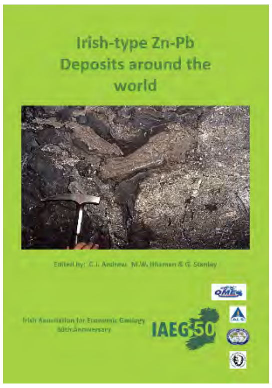

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Base-metal sulphides and barite in the Palaeozoic of SW Sardinia: from tectonically deformed SedEx and Irish-type deposits to post-Variscan hydrothermal karst and vein ores.

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Base-metal sulphides and barite in the Palaeozoic of SW Sardinia: from tectonically deformed SedEx and Irish-type deposits to post-Variscan hydrothermal karst and vein ores

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Abstract Stratabound Zn-Pb-Ba orebodies are hosted in the Lower Cambrian carbonates and Ordovician lithologies of SW Sardinia (Italy). Two groups of genetically distinct ore types are known in the Cambrian: (1) syngenetic(?)-early diagenetic massive sulphides consisting of pyrite>>sphalerite>>galena and barite layers in tidal dolomites, interpreted so far as SedEx-type ores; (2) late-diagenetic replacement and breccia-hosted ore bodies in shallow water limestone with a higher Pb/Zn ratio and a sphalerite>galena>>pyrite association, which have been classically interpreted as MVT ores, but could be easily classified as Irish-type deposits. At the regional scale, most economically significant deposits in SW Sardinia were primarily located along long-living synsedimentary faults. Ordovician stratabound ores, consisting of barite>galena>>sphalerite, were economically less significant than the Cambrian mineralizations. The SW Sardinia ores, together with their host rocks, have been affected by Variscan tectonics, which produced two folding phases, characterized by sub-vertical axial planes-oriented E-W and N-S, and associated inverse faults. A pervasive cleavage, locally overprinting the sedimentary bedding, associated with the N-S-striking folds, strongly deformed the limestone-hosted mineralization, locally increasing the original thickness of the orebodies.

During the emplacement of the Variscan granites, contact metamorphism and metasomatism modified both the original mineralogy and the chemical composition of the stratabound ores (e.g., adding Cu, F, As). The late-Variscan deposits consist of skarn bodies around the intrusions or along fault zones, and of high-temperature (HT) vein systems developed along regional tectonic lineaments. From Permian onwards, SW Sardinia experienced several hydrothermal phases, comparable with those occurring in other European terranes. The associated ores consist of low-temperature (LT) veins and palaeokarst breccia fillings in the Cambrian limestone, containing mainly Ag-galena and barite mineralization.

Keywords: Sardinia, Cambro-Ordovician, Variscan tectonic deformation, hybrid SedEx-MVT deposits.

Introduction

In the first decades of the 20th century, the Iglesiente-Sulcis district in SW Sardinia (Italy) was one of the most important mining areas for base metal ores in Europe, with more than 50 active mines of lead, zinc, and copper with local barite and fluorite (Fig.1). Most base-metal ores are hosted in Lower Palaeozoic carbonate rocks, in the form of stratabound orebodies and show tectonic deformation and weak metamorphism. The pre-Variscan lead-zinc and barite ores have been broadly divided into two subtypes: sedimentary exhalative (SedEx) and Mississippi Valley-type (MVT) deposits (Boni *et al.*, 1996). It is widely accepted that the distinction between the world-known SedEx and MVT deposits can be quite subjective, because some SedEx ores have also replaced their carbonate host, whereas a number of MVT deposits display laminated ore textures and were formed in an early-diagenetic environment (Leach *et al*., 2005). The classification of the Sardinia subtypes is related to two main features: 1) the SedEx deposits have marked synsedimentary or early diagenetic features, 2) the MVT are mostly hosted in limestone breccias as discordant bodies. The Irish-type Zn-Pb deposits are generally stratabound and structurally controlled and represent a distinctive

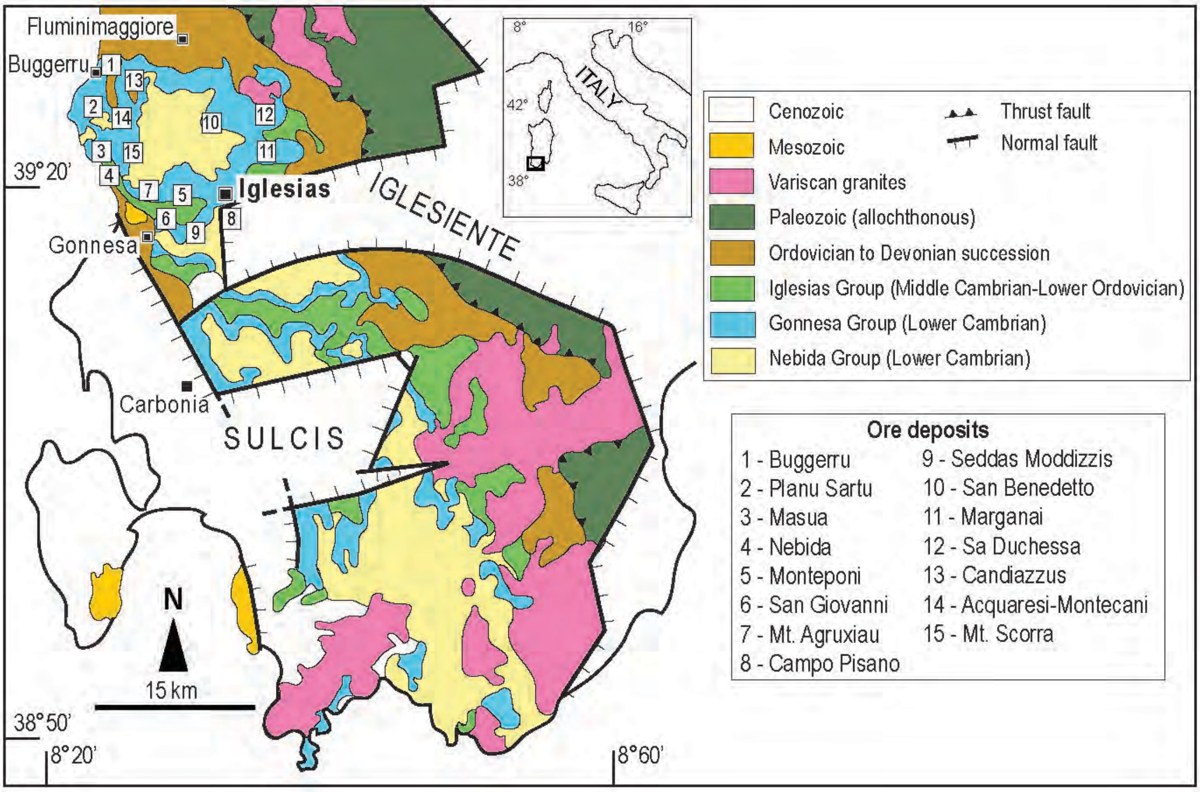

Figure 1: *Geologic sketch map of southwest Sardinia with location of the Cambrian deposits; the Candiazzus, San Benedetto, Seddas Moddizzis, and Campo Pisano orebodies are considered to be SedEx-type sulphides, whereas Buggerru, Planu Sartu, Masua, Monteponi, San Giovanni, Mount Agruxiau, Marganai, Sa Duchessa, Mount Scorra, Montecani, and Acquaresi ores are MVT-type sulphides and barite (modified from Bechstädt & Boni, 1994). The Ordovician ores are not shown in the figure.*

sub-class in the family of the carbonate-hosted zinc-lead ores, having geological features and ore formation processes models that are hybrids between SedEx and MVT deposits (Wilkinson & Hitzman, 2014; Ashton *et al*., 2015; Yesares *et al*., 2019).

In this text we provide a review on the state of knowledge of the mineralization in SW Sardinia, which, unfortunately, after the closure of the mines in the last decades of the 20th century, has not progressed further. We also intend to discuss if, considering their peculiar characteristics, at least part of the Zn-Pb ores hosted in the Palaeozoic of Sardinia could be considered interesting examples of Irish-type deposits. The text also mentions the late- and post-Variscan lead-silver hydrothermal mineralization in veins and palaeokarst, which are widespread in the Iglesiente-Sulcis district and overprint the former ores (Boni *et al*., 1996). To the already published information, we have added some preliminary mineralogical and geochemical data deriving from current research, aimed at better understanding the genesis of the stratabound ores.

Geological setting

The geology of Southwestern Sardinia is largely dominated by Cambro-Ordovician rocks of sedimentary origin (Fig. 1). The geological units in the Iglesiente-Sulcis mining district are low-grade metamorphic rocks of epizonal facies and belong to the so-called "External zones" of the Variscan orogen (Carmignani *et al*., 1994; Franceschelli *et al*., 2005). The Lower Cambrian succession is subdivided into the basal Nebida Group, which consists of 400 to 500m of siliciclastic sedimentary rocks, with carbonate intercalations toward the top, and the overlying Gonnesa Group, which consists of 300 to 600m of dolomites and limestones (Bechstädt & Boni, 1994) (Fig. 2). The development of the carbonate platform in the Cambrian follows a multi-stage evolution (Bechstädt & Boni, 1989, 1994), including the evolution from a terrigenous carbonate ramp or a rimmed shelf attached to an easterly continental area (Nebida Group) to an isolated, subsequently flooded, carbonate platform (Gonnesa Group). The carbonate sediments belonging to the Gonnesa Group were segmented: tidal dolomites of the Santa Barbara Formation (Fig. 3a), drowned lagoonal limestones of the San Giovanni Formation (Fig. 3b), and finally covered by terrigenous clastic rocks deposited in an open marine environment (Iglesias Group) (Fig. 4).

The main control of the evolution of the Cambrian platform was a strong tensional tectonism (rifting to drifting stages, Bechstädt & Boni, 1989, 1994), mirrored by abrupt facies changes, and coupled with differences in thicknesses and an abundance of breccias at several stratigraphic levels (Fig. 3b). The limestones of the San Giovanni Formation, consisting of microsparites represent, at least partially, recrystallized peloidal mudstones to wackestones. These facies are considered to

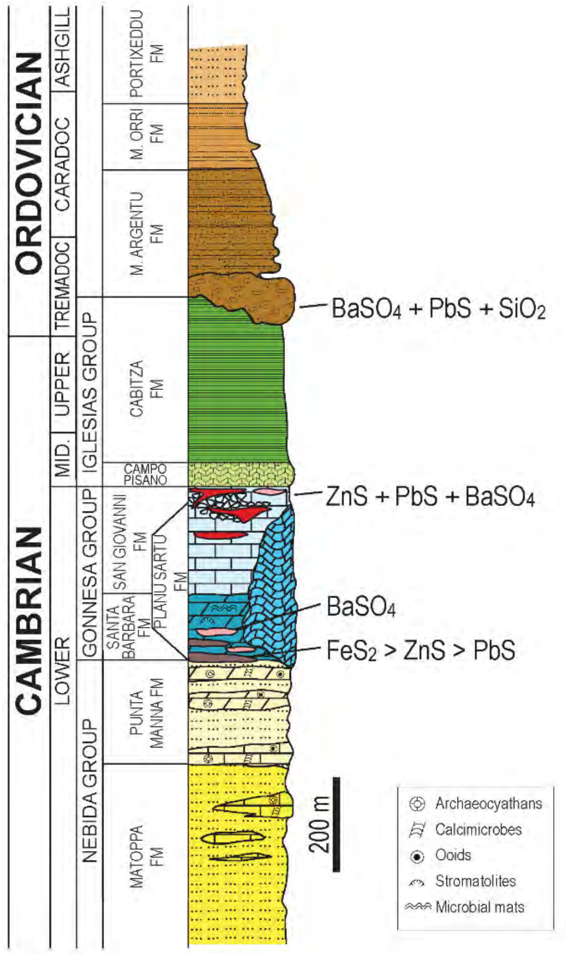

Figure 2: *Stratigraphic column of the Cambro-Ordovician lithologies in SW Sardinia with the location of the main mineralizations (modified from Bechstädt & Boni, 1994).*

be indicative of uniform and deeper low energy conditions, typical of a flooding stage. The San Giovanni Formation locally corresponds to the so-called "Ceroide" (i.e., waxy) limestone facies, which consists of a microcrystalline marble-like white limestone. Middle and Upper Cambrian-Lower Ordovician strata are represented by nodular limestones of the Campo Pisano Formation (Iglesias Group, 50–80m), and overlying slates of the Cabitza Formation (Iglesias Group, 400 m) (Fig. 2). The inset of the Iglesias Group might be related either to tectonic instability (Fig. 4) or, as it is the case of other Cambrian successions in the Mediterranean realm, it might indicate an additional eustatic control (Orgeval *et al*., 2000; Liñán *et al*., 2016).

Tensional tectonics was probably directly controlling the inset of the stratigraphically lowermost "SedEx" mineralizations, located at the base of the tidal dolomites of the Gonnesa Group and characterized by an association with synsedimentary faults (Fig. 4).

The Palaeozoic successions exposed in SW Sardinia show clear evidence of tectonic instability also during Ordovician (Cocco *et al.*, 2018, 2023), as the Cambrian to Lower Ordovician strata are sealed by an angular unconformity with Middle-Upper Ordovician sediments, characterized at the base by variably thick conglomerates (the so-called "Ordovician Puddinga") (Bechstädt & Boni, 1994) (Fig. 3c). This sedimentary relationship is considered to be indicative of a tectonically driven uplift, followed by erosion and continental reworking. This event has been called "Sardic phase" and is assumed to have been characterized by broad folds with subvertical E-W-trending axial planes (e.g. Carmignani *et al*., 1994; Puddu *et al*., 2018, 2019; Cocco *et al.*, 2023). Following the "Sardic phase", only sparse Silurian and Devonian sedimentary rocks were deposited in the Iglesiente-Sulcis area, and the whole of the Palaeozoic succession, with the exception of Upper Carboniferous and Permian, was then affected by the Variscan orogeny.

As a fragment of the Variscan orogen (Carmignani *et al.*, 1994), the Sardinian basement is subdivided into three tectono-metamorphic zones: i) a "foreland zone", outcropping in SW Sardinia, with low-grade or no metamorphism, ii) a "nappe-zone", in southeastern and central parts of Sardinia, affected by low- to medium-grade metamorphism, and iii) an "inner zone", in northern Sardinia, characterized by medium- to high-grade metamorphic signatures (Carmignani *et al.*, 1994).

The Iglesiente-Sulcis district is located in the "foreland zone" (Carmignani *et al.*, 1994; Funedda, 2009). In this area, the Variscan orogeny is characterized by two well distinct deformation phases. The first one produced E-W-trending folds with subvertical axial planes, accentuating former structures associated with the Sardic phase (Carmignani *et al.*, 1994). The second phase is characterized by W-verging thrusts and N-S-trending folds with subvertical axial planes and by a penetrative N-S-trending (axial plane) cleavage (Carmignani *et al.*, 1994). The overprinting of the two-fold systems, both characterized by subvertical axial planes, perpendicular one to another, produced a complex deformation scheme of the sedimentary successions, which follows the type 1 "dome-and-basin" interference pattern of Ramsay (1967).

At the end of the main Variscan orogeny, the deformed basement was intruded by post-collisional granites. The intrusions have recently been placed into two magmatic peaks that resulted in the emplacement of the Sardinian batholith at 305 and 290 Ma (Conte *et al*., 2017). Within the contact aureoles, the carbonate rocks were recrystallized and replaced by a calcic skarn-type assemblage including wollastonite, garnets, hedenbergite, tremolite, diopside and chlorite (Aponte *et al.*, 1988). Variscan tectonics and magmatism were followed by a long continental period, with associated erosion and deep karstification of the Cambrian carbonates. Upper Carboniferous (Westphalian-Autunian) sparse lacustrine deposits (San Giorgio Fm, Barca & Costamagna, 2003a), as well as Permian volcano-sedimentary rocks (Barca & Costamagna, 2006) locally occur in the district.

Triassic sediments are rare (Cocozza & Gandin, 1976; Barca

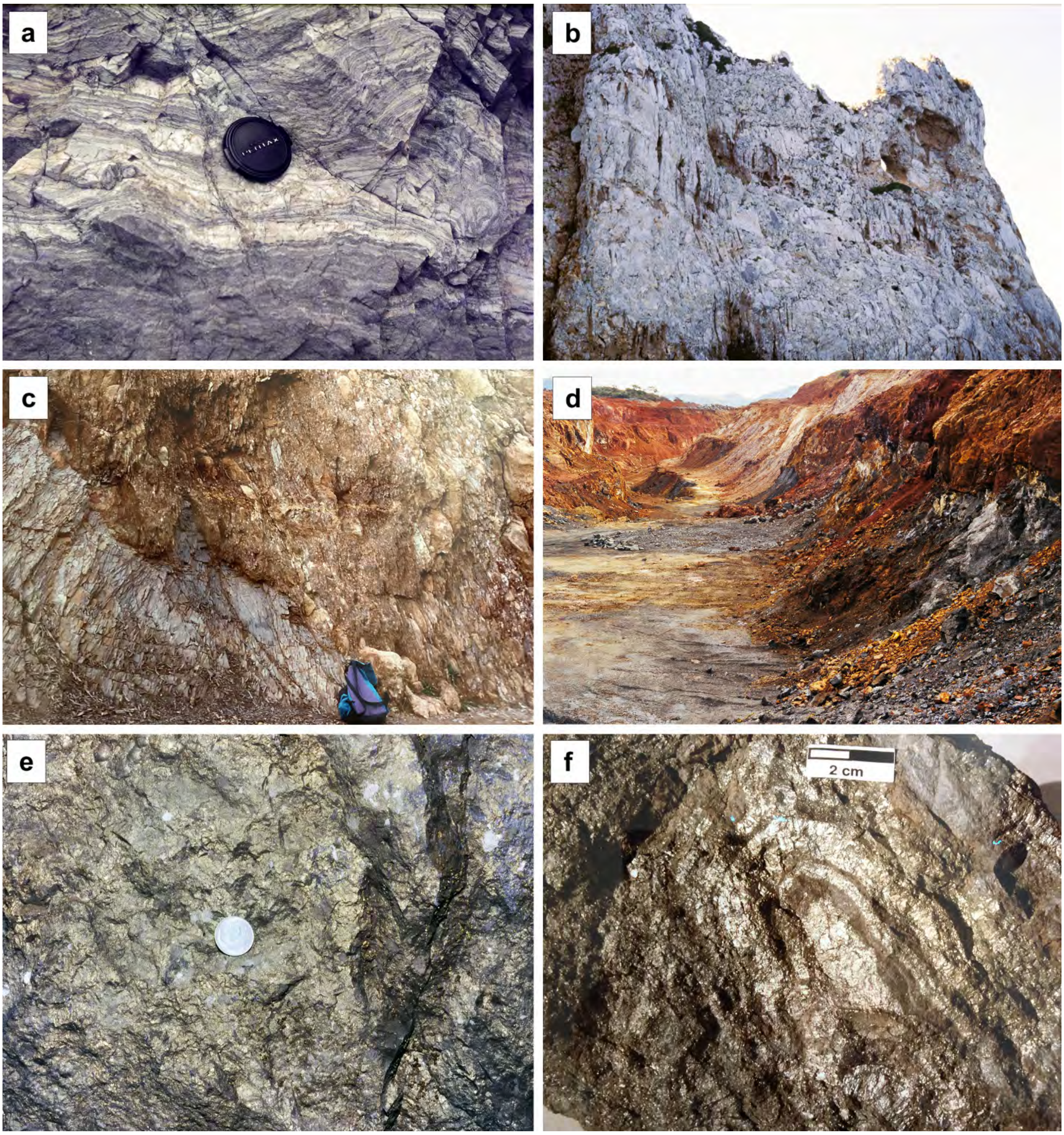

Figure 3: a). *Tidal dolomites, Santa Barbara Fm, Lower Cambrian (Iglesias Valley);* ***b)***. *Megabreccia in Ceroide limestone, San Giovanni Fm, Lower Cambrian (Buggerru);* ***c)***. *"Puddinga" at the unconformity between Cambrian slates and Ordovician conglomerate, Lower Ordovician (Nebida);* ***d)***. *Iron gossan in the old Genna Luas quarry (Iglesias);* ***e)***. *Massive sulphides (pyrite>>sphalerite) in the Campo Pisano mine (Iglesias);* ***f)***. *Concretion of alternating pyrite and sphalerite from the Campo Pisano mine (Iglesias).*

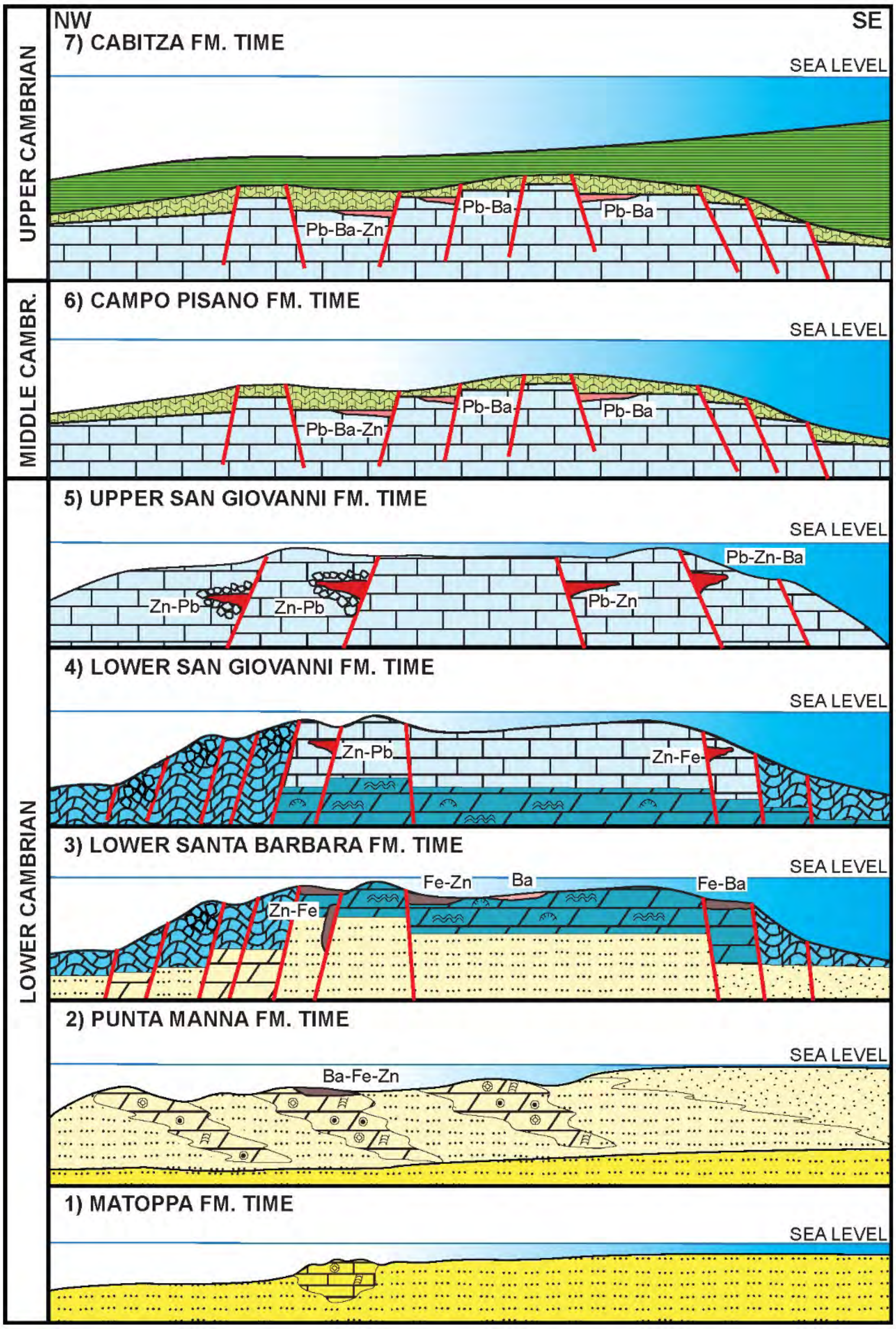

Figure 4: *Palaeogeographic cross-section from Nebidan to Cabitzan time, showing the main stages of platform evolution: (1) terrigenous-carbonate homoclinal ramp with algal-archaeocyathan mounds; (2) carbonate-terrigenous ramp or rimmed shelf with an ooid-shoal complex prograding westwards; (3) isolated platform aggraded to sea level: on the western and eastern border of the platform, slumpings and debris-flow breccias occur; (4) isolated, flooded platform; (5) isolated platform with raised margins and deep interior; (6) drowning and segmentation of the platform: small horst and graben development with deposition of nodular limestone; (7) siliciclastic deposits covers the former platform. Mineralization episodes are associated with the beginning of stage 3; ore deposits (MVT-Irish type) are also located in the lithologies deposited in stage 4 and 5, even if the timing of this mineralization might be well after the deposition of the host rock (modified from Bechstädt & Boni, 1994).*

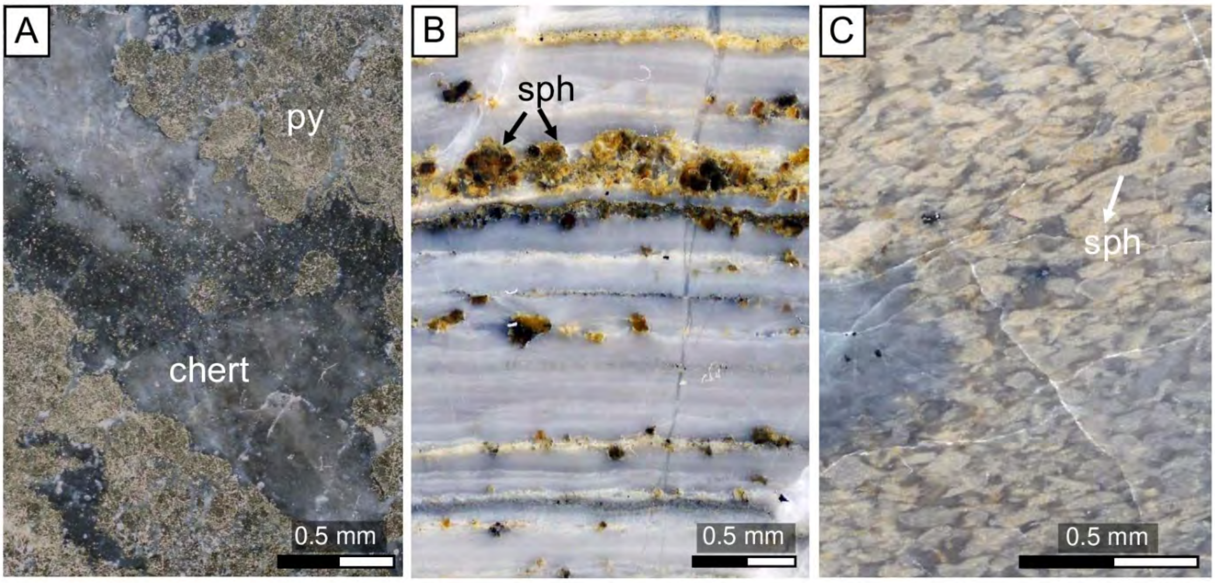

Figure 5: *Selected areas from polished samples from different Cambrian mineralized zones.* ***A****). Massive pyrite in chert (Genna Luas mine);* ***B****). Reddish sphalerite and pyrite concretions in "Ceroide" limestone; the layering is tectonic (Masua mine Cantiere Marx);* ***C****). Micro-peloidal, deformed "Yellow sphalerite" in "Ceroide" limestone (Massa Pozzo 3 San Giovanni mine). (sph) sphalerite, (py) pyrite.*

& Costamagna, 2003b), as well as sporadic Jurassic and Cretaceous sediments outcropping along the western coast. Undated sedimentary units (Permo-Triassic to Quaternary?) are also present in the palaeokarstic network of cavities throughout the Cambrian carbonates in the whole Iglesiente-Sulcis region.

Stratabound Ores

Cambrian Ores

The pre-Variscan, stratiform and/or stratabound orebodies are hosted in the Lower Cambrian carbonate rocks and in the basal Ordovician lithologies (Fig. 2), both affected by Variscan tectonics. Two groups of genetically distinct ore types are known in the Cambrian. The first group is represented by syngenetic(?)-early diagenetic massive sulphides (e.g.: Genna Luas, Campo Pisano, San Benedetto, Candiazzus), consisting of pyrite>>sphalerite>>galena together with barite layers in tidal dolomites, which are interpreted as SedEx-type ores (Bechstädt & Boni, 1994; Boni *et al.*, 1996) (Fig. 1). The second group of ores, having higher Pb/Zn ratio and much less pyrite (e.g.: Monteponi, San Giovanni, Nebida, Masua, Planu Sartu etc.), occur as late-diagenetic replacement bodies and void-filling breccia cements in the Gonnesa limestone (Fig. 1). The latter have been interpreted as MVT ores (Bechstädt & Boni 1994; Boni *et al.*, 1996), but could easily be classified as Irish-type deposits.

The SedEx-type deposits occur in the Cambrian upper Punta Manna to lower Santa Barbara Formations (Fig. 2) and formed during the tensional tectonic event that caused the isolation of the carbonate platform from the continent (Fig. 4) and the onset of local basin development. (Figs. 3d to 3f). The ores consist of stratiform massive sulphide bodies (average grade of 8 wt.% Zn), which laterally grade into barite horizons). In the western Iglesiente area sulphides are more common than barite, while in the more southern Sulcis and eastern Iglesiente Ba(Sr)-sulphates are dominant. Barite occurs as thin layers (from few cm to a maximum of 2m thick), interbedded with dolomite and traces of pyrite.

In the massive sulphide ores, botryoidal melnikovite-pyrite (Kucha & Viaene, 1992) and microcrystalline dark sphalerite is more abundant than galena. The orebodies can reach several meters in thickness, as for example in the Genna Luas mine, where the mineralization was characterized by concretional structures and several generations of breccias. The dolomite host rock is dark, strongly silicified (Fig. 5a) and locally contains barite crystals and fragments. The sulphide layers, apparently parallel to the main Cambrian stratification, are generally disrupted by syn-diagenetic deformation, although a strong displacement by Variscan structures has also been commonly observed (Figs. 6a to 6c & 6e to 6f). Some of the main sulphide bodies are clearly discordant to stratification. Even if this discordance can be partly related to the effects of Variscan deformation, several of the economically significant deposits (e.g. the Genna Luas-Campo Pisano complex and the San Benedetto and Baueddu orebodies) are located along regional faults that were possibly active already during sedimentation. This matches with the accepted models of emplacement of this mineralization type (Bechstädt & Boni, 1994), which originates from a fluid discharge through feeder channels in shallow depositional troughs controlled by reactivated syn-sedimentary faults (Boni *et al.*, 1996). New mineralogical and geochemical data on the stratabound ores have been obtained with SEM-EDS (University of Torino, Italy) and electron probe microanalysis (EPMA) (Natural History Museum, London, UK). The most significant character of the SedEx-type deposits is the abundance of iron in form of massive pyrite, whose amount highly exceeds that of sphalerite and galena (Figs. 7a to 7f, & 7i). From the new geochemical analyses, it was possible to determine that the iron content in sphalerite is not very high (0.87 wt.% on average). Other trace elements in sphalerite are

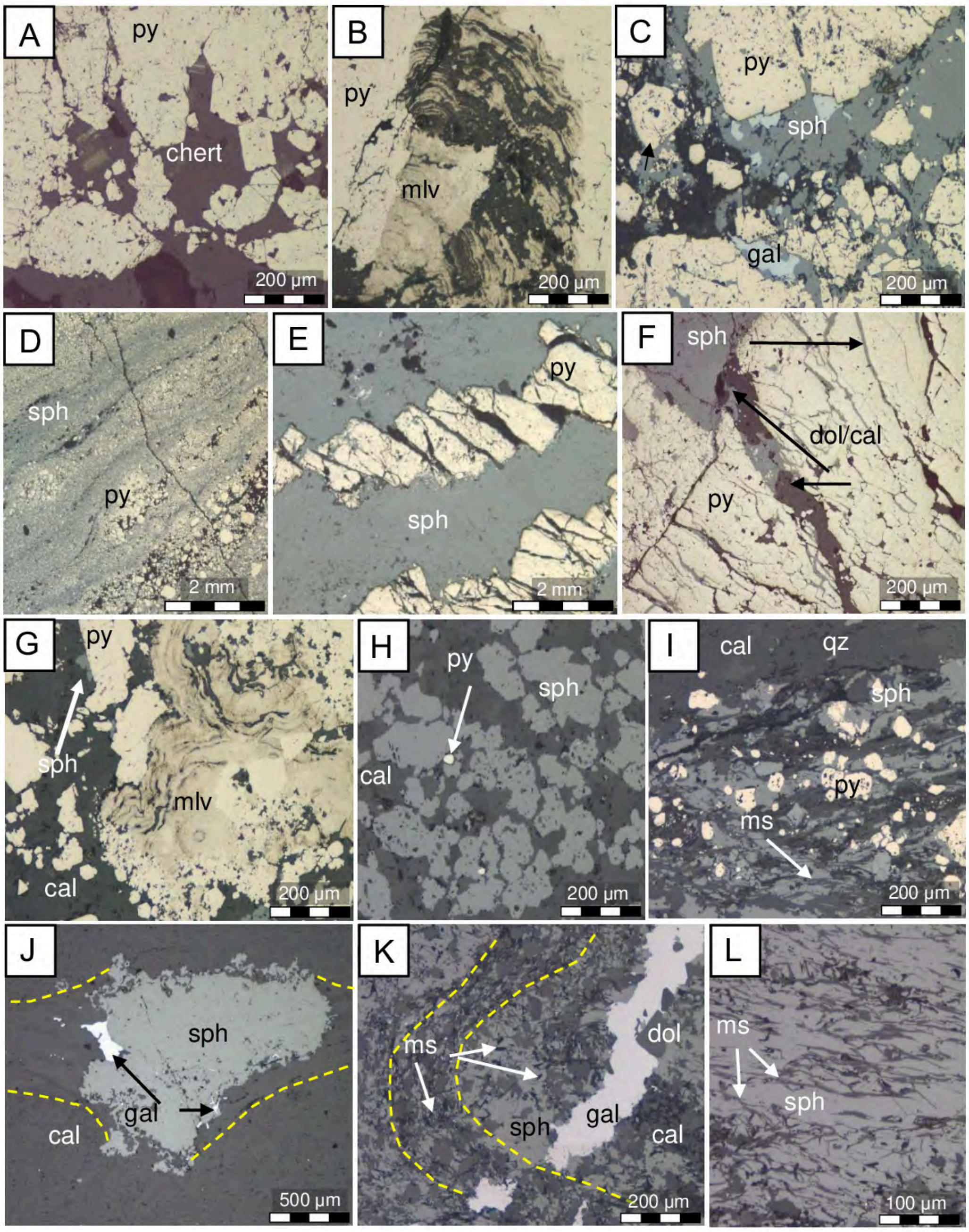

***Figure 6**: Images in reflected light microscopy of the different mineralization types. From A to F: "SedEx-type" ores. From G to I: "MVT-type" ores; **A)**. Fragmented pyrite in black chert (Genna Luas mine); **B)**. Massive pyrite with remnants of botryoidal melnikovite core (Genna Luas mine); **C)**. Pyrite and sphalerite in breccia. Minor galena associated with sphalerite. The arrow indicates a recrystallized pyrite crystal from a previous framboid (?) (Candiazzus mine); **D)**. Sedimentary structures consisting of sphalerite and pyrite in layers folded due to syndiagenetic deformation (Candiazzus mine); **E)**. Fragile deformation of a pyrite layer surrounded by sphalerite (boudinage). Sphalerite has a more ductile behavior (San Benedetto mine); **F)**. Fractured pyrite. Sphalerite and calcite/dolomite fill the fractures in pyrite (Campo Pisano mine); **G)**. Botryoidal melnikovite in the core of euhedral recristallized pyrite and sphalerite (San Giovanni mine Massa Pozzo 2); **H)**. Peloidal sphalerite in "Ceroide" limestone (San Giovanni mine Massa Pozzo 2); **I)**. Folded pirite and sphalerite layer. Quartz in the pressure shadows of pyrite, and muscovite isoriented crystals along schistosity planes (Masua mine Cantiere Albasini); **J)**. Ovoidal sphalerite nucleous in "Ceroide" limestone. Yellow lines define the trace of calcite pressure shadows (Masua mine, Cantiere Marx); **K)**. Deformed sphalerite layer cut by a galena microvein; isoriented muscovite crystals underline the ductile deformation. Dolomite crystals occur in sphalerite (Masua mine Cantiere Tetto San Marco); **L)**. Band of iso-orientated crystals of Ba-muscovite in sphalerite (Masua mine Cantiere Tetto San Marco); *(sph) sphalerite, (py) pyrite, (gal) galena (cal) calcite; mlv (melnikovite); dol (dolomite); ms (muscovite).*

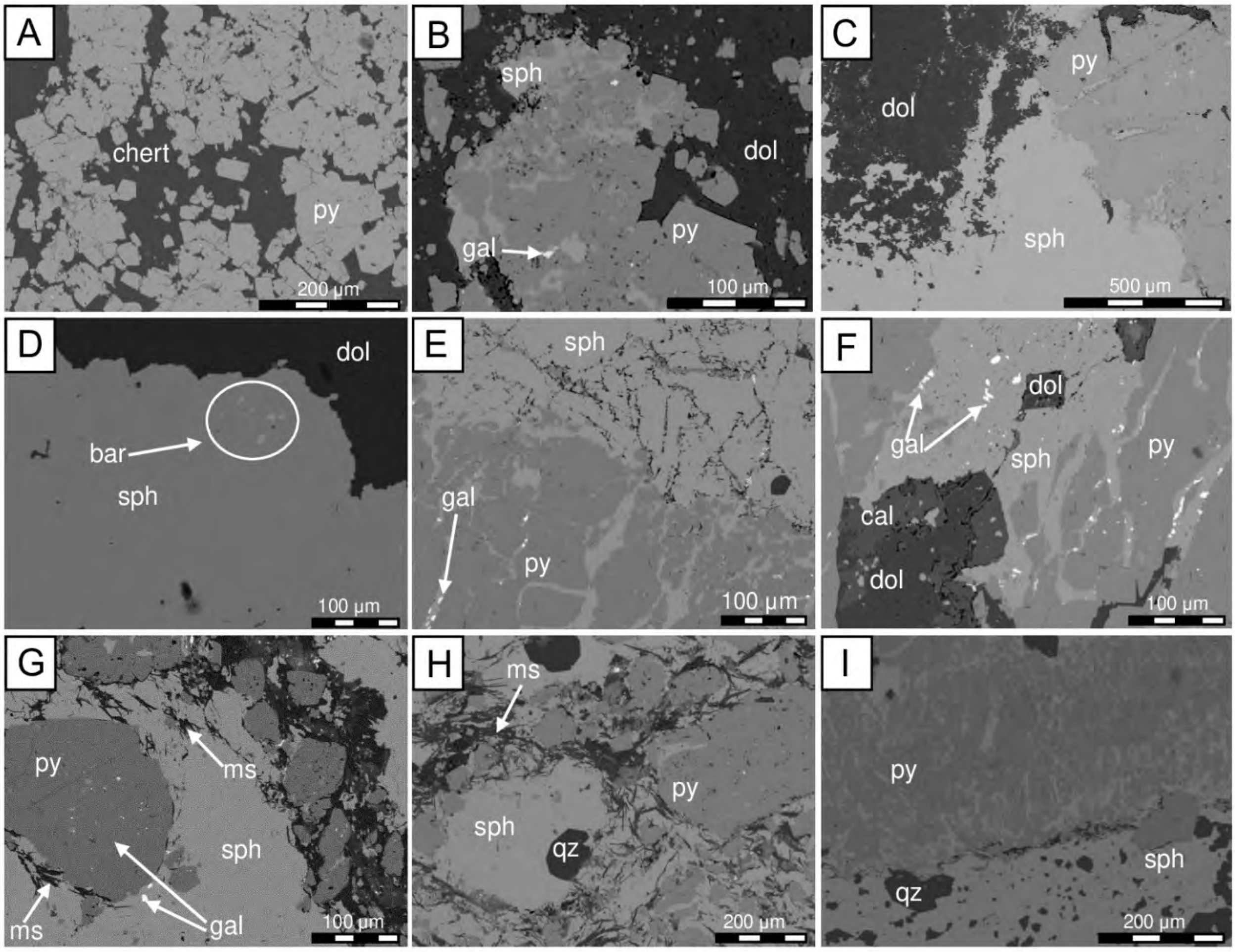

*Figure 7: BSE images of "SedEx"-type ore: **A**). Massive euhedral pyrite in chert (Genna Luas mine); **B**). Sphalerite and pyrite association. Minor galena inclusions in pyrite (Genna Luas mine); **C**). Massive pyrite and sphalerite in dolomite (Gennarutta mine); **D**). Barite inclusions in sphalerite (Gennarutta mine); **E-F**). Fractured pyrite. Sphalerite and calcite/dolomite fill the fractures of pyrite. Minor galena occurs associated with sphalerite (Campo Pisano mine); **G**). Pyrite and sphalerite in deformed ores. Schistosity is highlighted by platy crystals of Ba-bearing muscovite surrounding pyrite. Galena inclusions in pyrite and sphalerite (Candiazzus mine); **H**). Ba-bearing muscovite surrounding deformed sphalerite and fragmented pyrite (San Benedetto mine); **I**). Fragmented pyrite partially replaced by sphalerite (San Benedetto mine). (sph) sphalerite, (py) pyrite, (gal) galena, (bar) barite, (cal) calcite, (dol) dolomite, (ms) muscovite, (qz) quartz. BSE images from JEOL JSM IT300LV- 20 kev, 5 nA; 15 sec frame acquisition.*

on average: Mn (0.05wt.%), Cu (0.07wt.%), Pb (0.29wt.%), Cd (0.27wt.%), and Ge (0.06wt.%) (Table 1, WDS analysis). Trace elements detected in undifferentiated pyrite (i.e., including collophorm pyrite 1 and crystalline pyrite 2 types) are: Co (0.01wt.%), Cu (0.06wt.%), Zn (0.54wt.%), As (0.06 wt.%), Pb (0.44wt.%), and Cd (0.02wt.%) (Table 1).

The main elements contained in galena are: Fe (0.07wt.%) and Zn (0.28wt.%) (Table 1, WDS analysis). The new investigations allowed detecting also Ba-bearing muscovite (Hetherington *et al.*, 2003) in several shaly intervals (Figs. 7g to 7h).

Several types of MVT stratabound deposits are present in the upper Gonnesa Group, in the San Giovanni Formation, particularly in "Ceroide" facies. These ores include several horizons containing sphalerite>galena>>pyrite, and more rarely barite. Stratabound ores in the San Giovanni Fm, despite having a lower grade (about 4-5 wt.% Zn+Pb) than the massive SedEx deposits, are characterized by thicker and more continuous mineable horizons, which can be followed throughout the whole district.

The most characteristic among the MVT ores are the so-called Yellow Sphalerite "Blendosi" (i.e., sphalerite-rich), which occur as broadly developed "horizons" consisting of diffused impregnations of pale-yellow sphalerite with subordinate pyrite, hosted in a peloidal mudstone facies (Brusca & Dessau, 1968; Bechstädt & Boni, 1994) (Figs. 5c, 6h & 8a). This ore type has been detected mainly in the "Masse" (=Orebodies) 1, 2 and 3" of the San Giovanni mine and in the Nebida mine (Fig. 1). However, the most economically significant ore concentrations (Zn>Pb) of the San Giovanni Fm occur in cement and matrix of multigenerational breccias, which have variable degrees of fitting (Fig. 8b,d). These host breccias have two possible origins: 1) they could be of a fully sedimentary nature and have been formed as debris flows along fault scarps, in the areas

Ore mineral	Sphalerite					Galena					Pyrite				
Number of analyses	33					6					26				
Element (wt%)	Low	High	Mean	Median	SD	Low	High	Mean	Median	SD	Low	High	Mean	Median	SD
Mn	0.04	0.05	0.05	0.05	0.01	<dt	<dt	-	-	-	<dt	<dt	-	-	-
Fe	0.34	1.98	0.87	0.76	0.44	<dt	0.07	0.07	0.07	-	45.49	47.59	46.87	46.97	0.49
Co	<dt	<dt	-	-	-	<dt	<dt	-	-	-	<dt	0.01	0.01	0.01	-
Ni	<dt	<dt	-	-	-	<dt	<dt	-	-	-	<dt	<dt	-	-	-
Cu	0.04	0.09	0.07	0.07	0.02	<dt	<dt	-	-	-	0.04	0.07	0.06	0.06	-
Zn	64.10	66.71	65.77	65.82	0.73	0.13	1.48	0.57	0.28	0.57	0.04	1.75	0.54	0.54	0.42
As	<dt	<dt	-	-	-	<dt	<dt	-	-	-	0.05	0.07	0.06	0.06	0.01
Sb	<dt	<dt	-	-	-	<dt	<dt	-	-	-	<dt	<dt	-	-	-
Pb	0.15	0.57	0.29	0.20	0.17	83.23	84.35	83.92	83.98	0.40	0.12	0.82	0.44	0.41	0.25
Ge	<dt	0.06	0.06	0.06	-	<dt	<dt	-	-	-	<dt	<dt	-	-	-
Cd	0.22	0.32	0.27	0.27	0.03	<dt	<dt	-	-	-	<dt	0.02	0.02	0.02	-
Ag	-	<dt	-	-	-	<dt	<dt	-	-	-	<dt	<dt	-	-	-
S	32.07	33.70	33.00	33.03	0.36	13.62	13.87	13.76	13.76	0.11	52.75	54.90	53.92	53.98	0.55

dt: detection limit; -no value calculated;SD: Standard Deviation; CAMECA SX100, 20 Kev, at 20 nA

Table 1: *Summary statistics for trace element concentration in ores from SEDEX-type ores analysed by EPMA.*

Ore mineral	Sphalerite					Galena				
Number of analyses	61					6				
Element (wt%)										
	Low	High	Mean	Median	SD	Low	High	Mean	Median	SD
Mn	<dt	0.01	0.01	0.01	-	<dt	<dt	-	-	-
Fe	0.03	1.11	0.42	0.18	0.41	0.06	0.08	0.07	0.07	0.01
Co	<dt	<dt	-	-	-	<dt	<dt	-	-	-
Ni	<dt	<dt	-	-	-	<dt	<dt	-	-	-
Cu	0.01	0.06	0.04	0.04	0.01	<dt	<dt	-	-	-
Zn	64.31	67.13	66.02	65.98	0.58	0.08	0.24	0.16	0.16	0.07
As	0.01	0.03	0.02	0.02	0.01	<dt	<dt	-	-	-
Sb	<dt	<dt	-	-	-	<dt	<dt	-	-	-
Pb	0.12	33.53	11.36	0.26	16.02	83.64	84.55	84.06	84.02	0.39
Ge	<dt	<dt	-	-	-	<dt	<dt	-	-	-
Cd	0.20	0.75	0.36	0.36	0.11	<dt	<dt	-	-	-
Ag	0.09	0.10	0.10	0.10	0.01	<dt	<dt	-	-	-
S	32.55	33.81	33.08	33.02	0.29	13.65	13.91	13.76	13.78	0.09

Ore mineral	Pyrite 1					Pyrite 2				
Number of analyses	7					21				
Element (wt%)										
	Low	High	Mean	Median	SD	Low	High	Mean	Median	SD
Mn	<dt	<dt	-	-	-	<dt	0.01	0.01	0.01	0.01
Fe	42.75	45.69	44.51	44.92	1.15	43.53	47.60	46.79	47.06	0.87
Co	0.01	0.03	0.02	0.01	0.01	0.01	0.02	0.02	0.02	0.01
Ni	0.05	0.07	0.06	0.06	0.01	<dt	<dt	-	-	-
Cu	0.05	0.07	0.05	0.05	0.01	<dt	<dt	-	-	-
Zn	0.03	0.70	0.23	0.14	0.27	0.04	0.74	0.20	0.16	0.20
As	0.10	0.23	0.17	0.18	0.06	0.06	0.06	0.06	0.06	-
Sb	<dt	<dt	-	-	-	<dt	0.02	0.02	0.02	-
Pb	1.11	4.38	2.48	1.69	1.40	0.19	6.48	1.33	0.46	2.13
Ge	<dt	<dt	-	-	-	<dt	<dt	-	-	-
Cd	<dt	<dt	-	-	-	<dt	<dt	-	-	-
Ag	0.06	0.08	0.07	0.07	0.01	<dt	<dt	-	-	-
S	49.39	53.18	50.46	50.38	1.34	50.41	54.69	53.82	53.99	0.93

dt: detection limit; -no value calculated; SD: Standard Deviation; CAMECA SX 100, 20 Kev at 20 nA.

Table 2: *Summary statistics for trace element concentration in ores from MVT-type ores analysed by EPMA.*

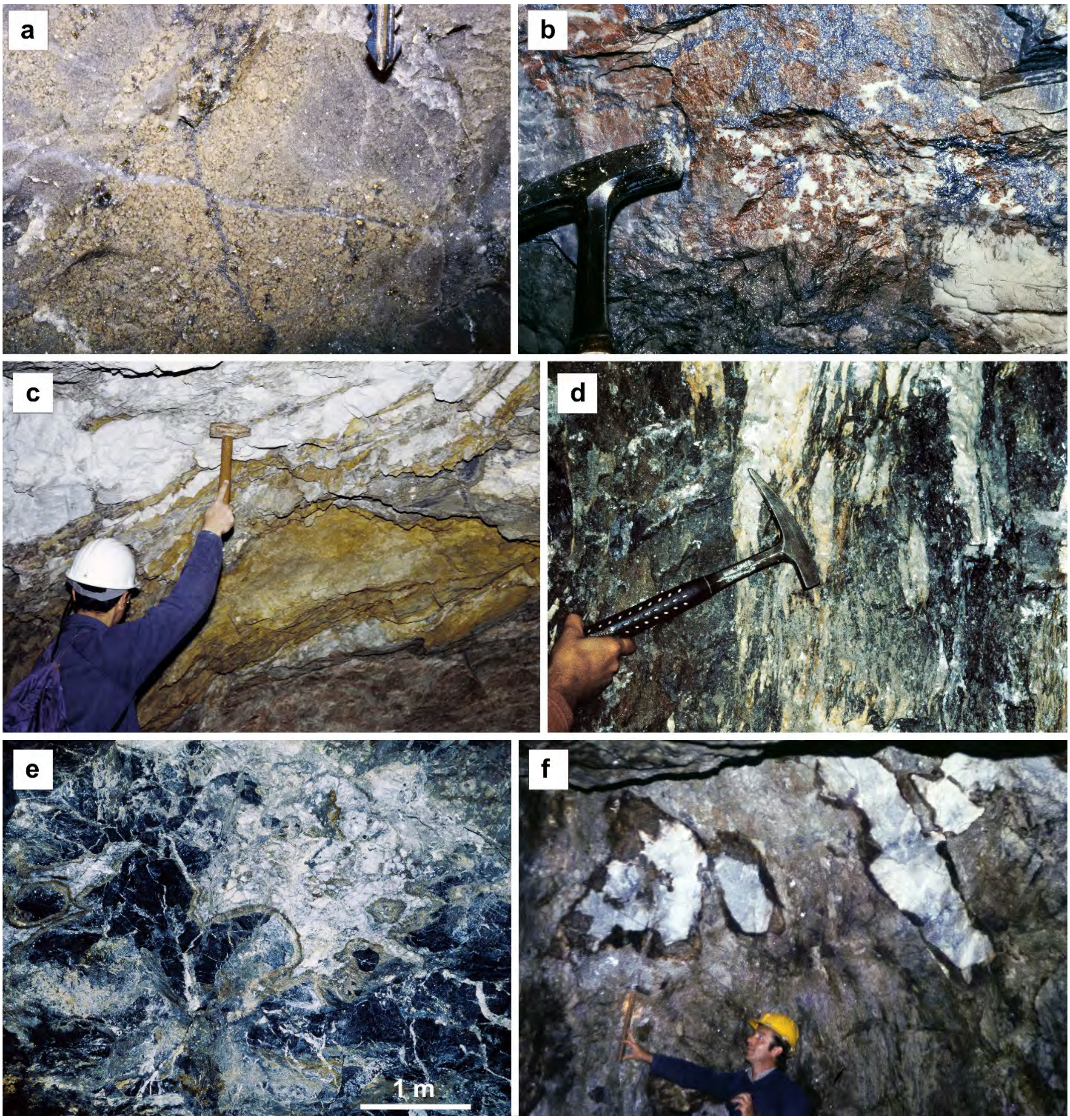

***Figure 8**: MVT deposits: **A**). "Yellow" sphalerite replacing peloidal mudstone in the San Giovanni Fm, Massa Pozzo 2, San Giovanni mine (Gonnesa); **B**). Massive concentration of red sphalerite and galena in the San Giovanni Fm, Monteponi mine (Iglesias); **C**). Deformed sparry calcite in the San Giovanni Fm, Seddas Moddizzis mine (Iglesias); **D**). Strongly deformed breccia with carbonate clasts and sulphides in matrix and cement, Planu Sartu mine (Buggerru); **E**). Cockades in a breccia of black "Ceroide" limestone, San Giovanni Fm; the clasts are wrapped by several generations of sulphides, Masua Mine (Nebida); **F**). "Ceroide" limestone clasts wrapped in several generations of sulphides. The mineralogy has been modified to a skarn association because of contact metamorphism, Sa Marchesa mine (Narcao).*

proximal to the NW-SE margins of the carbonate platform (Fig. 3b) (Bechstädt & Boni, 1994), or, 2) they could be fault breccias or hydrothermal breccias, associated with Cambrian tensional faults. Distinguishing between the two is not trivial, because the limestone-hosted mineralization has been affected by pervasive ductile deformation during the Variscan orogeny, with both the sulphides and the breccia clasts having been foliated and displaced along the N-S cleavage (Fig. 5b & 8d). In particular, all the "Ceroide"-hosted ores in breccias present a marked "prolate" strain (Arthaud, 1963; Ramsay, 1967; Ramsay and Huber, 1984; Weijermars, 1997). The ore bodies are generally associated with metre sized elongated pods and layers of sparry calcite (Fig. 8c), folded together with the host limestone.

In all the MVT deposits pyrite is extremely scarce (Fig. 9a-b)

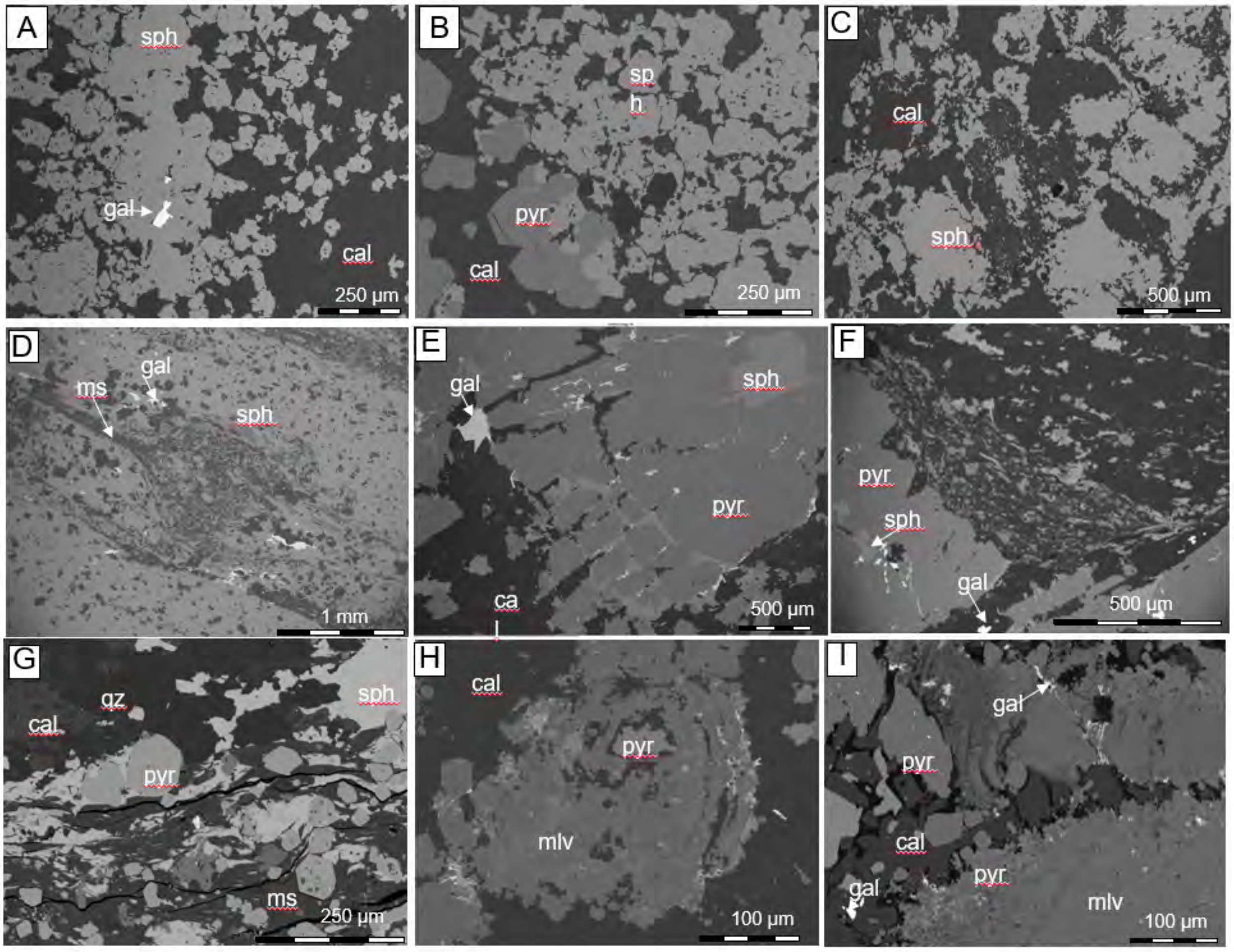

***Figure 9:** BSE images of MVT-type ore: **A**). "Blendosi" ore. Sphalerite impregnations with minor galena in Ceroide limestone (San Giovanni mine, Massa Pozzo 2); **B**). "Blendosi" ore. Sphalerite and pyrite impregnations in peloidal Ceroide limestone (San Giovanni mine, Massa Pozzo 2); **C**). Cockade-sphalerite (Masua mine, Cantiere Marx); **D**). Sphalerite and galena crystals strongly deformed. Ba-muscovite wisps define deformed foliation planes (Masua mine, Cantiere Tetto San Marco); **E**). Pyrite crystals strongly fractured during deformation. Sphalerite and galena are deformed ductily and fill fractures in pyrite; **F**). Recrystallized pyrite and sphalerite along strain shadows of pyrite porphyroclasts (Masua mine, Cantiere Albasini); **G**). Mineralization along cleavage planes (Masua, Cantiere Albasini); **H-I**). Pyrite-melnikovite and recrystallized pyrite (San Giovanni mine, Massa Pozzo 2). (sph) sphalerite, (py) pyrite, (cal) calcite, (mlv) pyrite-melnikovite, (dol) dolomite, ms (muscovite).*

BSE images from JEOL JSM IT300LV- 20 kev, 5 nA; 15 sec frame acquisition.

and sphalerite is low in Fe (<1 wt.% on average), whereas galena associated with macrocrystalline barite is increasingly more abundant towards the top of the Cambrian succession. In several deposits, as the Masua and Nebida mines along the western Iglesiente coast, there are orebodies showing cockade-like concretionary structures consisting of zoned sulphides (pyrite and reddish sphalerite) associated with sparry calcite (Fig. 8e,f, 9c). These structures, which are only slightly deformed, could be a late product of late mineralization along dilatational faults, developed during the late phases of Variscan orogeny, as hypothesized by Frenzel & Woodcock (2014). As in the SedEx deposits, local remnants of pyrite-melnikovite concretions have been found in the MVT-ores (Fig. 6g, 9h-i).

Recent investigations allowed detecting Ba-rich micas (Fig. 9d,g) also in association with the "Ceroide"-hosted ores, similar to the SedEx mineralized intervals.

The main trace elements in sphalerite are on average: Fe (0.42 wt.%), Mn (0.01 wt.%), Cu (0.04 wt.%), Pb (11.36 wt.%), As (0.02 wt.%), Cd (0.36 wt.%), and Ag (0.10 wt.%) (Table 2). Trace elements in pyrite 1 are Co (0.02 wt.%), Ni (0.06 wt.%), Cu (0.05 wt.%), Zn (0.23 wt.%), As (0.17 wt.%), Pb (2.48 wt.%), and Ag (0.07 wt.%) (Table 2). In pyrite 2 the number of elements and their contents are lower: Mn (0.01 wt.%), Co (0.02 wt.%), Zn (0.20 wt.%), As (0.06 wt.%), Sb (0.02 wt.%), and Pb (1.33 wt.%) (Table 2). Trace elements in galena are fairly limited: Fe has a mean value of 0.07 wt.%, and Zn of 0.16 wt.% (Table 2).

Ordovician Ores

Ordovician stratabound ores mark the angular unconformity between the pre-Sardic phase sedimentary rocks, including partly eroded Cambrian to lower Ordovician units, and Upper

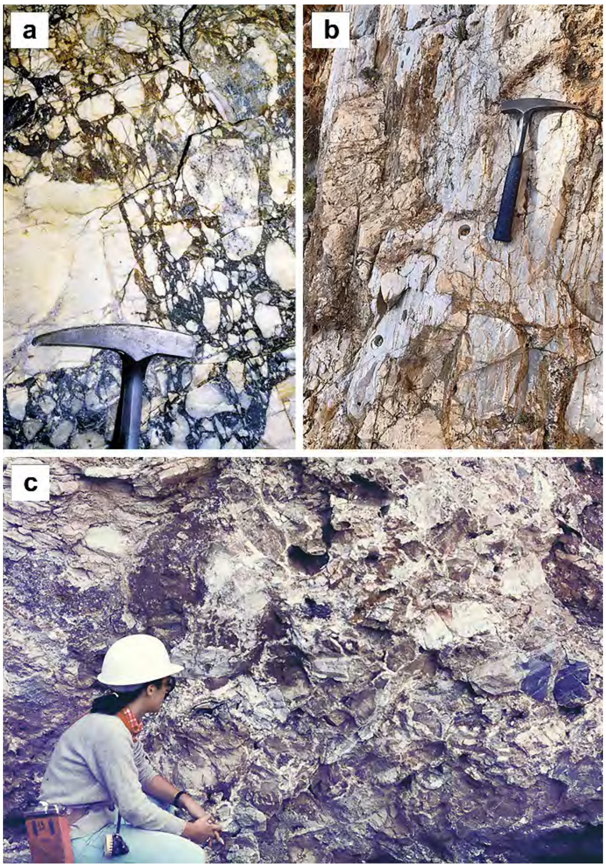

Figure 10: A). Skarn breccia: the clasts are marble and, in the matrix, and cement Zn-Pb-Cu-sulphides and an association of hedenbergite, epidote, and chlorite occur, Su Zurfuru mine (Fluminimaggiore); B). "Geodic" hydrothermal Fe-dolomite, (Nebida); C). "Ag-rich" palaeokarst breccia: carbonate clasts are partially replaced by barite; the cement consists of quartz, barite, Ag-galena, ankerite and calcite, Scavi Pisani San Giovanni mine (Gonnesa).

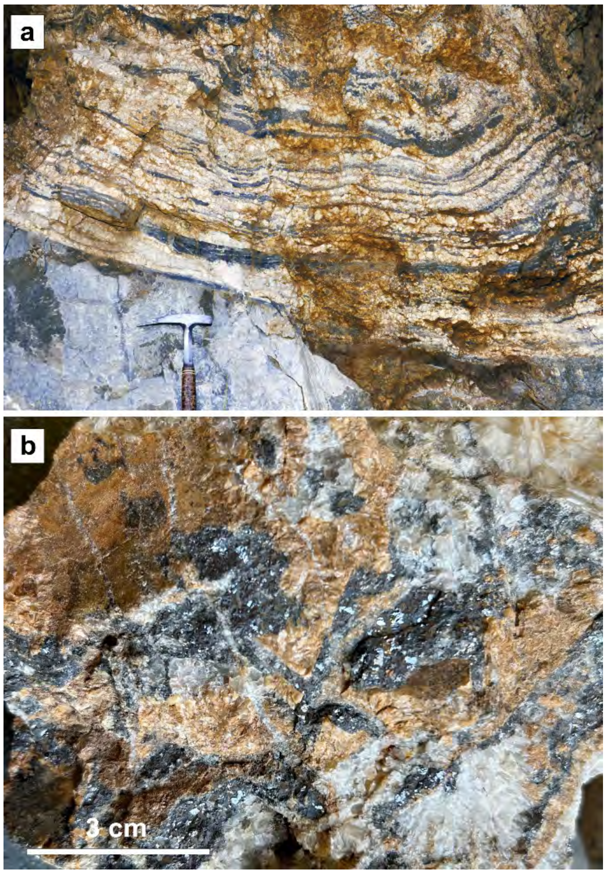

Figure 11: A). Internal sediment in palaeokarst, replaced by barite (white) and quartz (black), Fossa Is Bois Barega mine (Carbonia); B). "Ricchi Argento" ore sample in palaeokarst, Ag-rich galena, barite and ankerite, Grotta Pisani San Giovanni mine (Gonnesa).

Ordovician slates. The Ordovician hosted ores, which were economically less significant than those hosted in the Cambrian, consist mostly of barite (30 – 60wt.% $BaSO_4$) and galena, with traces of sphalerite and Cu-sulphosalts (Bechstädt & Boni, 1994; Boni *et al.*, 1996). When the unconformity marks the boundary between the Cambrian carbonates and the Upper Ordovician conglomerates and slates (i.e. when the Cabitza Formation is completely eroded and the conglomerates directly overlay the San Giovanni or Santa Barbara Formations), the mineralization occurs as veins and pods developed below the unconformity. Minor barite is also present in the Upper Ordovician conglomerates and breccias (e.g., Monte Segarino mine), as well as in the basal Caradocian-Ashgillian slates. The lithologies hosting the barite mineralization are pervasively silicified, resulting in a massive silica horizon (locally known as "Quartzite"), which contains sporadic galena. Previous studies (e.g., Bechstädt & Boni, 1994; Boni et *al.*, 1996) inferred that during the post-Sardic burial diagenesis (?) the Cambrian carbonates remained as buried fault-bounded structural highs within the sedimentary basin. In this setting, the overlying Ordovician slates (locally present in the sequence) formed an impermeable cover above either the carbonates or the conglomerates along the unconformity with the Cambrian sequence. The staking of variably permeable rocks acted as an effective trap for metal-bearing fluids that migrating within the basin could mineralize the top of carbonates below the Sardic unconformity and the carbonate fraction of the conglomerate (Boni *et al.*, 1992). In this regard, it is also interesting to observe a significant Ba enrichment in the rocks proximal to the Sardic unconformity (Cabitza slates and Mt. Argentu Fm) (Battaglia & Gherardi, 2017).

The Ordovician-hosted ores cannot be considered either SedEx or MVT. However, their metal association, consisting of Ba, Pb, minor Zn with only traces of Cu and Ag, is very similar to that recorded in the Cambrian deposits. This may be evidence for mineralizing fluids that, despite being originating at different stages and ending with different mineralization styles, tapped into a common source of metals. New investigations conducted on the different Ordovician pyrites resulted in trace element compositions of Cu (0.03 wt.%), As (0.06 wt.%), Pb (0.04 wt.%), and Cd (0.03 wt.%).

Late to Post-Variscan ores

Deformation and metamorphism effects on the pre-Variscan ores

As mentioned before, the effects of deformation and low-grade regional metamorphism on the pre-Variscan ores in SW Sardinia include changes in: (a) the geometry of sulphide orebodies, and (b) the mineralogy and textures of the ore and gangue minerals. Major and trace element contents of minerals were also probably modified. At first sight, in the Iglesias-Nebida-Masua areas the stratabound ore bodies have been tectonically tilted to a vertical position. This had various implications and it made possible the development of supergene alteration profiles after sulphide exhumation, which eventually produced widespread "non-sulphide" (secondary) calamine deposits (Boni *et al.*, 2003). Secondly, as anticipated before, the Variscan tectonics produced a pervasive ductile deformation of the limestone breccia-hosted MVT ores, bearing to the development of a strong foliation and redistribution of both the sulphides and the breccia clasts along the N-S cleavage, which locally thickened the orebodies in respect to their original width (Fig. 8d). At the microscale, the ductile deformation is evidenced by the presence of boudinage (Figs. 9d, 9g), pressure shadows (Fig. 6j) and microfolds marked by deformed wisps of Ba-micas (Fig. 6k) in the mineralized facies. The SedEx ores, being richer in pyrite, developed preferentially a brittle deformation, where sphalerite shows significantly more ductile behaviour relative to pyrite (boudinage) (Fig. 6e).

Contact metamorphism, metasomatism and Variscan granitic magmatism also had a strong impact on the previously deposited stratabound ores, modifying not only their previous structure and mineralogy, but also adding new elements, (most commonly Cu, see the Sa Duchessa mine), to the already present Zn-Pb-Ba and Fe association. Newly formed late-Variscan ore deposits consist of several skarn occurrences around leucogranite intrusions (Fig. 10a), or along marginal fault zones to the granitic plutons. In several localities the skarn ores occur at the same stratigraphic positions as the stratabound mineralization. Also prominent was the formation of high temperature vein systems, which were emplaced along tectonic lineaments of regional importance (e.g., Montevecchio-Ingurtosu, Moroni *et al.*, 2019; Santa Lucia, Su Zurfuru, Aponte *et al.*, 1988, etc.). These late Variscan ores contain a higher variety of elements than the Cambro-Ordovician ores, including F, Cu, Sb, W, Bi, Sn, and REEs. (Valera & Zuffardi, 1968, 1970; Venerandi Pirri, 1971; Verkaeren & Bartholomé, 1979; Aponte *et al.*, 1988; Naitza *et al.*, 2015, 2019; Moroni *et al.*, 2019; Deidda *et al.*, 2023).

Post-Variscan ore deposits

In the period spanning between the end of Variscan orogeny (Upper Carboniferous) and the beginning of Alpine cycle (Tertiary), southwestern Sardinia experienced several hydrothermal episodes, comparable with those recorded in other European terranes (Muchez *et al.*, 2005). These hydrothermal episodes resulted in a widespread replacive dolomitization ("Geodic dolomite") (Fig. 10b) of Lower Palaeozoic carbonates (Boni & Iannace, 1989; Boni *et al.*, 2000), which had an alleged Permian (270Ma ?) age. This dolomitization consisted in a pervasive process that overprinted former sedimentary and tectonic structures and was caused by warm (80-120°C), reducing and saline (20 wt.% eq. NaCl) fluids (Boni & Iannace, 1989). As many other hydrothermal dolomites in the world, the "Geodic dolomite" shows zebra-like features and saddle-shaped crystals (Fig. 10b).

Post-Variscan hydrothermal ores in SW Sardinia are not directly related to any intrusive bodies. They consist of lower temperature veins developed parallel to important late-Variscan structures (i.e., Marganai) (Arthaud & Matte, 1977) and of palaeokarst fillings in the carbonates of the Gonnesa Group (i.e., San Giovanni and Barega mines) (Fig. 10c, 11a,b). The mineral assemblage is dominated by barite and Ag-rich galena (Figs. 11a,b) (Ag=2 wt.%) (Brusca & Dessau, 1968; Boni, 1986; Bechstädt & Boni, 1994). New investigations allowed to determine that tetrahedrites are very common in these ores and include Ag-tetrahedrites (Ag=15wt.%), Zn-tetrahedrites (Zn=6-8wt.%), and Hg-tetrahedrites (Hg=8-17wt.%). Polibasite, freibergite, bournonite and argentite have also been found. Calcite, quartz and ankeritic dolomite are the main gangue minerals. The timing of these ores is not well understood; however, based on field relationships, and the cross-cutting relationship with the hydrothermal "Geodic dolomite", the mineralized veins and palaeokarst bodies appear to be younger than this dolomitization event. The ores in the palaeokarst network occur as cements of multistage collapse breccias or, more rarely, as replacement of both cement and the matrix of internal sediments. Ag-rich ore tonnages are quite low but, owing to their high Ag content, these deposits were originally exploited by the Phoenicians and Romans and then by the Pisans in the Middle Age.

Discussion

Irish-type Zn–Pb deposits consist primarily of stratabound sphalerite, galena, and iron sulphides, as well as barite, hosted in carbonate sedimentary rocks. These deposits have been considered as hybrids between SedEx and MVT ores (Wilkinson & Hitzman, 2014). In Ireland they are mostly associated with extensional faults, which originated during the development of Upper Palaeozoic sedimentary basins (Yesares *et al.*, 2019). These features can also be found in the Sardinian Lower Palaeozoic deposits, even if in the latter case the SedEx nature of some Cambrian ores is much more evident than in the Irish deposits. The SW Sardinia SedEx ores are located at the stratigraphic boundary between the sandstones of the Nebida Group and the tidal dolomites of the Gonnesa Group, marking the fragmentation of a continental bordering ramp and the onset of the development of a carbonate platform, and are strictly associated with extensional tectonics and fluids circulation through deep faults. The thin barite horizons associated with the SedEx ores show evidence of syn-diagenetic replacement of the host dolomites, whereas the sulphide bodies consist of massive accumulations of pyrite-melnikovite, with layers of sphalerite and rare galena. Sphalerite ores have average Fe values of 0.87 wt.% and contain Mn, Cu, Cd, and Ge as trace elements. In pyrite Co, Cu, As, Cd, Pb and Zn have been detected, even though the values of the latter two elements could be also ascribed to sphalerite and galena micro-inclusions.

Strontium and sulphur isotopes of barite in the SedEx ores are consistent with values of Cambrian seawater (Bechstädt & Boni, 1994), while sulphur isotopes of sulphides in the same stratigraphic position are consistent with their formation through bacterial sulphate-reduction (Brusca & Dessau, 1968; Boni *et al.*, 1996).

The limestone-hosted sulphide ores (defined as MVT by Boni *et al.*, 1996) are different from the SedEx style sulphides, both in their mode and time of emplacement, and in their behaviour during the Variscan deformation. Their iron content (pyrite) is much lower, whereas Zn and Pb predominate, but their mineralization grade is not very high (6 wt.% Zn+Pb on average). Several complex types of ores occur, which range from Zn-rich at the base of the "Ceroide" limestone, to Pb-rich at its top. The Zn-rich ore deposition starts with syn-diagenetic "yellow sphalerites" that replace a peloidal mudstone facies and continues with darker sphalerites cementing several generations of breccias. Galena is associated with the breccia-type mineralization.

Sphalerite is the main ore mineral in SW Sardinia, but galena and pyrite are also ubiquitous throughout the deposits. Iron and minor elements (e.g., Cd, Cu, Mn, Pb, As, and Ag) are commonly incorporated into the crystal structure of sphalerite or are present in minerals forming micro-inclusions within the sphalerite. The same should be considered for pyrite, which in Sardinian ores shows local evidence of transformation from amorphous pyrite-melnikovite (pyrite 1) to a crystalline phase (pyrite 2). Pyrite 1 contains traces of Co, Ni, Cu, Zn, As, and Ag, as well as barite micro-inclusions, whereas in pyrite 2 the number of elements and their contents are lower, this is possibly indicating that trace element were lost through the recrystallization process.

Trace elements content in sulphides is controlled by a number of factors, including P-T-pH-Eh conditions, fO_2 and fS_2 (Cook *et al.*, 2009; Pfaff *et al.*, 2011; George *et al*., 2016; Frenzel *et al.*, 2016). During the past decade numerous studies have focused on the trace element contents of sphalerite, galena and pyrite in carbonate-hosted deposits (e.g., Ye *et al*., 2011; Bauer *et al.*, 2019; Hu *et al*., 2021; Wei *et al.*, 2021), with few studies dealing with the fate of trace elements in sulphide systems that have undergone deformation and metamorphism during orogenic events (Lockington *et al.,* 2014; Cugerone *et al.*, 2020, 2021; Zhao *et al.,* 2021; Paradis *et al.,* in press). However, so far there have been no specific studies on trace element behaviour in the Lower Palaeozoic sulphides of SW Sardinia.

Galena from stratabound deposits in Cambrian rocks show a narrow variation of Pb isotopic composition: from these analyses it has been hypothesized that lead was sourced from a lower crustal component and matching with the Precambrian basement (Boni & Köppel, 1985). The deposition age of the SedEx-type ores should be considered syn-Cambrian, associated with the extensional tectonics at the base of the Gonnesa Group. The age of the MVT deposits in the "Ceroide" limestone is more difficult to determine, especially because the mineralization was probably deposited at different times. Orgeval *et al.* (2016) inferred that most of the MVT deposits in Sardinia would have formed during the inter-Ordovician Sardic tectonic phase, and over a relatively short time interval (ca. 70Ma) is considered to have occured between Cambrian sediment deposition and MVT Pb–Zn ore formation.

The Sr isotopes of Ordovician-hosted barites show higher radiogenic values than Ordovician seawater, which could be derived from Lower Palaeozoic siliciclastic host rocks (Boni *et al.*, 1996). Also, the Pb isotopes of Ordovician galenas are more radiogenic than the Cambrian-hosted ones, while their metal sources point to the silicates contained in Cambrian-Ordovician sandstone and slate.

Late- to post-Variscan mineralization developed through the following distinct, although partially superimposed, hydrothermal systems (Boni *et al.*, 1990; Bechstädt & Boni, 1994): (1) granite-related hydrothermal fluids, which resulted in the formation of skarn and high-temperature veins when metal-rich magmatic fluids, eventually mixed with a meteoric component; (2) high-salinity and colder hydrothermal fluids, which initiated the epigenetic dolomitization, as well as later silicification and vein and karst mineralization. These hydrothermal episodes occurred under conditions of low fluid/rock ratio, with fluids mostly sourced from formation water with a minor contribution from an external radiogenic source of metals; (3) fresh and cold meteoric waters, which precipitated mostly calcite with only minor ore and arguably lasted well beyond the Permo-Triassic. Lead isotopes from ore and gangue minerals of the late- to post-Variscan deposits suggest that the metals budget of mineralizing fluids was sourced from the Cambrian ores and their carbonate host rocks, and by the Variscan granites together with Lower Palaeozoic clastic sediments. Low temperature deposits show a strong Cambrian component. Extensional tectonics either related to Permian wrench fault tectonics (Arthaud & Matte, 1977) or to early Alpine rifting likely triggered the circulation of saline and mildly warm brines, from which the low-temperature and palaeokarst-hosted ores were deposited (Bechstädt & Boni, 1994). Comparable hydrothermal activity occurred during the same period in other European terranes, including the Central European Variscides (Germany and Switzerland), the Massif Central (France), the Cantabrian Mountains and the Catalonian Coastal Ranges (Spain) (Boni *et al.*, 1992, 2002 and references therein).

Conclusions

On the basis of the most accepted definition of Irish-type ores ("stratabound, stratigraphically and structurally controlled base metal deposits in carbonate rocks") (Wilkinson & Hitzman, 2014; Yesares *et al.*, 2019), the Lower Palaeozoic-hosted mineralization of SW Sardinia can only partly be classified as "Irish-type". In fact, the massive sulphides at the base of the Gonnesa Group (Santa Barbara Fm) with their abundance of pyrite locally associated with Fe-rich sphalerite, are quite different from the typical Irish-type ores (at least in Ireland). These sulphides do not appear to have replaced a previous carbonate lithotype but might have been deposited syngenetically on the sea floor or along active faults/feeder channels.

On the contrary, it is reasonable to consider that, as is the case of most Irish deposits (Wilkinson & Hitzman, 2014), that a significant part of sulphides as well as barite in the limestone-hosted orebodies formed through replacement of the carbonate host (San Giovanni Fm), during several diagenetic and post-diagenetic stages. This is self-evident not only for the "Yellow sphalerite" ores that replaced the peloidal mudstone facies, but also for the barite-galena enrichments at the boundary between the Gonnesa Group carbonates and the slates of the Iglesias Group. The sulphides in the cement and matrix of the multi-generational breccias, which are particularly abundant close to the Cambrian platform margins and along several NW-SE tectonic lineaments, also demonstrate that the structural control on the mineralization in specific areas of SW Sardinia. Other evidence of tectonic control is bound to the small Ordovician deposits, with the Cambrian carbonates acting as structural highs that followed a pattern of already active lineaments.

The deposition of post-Variscan ores was also subjected to structural control: the lineaments hosting the veins and palaeokarst orebodies were conditioned by the extensional tectonics active at the end of the Variscan orogeny, that lasted throughout the Mesozoic.

Because of low-grade metamorphism of the Lower Palaeozoic ores and host rocks caused by the Variscan orogenic phase, no useful genetic information can be obtained fluid inclusions measurements or stable isotopes of ore and gangue minerals. Also, the stable isotope data of carbonate rocks and calcite gangue associated with Cambro-Ordovician sulphides (Boni *et al.*, 1988) seem to be relatively uncertain, again due to the later overprint experienced during the Variscan orogeny. Furthermore, the Variscan orogeny might have affected the nature and amounts of trace elements in the ore minerals (e.g., Ba and Zn in several micas, Fe, Ge, Cd in sphalerite). Of course, this was not the case for the post-Variscan barite and Ag-rich galena orebodies, which because of their more recent age remained unchanged from any recrystallization or deformation process.

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