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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,  $16\cdot60\pm0\cdot05$ Å; b,  $27\cdot04\pm0\cdot08$ Å; c,  $50\cdot34\pm0\cdot15$ Å;  $\beta$ ,  $94^{\circ}$   $10'\pm10'$ ; space group A 2/a), at the Benalt mine, Caernarvonshire, Wales, and in Aroostook County, Maine. Bannisterite, a new mineral, occurs at Franklin, New Jersey (a,  $22\cdot20\pm0\cdot07$ Å; b,  $16\cdot32\pm0\cdot05$ Å; c,  $24\cdot70\pm0\cdot08$ Å;  $\beta$ ,  $94^{\circ}$   $20'\pm10'$ ; space group A2/a) and at the Benalt mine, Wales. Both minerals have similar pseudocells: a,  $5\cdot53$ Å; b,  $3\cdot3$ Å; c, 25Å;  $\beta$ ,  $94^{\circ}$ . The chemical analysis of ganophyllite from the Harstig mine, Sweden, is: SiO<sub>2</sub>,  $39\cdot67$ %; Al<sub>2</sub>O<sub>3</sub>,  $7\cdot95$ ; Fe<sub>2</sub>O<sub>3</sub>, 0·90; MnO,  $35\cdot15$ ; CaO,  $1\cdot11$ ; MgO,  $0\cdot20$ ; PbO,  $0\cdot20$ ; K<sub>2</sub>O,  $2\cdot70$ ; Na<sub>2</sub>O,  $2\cdot18$ ; Li<sub>2</sub>O, trace; H<sub>2</sub>O,  $9\cdot79$ ; total,  $99\cdot85$ . The chemical analysis of bannisterite from Franklin Furnace, New Jersey, is: SiO<sub>2</sub>  $46\cdot20$ %; Al<sub>2</sub>O<sub>3</sub>,  $4\cdot74$ ; MnO,  $23\cdot02$ ; FeO,  $6\cdot40$ ; ZnO,  $4\cdot67$ ; CaO,  $1\cdot52$ ; MgO,  $1\cdot99$ ; Na<sub>2</sub>O,  $0\cdot29$ ; K<sub>2</sub>O,  $1\cdot21$ ; H<sub>2</sub>O,  $9\cdot74$ ; total,  $99\cdot78$ .

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,  $22\cdot05$  Å $\pm0\cdot06$  Å; c,  $17\cdot70\pm0\cdot06$ ;  $\alpha$ ,  $124^{\circ}$  49';  $\beta$ ,  $95^{\circ}$  58';  $\gamma$ ,  $120^{\circ}$  00' (angles $\pm5'$ ). In the trigonal subcell, a',  $3\cdot2$  Å; c',  $36\cdot4$ . Small distorted trigonal subcells for ganophyllite have a',  $3\cdot38$  Å; c' 37·7, and for bannisterite have a',  $3\cdot264$  and c', 37 Å.

GANOPHYLLITE, 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° 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: Mo- $K\alpha_{av} = 0.7107$  Å, Cu- $K\alpha_{av} = 1.5418$  Å, Cr- $K\alpha_{av} = 2.2909$  Å. Roth ganophyllite and bannisterite have small monoclinic subcells, similar in projection on  $\{010\}$  with a, 5.5 Å; c, 25 Å;  $\beta, 94^\circ$ . The *hol* patterns of ganophyllite and of bannisterite (fig. 3), and the  $h.\overline{2h}.l$  (fig. 3),

<sup>1</sup> Personal communication.

	Ganop	hyllite	Bannisterite		Stilpn	omelane
	Harstig Mine, Sweden Harvard No. 10118	Franklin Furnace, N.J. Harvard No. 89837	Franklin, N.J. Harvard No. 10857		Deer Island, Maine Present study	Crystal Falls, Michigan Eggleton and Bailey, 1965
Symmetry	monoclinic	monoclinic	monoclinic		triclinic	triclinic
8	$16.60 \pm 0.05  { m \AA}$	$16.59 \pm 0.05 \text{ Å}$	$22 \cdot 20 \pm 0 \cdot 07$ Å	a	$22.05\pm0.06~{ m \AA}$	$21.724\pm0.004~{ m \AA}$
q	$27.04 \pm 0.08$	$27.08 \pm 0.08$	$16.32 \pm 0.05$	q	$22.05\pm0.06$	$21 \cdot 724 \pm 0 \cdot 004$
Q	$50.34 \pm 0.15$	$50.36\pm0.15$	$24 \cdot 70 \pm 0 \cdot 08$	ల	$17.70 \pm 0.06$	$17.740 \pm 0.004$
θ	$94^{\circ} 10' + 0^{\circ} 10'$	$94^{\circ} 10^{\prime} \pm 0^{\circ} 10^{\prime}$	$94^{\circ} \ 20^{\prime} \pm 0^{\circ} \ 10^{\prime}$	8	$124^{\circ} \ 49^{\prime} \pm 0^{\circ} \ 05^{\prime}$	$124{\cdot}14{\pm}0{\cdot}015^{\circ}$
Vol.	$22536  { m \AA}^3$	$22560  { m \AA}^3$	$8924 \text{ Å}^{3}$	ø	$95^{\circ} 58' \pm 0^{\circ} 05'$	$95.86^{\circ}\pm 0.023^{\circ}$
Space group	Aa  or  A2/a	Aa or $A2/a$	Aa  or  A2/a	~	$120^{\circ} \ 00' \pm 0^{\circ} \ 05'$	$120{\cdot}00^{\circ}{\pm}0{\cdot}02^{\circ}$
Mon	voclinic pseudocell			Vol.	5117 Å <sup>3</sup>	
в	5.53 Å	5-53 Å	5.55 Å	°*	0.06262	
q	13.52	13.54	3.264	$p^*$	0-07586	
v	25.17	25.17	24.70	с <b>*</b>	0.08237	
B	$94^{\circ} 10'$	$94^{\circ} 10'$	94° 20'	<del>د</del> *	43°37′	
Vol.	1878 Å	$1880  \mathrm{A^3}$	446 Å <sup>3</sup>	*9	56° 45'	
				*.	46° 44'	
	Pseudo-space-group					
	Ia or $I2/a$	Ia  or  I2/a	A2, Am, or A2/m		Calculated angles, spe	vial relationships
	Calculated angles				$\begin{array}{l} \alpha \ = \ \cos^{-1} - 1 \\ \beta \ = \ \cos^{-1} - \alpha \end{array}$	1b/24c /12c
-	$\beta = \cos^{-1} - 2a/9c = 94^{\circ} 1!$	2' - F	$3 = \cos^{-1} - a/12c = 94^{\circ} 18'$		$\alpha^* = \cos^{-1} 2c$ $\beta^* = \cos^{-1} 5c$	*/3b* */12a*

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

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 $2h.\bar{h}.l$ , 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  $h.2\overline{h}.l$  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 Å appears to represent the interstratification of four successive equal layers, alternately arranged, with basal spacing of 12.5 Å. The basal spacing of these layers is not significantly changed by heating overnight at 120° C ( $d_{004}$ , 12.55 Å) or by glycolating ( $d_{004}$ , 12.55 Å) or by exposing to a humid atmosphere ( $d_{004}$ , 12.53 Å). The body-centred pseudocell with a, 5.5 Å; b, 13.5 Å; c, 25 Å;  $\beta$ , 94° 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:  $a' = a/3 \tan 58^{\circ} 35' = b/8 = 3.38$  Å,  $c' = 3d_{004} = 37.7$  Å. 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  $a' = a/4\sqrt{3} = 3.1$  Å,  $c' = 3d_{001} = 37$  Å.

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. 1*a*. The optical orientation of the lathlike cleavage flakes from Franklin as found by Campbell Smith

	T	Jammiatanita					-	Ganophy	llite		
	Frankling	in Furnace,	N.J.		l				Measu	red	
Cal	culated*	W	easured	,	Calc	$ulated \dagger$	Har	stig, Swe	den	Frank	lin, N.J.
		Single crystal‡	Pow	der film§ 5464	Harsti	g, Sweden	Single crystal	Powe	ler film§	Powc 15	ler film§ 1499
hkl	d (Å)	. I	Ι	d (Å)	hkl	d (Å)	I	Ι	<i>d</i> (Å)	I	d (Å)
011	13.61	ΜΛ	]	1	ļ			1	1	1	
002	12.31	80	100	12.33	004	12.55	ల	100	12.53	100	12.59
ΠĪ	11.81	ບ	l	ļ	022	11.90	υ	67	11.86	67	11.95
111	11.39	Ð	-	11-45							
200	11.07	ΜΛ		ļ							
$21\overline{1}$	8.772	м	ଦା	8-779							
$20\overline{2}$	8.562	w		ļ							
211	8.418	w	67	8.428							
020	8.163	હ	I	ļ							
202	7-937	mw	-	7.954							
120	7.657	e		ļ							
Bannist 90 · h 16	erite from F1 -32	ranklin Furna 1 Å · R 94° 90	ace, N.J.,	d <sub>hki</sub> calculate erom 4 a or	$\begin{array}{c} \operatorname{dfrom} a, \\ 4^{9/a} & \operatorname{All} \end{array}$	‡ Sing	le crystal int n natterns t	tensities es aken with	stimated visu different exi	ally from V	Veissenberg es and diffe

† Ganophyllite, Harstig, Sweden,  $d_{AB}$  calculated from  $a_r$ , 16-60; b, 27-04; c, 50-34 Å; g, 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=2m* and *d*-spacings are listed for *hkl* reflections with *h/3+k/2+l/2=2m* and *d*-spacings are listed for *hkl* reflections consistent with space group *Aa* or *A2/a* are too weak to appear on the powder photograph (except calculated *d*-spacings listed for  $d \ge 3.0$  Å. 22.2

126 and 140).

radiations: c = cut-off at centre of film. Broad reflections designated  $\S$  114-59 mm camera; film measurements corrected for shrinkage. Lower limit of 29 measurable is approximately 8°. Bannisterite, as b, reflections observed to be absent = a.

and ent powder film 15464 and ganophyllite, powder film 15441, Mn-filtered Fe radiation, Fe- $K_{aw} = 1.9373$ ; ganophyllite, powder film 15499, V-filtered Cr radiation, Cr- $K_{aw} = 2.2909$  Å.

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

	μ. α	an and such a					C	Janophyl	lite		
	Franklin	h Furnace, 1	V.J.						Measure	q	
Cal	culated	W	casured		Cal	culated Sundam	Ha	rstig, Sw	eden	Frank	lin, N.J.
		Single crystal	Pou 1	der film 5464	Sarse in Tr	, Dwenen	Single crystal	Powa 15	er film 441	Powe 11	ler film 5499
hkl	d (Å)	Ι	Ι	d (Å)	hkl	<i>d</i> (Å)	Ι	Ι	d (Å)	Ι	d (Å)
013	7.331	ΜΛ	1	I							
$11\overline{3}$	7.107	w	4	7.106	026	7.107	ΜΛ	က	7.239	I	7-111
113	6.826	m	က	6.821	040	6.740	W	61	6.800	T	6.750
022	6.803	ΜΛ		]							
$31\overline{1}$	6.605	W	1	6.608							
$12\overline{2}$	6.579	νw	[								
220	6.570	5	]	[							
122	6.427	ΜΛ		]							
311	6.378	ΜΛ	61	6.382							
$21\overline{3}$	6.313	w		I	126	6.394	W				
004	6.154	w	ľ	6.162	008	6.275	шW	4	6.375	4	6.274
					140	6.258	W			I	6.238
213	5.931	ΜΛ	I	5.934	044	5.952	МЛ			I	5.939
$22\overline{2}$	5.907	w	]	1							
222	5.692	W	]	]							
$20\overline{4}$	5.562	тw	ŋ	5.562							
400	5.534	тw		I							
320	5.473	W									
$31\overline{3}$	5.385	ಸ	I	[							

	ł	(	<u>.</u> .		-							-										,	ī	1
			lin, N.J	der film 5499	d (Å)							$5 \cdot 11$						I				I	I	I
		pə.	Frank	Pow I	Ι							9						I						[
	llite	Measur	veden	der film 5441	d (Å)							5.116										4.707	4.631	
	Ganophy		vrstig, Sv	Pow	Ι							9						I				1	ଟା	I
	•		H <sub>0</sub> H	Single crystal	Ι							m						ΜΛ				ΜΛ	W	ΜΛ
(-aaron) T			ulated	, Sweden	d (Å)							5.112						4.847				4.704	4.625	4.596
TUTOTT			Calc	Harstıg	hkl							320						$32\overline{4}$				0.2.10	324	048
			'n	der film 5464	d (Å)	1		5.196			1		I		I	4.911						4.709	1	4.593
		, N.J.	Measure	Power	Ι			ŝ		I	1	1	l	ļ	ļ	I	ļ	l	ļ	ļ	ļ	I	ļ	10
	Rannietanita	lin Furnace		Single crystal	Ι	м	5	M	н	m	ш		ΜΛ	w	w	w		м	ΜΛ	ΜA	w	w	ಣೆ	mw
		Frank	ulated		d (Å)	5.316	5.203	5.195	5.187	5.173	5.149	5.112	5.053	5.035	4.914	4.912	4.899	4.861	4.822	4.762	4.737	4.715	4.692	4.596
			Calc		hkl	031	$41\overline{1}$	$40\overline{2}$	$13\overline{1}$	204	131	$32\overline{2}$	411	313	024	402	322	$12\overline{4}$	$23\overline{1}$	231	124	015	$11\overline{5}$	$22\overline{4}$

						(					
		Pannistorito	_				)	Ganophy	llite		
	Frank	clin Furnac	e, N.J.						Measure	pa	
	Calculated		Measur	ed	Calc	ulated	Ha	trstig, Sr	veden	Frankl	in, N.J.
		Single crystal	Pow 1	der film 5464	narsug	, sweden	Single crystal	Pow	der film 5441	Povd 15	er film 499
hkl	d (Å)	Ι	Ι	d $(Å)$	hkl	d (Å)	Ι	I	d (Å)	Ι	d (Å)
420	4.581	sm	ł								-
$41\overline{3}$	4.570	шw	l	ļ							
$21\overline{5}$	4.456	ΜA	1								
$42\overline{2}$	4·384	]	1	!	062	4.437	M	4	4.406	5	4.443
224	4.369	M	I	Ţ						I	
$33\overline{1}$	4.346	1	]	-1							
331	4.279			1							
413	4.279	шw	õ	4-280							
$40\overline{4}$	4.279	ಹ	١								
$51\overline{1}$	4.264	mm	1	T							
133	4-257	ΜΛ	l	-	$34\overline{2}$	4.255	m	I	4.250	-	4.249
$23\overline{3}$	4.233	ΜΛ	ļ	T							
215	4.228	ΜΛ	1	1							
$32\overline{4}$	4.211	ļ	I	4.211							
422	4.209	1	1								
511	4.160	1		7	00.12	4.183	ms	9	4.180	12	4.175
233	4.136	ΜA	I	1	342	4.175	ΜΛ			1	
315	4.110	ΜΛ			$32\overline{8}$	4.100	m	61	4.090	4	4.098

					LABLE L	T (com.)					
		Ramietorit					)	Janophyl	lite		
	Frank	lin Furnac	e, N.J.						Measur	pa	
-	Calculated		Measure	<i>q</i>	Calc	ulated	$H_a$	rstig, Su	eden	Frankl	in, N.J.
		Single crystal	bowd 15	ler film 464	nursug	, oueden	Single crystal	owo 1	ler film 5441	Powod	ler film 499
hkl	d (Å)	Ι	Ι	d (Å)	hkl	d (Å)	Ι	Ι	d (Å)	Ι	d (Å)
900	4.103	ms)	15b	(4.103)							
010	600.1	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~		to	080	2006	ł	U	090.6	c	070.6
	600' <del>1</del>	(SIII		200.F)	000 24 <u>6</u>	106.6	Ξ.	<b>.</b> .	606.6	סמ	216.0
333	3-795	ŧ !	x	3.793	328	3.837	5 <b>B</b>	101	3.840	101	3.833
$42\overline{4}$	3.791		1		}	, , ,	:	I	1	l	
600	3.690	W	I	3.691	346	3.723	Û	4	3.726	4	3.723
$24\overline{2}$	3.685	шw	l	ļ							
340	3-573	мл	9	3.571							
135	3.570	ΜΛ	l	I							
017	3.438	ms	l		0.2.14	3.464	$\mathbf{ms}$	6	3.463	18	3.464
$^{433}$	3.438		ļ	ļ							
<u>1</u> 17	3.436	so	20	3.436							
$53\overline{1}$	3.431	]	ł	I							
044	3.403	sm	1	3.401	$36\overline{4}$	3.404	I	l	1	I	
342	3.397	]	ł		080	3.380	ΜΛ	Į	]	]	[
117	3.360	s	10	3.360	0.6.10	3.380	W	!	]	1	[
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## M. L. SMITH AND C. FRONDEL ON

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GANOPHYLLITE, BANNISTERITE, AND STILPNOMELANE

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		ulated	d, Å	2.760	2.758	2.757	2.742	2.738	2.694	2.672	2.621	2.597	2.542	2.521	2.510	2.461	2.459	2.428	2.384	2.289	2.230	2.205	2.151	2 2.130	2.118	2.089	2.089	2.084	2.042	2.026	2.014	2.001						
ł	l	Calc	hkl	600	$38\overline{6}$	3.2.16	3.6.12	$60\overline{4}$	386	3.4.14	3.6.12	$60\overline{8}$	3.8.10	626	00.20	608	3.8.10	3.10.0	$6.0.\overline{1}2$	$3.8.\overline{14}$	6.0.12	3.8.14	6.0.16	3.10.1	6.4.12	6.2.14	684	$3.12.\overline{2}$	3.8.18	6.6.14	6.2.18	6.0.16						
is starita	lin, N.J. ter film	464	p	2.753					2.705		2.638	2.606				2.483	2.460	2.410	2.384	2-329	2.301	2.246	2.223	2.202	2.162	2.114						1.998						
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and by us is shown in fig. 1b. 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

	1	<b>2</b>		1a	2a
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		$\mathbf{Fe^{3+}}$	0.36	_
MnO	35.12	23.02	Mn	16.14	2.56
FeO	_	6.40	$\mathbf{Fe^{2+}}$	<u> </u>	0.70
ZnO		4.67	Zn	_	0.45
PbO	0.50		Pb	0.03	<u> </u>
ĊaO	1.11	1.52	Ca	0.62	0.21
MgO	0.50	1.99	Mg	0.16	0.39
Na <sub>2</sub> O	2.18	0.29	Na	2.29	0.01
K <sub>2</sub> Ō	2.70	1.21	K	1.87	0.50
H <sub>2</sub> O	9.79	9.74	H <sub>2</sub> O	17.70	4.27
Sum	99.85	99.78	0	70.30	17.73
Sp. gr.	2.84	2.92			

TABLE III. Chemical composition of ganophyllite and bannisterite

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

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

1a. Ganophyllite, atoms per 88 oxygen.

2a. 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. 1c. When these crystals are fractured they form cleavage laths similar to fig. 1b. 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.	α	β	γ	2V
	Ganophyllite*			
1	1·573, yellow- brown	1.603, colourless	1.604, colourless	$26^{\circ}$ , $\mathbf{r} < \mathbf{v}$
<b>2</b>	1.573, dark brown	1.611, pale brown	1.613, pale brown	small, $\mathbf{r} < \mathbf{v}$
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, $r < v$
	Bannisterite			
6	1.545,	1.586, —	1·589, —	med., $r < v \mod$ .
7	1.547,	1.588,	1.588,	small, $\mathbf{r} < \mathbf{v}$
8	1.544, nearly colourless	1 586, brown	1.588, brown	small, $\mathbf{r} < \mathbf{v}$ weak
9	1·574, nearly colourless	1.611, pale yellow	1.612, pale yellow	35°†
10	— nearly colourless	1 609, ochre buff	1.610, ochre buff	17°†

- 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.
- ‡ α near [001],  $\beta = [010]$ , γ 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 lathlike 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 singlecrystal 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  $h.\overline{2h}.l$  and hhl patterns of stilpnomelane. The  $h.\overline{2h}.l$  (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  $+60^\circ$  from  $2h.\overline{h}.l$ , 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° 35' = 3.264 Å,  $c' = 3d_{002} = 37$  Å. The ideal relationship for a' is:  $a' = a/4\sqrt{3}$ . There are 26<sup>2</sup>/<sub>8</sub> 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  $120^{\circ}$  ( $d_{002} = 12.30$  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 stilpnomelanelike 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 Å) quadrupled in the true cell  $(b \sin \gamma = 6 \times 3.2 Å)$ ; monoclinic bannisterite is twolayered, also with subcell a quadrupled in the true cell  $(b = 5 \times 3.264 Å)$ ; monoclinic ganophyllite is four-layered with subcell a tripled in the true cell  $(b = 8 \times 3.3 Å)$ . 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 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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