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NEW PHOSPHATE AND ARSENATE MINERALS FROM MIEDZIANKA NEAR CHĘCINY (HOLY CROSS Mts)

INTRODUCTION

Almost fifty years have passed since the Miedzianka Mine closed but its bluish and greenish minerals, still present on old waste heaps and in quarry walls, remain of interest to mineralogists.

Miedzianka is a hill, 354.5m high, of folded Middle to Upper Devonian stromatoporoid-coral limestones. These limestones are cut by longitudinal Variscian faults. Subsequent Cainozoic deformations resulted in rejuvenation of the older structures and the development of transverse-, oblique- and strike-slip faults (Czarnocki 1929; Rubinowski 1971). Cambrian, Zechstein, Triassic and Jurassic formations unconformably cover the Miedzianka limestones. Fluvioglacial Pleistocene sands also occur locally.

THE PRIMARY AND SECONDARY ORE DEPOSIT OF MIEDZIANKA – CHARACTERISTICS IN BRIEF

The primary mineralization at Miedzianka is commonly considered to be hydrothermal - of crevice-vein form (Rubinowski 1958; 1971) and to be related to the system of longitudinal Pre-Zechstein faults. Subsequent stages of mineralization occurred in several steps under changing tectonic conditions and over a long period of time (Balcerzak et al. 1992). Primary sulphide veins were divided by Balcerzak et al. (1992) into four types:

- *galena*
- *chalcopyrite*
- *calcite-tennantite*
- *chalcocite*

The sulphides crystallized from hydrothermal solutions at high- to low temperatures (Wojciechowski 1958; Rubinowski 1958; Balcerzak et al. 1992).

The primary deposit at Miedzianka was significantly changed, especially after the Triassic and most intensively in the Eocene-Pliocene interval of the Cainozoic. As a result of Variscan tectonics, chinks, faults and joint fissures were

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formed that allowed downward percolation resulting in karstification and the alternation of primary sulphides. The changing climate and groundwater levels were additional contributing factors. The primary sulphides were altered, in several stages and mostly during the Alpine epoch, to carbonates and sulphates of Cu, Pb, Zn, Ba and Ca, to oxides and hydroxides of Fe, Cu, Mn, Sb and Co and to arsenates. Some new sulphates and arsenates were described by Wieser and Żabiński (1986); their origin has been linked with that of tennantite $Cu_3AsS_{3.25.}$
Several tens of minerals from Miedzianka were investigated during the present study. Apart from those that are well known, five new minerals were found - three phosphates and two arsenates.

EXPERIMENTAL

- Introductory observations of the minerals from the Miedzianka limestone quarries and old waste heaps were carried under a binocular microscope.

- Powder X-ray diffraction patterns were obtained using a Philips PW 3710 diffractometer, Cu $K_{\alpha 1}$ radiation, with graphite monochromator; step scanning - $0{,}02^0$, time limit - 2 secs.

- EDS spectra of some samples were recorded using a Philips XL 30 TMP ESEM scanning electron microscope.

- IR spectra were made on an IR SPECORD 71 (KBr pellets: 2 mg samples with 700 mg KBr) to confirm the presence of phosphate and arsenate anions.

CHARACTERISTICS OF NEW PHOSPHATES AND ARSENATES

The following minerals have been found for the first time at Miedzianka:

pseudomalachite $Cu_4[PO_4 | (OH)_2]_2$
hentschelite $CuFe_2[(PO_4)_3 | F]$
fluorapatite $Ca_5[(PO_4)_3 | F]$
cornubite $Cu_5[AsO_4 | (OH)_2]_2$
austinite $CaZn[AsO_4 | OH]$.

Surprisingly, **pseudomalachite** was recorded in more than ten samples and, in five of these, it was the main mineral. Macroscopically, it is not different from malachite; its colour is emerald green and it forms small bunches in some samples but, more usually, green and pale-green crusts or fine-grained masses are developed. The electron microscope pattern reveals the microgranular morphology of the pseudomalachite bunches.

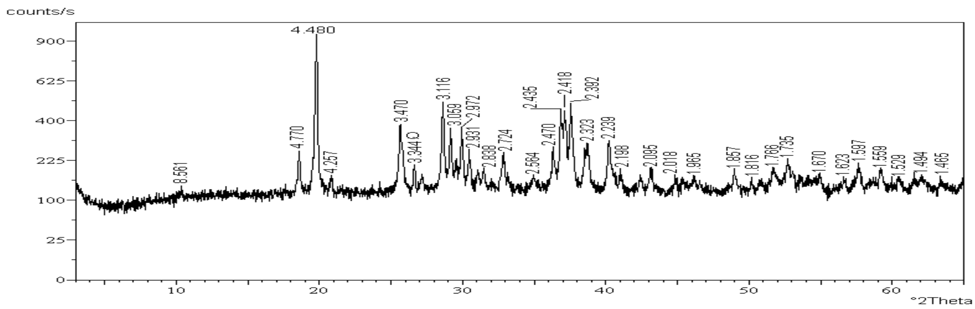

Fig. 1. X-Ray diffraction pattern of pseudomalachite with traces of quartz (Q).

The X-ray diffraction patterns of the pseudomalachites (Fig. 1) have elevated and oscillating backgrounds and numerous reflections, some sharp and some broadened. Some peaks are in slightly different positions when compared with standards; this is due to differences in their chemical composition. Their arsenian analogue is cornwallite $Cu_5[AsO_4|(OH)_2]_2$. It is therefore possible that substitution of phosphatic- by arsenic ions is the cause of the slight shift of the pseudomalachite peaks towards those of cornwallite. This phenomenon, as observed in the Miedzianka samples, is confirmed by the presence of a delicate As peak on EDS spectra.

The infrared spectrum of a pseudomalachite sample shown on Fig. 2A is identical to that presented by Holeczek and Janeczek (1991). Phosphate anions $(PO)_4^{3-}$ can be substituted by arsenate anions $(AsO_4)^{3-}$.

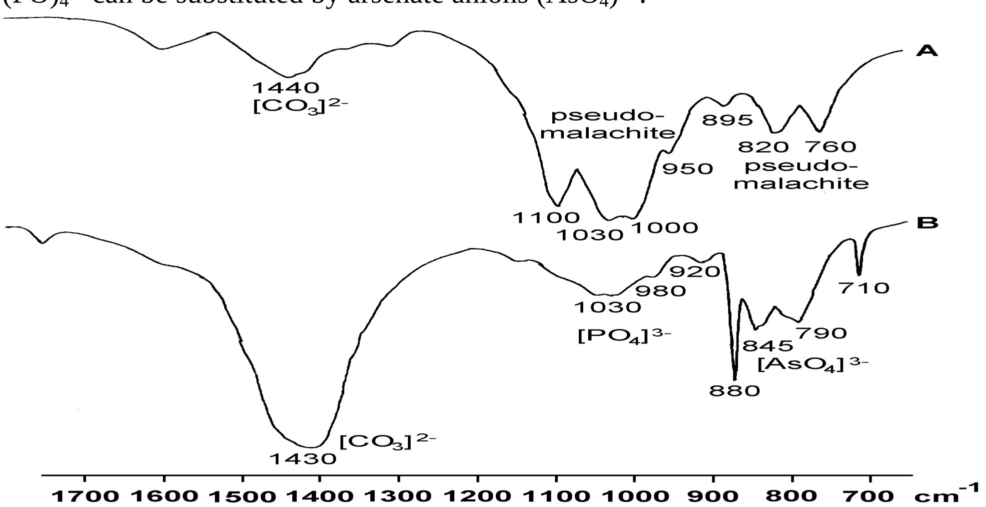

Fig. 2. Infrared absorption spectra of pseudomalachite (A) and austinite (B).

One of the pseudomalachite-bearing samples shows the low peaks of the Cu-Fe phosphate **- hentschelite**.

In addition, **fluorapatite** has been detected in two samples. These were collected in the fault zone in Miedzianka quarry, where together with calcite and illite, they form earthy concentrations cut by veinlets of calcite, clay minerals and fluorapatite.

The occurrence of phosphates in the Miedzianka deposit is probably connected with secondary activity involving phosphatic ions descending into the Miedzianka limestones in hydrothermal fluids during the Alpine epoch. The source of the phosphatic ions may have been the phosphatic concretions that are very common in the Lower Carboniferous and Cretaceous deposits in the vicinity of Miedzianka. Some of these ions contributed to the development of fluorapatite and others, with Cu ions, formed pseudomalachite.

In addition to the phosphates, two arsenates have been recorded for the first time at Miedzianka: **cornubite** and **austinite**. Cornubite (a few percent) occurs as an admixture with malachite, quartz and pseudomalachite. As it is also green in colour, it is virtually impossible to distinguish it macroscopically or with a binocular from malachite. This mineral forms green bunches, emerald-green greasy masses and green and white-green layers. Cornubite and cornwallite are two polymorphic varieties: the former is triclinic, the latter monoclinic. Cornubite and cornwallite also explicitly differ in the intensities and positions of their spectral peaks.

Austinite was found in association with calcite, conichalcite and quartz. It forms white mossy crusts on apple-green bunches on calcite. In the literature, it is usually described as white or colourless. In our sample, austinite reflections (beside calcite peaks) are very strong and in good accordance with the ICDD(37-0445) pattern (Fig. 3). Arsenate bands can also be seen on the IR spectra (Fig. 2B). The apple-green mineral substrate of the austenite is possibly conichalcite $CaCu[AsO_4 | (OH)]$ – some conichalcite reflections are identical to those of austenite but some are characteristic only of conichalcite.

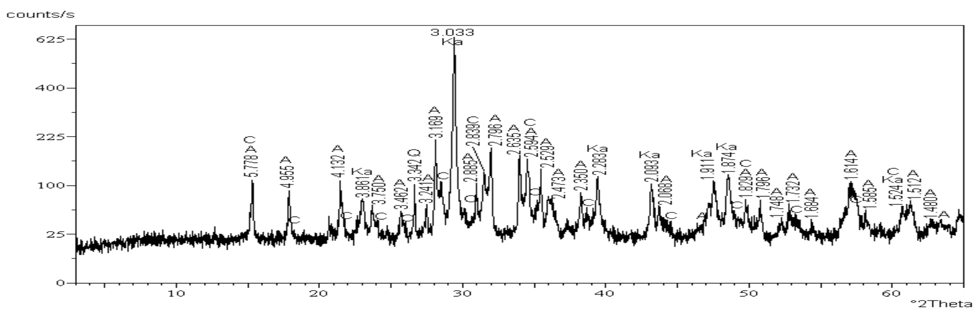

Fig. 3. X-Ray diffraction pattern of austinite (A) with calcite (Ka), conichalcite (C) and quartz (Q).

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