

OXIDATION-REDUCTION CHEMISTRY OF LECHUGUILLA CAVE SEEPAGE

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Abstract: Groundwater generally becomes increasingly reduced (decreasing Eh) with depth from the soil surface, and therefore seepage is a potential source of dissolved Mn, Fe, and NH_4 to caves. In Lechuguilla Cave, both abiotic and biotic processes have contributed to the origin of a vast array of secondary speleogenetic features which are enriched in Fe and Mn oxides. Existing chemical and physical properties of Lechuguilla Cave pool water indicates oxidizing conditions, with dissolved Fe and Mn below detection, and N existing primarily as NO_3 . However, the redox chemistry of the cave seepage has not been well-studied. The objective of this study was to characterize the redox status of Lechuguilla Cave seepage and to test the hypothesis that seepage entering the cave from the overlying vadose zone is a potential source of dissolved Fe, Mn, and inorganic N (as both NH_4 and NO_3). If present in seepage, Fe, Mn, and NH_4 will oxidize in the cave environment, resulting in non-detectable concentrations in cave pools. Seepage was collected from eight locations in the cave and analyzed for field parameters (pH, EC, dissolved $\text{O}_2(\text{g})$, Eh, temperature) and concentrations of dissolved Fe (Fe^{2+} + total Fe), Mn, NO_3 + $\text{NO}_2\text{-N}$, and $\text{NH}_4\text{-N}$. Results indicate that low organic C concentrations prevent the occurrence of complete anaerobic conditions in seepage, but the concentrations of Mn and NH_4 indicate that slightly reducing conditions can exist. Iron concentrations were below detection ($<0.06 \text{ mg L}^{-1}$) in all samples, and N existed primarily as NO_3 . Field-measured Eh values obtained using a Pt electrode (Eh_m) did not correlate with computed Eh values for various redox couples (Eh_c), and the poor agreement between Eh_c values for the different couples indicates the absence of redox equilibria in the samples. Rather than characterization of redox status according to Eh, seepage is classified as ranging from oxic to suboxic. This redox classification indicates that Lechuguilla Cave seepage can generally be expected to contain low concentrations of organic C and dissolved Mn, dissolved $\text{O}_2(\text{g})$ ranging from $1 \mu\text{M}$ to $>30 \mu\text{M}$, but with Fe below typical analytical detection limits.

INTRODUCTION

Lechuguilla Cave is located in the Guadalupe Mountains of southeastern New Mexico and is known as one of the world's finest examples of H_2SO_4 speleogenesis. Since its discovery in 1986, Lechuguilla Cave has provided researchers with unique opportunities in the study of speleogenesis, geology, microbiology, and geochemistry (e.g., Davis, 2000; DuChene, 2000; Northup et al., 2000; Polyak and Provencio, 2001). Numerous isolated pools of water exist throughout Lechuguilla Cave; and consequently, many of these pools have been studied to characterize their major ion and trace element compositions. Results from approximately 200 water samples collected by various researchers between 1986 and 1999 show that the majority of Lechuguilla Cave pools are dominated by Ca, Mg, HCO_3 , and SO_4 due to interaction of groundwater with calcite (CaCO_3), dolomite [$\text{CaMg}(\text{CO}_3)_2$], and massive gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) (Turin and Plummer, 2000). Typical Lechuguilla Cave pool water has a pH between 7.5 and 8.5, a Mg:Ca molar ratio greater than one, contains a $\text{CO}_2(\text{g})$ partial pressure (P_{CO_2}) greater than atmospheric

($10^{-3.5}$ atm), and is usually oversaturated with respect to calcite and dolomite. Water at Lechuguilla's deep point (Lake of the White Roses, -480 m) contains a higher P_{CO_2} and a lower (<1) Mg:Ca molar ratio, and therefore is believed to represent the regional Capitan Aquifer (Turin and Plummer, 2000).

Although the chemical and physical characteristics of Lechuguilla Cave pool water have been well-characterized, the chemical composition of seepage has received less attention. Seepage is defined as water which enters the cave environment from the overlying vadose zone, usually as ceiling drips or slow-flowing water emanating from bedrock. Conceptually, typical Lechuguilla Cave pool water will be different from seepage to the extent that it is influenced by $\text{CO}_2(\text{g})$ outgassing, oxidation, mineral precipitation, dilution, or evaporation. Cave seepage originates primarily as surface water which infiltrates into overlying soils, and aerobic microbial decomposition of dissolved organic C tends to deplete the available $\text{O}_2(\text{g})$ and increase the (P_{CO_2}) in percolating waters. As a result, the oxidation-reduction (redox) potential, expressed in terms of Eh, typically decreases in ground water isolated from the

Table 1. The standard potential (E°) and Eh (pH = 7, 25 °C) for selected redox couples in groundwater.^a

Reaction	E° (Volts)	Eh (Volts)
$4\text{H}^+ + \text{O}_2(\text{g}) + 4\text{e}^- = 2\text{H}_2\text{O}$	1.23	0.816
$\text{MnO}_2 + 4\text{H}^+ + 2\text{e}^- = \text{Mn}^{2+} + 2\text{H}_2\text{O}$	1.23	0.544
$\text{NO}_3^- + 2\text{H}^+ + 2\text{e}^- = \text{NO}_2^- + \text{H}_2\text{O}$	0.845	0.431
$\text{NO}_2^- + 8\text{H}^+ + 6\text{e}^- = \text{NH}_4^+ + 2\text{H}_2\text{O}$	0.892	0.340
$\text{Fe}(\text{OH})_3 + 3\text{H}^+ + \text{e}^- = \text{Fe}^{2+} + 3\text{H}_2\text{O}$	0.975	0.014
$\text{SO}_4^{2-} + 10\text{H}^+ + 8\text{e}^- = \text{H}_2\text{S}(\text{aq}) + 4\text{H}_2\text{O}$	0.301	-0.217

^a Langmuir, 1997. Eh assumes $P_{\text{CO}_2} = 0.2$ bar, $[\text{Mn}^{2+}] = 10^{-4.74}$ M, $[\text{Fe}^{2+}] = 10^{-4.75}$ M, and $[\text{NO}_3^-] = [\text{NO}_2^-] = [\text{NH}_4^+]$.

atmosphere. Eh is related to the activity of electrons (e^-) in solution, and similar to pH, is a master geochemical variable which controls the chemical behavior and mobility of nutrients and trace metals in groundwater.

The rate and extent of Eh decline in percolating ground water is a function of both the rate of $\text{O}_2(\text{g})$ replenishment and the availability of organic C and other reductants (Langmuir, 1997). Accompanying the decrease in Eh are the shifts in chemical equilibria between various redox couples (Table 1). In the absence of $\text{O}_2(\text{g})$, microbial oxidation of organic C is followed by reduction of NO_3^- and NO_2^- , MnO_2 , and $\text{Fe}(\text{OH})_3$; under extremely reducing conditions, SO_4^{2-} can be reduced to $\text{H}_2\text{S}(\text{g})$. Under neutral pH conditions, the Eh of natural shallow and deep ground water environments generally ranges between 0 and 0.20 V (Garrels and Christ, 1965). Therefore, depending on the extent of locally-reducing conditions in the vadose zone, seepage is a potential source of redox-indicator elements to

the cave, such as Fe, Mn, and various forms of N (NO_3^- plus NH_4^+) (Table 1).

Some of the most exemplary features of Lechuguilla Cave are the result of H_2SO_4 speleogenesis which occurred during the late Miocene and Pliocene, under conditions much different than exist today (Jagnow et al., 2000). However, Lechuguilla Cave also contains many spectacular examples of actively-growing dripstone and flowstone speleothems, in contrast to nearby Carlsbad Cavern where the majority of speleothems are inactive (DuChene, 1997). Dripstone and flowstone in Lechuguilla Cave tend to be concentrated in areas containing seeping water, and occur in various colors, such as white, brown, yellow, red, and orange. Some spectacular examples of colored dripstone and flowstone in Lechuguilla Cave occur in the Liberty Bell Area, Tower Place, Treehouse, and Vesuvius (Fig. 1).

The presence of dissolved Fe, Mn, and humic substances in cave seepage is known to influence the color of

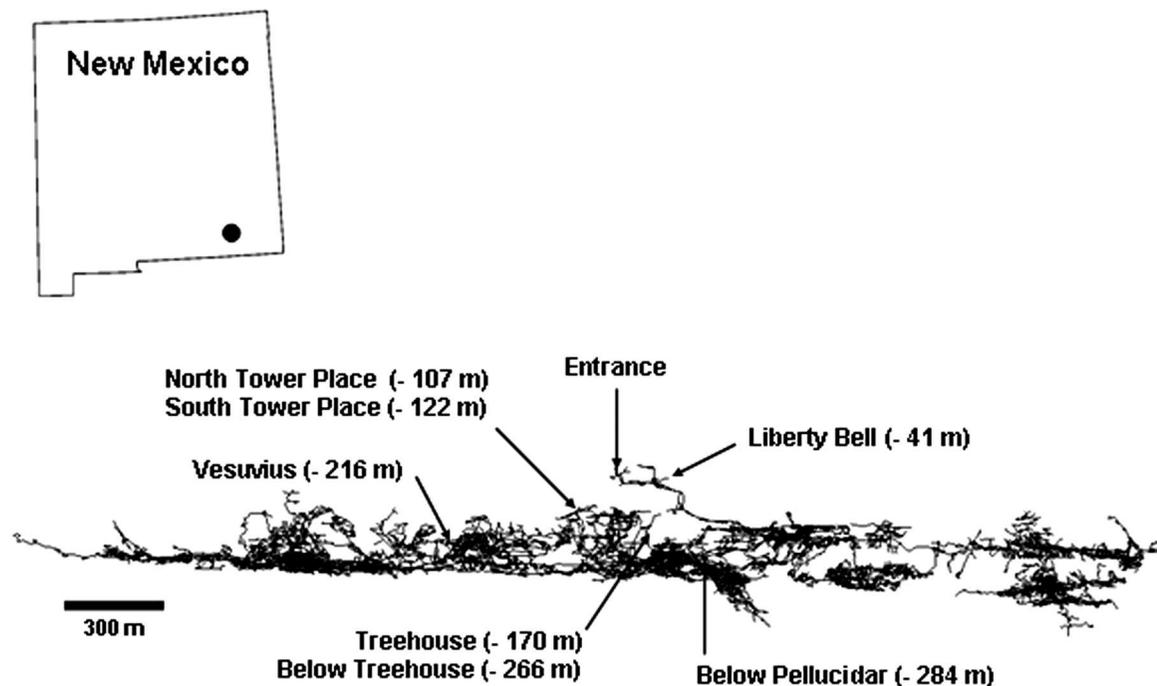


Figure 1. Map of Lechuguilla Cave (profile) showing the general locations and depths below entrance for cave seepage sampled during this study (survey data provided by Carlsbad Caverns National Park, July 13, 2006).

Table 2. Summary of historical analyses for redox-sensitive elements in Lechuguilla Cave pool and seepage water (compiled from Turin and Plummer, 2000).

Parameter	Fe		Mn		NH ₄		NO ₃		NO ₂	
	Pools	Seepage	Pools	Seepage	Pools	Seepage	Pools	Seepage	Pools	Seepage
No. Observations	87	8	87	8	32	1	151	10	25	1
No. Detections	6	0	1	0	17	0	151	10	0	0
Detection Frequency (%)	6.9	0	1.2	0	53	0	100	100	0	0
Mean of Detectable Values	0.01	NC	0.002	NC	0.05	NC	10.7	10.2	0	0.02
Median Detection Limit	0.02	0.02	0.02	0.02	0.02	0.05	NR	NR	0.02	0.02
Minimum Detection Limit	0.01	0.01	0.002	0.01	0.02	0.05	NR	NR	0.02	0.02
Maximum Detection Limit	0.20	0.20	0.02	0.02	0.05	0.05	NR	NR	0.02	0.02

NC = not calculated due to 0% detection.

NR = not reported due to 100% detection.

many speleothems (White, 1997) and may also serve as a potential energy source for a variety of microorganisms (Northup et al., 1997). However, the role of dissolved Fe and Mn in present-day Lechuguilla speleothem formation has not been evaluated. Poorly-crystalline Mn oxides are common in the cave environment, and it has been suggested that certain types of hydrous Mn oxides in Lechuguilla Cave may be secondary speleogenetic by-products, or perhaps even unrelated to speleogenesis (Polyak and Provencio, 2001). Both abiotic and biotic precipitation of Fe oxides is also common in Lechuguilla, with possible sources of reduced Fe existing as impurities in limestone, or as ferrous iron (Fe²⁺) in infiltrating water and cave pools (Northup et al., 2000; Northup and Lavoie, 2001). Elevated concentrations of inorganic N in selected Lechuguilla Cave pools (Turin and Plummer, 2000) raise additional questions regarding sources of N in the cave. While inorganic N in caves is sometimes derived from guano, the only known guano deposits in Lechuguilla are the historic deposits mined in 1914 from the entrance pit. The source of N in most caves is believed to originate as either NH₄ or NO₃ in ground-water seepage (Northup and Lavoie, 2001).

In a recent study of Lechuguilla Cave pools, Levy (2007) evaluated the redox status of selected pools by measuring dissolved O₂(g), dissolved organic C (DOC), Eh, Fe²⁺ plus total Fe, Mn, NO₃, and NH₄. Results of the redox evaluation indicated an oxic pool environment (Langmuir, 1997) with dissolved O₂(g) levels in equilibrium with the ambient atmosphere, N present as NO₃, and non-detectable concentrations of DOC, Mn, Fe, and NH₄. A review of historical data indicates that the number of both pool and seepage samples previously analyzed for Fe, Mn, and inorganic N is limited (Table 2). While the frequency of historic Fe and Mn detection was higher for the pools when compared to seepage, the number of pool samples analyzed (N = 87) was greater than the number of seepage

samples (N = 8), and the measured Fe and Mn concentrations were near the limit of detection. Nitrite (NO₂) is an unstable intermediate produced during nitrification (Stumm and Morgan, 1996) and was below detection in all pool (N = 25) and seepage (N = 1) samples. Thirty-two pool samples were analyzed for NH₄, with a 53% frequency of detection and a mean concentration also near the detection limit. A single seepage sample was analyzed for NH₄ (<0.05 mg L⁻¹). Prior analysis for NO₃ in pools (N = 151) and seepage (N = 10) indicate that NO₃ was detected in 100% of the samples, and that the mean NO₃ concentration in both types of water is approximately 10 mg L⁻¹ (Table 2).

The objective of the current study was to characterize the redox status of Lechuguilla Cave seepage to test the hypothesis that ground water entering the cave from the overlying vadose zone is a potential source of dissolved Fe, Mn, and inorganic N (as NO₃ and NH₄) to the cave system. A sampling protocol was developed to chemically-preserve the various forms of inorganic redox species and to analyze the samples using lower detection limits. If present in seepage, dissolved Fe and Mn will eventually oxidize and precipitate in the cave environment, resulting in non-detectable concentrations in pools. Inorganic N may be present as NO₃ and/or NH₄ in seepage, but will oxidize to NO₃ which becomes the main species of inorganic N in Lechuguilla Cave pools. Therefore, there could be a higher frequency of detection for any given reduced species (Table 1) in near-surface seepage, compared to seepage from lower elevations which may be more oxidized due to relatively longer periods of exposure to atmospheric O₂(g) in the cave.

STUDY LOCATIONS

Seepage collection sites in Lechuguilla Cave were located in the Entrance Series (Liberty Bell Area), the

Table 3. Lechuguilla Cave seepage sampling locations (2005–2006).

Drip Location	Aproximate Seepage Elev. (m) ^a	Collection Station	Tie-in Station	Distance (m)	Azimuth (degrees FS) ^b	Inclination (degrees FS)
Liberty Bell Area (sADR1)	-41	sADR1	sADR0	5.73	10	-34
		sADR0	ADR0	6.25	40	+7
Liberty Bell Area (sADR2)	-41	sADR2	sADR1	9.14	178	+30
Below Pellucidar	-284	sEC30A	EC30	10.5	272	+39
North Tower Place	-107	sFLVV7	FLVV7	3.05	267	-27
South Tower Place	-122	sFLVV8	FLVV8	12.2	75	+21.5
Below Treehouse	-266	EY24
Treehouse (sECR11B)	-170	sECR11B	sECR11A	29.8	30	+17
		sECR11A	ECR11	5	0	+90
Vesuvius	-216	sJF11A	JF11	4.90	165.5	-6.5

^a Below entrance datum.^b Degrees foresight with Suunto from tie-in station.

Western Branch (Below Pellucidar, Treehouse), and the Southwestern Branch (Tower Place, Vesuvius) of Lechuguilla Cave (Fig. 1). Eight specific drip locations were sampled during four separate trips into Lechuguilla Cave led by the author during June 13 to 18, 2005 and during June 12 to 17, 2006 (trip reports on file at the Cave Resources Office, Carlsbad Caverns National Park). The specific sampling locations with survey tie-in information are given in Table 3 and represent elevations ranging from -41 m below the Entrance (Liberty Bell Area) to -284 m below the Entrance (Below Pellucidar).

MATERIALS AND METHODS

SAMPLE COLLECTION AND FIELD MEASUREMENTS

Water sampling procedures followed standard methods used for the collection and preservation of water samples (Eaton et al., 2005). Seepage samples were collected from the various drip locations into polyethylene beakers and immediately transferred into clean-certified sample bottles. Samples collected for determination of redox-sensitive species (Fe, Mn, NH₄-N, NO₃-N) were not filtered to minimize the effects of sample oxidation. Each sample was split into four bottles: (1) a filtered (0.45 μm), unpreserved sample for analysis of Ca, Mg, HCO₃, Cl, K, and SO₄, (2) an HCl preserved sample for analysis of total organic carbon (TOC), (3) a HNO₃ preserved bottle for analysis of Fe and Mn, and (4) a H₂SO₄ preserved bottle for determination of both NH₄-N and NO₃ + NO₂-N. (Note: because NO₂-N is an unstable intermediate in the environment, the concentration of NO₃ + NO₂-N is used as a measure of NO₃-N because it allows for chemical preservation of the sample). Two field cave blanks (2005 and 2006) were also prepared by preserving and filtering analytical-grade distilled water into clean sample bottles containing the appropriate preservative while in-cave (Lake Lechuguilla) to evaluate the potential for sample contamination during sampling.

Field measurements of pH, temperature, and electrical conductivity (EC) were made using a combination HACH® (Loveland, CO) ion-selective electrode instrument which was calibrated using standard solutions before each use. Determination of Fe²⁺ and dissolved O₂(g) was also conducted in the field using a HACH® DR-850 colorimeter. Redox potential (Eh) was measured using a combination Pt/Ag-AgCl electrode and standardized to the Standard Hydrogen Electrode using Zobell Solution (Eaton et al., 2005).

Following collection and transport to the surface, the samples were stored at approximately 4 °C and then shipped to SVL Analytical, Inc. (Kellogg, ID) for chemical analyses using methods of the United States Environmental Protection Agency (USEPA, 1983): TOC (Method 415.1), Cl (Method 300.0), Ca, K, Mg, Na, Fe, Mn, Si (Method 200.7), NO₃ + NO₂-N (Method 353.2), NH₃-N (Method 350.1), carbonate alkalinity (Method 2020B), and SO₄ (Method 300.0). Laboratory quality control samples included duplicates, matrix spikes, and laboratory control samples.

GEOCHEMICAL MODELING

The major ion chemistry data were input into the geochemical speciation model PHREEQC which uses an extended Debye-Hückel equation for ion activity calculations (Parkhurst and Appelo, 1999). PHREEQC was used to calculate *P*_{CO₂} (g) and mineral saturation index (*SI*) values for various carbonate, sulfate, and silicate minerals, defined as:

$$SI = \log\left(\frac{IAP}{K_{sp}}\right) \quad (1)$$

where:

IAP = ion activity product observed in solution
K_{sp} = theoretical solubility product at field temperature

A positive *SI* indicates that the solution is oversaturated with respect to a given solid phase which could potentially

precipitate, while a negative *SI* indicates undersaturation with a solid phase which could potentially dissolve. When *SI* = 0, the solution and solid phase are in apparent equilibrium. In this study, apparent equilibrium is defined when *SI* values are between -0.50 and +0.50 due to inherent uncertainties in the available thermodynamic data.

Redox equilibrium was evaluated by comparing Eh values computed using PHREEQC (E_h) for the following redox couples: $O_2(aq)/H_2O$, NH_4^+/NO_3^- , $N_2(aq)/NO_3^-$, and $Mn^{2+}/MnO_2(s)$. The theoretical voltages for these couples are related to their standard electrode potentials (E°) (Table 1) through the Nernst equation:

$$E_h = E^\circ + \frac{2.303RT}{nF} \log\left(\frac{a_{Ox}}{a_{Red}}\right) \quad (2)$$

where:

$$R = 8.314 \times 10^{-3} \text{ kJ deg}^{-1} \text{ mol}^{-1}$$

T = absolute temperature

n = number of electrons (e^-)

F = Faraday's constant (96.42 kJ volt $^{-1}$ mol $^{-1}$)

$\frac{a_{Ox}}{a_{Red}}$ = ratio of the activity products of oxidized to reduced species

In theory, redox equilibrium exists when values of E_h for the various redox couples are in agreement; however, dissimilarity between E_h values would indicate redox disequilibrium, and the absence of a master system Eh (Lindberg and Runnells, 1984).

RESULTS AND DISCUSSION

QUALITY ASSURANCE/QUALITY CONTROL

Calculated percent recovery from the laboratory control samples ranged from 95.3% to 108%, while percent recovery from matrix spikes ranged from 92% to 116%. Relative percent differences ranged from 0% to 8% for laboratory duplicates and cation-anion balances for all samples were within 5%. Therefore, all values for the laboratory control samples, matrix spikes, and laboratory duplicates were within acceptable limits (USEPA, 1994). Analytical results from the two cave blanks (2005 and 2006) were below detection for all constituents except for low levels of Ca (0.085 and 0.235 mg L $^{-1}$), Cl (0.23 and 1.24 mg L $^{-1}$), and NH $_4$ -N (0.04 mg L $^{-1}$ in 2006).

FIELD MEASUREMENTS

The pH of seepage ranged from 7.67 to 8.50 and the EC ranged from 357 to 583 $\mu\text{S cm}^{-1}$ (Table 4), comparable to the chemistry of typical Lechuguilla pools (Turin and Plummer, 2000; Levy, 2007). The measured Eh values (420 to 460 mV) in seepage are consistent with water that is in contact with the atmosphere and saturated with dissolved O $_2$ (g) (Langmuir, 1997). Field results for Fe $^{2+}$ were below detection (<0.03 mg L $^{-1}$), also reflecting the presence of dissolved O $_2$ (g) and an absence of moderately-reducing

Table 4. Selected field and redox parameters for Lechuguilla Cave seepage samples.

Location	Sample Date	pH	EC ($\mu\text{S cm}^{-1}$)	Eh (mV)	Total Fe (mg L $^{-1}$)	Fe $^{2+}$ (mg L $^{-1}$)	Dissolved O $_2$ (g) (mg L $^{-1}$)	TOC (mg L $^{-1}$)	Mn $^{2+}$ (mg L $^{-1}$)	NO $_3$ /N (mg L $^{-1}$)	NH $_4$ /N (mg L $^{-1}$)
Liberty Bell Area (sADR1)	6/18/05	8.30	390	NM	<0.06	NM	NM	<1.0	<0.004	0.84	0.03
	6/17/06	7.79	380	420	<0.06	<0.03	7.8	<1.0	<0.004	0.85	0.04
Liberty Bell Area (sADR2)	6/18/05	NM	NM	NM	<0.06	NM	NM	1.1	0.0066	2.16	0.15
	6/17/06	7.77	412	419	<0.06	<0.03	7.7	1.3	<0.004	2.36	0.05
Below Pellucidar (sEC30A)	6/13/05	7.87	357	454	<0.06	<0.03	8.8	<1.0	<0.004	0.68	<0.03
North Tower Place (sFLVV7)	6/16/05	8.50	583	460	<0.06	<0.03	7.0	1.3	<0.004	0.71	<0.03
South Tower Place (sFLVV8)	6/16/05	7.92	567	460	<0.06	<0.03	7.1	1.2	0.0063	0.71	0.04
Below Treehouse (EY24)	6/13/06	7.67	423	434	<0.06	<0.03	7.7	<1.0	<0.004	0.84	0.20
Treehouse (sECR11B)	6/13/06	7.74	381	425	<0.06	<0.03	7.8	<1.0	0.013	0.74	0.19
Vesuvius (sJF11A)	6/16/06	8.03 ^a	547 ^a	NM	<0.06	NM	NM	<1.0	<0.004	1.32	0.04

NM = not measured.

^a Laboratory measurement.

conditions. Although dissolved $O_2(g)$ measurements were conducted immediately upon sample collection, introduction of atmospheric $O_2(g)$ could not be completely avoided. However, the mean concentration of dissolved $O_2(g)$ in seepage (7.7 mg L^{-1}) is lower than the mean of 8.5 mg L^{-1} measured in selected pools (Levy, 2007). This suggests that seepage is probably not completely devoid of dissolved $O_2(g)$ prior to entering the cave, but also that the samples had not yet completely equilibrated with atmospheric $O_2(g)$. No significant correlations existed between dissolved $O_2(g)$ concentrations in seepage and either temperature or elevation within the cave.

REDOX-INDICATOR SPECIES

The TOC values in Table 4 are the first reported for Lechuguilla Cave seepage, and ranged from <1.0 to 1.3 mg L^{-1} , consistent with those previously reported for Lechuguilla pools (Turin and Plummer, 2000; Levy, 2007). Although the TOC concentrations are probably too low to produce complete anaerobic conditions, the detectable concentrations of NH_4-N and Mn in some samples indicates that slightly reducing conditions can exist in seepage. The reduced form of N (NH_4) was detected in the majority of samples, ranging from 0.03 to 0.20 mg L^{-1} as NH_4-N (Table 4). Nitrate, however, was the dominant form of inorganic N present, with NO_3-N concentrations on the order of 1 to 2 mg L^{-1} (4.5 to 8.9 mg L^{-1} as NO_3). While Fe concentrations were below detection ($<0.06 \text{ mg L}^{-1}$) in all samples, seepage from certain locations near the surface (Tower Place, Liberty Bell, Treehouse) contained higher concentrations of Mn (0.006 to 0.013 mg L^{-1}) compared to those collected from greater depths (Below Pellucidar, Below Treehouse, Vesuvius). The higher frequency of Mn detection near the surface relative to the deeper samples can be explained by shorter exposure time to the cave atmosphere, allowing less time for Mn to oxidize and precipitate.

Generally consistent chemistry results were obtained at each of the two Liberty Bell Area locations when the 2005 and 2006 data are compared (Table 4). The higher NO_3-N and TOC concentrations at location sADR2 compared to sADR1, however, also illustrate the chemical variation that can occur between two seepage locations in close proximity. In 2005, Mn (0.0066 mg L^{-1}) and NH_4-N (0.15 mg L^{-1}) concentrations at location sADR2 were higher compared to 2006, perhaps due to increased soil saturation levels following above-average precipitation (Burger, 2005). However, a shelfstone pool which receives seepage directly from sADR2 contained Mn, Fe, and NH_4-N either at or below the detection limit (Levy, 2006). These observations support the hypothesis that such redox-indicator species in seepage eventually oxidize in the cave environment, resulting in lower concentrations in pools. The lower Mn concentration measured Below Treehouse ($<0.004 \text{ mg L}^{-1}$) compared to the higher concentration in the Treehouse (0.013 mg L^{-1}) provides additional evidence for Mn oxidation and precipitation along flow paths (Table 4).

The presence of low to non-detectable concentrations of Fe and Mn in Lechuguilla Cave seepage, coupled with measurable TOC concentrations in some of the more highly-decorated areas (Liberty Bell, Tower Place), is consistent with speleothem coloration by humic substances originating from decomposition of plant materials in overlying soils. Speleothem coloration can be caused by the presence of pigmenting substances, such as Fe and Mn oxides. However, humic substances have been shown to impart tan, orange, and brown colors when incorporated into calcite, and are considered to be the primary cause of most coloration observed in cave travertine (White, 1997).

MAJOR ION CHEMISTRY AND GEOCHEMICAL MODELING

The major ion chemistry of seepage is difficult to distinguish from typical cave pool water, which is variable with respect to Ca:Mg: HCO_3 ratios, contains elevated $P_{CO_2(g)}$ concentrations and a pH between 7.5 and 8.5. The results of geochemical modeling (Table 5) indicate equivalent mineral solubility controls and calculated $P_{CO_2(g)}$ concentrations previously reported for Lechuguilla pools (Turin and Plummer, 2000; Levy, 2007). Seepage was usually in equilibrium with calcite and magnesite, and sometimes oversaturated with respect to dolomite, while high degrees of gypsum undersaturation were calculated. Silica concentrations appear to be controlled by chalcedony rather than quartz. The majority of calculated $P_{CO_2(g)}$ levels were approximately 10 times higher than atmospheric (Table 5). The similarities in pH and calculated $P_{CO_2(g)}$ values between seepage and pools are at least partially attributed to disequilibrium of seepage chemistry as it unavoidably contacts the cave atmosphere during sampling.

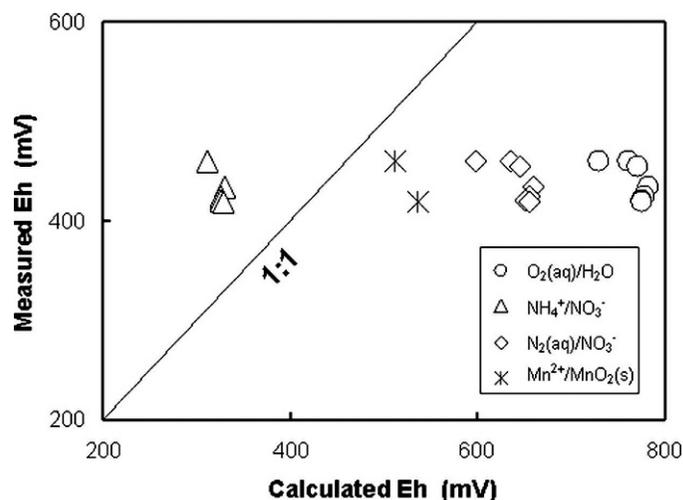
Nernstian Eh_c values computed using PHREEQC are shown in relation to their respective field-measured Eh_m values on Figure 2. These data illustrate that a relatively narrow range in Eh_m values exists compared to the wide range in Eh_c values computed for the various redox couples. The poor agreement between the Eh_c values illustrates the lack of internal redox equilibrium in the seepage samples, and deviation of the data points from the 1:1 line indicates the difficulty in determining a controlling system Eh when using a Pt electrode in the field. The lack of agreement between Eh_c and Eh_m values in ground water has been documented in many natural waters and is attributed to factors such as: (1) inaccuracy of the Pt electrodes caused by surface poisoning and/or electrode drift in poorly-poised systems, (2) slow redox kinetics and disequilibrium between redox couples, and (3) Eh_m values resulting from measurement of mixed potentials which do not correspond to a single redox couple (Langmuir, 1971; Lindberg and Runnells, 1984; Langmuir, 1997).

EVALUATION OF SEEPAGE REDOX STATUS

The aqueous concentrations of the redox-sensitive species of O, N, Mn, and Fe in conjunction with field-measured Eh values (Eh_m) are consistent with the presence of oxidizing conditions in Lechuguilla Cave seepage. The

Table 5. Mineral saturation index (SI) values and P_{CO_2} (g) values calculated using PHREEQC (Parkhurst and Appelo, 1999).

Mineral Phase	Liberty Bell Area (sADR1)	North Tower Place (sFLVV7)	South Tower Place (sFLVV8)	Vesuvius (sJF11A)	Treehouse (sECR11B)	Below Treehouse (EY24)	Below Pellucidar (sEC30A)
Calcite (CaCO ₃)	0.18	1.13	0.20	0.36	-0.06	-0.05	0.18
Dolomite [CaMg(CO ₃) ₂]	0.43	2.4	0.77	1.2	0.20	0.02	0.61
Magnesite (MgCO ₃)	-0.24	0.72	0.07	0.36	-0.24	-0.43	-0.07
Gypsum (CaSO ₄ ·2H ₂ O)	-2.4	-2.2	-2.6	-2.6	-2.9	-2.0	-2.8
Chalcedony (SiO ₂)	-0.22	-0.20	-0.23	-0.15	-0.12	-0.12	-0.17
Quartz (α -SiO ₂)	0.28	0.30	0.27	0.35	0.39	0.38	0.34
log P_{CO_2} (g)	-2.5	-3.1	-2.6	-2.5	-2.4	-2.4	-2.5

Figure 2. Nernstian Eh values (Eh_c) computed using PHREEQC versus field-measured Eh values (Eh_m) measured with a Pt electrode.

seepage contains around 1 mg L^{-1} of TOC, compared to the median DOC concentration of 0.7 mg L^{-1} for U.S. ground water (Leenheer et al., 1974). However, approximately 3 to 4 mg L^{-1} of organic C is typically required for groundwater to become completely anaerobic (Langmuir, 1997). The low concentrations of Mn and $\text{NH}_4\text{-N}$ and non-detectable Fe concentrations are consistent with the low concentrations of organic C present in the seepage.

Because of the difficulty in obtaining thermodynamically-meaningful Eh measurements in most natural waters, Berner (1981) proposed a simplified redox classification scheme which is broadly-based on the presence or absence of either dissolved $\text{O}_2(\text{g})$ or $\text{H}_2\text{S}(\text{g})$. According to Berner's widely-accepted classification, measurable dissolved $\text{O}_2(\text{g})$ indicates an *oxic* environment, whereas the absence of dissolved $\text{O}_2(\text{g})$ indicates an *anoxic* environment. In recent years, scientists have suggested that the Berner (1981) classification of oxic environments be divided into *oxic* and *suboxic* (Langmuir, 1997). With this revision, oxic environments contain more than $30 \mu\text{M}$ (1 mg L^{-1}) of dissolved $\text{O}_2(\text{g})$ with Mn below detection and organic matter absent. Suboxic environments contain low amounts of dissolved organic matter and dissolved $\text{O}_2(\text{g})$ from $\geq 1 \mu\text{M}$ to $< 30 \mu\text{M}$, with detectable Mn but with Fe below detection. While it was not possible to obtain in situ measurements of dissolved $\text{O}_2(\text{g})$ in ground water prior to exposure to the cave atmosphere, field sample preservation with subsequent analytical determination of redox-sensitive elements indicates that the redox status of ground water entering Lechuguilla Cave ranges from oxic to suboxic.

CONCLUSIONS

Characterization of seepage redox chemistry from selected areas of Lechuguilla Cave supports the hypothesis

that ground water entering the cave as seepage is a potential source of dissolved Mn and inorganic N (as both $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$) to the cave environment. Organic C concentrations in the seepage are generally low, and therefore redox conditions can be classified as ranging from oxic to suboxic, with N present primarily as $\text{NO}_3\text{-N}$ and dissolved Fe concentrations below detection. Once the seepage enters the cave environment, dissolved $\text{O}_2(\text{g})$ concentrations increase, organic C continues to oxidize, Mn oxidizes and is precipitated or adsorbed, and NH_4 oxidizes to NO_3 . As a result, water in standing pools has a tendency to contain concentrations of Fe, Mn, and $\text{NH}_4\text{-N}$ most often below common analytical detection limits. Comparison of E_{h_m} values obtained in the field using a Pt electrode, and E_{h_c} values computed using the analytical results for various redox couples, demonstrates a lack of internal redox equilibrium in seepage. Therefore, future studies related to redox chemistry of Lechuguilla Cave pools or seepage should avoid the use of measured E_{h_m} values to calculate the aqueous equilibrium concentrations of redox-sensitive elements.

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