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## *The related layered minerals ganophyllite, bannisterite, and stilpnomelane*<sup>1</sup>

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*Summary.* Two monoclinic minerals formerly classified as ganophyllite have been differentiated on the basis of single-crystal X-ray data. True ganophyllite occurs at the Harstig mine, Pajsberg, Sweden ( $a$ ,  $16.60 \pm 0.05$  Å;  $b$ ,  $27.04 \pm 0.08$  Å;  $c$ ,  $50.34 \pm 0.15$  Å;  $\beta$ ,  $94^\circ 10' \pm 10'$ ; space group  $A 2/a$ ), at the Benallt mine, Caernarvonshire, Wales, and in Aroostook County, Maine. Bannisterite, a new mineral, occurs at Franklin, New Jersey ( $a$ ,  $22.20 \pm 0.07$  Å;  $b$ ,  $16.32 \pm 0.05$  Å;  $c$ ,  $24.70 \pm 0.08$  Å;  $\beta$ ,  $94^\circ 20' \pm 10'$ ; space group  $A 2/a$ ) and at the Benallt mine, Wales. Both minerals have similar pseudocells:  $a$ ,  $5.53$  Å;  $b$ ,  $3.3$  Å;  $c$ ,  $25$  Å;  $\beta$ ,  $94^\circ$ . The chemical analysis of ganophyllite from the Harstig mine, Sweden, is: SiO<sub>2</sub>, 39.67%; Al<sub>2</sub>O<sub>3</sub>, 7.95%; Fe<sub>2</sub>O<sub>3</sub>, 0.90%; MnO, 35.15%; CaO, 1.11%; MgO, 0.20%; PbO, 0.20%; K<sub>2</sub>O, 2.70%; Na<sub>2</sub>O, 2.18%; Li<sub>2</sub>O, trace; H<sub>2</sub>O, 9.79%; total, 99.85. The chemical analysis of bannisterite from Franklin Furnace, New Jersey, is: SiO<sub>2</sub>, 46.20%; Al<sub>2</sub>O<sub>3</sub>, 4.74%; MnO, 23.02%; FeO, 6.40%; ZnO, 4.67%; CaO, 1.52%; MgO, 1.99%; Na<sub>2</sub>O, 0.29%; K<sub>2</sub>O, 1.21%; H<sub>2</sub>O, 9.74%; total, 99.78.

Both ganophyllite and bannisterite show a structural resemblance to stilpnomelane from Deer Isle, Maine, in projection on selected zones. All three have a micaceous cleavage parallel to {001} in the orientations here taken. Stilpnomelane is triclinic, pseudotrigonal, and pseudomonoclinic. In the triclinic cell,  $a = b$ ,  $22.05 \pm 0.06$  Å;  $c$ ,  $17.70 \pm 0.06$ ;  $\alpha$ ,  $124^\circ 49'$ ;  $\beta$ ,  $95^\circ 58'$ ;  $\gamma$ ,  $120^\circ 00'$  (angles  $\pm 5'$ ). In the trigonal subcell,  $a'$ ,  $3.2$  Å;  $c'$ ,  $36.4$ . Small distorted trigonal subcells for ganophyllite have  $a'$ ,  $3.38$  Å;  $c'$ ,  $37.7$ , and for bannisterite have  $a'$ ,  $3.264$  and  $c'$ ,  $37$  Å.

**G**ANOPHYLLITE, a complex manganese silicate, was first described from the Harstig mine, Pajsberg, Sweden, by Hamberg (1890). It has since been found at Franklin, New Jersey, at the Benallt mine in Wales and in the metamorphosed sedimentary manganese

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deposits of Aroostook County, Maine. A reported occurrence near San Jose, California, was disproven during the present study.

The first evidence that two different but closely related minerals have been confused under the name ganophyllite is found in the observations by Campbell Smith (1948) on the optical orientation and dehydration of crystals from the Benallt mine and from the Harstig mine. The crystals from Harstig are monoclinic with a micaceous cleavage on {001} in the orientation of Hamberg (1890). The optical orientation of

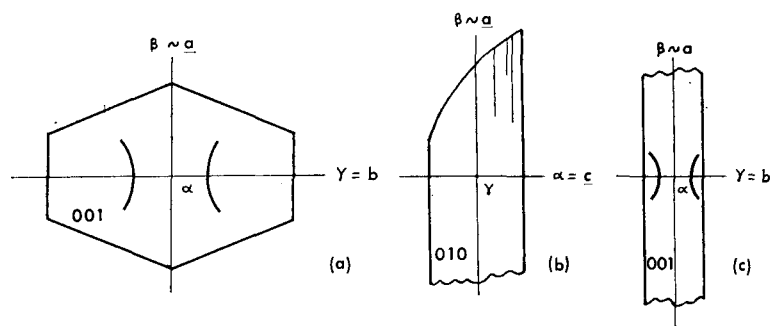


FIG. 1 *a*, Optical orientation in cleavage flake of Harstig ganophyllite; the *a*, *b*, and *c* axes of Hamberg (1890) and of the present study are parallel. *b*, lath-like crystal of Franklin ganophyllite resting on flat side, (010), showing trace of (001) cleavage. *c*, same, cleavage flake on (001).

the Harstig crystals (ganophyllite) found by Hamberg, and confirmed by Campbell Smith with the aid of X-ray single-crystal data, is shown in fig. 1. Campbell Smith observed that some of the crystals from the Benallt mine had the same optical orientation as the Harstig material, and that others had a different optical orientation as shown in fig. 2. On slight loss of water by heating or by desiccation, the two optical types were found by him to behave differently. In the Harstig material, the optic angle decreases to zero and then opens out in the plane at  $90^\circ$  to the original position. In the Benallt material with  $\beta \parallel [010]$  the optic angle increases without change of orientation.

We have confirmed these observations, and have found that these two types of crystals also occur at Franklin, New Jersey. Study by X-ray single-crystal and powder methods together with a new chemical analysis of the Franklin material has established that two different minerals occur in the Benallt and Franklin specimens. These minerals are closely related to each other and to the complex iron silicate stilpnomelane. The name ganophyllite is here restricted to the original

material from Harstig, Sweden, and the name bannisterite is proposed for the new phase.

The established localities for ganophyllite are the Harstig mine in Sweden; Franklin, New Jersey; the Benallt mine, Caernarvonshire, Wales; and Aroostook County, Maine. The occurrence in the metamorphosed sedimentary manganese deposits in Maine was first recognized in 1952 by Charles Milton, U.S. Geological Survey.<sup>1</sup> Bannisterite

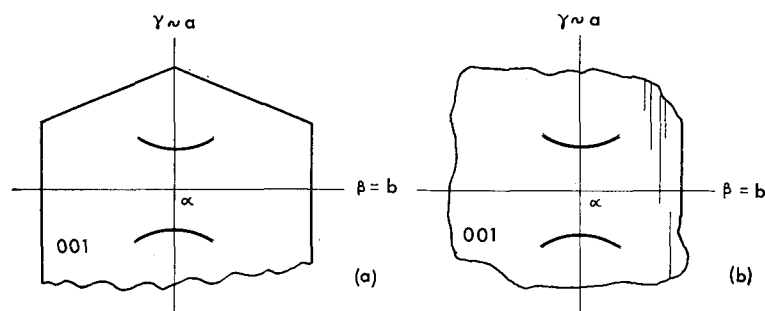


FIG. 2 *a*, Optical orientation in cleavage flake of Benallt bannisterite (from Campbell Smith, 1948). *b*, cleavage flake of Franklin bannisterite showing trace of the (010) cleavage.

occurs at the Benallt mine and at Franklin. This mineral also has been independently identified by R. Sadanaga, Y. Takeuchi, and T. Kato of the Mineralogical Institute, University of Tokyo, at the Ananai mine, Kochi, Japan.<sup>1</sup> These authors also recognized, by X-ray study, the separate identity of this mineral and ganophyllite.

#### *Ganophyllite*

*X-ray data.* Unit cell data for ganophyllite from Harstig, Sweden, and from Franklin, New Jersey, (the analysed sample of Larsen and Shannon, 1922) are compared with data for bannisterite from Franklin, New Jersey, and with stilpnomelane from Deer Isle, Maine, in table I. The data have been obtained by a combination of Weissenberg and precession camera techniques using various wave lengths of X-radiation:  $\text{Mo-K}\alpha_{\text{av}} = 0.7107 \text{ \AA}$ ,  $\text{Cu-K}\alpha_{\text{av}} = 1.5418 \text{ \AA}$ ,  $\text{Cr-K}\alpha_{\text{av}} = 2.2909 \text{ \AA}$ . Both ganophyllite and bannisterite have small monoclinic subcells, similar in projection on {010} with  $a$ ,  $5.5 \text{ \AA}$ ;  $c$ ,  $25 \text{ \AA}$ ;  $\beta$ ,  $94^\circ$ . The  $h0l$  patterns of ganophyllite and of bannisterite (fig. 3), and the  $h\bar{2}h.l$  (fig. 3),

<sup>1</sup> Personal communication.

TABLE I. Unit cell data for ganophyllite, bannisterite, and stilpnomelane

	<i>Ganophyllite</i>		<i>Bannisterite</i>	<i>Stilpnomelane</i>	
	<i>Harstig Mine, Sweden</i> <i>Harvard No. 10118</i>	<i>Franklin Furnace, N.J.</i> <i>Harvard No. 89837</i>	<i>Franklin, N.J.</i> <i>Harvard No. 10857</i>	<i>Deer Island, Maine</i> <i>Present study</i>	<i>Crystal Falls, Michigan</i> <i>Eggleton and Bailey, 1965</i>
<i>Symmetry</i>	<i>monoclinic</i>	<i>monoclinic</i>	<i>monoclinic</i>	<i>triclinic</i>	<i>triclinic</i>
<i>a</i>	16.60 ± 0.05 Å	16.59 ± 0.05 Å	22.20 ± 0.07 Å	22.05 ± 0.06 Å	21.724 ± 0.004 Å
<i>b</i>	27.04 ± 0.08	27.08 ± 0.08	16.32 ± 0.05	22.05 ± 0.06	21.724 ± 0.004
<i>c</i>	50.34 ± 0.15	50.36 ± 0.15	24.70 ± 0.08	17.70 ± 0.06	17.740 ± 0.004
$\beta$	94° 10' ± 0° 10'	94° 10' ± 0° 10'	94° 20' ± 0° 10'	124° 49' ± 0° 05'	124.14 ± 0.015°
Vol.	22536 Å <sup>3</sup>	22560 Å <sup>3</sup>	8924 Å <sup>3</sup>	95° 58' ± 0° 05'	95.86° ± 0.023°
Space group	<i>Aa</i> or <i>A2/a</i>	<i>Aa</i> or <i>A2/a</i>	<i>Aa</i> or <i>A2/a</i>	120° 00' ± 0° 05'	120.00° ± 0.02°
	<i>Monoclinic pseudocell</i>			Vol.	5117 Å <sup>3</sup>
<i>a</i>	5.53 Å	5.53 Å	5.55 Å	<i>a</i> *	0.06262
<i>b</i>	13.52	13.54	3.264	<i>b</i> *	0.07586
<i>c</i>	25.17	25.17	24.70	<i>c</i> *	0.08237
$\beta$	94° 10'	94° 10'	94° 20'	$\alpha^*$	43° 37'
Vol.	1878 Å	1880 Å <sup>3</sup>	446 Å <sup>3</sup>	$\beta^*$	56° 45'
	<i>Pseudo-space-group</i>			$\gamma^*$	46° 44'
	<i>Ia</i> or <i>I2/a</i>	<i>Ia</i> or <i>I2/a</i>	<i>A2, Am, or A2/m</i>	<i>Calculated angles, special relationships</i>	
	<i>Calculated angles</i>			$\alpha = \cos^{-1} -11b/24c$	
	$\beta = \cos^{-1} -2a/9c = 94^\circ 12'$	—	$\beta = \cos^{-1} -a/12c = 94^\circ 18'$	$\beta = \cos^{-1} -a/12c$	
				$\alpha^* = \cos^{-1} 2c^*/3b^*$	
				$\beta^* = \cos^{-1} 5c^*/12a^*$	

$2h.\bar{h}.l$ , and  $hhl$  patterns of stilpnomelane are very similar, with only the weak superlattice reflections appearing different. More pronounced are the variations in the  $0kl$  patterns of ganophyllite, of bannisterite, and of stilpnomelane, illustrated in fig. 4. The pattern differences are consequent to different numbers of trigonal subcells being packed

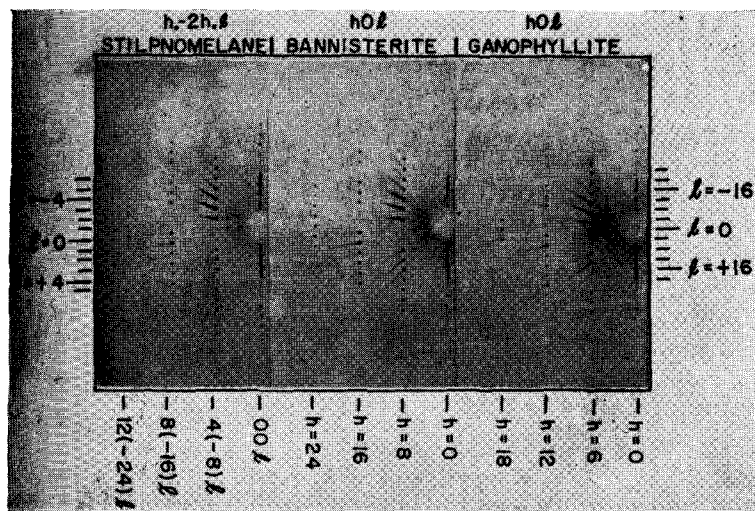


FIG. 3. The  $h0l$  patterns of ganophyllite and of bannisterite and  $h.\bar{2}h.l$  pattern of stilpnomelane (Buerger precession photographs). Note similarity of patterns for reflections corresponding to the subcell.

parallel to  $b$  in ganophyllite (8),  $b$  in bannisterite (5), and parallel to  $b \sin \gamma$  (or  $a \sin \gamma$ ) in stilpnomelane (6).

Ganophyllite has a micaceous cleavage parallel  $\{001\}$  and secondary cleavages parallel  $\{100\}$  and  $\{010\}$ . A modified layer structure, possibly a combination of a sheet and chain structure, is indicated. The very large repeat period of  $c = 50 \text{ \AA}$  appears to represent the interstratification of four successive equal layers, alternately arranged, with basal spacing of  $12.5 \text{ \AA}$ . The basal spacing of these layers is not significantly changed by heating overnight at  $120^\circ \text{ C}$  ( $d_{004}$ ,  $12.5 \text{ \AA}$ ) or by glycolating ( $d_{004}$ ,  $12.55 \text{ \AA}$ ) or by exposing to a humid atmosphere ( $d_{004}$ ,  $12.53 \text{ \AA}$ ). The body-centred pseudocell with  $a$ ,  $5.5 \text{ \AA}$ ;  $b$ ,  $13.5 \text{ \AA}$ ;  $c$ ,  $25 \text{ \AA}$ ;  $\beta$ ,  $94^\circ$  contains two layers, and the other two layers are related to these by an  $A$ -centring and an  $a$ -glide.

The axial elements derived for the monoclinic pseudocell (table I) are:  $a:b:c = 0.409:1:1.862$ ;  $\beta = 94^\circ 10'$ . Those derived for the true cell are:  $a:b:c = 0.614:1:1.862$ ;  $\beta = 94^\circ 10'$ . The axial elements reported in the original description of ganophyllite (Hamberg, 1890) correspond to those derived for the monoclinic pseudocell in the present

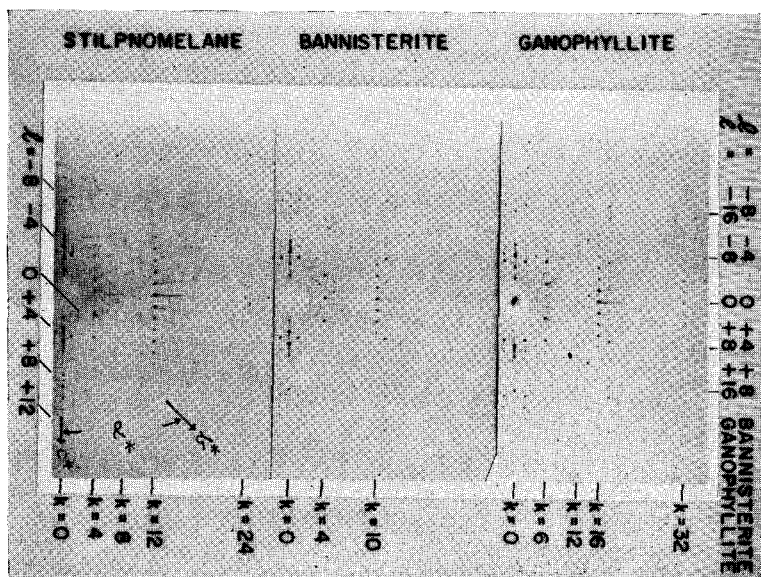


FIG. 4. The  $0kl$  patterns of ganophyllite, bannisterite, and stilpnomelane (Buerger precession photographs). Note the similarity of patterns for reflections on row lines  $k = 16$  in ganophyllite,  $k = 10$  in bannisterite, and  $k = 12$  in stilpnomelane.

The  $0kl$  of stilpnomelane is pseudo-orthogonal with  $\cos \alpha^* = \frac{2}{3}c^*/b^*$ .

study:  $a:b:c = 0.4130:1:1.8309$ ;  $\beta = 93^\circ 21'$ . These were derived by Hamberg from approximate measurements of forms  $\{010\}$ ,  $\{001\}$ ,  $\{110\}$ , and  $\{011\}$ . We have kept the original orientation of Hamberg, although this departs from the convention in having  $c > a$ , in order to designate the micaceous cleavage as  $\{001\}$ . In the preliminary announcement of two distinct phases, the  $a$  and  $c$  axes were interchanged, according to the convention  $a > c$ ; ganophyllite is phase A and bannisterite is phase B of Lindberg (1965, A152-A153). The indexed X-ray powder data for ganophyllite are given in table II. Only the reflections corresponding to the monoclinic pseudocell are strong enough to appear on the powder pattern.

Ganophyllite has pronounced pseudotrigonal symmetry, with a pseudo-threefold axis normal to (001), the plane of the micaceous cleavage. A small distorted trigonal subcell, defined by the primed unit-cell edges, is related to the true cell by:  $a' = a/3 \tan 58^\circ 35' = b/8 = 3.38 \text{ \AA}$ ,  $c' = 3d_{004} = 37.7 \text{ \AA}$ . The ideal relationship is  $a' = a/3\sqrt{3}$ . The true cell of ganophyllite contains 64 distorted trigonal subcells. Stilpnomelane has a similar trigonal subcell as reported by Eggleton and Bailey (1965) with  $a' = a/4\sqrt{3} = 3.1 \text{ \AA}$ ,  $c' = 3d_{001} = 37 \text{ \AA}$ .

*Chemical composition.* Chemical analyses of ganophyllite have been reported from the Harstig mine, Sweden (table III) and from Franklin, New Jersey (Larsen and Shannon, 1922). Analyses of bannisterite are available on material from Franklin (table III, also Foshag, 1936) and from Japan (Yoshimura, Shirozu, and Hirowatari, 1955). The chemical composition is complex and varies somewhat even in different specimens from the same locality. The main variations are in the mutual substitutions of divalent cations, although manganese is always dominant. Additional variations occur in the ratios of other constituents. A distinction between octahedral and tetrahedral aluminum and between water molecules and hydroxyl ions cannot be made at the present time. Attempts to calculate a possible formula unit for ganophyllite based upon chemical analysis, measured volume, and specific gravity indicate a total of 88 oxygen atoms (including oxygen, hydroxyl, and water) in the monoclinic pseudocell ( $Z = 12$  for true cell). This value corresponds to 16.5 oxygen plus hydroxyl plus water in the trigonal subcell of ganophyllite, or 33 if  $c'$  is doubled. This is a larger number of total oxygen than is suggested by analogy to stilpnomelane. The trigonal subcell content of stilpnomelane as determined from a chemical analysis by Ayres, the cell volume, and the measured density calculates to  $O + OH = 15$ , but the final structural subcell accounts for even less oxygen,  $O \pm OH = 14$  (Eggleton and Bailey, 1965).

The calculated specific gravities for 16.5, 15, or 14 oxygen plus hydroxyl plus water in the trigonal subcell of ganophyllite correspond, respectively, to 2.875, 2.614, and 2.440; the measured specific gravity is 2.84. In the present study, it appears significant that the trigonal subcell content of bannisterite, discussed elsewhere in this paper, also calculates to a total of 16.5 oxygen plus hydroxyl plus water.

*Optical properties.* The optical orientation on the perfect cleavage as found by Hamberg (1890), W. Campbell Smith (1948), and us for the Harstig crystals is shown in fig. 1a. The optical orientation of the lathlike cleavage flakes from Franklin as found by Campbell Smith

TABLE II. X-ray powder data for ganophyllite and bannisterite

<i>Bannisterite</i> <i>Franklin Furnace, N.J.</i>					<i>Ganophyllite</i>						
<i>Calculated*</i>		<i>Measured</i>			<i>Calculated†</i> <i>Harstig, Sweden</i>		<i>Measured</i>			<i>Franklin, N.J.</i>	
<i>hkl</i>	<i>d</i> (Å)	<i>I</i>	<i>I</i>	<i>d</i> (Å)	<i>hkl</i>	<i>d</i> (Å)	<i>I</i>	<i>I</i>	<i>d</i> (Å)	<i>I</i>	<i>d</i> (Å)
011	13.61	vw	—	—	—	—	—	—	—	—	—
002	12.31	s	100	12.33	004	12.55	c	100	12.53	100	12.59
11 $\bar{1}$	11.81	c	—	—	022	11.90	c	2	11.86	2	11.95
111	11.39	c	1	11.45							
200	11.07	vw	—	—							
21 $\bar{1}$	8.772	w	2	8.779							
20 $\bar{2}$	8.562	w	—	—							
211	8.418	w	2	8.428							
020	8.163	a	—	—							
202	7.937	mw	1	7.954							
120	7.657	c	—	—							

\* Bannisterite from Franklin Furnace, N.J.,  $d_{hkl}$  calculated from  $a$ , 22.20;  $b$ , 16.32;  $c$ , 24.70 Å;  $\beta$ , 94° 20'; space group  $Aa$  or  $A2/a$ . All calculated  $d$ -spacings listed for  $d \geq 3.0$  Å.

† Ganophyllite, Harstig, Sweden,  $d_{hkl}$  calculated from  $a$ , 16.60;  $b$ , 27.04;  $c$ , 50.34 Å;  $\beta$ , 94° 10'. All calculated  $d$ -spacings  $> 2.7$  Å, and those calculated  $d$ -spacings  $< 2.7 > 2.0$  Å consistent with measured  $d$ -spacings are listed for  $hkl$  reflections with  $h/3 + k/2 + l/2 = 2n$  and for  $h0l$ ,  $h = 6n$  ( $l = 4n$ ). Other reflections consistent with space group  $Aa$  or  $A2/a$  are too weak to appear on the powder photograph (except 126 and 140).

‡ Single crystal intensities estimated visually from Weissenberg and precession patterns taken with different exposure times and different radiations: c = cut-off at centre of film. Broad reflections designated as b, reflections observed to be absent = a.

§ 114.59 mm camera; film measurements corrected for shrinkage. Lower limit of  $2\theta$  measurable is approximately 8°. Bannisterite, powder film 15464 and ganophyllite, powder film 15441, Mn-filtered Fe radiation,  $Fe-K_{\alpha V} = 1.9373$ ; ganophyllite, powder film 15499, V-filtered Cr radiation,  $Cr-K_{\alpha V} = 2.2909$  Å.



<i>Bannisterite</i> <i>Franklin Furnace, N.J.</i>				
<i>Calculated</i>		<i>Measured</i>		
<i>hkl</i>	<i>d</i> (Å)	<i>Single crystal</i>	<i>Powder film 15464</i>	
		<i>I</i>	<i>I</i>	<i>d</i> (Å)
013	7.331	vw	—	—
113	7.107	w	4	7.106
113	6.826	m	3	6.821
022	6.803	vw	—	—
311	6.605	w	1	6.608
122	6.579	vw	—	—
220	6.570	a	—	—
122	6.427	vw	—	—
311	6.378	vw	2	6.382
213	6.313	w	—	—
004	6.154	w	1	6.162
213	5.931	vw	1	5.934
222	5.907	w	—	—
222	5.692	w	—	—
204	5.562	mw	5	5.562
400	5.534	mw	—	—
320	5.473	w	—	—
313	5.385	a	—	—

TABLE II (cont.)

<i>Ganophyllite</i>						
<i>Calculated</i>		<i>Measured</i>				
<i>Harstig, Sweden</i>		<i>Harstig, Sweden</i>			<i>Franklin, N.J.</i>	
<i>hkl</i>	<i>d</i> (Å)	<i>Single crystal</i>	<i>Powder film 15441</i>		<i>Powder film 15499</i>	
		<i>I</i>	<i>I</i>	<i>d</i> (Å)	<i>I</i>	<i>d</i> (Å)
026	7.107	vw	3	7.239	1	7.111
040	6.740	w	2	6.800	1	6.750
126	6.394	w	—	—	—	—
008	6.275	mw	4	6.375	4	6.274
140	6.258	w	—	—	1	6.238
044	5.952	vw	—	—	1	5.939

TABLE II (cont.)

<i>Bannisterite</i> <i>Franklin Furnace, N.J.</i>					<i>Ganophyllite</i>						
Calculated		Measured			Calculated		Measured				
		Single crystal	Powder film 15464		Harstig, Sweden	Harstig, Sweden			Franklin, N.J.		
<i>hkl</i>	<i>d</i> (Å)	<i>I</i>	<i>I</i>	<i>d</i> (Å)	<i>hkl</i>	<i>d</i> (Å)	<i>I</i>	<i>I</i>	<i>d</i> (Å)	<i>I</i>	<i>d</i> (Å)
031	5.316	w	—	—							
41 $\bar{1}$	5.203	a	—	—							
40 $\bar{2}$	5.195	w	5	5.196							
13 $\bar{1}$	5.187	m	—	—							
204	5.173	m	—	—							
131	5.149	m	—	—							
32 $\bar{2}$	5.112	—	—	—	320	5.112	m	6	5.116	6	5.111
411	5.053	vw	—	—							
313	5.035	w	—	—							
024	4.914	w	—	—							
402	4.912	w	1	4.911							
322	4.899	—	—	—							
12 $\bar{4}$	4.861	w	—	—	32 $\bar{4}$	4.847	vw	—	—	—	—
23 $\bar{1}$	4.822	vw	—	—							
231	4.762	vw	—	—							
124	4.737	w	—	—							
015	4.715	w	1	4.709	0.2.10	4.704	vw	1	4.707	—	—
11 $\bar{5}$	4.692	a	—	—	324	4.625	w	2	4.631	—	—
22 $\bar{4}$	4.596	mw	10	4.593	048	4.596	vw	—	—	—	—

TABLE II (cont.)

<i>Bannisterite</i> <i>Franklin Furnace, N.J.</i>					<i>Ganophyllite</i>						
<i>Calculated</i>		<i>Measured</i>			<i>Calculated</i> <i>Harstig, Sweden</i>		<i>Measured</i> <i>Harstig, Sweden</i>			<i>Measured</i> <i>Franklin, N.J.</i>	
<i>hkl</i>	<i>d (Å)</i>	<i>Single crystal</i>	<i>Powder film 15464</i>	<i>d (Å)</i>	<i>hkl</i>	<i>d (Å)</i>	<i>Single crystal</i>	<i>Powder film 15441</i>	<i>d (Å)</i>	<i>Powder film 15499</i>	<i>d (Å)</i>
		<i>I</i>	<i>I</i>				<i>I</i>	<i>I</i>		<i>I</i>	
420	4.581	ms	—	—							
413	4.570	mw	—	—							
215	4.456	vw	—	—							
422	4.384	—	—	—	062	4.437	w	4	4.406	2	4.443
224	4.369	w	—	—							
331	4.346	—	—	—							
331	4.279	—	—	—							
413	4.279	mw	5	4.280							
404	4.279	a	—	—							
511	4.264	mw	—	—	342	4.255	m	1	4.250	1	4.249
133	4.257	vw	—	—							
233	4.233	vw	—	—							
215	4.228	vw	—	—							
324	4.211	—	1	4.211							
422	4.209	—	—	—							
511	4.160	—	—	—	00.12	4.183	ms	6	4.180	12	4.175
233	4.136	vw	—	—	342	4.175	vw				
315	4.110	vw	—	—	328	4.100	m	2	4.090	4	4.098

TABLE II (cont.)

<i>Bannisterite</i> <i>Franklin Furnace, N.J.</i>					<i>Ganophyllite</i>						
<i>Calculated</i>		<i>Measured</i>			<i>Calculated</i>		<i>Measured</i>			<i>Franklin, N.J.</i>	
		<i>Single crystal</i>	<i>Powder film 15464</i>		<i>Harstig, Sweden</i>		<i>Harstig, Sweden 15441</i>			<i>Powder film 15499</i>	
<i>hkl</i>	<i>d (Å)</i>	<i>I</i>	<i>I</i>	<i>d (Å)</i>	<i>hkl</i>	<i>d (Å)</i>	<i>I</i>	<i>I</i>	<i>d (Å)</i>	<i>I</i>	<i>d (Å)</i>
006	4.103	ms	15b	4.103 to 4.089	066	3.967	m	6	3.969	9	3.972
040	4.083	ms	—	—	346	3.897	c	2	3.902	2	3.898
140	4.014	vw	—	—	328	3.837	w	2	3.840	2	3.833
333	3.795	—	8	3.793	346	3.723	c	4	3.726	4	3.723
424	3.791	—	—	—	0.2.14	3.464	ms	9	3.463	18	3.464
600	3.690	w	1	3.691	364	3.404	—	—	—	—	—
242	3.685	mw	—	—	080	3.380	vw	—	—	—	—
340	3.573	vw	6	3.571	0.6.10	3.380	w	—	—	—	—
135	3.570	vw	—	—	3.4.10	3.348	m	2	3.352	3	3.346
017	3.438	ms	—	—							
433	3.438	—	—	—							
117	3.436	s	20	3.436							
531	3.431	—	—	—							
044	3.403	ms	1	3.401							
342	3.397	—	—	—							
117	3.360	s	10	3.360							
217	3.355	w	—	—							

TABLE II (cont.)

<i>Bannisterite</i> <i>Franklin Furnace, N.J.</i>					<i>Ganophyllite</i>						
<i>Calculated</i>		<i>Measured</i>			<i>Calculated</i>		<i>Measured</i>				
					<i>Harstig, Sweden</i>		<i>Harstig, Sweden</i>		<i>Franklin, N.J.</i>		
<i>hkl</i>	<i>d</i> (Å)	<i>Single crystal</i>	<i>Powder film 15464</i>	<i>d</i> (Å)	<i>hkl</i>	<i>d</i> (Å)	<i>Single crystal</i>	<i>Powder film 15441</i>	<i>Powder film 15499</i>	<i>I</i>	<i>d</i> (Å)
—	—	—	1	3.308	3.2.12	3.348	w	—	—	—	—
622̄	3.303	—	—	—	364	3.324	—	—	—	—	—
051	3.237	m	1	3.237	084	3.266	vw	—	—	—	—
533	3.237	—	—	—							
217	3.216	w	1	3.212							
442̄	3.211	—	—	—							
317̄	3.208	vw	—	—							
151̄	3.208	w	—	—							
435	3.131	—	1	3.129	0.4.10	3.168	vw	—	—	—	—
008	3.079	s	12	3.077	0.0.16	3.138	s	25	3.138	25	3.134
208̄	3.024	w	2	3.021	3.2.12	3.135	w	—	—	—	—
					368̄	3.111	—	—	—	—	—
					368	2.992	—	9	2.980	4	2.994
			3	2.968	088	2.974	vw	—	—	—	—
			1	2.905	382̄	2.876	w	4	2.901	—	—
			2	2.838	382	2.851	s	5	2.857	—	—
					0.4.16	2.845	mw	—	—	—	—
					3.4.14	2.825	m	—	—	—	—
			8	2.789	0.6.14	2.805	m	4	2.808	6	2.804

TABLE II (cont.)

Bannisterite, Franklin, N.J. Powder film 15464		Ganophyllite						Bannisterite Franklin, N.J. Powder film 15464		Ganophyllite					
		Calculated		Harstig, Sweden		Franklin, N.J.				Harstig Powder film 15441		Franklin, N.J.			
				Single crystal	Powder film 15441	Powder film 15499	Powder film 15499								
<i>I</i>	<i>d</i>	<i>hkl</i>	<i>d</i> , Å	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>		
7	2-753	600	2-760	mw	—	—	—	—	—	3	1-930	2	1-973	4	1-968
		386	2-758	vw	—	—	—	—	—	1	1-916	2	1-929	3	1-924
		3.2.16	2-757	m	—	—	—	—	—	1	1-885				
		3.6.12	2-742	mw	—	—	—	—	—	1	1-860				
		604	2-738	s	3	2-740	6	2-735	1	1-831				1	1-823
1	2-705	386	2-694	s	13	2-696	21	2-696	1	1-786					
		3.4.14	2-672	mw	—	—	1	2-675	1	1-754	4	1-761	9	1-757	
15	2-638	3.6.12	2-621	mw	1	2-616	1	2-619	2	1-720	2	1-724	1	1-725	
11	2-606	608	2-597	s	9	2-598	12	2-595	4	1-708	2	1-694	1	1-702	
		3.8.10	2-542	m	1	2-547	3	2-540	1	1-668			3	1-692	
		626	2-521	vw	1	2-524	—	—	2	1-657	2	1-675	3	1-677	
		00.20	2-510	m	1	2-507	4	2-505	3	1-633	1	1-629	1	1-633	
1	2-483	608	2-461	m	9	2-465	12	2-461	7	1-614	3	1-621	9	1-621	
1	2-460	3.8.10	2-459	s	—	—	—	—	8	1-599	3	1-608	6	1-607	
10	2-410	3.10.0	2-428	mw	—	—	1	2-434	1	1-573	1	1-579	2	1-577	
9	2-384	6.0.12	2-384	s	4	2-384	7	2-382	3	1-561	2	1-568	3	1-567	
1	2-329	3.8.14	2-289	m	2	2-292	5	2-290	1	1-546	1	1-553	1	1-554	
1	2-301	6.0.12	2-230	ms	2	2-232	3	2-232	2	1-537	1	1-539	2	1-522	
4	2-246	3.8.14	2-205	ms	4	2-210	9	2-207	2	1-516					
3	2-223	6.0.16	2-151	ms	2	2-149	3	2-148	1	1-505	2	1-465			
1	2-202	3.10.12	2-130	—	—	—	1	2-132	2	1-451	2	1-456	3	1-455	
5	2-162	6.4.12	2-118	w	—	—	1	2-117	2	1-442					
1	2-114	6.2.14	2-089	mw	2	2-089	3	2-083	1	1-430			1	1-424	
		684	2-089	—	—	—	—	—	2	1-407			3	1-419	
		3.12.2	2-084	—	—	—	—	—	2	1-386			1	1-381	
		3.8.18	2-042	m	2	2-045	6	2-041	2	1-367			1	1-363	
		6.6.14	2-026	—	—	—	—	—	1	1-349					
		6.2.18	2-014	w	1	2-019	—	—	1	1-343					
2b	1-998	6.0.16	2-001	m	1	2-000	—	—	1	1-332			1	1-334	
									1	1-320	3	1-322	1	1-323	
									1	1-311	1	1-314	2	1-314	
									1	1-300					
									1	1-287					
									1	1-278					
									1	1-269					

and by us is shown in fig. 1*b*. Our optical data were obtained on crystals from these localities that had been identified and oriented crystallographically by single-crystal X-ray methods. A summary optical description is given in table IV.

The sub-radial or divergent groups of elongate laths or blades that characterize the Franklin ganophyllite generally are tightly intergrown

TABLE III. Chemical composition of ganophyllite and bannisterite

	1	2		1 <i>a</i>	2 <i>a</i>
SiO <sub>2</sub>	39.67	46.20	Si	21.55	6.08
Al <sub>2</sub> O <sub>3</sub>	7.95	4.74	Al	5.08	0.74
Fe <sub>2</sub> O <sub>3</sub>	0.90	—	Fe <sup>3+</sup>	0.36	—
MnO	35.15	23.02	Mn	16.14	2.56
FeO	—	6.40	Fe <sup>2+</sup>	—	0.70
ZnO	—	4.67	Zn	—	0.45
PbO	0.20	—	Pb	0.03	—
CaO	1.11	1.52	Ca	0.65	0.21
MgO	0.20	1.99	Mg	0.16	0.39
Na <sub>2</sub> O	2.18	0.29	Na	2.29	0.07
K <sub>2</sub> O	2.70	1.21	K	1.87	0.20
H <sub>2</sub> O	9.79	9.74	H <sub>2</sub> O	17.70	4.27
Sum	99.85	99.78	O	70.30	17.73
Sp. gr.	2.84	2.92			

1. Ganophyllite, Harstig mine, Sweden; Hamberg, 1890, anal.

2. Bannisterite, Franklin Furnace, New Jersey; J. Ito, anal.

1*a*. Ganophyllite, atoms per 88 oxygen.

2*a*. Bannisterite, atoms per 22 oxygen.

and when broken apart tend to form laths that rest on the perfect cleavage. Rarely prismatic-bladed crystals of monoclinic habit occur projecting into cavities. The crystal faces are rounded and dull, as if by solution, and do not permit optical goniometry. They are very thin perpendicular to (010) and are elongated parallel to (100). In this position under the microscope they show an oblique rounded termination; the obtuse bisectrix  $\gamma$  coincides with [010], and the optical normal  $\beta$  is either parallel to [100], or is inclined thereto at an angle not greater than a degree or two. There is a perfect cleavage at right-angles to the flattening, on {001}, and the acute bisectrix  $\alpha$  is perpendicular thereto. The optical orientation is shown in fig. 1*c*. When these crystals are fractured they form cleavage laths similar to fig. 1*b*. A few crystals were twinned on (100) with symmetrical extinction at a very small angle.

Several difficulties in the earlier optical descriptions may now be mentioned. Larsen and Shannon (1922) give precisely the same optical

orientation as that shown in fig. 1c for crystals resting on the flat side and note both the occurrence of a cleavage cutting the thin edge, corresponding to (001) in our orientations, and of twin lamellae parallel thereto. It seems likely that there has been some confusion between euhedral crystals resting on (010) and cleavage laths resting on (001).

TABLE IV. Optical properties of ganophyllite and bannisterite

Ref.	$\alpha$	$\beta$	$\gamma$	$2V$
<i>Ganophyllite*</i>				
1	1.573, yellow-brown	1.603, colourless	1.604, colourless	$26^\circ$ , $r < v$
2	1.573, dark brown	1.611, pale brown	1.613, pale brown	small, $r < v$
3	1.570, straw yellow	1.610, colourless	1.611, colourless	—
4	1.563, —	1.593, —	1.593, —	v. small, $r < v$
5	1.571, dark yellow-brown	1.610, pale yellow-brown	1.611, pale yellow-brown	small, $r < v$
<i>Bannisterite†</i>				
6	1.545, —	1.586, —	1.589, —	med., $r < v$ mod.
7	1.547, —	1.588, —	1.588, —	small, $r < v$
8	1.544, nearly colourless	1.586, brown	1.588, brown	small, $r < v$ weak
9	1.574, nearly colourless	1.611, pale yellow	1.612, pale yellow	$35^\circ$ †
10	— nearly colourless	1.609, ochre buff	1.610, ochre buff	$17^\circ$ †

1. Harstig; Larsen and Shannon, 1924; pleochroism from Hamberg, 1890.

2. Harstig; new data.

3. Benallt; Campbell Smith, 1948; approximate values, Na light.

4. Franklin; Larsen and Shannon, 1922.

5. Franklin; new data.

6. Franklin; Foshag, 1936.

7. Franklin; Larsen, unpublished note, 1936.

8. Franklin; new data.

9 and 10. Benallt; Campbell Smith, 1948; approximate values, Na light.

\*  $\alpha$  near [001],  $\beta$  near [100],  $\gamma = [010]$ .

† 2E.

‡  $\alpha$  near [001],  $\beta = [010]$ ,  $\gamma$  near [100].

A further inconsistency is the statement of Larsen (1921), to which attention has been drawn by Campbell Smith (1948), that  $\beta \parallel [010]$ . This has been here traced (in the original manuscript of 'U.S. Geological Survey Bulletin', 679, preserved in the Harvard files) to an error of transcription by Larsen from Hamberg's correct original description. Hamberg's erroneous indices of refraction for the Harstig material are cited by Larsen (1921); these were corrected by Larsen and Shannon (1924) and are given in Larsen and Berman (1934). As noted beyond,



ganophyllite and bannisterite have approximately the same indices of refraction but the optical orientation and the optical absorption are different (table IV).

Ganophyllite was reported by Rogers (1919) as tiny crystals from near San Jose, California, on the basis of a manganese test and on a correspondence in indices of refraction with the (erroneous) values originally reported by Hamberg (1890) for the Harstig material. Rogers's crystals were here analysed by electron-microprobe techniques and were found to be a manganese phosphate unrelated to the minerals at hand.

#### *Bannisterite*

Two types of so-called ganophyllite have been described from Franklin. One type, originally recognized by Palache (1910) and later described by Larsen and Shannon (1922, 1924), occurs as groups of small, pale-brown, lath-like crystals associated with rhodonite, willemite, and axinite in thin veinlets that cut the massive ore. This material is identical with the Harstig material and is described above under the name ganophyllite. A second type of material from Franklin was originally described and analysed by Foshag (1936), although he did not know that the material differed crystallographically from the lath-like ganophyllite crystals. This so-called 'ganophyllite' occurs as aggregates of anhedral dark-brown plates that are as much as 5 cm across cleavage surfaces. It is associated with a greenish-black manganoan amphibole, calcite, and baryte. A chemical analysis by Jun Ito, cited in table III, together with the optical and X-ray studies described below, establishes that this mineral is a layered mineral related to but different from ganophyllite. The name bannisterite is proposed for this new mineral in honour of Dr. Frederick A. Bannister, for some years keeper of Minerals in the Mineral Department, British Museum (Natural History), whose X-ray work done in connection with the study by W. Campbell Smith of the Benallt material helped establish the existence of the mineral. The name has the approval of the Commission on New Mineral Names of the International Mineralogical Association.

*X-ray crystallography.* The unit cell dimensions obtained by single-crystal measurements are given in table I, and indexed X-ray powder spacing data are given in table II. The space group, like that of ganophyllite, is either  $Aa$  or  $A2/a$ . Tests for piezo-electricity were negative. Dimensionally, bannisterite is related to ganophyllite in that  $c$  of the

former is half that of the latter, and  $a$  of the two minerals is in the ratio of 3:4. As in ganophyllite, there is a marked pseudocell with  $a$ , 5.5 Å;  $c$ , 25 Å;  $\beta$ , 94°, as projected on (010). In terms of true cells, ganophyllite is a four-layered mineral with  $a$  tripled and bannisterite is a two-layered mineral with  $a$  quadrupled. Stilpnomelane also has true  $a$  quadruple the  $a$  of a monoclinic subcell. The  $h0l$  pattern of bannisterite (fig. 3) has similarly disposed reflections as those observed on the  $h.2\bar{h}.l$  and  $hhl$  patterns of stilpnomelane. The  $h.2\bar{h}.l$  (fig. 3) and the  $hhl$  (not shown) of stilpnomelane superimpose in every detail, and are each obtained by rotating the reciprocal lattice on  $c^*$  exactly +60° from  $2h.\bar{h}.l$ , a unique net that represents a mirror plane, in stilpnomelane, for triclinic lattice points with  $h-k = 3n$ .

Values of  $b$  in ganophyllite and  $b$  in bannisterite are not rationally related, although lengths corresponding to  $b/8 = 3.38$  Å in ganophyllite and  $b/5 = 3.264$  Å in bannisterite are dimensionally similar. The ratio of  $b$  of bannisterite to  $a \sin \gamma$  or  $b \sin \gamma$  of stilpnomelane approximates 5:6. A polymorphic variation of stilpnomelane has been found that will be described independently.

The pronounced trigonal symmetry exhibited by ganophyllite and by stilpnomelane is also present in bannisterite. A small distorted trigonal subcell may be defined for bannisterite by the relationship:  $a' = b/5 = a/4 \tan 59^\circ 35' = 3.264$  Å,  $c' = 3d_{002} = 37$  Å. The ideal relationship for  $a'$  is:  $a' = a/4\sqrt{3}$ . There are  $26\frac{2}{3}$  trigonal subcells in the true cell of bannisterite. Concomitant to the tripling of true cell  $d_{002}$  to obtain trigonal  $c'$ , three monoclinic unit cells of bannisterite stacked about an axis  $\perp(001)$  are required to accommodate a whole number (80) of trigonal subcells.

The basal spacing of bannisterite is not significantly affected by heating overnight at 120° ( $d_{002} = 12.30$  Å), or by glycolating ( $d_{002} = 12.35$  Å), or by exposing to a humid atmosphere ( $d_{002} = 12.33$  Å).

*Optical properties.* The optical orientation of bannisterite from Franklin is shown in fig. 2. This material is anhedral and the position of the crystal axes was established by single-crystal X-ray study. The optical orientation is identical with that reported by Campbell Smith (1948) for certain crystals in which the plane of symmetry was established by an X-ray method (fig. 2a). Microscopically, a second, indistinct cleavage was noted in the Franklin material; the trace of this on (100) is parallel to the  $c$ -axis. No twinning was observed. A summary optical description is given in table IV.

The indices of refraction of the Franklin material are slightly lower

than those of the Benallt crystals and of ganophyllite. Variation in water content, as demonstrated by Campbell Smith (1948), and compositional variation involving the cations, as shown by the reported analyses, presumably are the major factors involved.

The orientation of the optical directions  $\beta$  and  $\gamma$  relative to the crystallographic  $a$  and  $b$  axes differs in ganophyllite from bannisterite. If the structures of these minerals, and of stilpnomelane, are based upon pseudo-trigonal subcells with non-equivalent  $a_1$ ,  $a_2$ , and  $a_3$  axes the  $\beta$  and  $\gamma$  optical directions will have different components parallel to  $a_1$ ,  $a_2$ , and  $a_3$ . It is tentatively suggested that the projection of the crystal structure upon  $a$  of ganophyllite and upon  $a$  of stilpnomelane is similar; and upon  $a$  of bannisterite and  $b$  of stilpnomelane, where  $a = b = 22.05$ ,  $\gamma = 120^\circ$  in stilpnomelane.

*Chemical composition.* A possible formula unit for bannisterite, calculated from the analyses, table III, the measured unit cell volume, and the specific gravity, indicates a total of 22 oxygen atoms (includes  $O + OH + H_2O$ ) in the small  $A$ -centred monoclinic pseudocell (table I),  $Z = 20$  in the true cell. This value corresponds to 16.5 oxygen atoms in the trigonal subcell of bannisterite, the same number as derived for ganophyllite by similar calculations. This exceeds the 15 total ( $O + OH + H_2O$ ) derived by similar calculations for the structurally related but not identical mineral, stilpnomelane. Calculated specific gravities for 16.5 and for 15 total oxygen atoms in the trigonal subcell of bannisterite are 2.936 and 2.669, respectively. The larger number of oxygen atoms appears to represent the best value, but an analysis of the crystal structure is required to determine the mutual substitution of various cations in sites related by symmetry operations.

#### *Classification and summary*

The classification of polytypes of mica by their stacking sequence has been outlined by Smith and Yoder (1956) and by Ross, Takeda, and Wones (1966). It may be expected that the formation of a new group of layered minerals will follow the established principles by which stacking sequences may be varied. These include, for polytypes of mica, the number of layers involved in the stacking sequence and the relative rotation of layers. The crystal structures of stilpnomelane-like minerals are not known. The available data—space group criteria including additional special conditions that limit the observed reflections, and the unit cell parameters—suggest that the formation of layered minerals with structures related to stilpnomelane involves

not only a possible rotation of successive layers perpendicular to the  $ab$  plane, but also an offset of layers giving different translation vectors within the  $ab$  plane. An apparent offset of layers may be accomplished by the selective occupancy or vacancy of corresponding spaces in one of several subcells, concomitant with small changes in chemical composition, without requiring additional rotations between layers involved in the stacking sequence. Evidence has already been found for several polymorphic variations in stilpnomelane.

Small trigonal or small monoclinic subcells may be defined common to ganophyllite, bannisterite, and stilpnomelane. Triclinic stilpnomelane is single-layered with monoclinic subcell  $a$  (units of  $5.5 \text{ \AA}$ ) quadrupled in the true cell ( $b \sin \gamma = 6 \times 3.2 \text{ \AA}$ ); monoclinic bannisterite is two-layered, also with subcell  $a$  quadrupled in the true cell ( $b = 5 \times 3.264 \text{ \AA}$ ); monoclinic ganophyllite is four-layered with subcell  $a$  tripled in the true cell ( $b = 8 \times 3.3 \text{ \AA}$ ). Ideally, the layers are stacked so that  $\beta = \cos^{-1} a/12c$  in stilpnomelane and in bannisterite and  $\beta = \cos^{-1} 2a/9c$  in ganophyllite. The stacking sequence by which  $a$  of the  $n$ th layer may be projected upon  $a$  of the original layer along an axis perpendicular to (001) is 6 layers in the monoclinic subcell common to the three minerals, 12 layers in the true cell of stilpnomelane, 24 in bannisterite, and 36 in ganophyllite. There are 16 trigonal subcells in the true cell of stilpnomelane, 80 in three unit cells of bannisterite, and 64 in the true cell of ganophyllite.

It is anticipated that an analysis of the structures of these minerals will show a common structure for the group.

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