

FRANCESCO GREGORIO \*, PIERFRANCO LATTANZI \*, GIUSEPPE TANELLI \*

A CONTRIBUTION TO THE GENETIC KNOWLEDGE  
OF THE SKARN-SULFIDES DEPOSIT OF VALLE DEL TEMPERINO  
(CAMPIGLIA MARITTIMA, TOSCANA):  
SPHALERITE, PYRITE AND PYRRHOTITE ASSEMBLAGE

RIASSUNTO. — È stata studiata per via ottica, diffrattometrica e spettrochimica (microsonda elettronica) la stretta associazione di sfalerite, pirite e pirrotina recentemente individuata nel corpo minerario più meridionale del giacimento della Valle del Temperino. I tre minerali si trovano associati con calcopirite, magnetite, ilvaite, quarzo e ridotte quantità di ematite, mackinawite, bismutinite, hedenbergite e fluorite. La sfalerite mostra tessituralmente di essere l'ultimo minerale nella sequenza paragenetica dei minerali metallici. Il suo massimo campo termico di formazione è stato fissato fra i 330° C (limite di stabilità dell'associazione calcopirite + pirrotina) e i 200-210° C (limite di stabilità della cubanite cubica, dallo smescolamento della quale sono stati interpretati provenire gli inclusi di calcopirite e mackinawite presenti nella sfalerite). Il contenuto in FeS delle sfaleriti, compreso tra  $21,3 \pm 0,6$  e  $17,2 \pm 0,5$  moli %, porta ad una  $f_{S_2}$  di formazione compresa tra i limiti definiti dalle associazioni tampone: pirrotina esagonale disordinata + pirite, e pirrotina « esagonale » ordinata + pirrotina monoclina. Le indagini diffrattometriche e ottiche sulla pirrotina del deposito hanno messo in evidenza che questa è costituita da un'intima associazione di pirrotina « esagonale » ordinata e pirrotina monoclina, in relazioni tessiturali tali da rendere plausibile, almeno in parte, una loro formazione da un'unica fase di pirrotina esagonale disordinata. Le informazioni raccolte si adattano bene al diagramma di fase ZnS-FeS-S, portando così a concludere che le sfaleriti sono cristallizzate o per lo meno riequilibrate in un ambiente in cui la fugacità di  $S_2$  era controllata dalla associazione dei solfuri di ferro.

ABSTRACT. — The sphalerite-pyrite-pyrrhotite assemblage recently found in the skarn-sulfides deposit of Valle del Temperino has been studied by optical, X-ray diffraction and electron probe investigations. The three minerals are associated with chalcopyrite, magnetite, ilvaite, quartz and minor quantity of hematite, mackinawite, bismuthinite, hedenbergite and fluorite. The pyrrhotite shows to be an intergrowth of ordered « hexagonal » pyrrhotite and monoclinic pyrrhotite. The sphalerite is characterized by a FeS content between  $17.2 \pm 0.5$  and  $21.3 \pm 0.6$  mole %.

The collected data match very well with the phase relations of the ZnS-FeS-S system, thus suggesting that sphalerites were crystallizing in an environment where  $f_{S_2}$  was buffered by the assemblages disordered hexagonal pyrrhotite + pyrite and ordered « hexagonal » pyrrhotite + monoclinic pyrrhotite, and in a thermal field ranging between 200-210° C and 330° C.

\* Istituto di Mineralogia, Petrografia e Geochimica dell'Università di Firenze.  
Centro di Studio per la Geologia Strutturale e la Minerogenesi dell'Appennino del C.N.R. -  
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## Introduction

A sphalerite, pyrite and pyrrhotite assemblage <sup>(1)</sup> was found in a recent mined ore body of the Valle del Temperino skarn-sulfides deposit. The ore body is located in the Pozzo Earle's area, between the second and the third level, about 140 m a.s.l..

The mineralized bodies of the deposit are completely embedded in the marble deriving from the liassic limestone formation « calcare massiccio » metamorphosed by the pliocenic granitic intrusion. The ore bodies are strictly associated with a femic monzonitic porphyry, 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.

According to CORSINI and TANELLI (1974) and BERNARDINI et Al. (1974), to which the reader is referred for a more complete description of the geological setting and of the ore structure of the deposit, sphalerite, pyrite and pyrrhotite occur in several parts of the Valle del Temperino deposit, but, to our knowledge, the assemblage of the three phases was never found before. For this reason, and considering the potential importance that such an assemblage holds in order to define the environmental parameters of formation, several samples have been studied by optical, X-ray diffraction and electron probe investigations.

## Experimental procedures and results

Samples were collected directly from the mine opening and their study in polished section revealed the following mineral association: magnetite, pyrrhotite, pyrite, chalcopyrite, sphalerite, ilvaite, quartz, together with minor quantity of hematite, mackinawite, bismuthinite, hedenbergite and fluorite. Magnetite is present both as pseudomorph on hematite lamellae, which are frequently observed as remnants, and as nodules. Pyrrhotite, which occurs as an intergrowth of large lamellae frequently embedding magnetite, resulted, at X-ray diffractometer and microscopic investigations, to be a mixture of the hexagonal and monoclinic types (fig. 1). The mixture was identified by the doublet in the X-ray diffraction tracing at the location of 102 reflection for the « hexagonal » pyrrhotite, with the high angle peak significantly lower in intensity than the other (ARNOLD, 1966; TAYLOR, 1971). In spite of the fact that our analyses did not enable us to detect directly the different types

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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 ».

which form the so called « hexagonal » pyrrhotite group, it is conceivable to regard the « hexagonal » pyrrhotite determined as one or more of the several types of low temperature ordered « hexagonal » pyrrhotite of SCOTT and KISSIN (1973) and SCOTT (1974), which correspond to the 5C, 11C and 6C types of NAKAZAWA and MORIMOTO et Al. (1975).

Both pyrrhotite and magnetite may be replaced by chalcopyrite, which presents typical « lensatic twins », according to the nomenclature of KELLY and CLARK (1975). Pyrite is present both in coarse subhedral grains and in colloform nodules in pyrrhotite. All the above mentioned minerals are earlier, from a textural point of

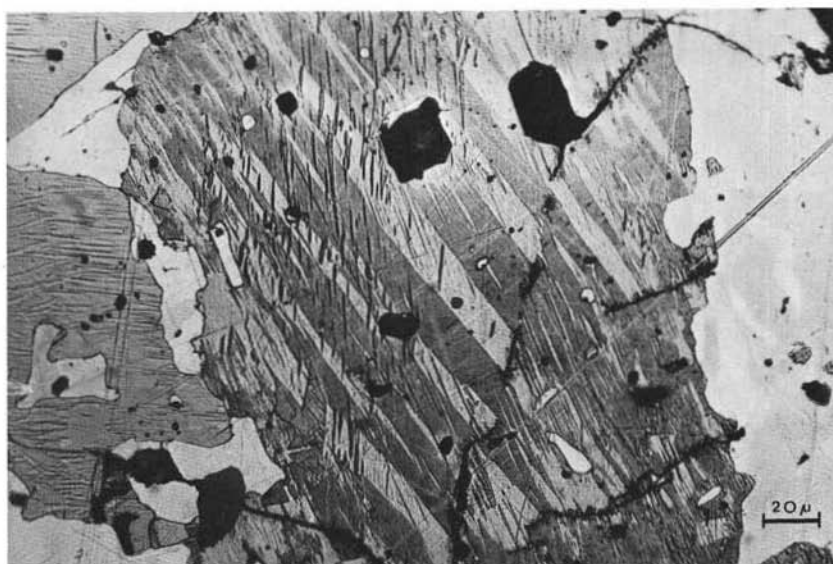


Fig. 1. — Polished section VT-X 1E; oil immersion, parallel Nic., etched HI 47 %. Central area: twinned « hexagonal » pyrrhotite and thin lamellae of monoclinic pyrrhotite with vertical orientation. The strict relation between fractures and twins indicates the latter to be of deformation origin. Right area: chalcopyrite (white and grayish white). Left area: chalcopyrite and a grid-like intergrowth of « hexagonal » pyrrhotite and monoclinic pyrrhotite. The textural relationships between these two phases suggest that they are the product of unmixing from disordered hexagonal pyrrhotite. Black is quartz.

view, than sphalerite, which is characterized by bleb-like inclusions of chalcopyrite, pyrite, chalcopyrite + pyrrhotite and an intergrowth of chalcopyrite + mackinawite.

Sphalerite has been electron-probed by a Philips-Norelco AMR/3 instrument (TANELLI, 1969, 1970). Preliminary scanning sets for Zn and Fe were carried out in different grains of several polished sections, successively.

Taking account this data, several points of ten grains present in two different polished sections were analysed for Zn, Cu, Fe, Mn and Cd. Pure metals were used as standards, and each element on each point was counted three

TABLE 1

Mole % FeS in sphalerite of Valle del Temperino associated to « hexagonal » pyrrhotite, monoclinic pyrrhotite and pyrite (relative error = 3%)

polished section VT-X 1C			polished section VT-X 1E		
18,6	18,6	18,0	17,3	20,5	19,4
19,9	20,2	20,4	18,0	17,9	17,6
20,9	20,9	20,3	20,3	18,6	18,7
19,8	18,9	18,4	18,8	17,2	17,2
21,3	20,6	20,7	20,3	19,3	19,7

The three values on the same line are referred to the three analysed points of the same grain.

times. The measured intensities were corrected for dead time, background and filament drift, and the measured concentrations for fluorescence, absorption and atomic number effects, applying a modified DUNCUMB and JONES (1969) program

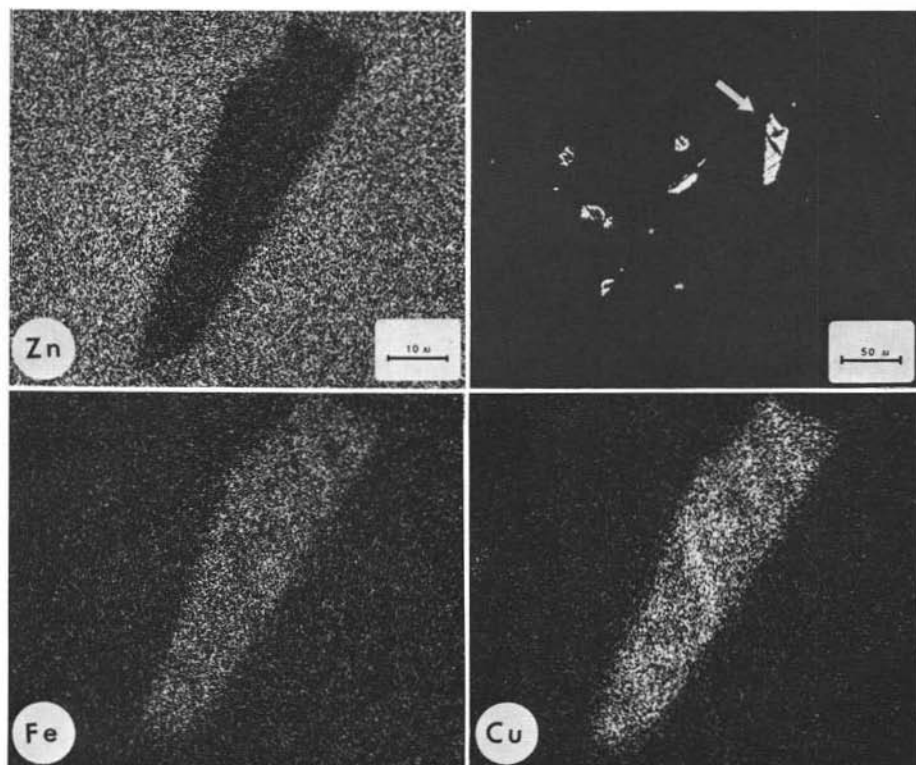


Fig. 2. — Polished section VT-X 1C. Top-right: Photomicrograph, oil immersion, crossed Nic. Intergrowths of chalcopyrite (blackish gray) and mackinawite (white) included in sphalerite (black). The arrow shows the inclusion, whose electron probe X-ray images are presented in the other pictures.

to the CII 10070 computer of the Centro di Calcolo dell'Università di Firenze.

In Table 1 are reported the FeS (mole %) content of the points the analyses of which, expressed by weight % of the sulfides, closed between 98 and 102. In all the analysed points Mn was detected in a mean concentration of 0.38 mole % MnS, with a deviation from point to point included between the reproducibility limits of the whole methodology (10% according to CORSINI et AL., 1975). The presence of Cd and Cu was not revealed above their detectability limits, estimated respectively in 0.09 and 0.08 wt% of the element, following the procedure reported in CORSINI and TANELLI (1974).

Spectrochemical data for mackinawite were collected by electron probe analyses in the same polished sections where the sphalerite were probed. Unfortunately the small size of the mackinawite grains (cross section between 1-5  $\mu$ ) prevents from characterizing the mineral by a formula. On the other hand, the collected qualitative informations, together with the optical features of the grains, enable us to regard them as a Ni- and Co-free mackinawite (estimated detectability limit of Ni and Co = 0.09 wt%). Cu was detected in all the analysed points, but we cannot say whether this element, which is generally present, together with Ni and Co, in the analyses of the major part of natural mackinawites, is really present in mackinawite of Valle del Temperino, or it arises from chalcopyrite interference (EVANS et AL., 1964; BERNER, 1964; CLARK and CLARK, 1968; TAYLOR and FINGER, 1971; SCHOT et AL., 1971; ZÓKA et AL., 1973; MUKHERJEE, 1976). In Figure 2 and 3 an electron probe scan and pictures of an inclusion of chalcopyrite + mackinawite in sphalerite are reported. From these figures it is in particular evident the opposite trend of the concentrations of Cu and Fe, which is related to the different distribution that chalcopyrite and mackinawite have in the inclusion.

### Discussion and conclusion

Phase relations in the ZnS-FeS-S system are well known above 300° C after studies of BARTON and TOULMIN (1966), BOORMAN (1967), SCOTT and BARNES (1971) and SCOTT (1973); numerous examples of their applications at natural associations are found in literature. At the contrary, the phase relations are not well known at the low temperature to which monoclinic pyrrhotite becomes a stable phase. The most complete diagram is that reported in Figure 4, proposed by SCOTT and KISSIN (1973) and SCOTT (1974). This diagram, as pointed out by SCOTT (1974), was drawn combining few experimental points with analyses of naturally occurring sphalerites from low-temperature assemblages and knowledge of the Fe-S system. The diagram is referred to a pressure around 1 bar, and the major uncertainties concern the general locations and slope of the univariant boundaries: disordered hexagonal pyrrhotite + ordered « hexagonal » pyrrhotite + sphalerite, and: ordered « hexagonal » pyrrhotite + monoclinic pyrrhotite + sphalerite, for which there are

no data. However these univariant boundaries must emanate, taking into consideration the phase relations in the system Fe-S, from the invariant point at the temperature of 262° C and FeS =  $20.7 \pm 0.6$  mole %, and from the invariant point at the temperature of 254° C and FeS content in sphalerite around 17.3 mole %.

CORSINI and TANELLI (1974) reported that the mineralizations of Valle del Temperino should be formed at low or moderate pressure, i.e. in such a condition that the Scott and Kissin diagram becomes potentially applicable.

The upper thermal limit of formation of sphalerite can be fixed at about 330° C (CORSINI and TANELLI, 1974). This temperature was deduced considering that the

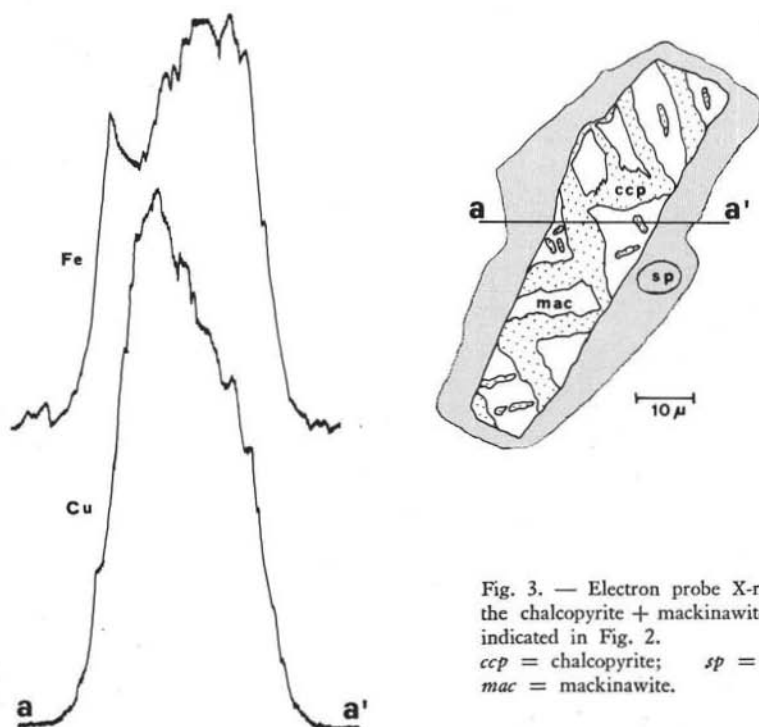
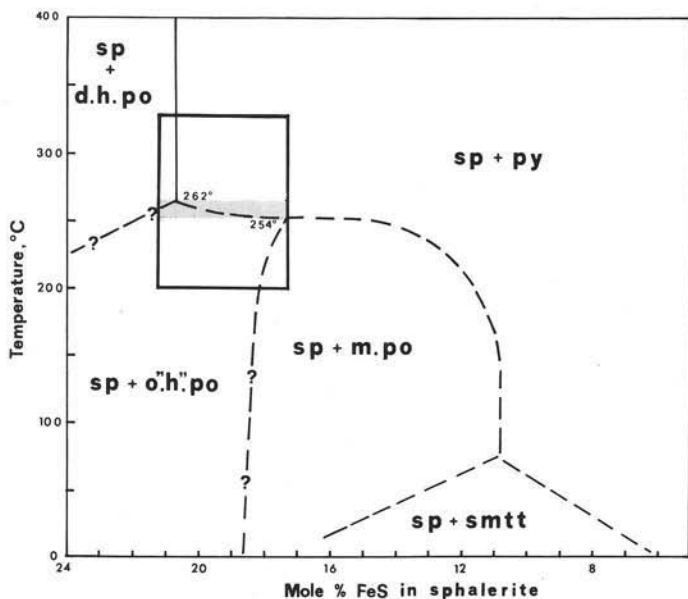


Fig. 3. — Electron probe X-ray scan of the chalcopyrite + mackinawite inclusion indicated in Fig. 2.

*ccp* = chalcopyrite; *sp* = sphalerite;  
*mac* = mackinawite.

sphalerite is later than the assemblage chalcopyrite + pyrrhotite, the textural features of which do not show to be formed by unmixing, and that the assemblage chalcopyrite + pyrrhotite, according to YUND and KULLERUD (1966) and SUGAKI et Al. (1975), is no more stable over 330° C. This value of 330° C disagrees with the temperature we should deduce following RAMDOHR (1969, pp. 91 and 526) interpretation of the « lensatic twins » which are present in the chalcopyrite of the samples studied. In fact, Ramdohr regards these twins as inversion twins related to the polymorphic phase transformation cubic chalcopyrite → tetragonal chalcopyrite which occurs, according to YUND and KULLERUD (1966), around 550° C. However, recent experimental studies of the Cu-Fe-S system (CABRI, 1973; BARTON, 1973)

pointed out that chalcopyrite does not undergo any polymorphic transformation from its upper stability limit at 557° C down to at least 300° C. KELLY and CLARK (1975), both in the light of the above mentioned experimental informations and of their own study on deformation of chalcopyrite, claim that the «lensatic twins» could be related to lattice strain during thermal contraction of chalcopyrite. Therefore the presence of such twins in the chalcopyrite of Valle del Temperino is not



*sp* = sphalerite; *d.h.po* = disordered hexagonal pyrrhotite; *o.h.po* = ordered (hexagonal) pyrrhotite; *m.po* = monoclinic pyrrhotite; *py* = pyrite; *smtt* = smythite.

Fig. 4. — T-X projection of a portion of the system FeS-ZnS-S at low temperature and pressure (SCOTT and KISSIN, 1973; SCOTT, 1974). The rectangular area inside the diagram shows the possible field of formation of the analysed sphalerite. It has been outlined on the basis of: the lower (17.2 m%) and the higher (21.3 m%) FeS content in sphalerite; the lower thermal stability limit of cubic cubanite (200°-210° C); and the higher thermal stability of the assemblage chalcopyrite + pyrrhotite (about 330° C). The shaded area inside the rectangle, delimited by the temperature of 262° C (lower stability limit of disordered hexagonal pyrrhotite + pyrite) and 254° C (higher stability limit of monoclinic pyrrhotite), shows the conditions characterizing partly or completely the formation environment of sphalerite.

«in contrast» with the maximum temperature of formation of 330° C deduced from the stability limit of the chalcopyrite + pyrrhotite assemblage.

Some informations on the minimum temperature of formation of sphalerite can be obtained taking into consideration the intergrowths of chalcopyrite + mackinawite included in sphalerite. Based on our present knowledge of the Cu-Fe-S system, it would appear that the assemblage chalcopyrite + mackinawite is not an equilibrium assemblage. RAMDOHR (1969, pp. 185, 538, 679) interprets the chalcopyrite + mackinawite inclusions in sphalerite as a product of unmixing from «an

original complex product of disintegration in sphalerite». This original complex product was considered to be the so called «chalcopyrrhotite», a phase that, according to YUND and KULLERUD (1966), could be regarded as cubic or tetragonal cubanite, the former stable down to 252° C, and the latter from 252° C to 213°C. Below this temperature, the stable phase is orthorhombic cubanite. More recently, CABRI (1973) and CABRI et Al. (1973) pointed out that the low temperature form of cubanite undergoes between 200° and 210° C an unreversible transition into cubic cubanite, and that during the experiments attempting to reverse the transition, chalcopyrite was observed to exsolve from a cubic cubanite matrix, resulting in an X-ray powder diffraction pattern that may be misinterpreted as that of a tetragonal cubanite single phase.

Conceivably, modifying Ramdohr's interpretation to the most recent acquired experimental informations, we can regard the chalcopyrite + mackinawite intergrowth as the unmixing product below 200°-210° C and at low  $f_{S_2}$  from cubic cubanite initially separated from sphalerite. Therefore, we could fix at 200°-210° C the lower thermal limit of formation of the analysed sphalerite.

This temperature agrees with the inferred thermal stability field of mackinawite, which is considered, on the basis both of natural occurrence and thermal experimental results, as a low temperature and pressure mineral (ARNOLD, 1967; TAYLOR and FINGER, 1971; SCOTT, 1974). In general the experimental results suggest mackinawite to be stable up to 130°-250° C in function both of the Ni, Co and Cu content and the  $f_{S_2}$  of the environment of formation. An increase of the metal content raises the breakdown temperature, while a reverse effect is imputed to  $f_{S_2}$  (CLARK and CLARK, 1968; TAKENO and TAYLOR, 1971; SCHOT et Al., 1971; ZOKA et Al., 1973; MUKHERJEE, 1976).

In Figure 4, the lower and the higher temperature of formation of the sphalerite, fixed respectively at 200°-210° C and 330° C, have been used, together with the lower ( $17.2 \pm 0.5$  mole %) and the higher ( $21.3 \pm 0.6$  mole %) FeS content in sphalerite, to outline the heavy-lined rectangle. From this figure we can notice that the FeS content and the thermal field of formation of the analysed sphalerite, superimposed to the Scott and Kissin diagram, indicates a  $f_{S_2}$  of formation included between the limits fixed by the assemblages: disordered hexagonal pyrrhotite + pyrite + sphalerite and ordered «hexagonal» pyrrhotite + monoclinic pyrrhotite + sphalerite. According to NAKAZAWA and MORIMOTO (1971) and SCOTT (1974), disordered hexagonal pyrrhotite is unstable at low temperature. Synthetic crystal of disordered hexagonal pyrrhotite, cooled from its stability field, acquire one or more of the many low or intermediate temperature structure types. Taking into consideration both this high rate of reaction of disordered hexagonal pyrrhotite and the refractory properties of sphalerite, we can regard the analysed sphalerite as to be crystallized, or at least re-equilibrated, in such a conditions that  $f_{S_2}$  was buffered by the assemblages: disordered hexagonal pyrrhotite + pyrite and ordered «hexagonal» pyrrhotite + monoclinic pyrrhotite.



In a simplified model, we can see the Fe-rich sphalerite to be formed in equilibrium with the association disordered hexagonal pyrrhotite + pyrite, at a temperatures higher than 262° C (lower stability limit of the assemblage disordered hexagonal pyrrhotite + pyrite <sup>(2)</sup>) and lower than 330° C; the sphalerite with an intermediate iron content to be formed in equilibrium with the association ordered « hexagonal » pyrrhotite + pyrite at a temperatures between 262° C and 254° C (higher stability limit of monoclinic pyrrhotite); and finally, the Fe-poor sphalerite to be formed in equilibrium with the association ordered « hexagonal » pyrrhotite + + monoclinic pyrrhotite at a temperatures lower than 254° C and higher than 200°-210° C. Owing to the low temperature instability of disordered hexagonal pyrrhotite, we have not found it in the samples, but the noticed exsolution textures of ordered « hexagonal » pyrrhotite + monoclinic pyrrhotite assemblage suggests its presence at high temperature.

No regular zonality in the distribution of Fe in the grains of sphalerite has been detected, as it would be to expect if the sphalerite formation had followed strictly the above mentioned simple model. At the contrary, we noticed an irregular distribution of the Fe content in sphalerite. Therefore, it can be easily inferred the sphalerite formation environment to be characterized by irregular and partially cyclic variations within the over described chemical-physical limits and general trend of formation. These irregular variations in the environment of formation are in agreement with the shallow formation of the Valle del Temperino deposit, as pointed by the geological evidence (CORSINI and TANELLI, 1974).

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(2) Actually the disordered hexagonal pyrrhotite (type 1C) is stable in equilibrium with pyrite down to 308° C, and below this temperature down to 262° C the type MC is the stable phase in equilibrium with pyrite (SCOTT, 1974). The MC type belongs to the ordered « hexagonal » pyrrhotite, but owing to its compositional similarity with the S-rich member of the 1C type, the  $f_s$ , buffering action of the association MC + pyrite and 1C + pyrite can be considered the same. Therefore, with the sole object of defining the environmental parameters, it is reasonable to consider the MC type as a disordered hexagonal pyrrhotite.

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