YEATMANITE AND MAGNUSSONITE FROM THE GARPENBERG NORRA MINE, BERGSLAGEN ORE PROVINCE, SWEDEN

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Abstract

Yeatmanite, $Mn^{2+}_9Zn_6Sb^{5+}_2Si_4O_{28}$, and magnussonite, $Mn^{2+}_{10}As^{3+}_6O_{18}(OH,Cl)_2$, occur with major willemite, zincite, rhodochrosite, alleghanyite and iron-free sphalerite, and minor barite, gahnite, franklinite and silver in granular Mn–Zn skarn in the ore zone of the stratabound Pb–Zn–Ag–Cu deposit at Garpenberg Norra, Sweden. Electron-microprobe analyses of yeatmanite reveal local variations in the Mn:Zn ratio, from 3.3:6.7 to 3.6:6.4. A surplus of tetrahedrally coordinated Zn over Mn is documented, as well as alteration of an unknown phase along the rim. Magnussonite shows a sum of 9 Me^{2+} to 6 arsenic atoms and an intermediate Cl content of 0.6–0.7 atoms per formula unit proxying for OH. On a limited scale, a remarkable mineralogical similarity exists between the Garpenberg Norra sulfide deposit and the famous Sterling Hill and Franklin Fe–Mn–Zn oxide deposits in New Jersey.

Keywords: yeatmanite, magnussonite, ore mineralogy, electron-microprobe analysis, Garpenberg, Sweden.

Sommaire

La yeatmanite, $Mn^{2+}gZn_6Sb^{5+}_2Si_4O_{28}$, et la magnussonite, $Mn^{2+}_{10}As^{3+}_6O_{18}(OH,Cl)_2$, sont présentes dans un skarn granulaire Mn–Zn à willemite, zincite, rhodochrosite, alléghanyite et sphalérite dépourvue de fer, avec comme minéraux accessoires barite, gahnite, franklinite et argent; l'échantillon provient de la zone minéralisée du gisement de Pb–Zn–Ag–Cu, conforme à la stratification, à Garpenberg Norra, Suède. Les analyse de la yeatmanite à la microsonde électronique révèlent des variations locales du rapport Mn:Zn, allant de 3.3:6.7 à 3.6:6.4. Un surplus de Zn à coordinence quatre par rapport au Mn est indiqué, de même qu'un liseré d'altération formant un minéral méconnu en bordure des grains. La magnussonite fait preuve d'une somme de 9 Me^{2+} par rapport à six atomes d'arsenic, et une teneur intermédiaire en Cl (0.6–0.7 atomes par unité formulaire) en remplacement du OH. Sur une échelle réduite, une ressemblance minéralogique remarquable est à signaler entre le gisement de sulfures de Garpenberg Norra et les gisements bien connus de Sterling Hill et Franklin, dans le New Jersey, où le minerai est plutôt un assemblage d'oxydes de Fe–Mn–Zn.

(Traduit par la Rédaction)

Mots-clés: yeatmanite, magnussonite, minéralogie du minerai, analyses à la microsonde électronique, Garpenberg, Suède.

INTRODUCTION

Yeatmanite, a rare zinc – manganese – antimony silicate known from the Franklin and Sterling Hill deposits, New Jersey, U.S.A., coexists there with arsenates and antimonates in willemite – franklinite – zincite ore (Dunn 1995). Magnussonite, a manganese arsenite first found at Långban in Sweden (Gabrielsson 1956), was later identified at Sterling Hill. A compositionally closely related phase is also known from the Brattfors mine, Nordmark, Sweden (Dunn & Ramik 1984). These phases are here described from the Garpenberg Norra mine in Dalarna County, Sweden. The Bergslagen mining district in south-central Sweden consists of metamorphosed Paleoproterozoic (1.8– 1.9 Ga) felsic metavolcanic and metasedimentary rocks belonging to the Svecofennian Domain of the Baltic Shield (Allen *et al.* 1996). In the Garpenberg area, the orebodies are confined to hydrothermally altered volcanic rocks of rhyolitic to dacitic composition and marble surrounded by early orogenic granitic rocks. Two mines are currently being operated by the Boliden Mineral Company, the Garpenberg Odalfält mine and the Garpenberg Norra mine (lat. 60°20'N, long. 16°14'E);

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the latter carries the mineral association of interest here (Fig. 1). In the stratabound deposit of Zn–Pb–Ag–(Cu) ore, the sulfides are concentrated in four bodies occurring in dolomitic marble, magnesian skarns, and silicarich altered volcanic rocks (Sandecki 1983). Late veins carrying barite, apophyllite, calcite and laumontite occur within the calc-silicate skarns, as well as pods of fluorite and anhydrite, indicating an episode of late-stage (postmetamorphic) hydrothermal activity. Manganese sulfides are locally common in dolomite as ferrous alabandite coexisting with pyrite and as rambergite (hexagonal MnS) in drusy tremolite skarn.

Zetterqvist & Christoffersson (1996) reported on the occurrence of Mn-bearing skarn rocks within the ore zone. Especially in the deeper parts of the mine, between the 865 and 980 m levels, such mineralization consists of pods of rhodonite, tephroite, willemite, manganoan clinopyroxene, and Mn-bearing calcite (Holtstam 2002). Within these pods of skarn, assemblages of several minerals typical of Långban and Franklin ores have been identified (e.g., native lead, manganosite, and lead silicates). A total of about 80 mineral species have been identified from the Garpenberg Norra deposit (Nysten, unpubl. data). Hydrothermal deposition of high concentrations of Mn, Sb, As and Ba on, or just below, the seafloor in a back-arc environment in carbonate beds associated with felsic volcaniclastic rocks has recently been suggested for Sjögruvan in Bergslagen by Holtstam & Mansfeld (2001). A similar setting may be applicable to Garpenberg, with subsequent prograde metamorphism up to amphibolite-facies conditions producing the skarn assemblages found today. Peak conditions of metamorphism at Garpenberg are estimated to be $T \approx 550^{\circ}$ C and P < 3.5 kbar (Vivallo 1984). These conditions are consistent with temperature estimates obtained on co-existing spinels in this study (see below). At the border between sulfide ore and dolomite, lenses consisting of Zn-Mn-rich silicates and Mn carbonate host rare Sb-As phases formed during peak to retrograde conditions.

MINERAL PHASES

Yeatmanite

Yeatmanite, $Mn^{2+9}Zn_6 Sb^{5+2}Si_4O_{28}$, was described as a new mineral from Franklin by Palache *et al.* (1938). Dunn & Leavens (1980) gave additional information concerning optical, chemical, paragenetic and XRD data. The crystal structure was studied by Moore (1966), Moore *et al.* (1976) and Kato (1986), who pointed out a relationship between katoptrite and yeatmanite. The mineral can be regarded as a 2:1 layer silicate with one sheet of octahedra containing (5Mn + 2Sb) surrounded by layers of tetrahedra consisting of Zn₃Mn₂Si₂.

Magnussonite

Magnussonite was originally found in the Hindenburg ore at Långban in 1919 and recognized by Flink (1920) as an unknown mineral. It was described much later by Gabrielsson (1956), who suggested the formula (Mn²⁺,Mg,Cu)₅(OH,Cl)(AsO₃)₃. A second find made at Sterling Hill in 1934 provided material analyzed by L.H. Bauer, but it was identified as magnussonite by Frondel (1961), partly based on Bauer's data. Moore (1970) and Moore & Araki (1979) determined the crystal structure (cubic, space group Ia3d), and Dunn & Ramik (1984) gave new chemical data and changed the formula to $Mn^{2+}10As^{3+}6O_{18}(OH,Cl)_2$. Hålenius & Lindqvist (1996) investigated the optical character of both natural and synthetic material; they showed that the green color is due to Fe²⁺, and that the symmetry of natural magnussonite may be lower than cubic, on the basis of very weak birefrigence and distinct pleochroism.

METHODS OF INVESTIGATION

Polished rock sections were studied under the polarizing microscope, and both powder and single-crystal X-ray diffraction was used as an aid in mineral identification (Philips PW 1710 X-ray powder diffractometer, CuKα and Nonius κ-CCD single-crystal diffractometer equipped with CCD area detector, $MoK\alpha$ radiation). Electron-microprobe analyses were performed mainly on the Sb- and As-bearing phases and, to some extent, on associated minerals with a Cameca SX 50 instrument (20 kV, 20 nA, beam size 1-2 µm). The following standards, emission lines, and counting times were employed: MgO (MgK α) 60 s, wollastonite (CaK α) 10 s, MnTiO₃ (MnK α) 20 s, hematite (FeK α) 30 s, Cu metal $(CuK\alpha)$ 30 s, sphalerite $(ZnK\alpha)$ 30 s, GaAs $(AsK\alpha)$ 60 s, LiF (FK α) 40 s, vanadinite ClK α) 30 s, stibute (SbL α) 30 s. Data reduction was made using a Cameca version of the PAP routine (Pouchou & Pichoir 1991).

COMPOSITION OF THE MINERALS

Equigranular pale pink rhodochrosite and pale yellowish to greenish willemite, with grain sizes up to 2 mm, constitute the main minerals of the specimen investigated, collected at the 900 m level in the mine. Dark brown angular to rounded crystals of yeatmanite are found as an impregnation within these minerals. Individual crystals may reach 1 mm, but are mostly smaller. To the author's knowledge, this is the third occurrence of this rare mineral after Sterling Hill and Franklin. A weak banding can be discerned in the skarn rock, with dark reddish brown alleghanyite in contact with grey tephroite on one side, and with pink rhodochrosite and pale green willemite on the other. The alleghanyite was



FIG. 1. Geological map of the Bergslagen ore district, showing the location of the Garpenberg Norra deposit (modified after Ripa 2001).

identified by both powder and single-crystal X-ray diffraction; the single-crystal unit-cell parameters, *a* 8.10, *b* 4.82, *c* 10.89 Å (all ±0.01), β 108.7°, suggest that it is a magnesian variety; no chemical analyses were done, however. Sphalerite, totally devoid of Fe within the limits of detection, is also dispersed throughout the matrix. Light orange-red, manganiferous zincite is present in one part, as submillimetric anhedral crystals together with yeatmanite in a podlike concentration. Magnussonite is rare, but occurs nearby, although not in direct contact with yeatmanite, as grass-green to bluish green, and rarely, red-brown anhedral grains in the willemite matrix. Additional phases are silver, barite, franklinite, and gahnite (Fig. 2A).

Yeatmanite

The internal parts of two crystals have been analyzed. A complex dark alteration rim of an unknown phase is variably developed, as seen from back-scattered electron (BSE) images (Figs. 2B, C). The average composition of 10 points taken within crystal A and B, respectively, is given in Table 1; an empirical formula obtained from crystal A may be given as: $[(Mn_{4.59}Mg_{0.41})_{\Sigma5}Sb_{2.02}]$ [Zn₆(Mn_{3.25}Zn_{0.71})_{Σ 3.96](Si_{3.95} Fe³⁺_{0.09})_{Σ 4.04O₂₈.}}

TABLE 1. COMPOSITION OF YEATMANITE, MAGNUSSONITE, AND AN UNKNOWN ALTERATION-INDUCED PHASE, GARPENBERG NORRA MINE, SWEDEN

Sample	yeatmanite A		yeatmanite B		magnussonite		alt. phase
	<i>n</i> = 10	[σ]	<i>n</i> = 10	[σ]	<i>n</i> = 6	[σ]	n=2
SiO ₂ wt.%	13.99	[0.12]	13.81	[0.14]	n.d.		10.88
Sb ₂ O ₅	19.22	[0.12]	19.44	[0.19]	n.d.		21.79
As ₂ O ₃	n.d.		n.d.		46.75	[0.66]	1.79
CuO	n.d.		n.d.		1.14	[0.26]	n.d.
MnO	32.72	[0.23]	34.17	[0.19]	46.37	[0.85]	26.92
ZnO	32.13	[0.25]	30.44	[0.23]	2.86	[0.70]	25.14
FeO	0.36	[0.02]	0.40	[0.02]	0.72	[0.10]	0.56
MgO	0.97	[0.04]	0.92	[0.04]	0.08	[0.03]	0.87
CaO	n. d.		n.d.		0.02	[0.01]	1.56
Cl	n.d.		n.d.		1.88	[0.08]	n.d.
H_2O (calc.)					0.94		
Total	99.39		99.18		100.76		89.51
-O = Cl					-0.41		
Total					100.35		
Si apfu	3.95		3.91		Cu ²⁺	0.18	
Sb ^{5‡}	2.02		2.05		As ³⁺	6	
VIMn ²⁺	4.59		4.61		Mn ²⁺	8.30	
^{IV} Mn ²⁺	3.25		3.58				
Zn	6.71		6.37		Zn	0.45	
Fe ³⁺	0.09		0.09		Fe ²⁺	0.13	
Mg	0.41		0.39		Mg	0.03	
					CI	0.67	
					OH	1.33	
					ΣMe^{2+}	9.09	

n.d.: not detected. Alt. phase: alteration-induced phase (dark in BSE image). The electron-microprobe data are recalculated on the basis of 28 atoms of oxygen in the case of yeatmanite, and six atoms of arsenic in the case of magnussonite.







FIG. 2. A. Photomicrograph showing barite (Brt), sphalerite (Sp), magnussonite (Mag), willemite (Wil) and rhodochrosite (Rds). BSE image. B. Photomicrograph showing willemite, unaltered yeatmanite and alteration phase. The composition of the most altered part (darkest BSE) is given in Table 1. Note the patchy pattern of alteration and the fractured surface resulting from interaction with the electron beam. BSE image. C. Photomicrograph showing incipient alteration on the rim of yeatmanite. Note the radial pattern of alteration perpendicular to the rim. BSE image.

The alteration at the rim is quite heterogeneous and of unknown character. Most of the yeatmanite crystals show a slight alteration with a tendency of radial growth at the rim, whereas other grains may be severely decomposed, showing a patchy development of the alteration (Figs. 2B, C). A comparison of the unaltered part of a crystal and three altered areas with darker BSE image shows a slight decrease in Mn and Zn, a slight increase in Sb, Ca and As, whereas Si is almost constant. The low total ($\approx 90 \text{ wt\%}$) for this alteration-induced phase is certainly due to a high content of volatile elements (H₂O?), because the mineral is very sensitive to the electron beam, leaving a heavily fractured surface at the analyzed spot. The average result of two analyses of the most altered part (with the darkest BSE) of a yeatmanite crystal is given in Table 1, and the crystal is shown in Figure 2B. In polished section, the unknown phase has lower reflectance than yeatmanite and partly shows brown internal reflections. Anisotropy is weak or absent. In the author's opinion, this must be a new mineral species.

Yeatmanite coexists with manganiferous willemite $[(Zn_{1.81}Mn_{0.145}Mg_{0.05})_{\Sigma 2.01}SiO_4]$ showing a strong green response to shortwave ultraviolet radiation, zincite [Zn_{0.99}Mn_{0.01}O] and rhodochrosite [(Mn_{1.66}Ca_{0.17} $Mg_{0,17}\Sigma_2(CO_3)_2$]. Anhedral crystals of sphalerite with a comparably high reflectance and white internal reflections are also a common constituent of this assemblage; the ZnS is pure, without any detectable Fe or Mn. The detection limit for these elements is estimated to 0.03– 0.05 wt%. Colorless secondary sphalerite of this type filling cracks in Mn-skarn has been noted elsewhere in the ore (Nysten, unpubl. data). Zoned subhedral crystals of gahnite $[(Zn_{0.99-1.04}Mn_{0.01-0.05})(Al_{1.86-1.82})$ $Fe_{0,10-0,19}O_4$, with a slight depletion of Mn and Fe^{3+} in the core, and euhedral franklinite $[(Zn_{0.80}Mn_{0.19})]$ $Mg_{0.01}$ $\Sigma_{1.00}$ (Fe³⁺ $_{1.73}$ Al $_{0.16}$ Mn³⁺ $_{0.05}$ Mn²⁺ $_{0.03}$ Ti $_{0.03}$ $\Sigma_{2.00}$ O₄] up to 0.3 mm in size also occur dispersed in willemite. Mostly, these spinel phases occur in approximately equal amounts without having mutual grainboundaries, although a few very small grains that are in contact have been encountered. Tiny inclusions of zincite(?) also are found within gannite. The fine-grained exsolution texture between franklinite and gahnite reported by Carvalho & Sclar (1983) from Sterling Hill has not been observed at Garpenberg. Given the above compositions of gahnite and franklinite from Garpenberg, and assuming equilibrium conditions, the gahnite component in franklinite gives a temperature of 550°C and the franklinite components in gahnite give 530 to 640°C for core and rim compositions, respectively, on the basis of the thermometer determined by Carvalho & Sclar (1983) for the $ZnFe_2O_4 - ZnAl_2O_4$ binary system. Their calibration curve seems to be more reliable for franklinite-rich compositions. The effect of Mn and Ti present in spinel from Garpenberg is not known, however.

Powder X-ray diffraction (XRD) was attempted in order to determine the cell dimension of yeatmanite, but

the small grain-size made separation difficult, and a sufficiently clean sample could not be obtained. The strongest peaks of yeatmanite were identified, and they are reasonably well separated from interfering peaks due to willemite and rhodochrosite. The low symmetry of yeatmanite, however, precluded a reliable dataset to be obtained for calculation of accurate unit-cell data. Furthermore, the alteration phase contributes peaks, adding to the ambiguity.

Magnussonite

The composition of a few crystals has been determined, and a representative dataset is given in Table 1. Normalizing to six atoms of As gives an anomalously low total for the divalent cations compared to the currently accepted formula. The chlorine content is also rather high compared to previously published data (Dunn & Ramik 1984, Hålenius & Lindqvist 1996). The composition may be given as: $(Mn_{8.30}Zn_{0.45}Cu_{0.18}Fe_{0.13}Mg_{0.03})_{\Sigma9.09}As^{3+}_{6}O_{17.09}(OH_{1.33}Cl_{0.67})_{\Sigma2.00}$.

Single-crystal determinations of the unit-cell parameter of magnussonite range between 19.72 ± 0.03 Å (bluish green grains) and $19.67-19.69 \pm 0.03$ Å (red-brown grains), values that are close to that given by Moore & Araki (1979), 19.680(4) Å. No evidence for a deviation from cubic symmetry was present. Note that analytical data for the red-brown magnussonite are lacking.

DISCUSSION

The ratio between Mn and Zn in yeatmanite from the type locality is known to vary only slightly from sample to sample (Dunn & Leavens 1980). At Garpenberg, a variation in Mn:Zn was found even among adjacent crystals in the same sample. At this locality, the proportion of tetrahedrally coordinated elements varies from Mn:Zn = 3.3:6.7 in crystal A to 3.6:6.4 in crystal B. Kato (1986) determined the structure based on a sample with Mn:Zn = 4:6 (#06290 analyzed by Dunn & Leavens 1980). He also proposed full order between tetrahedral Mn and Zn for this sample. For crystals #9371 and 22621 (Dunn & Leavens 1980), the Mn:Zn ratio is 3:7, however. The distribution of the additional zinc atom over the Mn sites in these samples was also discussed by Kato, who left the question of order open. The composition of crystal A from Garpenberg approaches this ratio.

Dunn & Ramik (1984) gave data for magnussonite from both Långban and Sterling Hill. They showed a marked difference in chlorine content (0.3 Cl per formula unit for Långban and 0.7 Cl *pfu* for Sterling Hill). Material from Garpenberg shows the same level of Cl as that from Sterling Hill, but the As content is much higher, and the sum of divalent cations is 9, not 10. The reason for these variations is not fully understood. A LIF wavelength-diffracting crystal was used in the analysis to avoid possible overlap between AsK β and MnK α lines. The crystal-structure model of Moore & Araki (1979) with Mn⁺ (sic!) and a high residual (*R* =11.2%), together with the fact that natural magnussonite may be optically weakly anisotropic (non-cubic?) (Hålenius & Lindqvist 1996), suggest that the true stoichiometry may be more complex than anticipated.

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