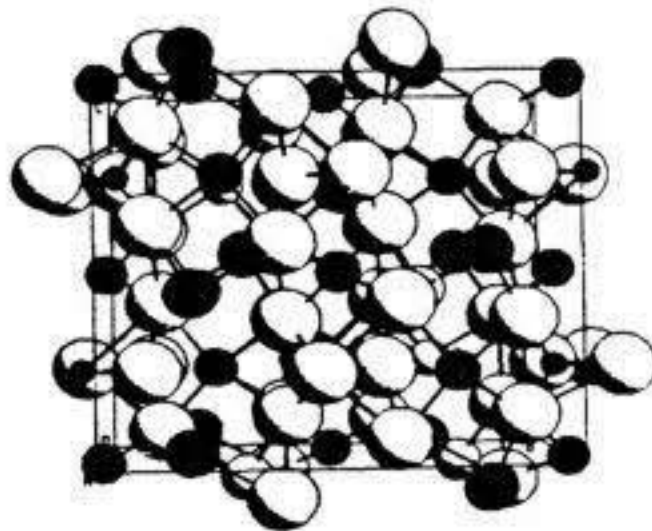


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COMPOSITIONAL VARIATIONS OF NATURAL AND SYNTHETIC  
LEAD SILICATES OF LÅNGBAN-TYPE

Doctoral Thesis  
by  
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GANOMALITE, MARGAROSANITE AND MOLYBDOPHYLLITE FROM LANGBAN,  
SOUTH-CENTRAL SWEDEN, AND SYNTHETIC EQUIVALENTS.

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**Abstract**

Paragenetic, compositional and crystal structural data for ganomalite, margarosanite and molybdophyllite from the Långban deposit are presented. It is shown that the Mn content of both natural and synthetic ganomalite phases may deviate from the ideal formula  $Pb_9Ca_5Mn(Si_2O_7)_3(SiO_4)_3$ , the maximum incorporation of Mn being dependent upon temperature of formation. Varying Mn content has also been recorded in margarosanite.  $Pb(Ca,Mn)_2Si_3O_9$ , a vug or fissure mineral often associated with celsian. The hexagonal unit-cell of molybdophyllite has been determined at  $a_0 = 9.32 \text{ \AA}$  and  $c_0 = 27.39 \text{ \AA}$ . The true mineral composition is still unknown but a tentative ideal formula is given as

$Pb_9Mg_9Si_9O_{24}(OH)_{24}$ , (Z=2). In relation to this formula all analyzed molybdophyllites show a lowering of the lead content of at least 10% which is assumed to be due to loss of loosely bound interlayer lead. A new mineral, macroscopically very similar to molybdophyllite but with a Pb:Mg:Si ratio of 3:2:2, has also been identified. Its hexagonal unit-cell parameters are  $a_0 = 9.34 \text{ \AA}$  and  $c_0 = 36.79 \text{ \AA}$  and the layer thickness is increased from 13.7  $\text{\AA}$  to 18.4  $\text{\AA}$  as compared to molybdophyllite.

## Introduction

Lead is one of the characteristic elements creating the unique mineral variety at the Långban deposit, near Filipstad, south-central Sweden. Among lead compounds there is especially a suite of silicates which are very uncommon in the rest of the world or only known from the Långban locality.

The following lead silicates have so far been recorded at Långban or satellite deposits: kentrolite and barysilite in combination with manganese, melanotekite and jagoite in combination with iron, molybdophyllite in combination with magnesium, and the calcium-lead silicates margarosanite, ganomalite, nasonite, roeblingite, hyalotekite (B-bearing) and joesmithite (with additional Mg and Be).

In this study ganomalite, margarosanite and molybdophyllite have been subject to closer investigation with respect to chemical variation and paragenetical relations of the minerals. It has been attempted to get more information about their stability conditions by means of synthesis experiments.

## Ganomalite

### *Recent compositional and crystal structural data*

Ganomalite is an apatite-related, hexagonal sorosilicate, containing both isolated and double silica tetrahedra. Its crystal structure was shown by Engel (1972) to be a hybrid between chlorine-vacant nasonite,  $\text{Pb}_6\text{Ca}_4(\text{Si}_2\text{O}_7)_3\text{Cl}_2$ , and an apatite structural element. The size of the hexagonal unit-cell was given as  $a_0=9.85 \text{ \AA}$ ,  $c_0=10.15 \text{ \AA}$ . The chemical formula was proposed to be  $\text{Pb}_3\text{Ca}_2\text{Si}_3\text{O}_{11}$  ( $Z=3$ ) with no hydroxide ions present in contradiction with earlier assumptions.

This structural concept was essentially confirmed by Dunn et al. (1985) who suggested that the space group of the lattice (unitcell parameters:  $a = 9.82 \text{ \AA}$ ,  $c = 10.13 \text{ \AA}$ ) is in analogy with the isostructural low-temperature lead germanate.

Table 1. Hydrothermal syntheses of ganomalite at varying temperature and Mn-content ( $P_{H_2O}=1$  kbar, run duration 1 week).

Run no	Initial Mn/(Mn+Ca)	Temp. (°C)	Crystalline products	
			Final Mn/(Mn+Ca) in ganomalite	Other phases
85139	0.25	200	0.03	ala, bsl
84136	0.50	250	0.05	ala, bsl
85135	0.00	250	0.00	ala
84131	0.33	300	0.08	ala, bsl, br
84130	0.00	300	0.00	mrq
84177a)	0.33	300	0.08	bsl
84128	0.25	400	0.14	ala, bsl
84127	0.00	400	0.00	mrq, ala
84132	0.00	500	0.00	mrq
84133	0.25	500	0.20	ala, mas
8365	0.00	630	0.00	ala
85141	0.25	650	0.22	bst
85142	0.50	650	0.22	bsl

#### Abbreviations

ala = alamosite, br = braunite, bsl = barysilite, bst = bustamite, mrq = margarosanite, mas = massicot

a) First heated to 400°C during one week and then the temperature was lowered and kept constant at 300°C for one month.

Table 2. Unit-cell dimensions of synthetic and natural ganomalites with varying Mn-content.

Run no	Mn/(Mn+Ca)	Temp. (°C)	a <sub>0</sub> (Å)	c <sub>0</sub> (Å)	Volume (Å <sup>3</sup> )
85135	0.00	250	9.920(8)	10.14(1)	863.9
84133	0.20	500	9.831(8)	10.18(1)	853.1
85142	0.22	650	9.798(8)	10.17(1)	845.6

#### Natural ganomalites

Sample	Mn/(Mn+Ca)	a <sub>0</sub> (Å)	c <sub>0</sub> (Å)	Volume (Å <sup>3</sup> )
831018	0.08	9.865(6)	10.17(1)	857.5
331067	0.15	9.850(8)	10.18(1)	853.0
760393	0.21	9.817(5)	10.14(1)	846.4

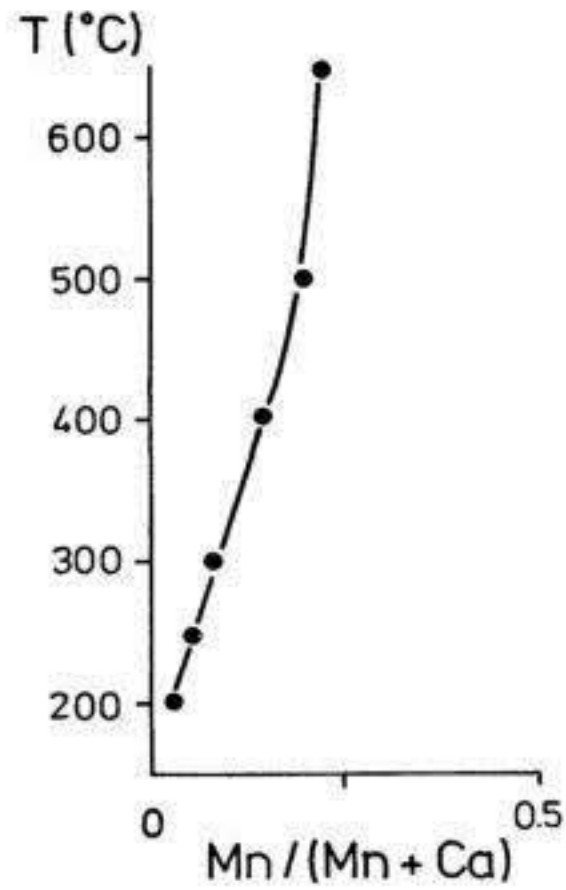


Fig. 1. Temperature-composition diagram showing the maximum manganese incorporation in ganomalite.

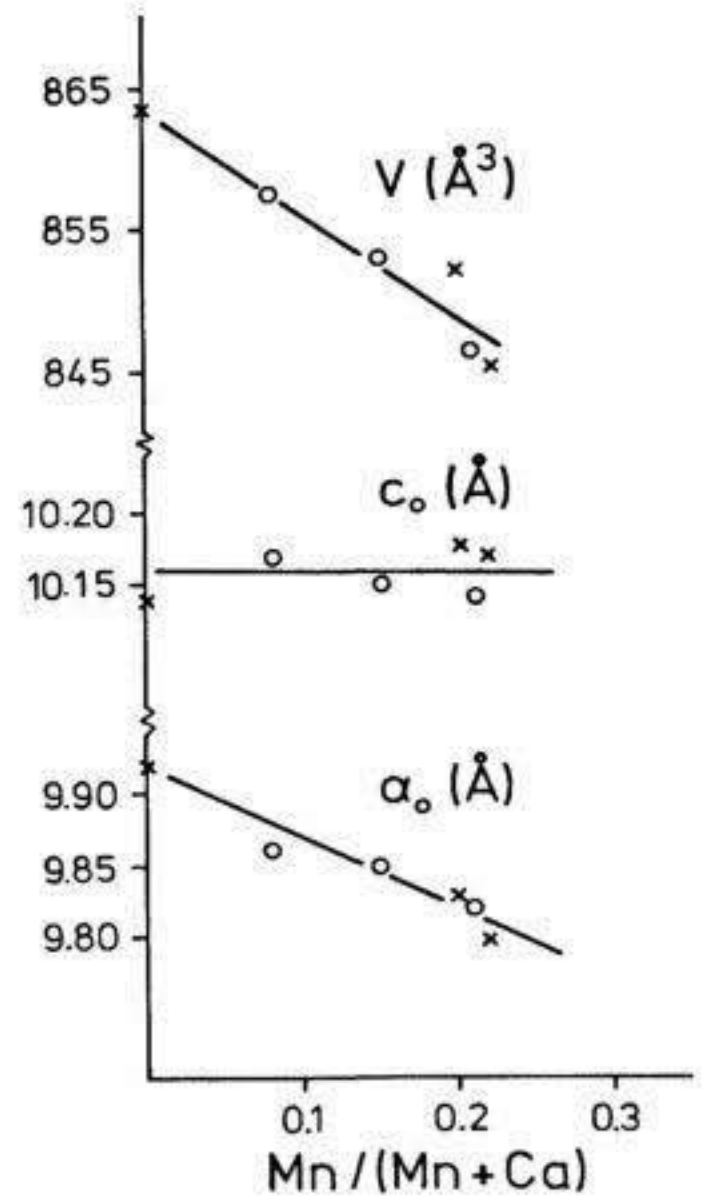


Fig. 2. Unit-cell dimensions of ganomalite with varying Mn-content. Circles and crosses refer to natural and synthetic phases respectively.

$Pb_5(Ge_2O_7)(GeO_4)$ . They also claimed that manganese is an essential component of ganomalite, constantly replacing Ca on one of six possible sites. Thus, they arrived at a composition of  $Pb_9Ca_5MnSi_9O_{33}$  (Z=1) which is now the officially approved ganomalite formula.

#### *Synthesis experiments.*

The results of hydrothermal synthesis experiments, carried out at various temperatures with starting oxide mixtures corresponding to ganomalite compositions of various Ca:Mn ratios, are given in Tab. 1 and compiled as a phase diagram in Fig. 1.

The results show that ganomalite is apparently a stable structure even in Mn-free environment and that the ability of ganomalite to incorporate manganese ions into the structure is temperature-dependent. The formation of ordered ganomalite with a Ca:Mn ratio of 5:1 (Dunn et al., 1985) should thus require a minimum temperature of approximately 450°C. At still higher temperatures the Mn-content of ganomalite may grow up to a Mn:(Ca+Mn) ratio of 0.22 (650°C). At temperatures below 450°C there is a steady decrease of the maximum Mn-content. This decrease seems not to be due to kinetical effects but is rather an equilibrium trend as indicated by reversed syntheses (run nr. 84177). The unit-cells of the synthetic phases as determined by X-ray powder diffraction analysis are listed in Table 2. The shrinkage of the ganomalite unit-cell as a function of increasing Mn-content is illustrated in Fig. 2, showing a rapid decrease of the a-axis whereas the c-axis (parallel to the length axis of tetrahedral silica doublets) is maintained constant.

In Fig. 3 typical morphologies of ganomalite crystals, synthesised at different temperatures, are shown. At intermediate temperatures (around 400°C) a tabular habit is easily recognized. At higher temperatures (630°C) this trend is lost and the ganomalite becomes more equant or short prismatic. While Swedish ganomalites are generally irregular in shape, tabular habit being only occasionally observed, Dunn (1979) has described ganomalite from Franklin, New Jersey, forming distinctly tabular crystals but with still more simplified morphology than



A.



B.

Fig. 3. SEM images of synthetic crystals of ganomalite formed at two different temperatures, 400°C (A) and 630°C (B), showing typical morphologies (see text). Length of bar 10  $\mu\text{m}$ .

the present synthetic phase.

*Paragenetical and chemical data for ganomalite from the Långban district*

*Ganomalite samples.*

831018, Jakobsberg: Pearly, colourless grains of ganomalite in a calcite-phlogopite rock, carrying hausmannite and Zn-rich jacobsite. The calcite is very poor in manganese and is non-fluorescent, whereas the phlogopite is poor in both manganese and barium. The sample is rich in disseminated native copper, often mobilized into grain boundaries and along cleavage surfaces of other minerals. Disseminated grains of macedonite, svabite and occasionally crednerite are also found.

g14888 and 331067, Jakobsberg: Both samples contain colourless, greasy to pearly ganomalite in a rock matrix of mica, calcite and jacobsite. In g14888 the jacobsite is carrying nearly 2 weight-% of  $TiO_2$  which is unusually high for spinels from the Långban district. In both cases the phlogopite mica is enriched in barium and manganese. In sample 331067, which also contains macedonite, the Mn ionic content of the octahedral mica layer may rise to 30%. The rocks which are traversed by small fissures of native lead and subordinate copper also contain minor barite and svabite.

g14906, Långban: Abundant ganomalite forming anhedral, translucent grains with pearly lustre in a rock composed of calcite, manganoan phlogopite and jacobsite. Manganoan diopside and Mg-rich tephroite are present as small inclusions in ganomalite. Native lead occurs as narrow fissure fillings.

14883, Långban: Subhedral crystals of ganomalite with very pale brownish colour and greasy lustre in close association with tephroite (Te70Fo30) and Mn-rich phlogopite.

38957, Långban: Greasy, translucent, colourless ganomalite grains are impregnating a calcite-rich groundmass with subhedral, Mg-enriched jacobsite, containing up to 25 mole-% of the



magnesioferrite component, manganous phlogopite, yellow andradite, manganous diopside, tephroite (Te70Fo30) and minor amounts of bindheimite and barysilite. Native lead is found as fissure fillings and as inclusions in ganomalite.

760393, Långban: Greasy, translucent, colourless to very pale brownish crystals of ganomalite, occasionally with tabular habit, are embedded in a matrix of calcite and Mg-rich jacobsite. Closely associated with ganomalite occurs tephroite (Te76-Fo24). Small amounts of barytocalcite are found enclosed by calcite. Fissures of native lead are traversing the rock.

14908, Långban: Colourless ganomalite in a medium-grained, heterogenous skarn rock consisting of calcite, jacobsite and manganous phlogopite, partly accompanied by pyroxene, partly by Mg-rich tephroite (Te71Fo29). Small amounts of barytocalcite and bindheimite are also present.

#### *Paragenesis*

Paragenetically, Magnusson (1930) assigned the formation of ganomalite, occurring as skarn silicate in hausmannite-impregnated dolomite, to the later stage of the B-period of his paragenetical scheme, which would involve a certain lowering of the temperature as compared to earlier formed lead silicates of kentrolite/melanotekite type commonly accompanied by braunite. The mode of occurrence of ganomalite in the present rock samples makes it difficult to delineate the pertinent mineral paragenesis. Generally, calcite, phlogopite (usually Mn-rich) and jacobsite constitute the minerals most intimately associated to ganomalite. There are, however, some differences between the ganomalite assemblages from Långban and Jakobsberg. A close paragenetical relationship between ganomalite and tephroite (Mg-rich) is exclusively characteristic for Långban samples. The jacobsite composition also varies, being Mg-enriched at Långban and Zn- or Ti-enriched at Jakobsberg. Ti enrichment is also evidenced by locally abundant macedonite inclusions in the Jakobsberg samples.

Among other minerals repeatedly present in the samples but not necessarily related to the ganomalite formation are noticed sva-bite and barite at Jakobsberg and barytocalcite and bindheimite at Långban. Conspicuously frequent is the occurrence of thin fissures of native metals, predominantly lead at Långban and copper at Jakobsberg. In some cases native lead is also directly associated to ganomalite. This type of narrow fissures may possibly have formed much earlier than usually assumed.

#### *Chemistry*

Obviously, there is some disagreement between the general feature of the synthetic ganomalite system as outlined in Fig. 1 and the definition of ganomalite as a strictly ordered phase with a fixed Ca:Mn ratio of 5:1 as proposed by Dunn et al. (1985). The possibility that Ca-Mn ordering is not fully attained in the laboratory experiments, which would require some modification of the given phase diagram, does not change the facts that Mn-free ganomalite is really a stable phase and that Mn can enter the structure beyond the value of the given ordered composition. The results of electron microprobe analysis of the present ganomalites, given in Table 3, show that the majority have a composition close to the accepted one, but there are two exceptions with deviating Ca:Mn ratios in agreement with those found for the synthetic phases. For one Långban sample (760393) the Mn:(Mn+Ca) ratio is raised to 0.21 instead of the ordered value 0.17, which possibly could be the result of a higher temperature of formation. For one Jakobsberg sample (831018) the same ratio is lowered to 0.08. The assemblage of this ganomalite contains both hausmannite and jacobsite, but is quite unique in some respects. The jacobsite composition is thus characterized by an unusually high zinc content whereas accompanying phlogopite and calcite are both extremely depleted in manganese. The formation of this particular ganomalite is most likely due to lack of available Mn rather than a lowering of the temperature.

Table 3. Microprobe analyses of natural ganomalites from Långban in wt%.

Sample	831018	14906	38957	g14888	331067	g14908	14883	760393
SiO <sub>2</sub>	18.38	19.15	19.06	18.54	18.36	18.90	18.83	18.21
Al <sub>2</sub> O <sub>3</sub>	n.d.	n.d.	n.d.	0.07	0.08	n.d.	n.d.	n.d.
CaO	10.65	9.95	9.75	9.79	9.75	9.52	9.65	9.60
MnO	1.19	1.86	1.85	2.17	2.18	2.20	2.32	3.09
MgO	n.d.	n.d.	n.d.	0.05	0.02	n.d.	n.d.	n.d.
PbO	69.18	69.37	69.00	69.20	68.80	69.27	66.38	68.97
BaO	n.d.	n.d.	n.d.	0.00	0.29	n.d.	n.d.	n.d.
Cl	n.d.	n.d.	n.d.	0.05	0.07	n.d.	n.d.	n.d.
Total	99.40	100.33	99.66	99.87	99.55	99.89	100.18	99.87

## Recalculation based on 33 oxygen atoms

Si	8.94	9.14	9.15	8.97	8.94	9.11	9.05	8.85
Al	-	-	-	0.05	0.05	-	-	-
Ca	5.55	5.07	5.06	5.07	5.08	4.92	4.97	5.00
Mn	0.50	0.75	0.75	0.89	0.90	0.90	0.96	1.29
Mg	-	-	-	0.05	0.02	-	-	-
Pb	9.06	8.91	8.93	9.02	9.02	8.97	8.99	9.03
Ba	-	-	-	0.00	0.00	-	-	-
Cl	-	-	-	0.05	0.06	-	-	-
Mn/(Mn+Ca)	0.08	0.13	0.13	0.15	0.15	0.16	0.16	0.21

n.d.: not determined.

*Conclusions*

As a result of the above studies of synthetic and natural ganomalite it may be concluded that the compositional variations of the mineral can be described by the general formula  $Pb_x(Ca,Mn)_y(Mn,Ca)(Si_2O_7)_z(SiO_4)_x$ .

It is also suggested that ganomalite in the Långban district is typically formed within a temperature interval of 450 to 500°C, in agreement with earlier opinions (Magnusson, 1930) that the formation occurred after the first strong peak metamorphism.

**Margarosanite***Crystal structure*

The details of the crystal structure of margarosanite,  $PbCa_2Si_3O_9$ , were clarified by Freed & Peacor (1969). They arrived at a triclinic unit-cell with  $a=6.77$  Å,  $b=9.58$  Å,  $c=6.72$  Å,  $\alpha=110.4^\circ$ ,  $\beta=103.4^\circ$ ,  $\gamma=83.02^\circ$ , space group  $P_1$ ,  $Z=2$ .

The silica tetrahedra are bonded together in groups of three-membered rings, forming separate planes between which edge-shared chains of irregular Ca(1)-octahedra are located, laterally coupled to each other by regular Ca(2)-octahedra. The 7-coordinated Pb-polyhedra cross the plane of silica tetrahedra and complete a three-dimensional network by combining Ca(1)-chains from alternating planes.

The crystallographic direction of the Ca(1)-chains is (101) which is also the c-axis of the derived pseudo-cells of orthorhombic and monoclinic symmetry. In margarosanite crystals this direction is easily recognised as the axis of elongation.

*Synthesis*

Under hydrothermal conditions Ito (1968) succeeded in producing artificial margarosanite at a temperature of 300°C and a pressure of 2 kbars. The crystals had an acicular appearance.

reminding of the habit of natural margarosanite from Franklin, New Jersey, USA.

In the present experiments, carried out at 1 kbar, Mn-free margarosanite was hydrothermally synthesized from equivalent oxide mixtures at temperatures ranging from 350°C to 600°C, higher temperatures not being tried.

At 350°C the yield was far from complete. At still lower temperatures there was no trace of margarosanite and instead various unidentified phases were formed.

Syntheses performed at 550°C with varying run times show that margarosanite is not the first crystallization product. Instead, ganomalite is first formed, not being transformed into margarosanite until after some hours of duration.

When introducing manganese in the system, the yield of margarosanite was conspicuously reduced. To a great extent lead was instead consumed in the formation of barysilite,  $Pb_8Mn(Si_2O_7)_3$ . The presence of barysilite and various other phases rendered it difficult to identify and chemically analyse the margarosanite phase.

Yet, approximate results of electron microprobe analysis of separate margarosanite grains seem to indicate that the incorporation of Mn into the structure is favoured with increasing temperature.

At 400°C the maximum substitution of Mn for Ca is around 10%, being nearly doubled at 600°C.

All margarosanite crystals, obtained in the present experiments, were developed as slender laths, independent of temperature of formation.

#### *Margarosanite specimens*

All the samples come from the Långban mine; when known, the name of the stope is also given.

336347: Radiating laths of colourless margarosanite, together with Mn-free calcite and celsian, form distinct thin fissures in a fine-grained braunite-bearing, micaceous skarn rock. In short-wave ultraviolet light the margarosanite fluoresces in red, changing to bluish-white at altered surfaces.

30810: Thin layer of small and colourless margarosanite needles associated with prehnite and barite in a distinct fissure environment of a micaceous augite skarn rock. This margarosanite shows strongly bluish-white fluorescence (SW) changing to purplish red.

730146 (Upper Bolivia stope): Clusters of slender laths of colourless, non-fluorescent margarosanite, closely associated with Mn-free calcite, barite (with a Sr:(Sr+Ca) ratio of 0.12), hedyphane and prehnite, are found as fissure fillings in mica-bearing braunite ore.

30640: A calcite-manganian phlogopite rock is traversed by distinct fissures of large margarosanite laths, accompanied by Mn-free calcite, barite (Sr:(Sr+Ca)= 0.08), svabite as well as ganomalite. The co-existence of margarosanite and ganomalite has never been reported earlier. The margarosanite fluoresces (SW) with a very pale red colour.

170786, 180015, 670015: Bundles of colourless laths of margarosanite, up to 20 mm in length, occur in a fissure- and vug-like pattern in a strongly heterogeneous rock matrix. The margarosanite is accompanied by Mn-free calcite, barite (Sr:(Sr+Ca)= 0.09), apophyllite, celsian and brownish red aegirine-augite. The short-wave fluorescence colour is heavy red with a purplish tint in all samples.

30165 (Australian stope): Fissure margarosanite accompanied by Mn-free calcite, barite (Sr:(Sr+Ca)=0.07) and prehnite. Minor amounts of reddish brown pyroxene, celsian and melanotekite also occur close to margarosanite. The colourless margarosanite fluoresces reddish violet in short-wave ultraviolet light.

31209: In a micaceous andradite skarn rock, white margarosanite is found partly as mm-thick planar fissures, partly as coating upon irregularly curved rock surfaces. Prehnite and minor apophyllite are associated with the margarosanite which shows purplish red fluorescence (SW) colour, locally changing to bluish white as a result of secondary alteration.

#### *Paragenetical relations*

The present and earlier descriptions (Flink 1917a and 1917b, Aminoff 1918a, Flink 1923) of Långban margarosanite assemblages show that they contain typical vug and fissure minerals, such as apophyllite, nasonite, trigonite, prehnite and native lead, thus suggesting a low to moderate temperature of formation.

It may also be noted that potassium-free celsian, not earlier reported as accompanying margarosanite, is present in nearly half of the samples here. Contrary to potassium-rich varieties, pure celsian is generally occurring as a fissure mineral of adularian affinity, again indicating a moderate temperature of formation.

Magnusson (1930) considered margarosanite to be formed during period C of his paragenetical scheme.

#### *Chemistry*

The results of chemical analyses by electron microprobe measurements (WDS and/or EDS) are given in Table 4. The only major compositional variation is recorded for the amount of manganese substitution, the Mn:(Mn+Ca) ratio varying from 0.02 to 0.11.

The reason for this variation is difficult to evaluate. It could be witnessing of temperature variations or simply reflecting the availability of manganese at time of formation. Most often the immediate environment of the margarosanite crystals seems to be depleted in Mn.

For comparison, recently published analyses of margarosanites from Franklin (Dunn, 1985) may be cited. They show a Mn:(Mn+Ca)

Table 4. Chemical composition in wt% of natural margarosanites from Långban.

Sample	336347	30810	730146	180015	g170786	30165	30648	67097	31209
SiO <sub>2</sub>	34.16	34.31	35.53	34.16	33.97	34.24	34.52	32.99	33.05
Al <sub>2</sub> O <sub>3</sub>	n.d.	n.d.	n.d.	n.d.	n.d.	0.05	0.05	n.d.	n.d.
CaO	20.46	20.88	21.35	18.81	19.32	19.41	21.06	18.30	18.19
MnO	0.47	0.52	0.79	1.67	1.67	1.97	2.70	2.75	2.75
MgO	n.d.	n.d.	n.d.	n.d.	n.d.	0.07	0.05	n.d.	n.d.
PbO	45.19	42.81	42.36	44.09	45.11	41.86	41.34	44.89	45.08
BaO	n.d.	n.d.	n.d.	n.d.	n.d.	0.00	0.24	n.d.	n.d.
Cl	n.d.	n.d.	n.d.	n.d.	n.d.	0.00	0.00	n.d.	n.d.
Total	100.28	98.52	100.03	98.73	100.07	97.60	99.96	98.93	99.07

## Formula proportions based on 9 oxygen atoms

Si	2.99	3.00	3.02	3.03	2.99	3.01	2.95	2.97	2.97
Al	-	-	-	-	-	0.01	0.01	-	-
Ca	1.92	1.95	1.94	1.79	1.82	1.82	1.93	1.76	1.75
Mn	0.04	0.04	0.06	0.11	0.13	0.15	0.20	0.21	0.21
Mg	-	-	-	-	-	0.01	0.01	-	-
Pb	1.06	1.01	0.97	1.06	1.07	0.99	0.95	1.09	1.09
Ba	-	-	-	-	-	0.00	0.01	-	-
Cl	-	-	-	-	-	0.00	0.00	-	-
Mn/(Mn+Ca)	0.02	0.02	0.02	0.04	0.07	0.08	0.09	0.11	0.11

n.d.: not determined.



ratio never exceeding 0.02 and some content of zinc which is not to be found in the Långban material.

Refined unit-cell parameters for some natural Mn-bearing margarosanites as well as for a Mn-free phase are given in Table 5 (Guinier-Hägg photographs,  $\text{CuK}\alpha_1$ , internal standard=Si).

### **Molybdophyllite**

#### *Synthesis*

Several attempts were made to produce molybdophyllite by hydrothermal synthesis. A wide range of temperatures (200-600°C) was tried as well as varying chemical environment (e.g. presence of carbonate ions), but in no case formation of molybdophyllite could be proved.

Electron microscopy studies of reaction products formed at temperatures in the range of 300-500°C occasionally revealed the presence of thin flakes with a composition close to molybdophyllite but the yield was too low to allow final identification. The main part of the reaction products consist of various hitherto unknown phases.

#### *Molybdophyllite samples*

All the samples under investigation are from Långban, the only locality at which the mineral with certainty has been found so far.

02154, 070315, 12413: Coarse, colourless flakes of molybdophyllite in calcite-braunite rocks with subordinate dolomite and serpentine. In sample 02154 the molybdophyllite flakes are located in calcite vugs which also contain minor norsethite. The molybdophyllite of sample 12413 contains small inclusions of nearly Mn-free phlogopites.

191581, 10168, 12426, 31238, 980568, 30825: Large, colourless flakes of molybdophyllite in calcite-hausmannite rocks of varying grain size and generally containing subordinate dolomite

Table 5. Refined unit-cell dimensions for natural Mn-bearing margarosanites from Långban, and one Mn-free synthetic variety. The estimated error is generally below 0.5%.

Sample	Mn/(Mn+Ca)	a <sub>0</sub> (Å)	b <sub>0</sub> (Å)	c <sub>0</sub> (Å)	α (°)	β (°)	γ (°)	Volume (Å <sup>3</sup> )
30810	0.02	6.727	9.531	6.718	110.35	102.82	83.26	393.40
30165	0.08	6.748	6.508	6.685	110.14	102.82	83.14	392.16
31209	0.11	6.730	9.522	6.668	110.18	102.99	83.04	390.37

Synthetic sample (run no 85155).

0.00	6.693	9.486	6.645	109.52	102.48	83.91	390.94
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Table 6. Microprobe analyses (wt%) of common molybdophyllite (sample 191581), Pb-depleted molybdophyllite (sample 10168) and "18 Å-molybdophyllite" (sample 740945) from Långban.

Sample	191581		10168		740945	
		std dev		std dev		std dev
SiO <sub>2</sub>	18.25	0.16	24.31	0.13	12.42	0.25
Al <sub>2</sub> O <sub>3</sub>	0.32	0.02	0.64	0.02	0.35	0.03
MgO	11.94	0.11	15.58	0.30	7.98	0.12
MnO	0.18	0.04	0.53	0.04	0.03	0.04
CaO	0.01	0.01	0.00		0.01	0.02
PbO	59.47	0.52	50.94	0.45	70.92	0.09
BaO	0.25	0.11	0.41	0.15	0.13	0.05
Cl	0.00		0.18	0.13	0.07	0.02
F	n.d.		n.d.		0.05	0.02
Total	90.42		92.59		91.96	

n.d.: not determined.

and serpentine. Among other minerals occasionally found closely associated with molybdophyllite may be mentioned morelandite in sample 191581, brucite in sample 10168 and barytocalcite and barite in sample 31238. There is no obvious tendency for molybdophyllite to form distinct fissures with exception for sample 30825.

#### *Paragenetical relations*

With regard to mode of occurrence of the investigated molybdophyllites, it is a general feature that their immediate environment is depleted in manganese in spite of the fact that they are all hosted in rocks rich in manganese oxides. Besides calcite the minerals most closely associated to molybdophyllite are principally barium- and/or magnesium compounds. Some of these may indicate lower to moderate temperatures of formation.

In his paragenetical scheme, Magnusson (1930) assigned molybdophyllite to period C, corresponding to post-peak metamorphic conditions characterized by vug fillings.

#### *Chemical and structural data.*

The handbook formula of molybdophyllite is usually given as  $Pb_2Mg_2Si_2O_7(OH)_2$ . The mineral was first described by Flink (1901) who found that the Pb:Mg:Si ratio was close to 1:1:1. He also stated the hexagonal character of the mineral.

From Laue photographs, Aminoff (1918b) drew the conclusion that the mineral was rhombohedral, belonging to the ditrigonal-discalenohedral crystal class. No successful crystal structure determination has so far been accomplished due to difficulties in obtaining single crystals of proper quality. The structural pattern of molybdophyllite is thus still unknown except for the fact that it should be based upon a layer lattice in view of the high elastic flexibility characterizing the mineral flakes, which are not much more brittle than mica.

The chemical composition as determined by electron microprobe

analysis (WDS and/or EDS) is more or less the same for all the molybdophyllites investigated here (see above), except for sample 10168 which is extremely depleted in lead. The results of the chemical analysis of sample 191581, representative for most molybdophyllites, and sample 10168 are given in Table 6.

In order to check the content of volatile components the behaviour of molybdophyllite during heating was also studied, hand-picked crystals (20 mg) being equilibrated in air at successively higher temperatures at atmospheric pressure. Up to a temperature of 400°C the weight loss was limited but increased then rapidly, especially in the range 450-550°C, with destruction of the molybdophyllite lattice and formation of other phases of unknown composition. The weight loss of approximately 8%, recorded during this break-down process, delimits the maximum hydroxyl water content of the mineral.

To obtain more structural data a small crystal flake of the sample 980568 was analysed in an X-ray single-crystal diffractometer (Philips PW 1100). An approximate hexagonal unit-cell could be outlined, which was further refined from Guinier-Hagg photographs ( $\text{CuK}\alpha_1$ , internal standard = Si) of powdered material, giving the cell parameters  $a_0=9.32(2)$  Å and  $c_0=27.39(7)$  Å. Slightly higher values, 9.47 and 27.9 Å respectively, are reported by P.B. Moore (University of Chicago, personal communication, 1987) who also claims that the space group is  $P6_322$  (182).

An indexed X-ray powder diffraction pattern of the mineral is shown in Table 7.

From the structural characteristics and the results of chemical analyses and weight loss measurements it may be proposed that the ideal molybdophyllite formula is  $\text{Pb}_9\text{Mg}_9\text{Si}_9\text{O}_{24}(\text{OH})_{24}$  ( $Z=2$ ), assuming that there are no other anions present (e.g. carbonate groups).

In relation to the proposed ideal composition, however, all the investigated molybdophyllites are more or less deficient in lead. A representative formula of most samples (as taken from the analysis of sample 191581) could thus be given as

Table 7. X-ray powder diffraction pattern for molybdophyllite from Langban (sample 980568). Intensities obtained visually.

I/I <sub>0</sub>	d(obs)	d(calc)	h k l
80	14.230	13.720	0 0 2
45	8.160	8.114	1 0 0
40	4.689	4.685	1 1 0
5	4.410	4.433	1 1 2
10	4.039	4.057	2 0 0
5	4.000	4.013	2 0 1
5	3.429	3.430	0 0 8
10	3.284	3.273	1 1 6
60	3.073	3.067	2 1 0
20	3.040	3.035	2 0 6
		3.048	2 1 1
40	2.989	2.993	2 1 2
20	2.842	2.855	1 0 9
70	2.701	2.705	3 0 0
75	2.684	2.692	3 0 1
		2.677	2 1 5
5	2.629	2.620	2 0 8
70	2.411	2.416	2 1 7
10	2.341	2.342	2 2 0
10	2.284	2.287	0 0 12
5	2.251	2.250	3 1 0
10	2.220	2.221	3 1 2
40	2.022	2.019	3 1 6
		2.023	4 0 1
10	1.980	1.980	4 0 3
5	1.925	1.926	3 0 10
20	1.862	1.862	3 2 0
5	1.834	1.834	3 0 11
		1.833	2 1 12
100	1.772	1.771	4 1 0



This composition requires a water content of 6.8 wt-% as compared to the observed weight-loss maximum value of 8% and the approximate value 9.1% indicated by the chemical analysis. The calculated density is 4.60 as compared to the measured value 4.717 (Flink, 1901) and the value 4.98 calculated for the ideal formula. The chemical composition of sample 10168, still giving a typical molybdophyllite X-ray pattern, seems to be the result of an extreme leaching of lead. The corresponding formula could be  $\text{Pb}_{5.2}\text{Ba}_{0.1}(\text{Mg}_{9.5}\text{Mn}_{0.2}\text{Al}_{0.3})\text{Si}_{19.0}\text{O}_{24}(\text{OH})_{16.3}\text{Cl}_{0.1}$  with a required water content of 6.5 wt-% as compared to the analytical "difference by weight" value of 7.4%.

The extreme layer lattice character of molybdophyllite could explain easy removal of loosely bound interlayer lead ions. The mineral is very sensitive to treatment of even diluted hydrochloric acid (0.1 M), which is transforming the transparent flakes into chalk white opaque by precipitation of lead chloride but without completely destroying the molybdophyllite structure. At such a treatment marginal zones are observed to maintain their transparency, which may depend on an original edge-wise removal of lead ions from the crystals.

When comparing the present data with the wet-chemical analysis given in the original molybdophyllite description (Flink, 1901) it may be noted that similar lowering of the Pb:Si ratio is recorded and that the water content was stated as 6.32 wt-%.

Awaiting further studies, it may be emphasized, that the ideal formula given above, from which the natural molybdophyllite formulas have been derived, is highly speculative.

#### *Molybdophyllite-like minerals*

According to P. B. Moore (University of Chicago, personal communication, 1987) there exists a monoclinic polymorph of molybdophyllite which was not to be found among the present samples.

In one sample (740945), however, crystals of the same general

Table 8. X-ray powder diffraction pattern for "10 Å-molybdophyllite" from Långban (sample 740945). Intensities obtained visually.

I/I <sub>0</sub>	d(Å)	d(Å)	h k l
100	16.627	16.395	0 0 2
45	9.239	9.197	0 0 4
10	6.694	6.753	1 0 3
40	6.159	6.131	0 0 6
45	4.676	4.671	1 1 0
45	4.630	4.634	1 1 1
50	4.544	4.527	1 1 2
60	4.324	4.365	1 1 3
60	4.177	4.165	1 1 4
60	4.047	4.045	2 0 0
10	3.877	3.842	2 0 3
5	3.685	3.679	0 0 10
60	3.287	3.277	1 1 8
70	3.068	3.066	0 0 12
45	3.039	3.037	2 0 6
45	3.007	3.016	2 1 2
20	2.889	2.890	1 1 10
90	2.699	2.697	3 0 0
20	2.653	2.643	2 1 7
20	2.627	2.628	0 0 14
15	2.426	2.420	1 1 13
60	2.338	2.336	2 2 0
15	2.322	2.319	2 0 13
10	2.294	2.294	2 2 3
5	2.265	2.264	2 2 4
45	2.243	2.244	3 1 0
60	2.226	2.227	3 1 2
45	2.187	2.183	2 2 6
20	2.149	2.146	3 1 5
20	1.871	1.872	1 1 18
20	1.859	1.858	2 2 12
15	1.820	1.819	3 2 4
60	1.787	1.766	2 1 17
20	1.756	1.757	4 1 2
20	1.746	1.746	2 2 14
15	1.575	1.576	2 1 20
60	1.554	1.556	3 3 1
45	1.510	1.511	3 1 18

appearance as molybdophyllite were shown to be deviating in both chemistry and structure. The layer thickness of this new mineral has increased by one-third from nearly 14 Å to 18 Å. Refinement of its hexagonal unit-cell parameters has given the values  $a_0=9.34(2)$  Å and  $c_0=36.79(0)$  Å. Reflections of the X-ray powder pattern obtained from Guinier-Hagg photographs (CuK internal standard = Si) are shown and indexed in Table 6.

At the same time, as shown by the chemical analysis in Table 6, the lead content has increased by one half in comparison to ideal molybdophyllite, the cation ratio Pb:Mg:Si being changed to 3:2:2.

Most probably this "18 Å-molybdophyllite" is derived from ordinary molybdophyllite by addition of an extra lead hydroxide/ (carbonate) layer. The 18 Å X-ray reflection is persistent upon heating up to 400°C, excluding the possibility that we are dealing with lattice expanded by hydration like smectite.

Except for "18 Å-molybdophyllite", sample 740945 (maximum dimension = 3 cm) consists primarily of hausmannite and barytocalcite. Minor amounts of calcite, aegirine-rich pyroxene, apatite and macedonite have also been identified.

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