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HYDROHETAEROLITE FROM THE ORZEŁ BIAŁY MINE (UPPER SILESIA) AND THE PROBLEM OF ZINCDBRAUNITE

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Abstract. Dark brown and black substance filling fissures and forming horizontal interlayers in the Triassic dolomites and galmeis has been found in the Zn—Pb ore deposit in the Orzeł Biały mine near Bytom (Upper Silesia). X-ray examination has shown that this substance contains hydrohetaerolite with cell parameters $a_0 = 5.75$, $c_0 = 8.99$ Å, which are close to corresponding parameters of hydrohetaerolite reported from Leadville and Sterling Hill, USA (McAndrew 1956, Wadsley 1955). Heated in air up to 1000°C hydrohetaerolite transforms into hetaerolite, the cell parameters of which are $a_0 = 5.733$ and $c_0 = 9.253$ Å. Microscopic examinations in reflected light and electron microprobe analysis have shown that hydrohetaerolite is accompanied by another phase — amorphous one or with only partly ordered atomic arrangement (Mn—Pb phase). As follows from chemical analyses, the substance in question is very similar to that reported by Nienadkiewicz (1911) from Olkusz (Cracow region) and called by him zincdibraunite.

In 1911 Nienadkiewicz reported the occurrence of a manganese-zinc ore found in Zn—Pb ore deposit of the Olkusz environs (Cracow region). It was found to occur as earthy masses of chocolate-brown colour filling lenticular empty spaces and irregular fissures within oxydized zinc ores (galmeis). The brown mass consisted essentially of manganese, zinc, lead and water (tab. 2). On the basis of chemical data, Nienadkiewicz considered this substance to be a new mineral of the chalcophanite group displaying essential formula $ZnO \cdot 2MnO_2 \cdot H_2O$ and containing admixtures of lead, calcium and other elements. Consequently, he proposed to call it zincdibraunite. Lack of full mineralogical data concerning this substance has not allowed to place zincdibraunite correctly in the classification scheme of minerals. Thus, this mineral has not been accepted by International Mineralogical Association.

Recently, the author of this paper has found similar dark brown and black earthy substance in oxidation zone of Zn—Pb ore deposit in the Orzeł Biały mine near Bytom (Upper Silesia). This substance either fills fissures or occurs as horizontal interlayers within dolomites or galmeis and closely resembles the ore described by Nienadkiewicz (1911). On the basis

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of chemical and X-ray examinations the crystalline phase of this substance has been identified as hydrohetaerolite.

Hydrohetaerolite is a hydrated zinc and manganese oxide of the formula $\text{HZnMn}_{2-x}^{3+}\text{O}$, $x \approx 0.4$ (McAndrew 1956). Its crystals display tetragonal symmetry and belong to the space group $D_{4h}^{19} - I 4_1/\text{amd}$; $Z = 4$. It is isostructural with hausmanite and thus shows deformed spinel structure (due to Jahn-Teller effect). Hydrohetaerolite is a rare mineral occurring in oxidation zones of Zn—Pb ore deposits. Till now its occurrence has been reported from Leadville, Colorado; Sterling Hill and Franklin, New Jersey; Philipsburg, Montana (Fronzel, Heinrich 1942).

More detailed megascopic observation of the material found in the Orzeł Biały mine containing hydrohetaerolite identified by means of X-ray methods has allowed to distinguish following forms of its aggregates:

- 1) earthy, loose masses dark brown in colour — sample MK-71 (phot. 1)
- 2) dark brown and black, massive granules — sample MK-72 (phot. 2)
- 3) black, porous coke-like substance — sample MK-96 (phot. 3)
- 4) black, botryoidal forms — sample MK-96b

Examination of polished sections of granules (MK-72) and of porous coke-like substance (MK-96) have shown heterogeneous material. Sample MK-72 consists mainly of light cream — coloured substance with pinkish shade, showing no anisotropy and no noticeable internal reflections. It displays collomorphic structure. When using higher magnifications micro-intergrowths of a grey phase can be noticed in it. Sample MK-96 contains much more of the latter phase which thus can be identified more in detail by means of optical methods (Phot. 4). It is distinctly anisotropic and exhibits microcrystalline structure and red internal reflexions. Reflectivity of the grey phases measured by means of MPV photometer of Ortholux-Pol microscope (Leitz-Wetzlar) for different wave lengths varies between $R = 13.3$ and 19.3% . Reflectivity of the grey phase was found to be distinctly lower than of the light-cream one. According to Uytendogaardt and Burke (1972) R for hydrohetaerolite is approximately $15-20\%$.

The separation of hydrohetaerolite from the coexisting phase was impossible by any means.

All the megascopic varieties of the substance in question have been examined by means of X-ray powder method using VEM apparatus. Powder photographs have been taken in cameras 114.6 and 57.3 mm in diameter by applying Fe-filtered, $\text{CoK}\alpha$ radiation ($\lambda = 1.788896 \text{ \AA}$). The 35 kV voltage and 10 mA current were used and time of exposition was 10 hrs. Values of interplanar spacings and cell parameters, calculated by means of the least square method for MK-72 and MK-96 are presented in table 1. The values are characteristic for hydrohetaerolite. It should be emphasized that in spite of microscopical differences observed in polished sections of both examined substances their X-ray patterns contain exclusively the lines characteristic for hydrohetaerolite. Only one very weak line of psilomelane ($d = 2.431 \text{ \AA}$) has been found to occur in powder photo-

graph of the sample MK-96. Powder photographs of the sample MK-96b display scarce and very weak lines and this sample should be more detailed examined.

The results of chemical analyses of samples MK-72 and MK-96 are presented in table 2 together with those of hydrohetaerolites from Sterling Hill and Leadville as well as of zincdibraunite from Olkusz. The chemical analysis has been carried out by means of atomic absorption spectroscopy whereas water content has been calculated on the basis of ignition losses and controlled by Penfield method. Because the analyzed material has been found to be heterogeneous, it has been impossible to calculate the formula of hydrohetaerolite on the ground of chemical data. In general, when compared with hydrohetaerolite from Sterling Hill and Leadville, samples MK-72 and MK-96 display similar contents of Mn and H_2O but are distinctly lower in Zn. This deficiency is compensated by considerable amount of Pb which has not been found in samples from the American ore deposits. If considerably higher water content is not taken into

Table 1

X-ray powder data for hydrohetaerolite

Hydrohetaerolite from Leadville (McAndrew 1956)		Hydrohetaerolite from Orzeł Biały mine (Upper Silesia)			
		Sample MK-96		Sample MK-72	
<i>I</i>	<i>d</i> (Å)	<i>I</i>	<i>d</i> (Å)	<i>I</i>	<i>d</i> (Å)
1/2	4.82	—	—	—	—
1/2	3.34	1/2	3.356	—	—
7	3.02	3	3.020	4	3.037
4	2.87	1	2.869	1	2.929
8	2.66	7	2.649	4	2.679
10	2.47	10	2.471	10	2.491
1	2.25	1	2.249	—	—
1	2.13	1	2.123	—	—
2	2.03	1	2.028	1	2.042
1	1.773	—	—	—	—
2	1.723	1	1.719	—	—
2	1.686	1	1.675	—	—
1	1.613	1	1.613	—	—
5	1.570	7	1.570	4	1.578
8	1.508	9	1.509	9	1.509
4	1.434	3	1.438	4	1.443
1/2	1.412	—	—	—	—
1/4	1.312	—	—	—	—
tr.	1.299	—	—	—	—
tr.	1.283	—	—	2	1.270
3	1.263	1/2	1.269	—	—
$a_o = 5.73 \text{ \AA}$		$a_o = 5.75 \text{ \AA}$		$a_o = 5.78 \text{ \AA}$	
$c_o = 9.00 \text{ \AA}$		$c_o = 8.99 \text{ \AA}$		$c_o = 8.97 \text{ \AA}$	

Table 2

Chemical composition of hydrohetaerolites and zincibraunite

	Sample MK-72 Orzeł Biały mine **		Sample MK-96 Orzeł Biały mine **		Hydrohetaerolite Sterling Hill Frondel, Heinrich (1942)		Hydrohetaerolite Leadville Frondel, Heinrich (1942)		Zincibraunite Olkusz Nienadkiewicz (1911)	
	weight %	mol. ratio	weight %	mol. ratio	weight %	mol. ratio	weight %	mol. ratio	weight %	mol. ratio
ZnO	27.70	0.3404	22.04	0.2708	33.43	0.4108	37.56	0.4615	23.28	0.2061
MnO ₂	—	—	—	—	—	—	—	—	52.27	0.6013
Mn ₂ O ₃	58.92	0.3732	57.91	0.3668	60.44	0.3829	56.00	0.3547	—	—
H ₂ O	4.17	0.2316	7.66	—	3.89	0.2159	4.36	0.2420	13.59	0.7543
PbO ₂	—	—	—	—	—	—	—	—	6.89	0.0288
PbO	7.40	0.0331	13.19	0.0591	—	—	—	—	0.54	0.0024
Fe ₂ O ₃	0.06	0.0037	—	—	0.77	0.0048	—	—	1.28	0.0080
CaO	0.13	0.0023	—	—	—	—	—	—	0.94	0.0168
SiO ₂	—	—	—	—	1.71	0.0285	2.69	0.0448	0.06	0.0009
Al ₂ O ₃	—	—	—	—	—	—	—	—	0.12	0.0012
BaO	0.94	—	—	—	—	—	—	—	trace	—
Total	99.34	—	100.80	—	100.24	—	100.61	—	99.48*	—
Density	—	—	—	—	4.85	—	4.64	—	4.63	—

* Including Tl₂O₃ + K₂O (0.51) and traces of Cu, Co, Cd.

** Analysed by mgr M. Swiercz.

account chemical composition of zincibraunite from Olkusz described by Nienadkiewicz (1911) is close to that of the samples from the Orzeł Biały mine.

In order to check whether the microscopic diversity of the samples under examination in due to chemical heterogeneity and to determine the role of lead in hydrohetaerolites, samples MK-72 and MK-96 have been examined by means of electron microprobe. The results of these investigation will be published in detail in one of the next papers. As follows from preliminary data, two phases observed microscopically display different chemical composition. Linear scan has shown that while Mn concentration is nearly constant, the contents of Zn and Pb vary considerably and this variation display opposite tendency. Lead concentrates essentially in light-cream phase containing only up to several per cent of zinc. On the other hand, Zn definitely prevails in grey phase while lead occurs in it in minute amounts or not at all. The higher concentration of Zn correlates with higher amount of oxygen. In both phases no traces of sulphur have been found by means of electron probe microanalysis.

On the basis of the above data it is merely possible to identify for certain only one, crystalline phase — hydrohetaerolite. The presence of this mineral in the examined samples has been evidenced by means of X-ray diffraction patterns (tab. 1). As follows from the results of electron probe microanalysis, hydrohetaerolite is represented by the phase which in polished section appears to be grey, anisotropic one. This phase is usually rich in Zn and contains only small amounts of Pb. This is confirmed by the values of cell dimensions (tab. 3), which are close to those of cell parameters of hydrohetaerolite from the American ore deposits containing no lead. It should be emphasized that presence of Pb ions in crystalline lattice of hydrohetaerolite would cause a distinct increase of its cell parameters. The second, light-cream coloured phase contains nearly total amount of lead found in the examined samples. Because of isotropy and lack of reflections on its X-ray powder patterns, this substance is supposed to be amorphous. However, it seems also possible that this phase belongs to psilomelane group but displays weakly ordered atomic arrangement since the strongest reflections of minerals of this group may coincide with those which are characteristic for hydrohetaerolite. As already mentioned, the X-ray pattern of the sample MK-96 contains one weak line 2.431 Å of psilomelane.

Sample MK-72 has been subjected to thermal analysis using Hungarian derivatograph of Pauliks and Erdey's system. DTA curve displays endothermic effects at 380°, 690° and 820°C (fig. 1) whereas the TG one indicates gradual loss of weight in the temperature range 20—900°C which amounts to 4.5 per cent.

X-ray examination of the sample MK-72 heated subsequently at temperatures 400°, 600° and 900°C has shown gradual transition of hydrohetaerolite into hetaerolite accompanied by distinct increase of c_0 parameter whereby a_0 remains nearly constant (slightly diminishes). It can be noticed that the $c_0 : a_0$ ratio varies from 1.55 to 1.58 for hydrohetaerolite and from 1.59 to 1.61 for hetaerolite. X-ray diffraction patterns of heated MK-72 and other samples from the Orzeł Biały mine up to 900°C consist of numerous sharp lines typical for hetaerolite (tab. 4). This phenomenon

Table 3

Cell constants of the hydrohetaerolite and hetaerolite

Hydrohetaerolite	a_o (Å)	c_o (Å)	$c_o : a_o$
Leadville (Fron del, Heinrich 1942)	5.71	9.04	1.583
Leadville (McAndrew 1956)	5.73	9.00	1.571
Orzeł Biały mine sample MK-96	5.75	8.99	1.563
Orzeł Biały mine sample MK-72	5.78	8.97	1.552
Hetaerolite	a_o (Å)	c_o (Å)	$c_o : a_o$
Orzeł Biały mine sample MK-72 heated up to 1000°C	5.733	9.253	1.614
Sterling Hill (Fron del, Heinrich 1942)	5.75	9.168	1.594
Sterling Hill (McAndrew 1956)	5.73	9.24	1.613
synthetic (Mason 1947)	5.72	9.24	1.615

indicates better ordering of its atomic arrangement in comparison with original hydrated mineral. It should be emphasized that X-ray diffraction patterns of samples heated up to 900°C show no additional lines of any other phases except of those of hetaerolite. Cell dimensions of the latter mineral clearly indicate that Pb does not cause any dilatation of its lattice. It is thus concluded that the amorphous phase contained in the original sample was not subjected to recrystallization.

The obtained results are quite concordant with the observations of McAndrew (1956). Hetaerolite obtained by this author on heating hydrohetaerolite from Leadville up to 900°C, displayed very close cell parameters which are in turn very similar to those of synthetic $ZnMn_2O_4$ obtained and analysed by Mason (1947). On the other hand, these are slightly different from cell dimensions of hetaerolite from Sterling Hill (Fron del, Heinrich 1942).

Infrared absorption analysis of the samples in question has been carried out using UR-10 (Zeiss) spectrophotometer. Samples have been prepared by applying KBr discs technique (0.7–0.8 mg of the substance plus 300 mg KBr). Infrared absorption spectra of hausmannite, sample MK-72 (containing hydrohetaerolite) and of sample MK-72 heated up to 1000°C (containing hetaerolite) are presented in fig. 2. All three samples display

similar spectra, indicating analogous structure of their metal-oxygen groups. No influence of the amorphous phase on the spectra is observed. Within the range of 400–700 cm^{-1} occur three distinct absorption bands. The position of absorption maxima of hausmannite and of the sample MK-72 is similar (hausmannite: 415, 520, 622 cm^{-1} and weaker band 600 cm^{-1} ; sample MK-72: 405, 530, 623 cm^{-1}). After heating sample MK-72 to 1000°C the above bands are distinctly displaced towards higher wave numbers (420, 545, 637 cm^{-1} and weaker bands 610, 665 cm^{-1}). This effect is probably due to a decreasing of metal-oxygen bonds length when compared with unheated sample.

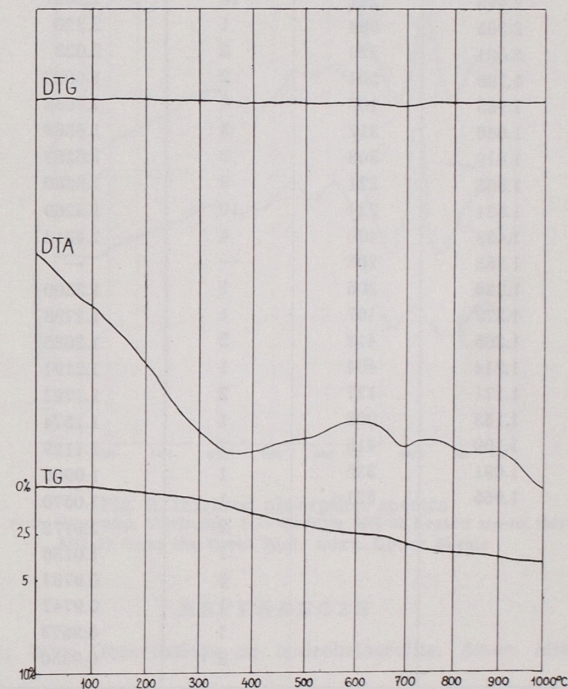


Fig. 1. DTA and TG curves of the sample MK-72 from the Orzeł Biały mine, Upper Silesia

As follows from the results of spectrophotometric and X-ray study, dehydration of hydrohetaerolite is accompanied by a decreasing of bond length within metal-oxygen coordination groups (displacement of absorption bands towards higher wave numbers) whereas the distances between these groups increase along Z axis (distinct rise of c_o parameter). Because of heterogeneity of examined substances (admixture of amorphous phase), more precise determination of the role of hydrogen in hydrohetaerolite structure has not been possible.

Table 4

X-ray powder data for hetaerolite

Sterling Hill N.J. (Fron del, Heinrich 1942)			Sample MK-72 from the Orzeł Biały mine heated up to 1000°C		
I	d (Å)	hkl	I	d (Å)	hkl
1	4.880	101	—	—	—
7	3.051	112	8	3.037	112
4	2.860	200	3	2.858	200
9	2.703	103	9	2.719	103
10	2.465	211	10	2.4697	211
3	2.305	004	1	2.320	004
3	2.021	220	2	2.023	220
3	1.796	204	2	1.8022	204
5	1.755	105	4	1.7636	105
4	1.686	312	3	1.6868	312
3	1.619	303	2	1.6252	303
5	1.563	321	9	1.5680	321
8	1.521	224	10	1.5269	224
4	1.433	400	4	1.4313	400
1	1.353	206	—	—	—
3	1.326	305	1	1.3300	305
2	1.279	107	1	1.2798	107
3	1.265	413	2	1.2685	413
1	1.214	404	1	1.2191	404
5	1.171	127	2	1.1791	127
4	1.153	008	1	1.1574	008
4	1.109	415	2	1.1129	415
3	1.091	335	1	1.0906	335
2	1.055	521	1	1.0570	521
—	—	—	2	1.0172	—
			1	1.0136	—
			3	0.9787	—
			1	0.9742	—
			1	0.9573	—
			2 r	0.9350	—
$a_o = 5.75 \text{ \AA}$			$a_o = 5.733 \text{ \AA}$		
$c_o = 9.168 \text{ \AA}$			$c_o = 9.253 \text{ \AA}$		

The mode of occurrence of the substances in question indicates their hypergenic origin. It is supposed that the process of their formation consisted first in absorption of Zn and Pb ions (contained in solutions circulating in weathering zone) on the precipitated manganese oxides. The substances thus obtained tended subsequently to recrystallize to form hydrohetaerolite phase, concentrating manganese and the vast majority of Zn ions. Lead, which because of different crystallochemical properties could

not enter this crystalline phase, formed a Mn-bearing amorphous or only poorly ordered (psilomelane?) phase.

Taking into account the obtained data, it is supposed that zincibraunite from Olkusz described by Nienadkiewicz (1911) was a substance similar to those examined by the writer of this paper and occurring in the Bytom region.

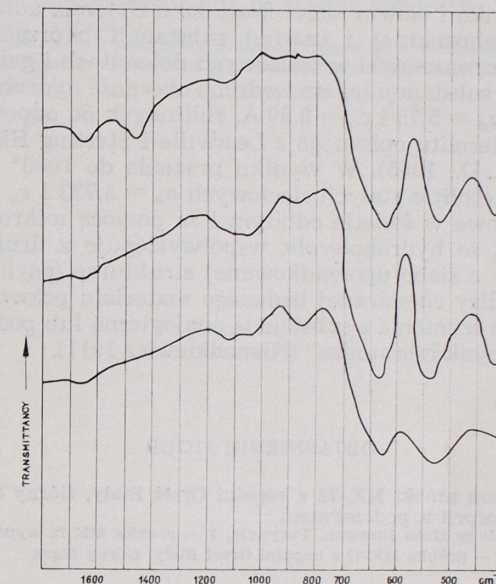


Fig. 2. Infrared absorption spectra
1 — Hausmannite from Ilmenau, Tübingen, 2 — Sample MK-72 heated up to 1000°C, 3 — Sample MK-72 from the Orzeł Biały mine, Upper Silesia

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HYDROHETEROLIT Z KOPALNI ORZEŁ BIAŁY (GÓRNY ŚLĄSK) A ZAGADNIENIE CYNKDYBRAUNITU

Streszczenie

W kopalni cynku i ołowiu Orzeł Biały koło Bytomia autorka napotkała skupienia ciemnobrunatnej i czarnej substancji tworzące wypełnienia szczelin i poziome warstewki w triasowych dolomitach i galmanach. Rentgenograficznie w substancji tej stwierdzono obecność hydroheterolitu o stałych sieciowych $a_0 = 5,75$ i $c_0 = 8,99$ Å, zbliżonych do odpowiednich parametrów hydroheterolitu opisanego z Leadville i Sterling Hill (Mc Andrew 1956, Wadsley A. D., 1955). W wyniku prażenia do 1000° hydroheterolit przechodzi w heterolit o stałych sieciowych $a_0 = 5,733$ i $c_0 = 9,253$ Å. Badania mikroskopowe w świetle odbitym i za pomocą mikroskopy elektronicznej wykazały, że hydroheterolit współwystępuje z drugą fazą, amorficzną, względnie o słabo uporządkowanej strukturze (psylomelan ołowiowy). Wyniki analizy chemicznej badanego materiału pozwalają przypuszczać, że mamy do czynienia z substancją analogiczną lub podobną do opisanego z Olkusza „cynkdybraunitu” (Nienadkiewicz 1911).

OBJAŚNIENIE FIGUR

Fig. 1. Derywogram próbek MK-72 z kopalni Orzeł Biały, Górny Śląsk
Fig. 2. Krzywe absorpcji w podczerwieni
1 — hausmanit ze złoża Ilmenau, Turynia, 2 — próbka MK-72 wyprażona do temperatury 1000°C , 3 — próbka MK-72 z kopalni Orzeł Biały, Górny Śląsk

Мария КУЛИГ

ГИДРОГЕТЕРОЛИТ ИЗ РУДНИКА ОЖЕЛ-БЯЛЫ (ВЕРХНЯЯ СИЛЕЗИЯ) И ПРОБЛЕМА ЦИНКДИБРАУНИТА

Резюме

В свинцово-цинковом руднике Ожел-Бялы близ г. Бытома автором были выявлены скопления темнобурого и черного вещества, выполняющего трещины и образующего прослойки в триасовых доломитах и в галмее. Рентгенографически в этом веществе определено присутствие гидрогетеролита с константами решетки $a_0 = 5,75$ и $c_0 = 8,99$ Å, сходными с соответственными параметрами гидрогетеролита, описанного из Ледвилл и Стерлинг Хилл (Мак Эндриу 1956, А. Д. Уэйдсли 1955). После прокаливании при 1000°C гидрогетеролит переходит в гетеролит с константами решетки $a_0 = 5,733$ и $c_0 = 9,253$ Å. Микроскопические наблюдения в отраженном свете и исследования с помощью электронного микроскопа показали, что гидрогетеролит сопровождается второй фазой, аморфной или характеризующейся слабо упорядоченной структурой

(свинцовый псиломелан). Результаты химического анализа исследуемого вещества позволяют предполагать, что рассматриваемое вещество аналогическое или сходное с цинкдибраунитом, описанным в руднике Олькуш (Ненадкевич 1911).

ОБЪЯСНЕНИЯ К ФИГУРАМ

Fig. 1. Дериwограмма образца МК-72 из рудника Ожел-Бялы, Верхняя Силезия
Fig. 2. Кривые поглощения
1 — гаусманит из месторождения Ильменау, Тюрингия, 2 — образец МК-72, прокаленный до температуры 1000°C , 3 — образец МК-72 из рудника Ожел-Бялы, Верхняя Силезия

PLATE I (PLANSZA I, ТАБЛИЦА I)

Phot. 1. Sample MK-71 from the Orzeł Biały mine, Upper Silesia, containing hydrohetaerolite and Pb phase; earthy, loose masses, dark brown in colour. No magnification.

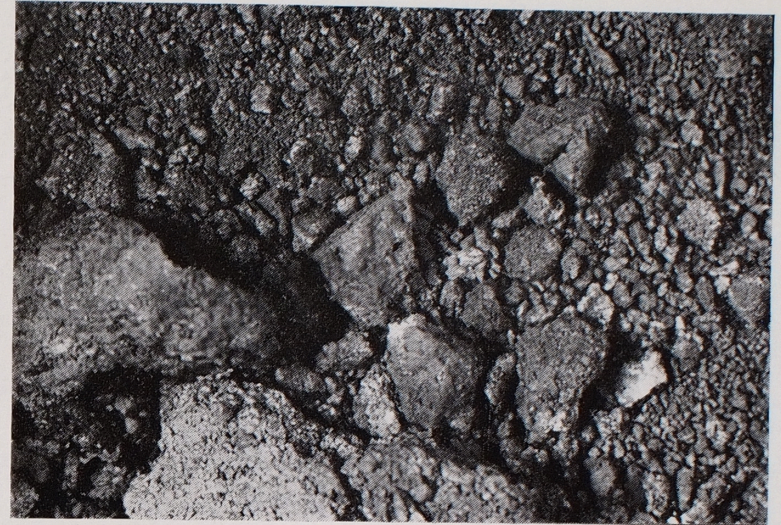
Próbka MK-71 z kopalni Orzeł Biały, Górny Śląsk. Skupienia ziemiste, czekoladowo-brunatne zawierające hydroheterolit i fazę Pb. Wielkość naturalna.

Образец МК-71 из рудника Ожел-Бялы, Верхняя Силезия. Землистые, шоколадно-буроватые скопления, содержащие гидрогетеролит и фазу Pb. Естественная величина

Phot. 2. Sample MK-72. Orzeł Biały mine, Upper Silesia. Hydrohetaerolite with coexisting Pb phase; dark brown and black, massive granules. Magn. $\times 5$

Próbka MK-72 z kopalni Orzeł Biały, Górny Śląsk. Hydroheterolit i współwystępująca faza Pb; zwięzłe granulki o barwie brunatnej i czarnej. Pow. $\times 5$

Образец МК-72 из рудника Ожел-Бялы, Верхняя Силезия. Гидрогетеролит в сопровождении фазы Pb; плотные зерна бурого и черного цвета. Увел. $\times 5$



Phot. 1



Phot. 2

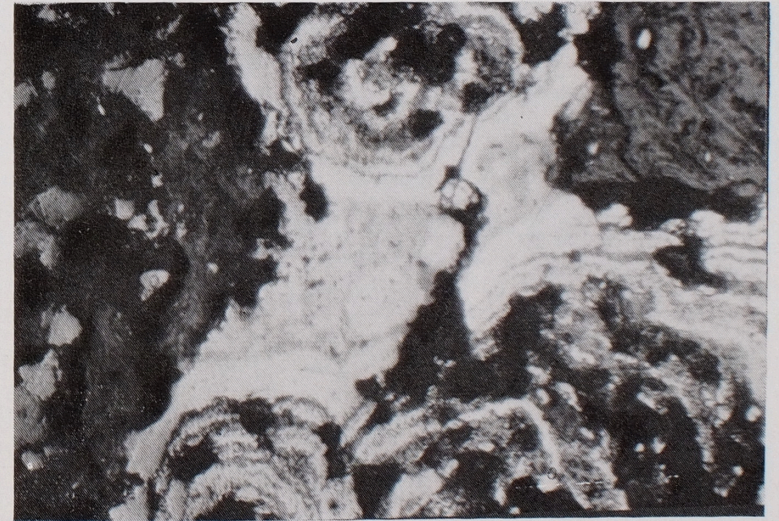
Maria KULIG — Hydrohetaerolite from the Orzeł Biały mine (Upper Silesia) and the problem of zincibraunite

PLATE II (PLANSZA II, ТАБЛИЦА II)

- Phot. 3. Sample MK-96, Orzeł Biały mine, Upper Silesia. Hydrohetaerolite with coexisting Pb phase; black, porous coke-like substance. Magn. $\times 3.5$
 Próbką MK-96 z kopalni Orzeł Biały, Górny Śląsk. Hydroheterolit i współwystępująca faza Pb; zwarte okruszki czarnej, porowatej substancji przypominające koks. Pow. $\times 3.5$
 Образец МК-96 из рудника Ожел-Бялы, Верхняя Силезия. Гидрогетеролит в сопровождении фазы Pb; плотные обломки черного пористого вещества, напоминающие кокс. Увел. $\times 3,5$
- Phot. 4. Sample MK-96, Orzeł Biały mine, Upper Silesia. Hydrohetaerolite (grey) and coexisting Pb phase (white). Reflected light, no analyser, magn. $\times 250$
 Próbką MK-96 z kopalni Orzeł Biały, Górny Śląsk. Hydroheterolit (szary) i współwystępująca z nim faza Pb (biała). Światło odbite, 1 nikol, pow. $\times 250$
 Образец МК-96 из рудника Ожел-Бялы, Верхняя Силезия. Гидрогетеролит (серый) в сопровождении фазы Pb (белое). Отраженный свет, 1 николю. Увел. $\times 250$



Phot. 3



Phot. 4

Maria KULIG — Hydrohetaerolite from the Orzeł Biały mine (Upper Silesia) and the problem of zindibraunite