The crystal structure of ganophyllite; monoclinic subcell

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Abstract

The crystal structure of monoclinic subcell ($a'=5.534$, $b'=13.565$, $c'=25.09\text{\AA}$, $\beta'=93.96^\circ$, $I2/a$) of ganophyllite has been determined and refined to an R of 0.078. The structure of true cell ($a=3a'=16.60$, $b=2b'=27.13$, $c=2c'=50.18\text{\AA}$, $\beta=\beta'=93.96^\circ$, $A2/a$) can be explained based on this average subcell structure. This mineral is a modified layer structure as suggested by Smith and Frondel (1968). The octahedral (sheet) layer is curved like a sine wave along the b -axis and is sandwiched by two tetrahedral layers, each composed of triple chains. The upper and lower chains sandwiching the octahedral layer are always at the outside of the curvature and the small tetrahedral layer is inside. Thus the layer misfit is elegantly minimized in this structure. The interlayer cation is eight coordinated to four oxygens or hydroxyls at the edges of the chains and to four water molecules. The ordering of interlayer cations and water molecules followed by the site preference of aluminum in the tetrahedra, and resultant slight changes in polyhedra of the subcell structure explain why ganophyllite has a large cell. The structural formula of ganophyllite determined from X-ray microprobe and structure analyses is $(\text{K}, \text{Na}, \text{Ca})_x \text{Mn}_8(\text{Si}, \text{Al})_{12}(\text{O}, \text{OH})_{32}(\text{OH})_4 \cdot n\text{H}_2\text{O}$, with $x=1\sim 1.5$, and $n\geq 4$; $Z=24$ in the true large cell. The average monoclinic subcell structure also can explain the structure of triclinic polytype recently found by Jefferson (1978).

Introduction

Ganophyllite is a rare 'layered' manganese silicate which has a complex chemical composition. This mineral was first described by Hamberg (1890). Smith (C.) (1948) found that two different but closely related minerals had been confused under the same name ganophyllite on the optical orientation and dehydration of crystals. Smith (M. L.) and Frondel (1968) confirmed these observations and the more common one was referred to as true ganophyllite and the less common one was named bannisterite. They determined the cell dimensions and space groups of these two minerals but did not determine the crystal structures.

Recently, Jefferson (1978) found the presence of triclinic polytype in ganophyllite besides monoclinic polytype described by Smith and Frondel (1968) and wrote that these two polytypes can be interpreted by a structural column

concept.

Smith and Frondel (1968) suggested that ganophyllite is to be a modified layer structure, possibly a combination of an (octahedral) sheet and (tetrahedral) chain structure. In 1968, the author also had a conviction that the tetrahedral layers in this mineral should be triple chains considering the restriction given by the symmetry of space group and the cell dimensions (Kato *et al.*, 1969). This idea was proved to be correct by the present structure analysis of the subcell of monoclinic polytype. It has been also found that the obtained average subcell structure can explain the true structure of these polytypes if the ordering of the interlayer cations and the combined water molecules followed by the site preferences of Al in the tetrahedral sites is taken into account.

Sample description

The ganophyllite samples from two localities were used. One is from the Benallt mine, Rhiw, Carnarvonshire, Wales and supplied by British Museum

TABLE 1. Cell dimensions of ganophyllite.

Monoclinic polytype (Space group, $A2/a$)					
	1	2	3	4	5
a	16.60(5) Å	16.59(5) Å	16.54(5) Å	16.67(5) Å	16.60(2)
b	27.04(8)	27.08(8)	27.01(2)	27.09(6)	27.13(4)
c	50.34(15)	50.36(15)	50.25(5)	50.22(9)	50.18(8)
β	94°10'(10')	94°10'(10')	94°37'(12')	93.37°(5)	93.96°(3)
Subcell (Space group, $I2/a$)					
$a' = \frac{1}{3}a$	5.53 Å	5.53 Å	5.51 Å	5.56 Å	5.53 Å
$b' = \frac{1}{2}b$	13.52	13.54	13.50	13.50	13.57
$c' = \frac{1}{2}c$	25.17	25.17	25.12	25.11	25.09
$\beta' = \beta$	94°10'	94°10'	94°37'	93.37°	93.96°
Triclinic polytype (Space group, $P\bar{1}$ or $P1$)					
	6				
a	16.54(5) Å				
b	54.38(9)				
c	28.52(8)				
α	127°28'(16')*				
β	94°04'(12')				
γ	95°50'(12')				

1: Harstig, Sweden (Smith and Frondel, 1968). 2: Franklin Furnace, N.J. (Smith and Frondel, 1968). 3: Swedish origin (Jefferson, 1978). 4: Benallt mine, Wales (This study). 5: Harstig, Sweden (This study). 6: Swedish origin (Jefferson, 1978).

*See note in text (p. 10).

(Specimen Number, B. M. 1944, 36). This sample was described by Smith (1948). The other is from the Harstig mine, Pajsberg, Sweden and supplied by Smithsonian Institution (Specimen Number, B17240).

The cell parameters of these samples determined using a single crystal diffractometer are listed in Table 1 with those described previously for comparison.

The chemical composition of these samples was determined by X-ray microprobe analysis and is given in Table 2. Microprobe analysis of the Benallt ganophyllite was carried out by Dr. Haga, University of Tokyo, and the Harstig ganophyllite by Mr. Minami, Hiroshima University. The water content of the Harstig material was determined using micro T.G.A. by Dr. Tanabe. These results are discussed later.

TABLE 2. Chemical composition.

	Benallt mine Analyst: Haga			Harstig mine Minami and Tanabe	
	Wt. %	atomic ratio		Wt. %	atomic ratio
SiO ₂	39.49	9.71	12.00	40.35	9.88
Al ₂ O ₃	9.30	2.29 0.40		8.59	2.12 0.36
TiO ₂	—			0.06	0.02
FeO	0.20	0.04	8.00	0.42	0.09
MnO	36.27	7.55		35.90	7.45
MgO	0.02	0.01		0.24	0.09
CaO	2.67	0.70	0.93	0.76	0.21
Na ₂ O	0.13	0.06		1.03	0.50
K ₂ O	0.55	0.17		2.95	0.91
H ₂ O(+)	(11.37)			4.00	6.54
H ₂ O(—)				4.00	3.27
total	(100.0)			98.30	

Based on the assumption that the sum of cations in the tetrahedral and octahedral sites is 20.

Experimental

A crystal measuring 0.23×0.19×0.06 mm from Benallt ganophyllite was prepared for a Syntex P1 automated diffractometer with a graphite monochromator; by using MoK α radiation, reflections up to $2\theta=60^\circ$ were measured for

monoclinic subcell (space group, $I2/a$) at the variable scan speed mode.

A similar procedure was applied for a crystal measuring $0.15 \times 0.23 \times 0.05$ mm from Harstig ganophyllite. A Philips PW100 single crystal diffractometer was used to collect the intensity data. The 2θ - θ scans were used for these experiments.

The reflections for which $I \geq 3\sigma_I$ were considered to be significant, where σ_I is the standard deviation. The number of significant nonequivalent reflections were 1345 for the Benallt specimen and 1612 for the Harstig specimen. The absorption correction was applied using a program ACACA written by Prewitt.

Determination of the subcell structure

Smith and Frondel (1968) found that a subcell (space group, $I2/a$) can be considered for monoclinic polytype of ganophyllite (Table 1). They also suggested that ganophyllite is a modified layer structure, possibly a combination of a sheet and chain structure. The cell dimensions and the symmetry of space group determined by them restrict the arrangement of the tetrahedra in one layer, and the author also became convinced that the tetrahedral layer should contain triple chains instead of being a sheet (Kato *et al.*, 1969). It was also found that the manganese octahedral sheet and triple chains satisfy the symmetry restriction of space groups ($A2/a$ for the true large cell and $I2/a$ for the subcell) simultaneously.

The direct method of phase determination (MULTAN) was applied for the intensity data set for the Benallt specimen, and produced two solutions, both having manganese ions in an octahedral layer and triple chains, one at $z=0$ and the other at $z=1/4$. The latter proved to be the correct solution. The starting R was 0.43 and the refinement using alternatively full-matrix least squares and difference Fourier methods gave the final R of 0.145. This high value is due to the diffuseness of reflections.

Later, the author was able to obtain better crystallized material from Harstig. The parameters for the Benallt specimen was used as the starting values for the refinement and, in this case, the final R was 0.078.

Description of the structure and discussion

The obtained atomic parameters for the Harstig specimen are given in Table 3 and the selected bond distances and angles are listed in Table 4.

The crystal structure of the subcell of monoclinic ganophyllite is illus-

TABLE 3. Atomic positional and thermal parameters (monoclinic subcell).

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{31}	β_{23}
K	0.0	0.0	0.0	.1673	.0241	.0035	0.0	-.0042	0.0
Mn1	-.0060(3)	.0621(1)	.2372(1)	.0058	.0006	.0005	.0003	.0002	.0001
Mn2	.4970(4)	.1870(1)	.2447(1)	.0057	.0008	.0007	.0003	.0004	.0002
T1	.7996(10)	.4465(3)	.1515(2)	.0081	.0004	.0004	.0002	.0001	-.0001
T2	.8011(8)	.2188(3)	.1382(1)	.0219	.0013	.0006	.0001	.0003	-.0000
T3	.2982(5)	.1045(2)	.1287(1)	.0364	.0022	.0008	.0011	.0004	.0000
O1	.5320(28)	.1765(9)	.1144(5)	.0553	.0022	.0015	-.0001	.0062	-.0003
O2	.0412(32)	.1686(9)	.1130(6)	.0744	.0021	.0015	-.0016	.0063	.0004
O3	.8115(18)	.3349(6)	.1253(3)	.0237	.0004	.0006	.0001	.0008	-.0000
O4	.0364(16)	.5057(7)	.1292(3)	.0097	.0030	.0005	-.0002	.0002	.0001
O5	.2842(18)	.0209(8)	.0816(5)	.0099	.0026	.0023	-.0029	.0026	-.0021
O6	.3172(14)	.0667(7)	.1925(3)	.0078	.0028	.0006	.0009	.0002	-.0003
O7	.8188(16)	.1966(6)	.2007(4)	.0103	.0009	.0006	-.0000	.0005	.0003
O8	.8226(14)	.4408(7)	.2171(3)	.0085	.0009	.0005	.0003	.0000	.0001
OH	.3261(15)	.3209(6)	.2125(4)	.0056	.0006	.0008	-.0012	.0000	-.0003
H ₂ O1	-.0142(14)	.0679(7)	.0633(3)	.0069	.0006	.0004	.0002	.0006	.0000
H ₂ O2	.5588(16)	.0705(7)	.0624(4)	.0097	.0011	.0005	-.0010	.0006	-.0002

The anisotropic temperature factor has the form: $\exp - (\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{23}2kl + \beta_{13}2lh + \beta_{12}2hk)$.

trated in Figures 1 and 2.

The crystal structure of the true cell of monoclinic ganophyllite based on the subcell structure is illustrated in Figures 3 and 4. The (100) projection (Fig. 3) clearly shows how the layer misfit between large manganese octahedral and small (Si,Al) tetrahedral layers is eliminated. The manganese octahedral layer is curved like a sine wave along the b -axis and is sandwiched by the tetrahedral layers, each composed of triple chains. The upper and lower chains sandwiching the octahedral layer are always at the outside of the curvature and the small tetrahedral layer is inside. Thus the layer misfit is elegantly minimized in this structure. An interlayer cation (K, Na, Ca) lies near the center of four chain edges and maintains the charge balance. The interlayer cation is coordinated to eight anions; four oxygens or hydroxyls at the edges of the chains (2.457 and 2.510 Å) and four water molecules (3.139 and 3.164 Å).

A part of the (001) projection is shown in Figure 4. Two triple chains run along the a -axis at one level in the structure.

In the subcell structure, there are two sites, Mn1 and Mn2, for the octahedral cation. The Mn1 site coordinated to five oxygens and one hydroxyl. Mean distance of Mn1 to (O,OH) is 2.210 Å and that of adjacent (O, OH) is

TABLE 4. Interatomic distances and bond angles.

Mn1 Octahedron	Mn2 Octahedron	Interlayer cation
Mn1-O6 2.177(9) Å	Mn2-O6 2.278(9) Å	I-O5 (×2) 2.457(12) Å
Mn1-O6' 2.262(9)	Mn2-O7 2.163(10)	I-O5' (×2) 2.510(12)
Mn1-O7 2.233(8)	Mn2-O7' 2.284(9)	I-H ₂ O1(×2) 3.164(8)
Mn1-O8 2.159(8)	Mn2-O8 2.188(9)	I-H ₂ O2(×2) 3.139(9)
Mn1-O8' 2.212(8)	Mn2-OH 2.151(9)	
Mn1-OH 2.220(8)	Mn2-OH' 2.177(8)	
Mean Mn1-O, OH 2.210	Mean Mn2-O, OH 2.207	
T1 Tetrahedron		
T1-O3 1.653(9)	O3-O4 2.629(13)	O3-T1-O4 104.7(5) °
T1-O4 1.666(10)	O3-O4' 2.650(13)	O3-T1-O4' 106.4(5)
T1-O4' 1.656(9)	O3-O8 2.712(12)	O3-T1-O8 110.6(5)
T1-O8 1.644(8)	O4-O4' 2.771(13)	O4-T1-O4' 113.1(5)
Mean T1-O 1.655	O4-O8 2.720(12)	O4-T1-O8 110.5(4)
	O4'-O8 2.723(11)	O4'-T1-O8 111.2(4)
	Mean O-O 2.701	Mean O-T1-O 109.4
T2 Tetrahedron		
T2-O1 1.668(15)	O1-O2 2.823(23)	O1-T2-O2 116.2(7) °
T2-O2 1.657(17)	O1-O3 2.651(16)	O1-T2-O3 107.9(6)
T2-O3 1.610(9)	O1-O7 2.609(16)	O1-T2-O7 106.3(6)
T2-O7 1.593(9)	O2-O3 2.618(17)	O2-T2-O3 106.5(6)
Mean T2-O 1.632	O2-O7 2.622(18)	O2-T2-O7 107.6(6)
	O3-O7 2.663(12)	O3-T2-O7 112.5(5)
	Mean O-O 2.664	Mean O-T2-O 109.5
T3 Tetrahedron		
T3-O1 1.680(15)	O1-O2 2.716(23)	O1-T3-O2 107.4(7) °
T3-O2 1.690(17)	O1-O5 2.619(15)	O1-T3-O5 104.3(7)
T3-O5 1.636(12)	O1-O6 2.792(16)	O1-T3-O6 112.5(6)
T3-O6 1.677(10)	O2-O5 2.567(18)	O2-T3-O5 101.0(6)
Mean T3-O 1.671	O2-O6 2.793(17)	O2-T3-O6 112.1(7)
	O5-O6 2.845(15)	O5-T3-O6 118.3(6)
	Mean O-O 2.722	Mean O-T3-O 109.3

3.119 Å. The Mn2 site is coordinated to four oxygens and two hydroxyls. The corresponding values are 2.207 Å and 3.115 Å, respectively.

There are three tetrahedral sites in the subcell structure; T1, T2 and T3. This triple chain is formed by the combination of three 'single' chains; one within and two outside. The inner 'single' chain is composed of T1 tetrahedra with a mean T-O distance of 1.655 Å. The two outer 'single' chains are composed of T2 and T3 tetrahedra with a mean distance of 1.652 Å. However, the T3 tetrahedra at the outside edges of the chain is distorted as is the T2 tetrahedra in amphibole structures (Papike *et al.*, 1969).

If Smith and Bailey's data (Smith and Bailey, 1963) are applied for the obtained results, the expected site occupancy of aluminum in the tetrahedral sites is as follows: T1, 0.07; T2, 0.03; T3, 0.50. This indicates that most of

FIG. 1. A part of the (001) projection of the ganophyllite subcell structure showing the manganese octahedral sheet (a) and the triple chain (b).

FIG. 2. The (100) projection of the ganophyllite subcell structure.

FIG. 3. The (100) projection of the ganophyllite structure (monoclinic polytype).

FIG. 4. A part of the (001) projection of the ganophyllite structure showing triple chains and the manganese octahedral sheet.

the aluminum that replaces silicon in the tetrahedral sites is located in T3. Although the details of the mechanism of site preference of the aluminum in the tetrahedral sites in the true large cell structure is not known yet, it is reasonable to consider that the site preference of the aluminum in the T3 tetrahedra affects the ordering of the interlayer cations and water molecules. It is possible to assume that the interlayer cations lie apart 2.75 Å, for instance, along the *a*-axis. However, the results of chemical and structural analyses suggest that there is an ordering of the interlayer cations—the presence of vacancies in the expected interlayer cation sites in the average sub-cell structure.

If only one-third of the interlayer cation sites is filled, the expected structural formula is as follows;

The chemical composition of the Benallt ganophyllite seems to coincide with this formula (Table 2).

If one half of the interlayer cation sites are filled, the expected structural formula is as follows;

The results for the Harstig ganophyllite satisfy this formula.

Thus the number of the interlayer cations is variable and depends on the kind of the interlayer cations. The positive charge of the interlayer cation is about +1.5 per subcell. If divalent cation is dominant, the number decreases to about 1, and if alkali ion is dominant, the number increases to about 1.5. The number of water molecules coordinated to the interlayer ion also should show the similar trend following the change of the number of the interlayer ion.

Thus the general structural formula of ganophyllite is considered to be as follows;

Several comments should be given here about this formula;

1. The number of the aluminum replacing the silicon in the tetrahedral sites is about 2, that is, Si: Al=10:2.
2. Small portion of aluminum is in the octahedral sites.
3. Small portion of oxygens in T₁₂O₃₂ chain should be hydroxyl to maintain the charge balance. Most of the oxygen at the edge of T3 tetrahedron, O5, might be hydroxyl.

The site preference of aluminum in the tetrahedral sites, especially T3, results in the ordering of the interlayer cations and the water molecules. These ordering gives slight changes in the geometry of the tetrahedra in the average subcell structure (The β_{11} values of several atoms are very large and suggest that the shift along the a -axis must be the most significant). These can explain why ganophyllite has such a large cell.

Recently, Jefferson found the presence of triclinic polytype in ganophyllite (Jefferson, 1978; Table 1).^{*} The structure of this polytype can be explained by the monoclinic subcell structure (Fig. 5). In both polytypes, the arrange-

FIG. 5. The relationship among the subcell, true large cell of monoclinic polytype, and the cell of triclinic polytype (M: monoclinic, T: triclinic).

^{*} Note. The value of $127^{\circ}28'$ for α given by Jefferson (1978) is doubtful. If we adopt this value, the calculated value of $d(001)$ for triclinic polytype becomes $22.39\text{\AA}$ and does not coincide with the corresponding value of monoclinic polytype, $25.04\text{\AA}$. After careful inspection of his precession photographs in his paper, the author has reached a conclusion that he has selected a wrong direction as an axis, and the correct value must be about $118-119^{\circ}$. If we adopt 118.3° as the value of α , $d(001)$ of triclinic polytype becomes $25.11\text{\AA}$ and also it is possible to explain the structure scheme of triclinic polytype based on the subcell structure of monoclinic polytype.

TABLE 5. Triple chain silicates.

Name	(synthesized)	(synthesized)	(synthesized)	Jimthompsonite (Mg,Fe) ₁₀ Si ₁₂ O ₃₂ (OH) ₄	clinojim- thompsonite (Mg,Fe) ₁₀ Si ₁₂ O ₃₂ (OH) ₄	chesterite (Mg,Fe) ₁₇ Si ₂₀ O ₅₄ (OH) ₆
Structural formula	Ba ₄ Si ₆ O ₁₆	NaMg ₄ [Si ₆ O ₁₅ OH] (OH) ₂	Na ₂ Mg ₄ Si ₆ O ₁₆ (OH) ₂			
<i>a</i>	12.476Å	10.132Å	10.152Å	18.626Å	9.874Å	18.614Å
<i>b</i>	13.962	27.12	27.137	27.230	27.24	45.306
<i>c</i>	4.688	5.257	5.276	5.297	5.316	5.297
β	93°37'	106°54'	106.97°		109.47°	
Space group	<i>P</i> ₂₁ / <i>b</i>	<i>C</i> 2/ <i>c</i>	<i>C</i> 2/ <i>c</i>	<i>Pbca</i>	<i>C</i> 2/ <i>c</i>	<i>A</i> 2 ₁ <i>ma</i>
<i>Z</i>	4	4	4	4	2	4
Type of chain*	T	T	T	T	T	T+D
Reference	Filipenko <i>et al.</i> (1971)	Dritz <i>et al.</i> (1975)	Tateyama <i>et al.</i> (1978)	Veblen and Burnham (1978a, b)	Veblen and Burnham (1978a, b)	Veblen and Burnham (1978a, b)

* T: Triple chain, D: Double chain.

ments of the tetrahedral and octahedral layers are nearly the same. The different ordering pattern of the aluminum in the tetrahedral sites, the interlayer cations and water molecules must produce these two different polytypes. For instance, the interlayer cations clearly have different symmetry relation in these polytypes.

There are three 'layered' manganese or iron silicates which have $d'(001) = 12.5 \text{ \AA}$; stilpnomelane, bannisterite and ganophyllite. The crystal structure of stilpnomelane, $\text{K}_2\text{Fe}_{48}\text{Si}_{70}\text{Al}_2\text{O}_{180}(\text{OH})_{48}$ (idealized formula), was determined by Eggleton (1972). Stilpnomelane has a cell with $d(001) \sim 12.2 \text{ \AA}$, but the layer misfit is eliminated by the introduction of inverted tetrahedra into six-membered rings. The crystal structure of bannisterite, a layered manganese silicate which has a cell with $d'(001) \sim 12.3 \text{ \AA}$, has been determined by Threadgold (a private communication). Bannisterite is not chain silicate though Patterson projection ($u'0w'$) of ganophyllite and bannisterite are nearly the same.

Hitherto, several triple chain silicates have been described (Table 5). Among these, four triple chain silicates (except $\text{Ba}_4\text{Si}_6\text{O}_{16}$) and ganophyllite have a common feature that the cell dimension of b is about $27 \text{ \AA}$, and among them four are monoclinic and have the same space group $C2/c$ (if a and c are interchanged in ganophyllite). The octahedral layers in these structures listed in Table 5 are band like in amphiboles, sepiolite or palygorskite. However, the octahedral layer in ganophyllite is not band but sheet. Also, the triple chains in ganophyllite are a modified modeling derived from sheet—the split of a sheet into triple chains.

Hazen and Wones (1972) and Hazen and Burnham (1973) deny the presence of a mica, $\text{KMn}_3\text{Si}_4\text{AlO}_{10}(\text{OH})_2$, theoretically as the α of this structure becomes negative. This prediction has been confirmed also by Kato *et al.* (1979). The structure of ganophyllite seems one solution devised to minimize the layer misfit when Mn^{2+} ions occupy nearly all the octahedral sites in the trioctahedral mica structure, in a sense.

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