Titanian Aeschynite-(Y) from Trimouns (French Pyrenees); review of the minerals of the aeschynite group

by Michel DELIENS

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’aeschynite a été définie: l’aeschynite-(Y) titanifère. Le minéral se présente en prismes millimétriques transparents de couleur brun rosâtre. L’analyse chimique à la microsonde a permis d’établir la formule suivante: Ti_{2.20}(Y,Gd,Nd,Sm,Dy,Ce,Pr)_{0.06}(O,OH)_{6.0} soit idéalement: Ti_3(TH)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’aeschynite et conclut par une discussion au sujet de leur nomenclature.

Mots-clés: aeschynite-(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 aeschynite-(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)_{0.06} (O,OH)_{6.0} or ideally: Ti_3(REE)(OH)_{6}. 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 aeschynite group and concludes with a discussion about their nomenclature.

Key-words: titanian aeschynite-(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 FORTUNE 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, bastnasite, hollandeite, hinganite, ilmonite, monazite, synchisite and xenotime as well as a new variety of aeschynite described in the present paper. The samples containing aeschynite were kindly given to us by Pierre Gatel, president of the French Association of Micromineralogy.

Morphology and physical properties

The new variety of titanian aeschynite-(Y) is known in two specimens from Trimouns. The mineral occurs in little geodes within the white ordovician dolomite 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 aeschynite-(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: α = a in the elongation, β = c in the plane and γ = b perpendicular to the plane. This orientation is identical to that of an yttrian aeschynite from Switzerland and opposite to these of two aesthesites from Alaska (where α = b, β = c and γ = a) and from Ural (where α = a, β = b and γ = 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 and synthetic glasses of the Center of Volcanology of the University of Oregon for the RE elements. The Kα line was used for titanium and the Lα 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: 

\[(\\text{REE})_7\text{Ti}_2(\text{OH})_6\text{O}_8\]

or ideally with respect to the equilibrium of the charges:

\[(\\text{REE})_7\text{Ti}_2(\text{OH})_6\text{O}_8\]

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

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<tr>
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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, \(V = 323\) Å 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 Kα, Ni filter, d(hkl) in Å, visually estimated intensities.

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<th>dobs</th>
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</table>
Titanian aeschynite-(Y) from Trimouns 233

Table 3.

<table>
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<tr>
<th>Mineral</th>
<th>a(A)</th>
<th>b</th>
<th>c</th>
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<td>Nioboaeschynite-(Ce)</td>
<td>5.355</td>
<td>11.01</td>
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<td>5.396</td>
<td>11.085</td>
<td>7.585</td>
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<td>Nioboaeschynite-(Y)</td>
<td>5.34</td>
<td>10.97</td>
<td>7.38</td>
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<td>Tañtalian aeschynite-(Y)</td>
<td>5.308</td>
<td>10.983</td>
<td>7.463</td>
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<td>Taiyite-(Y)</td>
<td>5.18</td>
<td>10.92</td>
<td>7.30</td>
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<td>Titanoaeschynite-(Y)</td>
<td>5.174</td>
<td>10.76</td>
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<td>Vigezzite</td>
<td>5.36</td>
<td>11.028</td>
<td>7.559</td>
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<tr>
<td>Rynersonite</td>
<td>5.37</td>
<td>11.063</td>
<td>7.505</td>
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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 titanio-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 αἰσχύνη (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). Rammelsberg (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). Rammelsberg (1875) also give an analysis of 1867 that corresponds to the formula R₄Nbx(Ti, Th)₁O₁₄ with R = Ce, La, Y, Ca and Fe. Other definitions of aeschynite during the 19th century were: zirconium titanate accompanied by several tanta-
lates (Landrin, 1852); tantalate of iron, “Yttria” and lanthanum (Leymerie, 1859); titanio-niobate of Th, Ce, La, Dy, Y, Fe and Ca (de Lapparent, 1899). Hinteze (1938) regarded aeschynite as a niobate and a tantalate (thorite) of cerium metals, iron and calcium. He gave a review of the particularly complex formula proposed by several authors (Groth & Mieleitner, 1921; Koechlin, 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 Hinteze (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 titanoniobiate 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 nomenclatural rules applied for the REE minerals (Levinston, 1966), only the name aeschynite was preserved. The name priorite (Brögger, 1879) was then transformed into aeschynite-(Y).

The other two minerals were also deleted by Fleischer (1966): blomstrandline (Brögger, 1906) and lyndochite (Ellsworth, 1927) changed into aeschynite-(Y) and nioboaeschynite-(Y) respectively. Strunz (1970) defined the aeschynite group as being rhombo 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)₂O₆(OH)₆. This mineral is indeed a particularly titanium-rich aeschynite-(Y) [Ti₁.₄₋₅(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)

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<th>Mineral</th>
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<th>Fe</th>
<th>Ce</th>
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<th>Th</th>
<th>Ti</th>
<th>Nb</th>
<th>Ta</th>
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<td>-4</td>
<td>-8</td>
<td>-6</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Koechlin (1928)</td>
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<td>-4</td>
<td>8</td>
<td>6</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Tschernik (1908)</td>
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<td>2</td>
<td>4</td>
<td>19</td>
<td>12</td>
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</table>
Fig. 2 – Ternary diagram Ti-Nb-Ta for the aeschynite group minerals.
1. Titanian aeschynite-(Y): Trimouns, French Pyrenees (this paper)
2. Taiyite: South China (CHI LING YI, 1974)
4. Priorite: Miask, SSSR (DANA, 1946)
5. Thoro-aeschynite: Vishnevye Mts, Urals (FLEISCHER, 1966)
6. Priorite: Wolhynia, SSSR (DANA, 1946)
8. Blömstrsandline: Käbuland, Norway (FLEISCHER, 1966)
10. Aeschynite-(Nd): Inner Mongolia (ZHANG PEISHAN & TAO KEJIE, 1982)
11. Priorite: Arendal, Norway (DANA, 1946)
15. Blömstrsandline: European SSSR (FLEISCHER, 1966)
17. Aeschynite: Miask, SSSR (DANA, 1946)
19. Aeschynite: Hitterö (DANA, 1946)
22. Priorite: Urals (DANA, 1946)
25. Priorite: Swaziland (DANA, 1946)
27. Lyndochite: China (FLEISCHER, 1966)
30. Lyndochite: Renfrew County, Ontario (ELLSWORTH, 1927)
32. Vigezzite: Oresesco, Italian Alps (GRAESER et al., 1979)
33. Tantalaoeschynite-(Y): Borborema, N-E Brazil (ADUSU-MILL et al., 1974)
34. Tantalian aeschynite (Y): Siberia (Adusumilli 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 AB₂O₆. Vigezzitite (GRAESER et al., 1979) with formula (Ca,Ce)(Nb, Ta, Ti)₂O₆ 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 tantalum 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 Tar-rich 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 nioboaeschy-nite (ROSENBLUM & ROSIER, 1975),
3. Ti < 1 and Nb < Ta, corresponding to tantalaeaeschynite (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 tantalitaeeschynite 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 AB₂O₆. 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 definition 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 titanaeschynite-(Y) for this variety. To avoid confusion in the nomenclature, the former suggestion of ZHABIN et al. (1960) must be her definitively rejected. These authors proposed the name “titanoeschynite” 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 titanaeschynite.

Conclusion

1. The aeschynite group includes orthorhombic Pbnm minerals of which the general chemical formula is AB₂O₆ 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 tantaloeschynite (ADUSUMILI et al., 1974) is the species where Ta > Ti.

3. Blömandridine (BRÖGGER, 1906), priorite (BRÖGGER, 1879) and lyndochite (ELLSWORTH, 1927) are discredited minerals after comparison to aeschynite (FLEISCHER, 1966; LEVINSON, 1966). Priorite and blomstrandrandine 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 titanaeschynite-(Y).

“Taiyite” (CHI LING YI, 1974) is another example of less pure titanaeschynite.

Acknowledgements

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M. DELIENS
Institut royal des Sciences naturelles de Belgique
Section de Minéralogie et de Pétrographie
Rue Vautier, 29
B-1040 Bruxelles, Belgique

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