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NEW OCCURRENCE OF CLAUSTHALITE (PbSe) IN THE SUDETES (SW POLAND)

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Abstract. The presence of clausthalite in the area of old mining works near Dziećmorowice in the Sowie Mts (SW Poland) is reported here for the first time. The identification of the clausthalite is based on macro- and microscopic observations, reflectance measurements, chemical analyses and X-ray diffraction data. The clausthalite, together with uraninite, forms veinlets in a breccia comprising <50% calc-silicate rock fragments. Different polishing hardnesses suggest some variation in the mineral structure of individual clausthalite grains. Chemical spot analyses do not reveal elements other than Pb and Se though calculated unit-cell parameters may suggest minor substitution of S for Se.

Key-words: clausthalite, ore mineralization, Dziećmorowice, Sowie Mts, Poland

INTRODUCTION

The area near the village of Dziećmorowice in the Sowie Mts, SW Poland, has long been known to mineralogists and geologists. The mining history of the region dates back to the 16th century when silver-bearing ore was exploited in the Johann Georg mine (Steinbeck 1857; Sachs 1906; Dziekoński 1972). The works were reactivated in 1711 with the opening of the Gabe Gottes mine and two mines, the Gabe Gottes and the Kaiser Heinrich, were reported active twenty years later (Steinbeck 1857; Traube 1888; Petrascheck 1933; Dziekoński 1972). Both were taken over by the State Mining Authority in 1782. In 1856, von Kramsta founded the Gutes Glück Miners Organization. In 1864, bankruptcy brought mining to a close (Sachs 1906).

In over 500 years of prospecting and mining, numerous ore minerals had been described from the Dziećmorowice area. These include Fe, Ni, Co, Bi, Cu, Pb, Zn sulphides, sulphide-arsenides, arsenides and secondary phases, e.g., torbernite, au-

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tunite, annabergite and erythrite. Thus the finding in 2004 of a considerable amount of Pb selenide (clausthalite), a mineral not previously recorded there, was a surprise.

Three occurrences of clausthalite are known in Poland, i.e., in abandoned polymetallic deposits at Kowary and Kletno (Banaś 1965; Mochnacka 1967) and the Fore-Sudetic copper deposits (Kucha 1982; Piestrzyński 1996). The occurrence and the mineralogical characteristics of clausthalite from the Sowie Mts are documented here.

METHODS OF INVESTIGATION

The samples were found on a mine dump near Dziećmorowice (Fig. 1) by Krzysztof Łobos in 2004. The largest sample, weighing about 0.6 kg, contained veinlets of clausthalite and radioactive phases confirmed with a RKP-1 counter. Polished sections were prepared following standard procedures (Muszer 2000). Optical investigations were carried out using a Nikon Optiphot 2-Pol microscope at the Microscopy Laboratory of Ore Minerals of the Institute of Geological Sciences, University of Wrocław. Reflectance measurements were performed with a P101 Nikon photometer using an SiC-858 Zeiss standard.

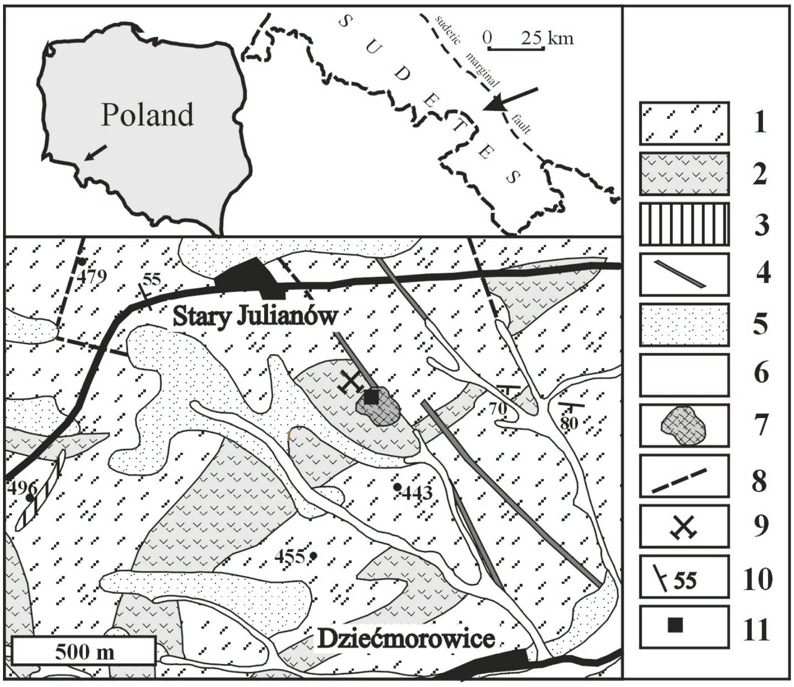

Fig. 1. Geological sketch map of the Dziećmorowice area (after Haydukiewicz et al. 1982)
1 – cordierite-bearing migmatites and homophanous migmatites, 2 – gneisses, 3 – amphibolites, 4 – quartz-barite and calcite-barite veins, 5 – till, 6 – alluvium, 7 – mining dump, 8 – faults, 9 – abandoned shafts, 10 – foliation, 11 – sampling points

Chemical spot analyses were performed with a JEOL JSM-55800LV scanning microscope (beam energy of 20 keV) at the Wrocław University of Technology. Clausthalite for XRD analyses was separated by handpicking from crushed rock under a binocular. About 25 mg of the material was used for the measurements which were carried out at room temperature on a powdered sample using a Siemens D5005 X-ray diffractometer (CoK_α Fe-filtered radiation, 2θ range 25–160°, step 0.02°2θ, counting time 3 s/step). The unit-cell parameter was calculated from eight reflections with a tolerance of 0.05°2θ using the WIN-METRIC programme. The X-ray analyses were performed at the Institute of Geological Sciences, University of Wrocław.

GEOLOGICAL BACKGROUND

The Dziećmorowice village lies within the Sowie Mts block (Grocholski 1967). The area is underlain by highly metamorphosed rocks, mainly gneisses and migmatites with inliers, lenses and tectonic blocks of granulite, amphibolite, serpentinite and calc-silicate rocks (Żelaźniewicz 1987; Gunia 1997). These are cut by porphyries, kersantites, aplites as well as quartz-barite and calcite-barite veins related to the Variscan orogeny (Dathe, Finckch 1906–1921; Haydukiewicz et al. 1982).

The gneisses are mainly biotite gneisses. A two-mica type occurs locally in the southern part of the Sowie Mts block. The gneisses are characterized by layering, lamination and augen structures. They are composed of quartz, feldspars and micas with subordinate garnet, cordierite, kyanite and sillimanite and accessory apatite, zircon and Fe oxides (Kryza 1981, 1995; Żelaźniewicz 1990).

Migmatites with stromatic, phlebitic and nebulitic textures also occur in the area investigated (Gunia 1997; Żelaźniewicz 1987, 1990). According to Smulikowski (1952), they are mostly vein migmatites (arterites) with veins of medium-grained two-mica granite following the gneiss foliation. In places, leucosome segregations pass into pegmatitic streaks or quartz veins. Some of the migmatites are layered rocks with alternate black (biotite) and white (quartz-feldspar) layers (Smulikowski 1952; Gunia 1985). Finckch (1923) suggested that the migmatites of all these types were formed by the metamorphism of greywackes and pelites.

ORE MINERALIZATION

Ore mineralization is associated with quartz-barite and barite-calcite veins which, in places, also contain fluorite (Buch 1802; Fiedler 1863; Förster 1875; Traube 1888; Petrascheck 1933). The veins follow Sudetic dislocations in the gneisses and migmatites of the Sowie Mts block (Kowalski 1977). During the exploitation of the ores, five veins were described and named and their names given to the mines: Gabe Gottes, Haus Hohenzollern, Gut Glück, Leopold, Wilhelmine; the sixth barite vein was not named (Traube 1888). Mining led to the recognition of mineralogical differences between the veins. The precise location of ore minerals within the veins is not possible due to the lack of documentation.

In the Gabe Gottes mine, silver-bearing galena occurred in barite-fluorite-quartz veins together with tetrahedrite, nickeline, smaltite, sphalerite, pyrite and Cu-bearing minerals (Hoehne 1935). In the Gut Glück mine, a calcite vein contained fine-grained smaltite, nickeline, chalcopyrite and, according to Petrascheck (1933), nickeline as inclusions in chloanthite. Chalcopyrite and tetrahedrite were identified in the Haus Hohenzollern vein (Traube 1888). Some tetrahedrite crystals reached 0.5 cm and were coated by chalcopyrite. In the now nonexistent hamlet of Kolonia (Schwarzgraben) near Dziećmorowice, a tetrahedrite-bearing vein also contained stephanite with freibergite (Petrascheck 1933). The Leopold and Wilhelmine veins contained mainly chalcopyrite. Fluorite with chalcocite, tetrahedrite, sphalerite and pyrite occurred in the unnamed barite vein (Traube 1888, Petrascheck 1933). In the Dziećmorowice area, apart from the Ni-Co ores, rammelsbergite with chloanthite and linneite were identified in a calcite vein (Hoehne 1936) and arsenopyrite in a quartz-calcite vein (Hoehne 1942). Annabergite and erythrite were also noted (Hoehne 1951, 1953).

During post-war prospecting by the Polish Geological Institute, the occurrence of bismutite, bismuthinite, magnetite, marcasite, bornite with covellite and radioactive minerals was noted. Lis and Sylwestrzak (1986) described Bi-bearing minerals in a tectonic zone trending 300–340^{o} and dipping 60–90^{o} to the SW. Bismuthinite occurs in 3–10 cm quartz-calcite veins with chalcopyrite, magnetite, arsenopyrite, sphalerite, cobaltite, nickeline, galena, marcasite, pyrite, pitchblende and secondary uranium--bearing phases. Bornite occurs with galena, sphalerite, covellite, chalcopyrite and pyrite in a quartz-barite vein, which follows an NW-SE tectonic zone. Minerals containing radioactive elements were also noted in tectonic zones. Uraninite, together with torbernite and pitchblende, occurs to a depth of 345 meters in a tectonic zone.

According to Petrascheck (1933), the barite veins (and ore mineralization) are related to Early Permian porphyries and the mineral paragenesis reflects low temperature crystallization. The barite-quartz veins formed at 150–220^{o}C based on ^{18}O and ^{34}S isotope data (Kowalski 1977).

THE DZIEĆMOROWICE CLAUSTHALITE

Clausthalite (PbSe) occurs in samples of tectonic breccia found on a mine dump between the villages of Dziećmorowice and Stary Julianów (Fig. 1). It forms irregular veinlets <0.5 cm thick filling spaces between fragments of calc-silicate rocks. The veinlets are particularly numerous in strongly brecciated samples and can comprise up to 50% of a sample (Fig. 2). The veinlets contain also blades of extremely anisotropic graphite and small amount of uraninite. Macroscopically, the clausthalite resembles galena but does not display the characteristic cleavage of the latter. The lustre, higher than that of galena, is typical of clausthalite. A polished surface lacks the triangular cavities typical of galena.

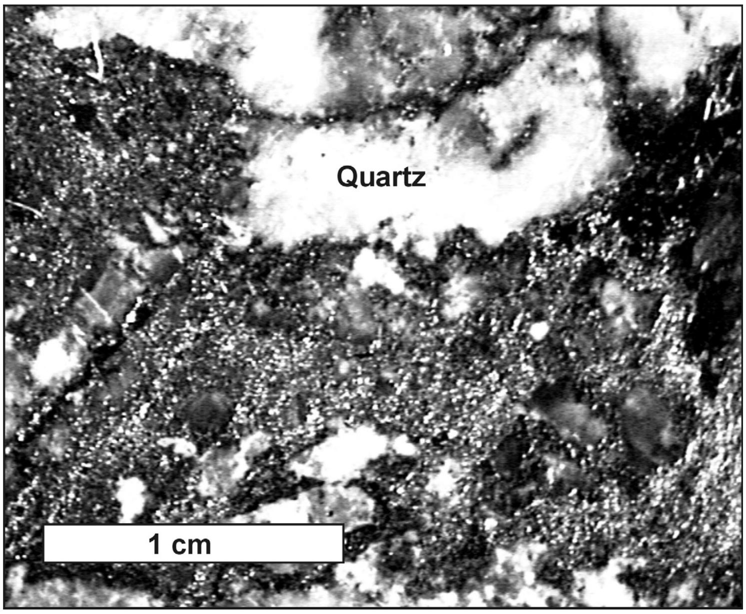

Fig. 2. Tectonic breccia with clausthalite veinlets (grey-silver) from Dziećmorowice.

Characteristically, the aggregates of clausthalite lack macroscopically discernible admixtures of other ore minerals that are typical of hydrothermal deposits. Microscopic observations reveal minute (5–10 μm) uraninites along the boundaries of, and within, the clausthalite grains. The clausthalite grains are xenomorphic and exhibit varying susceptibility for taking polish which may suggest a non-homogeneous composition.

Reflectance measurements in the range 440–700 nm show some differences between the investigated grains and various clausthalite standards (Table 1). The reflectance dispersion curve (Fig. 3) is similar in shape to that of a synthetic clausthalite given by Criddle and Stanley (1993). In reflected light, the clausthalite is isotropic and its reflectance R in white light is significantly higher than that of galena (Table 1).

Spot chemical analyses (Fig. 4) reveal a composition comprising Pb (73.38 wt.%) and Se (26.62 wt.%). No other elements were detected. The chemical composition of the investigated material differs from that of the IMA standard (Criddle, Stanley 1993) only by 0.38 wt.% for Pb and 0.58 wt.% for Se.

The X-ray diffraction pattern for the Dziećmorowice clausthalite corresponds well (Table 2) with the JCDP 85-237 clausthalite standard given by Wyckoff (1964). The unit-cell parameter, calculated within the constraints of a cubic crystal system from the eight reflections indexed (peak 111 was not used), is a = 6.108±0.001 Å, being slightly lower than the values of a typical clausthalite – a = 6.124 Å (*op. cit.*). This may indicate a minor substitution of S^{2-} (ionic radius: 1.74 Å) for Se^{2-} (ionic radius: 1.91 Å). The presence of S in the clausthalite cannot be detected in the EDS spectrum (Fig. 4) due to the much stronger overlapping signal from Pb.

TABLE 1

Comparison of R values for the Dziećmorowice clausthalite and clausthalite standards

λ	Clausthalite from Dziećmorowice	Clausthalite [1]	Clausthalite [2]	Clausthalite [3]	Clausthalite [4]
440	58.9	61.8	58.2	59.0	61.5
460	56.9	60.1	56.4	57.3	60.0
470	56.0	59.25	55.6		59.0
500	53.6	56.7	53.6	54.0	56.3
540	51.3	54.0	51.2	51.3	52.8
546	51.0	53.6	50.9		52.4
580	49.4	51.6	49.5	49.2	50.3
589	49.1	51.15	49.1		49.9
600	48.8	50.7	48.7	48.4	49.5
620	48.3	49.9	48.0	47.7	49.0
650	47.9	49.1	47.3		48.5
660	47.8	48.8	47.2	47.0	48.5
680	47.7	48.4	47.1	47.0	48.4
700	47.7	48.2	47.0	47.2	48.4

[1] Criddle A.J., Stanley C.J. 1993
[2] Criddle A.J., Stanley C.J. 1993
[3] Picot P., Johan Z. 1982
[4] Čvilova et al. 1988

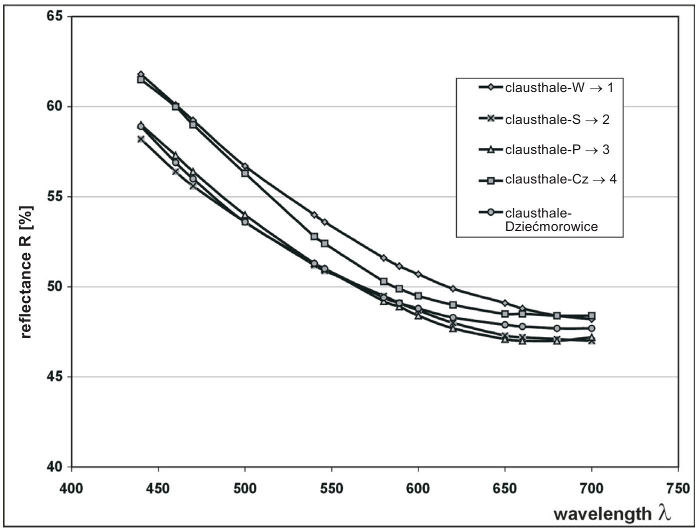

Fig. 3. Reflectance dispersion curves for various clausthalite standards and the Dziećmorowice clausthalite

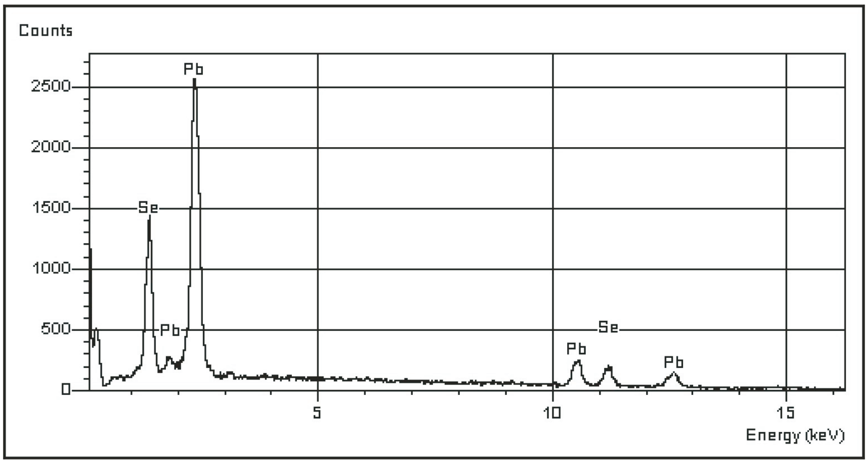

Fig. 4. EDS spectrum of the Dziećmorowice clausthalite

No spatial relationship of clausthalite with the Ni-Co and Pb-Zn-Cu phases that are well known in the Dziećmorowice area was noted. Apart from uraninite, no accompanying ore minerals were seen in the polished samples. Thus, the position of the clausthalite in the crystallization sequence of the ores from Dziećmorowice has not been established.

TABLE 2

XRD characteristics of the Dziećmorowice clausthalite compared with a typical pattern for this mineral (JCDP 85-237)

Clausthalite from Dziećmorowice			Clausthalite[1] JCDP 85-237	
h k l	d obs.	I/I_o	d	I
1 1 1	3.521	19	3.536	34
2 0 0	3.050	100	3.062	100
2 2 0	2.158	23	2.165	75
3 1 1	1.842	8	1.846	18
2 2 2	1.763	6	1.768	27
4 0 0	1.527	5	1.531	12
3 3 1	1.402	2	1.405	7
4 2 0	1.366	8	1.369	34
4 2 2	1.247	4	1.250	25

[1] Wyckoff 1964

The content of clausthalite in the analysed samples is high. For this reason, research focused on the origin of the clausthalite and its relationship with the natural radioactivity of the rocks in the Sowie Mts block has been initiated.

REFERENCES

BANAŚ M., 1965: New site of Pb, Hg, and Cu selenides in the Sudetes. *Bulletin L'Academie Polonaise des Sciences, Serie des Sciences Géologiques et Géographiques*, 13, 4, 267–271.

BUCH L., 1802: Geognostische Beobachtungen auf Reisen durch Deutschlad und Italien. Entwurf einer geognostischen Beschreibung von Schlesien. In: Leopold von Buch's Gesammelte Schriften, Bd. 1, Berlin.

CRIDDLE A.J., STANLEY C.J., 1993: Quantitative data file for ore minerals. London-Glasgow-New York-Tokyo-Melbourne-Madras. Chapman & Hall.

DATHE E., FINCKCH L., 1906–1921: Geologische Karte von Preußen und benachbarten Bundesstaaten. 1:25000 Charlottenbrunn.

DZIEKOŃSKI T., 1972: Wydobywanie i metalurgia kruszców na Dolnym Śląsku od XIII do połowy XX wieku. Ossolineum, Wrocław, 420 pp.

FIEDLER H., 1863: Die Mineralien Schlesiens mit Berücksichtigung der angrenzenden Länder. Breslau, 1–100.

FINCKCH L. 1923: Die stellung der Gabbros und Serpentynite Niederschlesiens und ihre Beziehungen zu den Gneissen und den Graniten. *Jahrbuch Preussischen geologischen L.A.B.* 42, 2, 825–838.

FÖRSTER B.R., 1875: Der Eulengebirgsgneiss und dessen Erzführung insbesondere bei Silberberg (preuss Schlesien). *Jahrbuch für Mineralogie, Geologie und Paläontologie*, 291–295.

GROCHOLSKI W., 1967: Tektonika Gór Sowich. *Geologia Sudetica* 3, 181–234.

GUNIA T., 1985: Pozycja geologiczna bloku sowiogórskiego i jego wpływ na paleogeografię paleozoiku Sudetów środkowych. *Geologia Sudetica* 20, 2, 83–116.

GUNIA P., 1997: Petrologia skał ultrazasadowych bloku sowiogórskiego. *Prace Geologiczno-Mineralogiczne. LXV.* Wyd. Uniw. Wroc. 1–65.

HAYDUKIEWICZ A., OLSZEWSKI S., PORĘBSKI S., TEISSEYRE A., 1982: Szczegółowa mapa geologiczna Sudetów 1:25000, arkusz Wałbrzych. Wyd. Instyt. Geol.

HOEHNE K., 1935: Quantitative chemische und erzmikroskopische Bestimmung von Arsen, Antimon, Zinn und Wismut in vorwiegend schlesischen Bleiglanzen. *Chemie der Erde* 9, 178–185

HOEHNE K., 1936: Über einige Arsen, Nickel, Kobalt, Silber, Wismut und Uranerzführende Kalkspatgänge der Grube Bergfreiheit zu Oberschmiedeberg im Riesengebirge. *Chemie der Erde* 10, 432–474.

HOEHNE K., 1942: Hydrotermale Verezung im Gefolge der Waldenburger Porphyrdurchbrüche. *Zeitschrift Berg.-Hütt.-u. Salinenw*, 90 Abh.

HOEHNE K., 1951: Zwei charakteristische Tonsteinlager in der Flözgruppe des unteren Hangendzuges (Westfal A) und ihre Bedeutung als Leitschichten im Waldenburger Bergbaugebiet (Niederschlesien). *Neues Jahrbuch für Geologie und Paläontologie* 7.

HOEHNE K., 1953: Ein neues Vorkommen von chromhatligen alumohydrocalcit im niederschlesischen Bergbaugebiet. *Neues Jahrbuch für Mineralogie, Monatshefte* 1, 45–50.

KOWALSKI W., 1977: Geochemia, mineralogia i geneza dolnośląskich złóż i wystąpień barytowych. *Archiwum Mineralogiczne* 33, 1, 107–160.

KUCHA H., 1982: Platinum-group metals in the Zechstein copper deposits, Poland. *Economic Geology* 77, 1578–1591.

KRYZA R., 1981: Migmatyzacja w gnejsach północnej części Gór Sowich. *Geologia Sudetica* 14, 7–100.

KRYZA R., 1995: Metamorphic evolution, In: Dallmeyer et al. (eds). Pre-Permian geology of Central and Eastern Europe. Springer Verlag. Berlin-Heidelberg, 351–359.

LIS J., SYLWESTRZAK H., 1986: Minerały Dolnego Śląska. Wydawnictwa Geologiczne, Warszawa.

MOCHNACKA K., 1967: Geologia polimetalicznego złoża w Kowarach (Dolny Śląsk). *Prace Geologiczne Komisji Nauk Geologicznych PAN Oddz. w Krakowie* 40, 1–67.
MUSZER A., 2000: Zarys mikroskopii kruszców. Wyd. Uniwer. Wroc., Wrocław, 233
PETRASCHECK W.E., 1933: Die Erzlagerstätten des Schlesischen Gebirges. *Arch. Lagerst. Forsch,* 59, 1–50.
PICOT P., JOHAN Z., 1982: Atlas of ore minerals. Elsevier, Amsterdam.
PIESTRZYŃSKI A., 1996: Okruszcowanie. Monografia KGHM Polska Miedź S.A. Lubin. CBPM Cuprum, 200–237.
SACHS A., 1906: Die Bodenschätze Schlesiens. Erze Kohlen Nutzbare Gestaine. Leipzig.
SMULIKOWSKI K., 1952: Uwagi o starokrystalicznych formacjach Sudetów. *Rocznik Polskiego Towarzystwa Geologicznego* 21, 67–124
STEINBECK E., 1857: Geschichte des schlesischen Bergbaues, t. I i II. Breslau.
ČVILOVA T.N., BEZSMERTNAJA M.S., SPIRIDONOV E.M., AGROSKIN A.S., PAPAJAN G.W., WINOGRADOV R.A., LEBEDEVA S.I., ZAVJALOV E.N., FILIMONOVA A.A., PETROV W.K., PAJTIAN L.P., SVEŠNIKOVA O.L., 1988: Sprawočnik – opredelitel rudnych minerałov w atroženom swietie. Nedra, Moskwa.
TRAUBE H., 1888: Die Minerale Schlesiens. Breslau.
WYCKOFF R.W.J., 1964: Crystal Structures, 1, 85–89.
ŻELAŹNIEWICZ A., 1987: Tektoniczna i metamorficzna ewolucja Gór Sowich. *Rocznik Polskiego Towarzystwa Geologicznego* 57, 203–348.
ŻELAŹNIEWICZ A., 1990: Deformation and metamorphism in the Góry Sowie gneissic complex, Sudetes, SW Poland. *Neues Jahrbuch für Geologie und Paläontologie* 179, 129–157.

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NOWE WYSTĄPIENIE CLAUSTHALITU (PbSe) W SUDETACH

Streszczenie

Polimetaliczna mineralizacja w rejonie Dziećmorowic (blok sowiogórski) obejmuje siarczki, arsenki i siarkosole Fe, Ni, Co, Bi, Cu, Pb, Zn. Minerały te występują w żyłach barytowo-fluorytowo-kwarcowych, kalcytowych, barytowych, kwarcowo-kalcytowych, które były eksploatowane już w XVI wieku i reprezentowały głównie źródło srebra i miedzi. Po II wojnie światowej stwierdzono także wystąpienia uraninitu oraz minerałów wtórnych (m.in. torbernit, autunit, annabergit i erytryn). Żyły są wieku waryscyjskiego i przecinają gnejsy i migmatyty oraz podrzędnie występujące amfibolity, skały wapienno-krzemianowe i granulity.

W roku 1984, na starej hałdzie między Dzećmorowicami i Starym Julianowem autorzy znaleźli fragmenty skały wapienno-krzemianowej (największy ok. 0,5 kg) z gęstą (do 50% obj.) siecią żyłek zbudowanych z clausthalitu. Jest to czwarte wystąpienie clausthalitu w Polsce, a pozostałe obejmują Kowary, Kletno oraz złoża rud

miedzi na monoklinie przedsudeckiej. Clausthalit z Dziećmorowic poddano badaniom mikroskopowym w świetle odbitym, punktowym analizom chemicznym na mikroskopie scanningowym i rentgenowskiej analizie dyfraktometrycznej.

Ziarna izotropowego clausthalitu są ksenomorficzne i zawierają wrostki uraninitu oraz grafitu, mają refleksyjność wyższą od galeny i nie wykazują obecności trójkątnych wykruszeń, charakterystycznych dla tej ostatniej. Krzywe dyspersji refleksyjności są zbliżone do krzywych podawanych w literaturze, podobnie jak wartość parametru komórki elementarnej *a* = 6,108±0,001 Å (standardowo *a* = 6,124±0,001 Å). Różnica ta może sugerować niewielkie podstawienie siarki za selen, aczkolwiek punktowe analizy chemiczne wykazały obecność tylko ołowiu – 73,38% wag. i selenu – 26,62% wag. Z uwagi na typ wystąpienia w formie luźnych bloczków i brak innych minerałów kruszcowych nie udało się ustalić pozycji clausthalitu w mineralizacji kruszcowej (Ni, Co, Pb, Zn i Cu) rejonu Dziećmorowic. Autorzy podejrzewają, że mimo pokaźnej koncentracji w znalezionych okazach clausthalit mógł uniknąć wcześniejszej identyfikacji z uwagi na makroskopowe podobieństwo do galeny.