

# THE HYDROUS BASIC ALUMINUM PHOSPHATES OF ŽELEZNIK (VASHEGY), SLOVAKIA (ČSSR)

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## INTRODUCTION

The primary zone of the siderite stocks and veins of hydrothermal-metasomatic origin is fairly unchanged from mineralogical point of view, their zone of oxidation, however, is often very interesting due to the abundance of the beautiful and sometimes rare secondary minerals occurring here.

In the primary zone of Železnik (Vashegy) beside ankerite and siderite only a few pyrite — often well crystallized — further chalcopyrite in still smaller amounts, quartz with micaceous hematite inclusions and as rarity, millerite can be found.

The MnO content of the siderite according to the known analyses amounts to 8,23 per cent, whereas its P<sub>2</sub>O<sub>5</sub> content reaches 0,55—0,58 per cent.

In the zone of oxidation of this locality the limonite is the dominating mineral. In its cavities beside very various and often beautiful Glaskopf pieces, limonite and goethite, respectively, stalactitic-rheniform, lacelike, branching out dendriform, often tarnished with metallic colours can be found. Železnik was the most excellent locality of the limonite occurring in splendid imitative shapes (*Fig. 1.*).

The well crystallized pyroluzite is not rare, manganite, however, is still rarer. The hematite occurred as Glaskopf or red ochre. Frequent was the well crystallized quartz as well as the calcite in water-clear, larger than one cm rhombohedrons (02 $\bar{2}$ 1) whose very interesting needle-like steep scalenohedral (54 $\bar{9}$ 1) crystals were described by MARIA VENDL. The aragonite occurred in wedge-like crystals and also as „*flos-ferr*”. There were rarer the native copper, cuprite, malachite as well as the gypsum, copiapite (janosite), diadochite and the delvauxite. The peculiarity of Železnik was, however, the occurrence of

three secondary phosphate minerals, that of the *evansite*, *variscite* and *vashegyite*. Of these minerals the *evansite* and *vashegyite* were first described from this locality [1, 2].

Beside the three basic aluminum phosphate minerals mentioned above, a further mineral — likely a basic aluminum phosphate — is noted by ZIMÁNYI [2] from this locality.

With the secondary phosphate minerals occurring here dealt F. ULRICH [3] and V. VESELY [4], the latter gave also the analysis of the *variscite*.

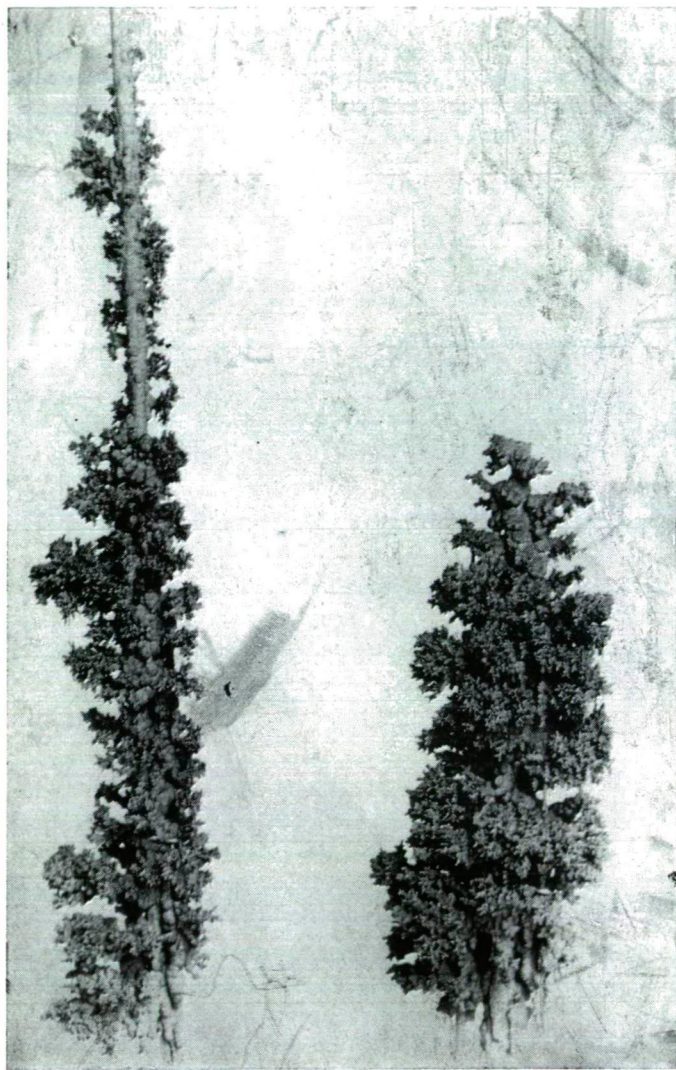


Fig. 1. Limonite from Železnik,  $\frac{1}{2}$  natural size

One of the authors collected before the World War I a fairly rich collection of the minerals of Železnik and they intend to communicate some new data on these minerals as follows.

#### EVANSITE

The evansite is longest known from this locality. This mineral is firstly collected by BROOKE EVANS in 1855 identifying, however, this mineral to be allophane. Only on the basis of the analysis of FORBES has been cleared this mineral to be a new species and it has been named by FORBES evansite in honour of its first collector.

This mineral is in Železnik long not to be found any more and only the old analyses given by FORBES were available.

The evansite covers as globular-stalactitic crust the wall of smaller cavities of the limonite or that of the graphitic slate. This crust of some millimeters in thickness is rarely colourless, commonly has a white-bluish or yellowish-brown colour and shows a pearly luster.

In the twentieth a far more rich and beautiful occurrence was found at Nižna-Slana (Alsósajó) in Slovakia (ČSSR) in the zone of oxidation of the siderite. The evansite from Nižna-Slana covers the limonite and the rock, respectively, with a globular-rheniform crust reaching half a centimeter thickness. Its colour varies from colourless through white to bluish, it is sometimes brown coloured by limonite. The colourless samples show a greasy luster and conchoidal fracture, the white-bluish pieces have a pearly luster showing a globular-layered separation. The material of this occurrence was not analysed up to date.

The refractive index of the evansite

from Železnik (white coloured)	from Nižna-Slana (colourless)
$n = 1,475 - 1,488$	$1,456 - 1,472$

and their specific gravity:

1,989	1,873
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The mineral pieces in collections in time become split and the more translucent parts become cloudy due to dehydration.

The results of analyses of selected samples are:

	Železnik white, of pearly luster	Nižna-Slana mostly colourless
Al <sub>2</sub> O <sub>3</sub>	40,14%	39,59%
Fe <sub>2</sub> O <sub>3</sub>	trace	trace
P <sub>2</sub> O <sub>5</sub>	20,17	20,03
H <sub>2</sub> O	38,23	40,30
insoluble	1,26	—
	<hr/> 99,80%	<hr/> 99,92%

The analysis of evansite from Nižna-Slana was carried out by Mrs. dr. E. RÓZSA. According to the both analyses the amount of the P<sub>2</sub>O<sub>5</sub> is higher and

the H<sub>2</sub>O content is lower than would be calculated on the basis of the formula of Al<sub>3</sub>PO<sub>4</sub>(OH)<sub>6</sub>·6H<sub>2</sub>O. It is to be noted that in the case of such gellike materials the ideal composition could not be expected, especially, if the samples were already collected about 50 years ago.

The dta curve of the evansite from Nižna-Slana is presented in Fig. 2-a. Beside the great endothermic peak about 200°C an other less expressed endothermic peak can be observed at 340°C, whereas at 1000°C an exothermic peak can be seen.

#### VARISCITE

The variscite from Železnik was firstly mentioned by K. ZIMÁNYI [5] and analysed by J. LOCZKA. An other analysis is known carried out by V. VESELY [4]. The variscite sample investigated by the authors was collected 50 years ago. It is microcrystalline, apple-green coloured and of waxy luster, its surface is botryoidal-nodular. Its specific gravity is 2,411.

The result of the analysis:

Al <sub>2</sub> O <sub>3</sub>	29,92%
Fe <sub>2</sub> O <sub>3</sub>	2,60
CaO	0,34
MgO	0,20
P <sub>2</sub> O <sub>5</sub>	41,35
H <sub>2</sub> O	24,39
insoluble	1,25
	<hr/>
	100,05%

On the dta curve of this mineral an endothermic peak can be seen at about 200°C. At about 430°C a little exothermic peak is to be noted (Fig. 2-b).

According to ULRICH [3] the vashegyite is younger than the variscite and it is formed from the variscite. In our opinion whereas *the vashegyite is very probable younger than the variscite, but it is formed in no conditions from this mineral.*

#### VASHEGYITE

The most interesting mineral of Železnik is the vashegyite. This white and only along the contact with limonite sometimes yellowish-brownish mineral, is amorphous, its pieces stick to the tongue.

The electronmicrographs of this materials were kindly carried out by Mrs. G. GRICAJENKO (Moscow) (Fig. 3, 4.). The authors express their gratitude for his kindness. According to these investigations the vashegyite shows no crystalline structure.

The first of the following two analyses was carried out by J. LOCZKA, the second by the authors.

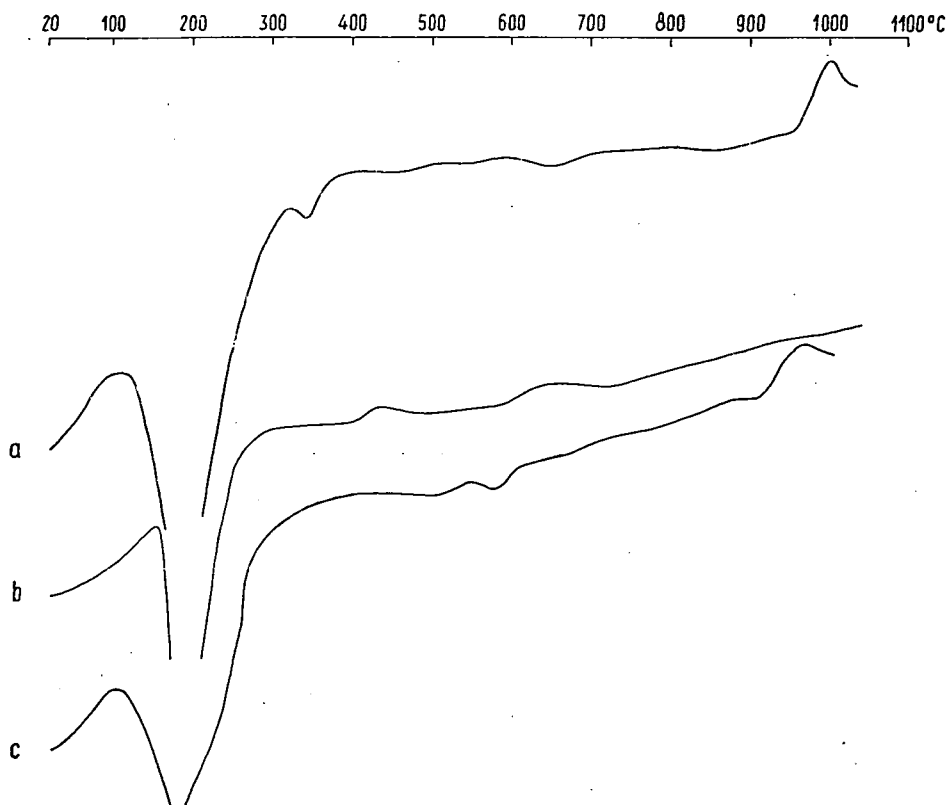


Fig. 2. Differential thermal curves of the samples: a) evansite from Nižna Slana, b) variscite from Železnik, c) vashegyite from Železnik

	1.	2.
Al <sub>2</sub> O <sub>3</sub>	28,33%	24,99%
Fe <sub>2</sub> O <sub>3</sub>	1,19	2,08
CaO	—	0,44
MgO	—	0,22
MnO	—	trace
Na <sub>2</sub> O	0,05	—
K <sub>2</sub> O	0,16	—
P <sub>2</sub> O <sub>5</sub>	31,32	33,09
H <sub>2</sub> O	38,97	38,61
insoluble	0,24	0,33
CO <sub>2</sub>	0,12	—
	<hr/> 100,38%	<hr/> 99,76%

The data of the analysis of the authors — as it was to be expected in the case of such a hydrous amorphous materials — would not give the formula that can be calculated on the basis of the data of LOCKA's analysis.



*Fig. 3.* Electronmicrograph of vashegyite,  $\times 30\ 000$



*Fig. 4.* Electronmicrograph of vashegyite.  $\times 20\ 000$

It was already noted by ZIMÁNYI that accompanied with the vashegyite a „loose, crumbling, almost flour-like, yellowish-white” material occurs. The material had been analysed by J. LOCZKA. In his mentioned paper ULRICH stated that this material consists of minute spherulites and that the tiny crystal-needles building up the spherulites show a + optical character in the longitudinal direction and their refractive index is 1,542—1,544.

This finely threaded material has been found also by the authors on their white, massive vashegyite samples, at the edges to the bedrock, on the wall of the cavities. This material occurs in a greater amount mainly along the contact between the vashegyite and the graphitic slate. The authors confirm ULRICH's statements, the tiny threads of the spherulites have positive optical character in their longitudinal direction and the refractive index is 1,544—1,547.

Among the analyses the first is LOCZKA's analysis, the second is carried out by the authors and the third by Mrs. dr. E. RÓZSA.

	1.	2.	3.
Al <sub>2</sub> O <sub>3</sub>	34,35%	29,48%	34,39%
Fe <sub>2</sub> O <sub>3</sub>	—	6,92	2,70
CaO	—	0,79	—
MgO	—	0,16	—
MnO	—	0,03	—
P <sub>2</sub> O <sub>5</sub>	31,93	29,15	29,80
H <sub>2</sub> O	34,11	33,73	33,02
insoluble	—	0,03	—
	100,49%	100,29%	99,21%

The probable formula for this mineral, calculated from the analyses, would be Al<sub>3</sub>(PO<sub>4</sub>)<sub>3</sub>·AlO·OH·12H<sub>2</sub>O.

On the dta curve of this sample, between 170—200°C a great endothermic peak and at about 970°C an exothermic peak can be seen (Fig. 2—c).

The mineral denoted by K. ZIMÁNYI as vashegyite is not homogeneous and on the basis of the analyses so far obtained a more or less probable formula for this mineral can not be given. *It can exactly be stated, that it is — in contrast to STRUNZ's opinion [6] — not identical with the evansite. This spherulitic mineral, however, composing the material of the dehydrating and crystallizing material of the amorphous „vashegyite” denoted by ZIMÁNYI [2] as questionable and as whawellite by F. ULRICH [3] can be rather considered as an independent mineral species than the mineral so far denoted as „vashegyite” because the analyses of this spherulitic minerals gave more congruent results.*

*It is proposed by the authors the name vashegyite for this mineral with a formula of Al<sub>3</sub>(PO<sub>4</sub>)<sub>3</sub>·AlO·OH·12H<sub>2</sub>O.*

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## REFERENCES

- [1] FORBES: Phil. Mag. Vol. 28. 1864. p. 341.
- [2] ZIMÁNYI, K.: Math. Term. tud. Értesítő XXVII. K. 1909. p. 64.
- [3] ULRICH, F.: Rozpravy České Akademie 31. Nr. 10.
- [4] VESELY, V.: Casopis Národního musea v Praze 1923.
- [5] ZIMÁNYI, K.: Math. Term. tud. Értesítő XXVI. K. 1908. p. 72.
- [6] STRUNZ, H.: Mineralogische Tabellen 3. Aufl. 1957.