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SUMMARY OF THE TIMING OF SULFURIC-ACID SPELEOGENESIS FOR GUADALUPE CAVES BASED ON AGES OF ALUNITE

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The H_2SO_4 caves in the Guadalupe Mountains, New Mexico, USA, such as Carlsbad, Cottonwood, Endless, Lechuguilla, and Virgin caves, formed during the late Miocene and early Pliocene (12-4 Ma). It has been demonstrated that the caves at the higher elevations are the oldest. The timing of speleogenesis was determined by the $^{40}Ar/^{39}Ar$ dating of the mineral alunite, which is a direct by-product of H_2SO_4 speleogenesis.

Five caves (Carlsbad, Cottonwood, Endless, Lechuguilla, and Virgin) in the Guadalupe Mountains of southeastern New Mexico, U.S.A., contain by-products of their H_2SO_4-related origin (Fig. 1). See Hill (2000) for an overview of the geology of these caves, and Jagnow *et al.* (2000) for a history of how this theory of speleogenesis developed for Guadalupe caves.

Caves formed by carbonic acid dissolution of limestone or dolostone usually leave no material trace of their origin. As Sasowsky (1998) noted, determining the age of what is not there has been a difficult task. However, caves formed by sulfuric acid-bearing water (H_2SO_4-speleogenesis) contain direct by-products of their origin. In the Guadalupe caves, Egemeier (1973) and Jagnow (1977) reported gypsum as a by-product of H_2SO_4-speleogenesis, and Hill (1987) reported gypsum and endellite (hydrated halloysite). More recently, Palmer & Palmer (1992), Polyak & Güven (1996), and Polyak & Provencio (1998) have reported that alunite, and other by-products such as hydrobasaluminite, also occur in these caves. Of these, alunite, $KAl_3(SO_4)_2(OH)_6$, is unique because it contains potassium which gives it the potential to be dated by the K-Ar or $^{40}Ar/^{39}Ar$ dating methods.

Alunite was sampled from Carlsbad, Cottonwood, Endless, Lechuguilla, and Virgin caves. William C. McIntosh at New Mexico Tech in Socorro, New Mexico used $^{40}Ar/^{39}Ar$ to date the fine-grained alunite from the Guadalupe caves (methods are found in Polyak *et al*. 1998). The deposits suitable for dating contained alunite (1-10 µm-sized crystals) mixed with hydrated halloysite (endellite). Purified samples (where the halloysite was removed) contained only tightly packed alunite.

Alunite can form by the alteration of aluminum- and potassium-bearing materials such as aluminosilicates (clays) in an environment of sulfide oxidation; i.e., high Eh, low pH (Kelepertsis 1989; Long *et al.* 1992; Rye *et al.* 1992). Similarly, during H_2SO_4-speleogenesis of the Guadalupe caves, alunite formed by sulfuric acid interaction with clays that contain potassium–clays such as illite and montmorillonite (Polyak & Güven 1996). For instance, in the Green Clay Room of Carlsbad Cavern, alunite was produced by the alteration of montmorillonite-rich clay. An alteration reaction for this situation may be expressed as follows:

$$2\ H_2SO_4 + 3[(K,Na)(Al_{1.24}Mg_{0.47}Fe_{0.29})(Si_{3.56}Al_{0.44})O_{10}(OH)_2 \cdot nH_2O]$$
$$\Leftrightarrow \quad 1\ [(K, Na)Al_3(SO_4)_2(OH)_6] + 1\ [Al_2Si_2O_5(OH)_4 \cdot 2(H_2O)]$$
$$+ 9\ SiO_2 + \text{residual } (Na^+, K^+, Fe^{2+}, Mg^{2+})$$

where the formula for the clay was determined from energy dispersive X-ray microanalysis of montmorillonite containing small amounts of illite and kaolinite. In these caves, the alteration reaction ceased when the supply of H_2SO_4 was terminated.

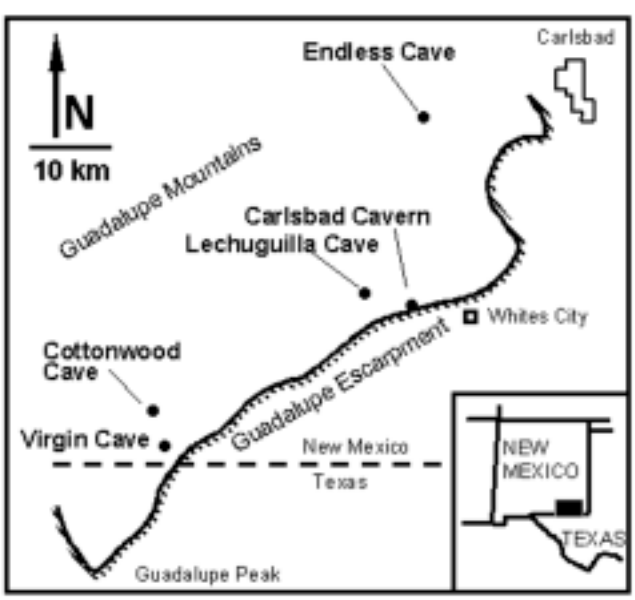

Figure 1. Study area map showing general location of five caves where the mineral alunite was collected.

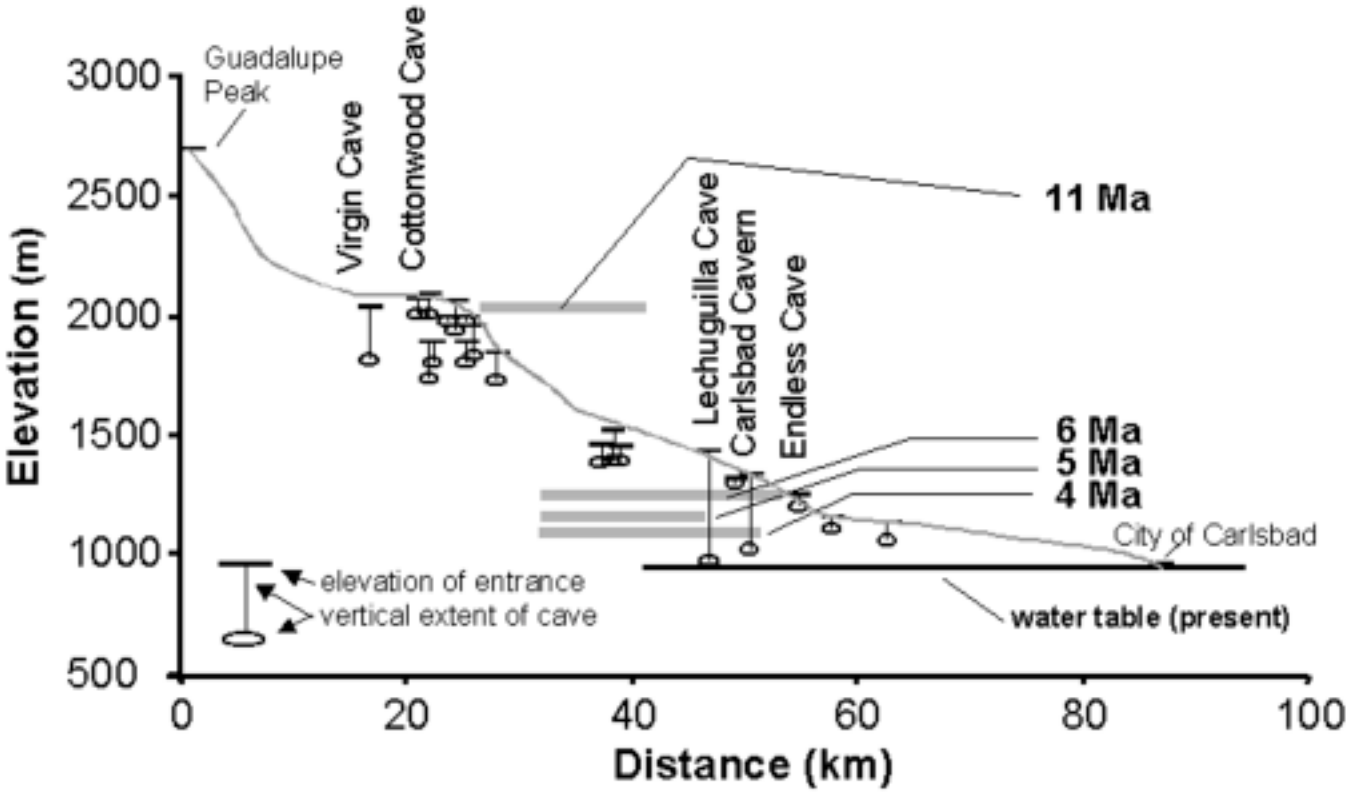

Figure 2. Profile of the Guadalupe Mountains from Guadalupe Peak to the city of Carlsbad. Locations of major caves are plotted on the profile according to their elevation. The gray line from Guadalupe Peak to the city of Carlsbad represents the surface elevation in the Guadalupe Mountains along the Guadalupe Ridge and the Capitan reef escarpment. Note the four elevation intervals where the timing of H_2SO_4-influenced speleogenesis has been established.

TIMING OF H_2SO_4-INFLUENCED SPELEOGENESIS

$^{40}Ar/^{39}Ar$ ages of alunite from Carlsbad, Cottonwood, Endless, Lechuguilla, and Virgin caves indicate that H_2SO_4-speleogenesis took place from the late Miocene to early Pliocene (12-4 Ma). These data represent four elevation intervals of speleogenesis (Fig. 2). Alunite in Cottonwood and Virgin caves at the higher elevations, 2000-2040 m, dates from 12.3 to 11.3 Ma (oldest dates). Two levels of Lechuguilla Cave are represented by alunite ages of 6.0 (Glacier Bay at an elevation of 1230 m) and 5.2 Ma (Lake Lebarge at an elevation of 1150 m). Glacier Bay in Lechuguilla Cave and Endless Cave, both at the same elevation of 1230 m, provided the same alunite age, ~6 Ma, even though they are located >20 km apart. Alunite from the Big, Green Clay, and New Mexico rooms of Carlsbad Cavern, at the elevation interval of 1090-1120 m, all have ages of 4.0-3.9 Ma. See Polyak *et al*. (1998) for a complete table and description of the age data.

CONCLUSION

H_2SO_4-speleogenesis took place at or near the water table (Hill 1987; Palmer & Palmer 2000). The relationship of the alunite ages with respect to elevation of the caves suggests an 1100-m apparent decline in the water table from 12 Ma to the present (Polyak *et al*. 1998). These correlations suggest that the Capitan aquifer water table was relatively flat during the late Miocene and Pliocene in areas of speleogenesis. Caves formed by the H_2SO_4-speleogenesis at any given period are located along the same elevation, as depicted by Jagnow & Jagnow (1992). Knowing the absolute timing of H_2SO_4 speleogenesis for the Guadalupe caves provides a framework for resolving long-sought questions regarding the caves and the mountains.

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