NCKRI SPECIAL PAPER 2

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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Cover Photo: Rift in Left Hand Tunnel, Carlsbad Cavern, a long fissure with many loops and branches. At several places in the Cavern, such as this example, there are deep approximately linear rifts through which hydrogen sulfide-rich water once rose. Aided by bacteria, the hydrogen sulfide reacted with oxygen derived from air to produce sulfuric acid. The floor of this passage, which is exactly the same elevation as nearby parts of the floor of the Big Room of Carlsbad Cavern, apparently represents a period of water table stability during one of the latest episodes of cavern enlargement (Palmer et al., 2009) (Photo by A.N. Palmer).

FOREWORD

The National Cave and Karst Research Institute is pleased to publish Dr. Doug Kirkland's monograph on the role of hydrogen sulfide on speleogenesis in the Guadalupe Mountains and western Delaware Basin. Dr. Kirkland's work builds on his many years of research in southeastern New Mexico and west Texas, and provides the most comprehensive overview of cave and karst phenomena in the greater Delaware Basin region in almost 20 years. His work incorporates and summarizes decades of research by previous workers, combined with new ideas he has developed on speleogenesis in the Guadalupe Mountains. We feel confident that this publication will serve as an important source book and milestone for future research in the Delaware Basin region for many years to come.

Lewis Land
Managing Editor
February 19, 2014

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ABSTRACT

This monograph provides a theory for multiple stages of speleogenesis related to production, transportation, and oxidation of hydrogen sulfide in the western Delaware Basin and along the margin of the basin in the vicinity of the Guadalupe Mountains (southeastern New Mexico, USA).

Large caves in the Guadalupe Mountains formed during the late Miocene and early Pliocene (~12-4 Ma ago). They originated dominantly from sulfuric acid (H_2SO_4), a powerful cave-forming agent that dissolved both limestone of an ancient sponge-algal reef—the Capitan Formation (Middle Permian; ~270-260 Ma ago)—and limestone and dolomite of age-equivalent, near-back-reef (shelfal) strata. The reef-front formed the boundary between the Guadalupe Mountains to the northwest and the Delaware Basin to the southeast.

The strong acid was produced as dissolved oxygen (O_2) from the earth's atmosphere reacted with aqueous hydrogen sulfide (H_2S) from the adjacent basin. The H_2S originated within and migrated from the Castile Formation (earliest Late Permian, ~260.0-259.8 Ma ago) because of the influence of two overlapping Late Tertiary events:

- transient high-heat flow, particularly in the western Delaware Basin, and
- eastward uniform tilting (ultimately by 1° to 2°) of the huge paleo-Guadalupe tectonic block (including the mountains and much of the basin).

The Castile before extensive Late Tertiary dissolution extended throughout the basin and consisted of thick (tens of meters), remarkably persistent, alternating beds of halite (NaCl) and anhydrite ($CaSO_4$).

Late Miocene artesian groundwater flowed within Permian aquifers eastward down the sporadically rising tectonic block. Much groundwater then rose along fractures generated or regenerated during the tilting and dissolved Castile evaporites at hundreds of local sites up to ≈30 km east of the shelf edge. Free convective flow resulted. Castile halite, in particular, became the vehicle of its own dissolution. To replace the sinking brine, the least dense, least saline, most solutionally aggressive groundwater persistently rose to the highest accessible elevation. The groundwater dissolved chambers vertically upward through thick-bedded halite until the voids contacted the smooth, intact base of a bed of Castile anhydrite (solubility ~1/140 of that of halite), all beds of which dipped uniformly eastward by <1-2°. The conduits, except for their anhydritic ceiling, were confined to the uppermost parts of halite beds and they are hypothesized to have been narrow (< ≈30 m), low (< ≈2 m), and elongated (≈30 km). They advanced westward by convective dissolution directly up the slight slope of the paleo-Guadalupe tectonic block. Many conduits eventually terminated at the nearly vertical face of the youngest-most Capitan paleo-reef or at the steep-to-shallow face of the youngest-most paleo-forereef, both of which were in side-by-side contact with beds of Castile anhydrite and halite.

Basinal stratal temperatures transiently increased shortly before and as the conduits were forming resulting in generation of billions of cubic meters of methane (CH_4). Much gaseous CH_4 ascended into the Castile evaporites at the same localities at which groundwater convectively rose and sank. The gas progressively dissolved within ambient water beneath a thick (~1 km) sealing cover of strata (chiefly red beds, carbonates, and evaporites) and reacted with SO_4^{2-} derived from dissolution of Castile anhydrite. The reaction, aided by enzymes of anaerobic microbes, generated many millions of metric tons of both aqueous H_2S and aqueous CO_2. The CO_2 reacted instantaneously with Ca^{2+}, liberated as $CaSO_4$ dissolved, replacing laminated, nodular, massive, and brecciated Castile anhydrite with permeable limestone. The anhydrite-encased limestone bodies, commonly with dimension, in plan, >30 m, formed at ~1000 scattered localities. Pressurized artesian groundwater transported the H_2S from the carbonate bodies into the conduits within overlying Castile halite. The groundwater then flowed up the homoclinal slope and by forced convection moved through fractures and pores of the Capitan Formation and adjacent shelfal carbonates, and descended to low levels because of a relatively high density imparted by dissolved halite.

The H_2S-charged, saline groundwater flowed sluggishly throughout the late Miocene and early Pliocene within a basin-margin carbonate aquifer that formed a narrow (~6 km) northeast-trending belt across the eastward-dipping paleo-Guadalupe tectonic block. The highest part of the belt, therefore, was to the far southwest. Here, west-to-

east-trending erosion initially removed the impermeable cover of mainly Salado and Rustler evaporitic strata (Late Permian; ~259.8-250.0 Ma ago) and groundwater initially fell allowing atmospheric O_2 to enter the uppermost level of incipient caves.

H_2S-H_2SO_4 speleogenesis occurred when H_2S degassed from cave pools and when atmospheric O_2 moved into the caves. The gaseous O_2 probably entered permeable carbonates that cropped out in southwestern highlands; it then descended laterally through fractures beneath sealing evaporites. The H_2S and O_2 dissolved within subaerial water on carbonate wall rocks and reacted completely (aided by bacterial enzymes) to form H_2SO_4. Then, over a span of ~8 Ma, each episodic uplift of the tectonic block resulted in further erosion of the cover, deeper descent of the groundwater table, further progression of speleogenesis southeastward along the belt, and deeper penetration of speleogenesis within carbonates of the cave belt.

Within 12 to ~50 km southeast of the cave belt, genetically related karstic processes formed deposits of native sulfur dispersed within biogenic limestone and encased within Castile and Salado anhydrite. The caves and the sulfur deposits owe their origin to a coincidence of essentially the same stratigraphic, tectonic, thermal, and biogenic events. The sulfur deposits occur along graben-bounding faults that breached both the Castile (~30% halite; ~0.5 km thick) and the directly overlying Salado (~85% halite; ~0.5 km thick) and extended to the surface. The faults guided hypogenic groundwater upward by forced convection, and during subsequent free convection, the returning brine locally increased the permeability of the steep fracture pathways through bedded anhydrite. Gaseous CH_4 migrated upward along the same pathways. It dissolved within water and reacted with SO_4^{2-} to generate porous $CaCO_3$ and, within at least three deposits, > 1,000,000 metric tons of H_2S.

Simultaneously, meteoric water flowing down the same pathways dissolved Salado halite (and gypsum) into which overlying Permian and Mesozoic strata collapsed forming large (up to many hectares), closed, karstic depressions. The dolines focused enormous volumes (up to many cubic kilometers) of saline, O_2-saturated (~2 to >4 mg/l) groundwater into the subsurface. The brine descended through the fault-tracking pathways along an inverted density gradient and discharged into underlying channel-fill sandstone. Where saline, O_2-bearing groundwater sinking along one course contacted relatively fresh H_2S-bearing groundwater rising along an adjacent course, elemental sulfur precipitated.

INTRODUCTION

The Guadalupe Mountains are located in southeastern New Mexico and west Texas (Fig. 1). Bounding the southeastern-facing front of the mountains, magnificently displayed in an escarpment, are a Middle Permian paleo-reef and its forereef—the Capitan Formation (Fig. 2). The reef escarpment extends ~65 km southwestward from near the city of Carlsbad, southeastern New Mexico, elevation ~960 m, to Guadalupe Peak, Trans-Pecos Texas, elevation 2,667 m, the highest summit in Texas (see DuChene and Martinez, 2000) (Fig. 3). The escarpment formed mainly during the last few million years as Upper Permian gypsum and halite in the Pecos River Valley just southeast of the reef eroded faster than the limestone reef and its partially dolomitized forereef. Directly northwest of the reef-escarpment in the Guadalupe Mountains of New Mexico are about 400 caves (Queen, 2009) of which more than 30 are major (Ford and Williams, 2007) including two of the world's largest, deepest, and most spectacular, Carlsbad Cavern (~50 km long, 315 m deep), and 5-6 km west of it, Lechuguilla Cave (~223 km long, 490 m deep). They are all relict having formed primarily in the late Miocene and early Pliocene, ~12 to ~4 Ma (million years) ago (Polyak et al., 1998) (Fig. 4).

Figure 1. Location of Guadalupe Mountains and Delaware Basin.

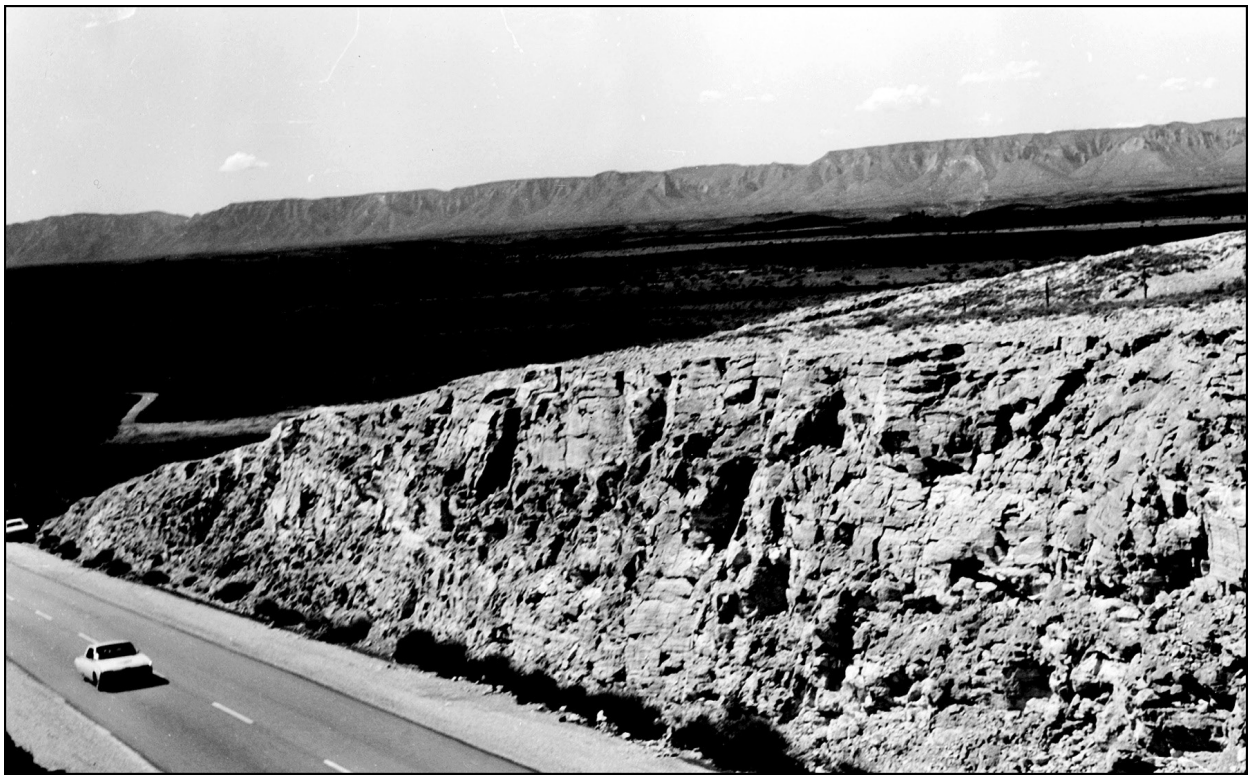

Figure 2. View to the far west showing in background the Capitan-reef escarpment—a prominent physiographic feature that extends southwest from near Carlsbad, New Mexico, to Guadalupe Peak, Texas; in foreground, road cut of Upper Permian Castile gypsum (Anhydrite III Member) along US Highway 62/180, 1.6 km north of the Texas-New Mexico boundary.

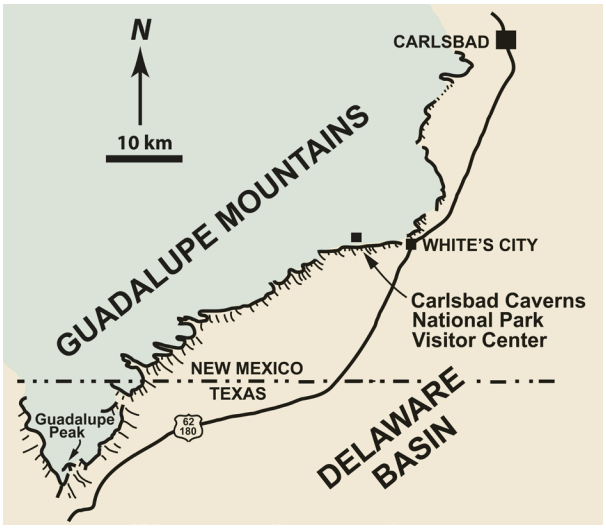

Figure 3. Location of reef escarpment, the approximate demarcation between the Delaware Basin to the southeast and the Guadalupe Mountains to the northwest.

Southeast of the mountain front in the adjacent west-central Delaware Basin several hundred meters beneath the surface are at least eight major accumulations or significant prospects of native sulfur (Smith, 1980)—three of which have a few million to many tens of millions of metric tons of original reserves. Exploration guidelines are few (Smith, 1980), and undiscovered deposits likely remain. One deposit is only 12 km southeast of Carlsbad Cavern. The native sulfur is dispersed within bodies of secondary limestone encased within Permian anhydrite. Karstic processes were an "intrinsically accompanying process" of the sulfur deposition (Klimchouk, 2007, p. 89).

A geographic and a genetic relationship exist between the caves of the Guadalupe Mountains and the large deposits of native sulfur. Both probably formed at about the same time; both probably owe their existence to a coincidence of essentially the same stratigraphic, thermal, biogenic, and tectonic events; and both probably owe their existence to great volumes of migrating methane (CH_4) that reacted with a virtually unlimited supply of sulfate anions (SO_4^{2-}). A by-product of the reaction—hydrogen sulfide—reacted with aqueous oxygen to form both sulfuric acid within the vadose environment of the caves and native sulfur within the phreatic environment of the sulfur deposits. Major differences between the genetic history of the caves and those of the sulfur deposits are chiefly the pathways followed by hydrogen sulfide from its environments of formation to its environments of oxidation and the mechanism by which the hydrogen sulfide was oxidized.

Objectives and Purpose of Investigation

Primary objectives are:

- to formulate a model for genesis of the hydrogen sulfide and for its transportation into caves of the Guadalupe Mountains;
- to formulate a model for genesis of the geographically and genetically associated huge subsurface karstic deposits of native sulfur, west-central Delaware Basin;
- to consider the similarities and differences between the two models; and
- to review evidence and arguments supporting aqueous CH_4 as the microbial foodstuff that resulted in the "waste-product," hydrogen sulfide.

A major purpose of the models is to stimulate further deliberations particularly those with a regional bent about the origin of both the caves and the sulfur deposits. The models can be considered both as "working hypotheses" and as "postulations," the consideration of which may stimulate debating, challenging, and reasoning that results in improved knowledge of these extraordinary cave and karst features.

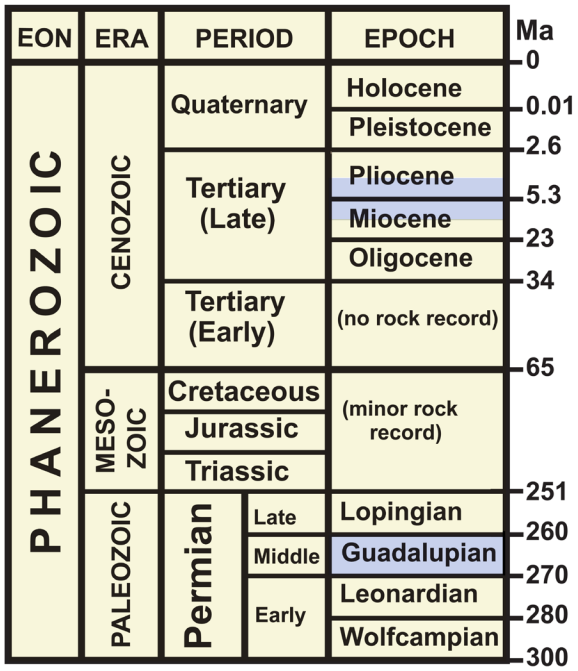

Figure 4. Time scale, Permian through Quaternary, for Delaware Basin and Guadalupe Mountains; the H_2S-H_2SO_4 caves occur within Middle Permian, Guadalupian age (shaded blue) carbonate rocks, but they formed about 250 million years later, in the Late Tertiary, specifically in late Miocene and early Pliocene (shaded blue) (Polyak et al., 1998).

SULFIDIC ORIGIN OF CAVES OF THE GUADALUPE MOUNTAINS

Geographic and Stratigraphic Setting of Caves

The locations of several of the more prominent caves of the Guadalupe Mountains are shown in Figure 5. Geographically, most large caves occur within a 6-km-wide band, referred to herein as the "cave belt," parallel to and directly northwest of the reef escarpment, and almost all caves reside within a 12-km-wide band (Hill, 1999) (Fig. 5). No long cave systems are known in the far western part of the Guadalupe Mountains (Fig. 1) (DuChene and Martinez, 2000). Stratigraphically, most cave passages occur within the Capitan reef and within an adjacent, correlative, shelfal carbonate—the Seven Rivers Formation—and most caves are close to the contact between these formations (Hill, 1987; DuChene and Martinez, 2000) (Fig. 6).

A Middle Permian sponge-algal reef, now represented by the Capitan Formation, extended for ~600 km around the perimeter of an ancient marine embayment (e.g., Adams and Frenzel, 1950; Newell et al., 1953). During its growth, the reef separated a lagoonal province situated on a surrounding shelf from the marine embayment, which coincided geographically with the structural Delaware Basin (Fig. 1). The reef grew upward and basinward as relative sea level rose (King, 1948). The upper forereef talus dipped steeply (maximum >50°; Mruk and Bebout, 1993) and the lower forereef talus dipped gently into the deep (hundreds of meters) marine embayment.

Three Middle Permian shelfal formations (in ascending order, the Seven Rivers, Yates, and Tansill) grade into the Capitan Formation (Fig. 6). Near the escarpment, the Capitan reef and forereef together have a maximum thickness of about 600 m (King, 1948, p. 61). The time-equivalent, marine, shelfal strata accumulated in shallow water (mostly <50 m). The Seven Rivers Formation consists primarily of bedded dolomite, and it is "possibly 600 ft" (183 m) thick near the reef (Hayes, 1964). The formation trends along an approximately 10-km-wide band parallel to and directly northwest of the reef. Near the reef, the Yates Formation consists of siliciclastics as

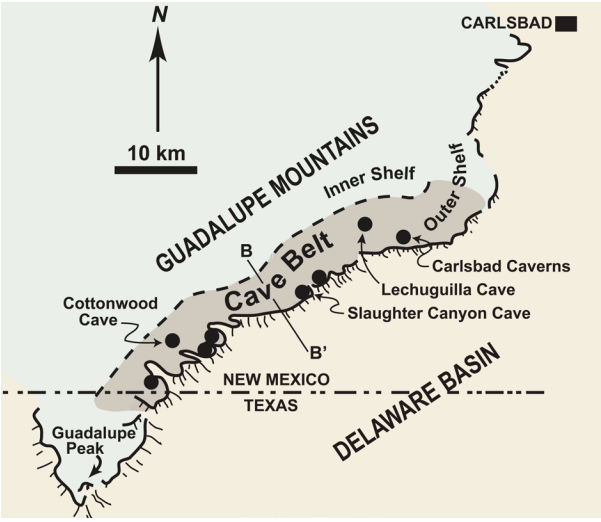

Figure 5. Location of cave belt, an elongate area 6 km wide just northwest of the escarpment that contains almost all caves in the Guadalupe Mountains (of which there are several hundred). Caves to the southwest are generally older than caves to the northeast (Polyak et al., 1998). Locations of selected large caves are shown by black circles (from Palmer and Palmer, 2000, their fig. 2); the outer shelf (the near back reef), as used in this study, is the zone between the outcropping Capitan reef and the northwestern margin of the cave belt. BB is line of cross section for Figure 20 (pre-tilting) and for Figure 25 (post-tilting).

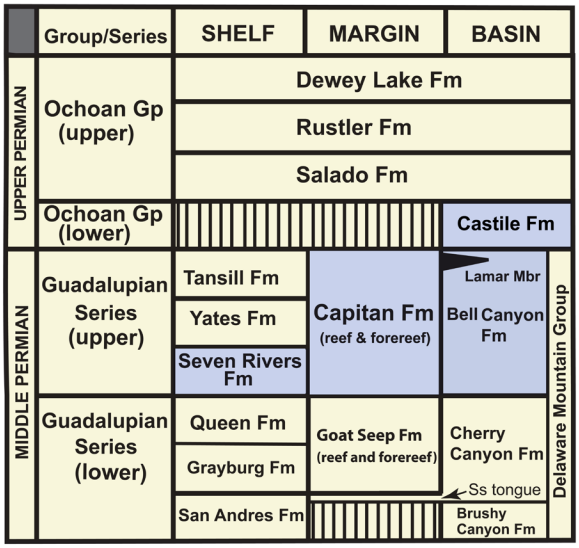

Figure 6. Stratigraphic chart of Middle and Upper Permian units (for shelf, margin, and basin) near the reef escarpment; vertical lines represent non-deposition and minor erosion; formations names that are colored blue played pivotal roles in the hypothesized process of cave formation. The Ochoan was originally established as a series equivalent to the Upper Permian (Adams et al., 1939). Lucas (2006) proposed that "Ochoa" and "Ochoan," because they represent "a very incomplete record of Late Permian," be considered, not a series, but a "lithostratigraphic group," which is how the terms have been used herein.

well as carbonates, and the Tansill Formation consists primarily of dolomite. Farther back from the reef the Seven Rivers, Yates, and Tansill consist of red beds and shallow-water evaporites, particularly gypsum.

A cross section transversally through the reef ~10 km north of White's City, New Mexico (Fig. 7), shows the stratigraphic relationship of the Capitan reef and forereef to the shelfal formations and to the time-equivalent Bell Canyon Formation. The cross-section also shows the stratigraphic relationship of the Capitan Formation to the youngest Upper Permian evaporites of the basin—those of the Castile Formation. The Castile consists predominantly of calcite-laminated anhydrite ($CaSO_4$) and anhydrite-laminated halite (NaCl), and the conformably underlying Bell Canyon consists dominantly of sandstone, siltstone, and intermittent tongues of limestone. Along the line of the cross section (Fig. 7), Castile evaporites are laterally juxtaposed against the steep-to-shallow face of the Capitan forereef and the steep face of the Capitan reef. The juxtaposition resulted from depositional onlap of the Late Permian Castile evaporites onto the Middle Permian Capitan reef and Capitan forereef. Although the Capitan is considered Middle Permian and the Castile Late Permian, the Castile evaporites—gypsum, halite, and calcite (or aragonite)—began to precipitate only a short time (probably within several thousand years) after the reef died from exposure and/or elevated salinity (e.g., Kirkland, 2003).

Peculiar Qualities and Unusual Origin of Caves

Caves of the Guadalupe Mountains have strange morphologies (e.g., Davis, 1980; DuChene, 1986; Hill, 1987, p. 22-23; 1996, p. 279; Palmer, 2006). They contain large rooms, many being >15 m in height and width, with flat floors and irregular vaulted roofs; and passages with abrupt and large-scale changes in cross-sectional area (Palmer and Palmer, 2000; Palmer, 2006). The immense size of rooms distinguishes caves in the Guadalupe Mountains from most other caves (Moore, 1960a). The Big Room of Carlsbad Cavern, with an area of ~3.3 hectares and a maximum height of nearly 100 m (Palmer et al., 2009), is among the largest chambers in the world (Fig. 8). Cave rooms and passages end abruptly without breakdown or major passage extensions and without relationship to surface topography; and cave entrances are random and form insignificant recharge points (e.g., Hill, 1996; p. 279; Hill, 1999). These various morphologic features are unlike those within caves created by aqueous carbonic acid (H_2CO_3), the acidic solvent that usually operates within carbonate terrain.

Moreover, caves of the Guadalupe Mountains harbor a strange suite of minerals unlike those found within the great majority of caves within carbonates (see Hill and Forti, 1986). Three caves contain native sulfur; particularly Lechuguilla Cave with several multi-ton deposits that amount to more sulfur than that within all

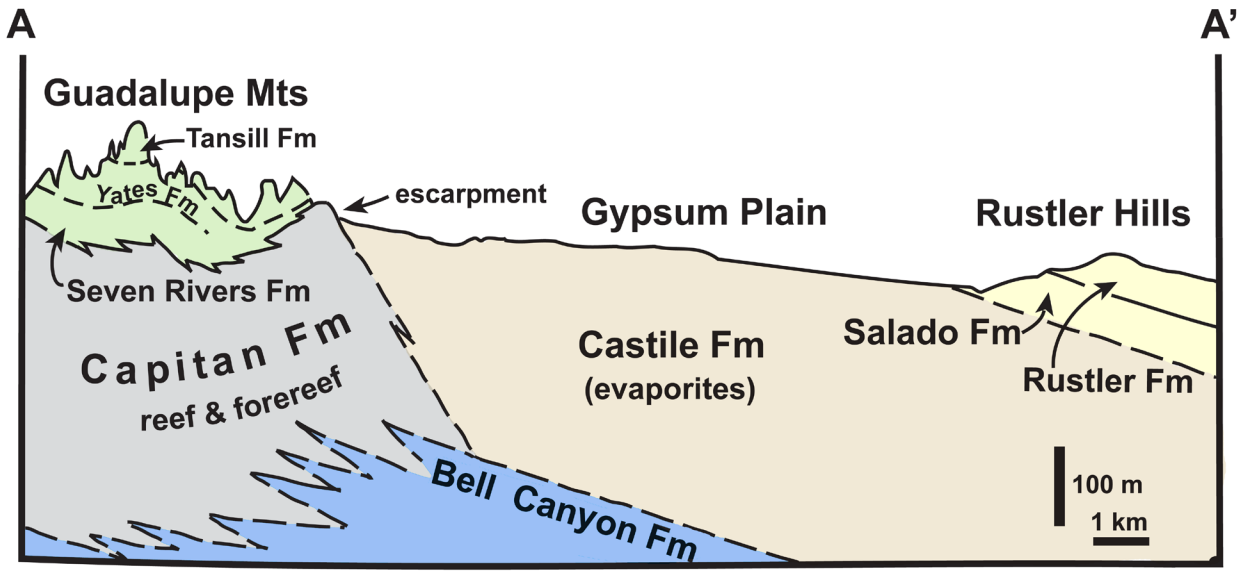

Figure 7. Vertically exaggerated cross-section from Guadalupe Mountains to Rustler Hills; the section crosses the escarpment where it is only a few tens of meters high; see Figure 13 for line of cross section; after Haigler (1962).

Figure 8. View of a small part of the Big Room in Carlsbad Cavern. Photo by A.N. Palmer.

other known caves of the world combined (Cunningham et al., 1993; Davis, 2000). Five caves contain the hydrated aluminosilicate mineral endellite [$Al_2Si_2O_5(OH)_4 \cdot 2H_2O$], and the rare sulfate minerals alunite [$KAl_3(SO_4)_2(OH)_6$] and natroalunite [$NaAl_3(SO_4)_2(OH)_6$] (e.g., Polyak and Provencio, 2000). Two caves contain the unstable mineral epsomite [$MgSO_4 \cdot 7H_2O$] (e.g., Hill, 1987, p. 131-132), and fourteen caves contain the common mineral gypsum [$CaSO4 \cdot 2H2O$], many deposits of which are massive (e.g., Hill, 1987, p. 43).

These unusual cave minerals formed either from reactions between sulfuric acid (H_2SO_4) and clay, dolomite, or limestone (e.g., Davis, 1980; Hill, 1987; Queen, 1994; Polyak and Güven, 1996; Palmer, 2006), or (for native sulfur) between hydrogen sulfide (H_2S) and oxygen (Spirakis and Cunningham, 1992; Cunningham et al., 1993). Furthermore, speleologists have concluded that rooms and passageways of the caves were dissolved not by the weak acid, H_2CO_3, but by the strong acid, H_2SO_4 (e.g., Egemeire, 1971; Jagnow, 1977; Davis, 1980; Hill, 1981, 1990, 2000; Kirkland, 1982; DuChene and McLean, 1989; Palmer and Palmer, 2000; Polyak and Provencio, 2001; Palmer 2006). Native sulfur and sulfuric acid both formed by reaction between the precursors O_2 and H_2S (e.g., Jagnow et al., 2000; Engel et al., 2004), but in the caves, almost all oxidation continued past the intermediate elemental-sulfur stage to yield H_2SO_4.

Role of Sulfuric Acid in Cave Formation

A general model has been formulated to explain how the caves of the Guadalupe Mountains formed dominantly from sulfuric acid (e.g., Egemeier, 1971; Buck et al., 1994; Engel et al., 2004; Hose and Macalady, 2006; Palmer, 2006). The model is based largely on investigations of active "H_2S caves" elsewhere in the world. A synopsis follows: Many passages and rooms in caves of these mountains have narrow fissures in their floors that descend several tens of meters along fractures, and pinch out at depth (Palmer et al., 2009) (Fig. 9). H_2S in solution within groundwater moved

Figure 9. Fissure in the Left Hand Tunnel of Carsbad Cavern. (see cover photo for full caption)

upward through fissures into the lower reaches of evolving caves of the ancestral Guadalupe Mountains (e.g., Palmer and Palmer, 2000; Kosa and Hunt, 2006b; DuChene and Cunningham, 2006). The groundwater table gradually fell, allowing atmospheric O_2—the other precursor of H_2SO_4—to enter the upper, subaerial parts of incipient caves through restricted pathways to the surface (see Hose and Macalady, 2006; Palmer, 2006). The H_2S, which was supplied to cave pools from below by diffusion and by flow of groundwater, degassed into the overlying cave atmosphere, and moved toward cave walls and ceilings by diffusion, thermal convection, and barometric winds (Hose and Macalady, 2006; Palmer, 2006). Gaseous H_2S and gaseous O_2 within the cave atmosphere then dissolved within drops and films of water on gypsum-coated cave walls and ceilings (Palmer, 2006). The dissolved gases reacted. One reaction pathway involved precipitation of native sulfur within the aqueous microenvironments. The reaction consumed the two gases, but the drops and films were re-charged with H_2S and O_2 from the cave atmosphere allowing more sulfur to form.

$$2H_2S + O_2 \rightarrow 2S + 2H_2O$$

Elemental sulfur, however, was a short-lived intermediary. The atmosphere of the caves supplied oxygen to the drops and films in relative abundance and at relatively high partial pressures (somewhat < 0.19 atmospheres), thus, additional oxidation, bio-catalyzed by sulfur-oxidizing bacteria, took place probably concomitantly with precipitation of sulfur to form sulfuric acid (e.g., Hose and Pisarowicz, 1999).

$$2S + 3O_2 + 2H_2O \rightarrow 2H_2SO_4$$

A second reaction pathway was possible. Certain sulfur-oxidizing bacteria form H_2SO_4 directly from aqueous H_2S and aqueous O_2, and they may have allowed the intermediate step (formation of native sulfur) to be bypassed (Palmer, 2009, p. 217).

The longer the drops and films of water remained exposed to the cave atmosphere, the more acidic they became (Palmer, 2006). The strong acid reacted wherever possible with limestone and dolomite. The reaction dissolved carbonates of cave walls and ceilings, precipitated gypsum, and released CO_2, which within water formed carbonic acid (H_2CO_3). This weak acid further enhanced speleogenesis by reacting with limestone to form calcium bicarbonate [$Ca(HCO_3)_2$] (see Palmer and Palmer, 2000), a substance that exists naturally only in aqueous solution. Expressed as equations, reaction of the acids with limestone and reaction of the by-products with water are:

$$H_2SO_4 + CaCO_3 + H_2O \leftrightarrow CaSO_4{\cdot}2H_2O + CO_2$$

$$CaSO_4{\cdot}2H_2O + H_2O \leftrightarrow Ca^{2+} + SO_4^{2-} + 3H_2O$$

$$CO_2 + H_2O \leftrightarrow H_2CO_3$$

$$H_2CO_3 + CaCO_3 \leftrightarrow Ca(HCO_3)_2 \leftrightarrow Ca^{2+} + 2HCO_3^-$$

Where a coat of gypsum (or less commonly, clay, silica, or biofilm) prevented sulfuric acid from reacting with carbonate walls and ceilings, aqueous sulfuric acid dropped onto cave floors or into cave pools where it reacted with limestone and dolomite commonly replacing the carbonate bedrock with gypsum (Queen, 1973; Queen et al., 1977; Hill, 1987; Buck et al., 1994; Palmer, 2006). The replacement occurred in a delicate balance with carbonate dissolution (Palmer and Palmer, 2000). Figure 10 shows vertical channels in a limestone block that formed by reaction of $CaCO_3$ with

aqueous H_2SO_4 dripping from the cave ceiling; a product of the reaction, gypsum, partially replaced the block (Palmer et al., 2009). Most gypsum, however, formed within cave pools not by replacement or by precipitation, but by recrystallization of gypsum that fell off cave walls into cave pools (Palmer, 2009, p. 219).

The water table within the cave belt progressively fell, and masses of cave gypsum became exposed, most of which were, in turn, dissolved within "fresh groundwater or within infiltrating seepage" (e.g., Palmer and Palmer, 2000). The ions Ca^{2+}, SO_4^{2-}, and, HCO_3^- were carried from the caves within groundwater.

Speleogenesis at any particular cave or cave level probably lasted for many tens-to-hundreds of thousands of years. H_2S-H_2SO_4 speleogenesis essentially ceased by mid-Pliocene, but vadose water continued to enlarge the caves by dissolving cave gypsum (Palmer, 2009, p. 224). Chiefly in the Pleistocene between 600,000-20,000 years ago, as estimated from $^{234}U/^{238}U$ ratios, groundwater from near the earth's surface infiltrated the caves (Ford and Hill, 1989). As the seeping water released CO_2 into the cave atmosphere, calcite precipitated and decorated the caves with speleothems.

Caves of the Guadalupe Mountains formed mainly above the water table, where water droplets formed

Figure 10. Deep rills in limestone column coated by gypsum (right, white), Far East of Lechuguilla Cave; height of column about 1 m. Photo by A.N. Palmer.

on cave surfaces chiefly by condensation. Alunite (potassium aluminum sulfate hydroxide) occurs within Carlsbad Cavern, Lechuguilla Cave, Cottonwood Cave (Fig. 5), and several nearby caves (Polyak et al., 2006). It requires a pH < ~4 to form. Such an acidic condition would have been "virtually impossible to achieve" in cave pools in contact with carbonate rock, but it could have been achieved readily within subaerial condensation (and within water of infiltration) on cave walls and ceilings (Palmer, 2006).

In addition, the sulfur isotopic composition of the cave gypsum (Fig. 12) generally falls within a range restricted to gypsum whose sulfate anions originated only from biogenic processes. The isotopic signature of the cave gypsum is consistent with cave formation above the water table by condensation-corrosion, a process in which the source of sulfur atoms would have been only from biogenic H_2S. The isotopic signature is inconsistent with cave formation beneath the water table in which the sulfur isotopic signature would have been altered significantly by sulfur atoms derived from sedimentary rocks (see Brown, 2006). The source of the adulterating sulfur (as sulfate anions) would have been a small fraction from dissolution of nearby Permian carbonates (see Staudt and Schoonen, 1995) and a large fraction from dissolution of nearby marine sulfate evaporites.

Cave formation above the water table is also supported by the large amount of gypsum in the caves compared to a relatively minor amount of native sulfur. Oxidation of H_2S above the water table was usually complete (yielding H_2SO_4, and subsequently, $CaSO_4 \cdot 2H_2O$), whereas oxidation of H_2S below the water table (i.e., within cave pools) was probably seldom complete, resulting in the intermediate oxidation product—native sulfur. Oxidation may have also been incomplete within drops and films of water where O_2 was overwhelmed by H_2S or where O_2 was in limited supply because passages and/or openings to atmospheric O_2 were restricted (personal communication, A.N. Palmer, 2013). The native sulfur shown in Figure 11 precipitated when the concentration of O_2 was somehow severely limited.

Attributes of Hydrogen Sulfide Transported to the Caves

Curious Sulfur Isotopic Composition

Speleologists working in Carlsbad Cavern before about 1980 believed that the voluminous gypsum in the cave came from nearby beds of marine gypsum

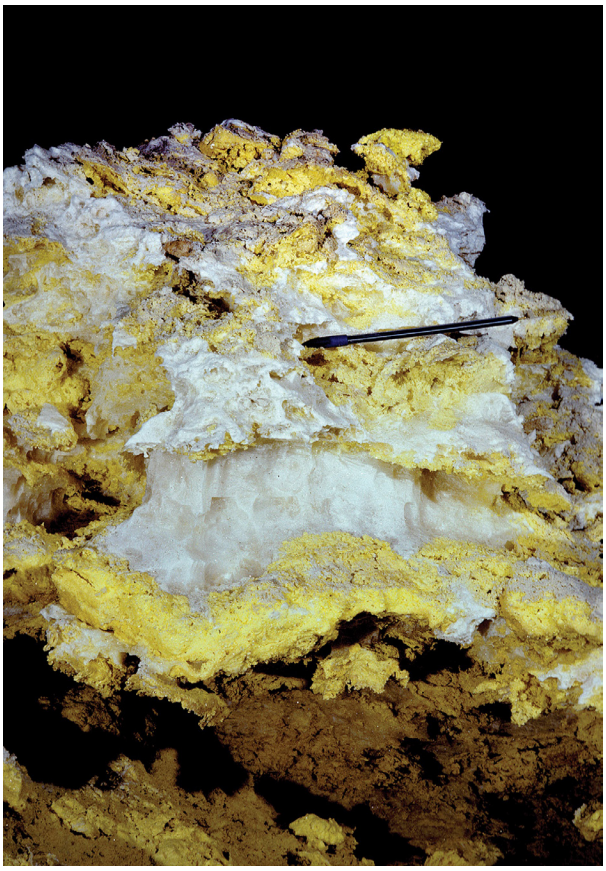

Figure 11. Native sulfur interlayered with gypsum; Southeastern Branch of the Voids area, Lechuguilla Cave (see pen for scale). Photo by A.N. Palmer.

(e.g., Bretz, 1949; Black, 1954; Good, 1957; Hayes, 1964; Bullington, 1968). These workers hypothesized that surface water and shallow groundwater dissolved Upper Permian marine gypsum of the nearby Delaware Basin and/or Middle Permian marine gypsum of the nearby inner shelf (far back reef) of the western Guadalupe Mountains (Fig. 13). Groundwater transported sulfate anions (SO_4^{2-}) and calcium cations (Ca^{2+}) from one or both of these sources into Carlsbad Cavern where gypsum precipitated within "local pooling" (Bretz, 1949) during "temporary conditions" and "as the waters cooled" (Good, 1957). Early students of Carlsbad Cavern communicated this account with hesitation, but they offered no other explanation (see Jagnow et al., 2000).

The massive gypsum deposits in Carlsbad Cavern did not form as early speleologists had envisioned. The primary evidence that invalidated this early hypothesis was analysis of samples of cave gypsum for the ratio between the number of atoms of ^{34}S and ^{32}S (Hill, 1981; Kirkland, 1982). The sulfur isotopic compositions were reported as the difference in parts per thousand from a standard (parts per thousand being equivalent to "per mil," "tenths of a percent" and the symbol, "‰"); the difference is designated "$\delta^{34}S$."

Permian marine gypsum in deposits near the caves (Fig. 13) are enriched in the ^{34}S isotope compared to sulfur within a standard—a sulfur-bearing iron meteorite found near the ghost town of Canyon Diablo between Flagstaff and Winslow, Arizona. The samples of marine gypsum have positive per mil values, and are described as "isotopically heavy"; in marked contrast, gypsum samples from Carlsbad Cavern are impoverished in the ^{34}S isotope, they have negative per mil values, and are described as "isotopically light" (Fig. 12). The sulfur-bearing minerals within the caves are depleted in ^{34}S by several percent (several tens of parts per thousand) compared to the ^{34}S composition of Late Paleozoic marine calcium sulfate (Fig. 12). The magnitude of this difference is highly significant. Based on such a wide divergence, the two suites of gypsum samples—those from Carlsbad Cavern and those from nearby Permian marine strata—are deemed unrelated.

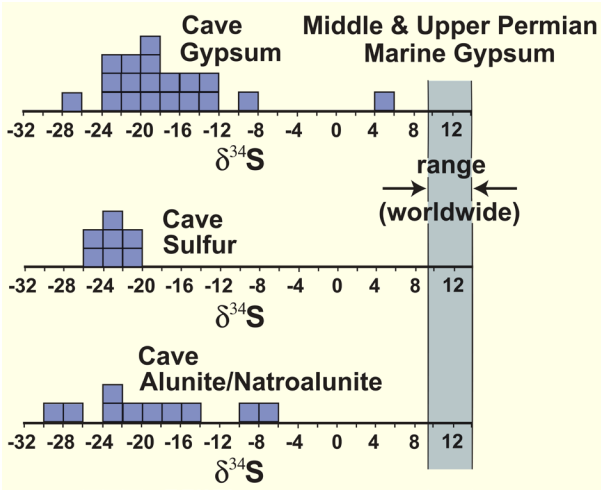

Figure 12. $\delta^{34}S$ values for samples of blocky gypsum, native sulfur, and alunite/natroalunite from caves of the Guadalupe Mountains, and for comparison (to right) range of $\delta^{34}S$ values for Middle and Upper Permian marine gypsum and anhydrite (light blue), which include values for the Castile and Seven Rivers Formations (after Claypool et al., 1980; Sarg, 1981; Kirkland, 1982; Hill 1987; DuChene in Hill, 1996, p. 449; Polyak and Güven, 1996). The wide divergence between values for the sulfur-bearing cave minerals and those for the Middle and Upper Permian marine gypsum indicates that gypsum within the caves was not derived from nearby deposits of marine gypsum.

The different origins of the two classes of gypsum are clearly displayed by their $\delta^{34}S$ values. Samples of Upper Permian, marine, Castile gypsum from near Carlsbad Cavern (Fig. 13) have positive $\delta^{34}S$ values and a narrow range, +11.3‰ to +12.0‰ (n=36) (Fig. 12) (Kirkland et al., 2000). Similarly, samples of Middle Permian marine gypsum from the nearby evaporitic facies of the Seven Rivers Formation (Fig. 13) have positive values and a narrow range, +8.7‰ to + 10.2‰ (n=8) (Fig. 12) (Sarg, 1981). On the other hand, samples of gypsum from Carlsbad Cavern have highly negative $\delta^{34}S$ values and a wide range, -25.6‰ to -13.9‰ (n=13) (Kirkland, 1982; Hill, 1987) (Fig. 12). In addition, samples of gypsum from Lechuguilla Cave, Cottonwood Cave, and McKittrick Hill Cave, and samples of other sulfur-bearing minerals from caves of the Guadalupe Mountains have negative $\delta^{34}S$ values similar to those of samples of gypsum from Carlsbad Cavern (e.g., Polyak and Güven, 1996) (Fig. 12). The collective range of $\delta^{34}S$ values for the sulfur-bearing cave minerals does not overlap with the $\delta^{34}S$ range of nearby Upper or Middle Permian, marine gypsum (Fig. 12). In fact, the range does not overlap with the $\delta^{34}S$ range of any deposit of Phanerozoic, marine-derived gypsum (or marine-derived anhydrite [$CaSO_4$], which generally replaces its hydrous sister mineral in the shallow subsurface).

All cave minerals bearing sulfur in the Guadalupe Mountains formed because of H_2S-H_2SO_4 speleogenesis (Palmer, 2006). An insignificant propensity existed for biased selecting of ^{32}S or ^{34}S as these minerals formed (e.g., Goldhaber, 1993; Ziegenbalg et al., 2012), therefore, the distinctive sulfur isotopic signature of the sulfur-bearing cave minerals must have been inherited from their precursor, H_2S, that moved into the caves and that participated in chemical reactions.

Microbial Derivation

The distinctive sulfur isotopic signature of the cave gypsum—highly negative $\delta^{34}S$ values having a wide range—indicates that its sulfur-bearing precursor, H_2S, almost certainly formed by a redox (red[duction] + ox[idation]) reaction mediated by anaerobic microbes. In near-surface Phanerozoic environments, the activity of sulfate-reducing microbes is probably the only way that H_2S with highly negative $\delta^{34}S$ values (i.e., << 0 ‰) can form (e.g., Dessau et al., 1962; Holser and Kaplan, 1966). Many types of organic matter, assisted by microbial enzymes, reduce $^{32}SO_4^{2-}$ to H_2S at a slightly faster rate than they reduce $^{34}SO_4^{2-}$ to H_2S, the ^{32}S–O bonds being slightly easier to break than the ^{34}S–O bonds. Thus, sulfate-reducing microbes generate H_2S enriched in ^{32}S and, if the system were open, they would leave behind sulfate anions enriched in ^{34}S.

The difference between the maximum and minimum $\delta^{34}S$ values for the sulfur-bearing cave minerals is broad (Fig. 12), e.g., 11.7‰ for gypsum from Carlsbad Cavern. Such a broad range compared, for example, to a

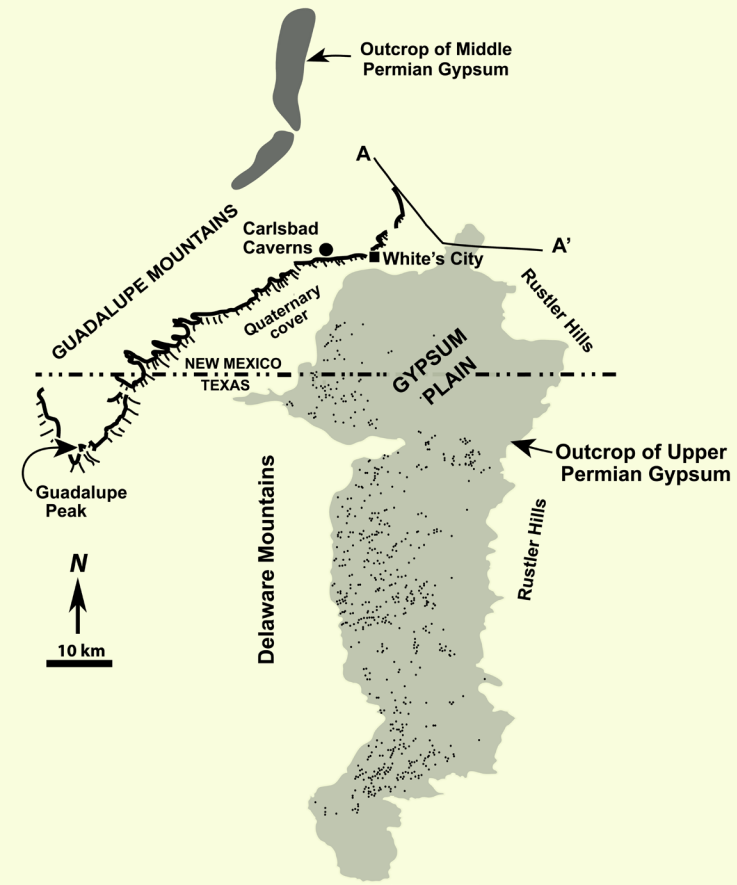

Figure 13. Location of Gypsum Plain, which consists predominantly of gypsiferous soil and scattered outcrops of Upper Permian (lower Ochoan) Castile gypsum; black dots show locations of castiles (secondary limestone masses that commonly stand in relief (Fig. 15)) (after Stafford et al., 2008b, their fig. 6a); where two or more dots are proximal, they may be connected into a single large castile; AA' is line of cross section for Figure 7; also shown are the locations (in the far back reef) of outcrops of Middle Permian Seven Rivers gypsum (dark gray) (after Sarg, 1981).

narrow range of about 0.7‰ for nearby Upper Permian, basinal, marine gypsum, suggests microbial derivation (e.g., Lein, 1974). The broad range results from variations in microbial strains, in rates of microbial reduction, in ambient temperatures during microbial activity, and in the degree of isolation of the aqueous sulfate being metabolized (e.g., Harrison and Thode, 1958; Coleman, 1985; Machel, 1992; Goldhaber, 2003).

Immense Quantity

A first-order approximation of the minimum weight of H_2S transported into caves of the Guadalupe Mountains can be calculated from the weight of cave gypsum. It takes ~0.2 metric tons of H_2S to produce one metric ton of cave gypsum. Judging from wide blocks of gypsum up to 10-m thick (e.g., Hill, 1987, p. 44-45; Spirakis and Cunningham, 1992; Davis, 2000) having a density of ~2.3 metric tons/m^3, the total weight of gypsum presently within the caves is large. Lechuguilla Cave contains "thousands of tons of massive or laminated gypsum" (Davis, 2000), and along more than 220 km of surveyed passageways, gypsum appears in many forms "including thick coatings on the passage walls, spectacular stalagmites and stalactites, delicate hairs, gypsum flowers, and massive deposits that sometimes fill passages" (Spirakis and Cunningham, 1992). An example is the remarkable gypsum chandeliers (Fig. 14). They formed late in the history of the cave as vadose seepage dissolved secondary gypsum from an overlying level and re-precipitated it as crystalline masses in an underlying level in which water tends to evaporate (personal communication, A.N. Palmer, 2013). As mentioned above, much gypsum, which is highly soluble in water (maximum ~2.5 g/l), has gone into solution and has been removed within groundwater (Hill, 1987, p. 48-49; Polyak and Provencio, 2001; Hose and Macalady, 2006). Remaining blocks of gypsum in the Big Room of Carlsbad Cavern usually lie in protected alcoves or under overhanging ceilings (Black, 1954). Water dripping from the ceiling has dissolved precise, vertical, cylindrical tubes through blocks of gypsum (Quinlan and Smith, 1968) (one hole is ~4 m long and only ~9 cm in diameter (Bretz, 1949)). The weight of gypsum in the caves before dissolution was huge (Hill, 1987, p. 87); from this original large weight, we can infer that many metric tons of H_2S moved into the caves, and reacted with O_2 to form H_2SO_4, which, in turn, reacted with either limestone or dolomite to form gypsum.

Also supporting introduction of a great weight of H_2S into the caves is the enormous weight of carbonate rock removed as the caves formed; more than 3,000,000 metric tons of limestone from the "Big Room" of Carlsbad Cavern alone (Hill, 1987, p. 79); and with its large galleries and extensive passageways, a truly immense tonnage from Lechuguilla Cave. Much, if not most, of this removal is attributable to H_2S-H_2SO_4 speleogenesis (Polyak and Provencio, 2001; Palmer, 2006), and because dissolution of one cubic meter of limestone requires 918 kg of H_2S (Palmer and Palmer, 2000), an immense weight of H_2S (millions of metric tons) apparently moved into developing caves of the Guadalupe Mountains.

Sources and Pathways of Hydrogen Sulfide: Previous Models

The source area from which microbial H_2S implicated in creating the caves formed is disputed (e.g., Brown, 2006). Two nearby source areas have been proposed.

Figure 14. Gypsum Chandelier, Ballroom of Lechuguilla Cave. Photo by A.N. Palmer.

The H_2S is thought to have originated by a microbially mediated redox reaction either southeast of the cave belt within Upper Permian calcium sulfate strata of the adjacent Delaware Basin, or northwest of the cave belt within Middle Permian calcium sulfate strata of the adjacent inner shelf (i.e., strata within the western Guadalupe Mountains) (Fig. 5).

While the caves were forming, both proposed source areas contained bedded anhydrite and near the surface bedded gypsum. Figure 13 shows the location of outcrops of Middle Permian Seven Rivers gypsum, which during the late Miocene and early Pliocene were more extensive; it also shows the general location of Upper Permian Castile gypsum either as scattered outcrops or situated just below a thin gypsiferous soil. Dissolution of the calcium sulfate minerals—gypsum and anhydrite—created sulfate anions that were both a potential oxidant and a potential source of the sulfur atoms within the H_2S molecules.

The basin contained abundant petroleum, particularly natural gas, while the caves were forming, and to the northwest, well behind the present-day reef escarpment, the inner shelf (Fig. 5) also possibly contained abundant petroleum while the caves were forming. If we consider the vast quantity of metabolizable organic matter required as a reductant, hydrocarbons (whether crude oil or natural gas) were probably the only viable contenders as reducing agents. They were both a potential reductant and a potential source of the hydrogen atoms within the H_2S molecules.

Which of these tectonic elements—the basin or the shelf—was the source of the H_2S has been earnestly contested. Proponents of a basinal source model include Davis (1980), Hill (1987, 1990), Polyak et al., (1998), and Palmer (2006), with C. A. Hill being the principal advocate. Proponents of a shelfal source model include DuChene (1986, 2009), DuChene and McLean (1989), Brown (2006), DuChene and Cunningham (2006), Stafford et al. (2008b; 2009), and Stafford and Nance (2009), with H. R. DuChene being the principal advocate. In addition, both basinal and shelfal proponents agree that the H_2S apparently entered the caves from below through fissures (Hill, 1987; Palmer and Palmer, 2000; Kosa and Hunt, 2006b; DuChene and Cunningham, 2006), but the pathways from where it originated to where it entered the fissures are also debated (Hill, 1996, p. 281; Brown, 2006; DuChene, 2009).

The Existing Shelfal Model

Pathway of Hydrogen Sulfide to Caves: Model of H. R. DuChene and K. I. Cunningham

Partially in response to the perceived paleohydrologic difficulty of transporting large quantities of aqueous (or gaseous) H_2S updip from the basin to the evolving caves, a model was proposed for transporting aqueous H_2S downdip within groundwater from the western, inner shelf (high elevations) to the evolving caves of the outer shelf (lower elevations) (e.g., DuChene and Cunningham, 2006; Brown, 2006; DuChene, 2009) (Fig. 5). (For this study, that part of the shelf within 6 km of the reef escarpment, the near back reef, is defined as the "outer shelf" (Fig. 5), and that part beyond 6 km, the far back reef, is designated as the "inner shelf.")

About 75 shelfal occurrences of sulfur are known within inner shelfal Middle Permian carbonates north and northwest of Carlsbad, New Mexico (Hinds and Cunningham, 1970, their fig. 4), and these occurrences provide direct evidence of the past presence of H_2S. Most "shows" occur within Permian formations older than those that are time equivalents of the Capitan Formation. Some cores of San Andres Limestone (Middle Permian, lower Guadalupian series; Fig. 6), for example, show thin coatings of sulfur on fractures and on bedding planes and small crystals of sulfur in vugs and in fractures. Southwest, west, and/or northwest of caves of the Guadalupe Mountains similar accumulations of native sulfur indicative of its precursor, H_2S, may have existed (or may exist) within Middle Permian strata of the inner shelf (i.e., within higher elevations of the ancestral (or present) Guadalupe Mountains) (e.g., DuChene, 2009) (Fig. 5).

Approximately twenty noncommercial metallic sulfide deposits occur northwest of the reef escarpment in the Guadalupe Mountains. They consist chiefly of pyrite (FeS_2) and sphalerite [(Zn,Fe)S] (Hill, 1993, her fig. 1). Sulfur combined within these minerals is isotopically light ($\delta^{34}S$, -1‰ to -15‰) (Hill, 1996, her appendix 2). These minor mineral deposits demonstrate that at least modest amounts of microbial H_2S were available to react with metallic cations to form sulfides, and the deposits support the past presence of H_2S on the inner shelf.

The possibility that the inner-shelf was the source of H_2S transported to the caves is based in part on analogy with current conditions on the shelf north and northeast of Carlsbad, New Mexico. Here, in Middle Permian

back-reef reservoir rocks, 0.9-1.2% H_2S is associated with shallow (mostly <1000 m) accumulations of degraded oil (DuChene, 2009, his figure 3). Anaerobic microorganisms apparently used fractions of the crude oil from these fields, particularly the paraffinic fraction (i.e., the alkanes), to reduce sulfate anions within associated pore water to yield the metabolic by-products CO_2 and H_2S. Similar accumulations of oil may have been present on the inner shelf west and northwest of the cave belt and may have contributed H_2S to groundwater that transported it to the outer shelf.

On the shelf northwest of the reef escarpment, however, present-day accumulations of oil within Middle Permian strata have not been discovered. Within several-to-several-tens of kilometers north and east of the Capitan reef vast accumulations (billions of barrels) of crude oil, now largely exploited, were trapped within Middle Permian shelfal carbonates (including carbonates of the Tansill, Yates, and Seven Rivers). Why crude oil was apparently not trapped within these same strata in the Guadalupe Mountains is uncertain (i.e., Hill, 1996, p. 354). Oil may have been swept away by hydrodynamic flow (Lindsay, 1998; DuChene and Cunningham, 2006; DuChene, 2009); it may have moved updip and escaped (Hill, 1996, p. 354-356); it may have been removed as reservoir rocks of the inner shelf were eroded; and/or it may have been displaced from traps by natural gas that subsequently escaped because of inadequate sealing.

From hydrologic principles alone, Brown (2006) concluded that H_2S that entered the caves must have been transported within groundwater "from an upflow direction" and, therefore, from higher elevations within inner shelfal strata "west or southwest" of the caves. He hypothesized that the necessary reductant was either "dissolved or particulate organic matter in water"; falling within his "dissolved" category are certain components of crude oil. The presence of crude oil within the western Guadalupe Mountains is indicated by the odor of petroleum from freshly broken limestone of the Grayburg Formation (Middle Permian, lower Guadalupian series; Fig. 6) (DuChene, 2009). Furthermore, within sparry calcite, "abundant hydrocarbon inclusions" occur within Middle Permian strata of "mid-shelf settings" (Scholle et al., 1992). The calcite, which also contains abundant inclusions of pyrite, occurs chiefly as a replacement of anhydrite or gypsum. Sparry calcite is "disseminated as pore fills or as isolated displacive and replacive crystals or nodules in micritic dolomites." The calcite is the youngest major diagenetic shelfal mineral (Scholle et al., 1992), and it probably formed primarily in the Miocene and Pliocene. Samples of the sparry calcite usually have isotopic signatures characteristic of genesis in part from organic matter (e.g., -12.8‰) (Scholle et al., 1992). The sparry calcite apparently formed from the microbially mediated reaction between fractions of oil and sulfate anions (probably derived from Middle Permian marine anhydrite), and the reaction would have generated a significant cumulative amount of H_2S some of which would have been transported downdip within groundwater.

Possible Deficiencies of Model

Despite the appeal of the shelfal source model, the quantity of H_2S required for speleogenesis in the Guadalupe Mountains (many millions of tons) was probably inadequate. Even if shallow accumulations of oil like those northeast of Carlsbad, New Mexico, were present on the inner shelf northwest of the present-day escarpment, the quantity of associated H_2S (see Brown, 2006) would have been insufficient to produce the vast quantity of H_2SO_4 required to dissolve the caves.

The biogenic H_2S implicated in genesis of the metallic sulfide deposits was hypothesized by Hill (1996, p. 384-388) to have come from the basin rather than from the inner shelf. These deposits of the inner shelf extend for several kilometers farther to the northwest than the cave belt, but sphalerite and pyrite can form from much lower concentrations of aqueous H_2S than that required for effective H_2S-H_2SO_4 speleogenesis.

Considering the amount of H_2S required for cave formation on the outer shelf (i.e., within the cave belt), if H_2S for cave formation came from the inner shelf, more evidence for past generation of H_2S might be expected within Middle Permian evaporitic strata of the far back reef. Such evidence might include strata of gypsum and/or anhydrite that contained scattered castile-like structures of secondary limestone (tens of meters across) highly depleted in ^{13}C. In addition, we might expect significant accumulations of natural gas, oil, and asphalt on the inner shelf, as well as major accumulations of native sulfur. Such evidence is wanting. A possible reason for its absence, however, is that much of the Guadalupian series has been stripped from the inner shelf (e.g., Boyd, 1958, p. 43; Sarg, 1981), and with erosion, critical evidence may have been lost.

H_2S was generated on the inner shelf northwest of the cave belt by reaction of fractions of oil with sulfate anions derived from Middle Permian anhydrite and gypsum, the best appraisal, however, appears to be that the quantity generated was less than the colossal amount required for speleogenesis in the outer shelf of the Guadalupe Mountains.

The Existing Basinal Model

Secondary Masses of Castile Limestone: Sites of Prolific Generation of Hydrogen Sulfide

Dotting the western outcrop area of the Castile Formation (lower Ochoan Group), throughout much of the western Delaware Basin, are hundreds of discrete masses of secondary limestone (Adams, 1944; Kirkland and Evans, 1976; Stafford et al., 2008b) (Figs. 13 and 15), many of which have only been partly exhumed out of surrounding Castile gypsum. Adams (1944) labeled these bodies "castiles" and he noted that they are "diagenetic," a term that (excluding weathering and metamorphism) includes all chemical, physical, and biological changes occurring to a lithified rock; in this instance, changes occurring to Castile anhydrite ~245 Ma after its inception. The castiles, in plan, commonly have maximum dimensions >30 m. They usually consist of isolated masses of limestone (Fig. 15); relatively few, however, consist of "laterally extensive horizons" or limestone "sheets" up to 2 m thick (e.g., Stafford et al., 2008b) (the "calcite ridges" of Miller, 1992). The castiles have a mean surface area of ~2,300 m^2, the largest having a surface area of ~40,000 m^2 (Stafford et al., 2008b).

These scattered bodies of diagenetic limestone while buried beneath hundreds of meters of chiefly upper Ochoan evaporitic strata (mainly the upper Castile and the Salado) were sites of generation of large quantities of microbial H_2S (Kirkland and Evans, 1976). The castiles and their buried counterparts are a crucial element of basinal source models (e.g., Hill, 1987, 1990), therefore, a summary of aspects of their nomenclature, morphology, distribution, and stratigraphy follows; in a later section, as Hill's basinal model is expanded and modified, their biochemical origin is considered.

Smith (1980) objected to Adam's use of the term "castile" or "castiles" for the carbonate masses because of possible confusion with the formation name, "Castile." Kirkland and Evans (1976), with similar objections in mind, termed

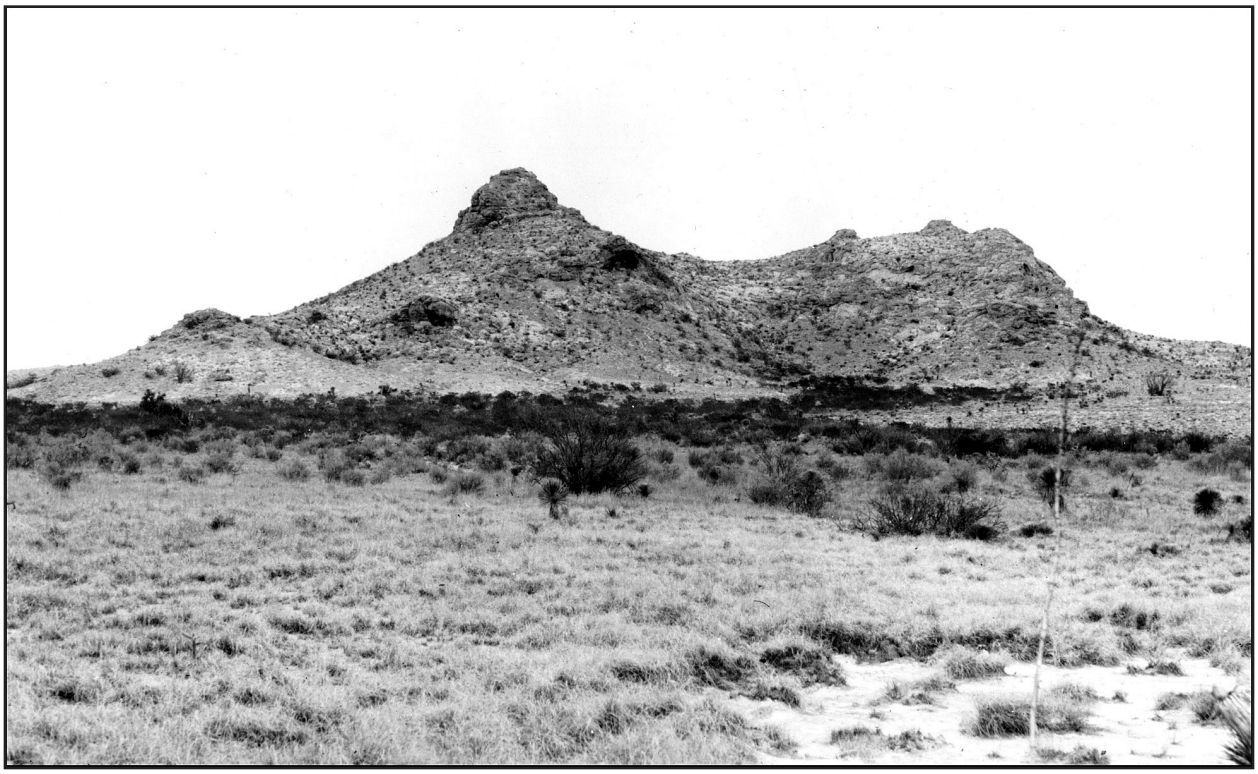

Figure 15. Typical castile on Gypsum Plain; it consists of biogenic limestone that has replaced Castile anhydrite; castiles commonly stand in relief because of differential erosion of the surrounding softer and more soluble gypsum; about 1,000 castiles of various sizes and shapes are located on the Gypsum Plain (Fig. 13) (Stafford et al., 2008b).

the structures "limestone buttes." Adams (1944), however, had noted that, "a more appropriate name than 'castiles' can hardly be imagined." The appropriateness was the similarity to the term "Castile" and to their physiographic expression as "castellated peaks" (although not all castiles stand in castle-like relief). Adam's terms "castile" and "castiles," after many decades of usage, are well ingrained, are widely used in geologic publications, are nearly always written with a lower case "c," and are apparently seldom confused with the name of their host formation. Therefore, I use "castiles," or its singular, for the many outcropping bodies of diagenetic limestone surrounded by and partly encased by Castile gypsum or by gypsiferous soil. For their subsurface equivalents—masses of limestone still fully encased within Castile gypsum or anhydrite, or both—I use "diagenetic limestone," or its equivalents, "secondary limestone" and "biogenic limestone."

About 1000 castiles crop out in clusters on nearly flat, open country that supports only sparse vegetation (Fig. 13) (Stafford et al., 2008b). Erosion of gypsum—softer and more soluble than calcite—has unearthed the limestone bodies and has left many standing in high relief (Fig. 15), some by as much as 40 m. From near the entrance to Carlsbad Cavern, a few castiles can be seen several kilometers to the southeast towering above gypsiferous soil ("gypsite").

The large (~1,800 km^2) geographic region in New Mexico and Texas from which the castiles rise has been designated the "Gypsum Plain" (Fig. 13). It consists mainly of gypsite-mantled Castile bedrock, dissolution-induced landforms (e.g., sinkholes, solution-subsidence troughs, and caves), of which there are an estimated 9,000 (Nance and Stafford, 2009), and sporadic outcrops of Castile gypsum that comprises ~8 % of the area in which the Castile is at or near the surface (Stafford et al., 2008a). The Gypsum Plain in New Mexico occurs southeast of the reef escarpment and northwest of the dolomitic Rustler Hills (Fig. 13); just to the south in Texas, the Gypsum Plain occurs east of the low-lying Delaware Mountains and west of the Rustler Hills (which stand in relief because of erosional resistant beds of dolomite) (Figs. 7 and 13).

The castiles are large-scale replacement features, calcite having replaced laminated, nodular, massive, and brecciated Castile anhydrite by a process termed "calcitization." The process occurred after subsurface conversion of gypsum to anhydrite but before near-surface conversion (by hydration) of anhydrite back again to gypsum (Moore, 1960b, p.74; Brown and Loucks, 1988). The depositional and structural fabric of Castile anhydrite is commonly preserved during the replacement, and the steep exposed limestone walls of many castiles magnificently display the characteristic laminations and microfolds of Castile gypsum and anhydrite (Kirkland and Anderson, 1970; Kirkland and Evans, 1976; Stafford et al., 2008b) (Fig. 16A). Almost all castiles before being exhumed in the latest Tertiary and Quaternary were probably fully encased within lower Castile anhydrite.

The Castile Formation near the eastern side of the Delaware Basin consists predominantly of thick (tens of meters) alternating sections of halite and anhydrite (Fig. 17) that collectively have a total thickness of 450-550 m. Here, in a narrow band, the highly soluble Castile evaporites have largely escaped the effects of dissolution (Fig. 18), which has otherwise greatly modified the thickness of the formation. Most beds of Castile halite in the west-central basin, for example, have completely dissolved (Fig. 18). Without the intervening halite members, the specific Castile anhydrite member from which a particular castile rises cannot usually be identified with certainty (apart from the challenging technique of varve correlation (Anderson and Kirkland, 1966)). The castiles, however, are concentrated in the western more elevated part of the Gypsum Plain where erosion has removed, at least, the Anhydrite IV Member and possibly all or much of the Anhydrite III Member. Just south in Texas, erosion has removed much of the Anhydrite II Member, and, just east of the erosional pinch out of the Castile (Fig. 18), much of the Anhydrite I Member. Most castiles, judging from their present geographic distribution, probably originated from replacement of the Anhydrite I and Anhydrite II members (Kirkland and Evans, 1976; Stafford et al., 2008b).

Cropping out on the northernmost part of the Gypsum Plain in New Mexico and on the easternmost part of the Gypsum Plain in Texas and New Mexico, are outliers of dolomite of the Rustler Formation, gypsum of the Anhydrite IV Member, and a mineral residue (chiefly gypsum) remaining after dissolution of halite within the Salado Formation. Castiles are nearly absent in these peripheral regions (Fig. 13), but beneath these outcropping stratigraphic units, within the lower Castile

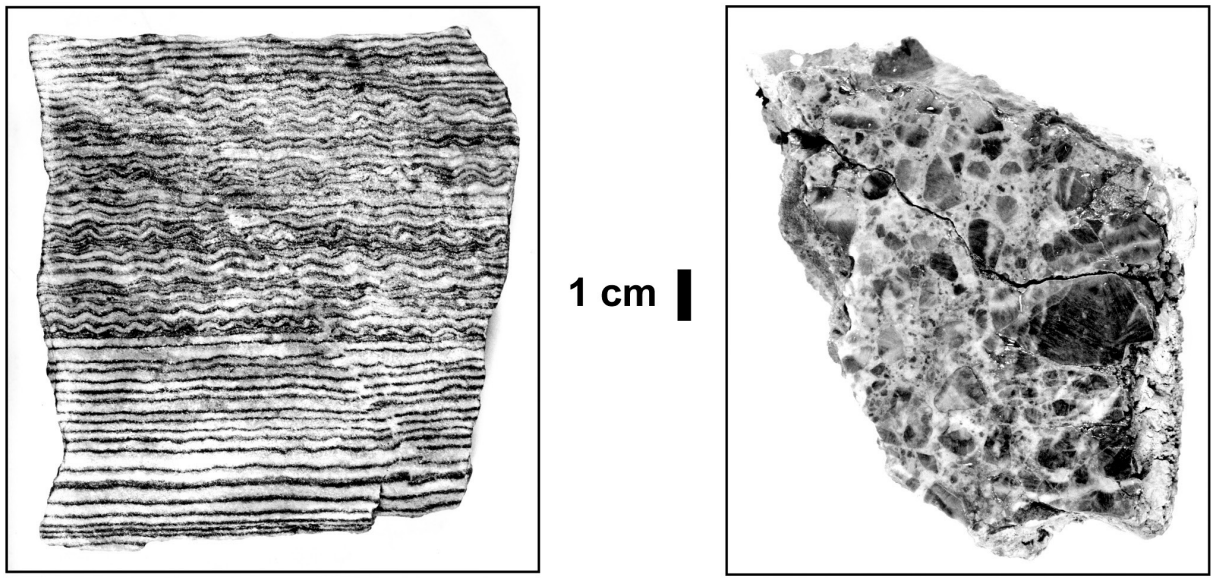

Figure 16. Typical samples from castiles of anhydrite replaced by calcite: **A.** Laminated calcite with microfolded laminae; virtually identical appearing samples consist of laminated Castile gypsum and calcite. **B.** Limestone breccia; brecciation occurred before calcitization of anhydrite clasts.

anhydrite member, equivalent masses of diagenetic limestone are probably present.

Major known deposits of native sulfur occur >100 m beneath the surface of the Gypsum Plain. The sulfur occurs within a carbonate lithology like that of the castiles except that the host rock contains elemental sulfur (e.g., Madsen and Raup, 1987; Smith, 1980). These rare deposits, discussed in a latter section, are apparently essentially "buried castiles" that enclose disseminations, replacements, and open-spaced fillings of sulfur.

	Members	Comments
Castile Fm	Anhydrite IV	Thickness 90-180 m; one halite interbed
	Halite III	Mixed anhydrite-halite; halite, max. thickness ~120 m
	Anhydrite III	Thickness in northern basin ~85-90 m
	Halite II	N basin, mostly ~60 m thick; 5 interbeds of anhydrite, < 1 m
	Anhydrite II	Thickness in central basin ~30 m
	Halite I	Maximum thickness ~125 m; no anhydrite interbeds > 3 mm
	Anhydrite I	Thickness in western basin ~52 m
	Basal Limestone	Thickness <1 m

Figure 17. Members of the Upper Permian Castile Formation; because of dissolution, thickness of the halite members, in particular, varies throughout much of the basin; thickness values are present day.

Most diagenetic masses of Castile limestone beneath the surface of the Gypsum Plain, despite having produced copious amounts of H_2S, are barren of native sulfur (see Zimmerman and Thomas, 1969, p. 18). One example, located ~5 km west of the Culberson sulfur deposit (Fig. 32), is the one-well Rustler Hills oil field. Its reservoir consists of secondary Castile limestone at a depth of ~140 m (Davis and Kirkland, 1970). Diagenetic masses of limestone beneath the Gypsum Plain barren of both native sulfur and crude oil have likely been encountered during exploration drilling, but, having no economic value, there was little-to-no incentive for documentation. Nevertheless, judging from the number of castiles exposed by erosion that completely lack native sulfur, that contain insignificant amounts of native sulfur, or that show no evidence of ever having contained significant accumulations of native sulfur, many sulfur-free limestone counterparts probably exist beneath the Gypsum Plain.

Pathway of Hydrogen Sulfide to the Caves: Model of C.A. Hill

Hill (1987) advanced the following explanation for the source and migration of H_2S from the Delaware Basin into the caves of the Guadalupe Mountains. During the Late Tertiary, masses of microbial limestone encapsulated

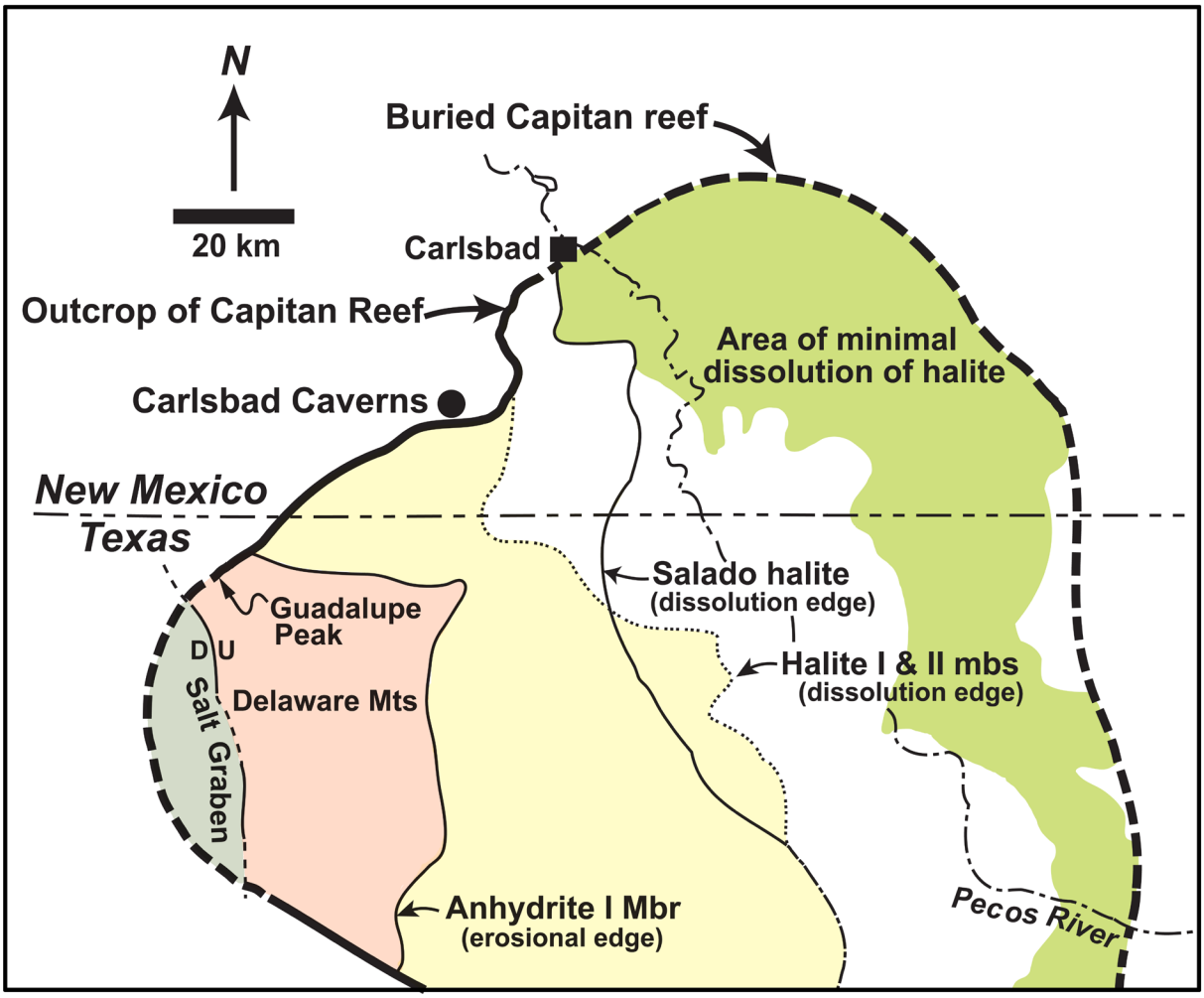

Figure 18. Subsurface dissolution edges for the Halite I and Halite II members of Castile Formation (dotted line) (which vary only insignificantly from one and another) and subsurface dissolution edge for halite within the Salado Formation (solid line) (Anderson et al., 1972). (West of the halite dissolution edge the Castile Halite I and II members are represented by a reduced section of micro-breccia consisting of gypsum, anhydrite, and minor calcite (Fig. 21B); and the Salado is represented chiefly by residual gypsum, anhydrite, dolomite, shale, and siltstone). The area of Delaware Basin largely unaffected by dissolution processes is green (Anderson, 1978, his fig. 1). Northeast of the vicinity of Carlsbad Cavern the Halite I and II members are proximal to the Capitan reef and forereef. Also shown is the subaerial erosion edge of the Anhydrite I Member of the Castile Formation.

within thick, bedded anhydrite of the lower Castile Formation were sites of generation of large quantities of gaseous H_2S that then migrated into underlying, widely extending beds of sandstone of the Bell Canyon Formation (the upper member of the Delaware Mountain Group) (Fig. 6). The gaseous H_2S subsequently migrated updip through permeable pathways into caves of the reef and adjacent shelfal carbonates.

Possible Deficiencies of the Proposed Pathway

Challenges to Hill's model are concerned not with generation of large quantities of H_2S within the Castile, for which there is much support, but with her hypothesized migration pathways within the Bell Canyon Formation and with her hypothesized phase of H_2S. According to Hill's model (1987, 1990), updip migration of gaseous H_2S occurred "along permeable sands," "along interfingerings of forereef carbonate beds," and/or "along northwest trending joints." However, gaseous H_2S, because of its buoyancy, would not have migrated downward from microbial loci within Castile anhydrite into the Bell Canyon sandstone (Brown, 2006). Even if gaseous H_2S were present in the upper Bell Canyon, it would not have migrated into the reef and into carbonate strata of the northwestern shelf through the "upper permeable sands," because these

channel-fill sandstones trend sub-parallel to the reef, not normal to it (DuChene, 1986; Brown, 2006). In addition, near the reef, "interfingerings of forereef carbonate beds" were possible (although unlikely) migration pathways for gaseous H_2S, but farther out into the basin such beds (e.g., the Lamar Member of the Bell Canyon Formation (Fig. 6)) consist of lithified carbonate mud of low permeability.

Gaseous H_2S, if it were under a sufficient pressure for a sufficient duration, might have migrated updip through connected pores of very fine-grained Bell Canyon sandstone and siltstone, and through northwest-trending joints. However, why would H_2S, many times more soluble than CH_4 or CO_2, have persisted in a gaseous state within an environment in which its aqueous solubility was further enhanced by the hydrostatic pressure of hundreds of meters of burial? Conceivably, H_2S dissolved within Bell Canyon pore water may have diffused into gaseous CH_4, and the mixture of gases may have migrated updip through the Bell Canyon Formation and into the Capitan where the H_2S was stripped from the CH_4. However, major problems remain: Why would an immense quantity of H_2S have resided in the upper Bell Canyon? What was its source? Moreover, could the modest quality of migration pathways within the upper Bell Canyon have conveyed the necessary volume of H_2S to the developing caves? Apparently, a significant volume of gaseous H_2S did not move updip into the Capitan and Seven Rivers carbonates through either Bell Canyon fractures or beds of sandstone.

The H_2S, wherever it was generated, was apparently transported to the caves not as a gas, but as a dissolved component within groundwater (Palmer and Palmer, 2000; Brown, 2006). While the caves were forming, groundwater within the Bell Canyon Formation, in response to the hydraulic gradient created by relief of the ancestral Guadalupe Mountains, moved slowly downdip though pores and through fractures probably at a rate of < 1 m per year (see Hiss, 1975, 1980; Wiggins et al., 1993; Lee and Williams, 2000). Within Bell Canyon sandstone, groundwater in which H_2S was dissolved could not have moved updip to the shelf edge, i.e., to the Capitan Formation, counter to this downward flow. A lateral and slightly upward passage of groundwater bearing dissolved H_2S through the Bell Canyon Formation is considered to be a view without strong ties to paleohydrology (Palmer and Palmer, 2000; Klimchouk, 2007, p. 75). Apparently, neither aqueous H_2S nor gaseous H_2S moved updip into reefal and shelfal carbonates through either Bell Canyon fractures or beds of sandstone.

Modified Basinal Model: Source of Hydrogen Sulfide and its Pathway to Caves

During their formation, Carlsbad Cavern, Lechuguilla Cave, and other large caves within the Guadalupe Mountains were extraordinary "sinks" for H_2S, the weight of H_2S oxidized to H_2SO_4 within the Capitan and Seven Rivers formations, as mentioned above, amounted to millions of metric tons. At the same time, the adjacent basinal Castile Formation was a prolific "generator" of H_2S, millions of metric tons having been generated at subsurface, microbial loci. Furthermore, the two principal formations, one harboring the "generators" and the other the "sinks," were proximal, the Castile Formation being laterally contiguous with the Capitan forereef and with the precipitous face of the Capitan reef (Figs. 7 and 20). While the "generators" of H_2S were active, they were sealed beneath hundreds of meters of virtually impermeable upper Ochoan evaporites (chiefly Salado halite and Rustler anhydrite); and, while the "sinks" of H_2S were active, the evaporites were gradually being stripped (over million of years) of these same thick sealing beds.

Following a historic timeline, the modified model of generation and transportation of H_2S to the caves of the Guadalupe Mountains is presented in five overlapping stages:

- formation of hydrologic pathways within anhydrite and halite of the Castile Formation;
- generation and migration of methane (CH_4) and its reaction with Castile sulfate anions (SO_4^{2-}) to form hydrogen sulfide (H_2S);
- transportation of aqueous H_2S through hydrologic pathways to the reef;
- removal from the cave belt of a cover of chiefly uppermost Permian evaporitic strata; and
- descent of the water table progressively from southwest to northeast, and concurrent oxidation of H_2S within caves along the cave belt progressive from southwest-to-northeast (and within specific caves from high elevation to low elevation).

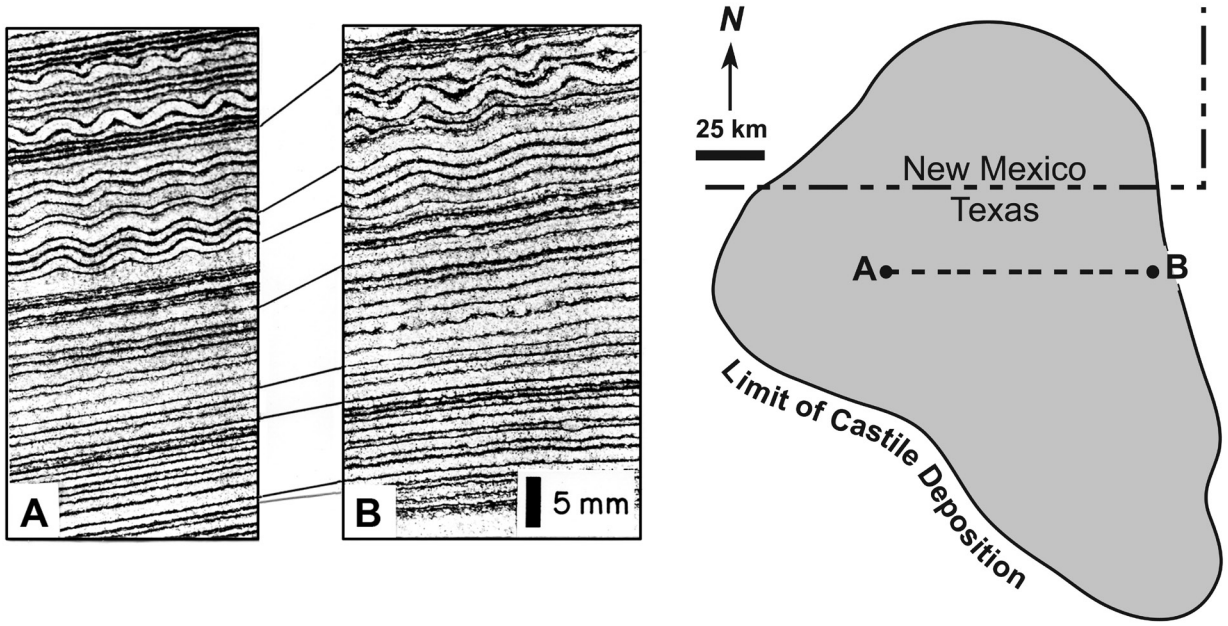

Figure 19. Correlative slabs of Castile Formation separated by 113 km demonstrating the remarkable stratigraphic consistency of calcite (dark) and anhydrite laminae (for additional correlations see Anderson and Kirkland, 1966; Dean, 1967; Anderson et al., 1972; Leslie et al, 1997; Kirkland, 2003). In the northwestern basin before tilting and dissolution of the Castile Formation, the thickness and the lithologic characteristics, at all scales, from beds to members, were usually remarkably consistent (exceptions were some beds of halite in the Anhydrite IV Member and, near the basin margin, disruption by gravity deposited beds.)

In addition, I consider the formation of curious, easterly trending, karstic, solution-subsidence troughs on the Gypsum Plain; and I compare and contrast the hypothesized conduits within Castile halite with a closely related karstic model—development of a void at the flat, halite crest of anhydrite-capped salt domes. Then, in a following section, I describe relatively recent removal of Rustler, Salado, and Castile strata.

Beginning of Intense Cavern Formation

Directly northwest of where the Capitan escarpment now trends (Fig. 3) Middle Permian carbonates of the reef and correlative carbonates of the outer shelf (near back reef) underwent only minor, sporadic speleogenesis for ~245 Ma (Hill, 1996, p. 276-278). Then, throughout ~8 Ma, from probably early late Miocene (or possibly latest middle Miocene) to early Pliocene (~12 to ~4 Ma ago), the carbonates experienced intense speleogenesis (e.g., Polyak et al., 1998; Polyak and Provencio, 2000). The Tertiary age assignments, which represent minimum ages (Palmer, 2006), are based on $^{40}Ar/^{39}Ar$ dating of the potassium-bearing cave mineral, alunite (e.g., Polyak and Provencio, 2000).

During speleogenesis in the Guadalupe Mountains, the Castile Formation of the Delaware Basin (which accumulated rapidly, ~260.0-259.8 Ma ago) had an extraordinarily uniform stratigraphic framework. Superimposed on this framework were two nearly concurrent Late Tertiary events.

- Heating of the crust, which caused abundant CH_4 to be generated and source beds to be overpressured.
- Tilting of the Guadalupe Mountains and most of the Delaware Basin to form the paleo-Guadalupe tectonic block; uplift of the block caused Permian strata to fracture or to re-fracture and provided the potential energy that on its release allowed karstic pathways to form.

(I referred to this ancient structural entity as the "paleo-Guadalupe tectonic block" or "ancestral Guadalupe tectonic block"; during the late Miocene, for example, it was shallower and probably more expansive (see DuChene and Cunningham, 2006) than its present-day tectonic descendant (the "Guadalupe tectonic block")).

The effect of these two major geologic events (heating and tilting) on Castile evaporites of the Delaware Basin probably led indirectly to cave formation in the Guadalupe Mountains.

Formation of Basinal Hydrologic Pathways

Hydrologic pathways within the Castile Formation probably began to form in the western Delaware Basin near the beginning of the late Miocene. The distinctive character of Castile stratigraphy was a pivotal factor in the formation of the aquifers.

Stratigraphic Framework of Castile Formation

Castile evaporites in the western basin before tilting of the ancestral Guadalupe tectonic block and before the ensuing dissolution consisted by volume of ~60% $CaSO_4$ (~6,000 km^3) and ~30% NaCl (~3,000 km^3) (see Hayes, 1964; Snider, 1966, his table 3; Anderson, 1978, his table 1). In the eastern basin, where Castile halite has been largely preserved (Fig. 18), the formation consists of eight members: a thin (<1 m) basal limestone, four thick (tens of meters) anhydrite members, and three thick (tens of meters) interstratified halite members (Anderson et al., 1972) (Fig. 17). The eight-member succession before extensive dissolution in the Late Tertiary was virtually basin wide.

The physical setting and the climatic conditions during Castile sedimentation resulted in remarkable lateral persistence of Castile beds and laminae. The rate of tectonic subsidence in the Delaware Basin during the Middle Permian exceeded the rate of accumulation of sediment, and, hence, the tectonic basin, as mentioned above, coincided with a deep marine embayment. Near the end of the Middle Permian, it was rimmed by the living Capitan reef, which eventually grew across the mouth of the embayment (e.g., Kirkland, 2003) transforming it into a large enclosed lagoon (Kendall and Harwood, 1989; Anderson, 1993; Anderson and Dean, 1995; Leslie et al., 1997). It was deep, initially ~550 m (Newell et al., 1953), and extensive, ~25,000 km^2, with substantial inflow (~50 km^3/yr) of marine groundwater (Kirkland et al., 2000); but a channel (strait) connecting it to the Permian ocean, as envisioned by R. H. King (1947), was absent (e.g., Kendall, 1988). During the early part of the Late Permian, Castile evaporites rapidly (~0.2 Ma) filled the enclosed lagoon with gypsum, halite, and a lesser volume (~10%) of calcite (or possibly initially aragonite).

Much evidence supports the "deep basin-deep water" interpretation for the Castile. It includes an extensive correlation network of undisturbed laminae (e.g., Fig. 19), a transitional contact between the deep-water Bell Canyon Formation (e.g., Anderson et al., 1972; Babcock, 1977) and the basal Castile Formation, an influx of gravity deposits (Leslie et al., 1997; Hovorka, 2000), a complete absence of desiccation surfaces (Hovorka, 2000), and a tendency for beds of halite to become more common as the basin filled (Dean and Anderson, 1978). There are abundant shallow-water and ephemeral saltpan fabrics within the Salado evaporites (Fig. 6) (e.g., Lowenstein, 1988), fabrics that are completely absent in the directly underlying Castile evaporites (Hovorka, 2000).

The dominant sedimentological control on the Castile brine body, the size of Lake Erie, was climate. Stream flow or runoff of fresh water into the basin from the surrounding arid desert had an insignificant influence on the evaporitic facies (Kirkland et al., 2000). With only modest regional variability, temperature and humidity affected evaporation over the entire brine body. Such external climatic factors fluctuated readily, and, consequently, they acted on the entire depositional environment within a short time (e.g., <1 yr); thus, across the deep-water basin most major and minor lithologic boundaries within the Castile sequence are nearly isochronous (see Kendall, 1988). Regional changes in Castile sedimentation, from calcium carbonate to calcium sulfate, and back again, and from calcium sulfate to sodium chloride, and back again, were abrupt, generally occurring within a season (Anderson et al., 1972; 1978). Such changes within both millennial cycles (Dean and Anderson, 1978) and seasonal cycles (e.g., Kirkland, 2003) produced evaporitic beds and laminae, respectively, that are "one of the few examples of true 'layer cake' stratigraphy" (Warren, 2006, p. 335), a stratigraphy in which "Walther's Law" does not apply (Kendall, 1988). Most Castile evaporitic beds, whether "millimeter thick laminae" or "meter thick beds," and whether halite, anhydrite, or calcite, extended throughout, at least, the northern basin. In support of such pervasive climatic control, Castile laminae from many drill cores from the northern half of the basin have been correlated precisely (to a faction of a millimeter) (e.g., Fig. 19) (see Anderson and Kirkland, 1966; Dean, 1967; Anderson et al., 1972; Dean and Anderson, 1982). The principle basis for correlation is the unique pattern formed by groups of laminae, each lamina usually having a slightly different thickness and uncommonly a slightly different lithologic character.

Beds of Castile halite once on-lapped the Capitan reef and forereef where they are now exposed. Presently,

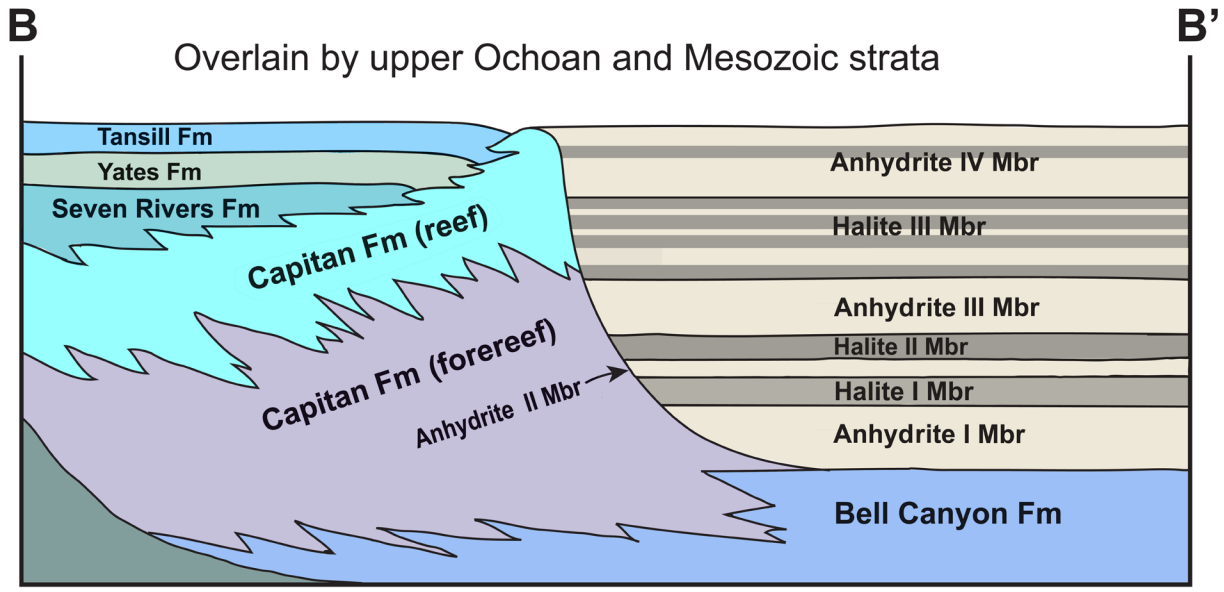

Figure 20. Diagrammatic northwest-southeast cross section through the central cave belt before uniform (homoclinal) tilting of the ancestral Guadalupe tectonic block, as it may have existed, for example, in the early Tertiary, showing relationship between members of the Upper Permian Castile Formation and the Middle Permian Capitan reef and forereef. Line of cross section BB' is shown on Figure 5. The precipitous face of the reef is based chiefly on data from B. L. Kirkland et al. (1999) and the steep upper forereef is based on data from Mruk and Bebout (1993). Before tilting, the Capitan, Tansill, and Castile formations were overlain by a thick section of upper Ochoan (Upper Permian) strata consisting primarily, in ascending order, of the Salado, Rustler, and Dewey Lake formations.

most beds of Castile halite, as mentioned, are missing from the westernmost Delaware Basin, but lithologic evidence of their past presence persists. Where dissolution has occurred, laminae of anhydrite once incorporated within the halite (Fig. 21A) remain as a jumbled "insoluble residue," and form a thin, distinctive, micro-breccia (Fig. 21B) termed a "blanket breccia" (Anderson et al., 1972; Anderson et al., 1978; Hentz et al., 1989, p. 42). The anhydritic micro-breccia survived dissolution because groundwater that dissolved the NaCl was saturated or nearly so with $CaSO_4$. "Every salt bed recognized on acoustical logs in the eastern side of the Delaware Basin has an equivalent bed of dissolution breccia in the western side of the basin…" Anderson et al., 1972; 1978). This determination is based primarily on definitive correlations between calcite-anhydrite laminae occurring just below beds of halite in the eastern basin with calcite-anhydrite laminae occurring just below beds of micro-breccia in the western basin. Thicknesses of the dissolution breccias range from a few centimeters to several meters, and the thickness of each bed of breccia is approximately proportional to the thickness of its correlative salt bed (Anderson et al., 1978).

Extensive dissolution of Castile halite moved eastward from the Guadalupe Mountain front (the Capitan reef complex) in the latest Tertiary and Quaternary. Within the subsurface, south of the latitude of Carlsbad Cavern, Castile halite has dissolved for a few kilometers to many kilometers into the basin (Fig. 18), but Castile gypsum, with a solubility ~140 times less than that of halite (Klimchouk, 2000), has been subjected to much less dissolution. Consequently, adjacent to the escarpment, beds of Castile gypsum presently come "…right up to the reef talus slopes" (written communication, D. B. Smith, 1970); to "within twenty feet of the reef" (Black, 1954); and, "to within as little as a few tens of feet" (Kelley, 1971). Like the beds of gypsum, the now missing beds of halite, with the exception of a few beds within the uppermost halite member (Anderson et al., 1972; Hovorka, 1990, p. 283), once extended to the northwestern margin of the basin (Anderson, 1978, p. 5; Kirkland, 2003). Figure 20, a diagrammatic cross-section normal to the trend of the cave belt before significant speleogenesis in the Guadalupe Mountains and before tilting of the tectonic block, shows the "face-to-face" configuration of the Capitan and Castile formations.

Early in the Tertiary, the boundary between each bed of Castile halite and each directly overlying bed of Castile anhydrite was persistent, smooth, and, nearly horizontal. Late in the Tertiary, each halite-anhydrite boundary, which represented an instant in geologic time, was persistent, smooth, and slightly inclined.

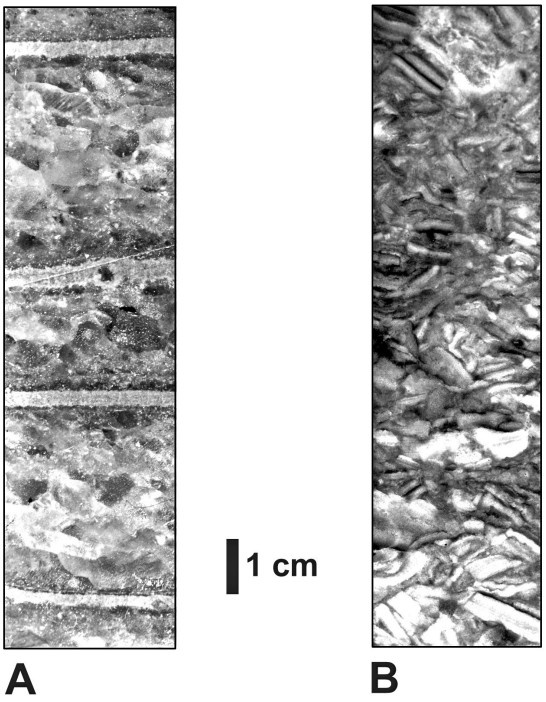

Figure 21. A. Typical core slab of Castile halite; laminae intercalated with thin beds of halite are dominantly anhydrite, are generally about 2-3 mm thick, and are repeated every 2-6 cm. ***B.*** Castile dissolution micro-breccia; photograph of thin (~2 mm) slab in transmitted light; clasts consist of fragments of anhydrite laminae remaining after halite has dissolved; such micro-breccias extend through much of the western basin and indicate past presence of halite. Approximately 0.3 m of anhydrite dissolution breccia is equivalent to 6-9 m of anhydrite-laminated bedded halite (Anderson et al., 1978).

Late Permian Burial of Cave Belt and Castile Formation by Salado, Rustler, and Dewey Lake Formations

In the latest Permian, following precipitation of the Castile evaporites, a huge area subsided (>150,000 km^2; see Lowenstein, 1988) including the Castile depositional basin, the fringing, extinct Capitan reef, and a wide—many tens of kilometers—shelfal area bordering the Delaware Basin (Lowenstein, 1988). The subsidence, including the area of the present Guadalupe Mountains, made space available for uppermost Permian strata to accumulate. Lithostratigraphic units that filled the "accommodation space" constitute the upper Ochoan Group (in ascending order, the Salado, Rustler, and Dewey Lake formations (Fig. 6)). Figure 22 shows the inferred depositional extent of the thickest of these formations—the Salado (dashed boundary)—and, for comparison, the depositional extent of the directly underlying Castile Formation.

The regional subsidence was augmented by the huge, rapidly deposited (~209,000 yrs; Anderson, 2011) load of Castile evaporites (a weight of ~ 27^{18} metric tons, based on a volume of ~10,000 km^3 and a mean density of ~2.7 g/cm^3). The great mass of Castile evaporitic sediments helped to depress the crustal surface, and the area in which the evaporites accumulated and beyond was isostatically depressed (part of the earth's crust literally sank to upper mantle depths).

As the crust slowly subsided, upper Ochoan halite, gypsum, dolomite, limestone, potassium-magnesium salts, and red beds (Fig. 6) filled the available space. The added mass of these shallow-water sediments, which eventually exceeded that of the Castile, contributed to continued crustal subsidence. The depression was filled by the close of the Permian, with most of the time of accumulation (~7 Ma) being represented by nondeposition and minor erosion. Near where the cave belt now trends, these latest Permian strata (upper Ochoan Group: the Salado, Rustler, and Dewey Lake formations) buried both the basinal Castile evaporites (lower Ochoan Group) of the basin and the marginal Middle Permian carbonates of the reef, forereef, and shelf by ~1 km (Fig. 20) (see Crysdale, 1987; Lowenstein, 1988; Garber et al., 1989; Ulmer-Scholle et al., 1993; Klimchouk, 2007, p. 76).

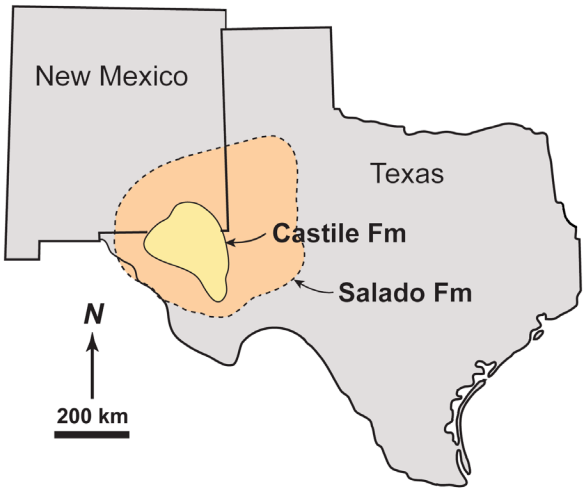

Figure 22. Depositional extent of the lower Ochoan Castile Formation (yellow) and approximate depositional extent of directly overlying upper Ochoan Salado Formation (orange, dashed boundary). Rapid deposition (~200,000 yrs) of ~10,000 km^3 of Castile evaporites helped to deform the surface of the crust downward allowing the Salado Formation—dominantly halite—along with carbonates, redbeds, and evaporites of the Rustler and Dewey Lake formations to cover the western Delaware Basin and Guadalupe Mountains with about 0.8-1.0 km of sedimentary strata. In the Late Tertiary, much of the thick Ochoan cover eroded from the Guadalupe Mountains and surrounding area.

Late Tertiary Tilting of the paleo-Guadalupe Tectonic Block

The southern Rio Grande rift, an active thermo-tectonic system of central New Mexico, extends into far west Texas (Seager and Morgan, 1979). The rift experienced renewed activity at 11 Ma (early late Miocene) and 6-4 Ma (latest Miocene-earliest Pliocene) (Lueth et al., 2005), times that coincide with pulses of intense speleogenesis in the Guadalupe Mountains (Polyak et al., 1998). These correlations imply that the major faults that episodically and uniformly tilted strata of the ancestral Guadalupe tectonic block were active at the same time as caves were forming in the mountains (Polyak, 1998; Polyak et al., 2006). Each episode of intense speleogenesis, of which there were at least three (Polyak et al., 2006), was apparently caused by a major increase in eastward tilting of the ancestral Guadalupe tectonic block. With each increase, the accessibility of H_2S, O_2, or both, to the developing caves increased; sulfuric acid production improved, and the intensity of speleogenesis in the Capitan Formation, Seven Rivers Formation, and, uncommonly, other shelfal units strengthened (see Polyak et al., 2006).

Tilting of the paleo-Guadalupe tectonic block culminated in its present 1-2° eastward dip (Hayes and Gale, 1957; Olive, 1957; Hentz et al., 1989; Hill, 1996, p. 219; DuChene and Martinez, 2000), the tilted province rising to the west by 17-22 m/km (King, 1948; Grauten, 1965) (Fig. 23). Strata of the ancestral Guadalupe Mountains and most strata of the Delaware Basin responded as a single structural unit, and with each episode of uplift the accrued gradient of the strata increased slightly. Episodes of tectonic deformation persisted through the late Miocene and early Pliocene, but by the mid-Pliocene they had ceased (DuChene and Cunningham, 2006, and references therein).

The uniform dip of Upper Permian strata throughout most of the basinal segment of the paleo-Guadalupe tectonic block was significantly disturbed at just a few places. Perturbations affecting the consistent eastward dip of Castile strata were principally sparse faulting (e.g., Smith, 1978, 1980; Hentz et al., 1989), minor folds (Kirkland and Anderson, 1970), and elongated anticlines adjacent to the northern Capitan reef (Anderson and Powers, 1978; Hill, 1996, p. 240). In addition, near Slaughter Canyon Cave (Fig. 5), a northwest-trending monocline underlain by a Pennsylvanian or older thrust fault extended into the basin (Hayes, 1964; Kelley, 1971). Castile strata throughout most of the Delaware Basin, except for such localized and generally minor structural disturbances, had (and still have) a similar gradient. Such a structural unit in which strata persistently exhibit the same dip is termed a "homocline," and the present-day basin has been subdivided into a "homoclinal province" and an "anticlinal province" (Grauten, 1965, his fig. 2), with the latter province occurring only in the far southwestern and far eastern parts. A structural contour map on the base of the Castile east of the Guadalupe Mountains and east of the lower-lying Delaware Mountains (Fig. 23) shows the approximate modern homoclinal configuration. The homocline encompassed not only the basin, but the Delaware Mountains, the Guadalupe Mountains, and along the mountain front, the Capitan reef and forereef. During the late Miocene, the eastward tilt was not as pronounced, the homoclinal slope probably extended further to the west, departures from the uniform upward dips were fewer, and strata of the ancestral Guadalupe tectonic block probably more closely approached a classic homocline.

The uniform dip of the homocline, however, was disturbed near where the cave belt now trends (e.g., Hunt et al., 2003). The disturbance resulted primarily from differential subsidence that occurred during Middle Permian time as the reef prograded into the basin over its own forereef debris and over basinal siliciclastics of the Bell Canyon Formation (Fig. 20). The progradation resulted in down-to-the-basin faults and associated folds (e.g., Hunt et al., 2003; Kosa and Hunt, 2006a, 2006b) on which the Late

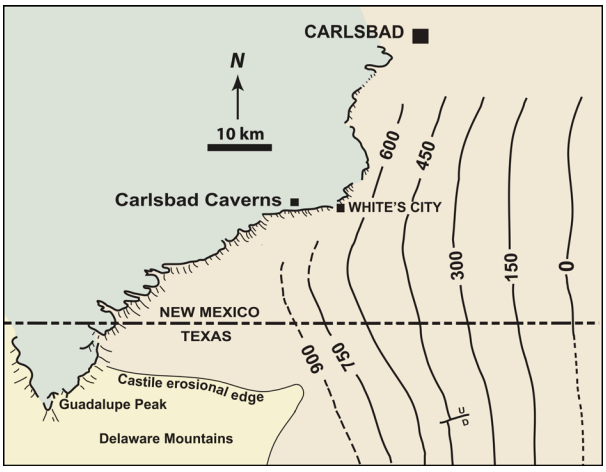

Figure 23. Structure contour map on base of the Castile Formation; contour interval, 150 m; map shows the general eastward, nearly homoclinal dip of the Guadalupe tectonic block; contours in New Mexico are after Dean (1967, his figure 8) and contours in Texas are after Hentz et al. (1989, their fig. 25); see also Grauten (1965, his fig. 2) and Hiss (1975, his fig. 15).

Tertiary regional uplift of the Guadalupe tectonic block was superimposed. The Late Tertiary tilting reactivated ancient Middle Permian joints and syndepositional faults and possibly created new ones. The fractures served as pathways for groundwater, as pathways for atmospheric oxygen, and as guides for cave development (e.g., Jagnow, 1977; Kosa and Hunt, 2006b).

Free Convective Dissolution

Shallow (<1,000 m) bedded evaporites—chiefly gypsum, anhydrite, and halite—underlie the earth's surface in many depositional basins. Such evaporites commonly interact with two principal categories of groundwater: One category, groundwater that descends from recharge surfaces above sedimentary strata is designated "epigene." This is the groundwater, for example, that descends from the surface into karstic features such as modern sinkholes. Another category, groundwater that ascends from underlying sedimentary strata is designated "hypogene." Such groundwater is unrelated to water infiltrating (or in-flowing) from either overlying or directly adjacent recharge surfaces (Klimchouk, 2007, p. 3). Hypogenic groundwater, usually artesian, may occur at substantial depth (hundreds of meters), and, under pressure, may rise via forced convection through fractures crossing bedding of non-evaporitic strata to contact evaporitic strata. Such hypogenic groundwater then initiates speleogenesis by free convection without direct connection to the surface (e.g., Anderson and Kirkland, 1980; Klimchouk, 2007; Stafford et al., 2008b).

Most epigenic groundwaters are fresh, and in such waters halite is exceedingly soluble 360 g/l at 20°C and 370 g/l at 50°C, with temperature differences having only slight effect. Even brines are strongly aggressive toward halite as long as they are significantly undersaturated with respect to NaCl (Ford and Williams, 2007, p. 45). As the salinity increases, however, the rate of dissolution decreases (Stiller et al., 2007). On contacting halite, undersaturated hypogenic groundwater approaches saturation, its density increases (commonly substantially), it descends, and a type of free convection begins: dense brines sink and simultaneously less dense groundwaters rise. Such convection has been termed "brine-density flow" (Anderson and Kirkland, 1980).

A similar process of free convection in the Castile, albeit without formation of brine, occurs when solutionally aggressive, hypogenic groundwater contacts anhydrite (or gypsum); $CaSO_4$ goes into solution, the aqueous solvent increases in density, it becomes gravitationally unstable, and it sinks (e.g., Kempe, 1996). Such anhydritic and halitic dissolution processes can be incorporated into the single term "density-driven flow," a term that applies to all circumstances in which a change in density of a fluid, either from an increase (or decrease) in temperature or from an increase (or decrease) in solute concentration, causes fluid flow. Density-driven flow may take place in either hypogenic or epigenic groundwater, and it may result from a relatively large increase in density, as when halite dissolves, or it may result from a relatively small increase in density, as when anhydrite and gypsum dissolve. Only a small relative increase or decrease in density (>0.01%) is enough to cause water to sink or to rise, assuming sufficient permeability is available. (In Gulf Coast sediments, dissolution and mass transfer of NaCl occurs even if sediments beneath halite have permeabilities as low as 0.01 md (Sarkar et al., 1995).) Where hypogenic groundwater actively dissolves a salt (e.g., gypsum, anhydrite, halite), the term "free convective dissolution" is applicable.

In laboratory experiments involving dissolution of halite by free convective flow of hypogenic water, the ascending fresh (solutionally aggressive) water and the descending nearly NaCl-saturated brine flowed simultaneously through a simulated fracture. The pathways were close, but the ascending pathway was separate and distinct from the descending pathway; the result was two-way flow (Anderson and Kirkland, 1980). The two fluids, acting almost as immiscible liquids, exhibited little interaction. Natural fractures contain micro-conduits that provide separate pathways for similar ascending and descending fluids. In such systems, the salinities of the rising and sinking groundwaters, which flow simultaneously and without turbulence, would probably be only marginally altered by diffusion and by commingling. In addition, density-driven flow initiated as solutionally aggressive, hypogenic groundwater contacts halite or anhydrite liberates potential energy. The liberation is manifest by the kinetic energy of hypogenic groundwater as it flows to form voids within halite and within anhydrite. If the hydrologic system were not dynamic, dissolution would cease.

Both halite and anhydrite commonly fuel natural hypogenic-induced convection, with these salts, in a sense, becoming the vehicle of their own annihilation. Aggressive water that dissolves halite increases in

density by up to 20%, whereas aggressive water that dissolves anhydrite, which under normal temperature conditions has a solubility equivalent to that of gypsum (Klimchouk, 2000), increases in density by up to only ~0.1% (see Klimchouk, 1997a). However, where hypogenic, solutionally aggressive groundwater, such as most artesian groundwater, contacts bedded anhydrite (or gypsum), the relatively slight increase in density due to incorporation of Ca^{2+} and SO_4^{2-} can easily result in density-driven flow. Such "natural convection" can form large caverns within anhydrite (Kempe, 1996). Indeed, free convective flow is apparently an effective mechanism for enlarging caves within limestone (e.g., Curl, 1966), although such enlargements, compared to those within anhydrite and gypsum, would occur at exceedingly slow rates.

The solubility of anhydrite increases by up to three times in the presence of a NaCl-rich brine (e.g., Klimchouk, 2000). Thus, as a brine substantially undersaturated with respect to $CaSO_4$ descends through fractures and through voids within bedded anhydrite, it is an effective solvent. Fresh hypogenic groundwater rising within a fracture pathway through a bed of anhydrite could, for example, potentially dissolve $\leq$ 2.5 g/l of $CaSO_4$, whereas NaCl-rich groundwater sinking through the same pathway could potentially dissolve > 4 g/l of $CaSO_4$. Halite is commonly associated with anhydrite; thus, hypogenic groundwater that dissolves halite forms a solvent for $CaSO_4$ that enhances permeability during its descent through anhydrite strata.

Two-way flow persists during convective dissolution as long as solutionally aggressive hypogenic groundwater contacts either halite or anhydrite. The rates of flow of the ascending and descending groundwater, however, depends on the character of

- the reservoir of the solutionally aggressive groundwater,
- the hydraulic pathway,
- the rising and sinking fluids (e.g., solute concentration, viscosity), and
- the reservoir for the sinking, nearly saturated brine.

The rate of flow decreases as the concentration of the descending brine increases because of a reciprocal relationship with viscosity (Anderson and Kirkland, 1980); and, given similar conditions, the rate of flow increases as the slope of pathways (<1° to 90°) increases through which aggressive water rises and through which saline water drains.

In early studies in the western Delaware Basin, artesian (hypogenic) groundwater was hypothesized to have played a critical role in forming present-day and ancient geomorphologic features as well as mineral deposits on and beneath the Gypsum Plain, namely:

- east-west trending "solution-subsidence troughs" (Olive, 1957),
- sulfur deposits (Hinds and Cunningham, 1970),
- castiles (Kirkland and Evans, 1976), and
- many karstic features within the Castile and Salado evaporites (Anderson, 1978; Anderson and Kirkland, 1980).

These suppositions have been supported by recent work. Many karstic features within the Castile formed during the Quaternary and Late Tertiary by hypogenic convective groundwater; free convective dissolution (involving density-driven flow) is widespread (e.g., Klimchouk, 2007; Stafford et al., 2008a; Stafford et al., 2008b, 2009; Nance and Stafford, 2009; Melville, 2009). Stafford (2008b), for example, states, that the "…Castile Formation exhibits a diagenetic history that has been dominated by hypogene processes with fluids, both water and hydrocarbons being delivered upward from permeable clastic units of the Delaware Mountain Group" (the group that consists of the Middle Permian Bell Canyon, Cherry Canyon, and Brushy Canyon formations (Fig. 6)). Inlet risers, wall channels, ceiling half tubes, and outlet cupolas "provide unequivocal evidence of dissolution driven by mixed convection from rising fluids" (Stafford, 2008b) ("mixed convection" being forced and free convection occurring together). The magnitude of the hypogenic processes is great: more than half (55%) of all sinkholes in Castile evaporites, for example, of which there are many hundreds, "…are the result of upward stoping of subsurface voids" (Stafford et al., 2008a).

Bell Canyon Formation: The Reservoir of Rising Aggressive Water

In the Late Tertiary in the western basin, a reservoir of groundwater under chiefly artesian pressure with substantial solutional aggressiveness for anhydrite and halite occurred several meters below the base of the Castile evaporites. The reservoir comprised an essential element

for prolonged and persistent convective dissolution within the Castile. The "holding reservoir" for the aggressive groundwater was porous sandstone of the underlying upper Bell Canyon Formation (Fig. 6). The sandstone, although limited in its transmissibility, provided an adequate rate of flow of groundwater. The Bell Canyon aquifer consists generally of very fine-grained, porous (22-27%), weakly cemented, silty, arkosic sandstone (Williamson, 1977). An upper sandstone unit of the Bell Canyon Formation—the Ramsey, a channel sandstone—has an average permeability of 39 md (Dutton, 2008).

The hydraulic conductivity of the Bell Canyon is variable on local and on sub-regional scales (Davies, 1983). Facies of the Bell Canyon with the greatest potential as a reservoir of groundwater were (and are) channel-fill sandstones (e.g., Dutton, 2008). Such reservoirs trend northeast-southwest, range from less than 0.5 km to more than 6 km in width, 1 m to more than 35 m in thickness, and up to 70 km in length (Williamson, 1977; Berg, 1979, his fig. 4).

Beds of upper Bell Canyon sandstone presently constitute an active regional flow system (Hiss, 1975, 1980). The few stock wells drilled into the Delaware Mountain Group, probably into the upper Bell Canyon, "have well yields ranging from 5 to 20 gallons per minute (0.3 to 1.2 l/sec)" (Nielson and Sharp, 1990). Movement of pore water within these siliciclastic beds, unlike movement of hydrocarbons, is unencumbered by capillary forces. It was "50 times" more difficult for typical Bell Canyon crude oil to move through sandstone of the upper Bell Canyon Formation, than it was for water (Nottingham, 1960); yet oil migrated through the upper Bell Canyon Formation, and is trapped in sandstone reservoirs in the central and eastern Delaware Basin (Berg, 1979, his fig. 1). Evidence for present-day artesian flow within the Bell Canyon include, an eastward dipping potentiometric surface (McNeal, 1965, his fig. 7), hydrodynamic entrapment of oil, and significant changes in water chemistry over short distances (Davies, 1983). Clearly, where a pressure gradient existed, groundwater flowed within sandstone of the upper Bell Canyon Formation. Artesian pressures during the Late Tertiary probably exceeded present-day artesian pressures (Lindsay, 1998), and flow rates were correspondingly greater.

Where permeability existed, hydraulic pressure during the Late Tertiary drove groundwater (by forced convection) from the Bell Canyon sandstone upward into Castile evaporites. Initial entry points into the lower anhydrite member—the Anhydrite I Member—were along joint and fault planes (e.g., Kirkland and Evans, 1976; Hill, 1990; Stafford et al., 2008b), and probably commonly at junctions of joint sets. Furthermore, artesian groundwater

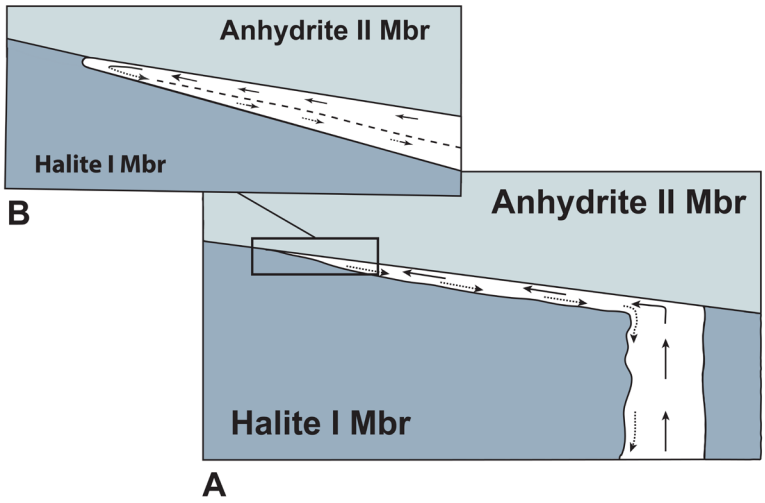

Figure 24. Diagrammatic representation of dissolution by hypogenic groundwater of Castile halite (dip greatly exaggerated): ***A.*** Vertical extending, chamber (white) formed in Halite I Member (dark blue) of the Castile Formation; on contacting the smooth base of the extensive and uniformly dipping (<<2° E) Anhydrite II Member (light blue), the void changed direction markedly, and directly below an anhydrite ceiling a probably narrow (< ≈30 m) and low (< ≈2 m) conduit advanced by dissolution for kilometers directly up the slope of the ancestral Guadalupe tectonic block. Solid arrows show upward flow during free convection of freshest groundwater (brackish-to-slightly saline), and dotted arrows show concurrent downward flow of concentrated brine. With dissolution of halite, an anhydrite residue, not shown, accumulated on floor of conduits (now represented by a micro-breccia (Fig. 21B)). ***B.*** Enlarged diagram of dissolution wedge at the uppermost part of advancing chamber; aggressive groundwater flowing upward along the top of the chamber came directly into contact with halite and actively dissolved NaCl. As it did so, the density of the groundwater increased, and under influence of gravity, its direction of flow diametrically reversed and nonaggressive brine descended along the bottom of the chamber, in part, through pores of anhydritic residue. Dashed line diagrammatically represents interface between fresher water at top and more saline (NaCl at or near saturation) below; dip of interface is greatly exaggerated, while conduits were forming, actual dip was probably < 0.5%.

along with overpressured water (forced out of shale) (Lee & Williams, 2000) rose into the upper Bell Canyon from deeper aquifers. The waters flowed through connected micro-openings along fault surfaces (slip faces). These waters helped re-supply both hypogenic groundwater that rose from upper Bell Canyon siliciclastics into the Castile evaporites (and ultimately moved upward and out of the basin) and nonaggressive brines that sank into Bell Canyon sandstone and ultimately moved downward and out of the basin or downward and into its depths.

Presently, much water within the upper Bell Canyon aquifer is highly saline (McNeal, 1965; Hiss, 1975). This was probably not the condition before inception of the Late Tertiary tilting and fracturing when beds of Bell Canyon sandstone, despite residing beneath a thick (>800 m) sequence of halite-rich evaporites, probably contained pore water that was only brackish-to-slightly saline. Three nearly stratigraphically adjacent, lithologic barriers of extremely low permeability (aquitards) prevented brine that may have originated within the overlying halitic section from sinking into Bell Canyon sandstone. One barrier, situated at the base of the Castile Formation, was a thin (< 1 m), basin-wide, laminated carbonate—the "Basal Limestone Member" (King, 1948; Anderson et al., 1972; Cys, 1978) (Fig. 17). Its petrography (Anderson et al., 1972) and its $\delta^{13}C$ values (0.0‰ to +2.5‰ (Magaritz et al., 1983, their fig. 5)) indicate that this member formed, not by diagenesis (Stafford et al., 2008b), but by sedimentation. A second barrier, 6-9 m below the base of the Castile (Anderson et al., 1972; Wilde et al., 1999; Tyrrell et al., 2006), the Lamar Limestone Member of the Bell Canyon Formation (Fig. 6), has a thickness of 30 m or more near the reef escarpment. It thins progressively into the basin and within 13 to ~30 km southeast of the escarpment pinches out (Tyrrell et al., 2006, their figure 2.23). A third barrier, and the most formidable, was the thick (~50 m) basal anhydrite of the Castile Formation (the Anhydrite I Member). Before being fractured during uplift, it was virtually impermeable.

Formation of Chambers and Breccias within the Basal Anhydrite Member of the Castile Formation

With tilting of the Guadalupe block, fractures breached the aquitards, and in the northwestern and west-central Delaware Basin solutionally aggressive groundwater under chiefly artesian pressure rose through the fractures into the Anhydrite I Member. Replacement of anhydrite by gypsum may have occurred along fractures, and the increase in volume of the gypsum may have closed micro-conduits and reduced or eliminated permeability (Stafford, 2008b). Expansion on gypsification has been

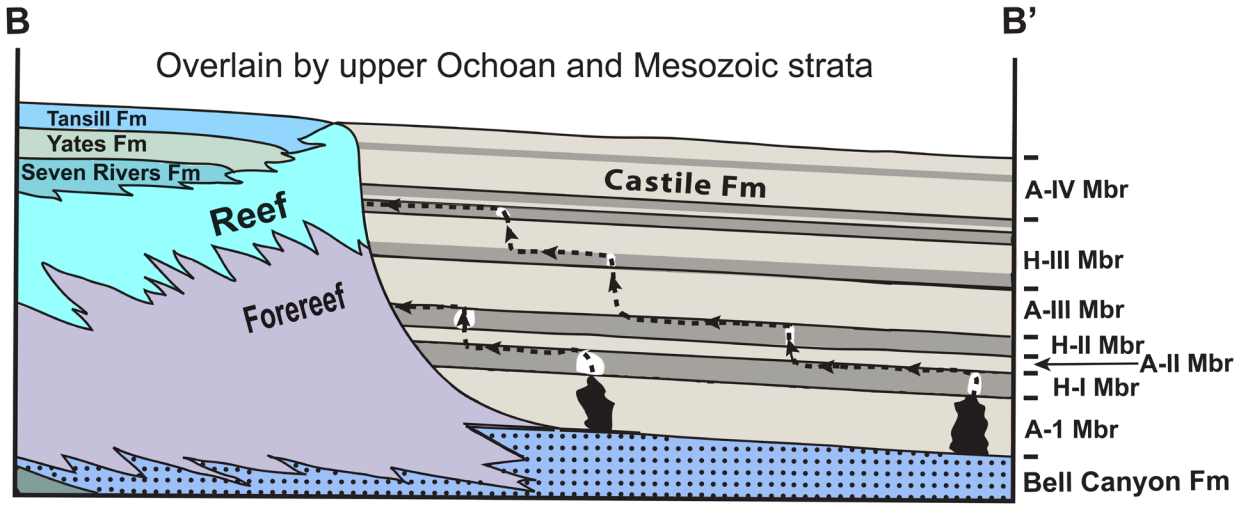

Figure 25. Diagrammatic northwest-southeast cross section through the central cave belt after uniform (homoclinal) tilting by <2° of the paleo-Guadalupe tectonic block as it may have existed in the early Pliocene (line of cross section BB' is shown in Figure 5); dip of beds is exaggerated. Two hypothetical, groundwater pathways are shown (of the many that are hypothesized to have existed) in which groundwater flowed (propelled by forced convection) from porous sandstone of the Bell Canyon Formation into the Capitan Formation. H_2S generated at the porous, biogenic carbonate masses (black) was transported in solution upward within the flowing, pressurized groundwater. The H_2S-bearing groundwater passed diagonally through intermittent fractures (as well as breccia chimneys and voids) within the anhydrite members (light gray), through dissolution chambers (white) within the halite members (dark gray), and for kilometers through conduits at the very top of halite beds.

documented for the Castile (Anderson and Kirkland, 1966, their pl. 4), but elsewhere it has seldom been substantiated (R. Evans, personal communication, 1990; Klimchouk, 2000), and deep within the Castile, expansion during gypsification may have been uncommon. However, if micro-conduits within fractures of the Anhydrite I Member were closed by expanding gypsum, they would have been reopened readily by free convective dissolution.

Most castiles contain a central core of calcitized anhydrite breccia (Hayes, 1964; Brown and Loucks, 1988; Stafford, 2008a, p. 166; 2008b) (Fig. 16B). The brecciated core apparently formed as bedded anhydrite collapsed into caves that formed as hypogenic groundwater, significantly undersaturated with respect to $CaSO_4$, rose through fractures, contacted bedded anhydrite, dissolved $CaSO_4$, increased in density, and descended gravitationally, all within the field of laminar flow. Subsequently, gaseous CH_4 may have migrated into the voids, ephemerally displaced water, diminished support of directly overlying anhydrite, and induced brittle failure (i.e., by fracturing) (see Bögli, 1980, p. 213). Displacement of the ambient groundwater removed both the buoyant force of the groundwater and the support provided by artesian-pressured and overpressured groundwater. The roof became unstable, and with its collapse into the void, directly overlying beds of anhydrite deformed by stoping, and in a cascading process, the caves filled with fragmented anhydrite. Before cementation and/or compaction, the breccia bodies had substantial permeability, the void space essentially equaling the volume of anhydrite removed (Davies, 1983).

Analogous caves (exceeding 200 m in dimension) within Zechstein gypsum or anhydrite of the Sangerhausen and Mansfeld districts, Germany, formed by this same process of free convective dissolution (Kempe, 1996). "About 100 cavities of this type are known in the region, encountered through the centuries in the course of mining operations at depths of up to 400 m at the base of the Zechstein gypsum" (Klimchouk, 2007, p. 26). In the Guadalupian backreef facies of southeastern New Mexico, "numerous hypogene caves occur where fluids rise through interbedded carbonates and evaporite rocks" (Stafford et al., 2008b; Stafford et al., 2009). The sinkholes at Bottomless Lakes State Park, ~23 km southeast of Roswell, New Mexico "are the product of subsurface dissolution of gypsum by upward leakage of groundwater from the karstic San Andres limestone" (Land, 2006). Most anhydrite breccias and most associated karstic features within the Castile and Salado formations of the Delaware Basin, however, owe their origin, not to dissolution of anhydrite ($CaSO_4$), but to dissolution of the much more soluble evaporite mineral, halite (NaCl).

Formation of Chambers, Breccias, and Conduits within the Basal Halite Members of the Castile Formation

Following tilting of the ancestral Guadalupe tectonic block, rising artesian groundwater at many localities in the northwestern and west-central basin eventually breached the Anhydrite I Member and contacted the base of the Halite I Member of the Castile Formation (Fig. 17). This latter member, free of anhydrite layers > ~3 mm thick, is, at ~125 m, the thickest of the three Castile halite members (Fig. 17). The rising solutionally aggressive artesian groundwater dissolved halite, and chambers grew vertically upward, a consequence of the most aggressive water available for dissolving NaCl—the freshest, least-dense water—continually rising directly to the very top of the growing void where dissolution took place (Fig. 24). The thin intercalated anhydrite laminae within the halite member provided essentially no impedance to upward dissolution. The resulting brine sank into the underlying sandstone beds of the upper Bell Canyon, removing the solute from the Castile.

The directly upward growing dissolution chambers within the Halite I Member were eventually blocked. Blockage occurred when advancing voids contacted the intact lower boundary of the thick (~30 m) overlying Anhydrite II Member (Fig. 24), a rock unit of relatively poor solubility and low permeability. The freshest, least-dense, most aggressive water, however, continued to rise; it turned a sharp angle directly beneath the anhydritic ceiling, and dissolved a void within halite directly up the slight tilt of the homoclinal block (Fig. 24). Advancement progressed within the bedded Halite I Member by free convective dissolution, the voids growing laterally westward and slightly upward just below the smooth base of the Anhydrite II Member, which dipped uniformly eastward by < 1° and which extended over thousands of square kilometers. The boundary of the Castile anhydrite members with underlying halite members did not differ greatly from a smooth, slightly sloping plane. Collapse of the westward advancing conduits was impeded by

the probably modest width of the voids, the presence of pressured water, and the strength of the anhydritic ceiling.

Above the Halite I Member, nearly vertical fractures probably intermittently and transversely cross the slightly tilted Anhydrite II Member. They are probably spaced sparsely because during uplift the intercalated, incompetent beds of Castile halite incorporated most strain. A fracture within the anhydrite ceiling intersected by a conduit provided incipient permeability that may have been slowly enhanced by free convective dissolution. The near-vertical fracture pathway may have eventually allowed pressurized groundwater, undersaturated with respect to NaCl, to flow transversally upward through the capping bed of anhydrite and to contact a directly overlying bed of halite (Fig. 25). The Anhydrite II, III, and IV members were less prone to dissolution by convecting hypogenic groundwater than the lower part of the Anhydrite I Member because groundwater dissolved much $CaSO_4$ during its upward passage through lower anhydrite strata and, thus, had limited potential for dissolving more.

Once groundwater transversally breached a bed of anhydrite, free convective dissolution once again created a nearly vertically trending chamber through the overlying bed of Castile halite until the void contacted the next intact bed of anhydrite. Then, an up-slope-trending conduit at the top of the bed of halite advanced by the same convective dissolution process directly beneath the eastward dipping and "capping" bed of anhydrite (Fig. 25). Solutionally aggressive groundwater for halite, for example, that rose transversely through the Anhydrite II Member formed vertical, upward trending chambers through the Halite II. Then, at the top of the Halite II, directly beneath the Anhydrite III, aggressive groundwater dissolved linear conduits up the slight slope of the paleo-Guadalupe tectonic block. Similarly, aggressive groundwater rising transversely within fractures across the Anhydrite III Member may have formed vertically trending chambers within the Halite III Member, followed by up-slope-trending conduits (beneath an anhydrite ceiling) within the member (Fig. 25).

Linear conduits within Castile halite propelled forward by free convection advanced up the slight grade of the homocline (Fig. 25). Each began at the widely distributed localities at which a buried body of permeable biogenic limestone was forming, or would soon form. The detailed configuration of the anhydrite ceiling within growing conduits (i.e., the "upside down topography") controlled precise directions followed by the advancing conduits. Specifically, the loci of continuously connected high points on the ceiling provided a track for the most aggressive groundwater—the freshest, least dense—to flow upward within conduits directly beneath the bedded anhydrite (Fig. 24A).

As groundwater with solutional aggressiveness for NaCl flowed up the low gradient, highly saline groundwater simultaneously flowed down the low gradient. The newly formed brine under the influence of gravity required only a slight downhill slope to induce flow. When uplift of the paleo-Guadalupe tectonic block ceased in the mid-Pliocene, for example, at a slope of ~20 m/km, its gradient was >1000 times greater than the gradient of the Amazon River from Manaus, Brazil, 1,610 km downstream to Belém, Brazil (online Columbia Encyclopedia). Some conduits departed slightly from linearity because of slight irregularities in the anhydritic ceiling, and because, as NaCl dissolved, gas may have rarely "salted out" to form temporary obstructive pockets. Furthermore, the path of conduits extending upward from different points of origin commonly coalesced because of chance alignment, and as conduits approached the margin of the basin, they may have received aggressive groundwater from several centers, each having different rates of flow.

The morphology of hypothesized conduits within Castile halite must be inferred. Halite because of its high solubility fails to crop out except in extremely arid climates, thus, accessible cave systems within halite are uncommon, and the body of knowledge about such cave systems is limited. Inferences about the morphology of caves within halite based on analogy are untrustworthy compared to those made for the morphology of caves within limestone or gypsum. Conduits within Castile halite are hypothesized to have had a narrow width ($< \approx 30$ m). Their narrowness is inferred because groundwater with maximum aggressiveness for halite moved upward as a "stream" directly beneath an anhydrite cap following connected subtle "highs" with only slight tendency for lateral departure, and, hence, for lateral dissolution. Furthermore, the conduits are hypothesized to have had a low ($< \approx 2$ m) height because high-density concentrated brine probably mantled their slightly dipping floor, shielding underlying halite from dissolution (Fig. 24 A and B); and they are hypothesized to have had a length that extended for up to several tens of kilometers (≈30 km).

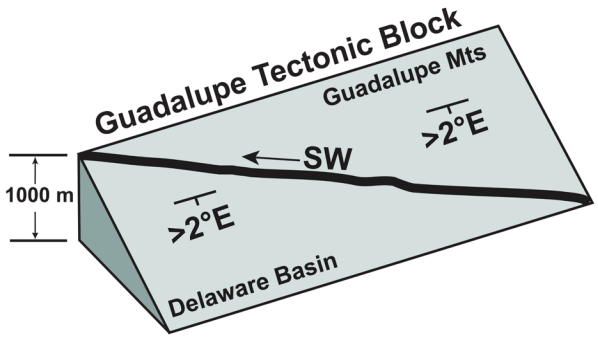

Figure 26. Schematic representation of southwest trending cave belt (black band) on eastward dipping homocline (the tilted Guadalupe tectonic block) showing that since early late Miocene, when tilting probably began, the most elevated part of the cave belt has been to the far southwest. Diagram explains the present >1,500 m difference in elevation between the top of youngest Capitan reef at Carlsbad, New Mexico, and the top of youngest Capitan reef near Guadalupe Peak, Texas.

Aggressive water within a conduit most actively acquired NaCl at a wedge-shaped dissolution apex (Fig. 24 B). It occurred at the westernmost part of a growing conduit, at that part with the highest elevation. Here, conduits probably thinned to less than a centimeter and aggressive groundwater propelled by free convection contacted Castile halite directly, dissolved NaCl, and moved toward saturation. The solvent then reacted to gravity, its direction of flow changed by 180°, and concentrated brine drained down the homocline in a direction diametric to that of the rising aggressive water (Fig. 24). Thus, a "stream" of moderately saline, medium-density, aggressive groundwater within each advancing conduit probably flowed up-gradient above a "stream" of NaCl-saturated (or nearly saturated), high-density, nonaggressive brine flowing down-gradient, the volume of water ascending equaling the volume of water descending. A thin residue of poorly soluble anhydritic debris mantled the halite floor of conduits (anhydrite laminae constituting 5-10-vol % of Castile halite).

Free convective dissolution of halite probably resulted in growth of conduits mainly during the early part of the multi-million-year interval in which the ancestral Guadalupe tectonic block was being episodically uplifted and tilted. The rate of growth of conduits is difficult to deduce. Compared to the rate at which dissolution of halite advanced vertically within the Halite I Member to create chambers, the rate at which dissolution of halite advanced laterally up a slight slope within the Halite I Member to create conduits was presumably slower. With each episode of tectonic uplift, the rate of advancement of conduits increased.

In laboratory experiments, distilled water dissolved a block of salt hypogenically through a capillary tube (1.5 mm in diameter) at a rate of one gram per minute in pulsating flow, and hypogenically by distilled water through a simulated fracture (1 mm in width) in two-way flow at a rate of descent of about 5 cm/sec (Anderson and Kirkland, 1980). These experiments support rather rapid dissolution through natural conduits. The rate of dissolution of Castile halite was persistent and probably always exceeded the rate of ductile closure of halite bounding conduits on their bottom and sides. The natural sinking brine, however, was relatively viscous, as considered above, which slowed its rate of descent, and, in turn, the rate of ascent of solutionally aggressive groundwater. Furthermore, friction between the fluid layers (Fig. 24B) and between the wall rock and the fluid layers increased as the length of conduits grew, decreasing the rate of flow. Because of the slight grade, the persistent need for aggressive water, and the persistent need for removal of brine from the system, many conduits probably advanced up the homocline at a rate of probably hundreds-to-thousands of years per kilometer.

Conduits within halite grew upward until many eventually contacted the Capitan reef or the steep Capitan forereef. Some conduits, however, contacted an anhydritic barrier that mantled parts of the forereef. This obstruction originated from Ca^{2+}-bearing

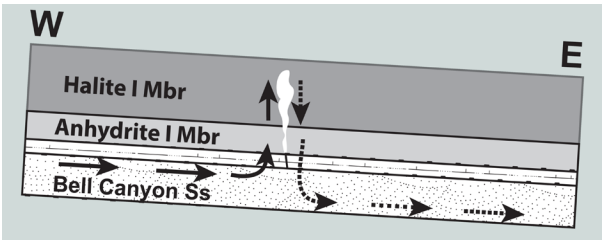

Figure 27. Diagram showing fresh-to-brackish groundwater (largely artesian) ascending from tilted Bell Canyon sandstone through a fracture into Castile anhydrite and Castile halite where dissolution occurred (white area), and brine from dissolution of Castile halite descending (dotted arrows) into the Bell Canyon sandstone. Within the Castile, the up and down pathways of convective flow were close, but separate. In the upper part of the bed of Bell Canyon sandstone, fresh-to-brackish groundwater flowed downward (from an updip direction) and rose into the Castile, whereas in the lower part of the same bed of sandstone, brine that descended from the Castile flowed in a downdip direction. Dip of beds is exaggerated.

spring water, and at places the anhydrite barrier was positioned between shallow-to-moderately dipping beds of Capitan forereef and slightly dipping beds of Castile halite.

The upper surface of the Capitan reef was exposed during deposition of Castile evaporites (e.g., McKee, Oriel, et al., 1967; Garber et al., 1989), and it experienced sporadic rainfall causing springs to flow from the lifeless reef into the Castile brine body. The volume of spring water that discharged annually, however, was probably small; only minor amounts of rainfall fell onto the reef both because the surrounding, flat desert failed to support orographic precipitation and because a seasonal, relatively cool, near-surface layer of air flowing from the ocean to the west reduced atmospheric convection (see Kirkland, 2003). Aridity was at a peak during precipitation of Castile halite, temperatures were unusually high, droughts were unusually long, and discharge from the springs was particularly low.

Where spring water discharged during the earliest Late Permian into the Castile brine body, it resulted in a thin barrier of gypsum consisting, in part, of gravity deposits that mantled the lower forereef. Following a minor pluvial event, and while Castile halite was the evaporite facies being precipitated, spring water near discharge points diluted the surface of the Castile brine causing halite to cease precipitating within a narrow marginal area. It also introduced Ca^{2+} (derived from dissolution by groundwater of reef and back-reef carbonates and back-reef gypsum). The Ca^{2+} reacted with excess SO_4^{2-} within the near-surface, marine-derived Castile brine, causing calcium sulfate to supersaturate, and inducing gypsum to precipitate adjacent to the reef. Gypsum accumulated where the slope of the forereef was below the angle of repose. With burial in the latest Permian by strata of the upper Ochoan Group (Fig. 6), the gypsum was replaced by anhydrite.

Conduits within Castile halite that advanced directly to the lower-to-middle forereef may have been blocked at some places by the spring-derived, anhydritic cover; with their upward and westward advancement obstructed, growth of conduits changed direction. Still within the uppermost part of a bed of Castile halite, they advanced by density-driven, free convective dissolution southwesterly up a decreased slope (e.g., < 0.5°; illustrated by the slope of the southwestern trend of the Capitan reef on the eastward dipping Guadalupe tectonic block (Fig. 26)). Such southwesterly-trending conduits within the halite members, probably relatively commonplace within the Halite I Member, advanced by convective dissolution parallel to the reef until the pressurized hypogenic groundwater within them encountered a pathway into the ancient reef.

Many conduits within the Upper Permian Castile halite terminated laterally against the Middle Permian Capitan reef. Near where the Capitan escarpment now trends, and before and during uplift of the Guadalupe block, the Halite III Member, for example, was probably in direct contact with the reef (Fig. 25), which had a dip that exceeded 80° (B. L. Kirkland et al., 1999). Furthermore, the Halite II Member of the Castile was in direct contact with the steep upper forereef, which had a maximum dip of ~65° (Mruk and Bebout, 1993). Its face was unable to retain spring-derived gypsum. Where conduits within halite members of the Castile were flush against the youngest-most reef or upper forereef, the H_2S-bearing groundwater flowed by forced convection through both fractures and pores into the basin-fringing rocks of limestone and dolomite, rocks that would eventually constitute the cave belt (Fig. 25).

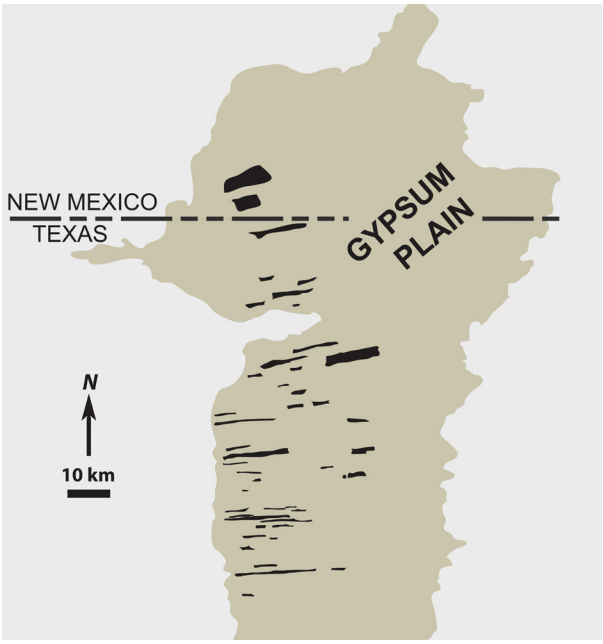

Figure 28. Distribution of solution-subsidence troughs on the Gypsum Plain; after King (1949) (New Mexico), and Hentz et al. (1989) and Hentz (1990) (Texas).

Bell Canyon Formation: The Repository of Sinking Brine

Groundwater within the Bell Canyon Formation during growth of conduits flowed under pressure (in large part artesian) upward into the halite members of the Castile Formation where it was transformed into dense brine inducing two-way flow. The brine sank, flowed down the conduits, and discharged into Bell Canyon sandstone. Relatively fresh, low-density, solutionally aggressive groundwater entered the Castile from the upper part of the underlying beds of sandstone, whereas solutionally nonaggressive, high-density groundwater—commonly saturated, or nearly so, with both NaCl and $CaSO_4$—sank from the Castile into the lower part of underlying beds of Bell Canyon sandstone (Fig. 27). The discharging brine then streamed down the homoclinal slope within Bell Canyon sandstone following the lowest, most permeable route. Most brine flowed northeastward or eastward across the basin, then moved upward under pressure into the Capitan aquifer, and near present-day Hobbs, New Mexico, flowed into San Andres Limestone (Fig. 6), and ultimately discharged into paleo-streams that extended to the ancestral Gulf of Mexico (see Hiss, 1975, 1980).

Some brine that descended into the Bell Canyon probably by-passed the Middle Permian easterly and northeasterly "escape routes" and moved directly downward through any available connected voids (e.g., interstitial pores and bladed cracks) into rocks within and beneath the Bell Canyon where it displaced less-dense water.

Such deep descending brines are expected. They are sequestered within the depths of probably most of the earth's major sedimentary basins, and in some basins, deep brine is the sole record of evaporitic deposition that has otherwise vanished (by dissolution) from the geologic record. A limit to downward flow of brine is either pore water with a greater density than that of the descending brine or an impermeable lithologic barrier, which beneath some sedimentary basins occurs thousands of meters below the contact of sedimentary strata within fractured igneous and metamorphic basement rocks (e.g., Möller et al., 1997).

Density-driven flow of brine from the Castile into the Bell Canyon was persistent, long lasting, and effective. In the early late Miocene, brine flowed slowly away from discharge points without interruption for many thousands of years and perhaps for many hundreds of thousands of years. Within this extended interval, solutes that resulted from dissolution of Castile halite and anhydrite (removal of which formed the chambers and conduits) could have easily been accommodated by Bell Canyon sandstone (e.g., Anderson, 1978, p. 56). Lambert (1983) concluded that the Bell Canyon was an ineffective repository of sinking Castile brine, but his assertion was effectively countered by Davies (1983) who presented evidence for active regional flow within the Bell Canyon.

A large volume of epigenic groundwater having NaCl in solution moved into Bell Canyon sandstone after H_2S-H_2SO_4 speleogenesis in the Guadalupe Mountains had ceased. The groundwater may have been derived, in part, from the western shelf as well as from the western Delaware Basin. Even today, epigenic- and hypogenic-derived brines from dissolution of Castile and Salado halite are probably flowing slowly down the homoclinal slope within Bell Canyon sandstone. These later phases of brine generation (latest Tertiary and Quaternary) were primarily responsible for the present-day, basinal distribution of chlorinity (a stand in for "salinity") that increases gradually eastward from fewer than 10 g/l in the western part of the basin to about 150 g/l along the eastern margin of the basin (Hiss, 1975). Diffusion and density-driven flow within the widespread area of brine-drainage smoothed heterogeneities of the salinity gradient.

Solution-Subsidence Troughs

A series of solution-subsidence troughs on the western Gypsum Plain trend parallel to regional dip and extend from near the latitude of Cottonwood Cave (Fig. 5) south for several tens of kilometers into Texas. These karstic features, which are abundant on the western Gypsum Plain of Texas, are commonly straight, narrow, shallow, flat-bottomed, surface depressions that trend to the east and east-northeast (Fig. 28). They are typically a few meters deep, 0.01 to 1.6 km in width, and 0.8 to ~16 km in length (Olive, 1957; Hill, 1996, p. 312). The troughs have been mapped in Texas and New Mexico by King (1949) and in Texas by Hentz et al. (1989, their pl. 1), and their linear easterly configuration on the Gypsum Plain is remarkably well displayed in "Google Earth." Their eastward (down-dip) limit does not extend beyond the updip limit of either sub-eroded Castile halite or sub-eroded Salado halite (Fig. 18) (Hinds and Cunningham, 1970; Smith, 1980, his fig. 2; Anderson, 1982).

The troughs were investigated by Olive (1957) who hypothesized that Castile gypsum was dissolved hypogenically along underground drainage channels following joints that extended parallel to the direction of regional dip, and that when the roofs above channels could no longer be supported, collapse ensued. Rather than being structurally controlled, could these modern solution-subsidence troughs (Fig. 28) be a surface manifestation of earlier formed Castile dissolution conduits? Such a karstic formation, which may have taken place during the Pliocene, would explain their lineation, their abundance, and especially their easterly dip directly down the slope of the Guadalupe tectonic block. South of the latitude of Carlsbad Cavern in New Mexico, the Anhydrite III and IV Members of the Castile and Quaternary alluvium may have obscured some solution-subsidence troughs (as well as some castiles). The unusual troughs probably exist because of dissolution of gypsum or anhydrite, or both, not because of dissolution of halite, which by the beginning of the Pleistocene, at the latest, had been pervasively removed from areas now encompassed by the troughs (Stafford et al., 2008a).

In the early late Miocene, a thick sequence (hundreds of meters) of primarily Rustler and Salado strata covered the western Delaware Basin the paleo-Guadalupe Mountains, and, in Texas, the area represented by the Delaware Mountains (and beyond). A prolonged phase of erosion, which extended through Pliocene time, followed that removed the covering strata. Runoff resulting from erosional dissolution of the thick section of Salado halite was rich in NaCl. During the latest Tertiary, some "runoff brine" possibly gained access into subsurface dissolution conduits within the Castile Formation. At that point, the conduits possibly became artesian escape routes for dense, saline meteoric water that originated in elevated ground.

The older phase of hypothesized convection, which was forced and which propelled groundwater up-gradient from east-to-west, may have ceased in the Pliocene as artesian pressures waned. A new phase of hypothesized convection (which was also forced) may have now propelled saline groundwater down-gradient from west-to-east. Under the influence of gravity, epigenic brine possibly flowed directly down the homocline within earlier-formed conduits and ultimately into the ancestral Pecos River, into major sinks being filled with alluvium, and into channel sandstone of the Bell Canyon Formation. The Ochoan-derived brine had substantial solutional aggressiveness for $CaSO_4$, and as brine flowed through remnant voids and through permeable breccias of anhydrite and gypsum within previous dissolution conduits, it may have put substantial $CaSO_4$ into solution and it may have formed solutionally enhanced linear caves. Air eventually infiltrated the conduits, which were restricted to a calcium sulfate lithology, support for the caves weakened, and overlying anhydrite and/or gypsum roof-rock collapsed. With settling and compaction, linear troughs possibly formed on the western Gypsum Plain, troughs that mimic the older dissolution conduits.

Comparison of Dissolution Conduits within Castile Halite with Dissolution Chambers at Crest of Halite Domes

The hypothesized dissolution conduits within Castile halite have few recognized karstic counterparts. The nearest analogue is possibly the nearly horizontal, commonly broad chamber that forms at the crest of flat-topped, commonly circular, anhydrite-capped salt domes. Such chambers opened and closed repeatedly with a period of several thousand years, a record preserved in overlying anhydrite caprock as bizarre sedimentary beds termed, "katatectic layers" (Goldman, 1933, p. 84; 1952, p. 6; Taylor, 1938, p. 12). At many domes, the cyclic karstic process is apparently still active. Crestal dissolution chambers form entirely within diapiric halite directly below the nearly horizontal base of anhydrite caprock. During their maximum open phase, chambers (~1 m high (e.g., Goldman, 1933, p. 92)) probably extend laterally for up to several kilometers. They grow laterally by convective dissolution that proceeds from the annular margin of a dome toward its central axis. Scattered pillars of anhydrite, yet-to-be-dissolved halite, and high-pressure water that rises from deep overpressured strata along the steep, permeable, annular, domal margin support the broad voids. The floor of chambers is covered by unconsolidated angular fragments—a residue of anhydrite laminae (~2-8 wt%) once intercalated within the halite (Taylor, 1938, p. 110). (The fragments are analogous to those that resulted from dissolution of Castile halite (see Fig. 21B)).

The central part of salt diapirs, in plan, rises slightly faster than the peripheral part (Goldman, 1952, p. 19). Thus, the extensive halite floor of developing crestal chambers tends to assume a convex configuration. During the early life of a chamber, much of its floor dips toward the outer

perimeter of a dome at a low angle (estimated at 1-3°). Groundwater most aggressively dissolves halite at that part of a chamber closest to the central vertical axis of the diapir, at that part of the floor of the chamber having the highest elevation. The resulting saturated (or nearly saturated) brine, because of its increased density, flows slowly down the slight incline to the outer margin of the dome. Forced convection of groundwater from outside the annular margin replaces departing brine; the inward-flowing groundwater is probably situated directly above the outward-flowing brine.

Topographically high areas on the halite floor of the void are preferentially dissolved because the inward moving groundwater within the uppermost part of the thin, ring-shaped chamber (directly below the anhydrite caprock) is aggressive for NaCl. The floor flattens progressively because downward dissolution of halite "highs" operates at a significantly faster rate than upward diapiric movement. The floor, which eventually approaches horizontality through persistent dissolution, is called a "salt mirror" by Fulda (1938), a "solution table" by Taylor (1938, p. 93). A significant slope no longer exists; brine ceases to flow toward the outer margin, and without free convective circulation, a stagnant layer of nonaggressive, saturated brine covers the horizontal diapiric crest. Downward dissolution of halite virtually ceases, and by deformation, the diapir moves slowly upward at ≈0.3 mm/yr (Kupfer, 1976). Within several thousand years, the chamber closes. During closure, the layer of uncemented, micro-fragments of anhydrite on the floor of the chamber accretes (underplates) onto the anhydrite caprock forming a katatectic layer (in reverse superposition; i.e., the lowest layer in the sequence of caprock layers being the youngest). Then, at the crest of the halite dome, beginning at the annular margin, a new cycle of karstic dissolution begins.

Both types of dissolution voids, the hypothesized channels within bedded Castile halite and the poorly documented ones within diapiric halite at the crest of flat-topped, anhydrite-capped salt domes, had (and have) a nearly uniformly smooth anhydritic ceiling, a slightly dipping floor, and an origin by dissolution of NaCl resulting from free and forced convection. The evaporitic karst systems, however, have morphologies that differ: although both systems probably had (and have) a low height, developing dissolution voids within the Castile were probably linear and narrow, whereas developing dissolution voids at the crest of salt domes tend to be ring-shaped and broad. Furthermore, whereas the floors of conduits within the Castile never approached horizontality, those within chambers at the crest of salt domes did so periodically.

Generation and Migration of Methane in Late Tertiary of Western Delaware Basin

A great volume of CH_4 was generated in the Delaware Basin just before and during speleogenesis in the Guadalupe Mountains. These two events—CH_4 generation in the basin and speleogenesis in the Guadalupe Mountains—are closely related genetically. Without a prolific, Late Tertiary episode of CH_4 generation, neither the caves of the Guadalupe Mountains nor the large subsurface deposits of native sulfur of the western Delaware Basin would have formed. In this section, I consider formation of the CH_4, its migration upward into the Bell Canyon, and its further migration upward into the lower Castile Formation.

High-Heat Flow

High-heat flow in the Delaware Basin began in the Oligocene, and it persisted and possibly intensified through the late Miocene (Barker and Pawlewicz, 1987, 1993). Compared to a geothermal gradient during the Holocene of 18°-21°C/km (1.0-1.2°F/100 ft) (Mazzullo, 1986) and to an estimated paleo-geothermal gradient during the Paleozoic of 30°C/km (1.6°F/100 ft) (Barker and Pawlewicz, 1987), the transient, high-heat flow of the Miocene resulted in a paleo-geothermal gradient of 40-50°C/km (2.2-2.7°F/100 ft) (Barker and Haley, 1986; Barker and Pawlewicz, 1987, 1993).

Support for the high late Miocene geothermal gradient—more than twice the modern gradient—is based chiefly on analysis of a myriad of microscopic particles of vitrinite. These vitrinite particles were derived from woody tissues of higher plants and they commonly reside abundantly within fine-grained, post-Silurian, sedimentary strata. The reflectance of polished particles of vitrinite as viewed under immersion oil with a microscope increases logarithmically with their level of maturation (essentially with the extent of their cooking; preeminent factors being *time* and, especially, *temperature* (e.g., Tissot and Welte, 1984, p. 222-223)). The vitrinite was extracted from its mineral matrix using strong acids in a technique termed "acid maceration." Strong acids dissolved mineral matter within samples of cores and well cuttings from about 50 wells, and insoluble particles of vitrinite within the residue were prepared for analysis.

The well samples were from widely distributed localities in and surrounding the Delaware Basin and throughout much of the represented geologic section (Pawlewicz et al., 2005). For the western Delaware Basin, using the percent of light reflected from each of many thousands of vitrinite particles, Barker and Pawlewicz (1987, 1993) reconstructed the Miocene paleo-geothermal gradient, the Miocene zone of generation of crude oil, and the underlying Miocene zone of generation of dry gas (i.e., natural gas consisting of >95% CH_4).

Brown (2004) attributed the anomalously high, thermal condition of the western Delaware Basin to "Cenozoic volcanics"; Barker and Pawlewicz (1987), on the other hand, attributed it to "magmatic bodies and thinning of the crust." Each of these heating events probably played a role. Extensive volcanism, which began in early Oligocene, occurred near the southwestern margin of the Delaware Basin (the Davis Mountain area) (Anderson, 1968; Parker and McDowell, 1987; Henry et al., 1994), but by the late Miocene its heating effects were reduced. The past presence of a deeply lying Late Tertiary body (or bodies) of magma in the northwestern Delaware Basin are inferred from ~30 Late Tertiary igneous sills and dikes, which—along with probably others undetected—were injected along faults into Paleozoic strata (Kelley, 1971; Calzia and Hiss, 1978). Furthermore, a late phase of Basin and Range deformation in the Miocene stretched both the crust and the uppermost mantle, and the consequent thinning extended westward into the Delaware Basin (Barker and Pawlewicz, 1987; Hentz and Henry, 1989; Hentz et al., 1989). Here, and in shelfal areas west of the basin, the crustal thinning allowed deep, hot material to move to shallower depths, and, thus, to contribute to the transient, high-heat flow.

Maturation of Kerogen and Cracking of Oil

Great volumes of petroleum (gas and oil) have been generated in the Delaware Basin. It has been generated primarily from maturation of a type of insoluble organic matter, termed "kerogen," dispersed within beds of Paleozoic marine shale and finely particulate marine carbonates. Molecules of kerogen commonly have remarkably high molecular weight, widely varying composition, and exceedingly complex composition (e.g., Tissot and Welte, 1984, their fig. II.4.8). Such molecules if subjected to a sufficiently high temperature over a sufficiently extended interval decompose systematically into a variety of petroleum components of lower molecular weight plus graphitic carbon.

Two principal episodes of generation of petroleum occurred within source strata of the Delaware Basin, a primary episode mainly during the Middle and Late Permian, and a secondary episode during the Late Tertiary. Paleozoic strata were nearly at maximum depth of burial and at (or nearly at) maximum temperature by the end of the Permian Period, and basinal source strata had generated huge volumes of crude oil (e.g., Hills, 1984; Hill, 1996, p. 351) much of which migrated out of the basin and into traps on the surrounding shelf. Heat flow in the basin apparently remained stable throughout the Mesozoic and Early Tertiary, and additional burial of Paleozoic strata was meager. Additional maturation of kerogen was likely to have been slight, thus, only relatively small volumes of new petroleum would likely have been generated. This situation changed with the advent of high-heat flow in the Late Tertiary. Paleozoic strata along especially the western side of the basin were subjected to higher temperatures than those achieved during the near-maximum burial of the Late Permian (Barker and Pawlewicz, 1987, 1993). The ephemeral, Late Tertiary heating event resulted not in generation of huge volumes of additional oil, but, importantly, in generation of vast volumes of dry gas.

The CH_4 of the Late Tertiary was generated in part from cracking of oil generated in the western basin more than two hundred million years earlier. The generation processes of the Late Paleozoic left a profusion of droplets of oil dispersed within Lower Permian and within older basinal finely particulate sedimentary strata, and, in addition, sporadic accumulations of trapped oil most of which were minor. With increasing Miocene stratal temperatures, the top of the principal zone of generation of dry gas moved upward. As it did so, oil within disseminated droplets and oil trapped within reservoirs were transferred into the zone of generation of dry-gas where it cracked systematically into progressively lower-molecular-weight compounds (chiefly hydrocarbons), and, ultimately, into large volumes of CH_4—the terminal hydrocarbon product.

Paleozoic kerogen dispersed within strata below a depth of >2 km in the western basin also decomposed during the Late Tertiary episode of maturation further generating

copious volumes of natural gas (Lee & Williams, 2000). Residual Lower-Permian-and-older kerogen, which had been nearly non-reactive since Permian time, was transferred into the rising zone of generation of dry gas—rising in response to the increasing stratal temperatures. The kerogen cleaved further than it had during the Late Paleozoic generating progressively smaller molecular fragments (those with several carbon atoms) and, ultimately, generating residual graphite and large volumes of CH_4.

Finally, increased stratal temperatures caused the top of the terminal stage of maturation, that of metagenesis, to move upward. Residual Paleozoic kerogen transferred into this zone—which was situated deep within the sedimentary section—was subjected to intense maturation. Particulate organic matter of all types, including vitrinite, trended toward graphite, and, concurrently, it generated remarkably large volumes of natural gas, the hydrocarbon fraction being exclusively CH_4 (e.g., Kopp et al., 2000).

Abnormal Fluid Pressure and Its Effects

Excess fluid pressures (overpressure) presently occur throughout much of the Delaware Basin within "deep Mississippian, Pennsylvanian, and Permian shales" (Lee and Williams, 2000). The excess pressures provide a mechanism for moving water and CH_4 into younger strata. Fluid pressure within overpressured strata exceeds normally expected hydrostatic pressure, which for a particular depth equals the fluid pressure exerted by an imaginary column of water extending vertically from the earth's surface to the depth in question (if fresh, a gradient of 9.74 kPa/m (~0.43 psi/ft)). The transient, high-stratal temperatures of the Late Tertiary initiated the abnormally high pressures, which coincide with the principal zone of generation of natural gas (Lee and Williams, 2000). The excess fluid pressures resulted from the generation of the natural gas (Lee and Williams, 2000; Hansom et al., 2003).

The basinal CH_4, as discussed above, was generated abundantly from either oil or kerogen within fine-grained Paleozoic strata. A unit volume of such organic matter on being subjected to the severe Late Tertiary maturation generated many unit volumes of natural gas (e.g., Lee and Williams, 2000). To reduce the excess volume, water along with natural gas, dominantly CH_4, attempted to move out of the source rocks through micropores and through pressure-induced microfactures. The fluids were unable to do so at a fast enough rate, and, therefore, probably beginning in the early Late Tertiary, fluid pressures within source strata increased substantially beyond their normally expected hydrostatic pressure. CH_4 and water generally escaped slowly. Faults, however, may have been generated or regenerated suddenly during episodes of tilting of the paleo-Guadalupe tectonic block or during the Basin and Range deformation, and CH_4 and overpressured water may have moved precipitously along micro-conduits of bladed fracture surfaces between high-pressured geologic sections and overlying lower-pressured geologic sections.

A second pressured hydrologic regime in the west-central and northwestern basin was established in the early Late Tertiary—an artesian system, as mentioned previously, in which groundwater flowed eastward driven by the topographic elevation of recharge areas high in the western ancestral mountains. The primary artesian aquifer, according to Lee and Williams (2000, their fig. 9), was not primarily sandstone beds of the Bell Canyon Formation, but the thin, continuous "third sand aquifer" of the underlying Bone Springs Formation (Lower Permian; Leonardian series) (Fig. 4) (see Montgomery, 1997). On the other hand, as the primary artesian aquifer, Stafford et al. (2008a, their figure 5) invoked sandstone of the Cherry Canyon Formation (Middle Permian; Guadalupian series (Fig. 6)). Artesian water, overpressured water, and CH_4 within some of these underlying aquifers probably moved upward along faults across hundreds of meters of Paleozoic section into the overlying Bell Canyon Formation. The pressurized fluids may have then migrated westward beneath Upper Permian evaporites within beds of Bell Canyon sandstone where they mixed with artesian groundwater moving eastward within the same beds of Bell Canyon sandstone (Lee and Williams, 2000, their fig. 9).

Migration of Methane into the Lower Castile

Strain associated with tilting of the ancestral Guadalupe tectonic block, as considered above, created and/or rejuvenated steep joints and steep basinal faults (e.g., Anderson, 1981). Furthermore, crustal extension during the associated Late Tertiary Basin and Range deformation created steeply dipping, northeast-trending, normal faults (Smith, 1978; Hentz and Henry, 1989; Crawford and Wallace, 1993). These deformations created fractures within outcrops near the western edge of the

Gypsum Plain (just south of the Guadalupe Mountains in the Delaware Mountains) (Fig. 13). They can be seen near the exposed contact between the Bell Canyon Formation and the Anhydrite I Member of the Castile Formation (King, 1948; Olive, 1957; Dietrich et al., 1983; Hentz et al., 1989) (Fig. 23). To the east, an extensive gypsite mantle and various karstic features obscure most fracture traces on the Gypsum Plain (Hentz et al., 1989, p. 36).

A great volume of gaseous CH_4, probably many billions of cubic meters, migrated within the Delaware Basin during the late Miocene and early Pliocene. CH_4 moved out of Permian source beds of Wolfcampian, Leonardian, and early Guadalupian age (Fig. 4), and probably out of Pennsylvanian and older source strata into carrier beds and into both new and reactivated fractures. Driven by its abnormally high pressure (Lee and Williams, 2000) and by its buoyancy, gaseous CH_4, wherever possible, moved persistently upward. Eventually, much CH_4 resided within beds of sandstone in the upper Bell Canyon Formation. Upward migration of earlier generated natural gas and crude oil had been blocked by the impermeable limestone barriers; but the barriers that protected the overlying anhydrite and halite from dissolution and the overlying anhydrite from reaction were now breached, and the newly formed fracture pathways allowed both CH_4 and fresh-to-brackish groundwater to rise into the Anhydrite I Member of the Castile Formation (Fig. 17).

Reaction between Methane and Sulfate Anions in Late Tertiary of Western Delaware Basin

Aqueous CH_4 has the thermodynamic potential of reacting with sulfate anions (SO_4^{2-}). The reaction is activated either thermally or enzymatically (i.e., catalytically). In the area of the Gypsum Plain, microbial enzymes caused the activation within the Castile and Salado formations. In this section, I consider the enigmatic biogenic process and the fate of the biogenic by-products: CO_2 and H_2S. In addition, I present sulfur isotopic data that support activation by microbes, and I argue that beneath the Gypsum Plain, thermochemical sulfate reduction of Castile anhydrite by CH_4 or by crude oil was an insignificant reduction process.

Sulfate Reduction by Enigmatic Microbial Processes

During the Late Tertiary, particular strains of anaerobic microbes were the agents that allowed CH_4 to reduce sulfate anions in the northwestern and west-central Delaware Basin. Much about these microbes however, remains a puzzle. In fact, the microbially mediated reaction between CH_4 and SO_4^{2-} was once thought to be impossible (e.g., Ivanov, 1968, p. 13). In the laboratory, working with various cultures of sulfate-reducing microorganisms, for example, Sorokin (1957) was unable to detect a reaction between CH_4 and SO_4^{2-}. Using pure cultures of sulfate-reducing bacteria, Davis and Yarbrough (1966), and much later, Harder (1997), were able to oxidize radioactive CH_4 ($^{14}CH_4$) by SO_4^{2-}, but at a nearly imperceptible rate. Presently, the specific taxon or taxa of sulfate-reducing microbes that can effectively oxidize CH_4 are unknown (e.g., Skyring, 1987; Widdel, 1988). That CH_4 can be the microbial foodstuff seems quite remarkable: This small molecule—the simplest, lightest, and most abundant of hydrocarbons—has a carbon-hydrogen covalent bond among the strongest of the hydrocarbons, and of all possible reactive organic compounds, it is the most stable (personal communication, W. L. Orr, 1989). Furthermore, compared to anaerobic oxidation of other metabolizable organic substrates, anaerobic oxidation of CH_4 provides only small amounts of energy for microbial functions (i.e., Wake et al., 1977; Valentine, 2002; Hinrichs and Boetius, 2002).

The perplexing issues surrounding this puzzle still hold, and the process remains a geochemical and microbiological enigma (Valentine and Reeburgh, 2000; Alperin and Hoehler, 2009). Although researchers recognized the process, known as "anaerobic methane oxidation," about 35 years ago, it remains poorly understood; "investigators have not been able to firmly establish the reaction mechanism, fully understand the factors that control oxidation rates, or isolate responsible organisms" (Alperin and Hoehler, 2010).

Nevertheless, within anoxic sediments of most present-day marine environments, within sediments associated with marine CH_4 seeps, and within, at least, some present-day saline lacustrine environments, sulfate anions are clearly reduced anaerobically; and it has been demonstrated "unequivocally" that the microbial reduction consumes CH_4 (Harder, 1997). The same or similar microbial process, although seldom recognized, also occur within anoxic terrestrial strata (e.g., Kirkland et al., 1995). The sum of the evidence for a microbial redox reaction involving oxidation of CH_4 and reduction of SO_4^{2-} within anaerobic marine

sediments is "compelling" (Valentine, 2002), and the process once deemed impossible is now identified as a major factor in global carbon cycling (Strous and Jetten, 2004). At a pH less than about seven, the overall reaction is expressed as:

$$SO_4^{2-} + CH_4 \rightarrow H_2S + H_2O + CO_3^{2-}$$

The marine microbes that mediated the modern reaction are probably the same as or related closely to those active within the Castile during the Late Tertiary. The microbes that promote the redox reaction are probably archaea and sulfate-reducing bacteria working as symbiotic aggregates (e.g., Hinrichs et al., 1999; Boetius et al., 2000; Valentine, 2002). There is, however, a "possibility that some archaea oxidize CH_4 without the need for a syntrophic partner bacterium" (Valentine and Reeburgh, 2000). Archaea, a separate domain of living organisms (along with Bacteria and Eukarya) exist within a variety of terrestrial, freshwater, and marine habitats (DeLong, 2003), but they are renown for surviving, and commonly thriving, within extreme environments—thriving, in part, because they usually completely lack competition. Like archaea, sulfate-reducing bacteria can tolerate wide variations in salinity, temperature, pressure, and pH (e.g., ZoBell, 1958; Postgate, 1979, p. 87). Given sufficient H_2O, CH_4, and SO_4^{2-} within their Castile habitats, growth of these puzzling CH_4-oxidizing bacteria and/or archaea would have confronted few ecological barriers; the principal ones being an unusually high (toxic) concentration of dissolved H_2S (e.g., Reis et al., 1991), a dearth of trace amounts of critical nutrients (NO_3^{-1}, PO_4^{3-}, etc.) (e.g., Ehrlich, 1990), a temperature > ~85°C (e.g., Machel, 1987), and a trace or more of dissolved O_2 (e.g., Pfennig et al., 1981).

Sulfur Isotopic Evidence for Microbial Sulfate Reduction

Samples of native sulfur from major and minor deposits of the western Delaware Basin have sulfur isotopic values that are isotopically light. Seven samples of native sulfur from minor occurrences associated with five castiles have $\delta^{34}S$ values that range from -15.1‰ to +9.2‰ with a mean of +1.6 and a median of +3.0 (data from Kirkland and Evans, 1976; Stafford, 2008a, his table A7). These values are more positive than $\delta^{34}S$ values for samples of native sulfur within the caves of the Guadalupe Mountains (Fig. 12); this is not unusual since sulfur isotopic fractionation imparted by sulfate-reducing microbes can vary with local environmental conditions. The mean $\delta^{34}S$ value for the samples of near-surface sulfur, however, is substantially less than the mean $\delta^{34}S$ of +11.6‰ (n=36) exhibited by Castile anhydrite and gypsum (e.g., Kirkland et al., 2000). This is true as well for three samples each from a different large deposit of native sulfur several hundred meters beneath the Gypsum Plain. The samples have $\delta^{34}S$ values of -4.7‰, -0.3‰ (Hill, 1996; her appendix 2), and +6.7‰ (Davis and Kirkland, 1970). The sulfur isotopic signatures of these surface and subsurface samples record the $\delta^{34}S$ values of the H_2S oxidized to form the native sulfur. Not only do the samples of native sulfur have relatively isotopically light signatures, but they also have a wide range of $\delta^{34}S$ values (21.8‰), characteristics that support a microbial origin for the H_2S. Residual anhydrite associated with sulfur mineralization at the Pokorny deposit has an isotopically very heavy value (a $\delta^{34}S$ of +26.6‰), which is also consistent with a microbial origin.

Potential for Sulfate Reduction of Castile Anhydrite by Thermochemical Processes

Stafford et al. (2008b) hypothesized that calcitization of Castile anhydrite and the accompanying generation of H_2S beneath the area delimited by the Gypsum Plain resulted from thermochemical sulfate reduction. Sulfate anions and organic matter—dominantly fractions of oil but also possibly CH_4 (Worden and Smalley, 2004)—react during this abiotic process to generate H_2S and CO_2. Significant thermochemical sulfate reduction, however, probably failed to occur within the Castile of the western Delaware Basin. This conclusion is based on the inferred ambient temperature during the postulated reaction, on the $\delta^{34}S$ values of samples of native sulfur from the minor surface accumulations, and on the $\delta^{34}S$ values of samples of native sulfur from the major subsurface deposits.

Almost all estimations of the temperature at which thermochemical sulfate reduction is initiated are >120°C (e.g., Claypool and Mancini, 1989; Heydari and Moore, 1989; Worden et al., 1995; Machel et al., 1995; Rooney, 1996; Heydari, 1997; Worden et al., 2000; Cai et al., 2004). Lower Castile evaporites were buried during calcitization by about 1 km of overburden (Barker and Halley, 1986; Crysdale, 1987; Luo et al., 1994, their figure 14; Dutton, 2008). Stratal temperatures at this depth, well below 120°C, were inadequate for a significant rate of thermochemical sulfate reduction, but they were probably nearly optimal for a high rate

of microbial sulfate reduction. Furthermore, within the upper Rustler Formation at the Culberson sulfur deposit (Fig. 32) (Crawford and Wallace, 1993, their figs. 5-7) and ~15 km south of the Culberson deposit at the Dutch Draw sulfur deposit (Salisbury, 1992), calcium sulfate reacted with CH_4 to yield sulfur and calcite at a depth of 0.5 km or less and at a temperature <<120°C.

If thermochemical sulfate reduction had operated, the basinal samples of native sulfur, rather than having isotopically "light" values and a broad range, would have had, in all likelihood, isotopically "heavy" values and a narrow range. H_2S generated via thermochemical sulfate reduction, with rare exception (e.g., Alonso-Azcárate et al., 2001), has an isotopic signature nearly identical to that of its parent anhydrite (e.g., Krouse, 1977; Orr, 1986; Goldhaber, 1993; Machel et al., 1995; Worden et al., 1995; Worden and Smalley, 1996; Worden et al., 2000; Cai et al., 2004). If the reaction between sulfate anions and hydrocarbons were caused by elevated temperatures instead of by microbial enzymes, the $\delta^{34}S$ values of native sulfur within the limestone host rock would probably have clustered near +11.6‰ (± 2‰), the mean $\delta^{34}S$ value for sulfur atoms combined within primary Castile anhydrite and gypsum. Instead, the $\delta^{34}S$ values have a wide range, a mean of +1.6 for near-surface sulfur, and a mean of +0.6 for subsurface sulfur.

Sulfate Reduction of Castile Anhydrite by Microbial Processes

Reaction between CH_4 and SO_4^{2-} probably occurred in the western basin during about an eight-million-year interval (~12 to ~4 Ma ago) primarily within the moderately buried (by ~0.8-1.0 km) lower Castile Formation. The reaction, intense at times, was mediated by sulfate-reducing microorganisms. The overall diagenetic redox reaction was identical to that which occurs within modern marine sediments; but the setting within the Castile Formation was terrestrial, and it took place about two hundred and fifty million years after lithification of evaporitic sediments of the Castile Formation.

Microbial enzymes greatly accelerate the rate of the reaction between CH_4 and SO_4^{2-} and allowed microbes to take advantage of energy released as the reaction proceeds. The onset of the reaction is nearly instantaneous and in most geologic settings, the rates are "extremely high compared to most inorganic geological processes" (Machel, 2001).

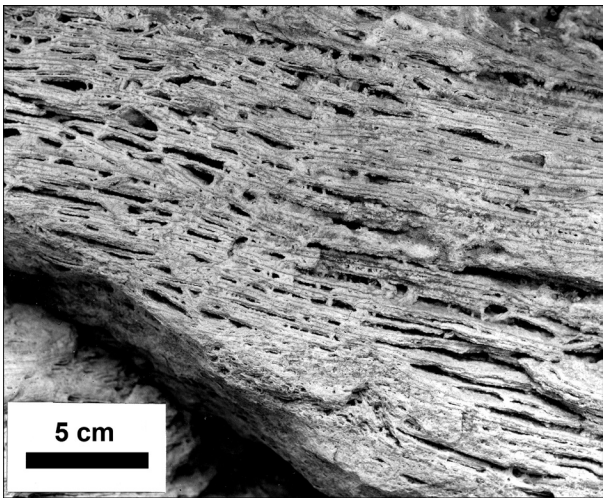

Figure 29. Outcrop of porous calcitized Castile anhydrite at a castile on the Gypsum Plain in which replacement of anhydrite by calcite resulted in porosity of approximately 25%; near the outer edge of castiles, replacement of bedded anhydrite commonly resulted in no macroscopically visible porosity, whereas the core of many castiles, consisted of a highly porous anhydrite breccia in which clasts were replaced by calcite (see Stafford et al., 2008b).

For their cellular carbon, the microbes assimilate dissolved CO_2, a by-product of the reaction, and/or fatty acids such as acetic acid (CH_3COOH) dissolved in trace amounts within ambient water (e.g., Jansen et al., 1984).

Microbes that inoculated reaction sites within Castile anhydrite were likely introduced in the Late Tertiary from an extraneous source. Probably not until after the tectonic block had been tilted and fractured did the lower Castile evaporites have the abundant living space and the required nutrients necessary for vigorous microbial growth. Modern sulfate-reducing bacteria are obligate anaerobes (Atlas, 1997, p. 990), and this was true of sulfate-reducing microbes within the Castile, whether they were bacteria and archaea working symbiotically, or archaea working alone (see Pfenning et al., 1981). Following the initial tectonic deformation and its attendant fracturing, microbes were probably transported within groundwater from anoxic niches within the Bell Canyon Formation upward through fractures into anoxic niches within the Castile Formation.

Microbial loci were scattered geographically within the subsurface of the western Delaware Basin. The locations of many microbial loci are presently represented by the castiles (Figs. 13 and 15). At the microbial loci, aqueous CH_4 and SO_4^{2-} reacted chiefly within the lower

anhydrite members of the Castile Formation. As the two constituents reacted, ambient water—in a sense, acting as a second catalyst—became a "refreshed solvent" for gaseous CH_4 and for local anhydrite. The same water was used repeatedly as a solvent during the redox reaction, in fact, the reaction created water as a by-product. Importantly, there were few limits on growth of the microbes, and probably only a small fraction of CH_4 that migrated into their habitats escaped consumption, carbon and hydrogen atoms within the CH_4 combining nearly wholly with oxygen and sulfur (from SO_4^{2-} anions) to form microbial biomass, and, in addition, CO_2, H_2O, and H_2S—the metabolic by-products expelled from the microbial cells.

Formation of Buried Limestone Masses and Generation of Hydrogen Sulfide

Anaerobic microbial agents were apparently actively forming H_2S in the widely distributed buried masses of biogenic limestone of the northwestern and west-central Delaware Basin at about the same time as aerobic microbial agents were actively forming H_2SO_4 in the caves of the Guadalupe Mountains. Furthermore, the limestone masses, which on differential erosion became castiles (Figs. 13 and 15), probably formed contemporaneously with and immediately after formation of the linear dissolution conduits within the uppermost parts of beds of Castile halite. The diagenetic carbonate masses were the habitats of the sulfate-reducing microbes. It is where they generated H_2S and CO_2, the microbial by-product CO_2 forming HCO_3^- and CO_3^{2-} ions within ambient water. As the microbes used SO_4^{2-} in their metabolism, anhydrite ($CaSO_4$) continuously dissolved to the limit of its solubility, as it did so, Ca^{2+} became available, and reacted with the CO_3^{2-} to precipitate $CaCO_3$. Calcitization resulted in nearly simultaneous solution of anhydrite and precipitation of calcite, a process that commonly accurately preserved the fabric of Castile anhydrite (Fig. 16A).

Calcitization occurred dominantly at interfaces between calcite and anhydrite. It progressed, for example, at the boundaries of the porous limestone masses outward into anhydrite bedrock at right angles to fracture planes along dual solution-precipitation fronts, and within breccia clasts at the boundary between anhydrite and biogenic calcite. The angular clasts of anhydrite-collapse breccias were particularly susceptible to calcitization because they provided an abundant surface area for dissolution and for microbial substrate. Clasts of anhydrite breccia in at least one large mass of diagenetic limestone were in place before calcitization (Crawford and Wallace, 1993), and all calcite breccias within the castiles and within the subsurface carbonate masses probably had this same paragenesis: brecciation of anhydrite followed by calcitization of clasts.

Many samples of limestone from the castiles and from their subsurface equivalents have significant porosity and permeability (Fig. 29). The brecciated cores of castiles at the time of their formation had a porosity that equaled the volume of mineral matter dissolved. Furthermore, replacement of $CaSO_4$ by $CaCO_3$ commonly created void space; the calculated quantities of compounds involved (the stoichiometry) indicate that the replacement reaction yields calcite with a porosity of 20-25% (e.g., Davis and Kirkland, 1970; Kreitler and Dutton, 1983; Machel, 2001). Similarly, where complete reduction of gypsum occurred and where H_2S failed to escape but became oxidized to native sulfur that filled pore space "…there are 3-4 parts of calcite to each part (by weight) of sulfur" (Ivanov, 1968, p. 104). Within individual castiles, an intermediate zone between the brecciated core and the peripheral zone commonly exhibits porous replacement calcite; it is vuggy and shows original lamination, although laminae are commonly distorted (Fig. 29) (Stafford et al., 2008b).

The peripheral zone of castiles is unbrecciated and is not macroscopically porous (Stafford et al., 2008b). Here, calcite appears to have replaced anhydrite volume-for-volume (Brown and Loucks, 1988), a replacement process that would seemingly not have created porosity. Enough porosity and permeability must have been created, however, to allow water, CH_4, and microbes to move to the reaction front, i.e., the boundary between biogenic calcite and primary Ochoan anhydrite. Reaction ceased at such a boundary when there was inadequate living space for the microbes, when CH_4 in solution was unable to move to the anhydrite-calcite boundary at a fast enough rate to maintain growth of the microbes, or when H_2S was unable to move away at a fast enough rate to avoid poisoning the microbes.

Calcitization would have failed to occur at the subsurface microbial loci unless the aqueous H_2S generated as a metabolic by-product was oxidized (to elemental sulfur) or unless pathways allowed it to escape. Its oxidation or

its escape prevented it from being concentrated to toxic levels (see Reis et al., 1991, 1992; Klimchouk, 1997b; O'Flaherty et al., 1998) allowing microbes to flourish for long spans. Calcitization intensified as microbial growth proliferated, with the rate of sulfate reduction being determined primarily by both the rate of introduction of CH_4 (the foodstuff) and the rate of removal of H_2S (the detrimental waste product).

Major occurrences of native sulfur are absent with the castiles (e.g., Hentz et al., 1989), but minor Quaternary occurrences occur within and near several castiles (e.g., Kirkland and Evans, 1976; Hill, 1996, p. 360-362; Stafford, 2008a, p. 139; Stafford et al., 2008b). These minor castile-associated sulfur deposits formed by reaction between H_2S and O_2 (like the native sulfur within major subsurface deposits and like that within Lechuguilla Cave). Could major deposits of associated sulfur have existed during the buried phase of castiles (i.e., before erosion exposed the limestone masses)? Probably not, as erosion removed the cover of evaporites, near-surface O_2-bearing water would have intruded, and dissolved O_2 within the shallow meteoric water would have reacted with the hypothesized large deposits of associated elemental sulfur eventually oxidizing them to H_2SO_4. The abundantly produced strong acid, would have reacted vigorously with the intimately associated limestone host rock to form caverns of substantial size within the carbonate masses, caverns that would be manifest within present-day castiles. Yet, Stafford (2008a, p. 92), during his comprehensive investigation of Castile karst, seldom found caves within calcitized evaporites; only eight such caves have been reported (Hill, 1996, p. 306; Stafford et al, 2008b). Furthermore, calcitized evaporites are usually observed within caves that consist primarily of laminated or massive gypsum (Stafford, 2008a, p. 118). The largest of such caverns, Dead Bunny Hole, with a length of ~440 m, is a hypogenic maze cave "developed in both laminated gypsum and calcitized evaporites" (Stafford et al., 2008a). Another large void within a castile, described originally as a natural cavern (Porch, 1917), is actually a 37-meter-deep vertical mineshaft dug in the early 1900s in search of sulfur (Stafford et al., 2008a). The mineshaft at three separate depths contains small voids (<10 m^3 each). Stafford et al. (2008a) attributed these minor voids "to sulfuric acid dissolution of the biogenic limestone." H_2S is still issuing from this mine (Richardson, 1905; Kirkland and Evans, 1976; Smith, 1980; Hill, 1996, p. 306), and the small isolated voids may represent late-stage dissolution; the strong acid being generated by near-surface oxidation (by aqueous O_2) of H_2S to native sulfur within shallow groundwater, and its further oxidation to H_2SO_4.

During the late Miocene and early Pliocene, when all castiles (i.e., all bodies of biogenic limestone) were buried, most H_2S generated *in situ* failed to react locally with O_2 to form native sulfur. Reaction failed because a thick (~1 km) cover of mainly Salado and Rustler evaporites (upper Ochoan) restricted influx of epigenic, O_2-bearing meteoric water and because hypogenic (largely artesian) water was an inadequate source of O_2. Brown (2006) concluded, "…most H_2S gas from the Castile Formation is likely to have been vented to the atmosphere" and Bodenlos (1973) concluded that many limestone masses "were not sealed against loss of hydrogen sulfide," but were "uncapped bioepigenetic systems." Similarly, Hentz et al., (1989)

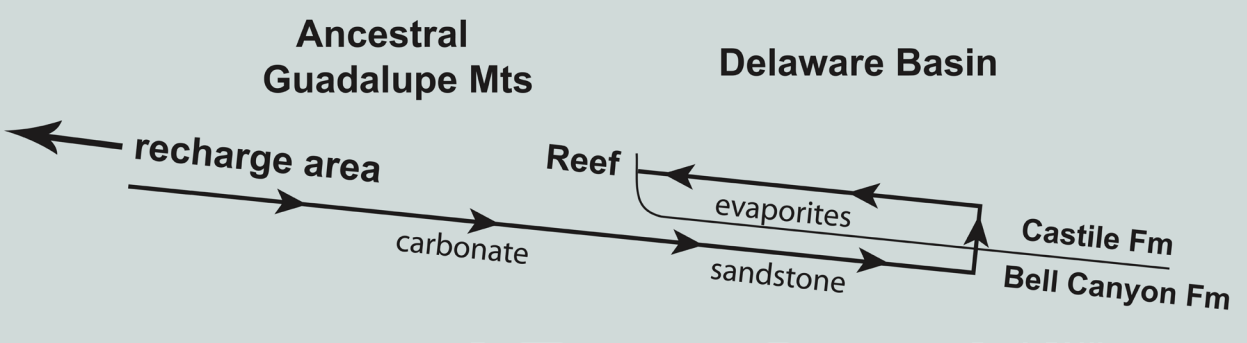

Figure 30. Profile showing hypothesized flow path of artesian groundwater that originated within Middle Permian (Guadalupian) strata during the late Miocene and early Pliocene (dip is greatly exaggerated). From recharge areas in elevated areas of the paleo-Guadalupe tectonic block, groundwater flowed for kilometers down a slight dip through Middle Permian carbonate and siliciclastics into the basin. It rose directly upward for, at most, several hundred meters through fractures and voids into Upper Permian evaporites. The artesian groundwater then backtracked and flowed for kilometers through conduits within Castile halite just beneath Castile anhydrite up a slight dip and into the Middle Permian extinct reef.

concluded that the castiles "…formed in a ground-water/ hydrocarbon circulatory system that lacked the seal (trap) necessary to cause extensive sulfur mineralization."

In the late Miocene and early Pliocene, however, almost all basinal H_2S-generating systems (i.e, the buried masses of secondary limestone) were probably capped. H_2S in solution in the lower Castile, with rare exceptions, failed to escape through vertically trending, karstic pathways within the thick overlying Ochoan strata (upper Castile, Salado and Rustler) to be vented into the atmosphere. Instead, much H_2S was transported within groundwater through the lateral- and slightly upward-trending conduits within Castile halite into the Capitan Formation and, eventually, into the slowly enlarging caves of the Guadalupe Mountains.

Transit of Hydrogen Sulfide-Charged Water through Conduits within Castile Halite into Capitan Formation

Late Tertiary H_2S-bearing groundwater within the dissolution conduits, which was under a pressure substantially greater than hydrostatic pressure, flowed up the homocline and into the Capitan Formation. The groundwater (brackish-to-saline) flowed upward from Bell Canyon siliciclastics through the subsurface masses of biogenic Castile limestone, which occurred dominantly within the Anhydrite I and Anhydrite II members. At these various microbial loci, the through-flowing groundwater dissolved the by-product, H_2S. (H_2S on a molar basis is nearly three times as soluble in water as CO_2 and ~75 times as soluble as CH_4 (Palmer and Palmer, 2000)). The rising nearly fresh-to-moderately saline groundwater held a greater concentration of H_2S in solution than any sinking NaCl-saturated brine with a molar concentration of about six (see Barrett et al., 1988; Duan et al., 2007).

The ascending groundwater moved upward by forced convection through the porous microbial limestone, fractured anhydrite, and dissolution chambers into the low, narrow, linear conduits in the uppermost part of Castile halite members. Then under substantial pressure, it migrated up to several tens of kilometers westerly directly up the slightly dipping homocline to the reef or to the forereef. The H_2S-bearing groundwater, acquired NaCl as it flowed westward, but the flowing groundwater probably seldom became saturated. Any H_2S that might have been forced out of solution by increasing salinity (i.e., that "salted out" into a gaseous phase) would have been carried forward (up the slope of the homocline) by the flowing groundwater. Forced convection (resulting from both artesian pressure and overpressure) dominated, and it resulted in the transportation of H_2S-bearing saline groundwater upward and westward. Free convection (resulting from density-driven flow), which had previously moved brine downward and eastward, greatly diminished or entirely ceased.

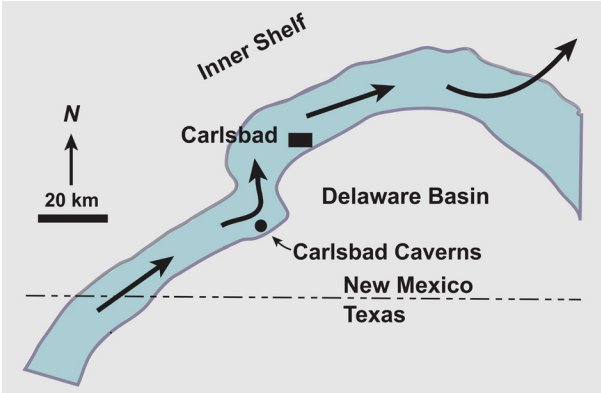

Figure 31. Inferred flow path of H_2S-charged, saline groundwater within the lower part of the ancestral Capitan aquifer (late Miocene and early Pliocene) (see Hiss, 1975, 1977, 1980). Rate of flow of groundwater within the paleo-aquifer was probably orders of magnitude slower than the rate of flow of groundwater within the modern aquifer. Groundwater within the paleo-aquifer eventually discharged into paleo-streams that drained into the ancestral Gulf of Mexico. The location of Carlsbad, New Mexico, and Carlsbad Cavern are shown for orientation.

Most H_2S-bearing brine within Castile conduits probably moved into the Capitan Formation of the Guadalupe Mountains through fractures, chiefly joints. A system of joints trends approximately perpendicular to the Capitan reef escarpment (e.g., King, 1948; Hayes, 1964; Jagnow, 1977). Although these joints are less developed than associated joints that trend parallel to the escarpment, the northwest-trending joints probably served as principal pathways into the Capitan reef and forereef. The permeability of these joints (including those within the partially dolomitized upper forereef (Melim and Scholle, 2002)) would have been enhanced by the NaCl-rich groundwater (see Palmer, 2009, p. 121) and by the acidity of the same H_2S-bearing groundwater. Furthermore, fracture openings and reef cavities in the Capitan were commonly occluded by anhydrite and halite (Darke and Harwood, 1990; Harwood et al., 1991), which would have been removed by under-saturated brine transported within the Castile conduits.

H_2S-bearing Castile brine was forced into the northwest-trending joints chiefly by artesian pressure. Judging from current hydrologic conditions (Hiss, 1975), the potentiometric surface of the Castile brine was greater than the potentiometric surface of groundwater within the Capitan reef. The hydrologic pressure of the Castile brine was more than adequate to move saline water into the Capitan; only a ~5-20% greater pressure would have been required to move various concentrations of saline water up the conduits than it would have taken to move fresh water up the conduits. The saline groundwater transported H_2S in solution and moved into a basin-margin aquifer—the Capitan paleo-aquifer—that coincided with much of the cave belt. Eventually the aquifer sequestered an abundance of H_2S-rich groundwater.

The Capitan reef, the older Goat Seep reef, and the adjacent, permeable outer shelfal carbonates presently constitute a modern aquifer that extends, in part, parallel to and just northwest of the Guadalupe Mountain front (e.g., Motts, 1968; Hiss, 1975, 1980). In the late Miocene and early Pliocene, the Capitan paleo-aquifer, the precursor of the modern-day aquifer, consisted of the same carbonate rocks. Groundwater that flowed westerly into the paleo-aquifer from the basinal Castile Formation was saline, whereas groundwater that flowed easterly into the paleo-aquifer from the back-reef, shelfal strata of the ancestral Guadalupe Mountains was fresh. On entering the ancient aquifer, the more saline, H_2S-charged, basinal-derived groundwater, because of its greater density, descended to a bottommost position. It then moved into the lower level of evolving caves within reefal carbonates and within adjacent shelfal carbonates.

Artesian groundwater that transported H_2S to the Capitan Formation within the cave belt had an unusual flow pattern (Fig. 30). From topographic areas of relatively high elevation, the groundwater flowed eastward down the paleo-Guadalupe tectonic block within shelfal aquifers. Beneath the Castile Formation, it continued flowing easterly, down-gradient, and parallel to bedding within basinal aquifers of low gradient. The flow of artesian groundwater then changed direction markedly, and for a short distance (< 1 km), it moved upward approximately vertically through fracture-directed and solutionally enhanced pathways transverse to bedding where it acquired H_2S. It then, once again, markedly changed direction, and in conduits within the upper part of Castile halite members, backtracked, and under pressure (chiefly artesian) flowed westerly, up-gradient, parallel to bedding through the "dissolution-produced aquifers" of low gradient until eventually finding passage into the Capitan Formation (Fig. 30).

Progressive Oxidation of Hydrogen Sulfide from Southwest to Northeast along the Cave Belt and from Higher to Lower Elevations within Individual Caves

Groundwater within the paleo-Capitan aquifer during the eight-million-year span during which the primary episode of speleogenesis took place (Polyak et al., 1998) transported H_2S in solution slowly to the northeast. The trend of the aquifer turned, and groundwater continued flowing slowly to the east-northeast, eventually discharging into the underlying San Andres Limestone (see Hiss, 1977, 1980) (Fig. 31). Compared to the velocity of flow within the modern aquifer, estimated to average about 1.5 m/day (Hiss, 1975, p. 198), the velocity of flow within the Capitan paleo-aquifer during the late Miocene and early Pliocene was greatly reduced. Factors causing the reduction were:

- Recharge areas were only partially stripped of their impermeable cover (i.e., upper Ochoan evaporitic strata).
- Permeability was only modestly enhanced (cavernous passageways were in the process of forming).
- Major outflow at Carlsbad, New Mexico, was absent (the Pecos River had not yet breached the aquifer, which it did about 0.6 Ma ago (Hiss, 1975)).
- Evaporites possibly partially plugged pores of the paleo-aquifer (e.g., Harwood et al., 1991).
- The dip of the paleo-aquifer through most of its history, at least, was less than that of the modern aquifer.
- Incised submarine canyons normal to the northern Capitan reef were filled with clastic debris having a lower permeability than the adjacent reef (Hiss, 1975, p. 74), and, thus, east-northeast flow through the aquifer was inhibited.

The sluggish flow of the Capitan paleo-aquifer did not readily flush the dissolved H_2S. Rather, near where the reef escarpment now resides within the lower part of the Capitan paleo-aquifer, joints and faults (those parallel to the escarpment) as well as connected pores allowed a

repository of moderately-to-highly saline groundwater charged with H_2S to flow slowly to the southeast. This repository of the H_2S-charged groundwater coincided with the developing cave belt.

Incipient caves must have initially been present for large caves to form from subaerially aqueous H_2SO_4 residing on cave surfaces. The incipient caves may have resulted from solutional enlargement of fractures by hypogenic artesian groundwater without involvement of H_2S (DuChene, 2009). Aqueous H_2S, a weak acid, however, conceivably played a role in dissolving the carbonates. Possibly, the incipient caves formed at a halocline separating saline, dense groundwater containing H_2S from overlying, fresh, less-dense groundwater containing O_2 (see Queen, 1994); the dissolved constituents may have reacted microbially near the top of the zone of saline sulfidic groundwater to form H_2SO_4 that, in turn, reacted with carbonates to form small subaqueous caves.

With tilting of the tectonic block, the Permian (Upper Ochoan) and Cretaceous sedimentary cover—consisting chiefly of Salado evaporites and Rustler carbonates and evaporites—began to erode. Erosion was probably initially most intense in the far west at high elevations of the ancestral Guadalupe Mountains. It then probably progressed gradually to the east to lower elevations of the mountains, most likely it tended to progress directly down the homocline. The narrow belt in which major caves of the Guadalupe Mountains evolved, consisting of, in particular, the Capitan Formation and the near-reef part of the Seven Rivers Formation, trended in a southwest-northeast direction across the eastward dipping Guadalupe homocline (Fig. 26). This configuration ensured that as the ancestral Guadalupe tectonic block intermittently rose the highest elevation of the cave belt was its southwestern part (as it remains today) (Fig. 26). This elevated part, which would probably have been subjected to more intense erosion, was likely to have been the first segment of the cave belt from which the virtually impermeable upper Ochoan, lithologic cover was removed.

Intense speleogenesis may have begun about 10 km northeast of where Guadalupe Peak, Texas, now rises (Fig. 3) (Polyak et al., 1998). Conceivably, however, sulfuric-acid caves may have been dissolved in a more elevated part of the cave belt, a part that may have once extended for several kilometers into Texas. Formation of such hypothesized caves beyond their present known limit would have taken place during the earliest history of uplift of the paleo-Guadalupe tectonic block. Later, during Basin and Range deformation, slip on the south-southeast trending border faults that now bound the Salt Basin graben (e.g., King, 1948) would have down-dropped the hypothetical caves and their Middle Permian host carbonates to be buried beneath Late Tertiary and Quaternary alluvium.

A primary control for speleogenesis in the Guadalupe Mountains (and for genesis of the large sulfur deposit beneath the Gypsum Plain) was not so much acquisition of H_2S, of which there was probably a large relative abundance, but, rather, acquisition of O_2. In fact, availability of O_2 was a limiting factor in cave development (Palmer and Palmer, 2000). Intense speleogenesis by H_2SO_4 demanded an abundant supply of O_2; on a molar basis, each metric ton of sulfuric acid that was generated required approximately two metric tons of molecular oxygen (see Palmer and Palmer, 2000). The reservoir for such an abundant supply of O_2 was one that atmospheric oxygen could best provide, which it did so chiefly to water of condensation within the subaerial part of caves. With each minor episode of uplift (of which there were almost certainly many), the water table descended progressively and intermittently from southwest to northeast along the cave belt. Similarly, within individual caves, the water table, responding to each episode of uplift, descended; and with major episodes of intense uplift, atmospheric O_2 entered the upper part of a new group of developing caves (Polyak, 1998; DuChene and Cunningham, 2006).

Gaseous H_2S and gaseous O_2 within the atmosphere of the caves repeatedly dissolved within the subaerial water of condensation, the habitat of sulfur-oxidizing bacteria and the site of H_2SO_4 formation. The amount of $CaCO_3$ dissolved by the H_2SO_4 depended on a relatively high concentration of CO_2 in the cave atmosphere; if aeration were too strong, the partial pressure of CO_2 would have dropped, and the H_2SO_4 would have lost much of its cave-forming potency (Palmer, 2006; 2009, p. 218-219). Entrances to nearly all large caves of the Guadalupe Mountains were (and are) few and small in relation to the size of the caves (e.g., Hill, 1999; Palmer, 2006), and they were completely absent until the largely evaporitic upper Ochoan cover was removed by erosion. The initial source of atmospheric oxygen for many caves was probably not through the small, sparse overlying entrances, which

probably developed late in the history of the caves, but rather from southwestern areas of the cave belt initially freed of the Upper Ochoan lithologic cover. Because of the slight dip of the aquifer (0.5° or less), a drop of a few meters in the water table opened several kilometers of the cave belt to aeration. Atmospheric oxygen may have moved laterally beneath the lithologic cover chiefly through permeable fractures within and parallel to the trend of the reef, and, hence, to the upper subaerial part of expanding caves. Such restricted pathways would have reduced aeration substantially.

Along the cave belt over a span of about eight million years, the groundwater table fell in progressive steps by a cumulative ~1,100 m, thus, caves to the northeast are generally younger than caves to the southwest (Polyak et al., 1998; Polyak and Provencio, 2000). Within particular caves, the water table fell with each episode of uplift. New cave levels apparently formed "whenever and wherever rising hydrogen sulfide emerged in large quantities at specific locations" (Palmer, 2006). Carlsbad Cavern and Lechuguilla Cave have three or four principal levels between an elevation of 1100 and 1370 m, the higher being ~6 Ma in age, the lower ~3.5 Ma (Ford and Williams, 2007, p. 246).

Dissolution of Castile and Salado Halite and Gypsum by Epigenic Groundwater

Both hypogenic karst systems—that within the Castile and that within the reef and adjacent shelf—lost their near confinement at latest by the close of the Pliocene, and an epigenic karst system became superimposed on the older hypogenic system (see Stafford, et al., 2008a). Erosion removed Lower Cretaceous sandy limestone (e.g., Lang, 1947), Upper Permian Dewey Lake red beds (if present), and most evaporites and carbonates of the Rustler, Salado, and, in addition, within the basin, the upper Castile and part of the lower Castile (e.g., Anderson and Kirkland, 1980). Erosion of the Salado Formation, for example, has resulted in complete removal of its dominant lithologic fraction—halite—from the northwestern shelf, from the reef, and from much of the western basin (Fig. 18). Denudation during the epigenic erosional phase exposed the castiles and resulted in extensive karstification on the Gypsum Plain. In addition, solutional denudation of Castile evaporites during the Pleistocene and Holocene exposed the Capitan reef and forereef along much of the northwestern margin of the basin to create the prominent escarpment that forms the Guadalupe Mountain front (Fig. 2).

The epigenic dissolution markedly changed the paleogeography of Castile halite. It has vanished (by dissolution) adjacent to the Guadalupe and Delaware mountains except in the subsurface just southwest of Carlsbad, New Mexico (Fig. 18); here the elevation of the Capitan Formation is low compared to elsewhere along the cave belt, and expression of the escarpment is slight. Presently, Castile halite south of White's City, New Mexico, is mostly several-kilometers-to-several-tens-of-kilometers downdip from the mountain front (Fig. 18).

Collapse breccia of Castile anhydrite in the northwestern Delaware Basin commonly lies directly upon blanket beds of micro-breccia. The clasts of the micro-breccia consist of millimeter-to-centimeter fragments of anhydrite (Fig. 21B) remaining after dissolution of Castile halite (Anderson et al., 1978; Anderson and Kirkland, 1980). Coarse collapse breccia, on the other hand, consists of much larger angular fragments mostly of laminated anhydrite ranging up to more than 30 cm in maximum dimension (Anderson et al., 1978). The clasts are now "closely spaced in a tight, interlocking pattern with little or no fine-grained anhydrite matrix" (Hentz et al., 1989).

Most coarse collapse breccias within the Castile originated following removal of halite by the epigenic groundwater. Anhydritic roofs collapsed by brittle failure as air displaced groundwater. "Many, but not all, beds of dissolution breccia are overlain by collapse breccia" (Anderson et al., 1978). Some bedded anhydrite apparently subsided gradually without extensive fracturing either by sagging or by settling into voids formed by halite dissolution. Where collapse has occurred, stoping usually diminished upward into Castile anhydrite, and most collapse breccias are overlain by intact beds of Castile anhydrite (and near the surface Castile gypsum). Rarely, however, breccia pipes of Castile anhydrite and gypsum stoped through to the surface (Anderson and Kirkland, 1980, their fig. 1; Wallace and Crawford, 1992; Crawford and Wallace, 1993; Stafford et al., 2008 a and b). Extensive Quaternary fracturing of beds of Castile anhydrite (due to widespread removal of Castile halite) allowed H_2S to move upward from reaction sites. Near the surface, it reacted with aqueous O_2 within groundwater to form scattered minor deposits of native sulfur (e.g., Porch, 1917).

The great volume of water that dissolved Salado and Castile (Ochoan) halite and, to a lesser extent gypsum and anhydrite, drained into the Pecos River and into major sinks just east of the Pecos River that filled ultimately with Tertiary alluvium (Malley and Huffington, 1953, their Pl. 1). These alluvial bodies, up to 460 m thick, are related to dissolution of halite within the lower Salado and, secondarily, to dissolution of halite within the uppermost Castile (Anderson et al., 1978). These centers of collapse into which Tertiary alluvium accumulated occur at the eastern part of "a front or 'wedge' of expanded dissolution" that in places has extended down-dip beneath overlying upper Salado halite and Rustler carbonates and evaporites for distances of up to 30 km (Anderson, 1978, 1981, 1982; Anderson and Kirkland, 1980). The thickness of the Tertiary alluvium filling the sinks is inversely proportional to the thickness of halite remaining within the Salado and uppermost Castile. The thick accumulations of alluvial fill are probably younger than both the caves of the Guadalupe Mountains and the major sulfur deposits beneath the Gypsum Plain. The accommodation space in which the alluvial bodies accumulated was created as Ochoan halite (primarily Salado halite) dissolved to form brine that descended through permeable pathways within the underlying Castile evaporites and drained into channel-fill sandstone of the upper Bell Canyon Formation, and eventually flowed out of the basin.

ORIGIN OF MAJOR DEPOSITS OF NATIVE SULFUR

Major subsurface deposits of sulfur are associated with graben-bounding faults (e.g., Smith, 1978; Hentz et al., 1989; Hentz, 1990; Hill, 1996, p. 366). The grabens clearly have an origin distinct from that of the solution-subsidence troughs (e.g., Hentz et al., 1990). Parallel faults form graben systems as much as 0.8 km wide and ~6.5 km long (Hentz et al., 1989, p. 39). The faults dip at 50-90°, are displaced by 15-75 m, and strike to the northeast (Hentz et al., 1989; Wallace and Crawford, 1992; Crawford and Wallace, 1993; Guilinger and Nestlerode, 1992). The graben-bounding faults probably extend (or extended) transversely through, at least, the upper Paleozoic section, and through a thin Mesozoic section now almost entirely removed by erosion.

Native sulfur occupies voids within massive replacement limestone, voids within and between replacement limestone clasts, and planar voids lined by finely crystalline drusy calcite. The major deposits occur several hundred meters beneath the Gypsum Plain within the northern and eastern part of the Rustler Springs sulfur district, Texas, an area of ~3,100 km^2 defined by scattered minor, near-surface, Quaternary deposits of native sulfur (e.g., Porch, 1917, his plate 9; Davis and Kirkland, 1970, their fig. 2; Hill, 1996, her fig. 196).

The locations of four important deposits of native sulfur relative to the cave belt are shown in Figure 32. Reserves of the Leonard Minerals deposit are unreported (see Hill, 1996, p. 365, for a description of the deposit). Original reported reserves of native sulfur at the Pokorny deposit (Klemmick, 1992) and at the Phillips Ranch deposit (Guilinger and Nestlerode, 1992) each probably exceed two million metric tons, and original reserves at the giant Culberson deposit probably exceed 75 million metric tons (Crawford and Wallace, 1993) (Fig. 32).

Similarities and Differences in Genetic Processes between the Caves and the Major Sulfur Deposits

The subsurface deposits of sulfur probably originated at about the same time as the caves, and the comprehensive genetic events that occurred at the major sulfur deposits and those that occurred at the caves demonstrate both similarities and differences.

Principal genetic events that were the same were:

- Hypogenic groundwater under pressure intruded Upper Permian basinal evaporites at various localities and convectively dissolved anhydrite and halite.
- Gaseous CH_4 intruded the evaporites at these same localities.
- SO_4^{2-} oxidized aqueous CH_4 biogenically resulting in large quantities of both permeable $CaCO_3$ and aqueous H_2S.
- Large quantities of aqueous O_2 oxidized the H_2S.

Principal genetic events that were different were:

- At the developing sulfur deposits, groundwater transported aqueous H_2S up steep grades (~90°) and laterally for < ~2 km, whereas at developing caves, groundwater transported aqueous H_2S up slight grades (<<2°) and laterally for < ≈30 km.
- O_2 at developing sulfur deposits was transported to reaction sites within saline, epigenic groundwater, whereas at the evolving caves O_2 was transported from the surface to aqueous reaction sites as a gas.
- Aqueous O_2 at evolving sulfur deposits reacted, probably mainly abiotically, within the phreatic zone with aqueous H_2S to generate native sulfur, whereas aqueous O_2 at evolving caves reacted biogenically with aqueous H_2S mainly within the vadose zone to generate H_2SO_4.

The Hydrologic Pathways

Hydrologic pathways at the major sulfur deposits differed markedly from hypothesized hydrologic pathways that extended up the homocline within Castile halite. At rare localities on the Gypsum Plain, micro-conduits within the steep, graben-bounding faults guided fresh, solutionally aggressive, hypogenic groundwater directly upward. This buoyant groundwater bypassed thick (tens of meters) barriers of bedded anhydrite (the Anhydrite members of the Castile Formation). Concurrently, in two-way flow, NaCl-rich, hypogenically-derived groundwater drained down the steep fault surfaces along adjacent pathways into the Bell Canyon aquifer. The density-driven, free convective dissolution enhanced the permeability of the fault conduits through beds of Castile anhydrite and formed voids within Castile halite. With dissolution of the halite, collapse breccias formed consisting predominantly of Castile anhydrite.

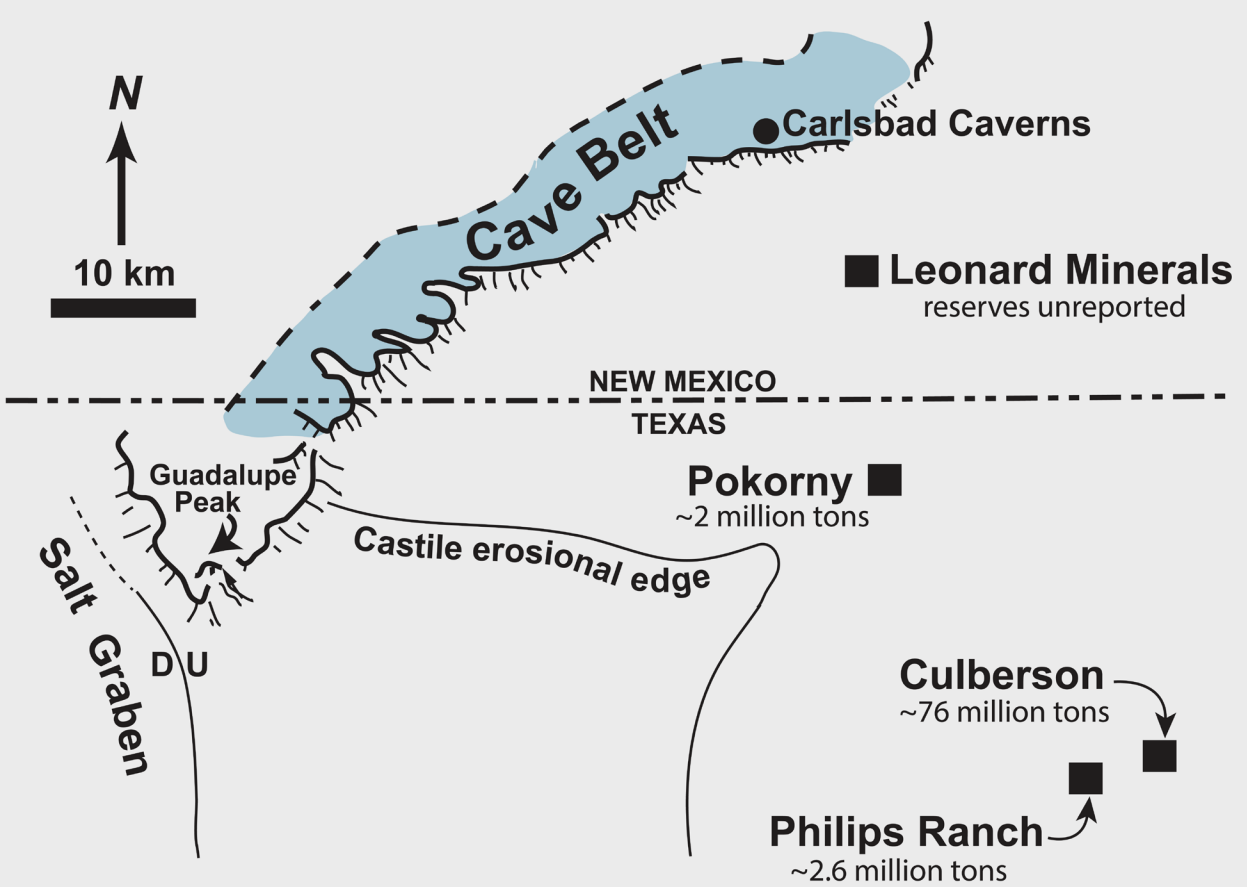

Figure 32. Location of two inactive sulfur mines (Culberson and Phillips Ranch) and two significant sulfur prospects (Pokorny and Leonard Minerals) beneath the Gypsum Plain, Delaware Basin (black squares) (after Smith, 1978, 1980) showing their relationship to the cave belt. Estimated original reserves of elemental sulfur, where known, are shown. The weight of the precursor, H_2S, would have been 6.2% greater than the weight of the original sulfur reserves. The locations of additional sulfur prospects are shown by Smith (1980, his fig. 2) and by Hill (1996, her fig. 196), and the locations of minor, near-surface, Quaternary deposits of sulfur are shown in Porch (1917).

During free convective flow, the upward and downward phases of hypogenic groundwater flowed simultaneously through caverns, breccias, and permeability-enhanced fault conduits. Eventually, an effective fault-tracking hydrologic pathway extended from the Bell Canyon sandstone directly upward through Castile anhydrite and halite into the overlying lower Salado anhydrite and halite. Such hydrologic pathways provided a migration route for gaseous CH_4, which moved into the Ochoan evaporite section as the pathways were forming or shortly afterward. Huge volumes of gaseous CH_4 eventually moved into what was, in effect, a large, robust, fermentation chamber where the gas dissolved within water and reacted with SO_4^{2-}. Judging from the volume of CH_4 consumed, some CH_4 may have migrated upward into the Ochoan evaporites along faults from deep (> 2 km), Lower Paleozoic (Devonian and older), unusually rich source beds.

The chemical and biological processes that formed H_2S and limestone at the major deposits of sulfur were the same as those that operated at diagenetic masses of limestone barren of significant sulfur (now commonly exposed as castiles). The primary locale of microbial CH_4 consumption at the sulfur deposits, whether it was stratigraphically low (Castile) or stratigraphically high (Salado, Rustler) within the evaporite succession, was determined, in particular, by the rates of introduction of CH_4 and groundwater, and by the permeability of the steep, fault-directed pathway. In addition, migration of sparse crude oil into the developing sulfur deposits may have thwarted upward stratigraphic movement of sulfur deposition by forming an "oil cap." Microbes at each of three major sulfur deposits (Fig. 32) consumed, at least, 1,000,000 metric tons of CH_4 (and at the Culberson deposit vastly more), and microbes at each of the major deposits, generated, at least, 1,000,000 metric tons of H_2S (and at

the Culberson deposit vastly more). Equivalent weights of H_2S were probably generated by larger masses of biogenic limestone, many now represented by larger castiles.

The Oxidizing Agent

Aqueous oxygen was clearly the oxidizing agent of H_2S at caves of the Guadalupe Mountains; dispute exists, however, as to the oxidizing agent at the major sulfur deposits. Was it O_2 or was it some other agent? To form the major sulfur deposits, prodigious weights of O_2 would have been required; ~35 million metric tons, for example, at the Culberson deposit (Fig. 32). This is perplexing: How could such a great weight of O_2 be transported for possibly as much as 1 km beneath the earth's surface where at a redox boundary (or redox boundaries) it reacted with H_2S? The O_2 must have been transported within groundwater, and because the maximum solubility of O_2 in groundwater is ~10 mg/l (e.g., Winograd and Robertson, 1982), huge volumes (cubic kilometers) of groundwater would have been required. Furthermore, the aqueous O_2 would seemingly have poisoned the obligate anaerobes that formed the H_2S. In addition, why would surface or near-surface, oxygen-bearing meteoric water sink through a transverse hydrologic pathway that extended for hundreds of meters from the surface to the Bell Canyon aquifer? More likely, it would seem, groundwater within the underlying Bell Canyon aquifer would have risen within the hypothetical transverse pathways (due mainly to artesian pressure) possibly to discharge at ancient springs such it does today at Rustler Spring and Castile Spring (for which the Castile Formation is named (Richardson, 1905)).

To circumvent this baffling problem, geologists have proposed other oxidizing agents for the major sulfur deposits, oxidizing agents that would have been readily available within the subsurface. The problem would be solved, for example, if either sulfate anions (SO_4^{2-}) or carbon dioxide (CO_2) were the oxidizing agent (Feely and Kulp, 1957; Davis and Kirkland, 1970; Ruckmick et al., 1979; Guilinger and Nestlerode, 1992; Guilinger, 1993; Miller, 1992; Klemmick, 1992, 1993). Little evidence, however, supports these agents (e.g., Davis et al., 1970). Moreover, most geologists who have investigated biogenic sulfur deposits have invoked aqueous O_2 as the oxidant (e.g., Ivanov, 1968; Smith, 1978, 1980; Davis and Kirkland, 1979; Hill, 1992; Machel, 1989, 1992, 2001; Niec, 1992; Spirakis and Cunningham, 1992; Wallace and Crawford, 1992; Crawford and Wallace, 1993; Klimchouk, 2007, p. 92). The agent that oxidized H_2S at major sulfur deposits beneath the Gypsum Plain was, in all likelihood, the same as that which operated at both the minor (near-surface) sulfur deposits and the caves of the Guadalupe Mountains, namely aqueous O_2.

Bacteria may have partly mediated the reaction between aqueous O_2 and aqueous H_2S. Ivanov (1968) used radioactive H_2S at the Shor-Su deposit, Uzbekistan, to show that bacterial enzymes catalyzed ~40% of the elemental sulfur. However, the reaction between aqueous O_2 and aqueous H_2S proceeds readily inorganically, and at the deposits beneath the Gypsum Plain sulfur oxidizing bacteria possibly failed to play an important role in precipitating elemental sulfur.

Source of Aqueous Oxygen

Artesian groundwater rising from the Bell Canyon sandstone was probably not the source of the aqueous O_2 that oxidized the H_2S. Several reasons depreciate this source:

- The quantity of O_2 required was so vast that artesian groundwater could not have supplied enough aqueous O_2 to restricted localities of major sulfur deposition. For example, within a reasonable time frame, could artesian (hypogenic) groundwater diluted by overpressured anoxic water forced out of shale have transported the ~35,000,000 metric tons of required O_2 to the restricted locality of the Culberson sulfur deposit?
- During its transportation eastward from mountainous recharge areas, dissolved oxygen within artesian water would have been diminished by reacting with dispersed particles of organic matter, pyrite, and siderite ($FeCO_3$). These constituents of the Bell Canyon occur predominantly within the siltstone lithofacies, which constitutes about 35% of the formation (Bozanich, 1979), and which has a hydraulic conductivity "not much lower than the sandstone" (Davies, 1983, p. 14).
- Late Tertiary pore water within Bell Canyon sandstone and within underlying Permian aquifers may have pervasively contained dissolved CH_4. Dissolved O_2 within artesian groundwater of the Bell Canyon might have reacted with the CH_4. The reaction, which is mediated by aerobic bacteria, forms CO_2 and H_2O. Apparently, the source of dissolved O_2 was not hypogenic artesian groundwater. As the oxidizing agent of H_2S, a source of dissolved O_2 within epigenic meteoric-derived water was more likely than a source of dissolved O_2 within hypogenic meteoric-derived water.

Descent of Epigenic Groundwater and Aqueous Oxygen into Late Permian Evaporites

The locales of major sulfur deposits apparently had a common characteristic: an efficient hydrologic, fault-tracking pathway that extended from the Bell Canyon upward through both the Castile evaporites (~30% halite; ~0.5 km thick) and the directly overlying Salado evaporites (~85% halite; ~0.5 km thick). Hypogenic groundwater, therefore, could move directly upward along the fault-directed pathway bypassing potential barriers—namely, interbeds of Castile anhydrite (~60 % of the formation) and interbeds of Salado anhydrite (~12% of the formation). Hypogenic groundwater that eventually reached the earth's surface and discharged at springs dissolved atmospheric O_2. Then, on dissolving upper Ochoan halite, the previous hypogenic groundwater became epigenic groundwater, and descended along the same fault-directed pathway in which it had ascended. Furthermore, epigenic, oxygen-bearing groundwater from overlying Rustler aquifers entered the pathways, dissolved Salado halite, and descended. Similarly, epigenic groundwater may have entered pathways from topographic structural troughs a possible surface manifestation of the grabens (e.g., Hentz et al., 1989, their fig. 35). Extensive removal of Salado halite followed, and dissolution formed a cavern into which overlying Permian, Mesozoic, and Cenozoic strata collapsed or subsided (see Miller, 1992; Crawford and Wallace, 1993). Collapse resulted in heterolithic breccias. Fractures radiated to the surface, allowing additional water to descend. A large (many hectares) catchment basin, a doline, formed that channeled huge volumes of water into the Salado Formation where it dissolved additional NaCl, in addition to $CaSO_4$ and $CaSO_4 \cdot 2H_2O$. The resulting saline groundwater—several-to-many cubic kilometers—descended by density-driven flow through the Castile and into the Bell Canyon. A huge volume of Salado halite (and a much lesser volume of calcium sulfate) went into solution, also possibly measured in cubic kilometers.

With dissolution of NaCl, the resulting brine became gravitationally unstable. It sank for hundreds of meters along a steep, transverse, "pipe-to-chimney-like" conduit through the evaporite succession. The concentration of the oxidant—dissolved oxygen—within the saline groundwater was low, but the volume of sinking saline groundwater was huge. The epigenic, oxygen-bearing brine sank (by forced convection) through an inverted-fluid-density gradient, as relatively fresh hypogenic groundwater continued to rise (also by forced convection) from Bell Canyon sandstone along separate, adjacent, and parallel pathways.

The dense, saline, epigenic groundwater driven by gravity transported O_2 deeply into the Castile evaporite section. A marine brine with a salinity five times that of seawater can transport (at ~22°C) ~4 milligrams of O_2 per kilogram of brine, and a marine brine with a salinity ten times that of seawater (i.e., a brine at saturation) can transport (at ~22°C) ~2 milligrams of O_2 per kilogram of brine (Kinsman et al., 1974). The dissolved-oxygen capacity of the dissolution brines closely approximates the dissolved-oxygen capacity of marine brines (Sherwood et al., 1991). Thus, the salty groundwater that descended from the Salado into the Castile could have transported about one-fourth to more than about one-half as much dissolved O_2 as a similar volume of fresh groundwater—if it were able to sink. Within the sinking brine, the deleterious effect on solubility of O_2 brought on by increasing temperature diminished as the salinity increased until at a salinity of ~250 g/kg it nearly disappeared (see Sherwood et al., 1991, their fig. 2).

An effective drainage system was required for disposal of the huge volume of sinking brine. Major Ochoan sulfur deposits probably formed only where graben-bounding faults intersect permeable, channel-fill sandstone of the upper Bell Canyon, such as channel sandstone that apparently underlies the giant Culberson sulfur deposit (Smith, 1980; Crawford and Wallace, 1993; Hill, 1996, p. 365). Brine that discharged into the relatively permeable channel sandstone flowed down the slight grade (probably < 0.5°) to the northeast and discharged into the Capitan and San Andres aquifers, the potentiometric pressure within the sandstone being greater than the potentiometric pressure within these aquifers (see Hiss, 1975).

Precipitation of Native Sulfur

Aqueous H_2S moved, in part by diffusion, away from sites of active microbial growth, and, at the same time, aqueous CH_4 moved, in part by diffusion, towards the same sites. Microbial growth occurred at contacts between anhydrite (the wall or fractured rock) and permeable diagenetic limestone. The limestone formed

virtually in place as dissolved CO_2 excreted from the enigmatic microbes reacted almost instantaneously with Ca^{2+} freed as $CaSO_4$ dissolved. Additional $CaSO_4$ persistently dissolved within ambient water as the Ca^{2+} reacted, and as SO_4^{2-} (also freed as $CaSO_4$ dissolved) reacted with CH_4.

Rising buoyant hypogenic groundwater and sinking saline epigenic groundwater flowed simultaneously in two-way flow. Much H_2S was sequestered within the relatively, fresh, hypogenic groundwater being propelled upward by artesian pressure, overpressure, and buoyancy. Where epigenic, O_2-bearing, saline groundwater sinking along one course contacted hypogenic, H_2S-bearing, brackish groundwater rising along an adjacent course, native sulfur precipitated within the pores of the secondary limestone. Both aqueous O_2 and aqueous H_2S, each harmful to the microbial agents if sufficiently concentrated, were eliminated at reaction interfaces separating the two-way flow. As native sulfur precipitated within pores of the limestone host rock, openings were obstructed resulting in redox interfaces shifting over time. At some deposits, sulfur deposition possibly occurred along a horizontal surface corresponding to a zone in which the rate of increase of fluid density with depth changed markedly (a pycnocline).

Oxygen, a crucial component for production of H_2SO_4 in caves of the Guadalupe Mountains, was in unlimited (although restricted) supply and it had a high partial pressure. It dissolved within drops and films of water on cave surfaces to support thriving colonies of sulfur-oxidizing bacteria. Oxidation of one metric ton of H_2S to H_2SO_4 required about four times more O_2 (by weight) than was required to oxidize one metric ton of H_2S to sulfur. Elemental sulfur was deposited within environments in which aqueous O_2 was relatively sparse and in environments in which sulfur-oxidizing bacteria that formed H_2SO_4 were apparently unable to function effectively. Specifically, sulfur was deposited within phreatic groundwater within the Ochoan basinal evaporite section (i.e., Castile and Salado) (some sulfur was also deposited within phreatic groundwater in caves of the Guadalupe Mountains, primarily, within cave pools of Lechuguilla cave (Cunningham et al., 1993; DuChene and Cunningham, 2006)). The second stage of the oxidation process at these locales, i.e., from native sulfur to sulfuric acid (H_2SO_4), failed to occur.

METHANE AS MICROBIAL FOODSTUFF

Microbial Foodstuff at the Subsurface Masses of Biogenic Limestone

Anaerobic reaction between CH_4 and SO_4^{2-} is common within modern marine sediments, but within sedimentary strata on land, the diagenetic reaction is uncommonly recognized and may be rare. However, the diagenetic reaction between CH_4 and SO_4^{2-} within Castile anhydrite in the northwestern and west-central Delaware Basin was paramount, the redox reaction of the Late Tertiary being indirectly responsible for the caves of the Guadalupe Mountains, for the castiles of the Gypsum Plain, and for the large native-sulfur-bearing limestone masses beneath the Gypsum Plain. The volume of CH_4 consumed by microbes was huge—billions of cubic meters—and some CH_4 from deep (thousands of meters) within the basinal sedimentary fill may have been involved. Reaction between CH_4 and SO_4^{2-} may still be occurring within the present-day Ochoan succession beneath the Gypsum Plain, but languidly because of diminished migration of thermogenic CH_4. In addition, where halite has been removed, oxygenated epigenic waters—deadly to the functioning microbes—have now penetrated deeply and extensively through fractures within gypsum and anhydrite evaporites of the Salado and Castile formations.

Support for the CH_4 fraction of natural gas as having been the dominant reductant of sulfate anions within Upper Permian strata of the Delaware Basin is summarized in the following sections. Higher-molecular-weight homologues within natural gas (i.e., ethane (C_2H_6), propane (C_3H_8), and other gases in the alkane series) probably also reacted with SO_4^{2-}; compared to CH_4, however, they were trivial reductants, their volumes being too small (e.g., <~5%). Furthermore, whereas both CH_4 and higher-molecular-weight natural gases were generated during the Late Tertiary within the deeply buried stratigraphic section (Lower Permian, and Middle and Lower Paleozoic), the higher-molecular-weight homologues may have been cracked predominantly to CH_4.

Negative Carbon Isotopic Values

Carbon isotopic analyses of samples of calcite from the castiles, samples of calcite from the major sulfur deposits, and samples of both crude oil and CH_4 from basinal reservoirs support CH_4 as having been the primary microbial foodstuff. (All isotopic analyses are reported as parts per thousand deviation from the $^{13}C/^{12}C$ ratio of a specimen of *Belemnitella americana*, an extinct, marine cephalopod mollusk that served as an early standard.) Twenty calcite samples from nine castiles have a $\delta^{13}C$ mode of -37.0‰; the most negative value being -39.2‰ (Kirkland and Evans, 1976). A sample of calcite from the Pokorny sulfur deposit has a $\delta^{13}C$ of -38.0‰ (Davis and Kirkland, 1970) and a sample of calcite from the Culberson sulfur deposit, a $\delta^{13}C$ of -49.0‰ (Crawford and Wallace, 1993) (Fig. 33). If oil were the dominant microbial foodstuff, we would be unable to account for these highly negative values. None of the fractions of the sparsely associated crude oil has such highly negative isotopic signatures. The benzene-soluble fraction of oil at the Pokorny sulfur deposit, for example, has a $\delta^{13}C$ of -26.1‰ (Davis and Kirkland, 1970), and the paraffinic and aromatic fractions of oil extracted from secondary limestone within the Castile section of the Culberson sulfur deposit (Fig. 32) have $\delta^{13}C$ values of -26.7‰ and -27.7‰, respectively (Crawford and Wallace, 1993). In general, oils within Permian reservoirs beneath the Castile fall into a $\delta^{13}C$ range of -27.2‰ to -28.2‰ (McNeal and Mooney, 1968) (Fig. 33).

Samples of CH_4 from Lower Permian and deeper Paleozoic reservoirs beneath the Castile, on the other hand, are considerably more negative, with $\delta^{13}C$ isotopic signatures in the range of -35.0‰ to -51.0‰ (n>18) (Stahl and Carey, 1975; written communication, R. S. Squires, 1980; Hill, 1996, her appendix 5) (Fig. 33). This range for CH_4 of the Delaware Basin falls within the $\delta^{13}C$ range of -30.0‰ to -55.0‰ for CH_4 produced during late stages of kerogen evolution (Tissot and Welte, 1984, their table II.6.1). Thus, thermogenic CH_4 easily accounts for the highly negative $\delta^{13}C$ values of samples of secondary limestone from both the castiles and the sulfur deposits, whereas crude oil does not.

Ten samples of calcite out of 20 from the castiles have $\delta^{13}C$ values more positive than -30‰ (and 18 of the 20 samples having $\delta^{13}C$ values more negative than -9‰) (Kirkland and Evans, 1976, their table 1) (Fig. 33). Because CH_4 is proposed as the primary reductant, we must account for these moderately elevated values. Carbon atoms within calcite of the castiles are not entirely

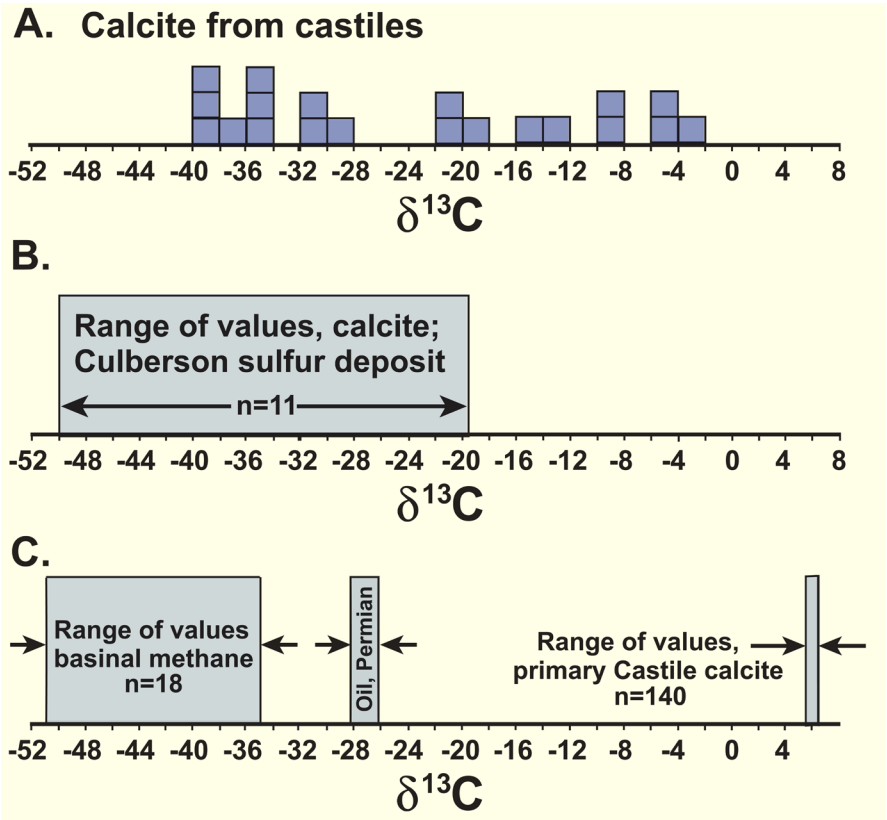

Figure 33. A. Histogram of $\delta^{13}C$ values for samples of secondary calcite from nine castiles on the Gypsum Plain (data from Kirkland and Evans, 1976); half of the samples have $\delta^{13}C$ values more negative than the most negative value for Permian oil; ***B.*** Range of $\delta^{13}C$ values for secondary calcite from Culberson sulfur deposit (data from Hill (1992) and Crawford and Wallace (1993)); samples are likely from the Salado Formation (which contains the largest ore body). ***C.*** Range of values for Lower Permian methane, Delaware Basin (data from R. S. Squires, written communication, 1980; Hill, 1996, her appendix 5); range of values for Permian crude oil and fractions of crude oil from Delaware Basin (data from McNeal and Mooney, 1968; Davis and Kirkland 1970; Crawford and Wallace, 1993); and range of values for primary Castile evaporitic calcite (W. E. Dean, written communication, 1990). Variation in $\delta^{13}C$ values for samples from the Castiles (***A***) probably result from differing proportions of carbon from methane (***C***, left) and carbon from Castile sedimentary calcite (***C***, right).

biogenic, but consist of a mixture of varying proportions of isotopically very light carbon ($\delta^{13}C \leq -35‰$) from CH_4 and isotopically very heavy carbon from primary sedimentary $CaCO_3$ ($\delta^{13}C \sim +6.0‰$; typical range, 5.5-6.5‰; n=140), which constitute the characteristic dark calcite laminae of the Castile Formation (Fig. 19). The isotopically heavy fraction of carbon within Castile sedimentary calcite (usually a minor component) originated in the Late Permian as CO_2 dissolved within seawater that had been concentrated by evaporation. The dissolved CO_2 reacted with Ca^{2+} to precipitate $CaCO_3$ that formed sedimentary laminae (possibly originally aragonite, but now calcite and rarely dolomite). The associated laminae of sedimentary calcite (Fig. 16A, left) persisted or recrystallized as biogenic calcite replaced laminae of Castile anhydrite, and their positive $\delta^{13}C$ values influenced the inclusive value of samples from the castiles. Sedimentary evaporitic calcite within the Castile ranges from ~3 to >80 wt% with a mean of ~10 wt% (see Anderson and Dean, 1995; Kirkland, 2003). Samples from limestone masses within the Castile, therefore, have carbon isotopic compositions that fall on a mixing line between the isotopic compositions of these two dominant carbon sources. Samples adulterated with even small amounts (e.g., 15 wt%) of isotopically heavy evaporitic $CaCO_3$ are likely to display $\delta^{13}C$ values that fall outside the field of thermogenic CH_4.

Eleven samples of calcite from the Culberson sulfur deposit have a more negative range ($\delta^{13}C$ of -49 to -20‰) than samples of calcite from the castiles (Fig. 33). This is probably because primary evaporitic calcite and dolomite are relatively sparse within Salado residual anhydrite; therefore, relatively little carbon having a markedly positive $\delta^{13}C$ value was available to adulterate the $\delta^{13}C$ of samples of the biogenic Salado calcite.

Two additional potential sources of relatively isotopically heavy carbon are HCO_3^- and CO_3^{2-} residing within pore water of sandstone beds directly beneath the Castile (Lee and Williams, 2000). Such anions, with a probable $\delta^{13}C$ range of -2.0‰ to -3.0‰ (Dutton, 2008), may have moved from the Bell Canyon into the overlying Castile, and may have transferred some of their carbon to the

secondary limestone masses. Another possible source of relatively isotopically heavy carbon was gaseous CO_2 (see Holmquest, 1965) that may have accompanied gaseous CH_4 that moved into the Castile. Such CO_2 may have had a $\delta^{13}C$ of about -3.0‰ (Ballentine et al., 2001, their table 1), and its carbon may have been incorporated into the secondary limestone masses.

Crude Oil: An Unimportant Reductant of Sulfate

Several subsurface, sulfur-bearing, limestone masses contain crude oil (Davis and Kirkland, 1970; Smith, 1978, 1980; Crawford and Wallace, 1993; Klemmick, 1993; Guilinger, 1993). The large carbonate-sulfur body that forms the Culberson sulfur deposit (Fig. 32), which extends from the lower Castile Formation upward into the overlying Salado and Rustler formations, is practically free of oil except for the basal Castile (Crawford, 1990). Sulfur-bearing limestone at the Philips Ranch sulfur deposit (Fig. 32), which is apparently confined to the Anhydrite I Member, "can be very oily" (Guilinger and Nestlerode, 1992; Guilinger, 1993). A mass of Castile limestone apparently lacking native sulfur forms the reservoir of the small, shallow Rustler Hills oil field (Davis and Kirkland, 1970). The nearby Screw Bean oil field, located about 18 km northeast of the Culberson deposit, has also produced minor volumes of oil from the Castile (Clark, 1990) (probably from porous diagenetic limestone). Oil within the Castile Formation migrated from the directly underlying Bell Canyon Formation, but it probably originated within deeper formations (Crawford and Wallace, 1993). Once within the Castile, fractions of the oil were degraded anaerobically by microbes to generate "heavy oil," and, among other by-products, CO_2 and H_2S.

The diagenetic masses of limestone within the Castile Formation are genetically analogous to the limestone caprock of salt domes. The limestone caprock of salt domes was initially thought to form by reduction of the underlying anhydrite caprock of salt domes by crude oil (Thode et al., 1954; Feely and Kulp, 1957). However, it now seems likely that CH_4 that migrated into the limestone caprock was the primary reductant (e.g., Posey, 1986; Saunders and Swann, 1994).

Crude oil was not a major reductant in the Castile. Its minor volume within the buried Castile limestone masses (with only insignificant amounts having been produced) indicates that to have served as the primary reductant of sulfate anions, fractions of the migrant crude oil had an inadequate volume. The total estimated weight of the reductant (the foodstuff) that entered sites of sulfur deposition within the Castile Formation (and that which entered the Salado Formation chiefly at the Culberson sulfur deposit) was clearly many thousands of times greater than the weight of crude oil observed at the various subsurface sulfur deposits. Middle and Lower Paleozoic strata of the Delaware Basin contain vast quantities of CH_4 (e.g., Hills, 1984) and relatively small quantities of crude oil, whereas equivalent strata on the surrounding shelf north and east of the basin contain relatively little CH_4 and vast quantities of crude oil; hence, for the basin, it is easier to envision CH_4 rather than fractions of crude oil as the primary reductant.

Could crude oil be sparse within the sulfur-bearing and sulfur-barren calcitized bodies because microbes consumed it? Probably not, if this were true, an obvious display of asphaltic compounds, refractory to microbes, would have remained. If oil had been the foodstuff at the giant Culberson deposit, an estimated 32 million m^3 (~200 million barrels!) of oil would have been required as a reductant (Smith, 1978; Ruckmick et al., 1979). Most crude oil contains a significant fraction of compounds containing N, S, and O—namely, resins (low-molecular-weight) and asphaltenes (high-molecular-weight)—that are neither readily dissolved within water nor effectively metabolized by microbes (e.g., Tissot and Welte, 1984, p. 467). Oil within Bell Canyon reservoirs contains about 10-wt% of such asphaltic compounds (K. A. Kvenvolden, written communication, 1966). If the cited values are representative and if oil were the foodstuff at the Culberson sulfur deposit, then at least 3.2 million m^3 (~20 million barrels) of viscous asphaltic material—the unmetabolizable fraction—would be expected within pores of the deposit. Yet, Smith (1980) reports, "Only a little asphaltic material and minor amounts of oil have been found." CH_4 or specific fractions of crude oil were the only organic constituents with sufficient volume to have served as principal reductants, therefore, the paucity of asphaltic residue and, in addition, the minor volume of oil encountered within the secondary deposits support the interpretation that CH_4 was the primary microbial foodstuff.

The Pokorny Sulfur Deposit, located beneath the Gypsum Plain about 30 km southeast of Carlsbad Cavern,

and about 32 km northwest of the Culberson deposit (Fig. 32), consists of a diagenetic mass of limestone about 200 m beneath the Gypsum Plain that contains dispersed elemental sulfur (Davis and Kirkland, 1970; Klemmick, 1992). Only small amounts of non-flowing crude oil were encountered in exploratory wells at the deposit (Klemmick, 1992). Oil occurs as stains on thin (< ~1 m) limestone intervals (Davis and Kirkland, 1970, their fig. 5), but sulfur crystals up to several centimeters in diameter are unstained (Klemmick, 1992). (These crystals probably formed from polysulfides, and yellow polysulfide-rich water flowed from the discovery borehole (W. E. Dean, personal communication, 1967)). Here too, the paucity of asphaltic residue and the minor volume of oil support CH_4 as having been the primary microbial foodstuff.

Asphaltic residue is unreported from the castiles, which again supports CH_4 as having been the primary reductant. If fractions of oil had been the primary reductant, a residue of resins and asphaltenes would be expected within pores of the castiles, and rather than being entirely or essentially devoid of asphalt, the limestone might fall into the category of a "tar-rich carbonate." Because asphalt is absent, fractions of oil were not primary reductants, leaving CH_4 as the only reasonable candidate. Furthermore, castiles of the Gypsum Plain are genetically related to the subsurface deposits of Ochoan sulfur and limestone beneath the Gypsum Plain (e.g., Kirkland and Evans, 1976; Smith, 1980), their carbonate petrologies, for example, being strikingly similar (Madsen and Raup, 1987). Since CH_4 was apparently the primary microbial foodstuff at the Ochoan sulfur deposits, it was apparently the primary foodstuff at the castiles as well.

Anaerobic Reduction of Sulfate Anions by Methane in Limestone-Hosted Sulfur Deposits Elsewhere

Elsewhere in the world, CH_4 is likely the primary reductant of sulfate anions at most, if not all, major deposits of biogenic sulfur (Mamchur, 1969). Examples include: caprock deposits of the US Gulf Coast (e.g. Posey, 1986), Miocene stratabound deposits of Poland (Niec, 1992; Böttcher and Parafiniuk, 1998), Miocene stratabound deposits of eastern Ukraine (Andrejchuk and Klimchouk, 2001), and late Miocene stratabound deposits of Sicily (Ziegenbalg et al., 2012). CH_4 was probably also the primary reductant at middle Miocene stratabound deposits of northern Iraq (see Al-Sawaf, 1977; Barker et al., 1979; Jassim et al., 1999). Samples of calcitized gypsum from Poland and Ukraine have $\delta^{13}C$ values that range from -32‰ to -65‰, a range considered a "diagnostic feature of bioepigenetic calcite recognized in major sulfur deposits around the world" (Klimchouk, 2007, p. 89). Such isotopically light carbon incorporated within the huge masses of secondary limestone that host these sulfur deposits could probably have been derived only from CH_4. That CH_4 was the likely reductant at major biogenic deposits elsewhere in the world supports CH_4 as having been the reductant of SO_4^{2-} at the large sulfur deposits beneath the Gypsum Plain.

Anaerobic Reduction of Sulfate Anions by Methane in Marine Diagenetic Environments

Anaerobic reduction of SO_4^{2-} by CH_4 is pervasive in modern marine sediments. An ever-available supply of SO_4^{2-} (~0.27 wt%) diffuses from overlying seawater into the sediments. In addition, on continental shelves, CH_4—both biogenic and thermogenic—is abundant, and commonly rises as seeps through oceanic sediments by buoyancy, by other sources of pressure, and by diffusion. The reaction between CH_4 and SO_4^{2-} within marine sediments, as mentioned above, is identical to that which occurred during the Late Tertiary within Castile and Salado anhydrite. The reaction in both diagenetic environments is (and was) mediated by microbes, and the enigmatic, biologic agents that operate today within modern oceanic sediments may be the same or related microbial species (or strains) as those that operated within anhydrite of the Ochoan group.

Significant seeps of petroleum (natural gas and/or crude oil) on the sea floor are designated "cold seeps" (e.g., Stakes, 1999; Aloisi et al., 2002; Orcutt et al., 2005). Associated near-surface components are hydrogen sulfide, sulfides of heavy metals (predominantly pyrite), and commonly massive accumulations of limestone. Ancient marine deposits of diagenetic limestone having lithologic and paleo-biologic characteristics similar to active, modern marine cold-seeps also rarely crop out on land (e.g., Peckmann et al., 1999; Clari and Martire, 2000). Limestone of both modern and ancient cold-seep deposits is depleted in ^{13}C (i.e., it is "isotopically light") (e.g., Jørgensen, 1992; Suess et al., 1999; Peckmann et al., 1999; Kotelnikova, 2002) attesting to its origin from organic matter. Furthermore, samples of the limestone commonly have highly negative $\delta^{13}C$ values

clearly derived directly or indirectly from CH_4 (either thermogenic, biogenic, or both). The H_2S generated at modern cold seeps supports an impressive mat of H_2S-oxidizing bacteria as well as an associated seep fauna, including tubeworms. The ecology of the seep fauna is built around bacteria, especially *Beggiatoa sp.*, that obtain their energy from reaction between aqueous O_2 and aqueous H_2S (e.g., Orcutt et al., 2005). The comprehensive processes that occur at modern cold-seep deposits of the world's oceans were duplicated, in many respects, by the comprehensive processes that occurred in southeastern New Mexico; these include microbial generation of H_2S at the calcite masses and its oxidation at the caves and at the sulfur deposits.

Furthermore, within shallow anaerobic sediments of the world's oceans, SO_4^{2-} oxidizes CH_4. The oxidation is apparently nearly pervasive in shallow oceanic sediments, but is most vigorous in sediments of continental shelves. Dissolved within seawater, O_2 diffuses downward through marine pore water for a few millimeters to more than one meter below the seafloor until it becomes exhausted (e.g., Jørgensen, 1982). Similarly, SO_4^{2-} within seawater—less reactive and in much greater concentration (>300 times)—diffuses downward even farther. Below its limit of diffusion (typically <1 m), a varied assemblage of anaerobic microbes (including methanogenic archaea) decomposes particulate organic matter by hydrolysis and by fermentation to generate CH_4 (e.g., Barker, 1956; McCarty, 1964). The upward diffusing CH_4 eventually contacts the downward diffusing SO_4^{2} (see Valentine, 2002). At the interface, anaerobic microbes (probably a consortium of archaea and bacteria) then bio-catalyze oxidation of CH_4 and the coupled reduction of SO_4^{2-} to form the metabolic "waste products," H_2S and CO_2 (e.g., Boetius et al, 2000; Hinrichs and Boetius, 2002). Most of the sulfur and carbon atoms are incorporated into pyrite and calcite, respectively. Little CH_4 escapes anaerobic oxidation to enter either the overlying O_2-bearing sediments or the O_2-bearing water column, the "sulfate-dependent methane oxidation" acting as a barrier (Valentine and Reeburgh, 2000). The microbially mediated reaction between CH_4 and SO_4^{2-} occurs collectively on a vast scale within the world's oceans, an estimated 100 trillion grams of CH_4 per year (Reeburgh, 1989), the amount of CH_4 consumed being approximately equivalent to 5-20% of the total annual flux of CH_4 to the atmosphere (Hinrichs and Boetius, 2002).

Anaerobic Reduction of Sulfate Anions by Methane in Terrestrial Diagenetic Environments Elsewhere

Conspicuous evidence of microbially mediated reduction of sulfate anions (SO_4^{2-}) by CH_4, or, for that matter, reduction of molecular oxygen (O_2) by CH_4, is uncommonly recognized within the Earth's terrestrial environments. In rare instances, *aerobic* bacterial cells (living and dead) are preserved ephemerally at and near the earth's surface as "paraffin dirt," which provides direct evidence that CH_4 has reacted with O_2 (Davis, 1952). Lithologic evidence of *anaerobic* microbial oxidation of CH_4 in terrestrial diagenetic environments is apt to be preserved prominently only where CH_4 has leaked into shallow strata having an absence of dissolved oxygen, a favorable concentration of SO_4^{2-} (e.g., >1000 ppm, Oehler and Sternberg, 1984, their fig. 14), and a favorable range of temperatures (e.g., ~40° to ~85°C). Evidence of such anaerobic oxidation consists of bleaching of redbeds by H_2S (such as occurs in some Mesozoic strata of the western USA (E. F. McBride, written communication, 1996) and above the Cement field of south-central Oklahoma (Donovan, 1974)), but especially from a combination of carbonate, sulfur, sulfate, and sulfide, replacements and/or pore-filling cements, and/or crystal growths, commonly with revealing isotopic signatures.

The redox reaction between CH_4 and SO_4^{2-} at several oil and gas fields in south-central Oklahoma had a magnitude that rivals that which occurred at the Culberson sulfur deposit (Kirkland et al., 1995). At the Cement, Velma, Carter-Knox, and several other fields, CH_4 migrated upward from complex Pennsylvanian structures across an angular unconformity into gently folded, gypsum-bearing Permian red beds. Sulfate-reducing microbes at the Cement field, for example, consumed an estimated 37 billion m^3 (1.3 trillion ft^3) of CH_4, and in the process generated millions of metric tons of the metabolic by-products, CO_2 and H_2S. The by-products reacted with associated cations—chiefly Ca^{2+}, Fe^{2+}, and Mg^{2+}—to form "chimneys" of bleached red beds, chiefly sandstone, cemented by calcite, dolomite, and lesser amounts of pyrite and marcasite (FeS_2), and, in addition, trace amounts of sphalerite, (Zn,Fe)S and galena, PbS. The carbonate minerals have $\delta^{13}C$ values as low as -39.2‰, and the sulfide minerals, $\delta^{34}S$ values as low as -37.9‰ (Kirkland et al., 1995). Other terrestrial examples in which anaerobic reduction of SO_4^{2-} by

CH_4 has played an important role are calcite-cemented sandstone along the flank of Butler Salt Dome, east Texas (Enos and Kyle, 2002), possibly the Beeri sulfur deposit, southern Israel (e.g., Druckman et al., 1994), and many low-temperature mineral deposits of copper, iron, lead, uranium, vanadium, and zinc within sedimentary strata.

SUMMARY AND CONCLUSIONS

An immense weight (millions of metric tons) of microbial hydrogen sulfide (H_2S) moved into caves of the Guadalupe Mountains during the late Miocene and early Pliocene (~12-4 million years ago). The H_2S reacted with O_2 chiefly within subaerial water of condensation to form sulfuric acid (H_2SO_4)—the primary cave-forming agent in the mountains. The caves formed within Middle Permian reefal limestone (the Capitan Formation) and within adjacent, time-equivalent, shelfal carbonates (particularly, the Seven Rivers Formation).

Pathways previously proposed for transporting the precursor, H_2S, to the caves are likely deficient. Neither large quantities of gaseous H_2S nor aqueous H_2S apparently migrated from the northwestern Delaware Basin *updip* into the evolving caves through siliciclastics of the Bell Canyon Formation (Middle Permian; Guadalupian series). Furthermore, large quantities of H_2S dissolved within artesian groundwater apparently did not migrate from elevated (mountainous) shelfal strata northwest of where the modern Capitan reef escarpment now exists *downdip* through permeable Middle Permian strata into the evolving caves. Instead, the H_2S involved in speleogenesis was probably transported into the evolving caves from the adjoining Delaware Basin through upward-inclined pathways within Castile halite (Upper Permian; lower Ochoan Group). The Castile Formation, a thick (~0.5 km) evaporite unit (originally ~30% halite, ~60% anhydrite, ~10% calcite), is confined to the basin.

Each Castile member, bed, and lamina—whether halite, anhydrite (probably initially gypsum), or calcite (possibly initially aragonite)—that formed by deposition and diagenesis in the Late Permian had, with few exceptions, an extraordinarily uniform thickness, lithology, and contact relationships over many thousands of square kilometers. Two approximately coeval Late Tertiary events superimposed on the consistent Castile stratigraphic framework resulted in intense H_2S-H_2SO_4 speleogenesis in the Guadalupe Mountains. These events were

- high-heat flow, particularly in the western Delaware Basin, and
- eastward tilting of the paleo-Guadalupe tectonic block, a huge homocline that included the Guadalupe Mountains and much of the Delaware Basin.

The transient, high-heat flow increased stratal temperatures in Permian and older petroleum-source strata, which, in turn, cracked dispersed crude oil and further decomposed dispersed kerogen to generate copious volumes of CH_4. In addition, the episodic and uniform easterly tilting during the late Miocene and early Pliocene (by a cumulative 1-2°) along with a nearly contemporaneous late-phase of Basin and Range crustal extension, created and rejuvenated fractures within the Paleozoic sedimentary section.

In the Delaware Basin near the beginning of the late Miocene, pressurized, nearly fresh artesian groundwater, which originated in the ancestral Guadalupe Mountains, moved upward from sandstone beds of the upper Bell Canyon Formation (Middle Permian) through the new and rejuvenated fractures into the directly overlying Anhydrite I Member (thickness ~50 m) of the Castile Formation. The artesian groundwater dissolved $CaSO_4$, the density of the solvent increased, it became gravitationally unstable, and Ca^{2+}- and SO_4^{2-}-bearing groundwater sank back into the Bell Canyon. Taking its place, under artesian pressure, the freshest, least-dense water available rose inherently to the highest accessible elevation. The continuous process of free convection created dissolution voids, and, subsequently, fractures and collapse breccias within the Anhydrite I Member through which CH_4, aggressive groundwater (rising), and nonaggressive groundwater (sinking) moved freely.

Hypogenic groundwater ascended through the solutionally enhanced, transverse pathways through the Anhydrite I Member and eventually contacted the base of the directly overlying Halite I Member (thickness ~125 m) of the Castile Formation. The rising groundwater readily dissolved the bedded NaCl, and the resulting brine sank. Simultaneously, groundwater with the greatest solutional aggressiveness for NaCl (that with the lowest density and the lowest concentration of solutes) rose continuously to the solution front where it, in turn, dissolved additional Castile halite.

The free convective process resulted in chambers being dissolved vertically upward within the Halite I Member until they contacted the intact base of the next overlying bed of anhydrite (namely, the base of the Anhydrite II Member), which dipped uniformly eastward over

thousands of square kilometers. Then, by the same process of convective dissolution, but in an abrupt change in dip (from ~90° to < ~1°) and in direction of dip (from upward to westward), anhydrite-capped voids advanced up the slight homoclinal slope for up to several tens of kilometers. The solvent, nearly saturated with $CaSO_4$, no longer readily dissolved anhydrite. The conduits, except for their smooth anhydritic ceiling, were confined to halite. The width of dissolution conduits is inferred to have been narrow (< ≈30 m); their height, low (< ≈2 m); and their length, long (up to tens of kilometers).

Halite dissolved most actively at the most elevated, thinnest, and most western part of growing conduits where solutionally aggressive groundwater directly contacted halite. Here, the convectively flowing groundwater abruptly and diametrically changed direction. Just beneath rising aggressive water (in a two-way stream), brine saturated with NaCl flowed easterly within conduits directly down the slight slope of the homocline, and passed through fractures, breccias, and voids within the Anhydrite I Member and drained into sandstone of the Bell Canyon Formation. Growing conduits continuously advanced westerly up the homoclinal slope as the ascending, aggressive groundwater dissolved halite. Many conduits eventually contacted the steep face of the reef or the steep face of the forereef; here Castile halite was flush against Capitan carbonates.

Within the basin, millions of cubic meters of gaseous CH_4 migrated from Lower Permian and deeper source strata upward into upper Bell Canyon sandstone just before, during, and just after formation of the conduits. Gaseous CH_4 moved upward through fractures or through anhydrite breccias into the lower anhydrite members of the Castile following the same pathways as the hypogenic, fresh-to-brackish groundwater. Within anoxic ambient water, sulfate anions (freed as anhydrite dissolved) reacted with aqueous CH_4. The reaction catalyzed by microbial enzymes formed H_2O, H_2S, and CO_2. Almost all CH_4 that invaded the Castile was probably transformed. The dissolved CO_2 (as CO_3^{2-}) reacted instantaneously with Ca^{2+} (which like SO_4^{2-} formed as anhydrite dissolved) to form diagenetic masses of $CaCO_3$, most ultimately having a maximum dimension, in plan, >30 m. Many limestone masses, exposed by later erosion, constitute the present-day castiles of the Gypsum Plain. The H_2S generated at the porous masses of subsurface limestone dissolved readily within the rising, pressurized, largely artesian groundwater. Forced convection transported the groundwater upward through the Castile dissolution conduits and into the Capitan Formation with a velocity of flow that exceeded that of free convection during construction of the conduits. The saline, H_2S-laden groundwater on reaching the ancient reef and forereef moved, wherever possible, through interconnected pores (particularly those along fractures) into the limestone reef, where, because of the relatively high density of the introduced saline groundwater, it descended to a low level.

The "cave belt" of the Guadalupe Mountains, a six-kilometer-wide band parallel to and including the Capitan reef, has a northeast-southwest trend across the uniformly eastward dipping, Guadalupe tectonic block. Because of this configuration, on uplift of the homoclinal tectonic block the highest elevation of the cave belt was to the southwest. Erosion, which generally progressed down the tectonic block from west to east, probably initially removed the stratal cover consisting primarily of Rustler and Salado evaporites (Upper Permian, upper Ochoa Group) from the most elevated southwestern part of the cave belt. In step with intermittent uplifts, erosional removal of the evaporitic cover from the cave belt probably progressed to the southeast over millions of years.

A primary control over both H_2S-H_2SO_4 speleogenesis in the Guadalupe Mountains and H_2S-S genesis in the Delaware Basin was availability of O_2. Abundant H_2S during the late Miocene and early Pliocene charged the sluggishly moving groundwater in the lower part of the ancestral Capitan aquifer, which over much of its extent coincided (in plan) with the cave belt. O_2 was dissolved within groundwater in the upper part of the aquifer in meager concentrations, and generation of minor quantities of aqueous H_2SO_4 at a pycnocline may have resulted in incipient caves. Intense speleogenesis began only when atmospheric O_2 became available to these initially formed caves. With sufficient tilting of the ancestral Guadalupe tectonic block and descent of the water table, gaseous O_2 from the earth's atmosphere initially entered the upper part of the most elevated incipient caves. The O_2 probably migrated laterally as a gas within northeast-trending fracture pathways from high ground to the southwest where the evaporitic cover was probably initially breached. Mediated by aerobic bacteria H_2S and O_2 from the cave atmosphere reacted within subaerial water of condensation, to form aqueous H_2SO_4. The strong acid, in turn, reacted with reefal and

shelfal carbonates initiating intense speleogenesis. Then, during an interval of ~8 Ma—with additional episodes of uplift, descent of the water table, and erosion of the cover—speleogenesis descended progressively in steps both within the slightly inclined (<0.5°) northeast-trending cave belt and within individual caves.

A genetic and geographic relationship exists between caves of the Guadalupe Mountains and large deposits of native sulfur (a few million to many millions of metric tons) beneath the adjacent Gypsum Plain. The deposits and the caves probably formed at about the same time, and they probably both owe their existence to a coincidence of essentially the same stratigraphic, thermal, biogenic, and tectonic events.

Similarities in the genetic history of both include:

- Hypogenic groundwater convectively dissolved Castile anhydrite and halite.
- Anaerobic microbes within the evaporite sequence mediated a reaction between CH_4 and SO_4^{2-} generating immense quantities of H_2S.
- Oxidation of the aqueous H_2S required immense quantities of aqueous O_2.
- Processes forming the caves and those forming the major deposits of sulfur required a lengthy period (probably many hundreds of thousands of years).

Differences in their genetic history include:

- At the sulfur deposits, O_2 oxidized H_2S to form native sulfur probably primarily inorganically within the phreatic realm, whereas at the caves, O_2 oxidized H_2S to form H_2SO_4 biogenically mainly within the vadose realm.
- At the major sulfur deposits, epigenic groundwater bearing O_2 dissolved halite of the Salado Formation (~85% halite; ~0.5 km thick); the resulting boost in density caused oxygen-bearing brine to sink directly downward along an inverted density gradient through a permeability-enhanced fault-tracking pathway to aqueous reaction sites within brecciated Salado anhydrite and brecciated and bedded Castile anhydrite. At the caves, however, gaseous O_2 from the earth's atmosphere probably moved laterally and slightly downward under a stratal cover by diffusion, thermal convection, and barometric winds to aqueous reaction sites within basin-margin carbonates.
- At the sulfur deposits, biogenic H_2S was supplied to reaction sites within hypogenic, relatively fresh groundwater that moved directly upward along steep, permeability-enhanced, fault-tracing pathways for meters to many tens of meters by buoyancy, artesian pressure, and overpressure.

At the developing caves, biogenic H_2S was supplied to reaction sites from basinal microbial loci (represented by the carbonate masses of the western basin). Within the uppermost part of beds of Castile halite, the H_2S-bearing groundwater, driven by artesian pressure and overpressure, flowed through conduits up a slight gradient (<<2%) for up to ≈30 km laterally. It then flowed into the Capitan reef and forereef, eventually into cave pools, degassed into cave atmospheres, and, eventually, moved to reaction sites on cave walls and ceilings.

Carbon-isotopic values of samples of the castiles support CH_4 as the microbial foodstuff. Half of 20 samples of calcite from the secondary masses of Castile limestone masses exposed at the earth's surface (the castiles) have $\delta^{13}C$ values in the range -39‰ to -28‰ (Kirkland and Evans, 1976). The carbon within these samples must have been derived entirely or largely from CH_4. Their values fall within the $\delta^{13}C$ range exhibited by thermogenic CH_4, but they fall outside the range exhibited by crude oil. To form the castiles, the subsurface masses of limestone, and the caves of the Guadalupe Mountains the basinal microbial agents required a huge volume of foodstuff (i.e., a reductant). Besides CH_4, probably only crude oil had a sufficient quantity to serve as a potential reductant, specifically, metabolizable fractions of crude oil. Middle Permian crude oil contains an asphaltic fraction (~10%) that microbes are unable to devour. The castiles and the buried sulfur-bearing limestone masses are virtually devoid of an asphaltic residue, an absence that supports CH_4 as the primary microbial foodstuff. Samples of calcite with $\delta^{13}C$ values more positive than -35‰ probably contain a significant fraction of inorganic carbon derived dominantly from minor amounts of Castile evaporitic calcite having a $\delta^{13}C$ of about +6.0‰. The presence of this fraction probably resulted in ten samples (out of 20) being displaced slightly-to-moderately from the field of calcite generated strictly or predominantly by CH_4.

CH_4 is the primary reductant at most, if not all, large biogenic sulfur deposits elsewhere in the world (e.g., US Gulf Coast, Poland, Ukraine, Sicily). In addition, these deposits are all associated with evaporites, and they all

have petrologic and isotopic characteristics remarkably similar to those of the castiles of the Gypsum Plain and to those of the large, limestone-hosted, sulfur deposits beneath the Gypsum Plain. These analogous traits support CH_4 as having been the dominant substrate (foodstuff) at microbial loci within the Castile Formation, loci that are now represented by masses of biogenic limestone.

A biogenic reaction between CH_4 and SO_4^{2-}, the same overall reaction that took place within the Castile during the Late Tertiary, is confirmed and is common within modern, shallow marine sediments and within marine sediments associated with seeps of CH_4. Bio-enzymes that catalyze the redox reaction are derived either from archaea or from a consortium of sulfate-reducing bacteria and archaea. The marine microorganisms that mediate the modern reaction are probably the same as or related closely to those active within the Castile during the Late Tertiary. Furthermore, many modern, cold-seep deposits of the world's oceans display processes—including SO_4^{2-} reduction by CH_4, and O_2 reduction by H_2S—duplicated ~12 to ~4 Ma ago by terrestrial processes operating collectively within the Castile, Capitan, and Seven Rivers formations.

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