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SULFURIC ACID SPELEOGENESIS AT THE NEW SECTION LEVEL OF CARLSBAD CAVERN ROUGHLY 6 MA

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Abstract—Alunite is a byproduct of the sulfuric acid speleogenesis of Carlsbad Cavern and other caves in the Guadalupe Mountains. It forms by the sulfuric acid alteration of clays of the illite and smectite groups hosted in the bedrock. Therefore, dating the alunite using $^{40}Ar/^{39}Ar$ determines the timing of speleogenesis and the position of the water table where, by our interpretation, speleogenesis largely takes place. In the Carlsbad Cavern–Lechuguilla Cave region, three "alunite levels" are known at 1230 m (6 Ma), 1180 m (5 Ma), and 1120 m (4 Ma). Even though Carlsbad Cavern has a large vertical extent, until now, only one "alunite level" has been documented (the Big Room level; 4 Ma). Here we report an age of natroalunite from the New Section of 5.7±0.1 Ma at 1210 m, which is largely consistent with the 6 Ma level. With a relatively flat water table setting back to 6 Ma within the Capitan aquifer and mass wasting rates for the Guadalupe Mountains, we interpret an incision rate of the Pecos River between 48 and 18 m/Ma in this region east of the mountain range, given that the river existed that far back.

INTRODUCTION

Timing of sulfuric acid speleogenesis (SAS) in the Guadalupe Mountains correlates well with elevation of the alunite/natroalunite deposits in those caves mainly formed by sulfuric acid (Polyak et al., 1998) often referred to as "sulfuric acid caves." This is due to (1) alunite being a byproduct of SAS and a dateable mineral, and (2) Miocene to Pliocene uplift and tilt of the Guadalupe Mountains tectonic block. The timing of SAS from 12 to 4 Ma reported by Polyak et al. (1998) is coincident with deposition of the Ogallala Formation and possible entrenchment of that formation by the early Pecos River (Hawley, 1993). Of the numerous SAS caves, the two largest, Carlsbad Cavern and Lechuguilla Cave, have the greatest vertical extents (>300 m and >450 m, respectively). In Lechuguilla Cave there are three dated levels of speleogenesis that produced alunite (alunite levels) at 1230, 1180, and 1120 m (above sea level) that define SAS that took place ~6, ~5, and ~4 Ma, respectively. In contrast, there is only one alunite level in Carlsbad Cavern at 1120 m that has been dated (~4 Ma). With a bigger entrance and evidence of large amounts of debris washing into Carlsbad Cavern over its history, most SAS byproduct materials have been removed from the upper parts of the cave. Here we report another alunite level in Carlsbad Cavern from the New Section. These alunite levels developed, as the caves did, along the water table, and therefore the timing and position of water tables at these times have potential to produce information about the geologic history of the Pecos River in southeastern New Mexico.

In the New Section near station G59, the walls of the cave are sandstone. The elevation at G59 is ~1210 m, which approximately correlates with the elevation of the Yates Formation sandstone just to the north of Carlsbad Cavern in Walnut Canyon. The New Section is part of the Guadalupe Room complex, which also includes Chocolate High and the Guadalupe Room, and is located at the northernmost extension of Carlsbad Cavern toward Walnut Canyon. Therefore, it is likely that the sandstone in the New Section is a Yates Formation sandstone tongue. One mile to the west is Spider Cave. This cave is capped by a sandstone unit at the same elevation, which is also probably a Yates Formation sandstone. Samples vp-2005-14 and -15 that contain natroalunite were collected from bedrock pockets in the sandstone walls near station G59 (Fig. 1) in the New Section. In some of these pockets, bluish hydrated halloysite (endellite) can be observed (Fig. 1). Near this area are zenithal ceiling tube-holes (Calaforra and De Waele, 2011)

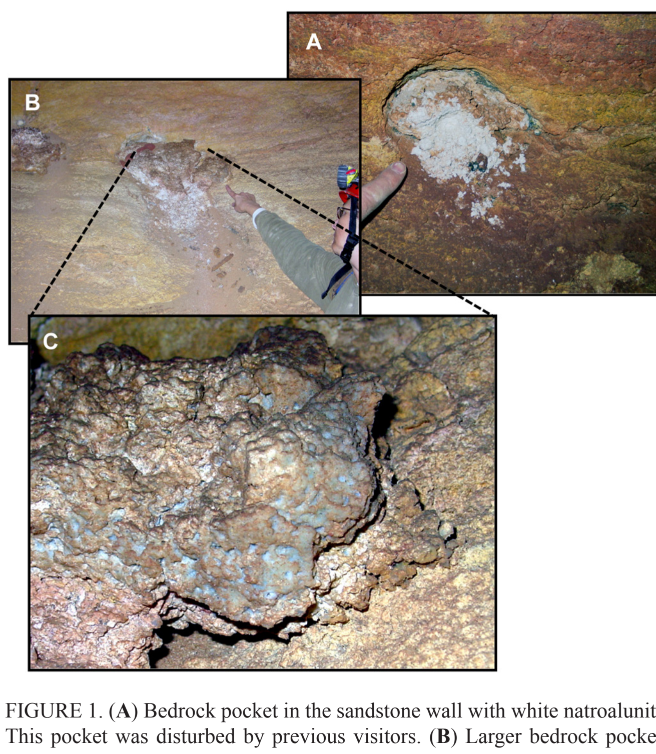

FIGURE 1. (**A**) Bedrock pocket in the sandstone wall with white natroalunite. This pocket was disturbed by previous visitors. (**B**) Larger bedrock pockets that have not been disturbed. Nothing was collected from the pristine pockets. (**C**) Inset of (**B**) exhibiting a bluish tint of hydrated halloysite.

and secondary chert deposits, both evidence of SAS (Fig. 2). This New Section level is also roughly coincident in elevation with alunite levels in Lechuguilla and Endless Caves that have $^{40}Ar/^{39}Ar$ dates of 6 Ma (Polyak et al., 1998).

RESULTS

Samples vp-2005-14 and -15 contain hydrated halloysite and natroalunite, both of which are byproducts of SAS (Polyak and Provencio, 2001). The natroalunite was separated for $^{40}Ar/^{39}Ar$ dating using a 25% HF solution, which was added to the sample for two hours, then centrifuged. The liquid containing dissolved impurities was decanted, and the separate was washed twice with 18 megaohm water, dried, and X-rayed. The XRD pattern showed nearly pure natroalunite (Fig. 3), which is the Na endmember of the alunite group (Roberts et al., 1990). Transmission electron microscopy and energy dispersive spectroscopy show pseudo-cubic rhombs of natroalunite crystals that contain minor amounts of K. Alunite is the K endmember of the alunite group minerals and is the most suitable for $^{40}Ar/^{39}Ar$ dating. Samples vp-2005-14 and -15, which are natroalunite, are not pure Na endmembers and contain enough K for dating. Two dates were measured at the New Mexico Geochronology Research Laboratory at the New Mexico Institute of Mining and Technology in Socorro, New Mexico. The $^{40}Ar/^{39}Ar$ age spectra show plateaus at 5.7±0.1 Ma for sample vp-2005-14 and 6.9±0.4 Ma for sample vp-2005-15. Integrated ages are 5.4±03 and 6.2±0.5 Ma, respectively (Fig. 4). The vp-2005-14 age plateau is tighter and appears better behaved, and thus, it probably represents the best age for the New Section SAS alunite level. The difference in ages likely represents inadequate amounts of K in sample vp-2005-15, but it could

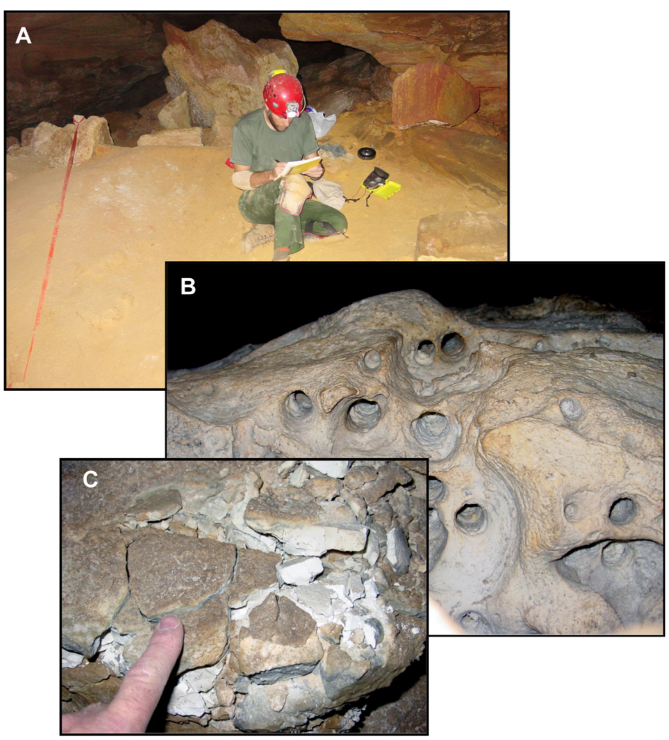

FIGURE 2. (**A**) Yellowish-orange floor sediment and rocks indicate that some of the New Section passage was formed in sandstone, probably the Yates Formation. Stan Allison for scale. (**B**) Bellholes in the ceiling of passage and (**C**) chert are indicators of sulfuric acid speleogenesis.

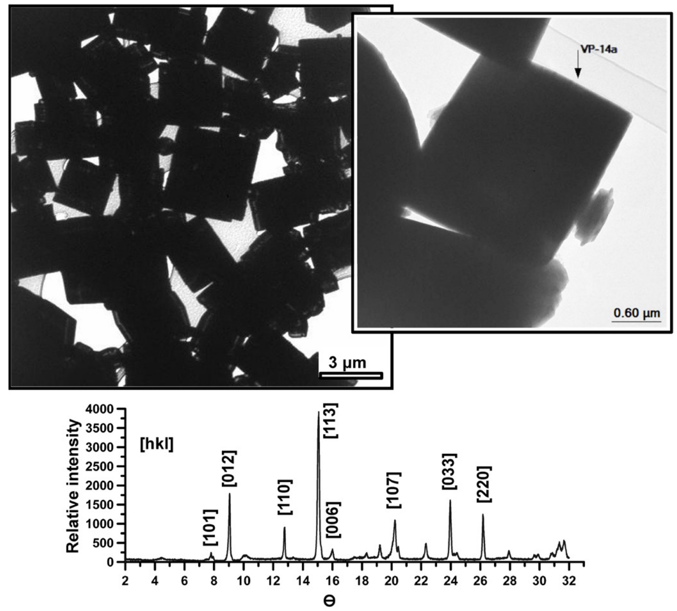

FIGURE 3. Transmission electron microscope image of natroalunite from the New Section (vp-2005-15) around 6 Ma. The crystals are µm-sized pseudo-cubes after processing with HF acid, which removes clay and other associated materials. The XRD pattern shows mostly purified natroalunite after treatment.

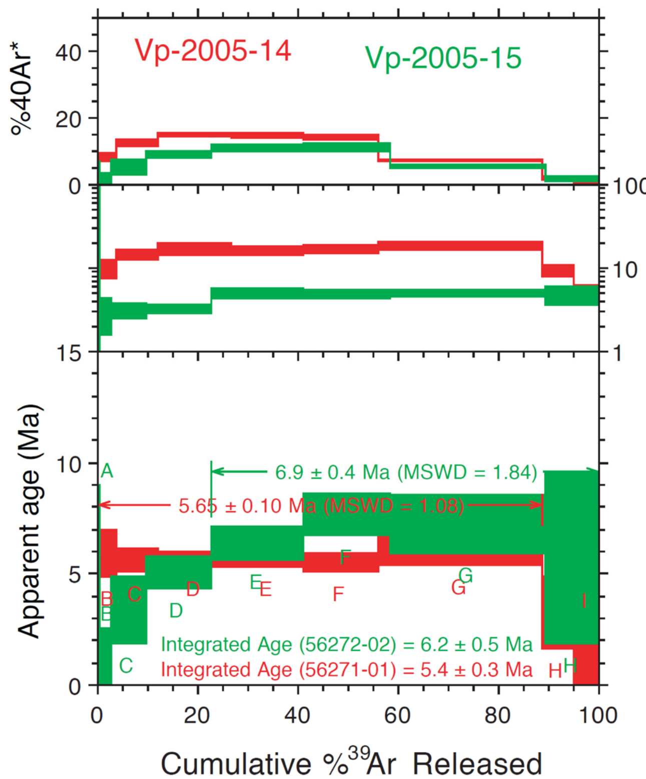

FIGURE 4. $^{40}Ar/^{39}Ar$ age spectra for the two natroalunite samples (vp-2005-14 and -15) from the New Section, Carlsbad Cavern. The results show that vp-2005-15 has considerably higher K/Ca than vp-2005-14. Both ages are centered around 6 Ma.

also reflect a timing of speleogenesis that extended at this level from ~6.9 to ~5.7 Ma. The importance of the natroalunite dates is that the timing of SAS at the New Section level centers near 6 Ma, as interpolated by the elevation of that level.

DISCUSSION

SAS byproducts are preserved in the Guadalupe Room complex of Carlsbad Cavern, and dating of alunite-group minerals in these byproducts has potential to define two new levels of SAS, the New Section level and the Guadalupe Room level. These two levels are equivalent in elevation to levels in Lechuguilla and Endless Caves, where the Guadalupe Room level is located equivalent to the 5 Ma level in Lechuguilla Cave and the New Section level is located equivalent to the 6 Ma level in both Lechuguilla and Endless Caves. Here, we have natroalunite in the New Section dated at 5.7 Ma, just below the 6 Ma level in Lechuguilla and Endless Caves (Fig. 5). Blue hydrated halloysite in the Guadalupe Room almost certainly has alunite-group minerals associated with it, showing that the 5 Ma alunite level might exist in Carlsbad Cavern as well, but those deposits have not been collected and dated.

The 6, 5, and 4 Ma alunite levels in Carlsbad, Lechuguilla, and Endless Caves show that these SAS events took place at the same elevations, which indicates that the water table of the Capitan aquifer was reasonably flat during these periods of SAS. Today, the water table in the Capitan aquifer between the Pecos River and these caves is relatively flat, given that the elevation of the Lake of the White Roses in Lechuguilla Cave believed to be the water table, is the same elevation as the Pecos River just south of the city of Carlsbad (Davis, 2000; Hill, 1987). This same setting 6–4 Ma suggests that the Pecos River, given it existed at this time, was at the same relative elevation as SAS and that the river has incised roughly 285 m (1230–945 m asl) in the past 6 Ma, an incision rate of ~48 m/Ma. For the past 4 Ma, the incision rate of the Pecos River is calculated to be 39 m/Ma. DuChene and Martinez (2000) determined an ~18 m/Ma downcutting rate of canyons on the eastern portions of the Guadalupe Mountains, which could represent a minimum incision rate. Given the Pecos River is ≥6 Ma (Hawley, 1993), the incision rate of the Pecos River could be as much as 48 m/Ma. Nevertheless, if there was uplift in the past 6 Ma, then this measured incision rate would be considered a maximum rate. We interpret that the Pecos River has incised sediment/bedrock at a rate between 48 and 18 m/Ma over the last 6 Ma in the Guadalupe Mountains region.

The overall timing of SAS in the Guadalupe Mountains (12 to 4 Ma; Polyak et al., 1998) is coeval with the timing of hydrothermal jarosite deposits related to Rio Grande Rift tectonic activity (10 to 0.4 Ma; Lueth et al., 2005), with the vast majority of the jarosite dates ranging from 7 to 3 Ma. The largest caves in the Guadalupe Mountains, Carlsbad, Lechuguilla, Spider, and the McKittrick Hill Caves, formed between 7 and 3 Ma toward the northeastern end of the mountain range. However, as DuChene and Martinez (2000) point out, the larger caves at higher elevations to the southwest were likely removed or fragmented by the greater mass wasting that has occurred over the last 12 Ma, compared to the northeastern end of the mountain range where the larger caves are located. Nevertheless, as suggested by Lueth et al. (2005), the SAS events that formed the

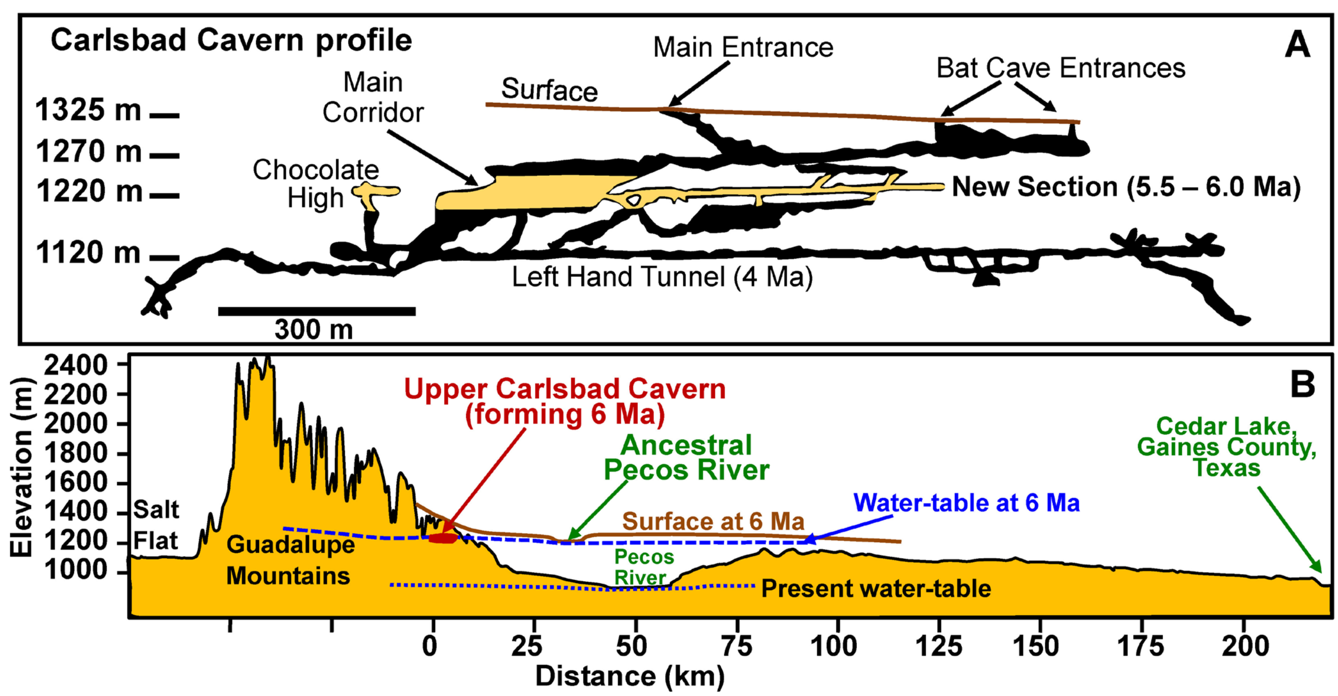

FIGURE 5. (**A**) West-east cross section of Carlsbad Cavern modified after CRF (1992) and Killing-Heinze et al. (2017). The yellowish-orange zone represents the parts of Carlsbad Cavern that formed by sulfuric acid speleogenesis ~6 Ma. Much of the Main Corridor and Chocolate High would have formed at this time, as well as nearby Spider Cave, Endless Cave, and portions of Lechuguilla Cave at this same 1210 m elevation. (**B**) West-to-east profile of the Guadalupe Mountains and southern High Plains showing the Pecos River Valley. A water table interpreted to have existed 6 Ma is placed on this profile through upper Carlsbad Cavern when this part of the cave was forming by sulfuric acid speleogenesis. This scenario provides a conceptual framework for the evolution of the Pecos River, if it existed 6 Ma.

large caves in the Guadalupe Mountains are probably linked to tectonic activity. Decker et al. (2018) interpreted the origin of hypogene spar caves and the hydrothermal calcite crystals (cave spar) that form druses in these caves formed at depth from upwelling CO_2 to have been triggered by tectonic and magmatic activity. Likewise, Polyak et al. (2017) presented a model for speleogenesis of Grand Canyon phreatic caves and the byproducts related to the origin of those caves to tectonic/magmatic activity. All of this supports a link between SAS events in the Guadalupe Mountains region and tectonic/magmatic activity, and the timing of these events indicates that this activity was related to Rio Grande Rift tectonism.

Regarding the overall origin of caves in the Guadalupe Mountains, a few renditions have been offered (DuChene and Cunningham, 2006; DuChene et al., 2017; Hill, 1987; Klimchouk, 2007; Palmer and Palmer, 2000; Polyak et al., 1998). Of these, two basic frameworks exist, which are the Alvarado Ridge model and the Basin and Range model. The Alvarado Ridge model suggests that a broad regional ridge formed before the Miocene that existed north and south along the Rio Grande Rift. In this model, DuChene and Cunningham (2006) suggest that the "Guadalupe Mountains tectonic block" was uplifted and tilted by the origin of the Alvarado Ridge roughly 35 Ma and that the water table slowly dropped down through the tilted strata. Klimchouk (2007) used this model to suggest that most of the large caves in the Guadalupe Mountains formed earlier than the Middle Miocene by hypogene speleogenesis that did not involve sulfuric acid, and that the sulfuric acid event was late stage along the water table and only modified the already existing large caves by enlarging them and depositing gypsum and alunite. The Basin and Range model suggests that the Guadalupe Mountains tectonic block was uplifted incrementally during the Miocene. Cave spar dated by U-Pb produce ages equal to or greater than 28 Ma on the higher southwestern end of the Guadalupe Mountains, suggesting that uplift of this tectonic block was initiated after 28 Ma and before deposition of fault spar in the Border Fault zone that yielded an age of 17 Ma (Decker et al., 2018). In this model, the Guadalupe Mountains undergo tectonic uplift in the Miocene, but there are likely incremental pulses of greater magmatic and tectonic activity that led to larger volumes of H_2S being oxidized near the water table, periodically forming sulfuric acid, large caves, and alunite and jarosite deposits.

VP-2005-14 and -15 collected near Sta G59 in the New Section of Carlsbad Cavern on the way to the Guadalupe Room consist of byproducts of SAS such as the alunite group minerals, for which natroalunite is the Na-rich endmember. $^{40}Ar/^{39}Ar$ ages of natroalunite from the New Section represent the timing of the SAS of the New Section along the water table as well as other passages in Carlsbad Cavern at that level ~6 Ma. SAS at ~6 Ma in Carlsbad Cavern, Lechuguilla Cave, and Endless Cave supports an interpretation that the water table was relatively flat in the Capitan aquifer. Therefore, Spider Cave, also at this 6 Ma elevation, likely formed during this time, and the Pecos River, if it extends back this far in time, was also at this level.

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