

THE PROBLEM OF CATION DEFICIENCIES IN SOME PHOSPHATES DUE TO ALTERATION PROCESSES

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ABSTRACT

Depending on their behavior with respect to alteration processes, phosphate minerals may be derived into four main groups. This study concerns one group having the general formula $A_xB_y(PO_4)_z(OH)_{n \geq 0}$ with $B = Fe^{3+}$ or Al, and particularly two cation-deficient phosphates from Central Africa: mitridatite and the new mineral eylettersite. In these phosphates alteration produces significant changes in the chemical composition with selective leaching of A ions and partial replacement of (PO_4) groups by (H_4O_4) , whereas the B ions are stable and the main structure remains. Changes are also observed in the physical properties according to the degree of alteration. Oxidation occurring in other phosphates of this group is also briefly discussed. The nomenclature of several phosphates must be reviewed in the light of alteration processes.

The importance of the alteration processes of the complex titanio-niobo-tantalates and their consequences have been outlined (L. Van Wambeke, 1970), it being shown that alteration by medium to low-temperature solutions is similar to weathering. Secondary deficiencies in the A positions are produced, whereas the elements occupying the B positions, such as Nb, Ta, Ti, and Fe^{3+} , are not affected. Moreover, the leaching is selective and concerns especially Na, the rare earths, Ca, and U in decreasing importance. The changes produced in the chemical compositions and physical properties, including the X-ray diffraction patterns obtained after heating, complicate both the nomenclature and the problem of age determination for these minerals. The aim of this paper is to outline the importance of similar alteration processes on some phosphates.

However, for the phosphates, the problem is further complicated by the fact that deficiencies due to alteration processes may occur in both the cation positions and in the anionic groups. Moreover, the stability of the phosphates differs sharply and it is evident that new data will be necessary in order to arrive at a better classification of the behavior of phosphates during alteration. Depending on their response to alteration, there are four main groups:

- (1) phosphate minerals relatively resistant to alteration processes;
- (2) phosphate minerals which become unstable and are destroyed by alteration;
- (3) phosphate minerals which are replaced by one or more new phosphates having different compositions and structures;
- (4) phosphate minerals showing deficiencies often in cations and anionic groups but with preservation of their structures.

Partial substitution of anionic groups in the phosphates has been proved only for some minerals and is mainly characterized by replacement of the (PO_4) group by (H_4O_4) and, sometimes, (CO_3) groups (McConnell 1965). When fluorine is present, it may also be replaced by (OH) through alteration. The leaching of cations, with or without oxidation of Fe^{2+} to Fe^{3+} , is less known in the literature. An example is the replacement of hühnerkobelite by alluaudite where leaching of selective cations and oxidation occur. Here the original structure remains with only minor changes in the parameters.

The first group of phosphates is characterized by the general formula $A_x(\text{PO}_4)_z(\text{OH})_{n \geq 0}$ where A is a cation or cations of the same group (*e.g.*, rare earths). They may also contain F or H_2O molecules. Deficiencies in A ions are almost absent in these phosphates despite the presence of easily leachable elements such as Ca and the rare earths. However, partial substitution of (PO_4) groups may occur. Examples are apatite, monazite, and xenotime.

In the second group of phosphates, the general formula is $A_xB_y(\text{PO}_4)_z(\text{OH})_{n \geq 0}$ but the B positions are occupied by relatively unstable cations. This group includes in particular secondary uranium phosphates such as autunite and phosphuranylite. These minerals are unstable and are rapidly destroyed by changes in the physicochemical conditions. They are characterized in the B positions by a leachable element.

The phosphate minerals of the third group also have the general formula $A_xB_y(\text{PO}_4)_z(\text{OH})_{n \geq 0}$ but the B positions are occupied by relatively stable cations. During alterations, they are replaced by one or more minerals with a different structure and leaching of cations occupying the A positions may occur. An example is the replacement of triphylite by tavorite and barbosalite characterized by leaching of Li and Na, partial oxidation of Fe^{2+} , and further hydration.

The fourth group consists mainly of phosphates in which alteration leads, in varying degrees, to deficiencies in both cations and anionic groups but which retain their structure with some changes in physical properties. Their chemical compositions may show wide ranges, depending upon the degree of alteration. These phosphates are mostly characterized by the general formula $A_xB_y(\text{PO}_4)_z(\text{OH})_{n \geq 0}$, where A is a leachable cation or a group of stable and leachable cations and B typically Fe^{3+} or Al. They show important deficiencies in the A positions and in the (PO_4) groups due to alteration.

Two highly cation-deficient phosphates were investigated:

- (i) calcium-phosphorus deficient mitridatites, and
- (ii) the new mineral eylettersite, which is a hydrated aluminium and thorium phosphate belonging to the crandallite series.

All specimens are from areas in Central Africa where weathering is particularly intense.

Knowledge of the alteration of such phosphate minerals is important not only from the viewpoint of the geochemistry involved, but from the practical aspect of geochemical prospecting.

THE CALCIUM-PHOSPHORUS DEFICIENT MITRIDATITES

Calcium-phosphorus deficient mitridatites have been found in several pegmatites of Central Africa: at Kobokobo in the Republic of Congo (Kinshasa) and at Kibingo, Kiluli, and Buranga in the Republic of Rwanda (L. Van Wambeke, 1969). At Kobokobo and at Buranga, mitridatite is formed after the minerals of the frondelite-rockbridgeite series, whereas at Kibingo mitridatite is an alteration product of hühnerkobelite-alluaudite together with cyrilovite. Both mitridatite and the associated frondelite or rockbridgeite have the same olive-green color but despite their identical color, mixture of these minerals easily can be detected by X-ray diffraction patterns. For large losses of Ca and P, the mitridatite becomes brown and the material is a mixture of highly altered and poorly crystallized mitridatite and limonite.

X-ray Diffraction Patterns of the African Mitridatites. The X-ray diffraction patterns of the African olive-green mitridatites were made with a Philips spectrometer using Cu $K\alpha$ radiation. The patterns obtained are essentially identical for all African mitridatites but show some variations in the d -values corresponding to differences in chemical composition and degree of alteration.

The X-ray diffraction patterns are very similar for both African and Soviet mitridatites (Chukhrov *et al.* 1958; Tarnovsky *et al.* 1968). The structure of mitridatite (Tarnovsky *et al.*, 1968) is hexagonal or pseudo-hexagonal.

For increasing grade of alteration, the dimensions of the unit cell increase, whereas the densities decrease. Also the crystalline state of the mineral decreases, the diffraction lines becoming broader.

Chemical Composition of African Mitridatites and an Associated Frondelite. Four chemical analyses were made of the purest materials available: three of mitridatites and one of an associated frondelite. The portions for analysis were carefully selected for purity after examination by X-ray diffraction and optical microscopy. The results of the new chemical analyses are compared with those of Soviet mitridatites in Table 1.

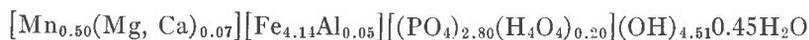
Of particular interest are the results for internal and external parts of the same Kobokobo sample, where appreciable differences in composition

COMPARISONS OF PHYSICAL PROPERTIES OF MITRIDATITES

	Unit-cell dimensions			Densities	
	<i>a</i> (Å)	<i>c</i> (Å)	<i>V</i> (Å ³)	calculated	measured
Mitridatite Usungeal unaltered (Tarnovsky <i>et al.</i> , 1968)	11.46	17.23	1960	3.20	3.28
Mitridatite Kobokobo already altered —internal zone—	11.50 ± 0.10	17.44 ± 0.08	1997	3.11	3.13
Mitridatite Kobokobo altered —external zone—	11.60 ± 0.10	17.48 ± 0.08	2037	3.03	3.03

have been found, especially for Ca and Fe³⁺. These results at first were inexplicable, so Ca, Fe, and P were redetermined by different methods to eliminate possible error or inhomogeneity of the samples. Since these tests gave similar results, it became apparent that differences in the degree of alteration were responsible for these chemical differences. This conclusion was fully confirmed by optical microscopy and density determinations. The differences are attributable to the sequence of crystallization in the pegmatite and subsequent hydrothermal alteration and weathering.

The frondelite associated with the analysed mitridatites of Kobokobo occurs in fibrous masses of olive-green color, often brownish superficially. The formula deduced from the chemical analysis (Table 1) is



Compared with the general formula of the frondelite rockbridgeite series, which is $A B_4(\text{PO}_4)_3(\text{OH})_5$ where



this oxidized frondelite is characterized by a higher degree of hydration due to partial substitution of tetrahedral hydroxyls H₄O₄ for (PO₄) groups. Compared with the general formula of the frondelite series, the total positive electric charge is almost conserved by substitution of (OH) by H₂O. Moreover, even taking account of the oxidation of Fe²⁺ occupying the *A* positions in Fe³⁺ calculated here in the *B* positions, this mineral

TABLE 1. CHEMICAL ANALYSES OF AFRICAN MITRIDATITES, AND OF A FRONDELITE

Analysed elements	Olive-green frondelite	Olive-green mitridatite ^a	Olive-green mitridatite ^b	Olive-green mitridatite ^c	Comparative analyses of Soviet mitridatites ^d	
	Ko/11/1	Ko/11/3A	Ko/11/3	KL/2/1	Usungeal Siberia	Novy Karatin Aertch-3 Novy Karatin Aertch-4
K ₂ O	n.d.	0.02	0.2	0.2	-	-
Na ₂ O	<0.2	0.10	<0.2	<0.2	-	-
Li ₂ O	<0.02	<0.03	<0.02	<0.02	-	-
CaO	0.01	12.59	4.70	4.27	17.68	16.68
BaO	tr	0.40	0.30	0.90	-	-
SrO	n.d.	0.03	<0.02	<0.02	tr	0.17
MgO	0.43	0.4	0.33	0.45	tr	0.60
MnO	5.71	-	-	-	0.57	-
MnO ₂	-	2.55	2.09	3.60	-	0.37
FeO	<0.20	<0.20	0.19	n.d.	1.13	-
Fe ₂ O ₃	52.78	39.67	47.90	46.95	38.15	38.60
Al ₂ O ₃	0.40	1.28	1.40	2.47	-	0.32
SiO ₂	0.04	1.22	0.90	1.50	-	-
P ₂ O ₅	31.62	30.32	30.00	27.39	32.62	30.84
TiO ₂	<0.01	tr	tr	-	-	-
CO ₂	-	n.d.	n.d.	n.d.	-	0.92
H ₂ O+	8.59	9.45	9.55	10.55	-	7.08
H ₂ O-	0.41	1.55	2.24	1.49	9.85	4.52
Insoluble	-	-	-	-	-	0.16
Total	99.98	99.58	99.70	99.77	100.00	100.22
						100.23

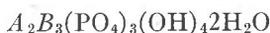
^aMineral impurities: quartz 0.7 % and MnO₂ as small nodules
^bMineral impurities: quartz 0.7 % an undetermined hydrated Al phosphate 1 % and MnO₂
^cMineral impurities: residual rockbridgeite 2 % and MnO₂; quartz 1 %
^dMineral impurity: quartz

Table 2: Optical Data of Calcium-Phosphorus Deficient and Unaltered Mitridatites

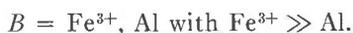
Properties	Calcium-Phosphorus deficient mitridatites - Central Africa				Unaltered mitridatites	
	Kobokobo - Kivu - Congo					
	External part KO/II/3	Internal part KO/II/3A	Buranga Rwanda	Kiluli Rwanda		Kibingo Rwanda
Color	yellow to yellow-brown	yellow to yellow-brown	brownish	brownish	brownish	yellowish brown
Crystalline forms	none	none	none	rare lamellae neg. elongation extinction angle 0°	rare lamellae neg. elongation extinction angle 0°	rare lamellae positive elongation
Pleochroism	none	none	none	none	none	yellowish brown to yellowish gray
Axial figures	uniaxial to biaxial - small	uniaxial to biaxial - small	no figures	no figures	no figures	biaxial
Mean index	1.805 to 1.825	1.785 to 1.815	1.805 to 1.835	1.805 to 1.84	1.79 to 1.815	1.755 to 1.775
Birefringence	low	low	low	low	low	low

has already lost part of the *A* ions, especially Mn. From our investigations, it is clear that the oxidized frondelites have all lost Mn by alteration and therefore their atomic ratio Fe/Mn increases gradually to values corresponding to those of rockbridgeites (higher than 8), particularly near the contact with mitridatites.

For mitridatite the general formula is (Chukhrov *et al.*, 1958):

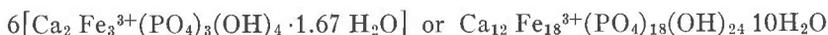


where



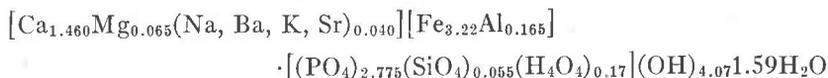
The *B* positions are occupied by stable cations, whereas the *A* positions are filled mainly by Ca, a leachable element.

Application to these data of the method proposed by McConnell (1967) gives the number of O per unit cell as 106 and $Z=6$. The structural formula of mitridatite is therefore

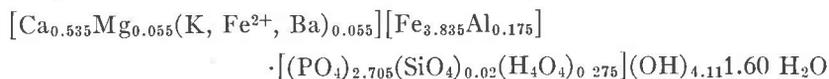


On the other hand, the effects of alteration on the physical properties are an increase in the volume of the unit cell and an accompanying decrease in the density. This increase in the volume of the unit cell and also of the total water content from about 10 percent to more than 12 percent H_2O in altered mitridatites and in their formula is consistent with a partial substitution of tetrahedral hydroxyls H_4O_4 for PO_4 (McConnell *et al.*, 1962; McConnell, 1965). Presumably the mitridatites have become deficient in P by alteration.

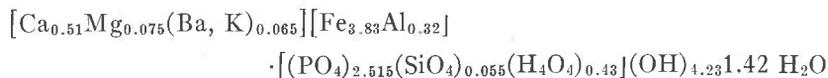
The structural formula for the three analysed mitridatites (Table 1) are: Sample Ko/11/3A—internal part, Kobokobo



Sample Ko/11/3 external part, Kobokobo

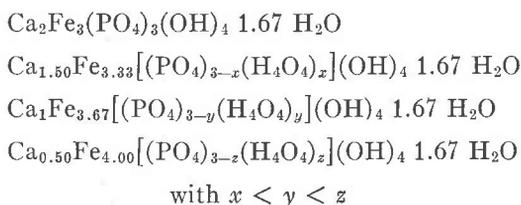


Sample Kl/2/1 Kiluli-Rwanda



These formulae clearly show the effects of alteration processes, here mainly weathering, on olive-green mitridatites. With increased alteration the value $B=3$ of the formulae (corresponding to the stable elements) Fe^{3+} and accessorially Al becomes higher, whereas the values $A=2$ and $(\text{PO}_4)=3$ (corresponding to the leachable elements) decrease. Also the hydration grade sharply increases beyond the theoretical value. The total positive electric charge in the three formulae is $+35.30$ and is similar to that of the unaltered compound with $1.67 \text{ H}_2\text{O}$ (35.34).

The leaching of Ca and P has led to an excess of Fe^{3+} in the formulae of altered mitridatites. By alteration the structural formulae theoretically become:



The values indicated for Fe must be slightly higher because of the substitution of (H_4O_4) for (PO_4) . These values well agree with the analysed mitridatites.

Nevertheless, both the refraction indices and the density measurements indicate that the Fe^{3+} in excess belongs to the structure. The structure of the mitridatites may thus readily accommodate the excess Fe^{3+} . This fact seems to be in relationship with the partial substitution of (PO_4) by (H_4O_4) as well as with the departure of A ions by leaching. The formation of limonite in highly altered materials changes the color from green to yellow-green and then yellowish brown.

The excess of Fe^{3+} in the formulae is due to *in situ* alteration of the mitridatites. It therefore constitutes an interesting parameter for characterizing the degree of alteration of these minerals. For unaltered mitridatites the (PO_4) value in the formula is about 2.9 because minor replacements by H_4O_4 may occur. The atomic ratio $\text{Fe}+(\text{Al})/\text{P}+(\text{Si})$ is thus 1.03 for unaltered analysed samples. The loss of (PO_4) groups by leaching reaches about the following values for our samples:

Internal part Kobokobo	13%
External part Kobokobo	30%
Kiluli	35%

Also some of the A ions, particularly Ca, have been leached out by alteration. The atomic ratio $(\text{Fe}+\text{Al})/(\text{Ca}+\text{other } A \text{ ions})$ is 1.5 in un-

altered mitridatites, but it must take into account the possible oxidation of Fe^{2+} , originally occupying the *A* positions, but calculated at Fe^{3+} in the *B* positions. The ratio 1.6 thus seems to be a maximum, Fe^{2+} being only an accessory *A* element in mitridatite. The loss of *A* ions, here mainly Ca, reaches about 25 percent of the *A* ions for the internal part of the Kobokobo mitridatite, about 74 percent for the corresponding external part, and 75 percent for the mineral of Kiluli. The results show that alteration is selective and concerns especially Ca and P for the mitridatites but the leaching rate of these elements is different, Ca being more easily leached out by about a factor of 2. These concepts become apparent from the compositional data contained in Table 1: decrease of the P and especially the Ca contents, larger amount of total water and abnormal high Fe^{3+} content. Therefore both atomic ratios $(\text{Fe}^{3+} + \text{Al})/(\text{Ca} + \text{other } A \text{ ions})$ and $(\text{Fe}^{3+} + \text{Al})/(\text{P} + \text{Si})$ increase approximately according to the degree of alteration. It follows that these altered mitridatites may be taken for a new species by their particular chemical compositions and formulae.

Optical Data and DTA. The optical properties of African mitridatites have been summarized in Table 2, where they are compared with mitridatites from the Kertch peninsula (Chukhrow *et al.*, 1958). The comparatively unaltered mitridatites of the USSR have lower mean refractive indices in conformity with their lower trivalent iron contents.

At Kiluli, Buranga, and Kobokobo the formation of mitridatite from frondelite or rockbridgeite is clearly observed and this alteration follows the cleavages. The primary minerals are biaxial positive and have higher refractive indices than the secondary altered mitridatites, and the primary minerals are characterized by a yellow to olive-brown pleochroism. Their birefringence is also much higher than that of mitridatite.

Locally, the Kobokobo samples contain inclusions of a hydrated Al phosphate (1 percent maximum) which often forms thin coatings on mitridatite and other phosphates. Under the microscope, this Al phosphate, which is probably a new species, occurs in flat prisms with $X = c$. It is biaxial positive with refractive indices $\gamma = 1.56$, $\beta = 1.558$, and $\alpha = 1.540$.

The DTA curve was made of the external part of the Kobokobo mitridatite, which shows a moderate endothermic effect with a maximum at 421°C and two well developed exothermic peaks at 750 and 1095°C . The most distinct exothermic peak at 750°C is somewhat different from that found for the Soviet mitridatites, where the maximum ranges from 675 to 705°C . It thus seems that a shift in the exothermic peak occurs as a result of alteration. The X-ray diffraction pattern obtained after heating

the sample to 950°C in air is very similar to the Soviet mitridatites (Chukhrov *et al.*, 1958)

EYLETTERSITE, ANOTHER CATION-DEFICIENT PHOSPHATE
IN THE CRANDALLITE SERIES

Eylettersite, a new hydrated Al and Th phosphate belonging to the crandallite series, has been found in the Kobokobo pegmatite already described (Safiannikoff *et al.*, 1967). Eylettersite occurs in pulverulent nodules of creamy white color. Most of the minerals in the crandallite series are intermediary substances among eylettersite, crandallite, and plumbogummite, all three of which are present at Kobokobo, the last one being rare. They have unusual chemical compositions because of intense alteration by hydrothermal and supergene solutions.

X-ray Diffraction Data. Eylettersite and thorian crandallite are hexagonal (rhombohedral) with space group $R\bar{3}m$. The entry of Th, U, and other A ions in substitution for Ca increases the value of c from about 16.13 Å in unaltered crandallite to about 16.70 Å for both eylettersite and thorian crandallite. Physical measurements for the analyzed eylettersites and the thorian crandallite are:

	Unit-cell dimensions			Densities	
	a (in Å)	c (in Å)	Volume (Å ³)	Calc.	measured (g/cm ³)
Eylettersite I (altered)	6.99±0.04	16.70±0.10	706.6	3.44	3.38±0.10
Eylettersite II (altered)	6.98±0.03	16.66±0.08	702.9	3.50	3.44±0.10
Thorian brandallite (altered)	6.98±0.04	16.72±0.08	705.4	2.94	2.85±0.12

The density measurements (pycnometric method) are particularly difficult because the minerals are often porous and pulverulent.

Chemical Compositions. Chemical compositions of two altered eylettersites and an altered thorian crandallite are given in Table 3. As and S were absent in all samples. Despite an abnormal high Al and Th content, the electron microprobe analysis shows a constant distribution of Th, P, and Al, suggesting the absence of amorphous aggregates of Th-or Al-containing substances. Part of the Si belongs to the structure, the remaining is in the altered zircon.

According to H. Strunz (1970), the general formulae for the minerals belonging to the crandallite series are:

TABLE 3. CHEMICAL ANALYSES OF ALTERED EYLETTERSITES AND A RADIOACTIVE CRANDALLITE

Elements analysed	Analyses corrected for impurities		
	Eylettersite I	Eylettersite II	Thorian crandallite
ThO ₂	18.43	20.10	6.70
UO ₃	3.05	3.10	1.50
CaO	0.72	0.55	1.25
BaO	1.45	1.90	0.60
SrO	0.1	0.2	0.30
PbO	4.62	3.11	0.2
Al ₂ O ₃	35.7 ^a	34.9 ^a	47.2 ^a
Fe ₂ O ₃	0.09	0.1	0.08
P ₂ O ₅	18.3	19.72	22.45
CO ₂	0.2	0.1	<0.1
SiO ₂	1.65	1.20	0.52
H ₂ O	15.0 ^a	14.4 ^a	19.4
ZrO ₂	0.95	1.0	-
Total	100.26	100.38	100.20
			100.26
			100.38
			100.20

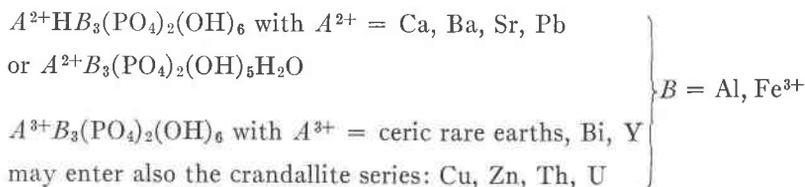
^a Elements retested by different methods

Mineral impurities

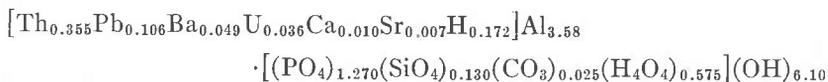
Eylettersite I: autunite 1.8 a 1.9 %; fluorapatite 0.9 %; limonite 0.1 %; highly altered zircon

Eylettersite II: autunite 1.3 %; fluorapatite 0.4 %; limonite and highly altered zircon

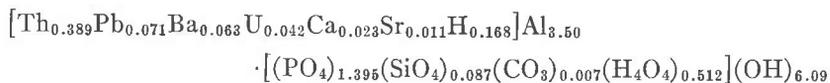
Thorian crandallite: autunite 0.3 %; fluorapatite 0.2 %; limonite.



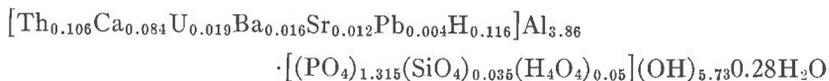
The minerals in the crandallite series are characterized in the *B* positions by elements stable to alteration processes whereas the *A* ions may or may not be removed by alteration. In the case of eylettersite, relatively stable *A* ions are Th, Ba, and Pb, whereas Ca, U, and to a lesser extent Sr are leached out by alteration. Altered minerals of this group show also deficiencies in P. The structural formulae (McConnell, 1967) for the analysed minerals are *Eylettersite I*¹



Eylettersite II



Thorian crandallite (an eylettersite most probably derived from a radioactive crandallite by alteration)



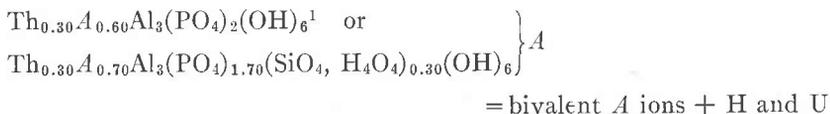
With alteration the value $B=3$ (of the formulae of unaltered minerals, increases, whereas the values $A=1$ and $(PO_4+SiO_4)=2$ (mainly Ca, U, P, and Si) decrease. The maintenance of the structure of the crandallite series can be explained only by partial substitution of (PO_4) and also (SiO_4) groups by tetrahedral hydroxyls. Also the density measurements and the degree of alteration of the two analysed eylettersites are in agreement with this concept.

The problem of the most probable formulae for the unaltered equivalents of the analysed minerals is much more difficult than for mitridatite.

In addition to Al in *B* positions, Th, Ba, and Pb are also relatively stable elements in the *A* positions. With increasing grade of alteration, these stable elements tend to increase their respective atomic percentages in the formulae. Considering the first eylettersite, two formulae are

¹ Probably U occurs as U^{3+} or U^{4+} in substitution for Ca^{2+} .

possible for the corresponding unaltered equivalent:

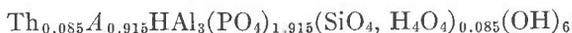


The second formula is the most probable because the entry of the tetravalent Th in the crandallite series is compensated by the partial substitution of (PO₄) groups by (SiO₄) groups and probably also by some tetrahedral hydroxyls as indicated by the presence of SiO₂ and the relatively low amount of P₂O₅ in all analysed materials.

Similarly, the most probable formulae for the unaltered equivalents of the eylettersite II and the radioactive crandallite are:



and



The total positive electric charge for the unaltered equivalents reaches +28.00. For the analysed minerals, the calculated positive charges are:

$$\text{eylettersite I: } + 28.11 \quad - \quad \text{eylettersite II: } + 28.17$$

$$\text{radioactive crandallite: } + 28.01$$

The small differences in the total positive electric charge are most probably related to the complexity of the chemical composition and also to the mineral impurities present. The total positive electric charge thus remains constant as for the altered mitridatites and confirms the absence of amorphous materials containing Al or Th.

As for mitridatites, the excess of Al constitutes an indication of the degree of alteration of eylettersites and thorian crandallites. The atomic ratio (Al+Fe)/(P+As+Si) of the unaltered minerals of the crandallite series is theoretically 1.5. However, this value becomes about 1.60 for these unaltered minerals because partial substitution of (PO₄) and (SiO₄) groups by (H₄O₄) has most probably occurred, these minerals being formed during the last stage of the pegmatite differentiation. The approximate losses of (PO₄)+(SiO₄) groups by alteration are eylettersite I 37 percent, eylettersite II 32 percent, and thorian crandallite 45 percent. The leaching of the A ions was selective and concerns Ca, U, and, to a far lesser extent, Sr. The contribution of the remaining A ions of the

¹ Obtained by multiplying 3.00×0.355/3.58 in the formulae given for the analysed mineral. U is considered here as U³⁺.

TABLE 4. DISTRIBUTION OF THE REMAINING AND LEACHED A IONS IN THE FORMULAS OF THE UNALTERED EQUIVALENTS OF THE ANALYSED MINERALS

	Distribution of the remaining A ions in the formulae				Remaining A ions (in at. percent)		Leached A ions (in at. percent)
	Th	Pb	Ba	leach- stable able Ca + U + Sr	% of A ions occupied	% of A stable positions occupied	Total loss %
Eylettersite I	0.30	0.09	0.04	0.04	43	47	53
Eylettersite II	0.335	0.06	0.07	0.07	45	52	48
Th-crandallite	0.082	0.003	0.012	0.09	10	19	81

altered minerals and the leached elements in the unaltered equivalent is given in Table 4.

It emerges (Table 4) that the analysed minerals have lost by alteration respectively 53, 48, and 81 percent of the *A* ions, particularly Ca and U. The leaching rate of Ca is higher than U^{4+} by a factor 2–2.5 for the complex titano-niobo-tantalates (L. Van Wambeke, 1970). However, here U is certainly more easily leached out than in these refractory minerals, autunite being formed inside eylettersites or radioactive crandallites as a result of alteration. Considering an approximate identical leaching rate for Ca and U, the unaltered equivalent of the eylettersite I had about the same atomic percentage for Th, U, and Ca in its formula. The Th in the unaltered equivalent of the second eylettersite remains prevalent, probably with U slightly higher than Ca in atomic percentage. The atomic distribution in the formula of the unaltered equivalent of the thorian crandallite was $Ca > U > Th$ and this last mineral is most probably derived from a radioactive-rich variety of crandallite.

Similarly to altered mitridatites, the analysed eylettersites and the thorian crandallite show an unusual chemical composition (Table 3) as a result of hydrothermal and supergene alteration, namely, a sharp decrease in the contents of leachable *A* ions and of (PO_4) and (SiO_4) groups accompanied by a higher content of stable elements, in particular Al.

Optical Properties. Refractive indices for the altered eylettersite and for the thorian crandallites showed appreciable ranges:

Thorian crandallite	1.575–1.60 mean value 1.585	} Uniaxial, low to very low birefringence
Eylettersite I	1.615–1.64 mean value 1.635	
Eylettersite II	1.625–1.66 mean value 1.645	

In general refractive indices higher than 1.62 characterize altered eylettersites, whereas the altered radioactive crandallites have indices of less than 1.62. Moreover, despite the presence of Th, U, and Pb in the altered radioactive crandallites, their refractive indices are lower than those of unaltered crandallites. This is a consequence of alteration. However, here, in contrast to mitridatite, the refractive indices decrease with alteration not only because of the higher degree of hydration but also because of their higher Al contents. It should be noted that Al has a significantly lower ionic refractivity than Fe^{3+} (McConnell, 1964).

Eylettersite is not only the first radioactive mineral in the crandallite series, but also the first hydrated Th phosphate found in nature, the mineral kivuite being often a mixture of thorian crandallite or eylettersite with phosphuranylite (L. Van Wambeke, 1958).

A HIGHLY ALTERED FLORENCITE

At Modubwe, Kivu, in the Republic of Congo (Kinshasa), a florencite occurs in microscopic fibrous nodules dispersed through a kaolinite mass in a cassiterite vein. Separation of the two minerals is not possible. The material gives the typical X-ray diffraction pattern of florencite besides that of kaolinite, though the broadening of the florencite lines indicates poorly crystallized material. The florencite content is difficult to determine with accuracy, but is 10 percent or more.

The refractive indices of this florencite are between 1.62 and 1.64, lower than that of unaltered florencite. X-ray fluorescence analyses show the presence of P, cerium earths, and Ca, besides Al and Si. A chemical analysis made on 100 g material gave the following results:

SiO_2 39.50% P_2O_5 1.27% H_2O^+ 14.75%

Al_2O_3 37.70% CaO traces H_2O^- 1.68%

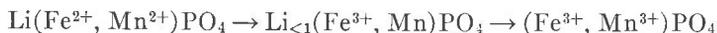
Fe_2O_3 4.29% RE oxides 0.90%

The low content of cerium earths, Ca and P found on analysis despite the small amount of florencite in the clayey material, together with the low refractive indices, indicate an altered phosphate. It seems that during alteration processes the mineral lost a large proportion of its cerium earths, P and probably Ca.

OTHER EXAMPLES OF ALTERED PHOSPHATES

In the mineralogical literature, altered phosphates retaining the structure of the original mineral are quite numerous. Many of these phosphates have Fe^{2+} in the *A* or *B* positions. Examples of these are the sicklerite and heterosite series, secondary minerals often formed by oxidation of the minerals belonging to the triphylite series:

triphylite series \rightarrow sicklerite series \rightarrow heterosite series



All these minerals have the same structure (Strunz, 1970) with minor changes in parameter values. Alteration processes, mainly weathering, lead to the oxidation of Fe^{2+} and Mn^{2+} , a progressive leaching of alkalis, especially Li and Na, and of Ca, and a slight decrease in the P content compensated by the entry of (OH) groups. The X-ray diffraction patterns show a decrease in the unit-cell dimensions from triphylite to heterosite. The oxidation of Fe and Mn and the leaching of Li, Na, and Ca leads to a sharp increase in the mean refractive indices to 1.68–1.69 for the triphylite series, to 1.74 for the sicklerite series, and finally to 1.86–1.90 for the heterosite series. Such phosphates derived from the triphylite series are regarded as distinct species, whereas the oxidized equivalents of the frondelite series also characterized by a loss of *A* ions are not distinct species.

The minerals ferrisicklerite and sicklerite can therefore be regarded as oxidized minerals of the triphylite series which have lost by alteration part of the *A* ions, especially Li. This last alkali metal has a very high leaching rate.

The situation is similar in the case of the minerals in the alluaudite series, which are oxidized alteration products of the varulite series. Here also oxidation is associated with a leaching out of alkali metals and Ca. Again, the mineral sigloite may be the oxidized equivalent of paravauxite.

ALTERATION AND NOMENCLATURE OF THE PHOSPHATES WITH GENERAL FORMULAE $A_xB_y(\text{XO}_4)_z(\text{OH})_{n \geq 0}$

The examples mentioned before concerning the triphylite, the frondelite, and the alluaudite series show that the nomenclature of several phosphate minerals must be reviewed taking into account the modifications of the physical properties and the chemistry due to alteration processes. Moreover, altered phosphates could be sometimes taken for a new mineral species because their particular compositions and formulae always showing an excess of stable elements. At present no general agreement exists for the nomenclature of oxidized and often leached iron-mangan phosphates which conserve the same structure as their unaltered equivalents. The problem of the nomenclature of several altered phosphates therefore requires a solution and I shall try here to give a possible suggestion. To avoid unnecessary names, the prefix oxy (for example oxyfrondelite) could be useful for designating an altered and oxidized phosphate with or without leached *A* ions. In the other phosphates of general formulae $A_xB_y(\text{XO}_4)_z(\text{OH})_{n \geq 0}$ where oxidation is absent or minor, the prefix keno as suggested by Permingeat for cation-deficient minerals

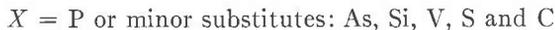
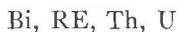
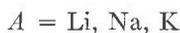
belonging to the pyrochlore group could be applied for designating cation-deficient phosphates characterized by an abnormal chemical composition. The minerals studied here could be named keno-mitridatite and keno-eylettersite. Partial substitution of tetrahedral hydroxyls for (PO₄) groups but without significant leaching of *A* ions may probably also occur in nature. The prefix hydroxy already used for apatite may be helpful for designating such highly hydrated phosphates, whether formed in particular conditions or by alteration.

MAIN CHEMICAL AND PHYSICAL CHARACTERISTICS OF ALTERED
PHOSPHATES WITH GENERAL FORMULA $A_xB_y(XO_4)_z(OH)_{n \geq 0}$

As was briefly described in the introduction, the behavior of phosphates minerals during alteration processes varies widely. This paper constitutes a first approach to the problem of the alteration of phosphate minerals having the general formula $A_xB_y(XO_4)_z(OH)_{n \geq 0}$.

The study is based mainly on two typical examples, the hydrated minerals mitridatite and eylettersite. The results of this study may be summarized as follows:

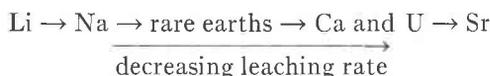
- 1) Alteration associated with relatively important changes in the chemical composition but only with minor changes in the original structure mainly concerns the phosphates of general formula $A_xB_y(XO_4)_z(OH)_{n \geq 0}$ and in particular those containing leachable *A* ions. In the formulae we have:



- 2) Alteration due to late hydrothermal solutions or (and) to weathering produces, especially in the case of originally hydrated phosphates (mitridatite, eylettersite), deficiencies in leachable *A* ions and P as well as an increase in hydration. Oxidation of Fe²⁺ and Mn²⁺ occurs when these elements are present in the *A* positions. The effects of alteration on unhydrated phosphates (sicklerite and varulite series) are mainly limited to a leaching of *A* ions and an oxidation of Fe²⁺ and Mn²⁺.

For the hydrated phosphates, deficiencies in *A* positions may reach

70 percent or more and 40–50 percent of (PO_4) groups may be substituted by H_4O_4 with preservation of the original structure. Present data indicate that leachable A ions are increasingly resistant to leaching in the following order:



Relatively resistant A ions to alteration processes are Ba, Pb, and Th.

- 3) The chemical composition of cation-deficient phosphates show an abnormally high content of stable B ions (here Fe^{3+} and Al), a higher degree of hydration and variations in the oxide contents even for the same mineral sample (*e.g.*, external and internal zones of the mitridatites of Kobokobo). The formulae of altered hydrated phosphates are thus very different from the theoretical formulae of unaltered equivalents. The atomic ratios $(\text{Al} + \text{Fe}^{3+})/\text{P}$ and $(\text{Al} + \text{Fe}^{3+})/\text{A}$ ions increase according to the degree of alteration.
- 4) The original structure of altered phosphates with formula $A_xB_y(\text{XO}_4)_z(\text{OH})_{n \geq 0}$ is preserved with only minor changes in the physical properties. The volumes of the unit cells of hydrated phosphates become slightly higher with increasing alteration. In the altered but non-hydrated phosphates where oxidation of Fe^{2+} or Mn^{2+} has occurred, the general trend is to a decrease in unit-cell size (triphylite→ferrisicklerite→heterosite). Most of the altered hydrated phosphates also show broad diffraction lines, indicating a small crystallite size or defects in crystalline organization.
- 5) The density decreases with alteration and shows a range for the same mineral specimen. Abnormally low density values may be obtained in highly altered phosphates compared with unaltered samples, especially when significant hydration has occurred.
- 6) The refractive indices also show a wide range due to the alteration. For altered hydrated phosphates with Al in the B positions the change is a decrease, whereas for those containing Fe^{3+} in the B positions there is an increase.
- 7) DTA curves of altered minerals are characterized by a shift in the peaks, but a complete interpretation of these changes is not possible at present.
- 8) The nomenclature of several altered phosphates of general formula $A_xB_y(\text{XO}_4)_z(\text{OH})_{n \geq 0}$ must be reviewed taking the alteration into account. Prefixes such as oxy, keno and hydroxy could be helpful for designating the type of alteration.

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