

Crystal chemistry of aeschynite-(Y) from the Western Alps: residual electron density on difference-Fourier map

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Abstract: Crystal structure and chemical composition of five crystals of non-metamict aeschynite-(Y) from the Western Alps were investigated. In the whole the structure previously determined on heat-treated crystals of aeschynite was confirmed. Nevertheless an interesting feature emerged from the structure refinements concerning the presence of a residual density maximum of approximately $3 \div 5 \text{ e}^-/\text{\AA}^3$ (C site) in the difference Fourier map. The addition of the C site to the structural model significantly improved the final *R* factors in all refined samples. The C site is asymmetrically located within an eight-fold cavity, similar in shape to that occupied by A cations. The short A–C distances led to the assumption that the presence of atoms in the C-site is coupled with structural vacancies in A. The implications in the calculation of chemical formulae are discussed.

Key-words: aeschynite-(Y), Ti-Nb-Ta-oxides, structure refinement, metamict minerals.

Introduction

Members of the aeschynite series (type formula AB_2O_6 , with A = Y, REE, Th, U, Ca... and B = Ti, Nb, Ta, W...) occur as late-stage minerals in granites, pegmatites, alkaline and carbonatite complexes, and hydrothermal veins. The crystal structure and the compositional variation exhibited by naturally occurring aeschynites confirm that they accommodate high contents of U and Th. As a consequence of the alpha-decay associated to these radionuclides, aeschynites are commonly found as metamict minerals. Previous crystal-chemical studies were mainly performed, therefore, on annealed natural metamict material or synthetic analogues (Aleksandrov, 1962; Komkov *et al.*, 1962; Aleksandrov, 1963; Komkov & Belopol'skiy, 1966). Over the last thirty years, a number of aeschynites from Alpine and sub-Alpine terrains have been described (Sommerauer & Weber, 1972; Graeser & Roggiani, 1976; Gramaccioli, 1977; Turconi, 1985; Albertini & Andersen, 1989; Bonazzi & Magnanelli, 1994). These samples, compared to those from older rocks, show only minor effects of radiation damage, and therefore

give the opportunity to examine natural material by means of single-crystal X-ray diffraction.

This work was undertaken to obtain structural data on untreated aeschynite crystals which show only faint effects of incipient radiation damage.

Samples

Granitic samples containing non-metamict or partially metamict aeschynite-(Y) from four different sites in the Western Alps (Table 1) were collected. Aeschynite-(Y) always occurs as minute tabular crystals, orange-brown to black in color, with resinous luster, and irregular to conchoidal fracture, scattered within miarolitic cavities in the rock.

Numerous crystals were separated by hand-picking and preliminarily screened on the basis of their optical properties. Crystals which did not exhibit evident darkening of color or appreciable lowering of birefringence were selected and their X-ray diffraction quality was checked by means of oscillating crystal photographs. Diffraction effects of crystals apparently single, ranged from weak powder-like diffraction cones to single broad spots. Five tiny single crystals suitable for

Table 1. Samples of aeschyanite-(Y) examined in this study.

	Sampling locality	Associated minerals
TR	Triolet Valley, Valle d'Aosta (Aosta, Italy)	Qtz + Or + Ab + Ms + Chl + Ttn + Zrn + Ant + Ilm + Ap + Cal + thorite + thorianite
MI	Miage Glacier moraine, Veny Valley, Valle d'Aosta (Aosta, Italy)	Qtz + Or + Ab + Ms + Ant + Ap + sinchisite
CE	Pizzo Cervandone (Novara, Italy)	Qtz + Ab + Ms + Bt
VV	Vigezzo Valley (Novara, Italy)	Qtz + Or + Ms + Bt + Mag + Ilm

Note: symbols for rock-forming minerals after Kretz (1983)

the structural study were selected and labelled according to the sampling localities (TR1 and TR2 = Triolet Valley, MI = Miage moraine, CE = Pizzo Cervandone, VV = Vigezzo Valley).

Chemical composition

Quantitative chemical analyses were carried out using a Jeol JXA-8600 electron microprobe equipped with a Tracor-Northern 5600 system. The analyses were performed using $K\alpha$ lines for Ca, Fe and Ti, $L\alpha$ for Y, Nb, and Ta, $M\alpha$ for W, Th and U. In order to avoid the intra-REE interferences, La, Ce, Dy, Er and Yb were determined on the $L\alpha$ peaks, and Nd, Pr, Sm and Gd on the $L\beta$ peaks. The REE standards used were those of Drake & Weill (1972). F, Eu, Tb, Ho, Tm were not included in the file since preliminary checks showed undetectable amounts of these elements. The results of the analyses are reported in Table 2. Analytical totals range from 96.82 to 97.79 wt.%, thus suggesting significant H_2O content. The presence of absorbed water, in fact, is a common feature of metamict or partially metamict Nb-Ta-Ti oxides (Ewing, 1975); on the other hand, the substitution of hydroxyl groups for oxygen atoms is required for the charge balance in the formula (Σ charge of cations ranging from 11.24 to 11.77 instead of 12.00). The presence of OH^- in the structure was already observed in the sample from Triolet Valley by means of infrared spectrometry (Bonazzi & Magnanelli, 1994). Among the B-type cations, titanium largely prevails and it almost fills the octahedral site in the crystals MI and TR1. On the other hand, VV shows the greatest amount of Nb and Ta substituting for Ti. An unusually high content of W, already detected in the sample from Triolet Valley (Bonazzi & Magnanelli, 1994), seems to be a common feature for all the aeschynites examined from the Western Alps. The dominant A-type cation Y fills over half the

site in all the crystals, which are also strongly enriched in intermediate and heavy REE, as expected for yttrium bearing minerals. Significant contents of Th and U are found in all samples. On the whole, the aeschynite-(Y) from Triolet Valley and Miage moraine, both related to the leucocratic facies of Mont-Blanc granite (D'Amico, 1974), are very similar as for their chemical composition. In particular, they are characterized by high contents of Ti. Even higher contents of titanium were only found in the aeschynite-(Y) from Tirmouns (French Pyrenees) while Nb and Ta were not detected (Deliens, 1991). Significant amounts of Nb are found in the sample from Cervandone and even higher contents in that from Vigezzo Valley.

X-ray data collection and structure refinements

Intensity data were collected by means of an Enraf Nonius CAD4 diffractometer using graphite-monochromatized $MoK\alpha$ radiation. Reflections were broad but no extra reflections were observed. Data corrected for Lorentz-polarization effects and for absorption using the semiempirical method of North *et al.* (1968) were consistent with the space group $Pnma$. Structure refinements were performed using the program SHELX (Sheldrick, 1976) starting from the atomic positional parameters of vigezzite ($CaNb_2O_6$) published by Giuseppetti & Tadini (1990). Scattering factors (Y *versus* Dy and Ti *versus* W for A sites respectively) as well as correction factors for anomalous dispersion were taken from the International Tables for X-ray Crystallography (Ibers & Hamilton, 1974). Convergence was rapidly obtained for an anisotropic model of the structure. However, the difference-Fourier synthesis calculated after the last cycle of refinement showed for each crystal the presence of an additional peak (here named C site) with an electron density ranging from 3.1

Table 2. Electron microprobe analyses (wt.%) and atomic ratios (on the basis of 3 cations) for aeschynite-(Y) from the Western Alps.

	TR1	MI	TR2	CE	VV
#	2	4	4	6	5
TiO ₂	48.93	46.89	42.26	42.89	31.04
Nb ₂ O ₅	2.22	1.33	3.69	6.56	13.23
Ta ₂ O ₅	0.25	-	0.35	0.83	13.71
WO ₃	2.14	2.72	7.25	4.20	2.93
CaO	0.14	0.08	0.27	0.03	0.20
FeO	-	-	-	0.32	0.66
Y ₂ O ₃	22.69	18.26	18.19	20.56	20.33
La ₂ O ₃	-	0.03	-	-	0.04
Ce ₂ O ₃	0.26	0.45	0.52	0.05	0.23
Pr ₂ O ₃	0.05	0.17	0.11	-	0.04
Nd ₂ O ₃	0.57	1.64	1.27	0.27	0.71
Sm ₂ O ₃	0.56	1.76	0.79	0.67	0.83
Gd ₂ O ₃	3.90	3.96	4.80	3.04	2.10
Dy ₂ O ₃	3.81	4.00	4.29	4.22	2.15
Er ₂ O ₃	2.06	2.46	1.87	2.28	1.22
Yb ₂ O ₃	1.58	1.78	1.25	1.48	0.96
ThO ₂	5.06	9.94	8.08	3.45	4.78
UO ₂	3.47	1.35	2.32	6.10	2.63
total	97.69	96.82	97.31	96.98	97.79
Ti ⁴⁺	1.946	1.949	1.811	1.798	1.406
Nb ⁵⁺	0.053	0.033	0.095	0.165	0.360
Ta ⁵⁺	0.004	-	0.006	0.013	0.225
W ⁶⁺	0.029	0.039	0.107	0.061	0.046
Ca ²⁺	0.008	0.005	0.017	0.001	0.013
Fe ²⁺	-	-	-	0.015	0.033
Y ³⁺	0.639	0.537	0.552	0.610	0.652
La ³⁺	-	0.001	-	-	0.001
Ce ³⁺	0.005	0.009	0.011	0.001	0.005
Pr ³⁺	0.001	0.003	0.002	-	0.001
Nd ³⁺	0.011	0.032	0.026	0.005	0.015
Sm ³⁺	0.010	0.034	0.016	0.013	0.017
Gd ³⁺	0.068	0.072	0.091	0.056	0.042
Dy ³⁺	0.065	0.071	0.079	0.076	0.042
Er ³⁺	0.034	0.043	0.034	0.041	0.023
Yb ³⁺	0.025	0.030	0.022	0.025	0.018
Th ⁴⁺	0.061	0.125	0.102	0.044	0.066
U ⁴⁺	0.041	0.017	0.029	0.076	0.035
Σ _{(B+C)cat.}	2.032	2.021	2.019	2.037	2.037
Σ _{(A)cat.}	0.968	0.979	0.981	0.963	0.963
Σ _{ch} *†	11.24	11.27	11.45	11.44	11.77

Note: # = number of analyses for each crystal;

*Σ_{ch} = sum of cation charge, assuming Fe as divalent and U as tetravalent.

e-/Å³ (crystal MI) to 4.6 e-/Å³ (crystal VV). We chose one (TR2) of the five structure refinements to check the reliability of this feature. Further re-

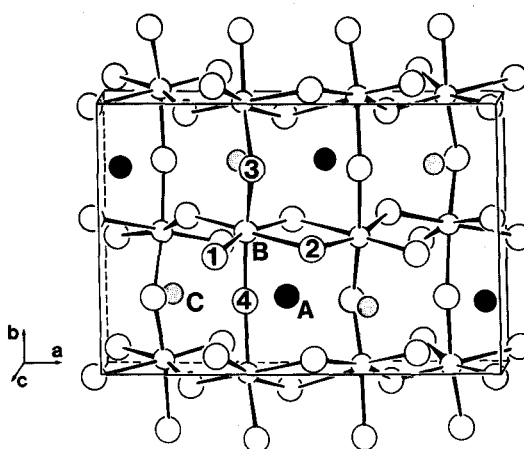


Fig. 1. Octahedral framework of aeschynite with A (black circles) and C (grey circles) cations.

finements were then performed with the C site included in the model. Coordinates, isotropic displacement parameter and occupancy factor (scattering factors of W versus vacancy) of the C site were left to vary without any constraint and the final *R* factor improved significantly. On the basis of the Hamilton test (Hamilton, 1965) (for TR2 crystal, $R = 4.26/3.59 = 1.187 > R_{4.520,0.005} = 1.015$), such an improvement should be considered highly significant. Therefore, the C site was included in the final model and the *R* factor became significantly lower for each crystal. Table 3 reports the unit cell parameters, determined by centering 25 reflections with θ angle ranging from 16 to 26°, together with some details of data collection and structure refinement. Atomic coordinates and equivalent isotropic parameters are given in Table 4.

Discussion

The crystal structure first determined by Aleksandrov (1962) on a heated crystal was substantially confirmed. The structural arrangement consists of a framework made up by sharing either corners and edges of (T,Nb)O₆ octahedra. In particular, pairs of edge-sharing octahedra are connected by corners to form double chains running along the *b* axis (Fig. 1). Double chains are linked by octahedral corners to provide the three-dimensional linkage. The structure projected down the *b* axis (Fig. 2) shows zig-zag bands of octahedral pairs and the large channels, centered by the

Table 3. Crystal data and experimental details.

<i>Crystal</i>	<i>TR1</i>	<i>MI</i>	<i>TR2</i>	<i>CE</i>	<i>VV</i>
space group	<i>Pnma</i>	<i>Pnma</i>	<i>Pnma</i>	<i>Pnma</i>	<i>Pnma</i>
cell parameters (Å)					
<i>a</i>	10.862(2)	10.803(2)	10.904(3)	10.881(2)	11.031(3)
<i>b</i>	7.483(3)	7.532(2)	7.490(3)	7.484(2)	7.448(2)
<i>c</i>	5.150(1)	5.180(1)	5.189(1)	5.156(1)	5.188(1)
<i>V</i> (Å ³)	418.6(2)	421.5(2)	423.8(3)	419.9(2)	426.2(2)
crystal size (µm)	60x120x210	60x60x90	30x150x270	120x60x45	60x180x200
θ - range (°)	2-30	2-30	2-32	2-30	2-30
scan mode	ω	ω	ω	ω	ω
scan width (°)	2.8	2.8	4.5	2.8	2.8
scan speed (°/min)	2.3	1.8	1.1	1.5	0.9
independent refl.	627	611	744	600	592
observed refl.	431	436	572	378	357
<i>F</i> _o > <i>n</i> σ(<i>F</i> _o)	<i>n</i> = 8	<i>n</i> = 8	<i>n</i> = 8	<i>n</i> = 6	<i>n</i> = 6
<i>R</i> _{merge} (%)	5.40	1.95	2.82	2.08	1.91
<i>R</i> (%) *	4.40	3.05	4.26	3.88	3.93
<i>R</i> (%)	3.40	2.65	3.59	2.89	3.08
<i>R</i> _w (%)	3.40	2.04	2.94	2.89	3.08

Note: * *R* index obtained for the model without the C site.

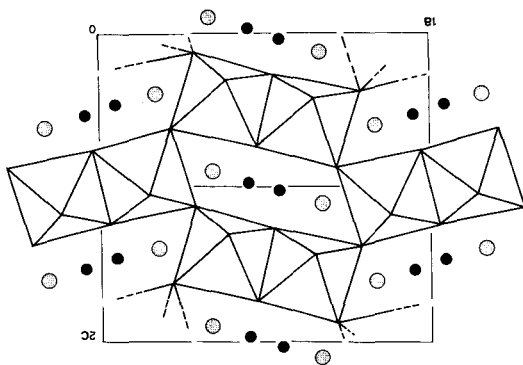


Fig. 2. Zig-zag bands of octahedral pairs with A (black circles) and C (grey circles) cations inside the channels (projection along the *b* axis).

screw diad axis, where the A and C sites take place. According to the nomenclature proposed by Britton & Dunitz (1973), the A-cavity ideally

corresponds to a C_{2v} (*n*.52) polyhedron (eight-fold coordination). The mean <A-O> distance, which shows a rough inverse relation to the Y content, ranges from 2.379 Å (CE) up to 2.406 Å (MI); a greater <A-O> distance was found in vigezzite (Giuseppetti & Tadini, 1990) where A is occupied by Ca and, to a lesser extent, by Ce. As for its shape, the C cavity closely resembles the A cavity. The electron density peak is asymmetrically located within the cavity, so that the C-O distances appear to be spread over a wider range than the A-O distances. There are six neighboring oxygens located at the vertices of trigonal prism (mean <C-O>_{VI} distances ranging from 2.29 to 2.33 Å), and two additional oxygens at longer distances (2.64 ÷ 2.66 Å). The quite short A-C distance (2.51 ÷ 2.57 Å) leads to the assumption that the presence of atoms in the C-site is coupled with structural vacancies in A ($\Sigma_{(A+C)cations} \leq 1.0$ a.p.f.u.). Due to the short C-O4 distances (2.02 ÷ 2.19 Å), we hypo-

thesized that only relatively small cations (B type cations) can enter the C site. The formula of aeschynite should then be written as $A_{1-x}B_2C_x(O, OH)_6$. This implies that the chemical formula should be calculated on the basis of $\Sigma_{(A+B+C)}\text{cations} = 3.0$ a.p.f.u., rather than $\Sigma_{B\text{cations}} = 2.0$ a.p.f.u.. The refinement of the occupancy factor for the C site led to a mean electron number ($1.4 \div 3.2$) corresponding, tentatively, to $0.06 \div 0.15$ a.p.f.u. of Ti or $0.03 \div 0.08$ a.p.f.u. of Nb, or $0.02 \div 0.04$ of Ta or W. The hypothesis that $\Sigma_{(B+C)}\text{cations}$ can be slightly greater than 2.0 accounts for the fact that aeschynite minerals usually show a Σ_B/Σ_A ratio >2 . According to Van Wambeke (1970) and Ewing (1975), both primary and secondary alteration could produce deficiency of the A-type cations. However, how to identify which chemical species and, correspondingly, how many atoms enter the C site is a fairly arduous task. In the crystals examined, $\Sigma_{B\text{cations}}$ only slightly exceeds 2.00; therefore, we arbitrarily assumed that W^{6+} enters the C cavity. The small ionic radius of W^{6+} accounts for the shortest C-O distance (C-O4 ranges from 2.02 and 2.19 Å).

The mean $\langle B-O \rangle$ distance ranges from 1.973 Å (TR1) to 1.989 Å (VV), in relation to the Nb+Ta/Ti+W ratio. In vigezzite, where Nb-Ta largely prevails on Ti (Graeser *et al.*, 1979), the $\langle B-O \rangle$ distance is 1.991 Å (Giuseppetti & Tadini, 1990), while a value of 2.021 Å was found for the mean octahedral $\langle Nb-O \rangle$ distance in the synthetic $CaNb_2O_6$ (Cummings & Stanley, 1970), which, however, crystallizes in the *Pbcn* space group (euxenite-type structure).

Chemical formulae

On the basis of the available data and keeping in mind the crystal-chemical relations discussed above, the following formulae were obtained:

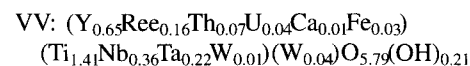
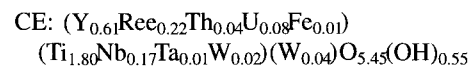
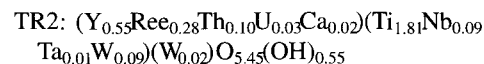
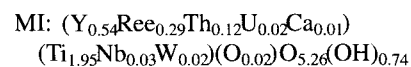
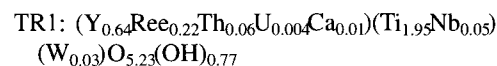


Table 4. Fractional atomic coordinates and equivalent isotropic displacement parameters together with their standard deviations in parenthesis.

		TR1	MI	TR2	CE	VV
A	x	.4503(1)	.4503(1)	.4513(1)	.4506(1)	.4529(1)
	y	.25	.25	.25	.25	.25
	z	.0333(2)	.0305(1)	.0344(1)	.0358(2)	.0402(3)
	U_{eq}	.0150(2)	.0075(1)	.0188(2)	.0111(3)	.0121(4)
B	x	.3593(1)	.3595(1)	.3588(1)	.3589(1)	.3579(1)
	y	.5137(2)	.5153(1)	.5119(2)	.5116(2)	.5077(2)
	z	.5446(2)	.5436(2)	.5427(3)	.5440(4)	.5436(3)
	U_{eq}	.0204(4)	.0122(3)	.0227(5)	.0152(5)	.0122(3)
C	x	.177(3)	.178(3)	.171(3)	.178(2)	.171(2)
	y	.25	.25	.25	.25	.25
	z	.603(6)	.598(6)	.607(5)	.602(4)	.595(4)
	U_{eq}	.023(7)	.011(5)	.020(5)	.024(6)	.019(7)
O1	x	.2868(5)	.2865(4)	.2873(6)	.2872(7)	.2886(8)
	y	.4354(9)	.4370(5)	.4381(8)	.4342(9)	.4338(12)
	z	.8778(12)	.8772(7)	.8780(9)	.8707(13)	.8803(18)
	U_{eq}	.024(2)	.014(1)	.025(2)	.016(2)	.021(2)
O2	x	.5262(6)	.5261(4)	.5269(6)	.5261(6)	.5260(7)
	y	.4568(8)	.4571(4)	.4576(7)	.4560(9)	.4555(12)
	z	.7373(12)	.7353(8)	.7367(10)	.7388(14)	.7379(17)
	U_{eq}	.025(2)	.016(1)	.026(2)	.017(2)	.019(3)
O3	x	.6190(8)	.6204(5)	.6182(9)	.6177(9)	.6169(11)
	y	.25	.25	.25	.25	.25
	z	.3114(19)	.3133(11)	.3165(15)	.3087(23)	.3175(25)
	U_{eq}	.024(3)	.016(2)	.029(3)	.018(3)	.018(4)
O4	x	.3506(8)	.3484(5)	.3524(8)	.3527(9)	.3548(12)
	y	.25	.25	.25	.25	.25
	z	.4361(19)	.4376(11)	.4393(15)	.4332(21)	.4337(28)
	U_{eq}	.023(3)	.016(2)	.026(3)	.015(3)	.020(4)

The mean electron numbers calculated for the site population obtained on the basis on the chemical data are in acceptable agreement with those obtained from the site occupancy refinement (Table 5). In this respect, it should be taken into account that small analytical errors in chemical data for heavy elements (*i.e.* Th and U, or heavy REE) lead to a substantial deviation in terms of mean electron number. Furthermore, the crystals examined appeared to be chemically zoned, and therefore we can not be quite sure that the portion analyzed is really representative of the whole crystal.

Table 5. Selected interatomic distances (Å), and mean number of electrons (n.e⁻) for the A, B and C sites.

	TR1	MI	TR2	CE	VV
A - O2(i)	2.323(6)	2.333(4)	2.342(6)	2.323(7)	2.335(9)
- O2(ii)	2.323(6)	2.333(4)	2.342(6)	2.323(7)	2.335(9)
- O3	2.326(9)	2.350(6)	2.336(9)	2.299(11)	2.311(13)
- O4	2.340(9)	2.379(6)	2.362(8)	2.309(11)	2.311(14)
- O1(i)	2.392(6)	2.397(4)	2.417(6)	2.388(7)	2.418(9)
- O1(ii)	2.392(6)	2.397(4)	2.417(6)	2.388(7)	2.418(9)
- O2(iii)	2.505(6)	2.531(3)	2.503(5)	2.501(7)	2.488(9)
- O2(iv)	2.505(6)	2.531(3)	2.503(5)	2.501(7)	2.488(9)
<A - O>	2.388	2.406	2.403	2.379	2.388
n.e ⁻ (ref)	44.9	47.8	50.5	47.1	43.4
n.e ⁻ (chem)	47.0	50.7	49.9	47.8	45.6
B - O1(v)	1.844(6)	1.833(4)	1.846(6)	1.844(7)	1.876(9)
- O2(iii)	1.924(6)	1.913(4)	1.926(6)	1.937(7)	1.962(9)
- O3(iii)	1.932(4)	1.929(2)	1.943(4)	1.956(5)	1.963(5)
- O1	1.977(6)	1.989(4)	1.985(5)	1.989(7)	1.985(9)
- O4	2.053(3)	2.076(2)	2.035(3)	2.041(4)	2.003(4)
- O2	2.110(6)	2.102(4)	2.130(6)	2.119(7)	2.146(8)
<B - O>	1.973	1.974	1.977	1.981	1.989
n.e ⁻ (ref)	22.7	22.5	24.0	24.1	34.6
n.e ⁻ (chem)	22.5	22.8	25.5	24.4	31.3
C - O4	2.07(3)	2.02(3)	2.16(3)	2.09(2)	2.19(2)
- O3(vi)	2.22(3)	2.22(3)	2.27(3)	2.22(2)	2.22(2)
- O1	2.31(2)	2.34(3)	2.36(2)	2.32(2)	2.40(2)
- O1(vii)	2.31(2)	2.34(3)	2.36(2)	2.32(2)	2.40(2)
- O2(viii)	2.40(2)	2.42(2)	2.35(2)	2.40(2)	2.38(2)
- O2(ix)	2.40(2)	2.42(2)	2.35(2)	2.40(2)	2.38(2)
- O1(x)	2.65(1)	2.65(1)	2.66(1)	2.65(1)	2.64(1)
- O1(xi)	2.65(1)	2.65(1)	2.66(1)	2.65(1)	2.64(1)
<C - O>	2.38	2.38	2.40	2.38	2.41
n.e ⁻ (ref)	2.3	1.4	2.2	3.2	3.0
n.e ⁻ (chem)	2.2	1.5	1.5	3.0	3.0

Note: symmetry codes are: *i*) x, y, -1+z; *ii*) x, 1/2-y, -1+z; *iii*) 1-x, 1-y, 1-z; *iv*) 1-x, -1/2+y, 1-z; *v*) 1/2-x, 1-y, -1/2+z; *vi*) -1/2+x, 1/2-y, 1/2-z; *vii*) x, 1/2-y, z; *viii*) -1/2+x, 1/2-y, 3/2-z; *ix*) -1/2+x, y, 3/2-z; *x*) 1/2-x, -1/2+y, -1/2+z; *xi*) 1/2-x, 1-y, -1/2+z

Conclusions

The A site deficiencies observed in a number of natural samples of aeschynite without marked evidence of alteration was to date explained as the consequence of pseudomorphic primary alteration (Ewing, 1975). However, taking into account the possibility that octahedral cations enter the C cavity too, values of the $\Sigma_{(B+C)cations}/\Sigma_A$ cations ratio greater than 2.0 can be due also to the presence of additional small-size cations in the C site. If this feature is primary or not is an interesting but not easy problem. As the presence of cations in C

must be coupled with structural vacancies in A, the $\square_A + Me_C$ pairs could be considered Frenkel defect pairs. We can venture the hypothesis that the observed electron density on C is due to accumulation of Frenkel defect pairs, which are known to occur at the first stages of metamictization (Ewing & Akimoto, 1994). According to Gong et al. (1996), the effects of α -decay damage in natural aeschynite is important in evaluating the long-term performance of this phase which may effectively be considered to incorporate actinides as waste loading. Further experimental work would

be necessary to explore this fascinating hypothesis.

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