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HYPOGENE CALCITIZATION: EVAPORITE DIAGENESIS IN THE WESTERN DELAWARE BASIN

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ABSTRACT: Evaporite calcitization within the Castile Formation of the Delaware Basin is more widespread and diverse than originally recognized. Coupled field and GIS studies have identified more than 1000 individual occurrences of calcitization within the Castile Formation outcrop area, which includes both calcitized masses (limestone buttes) and laterally extensive calcitized horizons (limestone sheets). Both limestone buttes and sheets commonly contain a central brecciated zone that we attribute to hypogene dissolution. Lithologic fabric of calcitized zones ranges from little alteration of original varved laminae to fabrics showing extensive laminae distortion as well as extensive vuggy and open cavernous porosity. Calcitization is most abundant in the western portion of the Castile outcrop region where surface denudation has been greatest. Calcitization often forms linear trends, indicating fluid migration along fractures, but also occurs as dense clusters indicating focused, ascending, hydrocarbon-rich fluids. Native sulfur, secondary tabular gypsum (i.e. selenite) and hypogene caves are commonly associated with clusters of calcitization. This assemblage suggests that calcium sulfate diagenesis within the Castile Formation is dominated by hypogene speleogenesis.

INTRODUCTION

Calcitization of evaporite minerals is a common occurrence and has been described in numerous settings associated with either bacterial sulfate reduction (BSR), thermal sulfate reduction (TSR) or infiltration of meteoric waters. Adams (1944) originally documented the occurrence of "castiles" within the Ochoan (Lopingian) (Fig. 1) rocks of the western Delaware Basin (Fig. 2A). Kirkland and Evans (1976) recognized these features as calcitized evaporites, which they termed "limestone buttes", and associated them with BSR and near-surface, methane seeps. Originally, calcitization within the Delaware Basin was only associated with isolated masses within the Castile and Salado Formations, including 71 limestone buttes physically documented (Fig. 2B) and over 100 estimated (Kirkland and Evans 1976). However, our study of the calcitized evaporites, in conjunction with our cave and karst studies in the region, has found that the occurrence of calcitization within the Castile Formation is far more extensive, including not only numerous, newly documented isolated masses but also laterally extensive calcitized zones. Additional calcitized evaporites occur in the carbonate facies on the margins of the Delaware Basin where anhydrite nodules have been replaced by calcite spar as gravity-driven meteoric waters passed downdip to the east through the Capitan Reef complex (Scholle et al. 1992).

Most previous studies of the Castile Formation have focused on its Permian deposition (e.g. Adams 1944, 1972; Anderson et al. 1972; Hill 1996), while occurrences of calcitization have long been noted to be associated with native sulfur deposits, including several ore bodies that have been mined economically (e.g. Wessel and Wimberly 1992). Recently calcitization has also been found to be associated with occurrences of hypogene karst (i.e.

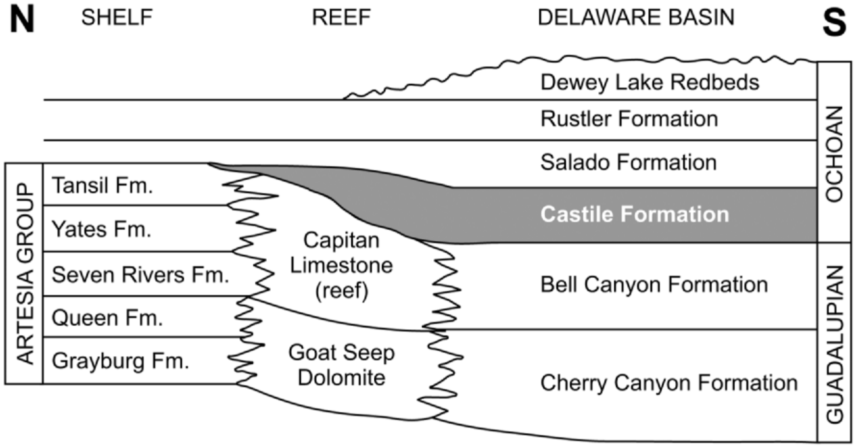

Figure 1. Stratigraphic north (Shelf) to south (Delaware Basin) section of significant lithologic units within the study area. Note the relationship between the Castile Formation (grey) and adjacent formations (adapted from Scholle et al. 2004).

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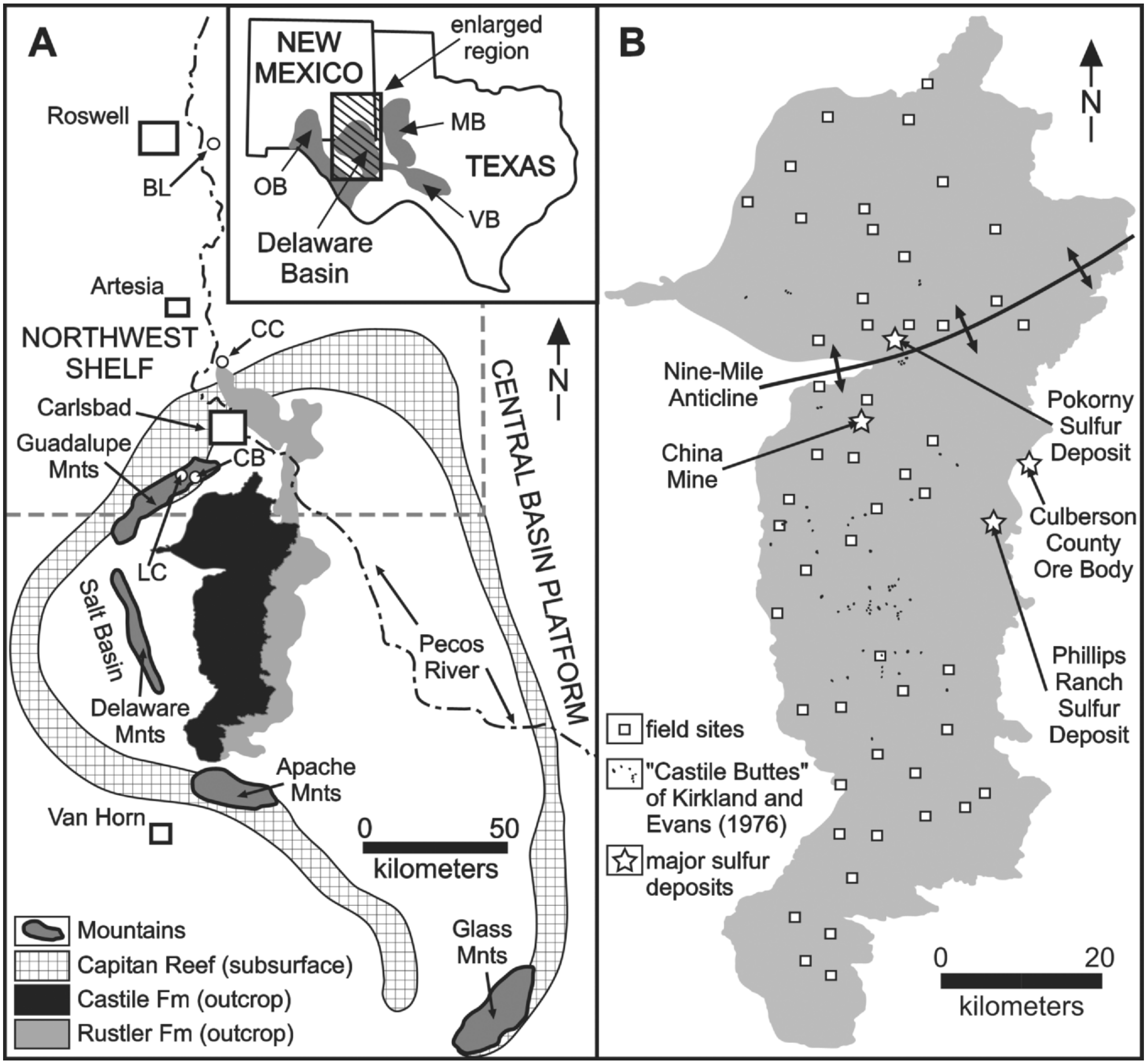

Figure 2. Castile Formation outcrop area. A) Regional overview of Castile Formation outcrop area in relation to the Delaware Basin, which is defined by the boundary of the Capitan Reef and Gypsum Plain (Castile and Rustler Formation outcrops). Features of interest include: BL – Bottomless Lakes; CC – Coffee Cave; CB – Carlsbad Cavern; and LC – Lechuguilla Cave. Inset shows location of expanded region and the Delaware Basin in relation to other major seas of the Permian, including: OB – Orogrande Basin; VB – Val Verde Basin; and MB – Midland Basin (adapted from Hill 1996; Klimchouk 2007; Scholle et al. 2004; and Stafford et al. 2008 a,b,c).; B) Enlarged Castile outcrop region showing the Nine-Mile Anticline, location of physically mapped field sites, "Castile Buttes" identified by Kirkland and Evans (1976) and major sulfur deposits (adapted from Hill 1996; Kirkland and Evans 1976; Stafford et al. 2008c; Wessel and Wimberly 1992).

cavernous porosity formed by ascending fluids within a confined or semi-confined system) (Stafford et al. 2008b,c) and selenite masses (Lock et al. 2004) within the Castile Formation.

Studies in Miocene gypsum deposits of the western Ukraine have found similar diagenetic assemblages of calcitized evaporites, native sulfur, selenite and extensive cave systems (Klimchouk 2007). These Miocene diagenetic assemblages have been attributed to hypogene speleogenetic processes similar to those observed in Mississippi Valley Type deposits. Salt dome caprock studies within the Gulf of Mexico contain complex diagenetic assemblages of anhydrite, calcitized evaporites, sulfur and abundant vuggy porosity, suggesting a similar diagenetic environment to that of Castile buttes (Lock et al. 2004).

Current research by the authors within the Castile Formation focuses on the diagenetic evolution of calcium sulfate rocks, with specific emphasis on the relationship between calcitized evaporites, native sulfur and secondary tabular gypsum (i.e. selenite), which consistently occur in clustered associations within the Castile outcrop area. Initial research focuses on the distribution and occurrence of calcitization within the Castile Formation, which is far more diverse and widespread than originally reported by previous investigators.

GEOLOGIC SETTING

The Castile Formation crops out over ~1,800 km^2 (Fig. 2) within the western Delaware Basin extending from the Castile dissolution front on the west, to the east where it descends into the subsurface beneath the Salado and Rustler Formations (Kelley 1971). The Castile Formation reaches a maximum thickness of 480 m in the subsurface, while it gradually decreases in thickness from east to west through the Gypsum Plain, until only a few meters of the lower Castile Formation remain on the western dissolution front (Kelley 1971). The outcrop area is part of the larger Gypsum Plain, a physiographic province located on the northern edge of the Chihuahuan Desert that includes extensive outcrops of the Castile and Rustler Formations (Fig. 1), but only minor residual outcrops of the Salado Formation.

At the time of deposition, the Delaware Basin was located within 5-10° of the equator on the western edge of Pangea (Lottes and Rowley 1990). Collision of the North American and South American-African plates during the Pennsylvanian produced the Ouachita Orogeny and block faulting within the Permian Basin, forming the Delaware Basin, Central Basin Platform and Midland Basin (Ross 1986). Throughout the Permian, high rates of sedimentation and subsidence dominated the Delaware Basin, with deposition of 3-5 km of strata (King 1942). Early to middle Permian (Wolfcampian to Guadalupian) strata include thick siliciclastic and carbonate sequences. Late Permian (Ochoan / Lopingian) evaporite strata were deposited as open marine circulation in the Delaware Basin ceased with the closing of the Hovey Channel (Adams 1972).

The Castile Formation was deposited during the early Ochoan (Lopingian) after the closing of the Delaware Basin at the end of Guadalupian time (Adams 1972). The Castile Formation is bounded below by clastic deposits of the Bell Canyon Formation (Guadalupian), on the margins by carbonates of the Capitan Reef (Guadalupian) and above by the largely evaporitic Salado and Rustler Formations (mid to late Ochoan / Lopingian) (Fig. 1) (Kelley 1971).

Castile evaporites were deposited as deep-water deposits within a density-stratified, closed basin, which filled the entire Delaware Basin (e.g. Adams 1944; Kirkland and Anderson 1970; Kendall and Harwood 1989). Castile sulfates have been traditionally defined as laminated to massive (Fig. 3), where laminae consist of mm to cm thick alternating layers of gypsum/anhydrite and calcite, including more than 260,000 individual laminae couplets, which have been correlated over distances up to 113 kilometers (Anderson and Kirkland 1966). These laminations have

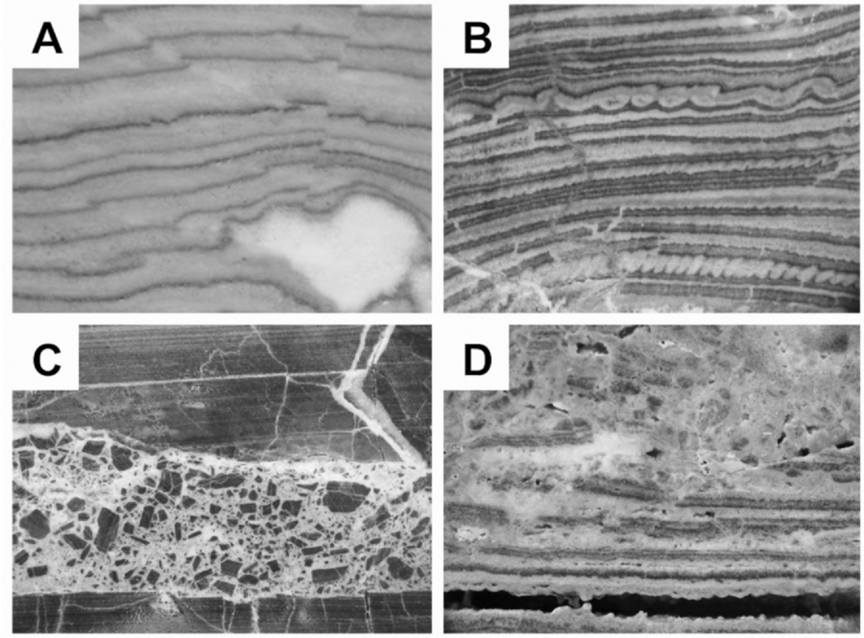

Figure 3. Slabs of Castile Formation bedrock. Image widths are ~10 cm. A) laminated and nodular gypsum; B) calcitization with preserved laminae including minor microfolding; C) calcitization showing a central zone of brecciation; and D) calcitization with vuggy porosity, laminae distortion and minor native sulfur.

been widely studied and are believed to represent annual varve sequences reflecting seasonal variations of basin salinity during deposition, where sulfate laminae represent dry periods and calcite laminae represent wetter periods (Anderson et al. 1972), similar to dry and monsoonal seasons seen in many semi-arid regions today.

Subsequent to Permian sedimentation in the Delaware Basin, the region has remained largely tectonically quiescent. Early Triassic, Laramide and Basin and Range tectonism resulted in uplift and regional tilting towards the east-northeast (Horak 1985). Broad anticlinal flexures oriented roughly east-west occur throughout the region in association with Laramide compression, beginning in the late Cretaceous (Dickenson 1981; Hentz and Henry 1989). Basin and Range (mid-Tertiary) extension affected the far western Delaware Basin, where the salt basin was down-dropped at least 500 meters (Friedman 1966); however, throughout the majority of the Delaware Basin this was limited to high angle fracturing, primarily represented by minimally offset joint sets oriented at ~N75°E and ~N15°W (Nance 1992). Since Permian time, the Delaware Basin region has been largely exposed to surficial processes, except during a brief period of marine inundation during middle Cretaceous deposition (Kelley 1971).

Although structural deformation appears to be minimal within the Castile Formation, diagenetic alteration is widespread. Original fabric alteration, largely associated with dehydration/rehydration processes of anhydrite/gypsum conversion, is common throughout the Castile Formation. This includes massive fabrics, showing no evidence of laminations, to diagenetic nodular fabrics with some semblance of the original laminations (Dean et al. 1975). In addition to calcitization and fabric alteration, deposition of native sulfur bodies (Klemmick 1992) and occurrences of large selenite masses are common (Hill 1996; Lock et al. 2004).

EVAPORITE CALCITIZATION

Calcitization of gypsum/anhydrite has been reported to occur primarily through three main processes, Bacterial Sulfate Reduction (BSR), Thermochemical Sulfate Reduction (TSR) and meteoric calcitization. Meteoric calcitization is commonly associated with dedolomitization where dolomites are converted to calcites through the simultaneous dissolution of dolomite and calcium sulfates and the precipitation of calcite (Back et al. 1983). Meteoric calcitization can also result solely from the dissolution of evaporite nodules and the precipitation of replacive calcite minerals. Unlike meteoric calcitization, both BSR and TSR require the presence of sulfate rocks and an organic carbon source (e.g. hydrocarbons) (Machel 1992). Sulfate is reduced and in the process hydrogen sulfide and calcite saturated fluids are formed, which either contemporaneously or subsequently precipitate as native sulfur and secondary calcite (Machel 1992). BSR occurs in a wide range of low temperature, sedimentary environments, including shallow groundwater aquifers, in the presence of low molecular weight organic compounds (Machel 1987). Because sulfate-reducing bacteria provide catalysts for sulfate reduction, environmental parameters including the availability of nutrients, the ability to remove waste products (H_2S) and thermal regime (0 to ~80°C) limit BSR (Ehrlich 1990). TSR generally occurs in higher temperature regimes (~100 to 180°C), as an inorganic processes (Machel 1998); however, thermodynamically TSR is possible at temperatures as low as 25°C (Worden and Smalley 1996). As with BSR, TSR will proceed as long as sulfate and organic compounds are present, but TSR does not require the active involvement of microbial organisms. Therefore, TSR can proceed in confined systems without the complete removal of hydrogen sulfide byproducts, which can become toxic for sulfur reducing bacteria (Machel 1992).

Kirkland and Evans (1976) identified calcitization in the Ochoan (Lopingian) evaporite facies of the Delaware Basin and noted that localized occurrences formed resistant "limestone buttes" that retained the lithologic texture of the original calcium sulfates that had been replaced (Fig. 3A,B). In the subsurface, many of these calcitized masses contain significant amounts of native sulfur, often forming vug-filling ore deposits. However, the presence of associated sulfur near the surface is limited to a few isolated occurrences because native sulfur rapidly oxidizes in the presence of meteoric waters. Based on their analyses of $\delta^{34}S$ and $\delta^{13}C$, Kirkland and Evans (1976) concluded that the occurrence of evaporite calcitization within the Delaware Basin was the result of BSR. Their $\delta^{34}S$ (CDT) values for anhydrite in the Castile Formation range from +9.6 ‰ to +11.5 ‰, while their $\delta^{34}S$ (CDT) values for native sulfur range from -15.1 ‰ to +9.2 ‰. Although the native sulfur values show a wider range of variability in $\delta^{34}S$ (CDT) values, samples were consistently depleted with respect to the anhydrite of the Castile Formation. They suggest this is consistent with normal variability in sulfate reducing bacteria processes (Kirkland and Evans 1976). Their $\delta^{13}C$ (PDB) values for depositional calcite laminae within the Castile Formation range from +5.0 ‰ to +6.7 ‰, which is consistent with marine deposition, while their $\delta^{13}C$ (PDB) values for calcitized evaporites range from -3.1 ‰ to -29.2 ‰ (mean is -23.5 ‰), which shows significant $\delta^{13}C$ depletion. This $\delta^{13}C$ depletion was attributed to ascending hydrocarbons, most likely methane, from the Bell Canyon and other formations of the Delaware Mountain Group. Therefore, Kirkland and Evans (1976) concluded that the limestone buttes of the Castile Formation were the byproduct of BSR in the presence of ascending methane.

Although, Kirkland and Evans (1976) suggest that calcitization in the Castile Formation is the result of BSR, their isotope data does not provide unequivocal proof. The observed $\delta^{34}S$ and $\delta^{13}C$ patterns could also result from TSR, although this is generally ruled out because evaporite rocks have not been buried to sufficient depths within the Delaware Basin to have induced TSR under normal geothermal gradients. However, Tertiary igneous dikes (Calzia and Hiss 1978) have been documented within the northern Delaware Basin which suggests significantly higher geothermal gradients in the past, but calcitized occurrences occur throughout the entire western portion of the Castile outcrop area. Some occurrences of secondary selenite have also been attributed to hydrothermal origins (Lock et al. 2004), which frequently crop out over several hundred square meters proximal to calcitized masses forming bodies that appear comparable in size to the more resistant limestone buttes (Stafford et al. 2008b). Although, Tertiary dikes are limited to the northwestern margin of the study area, Barker and Pawlewicz (1987) report that geothermal gradients within the entire region were as high as 40-50°C/km during the late Oligocene to middle Miocene during the initiation of Basin and Range extension, which is significantly above the lower temperatures limits where TSR is thermodynamically possible (Worden and Smalley 1996).

Native sulfur bodies are commonly associated with calcitized masses within the Ochoan (Lopingian) evaporites of the western Delaware Basin. Sulfur deposits are formed as either vug-fillings within calcitized masses or within breccias (e.g. breccia pipes and blanket breccias) primarily in the Castile and Salado Formations (Wessel and Wimberly 1992). Of these ore bodies, all have been associated with ascending fluid processes and calcitization, while several have been economically mined through Frasch processes where sulfur is extracted through the injection of super-heated waters, which melt sulfur so that it can be pumped to the surface. Major sulfur deposits within the Castile Formation include the Culberson Ore Body, the Pokorny Sulfur Deposit, and Phillips Ranch Sulfur Deposit (Fig. 2B) (Wessel and Wimberly 1992). The Culberson Ore Body is the largest sulfur ore body documented within the Delaware Basin with sulfur occurring as crystals that line or fill vugs and fractures (Wallace and Crawford 1992). Most of the Culberson Ore Body is developed in the Salado Formation within solutional breccias developed along high-angle faults (Fig. 4), which contain clasts of the Permian Rustler and Cretaceous Cox Formations and is associated with calcitization within the Salado and underlying Castile Formations (Wallace and Crawford 1992). Lee and Williams (2000) modeled hydrocarbon migration and ore genesis associated with Culberson County Ore Body and showed that the paleohydrogeology associated with sulfur mineralization and calcitization was a mixed hydrologic system dominated by basinal fluids derived from the Bell Canyon Formation and meteoric fluids migrating down gradient through the Cherry Canyon Formation (Fig. 5).

The Pokorny Sulfur Deposit (Fig. 2B) is completely developed within the Castile Formation within a calcitized mass, which is largely developed along three horizontal zones of brecciation (e.g. blanket breccias formed by halite dissolution and collapse) and bounded on the margins by high angle faults (Klemmick 1992). As with the Pokorny Sulfur Deposit, the Phillips Ranch Sulfur Deposit is developed entirely in the Castile Formation; however, the Phillips Ranch Sulfur Deposit (Fig. 2B) occurs directly above the

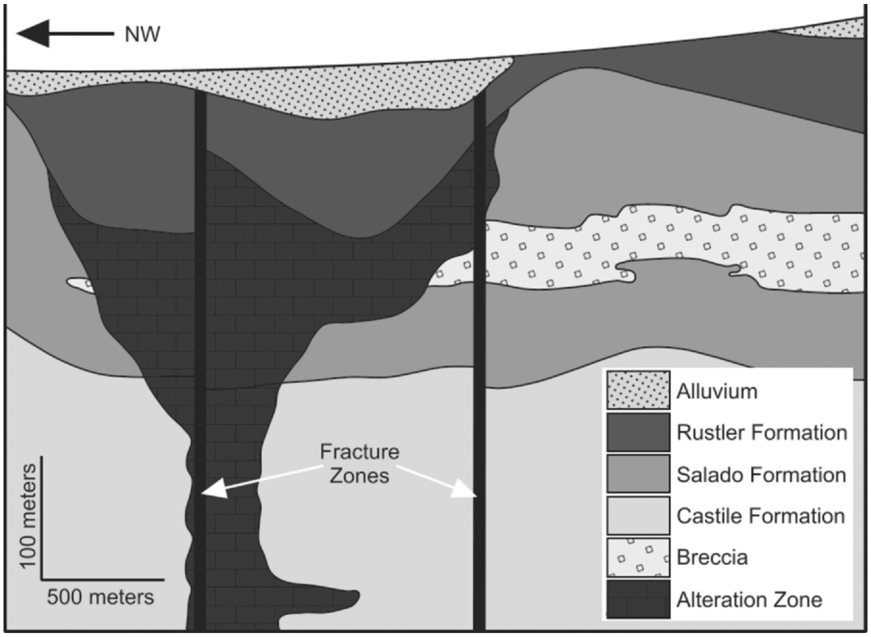

Figure 4. Simplified schematic diagram of the Culberson Ore Body showing the configuration of the "Alteration Zone", which contains native sulfur within calcitized evaporites (adapted from Wallace and Crawford 1992). Note the relationships between the "Alteration Zone", fracture zone, intrastratal breccia and different strata.

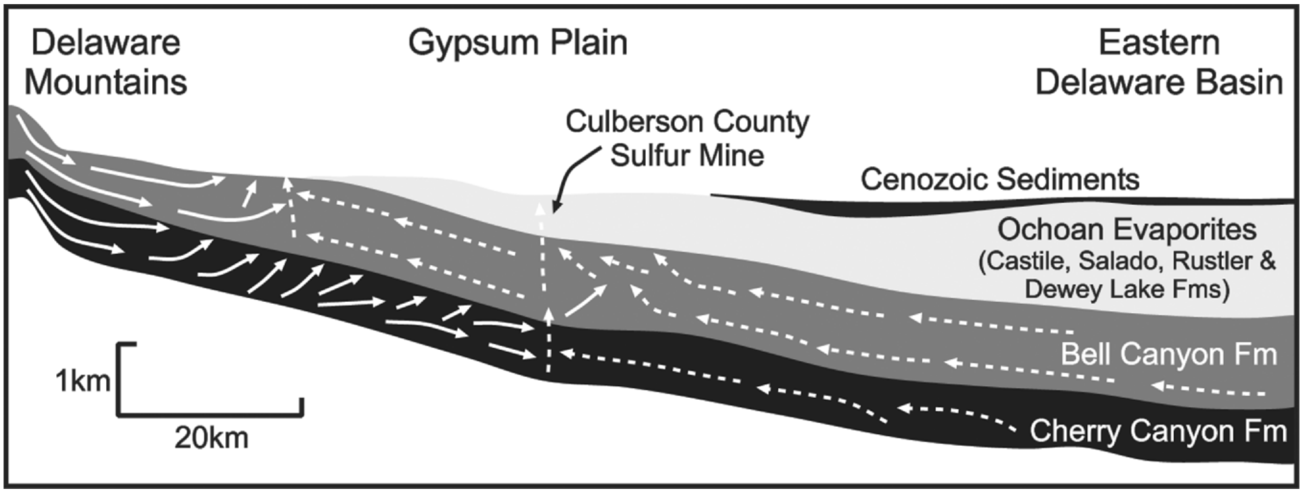

Figure 5. Simplified paleohydrology associated with calcitization and sulfur deposition of the Culberson County Ore Body. Solid arrows indicate flow paths of meteoric waters originating as groundwater recharge in the Delaware Mountains Paleohydrology. Dashed arrows indicate flow paths of basinal waters and associated hydrocarbons (adapted from Lee and Williams 2000).

Bell Canyon Formation along the contact with the Castile Formation in association with calcitization (Guilinger and Nestlerode 1992). Although not economically mined using Frasch processes, numerous exploration pits have been mined throughout the Castile outcrop area, some dating back to the late 19th century (e.g. China Mine, aka Hydrogenated Sulfur Mine) (Hill 1996). All occurrences of native sulfur within the Castile and Salado Formations have been associated with calcitization that occurred along solutionally enhanced transmissive zones (Wessel and Wimberly 1992), suggesting that hypogene speleogenesis is directly involved in sulfur mineralization, which has been validated by modeling of paleohydrology (Lee and Williams 2000).

Although, Kirkland and Evans (1976) reported evaporite calcitization within the Castile and Salado Formation, all of the calcitized masses that they documented occur within the outcrop area of the Castile Formation (Fig. 2B). Calcitization has been documented in the subsurface in the Salado Formation associated with native sulfur deposits (Wallace and Crawford 1992). Kirkland and Evans (1976) speculated on surficial exposure of Salado calcitization based on their limestone butte number 3, which did not exhibit laminated fabric. However, massive, sucrosic gypsum is common in the Castile Formation as a result of diagenetic alteration or depositional soft-sediment deformation (Dean et al. 1975); therefore, calcitized rocks of the Castile Formation do not have to show preserved laminations. No unequivocal evidence of surface exposures of calcitized Salado evaporites have been documented, and all surficial limestone buttes reported by previous studies occur within the Castile outcrop region; therefore, this study focuses on calcitization of Castile evaporites within the outcrop region. The surficial expression of limestone buttes within the Castile outcrop region is used as a proxy for evaluating the spatial distribution of calcitization processes.

CALCITIZATION OCCURRENCES IN THE CASTILE FORMATION

In order to evaluate the spatial distribution and occurrence of evaporite calcitization, a coupled field and GIS (Geographic Information System) based approach was undertaken as part of a larger study investigating speleogenesis and sulfate diagenesis within the Castile Formation. Fifty randomly selected, 1-km^2 regions where physically mapped within the Castile outcrop region using GPS navigation to conduct traverse line surveys at 100-meter spaced intervals within each individual 1-km^2 survey region (Fig. 2B). Field mapping included GPS locations and field sketching, including characterization of individual karst features, geologic features and geomorphic surfaces (Stafford et al. 2008c). Based on field mapping, digital air photos (DOQs - digital orthophoto quads) with a pixel resolution of one-meter were visually evaluated for the entire ~1,800 km^2 Castile outcrop region. Calcitized areas were identified based on their geomorphic expression, including topographic relief, low reflectance and lack of gypsofile vegetation, as compared with features physically documented during field mapping. A total of 1020 individual calcitized occurrences were documented (Fig. 6A), with an average surface area exposure of 2,296 m^2. Field checks of more than 100 individual calcitized occurrences identified through GIS analyses confirmed the techniques validity. Because of the one-meter resolution of air photos, only regions covering an area greater than one meter wide and more than ten square meters in total area were identifiable. This includes most exposed calcitized masses and calcitized sheets at least 30 centimeters thick, which become exposed as low relief

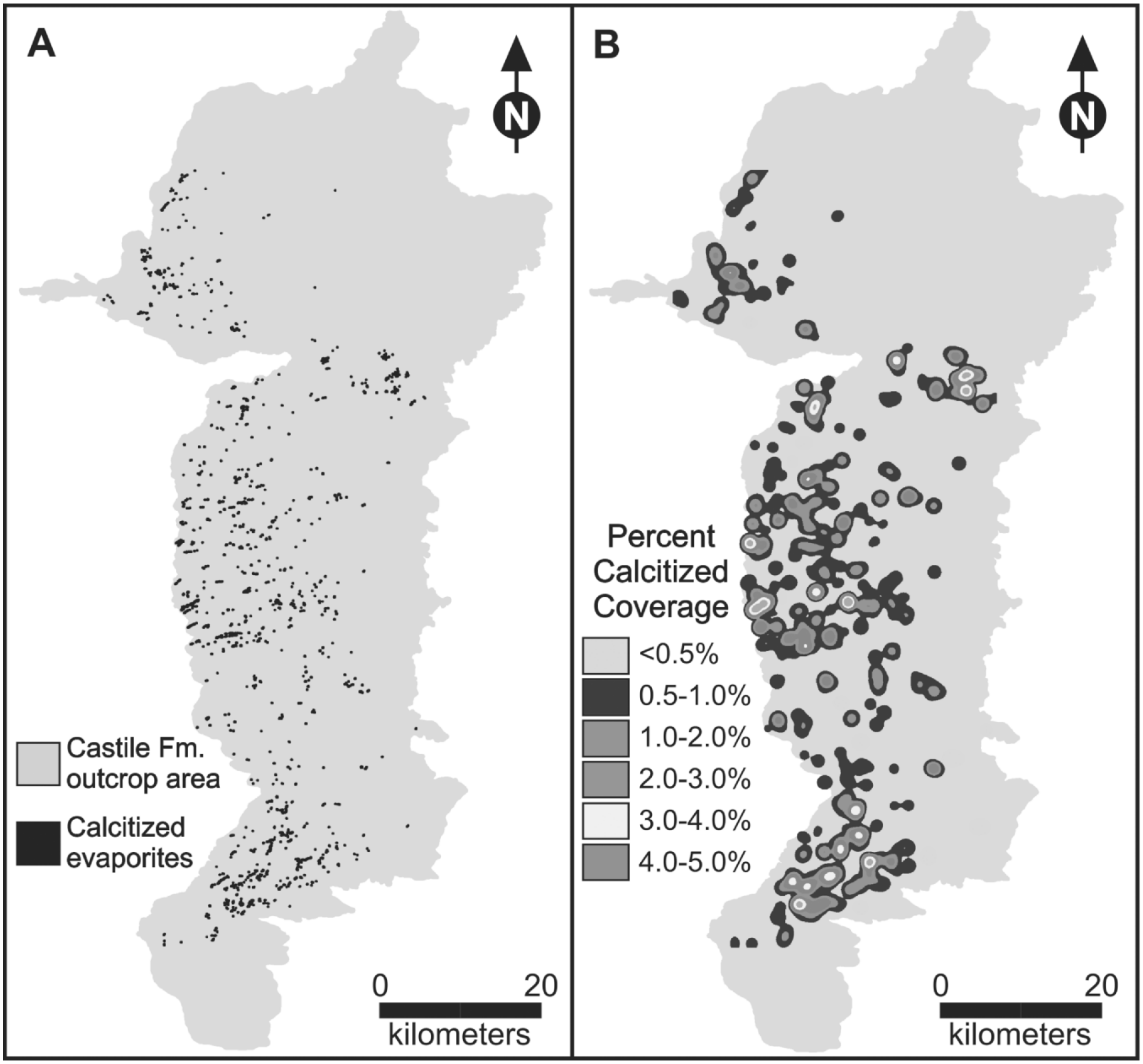

Figure 6. Distribution of calcitization within the Castile outcrop region (grey). A) Spatial distribution of occurrences of calcitization (black) identified through couple field mapping and GIS analyses of DOQs; B) Spatial analyses of calcitized occurrences showing clustered distribution of calcitization as a function of outcrop coverage. GIS analyses performed using ArcGIS 9.2.

ridges more than one meter wide, due to the gentle regional dip.

GIS analyses clearly show that calcitization is widespread in the western portion of the Castile outcrop area with a general decrease in calcitization abundance in the northern portion of the study area (Fig. 6A). The extreme northern and southern portions of the study area are effectively devoid of calcitization, while minor regions of calcitization occur scattered throughout the eastern portion of the Castile outcrop area. Spatial analyses of calcitization coverage throughout the study area indicate that the overall pattern of calcitization is highly clustered (Fig. 6B). Local calcitized occurrences are generally developed along linear trends oriented primarily at ~N70°E and ~N15°W; however, secondary linear trends of calcitization occur along orientations of ~N25°E, ~N55°E and ~N40°W (Fig. 6A). The linear trends of calcitization indicate mineral alteration along fractures within the Castile Formation (Hentz and Henry 1989), while the clustered nature of calcitization suggests focused diagenetic alteration within specific regions.

Based on field mapping, calcitized evaporites within the Castile outcrop area occur primarily in two distinct forms: 1) massive limestone buttes or "castiles" (Fig. 7) and 2) laterally extensive limestone sheets (Fig. 8). Lithologic fabric associated with calcitization can vary significantly. Most commonly, calcitization results in little fabric alteration, such that original fabrics (Fig. 3A), usually laminated but also massive and nodular fabrics, are preserved (Fig. 3B). Original fabric is often highly distorted where calcitized

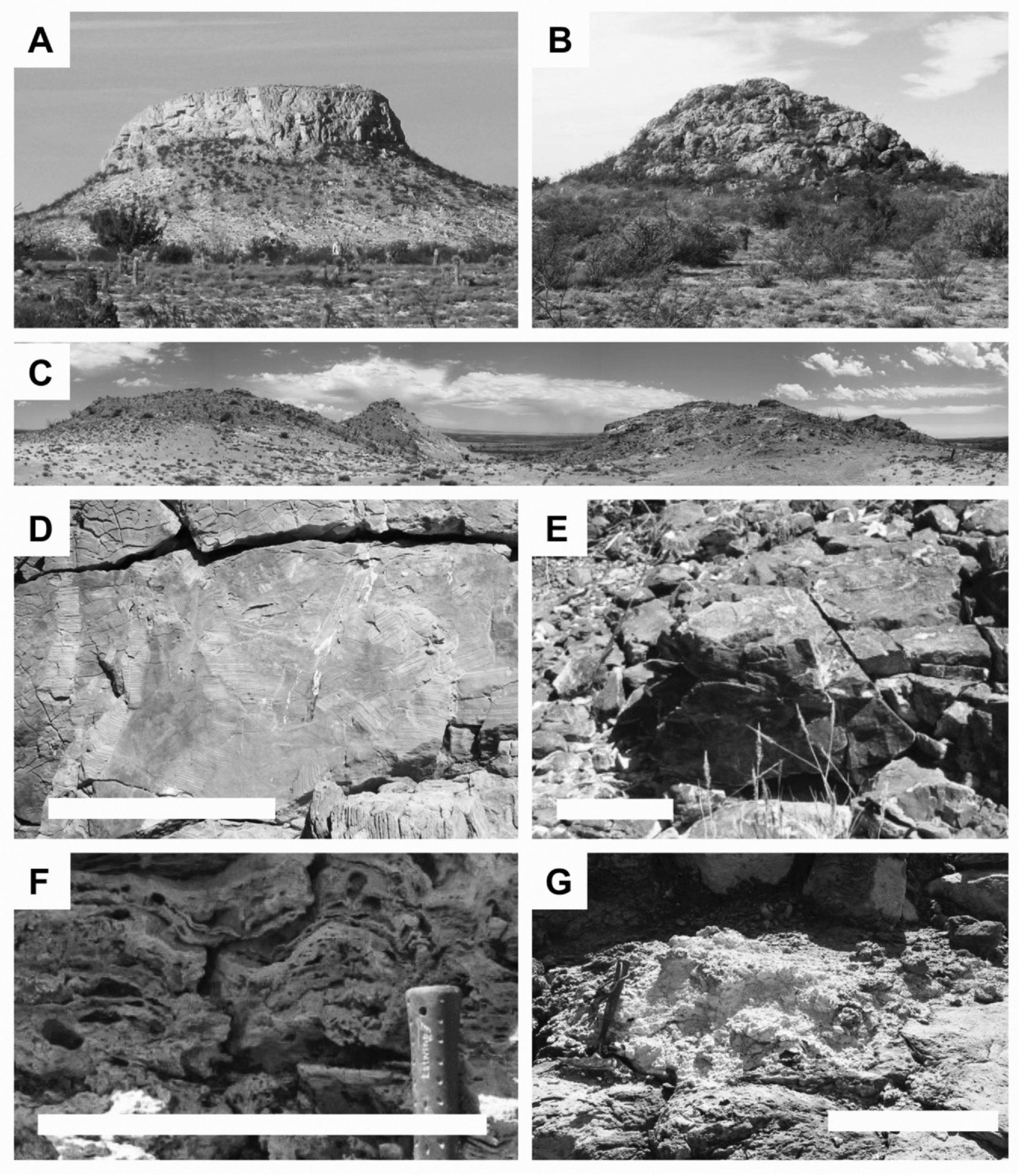

Figure 7. Calcitized masses and limestone buttes within the study area in Culberson County, Texas. White scale bars are ~25 cm long. A) large limestone butte ~40 m tall (note person in foreground for scale); B) typical limestone butte ~10 m tall (note person for scale); C) cluster of limestone buttes including three distinct calcitized masses that are ~20 m tall; D) typical brecciated core of calcitized masses; E) typical calcitization with preservation of original laminae distal to calcitized masses; F) typical calcitization with vuggy porosity proximal to calcitized masses; G) typical active vent and secondary gypsum powder associated with calcitized masses actively degassing hydrogen sulfide.

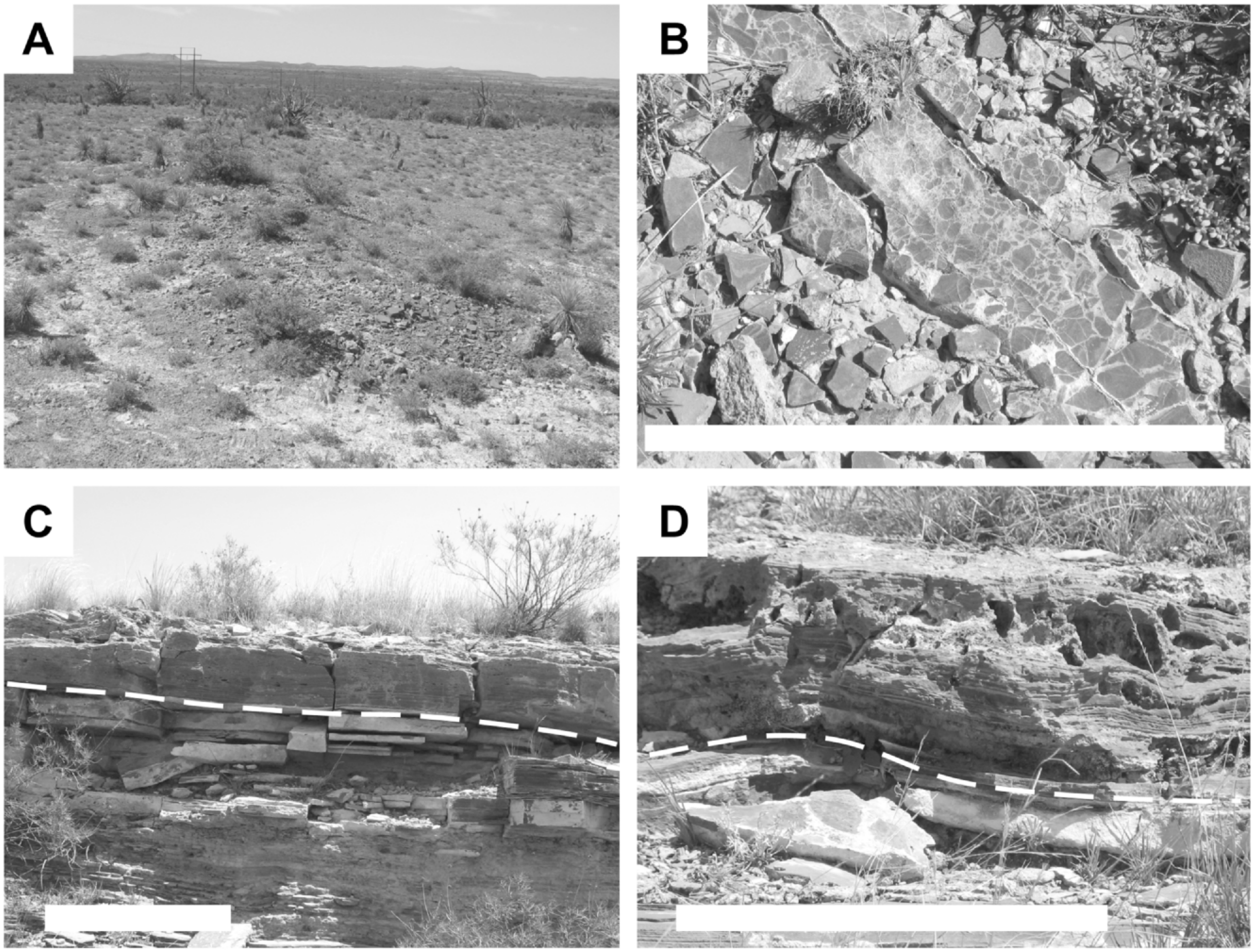

Figure 8. Calcitized sheets within the study area in Culberson County, Texas. White scale bars are ~0.5 m long. A) linear ridge of calcitization where calcitized sheet dips into the subsurface; B) central brecciated core of calcitized sheet; C) calcitization of immediately above the Bell Canyon, Castile Formation contact (dashed line delineates contact); D) vuggy porosity and laminae distortion of calcitization at Bell Canyon / Castile Formation contact (dashed line delineates contact).

masses have developed extensive vuggy-like porosity, such that laminations are observable but highly distorted (Fig. 3D). In addition to surface exposures, numerous calcitized zones have been identified within caves in the area (Fig. 9). In some cases, calcitization boundaries have been preserved between the calcitized and uncalcitized rocks showing direct lateral relationships.

Massive limestone buttes occur throughout the Castile outcrop region forming resistant topographic highs up to 40 meters higher than surrounding topography (Fig. 7A), although commonly less than 10 meters (Fig. 7B). Surficial expression of individual limestone buttes ranges from a few square meters (minimum documented coverage of 36 m^2) to several tens of thousands of square meters (maximum documented coverage of 40,687 m^2). They frequently occur in groups of several limestone buttes (Fig. 7C), either clusters covering several square kilometers or linear trends up to ten kilometers long, suggesting concentrated migration of hydrocarbons through these regions. Most individual limestone buttes contain a central core of highly brecciated calcitization (Fig. 7D), but the periphery usually shows little alteration of original fabric beyond mineral replacement (Fig. 3B; 7E). Occasionally, limestone buttes also contain a highly porous intermediate zone (Fig. 3D; 7F) between the breccia core and the largely unaltered periphery fabrics. The highly porous zone commonly shows evidence of original laminations, but laminae are highly distorted with abundant vuggy (Fig. 7F) to cavernous porosity (Fig. 9A), up to several hundred cubic meters in size. Several limestone buttes continue to actively degas hydrogen sulfide based on odor and the presence of highly porous, secondary gypsum precipitates at vent areas (Fig. 7G). This suggests that calcitization processes are still occurring in the subsurface or residual hydrogen sulfide from previous calcitization episodes has been trapped within the Castile Formation and is now degassing as surficial denudation provides preferential flow paths for releasing trapped gas

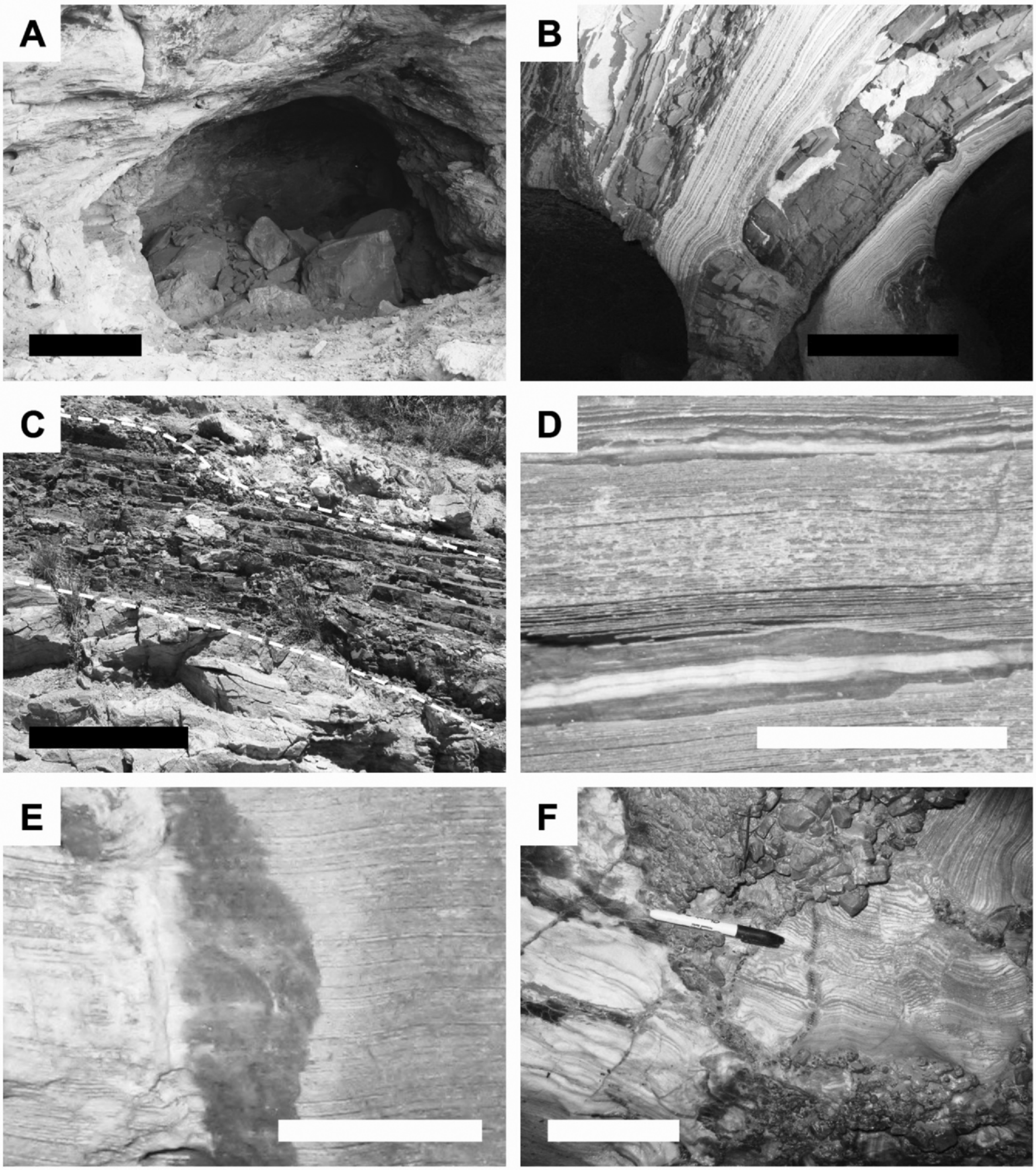

Figure 9. Calcitization associated with karst development within the study area in Culberson County, Texas. Black scale bars are ~1 m long. White scale bars are ~10 cm long. A) elliptical cave developed entirely within a calcitized mass; B) solutional cave passage containing calcitized sheets developed within folds; C) limestone sheet (bounded by dashed lines) dissected by solution entrenchment of karst arroyo; D) parallel contact between calcitization and original gypsum (white) showing alteration zone; E) perpendicular contact between calcitization (right side) and original gypsum (left side) showing alteration zone; F) acute angular contacts between calcitized breccia and laminated gypsum (white).

(Lock et al. 2004). Many of these degassing limestone buttes have been continually producing hydrogen sulfide for at least a century (Richardson 1905).

Laterally extensive limestone sheets are common throughout the study area, but generally occur within a 1-2 km radius of limestone buttes, suggesting that they are genetically related. Limestone sheets are generally decimeters thick, but have been observed up to 2 m thick. They commonly outcrop over large areas as residual clasts coating the ground surface (Fig. 8A) where overlying and underlying gypsum have been removed by dissolution; however, intact sheets are observed where calcitized zones dip into the subsurface, often forming linear or sinuous features that can be observed on aerial photos when they are at least 30 centimeters thick and several meters long. Usually, limestone sheets contain a central zone of brecciated material (Fig. 3C; 8B), such that the brecciated region and several decimeters above and below this zone are calcitized. Calcitized sheets have been identified at the base of the Castile Formation at the contact with the underlying Bell Canyon Formation (Fig. 8C). Although the Castile Formation has been traditionally characterized as having a depositional basal carbonate unit (Anderson et al. 1972), field observations at the contact suggest that this basal zone may actually be the result of calcitization. These calcitized regions are laminated, contain vuggy porosity (Fig. 8D) similar to that observed in many limestone buttes (Fig. 7D) and contain significant levels of hydrocarbons as evidenced by a strong fetid odor, while native sulfur deposits associated with calcitization have been mined at the Bell Canyon / Castile contact (Guilinger and Nestlerode 1992).

Calcitization associated with cave and karst development is widespread within the Castile Formation, suggesting that the two are genetically related; however, many caves were formed subsequent to actual calcitization. Dense clusters of caves are commonly found proximal to limestone buttes, with complete or partial solutional development within calcitized zones (Stafford et al. 2008b). Caves developed entirely in limestone buttes form small elliptical chambers (Fig. 9A) that are effectively large-scale vugs. Within many sinkholes and associated caves, thin, centimeter- to meter-thick lenses of calcitization are abundant, which are bisected by solutional cave passages (Fig. 9B) or incised karst arroyos (Fig. 9C). Portions of some larger caves are completely developed in limestone sheets, such that different levels of the caves are developed in alternating zones of gypsum and calcitized sulfate. Although caves intersecting the calcitized zones show similar textural patterns as surficial exposures, contact boundaries between original gypsum and calcitized zones are often preserved in passage walls. Preserved diagenetic boundaries include boundaries that are both parallel (Fig. 9D) and perpendicular (Fig. 9E) to laminations, as well as boundaries that cross laminae at acute angles (Fig. 9F). Commonly, these boundaries include a transitional zone of alteration averaging 1 cm wide (Fig. 9D,E). Kirkland and Evans (1976) noted no transitional boundaries between calcium sulfate and calcitization in the Castile Formation and suggested that a transitional zone did not exist. This may be due to the fact that they looked only at surface exposures and the transition zones have only been observed in caves where better preservation occurs. The 1020 identified occurrences of calcitization within the Castile outcrop region are highly clustered (Fig. 6B), although forming linear trends (Fig. 6A), with the greatest abundance of calcitization occurring along the western edge of the study area. The only major exception to this pattern is a dense cluster of calcitization that occurs along US HWY 652 in northern Culberson County, Texas, where limestone buttes are present on the eastern margin of the study area; however, these occurrences are also located along the axis of the structural high formed by the Nine-Mile Anticline (Fig. 2B) (Hill 1996). Because the regional dip of the Castile Formation and underlying Permian units is to the east-northeast, surficial denudation is greatest on the western edge of the Castile outcrop region and along the Nine-Mile Anticline where the base of the Castile Formation is at a higher elevation than in the northern and southern portions of the study area. The distribution of surficial exposures of calcitization is coincident with the degree of surficial denudation of the Castile Formation, indicating that calcitization is most intense proximal to the contact with the underlying Bell Canyon Formation, which has been proposed as the transmissive source region through which hydrocarbons were delivered to the Castile Formation.

SPELEOGENESIS IN THE DELAWARE BASIN

Speleogenesis has been traditionally associated with caves and karst; however, speleogenesis is not limited to the development of cavernous porosity. Instead, speleogenesis is simply part of the genetic evolution of soluble rocks, where void space ranging from sub-millimeter intragranular porosity to vuggy and cavernous porosity is created by dissolution, which may be subsequently filled by secondary deposits. Speleogenesis occurs in three basic diagenetic settings, based on the characteristics of the soluble fluids: 1) coastal, 2) epigene, and 3) hypogene (e.g. Ford and Williams 2007; White 1988). However, geologic systems are constantly evolving through time such that multiple episodes of different types of speleogenesis may occur within any system (e.g. Klimchouk et al. 2000).

Coastal speleogenesis is largely associated with the interaction of fresh and marine waters in coastal and island settings (Mylroie and Carew 1995). At the top of the fresh-water lens, dissolution is enhanced by the decay of organics, while at the margin and base of the fresh-water lens, dissolution is enhanced by the mixing of fresh and saline waters (Back et al. 1984). Epigene speleogenesis occurs in unconfined settings and is directly associated with meteoric precipitation (Palmer 1991). Dissolution is driven by gravity in the unsaturated, vadose zone and by hydraulic potential in the saturated, phreatic zone. Epigene secondary deposits may form either subaerially in the vadose zone, most commonly due to variations in void microclimate, or subaqueously in the phreatic zone, generally associated with changes in water chemistry (Ford and Williams 2007).

Hypogene speleogenesis occurs where dissolution is driven by a mixed hydrologic flow system, including significant components of both free and forced convection (Klimchouk 2007), where soluble fluids are delivered from underlying or adjacent transmissive zones. Hypogene systems do not form direct connections with surface process, but instead are associated with regional and basin-scale fluid movement where waters are delivered from deep sources or distal meteoric recharge areas. Hypogene speleogenesis is most commonly associated with hydrothermal or sulfuric acid systems, but in a broader context includes most geologic systems where fluids originating from lower depths or distal margins migrate vertically and laterally through overlying or adjacent soluble rocks, often not only forming complex solution features but also extensive, economic secondary mineral deposits (e.g. Mississippi Valley Type deposits) (Ford and Williams 2007).

In the greater Delaware Basin, hypogene processes appear to dominate the speleogenetic evolution of the area (e.g. Klimchouk 2007; Palmer 2006; Stafford et al. 2008a,b,c). The famous caves of the Guadalupe Mountains (Fig. 2A) (e.g. Carlsbad Cavern, Lechuguilla Cave) are developed in the Guadalupian forereef, reef (Capitan Formation) and near-backreef facies (Artesia Group). These massive caves and the extensive associated cavernous porosity in the Guadalupe Mountains, has been attributed to sulfuric acid dissolution, where rising anoxic fluids saturated with hydrogen sulfide mixed with shallower oxic fluids to produce aggressive, sulfuric acid-rich waters (Hill 1990; Palmer 2006). In the Guadalupian backreef facies (Artesia Group), numerous hypogene caves occur where fluids rise through interbedded carbonate and evaporite rocks (e.g. Bottomless Lakes) (Fig. 2A) (Land 2006). Because the rising fluids originate from lower carbonate aquifers, they are likely undersaturated with respect to calcium sulfate, such that significant dissolution occurs as fluids pass into gypsum/anhydrite interbeds. As a result, complex, three-dimensional, maze caves have formed within the interbedded evaporite sequences of the Artesia Group (e.g. Coffee Cave) (Fig. 2A; Stafford et al. 2008a). Within the Delaware Basin, numerous breccia pipes, subsidence troughs (Fig. 2A) and blanket breccias have been described in association with rising fluids through the Ochoan (Lopingian), basin-filling, evaporite sequences (e.g. Anderson et al. 1978; Bachman 1984). Anderson and Kirkland (1980) attributed the large, vertical breccia pipes to brine density convection, where fluids originating from lower carbonate units rose through overlying evaporite units. As the less dense, undersaturated water rose and dissolved overlying evaporitic beds, the resulting saturated / denser fluids simultaneously sank back to the lower carbonate aquifer, such that aggressive waters were continuously delivered to the upper solution front. With increasing void size, eventually ceiling collapse began stoping towards the surface such that large breccia columns were formed (Anderson and Kirkland 1980). Similarly, solution troughs and extensive blanket breccias have been described within these same Ochoan (Lopingian) rocks, where laterally migrating fluids dissolved halite interbeds, leaving behind residual blanket breccias from the simultaneous collapse of overlying beds (Anderson et al. 1978). Numerous examples of the dominance of hypogene speleogenesis occur throughout the greater Delaware Basin region, although the specific composition of the fluids and host rocks may differ.

Within the Castile outcrop region, evidence of both epigene and hypogene speleogenetic processes is extensive (Stafford 2006; Stafford et al. 2008b). Widespread epigene karst and caves occur within the study area in relation to modern surficial processes (Bachman 1980). However, hypogene processes appear to dominate the speleogenetic evolution of the Castile Formation (Stafford et al. 2008b). Recent work (Stafford et al. 2008c) has shown that cave development within the Castile Formation is highly clustered, suggesting that speleogenetic origin is largely associated with rising fluids, while surface expression is simply the result of breaching. Hence, more intense clustering of caves occurs along the western side of the Castile outcrop area similar to the patterns seen in calcitization distribution (Fig. 6B). Here, tectonic deformation, including basin tilting and fracturing, is most intense and surface denudation has been the most extensive, such that the lower strata of the Castile Formation which are proximal to the transmissive beds of the Bell Canyon Formation are exposed in outcrop (Fig. 5).

Additionally, morphometric features (i.e. inlet risers, wall channels, ceiling half tubes and outlet cupolas) present within many of the clustered caves provide unequivocal evidence of dissolution driven by mixed convection from rising fluids (Stafford et al. 2008b). Within the study area and throughout the Delaware Basin, breccia pipes and blanket breccias have been documented within the Castile Formation adding greater credence to the importance of hypogene processes within Castile evaporites.

DISCUSSION AND CONCLUSIONS

Evaporite calcitization within the Delaware Basin and specifically within the Castile Formation is far more extensive and widespread than was originally recognized by Adams (1944) and Kirkland and Evans (1976). Analyses of the occurrence and distribution of calcitization in the Castile outcrop area has identified numerous previously undocumented limestone buttes, as well as identification of the abundant occurrence of previously undocumented limestone sheets. Calcitization is most intense in the western portion of the study area where surface denudation has removed a greater portion of the upper Castile Formation and other overlying Ochoan (Lopingian) evaporites. Field observations of the Castile/Bell Canyon contact indicate extensive calcitization at the base of the Castile Formation. Numerous clusters of hypogene caves and masses of selenite are commonly associated with the clustering of surficial exposures of calcitization within the study area. These clustered associations indicate that ascending hypogene fluids have dominated the diagenetic evolution of the Castile Formation, which is supported by paleohydrology modeling within the Delaware Basin (Fig. 5) (Lee and Williams 2000). While the exact mechanism of sulfate reduction associated with calcitization in the Castile Formation remains unclear, ascending waters and hydrocarbons is consistent with most diagenetic patterns observed within the study area, suggesting that hypogene processes dominate the region.

This study, coupled with previous research on karst (Stafford et al. 2008b,c), native sulfur deposits (e.g. Wallace and Crawford 1992; Davis and Kirkland 1970) and limestone buttes (e.g. Kirkland and Evans 1976; Lock et al. 2004) within the Castile Formation indicates that calcitization within the Ochoan (Lopingian) evaporites of the Delaware Basin represents part of a complex speleogenetic evolution in the region. Ascending fluids established initial flow paths largely along fractures and bedding planes, through solution and brecciation (e.g. breccia pipes and blanket breccias). Because most calcitized masses and sheets contain central breccia zones, these initial transmissive flow paths established by ascending fluids were subsequently or simultaneously used by ascending hydrocarbons. Ascending hydrocarbons fueled sulfate reduction, resulting in calcite replacement of original calcium sulfate deposits along with the production of hydrogen sulfide. Calcitized rocks that show little original fabric alteration were likely well-connected to adjacent transmissive zones, such that hydrogen sulfide byproducts could be removed from the system easily. Calcitized rocks that show significant fabric alteration (i.e. laminae distortion and extensive vuggy porosity) were likely zones of enhanced mixing between hydrocarbon-rich and hydrogen sulfide-rich waters with associated higher flow rates. Hydrogen sulfide that did not completely escape the system was oxidized into native sulfur in many instances, which formed economic mineral deposits associated with calcitized masses. Although the origins of large selenite masses is still unclear, it is reasonable to assume that some selenite masses are the result of further oxidation of native sulfur, while others may be the result of ascending hydrothermal fluids or simply the solution and reprecipitation of original gypsum.

The widespread distribution of calcitization within the Castile Formation indicates that hypogene speleogenesis has significantly affected the diagenetic evolution of the region. Much of the hydrogen sulfide produced during calcitization appears to have been partially oxidized to native sulfur or oxidized to sulfuric acid, that subsequently converted limestone to secondary gypsum (selenite) within the region. Current theories on the origin of hypogene caves of the Guadalupe Mountains attribute calcitization within the Castile Formation as the source of the hydrogen sulfide that produced the sulfuric acid waters involved in speleogenesis (Hill 1990, 1987). However, minimal calcitization in the Castile Formation occurs proximal to the Guadalupe Mountains, instead most calcitization occurs farther to the south in northern Culberson County, Texas. This distribution of calcitization suggests that the diagenetic hydrogen sulfide of the Castile Formation is not likely the primary source of solutionally aggressive fluids for hypogenic, sulfuric acid speleogenesis in the Guadalupe Mountains. Future research needs to evaluate other possible sources of hydrogen sulfide generation in the greater Delaware Basin region or demonstrate geologically feasible mechanisms for delivering hydrogen sulfide from the known calcitized regions of the Castile Formation to the Guadalupe Mountains. Evaporite units of the backreef facies associated with either the Capitan or Victorio Peak reef masses appear to be more probable source areas for hydrogen sulfide associated with Guadalupe Mountain karst development (DuChene and Cunningham 2006; Queen 1994).

Calcitization within the Castile Formation is far more extensive and diverse than originally recognized. Research is currently being conducted to better constrain the geochemical relationships between evaporite calcitization, native sulfur, selenite bodies and hypogenic karst within the Castile Formation through isotopic and petrographic studies of closely related field occurrences. Detailed studies are being conducted on the transitional boundaries observed within caves, which will hopefully provide significant insight into the diagenetic alterations associated with calcitized evaporites, native sulfur and selenite within the Castile Formation.

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