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PECULIAR MINEROGENETIC CAVE ENVIRONMENTS OF MEXICO: THE CUATRO CIÉNEGAS AREA

NENAVADNO MINERALOGENO JAMSKO OKOLJE V MEHIKI: PODROČJE CUATRO CIÉNEGAS

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Abstract UDC 552.54:551.44(72)
Paolo Forti & Ermanno Galli & Antonio Rossi: Peculiar minerogenetic cave environments of Mexico: the Cuatro Ciénegas area
The karst area of Quatro Ciénegas (Coahuila, Mexico) represents an ideal site to study cave mineralogy, because it hosts caves of different age and genesis (karst, thermal, mine caves). Among the speleothems studied is worth to mention a nest of aragonite cave pearls found deep inside the Reforma mine characterized by the total absence of growing layers inside them. Despite only few studied caves (8), some 32 different cave minerals have been detected, one of which is new for the cavern environment (kingsmountite) and another one, still under study, which probably will result new for science. Due to the scientific interest of their chemical deposits it should be very important to protect in the future the natural cavities of the karst systems of Cuatro Ciénegas in order to preserve a scientific patrimony, actually only partially known.
Keywords: cave minerals, guano minerals, minerogenetic mechanisms, climate, Cuatro Ciénegas desert, Mexico.

Izvleček UDK 552.54:551.44(72)
Paolo Forti & Ermanno Galli & Antonio Rossi: Nenavadno mineralogeno jamsko okolje v Mehiki: področje Cuatro Ciénegas
Kraško ozemlje Quatro Ciénegas (Coahuila, Mehika) predstavlja idealno območje za preučevanje jamske mineralogije, saj so tam jame različne starosti in različnega nastanka (kraške, termalne, jamski rudniki). Med preučevanimi kapniki je vredno omeniti gnezdo aragonitnih jamskih biserov globoko v rudniku Reforma, za katere je značilna popolna odsotnost rastnih plasti (»letnic«). Kljub majhnemu številu preučevanih jam (8) je bilo odkritih 32 različnih jamskih mineralov, eden izmed njih nov za jamsko okolje (kingsmountite), drugi pa, ki je še v preučevanju, bo najbrž novo znanstveno odkritje. Zaradi znanstvenega pomena kemijskih odkladnin bi bilo zelo pomembno naravne jame kraškega sistema Quatro Ciénegas zaščititi, da bi s tem ohranili znanstveno dediščino, za zdaj šele deloma poznano.
Ključne besede: jamski minerali, minerali guana, mineralogeni mehanizmi, podnebje, puščava Quatro Ciénegas, Mehika.

INTRODUCTION

The natural caves are the seats of complex minerogenetic processes controlled by peculiar conditions existing in every single cave (Hill & Forti, 1997): hosting rock, cave sediments and circulating fluids are the most important factors controlling the development of the chemical deposits in caves. Forti (1996) stated that the hyperkarstic evolution occurs according to two chemical and physical contemporary processes: the corrosion/dissolution of pre-existing rocks and the deposition of speleothems with an extremely variable chemical composition.

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Recent researches, performed on internal cave deposits of European and extra-European locations, have brought to the identification of particular and extremely rare mineral phases, whose crystalline nature and chemical composition are strictly related to geological, climatological, lithological and hydrogeological continuously changing parametres (Frau *et al.,* 1998; Lattanzi *et al.*, 1998).

Some very different minerogenetical mechanisms may induce the deposition of crystalline and/or amorphous phases, that are stable as long as the environmental conditions remain constant. These "products" can easily change or slightly modify if the genetical conditions change (Benedetto *et al.*, 1998; Forti *et al.*, 1999, 2000, 2001).

In this framework the thermal caves, which have been characterised at least once during their evolution by the presence of fluids with complex chemistry, are extremely interesting, permitting the evolution of polygenetic complex chemical deposits, mostly, although not always, correlated to the "Sulphur cycle" (Forti, 1989; Frau & Sabelli 2000).

Another peculiar class of natural cavities is represented by the "mine caves", cavities without any natural entrance, which have been intersected by mine galleries or other artificial tunnels: their minerogenetic interest comes from the possible interaction between karst fluids and ore bodies (Forti 2005, De Waele & Naseddu 2005).

The karst area of Quatro Ciénegas (Coahuila, Mexico) represents an ideal site to study cave mineralogy, because it hosts caves of different age and genesis (karst, thermal, mine caves) and therefore the chemical deposits developed inside them should result quite different from cave to cave, allowing the detection of many simultaneous and/or subsequent minerogenetic mechanisms.

In the present paper the observed speleothems are described and the related minerogenetic mechanisms are discussed in detail.

THE KARST OF CUATRO CIÉNEGAS

Cuatro Ciénegas plain is a Natural Protected Area since 1994; it is located in the state of Coahuila, Mexico, in the Sierra Madre Oriental at the eastern edge of the Chihuahua desert (Fig. 1).

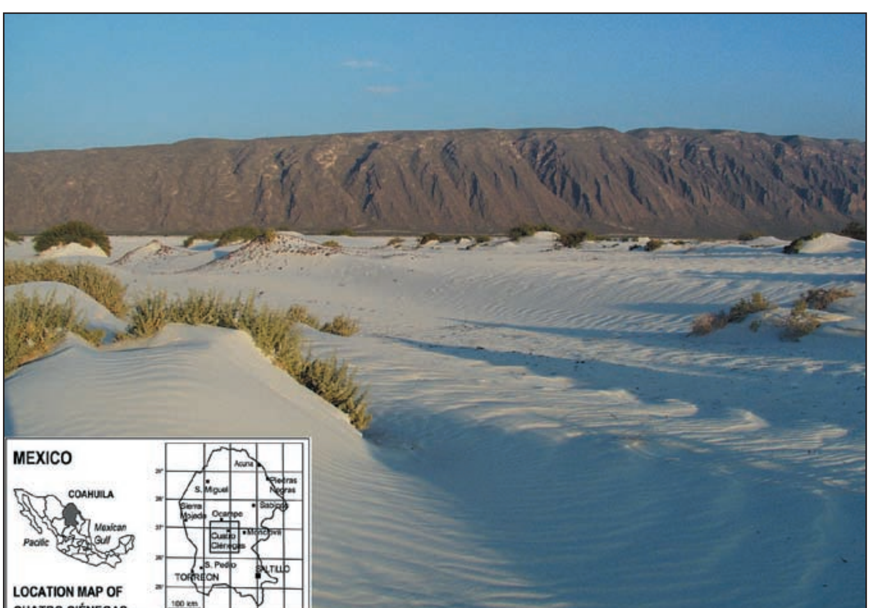

Fig. 1: Location map and a general view of the Cuatro Ciénegas desert.

This desert is characterized by a single period of rain, which normally consists of short but strong rainstorms in the summer period: they are caused by the moist air coming from the cyclones developing in the Mexican Gulf.

The rainiest period is September, with an average of 35 mm; anyway some years, particularly strong events may cause the fall of over 5 mm in a few hours, thus transforming the depressions in swallow ephemeral lakes.

Long rectilinear anticline ridges characterize the landscape of Cuatro Ciénegas whereas major valleys correspond to synclines. The most inclined slopes of major structures, mostly facing SW, often display vertical or overburden beds. Along them, deep transversal and longitudinal valleys form a typical trellis drainage pattern. In the pedemontane areas, several coalescent fluvial fans form a wide regular surface gently inclined, where streams display a disrupted and irregular pattern. Runoff is quite absent in these areas. The plains behave as endoreic basins where major storms form shallow lakes and ponds, the evaporation of which causes the formation of sulphates deposits. Eolian gypsum dunes occur in these areas.

Some of the major caves in the area of Cuatro Ciénegas are hypogenic in origin, created by rising thermal water. The best example is the Cueva Rancho Guadalupe, in the NE of Sierra la Fragua. This cave has a typical dendritic pattern and consists of maze conduits and spherical rooms (Bernabei *et al*., 2002).

Though it receives little rain, the Cuatro Ciénegas valley has abundant subterranean water, which creates hundreds of small pools, marshes, rivers, lakes (large, saline lakes locally called *lagunas or playas*), and canals with a unique biota of great interest to the international scientific community and at risk of extinction (Fig. 2).

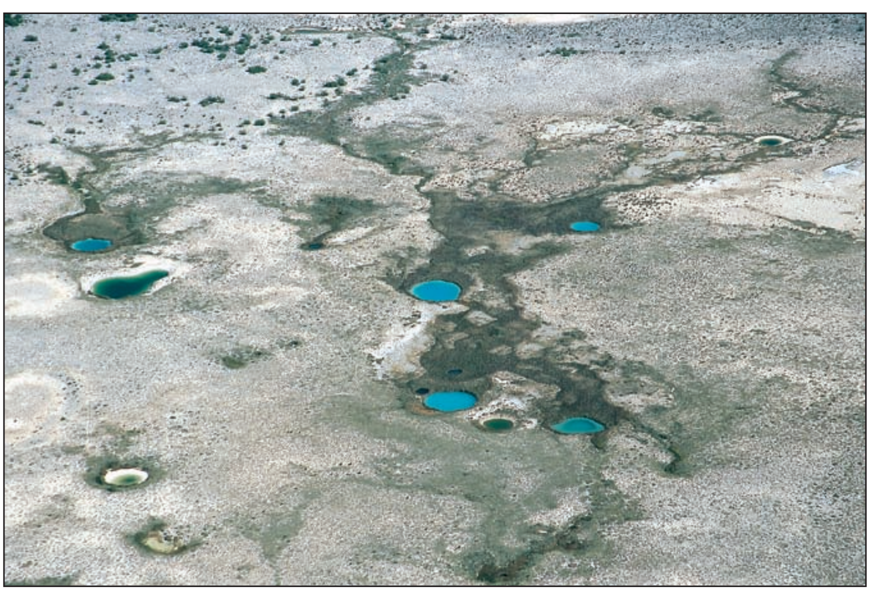

Fig. 2: Aerial view of the pools of the Cuatro Ciénegas desert.

A peculiar characteristics of the pools is the presence of living stromatolithes, which act as local primary agents of the food chain.

Despite the relevant ecological interest of the aquatic environment of Cuatro Ciénegas only in 2000 La Venta Exploring Team started a hydrogeological study of the pools and of high surrounding mountains proving that most of the pool recharge comes from karst structures; during this research over 60 caves were explored and mapped (Forti *et al.,* 2003).

The karst of Cuatro Ciénegas underwent a complex evolution over a very long span of time, which may be evaluated of several tens of millions years. Actually most of the karst systems show a rather inactive evolution, even if corrosion and/or depositional processes are still going on somewhere.

The speleogenetic mechanisms were very different among each other and therefore produced peculiar forms, which now allow reconstruction at least the mean steps of the complex evolution the caves of Quatro Ciénegas underwent.

This evolution may be subdivided into four principal types (Forti *et al*. 2003), which may be also regarded as subsequent stages being rather in chronological order even if some overlap occurred:

1. The genesis of mine caves (hyperkarst phenomenon)
2. The genesis of thermal caves (hyperkarst phenomenon)
3. The genesis of meteoric caves (karst phenomenon)
4. The development of biogenic forms inside previously formed caves (hyperkarst phenomenon)

The first two mechanisms are related to the uplifting of deep hot fluids, the third to the seepage of meteoric (rain) waters, the forth to the presence of huge bat communities, which colonized mainly the caves of the third type.

The study on the speleothems of the Cuatro Ciénegas caves, started in 2001, and it is far to be completed, but on the basis of the achieved results it is evident that this karst region can be considered as one of the most interesting in the world from the point of view of the hosted cave minerals.

This uncommon richness of mineralogical phases, most of which phosphates, is the direct consequence of the complex karst evolution this area underwent. Moreover, some of the "normal" karst caves became in the past (since several years ago) shelter for huge colonies of bats, thus allowing the accumulation of widespread guano deposits up to several metres thick: inside which microbiological reactions gave rise to an extraordinary variety of minerals.

Finally the karst springs are fed by mineralized waters uplifting from rather deep circuits and the peculiar climatic conditions of the desert of Cuatro Ciénegas inducing strong evaporations creating a "sabkha" type environment thus allowing the deposition of even very soluble minerals.

The scarcity of available time for the cave exploration and for mineral sampling obliged to restrict the mineralogical study to a rather small number of natural cavities. Anyway they have been selected to represent all the different environmental and minerogenetic conditions existing in Cuatro Ciénegas.

Among the analyzed caves there are mine caves (Reforma Mine), thermal caves (Cueva Rancho Guadalupe), karst cavities with bat colonies (Cueva Rossillo) and Cueva de los Murcielagos.

EXPERIMENTAL METHODS

A detailed analysis of all the samples by the stereoscopic microscope was performed to distinguish and to separate the different mineralogical phases present in each sample. Then the single phases were analysed by a powder diffractometre (Philips PW 1050/25), when the material was quantitatively enough and homogeneous, or by a Gandolfi camera (Ø: 114.6 mm, exposition: 24/48 hrs), when the material was scarce or inhomogeneous. Always the experimental conditions were: 40Kv e 20 mA tube, CuKα Ni filtered radiation (λ = 1.5418 Å). The analyses of the clay minerals were done not only over the natural samples but also after a glycerine treatment.

Almost all the samples analyzed by Gandolfi camera were later used to obtain images and chemical qualitative analyses through an electron scanning microscope (SEM Philips XL40) with an electronic microprobe (EDS-EDAX 9900) at the C.I.G.S. (Centro Interdipartimentale Grandi Strumenti) of the Modena and Reggio Emilia University.

THE MINE CAVES AND THEIR MINEROGENETIC MECHANISMS

The speleological interest of the mining areas around Cuatro Ciénegas is represented by the existence of "mine caves" (De Waele & Naseddu 2005, De Waele *et al*., 1999, 2001; Forti *et al*., 1999), karst cavities without any natural connection with the surface, which has been intersected by the mine galleries.

The oldest actually known karst (paleokarst) phenomena of the Cuatro Ciénegas area (Forti *et al*., 2003) are those connected with the formation of the metallic sulphides ore bodies, mainly consisting of lead, zinc and, in a lesser extent, of silver, extensively mined in the past (De Vivo & Forti 2002).

The area of Cuatro Ciénegas was one of the very first Mexican regions in which mining activities started since the first half of the 14^{th} century. These activities lasted until 1958, when the most important mine (the Reforma mine) was definitively closed because the reached depth, far below the water table, made the production costs higher than the exploitation profits.

The ore bodies consist of sulphides with some supergenic minerals, most of which carbonates, dispersed within a carbonate breccia or filling karst cavities (Vargas *et al*., 1993).

The fluids flowing inside the carbonate rocks developed caves along the bedding planes and the major discontinuities, mainly where the rock was highly fractured and therefore more permeable. These fluids simultaneously, or just after the development of the caves, filled them with lead and zinc sulphides as in the case of the Reforma Mine. Due to the progressive cooling down and loosing pressure of the thermal fluids, at the end of the mineral deposition, euhedral (middle thermality) quartz and finally low thermality calcite was formed.

In the first hypothesis (MVTOD) the caves filled by ore bodies should testify an old karst stage, partially connected to the seepage of meteoric waters, in a Cretaceous carbonate platform environment; in the second hypothesis the caves developed due to the uplifting of high temperature and pressure fluids, formed by the strong volcanic activity, which took place in the Upper Miocene (about 10-15 Myr BP).

This type of caves are practically never directly accessible and, even when intersected by mine galleries, they are hardly recognizable if completely deprived of the hosted ore bodies.

Their dimensions normally are of a few metres, but sometimes they are larger than ten metres. They exhibit an irregular shape without structural control; often they are rounded cavities elongated perpendicularly with respect to bedding. Good examples of such caves are visible inside the still accessible galleries of the Reforma Mine. These cavities are relatively rare worldwide and extremely important from the minerogenetic point of view: for example in Italy the mine caves of the Iglesiente (Sardinia) are the most known (De Waele *et al.* 1999, 2001).

Peculiar low-enthalpy reaction normally takes place inside such cavities, thus allowing the evolution of interesting and often rare speleothems and cave minerals.

In the area of Cuatro Ciénegas the mine caves are surely widespread even if they are actually very scarcely known.

This study took into consideration only a few cavities intersected by the main galleries inside the Reforma Mine: among them only the Cueva de los Cristales (Fig. 3) has a dimension of some tens of metres.

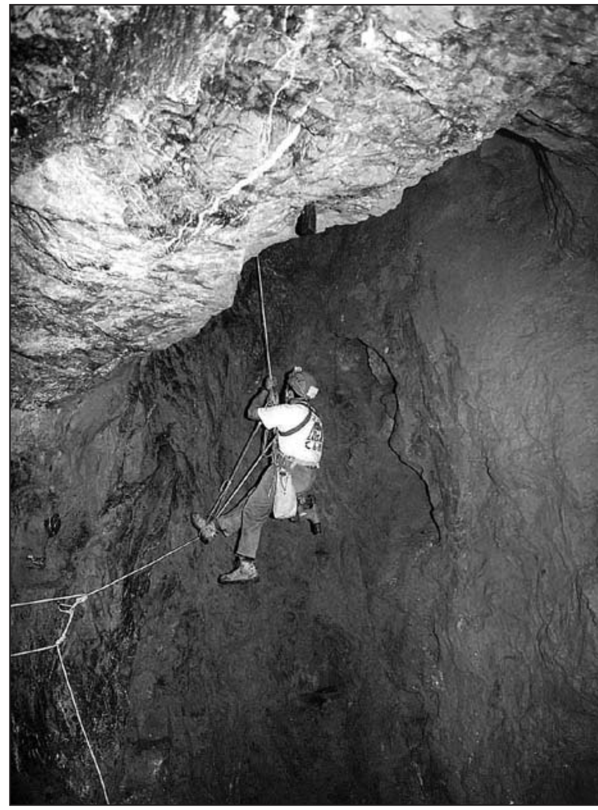

Fig. 3: The 30 metres high pit giving access to the Cueva de los Cristales inside the Reforma mine.

CUEVA DE LOS CRISTALES

It is a large cavity over 70 metres high and 100 long, developed along the big fault which controlled the deposition of the Pb/Zn sulphide ore bodies. Eight samples were taken from the wall of this cave where the primary minerals have been transformed to give rise to alteration compounds (Fig. 4).

The 6 detected minerals were:

Calcite: vitreous transparent euhedral rombohedral crystals up to 1 cm in size developed over iron hydroxides or as milky white to pale pink crusts;

Chlorite: it is an Mg, F fillosilicate; it consists of grains of different size with the same characteristics of the antigorite to which is always strictly associated;

Goethite: it is present as earthy from yellow to pale brown grains of different size;

Gypsum: it is present as thin dark grey layers covering the walls of small holes within the calcite crystals;

Hematite: it gave rise to a) small earthy reddish speleothems over sub-spherical hemi-transparent calcite grains or b) hard grains the powder of which has the typical bloody red colour.

Fig. 4: Cueva de los Cristales: transparent calcite crystals with hematite (A), illite (B) and goethite (C) within a broken speleothem.

LEVEL 12

A few more samples were collected in small karst cavities the "Level 12" gallery of the same mine, from 300 to 600 m from the entrance and at the end of this gallery. They consist of heterogeneous materials characterized by the presence of different mineral phases. The 6 detected minerals were:

Calcite: orange-yellow globular masses;

Goethite: it is present as earthy from yellow to pale brown grains of different size;

Gypsum: it is present as small lens-shaped aggregates of vitreous pale to dark grey crystals;

Hematite: it is strictly related to calcite and goethite;

Illite: this K fillosilicate is the major constituent of a clay and it consists of very small pale green-grey spheres over a black lithoid substratum;

Quartz: small euhedral transparent crystals.

The total number of the cave minerals found inside these mine caves (8) is by far lower than expected: in fact no lead or zinc compounds have been observed, while it is sure that such kind of minerals should be anyway present inside the karst cavities developed within the ore bodies.

In fact in a previous paper (Vargas *et al.*, 1993) cerussite, anglesite, smithsonite, hemimorphite, hydrozincite, hematite and limonite are reported as common supergene minerals of this mine. All of them have been well documented in the mine caves of Iglesiente (Hill & Forti, 1997), which are characterized by ore bodies and structural-lithological conditions very similar to those of Cuatro Ciénegas. Therefore it is logical to suppose that these minerals developed also inside the natural cavities of this mine.

But the principal ore body is actually completely flooded and therefore it is impossible to be reached; this fact is probably the main reason why these minerals have not been observed during the present study which has been focused only over the few mine caves existing in the upper part of the mine.

THE ARAGONITE CAVE PEARLS

One of the most important findings from the scientific point of view is a nest of aragonite cave pearls in which the internal growing layers were completely lacking (Forti, 2004).

Along the tunnel at the foot of the 170 m pit of the Reforma mine, several cave pearls nests were found lined with ultra-white pearls ranging from 1–2 mm to 2 cm in diameter (Fig. 5 left).

This tunnel was used by miners until just 50 years ago which would suggest that these speleothems only began to grow once the mine was abandoned, thus dating these formations at just half a century.

The largest pearls have a diameter of about 14 mm and the average size of their nuclei is 3 mm, therefore the average growth of those spleothems has been approximately 0.1 mm/year. Such a growth rate is considered average-average/fast for a carbonate speleothem in general and for a cave pearl in particular (Hill & Forti 1997).

Some of the pearls were found to have a cauliflower-shaped morphology, as a consequence of the coalescence of several single smaller pearls. This allows to state that the water supply to the nest should have been variable with periods of fast dripping followed by slow dripping or even completely dry periods, during which the originally insulated pearls cemented together. In fact cementation of different pearls may occur only if any kind of vibrations (induced by dripping) is completely avoided (Forti, 1983). Anyway, since composite pearls are quite rare, this would suggest that completely dry periods were far less frequent than the wet ones.

A mineral analysis by X-rays powder diffractions of the pearls has shown that the pearls consist of pure aragonite, the deposition of which is favoured when ions such as magnesium, lead and zinc, etc. are present in the feeding water (lead and zinc were originally extracted in the mine).

The cave pearls found in the Reforma Mine are extremely interesting because they completely lack growing layers (Fig 5, right), which would be of 0,1 mm/year if annual (Backer *et al.*, 1993). However, the Cuatro Ciénegas climate (dry/hot) would eventually have caused the development of many layers/year. In fact in such a climatic conditions, the relative long periods in between two subsequent rains surely avoid permanent dripping of infiltration water over the pearls nest, thus the development of the external layer would result stopped. If so, each rainfall or each series of close rainfalls would cause the development of one specific layer (Piancastelli & Forti, 1997).

Therefore the absence of concentric structure in the pearls of the Reforma mine is the result of very peculiar climatic conditions:

- Pearls must have a rather constant water supply during its growing.
- The chemical composition of the water supply must remain unchanged (irrespective of seasonal changes).

These seemingly simple conditions are in practice extremely difficult to be fitted in nature, which would explain why speleothems with no internal layers have been observed for the first time in the world here.

The Cuatro Ciénegas climate could hold the key to the evolution of these speleothems. Its aridity prevents most vegetal growth and soil covering, which in any case get quickly swept away by the regular strong winds. Therefore the infiltration water undergoes little or even none of the usual soil processes.

But this is not enough to explain the presence of the cave pearls in the Reforma Mine. The low rainfalls, high evaporation-transpiration, poor permeability around the mine could never guarantee a low but constant water supply in the tunnels. Therefore the water dripping into the pearl nests only occasionally may partially result from the rare rainfalls.

The constant presence of water in the depths of the mine is due to the daily temperature extremes typical of the Cuatro Ciénegas semi-arid climate and to the many man-made, interlinking tunnels on many different levels within the mountain, which in turn has a very stable temperature. These conditions allow for condensation, which would account for the constant presence of a few but continuously dripping water deep within the mountain.

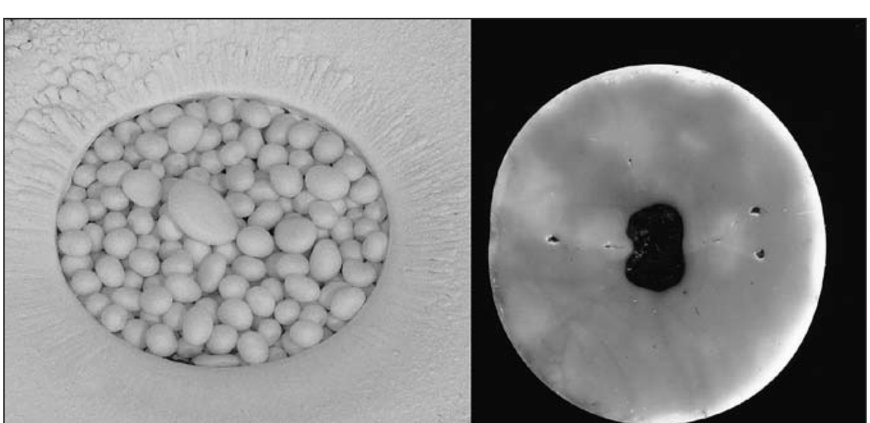

Fig. 5: The pearls nest of the Reforma mine (left) and a polished section of a cave pearl lacking of growing layers (right).

This condensation also explains the lack of any cyclicity in the depositional mechanism and, therefore, the absence of any (annual) growing layers. In fact the carbon dioxide content in condensation water is maintained stable due to CO_2 rather constant partial pressure within the mine over the year and the scarcity of meteoric water.

For these reasons the pearls found in the Reforma Mine has more far-reaching consequences. They have provided a method, based on the growth layers within a speleothem, for evaluating both qualitatively, as well as maybe quantitatively, the predominance of condensation over climatic-controlled water infiltration.

THE THERMAL CAVES AND THEIR MINEROGENETIC MECHANISMS

Some of the most interesting cavities of the Cuatro Ciènegas belong to this group; their genesis is linked to the uplifting of deep hot and chemically aggressive waters, which easily dissolve the rock during their slow movement toward the topographic surface. These waters were depleted of the heavy metals and of the other low solubility salts but represented the final stage of the processes, which gave rise to the mine caves.

The thermal caves, as well as the mine ones, are commonly called hypogenic, because they are generated by fluids coming from the depth (Forti, 1996). They normally lack of a natural entrance on the surface and when it is present, often it is the result of the demolition of the hosting outcrops by meteoric degradation.

The "pure" thermal caves are those whose development is exclusively controlled by the effect of thermal water uplifting, they are normally referred to as "monogenic": this kind of cavity is rare enough in the world and they have been described in details rather exclusively in the area of Budapest (Muller & Sarvary, 1977).

A "monogenic" cave is characterized by the presence of a reservoir of the thermal water (the equivalent of the magmatic chamber for a volcano), which consists of a huge "basal" chamber; several splitting and/or anastomized spherical cavities develop from the roof of such a chamber giving rise to a peculiar "branched tree" structure. The thermal caves of Cuatro Ciènegas belong to this category; therefore their importance exceeds the local interest (Fig. 6).

The Rancho Guadalupe cave, which is located just at the foot of the Sierra La Fragua, represents the best example of monogenic thermal cave.

It is a classical 3D maze cave with a net of conduits interconnecting large chambers all characterized by typical thermal corrosion forms. Due to the presence of some strange speleothems observed during the first visit, nine samples have been taken for an accurate mineralogical study, during the first exploration of this cave. Later, due to the peculiarity evidenced by the one sampled on top of an organic deposit rich in vegetal fibres up to 1 cm long, bird droppings and other animals excreta 4 more samples have been selected by the same deposit.

The study of the sampled speleothems confirmed the extraordinary importance of the secondary chemical deposits hosted in the Rancho Guadalupe cave (Forti *et al.*, 2004). Inside this cavity 18 different cave minerals have been observed (Tab. 1). Anyway the origin of only a few of them is directly related to the thermal processes which gave rise to the cave itself, others begun to grow after the thermal fluids definitively abandoned the cave and the meteoric waters entered the cave and finally some others were originated by the mineralization of some organic remains which were accumulated inside by small animals (mainly rodents) which use the cave as a shelter (Fig. 7).

Fig. 7: Cueva Rancho Guadalupe: a general view of a rodent shelter in a side passage close to the entrance of the cave where, beside whewellite, ardealite and sepiolite, a new still undefined mineralogical phase has been found.

The detected minerals are:

Aragonite: this polymorph of calcite is not common and it forms small milky-white to pale hazel-brown spheroidal grains;

Calcite: very common it is present as: a) radial aggregates of elongated (30x5 mm) vitreous, semitransparent,

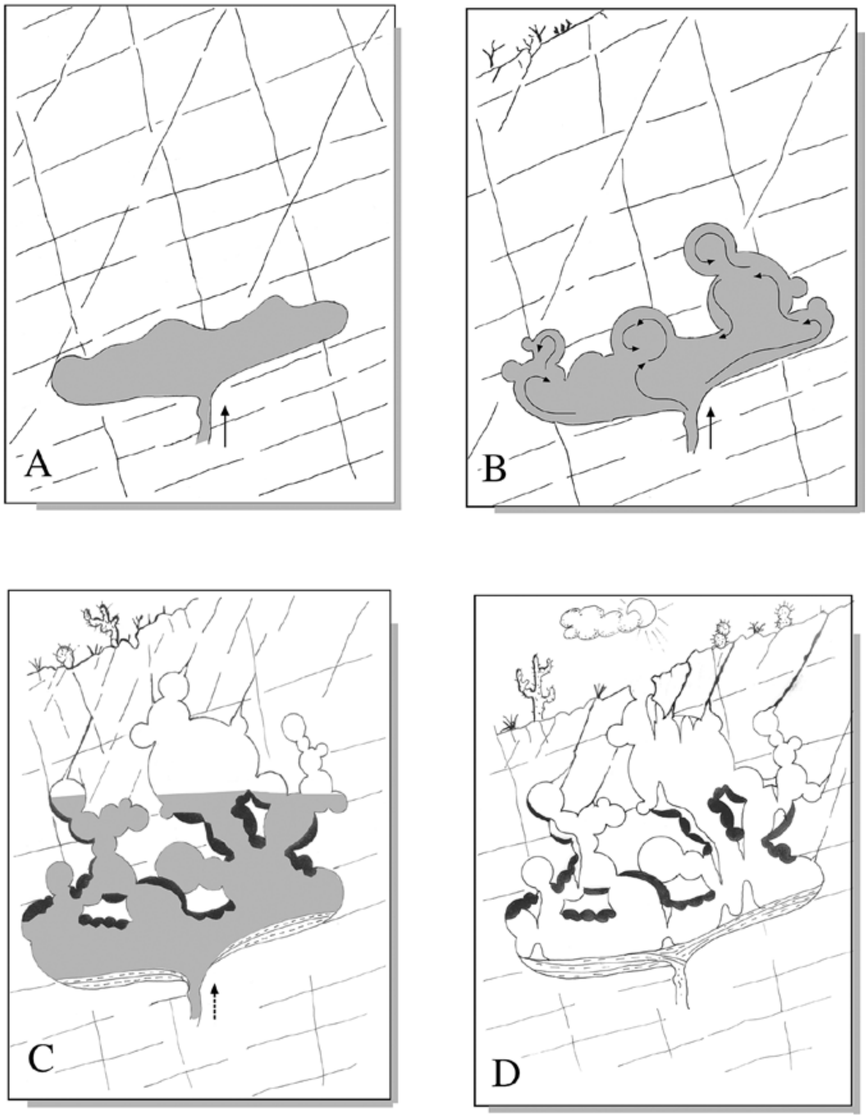

Fig. 6: Sketch for the evolution of the Rancho Guadalupe cave. A: due to the thickness and the low fracturation degree of the limestone, the uplifting of the thermal waters induces the development of a huge hydrothermal chamber in which they accumulates. B: The convective motions develop the upward evolution of a dendritic series of cohalescent subspherical voids. C: when part of the cave becomes partially unsaturated, the diffusion of CO_2 in the cave atmosphere allows for the development of some epiphreatic speleothems (cave cloud in black in the sketch) and the sedimentation over the cave floor of cave rafts, developed at the water-atmosphere interface; at the same time the meteoric seeping water starts the normal karst process in the unsaturated zone. D: the progressive erosion of the surface connects the cave to the exterior; the cave is then abandoned by the thermal waters. All the thermal forms and/or deposits are therefore fossilised, and meteoric seeping waters develop gravitational speleolothems (stalactites, stalagmites, flowstones…).

prismatic crystals which are often part of speleothems (flowstones); b) pale pink to brick-red hard material; or c) saccaroidal to powdery incoherent material;

Carnotite: this very rare uranil vanadate is present as small aggregates of canary-yellow small tabular crystals (SEM images in Fig. 8a,b);

Chlorapatite: it forms hard dark hazel-brown microcrystalline aggregates. The presence of Cl was confirmed by EDAX analyses;

Dolomite: it is present as aggregates of opaque, milky grains associated with sepiolite within the thick cave rafts deposit covering the whole floor of the thermal basal chamber;

Fluorite: it has been identified in a single sample: it consists of earthy and/or saccaroidal milky white grains within a speleothem (flowstone) on the wall of a small side bell shaped cavity;

Gypsum: it is present as: a) vitreous, milky crystals within a crust over a corrosion pocket of the wall; b) aggregates of small vitreous semitransparent dark-grey prismatic crystals;

Hydromagnesite: it gives rise very small spheroidal silky shining white aggregates of microcrystals. It is normally associated with monohydrocalcite (SEM image in Fig. 8c);

Monohydrocalcite: it normally consists of a earthy dust consisting of cream-white to pale hazel-brown micro spheres; sometimes it gives rise thin crusts and aggregates of small and fragile silky-lustre bladed crystals over the vegetable fibres (SEM images in Fig. 8d);

Niter: it presents: a) often as small effloresces of aggregates of thin transparent silky tabular crystals, often with a radial structure to simulate "an open book";

Tab. 1: Minerals identified in the karst systems of Cuatro Ciénegas: G – Cueva Rancho Guadalupe; L – Leona; M – Cueva de San Vicente (or de los Murciélagos); P – Cueva de Las Pinturas; R – Cueva Rosillo; Re – Reforma Mine; T – Tanche Nuevo; V – Vibora

Karst	**Mineral**	**Chemical formula ***	**System**	**Figure no.**	**References**
		HALIDES			
G	Fluorite	CaF_2	Cubic		Anthony et al. (1997), vol. III, 205
G	Sylvite	KCl	Cubic	9a	Anthony et al. (1997), vol. III, 545
		OXIDES			
R	Asbolane	$0.5[(Ni,Co)(OH)_2][MnO_2 \cdot nH_2O]$	Hexagonal		Anthony et al. (1997), vol. III, 26
R, Re	Goethite	α-FeOOH	Orthorhombic		Anthony et al. (1997), vol. III, 223
Re	Hematite	Fe_2O_3	Trigonal		Anthony et al. (1997), vol. III, 239
R	Lepidocrocite	γ-FeOOH	Orthorhombic	9f	Anthony et al. (1997), vol. III, 312
G	Opal-CT	$SiO_2 \cdot nH_2O$		8e	Smith (1998)
G, M, R, Re	Quartz	SiO_2	Trigonal		Anthony et al. (1995), vol. II, 672
		CARBONATES AND NITRATES			
G, Re	Aragonite	Ca[CO3]	Orthorhombic		Anthony et al. (2003), vol. V, 31
G,L,R,Re,T,V	Calcite	$Ca[CO_3]$	Trigonal		Anthony et al. (2003), vol. V, 101
G, Re	Dolomite	$CaMg[CO_3]_2$	Trigonal		Anthony et al. (2003), vol. V, 191
G	Hydromagnesite	$Mg_5[(OH)_2\|CO_3)_4] \cdot 4H_2O$	Monoclinic	8c	Anthony et al. (2003), vol. V, 310
G	Monohydrocalcite	$Ca[CO_3] \cdot$ H2O	Hexagonal	8d	Anthony et al. (2003), vol. V, 465
G	Niter	$K[NO_3]$	Orthorhombic		Anthony et al. (2003), vol. V, 497
		SULFATES			
G, L, R, Re, T	Gypsum	$Ca[SO_4] \cdot 2H_2O$	Monoclinic		Anthony et al. (2003), vol. V, 271
		PHOSPHATES AND VANADATES			
M, P, R	Apatite group	$Ca_5[(F,OH,Cl,O)\|(PO_4,CO_3)_3]$	Hexagonal	15d,e	Pau & Fleet (2002)
R	Ardealite	$Ca_2H[SO_4\| PO_4] \cdot 4H_2O$	Monoclinic	12c	Anthony et al. (2000), vol. IV, 23
L, R, T	Brushite	$CaH[PO_4] \cdot 2H_2O$	Monoclinic	9c,d	Anthony et al. (2000), vol. IV, 83
G	Carnotite	$K_2[UO_2\|VO_4]_2 \cdot 3H_2O$	Monoclinic	8a,b	Anthony et al. (2000), vol. IV, 96
G	Chlorapatite	$Ca_5[Cl\|(PO_4)_3]$	Hexagonal		Anthony et al. (2000), vol. IV, 111
R	Crandallite	$CaAl_3[(OH)_6\|PO_3OH\|PO_4]$	Trigonal		Anthony et al. (2000), vol. IV, 130
R	Kingsmountite	Ca4FeAl4[(OH)2|(PO4)3]2. 12H2O	Monoclinic	15a,b	Anthony et al. (2000), vol. IV, 282
R	Montgomeryite	Ca4MgAl4[(OH)2|(PO4)3]2. 12H2O	Monoclinic		Anthony et al. (2000), vol. IV, 387
R	Taranakite	K3Al5[(PO3OH6)3|(PO4)2] · 18H2O	Trigonal	15c	Anthony et al. (2000), vol. IV, 581
M, R	Variscite	Al[PO4]. 2H2O	Orthorhombic		Anthony et al. (2000), vol. IV, 621
M, P, R	Whitlockite	$Ca_9(Mg,Fe)[PO_3OH\|(PO_4)6]$	Trigonal	15d,e,f	Anthony et al. (2000), vol. IV, 653
		SILICATES			
Re	Illite	$(K,H_3O)Al_2[(H_2O,OH)_2\|(Si,Al)_4 O_{10}]$	Monoclinic		Brigatti & Guggenheim (2002)
G	Sepiolite	$Mg_8 [(OH)_2\|Si_6O_{15}] \cdot 12H_2O$	Orthorhombic	8e,f	Anthony et al. (1995), vol. II, 722
		ORGANIC COMPOUNDS			
R	Bitumen	nC_xH_y			
R	Guanine	$C_5H_3(NH_2)N_4O$	Monoclinic	9e	Anthony et al. (2003), vol. V, 265
G	Whewellite	$CaC_2O_4.H_2O$	Monoclinic	9b	Anthony et al. (2003), vol. V, 755
		NEW MINERAL(?)			
G	Unknown	Mg hydrated carbonate (?)			

*Classification and chemical formulae after Strunz & Nickel, 2001.

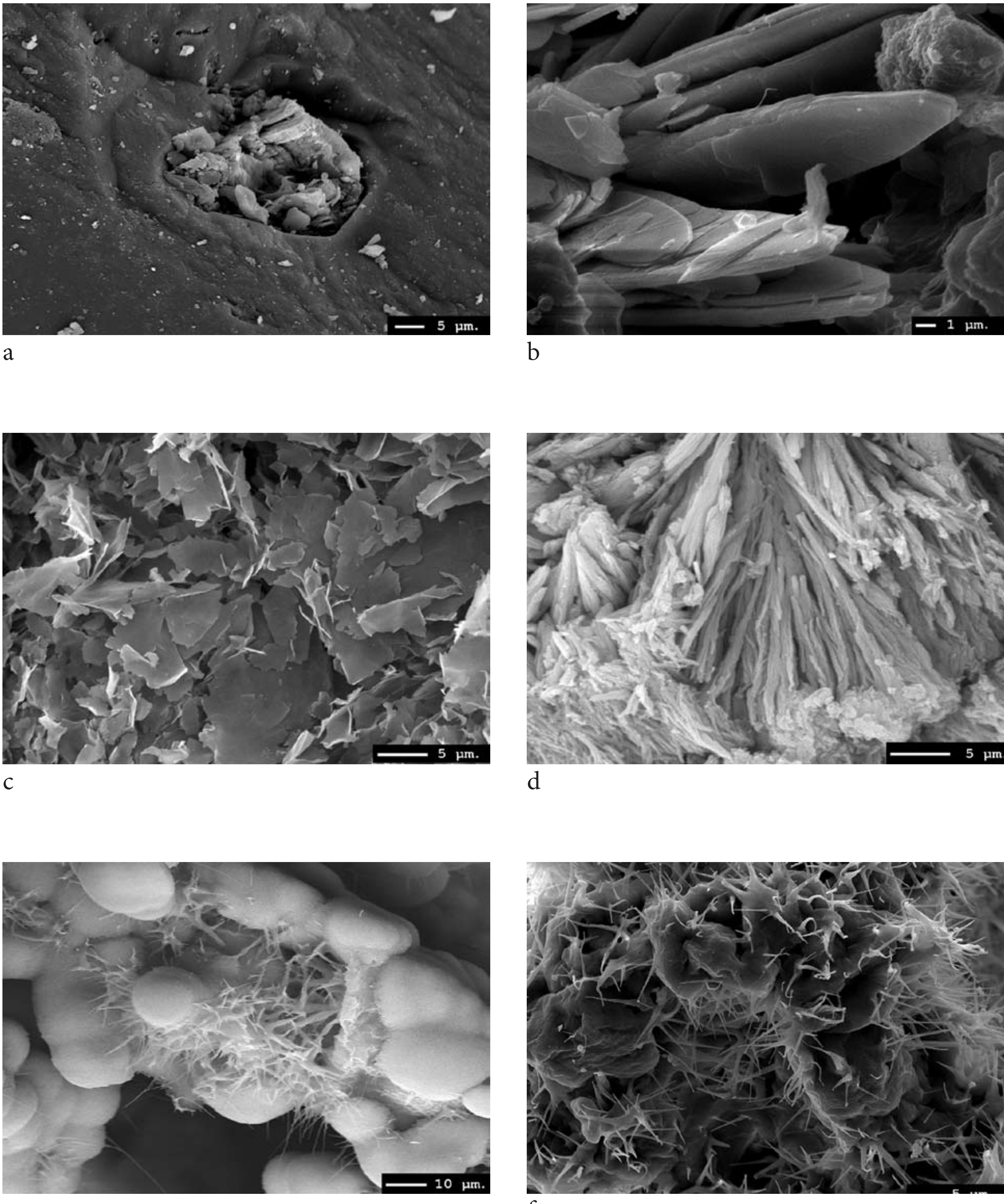

Fig. 8: SEM images of minerals from Cueva Rancho Guadalupe: a) inclusion of platy crystals of carnotite in tabular gypsum; b) magnification of a); c) aggregate of tabular crystal of hydromagnesite; d) fan like aggregate of platy crystals of monohydrocalcite; e) microspheres di opale-CT with fibrous sepiolite; f) fibrous sepiolite.

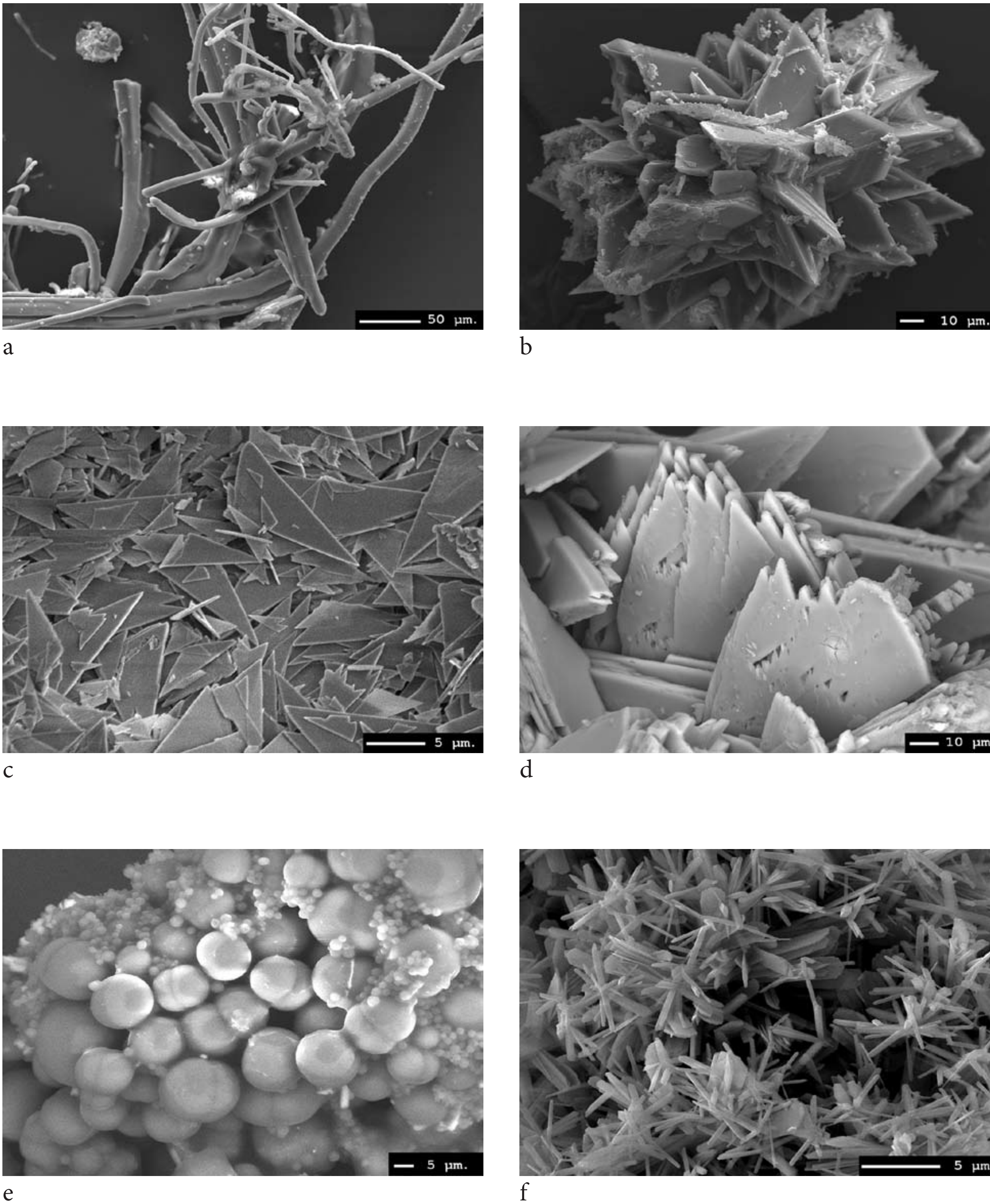

Fig. 9: SEM images of cave minerals from Cueva Rancho Guadalupe (a, b) and Cueva Rossillo (c, d, e, f): a) net of irregular fibres of sylvite; b) spheroidal aggregate of prismatic crystal of whewellite; c) aggregate of triangular plate crystals of brushite; d) close view of brushite crystals; e) aggregate of microspheres of guanine; f) star-like aggregates of lepidocrocite crystals.

b) sometimes as transparent crusts over the organic material;

Opal-CT: detected as incoherent milky white soft material like sawdust (SEM images in Fig. 8e);

Quartz: identified only by x-ray diffraction analyses within a thin gypsum-calcite speleothem;

Sepiolite: it gives rise to small hard milky white aggregates associated with dolomite within the cave rafts deposit covering the whole floor of the thermal basal chamber (SEM images in Fig. 8e,f);

Sylvite: observed as tuffs of vitreous, transparent bended filaments inside small pockets in the cave walls (SEM images in Fig. 9a);

Whewellite: this calcium oxalate monohydrate is present as small spherical aggregates of euhedral greasy, semitransparent prismatic crystals grown inside the coprolites (SEM images in Fig. 9b).

Anyway the uncommon richness and variety of the hosted cave minerals is not the principal reason of interest of this cave: in fact its importance from the mineralogical point of view depends on a mineral deposit, which has never been observed before in nature and which seems to be completely new for science. It is a highly crystalline magnesium compound, probably a hydrated carbonate, which is presently under examination to define univocally its structure and chemical formula. It occurs as extremely small (a few microns in diameter) milky white soft earthy spheroidal aggregates of tabular crystals inside organic materials (mainly vegetable fibres).

THE KARST CAVES AND THEIR MINEROGENETIC MECHANISMS

The most widespread karst phenomena are surely those connected with the seepage of meteoric water.

The karst forms induced by the diffuse and/or concentrated seepage are quite absent: in fact, even if the nature of the rock is carbonate and the fracturation degree is high, deep karst phenomena are normally scarcely developed and concentrated in very restricted areas. Most of the known cavities are sub-horizontal: they started as small interbedded conduits, which later have been widened by physical degradation starting from the entrance. Often they host plenty of speleothems even of huge dimension.

Sometimes the caves are fragment of old huge drainage tubes. Many of the cavities in the Sierra San Vincente and in the Cañon el Pedregoso are relict of old phreatic galleries developed in a period in which the rainfalls were by far higher than actually.

Often the karst caves do not host speleothems and/or cave minerals of interest: usually only calcite speleothems (stalactites, stalagmites, flowstones, etc…) are present, often with evident corrosion features induced by condensation processes. Among the cave minerals the crust and crystal aggregates of gypsum are fairly common: most of them are related to the dissolution of the discontinuous layers of this mineral present within the carbonate sequence, but some are generated by the oxidation of the sulphides associated to the ore bodies.

Normally the karst caves have scarce minerogenetic importance, but those, which have been and/or still are shelter for huge colonies of bats may exhibit a wide variety of secondary cave deposits. In fact actually the most active minerogenetic processes are related to the presence of guano deposits. Several thousand of years ago millions of bats colonized some caves, mostly of meteoric origin, after the active water flow stopped inside, thus allowing the development of widespread deposits of an incredible amount of guano (Fig. 10).

Fig. 10: Cueva Rossillo: one of the widespread large guano deposits.

The oxidation and mineralization processes of guano are strongly exothermic and release high quantity of H_2O and CO_2 thus inducing strong convective movements within the cave atmosphere, and producing a discrete amount of strong acids: mainly nitric (HNO_3), sulphuric (H_2SO_4) and phosphoric (H_3PO_4).

These processes may have strong morphologic consequences (Fig. 11), causing the development of peculiar condensation-corrosion forms like megascallops on the protruding walls and huge spherical domes in the cei-

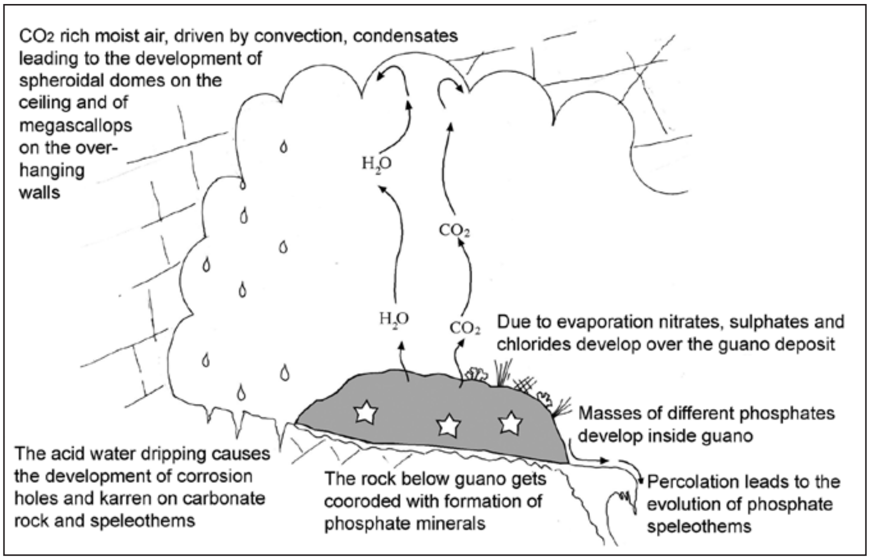

Fig. 11: Sketch of the morphological and mineralogical effect induced by guano deposits (Forti et al.*, 2004).*

lings or allowing for the evolution of corrosion furrows and/or holes in the cave floor.

The condensation water reacts with the carbonate rock, the other minerals eventually dispersed inside, the clay and sand deposits giving rise to many secondary minerals, among which the phosphates are the most widespread and may develop even as huge speleothems (Fig. 12).

Fig. 12: Cueva Rossillo: a) a thick phosphate flowstone developed in the final part of the cave; b) layers different in colour and/or texture are evident in a polished cross section; c) microsphere of pale yellow ardealite in a small void of the speleothem; d) the different layers observed with a polarizing microscope with crossed nicols.

CUEVA ROSILLO

It is a classical karst cave which has been deeply modified by the presence of an extremely large bat colony over a long time interval. The cave consists of a single huge gallery (average size 10 x 10 metres) some 1 km long. Its origin is related to important karst drainage below the groundwater level in a period in which the climate must be by far more humid than actually. The widespread presence of domes in the ceiling, megascallops in the walls and sponge-works on the floor is the direct consequence of the still occurring strong acid aggression due to the presence of huge fossil and/or actual guano deposits. The main cave gallery present on the floor a 5-7 m deep canyon developed when the lowering of the groundwater lever allowed for an epiphreatic to unsaturated evolution. Later the canyon was rather completely filled by sediments (mainly guano and its by-products): in the last century these sediments were intensely mined to produce fertilizers (Fig. 13).

Fig. 13: One of the many tunnels dug by guano miners in the floor of the main gallery of the Cueva Rossilo.

Where the guano leaking seeped along the limestone beds then gave rise to huge speleothems with inside layer of different thickness and colours, which often presented small cavities filled sometimes by pale vitreous crystals or dusty hazel-brown to pale pink grey material.

In one case, the seepage of organics leached by guano in the upper series of the cave developed small black stalactites, the colour of which was due to the presence of bitumen within the different growing layers of the speleothems (Fig. 14).

A total of 15 samples have been taken from sediments on the cave floor and from speleothems; the observed minerals are:

Apatite group: this generic name was given to hydroxylapatite, carbonate-hydroxylapatite, carbonate-fluorapatite and fluorapatite because it was rather impossible to discriminate among these phosphates. They are the most frequent phases in both the sampled sediments and speleothems. Their morphology resulted extremely variable: a) hard microcrystalline china-ware material,

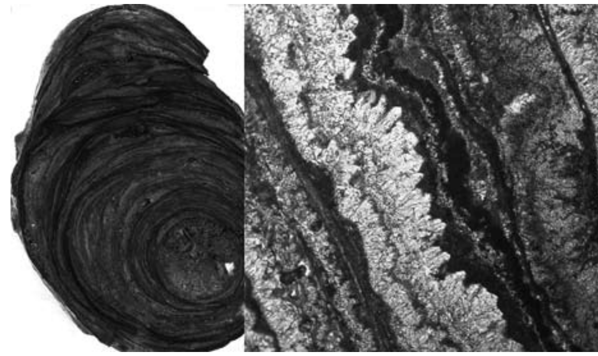

Fig. 14: Cueva Rossillo: polished section (left) of the black stalactite and a thin section (right) of it showing thin bitumen films adsorbed over calcite layers.

sometime layered with colours ranging from ivory to hazel brown, from pale brown to dark brown due to the dispersed presence of carbon rich phases; b) plastic light greasy pale pink powder, which sometime gives rise to small spheres, which in turn may be insulated or aggregated to form thin crusts; c) tuffs of radial aggregates of thin vitreous colourless to white acicular crystals; d) irregular grains of hard orange-red material (SEM images in Fig. 15d,e);

Ardealite: vary rare, it has been observed only in one sample where it was associated to gypsum within a small sphere of greasy pale lemon-yellow microcrystalline material (SEM image in Fig. 12c);

Bitumen: this organic compound is responsible for the pigmentation of the growing layers of a small dark brown calcite stalactite (5 x 2 cm) collected already broken close to the cave entrance. The concentration of this compound was high enough to allow a strong H2S smell while crushing the sample;

Asbolane: this Ni and Mn hydroxide is rare for the cave environment and in 4C was identified only in a couple of samples. It consists of small black earthy and spongy spheres within an earthy white material;

Brushite: common mineral which has been observed in several forms: a) thin crusts of vitreous, semitransparent milky white to pale greenish tabular crystals; b) aggregates of transparent lance shaped crystals; c) tuffs of thin elongated fairly bended crystals; d) aggregates of soft earthy grains, of small prismatic tabular crystals and of pale hazel-brown larger crystals; e) earthy milky white irregular grains; f) lens shaped aggregates of shining crystals within the earthy milky white material (SEM images in Fig. 9c,d);

Calcite: it is by far the most common mineral and consequently it is present in very different forms: a) in sub-spherical aggregates of radial elongated (30 x 5 mm) semitransparent vitreous prismatic crystals, similar to those observed inside some speleothems in a side cor-

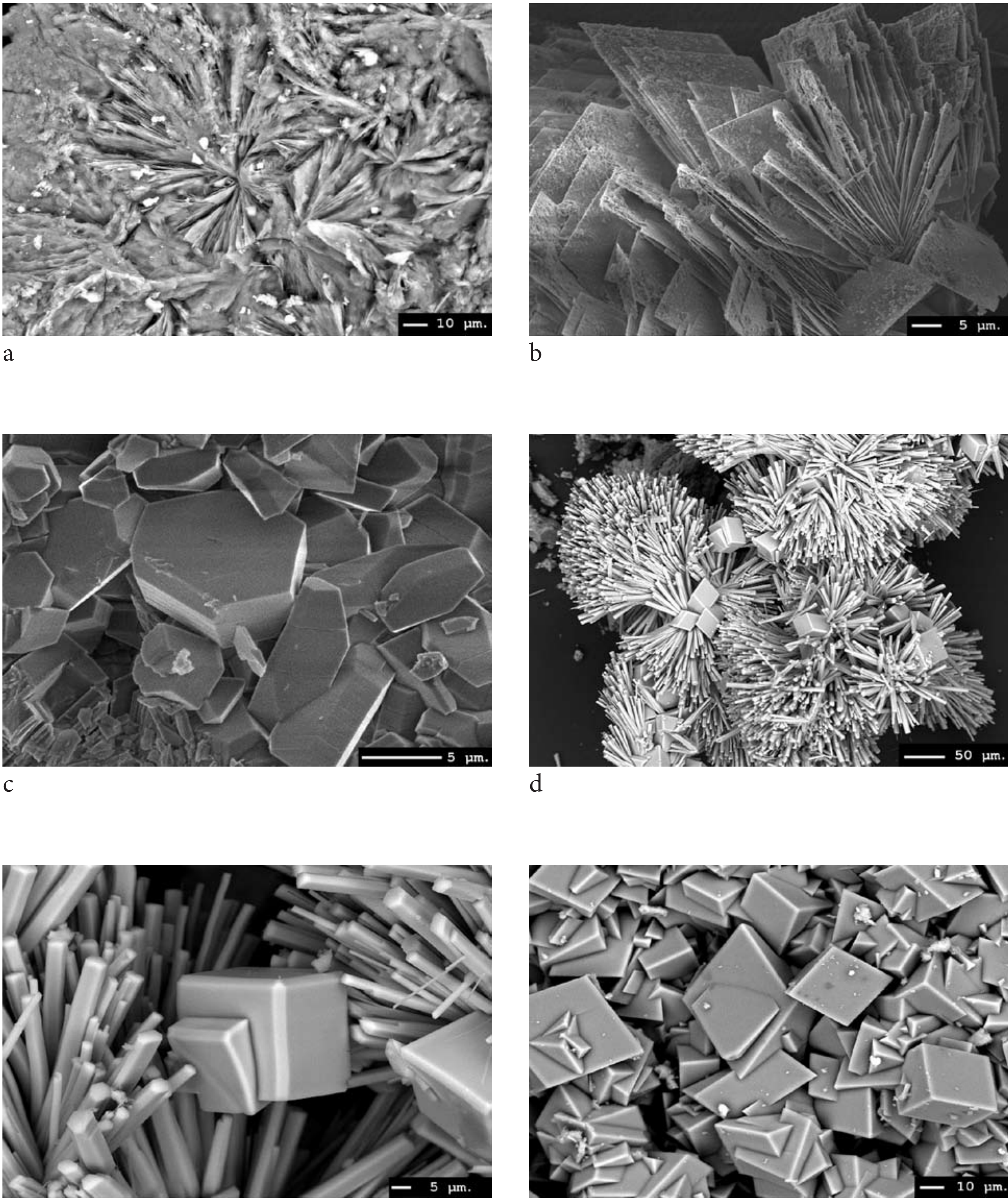

Fig. 15: SEM images of cave minerals from Cueva Rossillo (a, b, c) and Cueva de los Murcielagos (d, e, f): rose-like aggregates of tabular crystals of kingsmountite; b) tabular subparallel crystals of kingsmountite; c) prismatic ditrigonal crystals of taranakite; d) radial aggregates of fibrous crystals of apatite with rombohedral whitlockite; e) magnification of d) to put in evidence an overgrow of whitlockite; f) aggregate of euhedral rombohedral, sometime twinned, whitlockite crystals.

ridor; b) hard pale pink to brick-red microcrystalline material; c) as incoherent ochre-yellow sandy to dusty sediment;

Crandallite: extremely rare; it has been observed only in a single sample as thin irregular vitreous crust partially covering a yellow grain;

Goethite: it is present as earthy lemon-yellow to ochre-yellow grains;

Guanine: this rare organic compound gave rise to small black partially hard grains (SEM image in Fig. 9e);

Gypsum: rather common; it is present as: a) aggregates of fibrous silky-lustre micro crystals; b) vitreous lustre, transparent slightly grained, tabular prismatic crystal with a pseudo-square base;

Kingsmountite: it is always associated with montgomeryite and whitlockite; it is present as: a) thin small pale pink crusts or spheroidal aggregates of silky lustre, silver shining scaled crystals, which cover the walls of some cavities within the milky white material; b) aggregates of radial (open book) extremely thin silky blades over the surface of a single milky white grain (SEM images in Fig. 15a,b);

Lepidocrocite: this polymorph of goethite is fairly rare; it has been observed only in the alteration crust developed over an iron art craft (a small vessel or a cup) probably left by guano miners some tens of years ago and now found some 50 cm inside the fresh guano. The alteration crust consists of a millimetric layer of empty ochre-yellow to ruby red micro-spheres; at large magnification prismatic structures seem to be present over their surface. In this crust lepidocrocite is strictly associated with goethite, apatite and gypsum (SEM image in Fig. 9f);

Montgomeryite: it gave rise to small (Ø < 2.5 mm) pale yellow partially empty spheres, which consist of silky tabular radial crystals arranged in concentric layers;

Quartz: it has been found as cave mineral a single time over a sub-spherical grain of variscite. It consists of a hard thin transparent crust;

Taranachite: spherical soft aggregates of saccaroidal vitreous milky white micro-crystals (SEM image in Fig. 15c);

Variscite: very rare observed in a single sample where it is the nucleus of a rounded grain with the outer part made by quartz. It consists of lemon yellow microcrystalline material;

Whitlockite: semitransparent thin hard crusts with the outer surface smooth or consisting of semi-spheres of colourless or pale yellow to pale brown, vitreous, sometimes silky shining crystals covering the walls of some small empty voids within a china-ware material (SEM images in Fig. 15d,e,f).

CUEVA DE LOS MURCIELAGOS (BATS CAVE)

This cave has been drastically modified by guano miners, who left inside most of their art crafts like wood ladders and leaching structures: for this reason the cave is know also with the name of San Vincente mine. Anyway it is a classical karst cave, partially modified by the hyperkarst reactions connected with guano digestion.

Seven samples have been collected in this cave: three consist of fragments of small calcite stalactites, three of which consist of fragments of broken calcite stalactites (soda straw) and/or stalagmites; some pieces of flowstones consisting of honey yellow calcite are also present. Most of these samples are covered by a thin whitish powder. The other four samples are globular yellowish speleothems (up to 15 mm in diameter) the structure of which consists partially of pale yellow fibrous radial crystals and of a hard layered material with plenty of small cavities, sometimes covered by a thin semi-transparent calcite layer.

Beside calcite, the other observed minerals are:

Apatite: the phosphates hydroxylapatite, carbonate-hydroxylapatite, carbonate-fluorapatite and fluorapatite are grouped under this generic name, due to the difficulty to discriminate among them. They occur as: 1) small aggregates of fibrous pale-yellow material; b) vitreous semi-transparent layers over the fibrous material; c) crusts consisting of small milky white to cream yellow spheres;

Kingsmountite: this Ca, Fe, Al phosphate is easily recognized even at naked eye; it consist of: a) bladed millimetric bladed crystals with easy cleavage b) small crusts made by perfectly rounded shining yellow grains dispersed inside in an earthy whitish material;

Quartz: hard thin transparent crust in association with variscite;

Variscite: semitransparent thin hard crusts with smooth outer surface.

A few other karst caves have been sampled during the study (Leona, Las Pinturas, Tanche Nuevo, and Vibora) but they resulted of scarce mineralogical interest hosting only very common cave minerals (calcite, gypsum, hydroxilapatite and whitlockite) and therefore they will not be described here. Anyway their hosted chemical deposits are summarized together with those of all the other caves in the Tab. 1.

FINAL REMARKS

The mineralogical study of the secondary chemical deposits developed within the karst systems of Cuatro Ciénegas put in evidence the great variety of minerogenetic processes which were and/or are still active in this area: this is the reason why the number of observed cave minerals (Tab. 1) is very high in comparison to that normally present in a single karst area.

Moreover, the study of some of the caves in the area, even if not exhaustive, confirmed their extraordinary mineralogical interest: in fact in two natural cavities (Cueva Rossillo and Cueva Rancho Guadalupe) over 15 different cave minerals have been found, number which puts them among the most interesting caves of the world as for variety and richness of hosted mineralogical species.

Some of the 32 identified minerals (ardealite, asbolan, carnotite, crandallite, monohydrocalcite, montgomeryite, niter, sepiolite, sylvite, variscite, whitlockite) must be considered "rare" in the cave environment (Hill & Forti, 1997), while one Al, Fe, Ca hydrated phosphate (kingsmountite) has been cited for the fist time as cave mineral from Rossillo cave.

Previously this mineral was described by Dunn *et al.* (1979) from the Mine Foote, near Kings Mountain town, North Caroline (USA): the kingsmountite of Rossillo cave has the same morphology of the olotype, occurring as bladed tiny crystals, usually in radial hemispherical aggregates up to 1 mm in diameter. Kingsmountite is isostructural and therefore with an X-ray powder pattern similar to that of montgomeryite, but it may only be discriminate on the basis of chemical analyses because kingsmountite lacks of significative amounts of Mg.

While phosphate largely prevails in Rossillo cave due to the large amount of guano deposits, oxides and carbonates are the main cave minerals in the Rancho Guadalupe cave. In this cave it is worth of mention the presence of carnotite as small aggregates of bright, greenish-yellow plate crystals < 50 μm in length, as inclusion in tabular gypsum (Fig. 8 alb); this occurrence seems to be very similar to that of the Horsethief Cave, Wyoming (USA) (Mosh & Polyak, 1996).

In the Rancho Guadalupe cave there are several different silicate minerals: quartz, sequences of aligned micro-spheres (up to 15 μm in diameter) of opal-CT (Fig. 8e), and sepiolite (Fig. 8f), the origin of which should be related to diagenetic processes involving opal in an Mg-rich environment (the simultaneous presence of dolomite supports this hypothesis).

Among the organic compounds the guanine of Cueva Rossillo and wewellite of Cueva Rancho Guadalupe are worth of mention. The first of these compounds (Fig. 9e) gave rise to micro-spheres up to 20 μm in size and it is extremely rare for the cavern environment and up to present it was reported only from a few caves where it derived directly from bat guano mineralization. Whewellite of Rancho Guadalupe forms sub spherical aggregates of prismatic crystals (Fig. 9b): its origin is related to animal excreta (Martini *et al.*, 1990).

Finally the magnesium carbonate from Cueva Rancho Guadalupe, still under study, is highly probably to become not only a new cave mineral but probably new for science.

Beside this ongoing research, the mineralogical studies in the karst systems of Cuatro Ciénegas cannot be considered concluded, mostly those related to the mine caves.

As already written in the relative paragraph, the cave minerals observed in these caves are far to represent if not the totality at least a significant portion of those which should have developed in this environment: future research shall be surely addressed toward this topic.

Anyway the mine environment has already proved to be of noticeable interest and scientific importance: in fact a completely new kind of cave pearls has been observed in the Reforma mine.

It is thank to these cave pearls to be possible to realize a new method to define the relative ratio between condensation and seeping waters feeding a speleothem.

Due to the peculiarity and noticeable scientific interest of the secondary cave minerals of the karst systems of Cuatro Ciénegas it should be important that the natural cavities of such an area would be protected in the near future, in order to preserve their very high scientific patrimony, which actually is only partially known.

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