

## UNDERSTANDING ZACATÓN: EXPLORATION AND INITIAL INTERPRETATION OF THE WORLDS DEEPEST KNOWN PHREATIC SINKHOLE AND RELATED KARST FEATURES SOUTHERN TAMAULIPAS, MEXICO

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A system of water-filled sinkholes (known as cenotes) exists in southern Tamaulipas, Mexico (Figure 1), and is the result of a unique combination of speleogenetic factors. This system is composed of 18 different karst features that are on or near a large cattle ranch known as Rancho La Azufrosa. Zacatón, the deepest cenote in this system has been measured to over 350 meters deep, (Figure 1) and is the site of the world-record SCUBA dive (284 meters) by Jim Bowden in 1994 (Gilliam, 1994). This makes it the deepest known water-filled pit that has been explored by humans in the world. No previous scientific studies of

this extreme karst system have taken place, and it has only been limited work within the past two years that theories relating to the speleogenesis have been formed. Microbial interaction seems likely to affect karstification processes, and significant travertine structures appear to have a direct influence on the hydraulic connectivity between the bodies of water. Years of future research are being planned to document the extent of karstification in this deep hydrothermal system and interpret the geological history that has developed such an impressive example of hypogenetic karst.

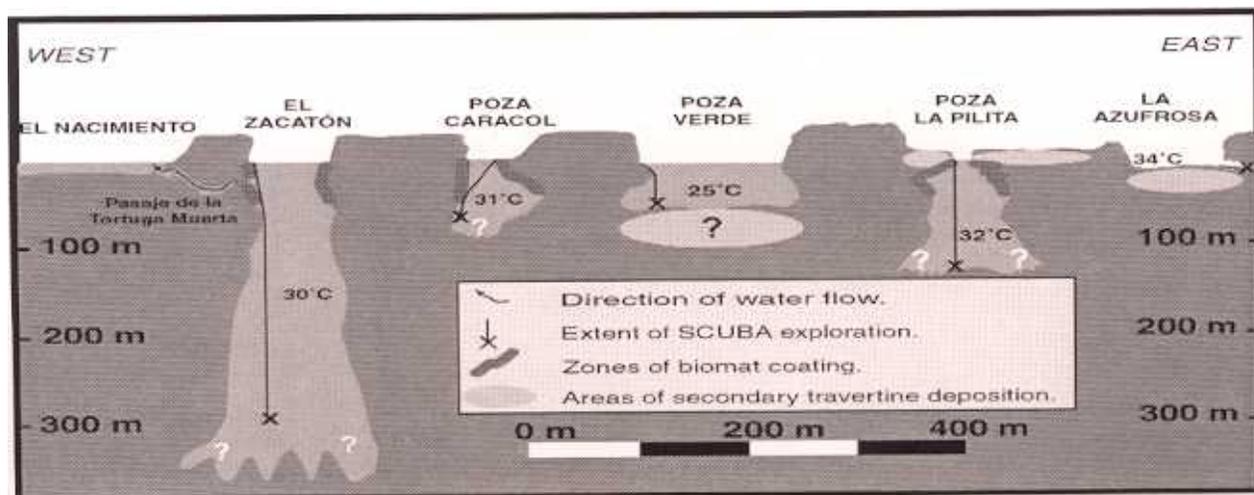


Figure 1: Generalized cross section of the cenotes of Rancho La Azufrosa. The limits of current exploration, locations of travertine deposition, and biomat-covered areas are represented.

### Geologic History

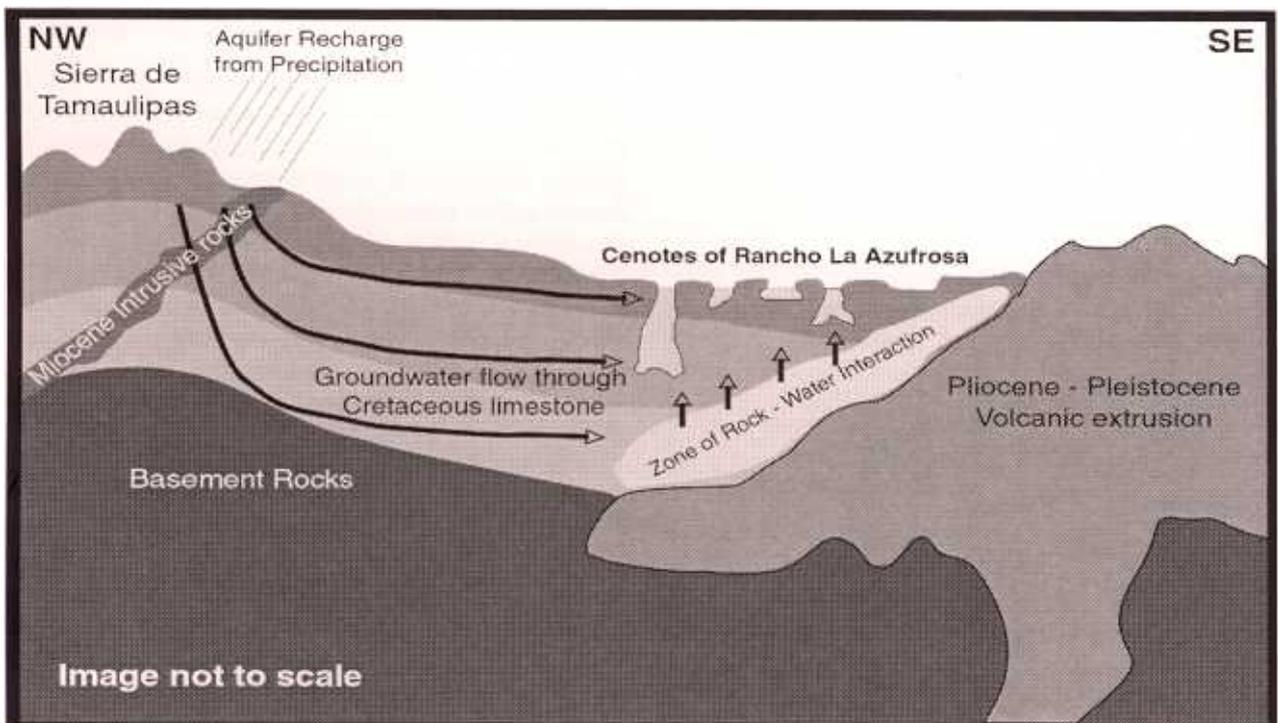
The cenotes of Rancho La Azufrosa are in the southern region of Tamaulipas, Mexico. The local geologic history presents conditions favorable for favorable for karstification processes. Thick beds of limestone were deposited during the Late Cretaceous as the ancestral Gulf of Mexico covered the area (Enos, 1989, Goldhammer, 1999). Following aerial exposure and lithification, these limestone beds were uplifted during the Laramide Orogeny (40 ma), forming the Tamaulipas Arch, a 200-kilometer long domal anticline that makes up the Sierra de Tamaulipas. The axial trace of this structure is immediately west of Rancho La Azufrosa.

By the late Oligocene, intrusive volcanic structures began to dissect the Sierra de Tamaulipas. Next, the extensive volcanic field around Villa Aldama became active in the late Pliocene, producing basaltic lava flows throughout most of the Pleistocene (Camacho, 1993). During the period of active volcanism, thick deposits of travertine were precipitated from springs discharging hydrothermal, mineralized water.

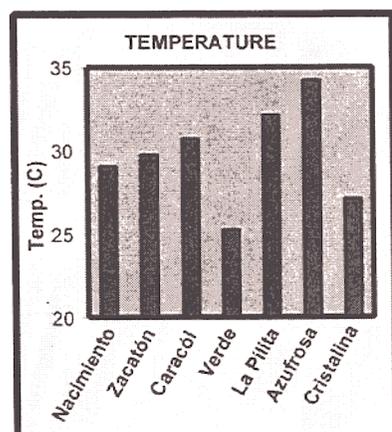
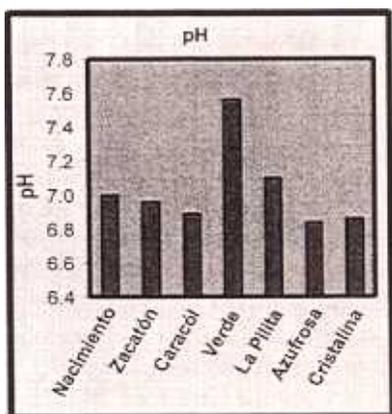
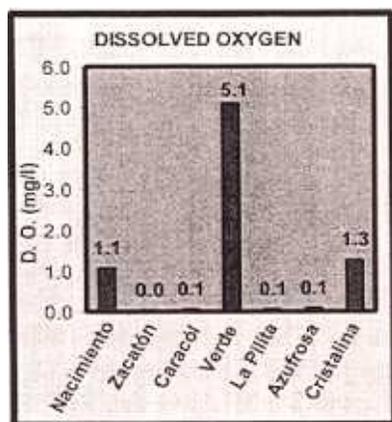
Surrounding geologic conditions allow for the development of this group of deep-seated subsidence shafts. The surface expression results from the collapse of large underground cavities that dissolved from circulating groundwater (White, 1988). Recharge from the Sierra de Tamaulipas moves down gradient through permeable karstified limestone until reaching the Pleistocene volcanic extrusion east of Rancho La Azufrosa where a fracture zone has provided a line of structural weakness. A groundwater-mixing zone occurs here as meteoric water comes into contact with hydrothermal, mineralized water adjacent to the volcanic extrusion (Figure 2). This zone provides an ideal environment for dissolution as the mixing waters adjust to chemically equilibrate with each other.

### Water Properties

Field parameters of pH, dissolved oxygen, and temperature were measured at each of the cenotes using a multi-parameter sonde (Figure 3). Vertical depth profiles of these characteristics indicate that the bodies of water are extremely homogeneous, showing little



**Figure 2:** Geologic cross section of the region showing important features that influence the speleogenesis of the cenotes.



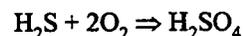
**Figure 3:** Graphs showing the basic water properties of the cenotes on Rancho La Azufrosa. The anomalous nature of Verde can be seen in contrast to that of the surrounding cenotes.

to no variation throughout the water column. The cenote, Verde, illustrates characteristics that deviate from those observed at the other cenotes and is the only one that has some stratification of physical parameters (Gary, 2000). Water samples collected at each of the cenotes and analyzed for major anion and cation concentrations and show that the chemical facies of all the waters is calcium bicarbonate. Significant levels of the sulfate anion ( $\text{SO}_4^-$ ) also are present. Sulfide ( $\text{H}_2\text{S}$ ) has been measured in both Caracól and Azufrosa at levels of 1.6 ppm and 1.04 ppm, respectively. In Zacatón, the volume of water is at least 9.5 million cubic meters (9.5 billion liters), so the dilution of sulfide anions may affect the measurement, which is limited to a detection limit of 10 parts per billion.

### Microbial Influence on Karstification

Biomats coating the walls of Zacatón, Caracól, and La Pilita appear as a thin, purple-red blanket, with some white filamentous areas. The mats are commonly underlain by dissolved calcium carbonate rock (Cretaceous limestone or Pleistocene travertine) that is either intensely etched “fingers” or a calcium carbonate “soup” that is as much as one meter deep. The bacteria that exist on the walls of the cenotes are suspected to be a type of photosynthetic purple bacteria that are autotrophic. A number of species from the genus *Thiobacillus* have been recognized to oxidize  $\text{H}_2\text{S}$  into  $\text{H}_2\text{SO}_4$  when grown in cultures (Ehrlich, 1995). The genus *Beggiatoaceae* is also a common sulfur oxidizer. Both of these forms are aerobic. There is an example of anaerobic sulfide oxidizing bacteria known as photosynthetic purple bacteria (*Chromatiaceae*). These types of bacteria are often found at groundwater interfaces, where they utilize the natural chemical gradients to capture energy (Banfield, 1997).

The occurrence of a type of bacteria likely related to the biomats at Rancho La Azufrosa can be found in some of the cenotes of the Yucatan Peninsula. Here, Pleistocene limestone is rapidly being dissolved in zones where bacteria are oxidizing  $\text{H}_2\text{S}$  into  $\text{H}_2\text{SO}_4$ .



The  $\text{H}_2\text{S}$  collects at the halocline where a mixing zone of seawater and freshwater occurs, and the bacteria convert it to sulfuric acid. This speeds up the dissolution rate of the limestone, creating large karst conduits along the horizontal interface of the mixing zone. The salt water below the halocline has waters that are highly concentrated with dissolved solids including sulfide values. It is suggested that the oxidation of hydrogen sulfide into sulfuric acid must be occurring if low pH values and high calcium

concentrations exist without exceedingly high alkalinities. The genus *Thiobacillus* is thought to be the strain of bacteria producing the hyper-acidic conditions at these Yucatan cenotes (Stoessell, 1993).

The immense cenotes at Rancho La Azufrosa have probably formed with aid from biological processes that have accelerated karstification. Hydrogen sulfide originates from the deep, hydrothermal contact zone created by local volcanism. This H<sub>2</sub>S rises through the water column and reacts with the purple sulfur bacteria that coat the calcium carbonate walls. Sulfuric acid is produced as bacteria consume available oxygen and H<sub>2</sub>S. Low dissolved oxygen values in the Zacatón, Caracól, and La Pilita reflect this reaction. The calcium carbonate substrate is exposed to a hyper-acidic environment as the sulfuric acid disassociates into the sulfate anion and hydrogen protons, dropping the pH to levels lower than would be expected in a limestone aquifer.

### Travertine structures

The 18 karst features that are included in the Zacatón system are primarily a series of circular sinkholes that exist within a 4-kilometer linear distance. Of these sinkholes, 8 have developed into shallow dolines that have floors of travertine. The origin of the travertine in these locations is associated with Pleistocene volcanism that was quite active just to the east of the study area. Rapid dissolution of limestone host rocks occurred as meteoric groundwater mixed with hydrothermal waters adjacent to the volcanic extrusion. These closed cenotes were once open, deep sinkholes that were most likely water-filled. Following a shift in the local geochemistry, mobilized calcium carbonate reached the surface and carbon dioxide equilibrated with the atmosphere, causing precipitation of calcite in the form of thick deposits of travertine that are typical of hydrothermal systems found in carbonate host rocks (Ford, 1989). Similar occurrences of massive travertine deposition have been documented in the travertine mounds of Tivoli, Italy (Folk, 2001).

The travertine floors are most common at present day water tables, but may also exist to some extent at lower, paleo-water levels. The cenote Verde has an extremely flat floor that is currently at 45 meters of depth. Such a level surface is atypical at the bottom of a large collapse structure and may, instead, be a travertine floor that formed at such time when climatic conditions forced a much lower water table. The anomalous water properties of Verde could be explained from this travertine structure. The cooler temperatures, higher pH, and significantly higher dissolved oxygen levels of Verde may be the result of shallow meteoric groundwater that is separated from the deep

hydrothermal groundwater seen in the other cenotes by a substantial travertine barrier similar to those now seen at the surface of other sinkholes in the area (Gary, 2000).

### Future Research

Understanding the vast and complex karst environment of the Zacatón system in northeastern Mexico proves to be a daunting task. Extreme conditions primarily related to deep sub-aquatic exploration severely limit access to collect data. To overcome the limits of human exploration and surveying, plans are being made to create detailed three-dimensional images of the phreatic voids of Zacatón. The Digital Wall Mapper (DWM) developed by Dr. Bill Stone in Wakulla Springs, Florida, (Stone et al., 2000) will be modified to withstand hydrostatic pressure in excess of 350 meters and dropped down the middle of the sinkhole. Imaging captured from this procedure will quantify the extent of karstification and identify potential side passages that may exist in the deeper zones. Spatial data collected from the phreatic zone of the cenote(s) will be combined with detailed digital elevation models (DEMs) created with laser radar (LADAR), and geophysical sensing of the travertine structures to produce a detailed three-dimensional image of the entire system. Applying information on chemical and physical parameters throughout the system will provide a scalar data set that can be interpreted to explain the speleogenesis of the world's deepest known phreatic sinkhole, Zacatón.

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