

Technical Article

A Survey of the Geochemistry of Flooded Mine Shaft Water in Butte, Montana

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Abstract. This paper outlines general trends in the geochemistry of the more than 10,000 km of flooded underground mine workings in the Butte mining district. The waters in question range in pH from 4 to 8, are all moderately to strongly reducing, and show a huge range in concentration of dissolved metals such as Al, As, Fe, Mn, and Zn. Metal concentrations and total acidity are highest in the Kelley mine shaft, which was the main dewatering station used to pump ground water from the underground mine complex during active mining operations. In contrast, metal concentrations are much lower in the outer portions of the district where many of the mines contain hydrogen sulfide formed by sulfate-reducing bacteria. In comparison to the other heavy metals, concentrations of Pb and Cu are quite low in the flooded mine shafts. An interesting inverse correlation between pH and water temperature is noted, which may be partly caused by exothermic pyrite oxidation reactions in the central portion of the district.

Key words: acid mine drainage; Butte; geochemistry; ground water; underground mines

Introduction

Although more famous for its pit lake, the Butte mining district (also known as the Summit Valley district) is also host to one of the most extensive flooded underground mine complexes in the world. An estimated 16,000 km of horizontal drifts connects over 30 vertical shafts over a land surface area of 12 km² to depths of up to 1.6 km below surface. Figure 1 is a digitized image showing the extent of the underground workings (modified from Duaiame et al. 2004). In this map, the horizontal workings are color-coded for depth below surface (referenced to the top of the Alice Mine, in the northern end of the district, which is at an elevation of 1900 m or 6260 ft). Of the workings shown, only a portion of those marked in yellow (top 300 m) are sufficiently shallow to be non-flooded. Also shown are the location of >30 mine shafts that are greater than 320 m (1000 feet) deep, many of which have head frames and mine buildings remaining today. The outline of the Berkeley open pit is shown in bold. The deepest portion of the pit prior to flooding was at an elevation of 1295 m (4260 ft). Quite a bit of the workings marked in yellow or green within the pit border were removed by the excavation of the open pit. Since the lake surface is currently at an elevation of roughly 1700 m (5260 ft), the workings shown in green are presently under water, whereas the workings shown in yellow are exposed above the water line. Workings shown in red and purple are beneath the bottom of the pit.

Most of the underground mine workings belong to the so-called “East Camp”, which is currently draining to the Berkeley pit lake, the lowest point in the local

ground water table. All of the East Camp mines produced copper, with variable quantities of zinc, silver, and lead from large, steeply dipping “Main Stage” veins (see Gammons et al. 2006). A set of mine workings in the SW corner of the district, known as the “West Camp”, were sealed off from the larger East Camp workings in the 1980s. These mines, serviced by the Emma, Travona, and Ophir shafts, were primarily producers of manganese (in the form of large rhodochrosite and rhodonite veins) as well as silver. Mine water in the West Camp drains to a pumping well located in the extreme SW corner of the flooded mine complex. Outlying mine workings are referred to as the “Outer Camp”, and include the Orphan Boy and Orphan Girl shafts near the present-day World Museum of Mining, and the Marget Ann mine, which is located off the NW edge of the map in Figure 1.

The Montana Bureau of Mines and Geology (MBMG) conducts a semi-annual inventory of mine waters from several of the flooded mine shafts in the East, West, and Outer Camps. The purpose of this paper is to summarize general trends in the geochemistry of the samples collected and analyzed by the MBMG. The next paper in this issue (Metesh 2006) goes into more detail about the hydrology of the mine flooding, which continues to this day.

The interested reader is referred to earlier papers by Gammons et al. (2003) and Pellicori et al. (2005) for a discussion of the stable isotope systematics of the flooded mine waters, and to Metesh (2004) for a detailed discussion of the relationship between the primary mineralogy of the ore bodies and the

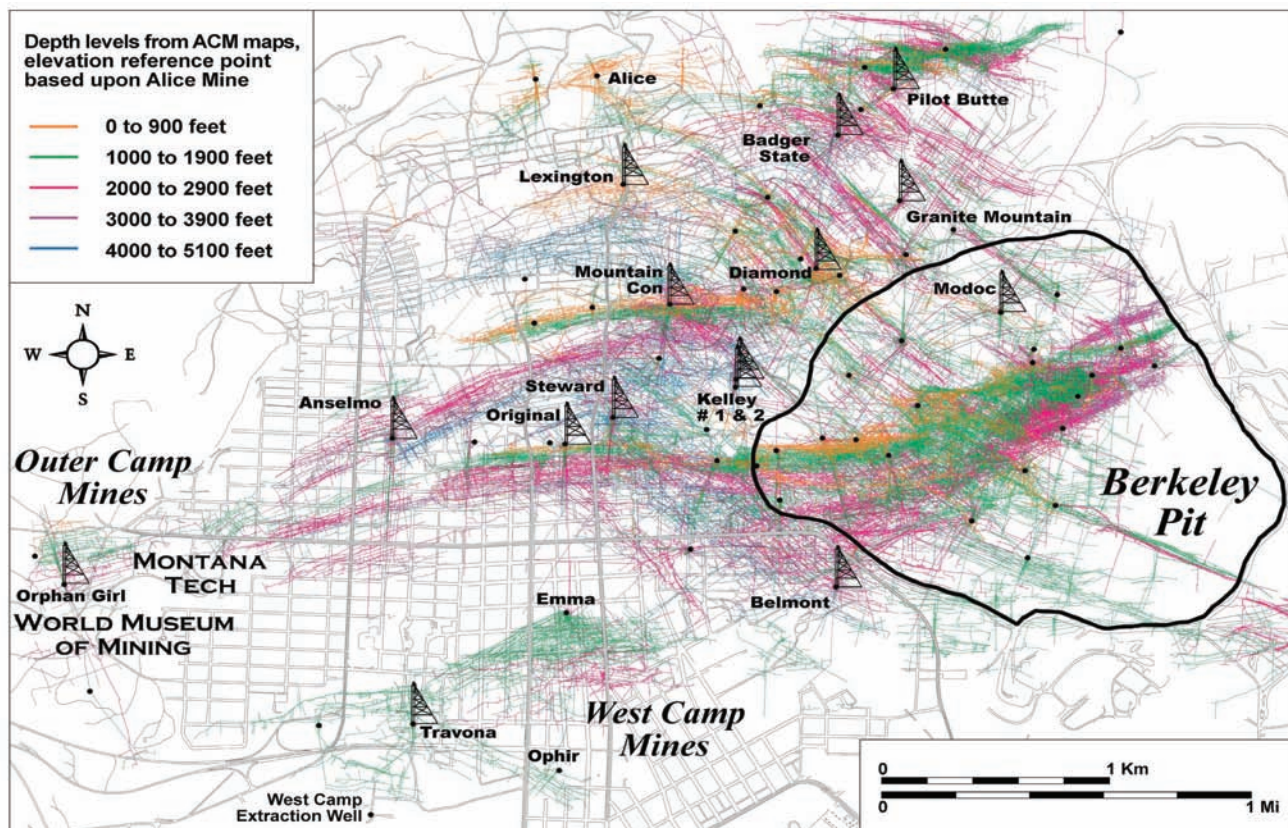


Figure 1. Map of the major mine workings in the Butte District. Solid circles are mine shafts at least 1000 feet (320 m) in depth. Shafts with head frame symbols have mine buildings and head frames that are still standing. The colors are coded according to depth below the elevation of the ground surface at the top of the Alice Mine, which is near the summit of Butte Hill (north-central portion of map). The map was digitized by MBMG personnel, and is based on unpublished Anaconda Mining Company records (modified from Duaiame et al. 2004).

resultant mine water chemistry. All of the data presented in this paper were taken from the MBMG's "Ground Water Information Center" database (GWIC 2006) which is published on the web. The MBMG has also published a large number of Open File reports summarizing the results of their semi-annual monitoring efforts (e.g. Metesh and Duaiame 2000, 2002; Duaiame and Metesh 2003).

Methods

Samples of mine shaft water are collected semi-annually by the MBMG. The majority of the samples have historically been collected using a point-source bailer (either steel or PVC) of roughly 5 L capacity, which is raised and lowered into the hole using a truck-mounted winch. Because the West Camp extraction well is continuously pumped to a treatment pond, samples of this water are simply collected at a spigot at the well head. Since about 2000, field parameters, including water temperature, pH, specific conductance (SC), oxidation-reduction potential (ORP), and dissolved oxygen, have been collected in the field using Hydrolab Datasonde multimeters. Chemical analyses are conducted by the MBMG

laboratory on samples previously filtered in the field to 0.45 μm . A routine analysis includes major and trace metals by ICP-AES, anions by ion chromatography (IC), and alkalinity by potentiometric titration. Although the laboratory also takes pH measurements, we have chosen to use the field pH values in this paper. Non-preserved samples of Butte mine waters often show changes in pH over a period of hours to days after collection, due either to oxidation of ferrous iron (with precipitation of hydrous ferric oxide and drop in pH), or exsolution of dissolved CO_2 gas (with a rise in pH).

Previous work by the MBMG has shown that some of the flooded mine shafts display vertical gradients in chemistry and temperature, whereas others have relatively minor changes with depth (Metesh and Duaiame 2002). Some mines have a thermocline and/or chemocline in the top 20 m of pooled water, which is probably due to tumbling of surface water or shallow ground water into the shaft (Metesh 2004). Figure 2 shows some example data from the Anselmo shaft. However, no detailed characterizations of vertical gradients in the mines have been attempted to date. For the sake of consistency, the majority of the mine shaft

samples have been collected from a depth of about 30 m below static water level, which is well below the location of the seasonal thermocline for the shafts that have been profiled.

General Geochemical Trends

Table 1 gives the chemical composition of 14 mine waters from the underground mine complex of Butte. This list includes most of the monitoring stations in the flooded mines where both water level and water quality information have been collected by the MBMG. With the exception of the Lexington mine, all of the samples were collected in the period 2000-2006, and each data point represents the average of all samples analyzed during this period. As seen in Table 1, the mine shaft waters vary considerably in chemical composition, depending on their location within the district. Although none of the mine shaft waters has a pH anywhere near as low as the Berkeley pit lake, many of the shafts nonetheless have extremely high total dissolved metal concentrations. By far, the worst water from a pH or toxic metals point of view is in the Kelley Mine (pH 4.6, 7700 mg/L SO_4 , 1770 mg/L Fe, 313 mg/L Zn, 186 mg/L Mn, 9.6 mg/L As). There are three possible reasons why this particular shaft should have an anomalous chemistry: 1) the Kelley Shaft was the location of large dewatering pumps that allowed mining to continue in the Berkeley Open Pit and subjacent underground workings; 2) between 1953 and 1962, the Anaconda Mining Company conducted underground block caving of the Cu-rich ore body in the Kelley Mine, a method that created enormous subterranean voids; and 3) the workings of the Kelley mine extend into what is now the Berkeley pit and into the area beneath the leach pads. Because of the first two points, the Kelley workings have had the greatest opportunity for ingress of air and subsequent oxidation of pyrite of any of the flooded mines. With respect to the third point, evidence presented in the companion paper by Metesh (2006) shows that the Kelley mine workings historically received a large amount of acidic water from decommissioned leach pad operations and nearby acidic springs that were dumped into the Berkeley Pit. During the first two years of mine flooding, hydraulic gradients were such that water pooling at the bottom of the pit infiltrated into the ground and outward into the underlying mine workings.

Overall, the mine waters show trends of decreasing metal concentration with increasing pH (Figure 3). Unlike the Berkeley pit lake, which contains a high concentration of both ferrous and ferric iron (Gammons and Duaiame 2006; Pellicori et al. 2005), dissolved iron in the mine shaft waters is mainly present in the

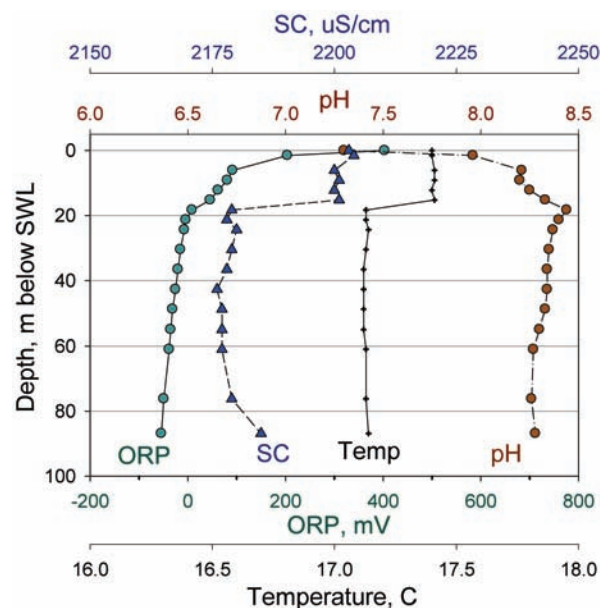


Figure 2. Vertical gradients in field parameters in the top 100 m of the flooded Anselmo Shaft, collected in July, 2000. Data are from Metesh and Duaiame (2002). The data show discontinuities in all parameters at a depth of 19 m below static water level (SWL). ORP = oxidation-reduction potential. Field ORP values were manually corrected from $E_{\text{Ag-AgCl}}$ to E_{SHE} (the standard hydrogen electrode) by adding +200 mV, which is the approximate potential of the Ag-AgCl reference cell used for the platinum ORP electrode (Nordstrom and Wilde 2005).

ferrous oxidation state (Pellicori et al. 2005). Likewise, dissolved arsenic is most likely present in its reduced As(+3) form (Roesler 2005) as the uncharged H_3AsO_3 species. The Butte mineral deposits were rich in As-bearing minerals such as enargite and tennantite-tetrahedrite. As well, many of the timbers used to support the underground mine workings were treated with arsenic trioxide (a by-product of smelting) as a preservative.

Factors Controlling Metal Mobility

The high grade veins of the Butte District are zoned with respect to their metal ratios and mineralogical composition, and this zonation has also imparted an important control on the geochemistry of the mine waters (Metesh 2004). The majority of the mines in the East Camp were mined primarily for Cu and Zn, although very substantial quantities of Pb and Ag were also locally recovered. In contrast, the mines of the West Camp and Outer Camp were mainly mined for Mn and Ag, with by-product Zn, Cu and Pb. The style of hydrothermal alteration is also strongly zoned, with intense phyllic and advanced argillic alteration in the central portion of the East Camp (near the Berkeley Pit), grading outward to weaker

Table 1. Chemical compositions of mine shaft waters in Butte. All data were taken from GWIC (2006), and represent the average of all samples collected during 2000–2006, with the exception of the Granite Mtn samples, which were collected during the 1990s. *SD* = standard deviation; *n* = number of samples; *ND* = not determined.

	Temp °C	pH SU	Eh mV, SHE	SC mS/cm	Ca mg/L	Mg mg/L	Na mg/L	K mg/L	Fe mg/L	Mn mg/L
East Camp										
Anselmo	16.0	6.49	+286	2.07	342	92	47	12.8	35.4	17.9
<i>SD (n = 10)</i>	(1.8)	(0.8)	<i>ND</i>	(0.21)	(27)	(17)	(6)	(1.2)	(13.2)	(6.0)
Belmont	13.4	6.85	+196	1.23	182	46	34	7.5	8.30	3.5
<i>SD (n = 3)</i>	(2.3)	(0.47)	<i>ND</i>	(0.02)	(11)	(2)	(4)	(0.51)	(0.37)	(13.3)
Granite Mtn	17.4	5.29	<i>ND</i>	3.19	551	206	33	23.6	72.5	66.3
<i>SD (n = 2)</i>	(0.0)	(0.0)	<i>ND</i>	(0.0)	(14)	(4)	(1)	(1.0)	(6.4)	(0.7)
Kelley	31.3	4.61	+244	6.80	491	395	83	62.9	1770	186
<i>SD (n = 9)</i>	(4.2)	(0.3)	<i>ND</i>	(1.63)	(15)	(109)	(21)	(12.9)	(680)	(61)
Steward	21.2	5.97	+350	3.14	491	153	44	31.7	249	30.5
<i>SD (n = 8)</i>	(3.1)	(0.5)	<i>ND</i>	(565)	(74)	(34)	(7)	(8.1)	(51)	(8)
Lexington	15.6	5.76	<i>ND</i>	2.58	347	104	49	6.6	22.1	107
<i>SD (n = 9)</i>	(1.0)	(0.58)	<i>ND</i>	(0.38)	(8)	(3)	(2)	(0.5)	(9)	(10)
Pilot Butte	19.3	5.70	+252	3.73	502	253	40	16.2	69.9	287
<i>SD (n = 2)</i>	(2.5)	(0.30)	<i>ND</i>	(0.56)	(18)	(26)	(3)	(0.8)	(29)	(146)
West Camp										
Travona	13.1	7.18	+65	1.25	176	47	41	5.7	1.83	5.5
<i>SD (n = 6)</i>	(0.4)	(0.30)	<i>ND</i>	(0.05)	(5)	(1)	(5)	(0.1)	(0.15)	(0.2)
Ophir	10.9	6.79	+345	0.88	112	31	25	4.6	1.54	11.7
<i>SD (n = 4)</i>	(0.3)	(0.8)	<i>ND</i>	(0.08)	(9)	(3)	(1)	(0.3)	(1.3)	(2.8)
Emma	16.3	6.84	+224	1.46	197	58	39	7.5	1.37	20.8
<i>SD (n = 6)</i>	(0.6)	(0.3)	<i>ND</i>	(0.10)	(5)	(2)	(2)	(0.7)	(1.4)	(8.8)
Pumping Well	11.8	7.18	+151	1.22	162	47	42	5.6	1.13	9.3
<i>SD (n = 9)</i>	(0.3)	(0.44)	<i>ND</i>	(0.02)	(10)	(2)	(4)	(0.5)	(0.1)	(13.8)
Outer Camp										
Orphan Boy	25.8	6.74	-49	1.64	227	61	126	10.5	0.1	4.8
<i>SD (n = 2)</i>	(0.9)	(0.11)	<i>ND</i>	(0.03)	(6)	(1)	(6)	(1.2)	<i>ND</i>	(0.3)
Orphan Girl	26.4	6.80	+75	1.63	217	59	117	10.2	0.2	4.4
(<i>n = 1</i>)	<i>ND</i>	<i>ND</i>	<i>ND</i>	<i>ND</i>	<i>ND</i>	<i>ND</i>	<i>ND</i>	<i>ND</i>	<i>ND</i>	<i>ND</i>
Marget Ann	10.2	6.87	-3	0.83	134	24	13	4.3	0.2	1.6
<i>SD (n = 4)</i>	(1.6)	(0.69)	<i>ND</i>	(0.06)	(19)	(1)	(1)	(1)	(0.1)	(0.4)
	SiO ₂	HCO ₃	SO ₄	Cl	Al	As	Cd	Cu	U	Zn
East Camp										
Anselmo	22	315	1124	34	50	155	9	8	23	12300
<i>SD (n = 10)</i>	(2)	(57)	(134)	(2)	(71)	(94)	(11)	(6)	<i>ND</i>	(9000)
Belmont	21	142	590	18	< 23	354	1	4	4	2790
<i>SD (n = 3)</i>	(1)	(42)	(11)	(2)	<i>ND</i>	(34)	<i>ND</i>	(2)	<i>ND</i>	(8)
Granite Mtn	26	<i>ND</i>	2390	12	192	7	9	189	<i>ND</i>	23600
<i>SD (n = 2)</i>	<i>ND</i>	<i>ND</i>	(35)	<i>ND</i>	(3)	(3)	(0.3)	(1)	<i>ND</i>	(424)
Kelley	78	<i>ND</i>	7740	25	34100	9610	36	47	8	313000
<i>SD (n = 9)</i>	(13)	<i>ND</i>	(2300)	(15)	(15900)	(4940)	(20)	<i>ND</i>	<i>ND</i>	(78400)
Steward	42	156	2320	38	691	2650	18	68	6	68900
<i>SD (n = 8)</i>	(10)	(106)	(570)	(3)	(307)	(1520)	(19)	(55)	<i>ND</i>	(25200)
Lexington	20	243	1570	40	< 37	140	116	8	<i>ND</i>	144000
<i>SD (n = 9)</i>	(2)	(37)	(50)	(1.1)	<i>ND</i>	(79)	(109)	(5)	<i>ND</i>	(17600)
Pilot Butte	35	35	3030	13	442	365	< 2	55	8	55900
<i>SD (n = 2)</i>	(4)	(49)	(510)	(7)	(349)	(162)	<i>ND</i>	(34)	<i>ND</i>	(33800)
West Camp										
Travona	18	342	401	37	41	114	< 2	< 3	16	8
<i>SD (n = 10)</i>	(1)	(24)	(20)	(8)	(58)	(14)	<i>ND</i>	<i>ND</i>	<i>ND</i>	(5)
Ophir	18	242	235	35	< 25	7	3	3	17	729
<i>SD (n = 4)</i>	(3)	(24)	(39)	(8)	<i>ND</i>	(6)	(2)	(2)	<i>ND</i>	(795)
Emma	19	417	512	41	< 26	17	39	14	23	16600
<i>SD (n = 6)</i>	(2)	(41)	(76)	(2)	<i>ND</i>	(10)	(34)	(18)	<i>ND</i>	(14300)
Pumping Well	17	342	396	41	< 28	109	< 2	2	25	11

<i>SD</i> (<i>n</i> = 9)	(1)	(10)	(11)	(1)	<i>ND</i>	(8)	<i>ND</i>	(1)	<i>ND</i>	(8)
					Outer Camp					
Orphan Boy	29	954	282	15	<25	7	<2	<3	62	14
<i>SD</i> (<i>n</i> = 2)	(3)	(32)	(3)	(0.1)	<i>ND</i>	(0.4)	<i>ND</i>	<i>ND</i>	<i>ND</i>	<i>ND</i>
Orphan Girl	25	780	303	17	<30	47	<1	<5	34	10
(<i>n</i> = 1)	<i>ND</i>	<i>ND</i>	<i>ND</i>	<i>ND</i>	<i>ND</i>	<i>ND</i>	<i>ND</i>	<i>ND</i>	<i>ND</i>	<i>ND</i>
Marget Ann	7.7	204	281	18	<25	2	<1	<3	13	3.0
<i>SD</i> (<i>n</i> = 4)	(2.1)	(36)	(36)	(1)	<i>ND</i>	<i>ND</i>	<i>ND</i>	<i>ND</i>	<i>ND</i>	(0.5)

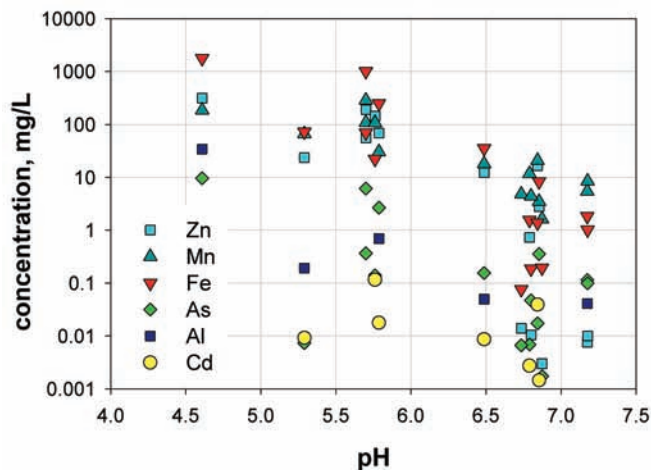


Figure 3. Relationship between pH and the dissolved concentration of Zn, Mn, Fe, and As; each data point represents the average of all samples collected at a given location during the period 2000 to 2006.

phyllitic and argillic alteration in the outer veins. Carbonate minerals such as calcite and rhodochrosite are absent in the center of the district, but become abundant as vein-forming minerals with distance outwards towards the peripheral zones.

Following this general pattern, the mine waters from the West Camp and Outer Camp, as well as the outer margin of the East Camp, all have near-neutral pH, elevated bicarbonate concentration, and relatively low metal concentrations. In contrast, mine waters closer to the Berkeley Pit have lower pH and higher metal concentrations.

Although a detailed discussion of mineral solubility controls on mine water chemistry is beyond the scope of this paper, a few generalities can be made. Most of the mine shaft water samples with sulfate concentrations greater than about 1000 mg/L are close to saturation with gypsum (Pellicori et al. 2005). Anhydrite (CaSO_4) was an abundant mineral in the early porphyry-style mineralization in the Butte District (Field et al. 2004), and as such is a likely source for much of the Ca and sulfate dissolved in the water.

However, an examination of the trends in Figure 4 shows that most of the waters with high sulfate concentrations have Ca: SO_4 ratios significantly less

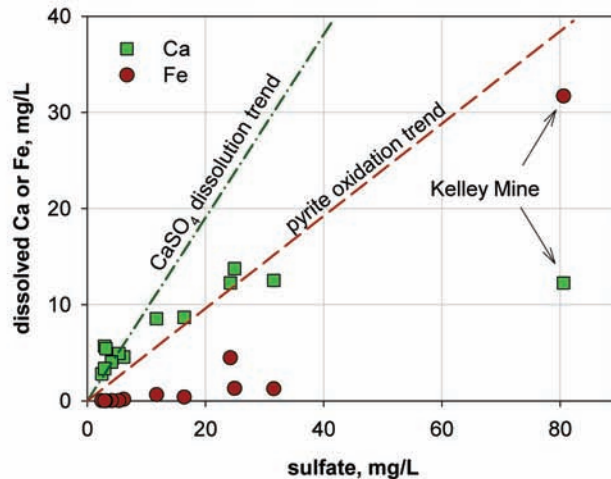


Figure 4. Relationships between the concentrations of dissolved Ca, Fe, and sulfate; as discussed in the text, Ca derived entirely from dissolution of gypsum or anhydrite would plot on the green (1:1) line, and Fe derived entirely from oxidation of pyrite would plot on the red (1:2) line. Each data point represents the average of all samples at a given location collected during the period 2000-2006.

than 1:1, indicating inputs of sulfate from sources other than gypsum or anhydrite dissolution. An obvious additional source of sulfate is the oxidation of pyrite and other sulfide minerals. The dashed line with slope 1: 2 in Figure 4 corresponds to the theoretical trend that would be expected between dissolved Fe and sulfate, if all of the sulfate was derived from pyrite oxidation. As shown, only the Kelley Mine plots close to the 1:2 line for Fe: SO_4 , which implies that most of the sulfate in this shaft most likely came from pyrite oxidation. Supporting this, Pellicori et al. (2005) presented stable isotopic evidence that aqueous sulfate in the underground mine waters of Butte is a mixture of sulfate with $\delta^{34}\text{S}$ of +1 to 3‰ from pyrite oxidation and sulfate with $\delta^{34}\text{S}$ of +10 to +18 ‰ from dissolution of hydrothermal anhydrite.

Several of the mine waters with high bicarbonate concentration are close to equilibrium with one or more carbonate minerals, including siderite, calcite, amorphous ZnCO_3 , and rhodochrosite (Gammons et al. 2003; Pellicori et al. 2005). In addition, several mine waters from the outer portions of the mine workings are sufficiently reducing to stabilize dissolved hydrogen sulfide at levels ranging from a few hundred $\mu\text{g/L}$ to

about 10 mg/L (data not shown in Table 1). These include the Marget Ann, Orphan Boy, and Orphan Girl mines from the Outer Camp, and the Travona and Ophir Shafts, as well as the ground water extraction well that drains the West Camp (Gammons et al. 2003; Roesler 2005). Although field ORP measurements from these shaft samples (Table 1) are seemingly too high to stabilize hydrogen sulfide, this compound is undeniably present based on the strong odor of the waters, and also by direct colorimetric analysis of dissolved sulfide using the Methylene Blue method (Gammons et al. 2003; Roesler 2005). It is known that field ORP measurements often give redox potential readings (Eh) that are inconsistent with theoretical Eh values calculated by independent measurement of SO_4^{2-} and H_2S (Langmuir 1997; Lindberg and Runnells 1984).

The sulfidic waters of the West and Outer Camps are characterized by a near-neutral pH, high bicarbonate alkalinity, and extremely low concentrations of heavy metals (such as Zn and Cu) that form insoluble sulfide minerals. Stable isotope work by Gammons et al. (2003) and Roesler (2005) has shown that the H_2S in the outer mine workings formed by bacterial sulfate reduction. It is not known what organic substrate the bacteria are using as an electron donor, although organic compounds derived from the decomposition of wood used to support the underground workings are a likely source. Based on unpublished Anaconda records, over 60 million board-feet (> 15 million meters) of timber went into the underground operations *annually*. Wood-framed mine stopes in the still-accessible Lexington Tunnel are in variable states of decay (see Figure 2F of Gammons 2006). Interestingly, concentrations of dissolved uranium are somewhat elevated in the sulfidic waters (>10 $\mu\text{g/L}$) compared to the East Camp waters (all <10 $\mu\text{g/L}$, with the exception of the Anselmo mine). This is somewhat surprising, considering the low solubility of uraninite under reducing conditions (Langmuir 1997).

Miscellaneous Observations

A few observations are deemed of sufficient interest to include at the end of this brief overview paper. First, considering the vast quantity of Cu and Pb produced from the Butte mines, it is somewhat surprising that dissolved concentrations of these two metals are so low. Dissolved Pb concentrations are typically below the method detection limit of 2 to 20 $\mu\text{g/L}$ (the detection limit varies with the dilution factor required prior to ICP analysis). The low Pb levels may be partly explained by the low solubility of anglesite (PbSO_4), especially for the more sulfate-rich waters, or galena (PbS) in the sulfidic waters of

the West Camp. However, it is also known that Pb^{2+} adsorbs more strongly than other divalent metal cations onto hydrous ferric oxide and jarosite (e.g. Stumm 1992), both of which are probably present in abundance as secondary minerals in the formerly oxidized but now submerged mine walls of the East Camp mine workings. The concentrations of dissolved Cu in the East Camp mine waters are also surprisingly low. Again, this may be partly due to adsorption of Cu^{2+} or Cu^+ onto secondary Fe minerals. However, we also speculate that some of the dissolved Cu may have been stripped from solution by precipitation of metallic Cu, or by conversion of pyrite to Cu-sulfide (covellite or chalcocite), in a manner similar to that which occurs during supergene enrichment of porphyry copper ore bodies (Brimhall et al. 1985; Sillitoe 2005). Although neither covellite nor chalcocite are stable at the Eh and pH conditions of the East Camp mine waters, it is conceivable that micro-environments of low redox potential exist on the submerged pyrite surfaces that are sufficient to form Cu-sulfide coatings on the underlying pyrite. Further experimental work is needed to confirm this hypothesis.

Figure 5 shows an intriguing inverse relationship between water temperature and pH in the underground mine complex. Based on the results of semi-annual sampling by the MBMG, the temperature of water in the mine shafts below a depth of 30 m does not vary with the time of year. Therefore, the apparent correlation between pH and temperature ($r^2 = 0.76$, excluding samples from the Orphan Boy and Orphan Girl shafts) requires some explanation.

One possibility is that there is one or more sources of geothermal heat in the flooded mine complex, centered near the Kelley Mine and the Orphan Boy/Orphan Girl workings. However, a second and possibly more intriguing possibility is that the warmer water temperatures are due to exothermic microbiological reactions. In the case of the Kelley Mine, the lower pH waters are influenced by pyrite oxidation, a reaction that is strongly exothermic and that is known to significantly raise the temperature of sulfide-rich waste rock or tailings piles undergoing microbially-catalyzed oxidation. It is possible that pyrite oxidation is continuing in the submerged, anoxic portions of the Kelley Mine via dissolved ferric iron. Although Fe(III) concentrations in the Kelley shaft are below the quantifiable limit (Pellicori et al. 2005), the detection limit for the Ferrozine method is rather high (well over 1 mg/L) when a large excess of Fe(II) exists, as is the case for the Kelley water. The dissolved Fe(III) present in these mildly acidic waters may be low compared to Fe(II), but nonetheless high enough to induce pyrite oxidation.

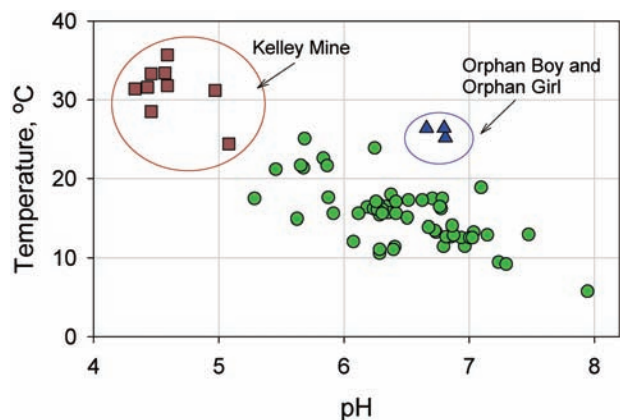


Figure 5. Relationship between water temperature and field pH for all mine shaft samples in GWIC (2006) collected during the period 2000 to 2006. All of the measurements were collected at a similar depth of roughly 30 m below the static water level.

Once consumed, the supply of dissolved Fe(III) could be replenished by dissolution of secondary Fe minerals on the mine walls, such as jarosite or ferrihydrite.

The cause of the elevated temperatures in the Orphan Boy and Orphan Girl mine shafts is less clear. However, these two mine shafts have the highest concentration of dissolved sulfide that have yet been measured anywhere in the Butte District (up to 10 mg/L in the Orphan Boy), and so it is conceivable that the warmer temperatures are in some way related to bacterial sulfate reduction or other anaerobic microbial reactions, such as fermentation. Additional data on vertical gradients in temperature within the mine shafts are needed to discriminate between the above hypotheses. This research is in progress, but it is too early to report results at this time.

A final observation: despite the fact that ground water discharged from the flooded underground mine workings is believed to account for as much as half of the total water volume in the Berkeley pit lake, the water quality of the mine shafts is generally much more benign than that of the pit lake. This has led previous workers (Gammons and Duaiame 2006; Madison et al. 2003; Pellicori et al. 2005) to conclude that much of the acidity, dissolved metals, and sulfate in the Berkeley pit lake were derived by in-situ processes, such as leaching of secondary minerals from weathered mine walls, or by sub-aqueous oxidation of pyrite and other sulfide minerals by dissolved ferric iron. Although compelling, these hypotheses are by no means proven, and await further field and laboratory research on the hydrology and geochemistry of the Butte mine waters.

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