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Fluid flow paths in fossil and active geothermal fields: the Plio-Pleistocene
Boccheggiano-Montieri and the Larderello areas

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Fluid flow paths in fossil and active geothermal fields: the Plio-Pleistocene Boccheggiano-Montieri and the Larderello areas

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Riassunto

Questa escursione, di un solo giorno, illustra le similitudini fra i sistemi geotermici fossili ed attuali, paragonando l'assetto strutturale dell'area mineraria di Boccheggiano-Montieri e del campo geotermico di Larderello. Ambedue le aree sono caratterizzate da circolazioni di fluidi nelle cataclasiti delle faglie dirette del Pliocene-Attuale e che hanno costituito i percorsi preferenziali per la circolazione. A partire da questi canali strutturali, i fluidi sono successivamente migrati verso le trappole strutturali principalmente ubicate in corrispondenza della Formazione delle Anidriti di Burano (Triassico superiore). Sia l'area di Boccheggiano - Montieri che di Larderello sono ubicate in Toscana meridionale, dove un diffuso magmatismo medio-crostale si è sviluppato contemporaneamente alla tettonica distensiva. La presenza quindi di magmatismo, strutture distensive e circolazione di acqua essenzialmente meteorica ha favorito la formazione di circolazione di fluidi idrotermali sia nella zona di Boccheggiano che in quella di Larderello. L'escursione ha quindi anche lo scopo di sottolineare l'importanza di studiare il "passato", cioè l'area mineralizzata di Boccheggiano-Montieri, per meglio capire il "presente", cioè il campo geotermico di Larderello.

La prima parte dell'escursione sarà quindi dedicata alle relazioni fra mineralizzazioni e strutture nella zona di Boccheggiano-Montieri; la seconda parte, invece, sarà invece dedicata alla visita del campo geotermico di Larderello e alle sue manifestazioni naturali. Alcuni dati del sottosuolo saranno infine illustrati e discussi.

Parole chiave: *geotermia, fluidi idrotermali, mineralizzazioni, Toscana meridionale*

Abstract

This one-day excursion aims to illustrate the similarieties between fossil and Present hydrothermal fluid paths, comparing the structural setting of the Plio-Pleistocene Boccheggiano-Montieri mineralized area and the Present Larderello geothermal field. Both areas are characterized by fluid flow throw cataclasites hosted within the Pliocene-Present normal faults. From these structural channels, fluids migrated toward structural traps predominantly located the Upper Triassic Anidriti di Burano Fm., one of the main detachment levels for the tectonic evolution of the Northern Apennines. Both areas are located in Southern Tuscany, where a diffuse intra-crustal magmatism developed contemporaneously to extensional tectonics. Magmatism, extensional structures and dominated meteoric water circulation enhanced hydrothermal fluid flow both in the Boccheggiano area and in the Larderello field. During this field trip we like to stress the importance to study the Past, i.e. the fossil geothermal systems, in order to better understand the Present, i.e. the Larderello field. The first part of this field trip is dedicated to the relationships between mineralization and structures in the Boccheggiano-Montieri mining area, whereas the second part of the day is addressed to the visit of the Larderello geothermal area and to its natural manifestations. Furthermore, data from the subsurface will be illustrated and discussed.

Key words: *geothermics, hydrothermal fluids, ore deposits, Southern Tuscany*
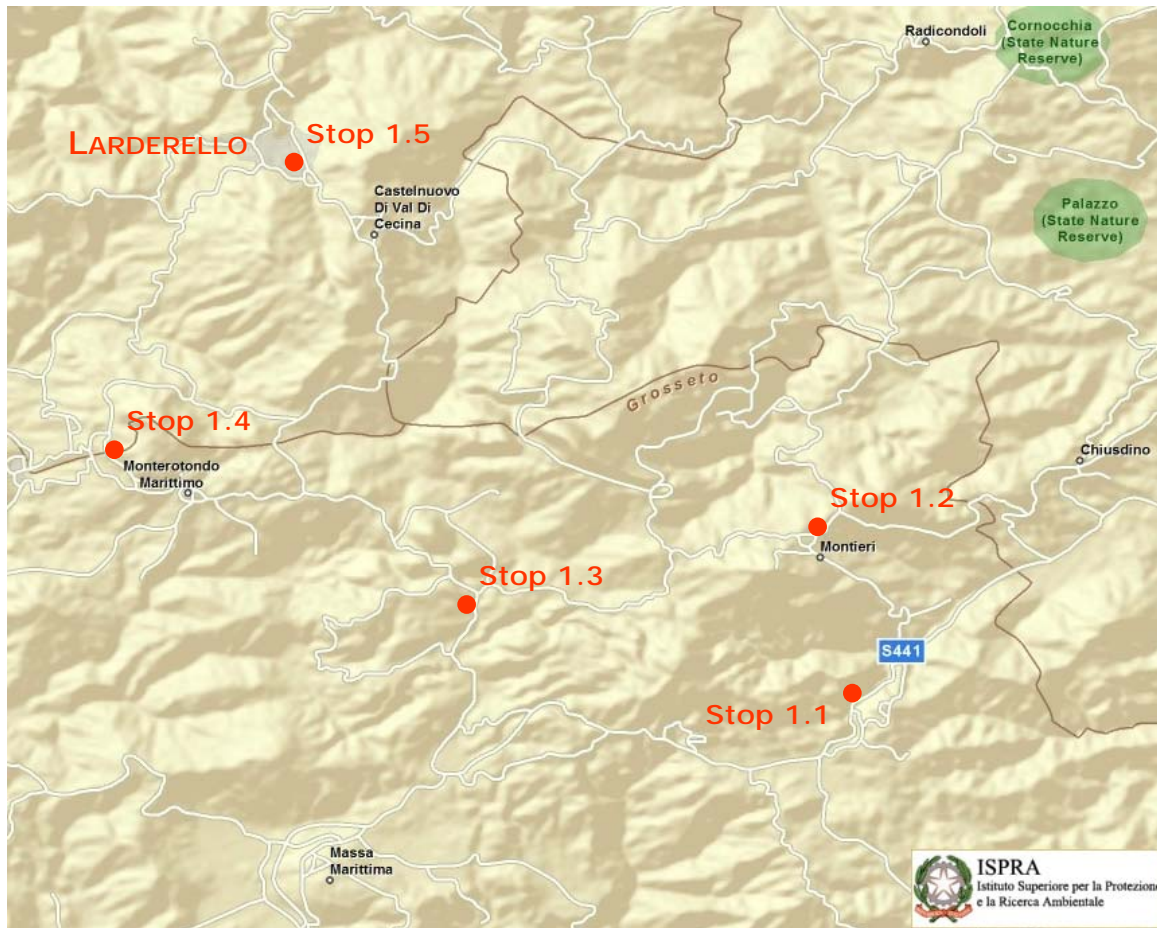
1. Introduction

The understanding of the fluid flow path in geothermal areas is a continuous task to better address the exploitation of the terrestrial heat, transported by geothermal fluids through a network of fractures. Relationships between geological structures and fluid flow in present geothermal fields are mostly derived through interpretation of borehole logs and geophysical data. However similar information can be achieved by studying exhumed geothermal systems, now resulting in mineralized areas, developed in epithermal and mesothermal conditions.

Southern Tuscany is an ideal region for comparing information from present and fossil geothermal systems. This field trip is organized in two parts: in the first half, we will visit the main outcrops of the Boccheggiano mineralized area (Rossetti et al., 2008; Liotta et al., 2010), developed during the cooling of the Montieri granitoid, emplaced at mid-crustal level during Late-Pleistocene at about 3-2 My (Boyce et al., 2003; Dini et al., 2005); in the second part of our excursion we will look at the Larderello geothermal field, visiting the so-called "first geothermal reservoir", cropping out close to the Monterotondo Marittimo locality (Fig. 1.1).
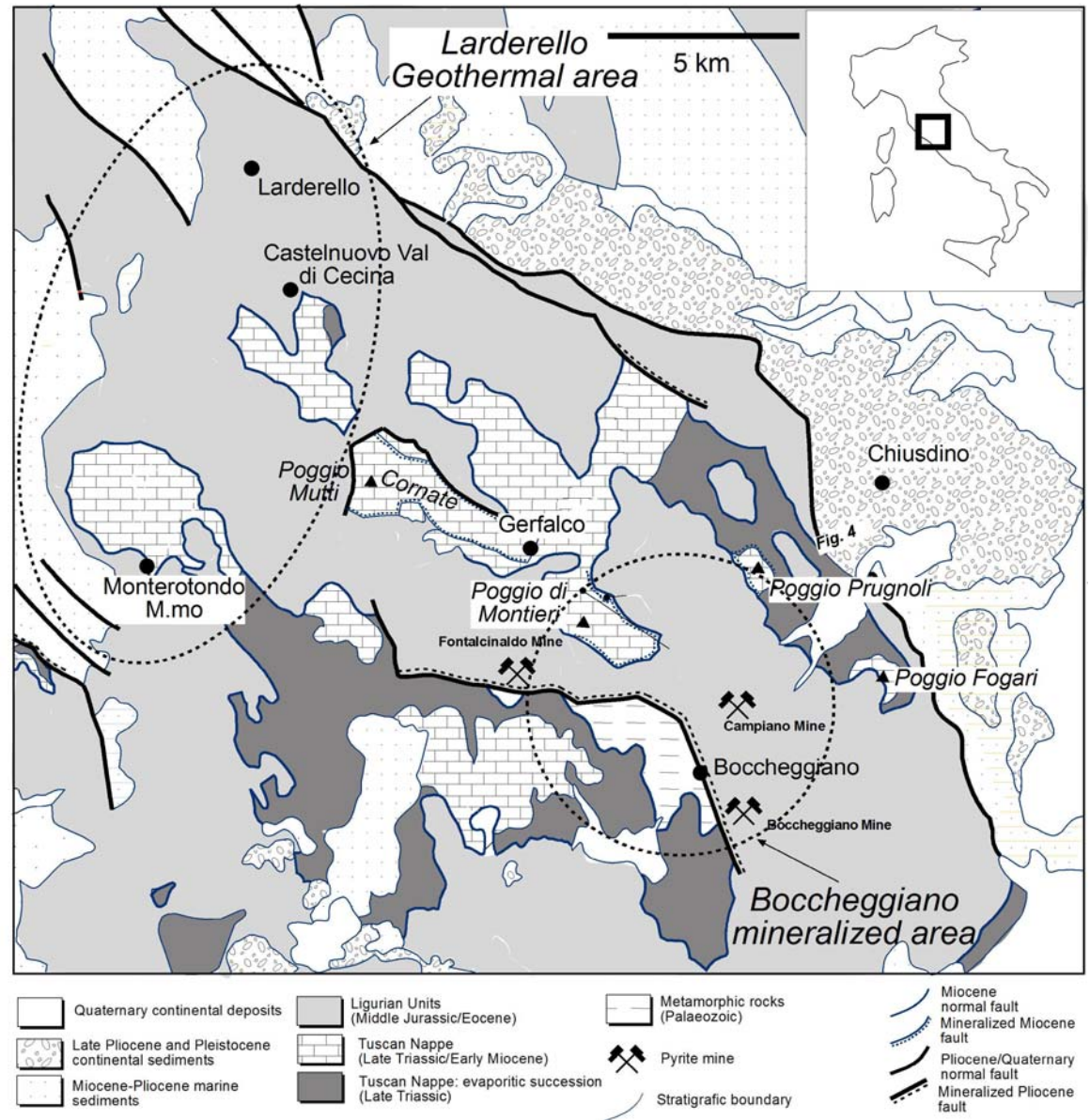

Fig. 1.1 - Geological sketch map of the Colline Metallifere area with highlighted the Larderello geothermal field and the Boccheggiano mineralized area.

The main goal of this field trip is to discuss the relationships between geological structures and fluid flow, comparing fossil and Present geothermal fields, that are supposed to be different just only for the age of the cooling mid-crustal magma.

2. Geological Setting

The Larderello and Boccheggiano areas are located in Southern Tuscany (Figs. 2.1, 2.2, 2.3), that is structurally located in the inner part of the northern Apennines. Its structural setting is consequence of two contrasting processes: the first related to the convergence and collision of the Adria microplate and the European plate, represented by the Sardinia-Corsica Massif (Molli, 2008, for a review); the second related to the extensional tectonics, which have been acting since the Early-Middle Miocene (Jolivet et al., 1990; Carmignani et al., 1994; Brunet et al., 2000). This extension migrated eastwards, affecting the entire northern Apennines.

The present crustal and lithospheric thicknesses, ranging between 22-24 km and 30-40 km respectively (Locardi and Nicolich, 1988), are the clearest evidence of the importance of this extensional process.

Since Late Miocene magmatism, becoming younger eastwards, accompanied extension. Magmas with both crustal and mantle geochemical signatures, intruded mostly at mid-crustal depths (Serri et al., 1993). Presently, Southern Tuscany is characterized by high heat flow, 120 mW/m^2 on average, with local peaks up to 1000 mW/m^2 in the Larderello geothermal area (Fig.2.1).
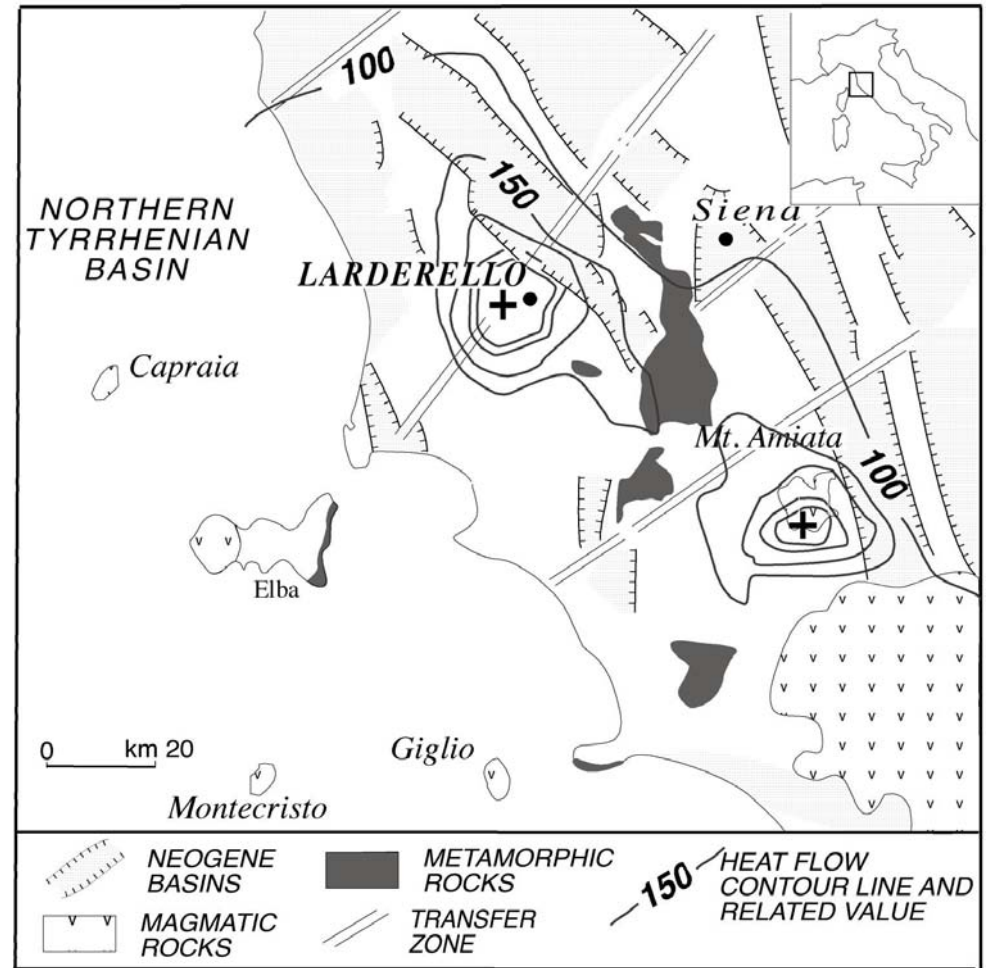

Fig. 2.1 - Structural sketch map of Southern Tuscany with regional heat flow contour lines (equidistance: 50 mW/m^2).The plus signs show the Larderello and Monte Amiata geothermal fields where heat low reaches 1000 mW/m^2 and 600 mW/m^2, respectively (from Bellani et al., 2004).

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This extensional setting was challenged by few Authors (Bonini et al.,1994; Bonini and Moratti 1995; Moratti and Bonini, 1998). This view led them to suggest a basically continuous (Bonini et al., 1999; Bonini et al., 2001; Finetti et al., 2001) or pulsing (Bonini and Sani, 2002) collisional process, active from the Cretaceous to Pliocene-Pleistocene times (Finetti, 2006). Reasons why these interpretations are not able to explain the evolution of the Northern Apennines are given in, e.g.: Faccenna et al. (2001), Brogi et al. (2005a, 2005b), Pauselli et al., (2006); Collettini et al. (2006), Brogi and Liotta (2008),Brogi, 2008; Barchi (2010), Brogi (2011).

The paleogeographic domains

The collisional process determined the stacking of tectonic units deriving from the palaeogeographic domains of the inner northern Apennines. These are, from the top (Fig. 2.2):

(a) The Ligurian Units, composed of remnants of Jurassic-Cretaceous oceanic crust and of its Jurassic-Cretaceous sedimentary cover;

(b) The Subligurian Units made up of arenaceous and calcareous turbidites Late Cretaceous-Oligocene age. Ligurian and Subligurian Units were thrust eastwards over the Tuscan Domain during Late Oligocene-Early Miocene.

(c) The Tuscan Nappe including sedimentary rocks, ranging from Upper Triassic evaporites (Anidriti di Burano Fm) to Jurassic-Cretaceous carbonates and Cretaceous-Lower Miocene marine clastic deposits (scaglia toscana group and Macigno Fm.). During the Early Miocene, the Tuscan Nappe, already involved in duplex structures, detached along the Upper Triassic evaporite level to thrust over the external Tuscan Domain and the inner part of the Umbria-Marche Domain.

(d) The metamorphic Tuscan Unit, belonging to the external Tuscan Domain, consists of greenschist-facies metamorphic rocks deriving from a Triassic-Oligocene sedimentary succession, similar to that one characterizing the inner Tuscan Domain.

The substratum of the Tuscan Domain was involved in the collisional stage determining isoclinal folds and duplex structures. It is composed, from the top, of Triassic quartzite and phyllite (verrucano group) and Palaeozoic phyllite.

(e) The Umbria-Marche Domain consists of continental-margin deposits from Triassic to Late Miocene; this Domain represents the external Zone of the Northern Apennines, where a fold-and-thrust belt developed from the Middle Miocene (Brozzetti et al., 2002).
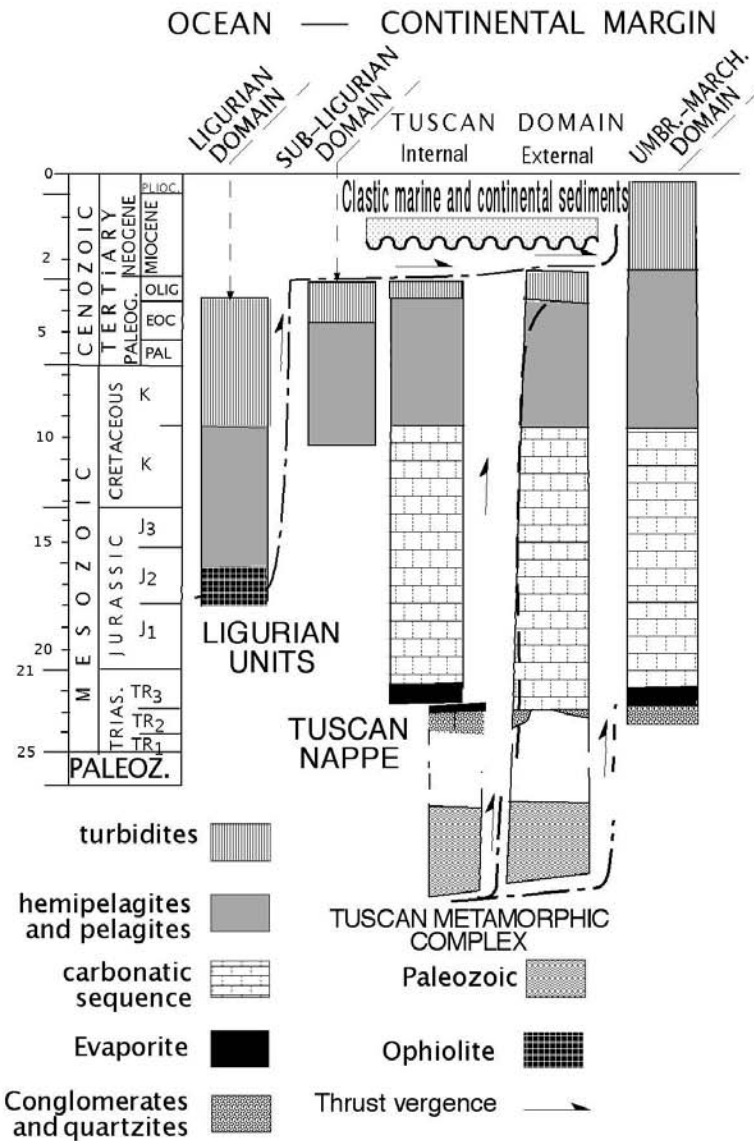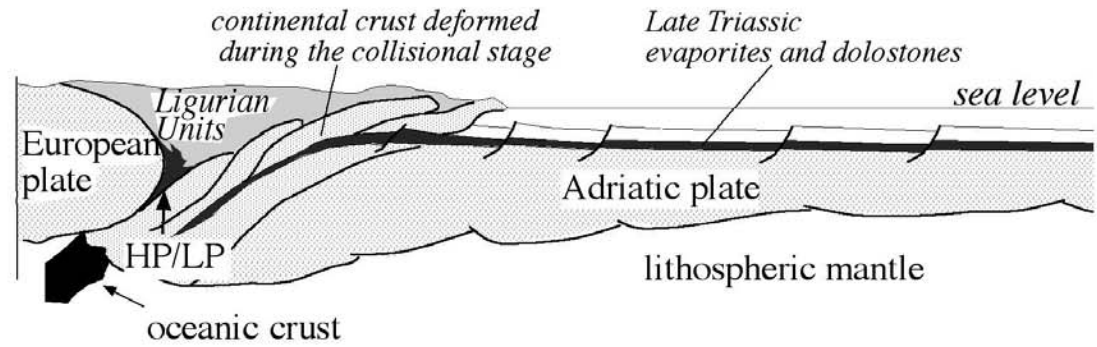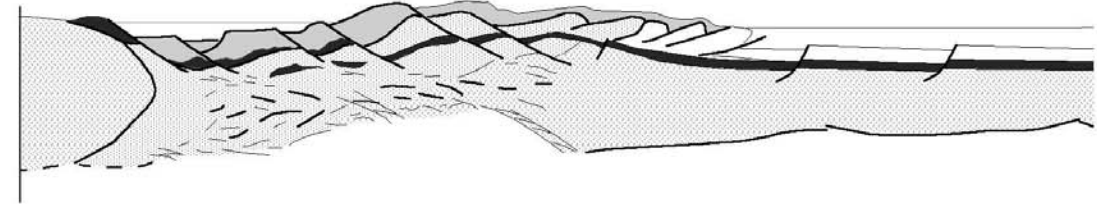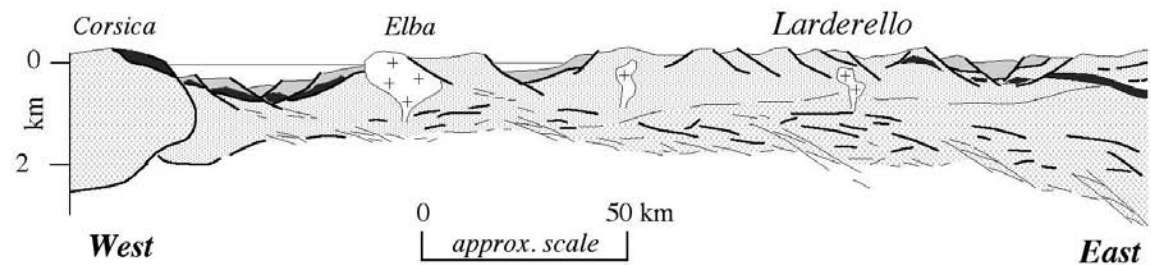
Fig. 2.2 - Left: relations among the different tectonic units of Northern Apennines and related palaeogeographical domains. Right: schematic crustal geological cross-sections showing the collisional and post-collisional evolution through the Northern Apennines (after Carmignani et al., 1994).

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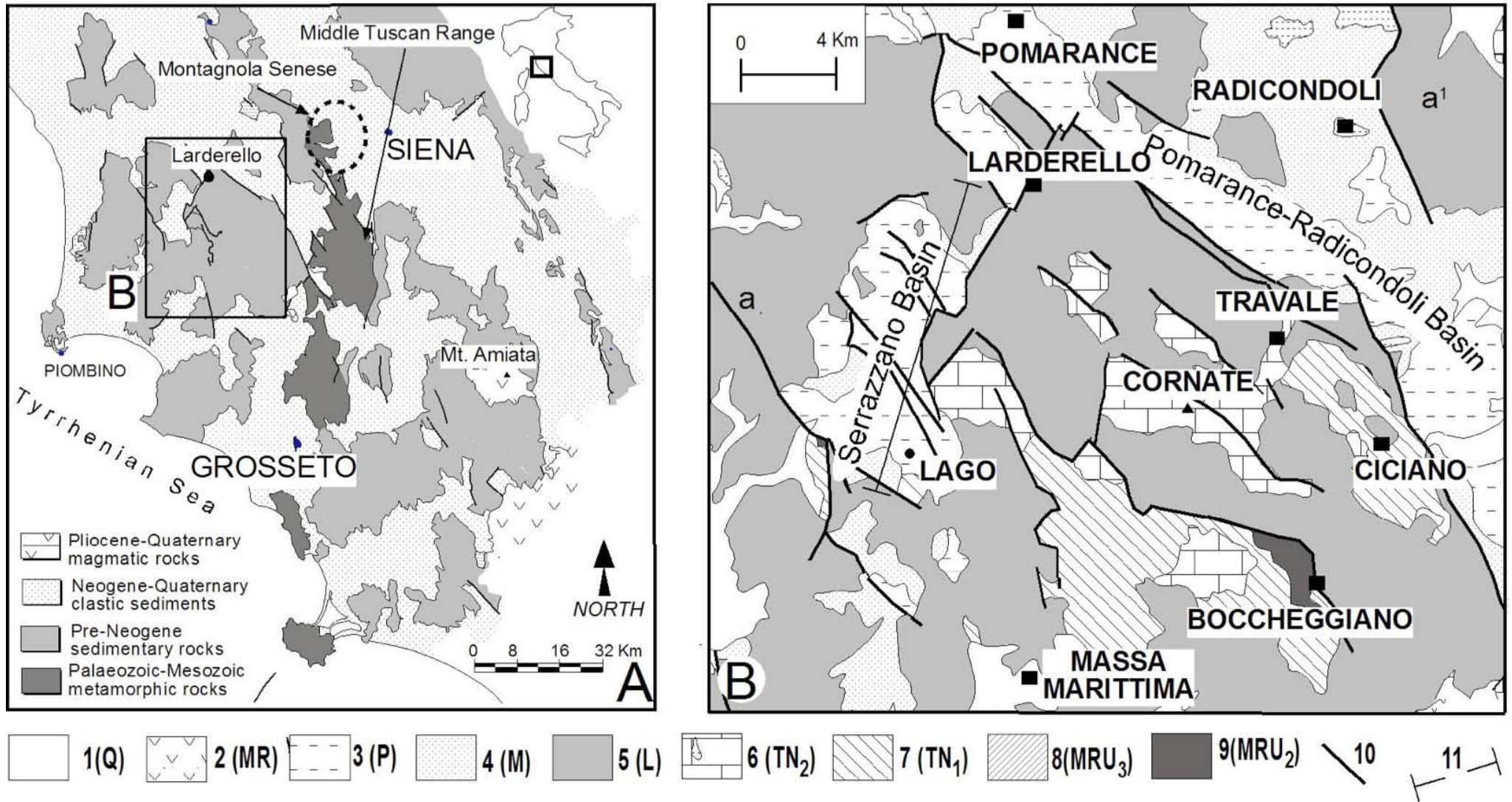
Fig. 2.3 - Geological sketch maps of **(A)** Southern Tuscany and **(B)** Larderello areas. Symbols: (1) Q: Quaternary continental deposits; (2) MR: Pliocene-Quaternary magmatic rocks; (3) P: Pliocene marine deposits; (4) M: Middle-Upper Miocene continental, brackish and marine sediments; (5) L: Ligurian Units (Jurassic - Oligocene); Tuscan Nappe: (6) TN$_2$: Late Triassic-Early Miocene sedimentary sequence; (7) TN$_1$: Late Triassic evaporites; (8) MRU$_3$: quartz metaconglomerate, quartzite and phyllite (Triassic Verrucano Group); (9) MRU$_2$: Palaeozoic phyllite; (10) normal fault; (11) trace of the geological section given in Fig. 4.1.

Compressional features

These are recognizable in the greenschist-facies metamorphic rocks cropping out both in the southern Middle Tuscan Range (i.e., Montagnola Senese and Monticiano-Roccastrada Ridge) and in the sedimentary cover (i.e., Larderello and Monte Amiata areas).

In the metamorphic rocks of the Montagnola senese area (Fig. 2.4) the Late Oligocene-Early Miocene compressional phase determined a planar, pervasive schistosity, mainly defined by sub-parallel orientation of micas and carbonate minerals (Liotta, 2002).

This schistosity is an axial plane foliation associated to isoclinal folds axes. These are roughly parallel to the NE-trending stretching lineation present on the S1 foliation. Kinematic indicators invariably show a transport direction toward the NE. During this contractional event, rocks belonging to the Verrucano Group overthrust the external Tuscan succession, thus determining the metamorphic conditions in which deformation occurred (i.e., the Montagnola Senese area, Liotta, 2002; Fig. 2.4).

At deeper levels duplex structures (Fig. 2.5) developed within the Verrucano Group in the greenschist metamorphic facies (Costantini et al., 1988; Elter & Pandeli, 1990; Brogi, 2008).

Concerning the sedimentary cover, thrusts were detected within the Tuscan succession in the Larderello and Monte Amiata area, now cropping out in isolated geological bodies (Nuclei toscani, Auctt.), surrounded by the Ligurian Units (Brogi et al., 2005). Thrusting occurred in very low-metamorphic conditions (Hillite-smectite paragenesis). The Upper Triassic evaporites and the Cretaceous-Oligocene clayey marls (scaglia toscana group) represented the main detachement levels. Particularly, the Upper Triassic Burano Anhydrites played as a regional decoupling horizon, favoring the development of a sub-horizontal cataclastic level (Fig. 2.6).
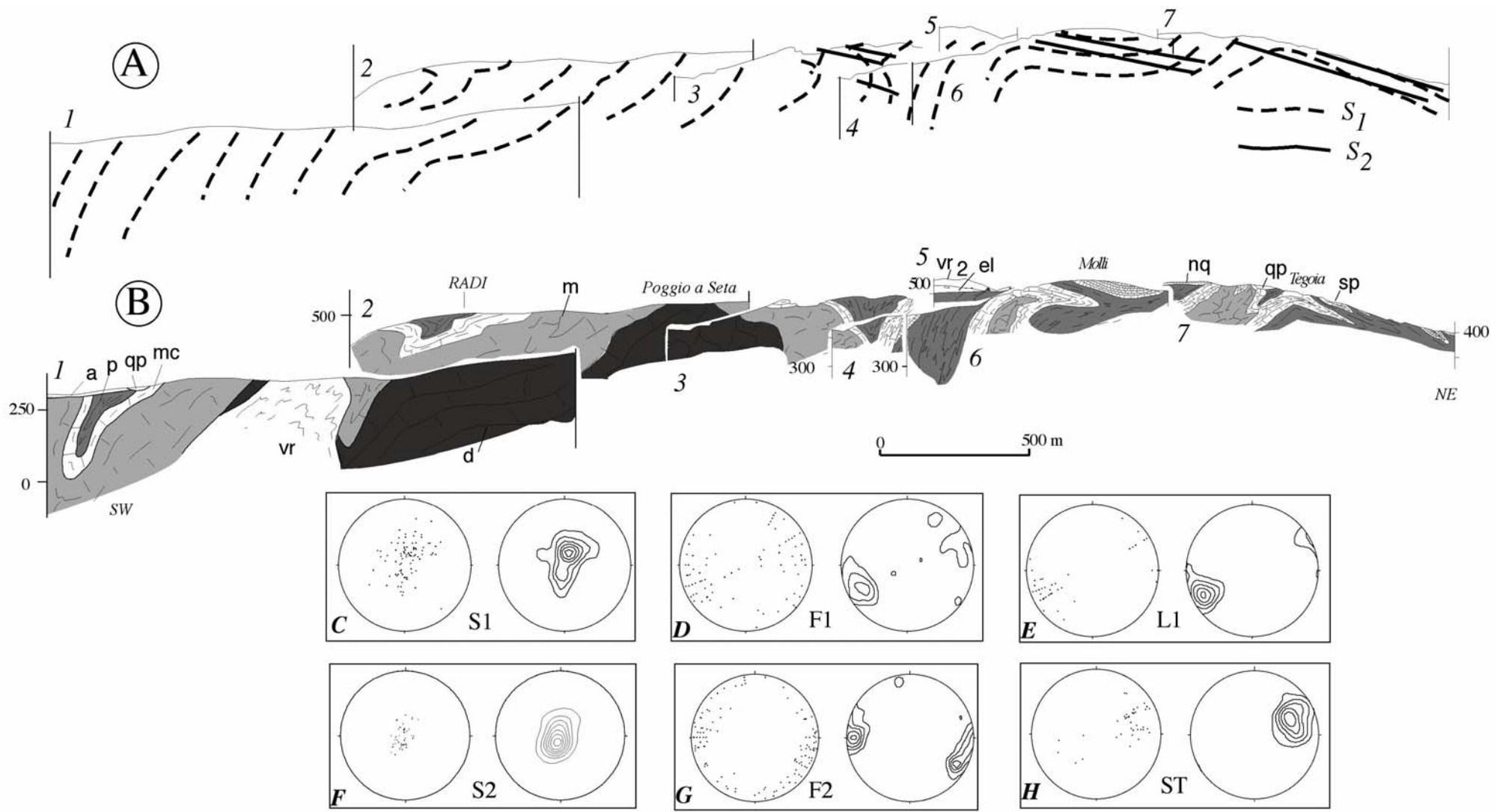
Fig. 2.4 - Geological cross section through the central part of Montagnola Senese area. A: sections showing the pattern of the S_1 and S_2 foliations. B: sections showing the pattern of bedding. Stereonets (lower hemisphere, equiangular net) of the structures related to the first (D_1) and second (D_2) deformational events, respectively. Symbols: vr - Verrucano Group (Ladinian-Carnian); d - Grezzoni Formation (Rhaetian-Norian); m - massive marble (Lower Liassic); mc - layered marble with cherts (Middle-Upper Liassic); p - metamorphic scaglia toscana fm. with marble breccias and siliceous phyllite (sp) interlayered (Cenomanian). Montepescali-Monte Quoio sub-unit: vr_2 - Verrucano Group (Ladinian-Carnian); Tuscan Nappe: el - Anidriti di Burano Fm. (late Triassic); nq - Neogene and Quaternary sediments.
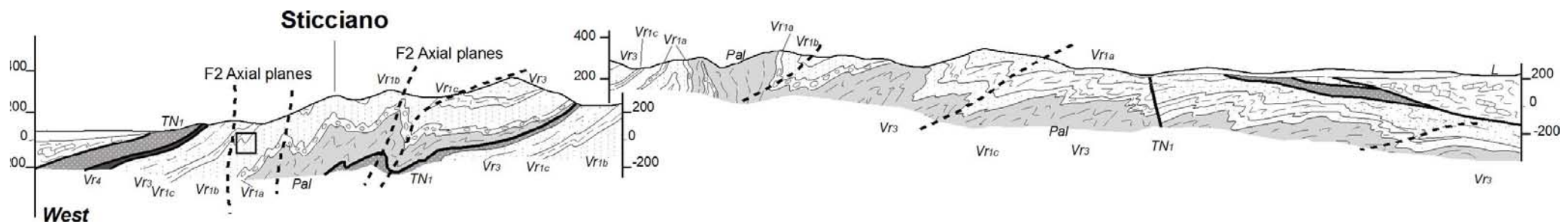
Fig. 2.5 - Geological sections across the Monte Leoni area showing the thrust affecting the Verrucano Group itself. Key: L - Ligurian Units; TN_1 - Tuscan Nappe, Anidriti di Burano Fm.; VR_4 - tocchi fm.; VR_3 - anageniti minute fm.; VR_1 - Civitella M.ma fm.: VR_{1a} - basal member; VR_{1b} - intermediate member; VR_{1c} - upper member; Pal - Farma fm. (From Brogi, 2008).

Extensional features

After the emplacement of the tectonic units, extension determined the lateral segmentation of the Tuscan succession and of the basal Verrucano Group through low-angle normal faults (Figs. 2.6 and 2.7). The main detachment levels are located: in the Upper Triassic evaporites, underneath the sedimentary cover, and within the Palaeozoic phyllite, underneath the Verrucano Group, already stacked in duplex structures.

This process, occurred in the Burdigalian-Messinian time span, determined the development of tectonic depressions (Fig. 2.8), where continental to marine Middle-Late Miocene sediments deposited (Brogi & Liotta, 2008).

Stretching is estimated in about 120% over 98 km, at least (Carmignani et al., 1994). Therefore, relics of the compressional structures remained preserved in the isolated geological bodies, made up of Tuscan Nappe and Verrucano Group (Figs. 2.5 and 2.6). In this framework, the Ligurian Units directly overlain the deeper structural levels, such as the Late Triassic evaporites, the Verrucano Group and the Palaeozoic phyllite. The previously formed compressional and extensional structures, were dissected by a new extensional event, which determined NW-SE normal faults. In the resulting tectonic depressions, marine sediments deposited
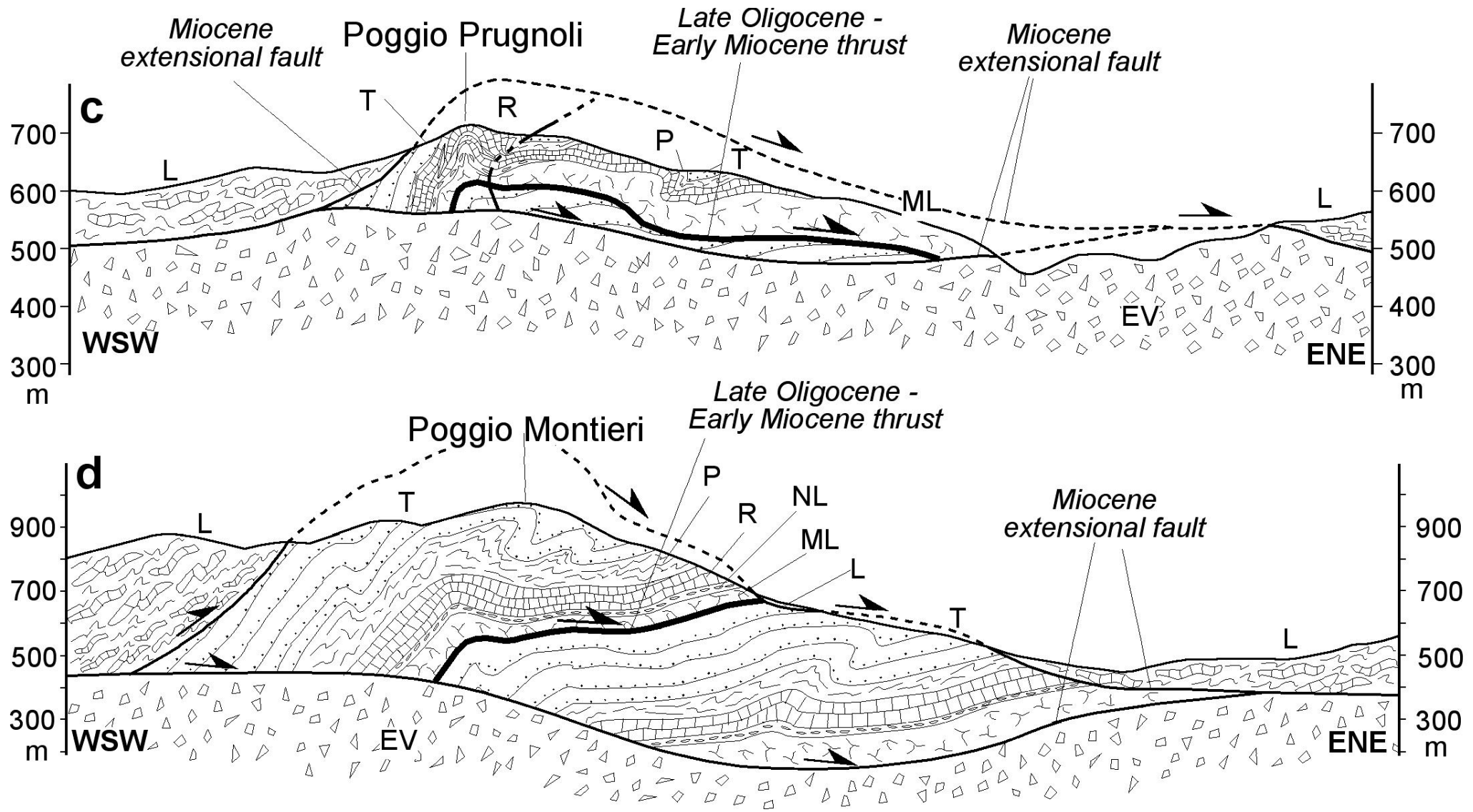
Fig. 2.6 - Geological sections through the Montieri and Poggio Prugnoli areas, illustrating the Tuscan Nappe as isolated geological bodies, where the Late Oligocene-Early Miocene compressional and Middle-Late Miocene extensional structures (indicated by thick arrows) are recorded; Symbols: L - Ligurian Units; Tuscan Nappe: T - Upper Oligocene - Lower Miocene terrigeneous turbidites; P Creataceous-Oligocene pelagic succession; R - Upper Jurassic Radiolarites; NL - Lower-Middle Jurassic nodular reddish limestone, cherty limestone, Posydonomia bearing marls; M - Lower Jurassic massive limestone; EV - Upper Triassic Anhydrites (from Brogi et al., 2005).
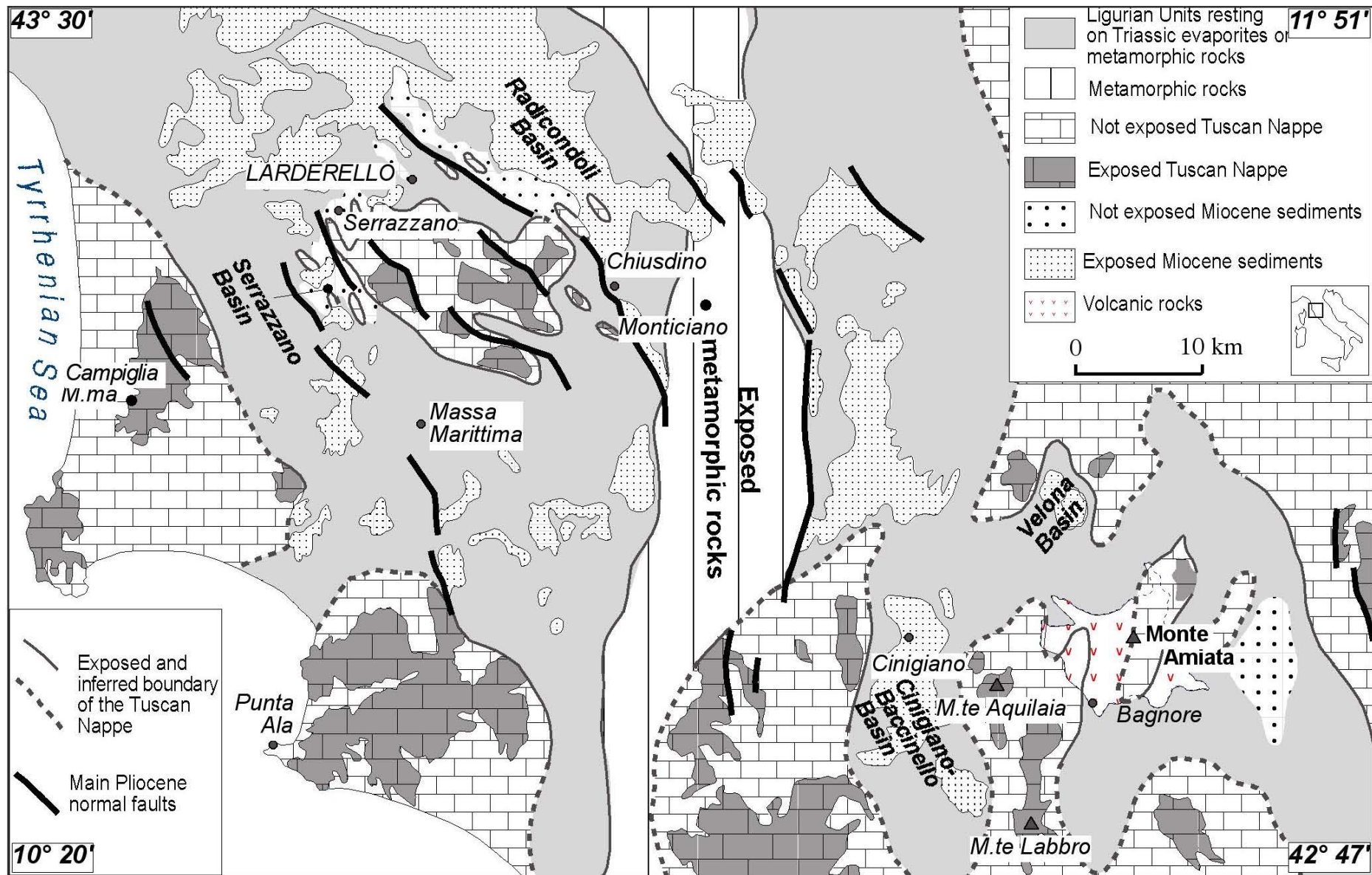
Fig. 2.7 - Tuscan Nappe segmentation and Middle-Late Miocene sediments in Southern Tuscany, as reconstructed from fieldwork, borehole data, and interpretation of seismic reflection lines. Gray pattern indicates where the Ligurian Units overlie the Late Triassic evaporites and/or the metamorphic rocks. The Middle-Upper Miocene deposits are located in the gap between two Tuscan Nappe segments.

during Early-Middle Pliocene (Fig. 2.8). This latter extensional event, mainly characterized by high-angle normal faults, produced a stretching in at least 7% over 98 km (Carmignani et al., 1994). The main tectonic depressions are dissected by SW-NE transfer zones.

In Southern Tuscany, the Pliocene extensional event is joined with widespread magmatism. Therefore, the geologic evolution of the area is characterized by the hydrothermal processes resulting from the interplay between ongoing extensional structures and cooling of granitoids at depth.
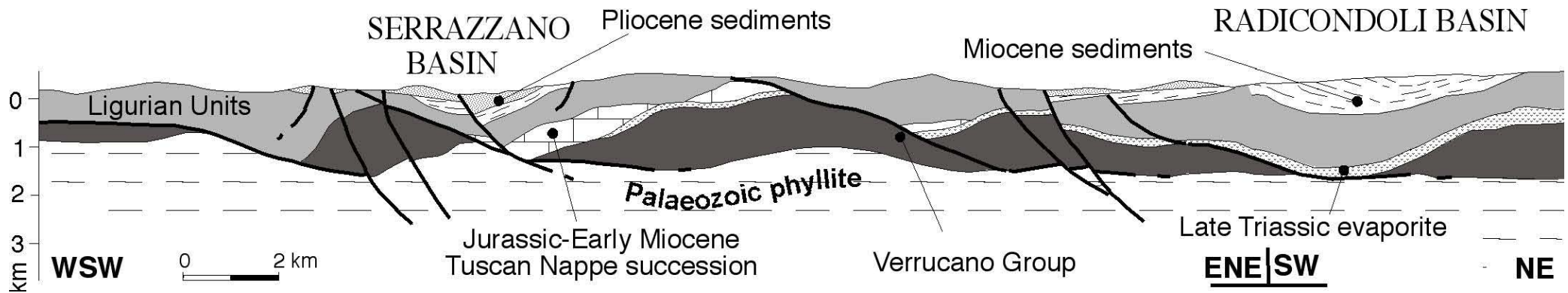
Fig. 2.8 - Geological cross section through the Larderello area and surroundings based on borehole stratigraphy, seismic reflection lines and field mapping, showing the lateral segmentation of the Tuscan Nappe and Verrucano Group (after Brogi and Liotta, 2008).

3. Fossil geothermal system: the Boccheggiano-Montieri area

In the following a summary of the geological setting of the Boccheggiano-Montieri is reported, on the basis of the data and interpretation proposed by Liotta et al. (2010).

In the Boccheggiano-Montieri area cataclasites deriving from the Late Oligocene-Early Miocene stacking of the tectonic units, from the Miocene low-angle normal faulting and from the Pliocene-Pleistocene high-angle normal faults are widely exposed (Fig. 3.1 and 3.2).

Fig. 3.1 - Geological sketch map of the Boccheggiano-Montieri area. References to other figures and geological sections are given. Mineralized Miocene and Pliocene normal faults are highlighted (from Liotta et al., 2010).
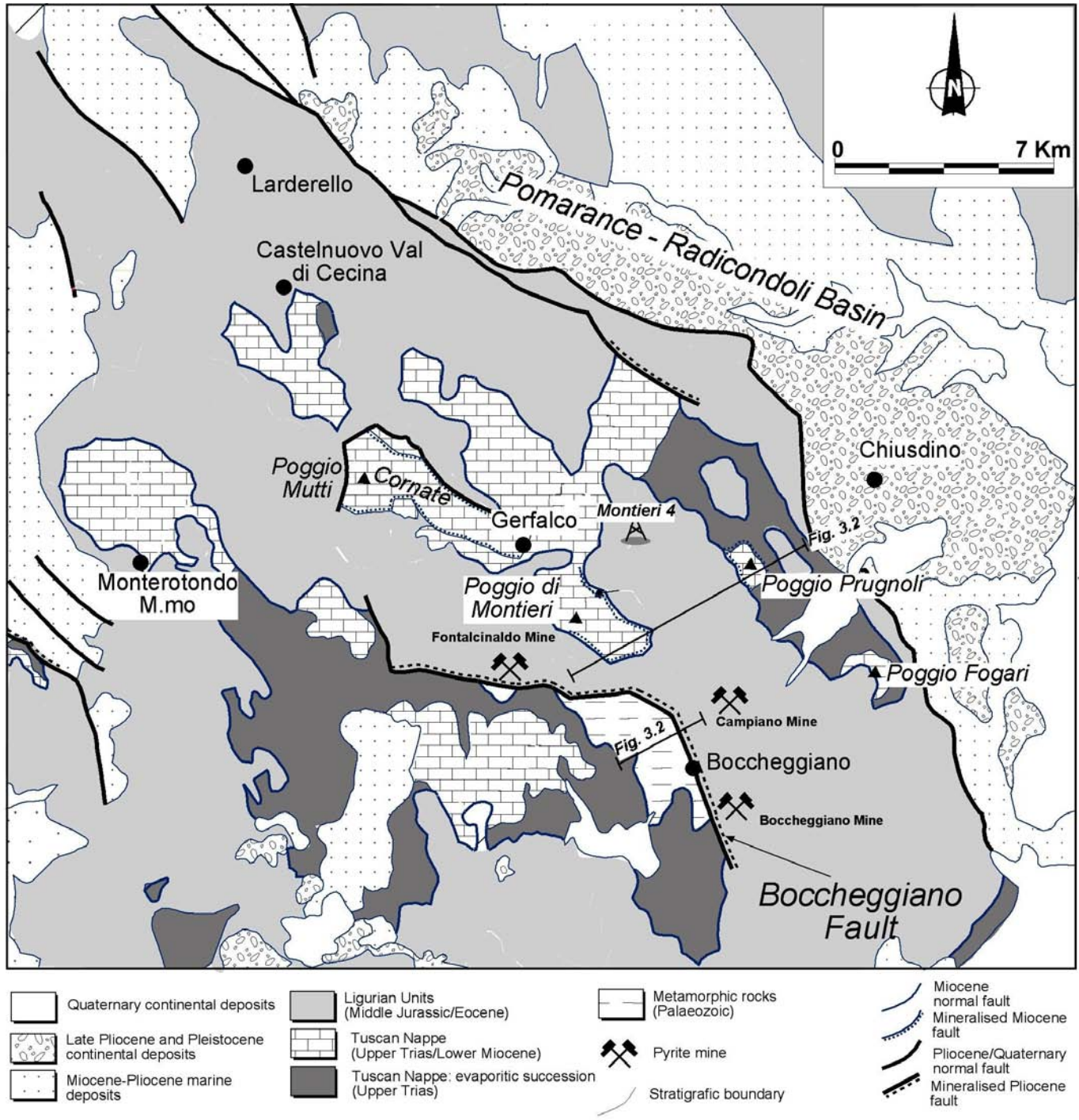
All cataclastic levels are locally mineralized. The structure is characterized by two isolated Tuscan Nappe geological bodies, internally deformed during the collisional stage of the northern Apennines, as indicated by the occurrence of a Late Oligocene thrust doubling the Tuscan Nappe succession (Fig. 3.2).

Middle-Late Miocene extensional tectonics developed low-angle normal faults, separating the presently named as Poggio Prugnoli and Poggio Montieri geological bodies. These faults show cataclastic levels localized at the base of the Ligurian Units and within the Late Triassic evaporite (Anidriti di Burano Fm).

In between the Poggio Prugnoli and Poggio Montieri areas, the Ligurian Units directly overlie the Upper Triassic evaporites. The NE dipping Boccheggiano Pliocene normal fault dissected the previously formed structural setting, thus juxtaposing the Ligurian Units (i.e., "Argille a Palombini", Early Cretaceous) to the Palaeozoic phyllite (Fig. 3.2). The 3,721-m deep Montieri 4 borehole (Boyce et al., 2003), drilled, for about 2,000 m, a monzogranite with an age of c.a. 3-2 My (Dini et al., 2005; Villa et al., 2006). Interpretation of seismic reflection lines (Rossetti et al., 2008) suggests that the Boccheggiano normal fault crossed, at depth, the Montieri monzogranite (Fig. 3.2).

These structural features, therefore, indicate that the mineralization characterizing the Boccheggiano fault zone and the entire Boccheggiano-Montieri area are related to the cooling of the monzogranite recognized at depth.
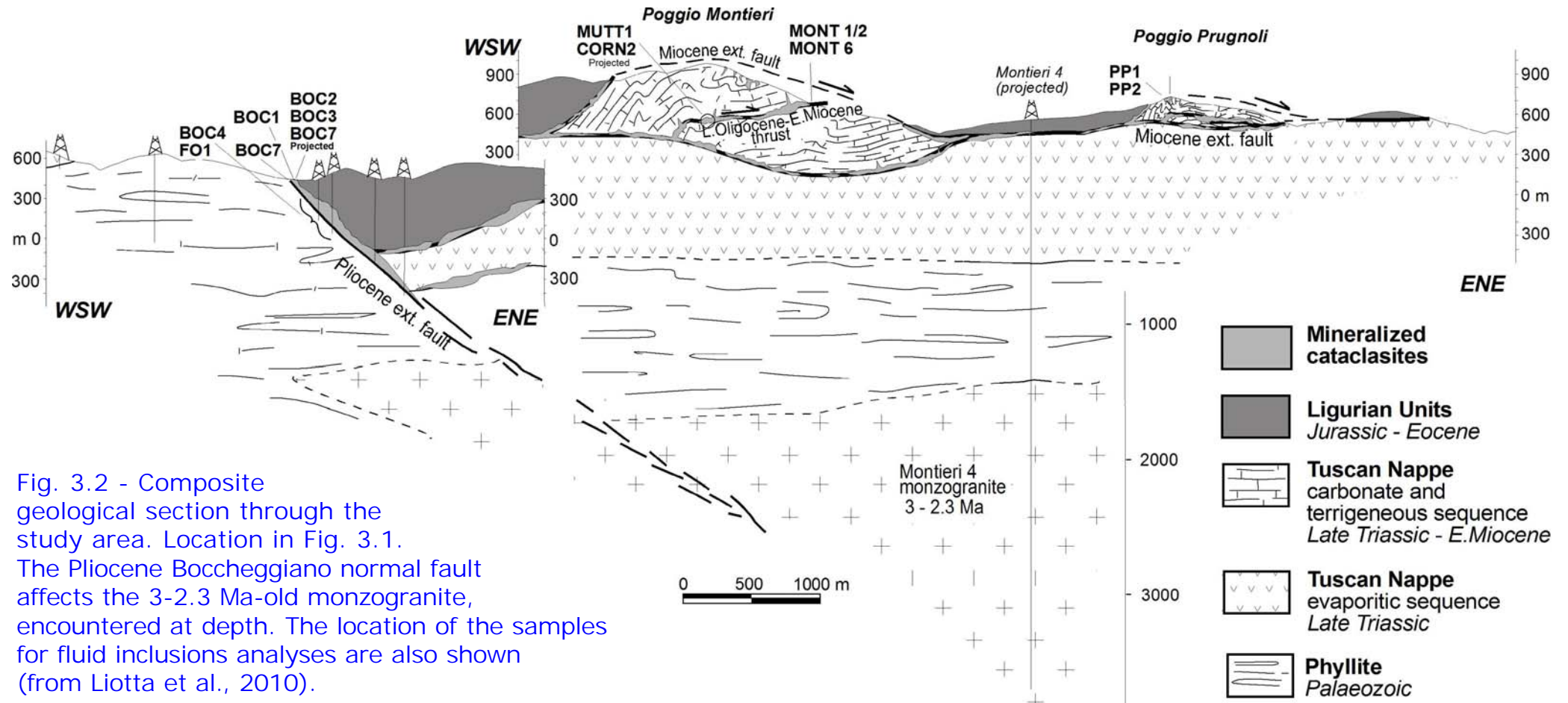
Fig. 3.2 - Composite
geological section through the
study area. Location in Fig. 3.1.
The Pliocene Boccheggiano normal fault
affects the 3-2.3 Ma-old monzogranite,
encountered at depth. The location of the samples
for fluid inclusions analyses are also shown
(from Liotta et al., 2010).

4. Present geothermal system: the Larderello geothermal field

The structure of the geothermal area is characterized by normal faults related to the Pliocene-Present time period. These structures cross-cut the already pre-existing compressional and extensional structures and tend to die out at depth, in correspondence of the present brittle-ductile transition. The upper boundary of this transitional zone is marked by a reflection seismic horizon, referred to as the K-Horizon (Fig. 4.1), interpreted as a fluid-filled fractured level (Cameli et al., 1993; Liotta & Ranalli, 1999).

Fig. 4.1 - **(a)** and **(b)**: unmigrated seismic line and its line drawing. In **(b)**, reflections with high contrast of acoustic impedance are highlighted by thick lines; dotted lines denote geological contacts; light grey lines indicate normal faults related to the third extensional event. **(c)**: geological interpretation. Symbols: Q - Quaternary sediments; P - Pliocene sediments; M - Miocene deposits; P - Pliocene deposits: M - Miocene deposits; Tuscan Nappe (FT): FT$_2$ - Lower Miocene-Rhaetian succession; FT$_1$ - Upper Triassic evaporites; Monticiano Roccastrada Unit (UMR): UMR$_3$ - Mesozoic-Paleozoic Group; UMR$_2$ - phyllite-quartzitic group; UMR$_1$ - Paleozoic micaschist group; BA - Gneiss Complex. Black triangles: intersections with other reflection seismic lines.
The trace of this geological section is shown in Fig. 2.3 (From Brogi et al., 2003).

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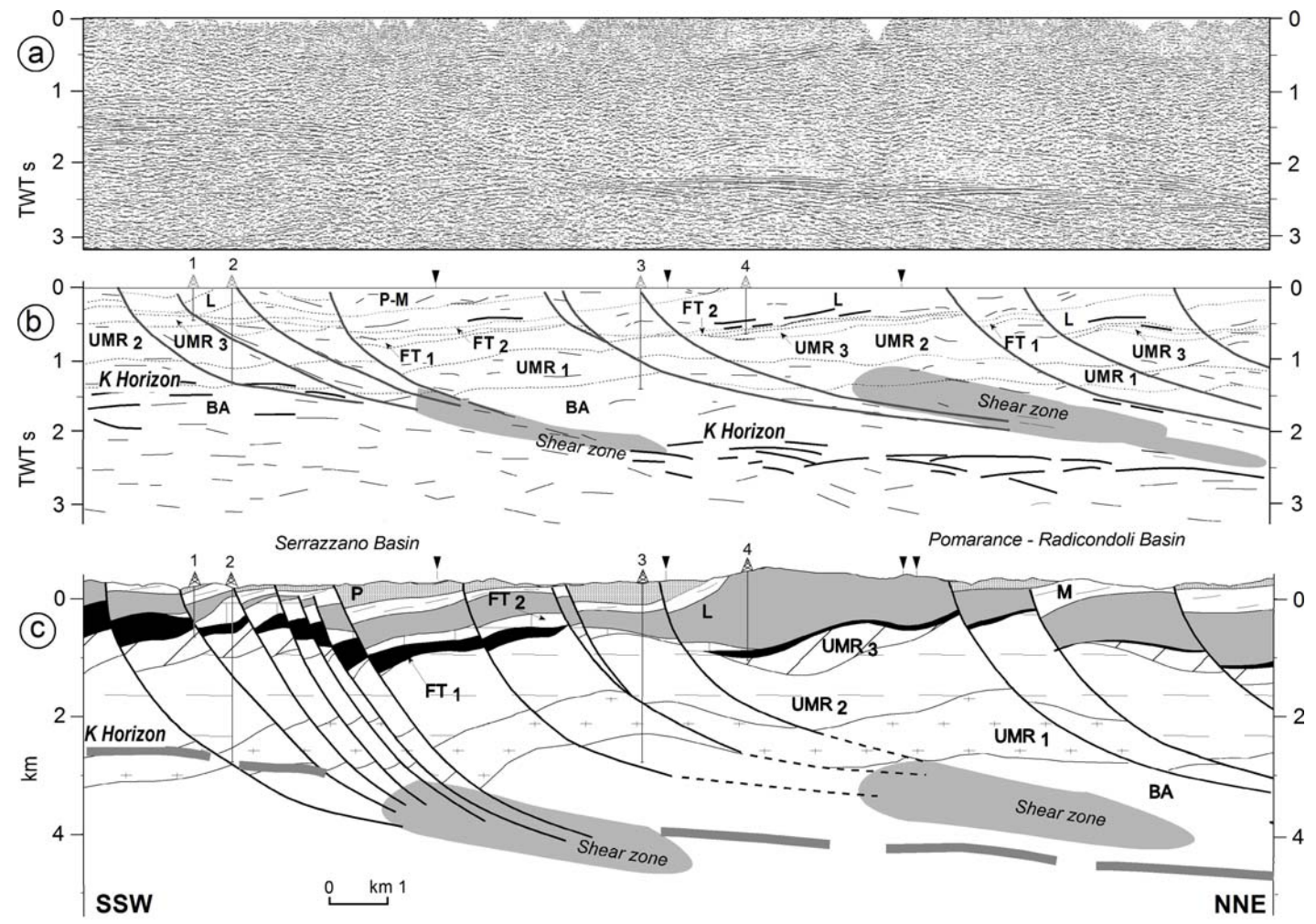
The lateral continuity of the K-horizon is interrupted by intersection with brittle shear zones where Pliocene-Present normal faults coalesce (Fig. 4.1).

Along these brittle shear zones, temperature data, measured at bottom holes, indicate local variations, with peaks and depressions (Fig. 4.2), thus implying that fluid flow is controlled by the extensional structures (Bellani et al., 2004). Two different reservoirs are exploited in the Larderello-Travale geothermal fields.
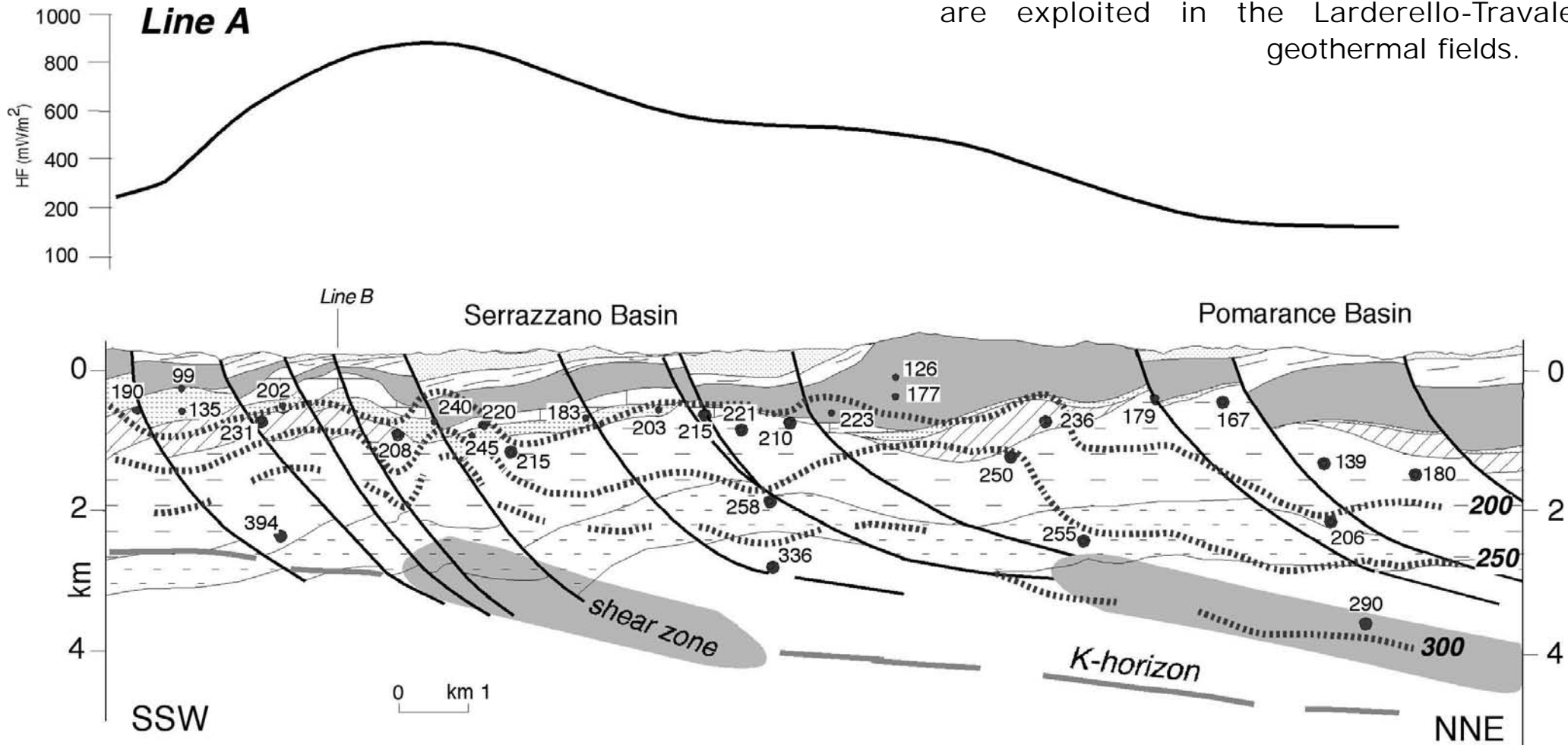
Fig. 4.2 - Geological cross sections, isotherms, and surface heat flow along a geological through the Larderello area (location is given in Fig. 2.3). Black circles represent temperature measurements in °C. Isotherms subject to the weakest control are denoted by a broken dashed line (From Bellani et al., 2004).

The reservoirs

The first reservoir is mostly located within the cataclastic level corresponding to the Late Triassic evaporites. Its depth ranges between 500 and 1000 m, approximately. This level was the main detachment level during the collisional and Early-middle Miocene extensional stages. A permeability of about 10^{-15} or 10^{-14} m^2 is estimated. The bulk of porosity derives from tectonic fractures, although the dissolution of the Late Triassic anhydride in presence of hot saline solutions, with the consequence collapse and rupture of the overlying carbonate rocks, can contribute to increase permeability. The second and deeper reservoir, exploited through boreholes down to 4000 m, is located in cataclastic rocks, linked to the Pliocene-Present extensional faults, within the metamorphic rocks. Here, the permeability is estimated in about 10^{-15} m^2.

The recharge area

The main recharge area is located in the Cornate area, where fractured limestones and cherty limestones belonging to the Tuscan Nappe, largely crop out.

The geothermal fluids

The Larderello geothermal system is vapor-dominated in both reservoirs. The meteoric water is the main source for the vapor, mixed with magmatic and metamorphic fluids, in a minor extent. A mantle signature is also present in the gas phase (Minissale et al., 2000). Since 1980's injection of wastewater has became an important feature of the exploitation strategy.

5. Field Stops

Stop 1.1: The Boccheggiano Fault

Take the road from Massa Marittima to Siena, through Prata village (Fig. 5.1). Going ahead for about 4 km more, on your left side, a little track (with an old bridge passing over the Merse creek) will bring you to the outcrop. This stop (43°05'47.7"-11°01'54.4") is located in the Boccheggiano pyrite mining district and we are looking at the Pliocene-Pleistocene mineralized Boccheggiano normal fault. This is a regional structure, almost 20 km long and characterized by two NNW-SSE segments, linked by an E-W striking segment. The attitude of the fault plane is constrained at depth trough borehole data. In the abandoned Campiano mine, it trends 170° N and dips 45°NE (fig. 5.2). A vertical throw of about 900 m was here estimated.

In this outcrop (Fig. 5.3), the footwall is made up of Paleozoic phyllite, while the hangingwall is constituted by Early Cretaceous shale and limestone belonging to the argille a palombini fm.

In the footwall, the Palaeozoic quartz-rich phyllite is interlayered with levels of quartzose metasiltite, metasandstone and minor metaconglomerate. The rock fabrics are characterized by isoclinal folds and pervasive S_2 schistosity (Chl+Ms+Qtz+FeOx±Ab), dipping 15° to SW. This folding event and the coeval synkinematic metamorphism is related to the Late Oligocene-Early Miocene collisional stage.

The Boccheggiano fault hangingwall is made up of Early Cretaceous interlayered shale and limestone of the argille a palombini fm. Limestone predominates on the shale beds, defining levels up to 20 m thick. Occurrence of pervasive pressure solution axial planar cleavage, at low angle with respect to the bedding, indicates a pre-faulting deformation, deriving from the collisional stage.

The fault zone is constituted of a footwall 25-m-thick damage zone, a 1-m-thick core zone, and a hangingwall damage zone about 40 m thick (Fig 5.3b). Pyrite is mainly concentrated in the hangingwall, extensively distributed in the 13-m-thick silicified rock mass, where the original sedimentary fabrics are totally lost. On the contrary, the sedimentary features are maintained in the rest of the hangingwall damage zone where pyrite is allocated within millimeter-thick quartz veins. The core zone consists of a black clay-rich incohesive fault gauge with 1-10 mm fragments (<30%) of Palaeozoic phyllite and quartz veins.

In the hangingwall damage zone, nearest to the fault core, intensity of deformation is higher, as suggested by the fracture frequency, here indicated by about 1 cm open fractures, spaced about 5 cm.

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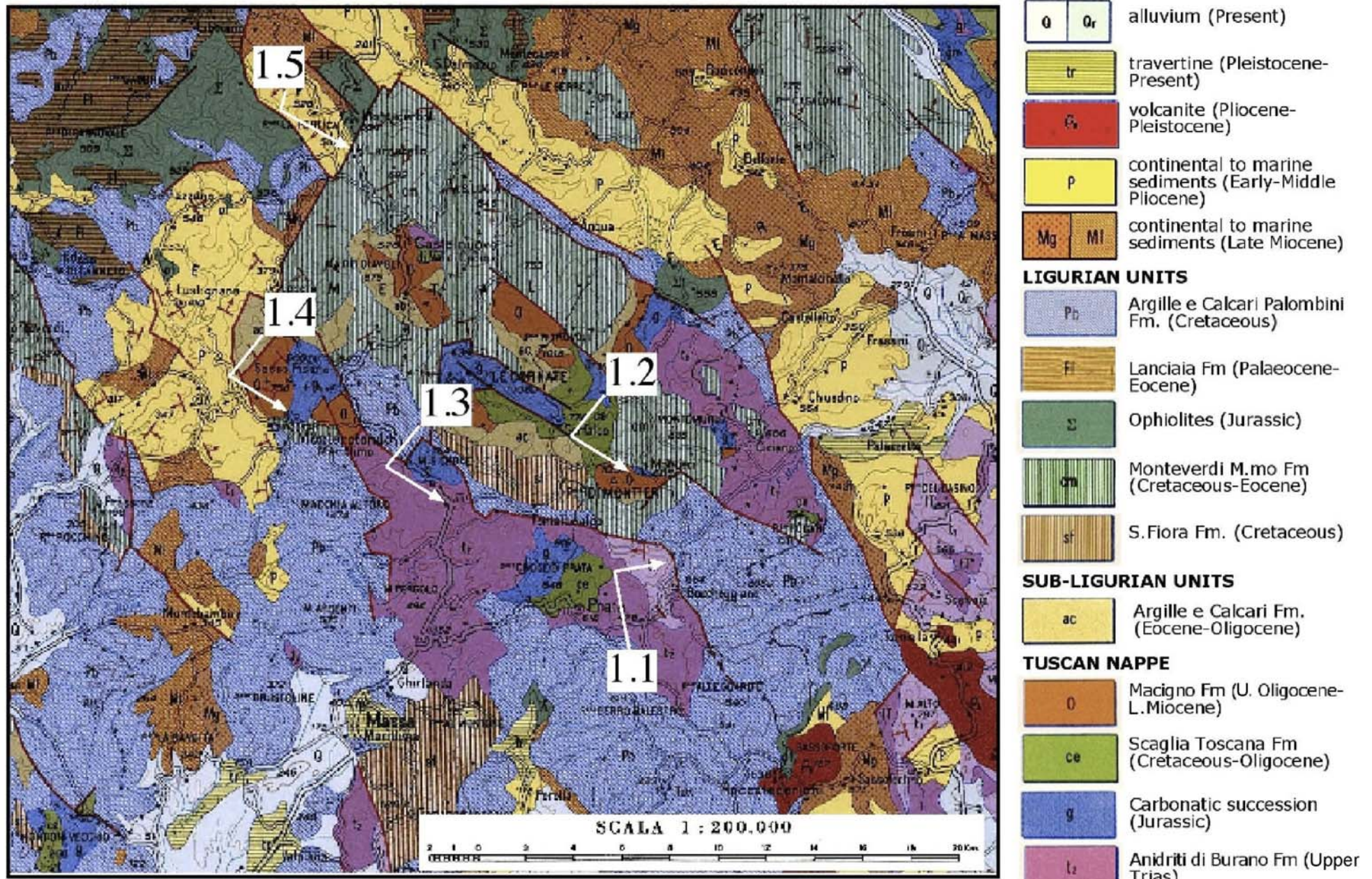
Fig. 5.1 - Location of the stops described in the text. The geological map is from Giannini et al., 1971 (modified).

Legend:

	alluvium (Present)
tr	travertine (Pleistocene-Present)
Gr	volcanite (Pliocene-Pleistocene)
P	continental to marine sediments (Early-Middle Pliocene)
Mg MI	continental to marine sediments (Late Miocene)

LIGURIAN UNITS

Pb	Argille e Calcari Palombini Fm. (Cretaceous)
Fl	Lanciaia Fm (Palaeocene-Eocene)
Σ	Ophiolites (Jurassic)
cm	Monteverdi M.mo Fm (Cretaceous-Eocene)
sf	S.Fiora Fm. (Cretaceous)

SUB-LIGURIAN UNITS

| ac | Argille e Calcari Fm. (Eocene-Oligocene) |

TUSCAN NAPPE

o	Macigno Fm (U. Oligocene-L.Miocene)
ce	Scaglia Toscana Fm (Cretaceous-Oligocene)
g	Carbonatic succession (Jurassic)
t₂	Anidriti di Burano Fm (Upper Trias)

TUSCAN METAMORPHIC COMPLEX

| t₁ | Verrucano Group (Trias) |

Legend:

- detritus and dump
- Quaternary continental deposits
- **Ligurian Units** Middle Jurassic/Eocene
- **Tuscan Nappe** Cretaceous/Early Miocene
- **Tuscan Nappe** evaporite succession Late Triassic
- **Metamorphic rocks** mainly Paleozoic phyllite
- Mineralised rocks
- Pliocene-Quaternary normal fault
- Miocene normal fault
- L. Oligocene-E. Miocene
- Borehole

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Fig. 5.2 - Schematic geological map and sections of the Boccheggiano mine district. The mineralization (quartz - pyrite, mainly) occurs within the damage zone of the Boccheggiano fault and along the boundary between the Palaeozoic phyllite and the Late Triassic evaporite (from Liotta et al., 2010).
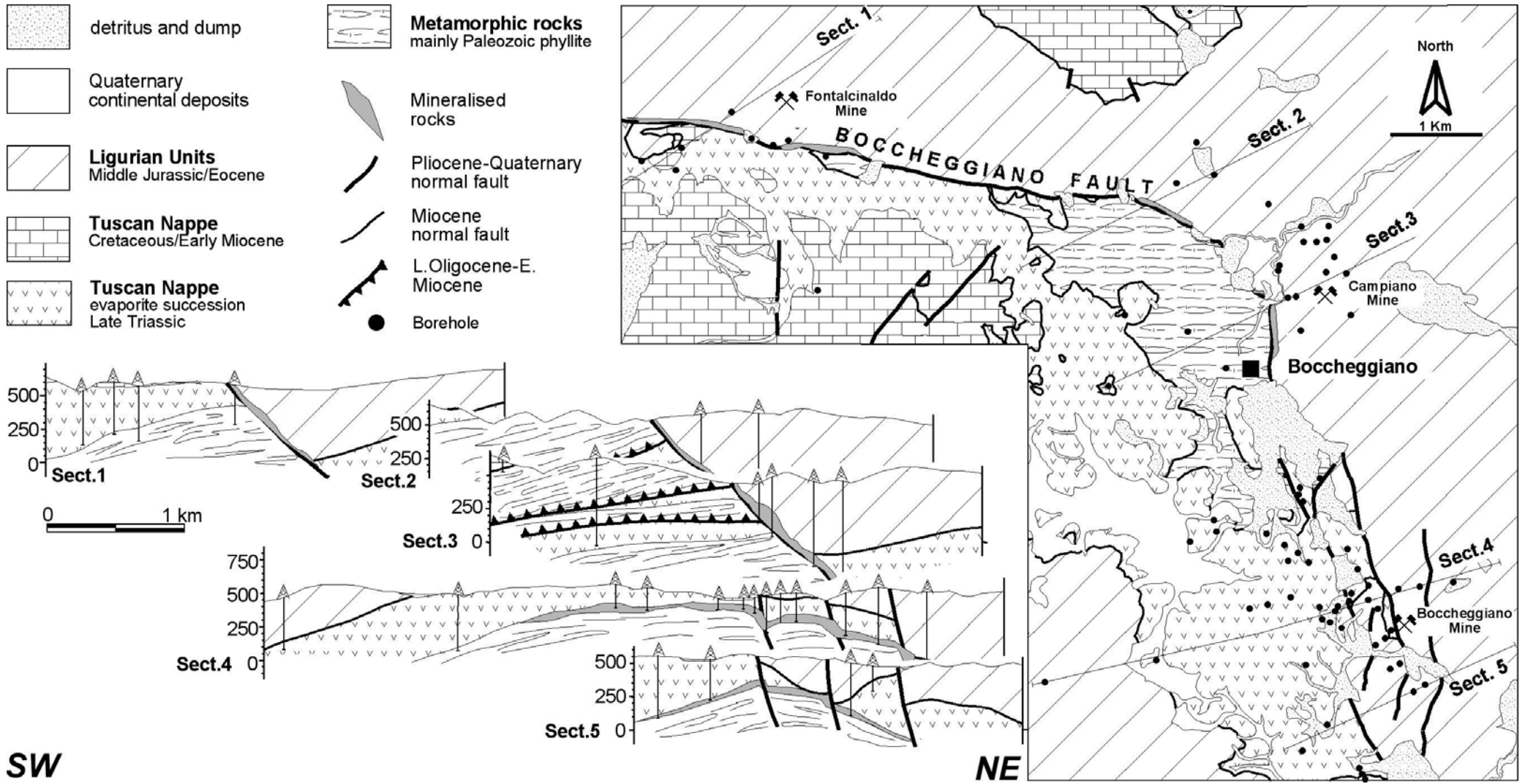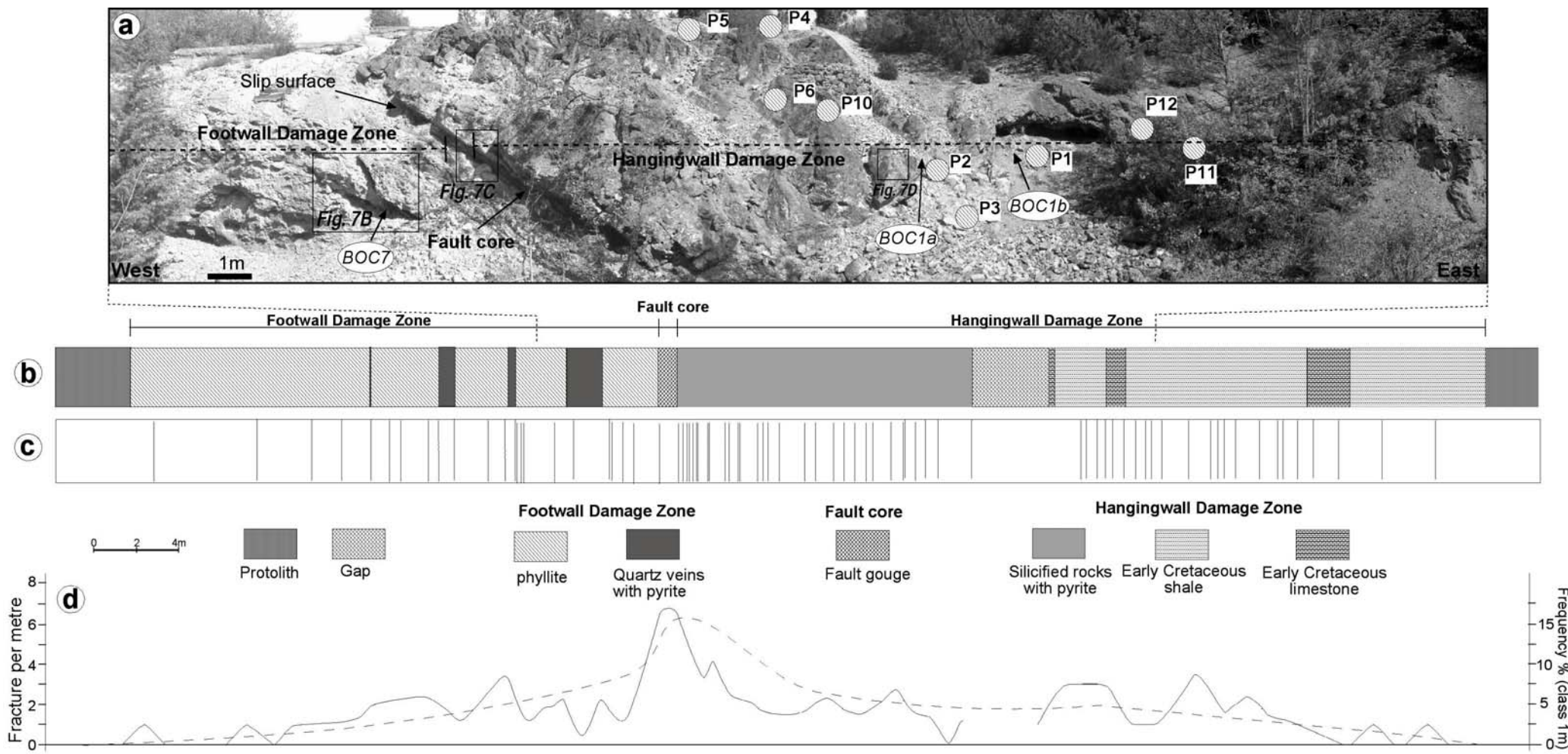
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Fig. 5.3a-d - **a**: The Pliocene Boccheggiano fault and its damage zone close to the Campiano mine. Location of samples BOC1 and BOC7 for fluid inclusions and for image analyses (from P1 to P12) are also shown. **b** and **c**: lithologic and fracture scan line along the indicated segment; **d**: fracture frequency in the damage zone.
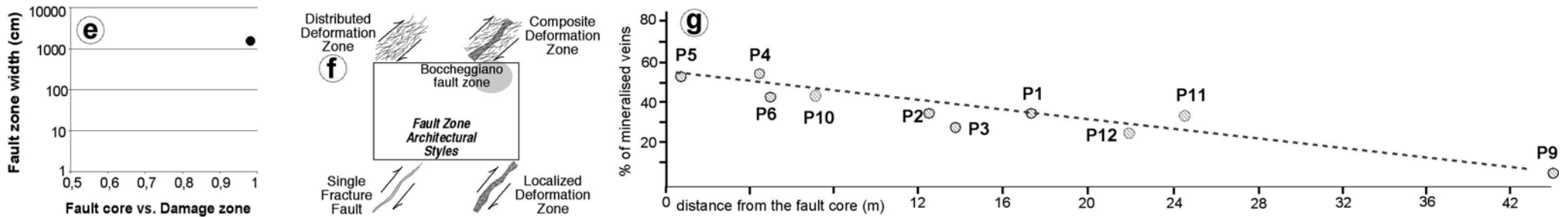
Fig. 5.3e-g - **e** and **f**: diagrams showing the high permeability of the fault following the methodology proposed by Caine et al. (1996); **g**: the minimum percentage of mineralized veins in the hangingwall varies from about 60% to 4% in 40 m, from the core zone to the hangingwall protolith (from Liotta et al., 2010).

Fracture frequency tends to decrease toward the undeformed rock (protolith), resulting in fractures spaced up to 260 cm (Fig. 5.3c). The fracture frequency distribution (Fig. 5.3c and 5.3d) indicates that: (1) the footwall is less deformed than the hangingwall; (2) the frequency peak is in the hangingwall, close to the core zone; (3) the damage zone is asymmetric, suggesting a lithological control during brittle deformation.

Mineralized veins tend to decrease from the core zone to the undeformed rock. An evaluation of this tendency is given by the vein/rock surface ratio, obtained by means of image analyses procedure. The outcomes (Fig. 5.3g) indicate that the percentage of mineralized veins in the rock-mass decreases from about 60 to about 4%, from the fault zone to the hangingwall protolith, following the fracture density decrease, as it was expected.

Considering their attitude and mutual relationships, fractures in the footwall and hangingwall can be related to Riedel shear fractures, developed during the fault activity (Fig. 5.4). In the footwall damage zone, R and P fracture surfaces are characterized by pyrite and iron oxides, indicating that these acted as pathways during fluid flow. In the hangingwall damage zone, fractures are related to R and R' fractures. Their average attitudes

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(Fig. 5.4a) are 150/30 and 240/70, respectively. These fractures became loci for fluid flow, thus resulting in intense mineralization with pyrite and quartz, both in the silicified (Fig. 5.4c and 5.4d) and not-silicified rock mass. Fractures in the clay-gauge are SW gently dipping shear foliations. Their attitude and structural relationships with the fault plane indicate that the kinematics of the Boccheggiano normal fault was characterized by a left lateral component (Fig. 5.4a). Noteworthy, the quartz elements dispersed within the fault gouge are often mantled with pyrite (Fig. 5.4j), indicating fluid flow and mineralization during the cataclasite development.
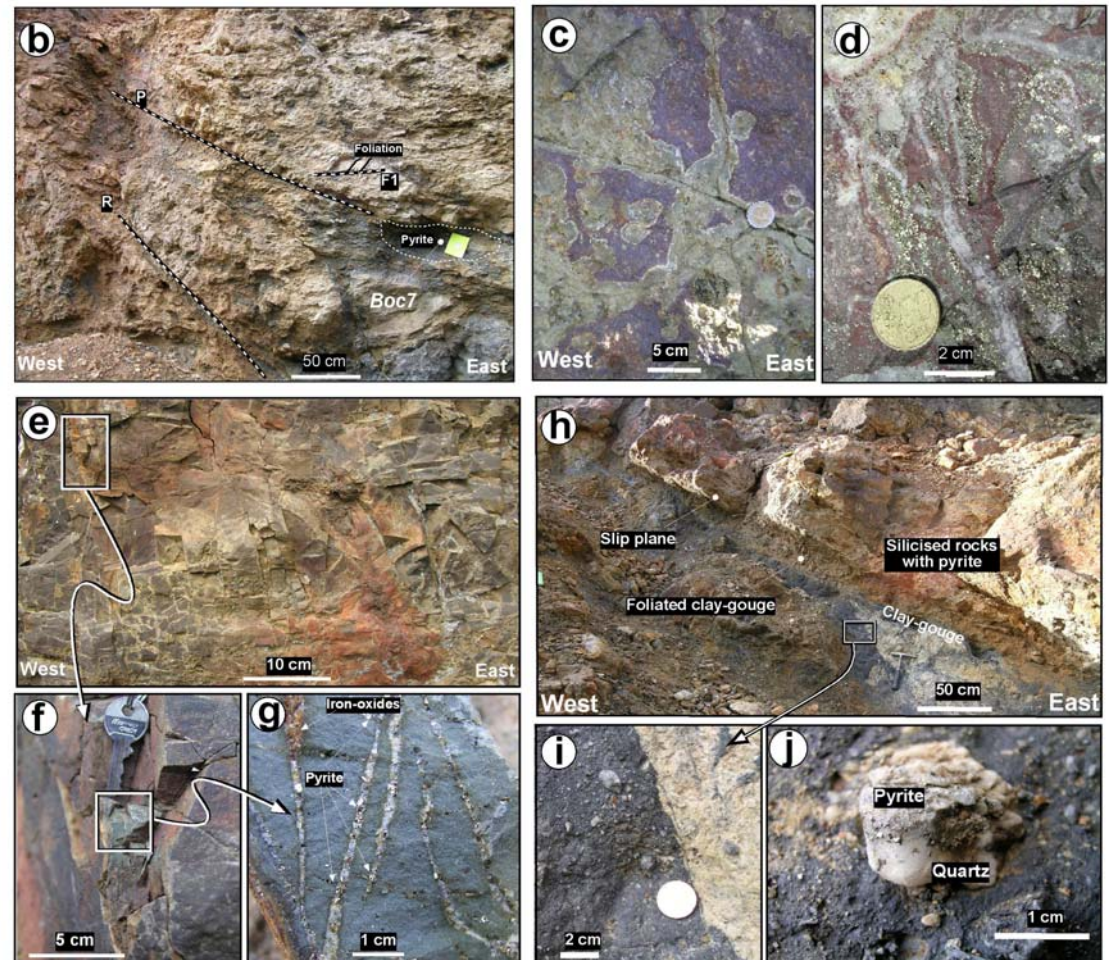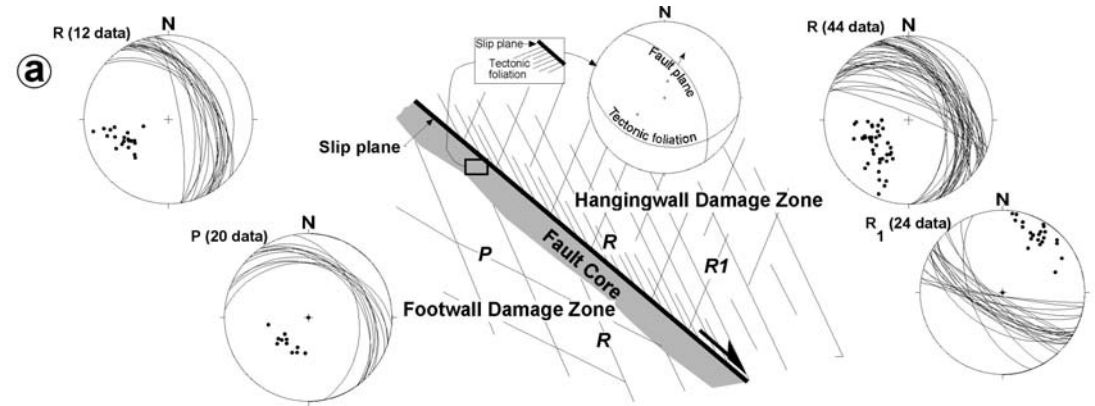
Fig. 5.4 - **a**: Sketch of the relationships among the Riedel shear fractures and the surface of the Boccheggiano fault. The fault kinematics is given by the relationships between shear foliations in the fault gouge and the fault plane. **b**: Palaeozoic phyllite from the footwall damage zone, displaying usually oxidized R and P shear fractures. **c** and **d**: Two photos from the hangingwall silicified rock mass; pyrite is generally concentrated along the margin of the quartz veins. **e-g**: Three photos from the no-silicified hangingwall rock mass: pyrite and quartz are concentrated in millimetric veins. **h-j**: Three photos, at different magnification, of the fault core zone: the cataclastic elements are often mantled with pyrite (from Liotta et al., 2010).

Microstructural features

Thin sections from the pyrite pockets of the footwall show syntaxial veins with elongate (about 0.4 mm long) blocky quartz texture and euhedral pyrite crystals (about 0.3 mm, on average), mainly concentrated along the median line of the vein (Fig. 5.5). Vein margins are generally sharp and smooth and form a pervasive network, among isolated elements of Palaeozoic phyllite (Fig. 5.5a). Within these latter, or at their margins, small euhedral crystals (about 0.1 mm) of pyrite can be recognized (Fig. 5.5c). Mineralization in the hangingwall shows two different textures, one for the silicified rock mass and the other for the rest of rocks belonging to the damage zone (Fig. 5.5b). Regarding the silicified rocks, a fine grain quartz texture highlights the areas where the silicifing fluid infiltrated the original limestone, produced metasomatism and deposited widespread small crystals of pyrite (Fig. 5.5d-f).

The boundaries of the silicified elements constitute the margins of syntaxial veins with a blocky elongate quartz texture. Pyrite in the veins is euhedral, with a 0.4-mm-long side, and it is generally located along the margins and/or along the vein median line (Fig. 5.5e-f). Differently, antitaxial veins characterize the rest of the hangingwall damage zone, further from the fault plane (Fig. 5.5g-i). These veins display a massive quartz texture, with relatively equant grains, with margins ranging from polygonal to irregular, with euhedral pyrite surrounded by unstrained quartz.

Fluid inclusions studies carried out on quartz from the hydrothermal veins indicate a main type of fluids that are characterized by two phase liquid rich-fluid inclusions (L+V): the first one, with homogenization temperatures ranging between 172 and 331°C and salinity between 0.0 and 8.8 wt% $NaCl_{equiv.}$; the second generation of fluid inclusions documents a later stage, with homogenization temperature from 124 to 288°C and salinity from 0.2 to 1.9 wt.% $NaCl_{equiv.}$

Stop 1.2: Montieri hydrothermal veins

Back to the main road and move toward Siena for about 1 km, reaching the cross-road to Montieri. Follow this windy street and cross all the village and park close to chapel located at the Poggio Montieri foot-hill. From here a track climbs over the hill. Follow this way for about 300 m, reaching the outcrop. The Late Oligocene-Early Miocene cataclasites, developed during doubling of the Tuscan Nappe, and the cataclasites deriving from the Miocene extensional events, located at the Ligurian Units/Tuscan Nappe boundary and within the Late Triassic evaporite, became channels for the flow of geothermal fluids.
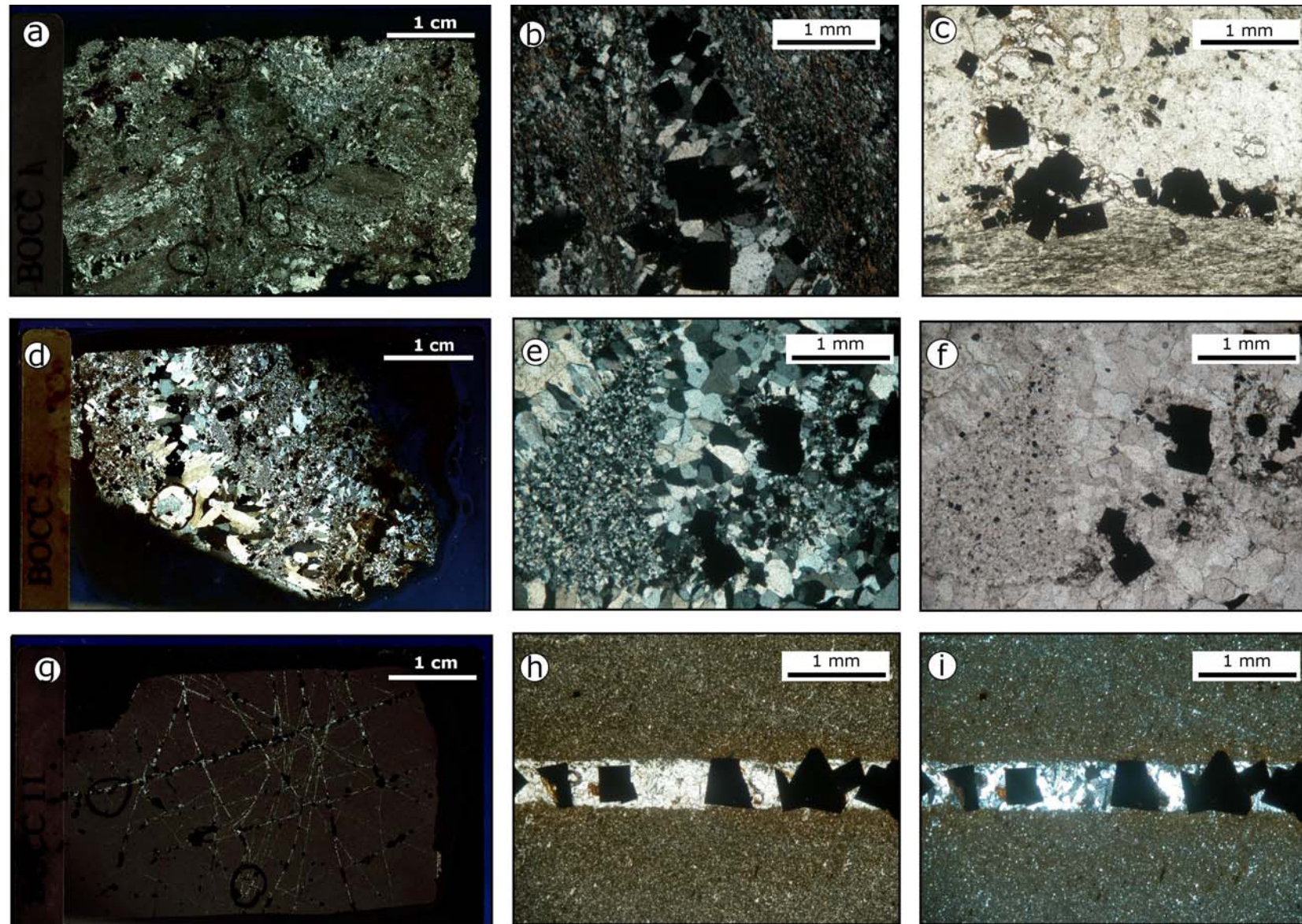
Fig. 5.5 - Microphotographs of the footwall and hangingwall damage zone. Footwall. **a**: clasts of Palaezoic phyllite surrounded by quartz veins with pyirite; **b** and **c**: syntaxial quartz vein with pyrite. Pyrite can be concentrated along the vein median line or, along the vein margins, as it is shown in c. Hangingwall: **d**: silicified rock mass; the syntaxial veins are characterized by large quartz grains; **e** and **f**: minute quartz grains in those parts where the metasomatism of the Early Cretaceous limestone occurred; **g**: network of quartz veins with pyrite; **h** and **i**: massive fabrics of the antitaxial quartz veins with pyrite (from Liotta et al., 2010).

We are looking at hydrothermal quartz veins hosted in the Macigno Fm, i.e. close to the boundary with the Ligurides Units, located at the top (43° 07' 49''- 11° 00' 54'').

Fluid inclusions studies carried out on samples from extensional and compressional cataclasites, indicate two types of fluid inclusions, the older, defined by a two phase liquid rich fluid inclusions (L+V), with temperatures ranging from 172°C and 280°C; the younger typified by V+L and V with homogenization temperatures ranging between 197° and 248°C.

Stop 1.3: Rocks hosting the Present first reservoir

From Montieri, continuing along the main road, toward Massa Marittima, we reach the cross-road where the directions to Monte Rotondo M.mo, Gerfalco and Larderello localities are indicated. Here (43° 07' 52.4" - 10°58' 50"), the Calcare Cavernoso Fm. crops out. These rocks derive from the Late Triassic anhydrides (Anidriti di Burano Fm.), sited at the bottom of the Tuscan Nappe. The Late Triassic evaporites represented the main detachment level during the collisional and post-collisional stages of the northern Apennines evolution. Tectonic activity and chemical processes, also induced by hydration and dehydration of the anhydrides, transformed the evaporite in a vacuolar carbonatic breccia, (Calcare Cavernoso Fm.) (Fig. 5.6).
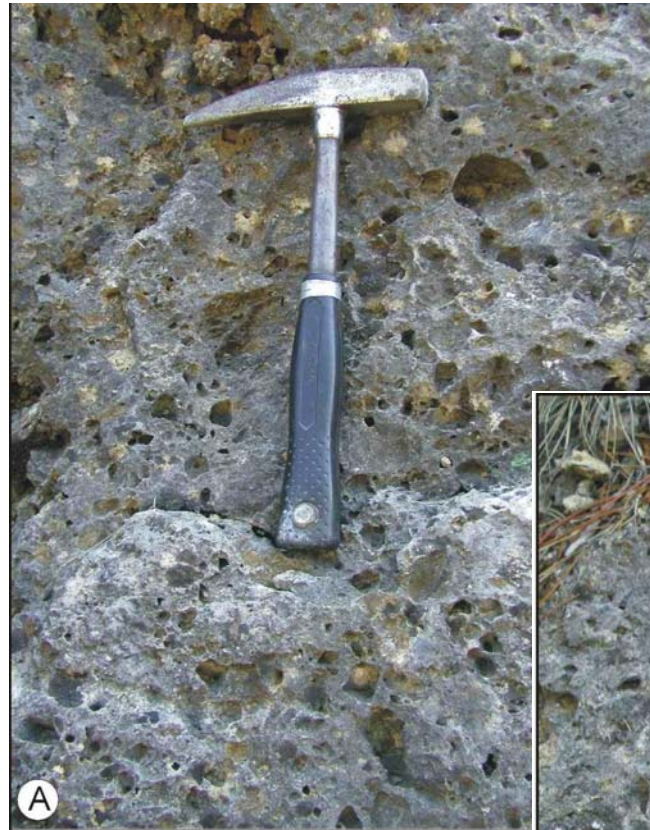
Fig. 5.6 - (A) Vacuolar carbonatic breccia (Calcare Cavernoso Fm.). The vacuoles were produced by dissolution of (B) the dolostone clasts, scattered in a carbonate matrix derived from alteration of the evaporite levels.

Undissolved dolostone clasts

The Calcare Cavernoso Fm., because of its brecciated texture (estimated permeability of 10^{-14} m^2) constitutes the main level hosting the Present first reservoir (both in the Larderello and in the Monte Amiata areas). The Calcare Cavernoso Fm. is also the main mineralised (mixed sulphides) horizon in the Colline Metallifere region.

Stop 1.4: Natural gas vents at Monte Rotondo Marittimo

Arriving to the Village, turn to the right side, toward the power plant and go ahead, up to the hill, reaching the Biancane locality (43°09'08.61" - 10°51'13.07"), a large whitish area with fumaroles (Fig. 5.7), located along the trace of a tectonic discontinuity.

In this stop, the first reservoir of the Larderello geothermal area crops out. This consists of fractured rocks related to the Upper Triassic, Jurassic and Cretaceous succession of the Tuscan Nappe (Fig. 5.8 and 5.9).

The Tuscan carbonatic succession is exposed in the southern side of the "il Monte" hill. At the top of the hill, the Macigno and "Scaglia toscana" fms. represent the impervious cover of this reservoir. The gas vent is interrupted at the boundary with the scaglia toscana group (Fig. 5.10).

The fumaroles are located in the Middle Jurassic radiolarites. These are deeply altered by hydrothermal circulation of hot fluids channelled to surface through a fractures network, mostly with an almost vertical attitude. Intersection between fractures and layering gave rise to loci for gas emission and growth of tiny crystals needles.

Stop 1.5: Visit to the Larderello Museum and "touristic" well

Leaving Monterotondo Marittimo, follow indication towards Larderello. The Museum, located in one of the first edifices built up during the initial period of industrial exploitation (XVIII century), hosts finds and tools from Etruscan and Roman periods, when the geothermal resources were mainly used for thermal baths, passing through the borax production of the XVII and XVIII centuries, to Present, with exploitation only devoted to provide electricity. Samples with minerals from the Larderello area are also proudly exhibited.

The so-called "touristic well" is a geothermal well drilling down the first reservoir. This well, when it is opened, gives rise to an impressive column of steam, at about 200°C.

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Fig. 5.7 - The fumaroles at Monterotondo Marittimo in the "Biancane" locality.
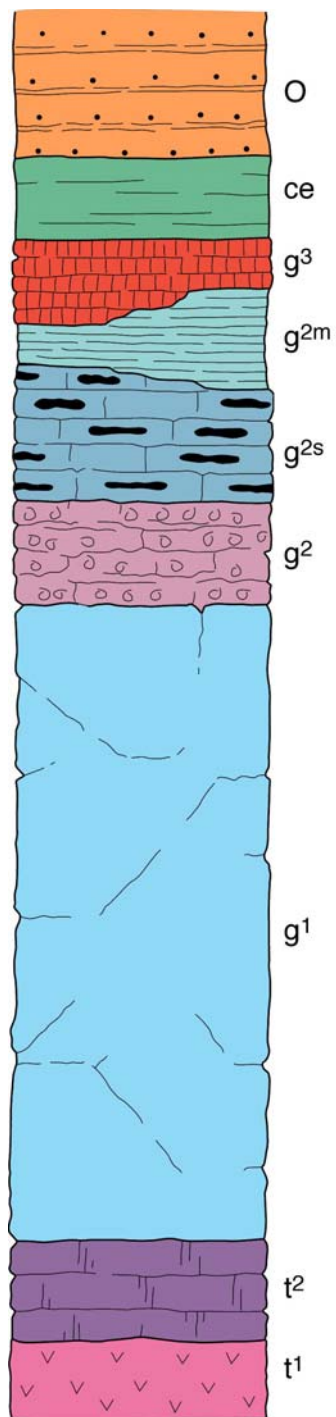
Fig. 5.8 - Tuscan Nappe stratigraphic succession. Key: **O** - Macigno Fm. (Upper Oligocene - Aquitanian); **ce** - "Scaglia toscana" fm. (Cretaceous - Oligocene); **g³** - Diaspri Fm., (Malm); **g²ᵐ** - Calcari e Marne a Posidonia Fm. (Dogger); **g²ˢ** - Calcare Selcifero Fm. (Middle-Upper Liassic); **g²** - Rosso Ammonitico Fm. (Lower-Middle Liassic); **g¹** - "Calcare Massiccio" Fm., (Lower Liassic); **t²** - Calcari e marne a *Rhaetavicula Contorta* fm. (Rhaetian); **t¹** - Anidriti di Burano e Calcare Cavernoso Fm. (Norian - Rhaetian).
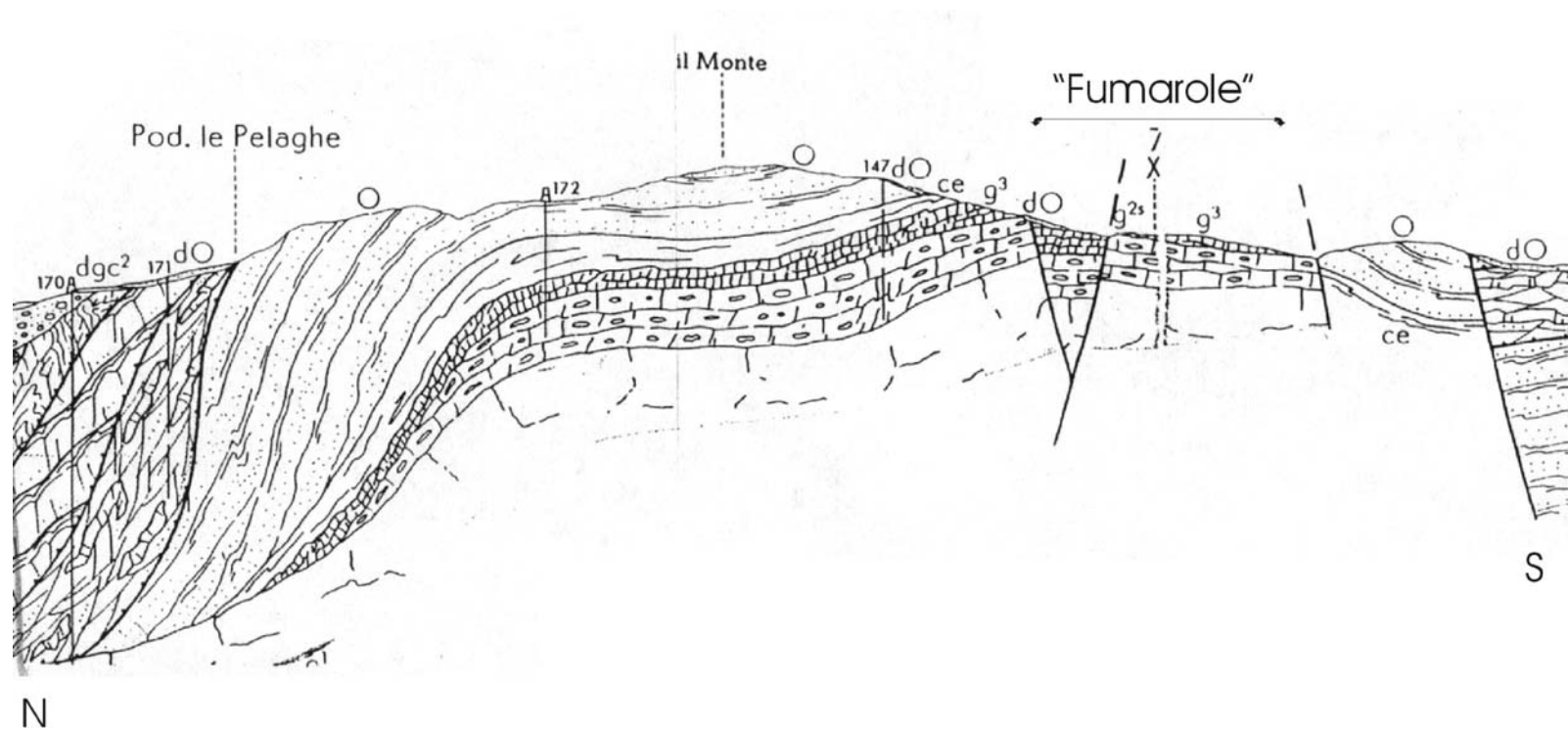

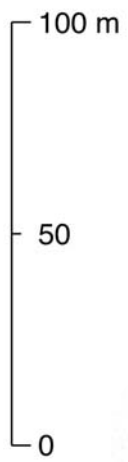Fig. 5.9 - Geological cross section through the Monterotondo M.mo area (From Lazzarotto, 1967). Key: **O** (Macigno Fm.) and **ce** ("Scaglia toscana" fm.) represent the impervious cover of the carbonatic reservoir, indicated by **g³**, **g²** and the below formations.
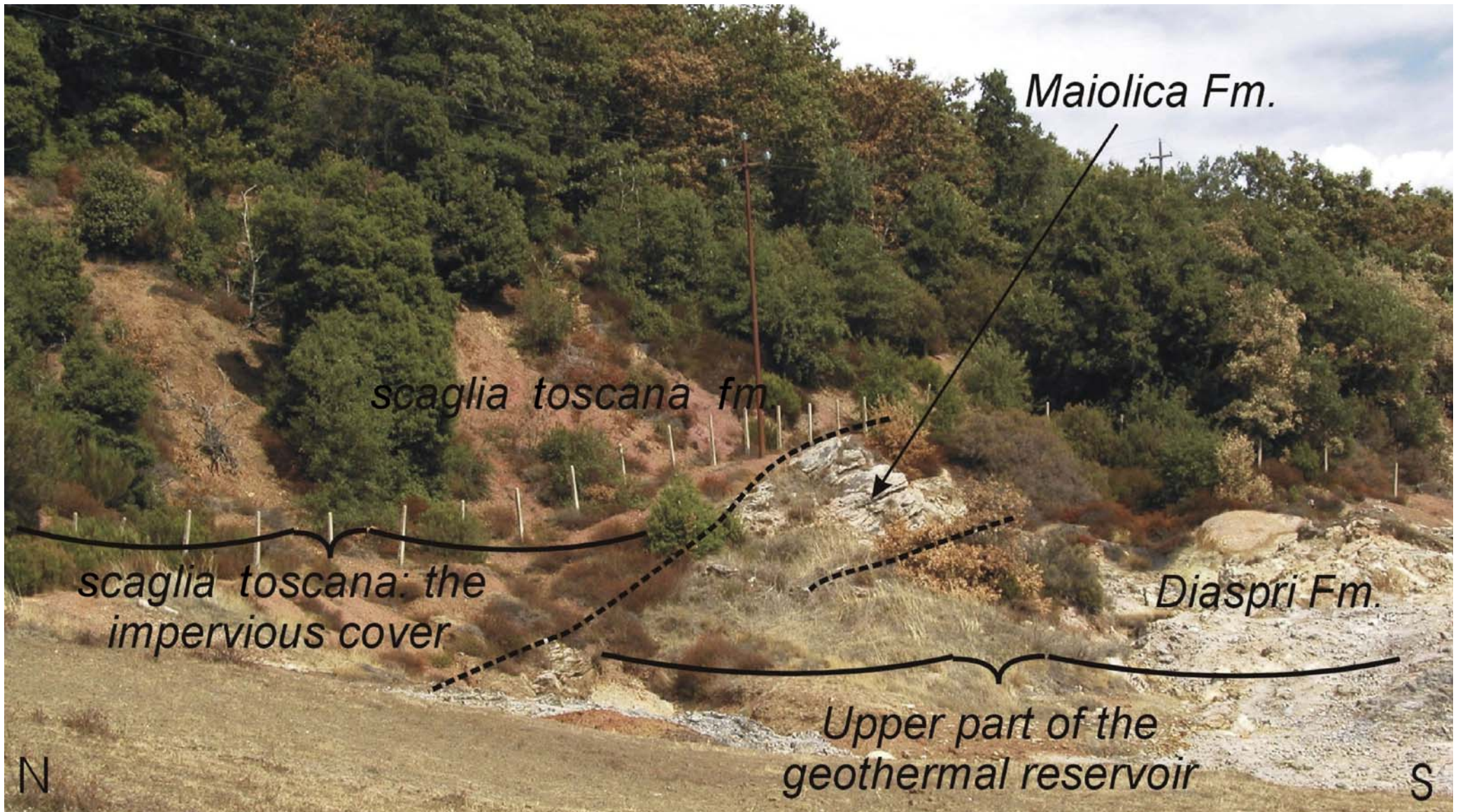
Fig. 5.10 - In the Monterotondo M.mo area the impervious cover of the uppermost geothermal reservoir corresponds to the "scaglia toscana" and Macigno fms.

6. Conclusions

The aim of this one-day field excursion is to underlain the similarity between a fossil, Pliocene-Pleistocene geothermal system, and the Present Larderello geothermal field.

In the Boccheggiano-Montieri area, fluid inclusions and structural data suggest that fluids flew through the cataclasites, representing structural channels of a single hydrothermal circuit (Fig. 6.1).
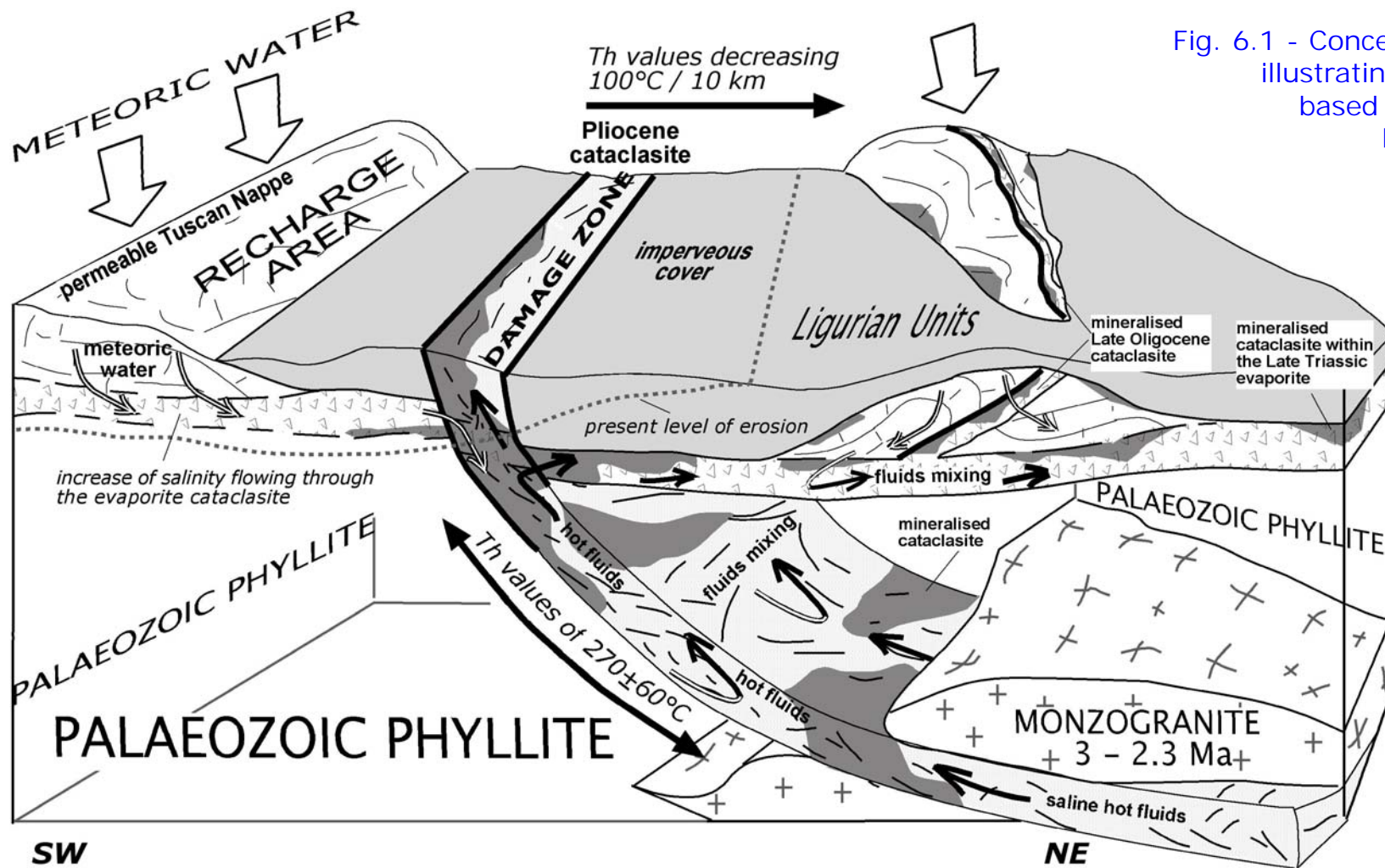
Fig. 6.1 - Conceptual cartoon, not to scale, illustrating the path of the fluid flow, based on the results of our study. Meteoric water infiltrated to depth through the damage zone of the Boccheggiano fault and trough the permeable Tuscan Nappe fractured and porous rocks. At depth, down to the monzogranite, heating and mixing with deep fluids originated hydrothermal mineralizing fluids, upflowing toward the surface and pervading the existing cataclasites and locally mixing with meteoric water (From Liotta et al., 2010).

A similar scenario (Fig. 6.2) is envisaged for the present day Larderello geothermal system where cooling granitoids are hypotized at depth of about 6-8 km. In this view, the deep reservoir is representing the Present analogue of the Boccheggiano fault damage zone, as well as the shallower reservoir is defined by the cataclasite within the late Triassic evaporites.
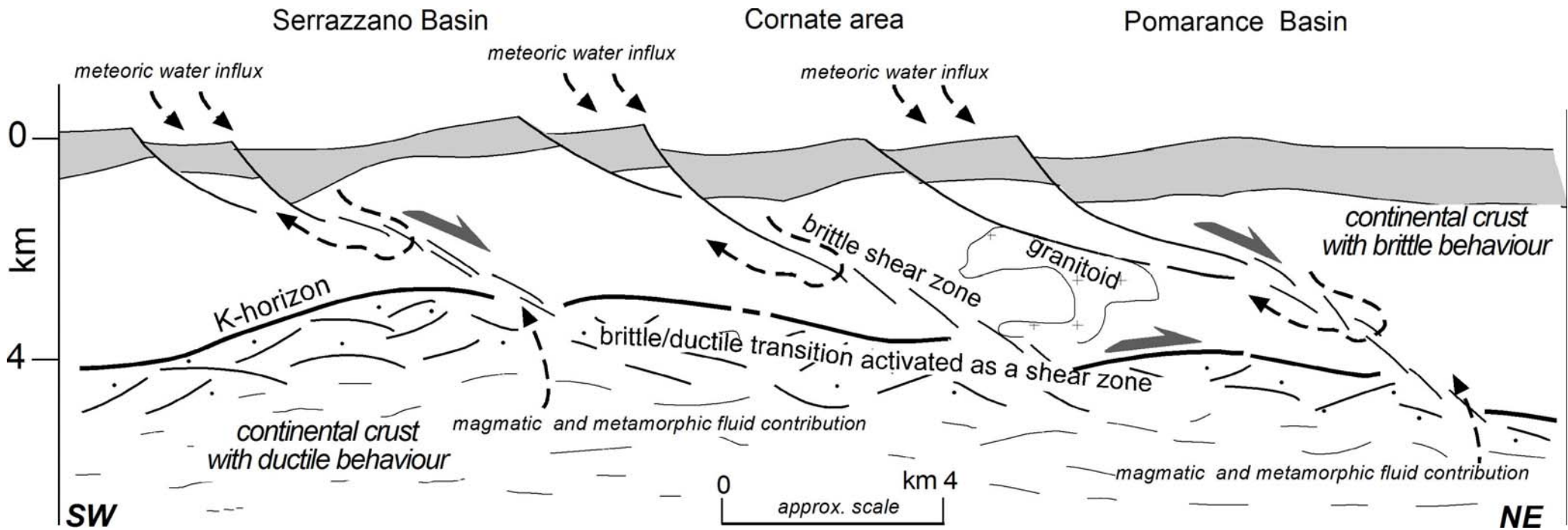
Fig. 6.2 - Geological interpretation of the Larderello geothermal area. The extensional shear zones and the top of the brittle-ductile transition are shown (thick arrows indicate the sense of shear). The shear zones act as hydraulic channels where geothermal fluid circulation is enhanced (dashed arrows). These shear zones are exploited and named as deeper reservoir. Light grey: sedimentary cover; the Calcare Cavernoso Fm. is located at the base of the sedimentary cover including the Upper Triassic evaporites at its base. In this level structural traps hosting geothermal fluids are located. An already cooled granitoid is delimited at the top by extensional structures.

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