

Plumbomicrolite from the Ploskaya Mountain, Keivy Massif, Kola Peninsula, Russia: composition and crystal structure

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ABSTRACT. — A sample of plumbomicrolite from Ploskaya Mountain, Kola Peninsula (Russia) was analyzed by electron microprobe and X-ray diffraction. A single crystal [$a = 10.571(1) \text{ \AA}$] was selected and the structure was refined in the space group $Fd\bar{3}m$ to $R_{\text{obs}} = 4.89\%$ and $R_{\text{all}} = 5.79\%$. Pb^{2+} was found to be completely ordered on the A site (*normal* structure). However, because the Y site was found to be partially occupied, the A cation may locally result in a six-, or seven-, or eight-fold coordination. Whenever two neighbour Y sites are vacant, six X atoms around the A position form a trigonally flattened octahedron, while a trigonal scalenohedron occurs when two Y sites around A are occupied. When only one neighbour Y site is occupied, the A cation assumes an asymmetrical seven-fold pyramidal coordination. Due to the stereoactive electron lone-pair of Pb^{2+} , this last coordination should be strongly preferred. The chemical data as well as crystal chemical considerations led to assign the following crystal chemical formula: $^A[\text{Pb}_{1.30}\text{Ca}_{0.29}\text{Na}_{0.08}\text{U}^{4+}_{0.03}]_{\Sigma=1.70}^B[\text{Ta}_{0.82}\text{Nb}_{0.62}\text{Si}_{0.23}\text{Sn}^{4+}_{0.15}\text{Ti}^{4+}_{0.07}\text{Fe}^{3+}_{0.10}\text{Al}_{0.01}]_{\Sigma=2.00}^X[\text{O}_6]^Y[\text{O}_{0.23}(\text{OH})_{0.25}]_{\Sigma=0.48}$.

KEY WORDS: *Plumbomicrolite, pyrochlore-group, Kola Peninsula, structure refinement, chemical composition.*

RIASSUNTO. — Un campione di plumbomicrolite proveniente da Ploskaya Mountain, Kola Peninsula (Russia) è stato analizzato mediante microsonda

elettronica e diffrazione a raggi-X. Un cristallo singolo [$a = 10.571(1) \text{ \AA}$] è stato selezionato e il raffinamento della struttura nel gruppo spaziale $Fd\bar{3}m$ ($R_{\text{obs}} = 4.89\%$, $R_{\text{all}} = 5.79\%$) evidenzia che il catione Pb^{2+} è completamente ordinato nel sito A (struttura *normale*). Comunque, poiché il sito Y risulta parzialmente occupato, il catione A può coordinare localmente sei, sette o otto anioni. Quando i due siti Y primiviciini sono vacanti, i sei anioni X intorno ad A formano un ottaedro compresso lungo l'asse ternario, mentre quando sono occupati si forma uno scalenoedro trigonale. Quando soltanto uno dei due primiviciini è occupato il catione A assume una coordinazione asimmetrica secondo una piramide esagonale. A causa della presenza del doppietto elettronico di non legame del catione Pb^{2+} , quest'ultima coordinazione dovrebbe essere preferita. I dati chimici insieme con considerazioni cristallochimiche hanno permesso di assegnare la seguente formula: $^A[\text{Pb}_{1.30}\text{Ca}_{0.29}\text{Na}_{0.08}\text{U}^{4+}_{0.03}]_{\Sigma=1.70}^B[\text{Ta}_{0.82}\text{Nb}_{0.62}\text{Si}_{0.23}\text{Sn}^{4+}_{0.15}\text{Ti}^{4+}_{0.07}\text{Fe}^{3+}_{0.10}\text{Al}_{0.01}]_{\Sigma=2.00}^X[\text{O}_6]^Y[\text{O}_{0.23}(\text{OH})_{0.25}]_{\Sigma=0.48}$.

INTRODUCTION

Minerals of the pyrochlore group typically occur as accessory minerals in granitic pegmatites, nepheline-syenite pegmatites, and carbonatites. They have cubic symmetry, space group $Fd\bar{3}m$, and general formula $A_{2-m}B_2X_6Y_{1-n} \cdot p\text{H}_2\text{O}$, where $m = 0.0-1.7$, $n = 0.0-1.0$ and $p = 0.0-2.5$ (Lumpkin *et al.* 1986). At $n = 0$, A is an eight-fold coordinated cation (mostly Ca and Na, less commonly or in

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minor amounts K, Sr, Ba, Sn^{2+} , Pb^{2+} , REE^{3+} , Y, Sb^{3+} , Bi^{3+} , U^{4+} , Th^{4+}) and B is an octahedrally-coordinated cation mainly including Nb, Ta, Ti^{4+} (or Sb^{5+} in the stibiconite group) and minor quantities of Fe^{3+} , Sn^{4+} and W^{6+} . On the basis of the B-site composition pyrochlore minerals are classified into three subgroups (Hogarth 1977): the root-names *pyrochlore* and *microlite* are given to the Nb- and Ta-dominant members, respectively, whereas the root-name *betafite* is assigned when $2\text{Ti} > (\text{Nb} + \text{Ta})$. The X position is mostly occupied by O^{2-} or, to a lesser extent, OH^- (Ercit *et al.* 1993, 1994; Nasraoui and Waerenborgh 2001), whereas Y may be O^{2-} , OH^- or F. In this type of structure, called *normal* pyrochlore, both the A and Y site can be partially vacant ($m \leq 2$, $n \leq 1$). On the other hand, the structure is called *inverse* pyrochlore when the A position is completely vacant and the Y site (or any positionally disordered A' position in the vicinity of Y) is occupied by large ionic radius cations (i.e., K, Ti^+ , Rb, Cs). A mixed *inverse-normal* pyrochlore structure has been described in cesstibantite and kalipyrochlore (Ercit *et al.* 1993, 1994).

In natural members, Pb is present at the divalent state and therefore should occupy the A site or, by analogy with pyrochlore-type compounds incorporating large cations, the A' site of the *inverse* pyrochlore structure. Pb-dominant members are known in the all three subgroups of pyrochlore minerals. Plumbomicrolite ($\text{Pb} = 0.44$ apfu) was first identified in the alluvial sands of the Kivu deposit (Democratic Republic of Congo) by Safiannikoff and van Wambeke (1961). Later, Skorobogatova *et al.* (1966) described two plumbopyrochlore samples ($\text{Pb} = 0.80$ and 0.62 apfu, respectively) occurring in the metasomatically altered granites from the Urals (Russia) and suggested the existence of a continuous plumbopyrochlore-plumbomicrolite series. Plumbobetafite ($\text{Pb} = 0.44$ apfu) was first identified in a dike cutting nepheline syenite of the Burpala massif, northern Baikal (Russia); owing to its metamict state, the mineral species was defined on the basis of the X-ray pattern shown after heating at 800°C (Ganzev *et al.* 1969). In all these minerals, as well as in the cation-deficient plumbopyrochlore from the Lovozero alkaline complex (Russia) described by Chakhmouradian and Mitchell (2002), Pb prevails on the other A-cations but never exceeds the

half-site occupancy. Indeed, pyrochlore minerals containing other large A-cations (i.e., K^+ , Cs^+) commonly exhibit high A-site deficiencies, which, in turn, usually correlate with high H_2O contents leading to stabilize the *inverse* pyrochlore structure. However, no full structural studies were done on Pb-rich pyrochlore minerals. On the other hand, a structural characterization of several synthetic $\text{Pb}_{1.5+x}\text{Nb}_2\text{O}_{6.5+x}$ compounds ($x = 0.0, 0.50, 0.81$, and 0.94) was provided by Bernotat-Wulf and Hoffmann (1982). According to these authors, the only phase in the $\text{PbO-Nb}_2\text{O}_5$ system which crystallizes with the cubic pyrochlore structure ($a = 10.567 \text{ \AA}$; $Fd\bar{3}m$) is $\text{Pb}_{1.5}\text{Nb}_2\text{O}_{6.5}$, the others having trigonal superstructures closely related to the cubic pyrochlore-type structure. In particular, the stoichiometric $\text{Pb}_2\text{Nb}_2\text{O}_7$ phase which corresponds to a fully occupied theoretical plumbopyrochlore crystallizes in the space group $P3m1$ ($a = 7.472$, $c = 28.351 \text{ \AA}$). In the $\text{PbO-Ta}_2\text{O}_5$ system, the existence of the defect-pyrochlore cubic phase $\text{Pb}_{1.5}\text{Ta}_2\text{O}_{6.5}$ was confirmed by Menguy *et al.* (1996) who also excluded, as previously suggested by Scott (1982), the existence of a rhombohedral phase $\text{Pb}_2\text{Ta}_2\text{O}_7$.

We were therefore interested in studying the structure of a pyrochlore-group mineral with the highest possible content of Pb. Voloshin *et al.* (1981) first reported that plumbomicrolite from amazonitic pegmatites of the Kola Peninsula has a composition close to the theoretical formula $\text{Pb}_2(\text{Ta},\text{Nb})_2\text{O}_7$. The chemical composition of a sample of this mineral from an amazonitic pegmatite vein cutting the Proterozoic gneisses and schists of the Kola Peninsula occurring at the Ploskaya Mountain was reported by Stepanov *et al.* (1982). According to these authors, the mineral contains PbO 44.0, Na_2O 0.63, CaO 2.80, SnO_2 4.45, Nb_2O_5 11.20, Ta_2O_5 33.46, Fe_2O_3 1.74, $\text{H}_2\text{O}(+)$ 1.31, and $\text{H}_2\text{O}(-)$ 0.20 wt.%, yielding to the chemical formula $^A[\text{Pb}_{1.36}\text{Ca}_{0.35}\text{Na}_{0.14}]_{\Sigma=1.85}^B[\text{Ta}_{1.06}\text{Nb}_{0.59}\text{Sn}^{4+}_{0.20}\text{Fe}^{3+}_{0.13}]_{\Sigma=1.98}^X[\text{O}_6]^Y[\text{OH}]$.

More recently, a plumbopyrochlore characterized by a high content of Pb (96 mol.% of the $\text{Pb}_2\text{Nb}_2\text{O}_7$ component) was reported from arfvedsonite-feldspar pegmatites associated with the rare-metal granites of the Khaldzan-Buregteg Massif of western Mongolia (Kartashov *et al.* 1992). Among these two extremely Pb-rich samples, plumbomicrolite from the Kola

Peninsula has been made available to us by Roy Kristiansen.

X-RAY CRYSTALLOGRAPHY
AND CRYSTAL-STRUCTURE REFINEMENT

A crystal fragment ($225 \times 255 \times 270 \mu\text{m}$) was selected for the X-ray single-crystal diffraction study. Unit-cell parameters, determined by least-squares refinement of the setting angles of 25 high- θ equivalent reflections on an automated diffractometer (Bruker P4), are shown in Table 1. Intensity data were collected using MoK α radiation monochromatized by a flat graphite crystal in ω scan mode. Intensities were corrected for Lorentz-polarization effects and subsequently for absorption following the semi-empirical method of North *et al.* (1968). A full-matrix least-squares refinement on F^2 was performed in the space group $Fd\bar{3}m$ (origin choice 2) using the program SHELXL-97 (Sheldrick 1997). Assuming a *normal* pyrochlore structure, the A cation was tentatively located at the Wyckoff position $16d$ ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$), B cation at $16c$ (0, 0, 0), X at $48f$ ($x, \frac{1}{8}, \frac{1}{8}$) and Y at $8b$ ($\frac{3}{8}, \frac{3}{8}, \frac{3}{8}$). Site-scattering values were refined using neutral scattering curves for A (Pb vs. \square), B (Ta vs. \square), X (O vs. \square) and Y (O vs. \square). A careful examination of the difference Fourier map did not reveal any electron density peak in the vicinity of the Y site, thus confirming the ordering of Pb on the A site (*normal* structure). Details of data collection and R indices are given in Table 1 whereas final atomic coordinates and anisotropic displacement parameters are reported in Table 2. The list of the

TABLE 1 – Data and experimental details for the selected plumbomicrolite crystal.

space group	$Fd\bar{3}m$ (origin choice 2)
cell parameters	$a = 10.571(1) (\text{\AA})$ $V = 1181.3(2) (\text{\AA}^3)$
crystal size (μm)	$225 \times 255 \times 270$
Wavelength	Mo-K α (26 mA x 50 kV)
theta-range ($^\circ$)	1 - 35
range of hkl	$0 \leq h \leq 16$ $0 \leq k \leq 16$ $0 \leq l \leq 16$
scan mode	ω
scan width ($^\circ$)	2.40
scan speed ($^\circ/\text{min}$)	1.00/6.00
number of parameters	14
collected reflections	708
independent refl.	140
refl. with $F_o > 4\sigma(F_o)$	104
R_{int} (%)	4.60
R_{obs} (%)	4.89
R_{all} (%)	5.79
$\Delta\rho_{\text{max}}$ ($\text{e}\text{\AA}^{-3}$)	2.30
$\Delta\rho_{\text{min}}$ ($\text{e}\text{\AA}^{-3}$)	-2.22
Extinction correction	None

TABLE 2 – Fractional coordinates and anisotropic displacement parameters of atoms for plumbomicrolite.

s.s.	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	U_{eq}	
A	58.5	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0.0237(8)	U_{11}	U_{11}	-0.0049(2)	U_{12}	U_{12}	0.0237(8)
B	49.4	0	0	0	0.0085(8)	U_{11}	U_{11}	-0.0010(2)	U_{12}	U_{12}	0.0085(8)
O	8.0	0.3154(9)	$\frac{1}{8}$	$\frac{1}{8}$	0.027(5)	0.014(3)	U_{22}	0	0	-0.001(3)	0.018(2)
Y	3.9	$\frac{3}{8}$	$\frac{3}{8}$	$\frac{3}{8}$	0.03(1)	U_{11}	U_{11}	0	0	0	0.03(1)

F/F_c data for plumbomicrolite is available from the authors upon request.

CHEMICAL COMPOSITION

The crystal used for the structural study (backscattered-electron image reported in Fig. 1) was embedded in resin and polished. The chemical composition was then determined using wavelength dispersive analysis (WDS) by means of a Jeol JXA-8600 electron microprobe. Major and minor elements were determined at 15 kV accelerating voltage and 20 nA beam current, with 30 s as counting time. The following lines were used: $\text{NaK}\alpha$, $\text{AlK}\alpha$, $\text{SiK}\alpha$, $\text{CaK}\alpha$, $\text{TiK}\alpha$, $\text{FeK}\alpha$, $\text{NbL}\alpha$, $\text{SnL}\alpha$, $\text{TaL}\alpha$, $\text{PbM}\alpha$, $\text{UM}\alpha$. F, K, Mn, Sr, Sb, Ba, La, Ce, Pr, Nd, Tl, and Th were measured but were found to be below the detection limit. The estimated analytical precisions are: ± 0.90 for Pb, ± 0.65 for Nb and Ta, ± 0.30 for Sn, and ± 0.10 for the other elements (wt % ox.). The crystal was found to be homogeneous within analytical error. The average chemical composition (4 analyses on different spots), the wt. % ranges of the oxides, and the standards employed are reported in Table 3.

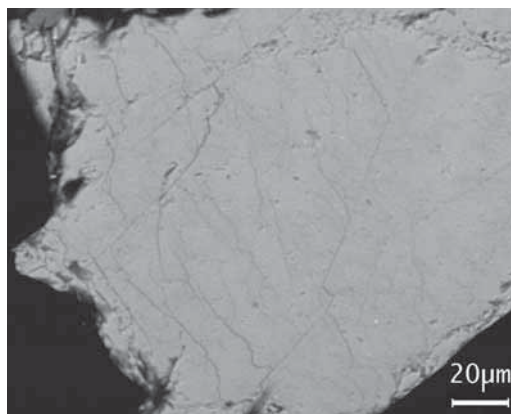


Fig. 1 – Backscattered-electron image (SEM) of a portion of the crystal used for the structural investigation.

CRYSTAL-CHEMICAL REMARKS

On the whole the crystal structure of the plumbomicrolite from Ploskaya Mountain is topologically identical to that of pyrochlores having a *normal* structure. Although Pb^{2+} , as a consequence of the stereoactive electron lone-pair,

TABLE 3 – Chemical composition (mean and ranges of wt. % of oxides) for the plumbomicrolite crystal and atomic ratios on the basis of $\Sigma B(\text{Ta}, \text{Nb}, \text{Si}, \text{Sn}, \text{Fe}, \text{Ti}, \text{Al}) = 2$.

	wt. %	range	atomic ratio	standard
Ta_2O_5	28.58	27.21 – 28.83	0.83	pure element
Nb_2O_5	12.90	12.11 – 13.39	0.62	pure element
SiO_2	2.19	1.62 – 2.44	0.23	kaersutite
SnO_2	3.47	3.10 – 3.58	0.13	pure element
Fe_2O_3	1.28	1.23 – 1.31	0.10	kaersutite
TiO_2	0.84	0.74 – 0.90	0.08	rutile
Al_2O_3	0.07	0.01 – 0.11	0.01	albite
PbO	45.39	44.20 – 46.29	1.31	pure element
CaO	2.51	2.18 – 2.63	0.29	kaersutite
Na_2O	0.37	0.32 – 0.46	0.08	albite
UO_2	1.24	0.99 – 1.45	0.02	pure element
total	98.84	98.14 – 100.29		

Note: All Fe was assumed to be Fe^{3+} and all Sn to be Sn^{4+} (see text).

usually displays a preference for low-symmetry sites, here is completely ordered on the A site (16d Wyckoff position, site symmetry $\bar{3}m$). In this sense, the case is different from the behaviour of Tl^+ in the structure of both the synthetic $TlNb_2O_5F$ (Fourquet *et al.* 1979) and in that of the Tl^+ -doped bariopyrochlore (Bindi *et al.* 2006), where the stereoactive Tl^+ cation exhibits asymmetrical coordinations in two different $32e$ positions (site symmetry $3m$) in the vicinity of Y site. However, because in plumbomicrolite the Y site was found to be partially occupied, the A cation may locally result in a six-, or seven-, or eight-fold coordination (Figure 2). Whenever two neighbour Y sites are vacant, six X atoms around the A position form a trigonally flattened octahedron, while a trigonal scalenohedron occurs when two Y sites around A are occupied. On the other hand, when only one neighbour Y site is occupied, the A cation assumes an asymmetrical seven-fold coordination (hexagonal pyramid). Due to its stereoactive electron lone-pair, this last coordination should be strongly preferred when A is occupied by Pb^{2+} . From a simple relationship, we can calculate the mean coordination number for the A position: $\langle A \rangle = 6 + 2y \sim 7$, y being the occupancy factor of the Y site. Thus, a local seven-fold coordination for Pb^{2+} ($\pm Na^+$) can be reasonably hypothesized, while eight-fold and six-fold configurations, if any, might occur around Ca ($\pm Na^+$) and U^{4+} ($\pm \square$), respectively.

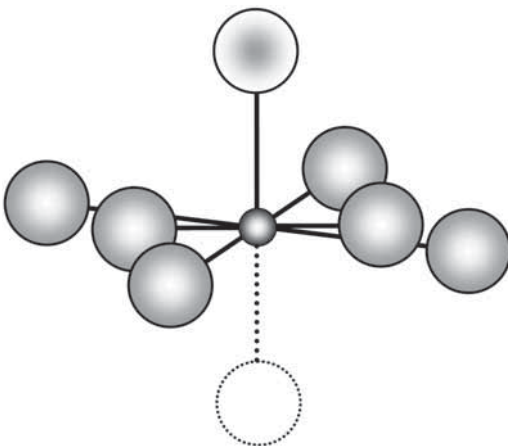


Fig. 2 – Coordination polyhedron of the A cation (small circle). O and Y atoms are in grey and white, respectively.

From the refined atomic coordinate (Table 2), the following bond distances can be obtained: A-X (x_6) = 2.702(7) Å, A-Y (x_2) = 2.289(1) (mean $\langle A-X, Y \rangle$ distance = 2.599 Å) and B-X = 1.993(3) Å. In keeping with the high content of Pb^{2+} at the A site, the $\langle A-X, Y \rangle$ distance is noticeably longer than that observed in calciobetafite from Campi Flegrei, Italy (2.490 Å; Mazzi and Munno 1983) where Ca and Na are the dominant cations on the A site or in betafite from Le Carcarelle, Vico Complex, Italy (2.467 Å; Camara *et al.* 2004) where the distance is further shortened by the presence of about 0.5 apfu of U^{4+} . On the other hand, the value of 2.599 Å observed in plumbomicrolite ($Pb = 1.30$ apfu) compares well with the value (2.614 Å) reported for the cubic $Pb_{1.5}Nb_2O_{6.5}$ compound (Bernotat-Wulf and Hoffmann 1982). If we consider a seven-fold AX_6Y polyhedron the mean $\langle A-X, Y \rangle$ distance is 2.643 Å in plumbomicrolite from Plonskaya Mountain and 2.660 Å in the $Pb_{1.5}Nb_2O_{6.5}$ compound.

Due to the possibility of A-site vacancies and the wider range of chemical substitutions at this site, the chemical formula of the pyrochlore group minerals is conventionally normalized to ΣB cations = 2.00. No uncertainty exists in assigning Nb, Ta and Ti to the B site. Likewise, Al and Fe^{3+} are commonly included in the chemical formula among the B cations. Indeed, ionic radius of octahedral Fe^{3+} (0.645 Å) is close to that of Nb and Ta (0.64 Å). On the other hand, more difficulties are found in assigning Sn and Si. According to Ercit *et al.* (1987), Sn could be present in both divalent (A site) and tetravalent (B site) state in the stannomicrolite from the type locality; nonetheless, the presence of substantial amounts of Sn^{2+} requires strongly reducing environments which are rather exceptionally attained by pegmatitic fluids. Phases with the general formula $Sn^{2+}_{2-x}(M_{2-y}Sn^{4+}_y)O_{7-x-y/2}$ ($M = Nb$ or Ta) with cubic pyrochlore related structures have been synthesized and characterized by X-ray diffraction, tin Mössbauer, density determinations, and chemical analyses by Birchall and Sleight (1975). According to these authors, Sn^{4+} enters the regular B octahedron while Sn^{2+} is actually not at the $\bar{3}m$ site of the ideal pyrochlore structure, being displaced from the A position by 0.38(2) Å. Although in our case no evidence of split site was found, we did not discard *a priori* the hypothesis that part of Sn were present on the A

site at the divalent state. Si-rich natural pyrochlores are widely reported in the literature and whether Si is truly hosted within the octahedral site of pyrochlore group minerals has been long debated (Hogarth 1977, 1989; Uher *et al.* 1998, Voloshin *et al.* 1989; Hogarth *et al.* 2000; Chakhmouradian and Mitchell 2002). Recently Bonazzi *et al.* (2006) have reported a crystal-chemical study combined with TEM-EDX investigations on pyrochlore samples with high SiO₂ content from Narssârssuk (Greenland). Although a portion of Si detected by EMPA was found to be concentrated in radiation-damaged portions, crystal chemical data suggested that substantial amounts (up to 0.24 apfu) enter the octahedral site. In particular it was hypothesized a local coupling of the Si → (Ti, Nb) and OH⁻ → O²⁻ substitutions leading to an increase of Si(OH)₆ groups in the structure upon hydration.

Taking the above considerations in mind, atomic ratios were tentatively calculated following different criteria for the Sn site-assignment (columns I, II and III in Table 4) and including/excluding Si in/from the mineral formula (rows 1 and 2 in Table 4). Assuming all Sn as Sn²⁺ in A and ΣB(Ta,Nb,Fe,Ti,Al) = 2 apfu (column I, row 2 in Table 4) an excess of A cations was found and this hypothesis was ruled out. Successive attempts to normalize the chemical data were made assuming Sn disordered on both the A and B sites [Σ(A+B) = 4.00; column II, Table 4) or assuming all Sn as Sn⁴⁺ in B (column III, Table 4). The site populations corresponding to a mean electron number of 58.0 and 50.1 for the A and B sites respectively (row 1, column III) match excellently the site scattering

values obtained by XREF (58.5 and 49.4, respectively). Thus, we assumed both Sn⁴⁺ and Si⁴⁺ to be hosted in the B site. The following crystal chemical formula was assigned accordingly: ^A[Pb_{1.30}Ca_{0.29}Na_{0.08}U⁴⁺_{0.03}]_{Σ=1.70}^B[Ta_{0.82}Nb_{0.62}Si_{0.23}Sn⁴⁺_{0.15}Ti⁴⁺_{0.07}Fe³⁺_{0.10}Al_{0.01}]_{Σ=2.00}^X[O₆]^Y[O_{0.23}(OH)_{0.25}]_{Σ=0.48}, with the occupancy of Y site obtained by XREF and the O²⁻/OH ratio at this site calculated to achieve the charge balance of the formula.

To verify the reliability of this assumption, the consistency between the observed B-O bond distances and the assumed cation populations was checked. Due to the complex chemical substitutions and the scarcity of crystal-chemical data in the literature, a comparison between the observed and theoretical bond distances in pyrochlore is not straightforward. Compared to the value of 1.962 Å observed in the Si-rich crystal from Greenland (sample 110a; Bonazzi *et al.* 2006), the <B-O> distance values observed in plumbomicrolite (1.993 Å) appears rather high, probably due to the significant content of Sn⁴⁺ (ionic radius = 0.690 Å) as well as the effect of the enlargement of the adjacent A polyhedron, which shares six edges with as many B octahedra. As shown by Kennedy *et al.* (1997) for a number of synthetic pyrochlore stannates of the type Ln₂Sn₂O₇ with Ln = Y, La, Pr, Nd, Sm-Gd, and Tb-Lu, the cubic lattice parameter displays a linear increase with increasing ionic radius of the cation located at the A site. In turn, the octahedral <Sn-O> distance increases linearly as a function of the *a* parameter. As a consequence, the octahedral distance shows a linear dependence on the ionic radius of the A cation. To model the effect of the ionic radius of the A cation (^A[i.r.]^{VIII}) on the octahedral bond distance and estimate the “pure” <Sn⁴⁺-O> value, the structural data reported by Kennedy *et al.* (1997) were used. From the linear equation: <Sn⁴⁺-O> = 1.85(1) + 0.18(1) ^A[i.r.]^{VIII} (Å) (*r* = 0.972), we estimated <Sn⁴⁺-O> = 2.081 Å for a <i.r.> = 1.25 Å which corresponds to the mean ionic radius weighted according to the A site population of our sample. To obtain the “pure” <B-O> distances for the remaining main cations located on B [i.e., Ti, Si, and (Nb, Ta, Fe³⁺)] we chose structural data of pure synthetic compounds from literature and corrected them for the “enlargement” induced by the cation in the adjacent A site. The following distances <Ti-O> = 1.953 Å (observed in Y₂Ti₂O₇; Becker and Will 1970), <Si-O> = 1.78

TABLE 4 – Mean electron numbers derived from chemical data using different criteria of normalization.

	I	II	III
1	e ⁻ _A = 66.3 e ⁻ _B = 50.2	e ⁻ _A = 66.8 e ⁻ _B = 50.2	e ⁻ _A = 58.0 e ⁻ _B = 50.1
2	A > 2	e ⁻ _A = 67.9 e ⁻ _B = 54.9	e ⁻ _A = 65.3 e ⁻ _B = 54.9

Note: Columns I, II, and III refer to different criteria for Sn site-assignment: as Sn²⁺ in A (I), distributed on both A and B (II) and as Sn⁴⁺ in B (III); rows 1 and 2 refer to the atomic ratio calculated including (1) or excluding (2) Si.

Å (mean value between those observed in $\text{Sc}_2\text{Si}_2\text{O}_7$ and $\text{In}_2\text{Si}_2\text{O}_7$; Reid *et al.* 1977), $\langle \text{Nb}, \text{Fe}^{3+}\text{-O} \rangle = 1.991$ Å [observed in $\text{CaNd}(\text{Nb}_{1.5}\text{Fe}_{0.5}^{3+})\text{O}_7$; Zhao *et al.* 2000] were corrected for the difference in $A[\text{i.r.}]^{\text{VIII}}$ and assuming arbitrarily the same linear behavior as found for the $\langle \text{Sn}^{4+}\text{-O} \rangle$ distance. On this basis, the “pure” B-O distances were assumed to have the following values: $\langle \text{Ti-O} \rangle = 1.994$ Å; $\langle \text{Si-O} \rangle = 1.843$ Å; $\langle \text{Ta}, \text{Nb}, \text{Fe}^{3+}\text{-O} \rangle = 2.009$ Å and $\langle \text{Sn}^{4+}\text{-O} \rangle = 2.081$. Due to the lacking of data for $\langle \text{Al-O} \rangle$ in pyrochlore structure, the Al content (0.01 apfu) was neglected and the site occupancies were recalculated accordingly. The theoretical distance obtained ($\langle \text{B-O} \rangle_{\text{calc.}} = 1.995$ Å) displays an excellent agreement with the observed value [$\langle \text{B-O} \rangle_{\text{obs.}} = 1.993(3)$ Å]. For this reason, it appears plausible that in this sample all the Si detected by EMPA is hosted in the structure of pyrochlore. On the contrary, in pyrochlore from Narssârssuk, Greenland (Bonazzi *et al.* 2006) only a fraction (up to 50%) of the Si detected by EMPA was assumed to enter the B site, whereas the remaining fraction enters the altered, radiation-damaged portions wherein the highest Si contents correlate with highest analytical deficits due to highest H_2O contents. In microlite from Ployaska Mountain, instead, the compositional homogeneity (Fig. 1) as well as the high analytical totals lead to exclude the presence of altered portions where Si might be incorporated.

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