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THE OCCURRENCE OF MONHEIMITE IN THE BOLESŁAW Zn-Pb ORE DEPOSIT NEAR OLKUSZ

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Abstract. In the Bolesław Zn-Pb ore deposit near Olkusz monheimite (Zn, Fe)CO_3 was found in mineralized breccia of Lower Triassic (Roethian) dolomites. The mineral was subjected to chemical, X-ray and IR spectroscopic analysis. Its occurrence in the part of the deposit not affected by weathering suggests that it owes its origin to the endogenic process of ore mineralization.

INTRODUCTION

Monheimite (ZnFe)CO_3 is a not too common mineral of zinc-lead deposits. According to Smirnov (1955), its occurrence is characteristic of those parts of the oxidation zone to which the access of oxidizing agents from the atmosphere is limited.

First informactions on monheimite occurrence in the Cracow-Silesian Zn-Pb deposits date from the second half of the 19 th cent. Gellhorn (1853, *vide*, J. D. Dana, E. S. Dana 1951) published chemical composition of ferrous smithsonite found in small ammounts in the former Maria mine near Bytom (weight %): ZnO — 39.15, FeO — 17.40, CaO — 12.74, CO_2 — 30.36, total — 99.65. Traube (1888) described monheimite from the former Elizabeth mine near Bytom, where it appeard in the form of fine rhombohedral brown crystals showing green tinge in transmitted light. The studies of Żabiński (1958) have revealed that galmeis occurring in the Matylda mine near Chrzanów have a high content of ferrous iron which appears in the form of isomorphous solid solution of carbonates (Zn, Fe)CO_3, i.e. as monheimite. The galmeis form granular, fairly massive aggregates, light brown-grey or yellowish in colour. Monheimite occurrences in the area of Bytom and Olkusz were also mentioned by Zawiślak (1971).

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The second author found recently monheimite in the Bolesław Zn-Pb deposit, where it forms greenish incrustations on fissure walls, in cavites and on fragments of mineralized breccia in Roethian dolomites.

GEOLOGICAL SETTING OF MONHEIMITE IN THE BOLESŁAW DEPOSIT

The zinc and lead ore deposit near Bolesław occurs in Middle Triassic dolomitized limestones (ore-bearing dolomites) and Lower Triasic diagenetic dolomites. Mineralization of a simple composition: ZnS, PbS, FeS_2 shows a nest-like distribution. The ore-bearing dolomites are mineralised over the almost whole area. Rich ore bodies are surrounded here by an aureole of poorer ore mineralization which the occurs almost on the whole area of the deposit. In the Roethian dolomites mineralization is confined to relatively small bodies of a diameter up to several dozen metres. Such nests are usually surrounded by an aureole of intense barite mineralization which is confined, as a rule, to some more porous or fissured dolomite beds. Barite mineralization is younger than ore mineralization.

Monheimite was found in the Roethian rocks, on the periphery of ore bodies, in intensely cavernous dolomites. The caverns are small, from some to a dozen or so millimetres in diameter, irregular, randomly distributed in the rock (Phots 1, 2). The cavernous structure of dolomites is presumably due to hydrothermal karst phenomena (Bogacz *et al.* 1970). This is evidenced by its occurrence in the vicinity of fissures as well as by the irregular, nest-like form of the cavernous parts, gradual grading cavernous parts into breccia and their intense mineralization. It has been found that marcasite and sphalerite forms impregnations and druses on the walls of caverns. Monheimite forms incrustations on the cavern walls and frequently also on sphalerite. It is readily discernible owing to its olive-green colour. This colour differentiates it from sphalerite, for which it can be easily mistaken only in the weathered parts, where the two minerals acquire a rusty-grey coating.

EXPERIMENTAL AND RESULTS

Microscopic studies

Microscopic observation has revealed that monheimite incrustations form a thin coating from 0.5 to 3 mm in thickness on crystalline secondary dolomite and sphalerite (Phots 3, 4). In places where marcasite is also present, the following sequence has been noted: marcasite-dolomite-sphalerite-monheimite. It follows, therefore, that monheimite is the youngest mineral, ending the cycle of ore mineralization. It forms crustifications along the cavities walls composed of aggregates of xenomorphic crystals up to 2 mm in size. In thin section monheimite is greenish, markedly birefringent and showing high relief which is positive relation to dolomite but lower than in sphalerite.

Monheimite crystals separated under the microscope were subjected to chemical, X-ray and infrared spectroscopic analysis.

Chemical analysis

Because of the small amount of monheimite available for investigation (sample designated as *BR-1*), it was first subjected to semi-quantitative analysis using emission spectroscopy (PGS-2 spectrophotometer). The following results were obtained:

Fe, Zn	— main components,
Ca, Mg	— about 1%,
Mn	— 0.0X%,
Cd, Pb, Si, Al	— traces ($<$ 0.01%).

The content of Zn and Fe, determined quantitatively by atomic absorption spectroscopy (Pye Unicam SP-90 B spectrophotometer), is: 27.0% Zn and 24.3% Fe.

From X-ray and IR spectroscopic investigations it appears that the sample studied contains about 6 weight % admixture of sphalerite and 3—4% of dolomite. Taking this into account, it can be calculated that monhemite contains 25.3 weight % Zn and 26.6 weigth % Fe. An approximate formula for monheimite is: $(Zn_{0.45}\ Fe_{0.54})CO_3$, so it represents an intermediate member of the isomporpous series smithsonite — siderite, showing slight quantitative prevalence of $FeCO_3$.

X-ray investigations

X-ray powder analysis of monheimite was made using both film and counter recording technique. Film technique was used to record reflections in the full range of Θ angles, so that unit cell parameters could be calculated (Table 1). A film photograph was taken for the sample that had been subjected to chemical analysis (*BR-1*), as well as for an additional sample (*BR*-1 a) obtained only in a minimal amount. A TUR M-60 diffractometer with a 114.6 mm diameter camera and filtered CoK_α radiation were used. Both samples have been found to contain sphalerite admixtures (about 6%) and some dolomite.

The X-ray diffraction pattern was taken primarily to check whether the mineral studies is in fact a member of the isomorphous series or a mixture of two carbonates. It was taken with a TUR M-61 diffractometer, using filtered CoK_α radiation. Although conditions enabling the best resolution were applied, no splitting of the strongest reflections was noted for the analyzed sample (*BR-1*). An X-ray diffractogram recorded under the same conditions for a mixture consisting of 50% siderite and 50 % smithsonite showed pronounced splitting of the reflections arising from these components.

Table 1 gives interplanar spacings for monheimite from the Bolesław deposit, along with d_{hkl} values for siderite and smithsonite published by Graf (1961) and those for monheimite from the Matylda mine (Żabiński 1960). As appears from the Table, d_{hkl} values and the unit cell parameters

Table 1

X-ray powder diffraction data of monheimites

hkil	d(Å) (1Å = 0.1 nm) Smithsonite, Graf (1961)	Monheimite from the *Matylda* Mine, Żabiński (1960)		Monheimite from the *Bolesław* Mine		Siderite, Graf (1961)
		a	*f*	*BR-1*	*BR-1a*	
$01\bar{1}2$	3.5509	3.56	3.57	3.5750	3.5750	3.5903
$10\bar{1}4$	2.7476	2.76	2.77	2.7847	2.7818	2.7912
$11\bar{2}0$	2.3264	2.33	2.33	2.3390	2.3370	2.3443
$11\bar{2}3$	2.1099	2.11	2.12	2.1283	2.1259	2.1318
$20\bar{2}2$	1.9460	1.95	1.96	1.9569	1.9576	1.9629
$02\bar{2}4$	1.7754	1.78	1.79	1.7864	1.7886	1.7952
$01\bar{1}8$	1.7023	1.71	1.72	1.7254	1.7215	1.7369
$21\bar{3}1$	1.5152	1.51	1.52	—	1.5199	1.5271
$12\bar{3}2$	1.4926	1.49	1.50	1.5006	1.5006	1.5050
$21\bar{3}4$	1.4114	1.41	1.42	1.4196	1.4217	1.4253
$03\bar{3}0$	1.3432	—	—	1.3516	1.3493	1.3535
$22\bar{4}0$	1.1632	—	—	1.1705	1.1693	1.1722
$40\bar{4}4$	0.9729	—	—	0.9794	0.9776	0.9814
a (Å)	4.653			4.686	4.670	4.689
c (Å)	15.025			15.272	15.205	15.373

a and *c* for monheimite from Bolesław are intermediate compared with the analogous values for siderite and smithsonite. Similar d_{hkl} values were obtained for monheimite from the Montevecchio deposit (Sitzia 1965). These results are consistent with chemical analysis and Vegard's law.

Infrared spectroscopic investigations

Infrared absorption spectra were obtained with a UR-10 (Zeiss-Jena) spectrometer, using KBr discs technique. Figure 1 shows a fragment of absorption spectrum in the wave-number region 700—900 cm^{-1}, in which ν_4 and ν_2 absorption bands, the most typical of anhydrous carbonates, appear.

Alongside of monheimite absorption bands at 741 cm^{-1} (ν_4) and 868 cm^{-1} (ν_2) there occur strong absorptions owing to the presence of dolomite admixture (close to 730 and 880 cm^{-1}). They are visible as inflexions on the slopes of monheimite bands.

According to Moenke (1962), the ν_4 and ν_2 bands of smithsonite occur at 743 and 870 cm^{-1} resp. whereas those of siderite at 737 and 865 cm^{-1} resp. The absorption bands recorded for monheimite from Bolesław take intermediate values suggesting, as X-ray data do, that it is an intermediate member of the smithsonite — siderite series.

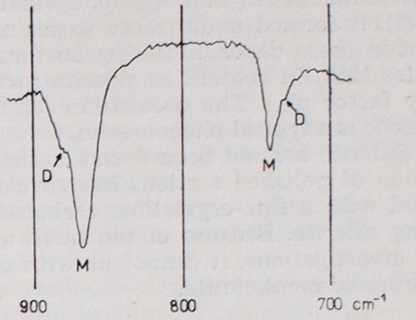

Fig. 1. IR absorption spectrum of monheimite from the Bolesław Mine
M — monheimite, *D* — dolomite admixture

Moenke and Żabiński (1963) found that isomorphic substitution of Zn^{2+} by Fe^{2+} in the crystal lattice of smithsonite has little effect on the position of its absorption bands. These authors recorded a value of 742 cm^{-1}* for the ν_4 band of monheimite from the Matylda mine near Chrzanów.

CONCLUSIONS

Monheimite found in the Bolesław deposit is an intermediate member of the isomorphous series smithsonite — siderite, showing a slight prevalence of Fe over Zn atomic fraction. In spite of this prevalence, the authors are inclined to treat it as ferrous smithsonite rather than zinc siderite because in the range $(Zn_{0.5}Fe_{0.5})CO_3$ — $FeCO_3$ the series in question seems to be discotinuous (Sitzia 1965).

The presence of monheimite in the Bolesław deposit, although its amount is small, provides some interesting information regarding the genesis of the deposit. Its occurrence in the part of the deposit not subject to weathering implies that it is a primary mineral, owing to endogenic ore mineralization. This statement is also substantiated by its close association with sphalerite — marcasite mineralization in cavernous dolomites, in which it ends the cycle of ore mineralization. Its appearance testifies to changes of the conditions under which ore mineralization proceeded. The precipitation of monheimite was presumably promoted by an increase in the Eh caused either by a decrease in the amount of sulphide sulphur which combined with Fe and Zn, or by the influx of surface water circulating in the Roethian dolomites and its mixing with the hydrothermal solution. It is worth noting that the final stage of mineralization involved precipitation of barite and this process requires an oxidizing environment. However, monheimite and barite have never been found together. From the general development of mineralization is can be inferred that monheimite is older than barite since it is associated with sphalerite — marcasite mineralization and its presence is an indicator of initiating changes of the physico-chemical conditions of mineralization.

The appearance of carbonates in the final stages of mineralization is typical of a great many ore deposits. Siderite rich in Zn (up to 5.6% ZnO)

* Due to a misprint, a value of 442 cm^{-1} was given instead of 742 cm^{-1} in the paper of Moenke and Żabiński (1963) (pers. comm.).

was found in Au and Ag epithermal vein deposits in Japan (Shikazono 1977). It formed under more oxidizing conditions than pure siderite present in these deposits. Basing on thermo-chemical data, Shikazono (1977) states that Zn content in siderite increases with increasing oxygen fugacity factor (f_{O_2}). The coexistence of barite or even haematite with such siderite is a typical phenomenon.

Siderite has not been found in the Bolesław deposit. However, examination of polished sections has revealed that the caverns are sometimes filled with a fine-crystalline carbonate mineral of brown colour, resembling siderite. Because of too small an amount of this mineral available for investigations, it cannot be with confidence wheather it is siderite or weathered monheimite.

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O WYSTĘPOWANIU MONHEIMITU W ZŁOŻU RUD Zn-Pb BOLESŁAW KOŁO OLKUSZA

Streszczenie

W złożu Zn — Pb Bolesław stwierdzono występowanie monheimitu $(ZnFe)CO_3$ wśród okruszcowanych brekcji w dolomitach retu. Znajduje się on tam na ściankach kawern, a także często na sfalerycie tworząc naskorupienia. Kawerny są drobne o rozmiarach od kilku do kilkunastu milimetrów (fot. 1, 2).

Pod mikroskopem można obserwować, że naskorupienia monheimitowe tworzą cienką powłokę o grubości od 0,5 do 3 mm, na krystalicznym wtórnym dolomicie i sfalerycie (fot. 3, 4). Tam gdzie występuje markasyt można prześledzić następstwo: markasyt — dolomit — sfaleryt — monheimit.

Przybliżony wzór monheimitu jest następujący: $(Zn_{0,45}Fe_{0,54})CO_3$, a zawartość Zn i Fe wynosi odpowiednio: 25,3 i 26,6% wag.

Z tabeli 1, gdzie zamieszczono wartości d_{hkl} i parametry komórki elementarnej a i c badanego minerału widać, że są one pośrednie w stosunku do analogicznych wartości dla syderytu i smitsonitu.

Położenie pasm absorpcji w podczerwieni również przybiera dla monhemitu wartości pośrednie między odpowiednimi wartościami dla syderytu i smitsonitu.

Wykonane badania wskazują, że monheimit rozpoznany w złożu Bolesław stanowi środkowe ogniwo szeregu izomorficznego smitsonit — syderyt z nieznaczną przewagą udziału atomowego Fe nad Zn.

Występowanie monheimitu w partii złoża nie objętej wietrzeniem pozwala przypuszczać, że może to być minerał pierwotny związany z endogenicznym procesem mineralizacji kruszcowej. Przemawia za tym również jego ścisły związek z mineralizacją sfalerytowo-markasytową w dolomitach kawernistych gdzie kończy on cykl mineralizacji kruszcowej.

OBJAŚNIENIE FIGURY

Fig. 1. Widmo absorpcyjne w podczerwieni monheimitu z kopalni Bolesław
M — monheimit, *D* — domieszka dolomitu

OBJAŚNIENIA FOTOGRAFII

Fot. 1. Kawerniste dolomity retu z kopalni Bolesław. 1/2 wielkości naturalnej
Fot. 2. Kawerniste dolomity retu z kopalni Bolesław. 1/2 wielkości naturalnej
Fot. 3. Mineralizacja kawern w dolomitach retu kopalni Bolesław. Światło przechodzące. 1 nikol. Pow. × 60
1 — monheimit, *2* — dolomit krystaliczny, *3* — sfaleryt, *4* — markasyt, *5* — dolomit mikrytowy
Fot. 4. Mineralizacja kawern w dolomitach retu kopalni Bolesław. Światło przechodzące. 1 nikol. Pow. × 60
1 — monheimit, *2* — dolomit krystaliczny, *3* — sfaleryt, *4* — markasyt, *5* — dolomit mikrytowy

Богуслав БОНК, Марэк НЕЦЬ

О ПРИСУТСТВИИ МОНГЕЙМИТА В МЕСТОРОЖДЕНИИ РУД Zn-Pb БОЛЕСЛАВ ВБЛИЗИ ОЛЬКУША

Резюме

В месторождении Zn-Pb Болеслав было обнаружено присутствие монгеймита $(Zn, Fe)CO_3$ среди брекчии доломитов рэтского возраста. Находится он на стенах каверн и довольно часто совместно со сфалеритом корки. Каверны обычно мелкие, их размеры колеблются от нескольких до 20 мм (фото 1, 2).

В поле зрения микроскопа можно наблюдать, что корки состоящие из монгеймита образуют тонкую оболочку толщиной от 0,5 до 3 мм на кристаллическом вторичном доломите и сфалерите (фото 3, 4). В местах присутствия марказита наблюдается последовательность: маркзит — доломит — сфалерит — монгеймит.

Приближённую формулу монгеймита можно записать как: $(Zn_{0,45}Fe_{0,54})CO_3$, а в весовых процентах Zn составляет 25,3% и Fe 26,6%.

В таблице 1, где показаны величины d_{hkl} и параметры a и c элементарной ячейки изучаемого минерала, видно, что они являются промежуточными для аналогических величин в сидерите и смитсоните.

Положение полос поглощения в ИК-спектре тоже является промежуточным для соответствующих величин в сидерите и смитсоните.

Проведённые исследования показывают, что монгеймит, обнаруженный в месторождении Болеслав, является средним звеном изоморфного ряда смитсонит-сидерит с незначительным преобладанием Fe над Zn.

Присутствие монгеймита в части месторождения, ниже зоны выветривания, делает возможным предположение, что может он быть первичным минералом, связанным с эндогенными процессами рудной минерализации. Свидетельством является тоже его тесная связь со сфалерито-марказитовой минерализацией кавернистых доломитов, в которых является он последним звеном цикла рудной минерализации.

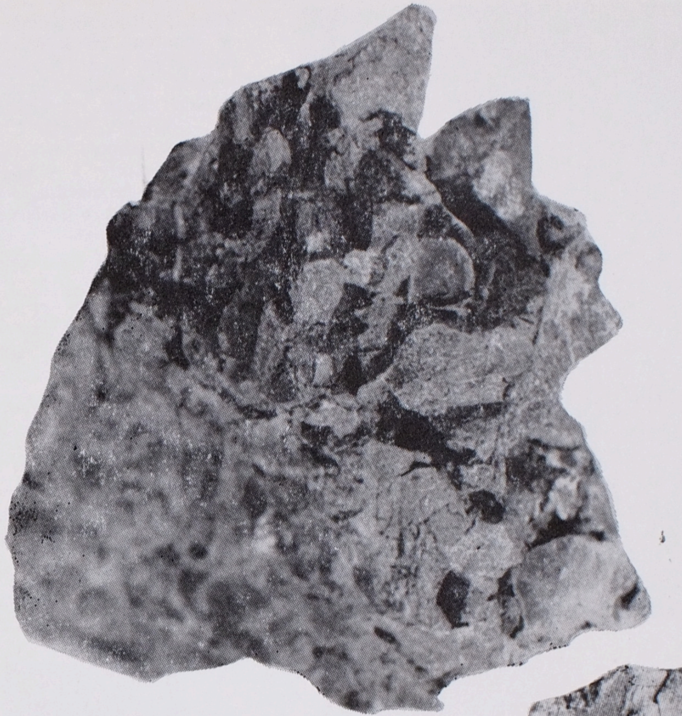
ОБЪЯСНЕНИЕ К ФИГУРЕ

Фиг. 1. ИК-спектр поглощения монгеймита из шахты Болеслав
M — монгеймит, *D* — примесь доломита

ОБЪЯСНЕНИЯ К ФОТОГРАФИЯМ

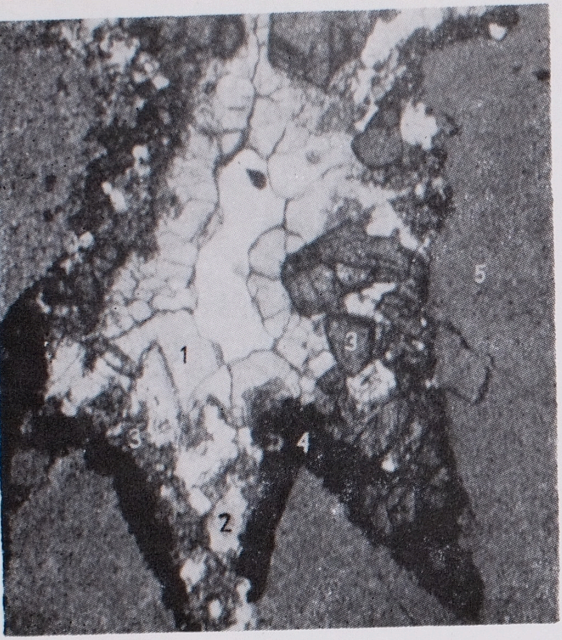
Фото 1, 2. Кавернозный доломит рэтского возраста 1/2 натуральной величины

Фото 3, 4. Минерализация каверн в доломитах рэтского возраста в шахте Болеслав. Проходящий свет. 1 николь. Увеличение около ×60
1 — монгеймит, *2* — кристаллический доломит, *3* — сфалерит, *4* — марказит, *5* — микритический доломит (вмещающая порода)



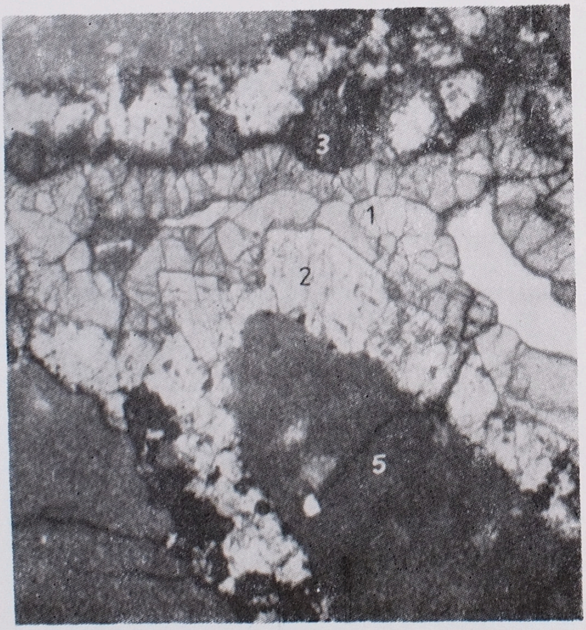
Phot. 1. Cavernous Roethian dolomites from the Bolesław deposit. 1/2 natural size

Phot. 2. Cavernous Roethian dolomites from the Bolesław deposit. 1/2 natural size



Phot. 3. Mineralization of caverns in Roethian dolomites from the Bolesław deposit. Transmitted light. 1 nicol. Magn. × 60

1 — monheimite, *2* — crystaline dolomite, *3* — sphalerite, *4* — marcasite, *5* — micritic dolomite (hostrock dolomite



Phot. 4. Mineralization of caverns in Roethian dolomites from the Bolesław deposit. Transmitted light. 1 nicol. Magn. × 60

1 — monheimite, *2* — crystaline dolomite, *3* — sphalerite, *4* — marcasite, *5* — micritic dolomite (hostrock dolomite