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The crystal structure of synthetic natrotantite

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Abstract. — Ideal natrotantite has the composition $Na_2Ta_4O_{11}$, space group $R\bar{3}c$, $a = 6.2092(1)$, $c = 36.619(1)$ Å, $Z = 6$. The structure of synthetic natrotantite has been refined by the Rietveld method to $Rp = 8.67$, $Rwp = 9.24$, $RB = 2.33$ % using X-ray powder diffractometer data. The structure consists of layers of (1) edge-sharing NaO_7 polyhedra and TaO_6 octahedra and (2) edge-sharing TaO_7 pentagonal bipyramids, alternating along Z. Natrotantite is topologically identical to, but not isomorphous with $Na_2Nb_4O_{11}$; the $Na_2Nb_4O_{11}$ structure is a monoclinic distortion of the natrotantite structure. The structure is also similar to that of calciotantite from which it differs in its layer (1) topology and in its layer stacking. Natural natrotantites are typically non-stoichiometric ; $Na_{2-x}Ta_4O_{11-x}(OH,F)_x$ is proposed as a more realistic formula for the mineral.

Key words : natrotantite, synthesis, X-ray, Rietveld method, crystal structure.

La structure cristalline de la natrotantite de synthèse.

Résumé. — La natrotantite idéale a la composition $Na_2Ta_4O_{11}$, le groupe spatial $R\bar{3}c$, $a = 6{,}2092(1)$, $c = 36{,}619(1)$ Å, $Z = 6$. La structure de la natrotantite de synthèse a été affinée par la méthode de Rietveld jusqu'à $Rp = 8{,}67$, $Rwp = 9{,}24$, $RB = 2{,}33$ % en utilisant les données obtenues par diffractométrie de rayons X sur une poudre. La structure est constituée de couches (1) de polyèdres NaO_7 partageant leurs arêtes avec des octaèdres TaO_6, et (2) de bipyramides pentagonales TaO_7 partageant leurs arêtes, alternant le long de Z. La natrotantite est topologiquement identique à $Na_2Ta_4O_{11}$ sans en être isomorphe ; la structure de $Na_2Nb_4O_{11}$ est une distorsion monoclinique de la structure de natrotantite. Cette structure est également semblable à celle de la calciotantite de laquelle elle diffère par la topologie des couches (1) et par l'empilement des couches. Les natrotantites naturelles sont non-stoechiométriques ; la formule $Na_{2-x}Ta_4O_{11-x}(OH,F)_x$ peut être considérée comme la plus réaliste pour ce minéral.

Mots-clés : natrotantite, synthèse, méthode de Rietveld, structure cristalline.

INTRODUCTION

Natrotantite was first encountered by Voloshin *et al.* (1981) in granitic pegmatites of the Kola Peninsula. On the basis of microprobe and powder X-ray diffraction data, they described it as monoclinic $NaTa_3O_8$. While examining tantalum oxide minerals of the Alto do Giz pegmatite, Brazil, we found a mineral similar in chemistry and optical properties to natrotantite (U.S. National Museum, sample no. NMNH 105002). Although agreement between chemical data for this sample and type natrotantite (Voloshin *et al.*, 1981) was only fair, we concluded that the two minerals were the same on the basis of identical powder diffraction patterns. In an attempt to resolve the problem of the chemical differences between the samples, a literature search was conducted for data on syntheses in the system $NaTaO_3$-Ta_2O_5. We were surprised to find poor agreement between the different studies ; no firm conclusions regarding the true composition of natrotantite could be derived from these data. However, more recent syntheses indicate a strong dependence of the results upon temperature (Chaminade *et al.*, 1972). With the intent to synthesize a compound isostructural with natrotantite, we decided to investigate the join $NaTaO_3$-Ta_2O_5 at 850°C.

NATROTANTITE

Chemistry

Chemical analyses of natrotantite from Alto do Giz were obtained with a MAC 5 microprobe operating in the wavelength dispersive mode. Operating conditions were : accelerating potentials = 15, 20 kV, sample current = 40 nA on brass, collection time = 10 s.. Standards were manganotantalite (Ta *La*), stibiotantalite (Nb *La*), microlite (Na *Ka*), orthoclase (K *Ka*), titanite (Ca *Ka*) and PbTe (Pb *La*). Ti and Sn were also sought but not detected. Data were reduced with a modified version of EMPADR VII (Rucklidge and Gasparrini, 1969) that uses the atomic number-absorption correction of Love and Scott (1978).

The microprobe analyses (Table I) of the Brazilian material do not agree well with those of the type material. To evaluate the precision of our results, the sample was analyzed twice, using two different sodium standards (microlite and synthetic $NaInSi_2O_6$). In terms of reproductibility of results, the precision was good. The analyses with microlite as a Na standard are averaged in table I ; use of $NaInSi_2O_6$ produced very similar results ($<Na_2O> = 3.6$ %), suggesting adequate absorption correction of the data. Voloshin *et al.* (1981) also analyzed their sample several times to evaluate the precision of their results. If the difference in composition between the two analyses is not real, it must be due to errors in ZAF correction of the microprobe data. However, the difference in Na_2O between the samples is approximately 50 % ; as it is improbable that the ZAF-type corrections of the two data reduction routines differ by this amount, much of the difference must be real.

	1	2	3	4	5
Na_2O	3.1	4.7	6.6	4.5	3.4
K_2O	0.06	---	0.0	0.0	0.0
CaO	0.3	0.08	0.0	0.0	0.0
PbO	0.6	0.9	0.0	0.0	0.0
Nb_2O_5	1.0	2.7	0.0	0.0	0.0
Ta_2O_5	94.3	91.3	93.5	95.5	96.6
	99.4	99.6	100.0	100.0	100.0

1. Natrotantite, Alto do Giz, Brazil (NMNH 105002).
2. Natrotantite, Kola Peninsula, USSR; Voloshin et al. (1981).
3. Ideal $Na_2Ta_4O_{11}$.
4. Ideal $NaTa_3O_8$.
5. Ideal $Na_2Ta_8O_{21}$.

TABLE I. — *Composition of natrotantite and chemically similar compounds.*

Compositions de la natrotantite et des composés chimiques voisins.

X-ray crystallography

A 2×10^{-6} mm^3 crystal fragment was extracted from the microprobe mount for X-ray studies. Gandolfi patterns (Table II), although weak, agree completely with the pattern reported for type natrotantite (Voloshin *et al.*, 1981). Voloshin *et al.* (1981) pointed out the correspondance between the X-ray powder diffraction patterns of synthetic $Na_2Ta_4O_{11}$ and natrotantite. They proposed the space group $C2/c$ for the mineral ; however, all data for it and that of Chaminade *et al.* (1972) for $Na_2Ta_4O_{11}$ can be completely indexed on a hexagonal-R cell of dimensions a = 6.21, c = 36.6 Å. Long-exposure precession photographs of the Alto do

	Natrotantite				$Na_2Ta_4O_{11}$		
	USSR		Brazil				
hkl	I (obs)	d (obs)	I (obs)	d (obs)	I (obs)	d (obs)	d (calc)
006	4	6.12	6	6.14	30	6.09	6.10
012	3	5.19	5	5.17	31	5.15	5.16
104	1	4.66	1	4.63	5	4.64	4.64
018	1	3.50	1	3.52	4	3.49	3.49
110					1	3.10	3.10
$00\underline{12}$	7	3.06	4	3.07	49	3.051	3.052
$10\underline{10}$			1	3.04	10	3.025	3.027
113	10	3.02	10	3.01	100	3.010	3.009
116	9	2.778	9	2.772	81	2.766	2.767
024	2	2.601	1	2.580	9	2.579	2.579
119	6	2.474	5	2.477	34	2.467	2.468
$01\underline{14}$					3	2.351	2.352
208			1	2.324	8	2.318	2.318
$02\underline{10}$					1	2.167	2.167
$00\underline{18}$,	4	2.038	3	2.042	15	2.032	2.034
211							2.029
122			2	2.022	4	2.023	2.020
214					1	1.984	1.984
125	1	1.973	1	1.958	8	1.958	1.958
$11\underline{15}$	5	1.926	4	1.934	31	1.919	1.919
217	1	1.884			1	1.894	1.894
128	3	1.849	1	1.858	3	1.858	1.857
300	6	1.799	6	1.791	46	1.792	1.792
$21\underline{10}$	1	1.783			5	1.778	1.777
$02\underline{16}$					5	1.743	1.743
$12\underline{11}$					1	1.735	1.735
306	1	1.727			11	1.720	1.720
$11\underline{18}$	6	1.707	5	1.717	35	1.701	1.702
$21\underline{13}$	1	1.648			3	1.648	1.648
$12\underline{14}$	1	1.595			3	1.605	1.605
$10\underline{22}$					1	1.590	1.590
$30\underline{12}$	8	1.556	5	1.549	48	1.547	1.552
223	8	1.548			15	1.543	1.540
$00\underline{24}$	3	1.527			10	1.527	1.526
$11\underline{21}$			3	1.535	20	1.520	1.520
226	2	1.509	2	1.504	16	1.504	1.504
131,	1	1.493	2	1.484	12	1.487	1.490
312							1.486
$12\underline{17}$					2	1.480	1.478
315	2	1.466			2	1.463	1.461
229	3	1.453	1	1.451	10	1.450	1.450
137	1	1.421			2	1.434	1.434
$21\underline{19}$	2	1.404			2	1.399	1.398
a	6.224(2)		6.199(2)		6.2086(3)		
c	36.76(2)		37.08(2)		36.618(2)		Å

USSR sample: data from Voloshin et al. (1981)
Brazilian sample: 114.6 mm Gandolfi camera, Ni-filtered Cu radiation. Corrected for shrinkage.
$Na_2Ta_4O_{11}$: Philips PW1710 powder diffractometer, automatic divergence slit, graphite-monochromated Cu Kα radiation.

TABLE II. — *X-ray powder diffraction data for natrotantite.*

Diagramme de poudre de la natrotantite.

Giz fragment confirm this assignment ; all aspects of the diffraction data indicate $R3c$ or $R\bar{3}c$ as possible space groups.

THE JOIN $NaTaO_3$-Ta_2O_5

Because of the diversity of results of separate studies of the join $NaTaO_3$-Ta_2O_5, each study is summarized in table III. To date, the phases $NaTaO_3$, $NaTa_3O_8$, $Na_2Ta_8O_{21}$ and L-Ta_2O_5 have been reported for the system. Of these phases, $Na_2Ta_4O_{11}$ of Chaminade *et al.* (1972) and Jahnberg (1970) most closely resembles natrotantite in terms of its X-ray powder diffraction pattern.

Reference	$Na_2Ta_4O_{11}$	$NaTa_3O_8$	$Na_2Ta_8O_{21}$	T (°C)
King et al. (1956)	T a=16.40 c=16.81	T a=7.81 c=7.66	---	from melt
Reisman (1962)	O a=6.00 b=7.66 c=5.08	O a=7.74 b=7.74 c=5.97	---	1300
Whiston & Smith (1965)	T a=7.86 c=7.15	---	T a=12.5 c= 3.92	1000
Jahnberg (1970)	R a= 6.209 c=36.618			1000
Chaminade et al. (1972)	---	---	O a=12.430 b=37.290 c= 3.900	1300
	H a= 6.208 c=36.659	---	---	900
T: tetragonal, O: orthorhombic, H: hexagonal P, R: hexagonal R				

TABLE III. — *Results of previous investigations of the join $NaTaO_3$-Ta_2O_5.*

Résultats des travaux précédents sur les composés de la série $NaTaO_3$-Ta_2O_5.

For the syntheses of the present study, the following starting materials were used : Ta_2O_5 (Puratronic, 99.99 %), Na_2CO_3 (Fisher, 99.99 %) and $NaHCO_3$ (Fisher, 100.2 %). The components were dried, weighed, thoroughly mixed and pressed into pellets prior to firing in an electric furnace. Heatings were done in a platinum crucible at 850°C for 4, 10 and 20 hours. All run products were characterized by X-ray powder diffractometry. Annealed reagent-grade BaF_2 and CaF_2, calibrated against U.S. National Bureau of Standards silicon (batch 640a) were used as internal standards in unit cell refinements.

The results of the study are shown in figure 1.

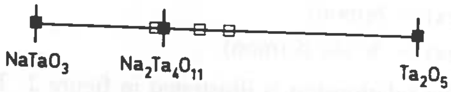

FIG. 1. — *The join $NaTaO_3$-Ta_2O_5 at 850°C.* Squares mark compositions investigated ; filled squares : single phase ; open squares : two phases.

La série $NaTaO_3$-Ta_2O_5 à 850°C. Les carrés indiquent les compositions étudiées ; carrés noirs : une phase ; carrés blancs : deux phases.

Three phases exist at 850°C : $NaTaO_3$, $Na_2Ta_4O_{11}$ and Ta_2O_5. Compositions more sodic than $Na_2Ta_4O_{11}$ produced mixtures of $Na_2Ta_4O_{11}$ and $NaTaO_3$; less sodic compositions produced mixtures of $Na_2Ta_4O_{11}$ and Ta_2O_5. The results of this study confirm the findings of Chaminade *et al.* (1972) for the join at low temperature (700-900°C). Unit cell parameters of all phases are given in table IV.

$NaTaO_3$	$Na_2Ta_4O_{11}$	Ta_2O_5
a: 3.8913(1)	a: 6.2086(3) c: 36.618(2)	a: 6.231(3) b: 40.18(2) c: 3.8890(4)
V: 58.923(5)	V: 1222.4(1)	V: 973.7(3)

TABLE IV. — *Unit cell parameters* (Å) *for phases of the join $NaTaO_3$-Ta_2O_5.*

Paramètres réticulaires (Å) *pour les phases de la série $NaTaO_3$-Ta_2O_5.*

$Na_2Ta_4O_{11}$

Structure analysis and refinement

Powder diffraction data for the compound $Na_2Ta_4O_{11}$ are given in table II. These data confirm that $Na_2Ta_4O_{11}$ is isostructural with natrotantite. This is surprising : chemical analyses (Table I) suggest either $NaTa_3O_8$ or $Na_2Ta_8O_{21}$ as possible compositions for natrotantite.

As shown earlier, the X-ray powder diffraction data for both natrotantite and $Na_2Ta_4O_{11}$ can be completely indexed on a R-centred cell, despite suggestions of Chaminade *et al.* (1972) and Voloshin *et al.* (1981) to the otherwise. The content of this cell is six formula units, *i.e.*

$Na_{12}Ta_{24}O_{66}$. The true cell is related to the monoclinic pseudo-cell proposed by Voloshin *et al.* (1981) by

$a(\text{hex}) = 1 / \sqrt{3}\ a(\text{mon})$

$b(\text{hex}) = b(\text{mon})$

$c(\text{hex}) = 3c \sin \beta\ (\text{mon})$

The relationship is illustrated in figure 2. The pseudocell is nearly identical to the true cell of the compound $Na_2Nb_4O_{11}$; comparison of the diffraction patterns of these compounds strongly suggests that the $Na_2Nb_4O_{11}$ structure is merely a monoclinic distortion of the $Na_2Ta_4O_{11}$ structure (Jahnberg, 1970). In order to assess the validity of this model, a structure refinement of $Na_2Ta_4O_{11}$ was initiated.

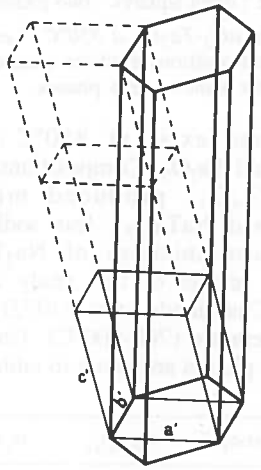

FIG. 2. — *Relationship between the hexagonal cell of natrotantite (bold rule) and its monoclinic pseudo-cell (light rule and dashed).*

Relation entre la maille hexagonale de la natrotantite (traits gras) et sa pseudo-maille monoclinique (trait fin et pointillé).

Because of the strong structural similarities between $Na_2Nb_4O_{11}$ and $Na_2Ta_4O_{11}$, the data of Jahnberg (1970) for $Na_2Nb_4O_{11}$ were used to generate the starting model for $Na_2Ta_4O_{11}$. Because $Na_2Nb_4O_{11}$ has a centric structure, the space group $R\bar{3}c$ was chosen for the refinement. The equation,

$$H = AM + C$$

where

$A = [2, 0, -2/3\ /\ 1, 1, -1/3\ /\ 0, 0, -1/3]$

$C = [-1/2, 0, 0]$

$M = [x, y, z]$ monoclinic

$H = [x, y\ z]$ hexagonal

was used to transform the coordinates of $Na_2Nb_4O_{11}$ to $R\bar{3}c$-compatible ones. The transformation placed Na at a 12c site with z = 1/6, Ta at both an 18e site with x = 0.364 and the 6b site and O at three sites : 36f (x = 0.055, y = 0.413, z = 0.197), 18e (x = 3/4), 12c (z = 0.406).

X-ray intensity data were collected with a Philips PW1710 automatic powder diffractometer using graphite-monochromated Cu*Ka* radiation. Beam divergence was controlled with an automatic divergence slit so that a constant area of the sample was irradiated (approximately 1.9 cm^2). The sample of $Na_2Ta_4O_{11}$ used for data collection was gently ground for 20 minutes prior to mounting in a sample holder. The data were collected in a step-scanning mode from 10° to 150° 2θ with a step size of 0.01° 2θ and a counting time of 5 s.per step.

Refinement was carried out using the Rietveld method with a slightly modified version of the program DBW 2.9 (Wiles and Young, 1981). Because of problems of the program with rhombohedral space groups, the structure was refined in the space group $P\bar{3}c1$, with all shifts constrained to comply with $R\bar{3}c$. Thus, the refinement was effectively conducted in $R\bar{3}c$. Data used in the refinement covered the interval 12-78° 2θ in 0.04° increments, chosen on the basis of space restrictions of the program. A small region in this range (21.5-24.9°) was excluded from refinement due to the presence of the (001) peak of very minor (< 1 %) contaminant Ta_2O_5. The profile function used was the modified Lorentzian of Khattak and Cox (1977), which gave a better fit to the data than a conventional Lorentzian or Gaussian function. The preferred orientation parameter was fixed at 0.0 because of the uncertainty of the morphology and cleavage of crystallites in the powder and because of the absence of any such data for the compound or natrotantite.

Refinement was done in three steps. First, the scale factor, cell parameters and 0° 2θ position were refined, with all structural parameters fixed at values for the transformed $Na_2Nb_4O_{11}$ starting model, and with a fixed background model based on visual estimation. In the second step, the half-width parameters, background (a quadratic function of 2θ), peak asymmetry parameter and overall isotropic temperature factor were included as variables. In the final step, all structural parameters were eventually allowed to vary, including individual isotropic temperature factors of the atoms, and the background model was expanded to a fourth order polynomial in 2θ.

The temperature factors of the atoms all converged on values higher than expected (*i.e.* those of $Na_2Nb_4O_{11}$) by a factor of 2 to 3 ; this may be due to absorption, which is not modelled by the program. In an attempt to evaluate the effect of the problem on the positional parameters, the temperature factors were fixed at expected values and the data were re-refined. Although the pattern R's increased by a factor of 1.5 and the Bragg R by a factor of 3, the positional parameters of the atoms experienced insignificant shift (mean absolute shift = 1.5 sigma, maximum absolute shift = 2.5 sigma). Thus, the problem does not affect the positional parameters significantly.

In the last cycle, 26 parameters (profile, lattice and structural) were refined simultaneously until all shifts were less than 0.1 sigma. Final values of the important profile parameters are given in table V ; lattice and structural parameters and final R-indices are given in table VI. A plot of the observed and calculated profiles is given in figure 3.

Preferred orientation parameter: 0.0 (fixed)

Asymmetry parameter: 1.04(4)

Halfwidth parameters:
U=0.127(9), V=-0.064(6), W=0.0263(9)

2θ(initial): 12.0°, 2θ(final): 78.0°, step: 0.04°

Number of datapoints: 1565

TABLE V. — *Profile information.*
Conditions d'obtention de profil.

Description of the structure

The general topology of the $Na_2Ta_4O_{11}$ structure is the same as that of $Na_2Nb_4O_{11}$; the two differ only in detail. The structure consists of alternations of two types of layer along Z (Figure 4). Each layer has edge-sharing arrangements, with adjacent layers connected via corners and edges. One layer consists of isolated TaO_6 octahedra in a sheet of NaO_7 capped octahedra. The other layer consists solely of TaO_7 pentagonal bipyramids. These shall be referred to as the octahedral and pentagonal bipyramidal layers respectively.

Atom	x	y	z	B (Å^2)
Na	0	0	0.3323(3)	3.1(3)
Ta(1)	0.3641(2)	0	1/4	3.14(4)
Ta(2)	0	0	0	3.36(7)
O(1)	0.052(1)	0.414(1)	0.1975(1)	2.2(2)
O(2)	0.750(2)	0	1/4	3.6(3)
O(3)	0	0	0.4074(4)	1.8(4)

Space group: $R\bar{3}c$, a=6.2092(1) c=36.619(1) Å

Rp=8.67, Rwp=9.24, RB=2.33 %

$Rp = \Sigma|y_i(o)-y_i(c)|/\Sigma y_i(o)$

$Rwp = \{\Sigma w_i[y_i(o)-y_i(c)]^2/\Sigma w_i[y_i(o)]^2\}^{1/2}$;
$w_i=1/(y_i+y_{bi})$

$RB = \Sigma|I_k(o)-I_k(c)|/\Sigma I_k(o)$

TABLE VI. — *Structural parameters.*
Paramètres structuraux.

Bond lengths and angles are given in table VII. The Ta octahedron is very regular. All Ta-O bond lengths are equal and all O-Ta-O angles are within 1.1° of the mean (90°). Conversely, the Ta pentagonal bipyramid is quite distorted. Axial Ta-O bonds (Ta(1)-O(1)) are shorter than equatorial bonds (Ta(1)-O(2), Ta(1)-O(3)), as is to be expected for this type of coordination polyhedron. However, there is considerable variation in equatorial bond angles and lengths which is merely a consequence of repulsion due to crowding of Ta-O bonds in the equatorial plane (<O-Ta-O> eq. = 78.2°), in conjunction with the high degree of edge-sharing of the bipyramids in the plane.

The Na polyhedron is also highly distorted. Each Na polyhedron shares three edges with three Ta bipyramids of one of the adjacent pentagonal bipyramidal layers. The sodium-capping oxygen bond is the longest of the polyhedron. Because this bond points alternately upward and downward from Na polyhedron to Na polyhedron within an octahedral layer, adjacent Na polyhedra link via edge-sharing to different pentagonal bipyramidal layers.

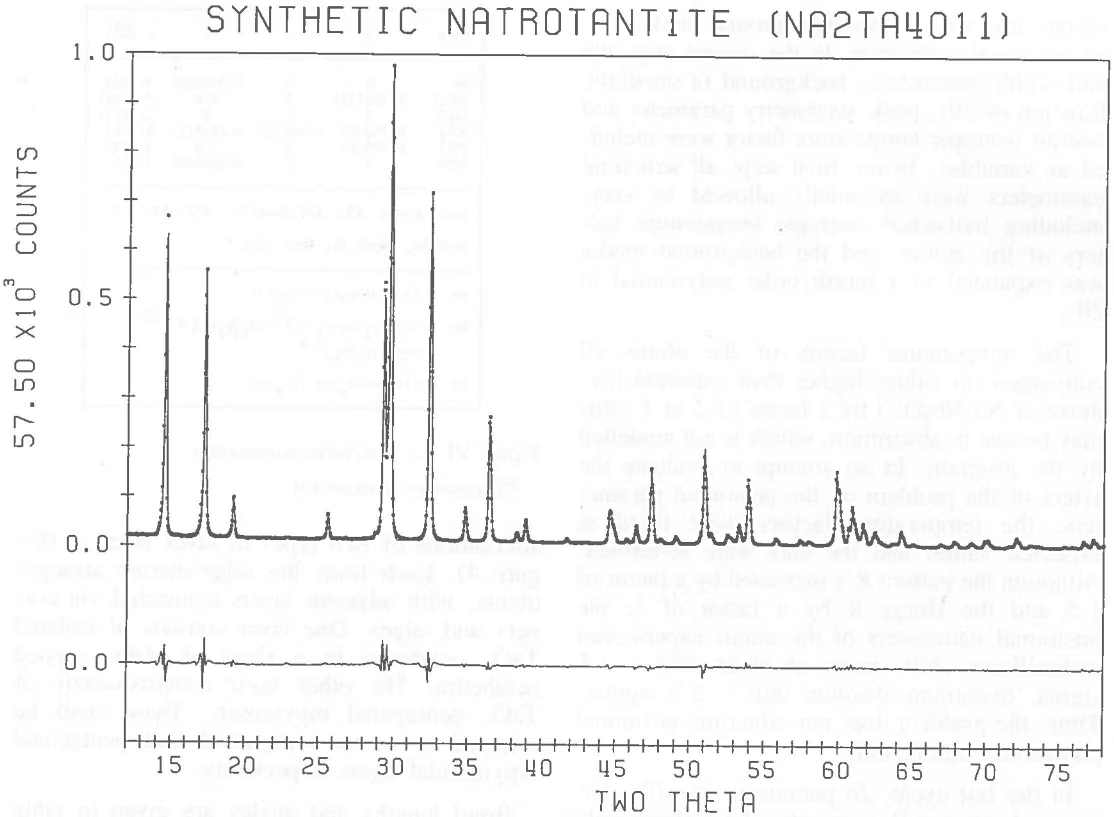

FIG. 3. — *X-ray powder diffractometer profile (Cu Ka) of natrotantite.* Above, squares : datapoints ; curve : calculated profile ; below, difference plot.

Profil de diffraction des rayons X sur poudre (Cu Ka) de la natrotantite. En haut, points de mesure et profil calculé ; en bas, différence entre mesure et calcul.

Comparison of the details of the $Na_2Ta_4O_{11}$ structure with those of $Na_2Nb_4O_{11}$ gives predictable results (Table VIII). $Na_2Ta_4O_{11}$ and $Na_2Nb_4O_{11}$ show no real differences in terms of polyhedral bond length distortion. In terms of bond angles, the M^{5+} polyhedra of $Na_2Ta_4O_{11}$ can be seen to be marginally less distorted than those of $Na_2Nb_4O_{11}$, at the expense of additional distortion in the Na polyhedron. Why the lower symmetry exists for this niobium oxide, and for niobium oxides versus tantalum oxides in general, is not fully understood ; unfortunately, what is in the literature to date is largely speculative in nature.

As pointed out be Jahnberg (1970), the structure of natrotantite ($Na_2Ta_4O_{11}$) is very similar to that of calciotantite ($CaTa_4O_{11}$), as calciotantite possesses alternating "octahedral" and pentagonal bipyramidal layers like natrotantite. The pentagonal bipyramidal layer of calciotantite is topologically identical to that of natrotantite. The octahedral layer (Figure 5) is similar to that of natrotantite, except that only one out of every two of the potential large-cation sites is occupied (in an ordered manner), and that the large-cation polyhedron is 8-coordinated. The difference in coordination of the large cation between the two structures is responsible for their different layer-stacking sequences. Seven-coordination of the large cation in natrotantite introduces an additional translation in the layer stacking that calciotantite does not have, resulting in a 36.6 Å *c* period in the latter compared to 12.3 Å in the former.

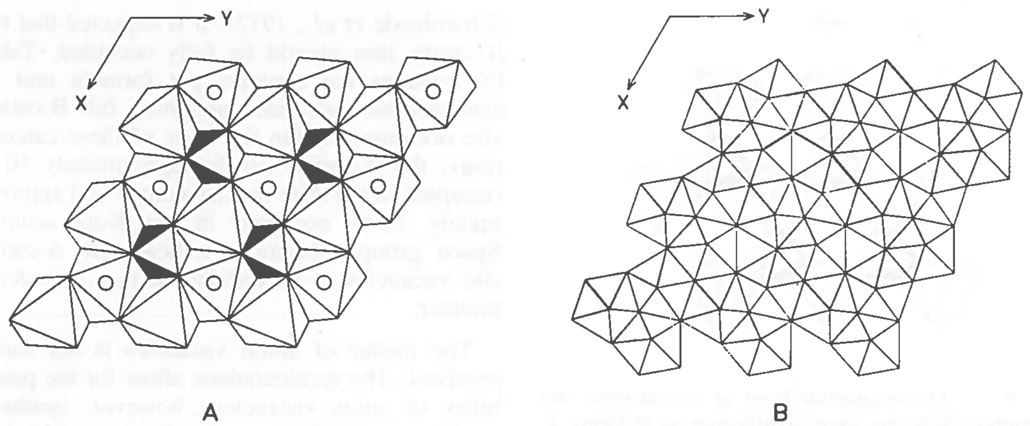

FIG. 4. — *Natrotantite structure.* (a) "Octahedral" layer. The small octahedra contain Ta, the large octahedra, sodium. Circles over the Na polyhedra mark the seventh oxygen in the true Na coordination polyhedron ; Na polyhedra without circles have their seventh oxygen below the plane of the figure. (b) Pentagonal bipyramidal layer.

Structure de la natrotantite. (a) couche "octaédrique". Les petits octaèdres contiennent Ta, les grands contiennent Na. Les cercles au-dessus du polyèdre sodique indiquent le septième oxygène dans le vrai polyèdre de coordination du Na. Les polyèdres sodiques sans cercle ont leur septième oxygène au-dessous du plan de figure. (b) couche de bipyramidales pentagonales.

TABLE VII. — *Selected interatomic distances* (A) *and angles* (°).

Distances interatomiques (A) *et angles* (°).

Ta(1) Pentagonal Bipyramid

Ta(1) - O(1)	x 2	1.95
- O(2)	x 2	2.00
- O(2)	x 1	2.40
- O(3)	x 2	2.01
⟨Ta(1) - O⟩		2.05
O(1) - O(2)	x 2	3.00
- O(2)	x 2	2.97
- O(2)	x 2	2.74
- O(3)	x 2	2.81
- O(3)	x 2	2.70
O(2) - O(2)	x 1	2.69
- O(3)	x 4	2.40
⟨O - O⟩		2.72

Equatorial Angles

O(2) - Ta(1) - O(2)	x 1	84.3
- O(3)	x 2	78.0
- O(3)	x 2	75.6
⟨O(eq) - Ta - O(eq)⟩		78.3

Axial-Equatorial Angles

O(1) - Ta(1) - O(2)	x 2	85.7
- O(2)	x 2	98.8
- O(2)	x 2	87.7
- O(3)	x 2	86.0
- O(3)	x 2	90.4
⟨O(ax) - Ta - O(eq)⟩		89.7

Ta(2) Octahedron

Ta(2) - O(1)	x 6	2.01	O(1) - Ta(2) - O(1)	x 6	91.1
			- O(1)	x 6	88.9
O(1) - O(1)	x 6	2.81	⟨O - Ta - O⟩		90.0
- O(1)	x 6	2.88			
⟨O - O⟩		2.85			

Na Polyhedron

Na - O(1)	x 3	2.48	O(1) - Na - O(1)	x 3	91.4
- O(1)	x 3	2.66	- O(1)	x 3	94.0
- O(3)	x 1	2.75	- O(1)	x 3	84.1
			- O(1)	x 3	94.8
⟨Na - O⟩		2.60	- O(3)	x 3	61.9
O(1) - O(1)	x 6	2.81			
- O(1)	x 6	2.88			
- O(3)	x 3	2.70			
⟨O - O⟩		2.82			

	$Na_2Ta_4O_{11}$		$Na_2Nb_4O_{11}$	
	Δ	σ^2	Δ	σ^2
$^{VI}[M^{5+}]$	0	1	2	2
$^{VI}[M^{5+}]$	51	10 (O_{eq}-M-O_{eq}) 23 (O_{eq}-M-O_{ax})	45,48	9,18 (O_{eq}-M-O_{eq}) 27,25 (O_{eq}-M-O_{ax})
$^{VII}[Na]$	3	150	3	104

$\Delta = 1/n\ \Sigma[(l_i - l_o)/l_o]^2 \times 10^4$; $l_o = 1/n\ \Sigma l_i$

$\sigma^2 = 1/n\ \Sigma(\theta_i - \theta_o)^2$; $\theta_o = 1/n\ \Sigma\theta_i$

TABLE VIII. — *Polyhedral distortion in $Na_2M_4O_{11}$ (M = Ta, Nb).*

Distortion des polyèdres dans $Na_2M_4O_{11}$ (M = Ta, Nb).

DISCUSSION : THE CRYSTAL CHEMISTRY OF NATROTANTITE

All samples of natrotantite and synthetic $Na_2Ta_4O_{11}$ are isomorphous, indicating that natrotantite ideally possesses $A_2^{+}B_4^{5+}O_{11}$ stoichio-

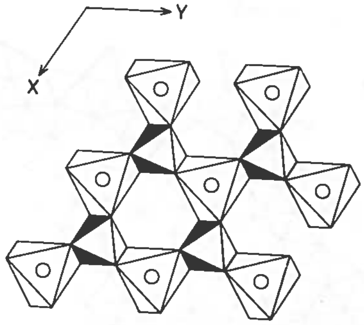

FIG. 5. — *The octahedral layer of calciotantite.* All symbols have the same significance as in figure 4. The eighth oxygen of the Ca polyhedron lies directly under the polyhedron, with the same lateral coordinates as the seventh oxygen.

Couche octaédrique de calciotantite. Les symboles ont la même signification que sur la figure 4. Le huitième oxygène du polyèdre Ca se trouve juste au-dessous du polyèdre, avec les mêmes coordonnées latérales que le septième oxygène.

	1	2
Na	0.93	1.40
K	0.01	----
Ca	0.04	0.01
Pb	0.03	0.04
Nb	0.07	0.19
Ta	3.93	3.81
A-site sum	1.01	1.45
Effective oxygen	10.54	10.75

Calculated on 4(Ta+Nb)

1. Alto do Giz, Brazil.
2. Kola Peninsula, USSR.

TABLE IX. — *Formula contents of natrotantites.*
Composition des natrotantites.

metry. The natural samples are all non-stoichiometric ; variable Na_2O and near-constant Ta_2O_5 + Nb_2O_5 of these samples suggest that partial A-cation vacancy, and perhaps anion vacancy is the norm for natrotantites. By analogy with behaviour in the pyrochlore group (Hogarth, 1977) and defect sodium ''oxyfluorotantalates'' (Chaminade *et al.*, 1972), it is expected that the B-cation sites should be fully occupied. Table IX contains the contents per formula unit of natrotantites, calculated assuming full B-cation site occupancies. On the basis of these calculations, the A-cation site is approximately 50 % occupied in the Alto do Giz sample and approximately 70 % occupied in the Kola sample. Space group restrictions indicate the A-cation site vacancies to be distributed in a disordered manner.

The matter of anion vacancies is not easily resolved. The recalculations allow for the possibility of anion vacancies ; however, synthesis studies suggest the opposite. Consequently, it is most likely that charge balance in A-cation deficient natrotantites is brought about by hydroxyl or fluorine substitution for oxygen. Unfortunately, this model has yet to be directly tested experimentally. Samples of natural natrotantites are less than 0.1 mm^3 in total volume, precluding powder IR spectroscopic examinations. Chaminade *et al.* (1972) did not detect O = F substitution in $Na_2Ta_4O_{11}$; however, the join needed to evaluate such substitutions. $Na_2Ta_4O_{11}$-$Ta_4O_9F_2$, was not investigated in his study. Andersson (1967) suggested O = OH substitution in $Na_2Nb_4O_{11}$, but did not test this model.

In conclusion, on the basis of the present understanding of natural and synthetic natrotantites, we propose that the formula of natrotantite is best written as :

$$Na_{2-x}Ta_4O_{11-x}(OH,F)_x$$

where $0.5 < x < 1.0$ in natural samples.

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