Heavy elements in the phosphorite from Kalaat Khasba mine (North-western Tunisia): Potential implications on the environment and human health

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ABSTRACT

Tunisia is one of the largest phosphate producers in the world (more than 10 million tons per year since the early nineties). The Kalaat Khasba mine (NW of Tunisia) has operated from 1893 until 1993 and data demonstrate that, in the phosphorites of Kalaat Khasba, Cd is enriched 105–208 times, when compared with shales, and U is enriched by a factor varying between 18 and 44. The general trend shows an increase in heavy elements content with decreasing particle size. On the other hand, concentrations of Sr, Cr and U exhibit the same distribution for the different size fractions. It was found that Cd concentrations exceed the allowed EC soil limits for growing crops. Hence, owing to the tailings exposure and to the mobilisation of the finest particles by rainfall and wind, Cd could have detrimental effects on human health and on the environment because a significant portion of Cd was found in the exchangeable form.

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1. Introduction

Phosphate rock (PR) is a general term that describes naturally occurring mineral assemblages containing high concentrations of phosphate minerals, which can be commercially exploited, either directly or after processing [1,2]. Phosphate rocks are widely used as raw materials for fertilizer production (80%), either in bulk, or after processing. These rocks can be effective crop P (phosphorus) sources for acidic soils [3]. As a minor constituent, phosphate is added to many dairy products, that is, detergents (12%), animal food supplements (5%) and other minor uses, such as, soft drinks, toothpastes, light bulbs, vitamins, flame-resistant fabrics, optical glass, safety match heads, cosmetics, shaving cream (3%) [4].

In general, the commercial-grade phosphate deposits contain more than 20% of P_2O_5, and is composed of Ca-phosphate minerals of the apatite group, such as hydroxylfluorapatite [$Ca_5(PO_4)_3(OH,F)$], carbonate fluorapatite [$Ca_5(PO_4,CO_3)_3(F,OH)$], also called francolite, and a low crystalline to cryptocrystalline variety of francolite called collophane. Both minerals occur as nodules or layers hosted in a calcareous or siliceous groundmass, commonly exhibiting greenish, brownish, yellowish or whitish colour. Francolite, with high carbonate (CO_3^{2-}) for phosphate (PO_4^{3+}) isomorphous substitution, is the highest reactive phosphate mineral and therefore the most suitable for direct application as fertilizer or soil amendment [5]. Other phosphates containing Fe, Mn and/or Al are seldom found in sedimentary basins [6,7]. The most common Fe- and Fe/Ca phosphates of such occurrences are: vivianite ($Fe^{2+})_3(PO_4)_2·8H_2O$, anapaite $Ca_2Fe^{2+}(PO_4)_2·4H_2O$, and mitridatite $Ca_2(Fe^{3+})_3(PO_4)_3O_2·3H_2O$. Pure fluorapatite contains 42% P_2O_5, and francolite, can contain up to 34% P_2O_5 and is more soluble in acids.

The reactivity of sedimentary PR is higher than that for igneous and metamorphic PR. The fundamental difference lies in the crystal chemistry of apatite, specifically the degree of isomorphous substitution of the phosphate anion by the carbonate anion. It has been demonstrated that the solubility of CO_3^{-2} bearing phosphate rock is higher than the solubility of pure fluorapatite having little or no carbonate substitution [8]. As carbonate substitution increases in phosphate rocks, the breakdown of the apatite structure is easier and thus P is released into the soil solution under acidic conditions. Therefore, the chemical and mineralogical features of PR are key factors in determining the reactivity and subsequent agronomic effectiveness of a certain PR.

The use of PRs may cause environmental hazards because they can contain potentially toxic elements, such as U, Th, REE (rare earth elements), Cd, As, Sb, V, Cr, Zn, Cu, Ni, etc. [9–11], depending on the

type and origin of the PR. The "defective" lattice of the carbonate fluorapatite (CFA) favors the incorporation of various trace elements in its structure [12], although adsorption phenomena onto mineral surfaces [13] can be also involved in this enrichment. Their study is important to clarify the general relationships in the behavior of elements in sedimentary rocks as well as for the agrochemical use of phosphorites because some trace elements in phosphorites are microfertilizers whereas others, such as U, are hazardous to the environment [14].

The presence of these metals, both in crops and in plants, depends largely on the soil chemistry and on the chemical form or speciation of the metal. Acidic environments generally increase the availability of all the metals present in soils and, on the other hand, the type of crop also influences the transfer factor of specific elements to the plants. For instance, Cd has the highest transfer factor for any plant and, therefore, is the most studied toxic element in fertilizers and soils [15].

Phosphate rocks of commercial-grade have been exploited in several countries in Middle East and in North Africa. Morocco is the major phosphate producer, whereas Jordan, Egypt, Tunisia, Algeria and Israel also play an important role in the world phosphates market.

In Tunisia, phosphorite deposits occur in several areas, such as the North-South Axis (Nosa) and in the Gafsa-Metlaoui region. Gafsa basin is one of the most geologically investigated areas in southern Tunisia. Previous studies carried out in the Gafsa-Metlaoui phosphate deposits, the most important phosphatic area in Tunisia, allowed the identification of sedimentological facies, depositional environment, diagenetic aspects [16], and geochemical characterization [17–21] of the region. The Kalaat Khasba deposit is the continuation of the Djebel Kouif deposit, in Algeria.

The Kalaat Khasba mine is located in a phosphate rich deposit which occurs in Paleocene/Eocene deposits from El-Kef region, 200 km to the West of Tunis near the Algeria border [22]. It is connected with the port of La Goulette, Tunis, by a metre-gauge railway (Fig. 1).

The ore grade is generally lower than that in the Gafsa region, and varies from 25 to 29% P_2O_5. The Eocene phosphate deposits outcrop to the North and to the South of Kalaat Khasba but, to the East, plunge beneath younger sediments. The phosphate bed is 4 m thick, but only the upper 3 m have been exploited currently. The rock is extremely hard and mining works require less mechanical support than in the case of the Gafsa mines.

The Kalaat Khasba mine has been operating since 1893 but due to the complete exhaustion of the reserves the Phosphate Company of Gafsa (CPG) stopped underground mining in 1993.

The main goals of this study are: (a) to carry out the geochemical and mineralogical characterization of the Kalaat Khasba (KK) phosphorites from mining tailings to investigate their polluting capability; (b) to compare the heavy elements concentrations in the KK samples and the concentrations of the same elements in other phosphate deposits occurring elsewhere; (c) to study the heavy elements partitioning in the different grain size fractions in order to obtain more information on the effect of particle size and heavy metal distribution in KK phosphorites, and (d) to assess the potential mobility and transportation of trace elements in natural environments.

This study should lead to a better understanding of the distribution of the potentially toxic elements in the KK phosphorites, the path by which these elements mobilize and become bioavailable and, finally, evaluate their impact to the environment and human health.

2. Experimental work

2.1. Sample collection, preparation and size fractioning

Four composite samples of phosphorites (KK1, KK2, KK3 and KK4) were collected from different tailing deposits located in the Kalaat Khasba area. Each composite sample consisted of a mixture of sub-samples taken from depths ranging from 0 cm to 10 cm in a 5 m × 5 m area. Samples were packed and sealed in polyethylene
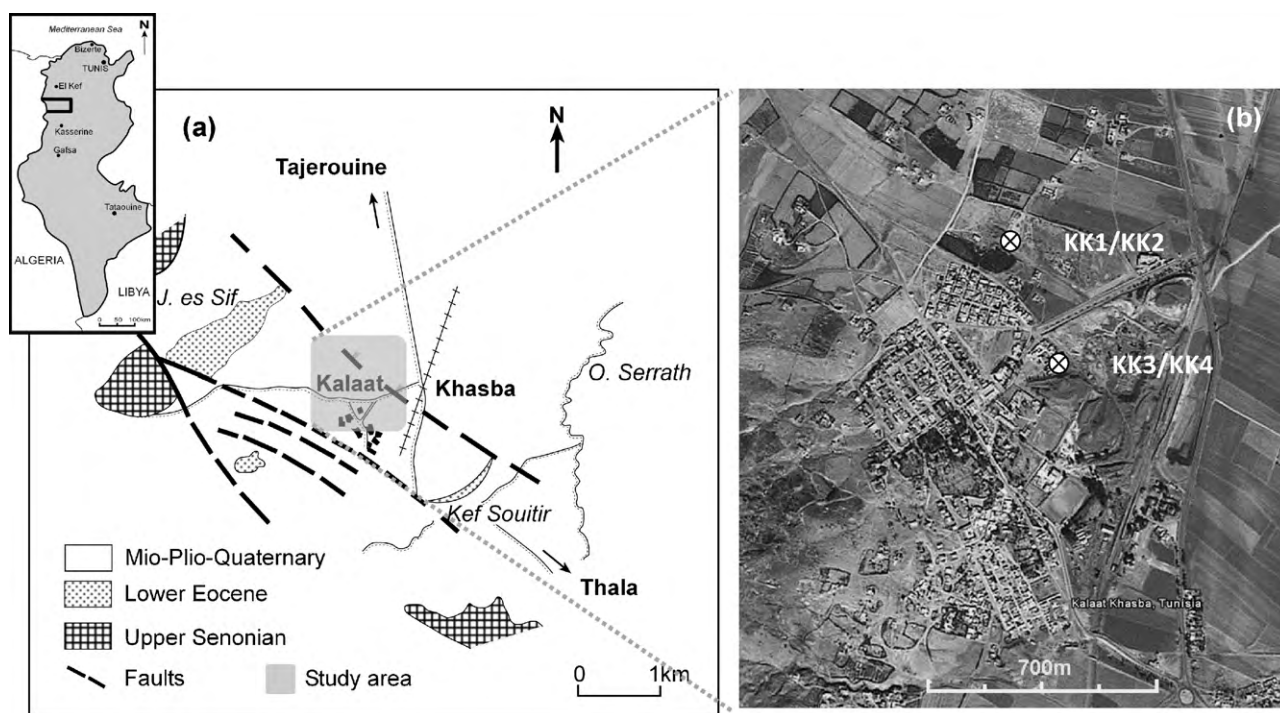
Fig. 1. (a) Geographic location of the studied area of Kalaat Khasba and local geological formations (adapted from [21]): Mio-Plio-Quaternary: alluvial sediments; lower Eocene - Métlaoui formation (bioclastic dolomite and limestone with some intercalations of clays and phosphorite layers); upper Senonian - Abiod formation (chalky limestones) and (b) image from Google Earth showing the location of the sampling points (⊗).

bags, transferred to the laboratory and then dried, at room temperature, for approximately 1 week. To determine the relationship between particle size and metals concentration the samples were dry-sieved using an electronically controlled electromagnetic sieve shaker. The different size fractions were identified as: >5000 μm; 2000–5000 μm; 1000–2000 μm; and <1000 μm. For all cases, the sieves were cleaned thoroughly, using distilled water, to allow the mesh to regain the correct pore size [23]. After homogenization aliquots of 30–50 g from each sample were milled to obtain fine powder using a mechanical agate mill.

2.2. Chemical analysis

All geochemical analysis (total sample and the different grain size fractions) were run at the ACME Anal. ISO 9002 Accredited Lab in Vancouver, Canada.

Total abundances of the major elements (in the form of oxides) are calculated from a 0.2 g aliquot sample analysed by inductively coupled plasma-atomic emission spectrometry (ICP-AES) following a lithium metaborate/tetraborate fusion and dilute nitric digestion (ACME, see http://acmelab.com). The detection limits for major elements were 0.01% for all elements except for Fe_2O_3 (in this case 0.04%). For the REE and trace elements analysis a 0.25 g aliquot of each powdered sample was heated in $HClO_4$–HNO_3–HCl–HF to fuming and taken to dryness (ACME, see http://acmelab.com) and the aliquot sample analysed by Inductively Coupled Plasma-Atomic Mass Spectrometry (ICP-MS). The detection limits for trace elements were as follows: 0.1 mg kg^{-1} for Cd, Cu, Ni, Pb, and U; 0.2 mg kg^{-1} for Co; 0.5 mg kg^{-1} for As and Sr; 1 mg kg^{-1} for Zn; 20 mg kg^{-1} for Cr, and Mn. The detection limits for REE elements were as follows: 0.01 mg kg^{-1} for Eu, Pr, Ho, Tb, Tm, and Lu; 0.03 mg kg^{-1} for Er; 0.05 mg kg^{-1} for Sm, Gd, Dy, and Yb; 0.1 mg kg^{-1} for La, and Ce; and 0.3 mg kg^{-1} for Nd. The LOI (loss on ignition) value, that is the weight loss determined after firing at 1100 °C over 1 h, corresponds to the evolution from the studied sample of all gaseous compounds being formed along the heating process, from both organic matter combustion and thermal decomposition of certain minerals. Sulphur (present in some phosphorite samples, such as KK3, under the form of gypsum) has not been analysed. The results of chemical analyses are shown in Table 1.

2.3. Chemical fractioning

The selective chemical sequential extraction (SCSE) technique was used to investigate the mode of occurrence of the metals in the selected samples and to establish the geochemical patterns of trace metals, which are useful for predicting their mobility into the environment, Samples KK1, KK2, KK3 and KK4 were treated sequentially with different reagents so that metals with different affinities for the mineral matrix could be liberated. 1 g of the homogenized samples was used to carry out sequential extractions.

The used procedure has followed the 6-step sequential extraction technique developed at the Geosciences Department of the University of Aveiro [24]. According to the authors, the following extractants and operationally defined chemical extraction steps were taken: Step 1: ammonium acetate (1 M NH$_4$Ac, pH 4.5) for water soluble and dissolved exchangeable ions, specifically adsorbed and some carbonates (exchangeable); Step 2: hydroxylamine hydrochloride (0.1 M NH$_4$OH·HCl, pH 2) for ions bound to Mn oxyhydroxides; Step 3: ammonium oxalate (dark) (0.175 M (NH$_4$)$_2$C$_2$O$_4$–0.1 M H$_2$C$_2$O$_4$, pH 3.3 – Tamm reagent in dark) for ions linked to amorphous Fe oxides; Step 4: H$_2$O$_2$ 35% for ions associated to organic matter (in this step sulphide-bound as primary sulphide minerals could not be totally leached out [25]); Step 5:

Table 1
Major (wt.%) and trace elements (mg kg^{-1}) contents in KK phosphorite.

	KK1	KK2	KK3	KK4
SiO$_2$	24.95	6.41	4.97	6.28
Al$_2$O$_3$	2.87	0.79	0.66	0.76
Fe$_2$O$_3$	0.78	0.41	0.37	0.38
MgO	2.21	2.18	0.84	2.19
CaO	35.46	47.44	49.00	46.78
Na$_2$O	0.80	1.06	1.19	1.06
K$_2$O	0.48	0.14	0.10	0.14
TiO$_2$	0.14	0.07	0.05	0.06
P$_2$O$_5$	22.06	30.23	32.78	30.32
LOI	9.8	10.8	9.5	11.6
As	11	11	11	11
Cd	48.8	44.9	62.5	45.0
Co	0.5	b.d.l.	b.d.l.	0.2
Cr	390	430	490	400
Cu	12	25	35	23
Mn	57	61	63	24
Mo	13.1	14.5	14.9	13.9
Ni	37	51	83	49
Pb	3	2	3	2
Sr	1385	1556	1903	1582
U	53.8	112.8	133.4	112.8
Zn	209	211	276	208
La	136.0	161.3	185.6	156.0
Ce	146.2	84.1	91.3	84.7
Pr	28.95	27.14	31.12	26.61
Nd	120.9	113.1	132.3	116.6
Sm	23.16	22.29	25.82	21.60
Eu	6.14	6.05	6.91	5.95
Gd	26.73	29.65	35.75	29.46
Tb	4.21	4.69	5.52	4.59
Dy	24.24	28.61	34.44	28.64
Ho	5.33	6.95	8.20	6.76
Er	16.03	21.46	25.66	21.56
Tm	2.16	3.05	3.59	3.02
Yb	13.10	18.87	22.33	18.32
Lu	2.06	3.17	3.73	3.11
LREE	455.21	407.93	466.14	405.51
HREE	100.00	122.50	146.13	121.41
TREE	555.21	530.43	612.27	526.92
Ratio	4.55	3.33	3.19	3.34

Abbreviations: b.d.l. (below detection limit: Co–0.2 mg kg^{-1}); light REE (LREE: La to Sm); heavy REE (HREE: Eu to Lu); TREE = sum of total concentration of rare earth elements; ratio = ΣLREE/ΣHREE.

ammonium oxalate (UV) (0.175 M (NH$_4$)$_2$C$_2$O$_4$–0.1 M H$_2$C$_2$O$_4$, pH 3.3 – Tamm reagent under UV radiation for ions associated to crystalline Fe oxides; Step 6: mixed acids (HCl + HNO$_3$ + HF) digestion for ions associated to matrix elements in lattice positions, resistant oxides and some sulphides.

The elements Ca, Cd, Cr, Cu, Mg, Mn, Ni, Pb and Zn were analyzed using an Atomic Absorption Spectrometer GBC906 model (AAS). The concentrations of PO$_4$-P, in filtered samples, were measured using a Shimadzu 2000 UV/VIS spectrophotometer after samples treatment using the molybdenum blue method [26]. P was expressed as % phosphorus pentoxide (P$_2$O$_5$). Arsenic, Mo and U were not analyzed as the chemical fractioning protocol was not implemented for these three elements.

2.4. Petrography and mineralogical analysis

Thin sections of the phosphorite samples were analysed using an optical polarizing microscope. The selected samples were characterized by X-ray powder diffraction (XRD) using a Philips PW1130/90 and X'Pert PW3040/60 equipment and CuKα radiation (λ = 1.54056 Å). The instrumental conditions adopted were as follows: voltage 40 kV; current 30 mA; slit 0.5 mm. Scans were run between 2° and 60° 2θ. Qualitative and semi-quantitative mineralogical analyses were carried out based on the criteria recommended by several authors [27–29]. For comparative purposes

only and bearing in mind the inherent difficulties, an attempt to semi-quantify the identified principal minerals, such as apatite, calcite, quartz, and feldspar was carried out based on the heights of their specific diffraction maxima, and on information provided by both chemical analyses (for instance, P_2O_5, CaO/P_2O_5, and MgO contents) and microscopic examination of thin sections (for instance, number of quartz and feldspar grains). Furthermore, the height of the diffraction maximum corresponding to 4.45 Å was used to estimate the relative content of phyllosilicates, clay minerals inclusive. As it can be seen in Table 1, sample KK3 shows the highest content in phosphate minerals and gypsum (Fig. 3b); sample KK1 has the highest content in quartz and calcite (Fig. 3a); samples KK2 and KK4 provided diffraction patterns similar to the one corresponding to sample KK1. For a better identification of detrital minerals existing in sample KK1, their concentration was increased through the dissolution of calcite with glacial acetic acid and hydrochloric acid (Fig. 3c). For a better identification of the clay minerals present in sample KK3, this has been finely ground, and oriented aggregates (O.A.) were prepared with the fine grained residue (undetermined particle size range) obtained from the partial dissolution of carbonate fluorapatite and calcite using 1 M HCl attack at room temperature for 3 h. The aim of this acid activation was to increase clay minerals concentration without affecting much their crystallochemistry.

2.5. WDS in electron probe and EDS analyses in scanning electron microscopy

From each collected rock sample, 2–3 pieces were separated, sawed and polished to carry out WDS and EDS analysis. The sulphides disseminated inside the phosphates have very small size (<10 μm) implying bad polishing of these and not permitting good conditions of analysis. The quantitative mineral analysis by wavelength-dispersive spectrometry (WDS) was done with a JEOL JXA 8500F Electron Probe Microanalyser (EPMA) at the LNEG Laboratory, in S. Mamede de Infesta, and the EDS analysis with a FEG-SEM Hitachi S4100 equipped with Rontes EDS System at the Electronic Microscopy Laboratory of the University of Aveiro.

The JEOL JXA 8500 F microprobe was operated at 20 kV accelerating voltage, 20 nA beam current and 1 μm beam size. The standards used for Ca, Zn, As, Fe and Mn WDS analysis were CdS, ZnS, AsGa, FeS_2 and $MnTiO_3$, respectively. The map analysis (300 × 300 points) was produced with the JEOL JXA 8500 F microprobe (20 kV accelerating voltage, 30 nA beam current, 1 μm beam size and 250 μs level time).

The Hitachi S-4100 was operated at 25 kV accelerating voltage, 20 nA beam current and 1 μm beam size.

2.6. Quality assurance

The accuracy and analytical precision of the ICP-MS and ICP-AES methods were verified against standard reference materials (standard SO17/CSB for major elements and REE, DS4 and DS5 standards for trace metals) and duplicate samples for each analytical set. The obtained analytical values were within the 95% confidence limits of the recommended values for this certified material. Overall analytical precision was ±3% for the analyzed heavy elements and REE.

The overall accuracy of the selective sequential extraction was estimated comparing the sums of the metal concentrations, for each geochemical phase of the selected samples, with the total concentration obtained after the hot mixed-acid digestion ($HCl + HNO_3 + HF$) of the same sample. The results obtained show that the differences between the total content of sediment and the sums of the individual phase concentrations do not exceed 20%.

3. Results

3.1. Petrographic and mineralogical characterization of the KK samples

In Tunisia, the phosphorites formed during the Paleocene/Eocene were found to be composed of apatite, calcite, dolomite, clay minerals (illite, smectite, sepiolite and kaolinite), quartz, opal-CT, and gypsum (occasionally) [17,30]. The KK phosphorite samples show a brownish to yellowish colour. The limestone/phosphate succession is of marine chemical origin. From the observation of the thin and polished sections in the optical microscope, equipped with both transmitted and reflected-light, it was possible to identify the presence of different phosphatic particles which could be divided into two categories depending on their origin: (a) collophane represented by pellets (rounded or sub-rounded (Pe) – see Fig. 2a and c), coprolites (faecal peloids, sub-rounded to pressed elliptic, showing a colour ranging from brownish white to brown and to almost black, depending on the organic matter content) and phosphatised fossils; (b) biogenic phosphate corresponding to well-preserved triangle-shaped teeth derived from sharks, such as Carcharodon sp. (Fig. 2a and b), and some skeletal fragments corresponding to small bones (OF) (Fig. 2c and d). In some un-phosphatized irregular limestone fragments, optical microscopy analysis has revealed small and greenish grains which were attributed to glauconite (Glau – see Fig. 2e and f).

Bulk mineralogy has been estimated from X-ray diffraction analysis carried out on KK1 to KK4 samples and from observation under SEM-EDS. XRD (Fig. 3) and SEM-EDS (Fig. 4 and Table 2) results revealed that the main mineralogical constituents are collophane (a low crystalline carbonate fluorapatite, and its microcrystalline fibrous variety, francolite), calcite (Cal), and gypsum (G). Detrital quartz (Qz), feldspar (F) and dolomite were identified as well. Clay minerals identified in KK samples include kaolinite (Fig. 4) and smectite, and the content of the last mineral being apparently higher in sample KK3. It must be added that there was some uncertainty in kaolinite and smectite identification, since it was only based on the peak (0 0 1) diffraction maxima of the clay minerals corresponding to ~7 Å and ~14 Å, respectively, shown on diffraction patterns of non-oriented powder samples. However, in the case of kaolinite the identification could be confirmed from information provided by the XRD pattern of oriented aggregate (O.A.) heated at 550 °C (disappearance of the reflexion ~7 Å), and on SEM-EDS information (Fig. 4). In the case of smectite the identification could be confirmed from information provided by XRD patterns of oriented aggregates (O.A.) obtained after glycerol-solvated (expansion of the 14 Å reflexion to ~17 Å), and after heating at 300 °C (collapse of the 14 Å reflection to 10 Å). Zeolites of the clinoptilolite–heulandite series were occasionally found in the studied samples (Fig. 4b).

3.2. Particle size fractionation and chemical characterization of the KK samples

Arsenic, Co, Cr, Cu, Mo, Mn, Ni, Pb, Sr, U and Zn distribution concentrations within the distinctive particle size fractions, together with the grain size values determined for the KK samples collected at four sampling sites are shown in Table 3.

The obtained results show that the dominant fraction in all the studied KK samples is the <1000 μm, accounting for about 77.5–87.2% of the total sample. Beji Sassi and Sassi [20] have proved that, in size fractioned phosphorite samples, Cd shows significantly higher concentrations in the fractions whose particle sizes range between 70 μm and 2 mm. In this work these fractions also showed higher P_2O_5 contents. This observation suggests that the finest particles could have been removed by rain and wind to long distances, and could be stocked in the sediment. Hence they could be bounded
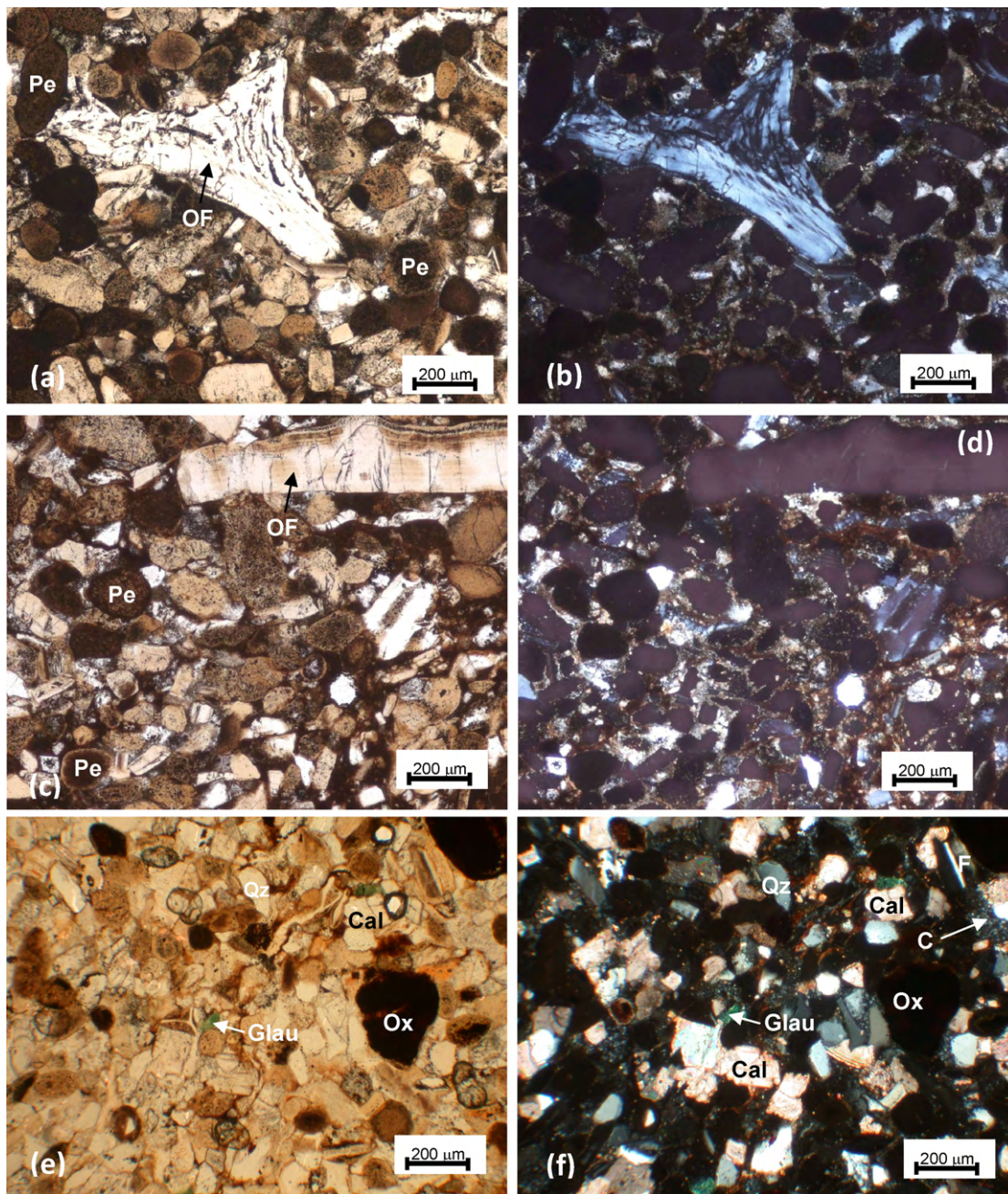
Fig. 2. Thin section photomicrographs obtained by optical polarizing microscopy of the Kalaat Khasba phosphorites. (a), (c) and (e) Plane polarized light. (b), (d) and (f) Cross-polarized light. Show phosphorites containing brownish pellets of collophane and set in a calcite cement. The views taken with polars crossed shows the isotropic nature of collophane and quartz grains showing grey colours. Grains outlined are Qz: quartz; Ap: apatite; C: clay minerals; Cal: calcite; F: feldspar; Glau: glauconite; OF: organic fragments; Pe: pellets; OX: oxides.

to the solid matrix by superficial interactions affected by sample specific surface area determining the adsorption capacity and the drainage to the groundwater.

KK samples were analyzed to quantify the major and trace elements, in order to define the potential damage that such wastes can cause to the environment. The analytical results obtained for KK samples are shown in Table 1. Chemical analysis for major elements revealed that the KK samples contained 35.46–49.00% CaO, 22.06–32.78% P_2O_5, 0.66–2.87% Al_2O_3, 0.37–0.78% Fe_2O_3, 0.84–2.21% MgO, and 4.97–24.95% SiO_2. The LOI values range between 9.5 and 11.6%.

The ratio CaO/P_2O_5 was found to be within the range 1.54–1.60 for the studied samples except KK3. This ratio is similar to nor-

mative carbonate fluorapatite (1.58). The difference observed in the sample KK3 is probably due to the presence of fluorapatite (CaO/P_2O_5 of fluorapatite is 1.32).

Table 4 shows that As, Co and Pb concentrations in the KK phosphorite samples are lower than those in Average World Phosphorite—AWP [33]. Moreover, average concentrations for the same elements are lower than those in Average Shale Composition—ASC [34].

The results also show that the As concentrations are similar to those found in phosphate samples from Morocco. Cobalt and Pb concentrations in the KK phosphorites were found to be much lower than those found in phosphate samples from other countries (Table 4). The average Co concentration in the studied samples
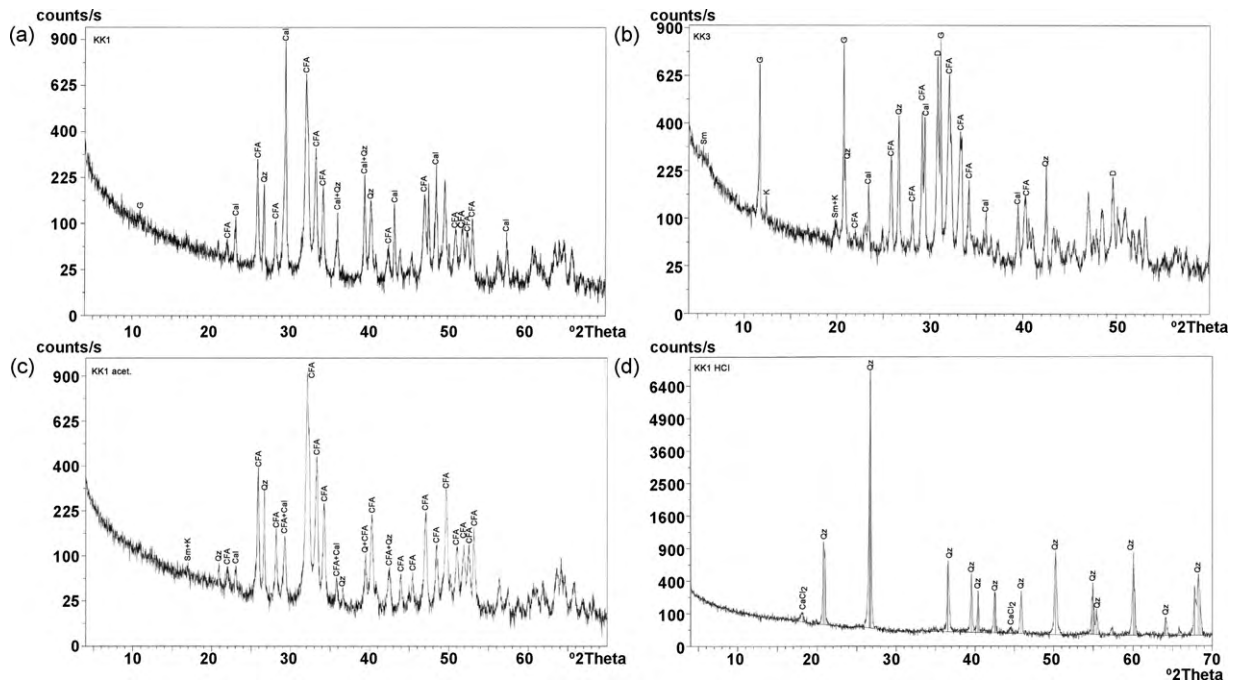
Fig. 3. Representative X-ray diffraction diffraction patterns of the KK samples: (a) KK1 sample; (b) KK3 sample; (c) KK1 sample treated with acetic acid; (d) KK1 sample treated with HCl; Cal: calcite; CFA: carbonate fluorapatite; D: dolomite; G: gypsum; Qz: quartz; K: kaolinite; Sm: smectite. Samples KK2 and KK4 provided diffraction patterns similar to the one corresponding to sample KK1.
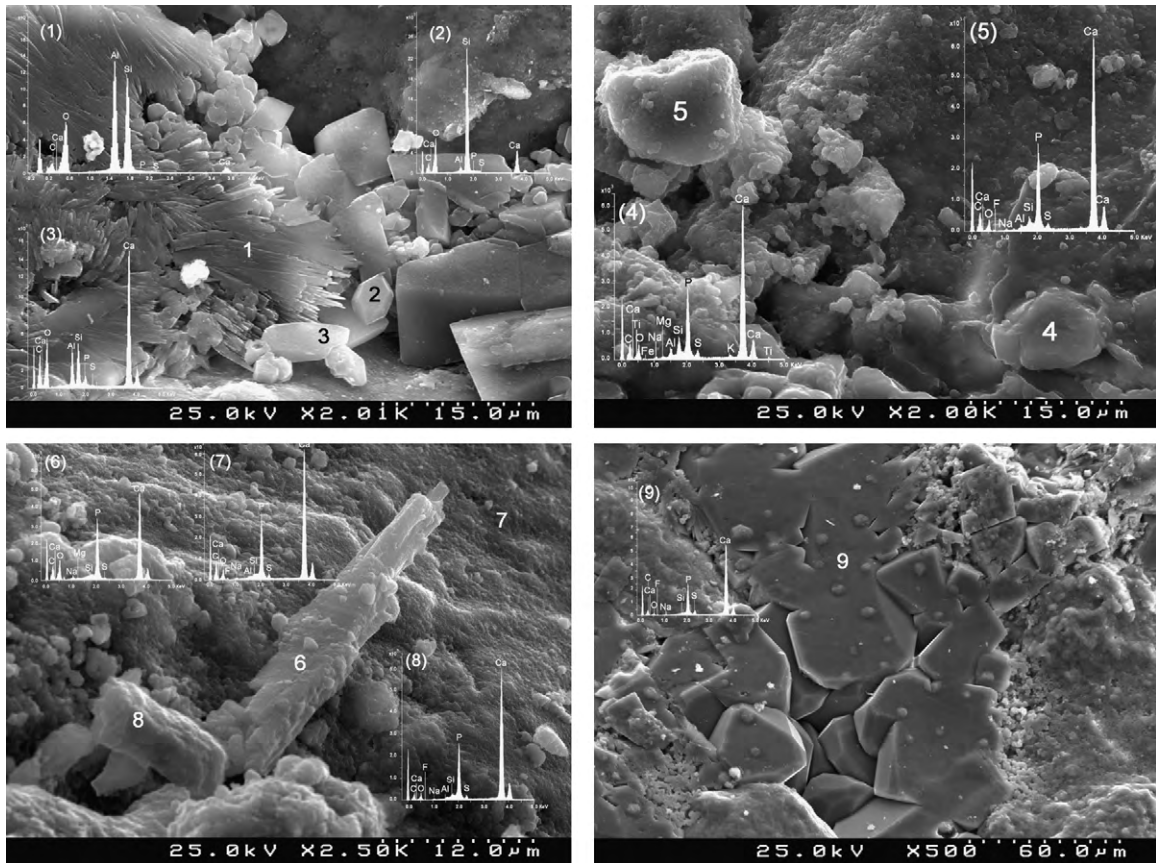
Fig. 4. SEM micrographs of the representative KK phosphorites showing the morphologies of the main constituents and their corresponding EDS spectrum of elements: 1: kaolinite; 2: zeolite (not identified); 3: calcite + kaolinite; 4–9: microcrystalline masses or well shaped crystals of fluorapatite showing [CO$_3$] and [SO$_4$] for [PO$_4$] substitutions.

Table 2
SEM-EDS chemical analysis (wt.%) of the main constituents of KK samples identified in Fig. 4.

	1	2	3	4	5	6	7	8	9
O	61.15	47.67	58.13	31.62	22.78	34.86	24.08	22.89	18.34
Ca	1.34	24.96	8.67	33.13	37.87	30.98	37.68	37.88	38.01
Al	16.37	3.90	1.46	1.33	0.62	–	0.44	0.50	–
Si	15.98	4.53	28.18	3.19	2.01	1.59	1.19	1.43	1.17
P	0.83	1.48	1.62	11.43	11.31	14.15	13.13	12.35	12.52
S	0.25	0.30	0.73	1.75	1.12	0.75	1.36	0.99	2.19
F	–	–	–	–	9.83	7.31	8.43	17.13	16.70
Na	–	–	–	0.61	0.40	0.52	0.38	0.90	1.93
Mg	–	–	–	0.22	–	0.10	–	–	–
Fe	–	–	–	0.30	–	–	–	–	–
K	–	–	–	0.85	–	–	–	–	–
Ti	–	–	–	0.24	–	–	–	–	–
Total	95.92	82.84	98.79	84.67	85.94	90.26	86.69	94.07	90.86

1: Kaolinite; 2: zeolite (not identified); 3: calcite + kaolinite; 4–9: microcrystalline masses or well shaped crystals of fluorapatite showing [CO₃] and [SO₄] for [PO₄] substitutions.

Table 3
Particle size distribution and associated trace metals concentration (mg kg⁻¹) in distinctive size fractions.

	Size fractions (μm)	Particle size (%)	As	Cd	Co	Cr	Cu	Mo	Mn	Ni	Pb	Sr	U	Zn
KK1	>5000	2.1	9	46.0	1	103	12	36	80	35	10	1409	62	248
	2000–5000	8.3	8	40.0	1	415	13	33	82	33	3	1366	59	198
	1000–2000	12.1	9	39.0	1	329	14	30	71	32	1	1371	58	185
	<1000	77.5	11	38.0	5	323	17	35	119	46	18	1282	50	271
KK2	>5000	4.0	5	36.0	b.d.l.	314	17	6	78	36	5	1199	64	201
	2000–5000	6.5	8	36.0	2	238	17	5	62	32	4	952	43	310
	1000–2000	7.1	7	20.0	2	121	16	4	69	25	3	1055	50	174
	<1000	82.4	9	29.0	5	322	25	9	115	48	13	1006	47	207
KK3	>5000	3.4	5	45.1	1	342	25	18	54	42	6	1656	100	244
	2000–5000	4.3	5	46.6	b.d.l.	304	21	16	47	37	2	1784	99	237
	1000–2000	5.4	6	49.6	b.d.l.	179	20	12	37	31	2	1785	111	245
	<1000	83.2	5	55.5	1	336	30	13	58	60	12	1823	103	310
KK4	>5000	0.0	–	–	–	–	–	–	–	–	–	–	–	–
	2000–5000	5.1	5	47.0	1	369	20	15	50	41	4	1400	84	250
	1000–2000	7.7	4	43.0	b.d.l.	151	19	11	38	36	3	1420	86	252
	<1000	87.2	4	38.0	1	208	25	12	43	46	13	1814	103	265

b.d.l.: below detection limit.

is 0.3 mg kg⁻¹, while the overall average for Tunisian phosphate samples is 0.75 mg kg⁻¹. The obtained results show that the Pb content in the samples is lower than the world's average range of 3–44.5 mg kg⁻¹ [35]. Pb concentrations in KK samples are similar to the values obtained for the phosphate samples from Jordan. Copper (Cu) concentrations in KK samples show values ranging between 12 mg kg⁻¹ and 35 mg kg⁻¹. The global range of Cu concentration is 5–130 mg kg⁻¹ [35], while the average concentration determined in the present study is 24 mg kg⁻¹, which is in agreement with the global range of Cu concentrations in phosphate rocks. According to the data shown in Table 4, the studied phosphate samples show similar mean concentration values as the phos-

Table 4
Comparison of the chemical composition (only trace elements in mg kg⁻¹) of the Tunisian raw phosphorites from KK mine (present study) with other phosphate rocks occurring in other countries (data from several authors).

	Present study			Jordan [31]	Morocco [32]	Pakistan [32]	Togo [11]	Tunisia [32]	USA [32]	AWP [33]	ASC [34]	Soil EC [47]	Fertilizer Canadá [48]
	Min	Max	Av.	Average values									
As	11	11	11	n.a.	10.7	n.a.	n.a.	2.0	7.7	23	13	8	75
Cd	44.9	62.5	50.3	23	21.6	7.2	44	53	12.5	18.0	0.3	1.5	20
Co	0.2	0.5	0.3	n.a.	0.75	9.4	2.5	0.75	2.83	7	19	n.a.	150
Cr	390	490	427	51	217	17	356	165	62.6	125	90	60	n.a.
Cu	12	35	24	n.a.	28.2	5.5	110	10.8	9.09	21.7	45	100	n.a.
Mn	24	63	51.2	n.a.	15.0	178	126	19.8	148	n.a.	850	n.a.	n.a.
Mo	13.1	14.9	14.1	n.a.	7.9	n.a.	8.5	5.63	6.68	n.a	2.6	n.a.	20
Ni	37	83	55	15	41.4	28	158	19.1	17.7	53	68	50	180
Pb	2	3	3	4	6.3	89	67	5.0	11.7	1–100	20	100	500
Sr	1385	1903	1606	n.a.	1331	n.a.	1429	1731	1104	1900	300	n.a.	n.a.
U	54	133	103	27	150.7	n.a.	n.a.	43.6	108	120	3	3	n.a.
Zn	209	276	226	121	279	67.2	465	308	104	195	95	200	1850

n.a.: data not available; AWP: Average World Phosphorite by Altschuler [33]; ASC: Average Shale Composition by Turekian and Wedepohl [34].; Soil EC: Permissible limit established by the Soil EC Directive [47]; Fertilizer Canada: Permissible limit established by the Canadian Food Inspection Agency [48].

phate samples from Morocco. The average Cu content of Tunisian phosphate rock was found to be 10.8 mg kg^{-1} [32], whereas the average Cu content of KK samples is clearly higher. Manganese (Mn) concentrations determined in the KK samples range from 24 mg kg^{-1} to 63 mg kg^{-1}. According to Table 4 the mean Mn concentration in KK samples (51.2 mg kg^{-1}) is clearly below the worldwide Mn concentrations for phosphates (149–2236 mg kg^{-1} [35]). However when they are compared with the Mn mean concentration for Tunisian phosphates (19.8 mg kg^{-1}) [32], KK samples are enriched in Mn. Nickel (Ni) concentrations determined in KK samples were higher than those determined in the set of phosphate samples from other countries, except those from Togo phosphorites (Table 4). Ni mean concentration determined in KK samples was found to be 55 mg kg^{-1}, while the overall average concentration for Tunisian samples was estimated at 19.1 mg kg^{-1} [32].

On the other hand, average Cd, Cr, Mo, Sr, U and Zn are relatively higher than those in ASC. Mean Cd concentration in KK samples was estimated to be 50.3 mg kg^{-1}, while the overall mean concentration in all the analyzed Tunisian samples was found to be 53 ± 1.6 mg kg^{-1}. KK samples show Cd concentration values similar to those found in Togo. The results of this study revealed that KK samples are enriched in Cd comparatively to the reference shale [34] factor ranging from 105 to 208. Chromium (Cr) concentration values determined in KK samples (Table 1) were found to be higher than the overall concentration of Cr determined in phosphate samples referred to other countries. Cr average content in KK samples (400 mg kg^{-1}) is also higher if compared with the average value for Tunisian phosphate samples (165 mg kg^{-1}) estimated by Sattouf in 2007 [32]. Molybdenum (Mo) concentrations determined in KK samples are relatively high when compared with the values from other countries, but they are similar to those estimated by Sattouf [32] for the Tunisian phosphate samples. Strontium (Sr) concentrations obtained in KK samples are similar to those obtained for the Tunisian phosphates (1705–1757 mg kg^{-1}; mean value of 1731 mg kg^{-1}) [32]. The KK samples were enriched in Sr comparatively to the reference shale by a factor ranging from 4.6 to 6.3. Similar factor values were obtained by Sattouf [32] for the Tunisian phosphorites (enrichment factor = 4.3). The studied KK samples are characterized by Sr/P$_2$O$_5$ ratios ranging from 5.14×10^{-3} to 6.27×10^{-3}, values which are similar to those obtained for other sedimentary phosphate rocks [32]. Uranium (U) contents determined in KK samples are within the range 54–133 mg kg^{-1}, and are higher than the values proposed by other authors for Tunisian phosphorites (26.7–50.2 mg kg^{-1} [32]). The U average value lies within the global range of U concentration values determined in other phosphate rocks (43.6–172 mg kg^{-1}) [32]. The results of this study revealed that KK samples are enriched in U comparatively to the reference shale [34] by a factor ranging from 18 to 44. The studied samples are characterized by high U/P$_2$O$_5$ ratios ranging from 2.4×10^{-4} to 4.1×10^{-4}, which are similar to the ratio values obtained for other sedimentary phosphate rocks [32]. From Table 4 it emerges that zinc (Zn) concentration varies significantly in the samples from different countries. The average Zn concentrations in KK phosphorites (averaging 226 mg kg^{-1}) are very similar to those found in the Tunisian phosphate samples (308 mg kg^{-1} [32]). Zn concentration values determined in KK samples are similar to the Zn concentrations determined in phosphate samples from Morocco.

Rare earth elements (REE) concentrations, the sum of the total REE (TREE), comprising light rare earths (LREE) and heavy rare earths (HREE) concentrations are shown in Table 1. REE concentrations determined in the KK samples vary from 530.43 mg kg^{-1} to 612.27 mg kg^{-1} with an average value of 556.21 mg kg^{-1}. All the studied samples show higher concentrations in LREE than in HREE (ratios ranging between 3.19 and 4.55).

3.3. Chemical fractioning of metals in KK samples

In order to identify the carrier phases of the selected trace elements in phosphorite samples, chemical fractioning was carried out in the KK samples. The results for Ca, Cd, Cr, Cu, Fe, Mg, Mn, Ni, P, Pb and Zn in the KK samples are shown in Fig. 5.

Cadmium content in the KK samples was estimated to be in the interval 44.9–62.5 mg kg^{-1} (Table 1). According to the results Cd content is associated with the residual fraction (41.7–58.9%), Mn oxides (18.1–33.5%) and exchangeable fraction (9.1–16.7%). Some Cd is also associated to the organic matter and, partially, to sulphide phases (8.4–14.5%). These results suggest that most of the Cd is present in relatively immobile forms.

The KK samples have Ca concentrations ranging from 25.4 to 33.6%. The main carrier phases for Ca are similar to those obtained for Cd: the residual fraction (51.0–68.2% related mainly to carbonate fluorapatite), Mn oxides and exchangeable fraction (21.6–30.3% and 7.7–14.5% respectively, associated to calcite). The partitioning data obtained for P shows that the highest percentage of extraction is found also in the residual fraction (carbonate fluorapatite as main bearing phase) or are linked to exchangeable and manganese oxide fraction. The results obtained for P are similar to those obtained for Ca and Cd.

Chromium content in KK samples was estimated in the range 390–490 mg kg^{-1}. According to the results 88.9–95.6% of the total Cr content is associated with the residual fraction, whereas 0.6–5.0% with the amorphous Fe oxides. Practically no Cr is associated with other fractions in accordance with the results yielded by the mineralogical studies.

Copper content in KK samples (12–35 mg kg^{-1}) is associated with the amorphous Fe oxides (28.0–57.7%), the residual fraction (15.4–28.0%), and the exchangeable fraction (9.6–20.0). Some Cu is also linked with both organic/sulphide phases (pyrite) and crystalline Fe oxides (9.6–14.3% and 7.7–12%, respectively). Cu is mainly associated with the clayey cementing matrix phase of the phosphorite.

Iron as expected, owing to the presence of iron amorphous oxides and hematite is basically found distributed into three fractions: insoluble residue (58.8–67.0%) and crystalline (13.4–18.9%) and amorphous iron oxides (11.2–16.4%). Also is observed that 3.2–6.7% of extraction is associated to H$_2$O$_2$ which could represent the contribution of the sulphide minerals (pyrite).

Magnesium was essentially extracted by ammonium acetate and by hydroxylamine hydrochloride (76.1–81.4%) which represents the presence of dolomite in the selected samples.

Manganese (concentrations in the studied samples ranging between 24 mg kg^{-1} and 61 mg kg^{-1}) appears associated to the exchangeable fraction but also it is associated with the insoluble residue and the Mn oxides. Mn associated to the ammonium acetate reagent could be explained by the dissolution of Mg/Ca carbonates, as Mn^{2+} can substitute for Mg^{2+} as well as Ca^{2+} in carbonate minerals, the more so for Mg in dolomite than for Ca in calcite. Specific adsorption of Mn at the surface of calcite is also possible [36].

Nickel content in the KK samples ranges between 37 mg kg^{-1} and 83 mg kg^{-1} (Table 1). In the analyzed samples the highest percentage of Ni extraction is distributed homogeneously between the exchangeable/Mn oxides bound fraction (24.2–34.6%) and with the residual fraction (21.1–38.5%). Nickel show the high percentage of extraction associated to ammonium acetate showing that this element might be related with the presence of clay minerals.

Lead content in KK samples was estimated to be in the range 2–3 mg kg^{-1} (very low contents), primarily associated with the carbonate and Mn oxides (48.9–57.9%) bearing phases fractions and with the residual fraction (23.7–31.7%) as well. The extraction
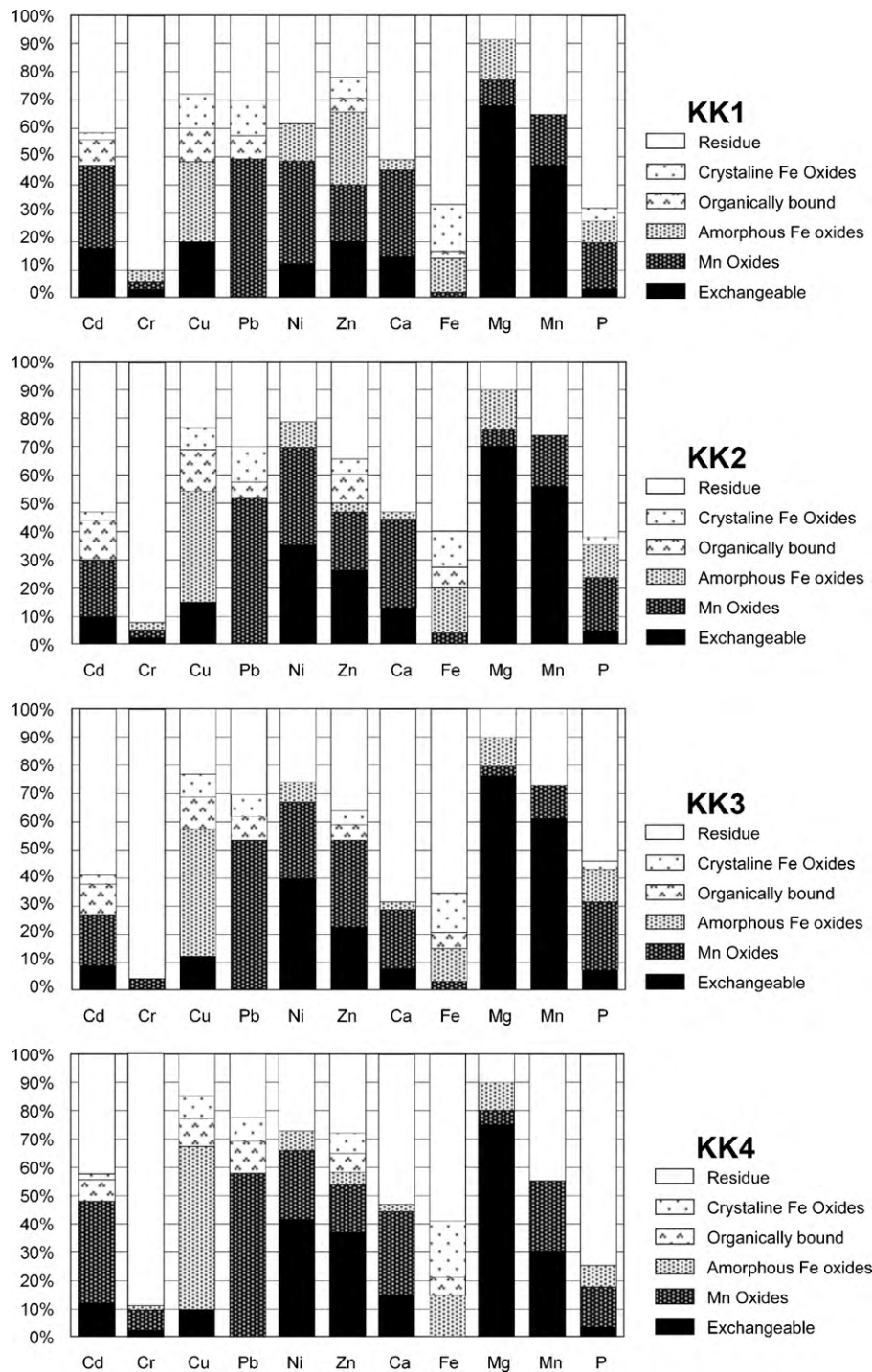
Fig. 5. Partitioning of Cd, Cr, Cu, Pb, Ni, Ca, Fe, Mg, Mn, P and Zn among the six chemical geochemical fractions of the KK1, KK2, KK3 and KK4 samples.

values of Pb with hydroxylamine can be attributed to the carbonate environment characterized by high pH values.

Zn shows clearly a high percentage of extraction associated to the two initial steps of extraction [exchangeable, Mn oxides and punctually to amorphous Fe oxides (see sample KK1)]. The relatively high concentration of exchangeable Zn (more than 30% in some samples), as the case of Ni, might be related with the presence of clay minerals (kaolinite and smectite) acting as adsorbents, thus retaining Zn through ion exchange and other processes [37]. Zinc is also extracted by H_2O_2 and HCl + HNO_3 + HF digestion showing that Zn is also associated to sulphide bearing phases (sphalerite).

4. Discussion

The previous studies carried out by Sassi [17] indicate that the formation of the studied phosphorites should have occurred in a confined, shallow, coastal, marine reducing environment rich in organic matter. The presence of gypsum, glauconite, dolomite, kaolinite and sharp-edged quartz grains in the KK phosphorite samples also support this proposal. Episodes of winnowing have led to the concentration of the grains, pellets and coprolites in particular in the phosphate layers. These variations in the environmental conditions are narrowly controlled by the fluctuations in the con-

Table 5
Enrichment factor (EF) for the KK samples compared with other worldwide phosphate deposits.

	As	Cd	Co	Cr	Cu	Mo	Mn	Ni	Pb	Sr	U	Zn
AWP	41	1711	3.4	12	12	23	n.d.	10	10	26	380	25
MP	26	2843	0.5	28	12	85	0.2	10	4	49	661	49
USP	35	3056	3.6	15	7	134	4.2	8	15	76	880	34
TP	n.d.	1426	0.4	11	12	23	0.5	10	12	13	n.d.	20
JP	22	778	n.d.	7	13	n.d.	n.d.	7	1	n.d.	565	19
KK	48	11631	0.4	91	18	267	1.4	24	4	104	794	70
Ratio	1.2	6.8	0.2	7.8	1.5	11.6	n.d.	2.4	0.4	4.0	2.1	2.8

The EF (enrichment factor) was calculated by normalizing all toxic elements concentration to Al concentrations of the average crustal rocks. The enrichment factor was calculated using the following equation: EF = (Cx/C$_N$)study/(Cx/C$_N$)crustal where: (Cx)study is the concentration of a given element in studied sample; (C$_N$)study is the concentration of Al in the studied samples; (Cx)crustal is the concentration of a given element in the crustal rocks; (C$_N$)crustal is the concentration of Al in the average crustal rocks, according the methodology proposed by Rudnick and Gao [38]. The Al$_2$O$_3$ concentrations for phosphate deposits are as follows: AWP (Average World Phosphorite) 1.8 wt.% [39]; MP (Morocco Phosphates) 1.3 wt.% [40]; USP (USA Phosphates) 0.7 wt.% [40]; TP (Togo Phosphates) 5.28 wt.% [11]; JP (Jordan Phosphates) 0.66 wt.% [31]; KK (Kalaat Khasba Phosphates) 0.74 wt.%; and for the average crustal rocks 15.4 wt.% [31].

finment, as well as, in the hydrodynamics and morphostructure of the basins [18].

KK phosphorites are enriched in As, Cd, Cr, Mo, Ni, Sr, U and Zn. The average concentrations of these elements is not different from the values proposed for other Tunisian phosphate rocks phosphorites [32]. The enrichment factor (EF), calculated according to Batarseh and El-Hasan [31], was used to establish the similarities between several worldwide phosphate deposits and the KK samples (Table 5). The ratio values between the individual elements EF's of the KK samples and AWP (Table 5) showed that the studied samples (KK) have relative ratios higher than AWP (12 times higher for Mo, 8 times higher for Cr, 7 times higher for Cd, 4 times higher for Sr, 3 times higher for Zn and 2 times higher for Ni and U). Other elements such as Cu and As show similar EF's trends.

These heavy metal enrichments are explained by ionic isomorphic substitutions that affect the apatite structure (replacement of Ca^{2+} for Na$^+$, Mg^{2+}, Sr^{2+}, Mn^{2+}, U^{4+}, Th^{4+}, Cd^{2+}, and REE [17,41,42]), and by adsorption onto the particle surfaces of Fe and Mn oxides, clay minerals, and calcite [12,42–43].

Reworking of phosphorites from Tunisian outcrops might be the factor responsible for the presence of phosphate grains with traces of Cd. The presence of Cd in KK phosphorites could be explained by the isomorphous substitution of Ca for Cd in the apatite structure. However, the affinity of Cd to the carbonate phase should also be emphasized.

The map analysis (300 × 300 points) of several elements, such as O, Cd, Si, Mg, P, Mn, Fe and Ca (Fig. 6), allowed withdrawing the following conclusions. According to the figure Ca and P concentrations show the same repartition which explains the similar results obtained in the selective chemical extraction. Indeed, these two principal components of apatite show a positive correlation. Also, Mg contents increase as Ca contents decrease, reflecting the substitution of Ca by Mg.

Cd, Mn and Fe coexist in the same phase, which is expressed by micro-inclusions. These elements are also contained in an area where oxygen and calcium contents are depleted.

The analysed sulphides disseminated inside the phosphates have very small size (<10 μm). The WDS results (Table 6) show high concentration in Zn (58.110–56.853 wt.%) and S (31.195–31.324 wt.%) suggesting the presence of sphalerite. These grains are also enriched in Cd (8.659–9.980 wt.%). Correlation values clearly show a good correlation between Cd and Zn ($r = 0.97$) in the KK samples. The results in Fig. 6b and Table 6 lead to the conclusion that Cd is associated with sulphide minerals (sphalerite) (Fig. 6b).

Similarly to many other phosphorites, no positive correlation between Cd and P$_2$O$_5$ ($r = 0.35$, $p < 0.05$) and between Cd and Ca ($r = 0.26$, $p < 0.05$) was found in the KK samples.

The results also indicate that Ca concentration decreases when Cd concentration increases. This phenomenon can be explained by

the substitution of Ca by Cd [17,41,42] due to their similar ionic radius and valence. Taking into account the characteristics of the reducing medium favourable to the formation of sulphides, Cd restored in the interstitial medium will replace Zn in the sphalerite [20]. Hatch and Leventhal [44] also proposed that high contents of trace metals, such as Cd and Zn, indicate deposition in the anoxic basis of the water column.

According to the obtained WDS results most of Co, Ni, and Cu contents are related with the presence of pyrite in KK samples.

WDS analytical data also indicates that the carbonate fluorapatite grains are enriched in uranium (Table 7). Altschuler et al. [45] have suggested that U is originally incorporated in CFA almost solely as U (IV), since phosphorites mostly form under low Eh conditions in association with abundant decomposition of organic matter (OM) [12,46]. Apatite, a common product of organic matter diagenesis, is known to incorporate substantial amounts of U in pore water during crystallization. Uranium as U^{IV} can substitute for Ca^{II} in the apatite structure, because of their close ionic sizes (0.97 Å and 0.99 Å, respectively). The U^{VI} can be fixed (adsorbed) only outside the structure (most probably as uranyl carbonate), because of its much larger ionic radius [10]. Significant pair correlation coefficients corresponding to a confidence level of 0.95 were obtained for U and P$_2$O$_5$ ($r = 0.99$), U and Ca ($r = 0.99$), and Sr ($r = 0.86$). In the studied KK samples, most of the U fraction seems to be held by the francolite phase, as suggested by the WDS results (Table 7). The obtained analytical results also indicate that the REE are mainly present in the carbonate fluorapatite grains.

Silicon (Si) and oxygen (O) distributions are similar and this is an indication of the presence of quartz. A good correlation also exists between Si and Al and justifies the presence of fine grained phyllosilicates, more precisely clay minerals (Fig. 6b).

Table 6
WDS results of selected minerals of sphalerite (Sphal) and pyrite (Pyr) in the Kalaat Khasba samples (wt.%).

Element	Sphal	Sphal	Pyr	Pyr
Zn	56.853	58.110	0.007	0.0041
S	31.195	31.324	47.331	51.250
Fe	0.487	0.488	43.159	43.190
As	–	0.006	–	–
Cd	9.980	8.659	0.036	–
Mn	0.039	0.025	–	–
Sn	–	–	–	0.009
Co	–	–	0.091	0.064
Sb	–	–	–	0.031
Cu	–	–	0.190	0.006
Ni	0.021	0.016	0.003	–
Au	–	–	4.031	–
Ag	–	–	–	0.010
Total	98.575	98.628	94.848	94.565
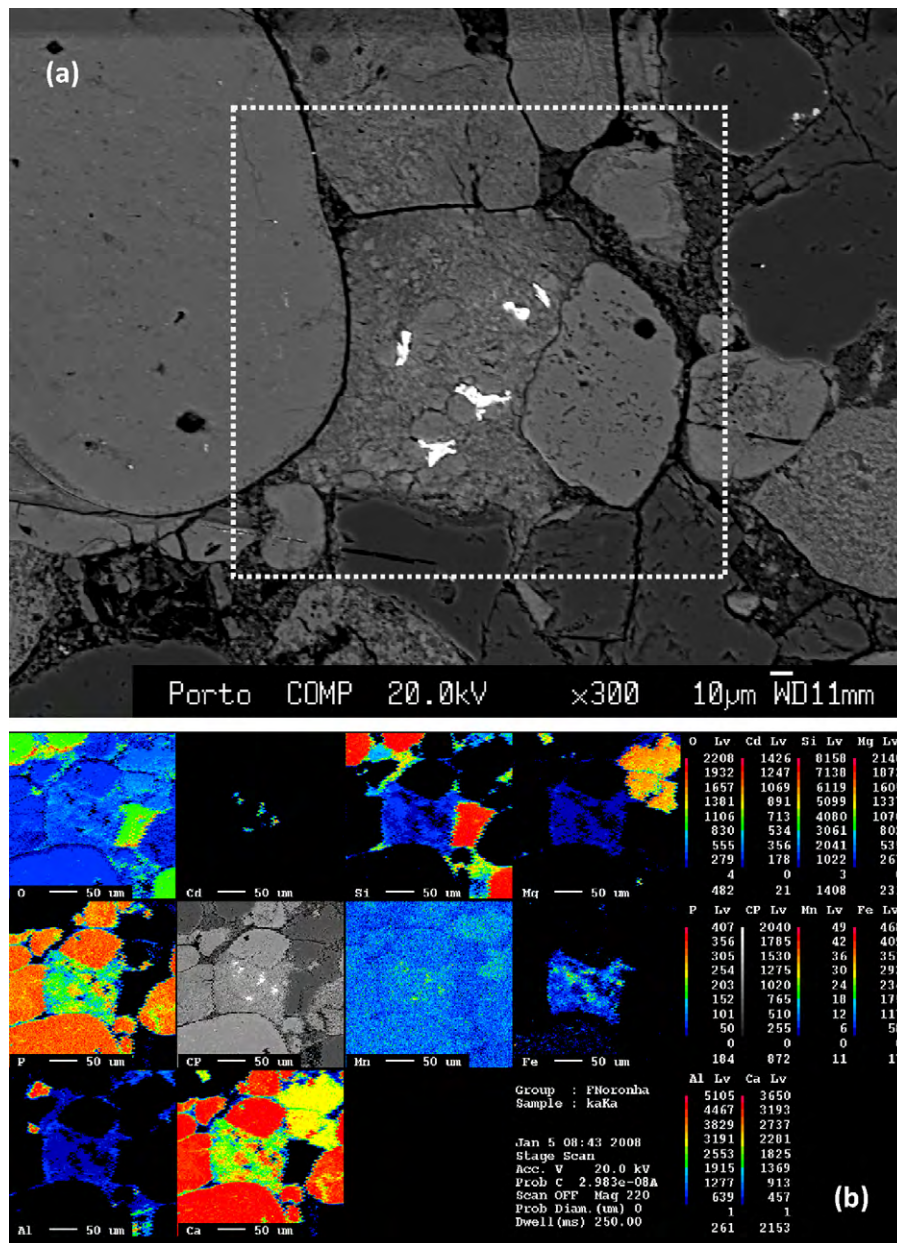
Fig. 6. (a) Rounded grains of calcium phosphate and some crystals of sphalerite (large density of electrons) enriched in cadmium. (b) The map of WDS analysis (300×300 points) of the sample represented in the square area. The phosphates correspond to the grains where O, P and Ca is present; grains of silicates (Si, O), one grain with Mg and Ca and a central zone with O, P, Ca and some fine grains containing Mg, Mn, Fe and Al were rich on Cd (Lv level of counts).

During the processing of these phosphorites, some of the mentioned trace elements are transferred to the fertilizers. Once in the soil, these trace elements can be partially assimilated by plants and when present in high contents can lead to hazardous consequences. To carry out the ecological evaluation of the phosphorites, concentrations of potential toxic elements were compared with their permissible limits for soils used for growing crops set up by the European Commission (EC) [47]. Considering that fertilizers are the phosphate final manufacturing product the trace metals concentrations were compared also with some Canadian fertilizers [48].

Arsenic, Co and Cu concentrations in KK samples are low enough and do not constitute either a health or a environment hazard. According to Dudka and Miller [49] As concentrations can reach $40 \, \text{mg kg}^{-1}$ without an appreciable toxicological or environmental hazard. Copper is present in sufficient quantities to meet the nutrient requirement of plants ($>3 \, \mu\text{g/g}$ and $<50 \, \mu\text{g/g}$). Also Co concentrations are sufficient low to cause any health or environmental risk. According to Sabila-Javied et al. [35] the toxic effects on plants are unlikely to occur if Co concentrations are below $40 \, \text{mg kg}^{-1}$, but small amounts are required for plant growth ($\sim3 \, \text{mg kg}^{-1}$). Ni concentrations are below the tolerable limit of $100 \, \text{mg kg}^{-1}$, proving that KK samples are compatible and safe with respect to Ni [35].

According to the obtained results Pb concentrations in KK phosphorites are not hazardous because the concentrations are below the permissible concentration limits for soils used for growing crops set up by the European Commission (soil EC – $100 \, \text{mg kg}^{-1}$ – [47]) and also for human health ($300 \, \text{mg kg}^{-1}$ [49,50]). The results from the selective chemical extraction show that Pb is associated with the organic and Fe-bearing oxide phases as well as in the residual phase. The uptake of Pb by plants depends on soil pH; for high

Table 7
WDS results of selected minerals of apatite (Ap) and carbonate fluorapatite (CFA) in the Kalaat Khasba samples (the presented values are expressed in wt.%).

Element	Ap	CFA	CFA
TiO_2	–	0.044	–
BaO	0.028	–	0.006
UO_2	–	0.380	0.008
Al_2O_3	0.023	0.026	0.082
Na_2O	0.157	1.309	1.380
P_2O_5	42.160	31.990	29.590
CaO	53.690	49.130	51.420
MnO	0.242	–	–
SO_3	0.019	3.600	2.510
MgO	0.049	0.129	0.190
FeO	0.362	0.014	0.137
SrO	0.067	0.213	0.249
HfO_2	–	0.003	0.013
Y_2O_3	–	–	0.190
ThO_2	–	0.045	–
ZrO_2	–	0.073	0.164
Dy_2O_3	–	–	–
F	5.370	5.290	5.620
Cl	0.199	0.021	0.034
La_2O_3	–	0.069	–
Ce_2O_3	–	0.030	–
Pr_2O_3	–	0.015	0.138
Nd_2O_3	–	–	0.092
Sm_2O_3	–	0.004	–
Gd_2O_3	–	–	0.033
Ho_2O_3	–	0.009	–
Er_2O_3	–	0.112	0.010
Yb_2O_3	–	–	–
Lu_2O_3	–	0.036	–
$F\equiv O$	2.261	2.220	2.366
Total	100.105	90.322	89.500

pH values, as those of the soils in the studied area, Pb becomes immobilized. The absence of labile forms of Pb is due to the low solubility of Pb-bearing minerals, and to the high affinity of Pb for metal oxides. Sabila-Javied et al. [35] indicates that during the fertilizer manufacturing process, the application of sulphuric acid either separates Pb in phosphogypsum or immobilizes it as insoluble Pb sulfate. The small transfer factor of Pb to plants also prevents its transfer. Plants do not take up Pb when its concentration in soil is below 300 mg kg^{-1}, and when taken up occurs, it accumulates in leaves rather than in fruits [50].

The average value for Zn concentration in the KK samples exceeds slightly the proposed EU limits (200 mg kg^{-1}). According to Sabila-Javied et al. [35] the Zn concentrations ranging from 25 mg kg^{-1} to 200 mg kg^{-1} are considered to be very positive for most field-grown crops.

Cadmium, Cr and U concentrations in KK samples are higher than the EC soil permissible limits for growing crops (1.5 mg kg^{-1}, 60 mg kg^{-1} and 3 mg kg^{-1}, respectively). According to the permissible limits the values of Cd in the KK samples are higher than the values established as limit for the Canadian fertilizers (20 mg kg^{-1}, Table 4).

The presence of high Cd and U concentrations in the studied KK samples is a major concern because of the high toxicity of both elements. Cd is classified as a Class 1 human carcinogen (Group B1) by the International Agency for Research on Cancer [51] and the World Health Organization [52]. The European countries have set up the limit of 10 mg kg^{-1} of Cd on phosphate rock [35]. The comparison of Cd mean concentration in KK samples with the European established upper limit for Cd suggest that significant quantities of Cd could be added into agricultural soils. According to the selective chemical extraction results a significant amount of Cd (9.1–16.7%) was found in the exchangeable form, implying that a large fraction of this metal is weakly bound, hence indicating that Cd may be highly bioavailable if the environment becomes acidic. KK samples

contain also higher concentrations of U than the EC soil permissible limits for growing crops.

During the preparation of fertilizer the Cd and U can either concentrate in the fertilizer or can go into the tailings. If Cd and U are concentrated in the fertilizer, it will be transferred to plants from where it can reach humans either directly or through the food chain. Cd and U can cause health hazard to humans by entering into their bodies through the following mechanisms: (i) direct inhalation of air borne particulates, (ii) food chain, (iii) absorption through skin and (iv) the direct radiation (in case of U). When inhaled, a fraction of the available Cd and U enters into the bloodstream. The reaction of the fraction passed into bloodstream depends upon factors such as the chemical and physical form of the element and the physiology of the person involved. Similarly, when Cd and U are ingested, the amount of it passing into the body fluids depends on the nature of the element and on the physiological conditions of the person concerned [52,53]. Cadmium has been associated to a lesser or greater extent with many clinical conditions including: anosmia, cardiac failure, cancers, cerebrovascular infarction, emphysema, osteoporosis, proteinuria and cataracts [53]. Uranium is chemotoxic, radiotoxic and a carcinogen. Because U is a radioactive substance, its effects on human health have been widely researched. Long-term exposure to U radionuclides can result in medical conditions such as kidney disease and the development of cancer [54].

The most important source of Cd and U exposure of the local population of Kalaat Khasba area is through dust and evidence of respiratory diseases was found originated by dust. However, dust in the tailings is dominated by the fine grain particles small enough to be inhaled. Iron oxyhydroxides admixed with dust, as well as, the potentially toxic metals present in the dust could be responsible for lung inflammatory problems. The ingestion of Cd and U found in certain foods and also in surface and groundwater must be also considered.

Analysis of chromium shows that the content of Cr in the KK samples is higher than that for the AWP and ASC (Table 1). In all KK samples, 90% of total Cr is associated to the residual fractions (Fig. 5) suggesting that Cr is present in the detrital mineral phases most probably in clay minerals. However the toxicity of Cr towards plants or animals depends on its oxidation state. For example, Cr(III) is an essential nutrient that helps the body consume sugar, protein, and fat, while Cr(VI) is considered to be carcinogenic [34]. Chromium and its compounds are known to cause cancer of the lungs, nasal cavity and para nasal sinus and suspected to cause cancer of the stomach and larynx.

Molybdenum (Mo) is also present in high concentrations in the KK samples. Plants require trace amounts of molybdenum (Mo) for normal growth. While animals also require trace amounts, they are more likely to be adversely affected by excessive Mo than plants [55]. In the Kalaat Khasba area (soils with high pH) Mo is largely be available to plants. This could be a problem because many animals cannot tolerate high Mo levels in their diets. Mo can impair utilization of copper (Cu) and other essential micronutrient, in particular if the diet is also relatively high in sulfur (S). A Cu–S antagonism lowers the biological availability of Cu by forming a Cu–Mo or Cu–Mo–S complex in the digestive tract. Forage Mo levels of 3 mg kg^{-1} and above will significantly reduce Cu availability from the diet [55].

Another important aspect is the fact that bioavailability of Cd, Cu, Ni, Zn could be enhanced in a marine environment due to their strong solubility in seawater or by the acidity of mine effluents [56]. Laboratory tests carried out by Gnandi et al. [57] showed that when in contact with seawater, heavy elements such as Cd, Cu, and Ni fixed by adsorption on sediment particles (manganese and iron oxides, clay minerals, carbonates, organic matter, and phosphate minerals) are highly solubilized, increasing the potential risk for the environment and human health.

5. Conclusions

The concentrations of heavy elements determined in KK phosphorites, investigated in the present study, are comparably lower than those determined for other phosphate rock deposits. However, like other phosphorites elsewhere in the world, they are highly enriched in several heavy elements, such as Cd, Cr, Mo, Ni, U and Zn, and REE. The results suggest that KK phosphorites can exert detrimental effects on human health and on the environment since the results of the sequential extraction showed that Cd, Cu, Ni, and Zn associated to bioavailable fractions (mainly with exchangeable ions, specifically adsorbed, carbonates and Fe and Mn oxides) could be significant.

These results suggest that the exploitation of the KK phosphorites as fertilizers could be a source of soil and surface/groundwater pollution. Trace element contents, specially the highest Cd and U concentrations, are critical for phosphates utilization, because the residual phosphogypsum produced during apatite processing may contain high contents of toxic elements. These elements could be removed by the action of water streams and/or wind and deposited in nearby areas.

The results lead to the conclusion that humans could be exposed to heavy metal risks through various pathways: inadvertently by inhalation and ingestion of heavy elements from phosphate rock dust; drinking water contaminated with heavy elements as the result of mining, milling, manufacturing and disposal processes; food chain, etc.

In order to evaluate the potential effects on human health and on the ecosystems it is important to carried out detailed studies on the potential toxic element distribution on soils and groundwater around the Kalaat Khasba site.

Acknowledgements

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