

Nb-Ta-Ti OXIDES IN GRANITIC PEGMATITES FROM THE TOPSHAM PEGMATITE DISTRICT, SOUTHERN MAINE

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ABSTRACT

Numerous bodies of granitic pegmatite intrude gneissic rocks in the Topsham pegmatite district, in southern Maine. Many of these pegmatites contain metamict, REE-bearing, complex Nb-Ta-Ti oxides. Initial reports identified this mineral as samarskite-(Y), an ABO_4 mineral with Nb, Ta and Ti at the B site and REE + Y dominant at the A site. However, electron-microprobe and X-ray-diffraction analyses of seven recently collected samples from various locations in the district reveal that the oxide mineralogy is complex, consisting of several oxide phases. When heated, five of the specimens examined recrystallized to high-T samarskite plus other phases. However, these specimens have U + Th greater than REE + Y at the A site, and thus are ishkawaite rather than samarskite-(Y). Ishkawaite was found in all of the locations studied except the Consolidated Number 2 Quarry. The only metamict-appearing sample collected from the Consolidated Number 2 Quarry is ferrocolumbite, an AM_2O_6 oxide. At the Stand Pipe Hill location, polycrase-(Y), an AB_2O_6 oxide with Y dominant at the A site and Ti dominant at the B site, occurs in addition to ishkawaite. Samarskite-(Y) is notably absent from the pegmatites studied.

Keywords: samarskite-(Y), ishkawaite, polycrase-(Y), Topsham pegmatite district, Maine.

SOMMAIRE

De nombreux massifs de pegmatite granitique ont été mis en place dans un socle gneissique dans le district de Topsham, dans le secteur sud de l'état du Maine. Dans plusieurs cas, ces pegmatites contiennent un oxyde complexe de Nb-Ta-Ti métamict et porteur de terres rares. Les rapports préliminaires font état de samarskite-(Y), à stoechiométrie ABO_4 , un minéral ayant Nb, Ta et Ti à la position B et les terres rares + Y à la position A. Toutefois, nos résultats d'analyses à la microsonde électronique et par diffraction X de sept échantillons prélevés récemment dans le district révèlent un assemblage d'oxydes complexe. Suite au chauffage, cinq des échantillons ont recristallisé à la samarskite et d'autres phases. Toutefois, ces échantillons contiennent davantage de U + Th que de terres rares + Y à la position A, ce qui en font des exemples d'ishkawaïte plutôt que de samarskite-(Y). L'ishkawaïte est présente à chaque endroit sauf la carrière Consolidated Number 2. Le seul oxyde qui paraît métamict à cet endroit est la ferrocolumbite, de stoechiométrie AM_2O_6 . Au site Stand Pipe Hill, nous avons trouvé le polycrase-(Y), oxyde à stoechiométrie AB_2O_6 , avec Y dominant à la position A et Ti dominant à la position B, avec l'ishkawaïte. La samarskite-(Y) serait absente des pegmatites étudiées.

(Traduit par la Rédaction)

Mots-clés: samarskite-(Y), ishkawaïte, polycrase-(Y), district de pegmatites de Topsham, Maine.

INTRODUCTION

Numerous bodies of granitic pegmatite intrude gneissic rocks in the Topsham pegmatite district, located in southern Maine, near the town of Topsham (Fig. 1). These pegmatites are generally tabular and commonly zoned. They range in thickness from 2 cm to at least 2 m (Shanin 1948). Wise & Frances (1992) have reported on the characteristics of granite

pegmatites from the Brunswick pegmatite field in which the Topsham pegmatites are located. Pegmatites in this district contain metamict, rare-earth-element-bearing complex Nb-Ta-Ti oxides. A single sample from Topsham, Maine has been analyzed, and identified as samarskite-(Y) (Lane 1937); subsequently it has been generally assumed that all samples of a black, glassy, metamict mineral from this district consist of samarskite-(Y) (King & Foord 1994). Our purpose in

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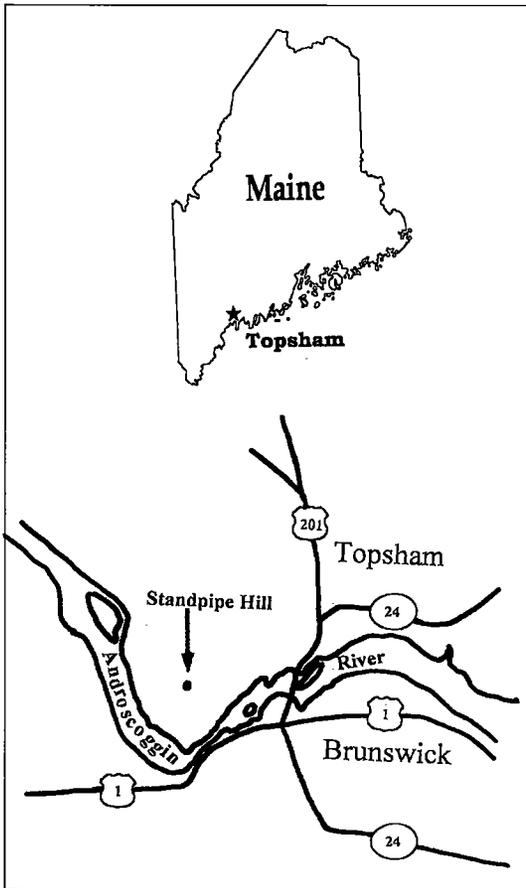


FIG. 1. Location map for the Topsham pegmatite district, eastern Maine.

this study was to examine metamict Nb–Ta–Ti oxides from the intermediate zones of five poorly zoned, rare-earth-enriched granitic pegmatites in this district (Fig. 1). Samples that resembled the description of samarskite-(Y) were chosen in order to confirm the identity of these specimens and to evaluate the chemical variations among the metamict oxides.

SAMPLES SELECTED AND ANALYTICAL METHODS

Samples analyzed with an electron microprobe and by X-ray diffraction include specimens from the Yedlin Location (YL), the Consolidated No. 2 Quarry (C2Q), the Russell Brothers Quarry (RBQ), Stand Pipe Hill (SPH) and the Swamp No. 1 Quarry (S1Q).

Electron-microprobe analyses were carried out at the University of Utah with a CAMECA SX-50 instrument using an accelerating voltage of 15 kV and a beam current of 30 nA. A 3- μ m beam size was used

to ensure analysis of inclusion-free phases. Peak overlaps involving the rare-earth-elements (REE) were avoided by using the $L\alpha$ peak positions for La, Ce, Eu, Gd, Tb, Ho, Tm and Yb, and the LB peak positions for Pr, Nd, Sm, Dy and Er. Standards used included: synthetic Y-niobate (Nb), manganotantalite (Ta), rutile (Ti), W metal (W), diopside (Ca, Si), hematite (Fe), rhodonite (Mn), YAG (Y), cubic zirconia (Zr), Sc metal (Sc), crocoite (Pb), cassiterite (Sn), synthetic UO_3 (U), and synthetic $NaTh_2(PO_4)_3$ (Th). The REE standards included the REE-doped glasses of Drake & Weill (1972), synthetic REE garnet compositions (U.S. National Museum numbers: S-65, S-67, S-68, S-87, S-90, S-92, and S-529), and synthetic REE phosphates (from the Smithsonian Institution). Matrix effects were corrected using a $\phi(\rho Z)$ correction procedure (Pouchou & Pichoir 1991).

X-ray-diffraction analyses were performed at the University of New Orleans using a Scintag XDS-2000 X-ray diffractometer. Samples were analyzed using an operating voltage of 35 kV and a current of 15 mA, with $CuK\alpha$ radiation, a scan step of $0.01^\circ 2\theta$ and a dwell time of 3 seconds. Standards for instrument calibration included corundum and quartz.

ISHIKAWAITE

Samarskite-(Y) and ishikawaite are both Nb–Ta–Ti oxides with the general formula ABO_4 . Both minerals have Nb dominant in the B site, and thus are differentiated from each other on the basis of A-site cation occupancy. Samarskite has been described as a mineral with Y + REE dominant at the A site (Komkov 1965, Sugitani *et al.* 1985, Černý & Ercit 1989). Thus Nickel & Mandarino (1987) recommended that the mineral name samarskite be changed to samarskite-(Y). Fleischer & Mandarino (1995) revised this definition of samarskite based on the work of Warner & Ewing (1993), and gave the formula for samarskite as $(Fe^{3+}, Y, Fe^{2+}, U, REE)(Nb, Ta)O_4$. However, as most of the samples in the dataset of Warner & Ewing (1993) have Y + REE dominant at the A site, we contend that the proper name should still be samarskite-(Y). It is clear that more work is needed to clarify the nomenclature of samarskite. Thus, further references in this paper to samarskite will be to the (Y + REE)-dominant phase, samarskite-(Y).

The currently accepted formula of the species ishikawaite is $(U, Fe, Y, Ca)(Nb, Ta)O_4$ (Fleischer & Mandarino 1995). Ishikawaite was first described as a uranium-rich, REE-poor mineral by Kimura (1922). It was later described as a uranium-rich variety of samarskite-(Y) (Ohashi 1924), although no data were presented to substantiate this relationship (Černý & Ercit 1989). In this study, the X-ray-diffraction pattern for recrystallized ishikawaite is found to be very similar to that for high-temperature samarskite-(Y) given by Sugitani *et al.* (1984, 1985). Thus, we infer that

TABLE 1. CHEMICAL COMPOSITION OF ISHIKAWAITE, POLYCRASE-(Y) AND FERROCOLUMBITE, TOPSHAM DISTRICT, MAINE

wt %	Ishikawaite					Columbite		Polycrase-(Y)	
	S1Q-1 avg	S1Q-2 avg	YL avg	SPH-1 avg	RBQ avg	C2Q avg	SPH-2 avg		
Nb ₂ O ₅	39.4	42.2	42.3	39.8	41.9	66.6			19.3
Ta ₂ O ₅	3.96	2.69	3.17	4.89	3.06	8.83			2.50
TiO ₂	1.08	1.33	3.39	4.07	3.66	2.91			25.3
ThO ₂	5.70	4.72	5.01	4.81	4.87	n.d.			5.10
UO ₂	28.3	29.6	21.8	22.0	20.9	n.d.			
U ₃ O ₈									20.2
La ₂ O ₃	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.			n.d.
Ce ₂ O ₃	0.07	0.06	0.09	0.08	0.09	n.d.			0.14
Pr ₂ O ₃	n.d.	n.d.	0.05	0.06	0.04	n.d.			n.d.
Nd ₂ O ₃	0.28	0.28	0.41	0.31	0.37	n.d.			0.38
Sm ₂ O ₃	0.33	0.26	0.45	0.34	0.44	n.d.			0.34
Eu ₂ O ₃	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.			n.d.
Gd ₂ O ₃	0.86	0.64	1.16	0.99	1.15	n.d.			1.06
Tb ₂ O ₃	0.09	0.03	0.11	0.11	0.09	n.d.			0.16
Dy ₂ O ₃	1.14	0.92	1.60	1.49	1.68	n.d.			1.75
Ho ₂ O ₃	0.28	0.23	0.40	0.35	0.41	n.d.			0.48
Er ₂ O ₃	n.d.	n.d.	0.11	0.06	n.d.	n.d.			1.63
Tm ₂ O ₃	n.d.	n.d.	n.d.	n.d.	n.d.	0.06			n.d.
Yb ₂ O ₃	0.23	0.27	0.28	0.51	0.29	0.04			1.85
Lu ₂ O ₃	0.08	0.08	0.09	0.11	0.05	0.05			0.38
Y ₂ O ₃	3.83	3.87	6.31	6.39	6.56	0.16			10.4
MnO	0.22	1.62	1.17	0.83	1.19	3.41			0.38
ZnO	n.d.	0.08	0.08	n.d.	0.06	0.05			n.d.
CaO	1.60	0.07	0.12	0.51	0.10	n.d.			2.82
SnO ₂	1.64	1.54	1.95	1.17	1.88	2.17			0.20
SrO	0.30	0.30	0.91	0.52	0.88	0.07			0.06
PbO	0.20	0.50	0.27	0.30	0.30	n.d.			1.01
WO ₃	0.43	0.20	0.55	0.66	0.51	0.29			0.25
Fe ₂ O ₃		3.85	5.52	5.09	5.78	1.68			2.52
FeO	4.56	5.50	3.85	3.90	3.70	13.5			
Al ₂ O ₃	0.07	n.d.	n.d.	0.04	0.05	n.d.			n.d.
SiO ₂	0.48	n.d.	n.d.	n.d.	n.d.	n.d.			n.d.
MgO	n.d.	0.10	0.12	0.08	0.12	0.33			0.04
Na ₂ O	n.d.	n.d.	0.05	0.09	n.d.	n.d.			0.05
Total	95.1	100.9	101.3	99.6	100.1	100.1			98.3

n.d. = not detected

ishikawaite is structurally equivalent to samarskite-(Y). The only difference between them lies in their A-site occupancy, with ishkawaite being the (U + Th)-dominant species, whereas samarskite-(Y) is the (Y + REE)-dominant species.

Analytical results: ishkawaite from the Topsham suite

Ishikawaite was identified at all sampled locations except the Consolidated No. 2 Quarry. Averaged compositions in terms of oxides are given in Table 1, and chemical formulae in Table 2. These compositions represent the average result of 15 analyses for sample RBQ, of 14 for samples YL and S1Q-1, and of 11 for samples SPH-1 and S1Q-2. The low analytical total for sample S1Q-1 is attributed to the presence of adsorbed molecular water, a common feature of metamict minerals (Ewing 1975a). Chemical formulae for ishkawaite were calculated on the basis of four atoms of oxygen (Table 2). Iron is typically present in samarskite-(Y) as both Fe²⁺ and Fe³⁺, and thus was partitioned in the calculation of the ishkawaite formula to yield a total of two atoms per formula unit, which is consistent with the general ABO₄ formula. This level of occupancy was achieved for all samples except S1Q-1. Because the site totals for S1Q-1 are low, no iron was converted from the divalent to trivalent state, as this would further lower the site totals. The B site is

occupied by Nb and Ta. Because both the A and B sites are octahedrally coordinated, Ti may occupy either the A or the B site. For purposes of recalculation, we have chosen to place all the Ti in the B site, as this gives improved totals. The slight deviation from unity in the A and B sites may be attributed to small errors in the analyses, which cumulatively affect the partitioning of Fe into ferrous and ferric states.

Occupancy of the B site is dominated by Nb, with only small amounts of Ta and Ti (Fig. 2). Samples from SPH, RBQ and YL all have similar B-site occupancies, whereas samples from S1Q have slightly less Ti. Plots of the dominant A-site cations (Figs. 3a, b) reveal that all specimens of ishkawaite are enriched in U + Th relative to REE + Y. Samples RBQ, SPH-1 and YL are only slightly enriched in U + Th, as they lie near the ishkawaite - samarskite-(Y) boundary. The two samples from S1Q have slightly higher concentrations of U + Th than the others. All samples have iron as the third most abundant element at the A site. However, iron occurs in the ferric state in samples SPH-1, RBQ and YL, whereas it is present in the ferrous state in samples from S1Q. It is important to note that these calculated Fe²⁺ and Fe³⁺ values represent post-metamictization values and may not reflect the

TABLE 2. CHEMICAL FORMULAE OF ISHIKAWAITE, TOPSHAM DISTRICT, MAINE (BASED ON FOUR ATOMS OF OXYGEN)

	S1Q-1 avg	S1Q-2 avg	YL avg	SPH-1 avg	RBQ avg
Nb	0.910	0.904	0.859	0.830	0.855
Ta	0.055	0.035	0.039	0.061	0.038
Ti	0.041	0.047	0.114	0.141	0.124
Sum B	1.006	0.986	1.012	1.032	1.016
Th	0.066	0.051	0.051	0.050	0.050
U ⁴⁺	0.322	0.312	0.218	0.226	0.210
La					
Ce	0.001	0.001	0.001	0.001	0.001
Pr			0.001	0.001	0.001
Nd	0.005	0.005	0.007	0.005	0.006
Sm	0.006	0.004	0.007	0.005	0.007
Eu					
Gd	0.015	0.010	0.017	0.015	0.017
Tb	0.002		0.002	0.002	0.001
Dy	0.019	0.014	0.023	0.022	0.024
Ho	0.005	0.003	0.006	0.005	0.006
Er			0.002	0.001	
Tm					
Yb	0.004	0.004	0.004	0.007	0.004
Lu	0.001	0.001	0.001	0.002	0.001
Y	0.104	0.098	0.151	0.157	0.157
Mn	0.010	0.065	0.045	0.032	0.045
Zr		0.002	0.002		0.001
Ca	0.088	0.004	0.006	0.025	0.005
Sc	0.073	0.064	0.076	0.047	0.074
Sn	0.006	0.006	0.016	0.010	0.016
Pb	0.003	0.006	0.003	0.004	0.004
W	0.006	0.002	0.006	0.008	0.006
Fe ³⁺		0.137	0.187	0.176	0.197
Fe ²⁺	0.195	0.218	0.145	0.150	0.140
Al	0.004			0.002	0.003
Si	0.025				
Mg		0.007	0.008	0.005	0.008
Na			0.004	0.008	
Sum A	0.956	1.014	0.988	0.968	0.984

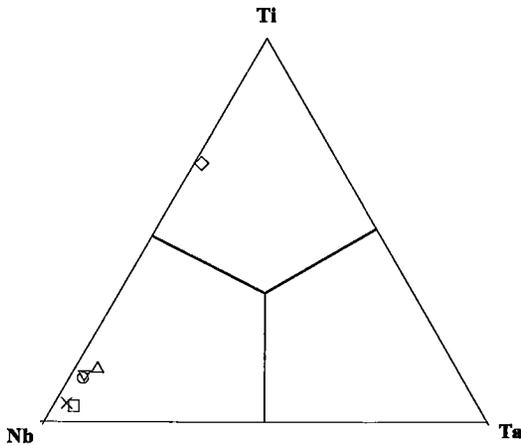


FIG. 2. Ti-Nb-Ta diagram showing major B-site occupancy of ishikawaite (samples S1Q-1, S1Q-2, YL, SPH-1 and RBQ) and polycrase-(Y) (sample SPH-2) from the Topsham district, Maine. Symbols are as follows: S1Q-1 (square), S1Q-2 (X), YL (circle), SPH-1 (triangle), RBQ (inverted triangle) and SPH-2 (diamond).

X-ray diffractometry

To confirm the above identification, all samples of ishikawaite were analyzed using X-ray diffractometry. Because the samples are completely metamict, recrystallization in a reducing atmosphere prior to X-ray analysis was necessary. Samples were heated in a quartz tube with a gas flow of 95% Ar and 5% H₂ at a temperature of 1100°C for 12 hours. This approach was chosen because Sugitani *et al.* (1984, 1985) reported that heating natural samples of samarskite in a reducing atmosphere yields a single crystalline phase considered to represent the samarskite-(Y) structure, whereas heating in air or an inert atmosphere yields several crystalline phases. It is important to note that the X-ray-diffraction peaks discussed below are compared to the high-temperature polymorph of Sugitani *et al.* (1985) simply for the purposes of identification; we are not implying that the high-temperature polymorph of samarskite-(Y) represents the original structure of the sample.

In contrast to the results of Sugitani *et al.* (1984, 1985), the X-ray-diffraction patterns of ishikawaite from Topsham reveal that several phases formed upon

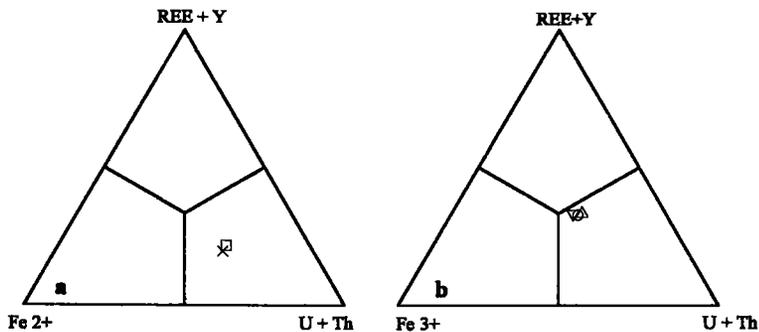


FIG. 3. (REE + Y) - Fe²⁺ (or Fe³⁺) - (U + Th) diagrams showing major A-site occupancy of Maine ishikawaite from the Topsham district, Maine. Symbols are as in Figure 2.

pre-metamictization values. Finally, S1Q-1 has more Ca at the A site, a feature which Ewing (1975b) attributed in metamict Nb-Ta-Ti oxides to early alteration prior to pseudomorphism. Thus the higher Ca content and the low oxide and cation totals for sample S1Q-1 suggest that it may be significantly altered.

A chondrite-normalized plot (Fig. 4) shows that for all samples of ishikawaite, the heavy REE (HREE) are enriched relative to the light REE (LREE) by several orders of magnitude.

recrystallization. These phases include ishikawaite, petscheckite [(U,Fe)(Nb,Ta)₂O₈] and an orthorhombic FeNbO₄ oxide. A representative X-ray-diffraction pattern is given in Table 3. The X-ray pattern correlates well with the samarskite-(Y) pattern of Sugitani *et al.* (1985). However, several significant peaks cannot be attributed to the samarskite structure. The most notable of these are at *d*_{obs} values of 4.007 and 3.172 Å. These peaks can be attributed to the presence of petscheckite as a subordinate phase. A comparison of the pattern

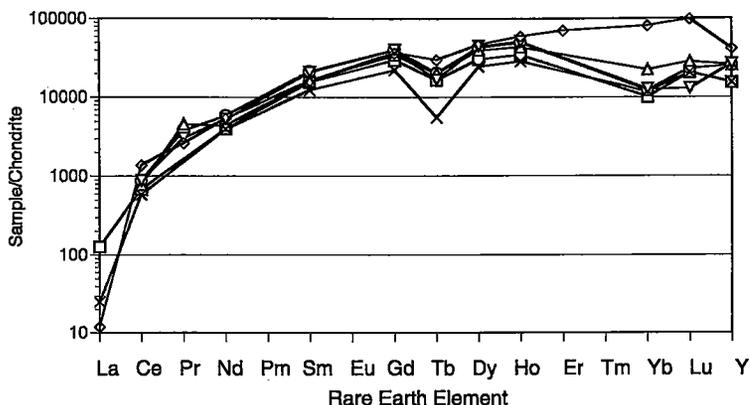


FIG. 4. Chondrite-normalized REE plot for ishikawaite and polycrase-(Y) samples from the Topsham district, Maine. Symbols are as in Figure 2. Note: Er is not plotted for the ishikawaite samples. The averaged value is low because, in many of the analyses, Er concentrations are below the detection limit.

for the Topsham sample that of petscheckite (PDF file 29-1426) reveals a strong correlation (Table 3). Finally, an extraneous peak that cannot be attributed to either of the above phases is observed at $d_{\text{obs}} = 3.584 \text{ \AA}$. A comparison of the X-ray data for the Topsham material to that for an FeNbO_4 oxide (PDF file 15-0019) reveals a strong correlation with this phase as well (Table 3). Thus, FeNbO_4 also may be present as an additional subordinate phase. Why these samples recrystallized to several phases rather than simply to a samarskite structure remains unclear.

POLYCRASE-(Y)

One sample of polycrase-(Y), a euxenite-group mineral, was identified from the Stand Pipe Hill location (SPH-2). The general formula for minerals of the euxenite group of Nb-Ta-Ti oxides is AB_2O_6 , in which A represents Y, REE, Fe^{2+} , Mn, Ca, Th, U, Pb and Sc, and B represents Nb, Ta, Ti, Fe^{3+} , W, Sn and Zr (Ewing 1976). The dominant cation at the B site is Nb in euxenite-(Y), Ta in tanteuxenite-(Y), and Ti in polycrase-(Y). Complicating the classification of euxenite-group minerals is their close chemical and structural relationship to aeschynite-group minerals (Černý & Ercit 1989). Aeschynite-group minerals [including aeschynite-(Ce), aeschynite-(Y), "priorite", and "blomstrandine"] have the same general AB_2O_6 formula as euxenite-group minerals. In most aeschynite-group minerals, Ti is the dominant B-site cation, and LREE are the dominant A-site cations. Thus in the older literature, "aeschynite" typically refers to aeschynite-(Ce). "Priorite" and "blomstrandine" are the names previously applied to the HREE-Ti-dominant

aeschynite-group minerals, and are now both considered to be equivalent to aeschynite-(Y). "Blomstrandine" was considered to be a Ti-rich variety of "priorite" (Komkov 1963). Thus, aeschynite-(Y), "blomstrandine" and "priorite" are all chemically equivalent to the euxenite-group mineral polycrase-(Y).

On the basis of a canonical discrimination analysis, Ewing (1976) suggested that the sum of the uranium oxides ("U") and ThO_2 may be critical in distinguishing "euxenite" [euxenite-(Y)] from "priorite" [aeschynite-(Y)]. Hanson *et al.* (1992) suggested that, by inference, this sum may be used to distinguish between polycrase-(Y) (a euxenite-group mineral) and aeschynite-(Y). Thus, if the sum of the uranium oxides ("U") is greater than ThO_2 , the mineral should be named polycrase-(Y), whereas if the sum of the uranium oxides ("U") is less than ThO_2 , the nomenclature is ambiguous.

Analytical results: polycrase-(Y) from the Topsham suite

The average result of ten analyses is given in Table 1, and the calculated chemical formula, in Table 4. The low analytical total is attributed to the presence of adsorbed molecular water, a common feature of metamict minerals (Ewing 1975a). The polycrase-(Y) formula was calculated on the basis of six atoms of oxygen. All FeO was converted to Fe_2O_3 , yet the total cations still significantly exceed three atoms per formula unit. For this reason, UO_2 was converted to the more oxidized U_3O_8 . This procedure yielded a sum of 3.041 atoms. Such a mixed oxidation state for uranium appears to be common in euxenite-group minerals.

TABLE 3. X-RAY DATA FOR HEATED ISHIKAWAITE,
HEATED SAMARSKITE-(Y), HEATED PETSCHCKITE,
AND FeNbO₄

Topsham Ishikawaite		Hi-T Samarskite-(Y) Sugitani <i>et al.</i> (1985)		Petscheckite PDF file 29-1426			FeNbO ₄ , PDF file 15-0019			
d _{obs}	I	hkl	d _{obs}	I	hkl	d _{obs}	I	hkl	d _{obs}	I
10.911	5									
9.780	8	010	9.927	15						
5.511	3									
4.007	35				001	4.020	100	030	4.58	10
								101	3.740	10
3.675	25	120	3.719	20				031	3.580	100
3.584	25									
		030	3.291	10						
3.172	65				110	3.210	100			
3.040	100	-121	3.098	100						
2.928	100	121	2.961	100				131	2.907	100
2.802	20	200	2.815	20				002	2.806	
								012	2.759	20
2.687	5	210	2.715	5						
2.570	25	002	2.611	25						
		-201	2.511	5						
2.494	35	040	2.478	20	111	2.510	80	200	2.497	100
2.463	15	220	2.440	10				102	2.446	60
2.423	15									
2.338	5	112	2.249	5				060	2.322	60
								230	2.196	40
2.169	10	-112	2.189	10				132	2.162	60
		230	2.141	10						
2.123	5		2.114	10						
		122	2.089	10						
2.072	10	032	2.050	5				231	2.045	60
2.011	5	-202	1.980	5	002	2.010	20	142	2.015	40
								161	1.973	40
1.893	25				211	1.861	20	202	1.864	60
1.837	35	202	1.853	25	300	1.850	30			
1.816	10	-241	1.780	5				062	1.788	60
1.750	15	320	1.754	10						
		222	1.735	10						
		241	1.723	5						
1.716	10									
1.698	25				112	1.697	40			
1.671	10									
		060	1.654	10						
1.637	10									
1.592	5	-123	1.603	15						
1.584	10									
		123	1.547	15						
1.529	15									
1.511	10							113	1.512	
1.487	5	242	1.484	10	221	1.492	20	310	1.495	
1.464	25							222	1.437	
		203	1.439	5	311	1.437	20	023	1.434	
1.433	10							311	1.432	
								132	1.427	
								040	1.404	
								231	1.400	
1.388	5									
1.366	5									
					302	1.360	10			
					103	1.307	10			
								041	1.352	
					410	1.212	10			
					411	1.161	10			

TABLE 4. CHEMICAL FORMULA OF POLYCRASE-(Y) SPH-2, TOPSHAM DISTRICT, MAINE

Nb	0.553	Th	0.074	Sm	0.007	Er	0.032	Ca	0.191
Ta	0.043	U	0.274	Eu		Tm		Sc	0.011
Ti	1.205	La		Gd	0.022	Yb	0.036	Pb	0.017
Sn	0.002	Ce	0.003	Tb	0.003	Lu	0.007	Fe ²⁺	
Fe ³⁺	0.120	Pr	0.001	Dy	0.036	Y	0.351	Mg	0.004
W	0.004	Nd	0.009	Ho	0.010	Mn	0.020	Na	0.006
Sum B	1.927							Sum A	1.114

The proportion of cations (in *apfu*, atoms per formula unit) is based on six atoms of oxygen.

TABLE 5. AVERAGE CHEMICAL FORMULA OF COLUMBITE C2Q, TOPSHAM DISTRICT, MAINE

Nb <i>apfu</i>	1.711	Tm	0.001	Sc	0.107
Ta	0.136	Yb	0.001	Sn	0.002
Ti	0.124	Lu	0.001	W	0.004
		Y	0.005	Fe ³⁺	0.072
Sum M	1.971	Mn	0.164	Fe ²⁺	0.642
		Zr	0.001	Mg	0.028
				Sum A	1.029

The proportion of cations (in *apfu*, atoms per formula unit) is based on six atoms of oxygen.

Hanson *et al.* (1992) suggested that the uranium oxide in polycrase-(Y) and aeschynite-(Y) from Trout Creek Pass, Colorado is U₃O₈. In this sample, U₃O₈ is significantly more abundant than ThO₂, which leads to the identification of the sample as polycrase-(Y).

The dominant cation at the B site is Ti (Fig. 2). Occupancy of the A site is dominated by REE + Y, with U + Th only slightly less abundant. The amount of Ca is also fairly high, suggesting that these samples may have undergone early alteration. A chondrite-normalized plot shows that the HREE are enriched in excess of two orders of magnitude over the LREE (Fig. 4). The polycrase-(Y) sample is also enriched in the HREE relative to ishkawaite.

X-ray diffractometry

The analyzed polycrase-(Y) sample is metamict, and was recrystallized prior to X-ray-diffraction analysis under the same conditions as ishkawaite. The X-ray pattern for this sample is difficult to interpret because, like ishkawaite, the sample recrystallized to several component oxides. These phases include petscheckite, niobian rutile and either polycrase-(Y) or aeschynite-(Y). Because of the considerable overlap in the peaks, it is difficult to determine if this last phase has an aeschynite-(Y) or a polycrase-(Y) (euxenite) type of structure. However, the chemical composition suggests that it is polycrase-(Y) rather than aeschynite-(Y).

FERROCOLUMBITE

Columbite occurs at many locations in the Topsham district (King & Foord 1994), but only one sample (C2Q) from the Consolidated Number 2 Quarry was analyzed in this study. An average result of 15 analyses of this sample is given in Table 1, and the chemical formula is reported in Table 5, calculated on the basis of six atoms of oxygen. Iron was partitioned to yield a total of three cations per formula unit. Fe is found to be the dominant cation at the A site; thus the sample is ferrocolumbite.

DISCUSSION

On the basis of a single analysis by Lane (1937), King & Foord (1994) reported that all occurrences of Nb-Ta-Ti oxide from the Topsham pegmatite district consist of samarskite-(Y). Quantitative electron-microprobe analyses and X-ray-diffraction data have shown that the oxide mineralogy of this district is more complex. The fact that all analyzed specimens have U + Th greater than REE + Y and recrystallize to a high-T samarskite structure leads to their classification as ishkawaite rather than samarskite-(Y). It should be noted that in the original analysis, Lane (1937) reported REE + Y > U + Th, thus it is correctly identified as samarskite-(Y). It is impossible to evaluate whether the mineral analyzed is samarskite-(Y) or if results of this analysis are in error, as the bulk sample analyzed may have contained inclusions of other phases. Ishkawaite samples from the Yedlin Location, Russell Brothers Quarry, and Stand Pipe Hill are all similar. They all show considerable overlap in the B-site cations and have a similar A-site occupancy, with U + Th only slightly greater than REE + Y. All have Fe³⁺ as the third most abundant element at the A site. Samples from the Swamp No. 1 Quarry are slightly different, as the B site has slightly less Ti than the others, and the A-site occupancy exhibits a significant enrichment in U + Th over REE + Y. In addition, Fe²⁺ rather than Fe³⁺ is the third most abundant element at the A site. Although both S1Q samples have a similar ratio of U + Th to REE + Y, one of the specimens (S1Q-1) is more enriched in Ca. This Ca enrichment, coupled with the low oxide and cation totals, may indicate that the sample underwent early alteration and thus, does not represent the original chemistry of the sample. Thus, it is likely that sample S1Q-2 more accurately represents the original composition of ishkawaite at this location.

A surprising discovery was that although one sample from Stand Pipe Hill is ishkawaite (SPH-1), polycrase-(Y) (SPH-2) also occurs at this location. In addition, the sample collected from the Consolidated No. 2 Quarry is ferrocolumbite; it is not known if any REE-bearing Nb-Ta-Ti oxides occur at this locality. In conclusion, samarskite-(Y), a mineral considered to commonly occur in the Topsham district, was notably absent from all of the locations studied.

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