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# HISTORY OF THE SULFURIC ACID THEORY OF SPELEOGENESIS IN THE GUADALUPE MOUNTAINS, NEW MEXICO

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*The history of events related to the sulfuric acid theory of cave development in the Guadalupe Mountains, New Mexico, USA, is traced from its earliest beginnings to the present. In the 1970s and early 1980s, when this hypothesis was first introduced, the reaction was one of skepticism. But as evidence mounted, it became more accepted by both the speleological and geological communities. Nearly 30 years after it was introduced, this theory is now almost universally accepted. In the last decade, the sulfuric acid theory of Guadalupe caves has been applied to other caves around the world. It has also impacted such diverse fields as microbiology, petroleum geology, and economic ore geology. This theory now stands as one of the key concepts in the field of speleology.*

The caves of the Guadalupe Mountains are located in southeastern New Mexico, near the city of Carlsbad. More than 300 caves are known in the Guadalupes, the most famous being Carlsbad Cavern and Lechuguilla Cave. The caves are believed to have formed by an unusual mode of speleogenesis–one involving sulfuric acid. This theory, as currently understood, is that hydrogen sulfide leaked upward along fractures from hydrocarbon (oil and gas) deposits in the nearby Delaware Basin. Upon reaching oxygenated meteoric groundwater in the Capitan aquifer, sulfuric acid formed, dissolving large voids in the rocks of the Capitan Reef Complex at or below the water table. Cave deposits that are related to this mode of speleogenesis are gypsum blocks and rinds (Fig. 1), native sulfur (Fig. 2), and the minerals endellite (hydrated halloysite) (Fig. 3), alunite, natroalunite, aluminite, hydrobasaluminite, tyuyamunite, and metatyuyamunite.

The topic of this paper is how the theory of a sulfuric acid speleogenesis developed in the Guadalupes, and who the key people were in this process. Only those events or people directly related to the sulfuric acid aspects of cave development will be discussed, although many other important geologic, mineralogical, hydrologic, and biological studies have been done in these caves. This paper is an expanded version of previous presentations given by Jagnow (1986, 1996, 1998).

## Pre-Sulfuric Acid Theory: (1920-1969)

The first geologist to study any Guadalupe cave was Willis T. Lee (1924, 1925a,b), although his publications were primarily of a popular nature. The first technical geologic study was done by J Harlan Bretz, who throughout the summer of 1948 with his dog (R. Riley, Bretz's daughter, pers. comm. 1984), inspected the passages of Carlsbad Cavern and other caves in the Guadalupe Mountains (New, Cottonwood, Black, Hidden, Mudgetts, and McKittrick). Bretz published his now classic *Carlsbad Caverns and other caves of the Guadalupe Mountains, New Mexico* in 1949, wherein he proposed the theory of a phreatic origin for these caves. But Bretz was mystified by the gypsum blocks in Carlsbad and McKittrick, calling them "gypsum flowstone" and stating (p. 454): "It seems that the gypsum can only be the consequence of local pooling during the vadose history, recording temporary conditions when sulfate alone was precipitated. The local source may have been the Permian (Castile) gypsum both outcropping and known in wells close to the base of the near by scarp and higher than these cave chamber floors."

Other investigators, following Bretz's lead, attributed the massive gypsum in the caves to a late-stage back-up of water where the source of the cave gypsum was the Castile Formation of the Delaware Basin (Black 1954; Gale 1957;

**Figure 1 (Top Left). Finely laminated (varved) structure in a gypsum block, Texas Trail, Big Room, Carlsbad Cavern. Photo by Dave Jagnow.**

**Figure 2 (Center Left). Massive sulfur deposits overlain by gypsum, then later penetrated by calcite stalactites, near Ghost Town (GDVB Survey), Lechuguilla Cave. Photo by Larry McLaughlin.**

**Figure 3 (Bottom Left). Blue-green endellite in Endless Cave. Largest piece of endellite is about 3 cm across. Photo by Peter and Ann Bosted.**

**Figure 4 (Top Right). Photo of Stephen Egemeier (left).**

**Figure 5 (Center Right). Speleologists Donald Davis, Michael Queen, Carol Hill, and Dave Jagnow at the Eighth International Congress post-convention field trip at Carlsbad Cavern in August 1981. Photo by Ronal Kerbo.**

**Figure 6 (Bottom Right). Diana Northup (left) and Penny Boston (right) collecting a sample of corrosion residue.**

Good 1957; Sanchez 1964; Bullington 1968). Davies & Moore (1957) also reported the presence of the mineral endellite in Carlsbad Cavern.

### SULFURIC ACID THEORY: FIRST DECADE (1970-1979)

Nearly 30 years elapsed before Bretz (1949) was challenged. Stephen Egemeier, in a 1971 report to Carlsbad Caverns National Park, briefly suggested that the large rooms of Carlsbad may have been dissolved by sulfuric acid. Egemeier (fig. 4) based his suggestion on the work he was doing for his PhD dissertation on the Kane Caves in Wyoming (Egemeier 1973).

In 1971-1973, David Jagnow undertook field work in the Guadalupes for his Masters thesis and, independent of Egemeier, also proposed a sulfuric acid origin for these caves. Jagnow (1977, 1978, 1979) attributed the source of sulfuric acid to the oxidation of pyrite in the Yates Formation, basing his model on the work he had done with David Morehouse in the Galena Limestone caves around Dubuque, Iowa (Morehouse 1968). Jagnow recognized that the massive gypsum deposits in Guadalupe caves were the end product of a sulfuric acid reaction.

Also at this time, Donald Davis–who had caved in the Guadalupe Mountains since 1960 and had seen Egemeier's 1971 report in the files of Carlsbad Caverns National Park while working there as a guide–began to consider the subject of sulfuric acid speleogenesis. The earliest published recognition of native sulfur in any Guadalupe cave (Cottonwood) proposed that sulfur was connected in origin to hydrocarbons. Davis (1973: 94) stated: "Petroleum and sulfate rocks, particularly gypsum and anhydrite, are plentiful (in the Guadalupe area)…I assume that the $H_2S$ was mobile in the groundwater and that its hydrocarbon source may have been either near or remote…the dense Yates sandstone just above the cave may have had a capping effect (for $H_2S$)".

Also in 1973, J. Michael Queen produced the first strong evidence that gypsum had replaced calcite and dolomite over a scale of tens of meters in Guadalupe caves. Queen, along with Art and Peg Palmer (Queen *et al.* 1977), explained the origin of this gypsum replacement by a brine mixing mechanism, where replacement supposedly took place at the interface between fresh water and hypersaline phreatic water bodies. The "brines" were believed to be derived from gypsum and halite units of the Castile Formation in the nearby Delaware Basin. Later, Queen (1981, 1994) considered that the reduction of sulfates could have taken place in anoxic brines beneath the fresh-water zone, in the same way as in seacoast aquifers, and that the mixing between fresh and saline waters could aid in speleogenesis. Queen was also of the opinion that the large cave passages dated from the Late Cretaceous-Early Tertiary Laramide uplift.

Davis in 1979, seeing conflicts and apparent inadequacies in the mechanisms proposed by Jagnow and by Queen *et al.*, first published a critique of Jagnow's pyrite theory, suggesting (citing Egemeier's previously neglected work) that $H_2S$ was a more significant source of sulfuric acid than pyrite. Davis (1980) then expanded this suggestion into a critical review of all the recent hypotheses of speleogenesis, and in this paper was the first to develop a coherent ascending-water model in which Guadalupe caves were viewed as having developed along rising limbs of deeply curving flow paths, where oxygenated meteoric water mixed with sulfidic brine which underwent additional oxidation at the air/water interface.

Concurrently, in the 1970s, Carol Hill was working on the mineralogy of Guadalupe caves. During the course of her mineralogical studies, Hill researched the endellite (hydrated halloysite) deposits in these caves (Fig. 3), and found from her readings that this mineral indicated the former presence of sulfuric acid. This origin corresponded to what Egemeier, Jagnow, and Davis had been hypothesizing, and, in late 1979, Hill had the first sulfur isotope determination performed on a sample of gypsum block collected from the Big Room, Carlsbad Cavern ($\delta^{34}S$ = -13.9‰). Hill immediately realized the importance of this analysis: the presence of isotopically light sulfur proved that the gypsum could not have been derived from the Castile Formation ($\delta^{34}S$ = +10.3‰, avg.), but had to have originated from hydrocarbons.

### SULFURIC ACID THEORY: SECOND DECADE (1980-1989)

Hill reported additional sulfur isotope analyses on gypsum and native sulfur in a manuscript she sent to Carlsbad Caverns National Park in 1980. She also presented a condensed paper of her data at the Eighth International Congress of Speleology in Bowling Green, Kentucky (Hill 1981), after which a number of Guadalupe researchers gathered at Carlsbad Cavern for a post-Congress field trip (Fig. 5). A short time later, Douglas Kirkland (1982) performed additional sulfur isotope analyses on the gypsum blocks of the Big Room.

In 1985, Stephen Egemeier died after a long illness, and his *Theory for the origin of Carlsbad Caverns* was posthumously published in 1987 with the help of the Palmers. Also in 1987, Hill published a lengthy bulletin on the *Geology of Carlsbad Cavern and other caves of the Guadalupe Mountains, New Mexico and Texas*. In this tome, Hill detailed the possible connection between the presence of sulfuric acid in the caves, with hydrocarbon and economic sulfur deposits in the Delaware Basin, and with Mississippi Valley-type (MVT) sulfide ore deposits in the reef. She also attributed the chert deposits in the Big Room of Carlsbad to a sulfuric acid mechanism. The fact that the New Mexico Bureau of Mines and Mineral Resources published Hill's work shows that this controversial theory was becoming accepted by the geological community.

In May of 1986, a breakthrough dig was made into inner Lechuguilla Cave. Lechuguilla was a virgin cave (beyond the first hundred meters) where all of the speleogenetic features remained pristine. This new discovery provided a unique opportunity to test and expand the ideas of a sulfuric acid speleogenesis model, so the thrust of cave research in the

Guadalupes changed in the late 1980s from Carlsbad to Lechuguilla. From 1986 until the present, Davis published numerous reports in *Rocky Mountain Caving* and elsewhere, documenting the mineralogical and geologic features that characterize a large sulfuric acid cave like Lechuguilla. Two papers from this time period that condense some of these observations related to a sulfuric acid speleogenesis are Davis (1988) and Davis *et al.* (1990).

In 1988, the Palmers began a geologic survey of Lechuguilla and other Guadalupe caves in order to help define the connection between the geomorphic features of the caves and past hydrologic and geochemical dissolution regimes. They also offered insights into the cave patterns present in sulfuric acid caves (Palmer 1991), and were the first to identify alunite, natroalunite, and dickite in Lechuguilla Cave (Palmer & Palmer 1992). Their geochemical/hydrological work from 1988 to the present is summarized in Palmer & Palmer (2000).

In late 1989, Kimberley (Kim) Cunningham of the U.S. Geological Survey initiated an ambitious cave-wide research program in Lechuguilla, utilizing both private and federal funding. This research program was multi-disciplinary and designed to attract investigators in the subdisciplines of cave geology, geochemistry, biology/microbiology, climatology /microclimatology, and paleontology, among others. Cunningham's efforts crossed many of these project lines (e.g., Cunningham & LaRock 1991). Those specifically related to the sulfuric acid theory involved a systematic determination of whole-rock sulfur isotope ratios and the concentration of gases and fluids in two-phase inclusions (Spirakis & Cunningham 1992). The consistent light isotopic ratios and the ubiquitous presence of light-chain aliphatic hydrocarbons suggested that the massive sulfur deposits had formed inorganically beneath the water table, probably in zones of favorable oxygen content (Cunningham *et al.* 1994).

## Sulfuric Acid Theory: Third Decade (1990-1999)

By the early 1990s the sulfuric acid theory had received wide recognition and acceptance among cavers and also by the geological community. This was, perhaps in part, due to Hill's (1990) paper in the *American Association of Petroleum Geologists Bulletin*, and to Palmer's (1991) paper in the *Geological Society of America Bulletin*, where he used Guadalupe Mountain caves as an example of a sulfuric acid-type hypogene speleogenesis.

In 1990, at the suggestion of Cunningham, Harvey DuChene submitted a proposal to Carlsbad Caverns National Park for a five-year inventory project on the mineralogy of Lechuguilla Cave. But, because of the desire of the National Park Service for a more comprehensive study, the scope of this project was expanded to include bedrock geology, paleontology, and speleogenetic features (DuChene 1996). Data on speleogenetic sulfur was published by DuChene in Cunningham *et al.* (1993, 1994), the mineralogical studies were summarized by DuChene (1997), and a description of bedrock features is included in this Symposium (DuChene 2000).

Late in 1992, shortly after the Palmers' find of alunite and natroalunite in Lechuguilla, Victor Polyak identified alunite and natroalunite in Carlsbad Cavern, and alunite in Virgin, Cottonwood, and Endless caves. Polyak, along with Cyndi Mosch (1995), then studied the uranium-vanadium minerals tyuyamunite and metatyuyamunite in Spider Cave, and Polyak, along with Paula Provencio (1998), discovered the minerals aluminite and hydrobasaluminite in Cottonwood Cave. All of these minerals are now considered to be speleogenetic in origin; i.e., related to a sulfuric acid mode of cave dissolution. Polyak *et al.* (1998) published $^{40}Ar/^{39}Ar$ dates on 10 samples of alunite in *Science*, establishing for the first time the approximate absolute ages of four elevation levels in five Guadalupe caves (12-4 Ma).

In the first half of the 1990s, Hill stopped working in the caves of the Guadalupe Mountains *per se*, choosing instead to try to understand how the caves fit into the overall regional geology. The results of Hill's regional geologic work were published in 1996 by the Society of Economic Paleontologists and Mineralogists (Permian Basin section): *Geology of the Delaware Basin–Guadalupe, Apache, and Glass Mountains, New Mexico and Texas*.

Because of the intriguing findings by Cunningham (1991a,b) of bacteria and fungi on mineral surfaces, Diana Northup began microbial studies in Lechuguilla in late 1989 and the early 1990s, utilizing techniques suggested by Clifford Dahm and Lauraine Hawkins (Northup *et al.* 1995; Cunningham *et al.* 1995). Northup's work, in turn, encouraged microbiologist Larry Mallory to begin studying cave bacterial communities that might be used to treat cancer and other diseases, and Penny Boston began studying caves as a parallel environment in the search for extraterrestrial life. Research findings in Lechuguilla eventually prompted Northup and coworkers to visit the Cueva de Villa Luz, Tabasco, Mexico to study microorganismal ecosystems operating in a sulfuric acid cave forming today (Hose & Pisarowicz 1999). In 1998, the team of Dahm, Boston, Northup and Laura Crossey was awarded a three-year, Life in Extreme Environments, National Science Foundation grant to study the geomicrobiological interactions within the caves corrosion residues (Fig. 6). The preliminary results of some aspects of this work are included in this Symposium (Northup *et al.* 2000). The fact that the National Science Foundation has supported their work in Lechuguilla Cave is confirmation that the sulfuric acid theory and related research has finally come of age.

## Conclusions

It has taken almost 30 years for the sulfuric acid theory of cave development to be accepted by the speleological and geological communities. What began as a "far-out" hypothesis in the 1970s has turned into a theory supported by a number of different lines of evidence–geologic, geochemical, mineralogical, and microbial. Now, at least six other caves or cave systems besides those in the Guadalupe Mountains of New Mexico are known to be, or are suspected of being, sulfuric acid caves: (1) the Kane caves, Wyoming, (2) Fiume-Vento Cave, Italy, (3) La Cueva de Villa Luz, Mexico, and (4) Las Brujas Cave, Argentina (Hill 2000); and in addition (5) the Kugitangtou caves, Turkmenistan (Klimchouk *et al.* 1995) and (6) the Redwall caves, Grand Canyon, Arizona (Hill *et al.* 1999). Also, the concept of $H_2S$ degassing of petroleum basins to produce sulfuric acid karst has been expanded to include the generation of hydrocarbon reservoirs (sulfuric acid oil-field karst; Hill 1995) and associated porosity (DuChene 2000); Mississippi Valley-type ore deposits (Hill 1994); and breccia pipe-type uranium deposits (Hill *et al.* 1999). It remains to be seen how this theory will affect other scientific disciplines in the future.

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