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POLYMETALLIFEROUS MINERALIZATION IN THE ASPROMONTE UNIT OF THE SOUTHERN CALABRIA (ITALY)

Abstract - Pyrrhotite and sphalerite mineralization of the Cartegì Locality (S. Roberto of Aspromonte - Reggio Calabria) was studied. This ore deposit is set in the Alpine Aspromonte Unit (Southern Sector of the Calabrian-Peloritan Arc). This Unit is characterized by a high-grade Variscan crystalline basement intruded by Late-Variscan plutonites, both interested by a strong greenschist facies Alpine overprint (P 5-8 Kbar, T 500 \pm 20°C).

Polymetallic mineralization is made up of a main discordant vein articulate in a network of small veins.

Minerographic studies show an association of pyrrhotite and sphalerite, with subordinate galena, chalcopyrite, fluorite and pyrite.

Pyrrhotite is hexagonal and always has a granoblastic structure with corrugation lamellae. It also shows evidence of dynamic stress, like sphalerite.

Chalcopyrite is often present as filling of fractures inside sphalerite. In sphalerite a second generation of pyrite can be seen. Late oxides and hydroxides are ubiquitous.

Geochemistry (major and trace elements) of studied minerals has also been carried out.

These latter analyses show a high Au content in some minerals. In galena, particularly, Au reaches a value of 0.683 ppm. Ag contents in pyrrhotite and galena are lower than 100 ppm with positive correlation towards galena.

Ni (100.8 ppm) and Co (15.7 ppm) values in pyrrhotite exhibit a low Co/Ni ratio (Brill, 1989). Sphalerite is ferriferous type.

Key words - Polymetalliferous mineralization, chemical features, CPA, Calabria.

Riassunto - *Mineralizzazione polimetallifera nell'Unità dell'Aspromonte della Calabria meridionale (Italia)*. È stata presa in esame la mineralizzazione a pirrotina e sphalerite di Contrada Cartegì (S. Roberto d'Aspromonte - Reggio Calabria). Essa si trova nell' Unita dell'Aspromonte (Settore meridionale dell'Arco Calabro-Peloritano). L'unità è caratterizzata da un basamento cristallino Varisico di alto-grado intruso da plutoniti tardo-Varisci entrambi interessati da una sovraimpronta Alpina in facies scisti verdi (P 5-8 Kbar, T 500 ± 20°C). La mineralizzazione polimetallica è costituita da un filoncello metallifero principale, discordante, con piccole vene ad esso associate.

Studi minerografici evidenziano un'associazione di pirrotina e sphalerite, con subordinata galena, calcopirite, fluorite e pirite. La pirrotina è esagonale ed ha sempre una struttura granoblastica con lamelle di corrugamento. Sono osservabili vari segni di stress meccanico come nella sphalerite. La calcopirite è spesso presente come riempimento di fratture nella sphalerite, nella quale è presente anche pirite di seconda generazione. Ossidi e idrossidi tardivi sono ubiquitari. Sui minerali studiati sono state condotte analisi chimiche sia degli elementi maggiori che in traccia. Queste ultime evidenziano, in alcuni minerali, contenuti di Au degni di rilievo. In particolare va sottolineato il valore di 0,68 ppm nella galena. L'Ag nella pirrotina e nella galena è inferiore a 100 ppm, con una correlazione positiva nei confronti della galena. I valori di Ni (100,8 ppm) and Co (15,7 ppm) nella pirrotina evidenziano un basso rapporto Co/Ni (Brill, 1989). La sfalerite è di tipo ferrifero.

Parole chiave - Mineralizzazione polimetallifera, caratteristiche chimiche, ACP, Calabria.

INTRODUCTION

Basal metal (Pb, Zn, Cu, Sn, Sb, As, Ag, Au), fluorite, barite and tungsten (scheelite) deposits are very well known in the Southern Sector of the Calabria-Peloritani Arc (CPA), where they were mined, in the past, at several localities. The mineralizations are associated to both Variscan low to medium-high grade metamorphics and to Late-Variscan plutonites of the crystalline basements of the CPA Alpine nappes.

Several studies have been devoted to mineral compositions and geo-petrographic features of these deposits (Bonardi *et al.*, 1982; Censi & Ferla, 1982; De Vivo *et al.*, 1993; Ferla, 1982; Omenetto *et al.*, 1986-88; Oteri *et* al., 1986; Saccà & Cimino, 1988; Saccà et al., 1992; 1996; 1995; Saccà & Saccà 1992, 1993; Saccà & Triscari, 1985). Because of the complex structure of the CPA Alpine building and its heterogeneous evolutive history, genesis of its mineralizations has been a matter of debate. According to recent studies (Messina & Saccà, 2001; Messina & Saccà, in progress) carried out on the Peloritani Belt, the metallogenic evolution, based on regional petrological and tectonic features of mineralizations and on their relationship in space and time, indicates that in metamorphic rocks they are Pre-Variscan (sedex or volcex) deposits re-mobilized in the Variscan and Alpine hydrothermal stages; in plutonites, they are related to the late-magmatic hydrothermal stage.

The aim of this paper is to characterize a pyrrhotite and sphalerite mineralization related to Late-Variscan

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Fig. 1 - Geological sketch map of the Aspromonte Unit. 1: Tertiary to Quaternary sedimentary cover; 2: Stilo Unit. 3 to 7 ASPROMONTE UNIT; 3: Late-Variscan plutonic rocks; 4: Variscan metamorphic rocks; 5: pervasively Alpine overprinted rocks; 6: partly Alpine overprinted rocks; 7: weakly Alpine overprinted rocks; 8: Cardeto Unit; 9: Africo Unit; 10: Stratigraphic boundary; 11: Direct fault; 12: Inverse fault; 13: Overthrust. *Outcrop

acidic plutonites of the Aspromonte Unit (Southern Calabria) as a contribution to the knowledge of the CPA polymetalliferous history. Particularly, it is part of a research programme whose purpose is to characterize metalliferous mineralizations in the Peloritani Mountains (Sicily) and in the Aspromonte Massif (Southern Calabria).

GEOLOGICAL SETTING

The Calabrian-Peloritani Arc joins the NW-SE tectonic direction of the Southern Apennines with E-W Sicilian Maghrebides (Amodio-Morelli et al., 1967; Bonardi et al., 1967; 1996). In the Southern Sector of the Calabrian-Peloritan Arc, the Aspromonte Unit crops out from the Aspromonte Massif (Calabria) to the Peloritani Mts. (Sicily). In Calabria, it extends from Taureana-Antonimina in the north, to Bova Marina in the south (Bonardi et al., 1979) (Fig. 1). The Passo di Cancelo to Antonimina line (Fig. 1) marks the northeastern tectonic contact between the Aspromonte Unit and the part of the overlying Stilo Unit which outcrops in the Serre Massif and consists of low to medium grade phyllites with granite intrusive (Bonardi et al., 1984b). The Fiumara Valanidi-Roccaforte del Greco fault, marks the southwestern tectonic contact with that part of the overlying Stilo Unit which outcrops in the Aspromonte Massif (Fig. 1) and consists of low to medium grade metamorphic rocks (Crisci et al., 1983). The Aspromonte Unit is without Cenozoic sedimentary cover and consists of a Variscan crystalline basement, made up of heterogeneous low to upper amphibolite-facies metamorphic rocks intruded by syn- and post-tectonic plutonites. In particular, in the area around Villa S. Giovanni the Variscan intrusive bodies are post-tectonic. The Variscan mineral points to low-P medium- to high-grade amphibolite-facies conditions. A tectono-metamorphic overprint of Alpine age affected the Aspromonte Unit, re-equilibrating the Variscan crystalline basement (Messina et al., 1992).

The Alpine mineral assemblages suggested a greenschist-facies conditions (P 5-8 kbar, T 50020°C) for the first event and higher T and lower P for the second one (Messina *et al.*, 1992). However, in the weakly reequilibrated area, the same two Alpine events developed under lower P-T conditions (Messina *et al.*, 1992). A Rb/Sr radiometric age determination (Bonardi *et al.*, 1987; Messina *et al.*, 1991) on samples of total rock and separated minerals confirmed the Alpine age of the metamorphic overprint, which was strong in the eastern portion of the Aspromonte Massif and weaker in the outer zone.

The Alpine tectono-metamorphic overprint, which involved the crystalline basement, developed along centimetre-to kilometre-thick shear bands.

In the area with weaker Alpine overprint a cataclastic to mylonitic deformation occurred. In the western area, from Scilla to Punta d'Atò (Fig. 1), the Alpine deformation produced mylonites, leading to the development of few very fine grain-sized neoblastic minerals (Messina *et al.*, 1992).

THE ORE DEPOSIT

Diffused polymetalliferous mineralization is developed along the contact between Late-Variscan plutonic rocks and Variscan metamorphic rocks of the Aspromonte Unit outcropping near Villa S. Giovanni (Fig. 1) (Vighi, 1951; De Vivo, 1980). The intrusive body, two mica Al-silicate-bearing leucotonalite to leucomonzogranites, varies in grain-size. The whole crystalline basement is crosscut by a network of aplitic dykes, which are the latest intrusions (Messina *et al.*, 1992).

In particular the examined ore deposit crops out in the S. Roberto territory (RC), near Cartegì (UTM 33SWC 123170), to the South of Serro Carnala (Fig. 1). It can be reached by the road connecting S. Roberto and Melia (Fig. 1).

The mineralization can be seen as a main metalliferous vein. It is mainly made up of pyrrhotite, pyrite and sphalerite, with smaller quantities of galena, chalcopyrite, fluorite and pyrite. The rock is a strongly altered aplitic granite. This is largely impregnated with metalliferous minerals, and constitutes a dyke emplaced in the gneiss (with quartz, albite, orthoclase, biotite and muscovite) of the Aspromonte Unit, outcropping in large areas. The rock is white on the new fractures and yellowish-brown on altered surfaces, where hydroxide altered epigenetic products prevail.

Fragments of mineralised host rock can be seen in the veins.

Studies have shown that the metalliferous minerals and associated veins fill the cracks in the rock, as a complex fracture or as a system of distensive faults with orientation slightly tilted vertically.

The direction of the veins is not clearly observable in the field, it could probably orthogonally penetrate the mountainside slope.

EXPERIMENTAL METHODS

The mineralogy and paragenesis of the deposits were studied by reflected and transmitted light microscopy and X-ray powder diffractions using CuK α radiation. Chemical analysis (electron microprobe) was carried out using an 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.

The results were corrected by 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. Samples are digested by HCL:HNO₃ (3:1) mixed reagent followed by ICP-MS analysis. Results give total concentrations for noble metals and partial concentrations for minerals making up the rocks, where materials were pure, tests were integrated by A.A. according to the following procedures: 300mg of powdered mineral bonded by heat to an HNO₃:H₂SO₄ 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 Recovery tests is between 98.8% and 102.6% of the theory. Laboratory reproducibility shows maximum oscillations lower than 2% for analytical determinations.

MINERALOGRAPHIC - STRUCTURAL CHARACTERISTICS

Under the microscopy the rock exhibits an autoallotriomorphic fine-grained fabric, made up, in order of abundance, of quartz, kaolinizated microcline and saussuritized plagioclase (albite) and subordinate sericite. Sericite developed after plagioclase. Widespread kaolinization and saussuritization indicate that the rock was affected by hydrothermal fluids.

The quartz is always rounded and somewhere contains rutile acicular microcrystals. This suggests that the quartz was not deposited at the same time during metalliferous mineralization. Going out from the contact, sericite is found next to the quartz, sometimes substituted by metalliferous minerals. Also muscovite and microcline have not been observed next to the contact. The feldspars do not show fractures or deformations. The texture of the metalliferous minerals can be compared with that of aplite quartz.

Microscopic study by reflected light shows an association of pyrrhotite and sphalerite with subordinate galena, chalcopyrite, fluorite and pyrite. Pyrite, pyrrhotite and galena are present in two generations.

On the whole according to De Vivo *et al.* (1980), the paragenesis is as follows: fluorite and pyrrhotite I; sphalerite and galena I; pyrite I and chalcopyrite; pyrrhotite II, galena II, pyrite II, marcasite.

Pyrrhotite is the most abundant mineral and is included almost in all minerals suggesting that it is the first mineral to be deposited. It is hexagonal and always has a granoblastic structure with corrugation lamellae. Evidence of dynamic stress, is shown. The extinction is often undulose. The anisotropy is marked and the colours vary from grey-yellow to grey-black.

Pyrrhotite is often altered to marcasite and pyrite II. The alteration is well observable along the fractures. Bird's eye (Fig. 2) and comb structures are both present. Pyrrhotite II can be found as filling of the fractures inside pyrrhotite I.

Sphalerite reddish-brown internal reflections can be seen at crossed nicols. There are no granules or iso-oriented lamellae of pyrite, pyrrhotite and chalcopyrite, which are common structures in other Peloritani mineralizations (Oteri *et al.*, 1986; Saccà & Cimino, 1988; Saccà *et al.*, 1992; Saccà *et al.*, 1996). (Fig. 3). But chalcopyrite is present as filling in the fractures and in wider areas, too (Fig. 4).

A first generation of pyrite can be seen sometimes inside the sphalerite.



Fig. 2 - Typical pyrrotite alteration known as "Bird's eye". Reflected light observation.

Galena I is rarely seen inside the pyrrhotite. Galena II is present in small areas inside all the other minerals. The alignment of triangular pits shows the lack of dynamical stress after deposition in galena II, too. Fluorite is present in quantities which vary from one area to another. Thin fractures are often found, filled with sphalerite and chalcopyrite and rarely with galena. Late oxides and hydroxides are ubiquitous.

CHEMICAL DATA

Chemical analyses concerning the main constituents, are carried out by SEM with EDS on pyrrhotite, chalcopyrite, galena and sphalerite (Table 1).

Trace elements data have been carried out on pyrrhotite and galena by ICP-MS (Table 2). Sphalerite is ferriferous with an average Fe content of about 5%. In galena, Au content reaches a value of 0.683 ppm, and Ag is present in smaller quantities than those recognized in most of the Peloritani mineralizations (Saccà & Saccà, 1993).





Fig. 3 - Galena (g) and sphalerite (s) with inclusions of chalcopyrite (c). Reflected light observation.

Fig. 4 - Chalcopyrite (c) as filling of the fractures inside sphalerite (s). Reflected light observation.

Tab. 1 - Representative chemical analyses (%).									
x	S	Pb	Fe	Cu	Zn	Total			
Galena	13.38	86.56				99.94			
Sphalerite	32.71		5.72		61.4	99.83			
Chalcopyrite	32.8		32.2	34.19		99.19			
Pyrrhotite	61.12		38.56			99.68			

Co content in pyrrhotite is markedly lower than what is usually found in volcano-genetic deposits (Frater, 1978). It is low even when compared with sedimentary deposits (Brill, 1989). Ni content is also low, but comparable with the content in remobilized vein deposits (Bralia *et al.*, 1979).

The Co/Ni ratio in pyrite which can usually give information on the genetic environment (Brill, 1989) is 3,9. Here it does not assume particular importance, because pyrite is a product of an alteration of pyrrhotite.

DISCUSSION

The granitic body outcropping in the Villa S. Giovanni area, was affected by mineralization processes. Chemical and microscopic characters of this mineralization are quite different from the other mineralizations outcropping in the Peloritani Mts. (Sicily). In particular, minerographic study of S. Roberto mineralization shows that some minerals, like pyrrhotite and galena, present two generations. Chalcopyrite and galena II

Tab. 2 - Trace-elements contents of galena, pyrrhoute and pyrite (ppm).											
	Ag	Al	Au	As	В	Ba	Bi	Cd	Со	Cr	Cu
Galena	75	20	0.68	10176	56	52.4	307.5	336	11	117	1329
Pyrrhotite	38.9	20	0.02	192	60	< 0.5	16.6	439	15	128	677
Pyrite	40.5	1.1	0.06	390	26.6	7.7	12.4	62	34.2	277	1.1
	Ga	Hg	La	Mn	Мо	Na	Ni	Р	Sb	Sc	
Galena	0.4	5.67	< 0.5	226	3.8	4	87	2	430	< 0.1	
Pyrrhotite	0.6	12.6	< 0.5	88	6.6	8	101	4	40	< 0.1	
Pyrite	8.5	10.2	< 0.5	156	4.2	5	8.6	3	70	< 0.1	
	Se	Sr	Te	Th	TI	Ti	U	\mathbf{V}	W	Zn	
Galena	14	2	0.64	< 0.1	0.36	78	< 0.1	28	0.2	5384	
Pyrrhotite	6	< 0.5	0.04	< 0.1	0.38	106	< 0.1	30	< 0.1	7307	
Pyrite	226	6.9	0.1	< 0.1	11	96	< 0.1	25	< 0.1	1200	

Tab. 2 - Trace-elements contents of galena, pyrrhotite and pyrite (ppm

are also observable as filling of fractures. They indicate a phase of late mineralization which probably could be correlated to Alpine event, which is also responsible for cataclastic effects for kink-bands and fragmentation.

The stars of sphalerite in the chalcopyrite are generally interpreted as the exolution products and are restricted to high-temperature deposits (Ramdohr, 1980).

The chemical study characterizes the mineralization. Co content in pyrrhotite is markedly lower than what is usually found in volcano-genetic deposits (Frater, 1978). It is low even when compared with sedimentary deposits (Brill, 1989). Ni content is also low, but comparable with the content in remobilized vein deposits (Bralia *et al.*, 1979).

The Co/Ni ratio in pyrite which can usually give information on the genetic environment (Brill, 1989) is 3,9. Here it does not assume particular importance, because pyrite is a product of an alteration of pyrrhotite. The presence of Au deserves particular emphasis,

The presence of Au deserves particular emphasis, which has been already found in the barite, siderite and galena mineralization of Linata (Saccà, 1983). The Linata area belongs to the Aspromonte Unit cropping out in the Peloritani Mts. (Sicily). The signallings of the Au presence in the mineralizations of the lower metamorphic grade Units, outcropping in the Sicilian part of the CPA, are more numerous. They are also referable to a late event which joins many CPA mineralizations, with different genesis too (Saccà, 1983; De Vivo *et al.*, 1993, 1998; Messina & Saccà, 2001; Messina & Saccà, in progress; Saccà *et al.*, 1995).

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