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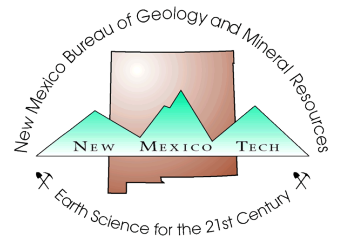
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# Origin of gypsum deposits in Carlsbad Caverns, New Mexico

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## Abstract

Gypsum within the Big Room of Carlsbad Caverns is greatly depleted in sulfur-34. This fact precludes most previously hypothesized origins for the gypsum and indicates that microbial agents played a part in its origin. The gypsum apparently resulted from reaction of calcium carbonate with sulfuric acid, which may have resulted from oxidation of pyrite in sandstone and siltstone of the Yates Formation (a mechanism proposed by Jagnow, 1979). An alternate explanation is that ground water bearing hydrogen sulfide moved from the Castile Formation into the phreatic zone of the cavern where the hydrogen sulfide was oxidized to yield elemental sulfur; with a lowering of the groundwater table, the sulfur, in turn, was oxidized to sulfuric acid within the vadose zone.

## Introduction

The source of large quantities of gypsum within Carlsbad Caverns and within some other caves of the Guadalupe Mountains is not fully understood. Various origins have been proposed (Bretz, 1949; Black, 1954; Good, 1957; Moore, 1960; Bullington, 1968; Palmer and others, 1977; Jagnow, 1979). Measurements of the sulfur isotopic composition of gypsum from Carlsbad Caverns indicate that most of these hypothesized origins are invalid.

## The gypsum masses

Several chambers within Carlsbad Caverns contain gypsum; the greatest volume occurs within the Big Room. In this chamber, tabular bodies of unstratified gypsum, up to 10 m thick, are sporadically distributed (Good, 1957). Within the gypsum blocks, vertical tubes, some with lengths in excess of 3.7 m and with diameters ranging from 2.5 cm to 30 cm, have formed by dripping water; some large blocks have lost more than 50% of their bulk by this action (Bretz, 1949). Those gypsum blocks that remain in the room usually lie in protected alcoves or under overhanging ceilings (Black, 1954), and locally the blocks are covered by flowstone and by stalagmites (Bretz, 1949; Good, 1957).

The gypsum masses of Carlsbad Caverns are thought by Palmer and others (1977) to be direct replacement of limestone—the Capitan Limestone of Late Permian (Guadalupian) age—with some blocks of gypsum displaying petrographic features of the carbonates such as pisolites, fossils, breccias, and primary pores. Jagnow (1979, p. 45), on the other hand, reports that the gypsum accumulated during a period of thousands of years by precipitation and sedimentation within ponded waters.

## Sulfur isotopic data

Six samples of gypsum were obtained (with permission) from the Big Room (fig. 1). The samples have an average  $\delta^{34}\text{S}$  value of  $-18.1$  parts per thousand (‰) and a range of  $-15.0$  ‰ to  $-22.0$  ‰ (table 1.) [Sulfur isotopic

data are reported in terms of  $\delta^{34}\text{S}$ , which represents the deviation of the  $\text{S}^{34}\text{-to-S}^{32}$  ratio in parts per thousand (‰) from the value 0.0450045, this value being the  $\text{S}^{34}\text{-to-S}^{32}$  ratio of sulfur in a standard troilite (FeS) in iron meteorites from Canyon Diablo, Arizona; the delta convention indicates that samples are enriched (positive  $\delta^{34}\text{S}$  values) or depleted (negative  $\delta^{34}\text{S}$  values) in sulfur-34 with respect to the standard.]

Upper Permian marine evaporites from west Texas and from other areas of the world have  $\delta^{34}\text{S}$  values with a mode of about  $+11$  ‰ (Thode and Monster, 1965; Holser and Kaplan, 1966; Claypool and others, 1980); the range for Upper Permian marine evaporites worldwide is  $+9$  ‰ to  $+13$  ‰,  $n = 200$  (Claypool and others, fig. 5). Thus, the sulfur isotopic composition of gypsum samples from the cave are markedly impoverished in sulfur-34 as compared to nearby bedded gypsum units of Permian age (Tansill, Yates, Castile, and Salado Formations).

A popular explanation for the gypsum of the caverns has been that it is derived from bedded marine evaporites nearby by dissolution, transportation, and reprecipitation (Bretz, 1949; Black, 1954; Bullington, 1968). The sulfur isotopic data presented in table 1 preclude this possibility. The data also preclude Good's (1957) proposal that warm water within a shallow, calcium-sulfate-saturated lake entered the cave through sub-

surface channels where, upon cooling, gypsum precipitated.

The gypsum of Carlsbad Caverns must have been derived from a sulfide formed by microbial reduction of a sulfate. No other mechanism is known that could reasonably account for the unusual isotopic signature of the mass of gypsum within the caverns. Microbial reaction leads to enrichment of sulfur-34 in residual sulfate and to depletion, commonly substantial, of sulfur-34 in diagenetic sulfide (Thode and others, 1954; Jones and Starkey, 1957).

TABLE 1—SULFUR ISOTOPE VALUES FOR GYPSUM SAMPLES; sample localities are shown in fig. 1.

Sample number	$\delta^{34}\text{S}$ ‰
1	-18.9
2	-15.2
3	-18.3
4	-19.3
5	-22.0
6	-15.0

## Origin of gypsum

Two hypothesized origins for the gypsum deposits of the Big Room of Carlsbad Caverns are in accord with the sulfur isotopic data (table 1). Both hypotheses involve reaction of calcium carbonate with sulfuric acid. This acid apparently resulted from either oxidation of pyrite (as proposed by Jagnow, 1979) or from oxidation of elemental sulfur.

The Yates Formation grades into and overlies the Capitan Limestone in the vicinity of Carlsbad Caverns (Hayes, 1964, fig. 27). Microscopic and disseminated crystals of pyrite and large concretions of pyrite occur within the Yates sandstone and siltstone. Within 3 km of the Capitan Limestone, the siltstone and sandstone beds of the Yates locally contain numerous nodules, up to approximately 5 cm in diameter, of limonite or goethite pseudomorphs after pyrite (Hayes, 1964, p. 35). The pyrite of the Yates, like most sedimentary pyrite, probably resulted from diagenetic reactions involving sulfate-reducing bacteria; hence the sulfur-34 concentration of the pyrite should be impoverished as compared to Permian marine gypsum and should be of approximately the same magnitude as the sulfur-34 concentration of the gypsum deposit of Carlsbad Caverns (table 1). Oxidation of the pyrite would generate sulfuric acid (Lindgren, 1933, p. 60 and p. 829) and, subsequently, reaction of the acid with the Capitan Limestone would result in gypsum, some of which might have accumulated within Carlsbad Caverns. A similar origin has been proposed for sulfate minerals within caves of central Kentucky (Pohl and White, 1965).

Another origin for sulfuric acid is oxidation of elemental sulfur, a reaction that may have played a part in the formation of the gypsum deposits of Carlsbad Caverns.

In Late Tertiary and Holocene times, a microbially aided reaction between hydrocarbons and calcium sulfate resulted in the generation of great quantities of hydrogen sulfide within ground waters of the Castile

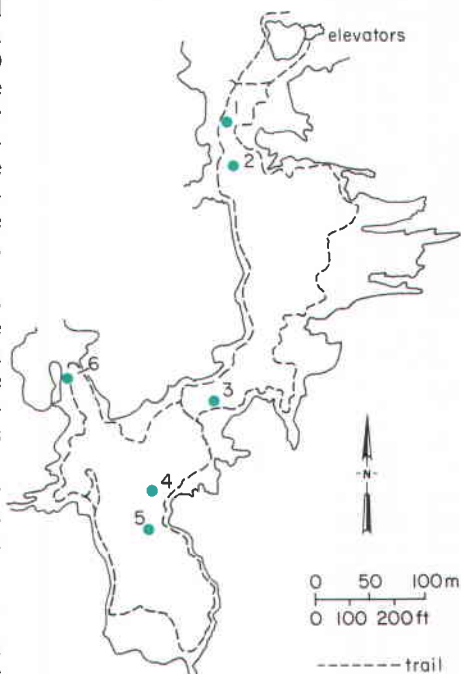


FIGURE 1—SAMPLE LOCALITIES IN BIG ROOM OF CARLSBAD CAVERNS; dashed line is trail (after map by Jagnow, 1979).

Formation (Davis and Kirkland, 1970; Hinds and Cunningham, 1970; Smith, 1978, 1980). Hydrogen-sulfide-rich ground waters may have moved through breccia zones within the Castile (Anderson and others, 1972; Anderson and others, 1978), through fractures, and through solution channels for distances of several kilometers or more into the Capitan Limestone, a major aquifer (Motts, 1968; Hiss, 1975), and hence into a cavern system of which the early Carlsbad Caverns were a part.

Oxidation of hydrogen sulfide within the phreatic zone of the caverns would result in precipitation of sulfur and in accumulation of sulfur within the cave. With a decrease in elevation of the ground-water table, the accumulation of sulfur would be exposed to moist, oxidizing conditions. Oxygen, sulfur, and vadose water, aided by the bacterium *Thiobacillus* sp., would react to form sulfuric acid. Transported into the phreatic zone by descending vadose waters, this acid would diffuse and would react with the limestone wall rock to form gypsum.

Because of their elevation and their distance from the reef front, movement of hydrogen-sulfide-bearing waters into other caves of the Guadalupe Mountains in which gypsum has accumulated may be hydrodynamically improbable. If so, Jagnow's (1979) explanation for the gypsum deposits of Carlsbad Caverns should receive additional support. Conceivably, pyrite within sandstone and siltstone of the Yates originated during the hypothesized influx of hydrogen-sulfide-bearing waters from the Castile into the cavern systems of the Guadalupe Mountains. If this were true, the diagenetic age of the pyrite, which is unestablished, would be late.

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### New book on porphyry copper deposits published

The University of Arizona Press recently announced publication of a 580-page book *Advances in geology of the porphyry copper deposits—southwestern North America*, edited by Spencer R. Titley. The cloth-bound book, which sells for \$35.00, presents findings of recent geologic studies. Part one contains interpretations of many aspects of ore genesis based on field and laboratory studies in accordance with advances made from 1960 to 1980, while part two describes specific deposits in detail. The book is available from the University of Arizona Press, Box 3698, Tucson, AZ 85722.

### Gallery of Geology



Photo by Glenn R. Osburn

Socorro Peak, a well known landmark in central New Mexico, is complex and interesting geologically. The mountain block is uplifted along normal faults that separate the low piedmont surfaces in the foreground from the steep slopes of the mountain. The most prominent features on the mountain are Miocene-age rhyolite domes and flows that cap "M" Mountain and the northern ridge ending in steep cliffs, and form Strawberry Peak (the pointed hill at the right edge of the photograph). Also prominent are very well indurated Miocene alluvial fan and mudflow deposits that form the large vertically striated cliffs just below the "M." Pennsylvanian sedimentary rocks of the Sandia and Madera Formations crop out further down the slope around the prominent white area. Note the well-bedded nature of these outcrops. These sedimentary rocks are truncated on the south by the northeast topographic margin of the Oligocene-age Socorro cauldron (an ash-flow cauldron similar to the young Valles cauldron in northern New Mexico). This topographic margin lies approximately in the gully that trends

diagonally 45 degrees downward to the left from the "M." Cauldron topographic margins often form very large and abrupt erosional unconformities. South of this unconformity, the cauldron-related rocks are thought to be more than 6,000 ft thick, whereas they are only 800 ft thick above the Paleozoic rocks on Socorro Peak. Here, these rocks form the gentle slope and lower cliff between the bedded Paleozoic rocks and the big cliffs of well-indurated fanglomerates. The cauldron-related rocks pinch out within a short distance to the north. A detailed description of the volcanic geology of the Socorro Peak area has been presented by R. M. Chamberlin in New Mexico Bureau of Mines and Mineral Resources Open-file Rept. 118 and in *New Mexico Geology*, May 1981, v. 3, no. 2. Several mines produced silver from veins in a fault block of Miocene rhyolitic rocks during the late 1800's. These mines were located in the small dark rounded hill above and to the left of the large white water tank.

—Glenn R. Osburn

### AN INVITATION TO OUR READERS

With the photo and accompanying description above, we would like to invite our readers to submit their own work to the **Gallery of Geology**. Excellent quality black-and-white photographs of a geologic feature or area and an accompanying geologic description (1-1½ pages in length) should be submitted to Marla D. Adkins-Heljeson, Editor, *New Mexico Geology*, New Mexico Bureau of Mines and Mineral Resources, Socorro, NM 87801. We look forward to seeing a wide selection of photographs of New Mexico's scenic geology.