

Technical Article

Geochemistry of Perched Water in an Abandoned Underground Mine, Butte, Montana

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Abstract. The Lexington tunnel is the last accessible underground mine working in the Butte, Montana mining district. Used as recently as 1993, the tunnel and adjacent workings have been abandoned for over 10 years. Although the Lexington tunnel is over 200 m above the regional water table, perched water is present over much of its extent. Mine water near the portal is moderately acidic (pH 4 to 5), with extremely high concentrations of metals, including Cu (up to 1000 mg/L) and Zn (up to 1400 mg/L). In the middle reaches of the tunnel, the quality of the water is much better, with near-neutral pH, high bicarbonate alkalinity, and lower concentrations of heavy metals. The low acidity and metal content is attributed to a lack of pyrite and other sulfides in this portion of the mine, as well as the presence of carbonate minerals, such as rhodochrosite (MnCO_3), in exposed veins. Sulfide minerals are more widespread further back in the tunnel, and are now oxidizing rapidly, leading to pockets of severe acid drainage (pH < 3, dissolved Zn up to 5000 mg/L).

Geochemical modeling suggests that the near-neutral waters – the most voluminous type encountered in the Lexington tunnel – are close to equilibrium saturation with rhodochrosite and hydrous Zn-carbonate ($\text{ZnCO}_3 \cdot \text{H}_2\text{O}$). The Eh of these waters is most likely controlled by redox reactions involving dissolved Mn^{2+} and secondary, Zn-rich, hydrous Mn-oxides. In contrast, the Eh of the acidic waters appears to be controlled by reactions involving Fe^{2+} and Fe^{3+} . Most of the acidic waters are saturated with K-jarosite, which forms delicate, straw-like dripstones at several localities. Decaying mine timbers could be an important renewable source of organic carbon for heterotrophic microorganisms, such as iron- and sulfate-reducing bacteria, especially deeper in the mine workings where the ground is saturated with anoxic ground water.

Key words: Butte; geochemistry; mine water; rhodochrosite; vadose zone

Introduction

The city of Butte, Montana is one of the most famous mining districts in the U.S., both from the standpoint of the mineral wealth produced (Meyer et al. 1968) and the resultant environmental damage (Dobb 1996; Langewiesche 2001). Large-scale mining in Butte began in the 1870s, and until the 1950s was mainly done by underground stoping of high-grade Ag-Cu-Pb-Zn veins. In the mid-1950s, the emphasis shifted to open pit mining of a lower grade porphyry Cu ore body. In 1982, all mining ceased temporarily, and the underground mine complex and adjacent Berkeley open pit began filling with ground water. Whereas the Berkeley pit lake is highly acidic and has extremely high concentrations of dissolved heavy metals (Davis and Ashenberg 1989; Gammons et al. 2003a; Jonas 2000; Newbrough and Gammons 2002; Pellicori et al. 2005), the majority of the flooded underground mine workings in Butte have a near-neutral to weakly acidic pH, and much lower metal content (Gammons et al. 2003b; Metesh and Duaiame 2000; Pellicori et al. 2005).

Of the estimated 15,000 km of underground mine workings under Butte Hill, the only workings that are

still accessible to humans are adjacent to the Lexington tunnel, a horizontal drift that was driven at the 400 level (400 feet (122 m) below the summit of Butte Hill) to access the northwestern portion of the underground mine complex. The purpose of this study was to conduct a geochemical inventory of mine water in the Lexington tunnel. The Montana Bureau of Mines and Geology (MBMG) regularly collects water samples from a number of monitoring wells and flooded shafts in the Butte mining district (Metesh and Duaiame 2000). However, all of these waters are located below the water table. The Lexington tunnel provides convenient, year-round access to mine waters that are located well above the present day regional water table. A better knowledge of the chemistry of these downward-infiltrating waters may help us to understand the mechanisms of weathering and acid mine drainage in the Butte District, as well as the geochemical evolution of underlying ground water.

Mining History

The Lexington tunnel heads roughly 1.5 km in a NE direction from the Syndicate open pit to the Lexington

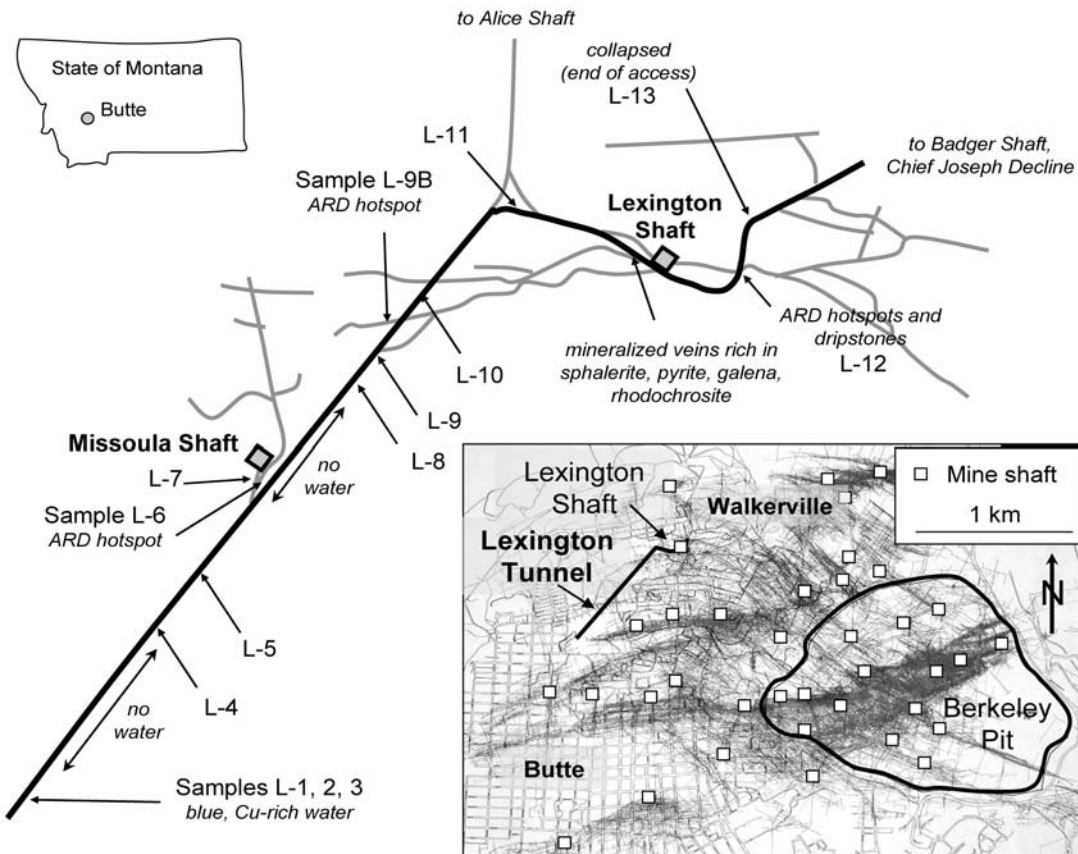


Figure 1. Map of the accessible portion of the Lexington tunnel, showing the location of samples collected in this study. The main Lexington tunnel is bold: side workings (mostly caved or sealed off) are shaded. Redrawn from “T400 Level Underground Map – Phase I Mine Plan” (New Butte Mining, circa 1990). The inset shows all major underground mine workings (thin black lines) in the Butte District (modified after Duaimé et al. 2004), as well as most of the major shafts. The approximate outline of the Berkeley Open Pit mine is shown in bold.

shaft (Figure 1). Sunk in 1876, the Lexington shaft was one of the original mines discovered on Butte Hill. According to local historians, the Lexington tunnel was built in the late 1800s so that operators of the Lexington mine could avoid the high ore taxes imposed by the city of Walkerville, which is adjacent to Butte. Rather than remove the ore at the shaft headframe in Walkerville, the mine owners would raise the ore to the 400 level, and then rail it through the Lexington tunnel to the portal at the Syndicate pit, which at that time was still on county land. Subsequent underground development off of the 400 level linked the tunnel to other underground workings in the northwestern portion of the Butte district, as well as the Berkeley open pit (via the Chief Joseph decline). The Lexington tunnel was re-opened in the late 1980’s by an Australian-owned company known as New Butte Mining. New Butte Mining explored the 400 level for several years before ending its underground operations in 1993, with little or no significant production. During the author’s visits in 2002 and 2003, the tunnel and adjacent workings had not been used for 10 years, during which time the

hydrology, chemistry, and biology was largely undisturbed. Improvements to the tunnel are in progress with the onset of a new underground miner training facility, which may change the quantity and quality of the mine water.

Like many of the early workings on Butte Hill, the Lexington tunnel was framed with timber, with a narrow gage railway to haul ore and equipment. Portions of the accessible tunnel are dry, whereas others carry appreciable amounts of water, up to 0.5 m in depth. All of the mine water in the Lexington tunnel is perched high above the present-day regional water table, which is more than 200 m below the 400 level. Judging from the oxidized appearance of the bedrock and mineralized veins, most of the accessible workings in the tunnel were above the pre-mining water table as well. However, pyrite and other sulfides (sphalerite, galena) become more widespread further back in the mine (near the Lexington shaft and beyond), indicating that some unoxidized ore is locally present. These pockets of previously unweathered sulfide minerals are now hot spots for

acid mine drainage. Based on hydrogeological investigations by the MBMG, water seeping through the floor of the Lexington tunnel eventually drains eastward to the Berkeley pit lake.

Methods

Most water samples described in this report were collected on Oct. 29, 2002. A representative set of field measurements and water samples were taken extending from the portal to the caved section past the Lexington shaft (Figure 1). The location of each water sample in the main tunnel was calculated using a calibrated hip-chain. A follow-up visit for additional samples was conducted on June 6, 2003.

The 2002 measurements collected in the field for each sample included pH, water temperature, specific conductivity (SC), and Eh. These measurements were recorded using two WTW Model 340i portable multimeters. The pH meter was freshly calibrated with pH 4 and 7 standards. Field Eh measurements were measured in mV with a Pt electrode, and were manually converted to true Eh using a temperature-sensitive correction factor that takes into account the difference between the standard potential of the Ag-AgCl half-cell reaction and the standard hydrogen electrode. A few samples collected in June of 2003 were also analyzed for alkalinity. Unfiltered and unpreserved samples were brought back to the lab and were titrated within 24 hours to a pH 4.5 endpoint, using a HACH digital titrator and 0.16N H₂SO₄ solution.

All samples of mine water were filtered in the field using a 60 cc polypropylene syringe and 0.45 µm PES syringe filters. The bottles were acidified back in the laboratory to 1% with trace metal HNO₃, and stored in the refrigerator for 3 weeks prior to ICP-AES analysis. The ICP analyses were performed at the Murdock Environmental Laboratory, Univ. of Montana, using EPA Method 200.7. Full analytical QA-QC protocols were followed, including Instrument Performance Checks every 10 samples, lab blanks, lab duplicates, and lab spikes. Accuracy of the analyses is estimated at ±5%.

Results

Figure 1 shows the location of the mine waters sampled during the field trips of October 29, 2002 and June 6, 2003. Field measurements and brief notes about the appearance of the waters are given in Table 1. Results of the ICP analyses are given in Table 2.

The mine waters sampled from the Lexington tunnel showed a large diversity in terms of appearance and chemical composition. Three waters connected by a ditch close to the entrance to the tunnel (L-1 to L-3) had moderately acidic pH (4.1 to 4.9), and a deep green color. In fact, the water itself was blue, owing to extremely high concentrations of dissolved copper (570 to 1010 mg/L). The green appearance was due to the combination of the blue water, and yellow-orange ochre lining the ditch (Figure 2A). Crystals of vivid blue CuSO₄ formed a “bathtub ring” above the water line.

Table 1. Field observations of mine waters from the Lexington tunnel

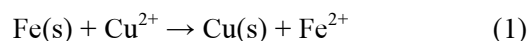
Sample	Location ^a	Date	Notes	SC ^b	pH	T°C	Eh ^c
L-1	107	10-02	blue-green water	17.7	4.53	0.3	488
"	"	6-03	"	18.0	4.50	-	-
L-2	125	10-02	blue-green water	19.9	4.15	2.6	510
L-3	180	10-02	blue-green water	18.3	4.93	3.7	470
L-4	380	10-02	colorless water, black crusts	1.49	6.80	5.3	353
L-5	410	10-02	colorless water, black crusts	2.54	6.97	5.4	353
"	"	6-03	"	2.14	6.46	5.7	-
L-6	500	10-02	colorless water	2.46	6.45	1.5	381
L-7	-	10-02	ARD hotspot, orange-red crusts	2.38	4.54	1.6	415
L-8	725	10-02	colorless water, red to black crusts	0.38	7.10	5.3	389
L-9	785	10-02	colorless water, red to black crusts	2.01	6.86	5.9	427
"	"	6-03	"	2.02	6.47	7.0	-
L-9 B	810	6-03	bad ARD hotspot in west drift	32.8	2.67	-	-
L-10	840	10-02	colorless water, black & white crusts	1.87	7.25	6.5	400
L-11	960	10-02	colorless water, black crusts	2.16	6.98	6.9	395
"	"	6-03	"	2.16	6.34	-	-
L-12	-	10-02	bad ARD seeps, soda straws	19.1	2.17	13.6	790
L-13	-	10-02	red precipitates, at caved tunnel	2.50	2.96	11.6	640

^ameters from the tunnel entrance, as measured with a hip chain; ^bmS/cm; ^cmV (SHE)

Table 2. Results of ICP metals analysis of mine waters from the Lexington tunnel; all data are in mg/L (ppm). Detection limits for a given analyte vary from sample to sample, according to the dilution factors used prior to analysis.

Sample	Al	As	Ca	Cd	Cu	Fe	K	Mg	Mn
L-1	389	<2.5	388	4.33	843	88.7	26	2390	1290
L-2	523	<2.5	394	5.09	1010	128	40	2980	1320
L-3	107	<2.5	373	5.37	572	57.7	<22	2400	1180
L-4	<.220	0.63	131	<.028	<.16	<.44	5.4	25.5	0.63
L-5	<.220	0.89	325	<.028	<.16	<.44	15	62.7	2.36
L-6	<.220	<.25	356	0.332	<.16	<.44	14	77.6	32.4
L-7	0.31	<.25	390	0.277	<.16	<.44	10	83.8	2.33
L-8	<.044	<.056	16.3	<.005	<.033	<.089	1.1	2.8	<.044
L-9	<.220	<.25	306	0.071	<.16	<.44	3.9	62.6	16.3
L-10	<.220	<.25	303	<.028	<.16	<.44	3.7	55.2	8.85
L-11	<.220	<.25	345	0.049	<.16	<.44	5.2	67.2	16.1
L-12	166	<2.5	443	11.0	45.1	841	<22	695	2840
L-13	0.48	<.56	342	<.055	<.33	1.49	<4.4	98.0	96.4
	Mo	Na	Ni	Pb	SO ₄	Sr	Si	Tl	Zn
L-1	1.22	235	4.36	<2.22	20300	2.81	17.4	6.76	1250
L-2	1.43	155	4.79	<2.22	24400	3.44	24.8	7.04	1420
L-3	1.38	248	4.33	<2.22	18000	3.11	9.7	6.51	1390
L-4	<.055	140	<.055	<.222	562	0.31	5.7	<.44	1.57
L-5	<.055	357	<.055	<.222	1740	0.85	6.7	<.44	3.64
L-6	0.154	155	0.074	<.222	1890	1.37	6.9	<.44	151
L-7	0.154	112	0.062	<.222	1790	1.61	7.1	<.44	139
L-8	<.011	62.3	<.011	<.0444	68	0.09	4.9	<.09	0.093
L-9	<.055	42.4	<.055	<.222	1199	1.03	8.2	<.44	49.7
L-10	<.055	39.4	<.055	<.222	973	1.00	8.0	<.44	16.4
L-11	<.055	40.2	<.055	<.222	1228	0.91	7.8	<.44	32.3
L-12	5.84	26.8	1.96	<2.22	23500	<.556	101	15.7	5490
L-13	<.11	16.4	<.11	<.444	1579	2.47	8.7	<.89	61.1

These waters were also extremely rich in sulfate (>18,000 mg/L), Zn (1250 to 1420 mg/L), and Mn (1180 to 1320 mg/L), as well as the common rock-forming elements Mg, Ca, Na, and K. Because of the moderately acidic pH, filtered Fe and Al were also highly elevated (Table 2). No visible flow of water was noticed near the portal, implying that these metal-rich waters are essentially puddles. Steel rails in the vicinity of L-1 to L-3 were extensively coated with pink, metallic copper, owing to the so-called “cementation” reaction:



Cementation has been used on a large scale in the Butte mining district since the 1940s to recover dissolved Cu from acid mine water, and is still used today to “mine” copper from the Berkeley pit-lake.

Further inside the tunnel, the majority of the waters sampled (L-4 to L-11) were colorless, with weakly acidic to neutral pH, moderately high SC (380 to 2500

μS/cm), and, with the exception of Mn and Zn, relatively low concentrations of heavy metals (Table 2). This water flows back towards the tunnel entrance at a slow rate of roughly 3-5 L/minute, but then seeps into the ground 400 m from the portal entrance. Mineral crusts and precipitates in this portion of the tunnel are dominantly dark brown or black, and were determined by SEM-EDX analysis to consist of poorly crystalline Mn oxy-hydroxide containing high amounts of Zn (15 to 19 wt%, based on semi-quantitative EDX analysis). White Al-hydroxide was also locally abundant (Figure 2B), presumably where slightly acidic water was mixing with the pH-neutral water of the main flow. The mineralogy of the secondary hydrous Mn-Zn oxides in the Lexington tunnel has not been determined, but based on other Zn-contaminated sites worldwide, it is most likely the phyllosilicate mineral hexagonal birnessite (i.e. Zn-substituted, hydrous MnO₂) (Tebo et al 2004; Toner et al. 2006). Similar Zn-rich hydrous Mn-oxides have recently been described from other abandoned mine sites in the Boulder Batholith (Shope et al. 2006).

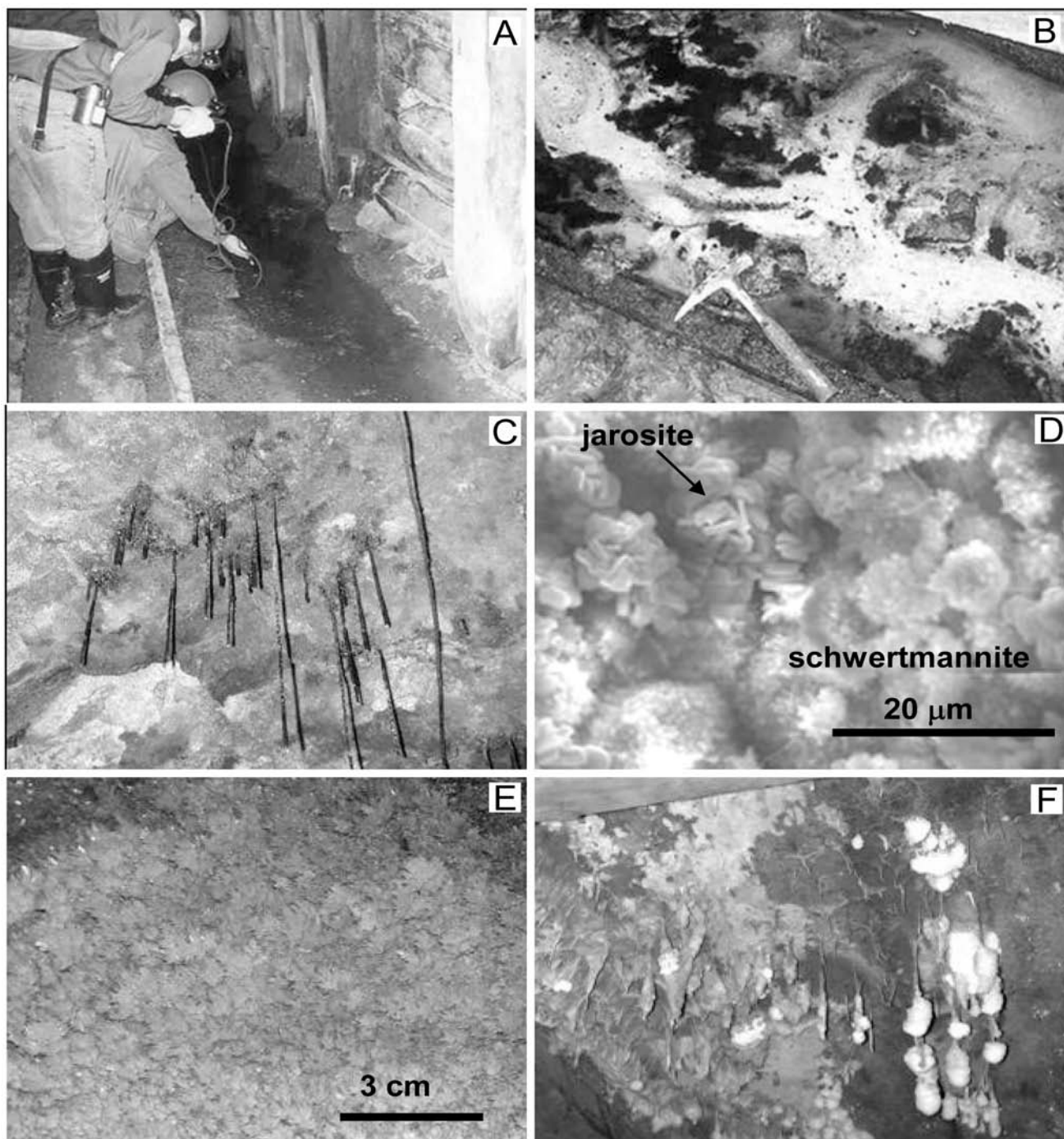


Figure 2. Photographs of the Lexington tunnel: A) Cu-rich water near the mine portal; B) pH-neutral water with abundant Al-hydroxide (white) and hydrous Mn-Zn-oxide (black) precipitates; C) Soda straws of jarosite and schwertmannite dangling from the roof of the mine near stop L-12. The straws were ~ 15 to 30 cm long, and were slowly dripping pH 2.2 water; D) SEM photograph of the interior of a dripstone, showing intergrown K-jarosite and schwertmannite; E) feathery gypsum crystals up to 1 cm long on mine walls near back of the tunnel; F) rotting timbers with fungus and biofilm.

The comparatively benign character of water in the middle section of the mine workings is explained by a paucity of sulfide minerals. Most of the rocks exposed were weakly altered granite or oxidized shear zones that lost their pyrite long ago (prior to mining) due to natural weathering processes. The

high Mn content of the waters is due to the presence of rhodochrosite (MnCO_3) in the veins and altered wallrock. Samples collected on Jun-04, 2003 at L-5, L-9, and L-11 contained 59, 44, and 184 mg/L alkalinity (as CaCO_3), respectively, indicating a moderate to high bicarbonate ion concentration. This

dissolved inorganic carbon most likely came from dissolution of rhodochrosite or calcite in the veins and altered wallrock; Roesler (2005) recently presented stable C isotope evidence to support this hypothesis.

Although the middle portion of the tunnel is dominated by pH-neutral water, isolated patches of orange-red precipitates and lower pH water (e.g. L-7, L-9B) attest to the presence of acid "hot spots". These were mainly found in side stopes, where mineralized shear zones containing relict sulfides cut the mine walls. This feature was best displayed at location L-9b, where water had extremely high SC (>30 mS/cm), and low pH (2.67). Further back in the mine workings, past the Lexington shaft, the mine waters became consistently acidic, with abundant orange-red mineral precipitates on the floors, walls, and ceilings of the open mine workings. The shift in character of the mine waters is explained by the increased presence of sulfide minerals (mainly pyrite and sphalerite, with lesser amounts of galena, chalcopyrite, and tetrahedrite-tennantite) in veins and mineralized shear zones exposed in the tunnel and side drifts. These sulfides are oxidized to a thin rind of secondary minerals on exposed surfaces, but are nearly fresh when broken, suggesting that this portion of the mine may have been saturated with ground water prior to mining. Because the water levels in the underground workings have been artificially drawn down by mining operations, the sulfides have been oxidizing for over 100 years, creating severe acid mine drainage. Mine walls in the vicinity were covered with a thick coating of ochre, feathery masses of gypsum (Figure 2E), and delicate needles of epsomite ($MgSO_4$). Sample L-12 was taken in a small puddle formed by drops of acidic water coming from the ceiling via straw-shaped dripstones (Figure 2C). The dripstones were examined by SEM-EDX, and were found to consist mainly of the minerals schwertmannite and K-jarosite. Jarosite is a very common secondary mineral in the Butte district, forming a yellowish film on exposed waste rock and tailings that contain actively-oxidizing pyrite. In the dripstone sample from the Lexington Tunnel, the jarosite contained up to 1 wt% Pb, indicating a possible solid solution of plumbian jarosite with K-jarosite. Figure 2D is an SEM photograph that shows the general appearance of the intergrown schwertmannite and jarosite crystals coating the interior of the dripstone formations. Water droplets collected from the end of the dripstones contained 5500 ppm Zn, 2800 ppm Mn, 840 ppm Fe, 45 ppm Cu, and 11 ppm Cd. The high Zn/Cu ratio of the waters is consistent with the abundance of sphalerite and relative scarcity of chalcopyrite in the veins exposed on the tunnel walls. The Lexington mine is located within the Peripheral Zone of the Butte

District, which is relatively Zn-rich and Cu-poor (Meyer et al. 1968; Miller 1973).

Discussion

Conceptual Hydro-geochemical Model

Figure 3 is a schematic diagram that illustrates the mine workings with respect to the location of the pre-mining and present-day water tables. The latter is artificially depressed due to continual drainage of ground water into the Berkeley pit-lake. The subsurface is subdivided into 4 hydro-geochemical zones. Zone I includes near-surface water stored in soil and highly weathered granite (regolith), Zone II includes bedrock above the pre-mining water table, Zone III is the area between the pre-mining and present-day water tables, and Zone IV comprises all mine workings that are below the current water table and are therefore completely flooded. Whereas Zone II water is of relatively good quality (near-neutral pH with low dissolved metal concentrations, with the exception of Mn and Zn), Zone III water includes pockets of very poor quality acid-sulfate water (e.g. samples L-7, L-9B, L-12, L-13). These localized pockets are concentrated along mineralized veins and shear zones rich in pyrite and other sulfide minerals. Other portions of Zone III that are less intensely altered and mineralized contain near-neutral mine water that is similar in composition to Zone II (e.g. samples L-10, L-11).

Of the various zones shown in Figure 3, Zone III is the region in which most of the active sulfide mineral oxidation and acid generation is expected to occur. Most primary sulfide minerals in Zones I and II oxidized long ago, through thousands of years of natural weathering. Some pyrite oxidation could have occurred in Zone IV during the 50 to 100 years of active underground mining, but such reactions would have essentially ceased following mine flooding, due to the extremely slow rates of diffusion of oxygen below the water table. Any acidic drainage that would have been generated during active mining operations in the deep mines would most likely have been flushed out of the mine workings during the 30+ years since the onset of wide scale mine flooding in 1982. This is consistent with the results of water quality monitoring of the Butte flooded mine complex by MBMG personnel (Metesh and Duaiame 2000).

One of the more enigmatic aspects of the Lexington tunnel is the occurrence of the Cu-rich water near the mine portal. The extremely high concentrations of Cu (and other metals, including Fe and Zn) in this water (Samples L-1 to L-3) cannot owe their origin to active oxidation of primary sulfide minerals, since such

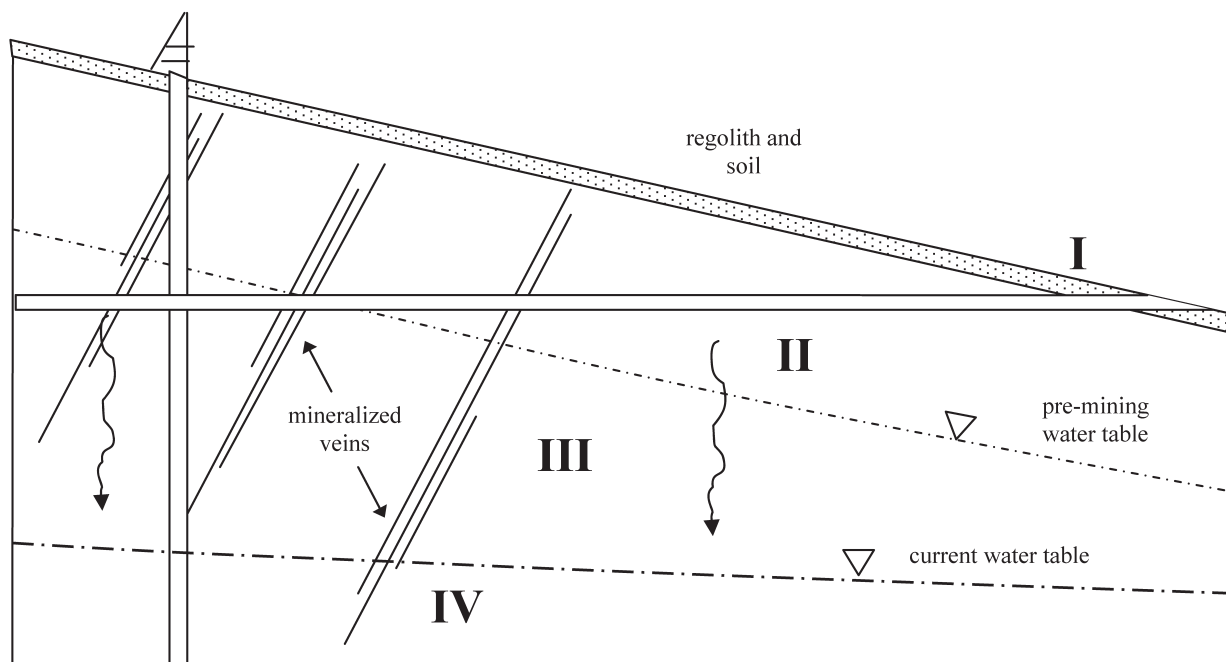


Figure 3. Conceptual hydro-geochemical model of the Lexington tunnel; the diagram is not to scale, and the location of the pre-mining and current water tables are conceptually drawn. See text for more discussion.

minerals in the near-surface would have been weathered long ago. Examination of the hanging wall of the Lexington tunnel above the Cu-rich water shows the presence of blue CuSO_4 along fractures and cracks, suggesting that the secondary mineral salts are pervasively distributed in the near-surface environment. It is proposed that the pool of metal-rich water near the portal entrance was formed by flushing of soluble salts (CuSO_4 , ZnSO_4) from the weathered bedrock and overlying regolith, forming a pool of metal-sulfate that is primarily dissolved during wet months, and crystallizes as efflorescent salts during dry periods. To explain the original concentration of metals in the regolith, the downward migration of dissolved metals during infiltration events must be balanced by upwards capillary migration of metals dissolved in pore waters during the dry months. The concentration of soluble heavy metals near the surface of the fractured bedrock ore body may be analogous to the formation of metal-sulfate “slickens” on the surface of mine tailings, such as those along Silver Bow Creek and the upper Clark Fork River, downstream of Butte (Moore and Luoma, 1990).

Geochemical Modeling

Eh-pH diagrams summarizing the geochemical conditions of the mine waters from the Lexington Tunnel are given in Figure 4. These were drawn using the program STABCAL (Huang 2001) with the MINTQA2 database option. In all of these diagrams, the stability fields of solids have been

shaded, and the measured Eh-pH of Lexington mine waters are shown with open circles.

Figure 4A shows the Fe-S- CO_3 - H_2O system, drawn for a total dissolved Fe concentration of 1 mg/L. The redox state of mine waters with pH between 2 and 5 appears to be buffered by equilibrium between dissolved Fe^{2+} and jarosite. For the strongly acidic waters (pH < 3), redox may also be influenced by the aqueous $\text{Fe}^{2+}/\text{Fe}^{3+}$ buffer. A single Fe speciation analysis of sample L-9B using the FerroZine procedure yielded a total dissolved Fe^{3+} concentration of 1450 mg/L, compared to a total dissolved Fe^{2+} concentration of 150 mg/L, indicating a high degree of oxidation, which is typical of vadose water. In contrast, most of the dissolved Fe in the deeper, water-saturated portions of the Butte mine workings is in the reduced Fe^{2+} state (Pellicori et al. 2005).

Figures 4B and 4D portray the Mn- CO_3 - H_2O and Zn-S- CO_3 - H_2O systems, drawn for total Mn and total Zn concentrations of 10 and 20 mg/L, respectively. The results suggest that the near-neutral mine water in the middle portion of the tunnel are near equilibrium saturation with rhodochrosite and hydrous Zn-carbonate. Oxidation of these waters could easily result in precipitation of Mn-oxides, as was evident from the abundant black crusts. Since the crusts were not pure Mn-oxide but rather a mixed Mn-Zn phase, the stability field of the oxide minerals should be enlarged, making them closer to equilibrium with the mine waters than they appear to be in Figure 4B. All

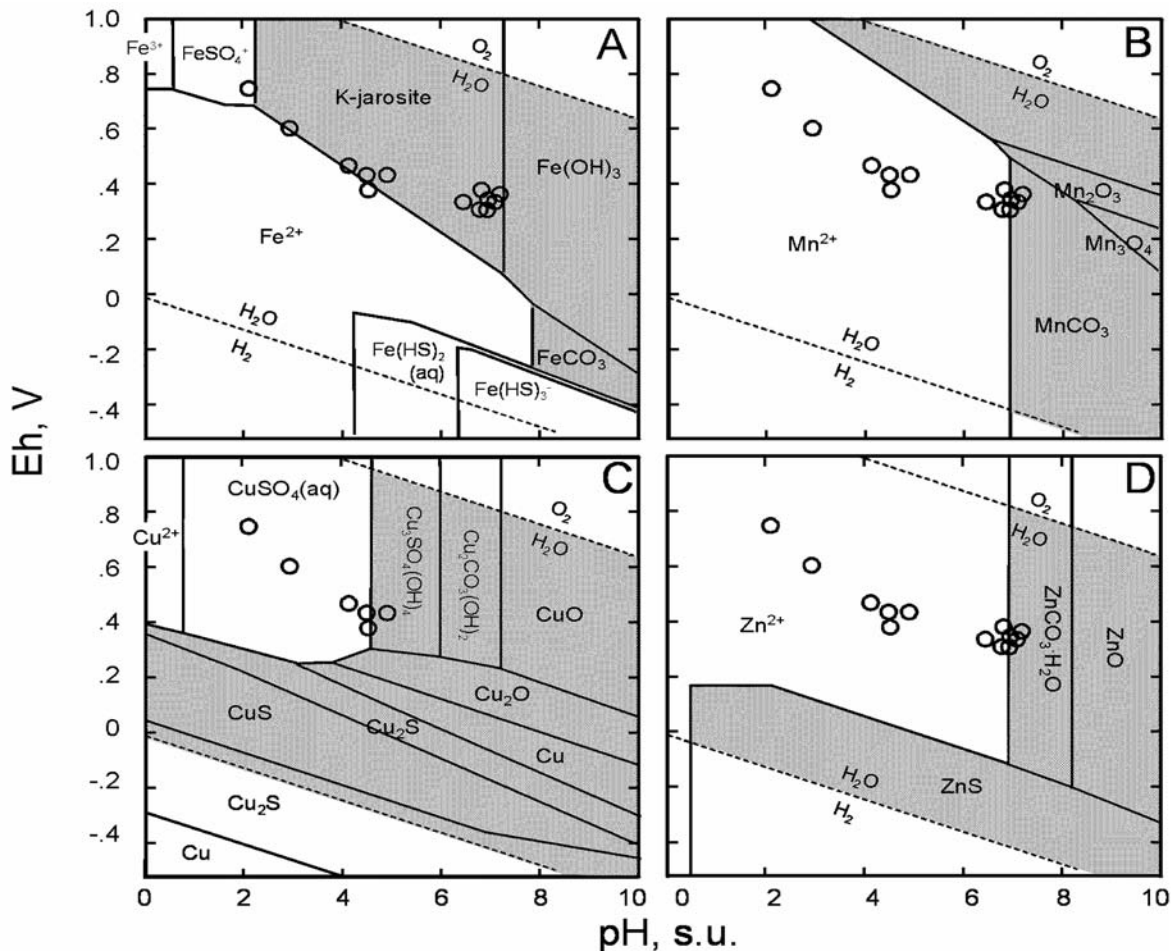


Figure 4. Eh-pH diagrams for water samples collected from the Lexington tunnel; the shaded regions show fields of predominance of solids within the stability limits of liquid water. Conditions of the diagrams: A) 1 ppm Fe, 1000 ppm S, 20 ppm C; 10 ppm K; B) 10 ppm Mn, 20 ppm C; C) 1000 ppm Cu, 7000 ppm S, 20 ppm C; D) 20 ppm Zn, 1000 ppm S, 20 ppm C.

of the waters with $\text{pH} < 5$ were strongly undersaturated with any pure Mn or Zn mineral.

Finally, Figure 4C portrays the Cu-S-CO₃-H₂O system, with solute concentrations set to reflect the conditions of the blue, Cu-rich water near the Lexington portal (Cu = 1000 mg/L; S = 7000 mg/L). These waters are close to saturation with the Cu-sulfate mineral antlerite (Cu₃SO₄(OH)₄), which is not surprising given the blue precipitates along the water line where the samples were collected. Any reduction in Eh could easily cause precipitation of cuprite (Cu₂O) or metallic Cu, as witnessed on the steel rails of the old narrow gage railroad. The strongly acidic seeps further in the mine are undersaturated with any Cu-bearing mineral. Because Cu concentrations of the near-neutral waters were below detection, these field samples are not plotted in Figure 4C.

Biology

Most of the Lexington tunnel and surrounding drifts are reinforced with timbers. Near the portal, these

timbers are well-preserved, and almost certainly have been treated. However, further back in the mine, many of the timbers were in an advanced state of decomposition. White fungus was locally abundant, occurring as delicate, spidery filaments coating the wood, or pendular masses hanging from the ceiling (Figure 2F). Small mushrooms of an unknown species were also growing on the wood.

During an earlier visit by the author to the Lexington Tunnel in March, 2002, a distinct (but faint) odor of H₂S was noted at one location several hundred meters from the entrance. This would indicate the localized presence of sulfate-reducing bacteria (SRB). SRB cannot tolerate oxygen, low pH, or high concentrations of toxic metals. However, the stagnant, near-neutral, sulfate-rich water present in much of the mine workings would be conducive to SRB, provided a source of organic carbon was present. Such a source could be provided by the decomposing wood supporting the mine workings. In October, 2002, the Eh values of the mine waters sampled were all above +350mV, and were therefore

too oxidized for SRB activity. However, it is possible that isolated pockets of bacterial sulfate reduction could occur in water-logged areas with low O₂ content. The likelihood of SRB activity is much greater below the regional water table, where oxygen is consumed by oxidation of pyrite and dissolved ferrous iron. Indeed, ground water being pumped out of the flooded West Camp mine workings of Butte has elevated concentrations of H₂S (> 0.2 mg/L), and recent stable isotopic work has confirmed that this dissolved sulfide owes its origin to bacterial sulfate reduction (Gammons et al. 2003b; Roesler 2005).

Conclusions

The Lexington Tunnel affords a unique window into geochemical processes that have occurred in the past throughout the Butte district, and are still occurring today. The data summarized in this report cover only a small portion of the vast network of abandoned underground mine workings in Butte. However, they are significant in that they are the only data that exist in the Butte district for perched ground water above the water table. The distribution of mine water types appears to follow a systematic trend from the mine portal to the interior of the mine workings, and this trend has been linked to the hydrogeology and mining history of the site. Water near the mine entrance was mildly acidic but was extremely rich in metals, with cyclic dissolution and precipitation of efflorescent metal-sulfate salts depending on changes in the humidity and elevation of the perched water table. The majority of the water further inside the tunnel had a near-neutral pH buffered by the presence of carbonate minerals in the veins and altered wallrock, and by a relative scarcity of pyrite. This water was close to saturation with the minerals jarosite, ferric hydroxide, rhodochrosite, hydrous Zn-carbonate, and hydrous Mn-Zn-oxide, and the redox state was likely controlled by reactions between dissolved Mn²⁺ and secondary hydrous Mn-Zn-oxides. Wallrock near the back of the tunnel was most likely below the pre-mining water table, and consequently, weathering of abundant sulfide minerals has created strongly acidic water saturated with K-jarosite and gypsum, with an Eh controlled by Fe²⁺/Fe³⁺ or Fe²⁺/jarosite.

The extreme variability of water chemistry types in the Lexington tunnel over a relatively short distance underscores the spatial heterogeneity that most likely occurs elsewhere in any fractured and mineralized bedrock system between the ground surface and the water table. It is within this hydrological zone that most pyrite oxidation takes place in the subsurface. In contrast, ground water below the water table has a more homogenous chemistry, due in part to a much less rapid rate of oxidation of sulfide minerals, and in

part to mixing, mechanical dispersion, and diffusion of solutes. Rotting timber in wood-framed underground mine workings may be a significant source of biodegradable carbon for micro-organisms. Previous studies have documented the widespread presence of bacterial sulfate reduction in outer regions of the Butte flooded underground mine complex.

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