



# Vein intersection zones and host rock composition as controlling factors in polymetallic *ore shoots* genesis: insights from the Southern Arburèsè five-element (Ni-Co-As-Bi-Ag) vein system (SW Sardinia)

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## Article

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## ABSTRACT

Several studies highlighted the role of chemical controls on the genesis of the five-element (Ni-Co-As-Ag-Bi) deposits, such as host rock composition and intersection between different hydrothermal systems. In the Arburèsè district (SW Sardinia), located in the Variscan low-grade metamorphic basement intruded by the Arbus (304 Ma) and Mt. Linas (289 Ma) plutons, the hydrothermal veins follow the contact with the Arbus pluton: in the northern part Pb-Zn ores prevail; conversely, in the southern branch they become five-element veins, showing a pinch and swell structure, breccia/cockades textures with alternating enriched (ore shoots) and low-mineralized zones. The overall mineral assemblages are: 1) native Bi and Ni-Co-Fe arsenides-sulfarsenides + quartz; 2) base-metal sulfides and sulfosalts + siderite; 3) late-stage quartz, followed by pyrite and calcite. New surveys in the area pointed out that important ore shoots occur: 1) where the veins are hosted in Silurian black shales, which can act as redox barrier; 2) at the intersection with earlier hydrothermal systems related to the Monte Linas pluton, where selective remobilization of As and Bi may have taken place. The vein system was explored only in its shallower parts, so it is possible that undiscovered ore shoots may be still present at depth.

**KEY-WORDS:** five-element veins, Arburèsè district, ore shoots, intersection zones, physico-chemical controls.

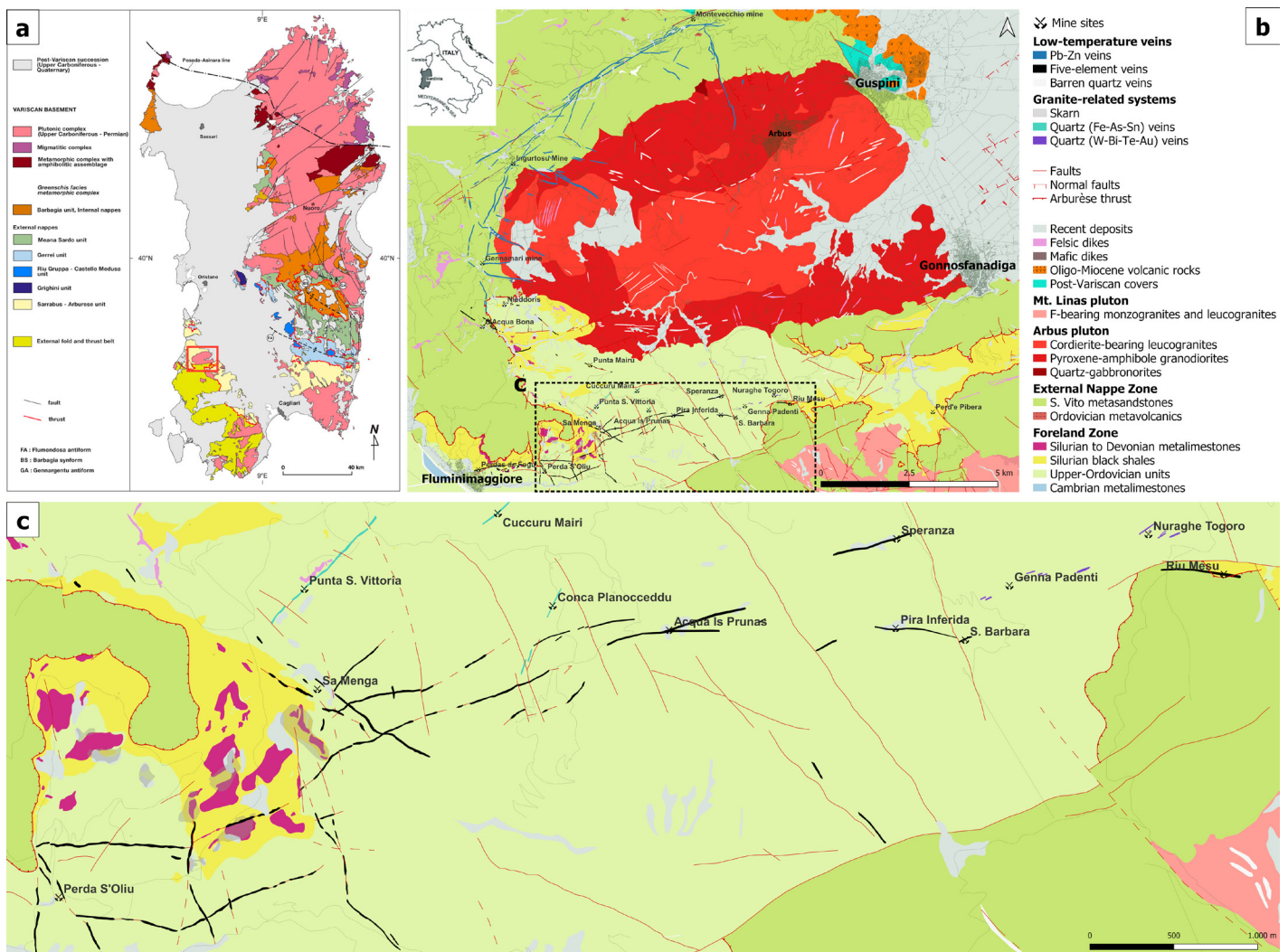
## INTRODUCTION

The “five element” vein type (Ni-Co-As-Ag-Bi) (Halls & Stumpfl, 1972; Kissin, 1992) is a class of hydrothermal ore deposits originated by low-temperature, very high-salinity fluids

and characterized by complex mineral assemblages, represented by native elements (Ag, Bi), Ni-Co arsenides and base metal sulfides/sulfosalts in quartz and carbonate gangue. Several models have been proposed to explain the precipitation of the ore shoots: 1) dilution and cooling through mixing of different fluids (Essarraj et al., 2005; Kissin, 1993; Marshall & Watkinson, 2000; Marshall et al., 1993); 2) interaction of the fluids with the wallrock (by leaching and by natural fracturing of carbon-rich lithologies) (Naumov et al., 1971; Markl et al., 2016; Burisch et al., 2017) or with Fe<sup>2+</sup> bearing minerals (Robinson & Ohmoto, 1973; Ondrus et al., 2003; Kreissl et al., 2018). Host rock chemistry and rheology, but also intersections with former hydrothermal systems seem to play a critical role, since they control the development and geometry of the veins, and they may act as sources of elements or as redox barrier. This research investigates the influence of these factors in the genesis of this class of deposits, focusing on the polymetallic five-element vein system of Southern Arburèsè (SW Sardinia, Italy), hosted in Paleozoic successions including carbonaceous black shales and granite-related ores.

## GEOLOGICAL SETTING AND ORE DEPOSITS IN THE AREA

The Arburèsè district is situated between the “Foreland Zone” and the “External Nappe Zone” of the Variscan basement of SW Sardinia (Fig. 1a). Outcropping geological units consist of low-grade



**Fig. 1 - Geological sketch map of the Arburès district (Mod. from Geological map of Sardinia in scale 1:25.000 by Regione Sardegna). a): the district (framed in the red rectangle) within the Variscan basement of Sardinia (mod. from Carmignani et al., 2016). b): overview of the district; c) detail of the Southern part of the district.**

to very low-grade metamorphic rocks, intruded by post-collisional granitoids (Fig. 1a,b). The Northern part of the district is dominated by the Arburès Unit (Barca et al. 1992), part of the Nappe Zone, made of Cambrian to Upper Ordovician siliciclastic rocks and minor calc-alkaline felsic metavolcanics, with some tectonic slices of Silurian black shales and metalimestones. On the other hand, the Southern part (Fig. 1c) is characterized by Upper Ordovician to Devonian rocks belonging to the Foreland Zone, consisting of metasandstones, metapelites and minor black shales and metalimestones (Carmignani et al. 2001, 2016). Post-collisional intrusive magmatism is represented by the 304 Ma (Cuccuru et al., 2016) Arbus pluton and by the 289 Ma (Boni et al., 2003) Mt. Linas pluton. The Arbus pluton is a composite intrusion, consisting of cordierite-bearing leucogranites at the core and pyroxene-amphibole granodiorites, with minor quartz-gabbrogranites at the outer shell (Secchi et al., 1991, 2022; Cuccuru et al., 2016); the Monte Linas pluton is represented by ilmenite-series ferroan, F-bearing monzogranites to leuco-syenogranites (Naitza et al., 2017). Two main types of ore deposits occur in the area: 1) granite-related high-temperature systems, such as skarns, Mo-W greisen

and Sn-As veins linked to the emplacement of the Mt. Linas pluton (Naitza et al., 2017); 2) low-temperature hydrothermal polymetallic veins (Dessau, 1935, 1936; Borghesan, 1945; Moroni et al. 2019a,b). Mo-W deposits mainly occur in the south-eastern sector of the district (Nuraghe Togoro and Perd'e Pibera old mines): they are represented by molybdenite ( $\pm$  wolframite, pyrite, and chalcopyrite) disseminations within greisen-altered rocks, and quartz-molybdenite, quartz-molybdenite-wolframite, and quartz-wolframite stockworks and veins hosted by greisen-altered granitoids and/or low-grade metamorphic rocks (Naitza et al., 2017).

The skarn deposits (Canale Ganoppi, Mitza Madeddu, S'Arritzoni mineworks) prevail in the south-westernmost part of the district and are mainly hosted in metasomatized early Devonian metalimestones (Mason Porcus Fm., Gnoli et al., 1990). They consist of green beds rich in epidotes, garnets and clinopyroxenes; sulfides such as sphalerite, galena, pyrite, arsenopyrite pyrrhothite and chalcopyrite occur as decimetric-sized lenses in agreement with the bedding planes or as tiny veinlets arranged without any preferential orientation (Sola, 1968).



Sn-As hydrothermal veins are constantly NE-SW directed throughout the whole area and exposed in several old mineworks (P.ta S. Vittoria – Perdu Cara; Conca Planocceddu; Cuccuru Mairi). They consist of steeply dipping quartz-arsenopyrite or quartz-chlorite-cassiterite veins with minor pyrite, chalcopyrite, and rare galena displaying banded to massive/disseminated textures (Borghesan, 1945; Sola, 1968; Naitza et al. 2017).

Low-temperature hydrothermal veins roughly follow the contacts of the Arbus pluton with the basement and, based on their dominant mineral associations, can be subdivided in two main categories: a) base metal sulfide veins (Pb-Zn-Ag), which are mainly hosted in the Arburèse Unit rocks, and mainly follow the Northern and Western margins of the Arbus pluton (Montevecchio, Ingurtosu and Gennamari mines: Cuccuru et al., 2016; Moroni et al., 2019a); b) five-element (Ni-Co-As-Ag-Bi) veins (Moroni et al. 2019b), extended at distance of 1-2 km to the southern margin of the pluton, mainly hosted in the low-grade metamorphic units belonging to the Foreland Zone (Nieddorri, Perda S'Oliu, Sa Menga, Acqua Is Prunas, Pira Inferida, and Riu Mesu mines: Dessau, 1936; Borghesan, 1945; Moroni et al., 2019b).

## METHODS

Field surveys and samplings were performed at the Sa Menga, Acqua Is Prunas, Pira Inferida abandoned mines in the five-element vein system of the Southern Arburèse district (Fig. 1c). As the underground mineworks (Fig. 2) are largely no longer accessible, the samples were collected from external outcrops, as well as from the dumps close to the main mine adits. 50 thin and polished sections from about 40 hand-selected samples were studied under transmitted and reflected light optical microscopy: 20 from Sa Menga, 25 from Pira Inferida and 5 from Acqua Is Prunas (where it was more difficult to find good samples). Further investigations were performed by SEM-EDS spot analyses and elemental mapping using a FEI Quanta 200 equipped with a ThermoFisher Ultradry

EDS detector at the CeSAR laboratory at Università di Cagliari under high vacuum conditions, acceleration voltage 25–30 Kv and spot size 5  $\mu\text{m}$ .

## RESULTS

### The ore shoots of the five-element system

The low-temperature five-element system is represented by 1 to 2m thick, ENE-WSW directed and almost constantly S dipping veins, whose continuity is broken by minor conjugate, similarly mineralized N-S to NW-SE veins (Perda S'Oliu and Sa Menga mines). The vein system is characterized by an overall pinch and swell attitude, with alternating *ore shoots* (roughly corresponding to the mine sites) and low-mineralized zones; along the way, it repeatedly crosscuts the granite-related mineralized occurrences, as the Medau Ganoppi Pb-Zn-Cu-Fe-As skarn and the various high-temperature vein systems (e.g., Nuraghe Togoro ENE-WSW quartz-wolframite (Bi-Au-Te) veins; Santa Vittoria-Perdu Cara NE-SW quartz-cassiterite and quartz-arsenopyrite veins). In the five-element system vein mineralization styles result from repeated filling of open spaces in a fault system; the vein filling largely displays disseminated, brecciated and banded textures (Fig. 3d, e, f). Banded textures include siderite and sulfide bands (mostly galena), often brecciated and cemented by late quartz. Brecciated textures including wall rock fragments are very common, cemented both by siderite and quartz; cockade textures are also frequent (Fig. 3a, c). Wall rock is variably bleached, sericitized and silicified (Fig. 3b). The mineralogical composition of the ores is quite complex and slightly changes in each of the studied mine sites. Sulfides such as galena, sphalerite and minor chalcopyrite  $\pm$  tetrahedrite are abundant; on the other hand Ni-Co arsenides and sulfarsenides show the greatest mineralogical and compositional variability in the ore, mainly occurring as relicts scattered in the sulfides or in the siderite-quartz gangue. The investigations mainly focused on the *ore shoots* of the Pira Inferida, Acqua Is Prunas and Sa Menga abandoned mines (Fig. 1c).



Fig. 2 - Some examples of still accessible abandoned mineworks. a) S. Barbara mineworks; b) Pira Inferida mineworks. In both situations it is possible to observe the exploitation voids of the vein.



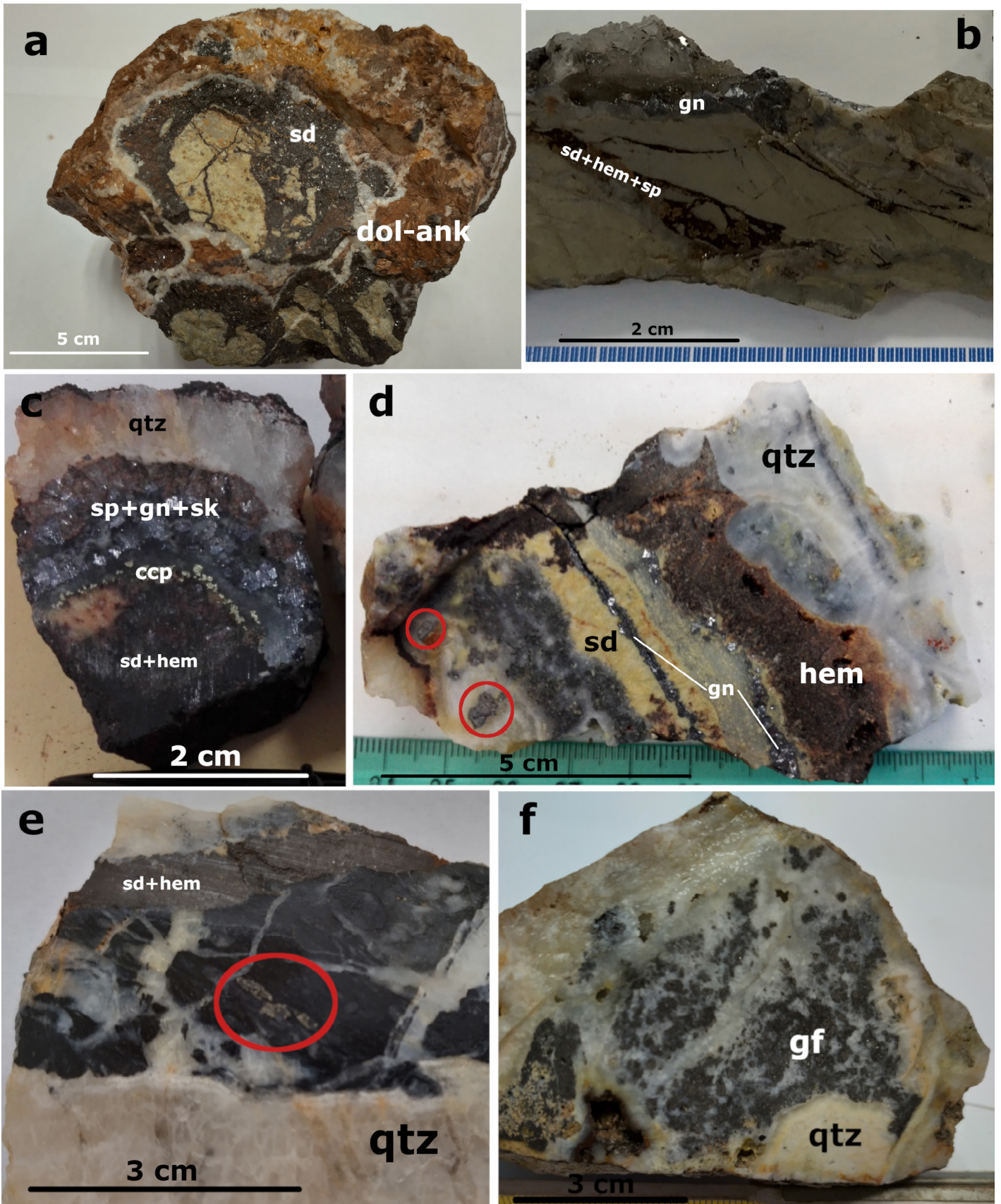


Fig. 3 - a) cockade texture from the S. Barbara mineworks: silicified wallrock fragments rimmed by siderite and quartz followed by dolomite-ankerite (dol-ank); b) bleached and silicified Silurian black shale from Sa Menga mine: foliation is partly filled by sulfides in siderite gangue; c) cockade from Sa Menga mineworks: alternating layers of quartz (qtz), sphalerite (sp) + galena (gn) enveloping some skutterudite (sk) aggregates, chalcopyrite (ccp) and siderite (partly altered in hemathite); d) banded texture from Pira Inferida mineworks consisting of alternate layers of siderite and galena, brecciated and cemented by late quartz: circled in red, Ni-Co arsenides/sulfarsenides aggregates; e) breccia from Acqua Is Prunas mine: black shales fragments in quartz gangue crosscut by a siderite (partly altered in hemathite) veinlet; circled in red, an aggregate of framboidal pyrite; f) disseminated texture from Acqua Is Prunas mine, consisting of gersdorffite (gf) in quartz gangue.



*Pira Inferida mine*

At Pira Inferida, the five-elements veins attain up to 2 m in thickness, cropping out discontinuously for over 1,5 km. Host rocks belong to the Upper Ordovician (Hirnantian) Rio San Marco Formation (Cuccuruneddu Member), which consists of rhythmic alternations of HCS sandstone layers separated by shales (Loi et al., 2023). Three main ore shoots are known in this area: namely the Speranza, the Pira Inferida and the Santa Barbara mineworks (Fig. 1c); the last two are of particular interest for this study, as they match intersection zones with granite-related, high-temperature systems: 1) the ENE-WSW directed and N dipping quartz-wolframite (Bi-Te-Au) vein swarm (Nuraghe Togoro veins: Deidda et al., 2021); 2) quartz-arsenopyrite-pyrite veins. Moreover, old

mine reports pointed out that during the ore exploitation in Pira Inferida mineworks some quartz-arsenopyrite-pyrite veins were encountered. These veins were not found to crop out on surface during the field survey, but numerous fragments of them have been found in the waste dumps close to the mine adits. From outcrop scale to microscope observations, the five-element ore resulted by superposition of at least two different mineral associations: a late siderite and base-metal sulfides-rich association is superposed on an early quartz Ni-Co-Fe arsenides-sulfarsenides/sulfantimonides association. The ore from Santa Barbara mineworks is characterized by a Ni-Co monoarsenide-sulfarsenide assemblage: nickeline (NiAs) is abundant and very rich in native Bi/bismuthinite ( $\text{Bi}_2\text{S}_3$ ) inclusions; it is overgrown by Co-rich, Fe-bearing gersdorffite ( $(\text{Ni},\text{Co},\text{Fe})\text{AsS}$ ) (Fig. 4a, c). Conversely, in samples belonging

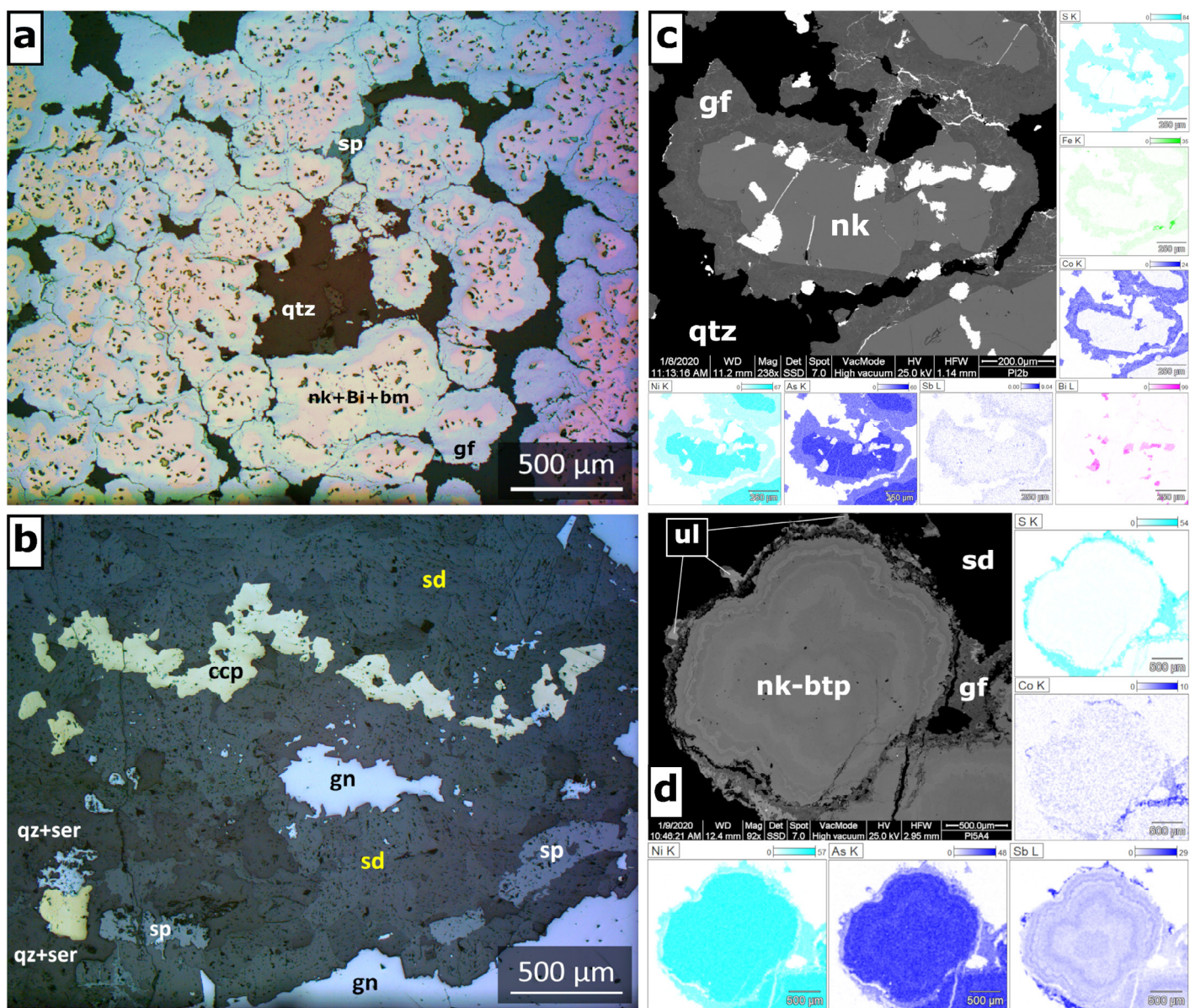


Fig. 4 - Reflected light photomicrographs, SEM backscattered images and EDS maps of samples from S. Barbara (pictures “a”, “b”, and “c”) and Pira Inferida mineworks (picture “d”). a) pink to pinkish yellow nickeline (nk) with abundant native Bi and bismuthinite (bm) inclusions, overgrown by gersdorffite (gf: white) in quartz (qtz) gangue; b) galena (gn: white), chalcopyrite (ccp: yellow) and sphalerite (sp: light grey) in siderite (sd) and quartz-sericite (qz+ser) gangue (grey); c-d) SEM backscattered images and EDS maps: c) almost pure nickeline (nk) crystal, overgrown by Fe-bearing, Co-rich gersdorffite (gf) in quartz gangue; d) nickeline-breithauptite (nk-btp) solid solution, overgrown by complex intergrowths consisting of Co-poor gersdorffite (gf) and minor ullmannite (ul) in siderite gangue (sd).



to the same vein but collected in the Pira Inferida mineworks located a little further west, far from the intersection zone with quartz-wolframite (Bi-Te-Au) veins, nickeline displays hardly any inclusion of Bi minerals (Fig. 4d), and shows a characteristic radial texture, with alternating layers rich in As or Sb (solid solution nickeline-breithauptite: Fig. 4d); it is overgrown by a complex mixture of Co-poor gersdorffite and ullmannite (NiSbS), sometimes enveloping some relicts of pure breithauptite. Di-tri-arsenides (e.g. rammelsbergite - safflorite, löllingite– (Co,Ni,Fe)As<sub>2</sub>, skutterudite – (Co, Fe, Ni)As<sub>3</sub> and their solid solutions were hardly found in the studied samples, although they are reported in the mine area. The abundant sulfide association is represented by galena with few tetrahedrite inclusions, minor low-iron sphalerite and chalcopyrite (sometimes in intergrowths with tetrahedrite) in siderite-quartz gangue; the sequence is closed by abundant quartz sometimes with little chalcopyrite disseminations, which represents the last mineralizing stage of the ore.

### Acqua Is Prunas mine

In this mine, the five-element veins are hosted in the late Ordovician (Katian) metasandstones of Domusnovas Fm. (Loi et al., 2023) and in Silurian (Llandovery) carbonaceous black shales of Genna Muxerru Fm. (Gnoli et al., 1990). The orebodies consist of two parallel E-W directed veins which run for a length of about 1 km along a verticalized and tectonized contact between Ordovician and Silurian units, as black shale fragments (sometimes containing framboidal pyrite aggregates) are commonly found in the veins (Fig. 3e), also where the wallrocks are the Ordovician metasandstones. In the western sector of the mine area (Conca Planuceddu), the five-element system clearly intersects a NE/SW and SE dipping quartz-arsenopyrite vein system. Distinctive features of the Acqua Is Prunas ore are the relative scarcity of sulfides and siderite, while, in the arsenide ore, nickeline is less abundant and Ni-Co di-arsenides (Fig. 5a) such as safflorite-löllingite (CoAs<sub>2</sub>-

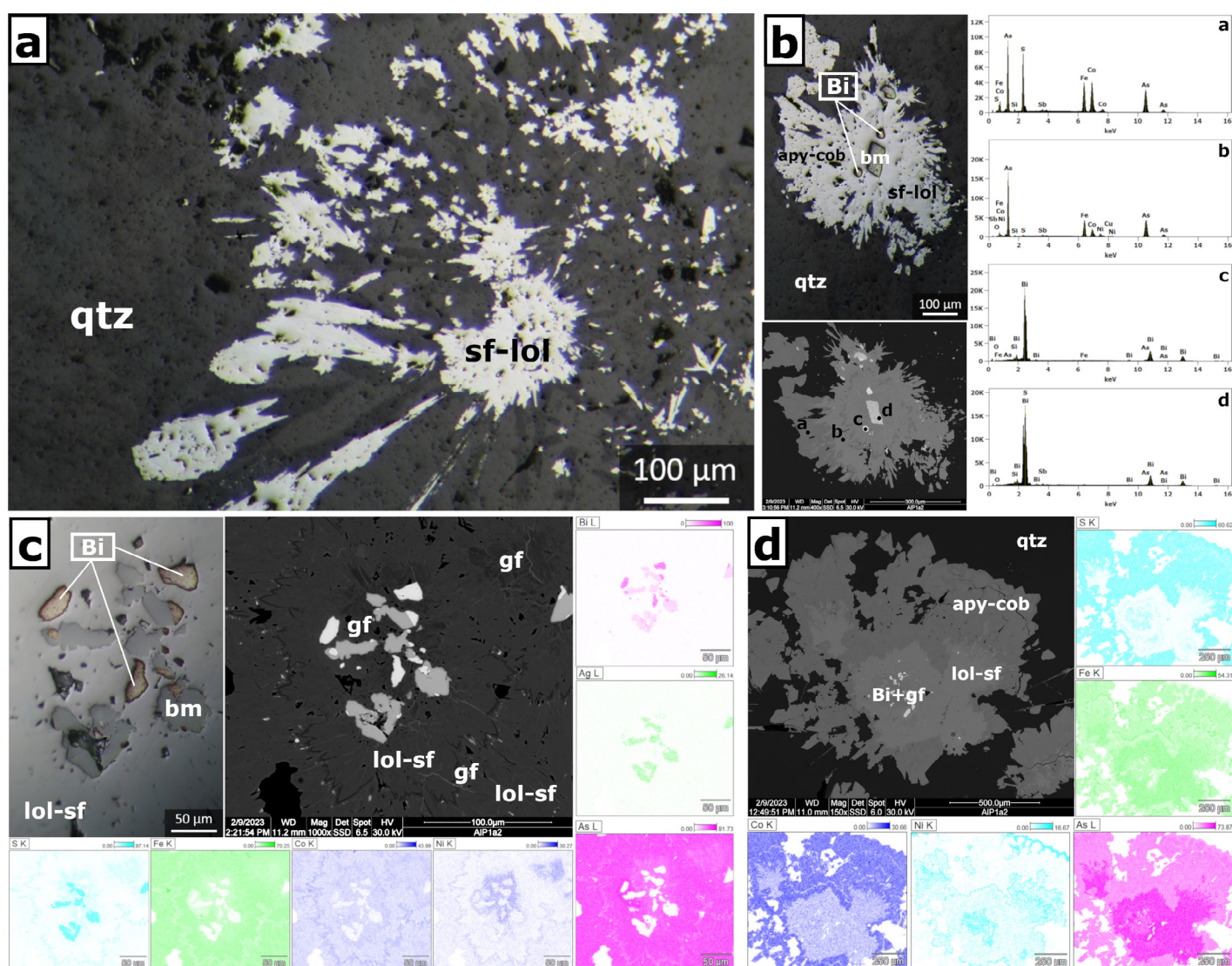


Fig. 5 - Photomicrographs, SEM-EDS images and maps of samples from Acqua Is Prunas mine. a) reflected light photomicrograph showing star-shaped aggregates of safflorite-löllingite (sf-lol) in quartz (qtz) gangue; b) photomicrograph and SEM-EDS spot analysis of a safflorite-löllingite (sf-lol) aggregate (point b) containing some native Bi (point c) and bismuthinite (bm) inclusions (point d), overgrown by a solid solution cobaltite-arsenopyrite (cob-apy) in quartz (qtz) gangue; c) native Bi and Ag-bearing bismuthinite inclusions overgrown by alternating gersdorffite (gf) and löllingite-safflorite (lol-sf) layers; d) native Bi droplets, overgrown by alternating gersdorffite (gf), löllingite-safflorite (lol-sf) and arsenopyrite-cobaltite (apy-cob) solid solutions in quartz gangue.

FeAs<sub>2</sub>) solid solutions rimmed by various Ni-Co-Fe sulfarsenides prevail (Fig. 5b, d), scattered in abundant quartz which represents the main filling of the veins. Solid solutions between cobaltite and arsenopyrite (possibly glaucodot (Co<sub>0.50</sub>Fe<sub>0.50</sub>)AsS or alloclasite Co<sub>1-x</sub>Fe<sub>x</sub>AsS) are quite common (Fig. 5b, d). Abundant native Bi and Ag-bearing bismuthinite inclusions (Fig. 5c) in the arsenides occur in the samples from the eastern sector of the mine, possibly related to a further intersection with the same quartz-wolframite (Bi-Te-Au) veins of Nuraghe Togoro system, cropping out in the neighboring valley of “Fosso Is Bandios” (Lauro, 1943).

**Sa Menga mine**

Silurian black shales are also the main host rock of the Sa Menga veins, which detach from the main E-W attitude of the vein field and run instead in a NW-SE direction. These veins distinctly crosscut the NE-SW and N dipping quartz-arsenopyrite veins of the Punta S. Vittoria granite-related system. Also in this case, the Sa Menga ore shoot displays peculiar characters: sulfides in siderite gangue are very abundant, mostly represented by galena, low-iron sphalerite, and chalcopyrite-tetrahedrite intergrowths (Fig. 6); Bi minerals are rare, and nickeline and di-arsenides are subordinate while skutterudite and gersdorffite (the latter sometimes overgrowing complex cobaltite-arsenopyrite or safflorite-löllingite solid solutions) prevail, notably as fragments included in sulfides (Fig. 6 a, e) and cemented by late-stage quartz. The observed

sequence of mineralization ends with small veinlets of pyrite and calcite which crosscut all previous minerals.

Despite of the mineralogical differences between the various ore shoots of the vein field, a general paragenetic sequence with three main mineralizing stages may be still schematized (Tab. 1): 1) early stage: native Bi and Ni-Co-Fe minerals (mono-arsenides/antimonides; di-tri-arsenides, sulfarsenides/sulfantimonides) in quartz gangue; 2) middle stage (that we may call the “Montevecchio event”): base-metal sulfides and Ag-sulfosalts in siderite gangue; 3) late stage: abundant quartz, followed by pyrite and calcite that seal the fractures.

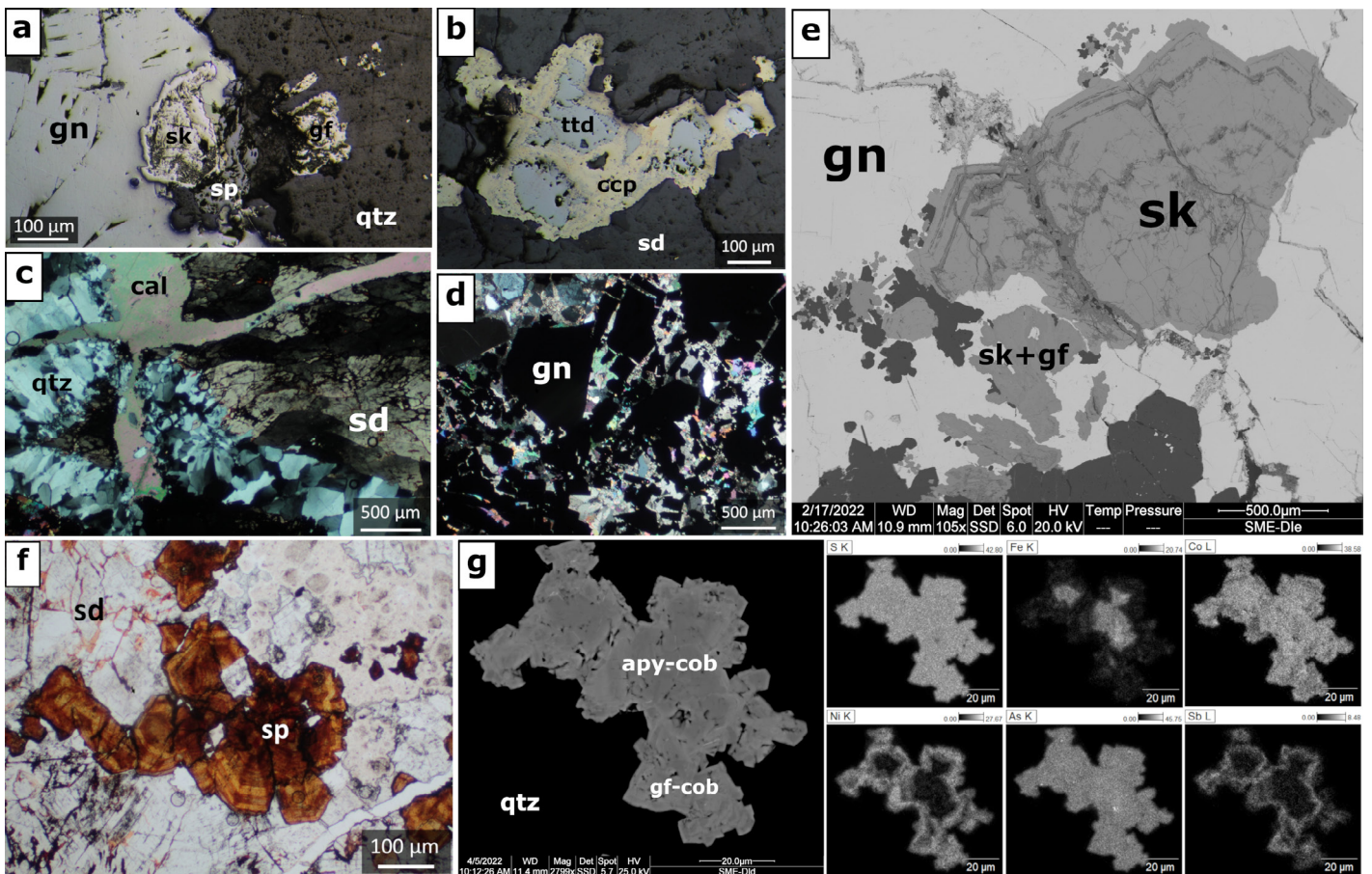
**DISCUSSION**

Field relationships, supported by optical microscopy and SEM-EDS analyses suggest that intersections between different hydrothermal systems and host rock composition played an important role in ore shoots precipitation in the five-elements vein system of the South Arburèse district. At Sa Menga and Acqua Is Prunas mines, where the five-element veins crosscut the quartz-arsenopyrite vein systems related to Mt. Linas pluton, As-rich phases like Ni-Co-Fe di-tri-arsenides (safflorite-löllingite, skutterudite) prevail over Ni-Co-Fe sulfarsenides; the same happens at the western sector of the Pira Inferida mine, where the five-element veins crosscut some quartz-arsenopyrite veins. Conversely, at the Santa Barbara mineworks in

**Table 1 - Overall paragenetic sequence of mineralization for the five-elements veins of the Southern Arburèse**

| Stages          |                                      | Native Elements                                  | Arsenides-Sulpharsenides | Sulphides and sulphosalts | Late stage |
|-----------------|--------------------------------------|--|--------------------------|---------------------------|------------|
| Ore minerals    | Native Bi                            | Bi   | ██████████               |                           |            |
|                 | Nickeline                            | NiAs;  | ██████████               |                           |            |
|                 | Breithauptite                        | NiSb;  | ██████████               |                           |            |
|                 | Safflorite-löllingite                | (Co,Fe)As <sub>2</sub>                           | ██████████               |                           |            |
|                 | Skutterudite                         | (Co,Ni)As <sub>3-x</sub>                         | ██████████               |                           |            |
|                 | Gersdorffite-cobaltite <sub>ss</sub> | (Ni,Co)AsS                                       | ██████████               |                           |            |
|                 | Ullmannite                           | NiSbS  | ██████████               |                           |            |
|                 | Arsenopyrite-Cobaltite <sub>ss</sub> | (Fe,Co)AsS                                       | ██████████               |                           |            |
|                 | Bismuthinite                         | Bi <sub>2</sub> S <sub>3</sub>                   |                          | ██████████                |            |
|                 | Tetrahedrite                         | Cu <sub>12</sub> Sb <sub>4</sub> S <sub>13</sub> |                          | ██████████                |            |
|                 | Sphalerite                           | ZnS  |                          | ██████████                |            |
|                 | Chalcopyrite                         | CuFeS <sub>2</sub>                               |                          | ██████████                | ██████████ |
|                 | Galena                               | PbS  |                          | ██████████                |            |
|                 | Pyrite/Marcasite                     | FeS <sub>2</sub>                                 |                          | ██████████                | ██████████ |
| Gangue minerals | Quartz                               | SiO <sub>2</sub>                                 | ██████████               | ██████████                | ██████████ |
|                 | Siderite                             | FeCO <sub>3</sub>                                |                          | ██████████                |            |
|                 | Calcite                              | CaCO <sub>3</sub>                                |                          |                           | ██████████ |





**Fig. 6** - Photomicrographs (reflected light: pictures “a-b”; transmitted light: pictures “c-d-f”), SEM backscattered images and EDS maps (pictures “e-g”) of samples from Sa Menga mine. a) skutterudite (sk) and gersdorffite (gf) relics (bright white) encapsulated by galena (gn: white), sphalerite (sp: light grey) quartz (qtz: grey); b) tetrahedrite (light grey), overgrown by chalcocyanite (yellow) in siderite gangue (gn); c) crosscutting relationships between different gangue minerals: siderite (sd), brecciated and cemented by late-stage quartz, crosscut by calcite veinlets; d) galena (gn) brecciated and cemented by late calcite; e) skutterudite relics (sk), partly rimmed by a thin layer of gersdorffite (gf) enveloped by galena (gn); f) zoned, brown sphalerite aggregate (sp) in siderite (sd) gangue; g) intergrowth arsenopyrite-cobaltite (apy-cob) solid solution (core: possibly glaucodot or alloclasite) overgrown by gersdorffite-cobaltite (gf-cob) slightly enriched in antimony.

the eastern sector of the same mine, in the intersection zone with the As-poor, Bi-rich granite-related quartz-wolframite veins of the Togoro vein system, monoarsenides (nickeline) and phases less rich in As such as gersdorffite and ullmannite are apparently favored, and the ore results strongly enriched in Bi minerals. A similar situation occurs in the eastern sector of the Acqua Is Prunas mine where abundant Bi phases are enclosed in the Ni-Co di-arsenides. Conversely, the quartz-arsenopyrite veins of Punta S. Vittoria and Conca Planoceddu show only minor bismuthinite inclusions, so the resulting ore shoots in the Sa Menga and the western part of Acqua Is Prunas mine areas contain little or even no bismuth minerals. Historical reports from some of the other old mines in the district (e.g., Perd’e’Fogu and Perda S’Oliu mines) confirm these observations, as they describe strong enrichment of the ores in intersection zones with granite-related quartz-arsenopyrite veins or even with sulfide mineralized skarns.

If the presence of the previous granite-related mineralization may represent an important control for mineral assemblage composition in the ore shoots, host rock chemistry might have played a very important role as redox conditioner (Markl et al., 2016; Burisch et al., 2017). In this way, the Silurian black shales

of the Arburèse district, particularly rich in reducing agents like carbonaceous matter and pyrite must be regarded as favorable environments for selective mineral precipitation from mineralizing fluids in ore shoots. The primary source of nickel and cobalt is still undefined, but it is reasonable that leaching of mafic facies of the Arbus pluton (Moroni et al., 2019b) or, possibly, of the Silurian black shales (Venerandi, 2007), may have played a role.

The five-element veins of the Arburèse district show many features in common with similar occurrences in other districts of Central-Western Europe (e.g., Southern Germany: Burisch et al., 2017, 2021). Similar mineral assemblages, origin from comparable low-temperature and highly-saline fluids and a probable post-Variscan age indicated by geological constraints (Deidda et al., 2021), suggest that they are probably related to the same large-scale geological frame (breakup of the supercontinent Pangea: Burisch et al., 2022). However, some non-negligible differences with the better known occurrences of Central Europe may be highlighted. In particular, no native Ag of primary origin has been observed, unlike in other important European five-element ores as: Annaberg-Buchholz, Erzgebirge (Guilcher et al., 2021); Odenwald, SW Germany (Burisch et al., 2017); Wittichen, Schwarzwald,



SW Germany (Staupe et al., 2012); Jáchymov, Krusne-hory, (Erzgebirge), Czech Republic, (Ondrus et al., 2003). In the South Arburèse district native Ag is reported by the ancient authors only (Traverso, 1909; Pelloux, 1921; Piepoli, 1934; Borghesan, 1945), and it was found in the shallower and oxidized parts of the veins: it must be considered as a secondary phase coming from alteration of Ag-rich primary minerals like tetrahedrite, and it has never directly observed in association with native bismuth or the Ni-Co arsenides. Thus, in the Arburèse district, the Ag-Bi-As-rich *native element stage* of mineralization established for five-element ores by Markl et al. (2016) and Burisch et al. (2017), seems to be limited to bismuth, while silver appears in the late paragenetic stages, mainly hosted by tetrahedrite. More remarkably, in the paragenetic sequence of the studied five-element veins there is no evidence of continuity between the native element – Ni-Co arsenides stage and the subsequent sulfide stage: Ni-Co minerals always occur as fragments, included in Pb-Zn sulfides and in the related gangue minerals, suggesting that Ni-Co phases and base metal sulfides represent two different hydrothermal pulses. This idea may be also supported by paragenetic evidence, as the local occurrence in the Ni-Co stage of aggregates consisting of solid solutions of cobaltite-arsenopyrite (possibly glaucodot or alloclasite), arsenopyrite and safflorite-löllingite, suggesting definitely higher temperatures of deposition (Fanlo et al., 2004, and references therein) than those established by the base-metal sulfide stage (<100°C: Moroni et al., 2019b). Another important evidence reinforcing this assumption is the occurrence of abundant native Bi droplets enclosed in the Ni-Co arsenides/sulfarsenides at the intersection zones. In fact, the temperature of fluids must have been greater than 270°C (Ramdohr, 1969; Ciobanu et al., 2005) to allow the remobilization of bismuth from quartz-wolframite veins, where it mostly occurs as complex mineral phases such as Bi-tellurides and sulfotellurides (Deidda et al., 2021).

## CONCLUSIONS

Overall observations (field surveys, microscopy studies and SEM-EDS analyses) carried out on the ores of five-element vein system of the Southern Arburèse district show that intersections with other hydrothermal mineral systems and host rock chemistry may be important controls in ore shoots deposition. These indications can be useful guidelines for further mineral explorations both in the studied area and in similar contexts at a wider scale. The five-elements vein system of the Southern Arburèse district until now has only been explored in its shallower parts, and it is possible that other ore shoots have yet to be discovered at depth.

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