

MINERALOGY AND ENVIRONMENT OF FORMATION OF THE Cu-Pb-Zn (Ag, Sb, As) MINERALIZATIONS IN THE NICCIOLETA DEPOSIT

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RIASSUNTO. — Nel giacimento a pirite massiva di Niccioleta (Toscana), gli stadi finali del processo minerogenico, legati all'attività idrotermale connessa con l'evento Appenninico, sono caratterizzati dalla deposizione di solfuri di Zn-Cu-Fe-Pb, cui seguono diversi minerali di As e Sb (arsenopirite, stibina, löllingite e numerosi solfosali, tra i quali tetraedrite argentifera).

Nella sequenza paragenetica, il primo minerale deposto appare essere la sfalerite, che reca tracce di deformazione meccanica sia duttile che fragile. I minerali successivi appaiono essenzialmente non deformati. La composizione chimica (microanalisi SEM/EDS) dell'arsenopirite e dei solfosali è assai variabile, a testimonianza di ricorrenti fluttuazioni dei parametri chimico-fisici dell'ambiente di deposizione.

Sulla base della successione paragenetica, di informazioni termometriche ricavate da dati isotopici e inclusioni fluide, nonché dei campi di stabilità dei vari minerali, la tendenza generale dell'evoluzione dell'ambiente dallo stadio a Zn-Cu-Fe-Pb a quello As-Sb può essere approssimata da una diminuzione di temperatura e attività dello zolfo, e da un aumento delle attività di arsenico e antimonio.

ABSTRACT. — Zn-Cu-Fe-Pb sulfides, followed by As-Sb minerals (arsenopyrite, stibnite, löllingite and several sulfosalts) were formed in the massive pyrite deposit of Niccioleta (Tuscany, Italy) during the hydrothermal activity related to the Apenninic event.

Mineral deposition began in an environment characterized by some tectonic disturbance, as recorded by deformation features in sphalerite. Later minerals appear to be essentially undeformed.

Chemical parameters of the environment were subject to fluctuations, as demonstrated by wide and random compositional variations of most studied minerals. The general evolution trend from the Zn-Cu-Fe-Pb stage to the As-Sb stage can be however be reasonably approximated by a decrease of temperature and activity of S_2 , and increase of activity of As and Sb.

Introduction

Niccioleta (Grosseto, Tuscany) is currently the major productive centre of the southern Tuscany pyrite district. Mining activity takes place today in massive bodies (hereafter referred to as Niccioleta A), completely enclosed within a quartzitic-phyllitic complex (Filladi di Boccheggiano formation = F.B.; Paleozoic-Triassic?). Early mining works exploited pyritic bodies (Niccioleta B) at the contact between the F.B. and the overlying dolomitic Calcare Cavernoso formation (= C.C.; Upper Triassic).

The geology, mineralogy and geochemistry of the Niccioleta pyrite deposits have been extensively studied in the last years (summary and references in LATTANZI & TANELLI, 1984). Current theories on ore genesis involve a Paleozoic-Triassic (?) volcano-sedimentary genesis of large massive pyritic bodies, which were metamorphosed and remobilized during the Apenninic event (Mid Tertiary to recent). In particular, to the Apenninic event is ascribed the emplacement of minor uneconomic Fe-Cu-Pb-Zn(As, Ag, Sb) mineral concentrations, in clear discordant attitude with respect to massive pyrite. With the aim of better understanding the environment of ore deposition during the Apenninic event, a study of these concentrations was undertaken, mainly focused on the mechanical behaviour of sulfide minerals, and on the chemical and textural characters of Fe-Pb-As-Sb phases.

Sampling and experimental

Samples for this study (table 1) were selected among about one hundred of hand specimens collected underground during repeated visits to Niccioleta A. A few additional samples from the nowadays inaccessible Niccioleta B, were kindly supplied by the mining staff. Mineral assemblages and textures were examined using standard reflected light microscopy, integrated, for sphalerite, by transmitted light observations on doubly polished thin plates. To bring out the features of mechanic deformation, sphalerite was etched with HI 57%, and chalcopyrite with a $\text{NH}_4\text{OH}/\text{H}_2\text{O}_2$ mixture. Microanalyses were performed on a Cambridge Stereoscan 250 scanning electron microscope, equipped with a Link 860 energy-dispersive spectrometer, in the electron microscopy and microanalyses laboratory of Nuovo Pignone S.p.A., Firenze. Accelerating potential was 20 kv. The following elements were determined: Cu, Ag, Zn, Fe, Cd, Mn, Co, Ni, As, Sb, Se and S. Pure elements were used as standards, except for S (pyrite) and Pb (galena, after determination of the peak profile on metallic Pb). The raw data were elaborated on-line via computer applying the program of STATHAM & JONES (1978). The precision of the measurements was estimated by repeating three times the analyses of selected points. Many analyzed minerals were extremely small in size, and contamination from neighboring phases could not always be avoided. Only analyses with no evidence of contamination, and with sums in % wt. between 98 and 102 were accepted.

Mineralogy

Sphalerite is by far the most abundant among Cu-Pb-Zn minerals at Niccioleta, and often the only one recognizable by eye. In doubly polished thin section, the stratigraphy of sphalerite appears to consist of three main units, A, B and C, characterized by color, Fe content and presence of inclusions of other minerals (LATTANZI, 1982). Fluid inclusion homogenization temperatures (not corrected for pressure) are between 225° and 300° C for units B and C (BELKIN et al., 1983). All sphalerite units show both brittle

TABLE 1
Mineral association of the studied samples

SAMPLE	LEVEL	ASSOCIATION (metallic minerals only)
NICCIOLETA A		
N5b	+127	sp,py,ccp,gn,tn,lz,mar
N5c	same	sp,py,ccp,gn,td,Pb-ss,bnn
N8a	+210	sp,py,ccp,gn,mar,Kb?
N10a	+198	sp,py,ccp,gn,td,tn,lz,mar,apy,Pb-ss
N10b	same	sp,py,ccp,gn,td,tn,x
N36	+175	sp,py,ccp,gn,td,
NA2	+210?	sp,py,gn,stb,brt,apy
NICCIOLETA B		
NC1	+350?	sp,py,ccp,gn,apy,Pb-ss,bnn

Abbreviations: *apy* = arsenopyrite; *bnn* = bournonite; *brt* = berthierite-like mineral (LATTANZI & TANELLI, 1980); *ccp* = chalcopyrite; *gn* = galena; *kb* = kobellite; *lz* = luzonite; *mar* = marcasite; *Pb-ss* = sulfosalts of the Pb-Sb-S₂ join; *py* = pyrite; *sp* = sphalerite; *stb* = stibnite; *td* = Sb-rich terms of the tetrahedrite-tennantite series; *tn* = As-rich terms of the tetrahedrite-tennantite series; *x* = Pb-Cu-Fe-Sb-As mineral (see text).

(brecciation) and plastic (formation of slip lines and deformation twins) deformation. A moderate annealing event has partly erased the deformation features (GREGORIO et al., 1980). Microprobe analyses indicate FeS contents between .9 and 8.4% moles, and small amounts (less than .5% weight) of Cu, Cd and Mn (GREGORIO et al., 1980).

Small amounts of tiny euhedral pyrite crystals, clearly recognizable from the coarse crystals of early massive pyrite, appear to have been deposited after sphalerite.

Chalcopyrite is diffuse, although never abundant. It is found, sometimes associated with the above described pyrite, along fractures or at the border of sphalerite grains. It partly replaces both the Fe- and the Zn-sulfide; the symptoms of the « chalcopyrite disease » in sphalerite (BARTON, 1978) are often very evident. Mechanic deformation and/or annealing textures in chalcopyrite are relatively rare (fig. 1).

Galena is similarly diffuse, but always in small amounts. Little galena may have been coprecipitated with the earliest sphalerite generation, but mostly it is later than

sphalerite, pyrite and chalcopyrite, and it partly replaces all these sulfides.

Following these minerals, a number of As-Sb-Fe-Cu-Pb(Bi,Ag) minerals were precipitated, in very limited amounts, accompanied by quartz-calcite (gypsum) gangue. They occur along fractures or at the borders of the previously formed Cu-Fe-Pb-Zn sulfides, often with evidence of replacement. These minerals can be grouped as follows:

1) phases of the Fe-As-S system: arsenopyrite, in tiny neat rhomb-shaped crystals, sometimes rimmed by löllingite (fig. 2), and marcasite. Textural relationships indicate that arsenopyrite does not belong to any equilibrium sulfur-buffering assemblage. The As/S ratio is therefore not applicable for geothermometry (KRETSCHMAR & SCOTT, 1976), and, indeed, it varies widely and randomly even in the same polished section (fig. 3). Microanalyses reveal the presence in arsenopyrite of several additional elements beside Fe, As and S (table 2). The compositional fields of arsenopyrite of Niccioleta in the Fe-As-S triangular diagram are compared in fig. 4 with compositional fields of arsenopyrite from other deposits. Some Niccioleta analyses appear to be slightly As- and/or Fe-rich. This however might be an analytical artifact, arising in particular, for As, from the use of elemental As as standard (KRETSCHMAR & SCOTT, 1976). Löllingite replacing arsenopyrite contains up to 2.8 wt% S;

TABLE 2

Minimum, maximum and average contents (wt%) of additional elements in arsenopyrite from Niccioleta

SAMPLE N11				SAMPLE N10a			
Element	min	max	\bar{x}	Element	min	max	\bar{x}
Cu	-	0.6	0.1	Cu	-	0.7	0.1
Pb	-	-	-	Pb	-	5.1	0.9
Zn	-	-	-	Zn	-	2.6	0.4
Sb	0.5	8.5	2.8	Sb	-	2.3	1.0
Se	-	1.2	0.1	Se	-	3.9	1.0

— = below detection limits, estimated at about 0.5 wt%. Co and Ni are always below detection limits.

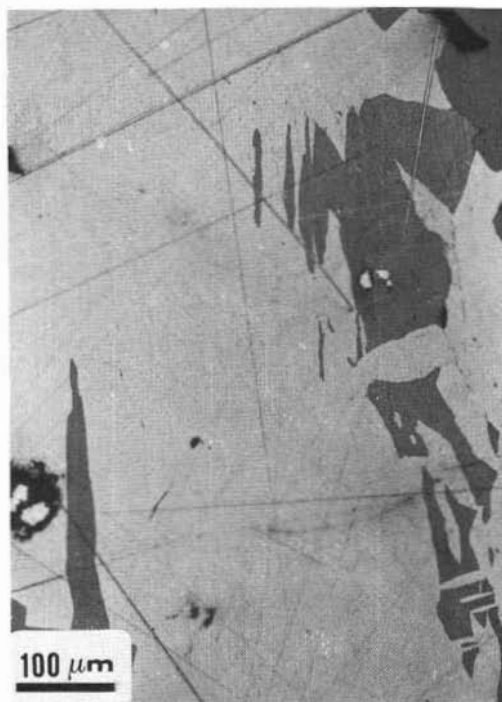


Fig. 1. — Photomicrograph showing detail of chalcopyrite after etching with $\text{NH}_4\text{OH}/\text{H}_2\text{O}_2$; some areas of abundant lensatic twinning, and no major deformation features, are shown.

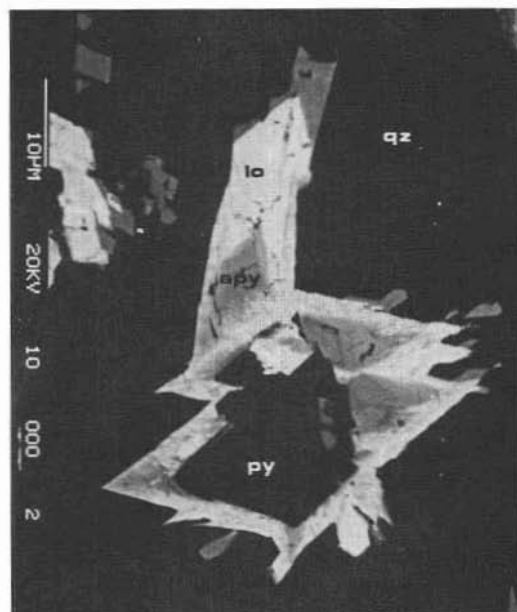


Fig. 2. — Backscattered electron image of löllingite (lo) replacing arsenopyrite (apy) and pyrite (py) in quartz gangue (qz).

2) phases of the Fe-Sb-S system: stibnite and a berthierite-like mineral (LATTANZI & TANELLI, 1980). The latter appears in some cases to replace pyrite and stibnite; in turn, supergenic transformation of it into stibnite

and pyrite (as documented for berthierite by RAMDOHR, 1980) is also observed;

3) phases of the Cu-(Fe)-Pb-Sb-(Bi)-S system:

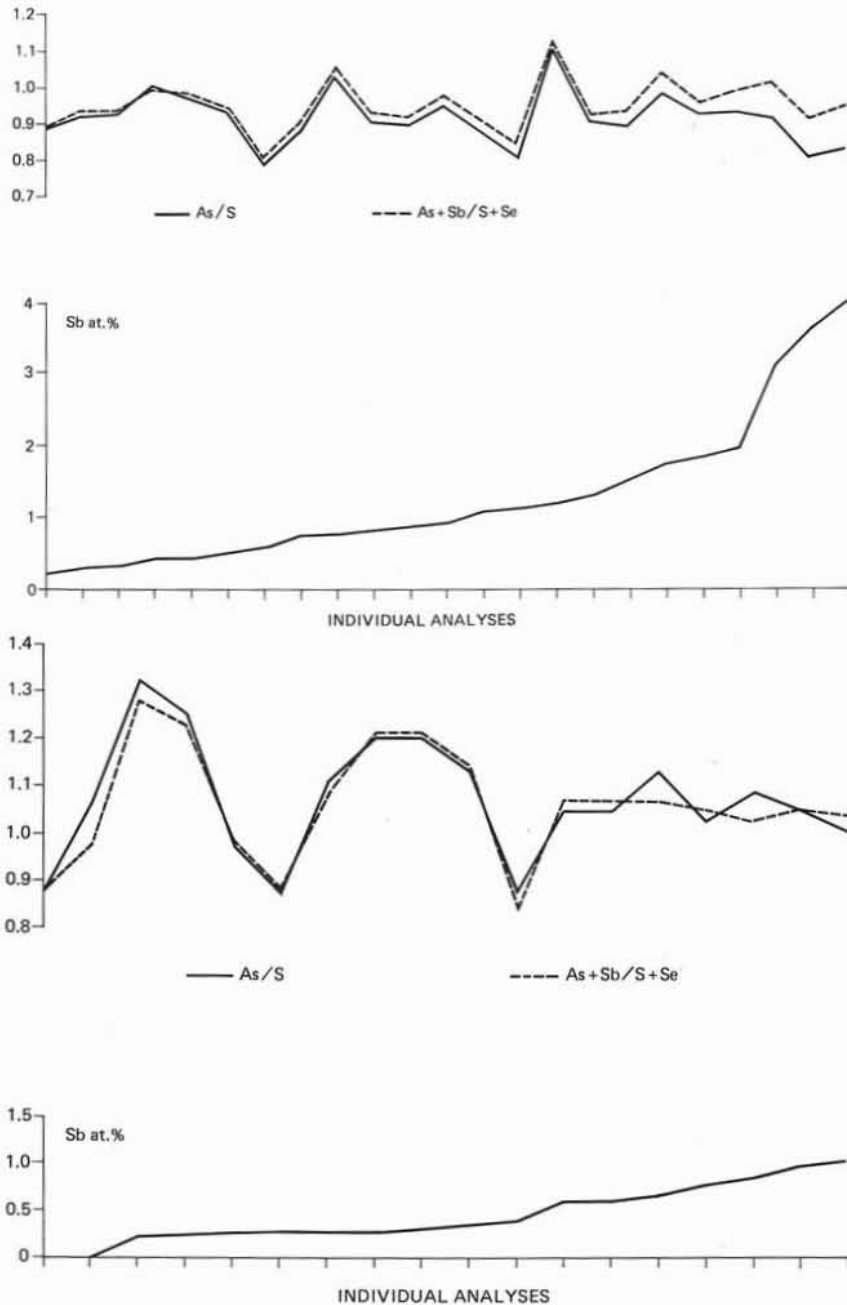


Fig. 3. — Variations of As/S and As+Sb/Se+S ratios in arsenopyrite, plotted in order of increasing Sb content. a): sample NCl; b): sample NIOa.

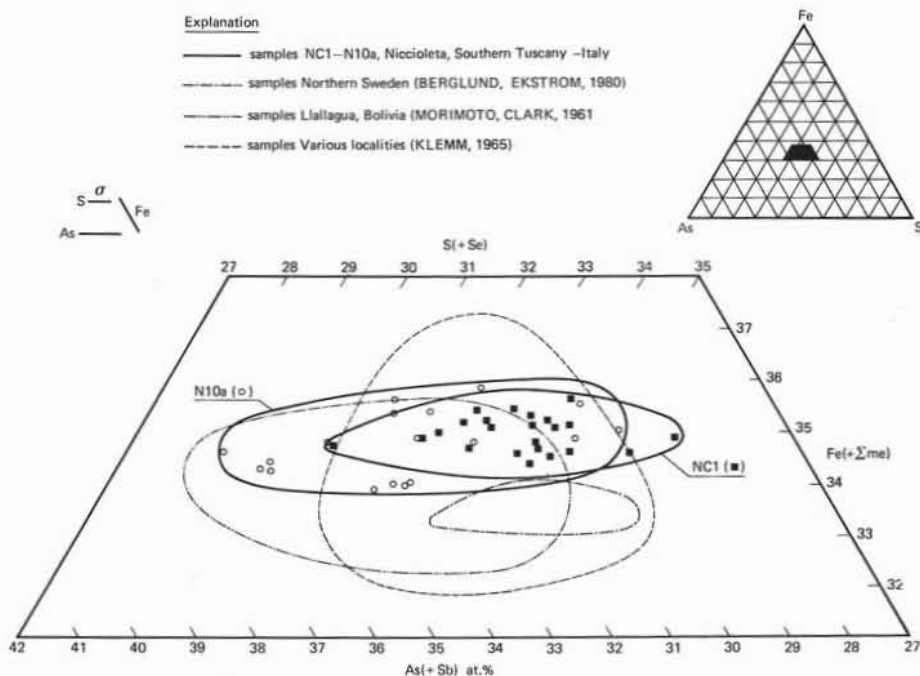


Fig. 4. — Compositional fields of arsenopyrite of Niccioleta, compared with other arsenopyrite analyses from literature.

- a) bournonite, CuPbSbS_3 (fig. 5). It contains small amounts of Fe, As and Se, and its sulfur content is somewhat lower than required for stoichiometry (table 3);
- b) a mineral tentatively identified, on the basis of the optical properties and of semiquantitative microanalysis, as kobellite, $\text{Pb}_5(\text{Bi,Sb})_8\text{S}_{17}$;
- c) an unidentified phase of approximate composition $\text{Pb}_2(\text{Cu,Fe})_4(\text{As,Sb})_2\text{S}_9$ (table 3). It occurs as a thin veinlet cutting across a pyrite crystal and its composition does not appear to be affected by analytical interference with the iron sulfide. Its qualitative optical properties in reflected light are: color (in oil) olive grey, fairly similar to tetrahedrite; bireflectance and anisotropy weak, with no vivid colors; internal reflections not observed;
- d) several phases of the pseudobinary $\text{PbS-Sb}_2\text{S}_3$ join (fig. 6). Many of them are apparently strictly ternary Pb-Sb-S phases, as they contain no other element, at least above detection limits (estimated at about .5 wt%); the sulfur content is somewhat lower than required for

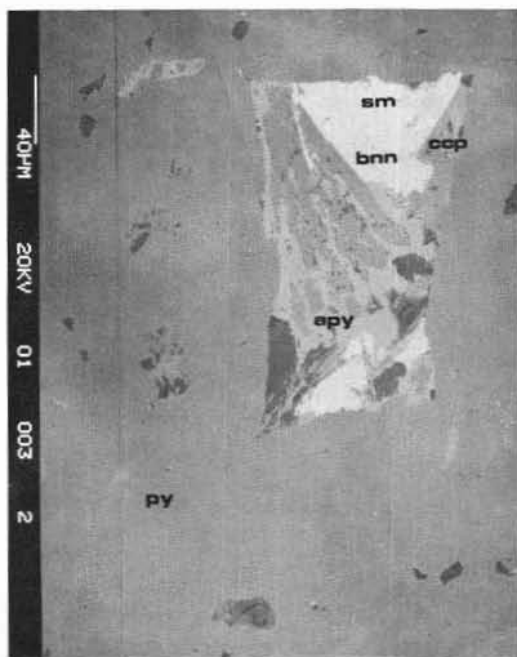


Fig. 5. — Backscattered electron image of a semseyite (*sm*) - bournonite (*bnn*) - chalcopyrite (*ccp*) - arsenopyrite (*apy*) assemblage within fractures of pyrite (*py*).

TABLE 3
Microanalyses of bournonite and of an unidentified mineral from Niccioleta

<u>BOURNONITE</u>			<u>UNIDENTIFIED MINERAL</u>					
SAMPLE NC1*			SAMPLE N5c			SAMPLE N10b°		
Element	wt %	atoms ⁺	Element	wt %	atoms ⁺	Element	wt %	atoms ^{°°}
Pb	41.5	1.04	Pb	42.4	1.09	Pb	35.9	2.15
Cu	12.8	1.05	Cu	12.5	1.04	Cu	11.6	2.27
Fe	0.9	0.08	Fe	-	-	Fe	7.6	1.69
As	-	-	As	1.7	0.12	As	1.0	0.17
Sb	25.5	1.09	Sb	22.8	0.98	Sb	19.5	1.99
Se	-	-	Se	0.5	0.03	Se	-	-
S	18.5	3.00	S	18.1	3.00	S	23.3	9.00
TOT.	99.2		TOT.	98.0		TOT.	98.9	

* = average of 4 analyses; ° = average of 3 analyses; °° = referred to 3 atoms of sulfur; °°° = referred to 9 atoms of sulfur; — = below detection limits, estimated at about 0.5 wt %.

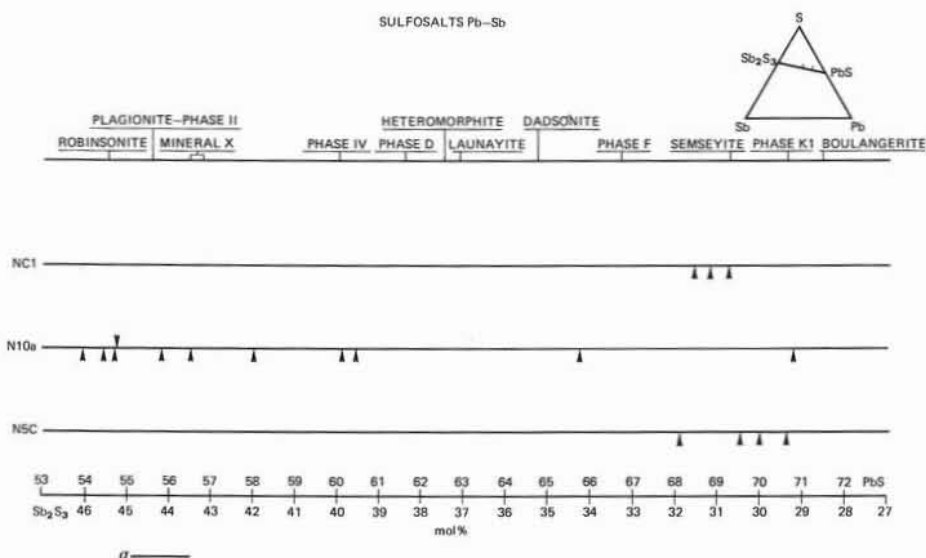


Fig. 6. — Individual analyses (arrows) of Pb-Sb sulfosalts of Niccioleta reported onto the PbS-Sb₂S₃ pseudobinary join according to their Pb/Sb atomic ratio, and compared with natural and synthetic phases occurring in the same compositional interval. Mineral X is described by JANKOVIC et al. (1977); all other phases are reported with the nomenclature and compositions given by CRAIG et al. (1973).

stoichiometry. Two analyzed points revealed presence of As (.5 wt%) and of Se (.7 wt%) respectively; other analyses show appreciable amounts of Zn and Fe, which however arise probably from contamination; notably, Fe contents (up to 3.1 wt%) are markedly higher than

experimental findings for similar phases by BORTNIKOV et al. (1982). These analyses were not reported in fig. 6. The identification of all the encountered phases is often difficult because the analytical error is relatively large, due to the partial overlap of the PbM_x and SK_x

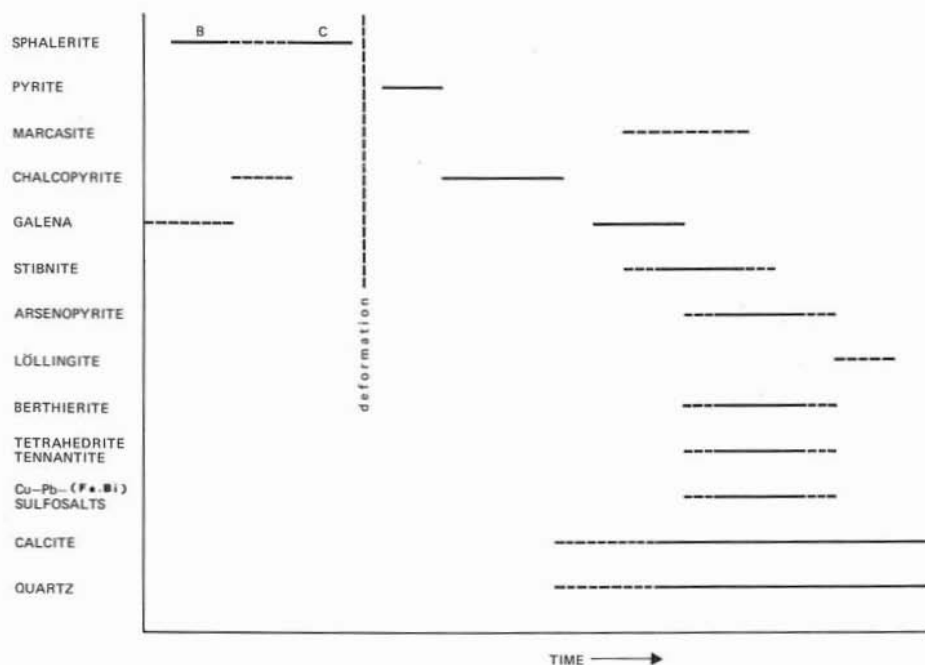


Fig. 7. — Inferred paragenetic sequence in the studied samples. *B* and *C* superscripts in sphalerite refer to types described by LATTANZI (1982).

radiations, the compositional limits, as well as stability fields, of many Pb-Sb-S phases are not clearly established (BORTNIKOV et al., 1982) and their optical properties are seldom distinctive. Taking into account these uncertainties, we have tentatively identified the following sulfosalts: sample N1c: semseyite ($Pb_{10}Sb_8S_{21}$); sample N5c: semseyite and boulangerite (theoretically $Pb_7Sb_4S_{11}$); sample N10a: robinsonite ($Pb_6Sb_{10}S_{21}$ according to CRAIG et al., 1973; see however BORTNIKOV et al., 1982), dadsonite and boulangerite. Moreover we notice analyses which may correspond to the « mineral X » of JANKOVIC et al. (1977) and to the synthetic « phase IV » (CRAIG et al., 1973) the presence of which in nature has so far never been reported;

- e) phases of the tetrahedrite-tennantite series, with Sb-rich members largely prevailing. Their general formula can be written as $(Cu,Ag)_{10+x}(Fe,Zn)_{2+y}(Sb,As)_{4+z}S_{13}$, with $x = .18$, $y = .46$, and $z = .32$. Ag content averages 2.2 wt%, and may be as high as 11.2 wt% (INNO-

CENTI et al., 1984). Tennantite is often supergenically altered to luzonite.

Evolution of the ore-forming environment

It is not always a simple task to establish the paragenetic sequence of the studied minerals, because representative mutual contacts are relatively rare. A possible sequence is reported in fig. 7. Chalcopyrite and, therefore, all minerals following it has been considered essentially post-deformation, because it lacks of abundant deformation textures, as opposed to sphalerite. The mechanic and annealing behaviour of the two sulfides are rather similar, thus any annealing event which might have erased all deformation features in chalcopyrite would probably have erased those in sphalerite as well (STANTON & GORMAN, 1968; GILL, 1969; CLARK & KELLY, 1973; ATKINSON, 1974; KELLY & CLARK, 1975).

For descriptive purposes, we can distinguish two main stages of mineralization. The first (Cu-Pb-Zn stage) was characterized by pre-

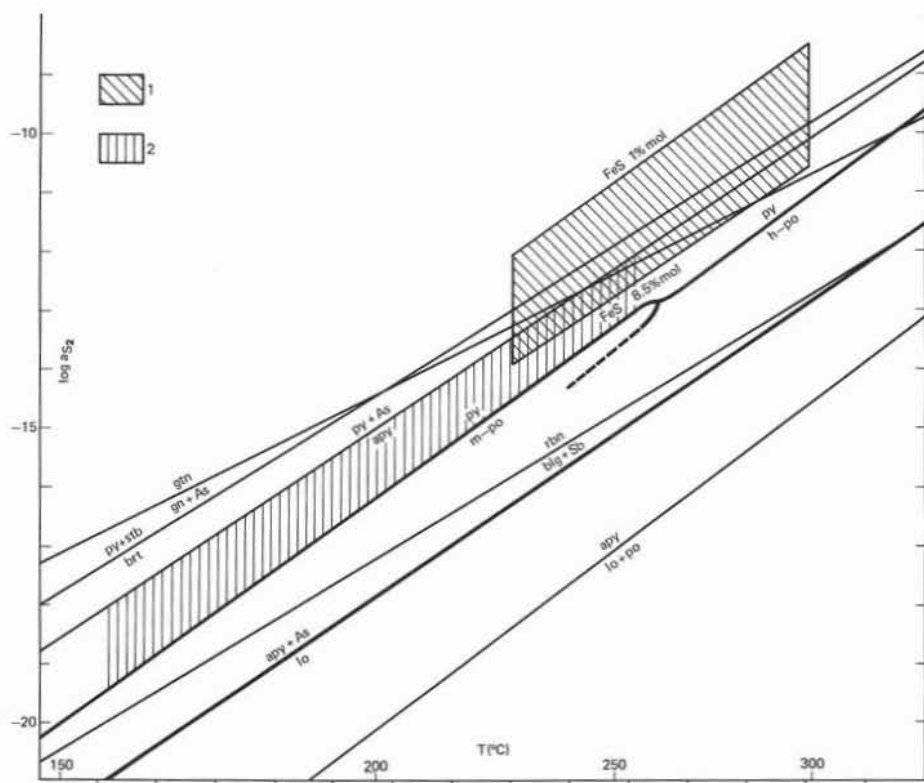


Fig. 8. — Activity of sulfur-temperature plot of sulfidation equilibria at low pressure pertaining to the studied assemblages. The low-temperature portion of most curves represent extrapolation from high temperature equilibria, thus its position is speculative. Field 1 defines the conditions of sphalerite formation as deduced from Fe content and fluid inclusion data; field 2 is the inferred possible range for the environment during deposition of As-Sb minerals. The sources of data for computing sulfidation equilibria are taken from BARTON & SKINNER (1979). Reactions involving robinsonite and boulangerite are shown for compositions $Pb_3Sb_{10}S_{21}$ and $Pb_3Sb_7S_{11}$ respectively (CRAIG et al., 1973).

Abbreviations: *apy* = arsenopyrite; *blg* = boulangerite; *brt* = berthierite; *gn* = galena; *gtn* = gratonite; *h-po* = hexagonal pyrrhotite; *lo* = loellingite; *m-po* = monoclinic pyrrhotite; *py* = pyrite; *rtn* = robinsonite; *stb* = stibnite.

precipitation of Zn-Cu-Fe-Pb sulfides, the second by the formation of Cu(Ag)-Fe(Zn)-Pb-Sb-As(Bi) minerals (As-Sb stage).

Pressure throughout both stages was most probably confined below 500 bars (TANELLI, 1977; LATTANZI e TANELLI, 1984).

The a_{S_2} - T environment during sphalerite deposition can be defined (fig. 8) on the basis of the previously reported FeS contents and fluid inclusion homogenization temperatures. As pointed out by GREGORIO et al. (1980), the sphalerite a_{S_2} - T field lies entirely within the stability field of pyrite, indicating that the large pyrite bodies acted as an effective sulfur buffer during sphalerite deposition.

Brittle and plastic deformation textures of sphalerite suggest that deformation of this mineral occurred at temperatures around 300° C and pressure not exceeding 500 bars (the boundaries between brittle and plastic behaviour of sphalerite: CLARK & KELLY, 1973; ATKINSON, 1974).

Thermal conditions during precipitation of the following minerals are somewhat speculative. Fluid inclusions in calcite filling sphalerite fractures may show homogenization temperatures as high as 370° C (BELKIN et al., 1983), but a generalized high thermal regime is in contrast with the preservation of mechanic deformation textures in sphalerite, which is very sensitive to annealing

(STANTON & GORMAN, 1968). For galena, deposition temperatures around 200°C are indicated by isotopic fractionation in pyrite-galena and sphalerite-galena pairs (CORTECCI et al., 1980, 1983). Isotopic and fluid inclusion temperature estimates of 160°-180°C are reported for late vug crystals of celestite (CORTECCI et al., 1983). Considering that As-Sb minerals appear to be later than phases of the Cu-Pb-Zn stage, we tentatively assume that precipitation of the As-Sb association took place essentially in the range 150°-250°C.

The wide compositional range, even at small scale, observed in arsenopyrite, Pb-sulfosalts and tetrahedrite (INNOCENTI et al., 1984), can be interpreted as: either mosaic equilibrium (KORZHINSKII, 1959), reflecting small scale fluctuations of activities of components, or disequilibrium precipitation.

It is possible to estimate the range of possible values of a_{S_2} during As-Sb stage on the basis of the following assumptions and observations:

- equilibrium conditions were at least approached at the deposit scale;
- arsenopyrite, berthierite-like mineral, Pb-sulfosalts and marcasite are more or less contemporaneous (fig. 7);
- the sulfidation equilibria pertaining to berthierite are applicable to the berthierite-like mineral;
- ignoring the small free energy change for the transformation marcasite-pyrite (about 1 Kcal/mol: GRONVOLD & WESTRUM, 1976), the occurrence of marcasite indicates that also in the As-Sb stage sulfur activity values were confined mostly within the stability field of pyrite.

The simultaneous occurrence of all conditions, considering the sulfidation reactions limiting the stability fields of the phases of interest, suggests that a_{S_2} values during the As-Sb stage were mostly confined between the reaction curves arsenopyrite/pyrite + As, and pyrite/monoclinic pyrrhotite (fig. 8). The inferred a_{S_2} - T field is indeed compatible with the stability of pyrite, arsenopyrite, berthierite, and robinsonite (which is, among the Pb-Sb-S phases encountered at Niccioleta, the one requiring, at constant temperature,

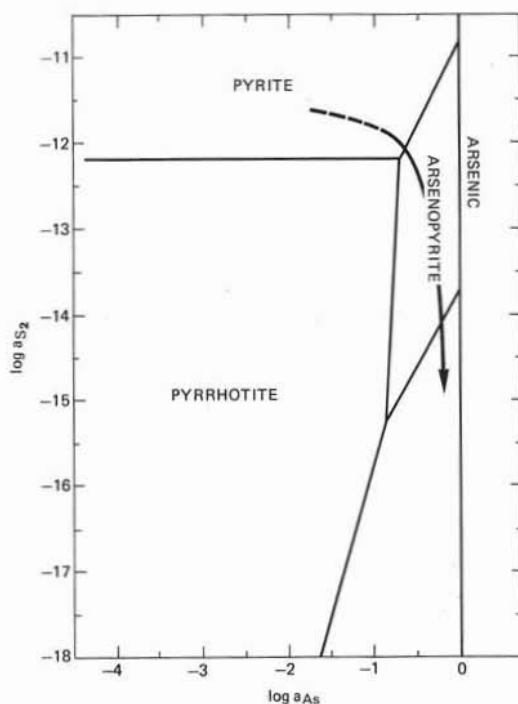


Fig. 9. — Possible evolution path (arrow) with respect to activities of sulfur and arsenic of the ore-forming environment from pyrite stability to formation of löllingite. The field boundaries for the various phases are calculated at 281°C (BARTON, 1969); at lower temperatures, their absolute positions will change, but it is assumed that the general topology does not vary.

the highest value of a_{S_2} to be formed), whereas it does not allow the formation of gratonite (which is, among the Pb-As sulfosalts, the one stable at the lowest value of a_{S_2} at constant temperature).

The final appearance of löllingite replacing arsenopyrite marks a drop of a_{S_2} across the sulfidation boundary arsenopyrite + As/löllingite. Pyrrhotite is exceedingly rare in the Cu-Pb-Zn-As-Sb mineralizations of Niccioleta, and, in particular, it does not occur in the studied samples. The topological relations in the system Fe-As-S as shown in fig. 9 indicate that, if a_{As} in the environment is high enough, it is possible the evolution from the stability field of pyrite to that of löllingite in absence of pyrrhotite.

From figs. 8 and 9 it appears that the general trend of the chemical environment throughout the As-Sb stage may be ap-

proximated by a progressive decrease of a_{S_2} . This in turn may have been the consequence of many factors; among them, a progressive decrease of total sulfur in solution, as it was separated by sulfide precipitation. In this respect, we recall that cotunnite ($PbCl_2$) has been found at Niccioleta A in vug association with euhedral pyrite, sphalerite and galena (LATTANZI & TANELLI, 1978). Cotunnite did not appear to be an alteration mineral, but the last crystallization product of the same environment from which the sulfides were precipitated.

Conclusions

As described by LATTANZI & TANELLI (1984), the Apenninic event at Niccioleta produced recrystallization and partial hydrothermal mobilization of the pre-existing sedimentary-exhalative pyritic bodies, then skarn formation and finally formation of the Cu-Pb-Zn and As-Sb associations.

Apparently, these two last stages of mineralization took place under similar conditions both at Niccioleta A and at Niccioleta B. Sphalerite (\pm galena) was the first

mineral to form, in a low pressure environment characterized by temperatures between 225° and 300° C, and by some deformative action, probably related to the post-tortonian distensive tectonics. Subsequent formation of pyrite, chalcopyrite and galena took place at temperatures down to about 200° C, in absence of significant tectonic phenomena. The following stage was characterized by introduction of As and Sb in the environment, at temperature possibly down to 150° C. Chemical activity of components may have fluctuated widely even at small scale, but the general evolution trend can be approximated by a drop of a_{S_2} , so that, in spite of the buffering capacity of the large pyritic bodies, formation of löllingite was eventually possible. A possible cause of a_{S_2} drop may have been the decrease of total sulfur content in the environment.

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