minerals

Review

The Ophiolite-Hosted Cu-Zn VMS Deposits of Tuscany (Italy)

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Abstract: Several Jurassic, ophiolite-hosted Cu-Zn VMS deposits occur in Tuscany. They are hosted by tectonic units of oceanic affinity (Ligurian Units), such as the well-known deposits of nearby Liguria. Industrial production was small and definitively ceased in the 1960s. Locally, massive ore (chalcopyrite-bornite-chalcocite) with an exceptionally high grade was found. The Montecatini Val di Cecina mine exploited the largest "bonanza" and, for few decades in the 19th century, became one of the most profitable copper mines in Europe. This study provides an updated review of these deposits. Tuscan Cu-Zn VMSs mostly occur in proximity of the contact between the serpentinite-gabbro basement and the overlying basalts. Chalcopyrite-pyrite stockworks occur in serpentinite-gabbro cut by dolerite dykes, while the largest massive sulphide bodies are hosted by polymictic-monomictic breccias at the base of pillow basalts. Early chalcopyrite ores were mechanically–chemically reworked and upgraded to bornite-rich nodular ore embedded in a chlorite, calcic amphibole, Fe-rich serpentine, quartz, andradite, ilvaite, and xonotlite assemblage. This bornite-rich ore contains substantial amount of sphalerite and pyrite and ubiquitous grains of clausthalite, hessite, tellurium, and gold. They represent a prime example of the sub-seafloor portion of a hybrid mafic-ultramafic oceanic hydrothermal system formed in an OCC along the slow spreading ridge of the Jurassic Piedmont-Ligurian Ocean. The peculiar mineralogical–textural character of the bornite-rich ore was driven by an interface coupled dissolution–precipitation process mediated by fluids.

Keywords: VMS deposits; ophiolites; slow spreading ridge; cataclasite; bornite; orebodies; northern Apennine

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1. Introduction

Tuscany, like many regions in Italy and Europe, dismissed mining exploitation after at least 3000 years of almost continuous activity. The Etruscans and Romans exploited copper, iron, and possibly tin, while, during the Middle Ages and the Renaissance, silver, copper, and iron became the most sought-after metals. With the 1800s' industrialization, deposits of all available elements were explored and exploited, e.g., base metals, silver, iron, tin, boron, antimony, and manganese. Then, there was the discovery of the supergiant Monte Amiata Hg district and the large, pyrite district of Maremma [1]. Most of these ore deposits are related to Neogene-Quaternary magmatic-hydrothermal activity [2]. However, there are also some volcanogenic massive sulphide (VMS) Cu-Zn deposits, hosted in Jurassic ophiolites, which triggered intense, albeit brief, mining activity during the 19th century. Massive ore (chalcopyrite-bornite-chalcocite) with an exceptionally high grade characterized these small deposits. The Montecatini Val di Cecina mine exploited the largest Cu-Zn sulphide "bonanza" in Tuscany (Figure 1) and, for few decades in the 19th century, became one of the most profitable copper mines in Europe. The large assets accumulated by the mining company were pivotal for the development of the chemical industry in Italy (Montecatini SpA, later transformed in Montedison SpA).

During the last 30 years, after mining cessation in Tuscany, several projects for the cultural valorisation of past mining sites have been developed and, nowadays, several mining parks are active [3]. Their cultural value is now well-recognized, as well as their economic impact on a region strongly based on tourism. If the relevance of mining seems to have faded, the scientific interest is still alive, and the Tuscan sites are a popular field trip destination for students of Earth Science courses at Italian and international universities, as well as a place where scientists from all over the world meet and discuss.

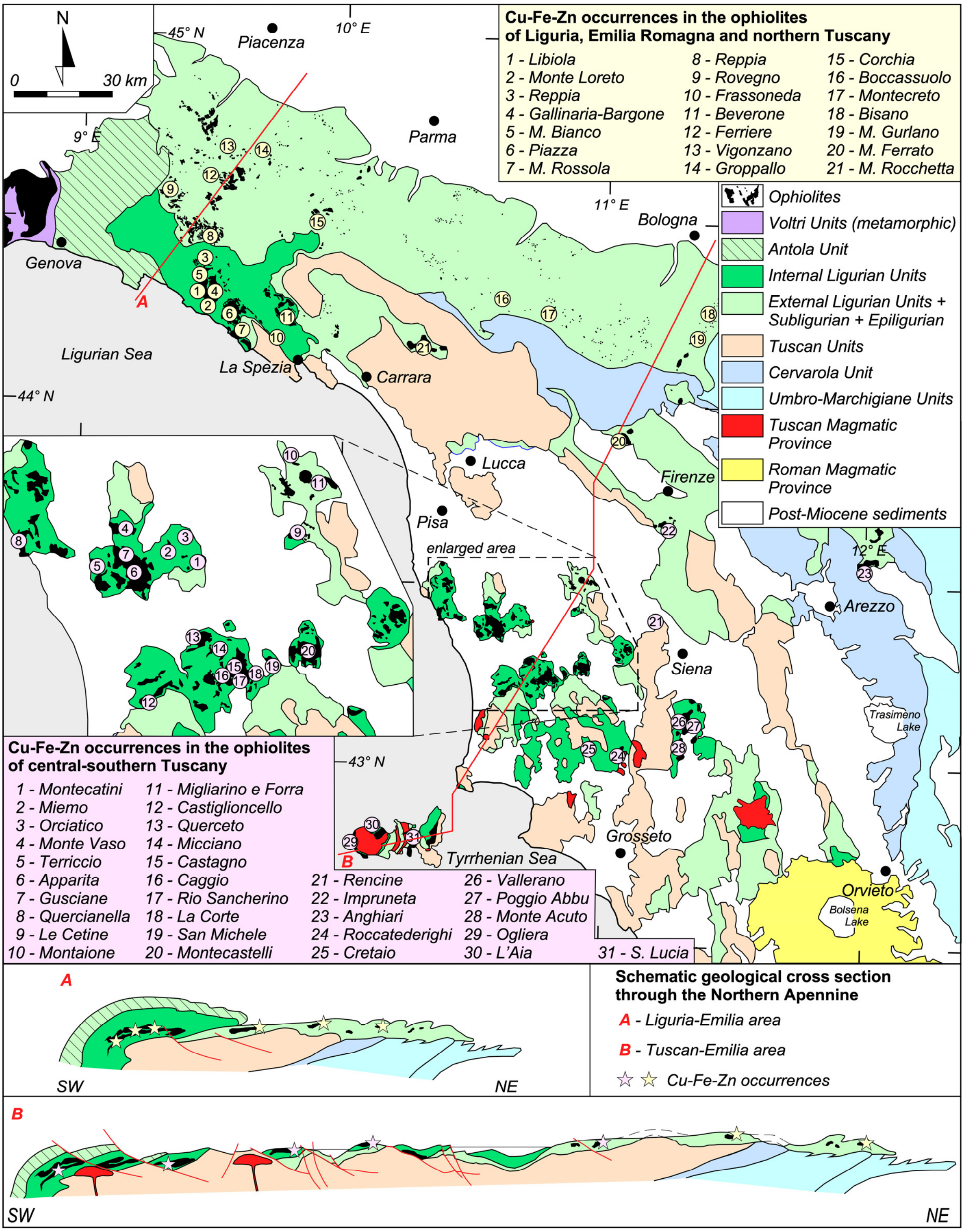

Figure 1. Simplified tectonic map of the northern Apennine, indicating the distribution of ophiolitic rocks and Cu-Zn VMS deposits in the internal and external Ligurian Units [4].

The reason for such scientific popularity is the great mineralogical and geochemical diversity of the Tuscan ore deposits, and the complexity of their geological and geodynamic setting [1,5,6]. This is a context in which very young magmatic-hydrothermal systems (ca. 8.5–4.5 Ma) have been exhumed to the surface by extremely rapid tectonic processes [7–9], and where some of them are only partially exhumed (ca. 4.0–1.5 Ma; [10]) or still active at depth (Larderello and Monte Amiata geothermal fields) [11,12].

The VMS Cu-Zn deposits hosted in the Jurassic ophiolites of central Tuscany have been poorly studied because their main exploitation ceased at the beginning of the 20th century and the modern industrial and scientific interest was polarized by pyrite, Sb, Ba, and Fe Tuscan deposits [6]. Despite this, a detailed mining exploration was developed in the late 1980s under the program "Ricerca Mineraria di Base" of the Italian Ministry of Industry (Law No. 752, 6 October 1982, Art. 4). Exploratory work was being conducted by the company RIMIN S.p.a. (ENI group) in collaboration with various scientists from Italian universities and other scientific institutions. The agreement No. 17 (Mineralizzazioni nelle ofioliti) focused on the ophiolitic outcrops of Liguria, but a significant part of the work (geology, petrography, geochemistry, and geophysics) was also conducted on the ophiolites of Tuscany. Multi-elemental analyses of about 2000 rock-ore samples were performed by ICP-AES and AAS after processing the samples by sodium peroxide fusion and acid digestion (Supplementary Material S1). The overall results were considered to be disappointing, and the huge amount of data remain deposited in the form of paper volumes in the Ministry's archives and are largely under-exploited scientifically [13].

This study is part of the PRIN-MUR 2017AK8C32 project, funded by the Italian Ministry of University and Research. It is aimed at making a reappraisal of the Tuscan VMS Cu-Zn deposits and defining: (i) their structural setting, (ii) their potential for precious critical metals, and (iii) the reactions involving their sulphides and gangue silicates. This contribution provides an updated geological and mineralogical review of these deposits based on available old mining map sections and reports, past scientific contributions, and the results of the RIMIN exploration, as well as new surface and sub-surface field work in accessible areas. Petrographic and whole-rock geochemical analyses have been performed on samples collected at the surface and in underground woks, as well as on the ore samples from the historical collection of the Natural History Museum of the University of Pisa. The Tuscan VMS Cu-Zn deposits have been generically described as being formed in the Jurassic ocean [6], but their strict association with the ultramafic oceanic basement has never been highlighted in the modern scientific literature.

Despite their small size, Tuscan ultramafic- and hybrid mafic/ultramafic-hosted VMS deposits provide valuable information for the ongoing definition of a genetic model for this sub-group of VMSs–SMSs [14,15]. This is a potentially relevant mineral resource worldwide not only for base metals, but for possibly recovering energy-critical metals like Co, Ni, Te, and Se from mafic/ultramafic-hosted deposits in orogenic and oceanic settings.

2. Geological Background

The northern Apennine fold and thrust belt (Italy) includes tectonic units derived from the Piedmont-Ligurian Ocean basin (Ligurian domain), which separated, during Jurassic-Cretaceous times, the Europe and Adria plates [16]. These tectonic units are characterized by the widespread occurrence of ophiolites (serpentinized peridotites, gabbros, and basalts) that locally host small Cu-Zn VMS deposits [17,18]. During the Alpine-Apenninic orogenic events, slices of the oceanic domain were thrusted on top of the continental crust of the Adria plate (Tuscan Domain) [19]. The thrusting of the Ligurian Domain units (Figure 1) started in the Late Cretaceous–Middle Eocene "Alpine" stage, controlled by the east-dipping subduction of the Ligurian ocean. Then, the tectonic overlap on the Tuscan Domain reached completion during the late Eocene-Quaternary "Appeninic" stage, driven by the west-dipping subduction of the Adria plate [19,20].

The Ligurian units of the northern Apennine can be divided into Internal Ligurian Units and the External Ligurian Units [21]. The Internal Units are made by Jurassic–Early

Paleogene sedimentary successions (radiolarites, limestones, and shales) deposited on the Jurassic basalt-gabbro-serpentinite oceanic crust. They are presently characterized by large outcrops of ophiolites showing a highly variable lithological composition [16]. Zones with a complete oceanic crust sequence (serpentinized peridotite-gabbro-basalt) laterally pass to sections without gabbro, as well as to sections where the beginning of sedimentation occurred directly on serpentinites, gabbro, and/or ophicalcites. The evidence of a widespread exhumation of serpentinized peridotites at the seafloor suggests that the Piedmont-Ligurian ocean was characterized by slow-spreading ridge and oceanic core complex (OCC) tectonics [16]. Conversely, the External Units lack the pre-Cretaceous succession and are distinguished for the peculiar occurrence of basal sedimentary mélanges (Upper Cretaceous) containing metric-kilometric blocks of ophiolites (Figure 1). The Jurassic ophiolites involved in the early accretionary wedge of the "Alpine" stage (Internal Units) provided the ophiolitic debris recorded in the Late Cretaceous, by the sedimentary mélanges of the Ligurian External Units [22].

Thus, rocks and VMS ores from the Jurassic slow-spreading ridge were firstly dispersed by the combined tectono-sedimentary effect of the "Alpine" deformation stage. Later, during the "Appenninic" stage, the Ligurian Domain units were emplaced onto the Tuscan Domain with a top-NE tectonic transport direction and then affected, from the Early–Middle Miocene, by extensional tectonics. The Tuscany and Northern Tyrrhenian basin experienced rates of extension much higher than Liguria, leading to the extreme tectonic dispersion of the ophiolitic units and ores observed in the study area (Figures 1 and 2) [4]. Such a strong lateral segmentation was controlled by low-angle normal faults, also influencing the development and localization of the Late Miocene-Quaternary sedimentary basins [23]. The current geographical dispersion of ophiolite outcrops in Tuscany is, therefore, due to the overlapping of several geological processes: the Cretaceous re-working of the ophiolite basement into the sedimentary mélanges (External Units), the lateral segmentation induced by compressional and extensional tectonics, and the final deposition of the sedimentary covers in the Neogene-Quaternary basins. Drilling exploration (for geothermal fluids and drinking water) has highlighted the presence of ophiolitic lenses even in areas lacking any surface evidence.

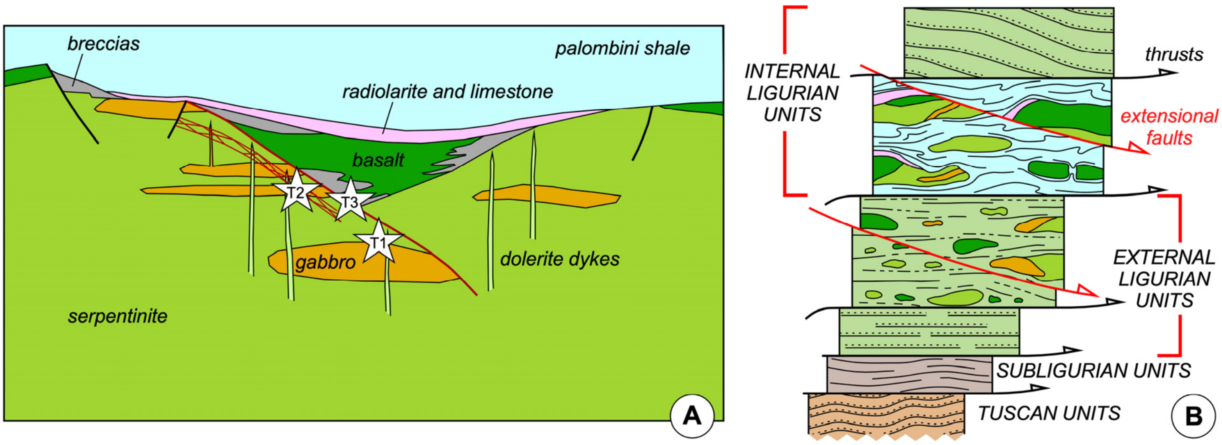

Figure 2. (**A**) Schematic reconstruction of the original oceanic succession of the Internal Ligurian Units (modified after [24]) showing the possible position of the Tuscan VMS Cu-Zn deposits (see the text for description and discussion of T1-, T2-, and T3-Type ores. (**B**) Sketch of the tectonic stack of ophiolitic units in the study area [25]. Both drawings are out of scale.

The Tuscan ophiolites can be geographically subdivided in seven main outcrop zones and several minor occurrences (Figures 1 and 3). The largest exposures, hosting most of the VMS ores, occur in central Tuscany, in the area between Pisa, Siena, Grosseto, and the Tyrrhenian coast: (1) Monti Livornesi, (2) Miemo, (3) Monterufoli, (4) Montecastelli, (5) Vallerano, (6) Murlo, and (7) Gambassi. The ophiolites occurring in the Gambassi area are hosted by External Liguride units, while the rest of the main ophiolite exposures belong to Internal Liguride units [26]. Each outcrop consists of both ophiolites and sedimentary covers but, due to the complex tectonic deformation described above, their relative proportion is quite variable. The ophiolite outcrops to the north of Cecina Valley (Monti Livornesi, Miemo, and Gambassi; Figure 3) are characterized by discontinuous, yet large exposures of pillow basalt overlying the serpentinite-gabbro oceanic basement. Conversely, the outcrops to the south of Cecina Valley (Monterufoli, Montecastelli, Murlo, and Vallerano) are dominated by the serpentinite-gabbro oceanic basement, while pillow basalt is less represented. In both areas, the serpentinite-gabbro oceanic basement is locally crosscut by dyke swarms of porphyritic dolerite. Their relationships with the pillow basalts still need to be clarified. The ultramafic rocks are usually represented by serpentinized harzburgite, but locally serpentinized dunite and lherzolite constitute important outcrops [27–29].

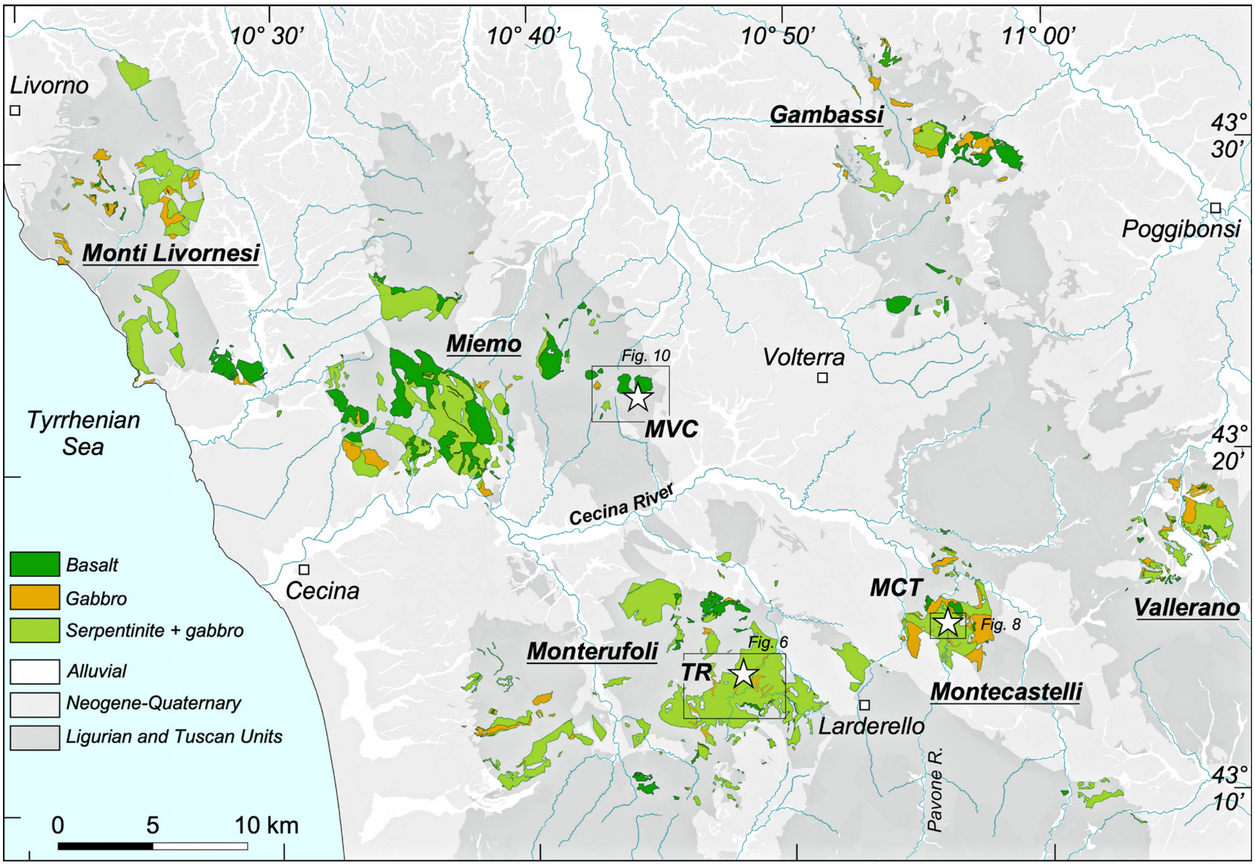

Figure 3. Geological map showing the different distribution of basalt, gabbro, and serpentinite in ophiolite outcrops south and north of the Cecina River valley (modified after http://www502.regione.toscana.it/geoscopio/geologia.html; accessed on 10 August 2023). The three key deposits described in the text are highlighted with white stars: TR—Trossa River; MCT—Montecastelli; and MVC—Montecatini Val di Cecina.

The Investigation of all the Internal Liguride outcrops in Tuscany allowed the reconstruction of a coherent pre-Apenninic framework for the Jurassic oceanic crust [24–26]. The deposition of radiolarite, limestone, and shale occurred on a very heterogeneous seafloor, characterized by strong lateral variations (Figure 2A).

Sedimentary covers may lay on pillow basalts, on serpentinized peridotites crosscut by dykes/laccoliths of gabbro, themselves cut by dolerite dykes, as well as, locally, also on gabbro bodies crosscut by dolerite dykes. This evidence, coupled with the pervasive serpentinization of the peridotites [27] and the lower hydration experienced by gabbro and basalt/dolerite bodies intruded in serpentinized peridotites [30,31], suggests a complex tectono-magmatic-hydrothermal evolution for the oceanic crust. The exhumation and hydration of mantle peridotites at the oceanic spreading ridge seem to have occurred progressively, allowing for the sequential intrusion of gabbro bodies, when the serpentinized peridotite was already partially exhumed at a plutonic depth, and dolerite dykes, when the system had reached a much shallower subvolcanic level. This scenario is consistent with a setting where OCC tectonics played along a slow spreading ridge in proximity of the ocean–continent transition, as already proposed by many authors for Alpine and Apennine ophiolites [14,16,28,32].

3. The Tuscan Cu-Zn VMS Deposits

This review focuses mostly on the Cu-Zn VMS deposits hosted in the ophiolite outcrops close to the Cecina Valley (Miemo, Monterufoli, and Montecastelli areas), because their original stratigraphy is relatively well-preserved (Internal Liguride units) and it is here that the main ore bodies occur. The overall industrial production has been very little. Montecatini Val di Cecina (MVC hereafter), the largest VMS deposit in the Tuscan ophiolites, produced around 50,000 tonnes of refined copper [13]. For the second deposit in terms of size, Le Cetine, a production of less than 1000 t of copper was recorded, while all the other small VMS occurrences in the Tuscan ophiolites provided a few thousand tonnes of copper in total [13].

Stratigraphic relationships (Figures 2 and 3), although complicated by tectonics and textural–structural features, allow for the identification of three different types of sulphide deposits [4,13]: T1-type—stockwork-dissemination ore in serpentinite and gabbro and, more rarely, in basalt; T2-type—nodular ore in cataclastic shear zones crosscutting the serpentinite-gabbro basement; and T3-type—nodular ore in breccia bodies in the contact zone between the serpentinite-gabbro basement and the overlying pillow basalts. The structural–textural relationships among ore types, and between ores and the ophiolite sequence, indicate that stockwork- and dissemination-ore (T1-type) formed early; then, they were re-worked during the brecciation processes that controlled the formation of the T2- and T3-type ores. T1-type ore forms independent bodies, may be found in close association with T2-type deposits, and occurs as fragmented clasts within T2-type and T3-type orebodies. The obvious textural difference between the T1 and T2/T3 types has been noted since the earliest scientific investigation [33,34] and led to the distinction between primary T1-type deposits, referred to as “filoni iniettati” (injected lodes), and T2-, T3-type reworked deposits, referred to as “filoni impastati” (kneaded lodes).

Many of the VMS deposits of the Tuscan ophiolites have a peculiar mineralogical–geochemical character that clearly distinguish them from the ophiolite-hosted deposits of Liguria (Figure 4; Supplementary Material S1): in Tuscany, the exploited ore minerals were predominantly chalcopyrite and bornite [35,36], while, in Liguria, they were mostly pyrite and chalcopyrite [37]. This explains why the high-grade “bonanza” of the relatively small MVC deposit produced almost twice as much copper as the larger Libiola deposit in Liguria [13,38]. Moreover, chalcocite may be locally abundant in Tuscany, contributing to the high grade of the orebodies. The last notable difference is the absence, in Tuscany, of important deposits totally embedded in the uppermost part of the pillow basalts, like the largest deposit in Liguria: Libiola [37].

Thanks to the sensitivity of the mining engineers who managed the mine in the 19th century, many ore and host rock samples from the Tuscan VMS deposits were donated to the mineralogical museums of Italian universities. The mines were visited and studied by all the major Italian and European geologists and mineralogists of the time, who left numerous scientific publications [33–35,39–42]. A few scientific papers about these deposits were published also in the second half of the 1900s [36,43]. The MVC mine is now a mining park and the underground works are still partially accessible, so we were able to conduct underground observation and sampling down to the fifth mining level. The rest of the smaller Tuscan copper mines, although abandoned for long time, are visitable using speleological techniques.

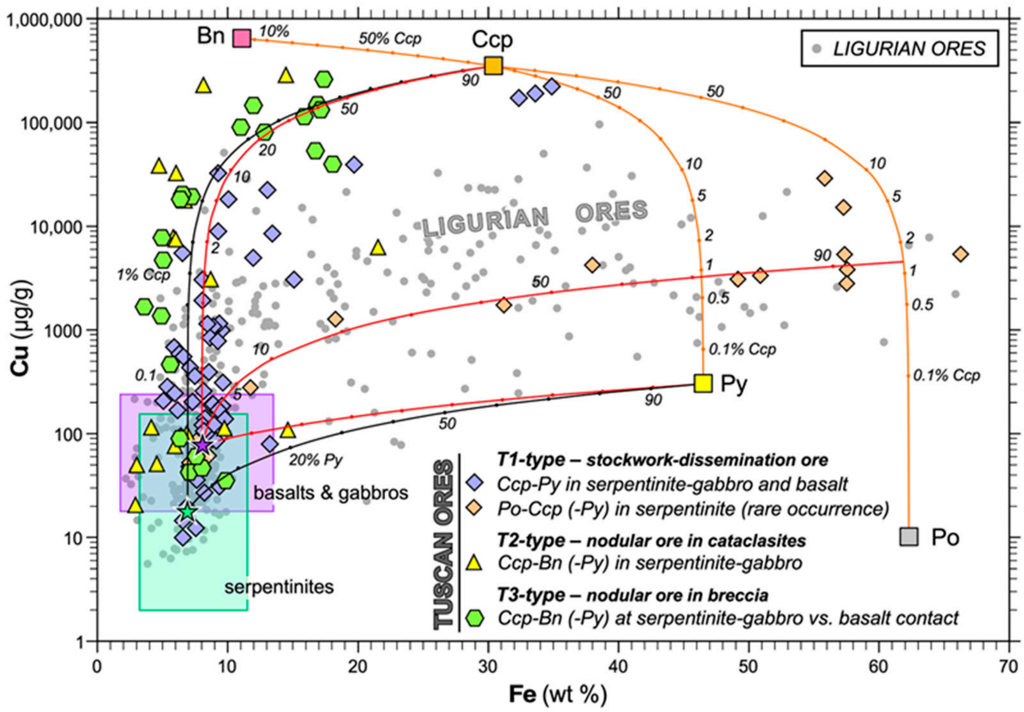

Figure 4. Semilogarithmic Cu vs. Fe diagram showing the distinct geochemical and mineralogical characters of the Tuscan and Ligurian Cu-Zn VMS ores [13]. Grey dots (Ligurian ores) are representative of the Libiola, Monte Loreto, Boccassuolo, Gallinaria, Monte Bardeneto, Monte Bianco, Corchia, Reppia, and Monte Rossola deposits. Tuscan ores are grouped coherently with the classification proposed in this contribution: T1-type) from Trossa, Roccatederighi, Riparbella, Miemo, Murlo, and Micciano deposits; T2-type) from Montecastelli deposit; and T3-type) from Montecatini Val di Cecina and Le Cetine deposits. Geochemical variability in non-mineralized oceanic crust, from both abyssal and ophiolitic settings, is indicated by green and violet boxes, with stars for the average composition (data from Earthchem.org; [44,45]). Square symbols indicate the nominal composition of the main sulphides involved in Cu-Zn VMS ores: Bn—bornite, Ccp—chalcopyrite, Py—pyrite, and Po—pyrrhotite. Incremental addition of sulphides to mafic and ultramafic oceanic rocks is visualized by red and black curves, while the orange curves highlight possible mixture between sulphide phases.

Based on the detailed descriptions left by previous authors, our underground surveys, and the availability of historical samples (Natural History Museum of Pisa University), the geometry of these deposits, as well as their mineralogy and geology, were placed in the stratigraphic and structural context of the ophiolitic Ligurian units of Tuscany. Three mining areas were studied in detail and used as a representative case study of each ore-type: Trossa Valley (T1-type), Montecastelli (T2-type), and Montecatini Val di Cecina (T3-type). Selected rock and ore samples provided by the Natural History Museum of Pisa University, as well as collected at the surface and from underground during the survey, were characterized by reflected/transmitted light, XRD, and SEM-EDS (methods in Supplementary Material S2).

3.1. T1-Type Ore (Stockworks and Disseminations in Serpentinite-Gabbro Basement)

This ore type mostly occurs in the area south of the Cecina Valley, where the ophiolite outcrops are dominated by the serpentinite-gabbro oceanic basement, while pillow basalts are almost lacking (Figure 3).

The best example of T1-type ore is represented by the Trossa river deposits (Castagno and Caggio mines), but many other small deposits were discovered throughout the area (e.g., Querceto, Montecastelli, and Gambassi mines; Figure 1). They consist of chalcopyrite stockworks and disseminations, with minor pyrite and bornite, hosted in serpentinite and intrusive bodies of gabbro (Figures 5 and 6). As already highlighted, these deposits provided a negligible production with respect to the deposits of the T3-type ore. Nonetheless, they are very important for understanding the Tuscan Cu-Zn VMS deposits.

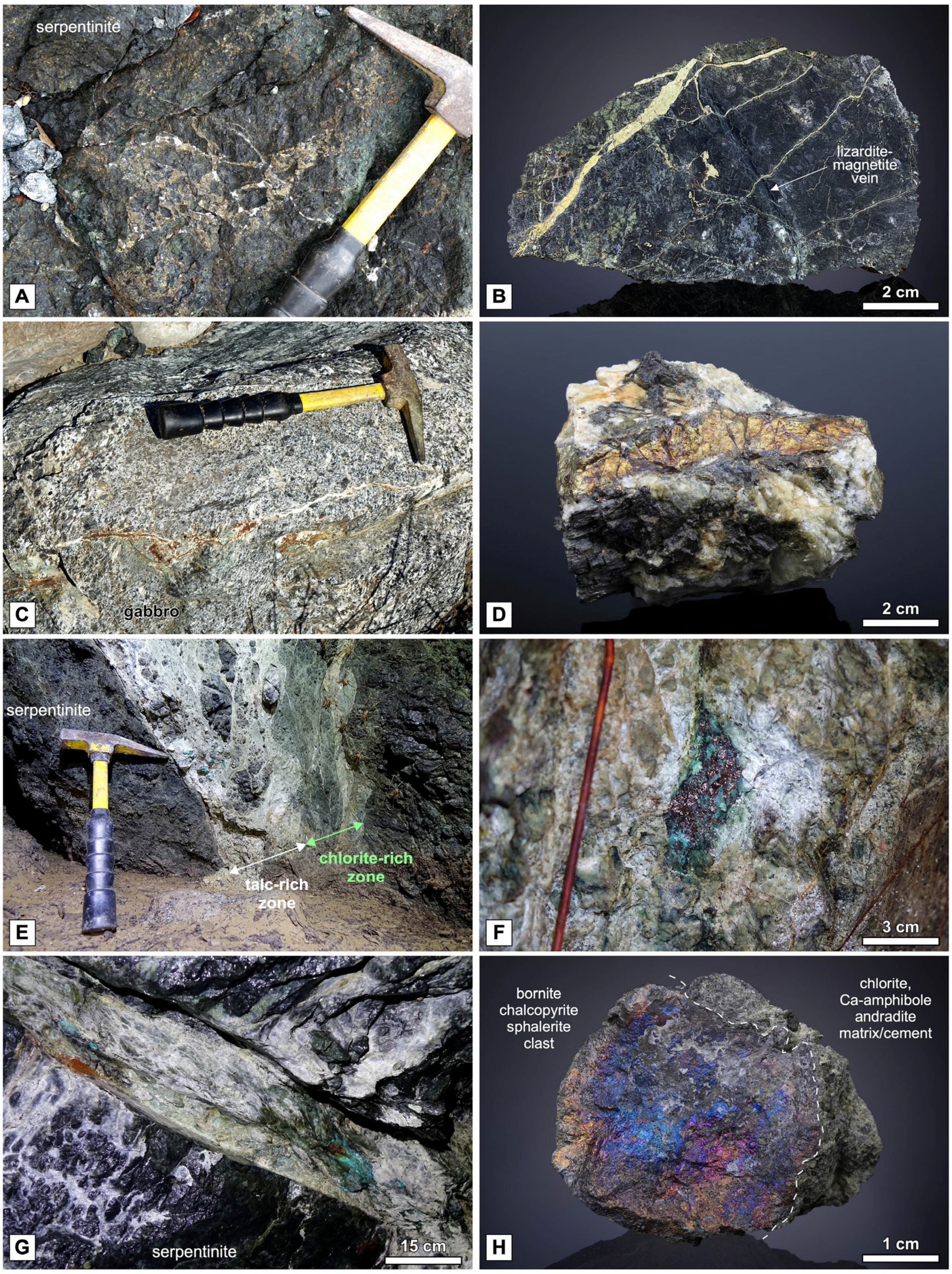

Figure 5. T1-type ore: (**A**) chalcopyrite-pyrite stockwork and disseminations in serpentinite, Trossa Valley; (**B**) chalcopyrite ± pentlandite veins up to 2 cm thick in serpentinite, Querceto mine; (**C**) chalcopyrite-pyrite veins hosted in gabbro, Trossa Valley; (**D**) a 2 cm thick chalcopyrite vein in gabbro, Castagno mine, Trossa Valley. T2-type ore: (**E**) chalcopyrite-bornite, serpentinite, and gabbro clasts in a cataclastic zone hosted by serpentinite, Querceto mine; (**F**) clast of bornite-chalcopyrite of 5 cm in cataclastic gabbro, Montecastelli mine; (**G**) serpentinite-hosted cataclastic zone with chalcopyrite-bornite clasts, Montecastelli mine; and (**H**) clast of chalcopyrite-bornite, 3 cm; Montecastelli mine.

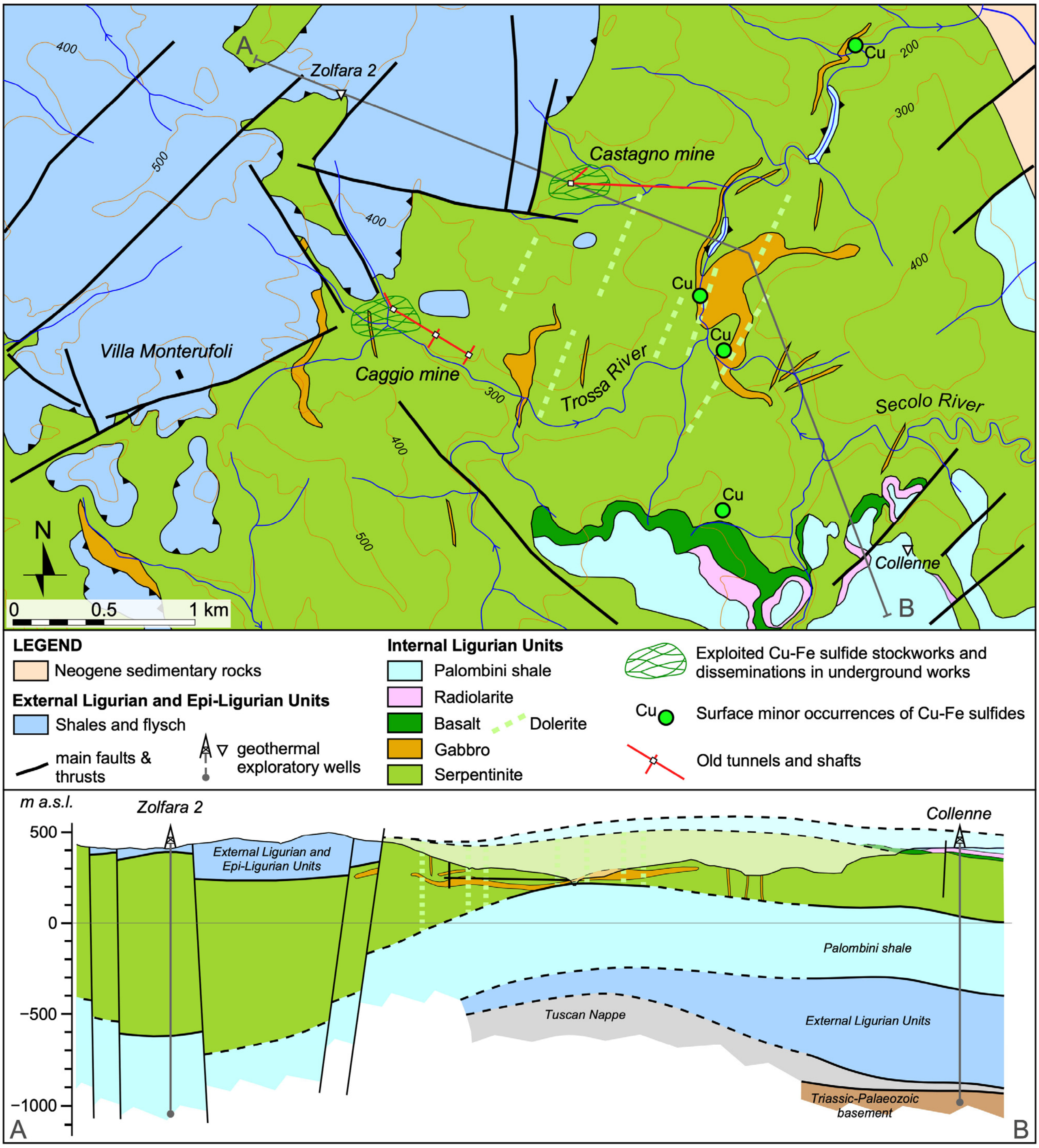

Figure 6. Interpretive geological map and cross section of the Trossa Valley showing the local geological setting of the T1-type ores exploited by the Castagno and Caggio mines (modified after http://www502.regione.toscana.it/geoscopio/geologia.html, accessed on 10 August 2023, on the base of new detailed mapping at surface and sub-surface).

The ophiolite outcrops that host T1-type deposits are usually characterized by an unusual amount of gabbro intrusions hosted in serpentinites, lately cut by dolerite dykes. The gabbro forms sub-horizontal, kilometric sills and laccoliths up to several hundred meters thick, connected to swarms of sub-vertical gabbro dykes, several hundred meters in length and from a few centimetres to a few meters thick. Gabbro is usually isotropic and ranges from fine-grained (micro-gabbro) to very coarse-grained (pegmatoid gabbro), with the most common type represented by "normal" gabbro with a cm size texture. Feeder dykes have a homogeneous coarse-grained texture, while sills-laccoliths commonly display a significant layering, sub-parallel to the contacts, outlined by the alternation of coarse- and fine-grained layers. Strongly deformed bands (flaser gabbro) sometimes occur inside the layered intrusions, as well as at the contact with the serpentinite host. Finally, swarms of sub-vertical dykes of porphyritic dolerite, several hundred meters in length and up to 4 m thick, crosscut serpentinite and gabbro. Serpentinite outcrops lacking gabbro intrusions are usually devoid of dolerite dykes.

3.1.1. Orebody Geometry and Local Geological Setting

The Trossa River Valley is one of the wildest areas in Tuscany, and it is quite surprising to observe the large number of mining shafts (some as deep as 150 m) and the many kilometers of tunnels that were dug in the 19th century, when the area could only be reached by travelling many hours by mule. The Trossa River deposits are hosted by a large sub-horizontal ophiolite lens, about 50 km^2 in size and up to 1 km thick, sandwiched between sedimentary sequences (mostly shale formations). The geometry of this ophiolitic lens is well constrained by deep fluvial incisions and some geothermal exploratory wells [26]. The bottom of the ophiolite lens is in in tectonic contact with Cretaceous shale, while the top locally maintains portions of the original sedimentary covers, represented by Jurassic radiolarites and Cretaceous limestone/shale, and it is overlaid by other tectonic units (Figure 6).

Serpentinite is the predominant lithology along the Trossa valley, but large, sub-horizontal sills of gabbro crosscut the slopes at variable elevations, and they are also intercepted at depth by several mining shafts and tunnels. Gabbro sills are up to 20 m thick, and they can be followed along strike for more than 1 km. They have an undulated attitude, tapering terminations, and even sudden interruption due to NE-SW and N-S faults. Swarms of sub-vertical gabbro dykes with variable strikes crosscut the serpentinite between the sub-horizontal tabular intrusion of gabbro. The largest sill of gabbro crops out along the Trossa river and gently dips to the W, forming the basal host rock of the orebodies. NNE-SSW trending, sub-vertical swarms of porphyritic dolerite dykes crosscut both serpentinite and gabbro, passing also throughout the mineralized area.

Chalcopyrite stockworks and disseminations are widespread all along the upper contact of the main sill of gabbro and into the serpentinite host [34,46]. However, their limited extension, both laterally and downdip, hampered the development of mining activity. The chalcopyrite veins are usually few mm–cm thick and few meters long, although in a few cases, they reached a thickness of half a meter and a continuity of tens of meters along strike/dip (Figure 5). Where serpentinite and gabbro are crosscut by the dolerite dykes, the chalcopyrite stockworks may continue into the latter rock as well. A minor amount of pyrite and sphalerite are commonly associated with chalcopyrite and, locally, pyrrhotite veins were also observed [46].

Variably oriented cataclastic shear zones crosscut the whole ophiolitic sequence, locally reworking sulphide stockworks and disseminations (Figure 5). Minor T2-type orebodies were exploited in the Trossa area, but the production was negligible. A few examples of this nodular ore were observed during the survey, showing clasts of massive chalcopyrite-bornite, as well as clasts of serpentinite and gabbro containing chalcopyrite veins. The matrix is dominated by chlorite and Ca-amphibole but, in some cases, andradite and talc were also detected by XRDP analyses.

3.1.2. Ore-Gangue Mineralogy and Textures

T1-type ore mostly consists of chalcopyrite stockworks and disseminations (Figures 5 and 7). Sphalerite and pyrite are ubiquitous but always in small amounts, while pyrrhotite (magnetic) veins are rather rare [46]. The veins are composed of massive microgranular sulphide, with minimal amounts of gangue minerals (Mg-rich chlorite and Ca-amphibole).

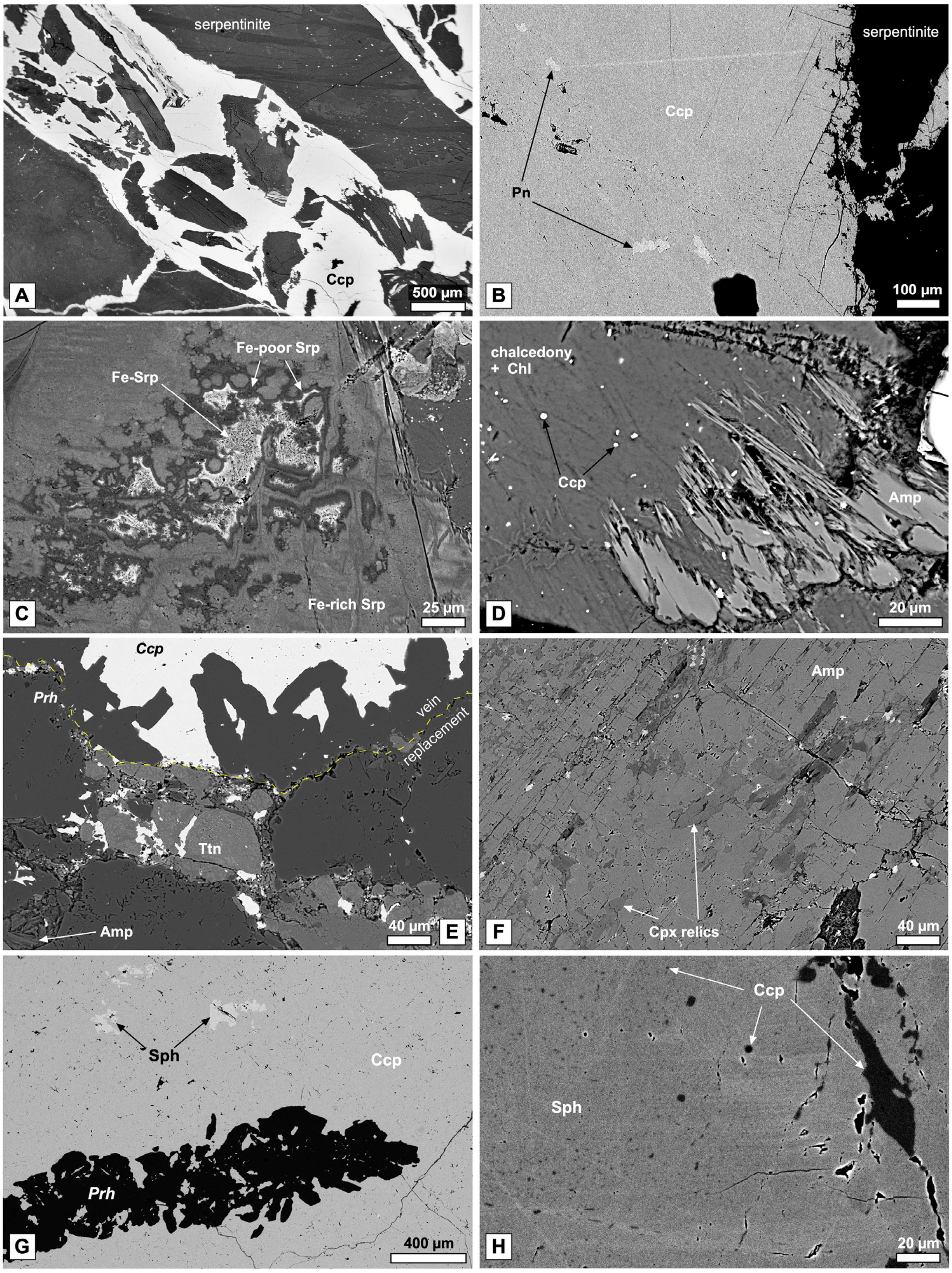

Figure 7. Textural details of the T1-type ore (SEM-BSE images): (**A**) chalcopyrite (Ccp) vein in serpentinite, Querceto mine; (**B**) pentlandite (Pn) grains in chalcopyrite, Querceto mine; (**C**) recrystallized serpentinite at the contact with chalcopyrite veins, Trossa Valley: iron-rich serpentine minerals (Srp) replacing a bastite; (**D**) a detail of the silicified serpentinite with Ca-amphibole (Amp), chlorite (Chl), and disseminated chalcopyrite, Caggio mine, Trossa Valley; (**E**) prehnite (Prh) and Ca-amphibole (Amp) replacing plagioclase in gabbro; titanite (Ttn) is partially replaced by rutile and ilmenite. Prehnite forms also idiomorphic crystal in the chalcopyrite vein, Libbiano mine; (**F**) Ca-amphibole replacing a pyroxene (Cpx) crystal in gabbro, Libbiano mine; (**G**) sphalerite (Sph) grains in chalcopyrite from a gabbro-hosted vein, Trossa Valley; and (**H**) chalcopyrite-disease and veinlets in sphalerite; Libbiano mine.

Locally, the stockworks develop true brecciated textures where the sulphide-cement embeds the clasts of the host rock. Veins hosted by serpentinite always contain small amounts of pentlandite in lozange-shaped grains, a few tens of microns in size. Very small octahedral crystals (1–5 μm) of sulphides, with an intermediate composition compatible with the cattierite-vaesite series, were identified by SEM-EDS in both serpentinite- and gabbro-hosted chalcopyrite veins. All these veins, when observed in preserved and tectonically undisturbed outcrops, do not show any association with bornite and chalcocite. The latter two minerals variably replace chalcopyrite veins and disseminations, only when T1-type ore is reworked along the cataclastic shear zones (T2-type ores). Cu-sulphides, ascribable to covellite and/or digenite-djurleite (reflected light, SEM-EDS, and XRDP data) are common in oxidized veins at the surface, where chalcopyrite is pervasively altered to Fe-hydroxides and Cu carbonates-chlorides.

Host rocks of T1-type ore experienced a significant hydrothermal alteration, mostly in proximity to the sulphide veins. The lizardite-chrysotile mesh-textured assemblage that forms a large part (>90% vol.) of the serpentinite was texturally re-organized in spherulitic aggregates of serpentine (Figure 7C) and variably replaced by aggregates of fibrous Mg-rich Ca-amphibole and microcrystalline quartz (Figure 7D). The new texture was highly porous, and needles of Fe-rich serpentine minerals grew in the residual cavities (Figure 7C). Chalcopyrite disseminations are more frequent in silicified portions. When the stockworks were hosted by gabbro, the hydrothermal alteration produced a pervasive replacement of plagioclase by a fine-grained aggregate of prehnite in tabular crystals (Figure 7E). The SEM-EDS analyses indicate that sodium was totally remobilized. Clinopyroxene was replaced by Mg-rich Ca-amphibole, titanite, and minor amounts of Mg-rich chlorite (Figure 7F).

3.2. T2-Type Ore (Cataclastic Zones in Serpentinite-Gabbro Basement)

Even this type of deposit mostly occurs in the area south of the Cecina Valley (Figure 3). The best example is the Montecastelli deposit, but many other small deposits were discovered throughout the area (e.g., Querceto, Libbiano, and Monterufoli). They consist of brecciated orebodies in cataclastic shear zones that are totally embedded in the serpentinite-gabbro basement. Even this type of ore deposit is usually hosted by serpentinite intruded by an unusual amount of gabbro and dolerite bodies. The overall geometric and textural characters of such intrusive bodies are like those introduced in Section 3.1.

The Montecastelli deposit is hosted in the large serpentinite-gabbro outcrop of the Pavone River (13 km^2; Figure 8). The deposit was intermittently explored and mined between 1832 and 1942 through the excavation of small open pits and underground works, providing a total production of few hundred tons of copper. The Montecastelli mine consists of about 1500 m of adits and drifts distributed over three levels from 195 m to 245 m above sea level (a.s.l.), connected by a main shaft and smaller inclined shafts (Figure 8). The description of the ore deposit is based on old mining reports/maps and few old scientific contributions [47], field work conducted at surface/underground, and the petrographic study of host rocks and ores.

3.2.1. Orebody Geometry and Local Geological Setting

The ophiolitic outcrop along the Pavone river is dominantly made up of serpentinized harzburgite intruded by sub-horizontal sills and sub-vertical dykes of gabbro. Large bodies of serpentinized dunite and lherzolite also occur [27,28,48]. In the northernmost area, the top of the ophiolitic sequence is preserved, and pillow basalts, as well as relics of sedimentary covers, overlie the serpentinite-gabbro basement (Figures 3 and 8). A few sub-vertical dykes of porphyritic dolerite occur in the mining area, crosscutting serpentinite and gabbro.

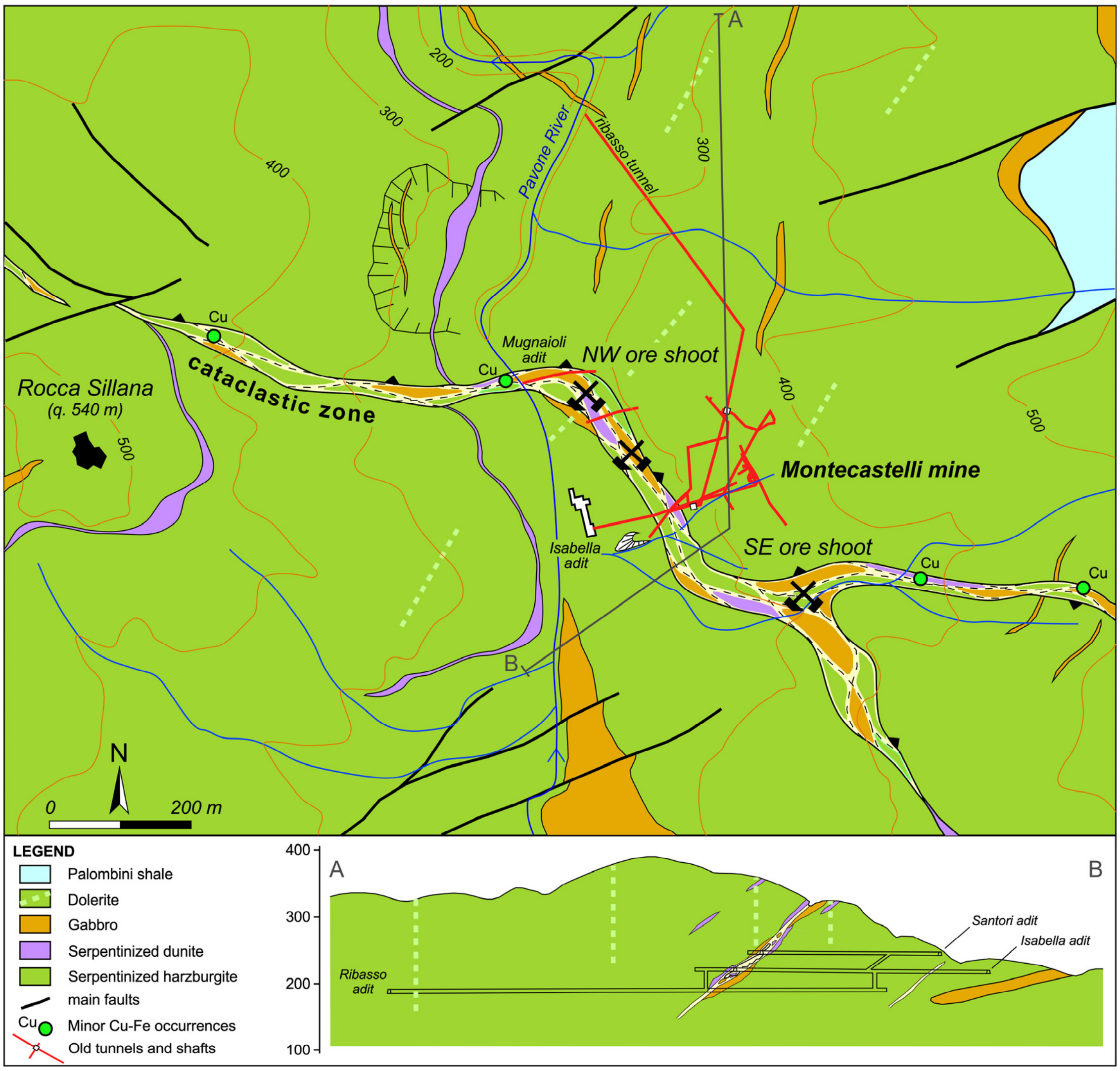

Figure 8. Interpretive geological map (**A**) and cross section (**B**) of the Pavone Valley showing the local geological setting of the T2-type ores exploited by the Montecastelli mine (modified after [48] on the base of new detailed mapping at surface and sub-surface).

The serpentinite-gabbro basement is crosscut by a NW-trending mineralized cataclastic zone with a variable dip to NE. It was explored from the surface (ca. 320 m a.s.l.) down to the third mining level (ca. 200 m a.s.l.) and along the strike for about 700 m. The thickness of the cataclastic zone is highly variable, from few meters up to 40 m, in correspondence with the richest ore-shoot (Isabella stope). The variable interplay of mechanical and hydrothermal reworking is responsible for the significant mineralogical heterogeneity of the mineralized cataclastic zone.

Clasts and decametric lenses of serpentinized harzburgite-dunite, gabbro, and dolerite are embedded in a matrix that ranges from soapy and whitish with pervasive foliation to competent and pale–dark green with a spaced cleavage. The soapy breccia matrix characterizes the northwestern zone of the deposit (Isabella-Grotta Mugnaioli stopes), while in the southeastern zone, the pale–dark green type progressively dominate. Both the matrix and the surfaces of the clasts display lineations with a very variable orientation. Plurimetric lenses of gabbro and serpentinite embedded in the cataclastic zone were exploited for their chalcopyrite (±bornite and chalcocite) stockworks that pre-date the cataclastic deformation (T1-type ore; this study and [47]). However, most of the production came from nodular sulphide ore (mm to dm in size) dispersed throughout the breccia matrix in the northwestern zone. Centimetric clasts of chalcopyrite-bornite-sphalerite are still observed nowadays at the surface exposures and in underground workings. The irregular, anastomosed nature of the cataclastic zone and the sudden closure along strike/dip of the ore shoots prevented the industrial progress of this deposit.

3.2.2. Ore-Gangue Mineralogy and Textures

Sulphide clasts of the nodular ore (T2-type) are mainly composed of chalcopyrite and bornite (Figure 9). In the southeastern, low-grade part of the mineralized cataclastic zone, chalcopyrite predominates. Here, the serpentinite-gabbro host rocks are strongly deformed and the sulphide stockworks are disrupted in angular-rounded clasts, but the breccia matrix lacks the pervasive hydrothermal re-working that characterizes the north western, high-grade part of the deposit (Isabella oreshoot). The chalcopyrite veins and clasts show minor concentrations of pyrite and Fe-poor sphalerite and rare crystals of Ni-Fe and Ni-Co sulphide. The breccia matrix contains comminuted amounts of host rocks (serpentinite and gabbro) and amounts of Mg-rich Ca-amphibole/chlorite and prehnite replacing the serpentinite-gabbro host, characteristics that are identical to the previously described T1-type ore.

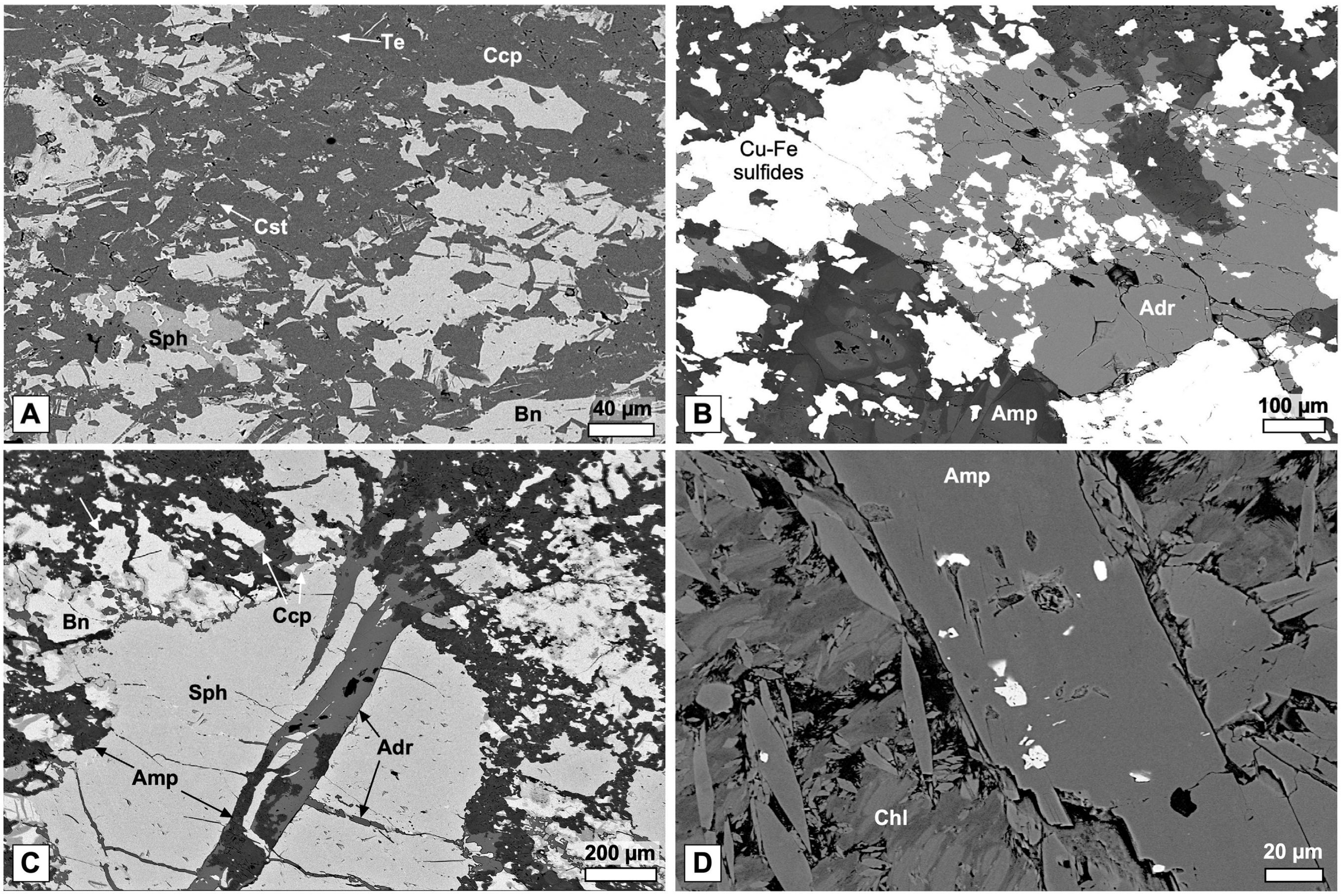

Figure 9. Textural details of the T2-type ore from Montecastelli mine (SEM-BSE): (**A**) typical massive intergrowth of bornite (Bn) and chalcopyrite (Ccp), locally involving Fe-poor sphalerite (Sph), with tiny dispersed grains of tellurium (Te) and clausthalite (Cst); (**B**) intimate intergrowth of sulphides, andradite (Adr), and Ca-amphibole (Amp) from the border of an ore nodule; (**C**) a vein of andradite and Ca-amphibole propagating through a clast of sphalerite embedded in the sulphide-silicate intergrowth; and (**D**) inclusions of chalcopyrite hosted by prismatic crystals of Ca-amphibole with interstitial chlorite, from the breccia matrix of nodular ore.

Moving north-westward along the strike, the thickness of the cataclastic zone increases and the matrix becomes more and more whitish and soapy. The mineral assemblage is still characterized by Mg-rich chlorite and Ca-amphibole, but talc, Fe-rich serpentine minerals, andradite, ilvaite, xonotlite, and titanite are common and, locally, dominate (Figure 9). The main ore shoots (Isabella and Grotta Mugnaioli stopes) are composed of pluri-decametric clusters of cm-dm clasts of a bornite-chalcopyrite-sphalerite assemblage, intimately intergrown with gangue silicates (mainly Mg-rich Ca-amphibole, andradite, and Mg-rich chlorite). Sulphide clasts are zoned, with a chalcopyrite-rich core and a bornite-rich rim, while sphalerite is evenly distributed. Micrometric grains of native tellurium, clausthalite, Ag-rich gold, and hessite were identified by SEM-EDS analyses (Figure 9). They are preferentially embedded in bornite and chalcopyrite. Their textures do not suggest any systematic replacive relationship between sulphides, although locally late chalcopyrite veinlets crosscutting bornite have been observed.

3.3. T3-Type Ore (Breccias at the Serpentinite/Gabbro Basement vs. Pillow Basalt Contact)

The MVC deposit, together with the smaller Le Cetine, Terriccio, Monte Vaso, Miemo, and other minor occurrences, belong to the T3-type and are localised to the north of Cecina Valley (Figure 2). Most of these mines are no longer accessible, but thanks to the sensitivity of the mining engineers who managed the mine in the 19th century (Aroldo and Augusto Schneider), many ore and host rock samples were donated to the mineralogical museums of Italian universities. The mines were visited and studied by all the major Italian and European geologists and mineralogists of the time, who left numerous scientific publications [33–35,41,42,44,45]. A few scientific papers about these deposits were published also in the second half of the 1900s [36,43]. The MVC mine is now a mining park and the underground works are still partially accessible; we were able to make underground observations and sampling down to the fifth mining level. Based on the detailed descriptions left by previous authors, our underground survey, and the availability of historical samples (Natural History Museum of Pisa University), the geometry of the MVC deposit, as well as its mineralogy and geology, can be placed in the stratigraphic and structural context of the Tuscan ophiolitic units. It can be considered as the most representative example of this deposit type in Tuscany.

3.3.1. Orebody Geometry and Local Geological Setting

The MVC deposit is hosted in a 2 km wide and 200 m thick lens of basalt, tectonically embedded in cretaceous shales (Palombini shale formation) [25]. Despite the strong disruption of the stratigraphy of the oceanic sequence, few relics of the original sedimentary cover (Jurassic radiolarite) are preserved at the top of the basalt, in the southern part of the outcrop (Figure 10) [49]. Thanks to the mining activity, we know that the bottom of the basalt lens is lined by several pluri-decametric lenses of serpentinite and gabbro. Larger, kilometric bodies of serpentinite and gabbro crop out one kilometre to the west of the MVC basalts (Figure 10). The basalt relics occurring on top of these serpentinite-gabbro outcrops (La Cavina) suggest that they could represent the original oceanic basement of the MVC basalt lens.

The present day displacement is consistent with the extensional tectonics—low-angle faults with a top-down-to-the-east sense of movement—that have affected these units since the Early–Middle Miocene [23]. Preserved examples of the pristine basalt vs. serpentinite-gabbro contact occur in the nearby areas of Miemo and Riparbella (Figure 2). Cu-Zn VMS occurrences are ubiquitous all along the preserved contacts (e.g., Miemo and Le Cetine), as well as along the basalt–shale tectonic contacts (e.g., Le Cetine, Terriccio, and Monte Vaso), where the basalt lenses have been detached from their original serpentinite-gabbro basement.

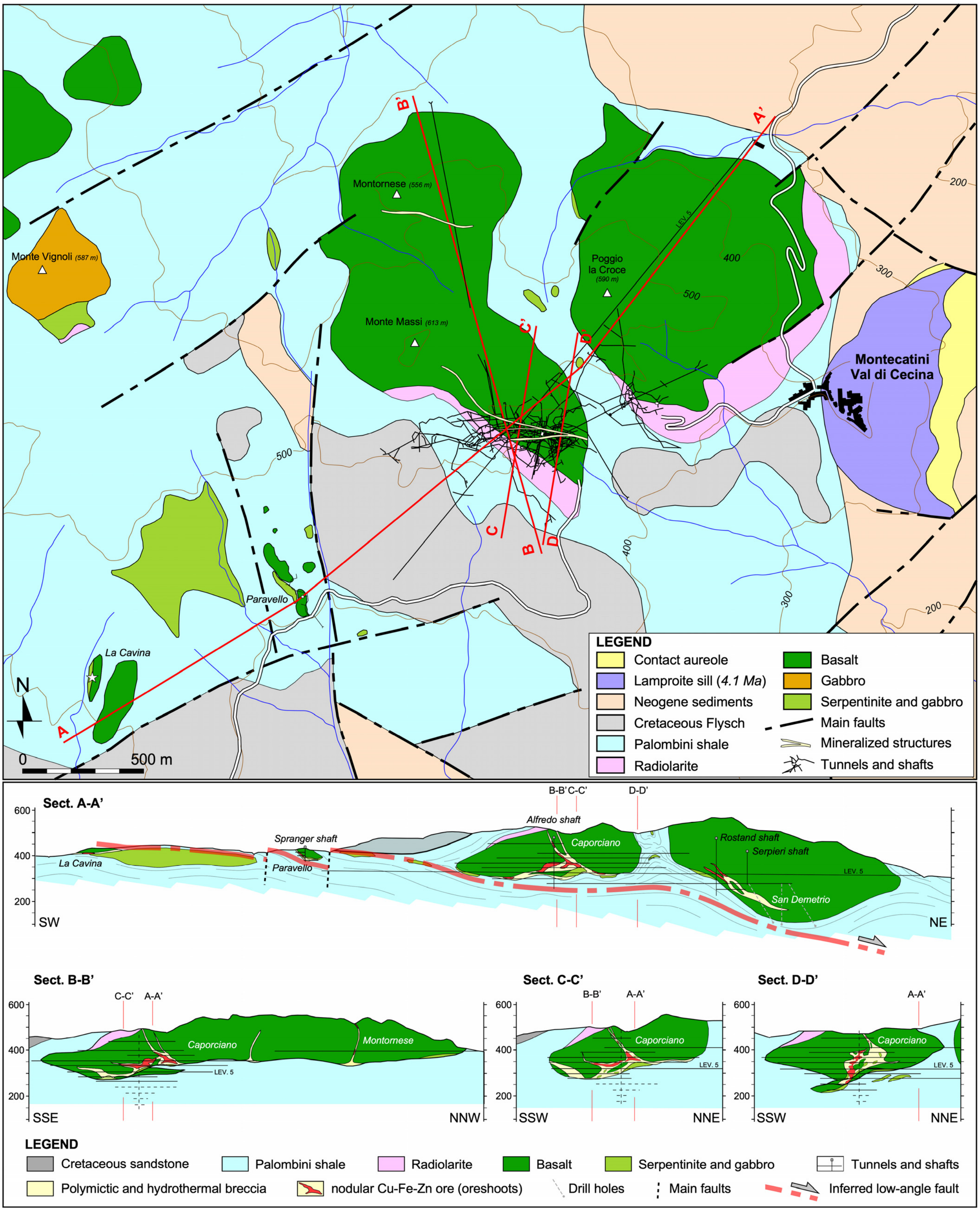

Figure 10. Interpretive geological map and cross sections (red traces in the map) of the Montecatini Val di Cecina area showing the local geological setting of the T3-type ores exploited by the MVC mine (modified after http://www502.regione.toscana.it/geoscopio/geologia.html, accessed on 10 August 2023, on the base of old mining reports/maps and new detailed mapping at surface and sub-surface).

The main MVC orebody (Caporciano) was discovered by digging into an E-W trending belt made by anastomosed breccia dykes, a few hundred meters long, hosted in strongly chloritised pillow basalts (Figures 10 and 11A). The two main mineralized structures, variably interconnected and separated by basalt septa, were very narrow at the surface (1–100 cm thick). In the most superficial part, the basalt host had undergone considerable oxidation, which is responsible for the typical red colouring to which the mining slang, yet misleading term, "gabbro rosso" is due. The matrix-supported breccia dykes contained abundant angular to rounded clasts, up to several centimetres across, of altered basalt, chalcocite, bornite, and chalcopyrite, in a pale green–red soapy chlorite matrix [35,50]. Native copper leaves and Cu carbonates/chlorides were also frequent. Chalcocite, native copper, and Cu carbonates/chlorides rapidly declined at depth, leaving an ore mineral association dominated by chalcopyrite, bornite and minor chalcocite, sphalerite, and pyrite. The two E-W-trending breccia dykes, steeply dipping to the north, maintained a limited thickness from the surface (477 m a.s.l.) down to the second mining level (390 m a.s.l.), where they merged into a single monomictic breccia body (Figures 10 and 11C), up to 50 m thick and 500 m long.

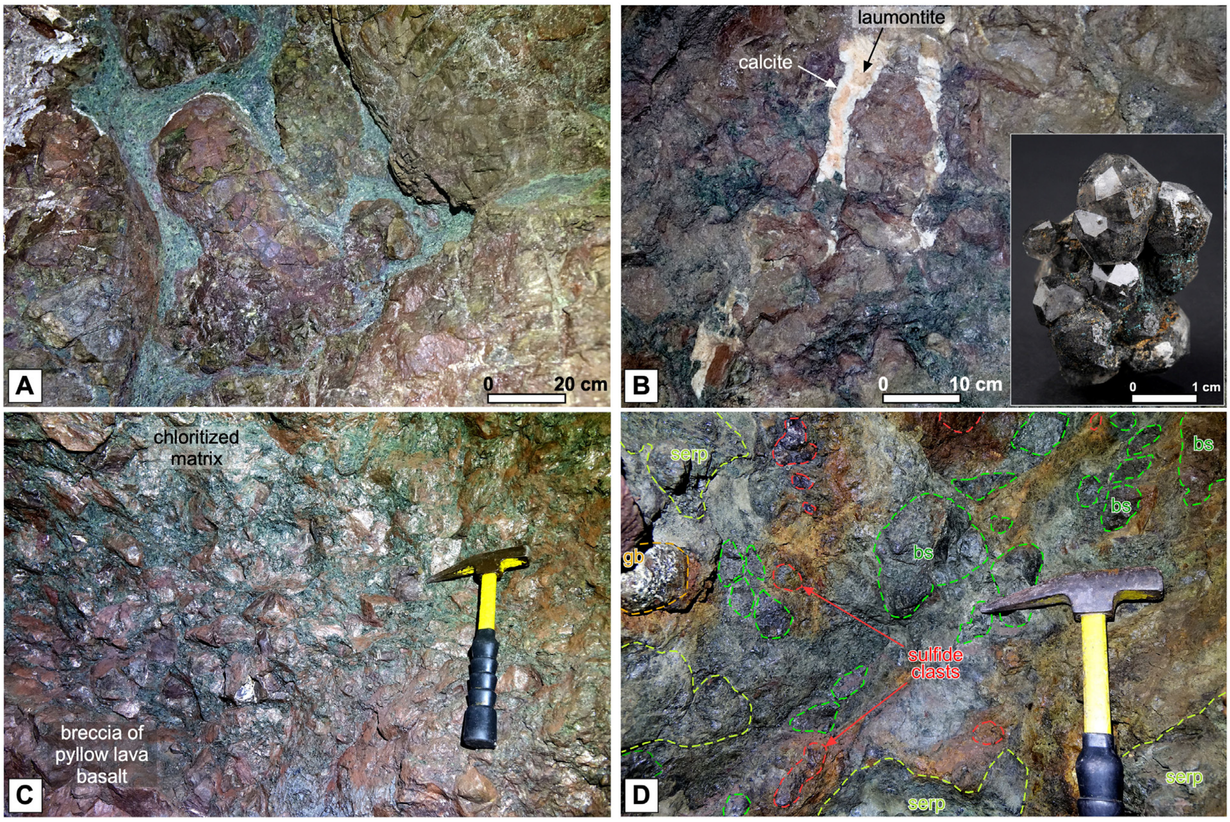

Figure 11. Host rocks and orebodies from MVC mine (T3-type ore): (**A**) epidotized pillow basalts embedded in a strongly chloritized matrix, Level 5 tunnel; (**B**) late calcite-zeolite veins crosscutting the mineralized monomictic breccia at Level 2. The inset shows a cluster of icositetrahedral crystals of analcime, embedding micro-fragments of bornite and chalcopyrite, from a calcite-natrolite-analcime vein crosscutting a large sulphide clast; (**C**) monomictic basalt breccia at Level 2; and (**D**) mineralized polymictic breccia from Level 3 (bs: basalt; gb: gabbro, serp: serpentinite).

From here down to the fourth level (345 m a.s.l.), although the deposit was still hosted by chloritized basalt, more and more exotic clasts of altered serpentinite and gabbro appeared and the breccia matrix became more heterogeneous, with colour variations from light green to whitish to dark green (chlorite, Ca-amphibole, talc; Figure 11D). At the third level (367 m a.s.l.), this polymictic breccia body became steeper and it reached its maximum dimensions (750 × 80 m; Figure 11D), showing the highest concentrations of ore.

The MVC bonanza contained huge amounts of clasts (millimetric to plurimetric in size) of almost pure chalcopyrite-bornite massive aggregates, as well as clasts of serpentinite and gabbro hosting high-grade chalcopyrite-bornite stockworks and disseminations. Massive sulphide clasts larger than 1 cm, although rounded, showed an irregular shape, suggesting their derivation from the re-working of original angular sulphide clasts. Locally, clusters of clasts were found whose reciprocal shape and distribution appeared to be arranged in the form of a jigsaw puzzle, reminiscent of the shape of a continuous tabular body of massive sulphide. Such a clusterized pattern was used by miners to chase the high-grade ore shoots for many meters along strike. The southern wall of the deposit, made by basalt, locally hosted large, rounded cavities filled by brecciated ore associated with veinlets of sulphides propagating into the host rock. At least half of the copper production at MVC came from the fine-grained sulphide clasts dispersed in the breccia matrix and from the clasts of stockwork-dissemination ore [50]. Between the third and fourth levels (345 m a.s.l.), the mineralized polymictic breccia body acquired a gently dipping attitude and began to follow the original basal contact of the basalt with the underlying serpentinite and gabbro basement. Large, pluri-decametric lenses of serpentinite and gabbro outlined the bottom of the MVC deposit and the lower tectonic contact between basalt and shales. Serpentinite and gabbro also occurred as isolated lenses dispersed in the orebody and into the footwall shales. At the fifth level (321 m a.s.l.), the size of the deposit decreased greatly (400×40 m), as did the metal content. The ore body, which, up to this point, had shown an extraordinary amount of chalcopyrite and bornite clasts, became progressively less rich in ore, and the bottom of the ore deposit was locally in tectonic contact with the shales. Nonetheless, scattered concentrations of sulphide clasts were found down to the eighth level (225 m a.s.l.), where a single block of massive chalcopyrite-bornite of 2000 t (>400 m^3) ended the MVC bonanza. Other basalt-hosted, low-grade breccia bodies were discovered in the 19th century during the exploration of the MVC deposit: the Montornese and the San Demetrio orebodies, respectively, to the north and to the east of the main Caporciano orebody (Figure 10).

The overall data from the literature [35] and our new observation at the surface and in underground tunnels indicate that T3-type ore developed mostly in a monomictic-polymictic breccia body (basalt $\pm$ serpentinite and gabbro), hosted by pillow basalt, close to the contact with the serpentinite-gabbro basement. Nonetheless, mineralization propagated upward into the basalt, developing thinner breccia dykes and, where original stratigraphy was preserved, they were eroded and mantled by the sediments of the Jurassic Ocean (radiolarite). The accurate projection of all the mining data (see cross sections in Figure 10) clearly indicates that, despite the variable orientation of the orebody, massive sulphide clasts were asymmetrically distributed, being strongly concentrated towards the southern wall of the deposit, i.e., in the original upper part of the breccia body. Finally, the lack of any Cu-Fe-Zn sulphide veins/disseminations in the tectonized shale that embeds the ophiolite-VMS lens suggests that the tectonic deformation during the Apennine orogenesis did not produce any significant chemical re-mobilization of Cu-Fe-Zn sulphides. This is consistent with the very low-grade metamorphism experienced by the Ligurian units and their shallow and distal position with respect to the Mio-Pliocene magmatic-hydrothermal systems that characterize the southern part of Tuscany (Figure 1). Even the nearby lamproite subvolcanic intrusion (4.1 Ma), on which the village of Montecatini Val di Cecina was built, produced negligible metamorphic-hydrothermal effects in the clay sediments at the top of the small laccolith.

3.3.2. Ore-Gangue Mineralogy and Textures

A description of the sulphide clasts/nodules of T3-type ore is provided by 19th-century authors, while the only modern petrographic description (reflected light) is reported in [43]. Bernardino Lotti gave a comprehensive description of the orebody geometry and host rocks, as well as a detailed macroscopic description of the sulphide clasts that match the characters of historical specimens in Mineralogical Museums (Figure 12) [35].

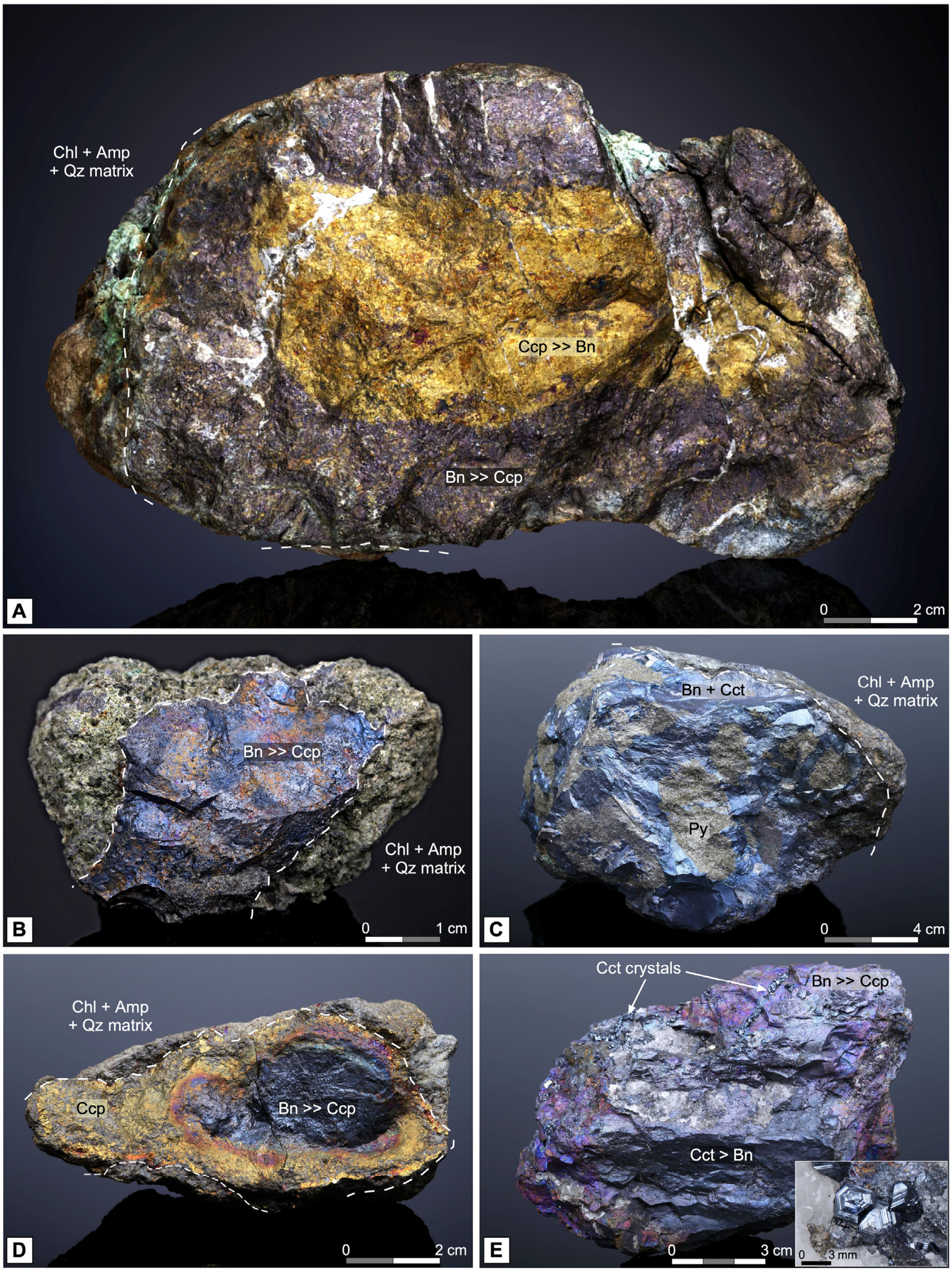

Figure 12. T3-type ore samples from MVC deposit provided by the Natural History Museum of Pisa University: (**A**) a typical, zoned, rounded clast with a chalcopyrite-rich core (Ccp) and a bornite-rich border (Bn); (**B**) an irregular clast of bornite-chalcopyrite wrapped into the chlorite-amphibole matrix; (**C**) an unusual, complex, clast made by pyrite aggregates cemented by bornite and chalcocite (Cct); (**D**) an example of the rare clasts showing reversal mineralogical zoning; and (**E**) a fragment of a large bornite-chalcopyrite clasts showing a pervasive replacement by chalcocite (Cct). Idiomorphic, twinned crystals of chalcocite (see the inset) occur in late fractures partially filled by calcite.

Most of the ore was composed by rounded, flattened clasts (from 1 cm up to several meters) made up of a core of chalcopyrite and a thick rim of bornite (Figures 12A, 13 and 14). There are examples of clasts formed by bornite alone or containing small chalcopyrite cores. Sulphide clasts with reversal zoning (Figure 12D) and a more complex brecciated structure (Figure 12C) are extremely rare. The bornite shell of the common clasts shows a highly variable thickness, and its outermost zone is intimately intergrown with gangue minerals (quartz, chlorite, Ca-amphibole, talc, and titanite; Figure 15). The same gangue minerals may also occur in the inner part of the clasts, although many of them are made exclusively of massive sulphides. The huge, tabular block of massive sulphides found at Level 8 (400 m^3), despite its larger size and different geometry, showed a similar concentric structure. Again, bornite formed the outer shell, as well as a network of interconnected structures embedding polyhedral volumes of chalcopyrite [35,50].

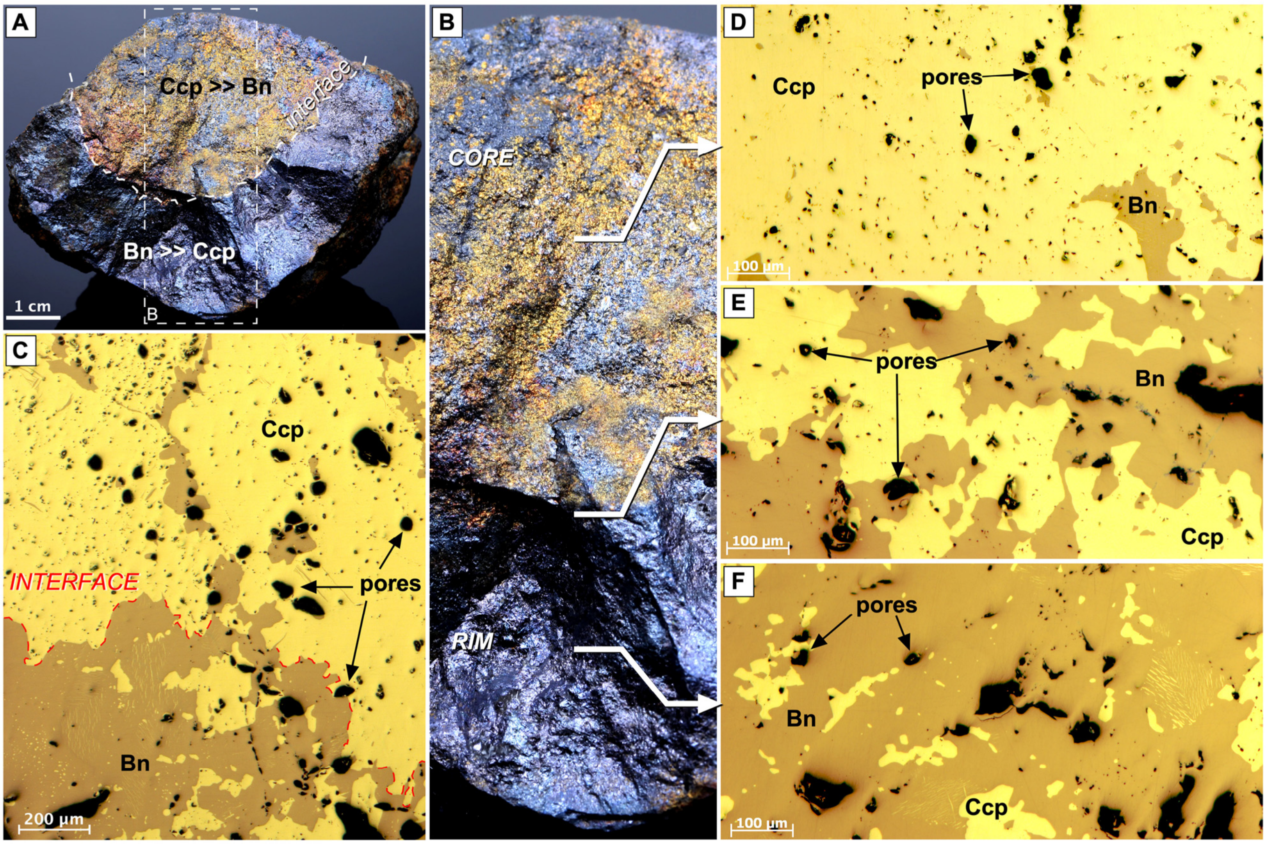

Figure 13. Textural details of the T3-type ore from MVC mine: (**A**) typical zoned clast (half) with chalcopyrite (Cpy) core and bornite (Bn) rim; **(B**) detail of the ore nodule; (**C**) reflected light detail of the interface between the Cpy and the Bn zones. Note the widespread porosity of the massive sulphides; and (**D**–**F**) reflected light details of the core, intermediate and rim zones of the sulphide nodule.

At the microscopic scale, the chalcopyrite cores and bornite shells appear to be more complex than macroscopically observed. Chalcopyrite cores contain a significant amount of bornite and vice versa. The interface between the two zones is indented and the chalcopyrite-bornite intergrowth does not change textural pattern, varying only the relative proportions of sulphides (Figure 13). The grain size ranges from sub-micrometric to few mm and the sulphides are riddled with many pores of a variable shape (ramified, rounded, and polyhedral) and size (from sub-µm up to 500 µm), sometimes arranged in arrays and clusters (Figures 13 and 14). There is clear textural evidence for the replacement of chalcopyrite by bornite, starting from the edge of crystals in cavities and along fractures and the crystallographic planes of chalcopyrite grains (Figure 14A). These textures were already described by previous authors [43].

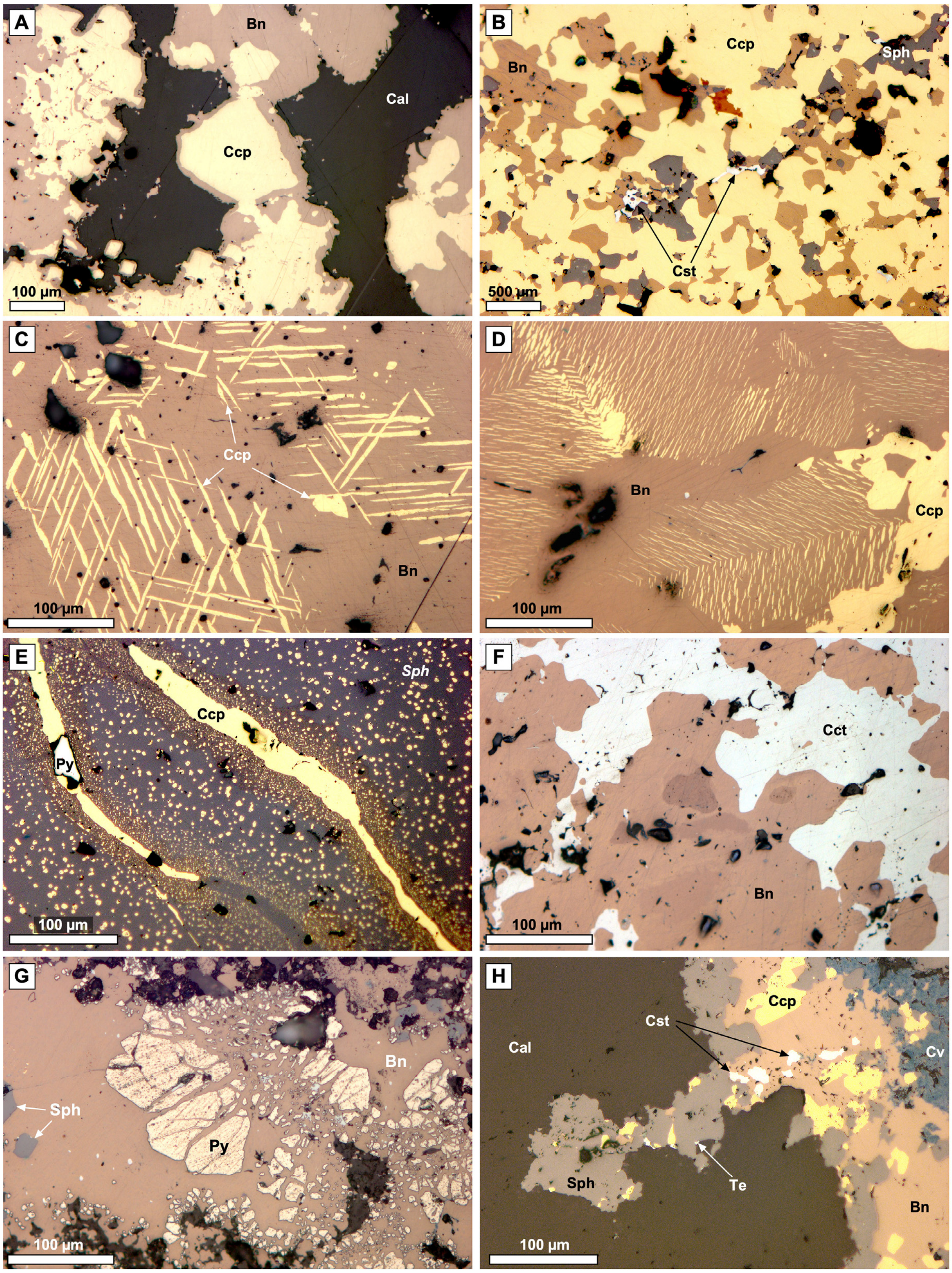

Figure 14. Textural details of the T3-type ore from MVC mine (reflected light): (**A**) chalcopyrite crystals (Cpy) replaced by bornite (Bn), from a cavity with calcite infill; (**B**) typical intergrowth of bornite, chalcopyrite and sphalerite (Sph) with some clausthalite (Cst); (**C**) bornite-chalcopyrite with lattice intergrowth texture; (**D**) another example of lattice-controlled texture between bornite and chalcopyrite; (**E**) chalcopyrite-pyrite veinlets cutting through earlier sphalerite inducing a spectacular "chalcopyrite-disease" effect; (**F**) bornite and chalcocite (Cct) intergrowth texture; (**G**) bornite replacing and cementing pyrite crystals; and (**H**) clausthalite and tellurium (Te) grains in a bornite-chalcopyrite-sphalerite aggregate.

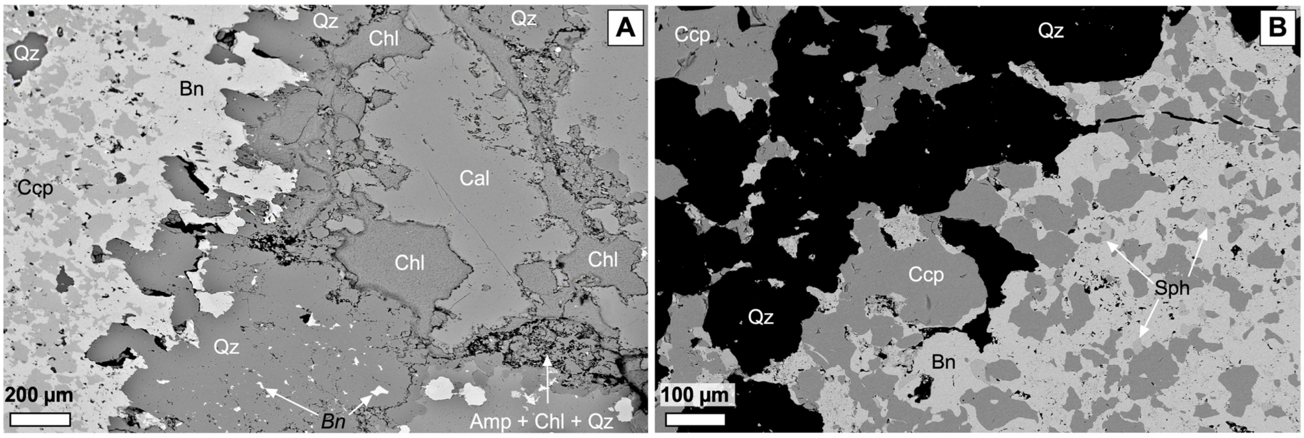

Figure 15. Textural details of the T3-type ore from MVC mine (SEM-BSE): (**A**) at the rim of sulphide nodules, bornite is intergrown with quartz, chlorite, and calcic amphibole. The external cavities show a sequential infill: first quartz, then amphibole + chlorite followed by chlorite alone. The residual voids were later filled by calcite; (**B**) gangue minerals, and clasts of strongly altered rocks, also occur in the internal part of sulphide nodules. In this case, subhedral-euhedral crystals of quartz form ribbons and clusters cemented by bornite, chalcopyrite, and sphalerite.

However, most of the chalcopyrite-bornite aggregates, in both the cores and shells, are mutually intergrown and interembayed (Figures 13 and 14B). The bornite of some zoned nodules is characterized by a ubiquitous lattice intergrowth texture with chalcopyrite spindles, lamellae, dendrites, and irregular grains (Figure 14C,D). The size of the chalcopyrite lamellae varies from extremely fine to coarse and, locally, they coalesce in continuity with the larger grains, forming the main intergrowth pattern.

Sphalerite is a ubiquitous mineral in MVC T3-type ore, but its modal abundance is highly variable. It occurs as isolated grains and larger microgranular aggregates in chalcopyrite, as well as in the bornite-chalcopyrite intergrowths. In few samples, coarse-grained aggregates of sphalerite are brecciated and cemented by chalcopyrite + pyrite. In this case, sphalerite is characterized by a pervasive "chalcopyrite disease" (Figure 14E). Pyrite is unevenly distributed: some nodules contain considerable amounts, but, in most cases, it is absent or rare. This sulphide occurs as relics of microgranular aggregates of subhedral-euhedral crystals brecciated and embedded in the bornite-chalcopyrite mass, and in cubic euhedral crystals associated with chalcopyrite (Figure 14G). Chalcocite has been considered, in the past, as a common mineral in the MVC deposit. However, the SEM-EDS study of the dark blue–black nodules in the historical collection of Pisa University Museum, classified as massive chalcocite, indicates that they are formed by an intimate intergrowth of chalcocite and bornite dominated by the latter one (Figure 14F). Only a few late veins and idiomorphic crystals in the fissures consist of pure chalcocite (Figure 12E).

Accessory minerals, already reported by previous authors [43], are hematite, magnetite, marcasite, covellite, and digenite. These authors also described small grains of a white sulphide (parallel polars) that was tentatively identified as galena. The new SEM-EDS study established that the frequent white grains of high reflectance (sub-µm to few tens of µm), generally embedded in bornite-rich zones, are not galena, but rather a mineralogical association including clausthalite, hessite, native tellurium, and, rarely, electrum/native gold (Figure 14B,H). This Te-Se-Ag-Au-Pb mineral association is like that described for the T2-type nodular ore in Montecastelli.

Gangue minerals are represented by quartz, chlorite, Ca-amphibole, talc, titanite, calcite, and zeolites. Quartz is unevenly distributed as subhedral-euhedral crystals (50–500 µm) embedded in sulphides (Figure 15B) and cryptocrystalline aggregates with chlorite and amphibole (Figure 15A). Iron-rich clinochlore dominate in the monomictic basalt breccia of the uppermost mining levels, while Ca-amphibole, talc, and titanite appear in the polymictic breccia in the lower levels (XRD and SEM-EDS from this study and [43]). These minerals are embedded in sulphides and mechanically re-worked into the fine-grained matrix of the breccia. Calcite, together with zeolites (analcime, laumontite, and natrolite) and datolite, occur as late infills of sulphide porosity and fractures in nodules and host rocks (Figure 11B) [35,51].

4. Discussion

A discussion of the overall data presented is now provided to re-evaluate the geological–mineralogical–geochemical characters of these deposits in the context of the available models on oceanic SMS deposits and VMS analogues implicated in orogenic belts. Far from being an exhaustive discussion, it is intended to be an updated framework to stimulate new detailed scientific research on these easily accessible natural analogues of oceanic hydrothermal systems. Four themes were addressed in the discussion: the effects of the Apennine orogeny on the Tuscan VMS, the origin of the mineralogically zoned nodules of the T3-type ore, the implication of their geochemical signature, and a possible genetic scenario of the deposits in an OCC context.

4.1. The Tuscan VMS Deposits in the Northern Apennine Framework

The overall geological, mineralogical, and geochemical characters of the ophiolite-hosted Tuscan Cu-Zn deposits are compatible with their derivation by the tectonic fragmentation of oceanic massive sulphide deposits (SMS) formed along the slow spreading ridge of the Jurassic Piedmont-Ligurian Ocean. They are hosted near the transition zone between the serpentinite-gabbro basement and the overlying basalts, and they are part of ophiolitic lenses that still preserve portions of the original sedimentary cover. Chalcopyrite stockworks and disseminations (T1-type; e.g., Trossa Valley) and their mechanically chemically reworked analogues (T2-type; e.g., the bornite-chalcopyrite Montecastelli ore) are mostly hosted in serpentinites intruded by gabbro tabular intrusions and dolerite dykes. The largest deposits of this area (T3-type; e.g., the bornite-chalcopyrite Montecatini Val di Cecina ores) are hosted in polymictic-monomictic breccias, partly interlayered with pillow basalt, directly in contact with the serpentinite-gabbro basement. All the most important Tuscan VMS deposits formed in sub-seafloor conditions (Figures 2, 6, 8, and 10). Unlike in the nearby Liguria mining district, in Tuscany, there are no large deposits formed on seafloor either during the progressive accumulation of pillow basalt or at the top of the volcanic pile itself (e.g., Libiola, Reppia, and Corchia deposits in Liguria) [37].

The apparent lack of major ore deposition on the seafloor is not the only distinguishing feature of the Tuscan district. Tuscan chalcopyrite stockworks-disseminations (T1-type) have similar sub-seafloor oceanic counterparts in Liguria, but Tuscany's reworked deposits (T2 and T3), with their bornite-rich association, constitute a prominent and distinctive character (Figures 4, 5, and 12). The mechanical and chemical reworking of the latter ores occurred in breccia volumes (T3-type) and along cataclastic zones (T2-type) that are clearly cut and offset by deformational structures—both compressional and extensional—related to the Apennine orogeny and its post-collisional evolution. As already stated, evidence of the chemical remobilization of Cu-Fe sulphides during the northern Apennine tectonic evolution is lacking and it is consistent with the very-low-grade regional metamorphism experienced by the Ligurian Units.

Klemm and Wagner [36] hypothesized that the unusual mineralogical paragenesis of the Tuscan VMSs was acquired during the hydrothermal remobilisation of "normal" pyrite-chalcopyrite VMSs, promoted by the emplacement of Miocene-Pleistocene granite intrusions into the shallow crust (Tuscan Magmatic Province; Figure 1). However, this hypothesis is not sustainable for two reasons (Figure 1): (1) the area of the occurrence of Tuscan VMS deposits is predominantly outside the Tuscan Magmatic Province; and (2) the few deposits close to igneous intrusions (Aia, Ogliera; Figure 1) that experienced metamorphic and hydrothermal effects maintained the pyrite-chalcopyrite paragenesis. In this framework, the spatial proximity of the MVC deposit to the small lamproite laccolith

(Figure 10) is purely coincidental, given also the minimal thermal–hydrothermal effects experienced by the Pliocene sediments at the upper contact of the intrusion [49].

Thus, the peculiar character of the ophiolite-hosted Tuscan Cu-Zn VMSs is not related to the Apennine orogenic and post-collisional events. It must have been acquired before the Upper Cretaceous, because similar ores occur in the External Liguride formations [37]. The most striking example is the bornite-rich deposit of Bisano (Emilia Romagna; Figure 1), hosted in ophiolitic olistoliths sedimented in Upper Cretaceous shales, and now exposed 90 km to the northeast of the study area. In the second half of the 1800s, hundreds of tons of bornite-chalcopyrite ore were extracted here, including a massive bornite block of ca 10 m^3 [52,53].

The geological cross sections from Figure 10 give the opportunity to discuss, at a local scale, the late tectonic evolution of the ophiolite lenses embedded in the Palombini shales (Internal Ligurian Unit). The cross sections clearly show how the basalt lens that hosts the MVC deposit and the serpentinite-gabbro lenses at its base can be restored to the serpentinite outcrop occurring about 1.5 km to the WSW (La Cavina-Paravello area) by an inferred low-angle fault with a top-down-to-the-east sense of displacement. This interpretation is also consistent with the occurrence of small relics of Cu-Fe-Zn ore along the exposed serpentinite-gabbro basement. Furthermore, the MVC basalt lens has been fragmented into two blocky boudins with convex exteriors (torn boudins [54]) and the enveloping foliation of Palombini shale was symmetrically drawn into the inter-boudin zone to varying degrees, resulting in scar folds. The absence of hydrothermal veining in the inter-boudin zone is further evidence for the scarce capacity of Apennine tectonic processes, when acting far from Miocene-Quaternary magmatic-hydrothermal activity, to produce important chemical remobilization effects.

All these deformational features are consistent with the extensional tectonics that have affected this area since the Middle–Late Miocene [23]. The net result was the lateral segmentation of the previously stacked units and the boudinage of the competent ophiolite blocks embedded in the incompetent shales of the Internal Ligurian units. The extreme geographic dispersion of the small Tuscan VMS deposits (ca. 20 occurrences over an area of 250 km^2) would seem related to the complex tectonic evolution, rather than to a hypothetical high spatial frequency of small hydrothermal systems in the original Jurassic oceanic crust.

4.2. The Zoned Sulphide Nodules (T2- and T3-Type Ores)

The unusual texture of the sulphide nodules in many of the Tuscan VMS deposits has fuelled scientific debate since the mid-1800s. Concentrically zoned nodules with chalcopyrite at the core and bornite at the rim from MVC were interpreted as being the result of: (1) sequential precipitation (cockade texture; [44]); and (2) desulfurization and Fe removal from chalcopyrite [45,55,56]. Reyer [45] attributed the process to the action of oxidizing aqueous fluids, while Mazzuoli [56] invoked electrolytic effects induced by unspecified electric currents. The few modern authors have not remarked on this texture.

The descriptions left by Lotti [35] and Schneider [50] leave no doubt. The large tabular blocks (up to 2000 t) of chalcopyrite with bornite at the edges and along the fractures clearly indicate that this is a fluid-mediated process of chalcopyrite replacement by bornite. The same is true for the smaller nodules preserved in historical museum collections (Figure 10). The fact that the smallest grains/nodules dispersed in the breccia matrix do not contain cores of relic chalcopyrite reinforces this interpretation [35].

The petrographic analysis produced in this study offers further details. First, the cores and shells do not consist of pure phases, but rather of mixtures of chalcopyrite and bornite, with the former dominant in the core and the latter in the shells. Then, the microtextural relationships between the two phases do not give unambiguous indications. Most chalcopyrite–bornite aggregates in both cores and shells are mutually intergrown and inter-embayed. In addition, bornite is characterized by ubiquitous lattice intergrowth texture with spindles, lamellae, dendrites, and irregular grains of chalcopyrite. In several cases, the geometric pattern of chalcopyrite lamellae transition to more irregular thicker dendrites, eventually blending in a single large grain. Similarly, chalcopyrite also shows analogous textures involving bornite spindles and lamellae.

The coexistence of the two minerals and their mutual intergrowth suggest near-equilibrium conditions, while lattice intergrowth textures are less easily interpretable. Similar lattice intergrowth textures between bornite and chalcopyrite were initially interpreted in terms of solid-state exsolution or unmixing processes [57]. Conversely, more recently, these textures have been interpreted as replacement reactions, mediated by hydrothermal fluids and driven along preferential lattice planes [58]. Because of the growing interest in the in situ recovery of copper, numerous experiments have been conducted to define the conditions for transforming more refractory sulphides into easily leachable ones [58,59]. These authors [58] investigated the fluid-mediated replacement of chalcopyrite by bornite between 200 °C and 320 °C in cuprous-chloride buffered solutions and they discussed, in detail, the reaction mechanism in terms of interface coupled dissolution–precipitation (ICDR; [60]). The textures obtained experimentally were strikingly like those observed in T2- and T3-type ores, as well as to those reported by other authors for massive sulphides from the Indian Ocean seafloor hydrothermal vents [61]. The replacement of chalcopyrite by bornite via an ICDR process is a viable process in the Tuscan VMSs, however, the exact mechanism involved—Fe removal vs. Cu input or a coupled mechanism—still needs to be clarified.

The propagation of the ICDR reaction is mediated by fluids and, therefore, a certain porosity (fractures and pores) should be maintained during the replacement process. The numerous pores observed in MVC sulphide nodules could be a witness to the essential pathways for fluid and mass transport between the bulk solution and reaction front [60]. Even the preferential distribution of clausthalite, tellurium, hessite, and gold/electrum grains in the bornite-rich shell of the T2- and T3-type ore nodules could be related to the ICDR process (Figure 14). The question to solve is the origin of these energy-critical and precious metal (Te, Se, Au, and Ag). They could be either remobilised from the primary sulphide (chalcopyrite ± pyrite) or introduced by the fluid responsible for the ICDR process itself. Further geochemical studies on bulk samples and in situ minerals will be able to clarify these aspects and, consequently, also the potential for energy-critical and precious metals of this type of deposits.

The chemical reworking of primary ores could result from multi-stage mineralisations, as observed in several ultramafic-hosted VMSs [14]. This is consistent with the complex hydrothermal evolution of OCC at slow spreading ridges and with evidence of multi-stage serpentinization [27] and Si-Ca-Fe-Mg metasomatism [32,62]. The off-axis emplacement of gabbroic magma within the footwall of collapsing OCC could possibly trigger secondary hydrothermal systems that overprint earlier ore concentrations [63].

4.3. Geochemical Signature of Tuscan vs. Ligurian VMS Deposits

The Tuscan VMS deposits display peculiar mineralogical–geochemical characters with respect to the better-known deposits from the Liguria district [37]. The geochemical exploration data plotted in Figure 4 (bulk rocks; [13]) visualize the difference, and the diagrams from Figure 16 provide additional insights. The Tuscan ores have highly variable Co/Ni ratios (from 0.03 up to 4; Figure 16) that strongly increase in high-grade samples (above 1% Cu), especially those from T1- and T3-type ores. Co/Ni ratios even higher than those in Tuscany are reached by ores from the Ligurian district. Such behaviour is well-known in ultramafic- and hybrid mafic/ultramafic-hosted VMSs and SMSs, where the maximum Co/Ni values are recorded by the most mineralised samples [64,65]. However, such high ratios are associated with very different Co and Ni concentrations for the Ligurian and Tuscan districts. Tuscan ores show concentrations of few tens of μg/g, rarely a few hundreds, of both metals that are comparable with the concentration in many oceanic VMSs and SMSs. The Ligurian district has both cobalt and nickel much higher than the Tuscan one, and the extreme Co/Ni values are controlled by the very high cobalt concentration of some deposits (Figure 16; e.g., Corchia mine with Co up to 4200 µg/g). This is consistent with the extreme cobalt enrichment in pyrite from Corchia deposits (up to 1.5 g/g; [18]) and other seafloor deposits at slow spreading ridges (Rainbow and Ashasze ultramafic-hosted systems) [15,65]. For the same copper concentration, Tuscan ores (Cpy-Bn rich) have a lower sulphide content than Ligurian ores (Py-Cpy rich), so the higher Co and Ni concentrations of Ligurian ones cannot be attributed to a major contamination from host rocks (Figures 4 and 16).

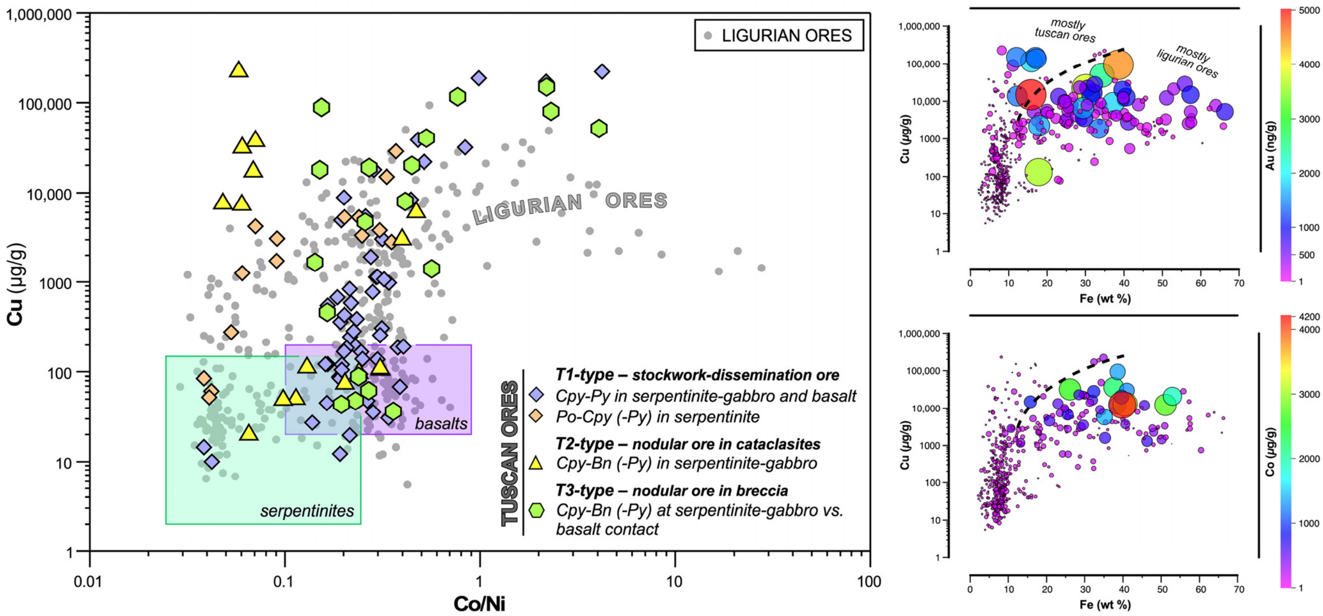

Figure 16. Logarithmic Cu vs. Co/Ni ratio diagram showing the Rimin exploration data set [13]. Both Ligurian and Tuscan minerals show a strong increase in Co/Ni ratio in samples with high copper contents. Bubble diagrams highlight the very distinct behaviour of Tuscan and Ligurian minerals. The Ligurian high-grade ores achieve high Co/Ni ratios in parallel with strong cobalt (and nickel) enrichment. In contrast, the Co/Ni variability in Tuscan ores does not correlate with a significant increase in cobalt. Gold concentration in both Ligurian and Tuscan ores tends to increase in ores with higher copper content.

The claimed difference between high-Co/Ni mafic- and low-Co/Ni ultramafic-hosted deposits [18,65] does not seem to be confirmed by the recent statistical treatment of VMS geochemical data [66]. Thus, although the nature of the substrate is likely to exert some control on the distribution of Ni and Co in SMS/VMS deposits, the Co/Ni ratio appears to have little discriminatory power. Other factors, like depositional temperature, physical-chemical conditions in the reactor zone, mineralisation intensity, and ore zone refining, may influence, to various extent, the concentrations of Co and Ni, masking the effects of substrate composition. Both Tuscan and Ligurian ores display a strong increase in Co/Ni ratio in high-grade samples/orebodies that is possibly consistent with a high mineralisation intensity [15]. However, the distinct Co and Ni concentrations in the two districts are less clear and still need to be investigated.

New investigations are needed to understand whether the chemical reworking of the Tuscan VMS (type T2 and T3) only produced an upgrade of Cu or also had effects on energy-critical/precious metals. A simple redistribution of Te, Se, Au, and Ag from the primary sulphides could have occurred, but a new addition of these metals by the fluid responsible for the chemical reworking cannot be discarded. Magmatic degassing from off-axis magmatic intrusions can be a potential source for such fluids, as suggested in the Semenov hydrothermal field [67], based on the occurrence of specific metal enrichment (Au, Ag, Se, Te, As, Sb, Tl, and Bi). Their emplacement could be controlled by faults developing during the collapse stage of the OCC [14,63].

4.4. Tuscan VMS and the Architecture of the Jurassic Oceanic Hydrothermal Systems

The orogenic and post-collisional Apennine tectonics segmented the ophiolites complicating the stratigraphic sequences but, at the same time, dissected the Jurassic magmatic-hydrothermal systems, making the sub-volcanic zone accessible for study. The Tuscan sub-seafloor deposits show a composite cross-section of the less accessible part of these systems (Figure 17) and, in the case of the MVC deposit, a concentration of cupriferous ore comparable in terms of metal content to the major seafloor deposits of the Ligurian district. The distinction between large, low-grade on-seafloor deposits in the Ligurian district and relatively large, high-grade sub-seafloor deposits in the Tuscan district could be merely coincidental, but lends itself to interesting speculation.

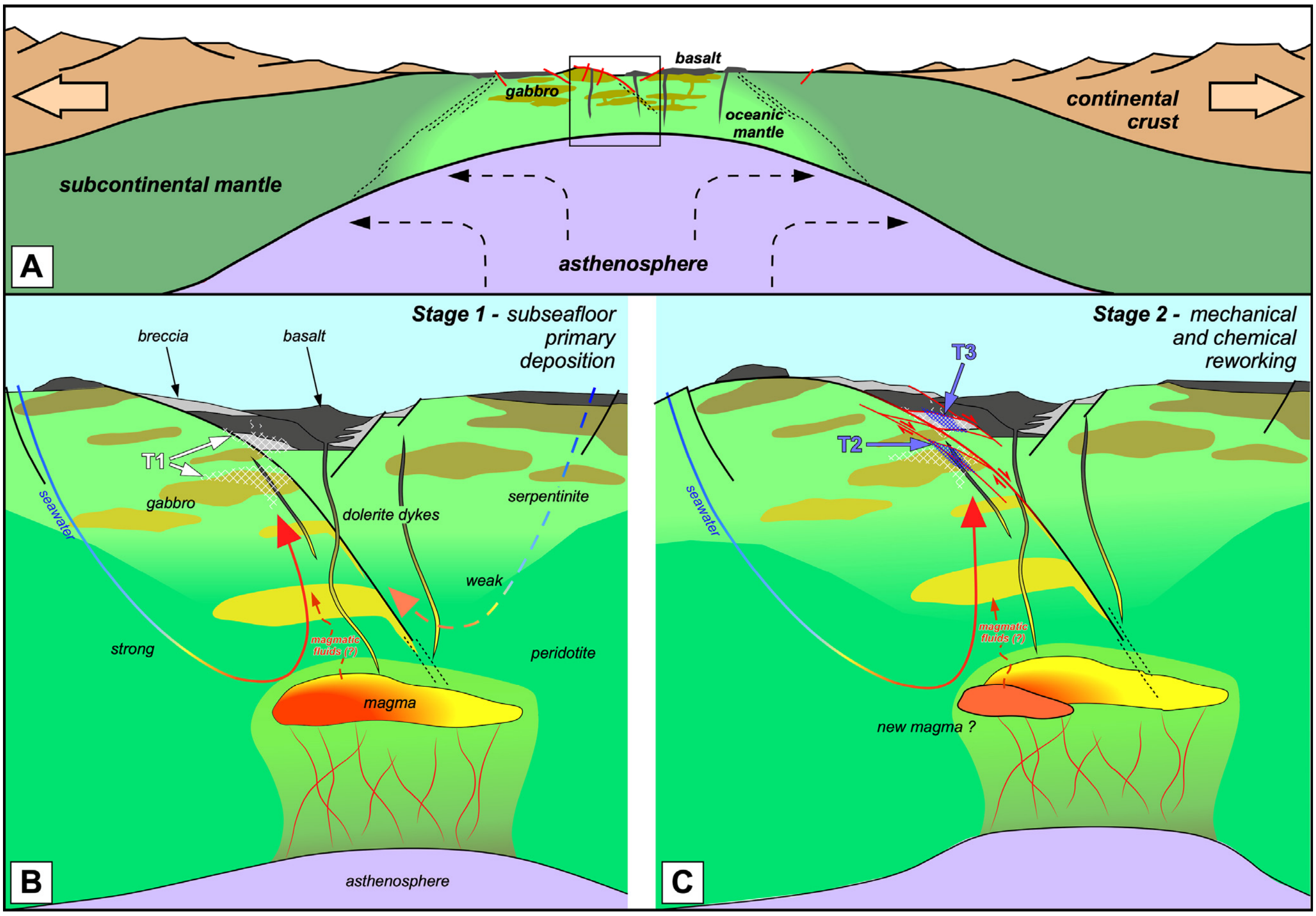

Figure 17. Schematic model of the formation of the mafic-ultramafic-hosted, Cu-Zn VMS deposits from Tuscany. (**A**) Schematic reconstruction of the heterogeneous lithosphere exposed in the Piedmont-Ligurian Ocean (modified after [16]). The box highlights the lithospheric portion enlarged in the model cartoons (**B**,**C**); (**B**) stage 1—sub-seafloor primary deposition: the T1-type ore formed by hydrothermal circulation in the footwall of the OCC detachment; and (**C**) stage 2—mechanical and chemical reworking: continuous exhumation of the footwall creates the conditions for a pervasive interaction with new fluids (magmatic fluids involved?). A substantial Cu upgrading of the ores is achieved at this stage.

Relatively large, low-grade, on-seafloor deposits could have been present in Tuscany, but perhaps they have been lost to erosion or are still buried in the Tuscan subsurface. The mineralized breccia dykes propagating upward, at the top of the MVC bonanza (Figure 10) could have reached the seafloor connecting to sulphide on-seafloor deposits.

However, it is possible that oceanic hydrothermal systems could be focused by OCC tectonics, dumping most of their metal load either into a single on-seafloor deposit or in a sub-seafloor one. Their coexistence, along the vertical of the same hydrothermal system, may not be obvious and is largely dependent on the competition between tectonic and magmatic processes. OCC activity induces a marked asymmetry of local portions of the slow spreading ridges. During the OCC stage, tectonic spreading dominates and magma is prevalently focused on the footwall of the system (gabbro intrusions and less basalt effusion). This modality and the normal magmatic spreading (formation of new mafic oceanic crust in the axial valley by magma focusing on the hanging-wall) alternate, producing the typical heterogeneity of slow spreading ocean floors [68]. A similar footwall–hanging-wall shift could be responsible for the prevalence of sub-seafloor and on-seafloor ores, respectively, in Tuscany (tectonic spreading) and Liguria (magmatic spreading). The Tuscan Cu-Zn VMSs may record a part of the OCC lifecycle, during which, the magmatic-hydrothermal activity was concentrated in the footwall of the detachment (Figure 17). In this case, the detachment and second-order cataclastic shear zones could act as structural traps preventing the fluids to be issued on the seafloor. Understanding the factors controlling the fluid-focusing at on-seafloor rather than at sub-seafloor levels would have important implications for VMS exploration strategies, as well as for the re-construction of oceanic paleoenvironments from ophiolite-VMS associations in orogenic settings.

Additional information is provided by the geo-mineralogical characteristics of the different ore types and host rocks described for Tuscan VMS deposits. T1- and T2-type ores are localized in serpentinite volumes that recorded a sequential story of magmatic injection, hydration, tectonic deformation, and multiple hydrothermal events. During the initial exhumation stage, the peridotites experienced reactive flow by undersaturated melts that produced dunitic channels (non-extrusive magmatic stage) [16,27,48]. Progressive exhumation and hydration to serpentinite was accompanied by the emplacement of dykes, sills, and laccoliths of gabbro, when the system was still at plutonic levels (plutonic magmatic stage) [16,48]. Further exhumation up to a subvolcanic level triggered additional hydration and the emplacement of the dolerite dyke swarms, together with the progressive accumulation of pillow lava at seafloor (subvolcanic–volcanic magmatic stage).

The hydrothermal process responsible for the primary mineralisation was triggered only in this stage (Stage 1 in Figure 17). Stockworks-disseminations and massive bodies of chalcopyrite + sphalerite + pyrite (T1-type ore and the precursor of T2- and T3-type ores) indistinctly overprinted serpentinite, gabbro, dolerite, polymictic-monomictic breccia, and pillow basalts, close to the contact between the serpentinite-gabbro basement and the overlying volcanic pile. The hydrothermal alteration produced a serpentine-calcic amphibole-quartz assemblage in serpentinite; gabbro was replaced by prehnite, calcic amphibole, and chlorite, while the basalt/dolerite rocks mostly experienced chloritization. A second hydrothermal stage concurred to re-work the primary ores, stabilising the bornite-rich assemblage and significantly upgrading the copper concentration of the ores (Stage 2 in Figure 17). Hydrothermal fluids were channelised along cataclastic shear zones in the serpentinite-gabbro basement (T2-type ore), as well as along the main contact with the overlying volcanic pile and in breccia bodies (T3-type ore; MVC bonanza). A different style of hydrothermal alteration developed at this stage. In addition to calcic amphibole and chlorite, the new mineral paragenesis included variable amounts of andradite, Fe-rich serpentine, talc, ilvaite, xonotlite, and titanite, depending on the rock type that underwent recrystallisation. Such a mineral assemblage is comparable to what is found in metasomatic rocks at the footwall of active detachments in OCC [62] and locally associated with ultramafic-hosted SMS deposits [64].

The integrated magmatic-tectonic-hydrothermal history recorded in the ophiolite-hosted Tuscan VMSs is consistent with an origin along the main detachment of a Jurassic OCC. The peculiar mineralogical–geochemical characteristics of these sub-seafloor deposits could be related to multiple hydrothermal events that were sequentially activated during the footwall exhumation of a collapsing OCC.

5. Conclusions

The Tuscan Cu-Zn VMS deposits, mostly hosted in the ophiolites of the Internal Ligurian units, were derived by the tectonic fragmentation of oceanic deposits formed along the slow spreading ridge of the Jurassic Piedmont-Ligurian Ocean, in proximity of the ocean–continent transition.

They represent a prime example of the sub-seafloor portion of a hybrid mafic-ultramafic oceanic hydrothermal system. Together with the deposits from the nearby Ligurian district, they provide an easy access to the roots of oceanic hydrothermal systems that are rarely well-preserved in orogenic ophiolites.

The Tuscan VMSs include primary chalcopyrite-pyrite stockwork-dissemination ore (T1-type), mostly hosted in serpentinite and gabbro, and bornite-rich ores (T2- and T3-type), hosted in serpentinite, gabbro, dolerite, and pillow basalts, produced by the mechanical and chemical re-working of T1-type ores.

The peculiar mineralogical–textural character of the bornite-rich ore (T2- and T3-type) was possibly acquired, during the oceanic evolution, through the fluid-mediated replacement of chalcopyrite by bornite driven by an interface coupled dissolution–precipitation process.

The high-grade Cu-Zn VMS deposits of Tuscany (T2- and T3-type) may represent the fossil analogue of a peculiar sub-type of hybrid ultramafic-mafic SMS deposits. They can be formed at subseafloor conditions when OCC tectonics allow for the mechanical and chemical reworking of sulphide ores by multiple injections of hydrothermal fluids.

A better understanding of these Cu upgraded ores would have important implications for VMS exploration strategies for Cu and energy-critical metals (Te, Se), as well as for the reconstruction of oceanic paleoenvironments from ophiolite-VMS associations in orogenic settings.

Ophiolitic olistoliths sedimented in the Upper Cretaceous sedimentary mélanges of the External Ligurian Units host disrupted portions of all the ore types, including bornite-rich ones. This is clear evidence that the unusual mineralogical paragenesis that characterizes the most important Tuscan VMSs was acquired before the Alpine and Apennine orogenic phases.

The geological reconstruction of the main Tuscan VMSs allowed for the identification of low-angle extensional faults displacing the volcanic portion of the ophiolite sequence from its serpentinite-gabbro basement. The deformation style and the sense of displacement match the post-collisional, extensional evolution proposed by previous authors for this part of the northern Apennine.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/min14030273/s1, Table S1: Selected geochemical data for Tuscan and Ligurian Cu-Zn VMS deposits; Method Chapter S1: Mapping and sample preparation, SEM-EDS and XRDP methods.

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Data Availability Statement: Old mining reports and maps used for this study are openly available in "DBGM—Data Base Geologico Minerario" (accessed on 20 February 2023) [https://www.pconti.net/dbgm] and the "Archivio Fotografico Montecatini" maintained by the Centro per la cultura d'impresa (accessed on 15 October 2022) [https://www.lombardiabeniculturali.it/archivi/complessi-archivistici/MIBA01ACC9/]. Reports, maps, and geochemical database (agreement No.

17—Mineralizzazioni nelle ofioliti) produced by RIMIN S.p.a. under the exploration program "Ricerca Mineraria di Base" of the Italian Ministry of Industry (Law No. 752, 6 October 1982, Art. 4) are part of the "Archivio RIMIN", available upon request from the "Ministero delle Imprese e del Made in Italy" (MIMIT).

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References

1. Dini, A. Ore deposits, industrial minerals, and geothermal resources. *Per. Mineral.* **2003**, *72*, 41–52.
2. Dini, A.; Gianelli, G.; Puxeddu, M.; Ruggieri, G. Origin and evolution of Pliocene- Pleistocene granites from the Larderello geothermal field (Tuscan Magmatic Province, Italy). *Lithos* **2005**, *81*, 1–31. [CrossRef]
3. Francovich, R.; Dallai, L. Colline Metallifere (Tuscany, Italy): Research and landscape enhancement of a mining district. *Archeosciences* **2010**, *34*, 277–287. [CrossRef]
4. Dini, A.; Boschi, C. I giacimenti cupriferi delle ofioliti toscane. *Riv. Mineral. Ital.* **2017**, *42*, 84–101.
5. Dini, A. I giacimenti minerari della Toscana. In *Guide Geologiche Regionali—Toscana*, 1st ed.; Conti, P., Conticelli, S., Cornamusini, G., Marroni, M., Eds.; Società Geologica Italiana: Roma, Italy, 2022; pp. 71–77.
6. Tanelli, G.; Lattanzi, P. Metallogeny and mineral exploration in Tuscany: State of the art. *Mem. Della Soc. Geol. Ital.* **1986**, *31*, 299–304.
7. Westerman, D.S.; Dini, A.; Innocenti, F.; Rocchi, S. Rise and fall of a nested Christmas-tree laccolith complex, Elba Island, Italy. *Geol. Soc. Lond. Spec. Publ.* **2004**, *234*, 195–213. [CrossRef]
8. Vezzoni, S.; Rocchi, S.; Dini, A. Lateral extrusion of a thermally weakened pluton overburden (Campiglia Marittima, Tuscany). *Int. J. Earth Sci.* **2018**, *107*, 1343–1355. [CrossRef]
9. Di Vincenzo, G.; Vezzoni, S.; Dini, A.; Rocchi, S. Timescale of a magmatic-hydrothermal system revealed by ^{40}Ar-^{39}Ar geochronology: The Mio-Pliocene Campiglia Marittima system (Tuscany, Italy). *Sci. Rep.* **2022**, *12*, 7128. [CrossRef]
10. Farina, F.; Dini, A.; Ovtcharova, M.; Davies, J.H.F.L.; Greber, N.D.; Bouvier, A.S.; Baumgartner, L.; Ulianov, A.; Schaltegger, U. Zircon Petrochronology reveals the timescale and mechanism of anatectic magma formation. *Earth Planet. Sci. Lett.* **2018**, *495*, 213–223. [CrossRef]
11. Gola, G.; Bertini, G.; Bonini, M.; Botteghi, S.; Brogi, A.; De Franco, R.; Dini, A.; Donato, A.; Gianelli, G.; Liotta, D.; et al. Data integration and conceptual modelling of the Larderello geothermal area, Italy. *Energy Procedia* **2017**, *125*, 300–309. [CrossRef]
12. Brogi, A.; Liotta, D.; Ruggieri, G.; Capezzuoli, E.; Dini, A.; Meccheri, M. An overview on the characteristics of geothermal carbonate reservoirs in southern Tuscany. *Ital. J. Geosci.* **2016**, *135*, 17–29. [CrossRef]
13. Rimin, S. Mineralizzazioni nelle ofioliti. In *Ricerca Mineraria di Base*; Italian Ministry of Industry: Roma, Italy, 1990; Volume 17.
14. Patten, C.G.C.; Coltat, R.; Junge, M.; Peillod, A.; Ulrich, M.; Manatschal, G.; Kolb, J. Ultramafic-hosted volcanogenic massive sulfide deposits: An overlooked sub-class of VMS deposit forming in complex tectonic environments. *Earth-Sci. Rev.* **2022**, *224*, 103891. [CrossRef]
15. Fouquet, Y.; Cambon, P.; Etoubleau, J.; Charlou, J.L.; Ondréas, H.; Barriga, F.J.A.S.; Cherkashov, G.; Semkova, T.; Poroshina, I.; Bohn, M.; et al. Geodiversity of hydrothermal processes along the Mid-Atlantic Ridge and ultramafic-hosted mineralization: A new type of oceanic Cu-Zn-Co-Au volcanogenic massive sulfide deposit. In *Diversity of Hydrothermal Systems on Slow Spreading Ridges–Geophysical Monograph Series 188*; Rona, P.A., Devey, C.W., Dyment, J., Murton, B.J., Eds.; American Geophysical Union: Washington, DC, USA, 2022; pp. 321–367. [CrossRef]
16. Rampone, E.; Sanfilippo, A. The heterogeneous Tethyan oceanic lithosphere of the Alpine ophiolites. *Elements* **2021**, *17*, 23–28. [CrossRef]
17. Bonatti, E.; Zerbi, M.; Kay, R.; Rydell, H. Metalliferous deposits from the Apennine ophiolites: Mesozoic equivalents of modern deposits from oceanic spreading centers. *Geol. Soc. Am. Bull.* **1976**, *87*, 83–94. [CrossRef]
18. Zaccarini, F.; Garuti, G. Mineralogy and chemical composition of VMS deposits of northern Apennine ophiolites, Italy: Evidence for the influence of country rock type on ore composition. *Mineral. Petrol.* **2008**, *94*, 61–83. [CrossRef]
19. Conti, P.; Cornamusini, G.; Carmignani, L. An outline of the geology of the Northern Apennines (Italy), with geological map at 1:250,000 scale. *Ital. J. Geosci.* **2020**, *139*, 149–194. [CrossRef]
20. Carminati, E.; Lustrino, M.; Doglioni, C. Geodynamic evolution of the central and western Mediterranean: Tectonics vs. igneous petrology constraints. *Tectonophysics* **2012**, *579*, 173–192. [CrossRef]
21. Elter, P. L'ensemble ligure. *Bull. Soc. Géol. Fr.* **1975**, *17*, 984–997. [CrossRef]

22. Marroni, M.; Meneghini, F.; Pandolfi, L. Anatomy of the Ligure-Piemontese subduction system: Evidence from Late Cretaceous–middle Eocene convergent margin deposits in the Northern Apennines, Italy. *Int. Geol. Rev.* **2010**, *52*, 1160–1192. [CrossRef]
23. Brogi, A.; Liotta, D. Highly extended terrains, lateral segmentation of the substratum, and basin development: The middle-late Miocene Radicondoli Basin (inner Northern Apennines, Italy). *Tectonics* **2008**, *27*, TC5002. [CrossRef]
24. Marroni, M.; Pandolfi, L. The architecture of an incipient oceanic basin: A tentative reconstruction of the Jurassic Liguria-Piemonte basin along the Northern Apennines–Alpine Corsica transect. *Int. J. Earth Sci.* **2007**, *96*, 1059–1078. [CrossRef]
25. Bertini, G.; Cornamusini, G.; Lazzarotto, A.; Maccantelli, M. Stratigraphic and tectonic framework of the Ligurian Units in the Castellina M.ma hills (southern Tuscany, Italy). *Boll. Soc. Geol. Ital.* **2000**, *119*, 687–701.
26. Nirta, G.; Pandeli, E.; Principi, G.; Bertini, G.; Cipriani, N. The Ligurian Units of Southern Tuscany. *Boll. Soc. Geol. Ital.* **2005**, *3*, 29–54.
27. Boschi, C.; Dini, A.; Baneschi, I.; Bedini, F.; Perchiazzi, N.; Cavallo, A. Brucite-driven CO_2 uptake in serpentinized dunites (Ligurian Ophiolites, Montecastelli, Tuscany). *Lithos* **2017**, *288–289*, 234–281. [CrossRef]
28. Tribuzio, R.; Thirwall, M.F.; Vannucci, R. Origin of the gabbro–peridotite association from the Northern Apennine ophiolites (Italy). *J. Petrol.* **2004**, *45*, 1109–1124. [CrossRef]
29. Rielli, A.; Boschi, C.; Dini, A. Tectonically driven carbonation of serpentinite by mantle CO_2: Genesis of the Castiglioncello magnesite deposit in the Ligurian ophiolite of central Tuscany (Italy). *Ore Geol. Rev.* **2022**, *149*, 105022. [CrossRef]
30. Serri, G.; Hébert, R.; Hékinian, R. Chemistry of ultramafic tectonites and ultramafic to gabbroic cumulates from the major oceanic basins and the Northern Apennines ophiolites. *Ofioliti* **1985**, *10*, 63–76.
31. Ferrara, G.; Innocenti, F.; Ricci, C.A.; Serri, G. Ocean-floor affinity of basalts from north Apennine ophiolites: Geochemical evidence. *Chem. Geol.* **1976**, *17*, 101–111. [CrossRef]
32. Coltat, R.; Branquet, Y.; Gautier, P.; Rodriguez, H.C.; Poujol, M.; McClenaghan, S.; Manatschal, G.; Boulvais, P. Unravelling the root zone of ultramafic-hosted black smokers-like hydrothermalism from an Alpine analog. *Terra Nova* **2019**, *31*, 549–561. [CrossRef]
33. Savi, P. Delle masse ofiolitiche toscane e delle miniere di rame che in esse si trovano. *Nuovo G. Lett.* **1839**, *38*, 67–94.
34. Meneghini, G. Della presenza del ferro oligisto nei giacimenti ofiolitici di Toscana. *Nuovo G. Lett.* **1860**, *37*, 47–80. [CrossRef]
35. Lotti, B. La miniera cuprifera di Montecatini (Val di Cecina) e i suoi dintorni. *Boll. Del R. Com. Geol. D'Ital.* **1884**, *15*, 359–394.
36. Klemm, D.D.; Wagner, J. Copper deposits in ophiolites of Southern Tuscany. *Ofioliti* **1982**, *2–3*, 331–336.
37. Garuti, G.; Bartoli, O.; Scacchetti, M.; Zaccarini, F. Geological setting and structural styles of Volcanic Massive Sulfide deposits in the Northern Apennines (Italy): Evidence for seafloor and sub-seafloor hydrothermal activity in unconventional ophiolites of the Mesozoic Tethys. *Bol. Soc. Geol. Mex.* **2008**, *60*, 121–145. [CrossRef]
38. Marini, L.; Saldi, G.; Cipolli, F.; Ottonello, G.; Vetuschi Zuccolini, M. Geochemistry of water discharges from the Libiola mine, Italy. *Geochem. J.* **2003**, *37*, 199–216. [CrossRef]
39. Burat, A. *Théorie des gites métallifères*; Langlois et Leclercq: Paris, France, 1845; p. 358.
40. Caillaux, A. Memoria sopra li depositi di rame contenuti nelle montagne serpentinose della Toscana e sopra alcune miniere di cinabro dello stesso paese. *Nuovi Ann. Delle Sci. Nat. Bologna* **1851**, *3*, 22–42.
41. Vom Rath, G. Ein besuch der kupfergrube Monte Catini in Toscana und einiger punkte ihrer umgebung. *Z. Dtsch. Geol. Ges.* **1865**, *17*, 277–310.
42. Reyer, E. Monte Catini. *Berg-Huettenmaennische Ztg.* **1882**, *34*, 325–327.
43. Bertolani, M.; Rivalenti, G. Le mineralizzazioni metallifere della miniera di Montecatini Val di Cecina (Pisa). *Boll. Soc. Geol. Ital.* **1973**, *92*, 635–648.
44. Deschamps, F.; Godard, M.; Guillot, S.; Hattori, K. Geochemistry of subduction zone serpentinites: A review. *Lithos* **2013**, *178*, 96–127. [CrossRef]
45. Stracke, A.; Willig, M.; Genske, F.; Béguelin, P.; Todd, E. Chemical geodynamics insights from a machine learning approach. *Geochem. Geophys. Geosyst.* **2022**, *23*, e2022GC010606. [CrossRef]
46. Meneghini, G. Prodotti delle Miniere e della Metallurgia—Rame (Bisano, Castagno, Caggio). In *Catalogo Descrittivo Esposizione Internazionale del 1862 Regno d'Italia*; Dalmazzo: Torino, Italia, 1862; Volume 1, p. 116.
47. Lotti, B. Sul giacimento cuprifero di Montecastelli in provincia di Pisa. *Boll. R. Com. Geol. D'Ital.* **1885**, *16*, 82–87.
48. Brogi, A.; Liotta, D.; Dini, A.; Rielli, A. Geology of Montecastelli Pisano (inner Northern Apennines, Italy): Normal and transfer fault zones affecting a dismantled ophiolite bearing orogenic wedge. *J. Maps* **2023**, *19*, 2242723. [CrossRef]
49. Mazzanti, R.; Squarci, P.; Taffi, L. Geologia della zona di Montecatini Val di Cecina in provincia di Pisa. *Boll. Soc. Geol. Ital.* **1963**, *82*, 1–69.
50. Schneider, A. *La Miniera Cuprifera di Montecatini Val di Cecina*; Barbera: Firenze, Italy, 1845; p. 91.
51. Biagioni, C.; Orlandi, P.; Cerri, M.; Angeli, A.; Lorenzoni, M. Montecatini Val di Cecina—La collezione del Museo di Storia Naturale dell'Università di Pisa. *Riv. Mineral. Ital.* **2017**, *42*, 144–160.
52. Meneghini, G. Rapporto alla Società Mineralogica Bolognese sul giacimento cuprifero di Bisano. *Nuovi Ann. Sci. Nat. Dell'Ist. Bologna* **1853**, *8*, 136–165.
53. Bombicci, L. Descrizione dei minerali metalliferi. *Mem. Accad. Sci. Dell'Ist. Bologna* **1873**, *4*, 83–90.
54. Goscombe, B.D.; Passchier, C.W.; Hand, M. Boudinage classification: End-member boudin types and modified boudin structures. *J. Struct. Geol.* **2004**, *26*, 739–763. [CrossRef]

55. D'Achiardi, A. *Mineralogia Della Toscana*; Nistri: Pisa, Italia, 1873; Volume 2, p. 402.
56. Mazzuoli, L. Appunti geologici sul giacimento cuprifero di Montecatini (Val di Cecina). *Boll. R. Com. Geol. D'Ital.* **1883**, *14*, 220–228.
57. Schwartz, G.M. Intergrowths of bornite and chalcopyrite. *Econ. Geol.* **1931**, *26*, 186–201. [CrossRef]
58. Zhao, J.; Brugger, J.; Ngothai, Y.; Pring, A. The replacement of chalcopyrite by bornite under hydrothermal conditions. *Am. Mineral.* **2014**, *99*, 2389–2397. [CrossRef]
59. Hidalgo, T.; Verrall, M.; Beinlich, A.; Kuhar, L.; Putnis, A. Replacement reactions of copper sulfides at moderate temperature in acidic solutions. *Ore Geol. Rev.* **2020**, *123*, 103569. [CrossRef]
60. Putnis, A. Mineral replacement reactions. *Rev. Mineral. Geochem.* **2009**, *70*, 87–124. [CrossRef]
61. Halbach, P.; Blum, N.; Munch, U.; Pluger, W.; Garbe-Schonberg, D.; Zimmer, M. Formation and decay of a modern sulfide deposit in the Indian Ocean. *Miner. Depos.* **1998**, *33*, 302–309. [CrossRef]
62. Boschi, C.; Fruh-Green, G.L.; Delacour, A.; Karson, J.A.; Kelley, D.S. Mass transfer and fluid flow during detachment faulting and development of an oceanic core complex, Atlantis Massif (MAR 30° N). *Geochem. Geophys. Geosyst.* **2006**, *7*, Q01004. [CrossRef]
63. Manatschal, G.; Sauter, D.; Karpoff, A.M.; Masini, E.; Mohn, G.; Lagabrielle, Y. The Chenaillet Ophiolite in the French/Italian Alps: An ancient analogue for an Oceanic Core Complex? *Lithos* **2011**, *124*, 169–184. [CrossRef]
64. Coltat, R.; Boulvais, P.; Riegler, T.; Pelleter, E.; Branquet, Y. Element distribution in the root zone of ultramafic-hosted black smoker-like systems: Constraints from an Alpine analog. *Chem. Geol.* **2021**, *559*, 119916. [CrossRef]
65. Marques, A.F.A.; Barriga, F.; Chavagnac, V.; Fouquet, Y. Mineralogy, geochemistry, and Nd isotope composition of the Rainbow hydrothermal field, Mid-Atlantic Ridge. *Miner. Depos.* **2006**, *41*, 52–67. [CrossRef]
66. Toffolo, L.; Nimis, P.; Tret'yakov, G.A.; Melekestseva, I.Y.; Beltenev, V.E. Seafloor massive sulfides from mid-ocean ridges: Exploring the causes of their geochemical variability with multivariate analysis. *Earth-Sci. Rev.* **2020**, *201*, 102958. [CrossRef]
67. Melekestseva, I.Y.; Maslennikov, V.V.; Tret'yakov, G.A.; Nimis, P.; Beltenev, V.E.; Rozhdestvenskaya, I.I.; Maslennikova, S.P.; Belogub, E.V.; Danyushevsky, L.; Large, R.; et al. Gold-and Silver-Rich Massive Sulfides from the Semenov-2 Hydrothermal Field, 13° 31.13′ N, Mid-Atlantic Ridge: A Case of Magmatic Contribution? *Econ. Geol.* **2017**, *112*, 741–773. [CrossRef]
68. Macleod, C.J.; Searle, R.C.; Murton, B.J.; Casey, J.F.; Mallows, C.; Unsworth, S.C.; Achenbach, K.L.; Harris, M. Life cycle of oceanic core complexes. *Earth Planet. Sci. Lett.* **2009**, *287*, 333–344. [CrossRef]