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Review

Campiglia Marittima Skarn (Tuscany): A Challenging Example for the Evolution of Skarn-Forming Models

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Abstract: Campiglia Marittima (hereafter Campiglia) has a long record of attracting interest on its ore deposits that have been intermittently exploited from the Copper Age to the late XX century. Since the XIX century, Campiglia has been a key locality for the debate on skarn-forming processes due to the presence of mining activities ensuring access to ever new rock exposures. The pioneering study of vom Rath and the comparison with attractive chemical model (e.g., Korzhinskii's theory) in the XX century made Campiglia a "classic" example of skarn ore deposit, from the causative intrusion to the marble host rock. In recent years, detailed field investigations integrated by petrographic, geochemical, and isotopic analyses revealed a more complex and stimulating geological history. The Campiglia skarn was later intruded by mafic magma causing textural reworking and chemical redistribution as well as the reverse telescoping process with Fe-Cu sulfides overprinting previously formed Pb-Zn ore. This work aims to trace the evolution of the scientific thinking on the Campiglia ore deposit by comparison with existing skarn-forming models and, ultimately, shows that the current skarn-forming model(s) cannot fully explain the textural and geochemical features of the Campiglia skarn.

Keywords: Campiglia Marittima; ore deposit; skarn

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1. Introduction

The geological heritage of Tuscany is one of the most varied, studied, and rich in history across Italy, from both the industrial and scientific point of view, representing an area of active research and educational training for Italian and foreign scientific institutions. Some localities are known worldwide for having sparked scientific debate on the formation of geothermal/hydrothermal fluids and mineral deposits since the XIX century. Some prominent examples are undoubtedly the Larderello–Travale geothermal field, the Elba Island Fe deposits, and the Monte Amiata Hg district.

Geologists need to be able to walk, map, and sample key outcrops in order to update theories on ore-forming events. Unfortunately, the Italian and international scientific community has lost many key outcrops due to the extensive closure of mining activities in Italy in the second half of the XX century; additionally, the scientific interest for ore-forming processes declined in this period. In Tuscany, prime examples are the closure (and consequent flooding) of several mines that were sites of major scientific breakthroughs in the last century (e.g., Campiano, Niccioleta, Fenice Capanne) and "gyms" for the training of many generations of geologists.

The present paper aims to describe a locality that has "survived" this fate, the Campiglia skarn system. It traces the evolution of scientific thinking through the works of authors that studied the igneous rocks and the related skarn deposits, stressing the role of accessibility for the development of new scientific scenarios on ore-forming processes.

2. Geological Setting and Past Mining Activities

Campiglia is located in the internal side of the Apennine chain, at the northern end of the Tyrrhenian Sea (Figure 1a). The current geological setting derives from the relative movements of the Sardinia–Corsica block and the Adria microplate, belonging to the European and African plates, respectively. The convergence between these plates began in the Late Cretaceous leading to Oligocene–Miocene continental collision ([1] and references therein). After the collision, the rollback of the Adria slab caused the eastward retreat of the subduction zone due to the eastward migration of the compressional front. The continental collision produced a stack of tectonic units, listed as follows from the top: 1. Ligurian Units, representative of the Ligure–Piemontese oceanic basin and related sedimentary covers; 2. Subligurian Units, mainly formed by sandstones and shaly-calcareous deposits; 3. Tuscan Units, representative of the former proximal side of the Adria continental margin deformed at shallow (Tuscan Nappe) to deeper structural levels ([1,2] and reference therein). Lithospheric extension followed the eastward migrating compressional front [3], generating a strongly thinned continental crust in southern Tuscany (20 to 25 km [4]) associated with magmatic activities traditionally known as the Tuscan Magmatic Province (TMP [5]).

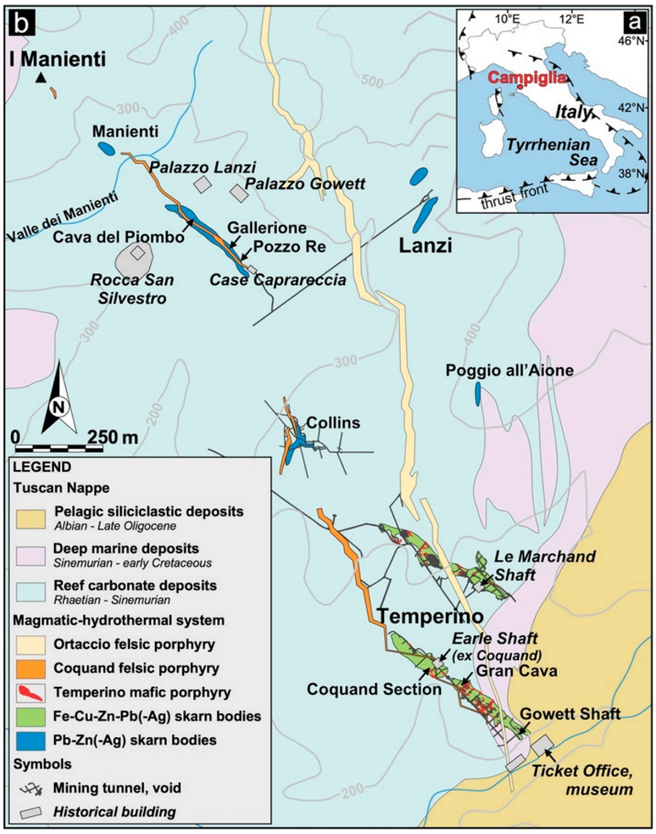

Figure 1. (**a**) Location of Campiglia in the northern Apennine chain. (**b**) Schematic geological map of Temperino–Lanzi area showing the main mining tunnels and historic buildings (e.g., Middle Age: *Rocca San Silvestro*; Renaissance: *Palazzo Lanzi*, *Case Caprareccia*; XIX-XX century: *Palazzo Gowett*, Earle, Le Marchand, and Gowett shafts).

The TMP consists of a series of crustal anatectic and mantle-derived intrusive and/or volcanic centers distributed on SW–NE lineaments that show a decreasing age moving northeastward (e.g., [6]), spatially and temporally correlated with the extensional phase (e.g., [7–13]). The magmatic activity led to HT-LP metamorphism in the host rocks, associated together with hydrothermal activities still active today [14], metasomatic rocks, and related ore deposits (e.g., Campiglia [15]; Castel di Pietra [16]; Elba Island [17,18]; Larderello [19]; Gavorrano [13]; Giglio Island [20]).

The Campiglia area is characterized by a N–S trending wedge-shaped horst delimited by high-angle extensional and strike-slip faults [8,21]. The horst is mainly made of Mesozoic carbonate formations of the Tuscan Nappe surrounded by Jurassic–Eocene ophiolitic-flysch rocks (Sub-Ligurian and Ligurian Units; Figure 1). The vertical displacement recorded by the lateral horst faults is of the order of a thousand meters causing juxtaposition, of the deeper formations of the Tuscan Nappe with the overlying Sub-Ligurian and Ligurian Units. The Campiglia area has been repeatedly affected by magmatic and hydrothermal events (e.g., [22]).

Campiglia is located in the center, both spatially and temporally, of the TMP in which several late Miocene–Pliocene plutonic, subvolcanic, and volcanic rocks were emplaced about 1 Ma [23]. Ore deposits and metasomatic rocks are spatially associated with magmatic bodies and they are exploited for different commodities such as Sn, Fe, Cu, Pb, Zn, and Ag. The exploitation dates back at least to the Copper Age and then developed intermittently during the first Millennium BCE, the Middle Ages, the Renaissance, the Industrial Revolution, and up until the 1970s ([24–27] and references therein). At present, a mine for raw ceramic materials is still active, exploiting the K-altered Botro ai Marmi granite [28]. This area was partly protected by local government, with the establishment of the Parco Archeominerario di San Silvestro [26,29], which includes several closed mines (e.g., the Temperino and Lanzi mines; Figure 1), that were once exploiting Fe-Cu-Zn-Pb(-Ag) skarn orebodies.

3. The Pioneering Studies on Campiglia Skarn Deposit

This section, far from providing an exhaustive review of the papers published on this area, is reporting on the contribution of studies on Campiglia ore deposit to the main advancements on hypotheses and models for skarn-forming processes. In this framework, the XIX century was a challenging scientific period worldwide. The growing demand for metals promoted a renewed interest for ore exploration and exploitation stimulating the scientific discussion on ore-forming processes (see [30]). Furthermore, the mining activities eased access to surface and underground rock exposures, ultimately sparking the scientific debate. In Tuscany, the resuming of mining activities started after the Congress of Vienna in 1815, attracting the best European mining scientists and engineers [31].

For sake of clarity, we will use the term "skarn" throughout the text, although at that time of some authors the term was not yet in use. In fact, Törnebohm [32] used the term "grönskarn" to describe pyroxene-garnet rocks in an Fe deposit in Sweden for the first time in 1875 and it will become of common usage much later.

The first description of the Campiglia skarn was proposed by Paolo Savi [33,34] based on the observations performed at the "Cava del Piombo", a Renaissance abandoned Pb-Zn(-Ag) mine still visible today near Rocca San Silvestro (Figure 1). Savi described texture and mineralogy of the skarn silicates and ore phases without proposing interpretations on timing and genesis of mineral formation. After Savi, Friedrich Hoffmann visited the abandoned works of Campiglia in 1830 providing a detailed description of skarn and magmatic rocks and hypothesizing contemporaneous formation/emplacement [35].

The year 1841 was important, as it was when two companies directed by the French geologists Amédée Burat and Henry Coquand re-started the exploration of the ore deposit. At that time, the mines had been abandoned for several centuries and exploration activities developed from the labyrinth of ancient tunnels, shafts, and voids. Coquand decided to explore with a vertical shaft (Coquand Shaft, now Earle shaft) and a transverse vertical section one of the Temperino skarn body. This section, known with the name of "Coquand Section", will influence scientific debate to the present day (Figure 2). In fact, Gerard vom Rath, based on this outcrop, described for the first time in the world the internal mineralogical zoning in a metasomatic body (Figure 2b), a typical feature for skarn bodies [36]. Furthermore, he recognized two different types of magmatic rock theorizing that the mafic porphyry represents the alteration of the felsic one. This misinterpretation, also due to the short time spent on the outcrop (as reported in [37]), will also condition the views of later authors such as Lotti [38,39].

Finally, we want to include in the earliest scientific investigators of the Campiglia ore deposit Alfred Bergeat. Bergeat, based on the same outcrops observed by the previous authors, proposed a detailed geological profile of the "Coquand Section" and an innovative idea on metasomatic-hydrothermal and magmatic events [40]. In this view, the hydrothermal-metasomatic event produced ilvaite and hedenbergite skarn bodies followed by the emplacement of mafic porphyry responsible for the formation of sulfide mineralization. The emplacement of felsic porphyry was the last event associated to the formation of epidosite for hydrothermal interaction with the skarn bodies. This sequence of events was not adopted by following authors, although correct, as it will be confirmed over 100 years later.

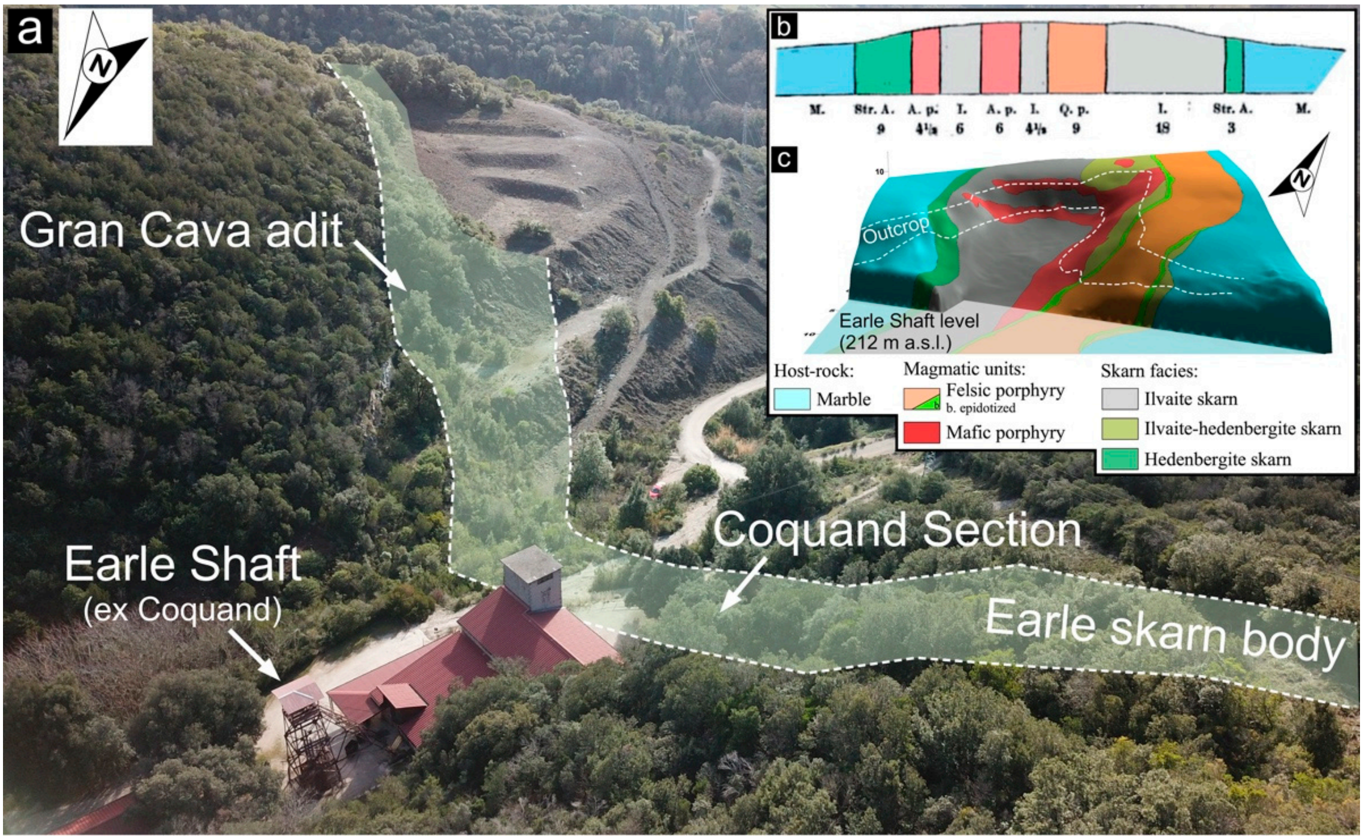

Figure 2. (**a**) Panoramic view of the Earle Shaft (Temperino mine) with schematic arrangement of Earle skarn body and location of the "Coquand Section". (**b**) First illustration of the "Coquand Section" by vom Rath (modified from [37]). Abbreviations are referred to: M.—Marmor (marble); Str.A.—Strahliger Augit (hedenbergite facies); A. p.—Augitporphyr (mafic porphyry); I.—Ilvait (Ilvaite facies); Q. p.—Quarzporphyr (felsic porphyry). The numbers referred to the thickness of each unit in feet. (**c**) Three-dimensional geological survey of the "Coquand Section" (modified from [41]). The picture represents the most recent representation of this historical-scientific outcrop.

4. Campiglia as Reference Locality for Skarn Deposit

Campiglia became a reference locality for skarn-forming processes during the XX century, when the interpretation on the sequence of magmatic/hydrothermal events and the comparison with attractive chemical theory made it an exceptional case study.

Francesco Rodolico, largely impressed by the work of Goldschmidt [42], described the temporal sequence that would be adopted by almost all later authors (e.g., [22,43–50]). Rodolico considered the mafic porphyry the first intrusion, in the reverse sequence with respect to Bergeat [40]. The mafic magma promoted the formation of ilvaite and hedenbergite skarn phases for metasomatism of the marble host-rock. The last magmatic event was the emplacement of felsic porphyry [51]. Rodolico was the first author to clearly invoke a direct genetic link between the emplacement of magmas (mafic porphyry), exsolution of hydrothermal fluids, and formation of skarn.

In the 1940 and 1950s, Korzhinskii published, largely in Russian, several papers developing the modern theory for metasomatic-forming processes. The ideas of Korzhinskii will spread mainly from the 1960s onward, with the publication of "The Theory of Systems with perfectly mobile components and processes of mineral formation" [52] and "The Theory of Metasomatic Zoning" [53]. The later authors applied this theoretical approach to discuss and explain the field and chemical data in skarn bodies (for a review see [36]). In this framework, also the case of Campiglia will be used by various authors to test Khorzinskii's theory.

In 1970, Bartholomé and Evrard [47] refined the mineralogical zoning describing an outward symmetric zoning sequence developed from the mafic porphyry toward the marble by successive steps with magnetite, followed by ilvaite, and, finally, clinopyroxene facies. These facies were produced by the change of fugacity of CO_2 over time in agreement with Khorzhinskii's theory. In addition, they described that skarn silicates can often be found an ilvaite–hedenbergite banded skarn zone. Burt [48,49] further elaborated the zoning sequence, inserting a quartz zone between the hedenbergite facies and marble (Figure 3). He defined a modified spatial-temporal evolution respect to [47] with the simultaneous development of all the facies, with the inner facies continuously replacing the outer ones. These results would be in agreement with chemical potential gradients set up between iron and silica-rich solutions and marble host-rocks. Finally, Corsini et al. [22] based on the [47] sequence, suggested that also the sulfides developed in sequential stages, in which the Cu-Pb-Zn ore were produced after silicates with chalcopyrite early, followed by sphalerite and late galena.

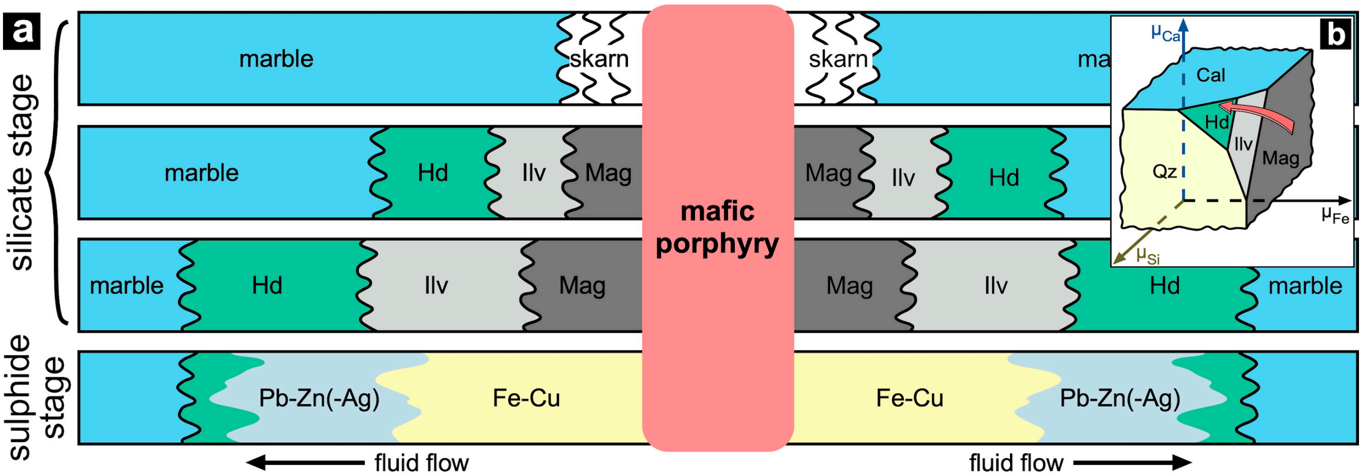

Figure 3. (**a**) Schematic illustration of the "classical model" of Campiglia skarn-forming event. Silicate stage is based on propagation reaction front model (modified from [36]) and mineralogical zoning [47]. Sulfide stage is based on [22] with spatio-temporal zoning of Fe-Cu sulfides (mainly pyrite, pyrrothite, and chalcopyrite) and Pb-Zn sulfides (sphalerite, and galena). (**b**) Chemical potential diagram for the Campiglia skarn (modified from [49]), based on Korzhinskii's theory. Red arrow indicates the successive skarn zones from the source toward the marble host-rock.

At this time, the field features (e.g., mineralogical zoning) and the sequence of the magmatic-hydrothermal events, as well as the historical scientific significance make Campiglia a "classic example" of a proximal exoskarn deposit (e.g., [54–56]) having all the typical features of the skarn-forming model (Figure 3) [36]. The closure of the last mining activities in 1979 resulting in the abandonment of the area, will make Campiglia a destination for sporadic geological studies on ore deposits [50,57] and field trips [58].

5. Campiglia: A New Skarn Model for the XXI Century

In the late XX century, mining and geological activities in Tuscany were headed to shut down. Meanwhile, archeological investigations were developing (e.g., under the guidance of Riccardo Francovich, University of Siena), with the first excavation campaign in 1984 of Rocca San Silvestro, a medieval village of miners, eventually leading to the establishment of the "Parco Archeominerario di San Silvestro" in 1996 [26,29]. The archeological-mining park would be pivotal for the following scientific activities, including geological ones, beginning with the signature in 2007 of the agreement between "Parchi Val di Cornia S.p.A." (park management public company), "Dipartimento di Scienze della Terra, Università di Pisa", and "Istituto di Geoscienze e Georisorse, Consiglio Nazionale delle Ricerche". From that moment, the Campiglia skarn would be the subject of a renewed geological interest through detailed field, petrographic, geochemical, isotopic, and geochronological studies. Furthermore, it is a customary stop for field trips on Tuscany ore deposits for Italian and foreign universities as well as for tourists and laymen (e.g., [59]).

The detailed field investigation performed at the surface and in all the underground levels of Temperino and Lanzi mines as well as in other minor mines (see [15]) started in 2008, allowing collection of data that eventually led to discovering scenarios for skarn formation significantly diverging from the classical exoskarn model. The reconstruction of the relative sequence of magmatic-hydrothermal events, based on robust spatial relationships between skarn, mafic, and felsic porphyries (Figure 4) testifies that the skarn was formed first, followed by emplacement of the magmatic units. The discovery of large primary skarn pockets filled by mafic porphyry (Temperino porphyry unit) is, to the author's knowledge, the first example in the world (Figure 5). Furthermore, two different types of felsic magmatic rocks (i.e., Coquand and Ortaccio porphyry units) have been identified.

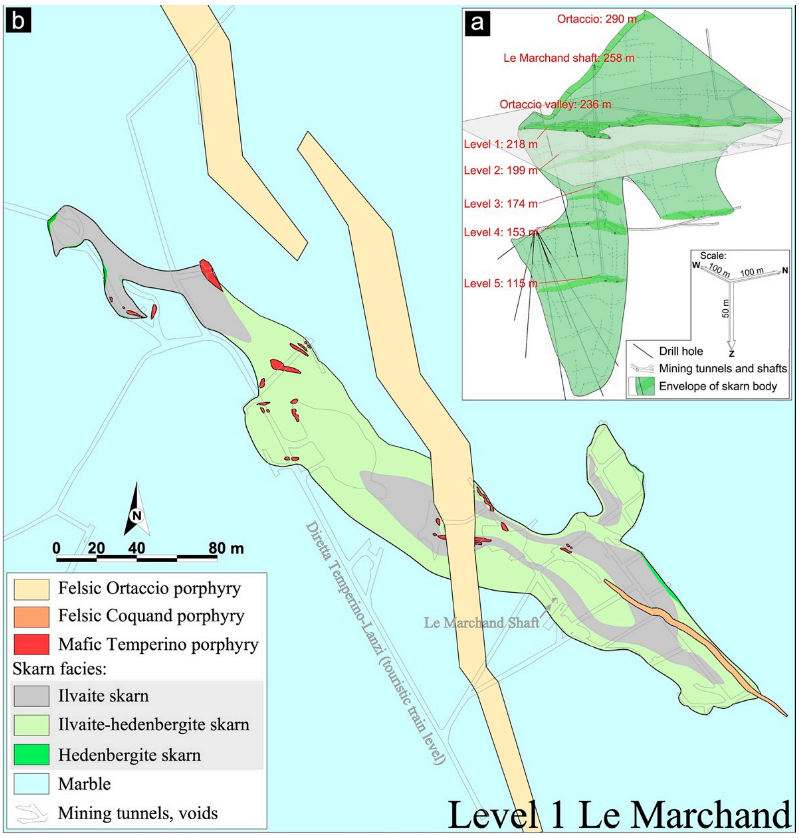

Figure 4. (**a**) Three-dimensional reconstruction of the Le Marchand skarn body (Temperino mine) based on geological survey and drill logs data. (**b**) Geological map of level 1—Le Marchand skarn body (Temperino mine) showing the distribution of the three facies and the relationships with magmatic rocks (following the methods reported in [15]).

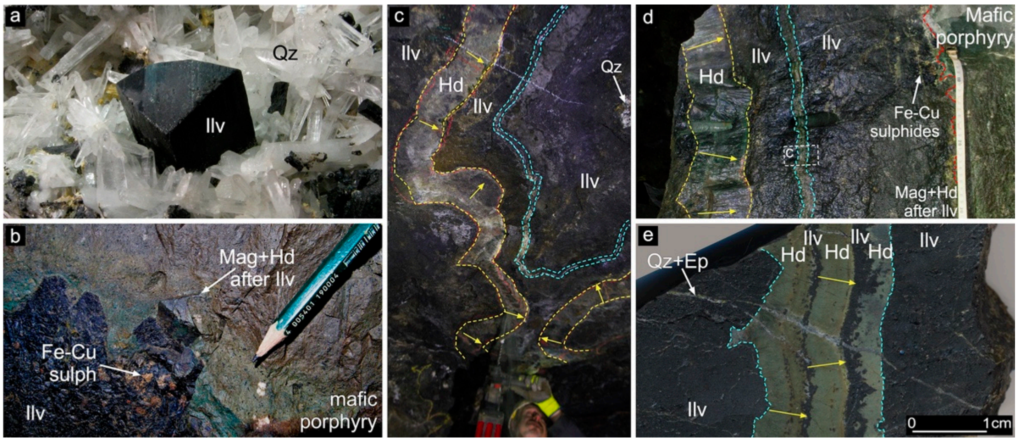

Figure 5. (**a**) Centimeter-size ilvaite crystal in skarn pocket associated with late quartz. (**b**) Euhedral ilvaite in a skarn pocket filled by mafic Temperino porphyry after ilvaite growth (level 3—Earle body). The first few centimeters of ilvaite are replaced by magnetite and hedenbergite. Additionally, Fe-Cu sulfides partially replace the ilvaite. (**c**) Banded ilvaite–hedenbergite skarn with centripetal sense of growth toward a pocket filled by late, low-temperature quartz (level 3—Earle body). (**d**) Same sequence of (**c**) with a pocket filled by mafic Temperino porphyry (level 3—Earle body). Fe-Cu sulfide veins and masses partially replacing primary skarn silicates. (**e**) Detail of the skarn sequence, with alternate millimetric bands of ilvaite and hedenbergite. Late quartz and epidote veins cutting the skarn. Yellow arrows indicate skarn mineral growth versors. See Figure 6 for location of images of skarn pockets (**c**,**d**).

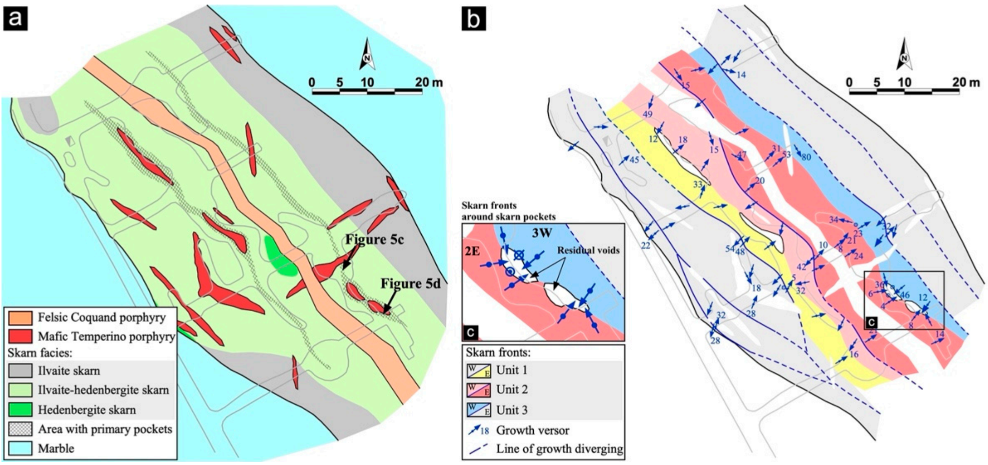

Figure 6. (**a**) Geological map of the middle part of level 3-Earle body (Temperino mine; modified from [15]). The main large primary skarn pockets are located inside the skarn body, as indicated by the hatched areas. (**b**) Skarn mineral growth versors (blue arrows - number referred to plunge) and traces of plane from which mineral growth versors diverge (blue lines - solid: well constrained plane traces; dotted: inferred plane traces; modified from [15]). The main large primary skarn pockets are located in the middle between two different planes at the contact between two skarn front units. In this figure, only the central skarn units are colored (yellow, pale and bright red, and blue colors). Note that some magmatic dykes cut the traces of plane from which mineral growth versors diverge. (**c**) Close-up of the contact zone between two skarn propagation front units, with primary skarn pocket (later filled by mafic porphyry); the skarn growth versors are centripetal with respect to the pockets.

The mineralogical zoning has been considered since vom Rath [37] to be a distinctive feature of the Campiglia skarn. Despite the intriguing bearings of zoning on the chemical scenario (e.g., [49]), actually the Temperino skarn bodies are not mineralogically zoned, and most of the external zones are formed by either ilvaite or hedenbergite, as visible, e.g., in the Coquand Section (Figure 2) [41], Level 3—Earle body [15], and Level 1—Le Marchand body (Figure 4). The primary magnetite zone was not observed but, instead, a magnetite and hedenbergite assemblage developed after ilvaite at the contact with the mafic porphyry (Figure 5b,d). This reaction was triggered by the heat released by mafic magma emplaced after skarn formation, a reaction reproduced also experimentally [60]. Furthermore, large volumes of skarn are formed by an alternance of primary millimetric to decimetric levels of ilvaite and hedenbergite (Figures 4 and 5c–e), with no evidence for reciprocal replacement. Ultimately, the model of propagation from the fluid source of multiple reaction fronts travelling at different velocities [36,49] can no longer be applied to the Campiglia skarn.

Further evidence for the lack of symmetrical skarn outward growth from a single axial zone is provided by the spatial orientation of growth versors for skarn minerals. In fact, the skarn developed outwards from multiple planes parallel to the skarn edges ([15]; Figure 6), while the large primary skarn pockets are in the central zone between two planes (Figure 6b,c). These pockets represent the voids remaining after the metasomatic process.

The crystallization geometry mimics textures observed in epithermal chalcedony-quartz veins (crustiform/comb/banded textures with vugs; e.g., [61]) and in agate [62,63], which are interpreted as crystallization in an open space. More recently, a similar interpretation has been proposed for other skarns (Serifos Island, Greece [64]; Madan ore field, Bulgaria [65]) prompting a reappraisal of metasomatic processes and their relations with tectonic activities, including the potential for creating large fluid-filled cavities in the upper crust.

The textural evidence for ilvaite and/or hedenbergite replacement by sulfides (Figure 5b,d), skarn breccia cemented by sphalerite–galena, and chalcopyrite–pyrite–pyrrothite veins in skarn, point to a late sulfide deposition after silicates, as also indicated by [22]. The sequence proposed by these authors follows a linear T-time evolution, from high-T skarn silicates, toward chalcopyrite and the last low-T sphalerite–galena ore. However, the Cu ores (Fe-Cu and Zn-Pb-Cu(-Ag) ore) are only associated to mafic Temperino porphyry (Temperino mine), while in other skarn bodies (e.g., Cava del Piombo and Lanzi mines), where igneous intrusions of Temperino porphyry are lacking, the Cu ore is also substantially missing (<1 wt%) with only the Pb-Zn(-Ag) ore occurring. This evidence, integrated by textural data, mine production records, and chemical analyses of drill hole samples suggest that the Zn-Pb(-Ag) ore was developed before the addition of Cu related to mafic Temperino intrusion. The overprinting of shallower, generally epithermal precious- and base-metal mineralizations on early, usually deep-seated mineralizations (e.g., porphyry type and Cu/Fe-skarn) is known as the telescoping process [66]. At Campiglia, a high-T Fe-Cu ore overprints a low-T Zn-Pb sulfide assemblage, so that the ore sequence can be defined as a reverse telescoping process. A similar scenario has been described in other skarn deposits such as the Kamioka mine (Japan; [67]), Madan ore field (Bulgaria; [68]), and Nikolaevsky Mine (Russia; [69]). Reverse telescoping may therefore have been an active process also in other ore districts, although it remained undiscovered because late fluids impacted the skarn leaving the magma behind; while at Campiglia, the causative magma intruded the telescoped skarn. Additional evidence of T increase, related to late intrusion of mafic magma in skarn, are (i) the magnetite and hedenbergite assemblage developed after ilvaite at the contact with the mafic porphyry and (ii) the overgrowths of Mg-rich pyroxene on early hedenbergite crystals [15].

Recently, the knowledge of the Campiglia magmatic-hydrothermal system benefited from a detailed geochronological investigation [23]. The skarn ore-forming system developed in <250 ka, with the formation of the Campiglia skarn and the associated Zn-Pb(-Ag) ore between ~5.38 and ~5.13 Ma while Fe-Cu ores formed at ~5.13 Ma, associated with the emplacement of a mafic porphyry (5.130 ± 0.043 Ma). The felsic Coquand and Ortaccio porphyry dykes emplaced in successive magmatic batches until ~4.74 Ma.

6. Conclusions

Campiglia is a reference locality for scientists studying skarn deposits. Here, rock exposures, both at the surface and underground, have stimulated the development of modern skarn-forming models. However, the Campiglia "classic" example of proximal exoskarn has been recently questioned, making Campiglia ore deposit a prime example of a distal Pb-Zn(-Ag) skarn that underwent a reverse telescoping process related to the late intrusion of mafic magma. The magma triggered several processes overprinting primary skarn silicate (e.g., replacement, overgrowth), as well as a late Fe-Cu sulfide deposition. Many other aspects are not explained by current skarn-forming theories and still need investigation. These includes skarn textures such as banded skarn and large primary pockets located in specific volumes of the skarn bodies at the contact between two propagating fronts (see [15]).

In summary, the Campiglia ore deposit is a natural laboratory for developing and testing theories on skarn formation (e.g., [36]), as was already perceived by vom Rath [37]. The opportunity to access rock exposures produced by mining activities and preserved by the archeological-mining parks have been (and are) essential in the advancement of knowledge on ore-forming systems. New generations of geologists will be trained on these outcrops and will make a contribution to issues that are still not understood.

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