

## Pyrophanite from Chvaletice (Bohemia)

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**SUMMARY.** Pyrophanite was found in quartz-rhodochrosite veins in hornstones of Algonkian pyrite-manganese ores. Photometric reflectance falls from  $R_0$  24 and  $R_E$  19 at 405  $m\mu$  to  $R_0$  18 and  $R_E$  15 % at 656  $m\mu$  (in air). Vickers microhardness (100 g load) demonstrates directional anisotropy, the average value is 611 kg/mm<sup>2</sup>. Besides the main constituents, subordinate to trace quantities of Mg, Si, Al, Ca, and Cu were recorded by a spectrographic analysis. Unit-cell dimensions are  $a = 5.131$  and  $c = 14.27$  Å. Electron-microprobe analysis gave MnO 43.3, FeO 3.8, MgO 0.05, TiO<sub>2</sub> 52.9, SiO<sub>2</sub> 0.1, total 100.15 %. The origin of the Chvaletice pyrophanite was most probably connected with a hydrothermal metamorphism of an Alpine-paragenesis type. The source of elements was older sedimentary, basic volcanic, and metamorphic mineral assemblages.

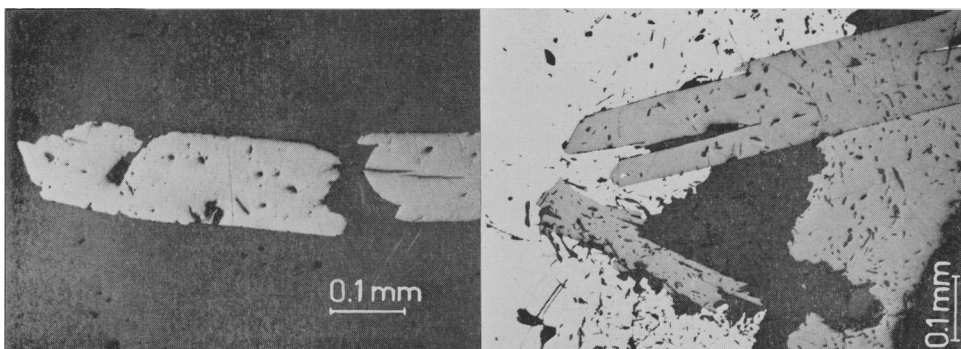
IN 1965 pyrophanite was found in the eastern part of the deep quarry of Chvaletice (3rd level) in the Iron Mts., west of Pardubice, East Bohemia. It occurs as an accessory mineral of quartz-rhodochrosite veins in finely grained grey-green or grey-brown hornstones. The hornstones belong to a metamorphosed sedimentary manganese carbonate horizon of the Algonkian Ore-Formation (Svoboda and Fiala, 1951). The thickness of the veins does not usually exceed several cm. Pyrophanite is accompanied by a pink-brown rhodonite, pyrrhotine, pyrite, infrequent neotocite, arsenopyrite, and microscopical chalcopyrite. Coarsely grained whitish-grey vein quartz and pink rhodochrosite surround and replace brecciated, sometimes deformed, pyrophanite crystals (fig. 1). Pyrrhotine and pyrite occupy fine fissures in pyrophanite, and the former surrounds its euhedral crystals (fig. 2). The vein quartz is penetrated and replaced by pyrite. The relation of pyrophanite to rhodonite is not clear.

In the hornstone, garnet and pyrrhotine prevail. The garnet is fully isotropic, mostly in anhedral and equant grains (0.08-0.16 mm); colourless grains have turbid, light pink-grey, translucent centres. Fine fibres of a monoclinic amphibole, rare rhodonite, clinozoisite or epidote, and pyrophanite can be found in the interstices. In places, the silicates are cemented by finely grained pyrrhotine. Near the vein boundary, rhodochrosite and rhodonite are penetrated by quartz veinlets, and so is rhodonite by rhodochrosite along cleavage directions.

According to the above observations, a probable succession of vein and hornstone minerals can be presented: garnet (spessartine?), rhodonite-pyrophanite-rhodochrosite-quartz-epidote or clinozoisite, amphibole (manganoean cummingtonite?)-arsenopyrite, pyrite, pyrrhotine-chalcopyrite-neotocite.

The origin of the minerals was hydrothermal metamorphism (Žák, 1965) most probably of the Alpine-paragenesis type. Titanium, manganese, iron, and other

elements were extracted by hydrothermal solutions from a tuffaceous manganese-carbonate sediment. The volcanic material of the sedimentary rocks was connected with intensive basic volcanic activity during the ore-formation. The typical eruptive rocks were gabbro–diabases with frequent ilmenite.



FIGS. 1 and 2: FIG. 1 (left). Pyrophanite in the vein quartz. Polished section. FIG. 2 (right). Euhedral pyrophanite in pyrrhotine (white) and rhodochrosite (dark grey). Polished section.

#### *Physical properties*

Thin black tabular or scaly pyrophanite crystals grow isolated or in aggregates into the vein quartz (fig. 3) and rhodochrosite (fig. 4). They reach ten mm in length, and their maximum thickness is about one mm. Trigonal striation of  $\{0001\}$  (fig. 5) is rare, and perfect  $\{02\bar{2}1\}$  cleavage was observed in a few cases only. The powder of the mineral is brown.

Microscopically, in transmitted light, thin tabular pyrophanite crystal fragments are dark red-brown to yellow-brown, translucent or transparent, and uniaxial negative. Thin transverse sections exhibit red-yellow or brown-yellow colours without any observable pleochroism. In reflected light, pyrophanite in quartz is grey and in transverse sections a weak or distinct reflection pleochroism between lighter and darker grey can be observed (cedar-oil immersion). Between crossed nicols in air, and especially in immersion, a strong anisotropy in grey colours and frequent red internal reflections are observable.

Photometric reflectance measurements were performed on pyrophanite polished sections, approximately parallel to the  $c$ -axis of the crystals (fig. 1), after repolishing the section with diamond paste. A Leitz Ortholux microscope, 8 filters ranging from 405 to 656  $m\mu$ , and a  $SrTiO_3$  standard (Leitz, Wetzlar) with reflectance values from

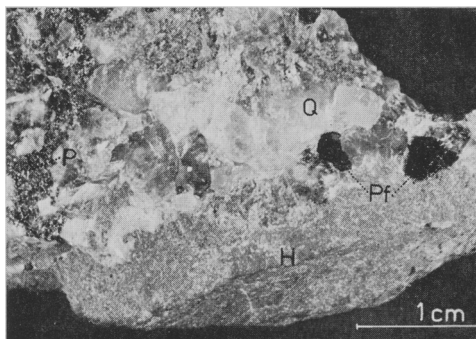
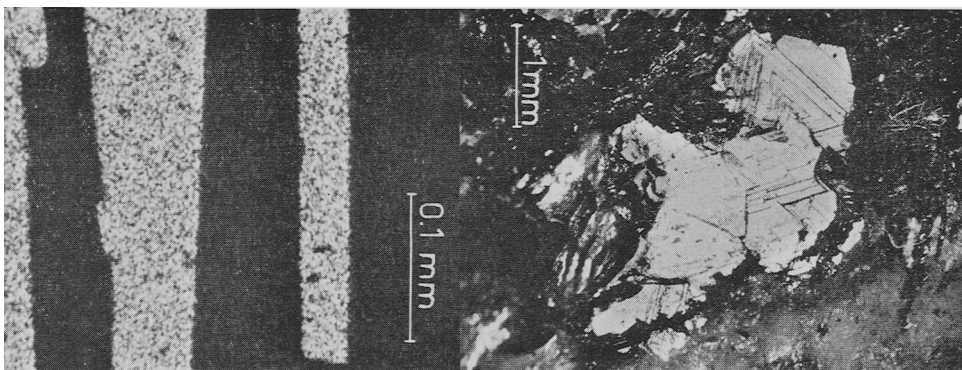


FIG. 3. Pyrophanite (black, Pf) in the vein quartz (Q) with pyrrhotine (P), rhodonite, and rhodochrosite on a hornstone (H). Photo by V. Šilhan.

19.3 % at 436 m $\mu$  to 16.7 % at 644 m $\mu$ . Reflectance values from several measurements on two crystals were averaged; the standard deviations did not exceed 1 % relative:

$\lambda$	405	436	480	527	546	589	644	656 m $\mu$
R <sub>E'</sub>	19.4	18.3	17.0	16.1	15.9	15.7	15.1	14.7 %
R <sub>O</sub>	23.7	22.1	20.3	19.4	19.0	18.8	18.2	17.8 %



FIGS. 4 and 5: FIG. 4 (left). Pyrophanite sections in rhodochrosite. Gold-coated polished section in Ti-K $\alpha$  radiation. Scanning picture by E. Rubeš. FIG. 5 (right). Trigonal striations on the basal plane of pyrophanite. Aggregate of pyrophanite scales in vein quartz. Photograph by V. Šilhan.

Vickers microhardness determinations were made of the polished section (fig. 1) using a Leitz Durimet microscope with 100 g load and 10 sec duration. The Vickers pyramid edges were set both at 45° to the trace of (0001) and parallel and perpendicular to the trace. In the latter position a microhardness anisotropism was observed: 545 kg mm<sup>-2</sup> parallel and 735 kg mm<sup>-2</sup> normal to the trace of (0001) (means of 4 measurements, 498 to 585 and 698 to 792 kg mm<sup>-2</sup>). In the diagonal position 5 measurements gave 581 kg mm<sup>-2</sup> (560 to 612). The average over both positions is 611 kg mm<sup>-2</sup>, which corresponds to >5 on the Mohs scale, and is somewhat lower than the average microhardness of ilmenite (Chukhrov and Bonshtedt-Kupletskaya, 1967).

X-ray powder data (table I) lead to cell dimensions in good agreement with those calculated for the chemical composition. Lattice constants have been given by Portnov (1963) and by Neumann and Bergstøl (1964) for pyrophanite from alkaline pegmatites, and by Ishikawa and Akimoto (1958), Shirane *et al.* (1959), and Posnjak and Barth (1934) for synthetic MnTiO<sub>3</sub>.

#### Chemical properties

A qualitative spectrographic analysis gave: major Ti, Mn, and Fe; minor ( $X$  to 0.5  $X$  %) Mg and Si; traces (<0.5  $X$  %) Al, Ca, and Cu; doubtful Cr, P, and V.

Electron-microprobe analyses were made for Mn, Fe, Ti, Mg, and Si using Cambridge Geoscan and Microscan-5 instruments. The specimen and standards were coated with graphite simultaneously after careful polishing. Pulses from specimen and standards were averaged over 4 points in each, using a one micron diameter electron

beam. The pyrophanite specimen from Chvaletice (fig. 4) shows transverse tabular crystal sections. As standards a pyrophanite from Stoksund, Norway, and microscopic spessartine grains in the hornstone country rock of the Chvaletice pyrophanite polished section were used. The Stoksund pyrophanite was a crystal plate from

TABLE I. *X-ray powder data for pyrophanite from Chvaletice. Guinier-de-Wolff camera, Cu-K $\alpha$  radiation. Indexed on a cell with  $a$   $5.131 \pm 0.005$ ,  $c$   $14.274 \pm 0.010$  Å, calculated from a quartz-calibrated pattern*

$d_{\text{obs}}$	$d_{\text{calc}}$	$I$	$hkl$	$d_{\text{obs}}$	$d_{\text{calc}}$	$I$	$hkl$	$d_{\text{obs}}$	$d_{\text{calc}}$	$I$	$hkl$
3.77 Å	3.772 Å	3	01 $\bar{1}$ 2	1.884 Å	1.886 Å	4	02 $\bar{2}$ 4	1.480 Å	1.481 Å	5	03 $\bar{3}$ 0
3.34*	—	1—	—	1.743	1.744	6	11 $\bar{2}$ 6	1.374*	—	1—	—
2.78	2.782	10	10 $\bar{1}$ 4	1.653	1.656	2	01 $\bar{1}$ 8	—	1.391	—	20 $\bar{2}$ 8
2.566	2.566	8	2 $\bar{1}$ 10	1.636	1.635	1b	3 $\bar{2}$ 12	1.356	1.359	2	1.0.1.10
2.258	2.258	2	11 $\bar{2}$ 3	1.519	1.520	5	21 $\bar{3}$ 4	1.282	1.283	2	4 $\bar{2}$ 20

\* Quartz lines (impurity).

Neumann and Bergstøl's original material (1964); it was brownish on the surface and microscopically homogeneous in polished section; a fragment  $2 \times 2$  mm was used for the microprobe study and the remainder (0.17g) for a chemical analysis. A chemical analysis of spessartine from the hornstone in the vicinity of the pyrophanite, by Z. Valcha, gave SiO<sub>2</sub> ~ 36 %, MgO ~ 0.9 %. The magnesium contents as found from the spessartine and from the Stoksund pyrophanite were in good agreement.

The quantitative analysis of the Stoksund pyrophanite by P. Povondra gave: MnO 32.00, FeO 14.22 (total iron), MgO 0.04, TiO<sub>2</sub> 51.83, SiO<sub>2</sub> (electron probe) 0.1, sum 98.19 %. The analysis was made on a potassium pyrosulphate fusion of the mineral, the iron being titrated with dichromate and the manganese with Complexon III, using triethanolamine to mask Fe and Ti. Magnesium was determined by atomic absorption. The 2 % deficiency in the analysis is best explained by oxidation and hydration of the pyrophanite (see also Neumann and Bergstøl, 1964); Fe<sub>2</sub>O<sub>3</sub>-MnTiO<sub>3</sub> isomorphism (Ishikawa and Akimoto, 1958) cannot explain the deficit. The difference between Bruun's analysis (Neumann and Bergstøl, 1964) and Povondra's is probably due to a somewhat different composition of their samples.

The electron-probe data were based on Povondra's analysis recalculated to 100 %, and were corrected for Ti-K $\alpha$  fluorescence due to Mn-K $\alpha$  and Fe-K $\alpha$  radiations (Springer, 1967), which leads to a reduction of the raw TiO<sub>2</sub> figure by 0.1 %. Owing to the similarity of the specimen and standard compositions, corrections for absorption (Birks, 1963) and atomic number (Springer, 1966) proved unnecessary; these corrections were small and antagonistic. Because of the inaccessibility of the correction formulae (see Springer, 1967) corrections for Mn-K $\alpha$  fluorescence due to Fe-K $\beta$  radiation were not applied.

Accordingly, the final electron-probe analysis of the Chvaletice pyrophanite is: MnO 43.3, FeO 3.8, MgO 0.05, TiO<sub>2</sub> 52.9, SiO<sub>2</sub> 0.1, total 100.15 %.

*Crystal chemistry*

The crystallochemical formula of the Chvaletice pyrophanite was calculated on the basis of 3 oxygen atoms in one-sixth of the hexagonal unit cell:  $(\text{Mn}_{0.92}\text{Fe}_{0.08}\text{Mg}_{0.002}\text{Ti}_{1.002}\text{Si}_{0.003})_{1.003}\text{O}_3$ . The proposed  $\text{Ti}^{4+}$ - $\text{Si}^{4+}$  substitution in pyrophanite appears probable, though the considerable difference in ionic radii enables only a limited substitution. Octahedral coordination of silicon, needed for the titanium positions in the pyrophanite lattice, has been found only in the high-pressure  $\text{SiO}_2$  modification stishovite; however, a limited reverse  $\text{Si}^{4+}$ - $\text{Ti}^{4+}$  diadochy in silicates has recently been suggested (Hartman, 1969; Gomes, 1969). A homogeneous silicon distribution in the Chvaletice pyrophanite was demonstrated by an electron-probe Si- $K\alpha$  scan of an abscissa (0.45 mm) nearly parallel with the {0001} trace of a crystal section. A constant silica content of 0.11 % was found and several heterogeneous inclusions of silicon bearing minerals gave markedly higher Si- $K\alpha$  intensities.

*Occurrences and origin of pyrophanite*

Pyrophanite has been found in two mineral assemblages, pegmatites of alkaline eruptive rocks and manganese-ore deposits (Portnov, 1963; Neumann and Bergstøl, 1964; Chukhrov and Boshstedt-Kupletskaya, 1967). From detailed descriptions of the latter assemblages (Hamberg, 1890; Campbell Smith and Claringbull, 1947; Lee, 1955) a close association of pyrophanite with hydrothermal veins or cavities in manganese ores, and with manganese silicate hornstone metamorphism, genetically related to hydrothermal activity, is apparent. Basic eruptives connected with Japanese occurrences indicate a possibility of a pyrophanite origin similar to that of the Chvaletice mineral.

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