SUMMER 2022

New Mexico EARTH MATTERS

Published by the New Mexico Bureau of Geology and Mineral Resources • A Research Division of New Mexico Tech

New Mexico's Sulfuric Acid Caves

New Mexico has some of the world's most spectacular caves. Each year, roughly half a million visitors flock to southeastern New Mexico to experience the underground splendor of Carlsbad Caverns National Park and hike in the rugged terrain of the Guadalupe Mountains. The area attracts more than just tourists. Scientists from all over the world study Carlsbad Cavern, Lechuguilla Cave, and other beautiful and enigmatic caves in the Guadalupe Mountains. These caves contain strange mineral deposits and large chambers that puzzled scientists and explorers for many years. We now know that these once-mysterious features are the result of an unusual cave-formation process known as *sulfuric acid speleogenesis* (cave formation by sulfuric acid).

Speleothems in Carlsbad Cavern. *Photo by Peter Jones*

What Are Sulfuric Acid Caves?

Caves can form in many ways. Lava tubes form as molten rock drains from inside cooling basaltic lava flows, sea caves form where waves erode into cliffs, and glacier caves form as streams cut through or under glacial ice. But the most common caves are solution caves, which form as water dissolves soluble rocks such as limestone or gypsum.

Most limestone caves result from carbonic acid, the weak acid formed when carbon dioxide (CO_2) gas dissolves in water. It is slightly corrosive to limestone and, with time, can form caves such as the extensive Mammoth Cave in Kentucky and Fort Stanton Cave in New Mexico. Most of these caves are *epigene* caves, which are formed by carbonic acid produced in CO_2-rich overlying soils and other surface sources. Epigenic limestone caves tend to be connected to the surface through sinkholes and sinking streams. Landscapes that contain these features are known as *karst*.

Most of New Mexico's largest caves are a little different. Carlsbad Cavern, Lechuguilla Cave, and most other large caves in the Guadalupe Mountains are karstic, but they were formed by sulfuric acid. This strong acid is responsible for their unusual mineralogy and morphology. Unlike epigene caves, sulfuric acid caves are a type of *hypogene* cave, which means that the acidic waters, or the ingredients that produce the acid, come from below Earth's surface. When they form, sulfuric acid caves are fed by rising groundwater that carries dissolved hydrogen sulfide (H_2S). Many hypogene caves are not directly connected to the surface, and the overlying land lacks the characteristic karst topography associated with epigene caves. Surface erosion exposed most sulfuric acid caves in the Guadalupe Mountains when they were intersected by downcutting canyons.

Hydrogen sulfide, the gas that gives rotten eggs their distinctive odor, is especially abundant in deep, oxygen-free environments associated with petroleum deposits or magmatic activity. Hydrogen sulfide is unstable in the presence of oxygen, so when rising groundwater is exposed to oxygen, it reacts to form sulfuric acid and elemental sulfur:

$$H_2S + 2O_2 \rightarrow H_2SO_4$$
(hydrogen sulfide + oxygen → sulfuric acid)

$$2H_2S + O_2 \rightarrow 2S^0 + 2H_2O$$
(hydrogen sulfide + oxygen → elemental sulfur + water)

This usually happens at or near the water table, where oxygen is plentiful in cave air and fresh water from the surface. Sulfuric acid can form below the water table if sulfidic groundwaters mix with oxygenated waters or when sulfidic streams pick up oxygen from the cave air. Sulfuric acid can also

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form above the water table in places where hydrogen sulfide escapes into the cave atmosphere and oxidizes on damp surfaces.

When sulfuric acid reacts with limestone on the walls and ceilings, it leaves behind crusts of the mineral gypsum (calcium sulfate).

$$H_2SO_4 + CaCO_3 + H_2O \rightarrow CaSO_4 \bullet 2H_2O + CO_2$$

(sulfuric acid + limestone + water → gypsum + carbon dioxide)

The newly formed gypsum builds up on the walls and ceilings, and most of it eventually slumps to the floor. Gypsum dissolves easily in fresh water, but these deposits can persist for millions of years if they are protected from drip water and other surface waters. Additional minerals can also result from hydrogen sulfide oxidation and sulfuric acid corrosion, such as elemental sulfur (see the chemical reactions above), clays such as hydrated halloysite (endellite), and clay-sized sulfate minerals such as alunite and jarosite. In addition to these, several other interesting speleogenetic minerals form in sulfuric acid caves.

Relatively few known caves in the world are actively forming by sulfuric acid speleogenesis. However, so-called *fossil* sulfuric acid caves are more common. Fossil caves experienced significant sulfuric acid corrosion at some point in the past, but not now. Carlsbad Cavern and Lechuguilla Cave are probably the best-known examples of fossil sulfuric acid caves. They have massive gypsum deposits and other evidence such as diagnostic minerals and cave patterns preserved from their sulfidic past.

History and Scientific Discovery

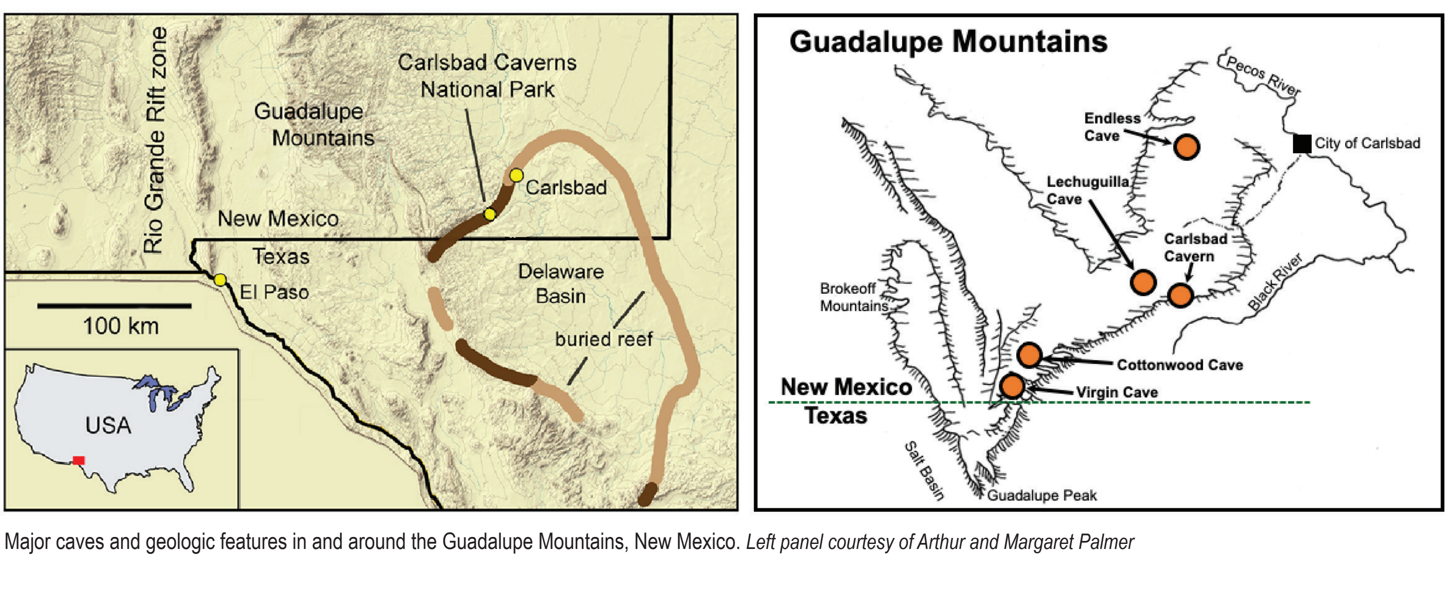
The famous geologist J Harlan Bretz ("J" was his entire first name) first proposed that Carlsbad Cavern formed deep below the water table. Bretz interpreted Carlsbad and other Guadalupe caves in the context of "normal" CO_2-driven karst processes that were commonly accepted at that time. However, he could not adequately explain the presence of the massive gypsum deposits and even concluded his article with a paragraph in which he puzzled about the origin of the gypsum:

> "What were the conditions under which deposition of calcium carbonate ceased in some of the caves, was succeeded by deposition of calcium sulfate, and that followed by a return of lime deposition and a re-solution of the gypsum? A more fundamental question deals with the precipitation of the sulfate. Obviously, the familiar explanation of escape of CO_2 does not apply. For these questions the writer has no answers."
>
> Bretz, J.H., 1949, Carlsbad Caverns and other caves of the Guadalupe Block, New Mexico: The Journal of Geology, v. 57, p. 402.

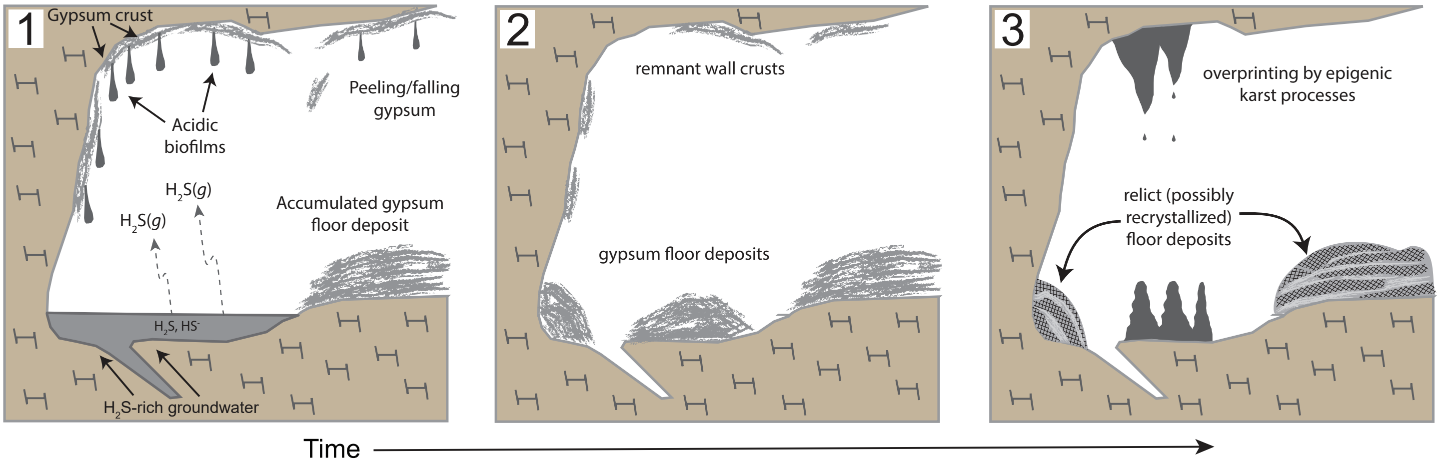
Indeed, that fundamental question of gypsum formation would take many years to answer, and the notion of sulfuric acid corrosion in Carlsbad did not arrive until the 1970s. Researchers proposed several different processes to explain the conversion of limestone to gypsum, including pyrite oxidation and chemical mixing with salt water. But eventually a new theory, developed to a large extent by Stephen Egemeier and expanded upon by Carol Hill, led to the hydrogen sulfide oxidation model that we now accept.

Egemeier did his dissertation research on Kane Caves in the Bighorn Basin, Wyoming, in the early 1970s. The Kane Caves consist of two relatively small caves with linear passages. Lower Kane Cave is an active sulfuric acid cave fed by H_2S-rich springs. Egemeier observed the abundant gypsum on the walls of Lower Kane Cave and attributed it to degassing and oxidation of hydrogen sulfide from a sulfidic stream that runs along the cave floor. He referred to the process of sulfuric acid corrosion and gypsum deposition as "replacement solution" and described the cave origin as

Massive gypsum deposits in the Big Room in Carlsbad Cavern. Vertical grooves represent places where drip water dissolved the gypsum. *Photo by Peter Jones*



Major caves and geologic features in and around the Guadalupe Mountains, New Mexico. *Left panel courtesy of Arthur and Margaret Palmer*



Evolution of a sulfuric acid cave chamber over thousands to millions of years. (The *(g)* indicates gas mixed in air.)

primarily occurring above the water table where gypsum crusts build up, collapse, and dissolve in the stream. Egemeier also argued that these same processes had formed Upper Kane Cave, which has similar morphologies and mineral deposits but no longer receives sulfidic waters. In the early 1980s, others, notably Carol Hill, Donald Davis, and Egemeier himself, extended this model to Carlsbad Cavern and the Guadalupe Mountains, taking into account the geologic history of the region and the potential for hydrogen sulfide oxidation both below and above the water table.

Other Lessons from Modern Analogues

Although active sulfuric acid caves are rare, they represent important analogues that allow us to directly observe the processes that occurred millions of years ago in New Mexico. Lower Kane Cave is one such analogue, and other well-studied examples include Cueva de Villa Luz in Tabasco, Mexico, and the Frasassi Caves in Italy's Marche Region. Geological studies of these caves allow speleologists to directly measure rates of limestone corrosion, link minerals and morphologies with sulfuric acid, evaluate the chemical signatures of sulfide oxidation, and study the fate of hydrogen sulfide in detail.

One of the most important lessons from these modern analogues is the importance of microbial activity. Hydrogen sulfide constitutes an abundant source of chemical energy (i.e., food) for certain bacteria and archaea. These *chemosynthetic* microorganisms live off hydrogen sulfide in the same way humans live off organic carbon. By analogy to us, they can be thought of as "eating" hydrogen sulfide and "breathing" oxygen. They produce elemental sulfur and sulfuric acid as metabolic waste. In doing so, they substantially speed up limestone dissolution and cave formation.

Early cave researchers did not recognize the importance of microorganisms, but with the growth of the field of geomicrobiology, bacteria and archaea have become central to our current understanding of sulfuric acid speleogenesis. Chemosynthetic organisms greatly speed up sulfide oxidation and sulfuric acid production, making these organisms responsible for most sulfuric acid production, limestone dissolution, and cave enlargement. Furthermore, these sulfide-oxidizing microorganisms form the base of a sulfur-powered food web, which usually includes endemic animals. While actively forming, sulfuric acid caves are hotspots for life in the subsurface.

Some of this microbial life is unusual and thrives in extreme habitats. In areas where hydrogen sulfide rapidly degasses into the cave atmosphere, highly acidic (pH 0 to 1) biofilms form on the walls and ceilings. Because of their shape and texture, these biofilms are known informally as *snottites* and are created by colonies of acid-adapted bacteria and archaea that thrive on hydrogen sulfide gas. Snottites and other microbial communities are associated with gypsum, elemental sulfur, and other minerals that form on cave walls. Other microorganisms fill cave streams with white microbial mats that speed up sulfide oxidation below the water table. A team of cave geomicrobiologists returned to Lower Kane Cave in the early 2000s and found that

A journey through time in the Frasassi Caves, a modern analogue for ancient sulfuric acid caves like those in the Guadalupe Mountains. Left: Actively forming gypsum wall crusts, with microbial biofilms and secondary sulfur minerals. Middle: An abandoned stream passage created during an earlier phase of cave development, with a water-table corrosion notch, feeder conduits, and characteristic bell-shaped passage. Right: A much older passage that still contains ancient gypsum deposits and water table features but has been overprinted by more recent speleothem formation. *Photos by Daniel Jones and Mackenzie Best* microorganisms in the stream consume most of the sulfide before it can escape into the cave's atmosphere.

Sulfuric acid caves don't stay active forever. As the local or regional hydrology changes, sulfidic groundwaters move or disappear entirely. When that happens, the chemosynthetic microbes diminish, sulfuric acid corrosion ceases, and the caves become overprinted by different processes. Surface water can enter the cave and modify sulfuric-acid-sculpted passages with epigenic carbonic acid corrosion, and fresh surface drips can wash away gypsum and precipitate calcium carbonate stalactites and stalagmites. The Frasassi Caves in Italy are a remarkable time capsule that shows this process.

Geologic History of Sulfuric Acid Caves in the Guadalupe Mountains

While many caves in the Guadalupe Mountains developed according to the general model of sulfuric acid speleogenesis described above, their specific developmental history has been controlled by the tectonic and hydrogeologic history of the region and the rock formations in which they developed.

Most of these caves are formed in the Capitan Reef, a complex of limestones and other marine rocks that were deposited between 265 and 259 million years ago along the shallow edge of an inland sea that is now the Delaware Basin. Sediments deposited deeper in the basin were rich with organic material which eventually became the productive petroleum reserves now associated with the basin. Eventually the sea dried up, filling the basin with salts as it evaporated and receded. After the end of the Permian Period, the Guadalupe Mountains were exposed to weathering and later tectonic uplift, which fractured the rock and created conduits for groundwater movement.

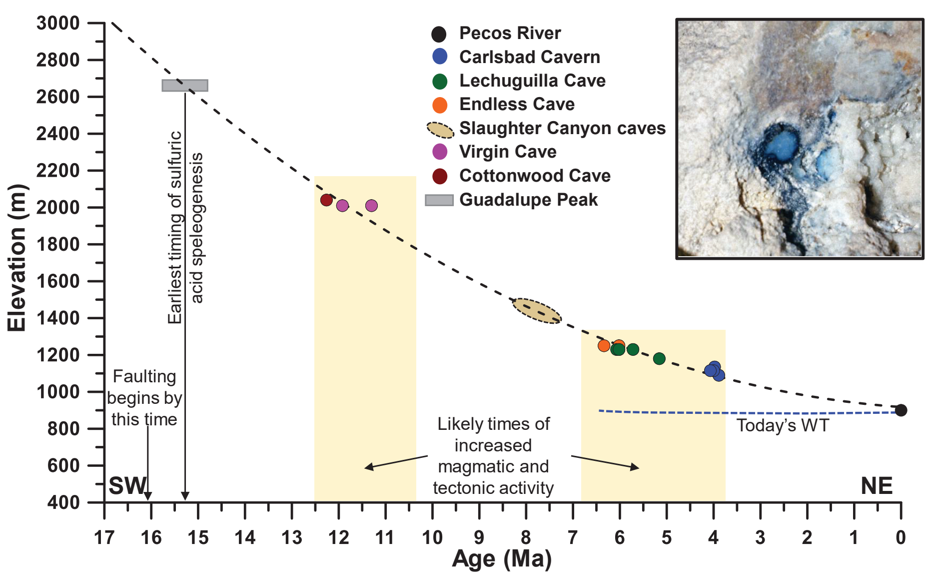
Sulfuric acid speleogenesis started when H_2S-rich groundwater and petroleum migrated westward in the northern part of the Delaware Basin. This migration occurred when the region tilted eastward during uplift and the subsequent opening of the Rio Grande rift. The most intense episodes of sulfuric acid corrosion started about 12 million years ago, as shown by radiometric dating of the mineral alunite ($KAl_3(SO_4)_2(OH)_6$). Alunite forms from the alteration of clay minerals under highly acidic conditions and would have formed by sulfuric acid corrosion just above the water table. The potassium in the alunite structure is slightly radioactive and decays slowly, so the origin of the mineral can be dated by $^{40}Ar/^{39}Ar$ geochronology methods.

Partially dissolved block of massive gypsum and hollow coralloid speleothems from the Southern Branch of Lechuguilla Cave. *Photo by David Harris, Harris Photographic*

The oldest known sulfuric acid caves in the Guadalupe Mountains, Cottonwood and Virgin Caves, formed 12 to 11 million years ago. Over the next 8 million years, sulfuric acid corrosion occurred at, just below, and just above the water table. As the mountain range rose, sulfuric acid speleogenesis within the Capitan Reef Complex migrated northeast along what is now the Guadalupe escarpment. Caves formed at progressively lower elevations as the water table dropped relative to the Capitan Reef, either because the region rose or the water table lowered as the land eroded. On the basis of alunite ages, sulfuric acid corrosion in Carlsbad Cavern and Lechuguilla Cave was most intense between 6 and 4 million years ago, with the Big Room in Carlsbad Cavern forming roughly 4 million years ago.

Today, sulfuric acid corrosion in these caves has nearly ceased. The robust sulfide-oxidizing microbial communities that thrived during periods of intense corrosion have given way to new and slow-growing microorganisms that rely on very scarce energy sources as they gradually etch away the cave walls. In the years since active sulfuric acid speleogenesis ended, fresh surface water has infiltrated the caves and precipitated the calcium carbonate stalactites, stalagmites, and other speleothems that now adorn the walls, floors, and ceilings.

Is sulfuric acid speleogenesis still occurring somewhere else in the Guadalupe Mountains today? Probably not, but we do not know for certain. For the most part, the process has drifted east, away from the mountains. If the mechanisms that allowed the hydrogen sulfide to migrate toward the reef are reactivated, sulfuric acid could once again impact the deepest reaches of Carlsbad Cavern and Lechuguilla Cave. Caves might be forming east of the Pecos River, where the Capitan Reef plunges beneath the gypsum and salt beds of the Delaware Basin. The basin has hydrogen-sulfide-rich waters associated with vast petroleum accumulations in the same strata that contain caves in the Guadalupe Mountains. Whether this acidic water is still dissolving the limestone is anyone's guess, but it is nice to think that new caves may be there for future scientists and explorers to discover.



Timing of major episodes of sulfuric acid speleogenesis based on the $^{40}Ar/^{39}Ar$ alunite ages from five caves in the Guadalupe Mountains (colored circles). The dashed curve represents the evolution of the water table over time, relative to today's water table within that aquifer near the city of Carlsbad. The inset photo shows a 1-cm-diameter pocket of blue hydrated halloysite with a black-manganese-rich rim exposed in the Guadalupe Room in Carlsbad Cavern. Alunite is intimately associated with these deposits.

Massive block of elemental sulfur in a passage near Ghost Town, Lechuguilla Cave, with John McLean for scale. *Photo by Kathryn Sisson-DuChene*

New Mexico and the International Year of Caves and Karst

Caves occur around the world and on all continents. About 20% of Earth's land surface is karst, where most caves, and most of the longest, largest, and deepest caves, occur. In recent years, caves have become recognized as one of the best and most diverse sources of paleoclimatic data for modeling modern climate change. Crystalline and sedimentary cave deposits preserve temperature, humidity, plant, animal, broad environmental, and human cultural information.

Caves and karst offer many other benefits to humanity. For example, karst aquifers are the sole or main water source for 700 million people. However, caves and karst also present many challenges to society. The cavernous and other highly permeable openings in karst make karst aquifers vulnerable to contamination, allowing pollutants to travel rapidly, with effectively no filtration, over long distances to water wells and springs. Caves and related cavities can also collapse, resulting in over $300 million per year in road damage in the United States alone.

The International Year of Caves and Karst was established in 2021 (and extended through 2022 to account for the COVID-19 pandemic) by the International Union of Speleology, which has over 260 partner organizations in 51 countries. The purpose of the Year is to teach the world about the importance and challenges of caves and karst, following the theme "Explore, Understand, Protect," since exploration is needed before research to make proper and sustainable protection possible.

The National Cave and Karst Research Institute (NCKRI) was created by the U.S. Congress to conduct and support cave and karst research, education, and management in the United States and internationally. NCKRI is administered by New Mexico Tech (NMT). Dr. Daniel Jones directs NCKRI's Academic Program at NMT, and Dr. George Veni is NCKRI's Executive Director, based at NCKRI headquarters in Carlsbad, New Mexico. NCKRI works in partnership with many individuals and organizations, such as this article's co-authors, retired petroleum geologist Harvey DuChene, and Dr. Victor Polyak from the University of New Mexico.

NCKRI is leading many International Year efforts and encourages everyone to participate. For more information about how to get involved with NCKRI and the Year, visit www.nckri.org and www.iyck2021.org.

By Daniel Jones, Victor Polyak, Harvey DuChene, and George Veni

Technical reviews kindly provided by Arthur Palmer and Louise Hose

For additional technical information, the 2006 New Mexico Geological Society Fall Field Conference Guidebook focused on Caves & Karst of Southeastern New Mexico: https://nmgs.nmt.edu/publications/guidebooks/57/

New Mexico
EARTH MATTERS

Volume 22, Number 2
Published twice annually by the
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A Research Division of
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Cover photo of Triassic-Jurassic unconformity exposed in Chama Wall, Rio Chama, New Mexico, by Paul Bauer

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Bureau News

Matt Heizler Receives Top Research Award

The New Mexico Tech 2022 Distinguished Research Award winner is Dr. Matthew Heizler, Principal Senior Geochronologist and Associate Director for Laboratories at the New Mexico Bureau of Geology and Mineral Resources at New Mexico Tech. Matt earned his Ph.D. from UCLA in 1993 and began work at the Bureau the same year as a geochronologist and thermochronologist, meaning that he studies the age and history of rocks. From the time of Matt's hiring, he and Dr. Bill McIntosh worked to build a state-of-the-art $^{40}Ar/^{39}Ar$ geochronology laboratory, which now serves students and professional researchers across the globe. Matt has published 213 peer-reviewed publications and written 30 successful proposals, bringing nearly $4 million to New Mexico Tech, and he has advised and mentored many students. His nominations for the award praised his expertise, accomplishments, research creativity, and collegiality.

Major Water Projects Receive Funding

The New Mexico nonprofit Thornburg Foundation has awarded grants to two new and consequential water projects. The first seeks to evaluate the coverage of groundwater monitoring efforts across the state and provide recommendations for improvements. The second is aimed at providing science-based learning opportunities on water topics to state legislators and other New Mexico decision-makers.

The U.S. Bureau of Reclamation's WaterSMART program has agreed to a cooperative grant in support of efforts to improve data access for regional, state, and federal agencies as well as other groups working on hydrologic modeling and water management in the Middle Rio Grande. This work is a continuation of Stacy Timmons's effort to implement the 2019 Water Data Act.

STATEMAP Earns Top Mapping Award in Nation

New Mexico's Geologic Mapping Program (STATEMAP) was awarded $668,850 through the federal STATEMAP program to continue detailed mapping of key areas in the state. This is the largest award ever received during the 30-year history of the program and the largest award to any state geological survey in the country this year. The grant also moved the Bureau to the top of the list for the largest cumulative total awarded to any state–a total of $6,681,600. A team of Bureau field geologists and contract mappers will focus on three regions: the Rio Grande watershed, the lower Pecos River watershed, and the I-40 corridor near Gallup. STATEMAP is funded by the USGS National Cooperative Geologic Mapping Program, with matching funds provided by the State of New Mexico.

Mike Timmons Selected as Interim Director while Nelia Dunbar Serves as Interim VP for Research

Bureau Director and State Geologist Nelia Dunbar was recently chosen as Interim Vice President for Research (VPR) at New Mexico Tech. Dr. Dunbar is now responsible for supporting and expanding the scientific and creative potential of a diverse group of academic faculty, research scientists, and engineers. The VPR plays a vital role in advancing the intellectual wealth and economic impact of the university's research activity, using them as drivers for the overall enhancement of the institution, the state, and the nation. The VPR also supervises 12 science and engineering research centers, including EMRTC, PRRC, MRO, and Langmuir Laboratory. Mike Timmons was selected as Interim Director and State Geologist. Mike previously served as Deputy Director and Manager of the Geologic Mapping Program.

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