Petrographic and isotopic evidence for late-stage processes in sulfuric acid caves of the Guadalupe Mountains, New Mexico, USA

Margaret V. Palmer¹* and Arthur N. Palmer²

Abstract:

Palmer M.V. and Palmer A.N. 2012. Petrographic and isotopic evidence for late-stage processes in sulfuric acid caves of the Guadalupe Mountains, New Mexico, USA. International Journal of Speleology, 41(2), 231-250. Tampa, FL (USA). ISSN 0392-6672. http://dx.doi.org/10.5038/1827-806X.41.2.10

Caves of the Guadalupe Mountains have experienced many modifications since their final phase of sulfuric acid speleogenesis several million years ago. Petrographic and geochemical data reveal details of the change from H₂SO₄ to CO₂-dominated reactions. The H₂SO₄ dissolution front acquired a coating of replacement gypsum with local pockets of anhydrite and by-products of altered clay, including Fe-Mn oxides. Alteration of bedrock beneath the gypsum produced a white micritized rind with small negative shifts in δ¹³C and δ¹⁸O. Solution basins contain records of the earliest post-speleogenetic processes: corroded bedrock, residual anhydrite, Fe-Mn oxides from fluctuating pH and Eh, mammillary calcite, and dolomitization. Later meteoric water removed or recrystallized much of the gypsum and early micrite, and replaced some gypsum with calcite. Mammillary crusts demonstrate fluctuating groundwater, with calcite layers interrupted by films of Fe-Mn oxides precipitated during periodic inflow of anoxic water. Condensation moisture (from local evaporation) absorbs CO₂ from cave air, corroding earlier features and lowering their δ¹³C and δ¹⁸O. Drips of condensation water deposit minerals mainly by evaporation, which increases δ¹⁸O in the speleothems while δ¹³C remains nearly constant. By forcing calcite precipitation, evaporation raises the Mg content of remaining water and subsequent precipitates. Dolomite (both primary and replacive) is abundant. In areas of low air circulation, water on and within carbonate speleothems equilibrates with cave-air CO₂, causing minerals to recrystallize with glassy textures. Fluorite on young evaporative speleothems suggests a recent release of deep-source HF gas and absorption by droplets of condensation water.

Keywords: sulfuric acid caves; isotopes; petrography; dolomitization; condensation

Received 19 February 2012; Revised 17 April 2012; Accepted 19 April 2012

INTRODUCTION

Caves of sulfuric acid origin retain diagnostic minerals and features that allow reconstruction of their geochemical history (Polyak & Provencio, 2001). This paper centers on caves in the Guadalupe Mountains, New Mexico, specifically their latest transition from H₂SO₄ to CO₂-dominated processes. Petrographic data reveal details of the change from H₂SO₄ to CO₂ equilibria. Much cave research today yields paleoclimate data from meteoric speleothems (Fairchild & Baker, 2012). Instead, this paper emphasizes processes specific to the caves themselves. Such information can help identify former conditions in similar caves, and is useful for organizing future studies of geochronology and paleoclimate.

Literature on speleogenesis in the Guadalupes is extensive (e.g., Jagnow, 1979; Davis, 1980; Hill, 1987, 1996; Egemeier, 1987; Queen, 1994, 2009a; Polyak et al., 1998; Palmer & Palmer, 2000; Northup et al., 2000; DuChene & Cunningham, 2006). The caves have a complex history of Permian and Mesozoic paleokarst produced by freshwater-saltwater mixing, plus Miocene-Pliocene sulfuric acid speleogenesis driven by H₂S from reduction of sulfates by petroleum. Argon dating of alunite [KAl₃(SO₄)₂(OH)₆], a by-product of sulfuric acid alteration of clay, reveals four major periods of cave enlargement at different levels from 12 to 4 Ma (Polyak et al., 1998).

FIELD SITES

The Guadalupe Mountains form a high dissected plateau in semi-arid southeastern New Mexico and western Texas, USA (Fig. 1). They consist of Permian carbonates of the Capitan reef and correlative back-reef strata. The Delaware Basin to the southeast contains fore-reef carbonates capped by thick evaporites. The Guadalupes owe their height to late
Permian, Mesozoic, and late Cenozoic uplift. Basinal and back-reef strata are prolific petroleum reservoirs. Guadalupe caves typically have ramifying patterns of irregular rooms and mazes, and a combination of steeply ascending and semi-horizontal passages (Fig. 2). Many rooms and passages contain narrow floor fissures that descend tens of meters along fractures and pinch at depth. These appear to have been the main inlets for H$_2$S-rich water during speleogenesis.

Three caves in Carlsbad Caverns National Park were investigated (Fig. 2): Carlsbad Cavern has the largest rooms, a surveyed length of 44 km, and vertical range of 315 m. Lechuguilla Cave is more complex, with dense arrays of interconnecting passages on many levels, a surveyed length of 210 km, and vertical range of 489 m. The water table is reached in at least two places. Both Carlsbad and Lechuguilla are located mainly in reef and back-reef rocks. Spider Cave is located about midway between the two other caves in the back-reef Yates Formation, a silty dolomitic limestone. It contains 6 km of maze passages mostly concordant with the bedding, with a vertical range of 41 m.

Cueva de Villa Luz, Tabasco, Mexico, serves as an active analog. It is a sulfuric acid cave in Cretaceous limestone in a tropical rainforest (Hose et al., 2000). It consists of 2 km of low-gradient stream passages fed by at least 26 groundwater inlets too small to explore. They converge to a spring of 200–300 L sec$^{-1}$ at 28 °C, slightly above mean surface temperature. Most inlets are anoxic, with H$_2$S = 300–500 mg L$^{-1}$, pH = 6.3–7.1, P$\text{CO}_2$ up to 0.1 atm, and slight calcite undersaturation. Other inlets are oxygenated and calcite-saturated, with pH ~7.2. Bacterial filaments line stream floors – white filaments of sulfur-oxidizing bacteria (e.g., *Thiobacillus*) in anoxic water, and red filaments of iron bacteria in oxygen-rich waters. A crust of replacive gypsum lines the walls and ceilings. H$_2$S in the cave air has a recorded maximum of 210 ppm, and gas masks are required.

**FIELD AND LABORATORY PROCEDURES**

In the three Guadalupe caves, geologic profiles were constructed from the entrances to the deep points with a tripod-mounted Brunton compass and tape, to augment previous maps. The Carlsbad survey extended to Lake of the Clouds (altitude ~1007 m), perched several tens of meters above the water table. In Lechuguilla the survey extended through several main passages and to the local water table at ~962 m. A surface theodolite survey connected the entrances...
and tied to geologic contacts. Bedrock features and minerals were included in the cave mapping, and small naturally broken fragments were obtained for analysis under National Park Service permit. Petrographic relationships were determined from thin-sections, X-ray diffraction, and scanning electron microscopy with energy-dispersive spectroscopy (SEM-EDS). Past chemical reactions were interpreted from mineral associations and C-O isotopes (Fig. 3). Mineral stability fields otherwise unavailable were calculated from thermodynamic data listed by Faure (1998). Chemical equilibria were calculated with the software PHREEQC (U.S. Geological Survey).

No numerical dating was done during this phase of our study. Published speleothem dates show much scatter (e.g., Hill, 1987), with many ages beyond the limits of the dating techniques. Asmerom et al. (2007) used U-series dating and δ18O values of a stalagmite from Pink Panther Cave (~25 km SW of Carlsbad) to distinguish Holocene wet and dry periods. Relatively low δ18O correlates with greater rainfall and faster stalagmite growth (Fig. 3). The climate was relatively dry from 12 to 7 ka and wetter since. A record of δ18O and δ13C over the past 164 ky was obtained by Brook et al. (2006) by coring a stalagmite in the Green Lake Room of Carlsbad (Figs. 2 & 3). It shows five episodes of cold-wet climate separated by warm-dry intervals, with no calcite deposited during the driest intervals. The highest δ13C values (~140–150 ka) indicate CO2 degassing, probably during wet periods. δ18O values are near the present ideal for calcite deposited by meteoric infiltration (discussed in next section).

WATER CHEMISTRY AND ISOTOPIES

Water infiltrating into Guadalupe caves today has a typical PCO2 of ~0.01 atm at stalactite tips, which decreases rapidly in mid-air and equilibrates to ~0.003–0.0006 atm in pools (additional data in Hill, 1987; Forbes, 2000; Turin & Plummer, 2000; Gregg Oelker, Altadena, Calif., personal communication, 1990). Incoming water has a high Mg+Ca expected of carbonate bedrock and dry climate. In more than half the pools, precipitation of CaCO3 by evaporation and degassing has driven molar Mg/Ca above 1.0, to as much as 6.5. More than 80% of dripwaters and pools are supersaturated with both calcite and dolomite.

Carbonate samples used for this paper are described in Appendix 1. Their δ13C and δ18O values are shown in Fig. 3. In the Guadalupes, δ13C of CO2 is ~20 to ~25‰ VPDB in soil (varies with vegetation type) and about ~15‰ in cave air (Gonzáles & Lohmann, 1988). Typical δ18O for local cave water is ~7.9 ± 1.0‰ VSMOW in drips and ~6.9 ± 0.7‰ in pools, with δ13C and δ18O near the global meteoric trend (Ingraham et al., 1990); δ18O VSMOW = 1.03(δ18O VPDB) + 30.86 (Faure, 1998, p. 304). Equilibrium of cave CO2 with local bedrock should produce calcite with δ13C of about ~4.5 to ~7.2‰ VPDB (fractionation data from Deines et al., 1974). At the present 14–20 °C in Guadalupe caves, meteoric water should deposit calcite with δ18O about ~7 ± 0.6‰ δ18O VPDB (Friedman & O’Neil, 1977), and δ13C of dolomite should be ~2.5‰ greater than that of calcite (Zheng, 1999). Scattered data probably reflects wet-dry cycles, with wet conditions yielding more negative δ13C (Hoy & Gross, 1982). The cave deposits have isotopes compatible with modern conditions, so no great environmental change is likely since they formed.

The green inset in Fig. 3 shows the major variables that affect the isotopic ratios of carbonate cave deposits. The following trends are of most concern in this paper: As infiltrating meteoric water releases CO2 to the cave air, the escaping gas is enriched in 13C, which raises the δ13C in the remaining water and in subsequent carbonate deposits. In contrast, evaporation of cave water preferentially removes 18O, causing a negative δ18O shift in the vapor. This causes a positive δ18O shift in the remaining water and in evaporative carbonate deposits (i.e., a shift toward the right in Fig. 3). Sequences of carbonate deposits tend to show a sharp increase in δ18O as degassing takes place – this trend can be seen down flanks of stalagmites and across floors to pools. Evaporation also has an effect – generally over longer time, with deposits away from pools and fringes of speleothems showing greater effect. The combined effect is a steep positive slope,

Fig. 3. Carbon-oxygen isotopic ratios of carbonate samples. Arrows in green box show isotopic trends caused by: (a) CO2 degassing in cave, or low water/bedrock ratio of infiltrating water; (b) Degassing and evaporation; (c) Evaporation, low water temperature, or dry climate; (d) Equilibrium with low-CO2 cave air, high water/bedrock ratio, or oxidation of hydrocarbons; (e) Subaerial corrosion, precipitates from condensation water, or high water/bedrock ratio; (f) Wet climate or high water temperature. MS (yellow) = trend of meteoric-water speleothems with increasing CO2 loss and evaporation (additional data in Hill, 1987, and Gonzáles & Lohmann, 1988). Georgia Giant (blue) = stalagmite in Carlsbad Cavern, mean ±1 std dev (Brook et al., 2006). Bedrock data averaged from Hill (1987, 1996). See text for details.
gradually diminishing in slope. Speleothems deposited chiefly by evaporation show a rightward shift in Fig. 3 (toward increasing δ13C) but with little or no increase in δ18O from degassing. See Lohmann (1988) for details.

When water vapor condenses on solid surfaces, it inherits some of the low δ18O of the water vapor. Also, the condensate absorbs CO2 from the cave air, acquiring δ13C that is much lighter than that of carbonate bedrock and most speleothems. Therefore, resulting corrosion residues show diminished δ18O and δ13C relative to the original carbonates. Condensation water can deposit carbonate minerals only by evaporation, since it is already at equilibrium with cave CO2. The initial deposits from this water are depleted in both δ18O and δ13C relative to speleothems deposited from meteoric water. Subsequent evaporative deposits continue to increase in δ18O but have rather steady δ13C, causing a trend toward the right (c) in Fig. 3.

If the evaporated water condenses on cooler surfaces above, it absorbs CO2 from the cave air (low in δ13C) and dissolves some of the carbonate substrate. This, in combination with the relatively low δ18O from the water, causes isotopes in the weathered carbonates to trend toward the lower left (e) in Fig. 3. Precipitates formed in drip-water from the condensate also show this trend.

Upwelling groundwater from hypogenic sources has apparently not been active for at least the past half million years. Isotopic values for mammillaries that were deposited soon after the last influx of H2S-rich water show low δ13C values, but not significantly different from those of more recent deposits from condensation moisture in equilibrium with cave air.

**LATE-STAGE PROCESSES AND FEATURES IN GUADALUPE CAVES**

The following sections concern processes that have operated in the caves during and after the last major phase of sulfuric acid speleogenesis, over roughly the last 4 My. Features described here are most diagnostic of cave conditions. A few have not been described before. Those that are well known are mentioned only briefly, and many of secondary importance are omitted.

**Sulfuric Acid Dissolution**

Oxidation of H2S to sulfuric acid takes place only in aqueous solution, so cave enlargement is limited to sulfide-bearing groundwater and streams in contact with an oxygen source, and to films and droplets of moisture that absorb H2S and O2 from the cave air. Sulfuric acid is produced by the H2S + 2O2 reaction (usually with intermediate steps) and is accelerated by microbial processes (Engel, 2004). Acidic water in direct contact with carbonate rock is quickly buffered by release of bicarbonate ions, maintaining a pH of about 6.3–7.2, while a continued influx of H2S and O2 is required to sustain the reactions. Passage widening in the Guadalupe caves tends to be greatest at former surfaces of streams or pools, but domed cross sections suggest that the greatest volume of carbonate dissolution was subaerial. In the Frasassi Cave System of Italy, an active analog of Carlsbad, Galdenzi et al. (1997) show that H2SO4 dissolution by condensation moisture on aerated surfaces is at least as rapid as in sulfide-rich streams and lakes below.

As carbonate rock dissolves, concentrations of Ca2+ from the rock and SO42- from the acid often increase enough to precipitate replacive (“speleogenetic”) gypsum. Negative δ34S values in the gypsum of Guadalupe caves suggests a biogenic H2S source (Hill, 1987). Chemical modeling shows that gypsum replacement requires the consumption of >0.014 mol L⁻¹ of sulfuric acid by carbonate dissolution. This process is predominantly subaerial. For it to occur subaqueously the water must already be at or near gypsum
PCO₂ in the cave can enhance bedrock dissolution. In a closed system, with no CO₂ loss, approximately two moles of calcite are consumed for each mole of gypsum deposited, and because the molar volume of gypsum is almost exactly twice that of calcite (within 1%), a 1:1 volume ratio of gypsum to calcite is preserved. In well-aerated caves, however, much of the generated CO₂ is lost, and the solutional capacity of the water is diminished (Palmer, 1991). If so, the speleogenetic gypsum occupies more volume than the original bedrock and the original textures are disrupted. Gypsum replacement of dolomite in a closed system yields a volume increase of only ~15%, and some original bedrock textures can be preserved.

The contact between bedrock and replacive gypsum contains rounded hollows, typically about 5–10 cm in diameter, where dissolution has been most intense (Fig. 4B). In the actively dissolving walls of Villa Luz these hollows are lined by anhydrite needles (Fig. 6). Anhydrite becomes sparse outward from the bedrock contact and apparently alters to gypsum with time. Anhydrite normally requires temperatures above 65 °C or humidity below ~75% (Hardie, 1967), neither of which is present in Villa Luz. Instead, carbonate dissolution must sometimes be rapid enough to bring both anhydrite and gypsum to supersaturation, allowing them to co-precipitate. We have not yet found anhydrite or its pseudomorphs along former reaction fronts in the Guadalupes, but some floor deposits contain residual anhydrite crystals (see Basin Sediments).

Replacive gypsum can preserve bedrock textures and grain shapes (Figs. 5 & 7). Rapid H₂SO₄ dissolution of carbonate releases CO₂ gas, and the increased saturation. As gypsum crusts cover the bedrock, additional acid diffuses inward through the gypsum to sustain carbonate dissolution, while the crusts thicken. Crystallization of gypsum can force slivers of bedrock and insoluble residue from the wall, leaving them “floating” in the crust (i.e., with no contact between fragments, Fig. 4A). Gypsum blocks occasionally fall to the floor, exposing corroded bedrock. The blocks can coalesce into moist glacier-like masses in which the outlines of bedrock fragments are identifiable only by a difference in gypsum crystal size, or by scattered µm-size inclusions of carbonate or Fe oxide (Fig. 5).

Fig. 5. Gypsum replacement textures. A) Ghosts of carbonate pisolites in backreef beds, converted to gypsum (Dry Cave, 15 km north of Carlsbad Cavern) Photo by Gosia Allison-Kosior. B) Relics of reef rock in gypsum are rare and are recognized by carbonate inclusions (shown), Fe oxides or differences in gypsum crystal size, PL. Notation for photomicrographs: PL = Plane-polarized light; XP = Cross-polarized light; RL = Reflected light; Red stain for calcite = Alizarin Red S.
$\text{H}_2\text{SO}_4$ alteration of clay typically produces alunite, hydrated halloysite, gibbsite, Fe-Mn oxides and hydroxides (hereafter simplified to “oxides”) and opal (Polyak & Güven, 2000; Fig. 4C). All can occur as inclusions in replacive gypsum or as residuum on weathered bedrock. Fe and Mn are most soluble at low pH and/or Eh and tend to precipitate when either variable increases. Stability fields for oxidized Fe minerals extend to lower pH and Eh than those of Mn, so the two are often segregated. Fe oxides are scattered throughout the replacive gypsum, while Mn oxides tend to concentrate along the carbonate contact where acidity is less intense (Fig. 8). As the gypsum thickens, oxides and clay residue are concentrated as irregular strands coated with opal (Fig. 9). Spilde et al. (2005) demonstrate microbial enhancement of Fe-Mn corrosion in the Guadalupe caves (cf. Fig. 10). Replacive gypsum in Villa Luz contains a ubiquitous, viscous red-brown biofilm. There are no obvious traces in the Guadalupe caves, although phosphate is present in scattered crandallite [CaAl$_3$(PO$_4$)(PO$_3$OH)(OH)$_6$] and fluorapatite [Ca$_5$(PO$_4$)$_3$F], which accompany Fe-Mn oxides and other alteration products of sulfuric acid at the bedrock contact (Fig. 10C). Phosphorus is removed from organic debris at low pH or Eh, and forms phosphates at alkaline pH (Blatt et al., 1980).

Deposits of elemental sulfur occur in many Guadalupe caves as the result of incomplete oxidation of H$_2$S. Sulfur is most stable at low pH, so it is generally distributed on or within non-carbonate materials that do not neutralize the acidity.

**Fig. 7.** Fabric-selective $\text{H}_2\text{SO}_4$ dissolution of limestone, Lechuguilla Cave. A) Replacive gypsum = gray, calcite = light sparkly tan, XP. B) Molds of former calcite are visible in PL. C) Slivers of corroded calcite floating in a gypsum-filled mold, XP.

**Fig. 8.** Bedrock-gypsum reaction front, Spider Cave. A) Gypsum containing corroded bedrock, clay, and alteration products, including Fe-Mn oxides. Arrow = location of B & C; XP, red stain for calcite. B) Detached crystals become increasingly corroded. Mn oxides (black) are concentrated at and near the bedrock contact. PL. C) Enlarged view of B. Decrease in crystal size is due to surface corrosion, not growth of internal pores. Fe-Mn oxides are attached to partially dissolved calcite crystals. Gypsum = gray; XP.
Micritic Rinds

Some dissolutional bedrock surfaces have been micritized (crystal size diminished to microscopic scale) to form coherent white rinds up to about 1 cm thick (Fig. 4). Many rinds have been intersected or removed by later dissolution, or are covered with gypsum and are disturbed by gypsum wedging. Where rinds intersect fossils in bedrock, the fossil outlines are still visible (Fig. 11). Thin micrite rinds are also present in Villa Luz at the gypsum-limestone contact where H$_2$SO$_4$ dissolution is active today (Fig. 12). Presumably that also once applied to the Guadalupe caves.

Micritic rinds on limestone show negative shifts in both $\delta^{13}$C and $\delta^{18}$O relative to the host rock (Fig. 3). The $\delta^{18}$O shift shows interaction of bedrock with meteoric water, and the $\delta^{13}$C shift shows the influence of cave-air CO$_2$. The changes are small because dissolution and reprecipitation were limited to thin zones along grain boundaries, while most of the original rock was unaffected (Fig. 11). Micritization by sulfuric acid alone should ideally produce no shift in $\delta^{13}$C, because H$_2$SO$_4$ does not contain carbon, and any CO$_2$ released by the reaction is derived from the limestone itself. Therefore the negative shift in $\delta^{13}$C shows some involvement with CO$_2$ in the cave air.
Insight is provided by epigenetic Mammoth Cave, Kentucky, where release of sulfuric acid by oxidation of pyrite in limestone has produced bleached micritic haloes. The haloes show an isotopic shift of −1.7‰ in δ¹⁸O from unaltered bedrock, but only −0.7‰ in δ¹³C (Fig. 3, CW347br–CW347c). The δ¹⁸O shift is caused by interaction with capillary water, and the δ¹³C shift shows interaction with CO₂ absorbed from the cave air. Elsewhere in the cave, white micritized rinds up to 3 cm thick are produced on limestone where CO₂-depleted water seeps into the cave and absorbs CO₂ from the cave air (Fig. 13; Palmer, 2007, p. 345). Both δ¹⁸O and δ¹³C are offset about −1‰ from the unaltered rock (Fig. 3, CW15br–CW15b). The isotopic shifts in these presently active examples resemble those in the apparently relict examples of the Guadalupe caves.

Dolomitization

Some of the micrite rinds are composed of dolomite. This is ordinarily not a common cave mineral but is widespread in Guadalupe caves, where it also forms many late-stage speleothems. Dolomite precipitation or replacement requires high Mg/Ca and CO₃²⁻ (thus high pH), and is favored by evaporation, high temperature, sulfate reduction, and much time. Thrailkill (1968) showed that the chemistry of water films on and near dolomite speleothems lies within the range of dolomite stability; and Polyak (1992) noted conversion of calcite to Mg-rich speleothems, including well-ordered dolomite. The main source of Mg in Guadalupe caves is dolomite bedrock. Dolomite
has been synthesized at >55 °C (Mandrikova et al., 1975), but this is well above the temperature of the present caves. Microbial sulfate reduction can catalyze dolomite precipitation (Wright & Wacey, 2004) but this requires anoxic conditions, which were uncommon in the late-stage cave environment. Thus evaporation and abundant time are the likely agents for most dolomite deposition in the Guadalupes.

If dolomite rinds form on limestone by simple replacement of Ca by Mg [i.e. \(2\ \text{CaCO}_3 + \text{Mg}^{2+} \rightarrow \text{CaMg(CO}_3\text{)}_2 + \text{Ca}^{2+}\)], no carbonate exchange is involved and there is ideally no isotopic shift. Intact fossil outlines in dolomite rinds support this process (Fig. 11). These rinds show a small negative shift in \(\delta^{13}C\) from limestone, as in calcite rinds, but less so in \(\delta^{18}O\) (Fig. 3, LG 212 & LG819). Differences in fractionation between calcite and dolomite may account for the smaller \(\delta^{18}O\) shift.

Some dolomite rinds have formed instead by direct precipitation (Fig. 3, LG805br–LG805c; Fig. 14) and show a large contrast in \(\delta^{13}C\) from the bedrock. Most contain varied morphologies as the result of changing chemical environments (Fig. 15). Some micrite rinds beneath speleogenetic gypsum are coated with younger, ~50 µm lenticular dolomite crystals with micritic cores (Fig. 14C). These probably formed by evaporitic wicking of moisture toward the aerated cave.

### Rills and Solution Basins

Sulfuric acid can become very intense in contact with insoluble material. In Villa Luz, measured pH on bacterial filaments and gypsum extends down to zero. Like a sponge, gypsum can retain moisture, which continues to absorb \(\text{H}_2\text{S}\) and \(\text{O}_2\) to become strongly acidic. Where the acid drips from the gypsum, narrow rills are corroded in the underlying carbonate rock, with intervening sharp spires (Fig. 16). On gentler slopes, acidic flows can produce channels up to ~15 cm wide, which resemble surface karren. These involve only thin films of highly aggressive water spread over a wide area, or draining along gypsum-bedrock contacts. Gentle slopes also acquire solution basins (Fig. 17), which are roughly circular, typically 15–30 cm in diameter, and up to 15 cm deep. Some form clusters with spillover channels between them. Where gypsum has been dissolved away by later meteoric water, the origin of these rills and basins may seem puzzling. Rills formed by sulfuric acid generally underlie bedrock surfaces that show no sources of meteoric water inputs. In many places the rills are overlain by smooth and nearly flat ceilings. Except at and near the land surface, carbonate rocks in the Guadalupes show no rills clearly attributed to meteoric water flow.

---

**Fig. 14.** Primary dolomite at \(\text{H}_2\text{SO}_4\) solution front, Lechugilla Cave. A) Dolomite rhomb at limestone-gypsum contact, XP, red stain for calcite. B) Primary dolomite rind in \(\text{H}_2\text{SO}_4\) basin invading limestone along calcite cleavage, XP. Isotopes distinguish between primary and replacive dolomite (see text and Fig. 3, LG805c). C) Lenticular dolomite crystals nucleated on micritic rind, XP.

**Fig. 15.** Late precipitates impregnating early micritic rind, Lechuguilla Cave, XP, red stain for calcite. 1 = bedrock; 2 = micritic \(\text{H}_2\text{SO}_4\) rind. Distortion shows that micrite was once moist and plastic. 3 = evaporative dolomite replacement of convoluted hydromagnesite layers lined with chalcedony balls. 4 = blocky calcite that grew beneath gypsum crust. Pores in crust are from gypsum dissolution.
Basin Sediments

Sediments in solution basins provide a record of post-solutional conditions. Three basins over a vertical range of 6 m were examined in the Near East of Lechuguilla Cave at ~1050–1060 m asl (Figs. 2 & 18). They lie deep in the cave with no interference from vadose recharge. Natural breakdown allowed minimally invasive sampling of their contents.

In the two lower basins (Fig. 18, basins 2 & 3), the bedrock floor has a dolomitic rind (A2) that is absent in the upper basin. In the lowest basin (3) all sediments are also dolomitized. This irregular distribution may indicate local sulfate reduction with microbially derived carbon as the reducing agent. In all basins the oldest sediment (B) consists of quartz silt (probably residuum from bedrock dissolution) and detrital carbonate. In Basin 2, bed B includes fragments of anhydrite and gypsum, artifacts of sulfuric acid speleogenesis. By that time, local sulfuric acid processes had apparently ceased.

Bed C consists of detrital limestone grains and fossils cemented by calcite, but free of quartz silt (Fig. 19). It is probably corrosion residue from high above, because nearby bedrock contains no such fossils. Dissolution along crystal interfaces reveals delicate fabrics, a typical product of condensation water, rather than sulfuric acid. δ^{13}C of dolomite in bed C (Fig. 3, LG805b) resembles that of evaporative speleothems. Carbonate debris has been micritized and impregnated by 1 μm Fe oxide crystals forming a mottled pattern, possibly microbial (Riding, 2000), which nearly obliterate the original textures. Mottled portions are cemented by calcite extending downward from the overlying mammillary crust. As in bed B, preservation of delicate shells suggests slightly alkaline water.

A mammillary crust (D) consists of calcite interbedded with Fe-Mn-rich laminae that suggest periodic influxes of anoxic water. Abruptly overlying D is a 5 mm very finely crystalline, dark brown-black bed (E) with few fossils and cut by desiccation cracks. EDS analysis shows Mn>Fe. Bed E is absent in the lowest basin. In Basin 2, bed E terminates upward in laminated domal Mn-rich structures (Fig. 20A). It is common for Fe oxides to precede Mn oxides (see Sulfuric Acid Dissolution, and example in Luiszer, 2009). Bed

Fig. 16. Near the Left Hand Tunnel, Carlsbad Cavern. A) Solution rills in limestone formed by acid drainage from gypsum. Note remnant gypsum on ledge. B) Fe-rich bedrock residuum at base of rills.

Fig. 17. Sulfuric acid solution basins in Near East, Lechuguilla Cave. A) Basins with rill infeeders, formed by acid drainage from former gypsum. B) Nearby water-level stains from a post-basin rise in water table; photo by Mark Tracy.
F of Basin 3 includes fine-grained botryoidal dolomite with balls and clusters of chalcedony typical of evaporitic speleothems.

All basin fills terminate upward in dolomitized cave rafts (formerly calcite) lined with chalcedony. The mammillary wall crust (D) beneath Basin 3 has also been irregularly dolomitized (Fig. 21). These conditions probably signify late-stage drying and evaporation. In all three basins, Fe or Mn deposits contain fenestrae cemented with calcite (Fig. 20B). The fenestrae formed in soft sediment; they do not intersect fossils. Some are coated with two stages of cement separated by detrital material, so they were true voids. This texture is common in peritidal microbial mats, either from biogenic gas or grain bridging (Scholle & Ulmer-Scholle, 2003). Most grains lie directly atop fenestrae without falling, which suggests biogenic gas. Alternatively, the voids may be partly tensional, because the contours of opposite walls crudely match, and they branch into desiccation cracks.

Fe-Mn oxides in the basin fills appear to be products of $\text{H}_2\text{SO}_4$ clay alteration. EDS scans show Si and Al peaks, as well as Fe and Mn. Some basins have overflowed, or have been breached by dissolution, so their contents dripped out. Ropy strands of microbial filaments, coated with Fe oxides, extend downward from them and have been coated by calcite (Fig. 22; Davis et al., 1990). The filaments resemble those of the acidophilic *Leptospirillum ferrooxidans* (Provencio & Polyak, 2001). Their presence implies that some basin fills had become anoxic and that oxidation, with microbial mediation, took place as the water drained out. Layer D of Basin 3 contains Fe oxide crystals that may be pyrite pseudomorphs, and SEM views of calcite mammillaries in the basin area show cubic pseudomorphs in solutional pores.
Calcite Replacement of Speleogenetic Gypsum

In scattered locations, calcite has replaced speleogenetic gypsum. The calcite consists of ~200 μm rhombs or blocky cement generally attached to bedrock surfaces. It contains gypsum inclusions and diagnostic fabrics of speleogenetic gypsum, including wedges of altered bedrock rind, clay residue, and Fe-Mn-rich strands. Some of the gypsum inclusions contain microscopic corroded calcite crystals (Fig. 23), showing the various generations of mineralization. The replacive calcite ends outward in a layered crust resembling that of speleothems. An example is located in Spider Cave near a former water level (Fig. 23C). Replacement apparently took place while gypsum was being partly dissolved by calcite-saturated water. Release of Ca$^{2+}$ from the gypsum led to precipitation of calcite by the common-ion effect (Palmer & Palmer, 2004). Dolomite is rarely precipitated by this process. In places calcite replacement has obscured earlier alteration fabrics (Fig. 23D). Isotopic values are not yet available for the replacive calcites.

Mammillary Crusts

Guadalupe caves contain a great variety of subaqueous and subaerial speleothems (Hill, 1987; Davis et al., 1990; Queen & Melim, 2006). Most are omitted from this discussion (e.g. calcite deposits from meteoric infiltration) in favor of those less understood.

Calcite mammillaries up to about 25 cm thick are common in the lower levels of many Guadalupe caves (Figs. 24 & 25). Deposited in standing water, they contain multiple layers, each precipitated over a wide vertical range (typically >20 m) like wallpaper. They coat all types of material, including the basin sediments described above. Their tops correlate over large areas and apparently represent former watertable stands, which correspond roughly to the lowest significant level of sulfuric acid speleogenesis (~1130 m asl in Carlsbad and slightly higher in the Western Borehole of Lechuguilla). The age of mammillaries at Lake of the Clouds exceeds 600 ka (from U/Th dating; unfavorable U/Pb values prevent obtaining older dates; David Decker, Univ. of New Mexico, personal communication, 2011).

The growth of calcite mammillaries was periodically interrupted by thin black layers of Fe-Mn oxides. Each black layer is a few tens of μm thick, with up to 10 individual laminae. Oxide layers seem too uniform to have originated directly as sulfuric acid residue from clay, and many are remote from clay-rich backreef beds. Instead, dissolved Fe$^{2+}$ and Mn$^{2+}$ may have been carried into the cave periodically by anoxic water from depth and precipitated in the aerated cave. However, EDS scans show that the Fe-Mn layers contain small amounts of Si and Al, which may indicate that local Fe-Mn oxides supplied by H$_2$SO$_4$ clay alteration were dissolved when the pools were anoxic. Microscopy and EDS scans of the cave mammillaries show that calcite precipitation ceased while the Fe-Mn layers were deposited. Analysis of the relevant equilibria shows that an (Fe$^{2+}$ + Mn$^{2+}$) concentration of only 0.1 mg L$^{-1}$, when oxidized, can produce enough H$^+$ to neutralize all HCO$_3^-$ in typical calcite-saturated cave pools and initiate carbonate dissolution.

Most Fe-Mn layers in the Guadalupes contain outward-facing shrub-like bodies apparently of microbial origin (Fig. 25D). Chafer et al. (1998) describe nearly identical examples in shallow surface streams fed by warm springs. Mn-oxidizing and -reducing bacteria have been identified in both Lechuguilla (Northup et al., 2003) and Spider (Spilde et al., 2005) and are still viable. Inorganic oxidation of Mn requires a pH of about 8, whereas the presence of Mn-oxidizing microbes allows it to precipitate at near-neutral pH (Ehrlich, 1995).

The oxide layers appear to terminate downward, away from oxidizing conditions, and most do not extend upward beyond the mammillaries. However, thin discontinuous oxide deposits coat walls up to at least 1170 m in Lechuguilla (Fig. 17) and also some mammillaries below 1130 m, leaving discrete water lines. Andrejchuk & Klimchouk (2001) describe a related example in Ukraine, where 50 years of mine dewatering lowered the water table in a gypsum cave, causing
Fe-Mn hydroxides to accumulate as yellow films on walls and as black deposits in clay beds.

After deposition of calcite mammillaries, evaporative dolomite replacement took place as water levels fell. In places dolomite formed overgrowths on the outer mammillary layer, and elsewhere it replaced calcite along crystal interfaces, penetrating mammillary layers to form a jagged contact and obliterating the original crystal fabric (Fig. 21).

Remaining mammillary pools are static, with very low $P_{CO_2}$ (mean = 0.0006 atm). Low $\delta^{13}C$ of mammillary calcite (Fig. 3, LG805, LG847) shows equilibrium with $CO_2$ in the cave atmosphere. In contrast, vadose infiltration has much higher $P_{CO_2}$ and produces perched pools at a variety of levels. Rapid degassing in these pools causes lateral growth of shelfstone at the water surface and high $\delta^{13}C$ values. Infiltrating water in Lechuguilla Cave ranges from oxic to suboxic, with minor concentrations of Mn but undetectable Fe (Levy, 2007). Fe-Mn deposits are rare in vadose pools because of comparatively uniform oxidation potential and a lack of anoxic recharge.

Villa Luz shows a contrast to the Guadalupe Fe-Mn coatings. Local reducing conditions occur in streams floored by dark gray sediment including detrital grains, authigenic pyrite, and carbonaceous muck, mainly from organic debris from skylights (rare in Guadalupe caves). $H_2S$ is present at water depths $>$15 cm, oxygen is below detection limit, and walls are black with a continuous coating of finely crystalline FeS and FeS$_2$. When exposed to air, the sulfides rapidly oxidize to sulfur and to Fe hydroxides and oxides as $\mu$m-size crystals (Fig. 26). Except in certain mammillaries (Fig. 26 B & C), our samples of Guadalupe wall coatings show no evidence of former pyrite.
Condensation Corrosion

High internal relief in the Guadalupe caves supports atmospheric convection driven by temperature and humidity gradients. Relative humidity in Carlsbad ranges from 100% to about 87% (McLean, 1971; Ingraham et al., 1990). Evaporation from warm and deep levels leads to condensation on cooler surfaces above. Many cave ceilings and high-level speleothems are corroded by this process. For example, the ceiling of the steeply inclined passage to Lake of the Clouds is highly corroded, while mammillary crust coats the local floors and walls. Apparently as the lake level dropped, condensation corrosion extended to ever-lower elevations while mammillary crusts continued to form below. In places there are conspicuous sub-horizontal boundaries between vadose speleothems and overlying corroded bedrock and speleothems (Fig. 27). Because most surfaces below the line are coated with botryoids (cave popcorn), this is known as the “popcorn line” (Hill, 1987; Queen, 1994, 2009b). Left Hand Tunnel contains a popcorn line about 3-5 m below the ceiling. Both thermal and humidity gradients are present. Two years of monitoring show relative humidities at or near 100% near the ceiling, and 87–96% near the floor, with almost uniform temperatures of 15–16 °C throughout (Paul Burger, National Park Service, personal communication, 2011). At the underlying Lake of the Clouds the mean temperature is 20 °C, which provides a strong thermal gradient.

Evaporation from pools can also be demonstrated isotopically by a decrease in δ¹⁸O values in the water vapor relative to pool water. Water in Lake of the Clouds has δ¹⁸O ~ −6.8‰ VSMOW (Ingraham et al., 1990), and if the overlying vapor were in equilibrium with the pool, the vapor would have δ¹⁸O of −16.4‰ (computational method in Faure & Mensing, 2005). In this case no more evaporation would be possible. Instead, the overlying water vapor has δ¹⁸O ~ −18.2‰ (Ingraham et al., 1990), lower than the equilibrium value, so further evaporation is possible.

Condensation greatly affects the isotopic signatures of both the water and corroded material. Condensation can shift the δ¹⁸O of evaporative water as much as +10‰ (Bottinga & Craig, 1969). In surface rainfall the earliest drops remove the most positive
δ¹⁸O from the vapor, and later ones are more negative; but the impact of moist air against a cold surface can bypass some of this fractionation by quickly condensing moisture with average isotopic values. Corroded surfaces show diminished δ¹⁸O and δ¹³C relative to the host carbonates (Fig. 3; see also the Micritic Rinds section and Sarbu & Lascu, 1997). The effect, but not the process, resembles the micritization beneath gypsum crusts during sulfuric acid speleogenesis. Condensation corrosion produces loose grains that easily fall away. In the weak carbonic acid there is much differential solution between grains of different crystal size or composition, and clay alteration is limited. As condensation corrosion proceeds, the isotopic shift caused by bedrock weathering is apparently cumulative, e.g., from H1 to H2 in Fig. 3, representing several increasingly weathered samples (Hill, 1987). Effects are most conspicuous in clay-rich back-reef beds, which produce a fluffy coating of red, yellow, brown and black, consisting of quartz silt, clay, and Fe-Mn oxides (Fig. 28). Purer carbonate bedrock simply weathers to light gray powder. The clay-rich beds in Spider Cave were apparently first altered in sulfuric acid conditions and later modified by condensation corrosion in CO₂-rich air (Fig. 29A). Corroded zones are fertile ground for microbiologically mediated Fe-Mn reactions (Northup et al., 2003). Alternation between speleothem growth and corrosion probably indicates wet-dry cycles, with carbonate precipitation during wet periods and corrosion dominating in dry periods.

Micritization by condensation water produces intricate internal solutional features at μm scales, a typical effect of capillary water (Fig. 29B). Many subaerial calcite speleothems have acquired white micritized rinds, most notably in Spider Cave (Fig. 30A). Isotopes from a broken stalactite show typical open-system calcite values for the unweathered portion (Fig. 3, SP808B), with offsets of −0.68‰ (δ¹⁸O) and −2.1‰ (δ¹³C) in the 5 mm white rind (SP808A). The significant change in δ¹³C shows interaction with subaerial CO₂. Much corroded material has fallen to the floor to form a soft and moist granular paste. It can produce layers on underlying surfaces, or, on walls, blobs with finger-like spears shaped by dripping condensation water. Where evaporation is limited, cementation is poor or absent, because condensation water is already at equilibrium with cave air and CO₂ degassing is insignificant.

Drip cones of calcite and other carbonate minerals can grow on the floor by evaporation. Most have central drip holes maintained by still-aggressive condensation water. Many cones have been largely replaced by evaporative dolomite and terminate outward in euhedral quartz. Some also show interaction with meteoric water.

When calcite precipitates, its δ¹⁸O is about 30‰ higher than in the host water, depending on temperature (Friedman & O’Neil, 1977). The initial calcite in Carlsbad drip cones should therefore have δ¹⁸O of roughly −8‰ VPDB, more negative than typical dripstone. But as evaporation proceeds, ¹⁸O is selectively removed from the water and δ¹⁸O in the deposits increases (e.g., to −4.81‰ for CB808 and −3.74‰ for CB905 in Fig. 3). This positive shift overlaps the values for speleothems formed in and around meteoric pools, but the two types of deposits can be distinguished by their shape and composition.

Vents are tubes or channels dissolved in bedrock by condensation corrosion in constricted areas. Many intersect rills formed by previous sulfuric acid. Vents are bordered by flaring rims of precipitates, usually oriented toward cave entrances, and apparently formed by evaporation of condensation water that wicks out of the corroded area. Samples CB803 and CB813 (Fig. 3) are evaporative deposits from condensation water that had corroded a rim. Note the highly negative isotopic ratios. However, an upward-facing vent near the Left Hand Tunnel has a popcorn rim with more positive isotopes, which suggest precipitation from meteoric water (Fig. 3, CB932). This popcorn may pre-date the vent.

Modification of Speleothems by Evaporation and Recrystallization

Many speleothems in Guadalupe caves terminate in evaporative precipitates that increase in Mg content away from their water sources (whether mete-
Evaporation has been much greater in well-aerated Carlsbad Cavern than in Lechuguilla Cave, as shown by the oxygen isotopes of pool water. In Carlsbad pools, δ¹⁸O = −3.6 to −6.8‰ VSMOW, and in Lechuguilla pools it is −7.0 to −8.0‰ VSMOW (Newton et al., 2001). This difference is also transmitted to carbonate pool deposits. At 17 °C these pools would precipitate calcite with δ¹⁸O = −3.5 to −6.6‰ VPDB and −6.8 to −7.7‰ VPDB respectively (Fig. 3).

Some carbonate speleothems have recrystallized to a glassy texture with clear euhedral crystals lacking growth layers. They appear to form in nearly closed cave environments, in which the water films on the speleothems, and perhaps interstitial water within, is very close to calcite saturation and in CO₂ equilibrium with the cave air, so mass transfer between water and speleothems is balanced. Glassy popcorn (Fig. 3, LG 344 and Fig. 30B) has an abnormally low δ¹³C that reveals long-term carbon exchange between cave-air CO₂ and calcite, with slight evaporation but no degassing. Spider Cave contains many calcite speleothems that have been recrystallized in this way. The cave has a single small entrance periodically blocked in the past by mass wasting, and recrystallization may have occurred during a period of lengthy blockage. Slow dripwater maintained a relatively high δ¹³C in the speleothems (e.g. Fig 3, SP808b). Later micritization turned the speleothem walls a ghostly white (e.g. Fig. 29A). The isotopic shift suggests that condensation corrosion was responsible (Fig. 3, SP808a).

**Evidence for Late-Stage Hypogenic Gases**

One of our main goals was to determine the manner in which sulfuric acid dissolution ceased in the Guadalupes; but at the end of this study we have only begun to find an answer. In brief, the last stages of sulfuric acid dissolution overlapped both temporally and spatially with what are usually considered post-speleogenetic events such as mammillary deposition. Below the levels of alunite-dated H₂SO₄ features and mammillaries, steep rifts extend downward that show evidence for very late sulfuric acid enlargement. For example, in Lechuguilla, the rift that extends well below the lowest mammillaries down to the water table in the Southeastern Branch contains bare, highly corroded bedrock walls with no mammillaries. Its lower
HF gas can be liberated by the attack of fluorine-bearing minerals by H₂S or H₂SO₄ (Maltsev and Korsunov, 1998). We first considered detrital fluorapatite [Ca₅(PO₄)₃F] as a possible source, but this is rare in the Guadalupe. It is more likely that HF was released by deep-seated processes on the fringe of the Rio Grande Rift zone (Fig. 1). Leuth et al. (2005) describe mines in the rift zone that contain thermal deposits such as fluorite, jarosite, and barite, which coincide in age with major speleogenetic episodes in the Guadalupe dated by Polyak et al. (1998) at 12–11 Ma and 6–4 Ma. DuChene & Cunningham (2006) suggest that the Guadalupe caves formed when their catchment area extended much farther to the west and included known petroleum-related sulfide sources. Most of this plateau was gradually down-faulted in the late Neogene, leaving the caves as inactive relics with only a small remnant of their former recharge. Fluorite crystals support the relation between the rift zone and the caves, and the possibility of upward leakage of exotic gases during recent minor tectonic pulses.

CONCLUSIONS

Micro-scale petrographic mapping is shown to be an efficient way to reveal the complex geochemical evolution of hypogenic caves such as those in the Guadalupe Mountains. Identifying mineral phases and relationships is the first step toward interpreting geologic processes. From there, the most likely hypotheses can be tested quantitatively with the aid of equilibrium chemistry and stable isotopes. The processes described here have greatly affected how the caves look today.

Numerical chronology has not been considered here. Available dates are few and widely scattered, and the history of events is complicated by spatial and temporal overlap and by fluctuating intensity and occasional repetition. Scattered late stages of sulfuric acid enlargement were contemporaneous with depositional features such as mammillaries at similar elevations elsewhere in the caves. Observations in this paper should help to decipher this genetic history. They may also improve the efficiency of numerical dating and paleoclimatology, and aid the recognition of diagnostic features in other sulfuric acid caves.

ACKNOWLEDGMENTS

Thanks to fellow researchers Victor Polyak, J. Michael Queen, Carol Hill, Donald Davis, Laura Rosales Legarde, Bogdan P. Onac, and Paul Burger for discussion of concepts over many years; Richard Zopf, Rick Olson, Paul Rubin, Mark Tracy, Brandon Taylor, Steve Worthington, Richard Maire, Jean-François Perrette, and Yves Prunier for help with the geologic surveys; Carlsbad Caverns National Park staff Stan Allison, Dale Pate, and Jason Walz for logistical help and Paul Burger for humidity and temperature data; Tom Kraemer (U.S. Geological Survey) for O-H isotopic data; John Andersland (Western Kentucky University) for help with SEM work; and the State University of New York Research Foundation for covering laboratory expenses. Thanks also to three anonymous reviewers whose suggestions helped to clarify the text.
REFERENCES

Andreffchuk V. & Klimechouk A., 2001 – Geomicrobiology and redox geochemistry of the karstified Miocene gypsum aquifer, western Ukraine: the study from Zoloushka Cave. Geomicrobiology Journal, 18: 275-295. http://dx.doi.org/10.1080/01490450152467796

Asmerom Y., Polyak V., Burns S. & Rasmussen J., 2007 – Solar forcing of Holocene climate: new insights from a speleothem record, southwestern United States. Geology, 35 (1): 1-4. http://dx.doi.org/10.1130/G22865A.1

Blatt H., Middleton G. & Murray R., 1980 – Origin of sedimentary rocks (2nd ed.). Prentice-Hall, Englewood Cliffs, NJ, 782 p.

Bottinga Y. & Craig H., 1969 – Oxygen isotope fractionation between CO2 and water and the isotopic composition of marine atmospheric CO2. Earth and Planetary Science Letters, 5: 285-295. http://dx.doi.org/10.1016/0012-810X(69)90054-8

Brook G.A., Ellwood B., Railback L. & Cowart J., 2006 – A 164 ka record of environmental change in the American Southwest from a Carlsbad Cavern speleothem. Palaeogeography, Palaeoclimatology, Palaeoecology, 237: 483-507. http://dx.doi.org/10.1016/j.palaeo.2006.01.001

Chafetz H., Akdim B., Julia R. & Reid A., 1998 – Mn- and Fe-rich black travertine shrubs: bacteriologically induced precipitates. Journal of Sedimentary Research, 68: 404-412.

Davis D.G., 1980 – Cave development in the Guadalupe Mountains: a critical review of recent hypotheses. National Speleological Society, NSS Bulletin, 42 (3): 42-48.

Davis D.G., Palmer M.V. & Palmer A.N., 1990 – Extraordinary subaqueous speleothems in Lechuguilla Cave, New Mexico. National Speleological Society, NSS Bulletin, 52 (2): 70-86.

Deines P., Langmuir D. & Harmon R., 1974 – Stable carbon isotope ratios and the existence of a gas phase in the evolution of carbonate ground waters. Geochimica et Cosmochimica Acta, 38: 1147-1164. http://dx.doi.org/10.1016/0016-7037(74)90010-6

DuChene H.R. & Cunningham K.I., 2006 – Tectonic influences on speleogenesis in the Guadalupe Mountains, New Mexico and Texas. In: Land L., Leuth V., Raatz W., Boston P. & Love D. (Eds.), Caves and karst of southeastern New Mexico. New Mexico Geological Society, 57th Field Conference: 211-218.

Egeimier S., 1987 – A theory for the origin of Carlsbad Caverns. National Speleological Society, NSS Bulletin, 49: 73-76.

Ehrlich H.L., 1995 – Geomicrobiology (3rd ed.). Marcel Dekker, New York, 719 p.

Engel A.S., 2004 – Microbial contributions to cave formation: new insights into sulfuric acid speleogenesis. Geology, 32 (5): 369-322. http://dx.doi.org/10.1130/G20288.1

Fairchild, J. & Baker, A., 2012 – Speleothem science: from processes to past environments. John Wiley & Sons, London, 448 p. http://dx.doi.org/10.1002/9781444361094

Faure G., 1998 – Principles and applications of geochemistry (2nd ed.). Prentice Hall, Upper Saddle River, NJ, 600 p.

Faure G. & Mensing T., 2005 – Isotopes: principles and applications (3rd ed.). John Wiley & Sons, Hoboken, NJ, 897 p.

Forbes J.R., 2000 – Geochemistry of Carlsbad Cavern pool waters, Guadalupe Mountains, New Mexico. Journal of Cave and Karst Studies, 62: 127-134.

Friedman I. & O’Neill J.R., 1977 – Compilation of stable isotope fractionation factors of geochemical interest. U.S. Geological Survey Professional Paper 440-KK: 49 p.

Galdenzi S., Menichetti M. & Forti P., 1997 – La corrosione di placchette calcaree ad opera di acque ulifere: dati sperimentali in ambiente ipogeo. International Union of Speleology, Proceedings of 12th International Congress of Speleology, La Chaux-de-Fonds, Switzerland: 187-190.

González L.A. & Lohmann K.C., 1988 – Controls on mineralogy and composition of speleothem carbonates: Carlsbad Caverns, New Mexico. In: James N. & Choquette P. (Eds.), Paleokarst. New York: Springer-Verlag: 81-101.

Hardie L.A., 1967 – The gypsum-anhydrite equilibrium at one atmosphere pressure. American Mineralogist, 52: 171-200.

Hill C.A., 1987 – Geology of Carlsbad Cavern and other caves in the Guadalupe Mountains, New Mexico and Texas. New Mexico Bureau of Mines and Mineral Resources Bulletin, 117: 150 p.

Hill C.A., 1996 – Geology of the Delaware Basin, Guadalupe, Apache, and Glass Mountains, New Mexico and West Texas. Society for Sedimentary Geology, Permian Basin Section, Publication 96-39: 480 p.

Hose L.D., Palmer A.N., Palmer M.V., Northup D.E., Boston P.J. & DuChene H.R., 2000 – Microbiology and geochemistry in a hydrogen-sulphide-rich karst environment. Chemical Geology, 169: 399-423. http://dx.doi.org/10.1016/S0009-2541(00)00217-5

Hoy R.N. & Gross G.W., 1982 – A baseline study of oxygen-18 and deuterium in the Roswell, New Mexico groundwater basin. New Mexico Water Resources Research Institute Report, 144: 95 p.

Ingraham N.L., Chapman J.B. & Hess, J.W., 1990 – Stable isotopes in cave pool systems: Carlsbad Cavern, New Mexico, USA. Chemical Geology, 86: 65-74.

Jagnow D., 1979 – Cavern development in the Guadalupe Mountains. Cave Research Foundation, Columbus, Ohio, 55 p.

Kirkland D.W. & Evans R., 1976 – Origin of limestone buttes, Gypsum Plain, Culberson County, Texas. American Association of Petroleum Geologists Bulletin, 60 (11): 2005-2018.

LaRock E. & Cunningham K.I., 1990 – The October 1999 Lechuguilla Microclimate study field trip. Denver, Colorado: National Speleological Society, Rocky Mountain Caving, 7: 27-33.

Leuth V.W., Rye R.O. & Peters L., 2005 – “Sour gas” hydrothermal jarosite: ancient to modern acid-sulfate mineralization in the southern Rio Grande Rift. Chemical Geology, 215: 339-360. http://dx.doi.org/10.1016/j.chemgeo.2004.06.042

Levy D.B., 2007 – Oxidation-reduction chemistry of Lechuguilla Cave seepage. Journal of Cave and Karst Studies, 69 (2): 351-358.
Lohmann K.C., 1988 – Geochemical patterns of meteoric diagenetic systems and their application to studies of palaeokarst. In: James N. & Choquette P. (Eds.), Paleokarst. New York: Springer-Verlag: 58-80.

Luiszer F., 2009 – Speleogenesis of Cave of the Winds, Manitou Springs, Colorado. In: Engel A.S. & Engel S.A. (Eds.), Select field guides to cave and karst lands of the United States. Leesburg, Va.: Karst Waters Institute, Special Publication 15: 119-132.

Maltsev V. & Korshunov V., 1998 – Geochemistry of fluorspar and related features of the Kugitangtou Ridge caves, Turkmenistan. Journal of Cave and Karst Studies, 60: 151-155.

Mandrikova N.T., Perozio G.N. & Fedyunina V., 1975 – Synthesis of protodolomite. Mineralogy, 220: 121-123.

McLean J.S., 1971 – The microclimate in Carlsbad Caverns, New Mexico. U.S. Geological Survey, Denver, Colorado, Open File Report 71-198: 67 p.

Newton B.T., Campbell A.R., Turin H.J., Phillips F.M. & Plummer M.A., 2001 – Stable isotopic investigation of cave pools in Carlsbad Caverns National Park, NM. Geological Society of America, Rocky Mountain and South-Central Sections, Abstracts with Programs, 33 (5):14.

Northup D.E., Dahm C.N., Melim L.A., Spilde M.N., Crossey I.J., Lavoie K.H., Mallory L.M., Boston P.J., Cunningham K.I. & Barns S.M., 2000 – Evidence for geo microbiological interactions in Guadalupe caves. Journal of Cave and Karst Studies, 62 (2): 80-90.

Northup D.E., Barns S., Yu L., Spilde M., Schelble R., Dano K., Crossey L., Connolly C., Boston P., Natvig D. & Dahm C., 2003 – Diverse microbial communities inhabiting ferromanganese deposits in Lechuguilla and Spider Caves. Environmental Microbiology, 5 (11): 1071-1086.

Palmer A.N., 1991 – Origin and morphology of limestone caves. Geological Society of America Bulletin 103 (1): 1-21.

Palmer A.N., 2007 – Cave Geology. Cave Books, Dayton, Ohio, 454 p.

Palmer A.N. & Palmer M.V., 2000 – Hydrochemical interpretation of cave patterns in the Guadalupe Mountains, New Mexico. Journal of Cave and Karst Studies 62 (2): 91-108.

Palmer A.N. & Palmer M.V., 2004 – Sulfate-Carbonate Interactions in the Development of Karst. Northeastern Geology & Environmental Sciences, 26 (1&2): 93-106.

Polyak V.J., 1992 – The mineralogy, petrography and diagenesis of carbonate speleothems from caves in the Guadalupe Mountains, New Mexico. MS thesis, Texas Tech University, Lubbock, TX. 165 p.

Polyak V.J., McIntosh W.C., Güven N. & Provencio P.P., 1998 – Age and origin of Carlsbad Cavern and related caves from 40Ar/39Ar of alunite. Science, 279: 1919-1922.

Polyak V.J. & Güven N. 2000 – Clays in caves of the Guadalupe Mountains, New Mexico. Journal of Cave and Karst Studies, 62 (2): 120-126.

Polyak V.J. & Provencio P.P., 2001 – By-product materials related to H2S-H2SO4 influenced speleogenesis of Carlsbad, Lechuguilla, and other caves of the Guadalupe Mountains, New Mexico. Journal of Cave and Karst Studies, 63: 23-32.

Provencio P.P. & Polyak V.J., 2001 – Iron oxide-rich filaments: possible fossil bacteria in Lechuguilla Cave, New Mexico. Geomicrobiology Journal, 18: 297-309.

Queen J.M., 1994 – Speleogenesis in the Guadalupe: the unsettled question of the role of mixing, phreatic or vadose sulfide oxidation. In: Sasowsky I.D. & Palmer M.V. (Eds.), Breakthroughs in karst geomicrobiology and redox geochemistry. Karst Waters Institute, Charles Town, West Virginia, Special Publication 1: 64-65.

Queen J.M., 2009a – Brine mixing as an initial stage of speleogenesis. In: Palmer A.N. & Palmer M.V. (Eds.), Caves and karst of the USA. Huntsville, Alabama: National Speleological Society: 280-282.

Queen J.M., 2009b – Post-drainage evolution of the caves of the Guadalupe Mountains, southeastern New Mexico and West Texas, USA. In: White, W.B. (Ed.), Proceedings of 15th International Congress of Speleology, Kerrville, Texas: International Union of Speleology, 2 (2): 964-970.

Queen J.M. & Melim L.A., 2006 – Biothems: biologically influenced speleothems of the Guadalupe Mountains, New Mexico USA. New Mexico Geological Society Guidebook to 57th Annual Field Conference: 167-173.

Riding R., 2000 – Microbial carbonates: the geological record of calcified bacterial-algal mats and films. Sedimentology, 47 (Supplement 1): 179-214.

Sarbu S.M. & Lascu C., 1997 – Condensation corrosion in Movie Cave, Romania. Journal of Cave and Karst Studies, 59: 99-102.

Scholle P.A. & Ulmer-Scholle D.S., 2003 – A color guide to the petrography of carbonate rocks: grains, textures, porosity, diagenesis. American Association of Petroleum Geologists, AAPG Memoir, 77: 474 p.

Spilde M.N., Northup D.E., Boston P.J., Schelble R.T., Dano K.E., Crossey L.J. & Dahm C.N., 2005 – Geomicrobiology of cave ferromanganese deposits: a field and laboratory investigation. Geomicrobiology Journal, 22: 99-116.

Thraillkill J., 1968, Dolomite cave deposits from Carlsbad Caverns. Journal of Sedimentary Petrology, 38: 141-145.

Turin H.J. & Plummer M.A., 2000 – Lechuguilla cave pool chemistry, 1986-1999. Journal of Cave and Karst Studies, 62: 135-143.

Wright D.T. & Wacey D., 2004 – Sedimentary dolomite: a reality check. In: Braithwaite C.J., Rizzi G. & Darke G. (Eds.), The geometry and petrogenesis of dolomite hydrocarbon reservoirs. Geological Society of London, Special Publication 235: 65-74.

Zheng Y.-F., 1999 – Oxygen isotope fractionation in carbonate and sulfate minerals. Geochemo Journal, 33: 109-126.
Appendix 1. Identification of samples in Fig. 1, showing approximate composition (from X-ray diffraction and EDS). Calcite, aragonite = CaCO$_3$; dolomite = CaMg(CO$_3$)$_2$; huntite = CaMg$_3$(CO$_3$)$_4$; hydromagnesite = Mg$_5$(CO$_3$)$_4$(OH)$_2$·4H$_2$O; quartz = SiO$_2$.

| Sample   | Composition (%) | Description                                                                 |
|----------|-----------------|-----------------------------------------------------------------------------|
| CB 801   | calcite 72      | finely crystalline precipitate after aragonite                               |
|          | aragonite 28    |                                                                             |
| CB 803   | 100             | finely crystalline precipitate                                              |
| CB 808   | 60              | finely crystalline precipitate                                              |
| CB 813   | 100             | corroded winged vent                                                        |
| CB 822c  | 100             | bedrock alteration rind                                                     |
| CB 831   | 97              | pop corn                                                                    |
| CB 839   | 25              | finely crystalline precipitate with sepiolite                               |
|          | 75              |                                                                             |
| CB 841c  | 94              | corroded bedrock                                                           |
| CB 842a  | 85              | botryoids                                                                  |
| CB 842b  | 51              | botryoids                                                                  |
| CB 845   | 97              | botryoidal blister                                                         |
|          | 3               | finely crystalline precipitate with sepiolite                               |
| CB 853   | 10              | finely crystalline precipitate bordering pool                               |
| CB 855   | 100             | finely crystalline precipitate bordering pool                               |
| CB 857   | 10              | finely crystalline precipitate in pool                                      |
| CB 903   | 41              | finely crystalline precipitate after aragonite                              |
|          | 51              |                                                                             |
| CB 905   | 9               | finely crystalline precipitate around drip cone                              |
|          | 89              |                                                                             |
| CB 909   | 100             | finely crystalline precipitate                                              |
| CB 915a  | 92              | finely crystalline precipitate (top)                                        |
| CB 915b  | 97              | finely crystalline precipitate with sepiolite                               |
| CB 915c  | 95              | finely crystalline precipitate with sepiolite                               |
| CB 915d  | 100             | finely crystalline precipitate (base)                                       |
| CB 917b  | 5               | drip cone                                                                  |
|          | 9               | subaerial rim                                                               |
| CB 932   | 90              | subaerial rim                                                               |
|          | 10              |                                                                             |
| CB 934b  | 100             | botryoids                                                                  |
| CW 15 br | 100             | bedrock, Mammoth Cave                                                      |
| CW 15b   | 100             | weathered rind on bedrock, Mammoth Cave                                    |
| CW347br  | 100             | bedrock containing pyrite, Mammoth Cave                                    |
| CW347c   | 100             | bedrock rind around pyrite, Mammoth Cave                                   |
| LG 62    | 100             | finely crystalline precipitate                                              |
| LG 212   | 100             | bedrock alteration rind                                                     |
| LG 344   | 86              | glassy crystals                                                            |
|          | 14              |                                                                             |
| LG 357a  | 3               | finely crystalline precipitate                                              |
| LG 357b  | 100             | finely crystalline precipitate                                              |
| LG 801   | 9               | finely crystalline precipitate                                              |
|          | 66              | mamillary crust                                                             |
| LG 805   | 100             | mamillary crust                                                             |
| LG 805br | 100             | limestone bedrock                                                          |
| LG 805a  | 17              | botryoidal basin fill                                                       |
| LG 805b  | 100             | basin fill                                                                 |
| LG 805c  | 40              | basin fill                                                                 |
| LG 813a  | 90              | finely crystalline pool precipitate                                         |
| LG 813b  | 10              | finely crystalline pool precipitate                                         |
| LG 819   | 100             | bedrock alteration rind                                                     |
| LG 847   | 11              | mamillary crust                                                             |
| SP 808a  | 100             | stalactite, corroded rind                                                   |
| SP 808b  | 100             | stalactite, recrystallized interior                                         |