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PYROPHANITE $MnTiO_3$ FROM STERLING HILL, NEW JERSEY

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ABSTRACT

Pyrophanite of composition $(Mn_{0.938}Fe_{0.055}Zn_{0.030})Ti_{0.980}O_3$ has been identified in the zinc- and manganese-rich ores of the Sterling Hill deposit, New Jersey. It occurs as anhedral grains up to 2 mm in length in association with gahnite, manganiferous augite, hendricksitic biotite and fluorescent Mn-calcite. Unit-cell dimensions: *a* 5.161(1), *c* 14.317(8) Å; microhardness in the range VHN_{100} 567–607; reflectance *R* (in %) 18–22 (460 nm), 16–19 (546 nm), 14–18 (600 nm). The pyrophanite is a product of high-grade metamorphism and is formed in Mn- and Ti-rich areas with lower-than-average $f(O_2)$.

Keywords: pyrophanite, gahnite, hendricksite, Sterling Hill, New Jersey.

SOMMAIRE

On a identifié la pyrophanite, de composition $(Mn_{0.938}Fe_{0.055}Zn_{0.030})Ti_{0.980}O_3$, dans le minerai zincifère et manganifère du gîte de Sterling Hill (New Jersey). Elle se présente en grains allotriomorphes, longs de 2 mm, associés à gahnite, augite manganifère, biotite hendricksitique et calcite manganifère fluorescente. Dimensions de la maille: *a* 5.161(1), *c* 14.317(8) Å; microdureté VHN_{100} 567–607; réflectance *R* (en %) 18–22 (460 nm), 16–19 (546 nm), 14–18 (600 nm). La pyrophanite résulte d'un métamorphisme intense et caractérise les régions riches en Mn et Ti et à fugacité d'oxygène anormalement basse.

(Traduit par la Rédaction)

Mots-clés: pyrophanite, gahnite, hendricksite, Sterling Hill, New Jersey.

INTRODUCTION

Pyrophanite $MnTiO_3$, the manganese analogue of ilmenite, has been observed in ore samples from the Sterling Hill mine near Franklin, New Jersey. This rare mineral had not previously been reported in the zinc- and manganese-rich Franklin–Sterling Hill ores and has only been found in a few localities in the world since its original description in the Pajsberg deposit in Sweden by Hamberg (1890). The present brief report provides additional information on its chemistry, characteristics and mode of occurrence.

MODE OF OCCURRENCE AND PHYSICAL PROPERTIES

The pyrophanite was found in samples taken from the footwall contact of the east limb of the orebody, approximately 10 m above the 500 level of the Sterling Hill mine. The samples were collected at about the 1000 N co-ordinate in October 1980. Megascopically, the samples consist of coarse-grained (1–2 cm) brown to greenish grey manganiferous augite with scattered rounded to euhedral grains of dark green gahnite and irregular patches of biotite and white calcite. The original, roughly 10-cm-diameter specimens were cut in order to prepare polished sections of gahnite as part of a study of that mineral (Sandhaus 1981). The cut and polished sections reveal that the gahnite grains are commonly sheathed by a narrow irregular rim of zincian biotite that appears to be a reaction product. The pyrophanite occurs disseminated within the pyroxene and within the white fluorescent Mn-calcite as anhedral to subhedral grains or aggregates up to 2 mm across; most grains, however, are less than 0.5 mm in their maximum dimension. Subsequent to our discovery of pyrophanite, Valentino (1983) found pyrophanite lamellae oriented on the (111) plane of magnetite that defines an exsolution texture with franklinite at Sterling Hill.

The reflectance of several grains was measured using a McCrone photometer; measurements were calibrated against pyrite, galena and magnetite that had previously been calibrated against Zeiss WTiC standard number 474253 and against a silicon standard provided by Dr. Hans Pauly of the University of Copenhagen as part of an I.M.A. Commission on Ore Microscopy test of interlaboratory accuracy. The ranges of reflectance values *R* (in %) observed at three arbitrary wavelengths are: 18–22 at 460 nm, 16–19 at 546 nm and 14–18 at 600 nm. These values are comparable to those reported by Žák (1971).

The microhardness was determined on a Tukon Microhardness Tester using a 100 g load for approximately 20 s. Vickers Hardness Numbers were found to lie in the range 567–607.

Examination of the pyrophanite under the ore microscope reveals that it is grey, and resembles ilmenite; it exhibits a weak bireflectance and a moderate anisotropism. On broken surfaces and locally within polished grains, the pyrophanite displays reddish internal reflections. The grains are

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anhedral and appear to have formed at the same time as the enclosing minerals.

An X-ray-diffraction pattern (Table 1) was generated from a 0.5- to 1-mm fragment in a Gandolfi camera. The unit-cell dimensions calculated in space group *R*3 on the basis of six of the seven lines are *a* 5.161(1), *c* 14.317(8) Å. These values compare well with those given in the ASTM file (PDF 12–435: *a* 5.137, *c* 14.29 Å). The cause of the slightly larger-than-expected cell dimensions of the Sterling Hill pyrophanite is not known.

Electron-microprobe analyses were performed on an ARL SEMQ using an operating voltage of 15 kV and a beam current of 15 nanoamperes. Four typical compositions of pyrophanite are given in Table 2 along with the composition of coexisting gahnite, pyroxene and Zn-biotite. The average composition of pyrophanite is equivalent to a formula of $(Mn_{0.938}Fe_{0.055}Zn_{0.030})(Ti_{0.980})O_3$. No evidence of compositional zoning was observed. The coexisting manganiferous pyroxene $(Ca_{0.44}Mg_{0.27}Mn_{0.15}Fe^{2+}_{0.07}Zn_{0.05}Na_{0.03}K_{0.03})(Si_{0.98}Al_{0.02})O_3$ approaches bustamite in composition; the Zn-biotite $[(K_{0.95}Na_{0.08})(Mg_{1.60}Mn_{0.39}Zn_{0.70}Fe^{2+}_{0.42}Ti_{0.13})(Si_{3.07}Al_{1.35})O_2(OH)_2]$ apparently is hendricksite. The gahnite is compositionally similar to that found in many localities (Sandhaus 1981) except for a slightly higher-than-normal manganese content (galaxite component).

It is apparent from Figure 1 that the pyrophanite from the Sterling Hill mine is similar compositionally to that from eight other localities and that naturally occurring compositions span the ilmenite–pyrophanite join.

TABLE 1. X-RAY POWDER-DIFFRACTION DATA FOR PYROPHANITE FROM THE STERLING HILL MINE

Reflection	d_{meas}	d_{calc}	Intensity
104	2.799 Å	2.794 Å	strong
110	2.576	2.581	moderate
113	2.274	2.270	weak
024	1.903	1.896	moderate
116	1.750	1.752	moderate
214	1.528	1.528	moderate
300	1.490	1.490	moderate

Cell dimensions calculated using least-squares unit-cell refinement of Appleman & Evans (1973); a 5.161(1), c 14.317(8) Å.

TABLE 2. CHEMICAL COMPOSITION* OF PYROPHANITE AND COEXISTING GAHNITE, PYROXENE AND BIOTITE FROM THE STERLING HILL MINE, NEW JERSEY

Oxide wt. %	Pyrophanite				Pyroxene		Gahnite		Zn-biotite	
TiO_2	50.7	50.5	54.3	48.1	0.2	0.2	0.1	0.1	2.0	1.9
MnO	42.8	41.7	44.4	43.9	9.4	9.3	0.6	0.7	5.3	5.3
FeO	2.7	2.7	2.4	2.4	4.3	4.0	5.9	5.5	5.7	5.9
ZnO	1.6	1.7	1.3	1.7	3.2	3.9	41.0	40.8	11.6	10.4
Al_2O_3	0.1	0.3	0.0	0.0	1.0	1.1	50.6	51.8	13.0	13.7
MgO	0.1	0.0	0.0	0.0	9.2	9.4	0.2	0.4	12.6	12.6
SiO_2	0.2	0.1	0.0	0.1	51.6	50.7	0.1	0.1	35.1	36.4
K_2O	0.0	0.0	0.0	0.2	0.1	0.1	0.0	0.0	8.8	8.5
CaO	0.1	0.1	0.3	0.2	21.3	21.3	0.0	0.0	0.0	0.0
Na_2O	0.1	0.0	0.1	0.1	0.9	0.8	1.1	1.1	0.5	0.5
Total	98.4	97.1	102.8	96.7	101.2	100.8	99.6	100.5	94.6	95.2

Cation formula-units based on 3 oxygen atoms

Ti	.979	.985	.998	.958
Mn	.931	.916	.919	.985
Fe	.059	.058	.049	.053
Zn	.030	.032	.023	.033
Al	.004	.010	.000	.001
Mg	.002	.000	.000	.000
Si	.005	.003	.001	.001
K	.001	.001	.001	.001
Ca	.003	.004	.008	.007
Na	.004	.002	.005	.007

average formula
$(Mn_{0.938}Fe_{0.055}Zn_{0.030})Ti_{0.980}O_3$

*determined by electron microprobe

ORIGIN OF THE PYROPHANITE

Pyrophanite has heretofore been reported from only a few types of geological setting: peralkaline rhyolites from Mont-Dore, France (Brousse & Maury 1976), nepheline syenite pegmatites from Baikalia, USSR (Portnov 1965) and the Oslo area, Norway (Neumann & Bergstøl 1964), and from Mn-rich hydrothermal veins in hornfels from Bohemia (Žák 1971). The host rocks in the Sterling Hill deposit have been interpreted in recent years as a Zn–Fe–Mn-bearing dolomite bed that was decarbonated when metamorphosed to sillimanite grade (Callahan 1966, Metsger *et al.* 1969, Frondel & Baum 1974). Squiller & Sclar (1980) reached a similar conclusion and proposed, in light of their own findings and those of previous workers, that the peak temperature of metamorphism was in the range 700–800°C at pressures of at least 3 kbar. They further noted that the composition of the oxide phases would be dependent upon variations in the proportion of metallic elements and local differences in the fugacity of oxygen. Haggerty (1976) reported that at high values of $f(O_2)$ and at high temperatures, Mn^{3+} can be stabilized in the spinel structure, whereas at lower values of $f(O_2)$ and with a dominance of Mn^{2+}, the rhombohedral [*i.e.*, pyrophanite] structure is decidedly preferred. The pyrophanite observed in this study occurs within a fresh coarse-grained matrix of pyroxene, calcite, gahnite and biotite, and certainly appears to be a product of the high-grade metamorphism. The traces of pyrophanite may well have formed in areas of slightly lower-than-average $f(O_2)$, as suggested by Haggerty (1976), but there is insufficient information to permit further speculation.

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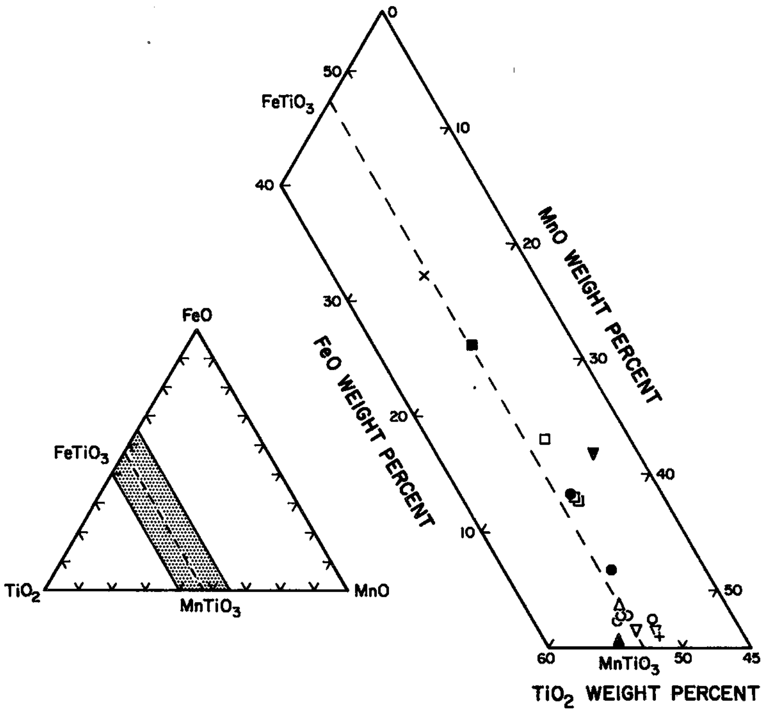

FIG. 1. MnO–TiO_2–FeO plot on which is shown the composition of pyrophanite from the Sterling Hill deposit (○) and from several other deposits: ● Norway (Neumann & Bergstøl 1964); △ Bohemia (Žák 1971); □ Massachusetts (Rumble 1976); □ Norway (Vokes *et al.* 1969); ▲ Baikalia (Portnov 1965); + Sweden (Hamberg 1890); × Australia [(Simpson 1929) cited in Palache *et al.* (1944)]; ▽ India (Sivaprakash 1980); ▼ France (Brousse & Maury 1976).

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