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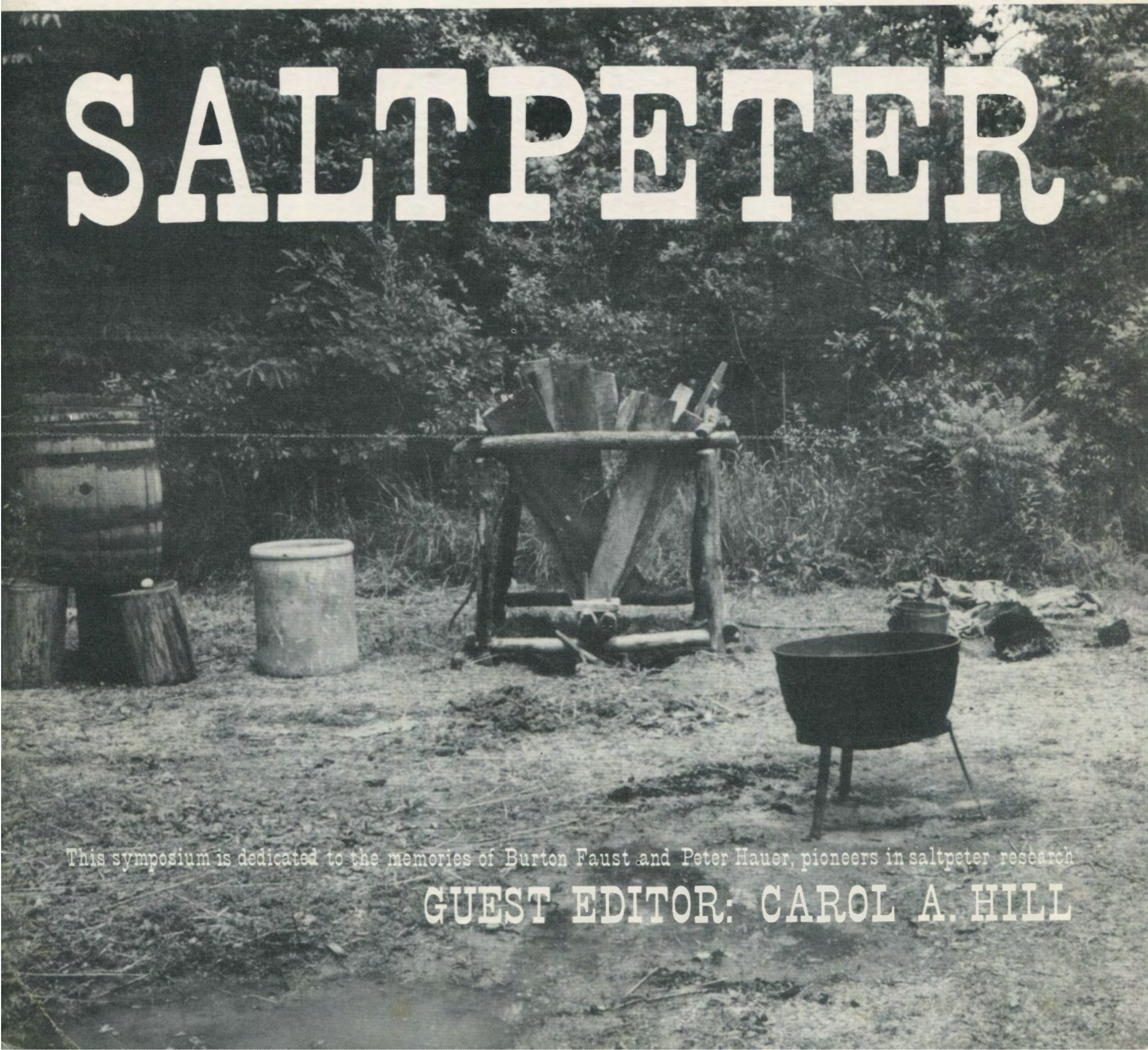
SALTPETER



This symposium is dedicated to the memories of Burton Faust and Peter Hauer, pioneers in saltpeter research

GUEST EDITOR: CAROL A. HILL

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INTRODUCTION TO THE SYMPOSIUM

What is the Origin of Saltpeter? "Bat guano" has always been the favorite answer to this question, yet over many a NSS convention campfire this question would be the favorite topic of conversation. Many cavers—people like Burton Faust and Pete Hauer, pioneers in saltpeter studies—felt that a bat guano origin could not explain the occurrences of saltpeter earth in caves they had visited.

Hill, in her paper "Origin of Cave Saltpeter," concludes that cave saltpeter derives from seeping groundwater, not bat guano. Rainwater picks up nitrate from organic debris in surface soils and transports it underground, where it accumulates in caves due to a lack of leaching and biological activity. Bat guano can enrich saltpeter earth in nitrate, but it is not the only, or even the major, source of nitrates in most saltpeter caves.

Where are the Nitrate Minerals in Saltpeter Earth? Old (early 1800) reports of crystallized nitrate minerals in saltpeter earth have never been verified by modern investigations. Upon analysis, crystals from saltpeter dirt always X-ray as sulfate (usually gypsum) minerals.

In her article "Mineralogy of Cave Nitrates" Hill concludes that nitrate minerals cannot exist in the crystallized state in southeastern caves. In the high humidity of these caves, nitrate minerals deliquese; that is, they absorb water from the air, dissolve in this water and then sink back into the cave dirt or wallrock. Only in dry southwestern caves can nitrate minerals crystallize from the dissolved state.

Are Microorganisms Involved in the Production of Cave Saltpeter? Burton Faust believed they might be. Burton felt that regeneration times (saltpeter earth after leaching regenerates nitrate in as little as 3 years) could only be explained by such a mechanism as bacterial production of nitrates. Burton's intuition proved right.

Carl Fliermans, a member of the Saltpeter Research Group, has shown that the nitrogen bacterium, *Nitrobacter*, occurs in large numbers on the walls, ceilings, and in the earth of saltpeter caves. Hill ("Origin of Cave Saltpeter") speculates that nitrogen is transported through limestone bedrock from the surface in the reduced (ammonium) state and is used as a food source by *Nitrobacter*, which produces nitrate as the end product of its metabolism.

What are the Chemical Steps in the Production of Saltpeter? Crystals of saltpeter (from which gunpowder is made) were obtained by leaching cave earth and combining the leachate with lye produced from wood ashes. The chemical changes that occurred were not understood by those who manufactured saltpeter in 1700's and 1800's, because the chemistry of ionic species was not then known.

Gary Eller (see "Chemical Aspects of the Conversion of Cave Nitrates to Saltpeter") duplicated this historic manufacturing process in an "action history" experiment funded by the National Geographic Society. This experiment produced the first saltpeter crystals obtained from cave sediment in over 100 years. Gary's demonstration is now part of an interpretative program put on by Mammoth Cave National Park for its visitors.

What is the History of Cave Saltpeter Use in America? Cave saltpeter was essential to our country's security in the Revolutionary War, War of 1812, and Civil War. It was also of utmost importance to the pioneers who faced wild animals and Indians in the western Territories.

The articles "Historical Geography of United States Saltpeter Caves" by DePaepe and Hill, "Confederate Niter Production" by Powers, "Saltpeter Mining Features and Techniques" by DePaepe, and "Confederate Saltpeter Mining in Northern Alabama" by Smith trace the historic use of cave saltpeter in the United States.

Where are Saltpeter Caves Located? Saltpeter caves are located exclusively in the southeastern United States. Is this geographic distribution truly a real phenomenon; or is it because this cave region was more densely populated when saltpeter production was economically profitable?

The locations of saltpeter caves are listed by Hill and others in "Saltpeter Caves of the United States". This list indicates definite boundaries beyond which saltpeter caves do not exist. The reason for this distribution is discussed by Hill in "Origin of Cave Saltpeter" in which she correlates the location of saltpeter caves with oak-hickory forest; *i.e.* more nitrate will be leached into caves in regions high in nitrous surface vegetation.

THE SALTPETER GROUP of the Cave Research Foundation was started in 1973 by a handful of people interested in the interdisciplinary challenges posed by saltpeter research. This research is both of a historical and a scientific nature. Saltpeter had been mined from this nation's caves from as early as the mid-seventeenth century to the late 1800's; indeed, as one of this country's most important early industries, saltpeter mining during its heyday was at the heart of the nation's economics and politics. Yet, the fundamental questions about saltpeter—its origin, the details of its manufacture—had never been answered. At the onset of our investigations we (the saltpeter researchers) were not even sure that nitrates existed in cave dirt. As William B. White, Chief Scientist for the National Speleological Society, jokingly once said: "Wouldn't it be ironic if the nitrate came from the woodash or some other source and all of the cave saltpeter miners' labors were in vain?" We really didn't think that the old-timers knew so little about their means of livelihood, but the question, although in jest, reflected our scientific ignorance of the subject. We knew we had to start at ground zero and build upon many disciplines—chemistry, geology, microbiology, history, geography—in order to solve the intricate interrelationships of saltpeter research.

The most basic questions asked by the saltpeter researchers at the beginning of their investigations are (at least partly) answered by the research papers presented in this Symposium.

The work of the Saltpeter Research Group is not finished. Many questions still need to be answered. The most fundamental of these questions concerns the precise interrelationship between the microbiology, biology and geology cycles in the cave. Many saltpeter caves still await adequate description; and the protection of saltpeter artifacts in these caves is crucial if we are to pass on this unique heritage to future generations. Those people interested in doing saltpeter research are encouraged to contact the Saltpeter Research Group of the Cave Research Foundation.

Carol A. Hill
Co-ordinator, Saltpeter Research Group

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Hill, C.A.; Duane DePaepe; P.G. Eller; P.M. Hauer; John Powers; and Marion O. Smith (1981)—Saltpeter Caves of the United States: *NSS Bulletin* 43:84-87.

SALTPETER CAVES of the UNITED STATES

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SALTPETER CAVES are not located uniformly throughout the United States but exist primarily in the southeastern United States (Table 1). The extent of known saltpeter cave locations is roughly south of the Mason-Dixon line, north of the southernmost Dixie states (Alabama, Georgia, Mississippi) and east of the Mississippi River (with the exception of Missouri and northernmost Arkansas) (Fig. 1).

Although the distribution of saltpeter caves is partly related to the general distribution of limestone caves (Fig. 1), there are definite geographic limits beyond which verified saltpeter caves do not extend. Hauer (1971) reported only one saltpeter cave in Pennsylvania. In the Civil War, the southern states had no natural supply of saltpeter within their area except from the cave regions of Virginia, Tennessee and Kentucky (see Powers, this issue). The caves of Texas and Arizona noted by Hauer (1972) are not true saltpeter caves (filled with nitrous clastic sediments), but are strictly bat guano caves (Campbell, 1925; Phillips, 1901). As discussed by Hill ("Origin of Cave Saltpeter", this issue), the deposits (saltpeter earth and bat guano) in these two types of caves may be completely unrelated in origin. One possible site outside the above geographic limits includes the saltpeter caves of the Lake Pepin, Minnesota, region (Le Sueur, 1700, p.25); this location needs modern verification.

This list of United States saltpeter caves was compiled by the authors from references in the literature and from personal visits to some of the caves. It is by no means complete. Anyone who can add to, amend, or correct the list should contact the authors.

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Table 1. List of Saltpeter Caves in the United States.

ALABAMA	
Bibb County	Saltpeter
	Saltpeter Sink
Blount County	Adcock
	Bangor
	Blowing Saltpeter
	Crump
	French's Saltpeter
	Horse
	Second
Calhoun County	Lady
	Little Weaver
	Meadows
	Oxford
	Weaver
Cherokee County	Daniel
Colbert County	Keeton
	McKinney
	Wolf Den
Cullman County	Saltpeter
DeKalb County	Manitou
Jackson County	Blue River
	Coon Creek Saltpeter
	Crossing
	Devers Cove Saltpeter
	Fabius
	Horse Skull
	Long Island Saltpetre
	Saltpeter
	Sauta
	Steele Saltpeter
	Tumbling Rock
	William's Saltpeter
Jefferson County	McClunney
Lawrence County	Melson
	Saltpeter
Lauderdale County	Collier
	Watkins Saltpeter
Limestone County	Indian
	Kendall Saltpeter
Marshall County	Cave Mountain (Long Hollow)
	Eudy
	Fort Deposit

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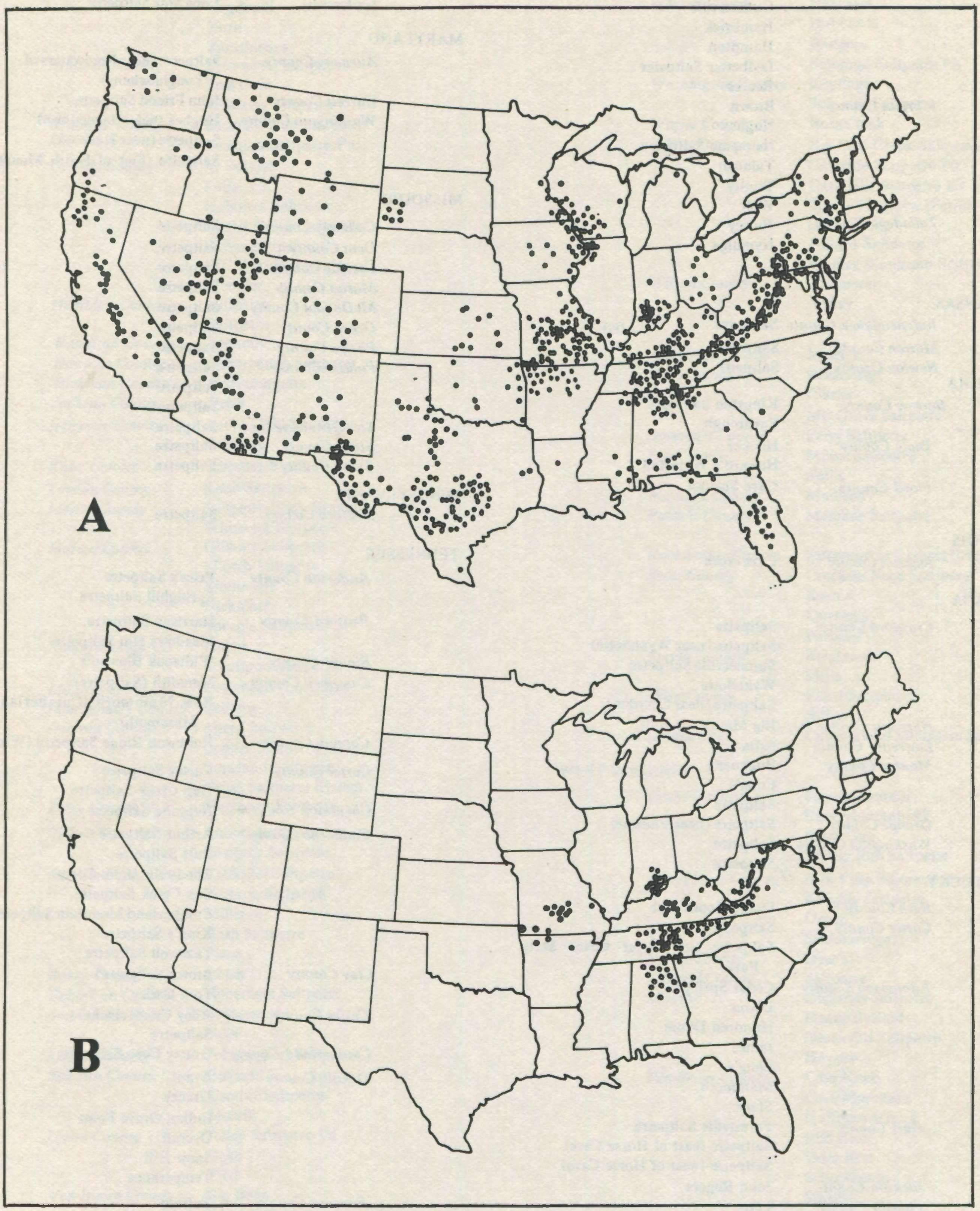

Figure 1. (A) Distribution of limestone caves in the United States (after Halliday [1966], with permission). (B) Distribution of limestone caves containing saltpeter deposits.

	Guntersville
	Hambrick
	Hampton
	Ledbetter Saltpeter
	Reeves
Morgan County	Brown
	Hughes
	Newsome Saltpeter
	Talucah
	Trinity
	Wolf
Talladega County	Hawey
	Kymulga

ARKANSAS

Independence County	Saltpetre
Marion County	Saltpetre
Newton County	Saltpetre

GEORGIA

Bartow County	Kingston Saltpetre
	Yarbrough
Dade County	Hooker
	Howard's Waterfall
Floyd County	Cave Springs

ILLINOIS

Jackson County	Cave creek

INDIANA

Crawford County	Saltpetre
	Saltpetre (near Wyandotte)
	Sumnerville Saltpetre
	Wyandotte
	Saltpetre (near Corydon)
Harrison County	Big Mouth (or Rat)
Lawrence County	Salts
Monroe County	Buckner's
	Coon's
	Saltpetre
Orange County	Saltpetre (near Valeene)
Washington County	Saltpetre
	Saltpetre

KENTUCKY

Bath County	Daniel Boone Hut
Carter County	Saltpetre
	Saltpetre (in Carter Caves State Park)
Edmonson County	Cedar Springs
	Dixon
	Hundred Dome
	James
	Long's
	Mammoth
	Short
Hart County	Forestville Saltpetre
	Saltpetre (east of Horse Cave)
	Saltpetre (west of Horse Cave)
Jackson County	John Rogers
Pulaski County	Petre
Rockcastle County	Great Saltpetre (or Crooked Creek)
	Owens Saltpetre
Wayne County	Saltpetre
	Triple Saltpetre
	Wind

[unknown]	Lone Star Saltpetre

MARYLAND

Allegany County	Saltpetre (near headwaters of Youghiogheny)
Garrett County	John Friend Saltpetre
Washington County	Hughes (near Hagerstown)
	Saltpetre (near Hancock)
	Saltpetre (foot of South Mountain)

MISSOURI

Callaway County	Saltpetre
Dent County	Saltpetre
Laclede County	Saltpetre
Maries County	Saltpetre
McDonald County	Saltpetre
Ozark County	Saltpetre
Phelps County	Saltpetre
Pulaski County	Saltpetre
	Saltpetre
	Saltpetre
Ste. Genevieve Co.	Saltpetre
Stone County	Saltpetre
Texas County	Saltpetre

PENNSYLVANIA

Bedford County	Saltpetre

TENNESSEE

Anderson County	Fritz's Saltpetre
	Springhill Saltpetre
Bedford County	Harrison Saltpetre
	Meadows Hill Saltpetre
Blount County	Whiteoak Blowhole
Campbell County	Meredith (Saltpetre)
	New Mammoth (Cumberland Mammoth)
Cannon County	Robinson Ridge Saltpetre (Window)
Carter County	Carter Saltpetre
	Gap Creek Saltpetre
Cheatham County	Neptune Saltpetre
Claiborne County	Arthur Saltpetre
	Buis Saltpetre
	Chadwells (John Greer)
	Cox Creek Saltpetre
	Cumberland Mountain Saltpetre
	King's Saltpetre
	Tazewell Saltpetre
Clay County	Brown Saltpetre
	Tom Dailey
Coffee County	Riley Creek (Duke)
	Saltpetre
Cumberland County	Grassy Cove Saltpetre
Dekalb County	Avant
	Gracey
	Indian Grave Point
	Overall
	Snow Hill
	Temperance
Fentress County	Buffalo
	Campbell Saltpetre
	Cobb Creek Saltpetre
	Copely Saltpetre
	East Fork Saltpetre
	Manson Saltpetre

	Yogdrasil
	York
	Zarathustra
Franklin County	**Crownover Saltpetre**
	Lost Cove
	Williams Saltpetre
Grainger County	**Dunville Gap Saltpetre**
	Jarnigan Saltpetre Pit
Grundy County	**A. Smartt**
	Fultz
	Hubbard Saltpetre
	Laurel Creek Saltpetre
	Payne Saltpetre
	R.C.(Ira) Winton No. 1
	Woodlee
Hamblen County	**Saltpetre**
	Saltpetre
Hamilton County	**Lookout**
Hawkins County	**Sensabaugh Saltpetre**
Hickman County	**Only Saltpetre**
Jackson County	**Peter**
Jefferson County	**Animal Hill Saltpetre**
	Saltpetre
Knox County	**Saltpetre Bluff**
Lincoln County	**Kelso Saltpetre**
Macon County	**Saltpetre (Lick Branch)**
	Whiteoak Saltpetre
Marion County	**Gillams Saltpetre**
	Martin Saltpetre
	Monteagle
	Nickajack
	Speegle Saltpetre
Maury County	**Hobbs**
	Southport Saltpetre
Monroe County	**Craighead (Lost Sea)**
Montgomery County	**Bellamy**
Overton County	**Allred Saltpetre**
	Cooper Saltpetre
	Copeland Saltpetre
	Great Saltpetre Chasm
Perry County	**Sheppard Saltpetre**
Pickett County	**Abbott Saltpetre**
	Eastport Saltpetre
Putnam County	**Calfkiller Saltpetre**
	Johnson Saltpetre
	Milligan
	Nash Saltpetre
	Petre
Roane County	**Eblen**
Robertson County	**Robertson Saltpetre**
Smith County	**Bridgewater**
	Piper
Stewart County	**Tobaccoport Saltpetre**
Sullivan County	**Buzzard**
	Caudill Saltpetre
	Morrill
Union County	**Jolley Saltpetre Pit**
	Oaks
	Wolf
Van Buren County	**Big Bone**
	Cagel Saltpetre
	Cane Creek Saltpetre
	DIG (Hitchcock's Peter Pile Pit)
	McElroy
	Rice
	W.R. Johnson Saltpetre
Warren County	**Henshaw**
	Hubbards
	Rodgers
	Solomon Saltpetre Pit
Washington County	**Keplinger**
	Solomon Saltpetre
Wayne County	**Ross Creek**
White County	**Big Lost Creek Saltpetre**
	Cassville Saltpetre Pit
	Cave Hill Saltpetre Pit
	Cherry Saltpetre (Petre)
	Lost Creek
	Pollard Saltpetre
	Walker Mountain Saltpetre
Wilson County	**Anderson**
	Valley

VIRGINIA

Allegheny County	**Mann's**
Bath County	**Breathing**
	Clarks
	Mt. Grove Saltpetre
Botetourt County	**Perry Saltpetre**
Lee County	**Minoc Saltpetre**
	Neil's
Madison County	**Madison**
Pulaski County	**Melbane Saltpetre**
Rockbridge County	**Saltpetre (at Natural Bridge)**
Scott County	**Crackers Neck Saltpetre**
	Kern's
	Lawson's
	Parsons
Smyth County	**Buchanan**
	Little
Wise County	**Faust Saltpetre**
	Ridge
[unknown]	**Cumberland Mountain Saltpetre**

WEST VIRGINIA

Grant County	**Cave Mountain**
	Cave Mountain #2
	Kline Gap
	Spring Run Saltpetre
Greenbrier County	**Alta Vista Saltpetre**
	Knights Saltpetre
	Organ
	Seldomridge
Hardy County	**Dyer's**
Mineral County	**Saltpetre**
Monroe	**Dicksons Saltpetre**
	Doane Ballard
	Greenville Saltpetre
	Haynes
Pendleton County	**Cave Knob**
	Cave Mountain
	Hoffman School
	Mill Run
	Peter Run
	Schoolhouse
	Sinnett
	Tory's
	Trout
Pocahontas County	**Lobelia Saltpetre**
	Snedegar's
Randolph County	**Crawford (or Wymer's)**
	Fortlick

DePaepe. Duane and Carol A. Hill (1981)—Historical Geography of United States Saltpeter Caves: *NSS Bulletin* 43:88-93.

HISTORICAL GEOGRAPHY of UNITED STATES SALTPETER CAVES

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SUMMARY

Saltpeter, an essential ingredient in gunpowder, is produced artificially from organic matter or can be obtained from the "nitre" earth and rocks of caves. Cave saltpeter mining started on a large scale in Virginia and West Virginia just prior to the Revolutionary War, when the colonists realized that they needed an inexpensive, dependable supply of gunpowder. After the Revolutionary War, among the first settlers to push into the westward territories were the "saltpeter chemists" searching for caves containing nitrous earth.

Many caves in Kentucky, Indiana, and Tennessee were mined on a small scale in the years between the two wars with Britain. The pace of saltpeter mining in caves again quickened immediately preceding the War of 1812. The price of saltpeter skyrocketed, and large-scale mining ventures were begun. The central region of Kentucky—especially the Mammoth Cave area—became famous for saltpeter mining and gunpowder manufacturing. After the war ended in 1815, the market price of saltpeter plummeted. Most mining activities in saltpeter caves closed, and the few remaining were reduced to "cottage" operations.

During the Civil War, the Confederacy had to depend almost completely on caves for its source of saltpeter. Both small- and large-scale operations were supported by the rebel government as most of the major caves in the deep South were worked for saltpeter.

The active cave saltpeter era ended in the late 1800's with the discovery of Chilean nitrate deposits and nitrogen fixation technology.

GUNPOWDER was introduced to Europeans either in the Twelfth or the Thirteenth Century: seven parts of saltpeter (potassium nitrate) mixed with five parts of charcoal and five parts of sulfur made "black powder". It is unknown when or where it was discovered that caves are rich in nitrous earth, but this fact probably was known in Europe by the late Sixteenth Century, because the American colonists brought such knowledge with them from Europe. Shaw (1979, p. 64), in *History of Cave Science*, does not refer to any early use of cave saltpeter by Europeans, although he does mention two later cave-mining efforts:

> **"The main exploitation of saltpeter caves has been in the USA, though two caves in France (the Grotte des Espelungues near Lourdes and one in the Gorge d'Enfer, Dordogne) were worked in 1793 when a lack of imports during the wars was causing a shortage of gunpowder."**


REVOLUTIONARY WAR

WAR of 1812

CIVIL WAR

Figure 1. Areal distribution of saltpeter caves during wartime peak production years. Maps by Duane De Paepe.

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Reliable technology for working cave deposits was brought to America in the late Eighteenth Century from France in Diderot's (1790) epic compendum of manufacturing knowledge, *Encyclopedie Methodique.*

The American colonists artificially produced their own saltpeter by piling compost (leaves and other vegetable matter) into heaps, moistening it with water or urine, and then sprinkling it with lime. Saltpeter was also obtained from the walls of old cellars, from stables, from underneath houses and barns, and from the "nitre" earth and rocks of caves (the older spelling, "saltpetre," comes from *sal petre,* salt of rock).

REVOLUTIONARY WAR

With the news of Lexington and Concord in 1775 came the realization that home methods for producing saltpeter were not sufficient for the impending war. "The colonies were scoured for black powder and less than 68 barrels were found." When Washington took command of his colonial army, he "made the alarming discovery that there was not more powder than sufficient to furnish each man with nine cartridges" (Hovey, 1897). Since limestone caverns were known to contain extensive niter deposits, the colonists' attention immediately turned to these. Men such as Thomas Jefferson and James Madison became cave hunters and mappers. Among the caves found by Jefferson was one he named for his friend James Madison, "Madison Cave," in Grotto's Ridge, Virginia. Madison Cave was mined of saltpeter during the Revolutionary War, the War of 1812, and the Civil War, perhaps the only cave to have this distinction. Eleven thousand pounds of niter were obtained from a large cave on Rich Creek, Kanawha River, Virginia. According to Hovey (1897), the bulk of the saltpeter used to make gunpowder during the Revolutionary War came from the caves of Virginia (Fig. 1).

One cave outside of Virginia that may have been mined during the Revolutionary War was Buckner's Cave near Bloomington, Indiana. Buckner's Cave contains the scratched name "L.V. Cushing" along with the date "Nov. 23, 1775" at the end of a passage which was re-excavated by modern explorers several years ago. Cushing's identity has not yet been verified, but he may have been an itinerant "saltpeter chemist" of that era prospecting for rich underground deposits of niter.

The *Journals of the Continental Congress,* June 10, 1775-July 28, 1775, record resolutions dealing with saltpeter recovery for the purpose of manufacturing gunpowder. The importance attached to saltpeter is demonstrated by the prominent figures (Robert Treat Paine, Richard Henry Lee, Benjamin Franklin, Philip Schuyler and Thomas Johnson) who were to "be a committee to devise ways and means to introduce the manufacture of salt petre in these colonies." The assigned task of this committee was summarized:

> "Whereas the safety and freedom of every community depends greatly upon having the means of defense in its own power, and that the United Colonies may not, during the continuance of their present important contest for Liberty, nor in any future time, be under the expensive, uncertain and dangerous necessity of relying on foreign importations for Gun Powder: And it being very certain from observation and experiment, that Salt Petre is to be obtained in great abundance from most parts of this Northern Continent."

Scientist-President Thomas Jefferson documented the quantity of saltpeter collected (Peden, 1955, p. 34) from at least 50 saltpeter caves on the Greenbrier and Cumberland rivers in Virginia and West Virginia. Yet, beyond these notations, little else was specifically recorded on saltpeter mining in caves for the Revolutionary War effort.

Figure 2. *Eye Draught Map* (1811) of Mammoth Cave, Kentucky. Courtesy of the American Philosophical Society Library.

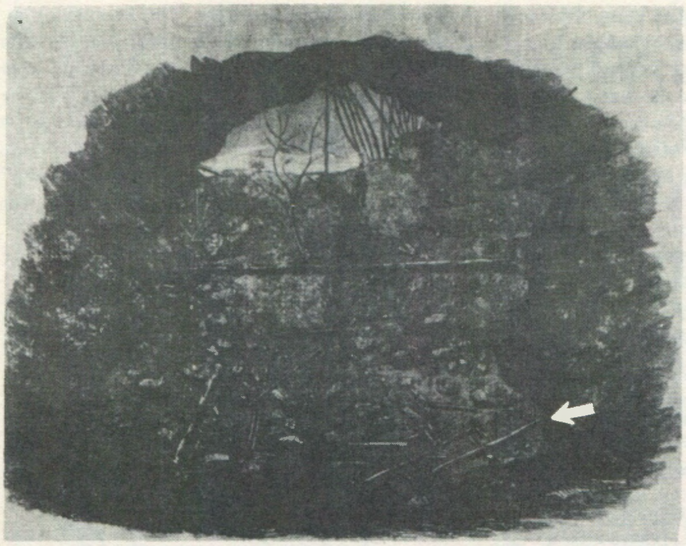

Figure 3. Entrance to Mammoth Cave, "View of the Mouth from the Interior." From the 1835 Lee Map. Arrow in lower right corner indicates what may be the channel log of a V-vat with 3 or 4 staves attached. V-vats were used at the cave entrance perhaps as early as 1798.

WESTWARD EXPANSION

The westward movement across the Appalachians began in earnest after the close of the Revolutionary War. The art of saltpeter recovery from cave sediments travelled the Wilderness Road westward through the Cumberland Gap. Local saltpeter was converted to homemade gunpowder by hunters and by settlers for protection against hostile Indians.

Among those who first pushed into the territory of Kentucky were the "strolling chemists"—men who hunted for saltpeter caves. By 1800, at least 28 Kentucky saltpeter caves had yielded more than 100,000 lbs of saltpeter (Hovey, 1897). Mining ventures in Kentucky caves became so lucrative that, in 1806, the industry attracted the attention of E.I. DuPont, proprietor of a very extensive gunpowder manufactory near Philadelphia. By 1810, there were six powder mills in Lexington, Kentucky. These mills received most of their niter from relatively few caves, such as Great Saltpetre Cave, on Crooked Creek in the Rockcastle area, approximately 40 miles from Lexington. Lexington, Kentucky became the marketing center for nitrates and gunpowder while Nashville, Tennessee was the outpost to the extreme southwest. An enthusiastic entrepreneur (Anon., 1806) of the time reported:

> "Already has salt-petre of this domestic manufactory been sent from Nashville to New York; already have contracts been offered to the government for the delivery of any quantity that may be necessary for the public service; and already are the neighboring inhabitants so expert in turning it to gunpowder, that in Tennessee this latter article is sold by retail to shooters at thirty-seven cents and a half, or three eights of a dollar the pound."

Gilbert Imlay, a captain in the American Army during the Revolutionary War and commissioner for surveying lands in the back settlements, stated in his geography (1797, p. 135) that saltpeter "...is discovered in greater plenty on the waters of Green River, than it is in any other part of Kentucky." Recent analysis of legal records show that Mammoth and Dixon caves, along the Green River, were mined for niter as early as the late Eighteenth Century; a land certificate dated 1798 included 200 acres and "two saltpeter caves" (Thomas, Conner, and Meloy, 1970). These two caves were probably mined continuously from 1798 until the end of the War of 1812. An 1810 visitor from Bowling Green, Kentucky, commented on Mammoth Cave: "it is arched over by a large ledge of rocks, from which issues a clean fountain; from this the workmen are supplied with a sufficiency of water for their saltpetre works (Anon., 1810)."

The first known map of Mammoth Cave, the "Eye-Draught" map, was drawn sometime before 1811, probably as a means of attracting investment capital for expansion of the saltpeter works (Fig. 2). Leaching vats ("the leeches") are shown at the cave entrance on the Eye Draught map. These first leaching vats at the entrance of Mammoth Cave were probably V-vats, perhaps on the order of 15 ft long and 4 ft wide at the top (Fig. 3).

WAR OF 1812

By the beginning of the Nineteenth Century, it was apparent to some Americans that a crisis was emerging in which Great Britain would seek to regain her lost colonies in the New World. In 1806, Dr. Samuel Brown, Professor of Chemistry at Transylvania University, Lexington, Kentucky, presented his views to the American Philosophical Society on the importance of developing the great Kentucky saltpeter caves for a time of national emergency (Brown, 1809, p.236). As a result of his appeal, speculators promoted the exploration and development of saltpeter caves throughout the karst regions east of the Mississippi River. Some caves, such as Donaldson's Cave at Spring Mill State Park, Indiana probably were mined only for home gunpowder needs, but other caves, such as the famed Wyandotte Cave near the Ohio River, the major transportation artery, produced nitrates for manufacture into government gunpowder.

In early 1812, prospects of another war with Britain caused the price of saltpeter to skyrocket, and saltpeter caves became what was early termed the "gold mines" of the day. "The nitre fever of 1812 rivaled the subsequent gold fever of 1849," (Hovey, 1897). "Profits were so great as to set half the Western world gadding after niter caves. Cave hunting, in fact, became a kind of mania" (Bird, 1837). The 1810 market price of 17 cents/lb for crude saltpeter, or "rough shot-petre" as it was called, increased to 75 cents to $1.00/lb during the war years. In 1812, Kentucky supplied 301,937 lbs of saltpeter to the war effort (Niles and Ogden, 1812) — almost the entire supply of powder used by the government. Five hundred pounds of saltpeter/day were mined from Mammoth Cave, Kentucky, and the contract for the supply of fixed alkali for the year 1814 was $20,000 (Meriam, 1844). When the war ended in early 1815, the market collapsed and the manufacture of saltpeter was suspended in most caves. The closure of Kentucky's saltpeter mining operations contributed to a regional depression which lasted into the 1820's.

Some of the most profitable saltpeter ventures of the War of 1812 were the mining operations of the Mammoth Cave region, located near the Green River in the "Barrens" country, a prairie land of rolling hills and knobs containing beds of cavernous limestone. These operations constituted a booming regional industry. At least 12 saltpeter caves recently have been surveyed by the Cave Research Foundation in the Mammoth Cave area; each of these caves contains some evidence of 1812 mining activity such as vats, tally marks, troughs, and other artifacts. A detailed discussion of the saltpeter caves of the Mammoth Cave region and, especially, of the works at Mammoth Cave itself, is given by Hill and DePaepe (1979).

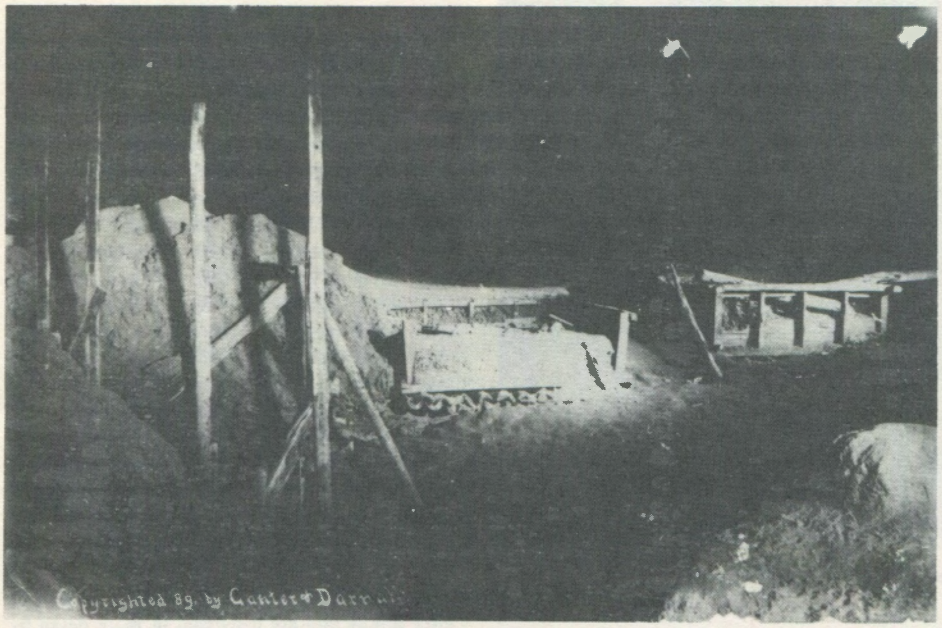

Figure 4. Leaching vats and pumping tower posts in the Rotunda of Mammoth Cave, ca. 1889. Photo by C.G. Darnall, from the Kentucky Library, West Kentucky University, Bowling Green.

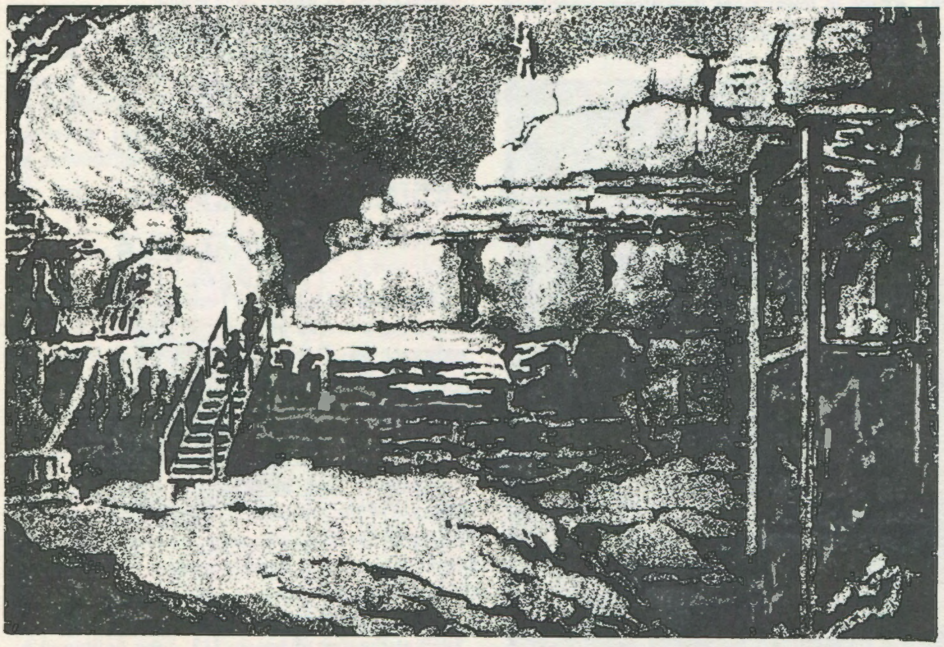

Figure 5. (above) "Entrance to Gothic Avenue," showing pumping tower in Booth's Amphitheatre, Mammoth Cave. Lithograph by T. Campbell.

Figure 6. (left) Boiling kettle formerly used at the Mammoth Cave saltpeter furnaces, now owned by Walter Davis, Brownsville, Kentucky (standing by kettle).

The method of operation at Mammoth Cave, perhaps the largest producer of saltpeter for the War of 1812, was as follows:

1) Miners were dispatched to cave passages to test the earth for nitrate. When the dirt was deemed profitable, the laborers would begin mining by first piling the loose breakdown along the cave walls. Then they would dig the nitrous dirt down to a depth of about 2 feet. The dirt becomes unprofitable with depth.

2) The cave dirt was transported by gunny sack and oxen to large square vats or "hoppers" within the cave where leaching occurred (Fig. 4). Water, piped into the cave from the surface, was directed into each hopper, wherein it seeped through the cave dirt and dissolved the soluble nitrate.

3) The nitrous liquid (or "mother liquor", as it was called) thus obtained drained from the vats into collection troughs. From the troughs, it was pumped from tall towers (Fig. 5) within the cave to the surface. Three pump towers provided gravity flow to transport the nitrate solution by wooden conduits to above the Historic Entrance. The solution was pumped up and allowed to flow downhill to the next tower, where it was pumped higher toward the surface. At the surface, the "mother liquor" was boiled in large vats or kettles called "evaporators" (Fig. 6) inside stone furnaces (Figs. 7 and 8).

4) The "rough shot-petre" crystals obtained upon the cooling of the liquid were sent to a refinery to be manufactured into gunpowder. The most notable refinery of the era was the DuPont powder works near Philadelphia.

BETWEEN THE WARS

At the close of the War of 1812, the large cave-mining operations ceased abruptly. Small "cottage" production sustained itself on local gunpowder consumption, and then only with

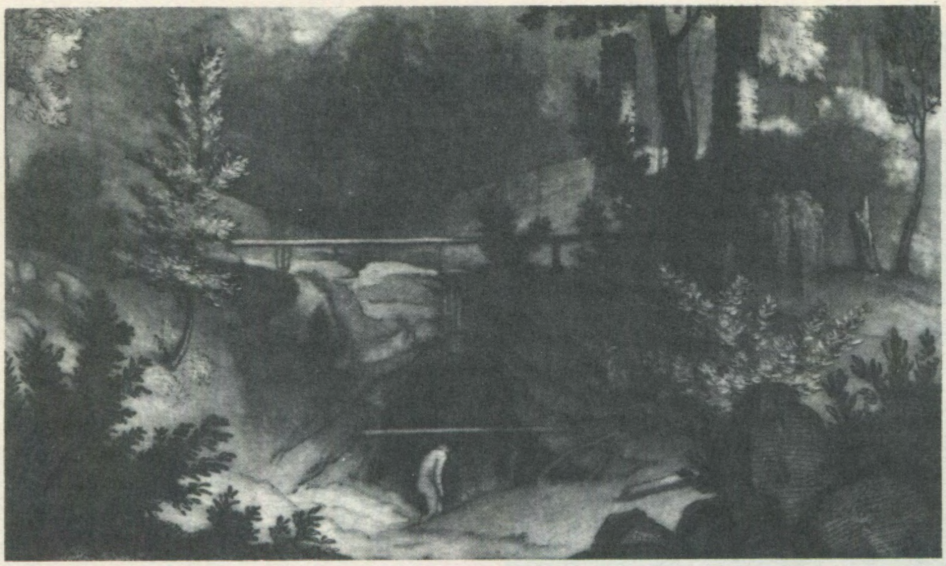

Figure 7. (above) "Mammoth Cave," showing ruins of two log pipelines and two stone furnaces. Engraving by J. Sartain, 1837, for *The American Monthly*.

Figure 8. (below) Entrance to Mammoth Cave, ca. 1890. Arrow in lower right indicates remnants of sandstone foundations of saltpeter furnaces. Courtesy of Ellis Jones, Cave City, Kentucky.

seasonal labor during times when agricultural pursuits permitted.

For home use small V-vats, rather than large square vats, were used for making lye and saltpeter. Home-production methods were utilized by the pioneers and by backwoods people before, during and after the three early wars (the Revolutionary War, War of 1812, and Civil War). Only as the 1900's approached did the home production of saltpeter cease.

THE CIVIL WAR

Union blockades of Southern ports forced the Confederacy to place heavy priority on developing its many saltpeter caves. The Civil War caused even larger-scale industrial operations than had the War of 1812. This period of niter mining is unsurpassed in the history of American caves. Kentucky, although the major producer during the War of 1812, was not a significant supplier to the Confederacy because of its weak sympathy with the Southern cause; likewise, Missouri was not an important saltpeter producer. In the deep South, however, the landscape was dotted with saltpeter recovery operations. Instructions for manufacturing saltpeter (LeConte, 1862) had been widely distributed by the Southern government early in the war. Niter production by the Southern planters was eminently successful and contributed to a prolonged military effort in the face of overwhelming Northern military-industrial might. Many of the big saltpeter caves maintained operations until directly threatened by invading Union troops. Big Bone Cave, Tennessee closed down when the Union encroached upon Nashville; Nickajack Cave, Tennessee was shelled by advancing Northern forces. Other caves, such as Sauta Cave, near Scottsboro, Alabama were better sheltered by location from the military onslaught. Confederate saltpeter mining and niter production are discussed in more detail by Powers and by Smith (this issue).

The bat caves of Texas also played a significant role in Southern saltpeter production. The San Antonio, Texas, region was particularly important for this type of nitrate recovery. In contrast to the clastic saltpeter sediments found in southeastern saltpeter caves, the source of nitrates in these caves was bat guano.

POST CIVIL WAR

The close of hostilities between the North and the South marks the end of the active cave-saltpeter era. During World War I, a feasibility study (Bailey, 1918) was conducted in more than 100 caves in Tennessee's Eastern Highland Rim to determine if cave sediment nitrate recovery would be advisable for the European military campaign. This investigation concluded that because of the availability of Chilean nitrates and nitrogen fixation technology, recovery of nitrates from sediments in American caves was no longer a practical alternative.

The last saltpeter miner died in the spring of 1959 at the age of nearly 113. John Salling as a youth had mined saltpeter for the Confederate Nitre and Mining Bureau. Burton Faust recorded an interview with the old gentleman at his mountain home along the Clinch River in Southwest Virginia (Faust, 1960) just before Salling's death. There, the living history of saltpeter mining in American caves fittingly concluded, where it began some 200 years before, in the cave region of Virginia.

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CONFEDERATE NITER PRODUCTION

John Powers

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SUMMARY

Caves played a major role in supporting the Confederacy's bid for independence. The Confederate Ordnance Department (later, the Nitre and Mining Bureau) successfully utilized the South's numerous but scattered caves to produce an adequate supply of nitrate for gunpowder despite military, political, and logistic disadvantages. Geographic, historic and economic factors led to success despite other handicaps; government assistance to niter producers and capable administration were especially significant. Had the majority of this country's saltpeter caves been north of the Mason-Dixon Line rather than south of it, the War would certainly have ended sooner.

THE STRUGGLE FOR SURVIVAL in the American wilderness coupled with vast distances from the mother countries demanded self-sufficiency on the part of the colonists. An abundant powder supply was essential for hunting and for protection against hostile Indians. Gunpowder contains 75 percent saltpeter; the rest is sulfur and charcoal. As early as 1630, the colonial government of Virginia passed an act pertaining to the acquisition of materials necessary for creating artificial niter beds. In the same year, Royal Governor John Harvey expressed his hopes for discovering a saltpeter cave.[1]

The earliest known American saltpeter manufacture was in 1639 in Massachusetts by Edward Rawson. His work prompted the colonial legislature to pass an act on June 14, 1642, which urged all families and towns to promote saltpeter manufacture.[2] When settlers began exploring the fertile valleys west of the Blue Ridge in the 1740's, they discovered a potential source of domestic niter in the numerous limestone caves there. In 1745, the Virginia Assembly passed an act to encourage production by offering a bounty on saltpeter.[3] Surveying and mapping saltpeter caves were essential to the fledgling industry. In 1770, Thomas Jefferson produced the first cave map in the United States (Madison Cave, Virginia).[4]

The War for Independence stimulated production of gunpowder. In view of the impending conflict, the Continental Congress in 1775 advised the colonies to collect saltpeter for making gunpowder. They also established a saltpeter committee to facilitate production; its members included Franklin, Paine and Jefferson.[5]

To better facilitate administration, the Continental Congress in November of 1775 divided the colonies into 4 districts, each overseen by a saltpeter committee; the committees were authorized to pay 40 cents per pound for saltpeter. By 1783, over 50 caves in one Virginia county alone were being mined for niter.[6] One famous cave (Cave Mountain Cave, near Franklin) contains a set of initials with the date, 1769.[7]

In the period following independence, the production of saltpeter lagged due to the cheaper price of niter imported from England. Local production continued in frontier areas, however, to supply powder necessary for hunting, mining and protection. The census of 1810 shows that 447,144 lbs of gunpowder were produced in the United States.[8]

The war of 1812 again terminated importation of English gunpowder. Production soared and expanded into new areas. Frontier settlement had greatly expanded the base area from which to locate saltpeter caves. Mammoth Cave, Kentucky supplied much of the young nation's new military needs.[9] Niter from Sauta Cave, Alabama provided gunpowder for the famous warship, *USS Constitution*. This cave continued production for over 50 years and would later become one of the Confederacy's most important sources of nitrates. Railway tracks were even installed in the cave to speed mining.[10] Another important southern cave, Nickajack Cave, near Chattanooga, Tennessee began production during the Mexican War.[11]

Over 100 years of production gave the Confederate States a broad base of experience, proved mining locations, and an established marketing system to rely on when they seceded from the Union. By 1860, many saltpeter caves had already been located, explored and developed (Fig. 1). In addition, the pattern of government encouragement had been established since the days of earliest settlement.

CIVIL WAR ERA TECHNIQUES

Saltpeter production in the South was successful because of many economic advantages. Saltpeter was easy to locate, extract and refine. It was cheaper than and superior to imported saltpeter, and the geographical dispersal of the sites lent itself to the character of the war and the decentralized supply system. Only scattered information exists about Confederate niter production. The records of the Ordinance Department and of the Nitre and Mining Bureau

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were destroyed by fire in the closing days of the war. Their chiefs, generals Gorgas and St. John, died before they could write histories of their operations.

Nitrous earth deposits from non-cave sources were more abundant and more widely distributed than were cave sources. Large quantities of nitrates were mined from underneath old dwellings, slave quarters, cattle sheds and barns; almost any old building held a potential deposit of nitrous earth under its floors.

If the earth was dry and loose and not subject to flooding, it necessitated further investigation. Simple tests could determine the presence of saltpeter. If the earth contained whitish, needle-like crystals which tasted cool and bitter, it was further tested. One simply scratched a furrow into the smooth surface of the earth and re-examined it after several days. If the earth again appeared smooth and even, it contained saltpeter. This test was unexplainably accurate.[13] If, after sprinkling some of the crystals into hot coals, they burned quietly with no sparkling or crackling, the earth definitely contained saltpeter.[14] These tests made no demands on the limited education of the average worker of that period.

Once nitrous earth was located, it usually was readily accessible and extraction was easy. Niter mining rarely involved extensive tunneling or quarrying. Of the 12 Virginia caves being mined in 1863, 10 had natural passages large enough to walk through. Many, such as Clarks, Buchanan and Burnsville (Breathing) saltpeter caves were large enough for donkeys and oxcarts.[15] Sauta Cave in Alabama had over one-half mile of oxcart tracks.[16] The majority of saltpeter caves in West Virginia had large, easily traversible passages; Sinnett, Trout and Greenville are among the best known.[17]

Niter production could be done on a small scale with ordinary farm implements: an iron pot, 3 or 4 tubs, several small water troughs, several coarse bags, a wheelbarrow, 4 barrels and several shovels.[18] Once everything was set up, it could actually be carried on by one man.[19] Refining was usually done at the powder factory, but could be done on site. The only additional equipment included several large kettles, a rake and additional troughs, barrels and buckets.[20]

The unusual dryness and stable temperatures in saltpeter caves preserve objects for great lengths of time.[21] Because locating the leaching equipment in the cave was advantageous (less distance to carry the unprocessed earth) and many caves had been mined for saltpeter since the Revolution, it seems probable that niter workers re-used much old equipment left from earlier days. Old water troughs, small bridges, ladders and other equipment can be found in the caves today, even though much has been carried off by overzealous collectors. Modern explorers of Breathing Cave, Virginia first used an old ladder still intact from saltpeter days.[22] In Sauta Cave, leaching pots and scaffolding are intact; wooden rails and metal railway cars are so well preserved that they could probably be used today.[23]

The extracted earth was dumped into 3 barrels.[24] Water leached through the first barrel was poured into the second and then into the third. Finally, the nitrous water was poured into a trough and lye was added to remove undesirable magnesium and calcium and to add potassium ions. Afterwards, the leachate was strained through cheesecloth and then boiled in open kettles.[25] This evaporated the water, causing saltpeter crystals to form. The crystals were strained out and the used water was returned to the first barrel for the next cycle.[26] Three men could produce 100 to 200 lbs of saltpeter in 3 days.[27] The 25 to 30 workers in Sauta Cave produced over 1000 lbs per day.[28]

CONFEDERATE PRODUCTION

Despite the industry's early development, the Confederacy suffered a serious shortage of niter in 1861. Years of peace, emphasis on agriculture and northern domination had hindered industrial development.[29] In 1861, only 2 small powder mills existed. Combined, they produced less than 30,000 lbs per year.[30]

Table 1. CSA niter production by districts, through 30 September 1864. Data from the *OR*, ser. 4, v. 3, p.698.

district	source	production (lbs)
1-4	caves	156,323
	other	346,271
5	other	238,907
6	other	2,008
7	caves	91,747
	other	98,560
8	combined	85,706
9	combined	225,665
10	other	34,716
11	——	na
12	other	820
13	——	na
14	other	29,913

Saltpeter remained an essential for war, as both nitroglycerin and gun cotton were still in the experimental stage.[31] One of President Davis's first acts authorized the buying of northern niter processing equipment and machinery.[32] The outbreak of hostilities closed off the North as a source of supply and demonstrated even more strongly the urgency of developing niter production.[33] In 1861, the Union initiated a naval blockade of southern ports to prevent importation of war goods and exportation of cotton.[34] Its increasing effectiveness stimulated increased efforts toward self-sufficiency by the domestic munitions industry.[35] The blockade caused freight charges for imported goods to rise over 100 percent the first year.[36]

Truly, self-sufficiency became necessary for the South's economic survival. The Confederacy quickly distributed and utilized all munitions captured from federal arsenals and forts seized at the time of secession. Even so, the new nation possessed barely a month's supply of gunpowder.[37] The urgent need compelled the Confederate government to accelerate domestic niter production. The economic and administrative assistance given to the industry illustrates its high priority.[38]

During the war's first year, the Confederate government worked indirectly through state contracts and private firms to develop niter production. Economic aids included loans, subsidies and guaranteed high prices for saltpeter. It allowed private firms a generous 75 percent profit ceiling.[39] The Confederate Congress passed an act authorizing the advancement of one-half the necessary capital for starting new niter works and enlarging existing ones.[40] By the end of 1861, the Ordnance Department, which then administered niter production, authorized its agents to pay 35 cents per pound, nearly triple the price in the North.[41] Despite economic encouragement, however, private production lagged, yielding only 10 percent of the year's total niter supply. The rest was imported.[42]

In 1862, the Ordnance Department started its highly successful importation system, but by August, 1864 sinkings, captures and reduction of ports had wrecked it.[43] The South was reduced to only two ports: Wilmington and Charleston.[44] The capture of Charleston in late 1864 all but ended importation, but domestic niter production increased.

President Davis continued to urge decreased dependence on foreign supplies and to emphasize developing domestic production.[45] Niter production soared 300 percent in 1862 and an additional 300 percent in 1863.[46] Domestic gunpowder cost only one-third that of imported powder because of the dangers of blockade-running and the long transportation distance.[47] Gunpowder produced with Confederate niter at the Augusta, Georgia powder factory cost only $1.08 per pound, while imported gunpowder cost $3.00 per pound.[48] In addition to being cheaper, domestic niter was of equal or superior quality. The May 3, 1863 *London Times* stated:[49] "Powder made in Augusta, Georgia is nearly up to the standards of the finest English powder and costs only four cents to make."

Col. George W. Rains, supervisor of the Augusta powder factory, stated that double refining of saltpeter produced a quality as pure as that from the famous Waltham Abbey powder works in England.[50] Col. (later General) Isaac M. St. John, CSA Nitre and Mining Bureau Chief reported that niter from caves in southwestern Virginia was of superior quality and could be quickly refined.[51] The unused Augusta powder after the war was employed by the U.S. Army at Fort Monroe School of Artillery Practice "on account of its superiority."[52]

By 1862, the growing needs of mass warfare proved too burdensome for the Ordnance Department. It was unable to handle all the work of extracting and processing niter and other minerals in addition to its major responsibility, making arms and ammunition.[53] Accelerating prices, inability to secure slave labor and transportation problems also contributed towards the creation of a separate, independent bureau.[54] On April 22, 1863, at the urging of General Josiah Gorgas, the Confederate Congress established the Nitre and Mining Bureau as a separate agency within the War Department.[55] The Bureau's purpose as stated in the Act was explicit:[56] "...the organization of a corps of officers for the working of nitre beds."

St. John was appointed superintendent over 3 majors, 6 captains, and 10 lieutenants who shared the same pay and allowances of similar grades in the cavalry.[57] By August, the Bureau had 400 men working 16 caves. It had produced 100,000 pounds of saltpeter by October.[58] The $1,000,000 niter appropriation in August, 1862 was almost one-third of the total Ordnance Department budget.[59] The Bureau's appropriation for January through June, 1864 was $9,500,000, nearly half of the total Ordnance Department appropriation.[60] For the same period in 1865, it rose to $12,500,000.[61]

Labor requirements became increasingly acute because of the conflict between larger niter production and the growing demand for soldiers. To alleviate the labor problem, especially in remote, mountainous areas such as West Virginia where apathy and unionist sympathies hindered hiring, the Secretary of War in May, 1862 ordered all army commands to detach details of men at the request of the Bureau's local officers to work niter caves and deposits in their respective areas.[62] In addition, they were to seize the men, equipment and caves of inefficient private producers.[63]

The government further eased the niter industry's labor problem by giving it the highest priority in conscripting Negro slave labor. Although private industry had been hindered by the reluctance of slave owners to have their slaves work far from home, and because the owners felt that the needs of agricultural production required them, niter mining became one of the 3 largest employers of Negro labor in industry.[64] In one Virginia county (Smith), 75 percent of all slaves were producing saltpeter.[65]

Conscription remained a thorn in the side of the Confederate supply system throughout the war; yet, the Bureau was barely touched. Its workers received the highest priority in exemptions from conscription. The first Conscription Act of 1862 exempted miners.[66] In 1864, due to urgent manpower needs of the decaying military picture, General Order No. 77 was issued. It revoked exemptions of all men ages 18 to 45 except those classified as experts.[67] The Bureau until then had been struggling along with a minimal 30,000 men. St. John threatened to resign over charges that his bureau harbored draft evaders, but Gorgas (Chief of the Ordnance Department) refused to accept it.[68] Due to St. John's and Gorgas's protests, President Davis granted the two agencies a "concession." They suffered only a 20 percent cut in personnel instead of 30 percent. No other Confederate agency was so favored.[69] By 1865, 70 percent of all able-bodied men engaged in supply who weren't artisans or mechanics were in the Nitre and Mining Bureau.[70]

The government also aided the niter industry in surmounting transportation difficulties. In 1862, the Secretary of War directed that saltpeter and powder would be given the highest priority in transportation.[71] Historical evidence on this subject is meager, but government control of all railroads and the prohibition on transport of non-essentials (to the war effort) certainly helped.

CONFEDERATE LEADERS

The niter industry was administered by competent leaders. Until 1862, along with its other duties, the Ordnance Department struggled to develop it. Ordnance Chief Josiah Gorgas created the Nitre Corps to begin surveying the South's niter resources. He persuaded the states to relinquish their supplies to the Confederacy. A West Point graduate and ordnance officer, he had gained much practical experience during the Mexican War and at various arsenals throughout the United States.[72] He experimented with new cartridge designs, designed new artillery, and familiarized himself with the making of gunpowder.[73] Robert Kean, head of the Bureau of War, praised Gorgas as a "talented administrator."[74] In addition to centralizing the Confederacy's niter supply, Gorgas pushed the bill which created the Nitre and Mining Bureau.[75]

The Chief of the Ordnance Department's Nitre Corps, George W. Rains, was also a talented and experienced leader. He was a graduate of West Point, ranking first in the Scientific Studies Curriculum. His career included military service in Mexico, teaching chemistry at West Point, and serving in the Army Engineers and Artillery.[76] Under Gorgas's direction, Rains enlisted agents to survey niter caves in Alabama, Tennessee, Georgia, western Virginia (now West Virginia) and Texas and visited many of these himself.[77] He built a larger niter refinery and powder factory at Nashville which shortly was producing 3,000 lbs per day.[78] In addition, Rains started construction of artificial niter beds and published a pamphlet to encourage local production.[79]

Isaac M. St. John was selected to head the newly created Nitre and Mining Bureau. He was probably one of the most talented administrators in the Confederate Army. A Yale graduate, the youngest in his class, he tried medicine and journalism before becoming a civil engineer.[80] Upon his selection to head the Bureau, his superior, General McGruder, regretted losing him, saying that he[81] "...has energy and talent beyond any that I have witnessed." St. John's psychological insight aided him greatly. He concentrated on what he controlled, not on what he didn't—*e.g.*, on transportation and on raising funds.[82] By the war's end, his talents were nationally recognized. Robert Kean praised his great energy, organizing talents and ingenuity, explaining that [83] "St. John created resources where none previously existed." Recognition of his accomplishments was illustrated by his promotion to General and selection to take over the floundering Commissary Department.[84]

NITRE AND MINING BUREAU

St. John seized the reins of the Nitre and Mining Bureau at a low point in the war. Many caves had been lost during the Union's Spring Campaign through the Shenandoah Valley. Production was struggling along.[85] Through him, the Bureau reacted successfully to the changing needs of war. His first action decentralized command while unifying control over the entire industry. He divided the Confederacy into 14 districts, each supervised by an experienced ordnance officer who enlisted labor from those subject to military duty.[86] Over these districts were 3 supervisory divisions: First Division (Alabama, Georgia and South Carolina), Second Division (Virginia, Tennessee, Kentucky and North Carolina), and Third Division (trans-Mississippi area).[87] This lent itself to the geographical diversity of the South's niter resources. It also reduced red tape. Officers didn't have to go through elaborate channels to impress a cave for production.[88] The Bureau became an efficiently running machine. Its central headquarters in Richmond was noted for its small number of officers.[89] Within 6 months, the Bureau had increased production to 2,000 lbs of powder per day, which almost met military needs.[90]

The Bureau expanded its labor force despite the losing course of the war. By July, 1862 2,771 Whites and 115 Blacks were developing Bureau-controlled niter works. This does not include private works.[91] Although the Bureau's high priority in impressing Negro slave labor greatly aided its operation, it also hired a large number of free Blacks.[92] It established a training program from which a small nucleus of skilled workers trained the unskilled.[93] St. John stated that better training offset the losses of niter works.[94] Despite conscription and the Army's reluctance to relinquish skilled workers, the Bureau contained almost 4,000 niter workers by 1863.[95] By September, 1864, due to Army impressment, desertion, conscription, capture, casualties and other losses, it numbered only 3,292 niter workers. Yet, due to their superior training, these workers provided 55 percent of the Confederacy's total niter supply. In contrast, the Union required over 80,000 men for its niter production.[96]

Decentralization also made production less vulnerable to Union destruction. Twenty-seven limestone caves were mined for saltpeter in Alabama, 25 in Virginia and many in Tennessee.[97] As territory was increasingly lost to Union forces, Nitre and Mining Bureau Commandant St. John concentrated more on developing niter production from non-cave sources.[98] North Carolina had no known caves, yet it became the district with most constant supply of niter. Enemy action had less effect on North Carolina and other coastal states.[99] From June through September, 1864, Virginia caves supplied only 24,133 lbs of saltpeter, while North and South Carolina and tidewater Virginia supplied 93,558 lbs.[100] By 1864, as cave areas were increasingly lost to the Union, production from other deposits exceeded that from caves.[101]

Despite military reverses and gradual loss of territory, niter production didn't decline until 1865.[102] Production of saltpeter in the Confederate heartland wasn't hampered until Sherman's march through Georgia in late 1864.[103] As caves were increasingly lost, St. John countered with the establishment of artificial niter beds at Columbia, Charleston, Augusta, Savannah, Selma, Mobile and elsewhere. These beds would have supplied 3 to 4 million lbs of saltpeter—enough to arm the South's cannon for several years—had not the Confederacy collapsed before the beds became ripe.[104]

The smallness and seclusion of the scattered niter operations rendered them seemingly unaffected by Union advance. Despite Union conquest and major raids in Tennessee, Kentucky, West Virginia and the Shenandoah Valley, many caves there continued to supply niter to the powder factories through 1864.[105] In Virginia, 12 caves were still operating in September, 1864. Buchanan Cave, one of the largest saltpeter-producing caves in the state, located near Saltville, was never captured.[106] Fifteen caves were still being mined in the Greensboro-Chattanooga area of Tennessee in 1863 despite constant harrassment by Union forces.[107] Even in unionist West Virginia, caves raided in Pendleton and Greenbrier counties were repeatedly re-opened. St. John reported the raiding by the 12th N.Y. Cavalry of a cave near Franklin in March, 1864.[108] Herndon Wagge, a resident of Franklin (and owner of Floyd Wagge's Cave), reported that his father worked in caves as a "petre monkey." He was captured by marauding Union cavalry and taken to a prisoner camp at Old High Town, then released upon his pledge not to engage in any more saltpeter production.[109]

Despite the weakness of the Confederacy, the Nitre and Mining Bureau expanded and increased production. By decentralizing production, maximizing the output of its workers, instituting efficient administration and providing governmental assistance, the Confederacy seldom lacked saltpeter.[110] The Augusta, Georgia powder factory had 70,000 lbs on hand at war's end.[111] St. John had developed production of saltpeter to the point where the Confederacy would have been independent of importation had the necessary territory been held.[112]

CONCLUSIONS

Saltpeter caves played a major role in supporting the Confederacy's bid for independence. Confederate niter production was successful because of geographic, historic and economic advantages, governmental assistance and capable administration. Most Southern leaders believed that if war came, it would be a short victorious one. When it did come, capable soldiers and engineers like General Gorgas, Colonel Rains, and General St. John utilized the South's natural resources to the utmost, given the difficulties of transportation and communication at that period. Had more of this country's caves been north of the Mason-Dixon Line, the war would certainly have ended sooner.

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CONFEDERATE SALTPETER MINING IN NORTHERN ALABAMA

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SUMMARY

A domestic gunpowder industry was successfully developed by the Confederate States of America during the Civil War years 1861-65. Brilliant administrators such as Gorgas, St. John, and Rains were able to increase production from virtually none in 1860 almost to the point of self-sufficiency before severe losses of territory in 1865 deprived the Confederacy of many of its sources of saltpeter, an essential ingredient.

Alabama caves were an important source of saltpeter. Surviving records of mining at Long Hollow Cave, Marshall County, and at other caves in northern Alabama, are unusually complete. From them is reconstructed an authentic picture of the administrative organization, production methods, and logistic problems of the Confederate Nitre and Mining Bureau.

ONE PROBLEM that the Confederacy succeeded in solving was the production of sufficient amounts of gunpowder. A "complete" account of this achievement has never been written, and the published references that exist tend to be of a general nature or serve as supporting data for a broader topic. The study of this subject has been hampered by the wartime destruction of many of the documents and by the subsequent failure of the highest-ranking personnel to write their memoirs. Although there are many facets to the story, the focus of this article will be upon the domestic production of saltpeter or niter, the main ingredient of gunpowder, from the limestone caves of northern Alabama, with particular attention given to the difficulties of an individual operation.

PRIVATE DEVELOPMENT

At the start of the war virtually no powder was manufactured in the South. The 1860 census lists only two small mills, one in South Carolina and one in Tennessee.[1] After secession, many local government officials, as well as private citizens, realized that if war did come, a domestic supply of gunpowder must be developed. In some states, as in Tennessee, military boards were established whose duties included making contracts with local producers of saltpeter.

Working closely with the Tennessee Military and Financial Board was Samuel D. Morgan, an influential citizen of Nashville. In the spring of 1861 he corresponded with people not only in his own state but in Arkansas and Alabama, encouraging them to commence saltpeter production from caves. Later he aided in the enlargement of Cheatham County, Tennessee's Sycamore Powder Mills, where much of the saltpeter produced in the area was blended with charcoal and sulphur, and made into powder.[2]

The immediate result of Morgan's solicitations was the discovery of both previously mined and potentially mineable saltpeter caves. In Tennessee he obtained information about a number of caves, including Nickajack, Lookout, Big Bone, and several unnamed caves in or near White County. For Alabama, 6 responses to Morgan are known. William Richardson Hunt, then chief of ordnance at Memphis, but later the Nitre and Mining Bureau officer at Selma in charge of iron mining,[3] forwarded saltpeter information from a Mr. Echols of Huntsville: "Wm or David Larkin Jackson County Ala owns a deposit from which Mr. Echols says he has purchased it by the waggon load from time to time for many years." In addition, he reported a "deposit" on the lands of "Dr H A Binford in Limestone Co" and "Dr. W^{m}. O. Winston of Talladega Co."[4] B. Lanier of Huntsville indicated that there was "a cave of Salt Peter at the mouth of Elk River in Lauderdale Cty" where "There has been a good deal of work done" but "The mine is not any Thing like Exasted."[5]

Referring to a notice by Morgan in the local paper, John D. Taylor of Guntersville volunteered, "And as for the dirt containing the Niter I am assurd by good men that there is an aboundence of it in the different caves of this (Marshall) County and all we lack is Some One to start the work."[6] Sam Tate, Superintendent of the Memphis and Charleston Railroad, reported a cave "2½ miles below Tuscumbia" with "an inexhaustable Supply of Rich Salt Petre earth in it."[7] James R. Harris of Winchester, Tennessee, who had visited caves in Jackson County "Convenient of access — and within Ten miles of Stephenson," asked where he could obtain four 100 gallon kettles.[8] But Nelson Robinson, a sixty-one year old farmer and lawyer of Bellefonte,[9] had the most positive news: "I have Succeeded in getting a company to go to work in the Sauta Cave, the best in the region with one hundred hands. They commenced on Monday last [May 6]." He further mentioned that he had men searching the mountains for other caves in addition to "starting a party to examine a large cave in DeCalb Co. near old fort Payne." The greatest difficulty, he thought, in mining the niter deposits was "in obtaining hands to work them — Such is the false military furor here to enter the army."[10]

Newspapers of the same period show that interest in locating saltpeter deposits was a public concern. The Tuscaloosa *Constitution* observed "there are several Saltpetre caves in Franklin County, Ala., which have been worked on a small scale" and suggested that a "competent mineralogist" should test them.[11] The Huntsville *Democrat* mentioned that in Morgan County "there are very rich saltpetre caves in Newsom's Sinks, very accessible, about fifteen miles from Whitesburg ...belonging to Mr. David Prince, who says, the Confederate States may work them at pleasure."[12] Whereas the Fayetteville, Tennessee *Observer* noted that Nashville had received "a large lot of sulphur" and that powder would be made there "as soon as the nitre (saltpetre) can be procured." Mentioning that niter had been made in North Alabama caves during the War of 1812, it was pleaded, "The business should be at once commenced. We cannot fight without powder. We cannot make powder without saltpetre. Who will see to it that the caves once worked to produce this absolute necesity are again worked and saltpetre made for market?"[13]

Jackson County's Sauta Cave, one of the caves worked before and during the War of 1812, was briefly mentioned several times. In June, 1861, the Montgomery *Advertiser* reported that the proprietors were daily "turning out a quantity," being under contract "to furnish a certain number of pounds monthly to a powder manufacturer in Nashville, Tennessee." It was claimed "some fifty hands" were employed at Sauta, with "the average yield" being "about three pounds of the salt to one bushel of earth, ten bushels of wood ashes being used in lixiviation."[14] About the same time the Huntsville *Advocate* reported that John D. Borin was one of the men in charge of the operation and that his company could "turn out 700 pounds per day."[15]

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GOVERNMENT PROMOTION

At the same time local expression of concern and early attempts toward actual saltpeter production were in process, the Confederate Government made similar efforts to insure that an adequate supply would be available. The Provisional Congress on February 20, 1861, passed "An Act to provide Munitions of War, and for other purposes," which included provision for the "establishment of powder mills and for the manufactory of powder."[16] In early May, in answer to a Congressional resolution asking if any measures had "been taken to promote and induce manufactures of arms and of powder," the Secretary of War reported that an agent, John C. Riddle, "has been dispatched to examine several caves on Little Bear Creek in Franklin County, and another in Blount County," Alabama.[17] In April Major Josiah Gorgas was assigned as the Confederacy's Chief of Ordnance and in that capacity one of his duties was to guarantee adequate powder supplies.[18] To this end he and President Jefferson Davis selected George Washington Rains, giving him full power to do what was needed.[19] Leaving Richmond July 10, 1861, Rains toured the South, selected Augusta, Georgia, as the site for the South's main powder mill, and proceeded to Nashville to make arrangements to increase powder production there. Saltpeter contracts with the Military and Financial Board were turned over to him, he visited some caves, and sent agents with authority to make contracts to investigate others. After several months Rains was relieved of his duties in Tennessee and subsequently devoted his full energies to the construction and operation of the successful Augusta Powder Mill.[20] During the fall he published a pamphlet, "Notes on Making Saltpetre from the Earth of the Caves" which was widely distributed and copied in many newspapers, including those of Alabama.[21]

As the duties of the Ordnance Department increased, Gorgas asked for the creation of a separate organization to supervise saltpeter production. On April 11, 1862, Congress accommodated and the "Nitre Corps" came into existence,[22] nominally under the supervision of the Ordnance Department, with Isaac M. St. John as chief. The saltpeter region was divided into districts with an officer in charge of each district who oversaw work details and production. The Corps worked so well that on April 22, 1863, Congress made it an independent entity of the War Department with the title "Nitre and Mining Bureau," and to its responsibilities were added the mining of iron, copper, lead, coal, and other minerals.[23]

SALTPETER MINING IN ALABAMA

Alabama was divided into two districts. William Gabbett commanded the northern district, No. 9, and William H. C. Price the southern district, No. 10. Later, as the Confederates were forced from Tennessee, Gabbett also acted as head of the middle Tennessee and extreme northwestern Georgia district and signed his correspondence as superintendent of districts 8 and 9.[24] Gabbett's territory was in the mountains and most of the saltpeter his men made came from caves. In Price's district, however, saltpeter was usually extracted from dirt underneath old buildings, and a potential source was created by constructing artificial niter beds.[25]

If the surviving records present an accurate picture, 1862 niter production in Alabama seems not to have met the optimism of the previous year. It was reported in March that only four caves were then being worked. Without naming any of the caves it was claimed that fourteen men working four and a half months, made 2,785 pounds at one operation, and at other sites 9,000 and 4,350 pounds were made, at a cost per pound, of 75 and 73 cents. It was urged that the government price for saltpeter be increased "to secure a continuance of the work."[26] Undoubtedly one of the caves being worked was Sauta, but spring brought General Ormsby M. Mitchel's invasion of northern Alabama which "occasioned a general suspension of work" at that site.[27] By late July only "two or three caves" were being worked in Alabama, but "more will soon be started by Bureau agents."[28]

Before the end of the year, after the Federals temporarily withdrew from the area, work was resumed at Sauta. Concerned about protection at cave sites, St. John asked for and received authority to "organize and arm the working forces."[29] An order was issued which allowed "a company of sixty-four non-conscripts to be raised and detailed to guard the Santa [Sauta] Cave."[30] This order was soon revoked and substituted by a similar one for the company "to guard and work" the cave, which was in line with St. John's belief that it was better that "the workmen guard their own works."[31]

For Alabama there are indications that the number of saltpeter cave operations increased after 1862. This is deduced from the increase in recorded incidences of discovery of such operations by the advancing Union forces. Specific information for 1863, however, is sparse. In April General Grenville M. Dodge, USA, alluded to a saltpeter works "near Decatur."[32] It is possible that this was the cave near the confluence of the Elk River with the Tennessee, since in May the location of such a cave was published on a map in a Northern newspaper under the headlines, "Col. Dodge's Expedition."[33] Or perhaps it was Morgan County's Trinity Nitre Works, from which during this time tools and provisions were moved to a place of safety by the superintendent, John L. Bartow.[34] Sauta Cave was still in operation as late as June, but probably within a few weeks work there was suspended for the final time.[35] The Union re-occupation of much of Alabama north of the Tennessee River and the movement of portions of General William S. Rosecrans' army through the state and into Georgia in late summer brought to light two more caves. On September 4th a detachment of Colonel Edward M. McCook's cavalry, moving southward from Valley Head, found the works at what later became known as Manitou Cave and captured the Confederate niter agent.[36] A private with that detachment noted they "passed a saltpeter Cave and Burned the works and the Saltpeter Mills."[37] The next day, while a large segment of the Union army was moving through Long Island Cove and up the western slope of Sand Mountain a cave which contemporary reports called either "saltpetre" or "Hill's" was located "where the rebels have been working the cave ever since the war began." This cave drew many soldier visitors, including Rosecrans himself.[38]

More is known about Confederate niter mining efforts in Alabama for 1864 than for any other period of the war. This is because official reports of Union raids were published, and of the recent acquisition of the papers of a Confederate Nitre and Mining Bureau officer.

Several sketchy 1864 reports mention saltpeter operations. In late January the 15th Michigan Mounted Infantry again destroyed "a quite extensive niter-works" at Manitou Cave "and captured 1 officer and 7 privates."[39] In mid-April Brigadier General John W. Geary with 800 men made a five day reconnaissance by boat down the Tennessee River from Bridgeport to near Triana and back. "At Wild Goat Cove," he reported, we "discovered places for manufacturing saltpeter."[40] A few days later a Nashville, Tennessee, paper listed the names of fifteen citizens and soldiers "direct from the nitre works near Paint Rock, (Ala.)" who had apparently quit the Confederacy. "Up to a short time since they had all been engaged in the nitre works."[41] That summer, on August 15, Major Alfred B. Wade, 73d Indiana Infantry, with a force of 100 men, crossed the Tennessee River and at the plantation of James Grantlin "destroyed a saltpeter-work belonging to the Confederate Government," and at Valhermosa Springs "effectively destroyed another saltpeter-work...breaking the kettles and burning the building." He noted there were "other works in the neighborhood, but I did not discover them."[42]

These reports deal with sites, generally on or near the Tennessee River, that were located by Union patrols. While interesting, little is actually learned about the individual operations. Who worked these sites, when they were started, how large and how productive they were are questions not easily answered. Some of the answers, for a few of the caves, are revealed in a collection of papers donated to the Georgia Archives in 1971, which give the largest amount of detailed information about Confederate saltpeter mining in Alabama known to date.

John Riley Hopkins, a prominent citizen of Gwinnett County, Georgia, was an officer at several niter works in Alabama. Within his papers are about 200 documents pertaining to that service, mostly dated 1864, including time sheets, lists of arms, types of tools used, names of workmen and slaves, ration and forage lists, requisitions, receipts, monthly reports, and various messages between sites.[43] Although a few references are made to Sauta Cave in Jackson County and Blue Mountain Cave in Calhoun County, the bulk of the material pertains to the Long Hollow and Big Spring works in Marshall and four sites in Blount County: Nixon's, Culpepper's, Little Warrior, and Cedar Mountain.[44] A close examination of these records reveals many of the daily struggles of Hopkins and his fellow workers to produce saltpeter.

LONG HOLLOW CAVE ALABAMA

As an example, because sufficient records exist, and the correct identity of the site is unquestioned, the Confederate mining efforts at Marshall County's Long Hollow Cave will be described at length. This cave, located in a bluff near the Tennessee River about ten miles below Guntersville, has been surveyed to a distance of 2,680 feet.[45] The mining was done in the first thousand feet of passage, a dry, straight natural tunnel five to ten feet wide and usually of walking height except for one crawl about one hundred fifty feet long. Physical evidence within the cave indicates that the miners excavated a layer of earth two to three feet thick. Also, the lack of piles of leached dirt inside the cave suggests that the leaching was done outside.

It is not known when work began at Long Hollow. Possibly it was before late April, 1864, when Hopkins was sent to the site with a small force of men. On a report, next to the names of workers W. H. Herrin and A. C. McMinn, was the notation "Old hand at Long Hollow," indicating that they had been there a considerable time.[46] Hopkins initially commanded ten men plus a wagon and team. On May 1st three men left and twelve men arrived. At mid-month came nine hands, including J. M. Blackwell, who had been recommended for "foreman in the cave," followed a few days later by a lone laborer.[47] Five of these newcomers deserted May 24th. Exclusive of the two "old hands" already mentioned, the entire force at Long Hollow had been transferred from other niter or associated works in northern Alabama and Georgia. Three, including Hopkins and his assistant superintendent, W. B. Stephens, came from Big Spring; six from Blue Mountain; three from Prater's Cave; two from Little River; five from Cedar Mountain; and eight from Cobb's Potash Works. During May one sick man was discharged, while two other sick men were sent to Big Spring.[48]

The Nitre Bureau expected Hopkins to be productive. This was indicated in a letter from his immediate supervisor, J. F. Martin: "We look to you for Saltpeter and dont intend that you shall Lack for anything that we can furnish."[49] Martin, at Big Spring, was assistant superintendent of District No. 9.

Besides orders, tools and supplies for Long Hollow came from Big Spring. Hopkins was instructed to give receipts for the tools he acquired from that work. While at Long Hollow, Hopkins receipted axes, picks, shovels, rock hammers, ovens and lids, tin plates, nails, buckets, drills, iron wedges, steelyards, wheelbarrows, an adz, a crosscut saw, a handsaw, a froe, a one inch auger, a spirit level, a kettle, a hatchet, a spade, a crowbar, and barrels of potash.[50]

Rations were sent from Big Spring by wagon once a week. The daily amount issued per man at Long Hollow was a half pound of bacon and one and a half pounds of meal, plus an occasional small amount of peas. Salt was not weighed daily. For instance on May 3d, only five and three-fourths pounds were issued to nineteen men to last eight days. There appear to have been two classifications of men at Long Hollow, since the rations from Big Spring were marked "L" for laborers and "G" for guards. With the rations for the men was sent forage, usually corn, for the animals, a yoke of oxen and two mules.[51] Sometimes when forage failed to last it was borrowed or bought locally by Long Hollow personnel. Then when the regular shipment of rations and forage arrived the borrowed amount was paid back.

Scarcity in all areas was a continuing problem for the niter workers. Martin made repeated requests that meal sacks and other items should be returned to Big Spring. On one occasion he requested Hopkins to "please dispense with the use of the ox team—so far as you can…our forage is getting verry scarce—and if your mule team can Carry on your works it will help us verry much in the way of feed." In the same note he requested nails to be sent back, "until our wagons returns from Blue Mountain we havent nails to Box what nitre we have made."[52] On another occasion he sent "all the paper that I can Spare" and promised to fill Hopkins' "requisition by the wagons—as far as in my power—but I think Some of the articles called for are not on hand."[53] Wood for construction at Long Hollow was cut and hauled to a local sawmill, then hauled back to the work site.[54] Late in May Martin asked Hopkins to "secure for me a Load of plank Suitable for nitre Boxes" because "we cant get any plank in this country."[55]

Early in the month Martin responded to a venture previously proposed by Hopkins. One of the Long Hollow workers, W. H. Herrin, apparently some time before had been engaged in niter making in a cave north of the river and had left some of the finished product there when the work was abandoned. Hopkins was told to "Use your discretion in regard to Leting Mr. Herrin cross the River. If you think it perfectly Safe for him to go—& he will bring out the nitre that he has on hand I have no objection to his going."[56]

Hopkins maintained a "Programme of labor & improvements" at Long Hollow which shows what work was actually done each day. From April 27 through May 7 at least four shelters for the workers, one cook shelter, one office shelter, and a furnace were built, plus grading and "Getting hopper floors."[57] By the 14th four hoppers and various troughs were built and in place, and the workers "Filled 1st hopper 2/5 full of dirt." On the next Monday, the 16th, the hopper was filled, the waterworks built, the settling trough fixed, and the crystallizing trough set up. Boiling commenced the next day and shelters were built for the new arrivals. On the 18th they "made 1st shoot of Nitre." Routine work continued with the work details for the 21st being "8 men for dirt = 2 hoppers — 1 boiling — 4 hauling — 2 wood — fixed office walls…filled 3rd hopper and began to fill 4th a little." The 23d saw the usual "dirt work — boiling" continue, plus construction of the 5th hopper. They also "finished making first box of nitre." The following day the 6th hopper was built, the "crystalization tray for draining nitre" was gotten ready, and the first box of niter was sent off. Normal work was maintained and by the 28th the eighth hopper was under construction.[58]

On the back of a note from Assistant Superintendent Martin were the following computations. "A bank of dirt" in "55 yds of the low passage" of Long Hollow Cave was estimated to contain 2,652 bushels of dirt which was "enough to fill 10½ hoppers of 252 Bu each."[59] But this dirt bank was not to be touched, the Federals raided the works before it could be dug.

Because of their proximity to the river there was constant fear of discovery. Each time a boat passed the miners were in a state of alarm. They received arms May 21st and drilled for the first time the same day. For their entire force they had only nineteen guns: six old rifles, caliber 58, eleven old muskets, caliber 69, and two new Belgium rifles, caliber 69. Ammunition included 429 cartridges and 413 caps for the older guns, and, after the 23d, 140 cartridges and "13 papers of caps" for the Belgium rifles.[60]

On May 28, just when Long Hollow was beginning to become productive Martin at Big Spring wrote Hopkins:

> You will hide your Kettles Tools
> & c Such as picks Shovels & Spades
> & c — Bring your cooking vessels
> axes — and all other articles that
> you can bring — in your ox wagon
> — and fall back on this place as
> Rapidly as possible — have the
> men to help the wagon up the
> mountain. I will send the mule
> team to meet you on the way —
> have your men bring all their guns
> — *act promptly*[61]

The next day, after preaching services were held, the order was apparently carried out, just in time for the men to escape capture.

Long Hollow probably had been for some time under Federal surveillance. On the 29th Lieutenant Colonel Charles H. Jackson of the 18th Wisconsin Infantry, commanding the Northern forces in the vicinity of Whitesburg, wrote his superior that there were "about fifty [rebels] at a saltpeter cave about one mile from here on the south side of the river," and asked, "Shall I take some men and go there?"[62] The answer was yes and two days later he reported the result: "I found about thirty men at the saltpeter works. They all fled to the mountains. We destroyed all their works, which were near, and fire in their furnaces."[63]

Niter making activites for Hopkins and his men were not over. On June 6 they were ordered to Blue Mountain to work in the cave there. About seven weeks later Hopkins and twenty men, including J. M. Blackwell and W. H. Herrin, were sent to Blount County's Cedar Mountain Nitre Works. Records from that operation reveal Hopkins was acting as assistant superintendent as late as October, 1864.[64]

During the last year of the war the headquarters of Nitre and Mining Districts 8 and 9 fluctuated between Blue Mountain and Montevallo. But Blue Mountain, the terminus for the Alabama and Tennessee Railroad,[65] was the more important. It was apparently the main supply center for the Nitre Bureau in north Alabama. Supplies from Blue Mountain were hauled by wagon to certain caves in the counties which served as local supply points, such as Big Spring in Marshall County and Little Warrior in Blount County. At the same time it can be assumed that much of the saltpeter that was made was sent back through Blue Mountain to the powder mill at Selma.[66]

Although the territory under Confederate control kept decreasing, Captain Gabbett's district continued to produce saltpeter until at least the last months of the war. Some of the same men, such as John D. Borin, who had been active at Sauta Cave in 1861, continued in the niter business throughout the war. Saltpeter production, though frequently interrupted by the enemy, never ceased entirely. On more than one occasion, after a site was raided, it was refurbished and worked again. But the primary reason for continuance of production, even after a site was permanently destroyed or abandoned, was there were always other caves to be worked or operations in progress that could be enlarged. Near the end of the war Colonel St. John stated, "It has...been the aim of the Bureau to work to the last our natural deposits, at times within the enemy's lines, and to examine carefully for new deposits in every possible locality," an effort that was maintained in Alabama.[67]

Available figures for saltpeter production in northern Alabama, from both caves and underneath buildings, was as of September 30, 1864, 225,665 pounds. This represented 13% of the Confederacy's total domestic production and, while lower than the Virginias (29.1%), Tennessee (15.9%), and Texas and Arkansas (23.5%), was nevertheless a significant accomplishment considering the few men involved. The force on September 30, 1864, for instance, was only 295 Whites and 88 slaves or free Blacks.[68]

At least fifty-five[69] caves in Alabama have been mined for saltpeter, and while it would be a mistake to assume they were all worked during the Civil War, certainly a large number were. Many were small one and two man operations, but as demonstrated in the above pages, some were sizeable government undertakings. The cessation of hostilities in 1865 and the invention of newer types of powder ended the use of saltpeter from American caves as an ingredient of gunpowder. Now all that remains from that obsolete mining process are a few piles of dirt, scattered wood fragments, pick marks, and a myriad of questions by speleo-historians.

FOOTNOTES

1. *Manufactures of the United States in 1860: Compiled from the Original Returns of the Eighth Census, under the Direction of the Secretary of the Interior:* Washington, v. 3, pp. 556,561.
2. G.W. Rains (1882) — *History of the Confederate Powder Works:* Augusta, Chronicle and Constitutionalist Printers, p.5; A.P. Van Gelder and Hugo Schlatter (1927) — *History of the Explosives Industry in America:* NYC, Columbia University Press, p.108.
3. U.S. Department of War (1880-1901) — *The War of the Rebellion: A Compilation of the Official Records of the Union and Confederate Armies*: Washington, 70 vols. in 128, ser. 4, v.2, p.778.
4. Samuel D. Morgan Papers, Tennessee State Library and Archives, Nashville — William R. Hunt to Morgan, 9 May 1861.
5. *ibid.*, B. Lanier to Morgan, 1 May 1861.
6. *ibid.*, John D. Taylor to Morgan, 11 May 1861.
7. *ibid.*, Sam Tate to Morgan,. 10 May 1861.
8. *ibid.*, James R. Harris to Morgan, 28 June 1861.
9. *1860 Census,* Alabama, Jackson County, Town of Bellefonte, page 84; T 3, R 6 E, p.24.
10. Morgan Papers — N. Robinson to Morgan, 10 May 1861. It is likely that Mr. Robinson was a kinsman of William Robinson, who operated Sauta Cave during the War of 1812.
11. As quoted in the Rome, Georgia *Tri-Weekly Courier,* 11 May 1861.
12. As quoted in the Nashville *Daily Patriot,* 8 June 1861.
13. Fayetteville, Tennessee *Observer,* 13 June 1861.
14. As quoted in the Columbus, Georgia *Daily Inquirer,* 1 July 1861.
15. As quoted in *ibid.*, 22 June 1861.
16. F.E. Vandiver (1952) — *Ploughshares into Swords: Josiah Gorgas and Confederate Ordnance:* Austin, University of Texas Press, p.57. See also: J.M. Matthews (Ed.) (1864) — *Statutes at Large of the Provisional Congress of the Confederate States of America:* Richmond, Stat. I, Ch. 4.
17. *OR,* ser. 4, v. 1, pp. 292-293.
18. Vandiver, p. 57.
19. *ibid.*, p. 75; Rains, p. 4.
20. *ibid.*, pp. 6, 7.
21. Two Alabama papers in which the pamphlet was copied were the Huntsville *Democrat,* 4 December 1861 and the Mobile *Advertiser and Register,* 26 March 1862.
22. J.M. Matthews (Ed.) (1862) — *Public Laws of the Confederate States of America Passed at the First Session of the First Congress: 1862:* Richmond, pp. 27-28.
23. Matthews, J.M. (Ed.) (1863) — *The Statutes at Large of the Confederate States of America, Passed at the Third Session of the First Congress; 1863:* Richmond, p. 114.
24. *OR,* ser. 4, v. 3, p. 702. See also: John R. Hopkins Papers, Georgia Department of Archives and History, Atlanta.
25. R.W. Donnelly (1956) — Scientists of the Confederate Nitre and Mining Bureau: *Civil War History* 2:80. The War ended before the beds matured.
26. Charleston *Courier,* 6 March 1862. The New York *Herald,* 20 April 1862, quoting the same source, says 6,000 pounds for the second site instead of 9,000.
27. *OR,* ser. 4, v. 2, p. 29.
28. *ibid.*
29. *ibid.*, p. 223.
30. *ibid.*
31. *Special Orders of the Adjutant and Inspector General's Office Confederate States, 1862*: v. 2, p. 566; *OR*, ser. 4, v. 2, p. 223.
32. *OR,* ser. 1, v. 23, pt. 2, p. 215.
33. New York *Herald,* 11 May 1863.
34. Expense account, April, 1863, for John L. Bartow, RG109, Confederate Papers Related to Citizens or Business Firms, Microcopy 346, Roll 46, National Archives, Washington.
35. Hopkins Papers — William D. Chadick to William Gabbett, June, 1863.
36. *OR,* ser. 1, v. 30, pt. 3, p. 354.
37. J.W. Rowell (1971) — *Yankee Cavalrymen:* Knoxville, University of Tennessee Press, p. 141.
38. Louisville *Daily Journal,* 19 September 1863; C.H. Kirk (Ed.) (1906) — *History of the Fifteenth Pennsylvania Volunteer Cavalry:* Philadelphia, Historical Committee of the Society of the Fifteenth Pennsylvania Cavalry, p. 228.
39. *OR,* ser. 1, v. 32, pt. 1, p. 129.
40. *ibid.*, pt. 2, pp. 663-668.
41. Nashville *Daily Times and True Union,* 21 April 1864.
42. *OR,* ser. 1, v. 39, pt. 1, pp. 463-464.
43. During his life Hopkins (1835-1909) was also a "school teacher, landowner, political aspirant, inventor, businessman, (and) lawyer." After the War he lived in Norcross, Georgia, where he pursued his diverse interests: operating "sawmills, cotton gins, and lathe shops," plus making an unsuccessful bid for the State legislature. Biographical sketch of John R. Hopkins, Manuscript Section, Georgia Department of Archives and History, Atlanta.
44. With the exceptions of Sauta and Long Hollow, the exact identities of these caves remain unproved, although there exist within the specified counties more than enough caves which legend or physical evidence indicate were mined for saltpeter. Blue Mountain Cave is probably either Weaver, Little Weaver, or Lady Cave, all located near each other at present day Anniston. Big Spring may have been the later commercially shown Guntersville Caverns, and while there are candidates for Cedar Mountain and Little Warrior, Nixon's and Culpepper's are a complete mystery.
45. Bill Torode and Chuck Hummel did the mapping 18 March 1970. Other names for the cave are Cave Mountain Cave, Alford Cave, and Barnard Cave. W.W. Varnedoe, Jr. (1973) — *Alabama Caves and Caverns*: Huntsville, privately printed, unpaged.
46. Hopkins Papers — Time sheet of Long Hollow C.S. Nitre Works, May, 1864. A.C. McMinn's name with the date 1864 was found on the cave wall by the writer in 1980.
47. *ibid.;* Hopkins Papers — J.F. Martin to Hopkins, 14 May 1864.
48. *ibid.*, April-May, 1864 time sheet.
49. *ibid.*, J.F. Martin to Hopkins, 14 May 1864.
50. *ibid.*, various receipts and letters.
51. *ibid.*, J.F. Martin to Hopkins, 8 and 23 May 1864; *ibid.*, rations issued at Long Hollow C.S. Nitre Works; *ibid.*, Forage consumed at Long Hollow C.S. Nitre Works.
52. *ibid.*, J.F. Martin to Hopkins, 23 May 1864.
53. *ibid.*, J.F. Martin to Hopkins, 6 May 1864.
54. *ibid.*, Lumber for Long Hollow.
55. *ibid.*, J.F. Martin to Hopkins, 28 May 1864.
56. *ibid.*, J.F. Martin to Hopkins, 6 May 1864. It is possible that Herrin (b. ca. 1830), a Georgia-born farmer living near New Hope, Alabama, had been earlier involved in procuring saltpeter from a cave north of the river in Marshall County. Herrin's signature has been found by modern-day cave explorer Bill Torode on the wall of Ledbetter Saltpetre Cave. *1860 Census,* Alabama, Marshall County, New Hope P.O., Tract 6, T 6, R 2 E, p. 13; Bill Torode, personal communication, 1973.
57. The writer does not know what the term "Getting hopper floors" here means, but possibly it involved the placement of the wooden slats in the sides of the hoppers to form a V-shaped "floor." It is not known what type of leaching vats or hoppers were used at Long Hollow, but at Nickajack Cave, Marion County, Tennessee, V-vats were used.
58. Hopkins Papers — Programme of labor & improvements, Long Hollow C.S. Nitre Works.
59. *ibid.*, J.F. Martin to Hopkins, 14 May 1864.
60. *ibid.*, Hopkins to W.H. Hall, 23 May 1864; *ibid.*, "Remarks" column, Rations Issued at Long Hollow C.S. Nitre Works, May 1864.
61. *ibid.*, J.F. Martin to Hopkins, 28 May 1864.
62. *OR,* ser. 1, v. 38, pt. 4, p. 348.
63. *ibid.*, p. 370.

64. Hopkins Papers — W.H. Hall to Hopkins, 6 June 1864; *ibid.*, List of Men sent to Cedar Mountain Nitre Works, 28 July 1864; *ibid.*, L.A. Mayo to T.J. Robinson, 7 September 1864; *ibid.*, John J. Black to T.J. Robinson, 22 October 1864.
65. *OR*, ser. 1, v. 32, pt. 2, p. 214.
66. This mill had a capacity at the end of 1864 to make 500 pounds of powder daily — *ibid.*, ser. 4, v. 3, p. 987.
67. *ibid.*, p. 696 — Isaac M. St. John to James A. Seddon, 1 October 1864.
68. *ibid.*, p. 698.
69. Varnedoe; Alabama Geological Survey reports; personal communications and observation.

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DePaepe, Duane (1981)—Saltpeter Mining Features and Techniques: *NSS Bulletin* 43:103-105.

SALTPETER MINING FEATURES and TECHNIQUES

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SUMMARY

Early saltpeter miners developed reliable methods for determining the amount of recoverable niter in individual deposits and sophisticated techniques for recovering the mineral. Process, technology, and tools were somewhat standard in all cave saltpeter operations. Specialized iron mattocks and wooden paddles were the basic mining implements. Leaching hoppers were of two basic types, V-vats and box vats. Heaps and walls of broken rock left by the miners are conspicuous features of many saltpeter caves. Glauber and epsom salts were sometimes collected as by-products of niter recovery.

EACH YEAR, thousands of visitors ramble along the historic passageways of famed Mammoth and Wyandotte caves, unaware that within a few feet are clear signs of nitrate mining, as distinct today as when made some 170 years ago. Many of these features were discovered only recently in these and other midwestern saltpeter caves. In commercial caves that were once mined of saltpeter, visitor trail improvements have eradicated much of the subtle, but interesting, telltale signs of the old time "petre-monkeys." There is a need for systematic programs to map remaining features, such as have already been conducted in Mammoth Cave National Park and other areas. Such inventories could enhance the interpretive value and assure planned preservation of the caves.

PROSPECTING FOR CAVE SALTPETER

Samuel Brown (1809), who was instrumental in the development of the cave saltpeter industry, recorded that:

> The workmen have different modes of forming an opinion with regard to the quantity of nitre with which the earth may be impregnated. They generally trust to their taste; but it is always considered as a proof of the presence of nitre, when the impression made on the dust by the hand or foot is in a very short time effaced. Where the nitre is very abundant the impression made to-day, will be scarcely visible tomorrow. Where there is a great deal of sand mixed with dust, it is commonly believed that a small quantity of pot-ash will suffice for the saturation of the acid.

A continuous testing program was carried on in the larger saltpeter caves to reveal those sections of cave sediments particularly rich in nitrate. Davies (1958, p.39) observed about West Virginia caves that "considering the amount of saltpetre earth that was easily accessible in some caves it is amazing how little was actually used. In addition it is quite puzzling why tortuous, small passages, as in Snedegars Cave, were exploited when more accessible deposits were left untouched."

MINING TECHNOLOGY AND TOOLS

After a cave was successfully tested for nitrate content and an adequate source of leachwater was found, a laborious process of sifting floor breakdown and gravel from saltpeter earth began. Often, this coincided with the necessary enlargement of a passage, or the construction of trails and ramps to major dig sites. Large breakdown blocks and constricted passages were broken apart by wooden or iron mauls and wooden gluts or by blasting with black powder. The sorted blocks and rubble were then carefully arranged in walls along the cave avenues, or in undulating heaps in rooms or trunk passages. Probably nowhere is this breakdown sorting more spectacular than in Dixon Cave, Kentucky, where Hovey and Call (1912, p.7) observed:

> Every foot of the floor was searched and overturned long ago by the industrious miners, who carried the niter-bearing earth outside to the vats and boiling tubs whose ruins are yet visible. The miners left the rocky fragments within the cavern piled in what might be described as transverse stony billows, of which we counted eighteen; each wave being forty feet through at the base, and rising thirty or forty feet above the true floor.

The original (ca. 1812) leaching vats are still visible in the entrance vestibule of Dixon Cave, and a rude, bevel-edged, wooden pry bar was discovered there a few years ago. Coach Cave, near Mammoth Cave National Park, contains a rock-lined passage in which an underground stream probably was the source of the leaching water. In the 1950's, a battered iron maul was discovered near the entrance to this passage; this tool was used to break up large breakdown blocks covering the nitrate bearing sediments so that they could be conveniently stacked along the narrow passage.

After cursory trail building, stone-slab steps, ladders, and sometimes tramways or bridges were installed for the transportation of the "petre-dirt" from the dig site to the leaching hoppers. Big Bone Cave, Tennessee, contains pegged wooden ladders and the "Skyway", a plank tramway built over the Bone Cave Branch vat complex. Hubbards Cave, Tennessee, has a Civil War era ladder joined in sections by thongs, pegs, and support poles in order to reach an upper level gallery. Among the more unusual mining appurtenances observed was a wooden windlass to

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Figure 1. Tally marks, Cedar Springs Saltpetre Cave, Kentucky. Photo by Al Scheide

lift nitrate-bearing earth from a deep pit in Haynes Cave, West Virginia. In the large-scale works in Mammoth Cave, Kentucky, Great Cave on Crooked Creek, Kentucky and Sauta Cave, Alabama, oxen and mules once pulled carts laden with "petre-dirt" along high, vaulted cave avenues. The Sauta Cave works utilized small, metal railroad cars and wooden rails. In contrast, the smallest of sediment-filled crawlways were meticulously carved out in sediment-poor Forestville Saltpeter Cave, Kentucky. Sometimes, dig sites along main trunk avenues include tally marks on walls and ceilings; these probably represent units of mined niter deposits (Fig. 1).

In all caves, illumination was an important consideration. Miners traversing long distances in Mammoth Cave developed a specially made, iron lard-oil lamp that carried over into the commercial era until as late as about 1920. Candles were sometimes utilized in stationary operations at the leaching vats, but faggot and bark torches were the most common form of mining illumination. Pieces of faggot torch were once so numerous in Tennessee's Nickajack Cave that they were a favorite packaged and labeled tourist souvenir.

There is a noticeable absence of metal tools from each of the cave saltpeter mining periods. An almost self-evident explanation for this is the scarcity of metal implements on the frontier; also, the mining tools could have had direct application to various agrarian pursuits and therefore may have been taken from the caves when the mining operations ceased. Not only were iron tools difficult to obtain, but their repair far from the settlements must have been a consideration of their use. Another explanation, one that has not been documented for niter mining, is the early folk belief that iron had the ability to chemically alter sediments with which it was in contact. On post-Colonial farms, wooden plows continued in general use long after metal plows were available, because of the belief that iron plows poisoned the soil and induced greater weed growth (R.H. Brown, 1948, p. 3). Nevertheless, imprints of iron mattocks in compacted cave sediments can still be seen, especially in the larger-scale operations. Recent investigations in Kentucky and Indiana 1812-era niter caves suggest that the saltpeter mattock was a specialized tool designed specifically for that trade. In fact, essentially identical tool imprints are distributed over surprisingly great distances. Imprints of iron, hoe-like tools from many niter caves indicate that the saltpeter mattock had a distinctively curved bit and was narrower than conventional mattocks. Numerous other site-specific tools were individually developed as situations dictated (Faust, 1955, pp. 10-11).

Figure 2. Iron mattock and wooden paddle, the basic saltpeter mining tools. Author's photo.

After the sediments had been cleared of rock fragments and had been broken up with a mattock, short wooden paddles with beveled edges served for scraping and digging the "petre-dirt" (Fig. 2). The highest concentrations of nitrates were to be found in only the top layers of sediment, and both mattock and saltpeter paddles had short handles, so as to be effective even in crawlways. The collected nitrate-bearing earth was then transported in rough-woven bags or wooden buckets to the leaching hoppers, usually located near the cave entrance. The lixiviated cave earth was believed to become reimpregnated with niter in three years (Meriam, 1844), and it was considered an inexhaustible mineral resource. Ancillary mined products were Glauber salts and epsom salts (Farnham, 1818), which were marketed for medicinal purposes.

Leaching vats, or hoppers, were of two general designs: V-vats and box vats. Other containers, such as barrels, were used as the situation demanded. Vats were employed to contain the collected sediments in order to effect gravity differential solution as the initial process in nitrate recovery. Current investigations have not yet conclusively assigned vat designs to specific time periods or an evolutionary state-of-the-art trend. Generally, however, box vats, such as those in Mammoth Cave (Fig. 3), were utilized with the larger operations and seem to be more prevalent during the War of 1812 period. They require a greater volume of water for leaching and are more often associated with bored or V-notched log pipelines.

Unfortunately, these wooden structures are often badly preserved, making design taxonomy difficult or impossible. Although box vats had the advantage of larger capacity over the V-vat design, apparent engineering shortcomings were the complicated underdrain system of halved hollowed logs and the increased difficulty of lixiviated earth transfer. The V-vat was extensively employed in cottage nitrate recovery, but the design probably did not originate with cave use. The V-shaped ash hopper and leachate barrel was a consistent pioneer design used for non-cave related tasks, such as soap making (Sloane, 1958, p. 105). Box vats and V-vats have been recorded as being emplaced on the surface for the calcium-to potassium-nitrate conversion process, although artifacts of this type are no longer in existence.

Regional clusters of saltpeter caves show similarities in mining features. However, detailed comparative studies made of artifacts and mining sites demonstrate important individual characteristics at each operation. It is therefore concluded that the technology of mining cave sediments for nitrates came about not so much as a "spill-over" caused by major successful operations, but was part of the arts and sciences that generally accompanied the roving pioneer folk who expanded ever westward in the latter years of the Eighteenth Century and the beginning years of the Nineteenth.

Figure 3. Box vats, Booth's Amphitheatre, Mammoth Cave, Kentucky. Author's photo

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CHEMICAL ASPECTS of the CONVERSION of CAVE NITRATES to SALTPETER

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SUMMARY

The procedure for producing saltpeter (potassium nitrate, or niter) from cave sediments was studied using laboratory and action history experiments. A sample of saltpeter was prepared for the first time in more than 160 years from Mammoth Cave, Kentucky saltpeter-rich sediments. The chemical steps of the process were identified, and the principal impurities were found to be sulfates derived from the sulfate-rich cave sediments. The cave saltpeter process was accomplished easily on a small scale by a single individual in about two days.

NITRATES have been valuable commercial commodities since at least 3100 BC, having value in medicine, meat curing, glass manufacturing, ceramics, explosives, and many other uses (Levy, 1955; Faust, 1967 and references cited therein). After Roger Bacon's study in the 1200's of the explosive mixture formed by saltpeter (niter, or potassium nitrate, KNO_3) and Berthold Schwartz's subsequent invention of firearms, saltpeter became one of the most historically significant of all manufactured chemicals. The importance of nitrates is illustrated by the fact that many of the greatest pioneering chemists of the Middle Ages and the 17th, 18th, and 19th centuries carried out studies on nitrates (Williams, 1975). Among these illustrious chemists were Agricola, Magnus, Diderot, Glauber, Machiavelli, Pelletier, Gmelin, Dumas, Lavoisier, Dupont, Rush, LeConte, Franklin, Pasteur, and Count Rumford (Faust, 1967). Numerous scholarly and practically oriented articles were written about the production of saltpeter and its uses, especially in gunpowder, throughout the Middle Ages (*e.g.*: Machiavelli, 1573 and Bate, 1634 [both as cited by Faust, 1967, p. 14]).

The North American continent contains few naturally occurring, commercially useful nitrate deposits. Of these, the nitrate-rich sediments in limestone caverns of the Appalachian region are the most historically significant (Hess, 1900; Faust, 1949, 1968 and references cited therein). Due to the importance of gunpowder in pioneer America, saltpeter production from cave sediments became perhaps the first chemical manufacturing process of significant size there (Miles, 1961; Maxom, 1932). The process achieved national urgency during the Revolutionary, 1812, and Civil wars, when blockades threatened to sever imports of essential gunpowder. Writers of this period, especially during the Civil War, prepared detailed treatises to encourage domestic saltpeter production to aid defense efforts (*e.g.:* Committee of Safety, 1775; Brown, 1809; Cutbush, 1825; Rains, 1861; LeConte, 1862). Many artifacts of cave saltpeter manufacture of Civil War and War of 1812 vintage remain to this day, in some cases preserved almost perfectly *in situ* by stable cave environments. After the Civil War, nitrates and gunpowder again were imported freely, and for all practical purposes the cave saltpeter process became extinct.* Later, the invention of the Haber process (1913) for fixing atmospheric nitrogen ended forever reliance upon natural deposits as a source for nitrate chemicals, and allowed nitrates to be manufactured in quantities and for uses unimaginable to the cave "petre monkeys."

It is evident that the manufacture of saltpeter from cave sediments has considerable historical interest, and many articles have been written on aspects of the subject (see papers by DePaepe and Hill, Powers, and Smith in this issue). As mentioned above, a variety of "recipes" have also been published that describe in step-by-step detail the procedure for obtaining saltpeter from cave earths. It is puzzling that the chemical details of the process, even as to the origin and identity of the native cave nitrate minerals themselves, have remained obscure (Hill, 1976). For these reasons, the historic cave saltpeter conversion process was duplicated using modern physico-chemical methods. The results are reported in this paper; historical, mineralogical, and geological aspects of this work are described in separate articles of this symposium.

PRELIMINARY CHEMICAL STUDIES

Although details vary among published cave saltpeter recipes, all involve the following steps:

Public domain material.

1. Locate nitrate-rich cave sediments.
2. Transfer the sediments to a leaching vat.
3. Leach soluble nitrates from the cave sediments.
4. Convert the nitrate-rich leachate to a saltpeter solution, using potash (wood ash) lye.
5. Boil down the leachate to obtain the crude saltpeter crystalline product.
6. Purify the crude saltpeter.

Among the common nitrate salts, only saltpeter (KNO_3) is sufficiently non-hygroscopic to form conveniently useful gunpowder in the moderately humid environment of eastern America (Hill and Eller, 1977; Hill, 1978). Therefore, in the cave saltpeter process, the conversion of naturally occurring nitrates into the pure potassium salt is crucial. The first three steps (above) serve to get nitrate ion into solution. The only chemical conversion in the entire process is step 4, in which potash lye, rich in potassium hydroxide, acts as an ion exchanger for the cations complementing the nitrate anion. Additionally, the highly alkaline potash lye removes calcium and magnesium by preciptating their highly insoluble hydroxides:

$$[\mathrm{Ca^+, Mg^+, NH_4^+}]\ (\mathrm{NO_3})\ \text{solution}$$

$$\mathrm{KOH}\ \Big\downarrow$$

$$\mathrm{K^+ + NH_4^+ + [NO_3]^- +} \underset{\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim}{\mathrm{Ca(OH)_2, Mg(OH)_2}}$$

---

* There are only two reports of post-Civil War cave saltpeter mining in this country: A small Rockcastle County, Kentucky cave was utilized as a saltpeter source by one family well into the 1900's, and there was an abortive post-1900 attempt to revive the Big Bone Cave, Tennessee operation (Roger Sperka and Duane De Paepe, personal communication).

Removal of impurities (principally sulfates) from the crude saltpeter product is accomplished by fractional crystallization (steps 5 and 6). The large temperature dependence of the solubility of saltpeter allows saltpeter recovery to be very efficient (Hill, *et al.*, 1974; Hill, 1978). Since common impurities (mainly sulfates) have solubilities with relatively small temperature dependences, a pure saltpeter product is easily attained (see Fig. 1).

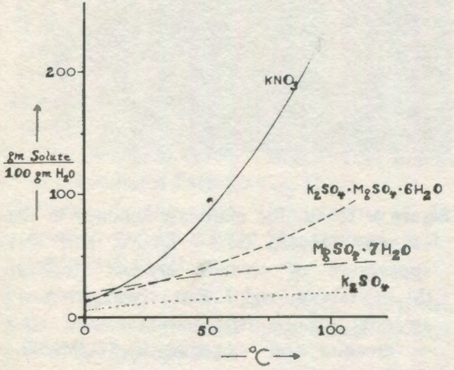

Figure 1. Solubility curves for niter (KNO_3), schoenite ($K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$), epsomite ($MgSO_4 \cdot 7H_2O$), and arcanite ($K_2SO_4$).

The first step in our study was to roughly quantify the distribution of nitrates in saltpeter caves. The procedure involved sampling a wide variety of sediments in several caves and analyzing for nitrate by the phenoldisulfonic acid spectroscopic method (Black, 1965). Some of the results for Mammoth Cave sediments are given in Table 1. The values generally are in the same range reported previously for sediments from Mammoth Cave (0.82%), but are seen to vary widely even among locations separated by only a few meters (Davies and Chao, 1959). It is seen that leached earths are generally high in nitrate, consistent with microbiological studies (Hill, *et al.*, 1974) but otherwise no clearcut pattern is discernible. Assuming a weight of about 220 lbs per bushel of cave earth and the quoted 2 to 6 lbs. of saltpeter produced per bushel, the required nitrate percentage is at least 1 to 3%, consistent with our determinations (Faust, 1967; Rains, 1861; LeConte, 1862; Brown, 1809).

Table 1. Nitrate percentages in Mammoth Cave, Kentucky sediments.

Sample origin	% NO_3
Black Chambers—loose surface soil	0.1 - 0.3%
Booth's Amphitheater—red soil in wall pocket	0.59%
leached earth in vat	0.30%
loose disturbed soil	0.10%
compacted sediments in contact with ceiling	0.15%
Gothic Avenue—gypsum soil	0.02%
Rotunda—leached earth in large vat	0.14%
Cleveland Avenue—main trail	0.28%
under wall ledge	0.08%
Audubon Avenue—loose undisturbed soil	0.79%
compacted soil	0.07%
disturbed clods in dug pit	0.18%
disturbed loose soil in dug pit	1.08%
mound of compacted soil	0.72%
Data from Davies and Chao (1959), Location Unspecified	
fresh guano	1.89%
dessicated guano (Chief City)	0.27%
cave fill beneath guano	0.39%
niter earth at saltpeter digging	0.43%
niter earth after leaching in saltpeter vats	0.01%

Next, we decided to carry out a laboratory conversion of cave sediments to saltpeter. Kingston Saltpeter Cave, Bartow County, Georgia, was extensively mined during the Civil War for saltpeter. A 560 g sample, analyzed at 2.4% nitrate, was collected in an extensively mined area of this cave. The sediments were stirred for 6 hrs with 500 ml of water, then filtered, and concentrated aqueous KOH was added to the filtrate until no further cloudiness was observed. The gelatinous hydroxide precipitate was filtered off and the solution was reduced in volume by one-half on a hotplate. The solution was filtered again to remove turbidity and reduced in volume to about 15 ml, whereupon needle crystals began to form. The solution was allowed to cool and was filtered a third time, giving 7.9 g of white needles and a thick, yellowish liquor. A second crop of light-tan needles was obtained when the filtrate was reduced to 5 ml. The needles were recrystallized easily from water to give high purity potassium nitrate (identified by infrared spectrum, taste, solubility, crystal habit, and combustion properties[Hill and Eller, 1977]). The final liquor was highly alkaline, indicating the presence of excess base. The leached earth was leached again, by the exact procedure outlined above, and a second crop of needles (0.6 g) was obtained. Based on the original 2.4% nitrate content of the cave earth, our recovery of saltpeter corresponds to a 42% yield. The quantity recovered is consistent with the amounts quoted in the historical recipes.

ACTION HISTORY EXPERIMENT

Historically at Mammoth Cave, cave sediments were leached in large, rectangular vats inside the cave, and the leachate was piped to the surface, where it was boiled down and purified (see DePaepe and Hill, this issue). At Big Bone Cave, Tennessee and Greenville Saltpeter Cave, West Virginia, arrays of large, V-shaped vats inside the caves were used for leaching and, again, boiling down and purification were done on the surface. A procedure more suitable for a scale smaller than these huge, factory-like operations, and the one more commonly used throughout Appalachia, involved removing the sediments from the cave and carrying out all subsequent operations on the surface in small, V-shaped vats constructed from rough-sawn lumber. Primarily because of the limited scale on which we wanted to carry out our studies, we chose the latter procedure (Fig. 2).

A preliminary field run was made at Lobelia Saltpeter Cave, West Virginia, where practical difficulties in the cave saltpeter process were identified. The actual action history experiment was carried out at Mammoth Cave National Park, Kentucky, where one of America's largest saltpeter manufacturies was located and operated before and during the War of 1812 (203,000 pounds of saltpeter were said to have been produced in Kentucky in 1810, much of it from Mammoth Cave [Faust, 1967]). A site was selected in Audubon Avenue which gave a good

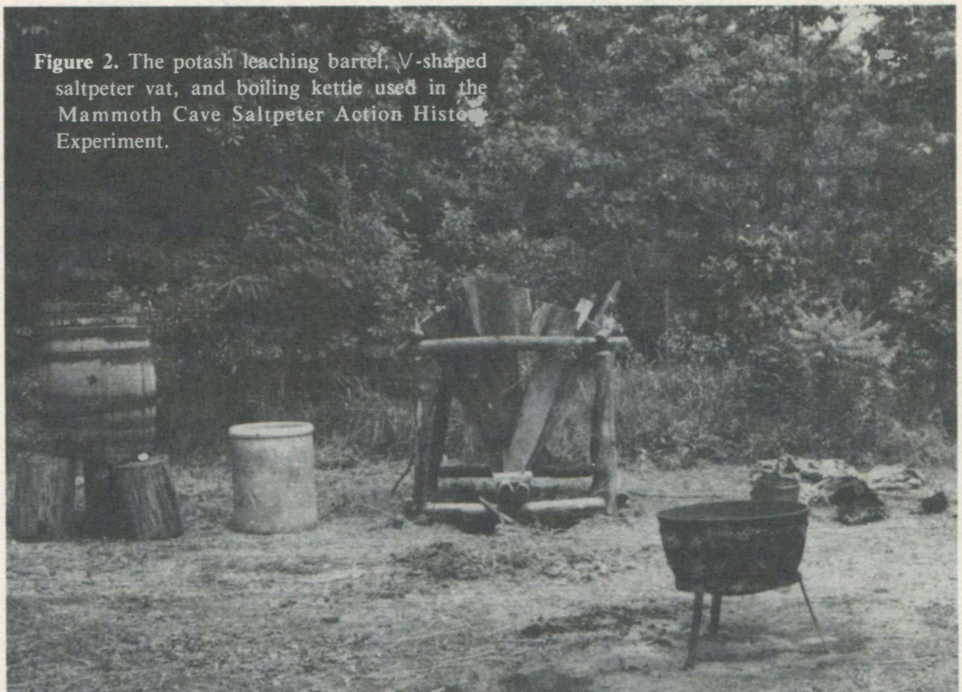

Figure 2. The potash leaching barrel, V-shaped saltpeter vat, and boiling kettle used in the Mammoth Cave Saltpeter Action History Experiment.

Figure 3. Peter Hauer digging saltpeter dirt with a saltpeter paddle in Audubon Avenue, Mammoth Cave During the Action History Experiment.

nitrate test (0.55% nitrate). Approximately one bushel (220 lbs) of the loosely compacted, red-brown soil was dug using an antique mattock and hewn saltpeter paddles and was carried from the cave in a gunny sack. Period costume (homespun shirts) and authentic lighting (lard oil lamps) were used during the mining operation (see Fig. 3).

The niter earth was placed in the leaching vat (lined with straw to prevent sediment leakage) and water (25 gal) was allowed to percolate slowly through the niter earth. The leachate was recycled through the vat for further extraction of nitrates. Concentrated potash lye liquor (5.4% potassium), prepared by leaching oak and hickory hardwood ashes in a wooden barrel, was added to the leach water until no further turbidity was produced. Gelatinous precipitates (referred to as "curds" in the old recipes) were removed by straining through cheesecloth, and the liquor was concentrated in an iron kettle ("evaporator") over an open fire. At a volume of about one quart, the first product separated from the "mother liquor" as tabular crystals of arcanite (K_2SO_4) (figs. 4a and 4b). At one pint, a thin surface layer of "grease and foam" (probably organic materials from the potash lye and cave soil) were successfully removed by adsorption onto turnip chunks. Concentration to 1 cup gave a mixture of arcanite crystals and schoenite ($K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$) crystals (Fig. 4c). At one-half cup, additional arcanite and needle crystals of niter (KNO_3) formed. Further concentration yielded almost exclusively niter crystals (Fig. 5a and 5b). Crystalline products were identified by physical and chemical properties, elemental analysis, and X-ray powder diffraction patterns by methods previously described (Hill and Eller, 1977). Quantitites obtained were schoenite (4.1 oz), arcanite (0.4 oz), and niter (1.6 oz). The once-leached niter earth was again leached with 25 gal of fresh water, and the above conversion and evaporation process was repeated. Again, only three crystalline products were observed: schoenite (1.0 oz), arcanite (1.1 oz), and niter (2.0 oz). The saltpeter was readily refined by fractional crystallization from water to give white needles of approximately 85% purity (based on potassium analysis). The total quantity of saltpeter obtained (3.5 oz, or 11% recovery of the total nitrate in the niter earth) indicates our leaching process is very inefficient and certainly does not approach the 2 to 6 lbs/bushel sometimes claimed in the old literature. The poor yield, however, could reflect our inexperience with the leaching and conversion process.

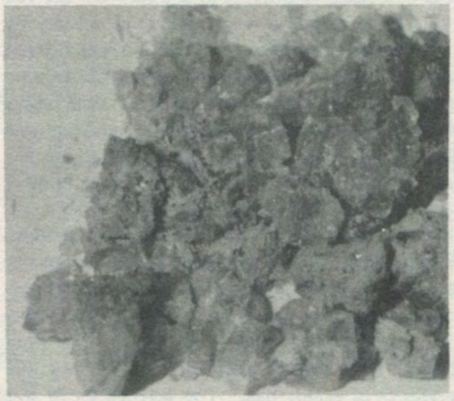

Figure 4. Crystalline materials obtained in the saltpeter process: (a) — (above, left) first appearance of arcanite crystals (K_2SO_4); (b) — (above, right) first crystal crop — arcanite; (c) — (left) second crystal crop — arcanite and schoenite ($K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$).

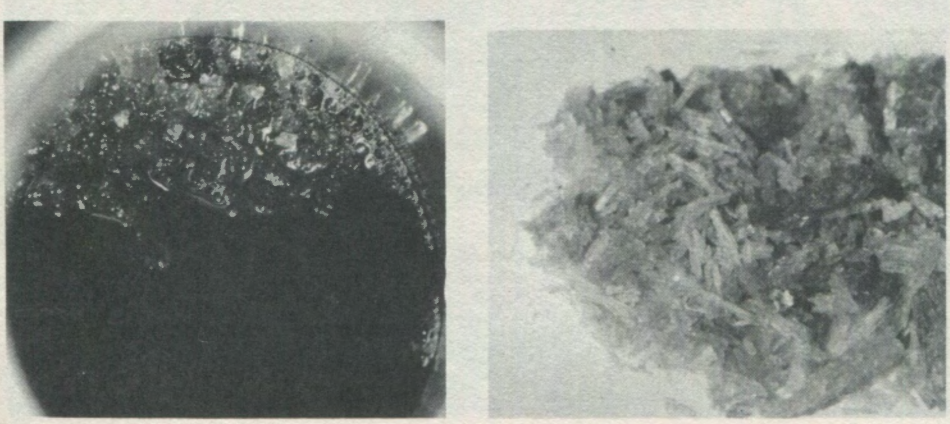

Figure 5. (a)—(left) Crystals of saltpeter forming from the mother liquor; (b)—(right) the raw saltpeter product.

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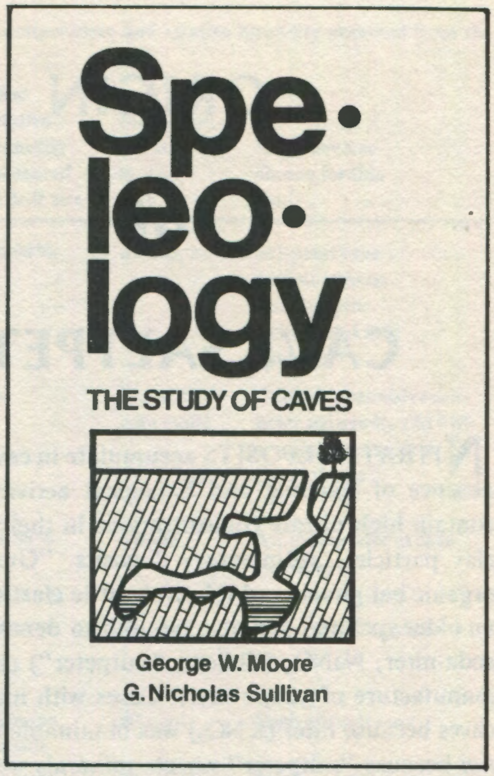

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THE STUDY OF CAVES

George W. Moore
G. Nicholas Sullivan

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John Schoenherr's drawing of a vampire bat, from *Speleology: The Study of Caves*, p. 102.

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ORIGIN of CAVE SALTPETER

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SUMMARY

Southeastern saltpeter caves have temperatures between 10 and 18°C and humidities between 90 and 99%. Saltpeter sediments are alkaline (pH 6 to 9), dry and porous (moisture 5 to 10 percent by weight) and non-organic (low levels of compost, guano and animal remains); sediments have nitrate concentrations ranging between 0.01 and 4.0 percent by weight, low total nitrogen (0.08 to 0.13 percent by weight) and relatively little phosphorus (0.1 to 1.4 percent by weight). Lixiviated cave sediments regenerate in nitrate in several years. Areal extent of cave nitrate is uniform; vertical concentration is in the top few meters of sediment. Nitrate is a minor constituent in some sulfate speleothems (up to 1 percent by weight). Surface and sinkhole limestones directly exposed to rainfall are leached of nitrate (1 to 2 ppm); sinkhole limestones in recessed, partly exposed positions have intermediate nitrate values (10 to 100 ppm); and protected cave limestones are enriched in nitrate (thousands of ppm in 30 cm deep cores). Nitrate concentration increases immediately at the sinkhole-cave boundary and is independent of limestone type or stratigraphy. Nitrobacter *bacteria populations on cave bedrock walls, ceilings and floor sediments are higher (6 x 10^5/g of sediment) and of a different species* (N. agilis) *than surface soil populations (1 x 10^3/g;* [N. winogradsky]).

Compost, animal remains, rat guano and bat guano do not account for the areal extent, vertical extent and regeneration of saltpeter earth nor do they explain saltpeter deposits that extend to cave ceilings or high (thousands of ppm) nitrate within limestone bedrock. Bat guano can enrich saltpeter earth in nitrate, but it is not the only, or even a major, nitrate source.

Surface soil nitrate transported into the cave by seeping groundwater is the most likely source of cave saltpeter. The proposed mechanism that drives seeping groundwater towards the cave is evaporation at the cave air-bedrock interface which produces a moisture density gradient within the limestone. Reduced nitrogen $(NH^{4}+)$ *is transported from the surface through the zone of aeration to cave bedrock and sediments where it is oxidized to nitrate by* Nitrosomonas *and* Nitrobacter. *The seeping groundwater model explains such characteristics of saltpeter caves and sediments as regeneration, areal and vertical extent, and nitrate within cave bedrock.*

NITRATE DEPOSITS accumulate in caves, deserts and the Antarctic due to the absence of leaching and biological activity. "Saltpeter caves" are caves which contain high nitrate concentrations in their primarily inorganic, clastic (sand and clay particles) sedimentary deposits. "Guano caves" contain primarily nitrous, organic bat guano and relatively little clastic sediment. "Saltpeter" (or "saltpetre", an older spelling) can also be used to denote a crystallized nitrate mineral such as soda-niter, $NaNO_3$ (Chilean "saltpeter") or niter, KNO_3 ("saltpeter" used in the manufacture of gunpowder). Caves with nitrous sediments were called "saltpeter" caves because niter (KNO_3) was obtainable by a lixiviation and conversion process, *not* because "saltpeter" nitrate minerals were visible in the cave sediments.

The origin of cave saltpeter has remained a mystery for over 400 years. The nitrogen cycle is complex and cave nitrates can theoretically derive from a variety of sources, both organic and inorganic. In this paper, seeping groundwater is investigated as a hydrologic mechanism transporting nitrate into saltpeter caves. "Seeping" groundwater is defined herein as water in the zone of aeration which moves by gravitational and capillary forces through rock pores and interstices rather than through enlarged joints, fractures and bedding planes.

CAVE NITRATE DEPOSITS

Previous Investigations

A popular technique of producing nitrates artificially in the 1700's and 1800's was to pile vegetative and animal debris into compost heaps, moisten it with water or urine and then sprinkle it with lime. Thus, for many years, it was assumed that organic material must be the source of nitrate in cave earth (Kain, 1819; Cornelius, 1819). This belief was widespread until Hess (1900) challenged the organic theory. Hess noted that the saltpeter sediments of Mammoth Cave and other eastern caves actually contained very little organic matter. He thought that cave nitrates were ultimately the product of nitrifying bacteria in surface soils above the cave; rain descending through these soils dissolved the soluble nitrate, percolated through cracks and fissures in the limestone and dripped from the cave roof into floor sediments. In Hess' model saltpeter caves merely acted as receptacles for surface-derived nitrates.

Although Hess' theory was original and had merit, many of his observations were faulty. First, Hess used as his argument against an organic, bat guano origin the tendency of bats to venture only a short distance into caves, a fact not strictly correct as was quickly pointed out by Nichols (1901). Second, Hess used the term "percolating" to mean "dripping" water; yet, dripping water never exists in close proximity to saltpeter earth. Nichols calculated that for every 8 parts of nitric acid in dripping cave water, 42 parts of lime will be deposited and thus the floor deposit would take the form of a stalagmite, a speleothem type never found in saltpeter cave passages. Nichols (1901) defended a bat guano origin for cave nitrates as have most subsequent investigators except Faust (1967, 1968), Moore and Nicholas (1964) and Pace (1971). Moore and Nicholas championed the rat guano theory of cave nitrates whereas Faust believed the nitrogen bacteria *Nitrosomonas* (which metabolically converts ammonia to nitrite) and *Nitrobacter*, (which converts nitrite to nitrate) aided in the production of cave saltpeter. Pace (1971) suggested that nitrifying microorganisms produced nitrate by utilizing ammonia in the cave air.

Inorganic, geologic sources of cave saltpeter have been practically ignored by all investigators except Hess. Seeping vadose groundwater and entrance drainage are hydrologic mechanisms for transporting nitrate into caves. Possible sources of nitrate to the groundwater are surface vegetation, ammonium-rich volcanic rock and limestones high in primary, depositional nitrate.

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Table 1. Pertinent factors and rationale for drilling in each study cave. Average annual rainfall, surface temperature and relative humidity obtained from the National Atlas (1970).

Cave	Location	Vegetation	Average annual rainfall	Average annual surface temperature	Average surface relative humidity	Cave temperature measured at drill site	Cave relative humidity measured at drill site	Maximum nitrate in drill core	Why cave was chosen for this study
Dixon Cave	Mammoth Cave National Park, Kentucky	Oak-hickory	130 cm/yr	13° C	60-70%	9-10° C	93-94%	2747 ppm	Saltpeter cave with numerous stratigraphic units at sinkhole entrance
Mammoth Cave	Mammoth Cave National Park, Kentucky	Oak-hickory	130 cm/yr	13° C	60-70%	—	—	No drill core made	Cave with extensive saltpeter sediments and with seepage-type sulfate speleothems
Carlsbad Cavern	Carlsbad Caverns NP, New Mexico	Cactus-sagebrush	35 cm/yr	17° C	30-60%	11°C	74-88%	6 ppm	Ammonia odor at cave entrance
New Cave	Carlsbad Caverns NP, New Mexico	Cactus-sagebrush	35 cm/yr	17° C	30-60%	15° C	88-89%	7 ppm	Extensive bat guano
Ellis Cave	Sandia Mts., New Mexico	Ponderosa Pine	40 cm/yr	11° C	40-60%	Same as outside	Same as outside	40 ppm	High altitude cave
Fort Stanton Cave	Capitan, New Mexico	Pinyon-Juniper	40 cm/yr	13° C	40-50%	8° C	83-97%	93 ppm	Similar to Dixon Cave but with different climate and surface vegetation
Malmquist Fissure	Wupatki National Monument, Arizona	Scrub pine, cactus-sagebrush	25 cm/yr	8° C	30-70%	12-16° C	39-80%	323 ppm	Cave in volcanic region; $NaNO_3$ mineralization
Flower Cave	Big Bend National Park, Texas	Cactus-sagebrush	3 cm/yr	18° C	30-60%	24° C	41%	129 ppm	Cave with rat guano; $Na_3(NO_3)(SO_4)\cdot H_2O$ mineralization

RESEARCH TECHNIQUES

Eight caves were chosen for cave nitrate experiments: Mammoth Cave, Mammoth Cave National Park, Kentucky; Dixon Cave, Mammoth Cave National Park, Kentucky; Carlsbad Cavern, Carlsbad Caverns National Park, New Mexico; New Cave, Carlsbad Caverns National Park, New Mexico; Fort Stanton Cave, Capitan, New Mexico; Malmquist Fissure, Wupatki National Monument, Arizona; Ellis Cave, Sandia Mountains, New Mexico; and Flower Cave, Big Bend National Park, Texas (Fig. 1). Characteristics of saltpeter caves and sediments were defined by empirical studies completed in Dixon Cave and Mammoth Cave, Kentucky. Non-saltpeter, southwestern caves were compared to Dixon and Mammoth Caves with respect to such parameters as bat guano, rat guano, ammonia in cave air, climate, regional volcanism and surface vegetation. Pertinent environmental parameters and rationale for drilling in each cave are listed in Table 1.

Drilling Procedure

Rock samples were taken from the entrance limestones of all the study caves except Mammoth. Dixon Cave was chosen as the control cave for the drilling experiments because it (1) contains saltpeter sediment, (2) has a natural, unaltered entrance, (3) lacks visitor contamination, (4) is easily accessible and (5) has a sinkhole entrance which exposes numerous stratigraphic limestone units. The premise of drilling was that biological material (bat guano, rat guano) should contaminate only the outer, surface layer of limestone whereas high nitrate values deep within the limestone would support a hydrologic origin.

A new technique was devised for obtaining drill samples (DS) from limestone bedrock: A 1350 watt alternator was set up at the cave entrance and used to power an electric concrete drill with a 0.3 m long, 1.3 cm diameter bit. Before drilling was begun, the bit was cleaned and lubricated with distilled water. The limestone was drilled and the powder captured until a 2.5 cm deep hole was made, at which time the drill bit was again thoroughly cleaned and washed with distilled water. This process was repeated until a hole had been drilled 22.5 to 30 cm into the bedrock. After drilling, the hole was filled with concrete and camouflaged. In relatively inaccessible Flower Cave, Big Bend National Park, Texas, a hand-driven star drill (1.3 cm diameter) was used. Samples were tested in the laboratory for nitrate, nitrite and, in two cases, phosphorus. Since nitrate is extremely soluble and phosphorus is extremely insoluble, comparison of these elements should indicate relative leaching of the bedrock by groundwater.

Sampling Techniques

Hand specimen bedrock samples were collected from each major stratigraphic unit above Dixon Cave; samples were also collected at 1.5-3 m intervals throughout the stratigraphic section of the Dixon Cave sinkhole and cave entrance zone. Samples were collected with a rock hammer. The rocks were later cut into sections (1 cm thick) with a rock saw parallel to the outer, weathered surface of the rock sample. These sections were then pulverized and sieved to a 100 mesh size before being analyzed for nitrate and nitrite. Nitrate analysis of each limestone sample was compared with noted lithologic features (*e.g.* micritic, oolitic, fossiliferous). All lithologic descriptions were determined by hand lens examination.

Nitrate concentrations in saltpeter sediment samples from different locations in Dixon Cave and Mammoth Cave were compared to one another and to those of other southeastern caves. Sediment samples were screened and tested for nitrate and nitrite. Saltpeter earth lixiviated in 1812 was collected in Dixon Cave; this earth had either been discarded by the saltpeter miners in floor mounds at the cave entrance, or shoveled onto cave wall ledges to regenerate in its nitrate content (Fig. 2). The lixiviated earth samples (LS) were sliced into parallel layers as they were removed from the cave wall ledges and were then subdivided into fine-grain and rock fractions. The small rocks and dirt clots of the rock fraction were pulverized and screened again before testing for nitrate and nitrite.

Mammoth and Dixon cave saltpeter earths were compared to the bat guanos of Carlsbad Cavern and New Cave, Carlsbad Caverns National Park, New Mexico in nitrate, total nitrogen and total phosphorus. Bat guano (BG) samples were pulverized, screened and tested for nitrate, total nitrogen and total phosphorus.

Speleothems precipitated from seeping groundwater (coatings and crusts) were collected from five of the study caves (Dixon, Mammoth, New, Fort Stanton and Malmquist). Speleothem samples (GS) were pulverized, screened and tested for nitrate (and in some cases X-rayed).

Water samples were not collected in the saltpeter passages of Dixon and Mammoth caves since no dripping or flowing water exists therein; however, *in situ* Eh and pH electrode measurements were made in surface springs in the Mammoth Cave region. Nitrate concentration in this spring water was analyzed in the laboratory (a few days later).

All sampling was done with the permission of the National Park Service, National Forest Service and Bureau of Land Management.

Chemical Analysis

The phenoldisulfonic acid method was used for nitrate analyses and the modified Griess-Ilosvay method for nitrite analyses (Black, 1965). About one-fourth of the analyses were completed by John Husler (chemist, Geology Department, University of New Mexico) and three-fourths by myself. The nitrite analyses were so low (less than 1 ppm regardless of nitrate content) that they were discontinued after about three-fourths of the samples had been analyzed. Total nitrogen and phosphorus in bat guano were analyzed by Carl White (chemist, Biology Department, University of New Mexico) using the Kjeldahl method (with K_2SO_4 and $CuSO_4$) and nitrates by the cadium reduction method (because of interfering organics, the phenoldisulfonic acid method could not be used on the bat guanos). Total phosphorus and water-soluble phosphorus were determined by John Husler using the molybdenum blue colorimetric method.

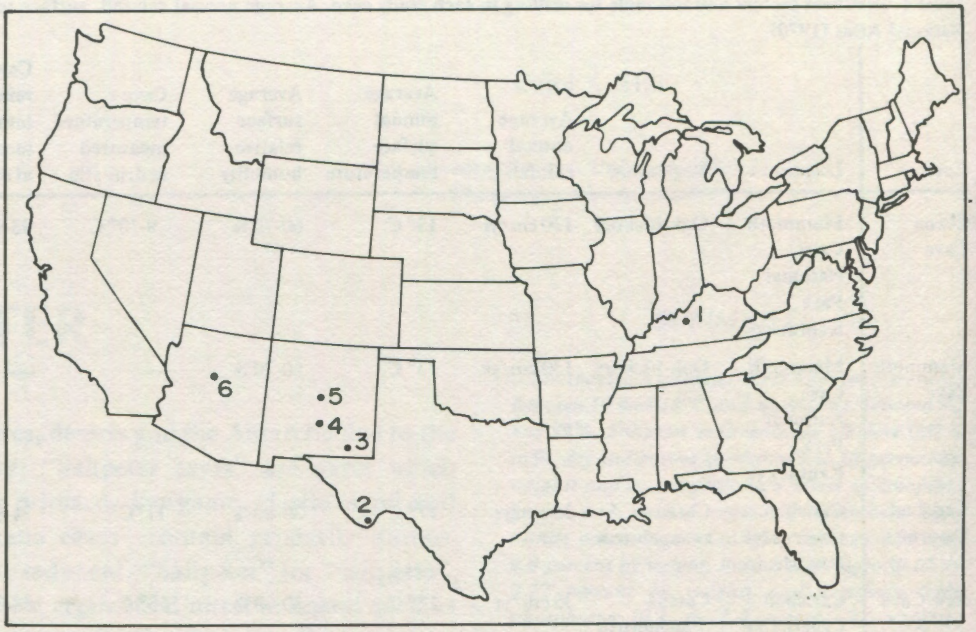


Figure 1. Location of caves: (1) Mammoth Cave and Dixon Cave, Mammoth Cave National Park, Kentucky; (2) Flower Cave, Big Bend National Park, Texas; (3) Carlsbad Cavern and New Cave, Carlsbad Caverns National Park, New Mexico; (4) Fort Stanton Cave, Capitan, New Mexico; (5) Ellis Cave, Sandia Mountains, New Mexico; (6) Malmquist Fissure, Wupatki National Monument, Arizona.

CAVES AND CAVE LOCALITIES

Dixon Cave

Dixon Cave is located 1.0 km from Mammoth Cave in Mammoth Cave National Park, Kentucky and is a short segment of cave passage isolated from the Mammoth Cave system by a terminal breakdown. Dixon Cave is approximately 300 m long, 12 to 21 m high and 9 to 12 m wide (Fig. 3). A small bat colony resides at the end of the cave.

Dixon Cave is developed in Upper Mississippian limestones of the Ste. Genevieve and Girkin formations and is capped by the Big Clifty Sandstone Member of the Golconda Formation, also of late Mississippian age (Fig. 4). The entrance sinkhole of Dixon Cave exposes the limestone members of the Girkin Formation to rainfall and weathering. The overhanging lip of the cave entrance partly protects the Paoli Limestone, the lowest member of the Girkin Formation. All members of the Ste. Genevieve Formation are in the cave, protected from weathering. Runoff water cascading over the lip of the cave entrance immediately sinks into the forest litter on the sinkhole slope and either descends into lower subterranean passages or seeps down-slope into the floor sediments at the cave entrance.

Figure 2. Regenerated saltpeter earth on wall of Fredonia Limestone, Dixon Cave, Mammoth Cave National Park. Dirt was shoveled onto ledge by 1812 saltpeter miners.

Other Caves

Mammoth Cave, Mammoth Cave National Park, Kentucky, is developed in the same

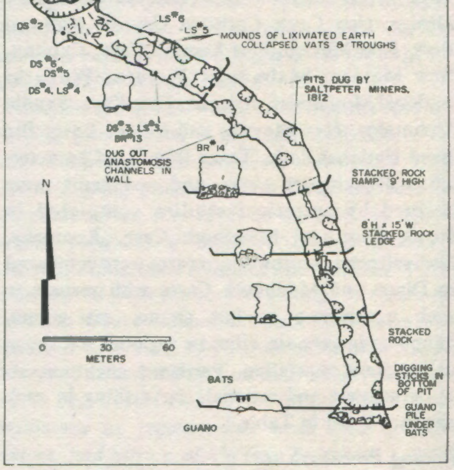


Figure 3. Map of Dixon Cave.

stratigraphic units as Dixon Cave. The top of the Beaver Bend Member marks the entrance ceiling of Mammoth Cave. Sediment and sulfate speleothem samples were collected in Mammoth Cave.

Carlsbad Cavern, Carlsbad Caverns National Park, is developed in the Permian limestones of southeastern New Mexico. The cave entrance is developed in horizontally bedded Tansill Limestone. Carlsbad Cavern is well known for its large bat population. Allison (1937) estimated that the cave had over 8.7 million bat inhabitants The bats reside in the Bat Cave section where guano has accumulated to great depths. Samples of recent bat guano were collected from Bat Cave. A colony of swallows resides at the entrance of Carlsbad Cavern and both the bats and swallows contribute to a fairly strong ammonia odor. A drill hole was made at the cave entrance approximately 15 m into the cave, along the left wall about 1.8 m off the visitor trail.

New Cave, Carlsbad Caverns National Park, New Mexico, is developed in the Capitan Formation, an unstratified reef limestone of Permian age. A drill hole was made in the bedrock wall just opposite, and about 12 m from, the entrance. The floor beneath the drill site is compacted bat guano; one sample of this guano and four samples of bat guano from further in the cave were analyzed for nitrate, total nitrogen and phosphorus. New Cave bat guano contains many bat bones and has been estimated to be 17,800 years old by Libby (1954). A cabonate speleothem sample collected from New Cave was also analyzed for nitrate.

Ellis Cave, located 0.15 km west of Ellis Ranch, Sandia Mountains, near Albuquerque, New Mexico, is a small, high altitude cave (2.4 km elevation) developed in Madera Limestone of Pennsylvanian age. A drill hole was made about 1 m inside the cave entrance. Cave temperatures and humidities closely reflect outside temperatures and humidities.

Fort Stanton Cave, located 11 km southeast of Capitan, New Mexico, is developed in Upper Permian San Andres Limestone. The San Andres contains gypsum as thick beds and lenses and it also contains minor interbedded dolomite. Fort Stanton Cave is similar to Dixon Cave, Kentucky in entrance size, entrance slope, type of cave passage and number of bat inhabitants, but it differs in regional climate and surface vegetation. One drill hole was made, and one sediment sample and one speleothem sample were collected from Fort Stanton Cave.

Malmquist Fissure is located 0.8 km southwest of Lomaki Ruin, Wupatki National Monument, Arizona. Since Malmquist Fissure is directly exposed to surface conditions along its entire length, cave temperatures and humidities closely reflect outside temperatures and humidities. Malmquist Fissure is developed in Kaibab Limestone of Permian age. The Kaibab at Malmquist Fissure is overlain by a thin layer of volcanic ash derived from the nearby, late Tertiary, San Franciscan volcanic fields. A drill hole was made approximately 21 m into the cave in a location sheltered from surface rainfall. Malmquist Fissure contains crystallized soda-niter ($NaNO_3$) which occurs along bedding plane seams in the Kaibab Limestone (Hill and Eller, 1977).

Flower Cave is a small solutional cave located in Big Bend National Park, Texas in Lower Cretaceous (Comanchean) Santa Elena Limestone. Flower Cave contains abundant amberat rat guano + dehydrated rat urine) which is in close proximity to crystallized darapskite ($Na_3(NO_3)(SO_4)\cdot H_2O$) speleothems. A drill hole was made 5 cm into the Santa Elena at the end of Flower Cave near the nitrate mineralization.

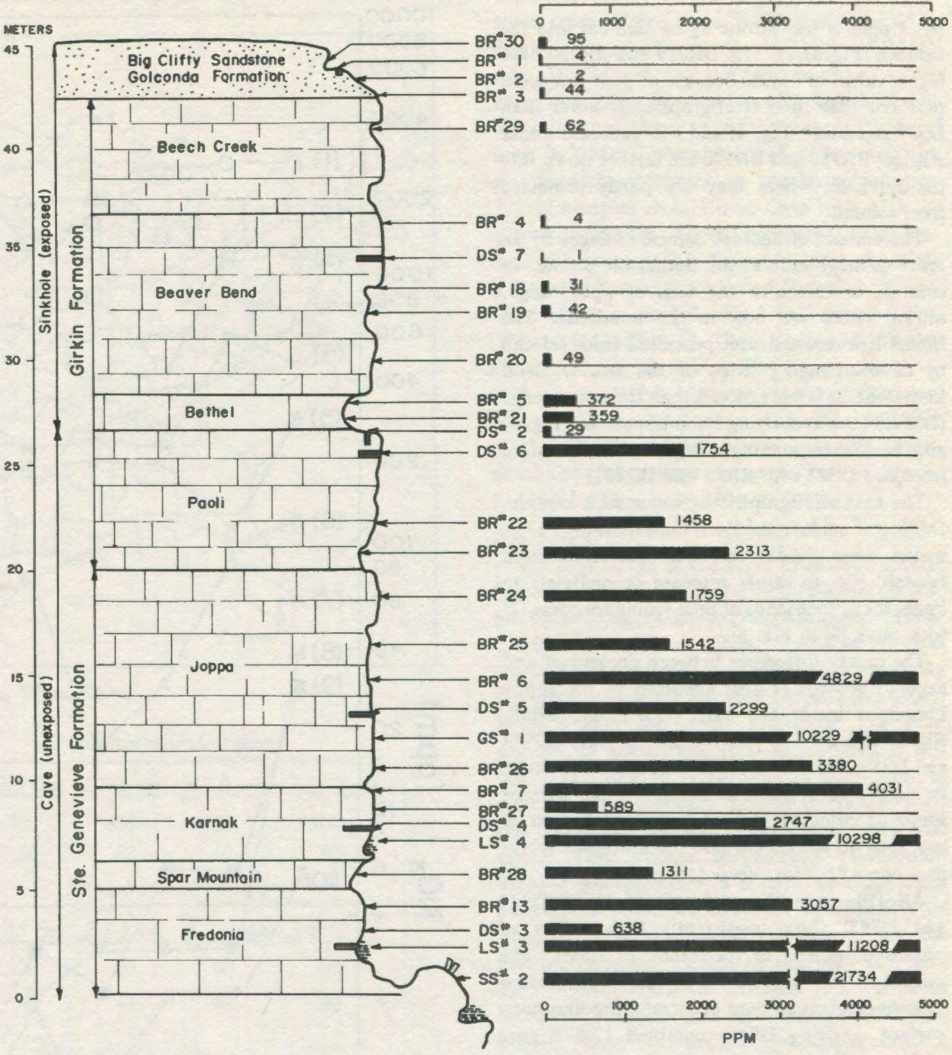


Figure 4. Stratigraphic section of Dixon Cave, Mammoth Cave National Park, showing maximum nitrate (ppm) of each bedrock sample (BR), drill site (DS), sediment sample (SS), lixiviated sample (LS) and speleothem sample (GS).

DRILLING RESULTS

Nitrate

All of the rock samples taken from drill holes (DS) in surface and sinkhole limestones exposed to rainfall are low (a few ppm) in nitrate, whereas all of the cave limestones protected from weathering yielded samples high (thousands of ppm) in nitrate (Fig. 5). Hand specimen bedrock (BR) samples collected within the Dixon Cave sinkhole also show this trend but on a smaller scale; limestone samples collected in positions directly exposed to rainfall have lower nitrate values than those collected in more protected positions (in recessed niches or under ledges) (see Fig. 4).

The Big Clifty Sandstone is variable in nitrate content depending on amount of exposure (Fig. 4). DS#1, obtained from an exposed upper surface of sandstone, has nitrate values of 4 ppm. Another exposed Big Clifty bedrock sample (BR#2) has less than 2 ppm nitrate, whereas a partly exposed piece (BR#3) has up to 44 ppm. Sample BR#30, collected under a recessed niche in the Big Clifty Sandstone, has nitrate values up to 95 ppm. The Beaver Bend Limestone shows a similar trend between exposed and unexposed limestone. BR#4 was exposed to weathering and has less than 4 ppm of nitrate. Drill Site #7 (DS#7) obtained from an exposed limestone face, has 1 ppm or less nitrate up to 22.5 cm into the bedrock (Fig. 5). BR#18, BR#19 and BR#20 have higher values of nitrate because of their protected positions; BR#18 is stratigraphically lower than DS#7 and BR#4 (Fig. 4) and was collected under a ledge; BR#19 and BR#20 are farther down into the sinkhole, where they are partly protected from rainfall.

The amount of bedrock nitrate changes by an order of magnitude at the Bethel Limestone. In contrast to values in the tens of ppm range, nitrate values are now in the hundreds. The Bethel is a recessed unit protected from rainfall by an overhanging ledge of the Beaver Bend Limestone. It is less exposed than the upper ledge (DS#2) of the underlying Paoli Limestone (Fig. 4) and has correspondingly higher nitrate values (compare DS#2 with BR#5 and BR#21).

The next stratigraphically lower rock sample, DS#6, was made in the Paoli Limestone only a few meters from DS#2, but well protected from rainfall. Nitrate values increase immediately to hundreds or thousands of ppm (compare curve [2] with curve [9] in Fig. 5).

The drastic difference between unexposed and exposed bedrock is also apparent in the Joppa Limestone inside the cave (DS#5 and BR#6, BR#24 and BR#25) and outside the cave (DS#8 and DS#9). Nitrate values in the Joppa Limestone inside the cave reach 4829 ppm while surface Joppa outcrops have nitrate values of 2 ppm or less, even up to 22.5 cm into the limestone (compare curve [3] with curves [11] and [12], Fig. 5).

All of the cave rock samples (DS#6, DS#5, DS#4 and DS#3) show consistently high values of nitrate (hundreds or thousands of ppm). The outermost few millimeters of limestone surface have the highest amount of nitrate; the limestone surface overlying DS#6 contained 17,871 ppm (1.8%, ten times more than the average of the first 2.5 cm of DS#6 [1754 ppm, or 0.18%]). In almost all of the drill samples and hand specimens collected, the outer layer had the highest nitrate content.

Beyond the first few centimeters of limestone, drill sample and hand specimen nitrate values vary as much between limestone stratigraphic units as they do within each unit. Variation between or within each unit may be caused by the type of limestone or by the presence of small cracks or vugs within the limestone which act as nitrate repositories (thus increasing the overall nitrate value for that 2.5 cm section). The type of limestone is probably the less important of these two factors. The Paoli Limestone is oolitic; the Joppa is fossiliferous, coarsely crystalline, dolomitic, oolitic and sparry; the Spar Mountain is micritic and finely crystalline; yet, none of these factors seem to relate to greater or lesser nitrate values. Chalk and Keeney (1971) came to the same conclusion: there is no well-defined relationship between the type of limestone and the nitrate content of that limestone.

The bedrock samples (BR#13 and BR#14) of the Fredonia Limestone show a possible decrease in nitrate away from the cave entrance. Near the

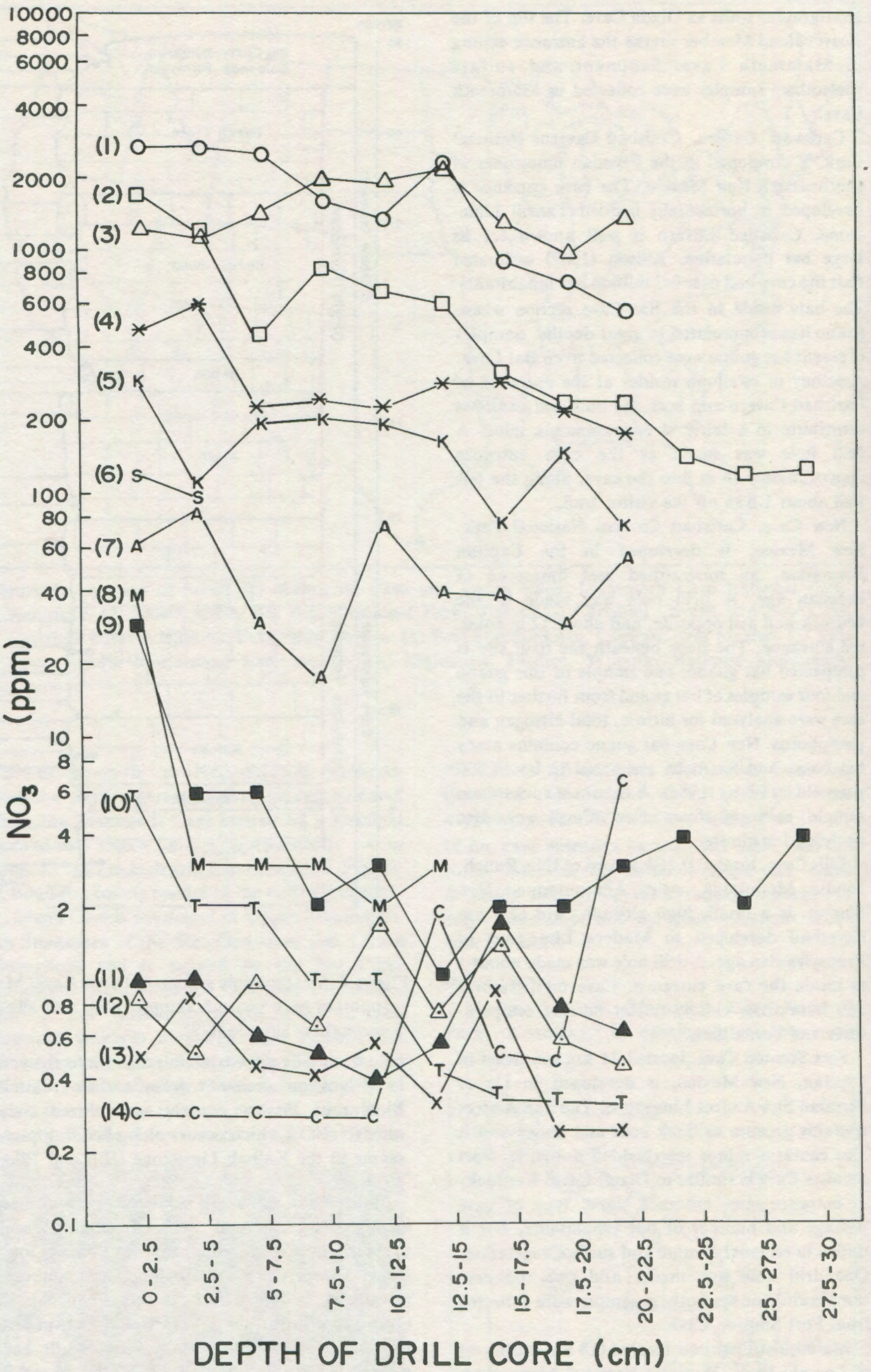


Figure 5. Nitrate in limestone bedrock: (1) Karnak Limestone (DS#4), Dixon Cave, Ky.; (2) Paoli Limestone (DS#6), Dixon Cave, Ky. (not exposed); (3) Joppa Limestone (DS#5), Dixon Cave, Ky.; (4) Fredonia Limestone (DS#3), Dixon Cave, Ky.; (5) Kaibab Limestone (DS#14), Malmquist Fissure, Ariz.; (6) Santa Elena Limestone (DS#15), Flower Cave, Tex.; (7) San Andres Limestone (DS#13), Fort Stanton Cave, N.M.; (8) Madera Limestone (DS#12), Ellis Cave, N.M.; (9) Paoli Limestone (DS#2), Dixon Cave, Ky.; (10) Tansill Limestone (DS#11), Carlsbad Cavern, N.M.; (11) Joppa Limestone (DS#8), on surface below Dixon Cave, Ky.; (12) Joppa Limestone (DS#9), on surface below Mammoth Cave, Ky.; (13) Beaver Bend Limestone (DS#7), Dixon Cave, Ky.; (14) Capitan Limestone (DS#10), New Cave, N.M.

Figure 6. Distribution of saltpeter caves compared with mean annual temperature (°C) (National Oceanic and Atmospheric Administration, 1974).

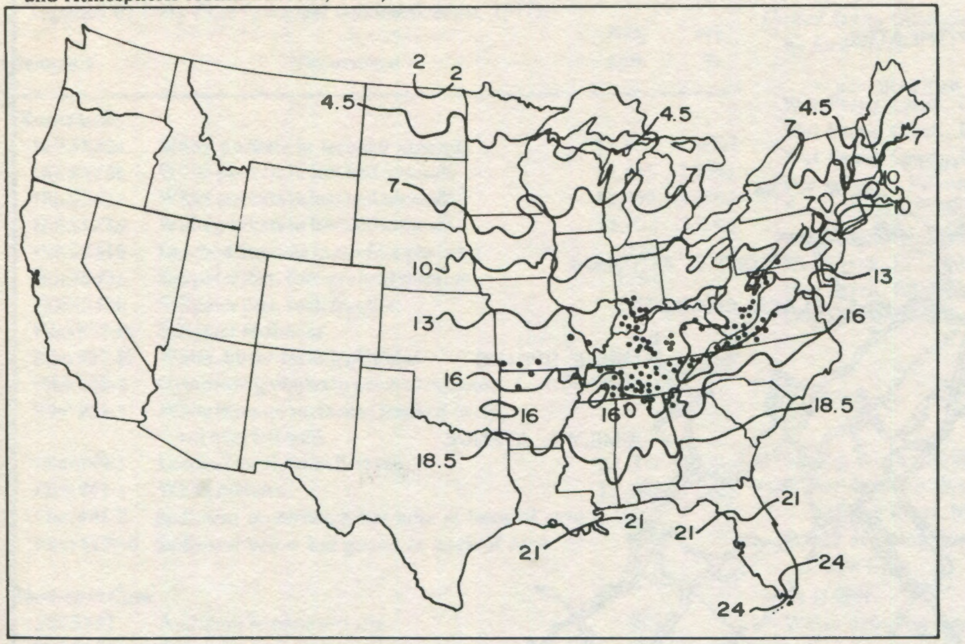
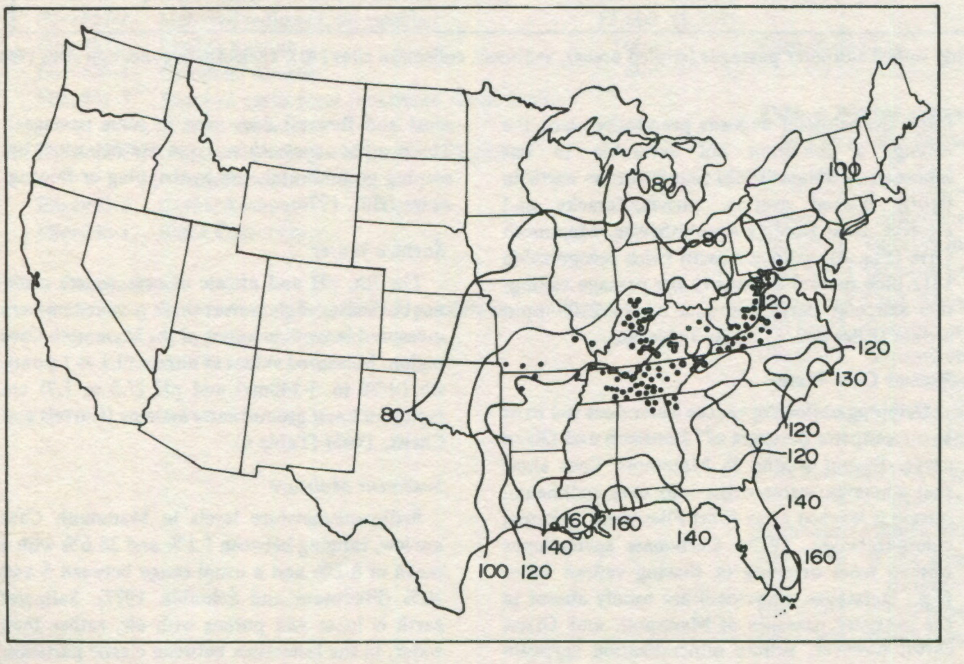


Table 2. Phosphorus in Paoli and Fredonia limestones, Dixon Cave.

Drill Site #2, Paoli Ls.	*Phosphorus (P_2O_5)(ppm)*			
	0-2.5 cm	*2.5-5 cm*	*5-7.5 cm*	*7.5-10 cm*
Total phosphorus	700	500	1000	1200
Water-soluble, organic phosphorus	50	40	40	40
Drill Site #3, Fredonia Ls.	*Phosphorus (P_2O_5)(ppm)*			
	0-2.5 cm	*2.5-5 cm*	*5-7.5 cm*	*7.5-10 cm*
Total phosphorus	200	60	40	50
Water-soluble, organic phosphorous	40	40	40	40

Figure 7. Distribution of saltpeter caves compared with mean annual rainfall (cm) (National Oceanic and Atmospheric Administration, 1974).



entrance, nitrate values in the Fredonia Limestone average 2858 ppm (BR#13) whereas 45 m down the passage they average 773 ppm (BR#14). Also, DS#3 (Fredonia) has average nitrate values lower than DS#4 (Karnak) and DS#5 (Joppa), two units sampled closer to the entrance. This trend may indicate a correlation of higher bedrock nitrate with proximity to the cave entrance

Drill samples from Dixon Cave were high in nitrate (thousands of ppm) compared to samples from non-saltpeter, southwestern caves, especially from the bat caves (Carlsbad Cavern and New Cave, which contained only 1 to 2 ppm; curves [10] and [14] of Fig. 5). Three caves—Malmquist Fissure, Flower Cave and Fort Stanton Cave — have intermediately high nitrate values (between 20 and 300 ppm; curves [5], [6], and [7] of Fig. 5). Crystallized nitrate minerals (soda-niter and darapskite) occur in two of these, Malmquist Fissure and Flower Cave.

Phosphorus

The first 10 cm of the Paoli Limestone (DS#2) (exposed) and of the Fredonia Limestone (DS#3) (unexposed) were analyzed for phosphorus (Table 2). Phosphorus is a minor constituent in most shales and limestones, carbonate rock averaging 400 ppm and shales 700 ppm (Krauskopf, 1967). Even though the Paoli Limestone has been exposed to weathering, total phosphorus in this unit is higher than average (up to 1200 ppm); in contrast, the Fredonia Limestone (unexposed) has lower-than-average values (less than 200 ppm). This inverse (to nitrate) relationship between phosphorus and amount of exposure is consistent with the extreme insolubility of phosphorus salts (solubility constants for the calcium phosphates range between $K=10^{-50}$ and 10^{-60}, compared to calcium nitrate with $K=2x10^{+1}$; Sillen and Martell, 1964). Phosphorus values have evidently remained constant since the deposition of the limestone and may reflect the amount of original organic material deposited in the limestone. Nitrate concentration, on the other hand, has probably changed continually since limestone deposition and lithification in direct correlation to the amount of exposure and leaching.

CHARACTERISTICS OF SALTPETER CAVES AND SEDIMENTS

The characteristics of saltpeter caves and sediments were defined from empirical data obtained in Dixon and Mammoth caves, from other studies of the Saltpeter Research Group, Cave Research Foundation, and from the literature.

Location

Saltpeter caves are not located uniformly throughout the United States but exist primarily in the southeast (see Hill, DePaepe, Eller, Hauer, Powers, and Smith, this issue).

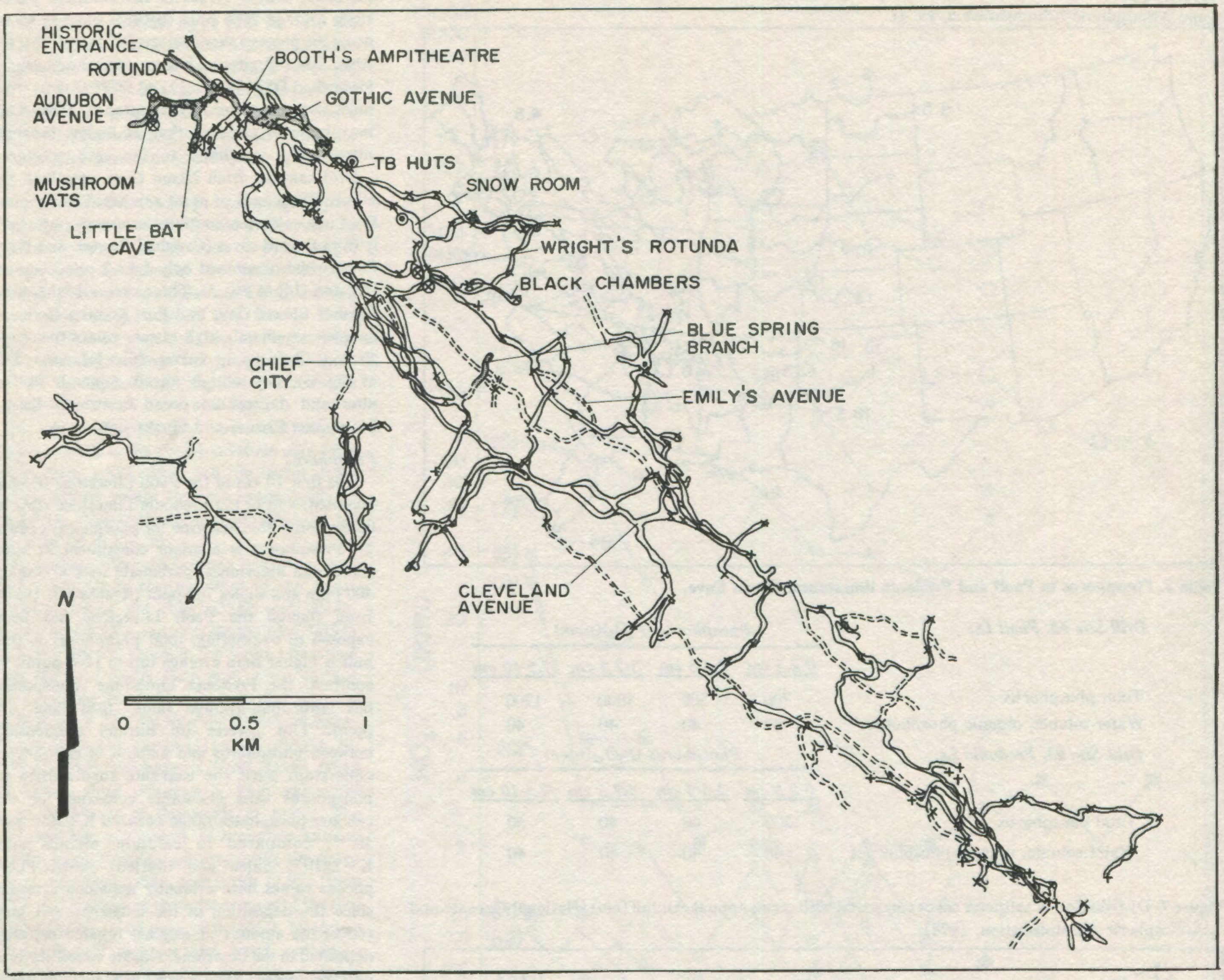


Figure 8. Map of a portion of Mammoth Cave, showing mined saltpeter passages (stipled areas), sediment collection sites (⊕), speleothem collection sites (◎) and Carl Fliermans' collection sites (X).

Mean Annual Temperature

Faust (1968) reported temperatures between 11°C and 14°C for saltpeter caves. Southeastern caves exist in temperate zones where the mean annual temperature (and therefore cave temperature) varies between 10°C and 18.5°C (Fig. 6).

Humidity

Humidity in southeastern United States is high partly because the annual rainfall is high (100 to 130 cm/yr, Fig. 7). Humidity within Mammoth Cave and Dixon Cave in the month of July measured between 93 and 94%. The estimated humidity range for southeastern saltpeter caves is 90 to 99%.

Air Circulation

Air circulation above saltpeter earth is a common but not an essential property. Davies (1958, pp. 21-23) noted that in Higginbothams Cave, the saltpeter deposits practically reach the ceiling, a condition not favorable to bat hibernation. Faust (1968) found nitrous earth in tightly packed grottos, niches, cracks and crevices. Near Booth's Amphitheatre, Mammoth Cave (Fig. 8), saltpeter earth (with recognizable 1812 pick marks) extends to the passage ceiling; this saltpeter earth contains up to 2100 ppm nitrate (Eller #82-A, 80-B; Table 3).

Vadose Cave Water

Dripping or flowing vadose water does not exist in the saltpeter passages of Mammoth and Dixon caves. Recent studies in Mammoth Cave show that wherever water drips into cave sediments, nitrate is leached away (Carl Fliermans, personal communication, 1977). Carbonate speleothems formed from dripping or flowing vadose water (*e.g.*, stalactites, flowstone) are totally absent in the saltpeter passages of Mammoth and Dixon caves; however, sulfate mineralization (gypsum crust and flowers) does exist in some passages. These sulfate speleothem types are deposited by seeping groundwater, not by dripping or flowing water (Hill, 1976).

Surface Water

The Eh, pH and nitrate of cave waters could not be measured; however, these parameters were measured in surface waters of the Mammoth Cave region. Measured values of nitrate (0.1 to 1 ppm), Eh (+78 to +140mv) and pH (7.5 to 7.7) are typical of karst groundwater systems (Garrels and Christ, 1965) (Table 4).

Sediment Moisture

Sediment-moisture levels in Mammoth Cave are low, ranging between 1.1% and 28.6% with a mean of 8.2% and a usual range between 5 and 10% (Fliermans and Schmidt, 1977). Saltpeter earth is loose and porous with air, rather than water, in the interstices between clastic particles.

Table 3. Nitrate values of sediment samples. All sample data labelled "Eller" supplied by Gary Eller (personal communication, 1977).

Sample #	Occurrence	NO_3 ppm	Wt. %
Dixon Cave			
Hill SS#2a	White pockets in leached mounds	15,660	(1.6%)
Hill SS#2b	White pockets in leached mounds	12,865	(1.3%)
Hill SS#2c	White pockets in leached mounds	12,059	(1.2%)
Hill SS#2d	White pockets in leached mounds	21,734	(2.2%)
Hill SS#15	Leached mounds (not white pockets)	9126	
Hill SS#3a	Saltpeter dirt, fine-grained fraction	1794	
Hill SS#3b	Saltpeter dirt, rock fraction	1108	
Eller#57-B	Saltpeter sediment	300	
Eller#57-E	White, bitter-tasting globules	40,000	(4.0%)
Eller#55-3	Gympsum globules in leached mounds	700	
Eller#51-1	White layer on surface of leached earth, vat near left wall	2500	
Eller#49-1	Leached earth from first vat	23,000	(2.3%)
Eller#41-1	White nodules	12,300	(1.2%)
Eller#41-2	Sediment underneath bat area at back of cave	6300	
Hess (1900)	Sediment below bat guano at back of cave	100	
Mammoth Cave			
Hill SS#1	Audubon Avenue test site	953	
Hill SS#11	Rotunda	483	
Hill SS#12	Wright's Rotunda	2955	
Hill SS#13	Near mushroom vats	2313	
Hill SS#14	Side passage by Wright's Rotunda	1103	
Davies and Chao (1959)	Rotunda	4300	
Hess (1900)	Cave earth	4700	
Eller#82-A	Sediment on ceiling, Booth's Amphitheatre	2100	
Eller#82-B	Loose sediment beneath rock, Gothic Avenue	700	
Eller#82-C	Undisturbed sediment, Booth's Amphitheatre	400	
Eller#80-A	Audubon Avenue, near Civil Defense supplies	7170	
Eller#80-B	Compacted sediment in contact with ceiling, Booth's Amphitheatre	1500	
Eller#80-C	Loose sediment, Booth's Amphitheatre	1000	
Eller#78-A	Loose sediments near mushroom beds	7850	
Eller#78-B	Earth from 1.5 m deep hole, Audubon Avenue	720	
Eller#78-D	Loose top sediment, Audubon Avenue	10,800	(1.1%)
Eller#57-A	Light red sediment, unspecified	12,000	(1.2½)
Eller#57-D	Emily's Avenue	6000	
Eller#55-4	Cleveland Avenue	800	
Eller#51-3	Leached earth from innermost vat at Booth's Amphitheatre	3000	
Eller#49-3	Light red soil from wall pocket at Booth's Amphitheatre	5900	
Eller#43-2	Gothic Avenue	2000	
Eller#45-1	Black Chambers	2800	
Fort Stanton Cave			
Hill SS#10	Sediment sample by DS#13 (possibly contaminated by bats and humans)	6003	

Table 4. Water analyses, Mammoth Cave region, Kentucky.

United States Geological Survey (unpublished October, 1971 data furnished by Jack Hess)			
	Nitrate (ppm)		
Wet Prong Creek, Edmonson County, Kentucky	2.6		
Wet Prong Creek, Edmonson County, Kentucky	1.5		
Wet Prong Creek, Edmonson County, Kentucky	1.2		
Bylew Creek, Edmonson County, Kentucky	3.0		
Bylew Creek, Edmonson County, Kentucky	0.9		
Bylew Creek, Edmonson County, Kentucky	1.8		
Dog Creek, Edmonson County, Kentucky	1.1		
Dog Creek, Edmonson County, Kentucky	1.8		
Dog Creek, Edmonson County, Kentucky	1.7		
Average	1.7		
Hill, this study			
	Nitrate (ppm)	*Eh(mv)*	*pH*
Spring, north side of Green River	0.45	+140	7.51
Water draining through forest litter, north side of Green River, Mammoth Cave National Park	0.10	-	-
Water dripping down entrance sinkhole, Dixon Cave	1.00	+ 78	7.71
Hess (1900)			
Water dripping from the roof of Mammoth Cave (perhaps contaminated by nitrate on ceiling bedrock ?), location unknown	5.71	-	-

Table 5. Percent nitrate in southeastern saltpeter caves. All sample data labelled "Eller" supplied by Gary Eller (personal communication, 1977).

Cave	County, State	Collector, Sample #	Nitrate wt. %
Kingston Saltpetre Cave	Bartow County, Georgia	Eller #468-E	2.4%
Triple Saltpetre Cave	Wayne County, Kentucky	Eller #72-C	0.2%
Petre Cave	Pulaski County, Kentucky	Eller #72-A	2.1%
Wind Cave	Wayne County, Kentucky	Eller #70-C	0.8%
Longs Cave	Edmonson County, Kentucky	Eller	<1.1%
Dixon Cave	Edmonson County, Kentucky	Hill and Eller	<4.0%
Mammoth Cave	Edmonson County, Kentucky	Hill and Eller	<1.2%
Wyandotte Cave	Crawford County, Indiana	Cox (1879)	2.0%

Table 6. Nitrate values of speleothems. Sample data labelled "Eller" supplied by Gary Eller (personal communication, 1977).

Sample #	Occurrence	NO_3 ppm	Wt. %
Dixon Cave, Mammoth Cave National Park			
Hill GS#1	Gypsum in seam on right wall by DS#5	10,229	(1.0%)
Eller #55-1	Gypsum growing on left wall	10,000	(1.0%)
Mammoth Cave, Mammoth Cave National Park			
Hill GS#2	Gypsum crust by TB Huts	173	
Hill GS#3	Gypsum crust by mirabilite area, Snow Room	6	
New Cave, Carlsbad Caverns National Park			
Hill GS#5	Black coating covering popcorn	44	
Fort Stanton Cave, Capitan, New Mexico			
Hill GS#4	Gypsum crust by DS#13	49	
Malmquist Fissure, Wupatki National Monument			
Hill GS#6	White powder, near $NaNO_3$ mineralization	2950	
Hill GS#7	White powder, before DS#14	2955	
Hill GS#8	White powder, before GS#6	2742	

Nitrate Concentration of Sediments

Nitrate content of saltpeter earth varies considerably between caves of different regions (Table 5) and also within the same cave, even over distances of only a few meters (Table 3). The taste of saltpeter earth is sometimes bitter and at other places imperceptible (McDermott, 1963), depending on nitrate concentration. Measured nitrate values in the saltpeter sediments of Mammoth and Dixon caves range between 0.01% and 4%, most commonly between 0.1% and 1.0%. The sediment mounds in the entrance zone of Dixon Cave contain the highest nitrate values.

Nitrate Concentration of Bedrock

Nitrate is also present on the limestone walls and ceilings of saltpeter caves. Rogers (1884) found nitrate on cave roofs and walls, far removed from organic matter supposed to be buried on the floor. Maxom (1932) measured 0.025% nitrate in the bedrock of a roof crevice in Great Saltpetre Cave, Kentucky. Carl Fliermans (personal communication, 1977) scraped the outermost bedrock layer off walls and ceilings in Mammoth Cave and, in many cases, found more nitrate in these scrapings than he did in the saltpeter floor sediments. The drilling results show that the outermost surfaces of limestone in Dixon Cave is very high in nitrate (1.8%) and that nitrate values remain high (in the thousands of ppm) up to 30 cm into the limestone (see discussion of drilling results).

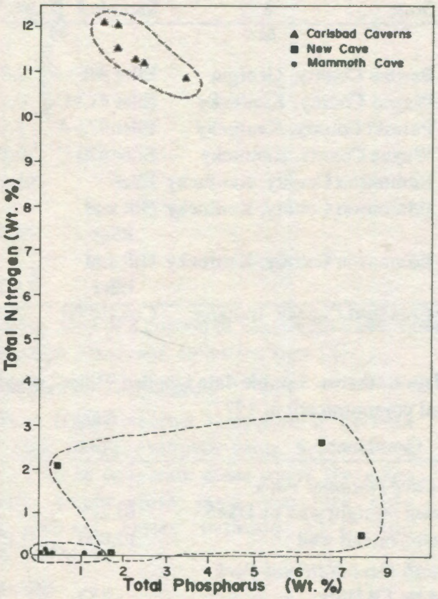


Figure 9. Total nitrogen and phosphorus in Carlsbad Cavern and New Cave bat guano and in Mammoth Cave saltpeter sediments.

Nitrate Concentration of Speleothems

Sulfate speleothems in Dixon and Mammoth caves were analyzed for nitrate (Table 6). Gypsum crust along the right wall (Hill GS#1) and left wall (Eller #55-1) near the Dixon Cave entrance both contained 1.0% nitrate. Two gypsum samples of crust were collected in Mammoth Cave, one by

Table 7. Nitrate, total nitrogen and total phosphorus in bat guano (BG) and in saltpeter sediment (SS).

Sample #	Location	NO_3 (ppm)	Total N_2O_5 (wt. %)	Total P_2O_5 (wt. %)
Carlsbad Cavern, Carlsbad Caverns National Park				
Hill BG#18	Bat Cave #1, youngest	<1	11.30	2.32
Hill BG#21	Bat Cave #2	20	12.09	1.89
Hill BG#19	Bat Cave #3	63	11.60	1.88
Hill BG#17	Bat Cave #4	517	12.10	1.63
Hill BG#20	Bat Cave #5, oldest	101	11.28	2.58
Hill BG#22	Bat Cave, bat guano underneath shaft	1754	10.90	3.45
New Cave, Carlsbad Caverns National Park				
Hill BG#1	Orange fraction, near jeep route	160	2.69	6.57
Hill BG#2	Black fraction, near jeep route	35	0.07	1.75
Hill BG#3	Black fraction, near path	<1	0.52	7.48
Hill BG#4	Orange fraction, near path	40	2.05	0.43
Hill BG#9	Guano beneath DS#10	6	-	-
Dixon Cave, Mammoth Cave National Park				
Hess (1900)	Bat guano underneath roosting area at end of cave	-	6.12	-
Hill SS#15	Saltpeter sediment	9126	0.11	0.16
Mammoth Cave, Mammoth Cave National Park				
Hill SS# 1	Audubon Avenue	953	0.07	1.00
Hill SS#11	Rotunda	483	0.05	0.29
Hill SS#12	Wright's Rotunda	2955	0.04	0.33
Hill SS#13	Near mushroom vats, Audubon Avenue	2313	0.08	1.44
Hill SS#14	Side passage off of Wright's Rotunda	1103	0.03	0.09

Table 8. Nitrate values of lixiviated saltpeter earth shoveled onto wall ledges by 1812 saltpeter miners, Dixon Cave. Sample data labelled "Eller" supplied by Gary Eller, (personal communication, 1977).

Sample #	Occurrence	NO_3 ppm	Wt. %
By DS#3, along right wall			
Hill LS#3-1a	Fine-grained fraction, outer layer	11,208	(1.1%)
Hill LS#3-1b	Rock fraction, outer layer	4147	
Hill LS#3-2a	Fine-grained fraction, middle layer	9392	
Hill LS#3-2b	Rock fraction, middle layer	1812	
Hill LS#3-3a	Fine-grained fraction, inner layer	6424	
Hill LS#3b	Rock fraction, inner layer	1546	
Along right wall			
Hill LS#4-1a	Fine-grained fraction, outer layer	10,557	(1.1%)
Hill LS#4-1b	Rock fraction, outer layer	6729	
Hill LS#4-2a	Fine-grained fraction, middle layer	10,295	(1.0%)
Hill LS#4-2b	Rock fraction, middle layer	7092	
Hill LS#4-3a	Fine-grained fraction, inner layer	9808	
Hill LS#4-3b	Rock fraction, inner layer	8103	
Along left wall			
Hill LS#5-1a	Fine-grained fraction, outer layer	9272	
Hill LS#5-1b	Rock fraction, outer layer	4483	
Hill LS#5-2a	Fine-grained fraction, inner layer	7930	
Hill LS#5-2b	Rock fraction, inner layer	5679	
Along left wall, near floor			
Hill LS#6-1a	Fine-grained fraction, outer layer	10,238	(1.0%)
Hill LS#6-1b	Rock fraction, outer layer	7970	
Hill LS#6-2a	Fine-grained fraction, middle layer	7221	
Hill LS#6-2b	Rock fraction, middle layer	9653	
Hill LS#6-3a	Fine-grained fraction, inner layer	6149	
Hill LS#6-3b	Rock fraction, inner layer	5573	
Leached dirt piled on left wall			
Eller #49-2	Fine-grained + rock fractions	10,000	(1.0%)

the TB Huts and the other near the Snow Room (Fig. 8); the sample nearest the Mammoth Cave entrance (TB Huts) contained 173 ppm nitrate and the sample farthest from the entrance (Snow Room) contained 6 ppm nitrate.

pH of Saltpeter Sediments

The saltpeter earth of Mammoth Cave is alkaline, with a pH range of 5.95 to 8.99 and a mean of 7.9 (Fliermans and Schmidt, 1977).

Nitrogen-Phosphorus Ratios

Hutchinson (1950) devised a convenient standard for comparing bat guanos of differing maturity and contamination. He plotted total nitrogen against total phosphorus and found that (1) low nitrogen and low phosphorus indicate a high concentration of inorganics in the guano, (2) high phosphorus and low nitrogen indicate highly decomposed and leached guano, and (3) high nitrogen and moderate or low phosphorus indicate relatively undecomposed and uncontaminated guano. The recent bat guano in the Bat Cave Section of Carlsbad Cavern is high in nitrogen and moderate in phosphorus content (Table 7 and Fig. 9), while the leached New Cave guano is relatively low in nitrogen and variable in phosphorus. The saltpeter sediments of Mammoth Cave have very low values of nitrogen and relatively low values of phosphorus compared to the bat guanos of Carlsbad Cavern and New Cave, indicating that the saltpeter deposits of Mammoth Cave contain a high concentration of inorganic material and a low concentration of bat guano. Davies and Chao (1959) described the saltpeter sediments of Mammoth Cave as clastic fills with quartz sand in the lower portion, gravel and coarse sand in the middle and upper portions, with a fine silt and clay surface layer.

Organic Material

The saltpeter earth of Mammoth and Dixon caves contains low levels of total inorganic matter (0.02 to 0.04%; Fliermans and Schmidt, 1977) no bat bones or hair and an almost complete lack of recognizable bat pellets (Hess, 1900), and no other animal remains. Recent guano deposits in the Bat Cave section, Carlsbad Cavern, are composed of guano pellets, bat bones and hair. The older, leached New Cave guano does not contain recognizable guano pellets, but has many bat bones. Four samples of saltpeter earth were collected from Mammoth Cave (Rotunda, SS#11; Wright's Rotunda, SS#12; side passage off Wright's Rotunda, SS#14; and Audubon Avenue, SS#1 [Fig. 9]) and one sample was collected from Dixon Cave (SS#15, Table 7). Examined petrographically and using a scanning electron microscope, the Wright's Rotunda and Audubon Avenue samples were found to contain less than 0.5% intact insectivorous bat guano pellets and isolated pieces of insect exoskeleton (Scott Altenbach, personal communication, 1976). The condition of these guano pellets and exoskeletal fragments suggest that they are of recent origin and have not been exposed to moisture. The isolated exoskeletal pieces were very similar to the intact guano pellets and were probably derived from the mechanical fragmentation of the guano pellets. The other three samples from Mammoth and Dixon caves contained no recognizable guano pellets or exoskeletal fragments. Unidentified rounded fragments were present in all five cave dirt samples; these fragments were not chemically analyzed (Scott Altenbach, personal communication, 1976).

Regeneration

Saltpeter earth, if returned to the cave after lixiviation, will regenerate in nitrate. Regeneration times of a few months (Cornelius, 1819), 3 to 5 years (Mitchell, 1806) and 8 to 10 years (Craig, 1862) have been reported. Craig (1862) suggested that dirt be carried into caves so as to become continuously charged with nitrate. Mitchell (1806) believed there was no end to the possible repetition of extracting and regenerating the nitrate ingredient of saltpeter earth.

Regeneration has occurred since 1812 in the lixiviated saltpeter earths of Dixon and Mammoth caves. Saltpeter earth after leaching contains less than 0.01% nitrate; lixiviated saltpeter earth in the Rotunda, Mammoth Cave analyzed by Davies and Chao (1959) contained 0.43% nitrate. This percent of nitrate in 30 liters of saltpeter earth produces (after conversion) 1.9 kg of crude saltpeter, which is close to the 1.4 to 2.3 kg reported by Croghan (1845) as having been produced in Mammoth Cave during the War of 1812. The 1812 lixiviated mounds of saltpeter earth at the entrance of Dixon Cave contain white, slightly bitter tasting, globules with up to 4% regenerated nitrate (Table 3, Eller #57-E). The lixiviated dirt shoveled up onto the wall ledges of Dixon Cave by the 1812 saltpeter miners contains up to 1.1% regenerated nitrate (Table 8). Removed from the walls in layers and divided into fine-grained and rock fractions, this lixiviated dirt was found to have nitrate values which steadily increase away from the cave wall. In all cases except one (LS#6-2, Table 8), the fine-grained fraction has a greater amount of nitrate than the rock fraction.

Nitrifying Bacteria

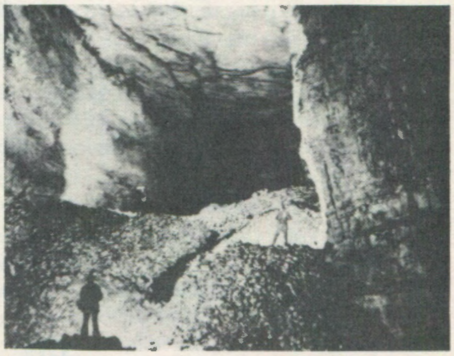
The nitrogen bacteria *Nitrosomonas* and *Nitrobacter* have been identified from the sediments and on the walls and ceilings of Mammoth and Dixon caves, Kentucky. An environment of free oxygen, phosphates, an alkaline pH and temperatures between 5°C and 40°C is required by these aerobic chemoautotrophic nitrifiers; darkness is favored and in the presence of strong light nitrification ceases. If living in the soil, the soil must be moist and aerated but not waterlogged or completely dry. Beyond a certain soil depth (approximately 2 m) *Nitrosomonas* and *Nitrobacter* cannot survive because of the lack of free oxygen (Gale, 1912). Other microorganisms must be present in the soil to decompose any organic matter as it is fatal to the activity of the nitric bacillus (Winogradsky and Omeliansky, 1900). A gram of sediment in Mammoth Cave contains an average of 6x10^5 *Nitrobacter* compared to less than 1x10^3 *Nitrobacter* in the surface soils above Mammoth Cave (Hill, Eller, Fliermans and Hauer, 1974). Of the *Nitrobacter* species present, the dominant species in Mammoth Cave is *Nitrobacter agilis* (85%), whereas the usually dominant species of *Nitrobacter* in surface soils, *Nitrobacter winogradsky*, makes up only 15% of the total cave *Nitrobacter* population. *Nitrobacter* population densities vary considerably among collecting sites but these densities do not correlate with nitrate concentrations or with the amount of moisture in the sediments at these sites (Fliermans and Schmidt, 1977). Lixiviation of cave sediments (1) removes excess and inhibiting nitrate, (2) selectively removes non-nitrifying bacteria from the system while having little effect on *Nitrobacter*, (3) adds water to a system whose biological activity is water limited, and (4) greatly enhances the efficiency of nitrate conversion (Fliermans and Schmidt, 1977). Once saltpeter earth has been leached of its nitrate, any ammonia added to the system is very rapidly oxidized to nitrate by the nitrifying bacteria *Nitrosomonas* and *Nitrobacter*.

Figure 10. A pit in Dixon Cave excavated by 1812 saltpeter miners.

Areal Extent of Saltpeter Deposits

Saltpeter earth was usually mined near cave entrances, but this may have been only an economic consideration. Hess (1900) reported saltpeter deposits in over 8 km of passages in Mammoth Cave. Nichols (1901) claimed that nitrates existed only in the entrance sediments of Wyandotte Cave, Indiana. Recently, Carl Fliermans (Fliermans and Schmidt, 1977) collected

Figure 11. Rock-piled main passageway of Dixon Cave.



about 150 samples of saltpeter earth from over 55 km of passages in Mammoth Cave ("X" in Fig. 8 mark Fliermans' collecting sites). Fliermans' analyses indicate that nitrate extends uniformly throughout Mammoth Cave as long as the floor sediment remains dry and that nitrate content of saltpeter deposits often varies more within a few meters than over larger distances. Nitrate concentrations may be exceptionally high near entrances; the sediment mounds and wall-ledge dirt at the Dixon Cave entrance have the highest nitrate values of any sediment samples collected.

Vertical Extent of Saltpeter Deposits

Nitrate is not vertically uniform throughout saltpeter earth but is usually concentrated in the top few meters of sediment. Saltpeter earth was reported to irregularly cover the floor of Great Saltpetre Cave, Kentucky, in some places 0.3 m and others 3 m in thickness (McDermott, 1963). In Dixon Cave, 1812 miners piled breakdown in the center of the passage and excavated 5 to 6 m deep pits along the cave walls (figs. 10 and 11). In Mammoth Cave, loose rocks were scraped of adhering dirt and then piled into neat walls along the sides of the passage (see p.108, this issue); saltpeter earth was then dug to a depth of 0.5 to 1 m while the underlying, unprofitable dirt was left untouched. The 1.5 m level of a recently excavated pit in Mammoth Cave was found to be much lower (720 ppm) in nitrate than the top sediment (10,800 ppm) (Table 3, Eller #78-B and #78-D).

There is a close similarity between the vertical extent of nitrate in cave saltpeter earth and in the nitrous caliche soils of the Chilean desert. In both locations nitrate is concentrated in the top few meters of the deposit. Mueller (1968) hypothesized that the Chilean nitrate deposits are derived from saline groundwater originating in the Andes Mountains. This groundwater accumulates in topographically low salt-pan basins between the western coastal foothills and the eastern mountains. Concentrated salts with relatively low solubilities (such as sulfates and chlorides) precipitate into the salt pans, whereas the more soluble salts (such as nitrates) ascend by capillary action up the slopes of the dry, coastal foothills and precipitate by evaporation near the surface of the porous soils.

THEORIES OF ORIGIN

Organic Theories

Vegetable debris, animal remains and rat guano are not present in sufficient quantities in most caves to account for the regeneration, areal extent and vertical extent of saltpeter earth; however, these theories may explain localized nitrate deposits in some caves. Rainwater percolating through the nitrous forest litter of the Dixon Cave sinkhole may diffuse laterally into bedrock and speleothems and down-slope into cave sediments thereby enriching the area near the cave entrance in nitrate. In Flower Cave, Big Bend National Park, Texas, the darapskite speleothems probably derive from the abundant amberat (rat guano + dehydrated urine) that exists in close association with the nitrate mineralization.

The two nitrifying microorganisms, *Nitrobacter* and *Nitrosomonas*, which occur in the sediments and on the walls and ceilings of Dixon and Mammoth caves could quickly regenerate saltpeter earth in nitrate providing there is a source of ammonia. One such source may be surface-derived nitrogen transported by seeping groundwater. In a purely inorganic system the stable aqueous species expected would be nitrogen (N_2aq) (Fig. 12); however, in an organic system surface microorganisms would reduce nitrogen in anaerobic interstitial waters of the lower soil zone to ammonium (NH_4^+). Calculated Eh-pH relationships (using the free energies tabulated by Garrels and Christ, 1965) predict that the ammonium ion should remain the stable species in the interstitial capillary water of the unsaturated zone (Fig. 13). When this capillary water encounters the cave, the ammonium ion in solution could be slowly and inorganically oxidized to nitrate, or it could be used as a nutrient source by *Nitrosomonas* and reduced to nitrite:

$$N^{-3} = N^{+3} + 6e^- \qquad (1)$$

$$3/2\ O_2^0 + 6e^- = 3\ O^{-2} \qquad (2)$$

$$NH_4^+ + 3/2\ O_2 = NO_2^- + 2H^+ + H_2O \qquad (3)$$

and then by *Nitrobacter* to nitrate:

$$N^{+3} = N^{+5} + 2e^- \qquad (4)$$

$$O_2^0 + 2e^- = 2\ O^{-2} \qquad (5)$$

$$2\ NO_2^- + O_2 = 2\ NO_3^- \qquad (6)$$

Figure 12. Eh-pH diagram of dissolved species of nitrogen in an inorganic system (after Berner, 1971).

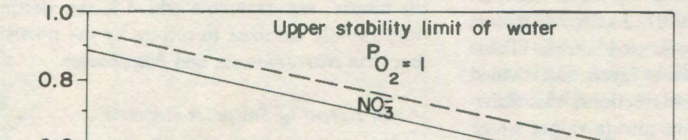
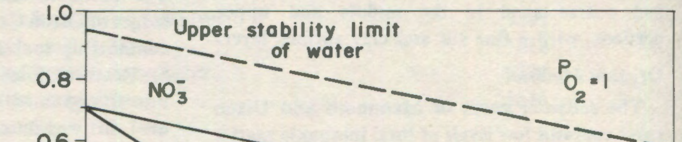


Figure 13. Eh-pH diagram of dissolved species of nitrogen in an organic system calculated using the free energies tabulated by Garrels and Christ (1965).



Pace (1971) also suggested that surface-derived ammonia is transported into the cave by seeping groundwater. Pace had the novel idea that this ammonia, upon reaching the cave, outgases into the cave air whereupon it is utilized by *Nitrosomonas* and *Nitrobacter.* This "cave air" theory is disproved by the drill data from Carlsbad Cavern. Nitrate values measured 6 ppm or less for entrance limestones exposed to odoriferous quantities of ammonia from bat and swallow urine (Fig. 5, Curve [10]).

Although bat guano is the most popular explanation of the origin of saltpeter deposits, upon close inspection this theory cannot account for many of the characteristics of saltpeter caves such as the general lack of bat guano, bat remains and the low concentration of nitrogen in saltpeter sediments. The presence or absence of clastic material is the primary difference between the mainly sedimentary saltpeter deposits of eastern caves and the organic bat guano deposits of western caves. Bat guano in Carlsbad Cavern and New Cave was mined intact as fertilizer whereas the saltpeter earth of Mammoth and Dixon caves was left in place after leaching. It is important to realize that both bat guano and saltpeter earth contain (and can be leached of) nitrate, but this by no means implies a similar origin for the two deposits. Texas cave bat guano was lixiviated and converted to gunpowder during the Civil War (Campbell, 1925; W.B. Phillips, 1901), but the primary commercial use of bat guano (containing high concentrations of both nitrogen and phosphorus) has always been as fertilizer.

Undoubtedly bats have supplied some guano to the saltpeter earth of Dixon and Mammoth caves, but bat colonies there were, and still are, relatively small. (It should be remembered that a bat population of thousands is small. Carlsbad Cavern has millions of bats). Dixon Cave has less than 100 individuals, which reside at the end of the cave (Fig. 3). The bat guano underneath the roosting area is composed of a mixture of excrement and fuzzy material from the bats' bodies together with clastic dirt (Hess, 1900). Before it became a major tourist attraction, Mammoth Cave was the wintering quarters for thousands of bats of five species, each species occupying a separate gallery or room relatively near the cave entrance (Lee, 1835). According to Hovey (1896) many of the bats occupied the passages called Big Bat Avenue (Audubon Avenue) and Little Bat Avenue (Fig. 8) where deposits of bat guano enriched the clastic saltpeter sediment in nitrate. Black, bat guano-enriched saltpeter earth was said to yield 3.2 to 4.5 kg of crude saltpeter per 30 liters of dirt, whereas unenriched clay sediment yielded only 1.4 to 2.3 kg (Cornelius, 1819). Davies and Chao (1959) reportedly found desiccated guano dust (38,000 years old) overlying rock, silt and sand in the Chief City Room, Mammoth Cave (Fig. 8). The small amount of bat guano (0.5% or less) in Mammoth Cave sediments indicate that the cave has also had fairly recent small colonies of bats but that, on the whole, bat guano is not abundant enough to explain such properties as regeneration. Regeneration of cave sediments reportedly takes place in a few years or less and is a process that is indefinitely repeatable. It is unlikely that small bat populations could uniformly regenerate nitrate in such short periods of time.

Another property that the bat guano theory does not adequately explain is the continuous areal extent of saltpeter earth. Although bats sometimes inhabit remote parts of a cave, usually these are solitary bats. Most bats congregate together by species in favorite roosting areas close to cave entrances. If bats were the only cause of nitrate in caves, then saltpeter earth should be abundant in passages close to cave entrances and almost completely absent further into the cave. The bat guano theory also does not account for saltpeter deposits that extend to cave ceilings or are packed in tight grottos, niches, or crevices where bats cannot roost.

Finally, the bat guano theory cannot account for high nitrate values found on cave ceilings, walls and up to 30 cm into limestone bedrock. The drilling results from New Cave, Carlsbad Caverns National Park, New Mexico, are extremely important to a proper interpretation of the high nitrate values in the Dixon Cave, Kentucky, limestones because they show that nitrate solutions do not move *into* the walls from saltpeter cave sediment. The compacted bat guano directly under DS#10, New Cave, is low in nitrate (6 ppm) indicating that these guanos have been leached by dripping vadose water. Yet, the New Cave bedrock drill sample (1 m above the guano) contains only a few ppm nitrate (Curve [14], Fig. 5) compared to thousands of ppm for the limestones of Dixon Cave. Apparently, nitrate leached from the New Cave bat guano exited in solution via cracks and joints in the floor rather than seeping into the limestone wallrock.

Thus, it is concluded that, although bat guano can cause saltpeter earth to be richer in nitrate, it is not the only, or even major source of nitrate to the saltpeter sediments of Dixon and Mammoth caves. The extent of bat guano contribution to saltpeter earth should be qualified by such evidence as quantity of recognizable bat guano and bat remains, size of bat populations and extent of nitrous earth. The nitrate in the deposits of Carlsbad Cavern is undoubtedly supplied by bats, whereas in Mammoth and Dixon caves, Kentucky, bats have contributed relatively minor amounts of nitrate to the saltpeter sediments.

Seeping Groundwater Theory

Theoretical considerations. The essential hypothesis of the seeping groundwater theory is that capillary vadose water transports nitrate from the surface through the zone of aeration and into the bedrock and sediments of saltpeter caves. The dynamics of water movement through the zone of aeration is only partially understood and has been little studied compared to water dynamics in soils and groundwater flow in the saturated zone (Stallman and Reed, 1969). This intermediate belt or "no man's land" of hydrology (Meinzer, 1942) contains water which is not normally affected by evaporation, but which moves slowly downward toward the water table at a rate dependent on the interaction of the forces of gravity, adhesive and cohesive molecular attraction and internal vapor pressure (which is less than atmospheric).

The extent to which evaporation occurs in the zone of aeration is questionable. Meinzer (1942) speculated that movement of air through natural openings (caves) may well have a tendency to dry out the rocks. Seeping water-type sulfate speleothems such as gypsum crust and flowers are evidence that evaporation occurs in caves. These speleothems are deposited in dry cave passages and are precipitated upon evaporation of sulfate-bearing solutions seeping through the pore spaces of the rock (Hill, 1976). The movement of capillary water toward a cave requires only that the pores at the surface of the cave wall have a lower capillary potential (*i.e.* a lower moisture content) than that of the surrounding limestone. The relative magnitudes of evaporation and incoming flow may vary with time, but eventually evaporation and inflow must balance.

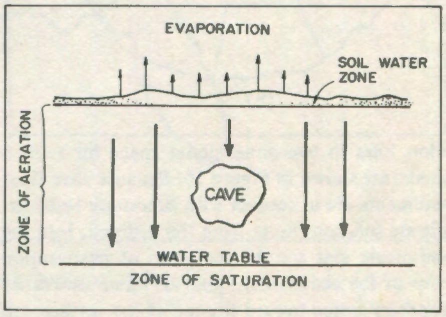


Figure 14. Idealized model of downward capillary flow through porous rock in the unsaturated zone under the influence of gravity.

Gravitational movement of water downward through a porous rock in the unsaturated zone may be expressed (within two orders of magnitude; Stallman and Reed, 1969) by Darcy's Law:

$$q = -K\nabla\Psi \qquad (7)$$

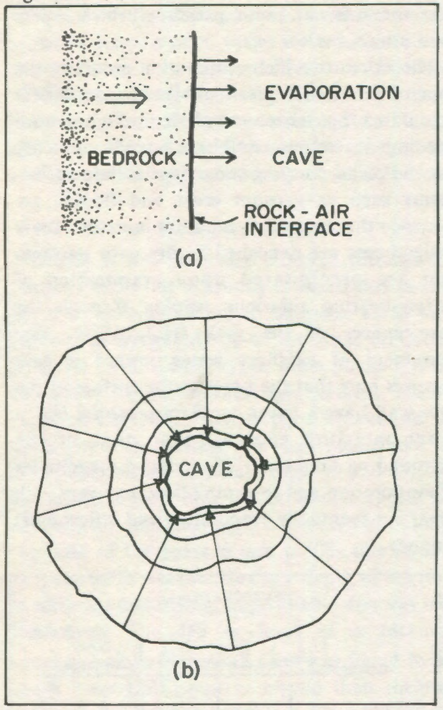
where q equals the volume of water per unit time crossing a unit area perpendicular to the flow, K equals the capillary conductivity (which is dependent on the properties of the fluid and medium) and $\nabla\Psi$ is the gravitational force represented by the negative gravity potential $\Psi = gz$ (z=height from a reference level) (Fig. 14). If evaporation and drying occur at the rock-air interface of a cave, a moisture density gradient within the rock should theoretically force capillary water to move toward the cave (figs. 15a and 15b):

$$q = K\nabla\Phi \qquad (8)$$

where $\nabla\Phi$ is the evaporative force and Φ is the moisture density potential. Capillary flow toward a cave is thus effected by the combined forces of gravity and evaporation:

$$q_t = -K\nabla\Psi \S K\nabla\Phi \qquad (9)$$

Figure 15. Density gradient of moisture (represented by dots) within rock produced by evaporation (a); capillary water flows toward the cave perpendicular to moisture density gradient (b).



Flow lines in two-dimensional space for such a model are shown in Figure 16. Because cave-floor sediments are in contact with limestone bedrock, nitrate solutions move from the bedrock, into the sediments and toward the zone of evaporation (top of the sediments), just as water moves by capillary action toward the top of the surface soil in the soil zone.

Indirect evidence for the groundwater theory. Seeping groundwater as a mechanism for transporting nitrates into caves has been reported to occur in many caves outside the Mammoth Cave region. Mawson (1930) found white encrustations and veinlets of nitrate in a central Australian cave which occur either as saturations in the rock pore spaces, as friable crystalline granular masses in pockets and veins, or more rarely as crystalline growths from the walls of vugs. Mawson thought downward-percolating water was the transporting agent for the nitrate impregnations. Brown (1809) reported nitrate within wallrock of the sandstone "rockhouse" caves near Lexington, Kentucky. The rock was highly impregnated with niter (KNO_3) and tasted strongly of saltpeter. The sandstone rock was leached rather than the cave earth since it yielded more nitrate (13.5 kg of saltpeter per 30 liters of sand) than the cave floor sediment. The nitrate was reportedly distributed through the whole rocky mass, cementing the siliceous particles together and filling up sandstone bedding planes and also veins and cracks across the strata (Phillips, 1818). Hess (1900) thought percolating water transported nitrate to these rockhouse caves.

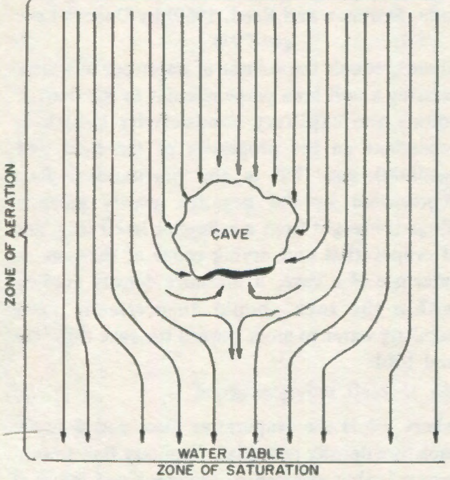


Figure 16. Idealized model of capillary flow toward a cave due to combined forces of gravity and evaporation.

In another occurrence, Stewart (1911) reported nitrate mineralization on the roof of an Idaho sandstone cave. The position of the deposit indicated to Stewart that the nitrate could have been carried only through the sandstone by percolating water and then deposited by evaporation. Mansfield (1927) also believed that groundwater caused the nitrate efflorescences and crusts on the roof of this same sandstone cave. A tunnel dug 18 m directly underneath the cave proved the existence of soluble salts within the mass of the sandstone, as the tunnel walls soon became white with a soluble, bitter-tasting coating. Mansfield considered the original source of nitrate to percolating water to be surface vegetation acted upon by nitrifying bacteria in the soil.

Davy (1821) extensively investigated caves in Ceylon which contained white efflorescent nitrate wall encrustations. These efflorescences crystallized in the dry season and disappeared in the wet season. The method of mining in the Ceylon caves was to chip off pieces of wall rock, powder it, and then leach the rock of its nitrate. In one of these caves, Memoora, there was reportedly no bat guano, yet the rock was strongly impregnated with nitrate; in the other caves, guano was present, but there was not the slightest trace of nitrate in the bat excrement. Davy concluded that the presence of bat excrement favors nitrification but is not indispensable. In Molfetta, another of the Ceylon caves, thin coatings and efflorescences of nitrate occurred on the limestone walls, and on removing these efflorescences others appeared within a few months time.

In all of these occurrences it appears to be the continuous supply of seeping groundwater which is responsible for the transportation of nitrate to the caves.

A seeping groundwater theory is consistent with the characteristics of saltpeter caves and sediments. It explains:

(1) low levels of nitrogen, bat guano, bat remains and other organic matter in saltpeter sediments; organic material in saltpeter earth is unnecessary for a groundwater origin of cave nitrate.

(2) the presence of *Nitrosomonas* and *Nitrobacter* in cave sediment and on cave walls and ceilings; dissolved ammonia in groundwater may be the source of nutrient to the nitrifying bacteria in the cave.

(3) the areal uniformity of saltpeter earth; descending groundwater seeps toward any dry cave passage regardless of its distance from the cave entrance.

(4) regeneration of nitrate within a few years' time; groundwater continuously seeps toward the cave, thus replenishing lixiviated cave dirt in nitrate.

(5) nitrate as a minor constituent in sulfate speleothems; nitrate is transported in seeping groundwater along with other soluble salts such as gypsum.

(6) high nitrate levels on the outermost surface of wall bedrock and in the outermost layer of regenerated saltpeter earth on cave wall ledges; groundwater movement is always towards the wall-cave air evaporation surface.

(7) highest nitrate concentration in the upper few meters of saltpeter cave sediment; groundwater movement is upward from the bedrock through the porous sediments and toward the surface of evaporation (just as occurs in the Chilean nitrate deposits), and toward the oxgenated region inhabited by the nitrifying bacteria *Nitrosomonas* and *Nitrobacter.*

(8) high (thousands of ppm) nitrate up to 30 cm within cave limestones; seeping groundwater continually transports measureable nitrate (oxidized from the ammonium when exposed to O_2) through the rock and toward the cave.

High nitrate 30 cm within the limestone bedrock is strong, indirect evidence for the applicability of the seeping groundwater theory. Dry cave conditions preclude movement of nitrate solutions into the bedrock and, even if sediment moisture conditions were sufficient to move nitrate toward the bedrock, the drilling results in New Cave, Carlsbad Caverns National Park, indicate that such movement does not occur. Because nitrate does not move into the wallrock from the cave, it may seep into the wallrock from above.

Source of nitrate to groundwater. Possible sources of nitrate to seeping groundwater are ammonium-rich volcanic rocks, primary depositional nitrate within the limestone, and organic material in overlying surface soils. Some rapidly cooled silicate volcanic rocks have high amounts of nitrogen (Baur and Wlotzka, 1968). Recent volcanic ash overlying Malmquist Fissure, Wupatki National Monument is possibly the source of the soda-niter mineralization and the nitrate saturations (up to 323 ppm, curve [5], Fig. 5) in the cave bedrock. Although volcanic rocks may explain localized cave nitrates such as those in Malmquist Fissure, this source is impossible for southeastern caves in non-volcanic areas.

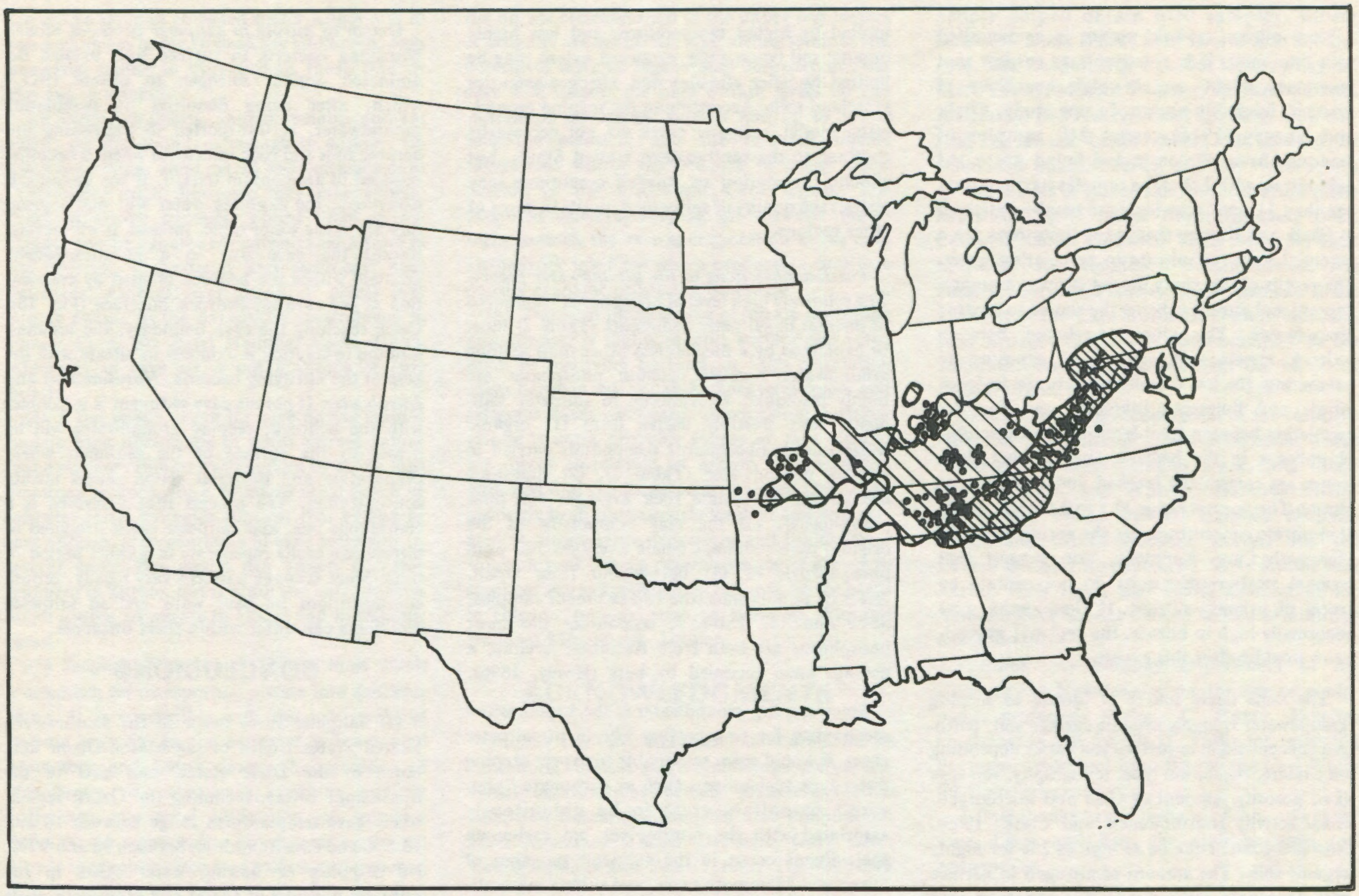


Figure 17. Distribution of saltpeter caves compared with "oak forest" (west) and "oak-hickory forest" (east) (National Atlas, 1970).

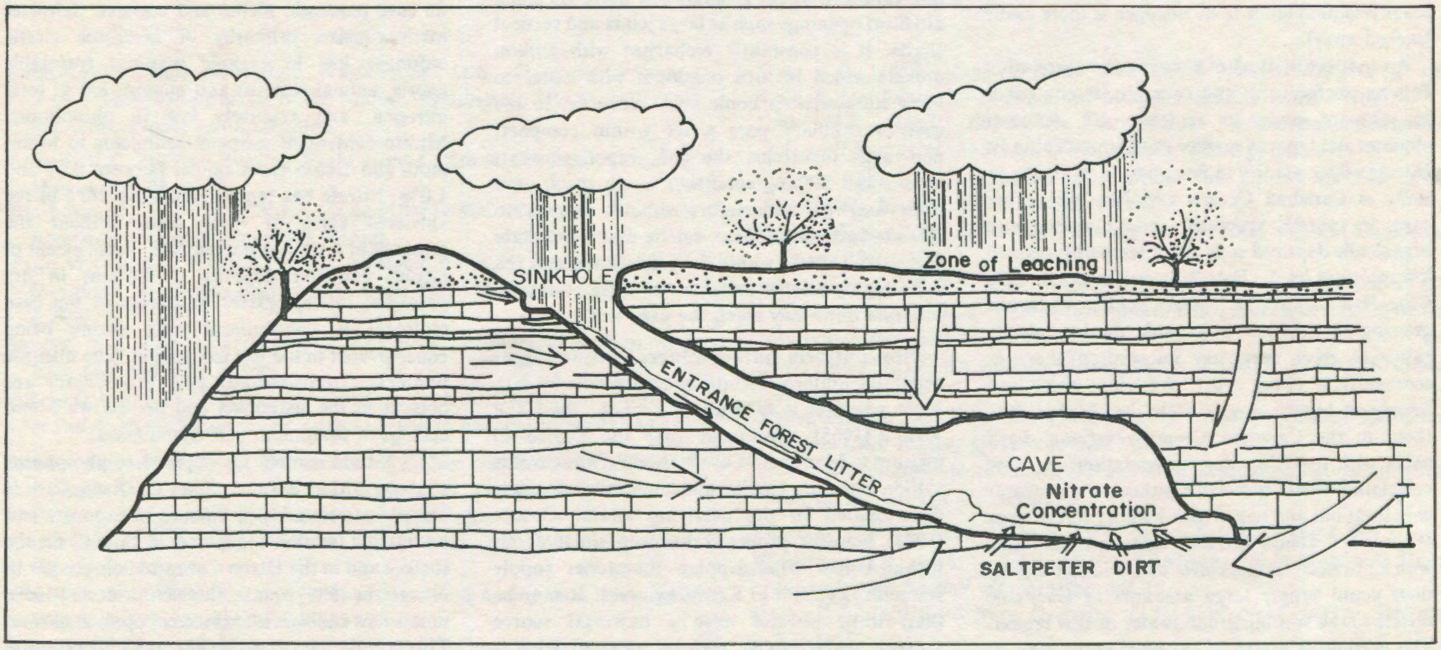


Figure 18. Idealized model of cave nitrate origin; the ammonium (NH$_4^+$) ion is transported by seeping groundwater (arrows) to the dry cave where it is oxidized to nitrate by the nitrifying bacteria, *Nitrosomonas* and *Nitrobacter.*

Since nitrous organic matter is co-deposited with lime mud, it is reasonable to suspect that limestones might contain high quantities of primary, leachable nitrate. In one study, Chalk and Keeney (1971) tested 210 samples of limestone from Wisconsin and found up to 164 ppm nitrate with 2/3 of the samples having values less than 11 ppm nitrate; these results indicated to Chalk and Keeney that many limestones are a potential source of nitrate to percolating water. The results of this study do not support primary, depositional nitrate as being the source to seeping groundwater. The close correlation between bedrock nitrate and amount of exposure to weathering, the low correlation between bedrock nitrate and limestone lithology, and the low correlation between soluble nitrate and insoluble phosphorus in the bedrock suggest that limestones are continually leached and recharged in nitrate. The normal range (0.1 to 3.0 ppm, Table 4) of nitrate concentration in the spring waters of Mammoth Cave, Kentucky, also suggest that regional stratigraphic units do not contain an excess of primary nitrate. If these units were abnormally high in nitrate, the regional groundwater would reflect this excess.

The most likely source of nitrate to seeping groundwater is highly organic surface soil. Nitrogen concentration in surface soil varies depending on climate, vegetation type, topography, soil type (*i.e.*, porosity, amount of clay) and microorganismal activity (Bartholomew and Clark, 1965). Nitrogen content can be as high as 2% for highly organic soils. The amount of nitrogen in surface soil decreases with rising temperature and increases with rising moisture content. Grassland soils readily retain available nitrogen whereas forest soils have lower amounts of nitrogen due to lower retention levels (*i.e.*, nitrogen is more easily leached away).

An indirect method of showing the correlation between surface soils and cave nitrate content is to compare caves in regions with different climates and types of surface vegetation (Table 1). Nitrate values are low (a few ppm) in the bedrock units of Carlsbad Cavern and New Cave, two caves in sparsely vegetated, arid climates with organically deprived soils, high temperatures and low moisture levels. Fort Stanton Cave and Ellis Cave, New Mexico, lie beneath coniferous forests growing on soils low in organic matter; nitrate values in these caves are lower than those in southeastern caves with overlying deciduous forests on highly organic soils, but higher than those in the Carlsbad Caverns National Park caves with overlying desert vegetation. A close correlation exists between southeastern saltpeter cave locations and oak or oak-hickory forest types (Figure 17). Dense surface vegetation combined with optimum temperature and rainfall conditions could supply large amounts of leachable nitrate to the seeping groundwater of this region. The northward extent of saltpeter caves may be limited by lower temperatures or by the wetness of northern caves; their southward extent may be limited by higher temperatures and less highly organic soil types; their westward extent may be limited by drier climates and nitrogen-retentive grassland soils. According to the seeping groundwater model, saltpeter caves are not necessarily confined to the southeastern United States, but climate, vegetation or rainfall conditions may restrict the quality of saltpeter deposits in caves of other regions.

Possible objections to the groundwater theory. The relatively high level of phosphorus (compared to nitrate) in saltpeter sediments (Table 7) must be explained by a mechanism other than seeping groundwater because calcium phosphates are highly insoluble. Phosphorus in saltpeter sediments may possibly derive from (1) organic water-soluble phosphorus compounds carried in seeping groundwater (Table 2), (2) limestone breakdown (carbonate rock averages 400 ppm phosphorus), (3) the clay component of the original cave sediment (shale averages 700 ppm phosphorus), or (4) bat guano from small, localized populations (the two sediment samples, SS#1 and 13, Table 7, containing the most phosphorus are both from Audubon Avenue, a passage once occupied by bats (Hovey, 1896).

Since seeping groundwater is the hypothesized mechanism for transporting nitrate to saltpeter caves, it would seem reasonable to expect seeping water-type speleothems such as carbonate "popcorn" or sulfate crust to be ubiquitously associated with the nitrate; yet, no carbonate speleothems occur in the saltpeter passages of Dixon and Mammoth caves, and sulfate mineralization occurs only intermittantly. The lack of popcorn carbonate speleothems may be related to the low acidity of capillary waters. When non-capillary vadose groundwater descends along air-filled openings such as large joints and vertical shafts, it is constantly recharged with carbon dioxide which in turn combines with water to form additional carbonic acid. However, in the case of capillary pore water within compact, non-vuggy limestone, the CO_2 vapor phase is absent and seeping solultions which reach cave walls may be undersaturated with respect to calcium carbonate. (Also, calcite may precipitate in vugs and cracks within the bedrock whereas the more highly soluble sulfates and nitrates stay in sollution until they reach the cave wall.)

Non-uniform sulfate mineralization versus relatively uniform nitrate concentration in saltpeter passages is difficult to explain. Pohl and White (1965) speculated that the source of gypsum to Mammoth Cave National Park caves is sulfide minerals (pyrite and marcasite) sparsely disseminated in the overlying strata. George (1974), however, proposed that evaporite intervals within Upper Mississippian limestones supply secondary gypsum to Kentucky caves. It may be that, while nitrates have a universal source (organic surface soils), gypsum mineralization is closely regulated by localization of evaporite rock or sulfide minerals in the overburden.

Origin of nitrate in saltpeter caves—a model. Nitrifying bacteria in surface soils oxidize deaminated organic nitrogen to nitrate (NO_3^-) which, after being dissolved by percolating groundwater, is transported to underlying anaerobic soils and rock interstices where it becomes reduced to ammonium (NH_4^+). If the bedrock is cavernous, the capillary water will not descend directly to the water table. Instead, it will deviate toward the cave due to a moisture-density gradient within the bedrock created by evaporation at the cave air-bedrock interface (Fig. 18). Upon reaching the cave boundary, the ammonium ion in solution is oxidized to nitrate with the help of the nitrifying bacteria, *Nitrosomonas* and *Nitrobacter.* If porous cave sediment is in contact with the bedrock, seeping groundwater will be drawn to the surface of the sediment where evaporation and bacterial action causes nitrate concentration. The process thus described is a continuous one, and saltpeter earth lixiviated of nitrate can easily regenerate in a short period of time. Since seepage patterns vary locally, nitrate concentrations on cave walls and in saltpeter sediments can differ within short distances.

CONCLUSIONS

(1) Saltpeter caves occur in the southeastern United States (south of the Mason-Dixon line, north of the Dixie states, and east of the Mississippi River), including the Ozark region, where cave temperatures range between 10 and 18.5°C and cave humidities between 90 and 99%. No dripping or flowing water exists in the saltpeter passages of Dixon and Mammoth caves and sediment moisture is low (5 to 10%). Air circulation above saltpeter earth is common but not essential; saltpeter sediment can completely fill cave passages, niches and crevices. Saltpeter earth consists primarily of inorganic clastic sediment low in organic material (vegetable debris, animal remains and guano), low in total nitrogen, and relatively low in phosphorus. Nitrate content of saltpeter sediments in Mammoth and Dixon caves ranges between 0.01 and 4.0%. Nitrate has regenerated since 1812 in the lixiviated earth of these caves without the presence of large bat populations. Areal extent of nitrous saltpeter deposits is uniform in dry passages; vertical extent of nitrate in the cave sediment is non-uniform with nitrate being concentrated in the top few meters. The nitrogen bacteria *Nitrosomonas* and *Nitrobacter* are present in the sediments and on the walls and ceilings of Mammoth and Dixon caves.

(2) Nitrate content (as opposed to phosphorus content) within the limestones at Dixon Cave is directly correlated with amount of exposure and leaching. Limestones exposed to rainfall on the surface and in the Dixon Cave sinkhole are low in nitrate (a few ppm) whereas protected cave limestones are high (thousands of ppm) in nitrate. This correlation of nitrate content with exposure occurs immediately (within a few meters) at the sinkhole dripline and is independent of lithology.

Limestone samples collected under ledges and in recessed niches in the Dixon Cave sinkhole always measured higher in nitrate than those directly exposed to rainfall.

(3) Vegetable debris, animal remains and rat guano are not abundant enough to account for the regeneration, areal extent and vertical extent of saltpeter earth; however, they may explain localized nitrate deposits. Forest litter in entrances may be a source of concentrated nitrate in the bedrock, speleothems and sediments near entrances. Amberat (rat guano + urine) may supply nitrate to the darapskite speleothems in Flower Cave, Big Bend National Park, Texas. Ammonia in cave air is not a source of cave nitrate.

(4) A bat guano origin for cave nitrate cannot explain high (thousands of ppm) nitrate values found on cave ceilings, walls and up to 30 cm into limestone bedrock, the continuous areal extent of saltpeter earth, saltpeter deposits that extend to cave ceilings, or regeneration of cave sediments in several years. Bat guano can enrich saltpeter sediment in nitrate, but it is not the only, or even major source, of nitrate in Dixon and Mammoth caves.

(5) Seeping groundwater is the most likely mechanism for transporting nitrate into saltpeter caves. It is compatible with the low levels of organic material in the saltpeter sediments of Mammoth and Dixon caves; the presence of *Nitrobacter* on cave walls, ceilings and in sediments; the areal uniformity of saltpeter deposits; the regeneration of saltpeter earth; the nitrate in seeping water-type sulfate speleothems; the nitrate concentration in the upper few meters of saltpeter sediment; the high nitrate levels in the outermost layer of regenerated saltpeter dirt on cave wall ledges; the high nitrate levels on the outermost surface of bedrock and up to 30 cm into the bedrock; and the reported nitrate saturations within the bedrock of many caves outside of the Mammoth Cave region. The proposed cause of seeping groundwater movement towards the cave is evaporation at the cave air-bedrock interface which produces a moisture density gradient within the limestone.

(6) The most likely source of nitrate to seeping groundwater is highly organic surface soil acted upon by nitrifying bacteria. A high correlation exists between oak or oak-hickory forest types and saltpeter caves. Primary, depositional bedrock nitrate is not a probable source of cave nitrate; the direct correlation of nitrate with exposure indicates that the limestones of Dixon Cave have probably been continuously leached and regenerated in nitrate since deposition and lithification. Volcanic rock is not a possible source of nitrate in southeastern saltpeter caves, but may be for caves in volcanic regions, such as those at Wupatki National Monument, Arizona.

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Bermuda Cave Exploration
Staging Area: St. George's West, Bermuda

Bermuda's islands boast one of the highest concentrations of limestone caves in the world, offering a unique opportunity for biological and geological study of these rare and fragile environments. Dr. Thomas Iliffe, a Research Associate at the Bermuda Biological Station, is investigating Bermuda's many caves.

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Team I: Sep 28-Oct 11
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MINERALOGY OF CAVE NITRATES

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SUMMARY

Nitrate minerals occur in dry southwestern United States caves, but do not crystallize in humid southeastern caves. At 12°C, the humidity at which nitrate minerals crystallize is 54% for nitrocalcite ($Ca(NO_3)_2 \cdot 4H_2O$) *and nitromagnesite* ($Mg(NO_3)_2 \cdot 6H_2O$), *74% for ammonia-niter* (NH_4NO_3), *79% for soda-niter* ($NaNO_3$), *and 92% for niter* (KNO_3).

The nitrate minerals niter, soda-niter, and darapskite ($Na_3(NO_3)(SO_4) \cdot H_2O$) *have been identified in non-saltpeter, southwestern caves. Niter (crystal size = 1.5 mm) occurs as a transparent, colorless to light brown, bitter-tasting wall crust in a lava tube near Socorro, New Mexico. Soda-niter also occurs as a crystalline wall crust, as two small stalactites, and as one small stalagmite with the Socorro niter. The Socorro soda-niter crystals are rhombohedral, 2 to 3 mm long, transparent, and colorless. Darapskite occurs in Flower Cave, Big Bend National Park, Texas, as cave "flowers", crust, "hair", flowstone, and stalactites. The darapskite is colorless with* $2V(-)=20\text{-}30°$, $\alpha=1.30\pm0.005$, $\beta=1.480\pm0.003$, $y=1.489\pm0.003$, $a=10.558(3)$, $b=6.870(2)$, $c=5.186(1)$ *and* $\beta=101.46.1(5)$.

NITRATE MINERALS are anisodesmic (ionic) structures containing discrete (NO_3^-) groups which are the same shape as $(CO_3^=)$ groups but of a slightly smaller size ($NaNO_3$ is isostructural with calcite and KNO_3 is isostructural with argonite). The shape of the complex (NO_3^-) anion is that of an equilateral triangle; the core atom (N) is in the center (Naray-Szabo, 1969). All nitrate minerals are highly soluble in water because the N-O electrostatic bond is much higher (1.67) than for oxygen-cation bonds (0.33 electrostatic bond unit). Nitrate minerals are optically negative with low refractive indices (n_α is extremely low) and have a strong, bitter-cooling taste. The natural nitrates are few in number and of rare occurrence due to their high solubility. Caves offer shelter and are therefore one of the few places where nitrate minerals can accumulate.

PREVIOUS INVESTIGATIONS

Six nitrate minerals have been previously reported from caves: niter (KNO_3), soda-niter ($NaNO_3$), ammonia-niter (NH_4NO_3), nitrocalcite ($Ca(NO_3)_2 \cdot 4H_2O$), nitromagnesite ($Mg(NO_3)_2 \cdot 6H_2O$) and darapskite ($Na_3(NO_3)(SO_4 \cdot H_2O)$). Descriptions of these nitrate cave minerals consist of either very old (early 1800) articles or scattered, later reports of limited detail.

Niter was reported by Davy (1821) as efflorescent wall encrustrations in the caves of Ceylon, by Mansfield (1927) as white efflorescences and crusts in an Idaho sandstone cave and by Mansfield and Boardman (1932) in the basaltic lava tubes of Socorro County, New Mexico.

Soda-niter was briefly mentioned by Bailey (1902) and Hutchinson (1950) as an encrustation in a small cave near Calico, California, by Mawson (1930) as a minor constituent with niter in a central Australian cave, and by Gale (1912) as coatings or even stalactites with niter on cave walls and ceilings.

Shepard (1857) reported ammonia-niter from Nickajack Cave, Tennessee, but gave no details of its occurrence. Mawson and Cooke (1906) reported a possible occurrence of ammonia-niter from the fissure caves at Elder Rock near Adelaide, Australia.

Ross (1914) noted the presence of very pure, elongated, white crystals of nitrocalcite in crevices of a southwestern guano cave. Mitchell (1806) supposedly found "crystals of salt-petre" (nitrocalcite) in the saltpeter earth of the limestone caverns of Virginia, Kentucky, and Tennessee; Palache, *et al.* (1951) noted that these reported eastern localities needed verification.

Larsen (1921) reported nitromagnesite from Madison County, Kentucky (probably Great Cave) and Cutbush (1825) from a cave near Corydon, Indiana.

Ericksen and Mrose (1970) briefly noted darapskite in a Death Valley, California cave, but gave no details of its occurrence.

It is interesting that, in all of the reported localities, nitrate cave minerals occur primarily as efflorescences or encrustations on cave walls and ceilings rather than as crystallized products in bat guano. Kasper (1934) found no crystallized nitrate minerals in the bat guano of Domica Cave, but did detect the presence of nitrate in solutions penetrating through the guano. Phosphates are the characteristic minerals found in bat guano; over 25 different phosphate guano minerals have been identified (Hill, 1976; Bridge, 1973).

MINERALOGICAL TECHNIQUES

All nitrate minerals were identified by the X-ray diffraction powder method, using Cu/Ni radiation and a 114.6 diameter Debye-Scherrer camera. Other identification techniques used were: distinctive taste, high solubility in water, a strong positive nitrate test (phenoldisulfonic acid method) and oil immersion. The indices of refraction were determined using white light. The immersion liquids were checked on a Fisher refractometer at the time the measurements were made. Indices above 1.40 were made using oils with an error range of ±0.001 and those below 1.40 with an error range of ±0.0005.

DESCRIPTION OF MINERALS

Niter, KNO_3

Both niter and soda-niter were identified from the Socorro bat caves, located 88 km south of Socorro, New Mexico. These tunnel caves, extending 2.4 km southward from a volcanic crater, were once parts of the same lava tube but have since been segmented by collapse into five separate sections. Roof thicknesses are 6 to 9 m. Bat guano occurs on the floors of all the caves, but the longest cave, Main Bat Cave, is the only cave that presently has a large bat colony. Temperature and relative humidity in Main Bat Cave in May, 1977, were 15.5°C and 43%, respectively.

Niter occurs in Main Bat Cave as a crust on the right wall approximately 9 m into the cave. The niter crust is about 2 m long and 0.3 m wide and extends from the cave floor-wall boundary up to a line demarcating a former bat guano level. The niter is either a regrowth or a remnant of abundant niter that once existed in the cave. Between 1899 and 1902 J.R. DeMier of Las Cruces, New Mexico mined about 125 tons of niter from Main Bat Cave (Mansfield and Boardman, 1932).

The niter in Main Bat Cave is massive-granular, transparent, and colorless to light brown (tinted by impurities from the bat guano). Taste is saline and cool. Many of the niter crystals

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(average size 1.5 mm) have rounded or embayed, partially dissolved edges (Fig. 1). The niter was identified by optical and X-ray diffraction techniques (Table 1). The X-ray pattern contains no diffraction maxima for any other nitrate minerals.

The close association of the niter wall crusts with former bat guano levels in Main Bat Cave suggests that both the potassium and nitrate may have derived directly from the bat guano or from the bat guano and basaltic rock.

Soda-niter, $NaNO_3$

Soda-niter was found in two southwestern caves: one occurrence was with niter in Main Bat Cave near Socorro, New Mexico; the other was in the Wupatki fissure caves near Flagstaff, Arizona (Hill and Eller, 1977).

The Socorro soda-niter occurs in Main Bat Cave 4 to 6 m from the entrance, along the right wall and 0.6 to 2 m above the floor, as a crystalline wall crust along cracks in the basalt (Fig. 2), and as two small stalactites 1 cm and 3 cm long. One tiny soda-niter stalagmite is located directly underneath the longest stalactite.

Soda-niter crystals are 2 to 3 mm long, massive granular, transparent, colorless and appear to have "melted" together to form clumps or aggregates of crystals. Taste is bitter, pungent and cooling. Some crystals show perfect rhombohedral cleavage (Fig. 3), while other crystals are badly altered and show dissolved, "eaten away" edges. The soda-niter was identified by X-ray diffraction.

The soda-niter dripstone (stalactites and stalagmite) and the soda-niter crusts of Main Bat Cave originated from solutions dripping and seeping into the cave from above. Possible sources of sodium and nitrate to the groundwater are the basaltic rock and/or surface vegetation.

Table 1. Optical data for niter, Main Bat Cave, Socorro, New Mexico.

Parameter	Observed	Previously Reported	Reference
Crystal System	Biaxial negative	Biaxial negative Orthorhombic	Larsen and Berman (1934)
Refractive Indices	$\alpha = 1.332 \pm .003$ $\beta = 1.504 \pm .005$ $\gamma = 1.500 \pm .005$	1.332 1.504 1.504	Larsen and Berman (1934)
2V (-)	6°	7°	Larsen and Berman (1934)
Habit	equant	equant or elong. ∥ *c*	Larsen and Berman (1934)

Figure 1. Niter crystals (1.5 mm long) with embayed edges.

Figure 2. Soda-niter crust developed along cracks in basalt, Main Bat Cave, Socorro, New Mexico. Length of pronounced, white, soda-niter seam in upper left is approximately 15 cm.

Figure 3. Rhombohedral soda-niter crystal, 2 mm long. Note embayed crystal in lower right.

Darapskite, $Na_3(NO_3)(SO_4)\cdot H_2O$

Darapskite, first described by Dietze (1891), is a widespread mineral in the Chilean nitrate deposits where it occurs alone and with other saline minerals in veins, pods, cementing material and cavities in the nitrate ore. Darapskite has also been reported as a mineral in the soils of the Antarctic (Claridge and Campbell, 1968). Ericksen and Mrose (1970) very briefly mention the presence of darapskite in saline materials from caves in the limestones of the Funeral Mountains, Death Valley, California, but give no details of its mineralogic properties or occurrence.

Flower Cave, located at the southern end of Big Bend National Park, is a small cave 15 m long and 6 m wide at the entrance. It ascends slightly as a crawlway to a terminal room 2 m in height and 3 m in diameter. Amberat (dehydrated rat urine + guano) is abundant on the walls of the room and is closely associated with the darapskite. Temperature and relative humidity in this chamber in March, 1977, were 24°C and 40%, respectively.

Five darapskite speleothem types exist in Flower Cave: flowers, crust, "hair", stalactites and flowstone. The darapskite flowers are white, opaque and consist of radiating "petals" which curve away from the center of the flower (Hill and Ewing, 1977) (figs. 4 and 5). These "petals" consist of alternating growth layers of translucent darapskite and opaque halite which are oriented parallel to each other, as well as to the bedrock wall (Fig. 6). The halite layers are 0.05 mm to 0.1 mm thick and the darapskite layers are 0.2 mm thick. The darapskite crystals within each darapskite layer are prismatic and are elongated along the *c*-axis perpendicular to the layering sequence. Sometimes these prismatic crystals terminate at the adjacent halite layers; sometimes individual crystals extend across the halite lines. Darapskite crystals average 0.1 mm in length and reach a maximum size of 0.2 mm (Fig. 7). Approximately one-half of the flower mass is halite and one-half is darapskite.

Darapskite-halite crust occurs as thin (1 to 20 mm), white patches attached to the walls of the terminal chamber. Some of these crusts have flaked off the wall onto the floor. Hanging down from the darapskite crust in one place is a very

Figure 4. "Baby" darapskite-halite flowers 1 cm in diameter. Note black beads of "amberat" on wall in close association with the flowers.

Figure 5. Darapskite-halite flower approximately 8 cm in diameter surrounded by darapskite-halite crust.

Figure 6. Alternating layers of light darapskite (0.2 mm) and opaque halite (0.05 mm) under crossed nichols. Note that some of the larger darapskite crystals are continuous across the halite layers.

Figure 7. Translucent, prismatic crystals of darapskite in plane polarized light. The small, dark inclusions are probably halite. The crystals are approximately 0.2 mm in length.

(next page) →

Table 2. Physical and optical properties of darapskite.

Properties	Flower Cave (this study)	Oficina Alemania, Chile. Ericksen and Mrose (1970)	Santa Catalina, Chile. Larsen and Berman (1934)
Habit	Prismatic *c*	Long prismatic; also thin tabular (100) elong. *c*	
Color	Colorless, transparent, vitreous	Colorless, transparent, vitreous	Colorless, transparent vitreous
Hardness	———	-2½	2.3
Cleavage	[100]	[100] perf. [010] good	[100] and [010] perf.
Specific Gravity	———	2.201 ± 0.005 at 22°C	2.20
Twinning	Polysynthetic twinning ∥ [100] rare	Polysynthetic twinning ∥ [100]	Polysynthetic twinning [100] similar to those of plagioclase
Optic sign	Biaxial (-)	Biaxial (-)	Biaxial (-)
2 V (meas)	20-30°	Small	27 ± 1°
2 V (calc)	32° 29'	29° 42'	26°
Dispersion	None observed	r>v strong	r>v rather strong
Indices of Refraction			
∝	1.391 ± 0.005	1.388 ± 0.005	1.391 ± 0.005
β	1.480 ± 0.003	1.479 ± 0.003	1.481 ± 0.003
γ	1.489 ± 0.003	1.486 ± 0.003	1.486 ± 0.003
Orientation			
X	*b*	*b*	*b*
Y			
Z	+13°(±1°) to *c*	+13 (± 1°) to *c*	12° to *c*

Table 3. X-ray data for darapskite.

(hkl)	$d_{calc.}$	d_{obs}	I/Io	Remarks	d_{obs}†	I/Io†
100	10.340	10.34	100		10.29	100
010	6.872					
110	5.723			vf	5.74	2
200	5.170					
001	5.076			vf	5.06	3
$\bar{1}01$	4.975					
101	4.228					
210	4.131	4.14	20		4.13	25
011	4.083					
$\bar{2}01$	4.059					
$\bar{1}11$	4.030			vf	4.05	2
		3.89	4			
111	3.601	3.57	15		3.585	13
$\bar{2}11$	3.495	3.51	25		3.522	25
300	3.447					
020	3.436	3.43	15		3.456	35
210	3.301	3.31	10		3.266	18
120	3.261					
		3.24	15	NaCl (111)		
$\bar{3}01$	3.167	3.16	10		3.188	18
310	3.081	3.08	5		3.077	2
211	2.976	3.01	10		2.953	7
$\bar{3}11$	2.876					
220	2.862					
		2.85	30		2.865	35
021	2.845					
$\bar{1}21$	2.827					
		2.82	100	NaCl (200)		
		2.70	1	vf		
121	2.667	2.66	5		2.666	9
$\bar{2}21$	2.623					
301	2.615					
$\bar{1}02$	2.590	2.587	25		2.594	30
400	2.585					
002	2.538					
$\bar{4}01$	2.521	2.525	8		2.534	7
$\bar{2}02$	2.488				2.502	1
311	2.444				2.423	2
320	2.433	2.428	10		2.436	13
$\bar{1}12$	2.424					
410	2.420					
012	2.381					
221	2.381					
$\bar{4}11$	2.366	2.365	1		2.378	3
102	2.356					
212	2.338	2.337	3		2.342	4
$\bar{3}21$	2.329					
030	2.291	2.307	5		(not listed)	
$\bar{3}02$	2.277			vf	2.292	1
120	2.236				2.250	6
112	2.229			vf		
$\bar{3}12$(r)§	2.162	2.182	1		2.176	4


Figure 4.


Figure 5.

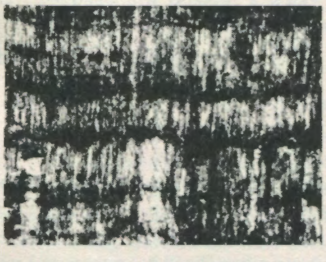
Figure 6.

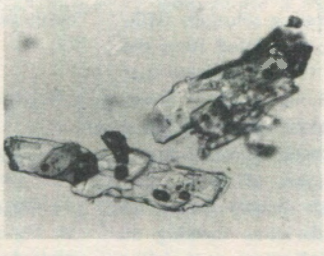
Figure 7.

Table 3 (Cont.)

(hkl)	$d_{calc.}$	d_{obs}	I/Io	Remarks	d_{obs}†	I/Io†
401	2.134					
202	2.114					
230	2.094			vf		
031	2.088				2.096	2
$\bar{1}31$	2.081					
321	2.081	2.080	12	Broad and diffuse	2.070	13
$\bar{1}22$	2.0682					
$\bar{5}01$	2.0681					
500	2.0680					
420	2.0657					
022	2.0413	2.040			2.040	2
411	2.0383					
$\bar{4}21$	2.0324					
$\bar{4}02$	2.0295					
212	2.0207					
$\bar{2}22$	2.0149					
131	2.0141					
		2.014	4			
$\bar{2}31$	1.9949				2.011	4
		1.9880	60	NaCl (220)		
$\bar{5}11$	1.9804				1.9885	1
510	1.9803					
$\bar{4}12$	1.9464				1.9625	1
122	1.9431	1.9430	10		1.9372	11
330	1.9078					
$\bar{3}22$	1.8982	1.8970	4		1.9106	11
231	1.8820					
302	1.8698					
331	1.8561				1.8671	2
421	1.8130					
501(r)§	1.7918	1.776	10	broad	1.7737	13
$\bar{6}01$	1.7436	1.750	2		1.748	3
$\bar{1}03$(r)§	1.7267	1.734	5		1.7288	10

* 114.6 mm Debye-Scherrer camera using Cu/Ni radiation.

† Darapskite (Ericksen and Mrose, 1970).

§ (r) indicates indices assigned by computer, but not used in final cycle of cell refinement.

fine hair-like strand approximately 2 cm long. Since this was the only "hair" found, it was not examined by X-ray diffraction and was only assumed to be composed of darapskite. In a small alcove above the terminal chamber crawlway darapskite-halite flowstone (approximately 40 cm long) cascades over a ledge. Small darapskite stalactites 1 cm by 0.5 cm have formed along the top and bottom parts of the flowstone.

The Flower Cave darapskite is colorless, transparent, has vitreous luster and, together with the halite, has a bitter-salty taste (Table 2). The cleavage [100] is pronounced. The darapskite does not fluorescence under short- or long-wave ultraviolet. The flower (darapskite + halite) phosphoresces green for approximately 5 sec after irradiation with short wave ultraviolet. Specific gravity measurements were not attempted because of small crystal size.

The X-ray diffraction data is in good agreement with the only previous measurement (Ericksen and Mrose, 1970) (Table 3). Diffraction maxima were indexed using the method of Appleman and Evans (1973). The indexed diffraction pattern is compatible with the $P2_1/m$ space group determined by Sabelli (1967). Unit cell parameters are: $a = 10.558(3)$, $b = 6.870(2)$, $c = 5.186(1)$ and $\beta = 101°46.1'(5)$. The calculated unit cell volume is 368.26 Å³.

Two lines (3.89 and 2.70) in the X-ray pattern do not match d-spacing values for either darapskite or halite. Normative mineralogical composition was calculated from a chemical analysis (Table 4) assuming all chlorine resides in the halite and all nitrate in the darapskite. The residual components in weight percent were: SO_4 (1.71%), Ca (0.93%), CO_3 (0.90%) and Na (0.456%). The 3.89 and 2.70 lines do not match the principal lines of $CaCO_3$, $CaSO_4 \cdot 2H_2O$, $CaSO_4$, or $NaCO_3$. There is a slight possibility of alpha-$NaSO_4$ (3.92 [100], 2.86 [90], 2.70 [90]).

Table 4. Chemical composition of cave flower from Flower Cave, Big Bend, Texas (analyzed by John W. Husler, Department of Geology, University of New Mexico).

	Wt. %		Wt. %
Na	32.85	Ti	<0.120
K	0.016	Al	<0.011
Ca	0.93	NO_3^-	12.80
Fe	0.028	Cl^-	28.00
Mg	0.054	$SO_4^=$	21.53
Sr	0.011	$CO_3^=$	0.90
Mn	0.005	$PO_4^\equiv$	0.01
		H_2O^-	3.45
		Total	100.72

The darapskite-halite speleothems formed from dripping (stalactites), flowing (flowstone) and seeping (flowers, hair, crust) water. The cave flowers deposited in layers by precipitation of soluble salts; each precipitated layer was subsequently forced outward parallel to the bedrock wall by subsequent precipitating solutions (Hill, 1976). Solubility products, calculated from the data of Sillen and Martell (1964), indicate that the darapskite ($K_d = 1.606 \times 10^{-3}$) layers precipitated first and the halite ($K_h = 2.045 \times 10^{-1}$) last, coating the already formed darapskite crystals. For thin layers of halite, subsequent darapskite crystals may nucleate on previous darapskite crystals, thus forming an optically continuous crystal across the halite layer. If the halite completely coats the darapskite, the succeeding layers crystallize in a different orientation. Each double layer (halite + darapskite) may reflect a separate depositional cycle corresponding to seasonal or yearly variations in surface precipitation. The closely associated amberat may be the source of the sodium, chlorine, sulfate and nitrate; seeping groundwater may dissolve these constituents and transport them to the site of darapskite crystallization.

STABILITY DISCUSSION

Nitrate minerals are hygroscopic (absorb moisture from the air) and deliquescent (dissolve in this moisture); that is, they are substances which have saturated solutions whose equilibrium water vapor tension is smaller than the vapor pressure of the surrounding air (Erdey, 1963). When the vapor pressure of the air (relative humidity) reaches a critical level, water condenses on the surface of the mineral and it dissolves.

The vapor pressure of water over a saturated solution of each nitrate cave mineral (except darapskite, whose vapor pressure has never been determined) is presented in Figure 8. The relative humidity at which a mineral will deliquesce is easily calculated from the following relation:

$$\text{Relative humidity} = \frac{\text{Vapor pressure of saturated solution. (T°C)}}{\text{Vapor pressure of water (T°C)}} \qquad (10)$$

The variance of relative humidity (at which deliquescence occurs) with temperature is shown in Figure 8; at vapor pressures above those plotted, the nitrate mineral will deliquesce and no longer exist in the crystallized state. For example, when cave relative humidity reaches 77% at 15°C

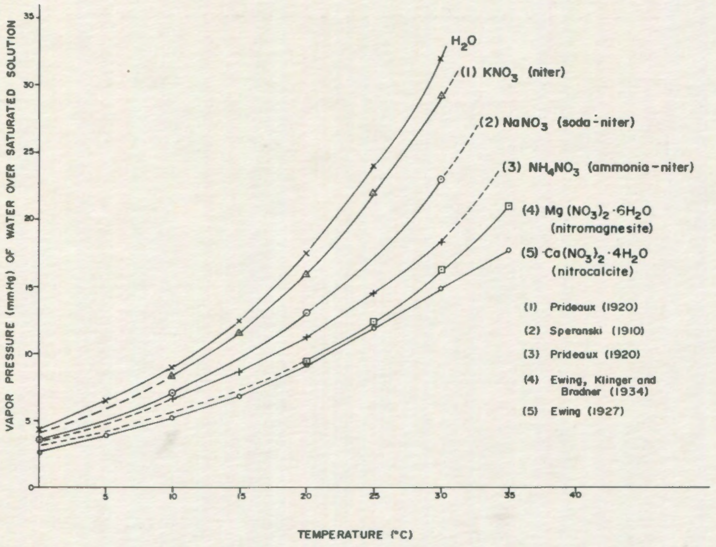

Figure 8. Vapor pressure of saturated solutions with respect to temperature.

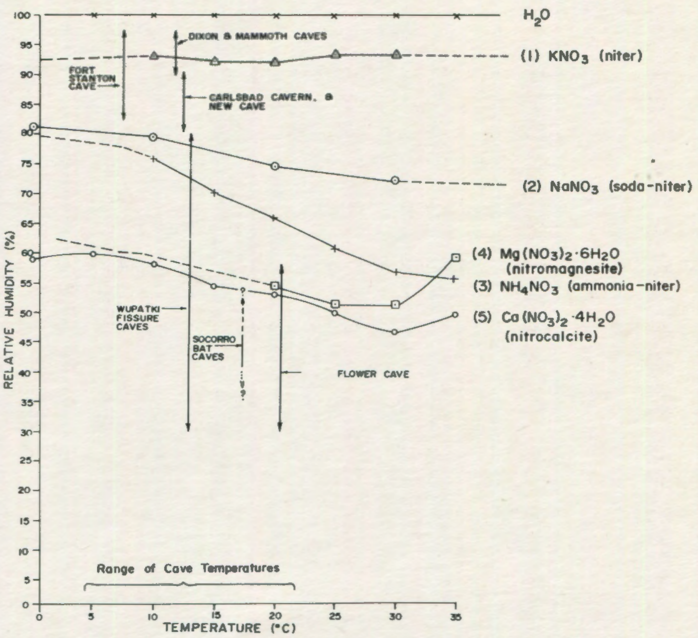

Figure 9. Stability of nitrate minerals in a cave environment

(Curve [2], Fig. 9), crystalline soda-niter will dissolve and seep into the surrounding sediment or bedrock.

Figure 9 is crucial to an understanding of why southeastern saltpeter caves do not contain crystallized nitrate minerals in their sediments or on their walls and ceilings. Niter is the only nitrate mineral that theoretically can crystallize in a humid (over 90%) southeastern cave (see Curve [1], Fig. 9). Early reports of nitromagnesite, nitrocalcite and ammonia-niter in the saltpeter caves of Virginia, Alabama, Tennessee and Kentucky are erroneous because the relative humidity of these caves far exceeds the equilibrium vapor pressure of these minerals (Curves [3], [4), [5], Fig. 9). Before nitrocalcite could crystallize from the dissolved nitrate within the bedrock and sediments of Dixon Cave, Kentucky, the cave humidity would have to decline from 93% to 54%. Ability to lixiviate cave sediments of calcium and nitrate is proof that these ions are truly present in the dissolved state within saltpeter caves; when saltpeter sediment is lixiviated the dissolved calcium and nitrate ions are removed and, upon evaporating the "mother liquor" leachate to dryness, a very deliquescent, nearly solid, thick "slurry" of nitrocalcite can be obtained (Maxom, 1932).

Crystallization of the Socorro and Wupatki soda-niter is the result of the usually low (less than 80%) relative humidity of these southwestern caves (Fig. 9). On the October, 1977, visit to Malmquist Fissure, Wupatki National Monument the humidity was an unusually high 80%; on this occasion the crystalline soda-niter had deliquesced and disappeared into the bedrock.

The stability of darapskite as a function of humidity could not be determined since the vapor pressure over a saturated solution of this salt is unknown. It may be reasonable to assume that the double salt darapskite crystallizes at low relative humidities, since both soda-niter ($NaNO_3$) and thenardite (Na_2SO_4) form in dry environments. Foote (1925), working in the system sodium nitrate-sodium sulfate-water found that darapskite forms from $NaNO_3$ and Na_2SO_4 at a transition temperature of 13.6°C. The Chilean, Death Valley and Flower Cave darapskites are all located in hot, arid climates where this transition temperature is exceeded. The Antarctic occurrence reported by Claridge and Campbell (1968) is somewhat problematic; its presence would indicate that darapskite can crystallize metastably at temperatures lower than 13.6°C.

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