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FLUORNATROMICROLITE, $(Na,Ca,Bi)_2Ta_2O_6F$, A NEW MINERAL SPECIES FROM QUIXABA, PARAÍBA, BRAZIL

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ABSTRACT

Fluornatromicrolite is a new mineral species of the pyrochlore supergroup (microlite group), with fluorine dominant at the second anion site. The type locality is the Alto Quixaba granitic pegmatite near Quixaba village, municipality of Frei Martinho, Paraíba, Brazil. Fluornatromicrolite forms adamantine green regular to flattened octahedral crystals in albite. The streak is white, the Mohs hardness is 5, and the calculated density is 6.568 g/cm^3. The chemical composition is $(Na_{1.10}Ca_{0.64}Bi_{0.15})Ta_{2.00}O_{5.91}F_{1.02}$, or, ideally $(Na,Ca,Bi)_2Ta_2O_6F$. The mineral is cubic, space group $Fd3m$, with a 10.4451(2) Å, V 1139.56(8) Å^3 and $Z = 8$. The crystal structure was refined to R = 0.034 using 2861 reflections obtained with Mo$K\alpha$ radiation on a four-circle automatic diffractometer. The structure is built up of TaO_6 octahedra and $(Na,Ca,Bi)O_6F_2$ polyhedra. The (Na,Ca,Bi)–F distances are significantly shorter than the (Na,Ca,Bi)–O distances.

Keywords: fluornatromicrolite, new mineral species, pyrochlore supergroup, microlite group, Quixaba, Paraíba, Brazil.

SOMMAIRE

La fluornatromicrolite est une nouvelle espèce minérale du supergroupe du pyrochlore, groupe du microlite, ayant une dominance de fluor au second site anionique. On l'a découverte dans la pegmatite granitique de Alto Quixaba, près du village de Quixaba, municipalité de Frei Martinho, à Paraíba, au Brésil. La fluornatromicrolite se présente sous forme de cristaux octaédriques réguliers ou applatis verts et adamantins dans l'albite. La rayure est blanche, la dureté de Mohs est 5, et la densité calculée est égale à 6.568 g/cm^3. Sa composition chimique est $(Na_{1.10}Ca_{0.64}Bi_{0.15})Ta_{2.00}O_{5.91}F_{1.02}$, ou idéalement, $(Na,Ca,Bi)_2Ta_2O_6F$. Il s'agit d'un minéral cubique, groupe spatial $Fd3m$, avec a 10.4451(2) Å, V 1139.56(8) Å^3 et $Z = 8$. Nous en avons affiné la structure jusqu'à un résidu R égal à 0.034 en utilisant 2861 réflexions prélevées avec rayonnement Mo$K\alpha$ et

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mesurées avec un diffractomètre à quatre cercles. La structure contient des octaèdres TaO_6 et des polyèdres $(Na,Ca,Bi)O_6F_2$. Les distances (Na,Ca,Bi)–F sont nettement plus courtes que les distances (Na,Ca,Bi)–O.

(Traduit par la Rédaction)

Mots-clés: fluornatromicrolite, nouvelle espèce minérale, supergroupe du pyrochlore, groupe du microlite, Quixaba, Paraíba, Brazil.

INTRODUCTION

A green mineral was observed from the Alto Quixaba pegmatite, Quixaba village, Frei Martinho, Paraíba, Brazil, by one of the authors (R.W.). The mineral was identified by X-ray powder diffraction as a member of the pyrochlore supergroup. A chemical analysis showed that the mineral is rich in fluorine. The material was characterized as a new member of the microlite group with dominant fluorine at an anion site.

The mineral and the name *fluornatromicrolite* were approved by the Commission on New Minerals and Mineral Names, International Mineralogical Association (IMA 1998–018). The name was given according to the chemical composition and by analogy with calciobetafite, described as a new species of the pyrochlore supergroup with Ca dominant at the *A* cation site (Mazzi & Munno 1983). Controversies about the mineral and the nomenclature of the pyrochlore supergroup delayed the publication of the new mineral for several years. When the paper on fluornatromicrolite was submitted for the first time, in 1998, there were problems because, although approved by the CNMMN–IMA, the name fluornatromicrolite did not match the nomenclature of Hogarth (1977), then still *de rigueur*. Today, however, the name *fluornatromicrolite* is perfectly in line with the newly approved system of nomenclature (Atencio *et al.* 2010).

Type specimens of fluornatromicrolite are deposited in the Mineralogical Collection of the Bergakademie Freiberg, Germany (No. 77975), and in the Mineralogical Collection of the Martin-Luther Universität Halle, Institut für Geologische Wissenschaften (no. 010356).

OCCURRENCE AND PARAGENESIS

The Alto Quixaba pegmatite is part of a swarm of granitic pegmatites near the village of Quixaba, Frei Martinho municipality, Paraíba State, northeastern Brazil. The pegmatite consists of two different vein-like bodies, each with limited outcrop; the first has a width of about 1.5 m, strikes 35° and dips east, the second strikes 60° and dips 80° west (Mousinho-Ferreira 1998). Both pegmatites are discordant with respect to the biotite schist host-rock, which strikes 50° and dips 75° southeast. The first pegmatite vein is sterile and without economic interest, whereas the second one shows distinctive mineralization. The main minerals are perthitic microcline, quartz and muscovite, with large amounts of albite and amblygonite. Accessory minerals are elbaite (mainly blue), tantalite-(Fe), tantalite-(Mn), green beryl and fluornatromicrolite.

PHYSICAL AND OPTICAL PROPERTIES

Fluornatromicrolite occurs as regular to flattened octahedral crystals up to 6 mm in size (Fig. 1). The color of the mineral is green, and the streak is white. The crystals have an adamantine luster and are transparent in thin fragments. The mineral is brittle and has a conchoidal fracture. Cleavage was not discernible. The Mohs hardness of fluornatromicrolite is 5. The density, measured with a pycnometer, is 6.49(6) g/cm^3, and the calculated density for Z = 8 is 6.568 g/cm^3. The difference may be due to the small quantity of the mineral used for the pycnometer measurement. The mineral is optically isotropic. The index of refraction measured by the immersion method is above 2.0 (wavelength 589 nm). An ellipsometric determination at 633 nm using a He–Ne laser yielded an index of refraction of 2.110 ± 0.025.

COMPOSITION OF THE MINERAL

Chemical analyses of the new mineral were made by means of energy-dispersive (EDX) as well as wavelength-dispersive (WDX) X-ray spectrometry. An EDX spectrum revealed Ta, Na, Ca, Bi, O, and F as the only elements present. Traces of Nb (<0.5 wt.%) were observed in only a few crystals.

The data from the WDX analysis were acquired using a CAMECA SX 100 electron microprobe operated at an acceleration voltage of 15 kV and a beam current of 10 nA. Seventeen chemical analyses were carried out on different spots of the sample. Standards used were albite (Na), fluorite (Ca, F), bismuthinite (Bi), and tantalum (Ta). For data reduction, the CAMECA program PAP was used. The results of the analyses of a crystal, according to an EDX analysis virtually free of Nb, are given in Table 1. The WDX microprobe analysis showed no Nb peak and a very weak Ti peak, but the peak:background relation (1.4) was too poor for a quantification of Ti. From the electron-microprobe data, an empirical formula (based on Ta = 2 *apfu*) can be calculated: $(Na_{1.10}Ca_{0.64}Bi_{0.15})Ta_{2.00}O_{5.91}F_{1.02}$. The occupancy of the second anion position by fluorine was confirmed by the structure analysis. The general formula of fluornatromicrolite is $(Na,Ca,Bi)_2Ta_2O_6F$. No zoning was observed in the analyzed crystal. A plot of the analytical data according to the Na, Ca, Bi cation relations is given in Figure 2.

An infrared spectrum was obtained in transmission mode using powder from a single crystal. No absorption attributed to OH or H_2O was observed.

X-RAY POWDER DIFFRACTION

The X-ray powder-diffraction pattern was recorded using a Philips Norelco diffractometer with Cu*K*α radiation and is reported in Table 2. The fluornatromicrolite sample from Quixaba shows no sign of metamictization. All the observed lines of the unheated material are sharp. From the powder-diffraction data, a cubic cell with a equal to 10.4451(2) Å and V equal to 1139.56(8) Å^3 was deduced.

CRYSTAL STRUCTURE

To avoid absorption problems, a sphere 0.4 mm in diameter was used for the data collection on a SIEMENS P4 four-circle diffractometer (Mo*K*α). A total of 2861 reflections up to $2\theta = 90°$ were measured. On the basis of a cubic structure, there are only 234 symmetry-independent reflections in the dataset. The empirical absorption correction was done with XEMP ($\mu = 423.6$ cm^{-1}); for the structure refinement, SHELXL–93 was used [R(F) = 0.034, wR(F^2) = 0.068]. Note that because of the delay incurred in publishing this article, a list of structure factors and a cif file could no longer be located.

Fluornatromicrolite belongs to the pyrochlore structure-type (Gaertner 1930, Chakoumakos 1984) (Fig. 3). The space group is $Fd3m$. According to the structure analysis, the sample has an 8*a* position fully occupied by fluorine. The refined occupancy is 0.95(5) and very close to the measured value. The 16*c* position (coordination number 8) is occupied by Na, Ca and Bi. The results obtained from the refinement for one cation are Na 0.528(6), Ca 0.314(6), and Bi 0.161(6). The values for Na and Ca are nearly identical to the results of the electron-microprobe analysis. The contribution of Bi is higher, but it is the element with the lowest fractional contribution to the *A* site; in this way, the error is higher. During the last cycle of structure refinement, the fractional occupancies of the 16*c* position were set to those values, known from the electron-microprobe analysis. This 16*c* position is coordinated by six atoms of oxygen and two atoms of fluorine. The F atoms are placed in opposing positions. The distances from the central ion to the F positions are significantly shorter [2.260(1) Å] than the distances to the O positions [2.655(4) Å]. Tantalum occupies the 16*d* position and is coordinated by six equivalent O atoms [distance Ta–O = 1.974(2) Å], which forms a nearly ideal octahedron. The TaO_6 octahedra are connected *via* corners, and the $(Na,Ca,Bi)O_6F_2$ polyhedra, *via* edges. The mineral contains eight formula units per cell. The coordinates of all atoms and selected interatomic distances and angles are presented in Tables 3 and 4.

TABLE 1. THE COMPOSITION OF FLUORNATROMICROLITE

	average composition*	range of results
Na_2O wt.%	6.39	6.28 - 6.47
CaO	6.96	6.81 - 7.23
Bi_2O_3	6.71	6.41 - 7.11
Ta_2O_5	76.81	76.54 - 77.38
F	3.63	3.55 - 3.70
less O=F	– 1.53	
Total	98.97	

The data were acquired with an electron microprobe. The average is based on 17 analyses.

TABLE 2. FLUORNATROMICROLITE: POWDER-DIFFRACTION DATA

I	d_{meas}	d_{calc}	*h k l*
31	6.023	6.030	1 1 1
33	3.148	3.149	3 1 1
100	3.015	3.015	2 2 2
27	2.610	2.611	4 0 0
6	2.396	2.396	3 3 1
<1	2.133	2.132	4 2 2
17	2.010	2.010	3 3 3, 5 1 1
59	1.846	1.846	4 4 0
15	1.765	1.766	5 3 1
1	1.652	1.652	6 2 0
10	1.592	1.593	5 3 3
47	1.574	1.575	6 2 2
17	1.507	1.508	4 4 4
11	1.463	1.463	5 5 1, 7 1 1
14	1.360	1.360	5 5 3, 7 3 1
8	1.306	1.306	8 0 0
2	1.276	1.276	7 3 3
1	1.231	1.231	6 6 0, 8 2 2
7	1.206	1.206	5 5 5, 7 5 1
23	1.198	1.198	6 6 2
18	1.168	1.168	8 4 0
7	1.147	1.146	7 5 3, 9 1 1
5	1.095	1.095	9 3 1
15	1.066	1.066	8 4 4
6	1.050	1.050	7 5 5, 7 7 1, 9 3 3
7	1.010	1.010	9 5 1, 7 7 3
16	1.005	1.005	6 6 6, 10 2 2
3	0.9739	0.9740	9 5 3
3	0.9418	0.9418	7 7 5, 11 1 1
7	0.9232	0.9232	8 8 0
8	0.9126	0.9126	9 5 5, 9 7 1, 11 3 1
<1	0.8956	0.8957	8 6 6, 10 6 0
7	0.8859	0.8859	9 7 3, 11 3 3
21	0.8828	0.8828	10 6 2
17	0.8704	0.8704	8 8 4, 12 0 0
4	0.8615	0.8615	7 7 7, 11 5 1

The values of *d* are quoted in Å.

FIG. 1. Fluornatromicrolite in albite from Quixaba, Paraíba, Brazil. Sample size 3.8 cm.

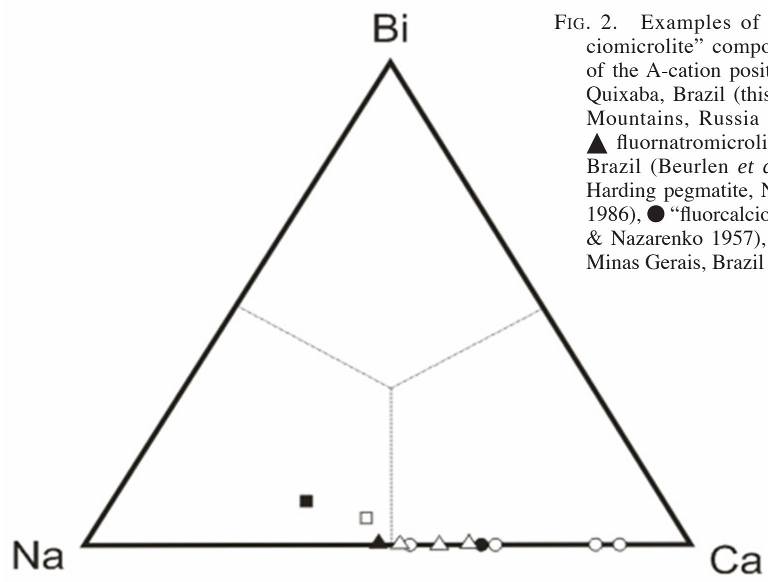

FIG. 2. Examples of fluornatromicrolite and "fluorcalciomicrolite" compositions according to the occupancy of the A-cation position. Symbols: ■ fluornatromicrolite, Quixaba, Brazil (this work), □ fluornatromicrolite, Altai Mountains, Russia (Zalashkova & Kucharchik 1957), ▲ fluornatromicrolite, Borborema pegmatitic province, Brazil (Beurlen *et al.* 2005), Δ "fluorcalciomicrolite", Harding pegmatite, New Mexico, U.S.A. (Lumpkin *et al.* 1986), ● "fluorcalciomicrolite", Koktogai, China (Borodin & Nazarenko 1957), ○ "fluorcalciomicrolite", Nazareno, Minas Gerais, Brazil (Pinto 2000).

DISCUSSION

Zalashkova & Kukharchik (1957) described a mineral from the Altai Mounains, Russia, with the composition $(Na_{0.94}Ca_{0.83}Bi_{0.08}Al_{0.06}Fe_{0.02})Ta_2O_6[F_{0.58}(OH)_{0.34}O_{0.08}]$ as "bismutomicrolite", a new variety of microlite. The composition is close to that of the Quixaba mineral, the *A* position is mainly occupied by Na, and the *Y* position, mainly by F. The name *fluornatromicrolite* thus should be applied to that material. Fluornatromicrolite with the composition $(Na_{0.93}Ca_{0.87}Sb_{0.03}Pb_{0.02}Sc_{0.01})_{\Sigma 1.86}(Ta_{1.98}Nb_{0.04})_{\Sigma 2.02}O_6F$ was described from the Borborema pegmatitic province, northeastern Brazil (Beurlen *et al.* 2005). According to Atencio *et al.* (2010), chemical compositions that correspond to fluornatromicrolite from other occurrences are avail-

TABLE 3. REFINED COORDINATES OF ATOMS IN FLUORNATROMICROLITE*

	x	y	z	occ.	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
Na	0.0	0.0	0.0	0.555	0.038(1)	0.038	0.038	-0.0098(7)	-0.0098	-0.0098	0.038(1)
Ca	0.0	0.0	0.0	0.325	0.038	0.038	0.038	-0.0098	-0.0098	-0.0098	0.038
Bi	0.0	0.0	0.0	0.075	0.038	0.038	0.038	-0.0098	-0.0098	-0.0098	0.038
Ta	0.5	0.5	0.5	1.0	0.0149(1)	0.0149	0.0149	-0.00072(6)	-0.00072	-0.00072	0.0149(1)
O	-0.1828(5)	0.125	0.125	1.0	0.020(1)	0.017(1)	0.017	0.006(1)	0.0	0.0	0.0183(6)
F	0.125	0.125	0.125	1.0	0.027(2)	0.027	0.027	0.0	0.0	0.0	0.027(2)

* $(Na_{1.11}Ca_{0.65}Bi_{0.15})Ta_2O_6F$, space group *Fd*3*m*, origin choice 2.

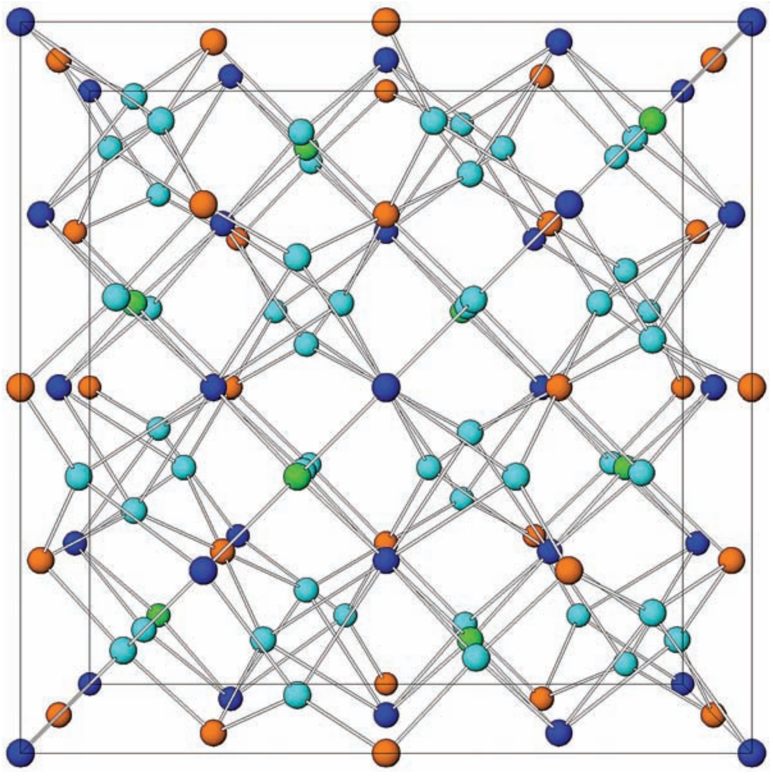

FIG. 3. The crystal structure of fluornatromicrolite, shown in a perspective view of the unit cell. Blue: (Na,Ca,Bi), orange: Ta, light blue: O, light green: F.

TABLE 4. FLUORNATROMICROLITE: SELECTED INTERATOMIC DISTANCES AND ANGLES

Me – F	2.260(0) Å	F – *Me* – O	81.22°
Me – O	2.655(4) Å	O – *Me* – O	62.28°
Ta – O	1.974(2) Å	O – Ta – O	88.12°

Me = (Na,Ca,Bi).

able in the papers by Ohnenstetter & Piantone (1992), Belkasmi *et al.* (2000), Huang *et al.* (2002) and Baldwin *et al.* (2005).

Related compositions, but with a dominance of Ca at the *A* position, *i.e.*, "fluorcalciomicrolite", were reported for example by Borodin & Nazarenko (1957); they found a composition $(Ca_{1.18}Na_{0.63}K_{0.19})_{\Sigma 2.00}(Ta_{1.80}Nb_{0.12}Ti_{0.04}Fe_{0.03})_{\Sigma 1.99}O_6(F_{0.66}(OH)_{0.34})$ for their sample from Koktogai (not further specified, apparently in Mongolian Altai, China). Pinto (2000) found compositions between $(Ca_{1.04}Na_{0.88}U_{0.02})_{\Sigma1.94}(Ta_{1.81}Nb_{0.15}Sn_{0.04})_{\Sigma2.00}O_6[F_{0.82}(OH)_{0.18}]{\bullet}nH_2O$ and $(Ca_{1.31}Na_{0.26}Mn_{0.01}U_{0.01})_{\Sigma1.59}(Ta_{1.82}Nb_{0.14}Sn_{0.04})_{\Sigma2.00}O_6[F_{0.50}(OH)_{0.40}]{\bullet}nH_2O$ for samples rich in fluorine. A positive correlation between the Na_2O and the F content was observed. Lumpkin *et al.* (1986) reported several compositions of microlite from the Harding pegmatite, New Mexico. All the datasets given show a dominance of Ca over Na at the *A* site. The second anion site is mainly occupied by F in several samples, and in other samples, mainly by OH or O. There are several compositions of "fluorcalciomicrolite" reported in the literature, *e.g.,* Lumpkin *et al.* (1986), Baldwin (1989), Ohnenstetter & Piantone (1992), Tindle & Breaks (1998), Huang *et al.* (2002), Geisler *et al.* (2004), Tindle *et al.* (2005), but a complete description is missing (Atencio *et al.* 2010).

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