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GALENA AND CHALCOPYRITE FROM THE
SKARN-SULPHIDE DEPOSIT « VALLE DEL TEMPERINO »,
CAMPIGLIA MARITTIMA, TUSCANY

SUMMARY. — Galena and chalcopyrite from the skarn-sulphide deposit « Valle del Temperino » (Campiglia Marittima, Tuscany) were studied by optical and electronprobe analyses.

The textural relationships evidence the chalcopyrite-sphalerite-galena paragenesis according to a crystallization from a metal-sulphur complex state.

The chalcopyrites from the inner and outer parts of the deposit show a remarkable compositional homogeneity, thus suggesting the same temperature of formation. On the other hand the compositional dishomogeneity of galena and its disequilibrium relationship with sphalerite point out the fact that no post-depositional event affected the whole system. The chalcopyrite-sphalerite-galena mineralization should have deposited after the contact metamorphic event correlated with the pliocene granitic intrusion and the chemical disequilibrium is to be imputed to f_{S_2} variations.

RIASSUNTO. — Le galene e le calcopiriti del deposito a solfuri della Valle del Temperino (Campiglia Marittima, Toscana) sono state studiate per via ottica e spettrochimica alla microsonda elettronica.

Le relazioni tessiturali mostrano una paragenesi calcopirite-blenda-galena in accordo con una cristallizzazione da complessi solfometallici.

Le calcopiriti delle diverse parti del deposito presentano una notevole omogeneità di composizione che suggerisce una stessa temperatura di formazione. D'altra parte la disomogeneità della galena e le relazioni di disequilibrio della stessa con la blenda indicano che il sistema non è stato riequilibrato da eventi post-deposizionali.

La mineralizzazione a calcopirite-blenda-galena si è depositata dopo il fenomeno metamorfico correlato con l'intrusione granitica e il disequilibrio chimico rilevato è da mettere in relazione con le variazioni di f_{S_2}.

Introduction.

Galena and chalcopyrite from the contact metasomatic skarn-sulphide deposit « Valle del Temperino » (Campiglia Marittima, Tuscany) have been studied by optical and spectrochemical investigations.

The mineralized bodies of the deposit are completely embedded in the marble deriving from the liassic limestone formation « calcare massiccio » metamorphosed by the pliocene granitic intrusion. The ore bodies are strictly associated with a femic monzonite porphiry, known as « porfido verde », and show, in spite of their irregular shape, a zoning of mineralization. The mineral association is characterized, in the inner zone, by the presence of ilvaite, magnetite, chalcopyrite and pyrrhotite and, in the outer, by hedenbergite, chalcopyrite and pyrite with some superpositions of the two associations as shown by a banded macroscopic texture. In some pockets of the upper part of the deposit, in direct contact with the marble, galena and sphalerite are associated with hedenbergite, chalcopyrite and pyrite. The whole mineralized body shows a marked outwards depositional trend.

This research, which follows a previous one on the sphalerite of the same deposit (CORSINI and TANELLI, 1974), to which the reader is referred for a more complete description of the geological setting and of the ore structure and relating bibliography, was carried out in order to obtain some information on:

1) the formation temperature of the chalcopyrite-sphalerite-galena assemblage ([1]), present in the upper zone of the mineral body, through the determination of the distribution coefficient (K) both of MnS and CdS between galena and sphalerite and of Se between galena and chalcopyrite, according to BETHKE and BARTON (1971);

2) the relationship between the chalcopyrites of the inner and of the outer zone through the determination of minor elements and of metal/sulphur ratio on the basis of the experimental work of YUND and KULLERUD (1966) and CABRI (1973).

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[1] According to BARTHOLOMÉ (1958): « mineral assemblage will refer to the set of minerals which are observed in direct contact with each other in an ore specimen. The words mineral association will be used more loosely ».

Experimental procedures.

Samples were collected directly from mine openings with special effort devoted to obtaining a representative sampling of different zones of the skarn-sulphide deposit. The microscope and electronprobe determinations were made on polished and thin-polished sections. The spectrochemical analyses of galena were carried out with the Philips-Norelco AMR/3 electronprobe (take-off angle 18°) of the Institute of Mineralogy, University of Florence, at an excitation potential of 30 kV. Galena was investigated for Pb, Mn, Fe, Cu, Zn, Se, Ag, Bi and Cd using a synthetic galena as a standard for lead, and pure metals (Alfa Inorganic Inc. Beverly, Mass. U.S.A.) for the other elements.

The spectrochemical analyses of chalcopyrite were carried out with a Cambridge-Geoscan electronprobe (take-off angle 75°) of the Department of Mineralogy and Petrology, University of Cambridge, U.K., at an excitation potential of 20 kV for S, Mn, Ag, and Cd and of 30 kV for all the other elements previously mentioned. In these analyses the standards used for galena were associated, for sulphur, to a pyrite from the Isle of Elba.

The measured intensities were corrected for dead-time, background and filament-drift and the measured concentrations for fluorescence, absorption and atomic number applying the DUNCUMB and JONES (1969) program to the IBM 360/44 computer of the Institute of Astronomy, University of Cambridge.

The analyses reported are average values from six to twelve different points on which each element was counted three times. The deviations from the several spot analyses of a same sample fall within the range of radiometric error. The overall precision of analyses was determined by repeating the determinations on selected areas of galena and chalcopyrite.

Microscopic analysis.

Chalcopyrite, sphalerite and galena assemblage.

This assemblage occurs only in the upper zones of the skarn-sulphide deposit in direct contact with marble. Sphalerite is always characterized by bleb-like inclusions of chalcopyrite in a typical « mottled

texture » (EDWARDS, 1965), which is particularly developed near the sphalerite-chalcopyrite and sphalerite-galena contacts. A drained area and a seriate arrangement of inclusions are frequently observed (fig. 1, *a* and *b*). In some cases the inclusions have a fragment-like shape, particularly when the contact sphalerite-chalcopyrite has a sharpcorner trend. Etching of sphalerite with HI has sometimes revealed an intergranular distribution of chalcopyrite (fig. 1, *c* and *d*). These textural relationships suggest a primary crystallization of chalcopyrite followed by crystallization of sphalerite toghether with some residual and/or replaced chalcopyrite. The early main crystallization of chalcopyrite might be confirmed by the selective replacement, particularly along the chalcopyrite-sphalerite contact, of chalcopyrite by galena which is the last mineral to crystallize (fig. 1 *b*).

Small amounts of pyrite and magnetite are associated with the above mentioned minerals while covellite and digenite are sometimes

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Fig. 1.

a) Bleb-like inclusions of chalcopyrite (white) in sphalerite (greyish black) along the contact. Note the draining zone and a polysinthetic twin of sphalerite.
Polished section M2-3, oil immersion; etched HI; N ∥ .

b) Replacement of chalcopyrite (greyish) by galena (greyish white) along the contact with sphalerite (blackish grey). Note the inclusions of chalcopyrite in sphalerite both parallel to the contacts and in a seriate distribution.
Polished section S7-2; air; N ∥ .

c) Fine aggregate of sphalerite grains (from greyish black to grey) with integranular and bleb-like inclusions of chalcopyrite (white).
Polished section M2-19; oil immersion; etched HI; N ∥ .

d) Coarse grain of sphalerite (from greyish black to light grey) showing a polysinthetic twinning with intergranular chalcopyrite (white).
Polished section M2-3; air; etched HI; N ∥ .

e) Chalcopyrite (whitish) replacing an iron sulphide (greyish, pitted) derived from pyrrhotite (whitish grey), with some remnants of magnetite (greyish black). The gangue mineral (blackish) is mainly hedenbergite.
Polished section M4-2; air; N ∥ .

f) Chalcopyrite specks and inclusions (white) in sphalerite (dark grey). Magnetite lamellae (blackish grey) are replaced by chalcopyrite. Note the magnetite nodules in a coarse subhedral pyrite grain (whitish).
Polished section E3-3; air; N ∥ .

present around chalcopyrite as supergene minerals. The gangue is mainly composed of hedenbergite, johannsenite and calcite and small amounts of quartz and ilvaite.
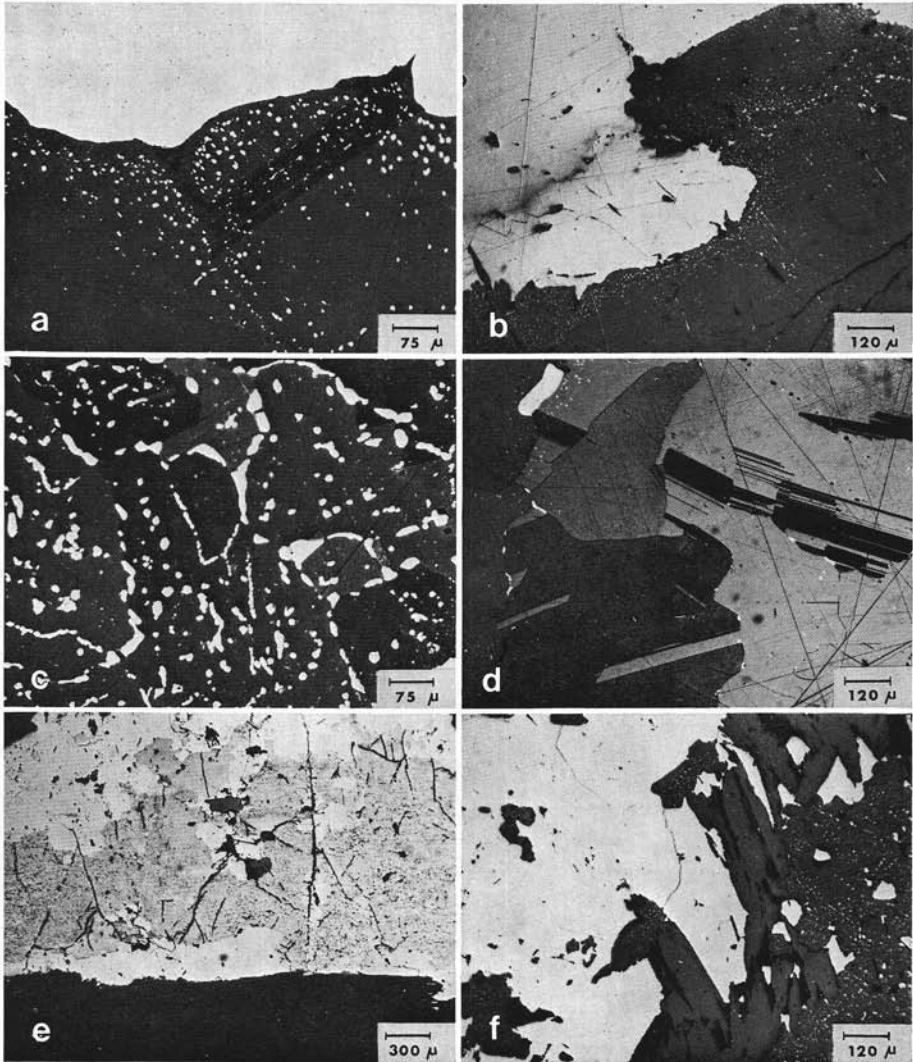

Fig. 1.

Chalcopyrite, pyrrhotite and magnetite assemblage.

This assemblage occurs in the inner zone of the mineralized body. Magnetite is present both as pseudomorph on hematite lamellae, which are frequently observed as remnants, and as nodules normally con-
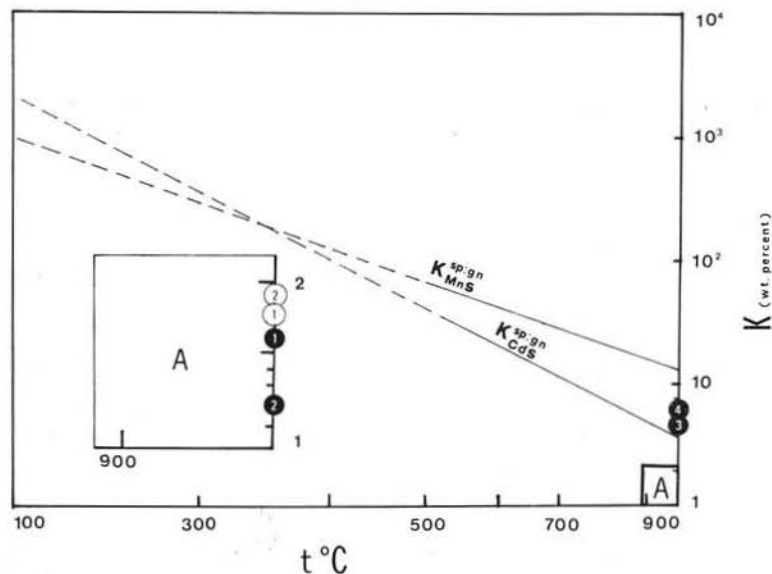

Fig. 2. — Variation of distribution coefficients with temperature for sphalerite and galena at equilibrium (after BETHKE and BARTON, 1971), with the values of the $K_{MnS}^{sp:gn}$ (solid circles) and $K_{CdS}^{sp:gn}$ (open circles) for galena and sphalerite from Campiglia Marittima. (Precision 42 percent; $1 = M2\text{-}2$; $2 = M2\text{-}3$; $3 = M2\text{-}19$; $4 = M4\text{-}103$).

taining small drop-like pyrrhotite and/or chalcopyrite inclusions. Pyrrhotite, which resulted to be hexagonal as well as monoclinic at x-ray diffractometer investigations, occurs as an intergrowth of large lamellae frequently embedding magnetite. Both pyrrhotite and magnetite lamellae may be replaced by chalcopyrite which in some cases is completely pseudomorph after pyrrhotite. Primary pyrite is present in coarse subhedral grains, strictly associated to magnetite and hematite, whereas secondary pyrite occurs in colloform nodules in pyrrhotite. The

association is completed by minor quantities of sphalerite, bismuthinite, marcasite and of another iron sulphide phase which appears to be an alteration product of pyrrhotite. This phase, which may be identified as the « intermediate product » of EINAUDI (1971), is replaced by chalcopyrite (fig. 1 e).

Three different types of sphalerite-chalcopyrite textures have been observed: star-like inclusions of sphalerite in chalcopyrite, mottled texture with a seriate distribution of chalcopyrite grains, and specks of chalcopyrite in sphalerite (fig. 1 f).

Bismuthinite is present as specks in chalcopyrite while marcasite is frequently associated with the chalcopyrite replacing pyrrhotite.

The gangue minerals are represented by ilvaite, quartz and minor quantities of hedenbergite and fluorite.

Electron probe analysis.

The analyses performed for those elements whose concentration was higher than the detectability limit, extimated to 99,7 percent level of probability, are reported in Tab. 1. The sulphide concentrations are also reported for the galena analyses in order to verify the overall accuracy. Chalcopyrites in the samples from the inner (E3-3 and E2-3) and outer (M2-3 and M2-19) zones of the deposit, show a remarkable similarity in their composition, expecially for what concerns the Me/S ratio which according to YUND and KULLERUD (1966), characterizes chalcopyrites of different formation temperatures. Therefore, assuming that no post-depositional homogenization has occurred, the results suggest that the $CuFeS_2$ of the inner and outer zones of the deposit are to be related to the same formation temperature. The analyses of galena and chalcopyrite show that selenium has never been detected while manganese and cadmium have been detected only in some of the galena samples. The values of the distribution coefficents $K_{MnS}^{sp:gn}$ and $K_{CdS}^{sp:gn}$, calculated for samples M2-2, M2-3, M2-19 and M4-103, using the sphalerite data obtained by CORSINI and TANELLI (1974) on the same polished sections, are plotted on the diagram of fig. 2 showing the relationship between distribution coefficients and temperature for sphalerite and galena at equilibrium (BETHKE and BARTON, 1971). The

position of the points representing our samples suggests that the ga-
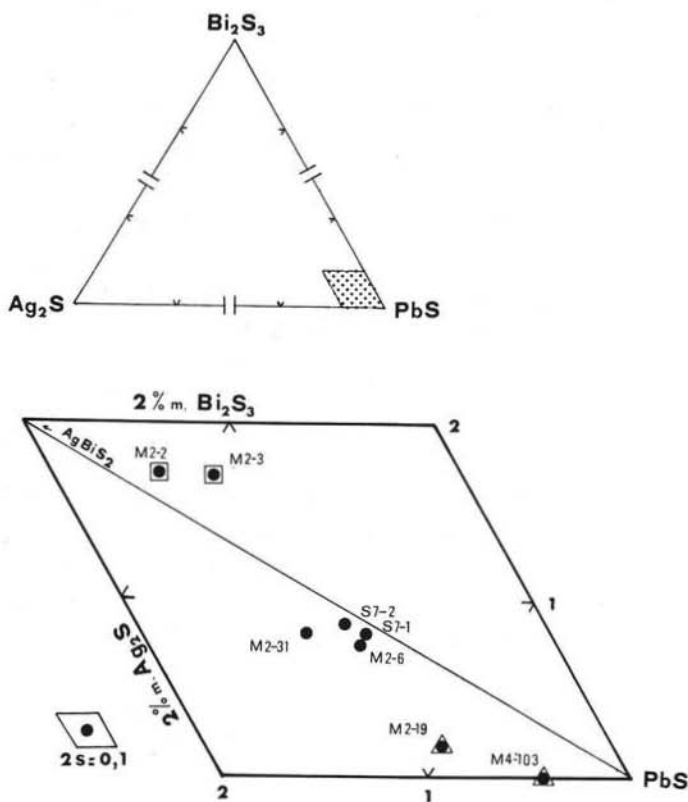lena and sphalerite from Campiglia Marittima are not at equilibrium.

Fig. 3. — Composition of galenas from Campiglia Marittima
reported in a portion of the PbS-Ag₂S-Bi₂S₃ system (the precision
is indicated by the small rhombus on the left; □ = Mn and Cd
present; △ = Mn present).

The results of all galena analyses reported (fig. 3) in the
PbS-Ag₂S-Bi₂S₃ diagram (MnS and CdS have been added to PbS)
point out the dishomogeneity in Ag₂S and Bi₂S₃ content, particu-
larly for the M2-2, M2-3, M2-19 and M4-103 samples collected in the
eastern part of the mineralized body (see fig. 1 CORSINI and TANELLI,
1974). No evidence of different steps of recrystallization — such as

an overgrowth of galena crystals — or of a continuos variation of physico-chemical conditions — such as a chemical zoning in a single galena crystal — has been detected. The compositional dishomogeneity suggests a chemical disequilibrium in the medium from which galena was crystallizing. It is extremely improbable for T and P to have changed, in the very restricted sampled area, in such a way as to account for the variations in the activities of the different components of the system.

Conclusions.

The internal compositional dishomogeneity of galena and sphalerite and the disequilibrium situation between these two minerals suggest that no remarkable post-depositional events have caused a re-equilibration in spite of the chemical homogeneity of chalcopyrite. Conceivably this homogeneity cannot be imputed to the thermal metamorphism related to the pliocene granitic intrusion, whose intensity, which caused the metamorphism of the liassic limestone, should have homogenized also the sphalerite in spite of its lower re-equilibration tendency in comparison with chalcopyrite (BARTON, 1970). The homogeneity of chalcopyrites may be imputed either to a re-equilibration occurred at room-temperature or to a same temperature of primary deposition, which should have varied between 260° and 334°C, as determined by CORSINI and TANELLI (1974) for the chalcopyrite of the inner zone. Of these two hypotheses the former seems to be less probable because of the dishomogeneity of galena which has an homogenization tendency of the same order of chalcopyrite (BETHKE and BARTON, 1971).

The chalcopyrite-sphalerite-galena paragenesis, analogous to the zoning of the whole mineralized body, agrees with a sequence of deposition from a Cu rich medium where all metals occur in sulphur complexe state (BARNES and CZAMANSKE, 1967). The textural relationship between chalcopyrite and sphalerite and the internal dishomogeneity of sphalerite and galena can be explained by fluctuations of f_{S_2}. Considering the close values of ΔG for Cu and Zn complexes, these fluctuations controlled both the crystallization and/or dissolution of chalcopyrite and sphalerite and the activity of FeS, Ag_2S, Bi_2S_3, MnS and CdS in the system.

TABLE 1. — *Microprobe analyses of galenas and chalcopyrites from Campiglia Marittima.*

GALENA				Concentrations (wt. percent)			
Sample	Mn (MnS)	Ag (Ag₂S)	Cd (CdS)	Pb (PbS)	Bi (Bi₂S₃)	Total	Association
M2-2	0.10(0.16)	1.30(1.49)	0.15(0.19)	81.40(93.94)	2.98(3.66)	(99.44)	ccp, sp, py, he, qz, cv, mag, hem
M2-3	0.13(0.21)	1.11(1.27)	0.10(0.13)	83.73(96.62)	3.04(3.74)	(101.97)	ccp, sp, py, he, calc
M2-6	—	0.89(1.02)	—	84.65(97.67)	1.32(1.62)	(100.31)	ccp, sp, py, calc
M2-19	0.06(0.09)	0.78(0.89)	—	85.84(99.06)	0.30(0.37)	(100.41)	ccp, py, sp, cv, di, he, il, qz
S7-1	—	0.83(0.95)	—	85.33(98.47)	1.45(1.78)	(101.20)	ccp, sp, he, qz
S7-2	—	0.89(1.02)	—	84.50(97.51)	1.46(1.80)	(100.33)	ccp, sp, py, he, calc
M2-31	—	1.08(1.24)	—	83.62(96.50)	1.42(1.75)	(99.49)	ccp, sp, py, he, qz
M4-103	0.07(0.11)	0.39(0.45)	—	86.24(99.52)	—	(100.08)	ccp, py, sp, he, qz

CHALCOPYRITE				Concentrations (wt. percent)			
Sample	Fe	Cu	Cd	S	Total	Formula	Association
M2-3	31.01	34.53	0.18	34.05	99.77	$Cu_{1.02\pm0.02} Fe_{1.05\pm0.03} Cd_{0.003\pm0.001} S_{2\pm0.03}$	see above
M2-19	31.05	34.73	0.15	33.74	99.67	$Cu_{1.04\pm0.02} Fe_{1.06\pm0.03} Cd_{0.003\pm0.001} S_{2\pm0.03}$	see above
E3-3	30.13	35.11	0.10	34.30	99.64	$Cu_{1.03\pm0.02} Fe_{1.01\pm0.02} Cd_{0.002\pm0.001} S_{2\pm0.03}$	hem, mag, ccp, py, il, he, qz
E2-3	30.56	34.92	0.12	34.10	99.70	$Cu_{1.03\pm0.02} Fe_{1.02\pm0.02} Cd_{0.002\pm0.001} S_{2\pm0.03}$	mag, po, ccp, he, il, qz

Limits of detectability (wt. percent)
Galena: Mn = 0.04; Fe = 0.05; Cu = 0.06; Zn = 0.09; Ag = 0.09; Cd = 0.09; Bi = 0.09; Se = 0.09
Chalcopyrite: Mn = 0.03; Zn = 0.08; Ag = 0.06; Cd = 0.09; Bi = 0.06; Se = 0.06

ccp = chalcopyrite; sp = sphalerite; py = pyrite; po = pyrrhotite; cv = covellite; di = digenite; mag = magnetite; hem = hematite; he = hedenbergite; il = ilvaite; calc = calcite; qz = quartz

The lower FeS content of the sphalerite associated with the chalcopyrite of the outer zone, points to an increased outwards f_{S_2}, which may account for the crystallization of galena beeing delayed till the temperature decreased, as requested by the lower Δ G value of Pb complexes in comparison with those of Cu and Zn.

REFERENCES

BARNES H. L. and CZAMANSKE G. K. (1967) - *Solubities and transport of ore minerals*. In Geochemistry of hydrothermal ore deposits, Edited by H. L. Barnes, New York, 334-381.

BARTHOLOMÉ P. (1958) - *On the paragenesis of copper ores*. Studia Universitatis Lovanium, Faculté des Sciences 4, Leopoldville.

BARTON P. B. Jr. (1970) - *Sulfide petrology*. Mineral Soc. Amer. Spec. Pap. *3*, 187-198.

BETHKE P. M. and BARTON P. B. Jr. (1971) - *Distribution of some minor elements between coexisting sulfide minerals*. Econ. Geol. *66*, 140-163.

CABRI L. J. (1973) - *New data on phase relations in the Cu-Fe-S system*. Econ. Geol. *68*, 443-454.

CORSINI F. e TANELLI G. (1974) - *Analisi alla microsonda elettronica delle blende del giacimento della Valle del Temperino (Campiglia Marittima, Toscana)*. Rend. Soc. Ital. Min. Petr. XXX, 205-221.

DUNCUMB P. and JONES E. M. (1969) - *Electron probe microanalysis: an easy-to-use computer program for correcting quantitative data*. Tube Investments tech. report *260*.

EDWARDS A. B. (1965) - *Textures of the ore minerals and their significance*. The Australasian Institute of Mining and Metallurgy, Melbourne.

EINAUDI M. T. (1971) - *The intermediate product of pyrrhotite alteration*. Am. Miner. *56*, 1297-1302.

YUND R. A. and KULLERUD G. (1966) - *Thermal stability of assemblages in the Cu-Fe-S system*. J. Petrol. 7, 454-488.