Volume n° 2 - from B16 to B33

Field Trip Guide Book - B18

32nd INTERNATIONAL
GEOLOGICAL CONGRESS

SKARN DEPOSITS IN SOUTHERNTUSCANY AND ELBA ISLAND (CENTRAL ITALY)

Leader: M. Benvenuti

Associate Leaders: M. Boni, L. Meinert

Pre-Congress **B18**

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Front Cover:
Historic site of Rocca San Silvestro in the Campiglia Marittima mining district

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Introduction

Aim and Localities of the Field Trip

IGC field trip B18 will investigate the classic skarn localities of Tuscany and the Island of Elba. Tuscany includes several different skarn types but the most famous, and the ones that we will visit on this field trip, are the Fe and Zn skarns at Isola d'Elba and in the Campiglia Marittima district. These are of historical, mineralogical, and economic importance. The field trip will start with a general overview at the historic site of the Etruscan town of Populonia. Following this, we will travel by ferry to the Island of Elba to examine the Fe-skarns at several localities. The second day we will focus on the classically zoned Zn-skarn system around Campiglia. The trip will conclude with a visit to the archeometallurgically interesting beach slags at the Baratti Gulf.

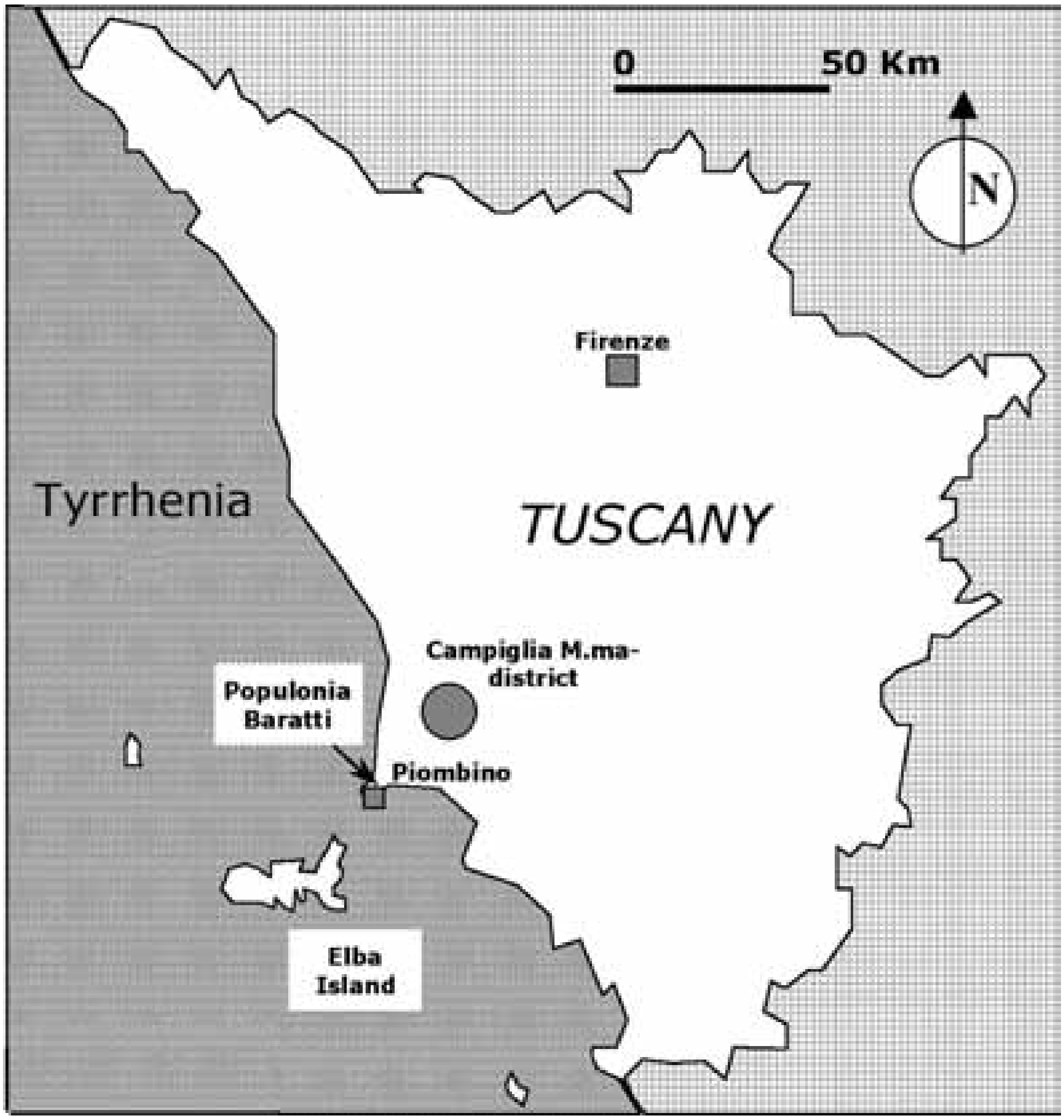

Figure 1 - Itinerary of the field trip.

Regional setting

Geology and geodynamics

The two areas which will be visited during our field trip (i.e., Elba Island and the Campiglia Marittima district: **Fig. 1**) belong to the Northern Apennines chain (**Fig. 2**). The Northern Apennines chain is mainly composed of a pile of NE-verging tectonic units, accompanied by second-order back-thrusts (Finetti et al., 2001). As schematically shown in **Fig. 3**, the uppermost are the Ligurian Units (or Ligurides), originally deposited in an oceanic realm (i.e. the Ligurian–Piedmontese sector of the Alpine Tethyan ocean). The Ligurian units, consisting of ophiolites with their Jurassic to Eocene sedimentary cover, tectonically overlie the Tuscan and Umbria–Marche units, originally deposited on the passive margin of the Adria Plate since the middle Triassic. The Tuscan and Umbria–Marche units consist of an upper 2000–3000 m-thick succession of Oligocene–Miocene age, formed by siliciclastic foredeep sediments, and a lower succession of Mesozoic–Cenozoic age, mainly composed of carbonate rocks. Both successions rest on about 1000–1500 m-thick Triassic evaporites (Burano Fm.), grading to dolomites in the Adriatic Sea area. The base of the thick evaporitic layer is a very important detachment plane for thrusting and gravity sliding. Due to time–space outward migration of the thrust front, Oligocene–Miocene tectono-stratigraphic units deposited in the foredeep system, become progressively younger eastward.

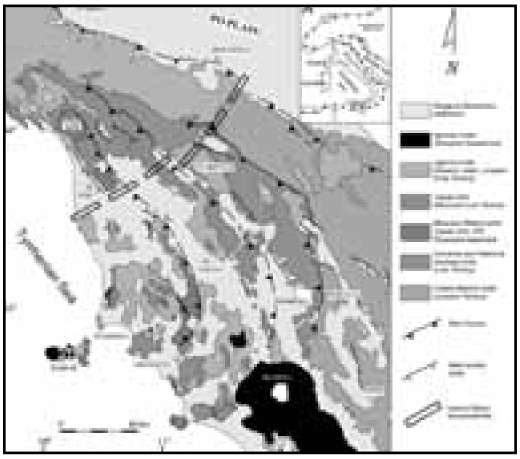

Figure 2 - Geological sketch-map of the northern Apennines (modified from Bonini et al., 2001).

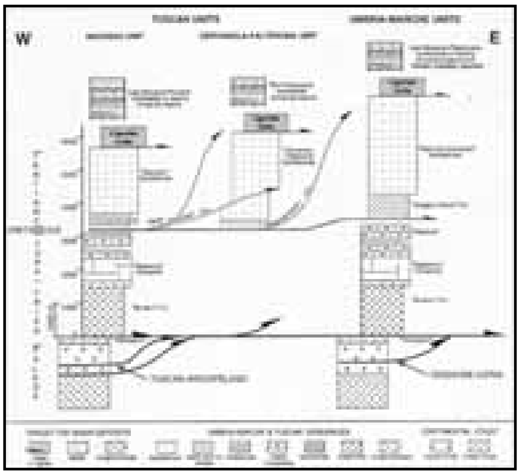

Figure 3 - Schematic stratigraphic columns of the Tuscan and Umbria-Marche units (from Finetti et al., 2001)

Neogene-Quaternary Magmatism

During the post-collisional phase of the Apenninic orogeny (from Late Miocene to Pleistocene), a large variety of magmatic bodies were emplaced at different crustal levels in the Northern Apennines hinterland (mainly in southern Tuscany). Volcanic to intrusive bodies were emplaced in the time span of 8 to 0.2 Ma, showing a trend of decreasing ages from west to east (Civetta et al., 1978; Ferrara and Tonarini, 1985; Peccerillo et al., 1987). They include crustal anatectic acid peraluminous rhyolites and granites, and a wide range of mafic to intermediate rocks such as lam-

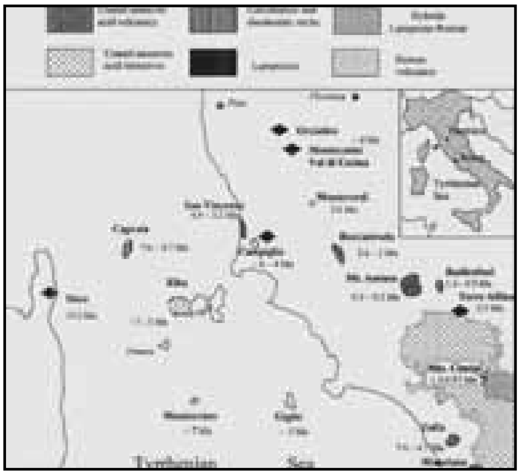

Figure 4 - Location and age of magmatic rocks of the Tuscany Magmatic Province (Peccerillo et al., 2001)

proites, high-potassium calcalkaline and shoshonitic rocks (**Fig. 4**). Rock compositions straddle the I and S fields of Chappel and White (1974), the most basic rocks being mainly I-type and the high-silica ones S-type (Peccerillo et al., 2001, and references therein). Most of the acid rocks appear to have undergone mixing and mingling with various types of mantle-derived calcalkaline to potassic melts (Poli, 1992). Mafic rocks, in fact, are commonly found as micro-granular enclaves and veins in most acid extrusive and intrusive bodies of the Tuscan Province. Several geochemical and petrological features, further suggest a heterogeneous mantle source for the mafic melts (Peccerillo, 1999). According to Peccerillo et al. (2001) the overall petrogenetic history for the Tuscan Province can be described in three main steps: 1) subduction-related metasomatism of upper mantle (both asthenospheric and lithospheric) by interaction with upper crustal material; 2) variable degrees of partial melting of heterogeneous mantle due to asthenospheric uprise, and formation of various types of magmas; 3) injection of mafic magmas into the continental crust, uprise of isotherms, onset of crustal anatexis, and acid-mafic magma mingling.

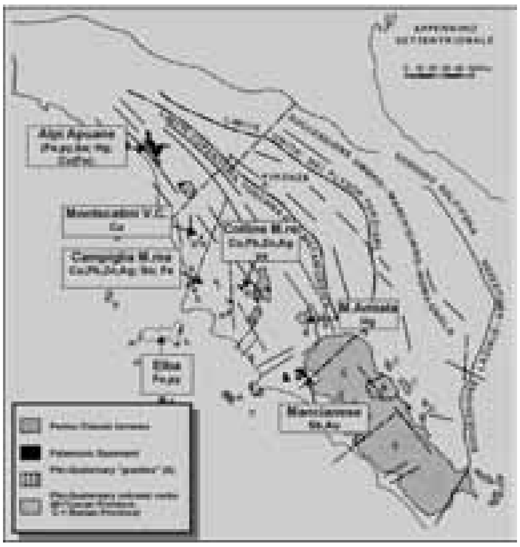

Figure 5 - The main mining districts of Tuscany (modified after Tanelli, 1983)

Ore Geology

For about 30 centuries, Tuscany has been one of the most important mining regions of Italy producing a large variety of resources, including pyrite, iron, base metals, geothermal steam and several industrial minerals and rocks (Lattanzi et al. 1994, and references therein). Today the mining industry in Tuscany is limited to industrial minerals (feldspars, halite), ornamental stones, and building materials. The Tuscan metallogenic province includes (**Figs. 5 and 6**): the Fe oxides deposits of Elba Island, the pyrite (± barite ± Fe oxides) deposits of southern Tuscany and Apuane Alps, the base-and precious-metals deposits of the "Colline Metallifere" district (southern Tuscany), the Hg deposits of the Monte Amiata area, the Sb deposits of the Capalbio-Monti Romani belt (cf. Cipriani, Tanelli, 1983; Tanelli, 1983). The newest addition to the metallogenic framework of Tuscany, is the discovery in the mid '80s of "Carlin-type" epithermal gold mineralization. Most of the Au prospects, of limited economic importance, are closely related to Sb deposits (Tanelli et al., 1991; Lattanzi, 1999).

A number of different skarn deposits occur in the southwestern portion of the Tuscan metallogenic province (**Fig. 7**): they include calcic iron skarns (Capo Calamita, Ginevro, Sassi Neri and Ortano at Elba Island; Niccioleta in the Colline Metallifere district) and lead-zinc(-copper) skarns (Temperino mine in the Campiglia M.ma district; Serrabottini near Massa Marittima). These deposits have been studied by Bartholomé, Evrard, 1970; Corsini et al., 1980; Dimanche, 1971; Tanelli, 1977; Lattanzi, Tanelli, 1985; Del Tredici (1990), Torrini (1990) and Dünkel (2002). According to Tanelli (1977) the Tuscan skarn deposits formed by replacement of Triassic

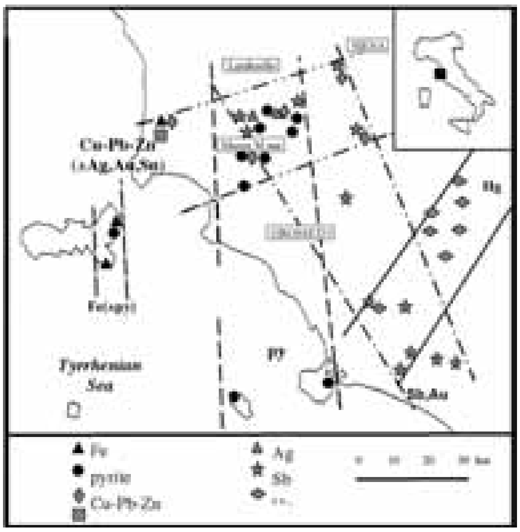

Figure 6 - Distribution of main ore types of southern Tuscany

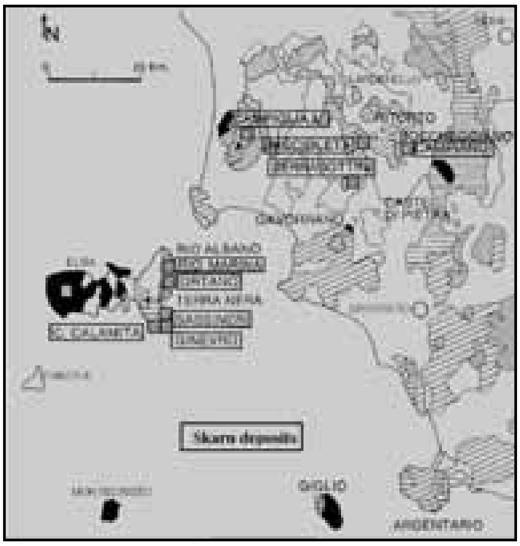

Figure 7 - Location of Tuscan skarn deposits (after Tanelli, 1977)

carbonate rocks of the Tuscan Unit by metasomatic processes triggered by the emplacement at shallow crustal levels of the Neogene magmatic rocks of the Tuscan Province. Skarn bodies may be in contact with magmatic rocks (e.g., at Temperino mine), or at various distances (Niccioleta, Ortano). The presence of magmatic rocks in close proximity to skarn bodies does not necessarily imply a genetic link: at Ginevro, for instance aplitic dikes appear to predate skarn formation (*cf.* Dimanche, 1971). Source(s) of elements for Tuscan skarn deposits are still poorly constrained. Corsini et al. (1980) maintain that isotopic composition of sulfur from the Temperino skarn deposit is compatible with a local, non magmatic source (i.e., sulfides/sulfates from Permo-Triassic country rocks). On the other hand, the uniform lead isotope composition of pyrite and galena from the Campiglia Marittima and Niccioleta deposits may reflect contribution of lead (and other metals?) from Neogene-Quaternary magmatic rocks (Lattanzi et al., 1991).

Elba Island

The geologic framework

Due to its location midway between Corsica and the Northern Apennines, Elba Island is a key element for the reconstruction of the tectono-stratigraphic evolution of the Apenninic chain after the opening of the Tyrrhenian basin. Other elements of interest are the presence of an extensive Mio-Pliocene magmatism, with attendant swarms of aplitic and pegmatitic dikes, as well as the occurrence of the world-famous iron ore deposits. Elba Island's long-living geologic history starts in the Palaeozoic, but its Alpine tectonic evolution begins in the Late Cretaceous - Early Tertiary with the consumption of the western Tethyan ocean (Ligurian-Piedmontese Basin). After the Upper Eocene-Lower Miocene collision and polyphase deformation of the European (Corsica) and Adriatic (Tuscany Domain) margins, in the Late Miocene-Pliocene/? Quaternary syn- and post-magmatic extensional events took place (Bortolotti et al., 2001).

The tectonic frame of central and eastern Elba Island is made up by the following nine major tectonic units (from the geometrically lowermost upwards): (1) Porto Azzurro Unit; (2) Ortano Unit and (3) Acquadolce Unit; (4) Monticiano-Roccastrada Unit, (5) Tuscan Nappe Unit and (6) Gràssera Unit; (7) Ophiolitic Unit with seven subunits; (8) Paleogene Flysch Unit and (9) Cretaceous Flysch Unit (Bortolotti et al., 2001 and references therein).

In eastern Elba the units of this tectonic pile are characterised by a general top to east vergence, and are separated each other by roughly NS verging overthrust surfaces. The various units, originally deposited in quite different palaeogeographic domains, were deformed and piled up into their present position during the compressional stage of the Apenninic orogeny, and later affected by an important extensional phase. This stage was also accompanied by the emplacement of several magmatic intrusions at shallow crustal levels (cf. Dini et al. 2002; Maineri et al., 2003, and references therein): the Monte Capanne pluton (6.9 Ma), the monzogranitic stock of Porto Azzurro (6.2-5.0 Ma), several swarms of aplitic and pegmatitic dikes (the latter almost exclusively found associated with the Monte Capanne pluton), and a laccolith complex made of subvolcanic porphyritic rocks (>8.5-6.85 Ma). Dini et al. (2002) suggest that the emplacement of the Monte Capanne pluton triggered the movement of an important extensional detachment fault (Elba Central Fault), which controlled the eastward translation of about 10 km of upper plate rocks (including Complex V with intruded laccolith complex) from their original position on the top of Monte Capanne pluton.

The Elba Central Fault caused intense fluid circulation and resulting pervasive hydrothermal alteration of porphyritic aplites and formation of the "eurites" (sericite replacing primary albite and K-feldspars) exploited at La Crocetta and Marciana mines (Maineri et al., 2003). At 6.2-5.0 Ma, the emplacement of the Porto Azzurro stock caused deactivation of the

Elba Central Fault, although additional eastwards tectonic translations took place along another major low-angle fault, the Zuccale fault (Pertusati et al., 1993). The emplacement of the Porto Azzurro pluton caused also a strong thermometamorphic imprint on the geometrically lowermost Units of the Elba structural edifice (namely, the Porto Azzurro, Ortano and Acquadolce Units). Crosscutting relationships between the Zuccale fault and aplitic dikes indicate that the detachment postdated, at least partially, the emplacement of the magmatic dikes. The last tectonic stage at Elba Island is mainly represented by N-S trending high-angle extensional faults, affecting the entire N-Tyrrhenian basin. This last episode ended before about 3.5 Ma (Keller and Pialli, 1990).

Geology, mineralogy and textures of Elba iron deposits

Iron ores from Elba Island have been mined without interruption for almost three millennia, since the early Etruscan mine workings (early 1st Millennium BC: Corretti and Benvenuti, 2001) up to about twenty years ago (1981, closure of the Ginevro mine). At least 60 million tons of Fe ore have been extracted from Elba deposits from ancient times to the present (data from Fabri, 1887; Pullè, 1921). To preserve this long mining tradition a "Mining and Mineralogical Park" has been recently established in eastern Elba (cf. Tanelli and Benvenuti, 1999).

As shown in **Figure 8**, the Fe deposits of Elba Island are restricted to a relatively narrow belt extending NS along the eastern coast of Elba Island, from Monte Calendozio (Rio Albano mine) to the Calamita promontory. The ore bodies range from stratiform to pod-like or vein-type, although the first appears to be dominant (Zuffardi, 1990). Stratiform Fe bodies are predominantly hosted by Palaeozoic-Triassic formations belonging to the Tuscan domain. Many Fe ores are associated with faults (Debenedetti, 1952; Gillieron, 1959): a first set of thrust faults, striking NS and dipping 30°-45° W, corresponding to the thrust surfaces among the various tectonic units, and two sets of normal, high-angle faults, one striking NS and dipping 30°-60° E, the other one with strike NE-SW and dips of 45°-70° to NW or SE.

As reviewed by Tanelli and Lattanzi (1986) there is disagreement in the literature about whether all of the Fe deposits are genetically associated with late-Apenninic granitic stocks or whether in some cases the intrusions simply metamorphosed and partly

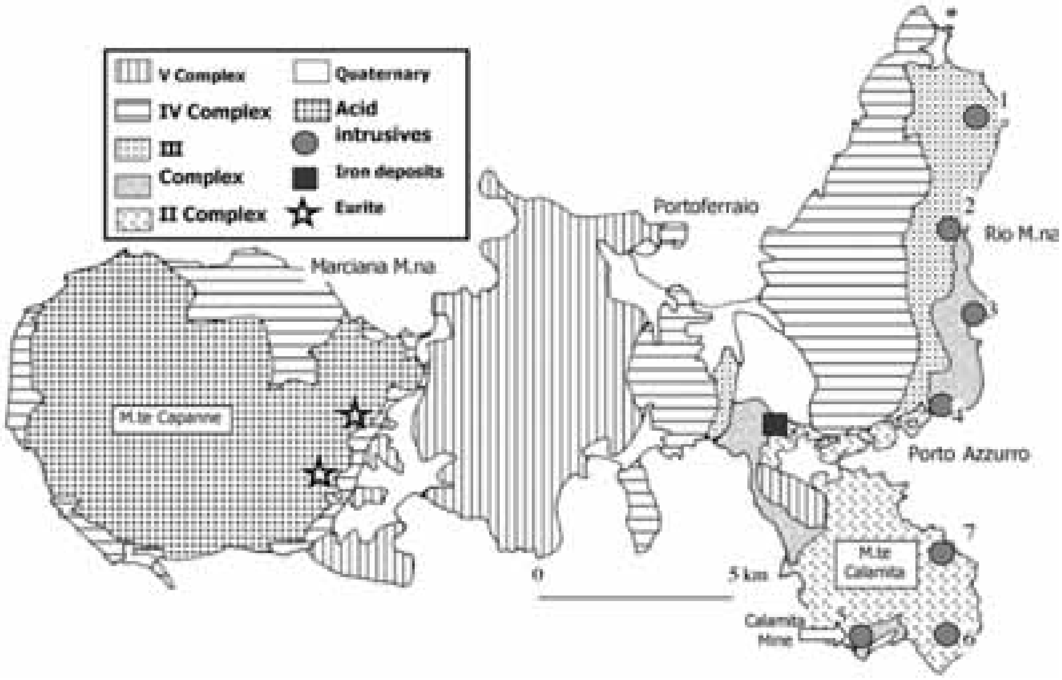

Figure 8 - Location of main iron deposits of Elba Island. Legend: 1) Rio Albano; 2) Rio Marina; 3) Ortano; 4) Terranera; 5) Calamita; 6) Ginevro; 7) Sassi Neri.

remobilised the iron ores that were formed, or at least pre-concentrated, in sedimentary and/or hydrothermal sedimentary environments of Triassic and/or Palaeozoic age (stage *ii* of Lattanzi et al., 1994).

Moving from Rio Marina towards the Calamita Peninsula, the association of iron ores with skarn bodies and/or aplitic dikes becomes more and more distinct. Even at Rio Marina skarn bodies were encountered at depth. Drilling and limited underground workings in the 1950s revealed the existence of hematite-pyrite skarn bodies replacing wedge-shaped carbonatic masses (the Vigneria limestones of Gillieron, 1959), which are now interpreted as tectonic slices of the overlying Jurassic to Oligocene carbonatic formation of the Monticiano-Roccastrada Unit (Bortolotti et al., 2001). Immediately south of Rio Marina town, very large skarn bodies with hedenbergite-ilvaite-epidote ± quartz, chlorite, magnetite, pyrite and pyrrhotite extend along the coast (Torre di Rio skarns, **Fig. 9**). Skarn minerals occur along schistosity planes of the Acquadolce calc-schists, as reported in detail by Lotti (1886, pp. 205-206). Moving southwards, other skarn bodies occur at Ortano, Porticciolo, Tignitoio and Capo d'Arco. The Ortano deposit shows a different ore mineralogy (pyrite, pyrrhotite ± hematite, magnetite), associated with pyroxene-epidote-ilvaite skarn bodies, which replace marbles and calcareous phyllites along a cataclastic horizon separating the Acquadolce Unit from the overlying Ortano Unit. Lenses of hematite + pyrite ± magnetite occur at Terranera within the Monticiano – Roccastrada Unit, and are in close proximity to skarn bodies cropping out at the nearby Punta delle Cannelle. The iron mineralization appears to be coeval and cogenetic with skarn development, based upon a 7.3 ± 0.4 Ma radiometric age of one hematite sample (Lippolt et al., 1995).

Fe ores and skarns of southeastern Elba Island are associated with aplitic dikes linked to the Porto Azzurro pluton. This association is particularly evident in the Calamita Peninsula (see **Fig. 8**), where several skarn-bearing iron deposits (Capo Calamita, Ginevro **(Fig. 9a)**, Sassi Neri, Stagnone) are hosted by the Porto Azzurro Unit. At Capo Calamita stratiform garnet (andradite)-rich skarn and lesser ilvaite-hedenbergite skarn (Torrini, 1990) developed mostly at the contact between the Mt. Calamita Formation and the overlying carbonatic formation ("crystalline dolostones and dolomitic limestones" of Bortolotti et al., 2001). The exploited ores were spatially associated with both types of skarn, and consisted of lenses and massive bodies of magnetite ± hematite, goethite and trace amounts of base metal sulfides. The Ginevro and Sassi Neri deposits appear to be higher temperature and more reduced than the other deposits. At Ginevro, for instance, skarn mineralization totally replaced the carbonate rocks and there is a great abundance of aplitic dikes (Dimanche, 1971; Del Tredici, 1990). The skarns contain ferropargasite, associated with grossular-almandine garnet and only minor amounts of hedenbergite, ilvaite and epidote. Finally, the Stagnone deposit was recognized through a drilling project, but was never exploited; no detailed information is thus available.

Primary ore mineralogy of Elba's iron deposits is relatively simple, being made up of Fe oxides. As a general rule, hematite is dominant in the northern deposits, whereas magnetite (±pyrite±Cu,Pb,Zn,As,Bi sulfides) is enriched in the skarn-associated deposits of the Calamita peninsula. Typically, magnetite occurs as pseudomorphs after primary hematite (mushketovite), as first suggested by Vom Rath (1870) and confirmed by Cocco and Garavelli (1954), Tanelli (1977), Torrini (190) and Dünkel (2002). Del Tredici (1990) has observed the same texture at Sassi Neri. Elba is especially famous worldwide for its beautiful crystals of hematite (variety "oligisto" = glaze iron) ± pyrite, most coming from the Rio Marina stopes. Deschamps et al. (1983) suggested that the hematite ±pyrite (±quartz) assemblage is paragenetically late, being derived from oxidation and remobilisation of primary pyrite. The final alteration products of primary Fe minerals are limonitic aggregates of variable types and morphologies (earthy, massive, concretionary, sometimes stalactitic), which were actively exploited in the past, especially at Rio Albano, Capo Bianco and Capo Calamita mines (cfr. Calanchi et al., 1976).

Figure 10 shows the two paragenetic sequences proposed for the Calamita iron deposit by Dünkel (2002) and Torrini (1990). The former author describes an early cassiterite+pyrite assemblage, which was not observed by Torrini (1990).

Sulfides, which are very rare or absent in the Rio Marina – Rio Albano deposits, are significantly more abundant in the magnetite-type deposits, where they normally form in a late paragenetic stage. Masses of Fe-Cu sulfides (pyrrhotite, pyrite, chalcopyrite ± malachite, azurite, chalcantite, etc.) were locally exploited at Capo Calamita at the contact between the garnet skarn and the magnetite lenses. (Torrini, 1990).

As mentioned previously, the genesis of iron deposits of Elba Island and other Tuscan districts (namely, Colline Metallifere and Alpi Apuane) is not well

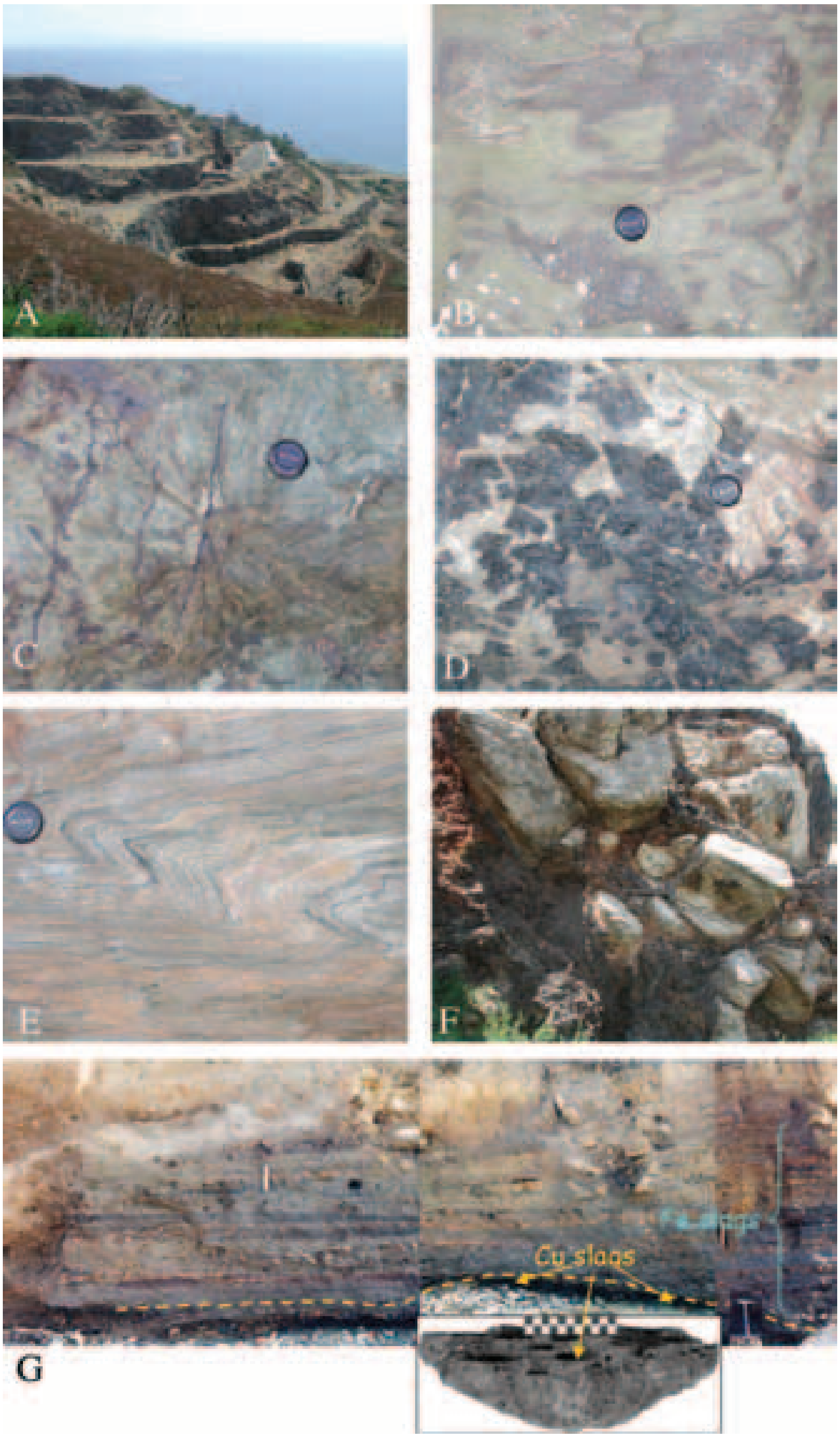

Fig. 9 - Photographs of Elba Fe skarn features: a) Open Fe Ginevro mine along the Elba coast b) Interlayered brown garnet and green pyroxene at Rio Marina c) Coarse-grained radiating crystals of hedenbergitic pyroxene cut by black ilvaite veins at Capo Calamita d) Euhedral black ilvaite crystals intergrown with hedenbergitic pyroxene at Rio Marina e) Isoclinally folded metasedimentary host rocks at Rio Marina f) Distal pyroxene-magnetite veins cutting marble at Capo Calamita g) Beach slag deposit from early mining activities along the Baratti Gulf.

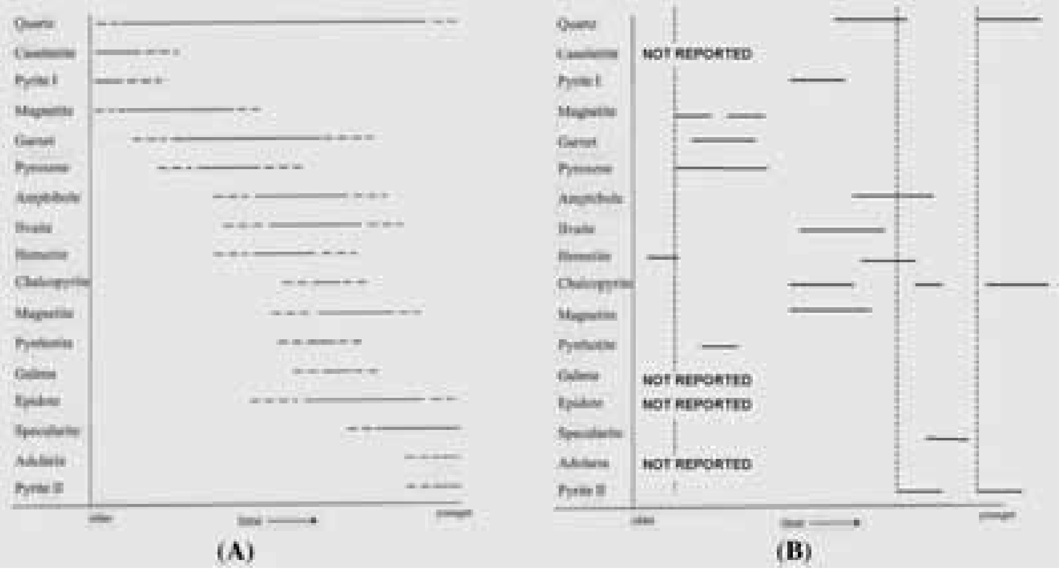

Figure 10 - Paragenetic sequences of the Capo Calamita iron skarn deposit. (A): Dünkel (2002); (B): Torrini (1990). The vertical dashed lines indicate deformation episodes.

understood. Descriptive models for the individual deposits are mostly incomplete and results of some research on specific deposits (Capo Calamita: Torrini, 1990; Sassi Neri: Del Tredici, 1990; Terranera: Seeck, 1998) are still largely unpublished. Radiometric age estimates of the hematite+adularia assemblages from Terranera and Rio Marina deposit fall between 6.4 ± 0.4 and 5.32 ± 0.11 Ma (U+Th vs He age of hematite and K/Ar age of associated adularia, respectively), i.e., the same time span as the Porto Azzurro stock (Lippolt et al., 1995). However, taking into account the regional framework, for which much more quantitative data are available (cf. Lattanzi et al., 1994), and the results obtained for the Calamita Peninsula deposits (Del Tredici, 1990; Torrini, 1990), Tanelli et al. (2001) suggest that the primary stage of iron concentration could have preceded (at least in part) the emplacement of the Porto Azzurro intrusion and related aplitic dikes (6.2-5.0 Ma), as well as the formation of skarn bodies.

Campiglia Marittima

Geologic framework

The ore deposits of Valle del Temperino, are located 2 km north of Campiglia Marittima (Livorno) village (**Fig. 11**). Several formations of the Tuscan Unit sequence crop out in this area, which can be described as a N-S trending wedge-shaped horst (“Campiglia Ridge”) bordered by high angle N-S and NW-SE trending faults on the western and eastern margins, respectively (Acocella et al., 2000). The Campiglia Ridge is made up of several formations, which belong to the Tuscan Unit, ranging from Liassic massive limestone (“Calcare Massiccio”) to Oligocene turbiditic sandstone (“Macigno”). The Tuscan Unit formations are tectonically overthrust by the allochthonous “Ligurian” and “Subligurians” Units, consisting of calcareous, marly and shaly turbidites of Upper Jurassic to Eocene age. The latter sequences are then unconformably overlain by Quaternary sediments, consisting of alluvium, fluvial and beach deposits (Giannini 1955; Giannini and Lazzarotto, 1967; Costantini et al., 1993; Bossio et al., 1993).

Magmatic activity strongly affected the Campiglia Marittima area in the Late Miocene-Lower Pliocene. Several kinds of both plutonic and volcanic bodies were emplaced, mostly with an overall acid to intermediate composition. The earliest emplaced magmatic body, cropping out in the Campiglia Marittima area is the “Granito di Botro ai Marmi”, dated at 5.7 Ma by Borsi et al. (1967). Most chemical data for the Botro ai Marmi stock plot in the syenogranite field; some rocks encountered in drill holes have granodioritic compositions (Lattanzi et al., 2001). The contact with the host rocks (mainly represented by the “Calcare Massiccio” formation) is marked by a N-S trending thermometamorphic aureole, approximately 5 km long, 1, 5 km wide and 300 m thick (Rodolico, 1945;

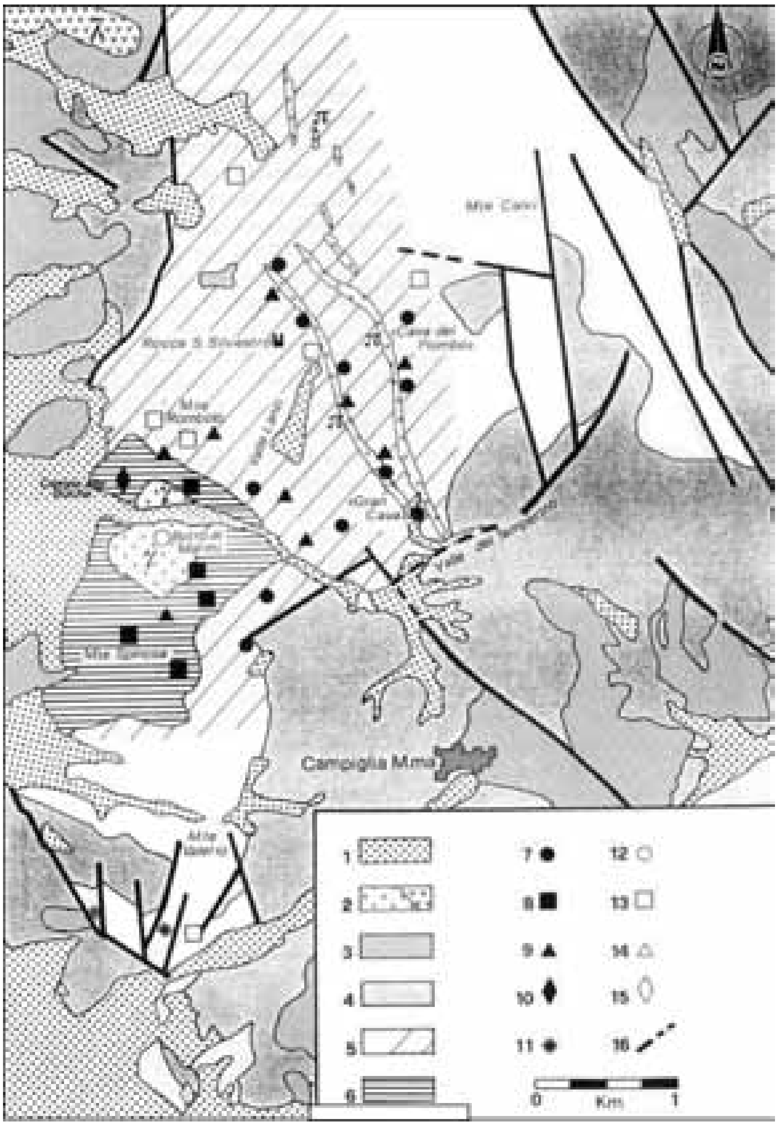

Fig. 11 - Geological map of the Campiglia Marittima district (modified after Tanelli et al., 1993). Key to symbols: (1) Neoautochtonous (Quaternary); (2) Magmatic rocks: quartzmonzonites (γ), quartzlatites (λ), porphyries (π); (3) Ligurian and Subligurian Units; (4) Tuscan Unit (Middle Jurassic-Oligocene): Posidonomya Marls, Radiolarites, Polichromous Schists, Macigno Sandstone; (5) Tuscan Unit (Lower Jurassic): "Calcare Massiccio" (Massive Limestone) partially metamorphosed to marbles (shaded areas), Reddish Limestone with Ammonites, Cherty Limestones; (6) Tuscan Unit (Lower-Middle? Trias) stratified dolomitic limestomes metamorphosed to grey marbles; (7) ilvaite-hedenbergite skarns (Cu,Pb,Zn±Sn) ; (8) diopside skarns (Cu,Fe±Sn); (9) Fe gossans; (10) supergene (?) Fe oxyhydoxide deposits; (11) Fe oxyhydroxide±cassiterite (supergene/placer) deposits;

Costantini et al., 1993). The dominant calcite-tremolite-diopside skarn assemblage suggests emplacement conditions characterized by temperatures ≤500°C and pressures ≤1 kb (Barberi et al., 1967).

Between 5 and 4 Ma, several swarms of porphyry dikes intruded the eastern part of the Campiglia area (Peccerillo et al., 1987). According to Rodolico (1931) and Barberi et al. (1967), three types of dikes can be distinguished: quartz-monzonite, monzonitic (also called "Green Porphyry") and potassic alkaline porphyries ("Yellow Porphyry"). The "Green Porphyry" ("Porfido Verde"), also known as "augitic porphyry", represents a diopside-bearing mafic differentiate, with intermediate silica contents, high Mg-V (64-71), Ni and Cr, and relatively low Al_2O_3 and Na_2O contents (Peccerillo et al., 1987). All the fertile skarn bodies exploited in the Campiglia Marittima district are closely related to the "Green Porphyry". The "Yellow Porphyry" and the quartz-monzonitic porphyry are acidic in composition (i.e., very similar to the the "Botro ai Marmi" intrusion), and display a strong potassic alteration. The extensive degree of alteration of the Campiglia porphyry dikes makes it difficult to establish whether the quartz-monzonite and "yellow" porphyries are both evolved products from the "Green Porphyry" or represent independent magmas (Peccerillo at al., 1987). For the same reason, the age of 4.3 Ma, obtained by Borsi et al. (1967) from the Yellow Porphyry, should be viewed with caution.

To the north of the Botro ai Marmi intrusion, the San Vincenzo rhyolites (actually quartz-latites according to Pinarelli et al., 1989) were erupted at about 4.4 Ma (Ar^{40}/Ar^{39} radiometric age: Feldstein et al., 1994). They probably resulted from mixing between a crustal “anatectic” melt and minor but significant amounts of subcrustal, mafic-internediate melt of possible calcalkaline affinity (Pinarelli et al., 1989; Ferrara et al., 1989).

According to Acocella et al. (2000) a releasing bend formed during right-lateral strike-slip faulting on the western margin of the Campiglia Ridge favoured the emplacement of the Botro ai Marmi intrusion. Pliocene extensional tectonics reactivated the strike-slip lineaments and probably controlled the Campiglia dikes as well as extrusion of the San Vincenzo rhyolites.

Ore geology and mineralogy

The Campiglia Marittima area has long been known for Cu-Pb-Zn(±Fe,Ag,Sn) skarn deposits (Corsini et al. 1980), which have been exploited since pre-Etruscan times up to a few decades ago. In the “Relazione Generale Mineraria” of 1975, the reserves in the district were estimated to be in the order of 250,000 tons at 4% Zn, 2% Pb, 0.8-1% Cu, and 20-70 g/t Ag, (with inferred reserves of about 700,000 tons: data from Cipriani and Tanelli, 1983). These deposits lie 1-2 km E and NE of the Botro ai Marmi stock, in strict spatial association with (4-5 Ma?) porphyry dikes; only minor skarn occurs in the immediate proximity of the intrusion (**Fig. 11**). A number of industrial minerals and rocks are also mined in the district.

The skarn-sulfide deposits of Campiglia Marittima can be subdivided between those outcropping in the area of Valle dei Lanzi (predominant Pb-Zn, mostly with galena>sphalerite: e.g., Cava del Piombo) and the Cu (Pb-Zn) orebodies from Valle del Temperino (**Fig. 11**). Both skarn complexes are completely enclosed in white marbles, derived from contact metamorphism of the Liassic “Calcare Massiccio” by the Botro ai Marmi and/or related intrusions. However, the skarn ores of the Campiglia area are not related to the Botro ai Marmi granite stock, but instead to the more extensive, though not outcropping, parent intrusion of the already mentioned network of Yellow and Green porphyry dikes.

The Valle del Temperino deposits occur in an area of about 0.4 Km^2 where they have been mined, even if on a small scale, from the surface at 250 m down to 50 m a.s.l. According to Corsini & Tanelli (1974) and Corsini et al. (1980), the skarn complex of Valle del Temperino consists of two west-northwest-east-southeast elongated masses, which appear to be strictly associated with the “Green Porphyry” (**Fig. 12**). The latter seems to be completely embedded in the orebodies, and is crossed by small mineralized veinlets bearing the calcite-epidote-quartz, K-mica and K-feldspar association (**Fig. 13a**).

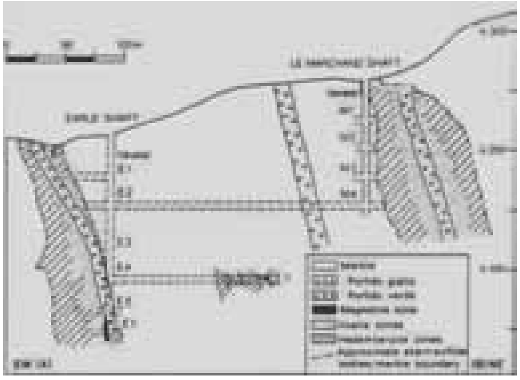

Figure 12 - Schematic cross section of the Valle del Temperino deposit (after Corsini et al., 1980)

The skarn complex consists of manganoan ilvaite (Table 1; up to 9.5 wt % MnO, after Rodolico 1931), hedenbergite-johannsenite pyroxene, quartz, calcite, epidote, and traces of andradite, rhodonite, fluorite and ferroactinolite (Bartholomé & Evrard, 1970). End member johannsenite of the solid solution hedenbergite-johannsenite series occurs near Rocca San Silvestro (**Fig. 13d; Table 1**). Epidote is particularly abundant in association with the Yellow Porphyry. Most common ore minerals include chalcopyrite, pyrrhotite, sphalerite, galena, pyrite, magnetite, hematite (traces), arsenopyrite, bismuthinite, mackinawite and galenobismutinite (Tanelli, 1977). Supergene minerals are only present in the upper levels of the mines and in small gossans.

According to Corsini et al. (1980), three zones of mineralization, namely with prevailing magnetite, ilvaite and hedenbergite occur between the Green Porphyry and the metamorphosed Liassic limestone (**Fig. 12**). The magnetite zone occurs only in the deepest levels of the skarn-sulfide deposit; it consists of a 1m thick, massive aggregate of coarse subhedral crystals of magnetite with quartz and traces of pyrite,

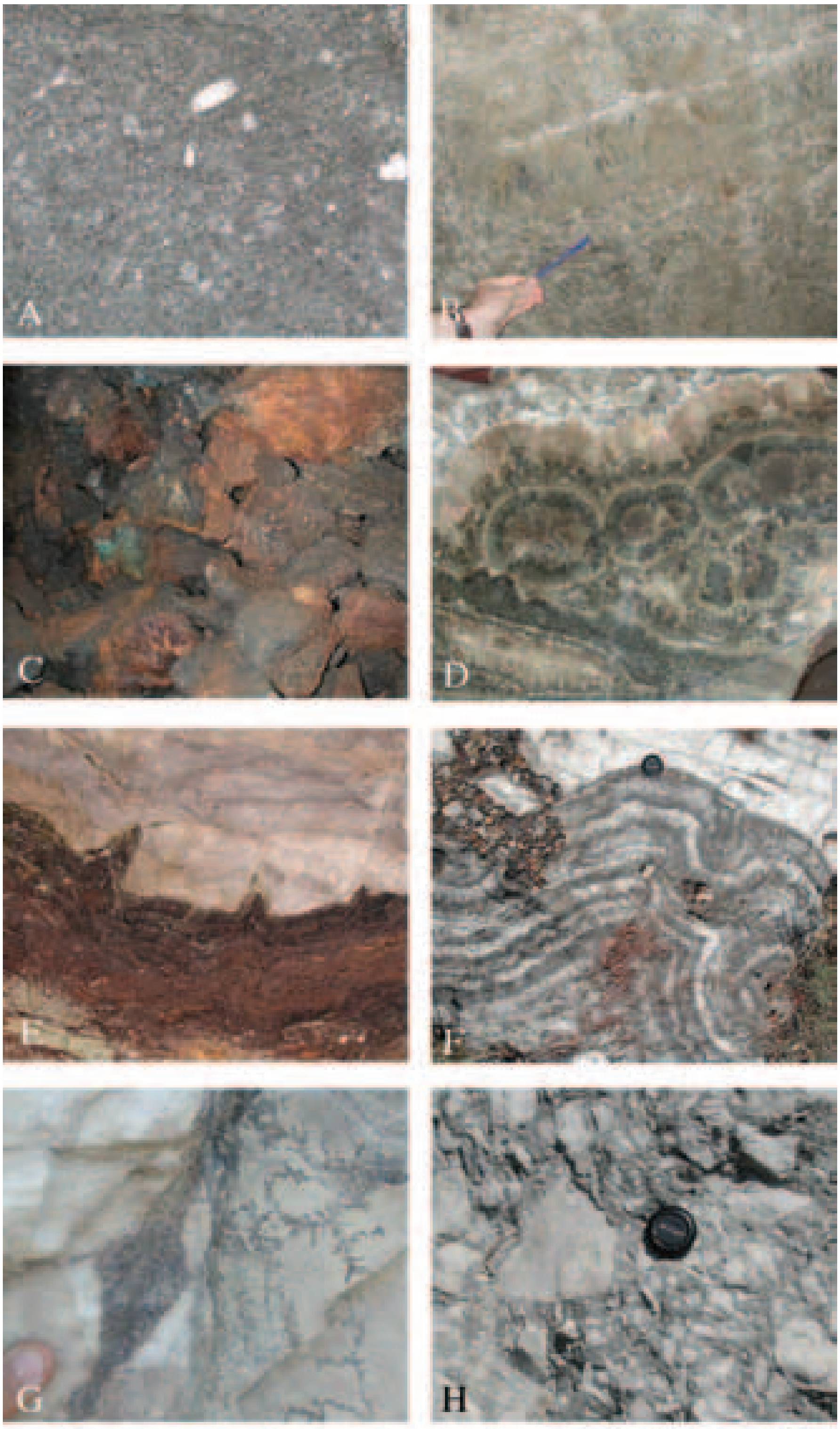

Fig. 13 - Photographs of Campiglia Marittima skarn features:
a) The "green porphyry" dike (underground mine gallery, V. Temperino)
b) Coarse-grained columnar hedenbergitic pyroxene (underground mine gallery, V. Temperino)
c) Sphalerite-rich stope fill from historic mining when Zn was not an economic commodity (underground mine gallery, V. Temperino)
d) Johannsenite from Grotta Johannsenite
e) Contact between banded johannsenite skarn and marble from Grotta Johannsenite
f) Metasomatic banding of Fe-Mn oxyhydroxides and carbonate from Campo alle Buche
g) Distal johannsenitic pyroxene vein and dendritic Mn oxide veinlets in marble near Rocca San Silvestro
h) Distal hydrothermal breccia with near Rocca San Silvestro

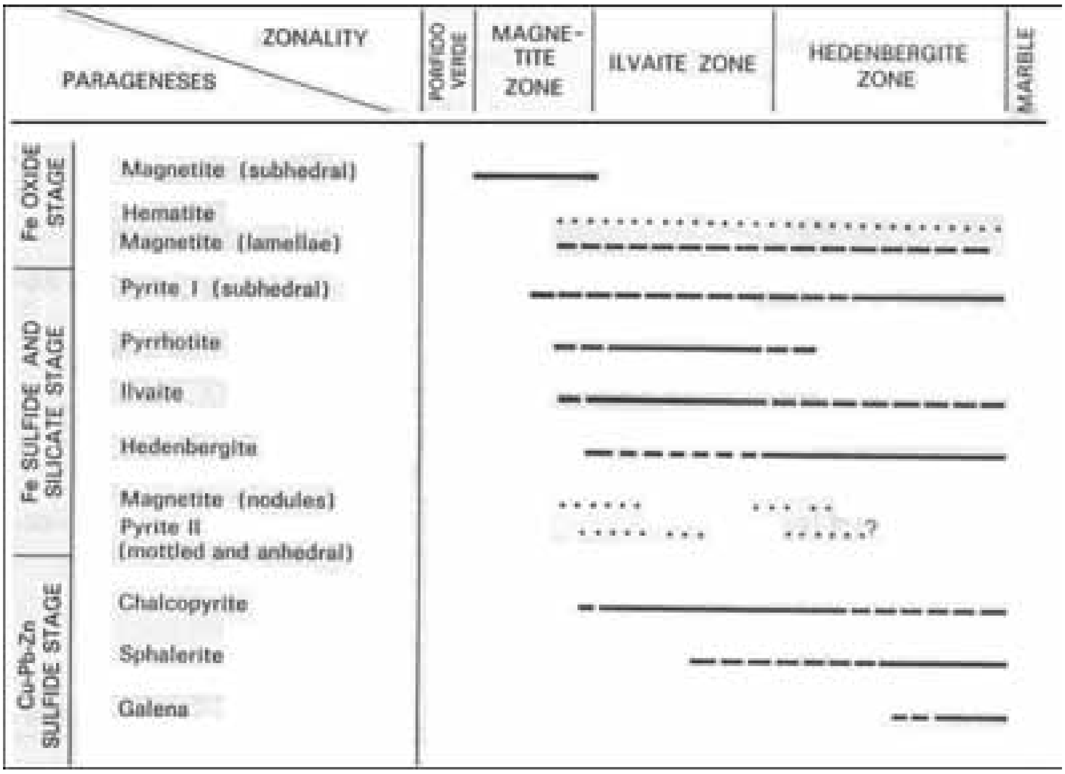

Figure 14 - Summary diagram of the space-time relationships as shown by the main minerals of the Valle del Temperino skarn-sulphide (after Corsini et al. 1980, Fig. 4)

pyrrhotite and chalcopyrite. The ilvaite zone occurs directly at the contact with the Green Porphyry: the typical ore assemblage consists of chalcopyrite and pyrrhotite, with minor magnetite, pyrite and Fe-rich sphalerite. Magnetite occurs here generally only as pseudomorphs after lamellar hematite. Pyrrhotite seems to be one of the earliest mineral phases, and is replaced by the other sulfides, as well as by magnetite. Sphalerite is quite late in the sulfide paragenesis and has an iron content ranging from 17.2 to 21.3 moles% FeS (Corsini and Tanelli, 1974). The hedenbergite zone is characterized both by well-developed, radiating and concentric aggregates of clinopyroxene with long fibers (**Fig. 13b**), and by marbles corroded and enclosed within the skarn bodies, showing that the skarn minerals were growing toward the limestone side of the complex (**Fig. 13e**). An increase in the Mn content of the clinopyroxene has been recorded, from manganoan hedenbergite (2.6 wt % MnO) in the core of the skarn body, to quite pure johannsenite (27.6 wt% MnO) at the contact with the marbles. The ore assemblage consists of chalcopyrite, pyrite, iron-poor sphalerite and finally of galena, with only minor lamellar magnetite and hematite remnants. Gangue minerals are quartz, calcite, epidote, minor ilvaite and andradite.

The ore mineral deposition at Valle del Temperino (Corsini et al., 1980) appears to have been a multi-stage process, which can be divided into three main stages (**Fig. 14**). The first corresponds to the deposition of iron oxides, mainly magnetite. Temporary changes of physicochemical parameters allowed hematite to form at first in the outer zones, and to be quickly reduced again to magnetite before the second stage took place. In the second stage, a first pyrite generation (I) was formed, then pyrrhotite, and then a second generation of pyrite (II). During this second stage, crystallization of ilvaite and hedenbergite took place. The third stage brought to the deposition of Cu-Pb-Zn sulfides, chalcopyrite being the first to precipitate, followed by sphalerite and finally by galena. The banded rocks contain ilvaite, hedenbergite, chalcopyrite and pyrrhotite. The replacement of ilvaite by hedenbergite and vice versa, indicates that these two minerals overlap.

As mentioned above, absolute age measurements and the geological reconstruction of the Campiglia area, indicate a Pliocene age for the formation of the Valle del Temperino skarn-sulfide complex. Regional stratigraphy indicates that the maximum thickness of the sediments over the "Calcare Massiccio" during the Pliocene was about 1500 to 2000 m (Bartholomé & Evrard, 1970). Based on mineralogy and S-isotope data Corsini et al. (1980) estimated that sulfide deposition at Valle del Temperino occurred during decreasing temperatures from about 400 °C to 250 °C. They also sugget that sources of sulfur for these deposits, may have been sulfate ($\delta^{34}S$ = 12÷14.6 ‰) and/or sulfide ($\delta^{34}S$ = 5÷12 ‰) associated with the Paleozoic/Mesozoic basement formations (namely, the "Filladi di Boccheggiano" and/or "Calcare Cavernoso"), both of them containing evaporites.

A different type of mineralization, consisting of layered iron minerals (mainly goethite, hematite, siderite ± marcasite, chlorite) and sparry calcite crystals, with apparently karstic features, occurs in the old mining locality of Campo alle Buche (**Fig. 13f**). This deposit has been exploited by both underground and open pit mine workings in the XIX-XX centuries, although there are evidences of older (Etruscan?) mining activity. According to Bertolani (1958) skarn sulfide mineralization occurs at some depth below the calcite-iron oxyhydroxides mineralization. The Campo alle Buche deposit has been regarded as a gossan-type ore by early authors (e.g. Ciampi, 1910); alternatively, it can be considered the product of late-stage, low-temperature hydrothermal fluids still related to the Pliocene magmatism which was responsible of the emplacement of the Cu-Pb-Zn(Ag,Sn) skarn bodies of the Campiglia Marittima district (*cf.* Tanelli, 1977; Tanelli et al., 1992).

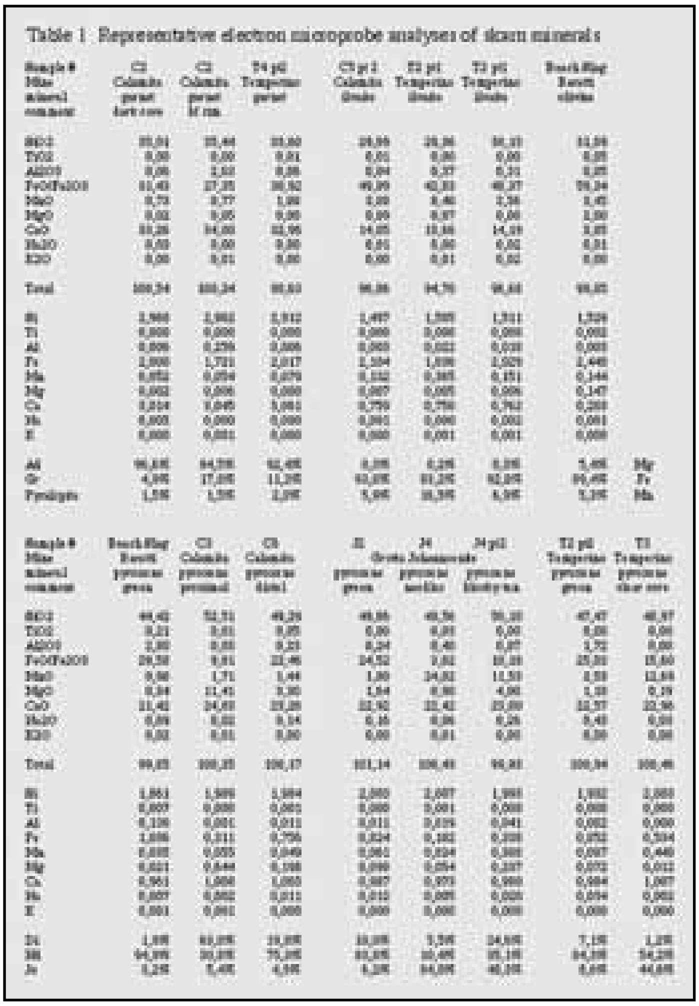

Table 1 Representative electron microprobe analyses of skarn minerals

A brief review of mining and metallurgy in Etruria Mineraria

Mineral resources of Tuscany have long been exploited, at least since Chalcolithic times, and were very important in the development of Etruscan and Roman civilizations; in medieval times, numerous city-states derived important revenues from mining exploitation and metal production. The same applies, on a larger scale, after the unification of Tuscany under the Medici government in the 16th century. Even in more recent times some mineral resources, such as the Elba iron ore, were successfully exploited.

However, despite their economic importance, the archaeology and history of the Tuscan mines has not been well studied. Recently, a joint project carried out by the Dipartimento di Scienze della Terra of Firenze and the Dipartimento di Storia Medievale of Siena with

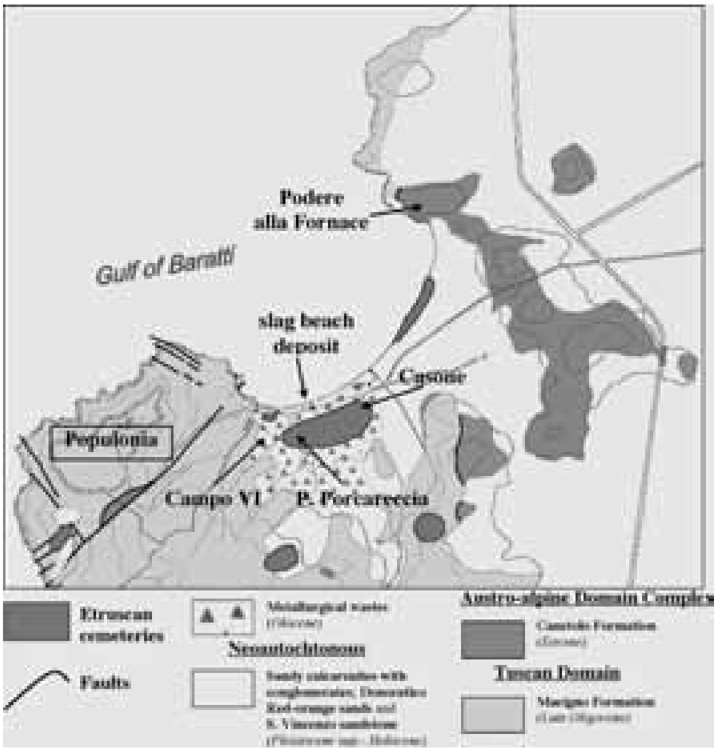

Figure 15 - Sketch map of the archaeometallurgical site of Populonia-Baratti (modified after Benvenuti et al., 2000)

the financial support of Regione Toscana (Tuscany Regional Government), has provided an exhaustive review of the mineral resources in Tuscany as a whole (Mascaro et al., 1991) with particular attention to the *Colline Metallifere* district (Cutero and Mascaro, 1995), from the double perspective of their geo-mineralogical and historical-archaeological background. These studies provide a detailed overview of all known mineral resources, from major deposits to minor occurrences, which could have been exploited by ancient miners.

A key role in the production and trade of metals (especially, but not exclusively, iron) in the Mediterranean area during the 1st Millennium BC, was played by the Etruscan town of Populonia. Populonia was an important metal production centre during Etruscan (7th-3rd century BC) and Roman (2nd century BC – 1st century AD) times. Such a prominent role was mainly due to its strategic location, midway between the large iron deposits of eastern Elba Island and the polymetallic Cu-Pb-Zn-Fe-Ag-Sn ores of the Campiglia Marittima area. The huge heaps of slags (probably in excess of 40,000m^3), discharged along the foreshore of the Gulf of Baratti could document a total iron production of some thousands tonnes of iron bloom (up to half a million tonnes according to Voss 1988). In the last ten years, a detailed research program on four main excavation sites in the Populonia-Baratti industrial zone (Poggio della Porcareccia, Casone, Campo VI and the Baratti beach deposit: **Fig. 15**) has been undertaken, with the aim of establishing the types and extent of metallurgical activities for iron and non-ferrous metals (mainly copper and tin), as well as on the provenance of smelted ores in the Etruscan and Roman periods. The main results so far obtained have been published elsewhere (Benvenuti et al., 2000, 2003a, 2003b, with references), and will be briefly summarized here.

From the analysis of stratigraphic relationships, morphological, mineralogical, textural, and chemical features of metallurgical materials the following can be concluded:

- although most archeometallurgical deposits at Baratti-Populonia can be ascribed to iron production, the existence of an earlier (and partly coeval) copper metallurgy can also be documented in the area, particularly from the slag beach deposits (**Fig. 9g**),
- two different types of copper slags, which could be related to different metallurgical steps, have been distinguished,
- the mineralogical and compositional features of some metallurgical scraps (Campo VI), dating to the 3rd century BC or earlier, provide evidence of local bronze production. In agreement with archaeological data, bronze was probably obtained by cementation, i.e., by adding unsmelted cassiterite to refined copper,
- trace element geochemistry (e.g., tin anomalous content of some iron slags: **Fig. 16a**) and Pb-isotope analyses indicate that iron ores came mainly from Elba and, to a lesser extent, from the Campiglia Marittima district (where Fe-Sn ores are common, e.g. at Monte Valerio); the latter district appears to be the most likely source area for smelted copper and,

possibly, for tin.

Field Itinerary

Elba Island (August 18, 2004)

Stop 1.1:

The ilvaite-hedenbergite skarn bodies of Torre di Rio

The area is characterized by a NW-plunging sequence of marbles and calc-schists (**Fig. 9e**) of variable size with minor grey/greenish quartzitic phyllites. They belong to the Acquadolce Unit of Bortolotti et al. (2001). Syn-metamorphic tight to isoclinal folds with a pervasive axial plane schistosity are well exposed. Deino et al. (1992) obtained a ^{40}Ar/^{39}Ar radiometric age of 19-20 Ma for this schistosity. A 1-metre thick, grey/whitish calc-schist level is well exposed along the road. Moving southwards from the Appiani Clock-Tower and along the coast, we can easily observe the gradational passage from calc-schists to the hedenbergite-ilvaite-epidote skarn bodies. Skarn bodies consist of almost monomineralic masses of garnet-epidote, hedenbergitic pyroxene and ilvaite (**Fig. 9b**), with associated quartz, chlorite and minor amounts of iron minerals (magnetite, pyrite and pyrrhotite), which justified limited exploitation activity in the past. Mesoscale textures clearly indicate that the replacement of minerals in the calc-schists by skarn minerals, occurred preferentially along the schistosity planes of the original rock, as pointed out by Lotti (1886,pp. 205-206). Ilvaite is here exceptionally abundant (**Fig. 9d**): it occurs in beautiful, centimetric black, prismatic crystals, with typical vertical striae and submetallic lustre. This is the type locality where ilvaite (so called after the Latin name of Elba Island: "Ilva") was first discovered and described in 1802 (Franchini et al., 2002).

Stop 1.2:

The Rio Marina mining area (seen from Torre di Rio)

Looking from the Appiani clock-tower to the NW, the landscape is dominated by the Rio Marina mines (from the left: Bacino, Zuccoletto, Valle Giove and Vigneria mines) and by the Torre del Giove hill (351 m), with the ruins of a castle of the XVIth century.

The Rio Marina ores are hosted in the Permo-Carboniferous (Rio Marina Fm.) and in the Triassic Verrucano Auctt.) metasiliciclastics of the Monticiano-Roccastrada Unit. The iron deposits of Rio Marina (as well as Rio Albano, to the north) consist of stratiform, massive or vein-like bodies, hosted by Trevisan (1950)'s Complex III rocks, preferentially at the contact between the Rio Marina Formation, or the Verrucano, and the overlying calcareous levels ("Calcare Cavernoso" Auctt.). According to some authors (cfr. Gillieron, 1959) at Rio Albano the setting of the orebodies is structurally controlled. Nevertheless, at least in the Valle Giove area, Deschamps et al. (1983) discovered a pyrite-bearing horizon within Verrucano Fm. ("Schistes verts minéralisés"), which they interpreted as a relic (syngenetic) of an iron protore. In the Rio Marina and Rio Albano deposits hematite ("specularite") is the main ore mineral which may show either a typical lamellar-micaceous habits or flattened, rhombohedral crystals, often covered by iridescent films of iron hydroxides. Pyrite is also common, predominantly as pyritohedra, although octahedra or cubes have been observed as well. Exogenous limonites, in massive or concretionary (sometimes stalactitic) forms may locally constitute the main ore minerals, especially at Rio Albano and other mineral showings to the north. It should be noted that in the 1950's-60's underground mine workings partly exploited a hematite+pyrite orebody associated with skarn silicates, known in the literature as "Rio Marina profondo" (= Rio Marina deep body").

Stop 1.3:

Along the Calamita mine road

After leaving Capoliveri, we pass by the tectonic contact between the Flysch Unit and the Porto Azzurro Unit, constituted by Mt. Calamita Fm. (Palaeozoic grey to brown micaschists, phyllites and quartzites locally intruded by aplitic dikes) and the Barabarca Fm. quartzites (Middle-Late Triassic). Just above the sea-village of Pareti (down the cliff) we can observe along the road some lenticular dark green bodies of amphibolites (tremolite + andesinic plagioclase + chlorite ± sphene, apatite) which Puxeddu et al. (1984) referred to WPB metabasites. We finally reach the former Calamita Mine Headquarters ("Palazzo"), which is one of several open pit and underground Fe mines along the coast (**Fig. 9a**).

Stop 1.4:

The Calamita mine: northern stopes

In this area thermometamorphic carbonate rocks occur. They consist mainly of stratified dolostones and dolomitic limestones, grey-whitish in colour, with rare phyllitic intercalations (Late Triassic?). To the east, along the road, there are outcrops of whitish saccharoid marbles (Hettangian?), massive or poorly stratified, with local grey dolomitic levels. These carbonate rocks may represent part of the original Mesozoic cover of the Mt. Calamita Fm.: more to the west, the quartzites of the Barabarca Fm. occur between the Mt. Calamita Fm. and the carbonate rocks. The latter have been affected by extensive metasomatism, which led to the development of two main types of skarn: a garnet (andradite)- skarn, quantitatively the most abundant, and an ilvaite-hedenbergite skarn (Torrini, 1990). Skarn bodies mainly occur at the contact between metacarbonates and the underlying Mt. Calamita Fm. The skarn is zoned from garnet-rich in the proximal southwest to pyroxene-ilvaite in distal zones (**Fig. 9c,f**), as is typical of most skarn systems (Meinert 1992, 1995, 1997).

Mining activity at Calamita probably dates back to Etruscan?-Roman times; according to Pullé (1921) at least 2 million tonnes of iron ore had been exploited in the period 1860-1920 by open pit mining, with iron reserves of approximately the same order of magnitude. The northern sector of the Calamita Mine is subdivided into several mine-working areas: Civetta, Albaroccia, Macei, Polveraio, Coti Nere. The exploited ores were associated with both types of skarns described above, and consisted of lenses and massive bodies of magnetite (±kenomagnetite, hematite). Additional phases include goethite and trace amounts of sphalerite, chalcocite, arsenopyrite, bornite and pyrite. Moreover, masses of Fe-Cu sulfides (pyrrhotite, pyrite, chalcopyrite ± malachite, azurrite, chalcantite, etc.) were locally exploited at the contact between the garnet skarn and the magnetite lenses (Torrini, 1990).

In the southern stopes of the Calamita Mine (not to be visited during this field trip) the exploitation activity focussed on several magnetite lenses associated with hedenbergite-ilvaite skarn bodies, beautiful examples of which can be observed just on the seaward cliffs (Punta della Calamita). A U-shaped trench (altitude: 112 m. a.s.l.), excavated in the metacarbonates and easily visible from the mine road separates the two main stopes (Vallone Basso and Vallone Alto). At the beginning of the past century the production mainly involved the limonitic gossan of iron ores, which were subsequently exploited almost exclusively for magnetite. At the so-called "Grotta Rame" (= Copper Cave) site, just below the U-shaped trench, veinlets of malachite, azurite, atacamite, paratacamite, etc. have been reported. At Vallone Alto, moreover, rare "organic" minerals like minguzzite ($K_3Fe(C_2O_4)_3 \cdot 3\ H_2O$) and oxalite ($FeC_2O_4 \cdot 2\ H_2O$) have been reported by Cocco, Garavelli (1954).

Campiglia Marittima district (August 19, 2004)

Stop 2.1:

Valle dei Lanzi. View from the Rocca San Silvestro; "Yellow Dike" with skarn envelope and nearby hydrothermal breccia

We will start the ascent to Rocca San Silvestro, an old medieval village built around the mining of base metals from shallow skarns and gossans. Here have been found also some remnants and slags with copper, lead and silver, derived from the early metallurgical works in this area. From the top of Rocca San Silvestro one can enjoy the panorama of Valle de Lanzi (Lanzi= from the german *Landsknechte*, who were at times working in the local mines), with the Botro ai Marmi granite in the background.

At the base of Rocca San Silvestro, along an internal road to the limestone quarries, it is possible to observe an outcrop of the "Yellow Porphyry", with thin skarn envelopes (**Fig. 13g**), as well as distal alteration features like a hydrothermal breccia and small Mn-oxide veins. (**Fig. 13h**) Around the "Yellow Porphyry", abundant concentrations of epidote also occur.

Stop 2.2:

Grotta Johannsenite (Gallerione)

From the upper part of the Valle dei Lanzi, we drive (walk) to the classical locality of Grotta Johannsenite (**Fig. 11**). Here we can observe the occurrence of very fine specimens (do not hammer the outcrop!!!) of Johannsenite occurring as pinkish rosettes and bands, replacing the marbles derived from "Calcare Massiccio" contact metamorphism (**Fig. 13d,e**). This Mn-pyroxene is a typical component of the Zn-skarn assemblage and represents here one of the end-members of of the hedenbergite-johannsenite solid solution.

Stop 2.3:

Mineral Museum of Valle del Temperino

We will visit the small, but very interesting Museum, set up in one of the old mine buildings at Valle del Temperino. The Museum is dedicated to the geology, mineralogy and mining history of this area and contains some spectacular mineralogical samples taken from the Cu- and Zn-Pb mines. Old maps of the mining districts are also among the exhibits and in a small, but well organized shop are sold several books on this theme and on the fauna and flora of the whole area.

Stop 2.4:
Underground Mine Valle del Temperino: Green Dike and Hedenbergite skarn

This Stop will take us underground in one mine gallery of the copper mine of Valle del Temperino. The mine is not active anymore, having been converted into a popular tourist attraction, and it's walls show the characteristic green patina of supergene copper minerals.. Nevertheless, there are still many interesting sites in the mine where geologists can observe the geological occurrence of the "Green Porphyry Dike" (**Fig. 13a**) thought to be genetically associated with mineralization, the marble host rocks, and hedenbergite skarns (**Fig. 13b**) with sphalerite and chalcopyrite. It is interesting to note that many of the old workings were backfilled with high grade Zn-ore, also occurring in the skarn, which was not economic in pre-industrial times (**Fig. 13c**).

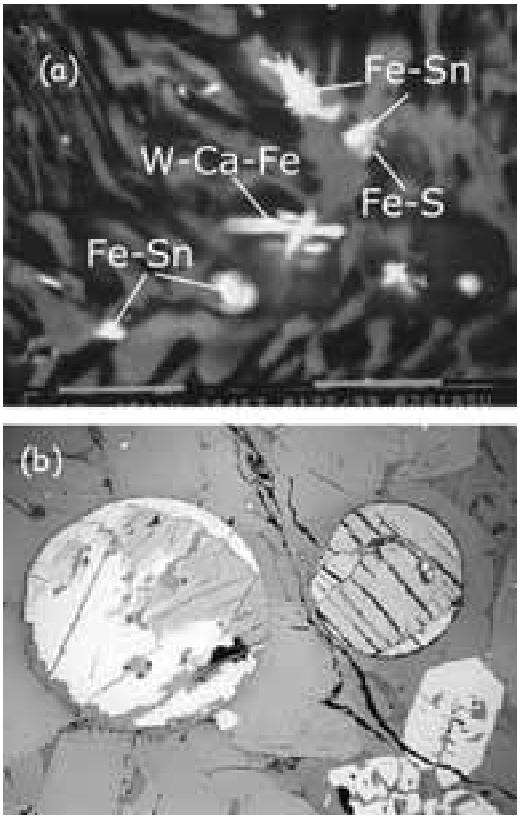

Figure 16 - Photomicrographs of archaeometallurgical samples from Populonia-Baratti: a) Backscattered electron image of partially smelted mineral charge showing micrometric globules of Fe-Sn phases (white), sometimes surrounded by Fe-S phases. The groundmass is composed of a glassy matrix and acicular crystals of hedenbergitic composition. Bar = 10 µm. b) Reflected light image of sulphidic droplets in (type-A) copper slags. Abbreviations: cc = chalcosite-djurleite; cv = covellite. Width of field: about 500 µm.

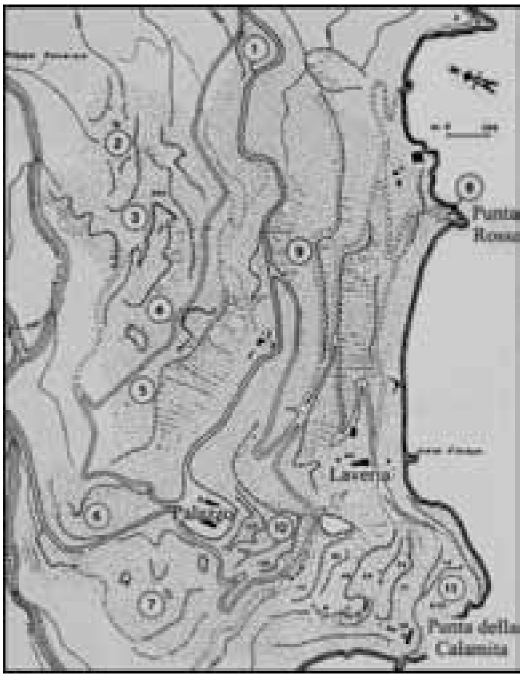

Figure 17 - Location of the principal mine workings at Calamita Mine (after Calanchi et al., 1976). Legend: 1. Civetta; 2. Albaroccia; 3. Nuova Zona; 4. Macei Alto; 5. Polverio; 6. Coti Nere; 7. Le Piane; 8. Punta Rossa; 9. Macei Basso; 10. Vallone Alto; 11. Vallone Basso.

Stop 2.5:
Mn-vein outcrops near mine exit along road to the "Gran Cava" pyroxene locality

Out of the underground adit, we walk up a small mine road characterized by interesting exposures of distal Mn-oxide veins and internal sediment-filled fractures, as well by hydrothermal breccias that directly overlie the underground ores. Such distal alteration features are common in the periphery of most skarn districts in the world. The road will bring us to the "Gran Cava", a small open pit also known as "Cava Etrusca", so called because it is thought to have been exploited already in Etruscan times. There we will observe coarse-grained hedenbergite pyroxenes and a well-exposed skarn-marble contact.

Stop 2.6:
Fe-Oxides at Campo alle Buche

Our last outcrop is situated at the westernmost

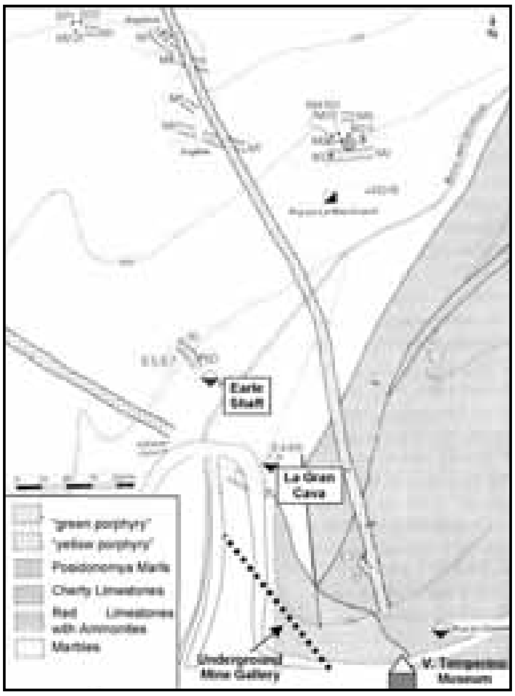

Figure 18 - Schematic geologic map of the Valle del Temperino deposit area (modified after Corsini and Tanelli, 1974)

extremity of the Campiglia area, in close proximity with a NNE-SSW trending fault. The old mining area of "Campo alle Buche" = literally "field with holes" was exploited for iron ore until the early decades of the twentieth century. The mineralized lithotype consists here of alternating bands of laminated Fe minerals (mainly goethite, hematite, siderite ± marcasite, chlorite) with calcite crystals (**Fig. 13f**). Interpreted as gossan-like deposits by early authors (e.g. Ciampi,. 1910). The Campo alle Buche mineralization probably represents the distal product, in a more oxidizing environment, of the same hydrothermal fluids that were associated with skarn formation.

The archaeometallurgical site of Populonia-Baratti (August 19, 2004)

Stop 2.7:

The beach slag deposit at Baratti

At the end of our visit to the Campiglia Marittima district, we move back towards Piombino, and take the road to Populonia. We enter the Parco Archeologico di Baratti. We leave the bus and reach the beach in order to observe the remains of the slag deposit, a poorly cemented heap of Etruscan and Roman slags discharged over an erosional terrace (**Fig. 9g**). The bottom portion of the deposit mostly consists of copper slags, clearly identifiable by the greenish spots (due to exogenous alteration of copper sulfides) on their surfaces. Preliminary analyses of the Baratti beach slag deposit led to the recognition of two main types of copper slags: type-A and type-B slags (Benvenuti et al., 2000). Type-A copper slags are characterized by a groundmass of dominant olivine, pyroxene, magnetite, and minor glass, with abundant metallic droplets, mostly fine aggregates of metallic copper, copper oxides (cuprite) and sulphides (covellite, chalcocite/dijenite) (see **Fig. 16b**). In type-B copper

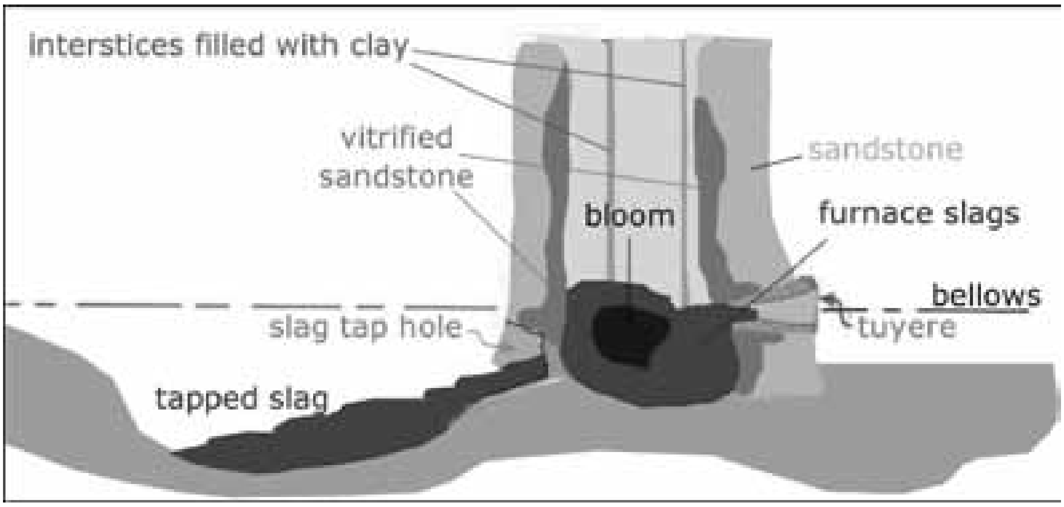

Figure 19 - Proposed reconstruction of Etruscan iron furnaces from Baratti (after Benvenuti et al., 2003b).

slags magnetite and cuprite are much less abundant, metallic copper is consistently absent, and the metallic globules (100-150μm in size) are mainly copper-iron-sulphur phases (matte) showing fine exsolution textures. These features could indicate a multi-stage copper smelting process, with type-B slags belonging to an earlier (matte production) stage than type-A slags.

The largest portion of the slag deposit consists of iron slags of different kinds (furnace slags, tapped slags, furnace conglomerates). The iron slags are mainly a silicate groundmass of fayalitic olivine (with up to 1.45% CaO) in an iron-rich interstitial glassy matrix (up to *c*25 wt.% FeO), which in itself is normally a eutectic of anorthite and fayalite. Wüstite, magnetite, hercynite and partially smelted, relic phases like quartz, hematite and scheelite (?), occur in variable amounts, and are especially abundant in furnace slags. Fayalite crystals in tapped slags occur as small laths associated with micrometric dendrites of wüstite, while in furnace slags both minerals show a significant increase in size. Unlike tapped and furnace slags, furnace conglomerates show abundant relics of hematite and quartz and a more silica-rich (and FeO-poor) glassy groundmass. Iron slags almost invariably contain droplets of metallic iron. Some iron slags are enriched in tin and may contain micrometric globules of iron-tin alloys, approximating FeSn and $FeSn_2$ in composition (**Fig. 16a**).

Fragments of smelting furnaces are also commonly present in the Baratti beach deposit. They are made up of local Macigno sandstone and baked clay, possibly derived from the terrigenous Canetolo formation (see **Fig. 18**). The baked clays show characteristic colour zoning from red to black, corresponding to increasing reducing atmosphere and temperatures in the furnaces. The reconstruction of Etruscan (and/or Roman?) iron furnaces proposed by Benvenuti et al. (2003*b*) is shown in **Fig. 19**.

If time permits, we will visit some of the Etruscan tombs located in the nearby archeological site.

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Back Cover:
field trip itinerary

FIELD TRIP MAP

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