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GEOCHEMICAL AND MINERALOGICAL FEATURES OF THE POLYMETALLIC DEPOSIT FROM ALÌ (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), related to Pre-Variscan intracontinental rifting, produced sedex-type Pb, Zn, F (Ag), Cu, W (As, Sb) ores. This paper focuses on the metalliferous stratabound mineralization outcropping in the Alì area (Tripi locality). It is part of sulphide ores, concordant with the regional foliation of the hosting unit (Fv2), very widespread in the Mandanici Unit (MaU). This unit is characterized by a Variscan low-P, polyphasic and plurifacial metamorphic overprint involving the basement. This metamorphic overprint exhibits a prograde zoning, from a chlorite zone of greenschist facies to an oligoclase-almandine zone of amphibolite facies. The metalliferous mineral association is formed by galena, sphalerite, pyrite, chalcopyrite, arsenopyrite and covellite. Quartz and fluorite among non-metalliferous minerals are predominant. Some minerals like quartz, fluorite, galena, sphalerite and pyrite are present in two generations, the second of which can be related to intense hydrothermal activity involving the whole Peloritani Belt. Trace-element contents of sulphide ores detected by Atomic Absorption and Inductively Coupled Plasma-Mass Spectrometry on powdered and selected samples of minerals have been determined. Major elements have been analyzed by Scanning Electron Microscopy. The Ag content is quite high in galena, relative to the same mineral of other Peloritani deposits in which this content is around 1000 ppm. Galena shows a high content of Sb (\bar{x} = 621) and lower values of Cd (\bar{x} =132) and Cu (\bar{x} =108) whereas in sphalerite the Sb content (\bar{x} = 134) is lower than Cd (\bar{x} = 1118) and Cu (\bar{x} = 1127). Mn is scarcely present in sphalerite, while galena shows higher contents. Fe content in sphalerite is about 6%, in agreement with Pressure-Temperature conditions of the Unit.

1. Introduction

Mineralization processes found in metamorphic rocks occur widely in many areas in the Southern Sector of the Calabria-Peloritani Arc (CPA), an Alpine arc-shaped structure connecting the Apennines to the Sicilian and North African Maghrebids.

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 [1-21].

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

This paper focuses on the metalliferous mineralization of Tripi (Fig. 1), outcropping in the Alì area, belonging to the Mandanici Unit (MaU). Interesting Ag contents in galena in the past have been mined in these ore deposits [22].

This study has been supported by geological, chemical and mineralogical analyses. Particularly, it is part of a research program whose purpose is to characterize metalliferous mineralizations of the CPA (Calabria-Peloritani Arc).

2. Geological Setting

The Peloritani Belt presently consists of seven Alpine units, which involve Variscan, or older, crystalline basements and Meso-Cenozoic covers [23, 24, 25, 26].

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

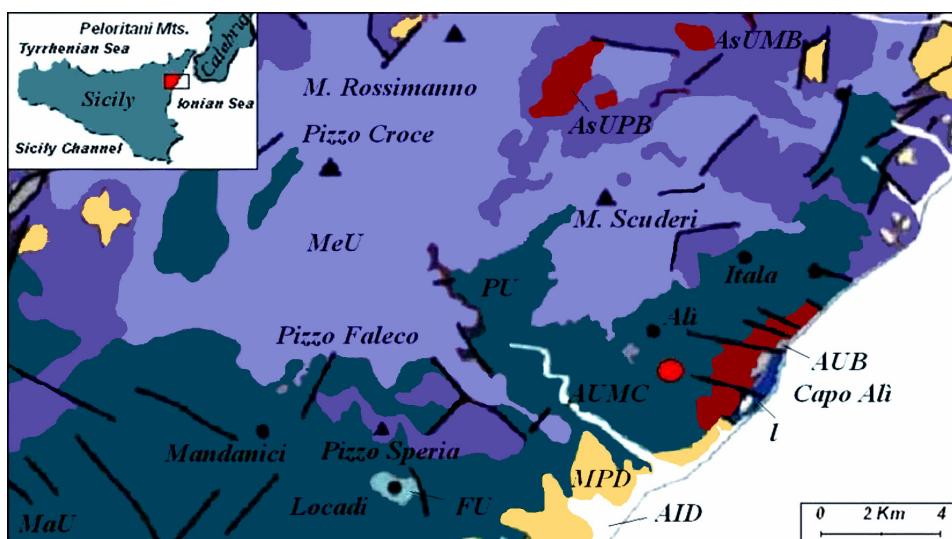
The Tripi mineralization is placed in the Mandanici Unit which crops out, along a SE-NW direction, from the Ionian Coast (Scaletta Zanclea-Taormina) to the Tyrrhenian Coast (Fiumara di Naso) [1, 2, 3, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41]. A complete reconstruction of its pre-Alpine and Alpine tectono-metamorphic history has recently been delineated by Messina *et al.* [26, 42, 43, 44] and Messina [23, 45, 46], according to these Authors, the Mandanici Unit is geometrically interposed between the overlying Mela Unit medium-grade metamorphic and the underlying low grade metamorphic Fondachelli Unit, with a maximum thickness of about 700 m. The tectonic contacts with the upper and lower units are marked by several meters-thick low-temperature cataclastic to mylonitic shear zones.

The Mandanici Unit consists of a basement, affected by a Variscan metamorphism (from the chlorite-zone of greenschist facies, to an oligoclasio-almandine zone of amphibolite facies) and by a localized Alpine low-P and low-T greenschist facies overprint, and of slices of Mesozoic sedimentary cover [26].

The basement is made up of hectometric to kilometric layers of phyllites grading to metarenites, with subordinate metric lenses of metabasites (amphibolites) and thick layers of impure marbles. Localized bodies of mafic meta-volcanics are also present.

In the Mandanici Unit discordant vein deposits are very widespread. These decimetre to metre-wide veins are concordant with the late-Alpine fractures and faults which irregularly cut the Variscan main foliation (F2).

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



● Tripi Mine

AID

AID - ALLUVIAL AND BEACH DEPOSITS (HOLOCENE).

MPD

MPD - MIOCENE-PLEISTOCENE DEPOSITS unconformable on the Calabria-Peloritani Arc and Maghrebien Chain Units.

AsUPB
AsUMB

AsU - ASPROMONTE UNIT. Variscan Plutonic Basement (AsUPB); Variscan Metamorphic Basement (AsUMB).

MeU

MeU - MELA UNIT.

PU

PU - PIRAINO UNIT.

MaU

MaU - MANDANICI UNIT.

AUMC
AUB

AU - ALÌ UNIT. Mesozoic cover (AUMC); Basement (AUB). l: Metamarls and metaradiolarites, metamarl-limestones and meta (?) - limestones, meta (?) - dolomites, cagneules; v: Verrucano type metasiltites and metarenites (Cretaceous- Upper Triassic).

FU

FU - FONDACHELLI UNIT.

Fig. 1 - Geological sketch map of the Peloritani Mountains (from Messina et al., 2004 modified)

The mineralised horizons are alternated within the schist sequences (lower dark-grey phyllites, upper green phyllites).

Fine-banded ores, rich in sphalerite, Ag rich galena and fluorite prevail in the Tripi areas and they are related to the alternation of iron (Mg)-carbonates and silica in the dark-grey phyllites grading to the paragonite marble [20].

3. The ore deposit

The Tripi mineralization, outcropping in the Ali area, is part of stratiform sulphide ore bodies, which are very widespread in the MaU.

The ore deposit consists, in order of abundance, of quartz, fluorite, galena, sphalerite, pyrite, chalcopyrite, arsenopyrite and covellite; smithsonite, gypsum, hydrozincite, limonite and malachite follow.

The stratiform ore body is concordant with the host-rock, consisting of phyllites, and has a syn-sedimentary pre-metamorphic genesis [3, 8]. It developed along the contact between carbonate layers and phyllites and has an extension of about 200 m.

The parallel alternated band structure of minerals (rhythmites) is often evident.

4. 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 areas without inclusions.

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 Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) analysis. Results give total concentrations for noble metals and partial concentrations of trace elements for minerals making up the rocks. Where materials were pure of inclusions, 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 Atomic Absorption (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.

5. Results and discussion

The Tripi ore-bearing metalliferous horizons are mainly made up of galena and sphalerite with scarce pyrite and rare chalcopyrite, arsenopyrite and covellite. Quartz and fluorite gangue minerals are predominant. Products of alteration such as oxides and hydroxides are also present.

Chemical analyses concerning the main constituents and trace elements are carried out by SEM with EDS (Table 1) and ICP-MS (Tables 2 and 3) on galena and sphalerite.

Galena (Fig. 2) follows sphalerite in terms of abundance and shows the characteristic black triangular pits with an arching alignment, which is a sign of dynamical stress related to metamorphic process. Two generations of galena are present, like has already been found in the stratiform ore body of Pancardo [12]. The second generation shows higher Ag contents than the first generation. The first is made up of fragments inside quartz; the second contains quartz I and pyrite. It is often fractured and the fractures are filled by quartz. Galena is sometimes replaced by sphalerite (Fig. 3).

The mineral chemistry (Table 2) shows very low Fe and Mn contents and higher values of Cu and Cd. Sb content is high ($\bar{x}= 621$) and comparable with that of Pancardo mineralization but lower than the Fiumedinisi discordant veins.

Sphalerite (Fig. 4) shows reddish-brown internal reflections and stocky habitus or slightly lengthened at crossed nicols. It is the most representative in terms of abundance and includes small relic grains of pyrite, pyrrhotite and rare chalcopyrite, in skeletal aggregates too. Two generations of sphalerite are present. The fractures have been cemented by quartz and pyrite II (Fig. 2). It is almost always pervaded by irregular quartz is partially replaced by smithsonite.

From a chemical point of view, sphalerite is ferrous with an average Fe content of about 5.15% (Table 1) and this is in good agreement with P-T conditions typical of the Unit. The Fe content is slightly lower than the Fiumedinisi discordant veins ($\sim 6.00\%$): Rosario, Cernicola, Migliuso, Due Fiumare, Lumbolo, Vacco and S.Carlo [8, 9, 10, 47] whereas it is comparable with the stratiform ore bodies of Molino di Giampileri and Pancardo [8, 12].

Sb ($\bar{x}= 134$) content is lower than Cd and Cu (Table 3). Sb values of the sample 5 in galena (3450 ppm) and sphalerite (8840 ppm) has been excluded from the average as it could be related to native antimony microinclusions, as already was emphasized in the same area, or to small areas of stibnite.

Pyrite (Fig. 5) is present in two generations: the first is made up of granules, often idiomorphic, inside quartz and sphalerite. The second generation consists of crystals filling the fractures in sphalerite (Fig. 2).

Chalcopyrite (Fig. 6) has been observed inside quartz in areas with irregular edges. It is also present inside sphalerite as relic grain and exsolution textures are rarely present.

Arsenopyrite is present in fragments inside quartz and sometimes shows polysynthetic twinning. Quartz is the main non- metalliferous mineral and looks like a milky mass. It is allotriomorphic and often alternates with sphalerite, fluorite and galena in a rhythmic deposition. Late litoclasts are filled with smithsonite, gypsum and contain hydrozincite, limonite and malachite patinas.

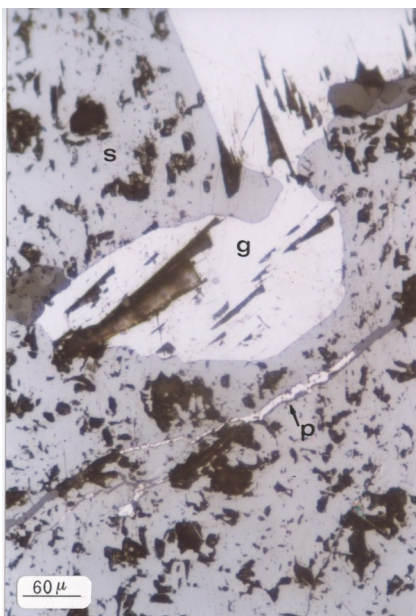


Fig. 2 - Galena (*g*) with signs of dynamical stress and sphalerite (*s*) with fractures cemented by pyrite II (*p*). Sphalerite replaces galena. Reflected light observation - // nicols.

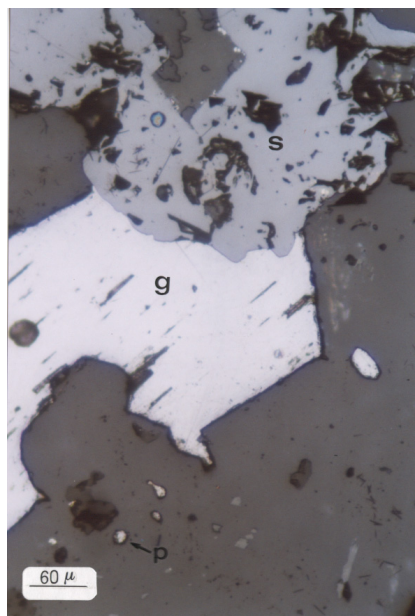


Fig. 3 - Sphalerite (*s*), galena (*g*) and granules of pyrite (*p*) inside quartz. Sphalerite replaces galena. Reflected light observation - // nicols.

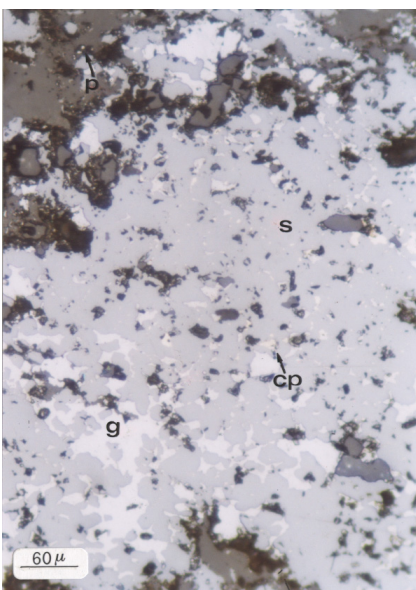


Fig. 4 - Galena (*g*) and rare crystals of chalcopyrite (*cp*) inside sphalerite (*s*). Granules of pyrite I (*p*) in quartz. Reflected light observation - // nicols.

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

SPHALERITE (S=33.06%; Zn=64.04%; Fe=2.88%)			GALENA (S=13.40%; Pb=86.60%)		
	mean ± s.d	n/4		mean ± s.d	n/4
S	32.09 ± 0.78	4	S	13.83 ± 0.37	4
Zn	61.49 ± 0.58	4	Pb	85.12 ± 0.47	4
Fe	5.89 ± 0.65	4			

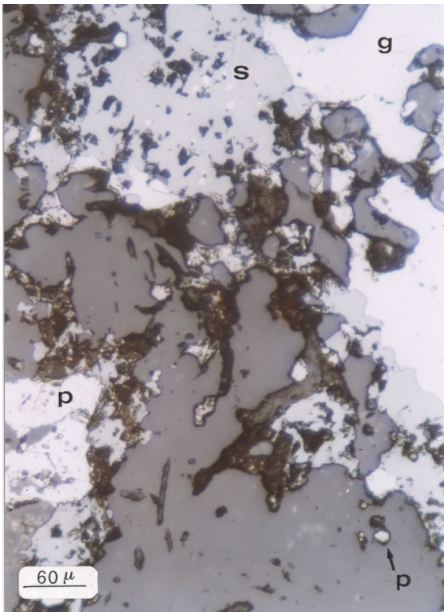


Fig. 5 - Galena (g), sphalerite (s) and pyrite(p). Pyrite is also present as granules inside quartz. Reflected light observation - // nicols.

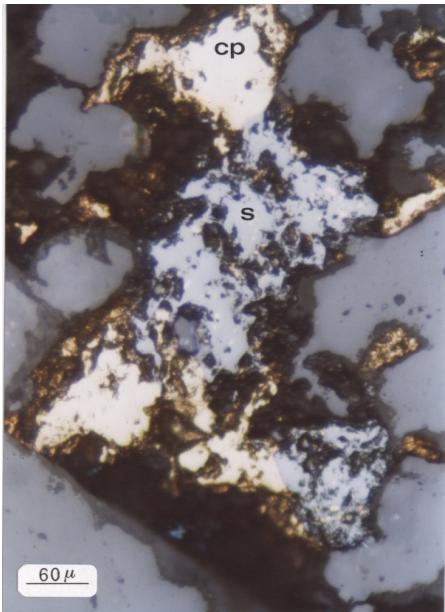


Fig. 6 - Sphalerite (s) and chalcopyrite(cp) inside quartz. Reflected light observation - // nicols.

The trace element data (Tables 2 and 3) have also indicated that the Cd content is much higher than the other stratiform mineralizations. The Mn content is comparable with that of the Molino di Giampileri mineralization [8]. Both Cd and Mn contents are however lower than in the vein mineralizations. Cu shows similar values or slightly lower than the Pancardo ore deposit. Also As, Ga and Hg are concentrated in sphalerite. Regarding the noble metals, the Ag (Tables 2 and 3) content is high in galena, relative to the same mineral of other Peloritani stratiform deposits and of discordant veins in which this content is variable from 500 ppm to 2000 ppm. The Au content reaches a value of 0.1 ppm in sphalerite.

Table 2
Chemical analyses of trace elements (ppm) in galena

GALENA											
Element	1	2	3	4	5		1	2	3	4	5
Al	2500	3200	1400	1200		Ni	1.4	1.4	1	<10	<2
Ag	975	790	850	694	1116	P	100	90	110	70	
Au	0.03	0.03	0.01		<0.2	Pd		<0.1			
As	4.3	3.6	2.7	<100	17	Pt		<0.002			<1
B	22.0	8.0	6.0			Se	<0.1	0.1	0.2		
Ba	8.0	5.3	4.7			Sc	0.4	0.2	0.3		
Bi	2.8	5	9.2	<100		Sb	329	570	725	860	3450
Ca	8500	5300	2000	2900	45	Sr	7.4	11	4.5		35
Cd	151	182	97	100	114	Te	0.02	0.03	0.04		<1
Co	0.9	1.3	1	<10		Th	0.5	0.5	0.5		
Cr	3.4	2.4	1.9	<10	<2	Tl	0.4	0.6	0.7		
Cu	36	158	78	160	313	Ti	10	10	<10		
Ga	0.9	1.2	0.5			U	0.4	0.4	0.7		
Hg	0.7	1.3	0.5	<10		V	5.0	<2	3.0		<3
La	5.2	3.9	4.8			K	600	300	200	200	1690
Mg	800	1800	400	600	26	W	<0.1	<0.1	2.1	20	
Mn	31	37	20	<100	13	Fe%	1.0	1.3	1.0	0.7	
Mo	0.17	0.28	0.08	<10	<0.5	Zn	>10000	>10000	>10000	35500	
Na	40	20	20	<100	8210						

6. Conclusions

The Tripi mineralization is included in the metalliferous mineralization province of the Peloritani Mountains, in particular in those hosted in the Mandanici Unit. They mainly occur as fine-banded ores, in the low-mid grade metamorphic schists with intercalated marble layers, related, according to Ferla and Omenetto [20], to Pre-Variscan intracontinental rifting associated to a basic magmatism [18].

Available data suggest that the Variscan tectono-metamorphic deformation phases and especially the intense hydrothermal activity correlated with the late phase of regional Variscan metamorphism are probably responsible for remobilization and concentrations

Table 3
Chemical analyses of trace elements (ppm) in sphalerite

SPHALERITE											
Element	1	2	3	4	5		1	2	3	4	5
Al	1300	900	1300	200		Na	1310	170	140	100	6470
Ag	157	270	200	109	306	Ni	3.9	4.0	4.7	<10	25
Au	0.15	0.17	0.07		<0.2	P	20	30	40	30	
As	35	26	35	100	3.0	Pb	<10000	<10000	<10000	40000	
B	833	128	157			Pd			1.1		
Ba	11	5.2	5.2			Pt			<0.002		
Bi	13	27	27	<100		Se	3.5	0.2	<0.1		
Ca	35100	9600	14300	5000	106	Sc	1.7	0.2	0.7		
Cd	1235	1119	898	1220	355	Sb	151	180	194	<10	8840
Co	8.9	10	11	10		Sr	5.1	2.5	2.5	<10	48
Cr	<0.5	1.4	1.7	<10	13	Te	0.1	0.1	0.1		<1
Cu	1215	1174	1147	980	382	Th	0.6	0.8	0.9		
Ga	5.3	5.0	5.0			Tl	0.4	0.5	0.4		
Hg	5.2	5.2	4.6	10		Ti	10	<10	10		
La	110	120	102			U	0.2	0.2	0.3		
Mg	<100	<100	100	<100	115	V	2.0	5.0	<2		
Mn	95	83	95	100	111	K	700	400	600	100	1310
Mo	0.84	0.1	0.22	10	<0.5	W	1.0	1.2	1.3	2250	

in vein- and stockwork-like orebodies. Some minerals like quartz, fluorite, galena, sphalerite and pyrite are, in fact, present in two generations, the second of which can be related to intense hydrothermal activity that involved not only the studied locality but the whole Peloritani Belt.

The Alpine metamorphic event then induced fracturing and reworking of the mineralised bodies and some kinds of enrichment in base metals and tungsten.

The presence of granules and lamellae of chalcopyrite inside sphalerite deserves attention. The rarity of chalcopyrite exsolutions in the sphalerite indicates T lower than 500 ° C and suggests the absence of hydrothermal Cu-rich fluids, in fact, in the Mandanici Unit the “chalcopyrite disease” texture is generally interpreted as the result of substitution phenomena, because the temperatures of metamorphic events affecting the Unit never reached 500 ° C, which is the temperature necessary to cause an exsolution-process [48, 49].

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

The analysis of trace elements (Tables 2 and 3) shows that Cd, Cu, Mn, As, Ga and Hg are concentrated in sphalerite whereas Sb is present mostly in galena, showing comparable values with those of other stratiform mineralizations, like Molino di Giampileri and Pancardo.

Ag content shows values around 1100 ppm in galena and lower values in sphalerite. The Ag presence in Peloritani minerals is widespread but shows variable values on average from 500 to 2000 ppm.

Particular emphasis must be paid to the presence of gold in the metalliferous minerals, whose contents in the Tripi mineralization (Tables 2 and 3) have however little economic importance if compared with the Au content in chalcopyrite (3 ppm) and arsenopyrite (6 ppm) of the Pomia Valley, near Bafia [13]. The Au values in the studied mineralization confirms the results of the latest research [11, 13, 21, 50, 47] on the presence of this element in some mineralizations belonging to the same Unit, such as in vein mineralizations belonging to the upper metamorphic grade Units too, thus supporting the hypothesis, already put forward by Ferla and Omenetto [20]; Messina and Saccà [21], that the presence of Au could be correlated to Alpine phenomena.

Therefore, this paper may be considered as a significant contribution to the reconstruction of the metallogenic evolution of the Peloritani Mountains concerning the stratiform and vein type ore deposits, since it completes the global delineated picture, also according to the reconstruction elaborated by Ferla and Omenetto [20].

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