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HYDROTHERMAL KARST AND Zn-Pb SULFIDE ORES

Kras hydrotermalny i kruszce cynkowo-ołowiowe w utworach krasowych

Abstract: This paper deals briefly with selected problems concerning the hydrothermal karst processes and the criteria for recognition of such processes in the Mississippi Valley type of deposits.

INTRODUCTION

By definition, the term karst includes the underground solution cavities, collapse breccias and related morphological features consequent upon the removal of soluble rocks. Habitually, when thinking of karst we have in mind a specific terrain showing characteristic relief and a system of caves produced by the action of aggressive, low-temperature meteoric waters. Only incidental consideration is given to caves and related features produced by hot solutions. The system of caverns produced by hot waters of any origin and the associated deformational and mineralogical features that are consequent upon the passage of aggressive hydrothermal solutions are indicated by the term „hydrothermal karst" (see e.g. Kunsky 1957, Maksimovich 1969).

The problem of hydrothermal karst refers among others, to the debatable question of the Mississippi Valley type of deposits (the MV deposits). The conclusion reached in recent years by many investigators is that a considerable part of Zn—Pb ores in these and similar deposits is closely associated with karst structures (see e.g.; Ohle 1951, 1959, Callahan 1964, 1974, Lelu 1966, King 1966, Ford and King 1966, Lagny 1969, 1974, Bogacz et al. 1970, Laurence 1971, McCormick et al. 1971, Rouvier 1972, Ridge and Smolarska 1972, Sass-Gustkiewicz 1974, 1975 a, b). No agreement, however, has been reached concerning the relationship between the karst structures and the ores resident in them.

Three main possibilities are here feasible (W a l k e r 1928): 1. the karst civities originated from hydrothermal solutions penecontemporaneously with the emplacement of ores; 2. the karst cavities were produced by cold meteoric waters before the introduction of hot, ore-bearing solutions and; 3. both, the karst cavities and the ores originated from the action of cold meteoric waters.

The possibilities (1) and (2) are favoured by exponents of hydrothermal origin of Zn—Pb sulfides (e.g. M c K i n s t r y 1955, M c C l e l a n d and W h i t e b r e a d 1965, H o a g l a n d et al. 1965, R i d g e 1968, B o g a c z et al. 1970, S a s s - G u s t k i e w i c z 1974, 1975 a, b). The possibility (3) has met with wide acceptance by geologists who advocate the sedimentary or exhalative-sedimentary origin of sulfides (e.g., L a g n y 1969, 1974, P a d a l i n o et al. 1971, R o u v i e r 1972, B e r n a r d et al. 1972, S m o l a r s k a and C h u T h u a n N h a 1972, S m o l a r s k a et al. 1973, B e r n a r d 1973).

In principle, the first possibility corresponds to the concept of „thermomineral karst" (K u n s k y 1957) or „hydrothermal karst" (B o g a c z et al. 1970). Also the second possibility cannot be regarded as distinctly separated from the hydrothermal karst processes, inasmuch as in the near surface regions the karst structures may result from a combined action of hydrothermal and cold meteoric waters.

The concept of hydrothermal karst is not new insofar as the general thought is concerned (V a n H i s e 1904). It has been touched upon throughout a number of papers devoted to the MV deposits. Indeed, in many descriptions of such deposits, the ore-filled solution cavities are assigned to the same processes whereby the ores have been deposited. Accordingly, if the ores are thought to be the products of hydrothermal solutions then a further inference and the next logical step is the assumption that such solutions are capable of producing the underground karst structures (W a l k e r 1928, L o c k e 1929, T r a i l 1939, O h l e 1951, 1959, M c C l e l l a n d and W h i t e b r e a d 1965, H a g n i and D e s s a i 1966, R a d a b o u g h et al. 1968, R i d g e 1968, B o g a c z et al. 1970, and others). Thus viewed the terms „thermomineral karst" and „hydrothermal karst" are modern expressions only of old ideas inherent to the hydrothermal interpretations of the MV deposits.

The controversy over the origin of the MV deposits has had its confusing impact upon the question of hydrothermal karst processes. With recent trend away from hydrothermal interpretations of Zn—Pb sulfide ores, it is not at all surprising that the concept of hydrothermal karst appears to be totally unacceptable for many geologists who support the sedimentary genesis of the MV deposits. Some of them go that far as to deny the very existence of hydrothermal karst processes (see B e r n a r d 1973, p. 65).

The following considerations are chiefly devoted to some selected aspects of the hydrothermal karst processes and deposition of sulfide ores in karst cavities. No attempt, however, will be made to enter again into the unterminable dispute concerning the origin of the MV deposits. Suffice it to reaffirm at this place the author's opinion, already expressed in earlier publications (see B o g a c z et al. 1970, 1972, 1973 a, b, 1975), that many of the MV deposits are best explained in terms of hydrothermal karst processes.

RECENT HYDROTHERMAL KARST PROCESSES

There is little doubt that hydrothermal solutions may be effective factors in speleogenesis (P á v a i - V a j n a 1931). Large quantities of carbonate sinter deposited by recent hydrothermal springs testify to intensive dissolution and cavernization of carbonate rocks by hot waters (W h i t e 1955).

Caves produced by hydrothermal waters have been recorded from various regions (for references see; M a k s i m o v i c h 1969). In Europe, the best known examples of such caves are presumably those from Hungary and Zbrasov in Czechoslovakia (P á v a i - V a j n a 1931, J a s k ó 1936, K u n s k y 1957, O z o r a y 1961, P a n o š 1961 and others). Admittedly, there is some uncertainty as to how much of the present cave system was formed by hydrothermal solutions and how much resulted from the action of cold or mixed waters. Notwithstanding such uncertainties, the nature of evidence is such as to confirm the conclusions arrived at by many authors that hydrothermal solutions are amongst the powerful agents dissolving carbonate rocks and producing the karst structures [1].

What is more to the point, the cave making hydrothermal waters frequently carry metals and deposit ore minerals (pyrite, marcasite, malachite iron hydro-oxides etc.). Such waters may well be regarded as the hydrothermal, ore-bearing solutions proper (see e.g. O z o r a y 1961, R o t k o 1962).

The hydrothermal caves contain residual materials and various products of solutional disintegration of the enclosing rocks. Such materials constitute the clastic cave deposits which in every respect are similar to those found in „ordinary", cold-water caves. The possible interference of hydrothermal and descending meteoric waters may account for sporadic occurrence of surficial materials in caves of hydrothermal or mixed ori-

[1] In agreement with the opinion held by many authors the term "hydrothermal solution" is used here for solutions of any origin showing temperature above that of ground waters in the near surface region. The question as to how the hydrothermal solutions dissolve and maintain their aggressivenes with respect to carbonate rocks is beyond the scope of this paper. For discussion, the reader is referred to the existing literature.

gin. It is conceivable that such surficial materials may include organic remains (compare: G a l e w s k i and G ł a z e k 1973).

The morphology of recent hydrothermal caves is poorly known. There is, however, a good reason to suppose that the underground karst cavities produced by hot and cold waters may display similar morphologies. This is also true of „karst tectonics", i.e. solution-collapse breccias, gravity faults and sagging fractures resulting directly from solutional thinning and cavern collapse.

The formation of extensive zones of solution-collapse breccias through the action of hydrothermal solutions brooks no denial. However, it should be borne in mind that with temperatures above 100°C, new brecciating factors come into action. These are: hydrothermal explosions and hydraulic fracturing.

The hydrothermal explosions (M u f f l e r et al. 1971) result from rapid expansion of water into steam. Such explosions disrupt the confining rocks and may drive the rock fragments upwards (L l o y d 1972). Parenthetically, it may be added that among the various causes of hydrothermal explosions there is the self-sealing of karst conduits by precipitating ores.

The hydrothermal explosions may lead to „chain reactions". For instance, with temporary increase in pressure, the solution is rammed into the enclosing rock, breaking it up by wedging the fractures open (B r i d g m a n 1952, K e n t s 1964). On the other hand, a sudden drop in pressure may cause the bursting apart of rocks and rock fragments into which the solutions have permeated under high pressure. Such phenomenon has been indicated by P h i l l i p s (1972) as „hydraulic fracturing" and is held to contribute to the formation of crackle and mosaic breccias [2].

CRITERIA FOR RECOGNITION OF HYDROTHERMAL KARST STRUCTURES IN THE MV DEPOSITS

Whilst the observation of recent hydrothermal springs leaves no doubts as to the reality of hydrothermal karst processes, the recognition of such processes in ancient rocks may be a matter of conjecture. Pertinent to our considerations is the question; how to distinguish the hydrothermal karst structures in the MV deposits from those effected by

[2] The karst breccias are here described by means of terms suggested by N o r t o n (1916). These terms are as follows: "crackle breccia" — one showing incipient brecciation with little or no displacement, "mosaic breccia" — whose fragments are detached but match along initial rupture planes, "rubble breccia" — characterized by a jumbled mass of rotated fragments and "pudding breccia" — whose fragments are embedded in a matrix composed of comminuted rock particles.

cold meteoric waters, in view of the fact that the morphology of karst structures is not conclusively diagnostic in this respect.

Important conclusions in this direction can be drawn from: 1. sulfide minerals infilling the cavities; 2. wall-rock alterations around the karst cavities and; 3. the overall geologic structure of the area.

As known, the sulfide precipitates may assume various forms. Such forms find their close counterparts among the calcite speleothems of ordinary caves. The sulfide precipitates have been repeatedly described and illustrated in many publications devoted to the MV deposits. Accordingly no further comment on this subject is here necessary. Suffice it to indicate that the majority of the crystalline or colloform sulfide incrustations are suggestive of phreatic conditions. The sulfide stalactites and stalagmites, diagnostic of vadose conditions, are very minor constituents of the karst ores and, in most instances, they represent the products of secondary remobilization processes rather then primary hydrothermal deposits.

What is the reliability of Zn-Pb sulfides as criteria for recognition of hydrothermal karst processes in view of the fact that the origin of these ores in the MV deposits is still disputable. To avoid begging the question, it is necessary to make to following statement: The presence of sulfide minerals can only then be diagnostic of hydrothermal karst processes if the sulfides are proved to have been precipitated from hot solutions penecontemporaneously with the formation of karst cavities.

The sulfide minerals may give valuable informations concerning the temperature of deposition, provided directly comparable examinations of fluid inclusions, trace element analyses and isotopic studies are carried out on sufficiently large number of samples. It is imperative that the samples are examined only with proper reference to the structure in which they occur. Randomly collected samples are of little value and may lead to grave errors in interpretation.

From the data hitherto collected from various MV deposits it appears that the temperature of sulfide deposition ranges between 75—200°C (see e.g. Roedder 1967, Heyl 1967, Miller 1969 and others). It is, however, to be admitted that the conclusions drawn from such methods are often controversial. In the uppermost parts of the crust (most of the MV deposited are localized near below unconformities!) the paragenetic sequence may be obscured by the appearance of remobilized, low-temperature sulfides superimposed upon those formed at higher temperatures. Thus, the statements of temperatures determined with respect to one sulfide may be incorrect with respect to the other. Accordingly, the best criterion and the real test of the methods in questions lies in what is shown by the relationship between the mineralized karst structures and the geological structure of the area (detailed geological maps!).

Extensive metasomatic wallrock alterations may also yield fair indications with regard to hydrothermal karst features in ancient rocks, in the same way as such alterations serve as guides to hydrothermal ores (see e.g. Lovering et al. 1949) [3].

As noted, in applying the sulfides as criteria for hydrothermal karst it is also necessary to prove that the emplacement of these minerals was essentially simultaneous with the formation of karst structures. Arguments for this can be drawn from the study of mineralized solution-collapse breccias.

MINERALIZED BRECCIAS IN THE MV DEPOSITS

As indicated by Jennings (1971), in no morphogenic system is collapse as significant as in karst. Accordingly, it is natural that in Zn-Pb deposits attributed to karst processes the solution collapse breccias are amongst the most prominent features.

The breccias in the MV depostis have recently been much discussed. Investigations, carried out independently in various ore districts have led to the theory, already widely accepted, of solution origin of most of the breccias in the MV type of deposits (Hoagland et al. 1965, Bogacz et al. 1970, Laurence 1971, McCormick 1971, Lagny 1974, Sass-Gustkiewicz 1974, 1975 a, b). No description of these breccias will be given here (the reader is referred to the existing literature). Only some selected problems shell be discussed, in as far as they refer to arguments concerning the origin of the breccias.

The solution surfaces at the base of the breccias, often stratified cave deposits beneath the rubble (residual clays, stratified ores and dolomitic sand), the dome-like vertical sections and irregular pattern in plan view are among the arguments for karstic origin of the breccia bodies (Sass-Gustkiewicz 1974, 1975 a, b).

The breccias in question did not result from a single collapse. For instance, in the Cracow-Silesian district (one of the representative areas for the MV deposits) it has been shown that the breccias resulted from a sequence of overlapping brecciation and mineralization stages (Sass-Gustkiewicz 1974, 1975 b). The process of brecciation was, in the course of development, spreading outwards, away from the central parts of the breccia bodies. What is more to the point, the successively younger minerals enclose the clastic fragments of earlier mineralization and brecciation stages (Sass-Gustkiewicz 1975 b). The last fact is of particular significance since it clearly shows the essential simultaneity of brecciation and ore mineralization.

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[3] The absence of alterations does not exclude the hydrothermal origin of karst cavities. With vigorous, integrated flow of solutions the alteration halo may be removed.

The formation of mineralized breccias in the Cracow-Silesian Triassic must have resulted from vigorous flow of the ore-bearing solutions (stagnant conditions are incompatible with the formation of solution-collapse breccias!). Inasmuch as the overall geologic picture of the area points to deep-seated sources of mineralizing solutions (see B o g a c z et al. 1975), the breccias in question are „hydrothermal collapse breccias" in the meaning of B r y n e r (1968).

The conspicuous developement of solution-collapse breccias in many Zn-Pb deposits is partly determined by the properties of the host-rock. As known, the commonest host-rock of such ores is a secondary, crystalline dolomite produced by metasomatic replacement of limestones and recrystallization of primary (early-diagenetic) dolostones (B o g a c z et al.,1975). Such dolomite exhibits abundant fractures of diverse origin [4], and may easily be broken into pieces under weak strains. In addition, the dolomite of this kind is prone to solutional disaggregation. The incipient stages of such disaggregation are characterized by the softening of the rock involved. The end-products are loose masses of „dolomitic sand" (see: T w e t o O g d e n and L o v e r i n g 1947, H e y l et al. 1955) which tend to fill the inter-fragmental voids in breccias. The disaggregated mass constitutes also the matrix for pudding breccias which tend to appear near the base of large solution-collapse structures. Significantly, the dolomite fragments suspended in such a matrix show self-brecciation which canot be accounted for by the solution collapse. The fragments are broken into pieces which, although displaced, still match along the planes of rupture. One possible explanation is that the opening of the fractures was initiated by the force of crystallization (G i g n o u x and A v n i m e l e c h 1937, S a w k i n s 1969). However, the work on further extension and wedging the fractures open appears to have been expended by a forcible injection of water-saturated dolomitic grains.

Although the sollution-collapse is presumably the most common, and certainly the most obvious cause of brecciation in the MV deposits, the hydrothermal explosions and hydraulic fracturing cannot be dissmissed from consideration. An objection to such processes hardly lies in the relatively low temperature attending the formation of the MV deposits (most if not all of these deposits are „low-temperature" and „low-pressure" hydrothermal deposits). Brecciation through hydrothermal explosions and hydraulic fracturing is to be expected also under relatively low pressure and temperature if the rocks involved are weakened by disagregation and solutional softening. The problem of hydrothermal explosions and hydraulic fracturing in the MV deposits may be one of recognition rather than existence.

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[4] Some of the fractures are related to processes involved in the formation of the dolomite (very small reduction in volume) and to the emplacement of the earliest sulfides by slow unintegrated transfer of solutions.

Before closing our discussion of the mineralized breccias in the MV deposits few words are needed concerning the debatable question of not uniform distribution of sulfides within the breccia bodies. The existence of barren and mineralized parts within the geometrically single breccia bodies has led some authors to consider the brecciation and mineralization as overlapping but essentially separate processes (H o a g l a n d et al. 1965, S a s s - G u s t k i e w i c z 1974, 1975 b). Admittedly, the breccias, as we see them today, may constitute a heterogeneous assemblage of structures that are not necessarily directly related in origin (notably where the meteoric karst processes are superimposed upon the earlier hydrothermal breccias or vice versa). However, in many instances the ore-bearing and the so called „barren" breccias (many of such barren breccias, on close inspection, contain sulfides) appear to have been „formed by the same solutions of much the same origin" (R i d g e 1968, p. 17). The striking difference in the degree of sulfide mineralization may, at least in some cases, result from the fact the „barren" breccias are the rock-matrix-breccias and having little open space between the rock fragments and blocks, they were less „hospitable" to ore-depositing solutions (R i d g e 1968).

In providing abundant open space for crystallization, the breccias, or at least some parts of them, are among the best receptacles of ores. Indeed, in some regions (for instance the Olkusz Mine in the Cracow-Silesian district — S a s s - G u s t k i e w i c z 1974, 1975 a, b) all the economic deposits are confined to solution-collapse breccias. In this connection it may well be recalled that among the various causes of precipitation of minerals from saturated solutions is the process of brecciacion itself (S h e l l e y 168, P h i l l i p s 1972). It has been shown that brecciation may suddenly reduce the pressure (this may happen with a sudden mass-failure of rocks). The supersaturation thus produced may by sufficient for sulfide crystals to be nucleated. Once the step of nucleation is passed „the cristallization will continue untill the supply of saturated solutions stops" (S h e l l e y 1968).

CONCLUDING REMARKS

The three possibilities concerning the origin of sulfide ores in karst cavities, listed at the beginning of this paper are neither mutually exclusive nor antagonistic. They all are likely to occur in nature (see: W a l k e r 1928, C a l l a g h a n 1974), but differ in their relative importance.

The thesis of this paper is that the hydrothermal karst processes (the possibility 1) are the most important in the formation of Zn-Pb sulfide ores in karst cavities of the MV deposits (compare also B o g a c z et al. 1970).

As noted, the concept of hydrothermal karst admitts an interference of hydrothermal and cold meteoric waters (the possibility 2). This is in keeping with what is known of recent hydrothermal karst processes. Accordingly, it seems resonable to suppose that the hydrothermal ore-bearing solutions, working their way upwards, might have also deposited the sulfide ores in karst structures that had been previously produced by low-temperature surface waters. Evidence supporting such a possibility is found in the well known and common association of the MV deposits with unconformities and ancient karst surfaces.

From the data available, it is impossible to estimate how much of the sulfide ores in the MV deposits was emplaced by hydrothermal solutions in meteoric caves. In the writer's opinion, only a very minor part of such ores can be accounted for in this way.

Ordinary meteoric karst caves and sink-holes are known to act as traps for sulfides precipitated through the action of microorganisms (see e.g., Caumartin 1963) or by leaching of sulfide minerals from the enclosing rocks. Such processes are effective in places where meteoric karst structures are superimposed upon the older, hydrothermal karst features or ore-bearing rocks.

The problem of sulfide remobilization and the formation of karst ores through the action of surface waters („meteorization" processes in the meaning of Rouvuer 1972) is beyond the scope of the present article. It should, however, be emphasized that the hydrothermal karst ores are highly unstable in the near-surface regions. No sooner are such ores emplaced than they may be subject to weathering and other alterations, given the appropriate geologic conditions and the access of meteoric waters. Such alterations involve not only oxidation processes but also intensive redistribution of metals [5].

Although evidence for remobilization is still disputable, on purely geological grounds there is no doubt that the supergene redistribution of metals may result in re-precipitation of zinc and lead sulfides (compare; Lovering 1934). Almost all the karst ores known as presenting evidence of hydrothermal origin, on close inspection, show also evidence of local remobilization. This evidence will not be detailed here. Suffice it to mention few examples from the Cracow-Silesian ore district. Arguments for supergene remobilization are here as follows: 1. the presence of galena precipitates in pre-Tertiary meteoric sink-holes (Panek and Szuwarzyński 1975), 2. the sphalerite dripstones of apparently ve-

[5] It is not out of place to recall here the significance of sulfuric acid that tend to form whenever the sulfide bearing rocks are invaded by oxidizing solutions. The sulphuric acid thus formed reacts with limestones to produce the soluble calcium sulphate and carbon dioxide which, in turn, increases the aggressiveness of ground waters and promotes further enlargement of caves (see, e.g., Evans 1900, Morehouse 1968, Picknett 1972).

ry recent origin (Sobczyński and Szuwarzyński 1975) and; 3. the euhedral galena crystals in the shells of molluscs in the Miocene sediments overlying the ore-bearing dolomite. The above facts lend evidence to re-precipitation of sulfides Such re-precipitation might have been effected, at least partly, by the action of H_2S rich ground waters resident in the Miocene sediments.

The unquestionable existence of the secondary supergene sulfides demands the examination of the part played by meteoric karst processes in the final shaping of Zn-Pb ores. However, in most instances, nearly all the evidence known to the present writer indicates that the rôle of meteoric karst processes is minor relative to that played by the hydrothermal karst processes.

It is realized that the hydrothermal karst processes are not necessarily the ore-forming processes, inasmuch as the hydrothermal solutions may or may not carry metals. In this situation it seems appropriate to reserve the term „thermomineral karst" (Kunsky 1957) for the ore-bearing hydrothermal karst structures, and to use the name „hydrothermal karst" as a comprehensive term to include, both, the mineralized and unmineralized karst structures produced by the action of hydrothermal solutions.

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STRESZCZENIE

Praca niniejsza ma charakter dyskusyjny. Dotyczy ona zagadnienia krasu hydrotermalnego, to znaczy zespołu form krasowych (jaskinie, brekcje zawałowe itp.) powstałych w wyniku przepływu roztworów hydrotermalnych przez skały węglanowe. Zdaniem autora zjawiska krasu hydrotermalnego odgrywają najistotniejszą rolę w procesie tworzenia się kruszców cynkowo-ołowiowych zaliczanych do złóż typu „Mississippi Valley i Śląska". W pracy podano wybrane przykłady współczesnego krasu hydrotermalnego oraz przedyskutowano niektóre sprawdziany rozpoznawcze kopalnego krasu hydrotermalnego. Jednym z takich sprawdzianów jest wypełnienie mineralne jam krasowych oraz zmiany w skale otaczającej struktury krasowe. Minerały siarczkowe można uważać za wskaźniki hydrotermalnych zjawisk krasowych tylko wówczas, jeśli istnieją dowody na hydrotermalne pochodzenie tych siarczków oraz dowody na to, iż siarczki zostały osadzone lub krystalizowały prawie równocześnie z powstawaniem form krasowych. Szczególną uwagę poświęcono w pracy tworzeniu się brekcji w warunkach krasu hydrotermalnego.

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