BULLETIN DE L'ASSOCIATION MINÉRALOGIQUE DU CANADA

THE CANADIAN MINERALOGIST

JOURNAL OF THE MINERALOGICAL ASSOCIATION OF CANADA

Volume 42 June 2004 Part 3

The Canadian Mineralogist
Vol. 42, pp. 697-704 (2004)

PETROGRAPHIC EVIDENCE FOR PRIMARY HAGENDORFITE IN AN UNUSUAL ASSEMBLAGE OF PHOSPHATE MINERALS, KIBINGO GRANITIC PEGMATITE, RWANDA

André-Mathieu FRANSOLET and Frédéric HATERT

Laboratoire de Minéralogie, Département de Géologie, Université de Liège, Bâtiment B18,
Sart Tilman, B-4000 Liège, Belgique

François FONTAN

Laboratoire de Minéralogie, Université Paul-Sabatier de Toulouse, 39, Allées Jules-Guesde, F-31000 Toulouse, France

ABSTRACT

A sample from the Kibingo granitic pegmatite, Rwanda, shows a striking assemblage of an alluaudite-group mineral with heterosite. The core of alluaudite *s.l.* is strongly pleochroic in blue green to pinkish grey hues, and is rimmed by an irregular border, weakly pleochroic in yellow brown to greenish yellow tints. The pleochroic core is very rich in Na (up to 9.35% Na_2O), whereas the yellowish green border is depleted in Na (3.75% Na_2O) and more oxidized. The decrease of the Na contents is not accompanied by significant variations of the ratio $Fe_{tot}/(Fe_{tot} + Mn)$. This mechanism represents the progressive transition of hagendorfite to alluaudite *sensu stricto*, and results from an oxidation, $Na^+ + Fe^{2+} \rightarrow \square + Fe^{3+}$. Heterosite exhibits cracks that are parallel to one of the cleavage directions, and that are favorable to the development of a product of alteration, identified as cyrilovite. Heterosite shows a chemical composition close to the idealized formula $(Fe^{3+}_{0.85}Mn^{3+}_{0.15})PO_4$, with a Mg content constant and quite low, *i.e.*, 0.023 Mg *apfu*. The Kibingo heterosite seems to be the Fe-richest member known so far. The heterosite corresponds to an oxidized Fe-rich member of the triphylite – lithiophilite series, a member that was initially in equilibrium with the primary hagendorfite. The ratio $Fe_{tot}/(Fe_{tot} + Mn)$ of the two minerals of this assemblage is different: the value is about 0.70 in hagendorfite, and 0.85 in the former triphylite. The temperature of formation of hagendorfite is estimated at about 600°C. Contrary to the information in the literature, the Kibingo pegmatitic body differs from the amblygonite pegmatite of Mwaka and could be a poorly evolved neighboring pegmatitic lens.

Keywords: hagendorfite, alluaudite, heterosite, phosphate mineral assemblage, Kibingo granitic pegmatite, Rwanda.

SOMMAIRE

Un échantillon provenant de Kibingo, Rwanda, montre une paragenèse remarquable d'un minéral du groupe de l'alluaudite avec l'hétérosite. Les plages d'alluaudite *s.l.* ont un noyau fortement pléochroïque dans les vert bleu à gris rosâtre, entouré d'une bordure irrégulière, colorée en jaune brun à jaune verdâtre, faiblement pléochroïque. Le noyau pléochroïque est très riche en Na (jusqu'à 9.35% Na_2O), et la bordure jaune verdâtre est nettement moins riche (avec 3.75% Na_2O) et plus oxydée; l'appauvrissement en sodium ne s'accompagne pas de variations significatives du rapport $Fe_{tot}/(Fe_{tot} + Mn)$. On passe donc

---

§ *E-mail address*: amfransolet@ulg.ac.be

progressivement de la hagendorfite à une alluaudite *sensu stricto*; cette transition progressive résulte d'un mécanisme d'oxydation, $Na^+ + Fe^{2+} \rightarrow \square + Fe^{3+}$. L'hétérosite montre une fissuration parallèle à une des directions de clivage et favorable au développement d'une phase d'altération, la cyrilovite. La composition chimique de l'hétérosite est proche d'une formule idéalisée $(Fe^{3+}_{0.85}Mn^{3+}_{0.15})PO_4$, avec une teneur en Mg constante et plutôt faible, soit 0.023 Mg par unité formulaire. L'hétérosite de Kibingo apparaît comme le terme le plus riche en fer actuellement connu. L'hétérosite est issue d'un terme riche en fer de la série triphylite – lithiophilite, initialement en équilibre avec la hagendorfite primaire. Le rapport $Fe_{tot}/(Fe_{tot} + Mn)$ est différent entre les deux minéraux de cette paragenèse: la valeur est de 0.70 dans la hagendorfite et de 0.85 dans la triphylite. La température de formation de la hagendorfite serait d'environ 600°C. Contrairement aux informations de la littérature, le gisement de Kibingo ne serait pas la pegmatite à amblygonite de Mwaka, mais une lentille pegmatitique voisine, moins différenciée.

Mots-clés: hagendorfite, alluaudite, hétérosite, paragenèse de phosphates, pegmatite granitique de Kibingo, Rwanda.

INTRODUCTION

The primary origin of alluaudite-group minerals, complex Na-, Fe- and Mn-bearing phosphates occurring in granitic pegmatites, was alluded by Fisher (1958), in his presidential address: "Quensel puts alluaudite in his supergene stage at Varuträsk; nevertheless, in some of its occurrences, it is definitely a primary mineral". However, this theme was not raised further in the literature dealing with genetic problems of the phosphates, especially with respect to the alluaudite-group minerals in a pegmatitic environment. These minerals are thus generally considered to be secondary products, derived from triphylite-group minerals by Na-for-Li metasomatic exchange, as suggested by Moore (1971). Although a metasomatic origin seems to be valid in many cases (Huvelin *et al.* 1972), caution has been expressed about the occurrence of alluaudite *sensu stricto* in the Buranga mine, Rwanda (Fransolet 1977, Héreng 1989). More recently, fillowite – alluaudite parageneses described from the Buranga and Rusororo granitic pegmatites, Rwanda, and from Kabira, Uganda, led to the conclusion that the alluaudite has a non-metasomatic origin (Fransolet *et al.* 1998).

In the context of our investigation of phosphates from granitic pegmatites of central Africa, the petrographic study of one sample has revealed striking textures that clearly demonstrate the syncrystallization of an alluaudite-group mineral, together with a member of the triphylite – lithiophilite series, oxidized later to heterosite. Although the results of this study concern only one specimen held by the Musée royal d'Afrique centrale at Tervuren, Belgium, and although the geological information about the host body is rather tenuous, we believe that this note will shed additional light on the genetic problem of the primary phosphate minerals in granitic pegmatites.

GEOGRAPHICAL AND GEOLOGICAL BACKGROUND

We carried out a study of a phosphate sample from the mineral collection of the Musée royal de l'Afrique centrale (M.R.A.C.), reference number RGM 5469. According to the general register of this institution, this sample originates from "Mont Kibingo, Gis. Mirudi, Ruanda".

According to the archives of the mining development deposited at the M.R.A.C., there is virtually no doubt that the following names, Kibingo or Kibinga (relating to a hill), Lemera and Mwaka, refer to the same body of granitic pegmatite. It is located 23 km west of Gitarama, along the Gitarama – Kibuye road (M. Errera, pers. commun.). Monteyne-Poulaert *et al.* (1962) located the Lemera pegmatite, south of Gatumba, along the Gitarama – Mwaka road, at the Lambert coordinates 29°38'E and 2°05'S, which exactly corresponds to the information in the archives.

There is no comprehensive geological description of this body of granitic pegmatite. The information found in the literature is rather sparse. According to the field observations from M.R.A.C. and the Geological Survey of Rwanda, and the geological map of Rwanda (Nyabisindu sheet, S3/29 NE, 1991), the Kibingo pegmatite is enclosed within black or dark grey schists, including whitish interlayers of quartzite, belonging to the pelitic Bulimbi Formation, in the Pindura Group (M. Errera, pers. commun.). The Pindura Group is generally considered to belong to the Mesoproterozoic (1600 to 1800 million years) (L. Tack, pers. commun.).

From a mineralogical point of view, Thoreau & Bastien (1954a) simply reported that the Mwaka pegmatite is similar to the Buranga body and represents a columbite-rich pegmatite, mined at that time by the Mirudi company ("Compagnie minière au Ruanda–Urundi"). Moreover, they mentioned the occurrence of lazulite, associated with huge irregular masses of montebrasite in close proximity to the quartz core (Thoreau & Bastien 1954b). Varlamoff (1961) pointed out that pegmatites "*à noyau riche en amblygonite avec cristaux géants de spodumène et autres phosphates*" (exhibiting an amblygonite-rich core with giant crystals of spodumene and other phosphate minerals), belonging to type 6 of his classification, also crop out south of the pegmatitic field of Gatumba, in the Mwaka mine concessions. According to Monteyne-Poulaert *et al.* (1962), the Lemera body is a pegmatite rich in slightly greenish mica, in niobotantalate minerals, in beryl, and in phosphate minerals. Finally, Van Wambeke (1969) gave a mineralogical description of three phosphates, "hühnerkobelite" (= Ca-rich alluaudite), cyrilovite and mitridatite, occurring in the Kibingo pegmatites (at about 20 km west of Kigarama, Rwanda). The author also mentioned the presence of heterosite accompanied by Fe- and Mn-oxides, and reported that "hühnerkobelite", which is distinctly pleochroic, alters to alluaudite of yellow color, weakly pleochroic. However, Van Wambeke (1969) did not describe the petrographic relationships between the two minerals.

DESCRIPTION OF THE PHOSPHATE ASSOCIATION

Sample RGM 5469 is rectangular, 25 × 15 × 15 cm, rather dense, dark green to black in color, with some purplish blebs and a few ocher specks. An investigation of thin sections under the polarizing microscope immediately reveals a polygranular texture of two groups of major minerals, as roughly equidimensional grains of variable size. All the grains are intensely colored, with very distinct pleochroism. Moreover, in crossed polars, a few grains display anomalous interference-colors owing to intense absorption or to a strong dispersion. These properties prevent accurate determination of optical features in conoscopic light.

Green grains of an alluaudite-group mineral, generally up to 0.5 mm across, and exceptionally up to 5 mm, constitute the first group of minerals. The larger grains show an undulatory extinction, with warped cleavage planes, and are intersected by fine-grained zones with a grain size of 30 up to 50 μm. This observation strongly suggests the presence of crushing caused by deformation subsequent to crystallization. Different cleavage planes can be seen; in some grains, the arrangement of these cleavage traces is similar to that already described by Huvelin *et al.* (1972) in the case of the specimen of calcium-rich ferri-alluaudite from Sidi-Bou-Othmane, Morocco. The grains of alluaudite *s.l.* have a rather complex coloring (Fig. 1), as they systematically exhibit a core strongly pleochroic in blue green to pinkish grey hues, rimmed by an irregular border, weakly pleochroic in yellow brown to greenish yellow tinges. These colors were pointed out by Van Wambeke (1969), who even measured the indices of refraction of "hühnerkobelite" and noted its pleochroism: *Z* greyish, *Y* turquoise blue, and *X* dark blue. Moreover, we note that the yellow brown to greenish yellow coloration takes form along the cleavages, isolating in this way small, strongly pleochroic parts of the grains. Whereas an interference figure in conoscopic light cannot be obtained on the grain's rim, we do know that the strongly pleochroic central part is biaxial positive with an apparently small 2*V*.

The second group of major minerals present on the specimen corresponds to heterosite occurring as equant grains with two orthogonal cleavage planes, and intensely pleochroic in violet to red brown with brownish grey tinges. This identification was checked by X-ray diffraction (powder method). The grains showing a weak pleochroism, yellowish brown to red orange, do not consist of ferrisicklerite; they represent sections virtually perpendicular to the optical axis of heterosite. The heterosite displays cracks that follow one of the cleavage directions; they resemble those reported by Fontan *et al.* (1976) in ferrisicklerite from Sidi-Bou-Othmane. Unlike Fontan *et al.* (1976), we are unable to define the orientation of the cleavage plane along the fissure. The fissures host an alteration product, yellowish to orange in color when observed in crossed polars, which forms strips with a thickness of about 20 to 30 μm. Data obtained by X-ray diffraction and electron-microprobe analysis served to identify cyrilovite, $NaFe^{3+}_3(PO_4)_2(OH)_4•2H_2O$, already mentioned by Van Wambeke (1969).

Among the accessory phases, there are poorly crystalline grains of phosphosiderite replacing yellow brown to greenish yellow alluaudite only. The grains of heterosite also are replaced by another brownish yellow mineral; it is very fine-grained, associated with opaque oxides, and could correspond to cacoxenite. These conspicuous examples of pseudomorphism derive from a late process of alteration. They are particularly visible along fractures, cracks or veinlets that cross-cut the sample and are filled with undetermined Fe (and Mn ?) oxides or hydroxides.

RESULTS OF THE CHEMICAL ANALYSES

The chemical analyses were performed with a Cameca SX–50 electron microprobe operating in the wavelength-dispersion mode, with an accelerating voltage of 15 kV, and a beam current of 10 nA. The following standards were used: graftonite from Kabira (P), Al_2O_3 (Al), hematite (Fe), pyrophanite (Mn), periclase (Mg), sphalerite (Zn), wollastonite (Ca), albite (Na) and sanidine (K).

Results of five representative electron-microprobe analyses on alluaudite *s.l.* are selected from a total of 41 data-sets, and classified according to decreasing Na contents (Table 1). Cation numbers are calculated on the basis of 12 PO_4 in the unit cell, and the $Fe^{3+} – Fe^{2+}$ contents are determined to maintain the electrostatic balance of 96 negative charges in the unit cell (Fontan 1978). The cation distribution in the various crystallographic sites of the structure, $[A(2)A(2)'][A(1)A(1)'A(1)''_2]M(1)M(2)_2(PO_4)_3$, calculated according to the method published by Moore (1971) and slightly modified by Hatert *et al.* (2000), is shown in Table 2 for two cases only, representative of the intensely pleochroic phase very rich in Na, and of the yellowish green phase of the cortex, distinctly less rich in Na but more oxidized (Fig. 1). If the proposal of Moore & Ito (1979) on the nomenclature of alluaudite *s.l.* is used in the case of Kibingo, a progressive transformation from hagendorfite, $Na_2Mn(Fe^{2+}Fe^{3+})(PO_4)_3$, to alluaudite *sensu stricto*, $NaMnFe^{3+}_2(PO_4)_3$, can be thus deduced (Tables 1, 2).

Among the 26 electron-microprobe analyses made on heterosite, results of two representative analyses are also given in Table 1. With the ratio $Fe_{tot}/(Fe_{tot} + Mn)$ varying between 0.86 and 0.83, the mineral is close to

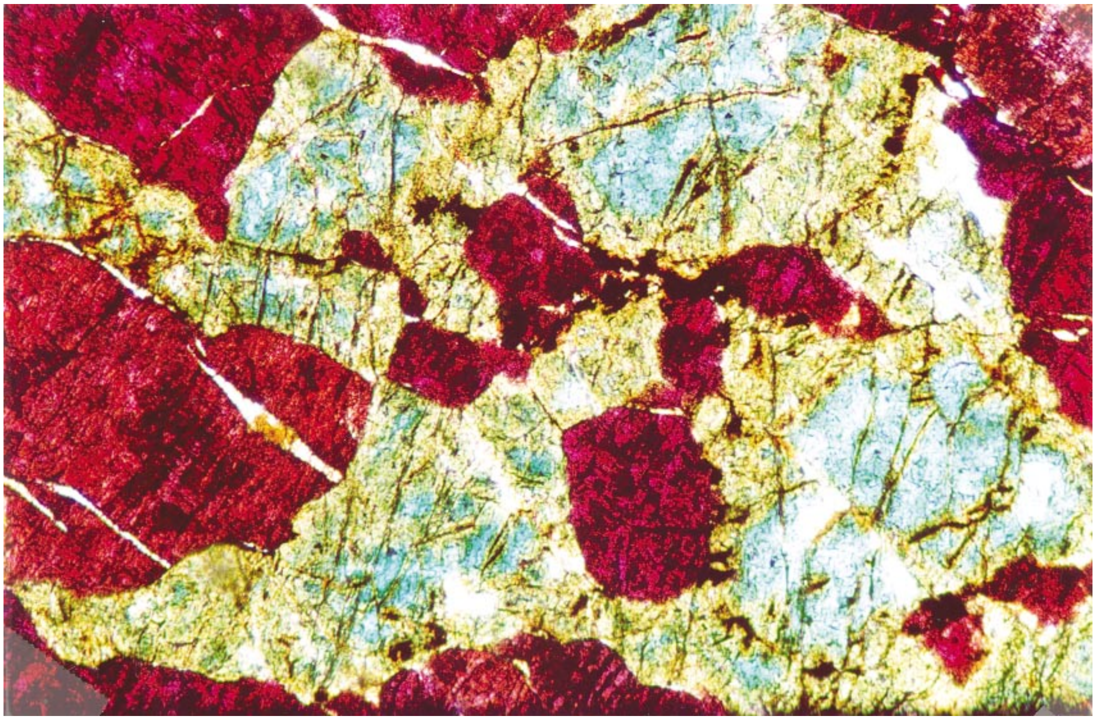

FIG. 1. Microphotograph (polarizing microscope, plane-polarized light) showing reddish purple grains of heterosite, and cores of blue-green hagendorfite rimmed by greenish yellow alluaudite *sensu stricto*. A few strips of cyrilovite are visible in the heterosite grains. Width of field of view is 3.0 mm.

the ideal formula $(Fe^{3+}_{0.85}Mn^{3+}_{0.15})PO_4$, with a constant and rather low Mg content of 0.023 *apfu* (atoms per formula unit).

The average result of five point-analyses performed on the cyrilovite strips is given in Table 1 as well, where it is compared with the theoretical composition, and with analytical results recently made on cyrilovite from Cyrilov, Czech Republic (Novák *et al.* 2000). The data obtained herein differ slightly from those given for the type locality. Moreover, we note a notable deficiency in Na, even if a possible replacement of Na by Ca is envisaged, as also suggested by Novák *et al.* (2000).

MINERALOGICAL DATA

In this section, we shall successively discuss relevant crystallochemical features of the hagendorfite, alluaudite *s.s.*, and heterosite, mostly deduced from the results gained from the electron-microprobe data.

Hagendorfite

Following the results obtained for the chemical composition of hagendorfite from Kibingo (Tables 2, 1), the Na-rich member is characterized by the presence of about 7.35 atoms of Fe, among which 5.3 Fe^{2+}, at the *M*(2) sites, the remainder of the eight cations being made up by 0.4 Mg *apfu* and 0.25 Al *apfu*. Zinc, whose presence in the phosphate associations at Kibingo was already mentioned by Van Wambeke (1969), plays an accessory role. At the *M*(1) sites, about 1.5 atoms Fe^{2+} and 2.5 Mn can be found. Finally, whereas the *A*(2)' site is almost fully occupied by 3.9 Na *apfu*, the *A*(1) site contains 0.8 Mn, 1 Ca and 2.2 Na *apfu*. Moore (1971) already reported that an occupancy of *A*(1) by about 50% of divalent cations results in an important content of divalent cations at *M*(2), particularly where the *A*(2)' site is completely occupied by Na. Among the 17 chemical compositions of alluaudite *s.l.* considered by Moore & Ito (1979), this characteristic appears in seven cases, among which three correspond to hagendorfite.

Alluaudite sensu stricto

The chemical composition of alluaudite *sensu stricto* invites a few comments as well (Table 2, sample 5). The Al content, about 0.65 wt.% Al_2O_3, corresponding to

0.25 cations of Al at *M*(2) per unit cell, remains virtually constant. The Mg content does not vary either. From the data given in Table 1 and the Na – Fe_{tot} – Mn diagram (Fig. 2), one can see that Na is notably depleted during the transformation of hagendorfite to alluaudite *sensu stricto*. Indeed, the amounts of Na clearly decrease from 9.35 to 3.75 wt.% Na_2O from the core of the alluaudite *s.l.* grains to their border. Moreover, Figure 2 shows that this depletion in sodium is not accompanied by an obvious variation of the ratio Fe/Mn. The Mn – Fe^{2+} – Fe^{3+} diagram proposed by Fisher (1957) confirms this relative constancy of the Fe/Mn value for the 41 electron-microprobe-derived compositions (Fig. 3). The slight fluctuation of the ratio $Fe_{tot}/(Fe_{tot} + Mn)$ in the alluaudite group can be seen from the Mg – Fe_{tot} – Mn diagram (Fig. 4) as well. This ratio fluctuates in the range of 0.73 to 0.68, a range that could in addition be affected by analytical errors. By its ratio $Fe_{tot}/(Fe_{tot} + Mn)$, the Kibingo alluaudite is relatively similar to that from the Tsaobismund pegmatite, characterized by $Fe_{tot}/(Fe_{tot} + Mn) = 0.75$, with 0.68 Mg per unit cell (Fransolet *et al.* 1986).

TABLE 1. REPRESENTATIVE RESULTS OF ELECTRON-MICROPROBE ANALYSES OF HAGENDORFITE, OF ALLUAUDITE *sensu stricto*, OF HETEROSITE, AND THE AVERAGE CHEMICAL COMPOSITION OF CYRILOVITE FROM KIBINGO, RWANDA

	1	2	3	4	5	6	7	8	9	10
P_2O_5 wt.%	41.82	41.86	42.85	43.40	42.03	44.47	45.62	28.49	29.30	29.40
Al_2O_3	0.63	0.66	0.70	0.60	0.59	0.00	0.08	0.32		0.02
[Fe_2O_3]	7.92	8.97	15.73	19.78	20.40	42.42	41.13	47.15	49.44	49.35
[FeO]	23.98	22.83	16.59	12.91	12.63					
[Mn_2O_3]						7.08	8.51			
MnO	11.45	12.79	13.33	14.32	12.9			0.40		
MgO	0.71	0.83	0.85	0.90	0.83	0.59	0.59	0.02		
ZnO	0.22	0.11	0.33	0.48	0.00	0.15	0.43			
CaO	2.77	2.97	2.93	2.89	2.72	0.08	0.32	0.43		0.53
Na_2O	9.35	7.63	5.71	4.12	3.76	0.00	0.06	5.50	6.40	6.15
K_2O	0.07	0.07	0.12	0.02	0.04	0.04	0.03	0.01		
[H_2O]								[14.86]	14.86	[14.93]
Total	98.92	98.72	99.14	99.42	95.90	94.83	96.77	97.18	100.00	100.38
Number of cations on the basis of fixed P contents **										
P *apfu*	12.000	12.000	12.000	12.000	12.000	1.000	1.000	4.000		
Al	0.252	0.263	0.273	0.231	0.235	-	0.002	0.063		
Fe^{3+}	2.020	2.285	3.915	4.861	5.176	0.848	0.802	5.892		
Fe^{2+}	6.798	6.465	4.589	3.527	3.561					
Mn^{3+}							0.143	0.168		
Mn^{2+}	3.287	3.668	3.735	3.961	3.685			0.056		
Mg	0.359	0.419	0.419	0.438	0.417	0.023	0.023	0.005		
Zn	0.055	0.028	0.081	0.116	0.000	0.003	0.008			
Ca	1.006	1.078	1.038	1.011	0.983	0.002	0.009	0.077		
Σ							1.019	1.012		
Na	6.144	5.009	3.662	2.609	2.459	-	0.003	1.770		
K	0.030	0.030	0.051	0.008	0.017	0.001	0.001	0.002		
R*	0.728	0.705	0.695	0.679	0.703	0.856	0.827			

In brackets: calculated values. R* = Fe_{tot} / (Fe_{tot} + Mn). Samples 1 and 2: representative electron-microprobe data for hagendorfite; 3 to 5: representative electron-microprobe data for alluaudite *sensu stricto* (** normalized on the basis of 12 P atoms per formula unit, *apfu*); 6 and 7: representative electron-microprobe data for heterosite (** normalized on the basis of 1 P *apfu*); 8 to 10: chemical composition of cyrilovite: 8 is the average result of five point-analyses (** normalized on the basis of 4 P *apfu*), 9 is the theoretical composition, and 10 presents the analytical data published by Novák *et al.* (2000).

TABLE 2. STRUCTURAL FORMULA OF ALLUAUDITE *s.l.*

	1	5		1	5
M(2) Σ = 8	0.252 Al 2.020 Fe^{3+} 0.359 Mg 0.055 Zn 5.314 Fe^{2+}	0.235 Al 5.176 Fe^{3+} 0.417 Mg 2.172 Fe^{2+}	*A*(1) Σ = 4	0.771 Mn^{2+} 1.006 Ca 2.223 Na	1.074 Mn^{2+} 0.983 Ca 1.943 Na
M(1) Σ = 4	1.484 Fe^{2+} 2.516 Mn^{2+}	1.389 Fe^{2+} 2.611 Mn^{2+}	*A*(2)' Σ = 4	3.921 Na 0.030 K 0.040 □	0.516 Na 0.017 K 3.467 □

Samples: 1 hagendorfite, 5 alluaudite *sensu stricto*. These sample numbers correspond to column numbers in Table 1. For *A*(1) and *A*(2)', see Hatert *et al.* (2000).

The trend of the plots of the 41 compositions of alluaudite *s.l.* in the triangular diagrams in Figures 2 and 3 constitutes an argument corroborating our hypothesis that the transition hagendorfite → alluaudite *sensu stricto* takes place progressively and not discontinuously, as is the case in the Quensel–Mason sequence triphylite – ferrisicklerite – heterosite (Fontan *et al.* 1976).

It must be pointed out that this transition hagendorfite → alluaudite *sensu stricto* is inferred in thin sections by the progressive and distinct variation of the absorption colors of the alluaudite *s.l.* (Fig. 1). The pinkish grey to greenish blue pleochroism of the core, which is Na-rich, is typical of Na- and Fe^{2+}-rich alluaudite-group minerals, such as the "hühnerkobelite" from Palermo, New Hampshire, U.S.A. (Moore 1965), the hagendorfite from Hagendorf-Süd, Bavaria, Germany (Strunz 1954) or from Angarf-Sud, Morocco (Fransolet *et al.* 1985). On the other hand, the external zone, in

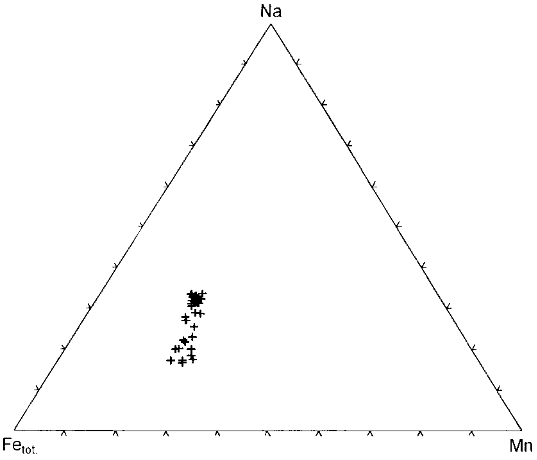

FIG. 2. Triangular diagram Na – Fe_{tot} – Mn, showing the compositions of hagendorfite in transition to alluaudite *sensu stricto*.

contact with grains of heterosite, shows a weak pleochroism in yellow brown to greenish yellow tinges, which is typical of Na-poor and Fe^{3+}-rich alluaudite-group minerals, such as those from Pringle, South Dakota (Fisher 1955, Boury 1981) or from Buranga (Fransolet 1975, Boury 1981). Thus at Kibingo, the distinct variations of absorption tinges constitute a valid argument to infer the presence of a deficiency in Na coupled with a concomitant oxidation of Fe^{2+} to Fe^{3+}, according to the substitution $\mathrm{Na} + \mathrm{Fe}^{2+} \rightarrow \square + \mathrm{Fe}^{3+}$. This substitution is not unusual, and recalls the oxidation mechanism already proposed by Quensel (1940) and by Mason (1941) in the phosphate associations from the Varuträsk pegmatite, Sweden. In addition, the absorption features also serve to justify the interpretation of the chemical data, as proposed by Fontan (1978). Note, however, that another explanation of the Na deficiency could be considered. As $\mathrm{NaMn_3(PO_4)(HPO_4)_2}$, a compound with the alluaudite structure, has been recently synthesized (Leroux *et al.* 1995), the insertion of protons at the *A*(1)'' site of natural alluaudite-group minerals cannot be excluded as a mechanism to maintain electrostatic balance.

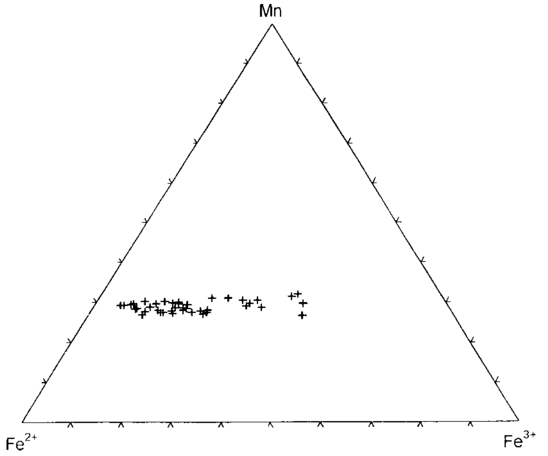

FIG. 3. Triangular diagram Mn – Fe^{2+} – Fe^{3+} of Fisher (1957), showing compositions of hagendorfite in transition to alluaudite *sensu stricto*.

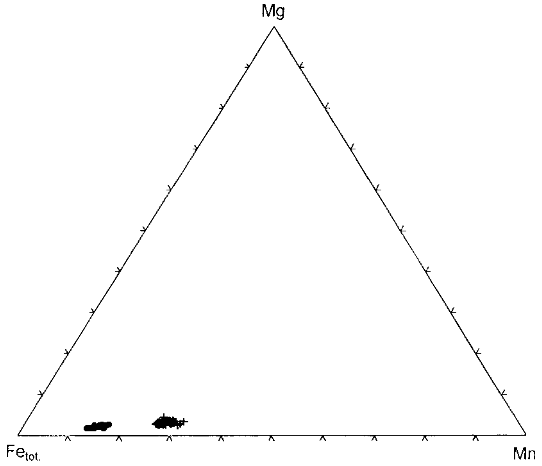

FIG. 4. Triangular diagram Mg – Fe$_{tot}$ – Mn showing the variations and the difference between the Fe/Mn values of heterosite (solid circles) and alluaudite *s.l.* (plus symbol).

Heterosite

The chemical composition of the Kibingo heterosite is noteworthy. A comparison with the data on the minerals of the triphylite group available in the literature and plotted in a Mg – Fe$_{tot}$ – Mn triangular diagram (Fig. 5) shows that the composition obtained herein is the richest in Fe known so far, being close to the Fe^{3+}PO$_4$ end member, and thus with a very low Mg content. As

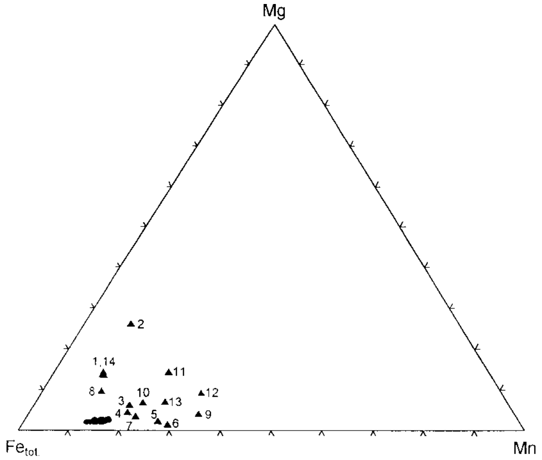

FIG. 5. Triangular diagram Mg – Fe$_{tot}$ – Mn indicating the Fe-rich composition of Kibingo heterosite (black circles) in comparison with: 1) triphylite from Angarf-Sud, Morocco, 2) triphylite from Newport, New Hampshire (Fransolet 1975), 3) triphylite from the Albères Massif, 4) heterosite from the Albères Massif, 5) ferrisicklerite from the Albères Massif (Malló *et al.* 1995), 6) triphylite from Kobokobo, Kivu, 7) heterosite from Tazarine-Est, Zenaga Plain, Morocco, 8) heterosite from Timoulal, Zenaga Plain, Morocco (Fransolet 1975), 9) ferrisicklerite from Sidi-Bou-Othmane (Fontan *et al.* 1976), 10) triphylite from Pénitence, Arize Massif, Ariège, 11) ferrisicklerite from the Trois Seigneurs Massif, 12) triphylite from the Aston Massif, 13) ferrisicklerite from the Aston Massif (Fontan 1978), 14) triphylite from Valmy, Albères Massif (Fontan & Fransolet 1986).

the Kibingo material has a ratio $Fe_{tot}/(Fe_{tot} + Mn)$ varying between 0.86 and 0.83 (Figs. 4, 5), it occurs in a compositional domain where the distinction of heterosite from ferrisicklerite on the basis of electron-microprobe data is tricky, particularly where this composition comes close to the $Fe^{3+}PO_4$ end member. Indeed, near this end member, ferrisicklerite and heterosite have virtually the same formula (Fontan *et al.* 1976). In the case of the Kibingo material, the distinction between $Li_{0.15}(Fe^{3+}_{0.85}Mn^{2+}_{0.15})PO_4$ and $(Fe^{3+}_{0.85}Mn^{3+}_{0.15})$ PO_4 remains optically possible owing to the distinct pleochroism. From Figure 5, one can see that triphylite from Newry and Angarf-Sud (Fransolet *et al.* 1984), from Valmy, Massif des Albères (Fontan & Fransolet 1986), and heterosite from the Timoulal pegmatite, Zenaga Plaine, Morocco (Fransolet 1975) are still richer in Fe than the Kibingo mineral but, however, with noticeable Mg contents. Taking into account their ratio $Fe_{tot}/(Fe_{tot} + Mn) = 0.80$, calculated with the data published by Malló *et al.* (1995), both triphylite and heterosite from other pegmatites in the Albères Massif have compositions similar to that of the Kibingo heterosite. Moreover, in both occurrences, the Mg content is low: about 0.05 Mg *apfu* in the samples of triphylite and heterosite from the Albères Massif, and 0.023 Mg *apfu* in the material from Kibingo.

Discussion of the Petrographic Relationships

Sample RGM 5469 from Kibingo held our attention because it clearly displays various peculiarities that characterize the close association of heterosite and alluaudite-group minerals. These major minerals occur as equant grains with sharp contacts, without any sign of replacement. According to Fontan *et al.* (1976), the presence of fissures within the heterosite grains (Fig. 1) could constitute an argument in favor of its secondary origin, as a product of oxidation of a mineral of the triphylite – lithiophilite series. In their study of the Sidi-Bou-Othmane ferrisicklerite, these authors reported that the oxidation of $Li(Fe,Mn)PO_4$ is accompanied by a shrinkage of the unit-cell volume of the precursor phase, as revealed by an anisotropic deformation-induced triggering of the fissures.

At Kibingo, the petrographic relationships clearly illustrate that a Fe-rich member of the triphylite – lithiophilite series and hagendorfite crystallized together from the melt. Hagendorfite is consequently of primary origin in this case. In the Mg – Fe_{tot} – Mn triangular diagram (Fig. 4), one can see that the Fe/Mn value is markedly different in the two major minerals of the paragenesis. During their syncrystallization, it seems clear that the structure of alluaudite accommodates Mn more easily than triphylite, which has an olivine-type structure. On the basis of data resulting from recent hydrothermal syntheses performed by Hatert (2002a, b), the temperature of formation of hagendorfite at Kibingo is estimated to be about 600°C at a pressure of 1 kbar.

The two cogenetic minerals were both affected by a stage of oxidation, well known within the phosphate associations of granitic pegmatites. It is clear that this oxidation is accompanied by alkali leaching. During the leaching of Li, triphylite is transformed into heterosite, whereas the progressive leaching of Na, originally in the *A*(2)' crystallographic site, leads to the alteration of hagendorfite to alluaudite *sensu stricto*. We tentatively suggest that a part of the leached Na leads to the precipitation of cyrilovite, $NaFe^{3+}(PO_4)(OH)$, in the fissures caused by the volume decrease resulting from the transformation of triphylite to heterosite.

A last point in the discussion deals with speculation about the type of pegmatite constituting the Kibingo body. If the hypothesis of Ginsburg (1960) on the degree of fractionation of a pegmatite-forming granitic magma and the evolution of the ratio Fe/Mn in minerals is accepted, as by Keller (1991) in checking the degree of differentiation of 46 pegmatite bodies of the Damara Sequence in Namibia, a question immediately comes up. Is the Kibingo pegmatite really a pegmatite of type 6 according to Varlamoff (1961), in other words, a complex pegmatite rich in amblygonite (Černý 1991)? With a ratio Fe/(Fe + Mn) of about 0.85 measured in heterosite, we are inclined to believe that the Kibingo pegmatite is not an "amblygonite-bearing" pegmatite such as the pegmatite at the Mwaka mine. We tentatively suggest that it could be another pegmatitic lens belonging to the swarm of the Mwaka – Lemera pegmatites, with a very limited degree of fractionation.

Acknowledgements

The authors acknowledge with thanks the help of Drs. Luc Tack and Michel Errera (Musée royal de l'Afrique centrale at Tervuren) for the geological information about the Kibingo mine. Philippe de Parseval (Toulouse) performed all the electron-microprobe analyses. The earlier versions of the manuscript were improved by a critical reading and constructive comments of V. Bermanec, B.P. Onac, S. Marincea, and R.F. Martin.

References

Boury, Ph. (1981): *Comportement du fer et du manganèse dans des associations de phosphates pegmatitiques*. Thèse de diplome, Univ. Liège, Liège, Belgique.

Černý, P. (1991): Rare-element granitic pegmatites. I. Anatomy and internal evolution of pegmatite deposits. *Geosci. Canada* **18**, 49-67.

Fisher, D.J. (1955): Alluaudite. *Am. Mineral.* **40**, 1100-1109.

________ (1957): Alluaudites and varulites. *Am. Mineral.* **42**, 661-664.

________ (1958): Pegmatite phosphates and their problems. *Am. Mineral.* **43**, 181-207.

Fontan, F. (1978): *Etude minéralogique et essais expérimentaux sur des phosphates de fer et de manganèse de pegmatites des Jebilet (Maroc) et des Pyrénées (France).*

Thèse de doctorat, Univ. Paul-Sabatier de Toulouse, Toulouse, France.

________ & Fransolet, A.-M. (1986): Les phosphates de Fe et Mn des pegmatites de Valmy, Massif des Albères (Pyrénées orientales), France. *Boletín de la Sociedad Española de Mineralogía* **9**, 391-396.

________, Huvelin, P., Orliac, M. & Permingeat, F. (1976): La ferrisicklérite des pegmatites de Sidi Bou Othmane (Jelibet, Maroc) et le groupe des minéraux à structure de triphylite. *Bull. Soc. fr. Minéral. Cristallogr.* **99**, 274-286.

Fransolet, A.-M. (1975): *Etude minéralogique et pétrologique des phosphates de pegmatites granitiques*. Thèse de doctorat, Univ. Liège, Liège, Belgique.

________ (1977): Le problème génétique des alluaudites. *Bull. Soc. fr. Minéral. Cristallogr.* **100**, 348-352.

________, Abraham, K. & Speetjens, J.-M. (1985): Evolution génétique et signification des associations de phosphates de la pegmatite d'Angarf-Sud, plaine de Tazenakht, Anti-Atlas, Maroc. *Bull. Minéral.* **108**, 551-574.

________, Antenucci, D. & Speetjens, J.-M. (1984): An X-ray determinative method for the divalent cation ratio in the triphylite–lithiophilite series. *Mineral. Mag.* **48**, 373-381.

________, Fontan, F., Keller, P. & Antenucci, D. (1998): La série johnsomervilleite – fillowite dans les associations de phosphates de pegmatites granitiques de l'Afrique centrale. *Can. Mineral.* **36**, 355-366.

________, Keller, P. & Fontan, F. (1986): The phosphate mineral associations of the Tsaobismund pegmatite, Namibia. *Contrib. Mineral. Petrol.* **92**, 502-517.

Ginsburg, A.I. (1960): Specific geochemical features of the pegmatitic process. *Int. Geol. Congress, Report 21st Session Norden, Part VXII, Proc. Sect. 17 Minerals and Genesis of Pegmatites*, 111-121.

Hatert, F. (2002a): *Cristallochimie et synthèse hydrothermale d'alluaudites dans le système Na–Mn–Fe–P–O: contribution au problème de la genèse de ces phosphates dans les pegmatites granitiques*. Thèse de doctorat, Univ. Liège, Liège, Belgique.

________ (2002b): The stability of alluaudite in granitic pegmatites: a study of the $Na_2(Mn_{1-x}Fe^{2+}_x)_2Fe^{3+}(PO_4)_3$ solid solution. *Int. Mineral. Assoc., 18th General Meeting (Edinburgh), Program Abstr.*, 91.

________, Keller, P., Lissner, F., Antenucci, D. & Fransolet, A.-M. (2000): First experimental evidence of alluaudite-like phosphates with high Li-content: the $(Na_{1-x}Li_x)MnFe_2(PO_4)_3$ series (x = 0 to 1). *Eur. J. Mineral.* **12**, 847-857.

Héreng, P. (1989): *Contribution à l'étude minéralogique de phosphates de fer et de manganèse de la pegmatite de Buranga, Rwanda*. Thèse de diplome, Univ. Liège, Liège, Belgique.

Huvelin, P., Orliac, M. & Permingeat, F. (1972): Ferrialluaudite calcifère de Sidi Bou Othmane (Jelibet, Maroc). *Notes du Service géologique du Maroc, Rabat,* **241**,32), 35-49.

Keller, P. (1991): The occurrence of Li–Fe–Mn phosphate minerals in granitic pegmatites of Namibia. *Commun. Geol. Surv. Namibia* **7**, 21-34.

Leroux, F., Mar, A., Payen, C., Guyomard, D., Verbaere, A. & Piffard, Y. (1995): Synthesis and structure of $NaMn_3(PO_4)(HPO_4)_2$, an unoxidized variant of the alluaudite structure type. *J. Solid State Chem.* **115**, 240-246.

Malló, A., Fontan, F., Melgarejo, J.-C. & Mata, J.M. (1995): The Albera zoned pegmatite field, eastern Pyrenees, France. *Mineral. Petrol.* **55**, 103-116.

Mason, B. (1941): Minerals of the Varuträsk pegmatite. XXIII. Some iron–manganese phosphate minerals and their alteration products, with special reference to material from Varuträsk. *Geol. Fören. Stockholm Förh.* **63**(2), 117-175.

Monteyne-Poulaert, G., Delwiche, R. & Cahen, L. (1962): Ages de minéralisations pegmatitiques et filoniennes du Rwanda et du Burundi. *Bull. Soc. belge Géol.* **71**, 1-13.

Moore, P.B. (1965): Hühnerkobelite crystals from the Palermo No. 1 pegmatite, North Groton, New Hampshire. *Am. Mineral.* **50**, 713-717.

________ (1971): Crystal chemistry of the alluaudite structure type: contribution to the paragenesis of pegmatite phosphate giant crystals. *Am. Mineral.* **56**, 1955-1975.

________ & Ito, J. (1979): Alluaudites, wyllieites, arrojadites: crystal chemistry and nomenclature. *Mineral. Mag.* **43**, 227-235.

Novák, M., Sejkora, J. & Cooper, M.A. (2000): Cyrilovite from Cyrilov, western Moravia, Czech Republic; new data on the type material. *J. Czech Geol. Soc.* **45**(1-2), 101-106.

Quensel, P. (1940): Minerals of the Varuträsk pegmatite. XVII. Further comments on the minerals varulite and alluaudite. *Geol. Fören. Stockholm Förh.* **62**(3), 297-302.

Strunz, H. (1954): Hagendorfit, ein neues Mineral der Varulith-Hühnerkobelit-Reihe. *Neues Jahrb. Mineral., Monatsh.*, 252-255.

Thoreau, J. & Bastien, G. (1954a): Lazulite et scorzalite de pegmatites du Congo belge et du Ruanda. *Bull. Acad. roy. Belgique, Classe des Sciences, Sér.* 5, **40**, 600-607.

________ & ________ (1954b) : Les phosphates des pegmatites du Ruanda occidental. *Bull. Acad. roy. Sci. coloniales* **25**(5), 1595-1603.

Van Wambeke, L. (1969): Présence d'hühnerkobelite, de cyrilovite et de mitridatite dans les pegmatites de Kibingo, Rwanda. *Bull. Serv. géol. Rwanda* **5**, 35-41.

Varlamoff, N. (1961): Matériaux pour l'étude des pegmatites du Congo et du Ruanda. IV. Pegmatites à amblygonite et à spodumène et pegmatites fortement albitisées à spodumène et à cassitérite de la région de Katumba (Ruanda). *Annales Soc. géol. Belgique* **84**, 257-278.

Received July 18, 2003, revised manuscript accepted March 26, 2004.