MINERALS OF THE SCHOENFLIESITE – WICKMANITE SERIES FROM PITKÄRANTA, KARELIA, U.S.S.R.

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ABSTRACT

Wickmanite, $MnSn(OH)_6$, schoenfliesite, $MgSn(OH)_6$, and manganoan schoenfliesite occur in separate low-temperature parageneses in hydrothermally mineralized skarns at Pitkäranta. Schoenfliesite occurs as crusts on cassiterite and shows moderate solid solution of MnO (up to 5 wt. %). The other minerals are very heterogeneous on a micro meter scale. Microprobe analyses show extensive solid solution between $MnSn(OH)_6$, $MgSn(OH)_6$ and an unnnamed $FeSn(OH)_6$ end member (up to 40 mol %). Complete solid solution is probably possible in favorable environments. The cell edge, refractive index, and density vary continuously with composition in the 3-component system. The $FeSn(OH)_6$ end member has an extrapolated a of 7.825.

SOMMAIRE

La wickmanite, $MnSn(OH)_6$, la schoenfliesite, $MgSn(OH)_6$, et la schoenfliesite manganifère se présente en paragénèses séparés be basse température dans des skarns minéralisés par processus hydrothermal à Pitkäranta, Karelia. La schoenfliesite se présente sous forme de croûtes sur la cassiterite, et contient MnO en solution solide (jusqu'à 5% en poids). Les autres minéraux sont nettement hétérogènes à l'échelle micromètre. Les analyses à la microsonde démontrent un vaste domaine de solution solide entre $MnSn(OH)_6$, $MgSn(OH)_6$ et le pôle extrême innommé $FeSn(OH)_6$ (jusqu'à 40% en mole). Sous conditions favorables, l'existence de solution solide complète est probablement possible. a, n et la densité varient de façon continue avec la composition dans le système à trois composantes. Le pôle extrême $FeSn(OH)_6$ possède une valeur de 7.825 pour a, après extrapolation.

(Traduit par la Rédaction)

INTRODUCTION

This work is the result of a cooperation that began in 1974 when Dr. Nefedov asked the Norwegian authors for assistance with microprobe analysis of Pitkäranta minerals. The wickmanites analyzed here were separated by Dr. Nefedov; the other minerals were picked from samples he sent to Norway. The descriptions of the physical properties and parageneses of the minerals were written by Dr. Nefedov, but he had no chance to comment on the chemical data before his sudden and untimely death. Dr. Nefedov's original X-ray data, referred to in the text, were lost after his death; the powder data tabulated here were measured from new films made in Oslo. An appreciation of Dr. Nefedov, written by several of his colleagues, is in *Zap. Vses. Mineral. Obshch.* **105**, 499 (1976).

GEOLOGICAL SETTING

The Pitkäranta mining district lies on the northwestern shore of Lake Ladoga in the Karelian SSR. The deposits were worked from 1807 to the 1930's, and produced relatively small quantities of Fe, Zn, Cu, Sn, and W from more than 40 small shafts. The workings are now flooded and inaccessible, but large dumps remain. The most comprehensive survey of the geology and mineralogy is that of Trüstedt (1907).

The ore deposits lay in two parallel horizons of carbonate rocks which form part of the Proterozoic cover to a group of Archean mantled gneiss domes (Eskola 1951). Zircons from similar gneisses in Finland have yielded U-Pb ages of 2500-2799 m.y. (Kuovo & Tilton 1966; Huhma 1976). By analogy with the Finnish areas, the remobilization of the gneisses, leading to the doming, probably occurred about 1900-1800 m.y. ago. Both the gneisses and their

cover are intruded by a large, post-kinematic epizonal pluton of rapakivi granite; similar granites in Finland have been dated to between 1570 and 1700 m.y. (Kuovo & Tilton 1966; M. Vaasjoki, pers. comm. 1977).

The lower of the two carbonate horizons is a limestone which has been metamorphosed to a cavernous diopside-garnet-amphibole-epidote skarn. The metamorphism preceded ore deposition, and may be related to the intrusion of the numerous pegmatites that cut the skarn. This horizon has been mined principally in the Old Mining Field. The main ore minerals were magnetite, chalcopyrite, sphalerite and cassiterite; these were in general mined from different parts of the horizon.

The upper horizon is a dolomite, which has largely been altered to serpentine in the ore-bearing areas. The serpentine has formed partly from pre-existing skarn minerals such as chondrodite and pyroxene, but mainly from silicification of dolomite. Serpentinization and ore deposition were apparently almost simultaneous. The serpentinites have been worked for disseminated magnetite, sphalerite, cassiterite, and scheelite in the New Mining Field and Ristaus, both of which lie stratigraphically above the Old Mining Field, and at Lupikko, about 5 km to the east. The Lupikko district is notable for its abundance of fluorite and vesuvianite, and for its beryllium mineralization (in vesuvianite and helvine).

The ore deposits are post-kinematic and geographically related to the rapakivi granites. The pre-existing cavernous skarns seem to have served as channelways for ore-bearing fluids emanating from the granites. The exact nature and temperature of the fluids have been debated, but the apparent association of serpentinization with ore deposition in the upper horizon implies temperatures below about 500°C (Eskola 1951; Saksela 1951).

The deposits are relatively rich in W, Sr, B, Be and other uncommon elements; as a result, the mineralogy is complex. The earlier studies list more than 65 minerals, and current research has identified more than 120 additional species, of which 10-20 remain to be positively identified (Nefedov 1967; Nikolskaya & Larin 1972; Saksela 1951; Nefedov, unpubl. data).

Among the species not previously reported from Pitkäranta are wickmanite – $MnSn(OH)_6$, and schoenfliesite – $MgSn(OH)_6$. Between these two end members we have found an extensive solid-solution series; such intermediate members (magnesian wickmanite/manganoan schoenfliesite) have not been described from other localities.

OCCURRENCE AND PHYSICAL CHARACTERS

Wickmanite

Wickmanite, $MnSn(OH)_6$, has been described from the Mn-Fe deposits at Långban, Sweden (Moore & Smith 1967), and from a nepheline-syenite dyke in Tvedalen, Norway (Åmli & Griffin 1972). At Pitkäranta it has been found in an altered garnet skarn from the dump of the Toivo shaft (Old Mining Field). The skarn consists of andradite, tremolite, calcite, chlorite, quartz, sphalerite, chalcocite, and small amounts of scheelite and cassiterite.

Small octahedral crystals of wickmanite, up to 1 mm on an edge, occur together with chlorite and chalcocite. The color varies from orange to greenish yellow, and less commonly from yellowish green to nearly colorless. The hardness is 3-4; cleavage was not observed. The mineral is optically isotropic, and the refractive index ranges from 1.714 to 1.780 (±0.003) within single grains. Crystals dissolve slowly in common acids. The powder pattern of the Pitkäranta wickmanite is very similar to that of the original material from Långban. Single-crystal X-ray studies show a primitive unit cell of cubic symmetry with a 7.85 ± 0.01Å. The density calculated from the X-ray data and the analysis is 3.716 g/cm^3.

Schoenfliesite

Schoenfliesite, $MgSn(OH)_6$, is the magnesium analog of wickmanite. It was originally described from the contact-metamorphic tin deposit at Brooks Mountain, Alaska (Faust & Schaller 1971); Pitkäranta is the second known locality. The original material consists of grains less than 10 μm in largest dimension, formed by late-stage hydrothermal decomposition of hulsite, $(Fe^{2+},Mg)_2(Fe^{3+},Sn)BO_5$.

At Pitkäranta, schoenfliesite has been found in lumps of chlorite-serpentine rock from the dump at shaft no. 1, Lupikko. This rock commonly contains relicts of chondrodite and diopside, as well as grains, lenses, and small veins of fluorite, calcite, dolomite, and magnetite. Spread in this matrix are small groups of prismatic crystals of cassiterite from a few mm to 7 cm long. The cassiterite is often covered with a fibrous crust of schoenfliesite, from 0.01-0.15 mm thick; the fibers are oriented normal to the surface. Many of the overgrowths are more complicated; the schoenfliesite is overgrown by a crust of calcite or fluorite, or by fluorite and then calcite. The outer crusts also consist of fibers oriented normal to the surface. Schoenfliesite was also found in rare thin veinlets; one of

these is cut by a vein of granular dolomite. The schoenfliesite fibers, in rare cases, are terminated on their outer ends by tiny cubic/octahedral crystals.

The schoenfliesite is transparent, colorless and optically isotropic with refractive index 1.667± 0.01. No cleavage was observed. The hardness is about 4; since fragments sink slowly in methylene iodide, density exceeds 3.32 g/cm³. The density calculated from X-ray and chemical data is 3.49 g/cm³. When warmed to 600°C the mineral becomes translucent and light brown. It does not melt even under a soldering iron, but dissolves slowly in concentrated HCl, HNO₃ and H₂SO₄.

The X-ray powder pattern of schoenfliesite (Table 1) is very similar to that of wickmanite. Indexing of a powder film made in Leningrad allowed deduction of a primitive cubic unit cell with *a* 7.77±0.01Å (by A. I. Komkov, VSEGEI), whereas the data in Table 1 give 7.79±0.01Å. The differences may reflect the compositional variability. These values are in agreement with that reported for synthetic material (Felten 1957; Strunz & Contag 1960; Faust & Schaller 1971).

Manganoan schoenfliesite

Manganoan schoenfliesite is used here to denote intermediate members of the wickmanite-schoenfliesite series with Mg>Mn. The mineral occurs, in the dump of the Lupikko shaft, in fragments of magnetite ore and in altered phlogopite-vesuvianite rock together with helvine, magnetite, sphalerite and calcite. It occurs in calcite as small octahedral crystals and grains, up to 3 mm on an edge, commonly intergrown

TABLE 1. X-RAY POWDER DIFFRACTION DATA FOR MANGANOAN SCHOENFLIESITE AND SCHOENFLIESITE

	Manganoan schoenfliesite, Pitkäranta, USSR [1]			Schoenfliesite Pitkäranta, USSR [1]		
hkl	d_{calc}Å	d_{obs}Å	I_{est}	d_{calc}Å	d_{obs}Å	I_{est}
111	4.493	4.495	7	4.495	4.495	6
200	3.892	3.890	10	3.893	3.898	10
220	2.752	2.754	6	2.753	2.758	6
310	2.461	2.462	2	2.462	2.465	2
311	2.347	2.344	5	2.347	2.349	4
222	2.247	2.245	3	2.247	2.250	2
321	2.080	2.078	1	2.081	2.082	1
400	1.946	1.944	3	1.946	1.944	2
331	1.786	1.786	2	1.786	1.786	2
420	1.740	1.740	5	1.741	1.741	5
422	1.589	1.589	4	1.589	1.589	3
511,333	1.498	1.497	2	1.498	1.496	2
440	1.376	1.376	1	1.376	1.375	0.5
441	1.355	1.351	0.5	1.355	–	–
433,530	1.335	1.334	0.5	1.335	–	–
531	1.316	1.315	2	1.316	1.316	2
442,600	1.297	1.297	3	1.298	1.296	2
620	1.231	1.231	3	1.231	1.230	2
533	1.187	1.188	1	1.187	–	–
622	1.173	1.173	2	1.174	1.172	1
444	1.123	1.123	1	1.124	–	–
711,551	1.090	1.090	2	1.090	–	–
640	1.079	1.080	2	1.080	–	–
642	1.040	1.040	4	1.040	–	–
731	1.013	1.013	3	1.014	–	–

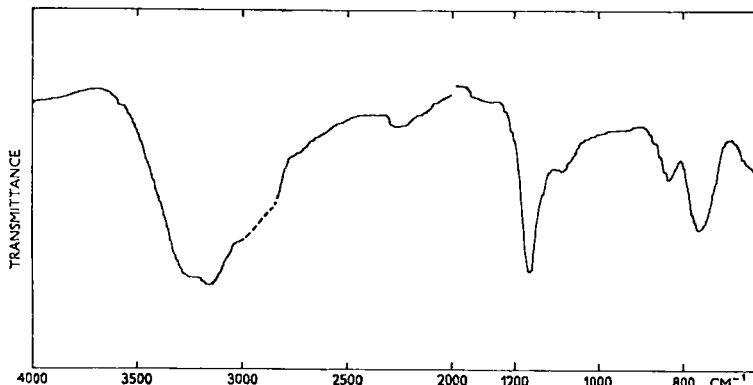[1] Debye-Scherrer camera, 9 cm diameter, Fe/Mn radiation, (λ = 1.93728 Å).

FIG. 1. Infrared spectrum of manganoan schoenfliesite; 0.05% on NaCl disc in Nujol oil; region of Nujol absorbance is stippled. Note change in scale at 2000 cm⁻¹.

with the beryllium borate, berborite (Nefedov 1967). In some samples manganoan schoenfliesite forms compact, granular aggregates, apparently pseudomorphous after cassiterite.

The crystals are yellow-orange to greenish yellow or yellow-green, and optically isotropic. The refractive index varies irregularly even within single grains, and ranges from 1.677 to 1.688. Other physical characteristics are similar to those of wickmanite and schoenfliesite; the same is true of the powder pattern (Table 1). The cell edge calculated from three powder films ranges from 7.77-7.80Å; these must be regarded as approximate values, since single grains vary widely in composition (see below). In the infrared spectrum of manganoan schoenfliesite (Fig. 1), the strong broad band in the region 3300-3000 cm^{-1} is due to the O-H stretching vibrations, and those at 1165 and 835 cm^{-1} represent the O-H bending vibrations. In general, these values are in agreement for those of synthetic $MgSn(OH)_6$ (Lorenzelli et al. 1964).

CHEMISTRY

Electron microprobe analyses were carried out using an XRL-EMX instrument housed at the Central Institute for Industrial Research, Oslo; accelerating voltage was 15 kV, sample current 0.03-0.05 μA. Data were reduced using the empirical correction factors of Albee & Ray (1970) with the following amendments:

$$\alpha^{SnO_2}_{Mg} = 1.7, \ \alpha^{MgO}_{Sn} = 1.45, \ \alpha^{H_2O}_{Sn} = 1.35$$

Standards were a mixture of natural and synthetic oxides and silicates. Ideal H_2O contents were assumed, as neither F nor Cl was detected during analysis.

The analytical data are presented in the form of averages and ranges in Table 2. The individual grains of wickmanite and manganoan schoenfliesite are compositionally heterogeneous on a scale of micrometers. The problem of precise repositioning of the microprobe beam for each set of three elements therefore led to relatively large spread in the analytical sums for the individual point analyses. In order to demonstrate the spread in compositions graphically, the three-component diagrams of Figure 3 were constructed by counting the relevant three elements simultaneously.

The wickmanite from the Toivo mine contains significant amounts of both Fe and Mg in addition to Mn (Table 2). The relative proportions of Fe, Mn and Mg vary considerably on a scale of a few micrometers whereas the content of Sn remains relatively constant. This variation does not appear to represent any consistent core-to-rim zoning, but is irregularly distributed in the analyzed crystal fragments. The only other element that has been detected by microprobe is zinc (<0.1%). The excess of (Fe+Mn+Mg) over Sn in the structural formula (Table 2) may reflect inaccurate analyses, or it may indicate that some Fe is trivalent and substituting for Sn. The analyses are probably not accurate enough to allow evaluation of Fe^{3+}/Fe^{2+} on the basis of stoichiometry. An optical spectro-

TABLE 2. MICROPROBE ANALYSES OF WICKMANITE AND SCHOENFLIESITE

| | Wickmanite | | Pitkäranta Manganoan schoenfliesite | | Schoenfliesite | | Långban Wickmanite | | Tvedalen Wickmanite | North Carolina Tetrawickmanite |
| | | | | | | | Moore & Smith (1967) | White & Nelen (1973) | Åmli & Griffin (1972) | White & Nelen (1973) |
	range	average (17 pts)	range	average (16 pts)	range	average (7 pts)				
SiO_2	–	0.0	0.1- 0.25	0.20	–	0.0	–	–	–	–
SnO_2	54.5- 56.4	55.1	55.8-58.1	56.9	57.7- 59.0	58.7	59.92	49.77	59.7	45.71
FeO	5.0- 10.7	8.5	1.2- 3.9	3.0	–	0.0	0.1	0.2	0.4	1.16
MnO	10.3- 18.8	15.3	5.2-14.4	6.9	2.0- 5.1	3.6	21.4	25.7	27.1	25.2
MgO	1.0- 3.5	2.4	5.7-13.2	10.7	13.9- 16.5	15.3	0.50	0.33	0.0	0.1
CaO	–	0.0	–	0.0	–	0.0	0.3	0.3	0.1	0.3
H_2O^*	(20.2)	20.2	(21.0)	21.0	(21.8)	21.8	(21.8)	(20.1)	20.3	(19.1)
Σ	99.0-102.2	101.5	96.3-99.4	98.5	98.6-100.6	99.4	104.02	96.4	107.6	91.57

Structural formulae on basis of (O) = 6

Si		–		0.008 } 0.979		–		–	–	–	–
Sn		0.977		0.971 }		0.966		1.025	0.919	1.029	0.889
Fe		0.316 }		0.108 }		– }		0.004 }	0.008 }	0.015 }	0.047 }
Mn		0.576 } 1.051		0.250 } 1.041		0.126 } 1.067		0.778 } 0.823	1.008 } 1.053	0.992 } 1.012	1.041 } 1.111
Mg		0.159 }		0.683 }		0.941 }		0.032 }	0.022 }	0.000 }	0.007 }
Ca		–		–		–		0.014 }	0.015 }	0.005 }	0.016 }
OH		5.990		5.999		6.002		6.245	6.216	5.860	6.221

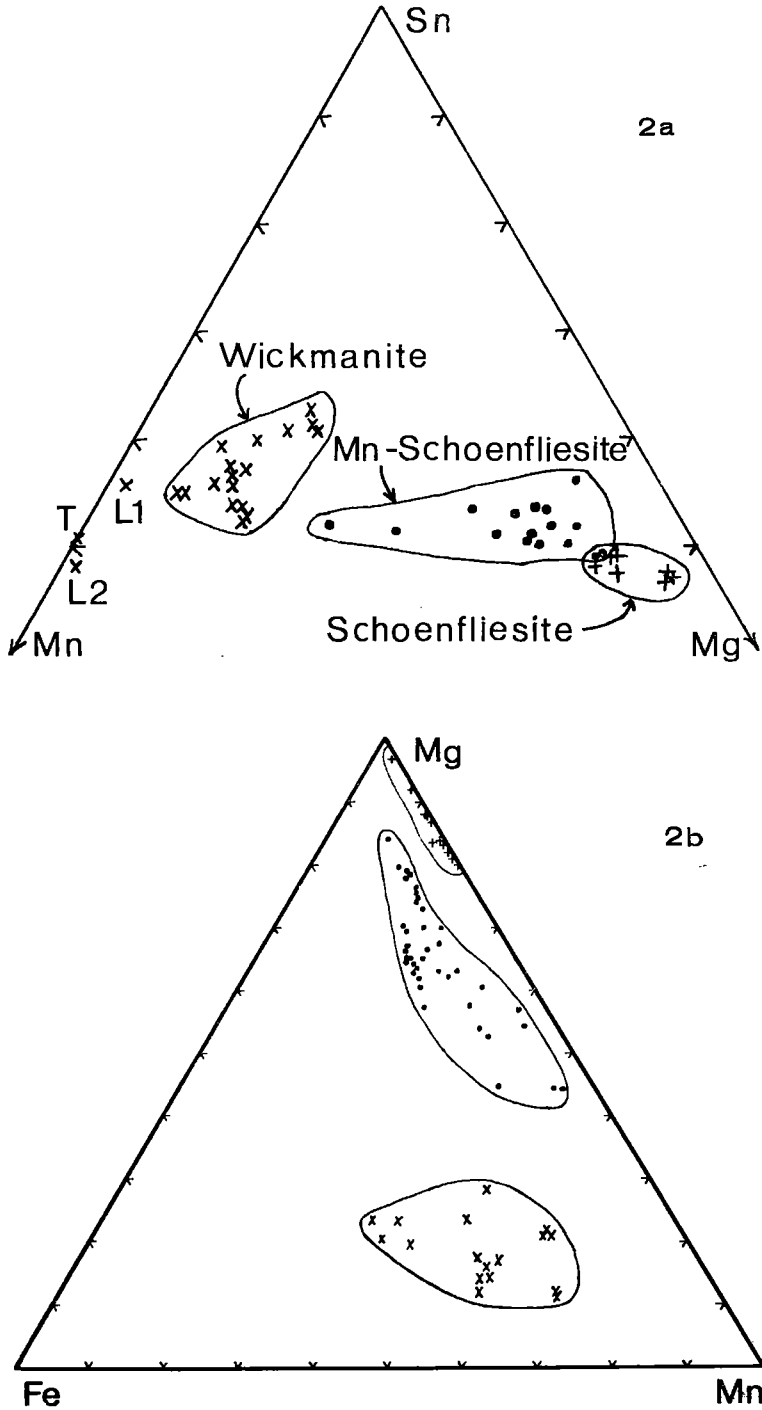* H_2O necessary to convert oxides to hydroxides.

FIG. 2. Chemical variations in the wickmanite-schoenfliesite series, plotted in atomic %. Wickmanite analyses: L1, Moore & Smith 1967; L2, White & Nelen 1973; T, Åmli & Griffin 1972. Others, this work.
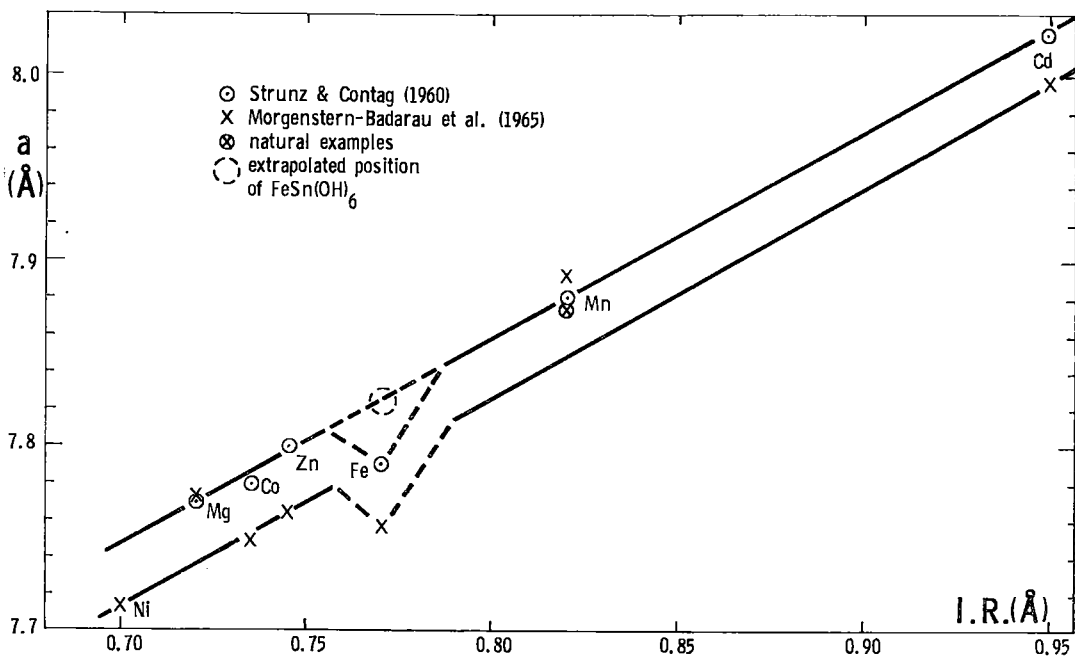a. Sn-Mn-Mg variation.
b. Fe-Mn-Mg variation.

FIG. 3. Relation between ionic radius (I.R.) and a for cubic $XSn(OH)_6$. Ionic radii are Shannon & Prewitt (1969) "IR" radii.

scopic analysis of the Toivo wickmanite showed both Zn and Ca to be present, though in amounts of <0.1%.

Previously analyzed wickmanites (Moore & Smith 1967; Åmli & Griffin 1972; White & Nelen 1973) contain Fe and Mg ranging from 0.1-1.16% FeO and 0.0-0.05% MgO. The Pitkäranta wickmanites, in contrast, show extensive solid solution towards both schoenfliesite and an iron end member.

The analyzed schoenfliesites show a much more restricted compositional range, and a notable lack of iron. The individual grains are too small to allow evaluation of their homogeneity; the observed heterogeneities are from grain to grain. The excess of (Mn+Mg) over Sn in the structural formula may be due to analytical error. However, the more Mn-rich members are more nearly stoichiometric (Fig. 2), and this may suggest that some of the excess in divalent cations is real. Faust & Schaller (1971) were unable to completely analyze the type schoenfliesite, but noted that microprobe checks showed very little Fe.

Manganoan schoenfliesite from Lupikko shows a very large variation in Mn/Mg ratio, and a relatively low and constant Fe content (Fig. 2). These variations, like those in the wickmanites, occur on a scale of micrometers. The

microprobe analyses again show an excess of (Fe+Mn+Mg) over Sn; even if all Fe were trivalent ($Fe^{2+}Sn^{4+} \rightleftharpoons Fe^{3+}Fe^{3+}$) this excess would still exist. A microchemical analysis (by I. A. Stolyarova) on material with an average $n=$ 1.678 gave MgO=10.75%, MnO=6.80%, FeO= 3.4%, ZnO=0.07%, in good agreement with the average of the microprobe analyses. The agreement suggests that the excess of (Fe+Mn+Mg) over Sn in our analyses represents a real non-stoichiometry. The same feature is observed in the analyses of wickmanite and tetrawickmanite given by White & Nelen (1973).

DISCUSSION

Crystal chemistry. A series of hexahydroxyostannates was synthesized by Strunz & Contag (1960), who assigned them to the space group $Pn3m$. Faust & Schaller (1971), citing the work of Morgenstern-Badarau et al. (1965), on MnSn(OH)$_6$, assigned the entire series of isometric hexahydroxyostannates to the space group $Pn3$.

The data of Strunz & Contag (1960) show a linear relationship between a and the ionic radius (in 6-coordination) of the divalent cations (Fig. 3). The Långban wickmanite (Moore & Smith 1967) and the Pitkäranta schoenfliesite plot on this curve, whereas Faust & Schaller's

(1971) synthetic $MgSn(OH)_6$ plots slightly below it. The data of Morgenstern-Badarau *et al.* (1965) for the Ni, Co, Zn and Cd hexahydroxyostannates define a parallel line 0.15-0.20Å below the first, but their data for $MgSn(OH)_6$ and $MnSn(OH)_6$ agree with those of Strunz & Contag (1960). This agreement, and the coincidence between the natural minerals and Strunz & Contag's data, lead us to prefer the upper line in Figure 3.

The one notable deviation from the a – ionic radius correlation is for $FeSn(OH)_6$; this is seen in both sets of experimental data. The anomalously small cell edge suggests to us that at least part of the iron in the synthesized material is trivalent; Fe^{3+} in 6-coordination would have an ionic radius of 0.55 (Shannon & Prewitt 1969). $FeSn(OH)_6$ has not been described as a mineral. However, Grubb & Hannaford (1966) have ascribed the dark color and magnetic properties of a cassiterite from Penepak Kauan, Malaya, to submicroscopic inclusions of $FeSn(OH)_6$. Their electron-diffraction study of the cassiterite yielded four lines that could be assigned to $FeSn(OH)_6$; three of these give a poorly-defined a of 7.7Å.

Figure 4 shows a as a function of relative concentrations of Mn, Mg and Fe^{2+}, assuming a of $Fe^{2+}Sn(OH)_6$ is 7.825 as predicted from Figure 3. The position of the Pitkäranta wickmanites in this diagram indicates that they should show a range in a from about 7.83 to 7.86; the average should be around 7.85, as was found by our single-crystal studies. We conclude that most, if not all, of the Fe in the Pitkäranta wickmanites is present as Fe^{2+}. The previously reported a values for $FeSn(OH)_6$ are in error, probably due to the presence of Fe^{3+}, and the correct value is about 7.83+0.01Å.

Figure 4 predicts that the manganoan schoenfliesites should have a ranging from 7.78 to 7.83, with an average of 7.81. In fact, our indexing of the powder patterns gave somewhat lower values. In view of the large variation in composition within single grains and from grain to grain, it is difficult to lay much weight on this small discrepancy. Substitution of Fe^{3+} for Sn could reduce a, but data on the refractive index (below) suggest that the content of Fe^{3+} must be small.

Refractive indices. The refractive index of Pitkäranta schoenfliesite is much greater than the apparent index of the synthetic material, but closer to that calculated from the Gladstone – Dale relation (Table 3). The small amounts of Mn may have influenced the refractive index.

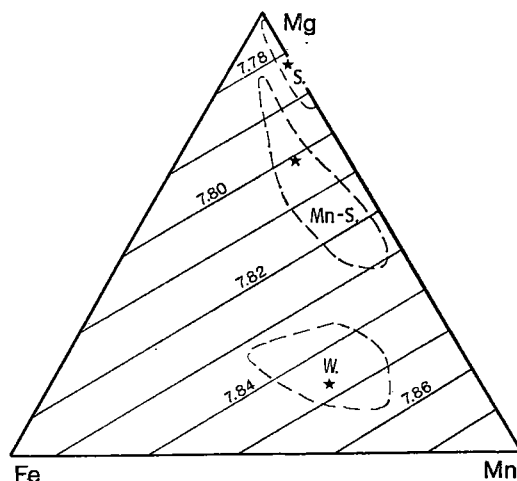The manganoan schoenfliesite shows a large range in n, paralleling a similar variation in Mn/

FIG. 4. Predicted variation of a with composition for $(Fe,Mn,Mg)Sn(OH)_6$, assuming a for $FeSn(OH)_6$ to be given by Figure 3. Outlined fields show compositional ranges (from Fig. 2b) and average compositions (*) for Pitkäranta minerals.

TABLE 3. DATA ON n, a_0 AND ρ_{calc} FOR ISOMETRIC $XSn(OH)_6$

$MgSn(OH)_6$	n	a_o	ρ_{calc}	reference
synthetic	–	7.78	–	Felten (1957)
"	–	7.79	–	Strunz & Contag (1960)
"	"1.590"	7.759	3.483	Faust & Schaller (1971)
calculated	1.685	–	–	"
Pitkäranta	1.667	7.78	3.49 (av.)	This work
$(Mg,Mn)Sn(OH)_6$				
Pitkäranta	1.677	7.77	3.534	This work
	1.688	7.80	3.575 (av.3.56)	
$MnSn(OH)_6$				
synthetic	–	7.88	–	Strunz & Contag (1960)
calculated	1.705	–	–	Moore & Smith (1967)
Långban	1.705	7.873	3.75 (meas. 3.65)	(corr. by White & Nelen (1973))
Långban	–	–	3.76	White & Nelen (1973)
Tvedalen	1.698	7.88	3.76	Åmli & Griffin (1972)
$(Mn,Fe,Mg)Sn(OH)_6$				
Pitkäranta	1.714	7.85	3.72	This work
	1.780		(av.)	
$FeSn(OH)_6$				
synthetic	–	7.79	3.89	Strunz & Contag (1960)
extrapolated	–	7.825	3.83	This work
Malaya	–	~7.7?	–	Grubb & Hannaford (1966)

Mg. If a linear relation between Mn/Mg and n is assumed, the extreme measured values of 1.677 and 1.688 correspond to Mn/Mg+Mn=0.24 and Mn/Mg+Mn=0.62, in close agreement with the range in the microprobe analyses (0.14-0.60). This may be regarded as evidence that most of the Fe is present as Fe^{2+}, since small amounts of Fe^{3+} would greatly increase the refractive index.

The refractive indices of the Pitkäranta wickmanites are much higher than those of the "purer" natural phases reported earlier (Table 3), and show a very large variation even within single grains. The small scale of this variation has made it impossible to identify its cause. Four grains which appeared to have n from <1.754 to >1.760 were mounted separately and analyzed by counting several points on each. However, no systematic variation of n with major-element composition could be seen. The explanation may lie in small variations in Fe^{3+}/Fe^{2+}, or in the concentration of a minor element such as Zn, on a scale of micrometers within each grain.

Genesis. Wickmanite and manganoan schoenfliesite crystallized during very late stages in the formation of a hydrothermal ore deposit. In this respect they resemble the Långban wickmanite (Moore & Smith 1967). The Tvedalen wickmanite, on the other hand, formed during the late hydrothermal alteration of a nepheline-syenite pegmatite dyke in the larvikite of the Oslo region (Åmli & Griffin 1972).

These phases would thus seem to have in common a low-temperature hydrothermal origin. The manganoan schoenfliesite from Lupikko is commonly intergrown with crystals of berborite which contain primary aqueous fluid inclusions. These inclusions have homogenization temperatures of <260°C (Nefedov 1967). Even allowing for a large pressure correction, it seems unlikely that the berborite – manganoan schoenfliesite intergrowths crystallized above about 350°C. A similar temperature might be inferred for the crystallization of wickmanite; the compositional differences between the two minerals probably reflect local differences in the composition of the ore-forming fluids.

The crystallization of schoenfliesite at Lupikko seems to represent late-stage reaction between serpentine and cassiterite in the presence of a volatile phase rich in H_2O, F and Be, but poor in Fe and Mn. Faust & Schaller (1971) found a stability field for synthetic $MgSn(OH)_6$ between 250-300°C. A similar temperature range is reasonable at Lupikko. The initial formation of serpentine by silica metasomatism of dolomite must have proceeded below about 500°C (Eskola 1951), and the formation of the late dolomite

veinlets cutting the schoenfliesite also implies low temperature.

We conclude that, under low-temperature conditions, there exists continuous isometric solid solution between $MnSn(OH)_6$ and $MgSn(OH)_6$. Although present data only demonstrate a solid solution of up to about 40% of the Fe^{2+} end member, the crystal chemistry suggests that the solid solution toward this end member should, in theory, also be continuous.

REFERENCES

ALBEE, A. L. & RAY, L. (1970): Correction factors for electron probe microanalysis of silicates, oxides, carbonates, phosphates and sulfates. *Anal. Chem.* 42, 1408-1414.

ÅMLI, R. & GRIFFIN, W. L. (1972): Three minerals new to Norway: wickmanite, leadhillite and hydrocerussite. *Norsk Geol. Tids.* 52, 193-196.

ESKOLA, P. (1951): Around Pitkäranta. *Ann. Acad. Sci. Fennicae,* ser. A27, 90 p.

FAUST, G. T. & SCHALLER, W. T. (1971): Schoenfliesite, $MgSn(OH)_6$. *Z. Krist.* 134, 116-141.

FELTEN, E. J. (1957): P.D.F. card, 9-27.

GRUBB, P. L. C. & HANNAFORD, P. (1966): Magnetism in cassiterite. *Mineralium Deposita* 2, 148-171.

HUHMA, A. (1976): New aspects to the geology of the Outokumpu region. *Bull. Geol. Soc. Finland* 48, 5-24.

KUOVO, O. & TILTON, G. R. (1966): Mineral ages from the Finnish Precambrian. *J. Geol.* 74, 421-442.

LORENZELLI, M. V., DUPUIS, TH. & LECOMPTE, J. (1964): Détermination de la structure des hexahydroxystannates, à l'état cristallin, par spectrométric d'absorption infrarouge (2-150 μ). *C. R. Acad. Sci. Paris* 259, 1057-1062.

MOORE, P. B. & SMITH, J. V. (1967): $Mn^{+2}(Sn^{+4}(OH)_6)$, a new mineral from Långban. *Ark. Mineral. Geol.* 4, 395-399.

MORGENSTERN-BADARAU, I., BILLIET, Y., POIX, P. & MICHEL, A. (1965): Sur de nouveaux hydroxydes mixtes $Mn^{II}Sn^{IV}(OH)_6$ et les composés isotypes $AB(OH)_6$. *C. R. Acad. Sci. Paris* 260, 3668-3669.

NEFEDOV, E. I. (1967): Berborite, a new mineral. *Dokl. Acad. Sci. USSR, Earth Sci.* 174, 114-117.

NIKOLSKAYA, ZH. D. & LARIN, A. M. (1972): Greisen formation of the Pitkäranta ore field. *Zap. Vses. Mineral. Obshch.* 101, 290-297 (in Russ.). *Chem. Abstr.* 78, 126839 j, 1973.

SAKSELA, M. (1951): Zur Mineralogie und Entstehung der Pitkäranta-erze. *Bull. Comm. Géol. Finlande* **154**, 181-231.

SHANNON, R. D. & PREWITT, C. T. (1969): Effective crystal radii in oxides and fluorides. *Acta Cryst.* **B25**, 925-946.

STRUNZ, H. & CONTAG, B. (1960): Hexahydroxostannate Fe, Mn, Co, Mg, Ca($Sn(OH)_6$) und deren Kristallstruktur. *Acta Cryst.* **13**, 601-603.

TRÜSTEDT, O. (1907): Die Erzlagerstätten von Pitkäranta am Ladoga-See. *Bull. Comm. Géol. Finlande* **19**, 333 p.

WHITE, J. S. & NELEN, J. A. (1973): Tetrawickmanite, tetragonal $MnSn(OH)_6$, a new mineral from North Carolina, and the stottite group. *Mineral. Record* **4**, 24-29.