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# Minerogenetic Mechanisms Occurring in the Cave Environment: An Overview

Bogdan P. Onac

*University of South Florida, bonac@usf.edu*

Paolo Forti

*Italian Institute of Speleology*

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# Minerogenetic mechanisms occurring in the cave environment: an overview

Bogdan P. Onac<sup>1,2</sup> and Paolo Forti<sup>3</sup>

### Abstract:

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Perhaps man's first motivation to explore caves, beyond using them as shelter, was the search for substances that were not available elsewhere: most of them were minerals. However, for a long time it was believed that the cave environment was not very interesting from the mineralogical point of view. This was due to the fact that most cave deposits are normally composed of a single compound: calcium carbonate. Therefore, the systematic study of cave mineralogy is of only recent origin. However, although only a limited number of natural cavities have been investigated in detail, about 350 cave minerals have already been observed, some of which are new to science. The presence of such unexpected richness is a direct consequence of the variety of rocks traversed by water or other fluids before entering a cave and the sediments therein. Different cave environments allow the development of various minerogenetic mechanisms, the most important of which are double exchange reactions, evaporation, oxidation, hydration-dehydration, sublimation, deposition from aerosols and vapors, and segregation. The cave temperature and pH/Eh strictly control most of them, although some are driven by microorganisms. The cave environment, due to its long-term stability, can sometimes allow for the development of huge euhedral crystals, such as those found in the Naica caves (Mexico), but the presence of extremely small yet complex aggregates of different minerals is far more common. Future development in the field of cave mineralogy will likely be focused mainly on hydrothermal and sulfuric-acid caves and on the role played by micro-organisms in controlling some of the most important minerogenetic processes in caves.

**Keywords:** cave minerals, mineralogy, processes, karst, lava tubes

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### INTRODUCTION

Caves are among the longest-lasting components of the environment and throughout their lifespan act as traps, accumulating physical, biological, and chemical deposits. It is well known that the chemical deposits (i.e., speleothems) are by far the most important for the aesthetic value of a given cave. At the same time, fewer people are aware of the fact that natural caves are among the most important minerogenetic environments of our planet.

Perhaps man's first motivation to explore caves was the search for substances that were not available elsewhere. In fact, from pre-historic times up to the present, many caves have been intensively mined. There is evidence that some ~30,000 years ago, humans were already entering caves in search of pigments (mainly iron and manganese oxides and hy-

drides) for personal use and to paint the cave walls (Fig. 1). Later, various natural cavities became true mines, from which a variety of minerals were extracted, as was the case of Monaca Cave, in Italy. This cavity is one of the best examples of an Eneolithic mine-cave (Larocca, 2005), preserving in its depths marks of hammers and chisels used in mineral excavation. Niter for use as a food stabilizer was mined by the Assyrians from small caves near the Tigris River as early as 4000 yr BP (Forti, 1983); about the same time, the native Americans in the Mammoth Cave region (USA) penetrated deep into the caves to search for mirabilite and epsomite (used in purgatives), and gypsum (used as fertilizer) (Farnham, 1820; Broughton, 1972; Tankersley 1996). More recently, the Incas mined salt speleothems inside the halite caves of the Atacama to supply their entire empire with salt (De Waele et al., 2009). Finally, until just a few years ago, millions of cubic meters of "guano" (a phosphate-rich cave soil/sediment) were still being extracted from caves worldwide to be used as a natural fertilizer (Abel & Kyrle, 1931; Badino et al., 2004; Onac et al., 2007).

It must be emphasized that the genesis of many of the minerals found in caves is unrelated to the existence of the cave itself; they were often brought in by flowing or seeping water or were exposed by the cor-

<sup>1</sup>Department of Geology, University of South Florida, 4202 E. Fowler Ave., SCA 528, Tampa, FL 33620, USA (bonac@usf.edu)

<sup>2</sup>"Emil Racovita" Institute of Speleology, Clinicilor 5, 400006 Cluj, Romania

<sup>3</sup>Italian Institute of Speleology, University of Bologna, Via Zamboni 67, 40126, Bologna, Italy (paolo.forti@unibo.it)



Fig. 1. Cave paintings in which the prehistoric man used red and black pigments extracted from floor sediments of a small cave in the Akakus Desert, Libya (photo: P. Forti).

rosion of the cave walls. By definition “a cave mineral is a secondary deposit precipitated inside a human-sized natural cavity”, where secondary means, a mineral derived from a primary mineral existing in the bedrock or cave sediment through a physico-chemical reaction (Hill & Forti, 1997). The generic term that encompasses all secondary deposits formed in caves is *speleothem* (cave).

The misbelief that caves are uninteresting from a mineralogical point of view persisted for a long time. This was mainly because by far the majority of speleothems consist of calcite and aragonite (over 90% of all cave minerals). Therefore, the systematic study of cave minerals started only some 50 years ago (White, 1961). However, although only a limited number of natural cavities have been investigated in detail, about 350 cave minerals have already been identified, some of which are entirely new to science (Hill & Forti, 1997; Back & Mandarino, 2008). Such an unexpected richness is the direct consequence of the leaching of various rocks and sediments by percolating waters prior to their entrance in caves, as well as the interaction of hydrothermal or hydrogen sulfide-rich fluids with the bedrock and cave sediments. Cave environments are home to several types of reactions (White, 1997); most of these are strictly controlled by changes in temperature and/or relative humidity, solution chemistry, pH/Eh, or are mediated by microorganisms. Moreover, different reactions can produce completely different mineral assemblages and/or different minerals from the same chemical compounds.

The aim of the present paper is to provide an overview of the evolution of cave mineralogy from the very early research of the XVIII<sup>th</sup> century up to the present, as well as to predict possible developments in the near future.

### SHORT HISTORY OF CAVE MINERALOGY

Almost all of the early descriptions of speleothems mentioned only calcite and/or aragonite (Shaw, 1992, 1997). A few papers did deal with a description of cave ice (Poissenot, 1586; Gollut 1592; Bell, 1744), and even fewer mentioned saltpeter (Sloane, 1707). None of these papers, however, can be considered a true mineralogical survey.

The first studies performed in caves were published only in the second half of the XVIII<sup>th</sup> century when analytical chemistry started to produce real sci-

entific results. These first papers were mostly related to Italian caves, simply because at that time, a large number of caves in that country had been documented and chemical studies were undertaken in various different universities throughout the country. However, the very first description of a cave mineral is that from 1767, when Fridvaldszky wrote about calcite in Dâmbovicioara Cave (Romania) in his scientific treatise *Mineralogia magni Principatus Transilvaniae*. A few years later, Bellitti (1783) described several thermal cavities near Sciacca (Sicily, Italy) and their chemical deposits (Verde, 2000). One of these was the Stufe di San Calogero Cave, at that time world renowned due to its transformation into a thermal bath as early as the Roman times. In his book, Bellitti describes the following minerals: sulfur, gypsum, and calcite.

The first written report of minerals found in a volcanic cave was authored by Spallanzani (1797) in his well-known “*Viaggio alle Due Sicilie*” (1792-1797). In this book, he describes the following minerals: alunogen, halotrichite, salammoniac, sulfur, and an undetermined iron sulfate found in Alum Cave, a small cavity developed at sea level in the volcanic tuffs of Vulcano Island (Fig. 2):

**“...but the most interesting object is a natural cave... from which a column of smoke continuously exits... Sublimated sulphur gives rise to conical yellow to pink stalactites up to 3 feet long and two inch [sic] thick. .... Some water springs out from the cave wall giving rise to some deposits over the lava beds consisting of stalactitic alum... sometimes with ammonium chloride... Deposits of iron sulphate are fairly common....”**

Another early paper describes a large nitrate deposit in the Pulo di Molfetta Cave, a meteoric cavity in Apulia, Italy (Giovene, 1784; Zimmerman, 1788). The cave minerals recognized by Zimmerman inside this cave were niter, nitrocalcite, nitratine, and nitromagnesite. During that time, in many European countries the strategic value of “niter”, a fundamental component of gunpowder, was extremely high; thus the



Fig. 2. Alum Cave, Vulcano Island (after Spallanzani, 1797).



caves in which it was found became exclusive properties of the King (Cesarotti, 1803; Forti & Palmisano, 1989). In this context, it must be mentioned that without the saltpeter exploited from Mammoth Cave and other caves in the Appalachians (Hill, 1979), the American civil war might have had a different ending (Gurnee, 1993).

All in all, by the beginning of the XIX<sup>th</sup> century, fewer than 10 papers had been published about some 10 minerals, all from the four caves mentioned above (Fig. 3). During the XIX<sup>th</sup> century, the development of cave mineralogy proceeded slowly, although a number of important caves were studied in detail around the world. These include Nickajack Cave (Tennessee, USA), where nitrammite (now called gwihabaite; Martini, 1996; Nickel & Nichols, 2009) was observed for the first time (Shepard, 1857); two caves on the islands of Mona and Moneta (Puerto Rico) from where hydroxylapatite (formerly called monite) and monetite were discovered (Shepard, 1882), and Skipton Cave (Australia), in which hannayite, newberryite, schertelite, and dittmarite were first identified (MacIvor, 1879, 1887).

But by far, the most important mineralogical study of the XIX<sup>th</sup> century was performed by Scacchi (1850), who studied a small tectonic cave developed at sea level in volcanic ash near Miseno Cap (Naples, Italy). In this cave, a small salt-water lake is present, in which hot fumarole exhalations come into direct contact with seawater, thus allowing rapid evaporation and the development of crusts consisting of various different minerals (mainly sulfates) (Bellini, 1901; Zambonini, 1907). In his study, Scacchi recognized 7 minerals (sulfur, halite, alum-(K), alunogen, halotrichite, voltaite, and misenite), with the latter new to science. Native sulfur, kaolinite, alunite, alunogene, and jarosite were mentioned from caves in Transylvania (Romania) in two monographs published by Koch (1878) and Bieltz (1884), respectively. All of these studies increased the number of known minerals formed within natural cavities; therefore, at the beginning of the XX<sup>th</sup> century, the number of known cave minerals and published papers on this topic increased to 50 and 250, respectively.

This relatively slow rate was maintained throughout the first half of the past century, and just after World War II, the number of papers on speleothems had approached 700, with descriptions of about 80 cave minerals. White published the first overview on this topic in 1961.

The study of cave minerals was strongly catalyzed by the publication of the first monograph of Hill (1976), and speeded up even more with the release of the second (Hill & Forti, 1986) and third (Hill & Forti, 1997) editions of the same book. At the beginning of the 3<sup>rd</sup> millennium, about 300 minerals from various cave environments had been described, and the number of published papers dealing with speleothems had reached nearly 5000. Over the past decade, the occurrence of at least 2 to 3 new cave minerals has been reported annually in dozens of papers (Onac, 2011a). It is therefore reasonable to assume that in the near future, given the availability of more sophisticated analytical facilities, this trend will be maintained (Fig. 3).

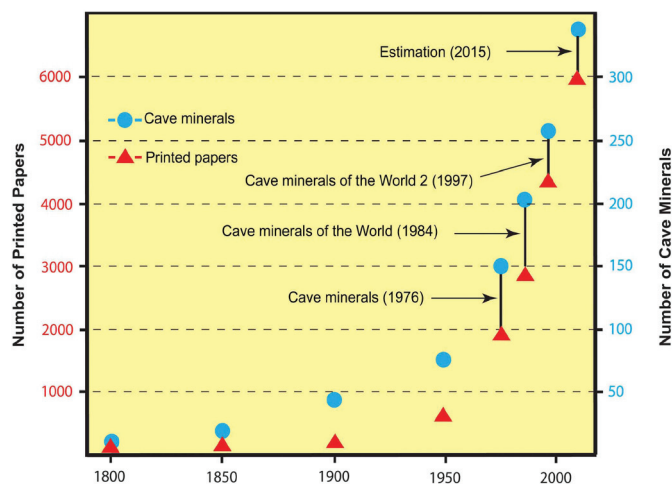


Fig. 3. The number of known cave minerals and of printed papers on cave mineralogy from the beginning of the XIX<sup>th</sup> century up to present.

### MINEROGENETIC MECHANISMS ACTING IN THE CAVE ENVIRONMENT

Although most of the chemical deposits precipitated in caves consist mainly of calcium carbonate, the cave environment accommodates a wide range of authigenic minerals belonging to all chemical classes (Back & Mandarino, 2008). Tens of mineral species were first identified in caves and only later identified outside them. A limited number of minerals are still restricted to caves (Garavelli & Quagliarella, 1974; Martini, 1978, 1980a, 1980b, 1983, 1992; Bridge & Robinson 1983). The reason for this situation is the chemical composition of the fluids and the geological formations with which they interact prior to entering the natural cavities. Four main types of solutions can interfere with the bedrock and cave sediments: meteoric, connate, juvenile, and seawater; all of these are responsible for transporting certain amounts of different ions. Ground water temperature can also be important as it controls the concentration of dissolved species. Essential in this context are the Eh and the pH, because many compounds dramatically alter their solubility in response to these environmental parameters.

Although water is definitely the most important carrier of ions and chemical compounds into the cave environment, other sources also exist (re-melted lava, fumarole vents, thermo-mineral fluids, etc.) and these may play an extremely important role in the deposition of cave minerals. However, one fundamental factor in the generation of diverse cave mineral assemblages is the cave itself, which is host to various minerogenetic mechanisms (White, 1997; Onac, 2005; Forti et al., 2006). Most of these are strictly controlled by cave temperature, relative humidity, and carbon dioxide partial pressure, and are often triggered by endemic microorganisms. Table 1 represents an attempt to synthesize these major processes and mechanisms (from higher to lower temperatures) acting in caves, along with their most common mineral products. Some of these processes and reactions (e.g., groups 1, 2, 3, 8.1, and 9) are restricted to highly peculiar cave settings, whereas all the others can, at least theoretically, be active in any ordinary cave.



Table 1. Main processes, mechanisms, and related temperatures, leading to deposition of minerals in caves.

PROCESS		MECHANISM / REACTION	T (°C)	COMMON PRODUCTS
1	Phase transition	1. Segregation	1000 ÷ 800	Silicates
		2. Sublimation	> 100	Sulfur, oxides, hydroxides
		3. Transition	< 50	Calcite
2	Thermal contact	Ion exchange/ Substitution of atoms	400 ÷ 50	Fluorite, opal, calcite
3	Cooling	Supersaturation	400 ÷ 0	Sulfates, halides, quartz, etc.
4	Air movement	Deposition from aerosols and vapors	100 ÷ 20	Sulfates, halides, opal
5	Solution	Evaporation	100 ÷ 0	Sulfates, halides, opal
6	Geochemical	Oxidation/Reduction Hydration/Dehydration Double replacement	100 ÷ 0	Si-, Al-, Fe oxides-hydroxides, sulfates, carbonates, sulfides, etc.
7	Karst	CO <sub>2</sub> diffusion	40 ÷ 0	Carbonates
8	Biogenic	1. Digestion, dissolution, double replacement, redox	60 ÷ 0	Phosphates, nitrates, sulfates, halides
		2. Guano combustion	600 ÷ 200	Phosphates, silicates
9	Water phase change	1. Freezing	< 0	Ice
		2. Segregation	< 0	Sulfates, halides, carbonates
		3. Sublimation	< 0	Ice

### Phase transition

At temperatures well-above 100°C, two different minerogenetic mechanisms (segregation and sublimation) are responsible for phase transition processes. These are however, restricted to volcanic caves/lava tubes, in which extremely high temperature (between 800 and 1000°C) are normal during the initial stage of development (Forti, 2005). At much lower temperatures, i.e., between 10 and 50°C, aragonite/calcite inversion is sometimes possible.

### Segregation

When a lava tube is only partially filled, oxidation processes occur in the atmosphere overlying the flowing molten lava. These reactions are strongly exothermic, with cycles of cooling and crystallization and re-melting of the rocks in the lava tube roof being induced (Fig. 4). Each of these cycles causes a partial segregation of compounds melting at higher temperatures, hence slightly changing the composition of the re-melted lava (Allred & Allred, 1998). If this process is repeated several times, it is possible that well-defined chemical compounds, with compositions completely different from that of the original lava, will be deposited. This is the case of volcanic glass (amorphous silica), which often gives a vitreous luster to some lava tubes, as well as pseudo-stalactites (pendants).

### Sublimation

When lava tube walls solidify while the temperature is still very high, sublimation processes may occur. They are related to fluids seeping out from the wall and/or fractures in the floor. The cooling of fumarole gases, enhanced when expelled in the cave atmosphere,

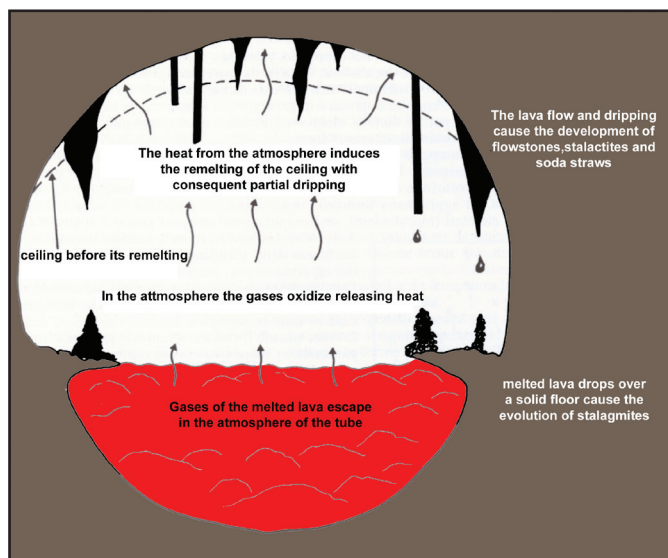


Fig. 4. Sketch of a lava tube in which partial re-melting of roof is induced by oxidation processes in the cave atmosphere (after Forti, 2005, modified).

sphere, allows for the deposition of sublimates of different minerals, the most common being sulfur. Other mineral compounds such as oxides, hydroxides, and even sulfate groups have been reported (Forti, 2005; Forti et al., 1996).

The first place where such a process was observed was the Cutrona lava tube on Mt Etna (Forti et al., 1994), in which the cave climate and the evolution of speleothems have been monitored since the cave's discovery (some 8-10 months after the end of the eruption which generated the cave) until the internal temperature reached equilibrium with that of the external environment. The fumarole activity, and therefore the process of sublimation, may last up to several months, but inevitably it stops, and most, if not all, speleothems precipitated disappear within days. This is partly due to their instability under low-temperature conditions but it is also a consequence of their delicate structure. Consequently, such deposits are rarely preserved once fumarole exhalation has ended.

### Thermal contact

When minerals in the cave rock walls are exposed over rather long time periods to high-temperature thermo-mineral fluids, they may undergo ion exchanges or substitution of atoms. A spectacular example of such a phenomenon has been reported from Faggeto Tondo Cave (Umbria, Italy) (Forti et al., 1989), where the calcite from a relatively large cave passage section has been completely replaced by fluorite (Fig. 5). Substitutions can also lead to the development of quartz and/or opal replacement, as reported worldwide in thermal caves (Dublyansky, 1997).

At lower temperatures, prolonged contact between limestone walls and thermal fluids may also be responsible for the precipitation of giant phreatic calcite crystals (De Vivo et al., 1987). In these settings, the development of crystals is not a direct result of precipitation from supersaturated solutions, but rather the result of the dissolution of grain-sized calcite crystals within the limestone and the simultaneous deposition of larger ones. There is a simple thermodynamic explanation for this, which is the ratio of mass to surface energy. This allows a solution to be undersaturated with respect to small crystals but oversaturated with respect to large ones.

### Cooling

The progressive cooling of thermo-mineral fluids may induce super-saturation with respect to many different minerals, because the solubility of most chemical compounds is temperature-dependent. When thermo-mineral solutions migrate upward, their temperature decreases as they approach the earth's surface, thus, the solubility equilibrium for many of the dissolved compounds can be reached or even surpassed. This process is responsible for most of the chemical deposits precipitated in the phreatic zone of many thermal caves. The presence of quartz, barite, celestine, and sulfides in such cavities is a consequence of this process (Dublyansky, 1997).

A unique example of cooling-related super-saturation is that which controls the solubility disequilibrium between anhydrite and gypsum (Fig. 6). This

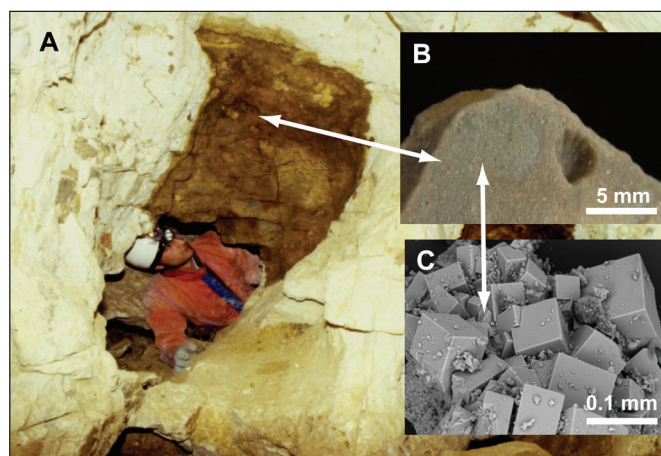


Fig. 5. Faggeto Tondo Cave (Italy): A) part of the limestone cave wall underwent molecular substitution into fluorite (photo: P. Forti); B) close-up view of fluorite (A. Rossi) and C) SEM microphotograph of fluorite crystals (E. Galli).

process has been found to be responsible for the formation of the world's largest gypsum crystals in the Cueva de los Cristales (Naica, Mexico; Fig. 7) (García-Ruiz et al., 2007). Up to 59°C (the temperature of thermo-mineral waters inside the mine), the solubilities of gypsum and anhydrite are about the same, but as temperature drops, gypsum becomes less soluble than anhydrite. Therefore, below this temperature, a solution that was originally saturated with respect to anhydrite becomes supersaturated with respect to gypsum, thus promoting the deposition of giant gypsum crystals and leaving the parent solution undersaturated with respect to anhydrite. The entire carbonate sequence of the Naica district (especially below the -240 m level) is rich in anhydrite produced by the

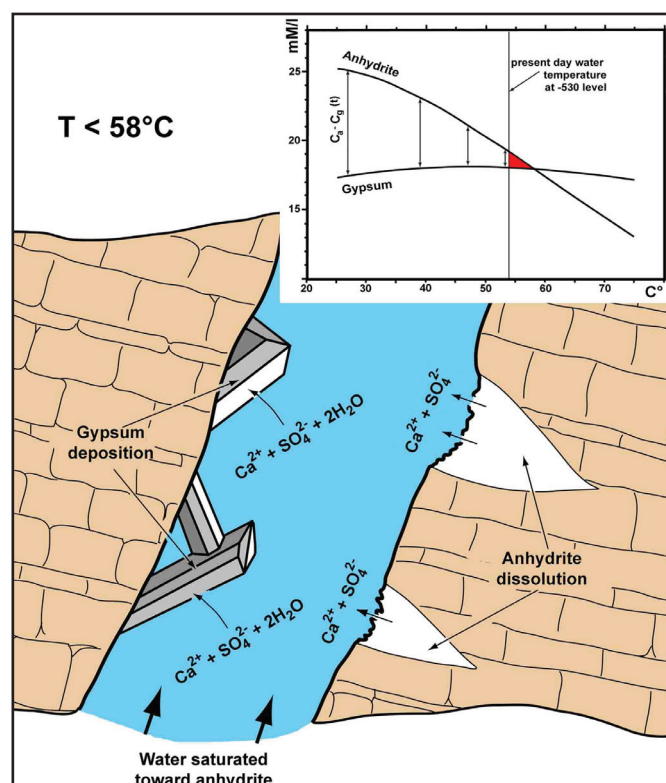


Fig. 6. The mechanism by which the giant gypsum crystals developed within Cueva de Los Cristales, Naica, Mexico) (after Forti, 2010).





Fig. 7. A general view of the giant gypsum crystals of Cueva de Los Cristales (Naica, Mexico; La Venta archive).

reaction between sulfuric acid (oxidation of sulfides) and limestone (García-Ruiz et al., 2007). This late-stage anhydrite continuously supplies the upwelling solutions with enough  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  to maintain them supersaturated with respect to gypsum and slightly undersaturated with respect to anhydrite.

#### Air movement

Air currents circulating inside caves can sometimes contribute to the deposition of peculiar speleothems made-up of different minerals, some of which are very soluble. Two possible mechanisms for the formation of these deposits involve aerosols and vapor condensation.

The deposition of minerals from aerosols is a rather uncommon process for most ordinary caves (Cigna & Hill, 1997), although the precipitation of certain unique speleothems such as needle-like calcite helictites (Cser & Gáboros, 1988), calcite crusts (Halbichová & Jančařík, 1983), gypsum crystals (Klimchouk et al., 1995, 1997), and coralloids (Hill, 1987) has been attributed to such a process. Great probability for aerosol-deposited speleothems exists in thermal caves (especially if water is flowing through them) where nodular calcite and opal popcorn have been reported by Pashenko & Dublyansky (1997).

Vapor condensation, however, is by far more frequent than aerosol deposition as a mechanism by which air currents can induce the deposition of cave minerals. This is an active process in most meteoric caves, especially where passage constrictions generate strong winds. The sudden “adiabatic” expansion cools the suspended vapors, which then condense at the mouth of the cracks or right after these narrow passages. The process is further enhanced by increased air turbulence, which commonly results in speleothems such as rims (often composed of gypsum; Hill, 1987) or anemolites (speleothem with a preferred orientation caused by air currents; Fig. 8). Fig. 8 shows anemolites growing in a downwind direction from vapors. However, the type of anemolites seen by most cavers form by a different process and grow in an upwind direction. In normal limestone caves with stalactites and stalagmites, gravitational solutions experience increased evaporation on the side facing the wind: the combination of these two processes (evaporation and vapors) can lead to the growth of coralloid anemolites into the wind.

The effect of vapor condensation induced by air movement is particularly evident within early-stage lava tubes when fumarole vents are still active in their interior. The interactions between these exhaled products and minerals previously precipitated due to evaporation can favor the deposition of very soluble compounds, generally sulfates (commonly thenardite) or halides.

The first lava tube where such deposits were observed was Cutrona Cave on Mt. Etna (Forti et al., 1994). The most common deposits of this kind are the extremely thin anemolite needles (hair-like filaments with a diameter of 0.1-0.5 mm and over 10-15 cm in length), which cover the sides of stalactites opposite the direction of fumarole flow through the cave (Fig. 9A). Anemolite genesis is related to the peculiar microclimatic conditions that develop immediately adjacent to stalactites exposed to fumarole vapors. In fact, the increase in gas turbulence near speleothems and the lowering of the temperature of the vapors as they are liberated in the cave atmosphere are responsible for the enhanced deposition of particles carried by the fluid itself. Other less common speleothems originating from the same process are rims and blisters. These develop along the upper part of the fractures along which the fumarole vapors enter the cave (Fig. 9B).

#### Dissolution/Reprecipitation

When evaporite rocks (salt, gypsum, etc.) dissolve in water percolating towards a cave,  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ , and  $\text{SO}_4^{2-}$  ions diffuse into solution. After entering the air-filled caves, these solutions become supersaturated with respect to one or more ions as a result of an efficient evaporation process that is controlled by the cave temperature and its relative humidity. Following this pathway, speleothems composed of very soluble minerals, such as halite, epsomite, mirabilite, and other sulfates were precipitated in the salt karst of the Atacama (De Waele et al., 2009) and in limestone and/or gypsum cavities throughout the world (Forti, 1996a). The very same process can also trigger

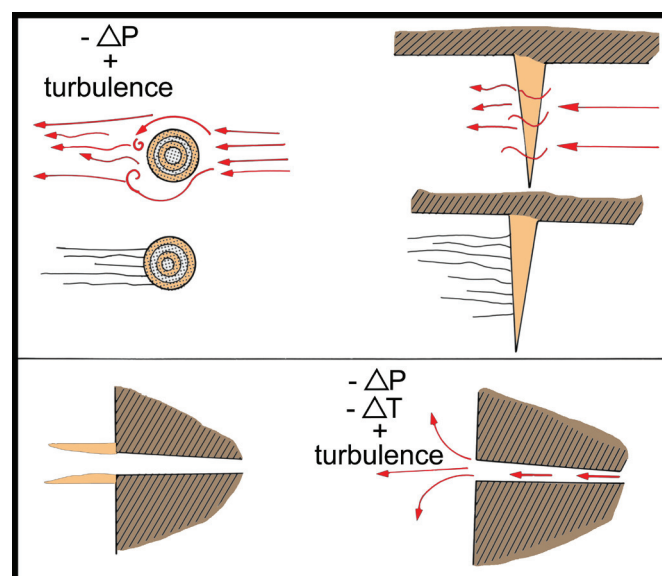


Fig. 8. Mechanism by which anemolites and rims develops from aerosols and vapors.



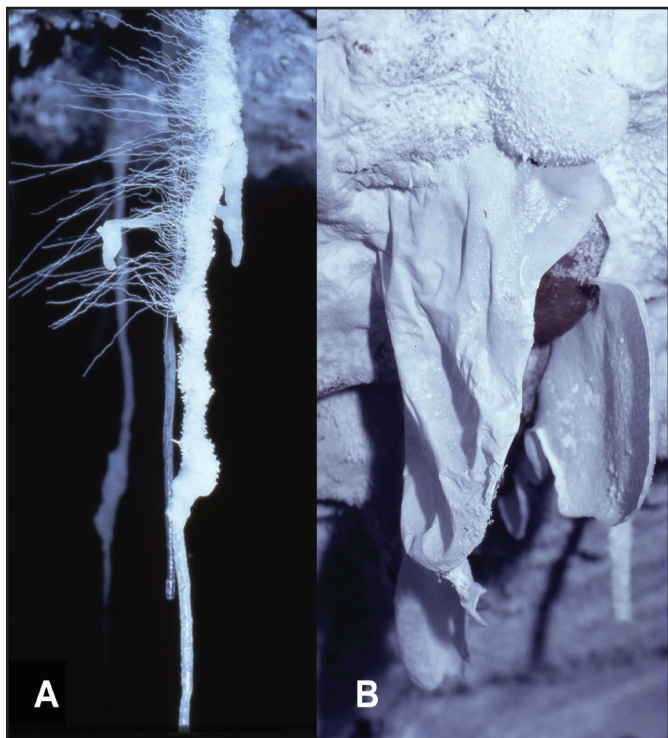


Fig. 9. Thenardite speleothems in Cutrona lava tube (Etna, Italy)  
A) anemolites; B) rims and blisters.

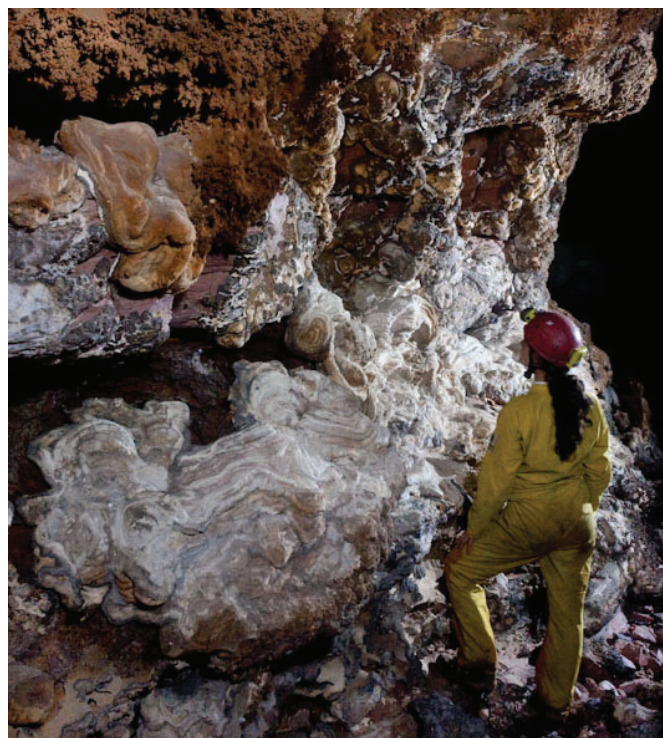


Fig. 10. Large opal flowstones in Cueva Guacamaya, a quartzite cave in Venezuela (photo: F. Sauro, Archivio La Venta).

the deposition of less soluble minerals, such as opal, which accumulates in large quantities in the quartzite caves of Venezuela (Fig. 10), or barite helictites (Forti, 1996b), found within small solutional cavities developed in barite veins in Sardinia (Fig. 11).

The dissolution/precipitation mechanism is also active within volcanic cavities. Once the temperature of lava drops below 100°C, liquid water can enter these cavities along fissures, or through porous surfaces, carrying various salts dissolved along the way. When dripping/seeping water comes in contact with a still-hot cave atmosphere, it rapidly evaporates, causing the deposition of large numbers of speleothems, normally consisting of highly soluble sodium, potassium, or magnesium sulfates and/or halides. This is certainly a “golden moment” for the decoration of volcanic caves, a time when not only the ceiling, but also the walls and the floor are completely covered by an incredible variety of polychromatic stalactites, soda straws, stalagmites, flowstones, popcorn, coralloids, etc. An exceptional example of this kind of decoration was found in the Cutrona lava tube on Mt Etna (Forti et al., 1994), but other cavities around the world are known to host similar formations (Jakobsson et al., 1992; Jónsson, 1994; Davies, 1998). Unfortunately most, if not all speleothems and cave minerals deposited via this dissolution/precipitation mechanism in a still hot volcanic cave are short lived; in fact, they rapidly dissolve as the cave temperature drops and the environment becomes more humid. In the Cutrona lava tube on Mt Etna, where snowfalls are normal during winter, the large evaporitic speleothems lasted for little more than one year (Forti et al., 1994). Probably, in drier areas such as deserts or similar environments, such speleothems may persist for tens or even hundred of years.

### Geochemical

The aerobic and anaerobic weathering of minerals within the host rock and/or their reaction with various ions and molecules dissolved in the seeping water can lead to the deposition of many different compounds, among which the most common are oxides & hydroxides, sulfates, carbonates, and nitrates. There are three main active minerogenetic mechanisms involved: oxidation/reduction (redox), hydration/dehydration, and double replacement reactions.

#### Oxidation/Reduction

Meteoric-derived groundwater seeping through a sequence of karst rocks creates an oxic mildly acidic microenvironment, in which pyrite and other sulfides disseminated in the limestone readily oxidize and hydrolyze into a variety of Fe oxides and hydroxides. This mechanism is mainly active in the vadose (air-filled) sectors of most caves. However, these processes also take place along epiphreatic conduits if the meteoric water supplies enough dissolved oxygen to maintain highly oxic conditions.

Another common process occurring in many cave environments involves the oxidation of hydrogen sulfide ( $H_2S$ ) to sulfuric acid ( $H_2SO_4$ ). In limestone caves, the expected product of this reaction is gypsum, especially in the form of moonmilk and cave flowers. When the environment is strongly acidic (pH ~1), the oxidation of  $H_2S$  results in the genesis of sulfur speleothems (Fig. 12) (Forti & Mocchiutti, 2004). For more information on the origin of sulfuric acid caves and their unique mineralogy, readers are directed to Hill (1987, 1995), Galdenzi & Menichetti (1995), Jagnow et al. (2000), Polyak & Provencio (2001), Palmer (2007), and Onac et al. (2009).





Fig. 11. Barite helicites in a natural cavity inside Silius mine (Sardinia, Italy) (photo: Paolo Forti).

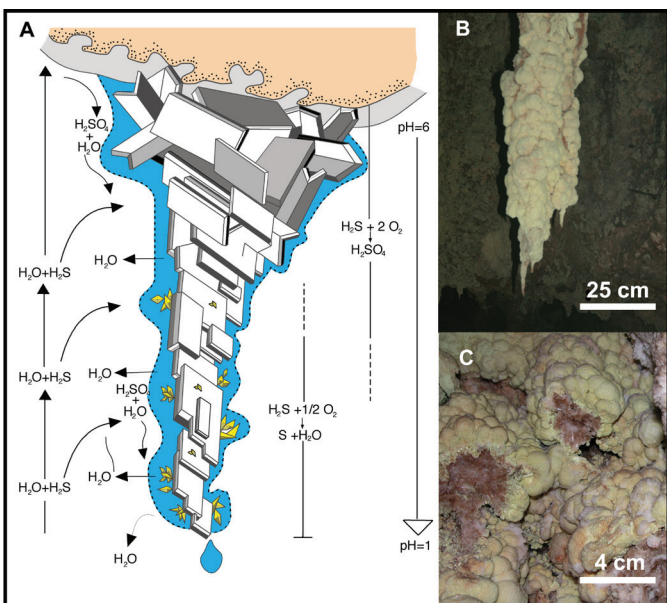


Fig. 12. A-C: Genetic sketch of a sulfur stalactite growing over a gypsum core in Cala Fatente Cave (Italy) (after Forti & Mocchiutti, 2004, modified).

The reduction processes are far less active in cave environments, which are normally slightly oxidizing, with redox potential (Eh) ranging from +0.4 to +0.6 V (White, 1976). In order for such processes to occur, anoxic conditions must prevail. Moreover, the presence of organic matter is required, as it is the oxidation of this material which supplies the energy needed for the endothermic reduction reactions to take place. Thus, if these processes occur, they are basically restricted to the phreatic or/and epiphreatic zone(s) of a given cave system. Sometimes, within the same cave passage, the geochemical boundary conditions change over time, switching the oxidizing and

reducing process on and off. The best examples of the formations found under such conditions are the so-called “bohnerz”, first described in the Dachstein-Mammuthöhle in Austria (Seemann, 1970) and later observed in other caves in Italy (Forti, 1987) and Romania (Onac, 1996).

The “bohnerze” are rounded dark brown to metallic black masses (Fig. 13A), somewhat similar to cave pearls; they consist of alternating lamina of iron oxo-hydroxides, with thin layers consisting of pyrite or marcasite crystals (Fig. 13B). They always form on underground streambeds and inside soft clay sediments with a relatively high organic content. Depending on the cave flow regime, the “bohnerze” evolve under both oxidizing (during dry seasons) and reducing (during floods) conditions, allowing for the evolution of the iron sulfides or their partial oxidation to oxo-hydroxides.

Although many important inorganic processes involve redox reactions, most such reactions are mediated by microorganisms, such as those related to sulfur, nitrogen, manganese, and iron cycles (see below in the Biogenic activity entry).

### Hydration/Dehydration

Many ionic compounds can incorporate water molecules into their solid structures (as expressed by the coefficient before the  $H_2O$  at the end of a chemical formula), a fact that impacts on their stability if the humidity fluctuates in the surrounding environment. The relative humidity in the atmosphere of most caves normally exceeds 85%. However, certain cave passages (sometimes the entire cave) are characterized by strong evaporative conditions, resulting in rather dry environments. In such settings, some hydrated minerals may lose part of their crystallization water and be converted into different compounds. On the contrary, in very humid areas of a cave, anhydrous compounds will absorb water from the cave atmosphere and be converted into hydrated minerals.

A common hydration/dehydration reaction reported from various different caves is that involving mirabilite ( $Na_2SO_4 \cdot 10H_2O$ ) and thenardite ( $Na_2SO_4$ ) (Bertolani, 1958). Mirabilite (stable under higher water vapor pressure) dehydrates completely to thenardite in a single step when the relative humidity drops. A similar, but more complex reaction is the dehydration of epsomite ( $MgSO_4 \cdot 7H_2O$ ) into hexahydrate ( $MgSO_4 \cdot 6H_2O$ ), and finally to kieserite ( $MgSO_4 \cdot H_2O$ ) (Bernasconi, 1962; White, 1997). Less frequently, other hydration/dehydration reactions (e.g., bassanite ( $CaSO_4 \cdot 0.5H_2O$ ) / gypsum ( $CaSO_4 \cdot 2H_2O$ ) (Forti, 1996b) or mbobomkulite / hydrombobomkulite (Martini, 1980a) can be encountered in caves.

### Double replacement reactions

This minerogenetic mechanism is characteristic of, but not restricted to limestone caves. It takes place between two compounds in which parts of each are interchanged to form two new minerals with the same ions. Typically, such reactions involve at least one carbonate compound (since caves are mostly developed in limestone and dolomite) and one more or less strong acid (carbonic, sulfuric, phosphoric, etc.). The presence of strong acids in the cave environment



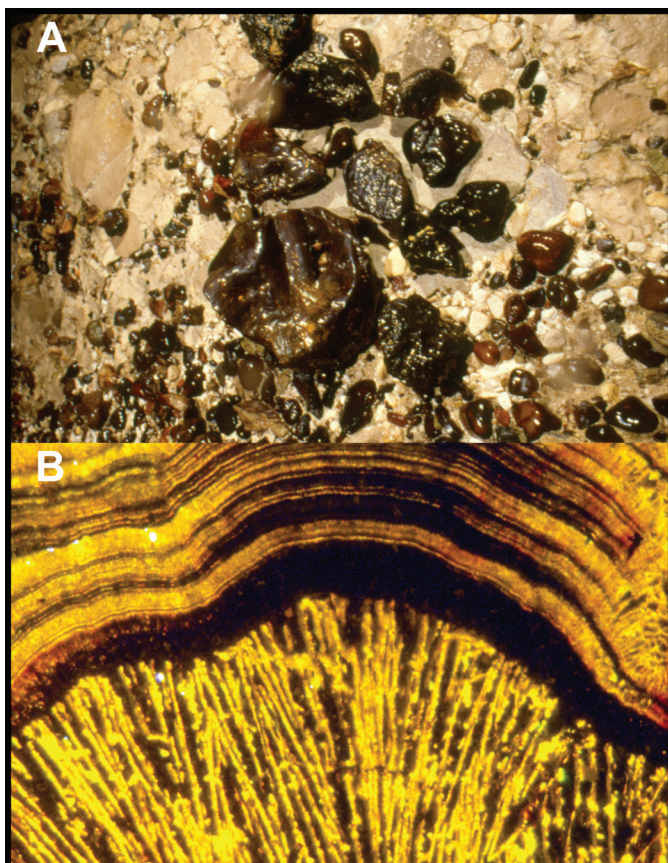


Fig. 13. Pod Lanisce Cave (Italy): A) bohnerz; B) thin section in which the transition between sulfides and oxides is evident (photo: P. Forti).

is usually related to oxidation processes (generation of sulfuric acid from pyrite or hydrogen sulfide; Pohl & White, 1965; Hill, 1987) and the presence of guano (phosphoric and nitric acids; Hill & Forti, 1997; Onac, 2000).

Sulfate, nitrate, and phosphate minerals are the final products of double replacement reactions taking place in caves. These minerals form a great variety of speleothems, from moonmilk to flowstones, and from helictites to euhedral crystals. Gypsum is by far the most common mineral being precipitated in a double exchange reaction.

In some circumstances, however, the double replacement reaction can also cause the precipitation of salts of a weaker acid, although the compounds of a stronger acid will be dissolved: the so-called common ion effect. Often, in the cave environment, this process is known as “incongruent dissolution” (e.g., the dissolution of gypsum/anhydrite driving the precipitation of calcite; Fig. 14) (Wollast & Reinhart-Derie, 1977; Calaforra et al., 2008). It is especially active in gypsum caves, where seeping water with a high  $\text{CO}_2$  content interacts with the gypsum bedrock (Forti & Rabbi, 1981). In these caves, most, if not all calcite formations are deposited via incongruent dissolution. Sometimes, peculiar speleothems, like the calcite blades of the Novella Cave (Italy) (Forti & Rabbi, 1981) and the floating half bubbles of Grave Grubbo Cave (Italy) (Chiesi & Forti, 1995) are attributed to this process. Thus, “incongruent dissolution” seems to be the second most active process in depositing calcite and/or aragonite speleothems in limestone caves, and it is by far the major mechanism in evaporite karst.

## Karst

The chemistry underlying the interaction between ground waters and carbonate rocks, the driving force of both karstification and speleothem deposition, can be expressed by a single simplified chemical reaction, known as the classical karst reaction:



in which, reaction from left to right consumes carbon dioxide to dissolve limestone, whereas the opposite reaction, precipitates calcite or aragonite out of the solution to form speleothems while  $\text{CO}_2$  escapes in the cave atmosphere. This reaction is responsible for the precipitation of ~95% of calcite and aragonite speleothems, representing over 97% of the total chemical deposits hosted in caves (Dreybrodt, 1988; Hill & Forti, 1997; Palmer, 2007; Onac, 2011a).

Obviously, this process is the dominant one in carbonate caves, but it is not restricted to this environment. In fact, reactions similar to this can cause deposition of calcite, aragonite, or any other carbonate mineral in non-carbonate rocks once two required

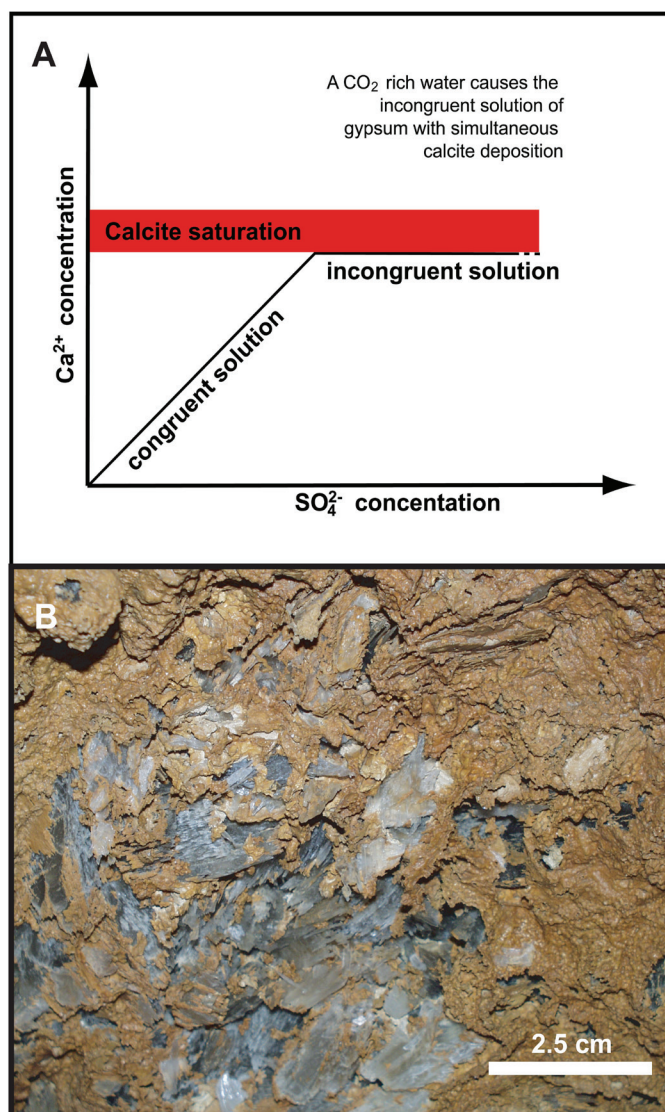


Fig. 14. A) Effect of the incongruent dissolution of gypsum rock by water with a relative high  $\text{CO}_2$  content; B) calcite crusts developing over gypsum crystals via incongruent dissolution (Novella Cave, Bologna, Italy) (photo: P. Forti).



conditions are met: a) a  $\text{CO}_2$ -enriched water source and b) availability of relatively large amounts of calcium, magnesium, or other cations in the solution. In order to satisfy the first condition, it is sufficient that a well-developed layer of soil covers the cave, whereas for the second, it is necessary for the water to dissolve  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and other ions as it passes through the formation(s) above the cave. While the first condition almost always exists, the lack of the second can prevent the deposition of carbonate speleothems. The cavities hosted in quartzites (e.g., Venezuela) and in almost any volcanic rock, provide examples of such restrictive environments.

An exception is represented by the lava tubes of Cheju Island (Korea), where flowstones, stalactites, stalagmites, helictites, conulites, gourds, and even cave pearls consisting of calcite and/or aragonite cover almost all of the cave walls and floors (Kashima & Suh, 1984). It is the unique environment of this island that has allowed such an exceptional development of calcite speleothems. Here, the lava tubes are covered by a thick bed of highly porous micro-coquina (a clastic limestone composed of cemented, sand-sized grain particles of shell detritus). Precipitations percolating through the soil are enriched in biogenic  $\text{CO}_2$ , producing carbonic acid that slowly dissolves the micro-coquina, becoming saturated with respect to  $\text{CaCO}_3$ . As soon as this supersaturated solution enters the lava tube, calcite or/and aragonite is immediately precipitated (Woo et al., 2000) (Fig. 15).

### Biogenic activity

The idea that living organisms can somehow influence the development of the secondary chemical deposits in caves is quite old (Shaw, 1997 and references therein). For the early visitors, the shape and internal structure of some speleothems (stalactites, stalagmites, coralloids, pool fingers, etc.) suggested the possibility that they had grown as plants (Tourneford, 1704). But since the second part of the XVIII<sup>th</sup> century, progress in chemical and geomicrobiological studies allowed the detection of the main mechanisms for the deposition of calcite and other minerals in caves. More recently, significant discoveries and detailed studies have updated our understanding of microbe-rock interactions and the way in which microorganisms mediate speleothem deposition (Northup & Lavoie, 2001; 2004; Barton, 2006; Jones, 2010).

Presently, it is well established that the enzymes synthesized by microorganisms can directly cause biomineralization and the production of substances that lead to the precipitation of minerals (e.g., by changing the pH in their surrounding), or they can provide nucleation support for different minerals (Northup et al., 1997; Boston et al., 2001).

The microbial processes in caves often involve redox reactions (Sasowsky & Palmer, 1994). The microbial players are varied, both aerobic microorganisms (chemiolithotrophs), which obtain energy directly from the oxidation of inorganic compounds, and anaerobic organisms (heterotrophs), which obtain energy from the oxidation of organic matter and reduce inorganic compounds. The best example of redox reactions driven by cave-dwelling microorganisms is the realm of guano (see below).

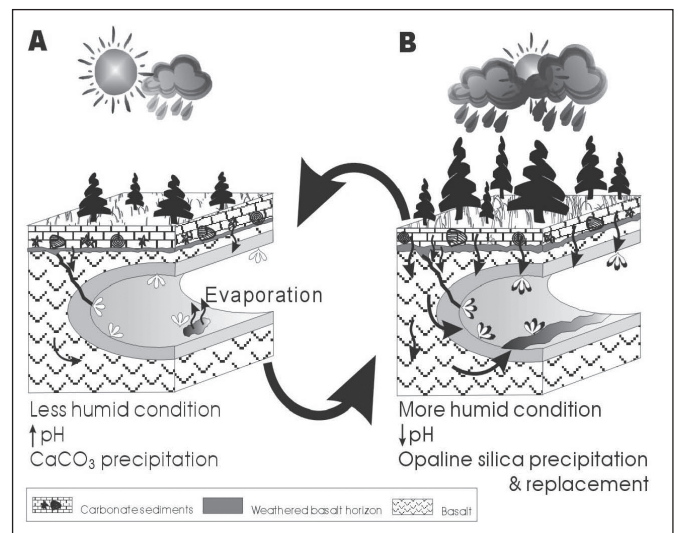


Fig. 15. Mechanisms by which calcite speleothems develops inside lava tube of Jeju Island (Korea) (after Woo et al., 2000).

Biologically driven processes act the same way irrespective of the type of rock in which the cave was formed, although some of them may be limited to specific unique environments. This is the case for those requiring large amounts of silica, normally restricted to volcanic and/or quartzite caves. In some of the volcanic cavities of Korea (Kashima et al., 1989), the development of silica coralloids and helictites seems to be strictly linked to the presence of certain diatom colonies (genus *Meolosira*), which are only present in the twilight zones of these caves. In addition to this proven biological control of speleothem deposition in a silica-rich cave environment, there are other cases in which microorganisms clearly mediate the precipitation of silica (opal, opal-CT, or quartz) speleothems (e.g., the filamentous organic structures reported from Caverns of Sonora by Onac et al. (2001).

Furthermore, in many of the lava tubes from Pico Island (Azores) or from Rapa Nui (Easter) Island, weathering of basaltic rocks has triggered the precipitation of large amounts of amorphous silica moonmilk. This deposit is extremely rich in organic matter, suggesting that microorganisms control the weathering process (Forti, 2005; Calaforra et al., 2008). On Pico Island (Azores), the Argar do Carbalo volcanic cave probably hosts the world's largest deposit of opal flowstone (up to 5-6 m in length and over 1 m in thickness), which appears to have formed through the diagenesis of the silica moonmilk (Forti, 2001).

Generally, all biologically driven processes are complex and begin with "digestion" which involves a variety of biochemical reactions. These processes require the presence of abundant organic deposits above and/or inside the cave and long periods of time. The most complex digestion processes relevant to the precipitation of nitrate and phosphate minerals are those taking place within guano deposits. A suite of dissolution, double replacement, and redox reactions is responsible for the deposition of a variety of nitrate, phosphate, and sulfate minerals in caves.

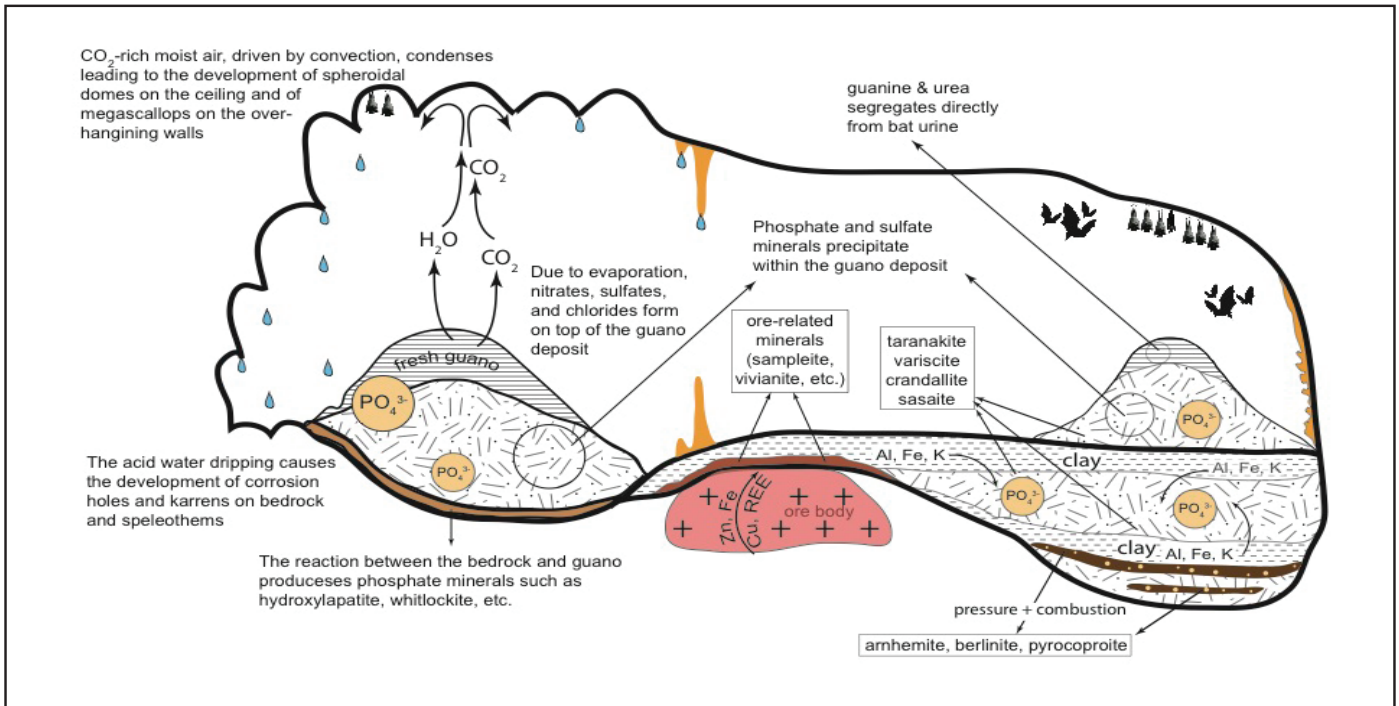


Fig. 16. Main minerogenetic and speleogenetic processes related to the presence of guano deposits.

**Precipitation of guano-related minerals**

The most common organic deposit in all types of caves is clearly bat guano, although bone breccias and the excrements of various animals are occasionally found. Guano is home for a variety of complex reactions (mostly biologically-driven), ultimately releasing nitric, phosphoric, and sulfuric acids (Forti, 2001), which then react with the carbonate bedrock or cave sediments to form over 100 secondary minerals (Onac, 2005, 2011b) (Fig. 16). Some of the guano related minerals, such as the organic compounds guanine and urea, segregate directly from the guano itself.

Nitrate minerals are highly soluble, therefore forming only under warm and dry (arid and semi-arid) conditions, a fact that limits their occurrence on the surface of the earth. However, nitrate minerals have been widely reported from well-ventilated caves, as well as from known caves in dry areas (Hill & Forti, 1997). Except for a very few occurrences where an inorganic origin has been documented (presence of overlying volcanic rocks supplying  $\text{NO}_3^-$  ions; Hill & Eller, 1977), the deposition of nitrates has been aided by the action of various nitrogen bacteria (e.g., *Nitrobacter*; Hill, 1981a, b).

Two main sources supply the  $\text{NO}_3^-$  ions in caves: a) decaying forest-litter in temperate humid climates and b) large guano deposits. The first source, with its associated biological processes, is by far the most important, and it is the only one that can justify the presence of very large deposits of cave nitrates (e.g., Saltpeter and Mammoth caves, USA) and their rapid regeneration cycle.

Although the reactions involving guano are identical in all types of caves (limestone, volcanic, etc.), the number of cave minerals precipitated is always greater in volcanic caves and ore-deposit mines, because the variety of different ions available in the rocks is much greater than in any ordinary limestone cave.

**The sulfur cycle**

The sulfur cycle (Fig. 17) involves redox reactions totally driven by microorganisms, which control each of the oxidizing and/or reducing steps and lead to the development of specific chemical cave deposits, mainly sulfates (Forti, 1989, 1996a; Forti & Salvatori, 1988). Under very low pH conditions (<1), sulfide-oxidizing bacteria are capable of precipitating native sulfur, as well as producing sulfuric acid. This has crucial implications for speleogenesis, during which a number of mineral by-products form (Polyak & Provencio, 2001; Audra & Hobléa, 2007; Onac et al., 2009).

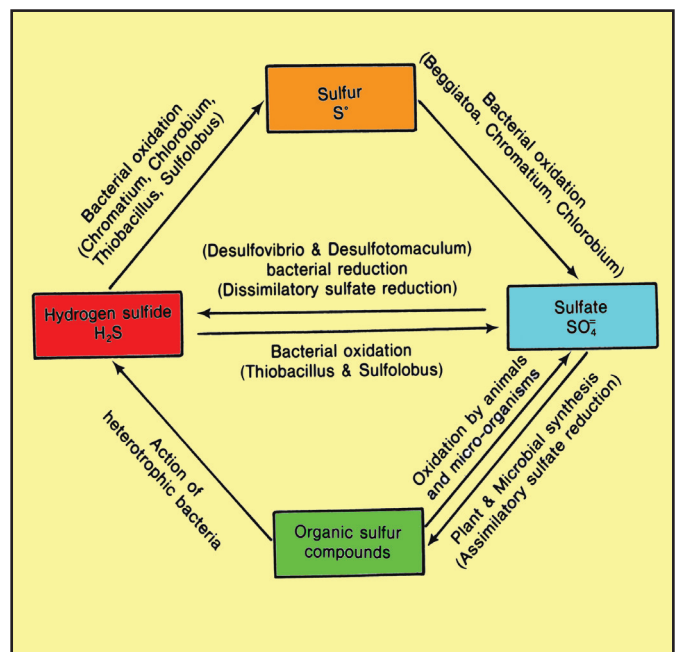


Fig. 17. Sulfur cycle-related minerals and their genetic pathways.

Table 2. Minerals directly related to the "Sulphur Cycle" (after Forti, 2001, modified).

	Minerals		Genetic mechanisms
1	<i>Sulfur</i>		Anaerobic reduction of sulfates, aerobic oxidation of sulfides in strongly acidic environment
2	<i>Gypsum</i>		Direct reaction of H <sub>2</sub> SO <sub>4</sub> with limestone or dolomite
3	<i>Calcite</i>		Incongruent dissolution of sulfates
4	Metal oxides & hydroxides	<i>Goethite, Hematite, Magnetite, Lepidocrocite, Braunitz, Pyrolusite, Romanechite, Hausmannite</i>	Final products of the sulfide oxidation
5	Metal sulfates	<i>Barite, Anglesite, Brochantite, Fibroferrite, Jarosite, Halotrichite, Melanterite, Rosenite, Zaherite</i>	Final product of the sulfide oxidation in presence of metallic ions
6	Metal carbonates	<i>Siderite, Aurichalcite, Azurite, Malachite, Cerussite, Rosasite, Hydrozincite</i>	Final products of the sulfide oxidation or of the mobilization of sulfates in carbonate environment
7	Metal phosphates	<i>Hopeite, Parahopeite, Tarbuttite, Scholzite, Tinticite, Sampleite</i>	Final products of the sulfide oxidation in presence of guano and/or bones
8	Silicates	<i>Opal and/or Quartz</i>	Deposition induced by pH lowering during the sulfide oxidation or sulfate reduction
		<i>Allophane, Halloysite-10Å</i>	Deposition in strongly acidic environment induced by sulfide oxidation
9	Sulfides	<i>Pyrite, Marcasite</i>	Anaerobic reduction of sulfates

Moreover, the sulfate generated by sulfur/sulfide oxidizing bacteria can be used as an oxidizing agent by sulfate-reducers. One such reaction produces bicarbonate, which can form complexes with calcium, causing the precipitation of calcite. On the other hand, sulfate reduction can also be responsible for the precipitation of dolomite (Palmer & Palmer, 1994).

The organic material produced during oxidizing processes involving the sulfur cycle often generates pseudo-stalactites of mucus (also known as mucolites or snottites). Over time, these may crystallize, generating different minerals, some of them direct products of redox processes, whereas many others form as a result of double replacement reactions involving sulfuric acid and limestone bedrock or cave sediments.

#### **Guano combustion**

A unique and rather rare minerogenetic mechanism, strictly related to guano, is its spontaneous combustion (Martini, 1994a). Naturally induced guano fires have been reported to occur in hot and arid climates, but also in temperate zones, in both limestone caves and lava tubes (Martini 1994a, b; Onac & White, 2003; Forti et al., 2004; Onac et al., 2006,

2007). This guano combustion commonly produces layers of ash or highly compacted sediment horizons (Fig. 18). Because guano combustion takes place at very high temperatures (>500°C), the mineral components of the cave sediments overlying or interbedded in the guano deposits react with each other and form extremely rare minerals (such as berlinite and hydroxyllestadite).

#### **Water phase change**

This final process simply involves the solidification of water, a process that takes place (with very few exceptions) when the temperature drops below 0°C. Ice speleothems inside most caves are ephemeral, but perennial ice blocks and large ice speleothems (stalagmites, stalactites, domes) have been reported even from regions where the mean annual temperature is above the freezing point (Racoviță & Onac, 2000; Yonge, 2004; Luetscher, 2005; Sivinskikh, 2005). In these locations, the cavities preserving ice over long periods of time are mostly limited to those with a single entrance and steeply descending passages. These are so-called "cold traps", in which the cold dense air sinks and accumulates during the winter, although



the warm, less dense summer air cannot displace the cold air body; this maintains the temperature of the cave below freezing. Under these conditions, the following three minerogenetic mechanisms are common: freezing, sublimation, and segregation.

### Freezing

The development of most ice formations occurs when warm water seeping along fractures and fissures in the caprock enters a cavity where the temperature is below 0°C. If the temperature remains below zero for a long time, the freezing of water creates giant ice blocks and speleothems (Fig. 19). Ice stalagmites and flowstones are far more abundant and larger than ice stalactites and/or draperies; this is because the air at the ceiling level is always slightly warmer than at the floor, thus hindering somewhat the evolution of such ice speleothems (Kyrle, 1929).

Ice stalagmites are formed by a mechanism similar to that of calcitic speleothems, the difference being that the seeping water freezes instead of depositing calcium carbonate. Both speleothem growth and the overall morphology are controlled by air temperature and drip frequency. The amount of ice deposited on stalagmite tips depends on how fast the water freezes. When this process is fast, water drops freeze almost instantly, causing an increase in length. When the process is slow, water drops first ooze down the sides of the stalagmite, contributing mainly to an increase in thickness. This is how the so-called “bamboo stalagmites” (Fig. 20) form and why the upper part of most ice stalagmites are expanded in the shape of a warclub.

### Sublimation

Sublimation processes are common in the entrance area of many caves when the external temperature is very low (below -10°C). The contrast between the cold, dry outside air and the relatively warm and humid cave air allows for the accumulation of “hoar frost”, consisting of large (up to 0.5 m in diameter) hexagonal tabular crystals of ice (Halliday, 1966; Lauriol et al., 1988; Sivinskikh, 2005; Ford & Williams, 2007).

Sublimation is the only active process in the Antarctica glacier caves, where it not only allows the development of ice crystals, but also the enlargement of the caves themselves, due to the heat transfer induced by the combined simultaneous processes of water vapor diffusion from the ice floor to the atmosphere and from this atmosphere to the condensation in hoar frost on the ceiling (Badino & Meneghel, 2001; Smart, 2004). This hoar frost is in general an extremely delicate and unstable ice speleothem that rarely lasts longer than a few months.

### Segregation

When a liquid crystallizes, the foreign ions and molecules (impurities) contained in it tend to be excluded from the crystalline structure of the newly formed compound. Similarly, the freezing of water causes the expulsion of all the impurities dissolved in the mother solution from the ice crystal lattice. If freezing causes the complete transformation of liquid water into ice, all the solute substances are forced



Fig. 18. Layer of thermally-transformed sediments within the guano deposit in Cioclovina Cave, Romania (from Onac et al., 2007, with permission).



Fig. 19. Giant ice speleothems in Eiskogelhöhle, Austria (photo: A. Danieli).

to precipitate giving rise to a wide range of minerals (most commonly carbonates and sulfates; Onac, 2011b). This process is particularly evident when the ice forms from rather concentrated solutions, because the transparency of the ice makes the segregation of the solute visible.

At the end of the segregation process, the compounds deposited form a layer of mineral powder (incoherent deposit of crystalline grains ranging from 10 to 50 microns in size) over the ice surface. The thickness of this layer is proportional to the amount of congealed water and the solubility of the minerals dissolved. The cryogenic calcite powders reported from a number of caves around the world form layers up to 10 mm (Zak et al., 2004, 2008; Fig. 21), whereas 20-mm layers of gypsum powder have been reported from Kungur gypsum cave, Russia (Fedorov, 1883; Dorofeev, 1989). All these deposits are ephemeral,





Fig. 20. "Bamboo ice" stalagmites in Kungur Cave, Russia (photo: P. Forti).

lasting only as long as the water remains frozen, because when the ice melts, the powder dissolves again. However, in caves that host perennial ice blocks and speleothems, the process of segregation not only contributes to the accumulation of flour-like cryogenic calcite fields, but it is also responsible, at least in Scărișoara Ice Cave (Romania), for the precipitation of an unique type of cave pearls (Viehmann, 1959) and the rare mineral ikaite (Onac et al., 2011a).

#### WHAT LIES AHEAD FOR CAVE MINERALOGY?

The systematic studies of cave mineralogy started only 50-60 years ago (Forti, 2002; Hill & Forti, 2007). At present, most mechanisms responsible for precipitating minerals in cave environments are well understood. Nevertheless, it is still possible that new processes will be discovered under very special cave settings, but the areas that deserve our greatest attention over the next several decades are: a) extensive search for new minerals and new cave minerals, b) geomicrobiology, c) paleoclimate and paleoenvironment, and 4) stable isotope geochemistry.



Fig. 21. Cryogenic calcite in Ice Cave, Romania (photo: B.P. Onac).

#### Extensive search for new minerals

In the last 20 years, on average, three new cave minerals per year have been discovered, although no more than 300 of the millions of known natural cavities have yet been subjected to systematic mineralogical studies. Therefore, there is a great possibility that minerals new in the cave environment will be discovered; some might be new for science. The systematic search for new cave minerals, especially in thermal and sulfuric acid caves (including those discovered in mines), may also shed light on similar processes and mechanisms occurring during emplacement of ore deposits or in acid sulfate alteration environments (Onac et al., 2011b).

#### Geomicrobiology

Caves hold an allure for scientists who have uncovered hundreds of bacterial strains never seen before. For example, creatures that evolved in Romania's Movile Cave (Sârbu et al., 1996) or New Mexico's Lechuguilla Cave (Northup et al., 2000) may have been isolated from other ecosystems for millions of years. Geomicrobiology is a field with great potential, which, until recently, has barely been investigated. Over the past 10 years, however, we witnessed a rapidly increasing number of such microbiological studies that showed the role of microorganisms on speleothem formation and speleogenesis (Boston, 2000; Boston et al., 2001; Northup & Lavoie, 2001; Barton & Northup, 2007; Macalady et al., 2007; Engel & Northup, 2008; Jones, 2010).

One of the most important areas for future research is that of further investigating the interactions between microbes and minerals in cave environments. This is certainly difficult, because microbial precipitation often mimics inorganic processes (Barton et al., 2001). Another intriguing target for the investigation of biogenic minerals is the provision of a window for the study of extraterrestrial life by studying the extremophiles living inside caves (Boston et al., 2006).

#### Paleoclimatic and paleoenvironmental studies

Over the past 20-30 years, it has clearly been shown that speleothems provide the most powerful terrestrial proxy for long periods of Quaternary paleoclimate history (Lauritzen & Lundberg, 1999; Lachniet, 2009). There are at least two reasons for this. First, speleothems are well suited for U/Th and U/Pb dating, so they act as precise geologic chronometers. Second, the growth of speleothems is linked to the Earth's atmosphere and hydrosphere in a number of ways, making them sensitive natural archives of climate change. Thus, scientists have been able to extract a wealth of information from carbonate speleothems (e.g., stalagmites and flowstones). Most climate events occurring outside a given cave have been preserved within the speleothem layers (Ford & Williams, 2007; Cheng et al., 2009; Drysdale et al., 2009; Asmerom et al., 2010). Speleothems precipitated in littoral caves are accurate recorders of past sea-level changes (Dorale et al., 2010; Tuccimei et al., 2010). Only recently scientists have begun to "read" such information from other cave minerals (Forti, 2008). For example, Calaforra et al. (2008)

studied the calcite-gypsum speleothems, which have proved to be highly sensitive with respect to climate and paleoclimate (Fig. 22). Other researchers have investigated the climate-controlled sulfur/gypsum speleothems deposition in hypogenic caves (Forti & Mocchiutti, 2004) and the diagenesis of aragonite to opal (Woo et al., 2000).

In addition, speleothems are useful in reconstructing the evolution of the environment (incision rates, uplift, etc.) and in the investigation of seismic activity (Polyak et al., 1998, 2008; Forti, 2004). Therefore, we envision a future, when most, if not all, cave minerals will become useful in providing scientists with available data on environmental changes over an extremely long time interval (from tens to even hundreds of millions of years).

### Stable isotope geochemistry

Across many earth and environmental sciences, the frontiers of research are moving rapidly forward as a result of fast-paced and revolutionary advances of analytical facilities. The emerging applications of recent advances in technology across a broad spectrum of inorganic stable isotope geochemistry started to impact the study of cave minerals. Oxygen isotopic variations in speleothems reflect changes in the isotopic composition of meteoric water and can be linked to climate, whereas, carbon isotopic variations can be traced to changes in regional vegetation (Dorale et al., 1998). Sulfur isotope analyses helps discriminate between various sources of this element when present in the composition of different cave minerals (gypsum, anhydrite, darapskite, etc.) (Bottrell, 1991; Hill, 1995; Onac et al., 2009, 2011b). The isotopic composition of nitrogen and chlorine in bat guano or phosphate minerals is critical to understanding paleoenvironmental conditions from caves in which no other clues are available (Johnston et al., 2010; Wurster et al., 2010; Onac et al., 2011c).

The important message coming from these studies is that vast new territories for exploitation in every aspect of cave minerals/deposits (i.e., deciphering the source of solutions precipitating cave minerals, temperature of deposition, hydrogeochemical and speleogenetic processes) become available using the new advances in stable isotope analytical geochemistry.

### CONCLUSIONS

Although not complete, this paper aimed to provide a general overview of the research conducted in the field of cave mineralogy and its scientific outreaches. It became clear from a number of papers published in the past few years that caves are among the most interesting minerogenetic environments in the world (Onac & White, 2003; Forti et al., 2006; Onac et al., 2006; Garcia-Ruiz et al., 2007; Forti, 2010). Moreover, the chemical deposits found in caves archive fundamental information needed for accurately reconstructing the dynamics of Quaternary climate changes. In the near future, the importance of speleothems as proxy for paleoclimate, paleoseismic, paleoenvironmental, paleotemperature, and sea-level changes will greatly increase.

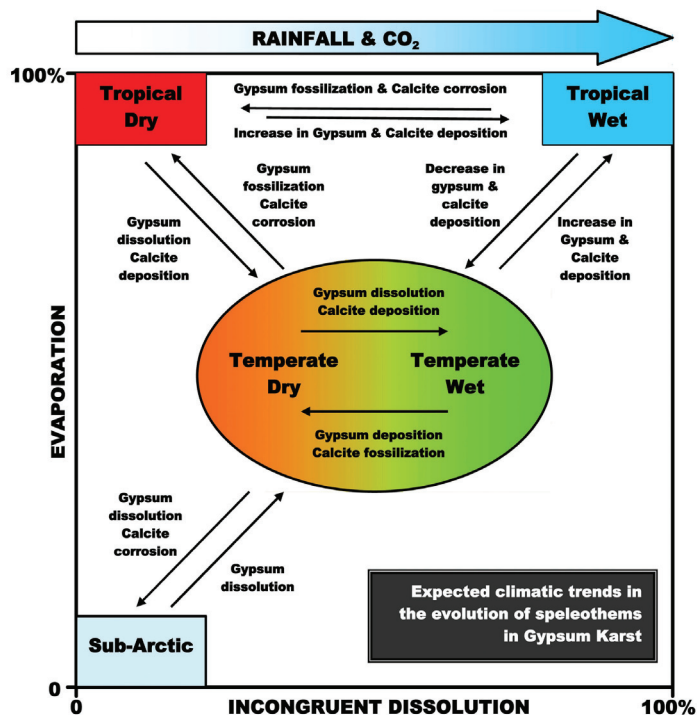


Fig. 22. Climatic induced effects on the calcite/gypsum speleothems within gypsum caves.

Beyond the esthetic rationale for preserving cave minerals/speleothems, there is or should be a moral imperative. Ultimately, our goal should be to protect the fragile speleothems that have taken hundred of thousands of years to form and may not be repeated on a human time scale.

We need to exercise restraint, while striking a balance between sampling speleothems (even broken pieces) and our scientific interests. Moreover, sampling for research purposes must always be kept to an absolute minimum to avoid exhausting the abundance of speleothems. If a proposed study requires the total destruction of a speleothem, the only proper decision is to avoid it until the research team is the possession of high-tech, non-destructive technologies (e.g., X-ray fluorescence, infrared, etc.) that will allow studies without irreversibly damaging the cave environment.

As we look back over the advances and new discoveries in the cave mineralogy field since the last edition of the book *Cave Minerals of the World* was published, we can predict that the science of cave minerals will continue to grow in both prominence and regard within the larger scientific community.

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