Revision 2

Pauloabibite, trigonal $NaNbO_3$, isostructural with ilmenite, from the Jacupiranga carbonatite, Cajati, São Paulo, Brazil.

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ABSTRACT

Pauloabibite (IMA 2012-090), trigonal $NaNbO_3$, occurs in the Jacupiranga carbonatite, in Cajati County, São Paulo State, Brazil, associated with dolomite, calcite, magnetite, phlogopite, pyrite, pyrrhotite, ancylite-(Ce), tochilinite, fluorapatite, "pyrochlore", vigezzite, and strontianite. Pauloabibite occurs as encrustations of platy crystals, up to 2 mm in size, partially intergrown with an unidentified Ca-Nb-oxide, embedded in dolomite crystals, which in this zone of the mine can reach centimeter sizes. Cleavage is perfect on {001}. Pauloabibite is transparent and displays a sub-adamantine luster; it is pinkish brown and the streak is white. The calculated density is 4.246 g/cm^3. The mineral is uniaxial; n(mean)$_{calc.}$ is 2.078. Chemical composition (n =17, WDS, wt.%) is: Na_2O 16.36, MgO 0.04, CaO 1.36, MnO 0.82, FeO 0.11, SrO 0.02, BaO 0.16, SiO_2 0.03, TiO_2 0.86, Nb_2O_5 78.66, Ta_2O_5 0.34, total 98.76. The empirical formula is $(Na_{0.88}Ca_{0.04}Mn^{2+}_{0.02})_{\Sigma 0.94}(Nb_{0.98}Ti_{0.02})_{\Sigma 1.00}O_3$. X-ray powder-diffraction lines (calculated pattern) [d in Å(I)(hkl)] are: 5.2066(100)(003), 4.4257(82)(101), 3.9730(45)(012), 2.9809(54)(104), 2.3718(88)(2-13), 1.9865(28)(024), 1.8620(53)(2-16), and 1.5383 (30) (300). It is trigonal, space group: R–3, a = 5.3287(5), c = 15.6197(17) Å, V = 384.10(7) Å^3, Z = 6. The crystal structure was solved (R_1 = 0.0285, wR_2 = 0.0636 for 309 observed reflections). Pauloabibite is isostructural with ilmenite and is polymorphic with isolueshite (cubic) and lueshite (orthorhombic). The name is in honour of Professor Paulo Abib Andery (1922-1976).

Keywords: pauloabibite, new mineral, carbonatite, ilmenite structure, crystal structure, chemical composition, Jacupiranga mine, Cajati, Brazil

INTRODUCTION

Pauloabibite (IMA 2012-090), trigonal $NaNbO_3$, is polymorphic with isolueshite (cubic) and lueshite (orthorhombic) (Table 1). Natroniobite, a poorly described mineral (Bulakh et al. 1960), may be a monoclinic polymorph of $NaNbO_3$, or a mineral with formula $NaNb_2O_5(OH)$, related to fersmite (Chakhmouradian et al. 1997, Chakhmouradian and Mitchell 1998). Chakhmouradian and Mitchell (1998) investigated a museum specimen labeled "natroniobite" (not the type specimen) and concluded that it is a "complex aggregate of lueshite and its replacement products, set in a matrix of dolomite and fluorapatite". Monoclinic synthetic compounds with formula $NaNbO_3$ are known (*e.g.* Solov'ev et al. 1961; Johnston et al. 2010), but the X-ray diffraction pattern of natroniobite does not match those of these other compounds.

Pauloabibite is trigonal, isostructural with ilmenite and other *R*–3 oxides which display a crystal structure formed by the hexagonal close packing of oxygen atoms, with two-thirds of the octahedral interstices occupied by two unique sites of di- and tetravalent or uni- and pentavalent cations. In corundum and other *R*–3*c* oxides, two-thirds of the octahedral interstices are occupied by trivalent cations in one unique site. Data for these minerals are included in Table 2.

The synthetic analogue of pauloabibite has been studied by several research groups. It was reported by Kinomura et al. (1984) and Kumata et al. (1990) from a two-step synthesis method, involving the preparation of $Na_8Nb_6O_{19}\cdot 13H_2O$ followed by hydrothermal reaction with NaOH in a silver-lined vessel at 250°C. It was also prepared directly in one step under mild hydrothermal conditions by lowering pH and using close-to-stoichiometric amounts of reagents at 240°C (Modeshia et al. 2009; Johnston et al. 2011). The equivalent to lueshite (space group *Pbnm*) was not yet synthesized, but phase transitions in natural lueshite were observed in the sequence: *Cmcm* at 575°C, *P*4/*mbm* at 625°C, and *Pm*–3*m*, equivalent to isolueshite, at 650 °C (Mitchell et al. 2014).

The name is in honor of Professor Paulo Abib Andery (1922-1976), Department of Mining Engineering at the Polytechnic School, Universidade de São Paulo, who developed a flotation process for Serrana SA Mining, resulting in an apatite concentrate that is used as raw material for the production of phosphoric acid and a calcite tailing that is used for the manufacture of cement. He founded the mining research facility known as Paulo Abib

Engenharia in the early 1970s, a pioneering institution in developing ore dressing technology in Brazil.

Type material (specimen number DR740) is deposited in the Museu de Geociências, Instituto de Geociências, Universidade de São Paulo, Rua do Lago, 562, 05508-080 - São Paulo, SP, Brazil.

OCCURRENCE

The mineral occurs in the Jacupiranga carbonatite (24°43'47"S, 48°06'37"W), Cajati County, São Paulo State, Brazil (Menezes and Martins 1984). This property is located near the Southern border of the Jacupiranga Igneous Complex, an alkaline intrusion that was formed in a continental-rift environment in the Early Cretaceous, with the age estimated at 130 m.a. (Roden et al. 1985), that outcrops in an area of 65 km^2, and constitutes dunites and peridotites in its Northern part and jacupirangite, ijolite and nepheline syenites in the Southern; the carbonatite plug is totally intruded into jacupirangite.

The carbonatite has been extensively mined since the late 1960's for the production of apatite and calcite; the average composition is 74% carbonates (calcite, dolomite and ankerite); 12% fluorapatite, 8% magnetite 2% phlogopite, 2% olivine, 1% sulphides and 1% of other accessory minerals (Alves 2008). It formed as a series of 5 successive intrusions. The oldest carbonatite, C1, was probably derived from a magma somewhat different chemically from those producing carbonatites C2 through C5. The precipitation of carbonatite C2 probably went to completion independently of C3 through C5, whereas carbonatites C3 through C5 probably were precipitated from successive batches of magma representing a continuum in time and magmatic evolution (Gaspar and Willye 1983). Paulobabite was found in the transition between the intrusions C2 and C3, where the carbonatite is coarser and a pyrochlore-group mineral is present as an accessory mineral; in this zone two other unique species were found: quintinite (Chao and Gault 1997) and menezesite (Atencio et al. 2008). Associated minerals are dolomite, calcite, magnetite, phlogopite, pyrite, pyrrhotite, ancylite-(Ce), tochilinite, fluorapatite, "pyrochlore", vigezzite, and strontianite. Pauloabibite occurs embedded in dolomite crystals, which in this zone of the mine can reach centimetre sizes.

HABIT AND PHYSICAL PROPERTIES

The mineral occurs as encrustations of platy crystals to 2 mm in size in dolomite. Crystals are partially intergrown with a still unidentified Ca-Nb oxide (Figures 1 and 2). Cleavage is perfect on {001} and parting was not observed. Pauloabibite is transparent and displays a sub-adamantine lustre; it is pinkish brown and the streak is white. It is non-fluorescent under short (254 nm) or long wavelength (366 nm) ultraviolet radiation. The Mohs hardness was not measured due to the small crystal size. Fracture is irregular and the grains are fragile due to perfect cleavage. Density was not measured due to the paucity of material but the calculated density is 4.246 g/cm^3 (based on empirical formula). Optically the mineral is uniaxial; $n(\text{mean})_{\text{calc.}}$ is 2.078 using the Gladstone-Dale relationship (Mandarino 1979), higher than that of available immersion liquids.

MINERAL CHEMISTRY

Pauloabibite crystals were embedded in epoxy resin and polished. Chemical analyses (17) were completed with a JEOL JXA-8900 electron microprobe (WDS mode, 15 kV, 20 nA, ~1 μm beam diameter). Analytical results are represented in Table 3. No elements with Z > 8 other than those reported were indicated by EDS. The empirical formula [based on 3 O *apfu*] is: $(Na_{0.88}Ca_{0.04}Mn^{2+}_{0.02})_{\Sigma 0.94}(Nb_{0.98}Ti_{0.02})_{\Sigma 1.00}O_3$. The ideal formula $NaNbO_3$ yields the following wt% oxide values: Na_2O = 18.91, Nb_2O_5 = 81.09, Total 100.00.

CRYSTAL STRUCTURE DETERMINATION

Very strong preferential orientation effects were observed in the powder X-ray diffraction data (XRD) due to the perfect {001} cleavage. The observed pattern probably would be of little value due to a huge difference between calculated and observed intensities of reflections. We

present only the model X-ray powder diffraction pattern (Table 4) calculated from the determined structure model using the XPOW program by Downs et al. (1993).

A single crystal (0.09 × 0.07 × 0.06 mm) was selected for intensity measurements on a Bruker X8 APEX2 CCD diffractometer using graphite-monochromatized Mo*K*α (λ = 0.71073 Å) radiation. Data were collected to a 2θ value of 65° and the X-ray absorption correction was calculated by the MULTI-SCAN method using the Bruker program SADABS (Sheldrick 1996). The crystal structure was solved using direct methods and refined using SHELX97 (Sheldrick 2008). Due to the measured major element chemistry, for simplicity, the structure was refined using the ideal formula, $NaNbO_3$, as the overall effects of minor elements (Ca, Mn and Ti) on the final structure results are negligible. Details about the data collection and structure refinement are summarized in Table 5. The final atom coordinates and anisotropic thermal displacement parameters are listed in Table 6. Selected bond distances, angles and bond valence calculations using the parameters given by Brese and O'Keeffe (1991) are in Table 7. Structure factors for pauloabibite and the CIF file are provided as deposited material[1].

[1] Deposit item AM-14-XXX, CIF and structure factors. Deposit items are available two ways: For a paper copy, contact the Business Office of the Mineralogical Society of America (see inside front cover of recent issue) for price information. For an electronic copy visit the MSA web site at http://www.minsocam.org, go to the *American Mineralogist* Contents, find the table of contents for the specific volume/issue wanted, and then click on the deposit link there.

Pauloabibite ($NaNbO_3$) is isostructural with ilmenite. It has a layered structure, in which NaO_6 and NbO_6 distorted octahedra share edges to form fully ordered Na and Nb layers that are stacked alternating along the **c** axis (Figure 3). The mean Nb–O (2.004 Å) and Na–O (2.412 Å) distances are in agreement with those determined by Modeshia et al. (2009) in their work on synthetic $NaNbO_3$ isomorphic with ilmenite: Nb–O (2.01 Å) and Na-O (2.41 Å). Isolueshite, the cubic polymorph, and lueshite, the orthorhombic polymorph, display modified perovskite structures, with distorted NaO_{12} cuboctahedral polyhedra and NbO_6 octahedra (Krivovichev et al. 2000; Mitchell et al. 2014).

IMPLICATIONS

Much work has been carried out on the synthesis of alkaline niobates because of their excellent nonlinear optical, ferroelectric, piezoelectric, electro-optic, ionic conductive, pyroelectric, photorefractive, selective ion exchange, and photocatalytic properties. For example, lead-free potassium and sodium niobates are potential substitutes for lead zirconium titanate (PZT, $PbZr_xTi_{1-x}O_3$, one of the world's most widely used high-performance piezoelectric ceramics). The high lead content in PZT introduces serious concerns about environment pollution during the fabrication, use and disposal of the materials, and therefore, because increasing attention has been paid to environmental issues nowadays, potential substitutes are urgently being examined (Wu et al. 2010).

$NaNbO_3$ is known to exhibit a rich polymorphism based on the perovskite structure, with a number of displacive transition occurring over a range of temperatures, which may also be sensitive to both pressure and crystallite size. Doped forms of the material are currently the focus of much attention because of their piezoelectric properties (Modeshia et al. 2009).

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295 Table 1. Comparative data for $NaNbO_3$ polymorphs.
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Mineral	pauloabibite	isolueshite	lueshite	natroniobite
Formula	$NaNbO_3$	$NaNbO_3$	$NaNbO_3$	$NaNbO_3$ (?)
Crystal system	trigonal	cubic	orthorhombic	monoclinic (?)
Space group	$R\bar{3}$	$Pm\bar{3}m$	*Pbnm*	n.d.
a (Å)	5.3287(5)	3.909(1)	5.5269(10)	
b (Å)			5.5269(10)	
c (Å)	15.6197(17)		7.8180(10)	
V (Å^3)	384.10(7)	59.73(3)	238.81	
Z	6	1	4	
Strongest lines in	5.2066 (100)	3.915 (30)	3.91 (100)	4.81 (70)
XRPD pattern;	4.4257 (82)	2.765 (100)	2.77 (70)	3.77 (20)
d in Å (I_{rel})	3.9730 (45)	1.953 (50)	1.96 (70)	3.05 (100)
	2.9809 (54)	1.747 (10)	1.748 (20)	2.97 (20)
	2.3718 (88)	1.594 (30)	1.60 (30)	2.77 (20)
	1.9865 (28)	1.380 (20)	1.382 (10)	2.68 (50)
	1.8620 (53)	1.234 (10)	1.302 (10)	1.72 (30)
	1.5383 (30)	1.042 (10)	1.234 (10)	1.61 (30)
Calculated density (g cm^{-3})	4.246	4.57	4.559	4.4 (meas.)
Color	pinkish brown	brownish-black	black	yellowish, brownish, blackish
Luster	vitreous	adamantine		
Optical class	Uniaxial	Isotropic	Biaxial (–)	Biaxial (–)
n	2.078 (mean,	2.200	2.29-2.30	
α	calc.)		(mean)	2.10-2.13
β				2.19-2.21
γ				2.21-2.24
2V (meas.) (°)			46	10-30
Reference	this proposal, calculated XRPD pattern	Chakhmouradian et al. (1997); Krivovichev et al. (2000)	Safiannikoff (1959); Mitchell et al. (2014)	Kukharenko et al. (1965)

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299 Table 2. Chemical composition and crystallographic data for pauloabibite and related minerals.

mineral	formula	Space group	a	c	reference
corundum	Al_2O_3	*R*-3*c*	4.7570(6)	12.9877(35)	Kirfel and Einchhorn (1990)
akimotoite	$MgSiO_3$	*R*-3	4.78(5)	13.6(1)	Tomioka and Fujino (1999)
eskolaite	Cr_2O_3	*R*-3*c*	4.9607(10)	13.599(5)	Newnham and de Haan (1962)
karelianite	V_2O_3	*R*-3*c*	4.99	13.98	Long et al. (1963)
hematite	$Fe^{3+}{}_2O_3$	*R*-3*c*	5.0355(5)	13.7471(7)	Maslen et al. (1994)
geikielite	$MgTi^{4+}O_3$	*R*-3	5.0567(0)	13.9034(2)	Liferovich and Mitchell (2006)
ilmenite	$Fe^{2+}Ti^{4+}O_3$	*R*-3	5.070(1)	14.064(3)	Waerenborgh et al. (2002)
ecandrewsite	$ZnTi^{4+}O_3$	*R*-3	5.090(1)	14.036(2)	Birch et al. (1988)
pyrophanite	$Mn^{2+}Ti^{4+}O_3$	*R*-3	5.13948(7)	14.2829(4)	Kidoh et al. (1984)
tistarite	$Ti^{3+}{}_2O_3$	*R*-3*c*	5.158	13.611	Ma and Rossman (2009)
melanostibite	$Mn^{2+}(Sb^{5+},Fe^{3+})O_3$	*R*-3	5.226(5)	14.325(5)	Moore (1968)
brizziite	$NaSb^{5+}O_3$	*R*-3	5.301(1)	15.932(4)	Olmi and Sabelli. (1994)
pauloabibite	$NaNbO_3$	*R*-3	5.3287(5)	15.6197(17)	This paper

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Table 3. Analytical data for pauloabibite (mean of 17 point analyses).

Constituent	wt%	Range	Standard deviation	Probe standard
Na_2O	16.36	13.39-19.40	1.60	jadeite
MgO	0.04	0.00-0.19	0.06	dolomite
CaO	1.36	0.16-5.38	1.52	anorthite
MnO	0.82	0.06-1.73	0.46	rhodonite
FeO	0.11	0.00-0.65	0.16	siderite
SrO	0.02	0.00-0.22	0.06	celestine
BaO	0.16	0.00-0.83	0.22	barite
SiO_2	0.03	0.00-0.11	0.03	quartz
TiO_2	0.86	0.06-1.98	0.74	rutile
Nb_2O_5	78.66	72.10-84.32	3.84	Nb metal
Ta_2O_5	0.34	0.00-0.91	0.29	Ta metal
Total	98.76			

Table 4. X-ray powder diffraction data for pauloabibite.

$d_{calc.}$(Å)	$I_{calc.}$	h	k	l
5.2066	100	0	0	3
4.4257	82	1	0	1
3.9730	45	0	1	2
2.9809	54	1	0	4
2.6644	13	1	1	0
2.6033	3	0	0	6
2.3718	88	2	-1	3
2.3718	9	1	1	3
2.0089	4	1	0	7
1.9865	28	0	2	4
1.8620	53	2	-1	6
1.8620	16	1	1	6
1.7981	8	0	1	8
1.7335	8	3	-1	1
1.7023	5	-1	3	2
1.6040	15	0	2	7
1.5926	3	2	1	4
1.5926	21	3	-1	4
1.5383	30	3	0	0
1.4795	9	1	0	10
1.4752	5	0	3	3
1.4752	6	3	0	3
1.4542	14	1	1	9
1.3742	3	2	1	7
1.3322	4	2	2	0
1.2935	6	0	2	10
1.2906	6	2	2	3
1.2756	5	1	3	1

1.2631	5	3	1	2
1.2162	7	1	3	4
1.1859	5	2	2	6
1.1636	6	2	1	10

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Table 5. Summary of crystal data and refinement results for pauloabibite

Ideal chemical formula	$NaNbO_3$
Crystal symmetry	trigonal
Space group	*R-3* (no. 148)
a (Å)	5.3287 (5)
c (Å)	15.6197 (17)
V (Å^3)	384.10(7)
Z	6
ρ_{cal} (g/cm^3)	4.251
λ (Å, Mo*K*α)	0.71073
μ (mm^{-1})	4.60
2θ range for data collection	≤65
No. of reflections collected	1155
No. of independent reflections	309
No. of reflections with $I > 2\sigma(I)$	275
No. of parameters refined	18
R(int)	0.044
Final R_1, wR_2 factors [$I > 2\sigma(I)$]	0.029, 0.064
Goodness-of-fit	1.06

Table 6. Atom coordinates and displacement parameters ($Å^2$) for pauloabibite.

	x/*a*	*y*/*b*	*z*/*c*	U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Na	0	0	0.35846(17)	0.0136(5)	0.0147(8)	0.0147(8)	0.0113(12)	0.0000(0)	0.0000(0)	0.0073(4)
Nb	0	0	0.14867(3)	0.0068(2)	0.0064(2)	0.0064(2)	0.0075(3)	0.0000(0)	0.0000(0)	0.0032(1)
O	0.3239(5)	0.0532(6)	0.23828(16)	0.0095(5)	0.0089(12)	0.0099(12)	0.0098(11)	0.0014(9)	-0.0002(9)	0.0047(10)

Table 7. Selected bond lenghts, angles, and bond valence (BV) calculations in the refined pauloabibite structure.

Bond	Bond length	BV(v.u)	Σ
Nb-O	1.881(3)	1.084 (x3)	3.252
Nb-O	2.182(2)	0.481 (x3)	1.443
			4.695
Na-O	2.354(3)	0.226 (x3)	0.678
Na-O	2.469(3)	0.165 (x3)	0.495
			1.173
	Angles		
O-Nb-O	77.65 (11), 81.44 (10), 99.23 (14), 101.70 (9)		
O-Na-O	68.45 (11), 90.09 (12), 97.69 (8), 100.20 (10)		

Figure 1. Pinkish-brown pauloabibite intergrown with an unidentified Ca-Nb oxide, with dolomite (white) and tochilinite (black), from the Jacupiranga mine, Cajati, São Paulo, Brazil. Field of view: 4 mm.

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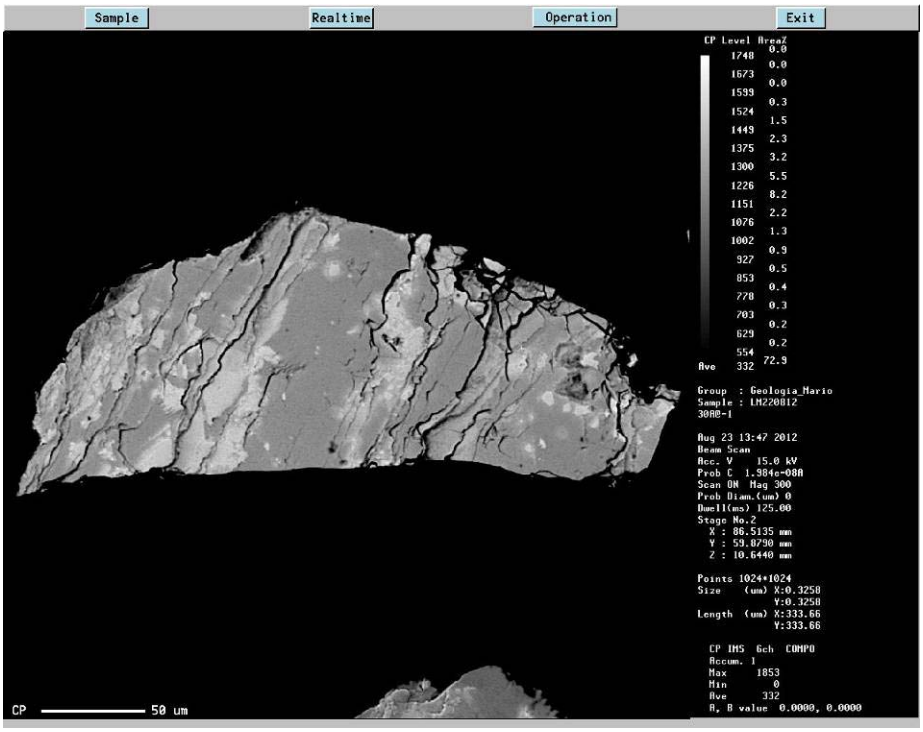

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357 Figure 2. Back-scattered electron image of pauloabibite (dark) intergrown with an

358 unidentified Ca-Nb oxide (light).

359

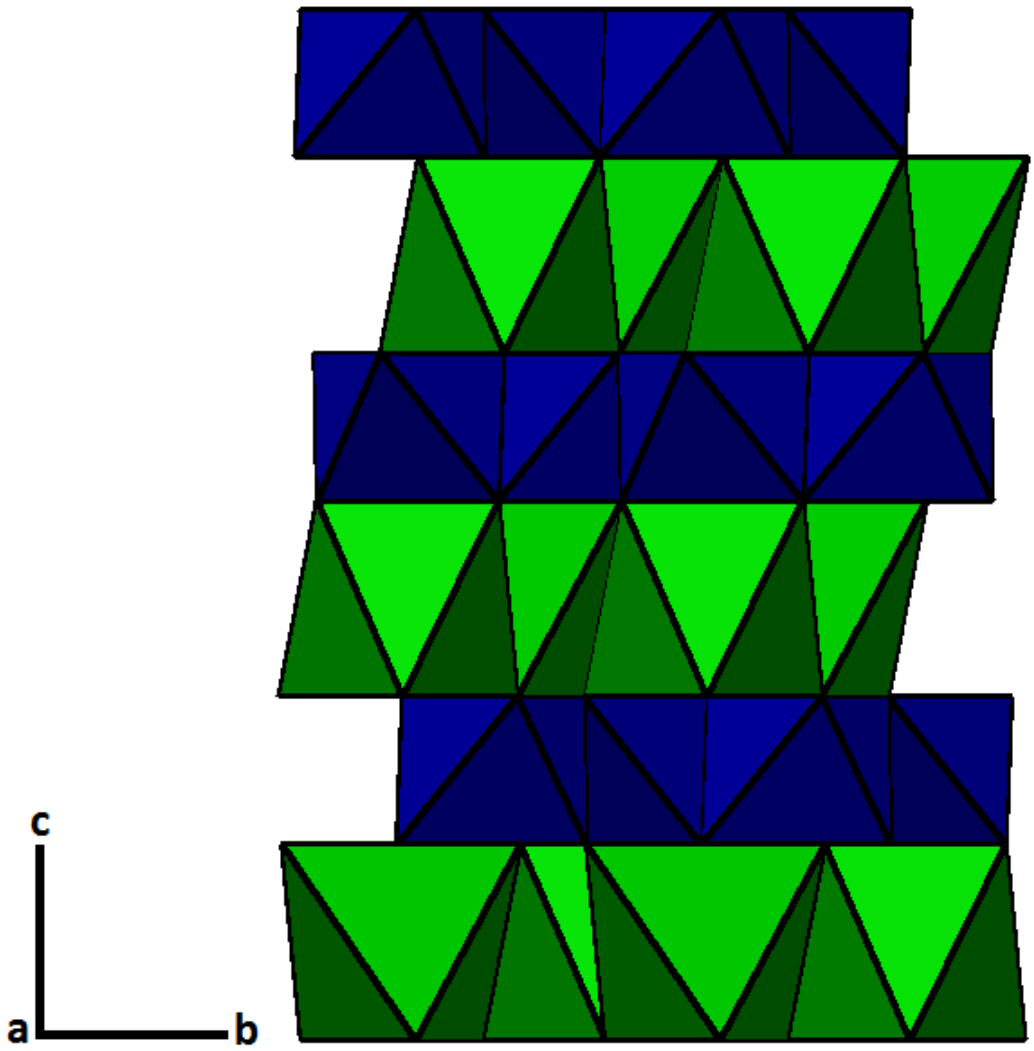
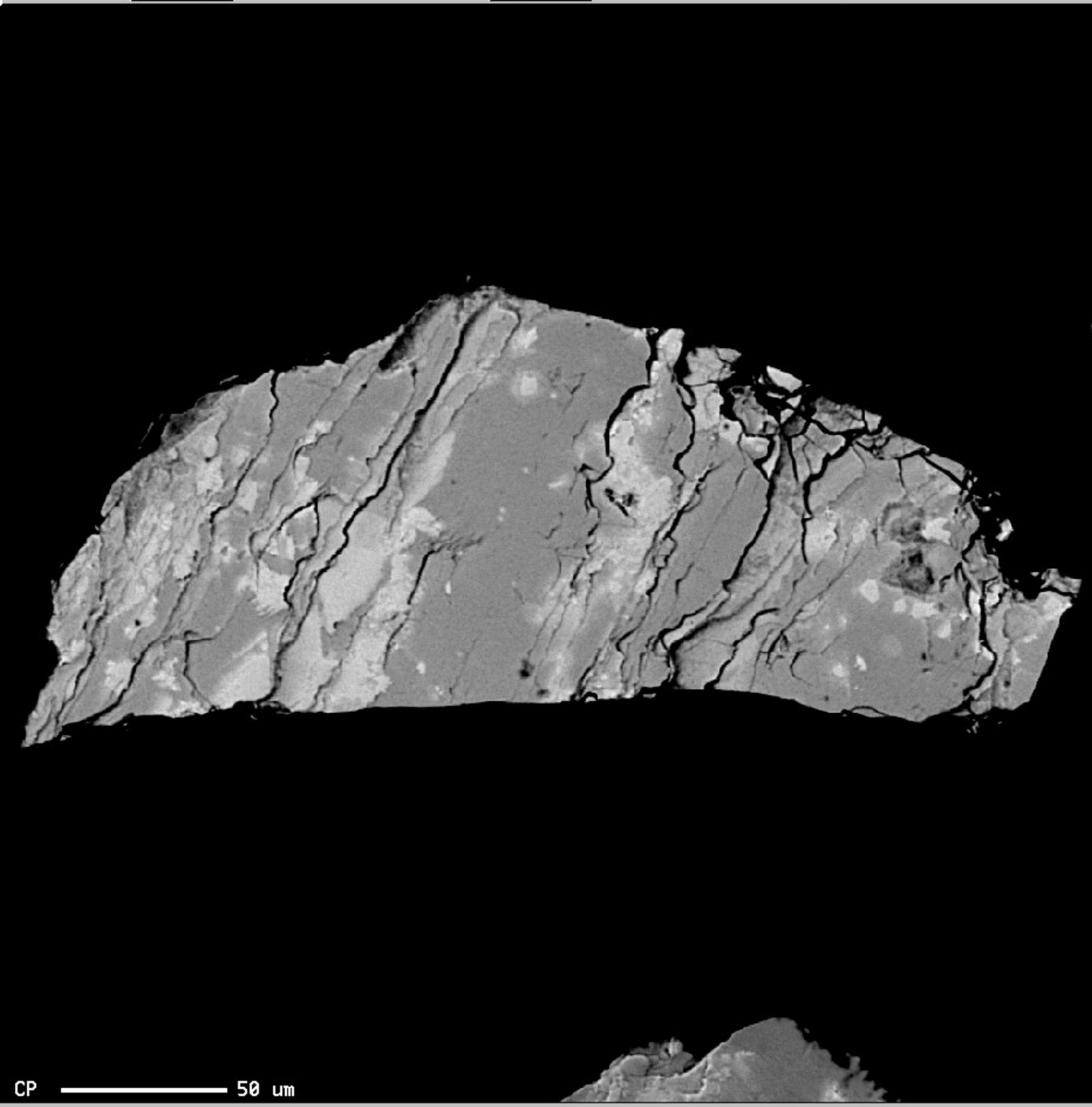


Figure 3. Crystal structure of pauloabibite. NaO_6 octahedra are green and NbO_6 octahedra are blue.

Sample | Realtime | Operation | Exit

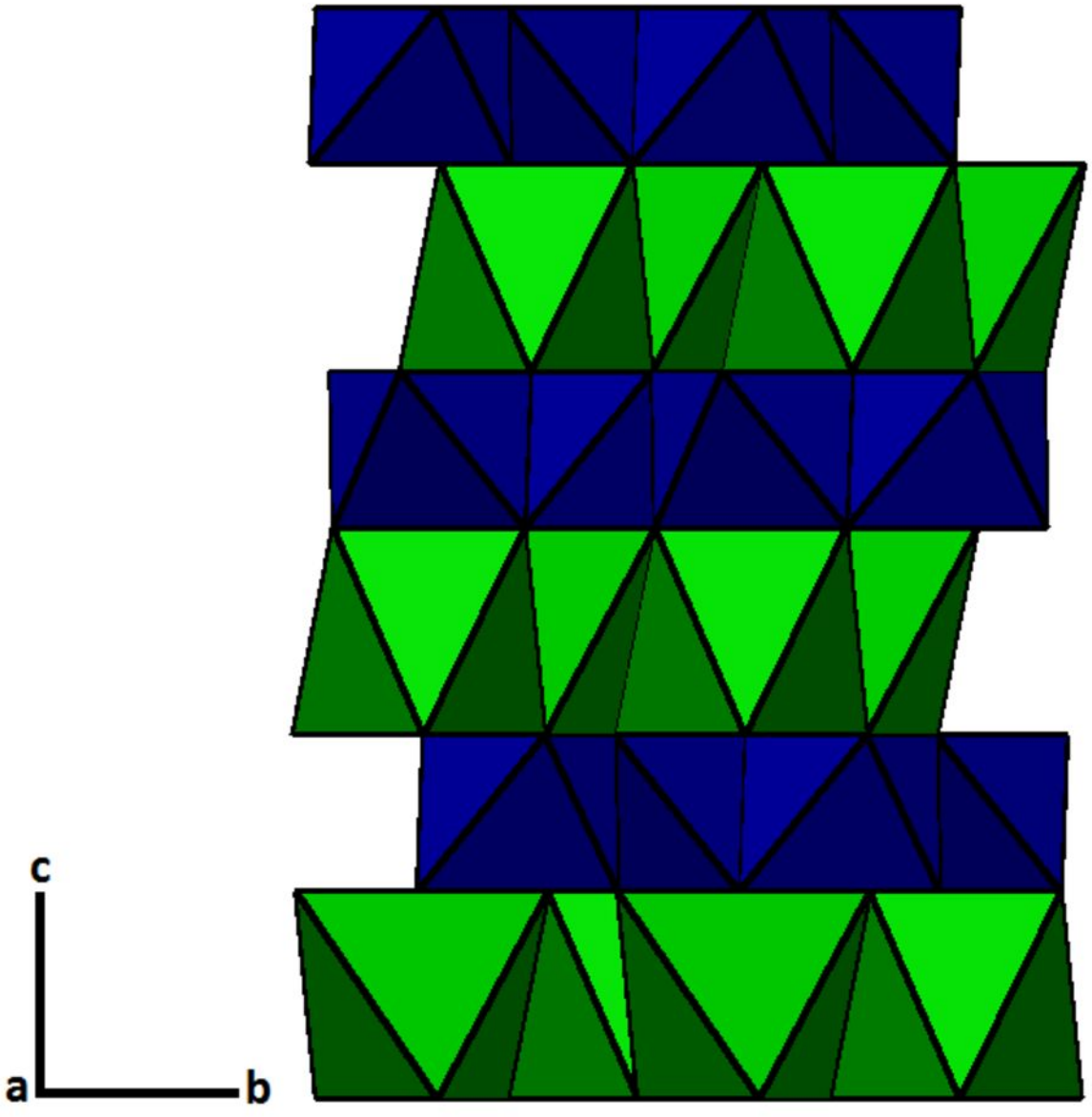


Group : Geologia_Mario
Sample : LM220812
30A@-1

Aug 23 13:47 2012
Beam Scan
Acc. V 15.0 kV
Prob C 1.984e-08A
Scan ON Mag 300
Prob Diam.(um) 0
Dwell(ms) 125.00
Stage No.2
X : 86.5135 mm
Y : 59.8790 mm
Z : 10.6440 mm

Points 1024*1024
Size (um) X:0.3258
Y:0.3258
Length (um) X:333.66
Y:333.66

CP IMS 6ch COMPO
Accum. 1
Max 1853
Min 0
Ave 332
A, B value 0.0000, 0.0000


c
a
b