

LECHUGUILLA CAVE POOL CHEMISTRY, 1986-1999

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In May 1986, cavers dug into Lechuguilla Cave, in southeastern New Mexico, USA. Subsequent exploration and research have demonstrated that Lechuguilla is a world-class cave, both in size and in speleological importance. Of particular interest to hydrologists and geochemists are the numerous isolated pools throughout much of the cave. Since 1986, close to 200 water samples have been collected and subjected to over 2000 individual analyses. Results of these analyses are collected and published here for the first time.

Dominant cations in the pool waters are calcium and magnesium; dominant anions are bicarbonate and sulfate. These characteristics reflect the limestone/dolomite host bedrock of the cave, modified to varying degrees by the cave's massive gypsum deposits, associated with the cave's early development. The overall chemistry of the water can be explained by a small number of geochemical processes, starting with evaporation and concentration of local rainfall, and dissolution of soil CO₂ and local bedrock. Within the cave, excess CO₂ is degassed, leading to precipitation of CaCO₃ and increased Mg²⁺:Ca²⁺ ratios. In some areas of the cave, infiltrating water encounters and dissolves gypsum, leading to increased CaCO₃ precipitation and increased SO₄²⁻:HCO₃⁻ ratios. In at least one location, massive evaporation has created a magnesium sulfate brine. Geochemical characteristics seem to confirm that the pool located at Lechuguilla's current deep point is actually the regional aquifer, suggesting that the cave's maximum air-filled depth has been reached.

In May 1986, a team of cavers digging in a guano cave a few kilometers west of Carlsbad Cavern broke through into cave passage, thus setting off one of the most remarkable events in American cave discovery and speleology—the exploration of Lechuguilla Cave. Within a week over 1050 m of cave had been surveyed to a depth of over 210 m (Bridges 1988). Lechuguilla quickly appeared on lists of the world's longest caves and is currently the deepest known limestone cave in the United States. The rate of discovery and surveying of Lechuguilla has been truly astounding, and exploration continues to this day. The cave had a total surveyed length of over 170 km and depth of 475 m as of November 2000. Due in large part to the stewardship of the National Park Service and the foresight of the caving community, science has been a part of exploration of Lechuguilla Cave since the beginning. Important studies in the fields of geology (Polyak *et al.* 1998), speleogenesis (Hill 1995, 2000; Jagnow *et al.* 2000), mineralogy (Polyak & Güven 1996, 1999; DuChene 1997), cave biology (Northup *et al.* 1992), cave microbiology (Cunningham *et al.* 1995), geomicrobiology (Dotson *et al.* 1999; Spilde *et al.* 1999; Northup *et al.* 2000), and microclimatology (Cunningham & LaRock 1991) have all been conducted within the cave.

One of the most striking aspects of Lechuguilla, located beneath the semi-arid Chihuahuan desert, is the large number of pools scattered throughout much of the vertical and horizontal extent of the cave (Fig. 1). With few exceptions, the pools show neither obvious interconnections nor visible inflow

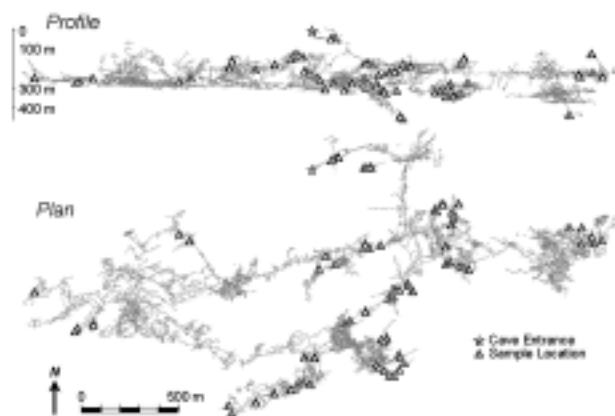


Figure 1. Map of Lechuguilla Cave, showing cave entrance and sample locations.

or outflow other than flowstone seeps and ceiling drips. The pools, therefore, generally represent isolated samples of vadose-zone water infiltrating along separate and independent flow paths. As early as June 1986, the potential geochemical significance of these pools was recognized, and the first sampling and analysis program was initiated. Since then, seven different researchers have collected close to 200 pool and drip-water samples from the cave and have performed over 2000 analyses.

GEOLOGIC SETTING

Lechuguilla Cave lies within the Permian Capitan Reef Complex of the Guadalupe Mountains in southeastern New Mexico and west Texas. These same rocks host nearby Carlsbad Cavern and numerous smaller caves. The geology and speleogenesis of these caves have been described at length by Hill (1987). The upper passages of Lechuguilla penetrate the backreef rocks of the Artesia Group, while the main cave rooms are within the massive Capitan reef (Palmer *et al.* 1991). While the Capitan reef in the Guadalupe Mountains is a relatively pure limestone, the overlying backreef deposits include a mixture of limestone, sandstone, and dolomite. As the water analyses reveal, the dolomite has a profound effect on the local water geochemistry.

Sulfuric acid speleogenesis theories for the Guadalupe Mountain caves were first proposed in the early 1970s and are now widely accepted as the primary mechanism of cave formation (Jagnow *et al.* 2000). Hill (1987) amassed an impressive collection of geologic, geochemical, and isotopic evidence that points to oxidation of hydrogen sulfide migrating from Delaware Basin oil and gas fields as the source of the sulfuric acid that dissolved the limestone and dolomite, forming the caves. Hill's report was published just as Lechuguilla Cave was first being explored; Lechuguilla's massive gypsum deposits, formed by the reaction of sulfuric acid and limestone, provided further confirmation of this theory, as well as a major control on pool chemistry. In fact, the combination of limestone and dolomite bedrock and gypsum cave deposits together explains the wide variations in water chemistry within the cave.

WATER SAMPLING PROGRAMS

Seven different researchers have conducted water chemistry studies in Lechuguilla Cave; their results are presented in Tables 1-3. In some cases the researcher associated sample locations with established survey stations. This has the great advantage of being a permanent and recoverable site identifier, readily capable of being computer plotted onto cave maps and being correlated to mineralogical maps. Unfortunately, the vast majority of water sample locations have only been identified by descriptions based on informal cave feature names. These names are not standardized and are not readily available in the computerized survey databases. Furthermore, names have already changed in the short history of Lechuguilla exploration; Bitter Water Pool, Briny Pool, and Gorilla Piss Pool all refer to the same small puddle! With the help of other Lechuguilla surveyors and scientists, we have attempted to assign survey stations to all of the sampling locations. Any future samplers are strongly encouraged to tie their locations into the established survey system.

SAMPLE SETS:

GO Samples. Gregg Oelker, formerly of Montgomery

Laboratories (Pasadena, CA), collected or coordinated the collection of 58 samples from the cave and three water supply samples between June 1986 and April 1990. pH and alkalinity titrations were conducted within 48 hours; remaining major-ion and trace-element analyses were performed on appropriately preserved (but unfiltered) samples using a variety of analytical techniques (ion chromatography, ion-specific electrode, atomic absorption/emission) in accordance with EPA protocols by Montgomery Laboratories. The results of these analyses were collated in an unpublished report (Oelker 1990). Oelker did not assign sample identification numbers; the numbers used in this paper (GO-1 through GO-61) correspond to their order in his report.

KC Samples. Kimberley I. Cunningham, formerly with the U.S. Geological Survey (Lakewood, CO), determined sulfate concentrations of six pools in April 1989. In-cave measurements were conducted using a Hach kit; reported values are the average of at least three analyses and are estimated to be precise to within 1 mg/L.

AP Samples. Arthur Palmer of the State University of New York-Oneonta and Margaret Palmer (Oneonta, NY) collected 17 samples between August 1988 and June 1994. pH and temperature measurements were conducted in the cave; remaining analyses were conducted in Oneonta and at the Illinois State Water Survey. Sample numbers shown are Palmer's, with the "AP" prefix added. The three 1988 Pellucidar samples were collected in support of an investigation of the formation of sub-aqueous helictites; these results were published by Davis *et al.* (1990). The remaining analyses have not been previously published.

WW Samples. Win Wright of the United States Geological Survey (Durango, CO) collected ten samples in October 1989 and February 1990. pH and temperature measurements and alkalinity titrations were conducted in the cave at the sampling site; additional analyses were conducted by the U.S. Geological Survey. The sample numbers shown in the tables were assigned by the authors. These data are published here for the first time.

DN Samples. Diana Northup of the University of New Mexico (Albuquerque, NM) coordinated the collection of 22 water samples in 1991 and 1992. In a few cases, in-cave pH measurements were made; other analyses were conducted at the University of New Mexico. Northup's research area is in microbiology rather than chemistry, and that directed her choice of analyses. Results of the 1991 analyses were presented in an unpublished report (Northup *et al.* 1992); the 1992 data are presented here for the first time.

JT Samples. Jake Turin (senior author of this paper) of Los Alamos National Laboratory (Los Alamos, NM) collected 27 cave water samples and one local aquifer sample between June 1992 and November 1999. pH and temperature were measured at the sample site using an in-cave calibrated pH meter and digital thermometer; alkalinity titrations, ion chromatography and ICP/AES (inductively-coupled plasma/atomic emission spectroscopy) analyses were performed on filtered and pre-

Table 1. Identification and description of cave and aquifer samples. The abbreviated table appearing here demonstrates the format of the full table, available on the internet at <http://www.caves.org/pub/journal/volume62.htm>.

Sample ID	Date Collected	Location Description	LCP/LEARN Survey Station	Field pH	Field T(C)
GO-1	6/1/86	Lake Lechuguilla	A10	8	
KC-1	4/16/89	Sulfur Shores	FNM13		
AP-LG1	7/89	Lake Louise, rafts, mam. pool	EC58	7.92	20.3
WW-2	2/25/90	Bitter Pool (Briny Pool)	FK5	8.25	
DN-MB-10	10/14/91	Lost Pecos River	MB10		
JT-LC92-01	6/6/92	Sugarlands	CA12	8.5	19.2
HD-LB1a	1/15/96	Liberty Bell Room: 1st pool from entrance	A9	8.54	

served samples at Los Alamos National Laboratory. These data are published here for the first time.

HD Samples. Helen Dawson of the Colorado School of Mines (Golden, CO) collected 58 samples between January 1996 and April 1997. pH measurements were made in the field using either a pH meter or pH indicator paper, field anion measurements were made using Hach kits, and cations were measured at the Colorado School of Mines by ICP/AES. One aspect of Dawson's work was repeated sampling of the same pool to determine temporal trends. While she used the same sample identification for each analysis, we have appended lower-case letters to her sample identifications to differentiate different sampling episodes. These data are published here for the first time.

Aquifer Samples. Eleven analyses of water samples from the regional Capitan aquifer are included in the tables for comparison purposes. These analyses include three samples collected by Oelker, one collected by Turin, and seven analyses published by Hill (1987: Table 2). The latter are given a "CH" prefix in the tables.

ANALYTIC RESULTS AND DISCUSSION

Eleven water samples from the regional aquifer and 197 samples of cave pool and drip water are listed and described in table 1, together with pH and temperature values where available. Location descriptions are as provided by the original researcher; corresponding survey stations are listed when possible. Figure 1 shows the cave pool sample locations, table 2 lists major-ion analyses and calculated saturation indices where appropriate, and table 3 lists trace element and minor-ion analyses. Note that only applicable samples appear in table 2 and table 3; i.e. a sample that was not analyzed for trace elements will not appear in table 3. Of the available data, the GO, WW, and JT sample sets have the most complete and directly comparable analyses. Excluding the Briny and Dilithium Pool samples, these three sets include 90 different samples.

In addition to the chemical analyses presented in this paper, a small number of Lechuguilla pool samples have been collected for stable isotope (Hill 1996: 321 & 452; Wright unpub. data) and tritium analysis (Turin & Plummer 1995; Wright unpub. data). A discussion of these results is outside the scope

of the present paper. We are currently involved in a major new isotopic study of Lechuguilla pools; the older results and new results will be presented and discussed in a future publication.

MAJOR-ION ANALYSES

The major ions found in Lechuguilla cave pool water include Ca^{2+} , Mg^{2+} , Na^+ , K^+ , HCO_3^- , Cl^- , SO_4^{2-} , and NO_3^- . The other major dissolved constituent present is SiO_2 . These nine parameters are listed in table 2, together with TDS (total dissolved solids) and, when possible, calculated SI (saturation indices) for calcite, dolomite, gypsum, quartz, and chalcedony, and calculated PCO_2 (partial pressure of CO_2).¹ Mean values and coefficients of variation for the eight major ions and silica for the 90 GO, WW, and JT samples are shown in table 4. All available analyses are plotted on a modified Piper diagram in figure 2. This plot differs from the familiar Piper diagram in that the cation axes have been rearranged to emphasize variations in the Mg:Ca ratio, and NO_3^- has been combined with Cl on the anion axes.² Figure 3 shows a plot comparing calcite and dolomite SI values for both cave pool and aquifer samples. Note that several of the AP alkalinity values are markedly lower than most other researchers' results. This phenomenon, possibly attributable to differences in analytical methods, has caused many of the AP points to appear as outliers, above and to the right of the bulk of the samples in the central field of figure 2, and below and to the left in figure 3.

¹ The SI and PCO_2 values were calculated using the SI program (based on the Debye-Hückel equation) for almost all of the samples; PHRQPITZ (based on the Pitzer equation and the MacInnes convention), was used for the three samples collected from the Briny Pool (samples GO-20, WW-2, and JT-LC95-02). In order to calculate SI values, relevant ion concentrations, pH, and temperature are all required. If no temperature was recorded, a value of 18.5°C (the average pool temperature measured for the JT cave samples) was assumed for cave samples, and a value of 23.0°C (the measured value for White City Well sample JT-LC94-06) was assumed for aquifer samples. If a pH or relevant ion concentration value was missing, SI values were not calculated. In two cases, reported values were judged extremely unlikely (the pH value of GO-33 and the Ca^{2+} concentration for DN-PL); these samples are not plotted nor are SI values reported.

² For a number of WW samples, alkalinity values were not available; for some DN samples, the reported alkalinity values were judged unreliable and for some AP samples no $\text{Na}^+ + \text{K}^+$ values were available. In these cases, missing values were estimated by charge balance; the estimated values are italicized in table 2. Note that these estimated values are used only for Figure 2; they were not considered reliable enough for SI calculations.

Table 2. Major-ion analyses and saturation indices (SI) of cave and aquifer samples. Values estimated by charge balance are italicized. SI is expressed as $(2/n) \log(IAP/K_{sp})$, where n is the number of ions per mineral formula (e.g. 2 for calcite, 4 for dolomite). The abbreviated table appearing here demonstrates the format of the full table, available on the internet at <http://www.caves.org/pub/journal/volume62.htm>.

Sample ID	Ca ²⁺	Cl ⁻	K ⁺	Mg ²⁺	Na ⁺	NO ₃ ⁻	SiO ₂	SO ₄ ²⁻	Total Alk. TDS as HCO ₃ ⁻ (calc.)	SI Calcite	SI Aragonite	SI Dolomite	SI Gypsum	SI Quartz	SI Chalcedony	log PCO ₂	
	(mg/L)									$(2/n) \log(IAP/K_{sp})$						(atm)	
GO-1	38.6	4.3	0.7	43.3	3.8	4.4	12.2	45	275	425	0.45	0.30	0.57	-2.2	0.36	0.06	-2.6
KC-1								17.5									
AP-LG1	40.08			27.47													
WW-2	60	4100	650	5400	4500	3900		23300	1,190	43100	0.43	0.24	1.65	-0.9			-2.6
DN-HB-1	23	3.0	0.62	29.5	4.75	3.32		19.5	61	145	-0.07	-0.22	0.08	-2.7			-2.6
JT-LC92-01	22.9	2.74	1.54	28.2	3.41	48.7	11.8	16.5	161	286	0.54	0.39	0.69	-2.8	0.32	0.03	-3.3
HD-LB1a	23	10	0.90	64.1	2.19	10.6	8.19	50.0	342	510	0.82	0.67	1.15	-2.4	0.17	-0.12	-3.1

Table 3. Trace-element and minor-ion analyses of cave and aquifer samples. The abbreviated table appearing here demonstrates the format of the full table, available on the internet at <http://www.caves.org/pub/journal/volume62.htm>.

Sample ID	Al	As	B	Ba	Br	Cr	Cs	Cu	F	Fe	Li	Mo	NH ₄	Ni	Pb	PO ₄	Rb	Sr	V	Zn	TOC	DOC
	(mg/L)																					
GO-1	<0.1	<0.002	<0.025	0.16		<0.01		<0.02	0.23	<0.02		<0.01		<0.02	<0.002			0.16		<0.02		
WW-2										12											1.78	1.70
DN-MB-10																						
JT-LC92-01	<0.1	<0.05	0.14	0.28	0.02				0.36	<0.01	0.02		<0.05			<0.05		0.13		<0.01		
HD-LB1a	<0.02	<0.05	0.028	0.084		<0.005		<0.002			<0.002	<0.01	<0.01	<0.01		0.08		0.094	0.004	<0.002	1	

The dominant cations in the cave pools are calcium and magnesium and the dominant anions are carbonate, bicarbonate and sulfate, reflecting the calcite and dolomite host bedrock and the gypsum deposits within the cave system. The distribution of these major ions is a product of the geochemical processes that affect local precipitation as it moves downward into the cave system. These processes, including evaporation, root-zone CO₂ enrichment, bedrock and gypsum dissolution, CO₂ degassing and speleothem precipitation, are described in detail in the geochemical evolution section below.

Although carbonate and gypsum elements dominate the chemistry of the pools, other major species are present as well, including silica, potassium, sodium, chloride and nitrate. Silica is derived from detrital sand and silt within the bedrock, especially in the backreef facies of the Artesia Group Yates Formation, which either contains or overlies most of the cave (Hill 1987; Palmer *et al.* 1991). The relatively low CV (Table 4) and clustering of SI values near zero (Table 2) suggest that silica concentrations are controlled by chalcedony solubility. No obvious bedrock sources of potassium, sodium, or chloride overlie the cave, and it is likely that these ions are derived from local atmospheric input, concentrated to varying degrees by evaporation both in the near-surface soil and in the cave itself. Table 5 shows averaged precipitation concentrations (reflecting both precipitation and dry fallout) and enrichment factors, calculated as the ratio of average pool concentration to average precipitation concentration. Enrichment factors for these three relatively nonreactive ions are similar, ranging from 27 to 36. Their nonreactive behavior is further demonstrated by their similar degree of variability (Table 4) and by positive correla-

Table 4. Mean concentrations and coefficients of variance for major ions and silica for 90 GO, WW, and JT samples (excluding Briny and Dilithium Pools).

Constituent	Average Concentration (mg/L)	Coefficient of Variation
Ca ²⁺	34.1	29%
K ⁺	0.9	44%
Mg ²⁺	36.9	29%
Na ⁺	3.7	41%
Cl ⁻	3.6	47%
NO ₃ ⁻	6.9	100%
SO ₄ ²⁻	42.6	97%
Total Alk. (as HCO ₃ ⁻)	234.1	22%
SiO ₂	11.3	28%

tions between the three (Na-Cl $r^2 = 0.52$; Na-K $r^2 = 0.41$).

Nitrate's reactive behavior is revealed by its low enrichment factor (Table 5) and high variability (Table 4). Two possible sources for nitrate in the cave pools are atmospheric deposition and in-cave biological activity, both natural and anthropogenic. Nitrate's relatively low enrichment factor suggests that some atmospheric nitrate is lost during infiltration, perhaps in the root zone. An in-cave nitrate source is indicated by high nitrate levels (>20 mg/L) found in areas with known guano deposits (Sugarlands, samples JT-LC92-01 and DN-SU), heavily traveled near-surface sites (Lake Lechuguilla, samples GO-1 to GO-5, and the Liberty Bell, samples GO-55 and GO-56), and a pool near a popular cave camping site that shows signs of microbiological colonization (Pink Dot Pool,

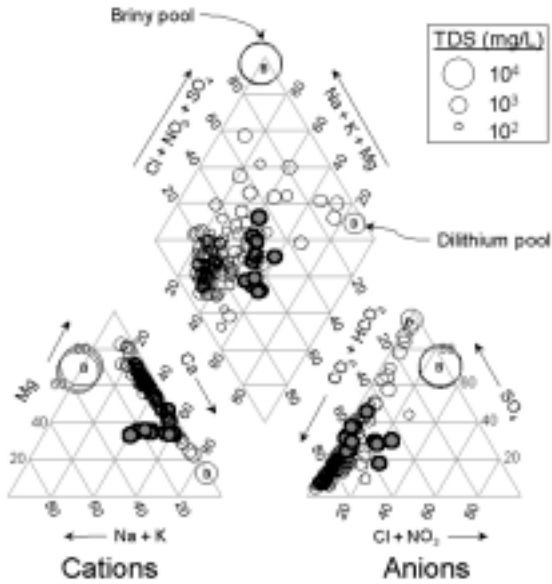


Figure 2. Piper diagram of water sample chemistry data with symbols proportional to log (TDS) for Lechuguilla cave pools (open circles) and aquifer samples (solid circles).

HD-46A samples). The spotty nature of these occurrences is reflected in the very high overall variability in nitrate concentrations (Table 4).

TRACE ELEMENT ANALYSES

Results of trace-element analyses with at least one detection are shown in table 3. In addition to these analyses, the JT, GO, and HD sample sets were analyzed for additional constituents shown in table 6; none of these additional analyses resulted in detectable concentrations at the detection levels shown in the table. (Iron concentrations reported for the WW samples were significantly higher than those reported by other

Table 5. Mean precipitation concentration at Guadalupe Mountains National Park, 1984-1997. Atmospheric deposition concentrations measured at Guadalupe Mountains National Park by the National Atmospheric Deposition Program (1998).

Constituent	Mean Concentration (mg/L)	Enrichment Factor (pool/precipitation)
Ca ²⁺	0.454	75
K ⁺	0.024	36
Mg ²⁺	0.039	954
Na ⁺	0.106	35
NH ₄ ⁺	0.222	0
Cl ⁻	0.135	27
NO ₃ ⁻	0.774	9
SO ₄ ²⁻	1.124	38
pH	5.258	

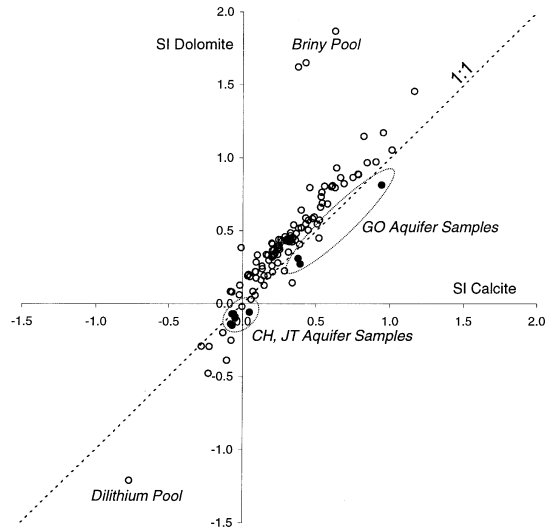


Figure 3. Plot of saturation index (SI) for calcite versus SI for dolomite. Cave samples are shown as open circles and aquifer samples as solid circles.

investigators, even when the same pool was sampled. This suggests that there may be an analytical problem with these samples.)

Most of the trace-element analyses resulted in non-detects, but a few interesting patterns emerge. Trace elements that were consistently detected include barium, fluoride, and strontium. All three of these elements have been associated with local sulfur and Mississippi Valley-type ore deposits (Hill 1996). Of these three, fluoride and strontium showed a positive correlation ($r^2 = 0.77$), and both appeared somewhat correlated to silica ($r^2 = 0.74$ for F, $r^2 = 0.51$ for Sr). This suggests that there may be a silicate mineral source of both fluoride and strontium in the pool waters. (The correlation does not appear to reflect similar geochemical behavior—if this were the case, fluoride and chloride would correlate closely, but their r^2 is only 0.29). Barium showed no significant ($r^2 > 0.10$) correlation with any other species.

Table 6. Additional trace elements and minor ions not detected in any analyses. Detection limits (mg/L) are given in parenthesis.

JT	GO	HD
Ag (0.005 - 0.05)	Ag (0.01)	(13 samples in table 3)
Cd (0.0002 - 0.002)	Be (0.005)	Ag (0.003)
Co (0.002)	Cd (0.003)	Cd (0.002)
I (0.01 - 0.02)	Co (0.025)	Co (0.005)
Mn (0.01)	Hg (0.001)	Mn (0.015)
NO ₂ (0.02 - 1)	Mn (0.02)	Ti (0.001)
S ₂ O ₃ (0.01 - 0.1)	Se (0.002)	
Sb (0.0002 - 0.1)	Ti (0.002)	
	Tl (0.005)	

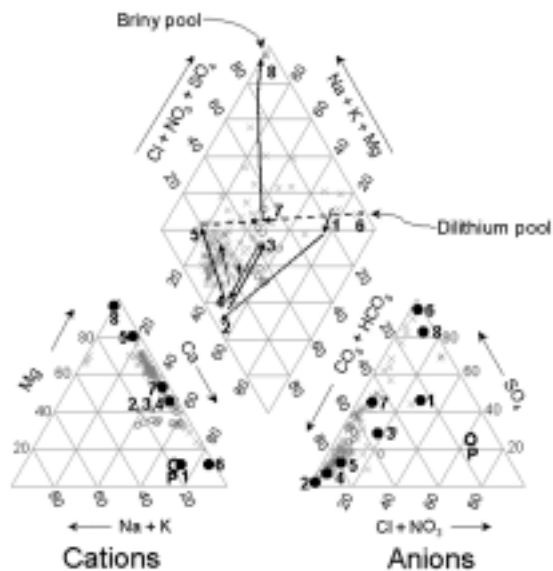


Figure 4. Piper diagram illustrating the modeled geochemical evolution of cave pool water. Refer to text for explanation.

TIME-SERIES ANALYSES

During the 14 years of analyses presented in this paper, numerous pools were sampled more than once. While this should provide an opportunity to look for water chemistry trends, that task is complicated by problems with pool identification caused by inconsistent use of survey station IDs and pool names, and the inevitable variability introduced by different sampling and analytical methods. When the data are carefully evaluated, most of the pools with repeated samplings show either constant chemistry (within 10-20%), or inconsistent “noisy” signals, with concentrations bouncing up and down.

One notable exception is Lake Lechuguilla, which was sampled eight times between 1986 and 1997 (samples GO-1 to GO-5 and HD-LL1a, b & c). The major-ion analyses for these samples are presented in table 7. Between 1986 and 1990, the pool showed a major increase in sulfate and nitrate concentrations, balanced by a slight increase in calcium and a decrease in alkalinity. This trend reversed itself between January 1996

and April 1997, with the latest samples returning to near-1986 values. Lake Lechuguilla is relatively close to both the cave entrance and the ground surface, and has experienced major water-level changes over the last decade. The chemical changes cannot be attributed to evaporative concentration, because chloride levels have not varied along with nitrate and sulfate. The changes may reflect the natural variability of precipitation chemistry, the introduction of pedogenic sulfate and nitrate, or human contamination. This phenomenon merits further monitoring and research.

GEOCHEMICAL EVOLUTION OF POOL CHEMISTRY

The major-ion geochemistry of the Lechuguilla pools is summarized in two plots: the modified Piper diagram (Fig. 2) and a plot comparing saturation indices for calcite and dolomite (Fig. 3). These plots suggest that the samples can be divided into four populations: Capitan aquifer water (including Lake of the White Roses), typical cave pool water, Briny Pool water, and Dilithium Pool water. The first two categories demonstrate the range of geochemical processes that determine the chemistry of water as it moves from the surface down toward the water table, while the last two examples are special cases; end-members of a particular process.

AQUIFER SAMPLES

The eleven aquifer analyses presented in table 2 break down into two distinct groups. The JT and CH analyses show water that is in equilibrium with calcite and dolomite, with an elevated PCO_2 of $10^{-1.8}$ atm. These points cluster close to the origin of figure 3. The GO samples, on the other hand, are supersaturated with respect to calcite and dolomite, show a lower PCO_2 of $10^{-2.8} - 10^{-2.2}$ atm, and extend upward from the origin of Figure 3 along a 1:1 line. This difference is due to degassing of the GO samples between sampling and analysis. The JT and CH analyses more accurately reflect actual aquifer conditions.

The aquifer water originates as precipitation at the ground surface. As the water infiltrates through the soil and root zone, evapotranspiration concentrates the dissolved ions, elevated biogenic CO_2 levels in the root zone force CO_2 into solution, and the resulting carbonic acid-enhanced water dissolves cal-

Table 7. Major-ion analyses of Lake Lechuguilla, 1986-1997.

Sample ID	Date Collected	Ca ²⁺	Cl ⁻	K ⁺	Mg ²⁺	Na ⁺ mg/L	NO ₃ ⁻	SiO ₂	SO ₄ ²⁻	Total Alk. (HCO ₃ ⁻)
GO-1	6/1/86	38.6	4.3	0.7	43.3	3.8	4.4	12.2	45	275
GO-2	3/30/88	31.1	4.2	0.9	42.7	4.4	4.3	12.0	52	250
GO-3	10/24/88	28.9	4.2	0.9	39.5	3.2	6.2	10.3	47	232
GO-4	6/1/89	41.1	4.1	0.9	49.8	4.3	11.9	12.0	130	202
GO-5	4/7/90	77.2	5.5	1.6	58.5	4.5	38.5	12.0	250	183
HD-LL1a	1/15/96	35	10	1.31	39.3	3.69	8.4		100.0	220
HD-LL1b	6/9/96						6.2		56.3	351
HD-LL1c	4/3/97		10				5.3		67.7	

cite and dolomite as it moves downward through the rock. The result is the high-PCO₂, calcite/dolomite-saturated water exemplified by the JT and CH aquifer samples. These samples show an average Mg:Ca molar ratio of 0.68, close to the predicted ratio of 0.78 for a calcite/dolomite equilibrated solution at 23°C, a measured aquifer sample temperature (Mg:Ca molar ratios at different temperatures were predicted using PHREEQC; Parkhurst 1995).

TYPICAL POOLS

Cave pool water starts in the same way as the aquifer water, as precipitation infiltrating through soil, evaporating, and dissolving CO₂, calcite, and dolomite. Before this water reaches the water table, however, it encounters cave passage with lowered CO₂ levels due to mixing with atmospheric air. As a result, CO₂ pressures in the cave (mean = 10^{-2.7} atm) are typically less than the 10^{-1.8} atm value of the aquifer samples but greater than the atmospheric level of 10^{-3.5} atm. Infiltrating water entering the cave thus degasses CO₂ and tends to become supersaturated with respect to carbonate minerals. The degree of supersaturation reached is largely a function of the difference between the soil-zone CO₂ pressure encountered during infiltration, which may be highly variable, and the CO₂ pressure within the cave. Supersaturation of calcite and dolomite occurs in a 1:1 ratio as a result of CO₂ degassing and most of the pool samples fall along that line in a plot of the saturation index of dolomite versus saturation index of calcite (Fig. 3). Evaporation of pool water would also cause supersaturation along a 1:1 line, but would lead to a correlation between saturation and chloride concentration. With the exception of the Briny Pool (discussed below), no such correlation exists.

Both calcite and dolomite are supersaturated in most of the pool samples showing that precipitation and re-equilibration is not instantaneous, and that kinetic factors determine observed chemistry. Although both calcite and dolomite precipitation are rate-limited, dolomite precipitation is particularly slow (Appelo & Postma 1996; Hill & Forti 1997). As a result, calcite preferentially precipitates, decreasing the degree of supersaturation of calcite relative to that of dolomite and increasing the Mg:Ca molar ratio of the water beyond the predicted equilibrium ratio of 0.90 at 18.5°C, the average cave pool temperature. Most of the pool samples have Mg:Ca molar ratios greater than one (mean, excluding Briny Pool samples, equals 1.9) and plot left of the 1:1 line on figure 3.

In some cave passages, water also encounters gypsum, formed during the original sulfuric acid dissolution of the cave (Hill 2000). Dissolution of gypsum adds both calcium and sulfate to the water, which can cause supersaturation and subsequent precipitation of calcite via the common-ion effect and incongruent dissolution of dolomite, if present. This precipitation mechanism has been identified as the source of subaqueous helictites in a number of Lechuguilla pools (Davis *et al.* 1990; Davis 2000). The lack of correlation between Mg and SO₄ in our data suggests that most water/gypsum interactions occur below dolomite bedrock horizons.

LAKE OF THE WHITE ROSES

The current deep point of Lechuguilla is Lake of the White Roses, in the cave's Far East section. The 30-m depth of this pool and its surveyed location relative to local groundwater elevations have led to speculation that the pool is, in fact, a window on the regional Capitan aquifer. The pool's chemistry, represented here by 3 samples (GO-53, WW-10 & DN-MNBX), supports this hypothesis. The samples' average Mg:Ca molar ratio of 0.82 more closely resembles the average aquifer sample ratio of 0.68 than the average cave pool (neglecting the Briny Pool) ratio of 1.9, and the calculated PCO₂ value of sample GO-53 of 10^{-1.7} atm is much closer to the average aquifer value of 10^{-1.8} atm than the average cave pool (without the Briny Pool) value of 10^{-2.7} atm.

DILITHIUM POOL

The Dilithium Pool (sample GO-37) is named for the spectacular selenite (gypsum) crystals that have apparently grown within the pool. It represents an extreme case of gypsum dissolution in Lechuguilla; it is the only pool in the cave that is gypsum-saturated and is, in fact, slightly supersaturated in gypsum. Despite the high Ca concentration, the very low alkalinity (73 mg/L HCO₃⁻) reported for the pool indicates that it is undersaturated with respect to calcite (SI = -0.77). This combination of gypsum supersaturation and calcite undersaturation is somewhat enigmatic. The Dilithium Pool is in a small chamber beneath a large room containing massive gypsum deposits, affording ample opportunity for feed water to become gypsum-saturated. Supersaturation could then be triggered by cooling, evaporation, or dissolution of a non-gypsum calcium or sulfate phase. Cooling of water at equilibrium with calcite and gypsum would produce the observed direction of changes in saturation, but a sufficient cooling mechanism is not obvious. Evaporation would tend to increase the saturation of both gypsum and calcite, and would result in elevated chloride concentrations. On the contrary, the Dilithium Pool chloride concentration is the lowest in the cave. On the senior author's 1992 visit to the Dilithium Pool, selenite needles appeared to be growing from pockets of mineral debris that had fallen into the pool from walls of the chamber. A sample of this debris was collected from the walls and analyzed by X-ray diffraction. It consisted primarily of quartz and calcite, with minor amounts of unidentified sulfate phases. Dissolution of this material could thus cause gypsum supersaturation, but cannot explain the calcite undersaturation.

None of these explanations is wholly satisfactory, and the Dilithium Pool problem merits further investigation. One possibility that cannot be dismissed is analytical error. A small error in the alkalinity measurement may explain the puzzling calcite undersaturation, while an error in the chloride measurement could restore evaporation as a valid explanation. Both alkalinity and chloride concentrations are low relative to the sulfate concentration, making this a challenging water to analyze accurately. Only one sample from the Dilithium Pool has been analyzed and explanations for the existing results will

likely remain speculative until confirmatory analyses are produced.

BRINY POOL

The Briny Pool (samples GO-20, WW-2, JT-LC95-02) (formerly called the Bitter Water Pool) represents another extreme in the range of chemical composition seen in the Lechuguilla samples. On the basis of both chemistry and morphology, it has previously been interpreted as the highly evaporated remnant of a much larger pool (Davis *et al.* 1990). The concentration of chloride in the pool suggests that as much as 99.99 percent of the original water has evaporated from that pool. Again, because of the kinetic barrier to dolomite precipitation, this has led to extensive supersaturation of dolomite (SI = 1.72) relative to calcite (SI = 0.48) and the highest Mg:Ca ratio (159) of the cave pool samples.

While many of the pools in nearby Carlsbad Cavern show evaporation effects due to the large natural entrance (Forbes 2000), with the exception of the Briny Pool, the pools of Lechuguilla, with no present-day natural entrance, show little evidence of evaporation. The presence of a ringtail skeleton near the Briny Pool suggests that at one time, there may have been a natural entrance nearby. An investigation into the mechanism and timing of such a major evaporation episode and its possible connection to a former cave entrance seems worthwhile.

GEOCHEMICAL MODELING

To illustrate the dominant processes in the geochemical evolution of the pool water, we performed a series of simple experiments with the geochemical modeling program PHREEQC (Parkhurst 1995). Results are summarized as a series of connected paths on the Piper diagram (Fig. 4). These simulations are intended to demonstrate the processes that produce "typical" Lechuguilla water, rather than any one specific pool. As discussed earlier, the different pools represent different independent flowpaths from the ground surface. Each flow path will have slightly different evaporation, bedrock, trace mineral, and PCO_2 characteristics, leading to the observed variability in chemistry.

The starting solution for the model was the average composition of local precipitation (Table 5). This composition is marked with a "P" on figure 4. In step 1, the composition of the precipitation was adjusted to reflect presumed plant uptake of nitrate in the root zone by decreasing the nitrate concentration to match the average cave-pool nitrate:chloride ratio. We then equilibrated the solution with calcite and dolomite bedrock (step 2) and represented evapotranspiration by removing sufficient water to match the average chloride concentration in the cave pools (step 3). Uptake of CO_2 in the root zone was simulated by increasing PCO_2 level to $10^{-1.5}$ atm while maintaining calcite/dolomite equilibrium (step 4). Note that although we modeled steps 1-4 sequentially and plotted them as such, in reality they all occur more or less simultaneously during infiltration.

As the water enters the cave, it degasses CO_2 , becoming supersaturated with respect to carbonate minerals, and begins precipitating calcite. As discussed earlier, this is a kinetically limited process. Because our simple model does not account for kinetics, we've simulated this process by decreasing PCO_2 to the average cave level, while maintaining equilibrium with calcite, but not dolomite (step 5). Three different step 5 arrows are shown on figure 4, representing different starting points, corresponding to slightly different soil PCO_2 levels. Note that these step 5 pathways traverse the bulk of the cave pool samples. The location of the different pools along the step 5 pathways reflects different degrees of calcite precipitation. At this point, we've simulated the major characteristics of the typical cave pool; simulating the chemistry of the Dilithium Pool and the Briny Pool required additional processes.

The Dilithium Pool chemistry differs from the other pools by its gypsum saturation. This pool was simulated by equilibrating the composition produced at the end of step 5 with gypsum (step 6). This point closely corresponds to the actual Dilithium Pool point (Fig. 4). The Briny Pool composition reflects a major evaporation episode; such a process is difficult to simulate using PHREEQC, which is limited to relatively dilute solutions. Furthermore, our simulation exercise was restricted to major ions and minerals and did not include minor minerals, such as celestite, magnesite, or hydromagnesite that are known to occur in Lechuguilla (DuChene 1997), and which will become important under high-evaporation conditions. Nevertheless, we explored the limits of our simulation by simulating the evaporation of a mixture of 92.5% "typical" pool water and 7.5% Dilithium Pool water. This mixing is shown in figure 4 as step 7, and the ensuing evaporation is step 8. As can be seen, this pathway moves in the general direction of the Briny Pool composition, but the simulated Briny Pool has higher magnesium and sulfate concentrations than the actual pool. Inclusion of additional magnesium and sulfate minerals in the simulation would help remedy this discrepancy.

CONCLUSIONS

The data presented here represent a major compilation of chemical analyses from one of the best-studied and most geochemically diverse caves in the world. The chemistry of the water is initially determined by precipitation chemistry, the bedrock that hosts the cave, and the gypsum deposits that date from the sulfuric acid formation of the caves. The water is then modified by present-day geochemical processes, including speleothem deposition, evaporation, and interaction with biological activity. Together, these processes result in diverse chemical compositions that reveal the complexity of the cave geochemical environment. The authors hope that these data will provide other researchers with the raw material for more in-depth analysis and characterization of cave processes.

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