

**THE NITRATE DEPOSITS OF ROCK CREVICES
IN THE UPPER MISSISSIPPI VALLEY**

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Acknowledgments

From the “fatty earths” of the alchemists to the present day, the subject of niter-rich soils has engaged the attention of the world’s greatest artists and scientists, among whom were Milton and Newton (Guerlac, 1954). The present dissertation is but a small contribution to the ever-increasing flood of nitrate literature since then, but even this much would have been impossible without the help of the following individuals and organizations.

The Cave Research Foundation and the National Speleological Foundation awarded grants in aid of my research. The Minnesota Pollution Control Agency funded me for several semesters to carry out an extensive literature review of nitrate in the surface and groundwater of southeastern Minnesota, during which I came across numerous additional nitrate references that I would not have otherwise. The Department of Earth Sciences, University of Minnesota, awarded me a Francis Gibson Fellowship and summer travel grants. The Minnesota Department of Natural Resources issued permits for sampling cave sediments in state parks and the Rockcastle Karst Conservancy provided access to Great Saltpetre Cave, Mt. Vernon, Kentucky, for sampling.

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For my minor in the History of Science, which played a big role in this dissertation, I much appreciated the advice of Dr. Sally Gregory Kohlstedt. This was especially relevant in the nitrogen literature, where I became convinced of the truth of Schmidt's (1982) remark that "a great deal of basic information on soil factors as they influence nitrification appeared decades ago, but is rarely retrieved and apparently destined for periodic repetition." Indeed, echoes of the original debate between Hess (1900) and Nichols (1901) continue to reverberate through the decades.

Finally, warm hugs for Cindy, who remained supportive throughout and was my companion on our long road trips through the Old Saltpeter Belt, and for the philosophical felines who kept me company in the middle of the night while drafting various publications over the years.

Abstract

Prompted by French fur-trader Pierre-Charles Le Sueur's 1700 report of caves containing saltpeter (potassium nitrate) along the Minnesota shore of Lake Pepin, this study located what are thought to be the original caves and revealed a hitherto unsuspected widespread district of cave nitrate deposits in the Upper Mississippi Valley (UMV). Of the 103 caves sampled from nine geologic formations, 67% had elevated nitrate concentrations (>50 ppm NO_3) in their sediments relative to surrounding surface soils (<10 ppm NO_3). These nitrate concentrations, up to 3.5 percent dry weight of sediment (35,000 ppm), are comparable to the concentrations found at Mammoth and Dixon caves, Kentucky, an historical nineteenth-century saltpeter mining locality, which range from 0.01 to 4 percent. But the Hill (1981) seeping groundwater model, which satisfactorily accounts for the nitrate deposits of the historic saltpeter caves of the southeastern United States, does not apply in the UMV. Through the application of geochemical and isotopic analysis to soil solutions it was concluded that the source of the nitrate was organic matter such as guano, scats, urine, carcasses, and plant materials, and that the nitrate accumulated because the cave roof protected the soluble nitrate ion from leaching and by blocking out sunlight, prevented plants from growing and thus extracting this nutrient. Le Sueur's claim of finding saltpeter (more likely, a saltpeter precursor, such as calcium nitrate) in Minnesota caves, for making gunpowder in the wilderness, is thus credible.

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“Nitre, that admirable salt, hath made as much noise in philosophy
as it hath in war.”

John Mayow, *Tractatus Quinque Medico-Physici*, 1674

Chapter 1

Le Sueur's Saltpeter Caves at Lake Pepin, Minnesota, and Wilderness Gunpowder Manufacture

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Summary

Prompted by French fur-trader Pierre-Charles Le Sueur's 1700 report of caves containing saltpeter (potassium nitrate) along the Minnesota shore of Lake Pepin, this study investigated nitrate concentrations in cave sediments along the Mississippi River bluffs in Minnesota and to a lesser degree the entire Upper Mississippi Valley. Elevated nitrate concentrations, up to 3.5 percent dry weight of sediment, were found in a wide variety of rock voids. These sediment nitrate concentrations are comparable to the nitrate accumulations found at Mammoth and Dixon caves, Kentucky, an historical nineteenth-century saltpeter mining locality, which range up to 4 percent. This is enough to show that Le Sueur's claim of finding saltpeter (more likely, a saltpeter precursor, such as calcium nitrate) in Minnesota caves, for making gunpowder in the wilderness, is credible, but other considerations raise serious doubts. In any case this is the earliest report of cave saltpeter from America, predating more probable French saltpeter manufacture from Missouri caves in 1720.

1.1 Introduction

Cressy (2011: 75) asserts that saltpeter (potassium nitrate), the most important component of gunpowder, "was the crucial link in the chain of chemistry and power, comparable in strategic importance to modern oil or uranium." The British Empire, for example, historically owed much of its strength to ready supplies of saltpeter obtained from India (Frey, 2009). Gunpowder was composed of 75 percent saltpeter combined with sulfur (10%) and charcoal (15%) but saltpeter had many other uses such as a meat preservative, a medicine, and a fertilizer (Calvert, 1961: 2) and among Native Americans it was used for work with dyestuffs (Browne, 1935).

In 1700, the French fur-trader Pierre-Charles Le Sueur (1657-1704), while ascending the Mississippi River, reported saltpeter caves in his Journal, which previous researchers (Halliday, 1968; Hill et al., 1981; Shaw, 1992: 52) have reasonably interpreted as being located along the west side of Lake Pepin, in Minnesota. According to the translation of Benard de la Harpe's version of Le Sueur's Journal, as published in Conrad (1971: 32-33), under the dates September 10 to September 14, 1700:

In these regions, a league and a half to the northwest, there is a lake named "Pein" which is six leagues long and more than a league wide. It is bordered on the west by a chain of mountains; on the other side, to the east, there is a prairie, and to the northwest of the lake a second prairie two leagues long and wide. Near by there is a chain of mountains which must be two hundred feet high and more than a half league in length. Many caves are found there in which bears hibernate in winter. Most of these caverns are more than forty feet deep and between three and four feet high. A few have very narrow entrances, and all of

them contain saltpeter. It is dangerous to enter them in summer because they are filled with rattlesnakes, whose bite is very dangerous. M. Le Sueur saw some of these snakes that were six feet long, although usually they are only about four feet.¹

There are several other versions of the translation, as discussed by Wedel (1974), and the one presented by Neill (1872: 41) gives different dimensions for the cave: "Most of the caverns are more than seventy feet in extent, and three or four feet high." Le Sueur's comments about the caves being inhabited by bears in winter and rattlesnakes in summer suggests that they were visited (by someone) throughout the year, and presumably there would have been a reason for this. Although not explicitly mentioned in Le Sueur's narrative, French fur traders could have sought out saltpeter to manufacture gunpowder, or perhaps as a meat preservative, in the absence of salt from saline springs (Jakle, 1969).

There was an extended French presence in the Upper Mississippi Valley (UMV) that would have required gunpowder from some source and the usual assumption is that all of it was imported. As early as 1686, the French fur-trader Nicolas Perrot established Fort St. Antoine on the Wisconsin side of Lake Pepin, near what is today Perrot State Park (Nute, 1930). Wedel (1974) presents a scholarly discussion of Le Sueur's presence in the UMV based on American, Canadian, and French archives. Le Sueur was involved with founding a post on what is now Prairie Island, Minnesota, in 1695. Perhaps his best known exploit was the establishment of "Fort L'Huillier" or "Fort Vert" at the site of a supposed copper mine on the Blue Earth River, in 1700, shortly after visiting the saltpeter caves (Hughes, 1908; Wood and Birk, 2001).

Trewartha (1938: 193) describes another one of Perrot's forts, this one along the Mississippi River in the vicinity of the lead mines near Dubuque, Iowa. The lead could be used to manufacture bullets:

Perrot's mines, as they were called, were worked more or less constantly by Indians and by white voyageurs who used the lead to supplement the fur trade. Penicaut in the journal of his ascent of the Mississippi with Le Sueur in 1700 states, "we found both on the right and the left bank the lead mines, called to this day the mines of Nicolas Perrot, the name of the discoverer."

In a strict sense, saltpeter, also called niter, refers to potassium nitrate, but it has also loosely been applied to sodium nitrate and even calcium nitrate (Needham, 1986: 95). What is called a "saltpeter cave" in the literature does not always mean a cave that actually contains saltpeter (potassium nitrate) but rather a precursor substance, historically known as "petre dirt," containing calcium nitrate, which must be converted into saltpeter by human activities such as lixiviation (leaching) with lye made from potash, and boiling (Hill, 1981). The manufacture of potash from wood ashes was a frontier technology in its own right (Miller, 1980).

Although Le Sueur described the Lake Pepin fissure-fill as "saltpeter" he was more likely referring to calcium nitrate. The prevailing humidity in Minnesota caves is too high for him to have encountered anything other than deliquescent salts, dissolved in the sediment, rather than crystallized saltpeter (Hill and Forti, 1997: 157). Apart from whitish snow-like efflorescences, not even experienced saltpeter prospectors could identify nitrate-rich sediments by sight and the usual confirmation was a bitter taste (Brown, 1809) until modern

chemical tests for nitrates were developed.

Gale (1912) and Mansfield and Boardman (1932), however, do not include Minnesota in their lists of states with nitrate deposits. Most historic American saltpeter caves are found in the southeastern United States. Minnesota lies well outside the classic "saltpeter belt" that runs from the Appalachians west to the Ozarks, so Le Sueur's description of saltpeter caves merits further scrutiny. While Le Sueur's account was discussed at a major saltpeter symposium (Hill et al., 1981) there is no record of anyone searching for this seemingly anomalous occurrence before the present study.

1.2 The Saltpeter Context

The earliest documented search for cave saltpeter in Europe was the 1490 exploration of Sophienhohle (Sophie's Cave) in Germany but the main occurrence and exploitation of this cave resource has been in the United States (Shaw, 1992: 52). The manufacture of saltpeter from cave sources was labor intensive and could only be justified when the price of saltpeter was high. More usually the raw material was obtained from "dungheaps, pigeon lofts, under floors and in crypts" and "dovecotes, barns, stables or outhouses" (Bull, 1990:5,7). Another source of saltpeter during the Middle Ages was niter beds, a sort of compost pile that was designed to generate saltpeter (Williams, 1975).

The production of saltpeter began in the American colonies as early as 1642, using niter beds (Calvert, 1961: 3). Suitable caves were generally lacking in

the New England colonies (O'Dell, 1990) and the earliest record of cave saltpeter in America dates from Le Sueur's visit to Minnesota in 1700 (Shaw, 1992: 52). Breckenridge (1925) asserted that saltpeter harvesting in Missouri began as early as 1720 when the French mining entrepreneurs Philip Francis Renault and M. La Motte opened the territory's first lead mines. Faust (1964: 42) states that Clark's Saltpetre Cave in Virginia was worked as early as 1740. Faust (1967: 67) surmised that the Kentucky "long hunters" must have made their own gunpowder in the remote trans-Appalachian wilderness in the years before the Revolutionary War, just as it was made at Fort Boonesborough in Kentucky (George, 1987). Thomas Jefferson's *Notes on the State of Virginia* describes saltpeter caves in that state (Jefferson 1995 [1787]:34). In the American West there are later examples of fur traders who manufactured gunpowder from cave deposits, such as General William Ashley in the 1810s (Breckenridge, 1925).

When the Revolutionary War began, the American colonists were cut off from British gunpowder imports and had to find their own sources of saltpeter. In 1775 the Continental Congress published a pamphlet giving directions for making saltpeter, providing enough for the American forces (Calvert, 1961: 5-7). E.I. du Pont came to America in 1800, bringing French technology, and soon established his Eleutherian Mills on Delaware's Brandywine River (Stapleton 2006). Some foresighted individuals anticipated the time when supplies of gunpowder would again be cut off. This time, however, the search for saltpeter was taken across the Appalachians. Samuel Brown, professor of chemistry at Transylvania University in Lexington, Kentucky, purchased Great Saltpetre Cave in Rockcastle County, Kentucky, in 1804 and hired an engineer to construct a

saltpeter works. The saltpeter was shipped to Lexington, which had six powder mills in operation by 1810. The technology developed at Great Saltpetre Cave was adopted at nearby Mammoth Cave, which was mined for saltpeter during the War of 1812 (George, 2005: 38). However, the market for domestically produced saltpeter collapsed after the war and extraction was terminated. It was cheaper to import saltpeter from British India than to transport it over the Appalachians or otherwise make it domestically (Calvert, 1961: 20).

During the American Civil War, the North had free access to imported saltpeter and had the ability to blockade the South, cutting off imports. The Confederate Nitre Bureau was established in 1862 and began to harvest saltpeter from caves, especially in Alabama, Georgia, Tennessee, and Virginia (Powers, 1981). Saltpeter was also manufactured using bat guano from caves in Missouri and Texas (Hutchinson, 1950: 396). Mammoth Cave was located in Kentucky, a state of mixed sympathies, which made it unsafe to restart mining operations there. The uneconomical, labor-intensive nature of these Confederate saltpeter workings is suggested by the fact that in areas captured by the Union Army, the caves were ignored by the North (Chandler, 1949).

As late as World War I, prospectors sought out natural nitrate deposits in the United States (Gale, 1917) in a tradition stretching all the way back to Le Sueur. The days of natural deposits were numbered, however, owing to the development of atmospheric nitrogen fixation, which involved converting the nitrogen of the atmosphere into ammonia, which could then be converted to nitrate. Although the electrical fixation of nitrogen had a lengthy history (Farrar,

1971), it was not until 1913 that the Haber-Bosch process (developed by Haber and industrialized by Bosch) became the first really successful nitrogen fixation method, being put into commercial operation in Germany and then around the world (Leigh, 2004: 140-154).

Useful overviews of saltpeter manufacture are provided by Partington (1960), Calvert (1961), Williams (1975), Needham (1980, 1985, 1986), O'Dell (1990), and the extensive annotated bibliography by Ball and O'Dell (2001).

1.3 Field and Laboratory Work

The location of Le Sueur's saltpeter caves is not identified on historic maps. Franquelin's 1697 map of the Upper Mississippi area, which had Le Sueur's input, predates the cave visit, and although a five-part map of the Mississippi River was compiled by the famous French cartographer Guillaume Delisle from Le Sueur's notes in 1702, and this map does label some mineral resources such as copper and lead mines, it does not depict the saltpeter caves (**Figure 1.1**). The Delisle map is reproduced and discussed in Wood and Birk (2001).

At this point we fall back on the narrative. The "chain of mountains" mentioned in Le Sueur's Journal tallies reasonably well with former islands in the ancestral Mississippi River in Goodhue County, Minnesota (Schwartz and Thiel, 1978: 303-304) of which Barn Bluff in the city of Red Wing is the best known example² (**Figure 1.2**). This series of linear, east-west ridges were once mesa-like islands in the river, slices of the hinterland separated by post-glacial stream

erosion, composed of bedrock, and not to be confused with the low, sandy, alluvial islands with which we are familiar today, such as nearby Prairie Island. In other early narratives describing Lake Pepin such as that by Jonathan Carver, the bluffs walling in the lake are described as "a range of mountains" (Gelb, 1993: 78) but the way in which Le Sueur delimits the lengths of the mountains suggests that we are dealing with discrete massifs, i.e., the bluff islands, rather than the river bluffs generally.

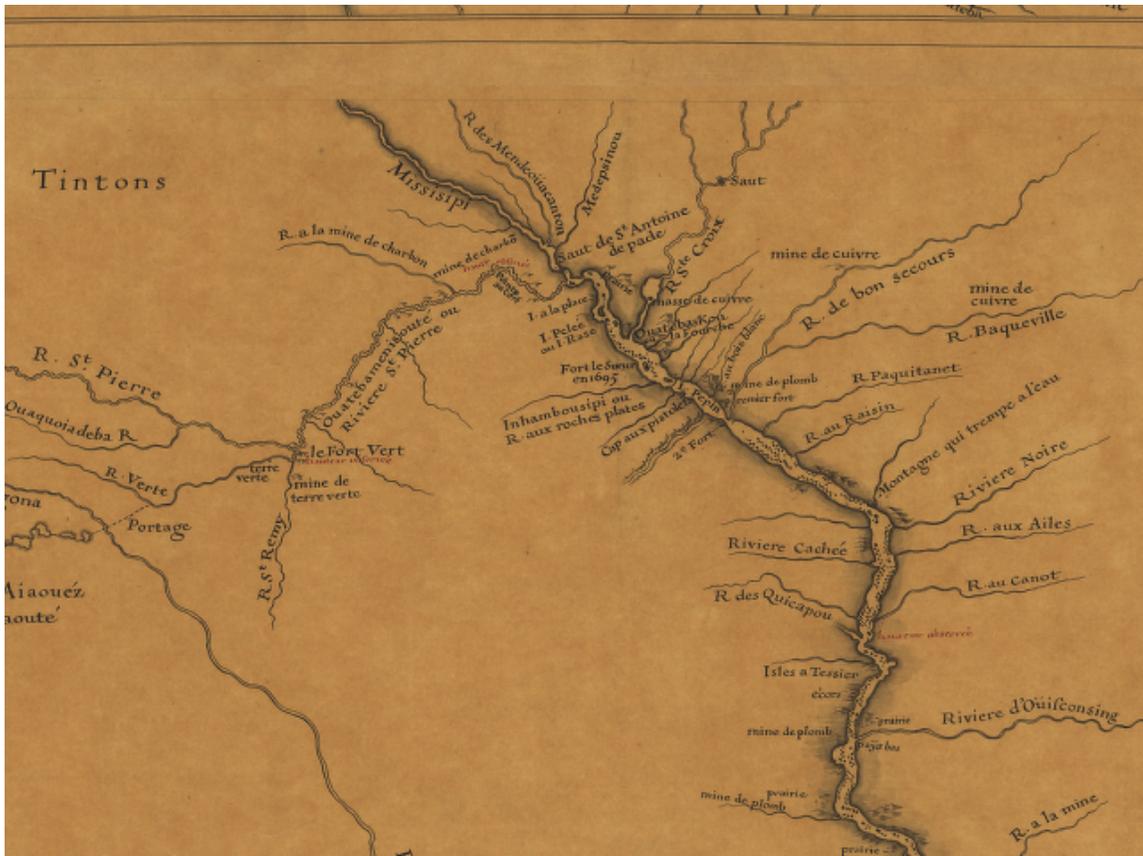


Figure 1.1. Delisle's 1702 map, based on Le Sueur's notes, showing the Upper Mississippi River. While depicting copper and lead mines, it does not show the saltpeter caves described in the latter's Journal.

Of the several possible Goodhue County "islands" the one that best matches Le Sueur's stated dimensions is the Sevastopol bluff, as I here refer to the bluff towering over the 1856 logging ghost town of Sevastopol (Rasmussen, 1935: 66-67) north of U.S. Highway 61 and east of the modern Sevastopol Road, in the northern half of Section 35 and the western half of Section 36, Township 113 North, Range 14 West (**Figure 1.3**). Le Sueur describes the "mountain" as "two hundred feet high and more than a half league in length." A French league was approximately 2.5 miles (Conrad, 1971: 5) so the proper bluff should be about 1.25 miles in length, which is fairly close to the one at Sevastopol, but the actual height of this bluff above the river is 350 feet, rather than 200 feet. Given that Le Sueur's dimensions appear to be estimated, this is the best we can expect.

The Sevastopol bluff was prospected for caves in 2004. A cave matching Le Sueur's stated dimensions in all but length (it was about one quarter as long) was located on private land along these bluffs (Brick, 2004) (**Figure 1.4**). While there is no way of knowing whether this was one of Le Sueur's caves, it became conceptually important during this investigation by revealing that the cave described by him matches a particular type of bluff crevice commonly found among these rock outcrops. These Le Sueur-type crevices (as they will be designated here) form where the bluff is gravitationally slumping away from the main rock mass along a rock joint, leaving a long, narrow, bluff-parallel crevice³ (**Figure 1.5**). But crevices 40 (or 70!) feet long, such as Le Sueur described, would represent serious lines of weakness in the bluffs. With this insight, it was surmised that the actual historic crevice(s) might no longer exist, having fallen down the bluff at some point during the past 300 years, to be replaced by a sub-

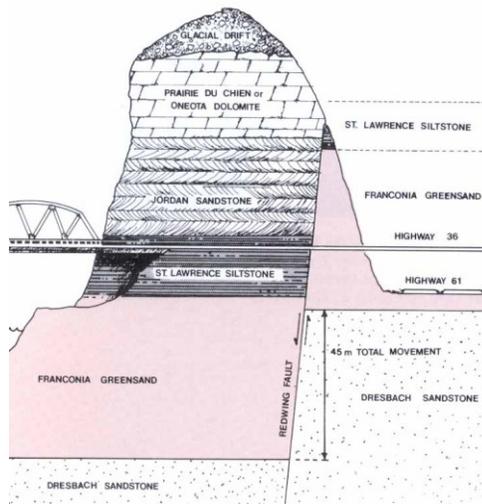


Figure 1.2. Geological cross-section of Barn Bluff, at Red Wing, MN, formerly an island in the post-glacial Mississippi River. From Ojakangas and Matsch, (1982: 240).

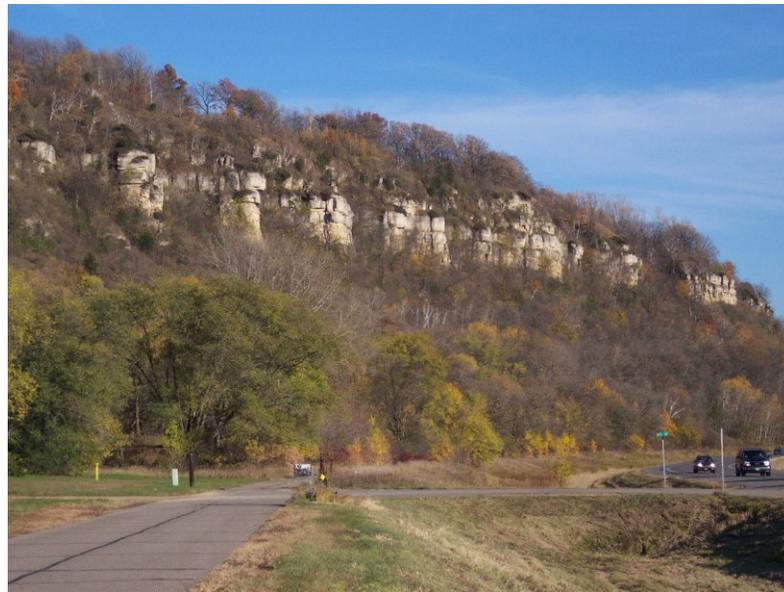


Figure 1.3. Sevastopol Bluff, near Red Wing, MN, showing Oneota dolomite outcrops. U.S. Highway 61 seen in the lower right corner. Photo by author.

sequent generation of newly-widened rock joints as the Lake Pepin bluffs undergo erosion and slope retreat.

When floor sediments from the Sevastopol crevice were tested they contained elevated nitrate, consistent with Le Sueur's narrative, suggesting that the presence of nitrate is characteristic of this physical setting rather than anomalous. This became the inspiration for a wider sampling program.

In Goodhue County, Minnesota, the Ordovician-age Oneota dolomite⁴ of the Prairie du Chien Group forms the hard caprock of the Lake Pepin bluffs, protecting the soft underlying Jordan Sandstone from erosion. In the dolomite layer there are two kinds of voids: those formed by chemical solution from flowing groundwater and the Le Sueur-type crevices formed by the mechanical widening of rock joints by gravitational slumping and always near the face of the outcrop. Many of these crevices have boulder ceilings through which tree roots have penetrated from above, along with descending soil, and appear unsafe to enter. The solutional caves, on the other hand, presumably formed in the dolomite at a much earlier time and are much more stable: uranium-series speleothem dating studies for caves in this rock layer elsewhere in southeastern Minnesota yield ages of a quarter of a million years (Lively, 1983). These much older solutional caves have been exposed by valley incision in geologically recent times, while the bluff crevices post-date the river valleys. The term "rockshelter" will be used to refer to truncated remnants of either of these two kinds as well as miscellaneous minor forms such as weathering voids.



Figure 1.4. Interior view of low, narrow crevice in the Oneota dolomite of Sevastopol Bluff, showing the sort of "saltpeter cave" that Le Sueur described. The crevice is approximately one foot wide, four feet high, 10 feet long, and contains nitrate-rich sediments. Photo by author, 2004.

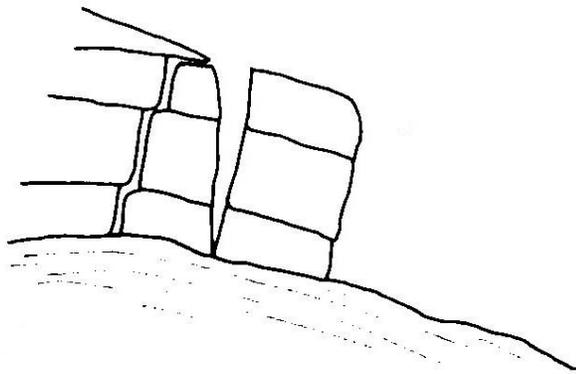


Figure 1.5. Cross-section showing how Le Sueur-type crevices develop along bluff lines. From Warwick (1976: 86).

Caves, crevices, and rockshelters, regardless of their size or geologic origin or whether they resembled the original Le Sueur-type crevice, were sampled in southeastern Minnesota, especially Dakota, Goodhue, Wabasha, and Winona counties; in western Wisconsin, especially Pierce County; in Allamakee County, Iowa; and at Upton Cave, Mississippi Palisades State Park, Carroll County, Illinois as part of a wider project to investigate nitrate concentrations in UMV cave sediments generally. Thus, rock outcrops on both sides of Lake Pepin and further up and downriver were investigated, not merely those in the immediate area suggested by Le Sueur's Journal. The most heavily prospected area, because of the public accessibility of the rock outcrops and the abundance of voids, was the linear ridge encompassed by Frontenac State Park along the Minnesota shore of Lake Pepin, where about two dozen features were sampled. For comparative purposes, sediments were also collected in Minnesota's two largest caves, Mystery Cave near Spring Valley, Minnesota and Niagara Cave near Harmony, Minnesota. Great Saltpetre Cave, Rockcastle County, Kentucky, which had a long history of saltpeter extraction (Engel and Engel, 1998), was also sampled. Sampling was conducted intermittently from 2004 through 2011.

Cave sediment sampling protocols were adapted from the research of Fliermans and Schmidt (1977) at Mammoth Cave, Kentucky. Floor sediments were collected with a trowel and placed in plastic bags, then transported at ambient temperature to the lab for processing within 24 hours. In the lab, sediments were sieved through fiberglass window screen, weighed, and splits taken for further processing. One split was weighed, desiccated in an oven, and reweighed to calculate moisture content. A second aliquot was placed in a

measured volume of distilled and deionized water in a Nalgene bottle, shaken to form a slurry, refrigerated, and left to settle overnight.

Surface soil control samples were also collected outside some of the caves, sometimes from surface soil beginning to enter the crevices from above but usually to either side of the cave and outside the apron of sediments spreading downslope from the cave, if such were there. Additionally, surface soils were systematically sampled along slope profiles provided by the wooden stairways in Frontenac and John Latsch state parks and along the tops of the bluffs.

Next, a preliminary indication of the nitrate content of the sediments and soils was made by dipping commercially available nitrate test strips, which yield semiquantitative values based on changing indicator colors, into the slurries. As a general rule surface soils are expected to have low nitrate concentrations because the highly soluble nitrate ion is easily leached by rainfall and, being a plant nutrient, nitrate is readily absorbed by roots. Indeed, Fliermans and Schmidt (1977) found that surface soils above Mammoth Cave were always less than 25 parts per million (ppm) nitrate-nitrogen ($\text{NO}_3\text{-N}$), which is equivalent to 110 ppm nitrate (NO_3), so this value was adopted as a lower limit for samples demonstrating nitrate enrichment. Solutions showing elevated nitrate concentrations were passed through a 0.2 micron filter and sent to the laboratory at the Department of Earth Sciences, University of Minnesota for chemical analysis.

1.4 Results

Of the nearly one hundred caves, crevices, and rockshelters sampled in the UMV from a variety of rock types (dolomites, limestones, sandstones, and basalts) that ranged in age from Precambrian to Pennsylvanian, about half had elevated concentrations of nitrate as determined by nitrate test strips.⁵ Subsequent laboratory analysis confirmed the indicator strips and provided quantitative values that could be related to the dry weight of sediment. High nitrate concentrations, up to 35,000 ppm, were widespread among rock voids on both shores of Lake Pepin and occurred as far south along the river as sampling was conducted, in Illinois. By contrast, none of the surface control soils showed more than 10 ppm nitrate.

Another topic of investigation was mining tools. Faust (1955) studied saltpeter mining tools from historical American caves. Apart from the largest operations, which employed diagnostic leaching hoppers and log pipelines, many of the tools used to harvest, transport, and process the cave sediments have other applications not unique to saltpeter mining. Examples are picks, shovels, and boiling kettles.

Although no mining tools or indications of mining were observed in any of the UMV caves, nearby archeological sites have the potential to contain mining artifacts. In 1727, under the directive of the Governor General of New France, the first French trading fort on the west side of Lake Pepin, Fort Beauharnois, was established. It was flooded in the spring of the following year,

rebuilt on higher ground, and subsequently abandoned (Kellogg, 1927). Traditionally, the fort was assumed to have been located at Sand Point near the town of Old Frontenac, but during a systematic archeological excavation in 1976, no French cultural remains were found (Birk and Poseley, 1978). This unfortunately precluded the possible identification of potential gunpowder-related implements in artifact inventories.

1.5 Discussion

The highest nitrate value obtained during this study was 35,000 ppm nitrate (equivalent to 3.5 weight-percent) from the dry, reddish sediment of an Oneota rockshelter in Rattlesnake Bluff, which forms the western end of Frontenac State Park. Thus, elevated nitrate is not confined to the Le Sueur-type crevices, which turned out to be in the minority among the kinds of rock voids encountered in the field. For comparison, the nitrate content of the Mammoth and Dixon caves, Kentucky, sediments examined by Hill (1981: 118) "range between 0.01% and 4%, most commonly between 0.1% and 1.0% [by weight]." This overlaps with the 3 percent to 5 percent nitrate historically reported for commercial concentrations in the surface soils⁶ of British India (Hutchinson 1917: 1). Many of the Minnesota cave sediments are thus sufficiently enriched in nitrate to be worth extraction.

Although it is theoretically possible to manufacture saltpeter from the UMV cave sediments based on the high nitrate concentration, a serious problem is presented by the amount of sediment available. According to George (2005: 22), describing saltpeter manufacture at Mammoth Cave more than a century

after Le Sueur, "Cave soils yielded 3–5 pounds of saltpeter per bushel." (A bushel of Mammoth Cave sediment was given as 227 pounds by Hill et al., 1983.) While it would be difficult to make explicit calculations in the absence of a complete inventory of all rock crevices bordering the perimeter of Lake Pepin, the author has the impression that at this rate of extraction the totality of them would be rapidly depleted of their sediment. It would then take years for the crevices to naturally replenish themselves with more sediment, as from rock disintegration and surface soil moving downwards through rock joints. Additional time would be required for intermixture with organic matter and the slow nitrification process. Craig (1862: 310) reported "that the earth in caves nitrifies itself sufficiently for extraction in eight or ten years" and this has been confirmed by more recent work (Northrup and Lavoie, 2001). Moreover individual Lake Pepin crevices are small, narrow, widely separated, and often difficult to get to, being located at the top of steep talus slopes at a considerable elevation above the lake so that even if a sufficient number of them were available, the amount of human labor involved would be enormous.

The source of the nitrate found in the cave sediments merits further discussion. The most widely accepted theory for the accumulation of nitrate in the large historic saltpeter caves of the southeastern United States such as Mammoth Cave involves the seeping groundwater model proposed by Hill (1981). Organic nitrogen, like that found in proteins, is converted to ammonia by bacteria in surface soils and drawn into the cave through the limestone walls by a moisture-density gradient created by evaporation at the bedrock/cave interface. Ammonia is then converted into nitrate by the nitrifying bacteria known to exist

in the cave sediments (Fliermans and Schmidt, 1977). This model accounts for the elevated nitrate concentrations obtained during this study from samples taken in Great Saltpetre Cave, Kentucky.

Hill (1981: 124) remarks, "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." Fliermans and Schmidt (1977), however, did find *Nitrobacter*, the nitrifying bacterium, in Minnesota soils. And historically, artificial niter beds have been operated with great success as far north as Sweden (Kaiserfeld, 2006). But Minnesota is located far outside Hill's optimal area and the conditions necessary for her model to work do not seem to apply here. Sediments taken from the driest parts of the largest Minnesota caves during this study, Mystery and Niagara caves, revealed total absence of nitrate (0 ppm).

Some other possible sources of the nitrate-nitrogen in the Lake Pepin crevices were excluded. The high nitrogen does not derive from host rock disintegration or dissolution, as nitrogen concentrations in this dolomite in neighboring Wisconsin are relatively low (Chalk and Keeney, 1971). Although some of the mesa "islands" are farmed on their summits, presumably involving the application of nitrogen fertilizer, the cave's nitrate-nitrogen does not match isotopically with the nitrogen of artificial fertilizer, nor does it match the nitrogen fixed by lightning, which is found in rainfall. Instead, it fits nitrogen that has been affected by microbial processes (Brick, Alexander, and Doctor, 2009). Moreover some high nitrate samples were obtained from voids in barren rock

pinnacles that could never have been farmed.

Rock crevices are sometimes thought of as merely smaller versions of much larger caves but there are some fundamental differences. In general many limestone solutional caves have an age predating the Wisconsinan ice advance, as known from speleothem dating, whereas the Lake Pepin crevices appear to be post-glacial features and quite ephemeral, as suggested during this study by instances where the cliff face had fallen away since a previous sampling trip.⁷

Because of this age and size difference, the sediment package in Mammoth Cave (for example) is much thicker, older, and more stable than the thin and chaotic accumulations of scats, carcasses, feathers, sticks, and leaves that strew the crevice floors. While on average the crevice sediment was less than several inches thick, in many of them it was a mere coating of rock dust and cryoclastic (freeze-thaw) debris, studded with scats, so that one sampling temporarily exhausted the site of sampleable material even though less than a one-gallon plastic bag of material was removed.⁸

A more useful way of looking at the Le Sueur-type crevices is in the light of the traditional division of caves into two zones: the entrance, or threshold zone, and the dark, or deep cave zone (Cubbon, 1976: 424-428). Crevices are basically all threshold environment, lacking the deep-cave zone entirely. The threshold zone is special in terms of its much higher nutrient flux. The crevice is an open system, usually with partial light, and animals are free to come and go, depositing organic matter⁹ in contrast to the much more static closed system of

the deep-cave zone, where animals are rare and nitrate accumulates by an entirely different mechanism, the one described by Hill (1981). The Le Sueur-type crevices also have a unique capacity to recharge themselves with sediment from above, more so than the other types of cave described. In terms of nitrogen flux and nutrient flux generally, the ephemeral crevices of the UMV might thus be called eutrophic (well-fed).¹⁰

Nitrate is very soluble and easily leached from cave sediments, so dry caves would be expected to harbor more nitrate than wet caves, and this was found as a general pattern. However, dampness was observed in some of the Minnesota crevices that had elevated nitrate, suggesting that leaching of nitrate and microbial denitrification (which takes place in anoxic, water-logged, settings) is possible, but that there is more than enough nitrogen replenishment from frequent additions of organic matter to compensate. This is corroborated by Hutchinson (1950: 403) who reported that Indiana caves are "mostly very wet," yet the cave earth was found enriched with nitrate, mostly from bat guano. Crevices, no matter where they are found, provide two essential conditions for nitrate accumulation: they protect the sediments from direct rainfall and thus decrease potential leaching, and by shutting out sunlight they prevent plant growth, which would otherwise utilize the nitrate as fast as it is generated.

Finally, any consideration of wilderness gunpowder manufacture should address the possible sources of sulfur used in the gunpowder formulation. In Europe, sulfur was often obtained from the volcanic deposits of southern Italy (Cressy, 2011). In America, Breckenridge (1925) suggested that French miners in

Missouri in the 1720s had access to saltpeter from the caves there, made charcoal from willow trees, and probably used sulfur that was generated as a by-product of smelting galena (lead sulfide).¹¹ However, no local source of sulfur was identified for potential use in the Lake Pepin area. Sulfur plays a complex role in the gunpowder formulation, such as lowering the ignition temperature and increasing the speed of combustion (Needham 1986: 111) but several writers have discounted its value entirely. According to Breckenridge (1925: 85-86), "If in some localities the obtaining of sulphur was at times so difficult, even so impossible, as to force its omission from the powder mixture, it could do no harm to omit it; for gunpowder made without sulphur is equally as powerful as with, since sulphur adds nothing to its power." More recently, Rae and Whitehead (2006: 369) asserted that "the sulphur and carbon could be replaced by other readily oxidized materials such as wood flour."

1.6 Conclusions

The occurrence of high nitrate concentrations in the sediments of UMV crevices revealed by this study is enough to show that Le Sueur's claim of finding saltpeter (more likely, a saltpeter precursor such as calcium nitrate) in caves along the shores of Lake Pepin in 1700 for making gunpowder in the wilderness is credible, but practical considerations raise serious doubts. This is the earliest report of cave saltpeter from America, predating more probable French saltpeter manufacture from Missouri caves in 1720.

The formation of a high-nitrate Le Sueur-type crevice goes something like this: the long, narrow crevices form by the widening of bluff-parallel rock joints, where the bluff is pulling away from the main rock mass. Over time, the crevices fill with sediment derived from rock disintegration and surface soil descending through the joints from above. Animal traffic and plant debris add organic matter that undergoes microbial nitrification, forming nitrate, which then accumulates because the cave roof protects the sediment from leaching and by shutting out sunlight, permits this plant nutrient to remain in the sediment.

1.7 Notes

1. The emphasis on Lake Pepin rattlesnakes was understandable, considering that even a century and a half later the pioneering Midwestern geologist David Dale Owen wrote of them (Owen, 1852: 57). According to Oldfield and Keyler (1989: 31), "Timber rattlesnakes den in areas of bluffs and steep rock outcrops on south and southwest facing hillsides. They are found near these rock outcrops during the spring and again in the fall."
2. Barn Bluff, the smallest of these post-glacial islands, was known historically as *La Grange Mountain*.
3. The Le Sueur-type crevice would be called a "crevice cave" according to Halliday (2004), who classifies them as a form of pseudokarst: cave-like features produced by nonsolutional processes. Cavers sometimes refer to them informally as "mechanical caves." Similar crevices are well known along the Niagara

Escarpment, a prominent dolomite cliff-former in the Midwest, but Hedges (1972) attributes these crevices to periglacial ice-wedge expansion over underlying shale rather than to gravitational slumping. See Cooper (1983) for additional examples of this type of cave.

4. The term "Oneota," a formal stratigraphic rock designation used by geologists, is not to be confused with its usage in archaeology to denote certain late pre-contact cultures. Dolomite is high-magnesium limestone.

5. In retrospect, fifty percent was a conservative estimate for the proportion of samples with elevated nitrate. Based on the surface control soils, none of which showed greater than 10 ppm nitrate-nitrogen, a lower cut-off value than 110 ppm could have been justified, which would have led to a higher proportion of elevated crevices, about two thirds.

6. Elevated nitrate can exist in these surface soils, unlike those of the UMV, because of the monsoonal climatic regime existing in Bengal.

7. Hedges (1972) interprets the Niagara Escarpment fissures as being Woodfordian (middle Wisconsinan) in age, but of course these fissures developed in a different geomorphic setting.

8. Hedges (1972) provides a description of this sort of fissure fill from the Niagara Escarpment and the difficulty of dating it. Sediment from the upper passages of Mammoth Cave has been dated at 2 million years old by the use of

magnetostratigraphy (Schmidt, 1982).

9. Several bird crevices were encountered during this study, with turkey buzzard chicks living in them, and the sediments of these crevices had especially high nitrate concentrations.

10. Schmid (1970) proposes a similar distinction between two types of caves, shallow and deep, based on their sediments. Crevice recharge follows Laville's (1976) model of "two fundamental stages" as it applies to rockshelters: (1) sedimentation, as by solifluction, and (2) "physical and chemical alterations" subsequently affecting the deposits.

11. Although Breckenridge's putative galena (lead sulfide) source for the sulfur is very plausible, he does not cite a reference for his assertion, and the documentary evidence suggests otherwise. It appears that Schoolcraft (1819) was Breckenridge's authority, but Schoolcraft nowhere states that the sulfur was derived from smelting galena, a process that he describes in detail. In fact, on page 131 Schoolcraft describes lead and sulfur as if they came from separate deposits, and on page 207 in the accompanying "Catalogue of the Minerals of the Western Country" sulfur is listed as a separate commodity derived from sulfur springs. On page 238, Schoolcraft visits a place called Sulphur Springs; to this day there is a small town on the Mississippi River, south of St Louis, Missouri, called Sulphur Springs, located near the lead mines that Schoolcraft described. I would suggest that this is a more likely source for the sulfur used to make gunpowder. Although Schoolcraft does not explicitly state that Renault and La

Motte made gunpowder, he describes working saltpeter caves and records that "60,000 lbs. of Gunpowder, manufactured by Ashley & Brown, Washington County" was "exported from Herculaneum, from December 31st, 1816, to June, 1818" (pp. 46, 47).

Chapter 2

Early Graphic Representations of Groundwater Nitrate Concentrations

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2.1 Introduction

Elevated nitrate concentrations in groundwater have become a concern worldwide, especially since the rise of artificial fertilizers after the Second World War, leading to increased monitoring. As one tool, time series analysis of groundwater nitrate concentrations has become commonplace. During the course of an extensive nitrate literature review for the Minnesota Pollution Control Agency, some early groundwater nitrate curves were found in the literature, dating to the mid-1880s English countryside.

2.2 Rothamsted Experimental Station

The context of these early groundwater nitrate curves involves the nineteenth century agricultural experiments of John Lawes (1814-1900) and Joseph Gilbert (1817-1901) at Rothamsted, the family estate of Lawes, located near Harpenden, Hertfordshire, north of London, UK. Rothamsted continues to this day as a research institute. Lawes established plots to test his new phosphate fertilizer,

but in 1843 turned to crop nutrient studies more generally, especially nitrogen, in the wake of the famous German chemist Justus Liebig's (1803-1873) controversial book, *Chemistry in Its Applications to Agriculture and Physiology*, published in 1840. For general overviews see Hall, 1917; Russell, 1942; Dyke, 1993.

Lawes financed the agricultural research, while Gilbert was an analytical chemist who had studied under Liebig. From 1877 to 1890, a younger worker, the chemist Robert Warington, Junior (1838-1907), was hired to assist Gilbert. Warington's most successful work was *The Chemistry of the Farm*, a slim volume that was translated into several languages and ran to 19 editions (Anon., 1938). Warington is better known today, however, as having discovered that nitrification is a two-stage process, even though it was the Russian microbiologist Sergei Winogradsky (1856-1953) who shortly thereafter isolated the specific bacteria responsible (Nutman, 1987). His father, Robert Warington, Senior (1807-1868), was a founder of the Chemical Society in 1841 and invented the ecologically balanced aquarium in 1850 (Hamlin, 1986).

Warington, Junior, had studied under the English chemist Edward Frankland (1825-1899), who was concerned with various forms of nitrogen in the Thames River as part of his work for a Royal Commission (Pickering, 1908; Hamlin, 1990: 171-174). Warington (1887) published a detailed account of his own nitrogen researches in an article titled, "A Contribution to the Study of Well Waters," summarizing the same material as "Lecture VI. Drainage and Well Waters" after a lecture tour in America, where it was published as *U.S. Department of Agriculture Experiment Station Bulletin No. 8* (Warington, 1892). The

remainder of this Historical Note largely concerns Warington's 1887 paper, which is three times longer than its 1892 abridgement.

2.3 Visualizing Groundwater Data

According to Bruno Latour, a French sociologist of science, the use of graphs is what distinguishes science from non-science (Smith et al., 2000). Yet it has also been observed that "the entire Scientific Revolution of the seventeenth century took place without graphs" (Hankins, 1999). The period during which Warington conducted his groundwater research falls squarely within what the great American historian of statistics, H.G. Funkhouser, dubbed "the golden age of graphics," from 1860 to 1890 (Funkhouser, 1937: 330). During this period, the German hygienist Max von Pettenkofer (1818-1901) prepared an interesting graph showing cholera morbidity in relation to groundwater levels in the city of Munich for 1873-1874 (Hume, 1925). The word "graph," however, had only been recently introduced into the English language in 1878 by the mathematician J.J. Sylvester (Hankins, 1999) and indeed Warington (1887: 534) himself refers to his graphical representations of groundwater nitrate from the mid-1880s as "charts."

Historically, Warington was not the first to detect nitrate in groundwater. According to Liebig (1849: 216), "It often happens that the well-water of towns contains a considerable quantity of nitre, which does not exist in the wells and springs outside the towns. Berzelius [1779-1848] detected nitrates in the well-water of the city of Stockholm. Margraf [1709-1782] also mentions its existence; and I, myself, have shown the presence of nitrates in the waters of twelve wells

in the town of Giessen, although they could not be detected in the waters of six wells separated 2300 paces from the town.” Likewise, the French chemist and agriculturist Jean Baptiste Boussingault (1802-1887) had detected nitrate in springwater in 1836, “due perhaps to farm sewage” (McCosh, 1984: 68). Of course, when regarded as a mineral constituent rather than as a contaminant, there was a long tradition of reporting “niter” (various nitrate salts) in medieval spa water analyses (Debus, 1962).

Warington had a keen understanding of what we would now call ambient groundwater monitoring, realizing that before you can conclude that a well is contaminated, you should have some notion of what the background levels are: “To form a correct judgment of any local water supply we must first know what is the composition of the pure waters of the district” (Warington, 1887: 523). He began by analyzing the chloride and nitrate concentrations of rainwater and of water that had percolated through the soil column and into the drain pipes under the Rothamsted fields. He usually did not analyze for the other chemical constituents. Nitrogen loss from the fields was of concern as part of the nitrogen balance equation, even though the idea of the nitrogen cycle had not yet been explicitly formulated (Aulie, 1971). Warington (1887: 521) used “the improved indigo method,” a colorimetric procedure, to quantify the nitrate, reporting the results as parts per million (ppm) nitrate-nitrogen, down to a claimed analytical precision of 0.01 ppm, which would be better than many current analyses.

Although artificial fertilizers existed in Warington’s day, they were apparently not common and he declares that “The amount of farmyard manure

at a farmer's disposal is so limited—about 1-2 tons per acre per annum—that its effect on the composition of the drainage water of any district must be very small, and almost negligible” (Warington, 1887: 519). He concluded that “Nitrates, being assimilated by plants, are generally almost entirely absent in the drainage from land bearing an actively growing crop” (Warington, 1887: 549).

Warington (1887: 520-548) next proceeded to discuss the well waters. The first British map to show groundwater contours in the Chalk, drafted by the hydrogeologist Joseph Lucas (1846-1926), had only recently appeared, in 1874 (Mather et al., 2004). Warington began analyzing groundwater from water wells downgradient from Rothamsted, in the village of Harpenden, where the wells were dug into the underlying Chalk aquifer. The Chalk is the largest aquifer in Britain, currently providing over 50% of the groundwater for England and Wales (Brenchley and Rawson, 2006: 393) and nitrate pollution has long been of concern there (Foster et al., 1982; Foster, 1993; Smith et al., 2010).

Warington (1887, Plate F) graphed the monthly groundwater data as parts per million nitrate-nitrogen, much as we do today (**Figure 2**). Before this it was not common to graph any constituents from groundwater analyses, merely to report them as tabular data. “The season chosen is that of 1885-86,” he explained, “which was a fairly normal one” (Warington, 1892: 109).

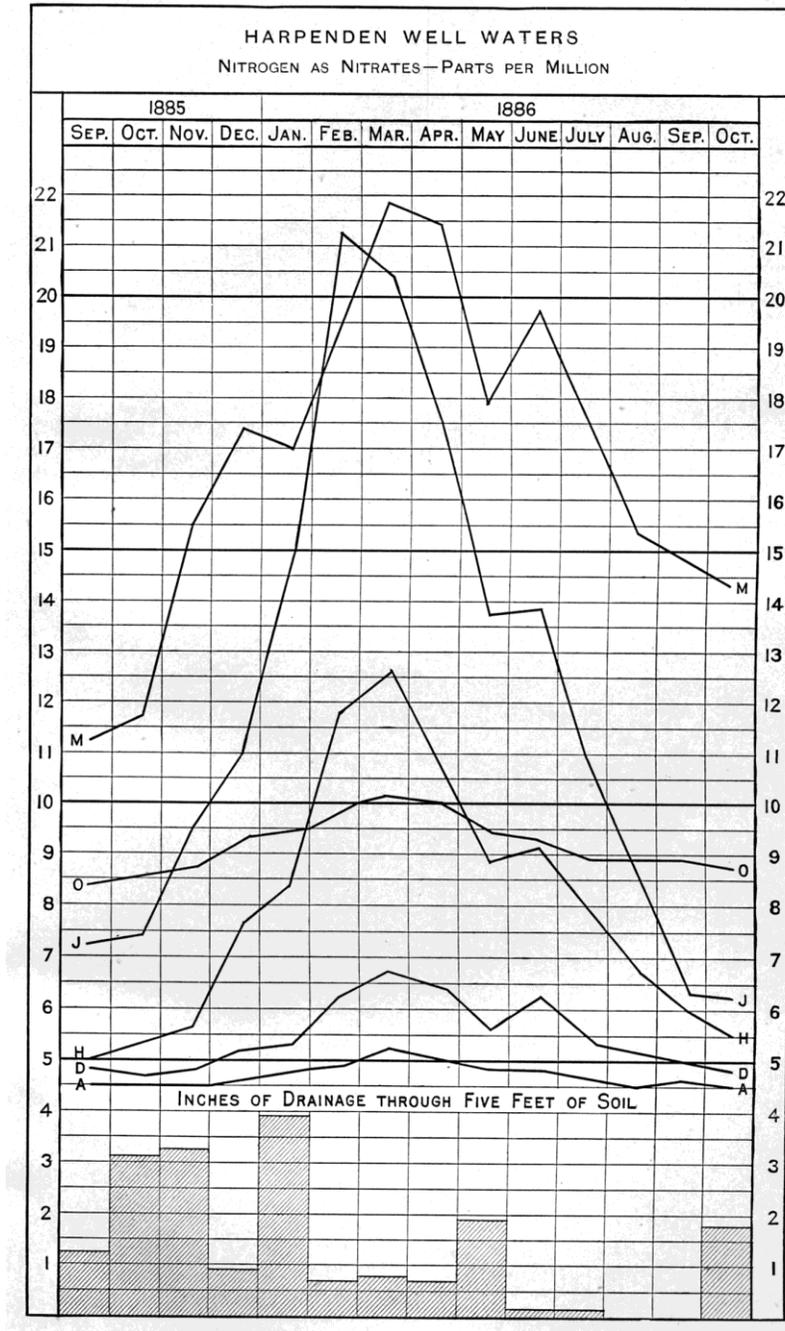


Figure 2. Warington's chart of the groundwater nitrate concentrations of "six typical well waters" from Harpenden, UK. This 1892 version of his original 1887 chart (Plate F) is clearer and easier to read. He considered "good wells" A and D uncontaminated, while "bad wells" H, J, M, and O were contaminated. From Warington, 1892, Plate XI.

Warington (1887: 520-521) studied 30 dug wells in Harpenden, to which he gave alphabetic designations. The Harpenden wells had 0 - 25 feet (0 – 7.6 meters) of overburden and terminated as deep as 214 feet (65 meters) in the underlying Chalk. In lieu of modern regulatory guidelines for contaminants, he used the average ambient concentration for his comparison value, above which he considered the water was contaminated, even if it did not have obvious health effects. The average concentration of nitrate-nitrogen in Chalk water for the agricultural district upgradient from Harpenden was 4.4 ppm, which was about what he found in the “uncontaminated wells” of the village (Warington, 1887: 550). This background nitrate he attributed to natural soil nitrification (see Kreitler and Jones, 1975, for a spectacular modern example of this phenomenon). On the other hand, Warington (1892: 108) attributed the source of nitrate in the contaminated village wells, ranging from 5 to 44 ppm nitrate-nitrogen, to highly localized “sewage contamination.” Compare this with the 11.3 ppm nitrate-nitrogen drinking water recommendation in the European Community since 1980 (Limbrick, 2003). He thus distinguished between diffuse and point sources of nitrate. Even so, the contaminated village well waters “were drunk apparently with impunity” (Warington, 1887: 532).

There were a variety of patterns, but Warington (1887, Table VIII) distinguished between wells that met background levels for chloride and nitrate (wells A-E) and those which did not (wells F-O). He graphed “six typical well waters” among the 30 well waters. Examples of two uncontaminated “good wells” (A and D) and four contaminated “bad wells” (H, J, M, and O) are shown in **Figure 2**. Warington (1887: 544) discusses the chlorine to nitrogen ratio, which

he separately graphed, distinguishing “chlorinous wells” (well M) from “nitric wells” (well J). Warington (1887: 518) properly recognized chloride as what we now call a conservative ion, whereas nitrate is a nutrient easily abstracted from groundwater by plants.

Warington’s (1887, Plate F) chart revealed seasonal leaching trends. Adjusted for rainfall variations, he explained that extended rainfall washes nitrate out of the soil and into groundwater and that there is usually a lag time before the impact is seen in the downgradient village wells. He described how nitrate declined during the growing season, even though nitrification in the warmer soil, mediated by bacteria, was at its peak, because plants absorbed nitrate. The groundwater nitrate increased again in winter, when accumulated nitrate was washed from the soil. Warington was aware of microbial denitrification (Hall, 1917: 219) but did not make any adjustment for it, and some later investigations (e.g., Howard, 1985) have justified this assumption. However, he was not aware of the complexities of dual-porosity groundwater flow through the Chalk, as highlighted by the so-called tritium anomaly, and other factors (Foster, 1975; Barker, 1993; Cook et al., 2007; Wang et al., 2011).

For such a short time span (one season) no long-term, secular trends could obviously be detected. Limbrick (2003) studied the baseline nitrate concentration in a different part of the Chalk aquifer, along the southern coast of England, between 1894 and 1946, observing a low but stable natural background concentration of about 1 ppm nitrate-nitrogen, but after 1946 it rose, marking the impact of artificial nitrate fertilizers on groundwater quality.

Warington (1892: 109-110) wrote that, "Chlorides, as we all know, have their principal origin in the common salt consumed in human diet." He thus usually regarded chloride in groundwater as a sign of human sewage contamination. Elsewhere, however, there were even higher proportions of chloride from deep wells in the Chalk, as shown by his mentor Frankland, and Warington (1887: 551) thought it "highly probable" that they reflected the original saline formation waters of the Chalk, a conjecture that has been confirmed by stable isotope studies (Price et al., 1993).

Even before groundwater nitrate toxicity was reported by the pediatrician Hunter Comly in 1945 (Lukens, 1987) it was suspected that nitrate in drinking water was deleterious because nitrate was often associated with the presence of pathogenic bacteria (Hamlin, 1990: 233). Pickering (1908), writing without a trace of irony in the days before nitrate toxicity was understood, declared that "In later years (1904) Warington was enabled to give these results a practical bearing on the supposed contamination of the Harpenden water supply, and he saved the community, at any rate, for a time, from adopting an expensive and, apparently, quite unnecessary system of sewerage."

2.4 Conclusions

Whatever conclusions were drawn from Warington's work, it brings together many of the approaches and concepts that the modern hydrogeologist takes for granted. He employed much of the basic conceptual tool kit used in modern groundwater consulting firms everyday. While Warington's groundwater nitrate

graphs might not be the very earliest in the literature, he himself has this to say: “The only published results I am aware of respecting the composition of well waters at different seasons of the year are the monthly analyses made by Dr. E. Frankland of the chalk well waters supplied respectively by the West Kent Water Company, and by the Colne Valley Water Company, and published in the Annual Reports of the Local Government Board” (Warington, 1887: 547).

Chapter 3

Isotopic Study of Nitrate from Upper Mississippi Valley Saltpeter Caves

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[Author's Note: This article documents the early stage of my research, when the sampling program was just getting started.]

Summary

There are two prominent theories for the source of nitrate in cave saltpeter: animal wastes, especially bat guano, and groundwater seepage. While it has been shown that the seepage theory works well for the saltpeter caves of the southeastern U.S., the other model works best for guano caves in the southwestern U.S. We used a dual isotope/geochemical approach to study the origin of nitrate-rich sediments from caves, crevices, and rockshelters in Minnesota and Illinois, comparing them with samples collected from Great Saltpetre Cave in Kentucky. The dual isotope approach analyzes both the $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ in the nitrate ion. In such an analysis, nitrates deriving from animal wastes can be distinguished from those derived by nitrification of organic matter in the soil. While there is some overlap, the isotopic results suggest that some of the nitrates from Minnesota caves derive from animal waste, while other nitrate deposits, having low phosphate concentrations, likely derive from groundwater seepage.

3.1 Introduction

Salt peter (potassium nitrate) is one of the three ingredients of gunpowder and up through the time of the American Civil War it was often obtained by processing cave sediments. While the vast majority of salt peter caves are found in the southeastern United States, the earliest known record of cave salt peter in this country is from Minnesota. In 1700, the French fur-trader Pierre-Charles Le Sueur reported salt peter caves along the west side of Lake Pepin while ascending the Mississippi River (Shaw, 1992). Le Sueur's comments about the caves being inhabited by bears in winter and rattlesnakes in summer suggests that the caves were visited with some frequency. Although not explicitly mentioned in his account, French fur-traders were interested in sources of salt peter to manufacture gunpowder. Documentary evidence indicates that the French were making salt peter from Missouri caves as early as 1720 (Breckenridge, 1925).

The exact location of Le Sueur's caves had been a topic of discussion since the 1981 Cave Research Foundation Symposium of salt peter researchers, but no one actually searched for the caves before this study, to the best of our knowledge. In 2004, one of us (G.B.) located small, narrow, crevice caves closely matching Le Sueur's description in outcrops of the Prairie du Chien Group carbonates along the Mississippi River bluffs near Red Wing, Minnesota (Brick, 2004). Laboratory analysis of sediments from these caves revealed nitrate concentrations more than 2% by weight. These concentrations fall within the 0.01 and 4% nitrate range reported by Hill (1981) from Mammoth Cave, Kentucky, a famous historical salt peter mining site.

There are two prominent theories for the accumulation of cave nitrates: the traditional guano theory and the seeping groundwater model (Hill, 1981). In the guano theory, the mineralization of nitrogenous animal wastes deposited in the caves is responsible for the nitrates, while in the seepage theory, surface soil nitrate is transported into the cave by seeping groundwater. The seepage theory best explains the saltpeter caves of the southeastern United States and the guano model works best for guano caves in the southwestern U.S. One goal of this project is to see if the cave nitrates in the Upper Mississippi Valley fit either theory.

We collected sediment samples from caves along the Mississippi River to help define the areal occurrence of the nitrate-rich cave sediments. The soluble major cations and anions in each sample were analyzed and the nitrate ions in selected samples were analyzed for $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$. Kendall et al. (2007) have shown that such nitrate isotopic analyses can help distinguish between different nitrate sources.

3.2 Materials and Methods

Caves, crevices, and rockshelters along the Mississippi River were sampled in Goodhue and Wabasha Counties, Minnesota; Pierce County, Wisconsin (not further discussed in this paper); and at Mississippi Palisades State Park, Carroll County, Illinois. The last was chosen as a comparison site in a different rock formation (Niagara Series dolomite). The crevices were generally bluff-parallel joints, widened by mass movement or block rotation. Some of the voids were

irregular rockshelters of solutional origin. For comparison, sediments were also collected in Great Saltpetre Cave, Mt. Vernon, Kentucky, which had a long history of saltpeter production (Engel and Engel, 1998). Sample locations are shown in **Figure 3.1** and listed in **Table 3.1**.

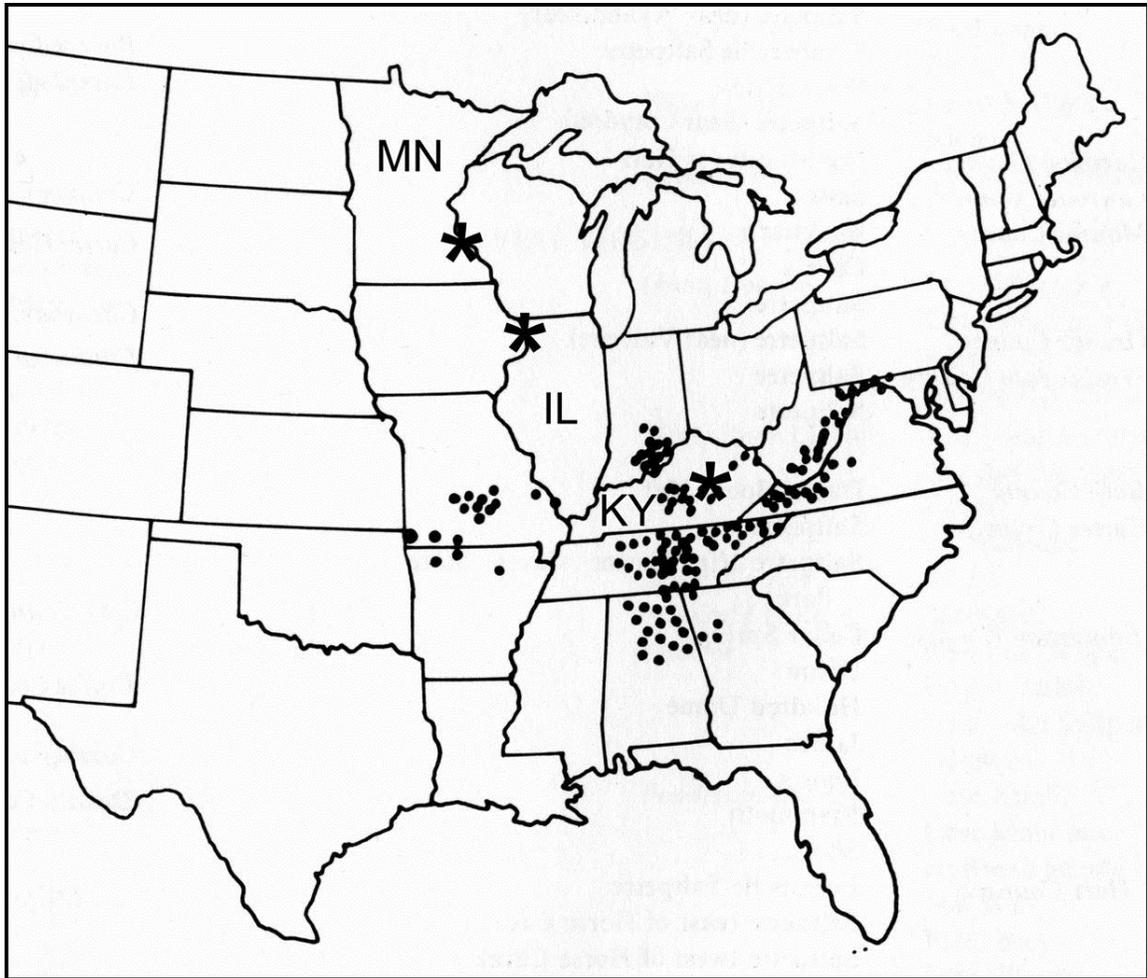


Figure 3.1. Location of sampling sites in Minnesota, Illinois, and Kentucky, marked as asterisks, plotted on map showing distribution of limestone caves containing saltpeter deposits (which includes Great Saltpetre Cave, Kentucky). Modified from Hill et al. (1981).

TABLE 3.1. Cave Sediment Sampling Locations				
(PDC=Prairie du Chien Group)				
Sample	Nitrate Strip (ppm)	Cave	Lithology	Location (by County)
Minnesota				
FSP-3.5f	>500	Rockshelter, solutional origin	PDC dolomite	Goodhue
PNP-E	250	Bluff-parallel crevice	PDC dolomite	Goodhue
PNP-M	500	Bluff-parallel crevice	PDC dolomite	Goodhue
Y-4	>500	Bluff-parallel crevice	PDC dolomite	Goodhue
Y-6	>500	Rockshelter, solutional origin	PDC dolomite	Goodhue
Illinois				
MPSP-3	>500	Bluff-parallel crevice	Niagaran Series dolomite	Carroll
MPSP-4	500	Rockshelter, solutional origin	Niagaran Series dolomite	Carroll
Kentucky				
GSP-3	>500	Great Saltpetre Cave, vat impression, Richard's Run.	St. Genevieve Limestone	Rockcastle
GSP-12	250	Great Saltpetre Cave, regeneration pile.	St. Genevieve Limestone	Rockcastle

Samples of floor sediments were collected with a trowel and placed in plastic bags and transported at ambient temperature to the lab. In the lab, the sediments were sieved through fiberglass window screen, weighed, and splits taken for further processing. One split was weighed, desiccated in an oven at 80°C for 3 days, and reweighed, to determine moisture content. A second aliquot was placed in a measured volume of deionized water in a Nalgene bottle, shaken, and left to settle overnight. A preliminary indication of the nitrate content was made using Merck nitrate strips. Solutions showing elevated nitrate concentrations were poured through filter paper to remove debris. The alkalinity was determined by colorimetric titrations, anion concentrations by ion chromatography, and cation concentrations by cation chromatography (Hautman and Munch, 1997). The soluble ion chemical compositions are reported relative to the dry sediment weight.

Nine samples showing elevated nitrate concentrations were analyzed at the USGS Reston Stable Isotope Laboratory for $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values. The sediment solutions were diluted to a nitrate concentration of approximately 1 mg/L (1 ppm). The diluted solutions were frozen, packed in dry ice, and shipped to Reston, Virginia. Nitrate samples are analyzed by bacterial conversion of nitrate to nitrous oxide and subsequent measurement in a continuous flow isotope ratio mass spectrometer (Sigman et al., 2001; Casciotti et al., 2002). Nitrogen isotope ratios are reported in parts per thousand (per mil) relative to N_2 in air (Mariotti, 1983). Oxygen isotope ratios are reported as per mil relative to VSMOW reference water and normalized on a scale such that SLAP reference

water is -55.5 per mil (Coplen, 1988, 1994). One-sigma precision of the analyses are ± 0.25 per mil for $\delta^{15}\text{N}$, and ± 0.5 per mil for $\delta^{18}\text{O}$.

3.3 Results

As our sampling of the Mississippi River bluff caves expanded, approximately one-third of the sites sampled showed elevated nitrate concentrations. Surface soils in the vicinity and caves sampled elsewhere in Minnesota, by contrast, showed virtually no nitrates. The results of the chemical analyses are shown in **Figure 3.2** and **Table 3.2**, and the isotopic results in **Figure 3.3** and **Table 3.3**.

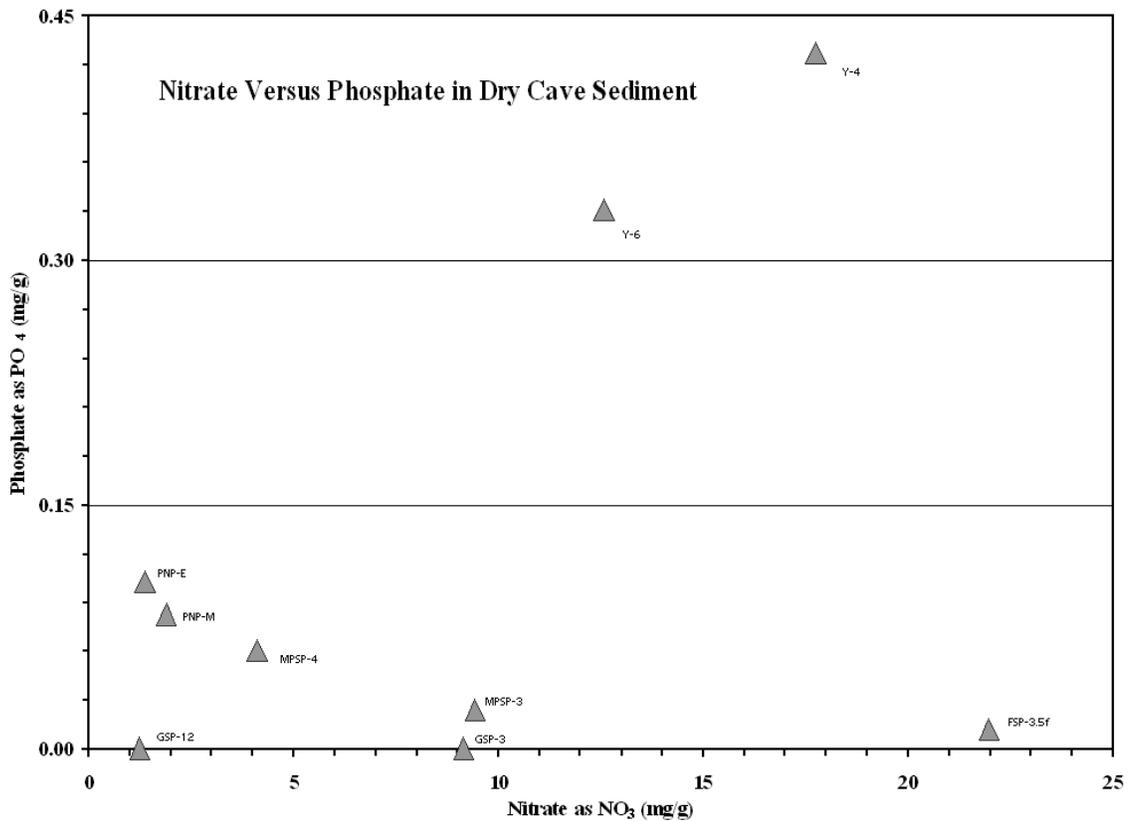


Figure 3.2. Plot of nitrate and phosphate concentrations in dry cave sediments.

TABLE 3.2. Chemical Analysis Reported as Milligrams Per Gram of Dry Cave Sediments												
Sample	Alkalinity as CaCO₃ (mg/L)	NO₃	Soil NO₃ %	Cl	PO₄	SO₄	Ca	Mg	Na	K	Sr	
Minnesota												
FSP-3.5f	47.3	21.98	2.20	0.810	0.013	8.239	4.142	3.067	0.228	1.209	0.004	
PNP-E	142.7	1.36	0.14	0.026	0.103	0.138	0.654	0.182	0.022	0.151	0.001	
PNP-M	114	1.89	0.19	0.031	0.083	0.314	0.700	0.211	0.027	0.116	0.001	
Y-4	65.7	17.75	1.77	0.217	0.427	2.960	4.916	1.426	0.092	1.437	0.004	
Y-6	78.8	12.57	1.26	0.279	0.331	7.083	2.457	2.073	0.240	1.283	0.002	
Illinois												
MPSP-3	54.3	9.42	0.94	0.898	0.025	27.545	4.914	5.337	0.349	0.516	0.012	
MPSP-4	50.5	4.11	0.41	0.777	0.061	4.757	1.075	1.242	0.330	0.216	0.003	
Kentucky												
GSP-3	22.6	9.15	0.91	0.234	0.001	1.022	1.989	0.166	1.010	0.086	0.013	
GSP-12	22.9	1.24	0.12	0.015	0.001	0.070	0.339	0.035	0.038	0.026	0.002	

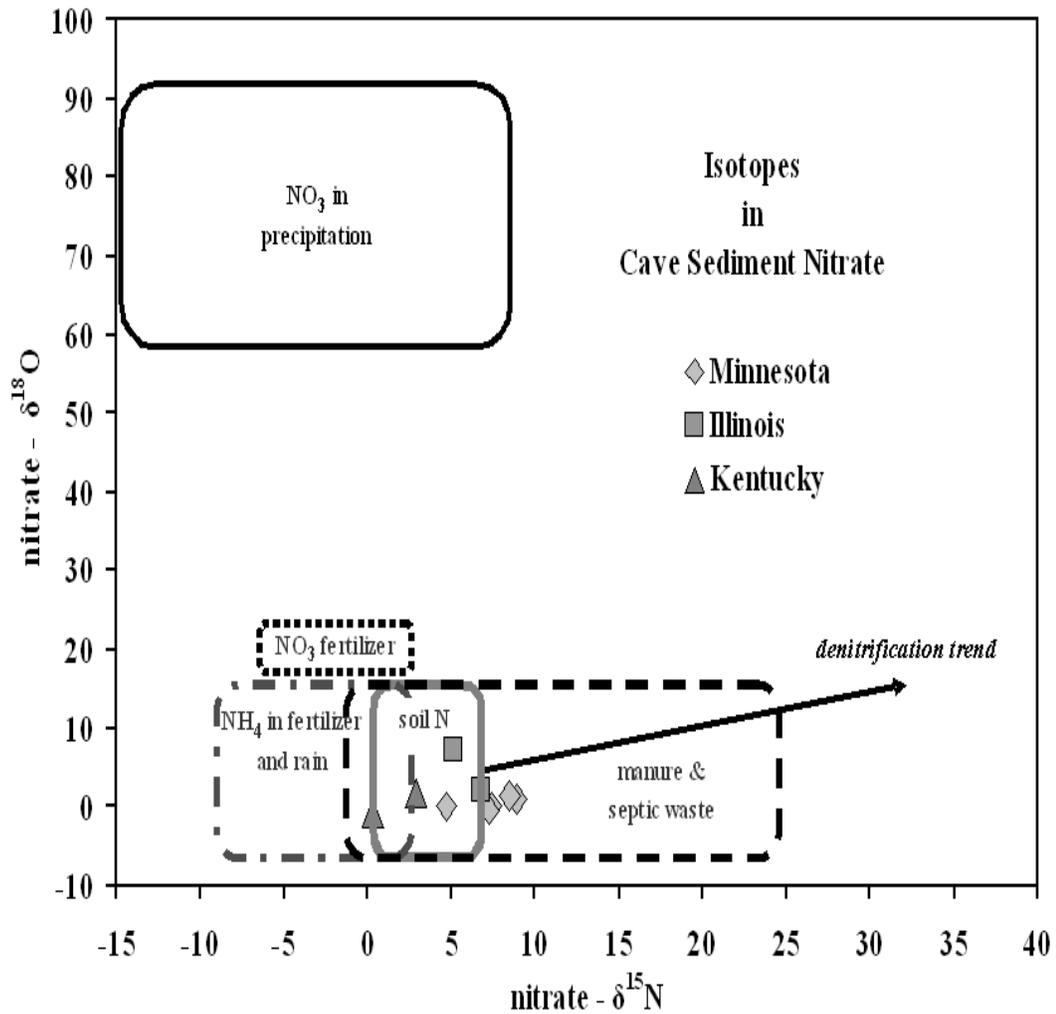


Figure 3.3. Plot of dual isotope analysis of nitrates in cave sediments. Enclosed areas represent known ranges of nitrate isotopic composition from various sources (modified from Kendall, 1998).

The chemical analysis shows that the soluble ions in these sediments are predominately calcium and magnesium nitrate. The magnesium/calcium molar ratio is greater than 1 for the samples FSP-3.5f, Y-4, Y-6 (Minnesota), and MPSP-4

(Illinois), which correlates with the observation that all of the rockshelters belong to this group (other samples were collected from the aphotic zones of caves or crevices). It is likely that being more exposed to convectional air currents along slopes increases the rate of evaporation in these settings, leading to the evaporative precipitation of calcium carbonate. There seems to be a fairly close relationship between the concentration of nitrate and that of chloride, except for the two Illinois samples (MPSP-3 and MPSP-4), which may indicate an independent chloride source for these two.

TABLE 3.3. Results of Dual Isotope Analysis of Nitrates from Cave Sediments.

Sample	NO ₃ as N (ppm)	Reston LabID	δ ¹⁵ N (AIR)	δ ¹⁸ O (VSMOW)	State
FSP-3.5f	1.003	G-12610	4.66	0.00	MN
PNP-E	0.997	G-12611	7.41	0.12	MN
PNP-M	1.003	G-12612	7.23	-0.32	MN
Y-4	0.987	G-12617	8.90	1.06	MN
Y-6	0.986	G-12618	8.46	1.46	MN
MPSP-3	0.996	G-12619	6.77	2.16	IL
MPSP-4	0.998	G-12624	5.08	7.19	IL
GSP-3	1.003	G-12625	2.88	1.59	KY
GSP-12	0.995	G-12634	0.25	-0.86	KY

3.4 Discussion

Our preliminary isotopic results for the 9 samples are displayed graphically in **Figure 3.3**. The spread between the 5 samples from Minnesota (FSP-3.5f, PNP-E,

PNP-M, Y-4, Y-6), the 2 samples from Illinois (MPSP-3, MPSP-4), and the 2 samples from Great Saltpetre Cave (GSP-3, GSP-12) is small (8.7 per mil for $\delta^{15}\text{N}$ and 8.15 per mil for $\delta^{18}\text{O}$). All of the samples appear to have been affected by microbial processes. Within this small range, the isotopic data suggest that Minnesota samples Y-2 and Y-4 derive from guano or animal waste, and this correlates with their higher phosphate content; a plot of nitrate versus phosphate concentrations in dry soil samples is shown in **Figure 3.2**. Here, FSP-3.5f (Minnesota), MPSP-3 (Illinois), and GSP-3 (Kentucky) show elevated nitrate concentrations, yet low phosphate values, suggesting a possible groundwater seepage origin. Two of the Minnesota samples (PNP-E and PNP-M) show disproportionately elevated phosphate to nitrate, which may indicate denitrification has occurred. The other four samples fall along a trend line with nitrate proportional to phosphate suggesting a manure source.

3.5 Conclusions

Stable isotope studies involving natural abundances of the dual isotopes $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ in the nitrate ion, coupled with analyses of the soluble cations and anions, have the potential to help discriminate between nitrate deposits in cave sediments formed primarily through the mineralization of animal waste, from those formed by the groundwater seepage mechanism. Further sampling and analysis will be required to extend these preliminary results.

Chapter 4

Geochemical Study of Nitrate from Upper Mississippi Valley Cave Sediments

4.1 Cave Nitrate Occurrences in the United States

Chemically bound or reactive nitrogen, N_r , is a component of all life on Earth. Amino acids, which contain nitrogen, are the basic building blocks of protein. There are three fundamental sources of N_r in the Earth's surface environment. Historically, the major source has been biochemical fixation of atmospheric elemental nitrogen by a small group of microbes called diazotrophs. A small secondary source of nitrate has been fixation by abiotic atmospheric processes such as lightning. Modern fossil fuel burning engines have added to this. During the last century a third source, the industrial fixation of nitrogen by the Haber-Bosch process, has surpassed all of the other sources combined and currently fixes two to three times as much nitrogen as the natural sources (Townsend and Howarth, 2010). Once generated, N_r tends to cascade through the environment (Galloway et al., 2003). Fixed nitrogen from all three sources is cycled and recycled by life on Earth through the biological Nitrogen Cycle.

The most widely accepted theory for the accumulation of nitrate in the large historic saltpeter caves of the southeastern United States such as Mammoth Cave involves the seeping groundwater model proposed by Hill (1981), some of which had been outlined by Pace (1971). Organic nitrogen, like that found in

proteins, is converted to ammonium and then nitrate by bacteria in surface soils. The nitrate ion is reduced again to ammonium lower in the profile and drawn into the cave through the limestone walls by a moisture-density gradient created by evaporation at the bedrock/cave interface. Ammonium is then reconverted to nitrate by the nitrifying bacteria known to exist in the cave sediments (Fliermans and Schmidt 1977). This model accounts for the elevated nitrate concentrations obtained during this study from samples taken in Great Saltpetre Cave, Kentucky.

The following geochemical analyses were undertaken to gain insight into which of these three sources was involved in the cave nitrate deposits that were observed in my field area in the Upper Mississippi Valley (UMV). The fact that Le Sueur discovered these crevice cave deposits in 1700 indicates that at least the original nitrate deposits were due to natural processes. However, Hill's (1981) "seeping groundwater model" was my original null hypothesis regarding the possible origin of the UMV nitrate deposits.

A terminological distinction that needs to be clarified at the outset is the difference between *nitrogen fixation* and *nitrification*. Nitrogen fixation involves the chemical combination of gaseous nitrogen (N_2) with other elements to form Nr compounds such as ammonia (NH_3) or nitrogen oxides (NO_x). Nitrification, by contrast, is the oxidation of ammonia to form nitrite (NO_2) or nitrate (NO_3). Combined forms of nitrogen readily undergo further chemical reactions, in distinction to atmospheric nitrogen, which is comparatively inert although it makes up 78% of the atmosphere. Many excellent reviews of nitrification have

been published since the early days, e.g., Warington (1878, 1879, 1884, 1891), King and Whitson (1901), Ingle (1920), Greaves (1922), Lees and Quastel (1946), Harmsen and Van Schreven (1955), Alexander (1977), Schmidt (1982), Prosser (1986), and De Boer and Kowalchuk (2001), among others. Nitrification studies specific to Minnesota include Halvorson (1949), Schmidt (1956), and Pastor et al. (1987). Reviews of nitrifying bacteria include Gibbs (1919), Meiklejohn (1953), Delwiche and Finstein (1965), Rosswall (1976), Belser (1979), Prosser (1986), Fiencke et al. (2005), and Jetten (2008).

According to Hill and Forti (1997), there are eleven nitrate minerals found in caves, several of which are extremely rare and need not be discussed here. Calcium nitrate (nitrocalcite) is best known from Kartchner Caverns in Arizona (Hill and Buecher, 1992). Native potassium nitrate is found in the caves of Ceylon (Hill and Forti, 1997). There are reports that potassium nitrate was present in the matrix of certain Kentucky sandstones, making the lixiviation step (see Chapter 6, below) unnecessary when manufacturing saltpeter from them (Hill, 1981). Sodium nitrate (nitratite) occurs as an encrustation from the Wupatki fissures in Arizona (Hill and Eller, 1977). Ammonium nitrate (nitrammite) is quite rare, having been reported from Nickajack Cave in Tennessee, and is usually associated with guano deposits (Hill and Forti, 1997).

Nitrate minerals are in some ways analogous to carbonates, but the deposition of nitrate minerals is often related to the evaporation of solutions, not carbon dioxide equilibrium reactions (Hill and Forti, 1997). Owing to their much higher solubility in water as compared with carbonates, nitrate minerals are

rarely found except where they cannot be leached away by invading waters and are thus characteristic of special locations such as deserts, Antarctica (where water is frozen), or in dry caves. Most nitrate minerals are hygroscopic, that is, they will absorb water from the atmosphere and, if enough water is present, deliquesce, or dissolve completely. In some environments, where there is a seasonal variation in temperature and humidity, nitrate minerals can deliquesce and thus disappear when the temperature and humidity is high, as in summer, and effloresce or reappear when temperature and humidity drops back down again, in winter (Hill and Forti, 1997).

4.2 Materials and Methods

The nitrates in this study apparently existed as concentrated soil solutions, between and coating the particles of cave sediments. During cold, dry periods the nitrates may have cycled through solid nitrate minerals, which deliquesced during warmer, higher humidity conditions. Or the nitrate ions may have only existed in solutions having never been concentrated or dry enough to crystallize as nitrate minerals.

In Goodhue County, Minnesota, the Ordovician Oneota dolomite of the Prairie du Chien Group forms the caprock of the Lake Pepin bluffs, protecting the soft, underlying Jordan Sandstone from erosion. In the dolomite layer, there are basically two kinds of voids: those formed by chemical solution from flowing groundwater, and crevices formed by the recent mechanical widening of pre-existing rock joints by gravitational slumping. The crevices are near the face of

the outcrop and are “ephemeral” in the sense that they are involved in recent cliff erosion and retreat, even though the joints themselves may be Devonian in age (Anthony Runkel, pers. comm.). Many of these crevices have boulder ceilings through which tree roots have penetrated from above, along with descending soil, and appear unsafe to enter. The solutional caves, on the other hand, presumably formed in the dolomite at a much earlier time, and are much more stable: uranium-series speleothem dating studies for caves in this rock layer elsewhere in southeastern Minnesota yield ages of a quarter of a million years (Lively, 1983). These much older solutional caves predate and have been exposed by geologically recent valley incision, while the bluff crevices post-date the river valleys. The term rockshelter will be used to refer to truncated remnants of either of these two kinds, as well as miscellaneous minor forms, such as weathering voids.

Caves, crevices, and rockshelters, regardless of their size or geologic origin, or whether they resembled the original Le Sueur-type crevice (see Chapter 1), were sampled in southeastern Minnesota, especially Dakota, Goodhue, Wabasha, and Winona counties; in western Wisconsin, especially Pierce County; in Allamakee County, Iowa; and at Upton Cave, Mississippi Palisades State Park, Carroll County, Illinois, as part of a wider project to investigate nitrate concentrations in UMV cave sediments generally (**Figure 4.1**). Thus, rock outcrops on both sides of Lake Pepin, and further up and downriver, were investigated, not merely those in the immediate area suggested by Le Sueur’s Journal. The most heavily prospected area, because of the public accessibility of the rock outcrops and the abundance of voids, was the linear

ridge encompassed by Frontenac State Park, along the Minnesota shore of Lake Pepin, where about two dozen features were sampled. For comparative purposes, sediments were also collected in Minnesota's two largest caves, Mystery Cave, near Spring Valley, MN, and Niagara Cave, near Harmony, MN. Great Saltpetre Cave, Rockcastle County, Kentucky, which has a known history of saltpeter extraction (Engel and Engel, 1998), was also sampled. Sampling was conducted intermittently from 2004 through 2011.

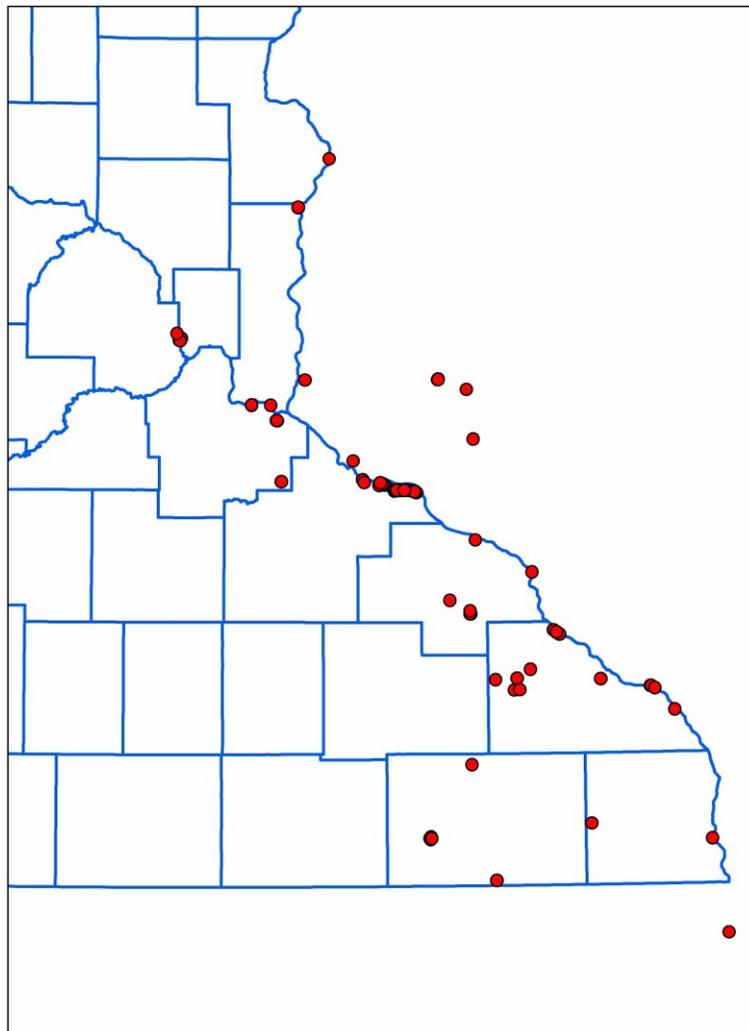


Figure 4.1. Cave sediment sampling locations in Minnesota, Wisconsin, and Iowa. Several other, more distant locations, in Illinois, Kentucky, and Tennessee, are omitted.

Surface soil control samples were systematically collected along slope profiles provided by the wooden stairways in Frontenac and John Latsch state parks and along the tops of the bluffs. Surface samples were also collected directly outside several caves, sometimes from surface soil beginning to enter the crevices from above, but usually to either side of the cave, and outside the apron of sediments spreading downslope from the cave, if such were present.

Sediment sampling protocols were modified from the research of Fliermans and Schmidt (1977) at Mammoth Cave, Kentucky. Floor sediments were collected with a trowel and placed in plastic bags and transported at ambient temperature to the lab for processing within 24 hours. In the lab, sediments were sieved through fiberglass window screen, weighed, and splits taken for further processing. One split was weighed, desiccated in an oven at 80°C for 3 days, and reweighed, to calculate moisture content. A second aliquot was placed in a measured volume of distilled and deionized water in a Nalgene bottle, shaken to form a slurry, refrigerated, and left to settle overnight.

In developing the sampling protocol, it was recognized that nitrification could take place in the sampling bag; indeed, this is the basis for a whole method of soil nitrate incubation studies (Eno, 1960). Many experiments have been conducted over the years to determine the optimum nitrification temperature (Panganiban, 1925; Russel et al., 1925). Holt et al. (1994) report that members of the genus *Nitrobacter* are mesophiles with a temperature optimum of 28°C. Below 5°C or above 55°C, nitrification ceases altogether. Removing sediments in the middle of a Minnesota winter, and bringing the samples into a warm laboratory,

could boost nitrification dramatically, unless the samples were either kept frozen or processed within 24 hours, in accord with the protocols of Fliermans and Schmidt (1977).

An experiment was performed to test whether hand shaking for 20 seconds, followed by a day for settling, was just as good as using a mechanical stirring device for 2 hours, followed by the same settling period. Dividing a sample into two portions, one of which was shaken, and the other stirred, as above, revealed no differences in nitrate concentration, likely owing to the high solubility of the nitrate ion in water.

A preliminary indication of the nitrate content of the sediments and soils was made by dipping commercially available Merck nitrate test strips, which yield semi-quantitative values based on changing indicator colors, into the slurries. The strips also indicate nitrite. As a general rule, surface soils are expected to have low nitrate concentrations because the highly soluble nitrate ion is easily leached by rainfall, and being a plant nutrient, nitrate is readily absorbed by roots. Fliermans and Schmidt (1977) found that surface soils above Mammoth Cave were “always less” than 25 parts per million (ppm) nitrate-nitrogen ($\text{NO}_3\text{-N}$), which is equivalent to 110 ppm nitrate (NO_3), so this value was initially proposed as a lower limit for samples demonstrating nitrate enrichment. Solutions showing elevated nitrate concentrations were passed through a 0.2 micron filter and analyzed by the Aqueous Geochemistry Laboratory at the Department of Earth Sciences, University of Minnesota. Selected filtered sediment solutions were analyzed for major and minor anions

using ion chromatography (EPA Method 300.0). A smaller set of the filtered soil solutions were analyzed for cations using ICP/AES (EPA Method 200.7) or ICP/MS (EPA Method 200.8+6020A) and alkalinity was determined using a digital titrator to a colorimetric endpoint. The general laboratory protocols followed are described in Alexander and Alexander (2008).

4.3 Results

Of the 171 samples collected from the 103 caves, crevices, and rockshelters that were sampled in the UMV, from a variety of rock types (dolomites, limestones, sandstones, and basalts) ranging in age from Precambrian to Pennsylvanian (**Table 4.1**), 67% had elevated concentrations of nitrate (>50 ppm NO_3) as determined by nitrate test strips. Subsequent laboratory analysis confirmed the indicator strips and provided quantitative values that could be related to dry weight of sediment. Of the samples sent to the lab, 74 anion analyses were performed, 33 of which also had cation analyses performed on them. High nitrate concentrations, up to 35,000 ppm ($\mu\text{g NO}_3/\text{g}$ dry sediment), were widespread among rock voids along both shores of Lake Pepin and occurred as far south as sampling was conducted, in Illinois (**Table 4.2**). By contrast, none of the surface control soils showed more than 10 ppm nitrate (**Table 4.3**).

Ion balances were calculated for samples where both cations and anions were analyzed. In some cases only anions, and in other cases, neither, were analyzed. Since all waters must remain electrically neutral, the cations balancing the anions, the ion balance serves as a QA/QC procedure. The calculation

compares the total milliequivalents per kilogram of cations and of anions. The difference between the two is then calculated as a percentage. An agreement of <5% is usually accepted within the Department of Earth Sciences, and <10% by the USGS. For the data set in **Table 4.2**, only four (CZC, FSP-3.6, PhilC, WC-2) of the 33 ion balances exceeded the 10% guidelines.

The water solutions described below are not surface waters or groundwaters, but rather soil slurries, or soil solutions diluted with distilled and deionized water. As such, only soluble constituents from the sediments are represented. The soluble constituents are reported as the concentrations in the sediments on a dry weight basis.

TABLE 4.1. Stratigraphic Distribution of Sampling Sites		
AGE	Formation	No. Samples
Pennsylvanian	Makanda Sandstone	7
Mississippian	St Genevieve Limestone	20
Silurian	Hopkinton Dolomite	6
Ordovician	Galena Group	6
	Platteville Limestone	4
	St Peter Sandstone	1
	Prairie du Chien Group	118
Cambrian	Jordan Sandstone	8
Precambrian	Keweenawan basalts	1

TABLE 4.2. Soil Solution Chemistry of Cave Sediment Samples (cont'd)		Alk	NO3-N	% Moisture	Soil %	MERCK	Cl	Br	CIBr	PO4-P	SO4	Sum	Cs	Mg	Li	Na	K	Sr	Ba	Fe	Mn	Si	Al	P	Sum	% Diff.	
CODE	LOCATION	mg/L as CaCO3	ug/g (soil)			ppm NO3	ppm (soil)	ppm (soil)	ratio	ppm (soil)	ppm (soil)	Anions	ppm (soil)	ppm (soil)											Cations		
Minnesota																											
Y-1	Young Property					10																					
Y-2	Young Property					0																					
Y-3	Young Property					150																					
Y-4	Young Property					200																					
Y-4 (2)	Young Property	65.7	235.2	10.71	1.7748	>500	12.7	<1	N/A	8.17	173.60	22.6	288.3	83.6	0.017	5.375	84.26	0.252	0.135	0.213	0.457	2.9	0.000	9.64	23.7	2.3	
Y-5	Young Property					40																					
Y-6	Young Property					250																					
Y-6(2)	Young Property					>500	36.7	<1	N/A	15.00	963.30	52.3	341.1	287.8	0	33.35	176.1	0.333	0.95	0.21	0.498	4.93	0.000	17.55	46.7	-5.6	
Y-7	Young Property					45																					
Y-8	Young Property					100																					
IC-36-1	Ice Cave					250																					
IC-36-2	Ice Cave					25																					
IC-37.5	Ice Cave	89.5	5721	1.86	0.0106	25	4.688	0.02	234	0.16	149.83																
MRT-1	Milwaukee Road Trestle					25																					
COV-1	Calacombs of Yucatan	11.5	14.788	15.75	0.0463	50	4.62	0.025	185	1.10	138.57																
COV-2	Calacombs of Yucatan					0																					
RDC	Reno Quarry Caves					10																					
SR-1	Shadow Falls	177.6	22.279	7.92	0.0475	100	59.916	0.208	288	0.01	1985.10																
EC-1	Echo C					5																					
EC-2	Echo C					5																					
LC-1	Ludlow C					0																					
PCC-1	Pancake C					5																					
SEN-1 (SC-1)	Sentry C					100																					
SEN-2 (SC-2)	Sentry C					50																					
WIC-1	W Ind Ck: Ridgeway C					75																					
WIC-2	W Ind Ck: Popcorn C					10																					
WIC-3	W Ind Ck: Popcorn C	10.66	133.126	3.66	0.3864	>500	6.21	0.025	248	1.62	142.89																
Clarke	Clarke C	16.58	34.8	0.99	0.0703	250	7.142	0.172	42	0.63	30.98																
Kmain	Knapp's C	8.85	55.22	3.75	0.1431	500	6.432	0.025	257	0.48	121.13																
Kpar	Knapp's C					50																					
Kupar	Knapp's C					0																					
Kilver	Knapp's C					0																					
LVC-1	Last Valley Cave	106.9	331.855	11.50	0.8240	>500	56.787	0.1	568	11.67	931.89	47.6	377.5	258	0	18.49	167.8	0.309	0.124	0.019	0.002	3.076	0.006	8.472	45.2	-2.8	
ACC	Around the Corner Cave					>500	224.168	N/A	N/A	16.82	1093.30	150.0	1037	809.4	0.018	170.4	364.8	0.964	0.736	0.094	0.781	5.372	0.070	20.76	135.1	-5.2	
DMVI	Damview Cave	121	1644.979	13.04	3.0722	>500	224.168	N/A	N/A	16.82	1093.30	150.0	1037	809.4	0.018	170.4	364.8	0.964	0.736	0.094	0.781	5.372	0.070	20.76	135.1	-5.2	
Dev	Devil's Cave					5																					
JL1	J.L. State Park Caves					5																					
JL2	J.L. State Park Caves	273	75.093	5.66	0.2913	500	10.832	0.02	542	1.52	72.96																
JL3	J.L. State Park Caves	N/A	207.897	5.66	0.6727	>500	32.033	0.206	156	1.91	920.21																
PCH-R	Priest's Cabin Hollow					0																					
PCH-HWS	Priest's Cabin Hollow					25																					
QB-1	Queens Bluff					50																					
QB-2	Queens Bluff					100																					
RHS	Raccoon Heaven Room					>500																					
RHS	Raccoon Heaven Side-Psg					>500																					
RHW	Raccoon Heaven Window					500																					
SKhc	Skunk Hollow C					10																					
TRfr	Tricorn C-frozen					50	6.632	0.02	332	0.26	31.27																
TRov	Tricorn C-oven					50	7.308	0.02	365	0.25	34.96																
TRm	Tricorn C-room					50	7.666	0.02	383	0.20	38.83																
TRC-1	Trout Run C	108.3	3.171	5.66	0.0085	25	7.459	0.005	1492	0.01	57.82	3.8	12.71	26.97	0.006	9.828	2.707	0.018	0.183	0.041	0.004	1.096	0.030	0.212	3.4	-6.3	
TRC-2	Trout Run C	61.4	2.332	2.91	0.0057	10.25	3.422	0.005	684	0.01	5.42																
TRC-3	Trout Run C	67.1	5.289	4.76	0.0142	25.50	3.229	0.005	646	0.32	6.41																
Wisconsin																											
BOV-1	Overlook Caves, BIV Park	233	72.656	8.84	0.1654	500	61.23	0.02	3062	0.19	85.53																
BC-1	Black's C					500																					
FC-1	Fuzzy Critter C					0																					
FC-2	Fuzzy Critter C					0																					
FC-3	Fuzzy Critter C					10																					
KSP-1	Kimickimic SP					40																					
SP-1	South Portal C					5																					
TF-DS	Tree Fork Cave					0																					
TF-Qo5	Tree Fork Cave					10																					
TF-HJ	Tree Fork Cave					25																					
TBPC-1	Trenton Bluff Prairie C	272.6	1265.969	6.54	2.6289	>500	328.39	1.2	274	0.10	2550.77	158.2	749.7	1120	0.051	132.9	558.5	0.921	0.158	0.056	0.809	0.718	3.875	2.865	149.6	-2.8	

CODE	LOCATION	Lithology	Alk mg/L as CaCO3	NO3-N ug/l (soil)	% Moisture	Soil %	MERCK ppm NO3	Cl ppm (soil)	Br ppm (soil)	Cu/Br ratio	PO4-P ppm (soil)	SO4 ppm (soil)	Sum Anions	Ca	Mg	Li	Na	K	Sr	Ba	Fe	Mn	Si	Al	P	Sum Cations	% Diff	
Wisconsin																												
WC-1	Webb Caves-Party C	PDC	38.9	274.412	8.26	0.6748	>500	14.84	0.1	148	0.10	111.84	23.1	198.7	142.2	0	14.51	34.61	0.415	0.137	0.017	0.002	2.093	0.012	1.046	23.1	0.0	
WC-2	Webb Caves-Facade C	PDC	93.4	55.492	2.91	0.1335	300	15.341	0.025	614	0.83	76.34	7.9	28.56	36.69	0.004	4.54	68.35	0.043	0.095	0.019	0.003	0.943	0.109	0.574	6.4	-10.6	
WC-3	Webb Caves-Facade C	PDC	66.2	28.187	0.99	0.0662	200	4.971	0.025	199	0.03	13.60	3.8	26.16	15.33	0	3.818	2.274	0.037	0.149	0.019	0.004	1.597	0.227	0.179	2.8	-14.8	
WC-4	Webb Caves-crawle	PDC	34.3	8.755	1.96	0.0200	50	6.07	0.005	1214	0.83	5.09																
BBT-1	Brady's Bluff Trail	Jordan SS					25																					
BBT-2	Brady's Bluff Trail	Jordan SS	247	273.145	2.06	0.5448	>>500	43.449	0.272	160	2.41	1119.63																
PP-1	Parrot Plaque	Jordan SS					25																					
Iowa																												
HOS	Mt Hosmer Overlook Cave	PDC	72	24.333	14.16	0.0487	50	6.293	0.01	629	0.89	214.55	7.9	36.28	54.87	0.017	5.675	2.288	0.052	0.166	0.008	0.002	1.564	0.014	0.27	6.6	-8.5	
Illinois																												
MPSP-1	Miss Pal SP- Sentinel Bluff C	Hopkinton Dolomite					>500	123.6	<1	N/A	0.92	2654.00																
MPSP-2	Miss Pal SP- Sentinel Bluff C	Hopkinton Dolomite	5.105	458	11.35	1.2392	>500																					
MPSP-3	Miss Pal SP- Sentinel Bluff C	Hopkinton Dolomite					>500																					
MPSP-3 (2)	Miss Pal SP- Sentinel Bluff C	Hopkinton Dolomite	54.3	305.9	13.04	0.9416	>>500	129.1	<0.1	N/A	1.15	3960.00	109.1	706.5	767.3	0.021	50.13	74.25	1.756	0.065	0.197	0.596	2.184	0.060	5.676	102.5	-3.1	
MPSP-4	Overlook Rockshelter	Hopkinton Dolomite	4.615	160.5	6.72	0.3614	>500	142.6	<1	N/A	3.24	795.90	32.4															
MPSP-4 (2)	Overlook Rockshelter	Hopkinton Dolomite	50.5	170.7	5.66	0.4106	500	142.9	<0.1	N/A	3.67	875.10	35.7	197.8	228.4	0	60.76	39.78	0.503	0.083	0.251	0.710	3.41	0.000	5.772	32.3	-4.9	
CIR-1	Cave in Rock	St Genv/SLL ls					25/50																					
FBC-1	Fountain Bluff C	Makanda SS					500	507.7	<1	N/A	0.66	2618.00																
FBC-2	Fountain Bluff C	Makanda SS	5.08	106.9	11.66	0.2650	500																					
FBC-3	Fountain Bluff C	Makanda SS			18.96	0.0000	10																					
BSS-1	Bell Smith Springs	Makanda SS																										
GC-1	Giant City SP	Makanda SS																										
GC-2	Giant City SP	Makanda SS																										
GC-3	Giant City SP	Makanda SS																										
Kentucky																												
GSC-1	Great Saltpetre C	St Genv/SLL ls					>500																					
GSC-2	Great Saltpetre C	St Genv/SLL ls					>500																					
GSC-3	Great Saltpetre C	St Genv/SLL ls	22.6	379.6	2.91	0.9150	>>500	42.9	<0.1	N/A	<0.5	187.70	32.7	365.1	30.48	0	185.5	15.79	2.477	0.055	0.14	0.031	1.407	0.209	0.216	29.3	-5.5	
GSC-4	Great Saltpetre C	St Genv/SLL ls																										
GSC-5	Great Saltpetre C	St Genv/SLL ls																										
GSC-6	Great Saltpetre C	St Genv/SLL ls																										
GSC-7	Great Saltpetre C	St Genv/SLL ls																										
GSC-8	Great Saltpetre C	St Genv/SLL ls																										
GSC-9	Great Saltpetre C	St Genv/SLL ls	19.25	32.13	3.19	0.0893	100/250	3.46	<5	N/A	<0.2	13.77																
GSC-10	Great Saltpetre C	St Genv/SLL ls					250	3.11	<5	N/A	<0.2	36.45																
GSC-11	Great Saltpetre C	St Genv/SLL ls	19.12	53.72	3.94	0.1804	250	3.11	<5	N/A	<0.2	36.45																
GSC-12	Great Saltpetre C	St Genv/SLL ls	22.9	50.6	4.76	0.1243	250	2.69	<1	N/A	<0.05	12.80	4.4	61	6.31	0.022	6.758	4.754	0.272	0.036	0.13	0.008	0.95	0.000	0	4.0	-5.0	
GSC-12(2)	Great Saltpetre C	St Genv/SLL ls																										
GSC-13	Great Saltpetre C	St Genv/SLL ls	25.7	620.32	7.24	0.9372	>500	42.94	<5	N/A	<0.2	1195.13																
GSC-14	Great Saltpetre C	St Genv/SLL ls																										
GSC-15	Great Saltpetre C	St Genv/SLL ls																										
GSC-16	Great Saltpetre C	St Genv/SLL ls																										
GSC-17	Great Saltpetre C	St Genv/SLL ls																										
Tennessee																												
TN-1	Saltpetre C	N/A					0																					
TN-2	Saltpetre C	N/A	38.9	42.835	6.54	0.1248	250	7.348	0.1	73	0.10	4.98	4.1	54.27	11.57	0	1.456	4.028	0.279	0.129	0.009	0.002	2.067	0.013	0.067	3.8	-3.5	
TN-3	Saltpetre C	N/A	9.6	272.94	2.91	0.9378	>500	12.646	0.1	126	0.10	58.04	21.2	313.9	64.19	0	5.163	21.75	1.203	0.079	0.008	0.002	0.318	0.005	0.026	21.8	1.2	

TABLE 4.3. Nitrate Values for Surface Control Soils				
CODE	LOCATION	COUNTY	DATE COLLECTED	NITRATE STRIP (ppm NO₃)
FSS-1	Frontenac SP	Goodhue	10/28/2011	0
FSS-2	Frontenac SP	Goodhue	10/28/2011	10
FSS-3	Frontenac SP	Goodhue	10/28/2011	10
FSS-4	Frontenac SP	Goodhue	10/28/2011	10
FSS-5	Frontenac SP	Goodhue	10/28/2011	10
FSS-6	Frontenac SP	Goodhue	10/28/2011	0
FSS-7	Frontenac SP	Goodhue	10/28/2011	0
FSS-8	Frontenac SP	Goodhue	10/28/2011	0
FSS-9	Frontenac SP	Goodhue	10/28/2011	0
FSS-10	Frontenac SP	Goodhue	10/28/2011	10
FSS-11	Frontenac SP	Goodhue	10/28/2011	0
FSS-12	Frontenac SP	Goodhue	10/28/2011	0
LSS-1	Latsch SP	Goodhue	11/8/2011	0
LSS-2	Latsch SP	Goodhue	11/8/2011	0
LSS-3	Latsch SP	Goodhue	11/8/2011	0
LSS-4	Latsch SP	Goodhue	11/8/2011	0
LSS-5	Latsch SP	Goodhue	11/8/2011	10
LSS-6	Latsch SP	Goodhue	11/8/2011	10
LSS-7	Latsch SP	Goodhue	11/8/2011	0

4.3.1 Nitrate

It has long been emphasized (e.g., Prince, 1923; Karraker, 1927; Schmidt, 1982; Parkin, 1987; Christensen et al., 1990; Murray et al., 1995) that the nitrate content of soils is subject to great variability. Schmidt (1982), for example, describes how the nitrate content of “a single farm site in Minnesota” varied widely even on the same date of sampling. Many of the crevices in this project were sampled only once and despite the inherent variability of nitrate concentrations they are valid spot concentrations. But it would not be safe to say that they represent a nitrate “average” for any given cave, without much additional sampling.

Nitrate concentrations in caves that were large enough to be sampled in multiple spots (rather than just once) were quite variable. The best Minnesota examples were the Oneota maze caves of Goodhue County, where samples taken as close as one meter apart sometimes had widely differing values. Samples taken in Miles Cave, for example, had nitrate strip values ranging from 50 to 500 ppm nitrate. This sporadic distribution is probably correlated with the former location of decaying organic matter, such as scats, urine, or carcasses, which may no longer be visible to the naked eye. Under drips, on the other hand, accelerated denitrification could be occurring. These are likely examples of microsites (Parkin, 1987; Christensen et al., 1990; Murray et al., 1995) or the “biogeochemical hot spots” concept described by McClain et al. (2003).

Several of the Mystery Cave outliers (caves along the South Branch of the Root River that almost certainly connect with Mystery Cave physically, although not large enough for human explorers to traverse the connection) were sampled and found to have high nitrate (>500 ppm) whereas samples from Diamond Cavern in Mystery Cave, one of the driest places in the latter cave and one of the few places where gypsum needles form, was found to have 0 ppm nitrate. There seems to be a nitrogen mineralization gradient (Pastor et al., 1984) from the periphery of the system to its deep interior.

While virtually all of the Merck strips showed zero *nitrite*, Damview Cave was exceptional in having a high nitrate concentration (3.1 wt%) in conjunction with high nitrite concentration (25 ppm). Nitrite is the precursor of nitrate, so this

would be expected. Too much nitrite accumulation, however, inhibits the respiratory activity of the soil (Tyler and Broadbent, 1960).

4.3.2 Nitrate and Soil Moisture (Figure 4.2)

Different investigators have reported a range of values for the optimum moisture content for nitrification. Early on, the famous microbiologist Waksman (1927) reported that “nitrate formation in soil is at a maximum with the highest moisture which will not saturate the soil.” Sabey (1969) related rates of nitrate formation to soil moisture tension. Stanford and Epstein (1974) noted that nitrogen production was optimized at “field capacity,” which for the 9 widely varying soils listed in their paper, ranged from 10.2 to 35.3% soil water content. Linn and Doran (1984) showed that nitrification of organic matter in the soil increased with moisture content until water filled 60% of the total pore volume. Above that, water-logging occurs, the attendant anaerobic conditions favor denitrification, and leaching also occurs. On the low end, therefore, sediments are water-limited, whereas on the high end they are aeration-limited.

The moisture values measured in the crevice sediments of this project ranged from <1% to 28% and are shown in **Figure 4.2**. Within Miles Cave alone, soil moisture was variable from 2.5 to 8.2%. The three Mystery Cave outliers that were sampled (Copeman’s Cave, Petrified Indian Cave, Windcourse Cave) were at the high end of the range, with from 18.0 to 27.5% moisture. The Diamond Caverns sample had a moisture content of 2.9% and was devoid of nitrate. Most of the samples are on the dry side for optimal nitrate production, with 65% of the

samples containing less than 10% moisture. Perhaps the sediments were damper when nitrification was occurring. *This suggests that the nitrification occurs during only parts of seasonal or longer moisture cycles.* Such moisture cycles would interact with the known temperature dependency for nitrate formation.

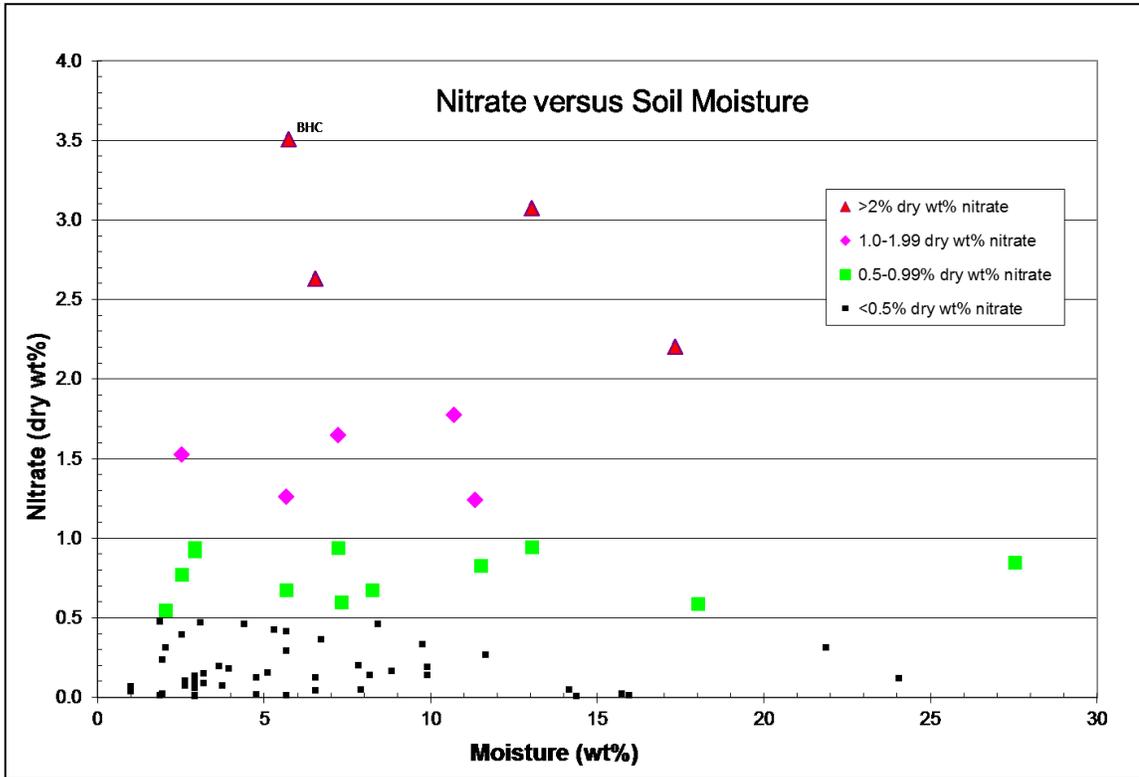


Figure 4.2. Dry weight-percent nitrate versus weight-percent sediment moisture.

The highest nitrate sediment sample (35,000 ppm), from Black Hole Cave (BHC), contained 5.75% moisture. The soil moisture in that soil had a nitrate concentration of about 5.7 g NO₃/100 g H₂O—just under a 1 Molal solution. All of that nitrate should have been in solution. That concentration is well below the solubility of Ca(NO₃)₂ in water, which is about 120 g/100 g H₂O at 20°C. *This*

observation is consistent with a hypothesis that the nitrates in these sediments are in concentrated soil water films.

The entire data set was divided into four series based on the concentration of nitrate: black squares (<0.5% dry weight of nitrate), green squares (0.5 to 1% dry weight of nitrate), magenta diamonds (1 to 2% dry weight of nitrate), and red triangles (>2% dry weight of nitrate). These four grades of sediment can be tracked through the sequence of scatterplots. In **Figure 4.2**, the low nitrate values are associated with 1 to 24% moisture; intermediate, 2 to 28%; high, 2 to 11%; and highest, 6 to 18%.

4.3.3 Piper Diagrams (Figures 4.3a and 4.3b)

Piper diagrams are used to classify and group natural waters and are useful for visualizing the major element chemistry of the soil solutions. The conventional, two-dimensional Piper diagram consists of coupled cation and anion trilinear diagrams with a lumped cation and anion quadrilateral between and above the two trilinear diagrams. Each of these three subdiagrams show the relative ionic abundance as a fraction of the total equivalents on that subdiagram. **Figure 4.3a** is a modified Piper diagram in which the concentration of the solutions is shown as a vertical line rising from the conventional Piper diagram. This permits the concentrated solutions to be visibly differentiated from the more dilute solutions. (Concentrated and dilute solutions with the same relative ion abundances plot at the same points in conventional Piper diagrams.) All of the elevated nitrate level solutions are concentrated solutions.

Most of the concentrated soil slurries from the UMV plotted in the upper apex of the quadrilateral field. Using Piper's (1944) classification scheme and original terminology for water-types, these waters are simultaneously classified as being in Area 1: alkaline earths exceed alkalis; Area 4: strong acids exceed weak acids; and Area 6: secondary salinity (non-carbonate hardness) exceeds 50 percent.

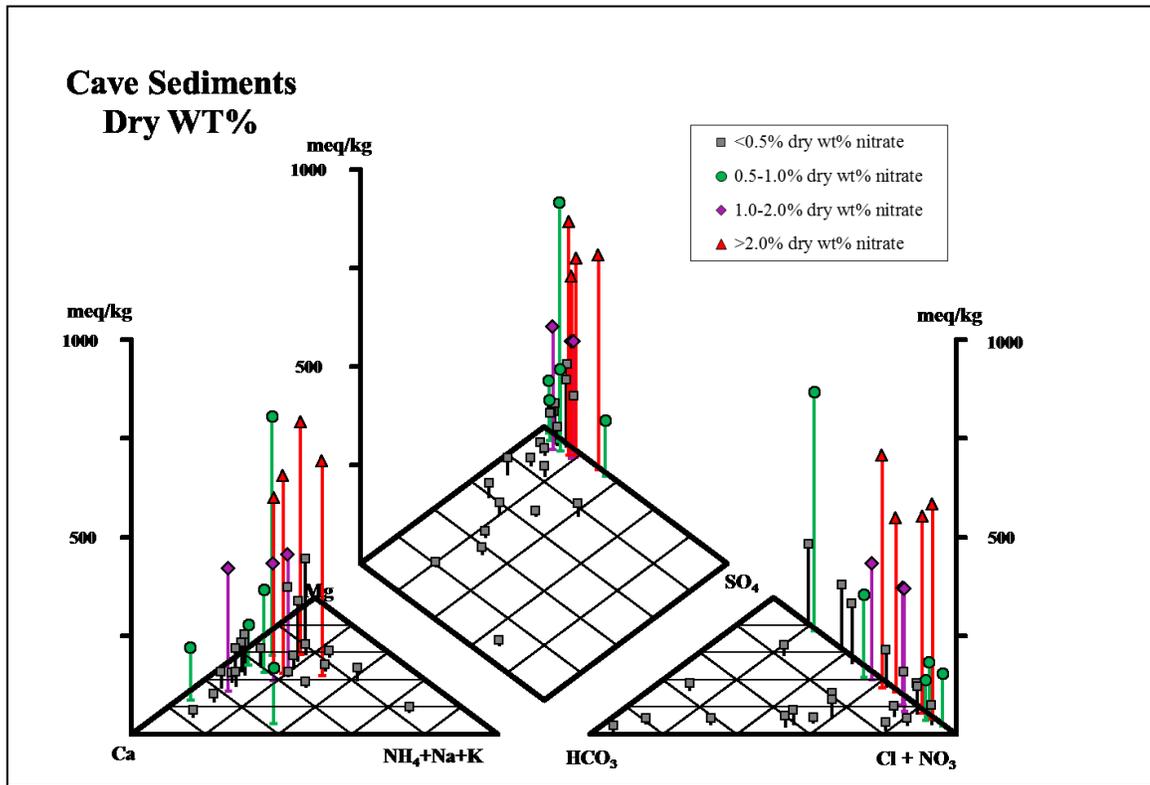


Figure 4.3a. Three-dimensional Piper diagram of sediment slurry solutions.

All solutions from sediments with >0.5 wt% nitrate and the most concentrated one third of the <0.5 wt% nitrate solutions plot along the SO_4 to $\text{Cl} + \text{NO}_3$ axis of the anion triangle, i.e., solutions from high nitrate sediments have

only small amounts of HCO_3 relative to the SO_4 , Cl , and NO_3 . These solutions plot near the top of the combined-ion quadrilateral. The least concentrated two thirds of the solutions from <0.5 wt% sediments contain significant to dominant amounts of HCO_3 . The cation triangle is more complicated but the solutions from the four highest nitrate sediments have Mg concentrations between 60 and 80%, Ca concentrations between 20 and 40%, and Na + K concentrations of 10 to 30%. The solutions from the high nitrate samples have Mg/Ca molar ratios >1.

Most of the samples were collected from voids in Prairie du Chien carbonates. Typically, Prairie du Chien groundwaters, like Minnesota waters generally, are calcium bicarbonate waters (Wall and Regan, 1994). The concentrated UMV cave sediment slurry waters in this study are different. Most of the concentrated UMV cave sediment waters contained cations plotting as magnesium-rich, while most of the anions plotted as nitrate/chloride rich with a few that were sulfate-rich. Thus, most of them could be called magnesium/calcium nitrate/chloride waters. *The excess of Mg compared to Ca is suggestive of a calcite precipitation mechanism operating on the most concentrated solutions.*

Figure 4.3b is a modified Piper diagram of the soil solutions for which cation analyses were not performed, because these samples generally had low nitrate according to the test strips. The same pattern as seen in **Figure 4.3a** is evident, showing that no bias was introduced to the anion pattern by the selection process.

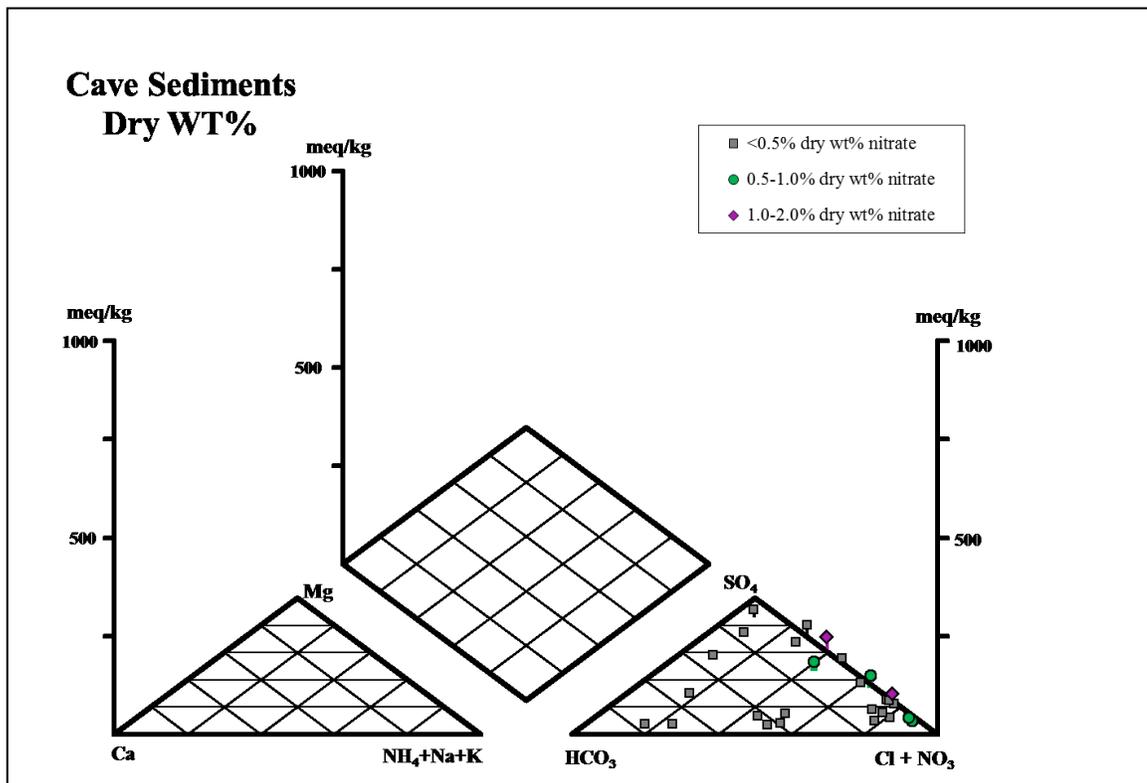


Figure 4.3b. Three-dimensional Piper diagram of sediment slurry solutions for which no cation analyses were performed.

4.3.4 Calcium / Magnesium Ratio (Figure 4.4)

The predominant soluble cations in the samples are calcium and magnesium. Calcium/magnesium ratios are a good indicator as to whether water has been flowing through limestone or dolomite, respectively (Jacobson and Langmuir, 1970). When the ratio is greater than one it indicates water that has flowed through limestone. When the ratio is around or less than one it suggests that the water flowed through dolomite or that evaporation has precipitated calcite, leaving excess magnesium behind. Since magnesium and calcium have significantly different ionic radii, the magnesium ion is excluded from the calcite

lattice with each successive recrystallization, concentrating magnesium in the residual (Murray, 1954).

For the total data set, the Ca/Mg ratio (on a molar basis) ranges from 0.27 (RBW) to 7.26 (GSC-3-2) with an average of 1.36. The high ratios are those belonging to the Mississippian limestone formations of the southeastern United States (GSC and TN series) while the low ratios belong to the Prairie du Chien Group dolomites. The data subset that includes the Prairie du Chien dolomites in Minnesota ranges from 0.27 (RBW) to 2.19 (PNP-E) with an average of 0.99. The fact that both end members of this range came from Frontenac State Park, and that all intermediate values compass the range of variation for Minnesota as a whole, suggests significant compositional variation within this lithological group.

Samples taken from higher, more exposed rock shelters along the Mississippi river bluffs show Ca/Mg molar ratios less than one, suggesting that evaporation has precipitated calcite and depressed the ratios (**Figure 4.4**). Some of these river bluffs are subject to thermals, i.e., warm, rising air currents on summer days, which increase evaporation. Examples of such samples are BH, DMVI, FSP-3.5f, GPCLL, RBW, and Y-6 from Minnesota; TBPC from Wisconsin; and MPSP-3 and MPSP-4 from Illinois. The most consistent pattern appears to be perhaps an evaporation/precipitation cycle or evaporation sequence whereby samples become more magnesium rich and nitrate rich with time. The caves studied here, however, are not exact analogs of the “closed basins” described by Hardie and Eugster (1970).

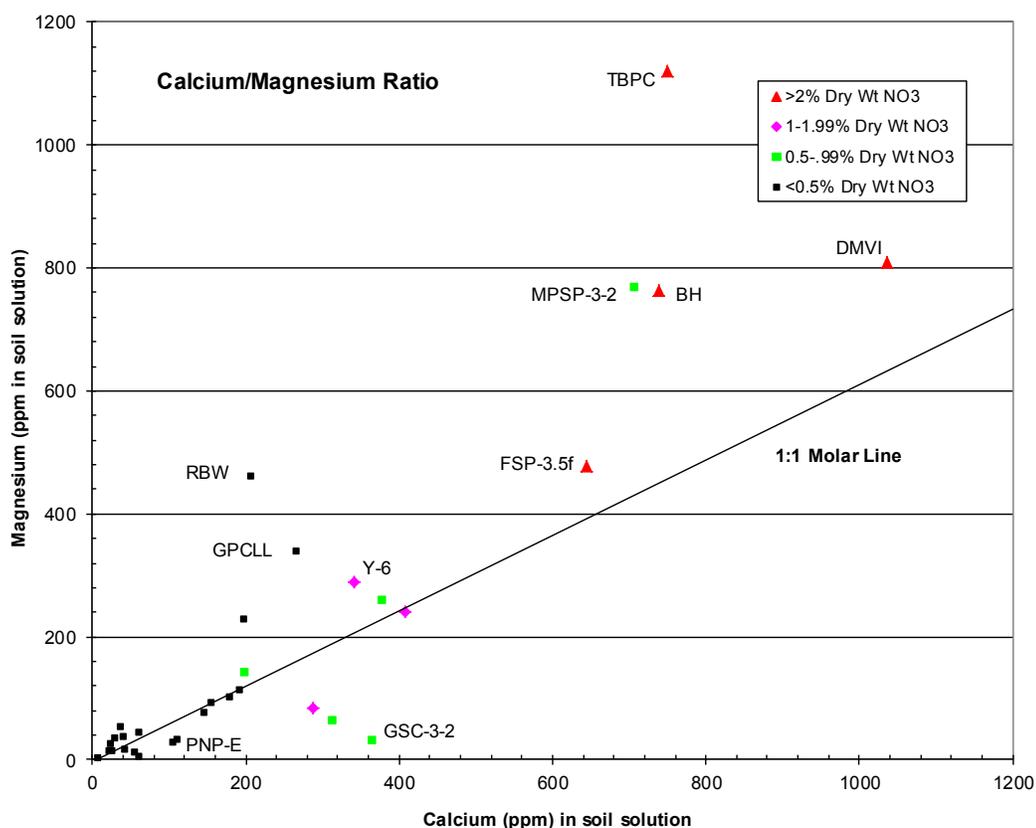


Figure 4.4. Calcium/magnesium ratio in the sediment slurry solutions.

4.3.5 Nitrate versus Calcium + Magnesium (Figure 4.5)

Figure 4.5 is a plot of NO₃ versus Ca + Mg on a molar basis. The red 1-to-2 molar line shows the locus of soil solutions from the sediments where the dominant nitrate species is a mixture of Ca(NO₃)₂ and Mg(NO₃)₂. Most of the samples with >0.5 wt% nitrate (green squares, magenta diamonds, and red triangles) plot between the 1-to-1 and 1-to-2 molar lines. The red triangle and green square above the 1-to-2 line indicate that some other cation in solution is necessary to balance the NO₃, perhaps Na in these cases. The points below the 1-to-2 line

indicate the presence of an additional significant anion: Cl, HCO₃, and SO₄, in these cases.

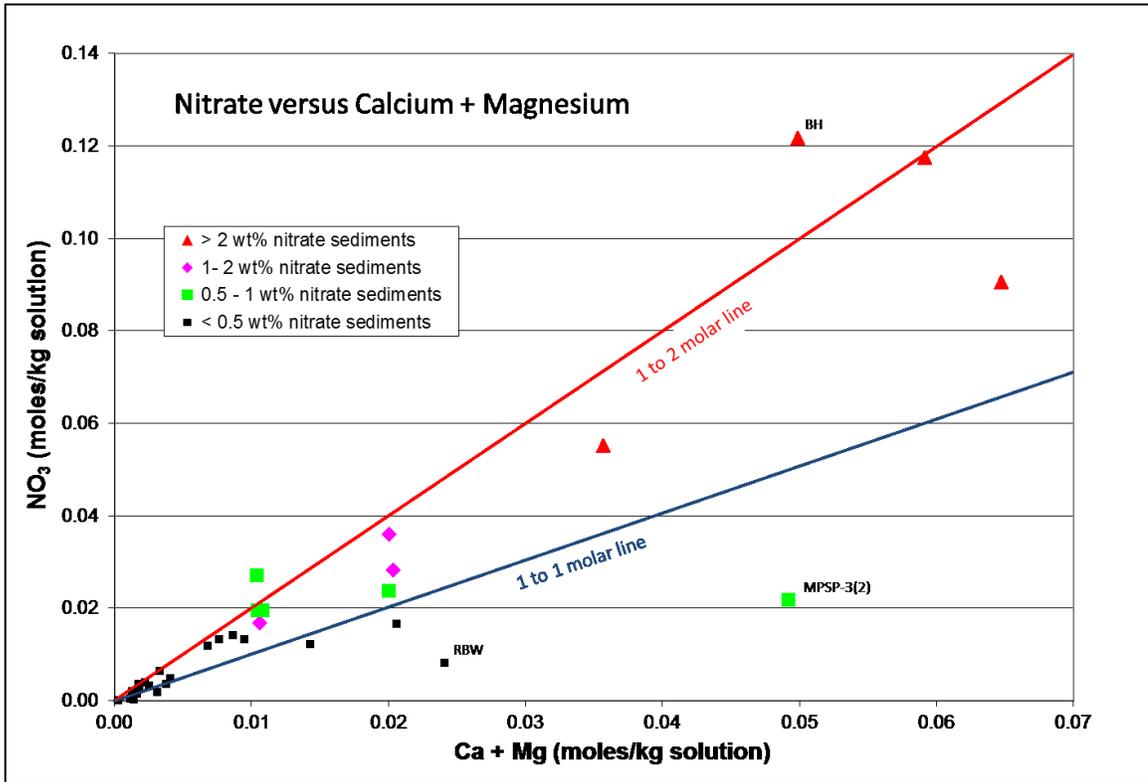


Figure 4.5. Nitrate versus calcium + magnesium in sediment slurry solutions.

The 1-to-1 molar line in **Figure 4.5** shows the locus of solutions that would result from the simple dissolution of calcite or dolomite with nitric acid. Some of the <0.5 wt% sediments solutions (black squares) plot along the lower end of the 1-to-2 line, some plot between the lines, and several plot along the 1-to-1 line. One black square (RBW) and one green square (MPSP-3-2) plot well below the 1-to-1 line. These two points indicate the importance of other anions in some soil solutions—sulfate in the case of MPSP-3-2. Some of these solutions from nitrate-rich sediments have a magnesium sulfate composition, similar to Epsom salts.

The low nitrate samples represent the first step in the multi-step process that produces the most concentrated nitrate sediments. *This suggests that the process leading to the highest nitrate levels moves through calcium/magnesium nitrate/bicarbonate compositions to magnesium nitrate compositions.*

4.3.6 Calcium versus Sulfate (Figure 4.6)

Gypsum (calcium sulfate) tends to be stable only in very dry conditions, such as those in the caves of the arid southwestern U.S., but it has been identified in Diamond Caverns, the driest passage in Mystery Cave, Minnesota (Calvin Alexander, pers. comm.).

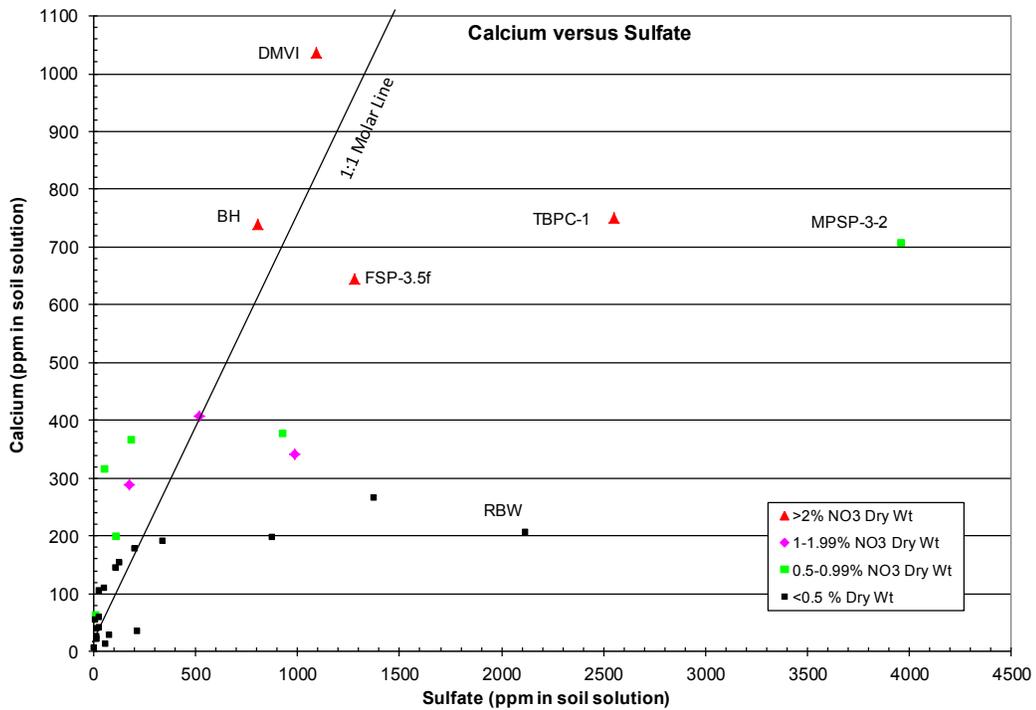


Figure 4.6. Calcium versus sulfate in the sediment slurry solutions.

In **Figure 4.6**, MPSP-3, RBW, and TBPC, are seen to have excess sulfate in relation to calcium. DMVI, by contrast, is enriched in calcium. Bird and bat guanos are well known to contain significant amounts of calcium sulfate (Hutchinson, 1950: 463), which is a possible biological source of calcium sulfate in the UMV waters. This could explain the general correlation of increased calcium sulfate with increased nitrate.

4.3.7 Strontium / (Calcium + Magnesium) Ratio (Figure 4.7)

According to Odum (1951), "Strontium moves in a cycle qualitatively resembling that of calcium but quantitatively different, and is about 1/500 as concentrated in most phases." Strontium behaves very much like the more-abundant calcium. However, the lattice fit is not perfect, so upon successive crystallizations of calcite and/or aragonite, strontium is released from the lattice and tends to concentrate in the residual (Holland et al., 1964). Also, during the dolomitization of limestones, magnesium tends to replace strontium (Goldschmidt, 1958: 248).

The strontium/(calcium+magnesium) molar ratio has an average of 5.2×10^{-4} for the entire data set. The highest value was for a Mississippian carbonate (GSC-3) and lowest for an Ordovician dolomite (TRC-1). The strontium/calcium molar ratio ranges from 3.7×10^{-4} (LVC) to 3.6×10^{-3} (PhilC), with an average of 9.5×10^{-4} . In the samples from the Prairie du Chien Group in Minnesota, the average Sr/Ca ratio is 7.3×10^{-4} . The average for the Mississippian limestones of Kentucky and Tennessee is higher, 2.3×10^{-3} . The two samples from Saltpetre Cave, Tennessee (TN-2 and TN-3) have a high Sr/Ca ratio, suggesting that

recrystallization has excluded strontium from the lattice, consistent with the cycling hypothesis presented above. Higher concentrations in the residual also correspond with elevated cliff crevices (BH and MPSP-3) where evaporation may have occurred. The strontium/magnesium molar ratio displays the same pattern as the Sr/Ca ratio, and for the same reasons (**Figure 4.7**).

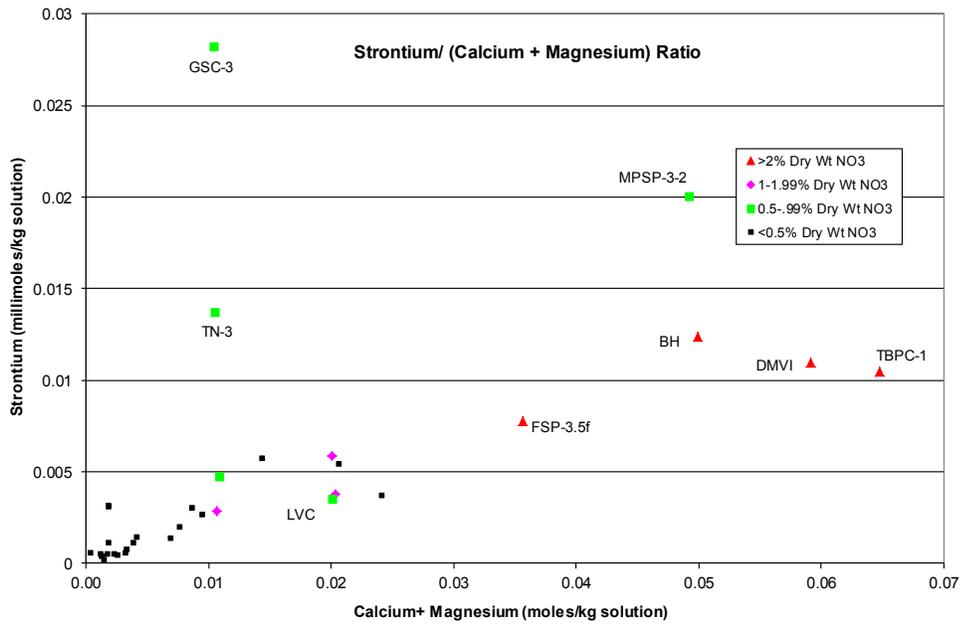


Figure 4.7. Strontium / (calcium + magnesium) ratio in the sediment slurry solutions.

4.3.8 Nitrate versus Chloride (Figure 4.8)

Nitrate and chloride are often indicators of impacted water quality. The chloride values shown here are the clearest indicators of which caves were impacted by liquid animal waste. As seen in **Figure 4.8**, the highest nitrates (BH, DMVI, FSP-3.5f, and TBPC) also have high chloride values. The exact source of the urine, whether bird or mammalian, has not been determined.

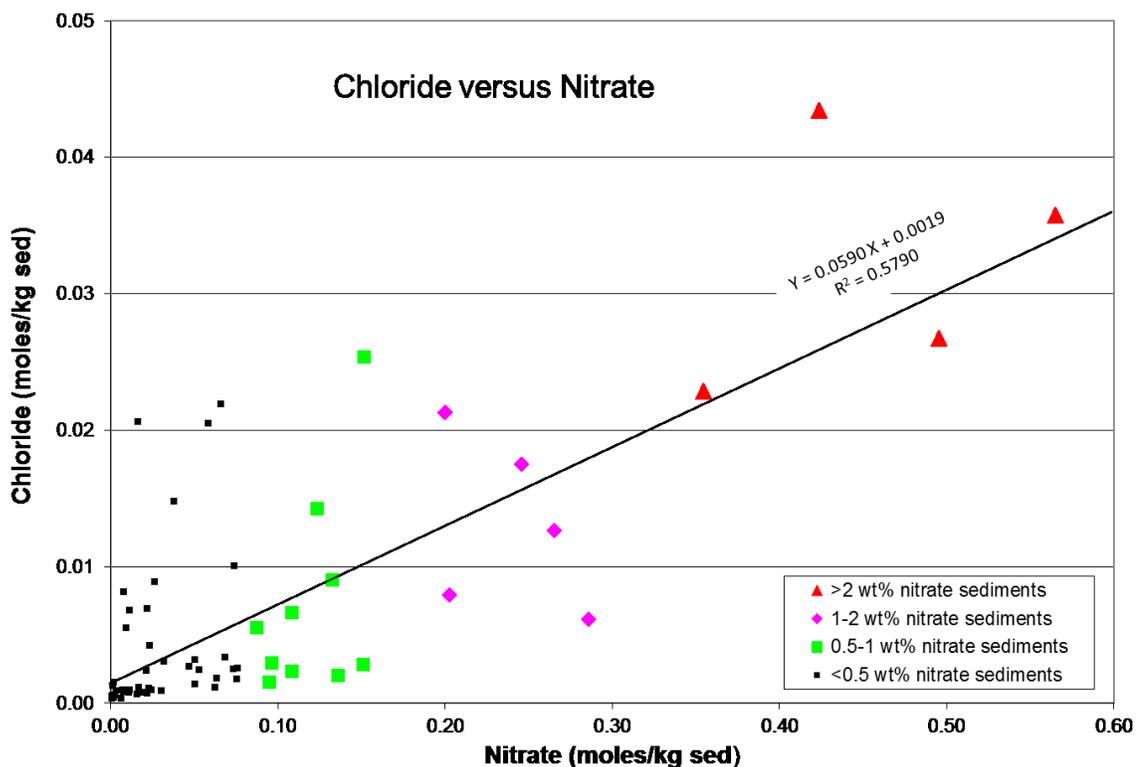


Figure 4.8. Nitrate versus chloride in the sediment slurry solutions.

The regression line shown in **Figure 4.8** indicates an apparent weak correlation, $R^2 = 0.58$, between nitrate and chloride in the soil waters. The processes that produce the highest nitrate contents also concentrate the chloride present in the samples. However, a wide range in the nitrate to chloride ratios is evident in the samples with lower concentrations of nitrate and chloride. Samples with elevated nitrate but low chloride are common—as are samples with elevated chloride but relatively low nitrate.

4.3.9 Sodium versus Chloride (Figure 4.9)

According to Panno et al. (2006) sodium and chloride can be used as indicators of the source of groundwater. Sodium enrichment is sometimes from burning vegetation (Drever, 1988), sometimes from parent material enrichment, as from the weathering of sodium-containing igneous rocks, and sometimes from soil dust (Gorham, 1961). Chloride enrichment is often due to animal wastes.

As plotted in **Figure 4.9**, a majority of samples are enriched in chloride relative to sodium. Samples DMVI, BH, and TBPC, are enriched in absolute amounts of sodium and chloride, suggesting a urine source, which is consistent with the observation of bird feathers at these sites.

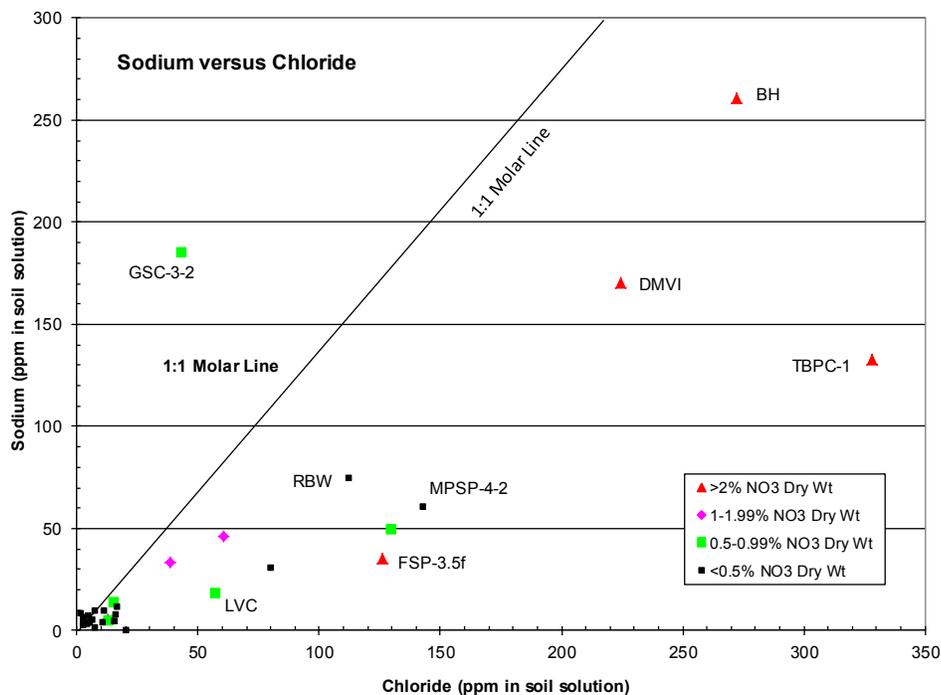


Figure 4.9. Sodium versus chloride in the sediment slurry solutions.

4.3.10 Chloride / Bromide Ratio (Figure 4.10)

Chloride and bromide are conservative ions often used to identify groundwater contamination (Davis et al., 1998; Hudak, 2003). According to Davis et al. (1998), “Atmospheric precipitation will generally have mass ratios between 50 and 150; shallow ground water, between 100 and 200; domestic sewage, between 300 and 600; water affected by dissolution of halite, between 1000 and 10,000; and summer runoff from urban streets, between 10 and 100.” Commercial “potash” fertilizer is actually sylvite, KCl, and typically has Cl/Br ratios in the 1000 to 10,000 range.

Figure 4.10 is a plot of the chloride and bromide contents of the soil slurries. Many of the samples collected were below the detection limits for bromine and so could not be included in the graph. In addition, for some of the highest nitrate samples (e.g., DMVI), the large nitrate peak in the IC anion analysis masked the small bromide peak, so these points could not be plotted. FBC-2 was removed because it came from a known “party cave” with a campfire ring and so contamination was suspected.

The Cl/Br ratios in a minority of samples with enough bromide to be accurately measured are in the range of atmospheric precipitation, i.e., with little evidence of the high Cl/Br ratios in artificial fertilizer. High nitrate samples BH and FSP-7 appear to contain chlorine and bromine from atmospheric sources. Samples TBPC-1 and FSP-3.5f are within the range for animal waste sources.

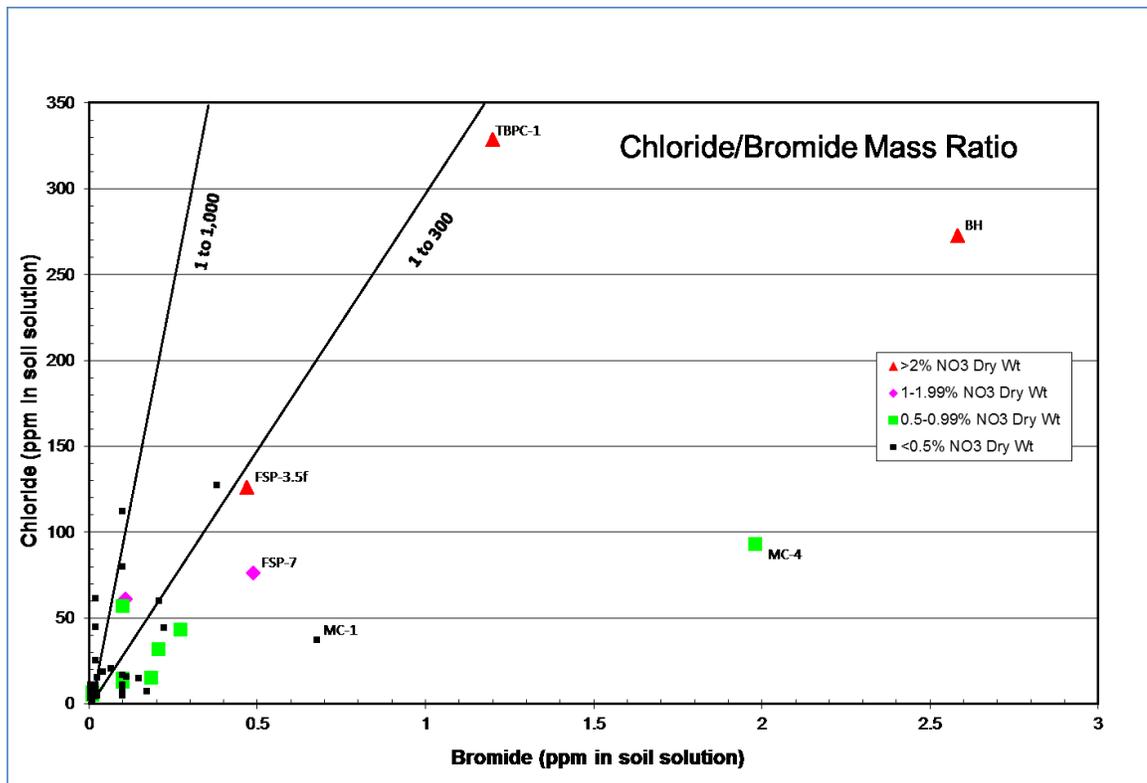


Figure 4.10. Chloride/bromide ratio in the sediment slurry solutions.

Two samples (MC-1 and MC-4) from Miles Cave in the city of Hastings, MN, have very low Cl/Br ratios. Miles Cave lies under a grain elevator and bromide-containing fumigants may have contaminated the cave. Miles Cave is also immediately adjacent to city streets and runoff from the streets may have contributed to the observed Cl/Br ratios.

4.3.11 Nitrate versus Soluble Phosphate (Figure 4.11)

While nitrate is very soluble, phosphate has low solubility. Phosphate is associated with vertebrate excretions (Hutchinson, 1950), so where we find elevated nitrate in the absence of phosphate it suggests that the nitrate is not

derived from animal wastes, but rather according to the seeping groundwater model described by Hill (1981).

The relationship between nitrate and soluble phosphate is shown in **Figure 4.11**, where the phosphate is seen to be two orders of magnitude lower than that of nitrate. However, it must be emphasized that the extraction method only picks up water-soluble constituents so there is likely a considerable amount of bound, insoluble phosphate, especially in the form of calcium phosphate, that is not showing up in the analyses.

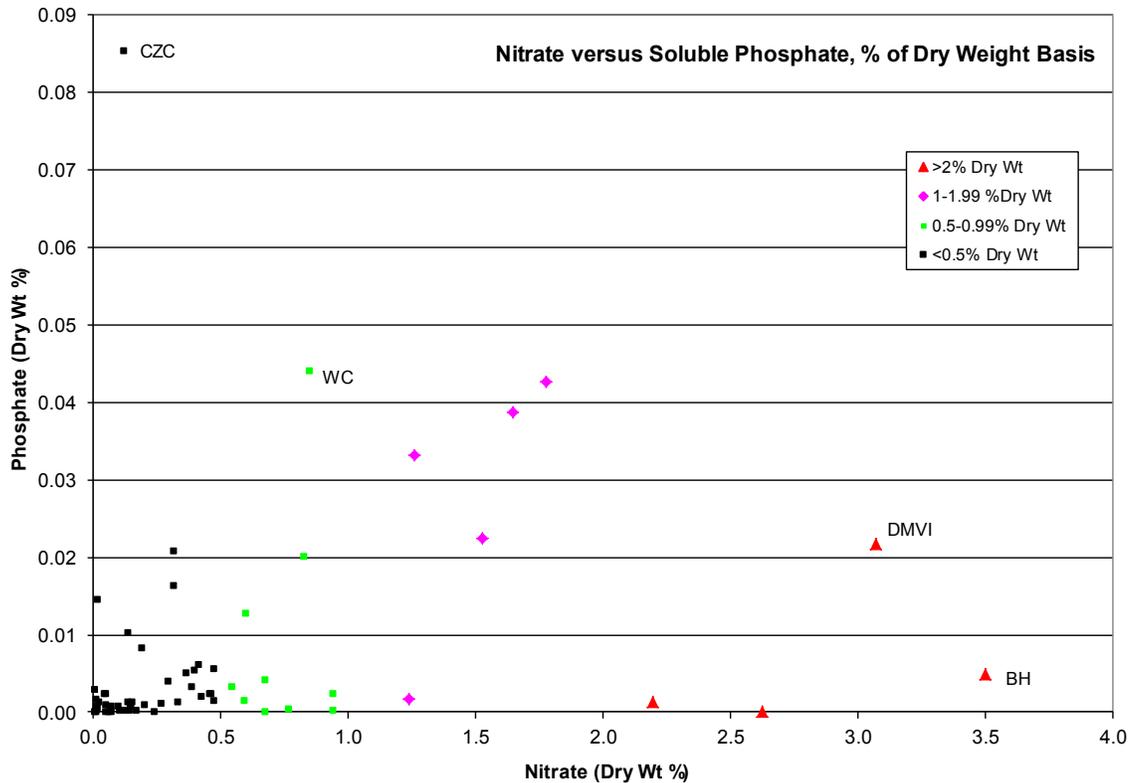


Figure 4.11. Nitrate versus soluble phosphate, % of dry weight basis.

The two samples from Saltpetre Cave, Tennessee (TN-1 and TN-2) had elevated nitrate, ranging from 0.12 to 0.94%. The data from Great Saltpetre Cave, Kentucky, was not plotted, because the phosphate was below the detection limits, but this suggests that the nitrate originates according to Hill's (1981) model, rather than being the excretion products of bats or other animals.

All of the higher phosphate values ($>0.02\%$) are from Minnesota caves. Sample CZC had the highest phosphate (0.855 ppm) while having low nitrate (0.1166 ppm). Furthermore, all of the lower phosphate ($<0.02\%$) associated with higher nitrate ($>1.0\%$) values also belong to Minnesota caves, except for the Trenton Bluff Prairie Cave (TBPC), located in Wisconsin. Among the sites sampled, the most anomalous were the "bird" caves, such as Poop Ledge Cave (PLC), where pigeon guano and feathers were directly observed, and the Trenton Bluff Prairie Cave, which contained living turkey buzzard chicks when sampled. There was a pronounced smell of ammonia in both, suggesting volatilization, as happens in rookeries (Lindeboom, 1984). However, while both of these caves had elevated nitrate, TBPC having the third highest value of nitrate in the data set (2.6%), only PLC also had elevated soluble phosphate as well, perhaps reflecting the freshness of the guano. These issues are examined further in the next section.

4.3.12 Sediment Fusion Analysis (Figure 4.12)

To quantify the amount of insoluble phosphate in the sediments, six samples were analyzed by Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES). Three of the samples (BH, PETI, and TBPC) were high-nitrate cave sediments, while the other three (LSS-4, S-5, and S-9) were surface control samples. The surface soils ranged from 0.0155 to 0.0751 wt% phosphate, whereas the cave sediments were significantly higher, ranging from 0.2160 to 0.6444 wt% phosphate. The phosphate values for the cave sediments as determined by fusion are considerably higher than the corresponding soluble concentrations, confirming that most of the phosphate present in the sediments is in the insoluble form. Since the surface soils (usually the most important parent material of the eventual crevice sediments) were revealed by sediment fusion to be low in phosphate relative to those sediments, it was concluded that the insoluble phosphate was not part of phosphate minerals, such as apatite, but rather added from biological sources within the crevice. Most of the surface samples, collected from Frontenac State Park, belong to the Frontenac Series, described in the Goodhue County Soil Survey as “soils formed in loess and residuum from limestone. The native vegetation was deciduous hardwood” (Poch, 1976). While the sediments, especially in the mechanical crevices, are largely allochthonous, residual clays from limestones are known to be low in phosphate, so that even with autochthonous sediments in limestone caves the amount of calcium phosphate deriving from the limestone would be quite small.

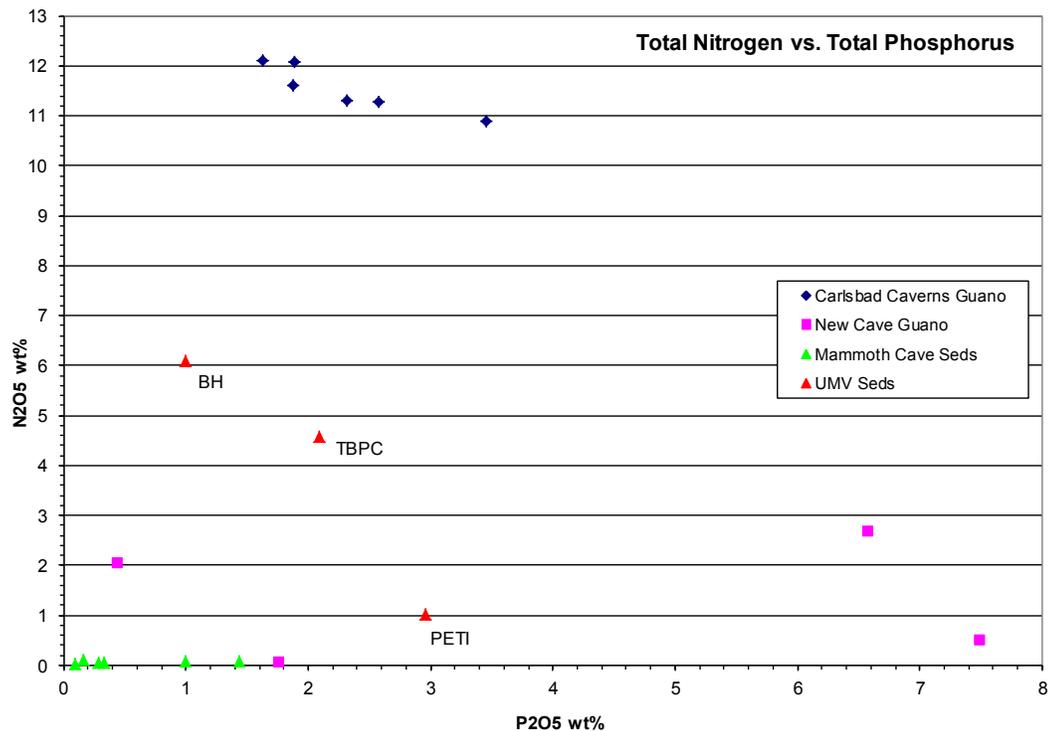


Figure 4.12. Total nitrogen versus total phosphorus, plotted with the data points from Hill's (1981) Figure 9.

This sediment fusion data set (Table 4.4) was plotted onto Figure 9 from Hill's (1981) paper, and is presented here as Figure 4.12. To maintain her conventions, the nitrate and phosphate from my study has been calculated as N_2O_5 and P_2O_5 , respectively. As explained by Hill (1981), fresh guano (such as that from Carlsbad Caverns) has a high nitrogen content, which decreases as the guano is weathered and leached, until it drops to the levels shown for the much older New Cave guano. While Hill (1981) has also plotted her Mammoth Cave sediments (which are clastic, not guano), which do not seem to contain much nitrogen, it is important to note that Hill's data set is incomplete—her high-nitrate samples from Mammoth and Dixon caves are not plotted at all, and it was

TABLE 4.4. Major Elements in Sediments as Compounds

Sample Name	Al ₂ O ₃ wt%	BaO wt%	CaNO ₃	CaSO ₄ .2H ₂ O	CaCO ₃	FeO wt%	K ₂ O wt%	MgCO ₃ wt%	MnO ₂ wt%	NaCl	Na ₂ O	P ₂ O ₅ wt%	SiO ₂ wt%	SrO ₂ wt%	TiO ₂ wt%	ZrO ₂ wt%	Total %
Cave Sediments																	
BH	2.89	0.0231	5.7624	0.6707	21.4968	9.7102	0.9130	23.4053	0.1269	0.2088	0.2773	0.4948	21.6003	0.0087	0.1156	0.0034	87.7117
PETI	3.44	0.0280	0.9684	0.0763	46.7077	1.3386	1.1136	11.5873	0.0623	0.0087	0.3359	1.4767	25.1425	0.0259	0.1633	0.0049	92.4763
TBPC	2.42	0.0218	4.3213	2.4936	26.4168	3.4751	1.1884	24.9204	0.1150	0.2952	0.1247	1.0455	22.2755	0.0094	0.1139	0.0033	89.2377

not clear why after the lapse of years (Carol Hill, pers. comm., 2013). This is why my data set (BH, PETI, and TBPC) seems to plot higher than Hill's (1981). These three points are higher in phosphate than Hill's Mammoth Cave sediments, which according to her criteria would suggest a guano, rather than seeping groundwater, origin. *The significant phosphate values in the cave as opposed to the surface sediments, in conjunction with the high nitrate values, again suggests that the nitrate is not accumulating by the Hill mechanism, where total phosphate should be negligible.*

4.4 Discussion

The word *guano*, as used in this dissertation, is used in the expanded sense of Hutchinson (1950), who employed the word with reference to all vertebrate feces, not merely those of birds and bats, leaving the context to clarify the specific meaning. Others have broadened the word further to include even invertebrates, e.g., cricket guano. Animals with a cloaca, such as birds, where the products of the digestive and urinary systems are mixed together before elimination, produce a far more nitrogenous guano than mammalian scat.

1. Birds and reptiles are uricotelic (Schmidt-Nielsen, 1988), excreting waste Nr in the form of uric acid, $C_5H_4N_4O_3$, a double heterocyclic compound. Uric acid in excrement is decomposed by microbes to form urea, $CO(NH_2)_2$, and carbon dioxide. Mammals eliminate waste Nr directly in the form of urea, the most nitrogenous of all animal substances (Kurzer and Sanderson, 1956). Urea from

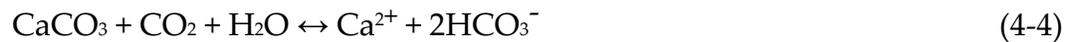
both sources reacts (by means of microbes) with water to form ammonia and carbon dioxide. These reactions can be summarized as:



2. Nitrification of ammonia/ammonium oxidizes the nitrogen atoms to nitric acid or nitrate ions and hydrogen ions in solution:



3. The ubiquitous dissolution of calcite with carbonic acid reaction produces calcium and bicarbonate ions:

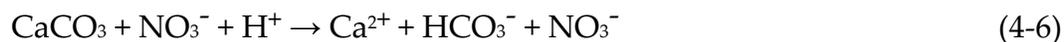


The analogous dissolution of dolomite with carbonic acid produces calcium, magnesium, and bicarbonate ions:



A combination of these two geochemical reactions is a major control on the composition of soil waters in carbonate terrains. Both reactions produce calcium + magnesium to bicarbonate equivalent ion ratios of 1 to 1. It is also important to note that the calcite reaction is reversible under near-surface conditions but the dolomite reaction is not. Dolomite is not observed to precipitate under near-surface conditions.

4. The nitric acid produced from the nitrification of ammonia reacts with the limestone and dolomite to produce calcium, magnesium, bicarbonate, and nitrate ions:



The calcium, magnesium, bicarbonate, and nitrate ions are produced with equivalent ratios of calcium + magnesium to bicarbonate to nitrate of 2 to 1 to 1.

The Prairie du Chien and other UMV carbonates are variable mixtures of limestone and dolostone. Limestones, however, have significant magnesium contents. Solution of these carbonates always produces solutions with 1 or <1 but >0 Mg/Ca (molar) ratios. The observed Mg/Ca >1 ratios in the sediment solutions require a mechanism to remove Ca or add Mg. The former process is well understood, observed, and dominates.

5. The equivalent excess of calcium + magnesium ions over bicarbonate ions in solutions produced by the nitric acid dissolution, when concentrated by drying, precipitates calcite but not dolomite, thereby increasing the Mg/Ca ratio of the residual soil solutions leading to $\text{Mg}(\text{NO}_3)_2$ compositions:



If no other ions complicated this process and it progressed to dryness the end result would be calcite and a mineral such as nitromagnesite, $\text{Mg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$.

6. Other soluble ions, sodium, potassium, chloride, and sulfate from the animal wastes and or rock and precipitation sources, lead to more complex ionic soil solution compositions—but the additional soluble anions accelerate the precipitation of calcite which further drives down the dissolved inorganic carbon content of the solutions.

There are four samples (BH, DMVI, FSP-3.5f, and TBPC-1) with dry weight sediment nitrate concentrations above 2%, and five samples (FSP-7, MPSP-1, PLC, Y4, and Y-6) with between 1 and 2% nitrate. As expected, in any scatterplots showing nitrate concentrations, these nine samples will stand out. But they also stand out in graphs involving other constituents. For example, in the calcium to magnesium plot, most of these samples are associated with higher calcium concentrations. This is to be expected considering that calcium is the major cation in the soil solutions that were generated from the sediments. Likewise, in the calcium sulfate plot, the absolute amounts of calcium sulfate are greater for most of these high nitrate samples, which makes sense given that calcium sulfate is a known constituent of guano (Hutchinson, 1950: 463).

Likewise, in the sodium versus chloride graph, the absolute amount of both ions is greater for these high nitrate samples, most of the low nitrate samples forming a cluster at <20 ppm of these constituents. In terms of the chloride/bromide ratio, the samples are mixed, with some above and some below the normal range of ratios, and they are comparable in bromide concentrations to the rest of the samples. Wide departures seem due to extraneous circumstances,

such as the presence of bromide fumigation (MC-1, MC-2, and MC-6). However, again, the samples show elevated chloride in an absolute sense.

It is distinctly notable that none of the samples from the southeastern United States plot within the two upper categories of nitrate concentration. It is not until we get to the third highest (GSC-3, GSC-14, TN-3) and lowest (FBC-2, GSC-9, GSC-11, GSC-12, TN-2) categories that we find these samples. Judging only from the data available in this study, it would appear that the UMV “saltpeter” caves are much richer in nitrate, even as the nitrate would be that much less economical to extract owing to the sporadic distribution of the small voids involved.

Chapter 5

Origin of Upper Mississippi Valley Cave Nitrate Deposits

5.1 Theories of Cave Nitrate Origin Since 1900

Salt peter has traditionally been associated with organic materials and processes, but within that framework the exact origin of the nitrate in caves has been contentious. In the words of Faust (1949), "There seem to be great differences of opinion between geologists, bacteriologists, agricultural chemists, and others, about the formation of salt peter in caves." While some of the uncertainties have been resolved since then, especially by Hill (1981), others remain.

Hess (1900), writing in the wake of Winogradsky's isolation of nitrifying bacteria, argued that guano could not be the source of nitrate in Mammoth Cave because the nitrate was found far beyond the passages that bats were known to frequent and because some of the richest nitrate deposits were devoid of the expected animal remains and organic matter. Instead, Hess suggested that the nitrate originated from the oxidation of organic matter by nitrifying bacteria in soils above the cave and was subsequently leached into the cave by soil water and redeposited. Caves thereby act merely as receptacles. The Dutch naturalist P.W. Lund, reporting on the Brazilian salt peter caves in 1839, had anticipated Hess in some respects except without the bacteria (Hill and Forti, 1997: 158).

Nichols (1901), however, countered Hess with the assertion that bats do indeed visit remote parts of the cave and that the ratio of phosphate to nitrate in the cave sediments was too high to be accounted for by supposing nitrates were brought in by percolation from surface soils. Nichols argued that the phosphate did not come from calcium phosphate in the autochthonous sediments—derived from the surrounding limestone, Hess had suggested—because these sediments contain a far greater proportion of phosphate than is found in residual clays of similar origin.

Hill (1981), in her landmark study of saltpeter caves, came to conclusions similar to Hess (1900), but with the crucial addition of capillary action, thus removing Faust's (1949) objections to groundwater transport. By drilling into the bedrock walls of these caves and analyzing the cores, she showed that high concentrations of nitrate, in the thousands of parts per million, exist up to 30 centimeters deep. She proposed what has become known as the "seeping groundwater model," which is a refinement of Hess's (1900) idea, with some insights by Pace (1971). Organic nitrogen, like that found in proteins, is converted to ammonia and then nitrate by bacteria in surface soils. The much more mobile nitrate ion is reduced again to ammonia lower in the profile and drawn into the cave through the limestone walls by a moisture-density gradient created by evaporation at the bedrock/cave interface. The saltpeter cave thus basically appears dry to visitors. In the wall rock and cave sediments themselves, the ammonium is reconverted to nitrate by the nitrifying bacteria known to exist there (Fliermans and Schmidt, 1977). In this scenario, the observed regeneration

of cave nitrate after exhausted sediment has been returned to the cave is readily explained.

Moore (1994) offered an alternative explanation for some of Hill's (1981) results. Likewise, Olson and Krapac (2001) reasserted the old guano theory at Mammoth Cave. They reported that six years after the lixiviation of nitrate-bearing cave sediments, the latter had not regenerated its nitrate content as expected and they concluded that it was due to the absence of the former bat, woodrat, and raccoon populations in the cave. But Craig (1862) found that it required from 8 to 10 years for regeneration to occur, as recently emphasized by Northrup and Lavoie (2001).

5.2 Climatic and Edaphic Factors

Hill (1981) remarked that "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." She emphasized that the distribution of the majority of classic saltpeter caves coincides with that of the distribution of oak-hickory forest in the southeastern United States. She suggested that this was probably because of abundant forest litter and that woodland soils do not retain fixed nitrogen as well as grassland soils. This correlation could be explained by the higher cation exchange capacity (C.E.C.) of grassland soils. Thick prairie Mollisols with high C.E.C. would retain ammonium far better than Alfisols or the thin, weathered Ultisols of the southeastern U.S., which have a lower C.E.C.

(Lutz, 1966; Stanford and Smith, 1972). The ammonium-fixing power of the soil is concentrated in the clay fraction (Allison et al., 1953; Nommik, 1957; Dhariwal and Stevenson, 1958; Sparks, 1999), and soil mineralogy and chemistry affect the transport of nitrate through the soil profile (Qafoku and Sumner, 2001).

Long before this, Jenny (1928) had discussed the extent to which his classic soil-forming factors influenced the concentration of nitrogen in soils. While these five factors are not independent variables, he arranged their order of importance for the nitrogen content of the soil as: climate > vegetation > topography and parent material > age. He concluded that “the total nitrogen content of the soil decreases in the United States from north to south in relation to temperature.” Confirmed by Post and Pastor (1985), this favors Minnesota.

Much of southeastern Minnesota, where the state’s caves are concentrated, belongs to the Maple-Basswood zone. However, Daubenmire (1936) quantified the actual tree species composition of the Big Woods (a prominent stand of Maple-Basswood in Minnesota and Wisconsin), finding that oaks and hickories still make up a certain percentage of the tree species; so the tree criterion seems somewhat arbitrary. Much of the vegetation along the cliffs of Lake Pepin, where the majority of my sampling sites are located, is algific, including ferns, aspens, and so forth. Furthermore, the present vegetation does not necessarily reflect conditions before extensive European settlement. So in the UMV, at least, there’s no clear correlation of nitrate deposits with vegetation types, consistent with the guano theory.

Hill (1981) reported that the classic saltpeter caves of the southeastern United States have stable temperatures ranging from 10 to 18°C and stable humidity between 90 and 99%. For the small, exposed UMV crevices, the air temperature will reflect more closely the range of ambient aboveground temperatures. For comparison, the range of average monthly temperature, as measured at the Rochester Airport in southeastern Minnesota, ranges from -11.8 to 21.5°C and the relative humidity from 56 to 87% (NOAA, 1985). These differences become irrelevant under the guano theory. Indeed, artificial niter beds have been operated with great success as far north as Sweden (Kaiserfeld, 2006).

Minnesota is located far outside Hill's optimal area and the conditions necessary for her model to work do not seem to apply here. Thus, the samples taken from the driest parts of the largest Minnesota caves during this study, Mystery and Niagara caves, revealed the total absence of nitrate (0 ppm). However, Hill's model presumably accounts for the elevated nitrate concentrations obtained during this study from samples taken in Great Saltpetre Cave, Kentucky.

5.3 UMV Guano Theory

The highest nitrate value obtained during this study was 3.5% weight-percent nitrate (equivalent to 35,000 ppm) from the dry, reddish sediment of an Oneota rockshelter in Rattlesnake Bluff, which forms the western end of Frontenac State Park. Thus, elevated nitrate is not confined to the Le Sueur-type crevices, which

turned out to be in the minority among the kinds of rock voids encountered in the field. For comparison, the nitrate content of the Mammoth Cave, Kentucky, sediments examined by Hill (1981) “range between 0.01% and 4% [by weight], most commonly between 0.1% and 1.0%.” This overlaps with the 3% to 5% nitrate historically reported for commercial concentrations in the surface soils of British India (Hutchinson, 1917: 1). Many of the Minnesota cave sediments are thus sufficiently enriched in nitrate to be worth extraction.

Some potential sources of the nitrate-nitrogen in the Lake Pepin crevices can be excluded. Elsewhere, the presence of geologic nitrogen is a significant source of detectable nitrogen in streams (e.g., Holloway et al., 1998; Holloway and Dahlgren, 2002). Chalk and Keeney (1971) suggest that geologic nitrogen can dissolve from Wisconsin limestones, but most of the crevices in my field area are tectonic, and not solutional, in origin. Moreover, because the amounts of water-soluble calcium and magnesium are much higher than any potential concentration of nitrogen in the rocks, you would expect to see significant carbonate speleothems (Sandler and Heaton, 1997), which are not found in the UMV crevices.

Although some of the mesa “islands” in which the crevices are located are farmed on their summits, presumably involving the application of nitrogen fertilizer, the cave’s nitrate-nitrogen does not match isotopically with the nitrogen of artificial fertilizer, nor does it match the nitrogen fixed by lightning, which is found in rainfall (Brick, Alexander, and Doctor, 2009). Moreover, some high nitrate samples were obtained from voids in barren rock pinnacles that

could never have been farmed. This should hardly come as a surprise, because nitrifiers were detected in barren rocky cliff environments in 1890—shortly after these bacteria were discovered (Gibbs, 1919).

The expanded definition of the word *guano*, in the sense of Hutchinson (1950), has been discussed in Section 4.4. Within the range of guano theories, the scats and urine of raccoons (*Procyon lotor*) were most frequently observed in the UMV caves. Mammalian urine is much more nitrogenous than scats and some of these locations probably conform to the “raccoon latrine” concept utilized by Page et al. (1998) among others. Bird caves, occupied by nesting turkey vultures (Coles, 1944), or ledges serving as pigeon lofts, were a distant second. Only Sevastopol Crevice had suspected bat skeletal material (species not identified), encountered in the sediment sample bag itself. As for the rat guano theory of Moore and Nicholas (1964), which attributes cave nitrate to packrats and woodrats (genus *Neotoma*) through their production of amberat (scats + urine), the *Neotoma* region is largely separate from the UMV (Schwartz and Odum, 1957). Finally, one unusual theory is that some nitrate deposits are due to passenger pigeon guano (reviewed by Brick, 2009), and the Mississippi River being a former flyway for these now extinct birds would help explain the multitude of Lake Pepin nitrate occurrences (at least historical ones), the lake being an expanded reach of the river. But it’s difficult to see how the pigeon guano could have gotten into the crevices from the groves of nut-bearing trees in which the birds were known to have roosted.

Nitrate is very soluble and easily leached from cave sediments, so dry caves would be expected to harbor more nitrate than wet caves, and this was found as a general pattern. However, dampness was observed in some of the Minnesota crevices that had elevated nitrate, suggesting that leaching of nitrate and microbial denitrification (which takes place in anoxic, water-logged settings) is possible, but that there is more than enough nitrate regeneration from frequent additions of organic matter. This is corroborated by Hutchinson (1950: 403), who reported that Indiana caves are “mostly very wet,” yet the cave earth was found enriched with nitrate, mostly from bat guano. What was measured during sampling was an *equilibrium* concentration of nitrate in the cave sediments. According to Jones and Schwab (1993), describing surface soils, “in periods of average or less than average precipitation, nitrate accumulates in the profile. In periods of above average precipitation, this nitrate can be flushed from the profile.” A similar observation was made by the French scientist Jean Baptiste Boussingault for garden soils as long ago as 1857 (McCosh, 1984: 139-140).

According to Schmidt (1982), “nitrification takes place in virtually all soils where NH_4^+ is present and conditions are favorable with respect to the major factors of temperature, moisture, pH, and aeration.” From this, it should not be surprising to find nitrate in crevice sediments, considering the amount of input of organic matter, in terms of the guano, scats, urine, carcasses, feathers, leaves, sticks, and so forth, which are regularly observed in such places. Crevices, no matter they are located, provide two essential conditions for nitrate accumulation: they protect the sediments from direct rainfall, and thus decrease potential leaching, and by shutting out sunlight they prevent plant growth,

which would otherwise extract this plant nutrient as fast as it formed. The concluding remarks of Hess (1900) that “the occurrence of nitrates in cavern earths is general,” is largely born out in the Upper Mississippi Valley, if not for exactly the same reasons he suggested.

5.4 Conclusions and Further Work

This study revealed a hitherto unsuspected widespread district of cave nitrate deposits in the Upper Mississippi Valley. There was little evidence that the nitrate deposits in the UMV study area were forming by Hill’s (1981) seeping groundwater model, but rather by the transformation of organic matter in situ. The presence of significant phosphate concentrations in the UMV nitrate deposits is strong evidence of this. Thus, the origin of cave nitrate deposits in the United States generally appears to be owing to more than one mechanism, as suggested by Faust (1949).

The formation of a high-nitrate Le Sueur type crevice goes something like this: the long and narrow crepuscular crevices form by the widening of bluff-parallel rock joints, where the bluff is falling away from the main rock mass. Over time, the crevices fill with sediment derived from rock disintegration and surface soil descending through the joints from above. Animal traffic and plant debris contribute organic matter that undergoes microbial nitrification, forming nitrate, which then accumulates because the cave roof protects the sediment from leaching and by shutting out sunlight permits this plant nutrient to remain in the sediment.

The occurrence of high nitrate concentrations in the sediments of UMV crevices revealed by this study is enough to show that Le Sueur's claim of finding saltpeter (more likely, a saltpeter precursor, such as calcium nitrate) in caves along the shores of Lake Pepin in 1700, for making gunpowder in the wilderness, is credible. This is the earliest report of cave saltpeter from America, predating more probable French saltpeter manufacture from Missouri caves in 1720.

Future study of this hitherto unrecognized subterranean environment, especially its microbiology and wildlife, as well as the factors promoting nitrification, along with further sampling to better define the seasonal and spatial distribution of nitrate, would yield valuable additional insights into the formation of nitrate deposits in the rock crevices of the Upper Mississippi Valley and elsewhere.

Chapter 6

Modeling Saltpeter Conversion with GEOCHEMISTS WORKBENCH™

6.1 Introduction

Hill et al. (1983) report the results of an “action history” experiment in which, carefully reproducing the techniques (in so far as they have been historically documented) of saltpeter conversion (manufacture) at Mammoth Cave, Kentucky, in the early nineteenth century, they were able to produce saltpeter starting from recently harvested cave sediments. While it became obvious that some of the secrets to increasing the yield are artisanal in nature, the broad outlines of the conversion process are well known enough that they can be modeled using GEOCHEMISTS WORKBENCH™ (GWB), a commercially available software package. The background and basis for this modeling program is given by Bethke (2008).

Hill et al. (1983) divided the saltpeter conversion process into three discrete steps, and these were followed as separate steps in the modeling, except for the first, which is a straightforward solubility step: (1) **lixiviation** (leaching) of nitrate from the cave sediments; (2) **double decomposition**, involving the addition of potash lye and the precipitation of calcium carbonate from solution; and (3) **fractional crystallization** by boiling to isolate pure potassium nitrate.

These steps will now be described in greater detail, along with a discussion of the graphic results in GTPLOT™.

6.2 Lixiviation

Lixiviation, also called leaching, took place inside Mammoth Cave. Ox carts were used to haul the “petre dirt,” or cave sediments, from remote passages to the Rotunda, where the dirt was shoveled into V-vats or larger wooden vats. When full, water from a spring outside the cave was poured on top, leaching the soluble nitrate (which is probably in the form of calcium nitrate), draining out the bottom. Usually, this fluid, dubbed “beer” or “liquor,” was drained through the vat several times to enrich the nitrate. Since this is a simple solubility step it was not separately modeled.

6.3 Double Decomposition

Calcium nitrate or lime niter, $\text{Ca}(\text{NO}_3)_2$, is the form in which the nitrate is likely found in the cave sediments themselves. Except at very high concentrations, nitrate is a deliquescent salt, dissolved in the soil, rather than a discrete mineral. The usual back-country test, in the absence of chemical assay, was a bitter taste, or sometimes that a recently-made soil impression would become undetectable over a period of time, presumably because of crystal turbation in niter-rich soils. Potassium hydroxide or potash lye, KOH , is a corrosive alkaline hydroxide derived from wood ashes, which is added to the leachate.

The basic formula involving the addition of potash lye and formation of calcium hydroxides is as follows:



While this reaction would be straightforward to set up in REACT, an equilibrium-based model, it does not likely represent the actual reaction occurring, which is open to the atmosphere. In the open system, atmospheric carbon dioxide dissolves in the water, forming bicarbonate, which reacts with the potassium hydroxide to form potassium carbonate. To model this in REACT, the carbon dioxide fugacity is set at 0.00035. As KOH is added, the expected precipitation of calcium carbonate occurs, which is thus removed from the system:



Since Hill et al. (1983) do not provide a chemical analysis of their starting materials, the amounts of the species listed in the BASIS were set according to their concentrations in sample BHC (Black Hole Cave), which had the highest nitrate concentration in my data set. The charge was set to balance on nitrate, the most abundant anion.

The reaction output, in the final step, shows calcite, aragonite, monohydrocalcite, and portlandite. The GtPLOT (**Figure 6.1**) was set as components in fluid (moles) plotted against reaction progress. As the reaction proceeds, and more KOH is added, the hydrogen ion concentration drops off

quickly at 0.4, as does the bicarbonate (which precipitates as the calcium carbonate).

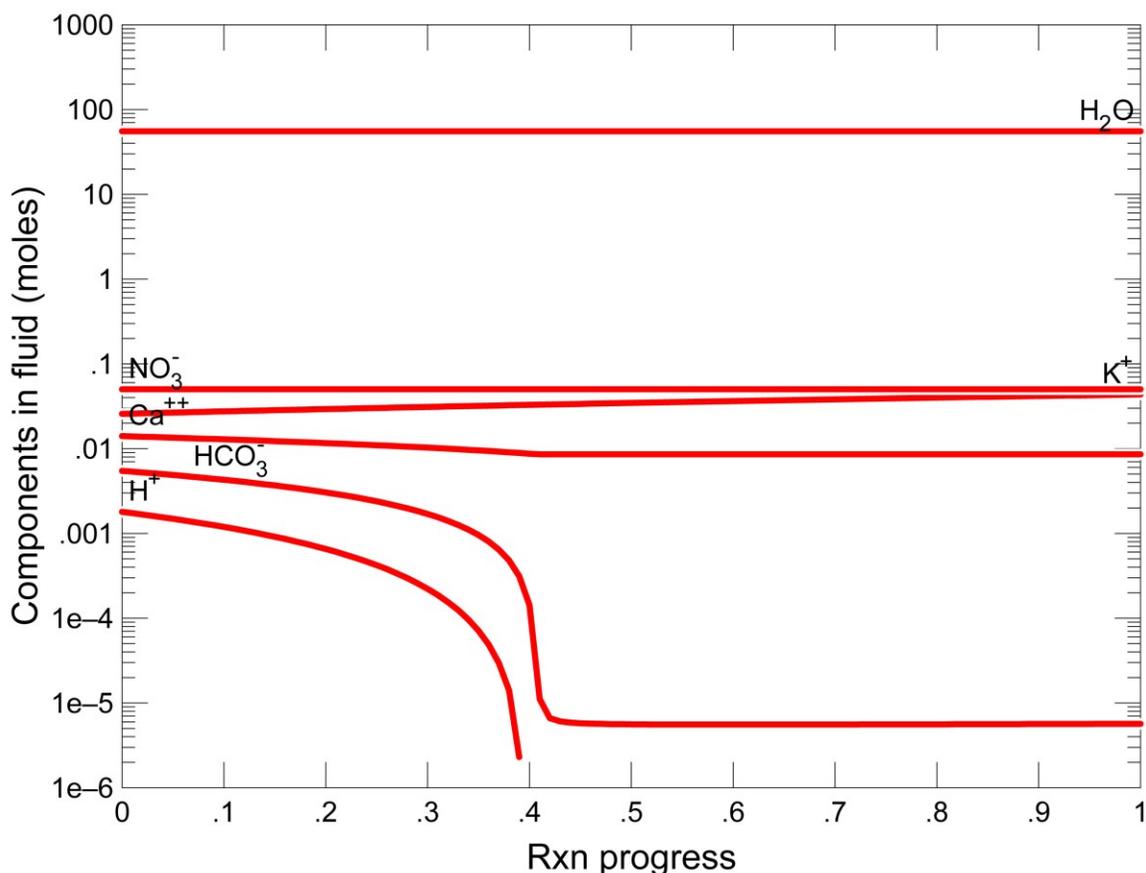


Figure 6.1. Double decomposition step with CO₂ fugacity = 0.00035.

Next, additional ionic species, as listed in the laboratory analysis for sample BHC, were successively added to the BASIS. The first to be added was chloride, and this did not significantly alter the results, the Cl declining slightly near 0.4—perhaps a dilution effect as the KOH is added. When both Cl and Na were added, the results were again the same. Although phosphate was a third species in the list, no run was made with it, as it was present in very small quantities in the actual analysis.

See Appendix D for a printout showing the BASIS species and reaction steps.

6.4 Fractional Crystallization

Hill et al. (1983) next studied the fractional crystallization step in saltpeter conversion, which involved boiling the crude KNO_3 solution to remove the other salts present. Basically, KNO_3 is more soluble in hot water than the other salts, so as the water evaporates, the other salts are precipitated, leaving KNO_3 behind (**Figure 6.4**). Historically, it was found that when KNO_3 initially precipitated, it was often darker and discolored, owing to impurities, not the white of the pure mineral, and so the impure crystals were re-dissolved in a kettle of water, boiled again, until purer crystals were secured. In historical saltpeter markets, the whiter the saltpeter, the higher its value.

Hill et al. (1983) successively isolated three salts from the kettle, before leaving niter behind. The first salt to precipitate as evaporation progressed was potassium sulfate, K_2SO_4 , also known as arcanite; then hydrated magnesium sulfate, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, or epsomite; and then a double salt, schoenite, $\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 6\text{H}_2\text{O}$.

In REACT, where the default value for the mass of water is one kilogram, the evaporation step is modeled by specifying the amount of water to be gradually subtracted; in this case, the value was set at -996 grams (so that 4 grams of water would remain). Since KNO_3 is not listed in the *thermo.dat* database of minerals provided by GWB, it cannot be separately specified as a

mineral precipitate in the program, so the final isolation of KNO_3 was considered complete for the purpose of this exercise when K and NO_3 were the only species left in solution, such that if the evaporation continued they would ultimately be precipitated.

For the modeling this step, the species concentrations in the BASIS were chosen so as to correspond to the molar amounts in Hill's salts, because an analysis corresponding to what would be found in an actual kettle of processed Minnesota cave sediment was not available. It should be noted, however, that all the ions going to make up Hill's salts are also found in the Minnesota sediments, so the assumption is justified.

In the evaporation itself, as with the double decomposition, it was found that fugacity was critical. If the system was not open to the atmosphere (CO_2 fugacity=0) then 3 minerals resulted: brucite, magnesium hydroxide, or $\text{Mg}(\text{OH})_2$, was the first mineral to appear, followed by arcanite, then epsomite (**Figure 6.2**). If however the CO_2 fugacity was specified, magnesite, magnesium carbonate, or MgCO_3 , was formed instead of brucite, followed by arcanite and epsomite as before (**Figure 6.3**). Interestingly, Multhauf (1976) mentions magnesium carbonate (historically known as magnesia alba) as one of the long-standing byproducts of saltpeter production that was casually discarded until it was recognized as an excellent mild cathartic (our modern Milk of Magnesia), pleasantly contrasting with the violent purgatives hitherto available.

See Appendix D for a printout showing the BASIS species and reaction steps.

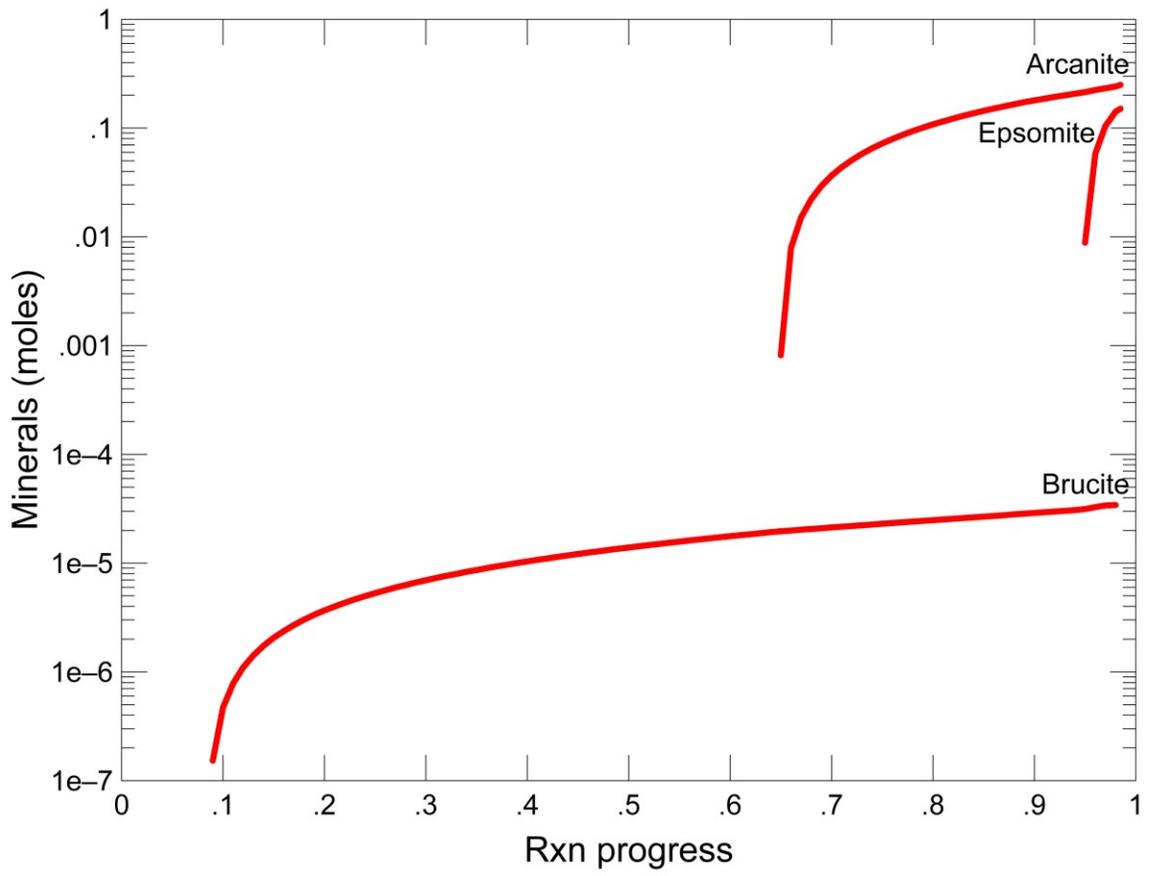


Figure 6.2. Evaporation step in a closed system.

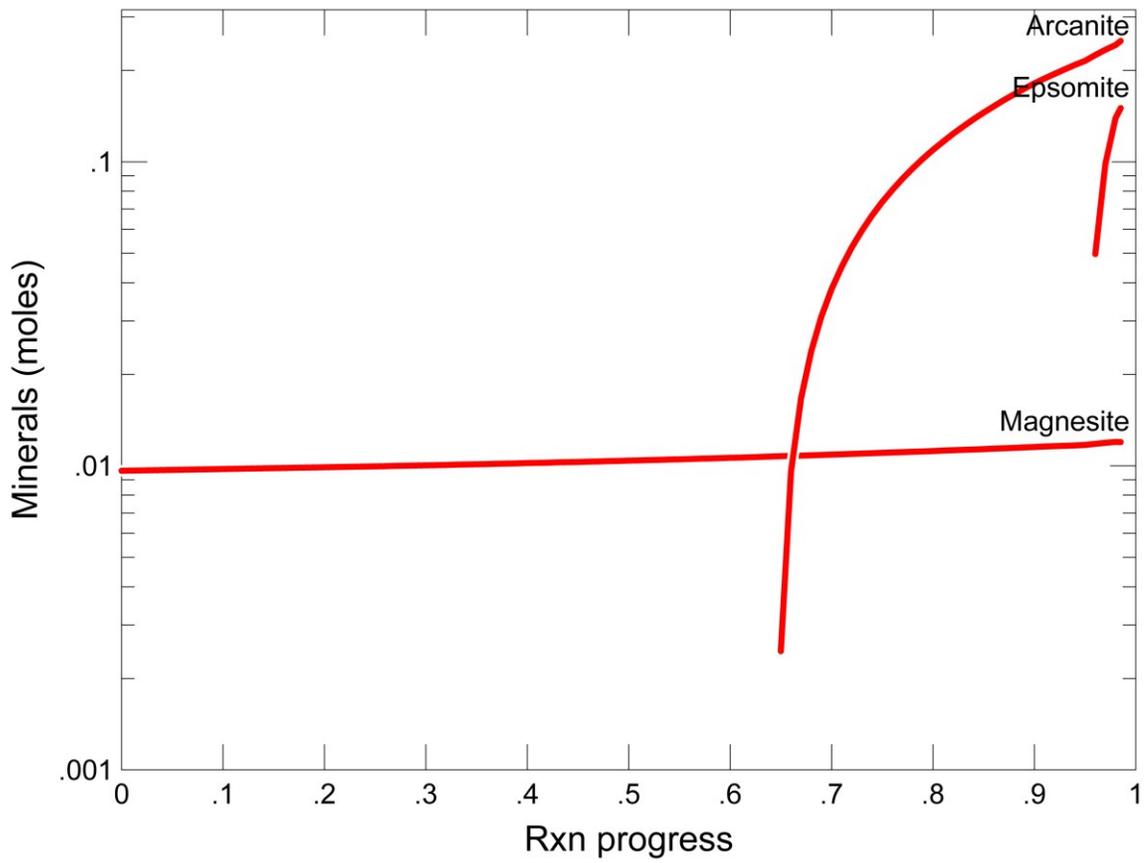


Figure 6.3. Evaporation step with CO₂ fugacity = 0.00035.

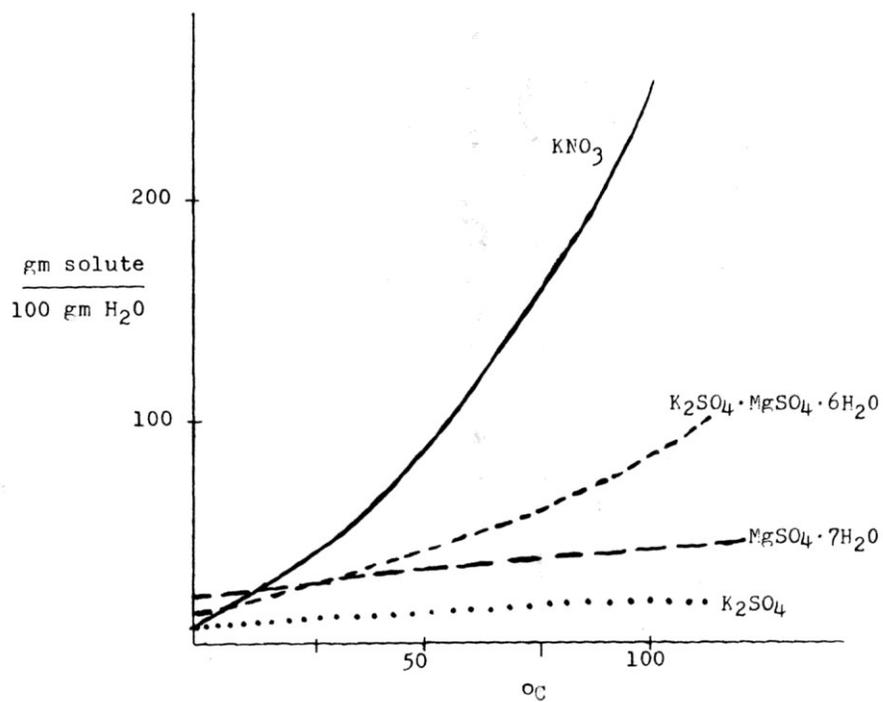


Figure 6.4. "Solubility curves for niter (KNO_3), schoenite ($\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 6\text{H}_2\text{O}$), epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$), and arcanite (K_2SO_4)" (Hill et al, 1983).

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APPENDIX A: CAVE SAMPLING LOCATIONS

All UTM coordinates belong to Zone 15, NAD 1983.

Sample ID	Remarks	UTME	UTMN	County	State
SGC	Strong's Cave	527509	5028877	Chisago	MN
MC	Miles Cave: 6 samples	512153	4952527	Dakota	MN
LMC	Lee Mill Cave: 2 samples	504939	4957037	Dakota	MN
KC	Korneski Cave: 8 samples	504951	4957111	Dakota	MN
MIE-1	Miesville Ravine Park crevice	513593	4934731	Dakota	MN
VR-4	Vermilion River Cave 4 (Hobo Cave)	512412	4952377	Dakota	MN
VR-3	Vermilion River Cave 3 (Horseshoe Cave)	512249	4952467	Dakota	MN
NC-1	Niagara Cave	576384	4818310	Fillmore	MN
DC	Diamond Cavern (MC 2): 2 samples	557143	4830175	Fillmore	MN
CM	Copeman's Cave	556913	4830513	Fillmore	MN
WC	Windcourse Cave	557332	4830935	Fillmore	MN
PIC	Petrified Indian Cave	557489	4830557	Fillmore	MN
RR-52	Root River at Hwy 52	569142	4852056	Fillmore	MN
Y-1	Young Property	542685	4933940	Goodhue	MN
Y-2	Young Property	543064	4934003	Goodhue	MN
Y-3	Young Property	543134	4934023	Goodhue	MN
Y-4	Young Property	543219	4934013	Goodhue	MN
Y-5	Young Property	543304	4933988	Goodhue	MN
Y-6	Young Property	543374	4933948	Goodhue	MN
Y-7	Young Property	543424	4933903	Goodhue	MN
Y-8	Young Property	543774	4933748	Goodhue	MN
WM-1	Wacouta Motors	542110	4933643	Goodhue	MN
SC-1	Sevastopol Crevice (alias Y-4)	543110	4934044	Goodhue	MN
CR-1	Chimney Rock	542440	4934412	Goodhue	MN
BB-1	Barn Bluff	537226	4935277	Goodhue	MN
OC	Overlook Cave: 2 samples	537756	4934499	Goodhue	MN
RBW	Rattlesnake Bluff West	546438	4932168	Goodhue	MN
RBS	Rattlesnake Bluff South	546518	4932023	Goodhue	MN
FSP-5	Frontenac State Park	551842	4931993	Goodhue	MN
FSP-6	Frontenac State Park	547418	4932173	Goodhue	MN
FSP-7	Frontenac State Park	547603	4932233	Goodhue	MN
FSP-10	Frontenac State Park	550577	4932223	Goodhue	MN
FSP-12	Angel's Roost (alias NACC)	549878	4932758	Goodhue	MN
FSP-11	Cold Crack	550157	4932253	Goodhue	MN
FSP-2	Not-a-Trail Cave	552713	4931728	Goodhue	MN
FSP-4	Coon Trap	552117	4931948	Goodhue	MN
FSP-9	Jordan Sandstone Tube	548173	4932223	Goodhue	MN
FSP-1	Peregrine Signage	552859	4931512	Goodhue	MN
LSTC	Le Sueur-Type Crevice	546636	4932245	Goodhue	MN
Phil Cave	Philosopher's Cave	546750	4932231	Goodhue	MN
FSP-3.5	Frontenac State Park	552543	4931759	Goodhue	MN
FSP-3	Point-No-Point Cave	552609	4931728	Goodhue	MN
FSP-3.6	Frontenac State Park	552501	4931783	Goodhue	MN
FSP-8	Greene Point Cave	547637	4932215	Goodhue	MN
NGPC	Near Greene Point Cave	547732	4932260	Goodhue	MN
NYR	Navy Yard Rockshelter	547327	4932244	Goodhue	MN
BHC	Black Hole Cave--highest nitrate	547529	4932225	Goodhue	MN
RFC	Red Flask Cave	549322	4932236	Goodhue	MN
SUC	Sit Up Cave	548872	4932214	Goodhue	MN
CZC	Corrosion Zone Cave	547203	4932227	Goodhue	MN
PLC	Poop Ledge Cave	547954	4932210	Goodhue	MN
IC-36	Ice Cave 36th Street	483831	4976054	Hennepin	MN
IC-37.5	Ice Cave Between 37th and 38th	483996	4975747	Hennepin	MN
MRT	Milwaukee Road Trestle	483185	4977987	Hennepin	MN
RQC	Reno Quarry Crevice	639365	4830751	Houston	MN
COY	Catacombs of Yucatan	604128	4835076	Houston	MN
SF	Shadow Falls	484325	4976517	Ramsey	MN
WIC-1	Ridgewalk Cave	568819	4896054	Wabasha	MN
WIC-2	Popcorn Cave	568616	4896060	Wabasha	MN
SEN	Sentry Cave: 2 samples	568647	4896837	Wabasha	MN
PCC-1	Pancake Cave	568673	4897036	Wabasha	MN
EC	Echo Chambers: 2 samples	562782	4900036	Wabasha	MN
LC-1	Lundberg Cave	570220	4917622	Wabasha	MN
LVC-1	Lost Valley Cave	510531	4956975	Washington	MN
Knapps	Knapps Cave	518517	5014723	Washington	MN
Clarc	Clarke Cave	518519	5014836	Washington	MN
QB-1	Queens Bluff	628310	4868350	Winona	MN
QB-2	Queens Bluff	628353	4868312	Winona	MN
JLSP-1	John Latsch SP ss crevice	592920	4891444	Winona	MN
JLC-1	John Latsch Cave	592996	4891393	Winona	MN
TRC	Trout Run Cave: 3 samples	576090	4876940	Winona	MN
WWRC-1	Whitewater River Cave	581582	4873848	Winona	MN
DEV	Devil's Cave	606685	4877251	Winona	MN
DMV	Damview Cave	594606	4890273	Winona	MN
ACC	Around the Corner Cave	593812	4890780	Winona	MN
TR	Tricorn Cave	593754	4890835	Winona	MN
SH	Skunk Hollow	586291	4880003	Winona	MN
WWRC	White Water River Cave	582357	4877291	Winona	MN
RH	Racoon Heaven	583069	4873890	Winona	MN
BVP	Buena Vista Park	586697	4908414	Buffalo	WI
KSP-1	Kinnickinnic SP	520440	4964329	Pierce	WI
BC	Black's Cave	569506	4947183	Pierce	WI
TF	Tree Fork Cave: 3 samples	559247	4964613	Pierce	WI
SP	South Portal Cave	559154	4964433	Pierce	WI
FCC	Fuzzy Critter Cave: 3 samples	559296	4964539	Pierce	WI
TBPC-1	Trenton Bluff Prairie Cave	534496	4940744	Pierce	WI
WC	Webb Caves: 4 samples	567551	4961623	Pierce	WI
BBT-1	Bradys Bluff Trail--Lower	621249	4875284	Trempealeau	WI
BBT-2	Bradys Bluff Trail--Upper	621472	4875290	Trempealeau	WI
PP	Perrot Post Historical Marker	622507	4874619	Trempealeau	WI
HOS	Mt. Hosmer Park Overlook Cave	644143	4803180	Allamakee	IA
MPSP-4	Mississippi Palisades SP Overlook RS	734934	4667988	Carroll	IL
MPSP	Uptons Cave: 3 samples	735043	4665811	Carroll	IL

APPENDIX B: FIELDNOTES

SAMPLE	DATE	FIELDNOTES
MINNESOTA		
Chisago County		
SGC	7/3/2011	Strong's Cave: T-joint in basalt below Taylor's Falls, driftwood in rear indicates entire cave floor submerges; L=22', H=20', W=2'.
Dakota County		
KC	8/14/2009	Korneski Cave, an Oneota maze cave in Schaar's Bluff, dry, thick red sed.
LMC	10/31/2009	Lee Mill Cave, an Oneota solutional cave in Schaar's Bluff, dry, thick red sed.
MEC	9/19/2009	Miesville Crevice, a small rock tube, dry, gravelly.
MC	10/31/2009	Miles Cave, large solutional Oneota maze cave, dry thick red sed, multiple sampling spots.
VR-1	2/26/2010	Ridge Cave (Vermilion River Cave No. 1)
VR-2	2/26/2010	Sawtooth Cave
VR-3	2/26/2010	Horseshoe Cave, an Oneota rockshelter with dry thick red sed.
VR-4	2/26/2010	Hobo Cave, used as living quarters with door.
Fillmore County		
CM	10/23/2010	Copeman's Cave
DC	7/13/2010	Diamond Caverns: driest part of Mystery II route.
NC	N/A	Niagara Cave
PIC (=PETI)	10/23/2010	Petrified Indian Cave
RR-52	N/A	Root River at Hwy 52, a horizontal PDC bedding plane.
WC	10/23/2010	Windcourse Cave
Goodhue County		
BB	6/24/2005	Barn Bluff cave in Oneota outcrop overlooking bridge, divided by pillar.
BHC	5/20/2011	Black Hole Cave: Oneota rockshelter with a "burned" appearance (maybe dead moss), thick dry reddish sed.
CR	5/21/2005	Chimney Rock, horizontal corrosional void near base

		of a rocky pinnacle, H=6"-18"; dry reddish sand, fresh coon scat.
CZC	5/20/2011	Corrosion Zone Cave: in Oneota cliff with several inches thick reddish sed, leaves, scats, tree roots.
FSP-1	9/12/2004, 11/21/2008, 6/29/2010	Oneota rockshelter along park trail, H=3', L=3', W=8', thin black soil.
FSP-2	9/12/2004, 11/21/2008, 6/29/2010	Oneota rockshelter along park trail, H=10', L=8', W=10'; moist brown clayey seds several inches thick.
FSP-3	9/12/2004, 11/21/2008, 6/29/2010	Point-No-Point Cave, from a named park feature; a mechanical bluff-parallel vertical joint in Oneota with skylight; H=8', L=15', W=3'. Thin patchy sed between boulders, bird droppings and feathers, crickets seen.
FSP-3.5	6/29/2005, 11/21/2008	Oneota rockshelter, dry and dusty, H=3', L=8', W=5'.
FSP-3.6	11/21/2008	Oneota rockshelter
FSP-4	10/24/2004	Coon Trap Cave: part solutional Oneota, but intersected by joint falling away from bluff, L=20'. Much coon scat and musty odor.
FSP-5	10/24/2004	Oneota rockshelter, H=3', L=12', W=5'.
FSP-6	12/5/2004	Mechanical joint containing dry soil, leaves roots; H=3', W=3" (too narrow to enter).
FSP-7	12/5/2004	Pancake rockshelter H=3', W=8', L=6'; dry reddish sandy sed; swallow's nest on ceiling.
FSP-8 (=GPC)	12/5/2004, 5/13/2011	Green Point Cave, Oneota rockshelter with upper (L=15') and lower levels; thick, reddish sandy sediments.
FSP-9	12/5/2004, 5/13/2011	Crawl tube L=20' along joint in Jordan SS, sampled as far in as I could reach, dry reddish sand.
FSP-10	6/5/2005	Oneota rockshelter H=2', L=4', W=6'; black sed.
FSP-11	6/5/2005	Cold Crack: bluff-parallel Oneota joint with sit-up room; damp brownish soil with coon scats.
FSP-12	6/5/2005	Angel's Roost Cave, so called from its altitude; an Oneota arch in bluff-parallel joint, solutional crawlway L=15', thick reddish sed.
LSTC	5/20/2011	Le Sueur-Type Crevice: mechanical joint in Oneota

		float-blocks, bluff-parallel, too small to enter, plugged with thick black colluvial soil.
NACC	10/4/2010	Natural Arch Crawlway Cave: large, shallow natural arch niche in Oneota cliff, entrance to crawlway (L=20', H=2', W=3') on R-side where sample was taken. Maybe same site as FSP-12.
NGPC	10/4/2010	Near-Green-Point Cave: Oneota crawlway divided by pillar, L=11', W=6', H=2'.
NYR	5/20/2011	Navy Yard Rockshelter: shallow spaces around Oneota boulders, L=7', W=15', H=1.5'.
OC	6/24/2005	Overlook Cave, Sorins Bluff, Red Wing, an artificial sandstone cave with abundant party debris.
PhilC	5/20/2011	Philosopher's Cave: mechanical joint with a stone seat, ceiling formed by large boulder.
PLC	10/4/2010	Poop Ledge Cave: an Oneota rockshelter with bird feathers and guano.
RBS	7/11/2009	Rattlesnake Bluff South, foothole at base of Oneota outcrop, top of talus wedge, southern aspect.
RBW	7/11/2009	Rattlesnake Bluff West, foothole at base of Oneota outcrop, top of talus wedge, western aspect.
RFC	10/4/2010	Red Flask Cave: Oneota rockshelter, flask-shaped in map view, containing dry, thick, reddish seds; H=2.5', L=9.5', W=4'.
SC (=Y4)	5/21/2005	Sevastopol Crevice: mechanical joint in dolomite block that has moved downhill, difficult to enter; bat bones in seds; H=4', L=12', W=18". Also collected surface soil above cave.
SUC	10/4/2010	Sit Up Cave: Oneota rockshelter just large enough to sit up in; L=9', W=3.5', H=3.5'; dry, thick reddish seds.
WM	8/19/2004	South face of ridge, above Wacouta Motors; dry sandy Oneota RS, H=1', W=4', D=2; cottonball-sized masses of a whitish mineral (gypsum?) on top of sand.
Y-1	8/11/2004	Pocket in Oneota outcrop, unenterable, H=1', L=2', acorns. On the Young (Y) property.
Y-2	8/11/2004	Roofed-over vertical joint in Oneota, unenterable, W=6", H=2'.
Y-3	8/11/2004	Oneota RS, L=30', H=5', D=6'; collected soil with

		whitish cast from below overhang.
Y-4	8/11/2004	Same as SC.
Y-5	8/11/2004	Standing height Oneota rockshelter, H=6', W=6', D=12'.
Y-6	8/11/2004	Hole in high vuggy Oneota outcrop, H=2', W=6', D=4', sample may have included scats.
Y-7	8/11/2004	Oneota RS near Devil's Stairway, collected dry, whitish soil.
Y-8	8/11/2004	Oneota RS, H=2', L=6', D=6', soil scraped off rock floor.
Hennepin County		
IC-36	2/19/2010	Ice Cave at 36 th Street, Minneapolis, collected below a waterfall notch.
IC-37.5	2/19/2010	Ice Cave at 37½ (midway along the city block), mechanical cave in the Magnolia Member, where club-shaped ice stalagmites seen; seds appear to be descended surface soil.
MRT	2/19/2010	Milwaukee Road Trestle, quarry facet near stairway, collected under Platteville ledge.
Houston County		
COY	9/4/2011	Catacombs of Yucatan: wet, well-decorated Oneota phreatic cave, samples obtained near junction of the 2 main passages from dry ledges above the floor.
RQC	9/6/2010	Reno Quarry Crevice: on unworked E slope of dolomite quarry in the Reno Unit, roofed by chockstones, H=10', L=6', W=1.5'. Seds may be very recent talus soil.
Ramsey County		
SF	2/19/2010	Shadow Falls ravine, collected seds from shallow overhang in St Peter SS near mouth of ravine near river level.
Wabasha County		
EC	7/5/2007	Echo Chambers, solutional Oneota cave, sampled both forks.
LC	5/15/2005	Lundberg Cave: Large Oneota solutional cave, sampled L side of T-branch, above stratified clays, where no animals could get to.

PCC	11/18/2007	Pancake Cave in Oneota finger ridge across valley from Sentry Cave; has drips; sampled dry brown mud; abundant coon bones.
SEN	11/18/2007	Sentry Cave in Oneota finger ridge; cherty gravel floor pavement with coon scats, under which are dry, tan, sandy seds, from which sample was taken.
WIC-1	7/5/2007	Ridgewalk Cave, high on cliff face, dry red seds with abundant coon scat.
WIC-2	7/5/2007	Popcorn Cave, crawl tube, H=2', L=12'.
Washington County		
CLARC	7/3/2011	Clarke Caves: solutional cave in red clastics, dry, thick, red seds, one sample taken.
Kmain	7/3/2011	Knapp's Cave: solutional cave in red clastics, dry, thick, red seds, multiple samples taken.
LVC	8/14/2009	Lost Valley Cave, in Oneota outcrops.
Winona County		
ACC	6/30/2010	Around-the-Corner Cave, a vertical joint with chockstone ceiling, descending tree roots and soil visible, a mechanical cave on Oneota bluff face of the "Hope" bluff; H=5', L=9', W=2'.
DMV	6/30/2010	Damview Cave, solution-enlarged crawlway along Oneota joint in the "Faith" bluff, view of Lock & Dam No. 5 from here; several inches of thick, abundant leaf litter and sticks inside cave; L=20', W=2', H=2'. Very steep and remote location.
DEV	6/29/2010	Devil's Cave: near-vertical joint in Jordan SS; party room at rear of cave with dry, thick, brown sand several inches thick, trash scattered about.
JLC	9/20/2009, 12/6/2009	John Latsch Cave, roomy walking height tectonic void along cliff face, near top of stairway on the "Charity" bluff; dry gravelly reddish-brown sandy seds.
JLSP-1	9/20/2009	John Latsch State Park Crevice, small cleft in Jordan SS near top of stairway on the "Charity" bluff.
JLSP-2	4/2/2010	Oneota boneyard void containing black earth with tree roots and scats.
PCH	8/28/2011	Priest's Cabin Hollow: Oneota maze cave high above the Whitewater River, many entrances; thick dry seds

		and abundant coon scats.
QB	6/25/2009	Oneota crevice near top of Queen's Bluff, in Great River Bluffs SP.
RH	10/30/2010	Raccoon Heaven: Oneota maze cave high above South Branch of Whitewater River, several entrances; thick dry sed and abundant coon scats.
SH	8/28/2011	Skunk Hollow Cave, Oneota solutional cave, rather wet.
TR	6/30/2010	Tricorn Cave: a mechanical cave on Oneota bluff face of the "Hope" bluff, with three passages, total L=19'; dry, tan sandy soil laced with abundant fine rootlets, fresh coon prints.
TRC	7/11/2009	Trout Run Cave, a solutional Oneota cave in Whitewater SP, well above stream level; collected from the dry parts.
WWR	12/6/2009	Multi-columned rockshelter with red sed on N bank of Whitewater River just downstream from Lamberton Mill Rd.
WWSP	7/11/2009	Rockshelter 100 feet upstream from TRC, sampled where crawlway with animal tracks starts.
WISCONSIN		
Buffalo County		
BVP	3/26/2010	Overlook Cave, an Oneota rockshelter in Buena Vista Park.
Pierce County		
BC	9/5/2004	Black's Cave, descending solutional Oneota crawlway, wet clay-rich sed covered with fungus.
FC	N/A	Fuzzy Critter Cave, solutional Oneota cave, moist red sed.
KSP	4/3/2005	Kinnickinnic SP: Oneota rockshelter that fits one person sitting, just above floodplain.
SP	1/26/2008	South Portal Cave, Oneota solutional cave, sampled from Blaze Dome, brown passage fill below black layer.
TF	9/11/2004	Tree Fork Cave, an excavated solutional Oneota passage.
TBPC	7/11/2009	Trenton Bluff Prairie Cave: an Oneota rockshelter

		with nesting turkey buzzard chicks inside.
WC-1	5/31/2009	Webb Caves: Party Cave, a long solutional Oneota rock tube with a standup room with flowstone at rear; sample collected at the bone deposit half way through, abundant coon scats.
WC-2,3	5/31/2009	Webb Caves: Façade Cave, 2 entrances, dry tan seds collected from ledge.
WC-4	5/31/2009	Webb Caves: horizontal Oneota crevice, L=12', dry brown seds, coon scats.
Trempealeau County		
BBT-1	3/26/2010	Brady's Bluff Trail, Perrot SP, Jordan SS joint in shaded ravine.
BBT-2	3/26/2010	Brady's Bluff Trail, where trail switches to ladder on bluff, thick seds in small pocket.
PP	3/26/2010	Perrot Post, ss niche at ground level.
ILLINOIS		
Carroll County		
MPSP-1,2,3	7/13/2008	Sentinel Bluff Crevice, Mississippi Palisades State Park; tectonic crevice near bluff edge, aphotic zone.
MPSP-4	7/13/2008	Overlook RS
Hardin County		
CIR	7/15/2008	Cave in Rock, on Ohio River, seasonal flooding of entire floor surface.
Jackson County		
FBC	7/15/2008	Fountain Bluff Cave, large rockshelter in Makanda SS; thick reddish sandy seds, party debris.
Pope County		
BSS	7/15/2008	Bell Smith Springs; sampled dry seds at shallow overhangs in the park.
Union County		
GC-1	7/15/2008	Giant City SP
GC-2	7/15/2008	Giant City SP
GC-3	7/15/2008	Giant City SP
IOWA		
Allamakee County		
HOS	9/5/2010	Overlook Cave, dolomite overhang at the Mt Hosmer overlook, Lansing, IA; W=4', L=4.5', H=3.5'.

KENTUCKY		
Rockcastle County		
GSC	7/17/2008	Great Saltpetre Cave
TENNESSEE		
Carter County		
TN	5/23/2009	Saltpetre Cave

APPENDIX C: SELECT CAVE MAPS

Korneski Cave

Leslie and Clarke Caves

Miles Cave

Priests Cabin Hollow

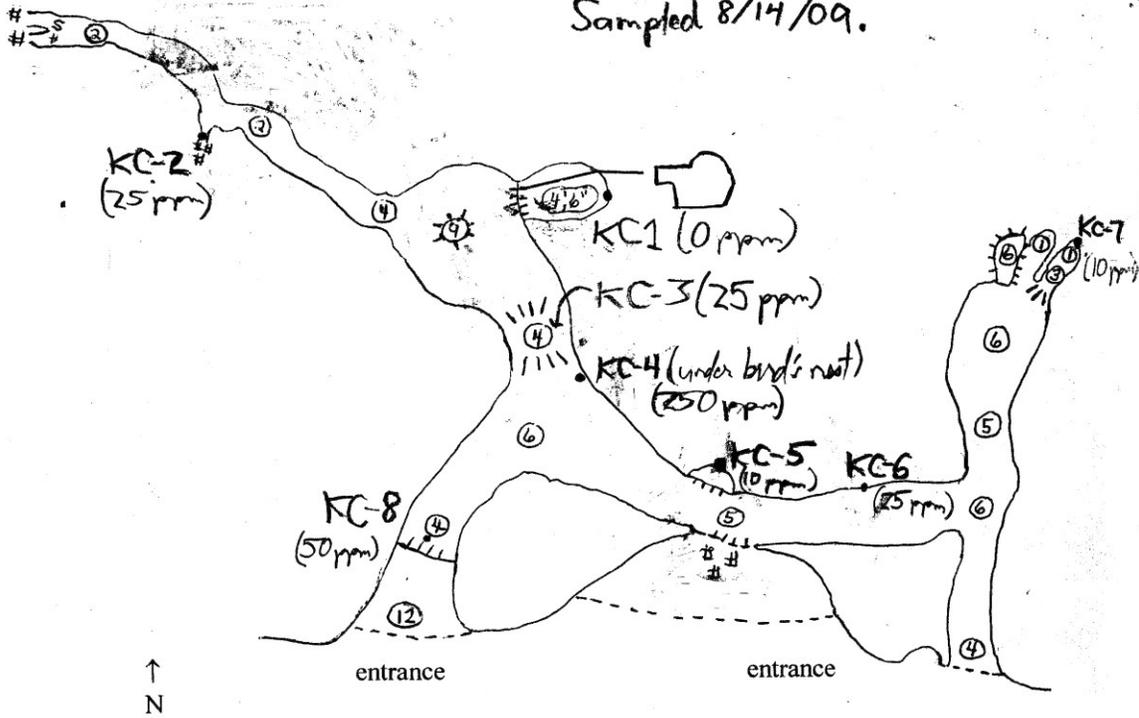
Great Saltpetre Cave

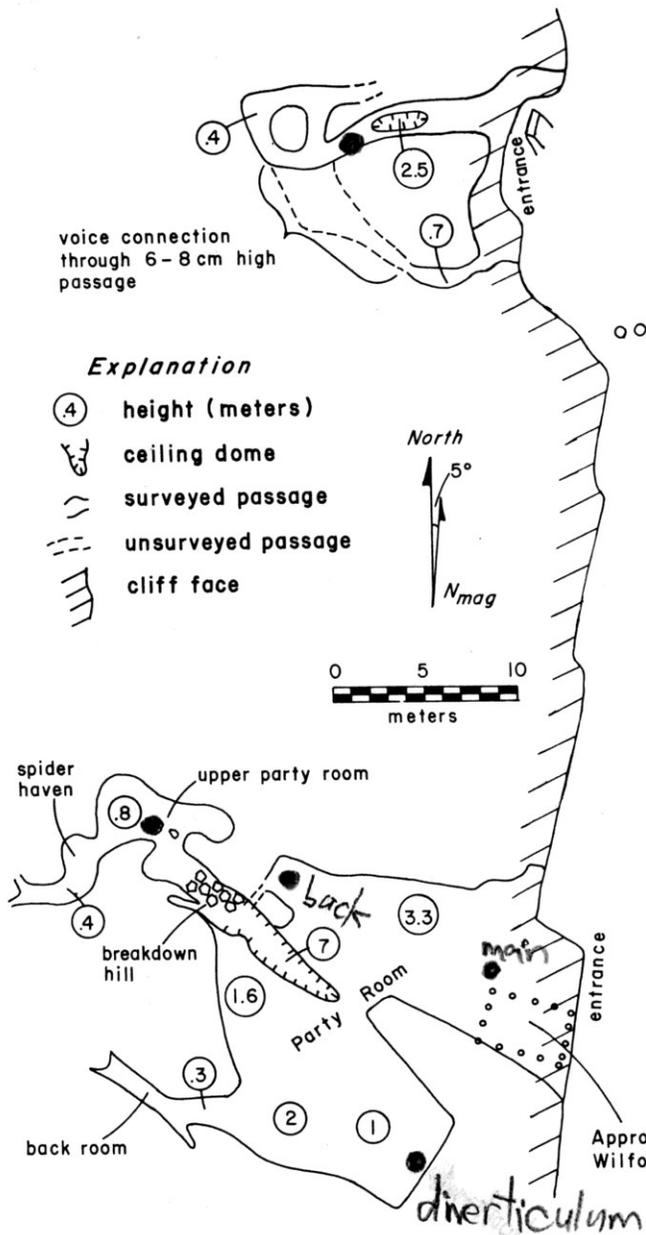
0 5 10
scale in feet

rough survey map
for
Korneski cave
Dakota county, Minnesota

Legend	
---	dripline
⊕	dome
⊙	pit
##	ceiling to low to crawl
S	squeeze
	ledge
/\	slope

Sampled 8/14/09.



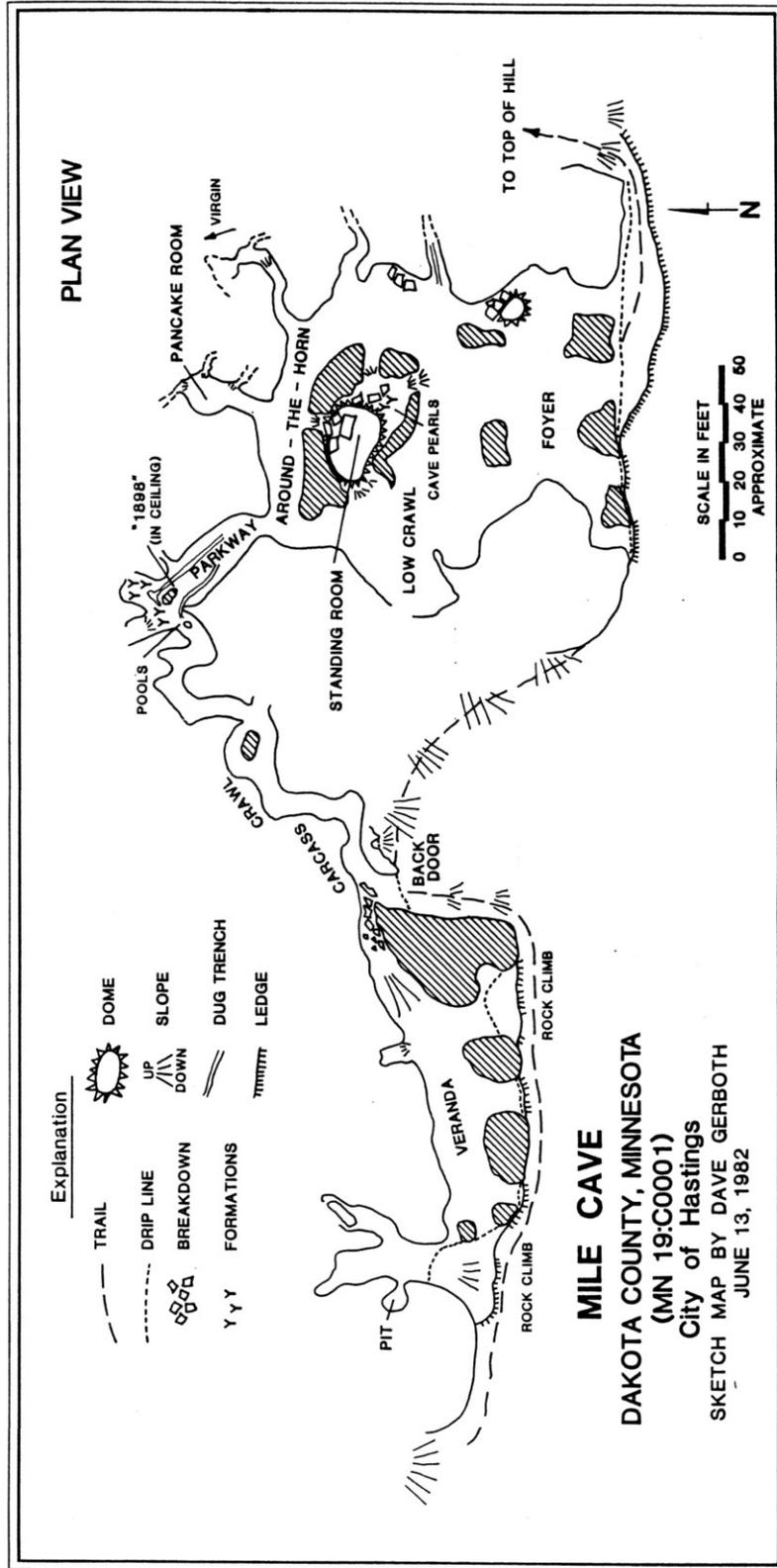


CLARKE CAVE
 Washington County, Minn.
 MCKS (321902)
 Length 30.4 meters

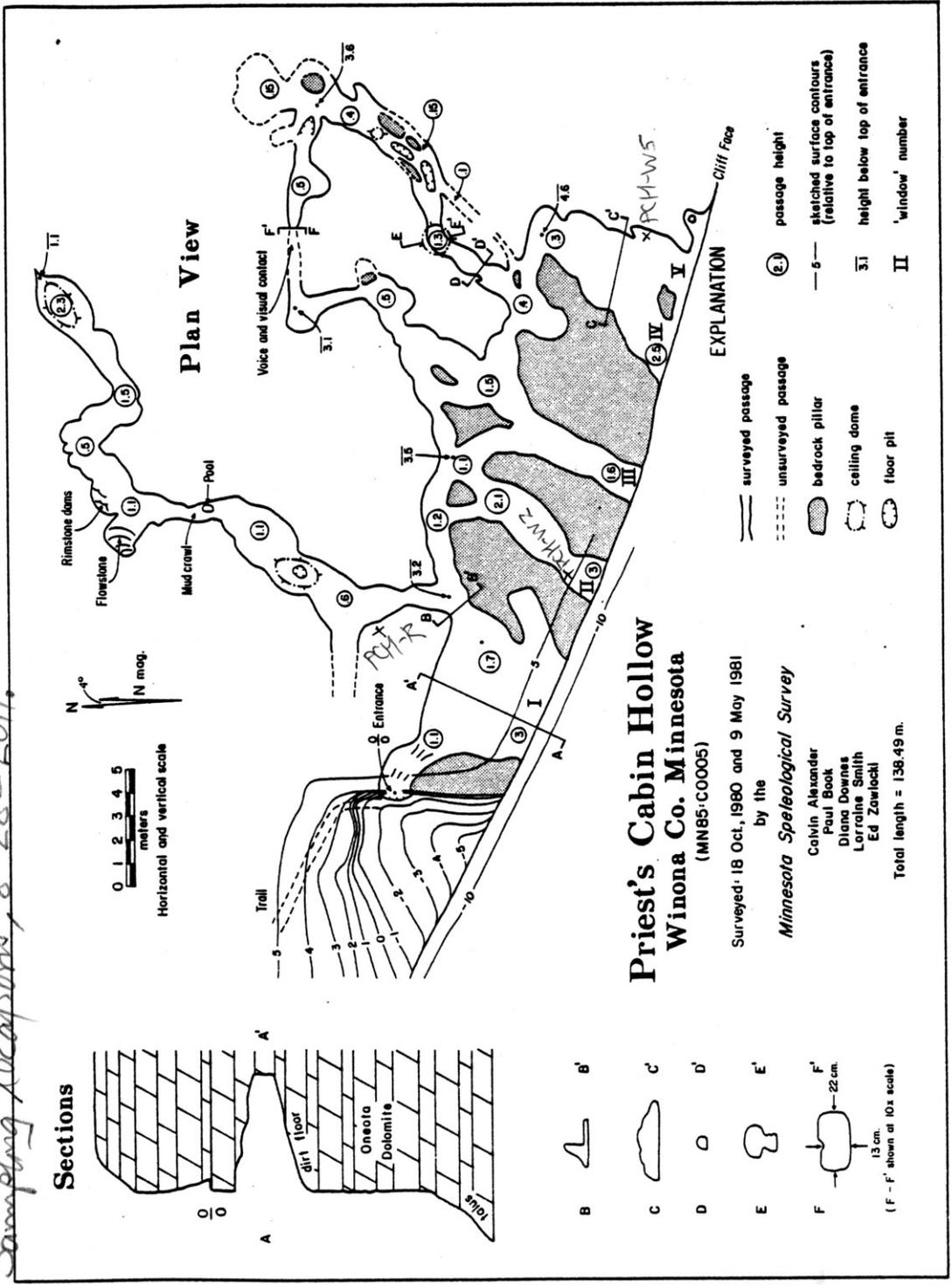
Tape and Brunton Survey
 April 20, 1980
 by the
 Minnesota Speleological Survey

Survey party :
 Carl Breske
 Anne Kress
 Lorraine Smith
 Margaret Daly
 Ed Zawlocki
 Calvin Alexander

LESLIE CAVE
 Washington County, Minn.
 MCKS (321901)
 Length 90.0 meters



Sampling locations, 8-28-2011



Great Saltpetre Cave

Rockcastle County, Kentucky

Suunto and Tape Survey

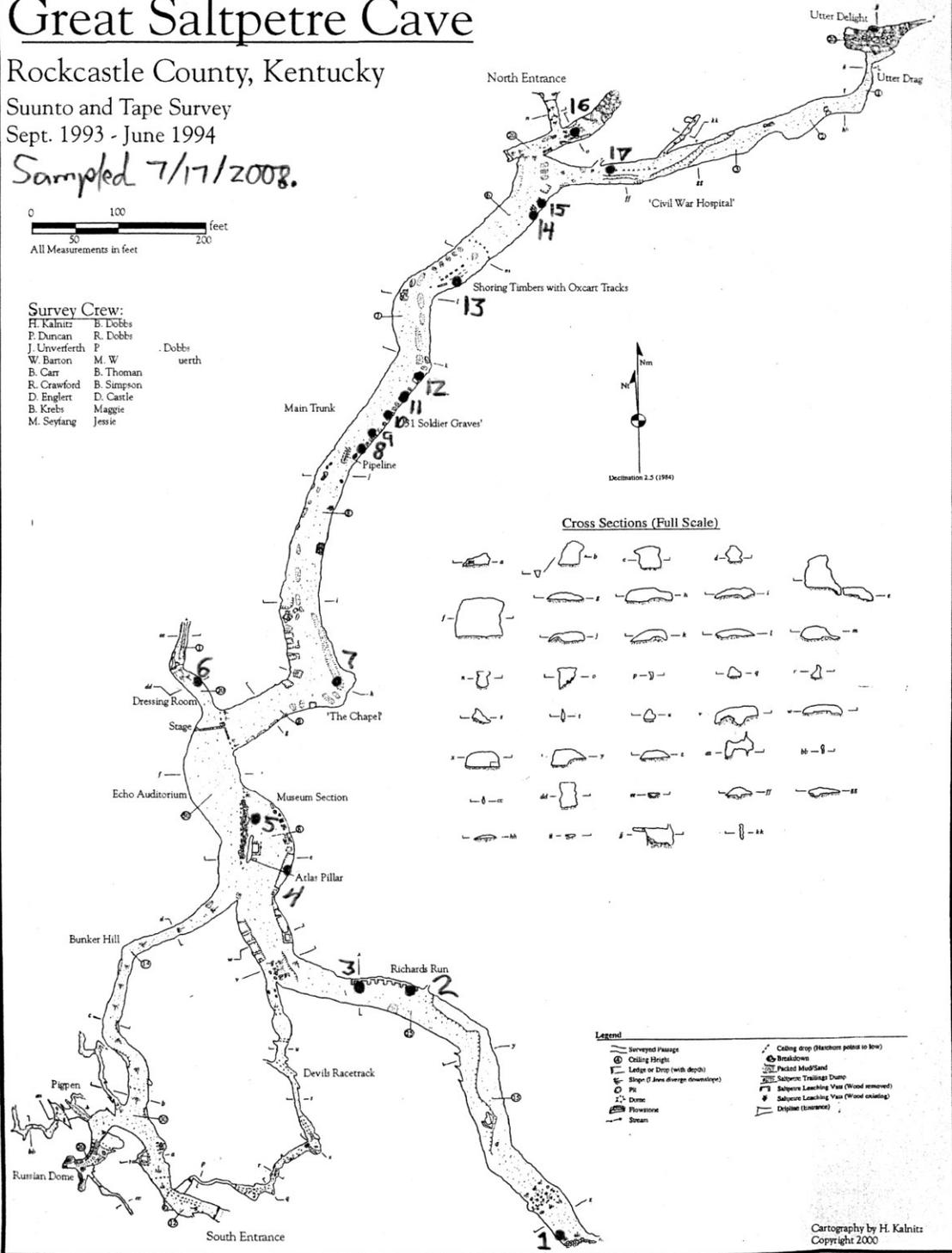
Sept. 1993 - June 1994

Sampled 7/17/2008.

0 50 100 200 feet
All Measurements in feet

Survey Crew:

H. Kalnitz	B. Dobbs	
P. Duncan	R. Dobbs	
J. Liverferth	P. Dobbs	
W. Barton	M. W. uerth	
B. Carr	B. Thoman	
R. Crawford	B. Simpson	
D. Englert	D. Castle	
B. Krebs	Maggie	
M. Seyfang	Jessie	



**APPENDIX D: GEOCHEMISTS WORKBENCH
REACTION OUTPUT**

Step # 0 Xi = 0.0000
 Temperature = 25.0 C Pressure = 1.013 bars
 pH = 9.000
 Ionic strength = 0.069753
 Activity of water = 1.000000
 Solvent mass = 1.000000 kg
 Solution mass = 1.005490 kg
 Solution density = 1.015 g/cm³
 Chlorinity = 0.000000 molal
 Dissolved solids = 5460 mg/kg sol'n
 Elect. conductivity = 4732.94 uS/cm (or umho/cm)
 Hardness = 1872.92 mg/kg sol'n as CaCO₃
 carbonate = 549.90 mg/kg sol'n as CaCO₃
 non-carbonate = 1323.02 mg/kg sol'n as CaCO₃
 Rock mass = 0.000000 kg
 Carbonate alkalinity = 549.90 mg/kg sol'n as CaCO₃
 Water type = Ca-NO₃

	moles remaining	moles reacted	grams reacted	cm ³ reacted
Reactants				

KOH	0.01782	0.0000	0.0000	

No minerals in system.

Aqueous species	molality	mg/kg sol'n	act. coef.	log act.
NO ₃ ⁻	0.04788	2953.	0.7873	-1.4237
K ⁺	0.02572	1000.	0.7873	-1.6936
Ca ⁺⁺	0.01351	538.6	0.4457	-2.2203
HCO ₃ ⁻	0.006600	400.5	0.8056	-2.2743
CaCO ₃	0.002384	237.3	1.0000	-2.6226
CaNO ₃ ⁺	0.002262	229.7	0.7998	-2.7424
CaHCO ₃ ⁺	0.0006564	66.00	0.8131	-3.2726
CO ₃ ⁻⁻	0.0005833	34.81	0.4130	-3.6182
OH ⁻	1.299e-05	0.2197	0.7938	-4.9868
CO ₂ (aq)	1.235e-05	0.5406	1.0000	-4.9083
CaOH ⁺	1.542e-06	0.08753	0.7998	-5.9090

KOH 6.625e-08 0.003696 1.0000 -7.1788
 (only species > 1e-8 molal listed)

Mineral saturation states

	log Q/K		log Q/K
Calcite	2.7924s/sat	Monohydrocalcite	1.7985s/sat
Aragonite	2.6275s/sat		

(only minerals with log Q/K > -3 listed)

Gases fugacity log fug.

Steam	0.03131	-1.504
CO2(g)	0.0003500	-3.456

	In fluid		Sorbed		Kd		
Original basis	total moles	moles	mg/kg	moles	mg/kg	L/kg	

Ca++	0.0188	0.0188	750.				
H+	-0.00297	-0.00297	-2.98				
H2O	55.5	55.5	9.95e+05				
HCO3-	0.0102	0.0102	621.				
K+	0.0257	0.0257	1.00e+03				
NO3-	0.0501	0.0501	3.09e+03				

Elemental composition		In fluid		Sorbed
total moles	moles	mg/kg	moles	mg/kg

Calcium	0.01882	0.01882	750.0	
Carbon	0.01024	0.01024	122.3	
Hydrogen	111.0	111.0	1.113e+05	
Nitrogen	0.05014	0.05014	698.5	
Oxygen	55.69	55.69	8.861e+05	
Potassium	0.02572	0.02572	1000.	

Step # 0 Xi = 0.0000
 Temperature = 25.0 C Pressure = 1.013 bars
 pH = 6.547
 Ionic strength = 0.063206
 Activity of water = 1.000000
 Solvent mass = 1.000032 kg
 Solution mass = 1.005013 kg
 Solution density = 1.015 g/cm³
 Chlorinity = 0.000000 molal
 Dissolved solids = 4956 mg/kg sol'n
 Elect. conductivity = 4519.06 uS/cm (or umho/cm)
 Hardness = 1399.24 mg/kg sol'n as CaCO₃
 carbonate = 177.61 mg/kg sol'n as CaCO₃
 non-carbonate = 1221.63 mg/kg sol'n as CaCO₃
 Rock mass = 0.000477 kg
 Carbonate alkalinity = 177.61 mg/kg sol'n as CaCO₃
 Water type = K-NO₃

Reactants	moles remaining	moles reacted	grams reacted	cm ³ reacted
KOH	0.01782	0.0000	0.0000	

Minerals in system	moles	log moles	grams	volume (cm ³)
Calcite	0.004765	-2.322	0.4770	0.1760
(total)			0.4770	0.1760

Aqueous species	molality	mg/kg sol'n	act. coef.	log act.
NO ₃ -	0.04811	2969.	0.7943	-1.4177
K+	0.02572	1000.	0.7943	-1.6898
Ca ⁺⁺	0.01172	467.5	0.4572	-2.2709
HCO ₃ -	0.003368	204.5	0.8114	-2.5634
CaNO ₃ +	0.002026	205.8	0.8060	-2.7870
CO ₂ (aq)	0.001800	78.83	1.0000	-2.7447
CaHCO ₃ +	0.0002983	30.01	0.8185	-3.6123

CaCO3	3.846e-06	0.3830	1.0000	-5.4150
CO3--	1.025e-06	0.06121	0.4258	-6.3600
H+	3.339e-07	0.0003348	0.8495	-6.5473
OH-	4.542e-08	0.0007686	0.8003	-7.4395

(only species > 1e-8 molal listed)

Mineral saturation states

	log Q/K		log Q/K
Calcite	0.0000 sat	Monohydrocalcite	-0.9939
Aragonite	-0.1649		

(only minerals with log Q/K > -3 listed)

Gases

	fugacity	log fug.
--	----------	----------

CO2(g)	0.05101	-1.292
Steam	0.03131	-1.504

	In fluid	Sorbed	Kd			
Original basis	total moles	moles	mg/kg	moles	mg/kg	L/kg
Ca++	0.0188	0.0141	560.			
H+	-0.00297	0.00180	1.80			
H2O	55.5	55.5	9.95e+05			
HCO3-	0.0102	0.00547	332.			
K+	0.0257	0.0257	1.00e+03			
NO3-	0.0501	0.0501	3.09e+03			

Elemental composition	In fluid	Sorbed	
total moles	moles	mg/kg	moles
		mg/kg	mg/kg
Calcium	0.01882	0.01405	560.3
Carbon	0.01024	0.005471	65.39
Hydrogen	111.0	111.0	1.113e+05
Nitrogen	0.05014	0.05014	698.8
Oxygen	55.69	55.68	8.863e+05
Potassium	0.02572	0.02572	1000.

Step # 10 $X_i = 0.1000$
 Temperature = 25.0 C Pressure = 1.013 bars
 pH = 6.653
 Ionic strength = 0.061879
 Activity of water = 1.000000
 Solvent mass = 1.000054 kg
 Solution mass = 1.004995 kg
 Solution density = 1.015 g/cm³
 Chlorinity = 0.000000 molal
 Dissolved solids = 4917 mg/kg sol'n
 Elect. conductivity = 4535.25 uS/cm (or umho/cm)
 Hardness = 1281.78 mg/kg sol'n as CaCO₃
 carbonate = 150.62 mg/kg sol'n as CaCO₃
 non-carbonate = 1131.15 mg/kg sol'n as CaCO₃
 Rock mass = 0.000595 kg
 Carbonate alkalinity = 150.62 mg/kg sol'n as CaCO₃
 Water type = K-NO₃

Reactants	moles remaining	moles reacted	grams reacted	cm ³ reacted
KOH	0.01604	0.001782	0.1000	

Minerals in system	moles	log moles	grams	volume (cm ³)
Calcite	0.005945	-2.226	0.5950	0.2196
(total)			0.5950	0.2196

Aqueous species	molality	mg/kg sol'n	act. coef.	log act.
NO ₃ -	0.04826	2978.	0.7958	-1.4156
K+	0.02750	1070.	0.7958	-1.6599
Ca ⁺⁺	0.01076	429.0	0.4597	-2.3058
HCO ₃ -	0.002855	173.4	0.8127	-2.6344
CaNO ₃ +	0.001876	190.5	0.8073	-2.8198
CO ₂ (aq)	0.001198	52.44	1.0000	-2.9217
CaHCO ₃ +	0.0002334	23.48	0.8196	-3.7183

CaCO3	3.846e-06	0.3830	1.0000	-5.4150
CO3--	1.104e-06	0.06591	0.4286	-6.3251
H+	2.613e-07	0.0002621	0.8502	-6.6533
OH-	5.787e-08	0.0009793	0.8017	-7.3335

(only species > 1e-8 molal listed)

Mineral saturation states

	log Q/K		log Q/K
Calcite	0.0000 sat	Monohydrocalcite	-0.9939
Aragonite	-0.1649		

(only minerals with log Q/K > -3 listed)

Gases	fugacity	log fug.
CO2(g)	0.03394	-1.469
Steam	0.03131	-1.504

	In fluid total moles	Sorbed moles	Kd mg/kg	L/kg
Ca++	0.0188	0.0129	513.	
H+	-0.00475	0.00119	1.20	
H2O	55.5	55.5	9.95e+05	
HCO3-	0.0102	0.00429	261.	
K+	0.0275	0.0275	1.07e+03	
NO3-	0.0501	0.0501	3.09e+03	

Elemental composition	In fluid total moles	Sorbed moles	mg/kg
Calcium	0.01882	0.01287	513.3
Carbon	0.01024	0.004291	51.29
Hydrogen	111.0	111.0	1.113e+05
Nitrogen	0.05014	0.05014	698.8
Oxygen	55.69	55.67	8.863e+05
Potassium	0.02750	0.02750	1070.

Step # 20 Xi = 0.2000
 Temperature = 25.0 C Pressure = 1.013 bars
 pH = 6.803
 Ionic strength = 0.060383
 Activity of water = 1.000000
 Solvent mass = 1.000076 kg
 Solution mass = 1.004971 kg
 Solution density = 1.015 g/cm³
 Chlorinity = 0.000000 molal
 Dissolved solids = 4870 mg/kg sol'n
 Elect. conductivity = 4546.23 uS/cm (or umho/cm)
 Hardness = 1157.86 mg/kg sol'n as CaCO₃
 carbonate = 116.99 mg/kg sol'n as CaCO₃
 non-carbonate = 1040.87 mg/kg sol'n as CaCO₃
 Rock mass = 0.000720 kg
 Carbonate alkalinity = 116.99 mg/kg sol'n as CaCO₃
 Water type = K-NO₃

Reactants	moles remaining	moles reacted	grams reacted	cm ³ reacted
KOH	0.01426	0.003565	0.2000	

Minerals in system	moles	log moles	grams	volume (cm ³)
Calcite	0.007190	-2.143	0.7196	0.2655
(total)			0.7196	0.2655

Aqueous species	molality	mg/kg sol'n	act. coef.	log act.
NO ₃ -	0.04842	2988.	0.7975	-1.4132
K+	0.02928	1139.	0.7975	-1.6317
Ca ⁺⁺	0.009741	388.5	0.4626	-2.3462
HCO ₃ -	0.002217	134.6	0.8141	-2.7437
CaNO ₃ ⁺	0.001715	174.2	0.8089	-2.8578
CO ₂ (aq)	0.0006599	28.90	1.0000	-3.1805
CaHCO ₃ ⁺	0.0001651	16.61	0.8210	-3.8678

CaCO3	3.846e-06	0.3831	1.0000	-5.4150
CO3--	1.202e-06	0.07180	0.4318	-6.2847
H+	1.850e-07	0.0001856	0.8511	-6.8028
OH-	8.150e-08	0.001379	0.8033	-7.1840

(only species > 1e-8 molal listed)

Mineral saturation states

	log Q/K		log Q/K
Calcite	0.0000 sat	Monohydrocalcite	-0.9939
Aragonite	-0.1649		

(only minerals with log Q/K > -3 listed)

Gases	fugacity	log fug.
Steam	0.03131	-1.504
CO2(g)	0.01870	-1.728

	In fluid	Sorbed	Kd			
Original basis	total moles	moles	mg/kg	moles	mg/kg	L/kg
Ca++	0.0188	0.0116	464.			
H+	-0.00653	0.000655	0.657			
H2O	55.5	55.5	9.95e+05			
HCO3-	0.0102	0.00305	185.			
K+	0.0293	0.0293	1.14e+03			
NO3-	0.0501	0.0501	3.09e+03			

Elemental composition	In fluid	Sorbed	
total moles	moles	mg/kg	moles
		mg/kg	mg/kg
Calcium	0.01882	0.01163	463.7
Carbon	0.01024	0.003047	36.41
Hydrogen	111.0	111.0	1.114e+05
Nitrogen	0.05014	0.05014	698.8
Oxygen	55.69	55.67	8.863e+05
Potassium	0.02928	0.02928	1139.

Step # 30 Xi = 0.3000
 Temperature = 25.0 C Pressure = 1.013 bars
 pH = 7.059
 Ionic strength = 0.058615
 Activity of water = 1.000000
 Solvent mass = 1.000100 kg
 Solution mass = 1.004936 kg
 Solution density = 1.015 g/cm³
 Chlorinity = 0.000000 molal
 Dissolved solids = 4811 mg/kg sol'n
 Elect. conductivity = 4548.63 uS/cm (or umho/cm)
 Hardness = 1023.49 mg/kg sol'n as CaCO₃
 carbonate = 72.60 mg/kg sol'n as CaCO₃
 non-carbonate = 950.90 mg/kg sol'n as CaCO₃
 Rock mass = 0.000855 kg
 Carbonate alkalinity = 72.60 mg/kg sol'n as CaCO₃
 Water type = K-NO₃

	moles remaining	moles reacted	grams reacted	cm ³ reacted
Reactants				

KOH	0.01248	0.005347	0.3000	

Minerals in system	moles	log moles	grams	volume (cm ³)

Calcite	0.008539	-2.069	0.8547	0.3154
(total)			0.8547	0.3154

Aqueous species	molality	mg/kg sol'n	act. coef.	log act.

NO ₃ -	0.04860	2999.	0.7996	-1.4105
K+	0.03106	1209.	0.7996	-1.6049
Ca ⁺⁺	0.008641	344.7	0.4661	-2.3949
CaNO ₃ +	0.001539	156.4	0.8107	-2.9039
HCO ₃ -	0.001373	83.38	0.8158	-2.9507
CO ₂ (aq)	0.0002274	9.958	1.0000	-3.6433
CaHCO ₃ +	9.146e-05	9.202	0.8226	-4.1236

CaCO3	3.846e-06	0.3831	1.0000	-5.4150
CO3--	1.333e-06	0.07961	0.4357	-6.2360
OH-	1.465e-07	0.002480	0.8053	-6.9282
H+	1.025e-07	0.0001028	0.8522	-7.0586
CaOH+	1.164e-08	0.0006615	0.8107	-8.0250

(only species > 1e-8 molal listed)

Mineral saturation states

	log Q/K		log Q/K
Calcite	0.0000 sat	Monohydrocalcite	-0.9939
Aragonite	-0.1649		

(only minerals with log Q/K > -3 listed)

Gases	fugacity	log fug.
Steam	0.03131	-1.504
CO2(g)	0.006444	-2.191

	In fluid	Sorbed	Kd			
Original basis	total moles	moles	mg/kg	moles	mg/kg	L/kg
Ca++	0.0188	0.0103	410.			
H+	-0.00832	0.000222	0.223			
H2O	55.5	55.5	9.95e+05			
HCO3-	0.0102	0.00170	103.			
K+	0.0311	0.0311	1.21e+03			
NO3-	0.0501	0.0501	3.09e+03			

Elemental composition	In fluid	Sorbed	
total moles	moles	mg/kg	moles mg/kg
Calcium	0.01882	0.01028	409.9
Carbon	0.01024	0.001697	20.29
Hydrogen	111.0	111.0	1.114e+05
Nitrogen	0.05014	0.05014	698.9
Oxygen	55.70	55.67	8.863e+05
Potassium	0.03106	0.03106	1209.

Step # 40 Xi = 0.4000
 Temperature = 25.0 C Pressure = 1.013 bars
 pH = 8.151
 Ionic strength = 0.056312
 Activity of water = 1.000000
 Solvent mass = 1.000128 kg
 Solution mass = 1.004880 kg
 Solution density = 1.015 g/cm³
 Chlorinity = 0.000000 molal
 Dissolved solids = 4728 mg/kg sol'n
 Elect. conductivity = 4534.03 uS/cm (or umho/cm)
 Hardness = 868.71 mg/kg sol'n as CaCO₃
 carbonate = 7.10 mg/kg sol'n as CaCO₃
 non-carbonate = 861.61 mg/kg sol'n as CaCO₃
 Rock mass = 0.001010 kg
 Carbonate alkalinity = 7.10 mg/kg sol'n as CaCO₃
 Water type = K-NO₃

Reactants	moles remaining	moles reacted	grams reacted	cm ³ reacted
KOH	0.01069	0.007129	0.4000	

Minerals in system	moles	log moles	grams	volume (cm ³)
Calcite	0.01009	-1.996	1.010	0.3728
(total)			1.010	0.3728

Aqueous species	molality	mg/kg sol'n	act. coef.	log act.
NO ₃ ⁻	0.04880	3012.	0.8024	-1.4072
K ⁺	0.03284	1278.	0.8024	-1.5792
Ca ⁺⁺	0.007376	294.2	0.4709	-2.4593
CaNO ₃ ⁺	0.001333	135.5	0.8132	-2.9649
HCO ₃ ⁻	0.0001283	7.790	0.8182	-3.9790
CaHCO ₃ ⁺	7.369e-06	0.7414	0.8247	-5.2163
CaCO ₃	3.846e-06	0.3831	1.0000	-5.4150

OH-	1.808e-06	0.03060	0.8079	-5.8355
CO2(aq)	1.721e-06	0.07536	1.0000	-5.7643
CO3--	1.527e-06	0.09122	0.4410	-6.1716
CaOH+	1.239e-07	0.007041	0.8132	-6.9967
KOH	1.221e-08	0.0006821	1.0000	-7.9131

(only species > 1e-8 molal listed)

Mineral saturation states

	log Q/K		log Q/K
Calcite	0.0000 sat	Monohydrocalcite	-0.9939
Aragonite	-0.1649		

(only minerals with log Q/K > -3 listed)

Gases	fugacity	log fug.
Steam	0.03131	-1.504
CO2(g)	4.876e-05	-4.312

	In fluid	Sorbed	Kd			
Original basis	total moles	moles	mg/kg	moles	mg/kg	L/kg
Ca++	0.0188	0.00872	348.			
H+	-0.0101	-5.59e-06	-0.00561			
H2O	55.5	55.5	9.95e+05			
HCO3-	0.0102	0.000143	8.67			
K+	0.0328	0.0328	1.28e+03			
NO3-	0.0501	0.0501	3.09e+03			

Elemental composition	In fluid	Sorbed	
total moles	moles	mg/kg	moles mg/kg
Calcium	0.01882	0.008722	347.9
Carbon	0.01024	0.0001427	1.706
Hydrogen	111.0	111.0	1.114e+05
Nitrogen	0.05014	0.05014	698.9
Oxygen	55.70	55.67	8.863e+05
Potassium	0.03285	0.03285	1278.

Step # 50 Xi = 0.5000
 Temperature = 25.0 C Pressure = 1.013 bars
 pH = 11.079
 Ionic strength = 0.057565
 Activity of water = 1.000000
 Solvent mass = 1.000131 kg
 Solution mass = 1.004966 kg
 Solution density = 1.015 g/cm³
 Chlorinity = 0.000000 molal
 Dissolved solids = 4811 mg/kg sol'n
 Elect. conductivity = 4792.50 uS/cm (or umho/cm)
 Hardness = 854.97 mg/kg sol'n as CaCO₃
 carbonate = 0.53 mg/kg sol'n as CaCO₃
 non-carbonate = 854.44 mg/kg sol'n as CaCO₃
 Rock mass = 0.001024 kg
 Carbonate alkalinity = 0.53 mg/kg sol'n as CaCO₃
 Water type = K-NO₃

Reactants	moles remaining	moles reacted	grams reacted	cm ³ reacted
KOH	0.008912	0.008912	0.5000	

Minerals in system	moles	log moles	grams	volume (cm ³)
Calcite	0.01023	-1.990	1.024	0.3779
(total)			1.024	0.3779

Aqueous species	molality	mg/kg sol'n	act. coef.	log act.
NO ₃ -	0.04884	3014.	0.8008	-1.4077
K+	0.03461	1347.	0.8008	-1.5572
Ca ⁺⁺	0.007185	286.6	0.4683	-2.4730
OH-	0.001533	25.94	0.8065	-2.9080
CaNO ₃ ⁺	0.001293	131.3	0.8118	-2.9791
CaOH ⁺	0.0001018	5.781	0.8118	-4.0830
KOH	1.087e-05	0.6071	1.0000	-4.9636

CaCO3	3.846e-06	0.3831	1.0000	-5.4150
CO3--	1.587e-06	0.09478	0.4381	-6.1579
HCO3-	1.567e-07	0.009516	0.8169	-6.8927

(only species > 1e-8 molal listed)

Mineral saturation states

	log Q/K		log Q/K	
Calcite	0.0000	sat	Portlandite	-2.8929
Aragonite	-0.1649		Ca(OH)2(c)	-2.8929
Monohydrocalcite	-0.9939			

(only minerals with log Q/K > -3 listed)

Gases fugacity log fug.

Steam	0.03131	-1.504
CO2(g)	7.028e-11	-10.153

	In fluid		Sorbed		Kd		
Original basis	total moles	moles	mg/kg	moles	mg/kg	L/kg	
Ca++	0.0188	0.00858	342.				
H+	-0.0119	-0.00165	-1.66				
H2O	55.5	55.5	9.95e+05				
HCO3-	0.0102	5.60e-06	0.340				
K+	0.0346	0.0346	1.35e+03				
NO3-	0.0501	0.0501	3.09e+03				

Elemental composition		In fluid		Sorbed	
	total moles	moles	mg/kg	moles	mg/kg
Calcium	0.01882	0.008585	342.4		
Carbon	0.01024	5.599e-06	0.06692		
Hydrogen	111.0	111.0	1.114e+05		
Nitrogen	0.05014	0.05014	698.8		
Oxygen	55.70	55.67	8.863e+05		
Potassium	0.03463	0.03463	1347.		

Step # 60 Xi = 0.6000
 Temperature = 25.0 C Pressure = 1.013 bars
 pH = 11.397
 Ionic strength = 0.059169
 Activity of water = 1.000000
 Solvent mass = 1.000131 kg
 Solution mass = 1.005066 kg
 Solution density = 1.015 g/cm³
 Chlorinity = 0.000000 molal
 Dissolved solids = 4910 mg/kg sol'n
 Elect. conductivity = 5074.21 uS/cm (or umho/cm)
 Hardness = 854.88 mg/kg sol'n as CaCO₃
 carbonate = 0.54 mg/kg sol'n as CaCO₃
 non-carbonate = 854.34 mg/kg sol'n as CaCO₃
 Rock mass = 0.001024 kg
 Carbonate alkalinity = 0.54 mg/kg sol'n as CaCO₃
 Water type = K-NO₃

Reactants	moles remaining	moles reacted	grams reacted	cm ³ reacted
KOH	0.007129	0.01069	0.6000	

Minerals in system	moles	log moles	grams	volume (cm ³)
Calcite	0.01023	-1.990	1.024	0.3779
(total)			1.024	0.3779

Aqueous species	molality	mg/kg sol'n	act. coef.	log act.
NO ₃ ⁻	0.04887	3015.	0.7989	-1.4085
K ⁺	0.03638	1416.	0.7989	-1.5366
Ca ⁺⁺	0.007102	283.3	0.4650	-2.4811
OH ⁻	0.003195	54.08	0.8047	-2.5899
CaNO ₃ ⁺	0.001269	128.9	0.8101	-2.9880
CaOH ⁺	0.0002082	11.83	0.8101	-3.7729
KOH	2.372e-05	1.324	1.0000	-4.6249

CaCO3	3.846e-06	0.3830	1.0000	-5.4150
CO3--	1.630e-06	0.09735	0.4345	-6.1498
HCO3-	7.689e-08	0.004669	0.8153	-7.2028

(only species > 1e-8 molal listed)

Mineral saturation states

	log Q/K		log Q/K
Calcite	0.0000	Portlandite	-2.2647
Aragonite	-0.1649	Ca(OH)2(c)	-2.2647
Monohydrocalcite	-0.9939		

(only minerals with log Q/K > -3 listed)

Gases fugacity log fug.

Steam	0.03131	-1.504
CO2(g)	1.655e-11	-10.781

	In fluid	Sorbed	Kd		
Original basis	total moles	moles	mg/kg	moles	mg/kg L/kg
Ca++	0.0188	0.00858	342.		
H+	-0.0137	-0.00343	-3.44		
H2O	55.5	55.5	9.95e+05		
HCO3-	0.0102	5.56e-06	0.337		
K+	0.0364	0.0364	1.42e+03		
NO3-	0.0501	0.0501	3.09e+03		

Elemental composition	In fluid	Sorbed	
total moles	moles	mg/kg	moles mg/kg
Calcium	0.01882	0.008585	342.3
Carbon	0.01024	5.558e-06	0.06642
Hydrogen	111.0	111.0	1.113e+05
Nitrogen	0.05014	0.05014	698.8
Oxygen	55.70	55.67	8.862e+05
Potassium	0.03641	0.03641	1416.

Step # 70 Xi = 0.7000
 Temperature = 25.0 C Pressure = 1.013 bars
 pH = 11.578
 Ionic strength = 0.060777
 Activity of water = 1.000000
 Solvent mass = 1.000131 kg
 Solution mass = 1.005166 kg
 Solution density = 1.015 g/cm³
 Chlorinity = 0.000000 molal
 Dissolved solids = 5009 mg/kg sol'n
 Elect. conductivity = 5354.61 uS/cm (or umho/cm)
 Hardness = 854.80 mg/kg sol'n as CaCO₃
 carbonate = 0.55 mg/kg sol'n as CaCO₃
 non-carbonate = 854.25 mg/kg sol'n as CaCO₃
 Rock mass = 0.001024 kg
 Carbonate alkalinity = 0.55 mg/kg sol'n as CaCO₃
 Water type = K-NO₃

Reactants	moles remaining	moles reacted	grams reacted	cm ³ reacted
KOH	0.005347	0.01248	0.7000	

Minerals in system	moles	log moles	grams	volume (cm ³)
Calcite	0.01023	-1.990	1.024	0.3779
(total)			1.024	0.3779

Aqueous species	molality	mg/kg sol'n	act. coef.	log act.
NO ₃ -	0.04889	3016.	0.7970	-1.4093
K+	0.03815	1484.	0.7970	-1.5170
Ca ⁺⁺	0.007022	280.0	0.4618	-2.4890
OH-	0.004861	82.25	0.8029	-2.4086
CaNO ₃ +	0.001246	126.6	0.8085	-2.9967
CaOH+	0.0003110	17.67	0.8085	-3.5996
KOH	3.767e-05	2.103	1.0000	-4.4241

CaCO3	3.846e-06	0.3830	1.0000	-5.4150
CO3--	1.674e-06	0.09994	0.4309	-6.1419
HCO3-	5.169e-08	0.003138	0.8137	-7.3761

(only species > 1e-8 molal listed)

Mineral saturation states

	log Q/K		log Q/K
Calcite	0.0000	Portlandite	-1.9101
Aragonite	-0.1649	Ca(OH)2(c)	-1.9101
Monohydrocalcite	-0.9939		

(only minerals with log Q/K > -3 listed)

Gases	fugacity	log fug.
Steam	0.03131	-1.504
CO2(g)	7.313e-12	-11.136

	In fluid	Sorbed	Kd			
Original basis	total moles	moles	mg/kg	moles	mg/kg	L/kg
Ca++	0.0188	0.00858	342.			
H+	-0.0154	-0.00522	-5.23			
H2O	55.5	55.5	9.95e+05			
HCO3-	0.0102	5.57e-06	0.338			
K+	0.0382	0.0382	1.49e+03			
NO3-	0.0501	0.0501	3.09e+03			

Elemental composition	In fluid	Sorbed		
total moles	moles	mg/kg	moles	mg/kg
Calcium	0.01882	0.008585	342.3	
Carbon	0.01024	5.575e-06	0.06662	
Hydrogen	111.0	111.0	1.113e+05	
Nitrogen	0.05014	0.05014	698.7	
Oxygen	55.70	55.67	8.861e+05	
Potassium	0.03819	0.03819	1486.	

Step # 80 Xi = 0.8000
 Temperature = 25.0 C Pressure = 1.013 bars
 pH = 11.705
 Ionic strength = 0.062389
 Activity of water = 1.000000
 Solvent mass = 1.000131 kg
 Solution mass = 1.005266 kg
 Solution density = 1.015 g/cm³
 Chlorinity = 0.000000 molal
 Dissolved solids = 5108 mg/kg sol'n
 Elect. conductivity = 5633.71 uS/cm (or umho/cm)
 Hardness = 854.72 mg/kg sol'n as CaCO₃
 carbonate = 0.55 mg/kg sol'n as CaCO₃
 non-carbonate = 854.17 mg/kg sol'n as CaCO₃
 Rock mass = 0.001024 kg
 Carbonate alkalinity = 0.55 mg/kg sol'n as CaCO₃
 Water type = K-NO₃

Reactants	moles remaining	moles reacted	grams reacted	cm ³ reacted
KOH	0.003565	0.01426	0.8000	

Minerals in system	moles	log moles	grams	volume (cm ³)
Calcite	0.01023	-1.990	1.024	0.3779
(total)			1.024	0.3779

Aqueous species	molality	mg/kg sol'n	act. coef.	log act.
NO ₃ -	0.04891	3017.	0.7952	-1.4101
K+	0.03992	1553.	0.7952	-1.4984
Ca ⁺⁺	0.006945	276.9	0.4588	-2.4968
OH-	0.006528	110.5	0.8012	-2.2815
CaNO ₃ ⁺	0.001224	124.4	0.8068	-3.0053
CaOH ⁺	0.0004103	23.30	0.8068	-3.4801
KOH	5.270e-05	2.942	1.0000	-4.2782

CaCO3	3.846e-06	0.3830	1.0000	-5.4150
CO3--	1.718e-06	0.1025	0.4275	-6.1341
HCO3-	3.933e-08	0.002388	0.8122	-7.4956

(only species > 1e-8 molal listed)

Mineral saturation states

	log Q/K		log Q/K	
Calcite	0.0000	sat	Portlandite	-1.6635
Aragonite	-0.1649		Ca(OH)2(c)	-1.6635
Monohydrocalcite	-0.9939			

(only minerals with log Q/K > -3 listed)

Gases fugacity log fug.

Steam	0.03131	-1.504
CO2(g)	4.145e-12	-11.383

	In fluid	Sorbed	Kd			
Original basis	total moles	moles	mg/kg	moles	mg/kg	L/kg
Ca++	0.0188	0.00858	342.			
H+	-0.0172	-0.00700	-7.02			
H2O	55.5	55.5	9.95e+05			
HCO3-	0.0102	5.61e-06	0.340			
K+	0.0400	0.0400	1.55e+03			
NO3-	0.0501	0.0501	3.09e+03			

Elemental composition	In fluid	Sorbed		
total moles	moles	mg/kg	moles	mg/kg
Calcium	0.01882	0.008585	342.3	
Carbon	0.01024	5.606e-06	0.06698	
Hydrogen	111.0	111.0	1.113e+05	
Nitrogen	0.05014	0.05014	698.6	
Oxygen	55.70	55.67	8.861e+05	
Potassium	0.03998	0.03998	1555.	

Step # 90 Xi = 0.9000
 Temperature = 25.0 C Pressure = 1.013 bars
 pH = 11.803
 Ionic strength = 0.064005
 Activity of water = 1.000000
 Solvent mass = 1.000131 kg
 Solution mass = 1.005366 kg
 Solution density = 1.015 g/cm³
 Chlorinity = 0.000000 molal
 Dissolved solids = 5207 mg/kg sol'n
 Elect. conductivity = 5911.53 uS/cm (or umho/cm)
 Hardness = 854.64 mg/kg sol'n as CaCO₃
 carbonate = 0.56 mg/kg sol'n as CaCO₃
 non-carbonate = 854.08 mg/kg sol'n as CaCO₃
 Rock mass = 0.001024 kg
 Carbonate alkalinity = 0.56 mg/kg sol'n as CaCO₃
 Water type = K-NO₃

Reactants	moles remaining	moles reacted	grams reacted	cm ³ reacted
KOH	0.001782	0.01604	0.9000	

Minerals in system	moles	log moles	grams	volume (cm ³)
Calcite	0.01023	-1.990	1.024	0.3779
(total)			1.024	0.3779

Aqueous species	molality	mg/kg sol'n	act. coef.	log act.
NO ₃ -	0.04893	3018.	0.7934	-1.4109
K+	0.04168	1621.	0.7934	-1.4805
OH-	0.008198	138.7	0.7995	-2.1835
Ca ⁺⁺	0.006870	273.9	0.4557	-2.5043
CaNO ₃ ⁺	0.001203	122.2	0.8052	-3.0136
CaOH ⁺	0.0005063	28.75	0.8052	-3.3897
KOH	6.880e-05	3.840	1.0000	-4.1624

CaCO3	3.846e-06	0.3829	1.0000	-5.4150
CO3--	1.762e-06	0.1052	0.4242	-6.1266
HCO3-	3.200e-08	0.001942	0.8107	-7.5860

(only species > 1e-8 molal listed)

Mineral saturation states

	log Q/K		log Q/K
Calcite	0.0000	Portlandite	-1.4750
Aragonite	-0.1649	Ca(OH)2(c)	-1.4750
Monohydrocalcite	-0.9939		

(only minerals with log Q/K > -3 listed)

Gases fugacity log fug.

Steam	0.03131	-1.504
CO2(g)	2.686e-12	-11.571

	In fluid	Sorbed	Kd		
Original basis	total moles	moles	mg/kg	moles	mg/kg L/kg
Ca++	0.0188	0.00858	342.		
H+	-0.0190	-0.00878	-8.80		
H2O	55.5	55.5	9.95e+05		
HCO3-	0.0102	5.64e-06	0.342		
K+	0.0418	0.0418	1.62e+03		
NO3-	0.0501	0.0501	3.09e+03		

Elemental composition	In fluid	Sorbed	
total moles	moles	mg/kg	moles mg/kg
Calcium	0.01882	0.008585	342.2
Carbon	0.01024	5.642e-06	0.06740
Hydrogen	111.0	111.0	1.113e+05
Nitrogen	0.05014	0.05014	698.6
Oxygen	55.71	55.68	8.860e+05
Potassium	0.04176	0.04176	1624.

Step # 100 $X_i = 1.0000$
 Temperature = 25.0 C Pressure = 1.013 bars
 pH = 11.883
 Ionic strength = 0.065625
 Activity of water = 1.000000
 Solvent mass = 1.000131 kg
 Solution mass = 1.005466 kg
 Solution density = 1.015 g/cm³
 Chlorinity = 0.000000 molal
 Dissolved solids = 5306 mg/kg sol'n
 Elect. conductivity = 6188.11 uS/cm (or umho/cm)
 Hardness = 854.56 mg/kg sol'n as CaCO₃
 carbonate = 0.56 mg/kg sol'n as CaCO₃
 non-carbonate = 854.00 mg/kg sol'n as CaCO₃
 Rock mass = 0.001024 kg
 Carbonate alkalinity = 0.56 mg/kg sol'n as CaCO₃
 Water type = K-NO₃

Reactants	moles remaining	moles reacted	grams reacted	cm ³ reacted
KOH	4.096e-17	0.01782	1.000	

Minerals in system	moles	log moles	grams	volume (cm ³)
Calcite	0.01023	-1.990	1.024	0.3779
(total)			1.024	0.3779

Aqueous species	molality	mg/kg sol'n	act. coef.	log act.
NO ₃ -	0.04895	3019.	0.7916	-1.4117
K+	0.04345	1690.	0.7916	-1.4635
OH-	0.009871	167.0	0.7978	-2.1037
Ca ⁺⁺	0.006797	271.0	0.4528	-2.5118
CaNO ₃ ⁺	0.001183	120.1	0.8037	-3.0219
CaOH ⁺	0.0005991	34.02	0.8037	-3.3174
KOH	8.597e-05	4.798	1.0000	-4.0656

CaCO3	3.846e-06	0.3829	1.0000	-5.4150
CO3--	1.806e-06	0.1078	0.4209	-6.1191
HCO3-	2.714e-08	0.001647	0.8092	-7.6583

(only species > 1e-8 molal listed)

Mineral saturation states

	log Q/K		log Q/K
Calcite	0.0000	Portlandite	-1.3231
Aragonite	-0.1649	Ca(OH)2(c)	-1.3231
Monohydrocalcite	-0.9939		

(only minerals with log Q/K > -3 listed)

Gases fugacity log fug.

Steam	0.03131	-1.504
CO2(g)	1.893e-12	-11.723

	In fluid	Sorbed	Kd		
Original basis	total moles	moles	mg/kg	moles	mg/kg L/kg
Ca++	0.0188	0.00858	342.		
H+	-0.0208	-0.0106	-10.6		
H2O	55.5	55.5	9.95e+05		
HCO3-	0.0102	5.68e-06	0.345		
K+	0.0435	0.0435	1.69e+03		
NO3-	0.0501	0.0501	3.09e+03		

Elemental composition	In fluid	Sorbed	
total moles	moles	mg/kg	moles mg/kg
Calcium	0.01882	0.008585	342.2
Carbon	0.01024	5.681e-06	0.06786
Hydrogen	111.0	111.0	1.113e+05
Nitrogen	0.05014	0.05014	698.5
Oxygen	55.71	55.68	8.860e+05
Potassium	0.04354	0.04354	1693.