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Manganese ferro-ferri-winchite from Harstigen, Filipstad, central Sweden

THE small, abandoned Fe–Mn mine at Harstigen (Lat. 59°47′, Long. 14°19′), Filipstad district, is the host of more than 100 different mineral species. The ore, which is of early Proterozoic age, consists of magnetite, hematite, and hausmannite in a dolomitic host rock which is surrounded by potassic meta-rhyolites. The ore may be classified as Långban-type. In this note we report on an unusually manganese-rich ferro-ferri-winchite which has been found on the mine dumps. Other Mn-rich amphiboles are known from Harstigen and Långban under the name richterite, and have been studied by Sundius (1945) and by Holtstam (1992). These may, however, easily be distinguished from the present sample by their colour, high Mg-content and also by the associated minerals.

The winchite phase occurs fairly abundantly in a restricted association, consisting of a dark green clinopyroxene intergrown with fine-grained hematite and yellowish-brown andradite. This matrix is cut by distinctly later veinlets of rhodonite, occurring as euhedral crystals embedded in fibrous to radiating ferro-ferri-winchite (Fig. 1), and minor baryte, galena, and calcite. The veinlets are structurally perpendicular to a foliation present in the skarn matrix. If the calcite is removed by HCl the amphibole is revealed as spherical aggregates up to 5 mm in size. It shows a distinct pleochroism in thin section, with greenish

FIG. 1. Photomicrograph showing radiating texture of manganese ferro-ferri-winchite. Parallel nicols. Scale bar – 250 µm.

yellow to dark grass-green colours. It was not possible to obtain exact optical data due to the fibrous habit of the amphibole aggregates.

Macroscopically the ferro-ferri-winchite resembles an iron-rich actinolite and it was not known to be of particular interest until one author (PN) performed a standard XRD test. The refined cell data based on 19 well resolved peaks are presented in Table 1. The powder pattern obtained strongly resembles that of arfvedsonite, a mineral normally not found in the geological environment (dolomite-hosted skarn rocks) occurring at Harstigen.

Mineral chemistry

Chemical analysis was performed by electron microprobe and the Fe^{2+}–Fe^{3+} ratio was determined by Mössbauer spectroscopy. The fine-grained fibrous habit of the sample caused some problems during the analysis resulting in low total sums. It was found that sample sections cut perpendicular to the fibres usually yielded higher total sums than sections cut parallel to the fibres. The result from the microprobe analysis, given in Table 1, represents the mean of 15 points obtained on several aggregates. Following the amphibole nomenclature (Leake, 1978) a standard formula may be written as $A_{0-1}B_2C_5T_8O_{22}(OH,F,Cl)_2$. Normalization of a structural formula to 46 negative charges resulted in almost exactly 8 Si (7.995) and a small deficiency in the $B+C$ type cations (6.87 instead of 7.00). It is not possible to adjust the number of $B+C$ and T cations to the theoretical 7:8 ratio since the sample does not contain Al which can be distributed between the tetrahedral and octahedral positions. Hence, the normalized formula can be shown as $(K_{0.16})_{\Sigma 0.16}$-$(Na_{1.10}Ca_{0.67}Mn^{2+}_{0.11})_{\Sigma 1.87}(Fe^{2+}_{2.31}Mn^{2+}_{1.36}$-$Fe^{3+}_{1.22}Mg_{0.12})_{\Sigma 5}Si_{8.00}O_{22}(OH)_2$, with the cation deficiency restricted to the B-type site. We regard this deficiency as an analytical error, and not caused by vacancies. Manganese was assumed to be divalent due to the presence of significant amounts of ferrous iron.

TABLE 1. Microprobe analysis (average of 15 points), and cellparameters of manganese ferro-ferri-winchite from Harstigen.

	wt.%		[Å]
SiO_2	50.55	a	9.943 (6)
TiO_2	n.d.	b	18.206(12)
Al_2O_3	n.d.	c	5.328 (4)
Fe_2O_3	10.22	β	103.96(7)°
FeO	17.46	V	936 (2) Å^3
MnO	10.92		
CaO	3.95		
MgO	0.50		
K_2O	0.79		
Na_2O	3.57		
Total	97.96		

n.d. = not detected.

Discussion

The amphiboles are divided into four groups based on the B group cation occupancy (Leake, 1978). Thus if $(Ca+Na)_B \geqslant 1.34$ the mineral belongs to the sodic-calcic group, which applies to the formula given above. Furthermore, if $(Na+K)_A < 0.50$ a discrimination diagram of $Mg/(Mg+Fe^{2+})$ versus Si per formula unit can be applied. This places the mineral under study well into the ferro-winchite field, although a total lack of Al and the high Mn-content point towards a ferro-ferri-winchite composition ($CaNaFe^{2+}_4$-$Fe^{3+}Si_8O_{22}(OH)_2$), where some ferrous iron is substituted by divalent manganese ($Mn^{2+}/(Fe^{2+}+Mn^{2+})$ = 0.39). The amount of Mn exceeds one atom per formula unit, hence the prefix manganese should be added (Leake, 1978), resulting in the name 'manganese ferro-ferri-winchite'. The composition of the sample can be described in terms of the hypothetical end members presented in Fig. 2, where the substitutions $Ca \rightleftharpoons 2\ Na$ and $Mn^{2+} \rightleftharpoons Fe^{2+}$ are shown.

The mineral is clearly of the sodic-calcic type, but taking into account the rather high sodium content a certain solid solution trend towards alkali amphiboles exists. Among these, arfvedsonite and kozulite are of particular interest since the former is the sodium analogue of ferro-ferri-

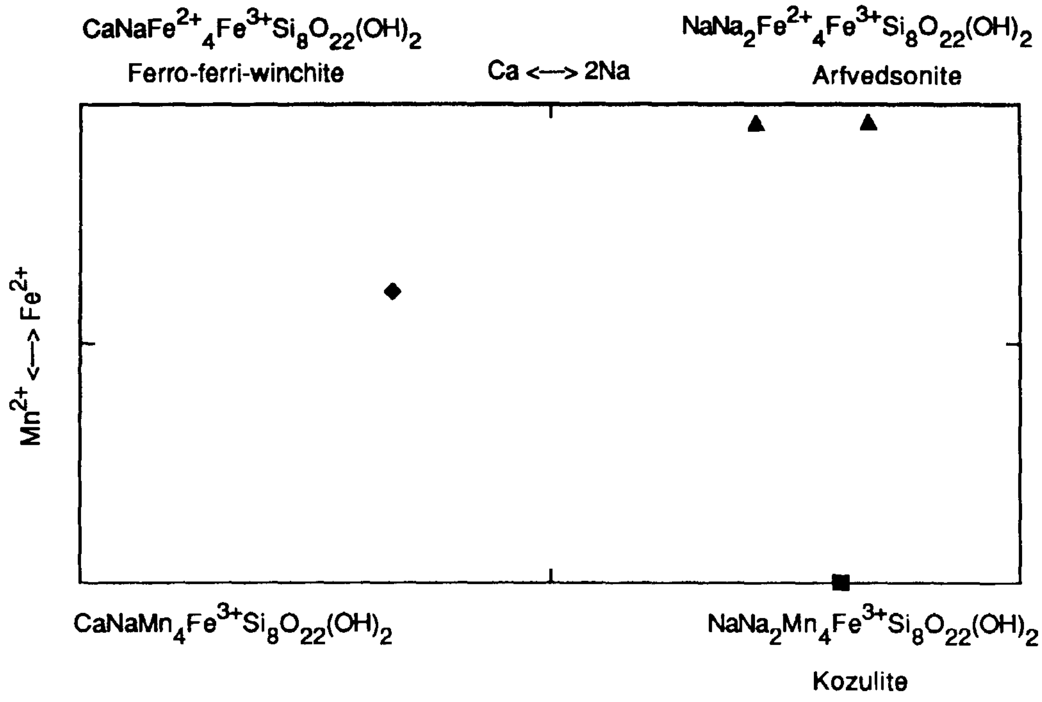

FIG. 2. Diagram showing the composition of manganese ferro-ferri-winchite from Harstigen (diamond) with respect to Ca–Na and Fe^{2+}–Mn^{2+} exchange. Kozulite (square; from Nambu *et al.*, 1970) and two arfvedsonites (triangles; from Hawthorne, 1983, samples 64 and 67) are plotted for reference.

winchite. Furthermore, a solid solution comprising Fe^{2+}–Mn^{2+} involves an unnamed component which could be called 'mangano-ferri-winchite' (lower left corner of Fig. 2), being the sodic-calcic analogue of kozulite. The latter mineral is of particular interest since it is known to coexist with Mn-silicates (e.g. rhodonite) at the Tanohata mine in Japan (Nambu *et al.*, 1969).

TABLE 2. ^{57}Fe Mössbauer parameters of manganese ferro-ferri-winchite obtained at 77 K

species	site	IS mm/s	ΔE_Q mm/s	fwhm mm/s	Int. %
Fe^{2+}	M(1)M(3)	1.27	3.13	0.35	49.8
Fe^{2+}	M(2)	1.28	2.63	0.35	15.7
Fe^{3+}		0.51	0.51	0.35	34.5

The half-widths (fwhm) were constrained to be equal. Int. = relative area.

Mn^{2+}–Fe^{2+} ordering

Since Mn and Fe occupy almost all the *C*-group positions, the sample is of potential interest with regard to the Mn^{2+}–Fe^{2+} ordering scheme in amphiboles (cf. Hawthorne, 1981). A first Mössbauer spectrum obtained at room temperature showed strong peak overlap, and a second spectrum was recorded at liquid nitrogen temperature to enhance the peak resolution. Also this spectrum shows considerable peak overlap for the Fe^{2+} doublets. However, the spectrum could be fitted satisfactorily with three doublets, assigned to $Fe^{2+}M(1)M(3)$, $Fe^{2+}M(2)$ and Fe^{3+}, as indicated in Fig. 3. A constraint used in the fitting procedure was to keep the half-widths of the different doublets equal. The resulting hyperfine parameters (Table 2) are similar to those obtained on calcic amphiboles at liquid nitrogen temperature (e.g. Skogby and Annersten, 1985). There is no indication of Fe^{2+} in the *M*(4) position.

Cation site occupancies as derived from the Mössbauer spectroscopy data and the normalized

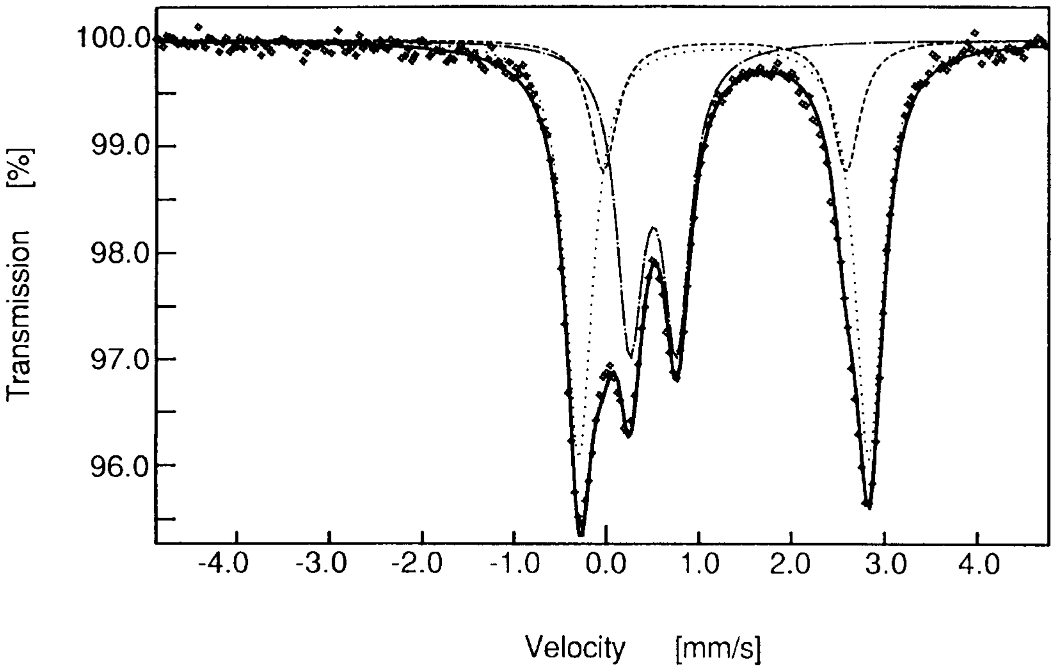

FIG. 3. Mössbauer spectrum of manganese ferro-ferri-winchite obtained at 77 K. Dotted doublet: $Fe^{2+}M(1)M(3)$; dashed doublet: $Fe^{2+}M(2)$; dashed-dotted doublet: Fe^{3+}.

structural formula are given in Table 3. All Fe^{3+} was assumed to occupy the $M(2)$ position, in accordance with XRD refinement studies on amphiboles which have shown a strong or complete ordering of Fe^{3+} in M(2) (cf. Hawthorne, 1983). The results indicate that Mn^{2+}, compared to Fe^{2+}, follows the ordering scheme $M(4) > M(1)M(3) > M(2)$. The observation that Mn^{2+} avoids the $M(2)$ site is in agreement with results obtained on tirodite (Hawthorne and Grundy, 1977) and arfvedsonite (Hawthorne, 1976).

In conclusion, this Mn-rich sodic-calcic amphibole from Harstigen shows compositional characteristics, including a large component of an hypothetic end-member, which although covered by the term 'manganese' is not specifically named in the currently accepted nomenclature.

TABLE 3. Site occupancies for manganese ferro-ferri-winchite

Site	Multiplicity	Occupancy*
Tetr.	8	1.00 Si
M(1)M(3)	3	$0.41\ Mn^{2+} + 0.59Fe^{2+}$
M(2)	2	$0.06\ Mn^{2+} + 0.28\ Fe^{2+} + 0.61Fe^{3+} + 0.06Mg$
M(4)	2	$0.05\ Mn^{2+} + 0.33Ca + 0.55Na$
A	1	0.16 K

* Occupancy numbers are based on the normalized formula and Mössbauer spectroscopy data.
The deficiency in the M(4) site ($\Sigma = 0.94$) is regarded as an analytical error.

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Hancockite from Jakobsberg, Filipstad, Sweden: the second world occurrence

HANCOCKITE, $CaPbAl_2Fe(SiO_4)_3(OH)$, the plumboan member of the epidote group is to date only reported from its type locality at Franklin, New Jersey (Penfield and Warren, 1899), where it appears in a rather restricted part of the mine, but locally in abundance, associated with andradite, franklinite, manganaxinite, willemite, barite and other minerals (Palache, 1935; Dunn, 1985). [The 'hancockite' reported by Neumann (1985) from Vestpolltind, Lofoten, Norway, does not qualify for the name as it is too low in Pb (~10% PbO).] During the examination of newly collected dump samples from the early Proterozoic Jakobsberg manganese–iron oxide deposit in the Filipstad district, Sweden (Lat. 59.83°N, Long. 14.11°E), a new hancockite-bearing paragenesis was found. The small deposit, mined mainly during the last century, consists of separate hematite and hausmannite ore bodies in association with silicate reaction skarns, enclosed by dolomitic marble. Like its more famous mineralogical counterpart, the Långban deposit (Moore, 1970), situated in the same district, is believed to result