

Titanian Aeschnite-(Y) from Trimouns (French Pyrenees); review of the minerals of the aeschnite group

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Résumé

Le gisement de Trimouns (Ariège, Pyrénées) renferme plusieurs niveaux de dolomies blanches d'âge Ordovicien, particulièrement riches en minéraux de terres rares. Parmi ceux-ci une nouvelle variété d'aeschnite a été définie: l'aeschnite-(Y) titanifère. Le minéral se présente en prismes millimétriques transparents de couleur brun rosâtre. L'analyse chimique à la microsonde électronique a permis d'établir la formule suivante: $Ti_{2,20}(Y,Gd,Nd,Sm,Dy,Ce,Pr)_{1,06}(O,OH)_6$, soit idéalement: $Ti_2(TR)(OH)O_5$. Système orthorhombique, groupe spatial *Pbnm* avec $a = 5,174$, $b = 10,76$, $c = 7,59$ Å et $Z = 4$.

L'auteur passe en revue les différents minéraux du groupe de l'aeschnite et conclut par une discussion au sujet de leur nomenclature.

Mots-clés: aeschnite-(Y) titanifère. Trimouns, France, nomenclature.

Abstract

The talc deposit of Trimouns (Ariège, Pyrenees) includes several dolomitic levels with an Ordovician age, that are particularly rich in rare earth minerals. Amongst these, a new variety of titanian aeschnite-(Y) has been defined. The mineral occurs as millimetric transparent prisms of which the colour is pinkish brown. Chemical analysis with electron microprobe leads to the formula: $Ti_{2,20}(Y,Gd,Nd,Sm,Dy,Ce,Pr)_{1,06}(O,OH)_6$, or ideally: $Ti_2(REE)(OH)O_5$. System orthorhombic, space group *Pbnm* with $a = 5.174$, $b = 10.76$, $c = 7.59$ Å and $Z = 4$.

The author reviews the minerals of the aeschnite group and concludes with a discussion about their nomenclature.

Key-words: titanian aeschnite-(Y), Trimouns, France, nomenclature.

Introduction

The talc deposit of Trimouns, near Luzenac, is located in the department of Ariège in the French Pyrenees. The deposit was extensively described by FORTUNÉ *et al.* (1980), MOINE (1982) and MOINE *et al.* (1982). Geological and metallogenetic data given by these authors are summarized in a more recent paper of Piret *et al.* (1990) dealing with the description of the new REE mineral trimounsite-(Y) that occurs in the same deposit. A rich-association of rare earth minerals is located in the dolomitic levels of the roof of the talc deposit. In addition to

trimounsite-(Y), the association includes allanite, bastnaesite, hellandite, hinganite, iimoriite, monazite, synchisite and xenotime as well as a new variety of aeschnite described in the present paper. The samples containing aeschnite were kindly given to us by Pierre Gatel, president of the French Association of Micromineralogy.

Morphology and physical properties

The new variety of titanian aeschnite-(Y) is known in two specimens from Trimouns. The mineral occurs in little geodes within the white ordovician dolomitic rocks. It consists of tiny striated tablets up to 1 mm in length, 0.6 mm wide and 0.1 mm thick (Figure 1). The crystals are flattened on (010) and elongated along {100}. The colour of the transparent tablets is pink to light brown with a vitreous luster. Cleavage {010} is perfect and {100} is good. Mohs hardness is between 5 and 6. Density measured in heavy liquids is higher than 4.2 g/cm³.

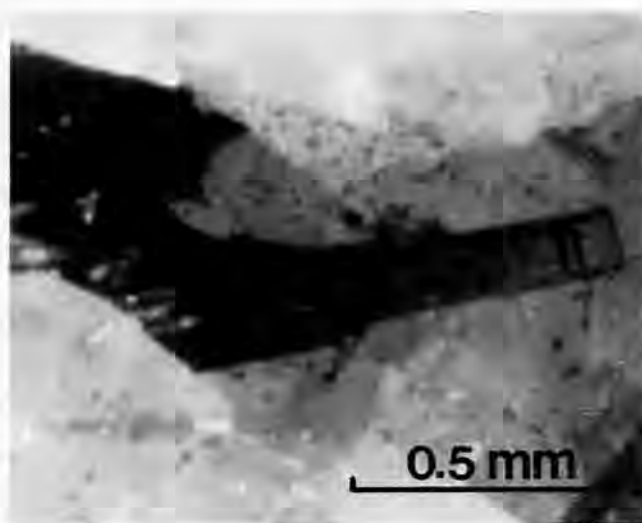


Fig. 1 – Flattened prism of titanian aeschnite-(Y) from Trimouns, associated with white crystals of dolomite.

Optical properties

Under the microscope, the tablets of titanian aeschynite-(Y) are colourless or very light brown, non pleochroic. The three indices of refraction are higher than 2.10. The mineral is biaxial negative with $2V$ near 80° . The optical orientation is as follow: $\alpha = a$ in the elongation, $\beta = c$ in the plane and $\gamma = b$ perpendicular to the plane. This orientation is identical to that of an yttrian aeschynite from Switzerland and opposite to these of two aeschynites from Alaska (where $\alpha = b$, $\beta = c$ and $\gamma = a$) and from Ural (where $\alpha = a$, $\beta = b$ and $\gamma = c$) (ROSENBLUM & MOSIER, 1975).

Chemical composition

Titanian aeschynite-(Y) was analyzed in the "Centre d'analyse par microsonde électronique pour les sciences de la Terre" (CAMST) of the University of Louvain-la-Neuve (analyst: J. Wautier). The standards were rutile for Ti and synthetic glasses of the Center of Volcanology of the University of Oregon for the RE elements. The K_α line was used for titanium and the L_α line for the rare earths. Titanian aeschynite-(Y) is anhydrous. The analytical results are summarized in Table 1. The experimental percentages represent the mean value of 11 analyses on two grains. The low total of 95.8% is due to the imperfect polish of the tiny scraps of crystal that could be used for the analyses. The empirical formula for 6 oxygens is: $Ti_{2.20}(Y_{0.53}Gd_{0.18}Nd_{0.11}Sm_{0.11}Dy_{0.09}Ce_{0.03}Pr_{0.01})_{\Sigma 1.06}O_6$ or ideally with respect to the equilibrium of the charges:

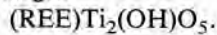


Table 1.

Chemical composition of titanian aeschynite-(Y) from Trimouns. 1: mean experimental percentages. 2: extreme percentages. 3: mole number for 6 oxygens

	1	2	3
TiO ₂	51,80	51,38	52,34
Y ₂ O ₃	15,80	13,42	19,12
Nd ₂ O ₃	5,62	3,55	7,24
Dy ₂ O ₃	5,19	4,65	5,52
Pr ₂ O ₃	0,29	0,01	0,50
Gd ₂ O ₃	9,83	9,51	10,54
Ce ₂ O ₃	1,47	0,90	1,88
Sm ₂ O ₃	5,80	4,16	6,43
Tb ₂ O ₃	n.d.		
Ho ₂ O ₃	n.d.		
Yb ₂ O ₃	n.d.		
	95,80		

Crystallography

The X-ray powder pattern of titanian aeschynite-(Y) is given in Table 2. The mineral is orthorhombic, space group *Pbnm*, with $a = 5.174(4)$, $b = 10.76(1)$, $c = 7.59(1)$ Å, $V = 323$ Å³ and $Z = 4$. The unit cell dimensions were calculated from the X-ray pattern. As shown in Table 3, no significant differences exist between the unit cell values for titanian aeschynite-(Y) and those of other minerals of the structural group of aeschynite.

Table 2.

X-ray powder pattern of titanian aeschynite-(Y) from Trimouns. 114.6 Debye-Scherrer camera, radiation Cu K α , Ni filter, $d(hkl)$ in Å, visually estimated intensities.

hkl	d _{calc}	d _{obs}	I _{vis}	hkl	d _{calc}	d _{obs}	I _{vis}
020	5,38	5,42	15	222	1,986	1,987	20
110	4,66	4,70	5	151	1,922	} 1,916	20
021	4,39	4,39	10	133	1,920		
111	3,97	3,96	10	004	1,898		
022	3,10	} 2,94	10	043	1,843	1,840	5
130	2,95		100	241	1,811	1,809	5
112	2,94	} 2,751	30	061	1,745	1,743	1
131	2,748			223	1,714	} 1,708	1
200	2,587	1,588	7	310	1,703		
041	2,535	2,536	3	242	1,674	1,674	2
140	2,387	2,389	1	134	1,596	1,594	3
141	2,277	2,279	5	153	1,563	1,564	7
221	2,229	2,225	5	330	1,554	1,552	7
123	2,094	2,096	1	331	1,523	1,525	2
231	2,022	2,025	1	322	1,507	1,504	2

Table 3.

Unit cell dimensions for 8 minerals of the aeschynite group. 1: Zhabin *et al.*, 1960. 2: Rosenblum & Mosier, 1975. 3: Adusumili *et al.*, 1974. 4: Kornetova *et al.* (in Adusumili *et al.*, 1974). 5: Chi Ling Yi, 1974. 6: this work. 7: Greaser *et al.*, 1979. 8: Foord & Mrose, 1978.

	a(Å)	b	c
Nioboaeschynite-(Ce) (1)	5.355	11.01	7.51
Nioboaeschynite-(Ce) (2)	5.396	11.085	7.585
Nioboaeschynite-(Y) (3)	5.34	10.97	7.38
Tantalian aeschynite-(Y) (4)	5.308	10.983	7.463
Taiyite-(Y) (5)	5.18	10.92	7.30
Titanaeschynite-(Y) (7)	5.174	10.76	7.59
Vigezzite (7)	5.36	11.028	7.559
Rynersonite (8)	5.37	11.063	7.505

The structure is a three-dimensional framework of (Nb,Ta,Ti) octahedra (Ti alone in the case of titanian aeschynite) that distinguish the minerals of the aeschynite group from other niobates and titano-niobates (columbite, fersmite, euxenite) of which the octahedra form isolated bi-dimensional groups (ALEKSANDROV, 1962).

The mineral of Trimouns and the aeschynite group

Aeschynite was discovered by BERZELIUS in 1828. The name originates from the Greek αἰσχυνή (shame) referring to the inability of the 19th century chemists to separate some of the constituents of the mineral at the time of the discovery (DANA, 1950). RAMMELSBURG (1875) published the original analysis of Berzelius: SnO₂ 0.5%, TiO₂ 56%, ZrO₂ 20%, Ce₂O₃ 15%, Fe₂O₃ or FeO 2.6% and CaO 3.8%. The early aeschynite was thus a complex oxide of Ti, Zr and Ce with minor Ca, Fe and Sn. It must be here stressed that: 1) zirconium is only mentioned as a minor element in a number of analyses of the 19th century and 2) niobium and tantalum appear to be missing in the analyses but were most likely not identified at that time (1928). RAMMELSBURG (1875) also give an analysis of 1867 that corresponds to the formula R₃Nb₂(Ti,Th)₃O₁₄ with R = Ce, La, Y, Ca and Fe. Other definitions of aeschynite during the 19th century were: zirconium titanate accompanied by several tantalates (LANDRIN, 1852); tantalate of iron, "Yttria" and lanthanum (LEYMERIE, 1859); titano-niobate of Th, Ce, La, Dy, Y, Fe and Ca (DE LAPPARENT, 1899). HINTZE (1938) regarded aeschynite as a niobate and a tantalate (thorate) of cerium metals, iron and calcium. He gave a review of the particularly complex formula proposed by several authors (GROTH & MIELEITNER, 1921); KOEHLIN, 1928 and TSCHERNIK, 1908). The number of cations appearing in the formula of the authors cited above are listed in Table 4. The more convenient analysis mentioned by HINTZE (1938) was

that of MACHATSCHKI (1932) with the formula XZ₂O₆ where X = Ca, Th, U and Ce and Z = Nb, Ta and Ti. From then onwards, this general expression was used for the minerals of the aeschynite group. Another mineral, of which the composition was very similar to that of the numerous aeschynites, has been described as priorite by BRÖGGER in 1879. It was in fact a titanoniobate of Y, Er, Ca, Fe and Th.

Only in 1966 were significant new data about the aeschynite group reported by FLEISCHER. This author reviewed 24 minerals of the aeschynite-priorite series and confirmed the general formula AB₂O₆, similar to that of MACHATSCHKI (1932). Aeschynite represents the cerian term whereas priorite is the yttrian one. In the same year, due to the nomenclatorial rules applied for the REE minerals (LEVINSON, 1966), only the name aeschynite was preserved. The name priorite (BRÖGGER, 1879) was then transformed into aeschynite-(Y).

Two other minerals were also deleted by FLEISCHER (1966): blömstrandline (BRÖGGER, 1906) and lyndochite (ELLSWORTH, 1927) changed into aeschynite-(Y) and nioboaeschynite-(Y) respectively. STRUNZ (1970) defined the aeschynite group as being rhombic dipyramidal, *Pbnm*. He mentioned 5 terms of the series:

- Y Ti NbO₆ (synthetic compound)
- (Y,Ce,Th,Na,U)(Ti,Nb,Ta)₂O₆ (Strunz named this mineral "priorite" although aeschynite-(Y) already has priority at that time)
- Ce Ti NbO₆ (synthetic compound)
- (Ce,Th,Ca)(Ti,Nb,Ta)₂O₆ or aeschynite (reference to BERZELIUS, 1828)
- Nioboaeschynite, a niobium-rich variety, see ZHABIN *et al.*, 1960.

Three additional minerals, belonging to the *Pbnm* structural group of aeschynite, were defined in the following years: taiyite, rynersonite and vigezzite. Taiyite, from Southern China (CHI LING YI, 1974) has the formula (REE,Al,Fe)(Ti,Si,Nb,Ta)₂(O,OH)₆. This mineral is indeed a particularly titanium-rich aeschynite-(Y) [Ti_{1.60}(Nb + Ta)_{0.15}] and the name was therefore refused by the commission on New Minerals and Mineral Names of the I.M.A. (Mineralogical Magazine 43, p. 1055, 1980) after its publication. Rynersonite (FOORD & MROSE, 1978) is a Californian species with formula Ca(Ta,Nb)₂O₆. It is chemically distinct from the defini-

Table 4.

Number of cations appearing in the formula proposed for aeschynite by Groth & Mieleitner (1921), Koechlin (1928) and Tschernik (1908)

	Ca	Fe	Ce	Y	Th	Ti	Nb	Ta
Groth & Mieleitner (1921)	—	2	—	4	—	8	—	6
Koechlin (1928)	—	2	—	4	—	8	—	6
Tschernik (1908)	3	4	8	2	4	19	12	2

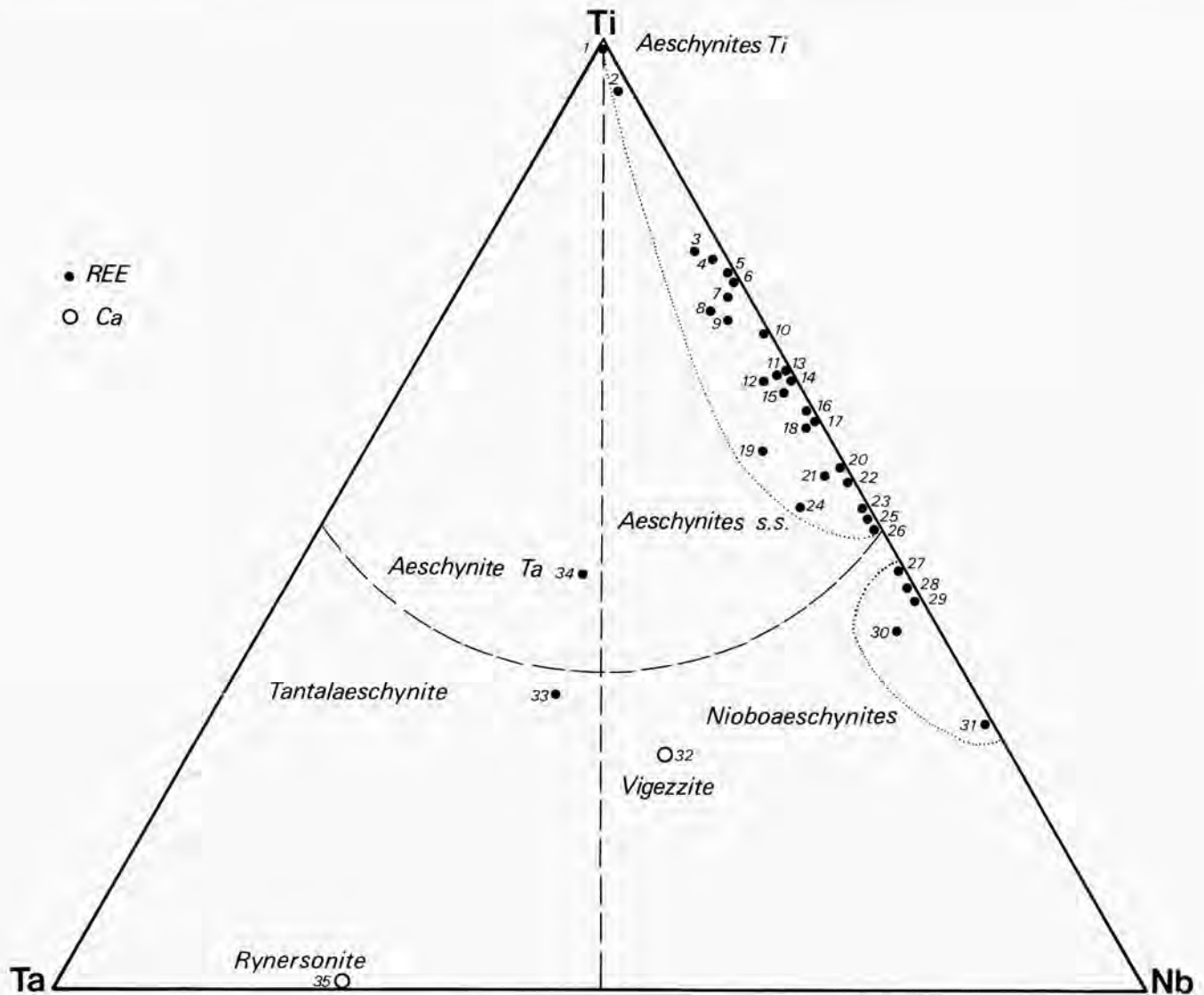


Fig. 2 – Ternary diagram Ti-Nb-Ta for the aeschnite group minerals.

1. Titanian aeschnite-(Y): Trimouns, French Pyrenees (this paper)
2. Taiyite: South China (CHI LING YI, 1974)
3. Blömstrandine: Ravsag, Norway (FLEISCHER, 1966)
4. Priorite: Miask, SSSR (DANA, 1946)
5. Thoro-aeschnite: Vishnevye Mts, Urals (FLEISCHER, 1966)
6. Priorite: Wolhynia, SSSR (DANA, 1946)
Priorite: Urstad, Hitterö (DANA, 1946)
7. Blömstrandine: Aktan massif, Uzbekhistan, SSSR (FLEISCHER, 1966)
8. Blömstrandine: Kabuland, Norway (FLEISCHER, 1966)
9. Aeschnite: Mongolia (FLEISCHER, 1966)
10. Aeschnite-(Nd): Inner Mongolia (ZHANG PEISHAN & TAO KEJIE, 1982)
11. Priorite: Arendal, Norway (DANA, 1946)
12. Sinicite: Ulashan, Mongolia (FLEISCHER, 1966)
13. Aeschnite: Vishnevye Mts, Urals (FLEISCHER, 1966)
14. Yttrium-aeschnite: Ilmen Mts, Urals, (FLEISCHER, 1966)
15. Blömstrandine: European SSSR (FLEISCHER, 1966)
16. Priorite: Eastern Siberia (FLEISCHER, 1966)
17. Aeschnite: Miask, SSSR (DANA, 1946)
18. Aeschnite: Ilmen Mts, Urals (FLEISCHER, 1966)
19. Aeschnite: Hitterö (DANA, 1946)
20. Aeschnite-(Nd): Inner Mongolia (ZHANG PEISHAN & TAO KEJIE, 1982)
21. Aeschnite: Vishnevye Mts, Urals (FLEISCHER, 1966)
22. Priorite: Urals (DANA, 1946)
23. Priorite: Eastern Siberia (FLEISCHER, 1966)
Priorite: Frikstad, Norway (DANA, 1946)
24. Aeschnite: locality unknown (FLEISCHER, 1966)
25. Priorite: Swaziland (DANA, 1946)
26. Aeschnite: Vishnevye Mts, Urals (FLEISCHER, 1966)
27. Lyndochite: China (FLEISCHER, 1966)
28. Nioboaeschnite-(Ce): Vishnevye Gor, Urals (ZHABIN *et al.*, 1960)
29. Nioboaeschnite-(Ce): Alaska (ROSENBLUM & MOSIER, 1975)
30. Lyndochite: Renfrew County, Ontario (ELLSWORTH, 1927)
31. Alumino-aeschnite: Vishnevye Mts, Urals (FLEISCHER, 1966).
32. Vigezzite: Orcesco, Italian Alps (GRAESER *et al.*, 1979)
33. Tantaloeschnite-(Y): Borborema, N-E Brazil (ADUSUMILI *et al.*, 1974)
34. Tantalian aeschnite (Y): Siberia (Adusumili *et al.*, 1974)
35. Rynersonite: San Diego County, California (FOORD & MROSE, 1978)

tion of aeschynite (HINTZE, 1938) as it is devoid of REE in the "A" term and of Ti in the "B" term of the general formula AB_2O_6 . Vigezzite (GRAESER *et al.*, 1979) with formula $(Ca,Ce)(Nb, Ta,Ti)_2O_6$ occurs in the Italian Alps. The authors considered this mineral of the aeschynite group as the first one with $Nb > Ta$. According to us however, the predominance of Nb compared to Ta rather appears to be characteristic of most aeschynites. Contrary to this, vigezzite is characterized by its high tantalium content and a relatively fair titanium content. The essential difference is that the "A" site of vigezzite is occupied by major Ca (12% CaO) with respect to the REE. It forms thus a distinct species in the aeschynite group. Vigezzite is the Nb equivalent of Tarich rynersonite.

With respect to the impact of the relative proportions of Ti, Ta and Nb (ratio Ti: Nb: Ta with Nb = 1) on the nomenclature of the aeschynite group, 3 possible situations exist:

1. $Ti > 1$, corresponding to aeschynite s.s.
2. $Ti < 1$ and $Nb > Ta$, corresponding to nioboaeschynite (ROSENBLUM & ROSIER, 1975),
3. $Ti < 1$ and $Nb < Ta$, corresponding to tantalaeschynite (Adusumili *et al.*, 1974)

It is clearly shown on the diagram of Figure 2 that most aeschynites s.s. ($Ti > 1$) are particularly rich in Nb and frequently devoid of Ta. This is the reason why ADUSUMILI *et al.* (1974) proposed the name tantalian aeschynite for an aeschynite ($Ti > 1$) with $Ti:Nb:Ta = 1.04:1:1.26$.

The mineral of Trimouns clearly belongs to the aeschynite group because of its space group *Pbnm* and its general chemical formula AB_2O_6 . Nevertheless it differs from the general definition by the lack of Nb and Ta in its chemical composition. The mineral does not exactly correspond to the redefinition of Hintze (1938) as niobotantalate of cerium metals, calcium and iron. The mineral of Trimouns represents thus an extreme titanium-rich term located at the "Ti" summit of the Ti-Nb-Ta diagram of Figure 2.

Therefore, we propose the term titanian aeschynite-(Y) for this variety. To avoid confusion in the nomenclature, the former suggestion of ZHABIN *et al.* (1960) must be here definitively rejected. These authors proposed the name "titanaeschynite" for an aeschynite of which Nb: Ti ratio was less than 0.5. As most aeschynites have an Nb: Ti ratio < 1 (frequently < 0.5), FLEISCHER (1962) had

already deleted that name. The former "taiyite" (CHI LING YI, 1974) in which Nb: Ti = 0.07 should therefore also be considered as a titanian aeschynite.

Conclusion

1. The aeschynite group includes orthorhombic *Pbnm* minerals of which the general chemical formula is AB_2O_6 with A = REE, Ca and Th, with accessory Fe, Mn, U, Na and Mg whereas B = Nb, Ta and Ti, with accessory Al and Si.
2. Aeschynite s.s. is the term characterized by A = REE predominated and B = Nb, Ta and Ti. Nioboaeschynite (ZHABIN *et al.*, 1960) corresponds to the variety with $Nb > Ti$ and tantalaeschynite (ADUSUMILI *et al.*, 1974) is the species where $Ta > Ti$.
3. Blömstrandine (BRÖGGER, 1906), priorite (BRÖGGER, 1879) and lyndochite (ELLSWORTH, 1927) are discredited minerals after comparison to aeschynite (FLEISCHER, 1966; LEVINSON, 1966). Priorite and blömstrandine are now aeschynite-(Y) and lyndochite is now nioboaeschynite-(Y).
4. Vigezzite (GRAESER *et al.*, 1979) is a niobian mineral of the aeschynite group characterized by the predominance of Ca with respect to the rare earth elements.
5. Rynersonite (FOORD & MROSE, 1978) is the term used for the aeschynite group mineral characterized by A = Ca (without REE) and B = Ta and Nb (without Ti).
6. The mineral of Trimouns is characterized by A = REE and B = Ti (without Nb nor Ta). We propose therefore to qualify this variety as titanian aeschynite-(Y).
"Taiyite" (CHI LING YI, 1974) is another example of less pure titanian aeschynite.

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