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GROWTH OF SPELEOTHEMS BELOW THE KARST-WATER TABLE: CONSIDERATION ON THE GENESIS OF SULPHIDE STALACTITES FROM THE UPPER SILESIAN Zn-Pb ORE BODIES – A DISCUSSION*

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Motyka and Szuwarzyński (1989), following their earlier paper (Forti *et al.*, 1986), discussed the origin of some sulphide speleothems found in Upper Silesian Zn-Pb ore deposits. They concluded that the sulphide stalactites – not always gravity controlled – could be formed in the phreatic zone, in cavities partly or entirely filled with gas. This hypothesis is a good explanation for the seemingly contradictory presence of "typically vadose" speleothems evidently formed during the phreatic ore-forming processes responsible for the bulk of Mississippi Valley-type deposits (cf. Dżułyński & Sass-Gustkiewicz, 1989).

However, besides the unquestionable field observations of the sulphide speleothems in the Silesian mines (see references in Motyka & Szuwarzyński, 1989) and the evidence for the existence of gas bubbles in the phreatic zone of this area, the authors also attempted to explain the mechanism of sulphide precipitation. They wrote: „Recent speleothems result from the evaporation of carbonates [*sic!*]. Of special importance is the evaporation from dropping karst water... If hydrogen sulphide is present in the gas bubble and heavy metals are contained in the solution, then sulphides may be precipitated." (Motyka & Szuwarzyński, 1989, pp. 425-426).

Many recent papers and modern textbooks dealing with karst processes indicate that this hypothesis is based on outdated premises (e.g. Jennings, 1985; Dreybroth, 1988; Ford & Williams, 1989). Thus, without further quotations and a detailed discussion, it is possible to conclude that: (1) recent precipitation of carbonate speleothems generally is the direct result of loss of

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CO_2 from the solution; (2) evaporation of dropping water is negligible in carbonate speleothem precipitation in the static zone of vadose caves, because the cave air is saturated with water vapor; (3) evaporation in carbonate karst is important only near the entrance of vadose caves (dynamic zone of microclimate), resulting in fast precipitation of microcrystalline speleothems having botryoidal (globulites) and wind-oriented stalactite-like forms (anemolites); (4) like carbonate speleothems, coarse crystalline sulphides could not have been precipitated during a fast process of evaporation; (5) the maintaining of solution drops on the cave roof and walls could not be related to capillary forces only. It is controlled by the relation of drop mass to the surface tension, solution/rock adhesion and the capillary forces of the solution; (6) the existence of gas bubbles under phreatic conditions can not be directly related to the balance between water input and output, but is controlled by gas solubility in solution at given conditions (pressure, temperature, and salt solution concentration); (7) hydrogen sulphide from gas bubble does not take part in the sulphide precipitation from solution at the gas/solution interface, but emanation of equivalent hydrogen sulphide from solution into a gas bubble is responsible for the precipitation of metal sulphide from solution at the solid/solution interface.

Instead of the suggested by Motyka & Szuwarzyński (1989) processes, other mechanisms of gas bubble origin and sulphide speleothems precipitation can be proposed. The kinetics of gas bubble formation and speleothem precipitation are controlled by changes of temperature and partial pressure of all gas components in solution during the development of the hydrothermal karst system.

Gas bubbles might have been emanated from solution when the solution pressure in karst channels dropped below the solubility treshold of a particular gaseous component in solution. Probably these bubbles were composed mainly of: (1) CO_2 from the host carbonate rocks formed by reaction with an acid solution; (2) H_2S from brines carrying sulphide matter, presumably as metal and hydrosulphide ions; (3) H_2O vapor from an overheated water solution as a consequence of a drop in pressure; and (4) saturated hydrocarbons, probably responsible for reducing conditions and supporting sulfur activity in the S^{2-} ionic form (Karwowski *et al.*, 1979; Kozłowski *et al.*, 1980).

Sass-Gustkiewicz (1985) distinguished three successive types of sulphide ores in Upper Silesian Zn-Pb ore deposits: (1) extended tabular bodies of metasomatic ore disseminated in host rocks; (2) less extended initial karst deposits abundant with crackle breccias filling little conduits; and (3) mature karst deposits with huge nest-like bodies of rubble breccias and fine internal sediments. Speleothems are typical of the mature karst deposits. They are thus related to the later stages of development of integrated hydrothermal karst conduits.

The pressure drop along with the development of integrated karst conduits, which replaced the earlier diffuse flow in minute pores, seemed to be a cause of gas bubble formation. A slight difference of solution pressure between the minute porosity of the wallrocks and the solution pressure in karst conduits may have persisted for a considerable time. During that time, it is very likely that gas vesicles were formed in the solution and concentrated at the top of karst conduits or in rubble breccia bodies as gas pockets (bubbles). Speleothems were precipitated at the solution/solid rock interface „almost perpendicular to the enclosing rock surface" (Motyka & Szuwarzyński, 1989, p. 421). Wherever pore solution having a higher partial pressure of H_2S were expelled from minute pores into a conduit filled with gas bubble of slightly lower H_2S partial pressure, sulphide speleothems could be formed. These speleothems were precipitated perpendicularly to the rock surface until the gravity force was less than surface tension, adhesion and capillary forces of the expelled drop of the solution. Along with diminishing pressure differences and/or higher flow velocity of the pore solution at the end of a growing speleothem, the gravity force prevails over the molecular forces in the solution and gravity-controlled endings could grow on a horizontal or oblique stalactite (cf. Pl. III, fig. 23 in Motyka & Szuwarzyński, 1989). Probably, most other irregularities in the morphology of the speleothems were caused by competition between the above mentioned controlling forces, which varied during the development of the karst system.

Also, a different explanation is possible for the origin of "stalagmites" which "are generally bent and/or broken" (Motyka & Szuwarzyński, 1989, p. 421). They represent tubes or cones of coarse crystalline sulphides located on the cavern floor and frequently broken and filled with fine crystalline and porous carbonates (Motyka & Szuwarzyński, 1989, fig. 4C). Similar forms were described for the first time from hydrothermal caves near Zbrašov in Moravia, Czecho-Slovakia, by Kunsky and Kašpar (1941) as a "geyser-like stalagmites", and then from hydrothermal caves in Budapest by Panoš (1960). These forms have been called "geysermites" (Panoš, 1960). Later on, similar forms were described by Nemec & Panoš (1967, *fide* Nuñez Jiménez, 1970) and studied in detail by Nuñez Jiménez (1970) from the Cuban cave Gran Caverna de Santo Thomas. All these forms were formed by solutions being forced from the cave bottom, frequently through the internal sediments or along fractures in the flowstone covering the cave bottom (Nuñez Jiménez, 1970, figs. 13 and 15). Such forms were called by Nuñez Jiménez (1970) "tremagmites" (from Greek *trema* – hole). Changes in composition of the solution resulted in precipitation of different minerals inside the axial hole. Aragonite, calcite, barite, gypsum and silica are the most common minerals (Panoš, 1960, 1961; Nuñez Jiménez, 1970). In the case of the Upper Silesian Zn-Pb ore deposits, coarse crystalline sulphides (mainly sphalerite) were the first to be deposited, followed later in the central hole by one or more generations of carbonates (mainly dolomite) or porous sphalerite (Sobczyński & Szuwarzyński, 1975; Motyka & Szuwarzyński, 1989: figs. 3 and 4).

The role of evaporation in the Silesian ore deposits seems to be of subordinate importance. In the case of faster flow through a conduit, the temperature of the solution was probably higher than the temperature of the host rock and evaporation was possible into gas pockets. However, this evaporation was balanced by condensation on the cooler walls of closed gas pockets. This mechanism was studied theoretically by Szunyogh (1984, 1990) and used to explain the spherical shape of chambers in Hungarian hydrothermal caves. This mechanism may be responsible for solution-reprecipitation processes of solids, including primary metasomatic ore disseminated in the pocket walls. Such a process would be a good explanation for the development of flowstone covers on pocket walls but not for the origin of speleothems with a feeding hollow in the centre (both stalactites and tremagmites).

Fluid inclusion studies of sphalerite and calcite (Karwowski *et al.*, 1980; Kozłowski, 1991), indicate solution temperatures of the Silesian ores in the range 90 - 140°C. The composition of the parent fluids range from brines (up to ca. 22 wt. % of NaCl with T_H ca. 123°C) in sphalerite to almost fresh water in the case of drusy calcite with T_H ca. 126°C. The solubility of H_2S is about 500 mg/dm^3 at 90°C and drops significantly with a rise in temperature. This suggests that the initial sulphide-depositing brines had even lower temperature than the fresh water depositing the later drusy calcite. This may suggest that the drusy calcite could have been precipitated by condensation waters according to Szunyogh's hypothesis.

These considerations suggest that the various kinds of speleothems in the Silesian Zn-Pb ore bodies were deposited by solutions expelled from minute pores into cavities filled with gas bubbles. The bubbles were formed due to a drop in pressure, when the disseminated and slow solution flow in pores was replaced by the faster solution flow in a conduit. The evaporation of brines and the subsequent condensation of water on cool rockwalls might be responsible for the origin of some reprecipitates – drusy calcite and gravity controlled sulphide speleothems.

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