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CHAPTER 2
Ore deposits, industrial minerals and geothermal resources

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2.1 HISTORICAL PERSPECTIVE

Together with Sardinia, Tuscany is the main mining region of Italy, where almost three millennia of exploitation yielded significant productions of iron, pyrite, base metals, silver, antimony, mercury, gold as well as industrial minerals and super-heated steam (Fig. 1). In addition to its economic relevance, the Tuscan metallogenic province remains of primary scientific importance due to the occurrence of diverse hydrothermal deposits associated with volcano-sedimentary, intrusive, metamorphic and geothermal environments of pre- Alpine and Alpine ages (Lattanzi *et al.*, 1994 and reference therein).

There are few indirect archaeological evidences indicating that exploitation of iron ores from Elba, Cu-Pb-Ag ores from Temperino and Massa Marittima, and tin ores from Monte Valerio was possibly accomplished since the VIII-VII century B.C until the Roman period. However, the archeometallurgical products and rare furnaces found along the coasts of the Elba Island and Tuscany (e.g. Populonia) indicate that extensive reduction of iron and copper minerals was accomplished in the Roman period (III century B.C.). Especially the iron industry grew to become the great economic resource of Populonia, drawing increasingly on the rich mineral deposits of the Island of Elba often mentioned in ancient texts (Diodorus Siculus, apocryphal writings of Aristotle).

After the fall of the Roman Empire, the ore deposits of Elba Island and «Colline Metallifere» (Massa Marittima area) fell in total oblivion for centuries. It was only in Middle Age (XI-XIV century) and Renaissance time (XVI-XVIII century) that mining activity flourished again in Tuscany, particularly in the Ag-Cu (-Fe) district of «Massa Metallorum» (now Massa Marittima in Southern Tuscany), but also in the Fe district of Elba Island. During the XIX century, exploration and exploitation of ore deposits in Tuscany took advantage by the production of the first geological maps and genetic studies of mineralogists and geologists from Italian and European Universities. After the Unification of Italy all mines became a state property and were granted in concession to different mining companies, up to 1990's, when the last pyrite mine in southern Tuscany (Campiano) shut down.

Today, the mining industry in Tuscany is facing the typical problems of most European regions, and extraction is currently limited to ornamental stones, building materials and a few industrial minerals such as raw ceramic material.

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2.2 METALLOGENY

The metallogeny of Tuscany is rather complex, and several aspects still await a definite answer.

According to Lattanzi *et al.* (1994), three main metallogenic epochs seem to be relatively well established in Tuscany: (i) a Lower-Middle Palaeozoic stage, leading to the formation of protores/preconcentrations of metals (e.g. the Ag-Pb- Zn Bottino deposit and the Hg Levigliani deposit in the Apuane Alps) strictly related to the Ordovician calcalkaline magmatism; (ii) an Upper Palaeozoic –Triassic Fe (and Ba) event, possibly related to a pre-Tethyan aborted rift, that is documented in various areas, such as Elba Island, Southern Tuscany and Apuane Alps; (iii) an Alpine event, well documented both in Apuane Alps and in Southern Tuscany (e.g. the epithermal Hg-Sb-Au deposits, the Cu-Pb-Zn sulfide ore bodies), characterized by hydrothermal systems triggered by both regional metamorphism and magmatism.

One of the most debated themes is the origin of iron-bearing deposits occurring in Tuscany (barite-iron oxide-pyrite deposits of Apuane Alps, pyrite deposits of Southern Tuscany and the iron ores of Elba Island). Total production from the three districts may be estimated in the order of 150 million tons ore: the Apuane deposits yielded about 0.5 million tons of pyrite + Fe oxides, whereas more than 80 million tons of high-grade mineral concentrate were obtained by exploitation of several pyrite deposits in Southern Tuscany (Niccioleta, Gavorrano, Boccheggiano, etc.), and not less than 60 million tons Fe ore have been extracted from Elba deposits from ancient times up to nowadays. A number of hypotheses have been put forward in the last two centuries in order to explain the genesis of Tuscan Fe deposits. They can be grouped in two basic genetic models (Tanelli and Lattanzi, 1986): (i) «plutonistic epigenetic», and (ii) «syngenetic/hydrothermal-metamorphic». According to the first model, ore genesis is a direct consequence of the intrusion of the Late-Alpine granitic plutons. In the first half of the past century, earlier scientists considered the Late-Alpine intrusions as the sources of heat and metals (e.g. Lotti, 1929). More recently, new epigenetic models have been proposed (Marinelli, 1983; Dechomets, 1985), according to which the intrusions acted as heat sources and promoted the circulation of hydrothermal fluids, although the source(s) of the fluids themselves and dissolved metals should be looked for elsewhere. Thus Marinelli (1983) suggested that Fe could derive from metasomatic reactions taking place at the peripheral portions of the intrusive bodies: chloride-rich metamorphic and/or connate waters would have been enriched in Fe through reaction with magmatic biotite. On the other hand, Dechomets (1985) proposes that hydrothermal fluids of dominant marine origin scavenged Fe from host rocks. The authors favouring the second genetic model («syngenetic/hydrothermal-metamorphic») acknowledge the importance of the Alpine tectono-magmatic event in reworking the iron ores, but believe that, at least as protores, they were formed in sedimentary and/or hydrothermal sedimentary environments of Triassic and/or Palaeozoic age (Deschamps *et al.*, 1983; Tanelli and Lattanzi, 1983; Zuffardi, 1990). According to these authors, the Late-Alpine extensional tectonics, metamorphism, magmatism and related hydrothermalism would be responsible for the more or less remobilisation and metamorphism of the metal preconcentrations.

2.3 THE FE DEPOSITS OF ELBA ISLAND

As shown in figure 1 and 2, the Fe deposits of Elba Island are restricted to a relatively narrow belt extending NS along the eastern coast of the Island (see Tanelli *et al.*, 2001 and reference therein). The ore bodies, even at the scale of individual deposit, occur in variable settings, from stratiform to pod-like or vein-type, although the first appears to be dominant (Zuffardi, 1990). Stratiform Fe bodies, either or not associated with veins and/or irregular masses, are «strata-bound», at least in the wider

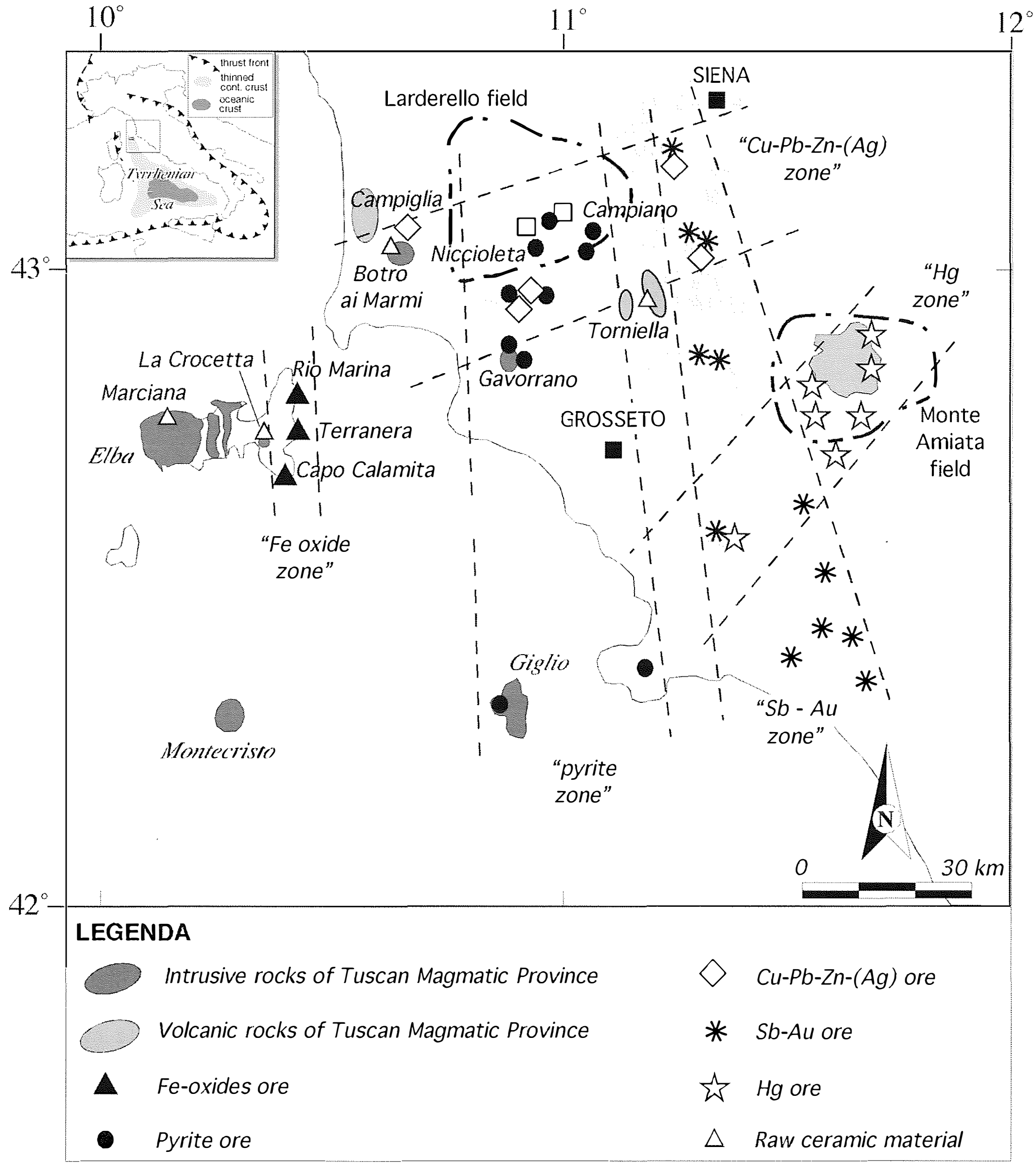
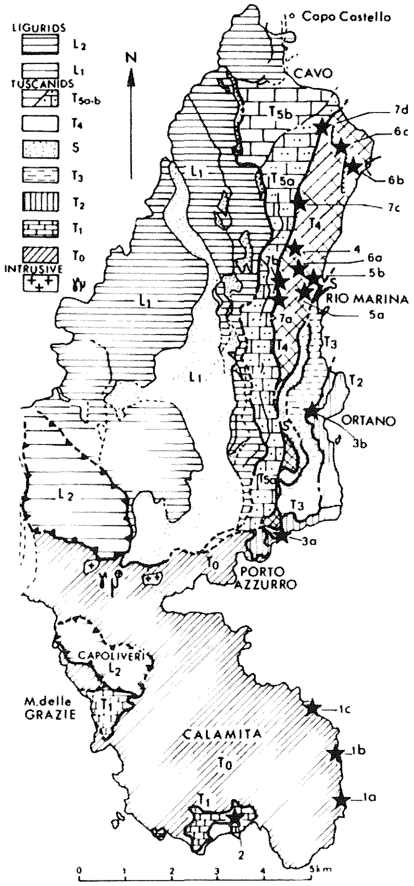


Fig. 1 – Major deposits and mineral belts of Southern Tuscany (modified after Tanelli and Lattanzi, 1983).

meaning of the word. In fact they are predominantly hosted by Palaeozoic-Triassic formations belonging to Tuscan Domain (Complex I, II and III; see Part III, Chap. 1).

Hematite (± pyrite, limonite) ores from Rio Albano up to Rio Marina mining area are neither directly associated with intrusive bodies (plutons, dykes) nor with skarn bodies of



Geological setting of the Eastern part of the Island of Elba, modified from PERRIN (1974):
- $\gamma\mu$: intrusive Eastern Elba Quartz monzonite.
- Lower Tuscan Units: T_0 = basement of the Calamita Unit; T_1 = carbonatic cover of the Calamita Unit; T_2 = Ortano Unit; T_3 = Unit of "Schists and Crystalline Limestones"; T_4 = Rio Marina Unit.
- Upper Tuscan Units: T_5a and T_5b = Limestone Units.
- Ligurian Units: S = interlayered serpentine; L_1 = Ophiolites; L_2 = Helminthoides bearing flysch.
- Iron Deposit: 1a = Ginevro; 1b = Stagnone; 1c = Sassi Neri; 2 = Calamita; 3a = Terra Nera; 3b = Ortano; 4 = Valle Giove; 5a = Bacino; 5b = Vigneria; 6a = Zuccoletto; 6b = Rialbano; 6c = Monte Calendozio; 7a = Valle di Catone; 7b = Rossetto; 7c = Le Conche, 7d = Fornacelle.

Fig. 2 – Geological setting and location of Fe ore deposits of Elba Island (modified after Deschamps *et al.*, 1983).

presumable magmatic affiliation. However, mineralogical, textural and fluid inclusion analyses of hematite+adularia assemblage from Valle Giove stopes at Rio Marina) (Deschamps *et al.*, 1983) would indicate that it formed through reaction of relatively hot (T= 310 °C) saline fluids with pyrite-biotite-quartz-bearing rocks. In addition, isotopic dating of the hematite+adularia assemblages from the same stope by Lippolt *et al.* (1995) point to ages of 6.4 ± 0.4 to 5.3 ± 0.1 Ma (U+Th vs. He ages of hematite and K/Ar age of associated adularia), i.e., very close to those estimated for the Porto Azzurro pluton (5.9 Ma; Maineri *et al.*, 2003).

Rio Marina is especially famous worldwide for its beautiful crystals of hematite (variety «oligisto» = glaze iron) and pyrite. Hematite may show either a typical lamellar-micaceous habitus, or rhombohedral, complex, crystals often covered by iridescent films of iron hydroxides; euhedral pyrite pyritohedra, octahedral and cubes are frequently associated with micaceous hematite and also embedded in soft chlorite aggregates.

Moving southwards from Rio Marina towards the Calamita Peninsula, the association of iron ores with skarn bodies and/or aplitic dykes becomes more and more distinctive.

Actually, skarn bodies were encountered in the Rio Marina mining area as well, although at depth (drillings in the Vigneria stopes). Immediately south of Rio Marina village, just a few metres after the old tower, decametric skarn bodies with hedenbergite, ilvaite, epidote, quartz, magnetite, pyrite, and pyrrhotite extend along the coast, replacing calcschists. Beautiful specimens showing ilvaite prismatic crystals, green and amethystine quartz and fibrous-prismatic hedenbergite have been collected here in the past. Moving southwards, other skarn bodies are encountered, often in association with Fe ores of variable size and economic relevance: at Ortano and Terranera pyrite, ematite, pyrrhotite and magnetite are associated with pyroxene-ilvaite-epidote skarn bodies. In this area, aplitic-pegmatitic dykes linked to the Porto Azzurro pluton frequently intersect (or are in close proximity to) Fe ores and skarn bodies. The Terranera deposit provided some of the most elegant and brilliant pyritohedra crystals of pyrite ever found in the island. The association between ores, skarn and aplitic dykes is particularly evident in the Calamita Peninsula, where several skarn-bearing iron deposits (Capo Calamita, Ginevro, Sassi Neri, Stagnone) are hosted by Complex I. The Capo Calamita deposit (Fig. 3) is characterized by the presence of two distinct type of skarn: a garnet (andradite)-rich skarn, quantitatively the most abundant, and an ilvaite-hedenbergite skarn.

The exploited ores were spatially associated with both types of skarns, and consisted of lenses and massive bodies of magnetite (± hematite, goethite) and trace amounts of base metal sulfides. However, magnetite was not the primary Fe mineral to form: the presence of magnetite with lamellar habitus and the presence of relic lamellar structures in euhedral magnetite are evidences of pseudomorphic replacement after earlier hematite. Of some interest is the presence at Ginevro and Sassi Neri of a relatively uncommon skarn mineral like ferropargasite, associated with grossular-almandine garnet, and only minor amounts of hedenbergite, ilvaite, and epidote.

As discussed more extensively elsewhere (cf. Tanelli and Lattanzi, 1986), none of the genetic models so far proposed for iron deposits of eastern Elba Island is completely satisfactory. Descriptive models for the individual deposits are largely incomplete, so that inferred genetic models are obviously qualitative and poorly constrained. Anyway, taking into account the previously reported textural, geological and geochronologic data, Tanelli *et al.* (2001) suggest that the stage of iron concentration

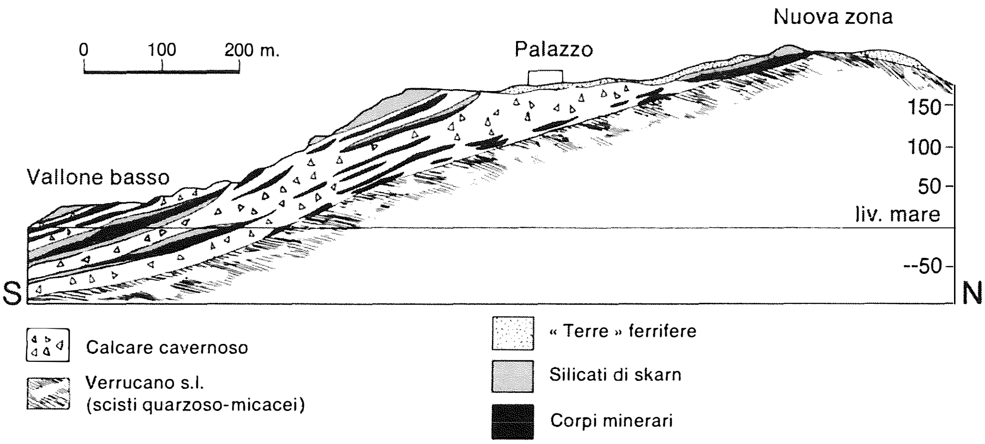


Fig. 3 – Simplified geological section of Capo Calamita Fe-skarn deposit (modified after Tanelli, 1977).

could have preceded (at least in part) the emplacement of the Porto Azzurro pluton and related aplites, as well as the formation of skarn bodies. In this scenario, fluids triggered from Porto Azzurro intrusion modified and remobilised mineralogy and structures of pre-Alpine (Palaeozoic-Triassic) Fe ore preconcentrations.

2.4 THE CU-PB-ZN SKARN DEPOSITS OF VALLE DEL TEMPERINO-VALLE DEI LANZI (CAMPIGLIA MARITTIMA)

The skarn-sulfide deposits of Campiglia M.ma area have been mined, on a rather small scale, for chalcopyrite, and minor sphalerite and galena. These deposits have been regarded as a classic example (Fig. 4) of a replacement skarn deposit formed by hydrothermal fluids related to the emplacement of porphyry dykes along fractures of limestones (see Corsini *et al.*, 1980, and reference therein). In the mine, two kinds of porphyry, «Porfido Giallo» and «Porfido Verde», have been observed. Such a subvolcanic products constitute a sub-vertical dyke swarm, trending NNW-SSE, that crosscut the thermometamorphic structures of marbles induced by the emplacement of Botro ai Marmi pluton. «Porfido Giallo» is monzogranitic in composition whereas the «Porfido Verde» has a more mafic composition, but a correct classification is precluded due to the strong alteration. Several skarn masses occur completely embedded in white marbles as well as at the contact between marble and porphyry dykes. The subvertical, elongated, geometry (pipe-like) of the three main masses is known owing to the detailed informations derived from underground works, that followed such structures from 400 m (at surface) to 50 m a.s.l.. The «Porfido Verde» is commonly completely embedded in the orebodies and is penetrated by small calcite-epidote-K-feldspar-quartz veins. «Porfido Giallo» (sometimes deeply epidotized) is occasionally associated with and/or embedded in the orebodies, always in the vicinity of a «Porfido Verde» dyke.

The skarn complex is almost entirely formed by manganoan ilvaite, and hedenbergite with

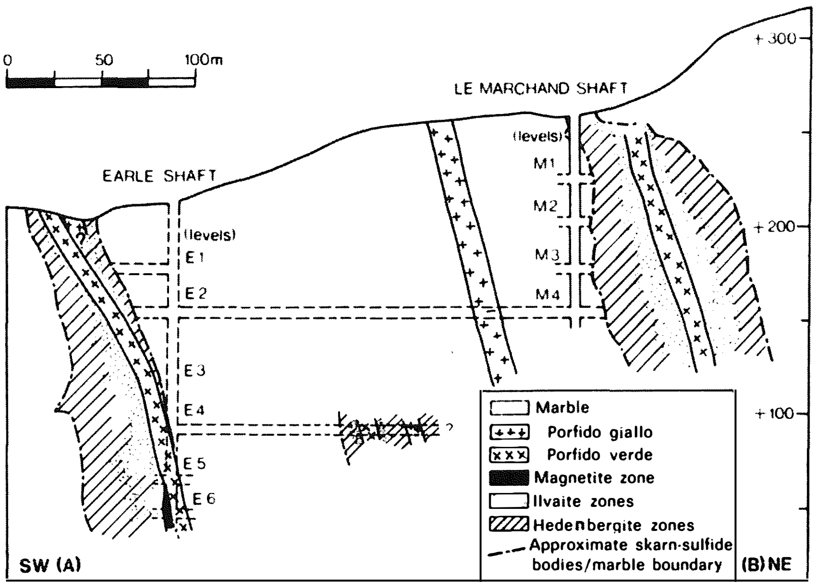


Fig. 4 – Schematic cross section of the Valle del Temperino deposit (modified after Corsini *et al.*, 1980).

quartz, calcite, epidote, johannsenite and traces of andradite, rhodonite and thaumasite. Ore minerals include chalcopyrite, pyrrhotite, pyrite, sphalerite, galena, magnetite and traces of bismuthinite, arsenopyrite, etc.. In particular, Cu-Fe ores are prevalent at Valle del Temperino, while Pb-Zn ores dominate at Valle dei Lanzi. Skarn bodies are zoned with an Ilvaite zone (substituted by a magnetite zone at the deepest levels) at the contact with the «Porfido Verde», followed by a distal hedenbergite zone that can change to a johannsenite zone at the external contact with marbles. The highest chalcopyrite-pyrrhotite concentrations occur in the ilvaite zone, whereas Pb-Zn sulfides tend to be concentrated in the external pyroxen-bearing zones. Nevertheless, the observation of rhythmic deposition of ilvaite, hedenbergite, chalcopyrite and Pb-Zn sulfides, and replacement of ilvaite by hedenbergite indicate that fluctuations of physicochemical parameters, with time and space, caused some overlapping of these relationships.

During the exploitation, many large cavities (up to several cubic metres) were encountered in the skarn mass, and spectacular groups of quartz crystals (max. 50 cm) and ilvaite crystals (max. 10 cm) were saved for public and private collections.

2.5 Pyrite ores and Cu-Pb-Zn-(Ag) sulfide ores of Southern Tuscany

One of the major mining resources of Tuscany (fig. 1) was pyrite which was exploited to produce H_2SO_4 and Fe-oxide pellets; the heat given off during the oxidation process was also exploited, yielding about 300 kWh energy per ton of treated pyrite. Mining for pyrite started at the end of the past century and stopped in the 1990's, when the last pyrite mine in southern Tuscany (Campiano) shut down; in this period about 100 million tons of high-grade mineral concentrate have been obtained and processed. According to their geologic settings, pyrite ores can be subdivided into three main groups (Tanelli and Lattanzi, 1983):

1) Lens-shaped (Fig. 5), near comformable massive pyrite bodies, in association with sulphate-carbonate lenses and skarn within phyllites (Paleozoic-Triassic?) belonging to the metamorphic basement (Niccioleta-I, Campiano-

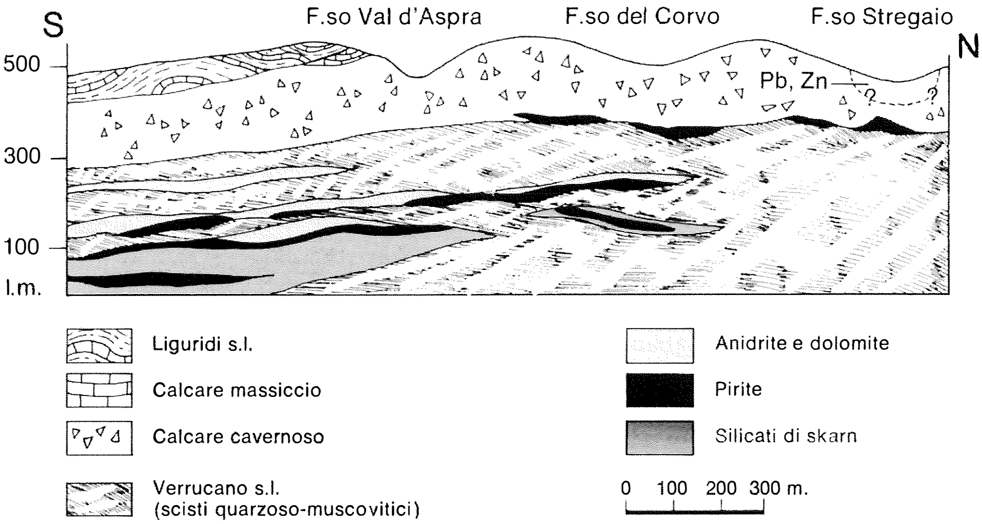


Fig. 5 – Simplified geological section of Niccioleta pyrite deposit (modified after Tanelli, 1977).

I, Serrabottini-I). Apart from Campiano-I, Cu-Pb-Zn grade in these deposits is uneconomic.

2) Lens-shaped bodies (fig. 5), partly discordant, associated with Upper-Triassic calcareous dolomitic formations («Calcare Cavernoso») at their bottom contact with phyllitic formations (Paleozoic-Triassic?) of the metamorphic basement (Boccheggiano-I, Niccioleta-II, Serrabottini-II, Gavorrano-I, Argentario). Higher Cu-Pb-Zn grade than group 1) but uneconomic.

3) Ore bodies (veins and masses) associated with Mio-Pliocenic, high-angle, extensional faults (Montoccoli, Ritorto), sometimes at the tectonic contact with Pliocenic intrusions (e.g. Gavorrano-II, Giglio Island). These mineralizations are of much smaller importance for extraction of pyrite, but in some cases they show economic Cu-Pb-Zn-(Ag) concentrations (Boccheggiano-II, Campiano-II, Fenice Capanne, Montieri-Gerfalco).

Many aspects of origin and evolution of these ores are still to be elucidated. However, Tanelli and Lattanzi (1983) considered the group 1) and 2) hydrothermal-sedimentary in origin (Palaeozoic-Triassic), possibly related to a pre-Tethyan aborted rift. Hydrothermal activity during Mio-Pliocenic magmatic events produced metamorphism, recrystallization and remobilisation of these ore bodies. Ore bodies of group 3), clearly emplaced in connection with Mio-Pliocenic tectonic and magmatic activity, and probably partially derived metals and sulphur from remobilisation of the former mineralizations [group 1) and 2)].

Niccioleta and Boccheggiano mines provided some of the finest groups of pyrite, cubic, crystals ever found in the world. Boccheggiano and Gavorrano mines also provided pyritohedral and complex cube-pyritohedral crystals. The latter are frequently deeply striated and are locally named «pirite triglifa». Niccioleta mine also provided metre-long gypsum crystals and good crystals of many other sulfides. Finally, Campiano mine produced incredible specimens of anhydrite in large lozange-shaped crystals (up to 30 cm) and in radiating groups of acicular crystals.

2.6 The Sb-Au and Hg epithermal deposits of Southern Tuscany

The most relevant addition in recent years to the metallogeny of Southern Tuscany is represented by the discovery in the mid'80s of «Carlin-type» (s.l.), carbonate hosted, epithermal Au prospects (Tanelli *et al.*, 1991). The Au prospects occur along a belt extending from Montagnola Senese to Monti Romani, which was previously known for the presence of Sb and Hg deposits (fig. 1). Sb-Au and Hg deposits show a strict association with structural highs where the «Calcare Cavernoso» of the Tuscan Nappe is directly overlain by the flyschoid, impermeable, Liguride Nappe (Fig. 6).

These deposits are associated with prominent hypogene and supergene alteration, and with recent or present-day thermal manifestations (travertines, hot springs, etc.). The deposits are localized in the peripheral parts of the Larderello and Monte Amiata geothermal fields, and their emplacement is ascribed to convective circulation of meteoric fluids triggered by recent (Pliocene-Quaternary) magmatic activity in the area.

Sb-Au mineralization consists of jasperoid and vuggy silica masses which replace carbonatic rocks (mostly Triassic «Calcare Cavrnoso») at the contact with the overlying argillaceous formations (Liguride Nappe). Ore minerals are stibnite, pyrite, native gold, base metal sulfides, orpiment, realgar included in chalcedony, coarse quartz, calcite, fluorite, barite, gypsum, alunite, clay minerals and kaolinite. In these deposits cinnabar is seldom found as thin earthy varnishes lining late fractures in ore. Beautiful specimens of stibnite in groups of well terminated, prismatic, striated, crystals (up to 20 cm) have been found in cavities of vuggy silica or embedded in spatic calcite veins. Secondary, whitishyellow-red, Sb oxides and sulphates frequently encrust the stibnite crystal faces.

Tuscany has long been a major mercury producer through the exploitation of the worldclass epithermal deposits of Monte

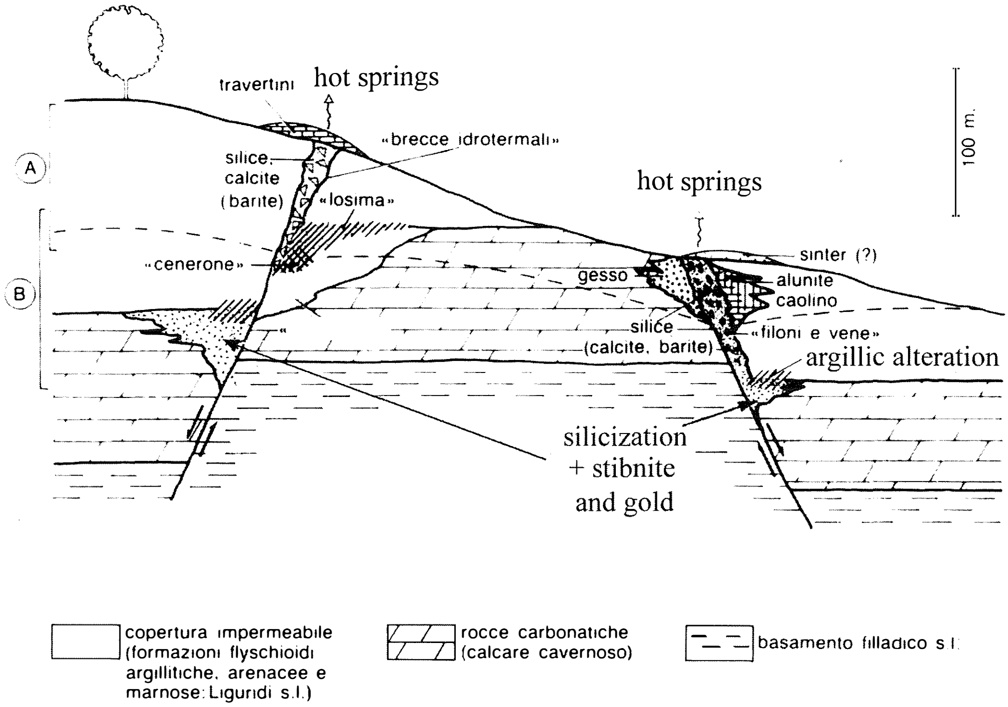


Fig. 6 – Schematic geological section of a Sb-Au deposits in Southern Tuscany (modified after Tanelli *et al.* 1991); (A) Quartz, calcedony, calcite ± Sb and Fe oxides and hydroxides, alunite, clay minerals, gypsum, barite, sulfides, sufates, Cl oxides, Sb sulfur oxides, gold; (B) quartz, calcedony ± clinozoisite, calcite, sericite, stibine, pyrite, marcasite, galena, sfalerite, tetraedrite, arsenopirite, cinabro, gold.

Amiata area. In the 1970's the Monte Amiata mines were gradually closed because mercury was progressively replaced in many industrial processes. Monte Amiata Hg deposits are spatially related to the Sb-Au ones, but cinnabar and stibnite do not occur in equal amounts in the same deposits and appear to exclude each other (Klemm and Neumann, 1984). In few Hg deposits, stibnite sporadically occurs as scattered and isolated aggregates of needles. Hg ores occur as cinnabar veinlets and impregnations (replacing carbonatic cement and matrix of host rocks), in limestones, calcarenites and sandstones (Liguride Nappe). Impregnations of cinnabar have been also found in Pliocene sands, and rare micro-crystals were observed in vacuoles of Monte Amiata lava flow. Cinnabar is associated with pyrite, marcasite, and minor realgar, orpiment, stibnite, metacinnabar, native mercury, with calcite, gypsum and celestite as gangue minerals. Sometimes the surfaces of open fractures in sandstones are covered by esthetic spherical and botryoidal aggregates of cinnabar named «fragole» («strawberries»).

2.7 The raw ceramic material deposits of Southern Tuscany

Among industrial minerals of Tuscany, raw materials for the ceramic industry are especially important (ca. 600,000 t/yr, about one third of total Italian production). The main activity was localized in four deposits (Marciana and La Crocetta in Elba Island, Botro ai Marmi near Campiglia M.ma and

Piloni di Torniella near Roccastrada; fig. 1) All these occurrence are associated with magmatic, acidic, rocks of the Tuscan Magmatic Province.

2.7.1 Marciana and La Crocetta (Elba Island)

At Marciana (western Elba), exploitation was focused on a lenticular, subvolcanic, body of porphyritic aplite (alkaly feldspar granite in composition) belonging to the Capo Bianco Unit. The mined rock is composed of a very fine-grained aggregate of albite, K-feldspar, quartz and magmatic muscovite that maintain the original magmatic, porphyritic, texture. Only minor alteration effects are visible (scarce pyrite-calcite-sericite disseminations and veinlets), hence the economic qualities of the rock (high alkali K_2O = 4 wt%, Na_2O = 4 wt%, and very low Fe, Ca and S contents) are the result of primary magmatic processes.

The La Crocetta mine (Maineri *et al.*, 2002) is located in central-eastern Elba, and represents the currently exploited portion of a mineralised area including the old mine of Buraccio to the north. Exploitation focuses on a pervasively sericitized, porphyritic, aplite sill belonging to the same intrusive unit exploited in Marciana (Capo Bianco Unit), which underwent significant potassium enrichment during sericitic alteration. The ore bodies are located along the hanging wall of the Central Elba Fault, a low-angle extensional lineament of regional significance. A later carbonatization stage, apparently associated with highangle extensional tectonics, locally overprinted the sericitized facies. It is expressed by carbonate ± pyrite ± quartz veins, with adverse effects on ore quality. Sericitization was accompanied by addition of potassium, and loss of Na (± Ca, Fe). Rubidium was not enriched along with potassium during sericitization, contrary to what would be expected for interaction with late-magmatic fluids. New ^{40}Ar-^{39}Ar data from eurites provide an isochron age of about 6.7 Ma for the sericitization, whereas the age of the unaltered protolith is ca. 8.0-8.8 Ma. Field evidence indicates the Central Elba Fault to be the main channel for the hydrothermal fluids. On the other hand, the involvement of heat and/or fluids contributed by the Porto Azzurro pluton, which crops out in the La Crocetta area, is ruled out by field, geochemical and geochronological data (^{40}Ar-^{39}Ar age of Porto Azzurro = 5.9 Ma, i.e. significantly younger than the sericitization event). Fluid inclusion studies suggest that sericitization was associated with a low-temperature (< 250 °C) hydrothermal system. Fluids were locally boiling, of variable salinity (4-17 wt% NaCl equiv.), and contained some CO_2 (XCO_2 = 0.027). Their ultimate source is not unequivocally constrained; meteoric and/or magmatic contributions may be possible. Low salinity (= 2.6 wt% NaCl equiv.), low temperature (< 250°C) fluids are associated with the late carbonate veining. They are considered to be of dominantly meteoric nature because of their low salinity. In summary, sericitization at La Crocetta is regarded as the product of a detachment fault-related, low temperature hydrothermal system, resulting from the structurally controlled focusing of meteoric and possibly magmatic fluids. Hence, potential targets for exploration for similar resources are represented by aplitic bodies located in the hanging wall of Elba Centrale Fault.

2.7.2 Botro ai Marmi (Campiglia M.ma)

The Botro ai Marmi feldspar deposit is associated with the apical part of a shallow sienogranitic to granodioritic intrusion closely associated with a porphyritic dyke swarm (both acid and mafic products), and several Cu-Pb-Zn skarn and Sn deposits. The economic value of the mined rocks lies in their high K (K_2O = 7.4 wt%), low Ca-Fe-S contents. Mineralogically, this high K content is expressed by the occurrence of two generations of K-feldspar; the first one is magmatic, whereas the second is late-magmatic/hydrothermal and replace plagioclase. Explanation for the high K content of this material include: 1) displacement toward the K-feldspar apex of the melt composition because of assimilation of carbonate country rocks (Poli *et al.*, 1989), and

2) late- to post-magmatic K-metasomatism. Recent studies (Lattanzi *et al.*, 2001 and reference therein) seem to favour the second mechanism, although the first one may have contributed as well. Specifically, fluids inferred to be in equilibrium with the second generation of K-feldspar show temperatures as high as 500 °C, with salinities up to 38 wt % NaCl and 19 wt % KCl. These features are typical of porphyry-related metalliferous deposits, also characterized by potassic alteration; however, in the Botro ai Marmi system the potassic alteration is metalpoor: metalliferous mineralization occurs in a later skarn to vein stage, and is mostly localized away from the intrusion.

2.7.3 Piloni di Torniella (Roccastrada)

The Piloni di Torniella deposit results from hydrothermal alteration of Quaternary (2.4 Ma) peraluminous rhyolitic lavas and domes, anatectic in origin. Field evidences suggest that the hydrothermal alteration was mainly controlled by high-angle fault systems. Hydrothermal kaolinite + alunite replace magmatic feldspar and glass. However, have been also described minor occurrences of sedimentary (re-worked?) kaolinite in small lacustrine basins; in these occurrences, of better economic quality, alunite is scarce or absent. In comparison with other deposits of this study, the chemical composition of mined rocks is widely variable, and S contents are locally high, because of the presence of alunite; in fact, alunite was also mined in the past, but nowadays it severely detracts from the quality of the ore. Even if there is no recent detailed research on the locality, the available information may suggest that this deposit represents an advanced argillic alteration assemblage formed in a shallow environment by meteoric fluids interacting with hot gases.

2.7.4 Conclusions

The main deposits of ceramic raw material in Tuscany are associated with acid magmatic rocks of the Tuscan Magmatic Province. Development of ore-grade material is the result of a combination to various degrees of magmatic and hydrothermal processes. Primary magmatic rocks are already characterized by comparatively high alkali, and low iron and calcium, contents. Therefore, in some cases (notably Marciana) they may represent ores in themselves. In other localities, the commercial qualities of the currently mined rocks arise from hydrothermal alteration, resulting in either K-enriched (Crocetta, Botro ai Marmi) or kaolinite (± alunite)-rich material (Piloni di Torniella). The nature of the fluids involved range from high-temperature, high salinity, presumably magmatic, fluids (Botro ai Marmi), to moderate temperature fluids of mixed magmatic and meteoric origin (La Crocetta), to presumably steam-heated meteoric fluids (Piloni di Torniella).

2.8 The Larderello and Monte Amiata geothermal fields

There are two important geothermal fields in Southern Tuscany (fig. 1): the Larderello field, and the Monte Amiata field. Shallow intrusive bodies, belonging to the Tuscan Magmatic Province, and hypothetical mafic injection and/or uprising mantle dome, seems to be the most plausible heat sources of these two geothermal areas, which were extensively drilled and exploited by ENEL (Italian Electricity Board) during recent decades.

The geothermal field of Larderello is a vapour-dominated system, one of the world's rare super-heated steam producing systems. The main reservoir of the Larderello field is found within a limestone formation (the «Calcare Cavernoso», Upper Triassic in age) belonging to the Tuscan Nappe. They rest on top of a schistose quartzitic rocks of Paleozoic-Triassic age which unconformably overly a metamorphic basement made up of phyllites, micaschists and gneisses. The cap rocks of the reservoir are represented by an impermeable flysch formation (the «Liguridi Nappe Complex») and by Neogene clay sediments. At

Larderello the first industrial extraction of boric acid started during the 18th century, while the possibility to generate electricity from geothermal steam was successfully proven for the first time in the world in 1904. In the late 1970s a deep exploration program through out the field significantly improved the knowledge on temperature distribution at depth, and productive levels were discovered in the deep-seated metamorphic basement. Peraluminous, leucogranites and monzogranites with significant F and B content, and their thermometamorphic aureoles, were found in several deep wells (between 2.5 and 4.5 km depth). The occurrence of intensely fractured zones inside the granites could represent a target for the future reservoir exploration. Intensive exploitation caused a pressure drop inside the reservoir with the consequent sharp decline in fluid production. To test the feasibility of increasing steam production water injection in the Larderello area started in 1979. From 1984, re-injection of waste water became an important part of the exploitation strategy, and the process was monitored by determining the isotopic and chemical composition of fluids.

The geothermal area of Monte Amiata is characterized by the presence of a Quaternary volcanic structure having a trachydacitic-latitic composition. This volcano is located on a wide structural high where Liguridi and Tuscan Nappe crop out. The main geological difference with Larderello is the nature of the metamorphic substratum, which consists mainly of Palaeozoic graphite-bearing phyllites and phyllitic quartzites, metasandstones, limestones and dolostones. Geothermal research in the Mt. Amiata area started in the 1950s and led to the discovery of several shallow reservoirs (160-220°C). The top of these reservoirs is located at a depth ranging from 400 m to 1000 m in correspondence to positive structures of the carbonate-anhydrite formation of the Tuscan Nappe. Based on experience gained from deep drilling in the Larderello field, the research in the Monte Amiata area was resumed in 1978: two deep exploratory wells were drilled to find additional fluid below the layers already under exploitation. At depths ranging from 1300 m to to 3000 m, water-dominated productive horizons have been discovered, with temperatures of 300 to 360 °C.