-}tetrahedron. A view of the cell content is represented in Figure 3 using Crystal Maker [24]. Final refinement parameters (Table 4) agree with this hypothesis.

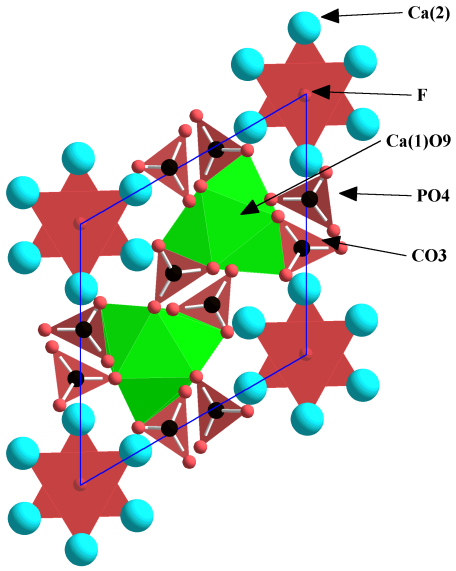

Figure 3. Projection of cell along [OO1] for natural carbonated fluoroapatite. CO_3^{2-} anions are presented on the faces of PO_4^{3-} tetrahedron.

Contrary than expected the cationic substitution, has not made an important modification of cell parameters. It is due to the lowest concentration of cadmium and manganese in the material [23]. However, the cadmium content as reported in Table 1 raises environmental problems because of its toxicity. This content (58 ppm) is considerably higher than the standards of cadmium content set by the European Union Countries for commercially produced phosphoric acid (less than 18 ppm) [25, 26].

CONCLUSION

Natural phosphate rock from the Hahotoe (Togo) ores have been characterized after elimination of clays contained in these rocks by washing and calcination at 800 °C for 4 hours. Chemical analysis performed on the final material shows high content of phosphate and some carbon due to carbonate ions and traces of cadmium and manganese. Infrared measurement gives a typical fluoroapatite spectrum and confirms the carbonated character of the material.

Structural characterization was realised by X-ray diffraction study. The full diffraction patterns have been attributed to hexagonal apatite type compound (SG: $P6_3/m$) and α quartz (SG: $P3_221$). Refinement of structural parameters allows the conclusion that the compound is a carbonated fluoroapatite with a poor substitution of cadmium and manganese for calcium.

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