

EVOLUTION OF A PLUTON-PORPHYRY-SKARN SYSTEM: THE TEMPERINO-LANZI MINE (CAMPIGLIA MARITTIMA, TUSCANY)

SIMONE VEZZONI

Dipartimento di Scienze della Terra, Università di Pisa, Via S. Maria 53, 56126 Pisa

INTRODUCTION

Skarn occurrences are well known worldwide and are hosted in several kinds of rocks of different ages; however, they are associated to carbonate rocks spatially related to magmatic bodies (Meinert *et al.*, 2005). Skarn deposits with the other CRDs (Carbonate Replacement Deposits; Megaw *et al.*, 1988) along with porphyry-type are the world's major source of Cu, Pb, Zn, Ag, and Au (Baker *et al.*, 2004). These deposits are potentially genetically linked (*e.g.*, Einaudi *et al.*, 1981; Megaw *et al.*, 1988; Titley, 1993) and, for these reasons, the knowledge of ore-forming processes in these magmatic-hydrothermal systems have prominent scientific and industrial relevance. Their economic significance is also testified by the scientific publications concerning skarns: 285 different skarn deposits were described until 1981 (Einaudi *et al.*, 1981), whereas 24 years later, that number increased at about 1700 deposits in more than 4000 publications (Meinert *et al.*, 2005). Scientific papers and mining reports have described these rocks since the 19th Century (*e.g.*, Beaumont, 1847; vom Rath, 1868), trying to understand their mechanisms of formation, the spatial relations with ore bodies and the morphologies of high-grade sulphides shoots. Although exceptional outcrops and three-dimensional (3D) data have been made available by mining activity all around the world, these topics are still debated. The results of skarn ore deposits studies have important implications for the mining industries, because they provide new methods and targets for exploration and exploitation.

In the 1950-60s the works by Korzhinskii (1965, 1968, and reference therein) were the basis of the modern theory on skarn formation. These ideas were later debated and expanded (*e.g.*, Burt, 1977; Einaudi *et al.*, 1981; Meinert *et al.*, 2005), with description of different mineral paragenesis and skarn zoning, typically related to the emplacement of magmatic bodies. In the last few years new issues are attracting researchers, such as the origin of skarn-forming fluids (magmatic-only *vs.* magmatic plus basinal and/or meteoric). This issue is of paramount relevance for skarns apparently unrelated to magmatic rocks (distal skarn; *e.g.*, Baker *et al.*, 2004; Samson *et al.*, 2008). Other open questions are the mechanism of metals transport from their source(s) to the site of deposition and the relations between skarns and other CRDs (Megaw *et al.*, 1988; Titley, 1993).

The present work contributes to the debate on skarn formation processes providing detailed field data integrated with petrographic, mineralogical, and geochemical-isotopic data from the Campiglia Marittima magmatic-hydrothermal system. This locality offers the opportunity for a 3D study of the geological bodies, thanks to past underground mining activities (during almost three millennia of ore exploitation), with additional data deriving from about 25 km of drill holes. Although the Campiglia Marittima skarn deposit is a deposit of small size (*ca.* 50 kt of base metals) and medium/low-grade (1.4% Cu; 3.8% Zn; 2.0% Pb), with modest economic interest, its geological characteristics make it an ideal site to study the skarn- and ore-forming processes (*e.g.*, Dill, 2010). Furthermore, it is one of the first skarn deposits studied in the world (Burt, 1982) by vom Rath (1868) and it has been considered as a classical example of replacement exoskarn (*e.g.*, Rodolico, 1931; Burt, 1977; Corsini *et al.*, 1980; Dill, 2010). The current skarn formation model (see Meinert *et al.*, 2005, for review) was also developed starting from the temporal and mineralogical characteristics described at Campiglia Marittima. The results of this work aim to contribute to the understanding of the processes occurring during skarn formation and ore deposition and the relationships with magmatism and active tectonics.

GEOLOGICAL BACKGROUND

The Campiglia Marittima area is located in the southern Tuscany at the centre, both spatially and temporally, of the Tuscan Magmatic Province (TMP; Innocenti *et al.*, 1992). This area is characterized by a N-S trending horst bounded by high-angle extensional faults and strike-slip faults. In this area the carbonatic formations of the Tuscan Nappe (Early Jurassic - Early Cretaceous) crop out widely, bordered by formations belonging to the Ligurian and Sub-Ligurian Domains to the west and by clayey and turbiditic successions of the Tuscan Nappe (Cretaceous - late Oligocene) to the east (Acocella *et al.*, 2000; Rossetti *et al.*, 2000; Fig. 1). The horst developed as a consequence of the extensional tectonics affecting the inner side of the Apennine thrust-and-fold belt. The extension produced a thinned crust (here *ca.* 22 km), a widespread magmatism involving both crustal anatexis and mantle-derived products (TMP), and a diffuse hydrothermal activity that is still active nowadays (*e.g.*, Barberi *et al.*, 1967; Dini *et al.*, 2005; Bertini *et al.*, 2006).

The Campiglia Marittima magmatic system is made by a major peraluminous monzogranite pluton (Botro ai Marmi; 5.7 Ma), cropping out at Botro ai Marmi; mafic and felsic porphyritic dikes crosscut the contact aureole of the monzogranite intrusion (Campiglia Marittima porphyritic dikes; *ca.* 4.4 Ma), and an early Pliocene rhyolitic extrusive complex (San Vincenzo Rhyolites; 4.3-4.4 Ma) covers the Ligurian units as well as the early Pliocene sediments to the west of the carbonate horst (Fig. 1; *e.g.*, Barberi *et al.*, 1967; Peccerillo & Donati, 2003).

Skarn and ore deposits occur in close spatial association with the intrusive rocks, in the form of (i) minor metasomatic rock masses at the pluton-carbonates contact (Barberi *et al.*, 1967), (ii) low-grade Sn-W-As-Bi ores (Sn *ca.* 0.4 wt.%; Venerandi-Pirri & Zuffardi, 1982), and (iii) the main Campiglia Fe-Cu-Zn-Pb(-Ag) skarn deposit (*e.g.*, Corsini *et al.*, 1980). The Campiglia Marittima skarn deposit consists of several bodies and veins that crop out discontinuously between Monte Spinosa to the south to Monte Coronato to the north (Fig. 2). Some of these skarn bodies surround small masses of mafic porphyry. Skarn bodies as well as mafic porphyries are crosscut by felsic dikes (*e.g.*, Bodechtel, 1968).

THE CLASSICAL CAMPIGLIA MARITTIMA SKARN MODEL

Campiglia Marittima skarn deposits are described as a classical example of exoskarn, whose formation started with the emplacement of the genetically linked magmatic rocks (mafic porphyry) that triggered the progressive replacement of marbles by skarn and the following deposition of sulphides during the waning stage of the metasomatic process (*e.g.*, Rodolico 1931; Bartholomé & Evrard, 1970; Corsini *et al.*, 1980). The skarn was described as having an outward symmetric mineralogical zoning with respect to a hypothetical axial mafic porphyry dike. A zoning sequence was proposed for both the main skarn minerals (porphyry - magnetite - ilvaite

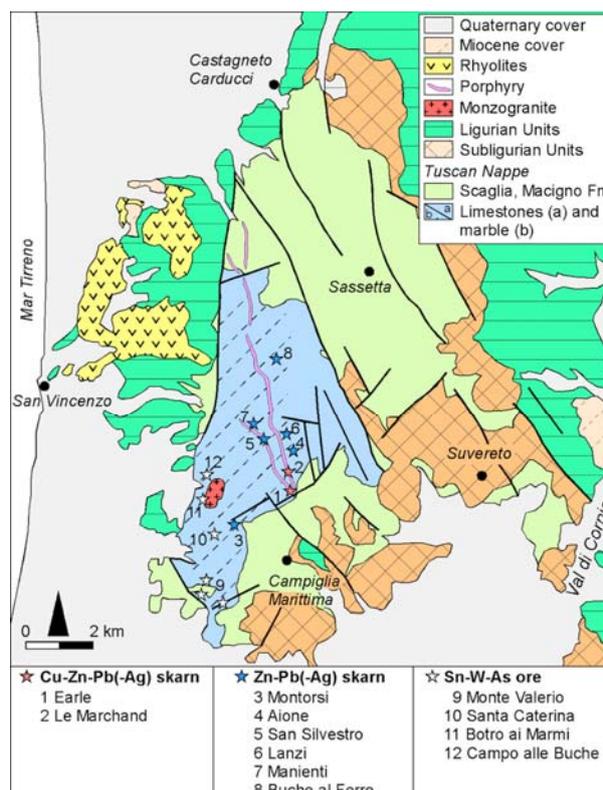


Fig. 1 - Schematic geological map of the Campiglia Marittima area. Stars indicate the main ore bodies (modified after Da Mommio *et al.*, 2010).

- clinopyroxene - marble) and the ore minerals (chalcopyrite + pyrrhotite in magnetite/ilvaite zones - sphalerite + galena in clinopyroxene zone) (Bartholomé & Evrard, 1970; Corsini & Tanelli, 1974). This evolution is in agreement with the classical model of Korzhinskii (1968) and theoretically consistent with the evolutionary paths proposed by Burt (1977) on the basis of chemical potential diagrams. Such a model was mainly developed for the Earle body at Temperino mine, making the Campiglia skarns a reference example for exoskarn formation processes until nowadays (*e.g.*, Dill, 2010).

FIELD AND LABORATORY METHODS

The working strategy was directed to progressively collect data for defining: 1) external geometry of skarn and porphyry bodies shapes; 2) internal skarn structures and mineralogical zoning; 3) petrography and chemistry of skarn silicates and ore minerals. The new detailed survey carried out both at outcrops and in all the accessible underground works (in particular, Temperino and Lanzi mines) allowed a detailed characterization (geometry, attitude) and sampling (for petrography, mineralogy, and geochemistry) of the magmatic and metasomatic units (Fig. 2). Underground mapping (*ca.* 20 km of mining tunnels) has been integrated with surface geological surveys over an area of 20 km². Direct field observations were integrated with data from mining reports and lithological/geochemical logs of 175 diamond and RC drill holes (*ca.* 25 km, performed by SAMIM S.p.A. for the last mining exploration program at Campiglia in the 1980s; SAMIM, 1983): these data lend support to the reconstruction, at even greater depth, of the 3D geometries of magmatic and metasomatic/ores units.

All this wealth of spatially referenced data led to produce a 3D visualization (axonometric projections) of the four main skarn bodies of the area. The 3D representation, integrated by the geological maps of all the underground mining levels and several geological sections allow to investigate the internal skarn structures, mineralogical zoning and morphologies of the ore shoots as well as the spatial relationships with the magmatic rocks.

Petrographic (thin and polished sections), mineralogical (XRD) and geochemical-isotopic (EPMA, XRF, ICP-MS, and O, H, Sr, Nd, Pb isotope) data integrate the detailed field, underground mapping and three-dimensional reconstructions.

RESULTS AND CONCLUSIONS

The data collected during this work led to a deep review of the classical Campiglia Marittima exoskarn model and suggest an alternative holistic model for the development of skarn and ore bodies in the regional-local tectono-magmatic setting. The striking novelty is represented by the relative timing of the mafic porphyritic magma, genetically linked to the skarn, which has been proved to intrude after -not before- the skarn formation. Furthermore, the three-dimensional reconstruction of skarn bodies as sigmoid-shaped, led to infer that the skarn

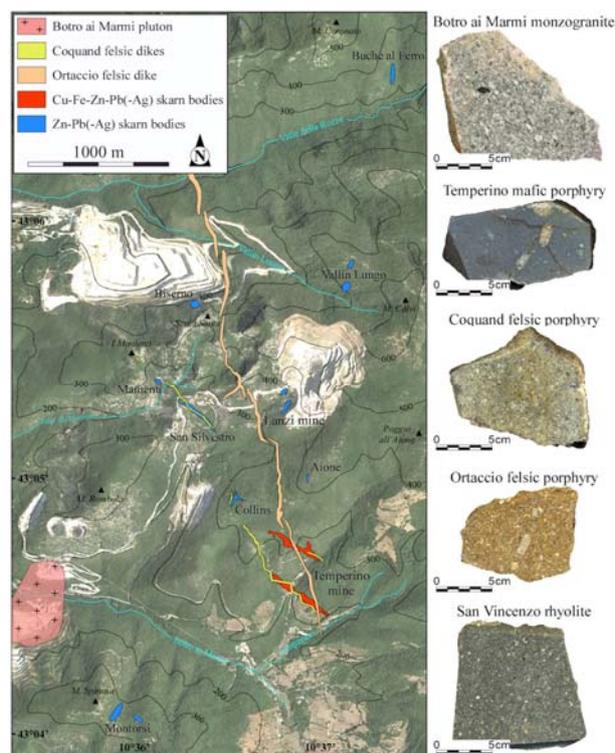


Fig. 2 - Geological map of the magmatic and hydrothermal units with scan images of rock slabs from the Campiglia Marittima magmatic rocks.

generated by fluid metasomatism after a sigmoid-shaped volume of fractured host marble. These damaged marble volumes thus acted as a relative low-pressure zone drawing metasomatic fluids from depth. The careful reconstruction of the fluid flow path during skarn formation by measuring the mineral growth direction and sense in all the tunnels of the Temperino and Lanzi mines disproves the current model of symmetrical mineralogical zoning from a single axial plane. Furthermore, the data point out an unexpected process during the “normal prograde to retrograde skarn evolution” in which a distal Zn-Pb(-Ag) skarn ore was overprinted by higher temperature Cu-Fe ore, typical of proximal skarn deposits. This new finding will help revision of the interpretation of other skarn deposits in the world that are known to show comparable features (*e.g.*, Kamioka skarn deposit, Japan; Mariko *et al.*, 1996; Madan ore field, Bulgaria; Bonev, 1977; Nikolaevsky mine, Russia; Rogulina & Sveshnikova, 2008). Finally, an unifying tectonic-magmatic-metasomatic model is proposed to overcome the difficulties in interpreting the overall Campiglia geological features, that are proved to be difficult to understand if tackled as single, isolated phenomena. This model shows as regional extensional tectonics and hydrothermal fluid transfer are intertwined with local magma-induced tectonics.

The model proposed for the Campiglia Marittima area can be used elsewhere as a guide in defining possible targets for ore and geothermal exploration.

ACKNOWLEDGEMENTS

This work has been partly supported by a fruitful cooperation between the Dipartimento di Scienze della Terra (University of Pisa), the Istituto di Geoscienze e Georisorse of Pisa (CNR) and the Parchi Val di Cornia S.p.A., and mineral collectors as well. Research was supported by the “Ministero dell’Istruzione, dell’Università e della Ricerca” of Italy (PRIN project: 2008PN8Z9K). We thank the “Parchi Val di Cornia S.p.A.” and, in particular, the “Parco Archeominerario di San Silvestro” for granting access and sampling in the Temperino and Lanzi mining area.

REFERENCES

- Acocella, V., Rossetti, F., Faccenna, C., Funicello, R., Lazzarotto, A. (2000): Strike-slip faulting and pluton emplacement in Southern Tuscany: the Campiglia Marittima case. *Boll. Soc. Geol. It.*, **119**, 517-528.
- Baker, T., Van Achterberg, E., Ryan, C.G., Lang, J.R. (2004): Composition and evolution of ore fluids in a magmatic-hydrothermal skarn deposit. *Geology*, **32**, 117-120.
- Barberi, F., Innocenti, F., Mazzuoli, R. (1967): Contributo alla conoscenza chimico-petrografica e magmatologica delle rocce intrusive, vulcaniche e filoniane del Campigliese (Toscana). *Mem. Soc. Geol. Ital.*, **6**, 643-681.
- Bartholomé, P. & Evrard, P. (1970): On the genesis of the zoned skarn complex at Temperino, Tuscany. *Int. Union Geol. Sci., Ser. A*, **2**, 53-57.
- Beaumont, E. (1847): Note sur les émanations volcaniques et metallifères. *Bull. Soc. Geol. Fr.*, **4**, 1249-1334.
- Bertini, G., Casini, M., Gianelli, G., Pandeli, E. (2006): Geological structure of a long-living geothermal system, Larderello, Italy. *Terra Nova*, **18**, 163-169.
- Bodechtel, J. (1968): Die Paragenesen der Skarnlagerstätten in den Monte di Campiglia-Toscana. *Freiberger: Forschungshefte*, **231**, 7-20.
- Bonev, I.K. (1977): Primary fluid inclusions in galena crystals. I. Morphology and origin. *Mineral. Dep.*, **12**, 64-76.
- Burt, D.M. (1977): Mineralogy and petrology of skarn deposits. *Rend. Soc. It. Mineral. Petrol.*, **33**, 859-873.
- Burt, D.M. (1982): Skarn deposits; historical bibliography through 1970. *Econ. Geol.*, **77**, 755-763.
- Corsini, F. & Tanelli, G. (1974): Analisi alla microsonda elettronica delle blende del giacimento della Valle del Temperino (Campiglia, Toscana). *Rend. Soc. It. Mineral. Petrol.*, **30**, 205-221.
- Corsini, F., Cortecci, G., Leone, G., Tanelli, G. (1980): Sulfur isotope study of the skarn-(Cu-Pb-Zn) sulfide deposit of Valle del Temperino, Campiglia Marittima, Tuscany, Italy. *Econ. Geol.*, **75**, 83-96.
- Da Mommio, A., Iaccarino, S., Vezzoni, S., Dini, A., Rocchi, S., Brocchini, D., Guideri, S., Sbrilli, L. (2010). Valorizzazione del geosito “Sezione Coquand”, Miniera del Temperino (Parco Archeominerario di San Silvestro Campiglia). *Atti Soc. Tosc. Sci. Nat., Mem., Ser. A*, **115**, 55-72.
- Dill, H.G. (2010): The “chessboard” classification scheme of mineral deposits: Mineralogy and geology from aluminum to zirconium. *Earth Sci. Rev.*, **100**, 1-420.

- Dini, A., Gianelli, G., Puxeddu, M., Ruggieri, G. (2005): Origin and evolution of Pliocene-Pleistocene granites from the Larderello geothermal field (Tuscan Magmatic Province, Italy). *Lithos*, **81**, 1-31.
- Einaudi, M.T., Meinert, L.D., Newberry, J. (1981): Skarn deposits. *Econ. Geol.*, 75th Anniversary Volume, 317-391.
- Innocenti, F., Serri, G., Ferrara, G., Manetti, P., Tonarini, S. (1992): Genesis and classification of the rocks of the Tuscan Magmatic Province: thirty years after Marinelli's model. *Acta Vulcanol.*, **2**, 247-265.
- Korzhinskii, D.S. (1965): The theory of systems with perfectly mobile components and processes of mineral formation. *Am. J. Sci.*, **263**, 193-205.
- Korzhinskii, D.S. (1968): The theory of metasomatic zoning. *Miner. Deposita*, **3**, 222-231.
- Mariko, T., Kawada, M., Miura, M., Ono, S. (1996): Ore formation processes of the Mozumi skarn-type Zn-Pb-Ag deposit in the Kamioka mine, Gifu Prefecture, Central Japan - A mineral chemistry and fluid inclusion study. *Res. Geol.*, **46**, 337-354.
- Megaw, P.K.M., Ruiz, J., Titley, S.R. (1988): High-temperature, carbonate-hosted Ag-Pb-Zn(Cu) deposits of northern Mexico. *Econ. Geol.*, **83**, 1856-1885.
- Meinert, L.D., Dipple, G.M., Nicolescu, S. (2005): World skarn deposits. *Econ. Geol.*, 100th Anniversary Volume, 299-336.
- Peccerillo, A. & Donati, C. (2003): Miocene-Quaternary magmatism in central-southern Italy. *Per. Mineral.*, **72**, 11-23.
- Rodolico, F. (1931): Ricerche sulle rocce eruttive recenti della Toscana - Le rocce del Campigliese. *Atti Soc. Tosc. Sci. Nat., Mem.*, **41**, 197-251.
- Rogulina, L.I. & Sveshnikova, O.L. (2008): The Nikolaevsky base-metal skarn deposit, Primorye, Russia. *Geol. Ore Deposits*, **50**, 60-74.
- Rossetti, F., Faccenna, C., Acocella, V., Funicello, R., Jolivet, L., Salvini, F. (2000): Pluton emplacement in the Northern Tyrrhenian area, Italy. *Geol. Soc. Am. Bull.*, **114**, 55-77.
- SAMIM (1983): Nota conclusiva sulle ricerche nella miniera di Campiglia Marittima (Zn-Pb-Cu) - (Toscana). Internal report, 36.
- Samson, I.M., Williams-Jones, A.E., Ault, K.M., Gagnon, J.E., Fryer, B.J. (2008): Source of fluids forming distal Zn-Pb-Ag skarns: Evidence from laser ablation-inductively coupled plasma-mass spectrometry analysis of fluid inclusions from El Mochito, Honduras. *Geology*, **36**, 947-950.
- Titley, S.R. (1993): Characteristics of high temperature carbonate-hosted massive sulfide ores in the United States, Mexico and Peru. In: "Mineral deposit modeling", R.V. Kirkham, ed. *Geol. Ass. Canada*, **40**, 585-614.
- Venerandi-Pirri, I. & Zuffardi, P. (1982): The tin deposit of Monte Valerio (Tuscany, Italy): Pneumatolytic-hydrothermal or sedimentary-remobilization processes? In: "Ore Genesis", G.C. Amstutz, G. Frenzel, C. Kluthet, eds. Springer, Berlin, **2**, 57-65.
- vom Rath, G. (1868): Die Berge von Campiglia in der Toskanischen Maremma. *Z. Deut. Geol. Ges.*, **20**, 307-364.