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Nb-Ta OXIDES FROM ELBA ISLAND PEGMATITES

Abstract — During a systematic mineralogical study of Elba pegmatites some Nb-Ta oxides were identified and characterized: microlite, uranmicrolite, titanowodginite, manganocolumbite, euxenite-(Y), polycrase-(Y). This is the first finding for all these minerals in this locality, with the exception of microlite.

Riassunto — *Ossidi di niobio e di tantalio nelle pegmatiti elbane.* Nel corso di uno studio mineralogico di dettaglio delle pegmatiti elbane sono stati identificati e caratterizzati alcuni ossidi di niobio e di tantalio: microlite, uranmicrolite, titanowodginite, manganocolumbite, euxenite-(Y), policrasio-(Y). Con l'eccezione della microlite si tratta di prime segnalazioni per questa località.

Key words — Nb-Ta oxides, Elba island, Italy.

INTRODUCTION

The (Li, Cs, F)-rich pegmatites of S. Piero in Campo, Elba island, are well known among mineralogists for pollucite and dachiardite, here discovered, and for museum samples of elbaite. Even if in the granodioritic pluton of M. Capanne very small pegmatitic veins are widespread, only some of them, located in the south-western margin of the pluton, near the locality of S. Piero in Campo, reach a considerable size, namely 3 to 10 m in length and 0.5 to 2 m in thickness.

These pegmatitic veins were mined at the beginning of this century for museum samples of tourmaline only. The most important veins are: «Grotta d'Oggi», «La Speranza», «Fonte del Prete», «Facciatoia».

Together with the Nb-Ta oxides described in the present work, a

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number of different minerals is known from these pegmatitic veins: besides quartz, orthoclase and albite, the most abudant accessory minerals are lepidolite, beryl and tourmaline. Less common to rare accessory minerals (MEACCI, 1985) are:

Oxides	: cassiterite, rutile, ilmenite, ilmenorutile, wolframoixiolite, magnetite.
Sulphides	: pyrite, arsenopyrite.
Sulphates	: brochantite.
Phosphates	: apatite, amblygonite, triplite, metatorbenite, xenotime.
Borates	: hambergite.
Wolframates	: huebnerite.
Zeolites	: natrolite, mordenite, dachiardite, epistilbite, heulandite, stilbite, laumontite, chabazite, analcite.
Other silicates	: spessartite, zircon, topaz, epidote, tourmaline, petalite, cookeite, pollucite, cordierite.

Some Nb-Ta-bearing minerals, namely microlite, wolframoixiolite and ilmenorutile were previously identified and studied. Microlite was firstly reported by CORSI (1881) and then described by MILLOSEVICH (1914). KLUGER and PERTLIK (1984) identified wolframoixiolite from Grotta d'Oggi, presenting chemical data, unit cell parameters and structural refiniment for this mineral. Ilmenorutile was reported in a paper by ORLANDI and SCORTECCI (1985); in the same work preliminary data on the presence of a mineral belonging to the manganocolumbite-manganotantalite series were presented.

The samples studied in the present work were collected in the dumps of «Fonte del Prete» vein, which is characterized by the conspicuous occurrence of Nb-Ta oxides and zeolites. Nb-Ta oxides occur as small (up to 1 mm in size) crystals in an intermediate fine-grained zone of the pegmatitic veins, in proximity of the contact with the host granodiorite. Less commonly they are associated with zeolites in the geodes of pegmatites.

EXPERIMENTAL METHODS

Identification and characterization of these minerals has been carried out by means of:

— X-ray methods: Weissenberg, precession and powder diffraction photographs.

— SEM study for morphology and chemical qualitative analyses.
— Electron microprobe analyses.

Cell parameters were determined for all the minerals, after correction for shrinkage, by least-squares refinement of powder diffraction patterns, obtained with a Gandolfi camera (114.6 mm in diameter, FeKα radiation). All the photographs presented in this work were obtained with a Philips PW515 Scanning Electron Microscope. Qualitative analyses were carried out by means of an EDAX equipment attached on this instrument. Quantitative chemical analyses were executed on a JEOL 50A electron microprobe in energy-dispersive mode. Standards used were: rutile (Ti), albite (Na, Al), anorthite (Ca), diopside (Mg), olivine (Fe), thorite (Th), synthetic PbO (Pb), synthetic NdF_3 (Nd), whereas metallic standards were used for the other elements. Working conditions: accelerating voltage 15 kV, sample current 2 nA measured on brass, counting time 100 live seconds.

MINERALOGY

Microlite and uranmicrolite

Microlite and uranmicrolite belong to the microlite subgroup of pyrochlore group, whose general formula is $A_{2m}B_2O_6(O, OH, F)_{1-n}.pH_2O$. In this group, subgroups are defined on the basis of the B atoms (Nb, Ta, Ti), whereas the different A atoms, e.g. K, Sn, Ba, REE, Pb, Bi, U give rise to the different mineralogical species. Microlite and uranmicrolite occur as small (up to 1 mm) crystals with {110} dominant and {111} poorly developed. Colour ranges from honey-yellow for microlite to a distinctive dark red-ruby for uranmicrolite. Owing to their high U-content uranmicrolites are metamictic and powder patterns were obtained after heating at 900°C for 10 hours. Uranium is always present in Elba microlites with highly variable contents; this probably indicates that domains of uranmicrolite may occur within microlite crystals. Chemical data, crystal-chemical formulae and unit cell parameters for microlite and uranmicrolite are reported in Table 1 and Table 2, respectively. As shown by these data, the samples from Elba island have (Nb+Ta) > 2Ti and Ta > Nb; therefore, according to the classification of HOGART (1977), pyrochlore and betafite-like minerals are absent.

Titanowodginite

The general formula of the minerals in the wodginite group is

TABLE 1 - *Microprobe analyses, crystal-chemical formulae (recalculated on the basis of six oxygen atoms) and unit cell parameters for three different crystals of microlite; n indicates the number of analyzed points.*

	1		2		3	
	n=5	range	n=8	range	n=8	range
Ta_2O_5	58.67	56.58 - 59.74	57.20	46.48 - 65.70	65.67	50.37 - 72.84
Nb_2O_5	9.34	6.31 - 12.27	14.84	10.97 - 19.80	8.80	6.57 - 16.32
WO_3	9.60	8.62 - 11.36	3.91	2.67 - 5.78	3.49	2.70 - 4.44
Y_2O_3	1.50	1.15 - 1.93	0.87	0.0 - 1.77	0.52	0.0 - 1.56
SnO_2	0.22	0.0 - 0.59	0.17	0.0 - 0.85	0.51	0.0 - 1.21
TiO_2	0.39	0.0 - 1.05	0.26	0.14 - 0.39	0.11	0.0 - 0.35
Na_2O	6.05	5.94 - 6.17	6.62	6.00 - 7.25	6.46	6.05 - 7.17
CaO	7.81	7.05 - 8.42	8.52	6.24 - 10.80	8.10	5.64 - 10.07
UO_2	4.40	2.64 - 5.93	6.34	0.0 - 14.04	4.85	0.0 - 13.64
Sum	97.98		98.73		98.51	
Na	0.93		0.98		1.00	
Ca	0.66		0.70		0.69	
U	0.08		0.11		0.09	
Ta	1.26		1.19		1.42	
Nb	0.33		0.51		0.32	
W	0.20		0.08		0.07	
Y	0.06		0.04		0.02	
Ti	0.02		0.01		0.01	
Sn	0.01		0.01		0.02	
Pb	—		—		—	

Cubic, *Fd3m*. 1. a=10.427(1) Å. 2. a=10.416(1) Å. 3. a=10.415(1) Å.

$A_4C_4B_8O_{32}$ with A = Mn, Fe^{2+}, C = Sn, Ti, Fe^{3+}, Ta, and B = Ta, Nb (ČERNÝ and ERCIT, 1985). Titanowodginite is a distinct mineralogical species (ERCIT *et al.*, 1985) which differs from wodginite in the presence of more titanium than tin in C position. In the present work only one sample of this mineral has been found, exhibiting prysmatic [001] brown crystals up to 0.3 mm in length (Fig. 1). Weissenberg photographs showed that the mineral is monoclinic with space group *C2/c* or *Cc*. Chemical data, crystal-chemical formula and unit cell parameters for titanowodginite are reported in Table 3.

TABLE 2 - *Microprobe analyses, crystal-chemical formulae (recalculated on the basis of six oxygen atoms) and unit cell parameters for two different crystals of uranmicrolite; n indicates the number of analyzed points.*

	1		2	
	n=4	range	n=8	range
Ta_2O_5	44.20	42.14 - 48.79	48.57	46.48 - 65.70
Nb_2O_5	13.51	11.92 - 14.33	14.25	10.97 - 19.80
WO_3	11.95	9.93 - 13.96	2.95	2.67 - 5.78
Y_2O_3	1.33	0.0 - 2.19	0.60	0.0 - 1.77
TiO_2	0.51	0.44 - 0.65	0.69	0.0 - 0.85
SnO_2	0.42	0.0 - 0.80	0.26	0.14 - 0.39
PbO_2	0.34	0.0 - 0.52	—	
Na_2O	6.60	5.43 - 7.84	6.17	5.00 - 7.62
CaO	3.35	2.74 - 3.87	4.72	4.12 - 15.22
UO_2	16.69	14.46 - 17.92	20.40	18.85 - 21.55
Sum	98.90		98.35	
Na	1.03		0.98	
Ca	0.29		0.42	
U	0.30		0.37	
Ta	0.97		1.09	
Nb	0.49		0.53	
W	0.25		0.06	
Y	0.06		—	
Ti	0.03		0.04	
Sn	0.01		0.02	
Pb	0.01		—	

Cubic, *Fd3m*. 1. a=10.401(1) Å. 2. a=10.402(1) Å.

Euxenite-(Y)

Euxenite-(Y) is a distinct species among the orthorhombic AB_2O_6 Y-Nb-Ta-Ti-oxides, with Y and Nb as major elements in the A and B sites respectively. It was found (Fig. 2) as small (up to 1 mm in length) opaque crystals, tabular {100} and elongated [001], with colour ranging from red-brown to dark-brown. Weissenberg photographs confirmed *Pbcn* as space group for euxenite-(Y). Chemical data, crystal-chemical formulae and unit cell parameters for

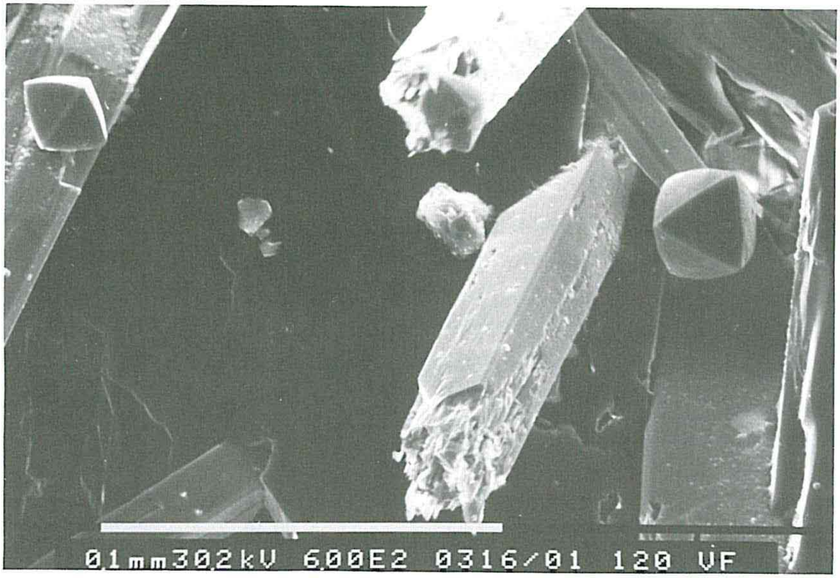

Fig. 1 - SEM photograph of titanowodginite. Octahedral microlite crystals are also present.

TABLE 3 - *Microprobe analyses, crystal-chemical formula (recalculated on the basis of 32 oxygen atoms) and unit cell parameters for titanowodginite; n indicates the number of analyzed points.*

	n=4	range
Ta_2O_5	68.22	67.93 - 68.50
TiO_2	11.07	10.28 - 11.88
MnO	10.96	10.53 - 11.23
SnO_2	5.44	5.10 - 5.85
Nb_2O_5	3.49	2.92 - 3.88
WO_3	0.33	0.0 - 0.78
ZrO_2	0.16	0.0 - 0.63
Y_2O_3	0.14	0.0 - 0.64
Sum	99.81	
Mn	3.67	
Ta	7.32	
Nb	0.62	
Zr	0.02	
Y	0.02	
W	0.02	
Ti	3.29	
Sn	0.85	

Monoclinic, *C2/c* (*Cc*). a=9.46(1) Å, b=11.37(2) Å, c=5.102(3) Å, β=91.4°.

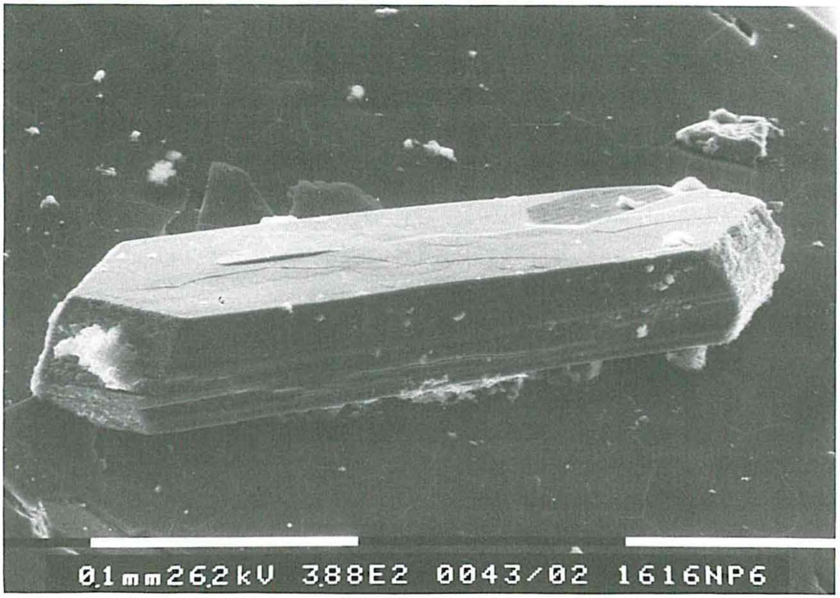

Fig. 2 - SEM photograph of euxenite-(Y).

euxenite-(Y) are reported in Table 4. Both samples of euxenite-(Y) are U-rich. The former one (analyses in the first two columns of Table 4) shows to be highly inhomogeneous in the yttrium to bismuth ratio.

Manganocolumbite

Manganocolumbite is the most common Nb-Ta oxide. It is found (Figs. 3 and 4) as tabular {100} and elongated [001] orange-red, vitreous, transparent crystals, up to 1 mm in length. They typically occur as inclusions in beryl, tourmaline and quartz, or in cavities associated with stilbite, quartz and orthoclase. Weissenberg photographs confirmed the orthorhombic symmetry of the mineral, space group *Pbcn*. Chemical data, crystal-chemical formulae and unit cell parameters for manganocolumbite are reported in Table 5. The general formula for the minerals in the columbite-tantalite group is $(Mn, Fe)_4(Nb, Ta)_8O_{24}$. Four end-members exist, namely manganocolumbite, ferrocolumbite, manganotantalite and ferrotantalite, depending on the dominant element in the two independent sites. The studied samples systematically have Nb > Ta, whereas iron is lacking. Therefore they can be classified as manganocolumbite.

TABLE 4 - *Microprobe analyses, crystal-chemical formulae (recalculated on the basis of six oxygen atoms) and unit cell parameters for two different crystals of euxenite-(Y). Analyses 1a and 1b, carried out on two points of the same crystal, were not averaged because of marked differences in several elements; n indicates the number of analyzed points for the second crystal.*

	1		2
	a	b	n=2
Nb_2O_5	32.41	22.69	15.04
Ta_2O_5	14.85	16.88	32.00
TiO_2	18.39	18.09	17.33
Y_2O_3	16.30	9.18	12.18
UO_2	9.56	9.31	11.76
Bi_2O_3	—	10.71	0.77
ThO_2	1.29	1.79	2.36
WO_3	1.94	2.39	0.23
MnO	1.04	—	1.22
CaO	1.13	1.14	1.22
FeO	0.37	1.93	0.36
PbO_2	0.86	1.01	0.80
Na_2O	—	0.83	0.68
MgO	0.56	0.63	0.42
Al_2O_3	—	0.54	—
Sum	98.81	97.12	96.37
Nb	0.90	0.69	0.48
Ta	0.25	0.31	0.61
Ti	0.85	0.92	0.91
Y	0.53	0.33	0.45
U	0.13	0.14	0.18
Bi	—	0.19	0.01
Th	0.02	0.02	0.04
W	0.03	0.04	—
Mn	0.05	—	0.07
Ca	0.07	0.08	0.09
Fe	0.02	0.10	0.02
Pb	0.01	0.01	0.01
Na	—	0.10	0.09
Mg	0.05	0.06	0.04
Al	—	0.04	—

Orthorhombic, *Pbcn.*
1. a=14.63(1) Å, b=5.632(1) Å, c=5.188(1) Å.
2. a=14.64(2) Å, b=5.571(2) Å, c=5.237(1) Å.

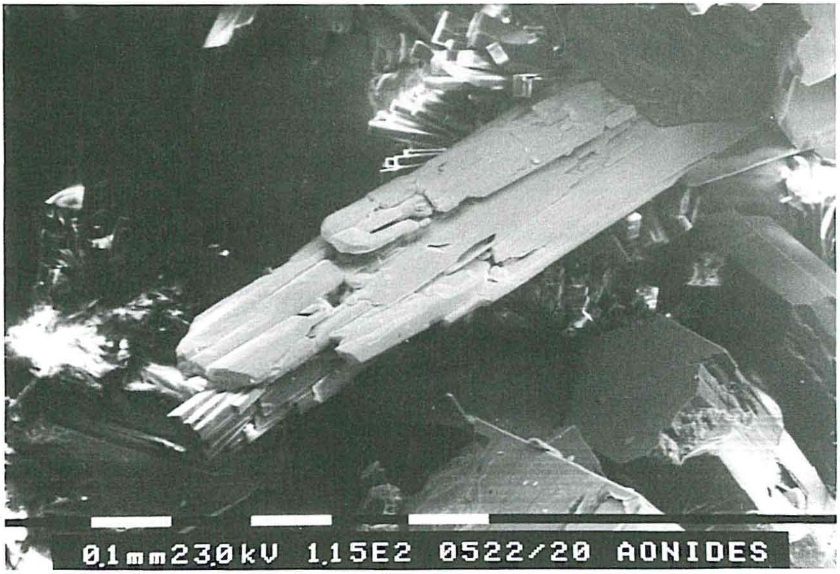

Fig. 3 - SEM photograph of manganocolumbite.

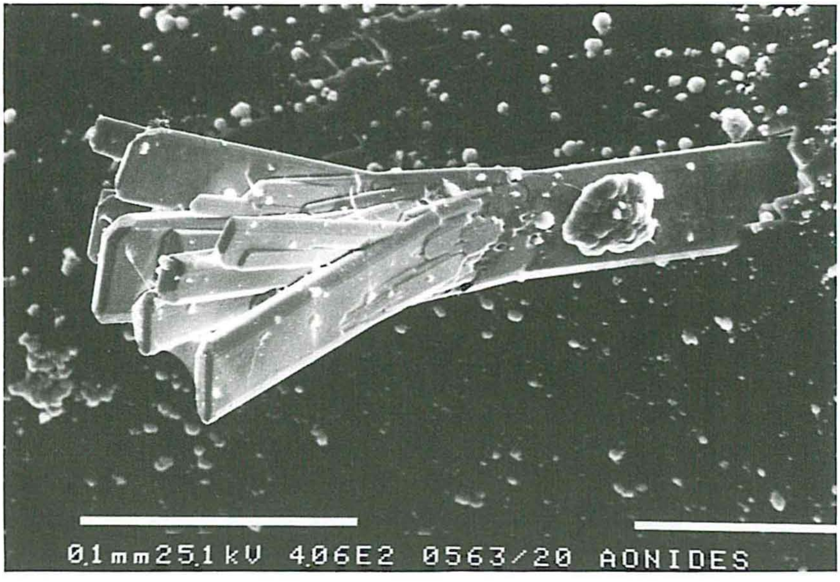

Fig. 4 - SEM photograph of manganocolumbite.

TABLE 5 - *Microprobe analyses, crystal-chemical formulae (recalculated on the basis of six oxygen atoms) and unit cell parameters for six different crystals of manganocolumbite; n indicates the number of analyzed points. Crystals no. 5 and no. 6 have been destroyed before the X-ray diffraction study was performed.*

	1		2		3	
	n=6	range	n=7	range	n=4	range
Nb_2O_5	41.11	35.68 - 44.87	44.64	42.10 - 49.64	36.70	25.09 - 47.31
Ta_2O_5	36.64	33.67 - 43.82	32.52	27.59 - 35.0	37.64	26.73 - 48.65
TiO_2	2.45	1.54 - 3.21	3.78	3.15 - 4.21	4.72	4.53 - 4.86
MnO	16.00	13.94 - 17.21	15.24	14.03 - 16.73	16.25	14.09 - 17.49
Y_2O_3	1.20	0.84 - 1.42	1.09	0.72 - 1.27	—	
UO_2	0.61	0.0 - 1.14	0.58	0.3 - 1.19	1.27	0.46 - 2.22
FeO	0.04	0.0 - 0.24	0.49	0.27 - 1.0	0.40	0.0 - 0.89
WO_3	0.59	0.28 - 0.80	0.41	0.17 - 0.74	0.62	0.48 - 0.96
SnO_2	0.32	0.0 - 0.61	0.44	0.0 - 0.67	0.86	0.55 - 1.03
CaO	0.05	0.0 - 0.30	0.03	0.0 - 0.18	0.24	0.0 - 0.43
Na_2O	0.04	0.0 - 0.24	0.05	0.0 - 0.21	0.17	0.0 - 0.44
MgO	—		0.08	0.0 - 0.17	—	
PbO_2	0.15	0.0 - 0.30	0.12	0.0 - 0.45	—	
ThO_2	0.04	0.0 - 0.40	—		0.49	0.0 - 1.44
Bi_2O_3	—		—		—	
Al_2O_3	0.07	0.0 - 0.25	—		0.24	0.0 - 0.95
Sum	99.34		99.47		99.60	
Mn	0.90		0.83		0.91	
Y	0.04		0.04		—	
Fe	—		0.03		0.02	
Sn	—		0.01		0.02	
Na	0.01		0.01		0.02	
Ca	—		—		0.02	
U	—		—		0.02	
W	0.01		0.01		0.01	
Th	—		—		0.01	
Al	—		—		0.02	
Mg	—		—		—	
Nb	1.23		1.29		1.09	
Ta	0.66		0.57		0.67	
Ti	0.12		0.18		0.23	

Orthorhombic, *Pbcn*. 1. a=14.359(9) Å, b=5.737(1) Å, c=5.091(1) Å. 2. a=14.388(6) Å, b=5.759(9), c=5.071(1) Å. 3. a=14.358(5) Å, b=5.729(1) Å, c=5.088(1) Å.

TABLE 5 - *(continued).*

	4		5		6	
	n=5	range	n=7	range	n=3	range
Nb_2O_5	44.75	43.07 - 45.68	45.23	44.61 - 46.13	48.64	47.16 - 50.84
Ta_2O_5	33.46	32.33 - 34.79	30.59	29.70 - 31.24	22.23	21.63 - 22.92
TiO_2	2.51	2.15 - 2.95	3.77	3.09 - 4.07	5.62	4.0 - 8.01
MnO	16.96	16.14 - 17.98	16.65	16.26 - 16.87	13.69	12.13 - 14.81
Y_2O_3	0.82	0.41 - 1.31	0.11	0.0 - 0.49	3.19	3.0 - 3.78
UO_2	0.35	0.0 - 0.80	0.86	0.0 - 1.61	1.48	0.91 - 2.24
FeO	—		0.29	0.0 - 0.53	1.73	1.22 - 2.59
WO_3	0.55	0.16 - 0.89	0.58	0.33 - 0.98	0.60	0.13 - 0.98
SnO_2	0.23	0.0 - 0.62	0.58	0.47 - 0.79	0.51	0.35 - 0.65
CaO	0.04	0.0 - 0.11	0.11	0.0 - 0.22	0.67	0.51 - 0.82
Na_2O	0.08	0.0 - 0.22	0.09	0.0 - 0.26	0.29	0.0 - 0.49
MgO	—		—		0.22	0.17 - 0.33
PbO_2	0.15	0.0 - 0.42	—		0.14	0.0 - 0.42
ThO_2	—		0.34	0.0 - 0.53	—	
Bi_2O_3	—		—		0.17	0.0 - 0.51
Al_2O_3	—		—		—	
Sum	99.89		99.20		99.18	
Mn	0.93		0.90		0.72	
Y	0.03		—		0.10	
Fe	—		0.02		0.09	
Sn	0.01		0.01		0.01	
Na	—		0.01		0.03	
Ca	—		—		0.04	
U	0.01		0.01		0.02	
W	—		—		—	
Th	—		—		—	
Al	—		—		—	
Mg	—		—		0.02	
Nb	1.30		1.31		1.36	
Ta	0.59		0.53		0.37	
Ti	0.12		0.18		0.26	

4. a=14.403(4) Å, b=5.747(1) Å, c=5.086(1) Å.

Polycrase-(Y)

Among the AB_2O_6 orthorhombic Y-Nb-Ti-Ta-oxides, polycrase-(Y) is the mineral with Y and Ti as major elements in the A and B sites respectively. This mineral occurs as small (0.2 mm long) opaque, brown-red crystals, tabular {100} and elongated [001]. It is associated with quartz, albite, orthoclase, lepidolite, elbaite, beryl and stilbite. Tiny apatite crystals are present on polycrase-(Y). For its very high U content, polycrase-(Y) results to be metamictic, and then almost completely amorphous to X-rays. Therefore, whereas chemical data were obtained on untreated material, it has been necessary to heat the mineral at 900°C for 10 hours to obtain X-ray diffraction data. Weissenberg photographs showed that polycrase-(Y) is orthorhombic, space group *Pbcn*. Chemical data, crystal-chemical formula and unit-cell parameters are reported in Table 6. Preliminary

TABLE 6 - *Microprobe analyses, crystal-chemical formula (recalculated on the basis of six oxygen atoms) and unit cell parameters for polycrase-(Y); n indicates the number of analyzed points.*

	n=2		
TiO_2	25.87	Ti	1.27
Nb_2O_5	18.74	Nb	0.55
Ta_2O_5	9.50	Ta	0.17
UO_2	27.24	U	0.39
Y_2O_3	11.51	Y	0.40
ThO_2	1.32	Th	0.02
MnO	0.15	Mn	—
Nd_2O_3	0.34	Nd	0.01
CaO	0.65	Ca	0.05
WO_3	1.72	W	0.03
Al_2O_3	0.57	Al	0.04
Na_2O	0.26	Na	0.03
Sum	97.87		

Orthorhombic, *Pbcn*. a=14.48(3) Å, b=5.559(6) Å, c=5.223(1) Å.

chemical data seems to indicate the occurrence of crystals with U > Y, which would represent a new mineralogical species. Work is in progress to identify this possible new mineral.

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