

## A STUDY OF SPHALERITE FROM THE CARBONATE-HOSTED Pb-Zn SULFIDE DEPOSITS OF THE EASTERN CHALKIDIKI PENINSULA, NORTHERN GREECE

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### ABSTRACT

A detailed textural and chemical study of sphalerite from Pb-Zn deposits in carbonate host-rocks from the Chalkidiki Peninsula, northern Greece, using doubly polished thin sections, indicates a complex evolution of the ore-forming system. Single crystals that attain 1.5 cm show evidence of fine growth-banding, leaching, and at least two stages of brecciation. "Chalcopyrite disease" has been detected along fractures and along grain boundaries in sphalerite; it represents the initial stages of replacement rather than exsolution. The proportion of FeS in the sphalerite is quite variable, between 1.8 and 18.7 mole %, among grains from the same sample, among samples from the same deposit, and among samples from the same mineralogical association in different deposits. This variability reflects variations in 1) the activity of FeS in the fluid, 2) the physicochemical conditions during precipitation (*i.e.*,  $f(S_2)$ , T), and 3) the "chalcopyrite disease" texture, or a combination of 1 and 2 where that texture is absent. On the basis of temperatures derived from fluid-inclusion data on sphalerite that coexists with pyrite and data on its composition (mole% FeS), we infer a sulfur fugacity of  $10^{-9.7}$  to  $10^{-13}$  atm. during sphalerite deposition.

**Keywords:** sphalerite, chalcopyrite disease, growth banding, fugacity of sulfur, Pb-Zn deposit, carbonates, Chalkidiki Peninsula, Greece.

### SOMMAIRE

Une étude texturale et chimique de la sphalérite de gisement Pb-Zn dans des roches hôtes carbonatées dans la péninsule de Chalkidiki, dans le nord de la Grèce, effectuée sur lames minces doublement polies, révèle une séquence complexe de déposition des sulfures. Les monocristaux, qui atteignent 1.5 cm, montrent des fronts de croissance très fins, des signes d'un lessivage et d'au moins deux stades de bréchification. On a décelé la texture dite «maladie de la chalcopyrite» le long de fissures et en bordure des grains de sphalérite; ce phénomène représenterait un remplacement plutôt qu'une exsolution. La teneur en FeS de cristaux uniques varie beaucoup, entre 1.8 et 18.7% (proportion molaire), d'un cristal à l'autre dans le même échantillon, d'un échantillon à l'autre d'un seul gisement, et parmi les échantillons montrant les mêmes associations minéralogiques des divers gisements. Cette variabilité serait due 1) aux changements en activité de FeS dans la phase fluide, 2) aux variations dans les conditions physicochimiques de précipitation (*i.e.*,  $f(S_2)$ , T), et 3) à la présence de la texture dite «maladie de la chalcopyrite», ou à la présence des facteurs 1 et 2 où cette texture est absente. À la lumière des températures obtenues de données obtenues sur les inclusions fluides dans la sphalérite qui coexiste avec pyrite,

et de sa teneur en FeS, on en conclut que la fugacité de soufre était de  $10^{-9.7}$  à  $10^{-13}$  atm. pendant la déposition de la sphalérite.

(Traduit par la Rédaction)

**Mots-clés:** sphalerite, «maladie de la chalcopyrite», fronts de croissance, fugacité de soufre, gisement Pb-Zn, carbonates, péninsule de Chalkidiki, Grèce.

### INTRODUCTION

The Olympias, Madem Laccos and Mavres Petres Pb-Zn massive-sulfide ore deposits are located in the Kerdyllion Formation, Chalkidiki Peninsula, northern Greece (Fig. 1). On the basis of available information, this formation represents the lowermost part of the stratigraphic column of the so-called Serbo-Macedonian Massif (SMM), whereas the uppermost member is referred to as the Vertiskos Formation.

These formations consist of variable proportions of biotite gneiss, two-mica gneiss, biotite-hornblende gneiss, microcline-plagioclase gneiss, amphibolites, marbles and pre-, syn- and postorogenic intrusive bodies (Kockel *et al.* 1977). Kockel *et al.* assigned a probable Precambrian age for the SMM on the basis of information existing for the similar geotectonic unit in Yugoslavia. The Serbo-Macedonian Massif has been subjected to at least three phases of deformation. The first, most likely Hercynian, is characterized by isoclinal folding, with axes trending and plunging to the north, whereas the other two are Alpine. The first took place from the Upper Jurassic to the Lower Cretaceous, with subsoclinal folds of variable trends; the second, of Tertiary age, is characterized by open folds and intense thrusting (Moundrakis 1985). Regional metamorphism has reached the almandine-amphibolite grade; the rocks were subsequently retrograded to the greenschist facies along shear zones and near postorogenic intrusive bodies (Demetriades 1974, Kockel *et al.* 1977, C. Kougoulis, pers. comm.). The metamorphic rocks of the SMM have been intruded by calc-alkaline postorogenic granites of Tertiary age (*e.g.* Stratoni granodiorite, 29 Ma) that show a spatial association with manganese-bearing Pb-Zn sulfides. These intrusive bodies are themselves ore-bearing (*e.g.*, Skouries Cu-Au granodiorite porphyry) and have also altered the surrounding rocks. Nicolaou & Kokonis (1980) suggested that this igneous activity has a

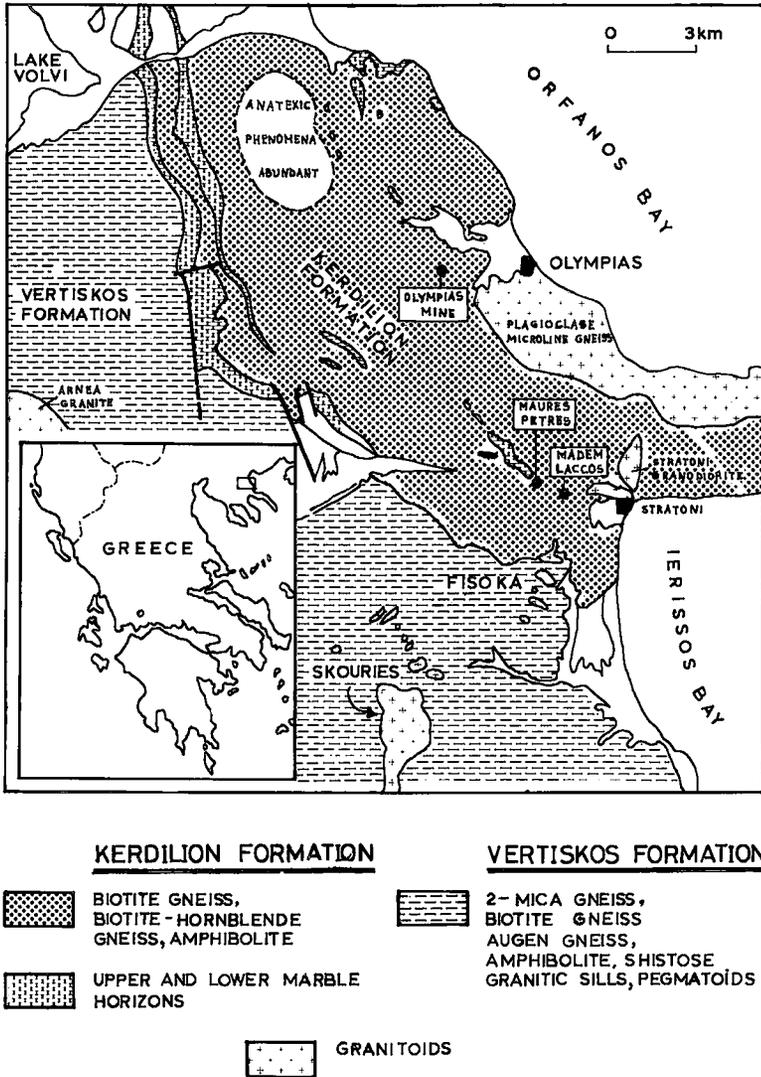


FIG. 1. Location map of the Pb-Zn massive sulfide deposits in Chalkidiki Peninsula (from Kockel *et al.* 1977).

genetic relation to the Pb-Zn-Mn metallogeny in the area.

The Pb-Zn sulfide ores referred to above occur along the contact between a lower marble horizon and a biotite gneiss, as well as within the marble (Kockel *et al.* 1977, Nikolaou & Kokonis 1980). The major minerals present in these ores are sphalerite, galena, pyrite, arsenopyrite and rhodochrosite, whereas the gangue mineralogy is represented by a combination of quartz and calcite.

These ore deposits are considered to be of metasomatic origin, with the hydrothermal fluids derived

from the Stratoni granodiorite (Fig. 1; Nikolaou & Kokonis 1980). The present study is an attempt to deduce the relationship between the mineralization event and deformation associated with metamorphism and to estimate certain geochemical parameters of ore deposition by unravelling the textural and geochemical features of the sphalerite associated with pyrite. This study forms part of a combined effort to gather information pertinent to the development of a scientifically sound and generally accepted genetic model for these Pb-Zn sulfide deposits. Such a model will provide us with the most

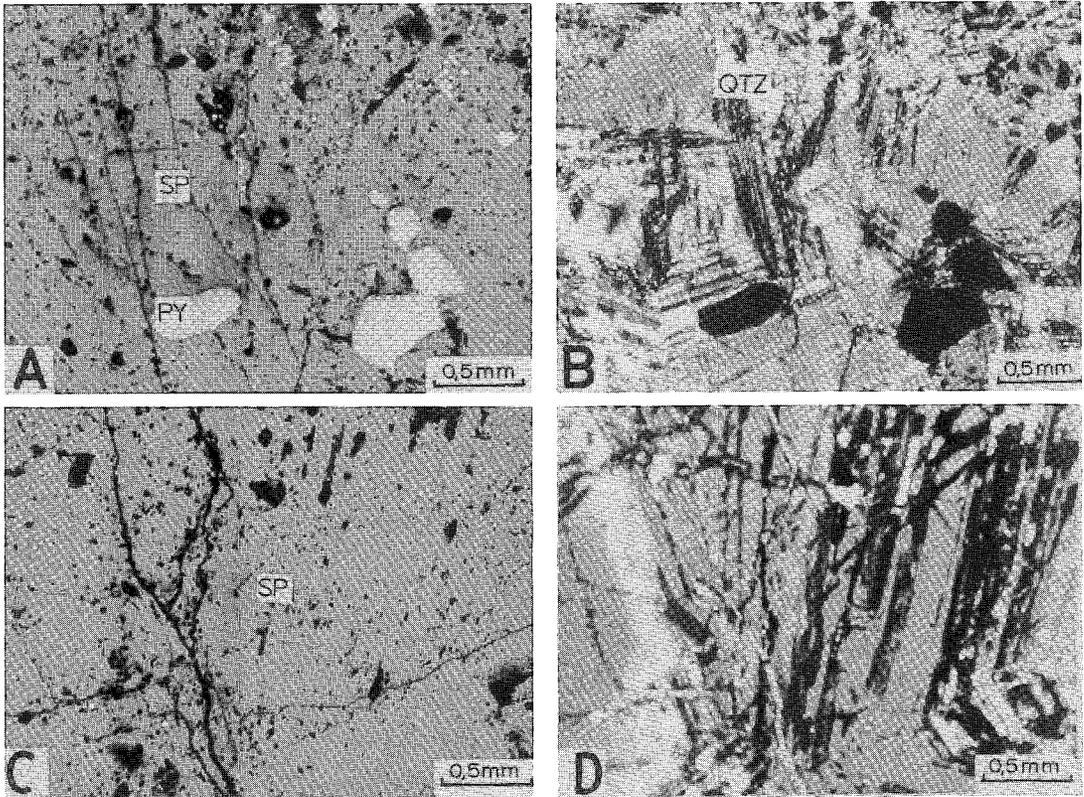


FIG. 2. Reflected (A,C) and corresponding transmitted (B,D) light photomicrographs of sphalerite (Olympias) (doubly polished thin section). Note the fine banding (B,D), which is also reflected in the chemistry.

suitable criteria for exploration for blind ores within the unexplored parts of the Kerdylion Formation.

#### CHARACTERISTICS OF THE ORE DEPOSITS

The ore deposits are stratabound (Nicolaou 1960, Nicolaou & Kokonis 1980) and generally compositionally banded. In addition, during recent visits underground at the Olympias mine, we noted the presence of fault-controlled mineralization as well (N. Bitzios & S.I. Kalogeropoulos, *unpubl. data*). Clastic ore commonly seen underground bears evidence of recrystallization. Two stages of brecciation may be deduced from a study of polished slabs of ore. The first stage consists of fragments of pyrite and sphalerite that are cemented by quartz, whereas in the second stage, fragments of the composite assemblage described above are cemented by sparry calcite.

#### CHARACTERISTICS OF THE SPHALERITE

The sphalerite exhibits a wide range of optical and

chemical variations; these can provide a wealth of information concerning conditions of deposition and subsequent metamorphism of sulfide-bearing rocks and ores (Barton & Toulmin 1966, Scott & Barnes 1971, Scott 1976). Uncovered doubly polished thin sections were used to decipher textural complexities and chemical variations in sphalerite (Figs. 2, 3). The chemical composition of the sphalerite in association with pyrite was determined by electron-microprobe analysis using the JEOL Superprobe 733. Operating conditions were as follows: 20 kV excitation voltage, 5 nA beam current, and 20 seconds counting time. Mineral standards were used, and on-line ZAF corrections were carried out using a PDP-11/04 computer. The error in the iron content of the sphalerite does not exceed 0.2 mole % FeS. In most cases, the iron content varies widely within a single grain (Fig. 3A, Table 1) and between grains (Fig. 3C). These properties, observed in sphalerite from the Olympias and Mavres Petres deposits, can also be extended to that from the Madem Laccos deposit, although our sampling in the latter was not systematic. Moreover, the internal texture in certain

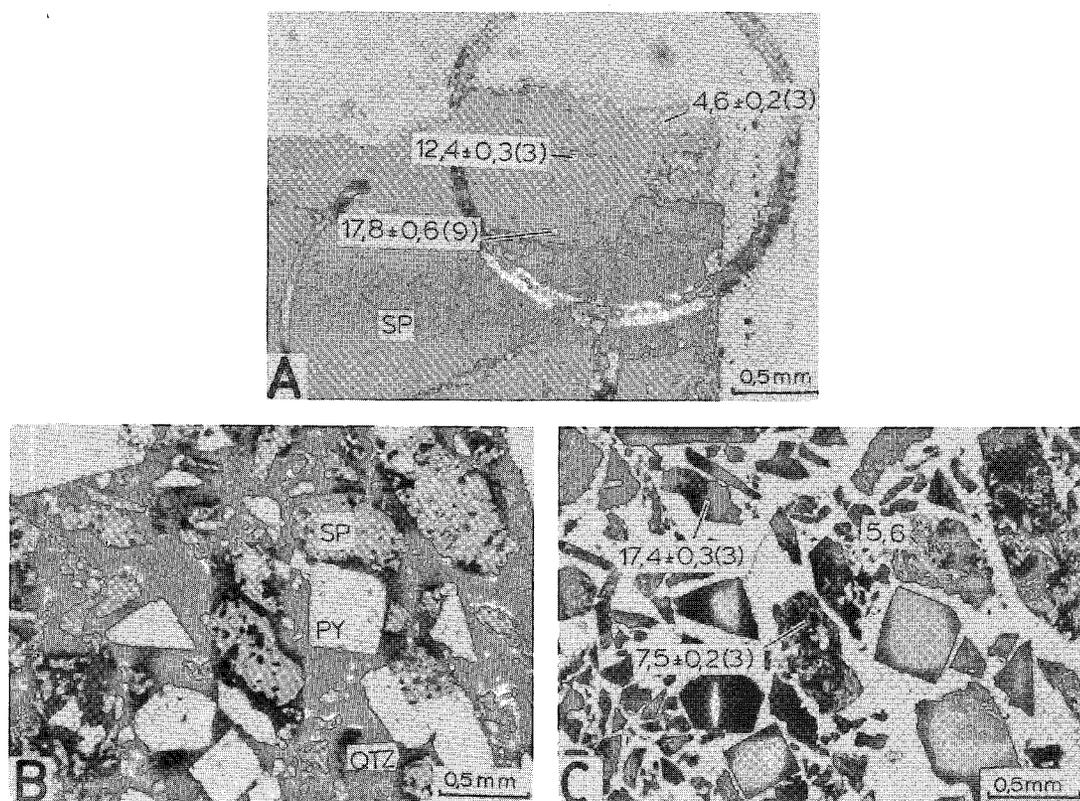


FIG. 3. Transmitted (A,C) and reflected (B) light photomicrographs of the breccia fragments. Sphalerite-bearing breccia fragments (B and C) are of different origin. Note the banding and chemical zoning (mole % FeS) in the sphalerite. Numbers in parentheses (in A and C) indicate the number of analyses performed (Olympias).

TABLE 1. COMPOSITIONAL ZONING IN A SINGLE GRAIN OF SPHALERITE, OLYMPIAS Pb-Zn SULFIDE DEPOSIT, EASTERN CHALKIOTIKI PENINSULA, NORTHERN GREECE

|           | Centre (n=5) | Intermediate (n=3) | Margin (n=3) |
|-----------|--------------|--------------------|--------------|
| Zn %      | 54.94(0.30)  | 58.50(0.78)        | 63.53(0.28)  |
| Fe        | 9.88(0.13)   | 7.13(0.15)         | 2.63(0.15)   |
| Cu        | -            | -                  | -            |
| Cd        | -            | -                  | 0.26(0.05)   |
| Mn        | 0.20(0.0)    | 0.33(0.05)         | 0.23(0.05)   |
| S         | 33.20(0.50)  | 32.50(0.36)        | 33.10(0.50)  |
| total     | 98.06(0.85)  | 98.46(0.76)        | 99.76(0.95)  |
| mole% FeS | 17.36(0.19)  | 12.40(0.26)        | 4.63(0.20)   |

Microprobe analyses performed using energy dispersion. Numbers in parentheses represent one standard deviation. n number of analyses.

sphalerite grains suggests the occurrence of hydrothermal leaching followed by redeposition (Fig. 3A).

The mole % FeS in sphalerite from the Olympias ore deposit [ $14.20 \pm 4.2(15)$ ;  $n = 59$ ] is not statistically different ( $t$  test) from that of the Mavres Petres sphalerite [ $9.4 \pm 5.2(15)$ ;  $n = 34$ ]. These data are presented in Figure 4. In general, sphalerite from deformed and metamorphosed lead-zinc sulfide deposits shows evidence of deformation twinning and a tendency to be homogeneous with respect to its iron

content. Since the host rocks have gone through at least three stages of deformation, regional metamorphism has reached the garnet-amphibolite facies, and the sphalerite in our case does not show evidence of deformation twinning and of chemical homogenization, it may be concluded that the deposition of the ore postdates deformation and regional metamorphism.

A study of the textural relationship between sphalerite and chalcopyrite reveals that the latter appears along fractures and grain boundaries (so-called "chalcopyrite disease"). The grains of sphalerite show a decrease in their iron content along preferred sites (Figs. 5, 6). This decrease may be due to one or a combination of the following two possibilities: (i) decrease of temperature and concomitant increase of the sulfur fugacity, with iron from sphalerite. Since the chalcopyrite primarily occurs cross-cutting sphalerite that is finely zoned with respect to its iron content, we suggest that the second process is the more attractive explanation of the observed texture.

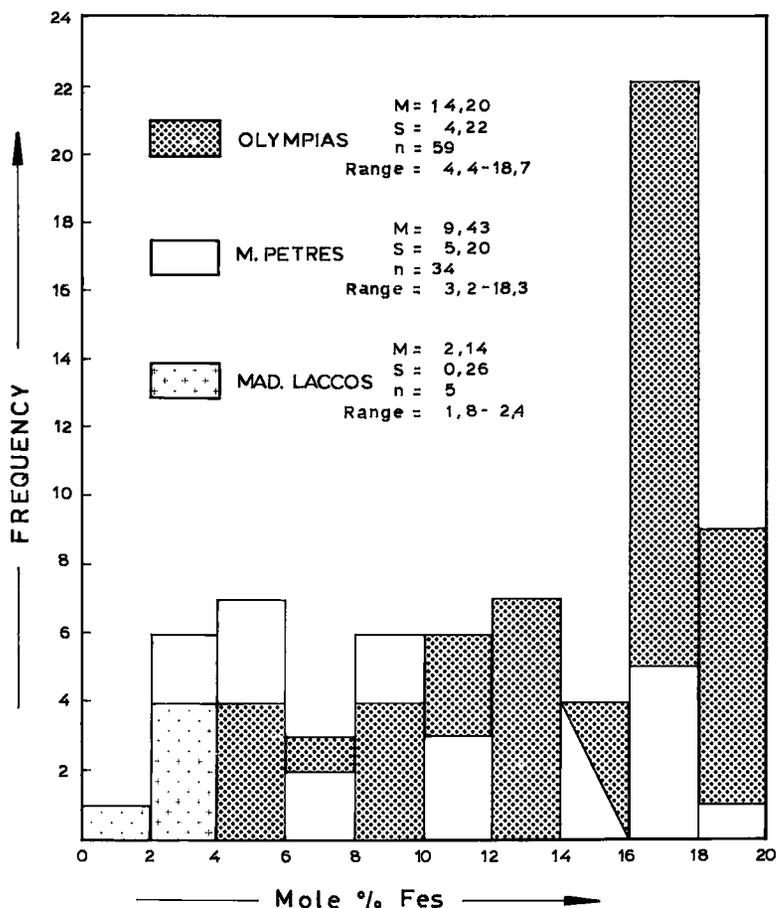


Fig. 4. Histogram of mole % FeS of sphalerite from Olympeas, Madem Laccos and Mavres Petres ore deposits. Mean (M), standard deviation (S), number of analyses (n) and ranges are also shown.

This texture may have been produced according to one or both of the following reactions:  $2 \text{FeS}^{\text{sp}} + \text{Cu}^{2+} (\text{in solution}) \rightleftharpoons \text{CuFeS}_2 + \text{Fe}_2^{2+} (\text{in solution})$ ,  $3\text{FeS}^{\text{sp}} + \text{FeS}_2 + 2\text{Cu}^{2+} (\text{in solution}) \rightleftharpoons 2\text{CuFeS}_2 + 2\text{Fe}^{2+} (\text{in solution})$ . Where the second reaction is valid, replacement features are found in the pyrite.

#### CERTAIN PARAMETERS OF THE GEOCHEMICAL ENVIRONMENT OF ORE DEPOSITION

We have chosen to present an overall estimate of the range of values of certain geochemical parameters of ore formation, for the following two main reasons: (i) it is not possible to statistically substantiate a correlation between fluid-inclusion data and iron contents in certain growth-zones in single grains of

sphalerite (K. Doryforos & S.I. Kalogeropoulos, in prep.). (ii) We cannot be certain as to whether or not each of these growth zones was in equilibrium with pyrite. Utilizing both the geothermometric data of fluid inclusions in sphalerite (not corrected for pressure) and its iron content, we can delineate the environment of ore deposition on an  $f(\text{S}_2) - T$  diagram (Fig. 7, Table 2), along with other geochemical parameters. The sulfur fugacity obtained from Figure 7 ranges from  $10^{-9.7}$  to  $10^{-13}$  atm.

#### DISCUSSION

The Pb-Zn sulfide ore deposits of the eastern Chalkidiki Peninsula, northern Greece, which occur

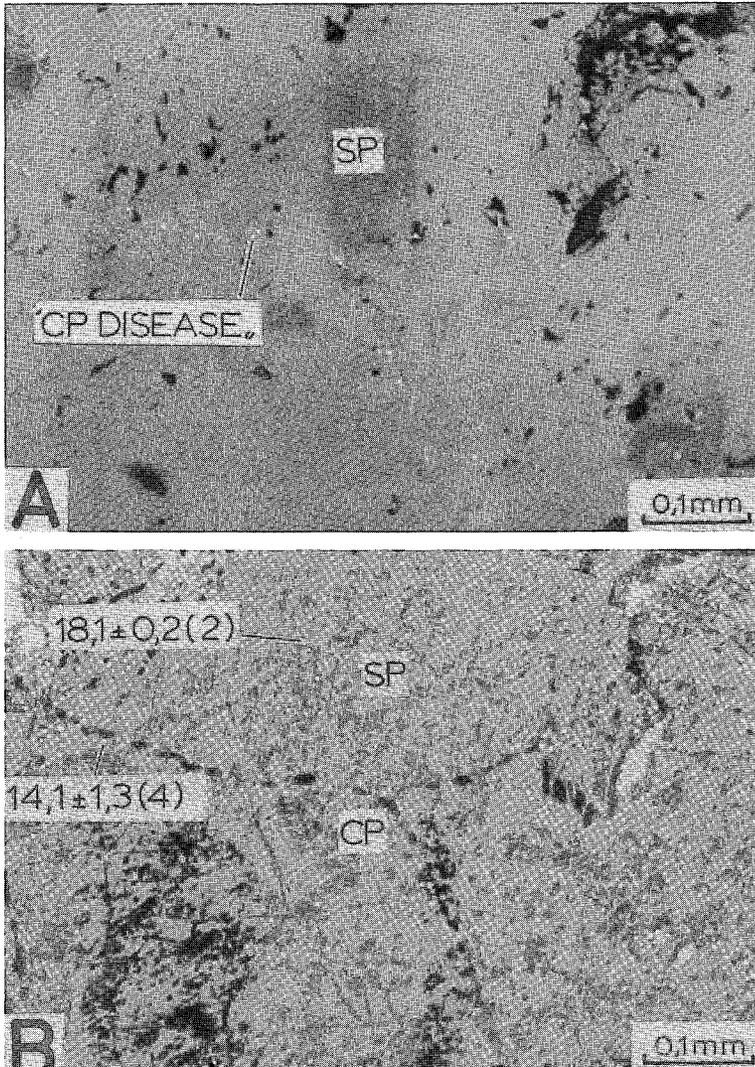


FIG. 5. Reflected (A) and transmitted light (B) photomicrographs of textures in sphalerite. Note that the presence of chalcopyrite along grain boundaries is coupled with a bleaching and removal of iron in the sphalerite (B) (Olympias).

mainly within marble and along a lower marble – biotite gneiss contact (Kockel *et al.* 1977, Nicolaou & Kokonis 1980), are fault-controlled, stratabound, and commonly stratiform. The host rocks have suffered at least three phases of deformation and have been regionally metamorphosed to the garnet-amphibolite facies. Along shear zones and Tertiary igneous stocks, this prograde sequence was followed by a retrograde metamorphic event (greenschist facies). The finely banded nature of single grains of

sphalerite, compositionally zoned with respect to their iron content, combined with the lack of deformation twinning, both suggest that deposition of the sphalerite postdates deformation and regional metamorphism. The recrystallization features detected are most likely due to the intermittent nature of the ore-forming hydrothermal activity. During sphalerite precipitation, this activity was dominated by saline solutions (22–25wt. % eq NaCl), temperatures ranging from 220 to 250°C, and sulfur fugaci-

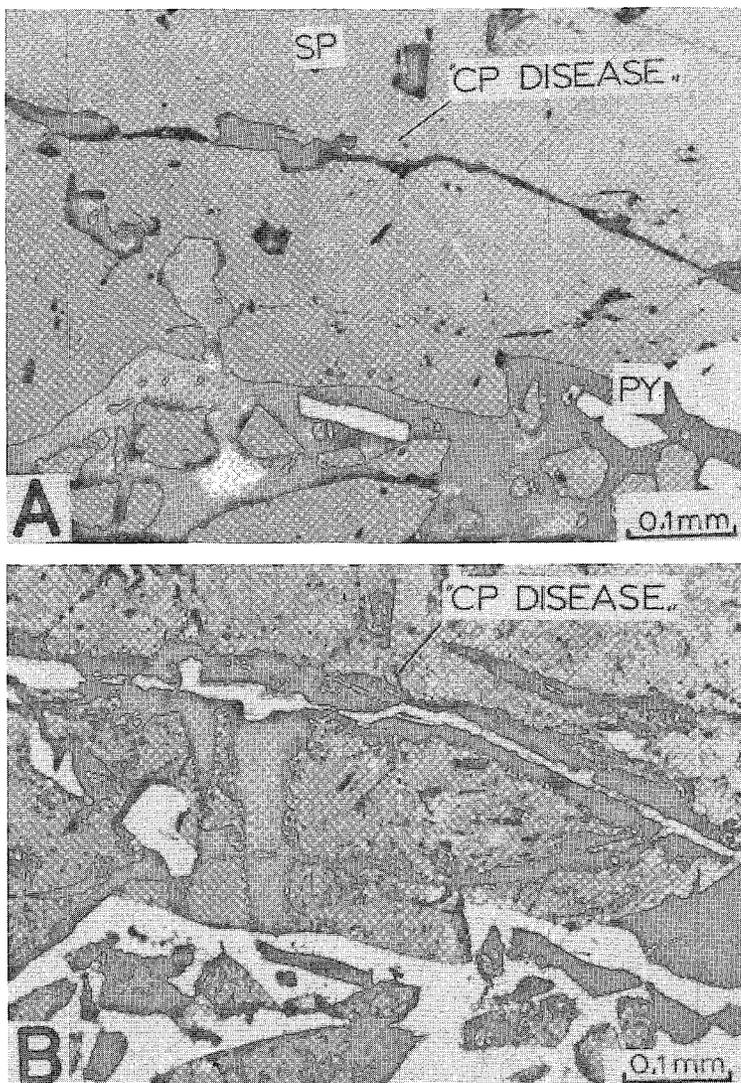


FIG. 6. Reflected (A) and transmitted light (B) photomicrographs showing fracture-controlled fine "chalcopyrite disease" texture, which results in partly opaque sphalerite (Olympias).

ties ranging from  $10^{-9.7}$  to  $10^{-13}$  atm. The temporal and spatial association of sulfide ore deposition and postkinematic igneous activity in the eastern Chalkidiki Peninsula does not necessarily imply that the sulfide ores represent a peripheral manifestation of ore-forming hydrothermal activity due to emanations from the nearby igneous stocks. This does not preclude the existence of predeformational mineralization which is now completely redistributed and reconcentrated through a Tertiary geothermal system set up by the post-kinematic igneous activity (e.g., near the Stratoni granodiorite).

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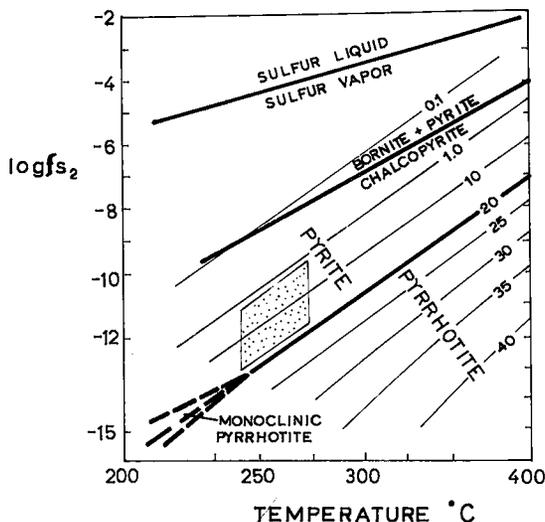


FIG. 7.  $\log fS_2 - T$  ( $^{\circ}C$ ) diagram for the Fe-Zn-S system showing the mole % FeS of the sphalerite in equilibrium with pyrite and pyrrhotite (Czamanske 1974). Note the outline on the field of sphalerite deposition.

TABLE 2. PARAMETERS OF ORE DEPOSITION, OLYMPIAS Pb-Zn DEPOSIT

| PARAMETER               | RANGE                  | SOURCE OF INFORMATION   |
|-------------------------|------------------------|---|
| Temperature             | 220 - 270 $^{\circ}C$  | fluid inclusions in sphalerite (Doryforos & Kalogeropoulos, in prep.) |
|                         | 235 - 387 $^{\circ}C$  | arsenopyrite geothermometry (Kalogeropoulos 1984)                     |
| Salinity                | 22 - 25 wt. %          | fluid inclusions (Doryforos & Kalogeropoulos, in prep.)               |
| Mole% FeS in sphalerite | 1.8 - 18.7             | this study  |
| $f(S_2)$ (atm.)         | $10^{-9.7} - 10^{-13}$ | this study  |

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