Schiavinatoite, (Nb,Ta)BO₄, the Nb analogue of behierite

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Abstract: The new mineral schiavinatoite (Nb,Ta)BO₄, the niobium analogue of behierite, has been found in a boron-rich pegmatite at Antsongombato, south of Betafo, in the Malagasy Republic, as portions of a greyish-pink bipyramidal crystal of Nb-rich behierite. Associated minerals are rhodizite, liddicoatite, spodumene, pollucite, danburite, apatite. The mineral is tetragonal, space group $I4_1/amd$, isostructural with behierite (zircon-type), with $a = 6.219(5)$, $c = 5.487(5)$ Å, $V = 212.2(5)$ Å³, $Z = 4$, $D_{calc} = 6.548$ g/cm³. The strongest lines in the X-ray powder diffraction pattern [d in Å (I, hkl)] are: 4.115(100,101), 3.110(84,200), 2.328(49,112), 1.598(42,312), 2.481(36, 211), 1.939(29,301), 1.646(25,321). Mohs's hardness is 8. Luster is vitreous, transparent in thin section, streak is white, the crystal is uniaxial (+) with average n = 2.30(5). The structure has been refined from single-crystal data, using 178 observed unique reflections to $R = 0.011$, $R_w = 0.014$.

Key-words: schiavinatoite, new mineral, behierite, niobium, tantalum, borate, crystal structure, chemical composition.

Introduction

Behierite is a very rare mineral found for the first time by Béhier (1960) in a pegmatite at Manjaka, Malagasy Republic (Madagascar), associated with red tourmaline ("rubellite"). Because of its aspect, the mineral was first considered to be zircon or xenotime; however, X-ray investigation and chemical analysis performed by Mrose & Rose (1961) on the only four crystals available, showed the mineral to be a new species, namely, a tantalum-rich borate (Ta, Nb)BO₄, isostructural with zircon, containing small amounts of niobium

and zirconium in the molar ratio Ta:Nb:Zr = 18:1:0.4.

Recently, during one expedition to the Malagasy Republic, one of us (F. P.) on examining a pegmatite with a mineral paragenesis similar to that occurring at Manjaka (see below) found a bipyramidal crystal looking like behierite. In view of the possibility of dealing with a second occurrence of this rare mineral, the crystal was submitted to the other authors of the present paper for crystallographic investigation and chemical analysis.

Single crystal X-ray diffraction data obtained

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Table. 1. Unit-cell data of schiavinatoite in comparison to behierite and similar synthetic compounds.

	(1)	(2)	(3)	(4)
a(Å)	6.206(5)	6.219(5)	6.2125(3)	6.2141(6)
c(Å)	5.472(5)	5.487(5)	5.4832(4)	5.4760(1)
V(Å³)	210.8	212.2	211.6	211.5

(1) Behierite (type specimen) from Manjaka (Mrose & Rose, 1961)
(2) Schiavinatoite (present work)
(3) Synthetic TaBO₄ (from Range et al., 1996)
(4) Synthetic NbBO₄ (from Range et al., 1988)

from a tiny fragment showed the mineral to be tetragonal, space group $I4_1/amd$, with unit-cell parameters very similar to those of behierite (Table 1). In view of the excellent quality of the fragment, the possibility of carrying out a structure refinement of the mineral was considered. Such a decision was favoured by the absence in the literature of refined crystal structure data for natural samples of behierite, the only available results concerning synthetic TaBO₄ and NbBO₄ (Range et al., 1988, 1996).

After the refinement, the occupation parameter of the metal site showed niobium to prevail over tantalum and the presence of boron was confirmed. For this reason, the possibility that the analyzed mineral represented a new species, i.e. the niobium-rich analogue of behierite, became evident. The presence of notable amounts of Nb, together with Ta, was also shown by preliminary SEM-EDS analysis. The prevalence of Nb over Ta in some portions of the crystal was definitively confirmed by accurate electron microprobe analysis, the average observed Nb/Ta ratio (in atoms) being about 53/47 (see below, Table 2, and Fig. 1).

Therefore, some parts of the behierite crystal (including the fragment used to obtain X-ray data) actually represent a new mineral, whose simplified formula is NbBO₄, or better (Nb,Ta)BO₄. The mineral has been named schiavinatoite (to be pronounced as "skee-ah-vee-nat-toh-ite") in honour of Professor Giuseppe Schiavinato (1915-1996) a distinguished Italian mineralogist, who considerably helped the development of mineralogical sciences in Italy. The mineral and the name have been approved by the I.M.A. Commission on New Minerals and Mineral Names (proposal 99-051).

Occurrence and paragenesis

The mineral was found at Antsongombato, south of Betafo, in a wild region in the highlands

of Central Madagascar, some tens kilometers south of the village of Mahaiza. The locality was already known at the beginning of the century for its production of fine gem-quality specimens of red tourmaline (Duparc et al., 1910). After a long period during which the locality was abandoned, in the autumn of 1998 a private company started prospecting and mining mineral specimens in some pegmatites in the area. These operations are still going on, especially following a sub-vertical highly evolved pegmatite dike 10 to 60 centimeters thick and about 400 meters long, which is hosted in marbles. This dike is mainly massive, but miarolitic cavities, up to some tens centimeters across, are locally present.

As a result of these recent activities, Antsongombato has rapidly become famous for its exceptional deep yellow crystals and gemstones of rhodizite. Furthermore, the discovery of a new mineral, londonite, corresponding to the caesium-rich analogue of rhodizite has been described recently from the same locality (Simmons et al., submitted). In this dike, borates of the behierite type are indeed very rare: after the discovery of the type specimen of schiavinatoite, only five additional crystals have been found so far, one of them reaching two centimetres in length. However, these crystals were left untouched and for this reason none of them has been exhaustively characterized yet.

The mineral has been found exclusively in the highly evolved portions of the dike, both in miarolitic cavities and in the massive rock, always in close association with rhodizite. Besides the typical rock-forming minerals of granitic pegmatites, the paragenesis includes spodumene, tourmaline (elbaite-liddicoatite series), danburite, Cs-rich beryl, pollucite, Mn-rich fluorapatite, U-rich microlite, xenotime, monazite, manganocolumbite, manganotantalite, huebnerite, and Hf-rich zircon.

Appearance and physical properties

Schiavinatoite was found as a small portion of one greyish-pink well-formed flattened bipyramidal crystal about 4 mm across, most of which is Nb-rich behierite (see Table 2 and Fig. 1); the observed forms are a first and a second order tetragonal bipyramid, and a tetragonal prism; no twinning has been observed. It is colourless in thin section and its lustre is vitreous. There is no fluorescence under both long and short wave UV light. The streak is white and the hardness is about 8; no

Table. 2. Chemical composition of selected points in the behierite-schiavinatoite crystal (wt%).

	1	2	3	4	5	6	7	8	9^	10	11	12	13	14	15	16	17^	18
Nb2O5	26.39	25.20	25.34	23.15	23.98	26.16	28.54	27.95	18.56	22.03	30.38	29.41	21.73	29.46	27.29	30.22	13.19	27.96
Ta2O5	60.33	60.55	58.46	64.26	60.97	58.91	58.96	57.45	70.60	63.11	56.71	56.87	63.95	56.51	56.75	57.17	63.32	57.73
B2O3*	16.42	16.14	15.85	16.19	15.89	16.13	16.76	16.37	15.98	15.71	16.89	16.66	15.77	16.62	16.09	16.92	13.43	16.42
total	103.14	101.89	99.65	103.60	100.84	101.20	104.26	101.77	105.14	100.85	103.98	102.95	101.45	102.59	100.12	104.31	89.95	102.11
Nb°	0.421	0.409	0.419	0.375	0.395	0.425	0.446	0.447	0.304	0.367	0.471	0.462	0.361	0.464	0.444	0.468	0.257	0.446
Ta°	0.579	0.591	0.581	0.625	0.605	0.575	0.554	0.553	0.696	0.633	0.529	0.538	0.639	0.536	0.556	0.532	0.743	0.554

	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
Nb2O5	31.39	32.01	29.74	26.02	25.75	27.74	30.31	26.05	20.30	30.24	30.29	28.80	31.34	29.42	28.04	31.69	27.85	29.01
Ta2O5	55.56	54.59	55.80	59.30	62.34	56.89	55.62	56.69	66.37	53.52	53.54	57.59	54.03	54.17	57.26	51.93	52.05	53.85
B2O3*	16.97	16.99	16.58	16.16	16.56	16.23	16.70	15.75	15.77	16.35	16.37	16.62	16.72	16.24	16.37	16.48	15.49	16.08
total	103.92	103.59	102.12	101.48	104.65	100.85	102.63	98.49	102.44	100.11	100.20	103.01	102.09	99.83	101.67	100.10	95.39	98.94
Nb°	0.484	0.494	0.470	0.422	0.407	0.448	0.475	0.433	0.337	0.484	0.485	0.454	0.491	0.474	0.449	0.504	0.471	0.472
Ta°	0.516	0.506	0.530	0.578	0.593	0.552	0.525	0.567	0.663	0.516	0.515	0.546	0.509	0.525	0.551	0.496	0.529	0.527

	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
Nb2O5	29.87	31.85	33.63	32.78	34.50	33.05	33.19	31.66	32.23	31.65	34.16	34.36	33.72	33.13	32.38	32.04	34.46	32.34
Ta2O5	53.02	53.36	50.67	51.32	50.30	50.26	49.10	48.76	51.43	51.96	50.24	50.15	49.35	50.47	50.35	51.23	50.34	50.00
B2O3*	16.18	16.75	16.79	16.67	16.96	16.57	16.43	15.97	16.54	16.48	16.86	16.90	16.61	16.63	16.41	16.46	16.96	16.35
total	99.07	101.96	101.09	100.77	101.76	99.88	98.72	96.39	100.20	100.09	101.26	101.41	99.68	100.23	99.14	99.73	101.76	98.69
Nb°	0.484	0.498	0.525	0.515	0.533	0.522	0.529	0.519	0.510	0.503	0.531	0.532	0.532	0.522	0.517	0.510	0.532	0.518
Ta°	0.516	0.502	0.475	0.485	0.467	0.478	0.471	0.481	0.490	0.497	0.469	0.467	0.468	0.478	0.483	0.490	0.468	0.482

* Calculated as explained in the text   ° Calculated on the basis of 4 oxygens   ^ These points probably correspond to altered material
The numbers correspond to those shown in Fig. 1; points from 39 to 54 are relative to schiavinatoite, the others to Nb-rich behierite.
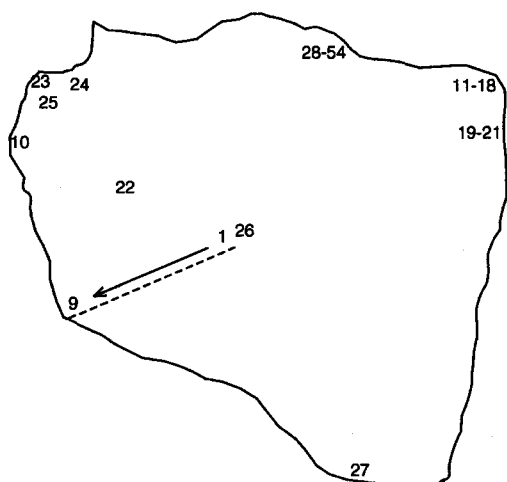
Fig. 1. A sketch of the polished section of the behierite-schiavinatoite crystal. The numbers correspond to the analyzed points reported in Table 2.

cleavage has been observed. The calculated density, using the X-ray data and the results from the chemical analysis (see below) is 6.548 g/cm³, a value sensibly higher than that of pure NbBO₄ (5.254 g/cm³).

The measurement of the optical properties of the mineral was difficult, in view of the very high indices of refraction. For this reason, and considering the satisfactory results we already achieved on dealing with other new minerals with high indices of refraction (Campostrini et al., 1999), we tried to measure the Brewster angle, using the optical goniometer. In this way, an approximate value of the mean index of refraction was obtained (n = 2.30 ± 0.05) almost coinciding with the value (2.310) calculated from the Gladstone-Dale relationship (Mandarino, 1981). The mineral is birefringent, optically uniaxial, positive.

The type specimen has been deposited in the collection of the Museo Civico di Storia Naturale, Milan, under the number MSNM M31137. This specimen is a fragment of pegmatite measuring 8 x 7 x 5.5 centimeters, with a portion of a miarolitic cavity showing corroded crystals of gray quartz, and well formed crystals of K-feldspar with deep red tourmaline. The behierite-schiavinatoite crystal is located between a tourmaline crystal and a deep yellow crystal of rhodizite, 1 cm across.

The type crystal of the mineral was removed for mineralogical characterization, leaving a small

fragment in place. At present, a considerable part of this crystal is included in a mount of epoxy resin and polished. This mount is also preserved in the collections of Museo Civico di Storia Naturale, Milan, with the same catalogue number as for the matrix specimen.

X-ray data collection and structure refinement

A grayish-brown fragment of the crystal having approximate dimensions of 0.10 x 0.10 x 0.10 mm was mounted on a glass fiber in a random orientation. A preliminary examination and data collection were performed with $MoK\alpha$ radiation (0.71073 Å) on an Enraf-Nonius CAD4 kappa axis diffractometer equipped with a graphite crystal monochromator on the incident beam. The unit-cell parameters reported in Table 1 and the orientation matrix for data collection were obtained from a least-squares refinement, using the setting angles of 25 reflections in the range $8 < \theta < 20°$. From the Laue symmetry $4/mmm$ and the systematic absences $h = 2n +1$ for $hk0$ and $2h + l \neq 4n$ for hhl, the space group was indicated to be $I4_1/amd$ (No.141): such an assignment was confirmed by refining the crystal structure. The data were collected at room temperature using the ω-scan technique up to a maximum 2θ of 80°; the scan rate varied from 1 to 20°/min, and the range (in deg.) was determined as a function of θ to account for the separation of the $K\alpha$ doublet. A total of 1395 reflections were collected, of which 203 are unique and not systematically absent (R_{int} 0.015).

Lorentz and polarization corrections were applied to the data as well as an empirical absorption correction as described in Demartin et al. (1991). Relative transmission coefficients range from 0.81 to 1.18. A secondary extinction correction was applied according to Zachariasen (1963). The structure was refined using full-matrix least-squares starting from the atomic coordinates reported in Range et al. (1996). The function minimized was $\Sigma w(|Fo|-|Fc|)^2$ and w taken as $4Fo^2/\sigma(Fo^2)$. The occupancy of the Ta/Nb site was also refined to account for the partial substitution of Ta by Nb. Scattering factors of neutral atoms for Ta, O and B were taken from Cromer & Waber (1974); anomalous dispersion effects were included in Fc.The values for δf' and δf" are those of Cromer (1974).

The final $R = \Sigma(|Fo|-|Fc|) / \Sigma|Fo|$ and $R_w = [\Sigma w(|Fo|-|Fc|)^2 / \Sigma wFo^2]^{1/2}$ are 0.011 and 0.014,

Table 3. Calculated powder diffraction pattern for schi-avinatoite.

h k l	d (Å)	I/I₀
1 0 1	4.115	100
2 0 0	3.110	84
2 1 1	2.481	36
1 1 2	2.328	49
2 2 0	2.199	14
2 0 2	2.057	3
3 0 1	1.939	29
1 0 3	1.755	19
3 2 1	1.646	25
3 1 2	1.598	42
4 0 0	1.555	11
2 1 3	1.528	11
4 1 1	1.454	9
4 2 0	1.391	9
0 0 4	1.372	2
3 0 3	1.371	5
3 3 2	1.293	13
2 0 4	1.255	8
3 2 3	1.255	4
4 3 1	1.213	9
5 0 1	1.213	2
2 2 4	1.164	7
4 1 3	1.164	6
5 2 1	1.130	3
5 1 2	1.115	9
4 4 0	1.099	2

Table 4. Average chemical composition (wt%) of schia-vinatoite.

oxide		3σ	range
Nb₂O₅	33.08	2.94	31.65-34.50
Ta₂O₅	50.37	2.55	48.76-51.96
B₂O₃*	16.60		15.97-16.96
Total	100.05		

*Calculated as explained in the text.

tors is available from the authors on request (or through the E.J.M. Editorial Office - Paris).

Owing to the impossibility of separating schia-vinatoite from behierite, no attempt to obtain an experimental X-ray powder diffraction pattern was performed. The calculated values based on the results of the structure refinement are reported in Table 3.

Chemical analysis

Several different points of a polished sample were analyzed using an Applied Research Laboratories electron microprobe fitted with six wavelength-dispersive spectrometers and a Tracor Northern energy-dispersive spectrometer. The system was operated at an accelerating voltage of 20 kV, a beam current of 300 nA and a counting time of 20 sec on the peaks and 10 sec on the backgrounds. Pure metal standards for Ta and Nb were employed. The results were processed for matrix effects using a modified conventional ZAF routine in the Tracor Northern TASK series of

respectively, for 178 reflections having I greater than 3.0 times the standard deviation. The highest and lowest peaks in the final difference Fourier were 0.9(2)/-0.9(2) e/Å³. All the calculations were performed on a 80486/66 computer using Personal SDP software (Frenz, 1991); a list of structure fac-

Table 5. Final atomic coordinates and ADP's (atomic displacement parameters) for schiavinatoite.

Atom	x	y	z	Beq(Å²)	Multiplicity*
M	0.000	0.000	0.000	0.257(2)	0.096
B	0.000	0.000	0.500	0.44(4)	
O	0.000	0.1792(2)	0.3239(2)	0.38(2)	

* Obtained using for the M site the atomic scattering factors of Ta.

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
M	0.00328(4)	U(1,1)	0.00322(6)	0	0	0
B	0.006(1)	U(1,1)	0.006(1)	0	0	0
O	0.0075(4)	0.0026(4)	0.0041(4)	0	0	0.0004(4)

The form of the anisotropic displacement parameter is:

$\exp[-2\pi^2\{h^2a^{*2}U(1,1) + k^2a^{*2}U(2,2) + l^2c^{*2}U(3,3)\}]$ where a*, and c* are the reciprocal lattice constants.

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter Beq defined as: $(4/3)[a^2\beta(1,1) + a^2\beta(2,2) + c^2\beta(3,3)]$

Table 6. Interatomic distances (Å) and angles (deg.) for schiavinatoite.

	(1)	(2)	(3)
M-O	2.098(1)	2.099(1)	2.095(2)
M-O	2.036(1)	2.034(1)	2.037(2)
O-M-O	64.20(8)		
O-M-O	33.58(5)		
O-M-O	69.39(6)		
O-M-O	135.8(5)		
O-M-O	80.29(3)		
O-M-O	157.00(7)		
O-M-O	92.27(1)		
B-O	1.475(1)	1.472(2)	1.469(2)
O-B-O	98.15(10)		
O-B-O	115.41(6)		

(1) Schiavinatoite
(2) Synthetic TaBO₄ (from Range *et al.*, 1996)
(3) Synthetic NbBO₄ (from Range *et al.*, 1988)

c

a   b

Fig. 2. The structure of schiavinatoite seen almost along [100].

programs. Since boron could not be detected by our microprobe, the concentration of this element was calculated on assuming the atomic ratio B/(Nb+Ta) = 1.

Of all the points measured, 16 showed Nb to prevail over Ta and can be considered to represent schiavinatoite; the average composition together with the range of variation is reported in Table 4, and leads to the chemical formula (Nb$_{0.52}$, Ta$_{0.48}$)BO$_4$, which is in excellent agreement with the corresponding formula (Nb$_{0.53}$,Ta$_{0.47}$)BO$_4$ obtained from crystal structure refinement. The Ta-rich zones (behierite) contain from 20.30 to 32.01 wt% of Nb$_2$O$_5$ and from 53.02 to 66.37 wt% of Ta$_2$O$_5$, corresponding to Nb 0.34 – 0.50 and Ta 0.50 – 0.66 atomic. Mn, Fe, and Ti are always below the detection limit; Hf and Zr are barely above this limit (~ .05 wt %).

Description of the structure and concluding remarks

Atomic coordinates and ADP's for schiavinatoite are reported in Table 5; selected interatomic distances are reported in Table 6, where they are compared with the corresponding data for synthetic TaBO$_4$ and NbBO$_4$. The mineral and its synthetic counterparts are isostructural with zircon, although the coordination polyhedra are much more distorted than in ZrSiO$_4$ (Fig. 2). The metal atom is eight-coordinated, with two groups of four equal M-O bonds measuring 2.098(1) and 2.036(1) Å, respectively, forming a distorted triangular dodecahedron. Boron is tetrahedrally coordi-
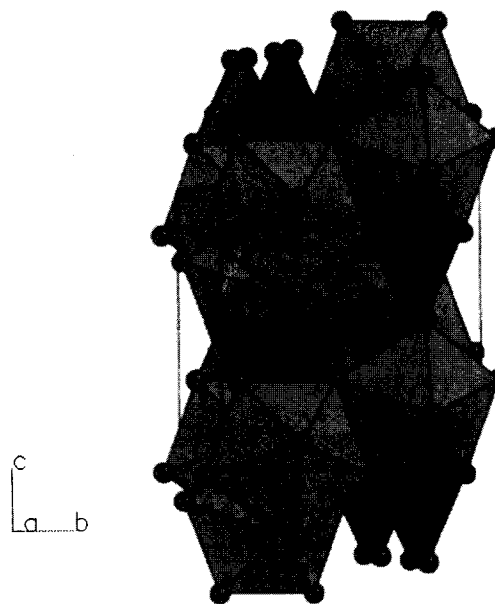
nated, with all the B-O distances equal to 1.475(1) Å, and statistically identical to those observed in the two synthetic phases. Instead of "borates", behierite and schiavinatoite could also be considered as complex oxides.

The structure consists of chains formed by edge-sharing BO$_4$ tetrahedra (corresponding to SiO$_4$ in zircon) and MO$_8$ dodecahedra (corresponding to ZrO$_8$) running parallel to [001]; these chains are linked together by edge-sharing dodecahedra. The edges common to tetrahedra and dodecahedra are considerably short (2.231(3) Å), with respect to the normal O...O non-bonding distances usually found in transition metal-oxygen polyhedra. According to Range *et al.* (1988), this shortening is not due to such edge sharing with the BO$_4$ tetrahedra, since it also occurs for the NbO$_8$ polyhedra of other phases such as, for instance, NaNb$_3$O$_8$ and NaTa$_3$O$_8$.

The occurrence of such rare borates of Nb and Ta in Madagascan pegmatites emphasizes the presence of exceptional conditions which have led to their formation, and a detailed physical-chemical study in this respect would be appropriate. At a first glance, an extraordinarily high value for the activity of borate ions in the depositing fluids would appear as one determining factor; such an idea is suggested by the presence of other species

very rich in B such as for instance rhodizite and danburite which contain about 40 wt% and 30 wt% B_2O_3, respectively, and are almost abundant; these figures are very high in comparison with the ubiquitous tourmalines, where the B_2O_3 content does not exceed 10 wt%.

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