Inactive Hydrothermal Hypogenic Karst in SW Sardinia (Italy)

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Abstract

In Sardinia, no active hypogenic caves have yet been discovered or described. Although there are a few thermal springs, mostly correlated to Quaternary volcanic activity, none of these thermal waters have interacted with carbonate rocks. Nevertheless, in the SW of the Island many metal ore deposits hosted in Cambrian limestones have been exploited over the last two centuries, allowing the discovery of so-called mine caves, some of which are clearly of hypogenic origin. These caves formed by thermal waters in a phreatic setting and are now located far above the water table and are no longer active, apart from some recent dripstone formation. The mine tunnels in Mount San Giovanni, near Iglesias and Gonnesa towns, have cut most of these caves: among them the well-known Santa Barbara cave, covered with barite crystals, Santa Barbara 2 cave, with its unique oxidation vents, and Crovassa Ricchi in Argento. Other hypogenic caves have been discovered in the mines of Campo Pisano and Monteponi (Iglesias), Mount Onixeddu (Gonnesa), and especially Masua (Iglesias). A very special case of hypogenic cave is the Corona ’e Sa Craba quartzite system, known for its barite crystals and rich in many mineral species. This chapter summarizes these known inactive hydrothermal and sulfuric acid caves.

Keywords

Hypogenic caves • Sardinia • Mine caves • Cave minerals • Quartzite cave

1 Introduction

Despite the fact that less than 10% of its surface is characterized by the outcropping of carbonate rocks, Sardinia is one of Italy’s most popular caving areas, hosting some of the most beautiful and extensive cave systems of the entire country. None of these caves, however, appear to be of hypogenic origin, and all most important systems are epigenetic ones in which surface runoff collects and flows downstream to the karst springs.

The only exception to this general rule appears to be the so-called mine caves, natural often bell-shaped voids inter-

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cepted by industrial mining activities in the SW of the Island. Mine tunneling occurred at various altitudes and extended deep below the surface, and even below the present sea level, thanks to an ingenious system of artificial lowering of the water table. This allowed discovering also natural voids deep below the natural water table level. These caves never extend for more than a couple of hundred meters and are characterized by a set of typical hydrothermal morphologies (cupolas, megascallops, etc.) and a wide variety of cave minerals. One of the richest mineralogical sites is the Corona 'e Sa Craba cave, near Barbusi, a unique hydrothermal cave carved in quartzite.

Here we summarize the present knowledge on this inactive hypogenic karst and its caves, with details on their speleogenesis, their morphology, and their secondary cave deposits.

2 Geographical and Geological Outline

All inactive hypogenic caves in Sardinia are located in the Iglesiente-Sulcis mining district, in the SW of the Island (Fig. 1). This area is characterized by almost hundred abandoned mines that mainly exploited ore deposits of lead, zinc, silver, and barium (Bechstadt and Boni 1996). Mine activities started around 600 B.C. with Sardinian (Nuragic) people followed by Phoenicians and Romans. These exploitations went on discontinuously in the Medieval age and developed industrially in the second half of the nineteenth century. The most important of these mines have been closed down in the period 1960–1990. The main Mississippi Valley-type Pb–Zn ores are hosted in the carbonate lithologies of the Cambrian sequence, constituting the oldest outcropping rocks of Italy. This poorly metamorphosed sedimentary succession starts

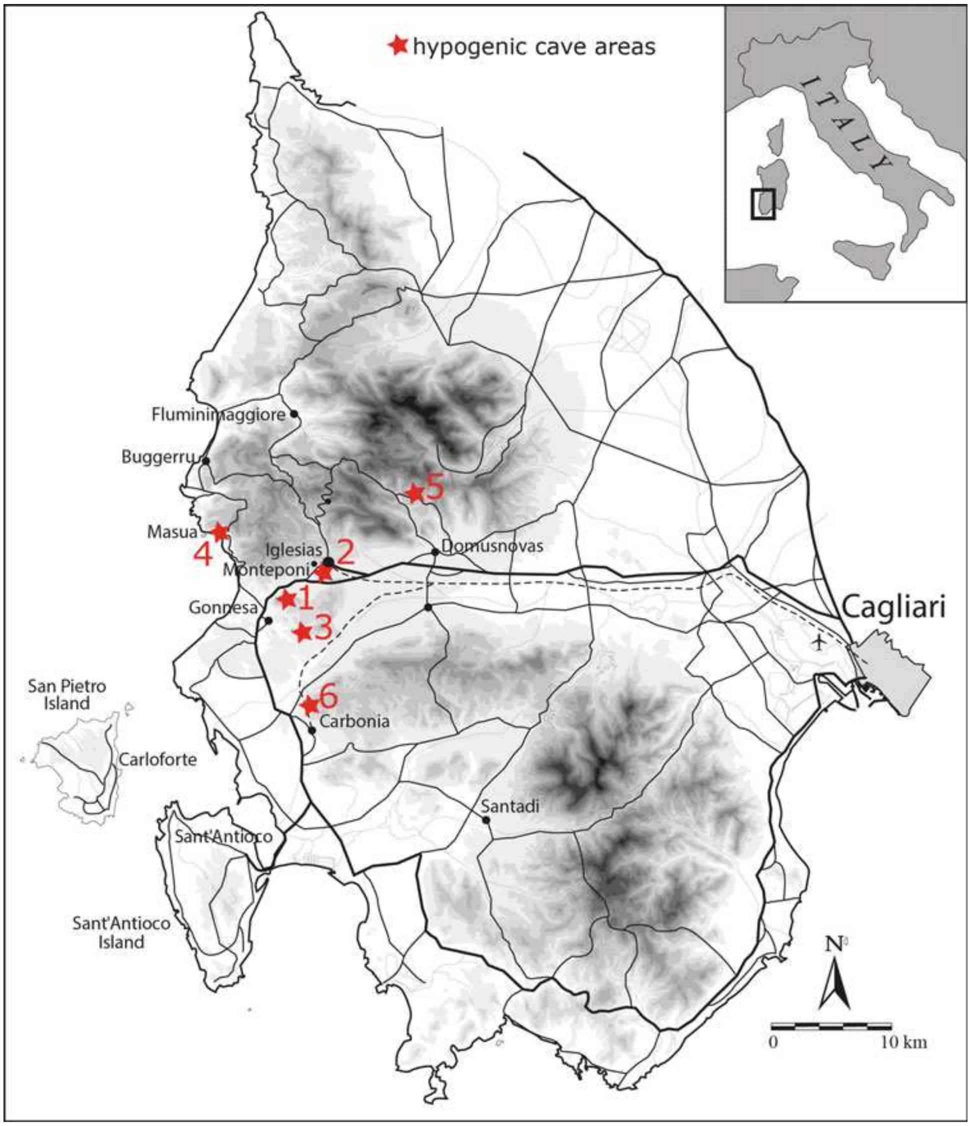


Fig. 1 Iglesiente-Sulcis area (SW Sardinia) and the main mine areas in which hypogenic caves have been encountered: *1* Monte San Giovanni; *2* Monteponi–Campo Pisano; *3* Monte Onixeddu–Monte Barega; *4* Masua; *5* Monte Guisi; *6* Corona 'e Sa Craba

with sandstones of the Nebida Group, followed by the dolomites and limestones of the Gonnesa Group and ending with the Nodular limestones and slates of the Iglesias Group. An angular unconformity separates these rocks from the overlying Ordovician and Silurian clastic sediments (Bechstadt and Boni 1996; Pillola 1989). This part of Sardinia was submerged again from Middle Ordovician to Middle Carboniferous, undergoing surface and subsurface erosion and corrosion during Late Carboniferous–Lower Triassic. Many of the hypogenic caves have probably formed during this continental period under thermal phreatic conditions (De Waele et al. 2013). A new transgression during Middle–Late Triassic submerged the area again, and most of the caves have been below the water table ever since. An intense tectonic and volcanic activity related to the opening of the Balearic and Tyrrhenian basins in the Oligocene–Miocene caused a renewal of circulation of thermal waters, probably remobilizing ore deposits and causing the deposition of many of the calcite spars and barite crystals found in the hypogenic caves. During the Quaternary, most of the higher located caves moved out of the phreatic zone and vadose speleothems could start developing, other caves were located in the epiphreatic or shallow phreatic zone with deposition of mammillary calcite (cave clouds), while others were located deep in the aquifer until very recently, when the mine exploitation required pumping the water level far below sea level (Cidu et al. 2011).

3 The Main Hypogenic Caves

Mines have occasionally intercepted caves since a long time, and some of these are mentioned in reports of the mine engineers. In an E–W striking longitudinal profile of Mount San Giovanni along the ore bodies of the "Ricchi in Argento" sector of the mine, many karst bodies and voids are clearly visible, some of which correspond to caves explored and surveyed almost a century later (Fig. 2). One of the most famous mine caves is the Santa Barbara cave, discovered in 1952 and, with reason, protected by the mine company itself because of its exceptional beauty. This cave has been surveyed by cavers from Bologna almost 30 years later (Fabbri and Forti 1981) and is now a show cave with limited visitors (Pagliara et al. 2010). A student in mine engineering and caver from Turin, who spent some time working in the mine in the late 1950s, also reports on some caves in San Giovanni mine (Fusina 1959), accurately describing some of the large caverns encountered by the mine tunnels. Well-organized exploration of the caves in the mines started when the exploitation of ores came to an end, in the late 1970s to early 1980s. Speleological exploration in the abandoned mines is still ongoing, and from time to time new caverns are discovered and surveyed.

Table 1 reports some of the most important hypogenic mine caves of SW Sardinia. Some mine caves of hypogene origin but of smaller dimensions are not reported in this table [e.g., Grotta Eraldo (Barega), Grotta di Monte Guisi (Domusnovas), Grotta del Gas and Grotta delle Budella (Masua)].

3.1 Mount San Giovanni

The most important and best-studied area for what concerns the hypogenic mine caves is the Mount San Giovanni, near Iglesias (De Waele et al. 2013). This mine has exploited the southern limb of the Iglesias syncline, composed of Cambrian limestones and dolostones sandwiched between the lower lying sandstones and overlying phyllites of the same age (Brusca and Dessau 1968). The over 100 km of mine galleries and shafts have allowed to discover more than 50 karst voids without any natural entrance at the surface, for a total development of around 4 km of cave passages. Most of these caves are of hypogenic origin and are now inactive except for some recent dripstone formation.

3.1.1 Santa Barbara Cave System

Surely the best-known hypogenic cave of Sardinia is the Santa Barbara system, composed of two caves developed along the contact between the "*Calcari Ceroidi*" of the San Giovanni and the "*Dolomia Rigata*" of Santa Barbara formations and separated vertically by only a few tens of meters (Fig. 3). Santa Barbara 1 develops between 180 and 227 m a.s.l. and was the first discovered during mining activities in 1952 (Fabbri and Forti 1981). It is famous because its walls and ceiling are entirely covered with brownish barite crystals (Rossetti and Zucchini 1956) and the main room is filled with large carbonate flowstones (Pagliara et al. 2010). The lower Santa Barbara II cave (between 52 to 145 m a.s.l.) (Fabbri and Forti 1986; Badino and Messina 2005) is instead poor in speleothems (except for the widespread presence of mammillary calcite coating the walls which formed in shallow phreatic conditions) and filled with a thick sedimentary sequence (Bini et al. 1988). This cave has a series of very spectacular corrosion morphologies, including megascallops, cupolas, and the extremely rare oxidation vents (De Waele and Forti 2006) clearly showing its hypogenic origin.

3.1.2 Crovassa Ricchi in Argento–Grotta Pisani–Grotta Quarziti

In the same mountain, but more to the west, a series of hypogenic caves has been unveiled along the Idina mine tunnel, at around 220 m a.s.l (Messina et al. 2005). Those are named Grotta Quarziti, in which a unique large hemimorphite flowstone has been found (Forti et al. 1999;

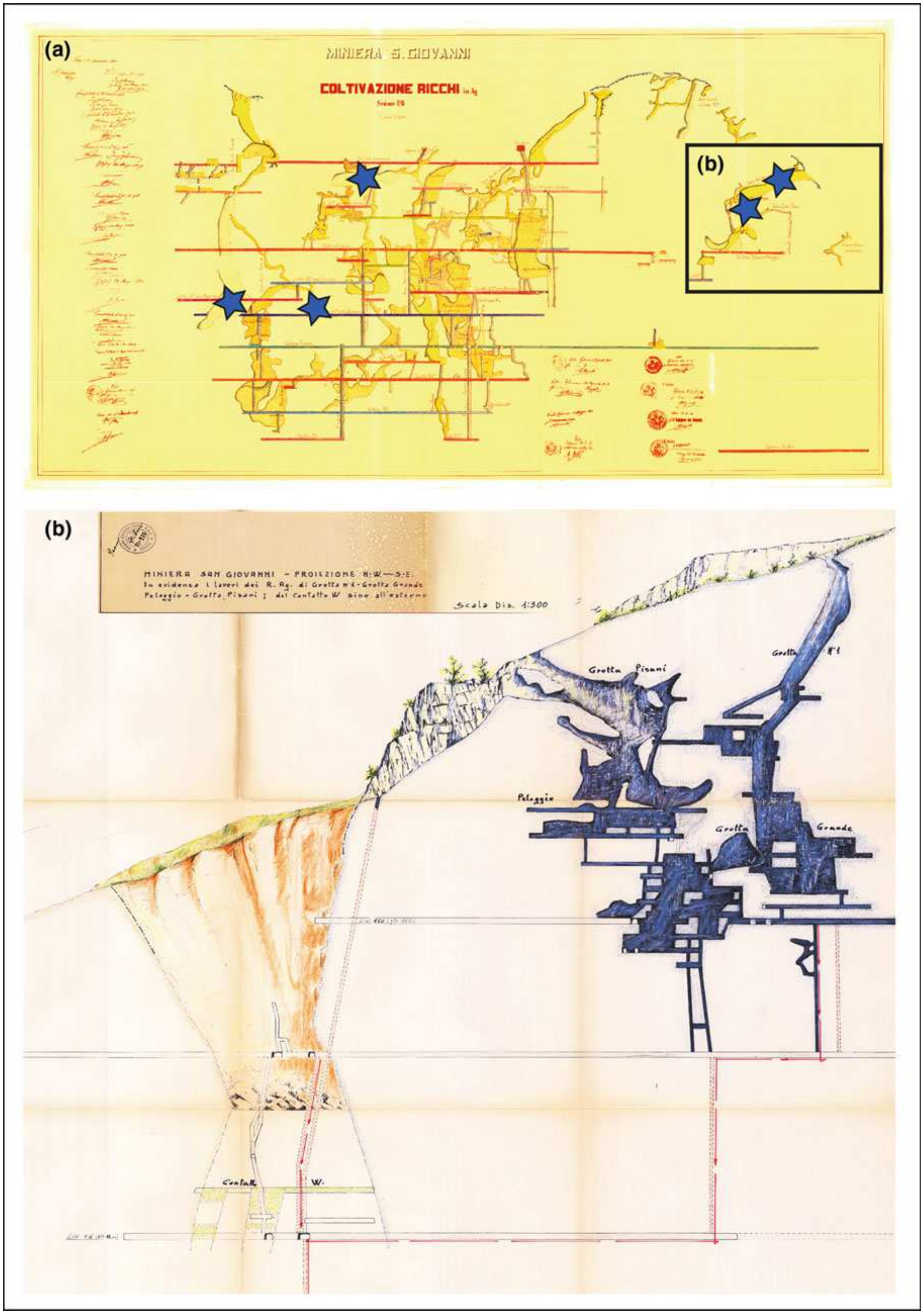


Fig. 2 E–W cross section through the "Ricchi in Argento" sector of San Giovanni Mine. **a** The *stars* indicate the caves signed on the map (they are mentioned with the word "Crevasse"); **b** detail of the western sector (inset **b** in **a**) with the Grotta Pisani and Grotta Grande mentioned. Both maps are from the first decade in the twentieth century

Table 1 List of the main hypogene mine caves of Sardinia and their specific volume

N°	Name of cave		Length (L) (in m)	Volume (V) (in m^3)	Specific volume (V/L) (in m^3/m)
210	Grotta S. Barbara	S. Giovanni	55	6000	110
639	Grotta della Colonna Egiziana	S. Giovanni	40	12,000	300
1122	Grotta Grande M. Onixeddu	Onixeddu	40	10,000	250
1381	Grotta delle Cinque Colonne	Onixeddu	25	1000	40
1527	Grotta Barega	Barega	60	70,000	120
1695	Grotta Phaff 1	Masua	35	18,000	510
1696	Grotta Phaff 2	Masua	35	17,000	480
1838	Crovassa de S'Azzurra	S. Giovanni	15	1500	100
1842	Grotta Eraldo	Barega	40	1500	40
1843	Grotta Cantiere S. Barbara	Monteponi	32	10,000	310
1872	Grotta delle Cupole	Masua	20	7000	350
2320	Grotta di S. Barbara 2	S. Giovanni	40	10,000	250
2405	Sa Crovassa de Trexentusu	S. Giovanni	75	30,000	400
2469	Crovassa Quarziti	S. Giovanni	40	20,000	500
2470	Grotta Pisani	S. Giovanni	60	24,000	400
2534	Crovassa "Ricchi in Argento"	S. Giovanni	100	90,000	900
2785	Grotta Grande di Pelloggio	S. Giovanni	30	3000	100
2789	Grotta di Albert n° 7	S. Giovanni	30	4500	150

Gázquez et al. 2015) (Fig. 4), and Grotta Ricchi in Argento, with thermal calcite spars covered with orange indurated crusts (Gázquez et al. 2013). At a higher level (around 275 m a.s.l), the Grotta Pisani cave still hosts the signs of ancient mining works.

3.1.3 Crovassa Azzurra

Close to the Idina Gallery, another mine adit (Peloggio level) allows to reach the well-known Crovassa Azzurra, at 218 m a.s.l. This cave is a small isolated room that was originally filled with exceptional blue aragonite flowstones. The morphology of the cave is typical of a hypogenic origin. Recently the mineralogy and geochemistry of these blue aragonite flowstones have been studied in great detail (Caddeo et al. 2011).

3.1.4 Massa Riccardo–Albert

Almost at the same altitude (226 m a.s.l), another mine gallery has cut several caves, some of which are vadose shafts, but others are of clear hypogenic origin. The two caves at Massa Riccardo are bell-shaped caves with nice cupola morphologies and speleothems (stalactites and stalagmites) composed of hydrozincite.

3.2 Campo Pisano–Monteponi

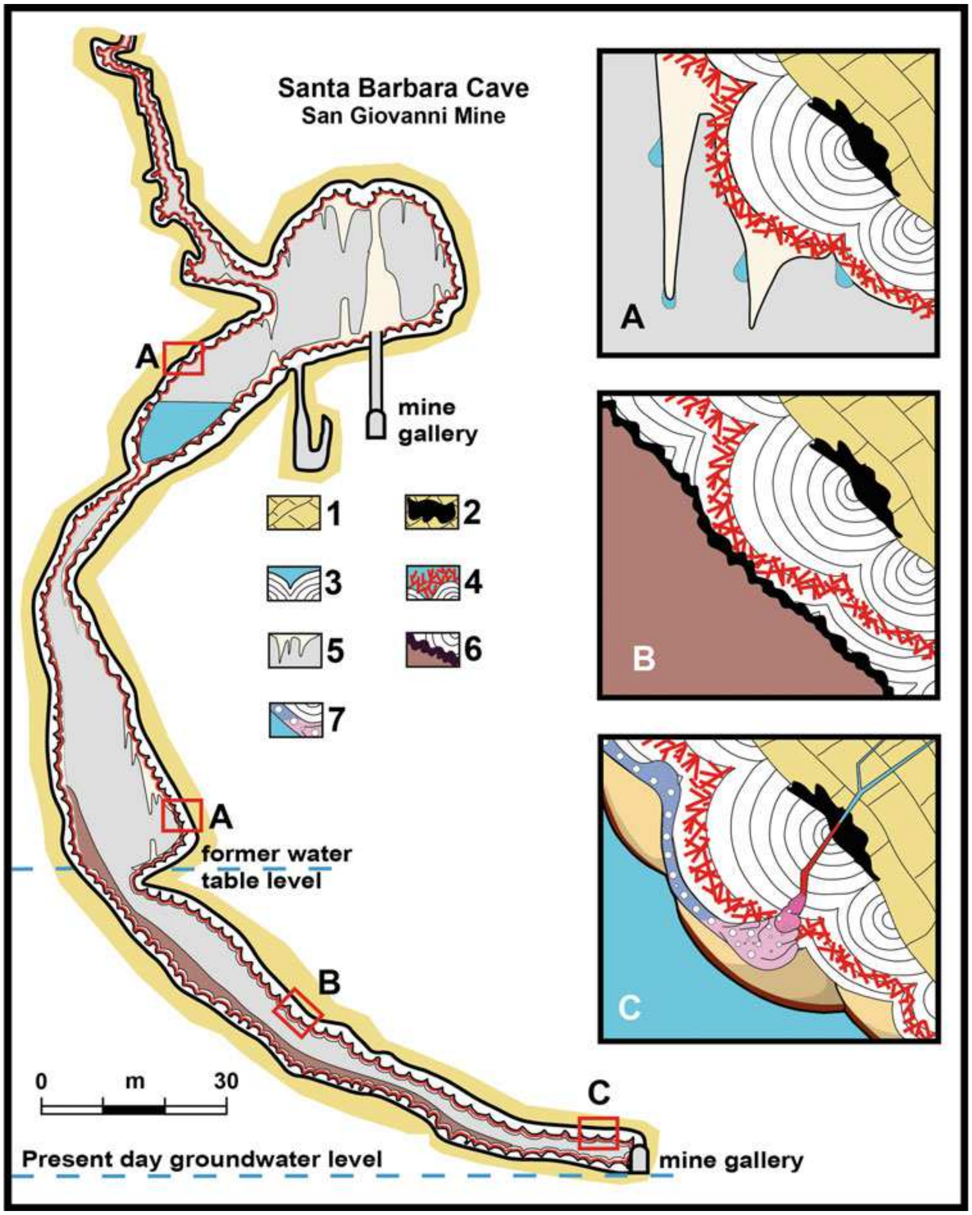
On the other flank of the Iglesias syncline two other mines have excavated over 100 km of underground galleries, encountering several mine caves, some of which are of clear hypogenic origin. These caves are typically bell-shaped isolated rooms of deep phreatic origin (Naseddu 1993). One of these is the Gran Sorgente that discharged over 1 m^3/sec into the mine and obliged the mine companies to carve an 8-km-long drainage gallery to allow the water to be drained from 8 m a.s.l directly to the sea at Funtanamare (Forti and Perna 1982; Civita et al. 1983).

3.3 Mount Onixeddu–Mount Barega

Another Cambrian limestone ridge outcrops a couple of kilometers south of the Iglesias syncline and contains a series of mines. Several mine caves have been discovered in Mount Onixeddu and are similar to the other mine caves of hypogenic origin (Sanna et al. 1999).

At the nearby Barega mine, a few mine caves have been discovered, in one of which (Grotta Eraldo) large

Fig. 3 Santa Barbara cave system: *1* Cambrian carbonate rocks; *2* MVT ore deposits (mainly galena and sphalerite); *3* mammillary calcite (cave clouds); *4* barite crystals; *5* vadose speleothems (stalactites, stalagmites, columns, etc.); *6* corrosion of cave clouds (and deposition of oxides–hydroxides, *black*) under clayey deposits (*brown*); *7* creation of bubble trails and oxidation vents. The evolution of the whole system was the same until the lowering of the groundwater level (not later than 250 ka) caused the differentiation of the processes above and below. In the upper part of Grotta Santa Barbara *1* and *2* vadose speleothems developed (*A*), while in the flooded parts oxidation processes induced the strong corrosion of the cave clouds below the thick clay deposits (*B*), while oxidation vents developed over the cave clouds not in contact with the mud (*C*)



sedimentary deposits of a sulfuric acid derived mineral halloysite were discovered (De Waele et al. 2008), together with nice barite crystals tapering the walls of the cave and filling a fracture (Naseddu 1993). A typical bell-shaped room covered with calcite crystals and also containing aragonite helictites has also been surveyed in this mine (De Waele and Messina 2004).

3.4 Masua

Another mine in which many hypogenic caves have been discovered is Masua, along the coast in front of the Pan di Zucchero islet (Forti et al. 1981). Several bell-shaped rooms are known (Phaff caves), some of which are entirely covered with calcite dogtooth spar, with crystals reaching several decimeters in length (Forti and Perna 1982) (Fig. 5). Fluid inclusions in these crystals and in barite and quartz have clearly demonstrated their thermal origin (De Vivo et al. 1987).

Two other caves have been discovered in this mine, both of which have clear signs of being formed under thermal conditions (Chiesi and Forti 1987). They are located in the mine level −42 m below sea level and became accessible when the mine pumped the water. The walls of both caves are covered with mammillary calcite (cave clouds), which in Grotta delle Budella cover corroded calcite crystals grown in thermal waters.

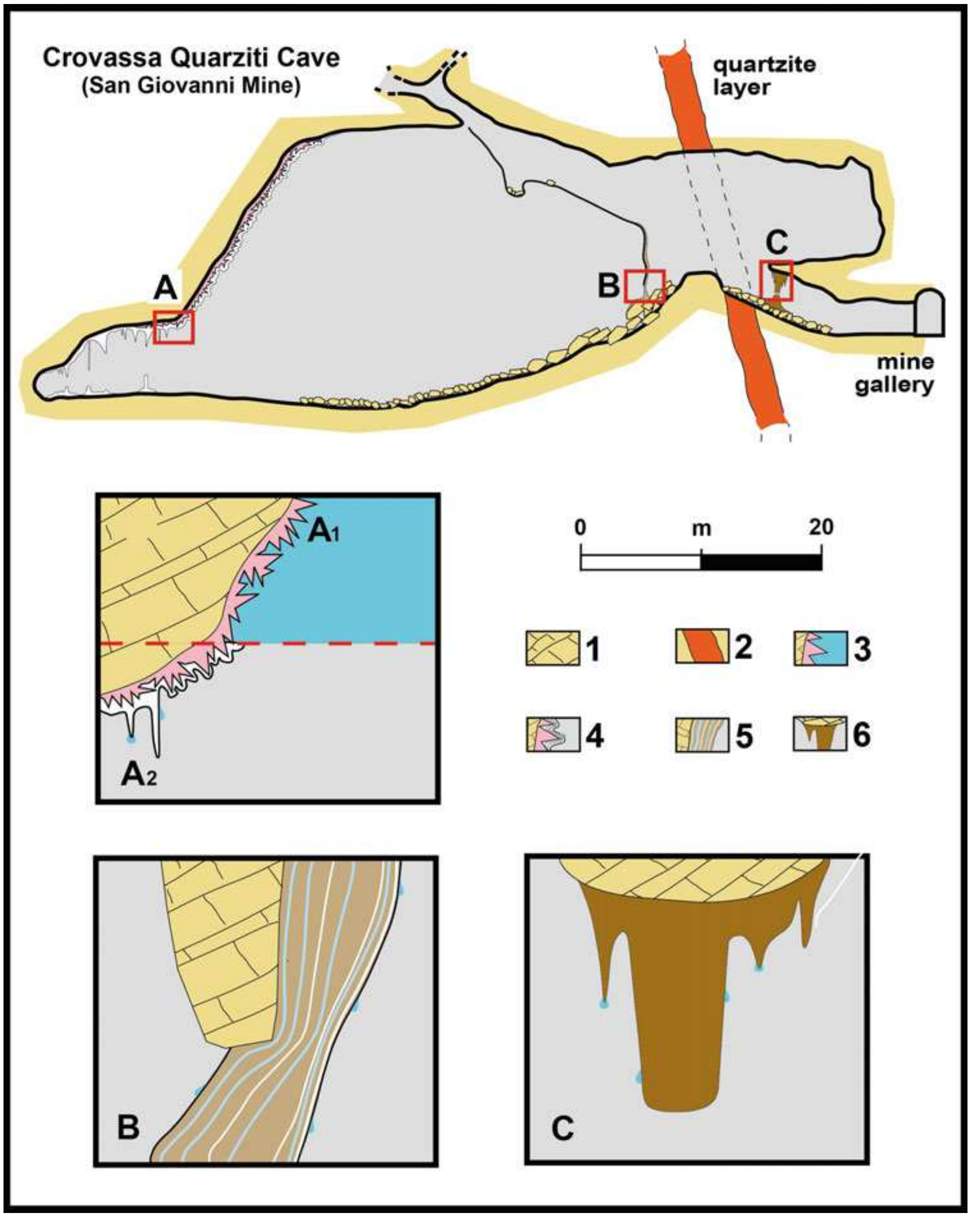


Fig. 4 Grotta Quarziti: *1* Cambrian carbonate rocks; *2* quartzite vein; *3* calcite dogtooth spar; *4* vadose calcite speleothems; *5* opal–hemimorphite–calcite flowstone; *6* hemimorphite dripstones. The thermal calcite macrocrystals (*A1*) represented the first stage in the chemical deposition. These calcites were later covered by cave clouds and after the lowering of the groundwater (ca. 250 ka) by gravitational speleothem formations (*A2*); during the latest vadose stage, an opal–hemimorphite–calcite flowstone (*B*) and a large hemimorphite dripstone (*C*) developed both being related to the quartzite layer and sulfide orebodies

3.5 Monte Guisi Cave

Monte Guisi is located 8 km north of Domusnovas, at the contact between Cambrian limestones and the granitic Variscan basement rocks. The intrusion of these granites has caused the limestones to be metamorphosed, also resulting in the emplacement of a calcic skarn deposit containing Pb, Zn, Fe, and Cu. The cave is carved in these skarns probably in several episodes, some of which are clearly of thermal hypogenic nature. The cave is a small labyrinth accessible by an accidental shaft and shows some clear hypogenic dissolution morphologies (cupolas, swiss cheese morphologies). It is only 70 m long, but it is of a great mineralogical interest (Moldovan et al. 2013).

3.6 Corona 'e Sa Craba Quartzite Cave

Close to Carbonia, near the small village of Barbusi, a 100 m thick quartzite vein scars the landscape forming a prominent N–S-oriented ridge. Within this quartzite, a 250-m-long cave has been carved (Sauro et al. 2014). The Corona 'e Sa Craba cave is renowned for its beautiful bluish barite crystals covering parts of its roof. The cave also hosts

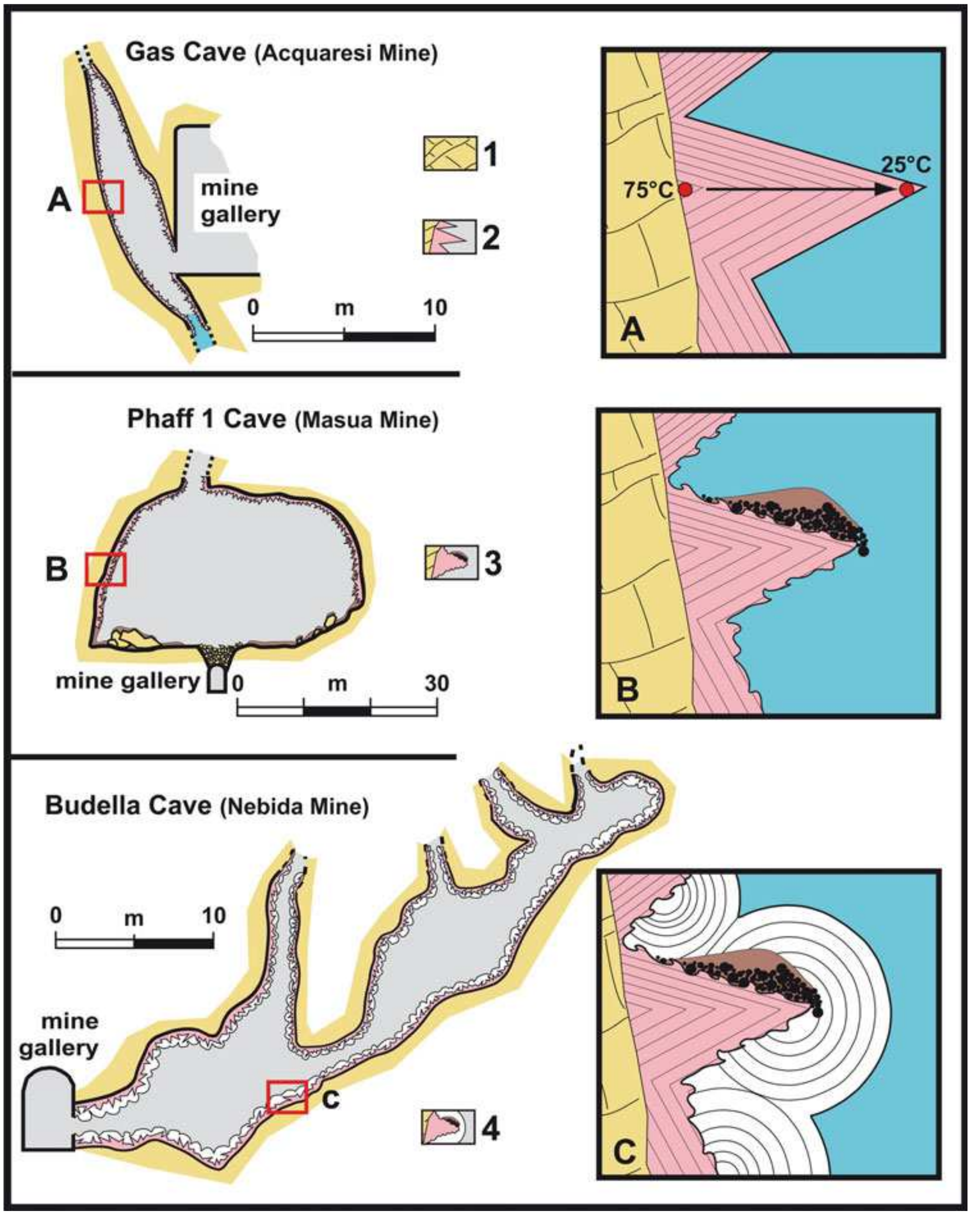


Fig. 5 Hypogene mine cave in the Masua area. *1* Cambrian carbonate rocks; *2* calcite dogtooth spar; *3* corroded calcite spars with oxidation residues; *4* mammillary calcite (cave clouds). The entire cave evolution occurred under phreatic conditions, and the first depositional stage was common to all caves and led to the evolution of thermal calcite dogtooth spar (*A*). Gas cave stopped its development at this stage. In the other two cavities, calcite macrocrystals underwent strong corrosion due to oxidation of the orebodies with deposition of oxides–hydroxides on the *upper* crystal faces (*B*); during a final stage, which took place only in the Budella cave, mammillary calcite (cave clouds) covered the corroded thermal calcite crystals (*C*)

other sulfates, besides many phosphates related to the presence of a large bat colony. Clear signs of intense corrosion in a thermal aquifer have allowed this quartzite cave to be defined as a hydrothermal hypogenic cave.

4 Morphological, Mineralogical and Geochemical Evidence for Hypogene Processes

Until recently, the speleological and scientific community did not regard the Iglesiente mine caves as being of hypogenic origin, despite the fact that several indices (i.e., fluid inclusion in calcite spars) were rather evident. This is mainly because many of these caves were not easily accessible (at least until the mines were closed), and abundant vadose speleothems cover and hide their typical hypogene characteristics. However, the shear size and shape of some of the voids clearly points to their origin in a thermal water body. The specific volume (the volume of the room divided by its major axis) of many of the mine caves clearly matches the typical values of those obtained in thermal caves (Frumkin and Fischhendler 2005) (Table 1).

Alongside this general morphology there are also several smaller subterranean parietal forms that indicate an origin in a setting of rising (thermal) fluids. Bubble trails, cupolas, and megascallops are widely present in many caves. Also local oxidation of the sulfide ores has enhanced the formation of sulfuric acid producing typical morphologies and replacement minerals (sulfates) (Audra et al. 2015). These processes probably occurred a long time ago, explaining the fact that gypsum, the most typical replacement mineral of sulfuric acid speleogenesis (SAS), is no longer present (De Waele et al. 2013). The unique oxidation vents in Santa Barbara 2 cave are clear evidence of these SAS episodes (De Waele and Forti 2006).

In addition to the morphological indicators that connect the genesis of the caves of the Sulcis-Iglesiente mining district to hypogene agents, there are a number of characteristic speleothems, whose presence indicates the ascent of deep-seated thermal waters and oxidation of Pb-Zn sulfides in the past. Typical secondary minerals found in the hypogenic caves are reported in Table 2. Note that many of these minerals are not associated with the active hypogene speleogenetic phases, but some (dogtooth calcite spars, and mainly oxides, hydroxides, silicates and sulfates) can be related to the cave-forming processes (Figs. 6a and 7b). The first vestige of high-temperature speleogenetic processes dates back to the Cambrian, as yellow speleothemic dolomite crystals (known as "dolomia gialla") filled small pockets of the carbonate bedrock. These primitive infillings are still visible in Santa Barbara Cave (Pagliara et al. 2010) and other locations in the Monte San Giovanni mine. In subsequent stages (Middle Ordovician–Middle Carboniferous), active oxidation of polymetallic sulfide orebodies took place as a consequence of the enhanced circulation of warmer meteoric water inside the system; this oxygen-rich water generated an intense alteration of sulfides and a partial re-mobilization of the ore bodies (De Vivo et al. 1987; Cortecci et al. 1989) and probably was responsible for deposition of massive metallic oxy-hydroxide deposits (Figs. 6b, 7b, d). Stable isotopes ($\delta^{18}O$ and $\delta^{34}S$) and micro-thermometry of fluid inclusions in barite from this period provide further support for this scenario of seawater–meteoric water mixing (Cortecci et al. 1989).

During this stage of sulfuric acid speleogenesis (SAS), precipitation of polymetallic oxy-hydroxides occurred in the upper, more oxygenated part of ore deposits, usually called *gossan* or iron cap. This intensely oxidized, weathered bedrock hosts iron–manganese oxides and quartz, often in the form of *boxwork* and pseudomorphs replacing the pyrite and primary ore minerals. This primitive stage of subaqueous speleogenesis and polymetallic oxy-hydroxides precipitation is clearly exposed in several caves of the Mount San Giovanni mine, including Massa Riccardo, Santa Barbara Cave, Crovassa Ricchi in Argento, and Grotta Quarziti (Figs. 3, 4, 6c, 7b, and 7d).

Massa Riccardo Cave shows massive goethite (α-FeO(OH)) and haematite (Fe_2O_3) deposits, which genesis preceded the precipitation of hydrozincite ($Zn_5(CO_3)_2(OH)_6$) (Fig. 6e), usually observed as white crusts, a few millimeters thick. The occurrence of hydrozincite could indicate a change in the pH of the solution, from acidic to more basic conditions, which enabled this mineral to precipitate. Likewise, Santa Barbara Cave hosts deposits of polymetallic oxy-hydroxides, including goethite, haeterolite ($ZnMn_2O_4$), hydrohaeterolite ($Zn_2Mn_4O_8 \cdot H_2O$), cesarolite ($PbMn_3O_7$ H_2O) and calcofanite ($ZnMn_3O_7 \cdot 3H_2O$), along with barite ($BaSO_4$), galena (PbS), sphalerite (ZnS), and cerussite ($PbCO_3$) (Pagliara et al. 2010). Phreatic and vadose conditions alternated from the Oligocene to the Pliocene, with periods of seawater ingression in the karst.

Subsequent stages were marked by the lowering of water temperature, as the solution reached the supersaturation in quartz (SiO_2) and calcite. First, quartz precipitated from highly saline solutions (13.3–23.3% NaCl eq.) at high temperature (70–112 °C). Later, water temperature decreased to 50–90 °C; then, rhombohedral and scalenohedral spars of calcite precipitated in voids of the bedrock from low-saline meteoric solutions (0.5–2.7% NaCl eq.) (De Vivo et al. 1987). This stage of relatively high-temperature and calcite precipitation is evidenced by the many widespread examples of calcite spars (sometimes tens of centimeters in size), covering the walls of most mine caves in the Sulcis-Iglesiente area, including Crovassa Azzurra (Caddeo et al. 2011), Crovassa Ricchi in Argento (Gázquez et al. 2013) (Fig. 7b), Grotta Quarziti (Fig. 7d), Grotta Barega (Fig. 7c), and the caves of the Masua mine (Figs. 5 and 6a) (De Vivo et al. 1987) among others (De Waele et al. 2013). Moreover, an additional phreatic stage of barite precipitation at around 50 °C has been suggested to occur in the setting of Corona 'e Sa Craba Cave (Sauro et al. 2014).

Further subaqueous freshwater conditions alternated with vadose stages during the Quaternary. During certain phase, the aquifer water level was relatively close to the level of the caves and subaqueous calcite speleothems precipitated, including mammillary calcite (cave clouds) and calcite crusts observed in the Capstan room of Masua mine (Fig. 5) and in the deeper levels of Santa Barbara Cave (Figs. 3 and 6d). These last calcite deposits formed at around 247 ± 17 ka (De Waele and Forti 2006) in epiphreatic conditions, by a slow mechanism of CO_2 degassing close to the water table; this appears to have occurred at temperature similar to the modern cave temperature (15–20 °C) or slightly higher, as suggested by $\delta^{18}O$ analyses of speleothemic carbonate (De Vivo et al. 1987). Interesting examples of low-temperature epiphreatic calcite speleothems have been described in Crovassa Azzurra, where cave clouds are exposed in the cave roof, whereas conical dogtooth calcite crystals, 5 to 10 cm in length, cover the walls to the height of roughly 3 m from the cave bottom. These calcite crystals probably formed during the Quaternary and indicate the position of the water level (~210 m a.s.l) at the time of formation. Cave clouds are also widely present in Santa Barbara 2 cave,

Table 2 Minerals of hypogenic mine caves in Sardinia

Mineral	Chemical formula	Mining area	Caves
Sulfides			
Galena	PbS	All	Many localities
Sphalerite	ZnS	All	Many localities
Cinnabar	HgS	Barbusi	Corona ‘e Sa Craba
Oxides/Hydroxides			
Cuprite	Cu_2O	Monte Guisi	Monte Guisi
Monteponite	CdO	Monteponi–Campo Pisano	Monteponi
Haematite	Fe_2O_3	M. S. Giovanni, Barbusi, M. Guisi	M. Riccardo, CSC, M. Guisi
Pyrolusite	MnO_2	Monte Guisi	Monte Guisi
Goethite	α-$FeO(OH)$	M. S. Giovanni, Barbusi, M Guisi	M. Riccardo, S. Barbara, CSC, M. Guisi
Lepidocrocite	$FeO(OH)$	Monte Guisi	Monte Guisi
Hetaerolite	$ZnMn_2O_4$	Mt San Giovanni	S. Barbara
Hydrohetaerolite	$Zn_2Mn_4O_8 \cdot H_2O$	Mt San Giovanni	S. Barbara
Cesarolite	$PbMn_3O_7 \cdot H_2O$	Mt San Giovanni	S. Barbara
Chalcophanite	$ZnMn_3O_7 \cdot 3H_2O$	Mt San Giovanni	S. Barbara
Coronadite (?)	$PbMn_8O_{16}$	Mt San Giovanni	S. Barbara
Carbonates			
Calcite	$CaCO_3$	All	Almost all locations
Siderite	$FeCO_3$	Monteponi–Campo Pisano	Monteponi
Smithsonite	$ZnCO_3$	Masua	Several caves
Aragonite	$CaCO_3$	All	Almost all locations
Cerussite	$PbCO_3$	Almost all	Many localities
Dolomite	$CaMg(CO_3)_2$	All	Almost all locations
Azurite	$Cu_3(CO_3)_2(OH)_2$	Monte Guisi	Monte Guisi
Rosasite	$(Cu, Zn)_2(CO_3)(OH)_2$	Monte Guisi	Monte Guisi
Malachite	$Cu_2(CO_3)(OH)_2$	Monte Guisi	Monte Guisi
Phosgenite	$Pb_2(CO_3)Cl_2$	Monteponi–Campo Pisano	Monteponi
Hydrozincite	$Zn_5(CO_3)_2(OH)_6$	Mt San Giovanni	Albert 7
Aurichalcite	$(Zn, Cu)_5(CO_3)_2(OH)_6$	Mt San Giovanni	Crovassa Azzurra
Dundasite	$PbAl_2(CO_3)_2(OH)_4 \cdot H_2O)$	Monte Guisi	Monte Guisi
Arsenates			
Ediphane	$Ca_2Pb_3(AsO_4)_3Cl$	Mt San Giovanni	S. Barbara
Sulfates			
Barite	$BaSO_4$	All	Corona ‘e Sa Craba, Barega, S. Barbara
Anglesite	$PbSO_4$	M. S. Giovanni, Monteponi–Campo Pisano, M. Guisi	San Giovanni, Monteponi, M. Guisi
Bianchite	$Zn_2Fe(SO_4)_3 \cdot 18H_2O$	Monteponi–Campo Pisano	Campo Pisano
Epsomite	$MgSO_4.7H_2O$	Mt San Giovanni	San Giovanni
Brochantite	$Cu_4SO_4(OH)_6$	Monte Guisi	Monte Guisi
Alunite	$KAl_3(SO_4)_2(OH)_6$	Barbusi	Corona ‘e Sa Craba
Basaluminite (= Felsőbányaite)	$Al_4(SO_4)(OH)_{10} \bullet 4H_2O$	Barbusi	Corona ‘e Sa Craba

(continued)

Table 2 (continued)

Mineral	Chemical formula	Mining area	Caves
Phosphates			
Tanarakite	$H_6K_3Al_5(PO_4)_8 \cdot 18H_2O$	Barbusi	Corona ‘e Sa Craba
Strengite Al rich	$(Fe, Al)(PO_4) \cdot 2H_2O$	Barbusi	Corona ‘e Sa Craba
Robertsite	$Ca_2Mn_3(PO_4)_3O_2 \cdot 3H_2O$	Barbusi	Corona ‘e Sa Craba
Spheniscidite	$(NH_4, K)(Fe, Al)_2(PO_4)_2(OH) \cdot 2H_2O$	Barbusi	Corona ‘e Sa Craba
Silicates			
Hemimorphite	$Zn_4Si_2O_7(OH_2 \cdot H_2O)$	Mt San Giovanni, M. Guisi	San Giovanni, M. Guisi
Shattuckite	$Cu_5(SiO_3)_4(OH)_2$	Monte Guisi	Monte Guisi
Plancheite	$Cu_8(Si_4O_{11})_2(OH)_4 \cdot H_2O$	Monte Guisi	Monte Guisi
Kaolinite	$Al_2Si_2O_5(OH)_4$	Mt San Giovanni	S. Barbara
Halloysite	$Al_2Si_2O_5(OH)_4$	Barbusi, Barega	Corona ‘e Sa Craba, Grotta Eraldo
Lizardite	$Mg_3Si_2O_5(OH)_4$	Barbusi	Corona ‘e Sa Craba
Chrysocolla	$(Cu, Al)_2H_2Si_2O_5(OH)_4 \cdot nH_2O)$	Monte Guisi	Monte Guisi
Quartz	SiO_2	Barbusi	Corona ‘e Sa Craba
Opal	SiO_2	Mt San Giovanni	San Giovanni

where they are intensely corroded (Fig. 6d), and in some caves in the Masua mine (e.g., Grotta delle Budella and Grotta delle Cupole) (Chiesi and Forti 1987). Although this kind of speleothem is typical of hypogenic/hydrothermal caves (e.g., Audra et al. 2009; Gázquez and Calaforra 2013, among others), some examples of cave clouds and other epiphreatic formations related to waters highly saturated in calcite have been described in non-thermal epigenic caves (e.g., D’Angeli et al. 2015).

During some periods, the karstic network was partially filled with detrital clayey sediments with significant amounts of Fe (8.4 wt%), Ba (3.8 wt%), K (2.9 wt%), and Zn (1.1 wt %), in addition to a great array of trace elements (Mn, Pb, Cu, etc.) below 0.5 wt% (Gázquez et al. 2013). Such high content of metals suggests that fine detrital materials interbedded in the carbonate sequence (mainly clay and silt) were decalcified and the insoluble residues incorporated into the subterranean flow. These red mud deposits are especially well preserved in Crovassa Ricchi in Argento (Fig. 7b) and Santa Barbara Cave (Fig. 7a). Oxidation of metallic ions in subaerial conditions in the wet clayey matrix lowered the pH and occasionally caused the corrosion of calcite spars and formation of orange indurated crusts (Gázquez et al. 2013). This is particularly well visible in the Phaff caves at Masua (Forti et al. 1981).

In Grotta Quarziti, goethite and haematite have been detected as a few centimeters thick layer on quartz substrate (Gázquez et al. 2015). Quartzite in this region formed during silicification events of tectonic breccia of dolomite clast (calcitic skarn), probably by fluids derived from deep-seated leucogranites during the Permian (Boni et al. 1992) or volcanic fluids in the Lower Oligocene (Sauro et al. 2014). Unlike in other caves of the Mount San Giovanni mine, in Grotta Quarziti the deposition of iron oxides probably occurred in subaerial conditions from a water film that flowed on the surface of the quartzitic substrate. During the Late Quaternary, high metal content in water supplied by mineralization in the host rock favored quartz dissolution and gave rise to relatively high concentration of H_4SiO_4 (aq) under neutral or slightly basic conditions. This produced subaerial hemimorphite ($Zn_4Si_2O_7(OH)_2 \cdot H_2O$) speleothem precipitation during the Late Quaternary in this and other caves (Fig. 7f) (i.e., Mount Guisi Cave; Moldovan et al. 2013; Gázquez et al. 2015) (Fig. 4).

Similar subaerial weathering processes have generated a wide variety of uncommon cave minerals, probably in “recent” times, such as anhydrous and hydrous sulfates and phosphates. In total, over 50 cave minerals have been described in these mine caves, enlarging the list originally published by De Waele and Forti (2005) (Table 1). This includes the recent discovery of the new cave minerals dundasite ($PbAl_2(CO_3)_2(OH)_4 \cdot H_2O$) and plancheite ($Cu_8(Si_4O_{11})_2(OH)_4 \cdot H_2O$) in Mount Guisi Cave (Moldovan et al. 2013) and several rare phosphates and sulfates in Corona ‘e Sa Craba Cave (Sauro et al. 2014). Also, during the Late Quaternary “conventional” carbonate speleothems formed in some of these caves, including stalagmites,

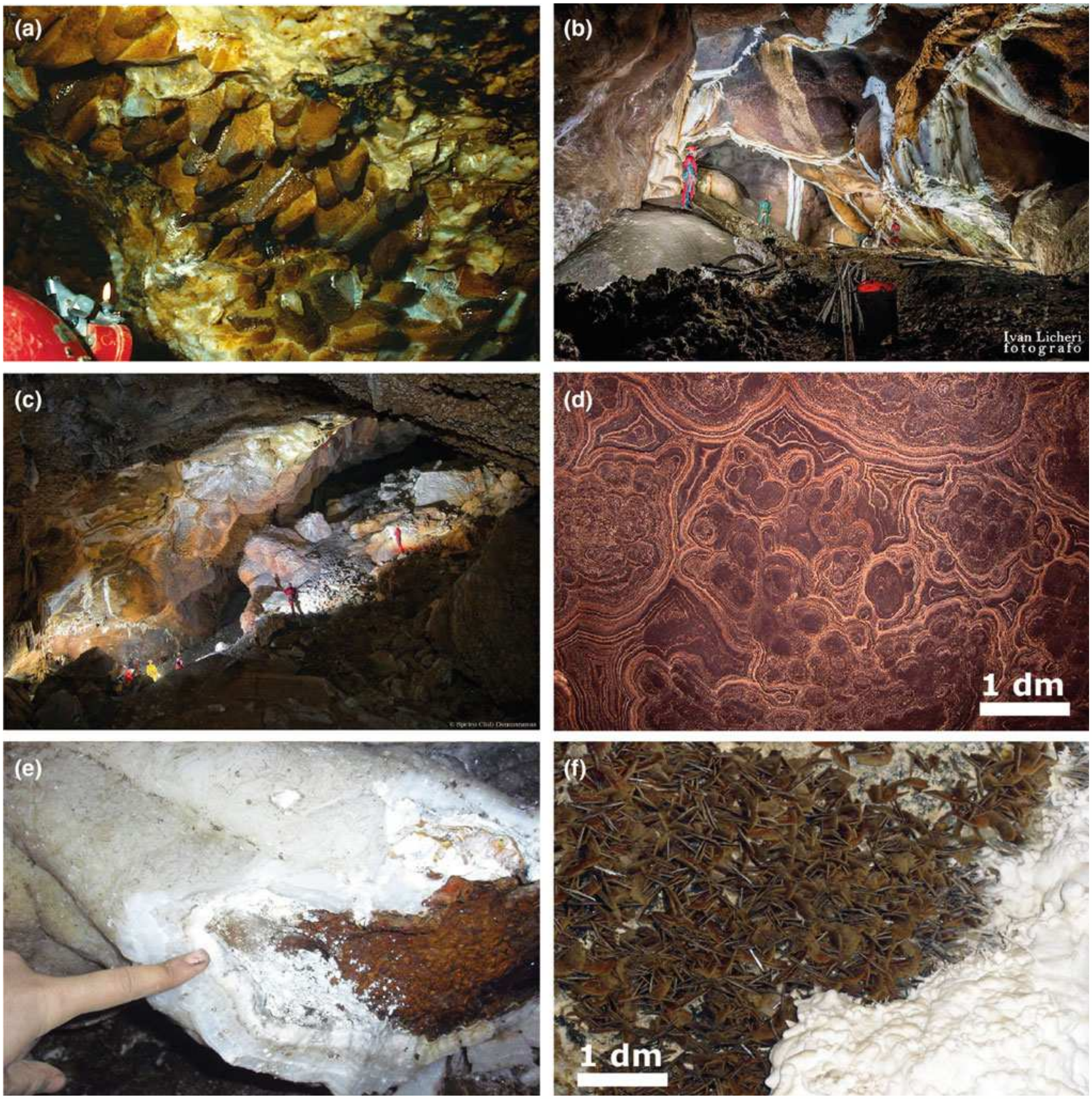


Fig. 6 Hypogene mine caves of Sardinia. **a** Big calcite dogtooth spar in one of the Phaff caves (Masua) (photograph Paolo Forti); **b** overview on the big phreatic chamber in Crovassa Ricchi in Argento cave. Note the rounded cave clouds and the dark oxide–hydroxide coating on the roof (photograph Ivan Licheri); **c** Grotta Pisani and the typical bell-shaped room with mammillary calcite covering the roof (photograph Michele Pili); **d** mammillary calcite (cave clouds) in Santa Barbara 2 cave, completely corroded and showing internal layering (photograph Paolo Forti); **e** 1-cm-thick white layer of hydrozincite coating the red-brownish oxides in the core of the sample and covered by white layered aragonite–calcite layers, Massa Riccardo Cave (photograph Fernando Gázquez); **f** brown centimeter-sized barite crystals covering the walls of Santa Barbara 2 cave (photograph Fernando Gázquez)

stalactites, and flowstones. Among them, the blue aragonite flowstone of Crovassa Azzurra deserves special mention (Fig. 7e). In this cave, subaerial aragonite precipitation was favored over calcite because of inhibition of calcite by relatively high Zn^{2+} concentrations (Caddeo et al. 2011).

5 Conclusions

Many caves discovered during mine tunneling in SW Sardinia have the typical characteristics of thermal hypogene caves. These wide, often bell-shaped voids have also been

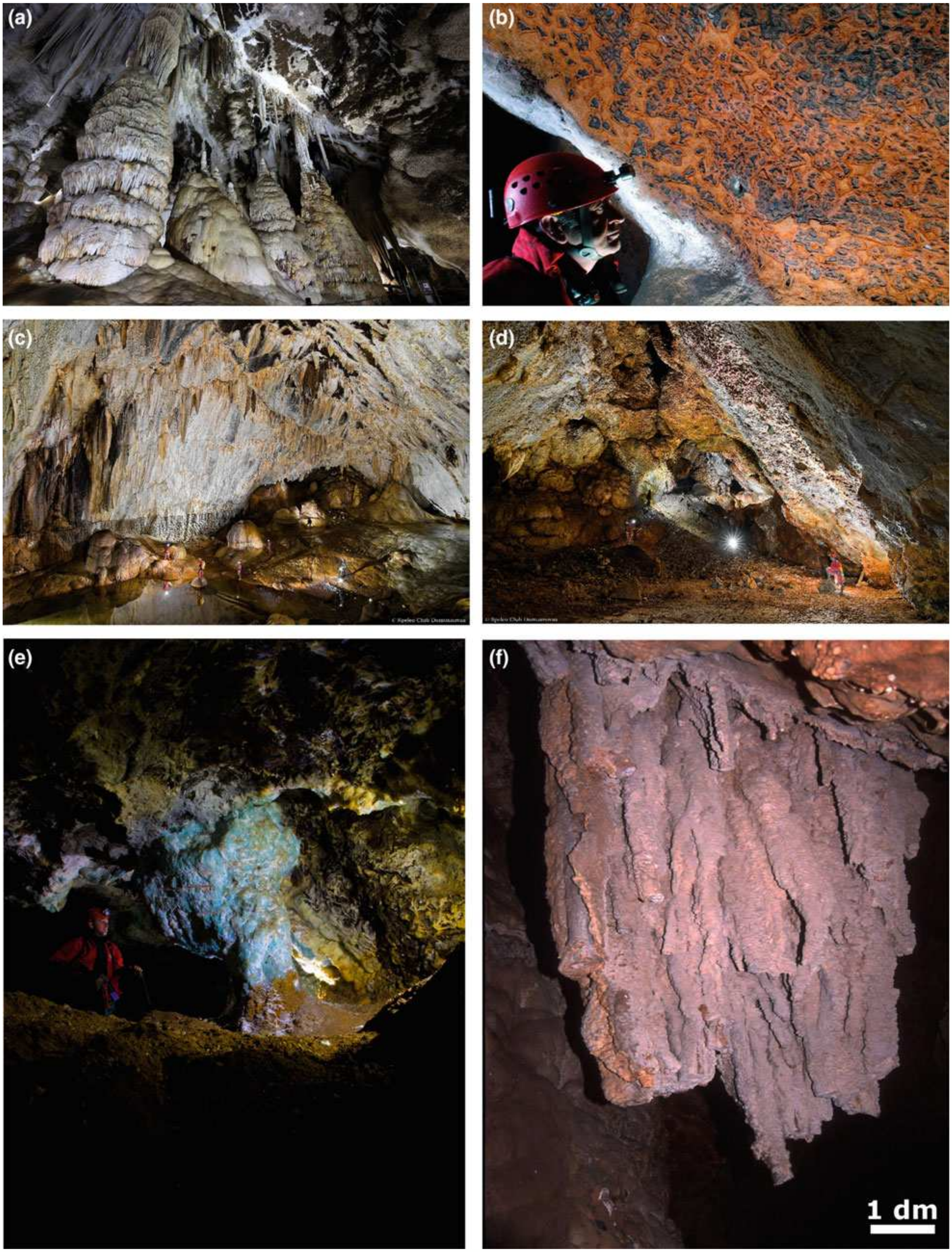


Fig. 7 **a** Santa Barbara 1 cave. Note barite-covered cave clouds (*dark*) on the roof and the giant vadose calcite flowstones (photograph Angelo Naseddu); **b** calcite ghosts with oxides in Crovassa Ricchi in Argento (photograph Victor Ferrer Rico); **c** the large room of Grotta Barega: the high water level can be seen as a dark horizontal line on the white cave walls (photograph Michele Pili); **d** the *bell-shaped* room in Crovassa Quarziti: the right wall is completely covered with calcite dogtooth spar (photograph Michele Pili); **e** *blue* aragonite pillar in the Crovassa Azzurra cave (photograph Angelo Naseddu); **f** the big hemimorphite flowstone in Crovassa Quarziti (photograph Angelo Naseddu)

encountered more than hundred meters below the present sea level, thanks to the fact that the water table was artificially lowered to allow Pb–Zn and barite exploitation. Although the typical hypogene features are often covered with vadose speleothems, or have been masked by the subsequent stages of cave formation and aquifer evolution, there is enough evidence that unmistakably shows these caves to have formed in thermal conditions. Also oxidation of the widespread sulfide ore bodies has caused the local creation of sulfuric acid speleogenesis conditions. One of the hypogene caves is unique for being developed in quartzite (Corona 'e Sa Craba cave) (Sauro et al. 2014). Others are well known for the presence of barite (Fig. 6f) covering the entire cave walls (i.e., Santa Barbara cave, Pagliara et al. 2010), or of thermal calcite dogtooth spars (Quarziti cave, Crovassa Ricchi in Argento (Gázquez et al. 2013), Phaff caves (Forti et al. 1981). Because of their unique setting, their morphological importance and their richness in secondary minerals, these caves deserve to be adequately protected.

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