

# The Caves of Naica: a decade of research

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## ABSTRACT

The caves of the Naica Mine have been the subject of study by scientists from up to seven countries over the past decade. Up to fifty research works have published to date, most relating to the origin of the giant selenite crystals of the Cueva de los Cristales. Nevertheless, a great deal of knowledge has been generated about other relevant aspects of the Naica system. This paper puts together the vast information available about the Naica caves, from the discovery of the Cueva de los Cristales in 2000 to the more recent investigations addressing mineralogy, microclimatology and the use of gypsum speleothems as a palaeo-environmental proxy. Special attention has been paid to novel research lines that have started to use the speleothems of Naica as a study case, particularly in fields such as Astrobiology and Planetary geology. Moreover, the conservation challenges which these caves will face in the near future as consequence of the end of mining activities have also been addressed in this article.

Keywords: Cueva de los Cristales, Cueva de las Espadas, gypsum, Naica; speleothems

## ***Las Cuevas de Naica: una década de investigación***

### RESUMEN

*Las cuevas de la mina de Naica han sido objeto de diversos estudios científicos en los que han estado implicados investigadores de hasta siete países distintos durante la última década. Más de cincuenta trabajos de investigación han sido publicados durante este periodo, algunos de ellos abordando el origen de los cristales de selenita gigante de la Cueva de los Cristales. Sin embargo, las investigaciones han ido más allá y han tratado otros aspectos relevantes del sistema de cavidades de Naica. En el presente artículo se hace balance de los resultados obtenidos durante la primera década de investigación, desde el descubrimiento de la Cueva de los Cristales en 2000, hasta trabajos más recientes centrados en la mineralogía, la microclimatología y uso de los espeleotemas yesíferos de las cuevas de Naica como indicadores paleoambientales. Se presta especial atención a las nuevas líneas de investigación que han empezado a estudiar recientemente estos espeleotemas desde el punto de vista de la Astrobiología y la Geología planetaria. Además, se tratan algunos de los desafíos de conservación a los que se enfrentan estas cavidades en la actualidad y su futuro incierto tras el cese de las actividades mineras, programado para los próximos años.*

*Palabras clave: Cueva de los Cristales, Cueva de las Espadas, espeleotemas, Naica, yeso.*

## VERSIÓN ABREVIADA EN CASTELLANO

### **Introducción**

*Las cavidades de la mina de Naica (Chihuahua, México) albergan los espeleotemas de yeso hidrotermal de mayor tamaño descritos a escala mundial. La Cueva de los Cristales, descubierta en 2000 a 290 m de profundidad, contiene cristales de yeso selenítico de hasta 11 m de longitud (Forti, 2010). Sin embargo, el interés científico suscitado por estas cuevas no radica exclusivamente en sus cristales gigantes (Fig. 1). De hecho, el hallazgo de la primera cavidad en Naica se remonta a los inicios del siglo XX, cuando las galerías mineras interceptaron la Cueva de las Espadas (nivel -120 m; Forti, 2010) (Fig. 2). En esta cavidad aparecen espeleotemas yesíferos de hasta 2 metros de longitud constituidos por un núcleo de selenita que posteriormente fue cubierto por capas sucesivas de carbonatos (aragonito y calcita) y yeso (Gázquez et al., 2012; 2013) (Fig. 3). Además, en estas cuevas se ha identificado una gran variedad de minerales, algunos de ellos descritos por primera vez en ambientes subterráneos. En el presente trabajo se han sintetizado algunos de los resultados obtenidos por las investigaciones llevadas a cabo en estas cavidades durante la última década, desde los estudios relacionados con la génesis de los cristales gigantes (García-Ruiz, 2007; Forti, 2010; Garofalo et al., 2010; Gázquez et al., 2012a), hasta los más recientes que abordan los procesos que tienen lugar en estas cuevas como potenciales análogos marcianos (Boston et al., 2012; Gázquez et al., 2012a; 2013a). Finalmente, se hace un resumen sobre las medidas de conservación adoptadas en relación con los cristales gigantes y algunas consideraciones sobre el posible futuro de estas cavidades.*

### **Entorno geológico y génesis de los cristales gigantes**

*El Distrito minero de Naica está localizado en el sector sur-central del estado de Chihuahua, al sur de México (Fig. 2). La mina de Naica es desde la segunda mitad del siglo XIX una de las explotaciones mineras de plata y plomo más importantes del mundo (Stone, 1959). Su entrada se encuentra a 1.385 m s.n.m. en la vertiente sur de la Sierra de Naica, una estructura anticlinal constituida por una formación carbonática de edad Aptiense-Cenomaniense que se extiende en dirección noroeste-sudeste (Franco-Rubio, 1978). La actividad magmática intrusiva, desarrollada en el Terciario y responsable de la mineralización, se caracterizó por el emplazamiento de diques félsico. La intrusión se produjo a través de un sistema de fracturas orientado en dirección noroeste-sudeste (Stone, 1959) (Fig. 2). Las características del agua subterránea del acuífero de Naica estuvieron y están íntimamente relacionadas con este sistema de diques y cuerpos magmáticos subterráneos, los cuales condicionan tanto su temperatura como su composición, dándole carácter hidrotermal (Forti, 2010).*

*El origen de los espeleotemas de yeso subacuáticos de las cuevas de Naica está ligado a la oxidación de sulfuros metálicos presentes en el entorno de la mina, lo cual dio lugar a una solución acuosa enriquecida en sulfatos que, a temperaturas superiores a 58 °C, provocó la precipitación de anhidrita (García-Ruiz et al., 2007; Forti, 2010). Posteriormente, y debido al progresivo enfriamiento del sistema, se produjo la disolución de la anhidrita, de forma que la solución quedaría ligeramente sobresaturada en yeso. A 58 °C la solubilidad del yeso y la de la anhidrita es similar (Forti, 2010). En consecuencia, los cristales de yeso de Naica se formaron ligeramente por debajo de esta temperatura, en un proceso muy lento condicionado por el equilibrio extremadamente estable entre la tasa de disolución de la anhidrita, que alimentaba el sistema con  $\text{SO}_4^{2-}$  y  $\text{Ca}^{2+}$  y la de cristalización de yeso, que consumía  $\text{SO}_4^{2-}$  y  $\text{Ca}^{2+}$  retirándolo de la solución y activando así la disolución de anhidrita (García-Ruiz et al., 2007) (Fig. 4). Este mecanismo se extendió durante más de un millón de años, como han revelado estudios experimentales en laboratorio (Van Driessche et al., 2011) y en la propia mina (Forti y Lo Mastro, 2008) (Fig. 5), así como las dataciones radiométricas de los grandes cristales (Sanna et al., 2010).*

### **Estudios mineralógicos, paleoambientales y microclimáticos**

*Los estudios mineralógicos en las cuevas de la mina de Naica han revelado la existencia de hasta 40 minerales distintos, 10 de los cuales han sido detectados por primera vez en un ambiente subterráneo (Forti et al., 2009) (Tabla 1). Además de las investigaciones relacionadas con el origen de los cristales gigantes, en estas cuevas se han estudiado otros espeleotemas peculiares como las “velas” de la Cueva de las Velas, cuyo origen está relacionado con procesos de evaporación y capilaridad (Bernabei et al., 2007) y las “espadas” de la Cueva de las Espadas, que han revelado oscilaciones del nivel freático en torno al nivel -120 m de la mina durante los últimos 60 ka (Gázquez et al., 2012a; 2013a) (Fig. 6). Los análisis isotópicos del yeso y*

los carbonatos precipitado en esta cavidad han permitido conocer variaciones en la composición y la temperatura del acuífero de Naica, así como las oscilaciones climáticas ocurridas durante el periodo en el que precipitaron (Gázquez et al., 2013a, b).

Otra interesante línea de investigación ha estado centrada en el estudio de las variables microclimáticas en la Cueva de los Cristales. Esta monitorización permitió detectar una disminución gradual de la temperatura del aire en esta cavidad desde el momento en el cual fue descubierta, como consecuencia de la falta de control sobre la apertura de la puerta que conecta la gran sala que alberga los cristales con las galerías vecinas (Fig. 7). Este hecho dio lugar a que se desencadenaran procesos de condensación sobre los cristales que han derivado en problemas de disolución y corrosión. A partir de 2007, se estableció un control exhaustivo sobre esta puerta, lo que ha permitido que la temperatura de la cavidad haya aumentado gradualmente hasta la actualidad (Badino, 2009).

### **La conservación de los grandes cristales**

A priori, se podría pensar que los cambios ambientales provocados por el descenso brusco del nivel freático en el acuífero de Naica (Fig. 8) representan la principal amenaza para la conservación de los grandes cristales tal y como los conocemos en la actualidad, principalmente debido a los procesos de condensación y disolución del yeso (Fig. 9). Sin embargo, el principal riesgo al que están sometidas las cuevas al nivel -290 m de la mina de Naica es el restablecimiento de las condiciones freáticas que se producirán en pocos años, cuando la actividad minera deje de ser rentable y cese la extracción de agua necesaria para mantener el nivel del agua por debajo del frente minero, que en la actualidad se encuentra en torno a 900 m de profundidad (Fig. 8). El coste económico que supone la extracción de 1 m<sup>3</sup>/s de agua de esta profundidad es tal, que mantener el nivel freático en su posición actual será inviable en el momento en el que cese la extracción de mineral. En consecuencia, en pocos años el nivel del acuífero volverá a su cota natural, en torno a 120 m de profundidad, coincidiendo con la parte más profunda de la Cueva de las Espadas. De hecho, este es el nivel al que se encontraba a principios del siglo XX cuando comenzó la explotación de la mina de Naica (Gázquez et al., 2012a). En consecuencia, los grandes cristales quedarán inaccesibles y bajo el agua del acuífero en pocos años.

## **Introduction**

Mine caves are natural subterranean voids, which are discovered accidentally as a result of human activity, usually being crossed by a mining gallery (Forti, 2005). Frequently, mine caves host uncommon secondary minerals with chemical composition linked to the nature of the ore bodies which are the subject of the mining extraction (Onac and Forti, 2011).

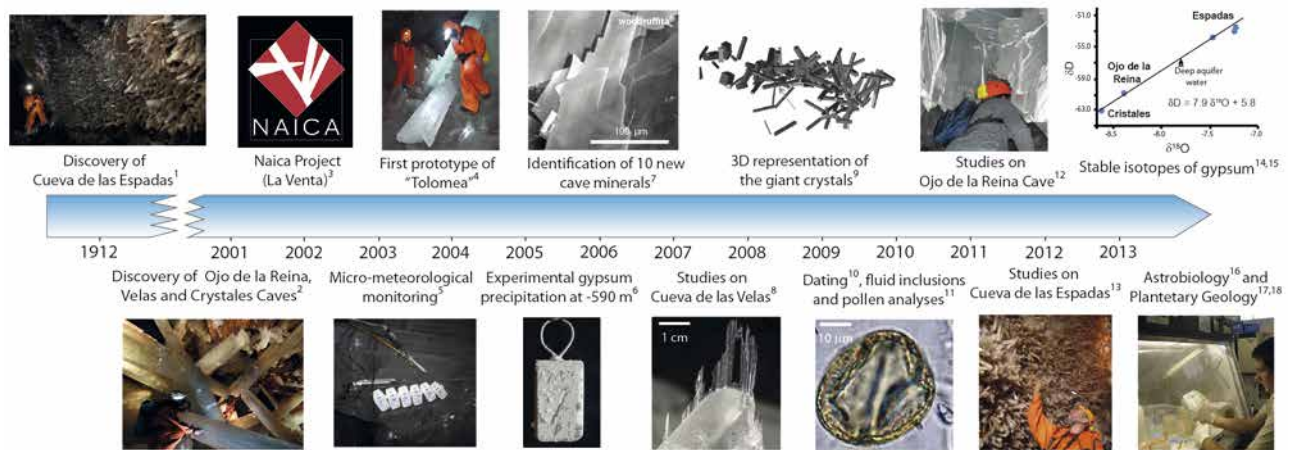
Among mines all over the world hosting natural caves, the mine of Naica is probably the most renowned due to the recent discovery of the largest gypsum crystals known to date (London, 2003). As the mining galleries reached the *Cueva de los Cristales* in 2000, the mine-workers found pure selenite crystals up to 11 metres long (Marín-Herrera et al., 2006; Badino et al., 2009), beating the size of the gypsum crystals of the giant geode of Pulpi (Almería, SE Spain; García-Guinea et al., 2002), discovered a few months before the *Cueva de los Cristales*.

In spite of the huge crystals having focused the attention of the media, research has been carried out not only in the *Cueva de los Cristales* in the Naica mine, but also in other natural cavities (Fig. 1). The *Ojo de la Reina* and *Cueva de las Velas* (at the -290 m level), as well as the *Cueva de las Espadas* (at the -120 m level),

host speleothems which have been investigated during recent years (Bernabei et al., 2007; Badino et al., 2011; Gázquez et al., 2012a; 2013a). Up to 40 different cave minerals have been found in the caves of Naica, 10 of which are new for cave environments (Forti et al., 2009). Nevertheless, the interest that has arisen around these concretions is not only because of their worth as speleological features, but also for other scientific fields such as Paleoclimatology, Astrobiology and Planetary Geology which have taken advantage of these speleothems, as will be discussed in the current paper.

In addition to studies addressing the mineralogy and genesis of speleothems, the caves of Naica have been used for microclimatological studies, in relation to the extreme environmental conditions that take place in the *Cueva de los Cristales*, where the temperature is around 45 °C and humidity over 90 % (Badino, 2007). Due to such especial characteristics, survey and investigation in these caves have required of the development of suits and breathing systems specifically designed for safe working conditions in extreme environments (Badino and Casagrande, 2007; Forti and Sanna, 2010).

The timeline of the exploration in the Naica Mine is also described in this article. We summarize the



**Figure 1:** Timeline showing some relevant milestones in research on the Naica caves. Some bibliographic references about these landmarks have been annotated: 1. Degoutin (1912); 2. London (2003); 3. Badino *et al.*, (2002); 4. Badino and Casagrande (2007); 5. Badino (2007); 6. Forti and Lo Mastro, (2008); 7. Forti *et al.*, (2007); 8. Bernabei *et al.*, (2007); 9. Badino *et al.*, (2009); 10. Sanna *et al.*, (2010); 11. Garofalo *et al.*, (2010); 12. Badino *et al.*, (2011); 13. Gázquez *et al.*, (2012a); 14. Gázquez *et al.*, (2012a); 15. Gázquez *et al.*, (2013a, b); 16. Boston *et al.*, (2012a); 17. Gázquez *et al.*, (2012c); Gázquez *et al.*, (2013b).

**Figura 1.** Línea temporal mostrando los hitos más relevantes derivados de las investigaciones en las cuevas de Naica. Se hace referencia a algunas reseñas bibliográficas más significativa al respecto: 1. Degoutin (1912); 2. London (2003); 3. Badino *et al.*, (2002); 4. Badino and Casagrande (2007); 5. Badino (2007); 6. Forti and Lo Mastro, 2008; 7. Forti *et al.*, (2007); 8. Bernabei *et al.*, (2007); 9. Badino *et al.*, (2009); 10. Sanna *et al.*, (2010); 11. Garofalo *et al.*, (2010); 12. Badino *et al.*, (2011); 13. Gázquez *et al.*, (2012a); 14. Gázquez *et al.*, (2012a); 15. Gázquez *et al.*, (2013a, b); 16. Boston *et al.*, (2012a); 17. Gázquez *et al.*, (2012c); Gázquez *et al.*, (2013b).

research carried out in the caves of the Naica Mine over the last decade, coinciding with the X anniversary of the beginning of the survey and the investigation in these unique cavities.

### Geological setting

The Naica Mine is located in the state of Chihuahua (Northern Mexico). The mine, in activity since the second half of the 19<sup>th</sup> century, is currently one of the most important of silver mines in the world. Mining extraction is centered in the Zn-Pb ore deposits enriched in silver. Every year a million tons of rock is extracted, obtaining 170 tons of silver and about 50,000 tons of lead (Giulivo *et al.*, 2007).

The current climate of the Naica region is typical of the Chihuahua desert with temperatures higher than 35-50 °C in summer, but slightly colder than in the neighbouring deserts of Sonora and Mojave. Annual precipitation is less than 250 mm, with most of the rainfall occurring in the monsoon season during late summer (Hoy and Gross, 1982).

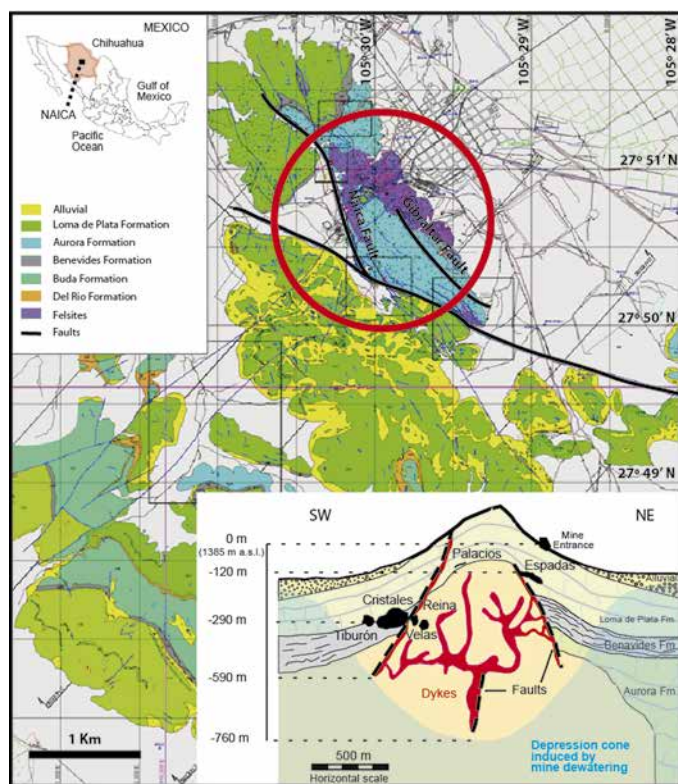
The entrance to the mine lies at 1,385 m a.s.l. on the southern face of the Sierra de Naica, an anticline structure consisting of carbonate rocks of Albian-Cenomanian age, which extends northeast to southwest. The stratigraphy comprises limestone and

dolostone interbedded clays and silts (Franco-Rubio, 1978). The area is characterised by a series of parallel structural ridges NW-SE oriented and over-thrusted toward the NE (Giulivo *et al.*, 2007) (Fig. 2).

Intrusive magmatic activity during the Tertiary is evidenced by felsic dikes emplaced in the carbonate series (Alva-Valdivia *et al.*, 2003), which are responsible for the mineralization in the mine. This part of the North American subcontinent was originally thought to be characterized by felsic dykes some 26.2-25.9 Ma old occurring within the carbonate sequences (Megaw *et al.*, 1988), although recently other authors date the dikes to 30.2 Myr BP (Alva-Valdivia *et al.*, 2003).

The contact between the groundwater and these igneous bodies created a hydrothermal system containing brines, which flowed along the lines of weakness, following the alignment of the dikes and faults (Ruiz *et al.*, 1985). In such a hypogenic system, the brines interacted with felsic materials and limestone, giving rise to new minerals (Megaw *et al.*, 1988). The development of the natural cavities in the Sierra de Naica Mountain is closely related to the main faults in this system, the Naica Fault and the Montaña Fault (Fig. 2) (Forti, 2010).

The gradual cooling of the aquifer water resulted in precipitation of low-temperature hydrothermal minerals. The mineral paragenesis comprises pyrite,



**Figure 2:** Location and geological setting of the Naica Mine (Chihuahua, Northern Mexico). The cross section of the Sierra de Naica Mountain shows the location of the main caves in the Naica mine, at the -290 m level (*Ojo de la Reina*, *Cueva de las Velas*, *Cueva de los Cristales* and the *Tiburón* Cave) and at -120 m deep (*Cueva de las Espadas*). The *Palacios* Cave, recently discovered at the -90 m level (Beverly and Forti, 2010), has also been represented.

**Figura 2.** Localización y entorno geológico de la Mina de Naica (Chihuahua, Norte de México). El corte geológico de la Sierra de Naica muestra la ubicación de las principales cuevas, al nivel -290 m (*Ojo de la Reina*, *Cueva de las Velas*, *Cueva de los Cristales* y *Cueva del Tiburón*) y a -120 m de profundidad (*Cueva de las Espadas*). También se ha representado la *Cueva de los Palacios*, descubierta recientemente al nivel -90 m (Beverly and Forti, 2010).

pyrrhotite, sphalerite, galena and chalcopyrite, all of which are formed from the hypersaline brines at high temperatures, in accordance with published data on fluid inclusions (Erwood, et al. 1979). During colder stages, precipitation of minerals, such as quartz, calcite, aragonite, anhydrite, and eventually gypsum, took place (Erwood et al., 1979; Forti, 2010).

### Discovery and survey of the Naica caves

In 1910, a group of mine-worker discovered the *Cueva de las Espadas* at a depth of 120 m, the first natural cavity intercepted by the galleries of the Naica Mine (Degoutin, 1912; Foshag, 1927). This cave is 80 m long

and its vertical development is 15 m. Its entrance is bounded by a sub-vertical fracture connected to the *Montaña Fault* and, at the time of the discovery, the cave mouth was completely covered by selenite gypsum crystals, some of them up 2 m long (Degoutin, 1912, Rickwood, 981).

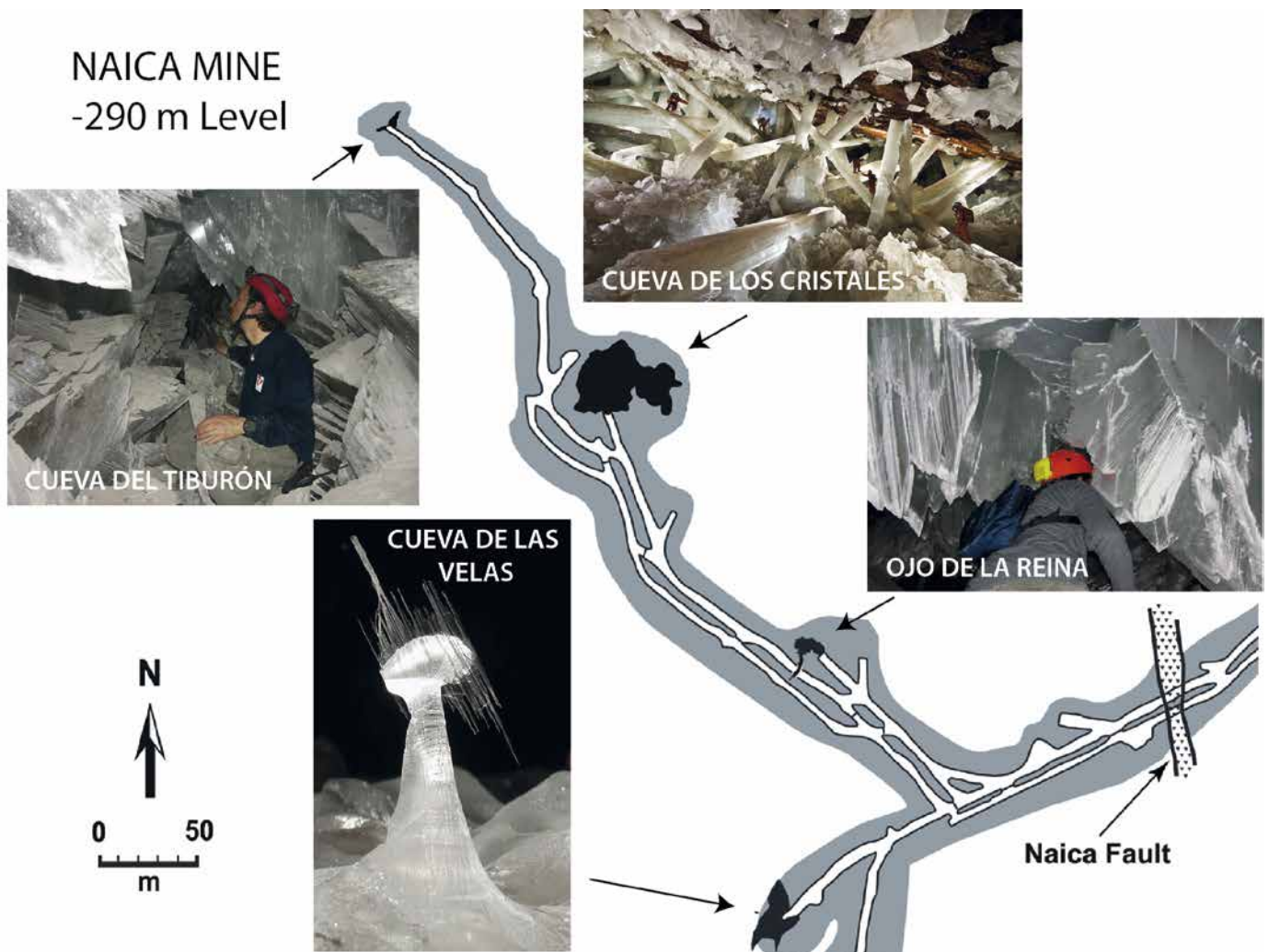
It was not until 2000 when the second natural cave was discovered in Naica. The *Ojo de la Reina* Cave was found in April 2000 by the brothers Eloy and Francisco Javier Delgado during an excavation at the -300 m level (De Vivo, 2007). Up to then, this mine level was immersed in the thermal aquifer of Naica; however, pumping of water for the mine dewatering enabled the miners to reach the cave. The *Ojo de la Reina* Cave consists of a narrow sub-vertical fracture parallel to the Naica fault, and it is totally filled with giant prismatic selenite crystals (Badino et al., 2011).

A few days later, the miners discovered the *Cueva de los Cristales*, hosting the largest gypsum crystals known to date. During these first immersions, the survival time did not exceed a few minutes due to the extreme conditions (almost 50 °C and 100 % humidity) because of the lack of suitable equipment (Badino and Casagrande, 2007). In January 2001, a first visit was carried out by a group of five people: geologists, engineers and one speleologist, guided by a mine-worker. Later, in May 2001, a group comprising five members of La Venta Exploring Team, an international non-profit association dedicated to developing multidisciplinary research projects all over the world, visited the Naica caves in order to take some photos and videos (De Vivo, 2007). The Venta Team accomplished a second visit to Naica in October 2002, when the first environmental measurements were carried out (47.38 °C and almost 100% humidity; Badino, 2007).

Because of limitations derived from such hostile environmental conditions, it was necessary to develop special suits and breathing systems for visiting this cave for more than ten minutes without risks for health. The suit prototype was named "Tolomea", whereas the cooling breathing system was baptized as "Sinusit" (Badino and Casagrande, 2007). This equipment allows the researchers to stay in such an extreme environment for over 60 min. The effect of heating on living organisms was not well known at that moment, so to avoid any possible risk the main physiological parameters (temperature, blood pressure, pulsations etc...) of any explorer were taken by spot measurements and/or continuous recording (Giovine, 2007; Giovine et al., 2009).

Several survey campaigns have been carried out in the Naica Mine during the first decade from the discovery of the *Cueva de los Cristales*. Remarkably,





**Figure 3:** Main caves at the -290 m level. Topography courtesy of the La Venta Team. Photos: the La Venta Team and Speleoresearch & Films.  
**Figura 3.** Cavidades principales al nivel -290 m. Topografía cortesía de La Venta Team. Fotos: La Venta Team and Speleoresearch & Films.

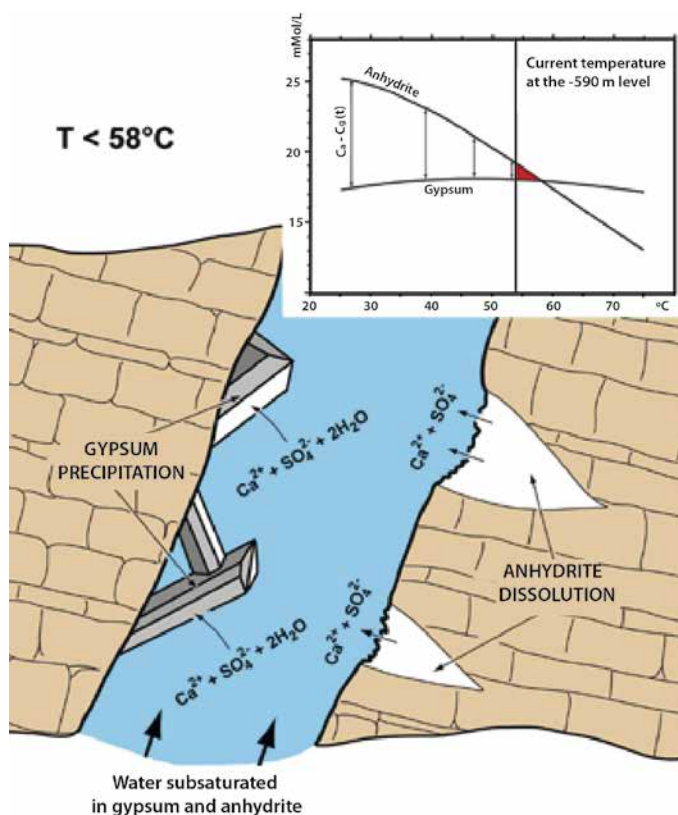
the La Venta Exploring Team and the Speleoresearch & Films company developed exhaustive documentation work comprising a documentary and a several shooting sessions producing a spectacular array of photos (Bernabei, 2007), some of them used to illustrate the current paper (Fig. 3). Besides, in 2007 a 3D topography of the *Cueva de las Espadas* and the *Cueva de los Cristales* was carried out by the company Virtualgeo by means of laser scanning technology (Tedeschi, 2007; Canevese *et al.*, 2009).

Topographic work was carried out between 2006 and 2007. The *Cueva de las Espadas*, *Cueva de los Cristales*, *Cueva de las Velas* and *Ojo de la Reina* Cave were mapped, as well as the nearby mine galleries (Badino *et al.*, 2009). In addition to the cave contours and profiles, up to 162 giant crystals were measured and geolocalized in the *Cueva de los Cristales* (Badino

*et al.*, 2009). This study revealed that the length of the crystal set describes a normal distribution, with the mode being around 4-6 meters. A preferred orientation in two directions has been also observed (290° and 320° N) (Badino *et al.*, 2009).

#### Research on the origin of the giant crystals

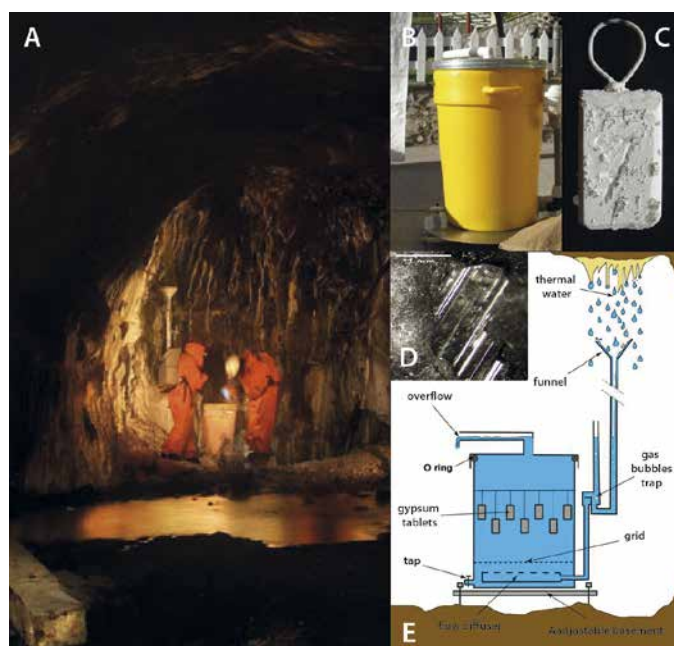
Several investigations have addressed the origin of the giant crystals of Naica. Research on stable isotopes, trace elements, fluid inclusions, and dating have enabled the establishment of a model in which the dissolution of anhydrite at temperatures around 58 °C gave rise to gypsum precipitation in the form of giant selenite crystals (García-Ruiz *et al.*, 2007; Forti, 2010).



**Figure 4:** Precipitation of selenite crystals in the Naica Mine. This mechanism is linked to the equilibrium between dissolution of anhydrite and gypsum precipitation at 58 °C, where the solubility of these minerals are almost the same (modified from Forti, 2010).

**Figura 4.** Precipitación de cristales de selenita en la Mina de Naica. Este mecanismo está ligado al equilibrio de disolución de anhidrita y precipitación de yeso a 58 °C, temperatura a la cual coincide la solubilidad de ambos minerales (modificado de Forti, 2010).

Before gypsum precipitation, oxidation of metal sulphides at high temperature enriched the groundwater in sulphates and led to the precipitation of anhydrite. Later, gradual cooling of the system caused dissolution of anhydrite, slightly supersaturating the water in gypsum below 58 °C (García-Ruiz *et al.*, 2007; Garofalo *et al.*, 2010). At 58 °C, the theoretical solubility of gypsum and anhydrite are the same, whilst below this temperature gypsum is the stable phase (Hardie, 1967) (Fig. 4). Studies on thermometry of fluid inclusions have revealed that precipitation of gypsum at the -290 m level occurred at around 55 °C (García-Ruiz *et al.*, 2007; Garofalo *et al.*, 2010), roughly coinciding with the theoretical value for the gypsum-anhydrite equilibrium. Besides, the similar isotopic signature ( $\delta^{34}\text{S}$  and  $\delta^{18}\text{O}$ ) found in gypsum, the widespread anhydrite in the mine and in the dissolved sulphate in the mine water confirmed this hypothesis (García-Ruiz *et al.*, 2007).



**Figure 5:** Gypsum precipitation experiments at the -590 m level (temperature over 51 °C and relative humidity of 100 %): A. Experimental laboratory at -590 m deep (Photo: La Venta Team and Speleoresearch & Films); B. Vessel in which the experiments were performed (Forti and Lo Mastro, 2007); C. Gypsum tablet covered with gypsum precipitates after 3.5 years (Sanna *et al.*, 2011); D. Selenite crystals precipitated on the surface of a gypsum tablet during the experiment (Forti and Lo Mastro, 2007); E. Sketch of the device placed at the -590 m level for the gypsum precipitation experiments (modified from Forti and Lo Mastro, 2008).

**Figura 5.** Experimentos de precipitación de yeso a -590 m de profundidad (temperatura en torno a 51 °C y humedad relativa de 100 %): A. Laboratorio experimental a -590 m de profundidad (Foto: la Venta Team y Speleoresearch & Films); B. Recipiente en el que se llevaron a cabo los experimentos (Forti y Lo Mastro, 2007); C. Tabletas de yeso cubiertas por concreciones yesíferas después de 3.5 años (Sanna *et al.*, 2011); D. Cristales de selenita precipitados sobre la superficie de las tabletas durante el experimento (Forti and Lo Mastro, 2007); E. Esquema del dispositivo colocado a -590 m para los experimentos de precipitación de yeso (modificado de Forti y Lo Mastro, 2008).

Garofalo *et al.* (2010) investigated fluid inclusions in speleothems from the *Cueva de los Cristales* and the *Ojo de la Reina* Cave, obtaining similar homogenization temperatures, mainly in the range between 50 – 58 °C. The fluid inclusions of the crystals from the *Cueva de las Espadas* (-120 m level) also produced homogenization temperatures in this narrow range, evidencing that the precipitation mechanisms at these two mine levels was analogue.

The incredible size of the selenite crystals in the Naica caves is attributable to the extremely low rates of nucleation and precipitation, which meant that the crystals grew very slowly. In fact, Forti and Lo



Mastro (2008) studied the current rate of hydrothermal gypsum precipitation in the Naica Mine. In 2006, these authors placed a vessel at the -590 m level in a hot location where thermal water with a temperature of more than 51 °C is still dripping out from the mine wall rock. Inside the vessel, 11 bars of prismatic polycrystalline gypsum were placed, suspended to act as a support for crystallization, in the absence of evaporation and constantly renewing the solution (Fig. 5). The results after two years revealed that the current gypsum precipitation rate is around 42 mm/ka. Most recently, Sanna *et al.* (2011) compared this data with growth rates estimated from U-Th dating of a giant crystal of the *Cueva de los Cristales*. They also established that these speleothems experienced an extremely slow growth ranging between 0.35 and 1.12 mm/ka, at least over the past 200 ka (Sanna *et al.*, 2010). These data are in total agreement with those obtained by Van Driesschea *et al.*, (2011) (0.5 mm/ka at 55 °C) from experimental precipitation of gypsum from the current water of the Naica aquifer. Therefore, it can be postulated that the giant crystals of Naica grew slowly, with the slowest growth rate known to date for a mineral (Van Driesschea *et al.*, 2011).

Another hot issue on the origin of the giant crystal has been the origin of the solution producing gypsum precipitation in the caves of Naica. Recent studies on strontium isotopes ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) in the Naica speleothems suggest mixing of thermal groundwater and fresh meteoric water during their precipitation.

Furthermore, the differences observed between the speleothems of the *Cueva de las Espadas* (higher  $^{87}\text{Sr}/^{86}\text{Sr}$ ) and the *Cueva de los Cristales* (lower  $^{87}\text{Sr}/^{86}\text{Sr}$ ) indicate greater contribution of the thermal reservoir of the Naica aquifer in the *Cueva de los Cristales* than in the *Cueva de las Espadas*, 170 metres shallower, which was more influenced by water of meteoric origin (Gázquez *et al.*, 2012b, d; 2013a). In addition, a recent work about stable isotopes of gypsum hydration water ( $\delta\text{D}$  and  $\delta^{18}\text{O}$ ) in the speleothems of Naica has enabled us to infer the isotopic composition of the original water from which gypsum precipitated in the Naica caves (Gázquez *et al.*, 2013a, b). The published values for  $\delta\text{D}$  and  $\delta^{18}\text{O}$  all describe a line that is close to the current meteoric water line for the Naica region. In addition, the isotopic composition of the current aquifer water fits this line. Consequently, it was concluded that the huge gypsum speleothems of the Naica caves precipitated from water of meteoric origin that changed in temperature and chemical composition along its flow path through the Naica aquifer.

### Mineralogical studies

The caves of the Naica Mine surprised the scientific community not only because of the giant crystals but also due to their mineralogical worth. Mineralogical analyses carried out by Forti *et al.*, (2009) revealed a completely unexpected mineralogical richness for



**Figure 6:** Some peculiar speleothems in the caves of Naica. A. “Sails” in the *Cueva de las Velas* generated by capillarity and evaporation (Bernabei *et al.*, 2007); B. Efflorescences composed of an admixture of Mg/Na soluble minerals (Badino *et al.*, 2011); C. *Espada* speleothems of the *Cueva de las Espadas*, comprising a core of selenite covered with layer of gypsum and aragonite (Gázquez *et al.*, 2012a) (Photos: the La Venta Team and S&F).

**Figura 6.** Algunos espeleotemas peculiares de las cuevas de Naica. A. “Velas” en la *Cueva de las Velas* generadas por procesos de capilaridad y evaporación (Bernabei *et al.*, 2007); B. Eflorescencias compuestas por una mezcla de sales solubles de Mg y Na (Badino *et al.*, 2011); C. “Espadas” en la *Cueva de las Espadas*, compuestos por un núcleo de selenita cubierto por capas de yeso y aragonito (Gázquez *et al.*, 2012a) (Photo: La Venta Team and S&F).



an environment apparently completely filled by gypsum: 40 minerals have been described, 10 of which are new for the cave environment (Table 1). These authors point out that minerals in the Naica caves developed in three different environments (deep phreatic, epiphreatic and aerated) (Forti *et al.*, 2009).

In particular, the *Cueva de las Velas* contains the majority of the cave minerals found in Naica (up to 17 minerals, 5 of which are new for cave environments) (Forti *et al.*, 2007). Moreover, this cave hosts a new variety of speleothems, called the "sails" (Figs. 3 and 6A), resulting from complex mechanisms of capillarity and evaporation (Bernabei *et al.*, 2007).

Recent studies on the genesis and evolution of the *Ojo de la Reina* Cave have addressed the origin of up to 6 very soluble minerals, most of them sulphates, on the large selenite crystal that cover the walls of this cave (Badino *et al.*, 2011). These authors established a model based on the opening of fluid inclusions embedded along gypsum planes. Dripping water rich in Mg and Na evaporated when it reached the cave atmosphere, giving rise to Na/Mg-sulphates and halite (Fig. 6B).

On the other hand, in the *Cueva de las Espadas* complex, speleothems comprising a high-purity selenite core covered by several layers of calcite, aragonite and gypsum have been found on the walls of the lower part of the cave. Recent studies have revealed that the *espada* speleothems recorded the water level fluctuations at around -120 m depth over the past 60 ka (Gázquez *et al.*, 2012a). The selenite core and gypsum layers formed under biphasic (water-rock) conditions when the cave was submerged under hydrothermal water. Meanwhile, the aragonite precipitation required triphasic (air-water-rock) conditions and occurred when the water table intercepted the cave, allowing the CO<sub>2</sub> exchange necessary for carbonate precipitation (Forti, 2007, 2010; Gázquez *et al.*, 2012a). An investigation on the morphological characteristics of these unusual speleothems was carried out by Calaforra *et al.* (2011), noting a gradation of the size of the *espada* speleothems from the bottom to the top of the lower part of the cave. These authors suggest that the differences in size of the *espadas* at different heights responds to a mechanism of higher evaporation on the phreatic surface around the level of the *Cueva de las Espadas* during the genesis of the *espadas*. The processes induced highest supersaturation at the air-water boundary, while progressively decreasing towards the bottom of the lake. Consequently, the biggest crystals developed on the bottom of the lake, while the size of the crystals progressively decreased towards the ceiling.

Environment	Mineral	Chemical formula
Ae - Ep	Aragonite	CaCO <sub>3</sub>
Ae	Anglesite	PbSO <sub>4</sub>
Ae	Anhydrite	CaSO <sub>4</sub>
Ae	Antlerite*	Cu <sub>3</sub> (SO <sub>4</sub> )(OH) <sub>4</sub>
Ae-Ep	Apatite	Ca <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> (C,F,OH,Cl,O)
Ae	Azurite	Cu <sub>3</sub> (CO <sub>3</sub> ) <sub>2</sub> (OH) <sub>2</sub>
Ae	Basanite	CaSO <sub>4</sub> ·1/2H <sub>2</sub> O
Ae	Blödite	Na <sub>2</sub> Mg(SO <sub>4</sub> ) <sub>2</sub> ·4H <sub>2</sub> O
Ae	Calcantite	CuSO <sub>4</sub> ·5H <sub>2</sub> O
Ae - Ep - Ph	Calcite	CaCO <sub>3</sub>
Ae - Ep - Ph	Celestine	SrSO <sub>4</sub>
Ph	Coronadite	Pb(Mn <sup>4+</sup> ,Mn <sup>2+</sup> ) <sub>8</sub> O <sub>16</sub>
Ae	Cu-pentahydrate*	Mg <sub>0.45</sub> Cu <sub>0.55</sub> (SO <sub>4</sub> ) <sub>2</sub> ·5H <sub>2</sub> O
Ae- Ep - Ph	Dolomite	CaMg(CO <sub>3</sub> ) <sub>2</sub>
Ae	Epsomite	Mg SO <sub>4</sub> ·7H <sub>2</sub> O
Ae	Fluorite	CaF <sub>2</sub>
Ae- Ep	Fraipontite	(Zn,Al) <sub>3</sub> (Si,Al) <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub>
Ae - Ph	Goethite	a-Fe <sup>3+</sup> O(OH)
Ae - Ep - Ph	Gypsum	CaSO <sub>4</sub> ·2H <sub>2</sub> O
Ae	Guanine	C <sub>5</sub> H <sub>3</sub> (NH <sub>2</sub> ) <sub>4</sub> N <sub>4</sub> O
Ae	Halite	NaCl
Ph	Hectorite*	Mg <sub>3</sub> Si <sub>4</sub> O <sub>10</sub> (OH) <sub>2</sub>
Ae	Hematite	-
Ae	Hexahydrate	Mg SO <sub>4</sub> ·6H <sub>2</sub> O
Ae	Jarosite	K <sub>2</sub> Fe <sup>3+</sup> <sub>6</sub> (SO <sub>4</sub> ) <sub>4</sub> (OH) <sub>12</sub>
Ae	Kieserite	MgSO <sub>4</sub> ·H <sub>2</sub> O
Ae	Magnetite	Fe <sub>3</sub> O <sub>4</sub>
Ae	Malaquite	Cu <sub>2</sub> (CO <sub>3</sub> )(OH) <sub>2</sub>
Ae	Nordstrandite	Al(OH) <sub>3</sub>
Ph	Opal	SiO <sub>2</sub> ·nH <sub>2</sub> O
Ae	Orientite*	Ca <sub>2</sub> Mn <sup>2+</sup> Mn <sup>3+</sup> <sub>2</sub> Si <sub>3</sub> O <sub>10</sub> (OH) <sub>4</sub>
Ae	Pirolusite	MnO <sub>2</sub>
Ae	Plumojarosite*	PbFe <sup>3+</sup> <sub>6</sub> (SO <sub>4</sub> ) <sub>4</sub> (OH) <sub>12</sub>
Ae	Starkeyite*	MgSO <sub>4</sub> ·4H <sub>2</sub> O
Ae	Szmikite*	MnSO <sub>4</sub> ·H <sub>2</sub> O
Ae	Szmolnokita*	FeSO <sub>4</sub> ·H <sub>2</sub> O
Ae	Woodruffite*	ZnMn <sub>3</sub> O <sub>7</sub> ·2H <sub>2</sub> O
Ph	Quartz	SiO <sub>2</sub>
Ae	Rozenite	FeSO <sub>4</sub> ·4H <sub>2</sub> O

**Table 1:** Cave minerals found in the caves of the Naica Mine. Ae= Aerial; Ph= Phreatic; Ep= Epiphreatic. \* New cave mineral (after Forti *et al.*, 2009).

*Tabla 1. Minerales encontrados en las cuevas de la Mina de Naica. Ae= Aéreo; Ph= Freático; Ep= Epifreático. \*Nuevos minerales de cueva para la ciencia (Forti et al., 2009).*

**Microclimate studies**

The first measurements of the environmental conditions in the *Cueva de los Cristales* were carried out in October 2002, producing 47.1 °C at the floor level and 47.4 °C at the 2 metre height (0.01 °C resolution), whereas humidity was almost 100% (Badino and Forti, 2005; Badino, 2007; Badino, 2009). In January 2006 the measurements were repeated, obtaining a temperature two degrees Celsius lower (45.5 °C) (Badino, 2007; Badino, 2009). Further measurements demonstrated that temperature in the *Cueva de los Cristales* decreased by 0.52 °C/year during the period between 2002 and 2007 due to a loss of heat by conduction towards the nearby mine galleries to the north-west, as well as by irradiation along the access corridor (Fig. 7) (Badino, 2007; Badino 2009). This fact demonstrates that the cave cooled until 2007 as a result of the artificial entrance generated when the mine galleries crossed it, suggesting mining activities have had a significant effect on the cave microclimate.

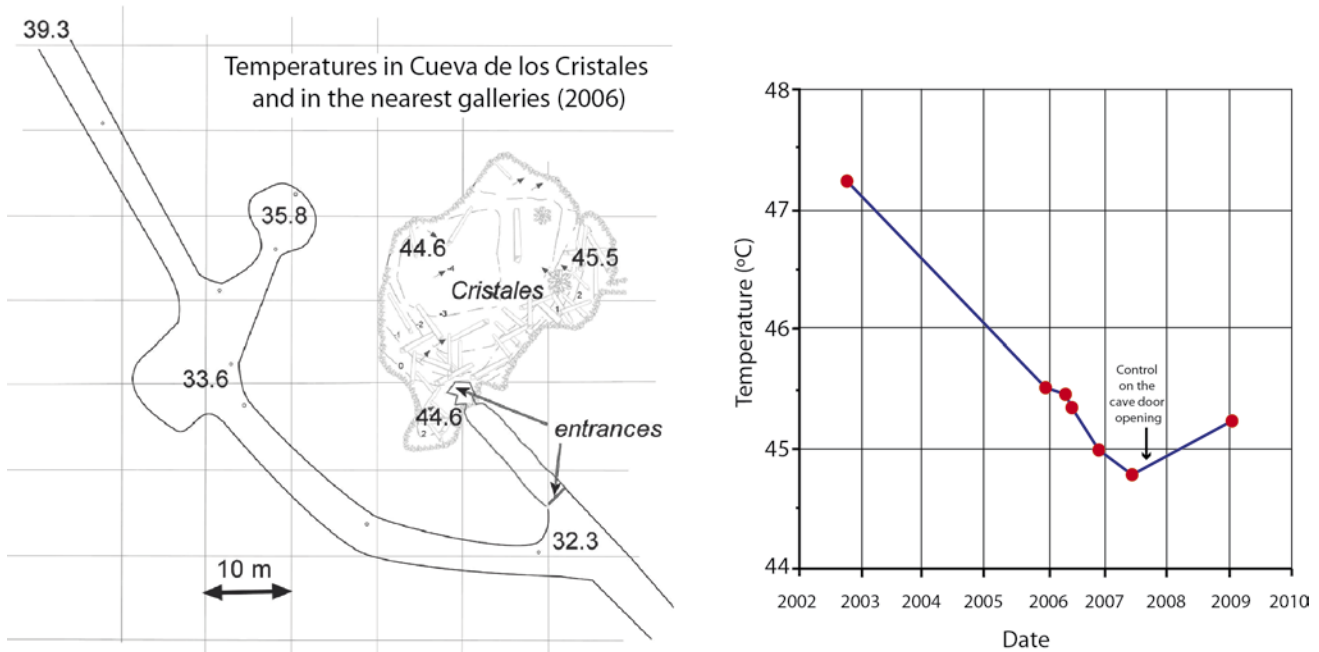
Monitoring of the environmental parameters revealed that the inner cave temperatures are not affected too much by the mining activities in the short term; however the hot air is forced into the entrance

corridor where the temperature is around 32 °C, causing a significant temperature increase and condensation on the walls of the cave entrance. Daily trends have been observed as a result of the opening of the doors (Badino, 2007).

At the end of 2007 the mine conduits surrounding the cave were closed to the airflow and their temperature quickly increased to approximately 40 °C. Air temperature increased due to a careful management of the opening of the internal door, which is now practically always closed, so that has almost stopped the temperature decrease of the *Cueva de los Cristales*. The temperature at the top (north-east) has become stable at around 45.5° C, whereas the temperature near the door, where there was a strong heat loss, increased by 0.7° C to 45.2° C in January 2009 (Fig. 7).

**Paleoenvironmental studies**

Speleothems have provided outstanding palaeoclimate records of continental environments all over the world (Fairchild *et al.*, 2006). The importance of speleothems is such that these deposits are currently considered an essential cornerstone of research



**Figure 7:** Air temperature in the *Cueva de los Cristales* and the surrounding mine galleries in 2006. The temperature of the cave decreased from the first measurements (2002) until 2007. From the end of 2007, the temperature has gradually increased due to the carefully controlled opening of the cave door (Badino *et al.*, 2009).

**Figure 7.** Temperatura del aire en la *Cueva de los Cristales* y las galerías adyacente en 2006. La temperatura de la cueva disminuyó desde las primeras medidas (2002) hasta 2007. Desde finales de 2007, la temperatura ha aumentado gradualmente gracias al cuidadoso control sobre la apertura de la puerta artificial que da acceso a la cueva (Badino *et al.*, 2009).

on palaeoclimate and present-day climate change (Lauritzen 2003).

In addition to research focused on carbonate speleothems and palaeoclimatology, the study of cave minerals has become more prominent over the past decade. In fact, several research studies have obtained palaeoenvironmental information from non-calcite cave minerals, such as gypsum (Gázquez *et al.*, 2011; Gázquez, 2012). Gypsum speleothems, in particular those of the Naica caves, have been used in several investigations as palaeoclimatic indicators because of the specific conditions required for their precipitation and the study of their geochemical composition (Garofalo *et al.*, 2010; Gázquez *et al.*, 2012a,b; 2013a).

This body of work is based on the U-Th dating obtained by Sanna *et al.*, (2010). These authors found that the innermost part of one of the largest crystals of the *Cueva de los Cristales* dates to  $169 \pm 101/-52$  ka, whilst a sample taken 4 cm far from the outer surface is  $34.5 \pm 0.8$  ka-old. In addition, the age of the gypsum crystals of the lower part of the *Ojo de la Reina* Cave was established in  $191 \pm 13$  ka. In contrast, the selenite core of the *espada* speleothems of the *Cueva de las Espadas* dates back to  $57 \pm 2$  ka, whereas the ages of the external aragonite layers were  $7.9 \pm 0.1$  ka and  $14.5 \pm 4$  ka.

Fluid inclusions studied carried out by Garofalo *et al.* (2010) suggest that the genesis of the gypsum speleothems in the caves of the Naica system was controlled by climatic forces. In fact, these authors identified pollen grains in fluid inclusions of a 35 kyr-old gypsum samples from a crystal of the *Cueva de los Cristales*. The characteristics of pollen grains found correspond to vegetation typical of a fresh-wet climatic period, radically different to the current arid climate of the Naica desert.

Furthermore, a genetic model based on water table fluctuations and mixture of fresh meteoric water and deep thermal water from the Naica aquifer has been established. This model justifies the salinity and composition differences in the fluid inclusion of the crystals formed at 290 m and 120 m deep, as a response to climatic variations (Fig. 8) (Garofalo *et al.*, 2010; Gázquez, 2012; Gázquez *et al.*, 2012a).

The most recent work has been focused on the stable isotopes analysis of gypsum (Gázquez, 2012; Gázquez *et al.*, 2013a, b). Investigations on isotopes of gypsum hydration water has revealed that  $\delta^{18}\text{O}$  of the Naica aquifer water ranged between  $-8.62$  and  $-7.23\text{‰}$ , whilst  $\delta\text{D}$  was between  $-63.04$  and  $-52.48\text{‰}$  over the past 200 kyr. The data are described by a line ( $\delta\text{D} = 7.97 \delta^{18}\text{O} + 5.81$ ) that is close to the current meteoric water line at the setting of Naica. The differences

observed between gypsum at  $-120$  m and  $-290$  m deep can be explained by selenite crystals forming under different climatic conditions. Changes in the main moisture source of precipitation (Pacific Ocean/Gulf of Mexico) affected the isotopic composition of the meteoric water in this area during the Quaternary (Gázquez, 2012; 2013a). More detailed investigations on the stable isotopes in the gypsum speleothems of Naica will enable the evolution of paleoclimate in the Naica setting over the past 1 Myr to be figured out.

### Implications for astrobiology and planetary geology

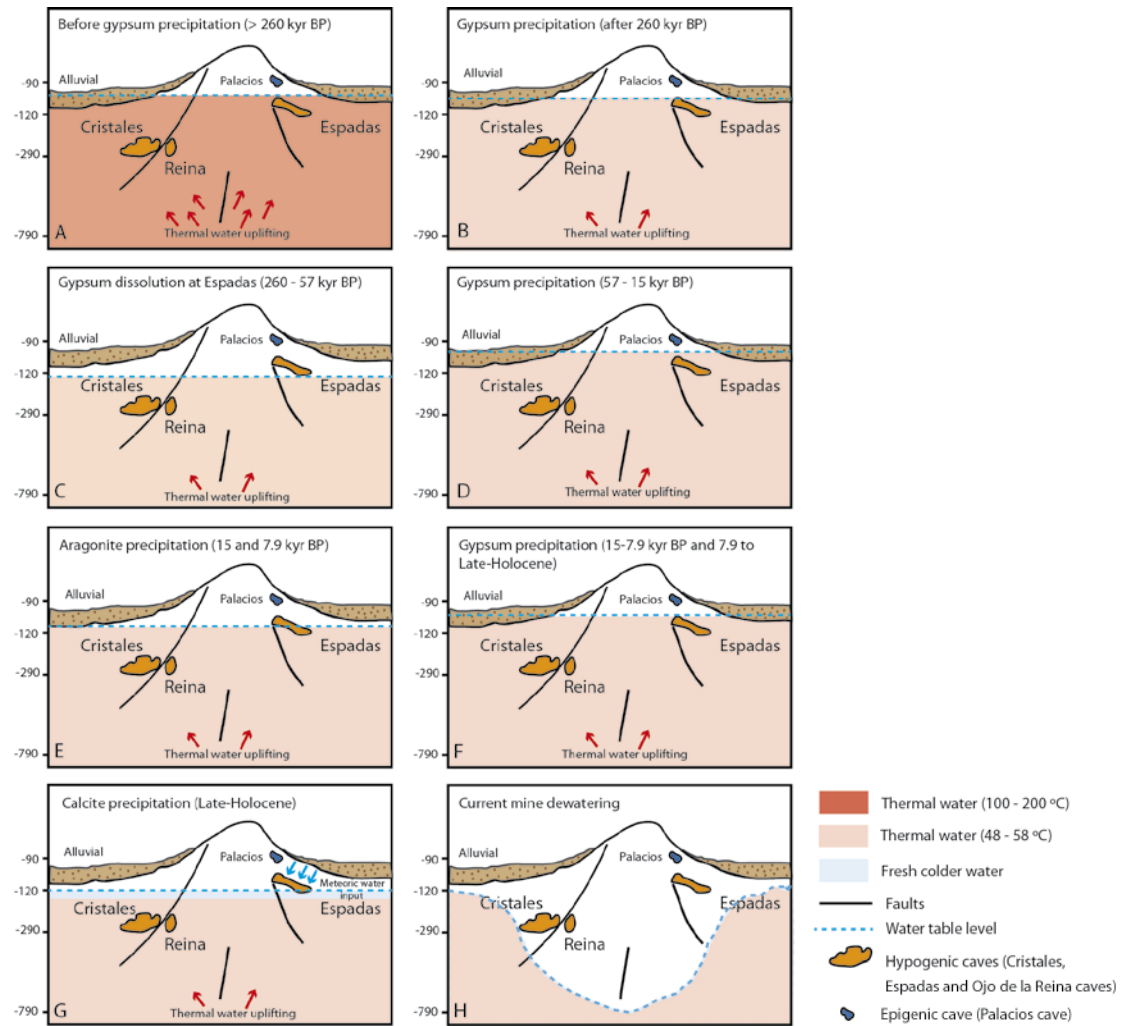
Terrestrial Analogue Sites (also called “Space Analogues”) are places on Earth with assumed past or present geological, environmental or biological conditions of a celestial body such as the Moon or Mars (Rull and Martínez-Frías, 2006). Caves have attracted great interest for Astrobiology and Planetary geology over recent years due to their particular environmental conditions, hosting diverse minerals and biological forms (Boston *et al.*, 2003).

In fact, there is growing evidence that subsoil and caves might be place for finding biological activity or biomarks on Mars (Boston *et al.*, 2003). Furthermore, caves (Baioni *et al.*, 2009; Cushing, 2012) and lava tubes (Cushing, 2012) have been recently detected on the surface of Mars, so the interest in caves and cave minerals here on Earth have exponentially increased. Ionizing radiations from the Sun, great daily temperature oscillations and the lack of liquid water are the main obstacles for life to exist on the surface of Mars (Boston *et al.*, 2003). Nevertheless, caves are protected from solar radiations, practically do not experiment daily temperature variations and are usually wet environments.

Ca-rich sulfates (probably gypsum) have been recently identified on the surface of Mars. Gypsiferous sands constitute dense dune fields in the Olympia Planum, around the Martian North Polar Cap (Massé *et al.*, 2011). Furthermore, in 2011 the Exploration Rover Opportunity found bright veins of a mineral, apparently gypsum that may be of hydrothermal origin. On the basis of this outstanding discovery, attention has been focused on the terrestrial gypsiferous formations. Recent studies have investigated gypsum crystals of Naica from a spectroscopic point of view by means of Raman and IR spectroscopy (Gázquez *et al.*, 2012c; 2013c). Due to its high-purity, the gypsum of Naica displays low fluorescence and thin-shaped Raman signals that also confirm its high crystallinity.

Taking into account that the ExoMars mission of the ESA, scheduled for launch in 2018 will be





**Figure 8:** Chronology and evolutionary stages of gypsum deposition within the Naica caves: A. Hydrothermal fluids uplifting at 100-120 °C along the three main regional faults at different levels inside the aquifer; B. The thermal water became supersaturated with respect to gypsum, and selenite nucleation took place very slowly in a phreatic environment at the -120 m level, where water first cooled down to the gypsum-anhydrite equilibrium temperature. During that period the water table kept in a narrow range between -90 m deep (the *Cueva de los Palacios*, where no evidence of hydrothermal gypsum occurs) and the -120 m level (the *Cueva de las Espadas*); C. Huge selenite speleothems also began growing within the *Cueva de los Cristales* and *Ojo de la Reina* Cave (at the -290 m level), whilst water table fluctuations in epiphreatic conditions produced gypsum corrosion phenomena at the level of the *Cueva de las Espadas* (-120 m); D. A new period of phreatic gypsum precipitation occurs in all caves; E. At the -120 level further oscillations in the water table produced two cycles of epiphreatic phase with aragonite layer deposition on submerged gypsum crystals at 15 ka and 7.9 ka, whilst inside the caves at -290 m level gypsum kept on precipitating; F. A new rise in the water table led to further gypsum crystallization in the *Cueva de las Espadas*. G. A short period of meteoric seepage was active in a vadose fast-cooling environment with deposition of a thin calcite cover; H. At the -290 level gypsum growth went on until a sudden change from deep phreatic to vadose conditions was caused by the depression cone associated with mine exploitation (modified from Sanna et al., 2011).

**Figura 8.** Cronología de las etapas de precipitación de yeso en las cuevas de Naica: A. Ascenso de fluidos hidrotermales (100-120 °C) a través de las tres fallas principales a diferentes niveles en el acuífero; B. El agua termal se saturó en yeso, y la nucleación de este mineral tuvo lugar con una tasa de precipitación extremadamente lenta en condiciones freáticas al nivel -120 m, donde el agua se enfrió más rápidamente hasta la temperatura a la cual la solubilidad del yeso y la anhidrita es similar. Durante este periodo el nivel freático osciló entre 90 m (*Cueva de los Palacios*, donde no aparece yeso selenítico) y el nivel -120 m (*Cueva de las Espadas*); C. Precipitación de los grandes cristales de la *Cueva de los Cristales* y *Ojo de la Reina* (-290 m) y corrosión en condiciones subaéreas de los cristales precipitados previamente en la *Cueva de las Espadas*; D. Nueva fase freática en todas las cavidades; E. Al nivel -120 m, nuevas oscilaciones del nivel freático produjeron ciclos de precipitación de yeso y aragonito entre 15 ka y 7.9 ka antes del presente, mientras que en el interior de la *Cueva de los Cristales* los grandes cristales siguieron precipitando; F. Una nueva subida del nivel freático produjo la precipitación de yeso en la *Cueva de las Espadas*; G. Un periodo breve de infiltración de agua meteórica a menor temperatura dio lugar a la precipitación de calcita en la *Cueva de las Espadas*; H. Al nivel -290, la precipitación del yeso continuó hasta la bajada abrupta del nivel freático debida a las labores mineras (modificado de Sanna et al., 2011).

equipped with a Raman spectrometer, investigation by Raman spectroscopy into minerals on Earth are essential for interpreting data coming from this further mission to Mars. On the basis of this evidence, gypsum speleothems from the Naica caves have been proposed to be included as reference materials in the mineral spectroscopy database for the Mars exploration (Gázquez *et al.*, 2012c; 2013c).

The relatively broad knowledge about the genesis of these huge selenite crystals acquired over the last decade can play an essential role for interpreting the origin of some Martian gypsum deposits, which suggest the presence of liquid water in the past. Data obtained from the Naica speleothems have an important astrobiological significance, since these cave minerals formed without the influence of solar radiation. The presence of spectroscopic signals linked to organic compounds and biomarkers in gypsum and Fe/Mn oxihydroxides, where the precipitation is usually mediated by microorganisms, will be an interesting issue to be studied in the future in relation to searching for current or ancient life on Mars.

The long-term persistence of microorganisms in geological materials is another relevant field in Astrobiology, particularly in cases in which life occurs in extreme environments. Boston *et al.* (2012a, b) performed DNA analysis and life cultures from the solution in fluid inclusions hosted within the gypsum crystals. They found microorganisms genetically close to other current organisms that have been identified from a variety of unusual and extreme chemical environments (Boston *et al.*, 2012a). These authors estimated that organisms recovered from inclusions may have been trapped within their crystalline time capsules from between 30-50 ka, depending on the position in which they were placed the inclusion in the crystals and the U-Th ages calculated by Sanna *et al.* (2010). Nevertheless, further analyses of fluid inclusions in the inner central part of the crystals might offer information on microorganisms living 1 Ma BP in the hydrothermal aquifer of Naica

### Preservation and use as a touristic resource

The caves of the Naica Mine have been subject to pressures of various kinds from the moment in which the cavities were crossed by the mining galleries. Spoliation has been a major threat for conservation of the giant crystals. Large gypsum crystals were extracted from *Cueva de las Espadas* by mine-workers and visitors who sold them to museums and mineral collectors. In fact, several large-size selenite crystals are currently exhibited in showcases at the British

Museum of London and the Smithsonian Museum of Washington. Regarding the *Cueva de los Cristales*, several attempts have been made to extract pieces of the giant crystals, as revealed by incisions and damage observed on their surfaces (Fig. 9A).

Nevertheless, collecting and pillaging are not the only threat for the speleothems of Naica. As mentioned above, the genesis of the giant gypsum crystals of Naica occurred underwater, in a very stable environment during a long span of time. Therefore, it is not surprising that the artificial dewatering of the mine dramatically affected the peculiar conditions in which gypsum precipitation occurs. It is estimated that gypsum precipitation stopped at a depth of 290 m around 1985, when the water table fell below the



**Figure 9:** Deterioration of the gypsum speleothems in the Naica caves. A. Saw marks on a gypsum crystal of the *Cueva de los Cristales*; B. Corrosion features due to condensation on the huge crystals; C. Condensation on a huge crystal; D. Dissolution-recrystallization of gypsum edges due to condensation; E. Evidence of spoliation of gypsum crystals in the *Cueva de los Cristales*; F and G. Mark on crystals due to sampling.

**Figura 9.** Degradación de los espeleotemas de yeso de las cuevas de Naica. A. Marcas de sierra en un cristal de yeso de la *Cueva de los Cristales*; B. Corrosión debida a procesos de condensación en un cristal gigante; C. Condensación sobre un cristal de yeso; D. Disolución-recristalización en las aristas de los cristales debido a la condensación; E. Evidencia dejadas por espolio de cristales en la *Cueva de los Cristales*; F y G. Marcas de muestreos en los cristales.

level of the *Cueva de los Cristales*. Such an abrupt shift from biphasic (water-rock) to triphasic (water-rock-air) conditions, gave rise sub-aerial processes occurring on the crystals surfaces, such as condensation and gypsum dissolution (Fig. 9B). The cave stopped being influenced by the hydrothermal water of the aquifer to then receive water from dripping. Obviously, the geochemical characteristics of dripping water are completely different from those of the phreatic solution. Incorporation of CO<sub>2</sub> into the cave atmosphere has led to carbonate precipitation on gypsum as observed in the *Cueva de los Cristales* and the *Ojo de la Reina* Cave (Badino *et al.*, 2011). Recrystallization, gypsum dissolution by condensing water and fluid inclusion opening have been also detected (Fig. 9D), mainly in the *Ojo de la Reina* Cave where Na-Mg sulphate crusts appear after the mine dewatering as a result of the cited mechanisms (Fig. 6B) (Badino *et al.*, 2011).

Temperature decreasing at the -290 m level was another consequence of the mine dewatering. As mentioned above, the temperature dropped by around 10 °C (from 55 to 45 °C) by 0.5 °C/year up to 2007. Temperature dropping triggered condensation on the crystals, so that at times the surfaces of the crystals display white patinas, tarnishing the selenite transparency (Fig. 9C). Fortunately, since late 2007, the temperature of the *Cueva de los Cristales* has progressively increased thanks to the carefully control of the door that isolates the cave from the colder mine galleries.

The impact of visitors, both scientific and touristic, on the cave's integrity has also been the subject of debate (Calaforra *et al.*, 2007). People can be rated as "cold objects" (at a temperature of around 37 °C) going into a hot and wet environment. Each "moving cold object" generates a cold aura around it, affecting the natural air movements in the cave and also the temperature of the surface of the crystal, so favoring condensation. Moreover, stepping on the crystals produces gypsum crushing by abrasion and breaking edges, which irreversibly destroys them (Fig. 9E).

As from 2008, visits into the *Cueva de los Cristales* have been limited to scientific purposes. Since then, the cavity has been closed with a steel door (not airtight) and more recently by a transparent veranda which protects the visitors from exposure to the hostile atmosphere. At the moment, around 2–3,000 people per year are permitted to visit the cave during weekends, but without opening the transparent door. It can be considered that tourists and non-specialist visitors are the major threat to the crystals, however scientific work can also produce severe damage in the Naica caves. Indiscriminate sampling and "over-sampling" represent a real threat for conservation of the

Naica caves (Fig. 9F and G) (Calaforra *et al.*, 2007). In our opinion, no speleothems should be taken from the cave walls and only gypsum fragments widespread in the caves should be collected. In the case of crystal sampling being needed, sites should be chosen that have a minimal visual impact. Preservation of this unique cave should be considered as mandatory for all the investigation carried out on the Naica caves.

### Final remarks

The extensive research conducted over the past decade has made the caves of Naica into the most studied cavity systems in the world. Investigations have addressed the genesis of the giant crystals, but also mineralogy, geochemistry and microclimatology. Nevertheless, these caves and their speleothems still represent a challenging mystery for the scientific community. How did environmental conditions remain unchanged over the past million years for gypsum precipitation in such a frail equilibrium? Are there more cavities in the Naica system hosting huge gypsum crystals? Why not in other sites around the world?

Meanwhile, new research lines arise around the larger gypsum crystals found to date, which have been recently proposed as paleoclimatic proxies and have started to be used in fields such as Astrobiology and Planetary Sciences. However, in spite of their indubitable scientific and aesthetic worth, the future of the Naica caves is uncertain. In addition to the human pressure to which the caves and their speleothems are subjected, the definitive cessation of the mining activity scheduled within the next 5 years represents the greatest threat for the preservation of these caves as we know them today. Currently, the maximum depth of the depression cone induced by the mine dewatering is placed below the -900 m level, thanks to pumping up to 1 m<sup>3</sup>/s. In the near future the Naica Mine will be considered as non-profitable, therefore pumping will be not necessary. As a result, the current induced groundwater level will quickly reach the 120 m depth level, where the natural phreatic level is. Unless the cessation of pumping is avoided, the caves of Naica will once again flooded by thermal water and hydrothermal gypsum will keep on precipitating for eternity.

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