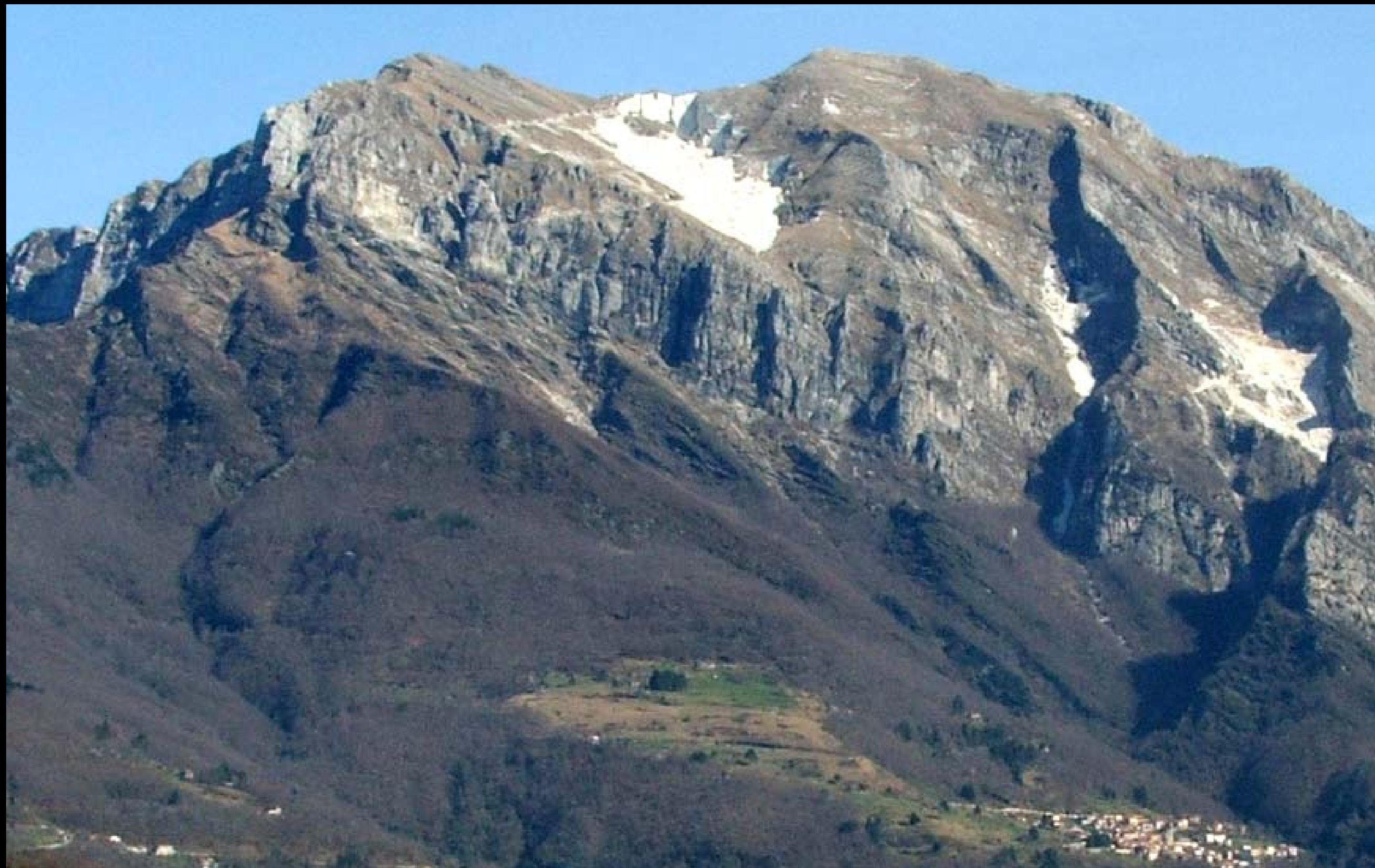
Geological Field Trips



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The Corchia Cave (Alpi Apuane): a 2 Ma long temporal window on the Earth climate

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The Corchia Cave (Alpi Apuane): a 2 Ma long temporal window on the Earth climate

85° Congresso Nazionale della Società Geologica Italiana - Pisa, 2010

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Riassunto

Il Monte Corchia è una delle località tipiche delle Alpi Apuane nella quale, nello spazio di pochi chilometri, è possibile discutere di aspetti di geologia strutturale, di problematiche relative all'attività estrattiva, geomorfologia fino ai processi di mineralizzazione del basamento. Quest'ultimo aspetto è di ulteriore interesse poichè l'area è stata oggetto di ricerche e sfruttamenti minerari anche in tempi relativamente recenti. È peraltro noto che all'interno della successione dei marmi della sinclinale del Monte Corchia si sviluppa la più lunga cavità carsica d'Italia (l'Antro del Corchia) con ben 52 km di gallerie e pozzi. Studi recenti stanno decodificando l'immenso archivio naturale del clima passato preservato all'interno delle concrezioni carbonatiche dell'Antro del Corchia e stanno ricostruendo con estremo dettaglio l'evoluzione climatica ed ambientale delle ultime centinaia di migliaia di anni di questa parte del bacino Mediterraneo.

Parole chiave:
Geologia, Mineralogia, Paleoclima, Alpi Apuane

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Abstract

Monte Corchia is one of the most typical geological structure of the Alpi Apuane but this is not the only peculiar aspect of this territory. Within a very small area it is possible to combine structural geology, marble exploitation, geomorphology and ore deposits.

The last point is of worth of interest because the area has been the subject of ore exploitation until the recent past. Within the marble succession of the Corchia synclinal core develops the longest Italian cave with 52 km of passages and galleries. Ongoing researches are exploring the huge paleoclimatic archives preserved within the carbonate concretion of the cave and are reconstructing, with extreme detail the climatic and environmental evolution of this sector of the Mediterranean basin.

Key words:
Geology, Mineralogy, Paleoclimate, Apuan Alps

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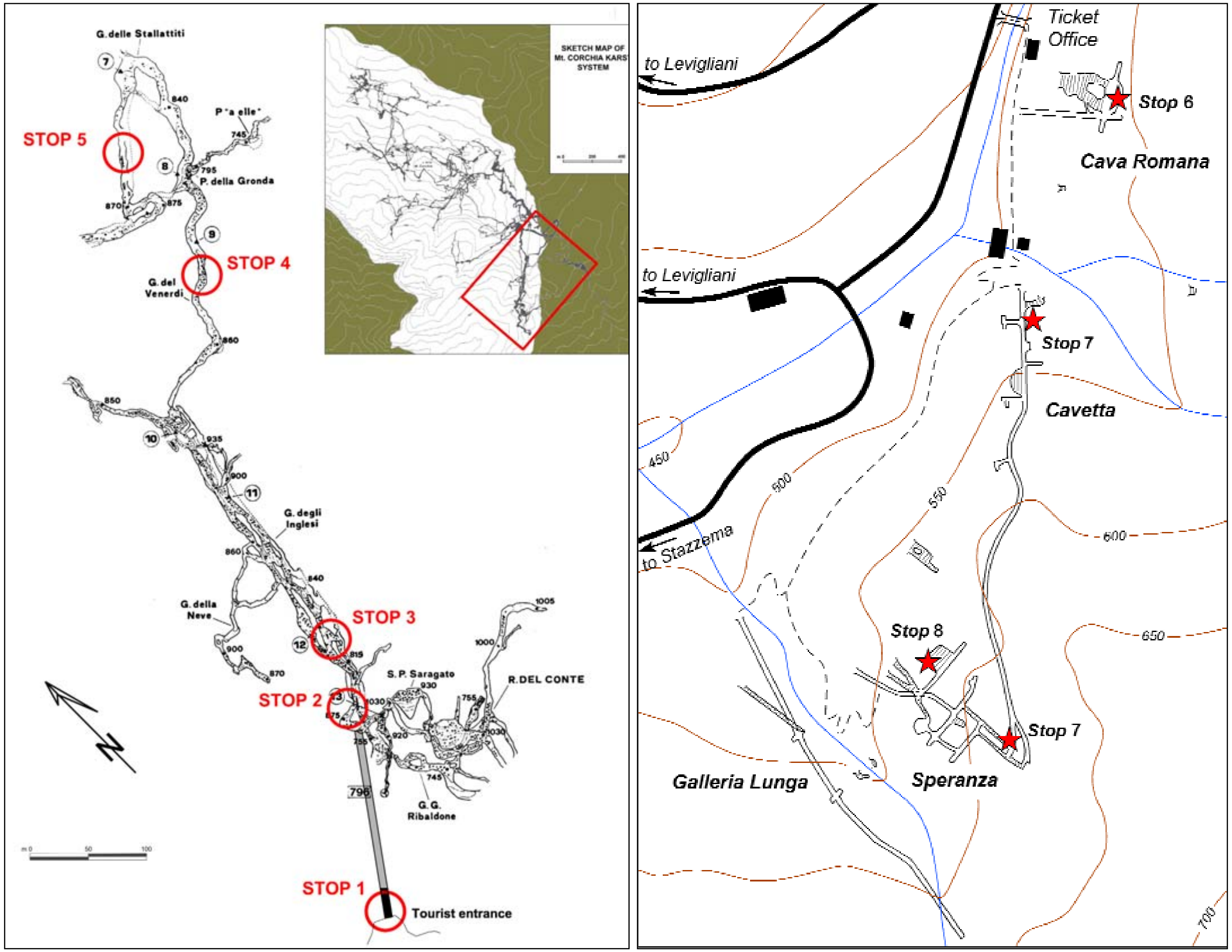

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1. Introduction

Monte Corchia (Northern Tuscany, Italy, Fig. 1.1) is one of the most emblematic geological structure of the Alpi Apuane but this is not the only peculiar aspect of this territory.
Within a very small area it is possible to combine geology, mineralogy, geomorphology and paleoclimatology with a warm and friendly welcome from the typical Apuan village of Levigliani. Within the Mesozoic carbonate succession (marble and dolostone) of the Corchia synclinal core, the longest Italian cave develops with 52 km of pits and galleries (Fig. 1.2).

Discovered the 11 October 1840 by Emilio Simi, a local naturalist, the Monte Corchia cave system has long been one of the most famous caves of Italy. Initial surveying of the cave dates to the second half of the 19th century, but systematic explorations began only during the first half of the 20th century. In 1934, speleologists from Florence attained the depth of about 540 m below the entrance, the greatest depth ever reach in the

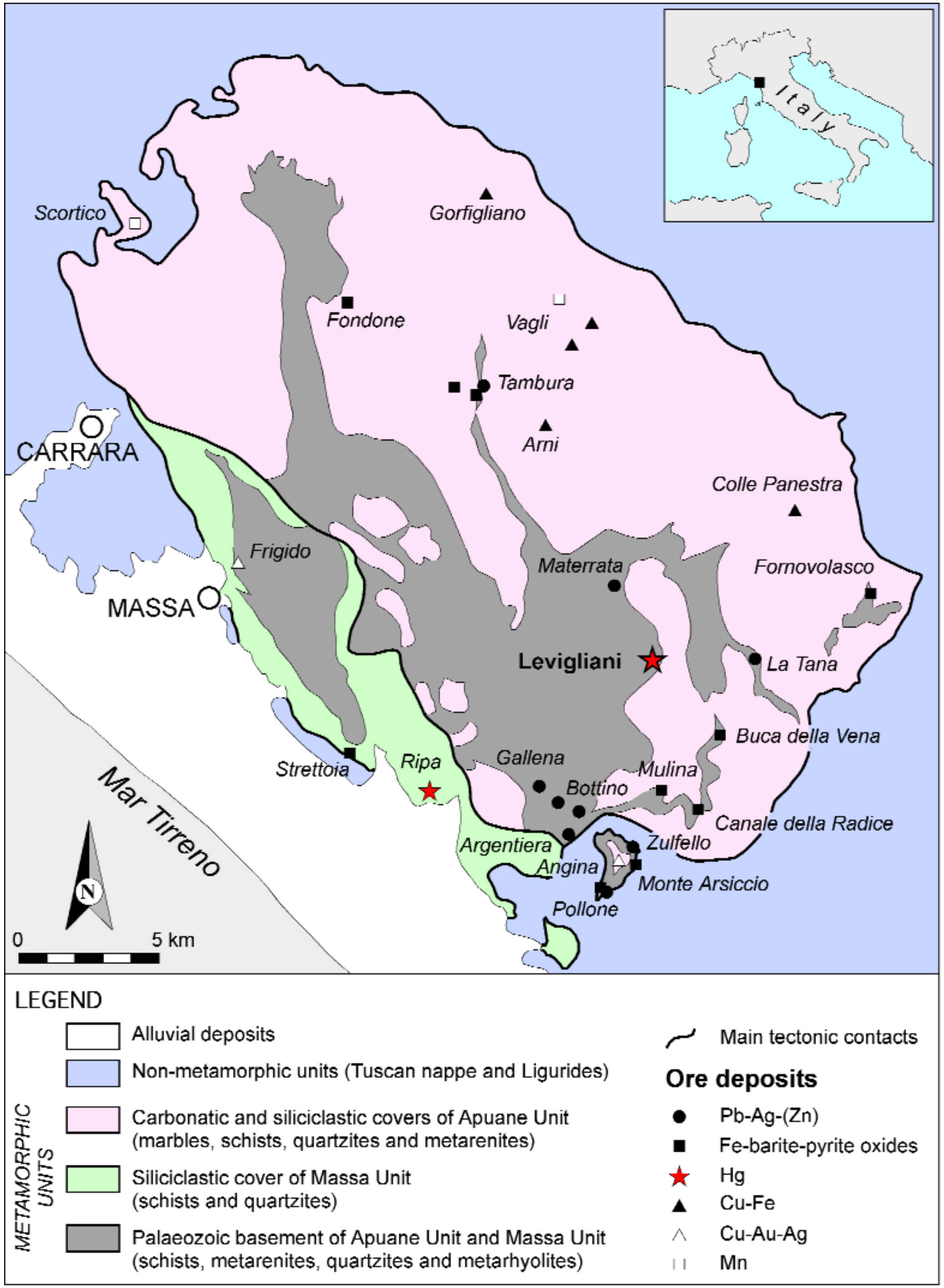

Fig. 1.1 - Sketch geological map of Alpi Apuane. The distribution of ore deposits inside the metamorphic units is also shown.

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world at that time. In the second half of the last century the Monte Corchia system attracted hundreds of speleologists from Italy and abroad. In the 1980s the collaboration, and some time the competition, among several Italian caving groups allowed the exploration of more than 50 km of cave passages with the depth reaching 1185 m.

Being part of the vast district of the Alpi Apuane, the Monte Corchia massif is a site of historical and modern marble exploitation, which represents one of the most traditional sources of local income. In the recent past (1985), the area of Monte Corchia has been included in the Alpi Apuane Regional Park and in the 2001 part of the cave system was opened to the public.

The opening of the tourist cave has shown that local economic benefits can arise from a more correct use of the landscape and by the additional incoming produced by tourism. A local cooperative (Cooperativa Sviluppo e Futuro Levigliani) has, in the last years, promoted important activity in the area for attracting tourism joining the different peculiarities of this land.

The Tuscan Speleological Federation (Federazione Speleologica Toscana) understood the new scientific potential of the cave, and has logistically and economically supported (since the 1998) researchers of the University of Pisa, INGV and CNR for using speleothems (cave concretions including stalagmites and stalactites) as an archive for reconstructing past climate conditions. So, in recent years, the Monte Corchia Cave system has turned out to be one of the most promising archives for reconstructing the paleoclimate and paleoenvironment in the Mediterranean basin (Drysdale et al. 2004, 2005, 2007, 2009; Zanchetta et al. 2007), with implications for the chronology of climatic events at the global scale (Drysdale et al. 2007, 2009). Owing to this new field of research, the Monte Corchia karst is not anymore seen as a locality where different aspects of local geology and geomorphology can be observed, but it is now studied as an unique system in which the geological structure conditioned the development of the cave and the history of deformation and mineralization have influenced the chemistry of drip waters from which speleothems precipitate. Moreover, the radiometric measurement of the concretions gives unique information on the timing of cave passages formation and then the recent uplift history of this sector of the Apennine. This field trip is an update synthesis of the work conducted by specialists who are currently working on this cave system from several points of view, which are producing a new and fresh holistic view of this environment.

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2. General geomorphological and geological framework of the Alpi Apuane

Monte Corchia is located in the southwestern part of the Alpi Apuane, a mainly calcareous mountain range, about 50 km long, 20 km wide and up to 1947 m high, in the NW of Tuscany (Fig. 1.1). The alpine-like landscape of this region is due to several factors, among which the complex structural setting plays a relevant role. In particular, the very steep beddings and the tectonic repetition of different rocks (mainly limestones and phyllites) have enhanced the role of differential erosion processes.
The present topography is presumed to be the result of heavy fluvial erosion accompanied by rapid tectonic uplift during early Pleistocene (Piccini et al., 2003b; Bartolini, 2003; Fellin et al., 2007). Glacial and periglacial processes reshaped the landscape during the last glacial stages, emphasizing the "alpine-like" features of the Alpi Apuane (Braschi et al., 1986).
In this respect it is interesting to remember that the first Quaternary glacial remain of the whole Apennine was discovered in the Alpi Apuane (Cocchi,1872; Stoppani, 1872). The Apuan glacial remains have very interesting characteristics: in fact, the Apuan chain contains the lowest glacial deposits of the whole Italian peninsula. In the most extensive phase of development the Equilibrium Line Altitude of the glaciers has been calculated for the internal areas at ca. 1200-1300 a.s.l. (Braschi et al., 1986); this is the lowest recorded in the Apennine chain. Several studies (e.g. see Federici, 2005 for a recent review) have reported the presence of at least 9 valley glaciers on the northern side of the Alpi Apuane with the estimated fronts located in an extraordinarily low position (down to 600 m a.s.l.).

Monte Corchia forms part of the main surface drainage divide of the Alpi Apuane, and it is located between the coastline of Mar Ligure and the inner basin of the Serchio River. For this reason, local climate is characterized by strong spatial variations as a function of elevation and distance from the sea. This mountain ridge is one of the rainiest parts in Europe. Mean annual rainfall exceeds 2500 mm over a large part of the chain and on the central ridges it is more than 3000 mm/yr (Rapetti and Vittorini, 1994; Piccini et al., 1999). Campagrina station, very close to Monte Corchia, has a mean annual precipitation of 3055 mm, one of the highest values in Italy.

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Karst geomorphology

Surface karst landforms are not well developed in the Apuane because the high relief and regional climatic conditions (i.e. high temperature excursions and rainfall up to 3500 mm/yr) enhance mechanical-denudation processes. In particular, mechanical erosion must have been very active during the last glacial and postglacial phases, destroying most of the previous surface karst landforms. Only in some restricted low-relief areas are small to medium-scale karst landforms. On the contrary, karst caves represent one of the most important morphological features of the Alpi Apuane: nine caves are deeper than 1000 m and 21 caves are longer than 3000 m. Most of the caves are percolation-vadose in origin with a predominance of vertical development. The deepest caves reach local piezometric surfaces at elevations between 350 and 550 m a.s.l.

Based on the vertical distribution of the phreatic and epiphreatic passages in the caves, three major generations of base-level caves can be identified (Piccini, 1997). In the largest cave system, the Monte Corchia Complex (Fig. 1.2), at least four levels are preserved, each cut vertically by a succession of percolation (vadose) caves (Piccini, 1997). In the central part of the massif, the uppermost level is preserved at an altitude of 1600-1700 m a.s.l., whilst the second and most widely developed generation occurs between 750 m to 1000 m a.s.l. In the Corchia Complex, the situation is slightly different, with the first generation lying above 1450 m a.s.l., and the second at between 1000 and 1200 m a.s.l.. The latter form a wide anastomosing network that was subsequently affected by a major phase of vadose entrenchment. Below 1000 m, most of the Apuan caves are located on the seaward side, and possess phreatic passages that drain towards the SW. Most of the third generation of phreatic caves is located at an altitude of 500 to 650 m. Phreatic tubes are also present at the bottom of the major vertical caves, adjacent to the modern piezometric level. Spring caves are still active on the NE side of Apuane, whilst on the seaward side they have been abandoned by valley downcutting. Here, a new generation of epiphreatic caves is now forming at elevations between 250 and 350 m a.s.l. There are few chronological elements by which to mark the age of the different stages of karst development in the Alpi Apuane.
However, we can assume that the oldest relict caves, including the upper level of Corchia cave, were formed during the early denudation stage of the metamorphic carbonate rock. Apatite fission-track dating provides a first constraint of exhumation timing. According to thermochronological data (Bigazzi et al., 1988; Abbate et al., 1994; Fellin et al., 2007), the metamorphic rocks were still buried some km depth at ~4.5-5.0 Ma. A second chronological constraint is the age of the alluvial-fan deposits in the basins surrounding the Apuane,

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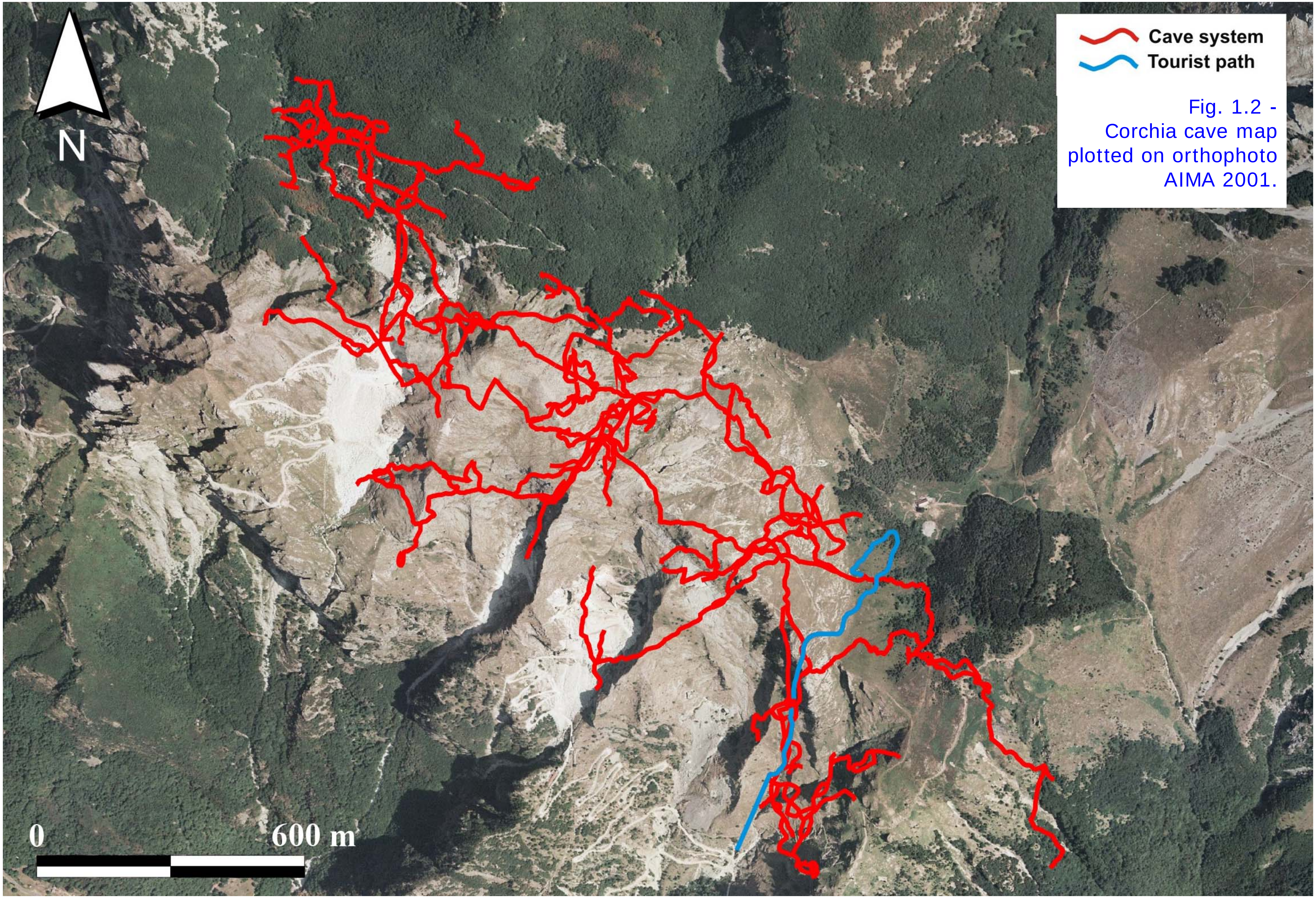

Fig. 1.2 - Corchia cave map plotted on orthophoto AIMA 2001.

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where pebbles belonging to the metamorphic core rest on Late Pliocene – Early Pleistocene lacustrine deposits (Calistri, 1974; Raggi, 1985; Bertoldi, 1988; D'Amato Avanzi and Puccinelli, 1988). The metamorphic core must have been exhumed by this stage. On this basis, we can take 3.0-2.5 Ma as a reasonable age estimate for the initial karstification of the metamorphic carbonate rock. This is agreement with the oldest U/Pb and U/U ages obtained from speleothems comprised between 1.5 and 2.0 Ma (Woodhead et al., 2006; Woodhead et al., unpublished data).

Geology of the Alpi Apuane

The Alpi Apuane represents a tectonic window that shows the deepest exposed levels (Tuscan Metamorphic Units) of the Northern Apennines (Fig. 1.1). The Northern Apennines is formed by a pile of tectonic units derived from the Adriatic continental margin (Tuscan Domain) lying below the westerly-derived "oceanic" Ligurian and sub-Ligurian accretionary wedge units (e.g. Elter, 1975; Carmignani and Kligfield, 1990; Molli and Vaselli, 2006 and references therein).

Two major tectono-metamorphic units are distinguished in the Alpi Apuane region: the Massa unit and the Apuane unit. A Paleozoic basement and a Middle Triassic succession with the higher-grade peak metamorphic assemblages, kyanite+chlorithoid in metapelites (references in Molli and Vaselli, 2006) characterize the Massa unit, which is well exposed in the westernmost part of the Alpi Apuane.

On the contrary, the Apuane unit shows a lithostratigraphic sequence made up of a Paleozoic basement (mainly phyllites and metavolcanics) unconformably overlain by a well-developed Upper Triassic (Ciarapica & Passeri, 1994)-Oligocene metasedimentary succession. The Mesozoic cover-rocks include thin Triassic continental to shallow water Verrucano-like deposits followed by Upper Triassic-Liassic carbonate platform metasediments comprising dolostones (Grezzoni Fm), dolomitic marbles and marbles (the famous "Carrara marbles"), which are followed by Middle Liassic-Lower Cretaceous cherty metalimestones, cherts and calcschists. Lower Cretaceous to Lower Oligocene sericitic phyllites and calcschists, with marble interlayers, are related to deep-water sedimentation during drowning of the former carbonate platform. The Oligocene-Early Miocene(?) sedimentation of turbiditic metasandstones (Pseudomacigno fm.) closes the sedimentary history of the domain.

The Alpi Apuane deformation structures are interpreted as formed during two main tectono-metamorphic regional events (D1 and D2 phases of Carmignani and Kligfield, 1990), which are regarded as a progressive

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deformation of the inner Northern Apennine continental margin during collision and late to post-collision evolution (e.g. Molli and Meccheri, 2000; Molli and Vaselli, 2006). During D1, SW to NE directed overthrusts and NE-facing tight to isoclinal recumbent folds with flat-lying axial surfaces were produced during deformation in mid-crustal conditions. In the following D2 history previously formed structures were refolded and the present-day geometry of the tectonic units and structures was achieved.

In the early stage of D2, folds associated with sub-horizontal crenulation axial planar foliation were formed, whereas later deformation was associated with semi-brittle and brittle structures, represented by kink and open folds, low- and high-angle faults (Molli and Meccheri, 2000; Ottria and Molli, 2000; Molli et al., 2010).
According to available P-T data (Molli and Vaselli, 2006 and references therein), peak metamorphism (temperature around 350-450 °C and pressure of 0.6-0.8 GPa) and early deformation D1 were realized at 27-20 Ma (Kligfield et al., 1986), while early stages of D2, developed at T higher than 250 °C, predated 11 Ma according to the zircon fission track data of Balestrieri et al. (2003) and Fellin et al. (2007). Latest stages of deformation, accommodating vertical movements locally exceeding 4 km, are achieved in the last 5 Ma as constrained by low-temperature thermochronometry, which suggests the transition at 100-120 °C at between 4 and 5 Ma in most of the metamorphic tectonic window (Abbate et al., 1994; Fellin et al., 2007 and references therein).

Ore deposits: history and metallogeny

The Alpi Apuane host a number of mineral deposits displaying a variety of mineralization styles and of elemental and mineral assemblages (Fig. 1.1; Lattanzi et al., 1994). According to Simonin's (1858) "romantic" ideas, the Etruscans founded the colony of Lucca and the port of Luna (now Luni, close to the town of Carrara) to exploit and trade the silver run out from the Pb-Ag deposits of Alpi Apuane. The same author suggests that the name itself of Luna (meaning "Moon") may support this hypothesis, since this is the "planet" to which the Etruscans consecrated silver. Although the presence of the Etruscans in the Luna area is reported in some historical documents, there are no definite archaeological proofs that they practiced mining activity in the Alpi Apuane (Tanelli, 1985). Thanks to the definite "romanization" of the Tuscan coast, in Caesarean age the Alpi Apuane became the site of intense marble exploitation. Luna rapidly became a famous, very elegant town, and the "marmor Luneense" one of the most appreciated marbles in the entire Mediterranean basin.

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After the fall of the Roman Empire, marbles and ore deposits of the Alpi Apuane (and all over Tuscany) fell in total oblivion for centuries. It was only in Middle Age and especially during late Renaissance time that mining activity flourished again in Alpi Apuane (Targioni Tozzetti, 1777), where Ag-Pb (Bottino and Argentiera mines) and Fe deposits (Buca della Vena, Monte Arsiccio and Fornovolasco mines) were actively exploited by the local noble families and the Grand Dukes of Tuscany (Medici family). After the “Medicean climax”, mining activities were drastically reduced, or eventually completely abandoned. It was only in the second half of XIX century that mining for Ag-Pb minerals and, subsequently Fe oxides, started again reaching a new climax in the period between the two World Wars. After the World War II, economical interest mainly focused onto barite and mixed barite-Fe oxide ores utilised as heavy muds for oil drilling, and concrete in building nuclear power plants respectively (Buca della Vena, Monte Arsiccio and Pollone mines).

Finally, the two small mercury ore deposits of Levigliani and Ripa were discontinuously exploited from Middle Age to 1970, never giving productions comparable to the larger Hg mines of Monte Amiata area (Southern Tuscany). However, the Levigliani mine is renown in Italy among mineral collectors and scientists for the common presence of native mercury in large droplets occurring in quartz veins. Levigliani Hg deposit also hosts a peculiar Hg-Zn-Fe sulfide association (cinnabar, zincian metacinnabar, mercurian sphalerite), and is the type-locality for the mercury-bismuth sulphosalt grumiplucite.
Today, the mining industry in Alpi Apuane is facing the typical problems of most European regions, and extraction is currently limited to ornamental stones (marble) and building materials.
Apart from the economic aspects, the Apuan metallogenic district remains of prime scientific importance due to the occurrence of diverse hydrothermal deposits associated with a peculiar metamorphic environment. Therefore ore deposit studies in this area may contribute to the understanding of fluid circulation and element mobilization occurred during the collisional and late to post-collisional evolution of this portion of the Tuscan Domain (e.g. Benvenuti et al., 1989; Lattanzi et al., 1992,1994; Costagliola et al., 1998; Dini et al., 2001).
As shown in Figure 1.1, Apuan ore deposits are preferentially located in the peripheral portions of the tectonic window, in proximity to tectonic contacts, and almost exclusively within the lower plate metamorphic units. They are especially concentrated in the southern part of the mountain massif, where the largest outcrops of Paleozoic formations occur. From the above picture, two main empirical controls of mineralization appear at a regional scale: (i) lithostratigraphic association, i.e. Paleozoic and Middle Triassic siliciclastic and volcanic formations of the metamorphic units; (ii) tectonic structures of the Apenninic orogeny. At the outcrop scale

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and down to the microscopic scale, mineralization is largely controlled by Apenninic early tectonic (D_1) and late tectonic (D_2) structures (Carmignani et al., 1978; Benvenuti et al., 1992; Costagliola et al., 1998; Dini et al., 2001). Conversely, field and textural evidence suggests that a number of ore bodies or pre-concentrations predate the Apenninic orogeny (Benvenuti et al., 1992; Dini et al., 2001), in agreement with the Paleozoic Pb-Pb model age of ore lead (Lattanzi et al., 1992).
The first established metallogenic epoch in Alpi Apuane is apparently related to lower Paleozoic bimodal volcanism represented by metarhyolites ("Porfiroidi") and metabasites of sub-alkaline affinity, presumably associated with the Caledonian cycle (Middle-Late Ordovician). Metal concentrations associated with this magmatism should be represented by originally stratiform, metal-enriched tourmalinites associated with metarhyolites in the Bottino-Gallena-Argentiera-Valdicastello area (Pb-Ag-Zn; Benvenuti et al., 1989), and by Hg mineralization associated with metabasites and metatufites in the Levigliani area (Dini et al., 2001). Due to the strong Apenninic overprint, the original characteristics of these concentrations are difficult to establish.

The existence in the Apuan area of a metallogenic event between the Variscan and Alpine cycles is still a matter of debate (Lattanzi et al., 1994). A Permo-Triassic metallogeny is conceivably associated with a pre-Tethyan aborted rift during which deposition of Norian dolostones (Grezzoni Fm) was initiated. In such a context, mineralization may be related to the concurrent alkaline mafic magmatism and/or to specific favorable paleogeographic environments (e.g. Ciarapica et al., 1985; Cortecci et al., 1985). The main expression of this inferred metallogenic event is considered the formation of sedimentary-(hydrothermal?) diagenetic Ba-Fe deposits in the Valdicastello-Fornovolasco belt (Pollone, Monte Arsiccio, Calcaferro, Buca della Vena and Fornovolasco mines).
The Apenninic orogeny was the main factor that accounts for the present setting of the deposits in the Alpi Apuane area. Several vein systems (most notably the Pb-Ag-Zn deposits at Bottino-Gallena-Argentiera-Pollone area, the Hg deposits of Ripa and Levigliani, the Cu-Au-Ag deposit at Buca dell'Angina, and the Cu-Fe deposit at Frigido) were emplaced at this time (cf. Benvenuti et al., 1992; Costagliola et al., 1998; Dini et al., 2001). The age of mineralization has not been established yet by isotopic dating; as previously stated, structural evidence suggests that there may have been early- (syn D_1) to late-tectonic (syn D_2) mineralising episode. Taking into account geochemistry, stable isotope and fluid inclusion data, the Apenninic metallogeny of the Alpi Apuane is the result of a synmetamorphic event under conditions that, at least in the initial stages, were not far from peak metamorphic conditions, and there is evidence that the involved metamorphic fluids derived (part of) the elements from remobilization of pre-existing (proto-)ores.

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3. The Monte Corchia

Geological setting

The geology of this area has been the subject of investigations since the late 1800s (Lotti, 1881; Zaccagna, 1932). At that time, the presence of east-dipping Mesozoic rocks between the Paleozoic exposures of the Valle del Giardino in the west and of Mosceta in the east (see Fig. 3.1a, b) was related with a west-facing overturned

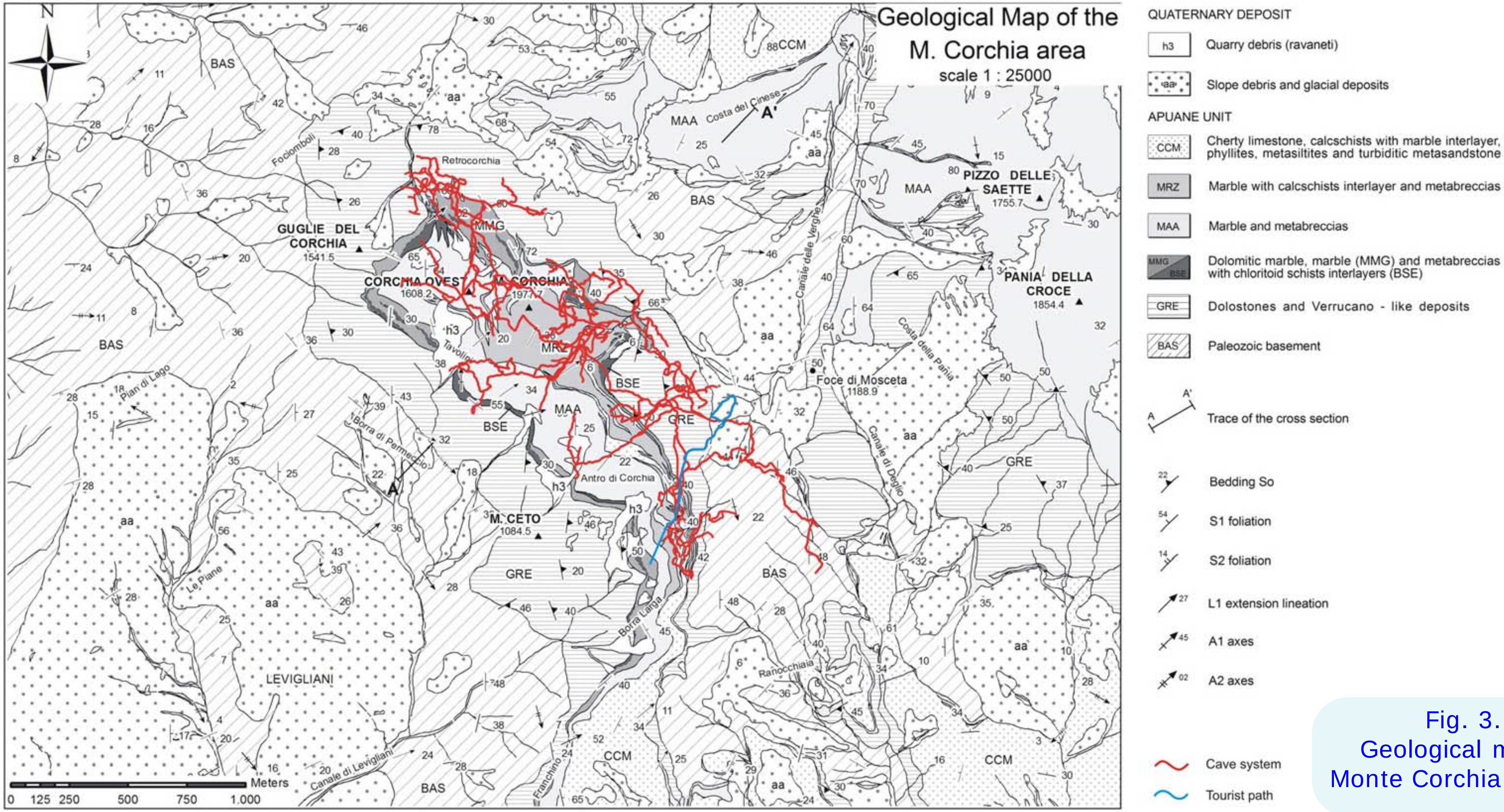

Fig. 3.1a - Geological map of Monte Corchia area.

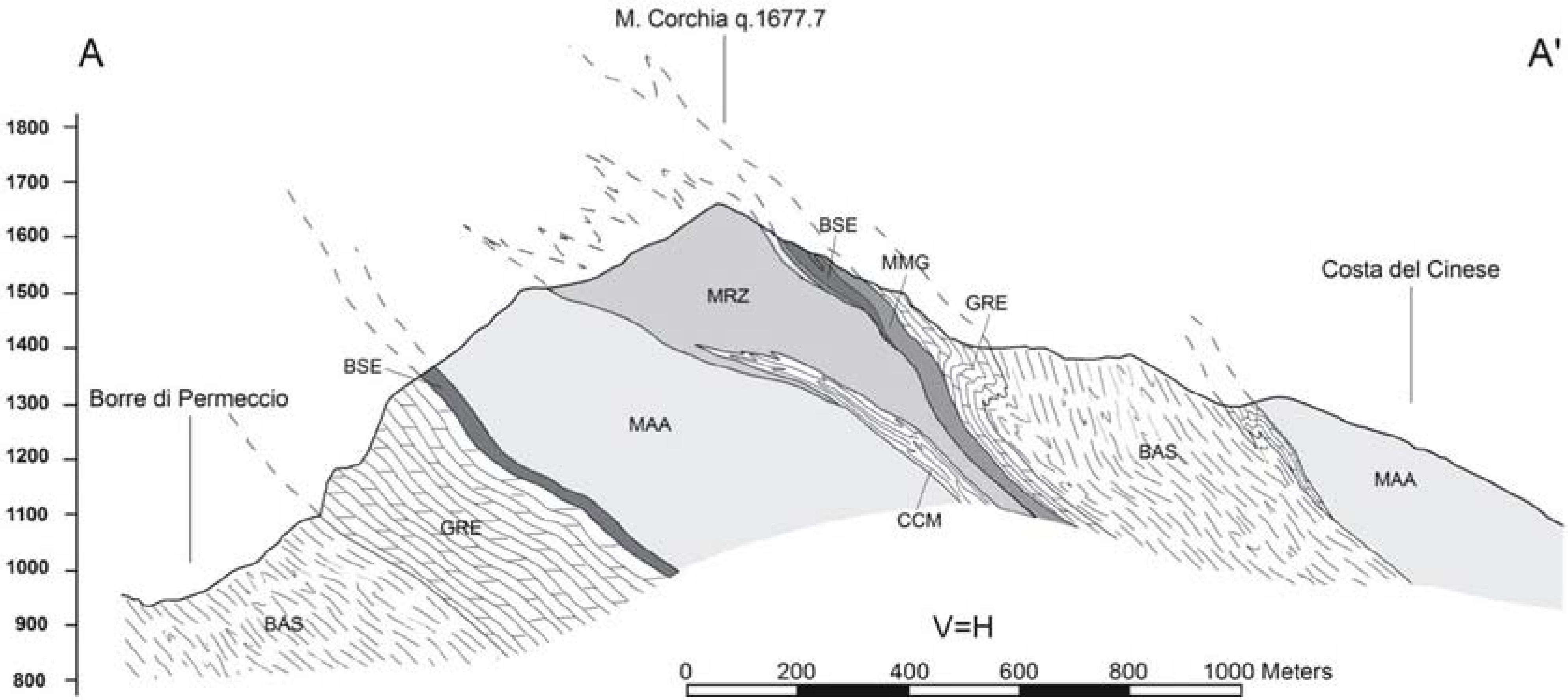

Fig. 3.1b - Cross profile of Monte Corchia.

syncline. A similar interpretation was followed later by Maxwell (1956). However, more recent structural studies have rejected this simplified view (Carmignani and Giglia, 1983; Carmignani et al., 2000). According to the new interpretation, the Corchia structure is the result of polyphase deformation during which an originally non-cylindrical eastward facing overturned syncline (D1) was refolded up to the present geometry showing the downward directed sense of younging.

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The geological map (Fig. 3.1a) and cross-section (Fig. 3.1b) enlighten some major features of the geology of the Monte Corchia area. A lateral termination of the D1 syncline is well exposed in the northern part of the map between the Monte Corchia peak and Fociomboli, where the hinge zone of the D1 Corchia syncline is exposed. In this zone, minor cartographic-scale M-structures and the related axial plane green schist foliation are refolded by open to tight east-facing D2 folds associated with a sub-horizontal crenulation cleavage. The youngest rocks in the core of syncline are the Late Jurassic cherty metalimestone in the northern part and the Late Jurassic to Cretaceous calcschists, metaradiolarites, chloritic marbles and Oligocene metasandstones in the southernmost part of the map.

About the 55% of Corchia Cave is developed in the Triassic dolostones (Grezzoni Fm) and 40% in Jurassic marbles. About the 5% of cave passages are carved in the Upper Triassic - Middle Jurassic Calcari Selciferi, “Brecce di Seravezza” or dolomitic marble. The boundary between dolostones and marbles does not seem to represent an important geological horizon for the origin of the cave. Only in the north-eastern sector some passages follow the contact between marble and dolostone.

An analysis of cave passage orientations shows that the highest and oldest level is more influenced by lithological planes, whereas the lower and youngest levels are controlled mainly by fracture patterns. This can be explained assuming that the first stage of cave development occurred when the relief was not so accentuated and the permeability of fracture was reduced by lithostatic load.

The Levigliani Hg deposit

The Levigliani deposit is located 2 km south of Monte Corchia (Figs. 1.1 and 3.2), and is hosted within the Paleozoic basement of the Apuane Unit cropping out below the carbonate core of the Corchia syncline (Dini et al., 2001). Specifically, the ore bodies occur within the lowermost part of the Late Ordovician metasandstones, quartzites and phyllites (MQP), near the contact with metarhyolites, and in strict association with pale-green layers of carbonate-chloritic phyllites (“metatufites”?) and calc-alkaline metabasites (Fig. 3.2 and 3.3). The metatufites are mainly constituted by syn-D_1 blastic phengite, chlorite, Fe–Mg–(Ca) carbonates, quartz, albite, and rare ilmenite as inclusions in the cores of carbonate crystals (Fig. 3.4). Rutile commonly occurs as small prismatic crystals oriented along S_1; its abundance sharply decreases toward the contacts with the MQP.

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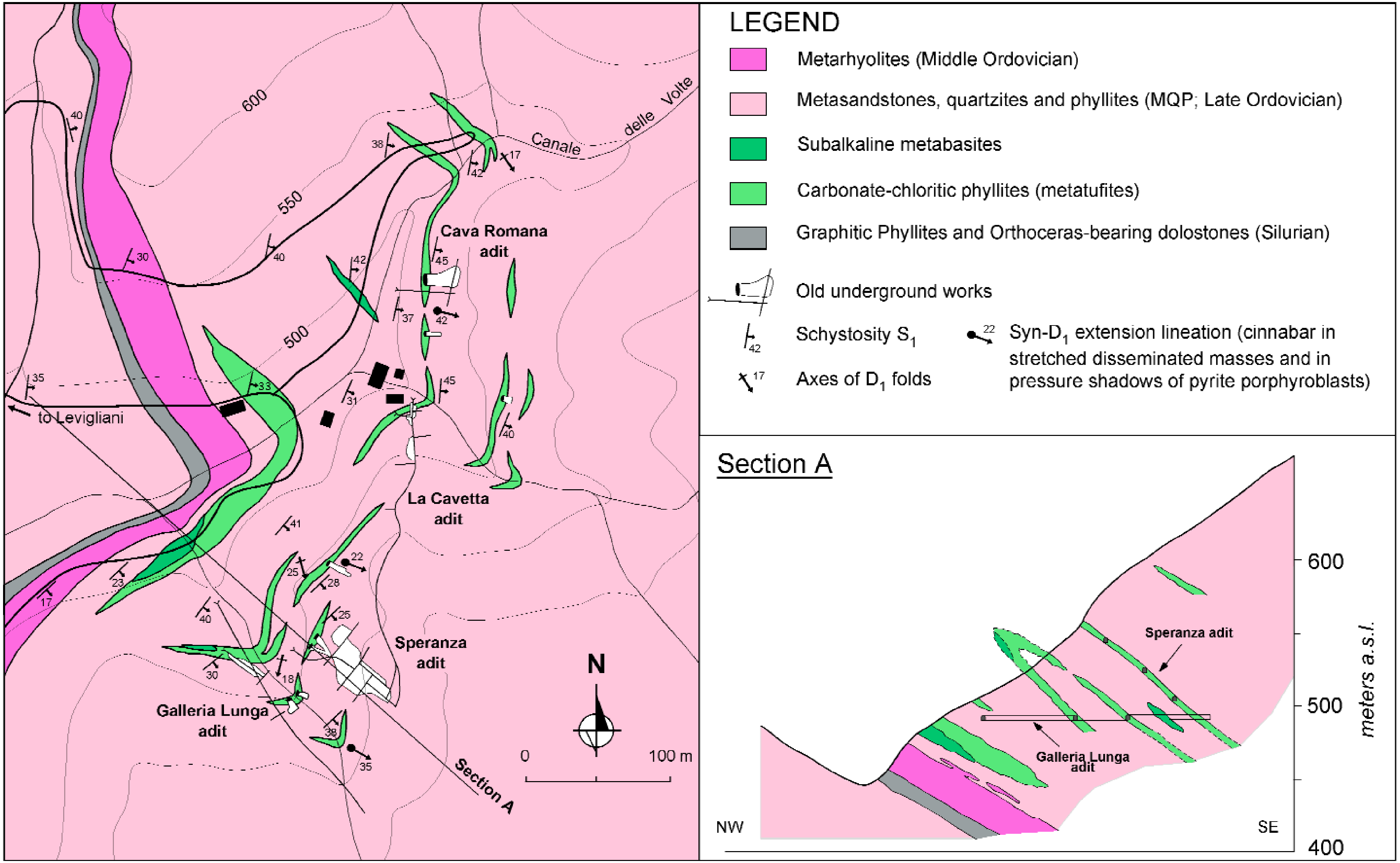

Fig. 3.2 - Detailed geological map and cross section of Levigliani Hg deposit.

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In the Levigliani area, MQP are implicated in a very complex tectonic structure, produced by the interference of Tertiary Apenninic deformation on earlier Variscan structures (Conti et al., 1991). Syn-D_1 deformation produced an axial plane schistosity (S_1), representing the main foliation in the field, while the second deformation episode (D_2) produced open folds and locally an evident crenulation cleavage (S_2). Relics of a pre-existing foliation have been tentatively attributed to a Variscan tectono-metamorphic event.

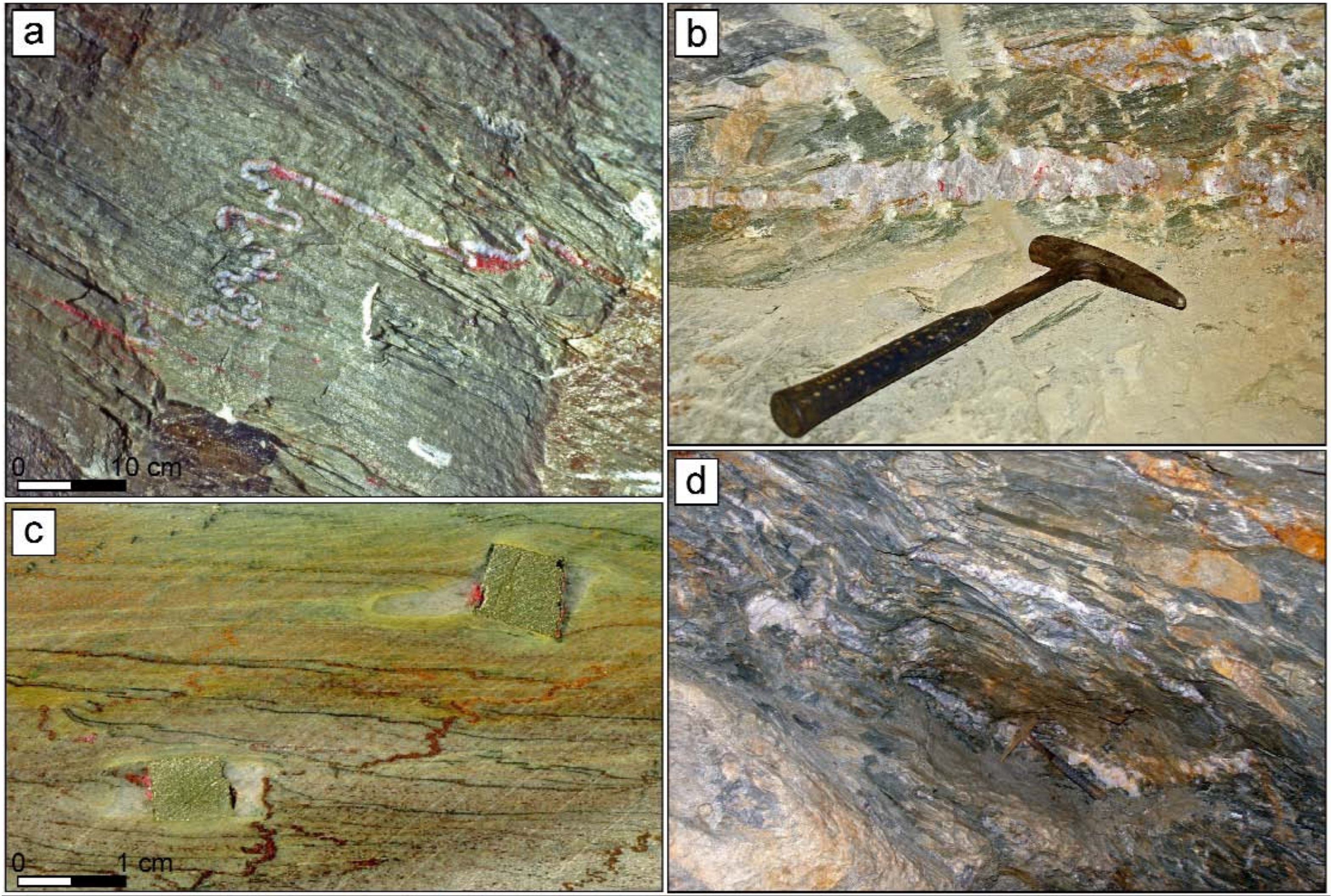

Fig. 3.3 - Examples of Hg ores at Levigliani. **a)** Cinnabar disseminations and an isoclinally folded quartz-cinnabar veinlet into a metatufite layer at Speranza adit; **b)** a quartz-carbonate-cinnabar vein hosted by metatufite, Speranza adit; **c)** polished slab of typical Levigliani metatufite showing two pyrite cubic porphyroblasts with quartz-cinnabar pressure shadows; also note some cinnabar disseminations and Fe-Mg (Ca) carbonate veinlets, Speranza adit; **d)** Quartz-carbonate veins containing native mercury and other Hg sulfides hosted by the grey phyllites of the Cavetta Tunnel.

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Metabasites were observed either as irregular green masses inside the metatufites, or as dyke-like bodies into the MQP (Fig. 3.2). Alpine (and Variscan?) metamorphic events caused a complete recrystallization of these rocks, with only minor iso-orientation of the lepidoblastic minerals. Albitized plagioclase phenocrysts, apatite and leucoxene-rimmed ilmenite represent the few relict mineral phases in some samples; by contrast, some well preserved magmatic textures are often present, leading to the distinction between blastoporphyric and blastophytic types (cf. Conti et al., 1993; Fig. 3.4). The mafic phases are completely replaced by syn-metamorphic chlorite, Fe–Mg–(Ca) carbonates, and oxides. The breakdown of the original magmatic minerals implies that the concentration of mobile elements does not reflect the original geochemical and petrologic features of the metabasites. However, a characterization of these rocks may be cautiously attempted using HFS elements, which are considered to be immobile during greenschist facies metamorphism (Winchester and Floyd, 1977 and references therein). The Levigliani metabasites show relatively low Nb/Y ratios (0.38–0.59), and relatively high Zr/TiO_2 ratios (0.029–0.037) indicating an andesite-dacite composition and a subalkaline affinity (Dini et al., 2001). Because of their stratigraphic position, close to the Ordovician metarhyolites, and their compositional affinity with metabasites from different outcrops in the Alpi Apuane, that are considered to represent a calc-alkaline compressional episode of Middle Ordovician age (Conti et al., 1993), a common origin is suggested.
The ore bodies exploited at Levigliani comprise two main horizons, 1–3 m thick and 100–150 m long, with an average grade of 0.3-0.5 wt.% Hg. Total Hg metal contained is estimated somewhere between 2000 and 5000 tonnes.

As previously said, Hg mineralization is strictly associated with pale-green metatufite layers, where it occurs both as disseminations, and as quartz–carbonate-sulfide veins (Fig. 3.3). Some quartz-carbonate veins containing native mercury and minor Hg sulfides propagate from metatufites into the MQP (e.g. at “Cavetta” adit). The disseminated ore is made up of millimetric clots and patches, forming levels where cinnabar (and metacinnabar) is flattened along S_1. In the disseminated ore, pressure shadows of cinnabar and quartz, coherently oriented with the D_1 extension lineation observed in the Levigliani area (Carmignani and Giglia, 1983), commonly develop around euhedral pyrite crystals (Fig. 3.3 and 3.4). The mineralized metatufite layers are isoclinally folded by D_1, leading to repetition of the ore at various elevations (Fig. 3.2).

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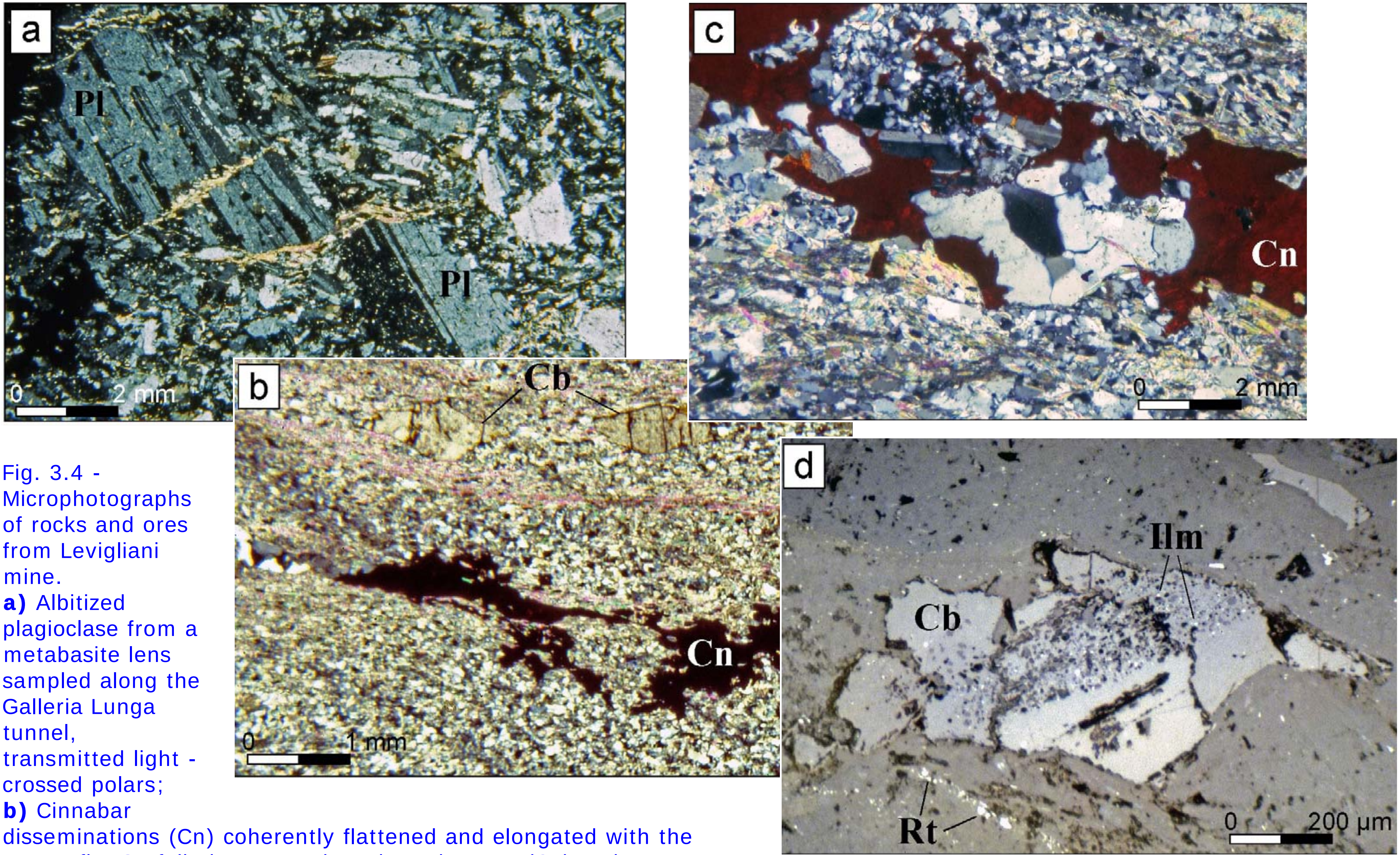

Fig. 3.4 - Microphotographs of rocks and ores from Levigliani mine.
a) Albitized plagioclase from a metabasite lens sampled along the Galleria Lunga tunnel, transmitted light - crossed polars;
b) Cinnabar disseminations (Cn) coherently flattened and elongated with the metatufite S1 foliation; note the oriented Fe-Mg (Ca) carbonate porphyroblasts (Cb), Speranza adit; transmitted light - crossed polars. **c)** detail of a cinnabar dissemination in the metatufites at Speranza adit; transmitted light - crossed polars; **d)** detail of a Fe-Mg (Ca) carbonate porphyroblast (Cb) with inclusions of ilmenite (Ilm); note the microcrystals of rutile (Rt) oriented along the S1 foliation, Speranza adit; reflected light - parallel polars.

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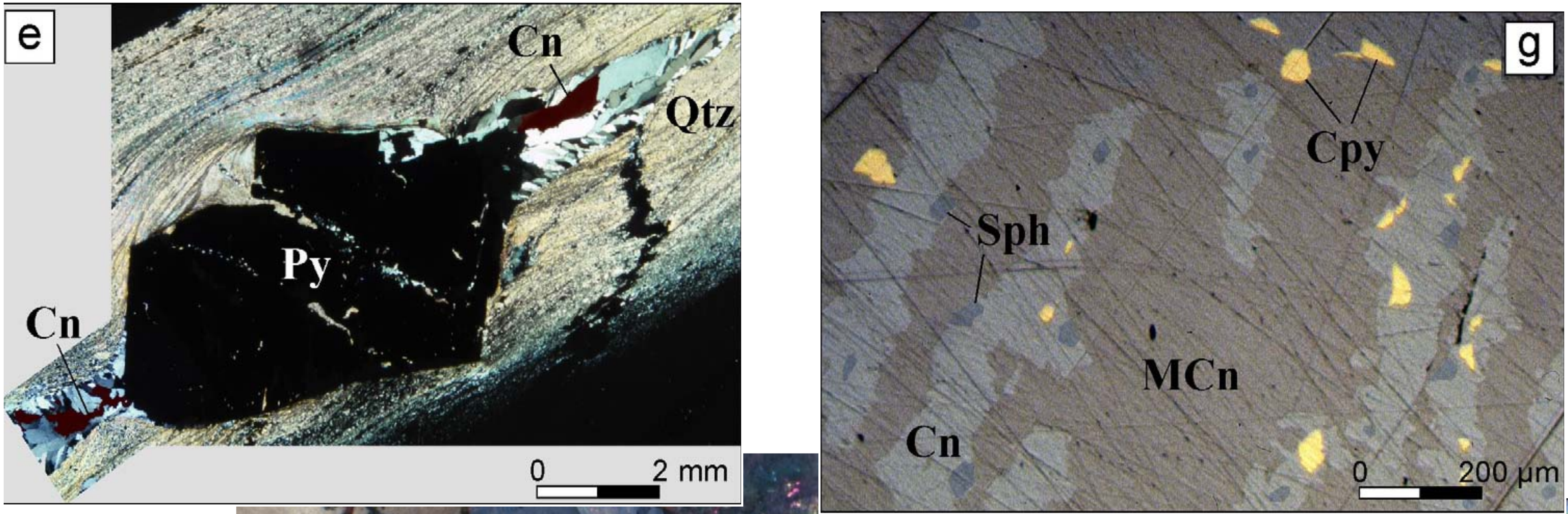

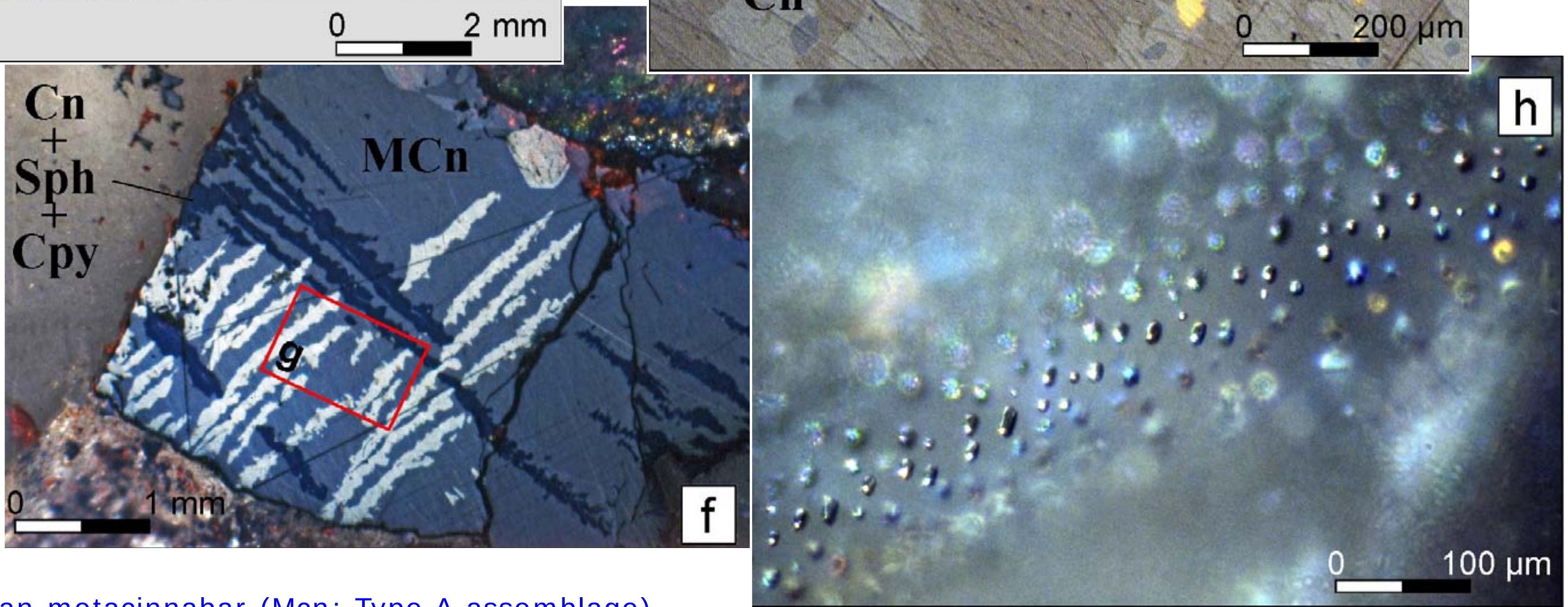

Fig. 3.4 - Microphotographs of rocks and ores from Levigliani mine. **e)** a cubic pyrite porphyroblast with pressure shadows of quartz and cinnabar, Speranza adit; transmitted light - crossed polars; **f)** a crystal of zincian metacinnabar (Mcn; Type A assemblage) replaced by cinnabar II, mercurian sphalerite and chalcopyrite (Cn+Sph+Cpy; Type B assemblage) as off-shoots penetrating the grain from the rim into the core, Speranza adit; reflected light - crossed polars; **g)** detail of Type B assemblage replacing zincian metacinnabar, Speranza adit; reflected light - planar polars; **h)** trail of small inclusions of native mercury in quartz from Cavetta adit; transmitted light - parallel polars.

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According to Dini et al. (1995), in both disseminated and vein mineralization two distinct Hg-bearing mineral assemblages can be recognized (Fig. 3.4): *A-type*, constituted by cinnabar I, zincian metacinnabarite and pyrite; *B-type*, made up of cinnabar II + mercurian sphalerite + pyrite ± native mercury ± chalcopyrite ± galena ± pyrrhotite. Both assemblages include variable amounts of gangue minerals, such as quartz, Mg-rich siderite, Fe-rich dolomite, calcite, muscovite, and albite. The *B-type* assemblage is present almost exclusively in the late stage veins controlled by D_2 structures. It is particularly well developed at "La Cavetta" adit. Here the Hg-filled cavities, that in other stopes usually do not exceed few millimetres, may reach a relevant size; in fact, as reported by Targioni Tozzetti (1777), during exploitation in the 18th century some very large cavities (containing about 1 tonne of native mercury) were found.
Dini et al. (1995, 2001), based on a detailed analysis of ore textures and mineral chemistry, suggested that *A-type* ore equilibrated at P–T conditions (P = 0.3–0.4 GPa; T = 385–350 °C) close to those established during the late evolution of the D_1 phase. According to the same authors, *B-type* ore assemblage overprinted and partially replaced the earlier *A-type* assemblage during the retrograde stages of the Alpi Apuane metamorphism, at temperatures not exceeding 250 °C. To the late retrograde stage should be ascribed the occurrence of the new mineral grumiplucite (a Hg–Bi sulphosalt described by Orlandi et al., 1998). The features of the fluid inclusions ($T_{h\ tot}$ 226-280 °C; wt.% NaCl equiv. 1.4-5.9; small amounts of low density CO_2) fall within the field previously established for fluids that circulated during the metamorphism in the Apuane metamorphic complex (Lattanzi et al., 1994), suggesting a syn-metamorphic nature of hydrothermal circulation at Levigliani.

In conclusion, at Levigliani, a strict spatial association between the Hg ore, and the Ordovician metatufite layers and metabasites can be observed. This association may be merely accidental; however, a possible genetic relationship between the metabasites and Hg mineralization must be considered, in view of the analogies existing between Levigliani and the early Paleozoic stratabound Hg deposits of the European Variscan terrains, including the very large deposit of Almaden (Spain), which is hosted in a lithostratigraphic context somewhat similar to Levigliani (Early to Late Silurian siliciclastic formations and mafic volcanics; Saupè, 1990). Admitting the existence, at Levigliani, of a Paleozoic metallogenic event, the Hg proto-ore (cinnabar disseminations) was locally reorganized/mobilized (in quartz carbonate veins) and, in part, conceivably lost by the system during the subsequent Apenninic metamorphism. The peculiar geochemical character of the

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Levigliani Hg ore (presence of Zn, Fe, and Bi), coupled with the peculiar temperature-pressure conditions reached during the Apenninic metamorphic event produced the complex mineral association described above (cinnabar, native mercury, zincian metacinnabar, mercurian sphalerite, grumiplucite) helping us to unravel part of the metallogenic puzzle of the region, and contributing to shed new light on the tectonometamorphic-magmatic evolution of this fragment of the Southern European Variscan belt.

The karst system

The karst system is developed inside the carbonate core of the Corchia syncline, almost completely enclosed by the non-karstifiable, low permeability basement (Fig. 3.1b). The presently known cave system occupies the northern part of this geological structure, while in the southern and lower sector, which corresponds to the Monte Alto ridge, there are no relevant explored caves.

The Corchia cave system is characterised by a high morphologic complexity. The whole system occupies a volume of rock about 2 km long, 1 km wide and 1 km high, gently dipping towards the SE. The system now has 15 entrances, the highest of which opens at 1637 m a.s.l., just below the summit of Monte Corchia.

The geological structure strongly controls the pattern of the cave, which is roughly elongated according to the main fold axial surface, that is to say along the strike of lithological beds and main cleavage. This is true for the major conduits, which represent the main collectors, whereas the secondary branches are mostly developed along fractures oriented ca. N-S.

About half of the cave passages are originated under phreatic or epiphreatic conditions, in places strongly modified by vadose incision or by local breakdown. These conduits are organized as complex 3D networks distributed from 450 to 1550 m a.s.l., having the shape of regular tubes or canyons and with a mainly horizontal pattern (Fig. 3.5).

Due to percolation or vadose flows, several high-gradient passages intersect the epiphreatic networks along the main fractures. These vertical caves, which show the typical features of deep alpine karst and are common features in the other areas of Alpi Apuane, are the present active drainage system from surface to the main collector level. The upper entrance is part of a steep canyon intercepted by surface erosion and modified by several collapses.

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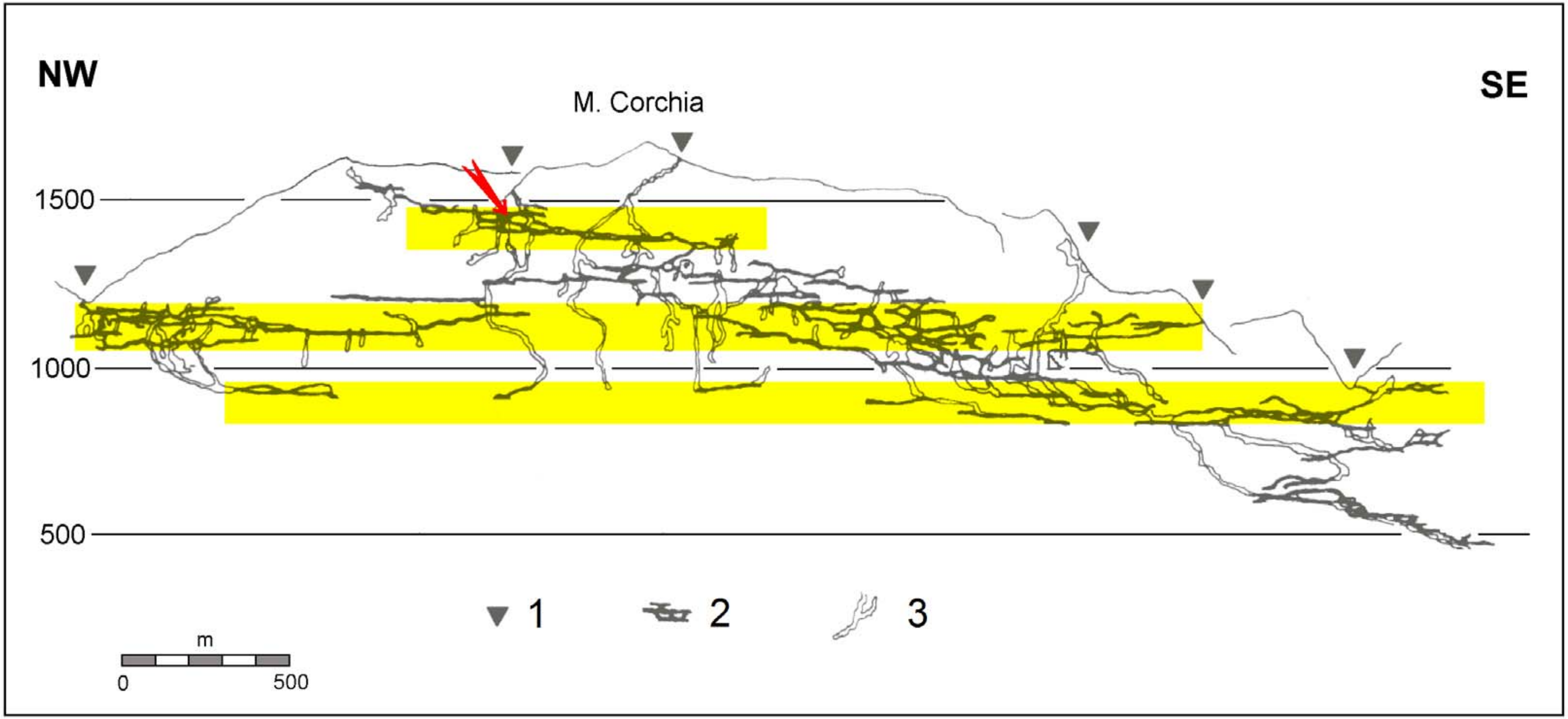

Fig. 3.5 - Sketch profile of Monte Corchia cave system. 1) Main entrances, 2) phreatic and epiphreatic passages, 3) vadose passages.

The canyon is a relict form, probably fed by a surface basin now completely destroyed by erosion (Piccini, 1991, 1994). At 1400 m a.s.l. the canyon encounters a well-developed level of relict phreatic tubes, locally modified by rock falls, which develops from NW to SE following the structural direction of main cleavage. Trending to the SE after a long and deep canyon of SW-NE oriented, phreatic morphologies became dominant and the galleries display well-preserved sections of elliptical tubes.

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The morphology of these galleries suggests a relevant recharge of allogenic waters, which deposited conglomerates with well-rounded exotic pebbles. These pebbles consist of non-metamorphic sandstones coming from the Tuscan or Ligurian nappes, lithologies which do not outcrop in the present day cave catchment, which thus implies a morphologic setting very different from the present one (Piccini, 1991, 1998). To the SE, the level closes with a large non-penetrable rockfall. In the last part, the conduit system preserves some ancient calcite deposits, now heavily altered and mostly broken because of the gravitational collapse of cave wall.
Several different generations of high-gradient caves cut this paleo-phreatic level, many of which are still active and are the present pathways of local infiltration water. More than one connection reaches a lower, almost horizontal level of phreatic tubes, which is located at an altitude of ca. 1300-1350 m. This level has a most irregular plane pattern without significant diversion. All the part of the cave system described above is completely carved in the marble rock.

In the north-western part of the cave, one of the vadose entrenchments descends northward and reaches a second and more developed level of phreatic and epiphreatic conduits at 1150-1200 m a.s.l.. Most of these galleries are carved in dolostone (Grezzoni Fm). The pattern is complex, and it is often difficult to recognize the main conduits from secondary ones.
In the SE sector the upper system of phreatic conduits (1300-1450 m a.s.l.) trends gradually down along large galleries heavily modified and incised by free flow of a large quantity of water. This large canyon intersects the major phreatic level of the karst complex at 1100-1200 m a.s.l. This level was probably connected with the NW section to form a single and ramified system of phreatic galleries. Deep canyons entrench some of these phreatic tubes, indicating a long phase of vadose incision close to the hydrological base level. Some vadose pathways lead to a further level of phreatic conduits located about 200 m below, between 900 and 800 m. The third cave level is still active in the inner part of the system, where an underground stream, whose mean discharge is presently around 0.15 m^3/s, flows in conduits partially water-filled. This circumstance is due to the occurrence of a structural dam that consists of low-permeability rocks (“Brecce di Serravezza” and “Scisti a Cloritoide”). Downstream of this structural obstacle the subterranean stream deepens with a long active canyon stepped by a series of waterfalls up to 40 m high. At an altitude of 600 m, the stream encounters a further level of water-filled phreatic conduits, which indicates another local perched piezometric level.
The stream flows along an unknown path, and then re-appears in the last section of the cave at 600 m a.s.l. The cave stream deeps towards the SE along a vadose canyon with a step-and-pool morphology until it reaches the present bottom of the cave, at 450 m a.s.l.

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General hydrology

The hydrological structure of the Corchia karst system consists almost exclusively of the carbonate core of the Monte Corchia-Monte Alto syncline, which is cut by the Torrente Vezza. No significant allogenic recharge occurs, except that in restricted areas on the east side of Monte Alto and in the lower part of the hydrological system. Dolomite and marbles are the main karst aquifers.

The catchment area is well depicted on the basis of several dye tests performed by the Federazione Speleologica Toscana (Roncioni, 2002 and references therein). The springs that drain Corchia are located in the valley of Torrente Vezza, a few hundred meters upstream of Ponte Stazzemese, at 176 m a.s.l. Water rises from several points in the left side of the Vezza stream channel, that is the opposite side with respect to the Corchia system, a few meters above the riverbed. Here there are several springs mantled by slope rock-fall, some perennial and some occasionally active, which together are named “Le Fontanacce” or “Cardoso” springs. A precise measure of discharge is difficult due to the characteristics of this group of springs, which are distributed along the riverbed. On the basis of the few measures, the mean discharge is though to be about 0.12 m^3/s (Piccini, 2002).

The feeding karst area is well defined, being bordered by a belt of Paleozoic basement. The cave stream disappears at the bottom of the cave, under a rock collapse, at an altitude of 450 m a.s.l. and about 3 km from Cardoso spring.

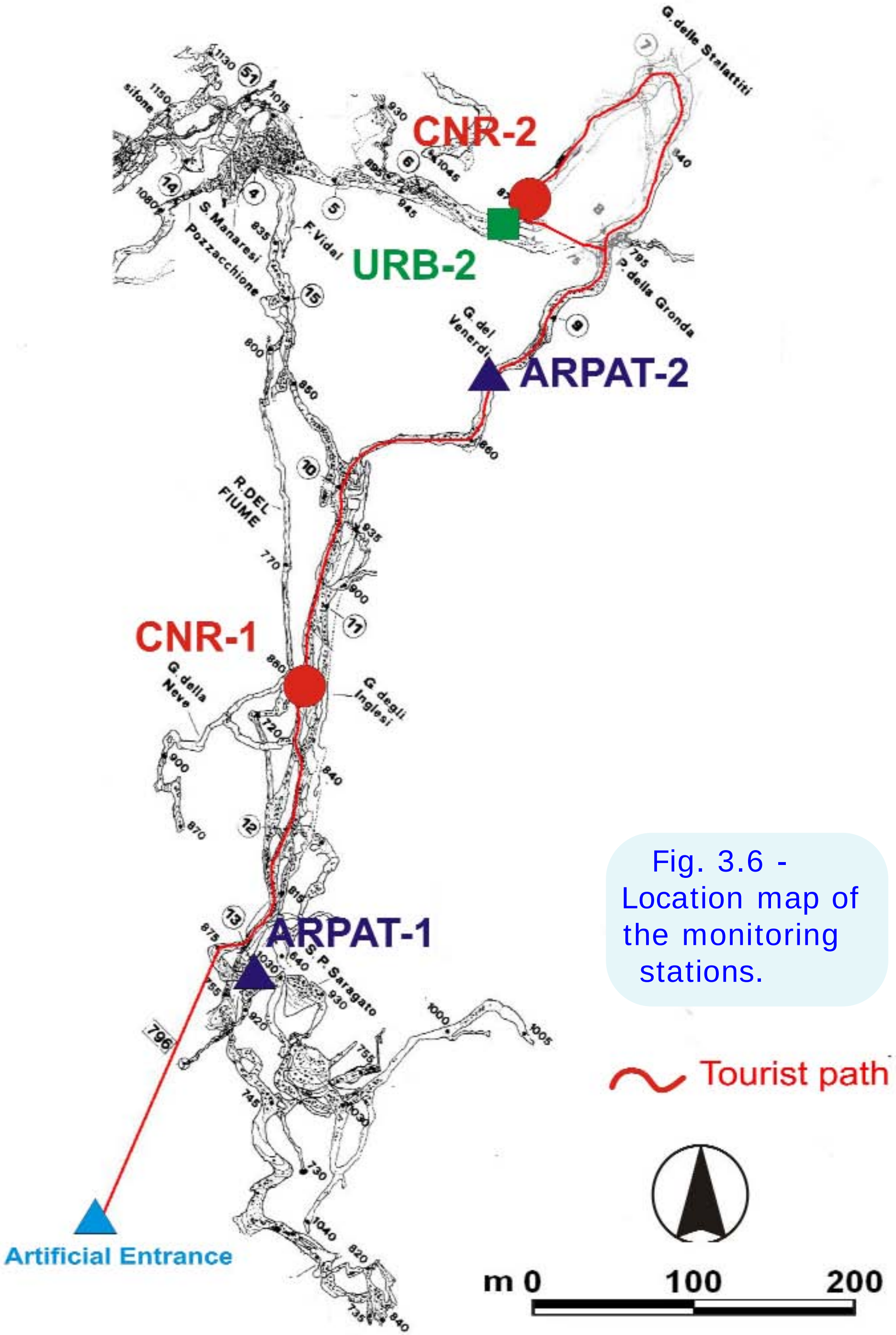

Fig. 3.6 - Location map of the monitoring stations.

The monitoring system, hypogean climate and water geochemistry

Hypogean climate

At Corchia Cave, meteorological monitoring has been in operation since 1998 by ARPAT (Agenzia Regionale per la Protezione dell'Ambiente, Toscana). Further monitoring stations for temperature (URB-1 and URB-2) were installed by the University of Urbino within the frame of the project supported by the Prof. M. Menichetti since 2005. Three meteorological stations have been installed along the tourist path (Fig. 3.6). Station ARPAT-1 is at the intersection of the tourist artificial tunnel and the natural path (870 m a.s.l.); station ARPAT-2 is located at "Galleria del Venerdì", about 1.4 km from the entrance at 830 m a.s.l.; station ARPAT-3 is located at "Galleria delle Stalattiti" near URB-2, at 840 m a.s.l. and about 2 km from the artificial entrance. Two meteorological stations (MT-1 and MT-2), measuring temperature, rain, wind speed and atmospheric pressure, have been installed on the Monte Corchia slopes at two different elevations.

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Figure 3.7 shows the temperature fluctuations of the two external stations (MT-1 and MT-2) and three inner stations (ARPAT-1, 2 and URB-2) during the year 2005. Typical fluctuations emphasize the extreme stability of stations ARPAT-2 and URB-2 compared to ARPAT-1, as expected for the deepest sectors of the cave. Station ARPAT-1 has a mean annual temperature significantly lower than the other two, due to the fact that it is located near two lower entrances through which cold air enters during winter, while ARPAT-2, which is more than 1 km from the entrances, is only marginally influenced by external temperature. In fact, the maximum fluctuation in temperature for station ARPAT-1 is 4 °C, corresponding to the minimum external temperature to 9.3 °C. For ARPAT-2, the temperature ranges from 7.6 °C to 9.0 °C.

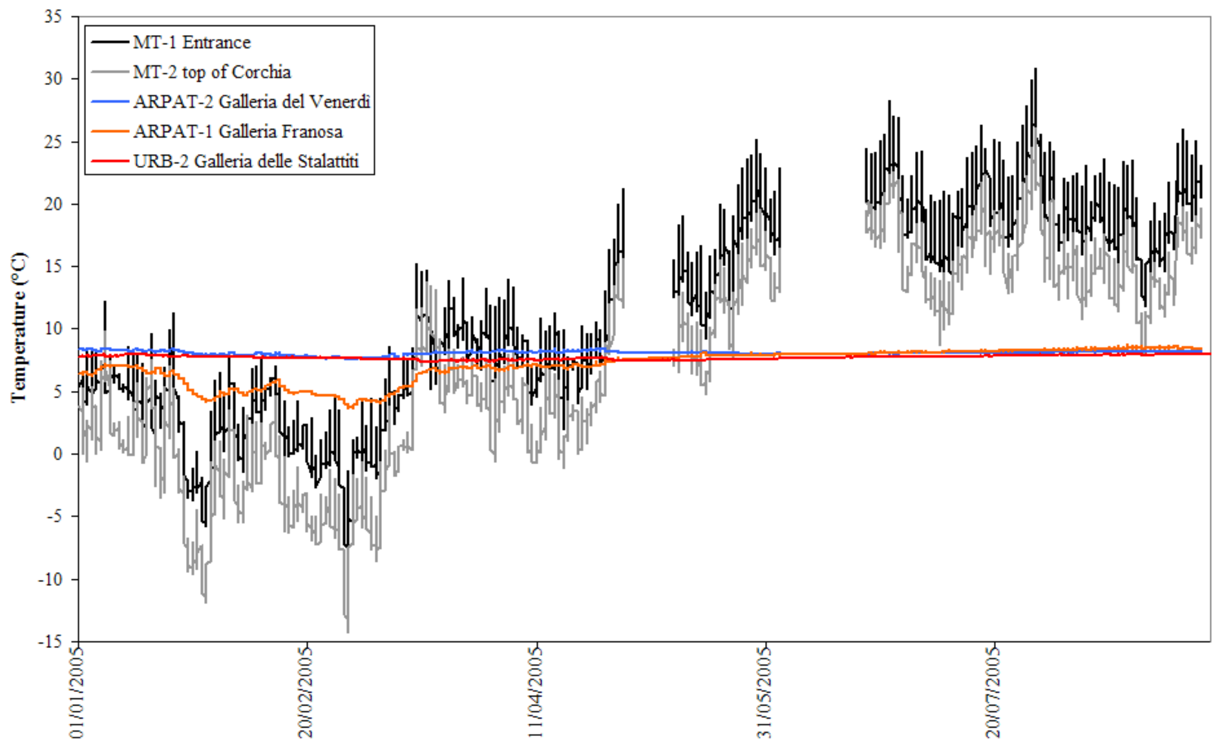

Fig. 3.7 - Temperature measured in different stations in the Corchia cave (see figure 3.6 for station locations). Note the significant stability of the Galleria delle Stalattiti.

During summer, the air flows downward and both the stations record the temperature of the air coming from upper entrances, which here is already in thermal equilibrium with the cave walls. The graph clearly shows than when the external temperature rises systematically above the mean cave temperature, the two stations reach soon almost the same temperature, indicating that the airflow changes direction.
The station URB-2 at the Galleria delle Stalattiti is relatively stable in terms of temperature, in agreement with its position, nearly 2 km from the nearest natural entrances. Temperature ranges from a minimum of 7.3 °C (in March) to a maximum of 8.1 °C (in October and November).

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Water geochemistry

In the last ten years, several chemical analyses of rain, surface and cave waters have been performed. Most of the cave water analyses have been obtained from sites along the tourist path, although some samples have been collected in the upper and less known sector of the karst system. These data have been extensively discussed recently by Piccini et al. (2008). Since April 2009 a monitoring program has been started and waters from 2 selected drip and one hypogean lake at the station CNR1 and CNR2 (Fig. 3.6) are collected every month for chemical and isotopic analysis. Here we summarize the most relevant chemical features of the cave waters useful for paleoclimatological interpretations in particular form the data obtained from the two stations.

Drips

Drip water samples have been collected over different parts of the cave (especially in the area of the tourist path) but only for CNR1 and CNR2 there are enough data for a meaningful characterization of the feeding waters. The longest sampling period is for CNR2 station.

The waters of the two drips and the lake are Ca-Mg bicarbonate waters (Figure 3.8a). The CNR1 drip is characterized by a higher percentage of bicarbonate than CNR2 and the lake (figure 3.8b). The latter ones have a relatively major content of sulphate. Moreover, the CNR2 and the lake show a higher content of magnesium (Figure 3.8c). These chemical differences could reflect the different bedrocks along the path of infiltrating rain waters at the two stations. In fact, CNR 2 is underlain by a thick layer including an impermeable basement of phyllite and metavolcanics, dolomite with the presence of “Grezzoni”. Instead at CNR1, the rock is a well karstified marble. Furthermore, the chemistry of CNR2 drip is extremely stable and characterised by an enrichment of Mg in relation to the calcium content if compared to the CNR1 drip and to the rainwater (Fig. 3.8d). This, with the fact that the CNR2 waters is characterized by higher content of dissolved solid and the above mentioned structural condition, supported the hypothesis of long residence time of the waters in the feeding the system compared to CNR1. Some tritium measurements confirmed that the CNR2 dripwaters are “older” than CNR1 ones (Piccini et al., 2008).

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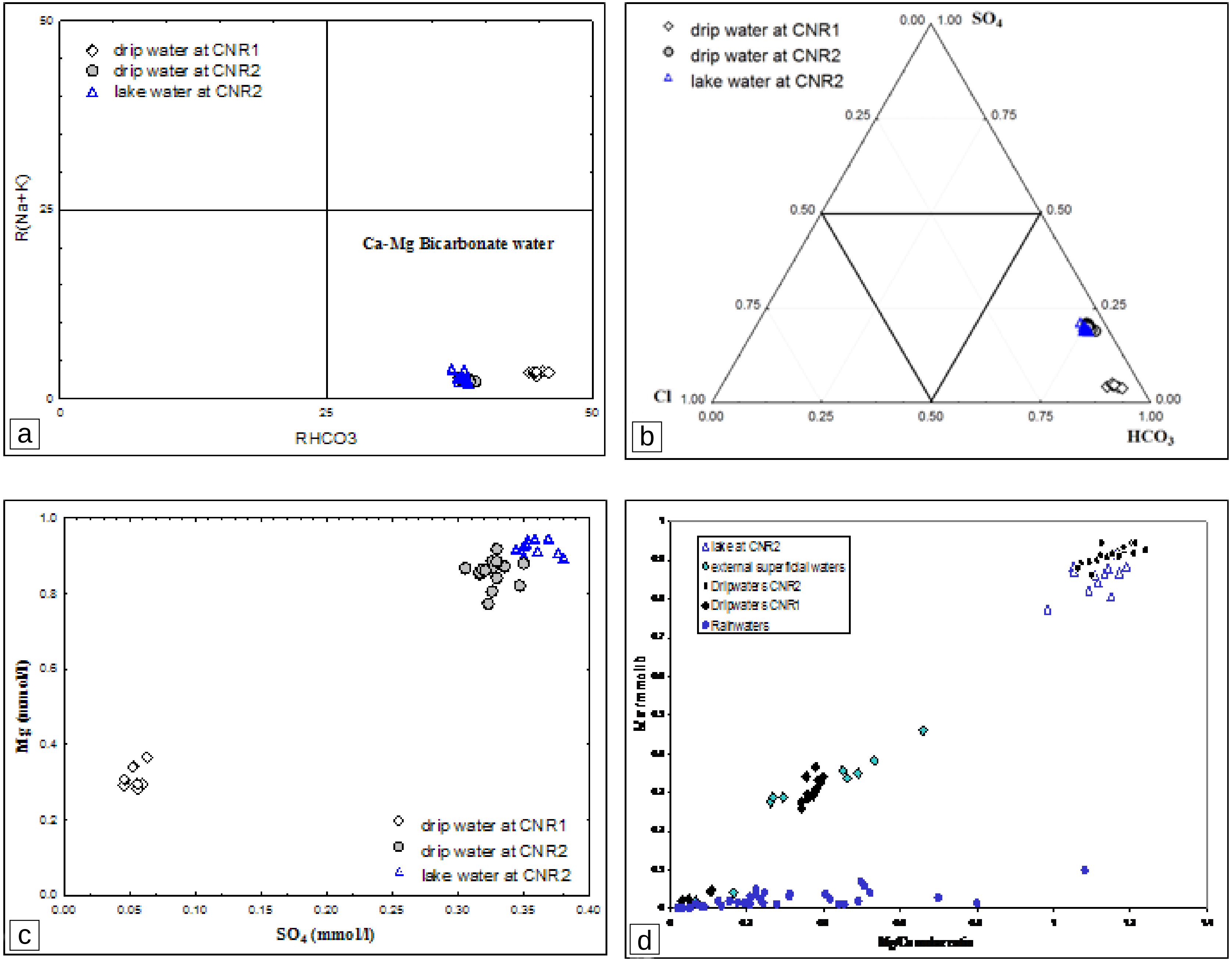

Fig. 3.8 - Water geochemistry of Corchia waters: **a)** Langelier-Ludwig classification diagram that identifies one water family, that is carbonatic waters; **b)** HCO3-SO4-Cl ternary diagram for drip waters and lake waters, that highlights the relative higher content on bicarbonate for CNR 1 drip and on sulphate for CNR 2 drip and lake waters; **c)** SO4 vs. Mg diagram for dripwater and lake waters; **d)** Mg/Ca molar ratio vs. Mg diagram for drip waters, rainwaters, superficial external and lake waters.

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Stable isotope water geochemistry

Figure 3.9 shows the Corchia waters plotted in the δ^2H_{H2O}-$\delta^{18}O_{H2O}$ diagram. Almost all waters plot closely to the Central Mediterranean Meteoric Water Line (CMMWL), with a deuterium excess (d) of 15 (Longinelli and Selmo, 2003). A few of the data points show lower d values without reaching the Global Meteoric Water Line (GMWL, with a d = 10). The spread of values is mainly due to CNR1 station, the drips collected at the entrance in the artificial gallery and the flowing waters (the latter collected only once in March 2005). The lower isotopic values, in particular those of the flowing waters, can be explained by infiltration of water derived from snow melting, usually characterised by lower d values (Mussi et al., 1998) and, possibly, derived from higher altitude recharge areas.

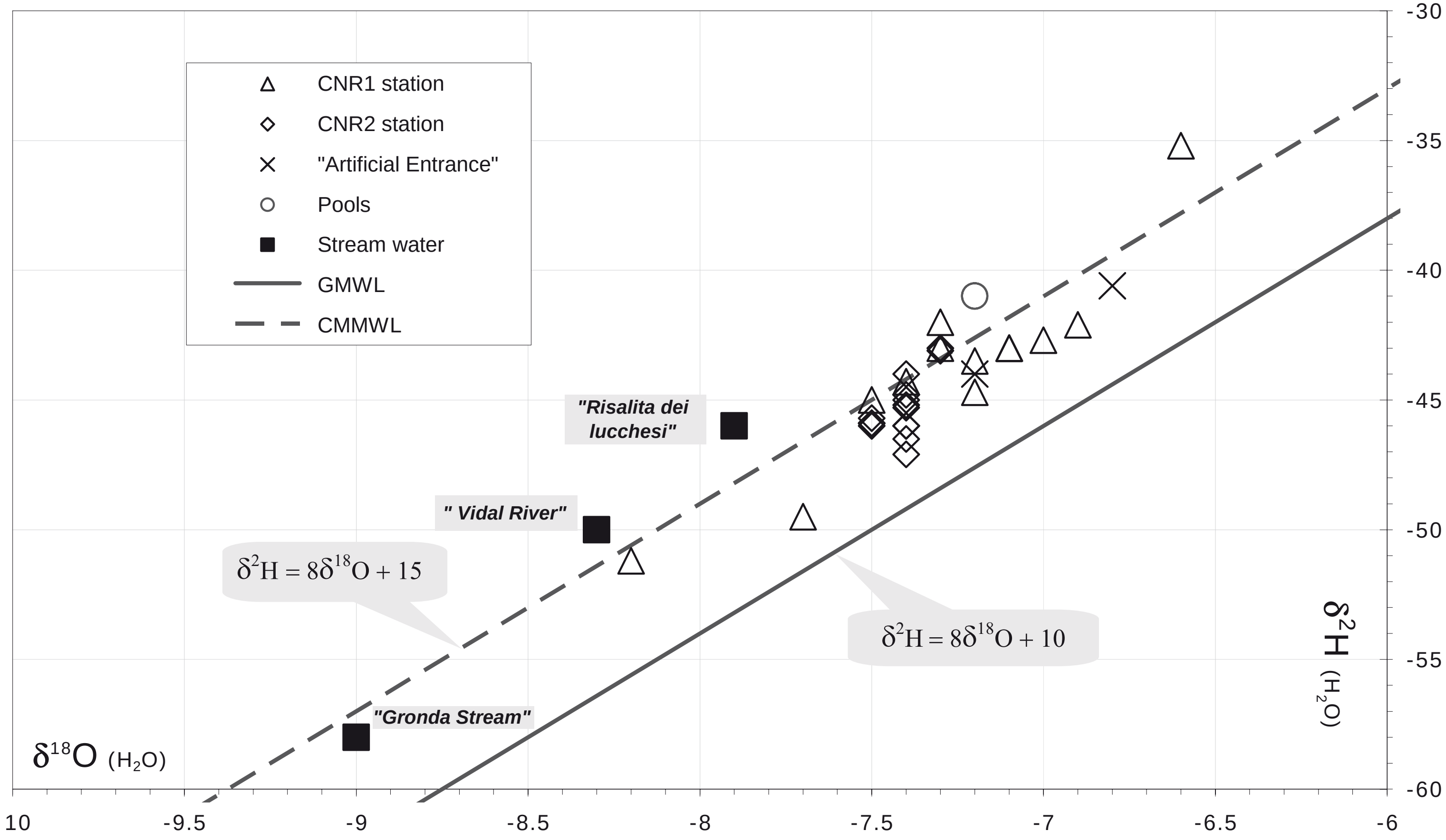

Fig. 3.9 - δ^2H_{H2O}-$\delta^{18}O_{H2O}$ diagram fro CNR1 and CNR2 stations (after Piccini et al., 2008). CMMWL: Central Mediterranean Water Line; GMWL: Global Meteoric Water Line.

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Figure 3.10 shows the oxygen isotope composition of the drip stations CNR1 and CNR2 along with four determinations of tritium content. In detail, the data show the substantial stability of station CNR2 (mean: -7.4±0.1 ‰) and a significantly higher variability for station CNR1 (mean: -7.3±0.4 ‰). The different behaviour of the two stations is replicated by the tritium data. On the hypothesis that there is no mixing of waters of different ages, the tritium data suggest residence times of ca. 50 years for CNR2, and values consistent with precipitation occurring within the year of sampling for CNR1. The data available do not support any significant differences in the altitude of recharge (ca 0.1 ‰ on average between CNR1 and CNR2, which can locally represent less than 100 m (Mussi et al. 1998), with the values of CNR1 likely to be influenced by seasonal effects and year-to–year rainfall isotopic variability, which is averaged out in the case of CNR2.

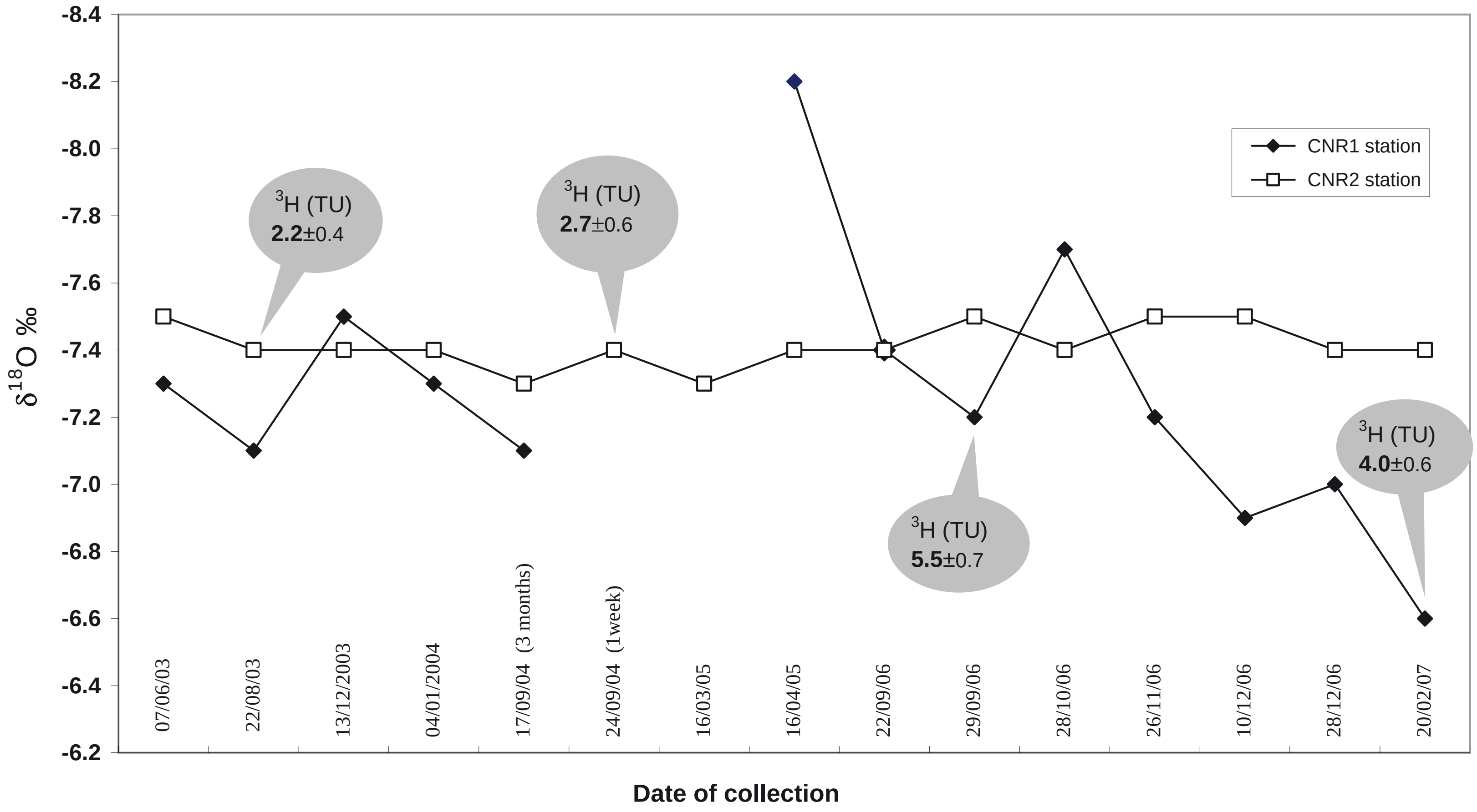

Fig. 3.10 - Oxygen isotopic composition of drip points CNR1 and CNR2 (after Piccini et al., 2008).

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Paleoclimatology

The increasing awareness about humanity facing at present the serious problem of global warming and its potentiality to cause significant climatic changes, which are caused or amplified by anthropogenic activities, poses important challenges for many fields of science. Although, Earth scientists can provide neither a political nor an economical answer to this problem, they can contribute to obtain a better knowledge of the climate system. The instrumental record is generally considered not to be long enough to give a complete picture of climatic variability. It is crucial, therefore, to extend the record of climatic variability beyond the era of instrumental measurements if we are to understand how large natural climatic variations can be, how rapidly climate may change, which internal mechanism drive climatic changes on regional and global scales, and what external or internal forcing factors control them. Overall, this is well summarized recently by P. Cox and C. Jones (2008) on Science where they stated: “Paleoclimatic data cannot tell us how to meet the challenge of managing 21st-century climate change, but they can help us to better understand the nature of this challenge”. Therefore, quantitative paleoclimate data are of paramount importance for understanding the climate system and offer past scenarios for testing climate models, which are at the base of our future projections.

Given predictions of future climate, changes in rainfall and water resources seem certain to have important socio-economic and political impacts in the Mediterranean region (Giorgi 2006). Understanding the variability of hydro-climate over different time scales is therefore an essential prerequisite for establishing predicted future climate change and its possible impact on human society (Mariotti et al., 2002). The Mediterranean region is both climate-sensitive and has an exceptionally long and rich history of human use, including some the world’s most important past civilisations. The investigation of natural archives which preserve information on climatic and hydrological changes in the last several thousands of years is of paramount importance to understand the causes and the potential impact of changes in the next future for this area (Robert et al., 2010).
Moreover, to understand which mechanisms transfer the climatic variability from the global to the regional scale it is necessary to have detailed regional proxy records with precise and accurate chronology.
Many marine- and ice-core records are celebrated within the palaeoclimate community because of the rich wealth of information they preserve. However, we still lack the means by which to date them precisely or to verify non-radiometrically based age models. Precise age control is vital for addressing many questions about palaeoclimate,

like the timing, duration and inter-hemispheric phasing of terminations, the duration and structure of interglacials, the timing and process by which the Earth plunges back into a glacial stage and so on.
Speleothems (cave calcite precipitates, e.g. stalagmites, stalactites, flowstones) are highly regarded in the international scientific community as archives of paleoenvironment and paleoclimate. This relies from the highly sensitivity of speleothem properties (e.g. chemical composition, growth rate) to environmental parameters (e.g. temperature, amount of rainfall, biological activity in the soil above the cave). However, the key of this success is the possibility to obtain a robust age control. Indeed, speleothems are arguably the most ideal material for U/Th dating (Richards and Dorale, 2003) because of their excellent preservation potential, particularly in deep cave systems. Developments in analytical techniques and technologies over the last 15 years have seen the amount of uranium required for a U/Th date fall by over three orders of magnitude, to the point where a precise and accurate age estimate can now be obtained from as little as a few billionths of gram of uranium using advanced plasma-source mass spectrometric techniques (Hellstrom, 2003).

Oxygen ($\delta^{18}O$) and carbon ($\delta^{13}C$) isotope ratios are amongst the most widely used climate proxies in speleothems studies (e.g. McDermott et al., 2006). The way in which $\delta^{18}O$ and $\delta^{13}C$ respond to climate through time varies markedly for different region to the Earth, so it is essential to have knowledge of the controlling factors at a given site. However, $\delta^{18}O$ and $\delta^{13}C$ offers important insights on change on local amount of precipitation (Bar-Mattehws et al. 2000), storm-track trajectory (especially when it is coupled with the study of fluid inclusions, e.g. Matthews et al., 2000) and change in typology of vegetation and biological activity of the soil over a cave catchment (Dorale et al. 1998). The study of trace-element variation in speleothems has accelerated dramatically in recent years (Fairchild et al., 2006), thanks to the development of the new techniques of laser ablation. Many studies show that Mg, Sr, Ba, P, U and Na are responsive to climatic change (e.g. Hellstrom and McCulloch, 2000). However, as with stable isotopes the relationships between climate and trace-element response appear to be location-specific (Fairchild et al., 2006). Fluorescence changes in speleothems reflect variations in the degree of humification of organic matter in the overlying soil (McGarry and Baker, 2000). The degree of humification is mainly controlled by temperature and rainfall amount and variations in fluorescence peak emission wavelength can act as proxy for these climatic parameters. So, speleothems are suitable material for multiproxy studies with high resolution, especially if accompanied by monitoring programme of the cave environment coupled with meterological data collected at regional scale.

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Paleoclimate studies on Alpi Apuane caves with special reference on Monte Corchia

The Alpi Apuane area preserves a high number of caves of particular interest for paleoclimatological purpose (Piccini et al., 2003a; Isola et al., 2005; Drysdale et al., 2006). They receive a high amount of rainfall triggered by the Apuane's orographic influence, which mainly traps eastward-moving moisture sourced from the Atlantic and the western Mediterranean Moreover, this area is close to the Gulf of Genoa, one of the most important area of cyclone formation in the Mediterranean. This concomitance of factors makes this area particularly suitable for studying past climatic changes and the role of North Atlantic over the Mediterranean circulation.
Today, the Earth Science Department of the University of Pisa, in collaboration with the Federazione Speleologica Toscana, INGV, IGG-CNR, the Earth Science Department of the University of Florence, the University of Newcastle, the University of Melbourne and the SUERC of Glasgow is studying several caves in the area: Antro del Corchia, Grotta della Renella, Tana che Urla, Tana di Mosciano, Grotta del Vento. Indisputably the most important scientific results have been obtained from Antro del Corchia.

One of the special characteristics of the Corchia speleothems is that they are virtually free of ^{232}Th (e.g. Woodhead et al., 2006; Drysdale et al., 2009) and are characterised by an elevated U concentration (ca. 5 to 25 ppm). This make the application of U/Th particularly successful and, recently this has allow to apply with excellent results the U/Pb technique (Woodhead et al., 2006). Therefore coupling different methods linked to the use of U-series, now it possible to affirm that Corchia (in particular Galleria delle Stallatiti) can preserve an almost continuous record of the climatic change during the last ca. 1.5 Ma or more. Results from extensive and careful reconnaissance work conducted over the last years showed that Corchia speleothems capture major palaeoclimate changes recorded in North Atlantic marine sediments at least for the last 400 ka.
Some outstanding examples are discussed below. Particularly significant is the oxygen isotopic composition of speleothem calcite, which can be mainly related to changes in the amount of precipitation over the catchment area (e.g. Drysdale et al., 2004). The amount of precipitation, in turn, seems to be related to changes in the Meridional Overturning Circulation through the amount of vapour masses released to this sector of Mediterranean (Drysdale et al., 2009). So that higher oxygen isotopic values in calcite are related to colder condition when vapour masses advection from the Atlantic are reduced. Whereas, lower oxygen isotopic values are usually related to climatic improvement and increase in vapour masses advected from the Atlantic to this region.

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The laghetto core: ca. 1,000000 years of continuous record of climatic changes

The "Laghetto basso" is a small pool within "Galleria delle Stalattiti" and was drilled in 2007-2008 (fig. 3.11a). This pool is now under an extensive monitoring program even if years of cavers explorations, work for the setting the tourist path and tourist frequentation have influenced the water chemistry and producing pollution.

A 200-μm resolution stable isotope record has been compiled from a 23-cm thick core (CD3 core, Fig. 3.11b, Drysdale et al. in progress). This record appears to be continuous and spans the period 0–0.960 Ma. Currently, its chronology is based on 12 U-Th ages and by tying sections of its isotope profile to other dated Corchia stalagmites. Nevertheless, comparison with Lisiecki and Raymo's 'LR04 benthic δ^{18}O stack' (2005) (a standard reference series for global ice-volume changes) and ice-core palaeotemperatures from EPICA (Antarctica, e.g. EPICA community members, 2004) shows it

Fig. 3.11 - **a)** Drilling operation within the "Laghetto basso"; **b)** The CD3 just extracted: it contains ca. 1 Ma of climate history.

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clearly preserves every glacial-interglacial transition of the last million years (Fig. 3.12). As far as we are aware, no other *radiometrically datable* continental record of this duration and continuity exists. It is interesting to note that the $\delta^{18}O$ record indicate a significant changes of the average values at ca 500 ka, which cannot seen so clearly in the marine record.

This may indicate a general rearrangement of hydrological cycle in this area (possibly reflecting some event at more regional scale, like changes in the amount of vapour advection from North Atlantic), though the general patter is maintained into the details. This observation is supported by the $\delta^{13}C$, which show a very similar features of the LR04 benthic $\delta^{18}O$ stack', but in this case must reflect more effect of climate on soil above the cave.

The last interglacial (MIS5e) and its end

The last interglacial is probably one of the most studied period of the Earth climate for its potential to represent a phase of climatic warming higher than current interglacial in absence of human perturbation. Evidence of millennial-scale cold events following the last interglacial optimum are well preserved in North Atlantic marine cores, Greenland ice, and pollen records from Europe (e.g. Dansgaard et al., 1993; Kukla et al., 2002 among others).

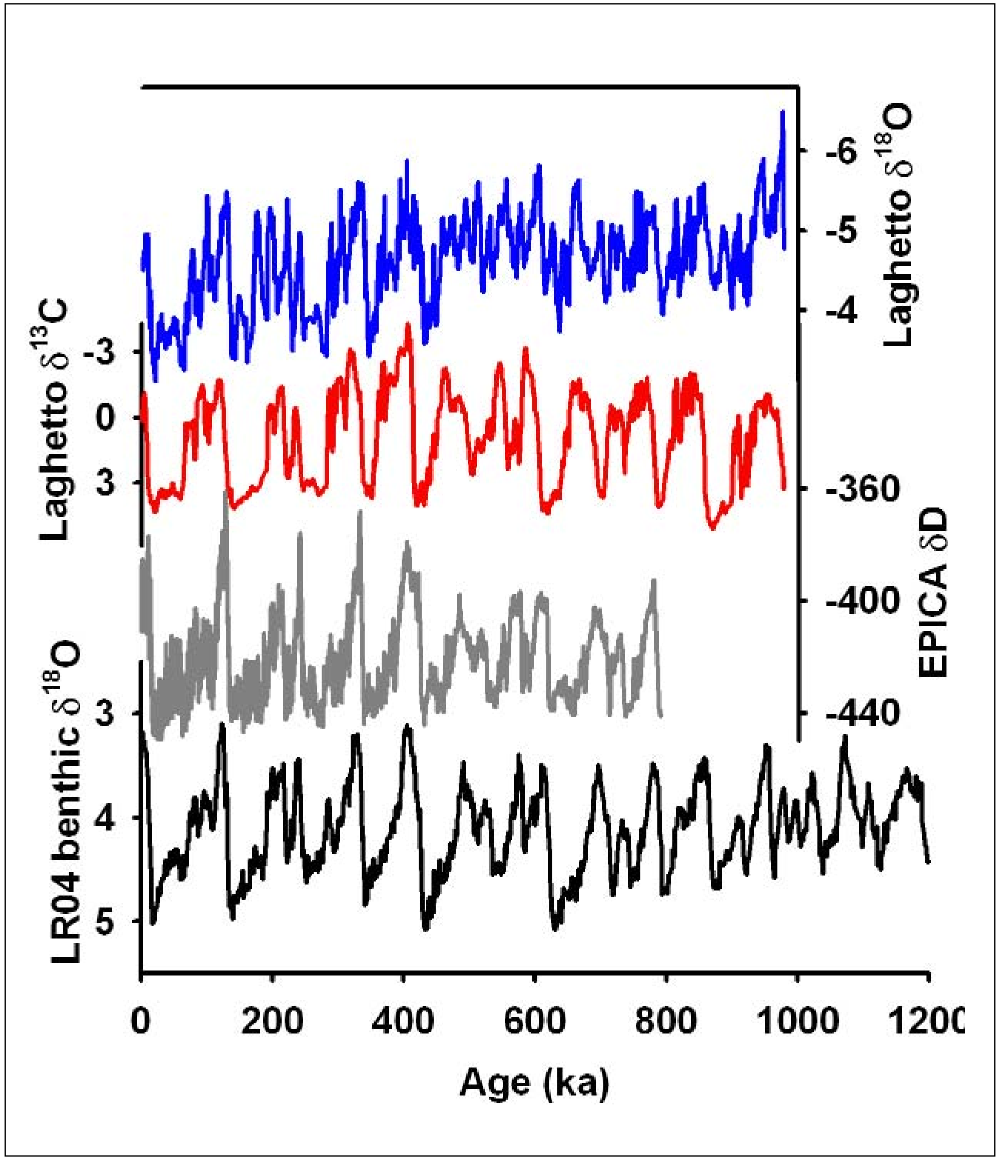

Fig. 3.12 - The "Laghetto core" isotopic record compared with some of the most famous records: EPICA δD (a proxy for paleotemperature, EPICA 2004) and LR04 benthic $\delta^{18}O$ stack (Lisiecki and Raymo, 2005). Note the impressive correlation.

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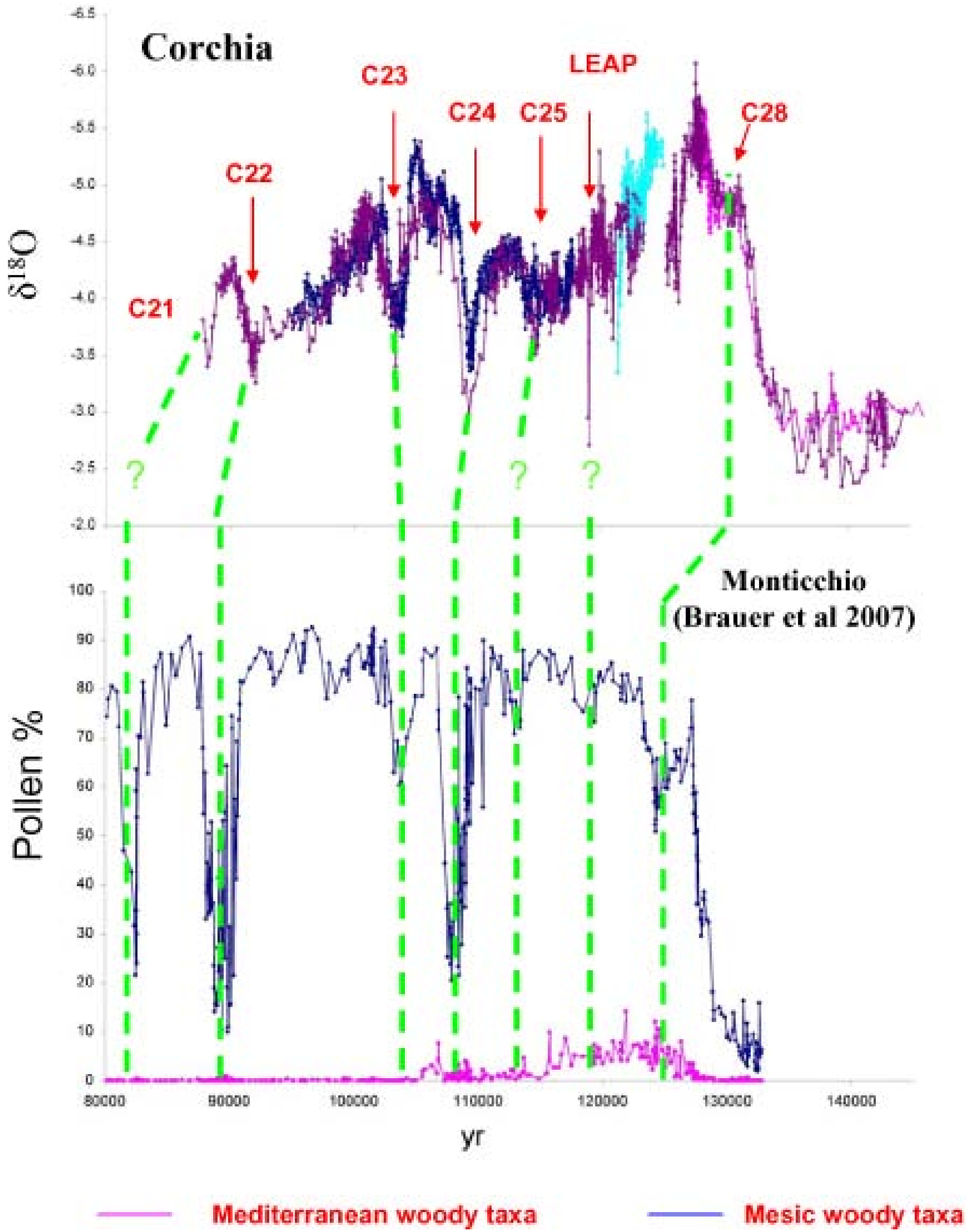

However, their timing was previously mostly undetermined by radiometric dating. A composite record formed by 4 different stalagmites has permitted to reconstruct a detailed paleoclimatic record between ca. 150 to 90 yr allowing to capture in detail some important climatic changes (Fig. 3.13). Detailed correlation with north Atlantic marine core record shows that the penultimate glacial termination (Termination II) commenced 141,000 ±2500 years before the present, too early to be explained by Northern Hemisphere summer insolation but consistent with changes in Earth's obliquity (Drysdale et al., 2009). This is particularly important because variations in the intensity of high-latitude Northern Hemisphere summer insolation, driven largely by precession of the equinoxes, are widely thought to control the timing of Late Pleistocene glacial terminations.

Fig. 3.13 - Comparison between the $\delta^{18}O$ record from Corchia Speleothems (different colour means record obtained from different stalagmites; after Drysdale et al., 2009 and unpublished data) and Monticchio pollen record (Brauer et al., 2007). Cold event after McManus et al., 1994; 2006. LEAP: late-Eemian aridity pulse (Sirocko et al., 2005).

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However, recently it has been suggested that changes in Earth's obliquity may be a more important mechanism and the data of Corchia substantially corroborated this last hypothesis (Hubert, 2006). Using these speleothems Drysdale et al. (2007) were also able to radiometrically dated important cooling events, which was responsible for the demise of the "Eemian forest" in southern Europe and close the last Interglacial. Figure 3.13 illustrate the comparison of this $\delta^{18}O$ record with the pollen record of Monticchio (Brauer et al., 2007), which is considered one of the best dated record of the last 140 ka in the Mediterranean region.
According to figure 3.13 there are evident differences between Corchia and Monticchio, even if some events appear chronologically consistent. From these figures (if the correlations proposed are correct) Monticchio chronology appears less robust than usually believed.

The Holocene hydrological changes and Sapropel S1 deposition
The small stalagmite CC26 has yielded one of the most remarkable and complete record of the Holocene for the Italian peninsula covering ca. the last 13 ka (so including the late part of the Late Glacial). The stable isotope record from CC26 supported by 17 uranium-series ages, indicates enhanced regional rainfall between ca. 8.9 and 7.3 kyr cal. BP at the time of sapropel S1 deposition (Zanchetta et al., 2007). Within this phase, the highest rainfall occurred between 7.9 and 7.3 kyr cal. BP (Fig. 3.14). Comparison with different marine and lake records, and in particular with the Soreq Cave record (Israel, Bar- Matthews et al., 2000), suggests substantial in-phase occurrence of enhanced rainfall between the Western and Eastern Mediterranean basins. However, minor events are also recognizable. It is interesting to note that the average $\delta^{18}O$ values of the first part of the Holocene are systematically lower than the second half of the Holocene (Giraudi et al., 2010). This suggests a progressive decreasing of moisture advection from the North Atlantic, in agreement with other evidence that report decrease amount of rainfall in the Mediterranean and in the Sahara region probably linked to progressive decrease in summer insolation (e.g. deMenocal et al., 2000).

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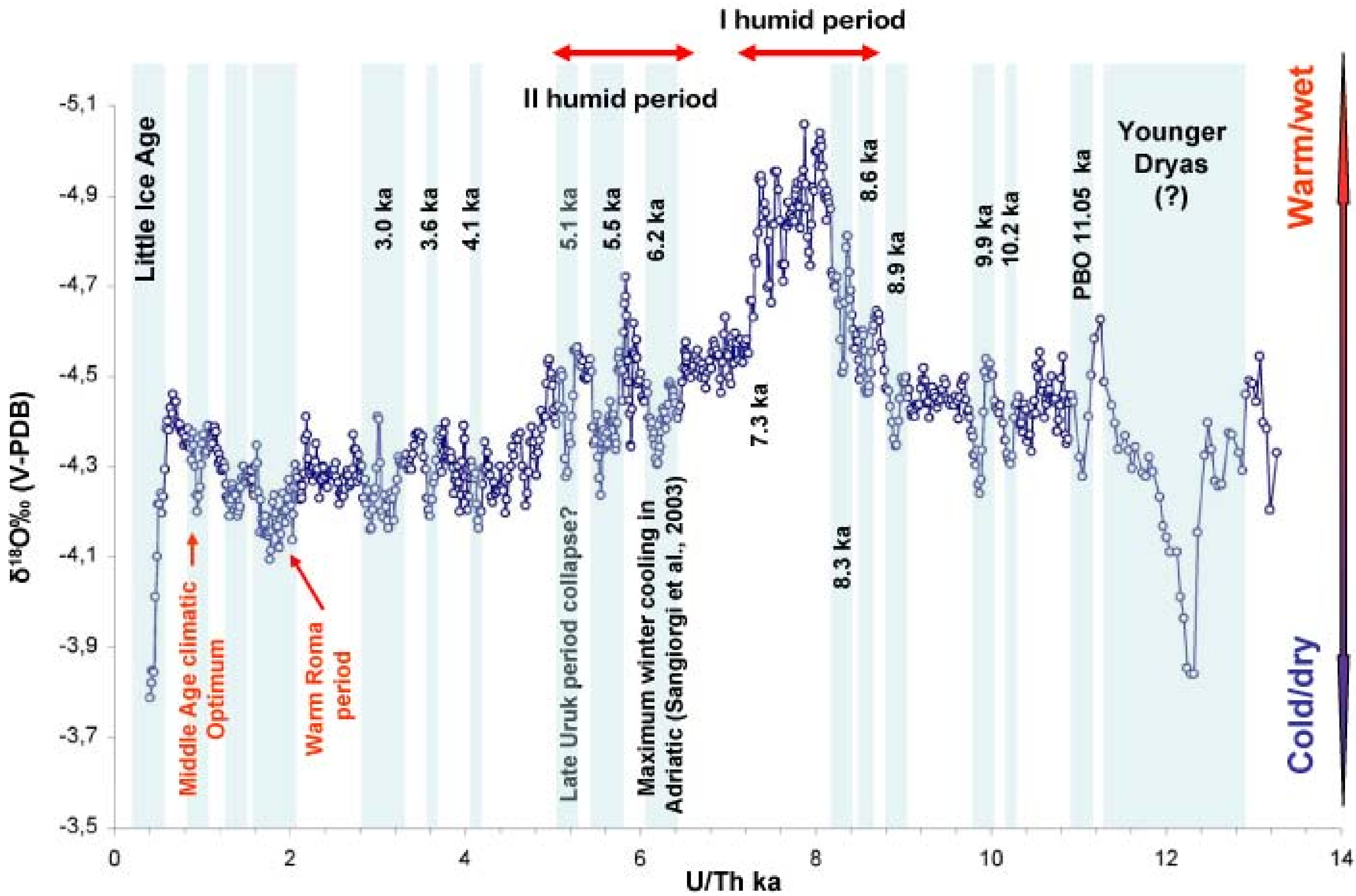

Fig. 3.14 - CC26 oxygen isotope record (after Zanchetta et al., 2007). Possible colder/drier events are highlighted (light grey box). Two wet phases during Holocene are also indicated.

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Field Stops

Corchia Cave

Stop 1: Corchia Cave Tourist entrance

The first stop is devoted to the introduction to the history of the exploration of Corchia Cave and its opening to the tourist (Fig. 3.15). From the artificial entrance a general view of the main structure of the Monte Corchia can be outlined and briefly discussed, as well as geomorphological features.

Stop 2: Galleria Franosa

The Galleria Franosa is the first passage we meet entering through the artificial tunnel. In the first and upper part it looks like a descending tubular phreatic tunnel.
Along the iron stair we observe a large and deep canyon-like gallery. The ceiling is very high while the floor consists of a steep debris slope. If we carefully look at morphology of the walls we can observe large rounded niches (scallops) and no sign of a progressive vadose entrenchment. We can so realize that this tunnel is not really a canyon but a conduit formed under phreatic conditions, whose ceiling and walls were probably reshaped by water flowing upward. In the last part a very peculiar deposit formed by small rounded pebbles cemented by sparitic calcite mantles the left wall. This sediment is probably due to in-site reworking of rock debris by upward flowing water during floods.

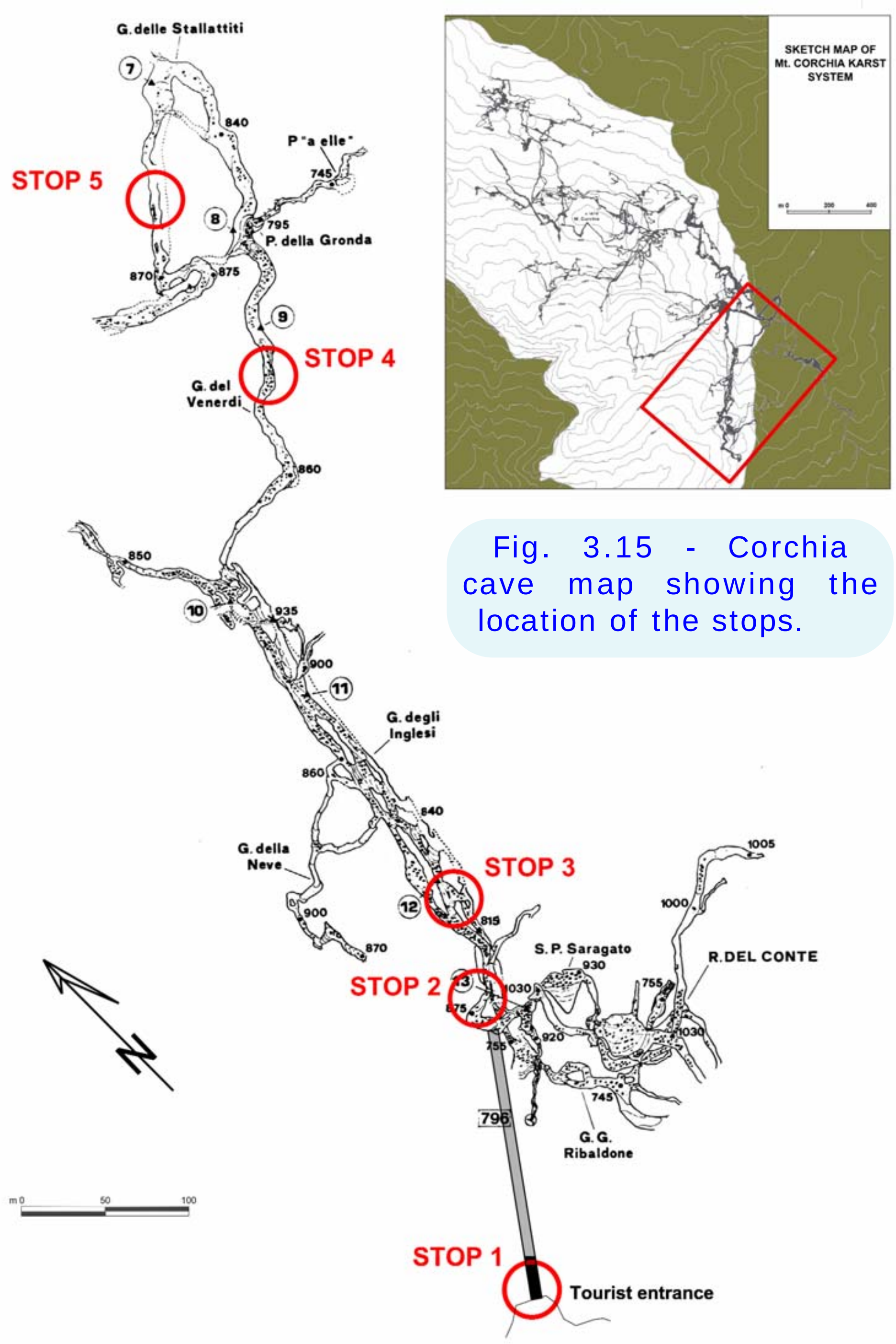

Fig. 3.15 - Corchia cave map showing the location of the stops.

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Stop 3: Galleria degli Inglesi

We are at the beginning of the Galleria degli Inglesi (Fig. 3.16), discovered by British cavers in the sixties coming from the upper entrance of Buca d'Eolo. Here we can observe three different tunnels along a fracture about NNW-SSE oriented. The lower passage shows a downcutting phase and leads to the rim of a 30 m deep pit (Pozzo Suzanne). In this part we found an alluvial deposit containing rounded exotic pebbles of non-metamorphic sandstone, whose provenance is still problematic. Probably, the pebbles come from an upper level of the cave system, through an unknown path. In fact similar pebbles can be found in the highest part of the Corchia complex (at 1450 m a.s.l.) and were probably deposited into the cave during the first phase of development of the karst, when the landscape of Alpi Apuane was very different from the present one.

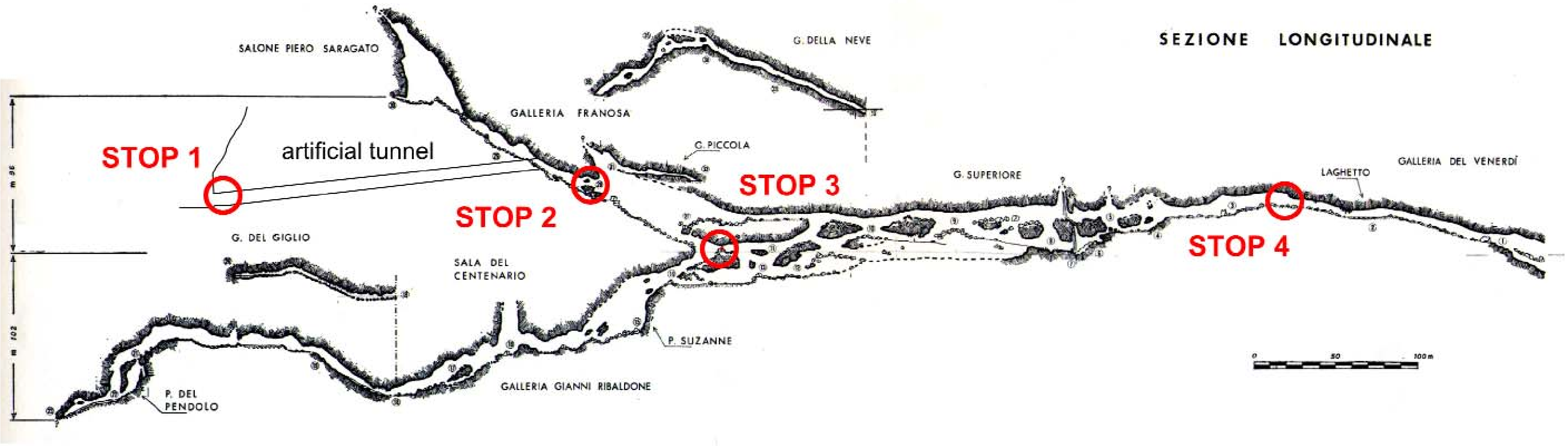

Fig. 3.16 - The cross profile of "Galleria degli Inglesi" showing the location of stops 1-4.

Stop 4: Galleria del Venerdì (first pool)

The Galleria del Venerdì is a large tunnel formed under phreatic condition by a water flow directed to SE. Ceiling pockets due to air bubbles or mixing corrosion testify the phreatic origin. Alluvial deposits consisting of sand and pebbles testify a phase of filling, anyway there are not clear forms due to incision under vadose condition, probably because the gallery was first almost completely filled with sediments. Almost certainly this part of the cave was deactivated first than the Galleria degli Inglesi, which was fed by the Galleria Firenze branch. Slow flowing waters progressively removed sediments during a long epiphreatic phase.

Stop 5: Galleria delle Stalattiti

This gallery is the most decorated of the whole Corchia system. Here we are ca. 400 m below the surface. In this gallery a first flowstone (older than ca 1.5 Ma?) covers a poorly preserved clastic deposit. On this old flowstone there are several phases of concretions represented by different stalagmite generations, with the most conspicuous phase seems to be related to Middle Pleistocene, whereas fewer stalagmites seems to be active during Holocene. Similar complexity is recorded in the flowstone stratigraphy, which was investigate using cores. Most of the stalagmites show a pop-corn like structure, which is due to phases of enhanced air flow in the cave and extremely reduced drip supply (most are visible in the lower part of the gallery). These structure can be found also in the stalagmite section and have been related to glacial conditions (e.g. Drysdale et al., 2004), when harsh climate was present outside the cave. In the central part of the very tall gallery series, white stalagmites are present. These are related to a generalised phase of aragonite deposition not well understood. Several broken stalagmites (plus a minor number collected in situ) was studied and dated as well as more than 6 m of flowstone cores. Radiometric ages indicated the most important phase of concretion was produced between ca. 100 to 800-900 ka, although this seems marked by some phase of partial interruption, probably due to local changes in the flow paths and/or climatic condition. We cannot rule out that some particular prominent phases of tectonic uplift can have regulated phases of depositions. However, carbon isotope composition from speleothems seems to suggest that the soil-epikarst system above the cave did not change much in the last million year.

The Levigliani mercury mine

The mining works of Levigliani (Fig. 3.17), abandoned since 1970, have been recently transformed in a touristic mining park (managed by Cooperativa Sviluppo e Futuro Levigliani a.r.l.). The old mining plants and the entrance of the underground works are now easily accessible and part of tunnels are safely and scenically lightened. The tourist visit of the Hg mine is part of the so-called “Corchia underground” project, developed to provide an interesting view of both natural and artificial underground cavities.
The outcrops of Hg orebodies can be observed in detail thanks to the several tunnels, ramps and openings excavated during the mining activity.

Stop 6: Cava Romana

This adit come first after the ticket office near the entrance of the mining park. A short crosscut drift (ca. 25 m long; 518 m a.s.l.), almost orthogonal to the main scistosity, allows the access at the base of an inclined excavation opening descending from the surface (entrance of the inclined room is at 535 m a.s.l.). An inclined green metatufite layer (max. 1 meter thick; N20 45E) with cinnabar disseminations and veinlets was exploited by room and pillar operations (Fig. 3.18a). The large pillar sustaining

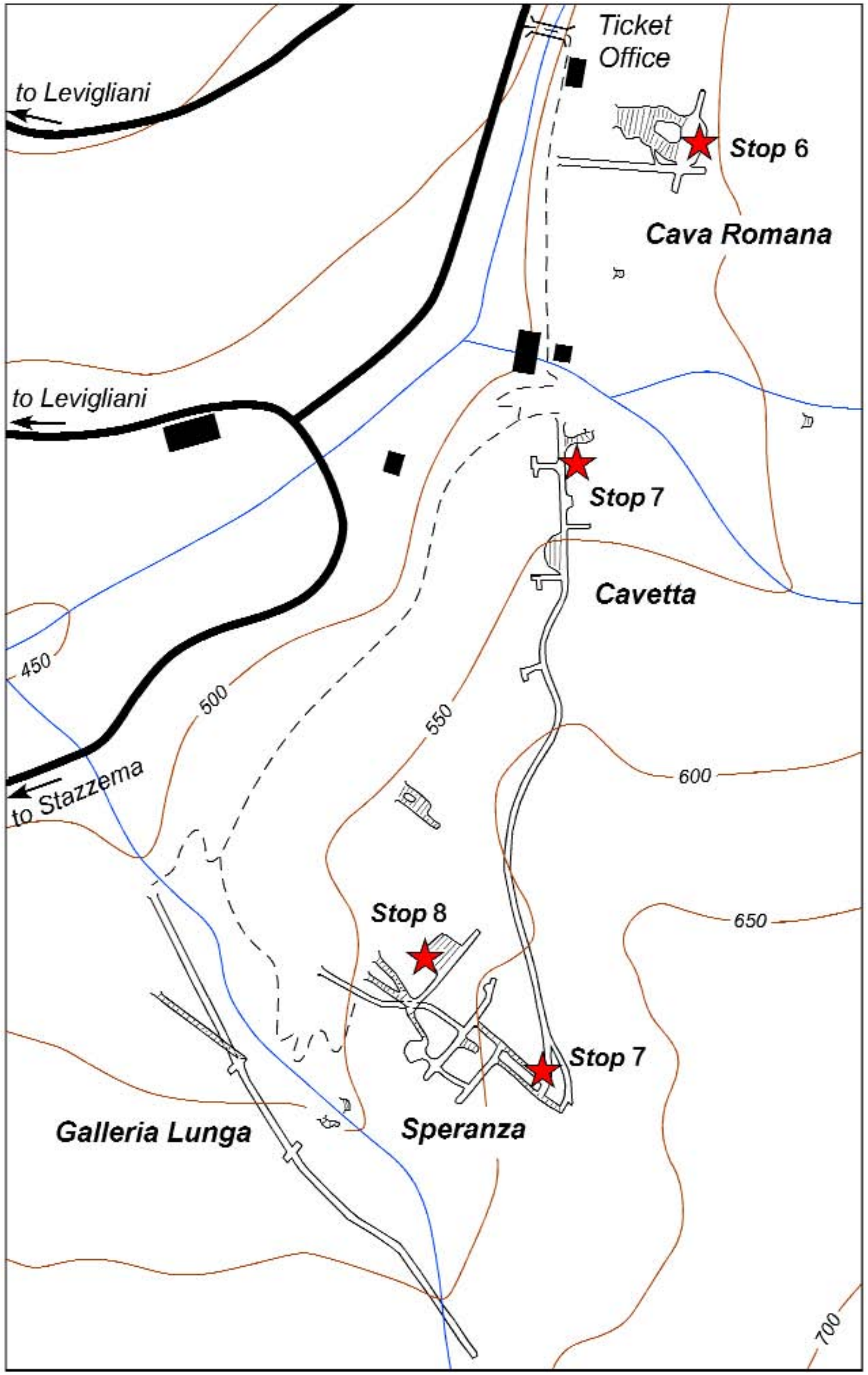

Fig. 3.17 - Schematic map showing the underground works at Levigliani mine and the geological stops.

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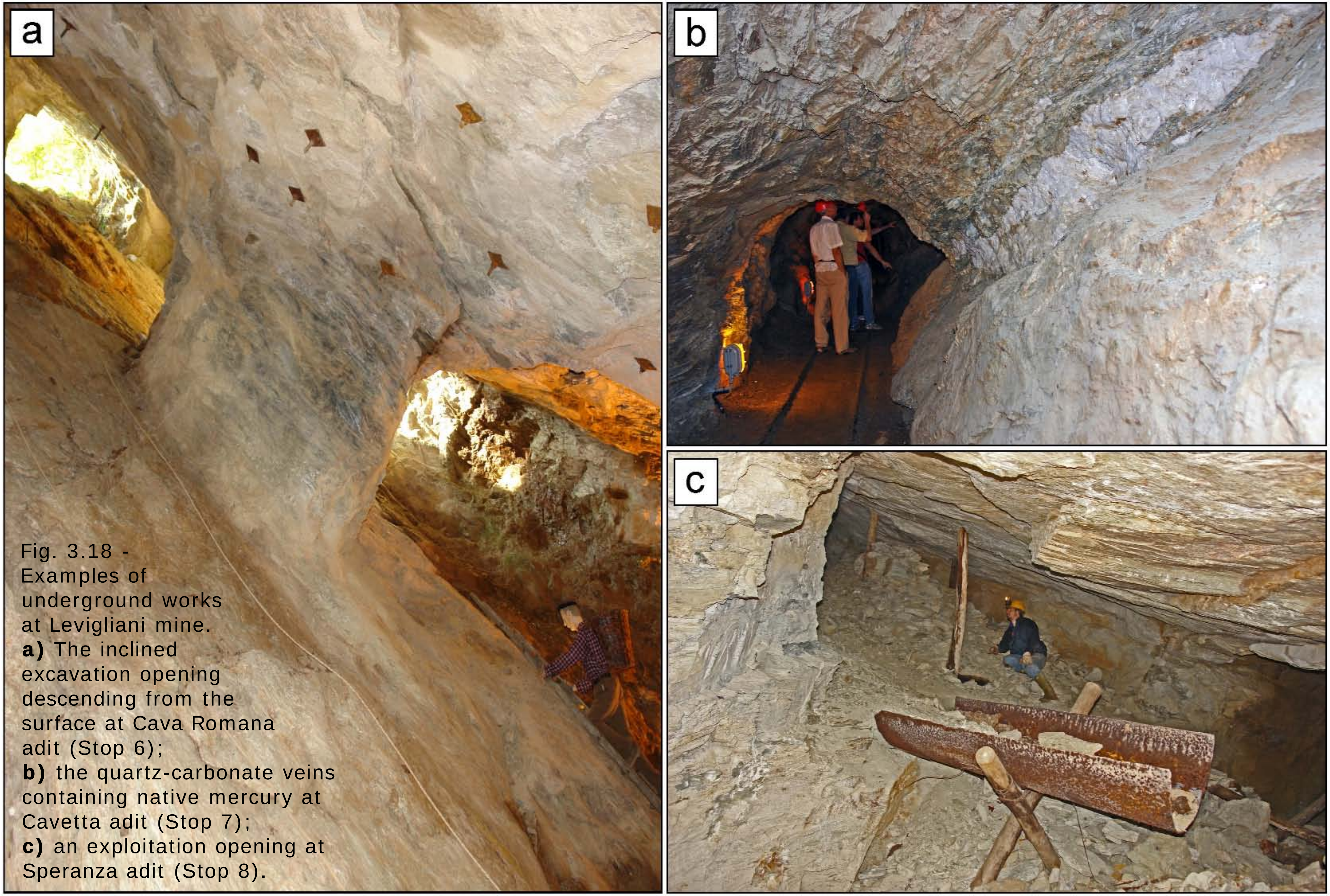

Fig. 3.18 - Examples of underground works at Levigliani mine.
a) The inclined excavation opening descending from the surface at Cava Romana adit (Stop 6);
b) the quartz-carbonate veins containing native mercury at Cavetta adit (Stop 7);
c) an exploitation opening at Speranza adit (Stop 8).

the hanging-wall is made by metatufite showing its typical structure/texture with several generations of strongly deformed Fe-Mg-carbonate veinlets and quartz-carbonate veins with cinnabar and rarely native mercury. Exploitation was continued few meters under the drift level leaving a large hole now filled by clear water. Coming back along the drift into the hanging-wall grey phyllites, few meters below the lower contact with metatufites, it is possible to observe a small quartz-carbonate veinlet with droplets of native mercury that crosscut the main scistosity. It may represents the escaping path of Hg-rich fluids derived by late-tectonic re-mobilization of disseminated cinnabar ore. Quartz contains many small fluid inclusions made by H_2O and Hg.

Stop 7: Cavetta Tunnel

After the entrance of Cava Romana adit the path crosses the remains of plants for mineral separation and mercury distillation. Then the path rise to the main mining area: the Cavetta adit (530 m a.s.l.). The Cavetta tunnel represented the access route to the main productive zone of the ore deposit. It was used for drawing off the ore from both the Cavetta (native Hg) and Speranza (cinnabar) adits, as well as for intake air and haulage. The Cavetta tunnel was driven along strike into a swarm of sub-parallel quartz-carbonate veins/veinlets with native mercury, cinnabar, mercurian sphalerite, pyrite, chalcopyrite, etc. (Fig. 3.18b and 3.19a-b). Here, about ten years ago were discovered tiny grey prismatic crystals of a new bismuth-mercury sulfosalt: the grumiplucite (Fig. 3.19d; Orlandi et al., 1998). Quartz veins display small cavities (1-10 mm^3) variably filled by native mercury; opening of such cavities by digging sometimes produces a weeping of mercury. During exploitation in XVIII century very large cavities were found. Targioni Tozzetti (1776) wrote: *"one time, after blasting, mercury weepeed for six minutes and the miners had not enough flasks that also two helmets were half-filled"*. The veins are hosted by grey phyllites placed at the hanging wall of a metatufite layer (the along strike continuation of that exploited at Cava Romana adit). Hg-rich quartz veins are well-exposed at the entrance of the tunnel and can be followed for several tens of meters inside. However, after about 70 m the number of Hg-rich veins suddenly decrease and the tunnel continue for about 130 m in barren grey phyllites until it reach the base of the Speranza adit. Here the tunnel enter a mineralized metatufite layer descending from the external outcrops placed on the opposite side of the hill (at ca. 573 m a.s.l.). Two parallel ramps connect three levels that explored/exploited disseminations and veins of cinnabar, zincian metacinnabar, mercurian sphalerite and pyrite. A beautiful isoclinally folded quartz-cinnabar vein associated with many flattened and elongated cinnabar disseminations can be observed at the base of the first ramp.

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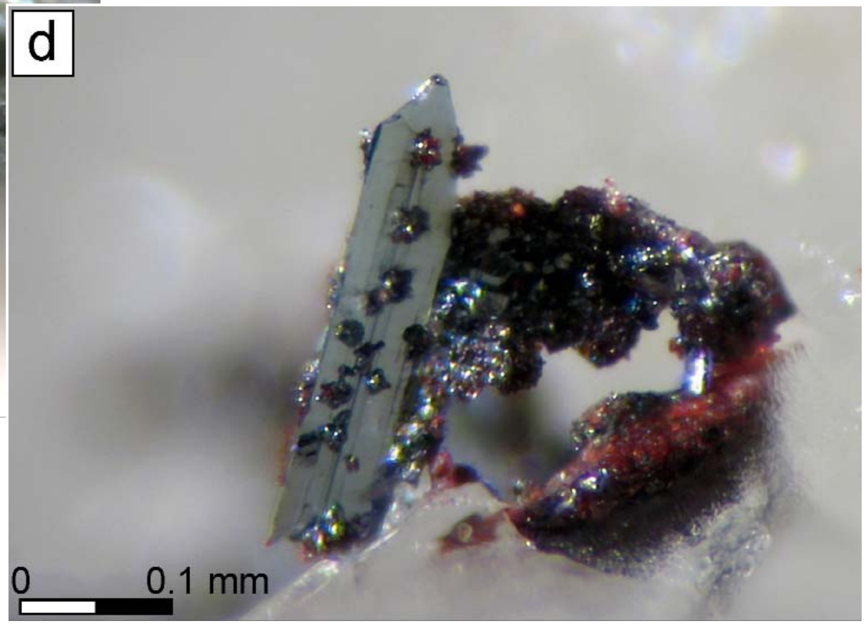

Fig. 3.19 - Microphotographs of minerals found into the vugs of quartz veins at Levigliani. **a)** a prismatic exagonal cinnabar crystal modified by rombohedron faces; Cavetta adit (Stop 7); **b)** droplets of native mercury associated with quartz and creamy dolomite; Cavetta adit (Stop 7); **c)** a crystal of zincian metacinnabar with quartz; Speranza adit (Stop 8); **d)** a tiny tabular crystal of grumiplucite ($HgBi_2S_4$) associated with cinnabar, mercurian sphalerite and native mercury; Cavetta adit (Stop 7).

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Stop 8: Speranza

From the entrance of Cavetta tunnel, a small trail leads to the upper mining adit (Speranza). First the path reaches the Galleria Lunga adit (535 m a.s.l.), then it rise up to the entrance of the Speranza excavation openings (ca. 573 m a.s.l.). The descending ramps follow a green metatufite layer with cinnabar disseminations and quartz-cinnabar veins (max. 1 meter thick; N45 30-45E). Several steps digged into the rock and a rope help the descent to the first level (ca. 564 a.s.l.). Here are exposed outcrops of mineralized metatufites with cinnabar disseminations and quartz veins containing cinnabar, zincian metacinnabar, mercurian sphalerite, etc. (Fig. 3.18c and 3.19c). A peculiar feature of this area is the presence of large cubic porphyroblasts of pyrite (up to 2 cm) with beautiful pressure shadows of quartz and cinnabar (Fig. 3.4c and 3.4e).

memorandum

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