

Endogene-supergene systems of epithermal deposits and occurrences of acid-sulfate and adularia-sericite type (cases from Bulgaria) — hypothesis and models

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А. Кунов — Эндогенно-гипергенные системы эпитеpмальных месторождений и рудопpоявлений кислотно-сульфатного и адуляр-серицитового типов — гипотеза и модели. (На примерах с территории Болгарии.) Эпитеpмальные месторождения кислотно-сульфатного и адуляр-серицитового типов принадлежат к самым важным источникам сырья и к самым интересным источникам информации для генетических интерпретаций и создания моделей. Широкое присутствие обоих типов на территории Болгарии предоставляет возможность сделать переоценку знаний о них и продолжать их изучение.

В статье обсуждены основные аспекты гидротермального и супергенного метасоматического минералообразования в эпитеpмальных месторождениях и рудопpоявлениях адуляр-серицитового и кислотно-сульфатного типов. На основании литературных данных о месторождениях разных частей мира и информации о болгарских примерах (главным образом — детальной минералого-петрологической характеристики пород) автором представлена идея о существовании эндогенно-супергенной системы в эпитеpмальных месторождениях. Показано, что при определенных обстоятельствах существует возможность рассматривать данные по эндогенным и экзогенным месторождениям в качестве единой общности. Такую общность можно принять как выражение единства между природными явлениями и человеческим мышлением. Показателями формирования и существования эндогенно-супергенных систем являются: их пространственная совместимость, зависимость между эндогенными и супергенными минерализациями, наличие метасоматического замещения и признаков метасоматической зональности, общие структурно-тектонические факторы, геоморфологические и климатические факторы и т.д.

Предложенные модели кислотно-сульфатного и адуляр-серицитового типов эпитеpмальных месторождений в значительной степени отражают изученность соответствующих болгарских примеров, но содержат и элементы широко известных моделей (Hedenquist, Lowernstern, 1994; Hedenquist et al., 1996; Fourmier, 1999; Chevez, 2000). Модели состоят из двух частей (эндогенной и супергенной) с соответствующей

Abstract. The epithermal acid-sulfate and adularia-sericite deposits are among the main sources of raw materials as well as among the most interesting subject of study and genetic modelling and conclusions on the mineral deposits. Both types have a broad occurrence in Bulgaria, which allows an extensive research on them.

Hereafter, discussing the main features of the epithermal mineralization a new hypothesis for an integrated endogene-supergene system is proposed. This idea is based on published evidences from worldwide as well as Bulgarian examples. Its core are the detailed mineralogical and petrological characteristics of the epithermal systems. It is suggested, that under some circumstances both endogene and supergene parts of the systems may be observed as an integrity. This integrity is observed as unanimity between the nature and human mind. Among the main prerequisites for the origin of such systems are spatial compatibility; dependence between endogene and supergene mineralizations; presence of metasomatic replacement and indications for a metasomatic zonation; common structural-tectonic agents; geomorphological and climatic agents; etc.

The proposed models for the epithermal mineralisations are based on Bulgarian occurrences, including some elements from the models of Hedenquist, Lowernstern (1994), Hedenquist (1994), Fournier (1999) and Chavez (2000). These models have an endogene and a supergene part with a respective metasomatic zonation.

The proposed hypothesis is obviously debatable and as any one hypothesis contains facts and suggestions. However, it is also supported by evidences from porphyritic systems, where a transition between hypogene and supergene mineralization was already suggested by Sillitoe (1973).

Some debatable points of the proposed hypothesis could be the cases where a significant gap in time between the primary and supergene mineralizations is established. However, in such cases usually as supergene processes are accepted to be only the recent ones, but those acting simultaneously with the endogene ore forming so far have been neglected. The recent geothermal and hydrothermal volcanic systems are the best proof of the simultaneous occurrence of both endogene and su-

метасоматической зональностью. На вертикальных колонках показано присутствие данного минерала в разных метасоматических типах, а также — установленные и возможные случаи конвергентности. Морфологические типы золотой минерализации и ее взаимоотношения с некоторыми сопутствующими гидротермальными минерализациями показаны символически.

Автор не отрицает дискуссионность предложенной гипотезы ввиду того, что в ней, как и во всякой другой гипотезе, содержатся и факты, и предположения. В тоже время он ссылается на Sillitoe (1973), который считает, что при минералообразовании в порфировых системах гипогенный эффект может перейти в супергенный.

При критических обсуждениях предложенной гипотезы очень часто проявляются ее недопонимание и отрицание. При этом, без ссылок на примеры, которые предоставляют современные гидротермальные системы, акцент негативной оценки обычно ставится на механическое объединение процессов и на разобщенность в миллионы лет между эндогенными и супергенными процессами. Тем не менее единство обсуждаемых типов происходит из смешанного характера флюидов, которого никто не отрицает и из конвекционных процессов. Оно заложено также в участии метеорных вод и атмосферного кислорода в эндогенных флюидах. Все эти факты хорошо известны оппонентам гипотезы, но они исключаются ими из доказательств во всех случаях, когда автор обсуждает общность эндогенных и супергенных систем на примере конкретных условий. В сущности основное критическое замечание оппонентов об огромном (в миллионы лет) разрыве во времени между эндогенными и супергенными процессами относится прежде всего к неосупергенезу, а супергенез, который непосредственно следовал за древними эндогенными минералообразовательными процессами, сбрасывается со счета.

pergene processes. The integrity of both processes is already recognized with the admission of the mixed character of the fluids, the convection and the participation of meteoric waters as well as atmospheric oxygen together with magmatic products into the forming of the endogene epithermal deposits.

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Key words: epithermal systems, acid-sulfate and adularia-sericite type, endogene-supergene systems, model.

Hydrothermal and supergene metasomatic mineral forming in the epithermal deposits — main aspects

During the last 15-20 years Lindgren's classification of the ore deposits (Lindgren, 1933) has been revived. Thus, the definition of epithermal deposits received a new popularity, especially concerning the gold deposits. Based on data from mineral inclusions (Berger, Eimon, 1983) it is broadly accepted that these deposits are formed under temperatures between 150° and 300°C and at 1-2 km depth.

The acquired worldwide data allowed the definition of two main epithermal types of

mineralizations. In both, gold is the main economic commodity. On the ground of the hydrothermal wall rock alterations and the associated to them ore minerals two main types have been distinguished: acid-sulfate and adularia-sericite (Hayba et al., 1985; Heald et al., 1987), respectively high-sulfidation and low-sulfidation (White, Hedenquist, 1995). Both types originate from contrast in chemistry solutions. Under conditions of high-sulfidation, the acid leaching is accomplished by acid solutions with moderate salinity, related to active volcanism (Hedenquist et al., 1994). The ores are hosted into fault zones and are related to the infiltration of solutions from earlier stages of leaching. Beside the residual silica in form of

"vuggy" quartz alteration halos of alunite, kaolinite, pyrophyllite and diaspore are also found (Hedenquist, 1995). Under conditions of low-sulfidation (White, Hedenquist, 1990) the ore-forming fluids have a low salinity, probably close to this of some active geothermal systems (Henly, Ellis, 1983). It is quite possible, that all together the low salinity, almost neutral pH and the conditions of deoxidization (dominantly sulfides) obstruct the transfer of copper, which may explain its lack in the low-sulfidation type of deposits. Several structural differences in both types are also found: dominantly disseminated mineralization for the low-sulfidation type and stockwork form for the high-sulfidation one. The low-sulfidation systems are a good example for physical chemical systems in disequilibrium and influence of chemical kinetics. The expressions of self-organization from mineralogical and structural aspect could be observed on precise targets. Русинов et al. (1966) describe rhythmic-layered quartz-adularia veins as result of self-organization in the Au-Ag deposit Doukat (Ohotsk-Chukotsk volcanic belt). Such rhythmic-layered quartz-adularia veins (with amethyst) are also a characteristic feature of the Madjarovo and Spahievo Ore Fields (Velinov et al., 1983, unpublished data). In „Метасоматизм и метасоматические породы.“ it has been remarked that the ideas of Коржинский (1955) for the "anticipating wave of acid components" and the deposition of the ores after the stage of acid metasomatoses during the late alkaline stage are too general and lack a precise character.

Acid-sulfate type of alteration

This type requires acid solutions (usually under $\text{pH} < 2$). It is also known as enargite-gold (Ashley, 1982), quartz-alunite-gold (Berger, 1986), high sulfuric (Bonham, 1984) and high-sulfidation (Hedenquist, 1987; White, Hedenquist, 1995). For this type the sulfur is of 4⁺ valence and is found as SO_2 . Велинов et al. (1978) describe the sulfide deposits from the Srednogie Zone of Bulgaria (Radka, Elshitsa, Krasen and Chelopech) as a particular "kolchedan" (copper-pyrite) formation*.¹ These deposits are characterized by the following features: alunite secondary quartzite (advanced-argillization), sulfosalts with a high level of oxidation of the arsenic (As^{5+}) — enargite, luzonite, lazarevichite; of the antimony (Sb^{5+}) — famatinite, stibioluzonite, as well as the absence of arsenopyrite, pyrrhotite,

etc. The role of the calderas as a hosting environment for the high-sulfidation type is limited, however, some examples as Rodalquilar (Spain) are given (Arribas, 1995).

Arribas (1995) accepts as crucial the identification of the alunite origin (magmatic-hydrothermal, steam-heated and supergene) or the acid-sulfate alteration, which may be realized by different processes in three main geological environments (Bethke, 1984; Rye et al., 1992). Which concerns the superficial and dynamic conditions of mineral deposition, the three opportunities (including also the supergene one) are possible and the spatial connection of every type of alunite with the ore is different. Therefore, a reliable identification is important for the mineral prospecting.

Adularia-sericite type of alteration

This type occurs from solutions close to neutral salinity ($\text{pH} \sim 7$), low temperature and low salinity (Heald et al., 1987; Berger, Henley, 1989). It has also been named as low sulfuric (Bonham, 1984), low-sulfidation (Hedenquist, 1987; White, Hedenquist, 1995), based on the 2-valence of the sulfur and its occurrence as H_2S . Meyer and Hemley (1967) conferred the different forms of potassium feldspar to the specific feature of the hydrothermal environment. From such point the occurrence of adularia is conferred to hot springs and epithermal deposits.

Hedenquist, Lowenstern (1994) emphasize on the permanent participation of the magmatic component in the geothermal systems of some volcanic arcs. At depth, the fluids of these systems have a neutral pH and low salinity (up to 1 weight % NaCl), but with a varying gas content (up to 4 weight % CO_2 and H_2S). These data as well as the mineralogy of the altered rocks show, that they are analogous to some epithermal systems with low-sulfidation type of deposits.

The existence of both contrast type of wall-rock alterations under epithermal conditions has been theoretically motivated by Каназирски (1996). The same has also defined their genetical incompatibility.

Supergene mineral forming

The evolution of the supergene systems is an extending in time complicated process. It needs a successful combination of convenient climatic environment, mineral composition

and petro-physical properties of the rocks (easily weathering minerals and high filtration properties), convenient hydrogeological and hydrochemical regimes (intensive washing, changing of the chemistry, the migration and exchange of the chemical elements). An essential element is the consideration of the supergene products as metasomatic ones and the search for elements of a metasomatic zonation. In difference to the endogene metasomatic column the deep zones of weathering here are accepted to be external ones. Чухров (1980) suggests that the deposition of minerals in the superficial and shallow part of the Earth occurs from different in origin solutions during their cooling. The deposition of products from them may happened under supergene temperature conditions. This way the endogene minerals in the supergene zone are deposited from ascending fluids. In difference the supergene minerals are deposited from descending solutions. This gives evidence to Чухров (1980) to accept the existence of convergence during the supergene and endogene mineral-forming. As examples, he shows such minerals as kaolinite, halloysite, smectite, palygorskite, zeolites, alunite, jarosite, etc.

Chavez (2000) discusses the supergene oxidation of some deposits, mainly of porphyry-type (copper and molibdenum). In the zone of oxidation the mineral parageneses reflect the geochemical changes of the solutions, which are the source for copper. The vertical and lateral location of the oxides is a function of the time (necessary for the "meteorization" and the accumulation of the metals from the decomposition of the sulfides), the composition and the chemical reactivity of the rocks, the pH of the solutions, the orientation and the density of the faults, the tectonic stability and the vertical fluctuation of the freatic level.

The first purposefully study in Bulgaria of a supergene mineralization, related to alunite rocks was made over the mineral occurrence Krousha from the Western Srednogorie Zone (Велинов et al., 1970). This study notices the role of the pH conditions and the broad access of oxygen for the origin of melaterite, halotrichite and alunogen. Beside the observations on the natural environment this study provides also the results from the laboratory experiments in three systems ($\text{FeSO}_4\text{-H}_2\text{O}$; $\text{FeSO}_4\text{-H}_2\text{O-Al}_2(\text{SO}_4)_3$; $\text{Al}_2(\text{SO}_4)_3\text{-H}_2\text{O}$) in varying pH conditions.

During the followed investigations the supergene mineralizations of some metasomatic rocks from the Srednogorie and the Rhodopes,

especially the so called "secondary quartzites" (advanced argillic rocks) and quartz-adularia metasomatites have been studied. So far, a study on the supergene end products of both epithermal type has not been carried out yet.

Endo-supergene metasomatic systems in the epithermal deposits and occurrences — arising, evolution, hypothesis, a model and discussion

During the hydrothermal and supergene mineral-forming many similar features, relations and interrelations are established. Some similar problems, as supergene metasomatic processes, the replacement of endogene by supergene ore and gangue minerals are discussed. Despite that fact, so far both products of the endogene and supergene minerals from the epithermal systems have never been treated as belonging to a single system. From the numerous definitions on the term "system", hereafter it is accepted as consisting of a multitude of elements, being in relation and interaction between each other and forming a determinate integrity. In their content the systems are complicated objects with different composition, structure and interrelations. In the hereafter presented hypothesis the endo-supergene system is accepted as following:

- an integrity where both acid-sulfate epithermal and supergene alterations occur;
- an integrity where both adularia-sericite epithermal and supergene alterations occur.

Hydrothermal and geothermal systems — genetic alternatives

Data from numerous studies as well as the results from isotopic investigations on the epithermal deposits show, that the hydrothermal fluids in low-sulfidation conditions are dominantly meteoric waters. Some systems also contain water and gases of magmatic origin (Hedenquist, Lowenstern, 1994; White, Hedenquist, 1995). In difference to them, the components under high-sulfidation conditions originate from an oxidized magmatic source, ascending to the close surface with little interaction between the rock environment and the waters at depth (Hedenquist, 1995; White, Hedenquist, 1995). In general the existing models on the epithermal systems re-

flect the idea of White (1955, 1957) as well as other authors for the conventional flow and mixing of both meteoric waters and magmatic fluids.

The geothermal system Broadlands-Ohaaki in New Zealand of low-sulfidation type is one of the best studied in the world (Simmons, Browne, 2000). The system is hosted in Quaternary volcanic rocks and Mesozoic meta-sediments. Browne (1986) relates the deposition of gold and silver with fluids coming from depth and their discharge into veins. Hedenquist (1990) describes the geochemistry and hydrological structure of the system starting from the surface up to its 2.5 km deep geothermal reservoir.

Based on the data from the studies of the high-sulfidation Cu-Au mineralization from Nansatsu (Japan) Hedenquist et al. (1994) show the following conditions being required for the deposition of the high-sulfidation mineralization:

- saturated in fluids crystallizing magma; low pressure and proximity to the surface (1.5-3 km); convenient metal fraction during the fluid transport.

- the fluid must be separated in rich in gases vapors and acid liquids;

- the rich in gases vapor phases (HCl and $\text{SO}_2 + \text{H}_2\text{S}$) during the ascending to the surface have to condense into meteoric waters; the formed acid chloride-sulfate fluids have to interact with the host rocks; the extraction occurs in the permeable zone of mixing;

- due to the mixing of the oxidized and salty liquids with meteoric water, the rich in metals liquids depose Cu sulfides, sulfosalts and Au.

Sillitoe et al. (1996) established the typomorphic mineralizations of the advanced (including also alunite, pyrophyllite, diaspore, native sulfure) and moderate argillic alteration (with adularia) in hydrothermally altered intermediate in composition rocks under condition of 2000 m water depth. This rises the idea for the genetic relation between the massive sulfides and some submarine conditions. As a result of active submarine hydrothermal activity Au, Ag, Sb and Hg have been deposited. Based on these evidences Велинов, Велинова (1999) propose a hypothetical empirical model for the Vitosha volcano-plutonic complex. This model includes some proven occurrences of adularia-sericite type as well as some occurrences of suggested advanced argillic type with high-sulfidation mineralization. This hypothetical opportunity is sug-

gested by the presence of debris from such altered rock in the buried pre-Tertiary river terraces and lake sediments. This model implants also the conclusion for a polygenetic origin of the alluvial gold of Vitosha, with its pragmatic significance.

The isotopic studies of Константинов, Косовец (1995) show, that in most cases the ore deposition with gold is determined by the mixing of gold-bearing fluids with meteoric waters, the last being able to extract and release gold from the host rocks. These data may also explain the partially mantle origin of the substance.

Кутыев, Шарапов (1979) admit that the forming of significant hydrothermal systems requires significant reservoirs and brines of highly mineralized waters of hypogene origin. Their mineralizations is determined by the extraction of different components during their interaction with the hosting rocks and the dissolution of the juvenile fluids. The origin of such systems may also occur during the ellision of inrestitial waters during the tectonical and/or thermal effect of deeply buried rocks.

Иванов, Станев (1982) examine the paleo-hydrogeological relations between the base-metals ore deposition and the volcanism from the Rhodopes and propose a thermo-ellisional model for the base-metals Tertiary mineralizations. The model suggests that the ore-forming hydrotherms are the interstitial waters of the deep hydrosphere during a long-term stable process.

The theoretical aspects for the origin of epithermal gold deposits in hydrothermal intrusion-related systems have been broadly discussed. Sillitoe (1973) and Wallace (1979) provided data for the occurrence of epithermal mineralizations in the shallow part of porphyritic systems. Sillitoe (1992), emphasizes on the numerous already established cases of direct connection between porphyritic and epithermal systems. Following Hedenquist et al. (1998) the porphyritic systems are related to the deep parts and the epithermal ones to the shallow parts of the intrusion-related hydrothermal systems. In the young volcanic arcs some geothermal systems, related to shallow intrusions are established. Data from deep drilling up to 3 km in such settings show that solutions with a pH close to the neutral are dominating. In difference, the active volcanic hydrothermal systems create only superficial high acid condenses originating from fumarol sources. The ultra-acid fluids with pH

from 1-1.5 are rich in Cl and SO₄. Available isotopic studies (Giggenbach, 1992a) suggest that they have been formed from condensation of both magmatic gases and meteoric waters. Hedenquist et al. (1998) accept that such condensation leads to the origin of acid waters, which in order are responsible for the advanced argillization especially in the porphyritic and high-sulfidation deposits.

Каназирски (1996) studied the field observed as well as the theoretically suggested zonation of the advanced argillization from the Asarel porphyry-copper deposit. He is the first who admits the existence of both spatial and genetic relation between both porphyritic and epithermal systems in this deposit. He also accepts that the change in the acidity of the fluids is responsible for the epithermal alterations in the upper part of the porphyritic system.

The metasomatic alterations are an important agent influencing the local re-distribution of the elements (Жаутиков et al., 2000). The gold mineralizations, belonging to different ore formations are accompanied by typical only to them metasomatic alterations. The modelling of the natural processes gives evidences for some practical conclusions. One of them is that the high fineness of the gold and its diverse morphology are characteristic for the lower parts of the ore bodies. The discovery of such gold morphology at superficial levels suggests a deep erosional level.

The model of Fournier (1999) treating the transition between magmatic and epithermal environments differs from all so far known models by its brittle-ductile stage. In sub-volcanic environment (1-3 km) the brittle-ductile stage occurs at temperatures 370-400°C. The fluids, mainly meteoric waters circulate under hydrostatic pressure in a brittle rock environment. The high salinity, mainly magmatic fluids under lithostatic pressure tend to concentrate into ductile rocks. The model suggests an episodic and temporary interruption in the closed brittle-ductile zone, which allows the discharge of fluids to the hydrothermal system.

Both epithermal types differ by the presence of ore as well as gangue minerals. The high-sulfidation type is characterized by the presence of enargite, kaolinite and alunite. In difference the low-sulfidation type contains electrum, adularia and calcite. Even though the temperature of mineral stability tend to be variable in relatively broad ranges, the pH of both environments is sharply different. Furthermore, the ore mineralizations tend to be

connected mainly to the zone of acid alteration (leaching). During the evolution of the systems, the earlier stage leads to the acid wall-rock alteration, in difference the later is the ore-forming one.

Supergene systems

An overview of the studies on epithermal gold deposits, with few exceptions, shows different levels of study of the endogene and supergene mineralizations. Evidently, the supergene mineralizations are better studied only in the porphyritic deposits. Such deposits from the Panagyurishte Ore Region of Bulgaria are rich in copper-containing as well as other supergene mineralizations (Токмакчиева, 1994).

Ферсман (1955) called "zone of hypergene" the upper part of the lithosphere, where the processes occur in low P-T conditions. The thickness of this zone locally may reach few thousands meters. According to Перельман (1961) three types of hypergene migration is found: biogenic, physico-chemical and mechanical. They are in close relation, therefore often they are found together. Of main importance for the migration of the elements are the climate and geological setting. These two agents play a different role concerning the depth. The hosting rock determine to a significant level the intensity of the processes.

In the hydrothermal systems, the hydrothermal fluids prevent the interaction between the atmospheric waters and the ore mineralizations. The starting point, where the zone of oxidation starts to develop is after the end of the hydrothermal stage. At this moment, the descending fluids can get in contact with the ores (Диман et al., 1982). As a result of the intensive oxidation of the metals, the compounds of the secondary hard phases form the zonation. During the following process of steadiness the dissolution slows down due to the forming of stable mineral associations.

Диман et al. (1982) modelling the interaction between atmospheric waters with concrete mineral parageneses comment also the change in the composition of the solutions with time and space. One of their main conclusions is that the acidity of the solutions determines to a significant point the behavior of the gold. If the primary ores miss gold of high finesses, but such is found in the supergene zone, then its supergene origin is quite probable.

There are many examples showing that the formed solutions as well as the ore composi-

tion influence the evolution of the supergene processes. The supergene mineralization from the alunite occurrence Krousha (Western Srednogorie Zone, Bulgaria) as well as the experimental results gave evidence to Велинов et al. (1970) to distinguish the following range of sulfate minerals formed during the oxidation of the pyrite:

pyrite → halotrichite; pyrite → melanterite (halotrichite) → rozenite → somolnokite; pyrite → jarosite.

The supergene processes are characterized by their dual and sometimes quite contradictory role: forming of epigenetic mineral deposits and the destruction of such already formed.

A broadly spread opinion is that in the supergene zone the weathering may lead to the occurrence of weathering crusts of unlimited thickness. However, Ивашов (1995) admits the existence of some barriers limiting this process. Following this hypothesis, the supergene products over the primary rocks play an important role in the preservation of the structure and composition of the primary mineral substance. This is explained by the locking role of the supergene products at a given stage of the process, depending on the scale of the operating supergene systems. As a result the so called quasi equilibrium (stable) supergene systems are formed: primary mineral substance — supergene products. If the supergene influence is not sufficiently intensive and no additional factors occur (e.g. tectonic), then the supergene processes temporary remain in a quasi equilibrium state. In that case the weathering may temporary slow down or even stop. The studies of Ивашов (1995) show that the locking role of the supergene products has a place, relatively to the level of organization of the mineral substance of the supergene systems. The same author formulates the law of the supergene zone: "Each one primary substance being in compact or crystal mineral state in the supergene zone is in a quasi equilibrium state with the supergene hosting environment as a result of the forming of supergene products, which lock further the weathering till the moment, when an additional external impact affects the supergene self-regulating system".

Endogene-supergene systems

The zones of oxidation of the different mineral deposits have been subject to numerous stud-

ies. Beside the supergene minerals formed at the expenses of the endogene mineralization, some supergene minerals occurring at the expenses of the metasomatic rocks have been occasionally described. Despite some obvious relations between the endogene and supergene mineralizations, so far, the processes responsible for their forming have been considered as successive, and the endogene and supergene mineralizations as separated units.

During the last 30 years have been created numerous models for the deposits of porphyritic and epithermal types. All of them have some common elements, the main being:

- an intrusion is always suggested;
- the presence of geothermal and volcanic thermal systems;
- the presence of magmatic fluids and meteoric waters;
- hydrothermal-metasomatic alterations;
- ores.

Different studies, hypotheses, computer modelling, etc., give evidences to extend the existing models or to the inclusion of some new and so far not used elements in them. This way have occurred the intrusion-related and intrusion-centered systems, the models with brittle-ductile zones, with dating of the processes, with endogene and supergene acid leaching, etc.

Modelling the evolution of the epithermal systems (Plumlee, 1994) based on the epithermal fluid systems from the Greed deposit (Colorado) shows that the epithermal ores, the mineral parageneses and zones are directly and strongly depending on the sub-surface hydrogeological processes, like boiling and fluid mixing.

Based on data on the mineral-forming processes in active as well as dead hydrogeothermal systems Щепев (1999) admits the large-scale hydrothermal mobilization, transport and discharge of mineral substances in them. The waters in such systems may be of meteoric, sedimentary-marine, marine or mixed (meteoric-marine) origin. Following the same author, most of these systems are not connected to magmatic sources. Where such connection is established then, it is limited only to a powerful heat flow and feeding from depth with CO₂ and other volatiles which act as catalisysts. Numerous similarities (structural, spatial, energetic, compositional, etc.) admit the existence of a geo-historical connection with palaeo-hydrothermal structures, in which had occurred most of the ore-forming processes over the Bulgarian territory.

Which concerns the contemporary hydrothermal systems, Петров (1977) emphasizes on the fact that they occur in areas with tectonic and volcanic activity, but also in areas without magmatism. In Bulgaria, thermal waters are found hosted in magmatic, metamorphic and sedimentary rocks. They have high negative values of $\delta_{18}\text{O}$ as well as δD and the interrelation between them shows the atmospheric waters as the main component in their forming.

The epithermal Ag-Au deposit Faride (Chile) is of adularia-sericite (low-sulfidation) type. It is suggested that the thermal evolution is responsible for the origin of two stage of mineralization. The first one is rich in gold, and the second one in silver. Beside many other conclusions, Camus and Skewes (1991) clearly show that the mineralogical peculiarities in the zone of oxidation directly reflect the distribution of the two types of primary ores. The redistribution of Au, Ag, Cu, Pb, Zn in the zone of oxidation depends on the Eh-pH conditions and the crucial role of the supergene mobility.

Based on the numerous examples hereafter it is suggested that the endogene and supergene systems of the epithermal occurrences in many cases could be observed as an integrity. The last can be adopted as unanimity between the natural datum and the human perception (thinking). The main criteria for the forming and existence of the endo-supergene metasomatic system are:

- spatial compatibility;
- dependence between endo- and supergene mineralizations;
- presence of metasomatic replacement and indications for a metasomatic zonation;
- common structural-tectonic agents;
- geomorphological and climatic agents.

The supergene part of the system can be complicated by the influence of some biogenic or technogenic agents.

Models of some endo-supergene metasomatic systems of epithermal ore deposits and mineralizations of acid-sulfate and adularia-sericite types

On the relatively small territory of Bulgaria numerous epithermal occurrences are found (Fig. 1). Most of them are located in the Srednogorie and the Rhodopes. Only two occurrences, one of each type, are established in the West

Balkan. The relation of most occurrences to the Alpine magmatism is clearly expressed.

Based on Bulgarian examples (Figs. 2, 3) some new models for the origin of the epithermal mineralizations are proposed. They are based on the hypothesis for a single endo-supergene metasomatic system occurring in the epithermal deposits. As it has already been mentioned an epithermal ore deposit is formed at shallow depth (1-2 km), temperatures between 150-300°C and low pressure. Based on the existing evidences I accept the thesis for the mixed character of the solutions. Following the endogene ore deposition, depending on the existing environment, like tectonic reworking, depth, geomorphological and climatic conditions, starts the supergene alteration of the ores and rocks. A decisive role for it have the access of oxygen and the acidity of the mixed solutions. After some examples from many presently active geothermal fields, it is admissible that the supergene mineral-forming starts to operate even during the endogene ore deposition. The supergenesis lasts longer, depending on the conditions and level of organization of the mineral substract. Supporting this suggestion are the numerous cases of recent mineral-forming.

A good example for a supergene mineralization is the gold-base-metals epithermal deposit Chala (Кунов, 1999). In this deposit the phosphates, sulfates, silicates and hydroxide minerals are dominating. Their distribution outlines a relatively well expressed zonation, which is complicated along faults, some of them being long-living. The studies of Кунов (2001) allow the determination of some features of horizontal as well as vertical zonation.

In Bulgaria, most of the epithermal occurrences of acid-sulfate type do not possess a significant richness of supergene minerals, when compared to those of the low-sulfidation type. The caolinite-alunite occurrence Klisoura (Велинов, 1971, 1973; Кунов et al., 2001) has a well expressed supergene zone. Its main features are the limited number of supergene minerals, the broad and almost all over occurrence of kaolinite, some zones with montmorillonite and jarosite.

These two examples of occurrences of both acid-sulfate and adularia-sericite type in Bulgaria as well as the numerous worldwide data from epithermal and porphyritic occurrence suggest:

- the conditions where the deposit is formed and the respective minerals determine the type of the mineralization;

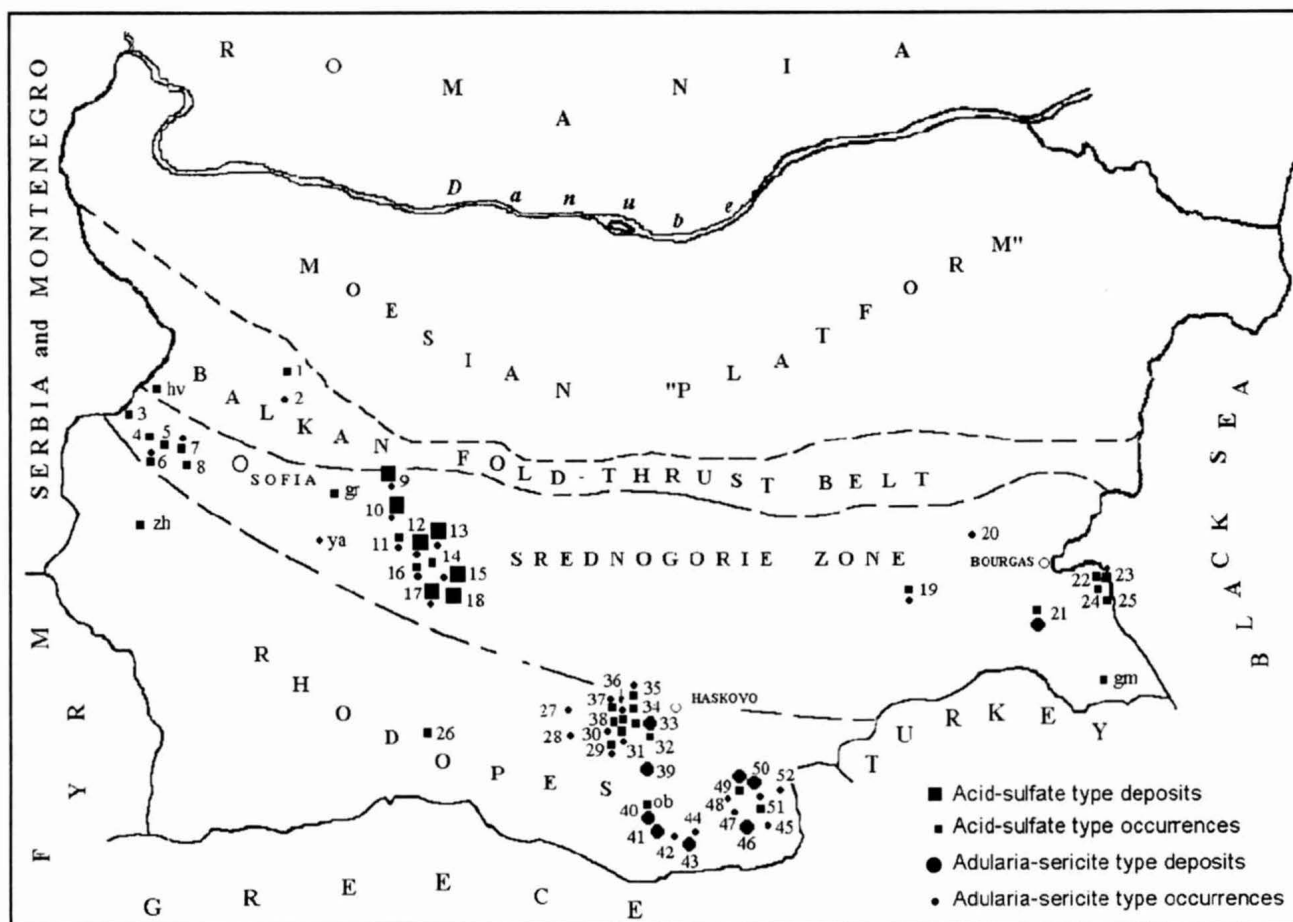


Fig. 1. Distribution of epithermal acid-sulfate and adularia-sericite type deposits and occurrences in Bulgaria (after Велинов and Кунов, 1996 and Кунов et al., 2003 with additions)

1 — Ignatitsa; 2 — Osenovlak; 3 — Krousha; 4 — Pishtene; 5 — Gourgoulyat; 6 — Breznik; 7 — Zlatousha; 8 — Klisoura; 9 — Chelopech; 10 — Asarel; 11 — Byalata prust; 12 — Krasen; 13 — Petelovo-Borova mogila; 14 — Pesovets; 15 — Radka; 16 — Chervena mogila; 17 — Elshitsa; 18 — Tsar Asen; 19 — Bakadzhik; 20 — Hadzhiite; 21 — Zidarovo; 22 — Alefo toumba, Sharlan bair; 23 — Kavatsite; 24 — Dyuni; 25 — Ropotamo; 26 — Stomanovo; 27 — Novakovo; 28 — Tri mogili; 29 — Gabrovo; 30 — Surnitsa-west; 31 — Surnitsa; 32 — Sirakovo; 33 — Spahievo with Chala; 34 — Sousam; 35 — Svetlina; 36 — Bryastovo; 37 — Boukovo (Pilashevo); 38 — Ramadansha chouka; 39 — Stremtsi; 40 — Obichnik; 41 — Zvezdel; 42 — Sedefche; 43 — Surnak; 44 — Ada tepe; 45 — Lensko; 46 — Rozino; 47 — Popsko; 48 — Chernichino; 49 — Madzharovo (Shish tepe, Gyurgen dere, Chatal kaya); 50 — Gaberovo; 51 — Gornoseltsi; 52 — Kamilski dol

supergene alunite: hv — Haidushki vruch; gr — Golyama Rakovitsa; gm — Gramatikovo; zh — Zhablyano; ob — Obichnik

superposed adularia-sericite type on listwaenites (Yamkite)

- the type of the mineralization (low or high sulfidation) is not the only one agent determining the mineral composition of the supergene part of the endo-supergene system;

- together with the climate, waters, geomorphological and erosional level, of peculiar importance for the supergene mineral-forming is the mineral composition of the primary ores.

- the supergene mineralization is of essential importance for the prospecting of unexposed ore mineralizations. It is not only an indicator about the ores at depth, but is also indicative for the expected ore mineralizations.

In support to these suggestions the next examples may be provided:

- the ore show Klisoura and the Chelopech deposit (acid-sulfate type) and Asarel (porphyritic type) have different supergene zones;

- the diversity of supergene minerals in the Asarel deposit (malchite, azurite, native copper, chrisokola, brochantite, chalkantite, melaterite, etc.) (Богданов, 1981; Токмачиева, 1994) is due to the presence of ore bodies (with pyrite, bornite, chalcopryrite, arsenopyrite, galena, sphalerite, tennantite-tetraedrite, enargite, molibdenie, etc.), located close to the surface;

- on the other hand, the Chelopech deposit (Терзиев, 1968; Богданов, 1981; Петрунов,

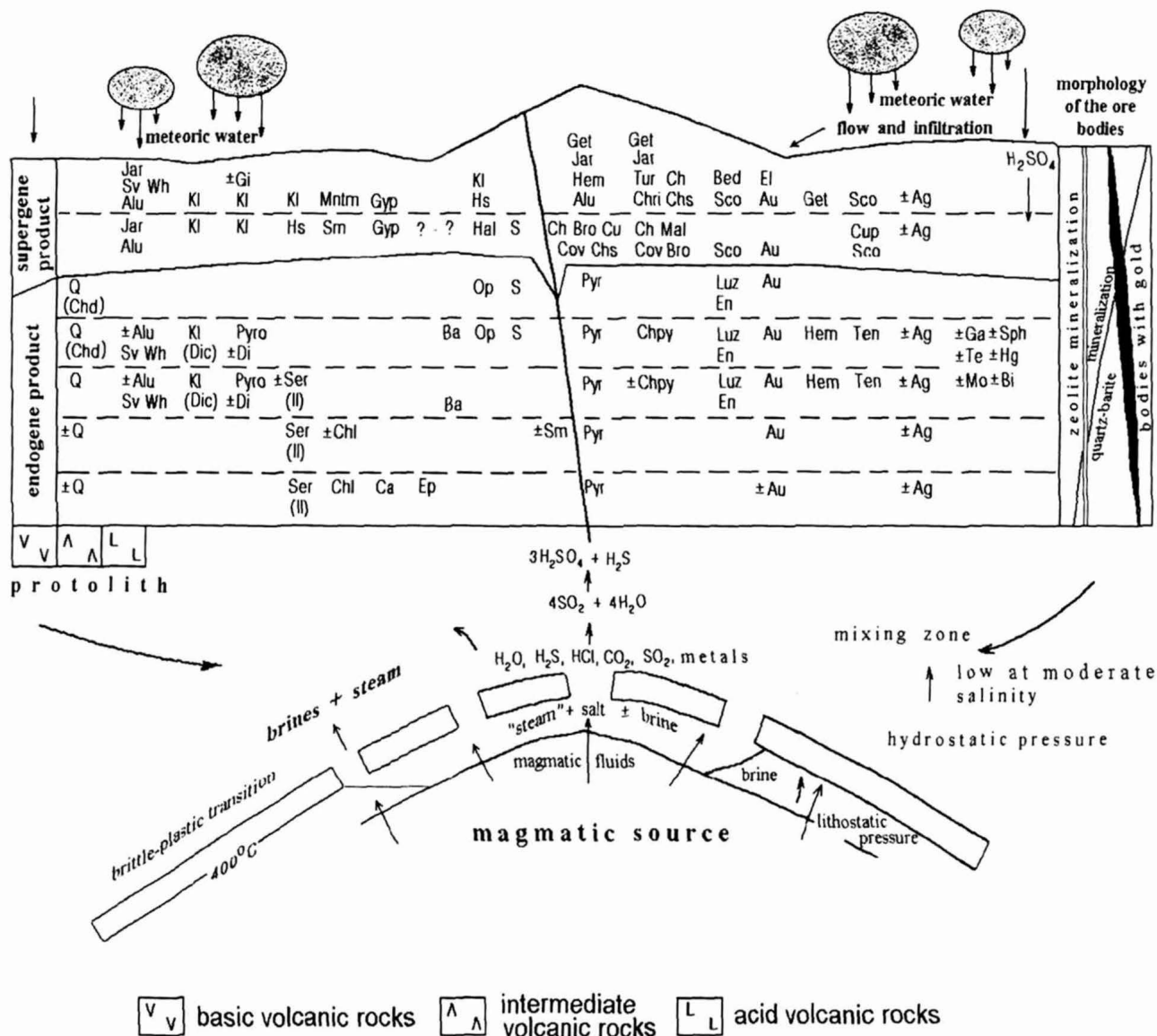


Fig. 2. Schematic model of endogene-supergene system of acid-sulfate (high-sulfidation) type epithermal gold and gold-bearing deposits and occurrences (with some elements of models of Hedenquist and Lowenstern, 1994; Hedenquist et al., 1996; Fournier, 1999; Chavez, 2000 and others).

Symbols: Ab – albite; Ad – adularia; Ag – native silver; Alu – alunite; Ame – amethyst; And – andalusite; Ang – anglesite; Anh – anhydrite; Ank – ankerite; Ap – apatite; Aspy – arsenopyrite; Azu – azurite; Au – native gold; Aug – augite; Auge – augelite; Ba – barite; Bea – beaverite; Bis – bismuthinite; Bor – bornite; Bt – biotite; Bro – brochantite; Ca – calcite, carbonates; Cac – cacoxenite; Cer – cerussite; Ch – chalcantite; Chd – chalcedony; Chl – chlorite; Chlap – chlorapatite; Chpy – chalcopryite; Chs – chalcocite; Chsi – chalkosiderite; Chry – chrysocolla; Cor – corkite; Coru – corundum; Cov – covellite; Cri – cristobalite; Cu – native copper; Cup – cuprite; Di – diaspore; Dic – dickite; El – electrum; En – enargite; Ens – enstatite; Ep – epidote; Eps – epsomite; Fau – faustite; Flap – fluorapatite; Flo – florencite; Ga – galena; Ge – geocronite; Get – goethite; Gi – gibbsite; Gyp – gypsum; Hal – halotrichite; Hem – hematite; Hsd – hinsdalite; Hl – halloysite; Hs – hydromica; Il – illite; Jar – jarosite; K-Fs – K-feldspar; Kl – kaolinite; Kts – ktenasite; La – landesite; Lab – labradorite; Laum – laumontite; Lus – lusonite; Mal – malachite; Mar – marcasite; Mel – melanterite; Mntm – montmorillonite; Mol – molybdenite; Ms – muskovite; Na-Alu – natroalunite; Nit – niter; Op – opal; Osa – osarizawaite; Pic – pickeringite; Pbgrm – plumbogummite; Pljar – plumbojarosite; Pr – prehnite; Pum – pumpellyite; Pyr – pyrite; Pyrm – pyromorphite; Pyro – pyrophyllite; Pyrt – pyrrothite; Q – quartz; Roz – rozenite; S – sulfur; Sco – scorodite; Sel – selenides; Ser – sericite; Sid – siderite; Sm – smectite; Smi – smitsonite; Som – szomolnokite; Sph – sphalerite; Sulfs – sulfosalts; Sv – svanbergite; Te – tellurium; Tel – telurides; Ten – tennantite; Tetr – tetrahedrite; To – topaz; Tri – tridymite; Tur – turquoise; Var – variscite; Ver – vermiculite; Viv – vivianite; Wav – wavellite; Wh – woodhouseite; Zun – zunyite

of chalcotrichite and melanterite in the ore show Krousha is an indirect indication to expect unexposed pyrite bodies. Thus, the presence of jarosite in the supergene zone suggests the presence of pyrite (pyrrhotite, marcasite) at depth. Instead, the presence of plumbogjarosite may be connected to a galena mineralization. To determine the protolite of the jarosite of main importance is the content of Al, which suggests the occurrence of alunite and pyrite. Such an example are the biverite and osarizavaite developed at the expenses of galena from the Chala deposit (Kunov and Petrov, 2001). The broadly occurring malachite and azurite are traditionally related to the presence of copper mineralizations. The turquoise found by Кунов (1986) motivated the drilling and further discovery of the Bryastovo base-metals deposit. The steady presence of some supergene minerals of Fe and Mn also reflect their capability for migration. The relation between the supergene mineralization and the gold as well as other precious metals, especially the platinum is more complicated. Such conclusions should be used very carefully as an exploration tool, because in the supergene zone new minerals may have different origin, including biogenic and technogenic one.

One of the main peculiarities of the superficial parts of the epithermal mineralizations is the fact that in them interfinger supergene minerals from the zone of oxidation as well as supergene minerals formed from the rock weathering, independently from the ore mineralizations, such as clays, hydromicas, mixed-layered minerals, etc. Usually the silicates are better preserved during the supergenesis, being more stable.

Out of doubt, the proposed models of the acid-sulfate as well as adularia-sericite type may be further developed. They are based on the so far available data from Bulgarian examples. These models reflect the dependence between the geochemistry and the mineral composition of the primary and the supergene products. The role of the tectonic and neotectonic processes may not be shown directly, but it is obvious that they are an important agent for the migration of both elements and fluids. An indirect indication for their role are the zonation and the higher mineralization in some areas.

Both models include also some elements from the models of Hedenquist and Lowenstern (1994), Hedenquist (1996), Fournier (1999), Chavez (2000). They consist of two parts, endogene and supergene with the re-

spective metasomatic zonation. The vertical columns reflect the presence of a mineral in the different metasomatic types, and also the established or probable cases of convergence. It is also possible to follow the different stages of evolution of the single minerals, during the endo-supergene processes. The right part of the models shows the morphological types of the gold mineralization, as well as its relation to some accompanying hydrothermal mineralizations.

Despite the similar general features of the gold mineralizations of both epithermal types, each one displays its own specific characteristics. This clearly shows the diversity of the natural processes and the impossibility to create a universal model.

Conclusion

The hypothesis for the existence of an integrated endo-supergene system as any one hypothesis contains facts and suggestions. It is well known that a hypothesis may be true only from a logical point of view. The theory differs from it by its factual authenticity.

Some debatable points of the proposed hypothesis could be the cases where a significant gap in time between the primary and supergene mineralizations is established. However, in such cases as supergene processes are usually accepted to be only the recent ones, but those acting simultaneously with the endogene ore forming have so far been neglected. The recent geothermal and hydrothermal volcanic systems are the best proof of the simultaneous occurrence of both endo- and supergene processes. The integrity of both processes is already recognized with the admission of the mixed character of the fluids, the convection and the participation of meteoric waters as well as atmospheric oxygen together with magmatic products into the forming of the endogene epithermal deposits.

The proposed hypothesis as any one hypothesis is debatable. However, it is also supported by evidences from porphyritic systems, where a transition between hypogene and supergene mineralization was already suggested by Sillitoe (1973) who wrote: "If it is correct to assume that porphyry systems crop-out at surface, then supergene alterations of their upper part might be expected to commence immediately upon cessation of hypogene mineralization. Moreover, the interaction of magmatic and meteoric fluids above the potassium sili-

cate altered core during mineralization suggests that hypogene effects may well be transitional to supergene ones...

A further possibility during the initial stages of supergene alteration of a porphyry copper system is the leaching of copper from unconsolidated ashes by acid solutions and its dissolution from sublimates by rain water with subsequent precipitation of the copper at deeper levels, perhaps aided by hydrogen sulfide in late stage volcanic gases."

The conclusions of Sillitoe may also be directly applied to the epithermal systems.

Based on the published evidences and personal studies some major conclusion are made:

- The definition of a endo-supergene system is based on real facts. Some cases of absolute dating showing a significant gap between the primary and supergene mineralizations may be due to the late initial of the supergene part. This may be interpreted as a discontinuance in time. However, other interpretations like a subjective including in the supergene system of minerals not related to it or formed at the expenses of minerals and rocks not belonging to the endogene systems may not be excluded. The recent geothermal and hydrothermal volcanic systems are the best proof of the simultaneous occurrence of both endo and supergene processes.

- In equal condition the primary mineral diversity is the main precondition for the abundance of supergene minerals. It is very important, that some characteristic minerals for both type, alunite and kaolinite for the high sulfidation and adularia and carbonates for the low-sulfidation, can be found in the opposite type. However, in such cases they are always imposed, being deposited by younger processes. The alunite originates from acid metasomatoses, caused by hydrothermal processes, superficial forming of acid-sulfate waters and after weathering and decomposition of sulfide minerals. In cases of imposing over low-sulfidation alterations the alunite is mainly of supergene origin. The so far known occurrences of hydrothermal alunite are quite a few, but theoretically such opportunity may not be excluded. When adularia is imposed over alterations of high-sulfidation type no alternative option to its hydrothermal origin exist, as its forming in supergene condition has never been proven.

- Some preliminary data suggest that mineralizations from both types may have quite similar supergene zones. The single deposits possess their own peculiarities and for the fea-

tures of the supergene zone of main importance are the primary mineralizations.

- The magmatic source has direct influence over the evolution of the endo and supergene processes. Some of its features, like the potassic or sodic tendency reflect also in hydrothermal and supergene metasomatic processes. Such role have for example played the arsenic and the phosphorus respectively, in the Stara Planina and the Rhodope Zone, where a strongly differentiation of respectively arsenates and phosphates is established.

- For both types of epithermal mineralizations the host rocks are of main importance for the supergene zone. This is well shown by the most frequent occurrence of phosphate mineralizations in the Rhodopes, where the primary rocks contain sufficiently apatite.

- Observing the endo- and supergene parts as belonging to an integrate system provides some opportunities to use the supergene part or some of its elements as indicators in prospecting of endogene ores and/or their estimation as separate raw-materials.

- The conditions in which the ore mineralizations and especially their supergene zones are formed, their near surface location and interaction with the ground waters suggest their influence over the ecosystems.

From such a point it is very important to know the endo- as well as supergene parts of the system, the forming of supergene minerals (sulfides, oxides, hydroxides, silicates, phosphates, pospho-sulfites, sulfites, arsenites, carbonates, etc) which result from the decomposition of the endogene rocks and minerals, their solubility and physico-chemical steadiness, the transport and discharge of elements, harmfulness, etc. At the same time it should be mentioned, that some Bulgarian occurrences of acid-sulfate type have enough reserves of alunite. From the last, based on a wasteless technology can be produced a product, which can be used as a coagulant for the purifying of the potable and waste waters.

The acid-sulfate (low-sulfidation) and adularia-sericite (high-sulfidation) deposits are a main source for economic commodities. They are also a very interesting subject for studies and modelling. The broad occurrence of both types in Bulgaria allows not only to extend further their studies (Велинов, 1995), but also to reconsider some already acquired knowledges on them. The hypothesis for an integrate endo-supergene system is a step towards the beginning of a new view in their investigation and is a prerequisite to expect other new and optional

ideas. Together with the studies on the epithermal systems some problems of the mineral convergence may also found their solution, thus limiting the domain of uncertainty and indefiniteness (Куюнов and Велинов, 1998). Without exaggerating the opportunities for discovering a large gold deposit in Bulgaria, a new untraditional view on the epithermal mineralizations may significantly increase the ore potential of the country.

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¹ This category corresponds to the VHMS class of deposits.