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Volcanogenic karstification of Sistema Zacatón, Mexico

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ABSTRACT

Deep phreatic shafts and travertine-capped sinkholes characterize Sistema Zacatón, an isolated karst area in northeastern Mexico. At a depth of at least 329 m, El Zacatón is the deepest known underwater pit in the world. Hypogenic karst development related to volcanism is proposed to have formed El Zacatón and is thought to have diminished since the late Quaternary peak activity. The resulting geomorphic overprint of Zacatón displays features similar to hydrothermal groundwater systems throughout the world. Other karst areas in northeastern Mexico are known for deep pits and high-flow springs rising from great depths, but differ from Zacatón in the speleogenetic processes that developed the caves. Sótano de Las Golondrinas (378 m), 200 km to the southwest of Zacatón, is among the deepest air-filled shafts in the world. The Nacimiento del Río Mante, 100 km to the west, is a large artesian spring that extends a minimum of 270 m below the water table. Although these three worldclass karst systems all formed in Cretaceous limestone and are located relatively close together, there are significant differences in lithology, tectonic setting, and geomorphic features. Geochemical, microbiological, and geomorphologic data for Zacatón indicate that cave formation processes are similar to those observed in other volcanically influenced systems.

Keywords: Zacatón, hypogenic karst, volcanism, Mexican caves.

INTRODUCTION

Study of the origin of limestone caves is a significant field of geologic investigation. Theories regarding the formation of large solutional voids have evolved dramatically over the past century. Early hypotheses claimed that a single mechanism, either chemical (Davis, 1930) or physical (Grund, 1910), was responsible for the development of all caves. However, more comprehensive modern theories are diverse and recognize the fact that multiple geologic factors influence cave development (Watson and White, 1985; Ford and Williams, 1989; Palmer, 1991). Certain theories postulate that hydrothermal and sulfuric waters act as agents of dissolution (Egemeier, 1981; Hill, 1987; Dublyansky, 2000). Theories proposed by Hill (1987) and Egemeier (1981) explain the speleogenesis of Carlsbad Cavern, New Mexico, and Lower Kane Cave, Wyoming, respectively, as hypogene caves that formed from water in which the aggressiveness was produced at depth. However, another method of speleogenesis is proposed to have formed Sistema Zacatón, which appears to have developed from hydrothermal karst processes associated with volcanic activity (Gary et al., 2003).

This paper focuses on the karst area of Sistema Zacatón, located in northeastern Mexico, which includes a number extremely deep, phreatic megasinkholes. El Zacatón (Fig. 1),

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Figure 1. El Zacatón is the deepest phreatic sinkhole in the world and extends at least 329 m below the water table. This mosaic photograph shows the entire diameter at the surface (113 m) and the floating grass islands known as "zacate." The cliff above the water is 21 m high. (Photograph courtesy Arthur Palmer.)

the primary feature, is the largest poza (phreatic shaft) in the system and may be the deepest such feature on Earth (Gary et al., 2003). The hypothesis that volcanic activity affects karst development here is inferred from a number of factors. Thick Cretaceous carbonates were moderately uplifted and fractured during late Laramide deformation (80–55 Ma; English and Johnston, 2004), and subsequent igneous events (Pliocene intrusive and Pleistocene extrusive) dramatically altered the local landscape of Sistema Zacatón (Camacho, 1993). In addition to this juxtaposition linking karstification and volcanism, water chemistry and isotopic data also support this theory. Finally, the expansive travertine deposits of Sistema Zacatón are consistent with the volcanogenic karstification hypothesis.

This study relies on observations and data collected from Sistema Zacatón and comparisons with similar karst systems. This region (Fig. 2) is known for some of the largest cave shafts in the world. Sótano de las Golondrinas is a renowned air-filled pit and is located ~200 km southwest from Sistema Zacatón in the Sierra Madre Oriental range. The Nacimiento del Río Mante lies 100 km west of Sistema Zacatón and is a deep phreatic cave located on the edge of the Sierra de El Abra. Detailed investigations regarding the origin of these two caves are limited, and definitive explanations of the speleogenesis of Golondrinas and Mante are not available (Hose, 2004). However, it is clear that Golondrinas, Mante, and El Zacatón have different and unique geomorphologic expressions (Fig. 3) and geologic contexts (Fig. 2); thus, it follows that the processes controlling their development are equally distinctive.

Sistema Zacatón is consistent with hydrothermal karstification, because many of the characteristic traits of these types of caves are present here. Dublyansky (2000, p. 292) defined settings and features of hydrothermal speleogenesis. All four of the major conditions have been observed at Sistema Zacatón as both active and paleokarst features: (1) elevated water temperatures (5–7 °C above mean annual air temperature); (2) large discharge volume; (3) oxidation of H₂S; and (4) mixing waters of contrasting chemistry. The setting at Sistema Zacatón has similarities to the volcanically driven hydrogeologic system at Mammoth Hot Springs in Yellowstone, Wyoming. Similarities to geologic processes, geochemistry, microbial activity, and travertine morphology in Mammoth Hot Springs support the hypothesis that volcanic activity has played a major role in the karst development of Sistema Zacatón.

GEOLOGIC SETTING OF NORTHEASTERN MEXICO

Major karst features in northeastern Mexico occur in Cretaceous (130–80 Ma) carbonate rocks. There is a wide distribution of carbonate facies in these units, because paleogeographic conditions varied both spatially and temporally. Lower Cretaceous rocks in the region are a thick (over 2000 m) buildup of forereef, reef margin, and back reef deposits that formed from late Neocomian through Albian time (Goldhammer, 1999). These units are now classified primarily as the El Abra and Tamabra Formations, and extend from the eastern edge of the Sierra Madre Oriental near Ciudad Valles (including the Sierra de El Abra) to areas 200 km west. Other Lower Cretaceous rocks of significance include the Lower Tamaulipas Formation, which crops out east of the Sierra Madre Oriental in the Sierra de Tamaulipas. No significant reef deposits have been identi-



Figure 2. Geologic map of northeastern Mexico showing the location of the deep karst shafts in the region (shown as bull's-eye circles). Major depositional and structural features are also represented.



Figure 3. Comparison of three deep karst shafts of northeastern Mexico shows the vertical profiles of the caves. Water-filled caves are shaded gray from the water table downward.

fied in this region (Goldhammer, 1999; Camacho, 1993; Enos, 1983; Enos and Stephens, 1993), but considerable rudist buildups are observed in the Sistema Zacatón area along the southeast flanks of the Sierra de Tamaulipas. Argillaceous limestone and shales dominate Upper Cretaceous deposits covering much of northeastern Mexico and are represented by the Aqua Nueva, San Felipe, and Mendez Formations (Camacho, 1993).

By the end of Cretaceous time, geomorphic processes were dominated by the advancing fold-and-thrust belt from the southwest. This Laramide development caused major uplifting and exhumation of younger, more easily eroded strata. Large thrust faults, overturned folds, and normal faults typify the Sierra Madre Oriental here, as thin-skinned deformation shaped the landscape (Suter, 1987). The Sierra de Tamaulipas is the expression of the Tamaulipas Arch, a 200-km-long domal anticline that formed in the Gulf of Mexico coastal plain east of the fold-and-thrust belt of the Sierra Madre Oriental. The Sierra de Tamaulipas is a result of basement-involved deformation and is a structural feature separate from the larger mountains of the Sierra Madre Oriental, 100 km to the west. Major uplift ceased in both the Sierra Madre Oriental and Sierra de Tamaulipas by the mid-Eocene, and in many locations Lower Cretaceous carbonates have since been above sea level (Ford, 2000).

During the Tertiary, igneous activity had a significant imprint on the regional geomorphology. Oligocene through Pliocene intrusive rocks dissect parts of the Sierra de Tamaulipas, and basalt flows were erupted along some frontal sections of the Sierra Madre Oriental. The most recent and largest single area of igneous rocks occurs along the Gulf of Mexico coast at the southeast flanks of the Sierra de Tamaulipas, downdip of the eastern limb of this anticline. This area is the Villa Aldama volcanic complex, which consists of Pliocene and Pleistocene lava flows and shield volcanoes. The most recent igneous rocks in this complex are dated at 250 ka (Camacho, 1993; Vasconcelos and Ramírez, 2004). Sistema Zacatón is 5 km from these rocks, and hydrothermal activity associated with Sistema Zacatón is inferred to result from this magmatic activity (Fig. 2).

SITE DESCRIPTION—SISTEMA ZACATÓN

Sistema Zacatón contains a diverse mixture of karst features that include: ramiform vadose cave passages (>2 km surveyed to date), broad overland travertine flows, collapse dolines, travertine-filled sinkholes, deep phreatic shafts, horizontal phreatic conduits, relict springflow travertine, and numerous minor karst features throughout the system (rillenkarren and others). The structural trends, aqueous geochemistry, travertine, and microbial communities of Sistema Zacatón are described in the following paragraphs.

Structural Trends

The most striking expressions of Sistema Zacatón are the large circular sinkholes (pozas) that dominate the immediate study area (Figs. 4 and 5). El Zacatón is the deepest of the sinkholes where Jim Bowden dove to 284 m below the water table (Gilliam, 1995). No walls are visible below 85 m, even with clear water providing visibility of 30 m or more. The lateral extent of El Zacatón at depth is unknown at this time. The primary trend of the pozas is roughly linear, N to S, and this coincides with the N-S-striking fractures that are observed in the area. This trend is parallel with the axial trace of the Tamaulipas Arch anticline (Fig. 2), and implies structural controls of speleogenesis related to Laramide uplift. A secondary E-W fracture trend is evident in the southern pozas. Upon initial inspection, all the pozas appear similar. However, substantial variations in water chemistry, rock type, and aqueous biological habitats indicate differences between the pozas. This wide distribution of characteristics raises questions regarding the sub-



Figure 4. Aerial photograph of Sistema Zacatón showing the major features of the study area. Numerous travertine-filled sinkholes are labeled and water-filled areas appear as black. The dry cave system of Caverna Cuarteles is shown as a gray-filled plan view map. A small water-filled cave (La Cristalina) on the north rim of Azufrosa may be the terminal resurgence for Caverna Cuarteles. Water flows under-ground from El Zacatón to the resurgence of El Nacimiento through a phreatic cave passage and then flows overland until becoming dispersed through broad honeycombed travertine deposits in the south of the area. Some of the pozas in the northern part of the study area are not shown in this figure, including the poza Alameda.

surface conduit system that connects or isolates each poza and provides the basis for some of the hypotheses relating to travertine formation.

Aqueous Geochemistry

Water samples have been analyzed for major-ion and traceelement geochemistry and some isotopes. These data are used to compare basic water types of the pozas and calculate calcite saturation indices (SI). A summary table for water analyses and



Figure 5. Profile view of the southernmost sinkholes of Sistema Zacatón showing zones of varying water types and travertine morphology. The poza Verde is hypothesized to have a travertine floor formed during periods of lower water-table levels (~50 m). This cap now serves as a flow barrier and can explain Verde's geochemical uniqueness, as compared to the deeper pozas on either side (La Pilita, Caracol).

selected field parameters is presented in Table 1, and a classification for three primary types of water is presented in Table 2. All calcite saturation indices (SI) calculated for the poza El Zacatón are negative, indicating undersaturated conditions (calcite dissolution). Verde has positive SI values (calcite precipitation), and Caracol, La Pilita, and Azufrosa have mixed SI values, although Caracol tends to be mostly undersaturated. Hydrogen sulfide (H₂S) is detected frequently in type-A waters, and Caracol repeatedly has the highest concentrations (1.40 mg/L at 18 m depth). Although some of the poza waters contain dissolved sulfide, sulfate concentrations are low in all of the analyzed waters (Table 1). Reducing conditions in type-A water would indicate low sulfate values, but sulfate is also very low in type-O and type-E waters. High Na (533 mg/L), K (135 mg/L), Cl (245 mg/L), B (1018 μ g/L, compared to values <100 μ g/L in other pozas), and total dissolved solids (TDS; 2746 mg/L) concentrations occur at Tule, and evaporation seems a likely cause. Tule may have such high evaporation rates because the surface water of Tule is cut off from groundwater circulation, possibly due to a travertine cap structure that isolates the deeper aquifer.

Stable isotopes have been applied as indicators of water cycle processes that reflect paleoclimatic variations. At Sistema Zacatón, eight samples were collected from the pozas for Hand O-isotope analysis in January 2003: Alameda, Tule, Poza Seca, Zacatón, Caracol, Verde, La Pilita, and Azufrosa. The measured D/H and ¹⁸O/¹⁶O ratios cluster along the meteoric water line (Craig, 1961), except for Tule water, which shows an evaporative signature. Tule is in the middle of the study area, and it has the largest diameter of all the pozas in Sistema Zacatón, but a depth of only 1 m. Evaporation enrichment for Tule based upon stable isotope data is consistent with the water chemistry (Table 2).

S isotopes may help to constrain the geologic processes that are the source of this element and determine the geomicrobiological cycles that occur in the water column and along the walls of the sinkholes. A single S-isotope analysis for Caracol yielded a δ^{34} S value of -8% Canyon Diablo Troilite (Smithebingale and Jenson, 1963; Schneider, 1970). The depleted δ^{34} S value is

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	°r‡	(hg/L)	N.D.	N.D.	210	526	508	490	N.D.	N.D.	302	730	637	N.D.	N.D.	250	577	608	N.D.	N.D.	793	759	685	290	765	667	600	556	505	744	572	263	742	709	Connon
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	Ca‡	(mg/L)	N.D.	N.D.	158	116	108	133	N.D.	N.D.	145	141	116	N.D.	N.D.	123	114	110	N.D.	N.D.	150	143	148	158	140	141	132	136	85	133	18	15	115	121	n brebue
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	Location		El Zacatón	Caraco	Caracol	Caraco	Caracol	Caracol	Poza Verde	La Pilita	La Azufrosa	La Azufrosa	La Azufrosa	La Cristalina	La Cristalina	Cav. Traver.	Poza Seca	Tule	Tule	La Alameda	La Alameda	Note: D.O. die													

Water type	Temp.	pН	Dissolved oxygen	Specific conductance	H,S	Proposed origin
	(°C)		(mg/L)	(mS/cm)	(ppm)	
Type A (anoxic)	~30° — 35°	6.5-6.8	0.01-0.9	730–950	0.01-2.0	Deep ground water
Type O (oxic)	Variable (seasonal)	7.2-7.9	2.5-7.5	600-750	0	Shallow ground water
Type E (evaporative)	Variable (seasonal)	8.5-9.0	7.5-9.0	2500-4000	0	Evaporative

TABLE 2. GROUNDWATER CLASSIFICATION SCHEME FOR SISTEMA ZACATÓN

indicative of biologic fractionation that occurs in thermal springs and is similar to that of hot springs in the Yellowstone area (Schoen and Rye, 1970).

Strontium isotopes have proven useful in comparing water chemistry from multiple sources and identifying possible mixing processes that account for variations in groundwater chemistry (Oetting et al., 1996). Limestone rocks of the study area are 110-87 Ma in age (Goldhammer, 1999), and the Sr-isotope ratio for these rocks ranges from 0.70730 to 0.70735 (Jones and Jenkins, 2001). Groundwater flowing solely through these rocks would be expected to have similar strontium isotopic values. Ten water samples collected from Sistema Zacatón were analyzed for 87Sr/86Sr ratios, and results of these analyses indicate that all waters have lower 87Sr/86Sr ratios than would be expected from equilibrium with host limestone (Fig. 6). This requires water contact with rocks that have a lower 87Sr/86Sr ratio, or possibly mixing of waters that have been in contact with mafic volcanic rocks. Mantle-derived rocks have typical 87Sr/86Sr values of to 0.7030-0.7050 (Faure, 1986). Assuming that adjacent Pleistocene basalt rocks have similar values, waterrock reactions could account for the low Sr-isotope values of the groundwater relative to the host marine limestone. This is consistent with a relationship between the groundwater moving through Sistema Zacatón and nearby volcanic rocks and supports the theory of volcanogenic karstification.



Figure 6. Strontium isotope data from Sistema Zacatón is interpreted to indicate that the karst waters are in contact or mixing with water in contact with Pleistocene volcanic rocks.

Travertine Analysis

Hydrothermal karst systems have distinct types of precipitated calcite that provide insight regarding hydrogeologic conditions that existed during mineral formation (Dublyansky, 2000). Several types of precipitated calcite exist in the study area: (1) thick travertine lids along water-table boundary zones in open sinkholes (Figs. 4 and 5); (2) subaqueous dogtooth spar in some type-A water; (3) broad overland travertine flows (Fig. 4); (4) subaerial speleothems in dry caves; and (5) paleo–spring flow travertine crusts.

Crystal Structure

Scanning electron microscopy was applied to examine crystal structure of dogtooth spar samples collected in La Pilita. Figure 7 shows a conglomerate of gothic-arch calcite crystals from a sample collected in La Pilita that displays crystal morphology that forms in sulfur-rich, hydrothermal aqueous environments (Folk et al., 1985). The curving triangular faces are thought to be the result of SO_4^{2-} ions that intermittently replace CO_3^{2-} ions in the calcite lattice structure. Groundwater conditions were different when the calcite precipitated, because the sulfate concentration in La Pilita waters is presently low (Table 1).



Figure 7. Scanning electron micrograph (SEM) of Gothic-Arch calcite crystal collected from the poza of La Pilita at a depth of 17 m. The triangular shape of crystals indicates that sulfate ions have replaced carbonate in the calcite lattice structure.

Isotopic Analysis

The great extent of travertine throughout Sistema Zacatón is significant because it can be an indicator of climatic changes (Soligo et al., 2002; Oppenshaw et al., 1997), reflect the rate of karstification (dissolution and reprecipitation of calcium carbonate) that has shaped the phreatic cave system, and record the geochemical conditions that existed during calcite precipitation (Coplen et al., 1994; Ivanovich and Harmon, 1992; Ludwig et al., 1992). A 50-cm-long core of travertine was collected in Caverna Travertina (Fig. 5) from a large mammalary calcite formation in the shallow underwater cave at a depth of 2 m, ~10 m in from the cave entrance. Subsamples at each end of the core bracket the time range of precipitation and were microdrilled, dissolved in acid, spiked with uranium and thorium tracers, and purified into separate uranium and thorium aliquots for mass spectrometric analysis at The University of Texas at Austin. Details of both chemistry and mass spectrometry procedures at The University of Texas are given in Musgrove et al. (2001). Measured ²³⁰Th / ²³⁴U ratios yielded ages around 3000 yr B.P. CT1a (the youngest subsample in the core) recorded an age of $2725 \pm$ 1060 yr. High thorium concentrations reduced the analytical precision. The subsample CT1z had much more accurate results, with a date of 2913 ± 158 yr. Both of these dates assume an initial ²³⁰Th/²³²Th ratio equivalent to theoretical average crustal values of 4.4×10^{-6} (Banner et al., 1990). The fact that the entire core is late Holocene is significant and indicates that calcite dissolutionreprecipitation remains active at Sistema Zacatón.

Microbial Biomats

Observations from years of exploratory diving at Sistema Zacatón have identified unique biologic coatings in three of the pozas: El Zacatón, Caracol, and La Pilita (Gary et al., 2003; Gary, 2004). These biomats generally appear as a thin, purplered blanket, with some white filamentous areas. The biomats are commonly underlain by calcium carbonate rock (limestone or travertine) that is expressed as either spar calcite fingers or an unconsolidated calcium carbonate soup that is as much as one meter deep. Biomats in Caracol and El Zacatón have a white powdery coating, which is thought to be elemental sulfur produced by bacteria in the mats. The biomats in these three pozas have thin, cohesive membranes, and in some cases gas bubbles collect beneath the biomat. The microbial communities in these pozas appear to change downward in depth. Shallow communities are typically green (algae and bacteria), and purple biomats become present at depths of ~3 m. Below the photic zone (100 m), or within dark phreatic tunnels, the walls are devoid of the thick mats, indicating that these are phototrophic communities. The bacteria that exist on the walls of the pozas may be a type of autotrophic, photosynthetic purple bacteria (Gary, 2004). The microbial communities of Sistema Zacatón are complex and diverse and may be similar to those developed in such settings as the Yellowstone, Wyoming, hydrothermal spring system (Barger, 1978; Fouke et al., 2000).

COMPARISON OF KARST DEVELOPMENT WITH OTHER SYSTEMS

Deep Shafts of Northeastern Mexico

Comparison of Sistema Zacatón with karstic systems in northeastern Mexico reveals distinct differences in the geologic setting and speleogenetic controls that form the deep cave shafts in this region. The deep shafts of Sótano de las Golondrinas and Nacimiento del Río Mante reflect a structural influence and are not associated with any current hydrothermal activity.

Sótano de las Golondrinas is the second deepest shaft in Mexico (Sprouse and Fant, 2002). The cave was first explored by Evans in 1967 and surveyed two months later to reveal a depth of over 330 m (Fig. 4), with an internal volume of roughly 6×10^6 m³ (Raines, 1968). The location of this immense shaft is in the Sierra Madre Oriental southwest of Ciudad Valles. Golondrinas lies on a major thrust fault in the Sierra Madre Oriental fold-thrust belt, which is a contact between the overthrust Lower Cretaceous Tamabra Formation and the Lower Cretaceous Aqua Nueva Formation (Sprouse and Fant, 2002). The shape of the shaft is controlled by fractures and joints, and dissolution appears to have occurred below 250 m depth from circulating groundwater. Golondrinas and other nearby shafts developed as chambers formed in phreatic limestone, and upward stoping of the ceiling occurred as material was removed from below (Raines, 1968).

Located on the eastern edge of the Sierra Madre Oriental fold-thrust belt, the Sierra de El Abra range has some of the world's highest flowing karst springs, including the Nacimiento del Río Mante (Ford, 2000). Sheck Exley explored this cave, diving to a depth of 267 m in 1988 and noted that the shaft continues at a steep angle (> 80°) as far as could be seen (Fig. 5) (Exley, 1994). The cave, classified as a deep phreatic lifting shaft, formed directly on the large normal fault plane that defines the eastern front of the Sierra de El Abra (Fig. 2). This fault controlled initial cave formation, as the passage runs directly down the structural dip. The Mante spring has a low base-flow discharge of 8 m³/s, but discharges during storm events can be as high as 250 m³/s (Fish, 1977; Ford, 2000). Water temperature has been measured at 23.5 °C (Harmon, 1971) and 26.2 °C (Fish, 1977), which reflects mean surface conditions. Water chemistry is Ca-HCO₃⁻ in character, with average $Ca^{2+} = 200 \text{ mg/L}$ and $CO_3^{2-} = 300 \text{ mg/L}$. Sulfate concentration has been measured at 400-500 mg/L at low baseflow conditions, and it decreases to <200 mg/L during high base flow. Water temperature and sulfate concentrations are directly correlated, and it is hypothesized that deeper, regional groundwater flow is reflected by an increase in temperature and sulfate (Mifflin, 1968; Mayer and Sharp, 1998). Conditions of low temperature and sulfate correspond to high discharge and are thought to reflect increased amounts of local, shallow groundwater flow (Fish, 1977). The mixing of these two groundwaters likely accelerates the dissolution of limestone at Mante and the other springs of the Sierra de El Abra.

Laramide deformation and uplift is dramatically different in the two areas of the Sierra Madre Oriental and the Sierra de Tamaulipas. Golondrinas and the deep shafts in the eastern Sierra Madre Oriental have been uplifted thousands of meters, and lie on the edge of the Cordilleran fold-and-thrust belt. Major collapse and cavern formation occurred postfaulting to create the vertical development of Golondrinas, and Mante formed directly in a normal fault. Sistema Zacatón certainly has structural influence, but it is quite different than the type seen in the Sierra Madre Oriental. The Sistema Zacatón area has not seen such dramatic structural deformation. In fact, beds only dip slightly to the east as a result of the thick-skinned folding of the domal anticline of the Tamaulipas Arch.

Modern Volcanic Karstification—Yellowstone Analogue

Mammoth Hot Springs in Yellowstone National Park, Wyoming, is a well-documented hydrothermal groundwater system that has developed in direct response to volcanic activity (Sorey, 1991; Sorey and Colvard, 1997; Pisarowicz, 2003). Many features and characteristics observed at Mammoth Hot Springs are similar to those of Sistema Zacatón. Mammoth Hot Springs has thick sequences of travertine deposits that form from emerging water supersaturated with calcium carbonate. The hydrothermal water is heated by magma at depth and rises through a zone of fissures and joints. It becomes supersaturated with calcium carbonate at depth due to highly elevated levels of CO₂ and flows to the surface (Barger, 1978). Hot springs are found north of Mammoth Hot Springs, and groundwater is known to flow through Mississippian limestone (Upper Madison Formation). Other caves and karst features, including travertine deposits, are found in this region. The source of most of the groundwater had been identified from isotopic signatures as meteoric (Barger, 1978). Studies on the distribution and diversity of geomicrobial communities have been done in this hydrothermal system, and the connection between volcanism and CaCO₃ dissolution and precipitation processes is likely interconnected with biologic activity (Fouke et al., 2000).

It is important to note that karstification processes at Mammoth Hot Springs and Sistema Zacatón are not identical. For instance, the geomorphic expression of Sistema Zacatón with large, deep sinkholes is not observed at Mammoth Hot Springs. The comparison of these two systems is proposed to demonstrate that hydrothermal karstification occurs near modern volcanically active zones, such as at Mammoth Hot Springs, and has likely been involved in the formation of Sistema Zacatón, although volcanic activity has subsided and the karstification processes are further developed there.

VOLCANOGENIC KARSTIFICATION HYPOTHESIS AT SISTEMA ZACATÓN

The speleogenesis of Sistema Zacatón is associated with Pleistocene volcanic activity. Geomorphic, biologic, and geochemical characteristics of Sistema Zacatón are consistent with features at Mammoth Hot Springs and other volcanically influenced groundwater systems. Northeastern Mexico is known for the deep shafts and caves, but the similarity of El Zacatón to these caves (specifically Golondrinas and Mante) ends with the fact that they are among the deepest in the world. A variety of contrasts exists between these karst areas.

Timing of significant karstification processes at Sistema Zacatón is reflected by a number of geologic controls, including deposition of a thick carbonate platform (Cretaceous), fracturing and jointing during late Laramide deformation (early Tertiary), and aqueous geochemical influence on groundwater by volcanic activity. All of these primary mechanisms are essential for the development of the karst system as it exists today. Nevertheless, the volcanic component is the most important for the morphology of Sistema Zacatón. Without elevated CO_2 and H_2S introduction to the system by volcanism, it is unlikely that this particular region of northeast Mexico would have developed the deep shafts in such a localized fashion.

The source of H₂S has two possible origins: (1) from volcanic activity and (2) from Cretaceous evaporite beds. The second source is considered to be much less likely due to the fact that evaporite deposits are regionally located within the carbonate facies of the Valles-San Luis Platform and the Golden Lane Atoll (Goldhammer, 1999; Enos, 1983, 1985; Enos and Stephens, 1993). Groundwater carrying H₂S from the Valles–San Luis Platform would have to travel a minimum of 120 km, cross a major thrust fault, normal fault, and move updip then downdip on both limbs of the Tamaulipas Arch to discharge at Sistema Zacatón. Groundwater carrying H₂S from the Golden Lane Atoll would require over 200 km of travel to reach Sistema Zacatón. Therefore, H₂S at Sistema Zacatón is thought to have its origin from local volcanic activity of the Villa Aldama volcanic complex, which lies only 3 km away. Increased levels of CO₂ would also likely be associated with this volcanic activity, and would accelerate the carbonate dissolution ability of groundwater in and around Sistema Zacatón.

In summary, it is proposed that Sistema Zacatón has developed through the following geomorphic events: (1) Deposition of thick limestone strata occurred during Late Cretaceous (110-80 Ma) time. (2) Late Laramide uplift of Sierra de Tamaulipas created an upland recharge zone and fractured the limestone in a N-S orientation during Late Cretaceous to early Tertiary (80–40 Ma). (3) Groundwater flow through fractures caused initial dissolution at a slow rate, and intermittent intrusive volcanic activity occurred in the area during the middle to late Tertiary (30-3 Ma). (4) Activation of Villa Aldama volcanic complex (hotspot) accelerated dissolution by increasing dissolved CO₂ and H₂S in groundwater, causing the formation of large phreatic galleries at depths down to 400 m during middle to late Quaternary (1.5 Ma to 200 ka) time. (5) Major collapse of many sinkholes exposed groundwater to the atmosphere, which allowed CO₂ to outgas and travertine lids to form at the water table within sinkholes during the late Quaternary (200 ka to present). (6) Cooling of the hydrothermal system occurred as volcanic hotspot activity slackened, and some sinkholes continued to collapse, including El Zacatón, as dissolution rates decreased during the late Quaternary to Holocene (50 Ka to present).

This hypothesized scenario explains how Sistema Zacatón may have formed. This does not imply that Pleistocene volcanism triggered karstification of Sistema Zacatón, but that volcanic activity altered the conditions to accelerate and focus dissolution processes dramatically in a relatively small area.

CONCLUSIONS

It is proposed that the deep phreatic caves of Sistema Zacatón developed under direct influence of Pleistocene volcanic activity. Accelerated karstification occurred as a result of increased dissolution and reprecipitation reactions that redistributed calcium carbonate, creating large subaqueous voids and expansive travertine deposits. Volcanism supplied elevated levels of dissolved CO_2 and H_2S to drive these reactions at increased rates. In fact, many features of Sistema Zacatón are more similar to characteristics of volcanically influenced groundwater systems, such as Mammoth Hot Springs in Yellow-stone, Wyoming, than to other deep sinkholes that occur in the same region of northeastern Mexico.

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