Holtite: a new mineral allied to dumortierite

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SUMMARY. Holtite, a new mineral allied to dumortierite, occurred as pebbles with stibiotantalite and tantalite on an alluvial tin lease near Greenbushes, Western Australia, and is named after the late H. E. Holt, Prime Minister of Australia.

The mineral is orthorhombic with a 11·905 Å, b 20·355 Å, c 4·690 Å, space group $Pmcn$, weak supercell $2a$, $2b$, c developed. Crystals are elongated along c, D 3·90±0·02, hardness $8\frac{1}{2}$, fluorescent. Optical properties α 1·743–1·746, mainly yellow, $\parallel$ [001], β 1·756–1·759, colourless, γ 1·758–1·761, colourless, $2V_\alpha$ 49–55°, $r < v$. X-ray powder data are given.

Chemical analysis gave SiO_2 20·30, Sb_2O_5 4·61, Al_2O_3 46·43, Ta_2O_5 11·24, Nb_2O_5 0·76, Fe_2O_3 0·27, MnO 0·05, TiO_2 0·09, BeO 0·05, B_2O_3 1·82, Sb_2O_3 13·89, H_2O^+ 0·38, H_2O^- 0·08, sum 99·97%. On a water-free basis the unit cell contains $Al_{24\cdot5}$ $Sb'''_{2\cdot56}$ $Ta_{1\cdot36}$ $Sb^v_{0\cdot76}$ $Nb_{0\cdot16}$ $Fe'''_{0\cdot10}$ $Be_{0\cdot05}$ $Ti_{0\cdot03}$ $Mn_{0\cdot02}$ $B''_{1\cdot40}$ $Si_{9\cdot09}$ $O_{66\cdot85}$. Compared with dumortierite, $4[(Al,Fe)_7BSi_3O_{18}]$ or 4 $(X_{10}O_{18})$, the holtite unit cell contains approximately $4(X_{10}O_{17})$.

Type material is preserved at the Government Chemical Laboratories, Perth, Western Australia.

IN 1962, the author re-examined two samples of alluvial stibiotantalite donated in 1937 and 1943 from Greenbushes, Western Australia (lat. 35° 50′ S., long. 116° 0′ E.). Amongst the stibiotantalite was a hard fluorescent mineral that could not be identified by optical, chemical, or X-ray powder methods.

A study of the mineral was commenced in 1965 using single crystal X-ray methods, which together with a complete analysis established a relationship with dumortierite, $4[(Al,Fe)_7BSi_3O_{18}]$. A unit cell content for the unknown mineral was calculated with a general similarity to dumortierite and approximately quadruple multiplicity.

The study confirmed that the mineral has a crystal structure like dumortierite but somewhat distorted because several light atom sites are occupied by 30·5% by weight of Sb, Ta, and Nb oxides. Such a large substitution of rare elements is unique among previous descriptions of dumortierite, which record only a minor replacement of Al by Fe'''.

The name holtite is after the Right Honourable Harold Edward Holt (1908–67), Prime Minister of Australia (1966–7). The new mineral was accepted by the Commission on New Minerals and Mineral Names, I.M.A.

Occurrence. The Greenbushes tinfield is in the south-west of Western Australia in an area of Pre-Cambrian greenstones and gneisses (metamorphosed basic lavas and sediments) together with granitic rocks and basic dykes.

The cassiterite has come from eroded tin-bearing lodes, and commercial concentrations were mainly in the pebble and boulder beds of the overlying Old Alluvium (Hobson and Matheson, 1949).

The first holtite specimen was donated in 1937 by H. J. McKay from the 'Enterprise' Mining Lease 369 and the second in 1943 by H. S. Barrymore who worked the former 'Enterprise' lease as part of Mineral Claim 1 at present leased as part of 'Leo' Mining Lease 665 by Greenbushes Tin No Liability.

The former 'Enterprise' is at the head of Bunbury Gully one mile south-south-east of Greenbushes township.

The site of the holtite occurrences on the lease is not recorded but the material donated by H. S. Barrymore is almost certainly from alluvial workings extended in 1943 south-east from the main road (Hobson and Matheson, 1949).

Mineralogy. The holtite-bearing samples are mainly stibiotantalite, tantalite, and holtite pebbles, 2–15 mm, with minor tourmaline, microlite, and quartz.

The holtite is present mainly as intergrown prisms and acicular coatings on the stibiotantalite and as parallel acicular to asbestiform replacements of the tantalite. Some pure holtite occurs as hard resinous pebbles composed of parallel needles often with S-shaped contortions. These rotational stress structures suggest that shearing forces accompanied the antimonial solutions that partially replaced the tantalite with stibiotantalite and holtite.

The predominant colour of holtite occurring as coatings varies from Ridgeway (1912) Light Buff 17'f to Cream Buff 19″d. Greenish pebbles are Deep Olive Buff 21‴d to Citrine Drab 21‴i, and brown pebbles are Russet 13'k to Mummy Brown 17'm. The streak is between white and Light Buff 17'f.

The lustre varies from dull in weathered pebbles to resinous for dense fibrous pebbles to vitreous for crystalline material.

Holtite is mainly very finely crystalline but a few crystals occur as large as 1 mm diameter. Some small pseudohexagonal prisms were also noted. Numerous grains have a good cleavage or parting parallel to $b\{010\}$, as suggested by Claringbull and Hey (1958) for the dumortierite from Garrah, India, described by Kilpady and Dave. The cleavage or parting planes are finely striated parallel to the elongation [001].

Holtite crystals have D 3·90±0·02 by sink-float method in Clerici's solution.

The hardness of dense fine-grained pebbles is $8\frac{1}{2}$ on Moh's scale. Pure holtite pebbles fluoresce dull orange in ultraviolet light λ 2537 Å and bright yellow with λ 3660 Å.

Optical properties. Refractive indices, α 1·743–1·746, $\parallel$ [001], β 1·756–1·759, γ 1·758–1·761 (calc. 1·74–1·80). Colour: α mainly yellow shades: Ridgeway Maize Yellow 19'f, Buff Yellow 19d, Pale Lemon Yellow 23, Strontian Yellow 23', also Cendre Green 35b and Grenadine Red 7, β and γ colourless. 2 V_{α} is 49–55°, optic axial plane is $b\{010\}$, multiple twinning on $m\{110\}$, dispersion $r < v$.

The grains become colourless on heating to 800 °C.

Chemistry. A 9 g. sample with D_4^{20} 3·90±0·02 by the pyknometer method of Ellsworth (1928) was prepared for the analysis (table I) by repeated electromagnetic and Clerici solution separations to better than 99·5% purity. The slight impurity consisted of fine inclusions of tantalite and stibiotantalite.

Most of the analysis was by standard methods. Si was determined after volatilizing

B as methyl borate and Sb as bromide, then complexing Ta and Nb with tartaric acid. Sb''' was determined by Groves (1949) modification of the Rowledge method for Fe'' analysis and Sb^V by difference.

The holtite unit-cell content (table I) is calculated including H_2O^+ and also on a water-free basis following Claringbull and Hey (1958), who recorded a similar combined water figure on gem dumortierite from Ceylon.

TABLE I. *Chemical composition and unit-cell contents of holtite including* H_2O^+ *and also on a water-free basis with corrected D.*

	I		2	3
SiO_2	20·30	Si	9·03	9·09
Sb_2O_5	4·61	Sb^V	0·76	0·76
Al_2O_3	46·43	Al	24·34	24·50
Ta_2O_5	11·24	Ta	1·36	1·36
Nb_2O_5	0·76	Nb	0·16	0·16
Fe_2O_3	0·27	Fe	0·10	0·10
MnO	0·05	Mn	0·02	0·02
TiO_2	0·09	Ti	0·03	0·03
BeO	0·05	Be	0·05	0·05
B_2O_3	1·82	B	1·40	1·40
Sb_2O_3	13·89	Sb'''	2·54	2·56
H_2O^+	0·38	H	1·12	—
H_2O^-	0·08	Σ	40·91	40·03
Total	99·97	O	67·02	66·85

1. Analysis by J. R. Gamble on sample with D_4^{20} 3·90±0·02.
2. Unit-cell contents calculated from 1 and based on D 3·90 and V 1136·5 Å^3.
3. Unit-cell contents calculated on a water-free basis, with D 3·91, V 1136·5 Å^3.

The water-free unit-cell content is $Al_{24·5}Sb'''_{2·56}Ta_{1·36}Sb^V_{0·76}Nb_{0·16}Fe'''_{0·10}Be_{0·05}Ti_{0·03}Mn_{0·02}B'''_{1·40}Si_{9·09}O_{66·85}$ which is approximately $4(X_{10}O_{17})$ compared with dumortierite $4[(Al,Fe)_7BSi_3O_{18}]$ or $4(X_{11}O_{18})$.

The constituent elements of holtite cannot be rationally grouped as in dumortierite. The Ta, Nb, and Sb ions most likely occupy a few random Al sites in the holtite unit cell.

Vlasov (1964) suggests the replacement of Al by Ta in silicate minerals. Being of similar ionic radius Nb and Sb ions should also appear in the same sites as Ta. The excess Al atoms could then be in the deficient Si sites as proposed by Hartman (1969) that Si deficiency is compensated by the entering of Al, Fe''', or Ti^{iv}, in this order of preference, into tetrahedral sites. Parker and Fleischer (1968) also point out the difficulty of replacement of SiO_4 tetrahedral complexes by tetrahedral or octahedral complexes of Ta and Nb.

A formula calculated on a basis of 72 oxygen atoms for direct comparison with dumortierite is unacceptable because the calculated specific gravity is then 4·21 compared with measured D 3·90±0·02.

A crystal structure analysis should resolve the doubtful positions of the heavy atoms.

X-ray data. Weissenberg photographs show holtite to have the same space group, *Pnma*, as dumortierite. The orientation *Pmcn* chosen for dumortierite by Golovastikov (1965) is adopted for holtite pending structure analysis.

TABLE II. *X-ray powder diffraction data for holtite, from diffractometer trace,* Cu-$K\alpha$.

hkl	I	d_{obs}	d_{calc}	hkl	I	d_{obs}	d_{calc}
110 } 020 }	100	10·28 Å	10·27 Å 10·18	351	6	2·430 Å	2·430 Å
200	32	5·93	5·95	510	24	2·362	2·365
130	34	5·89	5·90	431	16	2·355	2·357
220	24	5·12	5·14	370 } 002 }	24	2·344	2·346 2·345
040	32	5·08	5·09	280	26	2·338	2·340
111 } 021 }	3	4·26	4·27 4·26	460	4	2·237	2·237
031	14	3·86	3·86	181	2	2·202	2·198
150	14	3·85	3·85	202	2	2·181	2·182
211	2	3·62	3·62	132	2	2·173	2·179
221 } 041 }	14	3·46	3·46 3·45	451 } 222 }	2	2·137	2·138 2·133
330	6	3·44	3·43	511	6	2·113	2·112
060	3	3·39	3·39	371 } 142 } 281 }	10	2·094	2·098 2·096 2·094
141	3	3·31	3·31				
231	20	3·23	3·24	521 } 231 }	2	2·076	2·078 2·077
051	6	3·07	3·07				
400 } 151 }	22	2·97	2·98 2·98	461	4	2·018	2·019
260	40	2·94	2·95	312 } 242 }	2	2·010	2·009 2·005
321	8	2·895	2·900	600 } 322 }	6	1·981	1·984 1·980
420	10	2·840	2·855	390	4	1·965	1·964
331	3	2·762	2·767	620	4	1·945	1·948
251	2	2·731	2·731	332 } 480 }	4	1·934	1·935 1·934
161	7	2·679	2·678	062	4	1·930	1·929
440	8	2·571	2·569	162	2	1·910	1·904
080	8	2·543	2·544	342	4	1·873	1·877
261 } 411 }	2	2·492	2·496 2·494	plus 60 additional weak peaks to 1·171 Å			
071	2	2·473	2·471				

As with dumortierite the *hk*o layer of holtite is pseudohexagonal and the numerous strong *hk*o reflections dominate the powder X-ray pattern.

A parameter refinement using a least-squares computer program written by S. Hall for Weissenberg film measurements gave *a* 11·905±0·005 Å, *b* 20·355±0·005 Å, *c* 4·690±0·001 Å, $V = 1136·5$ Å³, axial ratios 0·5848:1:0·2304.

Powder X-ray films of holtite taken by the author give similar data to table II, measured from the powder diffractometer trace supplied by J. Graham except that the 221 reflection is the second strongest line on films.

The single crystal X-ray films exhibit strong thermal layers normal to *c* at spacings

of 2c and 3c. The layers produce a continuous shadow extending down to 3·5 Å on a powder X-ray film.

The Weissenberg photographs also show many weak diffraction spots based on a supercell with axes 2a, 2b, c. The extra reflections indexed on the supercell only have indices with odd values of h and k while equivalent supercell spots have markedly different intensities.

X-ray patterns taken of holtite powder and crystals after heating to 1000 °C showed no changes.

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