

Article

Non-Metamict Aeschynite-(Y), Polycrase-(Y), and Samarskite-(Y) in NYF Pegmatites from Arvogno, Vigezzo Valley (Central Alps, Italy)

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Abstract: At Arvogno, Vigezzo valley in the Central Alps, Italy, pegmatite dikes are unique in the scenario of a tertiary alpine pegmatite field because they show marked geochemical and mineralogical niobium–yttrium–fluorine features. These pegmatites contain AB_2O_6 aeschynite group minerals and ABX_2O_8 euxenite group minerals as typical accessory minerals including aeschynite-(Y), polycrase-(Y), and samarskite-(Y). They are associated with additional typical minerals such as fluorite, Y-dominant silicates, and xenotime-(Y). The Y–Nb–Ti–Ta AB_2O_6 and ABX_2O_8 oxides at the Arvogno pegmatites did not exhibit any textural and compositional features of oxidation or weathering. They are characterized by low self-radiation-induced structural damage, leading to the acquisition of unit-cell data for aeschynite-(Y), polycrase-(Y), and samarskite-(Y) by single-crystal X-ray diffraction. Aeschynite-(Y) and polycrase-(Y) crystals allowed for both to provide space groups whereas samarskite-(Y) was the first crystal from pegmatites for which cell-data were obtained at room temperature but did not allow for the accurate determination of the space group. According to the chemical compositions defined by Ti-dominant content at the B-site, the cell parameters, respectively, corresponded to polycrase-(Y), aeschynite-(Y), and the monoclinic cell of samarskite-(Y). Emplacement of Alpine pegmatites can be related to the progressive regional metamorphic rejuvenation from east to west in the Central Alps, considering the progressive cooling of the thermal Lepontine Barrovian metamorphic dome. Previous studies considered magmatic pulses that led to emplace the pegmatite field in the Central Alps. As an example, the pegmatites that intruded the Bergell massif were aged at 28–25 millions of years or younger, around 20–22 m.y.

Keywords: aeschynite-(Y); Arvogno; Central Alps; euxenite-(Y); NYF pegmatites; polycrase-(Y); samarskite-(Y); Vigezzo valley

1. Introduction

Complex REE–Nb–Ta–Ti oxides (aeschynite-, euxenite-, and samarskite-group minerals) are uncommon but locally important accessory phases occurring typically in the NYF (niobium, yttrium, fluorine) family and REL–REE (rare-element and rare earths) class (as per the listed pegmatites of allanite-, euxenite-, and gadolinite-type by Černý and Ercit [1]). Aeschynite- and euxenite-group minerals have a general formula AB_2O_6 where the eight-fold coordinated A-site, a square antiprism, is occupied by Y, REE, Ca, U, Th, Fe, while the six-fold coordinated B-site has a typical octahedra to form double chains in a zigzag pattern along the *b*-axis [2] occupied by Ti, Nb, Ta. and W. Aeschynite-group

minerals (AGMs) and euxenite-group minerals (EGMs) are orthorhombic, but the BO_6 stacking octahedra is different, leading to the $Pbnm$ space group in AGMs and to the $Pbcn$ space group in EGMs. Historically, samarskite-group minerals have the general formula ABO_4 and an $\alpha\text{-PbO}_2$ primitive structure [3,4]; Nb is dominant at the six-fold coordinated B-site, and the A-site is mostly occupied by REE, Ca, U, Fe^{2+} , and Fe^{3+} , although some studies placed Fe^{3+} in the B-site and Ti can occupy both sites [5]. The A-site in samarskite is occupied by REE, usually with a dominance of Y, but samarskite-(Yb) has also been reported [6].

Kjellmann [7] proposed a new nomenclature for samarskite-group minerals with a general formula ABC_2O_8 . Recently, a new structural investigation of non-metamict samarskite-(Y) from Laacher See, Eifel volcanic region, Germany, revealed a unique cation-ordered niobate structure related to layered, double tungstenates ABW_2O_8 by Britvin et al. [8]. These authors refined the crystal structure of samarskite-(Y) as monoclinic $P2/c$ and redefined the ideal formula to $\text{YFe}^{3+}\text{Nb}_2\text{O}_8$. The nomenclature was approved by the Commission on New Minerals, Nomenclature and Classification, International Mineralogical Association (IMA-CNMNC) and is leading to the end-member formula of samarskite-(Y), based on an ordered formula, ABX_2O_8 .

Yttrium-rare earths-oxide minerals typically contain elevated concentrations of U^{4+} and Th^{4+} and undergo self-radiation-induced structural damage leading to amorphization of formerly crystalline lattice. This crystalline-to-amorphous transition (metamictization) is followed by substantial changes of physical properties [9,10]. Such metamict phases are very prone to hydrothermal alteration, which commonly leads to substantial changes in the chemical composition of affected domains [11–15].

The Arvogno pegmatite dikes (Figure 1) are unique within the tertiary alpine pegmatite field [16,17] showing marked geochemical and mineralogical NYF features. These pegmatites contain aeschynite-(Y), polycrase-(Y), and samarskite-(Y) associated with further typical NYF minerals such as Y-rich fluorite, Y-rich spessartine, allanite-group minerals, gadolinite-(Y), and xenotime-(Y). This mineral assemblage and the chemical composition of minerals suggest that the examined pegmatites are typical examples of the NYF family enriched in Nb, Y, and other REE and F, fitting very well the definition of the NYF family [18,19].

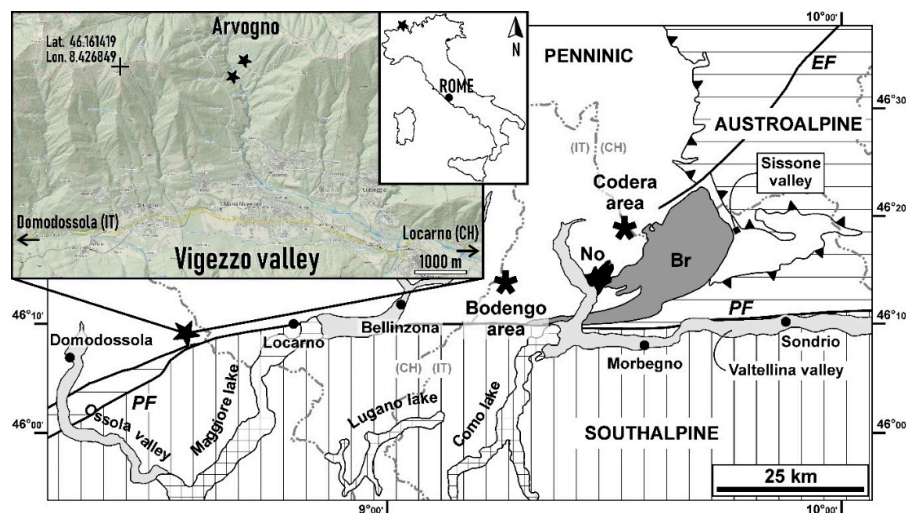


Figure 1. Simplified structural map of the Central Alps with the field of the Alpine pegmatites showing the locations of the Vigezzo, Codera, and the Bodengo areas. The thick black lines represent the Periadriatic Fault (PF), the Giudicarie Fault (GF), and the Engadine Fault (EF). The light-grey areas represent quaternary deposits along major valleys. The tertiary batholith of Bergell (Br) is in dark-grey, and the smaller, younger Novate stockwork intrusion (No) is in black. A detailed sketched map of the geographical location of the Vigezzo valley between Domodossola in Italy (IT) towards the west and Locarno in Switzerland (CH) is shown in the upper left of the figure. The location of the Arvogno pegmatites are shown with stars.

The crystal chemistry of these minerals was examined by means of EPMA analysis in the WDS (wavelength-dispersive spectrometry) mode, SEM (scanning electron microscope) in the EDS (energy-dispersive spectrometry) mode, and SCXRD (single-crystal X-ray diffraction). This study revealed that coexistent Y–Nb–Ti–Ta oxides from the Arvogno pegmatites are characterized by very low radiation damage [20–22] disregarding the rather high concentrations of U and Th, and it allowed to obtain the crystallographic determination by SCXRD at room temperature, as well as a Raman spectroscopy study for aeschynite-(Y), polycrase-(Y), and samarskite-(Y).

2. Geological Sketch

The tertiary, oligocenic, Alpine pegmatite field [16,17] is located in the Central Alps, within the SSB (Southern Steep Belt) of the Alpine nappes. It extends for ~100 km in an E–W direction and ~15 km in a N–S direction north of the Periadriatic Fault, from the Bergell massif to the east, and the Ossola valley to the west (Figure 1). The pegmatite field geographically overlaps the highest temperature domain of the Lepontine Barrovian metamorphic dome, and the zone of Alpine migmatization [23,24] indistinctly crosscutting the Alpine metamorphic nappes. The Centovalli line, an Alpine tectonic lineament considered a part of the Periadriatic Fault follows the E-striking depression of the Melezso river, developed along the Vigezzo valley, from Trontano in the Ossola valley (Italy) to the west, to Intragna, in the Maggia valley (Switzerland), to the east [25]. Along the Melezso River, Alpine nappes are vertical and locally stretched by a mylonitic deformation. These Pennine units were known as Antigorio, Pioda di Crana, Camughera, Moncucco, Isorno, Orselina, Bosco and Monte Rosa [26,27]. The main schistosity of Vigezzo and Centovalli valleys is characterized by a subhorizontal stretching lineation and dextral shear developed under amphibolite facies conditions. Many brittle structures, partly related to hydrothermal processes, also occur. They belong to mineralized faults, cataclasites, and fault breccias crosscutting the Pennine units of Vigezzo–Centovalli valleys [28] related to late-stage brittle deformation and hydrothermal processes that were active during late Alpine stage under variable P–T conditions.

3. Description of Pegmatite Dikes

Since the 1880s, the Vigezzo valley in the Central Alps, Italy, has been a classic Alpine-type locality for a number of Nb–Ti–Ta oxide minerals found in granitic pegmatites. The first alpine columbite was published by Strüver [29] from the pegmatites at Cravegna, Vigezzo valley. Zambonini [30,31] described in the pegmatites at Piano dei Lavonchi, Vigezzo valley, two new minerals, strüverite, renamed as a variety of Ta-rich rutile, and delorenzite, later redefined by De Pol and Minutti [32] as tanteuxenite-(Y). Roggiani [33] identified tapiolite at Piano dei Lavonchi and Albertini and Andersen [34] studied several Y–Nb–Ta–Ti oxides occurring at the “Bosco” pegmatite and described aeschynite-(Y), polycrase-(Y), and euxenite-(Y) in assemblage with gadolinite-(Y), monazite-(Ce), and xenotime-(Y).

The “Bosco” and “Fiume” dikes are located near the village of Arvogno, Vigezzo valley, were discovered and mined in the 1980s by local mineral collectors for rare REE–Nb–Ti–Ta oxides, phosphates, and silicate minerals [35]. The studied NYF pegmatites crosscut medium-grained two-mica orthogneiss, which belongs to the Pioda di Crana Lepontine nappe [36].

The “Fiume” pegmatite dike outcrops in the Melezso River for ~20 meters in length, up to 1 meter in width and shows straight contacts with the orthogneiss. It is pervaded by a set of late-stage brittle fractures respect to the orthogneiss foliation, and developed from the hosting rock throughout the pegmatite. The internal structure of the pegmatite consists of a fine-grained border-wall unit composed of K-feldspar, plagioclase, and quartz, a medium-grained intermediate unit composed of perthite K-feldspar, flakes of silvery-green muscovite, dark-brown platy crystals of siderophyllite-annite, albite, and quartz. Black nodules or crystals of AGMs and EGMs, up to two centimeters in diameter, exhibit conchoidal fractures. Black magnetite grains occasionally occur within this portion of the dike and within the host orthogneiss. The coarse-grained core zone is composed of white perthite K-feldspar, smoky quartz, and lamellar albite, cleavelandite variety [16]. This unit contains several

accessory minerals such as centimetric masses of orange yttrian–spessartine, massive pale-green and violet yttrian–fluorite. The core of the pegmatite hosts AGMs and EGMs, allanite-(Y), bismuthinite, monazite-(Ce), pyrophanite, titanite, uraninite, xenotime-(Y), and zircon as well. Secondary cavities in the core zone, formed after fluorite dissolution, are lined with albite, allanite-(Ce), microlite, pyrochlore, and rarely gadolinite-(Y), and late-stage minerals such as bavenite and milarite. The pegmatite also contains rare galena nodules associated with platy wulfenite crystals.

The “Bosco” pegmatite outcrops for 4–5 m and has 3–4 m in thickness. The dike has a decimetric coarse-grained border-wall zone composed of white K-feldspar, albite, brown quartz with rare accessory minerals including allanite-(Y), bismuthinite, magnetite, yttrian–spessartine, and thorium–monazite-(Ce). The hanging wall of the pegmatite in contact with the orthogneiss shows a lobate structure. The border zone, in the upper portion (upper end) of the dike, hosts albite, aeschynite-(Y), polycrase-(Y), xenotime-(Y) allanite-(Ce), yttrian–fluorapatite, zircon, and secondary cavities formed by the dissolution of yttrian–fluorite lined with gadolinite-(Y) and titanite [17]. The coarse-grained core zone is composed of euhedral pinkish to whitish perthite K-feldspar, brownish to colorless large masses of quartz and dark brown-black platy crystals of siderophyllite–annite, which host centimetric black granular masses of samarskite-(Y).

4. Analytical Methods and Terminology of REE

4.1. Wavelength-Dispersive Spectroscopy (WDS)

Chemical compositions of complex REE–Nb–Ta–Ti oxides were obtained from carbon-coated polished sections by means of an electron probe microanalyzer (EPMA) Cameca SX 100 (CAMECA, Gennevilliers Cedex, France) using the wavelength-dispersion mode (WDS). The following analytical conditions were applied: accelerating voltage 15 kV, beam diameter 5 μ m, beam current 40 nA, and counting times 20 s for Nb, Ta, Ti, Ca, Y and 30–60 s for the other elements. The following standards and lines were used: Ti (K_{α})—anatase (Hardargervida); Nb (L_{α}), Fe (K_{α})—columbite-(Fe) (Ivigtut); Ta (M_{α})—CrTa₂O₆; Mn (K_{α})—Mn₂SiO₄; Ca (K_{α})—wollastonite, W (M_{β})—CaWO₄; Na (K_{α})—albite (Amelia mine); P (K_{α})—Ca₅(PO₄)₃F; K, Al, Si (K_{α})—sanidine (Eifel); Mg (K_{α})—Mg₂SiO₄; As (L_{α})—lammerite (Guanaco), Y (L_{α})—YAG; Sn (L_{α})—SnO₂; U (M_{β})—U; Th (M_{α})—CaTh(PO₄)₂; Sc (K_{α})—ScVO₄; Pb (M_{α})—vanadinite (Mibladen); Zr (L_{α})—ZrSiO₄; La, Ce, Er, Yb (L_{α}); Pr, Nd, Sm, Gd, Dy, (L_{β})—La–Lu orthophosphates. Data were reduced using Correction for Quantitative Electron Probe Microanalysis [37]. Based on the counting statistics, the measurement error expressed as 2 σ was approximately <1 rel. % for concentrations around 20 wt.% and ~8 rel. % for concentrations around 1 wt.%. An empirically determined correction factor was applied to the coincidence of Ce M_{β} 2nd-order of Dy M_{β} and 3rd-order Y L_{β} with the F K_{α} line, Ce L_{γ} with the Gd L_{α} line, Tb L_{β} with the Er L_{α} line, Sm L_{γ} with the Tm L_{α} , and Tb $L_{\beta 2}$ with the Yb L_{α} line. In addition MgO, Al₂O₃, P₂O₅, K₂O, PbO₂, La₂O₃, and Pr₂O₃ resulted in below detection limits of EPMA (~0.05 wt.%).

Empirical formulae of aeschynite-(Y) and polycrase-(Y) were calculated assuming the sum of all cations = 3 (Table 1). The empirical formula of samarskite-(Y) was calculated on the basis of a six-fold coordinated X-site = 2 (Table 2). Based on the charge balance and the structural investigation by Britvin et al. [8], Fe is considered as trivalent and Mn as divalent.

Table 1. Representative chemical compositions (in wt.%) and mineral formulae (in apfu) of aeschynite-(Y) and polycrase-(Y) from Bosco and Fiume pegmatites at Arvogno.

Sample	Bosco1										Bosco2									
Analyses	64/1	65/1	66/1	67/1	68/1	69/1	70/1	27/1	28/1	29/1	30/1	31/1	32/1	33/1	34/1	35/1	36/1	37/1	38/1	
Mineral	A-(Y)	A-(Y)	A-(Y)	A-(Y)	A-(Y)	A-(Y)	A-(Y)	A-(Y)	A-(Y)	A-(Y)	A-(Y)	A-(Y)	A-(Y)	A-(Y)	A-(Y)	A-(Y)	A-(Y)	A-(Y)	A-(Y)	
WO ₃ (wt.%)	2.29	2.33	2.21	2.49	3.33	3.65	3.28	1.58	1.82	1.43	1.33	1.07	0.68	0.67	1.47	1.72	1.62	1.21	0.95	
Nb ₂ O ₅	11.6	11.5	12.0	12.4	13.4	13.7	12.7	20.4	21.0	21.2	20.2	21.8	22.2	21.9	20.9	21.0	20.4	21.7	22.0	
Ta ₂ O ₅	19.62	19.84	18.92	16.03	12.46	9.57	9.36	9.11	9.58	10.67	11.35	9.90	10.02	10.04	9.58	9.46	8.89	9.58	9.56	
SiO ₂	0.10	0.12	0.11	0.12	0.11	0.14	0.12	0.13	0.15	0.11	0.14	0.13	0.12	0.11	0.13	0.13	0.13	0.13	0.13	
TiO ₂	28.4	28.0	27.8	29.3	31.1	31.4	32.7	27.2	27.0	26.4	26.4	24.8	23.6	23.6	26.2	27.1	27.6	25.2	24.7	
ThO ₂	4.83	4.79	5.91	5.70	4.77	7.64	5.89	3.30	3.14	3.40	3.41	2.50	2.98	3.01	3.46	3.17	3.07	2.82	2.98	
UO ₂	2.37	2.37	2.73	3.20	3.44	4.22	4.52	7.68	6.13	6.19	6.67	9.58	10.24	10.39	6.34	6.22	7.46	8.89	9.01	
Sc ₂ O ₃	0.00	0.00	0.00	0.00	0.05	0.00	0.00	0.08	0.08	0.08	0.10	0.06	0.08	0.07	0.10	0.09	0.06	0.07	0.07	
FeOtot	0.82	0.84	0.88	0.85	0.71	0.80	0.55	0.86	0.88	0.93	0.90	1.31	1.83	1.88	0.90	0.86	0.86	1.11	1.47	
Y ₂ O ₃	21.1	20.7	20.3	21.1	22.3	20.2	21.8	21.2	21.8	20.7	20.5	18.3	16.9	16.9	20.7	21.2	21.2	18.8	18.2	
Ce ₂ O ₃	0.42	0.40	0.38	0.35	0.36	0.28	0.29	0.15	0.17	0.12	0.13	0.00	0.18	0.14	0.12	0.14	0.00	0.15	0.18	
Nd ₂ O ₃	0.85	1.04	0.76	0.71	0.55	0.61	0.49	0.16	0.17	0.19	0.30	0.32	0.31	0.36	0.25	0.00	0.15	0.21	0.29	
Sm ₂ O ₃	1.09	1.14	0.97	0.80	0.66	0.79	0.58	0.26	0.40	0.46	0.50	0.54	0.62	0.62	0.47	0.37	0.30	0.46	0.48	
Gd ₂ O ₃	2.33	2.48	2.32	2.20	1.99	2.00	1.88	1.54	1.83	1.97	2.10	2.31	2.28	2.38	1.99	1.84	1.59	1.96	2.10	
Tb ₂ O ₃	0.35	0.37	0.32	0.33	0.30	0.31	0.29	0.23	0.29	0.34	0.35	0.39	0.36	0.40	0.32	0.30	0.26	0.33	0.34	
Dy ₂ O ₃	2.23	2.28	2.20	2.15	2.18	2.24	2.13	2.04	2.21	2.52	2.52	2.93	2.91	2.80	2.31	2.14	2.02	2.45	2.68	
Ho ₂ O ₃	0.26	0.27	0.37	0.27	0.37	0.29	0.34	0.33	0.38	0.38	0.45	0.43	0.54	0.39	0.37	0.39	0.39	0.39	0.43	
Er ₂ O ₃	1.02	1.09	1.05	1.10	1.24	1.22	1.31	1.45	1.43	1.51	1.56	1.76	1.76	1.75	1.41	1.44	1.40	1.62	1.66	
Tm ₂ O ₃	0.47	0.49	0.46	0.41	0.40	0.35	0.38	0.39	0.38	0.41	0.45	0.46	0.44	0.44	0.37	0.40	0.40	0.42	0.43	
Yb ₂ O ₃	0.92	0.96	0.99	0.98	1.16	1.11	1.37	1.60	1.53	1.57	1.54	1.76	1.75	1.74	1.38	1.52	1.68	1.72	1.74	
Lu ₂ O ₃	0.16	0.09	0.15	0.05	0.08	0.01	0.05	0.09	0.14	0.13	0.15	0.05	0.10	0.12	0.10	0.14	0.15	0.11	0.14	
CaO	0.34	0.35	0.33	0.26	0.26	0.28	0.24	0.14	0.14	0.16	0.15	0.26	0.22	0.25	0.14	0.10	0.11	0.15	0.18	
MnO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.06	0.06	0.00	0.00	0.13	0.16	0.00	0.06	0.00	0.00	0.10	
F	0.16	0.18	0.16	0.14	0.00	0.00	0.00	0.00	0.00	0.00	0.12	0.00	0.00	0.00	0.00	0.10	0.11	0.00	0.00	
Total	101.7	101.6	101.3	101.0	101.2	100.9	100.3	99.9	100.7	100.8	101.3	100.6	100.2	100.1	99.0	99.8	99.8	99.4	99.8	

Table 1. Cont.

Sample	Bosco1										Bosco2									
Analyses	64/1	65/1	66/1	67/1	68/1	69/1	70/1	27/1	28/1	29/1	30/1	31/1	32/1	33/1	34/1	35/1	36/1	37/1	38/1	
Mineral	A-(Y)	A-(Y)	A-(Y)	A-(Y)	A-(Y)	A-(Y)	A-(Y)	A-(Y)	A-(Y)	A-(Y)	A-(Y)	A-(Y)	A-(Y)	A-(Y)	A-(Y)	A-(Y)	A-(Y)	A-(Y)	A-(Y)	
W ⁶⁺ (apfu)	0.037	0.037	0.036	0.040	0.052	0.057	0.051	0.025	0.028	0.022	0.021	0.017	0.011	0.011	0.023	0.027	0.025	0.020	0.015	
Nb ⁵⁺	0.322	0.323	0.338	0.345	0.361	0.375	0.345	0.562	0.573	0.581	0.558	0.613	0.633	0.627	0.581	0.576	0.562	0.610	0.621	
Ta ⁵⁺	0.329	0.335	0.321	0.268	0.203	0.157	0.153	0.151	0.157	0.176	0.188	0.167	0.172	0.173	0.160	0.156	0.147	0.162	0.162	
Si ⁴⁺	0.006	0.007	0.007	0.007	0.007	0.009	0.007	0.008	0.009	0.007	0.008	0.008	0.008	0.007	0.008	0.008	0.008	0.008	0.008	
Ti ⁴⁺	1.319	1.306	1.303	1.354	1.403	1.427	1.477	1.248	1.223	1.205	1.211	1.158	1.120	1.123	1.215	1.236	1.261	1.179	1.158	
subtot.	2.013	2.008	2.005	2.014	2.026	2.025	2.033	1.994	1.990	1.991	1.986	1.963	1.944	1.941	1.987	2.003	2.002	1.979	1.964	
Th ⁴⁺	0.068	0.068	0.084	0.080	0.065	0.105	0.080	0.046	0.043	0.047	0.047	0.035	0.043	0.043	0.049	0.044	0.043	0.040	0.042	
U ⁴⁺	0.032	0.033	0.038	0.044	0.046	0.057	0.060	0.104	0.082	0.084	0.090	0.133	0.144	0.146	0.087	0.084	0.101	0.123	0.125	
Fe ³⁺	0.042	0.044	0.046	0.044	0.035	0.040	0.028	0.044	0.045	0.047	0.046	0.068	0.097	0.099	0.046	0.044	0.044	0.058	0.077	
Sc ³⁺	0.000	0.000	0.000	0.000	0.003	0.000	0.000	0.004	0.004	0.004	0.005	0.003	0.004	0.004	0.005	0.005	0.003	0.004	0.004	
Y ³⁺	0.693	0.684	0.674	0.690	0.710	0.650	0.697	0.687	0.701	0.670	0.665	0.604	0.569	0.569	0.677	0.686	0.685	0.622	0.606	
Ce ³⁺	0.009	0.009	0.008	0.008	0.008	0.006	0.006	0.003	0.004	0.003	0.003	0.000	0.004	0.003	0.003	0.003	0.000	0.003	0.004	
Nd ³⁺	0.019	0.023	0.017	0.016	0.012	0.013	0.010	0.004	0.004	0.004	0.007	0.007	0.007	0.008	0.006	0.000	0.003	0.005	0.007	
Sm ³⁺	0.023	0.024	0.021	0.017	0.014	0.016	0.012	0.005	0.008	0.010	0.011	0.012	0.013	0.013	0.010	0.008	0.006	0.010	0.010	
Gd ³⁺	0.048	0.051	0.048	0.045	0.039	0.040	0.037	0.031	0.037	0.040	0.042	0.048	0.048	0.050	0.041	0.037	0.032	0.040	0.043	
Tb ³⁺	0.007	0.008	0.007	0.007	0.006	0.006	0.006	0.005	0.006	0.007	0.007	0.008	0.008	0.008	0.007	0.006	0.005	0.007	0.007	
Dy ³⁺	0.044	0.046	0.044	0.043	0.042	0.044	0.041	0.040	0.043	0.049	0.049	0.059	0.059	0.057	0.046	0.042	0.040	0.049	0.054	
Ho ³⁺	0.005	0.005	0.007	0.005	0.007	0.006	0.006	0.006	0.007	0.007	0.009	0.009	0.011	0.008	0.007	0.008	0.008	0.008	0.009	
Er ³⁺	0.020	0.021	0.020	0.021	0.023	0.023	0.025	0.028	0.027	0.029	0.030	0.034	0.035	0.035	0.027	0.027	0.027	0.032	0.033	
Tm ³⁺	0.009	0.009	0.009	0.008	0.007	0.007	0.007	0.007	0.007	0.008	0.009	0.009	0.009	0.009	0.007	0.008	0.008	0.008	0.008	
Yb ³⁺	0.017	0.018	0.019	0.018	0.021	0.020	0.025	0.030	0.028	0.029	0.029	0.033	0.034	0.034	0.026	0.028	0.031	0.033	0.033	
Lu ³⁺	0.003	0.002	0.003	0.001	0.001	0.000	0.001	0.002	0.002	0.002	0.003	0.001	0.002	0.002	0.002	0.003	0.003	0.002	0.003	
Ca ²⁺	0.022	0.023	0.022	0.017	0.016	0.018	0.015	0.009	0.009	0.011	0.010	0.017	0.015	0.017	0.009	0.006	0.007	0.010	0.012	
Mn ²⁺	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.003	0.003	0.000	0.000	0.007	0.008	0.000	0.003	0.000	0.000	0.005	
subtot.	1.061	1.067	1.067	1.063	1.054	1.050	1.056	1.056	1.061	1.054	1.061	1.080	1.109	1.114	1.055	1.042	1.047	1.053	1.082	
F ⁻	0.030	0.034	0.030	0.027	0.000	0.000	0.000	0.000	0.000	0.000	0.022	0.000	0.000	0.000	0.000	0.020	0.021	0.000	0.000	
O ²⁻	5.984	5.983	5.988	5.987	5.997	6.000	5.998	6.001	5.997	5.999	5.988	5.995	5.998	5.996	5.999	5.989	5.990	6.000	5.995	
REE + Sc + Y	0.87	0.87	0.85	0.85	0.87	0.81	0.85	0.83	0.86	0.84	0.85	0.81	0.79	0.78	0.84	0.84	0.83	0.81	0.80	
U/(Th + U)	0.32	0.33	0.31	0.35	0.41	0.35	0.43	0.69	0.66	0.64	0.66	0.79	0.77	0.77	0.64	0.66	0.70	0.75	0.75	
Nd/Yb	1.04	1.22	0.86	0.81	0.54	0.62	0.41	0.12	0.12	0.14	0.22	0.20	0.19	0.23	0.21		0.10	0.14	0.19	
Ta/(Nb + Ta)	0.50	0.51	0.49	0.44	0.36	0.30	0.31	0.21	0.22	0.23	0.25	0.21	0.21	0.22	0.22	0.21	0.21	0.21	0.21	
CV1	6.40	6.30	6.07	6.36	6.86	6.63	7.02	5.53	5.67	5.45	5.53	4.81	4.29	4.26	5.24	5.48	5.56	4.82	4.65	
CV2	-2.95	-2.92	-2.78	-2.78	-2.95	-2.53	-2.63	-2.86	-3.21	-3.09	-3.12	-2.88	-2.80	-2.78	-2.74	-2.87	-2.81	-2.61	-2.78	

Table 1. Cont.

	Bosco2					Bosco4					Fiume1								
#Analyses	39/1	40/1	41/1	42/1	17/1	18/1	19/1	20/1	21/1	1/1	3/1	4/1	5/1	6/1	7/1	8/1	9/1	10/1	11/1
Mineral	A-(Y)	A-(Y)	A-(Y)	A-(Y)	P-(Y)	P-(Y)	P-(Y)	P-(Y)	P-(Y)	P-(Y)	P-(Y)	P-(Y)	P-(Y)	P-(Y)	P-(Y)	P-(Y)	P-(Y)	P-(Y)	P-(Y)
WO ₃ (wt.%)	1.11	0.88	0.75	0.70	0.63	0.59	0.64	0.58	0.65	0.52	0.57	0.59	0.53	0.54	0.50	0.53	0.49	0.43	0.47
Nb ₂ O ₅	21.7	22.1	22.2	22.2	18.0	17.8	17.3	18.3	18.4	21.7	22.1	19.3	20.0	18.9	18.5	15.2	15.0	20.0	15.2
Ta ₂ O ₅	9.61	9.76	10.04	9.86	23.9	23.7	23.5	24.0	24.0	15.8	15.8	16.2	16.5	17.6	17.7	18.4	18.5	16.4	18.7
SiO ₂	0.12	0.12	0.13	0.12	0.11	0.12	0.14	0.12	0.13	0.13	0.14	0.12	0.12	0.11	0.12	0.12	0.12	0.14	0.13
TiO ₂	24.8	24.2	23.5	23.5	19.9	19.9	20.3	19.7	19.9	21.5	21.4	24.6	22.9	22.8	22.9	24.0	24.0	23.1	24.3
ThO ₂	2.93	2.86	3.04	3.06	3.00	3.02	3.25	2.77	2.88	3.77	3.72	2.95	2.53	3.51	3.63	3.59	3.58	3.61	3.48
UO ₂	8.81	9.52	10.08	10.14	4.90	5.29	5.37	4.35	4.67	3.79	3.88	6.20	6.70	6.72	6.90	9.06	8.98	6.01	9.42
Sc ₂ O ₃	0.07	0.07	0.06	0.07	0.35	0.35	0.32	0.33	0.32	0.05	0.00	0.00	0.00	0.00	0.06	0.00	0.00	0.00	0.00
FeOt _{tot}	1.38	1.50	1.83	1.89	1.45	1.59	1.51	1.58	1.56	1.66	1.66	0.80	1.26	1.38	1.45	1.18	1.16	1.27	1.21
Y ₂ O ₃	18.7	18.0	16.8	16.8	17.4	17.3	17.2	17.8	17.8	18.4	18.4	19.2	17.6	17.1	17.2	15.9	15.8	17.6	15.8
Ce ₂ O ₃	0.14	0.21	0.00	0.16	0.23	0.21	0.19	0.22	0.19	0.20	0.20	0.13	0.18	0.19	0.19	0.15	0.12	0.22	0.19
Nd ₂ O ₃	0.29	0.25	0.34	0.32	0.45	0.48	0.50	0.42	0.46	0.42	0.45	0.16	0.36	0.47	0.40	0.37	0.41	0.41	0.37
Sm ₂ O ₃	0.51	0.49	0.60	0.61	0.72	0.78	0.75	0.71	0.79	0.75	0.75	0.44	0.66	0.75	0.70	0.65	0.62	0.72	0.70
Gd ₂ O ₃	2.07	2.07	2.35	2.32	2.00	1.99	2.01	2.04	1.92	2.22	2.27	1.98	2.35	2.26	2.23	2.17	2.19	2.25	2.27
Tb ₂ O ₃	0.35	0.32	0.39	0.39	0.36	0.33	0.34	0.33	0.33	0.43	0.40	0.35	0.41	0.43	0.39	0.36	0.35	0.40	0.44
Dy ₂ O ₃	2.58	2.64	2.91	2.89	2.20	2.19	2.25	2.24	2.21	2.72	2.73	2.74	3.02	2.95	2.85	2.78	2.72	2.97	3.00
Ho ₂ O ₃	0.34	0.49	0.45	0.52	0.29	0.30	0.30	0.28	0.29	0.37	0.33	0.40	0.38	0.34	0.37	0.39	0.36	0.45	0.41
Er ₂ O ₃	1.63	1.69	1.77	1.81	1.12	1.09	1.08	1.17	1.14	1.41	1.45	1.71	1.71	1.54	1.48	1.52	1.49	1.58	1.52
Tm ₂ O ₃	0.41	0.43	0.38	0.44	0.61	0.57	0.58	0.60	0.59	0.50	0.52	0.57	0.58	0.57	0.55	0.55	0.55	0.54	0.57
Yb ₂ O ₃	1.74	1.73	1.77	1.75	1.48	1.47	1.44	1.51	1.46	2.03	1.99	2.11	2.00	1.83	1.79	1.51	1.52	1.95	1.58
Lu ₂ O ₃	0.13	0.15	0.14	0.14	0.30	0.32	0.31	0.27	0.31	0.23	0.26	0.25	0.23	0.22	0.21	0.16	0.17	0.26	0.16
CaO	0.18	0.20	0.26	0.20	0.94	0.88	0.81	0.89	0.86	0.41	0.44	0.16	0.31	0.32	0.34	0.21	0.20	0.32	0.23
MnO	0.12	0.07	0.16	0.10	0.36	0.33	0.27	0.30	0.30	0.22	0.23	0.06	0.12	0.16	0.17	0.09	0.13	0.14	0.10
F	0.00	0.00	0.00	0.00	0.12	0.00	0.12	0.12	0.13	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	99.6	99.8	100.0	100.0	100.9	100.6	100.5	100.7	101.3	99.2	99.7	101.0	100.4	100.7	100.7	98.9	98.5	100.7	100.2

Table 1. Cont.

	Bosco2					Bosco4					Fiume1								
#Analyses	39/1	40/1	41/1	42/1	17/1	18/1	19/1	20/1	21/1	1/1	3/1	4/1	5/1	6/1	7/1	8/1	9/1	10/1	11/1
Mineral	A-(Y)	A-(Y)	A-(Y)	A-(Y)	P-(Y)	P-(Y)	P-(Y)	P-(Y)	P-(Y)	P-(Y)	P-(Y)	P-(Y)	P-(Y)	P-(Y)	P-(Y)	P-(Y)	P-(Y)	P-(Y)	P-(Y)
W ⁶⁺ (apfu)	0.018	0.014	0.012	0.012	0.011	0.010	0.011	0.010	0.011	0.009	0.009	0.010	0.009	0.009	0.008	0.009	0.008	0.007	0.008
Nb ⁵⁺	0.611	0.627	0.635	0.635	0.529	0.525	0.512	0.538	0.536	0.627	0.636	0.545	0.576	0.547	0.537	0.452	0.449	0.572	0.447
Ta ⁵⁺	0.163	0.167	0.173	0.170	0.422	0.419	0.417	0.423	0.421	0.275	0.274	0.276	0.286	0.306	0.308	0.328	0.332	0.282	0.331
Si ⁴⁺	0.008	0.008	0.008	0.008	0.007	0.008	0.009	0.008	0.008	0.008	0.009	0.008	0.007	0.007	0.007	0.008	0.008	0.009	0.009
Ti ⁴⁺	1.163	1.144	1.120	1.120	0.972	0.974	0.995	0.962	0.968	1.033	1.024	1.155	1.095	1.098	1.104	1.188	1.190	1.101	1.188
subtot.	1.963	1.960	1.948	1.945	1.941	1.936	1.944	1.941	1.944	1.952	1.951	1.994	1.973	1.967	1.964	1.985	1.987	1.971	1.983
Th ⁴⁺	0.042	0.041	0.044	0.044	0.044	0.045	0.048	0.041	0.042	0.055	0.054	0.042	0.037	0.051	0.053	0.054	0.054	0.052	0.051
U ⁴⁺	0.122	0.133	0.142	0.143	0.071	0.077	0.078	0.063	0.067	0.054	0.055	0.086	0.095	0.096	0.098	0.132	0.132	0.085	0.136
Fe ²⁺	0.072	0.079	0.097	0.100	0.079	0.087	0.082	0.086	0.084	0.089	0.088	0.042	0.067	0.074	0.077	0.065	0.064	0.067	0.066
Sc ³⁺	0.004	0.004	0.003	0.004	0.020	0.020	0.018	0.019	0.018	0.003	0.000	0.000	0.000	0.000	0.003	0.000	0.000	0.000	0.000
Y ³⁺	0.620	0.602	0.567	0.567	0.601	0.599	0.598	0.615	0.609	0.626	0.622	0.638	0.595	0.584	0.585	0.556	0.554	0.594	0.546
Ce ³⁺	0.003	0.005	0.000	0.004	0.005	0.005	0.005	0.005	0.004	0.005	0.005	0.003	0.004	0.004	0.004	0.004	0.003	0.005	0.004
Nd ³⁺	0.006	0.006	0.008	0.007	0.010	0.011	0.012	0.010	0.011	0.009	0.010	0.003	0.008	0.011	0.009	0.009	0.010	0.009	0.009
Sm ³⁺	0.011	0.011	0.013	0.013	0.016	0.017	0.017	0.016	0.018	0.016	0.016	0.010	0.015	0.016	0.016	0.015	0.014	0.016	0.016
Gd ³⁺	0.043	0.043	0.049	0.049	0.043	0.043	0.043	0.044	0.041	0.047	0.048	0.041	0.050	0.048	0.047	0.047	0.048	0.047	0.049
Tb ³⁺	0.007	0.007	0.008	0.008	0.008	0.007	0.007	0.007	0.007	0.009	0.008	0.007	0.009	0.009	0.008	0.008	0.008	0.008	0.009
Dy ³⁺	0.052	0.053	0.059	0.059	0.046	0.046	0.047	0.047	0.046	0.056	0.056	0.055	0.062	0.061	0.059	0.059	0.058	0.061	0.063
Ho ³⁺	0.007	0.010	0.009	0.011	0.006	0.006	0.006	0.006	0.006	0.008	0.007	0.008	0.008	0.007	0.008	0.008	0.008	0.009	0.008
Er ³⁺	0.032	0.033	0.035	0.036	0.023	0.022	0.022	0.024	0.023	0.028	0.029	0.034	0.034	0.031	0.030	0.031	0.031	0.031	0.031
Tm ³⁺	0.008	0.008	0.008	0.009	0.012	0.011	0.012	0.012	0.012	0.010	0.010	0.011	0.011	0.011	0.011	0.011	0.011	0.011	0.012
Yb ³⁺	0.033	0.033	0.034	0.034	0.029	0.029	0.029	0.030	0.029	0.040	0.039	0.040	0.039	0.036	0.035	0.030	0.031	0.038	0.031
Lu ³⁺	0.002	0.003	0.003	0.003	0.006	0.006	0.006	0.005	0.006	0.004	0.005	0.005	0.004	0.004	0.004	0.003	0.003	0.005	0.003
Ca ²⁺	0.012	0.013	0.017	0.013	0.065	0.061	0.056	0.062	0.059	0.028	0.030	0.011	0.021	0.022	0.024	0.015	0.014	0.022	0.016
Mn ²⁺	0.006	0.004	0.009	0.005	0.020	0.018	0.015	0.017	0.016	0.012	0.013	0.003	0.007	0.008	0.009	0.005	0.007	0.007	0.006
subtot.	1.081	1.086	1.105	1.109	1.103	1.110	1.099	1.108	1.096	1.099	1.094	1.038	1.066	1.073	1.079	1.052	1.050	1.067	1.055
F [−]	0.000	0.000	0.000	0.000	0.023	0.000	0.025	0.025	0.026	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
O ^{2−}	5.997	5.998	6.001	6.001	5.988	5.996	5.985	5.991	5.985	6.002	5.996	6.001	6.004	6.000	5.999	5.997	5.998	5.996	5.995
REE + Sc + Y	0.81	0.80	0.78	0.79	0.79	0.79	0.79	0.80	0.80	0.84	0.84	0.84	0.83	0.81	0.80	0.77	0.76	0.82	0.77
U/(Th + U)	0.75	0.76	0.76	0.76	0.61	0.63	0.62	0.61	0.61	0.50	0.50	0.67	0.72	0.65	0.65	0.71	0.71	0.62	0.73
Nd/Yb	0.19	0.16	0.21	0.20	0.34	0.36	0.39	0.31	0.35	0.23	0.25	0.08	0.21	0.29	0.25	0.28	0.30	0.24	0.26
Ta/(Nb + Ta)	0.21	0.21	0.21	0.21	0.44	0.44	0.45	0.44	0.44	0.30	0.30	0.34	0.33	0.36	0.36	0.42	0.43	0.33	0.43
CV1	4.70	4.54	4.21	4.23	3.79	3.74	3.81	3.75	3.87	4.04	4.09	5.03	4.46	4.43	4.40	4.34	4.26	4.55	4.53
CV2	−2.78	−2.76	−2.72	−2.76	−2.69	−2.67	−2.57	−2.76	−2.82	−2.91	−3.01	−2.91	−2.80	−2.75	−2.71	−1.95	−1.83	−2.84	−2.18

Note: A-(Y) = Aeschnite-(Y), P-(Y) = Polycrase-(Y); empirical formula was calculated on the basis of sum of all cations = 3.

Table 2. Representative chemical compositions (in wt.%) and mineral formulae (in apfu) of samarskite-(Y) from Bosco pegmatites at Arvogno.

Sample	Bosco3										Bosco4							
#Analyses	43/1	44/1	45/1	46/1	47/1	48/1	50/1	51/1	12/1	13/1	14/1	15/1	16/1	22/1	23/1	24/1	25/1	
Mineral	S-(Y)	S-(Y)	S-(Y)	S-(Y)	S-(Y)	S-(Y)	S-(Y)	S-(Y)	S-(Y)	S-(Y)	S-(Y)	S-(Y)	S-(Y)	S-(Y)	S-(Y)	S-(Y)	S-(Y)	
WO ₃ (wt.%)	3.32	3.37	3.43	1.61	1.45	1.49	1.59	1.64	3.14	3.66	3.50	1.94	1.63	3.34	3.62	1.93	1.82	
Nb ₂ O ₅	26.7	27.5	26.4	25.4	25.7	25.8	26.7	25.1	22.1	26.2	26.2	27.6	26.1	27.2	29.0	28.0	27.7	
Ta ₂ O ₅	25.0	24.4	25.1	25.4	24.3	24.9	25.3	25.4	32.1	25.8	25.8	20.8	27.3	24.4	21.4	20.4	22.7	
SiO ₂	0.10	0.09	0.10	0.10	0.12	0.12	0.11	0.13	0.11	0.13	0.11	0.13	0.11	0.12	0.12	0.13	0.12	
TiO ₂	3.84	3.95	3.94	5.21	6.02	6.03	4.73	6.11	3.23	3.78	3.60	6.40	4.79	3.84	4.03	5.99	5.26	
ZrO ₂	0.51	0.51	0.54	0.49	0.50	0.54	0.31	0.61	0.48	0.57	0.48	0.50	0.39	0.49	0.49	0.52	0.40	
ThO ₂	2.58	2.60	2.65	2.57	2.81	2.74	2.59	2.34	2.64	2.73	2.71	2.60	2.41	2.81	2.94	2.97	2.90	
UO ₂	3.23	3.09	3.05	4.77	5.19	4.41	4.03	3.78	2.67	2.84	3.25	5.47	3.74	3.14	3.04	5.27	5.18	
Sc ₂ O ₃	0.78	0.78	0.71	0.63	0.58	0.67	0.73	0.66	0.92	0.86	0.82	0.56	0.95	0.69	0.70	0.61	0.69	
FeOtot	8.98	8.98	8.83	9.54	9.43	9.06	9.14	9.23	8.45	8.80	8.74	9.46	9.14	8.98	9.06	9.21	9.36	
Y ₂ O ₃	11.8	12.1	12.0	11.8	11.6	12.1	12.3	12.6	12.4	12.5	11.9	11.6	12.9	11.8	11.9	11.3	11.6	
Ce ₂ O ₃	0.14	0.17	0.17	0.00	0.13	0.17	0.14	0.00	0.16	0.17	0.17	0.13	0.00	0.18	0.17	0.18	0.00	
Nd ₂ O ₃	0.39	0.43	0.37	0.28	0.36	0.29	0.30	0.30	0.36	0.43	0.44	0.37	0.26	0.45	0.48	0.41	0.38	
Sm ₂ O ₃	0.74	0.67	0.69	0.62	0.61	0.65	0.60	0.65	0.74	0.74	0.74	0.65	0.54	0.77	0.76	0.68	0.66	
Gd ₂ O ₃	1.77	1.71	1.76	1.70	1.58	1.56	1.63	1.46	1.59	1.58	1.76	1.69	1.49	1.74	1.85	1.73	1.67	
Tb ₂ O ₃	0.39	0.42	0.41	0.41	0.38	0.39	0.36	0.39	0.39	0.32	0.43	0.38	0.31	0.40	0.40	0.40	0.42	
Dy ₂ O ₃	1.95	1.81	1.87	1.83	1.87	1.67	1.77	1.75	1.66	1.84	1.89	2.01	1.57	1.91	1.94	1.87	1.89	
Ho ₂ O ₃	0.26	0.22	0.21	0.23	0.24	0.21	0.22	0.19	0.20	0.28	0.22	0.30	0.24	0.20	0.24	0.26	0.17	
Er ₂ O ₃	0.88	0.94	0.88	0.92	0.89	0.84	0.82	0.89	0.75	0.80	0.90	0.98	0.80	0.95	0.86	0.93	0.93	
Tm ₂ O ₃	0.25	0.27	0.20	0.22	0.23	0.21	0.26	0.25	0.27	0.23	0.26	0.26	0.23	0.20	0.18	0.13	0.21	
Yb ₂ O ₃	1.75	1.78	1.73	1.79	1.78	1.75	1.85	1.81	1.55	1.64	1.71	1.83	1.64	1.75	1.79	1.72	1.78	
Lu ₂ O ₃	0.29	0.28	0.28	0.36	0.29	0.30	0.32	0.41	0.37	0.28	0.33	0.25	0.32	0.32	0.26	0.20	0.24	
CaO	0.19	0.20	0.18	0.11	0.12	0.09	0.23	0.14	0.12	0.16	0.19	0.16	0.26	0.17	0.20	0.16	0.17	
MnO	1.13	1.07	1.09	0.76	0.75	0.79	0.71	0.77	1.12	1.12	1.11	0.72	0.67	1.06	1.08	0.89	0.75	
Total	97.1	97.4	96.6	96.8	96.9	96.8	96.7	96.6	97.6	97.5	97.2	96.8	97.8	96.9	96.6	95.9	97.0	
W ⁶⁺ (apfu)	0.075	0.075	0.077	0.036	0.032	0.033	0.036	0.036	0.073	0.082	0.079	0.042	0.036	0.075	0.081	0.042	0.040	
Nb ⁵⁺	1.051	1.070	1.038	0.996	0.990	0.983	1.041	0.958	0.895	1.027	1.040	1.046	1.003	1.067	1.128	1.074	1.068	
Ta ⁵⁺	0.593	0.570	0.594	0.599	0.562	0.570	0.594	0.583	0.783	0.609	0.614	0.476	0.630	0.576	0.500	0.469	0.528	
Si ⁴⁺	0.009	0.008	0.009	0.008	0.011	0.010	0.009	0.011	0.010	0.011	0.009	0.011	0.009	0.011	0.010	0.011	0.010	
Ti ⁴⁺	0.251	0.255	0.258	0.340	0.385	0.382	0.307	0.388	0.218	0.246	0.237	0.404	0.306	0.251	0.260	0.382	0.337	

Table 2. Cont.

Sample	Bosco3										Bosco4							
#Analyses	43/1	44/1	45/1	46/1	47/1	48/1	50/1	51/1	12/1	13/1	14/1	15/1	16/1	22/1	23/1	24/1	25/1	
Mineral	S-(Y)	S-(Y)	S-(Y)	S-(Y)	S-(Y)	S-(Y)	S-(Y)	S-(Y)	S-(Y)	S-(Y)	S-(Y)	S-(Y)	S-(Y)	S-(Y)	S-(Y)	S-(Y)	S-(Y)	
Zr ⁴⁺	0.021	0.021	0.023	0.020	0.021	0.022	0.013	0.025	0.021	0.024	0.021	0.020	0.016	0.021	0.021	0.022	0.017	
subtot.	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	
Mn ²⁺	0.083	0.078	0.080	0.056	0.054	0.056	0.052	0.055	0.085	0.082	0.082	0.051	0.048	0.078	0.079	0.064	0.054	
Fe ³⁺	0.653	0.645	0.642	0.691	0.670	0.638	0.659	0.650	0.633	0.637	0.640	0.664	0.648	0.650	0.650	0.652	0.667	
subtot.	0.736	0.723	0.722	0.747	0.725	0.694	0.711	0.705	0.718	0.719	0.722	0.715	0.696	0.728	0.728	0.716	0.721	
Th ⁴⁺	0.051	0.051	0.053	0.051	0.054	0.053	0.051	0.045	0.054	0.054	0.054	0.050	0.046	0.056	0.057	0.057	0.056	
U ⁴⁺	0.063	0.059	0.059	0.092	0.098	0.083	0.077	0.071	0.053	0.055	0.063	0.102	0.071	0.061	0.058	0.099	0.098	
Sc ³⁺	0.059	0.059	0.054	0.048	0.043	0.049	0.055	0.049	0.072	0.065	0.063	0.041	0.070	0.052	0.053	0.045	0.051	
Y ³⁺	0.549	0.551	0.557	0.542	0.528	0.544	0.566	0.565	0.594	0.578	0.555	0.518	0.584	0.544	0.546	0.508	0.529	
Ce ³⁺	0.004	0.005	0.005	0.000	0.004	0.005	0.004	0.000	0.005	0.005	0.005	0.004	0.000	0.006	0.005	0.005	0.000	
Nd ³⁺	0.012	0.013	0.012	0.009	0.011	0.009	0.009	0.009	0.012	0.013	0.014	0.011	0.008	0.014	0.015	0.012	0.012	
Sm ³⁺	0.022	0.020	0.021	0.018	0.018	0.019	0.018	0.019	0.023	0.022	0.022	0.019	0.016	0.023	0.022	0.020	0.020	
Gd ³⁺	0.051	0.049	0.051	0.049	0.045	0.044	0.047	0.041	0.047	0.045	0.051	0.047	0.042	0.050	0.053	0.049	0.047	
Tb ³⁺	0.011	0.012	0.012	0.012	0.011	0.011	0.010	0.011	0.012	0.009	0.012	0.011	0.009	0.011	0.011	0.011	0.012	
Dy ³⁺	0.055	0.050	0.053	0.051	0.051	0.045	0.049	0.048	0.048	0.051	0.053	0.054	0.043	0.053	0.054	0.051	0.052	
Ho ³⁺	0.007	0.006	0.006	0.006	0.006	0.006	0.006	0.005	0.006	0.008	0.006	0.008	0.007	0.005	0.006	0.007	0.005	
Er ³⁺	0.024	0.025	0.024	0.025	0.024	0.022	0.022	0.024	0.021	0.022	0.025	0.026	0.021	0.026	0.023	0.025	0.025	
Tm ³⁺	0.007	0.007	0.005	0.006	0.006	0.006	0.007	0.006	0.008	0.006	0.007	0.007	0.006	0.005	0.005	0.004	0.006	
Yb ³⁺	0.046	0.047	0.046	0.047	0.046	0.045	0.049	0.047	0.042	0.043	0.046	0.047	0.043	0.046	0.047	0.045	0.046	
Lu ³⁺	0.008	0.007	0.007	0.009	0.007	0.008	0.008	0.010	0.010	0.007	0.009	0.006	0.008	0.008	0.007	0.005	0.006	
Ca ²⁺	0.017	0.018	0.017	0.011	0.011	0.008	0.021	0.012	0.011	0.015	0.018	0.014	0.023	0.016	0.018	0.015	0.015	
subtot.	0.987	0.980	0.980	0.976	0.964	0.955	1.001	0.962	1.017	1.000	1.004	0.965	0.996	0.977	0.981	0.957	0.980	
O ²⁻	7.487	7.456	7.455	7.456	7.384	7.326	7.449	7.337	7.519	7.485	7.503	7.373	7.413	7.464	7.468	7.363	7.432	
REE + Sc + Y	0.86	0.85	0.85	0.82	0.80	0.81	0.85	0.83	0.90	0.88	0.87	0.80	0.86	0.84	0.85	0.79	0.81	
U/(Th + U)	0.55	0.54	0.53	0.64	0.64	0.61	0.60	0.61	0.50	0.50	0.54	0.67	0.60	0.52	0.50	0.63	0.64	
Nd/Yb	0.26	0.29	0.25	0.18	0.23	0.20	0.19	0.19	0.27	0.31	0.30	0.24	0.18	0.30	0.31	0.28	0.25	
Ta/(Nb + Ta)	0.36	0.35	0.36	0.38	0.36	0.37	0.36	0.38	0.47	0.37	0.37	0.31	0.39	0.35	0.31	0.30	0.33	
CV1	-2.14	-2.07	-2.12	-2.00	-1.79	-1.71	-1.93	-1.69	-2.01	-2.01	-2.10	-1.74	-1.81	-2.13	-2.15	-1.95	-1.95	
CV2	-3.47	-3.55	-3.37	-3.37	-3.32	-3.25	-3.43	-3.33	-3.40	-3.57	-3.47	-3.36	-3.54	-3.46	-3.50	-3.12	-3.40	

Note: S-(Y) = Samarskite-(Y); samarskite formula was calculated on the basis of W + Nb + Ta + Si + Ti + Zr = 2.

4.2. Single Crystal X-Ray Spectroscopy (SCXRD)

Unit-cell data (Table 3) were obtained using a single-crystal diffractometer Rigaku-Oxford Diffraction Supernova (Rigaku Europe SE, Ettlingen, Germany) with an X-ray microsource (spot = 120 μm , λ = Mo K α , working conditions 50 kV and 0.8 mA) and equipped with a 200K Pilatus Dectris detector (DECTRIS Ltd, Baden-Daettwil, Switzerland). The measurements were performed using a 0–360° ϕ scan. The detector-to-sample distance was 68 mm. The unit-cell refinements were performed using CrysAlisPro software (Version CrysAlis_40_64.19a, Agilent Technologies Ltd., Santa Clara, CA, USA).

Table 3. Unit-cell parameters, obtained by single-crystal X-ray diffraction at room temperature, of aeschynite-(Y), polycrase-(Y), and samarskite-(Y) from Bosco and Fiume pegmatites at Arvigno.

	Bosco1	Bosco2	Bosco3	Bosco4	Fiume1
	aeschynite-(Y)	aeschynite-(Y)	samarskite-(Y)	polycrase-(Y)	polycrase-(Y)
<i>a</i> (Å)	11.043(3)	10.95(7)	9.9851(7)	14.736(6)	14.82(3)
<i>b</i> (Å)	7.477(2)	7.40(5)	5.6386(3)	5.605(1)	5.66(1)
<i>c</i> (Å)	5.201(9)	5.170(10)	5.1737(3)	5.184(2)	5.22(1)
α (°)	90.00	90.00	90.00	90.00	90.00
β (°)	90.00	90.00	93.061(5)	90.00	90.00
γ (°)	90.00	90.00	90.00	90.00	90.00
V. cell. (Å ³)	429.43(18)	419(4)	290.87(2)	428.2 (3)	438 (2)
space group	<i>Pbnm</i>	n.d.	n.d.	<i>Pcan</i>	<i>Pcan</i>
	* Skoda and Novak [38]	** Sugitani et al. [3,4]	*** Simmons et al. [6]	**** Britvin et al. [8]	***** Bonazzi and Menchetti [39]
	polycrase-(Y)	samarskite-(Y)	samarskite-(Yb)	samarskite-(Y)	aeschynite-(Y)
<i>a</i> (Å)	10.993	5.642	5.688(9)	9.8020(8)	11.031(3)
<i>b</i> (Å)	7.531	9.914	9.915(2)	5.6248(3)	7.448(2)
<i>c</i> (Å)	5.346	5.229	5.199(9)	5.2073(4)	5.188(1)
α (°)	90.00	90.00	90.00	90.00	90.00
β (°)	90.00	93.84	3.16(10)	93.406(4)	90.00
γ (°)	90.00	90.00	90.00	90.00	90.00
V. cell (Å ³)	442.6	292.88	292.76	286.59 (4)	426.2 (2)
space group	n.d.	n.d.	n.d.	<i>P2/c</i>	<i>Pnma</i>

* XRPD, cell data obtained upon heating the crystal to 650 and 750 °C (sample poz5); ** XRPD, cell data obtained upon heating the crystal to 1200 °C (sample Kawabe, Fukushima); *** XRPD, cell data obtained upon heating the crystal to 1100 °C (sample Little Patsy, Colorado); **** SCXRD, cell data obtained at room temperature; ***** SCXRD, cell data obtained at room temperature (sample VV).

4.3. Raman Spectroscopy

The Raman spectra of complex REE–Nb–Ta–Ti oxides (Figure 2f) were obtained from a polished section by means of a Horiba Labram HR Evolution spectrometer. This dispersive, edge filter-based system was equipped with an Olympus BX 41 optical microscope, a diffraction grating with 600 grooves per millimeter, and a Peltier-cooled, Si-based charge-coupled device (CCD) detector. After careful tests with different lasers (473, 532, and 633 nm), the 633 nm He–Ne laser with a beam power of 10 mW at the sample surface was selected for spectra acquisition to minimize analytical artefacts. Raman signal was collected in the range of 100–4000 cm^{-1} with a 100 $\times$ objective and the system being operated in the confocal mode, beam diameter was $\sim 1 \mu\text{m}$ and the lateral resolution $\sim 2 \mu\text{m}$, but due to the strong luminescence, in the region above 2000 cm^{-1} only the region 100–1200 cm^{-1} was processed. No visual damage of the analyzed surface was observed at these conditions after the excitation. Wavenumber calibration was done using the Rayleigh line and low-pressure Ne-discharge lamp emissions. The wavenumber accuracy was $\sim 0.5 \text{ cm}^{-1}$, and the spectral resolution was 2 cm^{-1} . Band fitting was done after appropriate background correction, assuming combined Lorentzian–Gaussian band shapes using the Voigt function (PeakFit, Version 4.12, Systat Software Inc, San Jose, CA, USA).

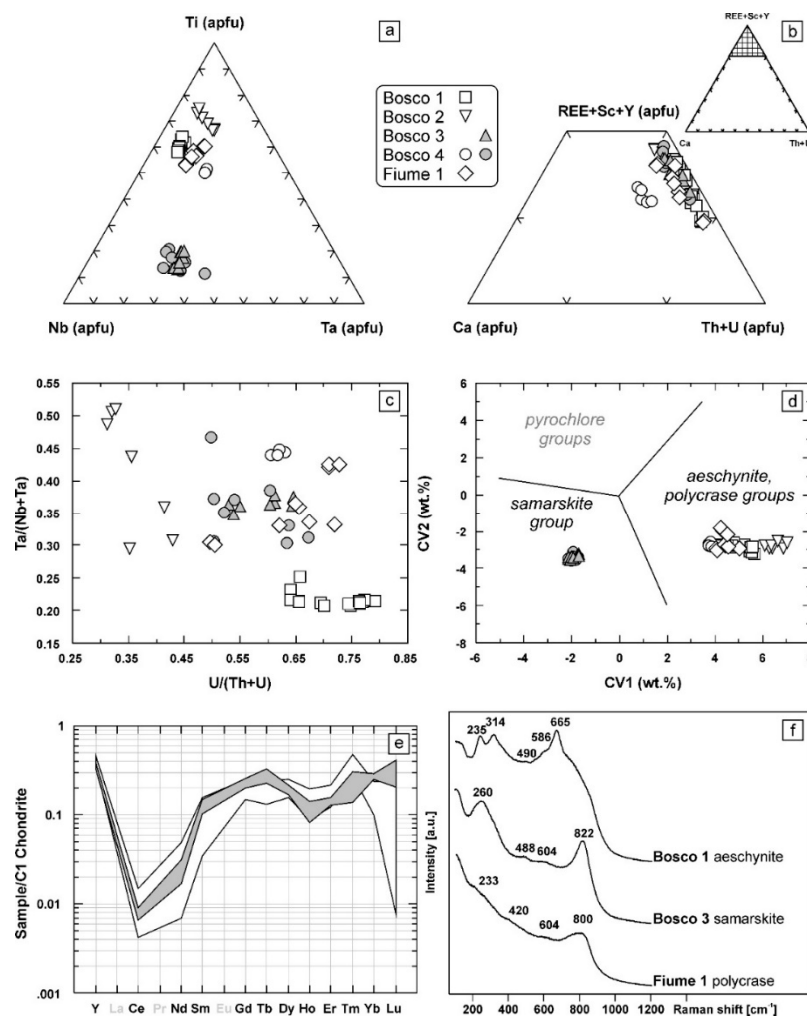


Figure 2. The composition of aeschynite-(Y), polycrase-(Y), and samarskite-(Y), plotted in terms of the Ti–Nb–Ta and (REE + Sc + Y)–Ca–(Th + U) apfu ternary plots are shown in (a) and (b). The quadrilateral plot of Ta/(Nb + Ta) and U/(Th + U) showing compositional variations of aeschynite-(Y), polycrase-(Y), and samarskite-(Y) are shown in (c). The CV2 versus CV1 Ercit [13] statistical diagram is shown in (d) and the chondrite versus normalized REE pattern of aeschynite-(Y), polycrase-(Y), and samarskite-(Y) from Arvogno is shown in (e). For all plots, aeschynite-(Y) and polycrase-(Y) are plotted in white and samarskite-(Y) in grey. Raman spectra of aeschynite-(Y) from Bosco1, samarskite-(Y) from Bosco3, and polycrase-(Y) from Fiume1 are shown in (f).

4.4. Terminology of REE

According to the IUPAC (International Union for Pure and Applied Chemistry), the term rare-earth elements (REEs) includes lanthanoids (Ln), yttrium (Y), and scandium (Sc). Due to the substantially smaller ionic radius of Sc with respect to the rest of the group, it frequently enters different crystal-structural sites via different substitutions, and therefore, Sc is commonly not included as a REE in geological sciences, and neither in this paper. Due to the lanthanide contraction phenomenon, the REE are further divided into larger LREE (light Ln, La–Gd) and smaller HREE (heavy Ln, Tb–Lu). Actinides, including Th^{4+} and U^{4+} show similar behavior, respectively, having a 0.94 Å and 0.89 Å ionic radius.

5. Hand Samples and BSE Description

The samples of Y–Nb–Ti–Ta oxides collected at the “Bosco” dike were, respectively, named Bosco1, Bosco2, Bosco3, and Bosco4 to maintain the original hand specimen description by Albertini and Andersen [34], while that collected at the “Fiume” pegmatite was named Fiume1.

Bosco1 are tabular prismatic crystals and occur in the border-wall areas of the coarse-grained dike associated with white K-feldspar and brown-smoky quartz. Bosco2 forms centimetric black, shiny masses with conchoidal vitreous fractures and occur in the border-wall areas of the coarse-grained dike with white K-feldspar and brown-smoky quartz. Bosco3 forms pluricentimetric black masses with granular fractures and occur at the core-grained dike embedded in brownish, vitreous massive quartz. Bosco4 forms idiomorphic millimetric crystals with prismatic-di-pyramidal habitus and a typical barrel-shape morphology. The crystals are black in color, opaque, show granular fracture, and occur in the border zone of the coarse-grained dike with white K-feldspar, albite, brown-smoky quartz, in association with magnetite and gadolinite-(Y). Fiume1 forms millimetric, black, vitreous masses and have conchoid fractures, rimmed by a reddish halo which extends a few millimeters within the K-feldspar. It was found in the border zone of the pegmatite associated with K-feldspar, black vitreous quartz, and silvery flakes of muscovite.

The individual grains of Y–REE–Nb–Ta–Ti-oxide minerals typically show well-developed zoning in BSE images (Figure 3). The Bosco1 sample—aeschnite-(Y)—had a volumetrically dominant homogeneous core only locally with weak oscillatory zoning inside and regular oscillatory zoning on the rim (Figure 3a) caused by variations in Ti, U, and Ta/Nb. The Bosco2 sample—aeschnite-(Y)—was more heterogeneous with irregular coarse oscillatory zoning rather randomly distributed within the grain (Figure 3b). The Bosco3 sample—samarskite-(Y)—was only slightly zoned; rather, the homogeneous core with slight sectorial zoning evolved to weak oscillatory zoning (Figure 3c) controlled by variations in Ti and U. The Bosco4 sample—polycrase-(Y) + samarskite-(Y)—consisted of rather homogeneous polycrase with euhedral to subhedral elongated grains of samarskite (Figure 3d). In the detailed image (Figure 3e), both minerals have slight oscillatory or irregular zoning. The Fiume1 sample—polycrase-(Y)—exhibited regular parallel oscillatory zoning in the center, and in the outer parts of the grains, irregular fine oscillatory zoning was developed (Figure 3f). The zoning evident from the BSE images was caused by variations in Ti, Nb, Ta, U, Y, and Ln due to its very different Z.

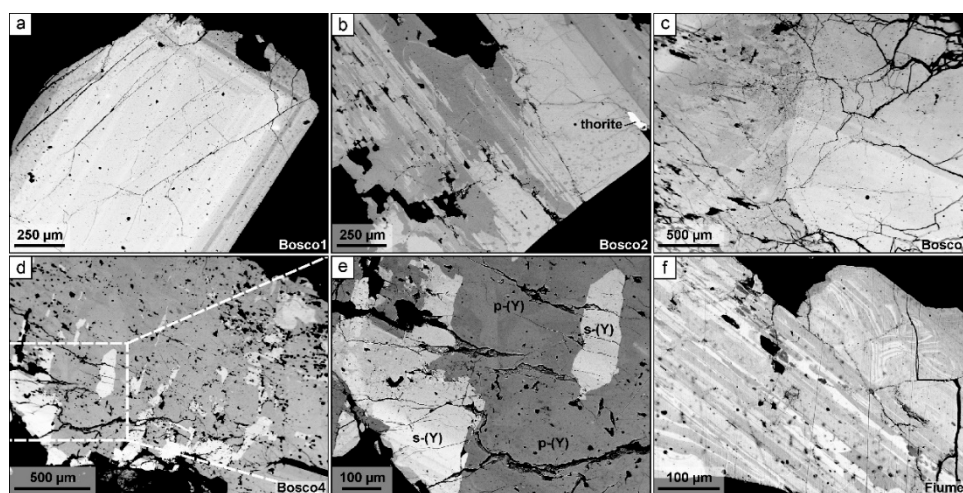


Figure 3. Back-scattered electron images of aeschnite-(Y) in (a) and (b) (Bosco1 and Bosco2), samarskite-(Y) in (c) (Bosco3), in (d) the polished section of intergrowth polycrase-(Y) (grey) with samarskite-(Y) (light grey), in (e) the detailed sample section (Bosco4), and polycrase-(Y) in (f) (Fiume1).

6. Mineral Chemistry of Aeschynite-(Y), Polycrase-(Y), and Samarskite-(Y)

Yttrium–niobium–titanium–tantalum AB_2O_6 and ABX_2O_8 oxides from Arvogno pegmatites showed common characteristics: they were free from weathering. No secondary reaction phenomena were observed nor the presence of exsolutions or hydrothermal secondary reactions typical when intergrowth with accessory secondary minerals such as fersmite, pyrochlore, thorite, thorianite or vigezzite, as it elsewhere occurs in the Alpine Tertiary pegmatites [40,41] or in other NYF pegmatite fields [15,38,42–44]. The representative chemical compositions of the studied oxides are reported in Tables 1 and 2. The analysis showed that AB_2O_6 phases have Y and Ti as dominant A- and B-site cations, respectively, and therefore, corresponded to polycrase-(Y) and/or aeschynite-(Y), which are undistinguishable from each other in chemical composition. The presence of both phases was unequivocally determined and identified under SCXRD. Samarskite group minerals have a general formula ABX_2O_8 ; they are represented by samarskite, ishikawaite, and calciosamarskite, respectively, Y, Fe, and Nb dominant A-, B-, and X-site cations [7,8]. At Arvogno, samarskite-(Y) was unequivocally identified under SCXRD; sample Bosco3 was samarskite-(Y), while Bosco4, which was also identified as samarskite-(Y), was intergrown with polycrase-(Y) as well. All samples were very depleted in LREE, particularly La–Nd, and also poor in Ca.

Bosco1 was aeschynite-(Y) and had the A-site mainly occupied by Y as the dominant REE which varied from 0.650 apfu (atoms per formula unit) to 0.710 apfu. Light rare-earths (Ce, Nd, Gd) varied from 0.034 to 0.056 apfu, HREE (Tb, Dy, Ho, Er, Tm, Yb, Lu) varied from 0.15 to 0.16, U/(U + Th) from 0.311 to 0.429 apfu, while Fe^{2+} from 0.028 to 0.046 apfu. The B-site had Ti dominant, which varied from 1.303 to 1.477 apfu, Nb from 0.322 to 0.375 apfu, Ta from 0.153 to 0.335, and W from 0.036 to 0.057 apfu. Bosco1 showed the highest Ti content among all the Arvogno AB_2O_6 oxides.

Bosco2 was aeschynite-(Y) in which the A-site had a Y dominant that varied from 0.567 to 0.701 apfu, LREE varied from 0.009 to 0.024, HREE from 0.139 to 0.203 apfu, U/(U + Th) from 0.640 to 0.771 apfu, and Fe^{2+} from 0.044 to 0.097 apfu. The B-site had Ti which varied from 1.120 to 1.261 apfu, Nb varied from 0.562 to 0.635 apfu, and Ta from 0.151 to 0.188 apfu, whereas W varied from 0.011 to 0.028 apfu.

Bosco3 was samarskite-(Y) where the X-site had Nb dominant which varied from 0.958 to 1.070 apfu, Ti varied from 0.251 to 0.388 apfu, Ta from 0.562 to 0.599 apfu, and W from 0.032 to 0.077 apfu. The A- and B-sites, respectively, had Y dominant that varied from 0.528 to 0.566 apfu, LREE from 0.027 to 0.034 apfu, HREE from 0.192 to 0.209 apfu, U/(U + Th) from 0.529 to 0.645 apfu, and Fe^{3+} varied from 0.638 to 0.691 apfu.

Bosco4 sample was characterized by the intergrowth of two phases: the dominant was polycrase-(Y), which was quite homogenous in composition; Y at the A-site varied from 0.598 to 0.615 apfu, LREE up to 0.031 apfu, HREE up to 0.175, U/(U + Th) from 0.606 to 0.631 apfu, and Fe^{2+} from 0.079 to 0.087 apfu. The six-folded octahedra B had Ti from 0.962 to 0.995 apfu, Nb from 0.512 to 0.536 apfu, and Ta up to 0.423 apfu. The subordinate phase was samarskite-(Y), which was quite heterogeneous in composition where the X-site had Nb dominant which varied from 0.895 to 1.128 apfu, Ti from 0.218 to 0.404 apfu, Ta from 0.469 to 0.783 apfu, and W from 0.036 to 0.081 apfu. The A-site had Y dominant that varied from 0.508 to 0.584 apfu, LREE up to 0.039 apfu, HREE varied from 0.179 to 0.195 apfu, U/(U + Th) from 0.498 to 0.673 apfu, and the B-site had Fe^{3+} that varied from 0.633 to 0.667 apfu.

Fiume1 was polycrase-(Y), and the A-site was mainly occupied by Y and varied from 0.546 to 0.638 apfu. The LREE varied from 0.016 to 0.031 apfu, HREE from 0.201 to 0.209, U/(U + Th) from 0.495 to 0.725 apfu, and Fe^{2+} from 0.064 to 0.089 apfu. The B-site had Ti which varied from 1.024 to 1.188 apfu, Nb from 0.449 to 0.636 apfu, Ta from 0.274 to 0.332 apfu, and W up to 0.009 apfu.

It is worth mentioning that Bosco3 and Bosco4 samarskite-(Y) was characterized by lower oxide analytical totals in the range of 97 wt.% with Fe^{3+} and Mn^{2+} showing significant vacancy at the B-site. When we looked at other samarskites worldwide, they were also partially vacant at this site—some more, some less [3–6,45]. The Fe and Mn oxidation states were determined in samarkites by bond valence calculation following Britvin et al. [8]. Taking into consideration that AGMs and EGMs have

sensible iron contents, future Mossbauer spectra may discriminate and quantify the amounts of Fe^{3+} and Fe^{2+} .

For comparison, Bonazzi and Menchetti [39] refined the crystal structure of a natural non-metamict aeschynite-(Y) and suggested a new structural formula $\text{A}_{1-x}\text{B}_2\text{C}_x\text{O}_6$ with an additional C-site. These authors assumed that W^{6+} enters the C-cavity, coupled with a corresponding vacancy in the A-site. The C-site is asymmetrically located within an eight-fold cavity, similar in shape to that occupied by A cations. The sample (VV Vigizzo) described and analyzed by these authors was collected at the “Bosco” dike. The empirical formula calculated with the structural formula obtained by the authors was very close to the Bosco1 analysis: $(\text{Y}_{0.65}\text{Nd}_{0.01}\text{Sm}_{0.02}\text{Gd}_{0.04}\text{Dy}_{0.04}\text{Er}_{0.02}\text{Yb}_{0.02}\text{Th}_{0.07}\text{U}_{0.03}\text{Ca}_{0.01}\text{Fe}_{0.03})_{0.94}(\text{Ti}_{1.41}\text{Nb}_{0.36}\text{Ta}_{0.22}\text{W}_{0.01})_{2.00}(\text{W}_{0.04})\text{O}_{5.79}(\text{OH})_{0.21}$

The chemical analysis reported by Bonazzi and Menchetti [39] highlights the deficient analytical total in respect to the data reported for Bosco1. Low total is related to elements not analyzed, such as Si, Tb, Ho, Tm, and Lu, that once added to the analytical total, would result in more than 99 wt.%.

7. Elemental Plots

The statistical approach developed by Ercit [13] allows to discriminate between (REE,U,Th)-(Nb,Ta,Ti) oxide species from REE-enriched granitic pegmatites. The studied samples fit very well the two regions of the Ercit plots. In the first region fall Bosco1, Bosco2, Bosco4, and Fiume1 samples related to the AB_2O_6 euxenite-aeschynite-group minerals (AGMs), and to the second region of the diagram fall Bosco3 and Bosco4, related to the ABX_2O_8 samarskite-group minerals (EGMs), as shown in Figure 2d.

The Ercit statistical diagram utilizes equations CV1 and CV2 calculated as follows: $\text{CV1} = 0.245\text{Na} + 0.106\text{Ca} - 0.077\text{Fe}^* + 0.425\text{Pb} + 0.220\text{Y} + 0.280\text{LREE} + 0.137\text{HREE} + 0.100\text{U}^* + 0.304\text{Ti} + 0.097\text{Nb} + 0.109\text{Ta}^* - 12.81$ (oxide wt.%); $\text{CV2} = 0.102\text{Na} - 0.113\text{Ca} - 0.371\text{Fe}^* - 0.167\text{Pb} - 0.395\text{Y} - 0.280\text{LREE} - 0.265\text{HREE} - 0.182\text{U}^* - 0.085\text{Ti} - 0.166\text{Nb} - 0.146\text{Ta}^* + 17.29$ (oxide wt.%); where, $\text{Fe}^* = \text{FeO} + \text{Fe}_2\text{O}_3 + \text{MnO}$; $\text{U}^* = \text{UO}_2 + \text{UO}_3 + \text{U}_3\text{O}_8 + \text{ThO}_2$, and $\text{Ta}^* = \text{Ta}_2\text{O}_5 + \text{WO}_3$.

The Ta (apfu) versus Nb (apfu) plot (Figure 4a) shows that the Bosco1 and Bosco2 samples have compositional variations in the Ta/Nb ratios and either form partial solid solutions with tantalaeschynite-(Y) [46] and with niobaeschynite-(Y) [47]. Bosco4 and Fiume1 are polycrase-(Y) and fall within the center of the diagram and they are quite clearly chemically distinguishable each other based on different Ta contents. Bosco3 and Bosco4 (grey) are samarskite-(Y) and fall in the upper-right end of the plot characterized by the highest Nb/Ta enrichment.

The Ti (apfu) versus Ta + Nb (apfu) plot (Figure 4b) identifies two fields represented by AB_2O_6 (Y, REE, U, Th) and ABX_2O_8 (Nb, Ta, Ti) oxides all aligned along a sloping line. Bosco3 and Bosco4 samarskites have lower Ti content than Bosco1, Bosco2 aeschynite-(Y), and Bosco4 and Fiume1 polycrase-(Y). The Ta + Nb content results were significantly higher for samarskites than aeschynites.

The Ti (apfu) versus Ca (apfu) plot (Figure 4c) shows Ca content was slightly higher for Bosco4 polycrase-(Y) in respect to Bosco1, Bosco2, and Fiume1. Bosco3 and Bosco4 samarskite-(Y) also showed the lowest Ti content. The Ti (apfu) versus U + Th (apfu) plot (Figure 4d) evidenced the variability of U + Th contents either for AGMs and EGMs from Arvogno.

The behavior of Y + Sc + REE (apfu) versus Ti (apfu) (Figure 4e) showed substantially equivalent contents of Y + Sc + REE for samarskite-(Y), aeschynite-(Y), and polycrase-(Y). Similar behavior was evidenced for U + Th (apfu) versus Y + Sc + REE (apfu) diagram (Figure 4f) as well where Bosco4 and Bosco3 samarskite-(Y) had sensible lower U + Th content than aeschynite-(Y) and polycrase-(Y). The U + Th content for Arvogno only partially agreed with the data reported by Hanson et al. [42], which proposed a higher U + Th content in polycrase-(Y) with respect aeschynite-(Y).

Ta/Ta + Nb (apfu) versus U/U + Th (apfu) (Figure 2c) had Bosco2, Bosco4, and Fiume1 aeschynite-(Y), polycrase-(Y), and samarskite-(Y) with strongly variable Ta/Nb and U/Th contents in respect to Bosco4 polycrase-(Y), which showed substantially equivalent contents.

The Ternary plot (Y + Sc + REE)-Ca-(U + Th) showed Bosco4 polycrase falls with lower uranium and thorium, and slight enrichment in calcium content (Figure 2b), while the Ti-Nb-Ta plot (Figure 2a) allows to well separate aeschynite-(Y) from samarskite-(Y) and quite well aeschynite-(Y) from polycrase-(Y).

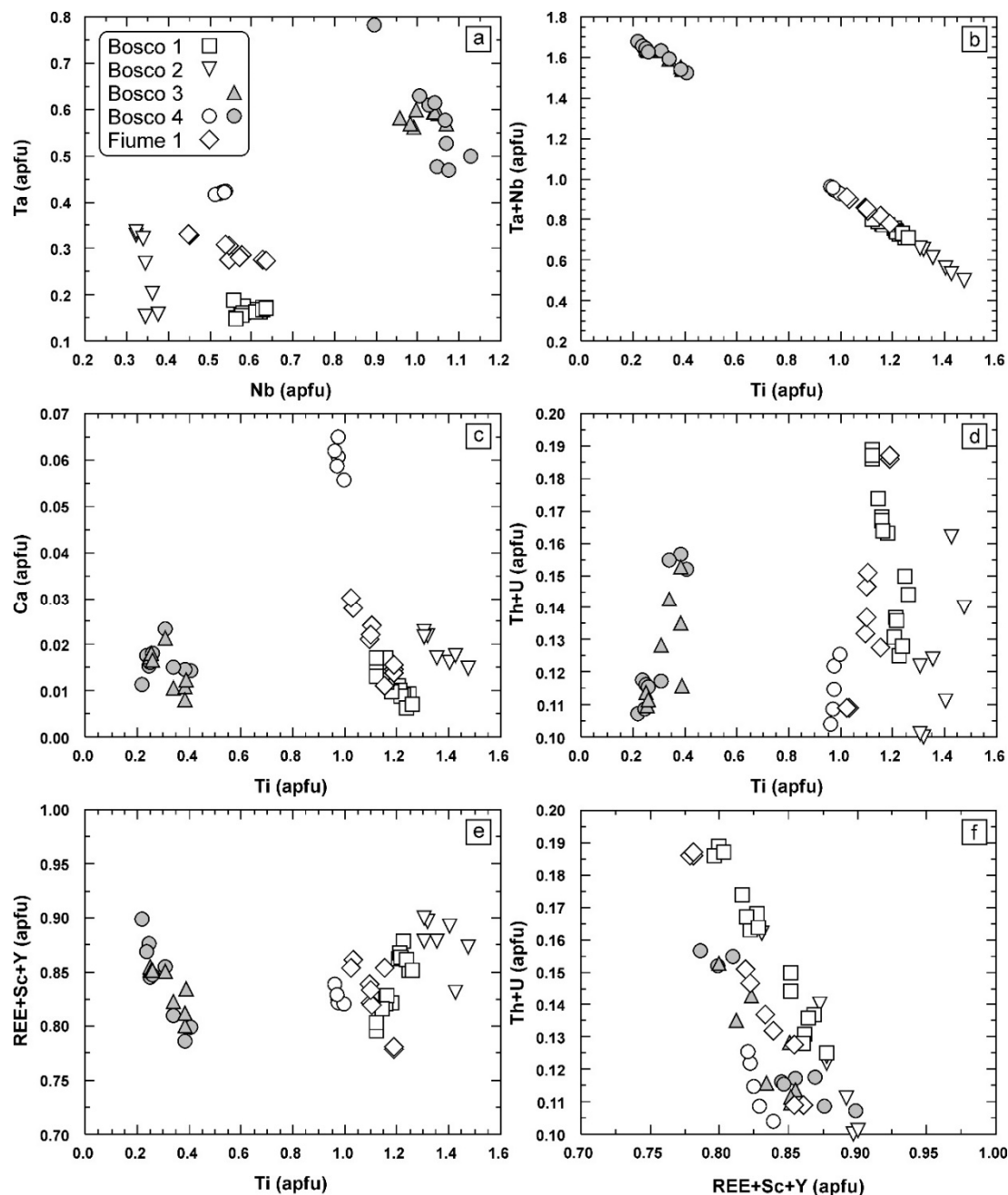


Figure 4. The quadrilateral plots showing compositional variations of aeschynite-(Y), polycrase-(Y), and samarskite-(Y) from (a) to (f). For all plots, the symbols plotted in white are aeschynite-(Y) and polycrase-(Y), and in grey samarskite-(Y).

8. REE Pattern and Fractionation Trends

Chondrite versus the normalized REE pattern [48] of AGMs and EGMs showed a strong depletion in the large LREE and enrichment in the medium and small HREE. The samarskite-(Y) pattern was the more enriched in HREE than polycrase-(Y), whereas the aeschynite-(Y) pattern was depleted in the heaviest REE with respect to polycrase-(Y), as shown in Figure 2e. The concentrations of La, Pr, and Eu were below the detection limit of EPMA.

A ratio of Nd/Yb was chosen to numerically characterize the degree of REE fractionation and the slope of the REE pattern. The highest slope (an average) showed samarskite-(Y) from Bosco3 equal to 0.22, Bosco4 to 0.27, then polycrase-(Y) from Fiume1 equal to 0.24, Bosco3 to 0.29, and Bosco4 to 0.35. Aeschynite-(Y) from Bosco1 equaled 0.76, while Bosco2 had a similar pattern for HREE as Bosco1, but in contrast to other samples, it was impoverished in LREE (Figure 2e) and it means that the Nd/Yb ratio was only at 0.18. All analyzed samples showed an M-type tetrad effect strongly evolved on T₃ and T₄ (Figure 2e). The tetrad effect is usually best developed in the first and third tetrad T_{1,3} [49], but some HREE-enriched systems can develop evolved tetrad effects on T₃ and T₄ as described by Škoda et al. [44]. The M-type tetrad effect was reported for evolved Li–F granites, fractionated pegmatites, and their associated minerals [49–55], as well as minerals crystallized from felsic magma-derived fluids [54–57] and is attributed to a distribution of REE among magmatic/solid and fluid phases. It is also frequently linked to the F-rich environment, but the sole role of F is questioned by Škoda et al. [44]. The presence of the tetrad effect complicates the interpretation of the REE fractionation as well as the role of crystallographic constraints controlling the entrance of REE into the structure and vice versa. The degree of Ta–Nb fractionation in Bosco1 aeschynite-(Y), expressed as Ta/(Nb + Ta) that decreases with increasing U–Th fractionation, expressed by U/(U + Th), whereas samarskite-(Y) and polycrase-(Y) showed a rather negative trend or no trend, respectively (Figure 2c). This behavior is controlled by crystallographic constraints or by coeval crystallization of U-, Th-, Ta-, and Nb-bearing accessory minerals, rather than by geochemical fractionation of the pegmatite. Similar fractionation behavior was observed in AGMs and EGMs from Třebíč pluton NYF pegmatites [38].

9. SCXRD Data

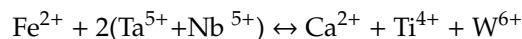
Although the samples investigated show sensible amounts of U + Th, they were all suitable for X-ray diffraction analysis. The cell data of the crystals studied are reported in Table 3 and include those for Bosco1, Bosco2, Bosco3, Bosco4, and Fiume1 samples. Complete intensity data were collected for all of them, but unfortunately, the crystal quality did not allow to obtain any structural data. The analysis of the systematic absences, given the quality of Bosco1 aeschynite-(Y) and Bosco4 polycrase-(Y) crystals, allowed for both to provide space groups Pbnm and Pcan. Fiume1 and Bosco2 samples did not allow the accurate determination of the space group, but according to the chemical compositions defined by Ti dominant content at the B-site, the cell parameters, respectively, corresponded to polycrase-(Y) and aeschynite-(Y), whereas the Bosco3 crystal provided the monoclinic cell of samarskite-(Y). In order to obtain information about the crystal chemistry of AGMs and EGMs, we compared our cell data of aeschynite-(Y) and polycrase-(Y) with those from Bonazzi and Menchetti [39] and Škoda and Novák [38], whereas the data on samarskite-(Y) were compared with those from Sugitani et al. [3,4], Simmons et al. [6], in addition to the very recent cell data obtained from crystal structures solved by Britvin et al. [8]. These data are reported in Table 3. If we compare the unit-cell volume of Bosco1 and Bosco2 aeschynite-(Y), we can observe that the Bosco1 volume is larger than Bosco2, likely because it had a higher Ti content, whereas, without structural information, it is more difficult to establish why Fiume1 had the higher cell volume of with respect to that of Bosco4, considering that these polycrase-(Y) have very similar chemical compositions.

Bosco3 samarskite-(Y) is the first crystal from pegmatites for which cell data were obtained by SCXRD technique at room temperature following the cell data of samarskite-(Y) occurring in sanidinites from Laacher See published by Britvin et al. [8]. Indeed, all previous crystallographic information reported in the literature provided cell data by powder X-ray diffraction obtained upon heating the crystals from 950 °C to 1110 °C in a reducing atmosphere [3,4,6].

10. Discussion

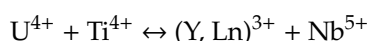
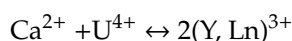
The compositions (REE,U,Th)–(Nb,Ta,Ti) AB₂O₆ oxide crystals from Arvogno ranged from aeschynite-(Y) (Bosco1, Bosco2) to polycrase-(Y) (Bosco4, Fiume1). The aeschynite-(Y) form individual crystals or aggregates, but polycrase-(Y) is usually intergrown with samarskite-(Y). In order to

discriminate the compositional variations described in the phase diagrams, a number of charge balanced equations are proposed for AGMs and EGMs. They are related to the mutual exchange vectors of elements for eight-folded square antiprism A-site and six-folded octahedra B-site, and they can be summarized as follows:



As can be observed, the exchange vectors are strongly variable at A- and B-sites for polycrase-(Y) and aeschynite-(Y) and no general rule can be discerned. The Nb/Ta ratio was strongly variable in polycrase-(Y) and aeschynite-(Y) and the (U + Th) content was sensibly variable and relatively higher in aeschynite-(Y).

As far as Bosco3 and Bosco4 samarskite-(Y) is concerned, the trend was rather homogeneous and the exchange vectors considered can be represented and described by Britvin et al. [8] as follows:



According to Ewing [58], both primary and secondary alteration could produce a deficiency of the A-type cations, but this is not the case for Arvogno aeschynite-(Y) and polycrase-(Y), which have high analytical totals. In addition, BSE images show no secondary mineral phases such as fersmite, pyrochlores, thorite or thorianite; these minerals are usually present when dissolution metasomatic or hydrothermal replacements occur. Low analytical totals measured for samarskites might reflect the possibility of incomplete occupancy (vacancies) in the B-site charge balanced by OH[−], but for all samples, Raman spectroscopy (Figure 2f) showed luminescence on laser at 473 nm, 532 nm, and 633 nm in the “water” region, and therefore, it was not possible to detect the presence of OH[−] or H₂O.

As described by Berman [59], the term “metamict” refers to the “non-crystalline pseudomorphs of material presumed to have been crystalline originally”. Mainly, radiation damage of the structure is the reason for a metamict state [9,58]. Owing to their significant concentrations in U and Th, the (Y-REE-U-Th)-(Nb-Ta-Ti) oxides usually experience strong structural damage resulting from the radioactive decay of actinides [10]. Although aeschynite-(Y), polycrase-(Y), and samarskite-(Y) from Arvogno showed sensible U + Th enrichments, no alpha decay of U and Th, which could cause volume expansion and damage to the crystal lattice of the mineral phases, which in turn may pass from a crystalline to an amorphous state, were observed. No secondary post-metamictization alterations were present as well [60]. If these alterations were present they would show hydration, Ca, and/or high-field strength element (HFSE) addition, in particular Si and Al, K, Ba or Sr, and result in a lowering of the analytical totals, but this is not the case for the Arvogno (Y-REE-U-Th)-(Nb-Ta-Ti) oxides. Behavior of HREE and LREE in AGMs and EGMs is generally distinct. Heavy rare-earths are most often located in EGMs, whereas LREEs are concentrated in AGMs [13]. This relation is likely controlled by crystallographic constraints, because the size of the A-site is larger in AGMs relative to EGMs [13,43]. However, aeschynite-(Y), polycrase-(Y), and samarskite-(Y) from Arvogno pegmatites have very low LREE contents and almost identical HREE patterns or even lowest in samarskite-(Y). These characters are similar in trend for (Y-REE-U-Th)-(Nb-Ta-Ti) oxide of Trout Creek Pass which exhibited very similar REE patterns [42].

Zoned patterns of Y-REE-U-Nb-Ta-Ti-oxide minerals from Arvogno pegmatites were not overprinted by later alteration processes and/or weathering as is typical in almost all pegmatites [38]. Hence, we examined in detail zoned patterns (Figure 3) which were studied in detail in other Nb-Ta-Ti-oxide minerals—mainly in columbite-group minerals [61,62]. Aeschynite-(Y) from Bosco1,2 had a simple zoned pattern with a rather homogeneous core and regular perfectly parallel oscillatory to irregular oscillatory zoning (Figure 3a,b). Polycrase-(Y) associated with samarskite-(Y) (Bosco4) was

rather homogeneous as well as intergrowth samarskite-(Y). Oscillatory zoning in polycrase-(Y) from Fiume1 was similar to the aeschynite-(Y) in Bosco2. The zoned patterns of the examined aeschynite-(Y) and polycrase-(Y) were similar to those described in columbite-group minerals [61], although only aeschynite had the same crystal structure. Except for the sample Fiume1 (Figure 3f), they represent typical primary crystallization [61,62]. Irregular oscillatory zoning as overgrowths on polycrase-(Y) (Figure 3f) did not show any corrosive textures, so it was also very likely primary. The observed zoned patterns in both aeschynite- and euxenite-group minerals were very similar to columbite-group minerals and suggest that AB_2O_6 minerals record crystallization of host pegmatite in a very similar way via compositional zoning; however, due to the metamictization, zoned patterns were overprinted by alterations and metamictization.

The backscattered image of Bosco4 contained bright areas of samarskite-(Y) which developed at the rim and was an elongated and skeletal crystal towards the core of the polycrase-(Y). It is not clear if samarskite-(Y) represents relics replaced by polycrase-(Y) or an exsolution phase which in turn is stable at the temperature of crystallization of the “Bosco” dike. Bosco3 formed homogeneous pluricentimetric black masses with granular fracture at the core zone of the dike embedded in brownish, vitreous massive quartz. Capitani et al. [63] described that the crystal chemistry of samarskite-(Y) fits better the aeschynite structure than the columbite (or ixiolite) structure. Indeed, large ionic radius cations like Y and U can be better accommodated in the larger A-site found in polycrase-(Y)-type structures, which in turn is the polymorph of aeschynite-(Y).

11. Conclusions

Previous crystallographic data from the literature on samarskite from pegmatites [3,4,6] were always obtained by XRPD (X-ray powder diffraction) and this is the first study where cell data on samarskite-(Y) from pegmatites were obtained by SCXRD at room temperature. Low analytical totals measured for Bosco3 and Bosco4 samarskites showed vacancy at the Mn^{2+} and Fe^{3+} site and this could be charge balanced by the entrance of OH^- in respect to O^{2-} . According to Britvin et al. [8], the sum of Fe and Mn in the M group was less than 1.0 apfu indicating the possibility of incomplete occupancy (vacancies) in the M-site.

Raman spectroscopy was unable to identify water but FTIR (Fourier Transform Infrared Spectroscopy) and TGA (thermal gravimetric analysis) in the future could provide additional information for the presence of hydroxyl or water in samarskites. Taking into consideration that AGMs and EGMs have sensible iron contents, future Mossbauer spectra may discriminate and quantify the amounts of Fe^{3+} and Fe^{2+} .

Yttrium–niobium–titanium–tantalum oxides from Arvogno have the ionic exchange $Fe^{2+} + (Nb + Ta)^{5+} U^{4+} + Ti^{4+} \leftrightarrow (Y, Ln)^{3+} + Nb^{5+} (Y^{3+} + REE^{3+}) + Ti^{4+}$ which mainly regulates the compositional transition from ABX_2O_8 samarskite-(Y) to polycrase-(Y) and aeschynite-(Y) with an AB_2O_6 crystal structure. According to Britvin et al. [8], the thermal behavior of metamict samarskite-group minerals never result in the complete restoration of the original pre-metamict crystalline phase.

Skoda and Novak [38] described the ionic exchange mechanism of AB_2O_6 with U + Th, and Ca are involved as well and Arvogno samples have almost constant U + Th contents and Ca content is relatively high only in polycrase-(Y). Furthermore, the chemical variations of Bosco4 polycrase-(Y) and Fiume1 polycrase-(Y) are regulated by a further Ti and Y increase and by a Ta decrease at Nb almost constant, while the further transition to aeschynite-(Y) is regulated by an Nb decrease as well. Moreover, Bosco4 polycrase-(Y) differs from Fiume1 polycrase-(Y) because its more relevant Ca content. The Nb/Ta ratio was virtually constant in samarskite-(Y), while it may be variable in polycrase-(Y) and aeschynite-(Y) also at constant Ti contents.

The Raman spectra of polycrase-(Y), aeschynite-(Y), and samarskite-(Y) showed a certain degree of crystallinity (Figure 2f) which was significantly lower than in their synthetic analogues [64] or annealed samples [65,66].

Unaltered euxenite-group minerals contained very little Si and Ca and the absence of an aqueous fluid, and (Y-REE-U-Th)-(Nb-Ta-Ti) oxide minerals from Arvogno experienced no dissolution–precipitation reactions that led to the formation of nanoporosity or diffusion reactions, which usually allow the remobilization of U and strategic metals, like HFSE, at the scale of the pegmatite.

Brittle structures crosscutting the Vigezzo–Centovalli Valley are related to hydrothermal processes: they belong to mineralized faults, cataclasites, and were active during the late Alpine stage under variable P–T conditions, but at the earlier stage, they did not affect Arvogno pegmatites, resulting as a set of rigid fractures only affecting the pegmatites after their emplacement.

Previous studies [12] assumed different magmatic pulses occurred to emplace the pegmatite field of the Central Alps. As an example, the pegmatites that intruded the Codera and Bodengo areas (Figure 1) hosting rocks were dated at 28–25 m.y. or younger, around 20–22 m.y. [14]. Emplacement of these pegmatites could be related to the progressive regional metamorphic rejuvenation from east to west in the Central Alps, considering the progressive cooling of the thermal Lepontine Barrovian metamorphic dome [67].

It is worth mentioning that pegmatites of Arvogno have high contents of fluorite and they may crystallize at significantly lower temperatures [68] with respect to the crystallization temperatures of pegmatites within the Masino–Bregaglia intrusion (Br in Figure 1), where the emplacement temperatures of pegmatite dikes occurred at least at 550 °C [14].

Ta/Nb fractionation is generally well developed in Nb–Ta-oxide minerals from the REL–Li (rare-element–Li-bearing) pegmatites. The REL–REE (rare-element and rare-earth element) pegmatites of allanite-, euxenite-, and gadolinite-type from Arvogno reveal the activity of F does not affect Ta fractionation [69,70] and no Ta-bearing oxides were observed in these pegmatites.

The bulk composition, geochemistry, and structural geology data will be the subject of a forthcoming publication that will provide the conditions of emplacement for these unique NYF pegmatites in the Alpine chain and may give indications on crystallization processes which occur among aeschynite- (Y), polycrase-(Y), and samarskite-(Y) from Arvogno.

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