THE BASIC MINERALOGIC, PARAGENETIC AND GENETIC CHARACTERISTICS OF THE SULPHIDE DEPOSITS EXPOSED IN THE EASTERN BLACK-SEA COASTAL REGION (TURKEY)

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ABSTRACT. — An attempt has been made to determine the mineral assemblages in various types of investigated sulphide deposits, the paragenetical relationships among the minerals, the order of their deposition and the genesis of single deposits, and the metallogeny of this region.

In general, there exist three genetical groups of the described deposits, such as:

a. Volcanic-sedlmentary-hydrothermal (Cu, Zn, Pb) deposits, occurring in rhyolitic and rhyodacitic pyroclastics. These deposits are the most favorable in view of economic importance.

Volcanic-sedimentary sulphide minerals weie precipitated contemporaneously with the host rocks, notably with rhyolitic or rhyodacitic pyroclasts, whereas the second-phase minerals in this type of deposits were segregated under hydrothermal conditions, but within the host rocks. These hydrothermal sulphide assemblages are mainly the products of remobilization of volcanic-sedimentary ores and the remobilization was caused by later hydrothermal solutions which circulated through the volcanic-sedimentary deposits. These solutions are related to later volcanic rocks.

b. Hydrothermal deposits (Cu, Zn, Pb) containing the mineral assemblages that are almost identical to those detected in the above-cited deposit types. The hydrothermal deposits occur in various rocks, such as rhyolitic, dacitic and andesitic pyroclasts, occasionally in volcanic rocks of the other types, or in granitoids, limestones, etc. The deposits of this type are limited in size and most of them are not of particular interest.

Hydrothermal deposits are genetically related to later rhyolitic and rhyodacitic reactivated volcanism, but a number of these deposits are the products of remobilization and redeposition of deeply-seated volcanic-sedimentary deposits.

c. Skarn-hydrothermal deposits are in most cases of small bulk and their mineral assemblages are the product of two phases. First, high-temperature assemblages may include various silicates like amphibole, pyroxene, epidote, garnet, etc., which are associated with magnetite, muschketowite and hematite. Second, hydrothermal phase is often characterized by abundant pyrite, followed by varying amounts of chalcopyrite, occasionally also by sphalerite and galena. The gangue minerals are quartz and calcite.

The skarn-hydrothermal deposits are partially juvenile owing to the presence of high-temperature minerals, such as amphibole, pyroxene, epidote, garnet, magnetite, etc., which may be genetically related to granitoid rocks occurring in the vicinity of these deposits. The sulphide assemblages accompanying skarn occurrences are hydrothermal in origin, but they are often products, of remobilization of primary volcanic-sedimentary ores.

INTRODUCTION

In the course of the last four years field studies and sampling of sulphide ores and surrounding rocks were carried out by the author as part of a comprehensive study by M.T.A. Institute, Ankara. Many reports and some papers on the mineral assemblages, paragenetic relationships as well as genetical characteristics of the investigated deposits and occurrences were written by the author in the interim, thus mineralogical and genetical peculiarities of the most interesting deposits exposed in the mentioned region will be discussed here.

Approximately 50 sulphide deposits and occurrences will be treated in this paper. The data piesented is based on field observations and examinations of more than 1,000 polished sections as

well as of numerous thin sections. Ore microscopic examinations were carried out by the author, and those of the rocks by S. Cvetic, D. Pesic, R. Stojanov and others. The micrographs of the ores were selected by the author.

To this day no reports or papers have been written as a study on the mineralogical-genetical characteristics of sulphide deposits from the described region, although interesting data has been reported by some authors.

Actually, many authors have genetically treated the sulphide deposits exposed in the region, although most of them have based their conclusions on magmatic-tectonic interpretations (1, 2, 3, 4, 5, 6, 8, 11, 12, 26, 27, etc.).

Previously the ore-microscopic examinations of samples from a number of deposits have been carried out by V. Kovenko (4), H. Schneiderhöhn (14), A. Kraeff (5, 6), A. Maucher (7) and G. Aslaner. (Also the data presented in a number of M.T.A. geological and prospection reports.)

The basic mineralogic study of samples from many sulphide deposits of this region has been carried our by M.T.A. experts, and the results were published in 1966 (28).

On the genesis of the deposits exposed in the described region the dominating opinion is that they are mostly hydrothermal and occasionally skarn-hydrothermal in origin.

However, A. Maucher (7) expressed that the Lahanos sulphide deposit is not hydrothermal, but volcanic-sedimentary in origin. This conclusion was not accepted by some authors (12, etc), especially due to the fact that hydrothermal assemblages are without doubt dominating in this deposit.

The author's field observations and ore-microscopic examinations of numerous sulphide deposits located in the region have shown that the volcanic-sedimentary type of deposits are more developed here, although these deposits are characterized, as a rule, by the presence of later hydrothermal sulphide phases (10,15,16,17,18,19, 20, 21).

The purpose of this paper is to present in detail the author's view on the paragenetic relations of the ore minerals, the host rock and the ore minerals, textural features, their successions, deposition temperatures, etc.

This psper includes the following deposits and occurrences:

- Murgul area: Anayatak, Çakmakkaya, Akarsen, Başköy Maden, Ishalka Köyü, Şahinkaya, the occurrences NE of Petek, Satip Dere.
- Artvin area: Kuvarshan, Irsa Maden, Zinkot I, II and III, Beşağıl, Umasen (Seyitli).
- The area between the towns of Rize and Sürmene: Tuncat I, Pilargivat, Sürmene, Taşhane (Gürpınardere), Maden Köy.
- The area S, SE, and SW of the city of Trabzon: Langaz, İdiya, Gümüşhane area (Hazine, Mağara, Kırkpavli, Deremaden), Köstere, Zigana, Ayman, Hozarak I and II, Eski Ocak (Yomra, Ördil)
- The area between the towns of Esbiye and Görele: Köprübaşı, Ketençukuru, Kepçelik, Oyraca, Eski Maden, Karalar, Lahanos, Kızılkaya.
- The area between the of towns Giresun and Fatsa: Akköy, Darıköy, Piraziz, Kirazören, İsrail Maden, Kovanlık, Karadere, Çatak, Çetili, Bakacak, Şıhman, Aytepe, Büyükgüre, Sineklik.

All of the described deposits are located in the eastern par of the Black-Sea coastal region, most of them between the towns of Ordu in the west and Murgul and Artvin in the east, notably in an area which is approximately 350 km in length and up to 50 km in width.

In the described region the following dominant genetical types of sulphide deposits were detected:

- a) Volcanic-sedimentary-hydrothermal,
- b) Hydrothermal,
- c) Skarn-hydrothermal.

The first type of deposits and occurrences are found at the following places: Anayatak, Akarsen, Çakmakkaya, Başköy Maden, Tuncat, Köprübaşı, İsrail Maden, Akköy, Zigana, Karalar, Lahanos, Kızılkaya and Kepçelik.

The second type of deposits belong to the hydrothermal type and are found at Şahinkaya, Ishalka Köyü, Satip Dere, Zinkot I, II and III, Beşağıl, Tuncat II, Sürmene, Taşhan, Gümüşhane (Hazine, Mağara, Kırkpavli, and Dere Maden), Köstere, Gezge, Ketençukuru, Oruçbey, Darıköy, Piraziz, Kirazören I, II and III, Kovanlık, Karadere, Çatak, Çetili, Bakacak, Şıhman, Aytepe, Büyükgüre, Sineklik.

The third type—skarn hydrothermal—are found at Ayman, Pilargivat, Langaz I, Hozarak, Eski Maden, Oyraca.

THE BASIC MINERALOGIC AND PARAGENETIC FEATURES OF THE VOLCANIC-SEDIMENTARY-HYDROTHERMAL SULPHIDE DEPOSITS

All of the presented deposits of this type are associated with rhyolitic or rhyodacitic pyroclastics (mainly volcanic breccia). Most of these pyroclasts are overlain by tuffs, occasionally by sandstones, tuffitic sandstones, marls and the like. These covers are mainly in the form of thin beds that are slightly or non-mineralized. Meanwhile, in many cases the overlying tuffaceous covers show geochemically anomalous contents of lead, zinc and copper.

As far as mineralogical assemblages of these deposits are considered, most of them are polymetallic, in general dominated by copper, zinc and lead minerals. The abundance of the mentioned minerals is strongly varying, even in a single deposit, but in most of them pyrite and copper minerals are dominant. Occasionally sphalerite or galena or both are predominant (Table 1). The chief lead mineral is always galena, so zinc is as a rule represented by sphalerite. Regarding the copper minerals the most abundant is chalcopyrite, except for some deposits (Kuvarshan, Irsa Maden) in which tetrahedrite ise also plentiful. Pyrite is always present, being sometimes massive. In some deposits of this type bournonite (Köprübaşı), enargite (Kuvarshan Irsa Maden, Kızılkaya) and bornite (Kuvarshan, Irsa Maden, Tuncat I, Maden Köy, Zigana, Köprübaşı) were also observed (Table 1). As a rule, marcasite is produced by the conversion of pyrite.

The volcanic-sedimentary-hydrothermal deposits and occurrences must have been formed in two phases:

- a) First phase, volcanic-sedimentary,
- b) Second phase, hydrothermal.

In most cases throughout the volcanic-sedimentary phase pyrite and chalcopyrite precipitated as the chief minerals, and they have been followed by a relatively small amount of sphalerite, galena, bornite, tetrahedrite and bournonite. The abundance of these minerals is varying depending on the locality, whereas bournonite is mainly lacking (Table 1).

During the second-hydrothermal phase minerals, analogous to the first phase, were deposited, but newly formed minerals were also detected in some deposits. Thus besides the above-mentioned

Table - 1

The mineral assemblages in the volcanic-sedimentary-hydrothermal sulphide deposits

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The gangue minerals in volcanic-sedimentary assemblages are dominated by chalcedony, or baryte, or both, whereas hydrothermal ores are occompanied by quartz, calcite, sericite, occasionally by baryte and various types of carbonates (siderite, ankerite, etc) (Table 1).

hematite.

THE ROCK ALTERATIONS

Throughout the hydrothermal enrichment of the volcanic-sedimentary ores, as well as later, the host and surrounding rocks have been variably altered. In the vicinity of hydrothermal sulphide veins strong wall rock alteration is commonly observed, notably silicification, pyritization, argillation, sericitization, occasionally also chloritization, and late-stage limonitization.

TEXTURES, STRUCTURES AND INTERGROWTHS OF VOLCANIC-SEDIMENTARY-HYDROTHERMAL ASSEMBLAGES

The minerals volcanic-sedimentary in origin show variations of forms considering that they were piecipitated in collidal forms. The most common forms are rounded, egg-shaped, ring-like and similar grains (Photos 1, 2, 3, 4, 7, 12,13, 14), whereas pyrite occurs in «bacterial» forms as well (Photos 8,10,11).

In the deposits Anayatak, (Çakmakkaya and Akköy the latter forms of pyrite are very common, but they were also observed in many other deposits of this type. Enclosure of minute dense grains of some metallic minerals in others or in the host rock is a very common feature in some deposits. Massive inclusions of chalcopyrite, pyrite, bournonite or tetrahedrite are known in a number of deposits of the described type (bournonite, tetrahedrite and pyrite inclusions in the Köprübaşı mine; chalcopyrite, pyrite and tetrahedrite inclusions in Kuvarshan and Irsa Maden deposits, etc). (Photos 17, 18). In many cases chalcopyrite, bournonite and tetrahedrite contain numerous pyrite inclusion, or various sulphides are enclosed in pyrite. Fine mixtures of sulphides, as well as their mixtures with host rock minerals are often visible, and they are very common in some cases. Rhythmical and particularly concentric textures and alternations of various ore and rock minerals are rather common, especially alternations of chalcopyrite and pyrite (Photos 1, 2, 3, 4, 5, 12, 13, 14).

As far as textures of the host rocks are considered they are very similar to the above described. The host rock minerals, particularly chalcedony, often appear in the form of rounded, egg-shaped, ring-like and similar grains, or these minerals alternate rhythmically or concentrically with the metallic ones (Photos 1,4,7, 14,15). When interlayers of chert are present in the ore-bearing pyroclasts, the former rock is also variably enriched in sulphides and it may contain residues of radiolaria.

Due to the fact that the intergrowths among the ore minerals and between the ore and host rock minerals are very intimate and that replacement structures are completely lacking, the author believes that the volcanic-sedimentary sulphide minerals have been deposited simultaneously with the host pyroclastic rocks. The occurrences of «mineralized bacteria» pyrite in the described assemblages perhaps signify its organic origin, especially due to the fact that the diameters of «bacterial» pyrite grains do not much differ in size.

In view of the mineralogic assemblages of the second-hydiothermal phase, they are almost identical to those belonging to the first one (Table 1) but all the other properties differ entirely. Namely, hydrothermal minerals occur along the fault and fracture systems in the pyroclasts and related sulphide associations, i.e. in the form of vein and veinlets or as metasomatic replacements.

A large variety of replacement structures were observed in numerous cases in the second phase mineral assemblages. Throughout the hydrothermal phase also crystalline sulphides and gangue minerals have been deposited. These often replaced and enclosed the first phase minerals as well as their rounded, egg-shaped, ring-like and other colloform grains, including the grains of «bacterial» pyrite. In general, the second phase minerals are very coarse or relativelly coarse, some of them are crystalline (quartz, pyrite, carbonates, baryte, enargite, sometimes also sphalerite) (Photos 23, 24, 25). These structural-textural features of the second phase minerals apparently differ from those that are characteristic of the minerals of the first—volcanic-sedimentary—phase.

EXSOLVED MINERALS

Contrary to the first-phase minerals, some hydrothermal minerals of the second phase often include geologic thermometers (exsolutions).

Due *to* the fact that the second phase assemblages in the described type of deposits are mineralogically and paragenetically very similar to those in the hydrothermal deposits, the data on the geologic thermometers will be treated together in a separate section.

THE BASIC PROPERTIES OF HYDROTHERMAL DEPOSITS

Numerous hydrothermal deposits and occurrences are known in the described region and some of them will be Treated in this paper. The presented data and conclusions are based on the results of investigations of about 30 deposits and occurrences studied by the author.

Actually, scarce volcanic-sedimentary pyrite, or even chalcopyrite can be detected in some of hydrothermal deposits, but the hydrothermal minerals are always predominant. Although hydrothermal sulphide deposits are distributed all over the investigated region, they are mostly concentrated to the south, southeast and southwest of the town of Ordu.

In the deposits of hydrothermal type, ore and gangue minerals occur in the form of veins and veinlets which are several centimeters to two meters thick. Most of the deposits of the said type, particularly those lying in the vicinity of Ordu, are characterized by quartz veins that are irregularly enriched by sulphide minerals. The ore-bearing quartz veins could be followed over a length from about several hundred meters up to several kilometers. Veins fill faults, fissures, or fractures, but rarely fault systems of various directions. The stockwork type was observed in some cases only.

The deposits of the described type appear in various rocks such as rhyolitic, rhyodacitic, dacitic and andesitic pyroclasts, further in spilitic tuffs, rhyolites, dacites, limestones, granitoids, etc.

THE ROCK ALTERATIONS

In all of the investigated deposits of the described type the alteration halo was observed being of various bulk and intensity but, in general, it extends as much as several up to several tens meters. As a rule, the minerals produced during the alteration processes are mixed, varying in individual cases depending upon the host and neighboring rock type, as well as of the properties of the hydrothermal solutions. In the stockwork type of deposits the mineralized parts of the rocks may be totally altered (Aytepe). Generally, the following alteration types were detected in the described deposits: silicification, pyritization, argillation, sericitization, chloritization and limonitization.

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MINERAL ASSEMBLAGES

The hydrothermal deposits and occurrences include a number of metallic minerals such as pyrite, chalcopyrite, galena and sphalerite, that are often accompanied by tetrahedrite, sometimes also by bournonite, bornite, enargite, pyrrhotite and hematite. The gangue minerals are quartz and calcite, occasionally followed by various carbonates (siderite, ankerite) and baryte (Table 2).

The abundance of pyrite is very variable, even inside a single deposit, although it is massive in some of them. In a number of deposits there are pyritic ores, containing appreciable or small amounts of copper, lead and zinc minerals (Büyükgüre, Zinkot, Seyitli, etc.). Galena and sphalerite are often plentiful, but chalcopyrite is rarely abundant. Meanwhile, the abundance of all of the sulphide minerals is strongly varying in all of the described deposits.

MINERAL TEXTURES AND STRUCTURES IN THE HYDROTHERMAL DEPOSITS

In the deposits of the described type, sulphide minerals do not occur in colloidal form, except for a few localities where the latest (epithermal) phase of replacement was recognized (Şıhman and some others). In most cases hydrothermal minerals, as a rule, occur in the form of grains of various shape and size often being coarse-grained and crystalline (pyrite, quartz, calcite, baryte, various carbonates, sometimes also sphalerite and enargite) with very apparent and well developed replacement structures both among the hydrothermal minerals and between these minerals and the host rock. Metasomatic replacements are, generally, most common.

SKARN-HYDROTHERMAL ORE DEPOSITS

Although the deposits and occurrences of this type are not the subject of particular interest, some of them have been investigated by the author.

A number of skarn-hydrothermal deposits were investigated such as those in Langaz (two localities), Ayman (five), Uzmesahor (one), Oyraca (one) and Eski Maden (two).

In this secdon ore deposits occurring in various rocks—such as limestones, marbles, diabases, tuffs, etc.—placed in the vicinity of the granitoids or related dykes will be discussed. Two phases of mineral deposition can be detected in this type of deposit: the first, being the one that produced contact silicates (actinolite, wollastonite, garnet, epidote, or some of them accompanied by magnetite, muschketowite and hematite), and the second one, hydrothermal, which included pyrite and chalcopyrite with lack or scarce galena and spalerite. The dominant second phase gangue minerals are quartz and calcite.

The skarn-hydrothermal deposits occur as relatively small metasomatic bodies, but also as veins or vein concentrations, lying occasionally in both granitoid and surrounding rocks.

The volcanic-sedimentary-hydrothermal deposits which include some skarn occurrences (Kuvarshan, Çayeli?) are not classified as the skarn-hydrothermal, as the skarn assemlages are of sporadical importance here.

TEMPERATURES DURING THE DEPOSITION OF HYDROTHERMAL SULPHIDE ASSEMBLAGES

In the described hydrothermal sulphide deposits, as well as in hydrothermal mineral associations that follow volcanic-sedimentary deposits, segregation temperatures have, generally, been very similar. Those will be discussed as follows:

 \overline{a} $Table - 2$ $\overline{}$

Direct evidence on the temperatures of described mineral assemblages is in general lacking, and any estimate or determination of temperatures must be based on indirect methods, i.e. on such properties as:

- Geological thermometers (solid solutions and exsolutions).
- Presence or lack of high-temperature minerals, which are known as products of contact metamorphism or similar.
- Other properities of minerals, such as grains and crystal forms and size, presence or lack of colloidal forms and other data.

In the skarn-hydrothermal assemblages the earliest minerals like amphiboles, pyroxenes, garnet, magnetite and others, apparently indicate high-contact temperatures; thus these temperatures must, no doubt, be above those that are characteristic of hydrothermal solutions. Sulphide minerals of the second phase have been deposited under hydrothermal conditions and moderate temperatures as neither exsolved minerals in chalcopyrite, nor in sphalerite were detected.

In the hydrothermal assemblages in both the volcanic-sedimentsry-hydrothermal and the hydrothermal deposits the following geologic thermometers were detected (Tables 1, 2):

- 1) Chalcopyrite exsolutions in sphalerite,
- 2) Pyrrhotite exsolutions in sphalerite,
- 3) Tetrahedrite exsolutions in sphalerite,
- 4) Chalcopyrite exsolutions in bornite,
- 5) Sphalerite exsolutions in chalcopyrite.

The properties of many minerals to be hosts for some compounds in form of solid solutions are well known and are described in detail in the literature (13). Some of the solid solutions can be stable almost at the room temperature and far below, or at high or relatively high temperatures only, especially if the solved «components» have not the great similarity of ionic radii. In many cases the solid solutions will be unstable with decreasing temperature, thus the guest component exsolves from the host mineral, forming exsolutionlamellae, bodies, etc. Many processes of the described type have been controlled by the lab-testings, and numerous data in view of solid solutions and exsolution temperatures of various compounds have been reported in literature (13).

In general, chalcopyrite solid solutions and exsolutions in sphalerite indicate a relatively moderate temperature, whereas exsolved pyrrhotite mainly occurs in sphalerite formed under relatively high temperature, especially if pyrrhotite is common in the host mineral and scarce or lacking in the ore.

Exsolved chalcopyrite in bornite has been observed in numerous hydrothermal sulphide deposits in the world, thus solid solutions of these minerals may be considered as indicators of hydrothermal conditions.

Although sphalerite exsolutions in chalcopyrite are believed by many authors to be the product of contact-metamorphism, in most cases to my experience sphalerite exsolutions in chalcopyrite indicate the earlier (katathermal) phase of hydrothermal mineralization.

The occurrence of exsolved tetrahedrite in sphalerite is rather rare and the data available in literature is scarce. However, the existence of exsolved tetrahedrite in sphalerite surely indicates the hydrothermal origin of both tetrahedrite and sphalerite and this conclusion could be supported by a number of findings of the author. Namely, in all the deposits in which exsolved tetrahedrite in sphalerite was detected by the author, the host mineral was always a normal member of the hydrothermal assemblage.

EXSOLUTIONS IN HYDROTHERMAL SULPHIDE MINERALS

Chalcopyrite and pyrrhotite exsolutions in sphalerite (Tables 1,2, and Photo 20).— In most of the examined hydrothermal sphalerites, chalcopyrite exsolutions were observed, being in some cases massive. The lack of exsolved chalcopyrite is a characteristic feature of the deposits with scarce sphalerite, or of those in which this mineral belongs to the latest replacement phase of hydrothermal deposition (Şıhman, Darıköy, etc.). In a number of deposits exsolved pyrrhotite was also seen, being occasionally massive (Anayatak and some others).

Exsolved chalcopyrite occurs as minute inclusions, but also as elongated grains (Photo 20), occasionally oriented in two directions. Chalcopyrite exsolved in the form of spindles was rarely found. In some sphalerites chalcopyrite exsolutions are zonally distributed, or they are concentrated inside some sphalerite lamellae.

Exsolved pyrrhotite appears in the form of minute inclusions, often submicroscopic in size, as well as in needle-shaped forms. In the latter case pyrrhotite may be oriented in one or two directions. Both of the exsolved minerals appear together or are separated.

Tetrahedrite exsolved from sphalerite (Table 1). — Was seen in a few localities only, notably in sphalerite from Irsa Maden, Kızılkaya, Akköy and Maden Koy. However, the author believes that new detectings of this type of exsolutions are to be expected, at least in sphalerites from Kuvarshan and Köprübaşı. Tetrahedrite exsolutions are occasionally common, occurring as minute inclusions in the host mineral, in places also as elongated grains (Photo 21).

Chalcopyrite exsolved from bornite (Table 1). — Detected in Irsa Maden, Tuncat I, Maden Koy and Zigana Maden. Often chalcopyrite is common, but its exsolutions are mainly fine and in many cases of submicroscopic size. In the latter case bornite becomes brighter megascopically as well as microscopically. Frequently chalcopyrite exsolutions in bornite are very dense, occurring as extremely thin needles (Photo 19). Thus, in some cases it is not clear if the question is of above-cited exsolutions, or bornite was exsolved from chalcopyrite. Due to the fact that both the host and exsolved minerals are often converted into covellite (and chalcocite), optical properties of the described mixtures may be very similar to those characteristic of the so-called « idaite».

Sphalerite exsolved from chalcopyrite (Table 2). — Observed in chalcopyrite from Seyitli (Artvin) and Eski Ocak, occurring in the form of «stars» of various sizes, rarely as elongated small bodies and minute lenses (Photo 22).

THE DEPOSITION TEMPERATURES OF HYDROTHERMAL SULPHIDE ASSEMBLAGES

Except for the earliest phases in some hydrothermal assemblages in which, as a rule, pyrite, quartz and occasionally sphalerite or chalcopyrite are present, hydrothermal sulphide assemblages are deposited under moderate temperature conditions, which correspond to mesothermal phase of hydrothermal activity. This conclusion is valid for hydrothermal mineral assemblages both in volcanicsedimentary-hydrothermal and hydrothermal sulphide deposits. In some deposits in the Murgul district (Anayatak, Çakmakkaya) pyrrhotile exsolutions are often massive, although pyrrhotite is scarce or lacking in the ore. Similar cases were also observed in some sphalerites from a number of localities such as Zigana, Piraziz, Başköy Maden. However, all of the described pyrrhotite exsolutions occur in earliest sphalerite only, and later deposited hydrothermal sphalerite does not contain massive pyrrhotite exsolutions. High-temperature hydrothermal chalcopyrite was found in Seyitli and Eski Ocak deposits, containing sphalerite exsolutions. However, these exsolutions were observed in some

chalcopyrite grains only and this fact, besides the other data, supports the author's opinion about the presence of the later chalcopyrite in the described deposits, and this chalcopyrite was deposited under moderate temperature conditions.

THE SUCCESSIONS IN HYDROTHERMAL ASSEMBLAGES

In both volcanic-sedimentary-hydrothermal and hydrothermal deposits the successions of hydrothermal sulphides and accompanied minerals are, in general, very similar and the data is presented together below.

Generally, the minerals are deposited approximately as follows:

Pyrrhotite-pyrite-quartz-sphalerite-enargite-tetrahedrite-bornite-chalcopyrite-galena-bournonitechalcopyrite II-baryte-carbonates.

The repeatedly deposited and exsolved minerals are not taken into consideration due to the fact that most of them are followers only, and their abundance is limited. Meanwhile, certain exceptions should be discussed here. First of all, it is to be accentuated that an appreciable part of chalcopyrite from Seyitli and Eski Ocak has been deposited before sphalerite. Quartz and pyrite belong to the earliest phases in most cases, but pyrite seems to be, as a rule, earlier. Actually, this conclusion may be acceptable only when silicification of the rocks, which often just precede the mineralization, is not taken into consideration. The typical example is the Köstere deposit in which sulphide assemblages have precipitated after formation of secondary quartzite. On the other hand, in a number of deposits quartz is also occurring as the product of the intermediate replacement phase, occasionally encountered in void spaces in early quartz in the form of crystals. In the vicinity of the town of Ordu the latter quartz is not rare. In the case of pyrite, besides its main phase, in a number of deposits it appears to be also later. Thus in the Zinkot area pyrite segregated throughout two phases, although pyrite II is not abundant.

It is very interesting to find pyrites occurring in the form of octahedron and pentagondodecahedron, detected in some deposits, being well developed in the Murgul district. In the latter case pyrite crystals are up to several centimeters in size. The problem of deposition temperature of the described pyrite is not solved yet, but it is believed that it has been the product of a «special» phase of hydrothermal replacements, in general. Finally, in some deposits (Seyitli, Maden Köy) quartz is older than pyrite, possibly also in some skarn-hydrothermal deposits. Regarding sphalerite it is the product of earlier phases in most of the localities or, at least of early intermediate ones. Occasionally, it seems to be partly epithermal (Şıhman, Darıköy).

The paragenetic position of some minerals varies depending on locality, like position of bournonite, which may be earlier (Şıhman) or later (Köprübaşı) than galena.

METALLOGENY

Rhyolitic and rhyodacitic volcanic-sedimentary rocks are very important as the hosts of *volcanic-sedimentary sulphide assemblages,* as these rocks have produced an appreciable amount of metal, particularly of copper, zinc and lead. The investigations described have demonstrated that the sulphide deposits of this type are developed in a very large area, at least between the towns of Ordu in the west and Murgul and Artvin in the east. This area extends in a length of approximately 350 km, and is up to 50 km in width (measured map distance).

The fact that volcanic-sedimentary sulphide assemblages occur in a large area, as a rule in rhyolitic-rhyodacitic pyroclasts, clearly indicates that multiple repeating of volcanic activity in a limited geologic period, which has produced these deposits, was not only intense but also widespread. The presence of volcanic-sedimentary sulphide deposits in this pyroclastic formation, as well as their lacking in pyroclastics of other types (andesitic, basic, intermediate, mostly in dacitic too) clearly demonstrate that the rhyolitic-rhyodacitic pyroclastic formation was the only one which produced the volcanic-sedimentary sulphide deposits in the investigated region.

The area investigated by the author may be a part of a larger metallogenic province. Consequently, this region must have been included in a large geosyncline, inside of which multiphase submarine volcanic activity took place and this activity produced various pyroclastic rocks, including the sulphide-bearing rhyolitic-rhyodacitic pyroclasts. The data is not available on the possibility that during the existence of the described geosyncline the parent magma had also produced typical rhyolites-rhyodacites and related hydrothermal sulphide deposits, but this possibility is not to be eliminated.

Hydrothermal sulphide assemblages in the volcanic-sedimentary sulphide deposits may have been the product of later phase, being deposited after the consolidation of the rhyolitic-rhyodacitic pyroclasts and related sulphides. *In this way complex volcanic-sedimentary-hydrothermal sulphide deposits must have formed* (Fig. 1).

Although the sulphide assemblages of the *first (volcanic-sedimentary) and second (hydrothermal) phase* are mineralogically very similar, they entirely differ regarding the way of their deposition and age. However, the hydrothermal sulphide assemblages in this type of deposits are the products of later volcanic activities, and these assemblages may be genetically explained in two ways:

1. By the new, hydrothermal, influx of the same metals during later, possible rhyolitic volcanism, which reactivated throughout and after the geosyncline folding, by which occasion sulphide minerals have deposited under hydrothermal conditions.

2. By the remobilization of volcanic-sedimentary sulphide deposits by later thermal waters which have circulated along the faults, fissures and void spaces within the primary deposits, and by the redeposition—this time hydrothermal—of dissolved material inside these deposits.

In trie author's opinion, much more detailed investigations, including detailed mapping, exploration, mining and particularly drilling, must be performed before giving a final answer regarding all these questions. Meanwhile, the author does not believe that reactivated volcanism produced the hydrothermal solutions which circulated through all of the investigated volcanic-sedimentary sulphide deposits and much less it is to be believed that these solutions always deposited hydrothermal sulphide minerals in volcanic-sedimentary sulphide deposits! This possibility is acceptable in some cases only. It is also to be pointed out that both of the volcanic-sedimentary and hydrothermal sulphide assemblages in volcanic-sedimentary-hydrothermal deposits are mineralogically very similar.

On the basis of the above-cited data it is to be believed that the hydrothermal sulphide assemblages in the described type of deposits are in most cases the product of hydrothermal remobilization of the primary volcanic-sedimentary sulphide deposits. This conclusion may also be supported by the fact that in a number of explored volcanic-sedimentary-hydrothermal deposits the influx-channels have not been detected at depth, or in these channels sulphide mineralization is almost completely lacking.

Finally, it is to be accentuated that volcanic-sedimentary-hydrothermal deposits do not occur outside the levels of the rhyolitic-rhyodacitic pyroclasts, except for some localities in which scarce sulphides appear. However, if the hydrothermal sulphide assemblages in the described type of deposits

Fig. 1 - Key map of the examined sulphide deposits.

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have always been the products of new hydrothermal influxes, these assemblages must have deposited both in the above cited pyroclasts levels and within the other parts of the stratigraphical column.

Regarding the *hydrothermal sulphide deposits* (Fig. 1) they are genetically related to the younger volcanic rocks, possibly to rhyolites-rhyodacites and occasionally to dacites. Hydrothermal deposits have probably formed almost contemporaneously with the hydrothermal sulphide assemblages included in the volcanic-sedimentary-hydrothermal deposits. Consequently, hydrothermal sulphide deposits exposed in the described region are believed to have been produced by the reactivated rhyolitic-rhyodacitic volcanism. This volcanism must have started under submarine conditions (geosyncline) and produced volcanic-sedimentary sulphide deposits. Throughout the final stage of the later geosyncline folding, rhyolitic-rhyodacitic volcanism has reactivated and produced the sulphide deposits of the hydrothermal type. However, a number of hydrothermal sulphide deposits may be the products of remobilization of deeply seated deposits volcanic-sedimentary in origin.

Opinions on the origin of the *skarn-hydrothermal deposits* (Fig. 1) are diverse, although the idea is prevailing that they are genetically related to the granitoids which are widespread to the south of the rhyolitic-rhyodacitic sulphide-bearing pyroclastics. In the author's opinion granitoids have been, in general, sterile in view of the influx of sulphides, except for molybdenite and associates. Actually, sulphides from skarn-hydrothermal deposits may also be the result of the remobilization of the volcanic-sedimentary ones. This conclusion is also supported by the fact that the skarn-hydrothermal deposits are located, as a rule, in the vicinity or along the contact with the volcanic-sedimentary sulphide-bearing formation (rhyolitic pyroclasts) discussed above. Consequently, granitoid magmatism should have been more or less sterile regarding its juvenile introduction of metals such as lead, zinc and copper.

THE AGE OF INVESTIGATED DEPOSITS

1. *Volcanic-sedimentary-hydrothermal deposits.* — The earlier as well as recent examinations of microfauna performed by the M.T.A. experts have demonstrated that the sulphide-bearing rhyolitic-rhyodacitic pyroclastic formation is of Cretaceous - Senonian age (Lower - Upper Senonian). These data are related to Artvin, Murgul, Kurdaze, Pazar, Ardeşen, Görele and Tirebolu (Köprübaşı) areas. The resulting conclusion is that during the existence of the described geosyncline rhyoliticrhyodacitic submarine volcanism developed throughout this limited period producing related pyroclastic formation. Consequently, the volcanic-sedimentary sulphide ores are exclusively located in this formation which represents a sequence only in the very thick complex of various volcanicsedimentaiy rocks.

The hydrothermal sulphide assemblages in the volcanic-sedimentaiy-hydrothermal deposits are, no doubt, later and they possibly are of Tertiary age.

2. *Hydrothermal deposits* are also later than the volcanic-sedimentary ones and they probably are of Tertiary age.

3. *Skarn-hydrothermal deposits* may be the latest sulphide deposits in the investigated region, although there is not enough data on their exact age.

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Photo 1 - Maden Köy (Çayeli), Volcanic-sedimentary ore: Colloidal textures of pyrite (bright gray, high relief), galena (gray) and chalcopyrite (light gray). These minerals are also concentric alternating. Hydrothermal pyrite and sphalerite (dark gray) are visible too, but they are scarce. Black: rhyolite pyroclast. Oil imm., $220 \times$.

Photo 2 - Maden Köy (Çayeli), Volcanic-sedimentary ore: Galena globules (gray) with aureoles of pyrite (high relief) and chalcopyrite (light gray) in the rhyolite pyroclast (black). Irregular grains of pyrite, chalcopyrite and sphalerite (dark gray) are hydrothermal in origin. Oil imm., $220 \times$.

Photo 3 - Maden Köy (Çayeli). Volcanic-sedimentary ore: Colloidal textures with very clearly developed concentric alternations of pyrite (light gray, pronounced relief), chalcopyrite (light gray) and galena (gray). Hydrothermal sphalerite (dark gray) occurs in the form of grains of various sizes and shapes. The groundmass is rhyolite pyroclast (black). Oil imm., $220 \times$.

Photo 4 - Tuncat I (Ardeșen). Volcanic-sedimentary ore: Rounded sphalerite grains (dark gray), rimmed by chalcopyrite (light gray) and pyrite (light gray, pronounced relief). Left and right: hydrothermal sphalerite (dark gray). The groundmass is rhyolite pyroclast. Oil imm., 200 <.

Photo 5 - Irsa Maden (Artvin). Volcanic-sedimentary ore: Colloidal textures of pyrite (light gray, high relief) and tetrahedrite (gray) in the rhyolite pyroclast (black). Oil imm., 180 ...

Photo 6 - Anayatak (Alurgul), Volcanic-sedimentary ore: Fine-grained mixture of pyrite (light gray, strong relief), and chalcopyrite (gray). This association is replaced by hydrothermal chalcopyrite (gray), which enclosed hyrothermal \mathbb{D} pyrite (light gray, strong relief). Oil imm., 180 s.,

Photo 7 - Çakmakkaya (Murgul), Volcanic-sedimentary ore: The groundmass is chalcopyrite (light gray). It contains the globules of transparent material (black) and the ring-shaped pyrite grains (light gray, high relief). Black: rhyolite pyroclast. Oil imm., $200\times$

Photo 8 - Anayatak (Murgul). Volcanic-sedimentary ore: «Bacterial» pyrite (light gray, pronounced relief), partly enclosed in chalcopyrite. Black: rhyolite pyroclast. Oil imm., 180×.

Photo 9 - Maden Köy (Çayeli). Volcanic-sedimentary sphalerite (gray) in rhyolite pyroclast (black). Oil imm., 220 ×.

Photo 10 - Anayatak (Murgu!). Volcanic-sedimentary ore: «Mineralized bacteria» pyrite (light gray) and sphalerite (dark gray) in chert (black). The groundmass of the «bacterial» grains is mostly represented by sphalerite, whereas pyrite is in the form of inclusions. Hydrothermal sphalerite (dark gray, with hardly visible L. chalcopyrite exsolutions) occurs as grains of various sizes, mainly in the central part of the fig. Oil imm., $220 \times$.

Photo 11 - Akköy (Giresun). Volcanic-sedimentary ore: «Bacterial» pyrite (light gray, pronounced relief) in chalcopyrite (light gray). Black: rhyolite pyroclast. Oil imm., 180 x.

Photo 12 - Tuncat (Ardeșen). Volcanic-sedimentary ore: In the chalcopyrite groundmass (bright gray) lie the globules of sphalerite (dark gray) and ring-shaped pyrite grains (light gray, pronounced relief). The multiple concentric alternations of pyrite and chalcopyrite are also visible. Black: rhyolite pyroclast. Oil imm., 220x.

Photo 13 - Maden Köy (Çayeli). Volcanic-sedimentary ore: Excellently developed concentric alternations of pyrite (light gray) and galena (gray) in the central part of the fig. In the corner: a number of grains of hydrothermal sphalerite (dark gray). Black: rhyolite pyroclast. Oil imm., $220 \times$.

Photo 14 - Akarşen (Murgul). Volcanic-sedimentary ore: In the rock groundmass three rounded grains are visible, consisting of concentric alternated chalcopyrite (light gray), galena (gray) and pyrite (light gray, pronounced relief). $80 \times$.

Photo 15 - Maden Köy (Çayeli). Volcanic-sedimentary ore: The colloidal intergrowths of pyrite (light gray, high relief) and chalcopyrite (fight gray). Black: rhyolite pyroclast. Qil imm.; $220 \times$.

Photo 16 - Akköy (Giresun). Volcanic-sedimentary ore: Colloidal textures of pyrite (light gray, strong relief) and chalcopyrite (light gray). Black: rhyolite pyroclast, Oil imm., 180×.

Photo 17 - Anayatak (Murgul). Volcanic-sedimentary ore: Chalcopyrite patches (light gray), contain numerous fine grains and inclusions of pyrite (light gray, pronounced relief). In the corner: few grains of hydrotermal pyrite. Black: the rock groundmass. Oil imm., $200\times$.

Photo 18 - Kuvarshan (Artvin). Volcanic-sedimentary ore: Very fine-grained mixture of pyrite (light gray, some relief) and tetrahedrite (gray). Above right, in the corner: Hydrothermal chalcopyrite (light gray) replaced both of the cited minerals. Variable coarse pyrite (high relief), and partly tetrahedrite, have been hydrothermally recrystallized. Oil imm., $220 \times$.

Photo 19 - Irsa Maden. (Artvin). Hydrothermal ore: Exsolved chalcopyrite (light gray) in form of «needles» and «spindles» in bornite (gray). White: hydroŀ. thermal pyrite (pronounced relief). The groundmass is carbonate. Oil imm., $200\times$.

Photo 20 - Köstere (north of Torul). Hydrothermal ore: Chalcopyrite exsolutions (white) in sphalerite (dark gray). Black: quartz, Oil imm., $180\times$.

Photo 21 - Irsa Maden (Artvin). Hydrothermal mineral assemblage: Sphalerite (dark gray) replaced by galena (almost white) and partly by tetrahedrite (gray). Minute tetrahedrite exsolutions in sphalerite are also visible. Oil imm., $180\times$,

Photo 22 - Seyitli (Artvin). Hydrothermal ore: Black sphalerite «stars» in chalcopyrite, Sphalerite has been exsolved from the host mineral. Oil imm., $180\times$.

Photo 23 - Irsa Maden (Artvin). Crystalline enargite (light to dark gray), hydrothermal
in origin. Black: carbonate. Oil imm., x nic., $180 \times$.

Photo 24 - Tuncat (Ardeșen). Hydrothermal ore: Crystalline pyrite, replaced and cemented by chalcopyrite (variable gray). Black: replaced rhyolite pyroclast. Oil imm., $200 \times$.

Photo 25 - Maden Köy (Çayeli). Hydrothermal mineral assemblage: The groundmass is sphalerite (dark gray), enclosing the crystals and grains of quartz (black). Sphalerite is replaced by galena (white). Oil imm., $220 \times$.