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Cover photo : Keir Vaughan-Taylor on Lake 2, Koonalda Cave, Nullarbor Plain. (Photo by Kevin Moore)

Back Cover : The Khan and Beagum in Kubla Khan Cave Tasmania (Photo by Garry K. Smith)

Secondary Minerals From Italian Sulfuric Acid Caves

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Abstract

Italy is a country hosting a large number of hypogenic sulfuric acid (SAS) speleogenesis caves, mostly located along the Apennine chain, but also in Campania (along the coastline of Capo Palinuro), Apulia (along the coastline of Santa Cesarea Terme) and Sicily.

Besides the typical morphologies related to their special geochemical origin (cupolas, replacement pockets, bubble trails, etc), these caves often host abundant secondary mineral deposits, mainly gypsum, being the result of the interaction between the sulfuric acid and the carbonate host rock. Native sulfur deposits are also well visible on the ceiling and roof, and peculiar sulfuric acid minerals such as jarosite, alunite, and other sulfates like copiapite, pickeringite, tschermigite, tamarugite (probably related to the weathering of native clay minerals) have been found in those caves.

The presence of typical SAS minerals, together with the morphologies, testifies the influence of rising acidic waters, that likely interact with the deep-seated Triassic evaporite deposits (along the Apennine chain), with volcanic sources or hydrothermal springs in the Tyrrhenian sea (in Campania) and with marine waters that infiltrate on the sea bottom and rise through deep faults (in Apulia). This paper describes the secondary minerals discovered in several caves, and discusses their origin and possible use in reconstructing the evolution of these cave systems.

Keywords: sulfates; speleogenesis; hypogenic caves; cave mineralogy

1. Introduction

Hypogene caves are widespread around the world and together with epigenic caves represent the most important types of karst systems (Klimchouk 2007). Despite the fact they can evolve in different lithologies (carbonates, evaporites and clastic rocks with soluble cement) and geological settings, they present similar cave patterns and the morphological features of rising flow (Klimchouk 2009). Because of the fact they are climate-independent and do not rely on infiltrating surface waters, the most famous and largest hypogene cave systems have been found in dry regions (*e.g.* Carlsbad caverns and Lechuguilla in the Guadalupe Mountains in New Mexico, Toca da Boa Vista and Toca da Barriguda in Bahia in Brazil, etc). In these areas hypogene cave systems can be preserved after their exhumation thanks to the dry weather conditions, with subduing secondary processes (*e.g.* epigenic infiltration, deposition of speleothems), which can cover the original hypogenic features (Klimchouk *et al.* 2016). Several types of hypogene caves are well known, such as sulfuric acid (SAS) caves, thermal limestone caves and intrastratal caves in gypsum (Klimchouk 2009). In Italy all these types of hypogene caves (Galdenzi and Menichetti 1995; De Waele *et al.* 2014) are documented, but here we focus in particular on sulfuric acid caves that are abundant especially along the Apennine Chain, in the Southeast Apulian foreland and in Sicily. Differently from sulfuric acid caves in the Guadalupe Mountains (Hose and Macalady 2006), along the Appennine chain the H_2S source is mostly related to deep-seated upper Triassic evaporites called "Anidriti di Burano Formation." (Martinis and Pieri 1964; Ciarapica *et al.* 1987) cropping out in several regions of Italy including Emilia-Romagna, Tuscany, Latium, Umbria, Marche, Apulia (Gargano), and also in Greece and Albania (Martinis and Pieri 1964).

We collected and analyzed samples coming from several sulfuric acid environments reported in Figure 1, in particular from Porretta Terme thermal spa underground tunnels (Emilia-Romagna), Monte Cucco and Faggeto Tondo caves (Umbria), Montecchio cave (Tuscany), Cavallone and Bove caves (Abruzzo), Cerchiara di Calabria and Cassano allo Ionio Caves (Calabria), Santa Cesarea Terme caves (Apulia), and Acqua Fitusa cave (Sicily).

2. Geological setting

Most SAS caves are located along the Apennine chain, where deep-rooted faults allow groundwaters to rise from depth. In many cases these rising fluids are rich in H_2S, and more or less thermal. Porretta Terme (Emilia Romagna), Cassano allo Ionio-Cerchiara di Calabria (Calabria), and Santa Cesarea Terme (Apulia) represent commercially exploited spas and thermal baths. Montecchio hosts a thermal lake at -100 m, Acqua Fitusa is related to a nearby thermal sulfuric spring, Monte Cucco, Faggeto Tondo, Cavallone and Bove caves are high up in the mountains and no longer directly related to thermal rising waters.

Porretta Terme spa is located in the Tuscan-Emilian Apennines and develops in the "Porretta Terme Formation.", in particular in the arenitic member called "Arenarie di Suvi-

Figure 1. Location of the caves object of this study. From the N to the S are reported: Porretta Terme caves in Emilia Romagna, Monte Cucco and Faggeto Tondo caves in Umbria, Montecchio cave in Tuscany, Cavallone and Bove caves in Abruzzo, Cerchiara di Calabria and Cassano allo Ionio caves in Calabria, Santa Cesarea Terme caves in Apulia, Acqua Fitusa cave in Sicily.

ana" characterized by Oligocene lithic arenites with a vertical stratification due to Apenninic tectonic movements (ISPRA). Several sulfuric thermal springs have been encountered in an artificial tunnel network realised in the XIX century. These old underground environments are similar to caves, and host a wide variety of secondary mineral deposits.

Monte Cucco and Faggeto Tondo caves are located in the Umbro-Marche Apennines in a fold-and-thrust belt dominated by Jurassic carbonate rocks of the "Calcare Massiccio Formation." (Pialli *et al.* 1998). Both caves are part of a huge sulfuric acid cave system, uplifted high above the present base level and now abandoned by the sulfuric waters. The cave is intersected by epigenic vadose shafts and hosts several active passages, unrelated to its hypogenic origin. Several fossil conduits still host a variety of secondary minerals related to SAS speleogenesis.

Montecchio Cave is situated in southern Tuscany, and is hosted in the massive Jurassic limestone of the "Calcare Massiccio Formation.", and in Lower-Jurassic well-bedded cherty limestone of the "Calcare selcifero di Limano" (Piccini *et al.* 2015). It is composed of several cave levels, the lowest of which (-100 m from the entrance) still hosts a thermal sulfuric acid pool.

Cavallone and Bove caves are located in the central Apennines, in the Majella National Park of Abruzzo, mainly characterized by fossiliferous marine limestones deposited during upper Cretaceous at the bottom of a tropical sea. The Majella massif is composed of an anticline fold structure (Patacca *et al.* 1992). Both caves are uplifted trunks of a huge SAS cave system now partly dismantled by surface erosion, but still holding evident signs of its speleogenetic past.

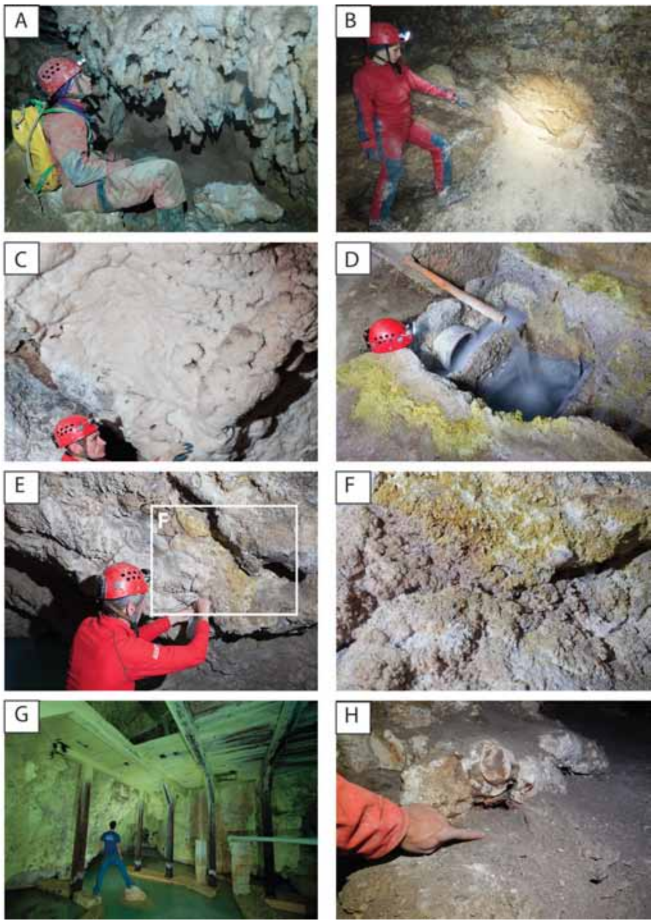

Figure 2. SAS minerals in several caves in Italy; A) Gypsum deposits in Faggeto Tondo cave (credits: J.De Waele); B) Alunite deposits in Cavallone cave (credits: M. Nagostinis); C) Gypsum in Sant'Angelo Cave in Cassano allo Ionio (credits: O. Lacarbonara); D) The yellow deposits are characterized by copiapite, tamarugite and pickeringite and are located in "Sorgente N°3" in Cassano allo Ionio (credits: O. Lacarbonara); E and F) The yellow deposits are characterized by copiapite and tschermigite and are located in Ninfee cave in Cerchiara di Calabria (credits: O. Lacarbonara); G) Sulfur deposits covering walls and ceiling in Gattulla cave at Santa Cesarea Terme (credits: M. Vattano); H) Gypsum deposits in Acqua Fitusa (credits: M. Vattano).

Cerchiara di Calabria and Cassano allo Ionio caves are located in the southern Apennines and develop in biogenic calcarenites of the "Cerchiara Formation." of Lower Miocene age (Selli 1957) and in Triassic dark-grey dolostone (Selli 1962), respectively. The underground karst network is composed of various caves and cave levels carved along the former sulfuric base level. The lowest level still contains active sulfuric water streams, used in the local spas.

Santa Cesarea Terme caves are located in the south-eastern Apulian foreland. They develop in micritic limestones and dolostones called "Calcari di Altamura" of Upper Cretaceous age (Azzaroli 1967). The four caves, all of modest dimensions, are carved at sea level and all have a direct access to the sea. Sulfuric thermal waters rise from the final parts of the caves where they meet seawater.

Acqua Fitusa cave is located in the eastern sector of the Sicani Mountains, in San Giovanni in Gemini, Sicily. It forms in the breccia member of the Upper Cretaceous known as "Crisanti Formation.", characterized by conglomerates and calcarenites with rudists and benthic foraminifera (Catalano *et al.* 2013).

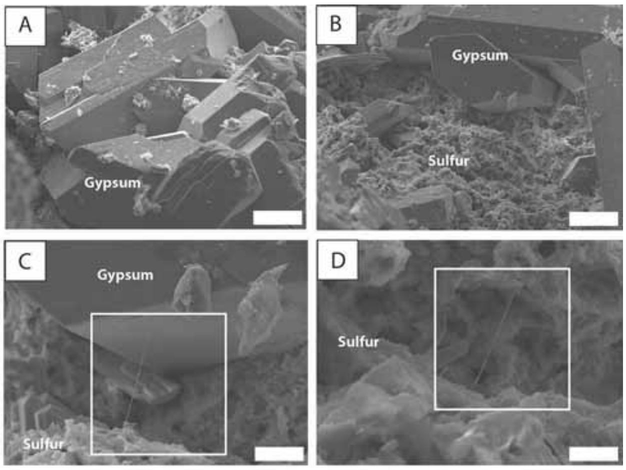

Figure 3. SEM images of gypsum and sulfur from Santa Cesarea caves; A) Gypsum crystals, the bar is 100 µm; B) Gypsum and sulfur crystals, the bar is 100 µm; C) In the white square it is possible to observe a filamentous structure between a gypsum crystal and sulfur minerals, the bar is 20 µm; D) In the white square it is possible to observe a filament in sulfur deposits, the bar is 10 µm.

Acqua Fitusa is a marvellous example of a sulfuric water table cave (De Waele *et al.* 2016), now disconnected from the active spring below.

3. Results

The collected samples have been analyzed using XRD methodology in Genova and Modena-Reggio Emilia Universities. Some preliminary analyses with Scanning Electron Microscope have been done in the laboratory of Bologna University.

In the following table (Table 1) the eleven SAS minerals found in these sulfuric acid environments are listed. These minerals generally occur as crusts or microcrystalline powdery deposits of pale white to yellowish and orange color. Larger crystals have also been found occasionally (mainly gypsum and sulfur) (Fig. 2).

Gypsum is derived from the typical reaction of sulfuric acid with pure limestone (calcite), producing also CO_2 (Galdenzi and Maruoka 2003). Sulfur is instead formed in extremely acidic conditions with the intermediation of micro-organisms. SEM images (Fig.3) from gypsum and sulfur deposits of Santa Cesarea Terme caves are shown below. Using a high magnification (20 µm and 10 µm) it is possible to observe microbial filaments (Fig.3C and D).

All the other sulfates, on the other hand, are all weathering products of sulfuric acid with the host rock, mainly Mg, Al, Fe, K, and Na - containing clay minerals. Among these, the K-jarosite and in particular alunite-group minerals are of extreme interest, because they allow to date the cave-forming process using the radioactive decay of the K-Ar chain (Polyak *et al.* 1998). Barite, found only in minor amounts in the Monte Cucco cave, might hint to a thermal origin, while fluorite in Faggeto Tondo cave clearly points to very acid and thermal conditions in the initial stages of cave development, before SAS speleogenesis became the dominant process (Forti *et al.* 1989).

4. Concluding remarks

In this study we report the results of mineralogical studies on secondary cave minerals formed by the interaction of sulfuric acid with the host rock. A total of 15 SAS caves have been visited and minerals have been collected. Also the artificial tunnels of a sulfuric thermal spa have been investigated.

Eleven minerals have been identified, most of which are sulfates (9), while native sulfur has been found in three locations and fluorite in only one cave. Besides the well-known SAS minerals (gypsum, jarosite, alunite), also less common minerals such as copiapite, tamarugite, tschermigite and pickeringite have been discovered. Copiapite-group minerals, besides volcanic caves close to fumarolic activity (Hill and Forti 1996), have been observed in mine environments and in particular in inactive mines of massive sulfide deposits in California (Jamienson *et al.*, 2005) and in Sardinia (Bini *et al.* 1986; De Waele and Forti 2005; Ara *et al.* 2013). It has also been reported from one sulfuric acid cave, Carlsbad Caverns (Mosch and Polyak 1996). Tamarugite and pickeringite have previously been described in relation with fumarolic activity in volcanic caves (Hill and Forti 1996), and in two sulfuric acid environments as well, Diana Cave in Romania (Puşcaş *et al.* 2013) and Aghia Paraskevi in Greece (Lazaridis *et al.* 2011). Tschermigite deposits have been discovered in thermal sulfidic serpents cave in France by Audra and Hobléa (2007) in association with alunogen and jurbanite, and in Lone

Table 1. The eleven secondary SAS minerals in the studied caves: PT = Porretta Terme, MC = Monte Cucco, FT = Faggeto Tondo, MT = Montecchio, CB = Cavallone-Bove; CC = Cerchiara di Calabria-Cassano allo Ionio, SCT = Santa Cesarea Terme, AF = Acqua Fitusa.

SAS Minerals	Chemical formula	PT	MC	FT	MT	CB	CC	SCT	AF
Gypsum	$CaSO_4$ $2H_2O$	x	x	x	x	x	x	x	x
K-Jarosite	$KFe(SO_4)_2(OH)_6$	x	x	x	x	x	x	x	
Sulfur	S^0	x		x				x	
Alunite	$KAl_3(SO_4)_2(OH)_6$		x		x	x			
Barite	$BaSO_4$		x						
Fluorite	CaF_2			x					
Natroalunite	$NaAl_3(SO_4)_2(OH)_6$					x			
Copiapite	$Fe^{2+}Fe^{3+}_4(SO_4)_6(OH)_2$ $*20H_2O$						x		
Pickeringite	$MgAl_2(SO_4)_4*22H_2O$						x		
Tamarugite	$NaAl(SO_4)_2$ $*6H_2O$						x		
Tschermigite	$(NH_4)Al(SO_4)_2$ $*12H_2O$						x		

Creek Fall Cave in eastern Transvaal, where it derives from pyrite oxidation and decay of guano, in the presence of clays (Martini 1983).

Some of these minerals can allow in the future to date the cave-forming process, with the possibility to constrain the formation of the very old caves of Cavallone and Bove, and maybe also Monte Cucco.

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SEM images were performed at the University of Bologna with the assistance of Prof. Giorgio Gasparotto.

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