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

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Abstract:

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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 H_2SO_4 to CO_2 -dominated reactions. The H_2SO_4 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 $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$. 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 CO_2 from cave air, corroding earlier features and lowering their $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$. Drips of condensation water deposit minerals mainly by evaporation, which increases $\delta^{18}\text{O}$ in the speleothems while $\delta^{13}\text{C}$ 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 CO_2 , 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

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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 H_2SO_4 speleogenesis to processes dominated by CO_2 equilibria. Much cave research today yields paleoclimate data from meteoric speleothems (Fairchild & Baker, 2012). Instead, this paper emphasizes processes and features 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 Guadalupe 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 H_2S from reduction of sulfates by petroleum. Argon dating of alunite $[\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6]$, 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 south-east contains fore-reef carbonates capped by thick evaporites. The Guadalupe owe their height to late

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Fig. 1. Location and geologic setting of the Guadalupe Mountains. Back-reef strata: T = Tansill, Y = Yates, S = Seven Rivers, Q = Queen, G = Grayburg.

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_2S -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 verti-

cal 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_2S = 300–500 mg L^{-1} , pH = 6.3–7.1, PCO_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_2S 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

Fig. 2. Maps and profiles of Carlsbad Cavern and Lechuguilla Cave (courtesy of National Park Service). E = entrance; C = Lake of the Clouds; G = Green Lake Room. Red dot = solution basins studied in Lechuguilla Cave. The Lechuguilla entrance is 5.82 km WNW of the Carlsbad entrance. The Spider Cave entrance is at 1295 m asl and 1.81 km WNW of the Carlsbad entrance.

Fig. 3. Carbon-oxygen isotopic ratios of carbonate samples. Arrows in green box show isotopic trends caused by: (a) CO_2 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- CO_2 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 CO_2 loss and evaporation (additional data in Hill, 1987, and Gonzles & 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.

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 $\delta^{18}\text{O}$ values of a stalagmite from Pink Panther Cave (~25 km SW of Carlsbad) to distinguish Holocene wet and dry periods. Relatively low $\delta^{18}\text{O}$ correlates with greater rainfall and faster sta-

lagmite growth (Fig. 3). The climate was relatively dry from 12 to 7 ka and wetter since. A record of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ 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 $\delta^{13}\text{C}$ values (~140–150 ka) indicate CO_2 degassing, probably during wet periods. $\delta^{18}\text{O}$ values are near the present ideal for calcite deposited by meteoric infiltration (discussed in next section).

WATER CHEMISTRY AND ISOTOPES

Water infiltrating into Guadalupe caves today has a typical PCO_2 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 CaCO_3 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 $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values are shown in Fig. 3. In the Guadalupe, $\delta^{13}\text{C}$ of CO_2 is –20 to –25‰ VPDB in soil (varies with vegetation type) and about –15‰ in cave air (Gonzles & Lohmann, 1988). Typical $\delta^{18}\text{O}$ for local cave water is -7.9 ± 1.0 ‰ VSMOW in drips and -6.9 ± 0.7 ‰ in pools, with $\delta^2\text{H}$ near the global meteoric trend (Ingraham et al., 1990); $\delta^{18}\text{O}$ VSMOW = $1.03(\delta^{18}\text{O VPDB}) + 30.86$ (Faure, 1998, p. 304). Equilibrium of cave CO_2 with local bedrock should produce calcite with $\delta^{13}\text{C}$ 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 $\delta^{18}\text{O}$ about -7 ± 0.6 ‰ $\delta^{18}\text{O}$ VPDB (Friedman & O'Neil, 1977), and $\delta^{18}\text{O}$ of dolomite should be ~2.5‰ greater than that of calcite (Zheng, 1999). Scatter in data probably reflects wet-dry cycles, with wet conditions yielding more negative $\delta^{18}\text{O}$ (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 CO_2 to the cave air, the escaping gas is enriched in ^{12}C , which raises the $\delta^{13}\text{C}$ in the remaining water and in subsequent carbonate deposits. In contrast, evaporation of cave water preferentially removes ^{16}O , causing a negative $\delta^{18}\text{O}$ shift in the vapor. This causes a positive $\delta^{18}\text{O}$ 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 $\delta^{18}\text{O}$ 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,

gradually diminishing in slope. Speleothems deposited chiefly by evaporation show a rightward shift in Fig. 3 (toward increasing $\delta^{13}\text{C}$) but with little or no increase in $\delta^{18}\text{O}$ from degassing. See Lohmann (1988) for details.

When water vapor condenses on solid surfaces, it inherits some of the low $\delta^{18}\text{O}$ of the water vapor. Also, the condensate absorbs CO_2 from the cave air, acquiring $\delta^{13}\text{C}$ that is much lighter than that of carbonate bedrock and most speleothems. Therefore, resulting corrosion residues show diminished $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ relative to the original carbonates. Condensation water can deposit carbonate minerals only by evaporation, since it is already at equilibrium with cave CO_2 . The initial deposits from this water are depleted in both $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ relative to speleothems deposited from meteoric water. Subsequent evaporative deposits continue to increase in $\delta^{18}\text{O}$ but have rather steady $\delta^{13}\text{C}$, causing a trend toward the right (c) in Fig. 3.

If the evaporated water condenses on cooler surfaces above, it absorbs CO_2 from the cave air (low in $\delta^{13}\text{C}$) and dissolves some of the carbonate substrate. This, in combination with the relatively low $\delta^{18}\text{O}$ 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 H_2S -rich water show low $\delta^{13}\text{C}$ 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 H_2S 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 H_2S and O_2 from the cave air. Sulfuric acid is produced by the $\text{H}_2\text{S} + 2\text{O}_2$ 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 H_2S and O_2 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

Fig. 4. Early micritized bedrock rinds. A) Secondary gypsum (top) with wedging and partial assimilation of bedrock, overlying white micritized and dolomitized bedrock rind, Lechuguilla Cave. B) White micritized crust on limestone, cut by solution pockets, Left Hand Tunnel, Carlsbad Cavern. C) White micritized, dolomitized bedrock rind in Lechuguilla Cave (1), overlain by residue from H_2SO_4 dissolution: 2 = Mn oxides; 3 = alunite, 4 = Al-rich clay and Fe oxides in gypsum. Upper scale in cm and mm. D) Contact between unaltered limestone (left) and micritized calcite rind, Carlsbad. Note disaggregation and diminished crystal size in rind.

al. (1997) show that H_2SO_4 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 Ca^{2+} from the rock and SO_4^{2-} from the acid often increase enough to precipitate replacive ("speleogenetic") gypsum. Negative $\delta^{34}\text{S}$ values in the gypsum of Guadalupe caves suggests a biogenic H_2S source (Hill, 1987). Chemical modeling shows that gypsum replacement requires the consumption of $>0.014 \text{ mol L}^{-1}$ 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

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.

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).

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 Guadalupe, but some floor deposits contain residual anhydrite crystals (see Basin Sediments).

Replacive gypsum can preserve bedrock textures and grain shapes (Figs. 5 & 7). Rapid H_2SO_4 dissolution of carbonate releases CO_2 gas, and the increased

Fig. 6. Anhydrite in solution pockets, Villa Luz: A) Felted anhydrite (lighter) and gypsum in enlarging H_2SO_4 solution pockets. Red stain for calcite, XP. B) Anhydrite needles with major growth perpendicular to bedrock contact, PL. C) Enlarged view of box in B, XP; anhydrite needles = bright. Box shows anhydrite rosettes.

PCO_2 in the cave can enhance bedrock dissolution. In a closed system, with no CO_2 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 CO_2 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.

Fig. 7. Fabric-selective H_2SO_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.

H_2SO_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, although phosphate is present in scattered crandallite $[\text{CaAl}_3(\text{PO}_4)(\text{PO}_3\text{OH})(\text{OH})_6]$ and fluorapatite $[\text{Ca}_5(\text{PO}_4)_3\text{F}]$, 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_2S . 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. 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.

Fig. 9. Fe-Mn strands formed during growth of replacive gypsum. A) Clay residue floating in replacive gypsum at contact with limestone, Lechuguilla Cave. Red stain for calcite, XP. B) Fe-Mn oxides, quartz silt (arrow), and clay residue in gypsum matrix (gray), XP. C) Fe-Mn oxide strands (black), same as B but PL. D) Same as B and C, but RL. Mn oxides = black, Fe oxides = yellow, clay inclusions = white. E) Enlarged view of Fe-Mn strand, with opal rind surrounding Fe-Mn oxides and clay residue, XP. B–E from Spider Cave.

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_2SO_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 $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ relative to the host rock (Fig. 3). The $\delta^{18}\text{O}$ shift shows interaction of bedrock with meteoric water, and the $\delta^{13}\text{C}$ 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 $\delta^{13}\text{C}$, because H_2SO_4 does not contain carbon, and any CO_2 released by the reaction is derived from the limestone itself. Therefore the negative shift in $\delta^{13}\text{C}$ shows some involvement with CO_2 in the cave air.

Fig. 10. Microbial textures in Fe-Mn oxides, Lechuguilla Cave. A) Oxide strands in replacive gypsum (arrow = corroded calcite), PL. B) Enlarged view shows apparent cell structures. C) Filaments coated with Fe-Mn oxides in a crandallite matrix, with clay-rich corrosion residue from back-reef beds, PL.

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 $\delta^{18}\text{O}$ from unaltered bedrock, but only -0.7‰ in $\delta^{13}\text{C}$ (Fig. 3, CW347br–CW347c). The $\delta^{18}\text{O}$ shift is caused by interaction with capillary water, and the $\delta^{13}\text{C}$ shift

Fig. 11. Detail of H_2SO_4 -micritized rind. A) Dolomitized micritic rind, Lechuguilla Cave, PL, red stain for calcite. B) Enlarged view of box in A: Corroded, dolomitized bedrock (above dashed line), PL. Fossil in rind shows that the rind was originally bedrock.

Fig. 12. Cueva de Villa Luz, Mexico: active micritization of bedrock (note fossils). Rind forms subaerially near an H_2S inlet and appears to be contemporary with replacive anhydrite-gypsum. A = PL. B = XP.

shows interaction with CO_2 absorbed from the cave air. Elsewhere in the cave, white micritized rinds up to 3 cm thick are produced on limestone where CO_2 -depleted water seeps into the cave and absorbs CO_2 from the cave air (Fig. 13; Palmer, 2007, p. 345). Both $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ 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 CO_3^{2-} (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

Fig. 13. Micritized limestone rind, Mammoth Cave, Ky., where low- CO_2 seepage has absorbed CO_2 from cave air. Despite different origin, isotopic shifts resemble those of Guadalupe rinds.

Fig. 14. Primary dolomite at H_2SO_4 solution front, Lechuguilla Cave. A) Dolomite rhomb at limestone-gypsum contact, XP, red stain for calcite. B) Primary dolomite rind in H_2SO_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.

has been synthesized at $>55^\circ\text{C}$ (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 Guadalupe.

If dolomite rinds form on limestone by simple replacement of Ca by Mg [i.e. $2\text{CaCO}_3 + \text{Mg}^{2+} \rightarrow \text{CaMg}(\text{CO}_3)_2 + \text{Ca}^{2+}$], 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 $\delta^{13}\text{C}$ from limestone, as in calcite rinds, but less so in $\delta^{18}\text{O}$ (Fig. 3, LG 212 & LG819). Differences in fractionation between calcite and dolomite may account for the smaller $\delta^{18}\text{O}$ shift.

Some dolomite rinds have formed instead by direct precipitation (Fig. 3, LG805br–LG805c; Fig. 14) and show a large contrast in $\delta^{13}\text{C}$ 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, $\sim 50\ \mu\text{m}$ 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 H_2S and 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 $\sim 15\ \text{cm}$ 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 Guadalupe show no rills clearly attributed to meteoric water flow.

Fig. 15. Late precipitates impregnating early micritic rind, Lechuguilla Cave, XP, red stain for calcite. 1 = bedrock; 2 = micritic H_2SO_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.

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.

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. $\delta^{13}\text{C}$ 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 $\text{Mn} > \text{Fe}$. 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. 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.

Fig. 18. Thin-section profiles of sediment in solution basins, Near East, Lechuguilla Cave, over a 6 m vertical range: 1, 2, 3 = highest to lowest. Red dye for calcite. A1 = limestone bedrock. A2 = dolomitized micritic crust. B = bedrock residue from H_2SO_4 corrosion (quartz silt, detrital carbonate, anhydrite laths). C = yellow, Fe-oxide-rich corroded bedrock from cave ceiling, dolomitized in Basin 3. D = mammillary crust, dolomitized in Basin 3. E = black, mainly Mn-oxide-rich, desiccation-cracked carbonate mud, absent in Basin 3. F = cave rafts, coated by 50 μm dolomite overgrowths and quartz in Basin 1; raft fabric and underlying mammillaries destroyed by evaporative dolomite in Basin 3, which ends upward in dolomite botryoids and chalcedony.

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 H_2SO_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.

Fig. 19. Basin 2C of Fig. 18: Fe-oxide-rich matrix around fossil shells corroded from ceiling. Fe oxide appears mottled (microbially?). A = PL, B = RL. C = enlarged view, PL.

Fig. 20. Microbial textures in basin fill. A) Layered domal Mn-oxide bodies at top of layer E, Basin 2, Fig. 18. PL. B) Fenestrae in layer C of Basin 1, cemented by mammillary calcite at top left, PL.

Calcite Replacement of Speleogenetic Gypsum

In scattered locations, calcite has replaced speleogenetic gypsum. The calcite consists of $\sim 200\ \mu\text{m}$ rhombs or blocky cement generally attached to bed-rock 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 sub-aqueous 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 $>20\ \text{m}$) like wallpaper. They coat all types of material, including the basin sediments described above. Their tops correlate over large areas and apparently represent former water-table stands, which correspond roughly to the lowest significant level of sulfuric acid speleogenesis ($\sim 1130\ \text{m}$ 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 back-reef 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. How-

ever, 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_2SO_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 $(\text{Fe}^{2+} + \text{Mn}^{2+})$ concentration of only $0.1\ \text{mg L}^{-1}$, 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 Guadalupe contain outward-facing shrub-like bodies apparently of microbial origin (Fig. 25D). Chafetz 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

Fig. 21. Invasive dolomite replacement of mammillary crust and bedrock below Basin 3, Lechuguilla Cave. Note irregular replacement front. Dolomite ends outward in evaporative chalcedony and finely crystalline dolomite. XP, red stain for calcite.

Fig. 22. Rusticles in the Near East of Lechuguilla Cave, have spilled from solution basins above to form the "Iron Curtain." These are bundles of microbial filaments lined with Fe-Mn oxides and coated by mammillary calcite (Photo by Mark Tracy).

Fig. 23. Calcite replacement of gypsum. A) Calcite containing debris from H_2SO_4 dissolution, Lechuguilla Cave (box enlarged in B), XP, red stain for calcite. B) Gypsum inclusion (gray) in calcite shows replacement of gypsum, XP. C) Calcite replacement of H_2SO_4 gypsum crust, Spider Cave. Corroded bedrock and Fe-Mn oxide strands (arrow) float in calcite that grades outward into a layered speleothem. Red dye for calcite, PL. D) Lechuguilla, XP: 1 = limestone, 2 = micritic rind, 3 = granular calcite after gypsum, with remnants of micritic rind and Fe-Mn oxide.

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 PCO_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 PCO_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 oxalic 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 μm -size crystals (Fig. 26). Except in certain mammillaries (Fig. 26 B & C), our samples of Guadalupe wall coatings show no evidence of former pyrite.

Fig. 24. Mammillary crust, Western Borehole, Lechuguilla Cave. Calcite sheets peel away from wall along Fe-Mn oxide laminae. Height of photo ~2.5 m.

Fig. 25. Mammillary crust in the Near East of Lechuguilla Cave has at least nine layers of Fe-Mn oxides. A) Bedrock coated with crust, PL, red stain for calcite. B) Enlarged view. Note domal, microbial (?) Fe-oxide-coated bodies (arrow). PL. C) Same, but RL. D) Layer in mammillary crust, Carlsbad, containing Fe-Mn-oxide shrubs, RL.

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 $\delta^{18}\text{O}$ values in the water vapor relative to pool water. Water in Lake of the Clouds has $\delta^{18}\text{O} \sim -6.8\text{‰}$ VSMOW (Ingraham et al., 1990), and if the overlying vapor were in equilibrium with the pool, the vapor would have $\delta^{18}\text{O}$ of -16.4‰ (computational method in Faure & Mensing, 2005). In this case no more evaporation would be possible. Instead, the overlying water vapor has $\delta^{18}\text{O} \sim -18.2\text{‰}$ (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 $\delta^{18}\text{O}$ of evaporative water as much as $+10\text{‰}$ (Bottinga & Craig, 1969). In surface rainfall the earliest drops remove the most positive

Fig. 26. Pyrite wall crust. A) Villa Luz. Wall coating below water level consists of Fe oxides after pyrite near H_2S inlet, PL. Fe oxide penetrates bedrock. Note lack of calcite precipitates and tiny Fe oxide cubes after pyrite (arrow). B) Outermost mammillary layer in Basin 3, Lechuguilla (Fig. 18), contains 5 µm Fe-oxide crystals, linked in a branching (microbial?) mass, similar to A, PL. Cave wall is toward the top. C) Enlargement of B, RL. Pyrite may have resulted from local sulfate reduction.

Fig. 27. The "popcorn line" in Left Hand Tunnel, Carlsbad Cavern. Walls and ceiling above are corroded, while botryoidal calcite is precipitated below.

$\delta^{18}\text{O}$ 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 $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ 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 CO_2 -rich air (Fig. 29A). Corroded zones are fertile ground for microbially 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 sub-aerial 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‰ ($\delta^{18}\text{O}$) and -2.1‰ ($\delta^{13}\text{C}$) in the 5 mm white rind (SP808A). The significant change in $\delta^{13}\text{C}$ shows interaction with sub-aerial CO_2 . 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 con-

densation water. Where evaporation is limited, cementation is poor or absent, because condensation water is already at equilibrium with cave air and CO_2 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 $\delta^{18}\text{O}$ 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 $\delta^{18}\text{O}$ of roughly -8‰ VPDB, more negative than typical drip-stone. But as evaporation proceeds, ^{16}O is selectively removed from the water and $\delta^{18}\text{O}$ 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-

Fig. 28: Residue from condensation corrosion in Spider Cave. A) Passage in backreef beds weathering to silt, clay, and Fe-Mn oxides. Much residue falls to the floor. Carbonate bedrock weathers light gray, finely crystalline, and fluffy. Calcite spar in bedrock is corroded to needles along the cleavage. B) Enlarged view; width = 0.3 m.

Fig. 29. A) Vadose speleothems in Spider corroded by condensation water, overlying older residue of silty clay and Fe-Mn oxides. Width = 0.7 m. B) SEM image of speleothem corroded by CO_2 -rich condensation moisture. Intricate internal skeletal porosity is typical. The earlier H_2SO_4 micritic rind predates speleothems and is usually indurated (see Fig. 4).

oric infiltration or condensation). Carbonate deposits around evaporative pools, fed by meteoric drips, grade outward from pasty hydromagnesite, huntite, dolomite and aragonite to indurated popcorn. Far from the water source, these minerals are accompanied by montmorillonite (smectite) and palygorskite clays typical of low-moisture alkaline conditions. The latest evaporative deposits are typically euhedral quartz, chalcedony, or opal. Many speleothems, including mammillaries, end outward in dolomite. Some evaporative aragonite and dolomite contain scattered $\sim 500 \mu\text{m}$ barite crystals (by-product of acid clay alteration?) accompanied by Fe-Mn oxides and siliceous residue (Fig. 31A). See Polyak & Provencio (2001) for a description of other evaporative minerals.

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, $\delta^{18}\text{O} = -3.6$ 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 $\delta^{18}\text{O} = -3.5$ 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 CO_2 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 $\delta^{13}\text{C}$ that reveals long-term carbon exchange between cave-air CO_2 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 $\delta^{13}\text{C}$ 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 Guadalupe; 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 H_2SO_4 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

Fig. 30. Recrystallized speleothems. A) Vandalized stalagmite in Spider with white micritized rind overlying recrystallized interior. Both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ are lower in the rind (Fig. 3, SP 808a-b). B) Glassy recrystallized popcorn (Fig. 3, LG 344) has anomalously low $\delta^{13}\text{C}$ from precipitation in condensation water, with almost no CO_2 degassing.

Fig. 31. Late-stage exotic minerals. A) Barite (gray) in floor crust, Left Hand Tunnel, Carlsbad Cavern. Red stain for calcite, XP. B) Fluorite crystals (black, isotropic) line carbonate popcorn, Lechuguilla, XP. Fluorite crystals are also found on gypsum elsewhere in the cave.

half contains many solution basins, and near the bottom are rafts and folia, but no mammillaries. This and a few similar routes were active long after most of the 4 Ma level (at roughly 1130 m in Fig. 2) had ceased to enlarge.

So far we see no evidence of anomalous sources of CO_2 . These would likely produce features with significantly lower $\delta^{13}\text{C}$ than those in Fig. 3. For example, Kirkland & Evans (1976) ascribe the origin of limestone buttes in the nearby Delaware Basin to reduction of gypsum by rising natural gas, resulting in a mean $\delta^{13}\text{C}$ of -24‰ , far below the values in Fig. 3. Trace amounts of gases such as SO_2 , COS , and CS_2 are present in Lechuguilla (LaRock & Cunningham, 1990), but there is so far no evidence that they have affected the cave or pose a danger.

The only mineralogical evidence we find for late-stage hypogenic gases (other than H_2S) consists of sparsely scattered 200 μm crystals of fluorite (CaF_2) on surfaces of gypsum and carbonate popcorn (Fig. 31B). The fluorite is not detrital, because its crystals have nucleated on the substrate, with euhedral faces extending outward. Concentration of fluoride is best explained by an influx of HF gas. Absorption of HF by droplets of condensation water in windy areas can concentrate the hydrofluoric acid and allow reactions with Ca-bearing minerals.

HF gas can be liberated by the attack of fluorine-bearing minerals by H_2S or H_2SO_4 (Maltsev and Korsunov, 1998). We first considered detrital fluorapatite [$\text{Ca}_5(\text{PO}_4)_3\text{F}$] 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.

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Appendix 1. Identification of samples in Fig. 1, showing approximate composition (from X-ray diffraction and EDS). Calcite, aragonite = CaCO_3 ; dolomite = $\text{CaMg}(\text{CO}_3)_2$; huntite = $\text{CaMg}_3(\text{CO}_3)_4$; hydromagnesite = $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$; quartz = SiO_2 .

Sample	Composition (%)						Description
	calcite	aragonite	dolomite	huntite	hydro-magnesite	quartz	
CB 801			72			28	finely crystalline precipitate after aragonite
CB 803	100						finely crystalline precipitate
CB 808			60			40	finely crystalline precipitate
CB 813	100						corroded winged vent
CB 822c	100						bedrock alteration rind
CB 831			97			3	popcorn
CB 839	25		75				finely crystalline precipitate with sepiolite
CB 841c	94					6	corroded bedrock
CB 842a	85		15				botryoids
CB 842b		51	49				botryoids
CB 845			97			3	finely crystalline blister
CB 853		10			90		finely crystalline precipitate bordering pool
CB 855		100					finely crystalline precipitate bordering pool
CB 857		10	90				finely crystalline precipitate in pool
CB 903	41	8	51				finely crystalline precipitate after aragonite
CB 905	9		89			2	finely crystalline precipitate around drip cone
CB 909			100				finely crystalline precipitate
CB 915a	92		8				finely crystalline precipitate (top)
CB 915b	97		3				finely crystalline precipitate with sepiolite
CB 915c	95		5				finely crystalline precipitate with sepiolite
CB 915d	100						finely crystalline precipitate (base)
CB 917b	5	9			86		drip cone
CB 932	90	10					subaerial rim
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					14	glassy crystals
LG 357a	3		97				finely crystalline precipitate
LG 357b			100				finely crystalline precipitate
LG 801	9		66			25	finely crystalline blister
LG 805			100				mammillary crust
LG 805br	100						limestone bedrock
LG 805a	17		80			3	botryoidal basin fill
LG 805b			100				basin fill
LG 805c	40		60				basin fill
LG 813a			90	10			finely crystalline pool precipitate
LG 813b			10	90			finely crystalline pool precipitate
LG 819			100				bedrock alteration rind
LG 847	11		89				mammillary crust
SP 808a	100						stalactite, corroded rind
SP 808b	100						stalactite, recrystallized interior