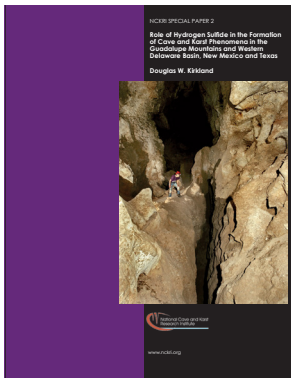


Douglas W. Kirkland

Role of hydrogen sulfide in the formation of cave and karst phenomena in the Guadalupe Mountains and western Delaware Basin, New Mexico and Texas.

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The caves of the Guadalupe Mountains are among the most spectacular in the world. Carlsbad Cavern, with the immense Big Room, and Lechuguilla Cave, the deepest cave in the U.S., are rightfully the most famous, but the area is riddled with hundreds of smaller caves distributed in a relatively narrow band (the 'cave belt') parallel to the Permian reef escarpment formed by the Capitan Limestone. Despite their iconic fame, a complete model for the speleogenesis of the Guadalupe caves has eluded researchers... until now.

The newest offering from the National Cave and Karst Research Institute, "*Role of Hydrogen Sulfide in the Formation of Cave and Karst Phenomena in the Guadalupe Mountains and Western Delaware Basin, New Mexico and Texas*" proposes a new model for speleogenesis and associated features. The author, Doug Kirkland, is not well known in the karst community, but has a long and distinguished record of studying evaporites, including the Permian evaporite deposits of the Delaware Basin. Accessing this broad background, this work also addresses the related topics of the origin of the native sulfur deposits in the basin and evidence for the anaerobic reaction of methane and sulfate as the primary driver of speleogenesis. The result is a complete and coherent model for the evolution of the karst features of the Guadalupe Mountains and surrounding area, which ties together a wide variety of data.

Leaning heavily on Palmer (2006, 2009), Kirkland starts by outlining the current speleogenesis model for the Guadalupe caves. Most workers agree these spectacular caves formed from the reaction of H_2S with O_2 above the water table, within the Capitan Formation and associated outer shelf facies. This reaction produced H_2SO_4 , a very strong acid, either through an intermediate S phase or more directly utilizing a biocatalyst. Sulfuric acid explains most of the unusual features of the Guadalupe Caves, including the unusually large rooms, the pattern of cave passages, and the presence of an assortment of minerals, including most notably gypsum, native sulfur, endellite, and alunite. In addition, the variable and negative isotopic values of the gypsum, first reported by Hill (1981) and Kirkland (1982), support a microbial origin for the H_2S precursor of that gypsum.

The primary controversy still surrounding Guadalupe speleogenesis is the origin of the H_2S . The two currently competing models, the *Basinal Model* of Hill (1987) and the *Shelfal Model* of DuChene and Cunningham (2006), differ in their source for the needed H_2S . The Basinal Model proposed a source in the basin to the east, where abundant castiles, discrete masses of diagenetic limestone, within the evaporites of the Castile Formation suggest H_2S generation via reaction with sulfate. Hill (1987) proposed migration of this H_2S through the Bell Canyon Formation, which interfingers with the Capitan foreereef. However, this model fails because it requires flow against the hydraulic gradient from the Castile Formation down into the underlying Bell Canyon. In addition, the Bell Canyon sands trend sub-parallel to the reef and would not channel flow to the cave belt. The Shelfal Model proposed instead that the H_2S originated in the shelf evaporites to the northwest and migrated downdip to the cave belt, consistent with the hydraulic gradient. According to Kirkland, the primary problem with this model is the absence of a sufficiently large source of H_2S for the quantity required for the amount of speleogenesis observed. The shelf sediments lack evidence, such as the castiles, of substantial H_2S generation.

To solve this controversy, Kirkland proposes a **Modified Basinal Model** where late Tertiary structural and thermal events triggered a series of relatively short-lived events in the adjacent basin that resulted in speleogenesis, castile formation, and the deposition of sulfur deposits. Kirkland then walks the reader through this series of events, carefully documenting each step. Kirkland's presentation provides enough background that the more casual reader should be able to follow the story. At the same time, a more advanced reader will be satisfied with the rigor of his arguments and thorough citation of relevant literature, both older and current.

Kirkland first summarizes the origin and stratigraphy of the Castile Formation and the overlying Salado, Rustler, and Dewey Lake formations. The interbedded anhydrite and halite of the Castile Formation and the way these beds terminate against the steep front of the Capitan reef are key to the model that follows. Kirkland proposes that aggressive artesian waters from the underlying Bell Canyon Formation entered the Castile during Late Tertiary uplift and propagated upward through free convective dissolution of the halite members. The slight structural dip of 1-2° to the east, and the relative insolubility of the anhydrite members (as compared to halite), produced channels that delivered these fluids to the Capitan. These fluids initially contained abundant methane derived from alteration of earlier formed oil during a Late Tertiary high heat flow event. Within the Castile Formation, a microbially mediated reaction of methane with sulfate resulted in the calcitization of the Castile sulfates. This reaction produced the large 'castile' masses of diagenetic limestone, and also generated large amounts of H₂S. The H₂S was then carried up dip along conduits at the base of anhydrite layers into the Capitan and shelf edge facies. There speleogenesis occurred at the water table when the H₂S reacted with atmosphere O₂ to produce H₂SO₄. Thus, Kirkland's model supports the existing model of speleogenesis by providing a large source of H₂S and documenting a viable pathway for its delivery to the cave belt in the Capitan and shelf edge facies.

Kirkland then turns his attention briefly to two related topics: the origin of native sulfur deposits to the east of the cave belt and a more detailed argument for methane, not oil, as the primary hydrocarbon source for the H₂S generated by microbes. The native sulfur deposits form in areas where the ascending methane-rich fluids followed fault-derived fractures through the Castile into the overlying Salado evaporites. There, according to Kirkland, H₂S was again generated, but reacted with O₂ in the phreatic zone to produce native sulfur within the diagenetic limestone instead of migrating into the more distant reef.

Although complex, the new modified basinal model proposed by Kirkland is coherent and compatible with the existing data, both from the caves and from the larger Delaware Basin region. The reader must be patient, as the careful explanations sometimes seem to wander off-topic. This patience will be rewarded, as each apparent digression eventually reveals more details on the way to a complete model. Although the larger stratigraphic picture is based on the classic early literature, the referencing and discussion are fully up-to-date in the more relevant sections related to speleogenesis. The figures are unsophisticated, with minimal color, so readers used to high-tech modern graphics may be tempted to discount them. However, each illustrates nicely the point being made and their simplicity often aids in understanding the complex ideas being presented.

Kirkland presents his model to "stimulate debating, challenging, and reasoning that results in improved knowledge of these extraordinary cave and karst features" (p. 4). In this, he has set the standard of discussion very high. His elegant model integrates the available data on tectonics, sedimentology, basin history, regional fluid flow, and speleogenesis into a satisfyingly complete narrative that is highly recommended for all interested readers.

References cited:

- DuChene H.R. & Cunningham K.I., 2006 - *Tectonic influences on speleogenesis in the Guadalupe Mountains, New Mexico and Texas*. In: Land L., Lueth V.W., Raatz W., Boston P. & Love D.L. (Eds.) - *Caves and Karst of Southeastern New Mexico*, New Mexico Geological Society Guidebook 57th Field Conference, p. 195-202.
- Hill C.A., 1981 - *Speleogenesis of Carlsbad Caverns and other caves in the Guadalupe Mountains*. In: Beck B.F. (Ed.) - *Proceedings of Eight International Congress of Speleology*, Bowling Green, Kentucky, **1**: 143-144.
- Hill C.A., 1987 - *Geology of Carlsbad Caverns and Other Caves in the Guadalupe Mountains, New Mexico and Texas*, New Mexico Bureau of Mines and Mineral Resources Bulletin **117**, 150 p.
- Kirkland D.W., 1982 - *Origin of gypsum deposits in Carlsbad Caverns, New Mexico*. *New Mexico Geology*, **4 (2)**: 20-21.
- Palmer A.N., 2006 - *Support for a sulfuric acid origin for caves in the Guadalupe Mountains, New Mexico*. In: Land L., Lueth V.W., Raatz W., Boston P. & Love D.L. (Eds.) - *Caves and Karst of Southeastern New Mexico*, New Mexico Geological Society Guidebook 57th Field Conference, p. 195-202.
- Palmer A.N., 2009 - *Cave Geology*. Cave Books, Dayton, 454 p.

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