

NOTES ON TAPIOLITE, WITH SPECIAL REFERENCE TO TAPIOLITE FROM SOUTHERN WESTLAND, NEW ZEALAND

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ABSTRACT

An occurrence of rare particles of the multiple oxide tapiolite in beach sands near Otorokua Point, southern Westland, New Zealand, is recorded. For this mineral the following data have been determined: $O_{Na} = 2.33 \pm 0.01$, $E_{Na} = 2.53 \pm 0.04$. $E-O = 0.20$. $O =$ pale brown, $E =$ reddish-brown to opaque. $E > O$. S.G._{25°C.} = 7.65. X-ray diffraction powder patterns show that the mineral has a true trirutile structure with unit cell dimensions of $a_0 = 4.750 \text{ \AA}$, $c_0 = 9.208 \text{ \AA}$, and with d -spacings and intensities that are comparable to those recorded for analyzed tapiolite from Brazil and Morocco, but distinct from the pattern yielded by unheated tapiolite from Skogsbole, Finland. The latter occurrence is shown to have a rutile structure but, after appropriate heat-treatment, a trirutile structure is developed with resultant denser packing of the atoms. Unit cell dimensions for ordered and disordered Skogsbole tapiolite, determined from quartz-calibrated Weissenberg films, are $a_0 = 4.752 \text{ \AA}$, $c_0 = 9.204 \text{ \AA}$, and $a_0 = 4.753 \text{ \AA}$, and $c_0 = 3.092 \text{ \AA}$ respectively.

INTRODUCTION

A recent examination of some specimens that were collected in southern Westland, New Zealand in the early part of 1954, led to the recognition of kobeite as a constituent of a granite boulder from the gravels of the Paringa River. In order to determine if this or other tantalum-niobium-titanium-bearing minerals might be represented in the heavy mineral assemblages of the local sands and silts, a careful study was made of a number of concentrates also obtained at that time. Kobeite has not been detected so far in any of these samples, but rare particles of tapiolite were isolated from two concentrates obtained by panning blacksand paystreaks on the beach just north-east of Otorokua Point, north-east of the mouth of Cook River (latitude $43^{\circ}25'$ South, longitude $169^{\circ}48'$ East).

Consequently this is the second tantalum-rich mineral that has been recorded from southern Westland but, unfortunately, neither mineral has been found in situ and both appear to be distinct rarities.¹ The only other tantalum-bearing minerals recognized and recorded from New Zealand are cassiterite and monazite (Hutton, 1950, pp. 656-658; 667-669) from southern Nelson and northern Westland, and yttriotantalite from Collingwood, Nelson (Morgan, 1927, p. 107); furthermore Morgan (1927, pp. 99) has stated that concentrates from Addison's, near Westport, Nelson, have been found to contain considerable amounts of Ta_2O_5 ,

¹ An occurrence of kobeite in boulders from Paringa River has been described recently (Hutton, 1957).

but in this instance the specific tantalum-bearing mineral or minerals have not been recognized.

MINERALOGY

After removal of ferromagnetic material, 9.6% and 10.2% respectively, from two 3 kg. samples the concentrates were screened² to give the following fractions: +32: 3.0%, 3.4%; -32+60: 30.8%, 32.6%; -60+115: 55.7%, 52.9%; -115+250: 0.8%, 0.5%; -250: 0.1%, 0.4% respectively. These fractions, the two finest grade sizes excepted, were carefully fractionated in Clerici solution that had been adjusted to a density of 4.0, and the heavy fraction of each grade-size was subsequently split electromagnetically into several fractions. The resultant material was then studied in oblique illumination with a binocular microscope.

Rare particles of tapiolite were found in the small concentrates attracted at 0.45 amps. and rejected at 0.3 amps.³ in both -16+32 and -32+60 mesh material. Garnet and monazite were the chief associates of tapiolite in these fractions, whereas, in the same size-fractions untreated in Clerici solution but electromagnetically separated, clinozoisite-epidote, clear brown and intensely dichroic tourmaline, non-metamict allanite, pale pink garnet, sphene, monazite, and composite fragments were recognized.

Tapiolite forms highly irregular conchoidally bounded particles with vitreous luster, that are opaque in oblique illumination except at the thinnest edges. In transmitted light very fine fragments of the mineral are translucent and deep brown to red-brown in color. All fragments appeared to be devoid of inclusions and free from any alteration phenomena. The refractive index of the ordinary ray was determined to be 2.33 ± 0.01 in sodium light, but a value for E is reported with considerable reservations, *viz.* 2.53_{Na} , because the intensity of absorption for the extraordinary ray only permitted one to obtain results reproducible within a range of ± 0.04 . Dichroism is intense with O=pale brown, E=deep reddish brown; opaque in thicker fragments; $E > O$. The specific gravity, determined for a collection of particles that had a total weight of 11.9 mgm., is 7.65 at 21° C., a figure that definitely points to a highly tantalian variety rather than to mossite. Isolated fragments of tapiolite were found to have a narrow range of magnetic susceptibility, since they were rejected at 0.40 amps. but attracted at 0.45 amps., with the Frantz separator set as for the main fractionation reported above.

Excellent x-ray diffraction powder patterns of the trirutile type were

² Tyler standard screen scale.

³ The Frantz separator was set as follows: tilt 10°, slope 15°.

obtained and the d -spacings and relative intensities (Table 1) are, except for quite minor points, closely comparable to those recorded by Tavora and Peixoto (1951, p. 451) and Permingeat (1955, p. 137) for tapiolite from Mecejana, Brazil, and Iguerda and Tazenakht, French Morocco, respectively. A number of very faint lines and the rather weak (505) reflection yielded by southern Westland tapiolite are not recorded by Permingeat (1955, p. 137, Table 1), although they may be seen in the author's own film yielded by Angarf, Plaine de Tazenakht tapiolite. Tavora and Peixoto (1951, p. 451, Table 1) do not record very weak reflections at 1.930 Å, 1.134 Å, .978 Å, although Tavora (1955, Fig. 6B) does indicate the presence of the (226) reflection, that is the second of the lines just noted, in his photograph of a tapiolite powder pattern. It

TABLE 1. X-RAY DIFFRACTION DATA FOR TAPIOLITE FROM WESTLAND, NEW ZEALAND AND SKOGSBOLE, FINLAND

Radiation: $\text{CuK}\alpha$ ($\lambda=1.5418$ Å). Camera Diameter: 114.59 mm.

hkl	New Zealand			Skogsbole, Finland						
	Unheated			Heated			Unheated			hkl
	d. meas. Å	d. calc. Å	I	d. meas. Å	d. calc. Å	I	d. meas. Å	d. calc. Å	I	
002	4.62	4.60	2	4.58	4.60	2				
101	4.22	4.23	3	4.22	4.22	3				
110	3.37	3.36	10	3.35	3.36	10	3.35	3.36	10	110
112	2.71	2.716	2	2.712	2.715	2				
103	2.58	2.58	9	2.572	2.578	9	2.58	2.59	9	101
200	2.375	2.374	5	2.371	2.375	5	2.37	2.37	5	200
004				2.300	2.301	<1				
113	2.265	2.267	2	2.265	2.265	2	2.27	2.27	2	111
210	2.125	2.125	1	2.125	2.126	1	2.12	2.12	1	210
202	2.114	2.111	1	2.112	2.112	1D				
211	2.067	2.070	2	2.069	2.071	2				
212	1.930	1.930	<1							
114	1.900	1.899	<1	1.900	1.899	1				
213	1.747	1.748	9	1.745	1.746	9	1.75	1.753	9	211
105	1.716	1.718	<1	1.714	1.717	1				
220	1.677	1.679	5	1.679	1.680	5	1.678	1.681	5	220
204	1.652	1.653	<1	1.651	1.653	1				
222	1.5775	1.577	1	1.577	1.579	1				
301	1.560	1.560	<1	1.562	1.562	<1				
006	1.534	1.535	2	1.533	1.534	2	1.546	1.546	2	002
310	1.501	1.503	5	1.502	1.504	5	1.503	1.505	5	310
312	1.429	1.429	1	1.428	1.430	1				
303	1.407	1.407	5	1.408	1.408	5	1.411	1.411	5	301
116	1.395	1.396	5	1.397	1.396	5	1.405	1.405	5	112
215		1.392			1.392					
224	1.357	1.357	<1	1.357	1.357	<1				
321	1.302	1.303	<1	1.304	1.305	<1				

I: Intensity, determined visually

D: Diffuse line.

B: Broad line.

TABLE 1. (continued)

New Zealand				Skogsbole, Finland						
hkl	Unheated			Heated			Unheated			hkl
	d. meas. Å	d. calc. Å	I.	d. meas. Å	d. calc. Å	I.	d. meas. Å	d. calc. Å	I.	
206	1.289	1.289	3	1.290	1.290	2	1.2985	1.296	2	202
107		1.268			1.267					
314	1.256	1.257	<1	1.258	1.258	<1				
323	1.212	1.211	4	1.210	1.210	4	1.212	1.213	4	321
305		1.200			1.201					
400	1.188	1.188	1	1.188	1.188	1	1.189	1.189	1	400
410	1.1525	1.152	<1		1.153		1.154	1.154	<1	410
402, 008	1.150	1.150	<1	1.151	1.151	<1				
411	1.144	1.1435	<1	1.145	1.144	<1				
226	1.134	1.133	3	1.134	1.133	2	1.139	1.139	2	222
330	1.120	{1.120}	3	1.120	{1.121}	1	1.121	1.1205	2	330
217										
118, 332	1.0895	1.089	<1	1.090	1.089	1				
413	1.0785	1.081	3	1.079	1.079	3	1.080	1.081	3D	411
316	1.075	1.074	3	1.074	1.074	2	1.079	1.079	3D	312
325		1.072			1.072					
420	1.063	1.062	2	1.063	1.063	<1	1.063	1.064	1	420
404		1.055			1.056					
208, 422	1.036	1.036	<1	1.036	1.036	<1				
307		1.012			1.012					
334		1.007			1.0075					
109	1.001	1.000	2	1.001	1.000	1	1.008	1.008	1	103
415	.978	.977	<1	.977	.977	<1				
424	.965	.965	<1	.965	.965	<1D				
228	.951	.950	<1	.950	.950	<1				
431, 501	.946	.945	<1	.946	.946	<1				
406	.940	.940	2	.9405	.940	2	.9435	.942	1	402
327, 510	.932	.932	2	.932	.932	2	.933	.932	1	510
416, 219	.923	.922	3	.922	.922	3	.929	.927	2	412, 213
318, 512	.915	.914	<1	.9145	.914	<1				
433, 503	.9085	.907	4	.908	.908	4	.910	.9085	4BD	431, 501
336	.906	.905	4	.905	.905	4	.9065	.9065	4D	332
1·1·10		.889			.888					
521		.878			.879					
426	.874	.874	3	.874	.874	3	.877	.8765	3	422
417		.866			.8665					
514		.863			.864					
309	.8605	{.860}	2	.859	{.8595}	2	.864	.863	1	303
2·0·10										
523	.849	.848	4	.849	.849	4	.8495	.849	3	521
505	.845	.845	2	.846	.845	1				
440	.840	.840	1	.8405	.840	1	.841	.840	1	440
408, 442	.827	.8265	<1	.827	.827	<1				
530	.815	.815	2	.815	.815	2	.8155	.815	1	530
329	.8095	.809	4	.809	.809	4				
532	.8035	.803	<1	.803	.803	1				
516	.7975	.797	5	.797	.797	5	.800	.799		512
525		.796			.796					
600	.793	.792	1	.7925	.7925	1	.7925	.792	<1D	600
444		.789			.790					
3·1·10		.785			.785					
602, 428	.782	.780	<1	.781	.781	<1				
611	.779	.7785	<1	.779	.779	2				

might be noted here that Tavora (1955, Fig. 6B) incorrectly labels the reflection at 1.001 \AA in his film as (104) instead of (109).

Employing powder patterns of southern Westland tapiolite, tentative values for a_0 and c_0 were subsequently refined to give $a_0 = 4.750 \text{ \AA}$ and $c_0 = 9.208 \text{ \AA}$; this leads to a ratio $a_0:c_0$ of 1:1.9385, that is intermediate in value to those recorded by Palache, Berman, and Frondel (1944, p. 775) for the tapiolite-mossite series, *viz.* 1:1.941 to 1:1.936, yet larger than the ratio of 1:1.942 reported by Tavora and Peixoto (1951, p. 451). Furthermore, the close relationship between the structures of tapiolite and rutile is clearly brought out if the value $c_0/3a_0$ for southern Westland tapiolite is compared with the ratio $a_0:c_0$ for rutile, *viz.* 0.646 and 0.644 respectively (cf. Goldschmidt, 1926, p. 18).

For comparative purposes a powder pattern was obtained with tapiolite from Skogsbole, Finland and, while the latter is comparable in a general way with the pattern yielded by southern Westland tapiolite, a considerable number of lines present in the film yielded by the latter mineral are absent from the former, but the relative intensities of the lines common to the two films are quite similar. Furthermore, there are significant shifts in the relative positions of several of the stronger lines; reflections at 1.411 \AA , 1.405 \AA , 1.139 \AA , 1.080 \AA , 1.079 \AA , and $.929 \text{ \AA}$ are especially noteworthy in this connection. If fragments of Skogsbole tapiolite are now heated in vacuo at 600° C. for $\frac{3}{4}$ hour a pattern is obtained that is identical to that yielded by southern Westland tapiolite, except for a very slight shift in the positions of lines due to somewhat different cell dimensions in the two cases, and a slight diffuseness in the reflections at high 2θ values in the film of the former mineral. However, if Skogsbole tapiolite is heated in vacuo at 1200° C. for one hour, the lines in the back-reflection region of the pattern are quite clearly and precisely resolved.

This situation is clearly indicative of an order-disorder relationship for the tetragonal compound $\text{Fe}(\text{Ta},\text{Nb})_2\text{O}_6$, a condition that has already been noted for tapiolite from Ross Lake, Northwest Territories (Hutchinson, 1955, p. 443), and for a number of AB_2X_6 compounds in general (Byström, Hök, and Mason, 1941, pp. 1-8). In most of the films yielded by unheated or disordered Skogsbole tapiolite traces of a number of weak lines, normally found in the ordered phase, were detected. This would seem to suggest that, in unheated tapiolite, domains exist in the crystals in which some degree of order is apparent, and others that are in a state of disorder. In an attempt to verify this situation a number of very small particles of unheated Skogsbole tapiolite, 0.1 mm. in diameter, were hand-picked, crushed in gum tragacanth, and x-rayed. The films yielded by these preparations appear to support the suggestion just of-

ferred since a number of the lines due to the trirutile structure are present although faint in some films, but only barely detectable in others.

After a number of attempts, a fragment of Skogsbole tapiolite was obtained that yielded a rotation photograph that was strictly of the rutile type. Measurements of rotation and quartz-calibrated Weissenberg films led to cell dimensions of $a_0 = 4.753 \text{ \AA}$ and $c_0 = 3.092 \text{ \AA}$, both values $\pm 0.002 \text{ \AA}$. This identical crystal fragment when heated in vacuo at 1200° C. for one hour yielded a - (or b -) axis rotation films with the same number of layer-lines as found for similar orientations of unheated tapiolite, but with many more reflections present than in similar films of the unheated mineral. The recrystallized mineral yielded c -axis photographs with six layer-lines compared with only two in the unheated mineral, and the 3rd layer of the former corresponds to the 1st layer of the latter. Furthermore, the reflections of the zero and 3rd layers are very much more intense than those in the 1st, 2nd, 4th and 5th layers, all of which are relatively weak. Accordingly a marked superlattice is evident in the trirutile or ordered form.

Measurements of the rotation and quartz-calibrated Weissenberg films yielded by heated Skogsbole tapiolite, give unit cell dimension of $a_0 = 4.752 \text{ \AA}$ and $c_0 = 9.204 \text{ \AA}$, $\pm 0.002 \text{ \AA}$. Now if we compare these data with the unit cell dimensions, $a_0 = 4.753 \text{ \AA}$ and $3 \times c_0 = 9.278 \text{ \AA}$, determined for the unheated or disordered Skogsbole tapiolite it is clear that the ordered form, with a trirutile structure, has a cell volume that is distinctly less than that of the disordered phase, namely 207.840 \AA^3 and 209.599 \AA^3 respectively. The specific gravities of unheated and heated Skogsbole tapiolite are interesting in this connection. For three fragments the following specific gravities were measured⁴ before and after heating to 1200° C. for one hour in vacuo; the weights of the particles used are recorded in parentheses in each case: 7.50, 7.51 (9.70 mgm.); 7.50, 7.51 (10.95 mgm.); 7.502, 7.508 (18.46 mgm.).

In Table 1 the measured and calculated d -spacings for unheated, but ordered, tapiolite from south Westland are set out and are compared with the data obtained for both the ordered and disordered phases of the Skogsbole mineral. In the ordered forms it should be noted that a number of weak reflections were found on Weissenberg films, which have not been detected in the powder patterns.

An attempt has been made to determine the amount of heat-treatment required to cause an approach to a state of order in Skogsbole tapiolite, and a summary of this work is set out in Table 2. In every case samples were sealed in vacuo in silica or high-silica glass capillaries; then each

⁴ These figures represent the average of five determinations in each instance.

TABLE 2. SUMMARY OF RESULTS OBTAINED BY HEAT-TREATMENT OF SKOGSBOLE TAPIOLITE

Temp. in °C.	Period of heating	Result
300	1, 2, 4, 8, 12, 24 hrs. 168 hrs.	Disorder maintained. Disorder maintained.
450	24 hrs. 48 hrs.	Disorder maintained. Slight amount of ordering.
500	1, 2, 3, 4, 5, 7 hrs. 15½ hrs. 24 hrs.	Disorder maintained. Almost completely ordered. Complete order.
600	5, 10, 15, 20 mins. 25, 30 mins. 35 mins. 45 mins.	Disorder maintained. Slight degree of order. Almost completely ordered. Ordered.
1200	1 hr.	Ordered.
1360	30 mins.	Slight amount of disorder.

tube was inserted in turn into an already heated furnace, and after the correct period of heating, the tube was withdrawn, and cooled rapidly to room temperature.

In films yielded by fragments heated at 1360° C., a marked diffuseness was evident in reflections at high 2θ values, and this effect may result from either of two situations: (a) the disordering temperature may have been reached, or (b) decomposition has commenced, but since no sintering together of fragments or dulling of the sharp edges of conchoidally fractured particles occurred as a result of heating, the first alternative is tentatively believed to be the more acceptable.

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