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ALLOPHANES FROM Zn-Pb SULPHIDE ORE BODIES IN THE "BOLESŁAW" MINE NEAR OLKUSZ

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Abstract. Allophanes were found to occur within marcasite concentrations in the Zn-Pb sulphide deposit "Bolesław" near Olkusz. They have been examined using chemical, X-ray, thermal and infrared spectroscopic methods. The occurrence of allophanes within marcasite showing no weathering phenomena indicates its origin during later stage sulphide mineralization.

INTRODUCTION

Allophane $m\text{Al}_2\text{O}_3 \cdot n\text{SiO}_2 \cdot p\text{H}_2\text{O}$ represents an X-ray amorphous substance, showing variable $\text{SiO}_2:\text{Al}_2\text{O}_3$ ratios. Its physical properties depend mainly on the hydration degree. Usually it forms compact, white or creamy aggregates displaying glassy lustre.

As follows from recent studies, allophanes are common constituents of soils, formed from silicate rocks and glasses by chemical weathering under tropical climatic conditions. Pure allophanes are met but sporadically. They can also be formed by the action of solutions, containing sulphuric or organic acids, on minerals or by low-temperature hydrotherms. Gradual ordering of their structure results in transformation into halloysite. Therefore, allophanes usually occur in younger deposits. Sometimes they are also reported to occur in carbonate rocks (Stoch, 1974).

In Poland, pure allophane was reported by Piotrowski to occur in limonitic iron ore deposit "Władysław" near Ilża (Piotrowski, 1934) and in bauxite clays in Mierzęcice near Będzin (Piotrowski, 1939) being accompanied by halloysite.

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It has been also found to occur in shales of the Carpathian flysch in Monasterzec (Michalek, Stoch, 1958) and other places (Badak *et al.*, 1962).

Allophane concentrations described by the present authors were found in Zn-Pb deposit "Boleslaw" in ore nests developed within Lower Triassic (Roethian) dolomites.

GEOLOGICAL CONDITIONS OF OCCURRENCE

Zinc and lead ore bodies of "Boleslaw" mine occurring within Roethian dolomites are composed of Zn-Pb sulphides accompanied by iron sulphides — mainly marcasite. Marcasite forms also locally their own ore bodies. A peculiar feature of this deposit is a widespread occurrence of hemicolloidal and colloidal ZnS modification, first of all of brunckite. Nests consisting of rich ores are usually surrounded by an aureole of dispersed sulphide mineralization accompanied by monheimite and by dispersed baryte mineralization.

Usually, iron sulphides appear abundantly at the peripheral parts of rich Zn-Pb ores, separating them from surrounding dolomites. These zones of marcasite envelopes are usually from a dozen to several tenths centimeter in width. They consist predominantly of marcasite breccia composed of crushed aggregates of this mineral cemented and mixed with clay and dolomitic fragments. Compact marcasite ore is less frequent, being product of replacement of dolomite rock. Brecciation of sulphides is probably due to volume changes during recrystallization of their primarily colloidal aggregates or to collapsing processes accompanying hydrothermal karst phenomena.

Allophane concentrations were found in two localities among cloddy marcasite in peripheral part of a large and rich Zn-Pb ore body. In the first case it fills a cavity within marcasite, 15 cm in diameter, whilst in the second one — it occurs at the boundary between marcasite and dolomite fragment embedded in the former, partly replaced by monheimite.

MEGASCOPIC AND MICROSCOPIC CHARACTERISTICS

Allophane in sample No 1 consists of two modifications. The first is white-creamy in colour, soft and brittle, showing pelitic texture. It passes gradually into the second one (*lb*), more compact and hard, displaying creamy-gray colouration. When freshly broken, the fragments of the latter modification show glassy lustre. In larger pieces, concentric-radial structures are observed, being better developed in allophane of the first modification (Phot. 1). The samples enclose gypsum crystals, forming characteristic rosette aggregates, up to 15 mm in size (Phot. 2). Specific gravity, determined using pycnometric method, was found to be 2.05 and 1.98 g/cm³ for samples *la* and *lb* respectively.

In sample No. 2 allophane occurs as white, powdery coatings at the contact between dolomite and cloddy marcasite.

Allophane aggregates are optically isotropic. Refractive indices have been determined using immersion method by means of Abbe's refractometer. They were found to be 1.49 and 1.48 for samples *la* and *lb* respectively. In surrounding marcasite allophane is filling fine, irregular pores, 0.01–1.0 mm in size (Phot. 3).

CHEMICAL STUDY

Both modifications — *la* and *lb* — occurring in sample No. 1 have been analyzed. Because of small amount of sample No. 2, no chemical study of it has been carried out. Silica and SO₃ have been estimated by gravimetric methods, alumina — by complexometric titration, H₂O[−] — by dehydration at 105°C for 2 hours and H₂O⁺ — using Penfield method. The remaining components have been determined by means of atomic adsorption spectroscopy using Pye Unicam SP-90 B instrument. The results of this study are presented in Table 1.

Table 1
Chemical analyses of allophanes from "Boleslaw"

Components	<i>la</i> weight %	<i>lb</i> weight %
SiO ₂	22.40	22.39
Al ₂ O ₃	32.47	31.95
Zn	1.07	0.65
Pb	0.54	0.01
Fe	0.36	0.15
CaO	2.78	1.27
MgO	1.71	0.73
K ₂ O	0.00	0.00
Na ₂ O	0.09	0.07
SO ₃	2.07	1.50
H ₂ O [−]	19.81	19.90
H ₂ O ⁺	15.99	20.48
Total	99.29	99.10

The SiO₂:Al₂O₃ ratio in both modifications is very similar, while H₂O⁺ contents in them differ considerably (Table 2). Both modifications, but particularly the *la* one, display high content of bivalent cations which may occur both as adsorbed ones or as sulphate admixture. The latter possibility is suggested by the presence of SO₃. Some part of Ca and Mg can also occur in carbonate phase. Direct contact of iron sulphides and allophane may suggest the presence of minute admixture of pyrite or marcasite too.

Table 2
Molecular ratios of main components in the investigated allophanes

Components	<i>la</i>	<i>lb</i>
SiO ₂	1.16	1.19
Al ₂ O ₃	1.00	1.00
H ₂ O	6.21	7.22

X-RAY STUDY

The results of X-ray examinations, carried out using TUR M-61 diffractometer by applying powder method, are presented in Fig. 1. X-ray patterns of all the samples examined (*la*, *lb*, 2) and of a comparative one from Monasterzec, are characterized by strong but diffuse peak, the maximum of which corresponds approximately to 3.35–3.44 Å (the whole band ranges from 3.70 to 3.00 Å). This indicates some ordering of structure of allophane in question.

Sample *la* was subjected to heating at 300, 900 and 1200°C for 5 hours. X-ray diffractometer patterns of the products thus obtained are presented in Fig. 1. No reflections are observed after heating at 300°C, indicating amorphous nature of the product. If allophane contains fine amounts of halloysite crystallites, its reflections are found to occur in the X-ray pattern (Czuchrov *et al.*, 1963). After heating at 900°C mullite is formed. At 1200°C mullite peaks are getting more sharp and there appear a strong, not identified reflection corresponding to *d*_{hkl} 4.11 Å (cristobalite ?).

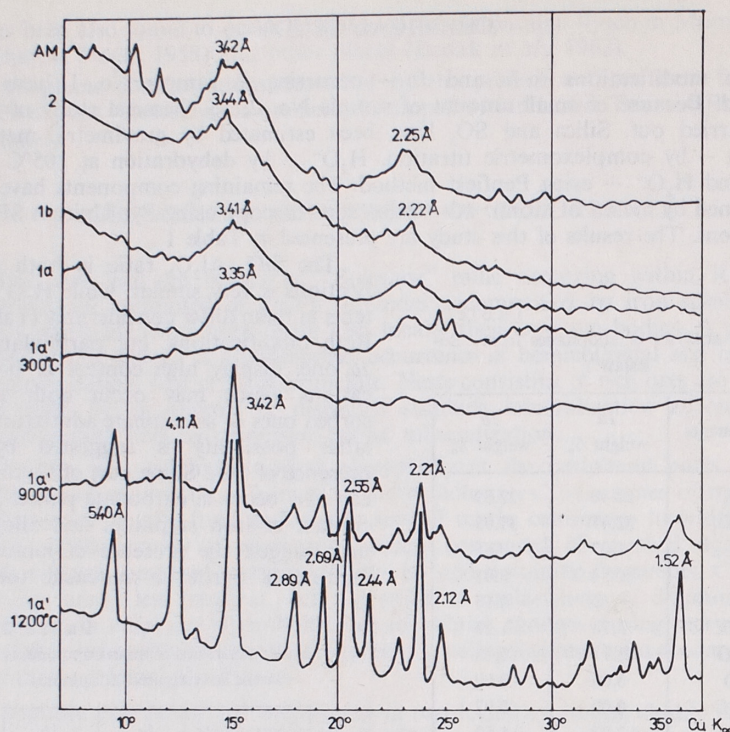


Fig. 1. X-ray diffractograms of allophanes
1a, 1b, 2 – allophanes from the "Boleslaw" mine, AM – allophane from Monasterzec, 1a' – 300, 900, 1200°C –
X-ray diffractograms of sample 1a heated to respective temperatures

THERMAL ANALYSIS

This analysis has been carried out by means of Hungarian "Derivatograph", allowing simultaneous recording of DTA, DTG and TG curves. DTA and TG curves of samples 1a and 1b are presented in Fig. 2. For both the samples we observe a strong endothermic effect between 60 and 400°C with the maximum at 253°C (1a) and 233°C (1b) caused by dehydration and dehydroxylation of allophane. Exothermic effects between 800 and 930°C with the maximum at 865°C (1a) and 880°C (1b) are due to mullite synthesis. Loss of weight recorded in TG curves are due to dehydration and dehydroxylation of allophane. Similar effects were reported for allophanes by White (1953) and Michałek and Stoch (1958).

INFRARED SPECTROSCOPIC STUDY

Absorption spectra of the allophanes studied (1a, 1b, 2) have been recorded in the range of wave numbers 400–3800 cm^{-1} by means of UR-10 Zeiss Jena spectrometer using KBr disk technique. The obtained spectrograms (Fig. 3) display several bands, usually broad and showing no subtle structure. The most intense of them correspond to the following ranges:

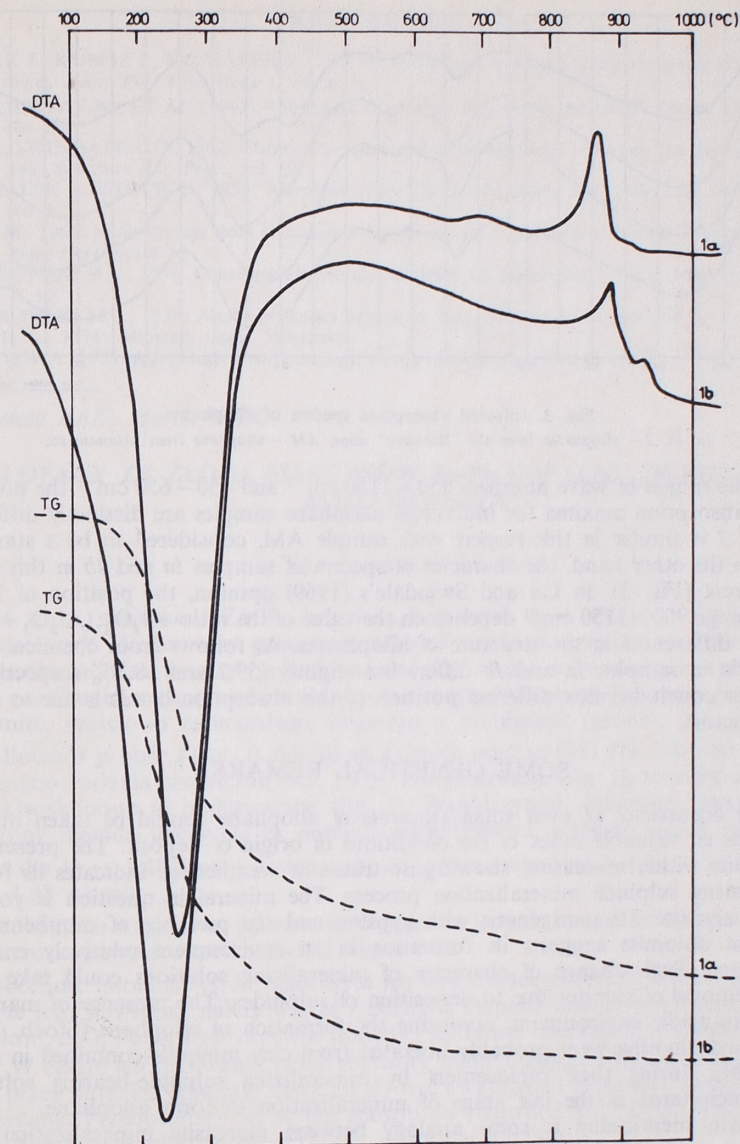


Fig. 2. DTA and TG – curves of allophanes from the "Boleslaw" mine

- 3400–3600 cm^{-1} – stretching vibrations of H_2O molecules and, probably, OH groups,
- 1600–1670 cm^{-1} – bending vibrations of H_2O molecules,
- 950–1150 cm^{-1} } stretching and bending vibrations of Si–O
- 450–650 cm^{-1} } and Al–O bonds

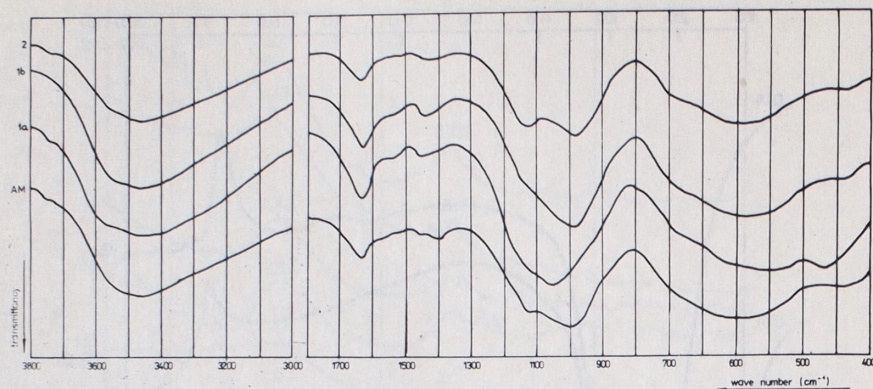


Fig. 3. Infrared absorption spectra of allophanes
1a, 1b, 2 — allophanes from the "Bolesław" mine, AM — allophane from Monasterzec

In the ranges of wave numbers $950-1150\text{ cm}^{-1}$ and $450-650\text{ cm}^{-1}$ the position of the absorption maxima for individual allophane samples are distinctly different. Sample 2 is similar in this respect with sample AM, considered to be a standard one. On the other hand, the character of spectra of samples 1a and 1b in this range is different (Fig. 3). In Lai and Swindale's (1969) opinion, the position of bands in the range $900-1150\text{ cm}^{-1}$ depends on the value of the ratio $\text{Al}_2\text{O}_3:(\text{Al}_2\text{O}_3 + \text{SiO}_2)$ and on differences in the structure of allophanes. As follows from chemical data, this ratio in samples 1a and 1b differs but slightly (59.2 and 58.8% respectively). It is thus concluded that different position of this absorption bands is due to structural factors.

SOME GENETICAL REMARKS

The occurrence of even small amounts of allophane should be taken into account as an valuable index of the conditions of origin of deposit. The presence of allophane within marcasite, showing no traces of weathering, indicates its formation during sulphide mineralization process. The mineral in question is younger than marcasite. Its paragenesis with gypsum and the presence of monheimite in adjacent dolomite suggests its formation in an environment relatively enriched in oxygen. Such change of character of mineralizing solutions could take place after removal of sulphur due to deposition of sulphides. The presence of marcasite indicates acidic environment, favouring the formation of allophane (Stoch, 1974). Silica and alumina were probably liberated from clay minerals contained in marly dolomites during their replacement by mineralizing sulphide-bearing solutions and precipitated in the last stage of mineralization to form allophane.

Worth mentioning is some analogy between marcasite mineralization with allophane, described in this paper, with marcasite deposit in Rudki (G. Świętokrzyskie — Holy Cross Mts.) where sulphides are accompanied by halloysite (Nieć, 1968). In the latter deposit halloysite has also been formed during the last mineralization stage, and cements brecciated marcasite. It is thus concluded that transformation of clay minerals, accompanying hydrothermal marcasite mineralization, is a typical and widespread process.

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ALLOFANY ZE ZŁOŻA SIARCZKÓW Zn-Pb KOPALNI „BOLESŁAW” KOŁO OLKUSZA

Streszczenie

W złożu siarczków Zn-Pb kopalni „Bolesław” koło Olkusza stwierdzono występowanie alofanów w gniazdach rudnych wśród dolomitów retu. W jednym przypadku alofan tworzył gniazdo o średnicy 15 cm w markasyt (próbki 1a i 1b), a w drugim występował na granicy markasytu i zanurzonego w nim fragmentu dolomitu, częściowo zmurszałego, bogatego w monheimit (próbka 2).

Alofan w próbce 1 (fot. 1) składał się z dwóch odmian (1a i 1b). Dla obu odmian wykonano badania chemiczne (tab. 1 i 2), rentgenowskie (fig. 1), termiczne (fig. 2) i spektroskopowe w podczerwieni (fig. 3). Współczynnik załamania światła wyznaczony metodą imersyjną za pomocą refraktometru Abbego wynosi dla 1a — 1,49, a dla 1b — 1,48. Gęstość oznaczono za pomocą piknomietru (1a — $2,05\text{ g/cm}^3$, 1b — $1,98\text{ g/cm}^3$).

Próbkę 2 ze względu na jej małą ilość poddano jedynie badaniom rentgenowskim i spektroskopowym w podczerwieni (fig. 1 i 3).

Obecność alofanu wśród markasytu nie wykazującego oznak wietrzenia wskazuje, że jego powstanie należy wiązać z późnymi etapami mineralizacji siarczkowej. Źródłem Al_2O_3 i SiO_2 były zapewne dolomity margliste otaczające skupienia siarczków. W czasie ich ługowania przez roztwory mineralizujące i zastępowania dolomitu przez siarczki, składniki ilaste mogły być uwalniane i częściowo przynajmniej rozkładane. Przedostające się w ten sposób do roztworu SiO_2 i Al_2O_3 wytrącały się w końcowym okresie mineralizacji w formie alofanu.

Zasługuje na uwagę pewna analogia, jakiej można się dopatrzeć między mineralizacją markasytową z alofanem w złożu „Bolesław” a złożem markasytowym w Rudkach w Górach Świętokrzyskich, w którym siarczkom towarzyszy haloizyt (Nieć, 1968). W złożu tym haloizyt tworzył się również w końcowym etapie mineralizacji (cementuje zbrekcjonowany markasyt), a powstał jak się przypuszcza w wyniku przeobrażenia otaczających złożę ilów illitowych. Przeobrażenie minerałów ilastych, towarzyszące hydrotermalnej mineralizacji markasytowej, wydaje się być zatem zjawiskiem typowym.

Fig. 1. DyfraktoGRAMY rentgenowskie allofanów

1a, 1b, 2 — allofany z kopalni „Bolesław”, AM — allofan z Monasterca, 1a' — 300, 900, 1200°C — dyfraktoGRAMY próbki 1a ogrzewanej do odpowiednich temperatur

Fig. 2. Krzywe DTA i TG allofanów z kopalni „Bolesław”

Fig. 3. Widma absorpcyjne w podczerwieni allofanów

1a, 1b, 2 — allofany z kopalni „Bolesław”, AM — allofan z Monasterca

OBJAŚNIENIA FOTOGRAFII

Fot. 1. Typowa tekstura allofanu z kopalni „Bolesław”. Pow. $\times 4$

Fot. 2. Gipsowe agregaty występujące wśród allofanów z kopalni „Bolesław”. Pow. $\times 4$

Fot. 3. Formy występowania skupień allofanów w markazycie z kopalni „Bolesław”, 1 nikol. Pow. $\times 100$

Богуслав БОНК, Марэк НЕЦЬ

АЛЛОФАНЫ ИЗ МЕСТОРОЖДЕНИИ СУЛЬФИДОВ Zn—Pb В ШАХТЕ “БОЛЕСЛАВ” ВБЛИЗИ ОЛЬКУША

Резюме

В месторождении сульфидов Zn-Pb шахты „Болеслав” вблизи Олькуша было обнаружено присутствие аллофанов в рудных гнездах среди доломитов ретского яруса. В одном случае аллофан образовал гнездо диаметром в 15 см в марказите (образцы 1a и 1b), а в другом присутствовал на границе марказита и погружённого в нём фрагмента доломита, частично разрушенного, богатого монгеймитом (образец 2).

Аллофан в образце 1 (фото 1) состоял из двух модификаций (1a и 1b). Для обеих модификаций были проведены химические (табл. 1 и 2), рентгеновские (фиг. 1), термические (фиг. 2) и ИК-спектроскопические (фиг. 3) исследования. Коэффициент преломления света, обозначенный по иммерсионному методу при помощи рефрактометра Абба, был равен для 1a — 1,49, а для 1b — 1,48. Удельный вес был обозначен при помощи пикнометра (1a — 2,05 г/см³, 1b — 1,98 г/см³).

Из-за небольшого количества, образец 2 был исследован только рентгеновским и ИК-спектроскопическим методами (фиг. 1 и 3).

Присутствие аллофана среди марказита, не обнаруживающего признаков выветривания, свидетельствует о том, что его происхождение надо связывать с поздними этапами сульфидного оруднения. Источником Al₂O₃ и SiO₂ были, по всей видимости, мергелистые доломиты, окружающие скопления сульфидов. Во время их выщелачивания минерализующими растворами и замещения доломита сульфидами, глинистые составляющие могли освободиться и, по крайней мере, частично распасться. Al₂O₃ и SiO₂ которые этим путём перешли в раствор, в последнем периоде оруднения выпадали в форме аллофана.

Большого внимания заслуживает некоторая аналогия, которую можно признать между аллофановым оруднением в залежи „Болеслав” а марка-

зитовым месторождением в Рудках в Свентокшиских горах, в котором сульфидам сопутствует галлуазит (Нець, 1968). В этом месторождении галлуазит образовался тоже на последней этапе оруднения (он является цементом для брекчированного марказита), а его происхождение связано, кажется, с преобразованием окружающих месторождение залежей иллитовых глин. Преобразование глинистых минералов, которое сопутствует марказитному оруднению, тоже кажется типичным явлением.

ОБЪЯСНЕНИЯ К ФИГУРАМ

Фиг. 1. Рентгеновские дифрактограммы аллофанов

1a, 1b, 2 — аллофаны из шахты “Болеслав”, AM — аллофан из Монастерца, 1a' — 300, 900, 1200°C — дифрактограммы образца 1a подогретого до соответствующей температуры

Фиг. 2. Кривые DTA и TG для аллофанов из шахты Болеслав

Фиг. 3. ИК-спектры поглощения для аллофанов

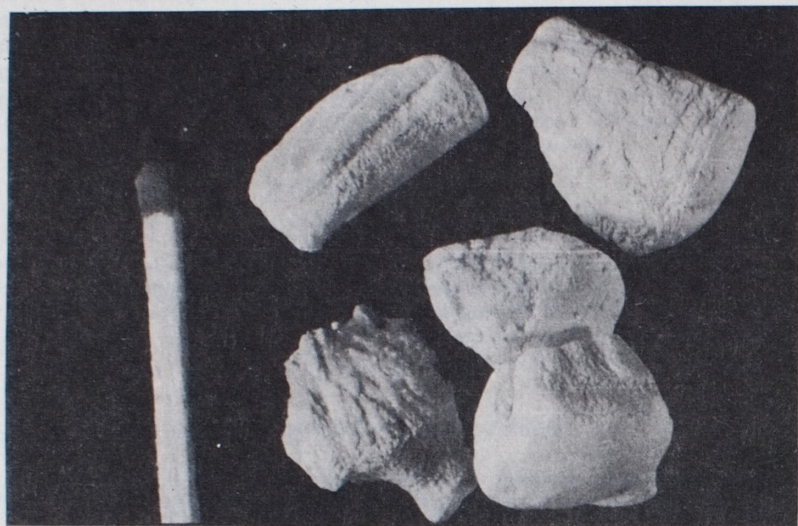
1a, 1b, 2 — аллофаны из шахты Болеслав, AM — аллофан из Монастерца

ОБЪЯСНЕНИЯ К ФОТОГРАФИЯМ

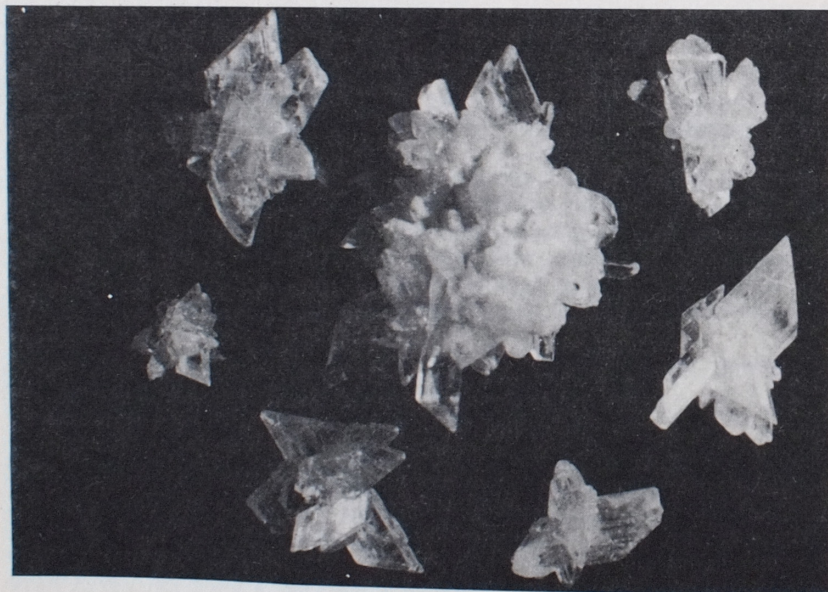
Фото 1. Типичная текстура аллофана из шахты Болеслав, увеличение $\times 4$

Фото 2. Гипсовые агрегаты, которые находятся среди аллофанов из шахты Болеслав, увеличение $\times 4$

Фото 3. Формы присутствия скоплений аллофанов в марказите из шахты Болеслав, 1 николь, увеличение $\times 100$

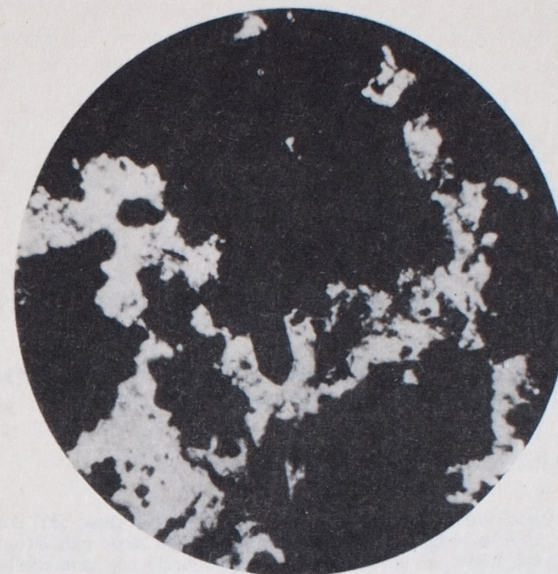


Phot. 1. Typical texture of allophanes from the "Bolesław" mine. Enlarged $\times 2$



Phot. 2. Gypsum aggregates occurring within allophanes from the "Bolesław" mine. Enlarged $\times 2$

Bogusław BAŁ, Marek NIEĆ - Allophanes from Zn-Pb sulphide ore bodies in the "Bolesław" mine near Olkusz



Phot. 3. Allophane aggregates in marcasite from the "Bolesław" mine. 1 nicol. Enlarged $\times 100$

Bogusław BAŁ, Marek NIEĆ - Allophanes from Zn-Pb sulphide ore bodies in the "Bolesław" mine near Olkusz