

The hōgbomite polytypes

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Summary. Single crystal X-ray examination has shown that hōgbomite forms a series of polytypes, designated nH or nR , with hexagonal or rhombohedral lattices and hexagonal unit-cell dimensions a 5.72 Å, c 4.6 × n Å. The polytypes arise by variation, in a manner as yet undetermined, of the stacking sequence of approximately close-packed oxygen layers with interstitial cations on fourfold and on sixfold sites; the composition of $1/n$ th of a unit-cell may be represented as $R_{1-0-1-6}^{2+} Ti_{0-2-0-4}^{4+} R_{3-7-4-3}^{3+} O_{7-6-8-0}^{2-} (OH)_{0-0-4}^{-}$, where $R^{2+} = Zn, Fe, Mg$, and $R^{3+} = Fe, Al$. The polytypes so far observed are $4H, 5H, 6H, 15H, 15R$, and $18R$. Minerals structurally related to hōgbomite are nigerite ($3H$) and taaffeite ($4H$). A new occurrence of hōgbomite, polytype $5H$, with composition $Ti_{1.7}Fe_{1.6}Mg_{6.3}Al_{18.8}Si_{0.2}O_{40}$, is described from a spinel-free paragenesis in a magnesian skarn at Mautia Hill, Tanganyika. Another new occurrence in an aluminous xenolith in the Cashel gabbro in Co. Galway, Ireland, is recorded. X-ray powder data are given for two of the polytypes.

SINCE its discovery by Gavelin (1917) in iron-rich skarns in Swedish Lapland, hōgbomite has been recorded, described, and analysed from a number of occurrences of widely differing paragenesis. Its morphological crystallography and its X-ray powder pattern have been discussed by various authors, to whose work detailed reference will be made below, but, in spite of the conflicting results obtained by these less fundamental techniques, it has not hitherto been the subject of single crystal X-ray study. The present study arose out of the examination of a new occurrence of relatively coarse, well crystallized hōgbomite in magnesium-rich skarns at Mautia Hill, Tanganyika, in the course of which it became apparent that the X-ray crystallography of hōgbomite presented some interesting and unsuspected complexities.

Material examined. Nine specimens of hōgbomite from seven of the fifteen recorded occurrences have been examined. References to the published descriptions are given in the lower part of table I. It suffices to add here that specimen 4 is off the rock figured by Gavelin (1917, figs. 2, 3), that specimen 8 is the dark variety of hōgbomite designated 'B' by Friedman (1952), and that specimens 7 and 11 are respectively

TABLE I. Unit-cell dimensions and polytype intergrowths in hōgbomite

Locality and no. of crystals examined	Principal polytype				Subsidiary polytypes
	<i>a</i>	<i>c</i>	<i>c/n</i>	polytype	
1 Castor (2)	5.72 Å	18.35 Å	4.59 Å	4H	—
2 Castor (1)	5.72	18.35	4.59	4H	15H
3 August (1)	5.72	18.35	4.59	4H	—
4 Perseus (1)	5.72	18.35	4.59	4H	—
5 Whittles (2)	5.72	18.40	4.60	4H	?15H + D
6 Mautia* (6)	5.718	23.02	4.604	5H	—
7 Transvaal-A (1)	5.72	23.01	4.60	5H	—
8 Macon Co. (1)	5.72	22.95	4.59	5H	4H
9 Cortlandt (2)	5.72	27.53	4.59	6H	?14H
10 Toombeola (2)	5.72	27.5	4.6	6H	4H + 15R
11 Transvaal-B* (1)	5.738	83.36	4.631	18R	—

1. Castor claim, Ruoutevare, near Kvikkjokk, Sweden (Gavelin, 1917). 19541.†
2. Castor claim, Ruoutevare, near Kvikkjokk, Sweden (Gavelin, 1917). BM 1925,1049.
3. August claim, Ruoutevare, near Kvikkjokk, Sweden (Gavelin, 1917). BM 1925,425.
4. Perseus claim, Ruoutevare, near Kvikkjokk, Sweden (Gavelin, 1917). BM 1923,1019.
5. Whittles, Pittsylvania Co., Virginia (Watson, 1925; Friedman, 1952). 79538.
6. Mautia Hill, Mpwapwa District, Tanganyika. 88280.
7. Dentz Farm, Letaba district, Transvaal (Nel, 1949). 19628.
8. Fairview Ridge, Macon Co., North Carolina (Friedman, 1952). 88279.
9. Smith and Ellis Quarry, Cortlandt, New York (Friedman, 1952). 35077.
10. Toombeola, Co. Galway, Ireland. 88283.
11. Dentz Farm, Letaba district, Transvaal (Nel, 1949). 19629.

* Unit-cell dimensions determined by diffractometry (see p. 575). Approximate values derived from single crystal photographs are *a* 5.72, *c* 23.01 Å for Mautia, and *a* 5.72, *c* 83.1 Å for Transvaal-B.

† Specimen numbers refer to the collections of the Department of Mineralogy and Petrology, University of Cambridge, except those prefixed BM, which refer to the collections of the Mineralogy Department, British Museum (Natural History).

from portions of the material separated for analyses A and B of Nel (1949).

Two specimens, 6 and 10, from new occurrences have also been examined. Specimen 6 is from an enstatite-tremolite-chlorite-hōgbomite-dolomite skarn at Mautia Hill, Tanganyika. An account of the hōgbomite- and sapphirine-bearing reaction skarns between the dolomitic marble and the yoderite-bearing schists (McKie, 1959) of Mautia Hill is in course of preparation. Hōgbomite there forms {0001} tablets up to 5 mm long, idiomorphic with respect to all other minerals (fig. 1),

and exhibiting a good $\{10\bar{1}0\}$ cleavage and a perfect $\{0001\}$ parting. It is pleochroic in thin-section, ω deep yellow, ϵ medium yellow, and is uniaxial negative (occasionally anomalously biaxial, $2V_{\alpha} \leq 15^{\circ}$) with ω 1.805, ϵ 1.783 (both ± 0.005).

Specimen 10 is from a corundum magnetite ilmenite högbomite-chlorite xenolith in the Cashel basic intrusion, near Toombeola, Co.

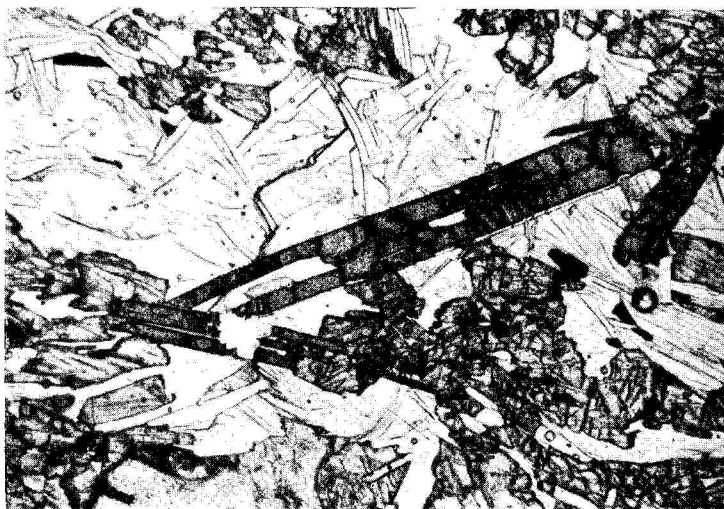


FIG. 1. Högbomite-chlorite-enstatite-tremolite-dolomite skarn. Three large högbomite tablets appear in the centre of the figure. A patch of dolomite occurs towards the left of the bottom edge. Tremolite is not visible. Plane polarized light, $\times 30$.

Galway, Ireland. Anhedral medium brown to light brown pleochroic högbomite and green spinel occur intergrown with magnetite in a corundum matrix traversed by pale chloritic veins. No clear replacement relationship is discernible between spinel and högbomite; some högbomite grains have spinel cores and some spinel grains are bounded against corundum or magnetite without any intervening högbomite. I am indebted to Dr. B. W. Evans for the gift of a portion of the xenolith and to Dr. M. G. Bown for generously making available to me the results of his single crystal X-ray study of this specimen.

Material from the högbomite occurrences in Norway (Schetelig, 1917; Kolderup, 1928 and 1936), on Samos in the Aegean (de Lapparent, 1946), in Turkey (Önay, 1949), in Czechoslovakia (Christophe-Michel-Lévy

and Sandrea, 1953), in the Cameroons (Sandrea, 1950), and in Russia (Moleva and Myasnikov, 1952; Bobrovnik, 1955; Kuzmin, 1960) was not available for single crystal X-ray study.

Unit-cell dimensions. The diffraction patterns of all the crystals of hōgbomite examined have been found to exhibit either hexagonal or rhombohedral symmetry. The dimensions of the hexagonal unit-cell are for each specimen a 5.72 Å, and c close to some multiple of 4.6 Å. The crystallography of hōgbomite can thus be described in terms of a series of polytypes of constant a , to each of which a symbol of the form nH or nR can be assigned, where H and R indicate hexagonal and rhombohedral lattice types respectively and n is given by $c = 4.6n$ Å.

The diffraction pattern of each specimen was studied by a -axis oscillation photographs, by zero and first layer a -axis Weissenberg photographs, and in some cases by c -axis oscillation photographs also. Unit-cell dimensions were evaluated by measurement of the zero layer a -axis Weissenberg photographs and more accurate values were determined for two specimens by diffractometry. The diffraction symbol was obtained by inspection of systematic absences on the Weissenberg photographs. Intergrown polytypes giving rise only to relatively weak distinguishable reflections were identified by measurement of the Weissenberg photographs.

The unit-cell dimensions of the principal polytype present in each specimen are listed in table I, where the presence of subsidiary intergrown polytype phases is also noted. Hōgbomite from the original Swedish localities is characteristically the $4H$ polytype, intergrown in the case of specimen 2 with $15H$ in approximately equal amount. The diffraction patterns of both crystals of the Whittles hōgbomite, specimen 5, exhibit streaks of moderate intensity joining reflections of constant h and k ; superimposed on these c^* streaks, which are indicative of pronounced disorder in the stacking of (001) layers of the structure, are reflections attributable to a $4H$ polytype and to a polytype of high n , possibly $15H$. Specimens 6 and 7, Mautia and Transvaal hōgbomite-A, are single-phase $5H$ polytypes and specimen 8, Macon County, is an intergrowth of $5H$ with $4H$ in notably smaller amount. The diffraction pattern of specimen 9, Cortlandt, has not been unambiguously determined; the dominant polytype is clearly $6H$ and relatively few weak reflections due to a polytype of high n , which may be $14H$, are also present on all photographs. Examination of oscillation photographs of specimen 10, Toombeola, by Dr. M. G. Bown has conclusively shown that three polytypes, $6H$, $4H$, and $15R$, with $6H$ clearly dominant, are

present in each of the crystals studied. Transvaal högbomite-B, specimen 11, is a single-phase $18R$ polytype, the only rhombohedral högbomite polytype so far found in isolation.

The unit-cell dimension a and the subcell dimension c/n exhibit slight variation, which cannot at present be correlated with composition. In crystals composed of more than one polytype the constituent phases have coincident a -axes and coincident c -axes. It is clear that, at least at Castor, different hand specimens of similar composition may contain different polytypes, but it would appear from the present investigation that there and elsewhere only crystals of one polytype or of one kind of polytype intergrowth occur within the compass of a single hand specimen.

The högbomite polytypes so far observed are, in order of increasing complexity, $4H$, $5H$, $6H$, $?14H$, $15H$, $15R$, $18R$, and D (— disordered stacking). One other polytype can be added to the list if the minerals nigerite ($3H$) and taaffeite ($4H$) with related unit-cell dimensions are considered; detailed reference to these two minerals will be made below.

Unit-cell contents. Chemical analyses and specific gravities are available for four of the högbomite specimens examined crystallographically. The chemical analysis¹ and the specific gravity given by Gavelin (1917) for Castor högbomite taken together with the unit-cell dimensions (table I) lead to a content of 31.7_1 oxygen atoms in the unit-cell, sufficiently close for the true oxygen content of the unit-cell to be assumed to be 32 atoms. Similarly, the chemical analysis and specific gravity of 3.80 given by Nel (1949) for högbomite-A from the Transvaal combined with the unit-cell dimensions of table I lead to a content of 39.62 oxygen atoms in the $5H$ unit-cell, sufficiently close for the true oxygen content to be 40 atoms. And for högbomite-B from the Transvaal the unit-cell dimensions of table I taken together with Nel's analysis and specific gravity 3.93 lead to a content of 47.5 oxygen atoms in the rhombohedral $18R$ unit-cell, sufficiently close for the true oxygen content to be 48 atoms.

The amount of högbomite available from Mautia Hill, Tanganyika, was inadequate for chemical analysis by classical methods, but a proximate analysis was very kindly made for me by Dr. J. V. P. Long on the scanning X-ray micro-analyser. The analysis is set down in table II. It was performed on two crystals of högbomite mounted in Araldite and polished with diamond paste on a lead lap. Yoderite, rutile, and iron

¹ Corrected for 7.11 % ilmenite (separately analysed), 15.25 % pleonaste (separately analysed), and 0.73 % SiO_2 (said to be secondary).

were used as internal, and 'specpure' aluminium and magnesium as external standards. Satisfactory correlation was obtained of Mg, Al, and Fe concentrations relative to yoderite and relative to the pure metal standards. The accuracy of the values listed in table II is uncertain, but at worst must be rather better than $\pm 10\%$ of each stated oxide percentage. X-ray micro-analysis determines the concentration of elements, giving no information about water content or the oxidation state of iron: it has been assumed provisionally that this h ogbomite is wholly ferrous and anhydrous.

TABLE II. Composition of h ogbomite from Mautia Hill, Tanganyika

	1		2
MgO	17.2	Mg ²⁺	6.3
FeO	7.8	Fe ²⁺	1.6
TiO ₂	9.1	Ti ⁴⁺	1.7
Al ₂ O ₃	65.2	Al ³⁺	18.8
SiO ₂	0.9	Si ⁴⁺	0.2
	<u>100.2</u>	O ²⁻	40.0

1. X-ray micro-analysis of h ogbomite from Mautia Hill, Tanganyika.
2. Unit-cell contents calculated from column 1 assuming 40 O²⁻ per unit-cell and that all the Fe found is divalent.

The specific gravity was estimated as 3.699 by measuring the loss in weight of a mercury-in-glass mass immersed in Clerici's solution in which a few grains of the mineral remained in suspension after being centrifuged for 10 minutes. The observed density and unit-cell dimensions and the chemical analysis lead to an oxygen content of 39.3₄ atoms in the 5H unit-cell, a satisfactory approximation to 40.

Comparison of the chemical composition of the four analysed h ogbomites of known polytype and of other analysed h ogbomites can conveniently be made in terms of the average cationic content of the common hexagonal unit-subcell containing eight anions, with dimensions $a' = a = 5.72 \text{ \AA}$, $c' = c/n \approx 4.6 \text{ \AA}$. The unit-subcell contents of all analysed h ogbomites are set down in table III with the exception of those corresponding to two analyses by Kuzmin (1960), both of which were made on admittedly impure material. The only analyses known to be of other than high quality are that of the Swedish h ogbomite, derived from the analysis of a mixture, and that of the Tanganyika specimen, a preliminary X-ray micro-analysis; the composition of the Gornaya Shoriya material is unusual and needs confirmation. The significant reported hydroxyl content of both Transvaal h ogbomites is probably

real although it appears to have little effect on their physical properties. One of the Russian högbomites, of unrecorded locality, analysed by Moleva and Myasnikov (1952) is characterized by having Zn^{2+} as one of its principal large cations. The small Si content of the two Transvaal

TABLE III. Unit-subcell contents in högbomite calculated to $\Sigma(O,OH) = 8$

	r	1	2	3	4	5	6	7	8	9
Ca^{2+}	0.99 Å	—	—	—	—	—	—	—	—	0.165
Mn^{2+}	0.80	0.004	0.004	0.037	0.006	—	0.003	—	0.007	—
Zn^{2+}	0.74	—	—	0.444	—	—	0.042	—	nil	—
Fe^{2+}	0.74	0.780	0.447	0.381	—	—	0.442	0.32*	0.499	0.041
Ti^{4+}	0.68	0.264	0.326	0.208	0.208	0.406	0.196	0.34	0.200	0.151
Mg^{2+}	0.66	0.710	0.983	0.731	1.153	1.017	1.000	1.26	0.929	0.171
Fe^{3+}	0.64	0.344	0.209	0.379	0.657†	0.419	0.318	—	0.321	0.411
Cr^{3+}	0.63	—	—	nil	0.012	—	0.042	—	nil	—
Al^{3+}	0.51	3.458	3.533	3.614	3.615	3.695	3.719	3.76	3.788	4.248
Si^{4+}	0.42	0.043	0.044	—	—	—	—	0.04	—	0.110
OH^-		0.381	0.427	—	—	—	—	—	—	0.225
O^{2-}		7.619	7.573	8.000	8.000	8.000	8.000	8.000	8.000	7.775
ΣR^{n+}		5.603	5.546	5.794	5.651	5.537	5.762	5.72	5.744	5.297
Sp. gr.		3.93	3.80	—	3.81	—	3.821	3.699	3.817	3.81
ω		1.848	1.820	1.837	—	1.85	1.850	1.805	1.850	1.851
ϵ		1.823	1.800	1.809	—	1.82	1.812	1.783	1.812	1.802
Polytype		18R	5H	?	4H+15H	?	?	5H	?	?

The cation radii, quoted from Ahrens (1952), are for sixfold coordination.

1. Högbomite-B, Transvaal (Nel, 1949).
2. Högbomite-A, Transvaal (Nel, 1949).
3. Zinc-högbomite, Russia. Analysis II of Moleva and Myasnikov (1952).
4. Högbomite, Castor, Sweden (Gavelin, 1917).
5. Högbomite, Smyrna, Turkey (Önay, 1949).
6. Högbomite, Russia. Analysis I of Moleva and Myasnikov (1952).
7. Högbomite, Mautia Hill, Tanganyika.
8. Högbomite, Russia. Analysis III of Moleva and Myasnikov (1952).
9. Högbomite, Shoriya Mountains, Siberia. Analysis III of Kuzmin (1960).

* Total Fe calculated as Fe^{2+} .

† Total Fe calculated as Fe^{3+} .

högbomites was attributed by Nel (1949) to impurities, but the finding of a similar content of Si in the Tanganyika högbomite by X-ray microanalysis demonstrates almost conclusively that Si^{4+} can be present, at least in small quantity, in högbomite.

The unit-subcell contents shown in table III display a certain degree of general similarity. The cation content does not approximate to a whole number, but lies between 5.54 and 5.79, of which an amount between 3.46 and 3.79 is accounted for by Al^{3+} , the difference being due to the principal larger cations, Fe^{3+} , Mg^{2+} , Ti^{4+} , Fe^{2+} , and Zn^{2+} , in

widely varying proportions. No simple stoichiometric composition for ideal högbomite is evident from the data of table III and in the absence of a crystal structure determination no detailed exposition of högbomite compositions is possible. It can, however, be concluded from the presence of Si^{4+} in the Tanganyika högbomite that some cations are probably on fourfold sites and it may be supposed on general grounds that Mn^{2+} , Zn^{2+} , Fe^{2+} , Ti^{4+} , and Mg^{2+} lie on sixfold sites; the remaining cations, Fe^{3+} , Cr^{3+} , and Al^{3+} , commonly occur in both fourfold and sixfold coordination. The uncertainty of the coordination of the dominant cation Al^{3+} precludes any attempt at significant quantitative grouping of cations in the högbomite unit-subcell. An appreciable content of Ti does, however, appear from the data of table III to be essential to the högbomite structure, although the influence of titanium concentration on the relationship of the stability field of högbomite to natural physical conditions rather than the presence of Ti as a crystal chemical requirement may well be critical. Högbomite compositions are shown in the $\text{MgO}-\text{Al}_2\text{O}_3-\text{TiO}_2$ system in fig. 2 with the divalent cations plotted as Mg and the trivalent cations as Al; they occupy a restricted area in the spinel-tiellite(pseudobrookite structure)-corundum field close to the spinel corner. In general terms the range of högbomite compositions may be represented as $R_{1.0-1.6}^{2+} \text{Ti}_{0.2-0.4}^{4+} R_{3.7-4.3}^{3+} \text{O}_{7.6-8.0}^{2-} (\text{OH})_{0-0.4}^-$; in analogous terms spinel appears as $R_{5.3}^{2+} R_3^{3+} \text{O}_8^{2-}$ and corundum as $R_{5.3}^{3+} \text{O}_8^{2-}$.

Preliminary structural conclusions. It is convenient at this point to consider what deductions about the structure of högbomite can be drawn from the dimensions and symmetry of the unit-cell and from an additional piece of evidence, the intensities of the 000*l* reflections of the specimens studied. The relevant data are set out in tables I and IV.

For each specimen the *a*-axis is close to 5.72 Å, a value corresponding to twice the O-O distance in close-packed planes of oxygen ions if an effective radius of 1.43 Å is assigned to O^{2-} . It would therefore seem reasonable to assume that högbomite is built with approximately close-packed planes of oxygen ions parallel to (0001). The manner in which the planes are stacked can be deduced from the observation that *c* for each specimen is some multiple *n* of 4.6 Å. For cubic close-packing (ABCA . . .) the repeat distance normal to the sheets is $\sqrt{6}$ times the oxygen separation within the close-packed sheets; for hexagonal close packing (ABA . . .) the factor is $\frac{2}{3}\sqrt{6}$. If the oxygen ions are cubic close-packed *c* should then be some multiple of 7.00 Å, and if hexagonal close-packed some multiple of 4.66 Å. The oxygen ions in högbomite

cannot, therefore, all be in cubic close-packing; they may be in hexagonal close-packing, but are more likely to be arranged in less simple sequences of close-packed (0001) layers. Thus the sequence in högbomite-4H may be ABABABABA, or ABABCBABA, or ABCABACBA, etc.

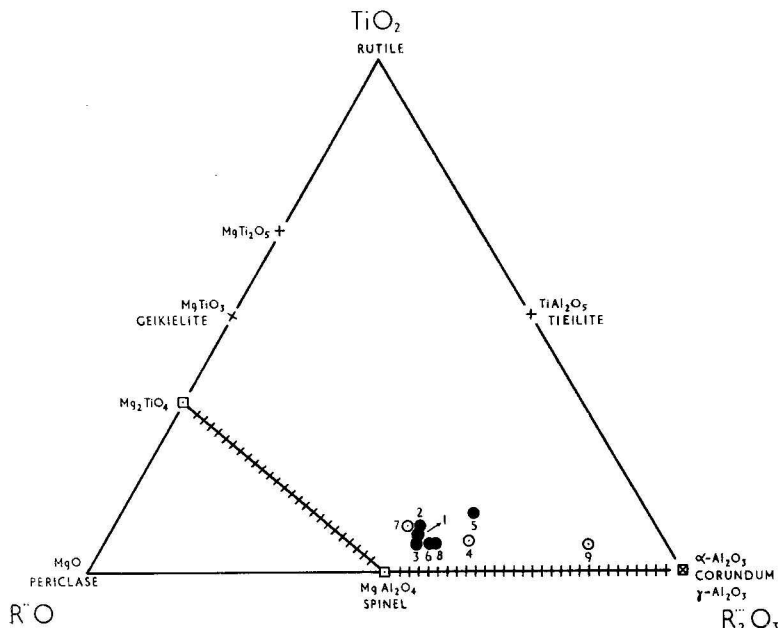


FIG. 2. Plot of högbomite compositions in the $MgO-Al_2O_3-TiO_2$ system with divalent cations represented as Mg and trivalent cations as Al. Numbers refer to the analyses of table III. Key: ● reliable högbomite compositions; ○ less satisfactory compositions; + phases of pseudobrookite structure; × phases of corundum-ilmenite structure type (hexagonal-close-packed oxygen); □ spinel end-members (cubic-close-packed oxygen); HHH spinel solid solutions.

The diffraction symbol of each specimen of högbomite listed in table I was determined by observation of the symmetry of a -axis oscillation photographs and of the systematic absences in $hh\bar{2}hl$, $h\bar{h}0l$, and $000l$ reflections on zero and first layer a -axis equ-inclination Weissenberg photographs. The diffraction symbol of each polytype, which does not vary for specimens of similar c -axial length, is shown in table IV. Polytypes with H lattices display Laue symmetry $6/mmm$ and have a c -glide plane when n is even, but mirror planes only when n is odd; polytypes

with R lattices display Laue symmetry $\bar{3}m$ and have no glide planes. The conclusion, based on the sequence of observed unit-cell dimensions, that the oxygen ions lie in a close-packed arrangement further limits the number of space groups possible for each polytype since close-packing is inconsistent with the presence of a simple rotation hexad.

Two other aluminate minerals with unit-cell dimensions related to those of the högbomites have for some time been recognized as having their oxygen ions in approximately hexagonal close-packing. Nigerite,

TABLE IV. Preliminary structural data for högbomite and related minerals

Polytype	c/n	Diffraction symbol	Possible space groups	Intensity of 000 l reflexions	
				absent for $l =$	strong for $l =$
Nigerite-3H*	4.62	$\bar{3}mP \dots$	$P\bar{3}m1, P\bar{3}1m$	—	?
Taaffeite-4H†	4.60	$6/mmmP6_3 \dots$	$P6_322$	$2n+1$?
Högbomite-4H	4.59–4.60	$6/mmmP \dots c$	$P6_3mc, P\bar{6}2c,$ $P6_3/mmc$	$2n+1$	$4n$
Högbomite-5H	4.59–4.60	$6/mmmP \dots$	$P\bar{6}2m, P\bar{6}m2$	—	$5n$
Högbomite-6H	4.59–4.60	$6/mmmP \dots c$	$P6_3mc, P\bar{6}2c,$ $P6_3/mmc$	$2n+1$	$6n$
Högbomite-15H	4.6	?	?	?	$15n$
Högbomite-18R	4.63	$\bar{3}mR \dots$	$R32, R3m,$ $R\bar{3}m$	$3n \pm 1$	$18n$

* Data quoted from Bannister, Hey, and Stadler (1947).

† Data quoted from Anderson, Payne, and Claringbull (1951).

described by Bannister, Hey, and Stadler (1947), has a 5.72 Å, c 13.86 Å, diffraction symbol $\bar{3}mP \dots$, and unit-cell contents $Pb_{0.04}Mn_{0.01}Fe_{0.39}^{2-}Zn_{0.59}Mg_{0.33}Sn_{1.77}Ti_{0.02}Fe_{1.57}^{3+}Al_{10.52}O_{22.16}(OH)_{1.84}$. It contains six close-packed (0001) oxygen layers and is an example of the 3H polytype, not yet observed in högbomite. Taaffeite, described by Anderson, Payne, and Claringbull (1951), has a 5.72 Å, c 18.38 Å, space group $P6_322$, and unit-cell contents $Mg_{3.6}Fe_{0.8}^{3+}Al_{15.0}Be_{4.7}O_{32}$. It is a 4H polytype analogous to the Swedish högbomites.

The existence of minerals of such divergent composition with structures related to, if not identical with, that of högbomite points to the extreme tolerance of the structure to variation in cation radius. Indeed, the tolerance is such that cations of radius 0.35, 0.51, 0.64, 0.66, 0.68, and 0.74 Å can substitute for one another as major constituents, the smaller ions on fourfold and the larger ions on sixfold sites, without affecting a or c/n to any considerable extent.

The unit-subcell common to högbomite and its analogues, with

dimensions close to $a' 5.72 \text{ \AA}$, $c' 4.6 \text{ \AA}$, thus contains eight oxygen anions, to which the coordinates $0 0 0$, $\frac{1}{2} 0 0$, $0 \frac{1}{2} 0$, $\frac{1}{2} \frac{1}{2} 0$, $\frac{1}{6} \frac{1}{3} z$, $\frac{2}{3} \frac{1}{3} z$, $\frac{1}{6} \frac{5}{6} z$, $\frac{2}{3} \frac{5}{6} z$ can be assigned, and, in the interstices between the approximately close-packed anions, eight sixfold and sixteen fourfold possible cation sites. However, of these twenty-four possible sites only 5.5 to 5.8 are occupied by cations in the average unit-subcell of högbomite (table III), 5.08 in nigerite, and 6.05 in taaffeite. While the actual distribution of cations over the possible interstitial sites cannot be determined from the data at present available, consideration of the systematic variation in intensity of the $000l$ reflections (table IV) enables some possibilities to be dismissed. A polytype nH produces strong $000l$ reflections only where l is a multiple of n ; of these the lowest angle reflection is that with indices $000n$. The hypothetical oxygen arrangement, to which there is no alternative, precludes the contribution of any significant amount of scattering from oxygen anions to the intensity of the $000n$ reflection. The cations must therefore be so distributed as to contribute as much scattering as possible to the high intensity of the $000n$ reflection; in particular there must be no large proportion of cations with z coordinates differing by $c'/2$. Although it would be idle to speculate further in the absence of detailed intensity data, it should be borne in mind that there may be essential differences in the cation content of adjacent unit-subcells, and that it must be significant that högbomite unit-cells always contain an even number of close-packed (0001) oxygen layers.

The analogy with the well-known polytypism of SiC (Thibault, 1944; Ramsdell, 1947) is close. There the structural unit common to all polytypes is hexagonal with $a' 3.073 \text{ \AA}$, $c' 2.513 \text{ \AA}$; it is simpler than the högbomite unit, containing only one atom of Si and one of C, and is, of course, of fixed composition. Stacking of the structural unit in various mixed hexagonal and cubic close-packed sequences produces a series of polytypes with hexagonal unit-cell dimensions $a = a'$, $c = nc'$. Strong $000l$ reflections appear only where l is a multiple of n . Polytypes may have either hexagonal or rhombohedral lattices; one is cubic. A great many SiC polytypes have been described, with unit-cells ranging in content from four to several hundred molecules of SiC. ZnS displays a closely similar series of polytypes (Smith, 1955).

In considering the relationship of högbomite to minerals of known structure particular attention must be paid to corundum and spinel, the formulae of which may be written as $\text{Al}_{5/3}\text{O}_8$ and $\text{Mg}_2\text{Al}_4\text{O}_8$ respectively. The composition of högbomite can be represented in simplified form as

ranging from $(\text{Mg,Ti,Al})_{5.5}\text{O}_8$ to $(\text{Mg,Ti,Al})_{5.8}\text{O}_8$. Corundum has hexagonal close-packed oxygen with aluminium occupying in a regular manner two-thirds of the sixfold interstices. The a -axis of corundum is at 30° to that in hōgbomite relative to the structure of the close-packed planes and c is $3 \times 4.32 \text{ \AA}$ (shorter than in nigerite since there are no large cations). Spinel has cubic close-packed oxygen with cations on both fourfold and sixfold sites. Synthetic spinels can be prepared with excess aluminium corresponding to titanium-free hōgbomite compositions; $\gamma\text{-Al}_2\text{O}_3$ has a defect spinel structure. Titanospinel in which (MgTi) substitutes for (AlAl) can also be synthesized. The length of the $[111]$ axis in spinel is $3 \times 4.67 \text{ \AA}$ and the sequence of oxygen planes is that of cubic close packing. Hōgbomite clearly bears some structural resemblance to both corundum and spinel, but it is neither a substituted corundum nor a substituted spinel.

The twinning of hōgbomite in the one specimen in which it has been observed (no. 10, Toombeola) contributes supporting evidence of the structural relationship of hōgbomite to spinel. The twins are quadruplets with their c -axes mutually inclined at 70.5° , corresponding to the angle between the normals to close-packed planes in cubic close packing, $[111] \wedge [1\bar{1}1] = 70^\circ 32'$. In the course of his examination of the twins with oscillation photographs Dr. M. G. Bown observed that occasionally the different individuals of a quadruplet might consist of different polytype intergrowths, for instance in one case the principal individual was $15R + 6H$ and one of the lesser individuals was $15R + 6H + 4H$. Another observation bearing on the relationship is that of the overgrowth of nigerite on the spinel gahnite such that $[0001]$ of nigerite is parallel to $\langle 111 \rangle$ of gahnite (Bannister *et al.*, 1947).

Another aluminate structure that it may be appropriate to mention is that typified by β -alumina, $\text{Na}_2\text{Al}_{22}\text{O}_{34}$, which has the space group $P6_3/mmc$ and unit-cell dimensions $a \ 5.548 \text{ \AA}$, $c \ 22.45 \text{ \AA}$ (Beever and Ross, 1937), not unlike those of hōgbomite- $5H$. The β -alumina structure is exemplified in a number of synthetic compounds (*vide* Donnay and Nowacki, 1954) and in the minerals hionite (Curien, Guillemin, Orcel, and Sternberg, 1956) and magnetoplumbite (Adensköld, 1938; Berry, 1951). It consists of blocks of approximately cubic-close-packed oxygen ions, with aluminium on fourfold and on sixfold interstitial sites, linked by a layer of sodium and oxygen ions not in close packing; it neither exhibits polytypism nor has $000l$ reflections that are strong only for $l = 5n$.

Dr. C. H. Kelsey and the author are at present engaged on the

determination of the crystal structure of högbomite-5H from Mautia Hill, Tanganyika.

X-ray powder pattern. Several högbomite powder patterns are in the literature. Christophe-Michel-Lévy and Sandrea (1953) indexed a powder pattern of 15 lines by means of Hull-Davey charts, finding a tetragonal unit-cell with a 8.34 Å, c 7.96 Å. Their d -spacings and intensities are consistent with the data of table V; their indexing cannot be accepted. Mikheev (1957) indexed a powder pattern of 41 lines by the same technique and found a hexagonal unit-cell with a 9.856 Å, c 22.43 ± 0.01 Å; he derived the right system, but chose a at 30° to its correct position. Kuzmin (1960) published unindexed d -spacings for three patterns of 48, 35, and 54 lines.

The low θ peaks on a diffractometer trace of högbomite from Mautia Hill, Tanganyika, were indexed from the single crystal data and the accuracy of the unit-cell dimensions was improved by measurement of θ for the $11\bar{2}0$ and $10\bar{1}7$ peaks on a diffractometer trace taken with Cu- $K\alpha$ radiation at 3 in. per degree of θ with AnalaR NaCl as internal standard and run six times over the range θ 15° to 17°. Assuming θ 15.866° for the 200 reflection of NaCl the unit-cell dimensions were evaluated as a 5.718 ± 0.002 Å, c 23.02 ± 0.01 Å. With these unit-cell dimensions and a knowledge of the relative intensities of all the relevant reflections from single crystal photographs, a diffractometer trace taken with Cu- $K\alpha$ radiation from θ 5° to 40° and a powder photograph also on Cu- $K\alpha$ were unambiguously indexed. The indexed powder data are shown in table V: the weakest lines (vw, vvw) were observed only on the photograph.

The unit-cell dimensions of Transvaal högbomite-B were similarly refined by measurement of θ for the $11\bar{2}0$ 0.1.1.23, and 0.1.1.26 peaks with reference to the 200 peak of NaCl in six runs over the range θ (Cu- $K\alpha$) 15° to 17°. Evaluation of the unit-cell dimensions as a 5.738 ± 0.001 Å, c 83.36 ± 0.05 Å combined with intensity data from single crystal photographs enabled a diffractometer trace over the range θ (Cu- $K\alpha$) 5° to 36° and a powder photograph taken with Fe- $K\alpha$ radiation to be unambiguously indexed (table V).

For the other specimens of högbomite examined by single crystal methods the separation of an adequate amount of sufficiently pure material for diffractometry was not possible, except in the case of specimen 7, another 5H polytype. The difficulty of separation of högbomite indeed makes the distinction of polytypes by powder methods of little practical interest.

TABLE V. Comparison of X-Ray powder data for hōgbomite, taaffeite, and nigerite

Hōgbomite-5H			Hōgbomite-18R			Taaffeite-4H			Nigerite-3H		
<i>d</i>	<i>I</i>	<i>hkl</i>	<i>d</i>	<i>I</i>	<i>hkl</i>	<i>d</i>	<i>I</i>	<i>hkl</i>	<i>d</i>	<i>I</i>	<i>hkl</i>
(Å)			(Å)			(Å)			(Å)		
*4.60	m	0005	*4.63	w	0.0.0.18	*4.57	m	0004	4.65	ms	10 $\bar{1}$ 1
4.54	mw	1012				4.35	mw	1012			
4.16	mw	10 $\bar{1}$ 3				3.85	vvw	10 $\bar{1}$ 3	4.01	m	10 $\bar{1}$ 2
*3.37	mw	10 $\bar{1}$ 5				*3.36	m	10 $\bar{1}$ 4	*3.36	vw	10 $\bar{1}$ 3
3.03	w	10 $\bar{1}$ 6	3.01	mw	1.0. $\bar{1}$.22						
			2.93	m	0.1. $\bar{1}$.23	2.95	mw	10 $\bar{1}$ 5			
*2.86	m	11 $\bar{2}$ 0	*2.87	s	11 $\bar{2}$ 0	*2.86	m	11 $\bar{2}$ 0	*2.84	vs	11 $\bar{2}$ 0
2.74	m	10 $\bar{1}$ 7	2.69	ms	0.1. $\bar{1}$.26	2.70	vvw	12 $\bar{3}$ 2			
			2.55	ms	1.0. $\bar{1}$.28	2.61	ms	1016			
2.49	ms	10 $\bar{1}$ 8	2.49	mw	0.1. $\bar{1}$.29						
*2.48	mw	2020									
*2.43	vs	11 $\bar{2}$ 5	*2.44	vvs	1.1. $\bar{2}$.18	*2.43	vvs	11 $\bar{2}$ 4	*2.42	vs	11 $\bar{2}$ 3
2.42	m	20 $\bar{2}$ 2	2.42	m	20 $\bar{2}$ 8						
2.36	vvw	20 $\bar{2}$ 3	2.36	mw	1.0. $\bar{1}$.31	2.38	vw	20 $\bar{2}$ 2			
2.27	mw	20 $\bar{2}$ 4	2.30	vw	2.0. $\bar{2}$.14	2.31	vwB	?			
*2.18	vw	20 $\bar{2}$ 5				*2.18	mw	20 $\bar{2}$ 4	*2.17	mw	20 $\bar{2}$ 3
			2.14	vvw	2.0. $\bar{2}$.20						
2.079	ms	20 $\bar{2}$ 6	2.081	m	0.2. $\bar{2}$.22	2.05	s	20 $\bar{2}$ 5			
			2.048	mw	2.0. $\bar{2}$.23				2.00	m	20 $\bar{2}$ 4
1.978	ms	20 $\bar{2}$ 7	1.990	mw	0.2. $\bar{2}$.25				1.981	w	11 $\bar{2}$ 5
			1.963	w	2.0. $\bar{2}$.26	1.925	m	20 $\bar{2}$ 6			
1.876	vw	20 $\bar{2}$ 8							1.847	md	20 $\bar{2}$ 5
									1.808	w	21 $\bar{3}$ 2
*1.733	vvw	21 $\bar{3}$ 5							*1.735	vw	21 $\bar{3}$ 3
						*1.720	vvw	20 $\bar{2}$ 8			
1.682	vw	21 $\bar{3}$ 6				1.684	vw	21 $\bar{3}$ 5			
1.665	vw	1.0. $\bar{1}$.13	1.665	mw	1.2. $\bar{3}$.23						
*1.648	vw	30 $\bar{3}$ 0									
1.623	wB	21 $\bar{3}$ 7	1.618	w	1.2. $\bar{3}$.26				1.647	s	21 $\bar{3}$ 4
1.596	vw	2.0. $\bar{2}$.11	1.589	vw	2.1. $\bar{3}$.28	1.596	mw	21 $\bar{3}$ 6	1.639	vvw	30 $\bar{3}$ 1
1.564	mw	21 $\bar{3}$ 8	1.572	mw	2.0. $\bar{2}$.41	1.576	vw	20 $\bar{2}$ 9			
					1.2. $\bar{3}$.29						
*1.550	mw	30 $\bar{3}$ 5	*1.558	mw	3.0. $\bar{3}$.18	*1.554	w	30 $\bar{3}$ 4			
			1.538	w	2.1. $\bar{3}$.31				1.544	s	20 $\bar{2}$ 7
*1.533	vvw	0.0.0.15									
1.511	mw	2.0. $\bar{2}$.12	1.505	w	2.0. $\bar{2}$.44	1.522	w	21 $\bar{3}$ 7			
			1.462	mw	0.2. $\bar{2}$.46	1.476	ms	2.0. $\bar{2}$.10	1.472	vwd	11 $\bar{2}$ 8
1.436	ms	2.0. $\bar{2}$.13	1.443	mw	2.0. $\bar{2}$.47	1.445	vvw	?			
*1.426	s	2240	*1.434	s	22 $\bar{1}$ 0	*1.428	s	2240	*1.433	ms	22 $\bar{4}$ 0
			1.403	vw	0.2. $\bar{2}$.49				1.416	ms	20 $\bar{2}$ 8

d-spacings ≥ 1.4 Å only are listed.

Sequence of intensities: vvs, vs, s, ms, m, mw, w, vw, vvw.

B = broad line or peak. d = doublet.

* = *h.k.i.nl.* lines that may be common to different polytypes.

The published *d*-spacings for nigerite have been converted from kX to Å units.

Accompanying the hōgbomite powder data in table V are data for the related minerals taaffeite and nigerite, quoted from Anderson *et al.* (1951) and Bannister *et al.* (1947) respectively. Common to all four

patterns are certain lines for which l is a multiple of n , including the strongest line, $11\bar{2}n$ near 2.43 \AA , and two other strong lines, $11\bar{2}0$ near 2.86 \AA and $22\bar{4}0$ near 1.43 \AA .

Stability and paragenesis. The $\text{MgO-Al}_2\text{O}_3\text{-TiO}_2$ system, in which magnesium hōgbomite may be a stable phase, has not so far been studied experimentally in the subsolidus region. The work of Berezhnoi and Gulko (1955) has, however, shown that hōgbomite has apparently no field on the liquidus; liquids of magnesium hōgbomite composition begin to crystallize spinel solid solutions at temperatures in the neighbourhood of 1900°C .

Preliminary heating experiments have shown that under dry conditions at 1 atmosphere in air hōgbomite-5H (specimen 6) begins to decompose at about 900°C . The first stage in the decomposition appears to be conversion to a 3H polytype and oriented exsolution of a phase that may be aluminous pseudobrookite. Under hydrothermal conditions at 825°C , $p_{\text{H}_2\text{O}}$ 2000 bars, partial decomposition to spinel, aluminous pseudobrookite, and rutile has been observed. The decomposition curve of hōgbomite, which in the absence of synthetic evidence may merely delimit a field of metastability, has not yet been determined; a series of decomposition and synthetic experiments is in progress.

In the absence of any adequate experimental study of the stability relations of hōgbomite interpretation of the petrographic evidence bearing on its paragenesis must necessarily be speculative, but certain common factors in its various occurrences can be discerned. In the iron ores of Ruoutevare fine-grained hōgbomite may be completely enveloped in titaniferous magnetite, or be interposed between pleonaste and magnetite grains, or occur in cracks within large pleonaste grains heavily dusted with exsolved ore (? hematite). Hōgbomite is here apparently in the main a primary phase in the crystallization of the iron-rich assemblage and in minor part an alteration product of pleonaste, a conclusion essentially in accord with that of Gavelin (1917). In its Norwegian occurrences the environment of hōgbomite is broadly similar: at the Rōdsand quarry, Sōndmōre, it occurs with ilmenite in a magnetite-corundum rock (Schetelig, 1917), in the Sogn district it is a common accessory in magnetite-ilmenite ores (Kolderup, 1928), and in the Bergen area it is associated with iron-ore minerals, but not always with spinel, at various localities in the Bergen anorthosites (Kolderup, 1936). In the Whittles, Virginia, emery hōgbomite occurs apparently as a primary phase in corundum-hercynite titaniferous-magnetite-hōgbomite assemblages;

it may be completely enveloped in magnetite, but is often interposed between spinel and magnetite, although spinel grains may be seen in contact with magnetite and corundum. The distinction made by Watson (1923 and 1925) in his descriptions of the Whittles occurrence between coarse euhedral original hōgbomite and 'cryptocrystalline' hōgbomite rimming spinel as a product of deuteric alteration would appear to be sound. In the Cortlandt, New York, emery hōgbomite was considered by Gillson and Kania (1930) to be an alteration product of spinel and Friedman (1952) in his more thorough study postulated its formation from spinel by titanium metasomatism through the partial substitutions $2(\text{Mg,Fe})^{2+} \rightarrow \text{Ti}^{4+}$ and $\text{Al}^{3+} \rightarrow \text{Fe}^{3+}$; hōgbomite does, however, occur at Cortlandt as an apparently primary phase in corundum-magnetite hōgbomite assemblages from which spinel is absent (specimen 9). In the Macon County, North Carolina, emery Friedman (1952) recognized the replacement sequence spinel \rightarrow hōgbomite-A (pale) \rightarrow hōgbomite-B (dark). In the Smyrna emery (Önay, 1949) hōgbomite mantles periclase in a diaspore rock and occurs characteristically as furlings in a calcite-corundum rock. In the Samos emery taosite, which may be hōgbomite (de Lapparent, 1947; Friedman, 1952; Agrell and Langley, 1958), is associated with diaspore, kaolinite, chloritoid, and magnetite. From Dentz Farm in the corundum fields of the eastern Transvaal Nel (1949) recorded the occurrence of cores of spinel rimmed by chlorite, corundum, and hōgbomite in aluminous lenses in serpentines, and at Frain in Moravia the alteration of pleonaste to hōgbomite in a serpentinized peridotitic pyroxenite was considered by Christophe-Michel-Lévy and Sandrea (1953) to be clearly demonstrated. In the Shoriya Mountains, about 250 miles SE. of Novosibirsk in Siberia, Kuzmin (1960) recorded hōgbomite from several corundum deposits of unspecified petrography; he suggested that it was a constant associate of corundum under conditions of excess Ti, Mg, and Fe.

Of the petrography of other hōgbomite parageneses, with the exception of that in Tanganyika, relatively little is known. In the Cameroons it occurs enclosed in pleonaste in a spilitic lava (Sandrea, 1950). Bobrovnik (1955) has described a sandstone containing detrital hōgbomite in the Ukraine.

Although not absolutely conclusive, there does therefore appear to be textural evidence for supposing that in its occurrences in aluminous or magnetite-rich hornfelses and xenoliths and in supposedly magmatic titaniferous iron ores hōgbomite may be a phase of primary crystallization, although in certain cases it seems to form overgrowths on, or occurs

as an alteration product of, spinel. At Mautia Hill in Tanganyika, however, the evidence is clear; högbomite there forms comparatively large crystals in an enstatite-tremolite-chlorite-högbomite-sapphirine-dolomite rock (fig. 1), the minerals of which show no evidence of mutual reaction and may be in equilibrium. The coarse-grained patches of dolomite are apparently stable in contact with enstatite and tremolite. Högbomite would seem to have crystallized as an alternative to spinel in an environment of relatively low Fe and high Ti concentration, although there is no other major mineral containing essential Ti present. Enstatite-spinel assemblages are well known, indeed cordierite-hyperssthene-spinel was considered by Tilley (1924) to be typical of the pyroxene-hornfels facies, but the physical conditions necessary for the stability of the assemblage have not been conclusively determined (Yoder, 1952; Roy and Roy, 1955). The effect of even small departures from the $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ system is not clear, but it would seem likely that the Ti content of the system may exercise a controlling influence on the stability of högbomite. In this context it may be relevant that högbomites of similar Ti content appear to have crystallized in conditions of widely varying Ti concentration. The physical conditions operative during the Precambrian regional metamorphism at Mautia Hill are uncertain, but it would seem probable that significantly high pressures may have been associated with moderate temperatures during the later stages of reconstitution of the neighbouring yoderite-bearing schists (McKie, 1959). The interest attaching to this högbomite occurrence lies particularly in the spinel-free paragenesis and in the clear evidence it provides of the crystallization of högbomite as an independent phase during the regional metamorphic reconstitution of the rock.

On the relative stability of the various högbomite polytypes there is little comment to be made. In other examples of stacking polytypism the crystallization of a particular polytype appears not to be simply dependent on relative thermodynamic stability, but to be controlled by the interplay of a variety of nucleation and growth factors such as the influence of impurities, or the development of screw dislocations; in the case of högbomite there is also the possibility, absent where compounds of fixed composition such as SiC are concerned, of control by composition.

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