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GROWTH OF SPELEOTHEMS BELOW THE KARST-WATER TABLE: CONSIDERATIONS ON THE GENESIS OF SULPHIDE STALACTITES FROM THE UPPER SILESIAN Zn-Pb ORE BODIES

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Abstract: Studies are presented on sphalerite and marcasite stalactites and curtains occurring in some ore bodies from the Upper Silesian Zn-Pb deposits. Forms of these speleothems are described along with the texture of minerals and the types of cavities in which speleothems were grown (original karst caves and open spaces formed during mineralization events). Conditions of their formation are described and genetic concept is proposed. The sulphide speleothems could be formed in the saturated (phreatic) zone, below the karst-water table, in cavities partly or entirely filled with gas.

Key words: speleothems, sulphide stalactites, ore bodies, Upper Silesia

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INTRODUCTION

Among the sulphide incrustations lining dissolution and dilatation cavities in Zn-Pb ore bodies of Upper-Silesia as in other Mississippi Valley-type deposits there occasionally occur forms which resemble dripstones known from carbonate speleothems of ordinary cold-water caves (devined by Moore, 1952; see also Thraikill, 1976). Dripstones are generally regarded as diagnostic of vadose conditions which, indeed, is the case with speleothems of ordinary caves. Although there is a controversy whether the dripstone-like sulphide incrustations in carbonate-hosted ores are parts of the main paragenetic assemblage or have resulted from secondary remobilization processes, the consensus is that such incrustations were produced under vadose conditions (e.g. Bogacz *et al.*, 1970; Smolarska & Chu Tuan Nha, 1972; Sass-Gustkiewicz, 1985). In the following considerations we raise questions with respect to such a generalized conclusion and present an alternative explanation of the incrustations discussed. The paper deals with sulphide speleothems from the Trzebionka and Pomorzany Mines (Fig. 1).

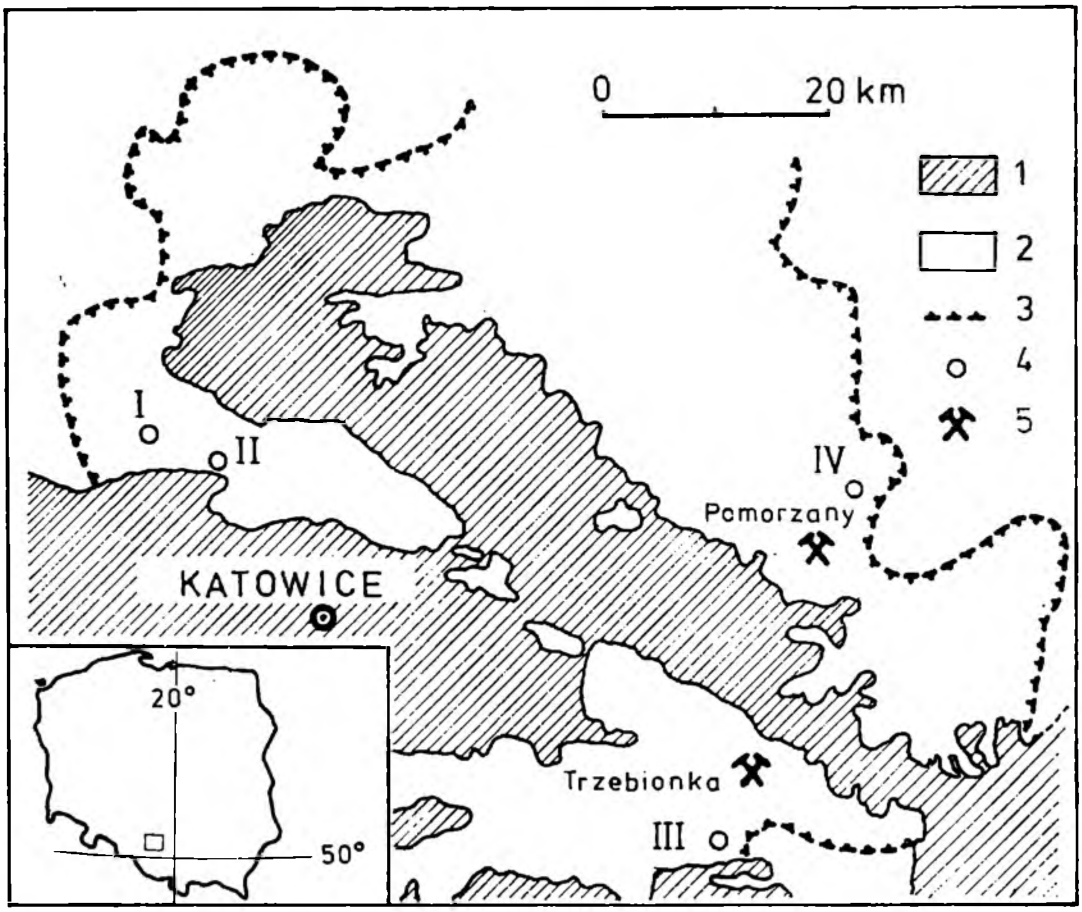

Fig. 1. Geological sketch of Upper-Silesian Zn-Pb ore district (without Jurassic and Cainozoic): *1* — Paleozoic (Upper Carboniferous and Permian); *2* — Triassic; *3* — boundary of ore district; *4* — localities of speleothems according to: *I* — Stappenbeck (1928), *II* — Wernicke (1930), *III* — Bartonec (1906), *IV* — Kuźniar (1925); *5* — localities of present investigations

UPPER-SILESIAN ORE BODIES

Ore bodies enclosing the speleothems consist of sphalerite with galena and marcasite and are hosted within the Triassic carbonate rock, in most cases within the dolomites of Lower Muschelkalk. Typical features allow one to classify these ore bodies as Mississippi Valley-type deposits (see Sass-Gustkiewicz *et al.*, 1982). The ores originated from the interaction between hydrothermal solutions and carbonate rocks. The accumulation of sulphides was associated with the leaching of significant amounts of carbonates.

Two ore-forming processes were distinguished depending on the proportions between leaching and precipitation rates (for details and references see e.g. Bogacz *et al.*, 1970; Dżułyński, 1976; Sass-Gustkiewicz, 1985): (1) metasomatosis – if volumes of both leached and precipitated matters were roughly similar, (2) hydrothermal karst – if leaching prevailed.

Similarity between the "hydrothermal" and "ordinary" karst features are obvious as far as the formation of cave system in carbonate rocks is considered. However, in the case of cavity-filling processes the analogies are much less evident. The bulk of sulphides which make up the ore accumulations in question has been introduced from source outside the host rock. These accumulations reveal features typical of the saturated zone (phreatic zone in the meaning of Choppy, 1985), whereas the cold-water accumulation were formed under vadose conditions, i.e. above karst-water table.

DESCRIPTIONS OF SPELEOTHEMS

Two main and coexisting groups of speleothems were observed: stalactites and curtains. These speleothems occur only within the ore bodies and their host rocks, at the depths up to 60 m below the recent surface. The typical sites

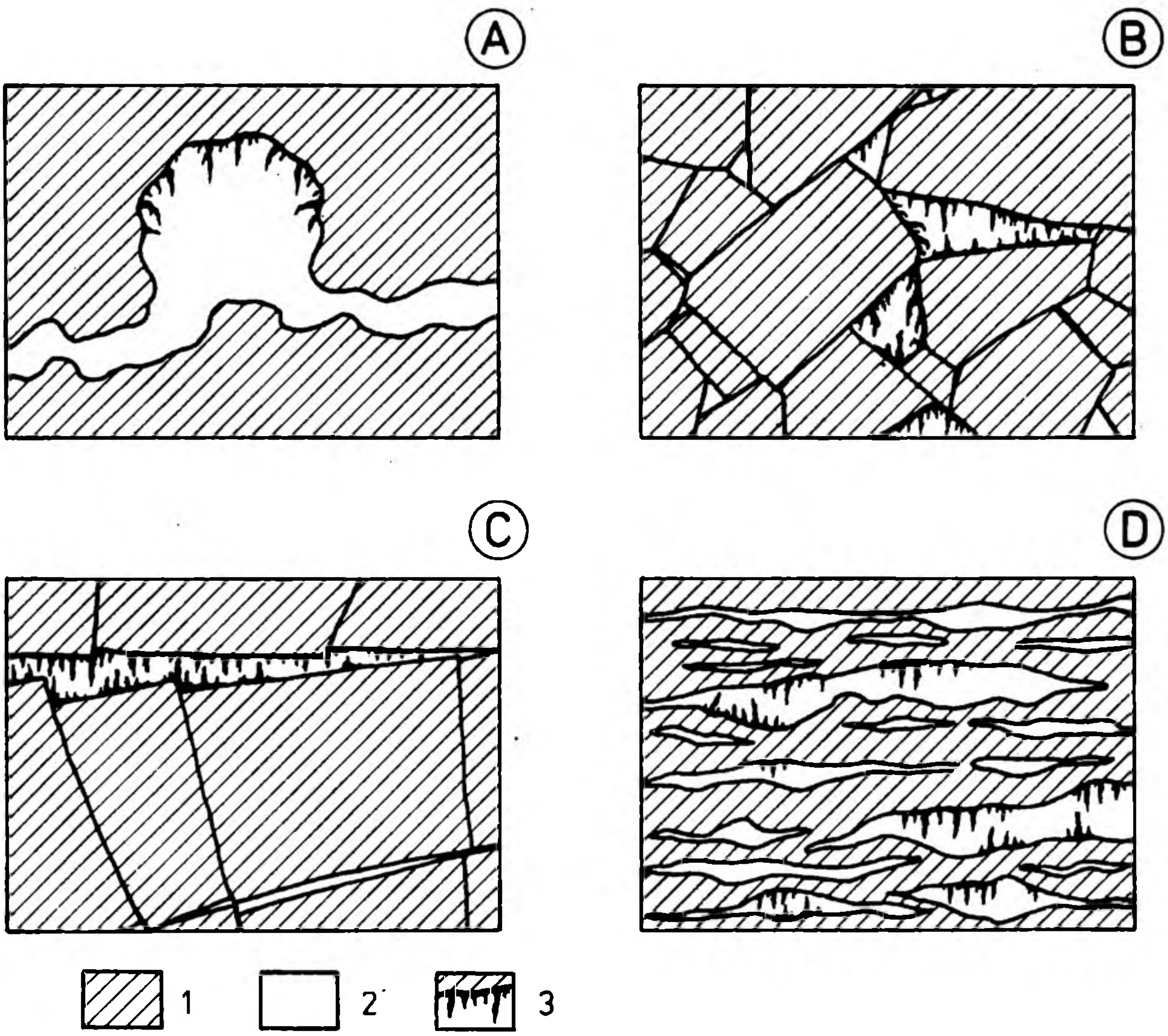

Fig. 2. Types of gas traps within Triassic carbonate formation: *1* – rock; *2* – void space; *3* – speleothems; *A* – part of original cave system; *B* – interfragmental spaces in breccia; *C* – crevices developed on bedding plane; *D* – open spaces within metasomatic sphalerite ore

of speleothems are (Fig. 2): dissolution cave systems, empty voids in solution-collapse and tectonic breccias, crevices developed on bedding planes and fissures (sag fractures), and cavities in metasomatic sphalerite ores.

Based on mineral composition, structures, textures and morphology, two types od sulphide speleothems have been distinguished:

(1) fine-crystalline ones, composed of minute sulphide crystals;

(2) coarse-crystalline ones, composed of large sulphide crystals accompanied by the fine-crystalline carbonates.

FINE-CRYSTALLINE SPELEOTHEMS

These speleothems are usually composed of marcasite, but in the Pomorzany Mine sphalerite ones were encountered, occasionally with some galena (occurrences of such speleothems in Upper Silesia are shown in Fig. 1, see also Kuźniar, 1925; Stappenbeck, 1928; Wernicke, 1931; Sass-Gustkiewicz, 1985). Galena stalactites were described from the Matylda Mine, near Trzebionka Mine (Bartonec, 1906).

The most typical form of the fine-crystalline speleothems are aggregates composed of numerous vertical hair-like stalactites. They are commonly linearly distributed, sometimes in wavy arrangement ("Ziegenbart" – Wernicke,

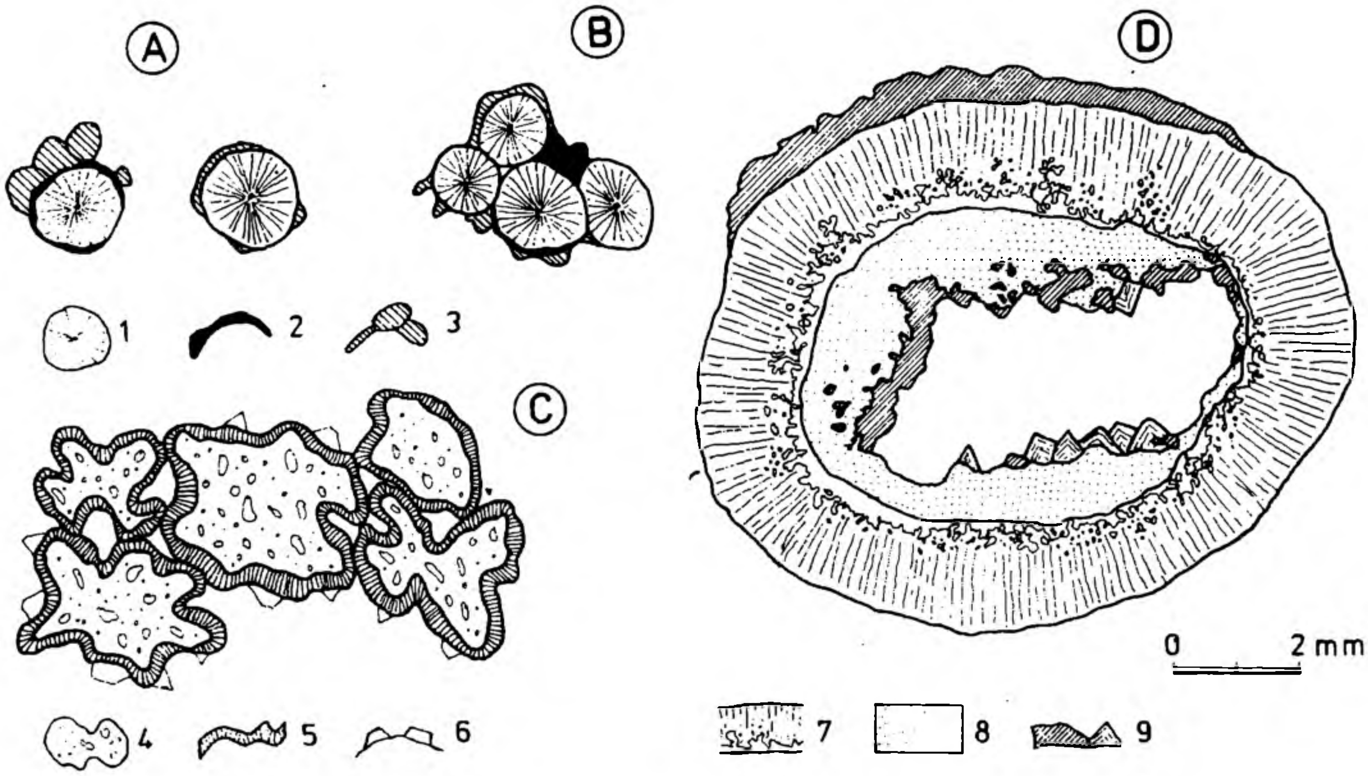

Fig. 3. Transversal sections of "stalactites": single (*A*) and aggregated (*B*) fine-crystalline marcasite forms, aggregate of sphalerite ones (*C*) and coarse-crystalline stalactite (*D*). *1* – marcasite rod; *2* – golden-coloured marcasite crusts; *3* – white marcasite crusts; *4* – porous sphalerite core; *5* – sphalerite crust; *6* – galena crystals; *7* – coarse-crystalline speleothem wall: dendritic carbonate layer covered with radially elongated sphalerite crystals; *8* – carbonate filling; *9* – crusts and druses of sphalerite and dolomite

1931). In some aggregates, the individuals are well developed, whereas in the other their intergrowths form curtains ("drapery macro-texture" – Sass-Gustkiewicz, 1985). Such forms may grow from the roof, bottom and/or the walls of the cavern always showing identical internal structure.

In cross-section the individual stalactites are circular, 0.3 to 2.2 milimetres in diameter (usually about 1 mm). Their length varies from 5 to 170 milimetres (usually about 30 mm). Some specimens reveal radial texture in cross-section. The surface of larger ones is covered with marcasite crust, sometimes composed of several sulphide layers (Fig. 3; Pl. I: 1). Sphalerite stalactites from the Pomorzany Mine are similar (Fig. 3; Pl. I: 2) but differ in size (2–8 milimetres in diameter and 20–50 milimetres long) and have more irregular cross-sections. The internal part of the individual stalactite consists of porous, fine-crystalline mass of sphalerite, occasionally showing concentric structure marked by small galena crystals or marcasite layers.

Sphalerite stalactites occur singly or in groups hanging from roofs of crevices developed along bedding planes (sag fractures). In some places more complicated forms occur (Pl. II: 1), in which the individual stalactites are connected by thin sphalerite curtains. In horizontal section the pattern of such curtain resembles cashmere shawl (Pl. II: 2).

COARSE-CRYSTALLINE SPELEOTHEMS

The most typical examples of this group are sphalerite tubes. Majority of them grow from the roofs of caves (for this reason, they have been called "stalactites" – Sobczyński & Szuwarzyński, 1975), but some may grow from the cave bottoms ("stalagmites" – *op. cit.*) and even from the walls of the open spaces. The "stalactites" are generally straight and vertical (Fig. 4). Moreover, the sphalerite tubes are occasionally inclined at various angles in various directions. Variability of orientation is revealed by some aggregates (Pl. III: 1). The "stalagmites" are generally bent and/or broken. In longitudinal cross-section of some tubes the stages of growth can be observed (Fig. 4). Tubes growing from the walls are bent down, i.e. their root parts are usually almost perpendicular to the enclosing rock surface. The end parts of such forms tend to be inclined to the bottom of the cavern (Pl. III: 2).

In most cases, however, the tubes in question exhibit a complicated internal structure (Fig. 3). The inner part consists of a thin layer of fine-crystalline calcium carbonate. The outer part (several times thicker) is built of radially elongated sphalerite crystals. Contact between both parts is complicated. The outer sphalerite zone may not be continuous. In some individuals only the spots of sphalerite were observed. This situation seems to result from two-stage formation process of such forms. At the first stage, thin carbonate tubes were formed resembling straw stalactites known from recent caves. Then, the change in the environmental conditions (i.e. the appearance of factors facilitating the precipitation of sulphides) led to the crystallization of sphalerite from the

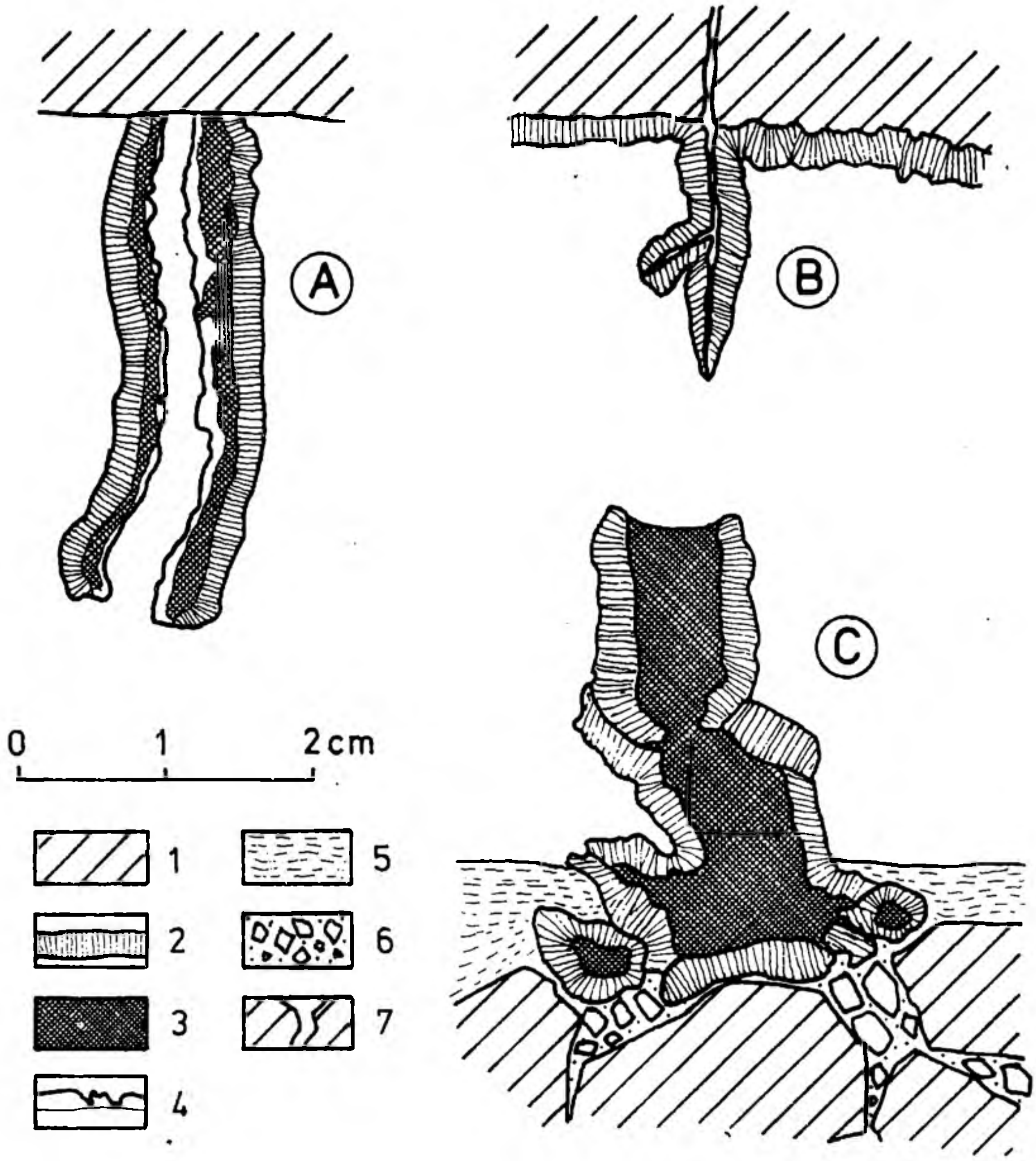

Fig. 4. Longitudinal sections of coarse-crystalline speleothems: "stalactite" (*A*), curtain (*B*) and "stalagmite" (*C*). *1* — dolomite bedrock; *2* — speleothem walls (as Fig. 3D, expl. 7); *3* — carbonate filling; *4* — crusts and druses of sphalerite and dolomite; *5* — fine cave sediment; *6* — dolomitic sand; *7* — dolomite debris

solution which percolated from the centre of tubes through the porous carbonate layer.

The inner parts of tubes are filled with carbonates. Fine-crystalline infilling is a dolomitic limestone. The "stalagmites" are completly filled, whereas in "stalactites" the empty spaces in their central parts are usually preserved. These spaces are encrusted with drusy sphalerite and dolomite crystyls (Figs. 3, 4). Sphalerite druses and crusts sometimes with scattered galena crystals occur also on the outer surfaces of the tubes.

The length of the tubes is usually several centimetres. The longer individuals are rare but one 67 centimetres long individual was found. The outer diameter varies between 7 and 15 milimetres. The thickness of walls varies between 2 and 3 milimetres but may reach even 6 mm in large forms.

Sphalerite curtains were also classified as the coarse-crystalline speleothems. Such curtains consist of two symmetric crusts composed of coarse-crystalline sphalerite (Fig. 4). The crusts are separated by a thin layer of fine-crystalline carbonate or by open crack. Curtains hang vertically from roofs and are usually located along the joints and fissures. Some of them grow directly from the walls. Apart from the simple tabular forms, the complicated curtains integrated with stalactites, aggregates of cross-cutting curtains, wavy or zig-zag ones have been observed.

FORMATION OF SPELEOTHEMS

The speleothems described could not have been formed in the same manner as those which originated in ordinary karst cavities. The speleothems in such caverns develop in a zone of aeration (e.g. Hill, 1976; Cabrol, 1978); this, however, is not the case with the sulphide speleothems under discussion. The formation of sulphide speleothems requires the reducing or, at least, neutral milieu. However, in the karst caves under vadose conditions the atmosphere is generally oxygenated (the free ventilation of cave system is one of the principle condition of speleothems formation). Existence of anoxic atmosphere in the aeration zone for the time span sufficiently long for the precipitation of speleothems seems unlikely.

Next problem is the distribution of speleothems within the host rock. The small agglomerations are randomly distributed, usually at considerable depths below the earth surface. The forms here discussed may grow in all possible directions including the horizontal orientation. Such a development is not the case with ordinary speleothem, the formation of which is gravity-controlled.

The features mentioned above allow us to conclude that the speleothems described were formed in the saturation zone, in trapped gas bubbles (this idea was presented by Forti *et. al.*, 1986). It cannot be precluded, however, that some forms were precipitated in the water-filled cavities supplied with concentrated metalligerous solutions through the micro-cracks and pores (similarly to formation of hydrothermal chimneys in deep sea, e.g. Boyce *et. al.*, 1983). The latter mechanism should be studied in detail as it provides a satisfactory explanation for a variety of speleothem orientations. In this paper authors deal only with the dexelopment of speleothems in gaseous environment.

GAS TRAPS

The formation of traps is conditioned by the impermeability of cave walls. Such situation may exist in parts of the original cave system, interfragmental spaces in breccias, crevices developed on bedding planes and open spaces within metasomatic sphalerite ores (Fig. 2). The existence of gas traps is well-known from the Zn-Pb ore mines in Upper Silesia. In February, 1967, a small cavern with water outflow was encountered in the Olkusz Mine close to the boundary with the neighbouring Pomorzany Mine (Wilk *et. al.*, 1971). Next year a drift, cut about ten metres above in dry rock, entered the breccia body causing the gas-and-rock outburst (composition of the gas was not analysed). After some time, water outflow took place. The rise of water table within the breccia can be explained by the degassing of the trap (Fig. 5).

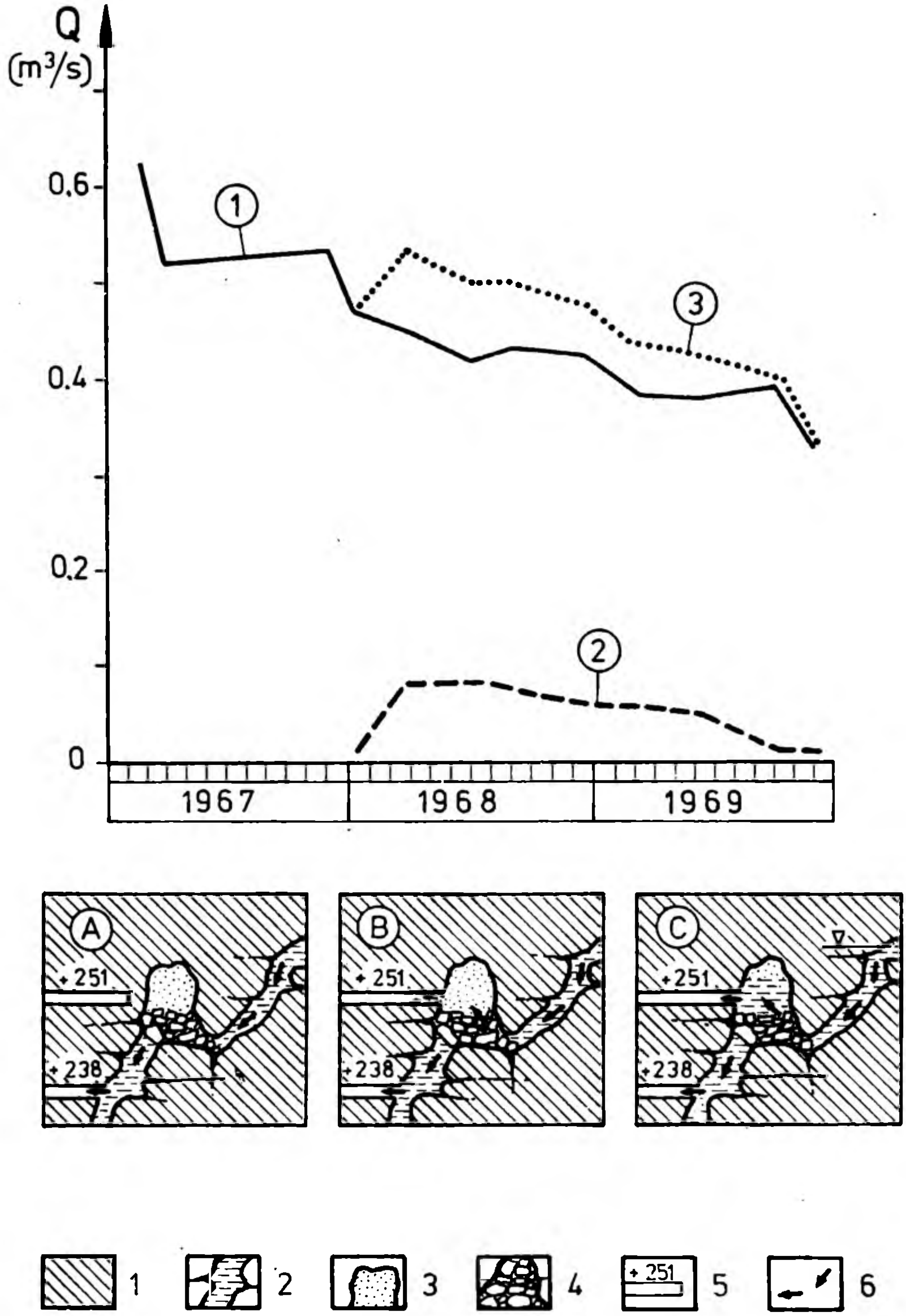

Fig. 5. Diagram of water output on level 238 (line 1), level 251 (line 2) and total (line 3). Interpretation of gas inflow: (*A*) — situation before digging up gas trap; *B* — gas inflow; *C* — water inflow. *1* — carbonate rocks; *2* — caves filled with water; *3* — caves filled with gas; *4* — caves filled with rock debris; *5* — mine gallery (with level designation); *6* — direction of water flow

Similar case is known from the Trzebionka Mine. In 1983 a drift cut in the dry, fine-crystalline dolomites encountered a cavern partly filled with dolomite rubble. The opening was accompanied by a gas outflow. The gas contain 20% of CO_2, other components were not identified. After several hours water outflow took place until the complete flooding of the drift. Carbonate precipitates ("calcite flotante") were on the surface of the outflowing water. These originated from the changes in CO_2 solubility during the pressure drop.

ORIGIN OF GAS BUBBLES

Three mechanisms can be proposed for the formation of gas bubbles in the Triassic aquifer.

(1) Oscillations of water table (and aeration/saturation boundary) could isolate some air-filled open spaces when the water table have risen.

(2) Gases could be generated in saturation zone during chemical and biochemical processes and could migrate and accumulate in the various types of traps. An illustration is the reaction between sulphuric acid (generated by the oxidation of sulphides) and carbonate wall-rock – a common process developing in water-saturated sulphide ore bodies (see Morehouse, 1968; Jakucs, 1977). Such a reaction yields significant amounts of carbon dioxide and presumably explains the origin of gas bubble from the Trzebionka Mine. Reaction of sulphuric acid with sulphides may produce hydrogen sulphide. The same gas is also a product of microbiological activity. Bacteria can also generate methane, carbon dioxide and other gases (see Caumartin, 1963; Leleu & Goni, 1974; Devigne, 1978).

(3) Gas bubbles can be produced during degassing of hydrothermal ore-bearing solutions. Studies of the recent hydrothermal fields, e.g. Salton Sea (White, 1969) and Cheleken (Lebedev, 1975) revealed the high contents of various gases (nitrogene, hydrogen, hydrocarbons, etc.). Apart from gas emanations accompanying the discharge of hydrothermal waters, gas bubbles trapped within the precipitates were reported (see Lebedev, 1975, figs. 86 and 90).

MECHANISM OF SULPHIDE PRECIPITATION

Recent speleothems result from the evaporation of carbonates. Of special importance is the evaporation from dropping karst water. Such a mechanism cannot be neglected in the case of the sulphide precipitates. However, some features must be considered which complicate this simple explanation. First of all, the balance must be achieved between the water input and output of water from the cavity. If the input dominates, the cavity will be filled with water and evaporation will stop. Moreover, the evaporation itself is also difficult to understand as the excess water vapor cannot be removed from the isolated gas bubble.

Therefore, it seems resonable to suggest that the speleothems described above originated from precipitation but without dropping of the solution from the cavity roof. If capillary forces are strong enough to maintain the drop on the roof, bottom or walls of the cavity, chemical reaction may proceeded at the interface between the solution and the surrounding gas. If hydrogen sulphide is present in the gas bubble and heavy metals are contained in the solution, then sulphides may be precipitated. Variable composition of the gas in the bubble may give rise to other chemical compounds deposited as speleothems: carbonates, sulphates, silicates, etc. Experimental data (see Leleu & Goni, 1974) proved that the amounts of hydrogen sulphide generated by the ordinary bacterial activity (i.e. about 10^{-3} mol/day) are sufficient to produce sulphide stalactites of the size described above.

SOURCE OF METALS

Position of the sphalerite and marcasite stalactites and curtains in relation to the formation time of ore bodies is not clear. Such speleothems could have formed either simultaneously with the emplacement of are bodies or during stages of their development, as a result of remobilization processes. In the former case, speleothems would be the integral part of the ore-forming process (see Sass-Gustkiewicz, 1985). In the latter case which seems to be more likely, the metals would be remobilized within the ore bodies by the solutions of a similar composition as that of recent underground waters circulating within the Triassic aquifer. These waters contain 0.2 – 3.0 ppm zinc, 0.0 – 0.9 ppm lead and 2.0 – 3.0 ppm iron (see Adamczyk, 1979). Such concentrations are high enough to produce the reactions of sulphide precipitation in the reducing milieu.

CONCLUSIONS

Although the hypothesis presented in this paper concerns the sulphide speleothems occurring in the Upper-Silesian Zn-Pb deposits, the conclusions are of more general importance and may be applied to other sphalerite, marcasite and galena stalactites (e.g. those described by Pošepny, 1887, or Perna, 1972). It seems highly probable that numerous non-carbonate stalactites occurring in various ore deposits are of similar origin. According to de Lafontaine (*fide* Beck, 1901) 81 mineral species may form speleothems (see also: Ford & Serjeant, 1964; Perna, 1972; Hill, 1976; Osmólski, 1976; Nieć, 1977; Savić, 1986).

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Streszczenie

O POWSTAWANIU NACIEKÓW W STREFIE SATURACJI: ROZWAŻANIA NAD GENEZĄ STALAKTYTÓW SFALERYTOWYCH I MARKASYTOWYCH W GÓRNOŚLĄSKICH ZŁOŻACH RUD CYNKU I OŁOWIU

Jacek Motyka & Marek Szuwarzyński

Praca zawiera wyniki badań autorów nad genezą sfalerytowych i markasytowych, spotykanych w obrębie niektórych ciał rudnych na obszarze Górnego Śląska (Fig. 1). Omawiane nacieki znajdowano dotąd wyłącznie w obrębie ciał rudnych i w ich najbliższym otoczeniu, na głębokościach większych niż 60 m poniżej powierzchni terenu. Spotykano je w poszerzonych fugach międzyławicowych i szczelinach, w nieregularnych kanałach krasowych, w przestrzeniach między okruchami brekcji krasowo-zawałowych i tektonicznych, a także w kawernach wśród metasomatycznych skupień sfalerytu (Fig. 2). W wymienionych pustkach stwierdzono albo pojedyncze formy bądź zespoły liczące od kilku do kilkuset osobników (Pl. I:2, II:1). Przeważają formy podobne do stalaktytów, z którymi współwystępują draperie (np. Pl. II:2, III:2). Są one zróżnicowane pod względem morfologii, składu mineralnego i struktury minerałów. Uwzględniając te cechy, wyróżniono dwie odmiany nacieków siarczkowych:

— zbudowane z minerałów siarczkowych o strukturze drobnokrystalicznej, znane z całej prowincji złożowej (Fig. 3; Pl. I:1, I:2);

— zbudowane z minerałów siarczkowych o strukturze grubokrystalicznej oraz drobnokrystalicznych węglanów, znane jedynie z kopalń „Trzebionka" (Fig. 4) i „Pomorzany" (Pl. III:1).

Wyniki badań skłoniły autorów do przyjęcia hipotezy, że opisane nacieki powstały w strefie saturacji, w uwięzionych tam pęcherzach gazowych. Wska-

zuje na to fakt, że ciała rudne, w obrębie których występują nacieki, w swej historii geologicznej nie znajdowały się w strefie aeracji, co jest uznawane za główny warunek ich rozwoju we współczesnych systemach krasowych. Inną okolicznością przemawiającą na rzecz tej hipotezy jest skład mineralny nacieków. Powstanie skupień siarczków wymaga atmosfery co najmniej obojętnej, a najlepiej redukcyjnej, co jest nie spotykane w przewietrzanych systemach krasowych. Dodatkowym argumentem jest także sposób rozmieszczenia nacieków w masywie skalnym, ponieważ występują one w niewielkich skupieniach, rozmieszczonych bezładnie w przestrzeni, zwykle na znacznych głębokościach w stosunku do powierzchni terenu. Niecodzienna jest także orientacja niektórych nacieków w obrębie poszczególnych skupień, bowiem rozwijały się one we wszystkich możliwych kierunkach, w tym także z dołu do góry albo poziomo, a więc niezgodnie z działaniem siły ciążenia.

Wyróżniono następujące, potencjalne pułapki gazu (Fig. 2): (a) części pustek krasowych (kanałów, jaskiń itp.), (b) przestrzenie między ziarnami w brekcjach krasowo-zawałowych, (c) poszerzone fugi międzyławicowe, (d) pustki powstałe w wyniku niepełnego zastąpienia węglanów podczas metasomatozy.

Dowody na istnienie pułapek zawierających gaz są znane z kopalń „Olkusz" i „Trzebionka". Podczas drążenia jednego z chodników w kopalni „Olkusz" nastąpił wyrzut gazu z okruchami skał, a później zaczęła wypływać woda (Fig. 5). Skład gazu nie został zbadany. Podobny przypadek zarejestrowano w kopalni „Trzebionka". W momencie przecięcia kawerny wypełnionej rumoszem dolomitowym nastąpił wyrzut gazu zawierającego około 20% CO_2. Inne składniki gazu nie zostały określone. Po kilku godzinach zaczęła wypływać woda, która po pewnym czasie zatopiła wyrobisko.

EXPLANATIONS OF PLATES

Plate I

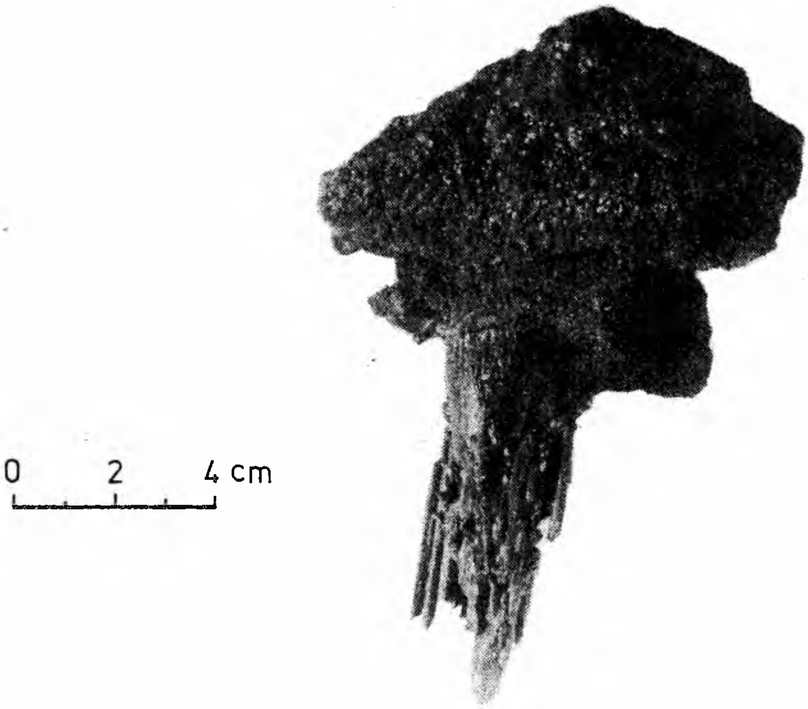
1 — Marcasite stalactites partly covered with marcasite crust. Pomorzany Mine
2 — Fine-crystalline sphalerite stalactites. Pomorzany Mine

Plate II

1 — Aggregate of fine-crystalline sphalerite speleothems. Pomorzany Mine
2 — Horizontal section through speleothem shown above; note characteristic pattern resembling cashmere shawl. Pomorzany Mine

Plate III

1 — Variability of orientation of coarse-crystalline stalactites. Pomorzany Mine
2 — Coarse-crystalline sphalerite tubes growing on cave walls: note characteristic bending of upper specimen. Trzebionka Mine



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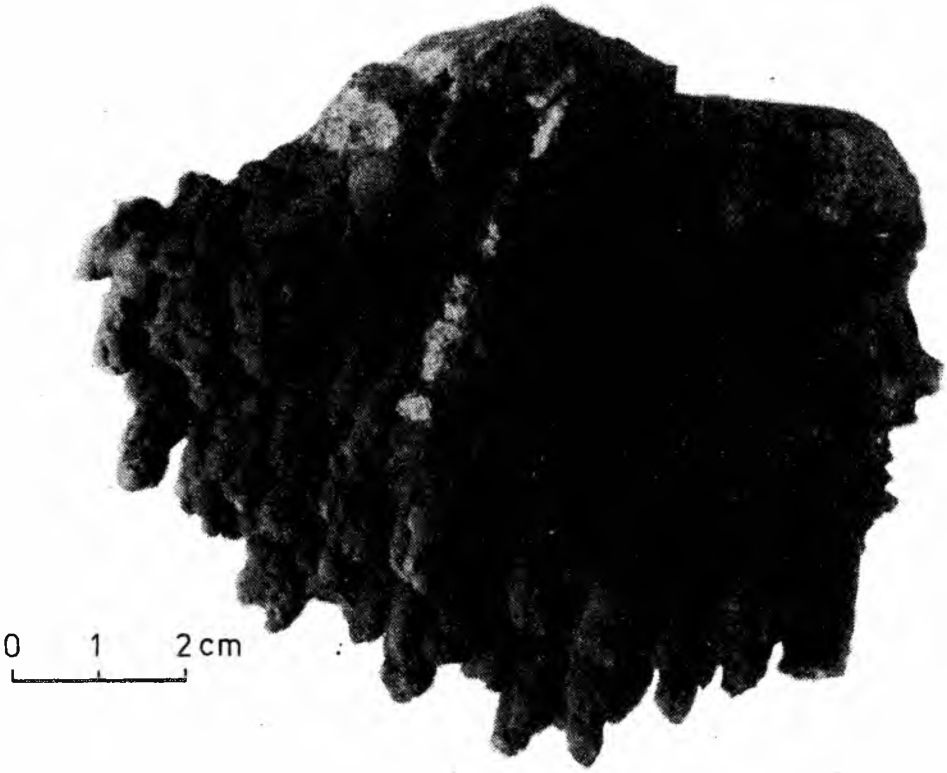

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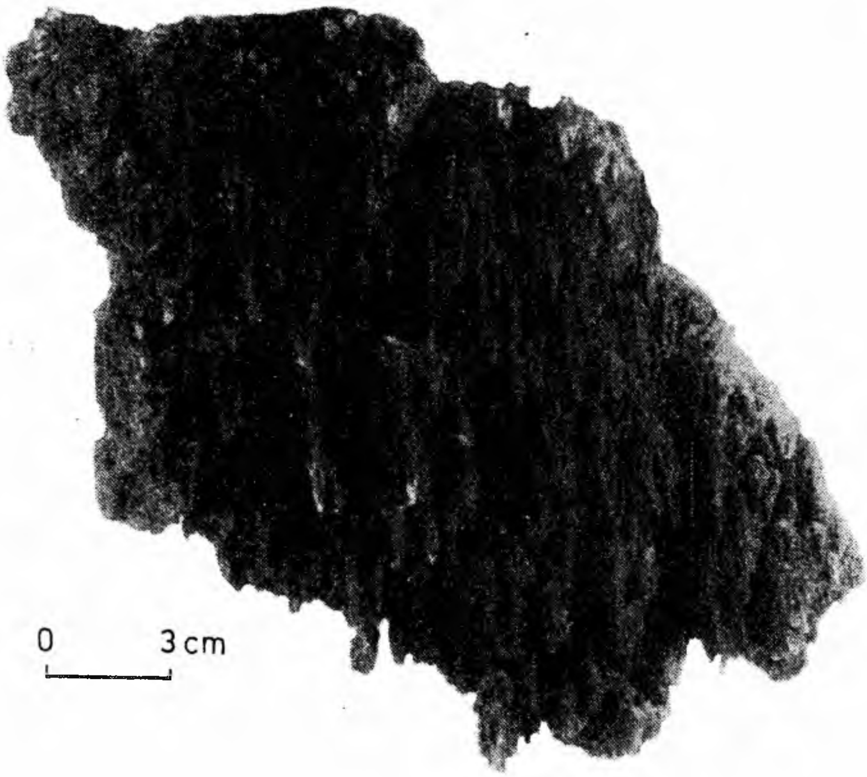

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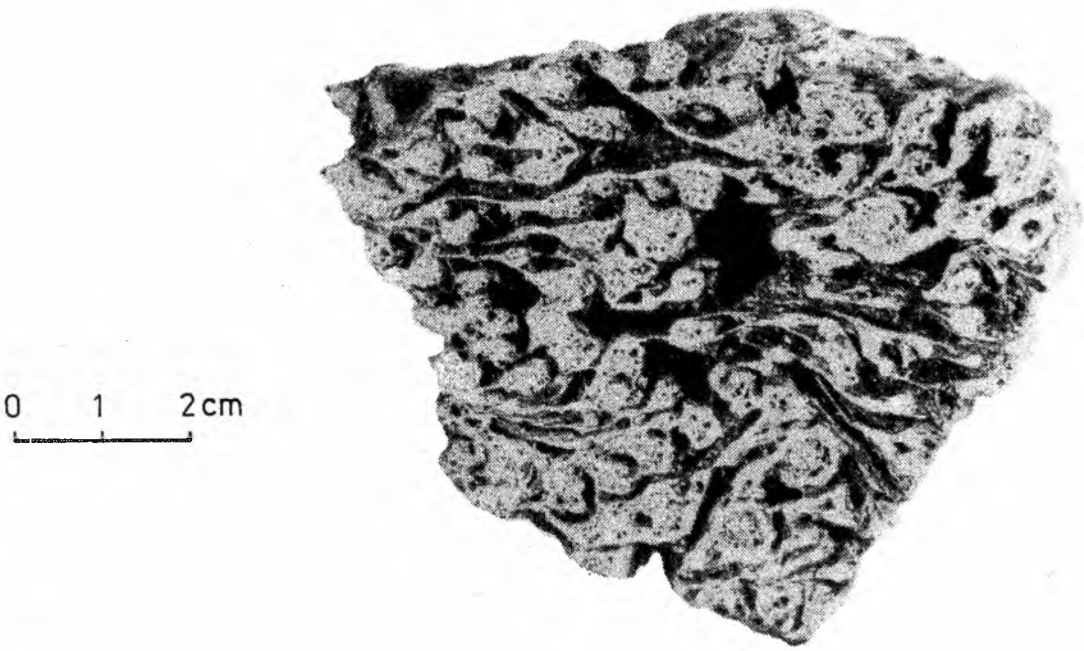

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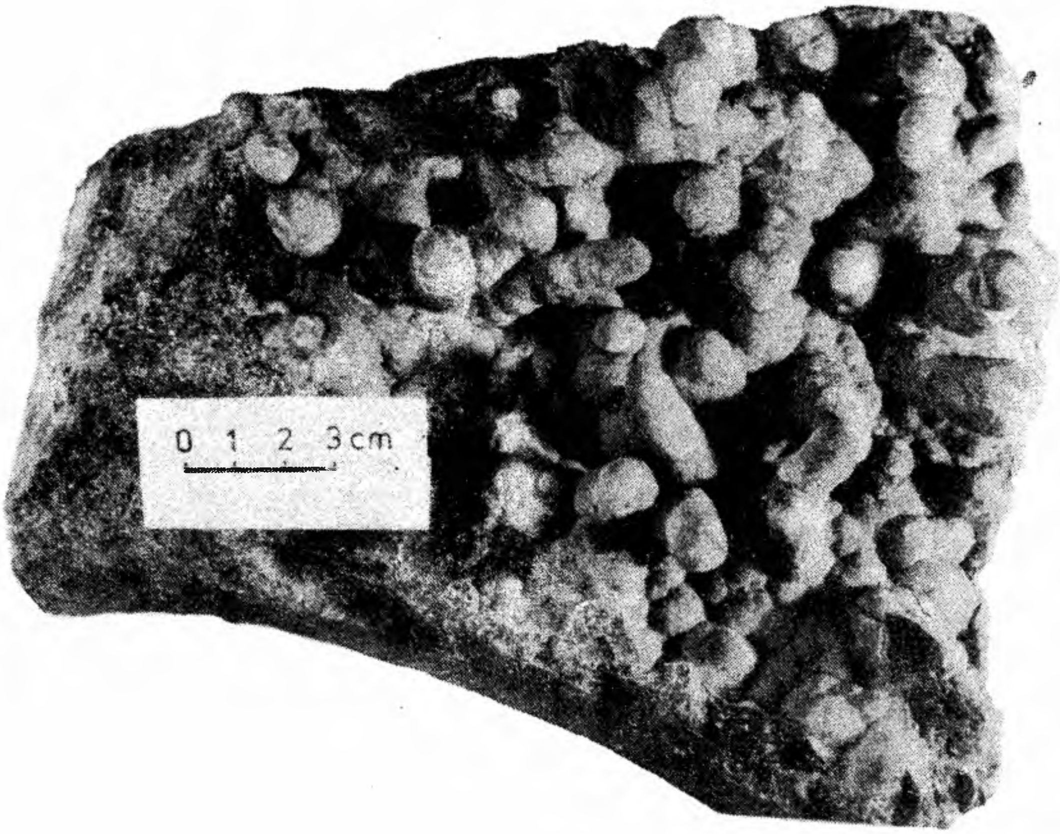

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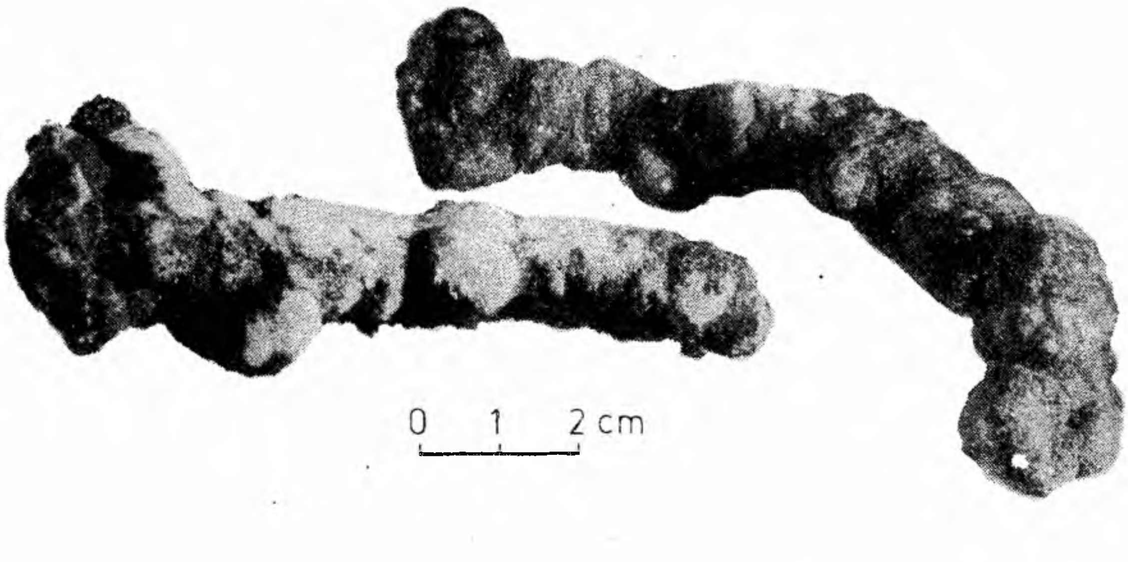

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