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Trace elements of Kef Es Sennoun natural Phosphate (Djebel Onk, Algeria) and how they affect the various Mineralurgic modes of treatment

N. Bezzi^a, T. Aïfa^b a*, S. Hamoudi^a, D. Merabet^a

^a *Laboratoire de Technologie des Matériaux et de Génie des Procédés (LTMGP), Faculté des Sciences exactes, Université de Béjaïa, 06000 Béjaïa, Algeria*

^b *Géosciences-Rennes, CNRS UMR6118, Université de Rennes 1, Bat.15, Campus de Beaulieu, 35042 Rennes cedex, France*

Abstract

Trace elements in particles of the phosphate ore and their behaviour in the various mineralurgic modes of processing were studied to: (i) locate the importance of these contents according to granulometry, their association with the existing mineralogical species, and (ii) check if the enrichment operations applied are compatible with a kind of processing. We used several methods of preconditioned analyses to (i) define the optimal meshes of release of the phosphatic elements and gangue minerals, (ii) identify the raw material mineralogical phases, the major elements chemical composition, their distribution into particle-size classes, and their thermal behaviour. X-ray fluorescence and ICP-MS allowed to identify 30 REE and transition metals. We obtained significant differences in the particle shapes, especially the fine ones and in the mineralurgic modes of treatment used, where the floatation processing is prevailing. A close relation between trace elements and various minerals (apatite, dolomite and silicates), through operations of substitution, is evidenced.

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Keywords: Phosphate-ore; trace elements; mineralogy; chemistry; granulometry; treatment; environment; characterization

* Corresponding author. Tel.: +33-223236785; fax: +33-223236097.
E-mail address: tahar.aifa@univ-rennes1.fr

1. Introduction

Trace elements have been playing an increasingly important part in the environment either as essential nutritional factors, or as toxic agents. Impurities in traces present in natural phosphates can contaminate the phosphate-enriched fertilizers, consequently the agricultural productions intended for food. At concentration levels higher above the normal threshold, trace elements can become toxic and adversely affect the quality of phosphates. The role of phosphates in the cycle of life is crucial and the importance of fertilizers is essential to ensure food for the world population. Thus, the industry of phosphatic fertilizers and of phosphoric acid, which absorbs more than 90% of the production of phosphate concentrates imposes requirements for the quality of the raw material. These requirements are in relation with the nature of impurities contained in the ore as well as with the importance of their effect on the manufacturing processes of fertilizers. The principal quality parameters of these ores are primarily defined by the limiting contents of major elements (P_2O_5 , MgO ,...) and existing trace elements (Cr, Sr, U,...)[1]. Indeed, at concentration levels higher than the normal threshold, these elements become toxic and adversely affect the quality of phosphates. They can then have an effect on the phosphate-enriched fertilizers, and consequently the agricultural productions intended for the food.

Nomenclature

BET	Brunauer-Emmett-Teller
DSC	Differential scanning calorimetry
IR	Infra red
SEM	Scanning electron microscope
TGA	Thermal gravity analysis
XRD	X ray diagram

Thus, the qualitative and quantitative knowledge of these elements and their localization in the phosphate ore has multiple implications, from a purely scientific or an industrial point of view. Indeed, certain trace elements are essential to life, such as the micronutrients cobalt, copper, iron, manganese, molybdenum, zinc, nickel, chromium, vanadium, tin,...[2,3]. Others are known for their noxious impact on man and their harmful effect [4] on the environment (arsenic, cadmium, mercury, lead,...), thus requiring us to identify and reduce the sources of emission. Indeed, although they are essential in minute quantities, the increase in their concentration in the environment can lead to toxic phenomena [5]. Other elements are not necessary for organisms and present toxic effects as of the low contents [6]. The geochemical behaviour of these elements is determined by their intrinsic characteristics (mass, load, atomic ray,...) and by their abundance. It is generally admitted that these elements are incorporated in structures determined by major elements according to their ionic characteristics. They are usually elements representative of apatite by various forms of substitution. One of the characteristics of the apatitic structure resides in its capacity to form solid solutions and to accept a large number of substitutes [7,8]. There is a competition on the sites of sorption between the major metals and cations, in particular Ca^{2+} [9] which decreases the retention of metals on the phosphatic particles. The most abundant and widespread phosphatic minerals belong to the apatite family. Apatite belongs to the hexagonal system (*Fig. 1a-d*) and is characterized by the general formula [10,11]: $M_5(XO_4)_3Y$, where M generally represents a divalent cation Ca^{2+} , Cd^{2+} , Pb^{2+} ,..., XO_4 a

trivalent anion PO_4^{3-} , AsO_4^{3-} , VO_4^{3-} , MnO_4^{3-} ,... and Y a monovalent anion OH^- , F^- , Cl^- [12,13,14]. The structure of hydroxyapatite allows many ionic substitutions: HPO_4^- can for example substitute for PO_4^{3-} [15,16,17]. The network of apatites still allows many other substitutions, generally more discrete than the previous ones. In this way, calcium is substituted by manganese, strontium, magnesium, sodium, potassium, copper, cadmium, lithium, iron, tin, lead, uranium, water and rare earths. Ion PO_4^{3-} can also be substitutable by SO_4^{2-} , SiO_4^{4-} , HPO_4^{2-} , AsO_4^{3-} and CrO_4^{2-} [18]. Ions SO_4^{2-} present with respect to PO_4^{3-} possibilities of substitution comparable with those of CO_3^{2-} for some SO_4^{2-} [7], or definitely lower for others [8].

On the basis of all these data, our study relates to the ore of Kef Es Sennoun layer (Djebel Onk) which has important rock phosphate reserves. The main required aim is to evaluate qualitatively and quantitatively the existing trace elements according to granulometry, mineralogy with their repercussions on the various modes of treatment such as: sifting, calcination, washing and floatation. The study should enable the exploitation company (Somiphos) to improve the quality of its products and contribute to the valorization of rejections, rich in toxic trace elements with a harmful environmental impact.

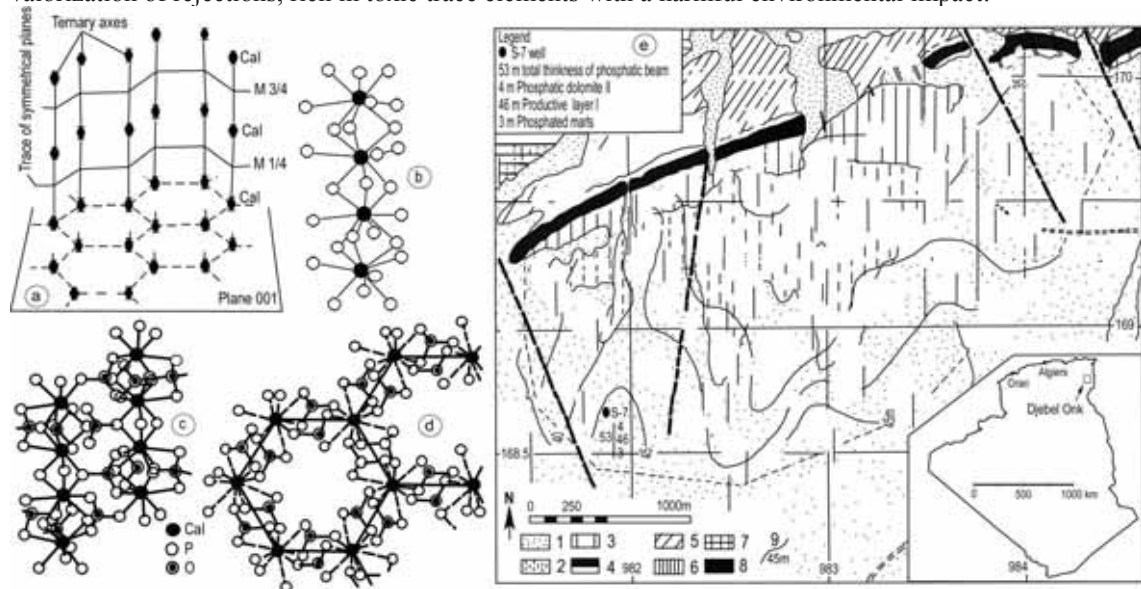


Fig. 1. Structure of apatite [28]. (a) the ternary axes are perpendicular to the plane 001 and are placed at the tops of jointed hexagons. The Ca^{2+} ions distributed on these axes are located appreciably at equal distance from the symmetry planes M1/4 and M3/4, themselves parallel with plane 001 (b) To each ion Ca_i of the ternary axes are associated 9 atoms O also distributed between the symmetry plane located above the ion Ca_i , the symmetry plane located immediately below, and the plane of ion Ca^{2+} (c) Ca_i -O columns are connected by ions P which form tetrahedrons PO_4 with 3 O of a column and 1 O of the following column (d) Projection onto plane 001 of the Ca_i -O columns and the PO_4 tetrahedrons which associate them. (e) Isopach map of the whole Kef Es Sennoun phosphatic beam ([19], modified). 1. Quaternary and Miocene: sands, gravels, clays, sandstones; 2. Lutetian: limestones, marls, clays, gypsum; 3. Ypresian: limestones with flint, marls, dolomites; 4. Thanetian (lower): phosphates; (upper): marls; 5. Mantiian: limestones, marls; 6. Danian: limestones, marls, clays; 7. Maestrichtian: limestones; 8. Outcropping phosphatic layer; 9. Contour of phosphatic thickness.

2. Outline on Djebel Onk natural phosphate

The phosphates of the area of Djebel Onk, located in the Southeast of Algeria, are part of a succession of sedimentary strata formed at the end of the Cretaceous-Eocene era. Djebel Onk is a calcareous mountainous solid mass, about twenty kilometres long. It comprises several sectors or phosphatic formations among which Kef Es Sennoun, the object of this study. It presents a layer of phosphate with

rather constant and homogeneous characteristics throughout the extent of the recognized layer, i.e. over a surface of $\sim 3.16 \text{ km}^2$ (3.5 km of length and 0.9 km of width). Its structure is mainly monoclinical, dipping 10° to 15° towards the South. Elevations are approximately 810 m to the Northeast and 710 m in the Southwest. The lithological succession of the Kef Es Sennoun layer is marked by the most important thicknesses of the phosphatic beam 35 to 45 m in the phosphatic basin of Djebel Onk. The maximum thickness of the productive layer is in the S-7 survey, with 46 m of phospharenites (*Fig. 1e*), without sterile guides, which is exceptional at the level of the Algerian-Tunisian and Moroccan phosphatic basin. The major part of the layer consists of dark phosphates, grey black, with variable granulometry, from fine (100 μm) to coarse (up to 1 mm). Clear, dark brown phospharenites (25% of the reserves) exist above dark phosphates in the northern part of the layer [19]. The phosphatic beam is made up, from top to bottom, of phosphated dolomite, the productive layer and marl-phosphate-dolomite alternations. Chemically, the productive layer is remarkable for its strong contents of P_2O_5 and its low contents in MgO, for both types of ores (dark and light). The average contents of P_2O_5 range between 25 and 27.9%, for a general average of 26.53%. The contents of MgO are constant and weak (2 and 3%) throughout the extent of the layer. The minerals of the gangues associated with the phosphated elements in the phosphatic rocks are many: quartz, calcite, dolomite, ankerite, siderite, feldspars, clays, gypsum, organic matters and others [20].

3. Preparation and characterization of Kef Es Sennoun natural phosphates

This study concerns two series of samples noted A and B obtained starting from natural phosphate extracted from the Kef Es Sennoun layer located in the Djebel Onk, whose particle sizes vary from 0 to 1500 μm . Series A is carried out according to operations of granulometric reduction, homogenization and reduction of volume (quartering). Thus, four samples representing the fractions: raw (PB), fine (PF), average (PM) and coarse (PG) of sizes (μm): 0-4000; < 40; 40-500 and >500 are obtained respectively. The B series consists of four samples obtained after processing by calcination at 900°C (PC); by scrubbing, designed to eliminate the major part of the siliceous and argillaceous particles (PD) and finally by floatation to separate the carbonates (rejection [RF]) from the phosphates (concentrated [CF]). These samples were subjected to characterization tests by various analysis methods (XRD, TGA, IR, DSC, SEM and BET), in order to better define their granulometric, petrographic, mineralogical, chemical and thermal characteristics. The knowledge of these characteristics should make it possible to direct the choices of beneficiation treatment and to understand the substitution processes of the trace elements in the matrixes of the phosphate and of the gangue. The characterization work brings out the following main points: On the granulometric level (*Fig. 2a*), the dimensional classification carried out by sifting revealed a unimodal curve, indicating the homogeneity of the grains of the raw phosphate. It also shows that the distribution of the general characteristics of the raw sample is made up of 75% (PM), 18% (PB) and 7% (PF). Thus, the average particle shape (PM) constitutes the mesh of optimal release of the separation of the phosphatic elements (class of arenites < 2 mm). From a chemical point of view, the best contents in phosphate ($\%\text{P}_2\text{O}_5$) and in elements of the gangue ($\%\text{MgO}$) are located within the beneficiation range of 90 to 250 μm (*Fig. 2b*), where the mesh of release of the phosphatic elements is also located [20]. The reduction in the frequency in these elements results in strong contents of MgO (PF, PG and RF) which are reflected on P_2O_5 outputs. The mineralogical study carried out by the XRD revealed that apatite is a strongly substituted francolite, in OH (hydroxyapatite) and in ions CO_3^{2-} (hydroxyapatite carbonate). Except in the dolomite (PG and RF), the presence of quartz, calcite and ankerite is not significant. All in all, the intensity of the peaks characteristic of the phosphatic elements and those of the gangue are in conformity with the various modes of treatment used (*Fig. 2c-d*). The analysis by infrared spectrophotometry highlighted the main bands attributable to phosphates, carbonates and OH hydroxyls ions of apatite.

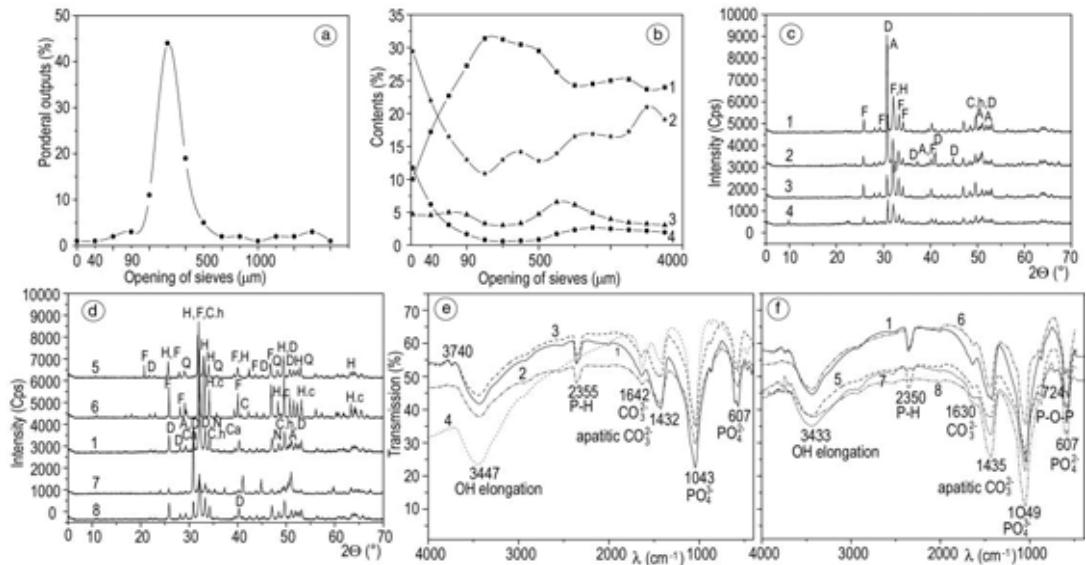


Fig. 2. (a) Granulometry by sifting and (b) chemical composition of the sample PB. 1: loss through combustion (PF); 2: P₂O₅; 3: MgO; 4: SiO₂. XRDs of the series of samples (c) A and (d) B. 1: raw phosphate (PB); 2: coarse phosphate (PG); 3: average-grained phosphate (PM); 4: fine-grained phosphate (PF); 5: scrubbed phosphate (PD); 6: calcinated phosphate (PC); 7: floatation rejection (RF); 8: floatation concentrate (CF). A: ankerite; C.h: carbonates hydroxyapatites; D: dolomite; F: fluorapatite; H: hydroxyapatite; Ca: calcite; H.c: calcium hydroxide; Q: quartz; N: nickel. IR Spectra of the two series of samples (e) A and (f) B. 1:PB ; 2:PG; 3:PM ; 4:PF; 5:PD ;6:PC ; 7:RF; 8:CF. λ: wavenumber.

However, the intensity of the rays characteristic of carbonates and phosphatic elements is clearly distinguished between the two series from the samples we studied. This difference is attributed to mineralogy for the A series, and to the specific mode of treatment for the B series (Fig. 2e-f). The TGA (Fig. 3a) showed a loss of principal mass attributed to the decomposition of carbonates in the 600°C<T<900 °C interval. It varies clearly according to granulometry (A series) and mode of treatment (B series). In fact, samples PF and PG recorded considerable losses (21.93 and 23.97% respectively), because of the abundance of strongly carbonated dolomitic cement [21].

DSC of sweeping for the treated samples, in particular by floatation (CF) highlighted two endothermic peaks at 71.65 °C and 360.20 °C, attributed to reactions of moisture water vaporization and of constitution water and organic matters respectively. The lack of peak characteristic of carbonates, for sample CF means that treatment by floatation is very effective to separate the carbonates-phosphates system (Fig. 3b).

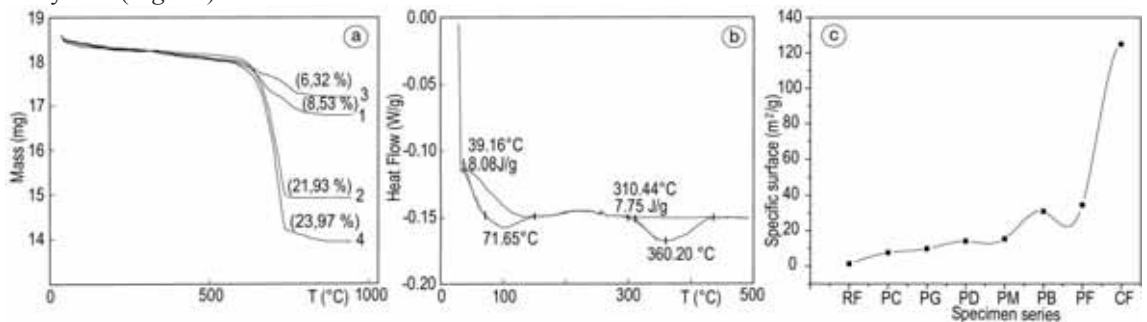


Fig. 3. (a) TGA of the phosphate samples. 1 :PB, 2 : PG, 3 : PI and 4 : PF, (b) DSC of the sample CF and (c) Specific surface of the phosphate samples PB, PG, PM, PF, PD, PC, RF and CF vs. type of the sample.

Specific measurements of surfaces through the BET method (Fig. 3c) show a clear difference as well for the samples of the A series as for those of the B series. The variation observed for the A series is primarily related to the smoothness of the grains, the chemical and mineralogical composition and the porosity (appearance of microcavities, according to SEM observations). For the B series, the difference is connected to the nature of the specific treatment used. The clear reduction in specific surface for calcinated phosphate (PC) can be attributed either to a recombination of calcium with fluorine or silicon, sealing the pores, or with a crystalline rearrangement of apatite [22]. The microscopic observations with the SEM (Fig. 4) highlight the presence of the principal minerals identified by XRD, like certain trace elements such as strontium, zirconium, barium, etc. The samples of the B series show a prevalence of apatites and a clear reduction in the elements of the gangue, in relation to their respective treatment. Micrographies of the A series show a great similarity regarding the shape and size of the microstructures. The phosphatic phase consists of grains with circular (oolites), rectangular (coprolites) and ovoid (pellets) sections, with dimensions ranging between 50 and 500 μm , cemented by carbonated aggregates (dolomite in particular), and a little clay and quartz.

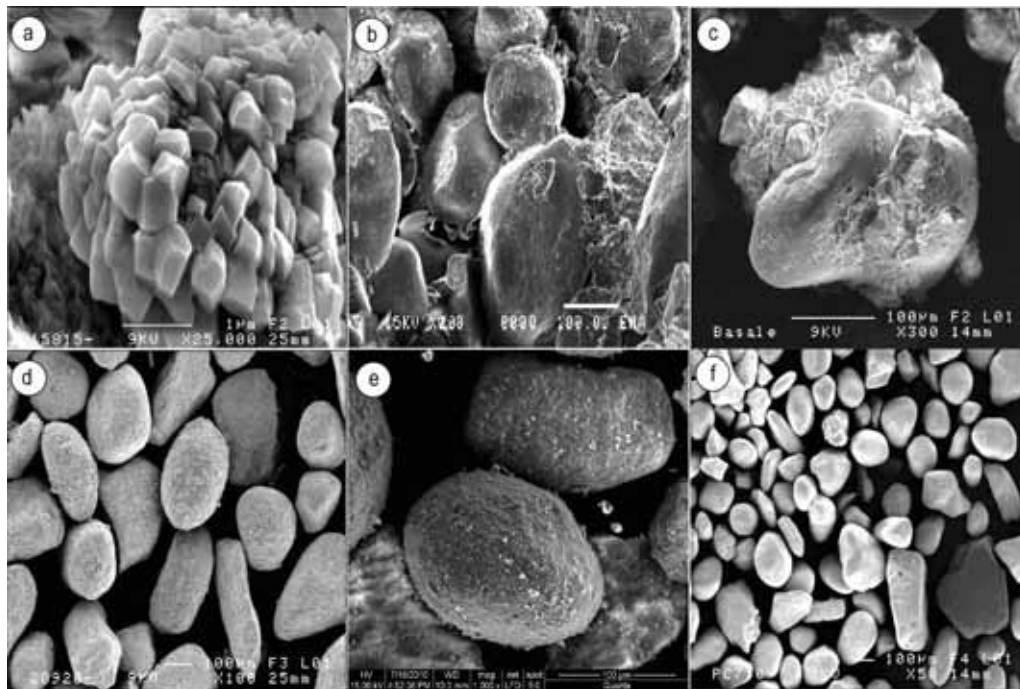


Fig. 4. Micrographies with SEM showing (a) : phosphate of the fine fraction (PF) : collection of rhomboedric shape of dolomitic crystals; (b) : raw phosphates (PB) : well-reorganized phosphate grains, coated with a dolomitic cement; (c) : phosphate of the coarse fraction (PG) : phosphate grain glued together with dolomitic crystals. (d) : floatation concentrate (CF), (e) : scrubbed phosphate (PD) and (f) : calcinated phosphate (PC) : phosphate grains of various shapes, without exogangue.

4. Study and analyses of trace elements

Qualitative and quantitative analyses of trace elements of the A series and their behaviour with the various modes of treatment (B series) were respectively given by (i) X-ray fluorescence, by means of a Philips PW1404 spectrometer, carried out at the Laboratoire des Matériaux de Grande Diffusion (Ecole des Mines d'Alès, France), (ii) mass spectrometry coupled to an inductive plasma (ICP-MS), with the

plasma gun of VG Plasmaquad II type, carried out at the Institut de Géosciences (Université des Sciences et Techniques de Montpellier, France).

4.1. Qualitative analyses of elements by X-ray fluorescence

The results yielded by the qualitative analyses (Fig. 5) did not show appreciable differences between the various samples (A series). In all cases, they highlight the presence of two groups of quite distinct elements by their intensities: (i) A group of major elements such as: phosphorus (P), calcium (Ca), strontium (Sr), sulfur (S), iron (Fe), molybdenum (Mo),... (ii) A group of trace elements such as: silicon (Si), magnesium (Mg), aluminium (Al), potassium (K), zinc (Zn), copper (Cu), sodium (Na),... These elements are distributed between several mineralogical phases [22], especially apatite (calcium (Ca), phosphore (P), strontium (Sr), sodium (Na), chrome (Cr), barium (Ba) and clays (aluminum (Al), silicium (Si), molybdenum (Mo), strontium (Sr), sodium (Na), nickel (Ni), zinc (Zn) and copper (Cu)).

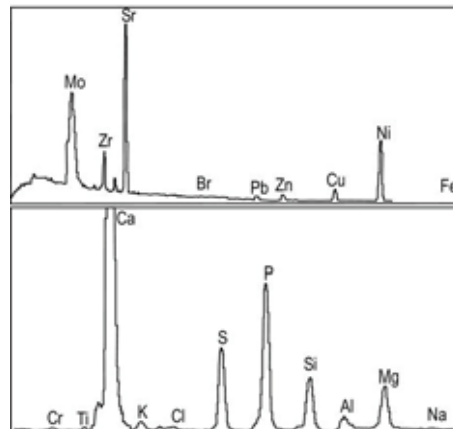


Fig. 5. Qualitative analysis by X-Ray fluorescence of the raw sample (PB).

4.2. Quantitative analysis of trace elements by ICP-MS

Chemical analyses of trace elements were carried out for the two series of samples (A and B) in a finely crushed state (<80 μm). This will allow us to study (i) their distribution into classes of particle-size (fine, average and coarse) and (ii) the effect of the treatment mode by calcination, scrubbing and floatation. The results of the analyses obtained for both series A and B (Table 1, Fig. 6a-f) highlight the presence of about thirty trace elements made up in majority of rare earths (scandium, yttrium) and all lanthanides except for promethium (lanthanum, cerium, praseodyme, neodyme, samarium, europium, gadolinium, terbium, dysprosium, thulium, ytterbium, holmium, erbium and lutecium) and of transition metals (vanadium, chrome, cobalt, copper, nickel, zinc, lead and ytterbium). However, alkaline-earth metals (strontium and barium), alkaline metals (cesium and rubidium) and two elements of the actinides family (thorium and uranium) are also identified. Concentration in these elements differs considerably according to the samples studied for both granulometric (PF, PM and PG) or treatment mode (PC, PD, CF and RF) level. A careful examination of the chemical composition of such elements enabled us to distinguish three main groups:

(i) *Group 1*, comprising low contents of trace elements (<10 ppm), and composed in majority of rare earths: cesium (Cs), rubidium (Rb), lutecium (Lu), ytterbium (Yb), thulium (Tm), holmium (Ho), terbium (Tb), europium (Eu), cobalt (Co) and scandium (Sc).

(ii) *Group 2*, comprising average contents of trace elements ($10 < T < 50$ ppm), and composed of actinides, metals of transition and lanthanides: lead (Pb), erbium (Er), dysprosium (Dy), gadolinium (Gd), samarium (Sm), praseodymium (Pr), barium (Ba), thorium (Th), uranium (U), copper (Cu) and nickel (Ni).

(iii) *Group 3*, comprising strong contents of trace elements (> 100 ppm), and composed of transition metals and lanthanides: vanadium (V), chromium (Cr), zinc (Zn), yttrium (Y), lanthanum (La), cerium (Ce) and neodymium (Nd). Strontium (Sr) which is classified separately because of its very high contents (> 2000 ppm), probably owing to a strong tendency to substitution in the apatitic structure and in the minerals of the gangue [1]. In addition, calculations of outputs or degrees of enrichment of each trace element, specific to each applied treatment mode compared to the raw sample (*Table 2*). The results obtained show significant differences, in particular for the process of floatation.

Table 1. Analyses of trace elements of groups (a) 1, (b) 2 and (c) 3 by ICP-MS for two series of the studied samples A and B.

(a)	Contents (ppm)							
	Series A				Series B			
	PB	PF	PM	PG	PC	PD	RF	CF
Cs	00.35	00.45	00.25	00.22	00.07	00.18	00.30	00.06
Co	00.82	01.67	00.41	00.45	00.57	00.52	00.38	00.12
Lu	01.57	01.24	01.41	00.61	01.51	01.65	01.45	00.48
Tm	01.54	01.26	01.36	00.61	01.49	01.64	01.44	00.50
Sc	02.84	02.50	01.81	01.08	02.51	02.47	02.26	00.85
Rb	05.65	08.41	03.46	03.16	01.54	02.72	03.99	00.95
Ho	04.16	03.58	03.73	01.60	04.01	04.42	03.85	01.32
Tb	03.16	02.81	02.78	01.18	03.16	03.31	02.89	01.02
Eu	05.39	05.10	04.87	02.08	05.58	05.92	05.07	01.76
Yb	09.30	07.60	08.11	03.63	08.86	09.90	08.75	02.88

(b)	Contents (ppm)							
	Series A				Series B			
	PB	PF	PM	PG	PC	PD	RF	CF
Er	11.48	09.96	10.41	04.47	11.48	12.31	10.83	03.76
Th	10.64	12.53	10.26	03.85	10.30	11.69	08.31	03.29
Pb	04.46	17.03	03.37	01.80	01.55	03.34	03.61	01.33
Dy	20.23	17.81	17.77	07.67	19.95	21.42	18.71	06.58
Sm	22.06	20.26	18.94	08.28	22.66	23.48	19.60	07.21
Gd	23.05	21.04	20.78	08.80	23.29	24.78	21.51	07.34
Pr	27.54	24.70	24.01	10.51	27.99	29.60	25.42	08.89
Cu	08.55	31.89	05.87	03.89	06.96	07.59	08.44	01.74
Ni	25.06	49.32	10.44	10.53	15.83	17.44	15.06	04.00
Ba	25.90	39.32	19.45	12.04	21.86	22.93	25.80	26.15
U	43.77	31.54	40.04	22.60	47.77	48.86	45.52	12.11

(c)	Contents (ppm)							
	Series A				Series B			
	PB	PF	PM	PG	PC	PD	RF	CF
V	66.45	110.38	40.84	33.56	49.92	50.00	48.25	21.53
Nd	117.33	104.86	102.22	44.60	119.37	125.41	108.10	37.98
La	124.59	105.52	108.27	48.59	127.20	132.46	117.93	39.29
Y	175.23	147.14	147.37	65.28	163.38	192.55	161.69	55.76
Ce	173.84	164.14	150.94	67.61	171.74	204.15	161.33	55.14
Zn	149.17	290.43	95.21	60.92	156.35	153.71	129.80	34.14
Cr	226.35	379.86	142.79	95.98	166.51	169.13	162.02	52.48
Sr	2258.41	1759.12	1812.34	1106.06	2347.20	2230.83	2449.10	605.96

5. Discussion

Taking into account characterization processes which show clearly differentiated mineralogical, granulometric, chemical and structural characteristics between the various samples, it is important to study their influences both on the identified trace elements and the granulometry.

In addition, in order to evaluate the performances of the treatment processing operations (granulometry, calcination, scrubbing and floatation) of each trace element, we carried out calculations of outputs or degrees of enrichment. These calculations are compared to the raw fraction (PB) content of each trace element. The results obtained (Table 2) show a strong influence for classes of particle-size (PF, PM and PG) as well as for the three applied treatment modes (PC, PD, CF and RF).

Table 2. Degree of enrichment or treatment outputs in trace elements of groups (a) 1, (b) 2 and (c) 3 of two series of the studied samples A and B.

(a)	Degree of enrichment (%)							
	Series A				Series B			
	PB	PF	PM	PG	PC	PD	RF	CF
Cs	---	28.57	37.41	80.00	48.57	14.28	82.85	---
Co	---	50.00	45.12	30.48	36.58	53.65	85.36	---
Lu	21.02	10.20	61.14	03.82	---	07.64	69.42	21.02
Tm	18.18	11.68	60.38	03.24	---	06.49	67.52	18.18
Sc	11.97	36.26	61.97	11.62	13.02	20.42	97.00	11.97
Rb	---	38.76	44.07	72.74	51.85	29.38	83.18	---
Ho	13.94	10.33	61.53	03.60	---	07.45	68.27	13.94
Tb	11.07	12.02	62.65	00.00	---	08.51	67.72	11.07
Eu	05.38	09.65	61.41	---	---	05.93	67.34	05.38
Yb	18.28	12.85	60.96	4.73	---	05.91	69.03	18.28

(b)	Degree of enrichment (%)							
	Series A				Series B			
	PB	PF	PM	PG	PC	PD	RF	CF
Er	13.24	09.32	61.06	00.00	---	05.66	67.24	13.24
Th	---	03.57	63.81	03.19	---	21.89	69.07	---
Pb	---	26.68	59.64	65.24	05.63	19.06	70.17	---
Dy	11.96	12.16	62.08	01.38	---	07.51	67.47	11.96
Sm	08.16	14.14	62.46	---	---	11.15	67.31	08.16
Gd	08.72	09.84	61.82	---	---	06.68	68.15	08.72
Pr	10.31	12.81	61.83	---	---	07.69	67.72	10.31
Cu	---	31.34	54.50	18.59	11.22	01.30	79.64	---
Ni	---	58.34	57.98	36.83	30.40	39.90	84.03	---
Ba	---	24.90	53.51	15.59	11.46	00.38	---	---
U	27.94	08.52	48.36	---	---	---	72.33	27.94

(c)	Degree of enrichment (%)							
	Series A				Series B			
	PB	PF	PM	PG	PC	PD	RF	CF
V	---	38.54	49.49	24.87	24.75	27.38	67.60	---
Nd	10.62	12.87	61.98	---	---	07.86	67.62	10.62
La	15.30	13.10	61.00	---	---	05.34	68.46	15.30
Y	16.03	15.90	62.74	06.75	---	07.72	68.17	16.03
Ce	05.57	13.17	61.10	01.20	---	07.19	68.28	05.57
Zn	---	36.17	59.16	---	---	12.98	77.11	---
Cr	---	36.91	57.59	26.43	25.28	28.42	76.81	---
Sr	22.10	19.75	51.02	---	01.22	---	73.16	22.10

Generally, the contents of these elements vary considerably according to the particle shape. In fact, except for erbium, thulium, ytterbium, lutecium and uranium, the concentration of the other elements is definitely marked in fine fractions (PF), rich in siliceous, dolomitic and argillaceous materials [23]. This distinction is particularly important for transition metals such as: vanadium, chromium, nickel, copper, zinc and lead which are associated with various mineral species of the gangue (clay, dolomite and silica). On the other hand, the average fraction (PM), rich in phosphates recorded relatively high contents for the following elements: strontium, lanthanum, ytterbium, lutecium, uranium, thulium and erbium, which are associated with the apatite network as mentioned previously. Strontium contents are high and vary according to classes of particle-size. The concentration of this element in the phosphate-rich fraction (PM) does not necessarily imply substitution of Ca^{2+} ions by Sr^{2+} in apatite, because of the ionic ray of Sr^{2+} (1.12 Å) which is higher than that of Ca^{2+} (0.99 Å), but much more with its surface adsorption on apatite crystals [1]. In addition, the degree of enrichment in trace elements varies considerably according to granulometric processes of separation (Table 2).

In fact, except for cesium, cobalt, rubidium and uranium, the coarse fraction (PG) recorded important enrichment outputs (>50%) for all the identified trace elements. This shows that the enrichment of these elements for such a phosphate ore type, can be correctly carried out by simple granulometric techniques of separation. Conversely, the fine fraction (PF) which recorded strong chemical contents gave very poor enrichment outputs for the major part of the trace elements (15% on average). For others, in particular transition metals such as cesium, cobalt, rubidium, thorium, lead, copper, nickel, barium, vanadium chromium and zinc, the enrichment outputs are almost worthless. This makes it possible to direct the treatment of such elements towards types of processes other than granulometry. In the case of average particle shape (PM), except for cobalt and nickel, the recorded outputs are weak (<50%) and variable from one element to another. This was to be expected, owing to the fact that particle shape PM is rich in phosphates and as trace elements are well expressed in the apatitic structure as well as in the endogangue and their enrichment remains complex.

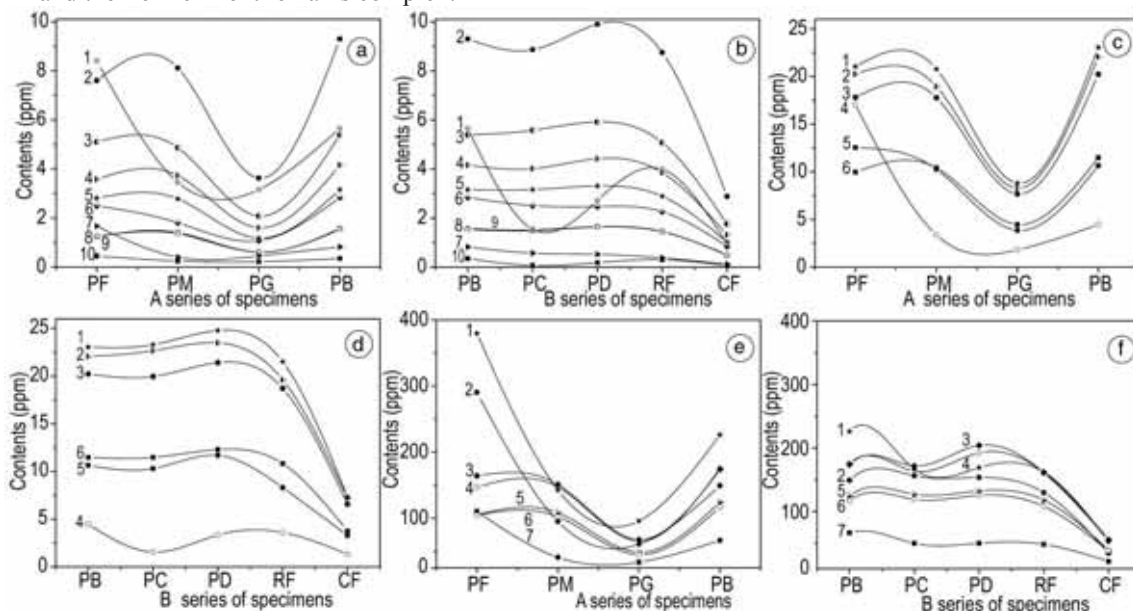


Fig. 6. Contents of trace elements of groups 1,2,3 for series of the samples (a,c,e) A and (b,d,f) B: [1: Rb; 2: Yb; 3: Eu; 4: Ho; 5: Tb; 6: Sc; 7: Co; 8: Tm; 9: Lu; 10: Cs], [1:Gd; 2: Sm; 3:Dy; 4: Pb; 5: Th; 6: Er] and [1: Cr; 2: Zn; 3: Ce; 4: Y; 5: La; 6:Nd; 7: V] respectively.

Taking into account these results, it clearly appears that the various modes of treatment we considered greatly influence the chemical contents of the trace elements identified, in particular the treatment by floatation (CF). In fact, except for barium, the near total of trace elements targeted saw their contents considerably decreasing for such a treatment. For treatments by calcination (PC) and scrubbing (PD), the chemical contents remain practically constant, and slightly vary from one element to another, in particular for the elements: zinc, strontium, lanthanum, praseodymium, neodymium, samarium, europium and gadolinium. In the case of sample rejection of floatation, the chemical contents recorded vary from one element to another, because of the diversity of mineral species constituting the gangue. *Table 2* clearly illustrates the enrichment outputs following the three processes of enrichment used (scrubbing, calcination and floatation) for all identified trace elements. According to these results, it clearly appears that the degree of enrichment in trace elements varies considerably according to the type of process. In fact, except for barium where no effect was noticed, outputs of the floatation process are highest for all the targeted elements. Metals such as: cesium, cobalt, rubidium, scandium and nickel recorded the highest outputs (>80%) for the concentrated sample of floatation (CF). This can be explained knowing that these elements could not float with carbonates, either because of their weight, or because of the type of reagent of floatation used as collector of carbonates or depressant of phosphates [24]. Uranium is known by its affinity with apatitic structure due to favorable substitution, its output is therefore much more important in the concentrated sample of floatation (CF). In the case of scrubbing process, enrichment outputs are very weak and sometimes even non-existent. This is related to the lack in the sample of fine particles rich in clays, silicas and dolomites, associated with a significant number of trace elements [23].

Enrichment outputs by calcination (PC), except for some cases (cesium, rubidium and lead), hardly exceeding 30%, remain insufficient. Trace elements of the class of Lanthanides (lanthanum, praseodymium, neodymium, samarium, europium and gadolinium) as well as uranium, zinc and strontium were not completely affected by this process because of their association or melting point to the endogangue, and thus remain difficult to extract by this process. Former geochemical studies [7,8] bearing on the association of chemical elements with phosphatic mineral phases (apatites, carbonates, silicates,...) showed that the network of apatites allows many substitutions, in particular for calcium. Thus, bivalent cations Ca^{2+} can be replaced by other bivalent cations such as Pb^{2+} , Sr^{2+} , Ba^{2+} , Zn^{2+} ..., or by monovalent Na^+ , K^+ , Li^+ ..., and trivalent cations La^{3+} , Eu^{3+} , Ga^{3+} , Al^{3+} ... [12,13]. Ion PO_4^{3-} can also be substituted by bivalent anion groupings CrO_4^{2-} , CO_3^{2-} , SO_4^{2-} , HPO_4^{2-} ... [14,25], trivalent VO_4^{3-} , AsO_4^{3-} , MnO_4^{3-} , and tetravalent SiO_4^{4-} , GeO_4^{4-} ... [26]. Finally, anions OH^- can be substituted by monovalent ions or anion groupings F^- , Cl^- , I^- , Br^- ..., bivalent CO_3^{2-} , O^{2-} , S^{2-} ... The substitution of the Ca^{2+} , PO_4^{3-} and OH^- ions by identical ions of valences can be total, except for ions Mn^{2+} and Mg^{2+} , whereas the incorporation of ions of different valences is limited and requires a compensation of loads in order to preserve the electroneutrality of the structure [12]. Various probable substitutions are related to usual rules of the diadochie: neighbor neighbour ionic rays, the safeguarding of electric neutrality, etc... For example Ca^{2+} (atomic ray 0.99 Å) is replaced more easily by Mg^{2+} (0.66 Å), Mn^{2+} (0.80 Å), Na^+ (0.97 Å), than by larger ions such as Sr^{2+} (1.12 Å), Ba^{2+} (1.32 Å) or K^+ (1.33 Å). Substitution of uranium in the apatitic structure is very probable because of very close ionic rays of ions Ca^{2+} and U^{4+} (0.97 Å).

Careful examination of all these data enabled us to confirm the substitution of elements: strontium, lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, dysprosium, erbium, copper, lead and uranium with apatite calcium [8,9]. Thus, all the trace elements identified in the phosphate ore we studied can be distributed into two main families:

- (i) family of apatite the apatite family: for strontium, chromium, barium, yttrium, uranium, thorium, as well as rare earths (lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, thulium, ytterbium, holmium, erbium and lutecium).
- (ii) family of silicates the silicate family: for strontium, nickel, zinc, copper, barium, chromium, cesium, lead, rubidium, scandium and vanadium.

It should be noted that the presence of rare earths (lanthanum, cerium, praseodyme, neodyme, samarium, europium, gadolinium, terbium, dysprosium, thulium, ytterbium, holmium, erbium and lutecium) in phosphates is related to their facility to enter the structure of apatites, where they replace calcium, sodium and strontium [27].

6. Conclusions

The characterization work carried out on Kef Es Sennoun raw phosphate allowed us to (i) define the optimal meshes for the release of the phosphated elements, (ii) identify minerals of the apatite and of the gangue, (iii) follow the evolution of the chemical composition of major and trace elements according to the size of grains, (iv) study the thermal behaviour and finally (v) evaluate specific surface according to various mineralurgic modes of treatment. The chemical analyses carried out on the raw ore highlighted the presence of two groups of quite distinct elements by their intensities: major elements (phosphorus, calcium, magnesium and silicon) and trace elements primarily made up of rare earths (lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, thulium, ytterbium, holmium, erbium and lutecium) and of transition metals (vanadium, chromium, cobalt, copper, nickel, zinc,...). These elements are distributed between several mineralogical phases, in particular apatite (calcium, phosphore, strontium, sodium, chrome, baryum) and silicates (aluminum, silicium, molybdene, strontium, sodium, nickel, zinc and copper). Generally, the concentration of trace elements considerably influences the various particle shapes (fine, average and coarse) and the modes of treatment used (calcination, washing and floatation). For granulometry, except for erbium, thulium, ytterbium, lutecium and uranium, the concentration of other elements is definitely marked in the fine fractions (PF), rich in siliceous, dolomitic and argillaceous matters. Among the modes of treatment suggested, nearly all the trace elements studied are enriched by the process of floatation (CF). The scrubbing process did not bring great changes in the treatment, because of its small proportion of fine particles, rich in clays, silicas and dolomites, associated to a significant number of trace elements.

The performances of the suggested enrichment processes are evaluated through the calculations of outputs or degree degrees of enrichment. They confirmed that the floatation process is the most adapted with very satisfactory outputs for most identified trace elements. Taking into account these results, the exploitation company of this material should define the most adequate enrichment plan, specific to each trace element and for each shape of particle: raw, fine, average and coarse. Thus, the floatation process could enter a phase of industrial development, making it possible to better develop this kind of material whose reserves are considerable and contribute particularly to environmental protection by certain trace elements considered to be toxic at the limiting contents.

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References

- [1] Bezzi N, Aïfa T, Merabet D, Pivan JY. Magnetic properties of the Bled El Hadba phosphate-bearing formation (Djebel Onk, Algeria): Consequences of the enrichment of the phosphate ore deposit. *J Afr Earth Sci* 2008;**50(2-4)**:255-267.
- [2] Devallois BV. Transferts et mobilités des éléments traces métalliques dans la colonne sédimentaire des hydrosystèmes continentaux. *PhD Thesis, University of Provence Aix-Marseille* 2009;277p.

- [3] Bech J, Suarez M, Reverter F, Tume P, Sanchez P, Lansac A. Selenium and other trace elements in phosphate rock of Bayovar-Sechura (Peru). *J Geochem Explor* 2010;**107**:136-145.
- [4] Chen A, Zhao Y, Qiang L, Qiao J, Tian Q, Liu X, 2009, Heavy metal contents and chemical speciations in swage-irrigated soils from the eastern suburb of Beijing (China). *J Food Agric Env* 2004;**7(2)**:690-695.
- [5] Maanan M, Zourarah B, Carruesco C, Aajjane A, Naud J. The distribution of heavy metals in the Sidi Moussa lagoon sediments (Atlantic Moroccan Coast). *J Afr Earth Sci* 2004;**39(3-5)**:473-483.
- [6] Sigg L, Behra P, Stumm W. Chimie des milieux aquatiques: chimie des eaux naturelles et des interfaces dans l'environnement. *Dunod Ed., Paris* 2001;567p.
- [7] Gulbrandsen RA. Chemical composition of phosphorites of the Phosphoria Formation. *Geochim Cosmochim Acta* 1966;**30(8)**:769-778.
- [8] McClellan GH, Lehr JR. Crystal-chemical investigation of natural apatites. *Am Mineral* 1969;**54(9-10)**:1374-1391.
- [9] Wang WZ, Brusseau ML, Artiola JF. The use of calcium to facilitate desorption and removal of cadmium and nickel in subsurface soils. *J Contam Hydrol* 1997;**25(3-4)**:325-336.
- [10] Masayuki O, 2006, Review specific physicochemical properties of apatite and their application to biomaterials. *Phosphor Res Bull*; **20**:25-32.
- [11] Shigeru S. Approach using apatite to studies on energy and environment. *Phosphor Res Bull* 2007;**21**:1-8.
- [12] Legeros RZ, Taheri MH, Quirolgico GB, Legeros JP. Formation and stability of apatite: effects of some cationic substituents. In: *Proceedings, 2nd International Congress on Phosphorus Compounds*, Boston (MA) 1980;89-103.
- [13] Panda A, Sahu B. Preparation and lattice constant measurement of (Ca + Cd + Pb) hydroxyapatites. *J Mater Sci Lett* 1991;**10**:638-639.
- [14] Marchat D. Fixation du cadmium par une hydroxyapatite phosphocalcique. Etude cinétique et Thermodynamique. *PhD Thesis, University of Limoges, France* 2005;206p.
- [15] Bouhaouss A, Bensaoud A, Laghzizil A, Ferhat M. Effect of chemical treatments on the ionic conductivity of carbonate apatite. *J Inorg Mater* 2001;**3(6)**:437-441.
- [16] Raynaud S, Champion E, Bernache-Assollant D, Thomas P. Calcium phosphate apatites with variable Ca/P atomic ratio I. Synthesis, characterisation and thermal stability of powders. *Biomater* 2002;**23**:1065-1072.
- [17] Landi E, Tampieri A, Celotti G, Vichi L, Sandri M. Influence of synthesis and sintering parameters on the characteristics of carbonate apatite. *Biomater* 2004;**25(10)**:1763-1770.
- [18] Isil A, Imamoglu S, Aydin F, Saydut A, Hamamci C. Determination of mineral phosphate species in sedimentary phosphate rock in Mardin, SE Anatolia, Turkey by sequential extraction. *Microchem J* 2009;**91(1)**:63-69.
- [19] EREM. Travaux de prospection et d'évaluation des phosphates de Djebel Onk, 2 tomes: géologie, 50p.; prospection et évaluation. *Report*, 1987;53p.
- [20] Bezzi N, Merabet D, Benabdeslam N, Arkoub H. Caractérisation physico-chimique du minerai de phosphate de Bled El Hadba - Tébessa. *Ann Chim Sci Mat* 2001;**26(6)**:5-23.
- [21] Bezzi N, Merabet D, Benabdeslam N, Pivan, JY. Enrichissement du minerai de phosphate à gangue carbonatée du gisement de Bled El Hadba-Algérie. *Les Techniques de l'Industrie Minérale* 2004;**23**:85-99.
- [22] Hamdadou M. Caractérisation pétro-minéralogique et séquentielle du gisement de phosphate de Djebel Onk (Algérie). *PhD Thesis, Ecole Nationale Supérieure de Géologie de Nancy, France*, 1996;299p.
- [23] Merabet D, Benabdeslam N, Bezzi N, Ikhlef T, Arkoub H. Influence de la composition chimique et minéralogique du phosphate noir du gisement de Djebel Onk (Tébessa) sur le procédé de traitement. *Ann Chim Sci Mat* 2004; **29(5)**:69-85.
- [24] Bezzi N, Merabet D, Pivan JY, Benabdeslam N, Arkoub H. Valorisation et enrichissement par flottation du minerai de phosphate du gisement de Bled El Hadba (Algérie). *Ann Chim Sci Mat* 2005;**30(2)**:171-186.
- [25] Chabou MS. Etude de la série phosphatée tertiaire du Djebel Onk (Algérie). Stratigraphie, pétrographie, minéralogie et géochimie. *PhD Thesis, University of Aix-Marseille III, France*, 1987;272p.
- [26] Audubert F, Carpena J, Lacout L, Tetard F. Elaboration of aniodine-bearing apatite iodine diffusion into a $Pb_3(VO_4)_2$ matrix. *Solid State Ionics* 1997;**95**:113-119.
- [27] Bonnot C. Le comportement des terres rares au cours de l'altération sous-marine et ses conséquences. *Chem Geol* 1980;**30**:119-131.
- [28] McConnel D. The cristal chemistry of apatite. *Bull. Soc. Française Minéral. Cristal.* 1974;**97**,240p.