OVERVIEW OF THE GEOLOGIC HISTORY OF CAVE DEVELOPMENT IN THE GUADALUPE MOUNTAINS, NEW MEXICO

CAROL A. HILL

17 El Arco Drive, Albuquerque, NM 87123-9542 USA carolannhill@cs.com

The sequence of events relating to the geologic history of cave development in the Guadalupe Mountains, New Mexico, traces from the Permian to the present. In the Late Permian, the reef, forereef, and backreef units of the Capitan Reef Complex were deposited, and the arrangement, differential dolomitization, jointing, and folding of these stratigraphic units have influenced cave development since that time.

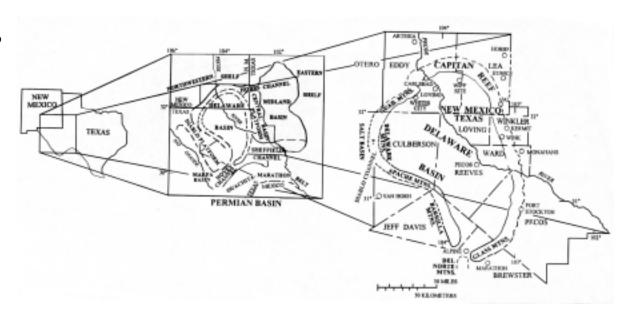
Four episodes of karsification occurred in the Guadalupe Mountains: Stage 1 fissure caves (Late Permian) developed primarily along zones of weakness at the reef/backreef contact; Stage 2 spongework caves (Mesozoic) developed as small interconnected dissolution cavities during limestone mesogenesis; Stage 3 thermal caves (Miocene?) formed by dissolution of hydrothermal water; Stage 4 sulfuric acid caves (Miocene-Pleistocene) formed by H2S-sulfuric acid dissolution derived hypogenically from hydrocarbons. This last episode is reponsible for the large caves in the Guadalupe Mountains containing gypsum blocks/rinds, native sulfur, endellite, alunite, and other deposits related to a sulfuric acid speleogenetic mechanism.

This paper provides an overview of events affecting cave development in the Guadalupe Mountains of New Mexico. Table 1 outlines the sequence of karst events, integrated with the regional geology. This overview is also intended to provide a geologic framework for the other papers in this Symposium.

The Guadalupe Mountains are located in southeastern New Mexico and west Texas (Fig. 1). The caves in these mountains are developed in the Capitan Reef Complex—a horseshoeshaped ring or belt of Permian-age limestone and dolomite rock ~8 km wide and ~650 km long that defines the perimeter

of the Delaware Basin. The Capitan Formation in the Delaware Basin is exposed in the northwestern Guadalupe Mountains section, the southwestern Apache Mountains section, and the southeastern Glass Mountains section, but is located in the subsurface on the eastern and northern sides of the basin. Its whereabouts is unknown in the western, Salt Basin side of the Delaware Basin (Fig. 1). Caves exist in all parts of the Capitan reef, including the eastern and northern subsurface sections and Apache and Glass Mountain exposed sections (Hill 1996, 1999a), but the largest number of accessible and spectacular

Figure 1. Location map of the **Delaware** Basin, southeastern New Mexico and west Texas. The caves are developed in the Capitan Reef Complex, which delineates the perimeter of the Delaware Basin (the western part



of the Permian Basin). The Capitan reef is exposed in the Guadalupe Mountains, Apache Mountains, and Glass Mountains, but occurs in the subsurface on the eastern and northern sides of the basin. Its location is unknown on the western, Salt Basin, side of the Delaware Basin (marked ?).

Table 1. Sequence of events for development of caves in the Guadalupe Mountains. Regional geologic events are taken from Hill (1996).

Time Interval

Events in Guadalupe Mountains

Paleozoic Permian		
Guadalupian	~255-251 Ma	 Deposition of the Capitan reef, basinal Bell Canyon Formation, and backreef Seven Rivers, Yates, and Tansill Formations. Dolomitization of backreef and forereef in Guadalupe Mountains and also parts of the Capitan reef in the Apache and Glass Mountains.
Ochoan	~251-250 Ma	 Deposition of the Castile Formation in the basin. Delaware Basin is tilted eastward. Probable first uplift and exposure of Guadalupe Mountains. Stage 1 fissure caves develop preferentially along a lithologic zone of instability between reef and backreef members.
Mesozoic		
Triassic-Jurassic	~250-135 Ma	 * Guadalupe Mountains remain emerged above sea level; marine environment replaced by deltaic, lacustrine, and fluvial environment. * Stage 2 spongework caves form under slow-diffuse circulation during limestone mesogenesis. Some spongework cavities filled with montmorillonite clay (~188 ± 7 Ma).
Cretaceous		
Comanchean	~135-95 Ma	* Shallow sea advances over Delaware Basin and Guadalupe Mountains, leaving behind a veneer of siliceous (now-summit) gravels. * Stage 1 caves fill with gravel to form "Type 2" dikes.
Gulfian	~95-65 Ma	* Late Cretaceous Laramide Orogeny begins in western U.S.; Guadalupe Mountain area uplifted thousands of meters above sea level. * Stage 2 spongework caves reactivated; calcite spar lines some Laramide caves (~90 Ma).
Cenozoic Tertiary		
Paleocene	~65-58 Ma	* Laramide uplift continues into the Early Tertiary. * Stage 2 spongework caves become further enlarged and integrated.
Eocene	~58-40 Ma	* Time of quiescence in the Guadalupe Mountains. Laramide uplift stops and an elevated plain exists over much of western U.S. * Stage 2 caves probably become stagnant.
Oligocene	~40-25 Ma	* Time of Trans-Pecos magmatic province; Tertiary extrusives and intrusives form in southern part of Delaware Basin; intrusive dikes reach across the Delaware Basin almost to the Guadalupe Mountains. * Transition from volcanic phase to Basin and Range phase in Delaware Basin area. Delaware Basin area tilts eastward and heats up. * Maturation and migration of hydrocarbons; H2S produced where hydrocarbons react with Castile anhydrite. * Time of emplacement of Mississippi Valley-type ore deposits (~40-20 Ma).
Miocene (Early,) ~25-12 Ma	* Maximum uplift of Guadalulpe Mountain block begins (~20 Ma). * Geothermal gradient of Delaware Basin area reaches ~40-50°C/km; time of maturation and migration of hydrocarbons. H2S produced when hydrocarbons react with evaporites. * Stage 3 thermal caves produced by hydrothermal circulating fluids; calcite spar fills Basin and Range fault zones and lines some cave passages (?).
Miocene (Late)	~12-5 Ma	 * Stage 4 sulfuric acid caves form where H₂S ascends into Capitan reef. Gypsum blocks and rinds, native sulfur, endellite and alunite form as a result of a sulfuric acid speleogenesis. * Stage 4 cave passages develop from southwest to northeast along the Guadalupe Mountains; 11.3 Ma for Virgin Cave to 3.9 Ma for the Big Room level of Carlsbad Cavern. * Large Stage 4 sulfuric acid cave passages cut across earlier 3 stages of cave development.
Pliocene	~5-2 Ma	 * Regional water table drops in response to base-level downcutting of the ancestral Pecos River. Caves develop along lowering water table levels. * Caves in higher, southeastern part of Guadalupe Mountains (e.g., Virgin) stop forming; caves in lower, northeastern parts (e.g., Carlsbad) continue forming at the water table. * As canyons downcut into the Guadalupe Mountain block, cave passages are intersected so that entrances form. * As the caves become air-filled, they become decorated with travertine.
Quaternary Pleistocene	~2 Ma-10 ka	* At ~600 ka the Capitan aquifer hydrologically connects with the Pecos River at Carlsbad. Possible time of water table draining out of Big Room-Lower Cave levels of Carlsbad and lower levels of Lechuguilla. * Air-filled caves continue to become decorated with travertine. Time of maximum decoration: ~600 ka and ~170-70 ka. * Animals inhabit air-filled caves.
Holocene	~10 ka-present	* Arid climate - travertine growth decreases. * Entrance air flow affects cave microclimates. * Pool chemistry evolves to present state.

caves are in the Guadalupe Mountain section. Over 300 caves are known in the Guadalupe Mountains. Carlsbad Cavern is perhaps the most famous of these caves, but it is neither the longest nor the deepest. Lechuguilla Cave is now the deepest (475 m) and longest (>170 km) cave in the Guadalupe

Mountains, the deepest and third longest limestone cave in the United States, and the fifth longest cave in the world. Guadalupe caves are characterized by their unusual mode of speleogenesis, which is reflected in their large passage size, ramiform morphology, and enigmatic deposits of gypsum,

native sulfur, endellite (hydrated halloysite), alunite, and uranium minerals.

The origin of Carlsbad Cavern and other caves in the Guadalupe Mountains has long been a subject of controversy. For more than 30 years, the prevailing theory had been that these caves formed like other caves; that is, by carbonic acid dissolution at or below the water table (Bretz 1949). But, since the late 1970s and early 1980s, this "normal" model of cave dissolution has been challenged by a new generation of speleologists (Jagnow *et al.* 2000). It is now nearly universally accepted that the caves of the Guadalupe Mountains are of "hypogene" origin, having developed where ascending H₂S, derived from hydrocarbons, became oxidized to sulfuric acid, which in turn dissolved out huge chambers at approximately the level (or levels) of the paleo-water table.

These large sulfuric acid caves, however, represent only the final chapter of cave development in a long history of periodic karstification in the Guadalupe Mountains. Porosity/karst development has occured in at least four stages throughout the diagenetic history of the Capitan Reef Complex, from Late Permian to the present. Thus, in order to understand the complete history of cave development in the Guadalupe Mountains, one must go back to the Permian, to a time when the great Capitan reef was growing upward around the intracratonic Delaware Basin.

This paper will only summarize the sequence of events in the Guadalupe Mountains from the Late Permian to the present; for a more detailed description, refer to Hill (1996).

PALEOZOIC

PERMIAN (GUADALUPIAN)

Guadalupian time (~255-251 Ma) in the Delaware Basin area was characterized by the growth of an extensive stratigraphic reef that separated the deep ocean basin from a shallow backreef shelf lagoon (Fig. 2). The classic model for the Delaware Basin in the Permian is that the basin was completely surrounded by the Capitan (and earlier reefs), and that sea water entered the basin through the Hovey Channel, located in the southern, Glass Mountains section of the basin (Fig. 1). However, Hill (1999b) challenged this classic paleogeograph-

ic map and placed the inlet (which she named the "Diablo Channel") to the basin on its western, Salt Basin side (Fig. 1, marked?). Hill claimed that this channel position could account for the absence of the Capitan reef between Guadalupe Peak and the Apache Mountains. It might also account for the extensive growth of the Capitan reef along the Guadalupe Mountain section of the basin (near where "fresh" upwelling sea water from the deep ocean was entering the Delaware Basin), and for less dolomitization of the Capitan reef in the Guadalupe Mountains, as compared to the Glass Mountains which would have been farther from the source of "fresh" sea water if the Hovey Channel had been non-existent.

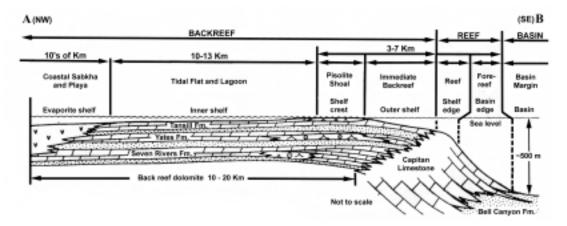
During Guadalupian time, when the Capitan reef was growing steadily upward and basinward in the Guadalupe Mountain area, a thick sequence of siliciclastics was deposited within the deep basin, and interbedded carbonates, siliciclastics and evaporites were deposited on the shallow lagoonal shelf behind the reef (Fig. 2). The Capitan Formation consists of two facies—a massive reef member composed of an organic framework and a thickly bedded forereef member. Both members grade laterally and vertically into each other and together reach thicknesses of 450-600 m in the Guadalupe Mountains. Time-correlative with the Capitan reef in the Guadalupe Mountains are the backreef Seven Rivers, Yates, and Tansill Formations of the Artesia Group and the basinal Bell Canyon Formation of the Delaware Mountain Group. These bedrock units deposited in the Late Permian were to influence all subsequent episodes of cave development in the Guadalupe Mountains (DuChene 2000).

CONTROLS ON CAVE DEVELOPMENT

Four properties of the Capitan in Late Permian time seem to have exerted control on later cavern development: (1) the arrangement of stratigraphic units; (2) differential dolomitization of these units; (3) joint patterns; and (4) positive structures (folds). All four controls first appeared in the Late Permian, although (3) and (4) have been modified by later tectonic and diagenetic events (Hill 1996).

Stratigraphy. As the Capitan reef was lithified in the Late Permian, the contacts between the reef-forereef and reef-back-reef facies became zones of structural weakness that were to

Figure 2. Facies patterns and depositional environments of the Capitan Reef Complex, Guadalupe Mountains, in Permian (Guadalupian) time, including the basin, forereef, reef, and backreef members. After Esteban & Pray (1983).



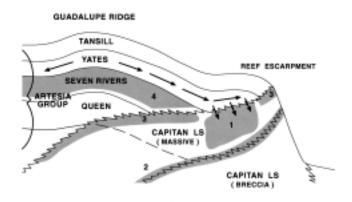


Figure 3. Four zones of preferential dissolution (shaded areas) in the Guadalupe Mountains: (1) below the Yates transition into the massive Capitan Limestone; (2) at the contact between the massive and forereef (breccia) members of the Capitan Limestone; (3) at the transition between the backreef Artesia Group members and Capitan Limestone; (4) immediately beneath the Yates Formation in the Seven Rivers. Arrows indicate movement of groundwater along impermeable siltstone in the Yates Formation. After Jagnow (1977).

become the focal point for later water movement and cave development. While some caves are developed within or beneath the Yates in the Seven Rivers Formation (Fig. 3), most of the major caves (e.g., Carlsbad, Lechuguilla) are developed at these reef-backreef and reef-forereef contacts (Jagnow 1977).

Figure 4. Idealized schematic diagram showing the distribution of dolomite in upper Permian units around the Delaware Basin. The upper Capitan in the **Guadalupe Mountains** is the only location where the Capitan is mostly undolomitized limestone. Diagonal lines show dolomitized rock, circles show rock with patchy dolomitization, white areas show limestone. The location of the Capitan and **Goat Seep formations** in the Salt Basin is unknown (?). After Hill (1996, 1999a).

Dolomitization. Dolomitization (or the lack thereof) has also exerted control on cave development in the Guadalupe Mountains. The Capitan reef was not dolomitized equally in all parts of the basin in the Late Permian (Fig. 4). In the Apache Mountains the Capitan reef is, in large part, dolomitized but its younger parts grade into limestone (Wood 1968). In the Glass Mountains, the reef facies of the Capitan is also more dolomitized than in the Guadalupe Mountains (King 1930), with textures varying from somewhat dolomitized and with complete preservation of fossils (e.g., in the Old Blue Mountain area), to only matrix replacement, to total replacement (e.g., in Jail Canyon) (Haneef 1993). In the Guadalupe Mountains, the oldest part of the massive reef facies (the lower Capitan) is partially dolomitized, whereas the upper Capitan is predominantly limestone. This thin belt of limestone extends northeastward along the mountain front but gradually becomes dolomitized just southwest of Carlsbad (Fig. 4). Thus, a thin "island" of limestone exists only in the upper Capitan in the Guadalupe Mountains, and it is this "island" of rock that hosts the majority of caves. Since dolomitization of the Capitan occurred primarily in the Late Permian (Melim 1991), it has acted as a control on dissolution ever since.

Joints. Joints are a primary structural control on cavern development, and the major trunk passages are usually aligned along joints that are either parallel or perpendicular to the reef front. Brecciation and crude bedding planes in the forereef slope, however, seem to (at least partly) control the location of some passages (e.g., the eastern part of the Western Borehole, Lechuguilla Cave; DuChene 2000). The age and origin of joints in the Capitan are controversial (Hill 1996). However, it appears reasonably certain that the initiation of jointing

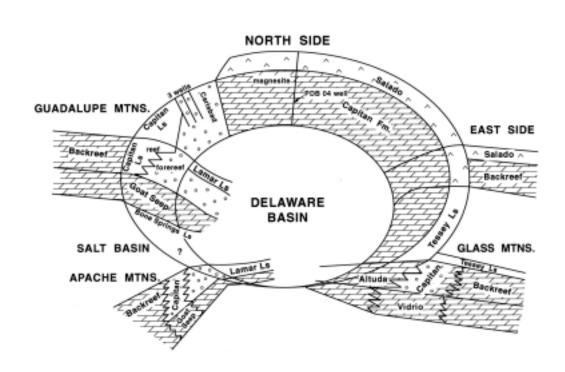




Figure 5. The relationship of major caves in the Guadalupe Mountains to positive structures (folds): (1) Reef anticline; (2) Guadalupe Ridge anticline; (3) Huapache monocline; (4) McKittrick Hill anticline (oval). Modified from Palmer & Palmer (2000).

occurred when the rock was being lithified in the Late Permian. Initial jointing probably occurred during the compaction phase of diagenesis in the Late Permian, and later jointing took place along these lines of weakness during tectonism—possibly during the Laramide and probably during Miocene Basin and Range block faulting. Similarly, initial cave development was along these Late Permian joints, with subsequent stages of karstification following along these same lines of weakness.

Positive Structures. Positive structures (e.g., anticlines) have been another control on cavern development. Carlsbad Cavern is located along the crest of the Reef anticline, Lechuguilla Cave and Cottonwood Cave are located along the Guadalupe Ridge anticline, the Slaughter Canyon caves are located along the Huapache monocline, and the McKittrick Hill caves are located along the flanks of the McKittrick Hill anticline (Fig. 5). The major large cave passages are concentrated along positive structures because these structures acted as avenues and traps for H₂S ascending into the reef. During the last (Stage 4) episode of cave development, sulfuric acid produced by oxidation of this H₂S dissolved out the large cave passages in the Guadalupe Mountains.

LATE PERMIAN (OCHOAN)

The Ochoan (~251-250 Ma) represents a time of dramatic change in sedimentation within the Delaware Basin. The inlet to the basin (whether the Hovey and/or Diablo Channels) became closed to marine waters so that the basin filled with thick sequences of evaporites and also with thinner sequences

of red beds (i.e., the Castile, Salado, Rustler, and Dewey Lake Formations; refer to Hill 1996 for a description of these units). The first uplift of the Delaware Basin probably occurred in Ochoan time, as evidenced by a Late Permian unconformity between the Dewey Lake Red Beds and Triassic rocks. The western edge of the basin was tilted eastward, and at least the western part of the Guadalupe Mountains was probably uplifted above sea level. This brought about the first episode of karsting in the Guadalupe Mountains.

STAGE 1 FISSURE CAVES

Stage 1 fissure caves are characterized by small fissure-like cavities filled with breccia, limy mudstone, siliciclastics, and/or calcite spar. Most Stage 1 caves are located at or near the reef/backreef contact (Hill 1987), a location suggesting that they formed in a zone of structural instability between the Capitan reef core and backreef shelf members. Although Stage 1 fissure karst is commonly intersected by Stage 4 sulfuric acid cave passages, it has also been identified in outcrop. Melim & Scholle (1989) and Scholle et al. (1992) identified an exposure episode in the Guadalupe Mountains during which an initial stage of meteoric leaching of originally aragonitic material occurred with the development of a large-scale, dissolutionenlarged fracture system. These surface-exposed fractures are filled with clast-supported breccia and blocky calcite, and are oriented mainly parallel to the Capitan reef trend, with a secondary orientation perpendicular to the reef trend (Melim 1991). Individual fractures average 1 m wide but they also occur in anastomosing sets averaging 10-20 m wide. Melim (1991) found the breccia fragments in these fractures to be dolomitized and of local origin without evidence of significant transportation, and also identified a dolomite alteration front or halo extending around the fissures for a distance of 5-10 cm into the reef rock. From this evidence, Melim concluded that this dissolution episode probably occurred in the Late Permian (Ochoan?).

The following origin seems likely for the Stage 1 fissure karst episode. Subsequent to the deposition of the Capitan Limestone and equivalent backreef facies, probably in Ochoan time, tectonic activity caused the first uplift and tilting of the Capitan reef. Fractures (joints) that had initially formed in response to differential compaction between the rigid reef and less competent backreef became enlarged into fissures due to tectonism and/or dissolution. Locally derived clasts were then displaced downward and partially filled these voids. The anastomosing nature of these fracture sets, with extensive pinching and swelling of individual fractures, is easiest to explain by dissolution-enlargement of already-existing fractures or joint sets (Melim 1991). However, solutional activity does not appear to have been extensive. Dissolution-enlargement occurred prior to at least one dolomitization stage because the walls of Stage 1 fissure caves and breccia clasts within the fissures are dolomitized. Stage 1 fissure caves developed along the zone of weakness between the reef/backreef and then became avenues for water movement, porosity enhancement, and dissolutional enlargement during the subsequent three stages of karstification.

MESOZOIC

TRIASSIC-JURASSIC

During the entire Mesozoic, up until the Laramide Orogeny in the Late Cretaceous, the Guadalupe Mountains were emergent just above sea level, and a marine environment was replaced by a deltaic, lacustrine, and fluvial environment. Probably at this time, the Capitan reef experienced its first "flushing out" and next episode of karstification.

STAGE 2 SPONGEWORK CAVES

The second episode of porosity/karst development in the Guadalupe Mountains involved the enlargement of pores and joints in the massive Capitan Limestone into three-dimensional mazes. "Spongework" consists of interconnected dissolution cavities of varied size in a seemingly random, three-dimensional pattern like the pores of a sponge (Palmer 1991). Essentially, these cavities are freshwater lens voids, where phreatic water creates a spongework array of passages. Hill (1987) described Stage 2 spongework cavities in the Guadalupe Mountains as being small and randomly oriented, with some being partly filled with montmorillonite clay.

In the early stages of cave-system formation, a complex, three-dimensional array of pores and joints of minimal cross-sectional area can develop in the rock, but the pores and joints are not necessarily integrated so that flow under these conditions is diffuse. As dissolution continues over time, this array expands, and there is a progressive integration of conduits and enlargement of small portions of the array to create a cave system that eventually becomes continuous from input to output (Ford & Ewers 1978). In such a situation the limestone becomes honeycombed along joints, fractures, and bedding planes, and small caves up to a few meters in extent can form.

Stage 2 spongework caves represent this type of early karst development in the Guadalupe Mountains. cavities/caves dissolved under phreatic conditions marked by the slow, diffuse circulation of aquifer water during limestone mesogenesis. Stage 2 spongework caves in the Capitan are exposed in the walls of the large cave passages as a threedimensional array of "Swiss-cheese"-like holes or cavities; some holes are large enough to crawl through, although most are not. Stage 2 spongework porosity/karst may have formed over a long period of time, or more likely during several episodes from the Mesozoic to early Cretaceous. The Triassic-Jurassic was a time of emergence for the Delaware Basin area, and it was also probably a time of extensive dissolution. Montmorillonite clay filling a small percentage of Stage 2 spongework cavities has a speculative K-Ar date of 188±7 Ma (early Jurassic) (Hill 1987).

CRETACEOUS (COMANCHEAN)

The Delaware Basin region remained stable for most of the

Mesozoic, but in the Early Cretaceous (Comanchean) a weak subsidence of the region permitted a shallow, epicontinental sea to transgress across the basin and over the top of the (then near sea level) Guadalupe Mountain area. Outcrops of Cretaceous rock can be found as lag gravels over the Tansill Formation near the edge of the reef escarpment, and these gravels also occur as remnants within Stage 1 fissure caves (the "Type 2" dikes of Hill 1996). This epicontinental sea withdrew from the area early in the Late Cretaceous in response to the Laramide Orogeny, and marked the last vestige of marine sedimentation in the Delaware Basin.

CENOZOIC (TERTIARY)

LARAMIDE PHASE, LATE CRETACEOUS - EOCENE

The long interval of relative quiescence in the Guadalupe Mountains during the Mesozoic was terminated by the Late Cretaceous-early Tertiary Laramide Orogeny. This tectonic event was responsible for the uplift of the entire western United States, and probably for more than 1.2 km of uplift in the Guadalupe Mountains area (Horak 1985). The Delaware Basin area was also subjected to broad arching during the Laramide, as can be seen in the Guadalupe and Delaware Mountains (King 1948). The steepest dip of this great Laramide arch is along its western flank; the crest of the arch was probably near the present summits of the southern Guadalupe Mountains because consequent streams radiate northeast, north, and northwest from this area.

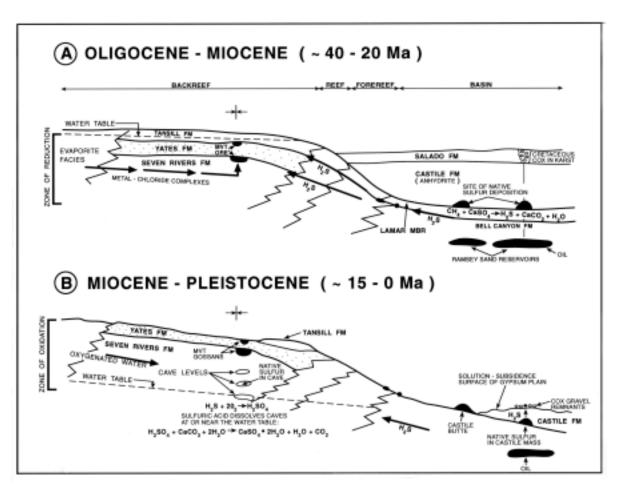
The effect of Laramide uplift on cave development in the Guadalupe Mountains is not known, but it must have caused at least a partial reactivation of water moving through the Capitan reef and consequently a further enlargement and integration of Stage 2 spongework caves. A preliminary Late Cretaceous (~90 Ma) date on cave spar (Lundberg *et al* 2000) attests to at least some Laramide dissolution at this time. This activity probably slowed during the quiescent Eocene, at which time water in the Capitan reef may have been relatively stagnant.

VOLCANIC PHASE - OLIGOCENE

A phase of extrusive and intrusive volcanism occurred in the Trans-Pecos, Delaware Basin area during the early-middle Oligocene (~40-30 Ma). No known volcanic rocks are exposed in the Guadalupe Mountains, but a number of northeast-trending intrusive dikes (both on the surface and in the subsurface) exist in the basin just southeast of the Guadalupe Mountains escarpment. The Oligocene to early Miocene (~40-20 Ma) may have also been the time of Mississippi Valley-type (MVT) ore emplacement in the Guadalupe Mountains (e.g., Queen of the Guadalupes mine; Hill 1996). As H2S began to ascend into the reef, it formed sulfide deposits in the reduced zone along structural (anticlinal) and stratigraphic (base of Yates Formation) traps where it mixed with metal-chloride complexes moving downdip from backreef evaporite facies (Figs. 2 & 6). Later, sulfuric acid caves formed along these same structural and stratigraphic traps in the oxidized zone.

Figure 6. Idealized model for the origin of caves, and also for Mississippi Valley-type (MVT) sulfides, in the Guadalupe Mountains. This figure shows a genetic connection between hydrocarbons and native sulfur within the **Delaware** Basin, and **MVT** deposits and sulfuric acid caves in the carbonatereef margin, although H2S could have also come from other

sources than



the basin *per se.* (A) In the late Oligocene-early Miocene, during the Tertiary tilting of the Delaware Basin, H₂S was generated in the basin by reactions involving hydrocarbons and anhydrite. The H₂S oxidized to native sulfur in the basin, and also some migrated from basin to reef to accumulate there in structural (anticlinal) and stratigraphic (base of Yates) traps. Metals moved downdip as chloride complexes from backreef-evaporite facies, and where they encountered ascending H₂S below the water table in the zone of reduction, they formed MVT deposits. (B) Later in the Miocene and also in the Pliocene to Pleistocene, continued uplift and tilting of the Guadalupe Mountain block and Delaware Basin area caused increased H₂S generation and migration of gas from basin to reef. Cave dissolution occurred in the same structural and stratigraphic position as earlier MVT deposits, where H₂S oxidized to sulfuric acid at or near the water table in the zone of oxidation. Cave levels correspond to a descending base level caused by the regional lowering of the Pecos River. From Hill (1996).

The importance of the volcanic phase to the caves of the Guadalupe Mountains is that it initiated a general heating up of the Delaware Basin. This heating was responsible for: (1) the setting up of convectional circulation patterns within the porous, spongeworked Capitan reef; (2) the beginning of the maturation and migration of hydrocarbons in basinal rock; and (3) the production of H₂S from the interaction of these hydrocarbons with Castile Formation evaporite rock (Fig. 6). The volcanic phase in Oligocene time, thus, "sets the stage" for the last two episodes of karstification in the Guadalupe Mountains.

BASIN AND RANGE PHASE - MIOCENE

The transition from the volcanic phase to the Basin and Range phase took place in the late Oligocene to early Miocene (\sim 30-20 Ma) and represents a time of change from Laramide compression to Basin and Range regional extension. By \sim 20 Ma, the main uplift and tilting of the Guadalupe Mountain block had begun.

STAGE 3 THERMAL CAVES

Stage 3 thermal caves are small caves characterized by crystalline dogtooth-spar linings (Fig. 7). Cavers call these "spar caves" or "geode caves" because of their spectacular spar crystals, which can be as large as footballs. Spar caves can be small individual caves exhibiting spar linings (e.g., Geode Cave, Crystal Ball Cave), or they can be small rooms or sparlined passages which have been intersected by later sulfuricacid dissolution (e.g., Diamond Chamber, Lechuguilla Cave).



Figure 7. A spar cave in the Guadalupe Mountains. Some of the dogtooth spar crystals lining the walls of this cave are as large as footballs. Photo by Alan Hill.

Stage 3 spar-lined caves exist in both the Guadalupe and Glass Mountains (Hill 1996).

From oxygen-isotope and fluid-inclusion studies, the dogtooth spar in these caves is known to have formed from ~30-65°C solutions. Thermal spar with similar isotopic values also permeates the Capitan reef filling pores and fault zones along the western escarpment of the Guadalupe Mountains (Hill 1996). Because the Miocene was a time when the geothermal gradient reached ~40-50°C/km (Barker & Pawlewicz 1987), Stage 3 thermal caves were thought by Hill (1996) to be most likely Miocene in age. However, the recent Laramide date of Lundberg *et al* (2000) challenges this assumption that all cave spar in the Guadalupe Mountains is Basin and Range age.

The following model can be invoked to explain the origin of Stage 3 thermal caves:

- (1) Surface water input into the Capitan reef in Miocene time was meteoric. As this cold meteoric water descended along faults and joints, it heated in response to the 40-50°C/km geothermal gradient, and a convective circulation pattern was set up in the Capitan reef and also in stratigraphic units below the Capitan.
- (2) As the convective water rose and cooled, the solubility of CaCO₃ gradually increased so that small (Stage 3) caves

were dissolved in a deep "solutional zone" by the "cooling corrosion" mechanism of Bögli (1980).

- (3) Although the solubility of CaCO₃ increased with the ascent of bathyphreatic fluid in the "solutional zone", it dropped sharply due to the loss of CO₂ in the shallower "depositional zone", so that solutions changed from aggressive to precipitative (Dublyansky 1995).
- (4) As Stage 3 caves formed in the "solutional zone" were shifted into the "depositional zone" by tectonic uplift and/or descent of the water table, cave walls became lined with dog-tooth spar. Conditions necessary for the growth of large spar crystals are: (a) solutions just barely saturated with respect to calcite; (b) a quiet, aqueous environment in which crystals can grow undisturbed; (c) enough time for crystals to grow large. All of these conditions must have been met in order for spar crystals to deposit in Stage 3 thermal caves from hydrothermal solutions.

STAGE 4 SULFURIC ACID CAVES

Later in the Miocene (12-5 Ma), and probably not long after the Stage 3 thermal cave episode, an entirely different mechanism created the last and most significant episode of karstification in the Guadalupe Mountains: Stage 4 sulfuric acid caves.

Description. The main caves/cave areas in the Guadalupe Mountains are: Carlsbad Cavern, Lechuguilla Cave, Cottonwood Cave, the Slaughter Canyon caves, and the McKittrick Hill caves (Fig. 5). These are located within 12 km of the reef escarpment (most are within 5 km); along the crests or flanks of anticlines or other positive structures (e.g., Reef anticline, Guadalupe Ridge anticline, Huapache monocline; Fig. 5); at the contact of major facies changes (Fig. 3); and between the limestone reef and more dolomitic backreef and forereef beds (Fig. 4).

The caves of the Guadalupe Mountains characteristically contain large rooms and passages (many are >15 m in height and width) along major elevation levels, with separate levels connected by steeply dipping passages (e.g., Main Corridor, Carlsbad Cavern), vertical tubular pits (e.g., Bottomless Pit, Carlsbad Cavern), or enlarged vertical fissures (e.g., Cable Slot, Carlsbad Cavern). In places, walls of large rooms and passages truncate Stage 1 fissure caves, are honeycombed with Stage 2 spongework caves, or truncate Stage 3 thermal caves lined with dogtooth spar crystals. Cave passages/rooms end abruptly without breakdown collapse or major passage extensions, and the caves lack a clear genetic relationship to surface topography. Intersections of caves with the land surface (entrances) are random and have no apparent relationship to recharge or resurgence points, either ancient or modern. Welldeveloped surface karst landforms (e.g., sinkholes) are not abundant.

Distinctive deposits in Guadalupe Mountain caves are thick floor blocks of massive gypsum (CaSO₄•2H₂O) and thinner wall rinds of gypsum; native sulfur (S) deposits; and colorful, waxy endellite [Al₂Si₂O₅(OH)₄•2H₂O] clay deposits. Alunite

[K₂Al₆(SO₄)₄(OH)₁₂], natroalunite [Na₂Al₆(SO₄)₄(OH)₁₂], tyuyamunite [Ca(UO₂)₂(VO₄)₂•5-8H₂O], and metatyuyamunite [Ca(UO₂)₂(VO₄)₂•3-5H₂O] are other speleogenesis-related cave minerals (Mosch & Polyak 1996; Polyak & Güven 1996, 2000).

Stage 4 caves are a result of combined bathyphreatic and water-table development (Hill 1987). Water table (shallow-water phreatic) conditions were responsible for the horizontal development of caves along certain levels (e.g., Big Room, Carlsbad Cavern), and bathyphreatic (deep-water phreatic) conditions were responsible for the strong vertical development of these caves (e.g., Main Corridor, Carlsbad). None of the caves are vadose in origin, with the possible exception of Queen of the Guadalupes, which might be a vadose domepit. Cave sediment, unlike that in vadose caves, is sparse and where it does occur it is usually (but not always) a coarse silt to fine-grained sand derived directly from the dissolution of siliciclastic facies in the bedrock (e.g., Sand Passage, Carlsbad Cavern).

Origin. Stage 4 caves are hypogenic, formed by acids of deep-seated origin (e.g., sulfuric acid), in contrast to epigenic caves, which form in the near surface where carbonic acid is derived from CO₂ in the atmospheric and soil zones (Palmer 1991). Hypogenic karst displays no relationship to recharge through the overlying surface, and cave passages are typically ramiform, network, or spongework patterns (Palmer & Palmer 2000).

Stage 4 caves in the Guadalupe Mountains were dissolved primarily by sulfuric acid. The source of the sulfuric acid was H₂S derived from hydrocarbons within the Delaware Basin (Fig. 6). Alternatively, it could have come from oil fields in the north part of the basin, from the backreef, or from deep source rocks below the Capitan reef (DuChene 1986; Hill 1990). A number of different lines of evidence point to a sulfuric acid/hydrocarbon origin for Stage 4 caves (Hill 1987, 1990):

- (1) Massive gypsum blocks (up to 10 m high) and native sulfur deposits (up to thousands of kilograms) in these caves formed as by-products of a sulfuric acid mode of dissolution. Epigenic, carbonic-acid caves do *not* contain these types of deposits.
- (2) The low-pH, sulfuric-acid indicator minerals endellite (hydrated halloysite), alunite and natroalunite occur in these caves.
- (3) High uranium, radon, and the minerals tyuyamunite/metatyuyamunite in these caves are all indicative of a H₂S system where uranium (and vanadium) have precipitated along a redox boundary interface (Hill 1995).
- (4) Other sulfuric acid caves are known worldwide, and these are also associated with hydrocarbons. Some of these caves are actively forming today by a sulfuric acid mechanism; e.g., Cueva de Villa Luz, Tabasco, Mexico, is a sulfuric acid cave related to hydrocarbons in the Gulf of Campeche. A milky-white river, with dissolved gypsum and sulfur, flows from the cave, and sulfur crystals are growing in areas where drip water has a measured pH of 0-3 (Palmer & Palmer 1998;

Hose & Pisarowicz 1999). Sulfur isotope values for sulfur and gypsum in Cueva de Villa Luz (δ^{34} S = -26 to -22‰; CDT) are within the same range as the sulfur and gypsum in Guadalupe Mountain caves (Fig. 8).

(5) The isotopically light composition of the massive gypsum, sulfur, alunite and natroalunite deposits in Stage 4 caves (Fig. 8) is the most convincing evidence for a sulfuric acid origin related to hydrocarbons. Only biologically aided reactions such as occur with hydrocarbons could have produced the large isotopic fractionations found in these deposits. Gypsum and native sulfur deposits in Guadalupe Mountain caves are significantly enriched in 32 S, and depletions in δ^{34} S as great as -25.6‰ for gypsum and -25.8‰ for sulfur have been measured (Fig. 8). The same isotopically light signatures also characterize alunite and natroalunite (Polyak & Güven 1996; Fig. 8).

The sulfur isotope results are crucial to understanding the hypogenic process of speleogenesis that produced the large Stage 4 cave passages in the Guadalupe Mountains. The evidence provided by the isotopic data demonstrates that the cave gypsum could not have been derived from Castile anhydrite beds by the local pooling model of Bretz (1949) or by the mixing model of Queen et al. (1977). The average isotopic composition of Castile gypsum and anhydrite is +10.3% (Fig. 8). If the cave gypsum had precipitated amicrobially from Castile brines, as modeled by these authors, then the cave gypsum and Castile Formation gypsum and anhydrite should have virtually identical isotopic compositions. The sulfur isotope data also discount an origin from pyrite as proposed by Jagnow (1977). Sulfide minerals (mostly pyrite) in the Guadalupe Mountains range from $\delta^{34}S = -9.3$ to +12.6% (mean = -2.2% for 20 samples; Fig. 8). Since there is no significant isotopic fractionation involved in the leaching of sulfides (less than 1‰), it is logical to conclude that the isotopically lighter cave gypsum and sulfur (mean = -16.8% for 22 samples) could not have derived from this source. Instead, the isotopically light deposits implicate a hydrocarbon connection for these caves (Hill 1990).

Cave dissolution by sulfuric acid. Hydrogen sulfide, generated from hydrocarbon reactions in the basin or elsewhere, migrated into the surrounding Capitan reef and accumulated in structural and stratigraphic traps (Fig. 6). Where it met with oxygenated meteoric groundwater descending to or below the water table along dipping backreef beds or joints in the overlying land surface it formed sulfuric acid (Palmer & Palmer 2000):

$$H_2S + 2O_2 = 2H^+ + SO_4^2 \tag{1}$$

$$2H^{+} + SO_{4^{-}} + CaCO_{3} = Ca^{2+} + SO_{4^{2-}} + H_{2}O + CO_{2}$$
 (2)

The sulfuric acid produced in (1) dissolved the Capitan reef limestone to produce the cave void, caused gypsum to precipitate or replace the limestone as blocks or rinds, and generated CO₂ (2). According to this model, vertical tubes, fissures and pits in Guadalupe caves are interpreted as having formed along injection points for H₂S (bathyphreatic dissolution), and hori-

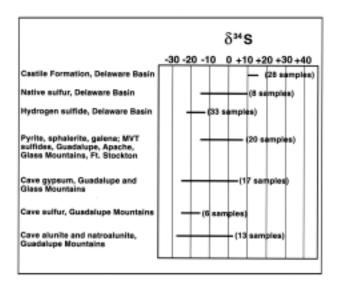


Figure 8. Range of sulfur isotope values for various types of deposits, Delaware Basin. Note that the cave gypsum and sulfur are significantly enriched in the light isotope of sulfur compared to the Castile Formation. The isotopically light composition of sulfur deposits in the basin (H₂S gas, native sulfur) and reef (sulfides and sulfur/gypsum cave deposits) resulted from bacterial sulfate reduction (BSR) reactions where sulfate solutions mixed with hydrocarbons to produce isotopically light hydrogen sulfide. Cave alunite and natroalunite values are from Polyak & Güven (1996). After Hill (1995).

zontal levels are interpreted as forming at the water table where dissolved oxygen was the most concentrated (water-table dissolution). This H₂S was also responsible for native sulfur deposits, which have been slowly oxidizing to gypsum when in the presence of meteoric water (Spirakis & Cunningham 1992; Hill 1995). A low-pH, sulfuric acid environment also caused clay minerals to reconstitute to endellite, alunite and natroalunite, and (ultimately) caused the precipitation of the secondary, later-stage, uranium-vanadium minerals tyuyamunite and metatyuyamunite. The above reactions (1) and (2) were most likely facilitated by microbial action. Microbes, from the time of speleogenesis until the present, have altered the geology of Guadalupe caves in ways that are just beginning to be discovered (Northup *et al.* 2000).

Age. The age of the Stage 4 sulfuric acid karst event is still somewhat controversial, but it appears that the beginning of Stage 4 dissolution may be somewhat older than the Pliocene-Pleistocene age ascribed by Hill (1987). Maximum uplift and tilting of the Guadalupe block is now believed to have occurred in the Miocene (20-5 Ma), which means that H₂S could have been migrating throughout the middle to late Tertiary with the potential for cave formation (K. Cunningham, pers. comm. 1995; Hill 1996).

Polyak et al. (1998) 40Ar/39Ar-dated the mineral alunite in

four Guadalupe caves, and established that these Stage 4 cave passages formed from about 12 Ma in the southwestern part of the reef (e.g., Virgin Cave) to about 4 Ma in the northeastern part of the reef (e.g., Carlsbad Cavern and Lechuguilla Cave). These absolute dates are very important because they correlate with the time of major uplift of the Guadalupe Mountains and the proposed time of migration of H₂S from the basin into the Capitan reef (Polyak & Provencio 2000). Since supergene alunite is known to form at or near the water table (Rye *et al.* 1992), the dates of Polyak *et al.* (1998) represent water-table development of the caves: bathyphreatic development would have been earlier or concurrent (but at a lower level).

BASIN AND RANGE PHASE - PLIOCENE

The large cave passages in the Guadalupe Mountains continued to form throughout the Pliocene (~5-2 Ma). During this time the discharge point for the Capitan aquifer was at Hobbs, New Mexico, ~110 km east of Carlsbad, rather than at Carlsbad as it is today (Hiss 1980). Therefore, water levels in Guadalupe caves during this time must have been at least partially controlled by the Hobbs discharge point. As canyons downcut into the uplifting Guadalupe Mountain block, cave passages were intersected and entrances formed (DuChene & Martinez 2000). Entrances allowed these caves to be inhabited by bats and other animals.

CENOZOIC (QUATERNARY)

PLEISTOCENE

By the Quaternary (~2-0 Ma), Basin and Range extension and uplift had decreased in the Guadalupe Mountain area, as had the geothermal gradient. The present-day geothermal gradient in the Delaware Basin is ~20°C/km as compared to ~40-50°C/km in the Miocene. The decrease in uplift and tilting in the Pleistocene was an important factor that could have halted the processes by which Stage 4 sulfuric acid caves formed.

Another late-stage impact on development of Guadalupe caves near the northeast end of the reef (e.g., Carlsbad and Lechuguilla) may have been a change in the hydrologic regime at ~600 ka when the Capitan aquifer began to discharge at Carlsbad Springs instead of at Hobbs (Bachman 1984). The relationship of cave development in the Guadalupe Mountains with respect to regional hydrologic events is still poorly understood, but it is known that Guadalupe caves must somehow have been related to past positions and levels of the ancestral Pecos River, and that the major cave levels are attributable to long periods of stability as defined by these former base levels. Dates on the cloud and folia linings in the lowest levels of Carlsbad Cavern (Lake of the Clouds) and Lechuguilla Cave (Lake of the White Roses) are >350 ka (uranium-series method; D. Ford, pers. comm.), and ~600 ka (electron spin resonance method; K. Cunningham, pers. comm.). Since cave clouds are believed to form in the shallow phreatic zone (Hill & Forti 1997), these dates could signify a time just before the water table dropped below the lowest cave level in response to the Hobbs-Carlsbad change in regional hydrologic regime (Hill 1996, 2000).

Sometime after Stage 4 cave passages became air-filled, they began to be decorated with travertine. The different speleothems and speleogens in Guadalupe caves are both diverse and noteworthy, and have been described by Hill (1987), DuChene (1997), Hill & Forti (1997), and Davis (2000). Pleistocene travertine deposition in Guadalupe caves appears to have occurred in two main episodes: around 600 ka and around the time of the Sangamon Interglacial (~170-70ka) (Hill 1987).

HOLOCENE

The Guadalupe Mountains area turned more arid in the Holocene (10 ka to present). This change in climate affected water percolation patterns and, thus, the deposition of travertine. Water percolation and entrance air-flow patterns, in turn, affected cave microclimates and the geochemistry of cave pools (Forbes 2000; Turin & Plummer 2000). Today, travertine is still actively forming in some caves (e.g., Lechuguilla), but is almost inactive in others (e.g., Carlsbad).

CONCLUSIONS

This paper is a synthesis of information that relates to the history of geologic events and cave development in the Guadalupe Mountains. In summary, these events are:

- (1) Late Permian. The Capitan reef and forereef facies and corresponding backreef and basinal facies were deposited in the Guadalupe Mountain area. The Guadalupe Mountains experienced their first uplift and exposure, and Stage 1 fissure caves formed along zones of weakness at the reef/backreef contact.
- (2) Mesozoic. The Guadalupe Mountain area remained stable and emergent just above sea level. The first "flushing out" of the Capitan reef produced Stage 2 spongework caves during limestone mesogenesis.
- (3) Late Cretaceous-Early Tertiary. The Laramide Orogeny uplifted the Guadalupe Mountain area at least 1.2 km above sea level. Stage 2 spongework caves probably enlarged, some may have been lined with calcite spar.
- (4) Oligocene-Miocene. Trans-Pecos volcanism caused the Delaware Basin-Guadalupe Mountain area to heat up. This initiated the maturation and migration of hydrocarbons, and created a pattern of convective hydrothermal water circulation in the Capitan reef. Stage 3 thermal caves formed; some may have been lined with calcite spar.
- (5) Miocene-Pleistocene. Tilting of the Delaware Basin eastward caused hydrocarbons to react with anhydrites in basinal rock to form H₂S. The main uplift of the Guadalupe Mountain block further caused this H₂S to migrate into the Capitan reef and there to become oxidized to sulfuric acid. This acid dissolved out the large cave passages and produced, as speleogenetic by-products, the gypsum blocks/rinds, native sulfur, endellite, and alunite found in these caves. Air-filled

parts of the caves became decorated with travertine and inhabited by animals.

(6) Holocene. The arid climate caused a decline in the amount of travertine deposition in Guadalupe caves. Cave microclimate and pool chemistry was affected by entrance air flow and water percolation patterns in the vadose zone.

ACKNOWLEDGMENTS

I thank Art Palmer, Peg Palmer, and Donald Davis for reviewing the manuscript. I also acknowledge Unocal Corporation for redrafting some of the figures of Hill (1996).

REFERENCES

- Bachman, G.O. (1984). Regional geology of Ochoan evaporites, northern part of Delaware Basin. *New Mexico Bureau of Mines and Mineral Resources Circular 184*: 22 pp.
- Bretz, J H. (1949). Carlsbad Caverns and other caves of the Guadalupe block, New Mexico. *Journal of Geology* 57 (5): 447-463
- Barker, C.E. & Pawlewicz, M.J. (1987). The effects of igneous intrusions and higher heat flow on the thermal maturity of Leonardian and younger rocks, western Delaware Basin, Texas. In Cromwell, D.W. & Mazzullo, L. (eds.). *Glass Mountains*. Society of Economic Paleontologists and Mineralogists Guidebook: 69-83.
- Bögli, A. (1980). *Karst hydrology and physical speleology*: New York, Springer-Verlag: 284 pp.
- Davis, D.G. (2000). Extraordinary features of Lechuguilla Cave, Guadalupe Mountains, New Mexico. *Journal of Cave and Karst Studies* 62(2): 147-157.
- Dublyansky, Y.V. (1995). Speleogenetic history of Hungarian thermal karst. *Environmental Geology* 25: 24-35.
- DuChene, H.R. (1986). Observations on previous hypotheses and some new ideas on cavern formation in the Guadalupe Mountains. In Jagnow, D.H. (ed.). *National Speleological Society Convention Guidebook, Tularosa, NM*: 96-100.
- DuChene, H.R. (1997). Lechuguilla Cave, New Mexico, U.S.A. In Hill, C.A. & Forti, P. Cave minerals of the world, 2nd ed., Huntsville, AL, National Speleological Society:343-350.
- DuChene, H.R. (2000). Bedrock features of Lechuguilla Cave, Guadalupe Mountains, New Mexico. *Journal of Cave and Karst Studies* 62(2): 109-119.
- DuChene, H.R. & Martinez, R. (2000). Post-speleogenetic erosion and its effect on cave development in the Guadalupe Mountains, New Mexico and west Texas. *Journal of Cave and Karst Studies* 62(2): 75-79.
- Esteban, M. & Pray, L.C. (1983). Pisoids and pisolite facies (Permian), Guadalupe Mountains, New Mexico and West Texas. In Peryt, T.M. (ed.). *Coated grains*. Berlin, Springer-Verlag: 503-537
- Forbes, J.R. (2000). Geochemistry of Carlsbad Cavern pool waters, Guadalupe Mountains, New Mexico. *Journal of Cave and Karst Studies* 62(2): 127-134.
- Ford, D.D. & Ewers, R.O. (1978). The development of limestone cave systems in the dimensions of length and depth. *Canadian Journal of Earth Sciences 15 (11)*: 1783-1798.
- Haneef, M. (1993). Lithofacies and depositional environment of Altuda, Capitan and Tessey Formations (Permian), Glass

- *Mountains, West Texas.* Unpublished MS Thesis, Sul Ross State University, Alpine, Texas: 208 pp.
- Hill, C.A. (1987). Geology of Carlsbad Cavern and other caves in the Guadalupe Mountains, New Mexico and Texas. New Mexico Bureau of Mines and Mineral Resources Bulletin 117: 150 pp.
- Hill, C.A. (1990). Sulfuric acid speleogenesis of Carlsbad Cavern and its relationship to hydrocarbons, Delaware Basin, New Mexico and Texas: *American Association of Petroleum Geologists Bulletin* 74(11): 1685-1694.
- Hill C.A. (1995). Sulfur redox reactions, native sulfur, Mississippi Valley-type deposits and sulfuric acid karst, Delaware Basin, New Mexico and Texas. *Environmental Geology* 25: 16-23.
- Hill, C.A. (1996). Geology of the Delaware Basin: Guadalupe, Apache and Glass Mountains, New Mexico and West Texas. Society of Economic Paleontologists and Mineralogists, Permian Basin section, Publication no. 96-39: 480 pp.
- Hill, C.A. (1999a). Origin of caves in the Capitan. In Saller, A.H., Harris, P.M., Kirkland, B.L., & Mazzullo, S.J. (eds.), Concepts in sedimentology and paleontology: Geologic framework of the Capitan Reef: Society of Economic Paleontologists and Mineralogists, Special Publication no. 65: 211-222.
- Hill, C.A. (1999b). Reevaluation of the Hovey Channel in the Delaware Basin, West Texas. *American Association of Petroleum Geologists Bulletin 83*(2): 277-294.
- Hill, C.A. (2000). Sulfuric acid, hypogene karst in the Guadalupe Mountains of New Mexico and west Texas, U.S.A. In Klimchouk, A., Ford, D.C., Palmer, A.N., & Dreybrodt, W. (eds.). Speleogenesis: Evolution of karst aquifers: Huntsville, AL, National Speleological Society: 309-316.
- Hill, C.A. & Forti, P. (1997). *Cave minerals of the world*. 2nd ed.. Huntsville, AL, National Speleological Society: 463 pp.
- Hiss, W.L. (1980). Movement of ground water in Permian Guadalupian aquifer systems, southeastern New Mexico and western Texas. In Dickerson, P.W. & Hoffer, J.M. (eds). *Trans-Pecos Region*: New Mexico Geological Society Guidebook, 31st Field Conference: 289-294.
- Horak, R.L. (1985). Tectonic and hydrocarbon maturation history in the Permian Basin. *Oil and Gas Journal* 83 (21): 124-125.
- Hose, L.D. & Pisarowicz, J.A. (1999). Cueva de Villa Luz, Tabasco, Mexico: Reconnaisance study of an active sulfur spring cave and ecosystem: *Journal of Cave and Karst Studies* 6 (1): 13-21.
- Jagnow, D.H. (1977). Geologic factors influencing speleogenesis in the Capitan Reef Complex, New Mexico and Texas. Unpublished M.S. Thesis, University of New Mexico, Albuquerque: 197 pp.
- Jagnow, D.H., Hill, C.A., Davis, D.G., DuChene, H.R., Cunningham, K.I., Northup, D.E. & Queen, J.M. (2000). History of sulfuric acid theory of speleogenesis in the Guadalupe Mountains, New Mexico and west Texas. *Journal of Cave and Karst Studies* 62(2): 54-59.
- King, P.B. (1930). *The Geology of the Glass Mountains*. Bureau of Economic Geology, University of Texas at Austin, pt. 1, no. 3038: 167 pp.
- King, P.B. (1948). *Geology of the southern Guadalupe Mountains, Texas*: U.S. Geological Survey Professional Paper 215: 183 pp.
- Lundberg, J., Ford, D.C. & Hill, C.A. (2000). A preliminary U-Pb date on cave spar, Big Canyon, Guadalupe Mountains, New Mexico, USA. *Journal of Cave and Karst Studies* 62(2): 144-146.
- Melim, L.A. (1991). The origin of dolomite in the Permian (Guadalupian) Capitan Formation, Delaware Basin, west Texas and New Mexico—Implications for dolomitization models: Unpublished PhD dissertation, Southern Methodist University, Dallas, Texas: 200 pp.

- Melim, L.A. & Scholle, P.A. (1989). Dolomitization model for the forereef facies of the Permian Capitan Formation, Guadalupe Mountains, Texas-New Mexico. In Harris, P.M. & Grover, G.A. (eds.). Subsurface and outcrop examination of the Capitan shelf margin, northern Delaware Basin. Society of Economic Paleontologists and Mineralogists, Workshop no. 13, San Antonio, Texas: 407-413.
- Mosch, C.J. & Polyak, V.J. (1996). Canary-yellow cave precipitates: Late-stage hydrated uranyl vanadate, uranyl silicate, and iron sulfate cave minerals (abs.). *Journal of Cave and Karst Studies* 58(3): 209.
- Northup, D.E., Dahm, C.N., Melim, L.A., Spilde, M.N., Crossey, Lavoie, K.H., Mallory, L.M., Boston, P.J., Cunningham, K.I. & Barns, S.M. (2000). Evidence for geomicrobiological interactions in Guadalupe caves. *Journal of Cave and Karst Studies* 62(2): 80-90.
- Palmer, A.N. (1991). Origin and morphology of limestone caves. Geological Society of America Bulletin 103: 1-21.
- Palmer, A.N., & Palmer, M.V. (1998). Geochemistry of Cueva de Villa Luz, Mexico, an active H₂S cave (abs): *Journal of Cave and Karst Studies* 60(3): 188.
- Palmer, A.N & Palmer, M.V. (2000). Hydrochemical interpretation of cave patterns in the Guadalupe Mountains, New Mexico. *Journal* of Cave and Karst Studies 62(2): 91-108.
- Polyak, V.J. & Güven, N. (1996). Mineralization of alunite, natroalunite, and hydrated halloysite in Carlsbad Cavern and Lechuguilla Cave, New Mexico. *Clays and Clay Minerals* 44 (6): 843-850.
- Polyak, V.J. & Güven, N. (2000). Clays in caves of the Guadalupe Mountains, New Mexico. *Journal of Cave and Karst Studies* 62(2): 120-126.
- Polyak, V.J., McIntosh, W.C., Güven, N. & Provencio, P. (1998). Age and origin of Carlsbad Cavern and related caves from 40Ar/39Ar of alunite. *Science* 279: 1919-1922.
- Polyak, V.J. & Provencio, P.P. (2000). Summary of the timing of sulfuric acid speleogenesis for the Guadalupe caves based on ages of alunite. *Journal of Cave and Karst Studies* 62(2): 72-74.
- Queen, J.M., Palmer, A.N. & Palmer, M.V. (1977). Speleogenesis in the Guadalupe Mountains, New Mexico—gypsum replacement of carbonate by brine mixing. Proceedings, 7th International Congress of Speleology, Sheffield, United Kingdom: 332-336.
- Rye, R.O., Bethke, D.M. & Wasserman, M.O. (1992). The stable isotope geochemistry of acid sulfate alteration. *Economic Geology* 87(2): 225-262.
- Scholle, P.A., Ulmer, D.S. & Melim, L.A. (1992). Late-stage calcites in the Permian Capitan Formation and its equivalents, Delaware Basin margin, west Texas and New Mexico—Evidence for replacement of precursor evaporites. Sedimentology 39: 207-234.
- Spirakis, C.S. & Cunningham, K.I. (1992). Genesis of sulfur deposits in Lechuguilla Cave, Carlsbad Caverns National Park, New Mexico. In Wessel, G. & Wimberley, B. (eds.). Native sulfur development in geology and exploration. Proceedings of Society for Mining, Metallurgy and Exploration, American Institute of Mining, Metallurgical, and Petroleum Engineers, Phoenix, AZ: 139-154.
- Turin, H.J. & Plummer, M.A. (2000). Lechuguilla Cave pool chemistry, 1986-1999. *Journal of Cave and Karst Studies* 62(2): 135-143.
- Wood, J.W. (1968). Geology of Apache Mountains, Trans-Pecos Texas. Bureau of Economic Geology, University of Texas at Austin: 32 pp., Text accompanying Geologic Quadrangle map no. 35.