

*Atti dell'Accademia Peloritana dei Pericolanti  
Classe di Scienze Fisiche, Matematiche e Naturali  
Vol. LXXXIV, C1A0601002 (2006)  
Adunanza del 28 novembre 2005*

**CHEMICAL AND MINERALOGICAL DATA OF THE  
METALLIFEROUS MINERALIZATION FROM S. CARLO MINE  
(PELORITANI MTS, NE SICILY, ITALY)**

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(Nota presentata dal Socio Aggregato Carmelo Saccà)

**ABSTRACT.** The mineralization processes in the Peloritani Belt (Southern Sector of the Calabria- Peloritani Arc) prevalently developed during the Variscan orogenesis producing Pb, Zn, Fe, As, Sb, Cu, Ag, W, etc. polymetalliferous ore-bearing horizons.

This paper focuses on the polymetalliferous mineralization recognised in the ancient S. Carlo Mine, which has already been subject of some studies and is part of an important discordant vein deposits system that are widespread in the Mandanici Unit (MaU). This Unit is characterized by a Variscan low-P, polyphasic and plurifacial metamorphic basement, exhibiting a prograde zoning, from chlorite zone of greenschist facies to oligoclase-almandine zone of amphibolite facies.

The Variscan main foliation (Fv2) is irregularly cut by mineralized veins of decimetric to metric width. They are also perpendicular to the Alpine mylonitic shear zones of metric thickness developing along the sub-horizontal tectonic contacts between the tectono-stratigraphic units. These vein deposits formed along late-Alpine systems of fractures and faults, after Peloritani nappe emplacement.

Minerographic study reveals a metalliferous mineral association mainly composed of tetrahedrite associated with, in order of decreasing abundance, chalcopyrite, bournonite, pentlandite, stromeyerite, arsenopyrite, scheelite, galena, sphalerite, pyrite, bismuthinite, boulangerite, jamesonite, covellite, bornite and argentite. Quartz, siderite and ankerite among non-metalliferous minerals are predominant.

This work has been supported by mineralogical studies and chemical analyses carried out by Atomic Absorption and Inductively Coupled Plasma-Mass Spectrometry on powdered and separated samples of minerals.

Geochemical data (major and trace elements) have allowed a detailed characterization of the minerals. They have revealed that the most significant minerals with Au contents around 1 ppm are tetrahedrite, sphalerite, chalcopyrite and bournonite. The presence of this noble metal in all minerals is important and shows that the mineralizing event is late and widespread.

The Ag content is generally about 2000 ppm in all metalliferous minerals, and is higher than those found in the same minerals of other Peloritani deposits in which this content is around 1000 ppm. Sphalerite and carbonates show very low Ag content.

Chalcopyrite, sphalerite, bournonite and tetrahedrite show high contents of Ni, As, Bi. Cd and Mn are concentrated in sphalerite. Fe content in sphalerite is on average > 6%, in agreement with pressure-temperature conditions (pressure from 2 to 3 kbar and temperature from 420 to 550 °C).

## 1. Introduction

Metamorphic-hosted mineralization occurs widely in many areas in the Southern Sector of the Calabria-Peloritani Arc (ACP), an Alpine arc-shaped structure connecting the Apennines to the Sicilian and North African Maghrebian Chains [8, 9, 10].

The Peloritani Belt is a very old mining area. The mineralization processes prevalently developed during the Variscan orogenesis producing Pb, Zn, Fe, As, Sb, Cu, Ag, W, etc. polymetalliferous ore-bearing horizons. Polymetalliferous mineralizations have been described by [11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31].

Genesis of Peloritani mineralizations is still a matter of debate because of the very complex structure of this Alpine building and of the heterogeneous evolutive history of its terrains.

This paper focuses on the mineralization of the ancient S. Carlo Mine (Fig. 1) where interesting Au contents in some metalliferous minerals have been ascertained.

In the documented epoch, between 1720 and 1764, Pb, Zn, Cu, Sn, Sb, As, Ag deposits in the Fiumedinisi zone (Peloritani Mountains) were known. The planimetry of the S. Carlo Mine in 1760 (in honour of Charles III of Austria) is reported in fig. 2. It was shown by Paillette [32], overseer and chairman of the metalliferous mines in Sicily and Calabria, in a his report published in 1842. The fig. 3, instead, shows the planimetry of the S. Carlo mine going back to about 1950 [33].

After a decline of this mining activity, also related to the earthquake of Messina, in 1908, new investigations were developed just after 1950, which suggested the exploitation of the more quoted copper than zinc and lead, but the works never were resumed. At present some parts of galleries of the mine can still be inspected, other parts are collapsed [34]. It will be possible a readaptation for tourist purposes.

This study has been supported by geological, chemical and mineralogical analyses based on selected samples from those parts of galleries which can still be inspected. Particularly, it is part of a research program whose purpose is to characterize metalliferous mineralizations of the ACP.

## 2. Geological Setting

The Peloritani Belt, at present, consists of an Alpine pile of several Africa-verging tectono-stratigraphic units, which involve Variscan, or older, crystalline basements and their Meso-Cenozoic covers [35, 36].

Mineralizations are present in the crystalline basements of all the units and in some Meso-Cenozoic covers, prevalently widespread in the middle of the Peloritani Mts., along a SE-NW trend, which is parallel to the nappes alignment. These ore deposits exhibit heterogeneous characteristics (structural site, habit, mineralogical association), different genesis and variable P-T conditions of their formation. These features are a consequence of the complex history of the Peloritani Belt.

The S. Carlo Mine is dislocated in the Mandanici Unit which crops out, along a SE-NW direction, from the Ionian Coast (Scaletta Zanclea-Taormina) to the Tyrrhenian Coast (Fiumara di Naso) [37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50]. A complete reconstruction of its pre-Alpine and Alpine tectono-metamorphic history has recently been



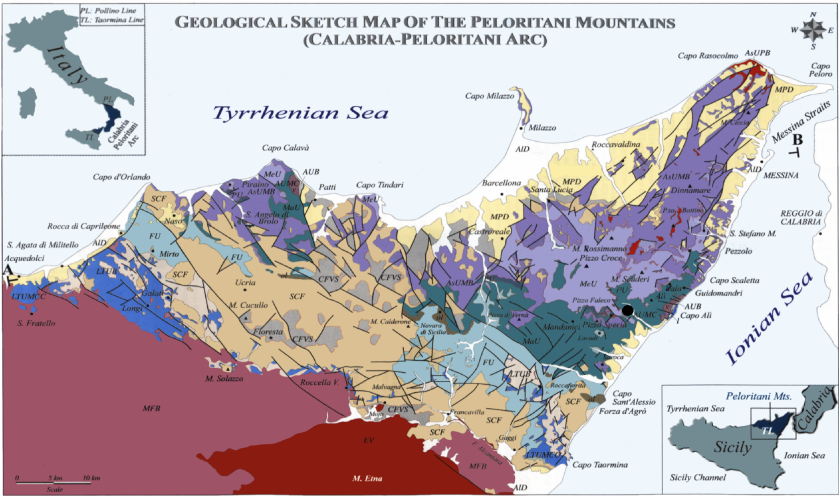


FIGURE 1. Geological sketch map of the Peloritani Mountains (after Messina et al., 2004; modified). ● S.Carlo Mine

delineated by [1, 2, 3, 4, 5, 6, 7]. According to these Authors, the Mandanici Unit is geometrically interposed between the overlying medium-grade Mela Unit and the underlying low grade Fondachelli Unit, with a maximum thickness of about 700 m. The tectonic contacts with the upper and lower units are marked by several metre-thick low temperature mylonites.

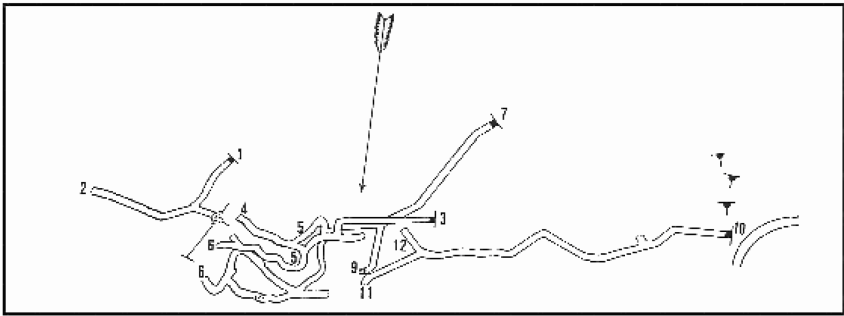


FIGURE 2. Planimetry of the S. Carlo mine in April of 1760. (The arrow points to the south).

The Mandanici Unit consists of a basement, affected by a Variscan metamorphism (from the chlorite-zone of greenschist facies to oligoclasio-almandine zone of amphibolite facies, and by a localized Alpine L-P and L-T greenschist facies overprint, and slices of Mesozoic sedimentary cover (Messina et al., 2004).

The basement is made up of hectometre to kilometre-thick phyllites passing to metarenites, with subordinate metric lenses of metabasites and thick layers of marbles. Localized bodies of meta-volcanics are also present.

Stratabound-sulphide ores in a quartz-fluorite gangue and millimetre to decimetre-thick galena or pyrite-bearing massive layers, concordant with the regional foliation of the unit (Fv2), inside of Variscan phyllites, are also present. The stratabound deposits are characterized by pyrite, chalcopyrite, pyrrhotite, sphalerite, Ag-rich galena, covellite, arsenopyrite, antimonite and tetrahedrite.

In the Mandanici Unit discordant vein deposits are widespread. These decimetre to metre-wide veins have developed along late-Alpine systems of fractures and faults which irregularly cut the Variscan main foliation (Fv2).

The S. Carlo Mine is part of an important discordant vein deposits system which are widespread in the Mandanici Unit.

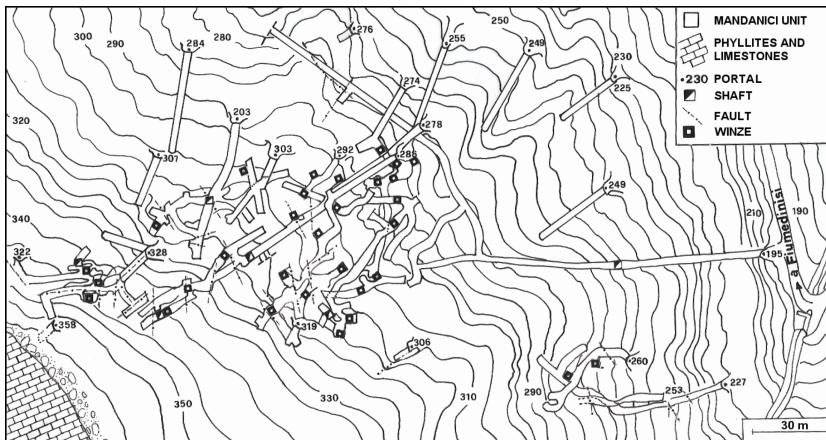


FIGURE 3. Planimetry of the S. Carlo mine going back to about 1950.

The mineralization consists of two vein systems:

- *the former* shows a NNE-SSW trend with a variable thickness from 1 to 5 m. These veins have developed along late-Alpine systems of fractures and faults which irregularly cut the Variscan main foliation (F2). The deposits consist of polymetallic sulphides, sulphosalts and tungsten-concentration in a quartz+siderite+ankerite gangue, in agreement with [51, 52, 53]. In the main stage of the mineralization tetrahedrite, bournonite, pentlandite, stromeyerite, scheelite, bismuthinite, boulangerite and jamesonite developed in addition to the common sulphides, such as chalcopyrite, arsenopyrite, galena, sphalerite, pyrite, covellite, bornite and argentite. In a last stage oxides, hydroxides and carbonates, like malachite and azurite, developed.

- *The latter* vein system of middle thickness is observable in the southern section of the Mine (Triscari and Saccà, 1982); it has an

E-W trend and consists of quartz and scarce chalcopyrite with traces of cubanite e tetrahedrite. Occasional small areas of pyrrhotite, pentlandite, pyrite, sphalerite, arsenopyrite and intergrowths of bornite-chalcocite are also present.

### 3. Experimental methods

The minerographic study was carried out by reflected light microscopy. The X-ray diffraction analyses (XRD) were carried out using  $\text{CuK}\alpha$  radiation. Chemical analyses (electron microprobe) were carried out using a SEM Cambridge instrument (Stereoscan 250) equipped with EDS Link AN 10.000, operated with an accelerating voltage of 20 KV. Pure metals were used as standard.

Collected spectra were processed by the analytical software of firm Link applying procedure ZAF 4. The measurements were carried out on rather pure areas. Chemical analyses of trace elements were carried out by ACME Analytical Laboratories Ltd in Vancouver, Canada. Powdered and separated samples of minerals were digested by  $\text{HCL}:\text{HNO}_3$  (3:1) mixed reagent followed by ICP-MS analysis. Results give total concentrations (or almost) for noble metals and partial concentrations for minerals making up the rocks. Where materials were pure, tests were complemented by Atomic absorption according to the following procedures: 300mg of powdered mineral bonded by heat to an  $\text{HNO}_3:\text{H}_2\text{SO}_4$  mixture (1:1) concentration, refluxed reaction for 2-3 hours until completely dissolved. The solution was analysed by AA Varian AA-1475 spectrophotometer, equipped with a Varian GTA-95 graphite oven. The adding method was used together with an absorption correction system by deuterium lamp. As and Se were determined by the same method and an accessory can be used to determine iodides or volatile elements.

The efficiency of the analytical method verified by known standards (Recovery tests) is between 98.8% and 102.6%. Laboratory reproducibility shows maximum oscillations lower than 2% for analytical determinations.

Whenever the minerals were pure enough the analyses also have been carried out by Neutronic Activation.

Finally, the  $\delta^{34}\text{S}$  value in tetrahedrite was determined by the method of [54]. The sample is oxidized in oxygen at  $>1100^\circ\text{C}$ , the  $\text{SO}_2$  produced is recovered and purified cryogenically and the  $^{34}\text{S}/^{32}\text{S}$  ratio measured by IRMS relative to a working reference  $\text{SO}_2$  gas, and recalculated as o/oo relative to the VCDT standard (VCDT = revised Canon Diablo Troilite scale).

### 4. Results and discussion

In the S.Carlo Mine **tetrahedrite** is the most abundant metalliferous mineral, displaying a structure from compact to microgranular. It is often fractured and the fractures are filled by **stromeyerite** together with smallest quantity of **argentite**. Inside other minerals can also be found diffusely, in small amounts (Fig. 4).

The most common minerals are:

**Chalcopyrite** (Fig. 5) has a microcrystalline structure. Oxides can be found along the fractures. It is also present inside sphalerite.

**Bournonite**, in often twinned granules, rims the tetrahedrite and is sometimes replaced too by **stromeyerite**.

**Pentlandite** is ubiquitous but is more frequent in the samples that were collected in the lower altitude galleries of the mine.

**Arsenopyrite**, often in idiomorphic crystals, is remarkably fractured.

Products of alteration (ferrous oxides) can be found along the fractures.

**Scheelite**, observable in ultraviolet short wave light, occurs as disseminated fine grains of mm size and patches of cm size deposited during an early stage of the mineral vein-filling process. They are preferentially aligned along the silicified fragments of the wall rock included in the ore bearing quartz (Triscari and Saccà, 1982).

**Galena** is rare and shows the cleavage planes.

**Sphalerite** shows reddish-brown internal reflections at crossed nicols. There are granules of pyrite, pyrrhotite and chalcopyrite, occasionally observable in lamellae iso-oriented, which are common structures in Peloritani mineralizations.

The data reported here refer exclusively to the first veins system.

Chemical analyses (Tab. 1 and 2) concerning the main constituents (determined by SEM) and trace elements (determined by ICP-MS and A.A) are carried on galena, chalcopyrite, sphalerite, tetrahedrite, bournonite, quartz, carbonate and phyllite (host rock).

Sphalerite is ferrous type with an average Fe content of about 6% (Tab. 1), and this is in good agreement with P-T conditions typical of the Unit (P from 2 to 3 kbar and T from 420 to 550 C).

Tetrahedrite is also characterized by a good Fe content (about 5%) and constantly shows low As contents.

As regards the noble metals, the Ag (Tab. 2) content is about 2000 ppm in all metalliferous minerals and is higher than that found in the same minerals of other Peloritani deposits in which this content is around 1000 ppm. Sphalerite and carbonates show respectively Ag values of 21 ppm and 14.3 ppm. The Au content reaches a value of 1 ppm in sphalerite.

Other trace elements, as Cd, Cr, Bi, are present in greater quantities inside specific minerals: Cd is prevalently concentrated in sphalerite; Cr reaches maximum values in tetrahedrite (1034 ppm) and slightly lower values in sphalerite (992 ppm); Bi, probably due to microinclusions of bismuthinite, is only scarcely present in sphalerite, while is greater in content in the tetrahedrite.

## 5. Conclusions

The mineralization of the ancient S. Carlo Mine is included in the vast picture of the metalliferous mineralizations of the Peloritani Mountains, in particular in those hosted in the Mandanici Unit. They mainly occur as discordant vein mineralizations, probably connected to hydrothermal activity and/or to the Alpine orogenesis (Ferla and Omenetto, 2000).

In particular, according to Ferla and Omenetto (2000) the metallogenic process appears to be connected to the presence of Pre-Variscan intracontinental rifting associated to a basic magmatism (Censi *et al.*, 2000).

Available data suggest that the Variscan tectono-metamorphic deformation phases and especially the intense hydrothermal activity correlated with the late phase of regional

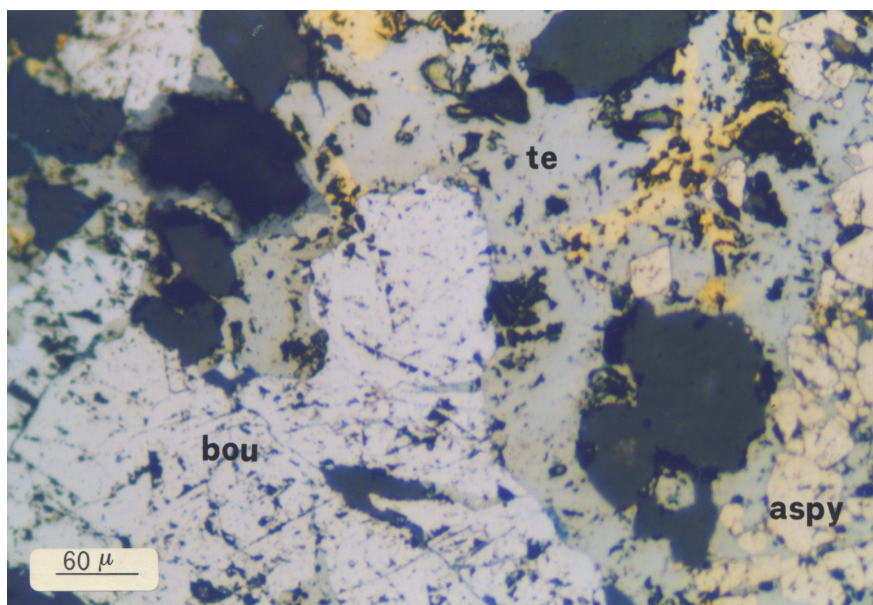


FIGURE 4. Tetrahedrite (*te*) with bournonite (*bou*) and highly fractured arsenopyrite (*aspy*). Reflected light observation - // nicols.

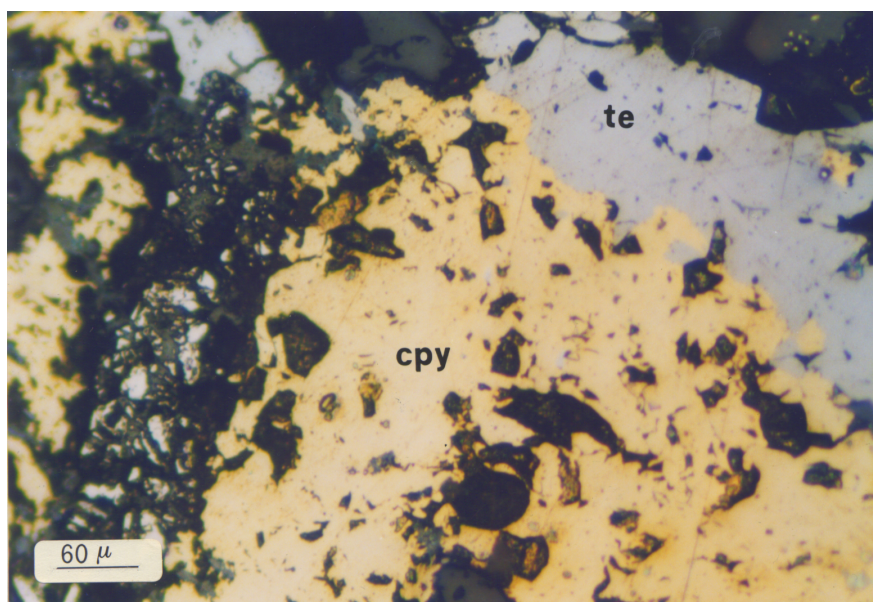


FIGURE 5. Tetrahedrite (*te*) and chalcopyrite (*cpy*). Reflected light observation -  $\perp$ vert nicols.



TABLE 1  
*Chemical analyses (%) of the main mineral phases*  
*(s.d. = standard deviation; n=number of significant analyses)*

<b>TETRAHEDRITE</b> S=25.37%; Cu=34.80%; Sb=29.64%; Fe=10.20%		
	<b>mean + s.d.</b>	<b>n / 20</b>
<b>S</b>	26.45 ± 0.50	20
<b>Cu</b>	36.62 ± 0.43	20
<b>Sb</b>	28.32 ± 0.40	20
<b>Fe</b>	5.29 ± 0.50	20
<b>As *</b>	0.41 ± 0.01	20
<b>Ti *</b>	1.25 ± 0.02	20
<b>Bi *</b>	0.52 ± 0.01	20

\* see tab. 2

<b>TETRAHEDRITE</b> S-isotope composition	
<b>% S</b>	35
<b>δ<sup>34</sup>S</b>	3

<b>GALENA</b> S=13.4 %; Pb=86.6%		
	<b>mean + s.d.</b>	<b>n / 4</b>
<b>S</b>	13.34 ± 0.25	4
<b>Pb</b>	86.34 ± 0.65	4

<b>BOURNONITE</b> S=19.75%; Cu=13.04%; Sb=24.68%; Pb=42.53%		
	<b>mean + s.d.</b>	<b>n / 6</b>
<b>S</b>	19.43 ± 0.40	6
<b>Cu</b>	12.90 ± 0.30	6
<b>Sb</b>	24.90 ± 0.42	6
<b>Pb</b>	42.30 ± 0.59	6

<b>SPHALERITE</b> S=32.9 %; Zn=67.1%		
	<b>mean + s.d.</b>	<b>n / 5</b>
<b>S</b>	32.20 ± 0.45	5
<b>Zn</b>	61.10 ± 0.40	5
<b>Fe</b>	6.70 ± 0.40	5

<b>CHALCOPYRITE</b> S=35.0%; Fe=30.4%; Cu=34.6%		
	<b>mean + s.d.</b>	<b>n / 5</b>
<b>S</b>	34.40 ± 0.60	5
<b>Fe</b>	30.10 ± 0.58	5
<b>Cu</b>	34.23 ± 0.45	5

<b>SIDERITE</b> FeO=62.01%; CO <sub>2</sub> =37.99%		
	<b>mean + s.d.</b>	<b>n / 5</b>
<b>FeO</b>	49.7 ± 0.8	5
<b>CaO</b>	5.31 ± 0.4	5
<b>MgO</b>	7.01 ± 0.4	5
<b>MnO</b>	3.08 ± 0.3	5
<b>CO<sub>2</sub></b>	34.9 ± 0.3	5

Variscan metamorphism are probably responsible for remobilization and concentrations in vein- and stockwork-like orebodies. The δ<sup>34</sup>S value in tetrahedrite (Tab. 1) are compatible with the hypothesis of a remobilization of the originally stratabound sulphides [55].

Alpine thrusting then induced fracturing and reworking of the mineralised bodies and some kinds of enrichment in base metals and tungsten (scheelite).

The presence of granules and lamellae of chalcopyrite inside sphalerite deserves attention. In the Mandanici Unit the temperatures of metamorphic events affecting the Unit never reached 500 C, which is the temperature necessary to cause exsolution-process,

TABLE 2  
Chemical analyses of trace elements (ppm)

<i>Minerals</i>	<b>Ag</b>	<b>Au</b>	<b>As</b>	<b>B</b>	<b>Ba</b>	<b>Bi</b>	<b>Cd</b>	<b>Co</b>	<b>Cr</b>	<b>Ga</b>	<b>Cu</b>	<b>Pb</b>
Chalcopyrite	>100	0.3	2589	38	7	179	1	50	26	1		
Bournonite	>200	0.5	1577	69	67	1985	5.5	17	7	0.2		
Sphalerite	21	1	328	604	8	<0.02	2481	33	992	8		
Tetrahedrite	2000	0.4	4122	777	70.5	5255	46	39	1034	2		
Carbonate	14.3	0.2	2391	2	37	4	0.5	274	1	0.5	1571	54
Quartz	2.8	0.01	227	1	2	9	0.04	3	<0.5	0.1	223	392
Phyllite	0.4	0.003	35	2	14	2	0.02	3	2	0.4	252	261
<i>Minerals</i>	<b>Mg</b>	<b>Mn</b>	<b>Mo</b>	<b>Na</b>	<b>Ni</b>	<b>P</b>	<b>Se</b>	<b>Sc</b>	<b>Hg</b>	<b>La</b>	<b>S</b>	<b>Sb</b>
Chalcopyrite	<100	2	0.5	65	883	30	15	0.1	41	<0.5		
Bournonite	<100	86	2	70	127	20	11.5	0.1	>100	<0.5		
Sphalerite	400	232	34	100	632	120	55	0.2	>100	<0.5		
Tetrahedrite	100	<1	29	195	694	220	35	0.3	>100	<0.5		
Carbonate	23600	15803	1	90	1183	50	0.3	2	5.3	<0.5	<0.01	897
Quartz	<100	1	0.01	80	55	10	0.1	0.1	1.2	<0.5	0.06	184
Phyllite	3700	954	0.07	130	13	550	0.1	2	0.3	13	<0.01	336
<i>Minerals</i>	<b>Sr</b>	<b>Te</b>	<b>Th</b>	<b>Tl</b>	<b>Ti</b>	<b>U</b>	<b>V</b>	<b>K</b>	<b>W</b>	<b>Fe%</b>	<b>Zn</b>	
Chalcopyrite	6	0.07	<0.1	0.02	205	<0.1	22	100	0.1			
Bournonite	9	<0.02	<0.1	0.75	420	<0.1	28	<100	<0.1			
Sphalerite	4	<0.02	1	2	<10	1.2	550	200	2			
Tetrahedrite	4	0.02	<0.1	0.06	12535	<0.1	464	<100	2			
Carbonate	29	<0.02	0.1	0.02	<10	0.1	4	300	1.5	>40	126	
Quartz	1	<0.02	<0.1	<0.02	<10	<0.1	<2	100	0.1	0.07	9	
Phyllite	8	<0.02	4.1	0.03	10	0.2	3	1100	<0.1	3	18	

therefore the iso-oriented lamellae present in the sphalerite of S. Carlo are generally interpreted as the result of substitution phenomena [56, 57].

From a chemical point of view (Tab. 1), the mineralization is characterized by a good iron presence in sphalerite (about 6 %) and is within the variability margins concerning iron content in this mineral in the Mandanici Unit vein mineralizations and in agreement with P-T conditions typical of the Unit.

Tetrahedrite is ferrous type (see data) and constantly shows low As contents.

Some trace elements (Table 2) appear to be concentrated preferably in particular phases: Cr in sphalerite and in tetrahedrite, Cd in sphalerite. Microinclusions of bismuthinite could justify the high Bi content in almost all the minerals, with the exception of chalcopyrite and sphalerite. Among noble metals Ag shows in the tetrahedrite values of about 2000 ppm and >100 e >200 in the chalcopyrite and bournonite respectively. Sphalerite and carbonates show very low Ag content. The Ag presence in Peloritani minerals is widespread but shows variable values on average of 500 ppm [58].

Particular emphasis must be reserved to the gold presence in the metalliferous minerals, whose content varies on average from 0.3 ppm in chalcopyrite to 1 ppm in sphalerite (Tab. 2); the results of the latest research (Messina and Saccà, 2001; Saccà *et al.*, 1995; 2002; 2003) on the presence of the element in some mineralizations belonging to the same Unit, as in vein mineralizations belonging to the upper metamorphic grade Units too, are therefore confirmed, thus supporting the hypothesis, already put forward by Ferla and Omenetto,

2000; Messina and Saccà, 2001, that even the presence of Au could be correlated to Alpine phenomena.

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Presented: November 28, 2005  
 Published on line on May 23, 2006