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The Naica Project – A multidisciplinary study of the largest gypsum crystals of the world[3]

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The caves of Naica (Chihuahua, Mexico) are perhaps the most famous mine caves of the world due to the presence of gigantic gypsum crystals. Nevertheless, very little research has been carried out on these crystals until now. An international multidisciplinary investigation started in 2006 with the aim not only to define the genesis and the age of the Naica gypsum crystals, but also to focus other important scientific aspects of these caves and to ensure a complete documentation and knowledge of these natural wonders which will not be accessible anymore in a few couple of years. The preliminary results of this, still in progress, research allow to date the giant crystals and to define the boundary conditions and the mechanisms which induced their development. For the first time pollens have been extracted from gypsum crystals and their analyses evidenced that some 35 Ky BP the Naica climate was cooler and more humid than today.

Introduction

The systematic study of "mine caves" has emphasized the high scientific interest of the minerogenetic processes active therein and consequently of the crystals that they sometimes host (De Waele and Naseddu, 2005).

From this point of view, the natural cavities crossed by mine galleries in Naica (Chihuahua, Mexico) (Fig. 1) have been world renowned for over a century, due to the dimension and purity of their gypsum crystals (Hill and Forti, 1997). Beside Cueva de las Espadas (Swords cave), unveiled at the beginning of the 20th century at the -120 level, where crystals up to 2 meters in length exist (Degoutin, 1912, Foshag, 1927, Rickwood, 1981), in the last 6-7 years mine galleries at the -290 level have intercepted several natural cavities, the most important of which are Cueva de los Cristales (Crystal Cave), Ojo de la Reina (Queen's Cave) and Cueva de las Velas (Sails Cave) (Fig. 1). All these caves host gypsum crystals much bigger that those in the Cave of the Swords. The largest of these crystals, over 13 m in length, has been found in Crystal Cave (Fig. 2) (London, 2003). Even if these crystals are by far the largest gypsum crystals in the world the scientific importance of the caves is not confined to this aspect: in fact many are their features worth to be studied, from biology to microclimate, from physiology to palynology etc.

The study of Naica caves and crystals is a part of a general research project which the owner of the mine, the Peñoles Company, committed to La Venta Exploring Team and Speleoresearch & Films in 2006 (Bernabei et al. 2009).

A workshop was organized at the end of the first year of the project, which was attended by researchers from 16 Universities of 6 Countries (Mexico, USA, Spain, Italy, Switzerland and Norway). The presented talks covered all the research fields of the project: from palynology to laser scanner techniques, from physiology to mineralogy, from climatology to speleogenesis, from geochemistry to documentation. When all the researches will be over (probably in 2011) a symposium will be organized in Mexico to share the results of the Naica project with the whole scientific community.

In the present paper, after a short geological outline of the area, the Naica project and its first achieved results within the field of earth sciences are presented.

Geological Setting

Naica mine is located in a semi-desertic region some 100 km southeast of Chihuahua, the capital town of the homonymous Mexican State bordering the USA (Fig. 1). The mine opens at 1385 m a.s.l. in the northern flank of the Sierra de Naica, a 12 km long, 7 km wide, anticline structure of carbonate formations oriented northwest-southeast. This antiform outcrops from a very extensive alluvial plain. At the regional scale the Naica carbonate sequence consists of limestone, dolomitic limestone and calcitic dolostone with lutitic interbeds overlying an Aptian evaporitic sequence. The carbonate sequence started its deposition during Albian age (Cretaceous) and its sedimentation went on for several tens of millions of years. In the mine location the whole ore body is within the carbonate sequence and up to now no trace of the Aptian evaporites has been found within cores drilled up to over 1 km in depth.

Tertiary intrusive magmatic activity, which characterized this part of the North American subcontinent, caused the development of acid dykes, some 26.2-25.9 Myr BP within the carbonate sequence (Megaw et al., 1988). Recent magnetometric studies have unveiled an igneous source at a depth of between 2.5 and 5 km, some 4 km south of Naica, while in 2007 a drilling close to the mine shaft met an igneous body about 1140 m below the surface.

The polysulphide (Pb, Zn, Ag) ore bodies are related to hydrothermal flows (Erwood et al., 1979) induced by the Tertiary dykes.

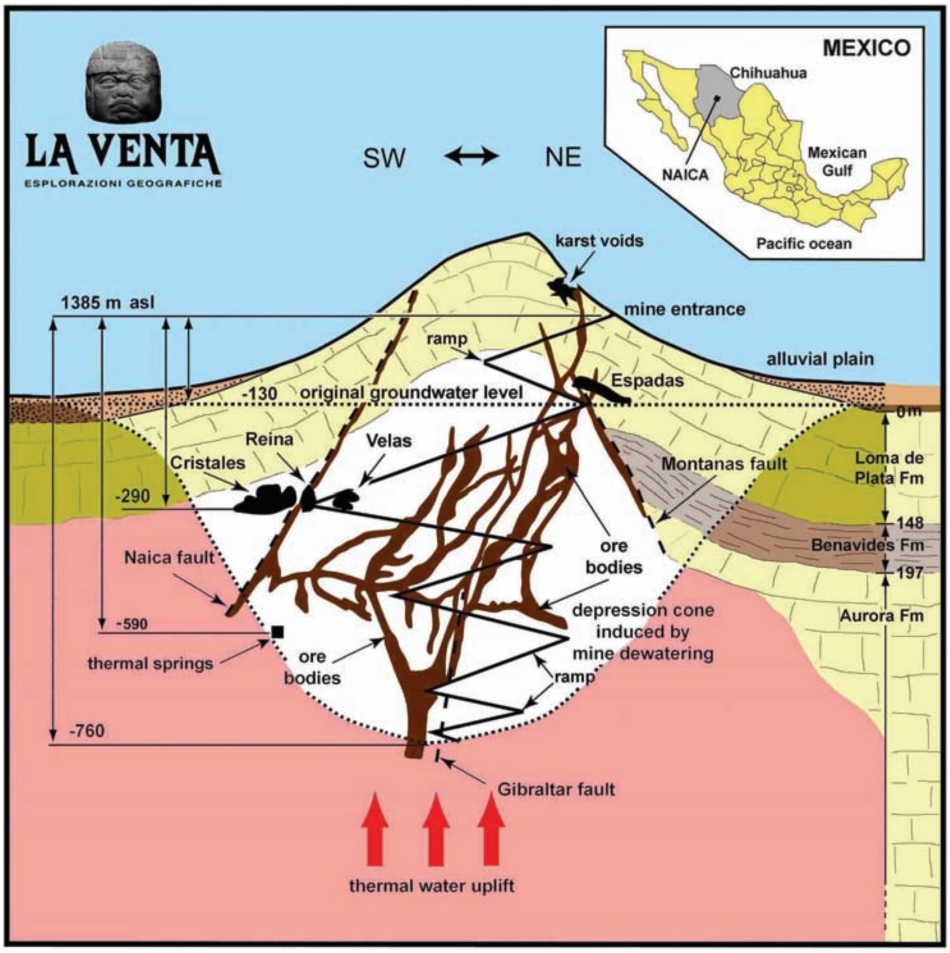

Figure 1. Sketch of the mine in which the main natural cavities, closely connected to the main faults, are related to the original groundwater

The mineral deposit (consisting mainly of pyrite, pirrotine, sphalerite, galena and chalcopyrite) displays chimney and manto shapes developed within dykes and hosting carbonate formations. The latter are consequently strongly altered and partially transformed into calcosilicates. During a later stage, when the thermal fluids got colder, calcite, anhydrite and quartz formed veins within the ore bodies (Stone, 1959).

Two different fault sets were the main structural controls for hydrothermal circulation and therefore for the location of the mineral deposits. The most important of them are the Gibraltar, Naica and Montaña faults (Fig. 1). These structures still control the thermal water flow within the Naica anticline: almost all the water springing in the deep mine galleries comes from fractures related to these faults. Their important role in water circulation is also confirmed by the fact that all the main karst caves are strictly related to them (Fig. 1). Mine activities have reached -760 below the mine entrance (level 0 at 1385 m a.s.l.), and they are some 630 m below the original groundwater level which was at -130 (1255 m a.s.l.): presently to maintain the mine galleries water free a dewatering of about 1 m^3/s is required.

All the Naica area is still under a thermal anomaly. Water springing in the mine galleries has a temperature close to 53°C. A recent study (García Ruiz et al., 2007) has demonstrated the meteoric origin of these waters, even if the average residence time within the thermal aquifer is rather long (over 50 years).

The end of the mining activities (some 5-7 years from now) will have as a consequence the flooding of the mine thus the gigantic crystals will be definitively drowned in 170 m of hot water.

The Naica Project

The aim of the four year project is to carry out a multidisciplinary research not only on various fields of interest in the Naica caves but also to search for a possibility to maintain this geological wonder at least partially available for future generations after the end of the mining activity.

The first research to start was obviously related to the presence of the 150 huge gypsum crystals (Badino et al., 2009) inside the Cueva de los Cristales: it was necessary to understand the mechanism by which such gigantic crystals grew and how long the environmental conditions allowing their development were maintained. In this respect the analyses of the huge, wide-spread fluid inclusions and small solid inclusions (in particular spores and pollens) proved to be fundamental together with U/Th gypsum analyses.

Another related field of interest is the study of the minerogenetic mechanisms which were active before, during and after the deposition of gypsum in order to clarify the relationships between the mine ore bodies, the cave speleogenesis, and the development of the gypsum crystals: a unexpected richness of diagenetic minerals, some of which new for the cavern environment, has been detected, thus allowing the detailed reconstruction of the evolution of these caves in the last half million years.

Other ongoing researches are focused on fields apart of geology: they deal with the physiologic behaviour of the human body when exposed to the Naica cave climates (Giovine et al., 2009), the possible presence of extremophile micro-organisms trapped within the huge fluid inclusion of the giant gypsum crystals (Boston, 2007), the study of new miniaturized devices to analyze the rock composition in non-destructive manner for space research, and to define the present day human impact on the caves and the better method to preserve them and to allow their public fruition in the future (Calaforra et al. 2007).

To answer all these questions a multidisciplinary task force has been organized (Fig. 3): presently some 40 scientists from 17 Universities and 2 Research Centres co-operate and more are expected to join in the near future.

Exploring and mapping Naica caves

Before starting scientific research inside these caves it was necessary to solve the problem of survival in such an hostile

Figure 2. A general view of the giant gypsum crystals inside the Cueva de los Cristales: explorers are equipped with refrigerated suits and breathing (photo by Paolo Petrignani, La Venta & S/F Archives)

environment (Badino and Forti, 2007). In fact, though small and not so complex, the caves of the Naica mine are a problematic habitat and it is impossible to venture inside without special equipment and suitable training, in order to avoid death in a few minutes.

The temperature in itself (45-48°C), isn't too high if compared to what can be found outside. But, without exception, external high temperatures are associated with a low humidity level and this fact allows cutaneous perspiration that induces the consequent cooling. This mechanism balances the heat transferred by the environment.

The Humidex Index, combining air temperature and humidity, makes it possible to represent in Humidex degrees, (Masterton and Richardson, 1979) the "temperature actually perceived" by the human body against the subjective evaluation of the sultry heat. In Cueva de los Cristales the Humidex Index ranges between 90 and 100 degrees, roughly, twice the value of the risk of death.

Apart from this unbearable heat for the human body, above 42°C, our cells degenerate, i.e. they cook. The temperature inside the cave is higher than that, so, there is a risk of burning. Survival techniques for longer periods had to take in serious consideration the risk of burns to the eyes and, even more devious and fatal, to the lungs.

For this reason, the first four expeditions were devoted to study the environment in which we had to operate.

The most important result achieved has been the understanding of the operating context: due to the environmental conditions, without specific technical precautions and suitable equipment any research is practically impossible. Thus specific materials and technologies have been developed: in particular, the refrigerated suits (Fig. 2), and the "crystal friendly boots" a footwear with a smooth and soft sole, made of a special mix that assures a perfect adherence above 40°C.

The usual stay was about one-two minutes in case of untrained personnel and up to ten minutes for the expert ones, but thanks to the developed techniques it is now possible to stay for more than one and a half hour.

But the environment appeared more hostile than expected and these prolonged stays caused unexpected and really dangerous situations of physiological stress. A correlated study of the matter became therefore part of the present project (Giovine et al., 2009).

Once solved the survival problems an extremely detailed survey of the Cueva de los Cristales was realised by using laser scanner techniques (Canevese et al., 2009), this because all the teams needed a reliable map to locate samples and/or field observations.

The genesis and evolution of the giant crystals

These studies were the first to be developed. Before the discovery of these caves four different reactions were known to cause the evolution of big gypsum crystals in cavern environment (Hill and Forti, 1997), evaporation, acid aggression, sulphide oxidation and incongruent dissolution. The study of the geochemical and physicochemical characteristics of the thermal aquifer evidenced the existence of a completely new mechanism for the genesis and evolution of these giant crystals (García Ruiz et al., 2007), which is based upon the gypsum-anhydrite solubility disequilibrium. At 59°C the gypsum and anhydrite solubilities are the same. At lower temperatures the solubility of gypsum becomes smaller than that of anhydrite (Fig.4).

Therefore, below this temperature a solution saturated with respect to anhydrite is automatically super-saturated with respect to gypsum, thus inducing the deposition of gypsum and a under-saturation with respect to anhydrite. Anyway to avoid the immediate stop

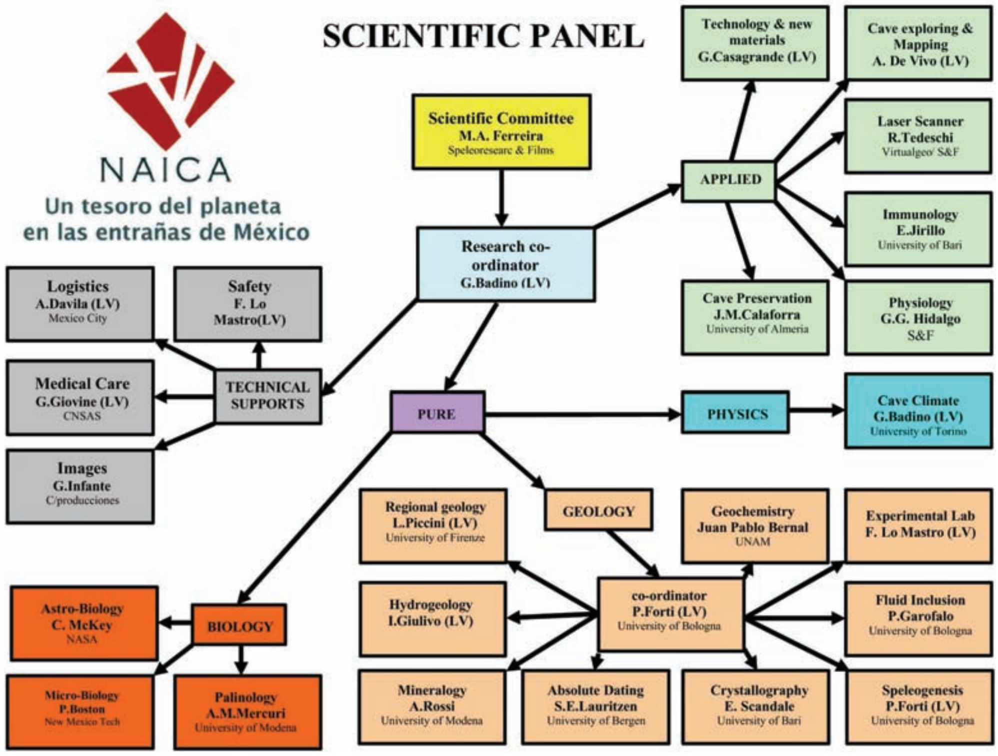

Figure 3. The Naica multidisciplinary team

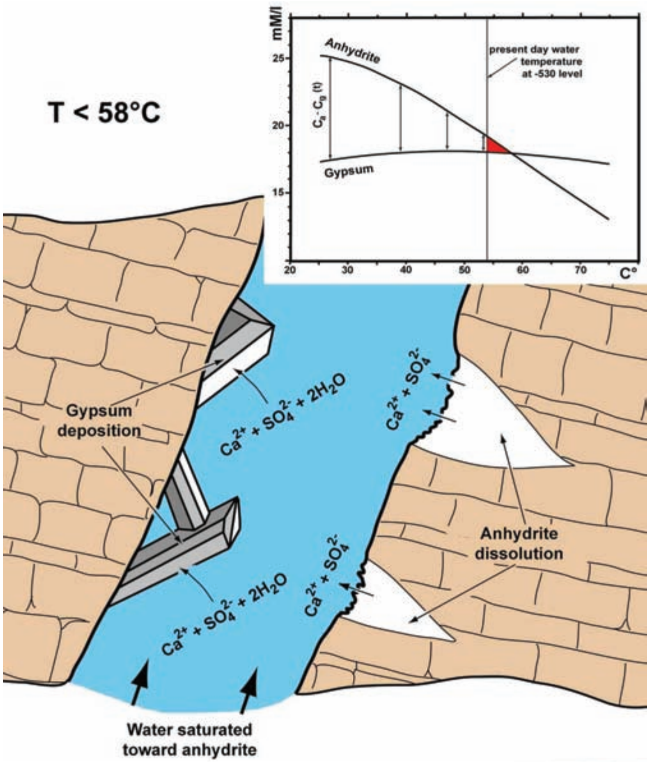

Figure 4. The development of the gypsum crystals induced by the gypsum-anhydrite solubility disequilibrium and (upper right) Gypsum-Anhydrite solubility diagram with evidenced (in red) the temperature range in the caves of Naica at the time in which gypsum crystals were growing

of this process the super-saturation with respect to gypsum must be maintained by introducing into the system new Ca^{2+} and SO_4^{2-} ions, which may be simply supplied by dissolution of new anhydrite (Forti, 2009).

Hydrothermal anhydrite lenses are dispersed in the whole carbonate sequence of Naica as a consequence of the late stage of the formation of the ore deposit and it allows for continuous supply of Ca^{2+} and SO_4^{2-} ions to maintain the uplifting solution supersaturated with respect to gypsum and slightly undersaturated with respect to anhydrite (Garcia Ruiz et al., 2007)

Such a small difference between the solubility of gypsum and anhydrite slightly below 59 °C provides a very stable mechanism to constantly maintain the crystallizing system close to equilibrium.

The role played by the anhydrite-gypsum solubility disequilibrium in the development of the Naica giant gypsum crystals is indirectly corroborated by the widespread presence of euhedral celestite ($SrSO_4$) crystals in the thin layer of clay and iron oxides just below the gypsum crystals of all the Naica caves and also trapped within them (Panieri et al., 2008). It is well known that the anhydrite structure hosts more strontium than does gypsum (Butler, 1973). Therefore, instead of being incorporated into the structure of newly forming gypsum, this excess strontium released through dissolution of anhydrite precipitated as a separate mineral phase. Another indirect proof of the active transformation of anhydrite to gypsum is given by the presence of microscopic gypsum crystals actively growing inside anhydrite lenses close to the Cueva de los Cristales (Garcia Ruiz et al., 2007).

The development of few huge crystals instead of many small ones is justified by the fact that the temperature drop was extremely slow (data from fluid inclusions demonstrate that the giant crystals developed in a temperature range between 55-58°C) over a relatively long time interval (Garofalo et al., 2009).

In order to evaluate the time interval in which the giant crystals developed several samples of already broken crystals have been taken from Cueva de los Cristales, Ojo de La Reina and Cueva de las Espadas to try to obtain dates by the ^{230}Th/ ^{234}U method.

A few samples were analysed by using thermal ionization mass spectrometry (TIMS) on a Finnigan 262RPQ instrument (Lauritzen et al., 2008), but this dating methodology proved to be inefficient due to the very scarce amount of uranium trapped within the gypsum. Only one sample taken some 50 mm below the outer surface of a prismatic crystal from Cueva de los Cristales gave a good result (34.544 ± 0.819 kyr).

In order to improve the U/Th dating it was then decided to use a multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) technology and a new extraction chromatographic method (Sanna et al. 2009). The first two achieved results are satisfactory: in fact even though the analysed samples display low uranium concentration and high background thorium level, the obtained ages are within reliable ranges. The first sample was taken from the inner core (some 13 cm from the outer surface) of a broken prismatic crystal in Cueva de los Cristales and gave an age of 164±48 kyr. The second one was taken at the entrance of the Ojo de la Reina cave, which is only a few tens of meters apart of Cueva de los Cristales: the sample was extracted from the base of a pinacoidal crystal a few centimetres apart from the contact with the limestone rock of the cave floor: its resulting age was 213 ± 12 kyr (Sanna et al., 2009).

Based on its location with respect to the hosting rock, the data of this sample should represent the very beginning of the gypsum deposition within the caves at the -290 level of the Naica Mine.

In order to test the validity of this assumption an experimental unit has been built, and placed in one of the “water springs” at -590 level, where the original thermal water, not yet contaminated, spills out from the ceiling of a mine gallery.

The experimental unit was planned to completely avoid the contact of the thermal water with the mine atmosphere in order to reproduce the condition of complete saturation existing inside the cave until the mine dewatering caused their emersion (Forti and Lo Mastro, 2008). Thus the single unavoidable difference existing between the present day water and that feeding the crystals in the caves until twenty years ago is its temperature which dropped to 51°C.

Other affecting factors, like variation of ionic effect as a consequence of the variation in salinity of the feeding solution (from the original 4-5% to the present day 2%) and the flux effect (the residence time of the solution inside the caves may be estimated in 1-2 days, while that inside the experimental vessel is only of 2-3 minutes), were not taken into consideration because their effect on the supersaturation was evaluated to be extremely scarce with respect to that of the temperature.

The device to reproduce the “cave conditions” for gypsum development (Fig. 5a) was installed at the end of 2006 and the experiment was successful. Euhedral gypsum monocrystals started growing (Fig. 5b) and the first available data covering an interval of over 480 days evidenced a very good correlation between crystal growth and time (Forti et al. 2009). The resulting average growth (corrected for the temperature factor) is 0.004 ± 0.0002 mm/yr. The experimentally measured growth rate gives an extrapolated age for the biggest crystals of 250000 yr, a value extremely close to that

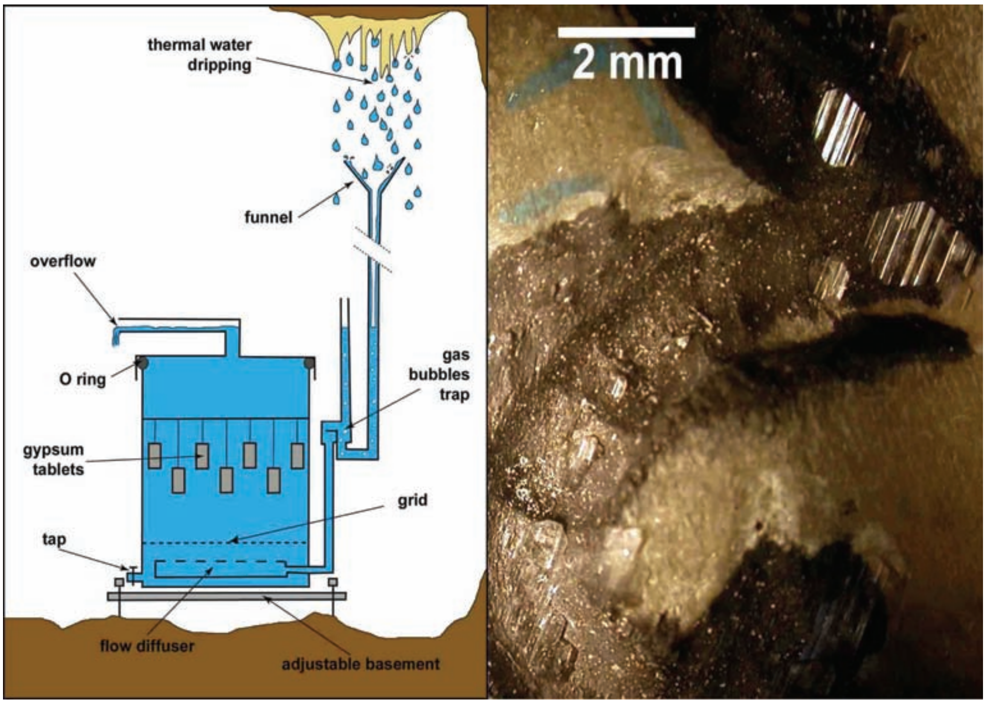

Figure 5. Left: the device placed at -590 to restore the conditions for the development of gypsum crystals; Right: gypsum crystals developed in about one year (photo Antonio Rossi, University of Modena, Italy)

obtained with U/Th method for the crystal of the Ojo de la Reina.

Considering the experimental errors which characterize both independent methods of dating, the agreement between the two values can be considered extremely good.

Using recent data on the dissolution kinetics of crystalline gypsum, (Jeschke, 2002), and assuming that dissolution and precipitation kinetics is symmetric around the saturation point (i.e. no nucleation threshold), the growing rate of 0.004 mm/yr converts to a supersaturation of about 1.005. This value corresponds to a nucleation probability (García Ruiz et al., 2007) less than 1 over 1 million which is reasonable for the growth of a hundred of giant crystals over a period of two-three hundred thousand years.

Finally it must be stressed that Naica caves are important not only for giant gypsum crystals, in fact they also host two new forms of gypsum. The first, named sails (Fig. 6a), have been discovered (Bernabei et al., 2007), inside the Cueva de las Velas. They are very thin fibres of gypsum, the evolution of which is closely related with the very first moment of the artificial lowering of the ground water table at Level -290. They are crystalline forms which have developed in a few days or months, about 20 years ago and their development and shape are totally controlled by capillary lifting and strong evaporation over the tips of the giant crystals pointing upward.

The second, named "gypsum hooks", were observed only in the upper part of Cueva de Las Espadas (Fig.6b). They are partially re-dissolved and bended crystals and their evolution was controlled by condensation and consequent strong heating of the crystal tips, when the cave became partially aerated during the latest phase of presence of thermal water (Forti et al., 2009).

The other chemical deposits

Even if 99% of the chemical deposits developed within Naica caves consist of gypsum, the scientific interest of the other deposits is very high. The mineralogical analyses are still in progress but already evidenced the presence of 40 different cave minerals, 10 of which (antlerite, hectorite, orientite, penta-hydriote-Cu, plumojarosite, starkeyite, szmikite, szmolnokite,and woodruffite, and an Al, Mg, Cu, Zn silicate) new for the cavern environment. Most of them developed in two distinct periods of oxidation of the ore bodies. In the first one, which occurred deep inside the thermal aquifer before and/or during the first stage of the deposition of the giant gypsum crystals, a large quantity of material was deposited but, due to the scarce variability of such an environment, only a few minerals developed (Panieri et al., 2008). This process was clearly controlled by micro-organisms, as testified by widespread biogenic structures preserved within these deposits

Figure 6. Left: Cueva de las Velas: a "sail" growing epitaxially over a pre-existing large gypsum crystal (photo by Tullio Bernabei, La Venta & S/F Archives); Right: gypsum hooks from Cueva de las Espadas (photo by Paolo Forti, La Venta & S/F Archives)

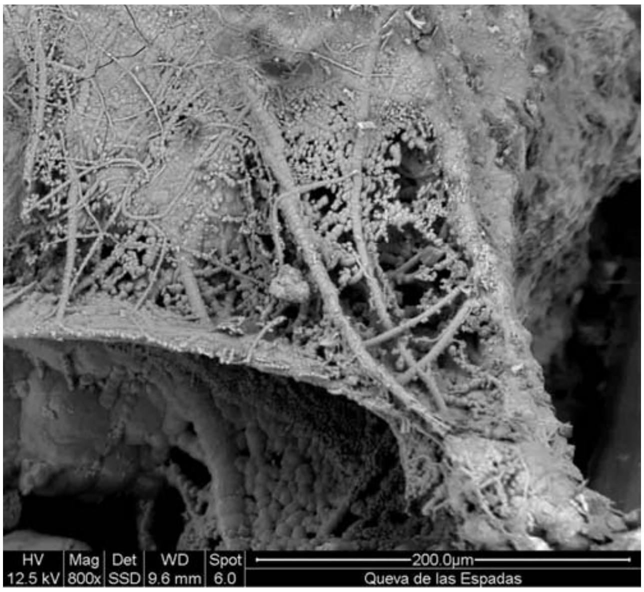

Figure 7. An electron microscope image of Fe/Mn oxides that fossilized clear biogenic forms (Laboratorio Grandi Strumenti, University of Modena, Italy).

(Fig. 7) and gave rise to the deposition of the following 9 minerals: calcite, coronadite, celestite, dolomite, fluorite, göthite, hectorite, opal and quartz (Forti et al. 2009). The genesis of hectorite $[Na_{0.3}(Mg,Li)_3Si_4O_{10}(F,OH)_2]$ was observed for the first time in a cave and is related to the pH decrease as a consequence of the ore bodies oxidation, which reduced the silica solubility enhancing also the opal and quartz deposition, and the increase of magnesium concentration in the feeding waters (Garofalo et al., 2009)

The second oxidation stage, started less than 20 years ago when mine dewatering allowed aerate conditions within the caves. In this case the process was totally abiotic as proved by the total absence of any biogenic form and it induced the deposition of small amounts of material but with an extremely high minera-logical variability due to the high number of active minerogenetic meghanisms (Table 1). 36 different minerals have been detected: anglesite, anhydrite, antlerite, apatite, aragonite, azurite bassanite, blödite, calcite, celestite, chalcantite, chrysocolla, dolomite, epsomite, fluorite, fraipontite, göthite, guanine, gypsum, halite, hematite, hexahydrite, jarosite, kieserite, magnetite, malachite, orientite, Cu-rich variety of pentahydrite, plumbojarosite, pyrolusite, rozenite, starkeyite, szmikite, szmolnokite woodruffite and an Al, Mg, Cu, Zn silicate, which is still under study and may result a new mineral for science).

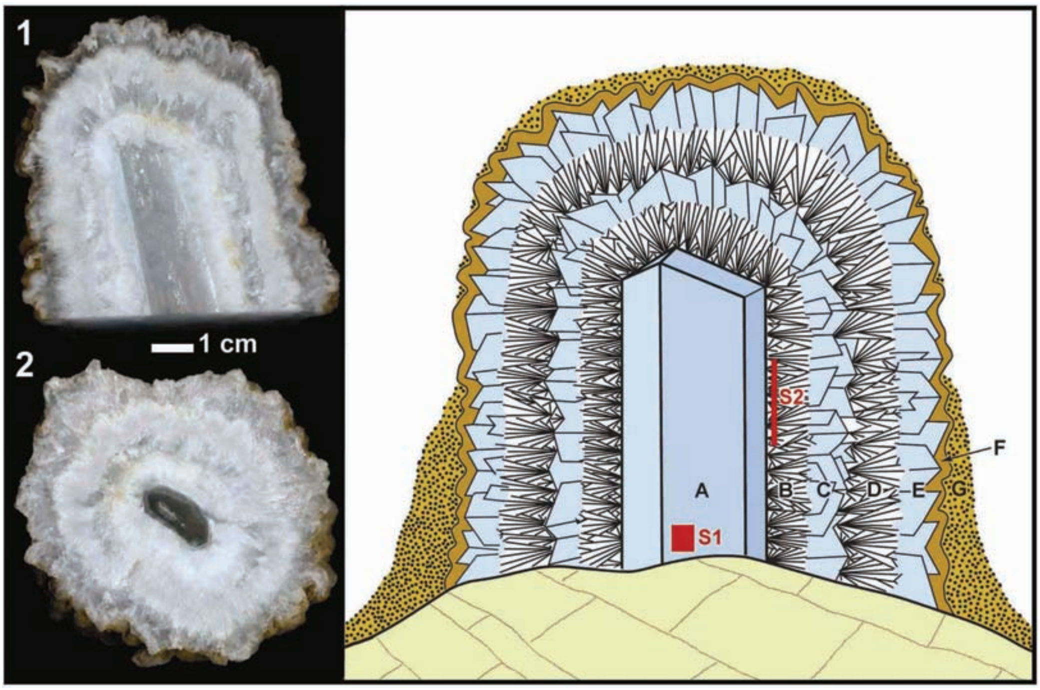

Figure 8. Vertical (1), horizontal (2) sections and graphical restitution of the pseudo-stalagmite grown inside the lake of the Cueva de las Espadas: A gypsum, B aragonite, C gypsum, D aragonite, E gypsum, F calcite, G clay and silt. S1 and S2 are the sampling point for the U/Th datings.

Finally some small "pseudo-stalagmites" developed at the bottom of the Cueva de las Espadas (Fig. 8) are worth of mention.

The analyses (FORTI, 2007) of a polished section of these speleothems evidenced the presence of an inner nucleus consisting of a prismatic gypsum euhedral crystal over which developed two white layers of acicular aragonite alternating with two layers of gypsum macrocrystals. Then the speleothem was covered with a thin layer (1-2 mm) of hazel-brown calcite and finally by poorly cemented clay-silty deposits, which represent the latest stage in the depositional sequence of this cave. During the low stand of the groundwater, the ingression of air in the upper part of the cave is responsible for the development of aragonite due to the diffusion of CO_2 into the thermal water. The subsequent highstand levels of groundwater re-established saturated conditions and therefore gypsum was deposited. The film of brown calcite corresponds to the definitive lowering of the thermal aquifer below the level of Cueva de las Espadas, which was started by a moderate flow of fresh water which induced the deposition of calcite instead of aragonite. This period was drastically interrupted by mining activities, which changed dramatically the hydrogeology of the whole area and also intercepted fresh water seepage feeding the cave, thus causing the deposition of the silt and clay deposits, which are the latest deposits in this cave. By using the thickness of all these different layers, it seems that the whole sequence of observed events (from layering of the gypsum crystals to silt deposition) took only a few thousand years.

To confirm these hypothesis two samples were taken from one of the pseudo stalagmites. The first one from the inner core of the gypsum macrocrystal (S1 in Fig. 8) and the second one from the first aragonite layer (S2 of Fig. 8) about 2 mm above the gypsum surface.

Both these samples were dated with the multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) technology (Sanna et al., 2009) and the obtained ages are respectively: 60 ± 0.7 Kyr for the core of the gypsum and 15 ± 2 kyr for the aragonite layer.

The age of the inner gypsum core should correspond to the beginning of a new step of gypsum deposition after a long corrosional period which caused the partial and /or total destruction of most of the largest gypsum crystals previously developed inside this cave.

The age of the first aragonite layer corresponding to the first fluctuation of the groundwater level gave an age which is in good agreement with the supposed one derived by the morfometric analyses of the 5 overgrowth layers, whose thickness suggest a rather constant time span of each of them. In the near future the radiometric ages of all the layers of the "pseudo-stalagmite" will allow for a detailed reconstruction of the fluctuation of the thermal groundwater level within the last 15 Kyr BP.

Stages in the development of the cave

Until recently, studies were focused on the mechanisms allowing for the development of the giant crystals, while the genesis and the evolutionary steps of the Naica caves were completely neglected. The thermal fluids responsible, since 25 Myr BP, of the evolution of the Naica ore bodies were always characterized by net deposition, therefore the permeability of the hosting formation was greatly reduced and no karst voids had the possibility to develop.

Very recently (1-2 Myr BP), tectonic stresses partially displaced the ore bodies giving rise to open joints and fractures closely related to three main faults (Naica, Gibraltar e Montañas), which control the uplift of the thermal fluids.

In the mean time the temperature of the thermal water lowered below 100-120°C and they became aggressive with respect to carbonate formations, thus small cavities had the possibility to develop at different levels inside the aquifer. This first stage of deep karst development was common to all the caves of Naica but it was surely short and the corrosion process not very effective. In fact, the presently known caves are small and they always correspond to scarcely widened fractures (Ojo de la Reina and Cueva de las Espadas) or bedding planes (Cueva de las Velas). The few corrosional features (mainly bell domes on the ceilings) did not allow for a detailed reconstruction of the cave evolution, which was in turn achieved by a multi-disciplinary analysis of the thick deposits hosted inside each cave (Fig. 9).

Table 1. Environmental control over the active speleogenetic processes and related temperature variations.

Environment	Processes	Chemical Deposits	T° decrease
Vadose	Organic matter mineralization deposition	Organic mineral and phospates	Very fast
	CO_2 diffusion	Calcite speleothem evolution	
	Acid aggression	Gypsum, metallic sulphate & silicate deposition	
	Inorganic oxidation	Oxide-hydroxide deposition	
	Evaporation	"sails" development, sulphate and halide deposition	
Epi-Phreatic	CO_2 diffusion	Aragonite deposition	Slow
Deep Phreatic	Organic oxidation	Oxide-hydroxide deposition and limestone corrosion	Extremely slow
	Gypsum/ anhydrite disequilibrium	Giant gypsum crystals and celestite development	

The evolutionary steps were several and complex ones, related to different speleogenetic mechanisms (corrosion, double exchange, acid aggression, CO_2 diffusion, condensation corrosion, etc). Even if they always were controlled by the presence of the thermal aquifer, the resulting evolution was somehow different from cave to cave, being, time by time, related to deep phreatic, epi-phreatic and vadose environments (Table 1).

From this point of view the most interesting cave is the Cueva de las Espadas, the evolution of which was characterized in time by several changes between these three environments, while the deeper caves (Cristales, Ojo de la Reina and Velas) suddenly changed from

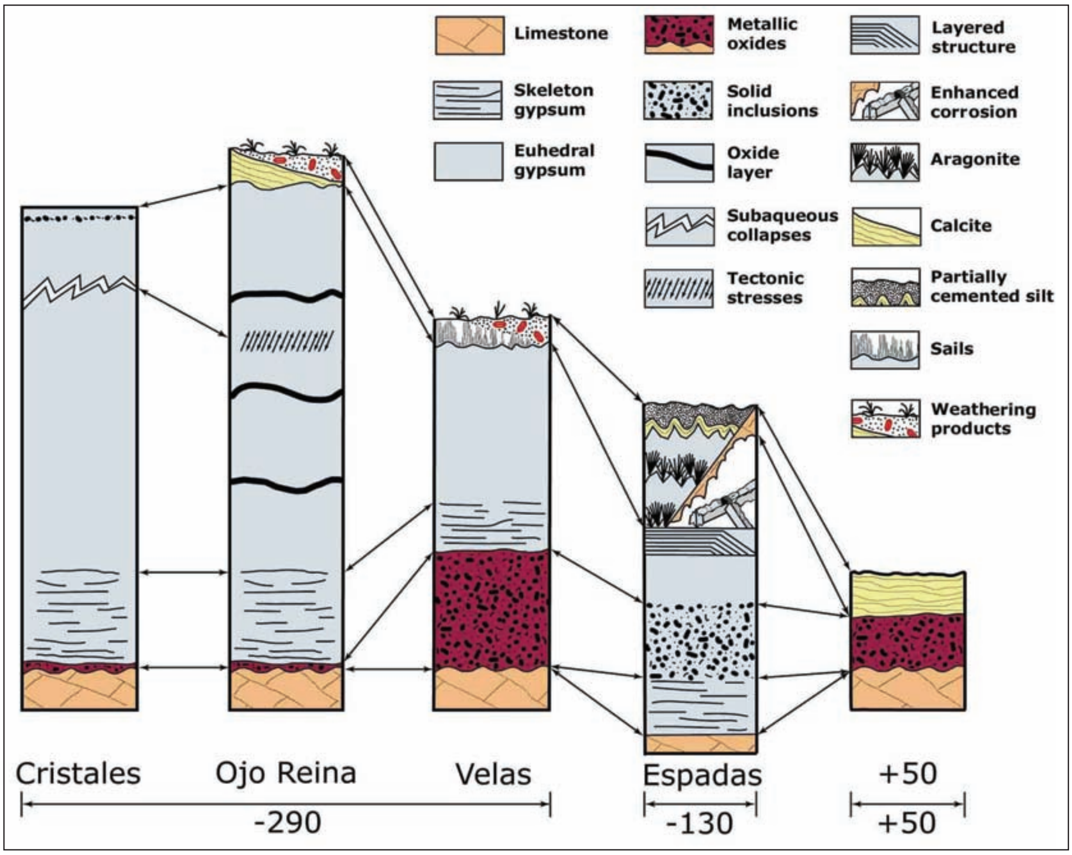

Figure 9. Stratigraphic sketch of the deposits present in each of the Naica caves and their relationships

deep phreatic to vadose conditions when the mine dewatering lowered the groundwater below the -290 level 20 years ago. The +50 cave is the only one in which the deposition of phreatic gypsum never occurred because the thermal water left it before its cooling down reached the gypsum-anhydrite equilibrium temperature.

The gypsum deposition went on until 20 years ago, when the mine exploitation caused the complete dewatering of the caves: anyway this fact did not represent the end of the cave development, which was characterized by a last stage active in all the cavities. The depression cone had relevant consequences on the cave development giving rise to the evolution of several new diagenetic minerals but also greatly enhancing the condensation corrosion and dissolution processes which, in a few years, will be responsible not only for the damage of the giant gypsum crystals but also for their complete destruction.

Fluid Inclusion Analyses

The study of fluid inclusions is aimed at determining the fundamental physical-chemical properties of the fluid that generated the giant gypsum crystals and its evolution in time and space (Garofalo et al., 2009). Fluid inclusions are abundant in all the studied samples and are commonly big (>200 ìm, Fig. 10). They were typically found along crystallographic planes (primary fluid inclusions).

About four hundred microthermometric measurements were carried out at the Department of Earth and Environmental Sciences of the University of Bologna with a Linkam THMSG 600 heating/freezing stage attached to an Olympus BX51 petrographic microscope. This stage is calibrated periodically using synthetic fluid inclusions (H_2O and H_2O-CO_2 fluids) and laboratory standards.

In all the occurrences the trapped fluid is mostly one-phase (liquid) at T_{lab}, and only occasionally two-phase (liquid-vapour). Freezing experiments show the presence of two aqueous fluids with distinct bulk salinity within the cave crystals: one in the range 3-6 $w_{\text{NaCl equiv.}}$(characterizing most of the fluid inclusion of the -290 caves) and the other between 7 and 8 $w_{\text{NaCl equiv}}$ (the highest values being observed mainly in the dark portion of the crystals of Cueva de las Espadas). Finally samples of the gypsum crystals actually developing close to the thermal springs in the mine galleries at -590 exhibited fluid inclusions with a even lower bulk salinity 1,8-2.0 $w_{\text{NaCl equiv}}$.

Laser Ablation-ICP-MS analyses were carried out at the Department of Chemistry and Applied Biosciences of the ETH-Zurich on 71 individual inclusions adjacent to those studied by microthermometry by using two UV 193 nm excimer lasers (GeoLasQ and GeoLasC, Lambda Physik, Göttingen, Germany) coupled with a quadrupole ICP mass spectrometer (ELAN 6100DRCplus, Perkin-Elmer, Waltham, Massachusetts).

Preliminary chemical analyses of single fluid inclusions by LA-ICP-MS show that, in addition to Ca and S, the major components of the cave fluid were Mg, Na, and K (in order of abundance), while Mn and Pb are minor and below the limit of detection in many inclusions. Only the fluid inclusions within the dark rims (rich in solid inclusion of oxides-hydroxides) of the crystals of Cueva de las Espadas, where Na and Mg reach high concentration ranges (10000-70000 µg/g), exhibit a relatively high Pb content (up to about 10000 µg/g).

The distribution of total homogenisation temperatures in Cueva de los Cristales display a mode in the 49-57 °C interval, which is rather undistinguishable from that of Las Espadas, while in Ojo de la Reina this interval is narrowed to 56-57°C. Hence, in contrast with the distribution of bulk salinity and Mg-Na concentration values, the total homogenisation occurs in a narrow range within the entire Naica karst-system.

A still open question is the definition of the mechanism responsible for this relatively high increase of Mg-Na content in the upper part of the thermal aquifer. These events may be explained by periods in which the Cueva de las Espadas was partially dissected from the main thermal aquifer, thus allowing for strong evaporation processes and consequent high concentration of Mg-Na ions in the residual water. On the basis of theoretical evaluation of ionic activities of the main ionic species present within the Naica aquifer (Garofalo et al., 2009), it was possible to demonstrate that the partial mixing of the hypersaline upper solution with the deeper less concentrated ones will constantly induce a slight supersaturation with respect to gypsum thus enhancing the growth of the giant gypsum crystals within the Cueva de los Cristales and Ojo de la Reina caves. Exceptional crystal growth was not possible in Cueva de las Espadas because of periods of high supersaturation induced by evaporation, which obviously induced a fast new nucleation.

Solid inclusions analyses

A detailed study of the solid inclusions trapped inside the crystals is being carried out. Some of the solid inclusions have shown a rich presence of "biogenic" organisms, fossilized by neo-formed minerals during the fist oxidation stage (Fig. 7). This discovery suggests that it might be possible to find, inside the large fluid inclusions often present inside the crystals, some micro-organism still viable for DNA genetic studies. Therefore a threefold research started: (1) to seek any viable living organisms that may be trapped in fluid inclusions and attempt to cultivate them, (2) to extract any DNA present in the fluid inclusions and identification of organisms or closest relatives (where possible), and (3) identification and analysis of any non-living organic material other than DNA that may shed light on any biological contents of the inclusions.

Water extracted from fluid inclusions of the gypsum crystals of Cueva de los Cristales have been fed in oxygen rich and oxygen depleted environments since more than one year. Biomats started to grow but the process is so slow that presently their amount still does not allow to perform experiments (P. Boston *personal communication*). In any case it has been demonstrated that living organisms were trapped inside the gypsum crystals at the time of their development and maintained at least some of their living activities up to present.

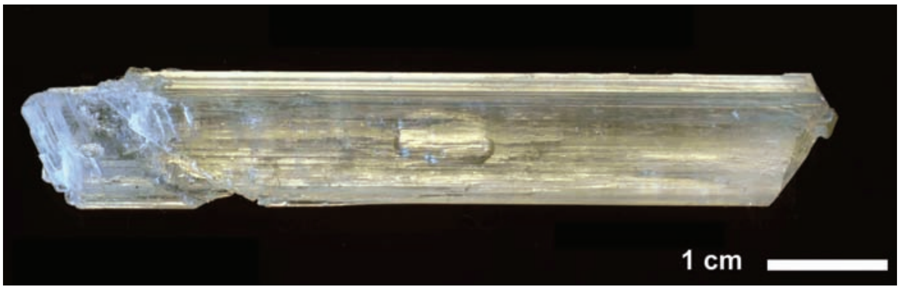

Figure 10. A huge biphasic fluid inclusion from Cueva de las Espadas (photo by Paolo Forti, La Venta & S/F Archives)

NASA is directly involved in these researches, and recently it has successfully tested a new miniaturized Raman spectrometer inside the Cueva de los Cristales. This apparatus will be sent in the near future to Mars for searching living micro-organisms (extremophiles) on the surface of that planet.

Amongst the Naica solid inclusions by far one of the most intriguing findings was the presence of well preserved pollen grains (Holden, 2008) trapped inside the giant gypsum crystals. Their presence inside the gypsum crystals may be explained only assuming that the meteoric water seepage brought them deep in the thermal aquifer from where the pollens were uplifted into the caves by the hot water feeding the crystals which consequently trapped them inside their structure.

Pollens and/or sporomorphs (Garofalo et al., 2009) have been found in all the analysed samples from all the Naica caves, but, up to present, detailed investigation have taken place only in Cueva de los Cristales. In this cave the pollens were extracted from the same crystal and the same area from which the absolute age of 34.544 ± 0.819 kyr was obtained. Extractions have been carefully repeated several times to be sure that the presence of pollens was not due to accidental pollution. Presently a total of over 40 pollen grains have been detected and some of them were perfectly preserved. Among these, pollens of *Quercus* cf. *garryana*, *Lithocarpus densiflora* cf., *Cupressus*, *Taxus*, *Plantago*, and *Lycopodium* sphores have been detected.

The pollen spectrum is representative of the vegetation existing in the feeding basin at the time of development of their deposition. Therefore they may allow for a paleo-climatic reconstruction for the area of Naica. Even still in progress the presently identified pollens are coherent with a humid broadleaf forest, presently existing in the S-Western areas of United States, suggesting that about 35 ky BP the Naica area was characterized by a much more humid climate than that present today.

Presently further fluid inclusion analyses and absolute dating of the hosting crystals are in progress to validate this paleo-environmental reconstruction.

Final remarks

Even if the research started only recently, some of the already achieved results are of extraordinary interest. A completely new mechanism for the development of the giant gypsum crystals based on the anhydrite-gypsum solubility disequilibrium below 59°C has been defined. Well preserved pollens have been found, for the first time in the world, trapped in euhedral crystals and they seem to be, together with the fluid inclusion and absolute dates, suitable proxy for paleoclimatic reconstructions. Microbiological search for extremophiles is very promising and the detection of new species is expected in the near future.

But all these researches must be completed in a short span of time.

In fact all the karst phenomena at the –290 level of Naica mine will remain accessible only for a few years, and as soon as the mining activities will stop (an event that is expected within 5-7 years), the uplifting of groundwater will submerge them under 170 m of hot water.

In reality, the giant crystals of Naica run the risk of destruction even earlier due to condensation processes. The walls of all the cavities of the –290 level, undergo a rather fast cooling due to the forced ventilation of the mine galleries. This process may bring in a short time the cave walls to have a temperature low enough, with respect to that of the uplifting vapours, so that the dew point will be reached and surpassed. When that happens, strong condensation will occur with the consequence of a fast dissolution of the giant gypsum crystals (Fernández-Cortés et al., 2006). This process has already started within the smallest cave at the –290 level (Ojo de la Reina), where the large gypsum crystals are presently intensively dissolved and transformed into calcite speleothems. In a couple of years condensation is expected to start also inside the Cueva de los Cristales.

Therefore a monitoring unit equipped with 20 sensors, with an accuracy of 4 mK, probably the most precise system of this kind ever brought inside a cave, was installed (Badino, 2009). Preliminary data seem to confirm a rather fast cooling trend (~0.5°C/yr).

Thus, one of the project main tasks is to decide the best way to preserve for future generations at least the memory and the records, or, even better, a significant part of this incredible underground world.

Speleoresearch and Films of Mexico City, in cooperation with La Venta, started the realization of full-length films documenting all the explorative and scientific aspects of the Naica caves: but it's not enough. Crystals Cave has been laser-scanner processed to obtain exact high definition 3D maps and eventual virtual reality trips.

But what is more worrying is the material conservation of the crystals. It would be nice to preserve at least a portion of these caves avoiding what happened in Cueva de las Espadas at the beginning of last century: crystals taken away and scattered in various, more or less important, mineralogical collections around the world.

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