Towards a better understanding of a Co-rich hydrothermal system: Punta Corna (Western Alps, Italy)

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Abstract. This study presents new geochemical, mineralogical, and petrographic data on the Co-Fe-Ni vein system of Punta Corna (PC) in the Western Alps, Italy. The mineralogical phases identified include arsenides belonging to the skutterudite and safflorite (Fe-Co-Ni tri- and di-arsenides) solid solutions, tetrahedrites, and sulfides. Gangue minerals comprise carbonates (mainly calcite, siderite, ankerite) and quartz. Field and mineralogical observations show a distinct geochemical zonation within the deposit system. No Co or Ni occur to the west, with only Fe-bearing minerals observed. Co-Ni arsenides are present in the central region, with a higher proportion of Ni di-arsenides than Co-bearing phases. To the east, Co arsenides prevail. Additional sampling, micro-textural characterization and geochemical investigations are going on, yet these preliminary observations agree with the genetical theories recently proposed for similar types of deposits and suggest that the hydrothermal system may have formed through a complex geological history, with multiple mineralizing events and variations in fluid composition and, possibly, temperature.

1 Introduction

The Co-Ni-bearing Punta Corna (PC) hydrothermal vein system is located in the western sector of the Alpine belt near the Lanzo Massif, Northern Italy. Despite being a historically known mining complex, exploited until the '90s, formerly for Fe and later for Co (used as a pigment), this vein system has received little scientific attention until recently.

In 2020, the Australian Junior Mining Company (Altamin l.t.d.) acquired the exploration license of ca. 22 Km^2 area around ancient mining galleries. The PC mining complex holds great potential from an economic standpoint, both for the main ores consisting of Co-rich arsenides, and for the poor exposure of the vein system, likely preserved at depth.

The literature lacks detailed information on the geochemistry of the deposit and high-resolution geological maps.

Preliminary paragenetic studies based on museum samples (Moroni et al., 2019 and ref. therein) suggested a multi-stage mineralizing process with early siderite, ankerite, quartz and baryte followed by deposition of Fe-Co-Ni di-triarsenides with native elements (As, Bi), and then base metal sulphides and tetrahedrite with siderite, ankerite, quartz and late baryte gangue.

There are analogies between the PC mineralization and the five-element vein-type deposits according to Kissin' (1992), to more recent studies (e.g., Markl et al 2016) as well as the mineralized veins in the world-class Bou Azzer ore district (Tourneur et al 2021).

Nevertheless, definitive constraints on the genetic conditions of the PC hydrothermal vein system are still missing.

In this work, we summarize geological, mineralogical, and geochemical data on a new set of surface samples of the poorly known Fe-Co-Ni-bearing Punta Corna ore deposit. Drilling is programmed for verifying the features of the vein system at depth. Moreover, we illustrate some investigations in progress about the possible sources of Co in the mineralization, about the age of the mineralizing process and about the characters of the fluid and its origin.

2 Geological setting

The ore bodies of the PC hydrothermal vein system are located in the Arnàs, Servin, Veil, and Autour valleys, some small offshoots of the Viù valley, close to the village of Usseglio (TO, Figure 1 A, B).

The Fe-Co-Ni-bearing veins extend for 2 Km along an east-west axis, from the "Lago dietro la Torre" lake to the "Torre d'Ovarda" peak, with elevations ranging from 2200 to 2900m. The average thickness of the outcropping veins is in the cm/dm range. Mineralized bodies are hosted in metabasites and, subordinately, in heavily foliated calcschists of the Internal Piedmont Zone tectonic unit (IPZ), a portion of oceanic lithosphere and its sedimentary cover related to the Middle-Jurassic Piedmont-Ligurian Ocean (Dal Piaz 1999, Figure 1). The IPZ is structurally located above the Gran Paradiso (to the North) and the Dora Maira (to the South) Units, which represent the external continental margin of the European Plate. With the subduction of the oceanic crust below the Adria plate leading to the Alpine orogenesis (90-35 Ma), the oceanic rocks of the IPZ registered an eclogitic peak metamorphism followed by green-schist facies re-equilibration during exhumation (35-23 Ma, Sandrone 1986). The rocks recorded several ductile deformations phases, while the mineralized veins are related to a post-metamorphic brittle event and are associated with faults and fractures. Two late steep E-W trending fault systems occur throughout the whole deposit. The first system is represented by a subvertical normal fault system, interacting with a diverging high-angle transtensional fault system.

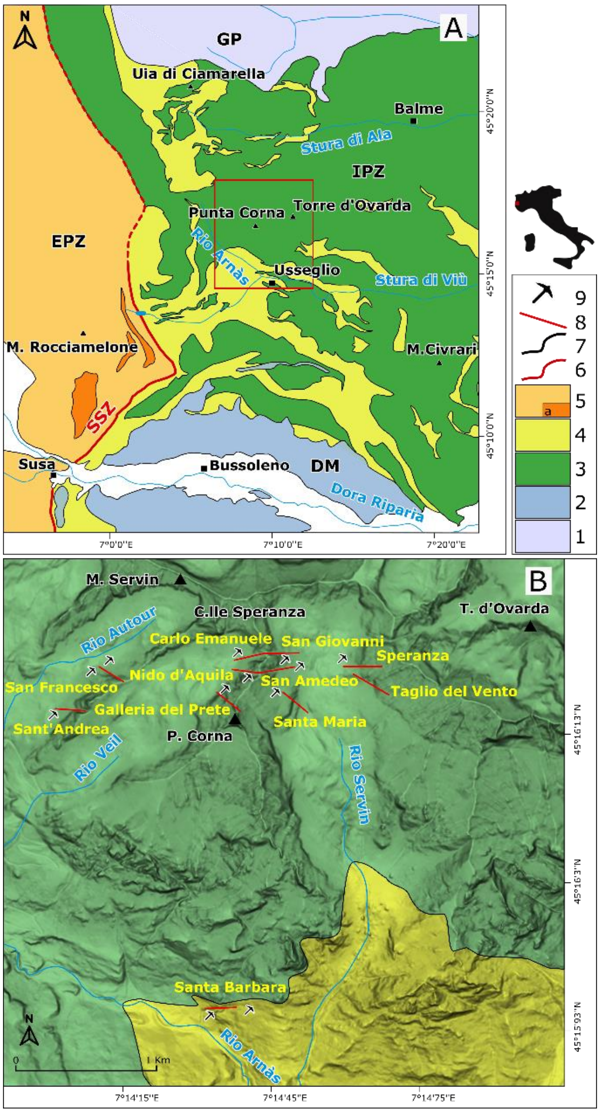


Figure 1. A) simplified tectonic sketch-map of the central sector of the Western Alps, modified after De Togni et al. 2021. In red is marked the location of the studied area. B) geological map of the studied area. *1* Gran Paradiso (GP); *2* Dora Maira (DP); *3* meta-ophiolites of the Internal Piedmont Zone (IPZ); *4* metasedimentary cover of IPZ; *5* oceanic metasediments with a) meta-ophiolite bodies of the External Piedmont Zone (EPZ); *6* Susa Shear Zone (SSZ); 7 tectonic contacts; *8* main mineralized veins; 9 ancient mining adits.

Field evidence of a geochemical zonation affecting the vein system occurs across the mining district. The presently accessible portions of the veins in the western sector characterized by Fe-bearing ores (siderite-ankerite). In contrast, the eastern sector displays high Co/Ni ore minerals (di- and tri-arsenides). It is worth mentioning the presence of Ag, mined since historical times, in the southernmost part of the ore district.
The ophiolite terranes in the surroundings of the studied area host several metamorphosed volcanogenic massive sulfides deposits (VMS) exploited in historical mines like Fragnè-Chialamberto, Uja di Calcante and Beth-Ghinivert, where recent studies signalled anomalous Co contents in the pre-metamorphic pyrite (Giacometti et al 2014). For this reason, we have started sampling variably deformed portions of some of these volcanogenic sulfides layers for evaluating them as possible sources for Co in the PC vein system.

3 Methods

Several samples collected in the field, both on surface and in the ancient mining tunnels, were cut to obtain thin and polished sections for optical microscopy (OM). The x-ray power diffraction (XRPD) analyses on carbonates, alteration and suprgene phases were carried out using a Rigaku SmartLab XE diffractometer in Bragg-Brentano geometry (CuKα radiation, Ni filter, generator operating at 40 kV and 30 mA, soller slit 2.5deg) equipped with a 2D HyPix-3000 detector. The detector was employed in 1D XRF-reduction mode to increase peak resolution and limit the background signal due to the fluorescence from Fe. In addition, each measurement was collected by mounting a frontal knife edge and a direct beam stop to reduce the background. The patterns were collected from 5 to 75º 2θ, with a step size of 0.02º and a scan speed of 1 º/min. The qualitative analysis was carried out with EVAluation software (Bruker), employing PDF-2 database.
Scanning Electron Microscopy equipped with Energy Dispersion Spectroscopy (SEM-EDS) was also employed for preliminary petrography and chemical semi-quantitative analyses. Carbon-coated thin polished sections were analyzed with a JEOL JSM-IT300LV SEM equipped with an EDS Energy 200 and an SDD X-Act3 detector (Oxford Inca Energy). The operating conditions were 20kV accelerating voltage, 5nA probe current, 30s counting time. The data were acquired and processed using the Suite AzTec ID, version 6.0(Oxford Instruments). Sample preparation, XRPD, and SEM-EDS were carried out at the Department of Earth Sciences, University of Turin.
Quantitative Microprobe analyses (EPMA) Wavelength Dispersion Spectroscopy (WDS) were performed at the University of Milan "Ardito Desio" on carbon-coated thin polished sections using a JEOL JXA – 8200 EPMA equipped with five wavelength-dispersive spectrometers. The analytical conditions for the electron beam were: accelerating voltage 15kV, beam current 5nA, beam diameter 1-2μm, and counting time for each element: 30s on peak and 10s on the background. Elemental concentrations were determined after applying φ(ρz) algorithm and corrections for X-ray fluorescence, absorption, atomic number (Z), and matrices and by evaluating spectral interferences.

4. Petrography, Mineralogy and Geochemistry

The new surface samples display abundant gangue minerals encompassing calcite, dolomite, siderite, ankerite, quartz, and baryte. Hydrothermal alterations of wall rock may often result in the

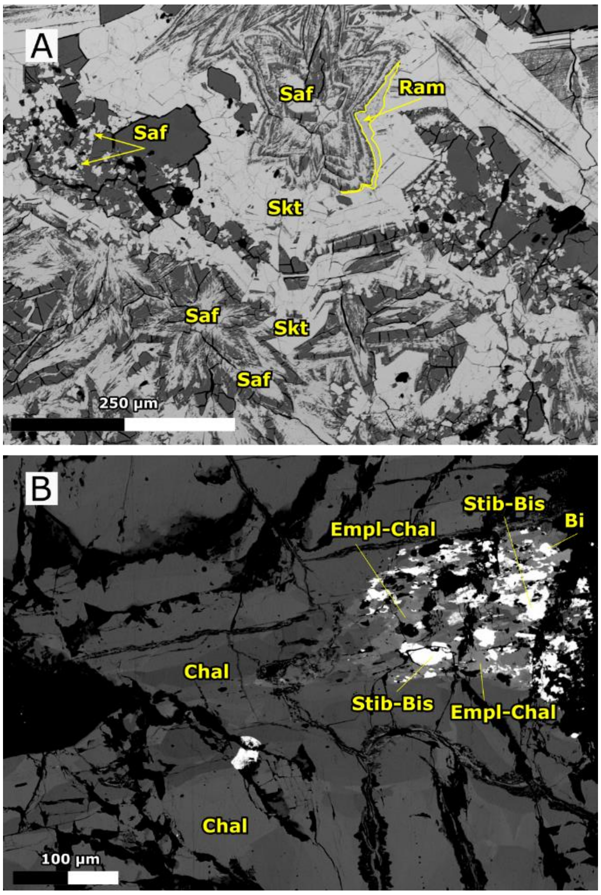


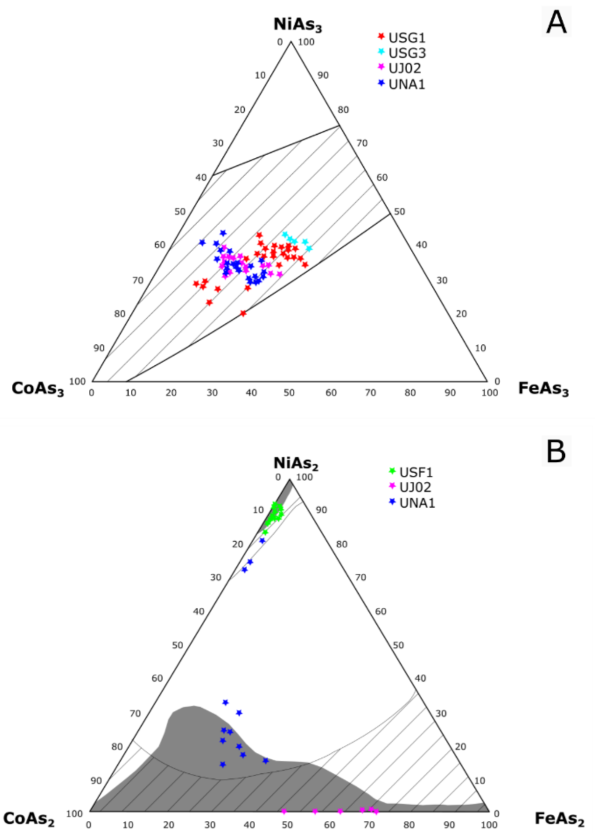
Figure 3. BSE images. A) coarse-grained safflorite I crystals exhibiting star-shaped twinning alternating with thin grained disseminated aggregates of safflorite II. Rammelsbergite rim and well-formed euhedral crystals of skutterudite can be observed. B) Sulfosalt belonging to emplectite-chalcostibite solid solution and stibnite-bismiuthinite solid solution.

presence of very fine-grained chlorite and white mica. Supergene oxidation of primary arsenides sulphides and siderite results in erythrite, annabergite, and abundant goethite. The veins exhibit a brecciated texture with clasts from the host rock, sometimes reaching centimetric sizes, cemented by a fine-grained gangue minerals matrix. Bladed siderite and euhedral quartz growing radially around brecciated clasts is also a typical texture of the mineralized veins. Veins can also present a banded structure with different compositional and textural layers. The ore minerals observed so far are represented by dominant Co-Ni di-triarsenides and base metal sulfides as those previously mentioned, although SEM and EPMA analyses helped in detecting additional sulfosalt minerals. Ore minerals show variable textures: from well-preserved coarse-grained to brecciated or fine-grained disseminated crystals. The precipitation sequence starts with carbonates and quartz, followed by arsenides. They are characterized by di-arsenides either overgrowing coarse-grained tri-arsenides Figure 2A,B) or disseminated along preferential directions or bands along the veins. Tri-arsenides (skutterudite series: (Fe,Co,Ni)As3) are often zoned, with banding marked by alteration products (erythrite, annabergite). Di-arsenides belong to the safflorite series: loellingite (FeAs2), clinosafflorite (CoAs2), and rammelsbergite (NiAs2)**.** The latter may often occur as a rim on di- and tri-arsenides. The last precipitation stage is represented by base metal sulfides (chalcopyrite, minor pyrite and rare sphalerite and galena), tetrahedrite and several Bi-rich sulfosalts intergrown with native Bi (FOTO). Rare droplets of secondary Ag sulfides were observed along rims of altered tetrahedrite crystals. Skutterudite composition is characterized by an average Co content of 9,25 wt%, Ni content of 7,65 wt% and Fe content of 4,93 wt%, but the compositions are quite homogeneous (**Errore. L'origine riferimento non è stata trovata.**, A). Di-arsenides, on the other side, present wide variation in composition, with a range in Co content varying from 3,16 wt% to 16,52, Ni content from 0 to 30,23 wt% and Fe content from 0,12 to 19,94 wt% (**Errore. L'origine riferimento non è stata trovata.** A,B).

Tetrahedrites belong to the tetrahedrite series and have low values of both Zn (ranging from 0,88 wt% to 6,46 wt%) and Ag (ranging from 0 to 0,87 wt%).

Beside Bi-Sb alloys, Bi-rich sulfosalts display highly variable compositions including horobetsuite (related to stibnite - bismuthinite solid solution) and Cu-rich varieties like wittichenite and emplectite-chalcostibite solid solution. It is worth noting that these Bi sulfosalts are especially characteristic of the post-metamorphic Au-bearing veins of the nearby Gran Paradiso nappe.

Figure 2. A) plot of skutterudite mineral series for the investigated veins. The solid-solution field for the system $FeAs_3$–$CoAs_3$–$NiAs_3$ is defined by shaded area, according to Roseboom (1962). B) plot of safflorite mineral series (system $FeAs_2$–$CoAs_2$–$NiAs_2$), compositional limits of natural Fe, Co, Ni diarsenides, according to Roseboom (1963) in dashed areas and Radcliffe & Berry (1968), full areas.



5. Work in progress

We are preparing a set of double polished sections from the new samples for fluid inclusion analyses in gangue minerals. From the same samples we are selecting portions with ore-related and post ore carbonates for performing U-Pb geochronology, together with carbonates from other post-metamorphic mineralized veins in the Gran Paradiso and Monte Rosa nappes. On the same samples also carbon isotope analyses will be performed for obtaining indications about origin of carbon gases in the fluids. Also, the origin of the great amount of Co in the PC vein system is a topic of interest. Therefore a series of pyrite-rich samples from the VMS deposits in the Western Alpine ophiolites are in preparation for testing their possible role as sources for hydrothermal Co enrichment. Preliminary EMPA analyses on cm-sized metamorphosed py-cpy layers located at the contact between metabasites and calcschists, in the Arnàs valley, have been promising so far by revealing anomalous Co contents (up to 2%) in irregularly zoned pyrites.

6. Conclusion

The data from the characterization of the new surface samples from the Co-rich post-metamorphic veins in the Western Alpine ophiolites at Punta Corna – Usseglio are revealing that the mineralized system is more complex than previously indicated from historical samples. Beside indications about the distribution of Co and Ni, the new data suggest a role to previously unknown Bi enrichments which also contribute to establish a possible link with the nearby domain of the Pennidic Gran Paradiso nappe. Therefore, the upcoming drilling campaign is bringing great expectation.

Because of the poor exposure of the PC veins, plenty of work is still needed to fully understand the features and the genetic process that led to the deposition of the hydrothermal system associated with Fe-Co-Ni arsenides. To gain further insight into these issues, fluid inclusion, geochronological and isotopical analyses will likely provide significant data for better defining the hydrothermal fluids and their components, the origin of the vein system and potentially explain the zonation. The fluid inclusion analyses will be focused in particular on potential reduction mechanisms/agents (e.g. hydrocarbons) proposed in various models in literature for hydrothermal Co-Ni mineralization. Last but not least the study of the metamorphosed exhalative pyrite ores in the western alpine ophiolites will be interesting for tracing possible Co sources for the PC mineral system and beyond. Further research and investigations could have significant implications for the evaluation of mineral resources and mining exploration in the region.

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