

**THE CRYSTAL STRUCTURE OF A MICROLITE-GROUP MINERAL  
 WITH A FORMULA NEAR  $\text{NaCaTa}_2\text{O}_6\text{F}$  FROM THE MORRO REDONDO MINE,  
 CORONEL MURTA, MINAS GERAIS, BRAZIL**

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ABSTRACT

We present electron-microprobe and single-crystal X-ray-diffraction data for a microlite-group mineral with a formula near  $\text{NaCaTa}_2\text{O}_6\text{F}$  from the Morro Redondo mine, Coronel Murta, Minas Gerais, Brazil. On the basis of these data, the formula is  $A(\text{Na}_{0.88}\text{Ca}_{0.88}\text{Pb}_{0.02}\square_{0.22})_{\Sigma 2.00} B(\text{Ta}_{1.70}\text{Nb}_{0.14}\text{Si}_{0.12}\text{As}_{0.04})_{\Sigma 2.00} X[(\text{O}_{5.75}(\text{OH})_{0.25})_{\Sigma 6.00}] Y(\text{F}_{0.73}\square_{0.27})_{\Sigma 1.00}$ . According to the new nomenclature for the pyrochlore-supergrout minerals, it is intermediate between fluornatromicrolite and “fluorcalciomicrolite”. The crystal structure,  $Fd\bar{3}m$ ,  $a = 10.4396(12)$  Å, has been refined to an  $R_1$  value of 0.0258 ( $wR_2 = 0.0715$ ) for 107 reflections (MoK $\alpha$  radiation). There is a scarcity of crystal-chemical data for pyrochlore-supergrout minerals in the literature. A compilation of these data is presented here.

*Keywords:* microlite group, “fluorcalciomicrolite”, fluornatromicrolite, crystal-structure refinement, solid solution.

SOMMAIRE

Nous présentons ici des données acquises avec une microsonde électronique et par diffraction X sur monocristal pour caractériser un minéral du groupe du microlite ayant une formule voisine de  $\text{NaCaTa}_2\text{O}_6\text{F}$ , provenant de la mine Morro Redondo, Coronel Murta, Minas Gerais, Brésil. Compte tenu de ces données, la formule en serait  $A(\text{Na}_{0.88}\text{Ca}_{0.88}\text{Pb}_{0.02}\square_{0.22})_{\Sigma 2.00} B(\text{Ta}_{1.70}\text{Nb}_{0.14}\text{Si}_{0.12}\text{As}_{0.04})_{\Sigma 2.00} X[(\text{O}_{5.75}(\text{OH})_{0.25})_{\Sigma 6.00}] Y(\text{F}_{0.73}\square_{0.27})_{\Sigma 1.00}$ . Selon la nouvelle nomenclature des minéraux du supergroupe du pyrochlore, il s’agit d’une composition intermédiaire entre fluornatromicrolite et “fluorcalciomicrolite”. La structure du cristal,  $Fd\bar{3}m$ ,  $a = 10.4396(12)$  Å, a été affinée jusqu’à un résidu  $R_1$  égal à 0.0258 ( $wR_2 = 0.0715$ ) en utilisant 107 réflexions (rayonnement MoK $\alpha$ ). Il y a une pénurie de données cristalochimiques pour les minéraux du supergroupe du pyrochlore dans la littérature. Nous présentons ici une compilation des données disponibles.

(Traduit par la Rédaction)

*Mots-clés:* groupe du microlite, “fluorcalciomicrolite”, fluornatromicrolite, affinement de la structure, solution solide.

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## INTRODUCTION

Pyrochlore-super group minerals have been studied in detail because of their interesting magnetic properties and advanced technological applications. The “geometrical frustration” concept is related to the incapacity of magnetic systems to satisfy simultaneously all the interactions (ferromagnetic and antiferromagnetic) between spins in order to minimize the total energy. The study of frustration among spins in the corner-sharing tetrahedra of pyrochlore-like structures of synthetic origin has contributed to a better understanding of new exotic low-temperature states, magnetic ordering (Wang *et al.* 2006, Normand 2009), and superconductivity, such as in  $\text{RbOs}_2\text{O}_6$  (Brühwiler *et al.* 2004). Titanate ( $\text{CaZrTi}_2\text{O}_7$ ) and zirconate ( $\text{Gd}_2\text{Zr}_2\text{O}_7$ ,  $\text{Er}_2\text{Zr}_2\text{O}_7$ ) pyrochlores play an important role in the development of long-term geological depositories of high-level radioactive waste such as plutonium (Laverov *et al.* 2010). Minerals of the pyrochlore super group have a formula  $A_{2-m}B_2X_{6-w}Y_{1-n}$  ( $m = 0$  to 2,  $w = 0$  to 0.7,  $n = 0$  to 1), in which the A site is normally occupied by Na, Ca, Ag, Mn, Sr, Ba,  $\text{Fe}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Sn}^{2+}$ ,  $\text{Sb}^{3+}$ ,  $\text{Bi}^{3+}$ , Y, Ce (and other REE), Sc, U, Th, □, or  $\text{H}_2\text{O}$ . The B site typically accommodates Ta, Nb, Ti,  $\text{Sb}^{5+}$ , W, and also  $\text{V}^{5+}$ ,  $\text{Sn}^{4+}$ , Zr, Hf,  $\text{Fe}^{3+}$ , Mg, Al, Si. The X site typically is occupied by O, but can include subordinate OH and F. The Y site is occupied by OH, F, O, □,  $\text{H}_2\text{O}$ , K, Cs, Rb. These minerals are commonly found in carbonatites, alkaline rocks and

granitic pegmatites (Lumpkin & Ewing 1992, Ercit *et al.* 1994, Zurevinski & Mitchell 2004). The pyrochlore super group includes minerals of the pyrochlore, micro-lite, roméite, betafite and elsmoreite groups.

There is a scarcity of crystal-chemical data in the literature. There are crystal-structure determinations published for only nine pyrochlore-super group minerals (Table 1). In this paper, we present results of electron-microprobe and single-crystal diffraction studies of a microlite-group mineral from the Morro Redondo mine.

## OCCURRENCE

The Morro Redondo pegmatite is located in the northern part of the Oriental Pegmatite Province of Minas Gerais (that extends 320 km east to west and 720 km north to south, reaching the southern part of Bahia and the northwestern part of Espírito Santo state. It was formed during the Brasiliano orogeny (also known as Araçuaí orogeny), dated from 600 to 450 million years ago. The pegmatite is located inside the Coronel Murta pegmatite field, which comprises tens of gem-bearing granitic pegmatites that have been extensively mined for the production of gem-grade elbaite (green, blue, red and multi-colored), gem-grade beryl (mostly “morganite”), ornamental quartz and perthitic K-feldspar (raw material for ceramic and glass industries).

Morro Redondo is the largest pegmatite found in this field: it has a length of 400 meters and an

TABLE 1. REFINED CRYSTAL-STRUCTURE DATA: CELL PARAMETER *a* AND OCCUPANCY OF THE SITES A, B, X AND Y

	<i>a</i> (Å)	A	B	X	Y	Ref.
fluorcalciomicrolite* – fluoratromicrolite intermediate member	10.4396(12)	$\text{Na}_{0.88}\text{Ca}_{0.88}\text{Pb}_{0.02}\square_{0.22}$	$\text{Ta}_{1.70}\text{Nb}_{0.14}\text{Si}_{0.12}\text{As}_{0.04}$	$\text{O}_{0.75}(\text{OH})_{0.25}$	$\text{F}_{0.73}\square_{0.27}$	(1)
hydroxykenomicrolite (from Vasin–Myk MtN.)	10.515(2)	$\square_{0.09}\text{Sb}^{3+}_{0.51}\text{Bi}_{0.01}\text{Na}_{0.31}\text{Pb}_{0.02}$	$\text{Ta}_{1.88}\text{Nb}_{0.12}$	$\text{O}_{0.69}(\text{OH},\text{F})_{0.31}$	$(\text{OH},\text{F})_{0.69}\text{Cs}_{0.31}$	(2)
hydroxykenomicrolite (from Tanco, Manitoba)	10.496(1)	$\square_{0.93}\text{Na}_{0.45}\text{Sb}^{3+}_{0.38}\text{Bi}_{0.02}\text{Pb}_{0.14}\text{Ca}_{0.06}$	$\text{Ta}_{1.88}\text{Nb}_{0.05}$	$\text{O}_{0.78}(\text{OH},\text{F})_{0.22}$	$(\text{OH},\text{F})_{0.56}\text{Cs}_{0.22}\text{K}_{0.01}$	(2)
kenoplumbomicrolite*	10.571(1)	$\text{Pb}_{1.30}\text{Ca}_{0.29}\square_{0.30}\text{Na}_{0.08}\text{U}^{4+}_{0.03}$	$\text{Ta}_{0.82}\text{Nb}_{0.67}\text{Si}_{0.23}\text{Sn}_{0.15}\text{Ti}_{0.07}\text{Fe}^{3+}_{0.10}\text{Al}_{0.01}$	$\text{O}_6$	$\square_{0.22}(\text{OH})_{0.25}\text{O}_{0.23}$	(3)
fluorcalciopyrochlore*	10.4200(7)	$\text{Ca}_{0.72}\text{Sr}_{0.07}\text{Mn}_{0.04}\text{Pb}_{0.01}\square_{0.69}\text{Na}_{0.37}\text{K}_{0.02}\text{Ce}_{0.03}\text{La}_{0.01}\text{Nd}_{0.01}\text{U}^{4+}_{0.02}$	$\text{Nb}_{1.72}\text{Ta}_{0.22}\text{Ti}_{0.16}\text{Sb}_{0.07}\text{Fe}^{3+}_{0.03}$	$\text{O}_{0.63}(\text{OH})_{0.37}$	$\text{F}_{0.62}(\text{OH})_{0.38}$	(4)
hydroxycalcipyrochlore*	10.3738(7)	$\text{Ca}_{0.72}\text{Sr}_{0.08}\text{Mn}_{0.04}\text{Pb}_{0.01}\square_{0.84}\text{Na}_{0.14}\text{K}_{0.04}\text{Ce}_{0.04}\text{La}_{0.01}\text{Nd}_{0.01}\text{U}^{4+}_{0.02}$	$\text{Nb}_{1.46}\text{Ta}_{0.54}\text{Ti}_{0.16}\text{Sb}_{0.24}\text{Fe}^{3+}_{0.08}$	$\text{O}_{1.63}(\text{OH})_{1.37}$	$(\text{OH})_{0.51}\text{F}_{0.46}$	(4)
hydropyrochlore	10.604(1)	$(\text{H}_2\text{O})_{0.99}\square_{0.99}\text{Sr}_{0.05}\text{Ca}_{0.01}$	$\text{Nb}_{1.85}\text{Ti}_{0.20}$	$\text{O}_{1.04}(\text{OH})_{0.94}$	$(\text{H}_2\text{O})_{0.88}\text{K}_{0.14}$	(5)
fluoratromoméite*	10.265(2)	$\text{Na}_{1.00}\text{Ca}_{0.80}\text{Mn}_{0.01}\square_{0.19}$	$\text{Sb}^{5+}_2$	$\text{O}_{0.66}(\text{OH})_{0.31}$	$\text{F}_{0.66}(\text{OH})_{0.05}\square_{0.06}$	(6)
hydroxycalcioroméite	10.277(1)	$\text{Ca}_{1.04}\text{Mn}_{0.07}\text{Sb}^{3+}_{0.65}\square_{0.23}\text{Na}_{0.01}$	$\text{Sb}^{5+}_{0.99}\text{Ti}_{0.71}\text{Fe}^{3+}_{0.19}\text{Al}_{0.06}$	$\text{O}_6$	$(\text{OH})_{0.51}\square_{0.09}$	(7)
hydroxycalcioroméite	10.311(7)	$\text{Ca}_{0.91}\text{Mn}_{0.08}\square_{0.37}\text{Sb}^{3+}_{0.27}\text{Fe}^{3+}_{0.18}\text{Al}_{0.10}\text{Na}_{0.10}$	$\text{Sb}^{5+}_{1.28}\text{Ti}_{0.72}$	$\text{O}_6$	OH	(8)
oxycalcibetafite*	10.2637(13)	$\text{Ca}_{1.23}\text{U}^{4+}_{0.50}\text{Na}_{0.18}\text{REE}_{0.03}$	$\text{Ti}_{1.09}\text{Nb}_{0.79}\text{Ta}_{0.01}\text{Zr}_{0.14}\text{Fe}_{0.04}$	$\text{O}_6$	$\text{O}_{0.98}\text{F}_{0.02}$	(9)
hydrokenoelsmoreite	10.352(1)	$\square_{1.33}(\text{H}_2\text{O})_{0.29}\text{Ca}_{0.06}\text{Na}_{0.02}$	$\text{W}_{1.46}\text{Fe}^{3+}_{0.54}$	$\text{O}_{1.70}(\text{OH})_{1.30}$	$(\text{H}_2\text{O})_{0.30}\text{K}_{0.20}$	(10)

\* Need to be completely described in order to be approved as valid species. References: (1) this work, (2) Ercit *et al.* (1993), (3) Bindl *et al.* (2006), (4) Bonazzi *et al.* (2006), (5) Ercit *et al.* (1994), (6) Matsubara *et al.* (1996), (7) Rouse *et al.* (1998), (8) Zubkova *et al.* (2000), (9) Cámara *et al.* (2004), (10) Ercit & Robinson (1994).

average thickness of 30 meters, has a N-S strike and dips 70°W. It shows a well-developed zoning, with a wall zone about 3 m thick, constituted of perthitic feldspar and quartz showing a graphic texture, with smaller amounts of dark muscovite plates, schorl and andradite. The intermediate zone is thick (about 10 m) and is constituted mostly of centimetric microcline and quartz grains, lighter brown centimetric muscovite plates, schorl, albite, montebasite and beryl crystals. The inner zone consists of a discontinuous quartz core, that in some areas can be up to 10 m thick, surrounded by albite-dominant replacement bodies with decimetric crystals of schorl.

This pegmatite was found in 1991; until 1996, inside the inner zone, tens of mid- to large-size cavities produced several hundreds of tonnes of quartz crystals (colorless, citrine or smoky), measuring up to 1 m long, as well as tens of small to mid-size cavities containing gem elbaite (green, blue, red or multi-colored crystals). What made this mine a legend was the discovery, in 1994, of a giant albite-dominant replacement body, near the northern edge of the pegmatite, containing several hundreds of small cavities, and closed spaced fractures mineralized in bicolored red-green elbaite crystals measuring up to 10 × 1 cm. Over one tonne of elbaite was produced, and it was considered the largest volumetric single find of gem-quality elbaite in the world. The empty cavity that resulted after this zone was mined out measures 15 × 10 × 10 meters.

Since then, all attempts at finding more mineralized cavities in the deeper parts of the pegmatite were unsuccessful. Two subsequent prospecting rotary-drilling campaigns failed to find more mineralized areas, and confirmed that the pegmatite has an atypical cross-section of a parallelogram measuring 30 × 40 meters.

After the mining operations were discontinued in 1997, intermittent and risky digging has been conducted by individual miners, who take the risk of digging into the safety pillars. One of these miners found the microlite crystal that is the object of this study in the vicinity of the cavity of the mined-out tourmaline zone, in the inner part of pegmatite, about 100 m south of its northern limit.

The main minerals of the Morro Redondo pegmatite are microcline, albite, quartz, muscovite, lepidolite, tourmaline, beryl, garnet, cassiterite, columbite-tantalite, amblygonite and microlite (Proctor 1984, Castañeda *et al.* 2001, Pedrosa-Soares *et al.* 2009).

#### MINERAL COMPOSITION

The green crystal fragment was embedded in epoxy resin, polished and carbon-coated to ensure conductivity. The chemical analysis was performed by means of JEOL JXA-8600 electron microprobe (WDS mode, 15 kV, 20 nA, 5 µm beam diameter and a Noran system for automation and data reduction). The analytical results are represented in Table 2. The empirical

TABLE 2. CHEMICAL COMPOSITION OF AN INTERMEDIATE MEMBER OF THE "FLUORCALCIOMICROLITE" – FLUORNATROMICROLITE SOLID SOLUTION

oxides	p1	p2	p3	p4	mean	atom	standards
Na <sub>2</sub> O wt%	5.49	5.55	5.66	5.49	5.55	Na <i>apfu</i>	0.88
CaO	9.97	10.17	9.79	9.98	9.98	Ca	0.88
MnO	0.09	0.08	0.07	<0.06	0.06	Mn	-
PbO	0.61	0.57	0.67	0.54	0.60	Pb	0.02
Ce <sub>2</sub> O <sub>3</sub>	0.18	0.20	<0.15	<0.15	0.10	Ce	-
ThO <sub>2</sub>	0.18	0.22	0.18	0.12	0.18	Th	-
						□	0.22
						ΣA	2.00
SnO <sub>2</sub>	<0.06	0.10	0.12	0.13	0.09	Sn	-
Al <sub>2</sub> O <sub>3</sub>	<0.02	<0.02	0.08	<0.02	0.02	Al	-
As <sub>2</sub> O <sub>3</sub>	<1.04	<1.04	1.20	1.20	0.60	As	0.04
Nb <sub>2</sub> O <sub>5</sub>	3.94	3.79	3.95	4.08	3.94	Nb	0.14
Ta <sub>2</sub> O <sub>5</sub>	74.8	75.4	74.9	75.4	75.13	Ta	1.70
SiO <sub>2</sub>	1.46	1.42	1.48	1.47	1.46	Si	0.12
						ΣB	2.00
						O	5.75
						OH	0.25
						ΣX	6.00
F	3.13	2.44	3.08	2.47	2.78	F	0.73
						□	0.27
						ΣY	1.00
O=F	-1.31	-1.02	-1.29	-1.04	-1.17		
Total	98.54	98.92	99.89	99.84	99.32		

Color of crystal: green. The structural formula is calculated on the basis of ΣB = 2 *apfu*. The following elements were found to be below the detection limits (wt%): Sr (<0.10), Ba (<0.16), La (<0.15), Bi (<0.16), Sb (<0.11), U (<0.20), Ti (<0.08), Fe (<0.07), K (<0.02) and Cs (<0.18). \*\* Amelia albite: pure, clear variety of albite from Amelia Court House, Virginia, U.S.A. \*\*\* REE3: a Ca-Al silicate glass.

chemical formula is  $(\text{Na}_{0.88}\text{Ca}_{0.88}\text{Pb}_{0.02}\square_{0.22})_{\Sigma 2.00}$   $(\text{Ta}_{1.70}\text{Nb}_{0.14}\text{Si}_{0.12}\text{As}_{0.04})_{\Sigma 2.00}$   $[\text{O}_{5.75}(\text{OH})_{0.25}]_{\Sigma 6.00}$   $(\text{F}_{0.73}\square_{0.27})_{\Sigma 1.00}$ .

### CRYSTALLOGRAPHY

A fragment of dimensions  $0.17 \times 0.12 \times 0.08 \text{ mm}^3$  was used for structural investigation. X-ray-diffraction measurements were made on an Enraf–Nonius Kappa-CCD diffractometer with graphite-monochromated  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Data were collected up to a  $2\theta$  value of  $60.5^\circ$ , with an average redundancy of 5. The data-collection geometry was strategically calculated by setting  $\phi$  and  $\omega$  scans with  $\kappa$  offsets. The data collection was performed with an exposition time of 8 s/degree. It took 24.6 minutes to collect 91 frames with a scan width of  $2^\circ$ . The final unit-cell parameter is based on the 1098 collected reflections with the following index ranges:  $-14 \leq h \leq 14$ ,  $-10 \leq k \leq 10$ ,  $-9 \leq l \leq 9$ . The COLLECT program (Enraf-Nonius 1997–2000) was used for the data collections, and the integration and scaling of the reflections were performed with the HKL DENZO–SCALEPACK system of programs (Otwinowski & Minor 1997). The face-indexed numerical absorption was calculated by the MULTI-SCAN method using the PLATON program. An extinction correction was applied, with a refined extinction coefficient of 0.0008(1).

The structure (Fig. 1) was solved using Patterson methods with SHELXS–97 (Sheldrick 2008). The model was refined on  $F^2$  by full-matrix least-squares

procedures with SHELXL–97 (Sheldrick 2008), within the WINGX program (Farrugia 1999) using anisotropic thermal displacement parameters. The anisotropic thermal displacement parameters for atoms sharing the same site were constrained to be equal. Scattering functions for neutral atoms were used for all atoms. In the final cycle of refinement, the weighting scheme used was  $w = [s^2(\text{Fo}^2) + (0.0262\text{P})^2 + 64.8762\text{P}]^{-1}$  where  $\text{P} = (\text{Fo}^2 + 2\text{Fc}^2)/3$ .

The software WINGX was used to analyze and prepare data for publication (Farrugia 1999). In the initial model, the starting positions for the A, B, X and Y sites were taken from a refinement of the “fluorcalciopyrochlore” structure (Bonazzi *et al.* 2006). Details about the crystal and data-collection parameters, structure determination and refinement are summarized in Tables 3 and 4. Selected cation–anion distances from the refined atomic parameters are consistent with the data in the literature (Table 5). A table of structure factors and a cif file are available from the Depository of Unpublished Data on the MAC website [document Microlite CM49\_615].

### RESULTS

The charge-balanced end-member  $\text{NaCaTa}_2\text{O}_6\text{F}$  is not at the center of the composition field of the species, but marks the boundary between fluornatromicrolite and fluorcalciomicrolite. Fluornatromicrolite is an IMA-approved mineral (Witzke *et al.* 1998), but the complete description has not yet been published. When

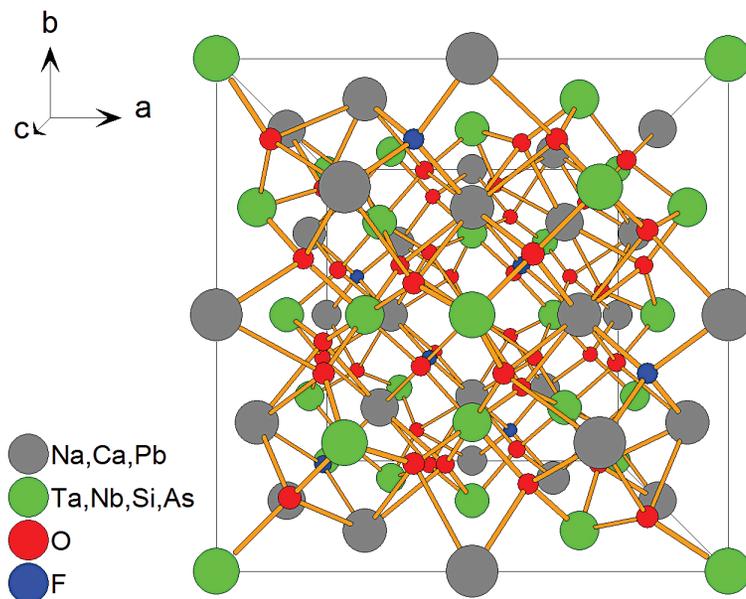


FIG. 1. Crystal structure of the microlite-group mineral from the Morro Redondo mine.

the manuscript on fluornatromicrolite was submitted for publication, although approved by the CNMMN-IMA, the name fluornatromicrolite did not match the nomenclature of Hogarth (1977). Today, however, the name fluornatromicrolite is perfectly in line with the new approved system of nomenclature (Atencio *et al.* 2010). Its type locality is Quixabá, Paraíba, Brazil, and the formula is  $(\text{Na}_{1.15}\text{Ca}_{0.70}\text{Bi}_{0.15})_{\Sigma 2.00}\text{Ta}_2\text{O}_6\text{F}$ . Some data on this mineral were published by Atencio (2000). Chemical analyses that correspond to fluornatromicrolite from other occurrences are available in the papers by Ohnenstetter & Piantone (1992), Belkasmí *et al.* (2000), Huang *et al.* (2002) and Baldwin *et al.* (2005). There are several compositions of “fluorcalciomicrolite” available 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.

The multiplicity of the *A* site (Na, Ca, *etc.*) is twice the multiplicity of the non-framework anion site (F, OH, O, H<sub>2</sub>O), and the most common *B*-site and *Y*-site components require 50:50 occupancy of *A* by two different valences. This mismatch of species “near the 50:50 mark” is very common in solid-state solutions.

Full structural refinement was carried out using as starting point the unit-cell parameters calculated from the microprobe-derived chemical analysis. The distribution of Na and Ca were assumed to be disordered at the *A* site, with each one occupying approximately 45% of this site. The cationic positions were assumed to be  $A(16d) = {}^A(\text{Na}_{0.88}\text{Ca}_{0.88}\text{Pb}_{0.02})_{\Sigma 1.78}$ ,  $B(16c) = {}^B(\text{Ta}_{1.70}\text{Nb}_{0.14}\text{Si}_{0.12}\text{As}_{0.04})_{\Sigma 2.00}$ ,  $X(48f) = {}^X[(\text{O}_{5.75}(\text{OH})_{0.25})_{\Sigma 6.00}]$ , and  $Y(8b) = {}^Y(\text{F}_{0.73})_{\Sigma 0.73}$ . As some typical *B*-site cations are incorporated at the *A* site in some synthetic pyrochlore structures such as bismuth-based pyrochlores (Cagnon *et al.* 2007), the presence of the 220-type reflections, which provide evidence of this kind of disorder, was investigated. They are absent, suggesting that the cations occupy the ideal

pyrochlore positions. The *B*-site occupancy was also constrained by the results from chemical analysis and set to full occupancy ( $\Sigma B = 2$  apfu). The occupancy of *A* and *B* sites was set to match the analytical data. The O and OH contents of the *X* (48f) position were calculated from charge-balance requirements. After the cationic contents of *A* and *B* sites were set, the *Y* position, located at 8*b*, was refined isotropically. The *Y* site displacement parameter was fixed as the average of the isotropic *U*-values of the positions *A* and *B*. The subsequent *Y*-position refinement was anisotropic, and the calculated occupancy was  $F_{0.73}$ . The final refined model with anisotropic parameters for *A*, *B*, *X* and *Y* sites converged to  $R_1 = 0.0258$ ,  $wR_2 = 0.0715$ , and is consistent with a cubic structure,  $Fd\bar{3}m$ , with the unit-cell parameter *a* equal to 10.4396(12) Å. The charge-balanced empirical formula obtained is  ${}^A(\text{Na}_{0.88}\text{Ca}_{0.88}\text{Pb}_{0.02}\square_{0.22})_{\Sigma 2.00}{}^B(\text{Ta}_{1.70}\text{Nb}_{0.14}\text{Si}_{0.12}\text{As}_{0.04})_{\Sigma 2.00}{}^X[(\text{O}_{5.75}(\text{OH})_{0.25})_{\Sigma 6.00}]{}^Y(\text{F}_{0.73}\square_{0.27})_{\Sigma 1.00}$ .

TABLE 4. WYCKOFF POSITION, SITE OCCUPANCY, COORDINATES AND EQUIVALENT ISOTROPIC DISPLACEMENT OF ATOMS IN AN INTERMEDIATE MEMBER OF THE “FLUORCALCIOMICROLITE” – FLUORNATROMICROLITE SOLID SOLUTION

	Wyckoff	occupancy	x	y	z	$U_{\text{eq}}$ (Å <sup>2</sup> )
A	16 <i>d</i>	0.89	0.5	0.5	0.5	0.0181(4)
B	16 <i>c</i>	1	0.0	0.0	0.0	0.0126(4)
O1	48 <i>f</i>	1	0.0684(9)	0.375	0.375	0.0207(16)
F	8 <i>b</i>	0.73	0.375	0.375	0.375	0.013(4)

$U_{\text{eq}}$  is defined as one-third of the trace of the orthogonalized  $U_{ij}$  tensor.  
Note:  $A = \text{Na}_{0.88}\text{Ca}_{0.88}\text{Pb}_{0.02}$ ;  $B = \text{Ta}_{1.70}\text{Nb}_{0.14}\text{Si}_{0.12}\text{As}_{0.04}$ .

TABLE 5. SELECTED CATION-ANION DISTANCES (Å) IN PYROCHLORE-SUPERGROUP MINERALS

	(A – X) × 6	(A – Y) × 6	(B – Y) × 6	Ref.
fluorcalciomicrolite* – fluornatromicrolite intermediate member	2.646(7)	2.2602(2)	1.979(3)	(1)
hydroxykenomicrolite (from Vasin–Mylk Mtn.)	2.73(1)	2.34(2)	1.978(5)	(2)
hydroxykenomicrolite (from Tanco)	2.72(2)	2.30(3)	1.963(5)	(2)
kenoplumbomicrolite*	2.702(7)	2.289(1)	1.993(3)	(3)
fluorcalciopyrochlore*	2.648(3)	2.2560(2)	1.972(1)	(4)
hydroxycalciooxyprochlore*	2.637(4)	2.2460(2)	1.962(1)	(4)
hydroxyprochlore	2.736(2)	1.90(7)	1.986(1)	(5)
fluornatromicrolite*	2.565(1)	2.2224(1)	1.9647(7)	(6)
hydroxycalcioroméite	2.5622(5)	2.2250(1)	1.9703(7)	(7)
hydroxycalcioroméite	2.574(3)	2.232(2)	1.975(2)	(8)
oxycalciobetafite*	2.552(3)	2.2222(2)	1.972(2)	(9)
hydrokenoelsmoreite	2.686(3)	2.2413(1)	1.933(3)	(10)

\*need to be completely described in order to be approved as valid species. References: (1) this work, (2) Ercit *et al.* (1993), (3) Bindi *et al.* (2006), (4) Bonazzi *et al.* (2006), (5) Ercit *et al.* (1994), (6) Matsubara *et al.* (1996), (7) Rouse *et al.* (1998), (8) Zubkova *et al.* (2000), (9) Cámara *et al.* (2004), (10) Ercit & Robinson (1994).

TABLE 3. CRYSTAL DATA AND DETAILS OF STRUCTURE REFINEMENT

Temperature (K)	293(2)
Crystal color	green
Crystal size (mm)	0.17 × 0.12 × 0.08
Formula weight	495.24
Crystal system	Cubic
Space group	$Fd\bar{3}m$
Unit-cell dimension <i>a</i>	10.4396(12) Å
Unit-cell volume <i>V</i>	1137.8(2) Å <sup>3</sup>
Z	8
Density (calculated)	5.782 g/cm <sup>3</sup>
Absorption coefficient	34.338
$F(000)$	1727
Reflections collected/unique	1098/107
Parameters	11 ( $R_{\text{int}} = 0.0336$ )
Goodness-of-fit on $F^2$	1.276
Final <i>R</i> indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0258$ , $wR_2 = 0.0715$
Largest diff. peak and hole	1.63 and –1.22 e.Å <sup>–3</sup>

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## REFERENCES

- ATENCIO, D. (2000): *Type Mineralogy of Brazil* (first ed.). Museu de Geociências – USP, São Paulo, Brazil.
- ATENCIO, D., ANDRADE, M.B., CHRISTY, A.G., GIÉRE, R. & KARTASHOV, P.M. (2010): The pyrochlore supergroup minerals: nomenclature. *Can. Mineral.* **48**, 673-698.
- BALDWIN, J.R. (1989): Replacement phenomena in tantalum minerals from rare-metal pegmatites in South Africa and Namibia. *Mineral. Mag.* **53**, 571-581.
- BALDWIN, J.R., HILL, P.G., FINCH, A.A., VON KNORRING, O. & OLIVER, G.J.H. (2005): Microlite–manganotantalite exsolution lamellae: evidence from rare-metal pegmatite, Karibib, Namibia. *Mineral. Mag.* **69**, 917-935.
- BELKASMI, M., CUNNEY, M., POLLARD, P.J. & BASTOUL, A. (2000): Chemistry of the Ta–Nb–Sn–W oxide minerals from the Yichun rare metal granite (SE China): genetic implications and comparison with Moroccan and French Hercynian examples. *Mineral. Mag.* **64**, 507-523.
- BINDI, L., ZOPPI, M. & BONAZZI, P. (2006): Plumbomicrolite from the Ploskaya Mountain, Keivy Massif, Kola Peninsula, Russia: composition and crystal structure. *Per. Mineral.* **75**(2/3), 51-58.
- BONAZZI, P., BINDI, L., ZOPPI, M., CAPITANI, G.C. & OLMI, F. (2006): Single-crystal diffraction and transmission electron microscopy studies of “silicified” pyrochlore from Narssârssuk, Julianehaab district, Greenland. *Am. Mineral.* **91**, 794-801.
- BRÜHWILER, M., KAZAKOV, S.M., ZHIGADLO, N.D., KARPINSKI, J. & BATLOGG, B. (2004): Superconductivity in the geometrically frustrated pyrochlore  $\text{RbOs}_2\text{O}_6$ . *Phys. Rev. B* **70**, 020503R.
- CAGNON, J., BOESCH, D. S., FINSTROM, N.H., NERGIZ, S.Z., KEANE, S.P. & STEMMER, S. (2007): Microstructure and dielectric properties of pyrochlore  $\text{Bi}_2\text{Ti}_2\text{O}_7$  thin films. *J. Appl. Phys.* **102**, 044102.
- CÁMARA, F., WILLIAMS, C.T., DELLA VENTURA, G., OBERTI, R. & CAPRILLI, E. (2004): Non-metamict betafite from Le Carcarelle (Vico volcanic complex, Italy): occurrence and crystal structure. *Mineral. Mag.* **68**, 939-950.
- CASTAÑEDA, C., ADDAD, J.E. & LICCARDO, A. (2001): *Gemas de Minas Gerais: esmeralda, turmalina, safira, topázio, quartzo, água-marinha e alexandrita*. Núcleo Minas Gerais, Sociedade Brasileira de Geologia, 228 p.
- ENRAF-NONIUS (1997–2000): COLLECT. Nonius BV, Delft, The Netherlands.
- ERCIT, T.S., ČERNÝ, P. & HAWTHORNE, F.C. (1993): Cesstibantite – a geologic introduction to the inverse pyrochlores. *Mineral. Petrol.* **48**, 235-255.
- ERCIT, T.S., HAWTHORNE, F.C. & ČERNÝ, P. (1994): The structural chemistry of kalipyrochlore, a “hydropyrochlore”. *Can. Mineral.* **32**, 415-420.
- ERCIT, T.S. & ROBINSON, G.W. (1994): A refinement of the structure of ferritungstite from Kalzas Mountain, Yukon, and observations on the tungsten pyrochlores. *Can. Mineral.* **32**, 567-574.
- FARRUGIA, L.J. (1999): WINGX suite for small-molecule single-crystal crystallography. *J. Appl. Crystallogr.* **32**, 837-838.
- GEISLER, T., BERNDT, J., MEYER, H.-W., POLLOK, K. & PUTNIS, A. (2004): Low-temperature aqueous alteration of crystalline pyrochlore: correspondence between nature and experiment. *Mineral. Mag.* **68**, 905-922.
- HOGARTH, D.D. (1977): Classification and nomenclature of the pyrochlore group. *Am. Mineral.* **62**, 403-410.
- HUANG XIAO LONG, WANG RU CHENG, CHEN XIAO MING, HU HUAN & LIU CHANG SHI (2002): Vertical variations in the mineralogy of the Yichun topaz–lepidolite granite, Jiangxi Province, southern China. *Can. Mineral.* **40**, 1047-1068.
- LAVEROV, N.P., YUDINTSEV, S.V., LIVSHITS, T.S., STEFANOVSKY, S.V., LUKINYKH, A.N. & EWING, R.C. (2010): Synthetic minerals with the pyrochlore and garnet structures for immobilization of actinide-containing wastes. *Geochem. Int.* **48**, 1-14.
- LUMPKIN, G.R., CHAKOUMAKOS, B.C. & EWING, R.C. (1986): Mineralogy and radiation effects of microlite from the Harding pegmatite, Taos County, New Mexico. *Am. Mineral.* **71**, 569-588.
- LUMPKIN, G.R. & EWING, R.C. (1992): Geochemical alteration of pyrochlore group minerals: microlite subgroup. *Am. Mineral.* **77**, 179-188.
- MATSUBARA, S., KATO, A., SHIMIZU, M., SEKIUCHI, K. & SUZUKI, Y. (1996): Romeite from the Gozaisho mine, Iwaki, Japan. *Mineral. J.* **18**(4), 155-160.
- NORMAND, B. (2009): Frontiers in frustrated magnetism. *Con-temp. Phys.* **50**, 533-552.
- OHNSTETTER, D. & PIANTONE, P. (1992): Pyrochlore-group minerals in the Beauvoir peraluminous leucogranite, Massif Central, France. *Can. Mineral.* **30**, 771-784.
- OTWINOWSKI, Z. & MINOR, W. (1997): Processing X-ray diffraction data collected in oscillation mode. *In* Methods in

- Enzymology **276** (C.W. Carter Jr. & R.M. Sweet, eds.). Academic Press, New York, N.Y. (307-326).
- PEDROSA-SOARES, A., CHAVES, M. & SCHOLZ, R. (2009): Eastern Brazilian pegmatite province. *4th International Symposium on Granitic Pegmatites, Field trip guide*, 1-28.
- PROCTOR, K. (1984): Gem pegmatites of Minas Gerais, Brazil: exploration, occurrence, and aquamarine deposits. *Gems & Gemology* **20**(2), 78-100.
- ROUSE, R.C., DUNN, P.J., PEACOR, D.R. & WANG LIPING (1998): Structural studies of the natural antimonian pyrochlores. I. Mixed valences, cation site splitting, and symmetry reduction in lewisite. *J. Solid State Chem.* **141**, 562-569.
- SHELDRIK, G.M. (2008): A short history of SHELX. *Acta Crystallogr.* **A64**, 112-122.
- TINDLE, A.G. & BREAKS, F.W. (1998): Oxide minerals of the Separation Rapids rare-element granitic pegmatite group, northwestern Ontario. *Can. Mineral.* **36**, 609-635.
- TINDLE, A.G., SELWAY, J.B. & BREAKS, F.W. (2005): Lid-dicoatite and associated species from the McCombe spodumene-subtype rare-element granitic pegmatite, northwestern Ontario, Canada. *Can. Mineral.* **43**, 769-793.
- WANG, R.F., NISOLI, C., FREITAS, R.S., LI, J., MCCONVILLE, W., COOLEY, B.J., LUND, M.S., SAMARTH, N., LEIGHTON, C., CRESPI, V.H. & SCHIFFER, P. (2006): Artificial 'spin ice' in a geometrically frustrated lattice of nanoscale ferromagnetic islands. *Nature* **439**, 303-306.
- WITZKE, T., STEINS, M. DOERING, T., SCHUCKMANN, W., WEGNER, R. & POLLMANN, H. (1998): Fluornatromicrolite, a new mineral from Quixabá, Paraíba, Brazil. *Int. Mineral. Assoc., CNMMN Submission* **98-018**.
- ZUBKOVA, N.V., PUSHCHAROVSKY, D.YU., ATENCIO, D., ARAK-CHEEVA, A.V. & MATIOLI, P.A. (2000): The crystal structure of lewisite,  $(\text{Ca}, \text{Sb}^{3+}, \text{Fe}^{3+}, \text{Al}, \text{Na}, \text{Mn}, \square)_2(\text{Sb}^{5+}, \text{Ti})_2\text{O}_6(\text{OH})$ . *J. Alloys Compounds* **296**, 75-79.
- ZUREVINSKI, S.E. & MITCHELL, R.H. (2004): Extreme compositional variation of pyrochlore-group minerals at the Oka carbonatite complex, Quebec: evidence of magma mixing? *Can. Mineral.* **42**, 1159-1168.

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