| 4th International Symposium *Karst Evolution in the South Mediterranean Area* 30 May / 2 June 2014 | Speleologia Iblea | Vol. XVI | pp. 65 - 71 | Ragusa 2016 |
|---|---|---|---|---|

# Grotta dell'Acqua Mintina a peculiar geosite with the smell of sulfur

Stefano Lugli[1], Rosario Ruggieri[2], Riccardo Orsini[2] & Giorgio Sammito[2]

[1]*Dipartimento di Scienze Chimiche e Geologiche, Università degli Studi di Modena e Reggio Emilia, stefano.lugli@unimore.it*
[2]*Centro Ibleo di Ricerche Speleo-Idrogeologiche Ragusa, info@cirs-ragusa.org*

**Riassunto**

La grotta dell'Acqua Mintina (comune di Butera, Caltanissetta, Sicilia) si estende per una lunghezza totale di 140 m nel Calcare di Base di età messiniana (Miocene superiore) ed è caratterizzata dalla spettacolare presenza di concrezioni e cristalli di zolfo nativo e gesso secondario. Lo zolfo si è formato sulle pareti e sul soffitto della grotto in cristalli fino a 1 cm di lunghezza e in concrezioni microcristalline di forma botroidale, a nuvola, a popcorn e a "mensola". Il gesso è presente in aggregati cristallini aciculari, prismatici e fibrosi con cristalli fino a 3 cm di lunghezza. La grotta mostra morfologie non compatibili con i consueti fenomeni carsici ma legate ad attacco acido su calcare. L'acido solforico è stato generato in corrispondenza della falda acquifera per miscelazione di acque ricche di $H_2S$ risalite dai sedimenti sottostanti con acque ricche in ossigeno infiltrate dalla superficie. Il gesso si è formato attraverso il fenomeno della condensazione-corrosione di acido solforico sulle pareti calcaree della grotta, mentre lo zolfo si è formato per degassamento di $H_2S$ e $CO_2$ al di sotto della superficie dell'acqua, con parziale ossidazione dell'acido solfidrico. L'acido solfidrico è stato a sua volta generato dalla degradazione dei sedimenti ricchi in materia organica del Tripoli che si trovano immediatamente al di sotto del Calcare di Base e/o per riduzione batterica del gesso primario della Formazione di Pasquasia affiorante al di sopra. La grotta, per la presenza di spettacolari concrezioni di zolfo e gesso, rappresenta un geosito di interesse nazionale da tutelare e conservare attivamente.

**Summary**

The Acqua Mintina cave (Butera, Caltanissetta, Sicily) cuts for a total length of 140 m the Messinian Calcare di base unit and is characterized by the spectacular, and fortunately still poorly degraded, presence of native sulfur and secondary gypsum. The sulfur occurs on the walls and ceiling in crystals up to 1 cm in length and centimeter-thick microcrystalline botroydal, cloud, popcorn, and folia concretions. Gypsum is present in acicular, prismatic and fibrous crystal aggregates consisting of crystals of up to 3 cm in length. The cave shows karst morphologies due to acid attack on limestone and not the usual dissolution by water flow. The organic-rich Tripoli sediments below the Calcare di Base unit and/or the bacterial reduction of gypsum from the Upper Gypsum unit probably provided the original $H_2S$. Sulfuric acid was generated when $H_2S$-rich water encountered oxygen-rich water at or near the water table. Gypsum formed by condensation-corrosion of sulfuric acid on the cave walls, while the sulfur concretion probably formed where $H_2S$ and $CO_2$ were outgassing below the water surface, with the $H_2S$ partially oxidizing to sulfur. The cave for its widespread presence of spectacular crusts of sulfur and gypsum crystals represents a rare and valuable geosite to be actively protected and preserved.

Key words: Sicily, Butera, sulfuric acid cave, gypsum

## Introduction

One of the peculiarity of Sicily is that the celebrated Italian island is hosting the most spectacular outcrops of the Messinian salinity crisis, one of the most impressive geological event that affected our planet in the Late Miocene between 5.97 and 5.33 Ma (Roveri at al. 2014 and references therein). The Mediterranena Sea was turned into a giant salina with the deposition of a thick sequence of evaporite minerals. One of the mineral associated with the salinity crisis is native sulfur, which formed mostly by complex late diagenetic processes at the expenses of gypsum.

Even though Sicily retained the world monopoly for sulfur extraction up to the beginning of the 20th century, the genetic mechanisms of its formation are poorly known. Virtually unknown is the very late occurrence of sulfur, the type forming through speleogenetic processes in the so-called sulfuric acid caves (Palmer and Hill, 2012). These processes are responsible for the formation of some of the largest and most famous cave systems in the world, such as the Guadalupe Mountains, New Mexico (Kirkland, 2014), the Cueva de Villa Luz, Mexico (Hose et al., 2000), and the Frasassi cave, Italy (Galdenzi and Maruoka, 2003). Probably the best example in Sicily

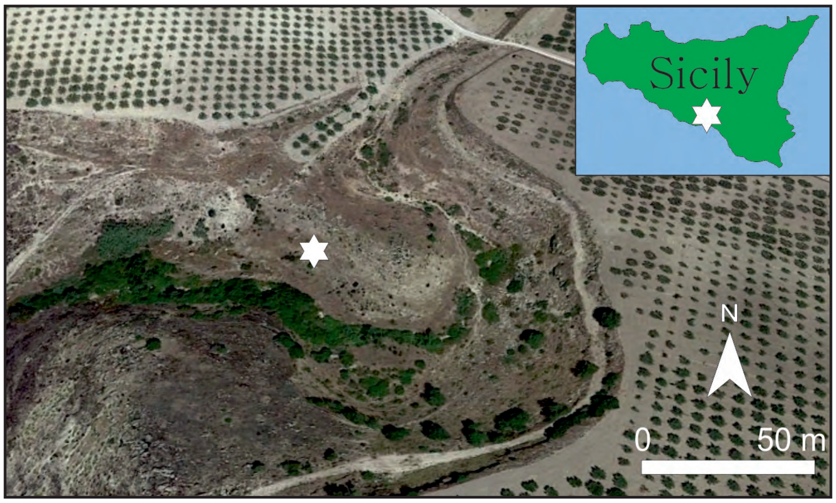


*Fig. 1: Map of the area with the location of the cave*

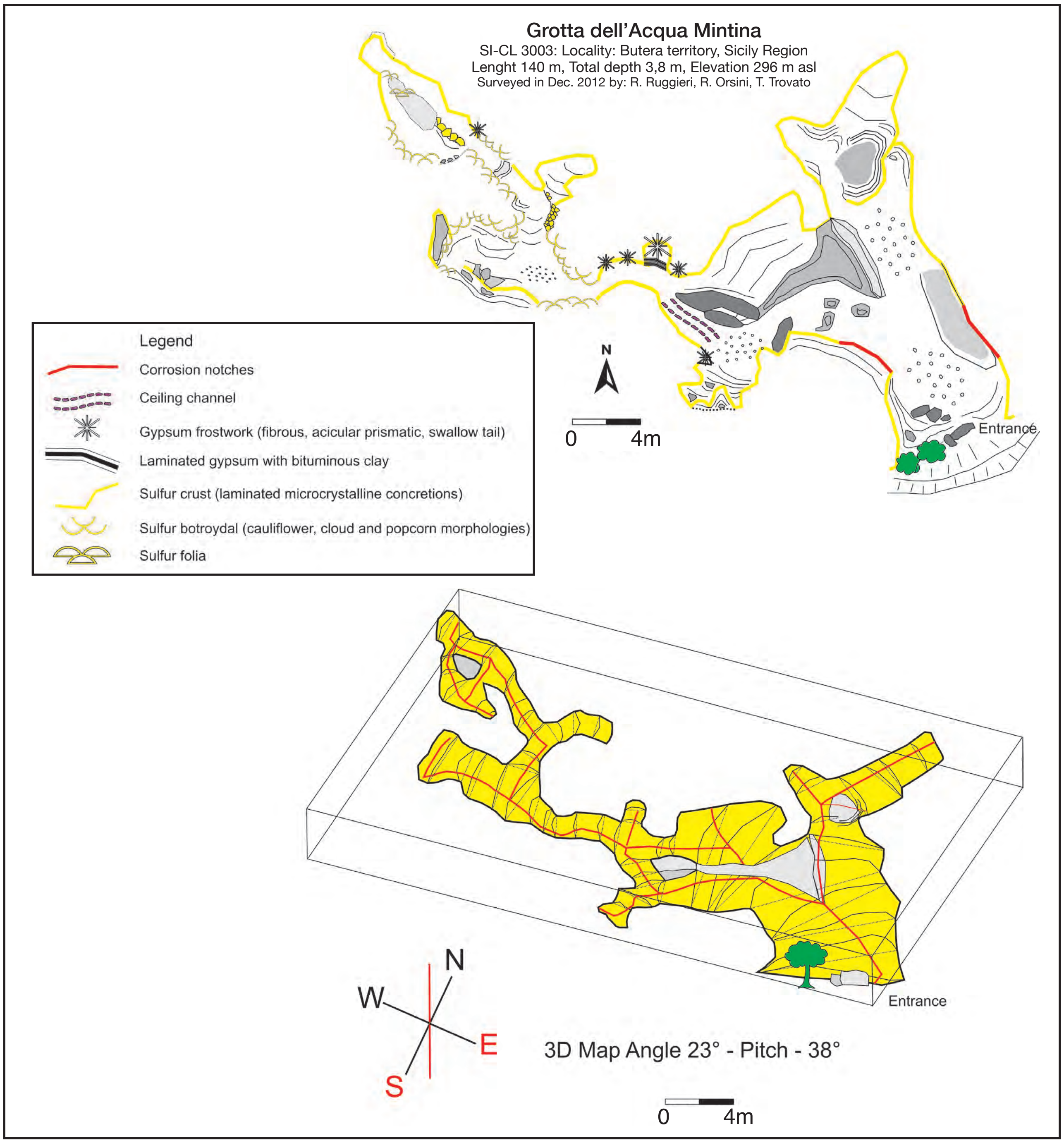


*Fig. 2: Map and 3D profile of the Acqua Mintina cave*


*Fig. 3: A. Part of the first large chamber. B. Collapse of gypsum layers in the second smaller chamber. C. Collapse of layers in the left branch. D. Widespread sulfur crust in the left branch of the cave.*

of this type of late occurrence is the Grotta dell'Acqua Mintina (cave of the sulfur water spring), which has the walls covered with sulfur and gypsum crystals formed by the sulfuric acid speleogenetic processes. This paper describes the characteristics of the Acqua Mintina cave and its geological feature, the aim is to contribute in rising the awareness on the importance of this occurrence and to promote its protection as a geosite.

## Geographic and geological setting

The cave entrance is perched about 20 m on the right bank of the Rizzuto stream, at 296 m of elevation, and is located approximately 2.5 km SW of the Butera village, in the Caltanissetta province The stream cuts a narrow valley, approximately 30 m deep, into the Miocene sediment (Fig. 1). The geological sequence starts with the pelagic to hemipelagic clays of the Licata fm. (Langhian to Serravallian) followed by the marl and diatomite alternance of the Tripoli Formation (Messinian). Resting on the Tripoli sediments is the carbonate unit of the Calcare di base (Messinian). Six Calcare di base layers are visible for a total thickness of about 8 meters. The Calcare di base facies is the type 3 of Manzi et al. (2010), which consists of breccia and laminate calcium carbonate sediments of clastic origin deposited by gravitational processes at the edge of structural highs, where the primary carbonate deposition was occurring. The clasts are well cemented and show cubic moulds up to a few millimeter in size originally occupied by salt crystals.

The cave developed in the lowest Calcare di base layer at its contact with the underlying Tripoli marls. The Calcare di base is capped by a selenite layer belong to the Upper Gypsum unit (Pasquasia Fm.; Manzi et al, 2009). The gypsum unit forms a discontinuous horizon reaching just a few meters in thickness. It consists bottom-grown vertically-oriented massive and banded selenite crystals up to 30 cm in size. The vertical sequence ends with the marl of the Lower Pliocene of Trubi Fm.

## Description of the cave

The cave have been explored and mapped by CIRS Ragusa in 2012. The cave opens at the bottom of the Calcare di base unit in correspondence of a laminated carbonate layer, with a strike of N 130° and a dip of 15°. The cave has a total length of 140 m, with a depth of 3.8 m, and formed along a main fracture system oriented N 280-300° crossed by another fracture set oriented N-S (Fig. 2). The largest chamber of the cave is located next to the entrance and is approximately 15 x 7 m across, with an average height of 2 m (Fig. 3A). Two distinct horizontal corrosion notches are present in the walls of the room, they may have marked the groundwater level. From this chamber one can reaches, to the right, a second smaller chamber, which has a lower ceiling affected by collapse (Fig. 3B-C). The left branch of the cave hosts the most abundant sulfur and gypsum mineralizations (Fig. 3D). A sort of discontinuous ceiling channel is present in the first part of the left branch (Fig. 4A), its surface is not flat but is punctuated by concave and domal-shaped irregularities covered by a hard brown mineralized crust of (Fig. 4B). Other morphologies are the collapse structures, especially in correspondence of a laminate horizon consisting of bituminous clay of thickness up to 50 cm-thick (Fig. 4C), while no stream sedimentary fillings are present into the cave.

The cave has been slightly modified in the past by a small-scale exploitation of sulfur. Some limestone blocks have been grouped to form a sort of small wall and are now covered as well by a sulfur crust (Fig. 4D).



*Fig. 4: A. Ceiling channel in the left longer branch of the cave. B. Corrosion pocket in the ceiling. C. Laminated bituminous clay layer with gypsum crystals up to 2 cm in size. D. Small wall made up of stones covered by sulfur crust.*

## Description of the mineralization

Native sulfur occurs on the cave walls in laminated concretions a few centimeters-thick consisting of microcrystalline, acicular crystals up to 1 cm in length (Fig. 5A-B), and millimeter-size bipyramidal crystals (Fig. 5C). Some of these concretion on the overhanging cave walls have a distinct shape resembling bracket fungi with a flat base and convex upper surface (Fig. 5D). Similar sulfur structures have been described as "folia" by Hose et al., 2000.

Associated with sulfur on the cave walls are also crusts consisting of aggregates of acicular, prismatic and fibrous gypsum crystals up to 3 cm in length (Fig. 6A). Some gypsum crystals are "swallow tail" twins (Fig. 6B). In some areas of the calcareous walls of the cave appear variously altered and exfoliated resembling a sort of "bread crust" (Fig 6C. These corroded areas of the limestone walls are covered with centimeter-thick deposits of acicular gypsum, which overlap dusty sulfur crusts (Fig 6D). In other areas, the sulfur crust have botryoidal and hemispherical shapes, such as cloud-, popcorn-, and cauliflower-like structures (Fig. 6E).

## Interpretation

The structural pattern of the cave, its location with respect to the relief, and the hydrogeological allogeneic charging regime in this part of the Rizzuto stream basin indicate

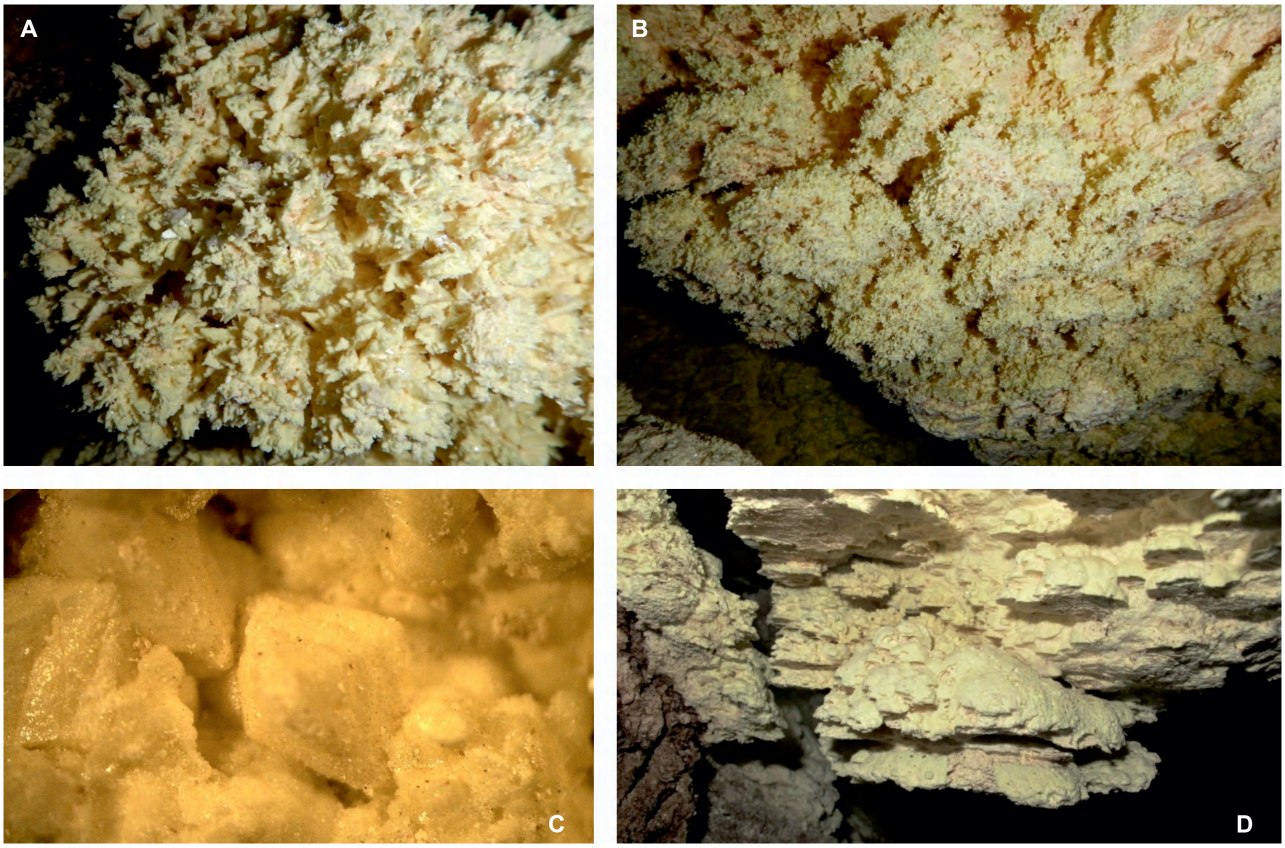

*Fig. 5: A-B. Aggregates of prismatic crystals of sulfur, the crystals are up to a few mm across. C. Photomicrograph of bipyramidal crystals of sulfur up to 2 mm across. D. Sulfur folia concretions up to 15 cm across. Notice the flat bottom and the convex upper surface.*

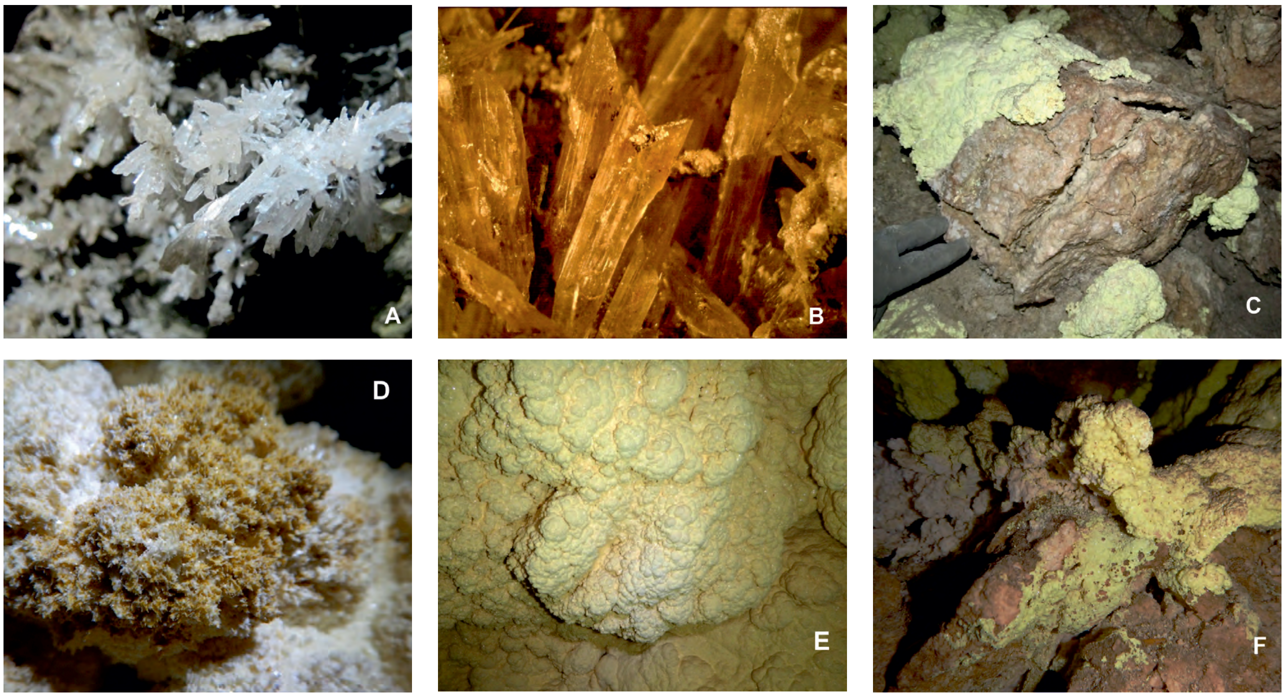

*Fig. 6: A. Aggregates of gypsum crystals up to 2 cm in size. B. Photomicrograph of prismatic and swallow tail gypsum twin aggregates, the crystals are up to 7 mm across. C. Sulfur crust formed on the altered and exfoliated limestone walls. D. Acicular gypsum with dusty sulfur, the cristals are a few mm across. E. Botryoidal and cauliflower-like sulfur structures, the field of view is about 30x25 cm. F. Sulfur crust (pale yellow) covering gypsum crystals (whitish) on the limestone walls. The field of view is about 30x25 cm.*

a geological context characterized by very low hydrodynamic speed. These observations, and other characteristics described below, suggest an origin of the karst system due to progressive enlargement of planar discontinuities, such as bedding planes, joints, and fractures by sulfuric acid corrosion. The presence in the system of an almost static water table would have favored evaporation/condensation and corrosion/precipitation processes, which produced the mineralization of native sulfur and gypsum inside the cave (Fig. 6F). This “partially confined karst



*Fig. 7: A. The sub-horizontal limit of the sulfur mineralizations (below) on the main conduct walls. B. Corrosion notches in the lower part of the walls in the entrance chamber.*

system", was then cut off and is now perched above the bottom of the valley by the erosional deepening of the Rizzuto stream, as a consequence of the tectonic uplift that affected this area. This hypothesis is supported by the sub-horizontal upper limit of the sulfur mineralizations on the main conduct walls (Fig. 7A), by the presence of corrosion notches in the lower part of the walls in the first chamber (Fig. 7B), and by the absence of phreatic morphologies and fluvial deposits inside the cave.

In particular, the described morphologic features are not consistent with caves created by aqueous carbonic acid ($H_2CO_3$), the acidic solvent that usually operates within carbonate rocks. The corrosion features, the altered walls, and the presence of sulfur and gypsum concretions suggest an origin of the cave by sulfuric acid attack on the limestone surface. In our case the $H_2S$ may have been originated by both, the organic-rich Tripoli sediments laying below the Calcare di Base unit and/or the bacterial reduction of gypsum from the Upper Gypsum unit irregularly capping the top of the carbonate unit. Sulfuric acid, in turn, was generated when $H_2S$-rich water encountered oxygen-rich water at or near the water table, which in our case was located at the interface between the fine-grained sediments of the Tripoli Fm. and the Calcare di base. The oxygenated groundwater was probably fed by meteoric infiltration, or exchange of air through openings to the surface. Gypsum formed by condensation-corrosion of sulfuric acid on the cave walls, while the sulfur concretion and folia may have possibly formed where $H_2S$ and $CO_2$ were outgassing below the water surface, with the $H_2S$ partially oxidizing to sulfur (Hose et al. 2000).

These processes are the late evolution of the phenomena which lead to the formation of the large Sicilian sulfur deposits (Ziegenbalg et al. 2010), largely related bacterial activity in the presence of hydrocarbons (Machel 2001). Also for the main sulfur deposits, the hydrocarbons required for the bio-chemical reactions were mostly coming from the Tripoli formation, which is particularly rich in organic matter (Catalano et al., 2016; Roveri et al., 2016).These preliminary genetic hypotheses will be verified through petrographic and isotope analyses on sulfur, sulfate, and carbonate minerals. The analyses are currently in progress.

## Conclusions

The Grotta dell'Acqua Mintina is a sort of treasure trove of great geological interest. In this relatively small underground space, produced by acid and not by water, it is possible to observe the results the phenomena which produced the famous Sicilian sulfur deposits throughot complex chemical reactions mediated by bacteria. Despite the limited exploitation activities conducted in the past, the spectacular crusts of sulfur and gypsum crystals are of great interest, both for educational purposes and for the research activities of the international scientific community.

Because of these important characteristics, the Grotta dell'Acqua Mintina has been proposed by CIRS Ragusa as a candidate for the list of Geosites of national importance under the Sicilian Regional Law 25/2012. Presently, the file is under consideratioǹ by the regional Geosite Scientific Commission.

## Acknowledgments

We thank Dr Salvatore Volpe for the valuable support on somoe aspects of this research.

## References

CATALANO R., DI STEFANO E., SPROVIERI R., LENA G. AND VALENTI V., 2016. The barren Messinian Tripoli in Sicily and its palaeoenvironmental evolution: suggestions on the exploration potential. Petroleum Geoscience, 22, 322 – 332.

GALDENZI S. AND MARUOKA T. 2003. Gypsum deposits in the Frasassi Caves, central Italy. Journal of Cave and Karst Studies 65(2), 111-125.

HOSE, L.D., PALMER, A.N., PALMER, M.V., NORTHUP, D.E., BOSTON, P.J, AND DUCHENE, H.R., 2000, Microbiology and geochemistry in a hydrogen-sulphiderich karst environment: Chemical Geology, v. 169, p. 399-423.

KIRKLAND, D.W., 2014. National Cave And Karst Research Institute Special Paper 2: Role Of Hydrogen Sulfide In The Formation Of Cave And Karst Phenomena In The Guadalupe Mountains And Western Delaware Basin, New Mexico And Texas". Environmental Sustainability Books. Book 3.

MACHEL, H.G., 2001. Bacterial and thermochemical sulfate reduction in diagenetic settings — old and new insights. Sedimentary Geology 140, 143–175.

MANZI V., LUGLI S., ROVERI M. & SCHREIBER B.C., 2009. A new facies model for the Upper Gypsum (Sicily, Italy): chronological and palaeoenvironmental constraints for the Messinian salinity crisis in the Mediterranean. Sedimentology, 56, 1937–1960.

MANZI V., LUGLI S., ROVERI M., SCHREIBER B.C. & GENNARI R., 2011. The Messinian "Calcare di Base" (Sicily, Italy) revisited. Geological Society of America Bulletin, 123; 347-370.

PALMER A. N. AND HILL C.A., 2012. Sulfuric acid caves. Encyclopedia of Caves, 810-818.

ROVERI M., FLECKER R., KRIJGSMAN W., LOFI J., LUGLI S., MANZI V., SIERRO F.J., BERTINI A., CAMERLENGHI A., DE LANGE G., GOVERS R., HILGEN F.J., HÜBSCHER C., MEIJER P.TH., STOICA M. 2014. The Messinian Salinity Crisis: past and future of a great challenge for marine sciences. Marine Geology, 352, 25-58.

ROVERI M., GENNARI. R, LUGLI S., MANZI V., MINELLI N., REGHIZZI M., RIVA A., ROSSI M.E., SCHREIBER B.C., 2016. The Messinian salinity crisis: open problems and possible implications for Mediterranean petroleum systems. Petroleum Geoscience, 22, 283-290.

ZIEGENBALG S.B., BRUNNER B., ROUCHY J.M., BIRGEL D., PIERRE C., BÖTTCHER M.E., CARUSO A., IMMENHAUSER A., PECKMANN J., 2010. Formation of secondary carbonates and native sulphur in sulphate-rich Messinian strata, Sicily. Sedimentary Geology, 227, 37–50.