Mine Water and the Environment (2003) 22: 141–148 © IMWA Springer-Verlag 2003

Technical Article

Geochemistry and Isotopic Composition of H_2S-rich Water in Flooded Underground Mine Workings, Butte, Montana, USA

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Abstract. Groundwater being pumped from the flooded West Camp mine workings of Butte, Montana, is elevated in hydrogen sulfide (H_2S), has a circum-neutral pH, and has high arsenic but otherwise low metal concentrations. The daily flux of H_2S and As pumped from the extraction well are each estimated at roughly 0.1 kg. Isotopic analysis of coexisting aqueous sulfide and sulfate confirms that the H_2S was produced by bacterial sulfate reduction. The mine waters are close to equilibrium saturation with amorphous FeS, amorphous ZnS, siderite, rhodochrosite, calcite, and goethite, but are undersaturated with orpiment (As_2S_3). The higher solubility of orpiment relative to other metal sulfides allows concentrations of dissolved arsenic (~ 100 µg/L) that are well above human health standards. The West Camp waters differ markedly from the acidic and heavy metal-rich mine waters of the nearby Berkeley pit-lake. These differences are partly attributed to geology, and partly to mining history.

Key words: Arsenic; bacterial sulfate reduction; Butte, Montana; geochemistry; hydrogen sulfide; mine waters; sulfur isotopes

Introduction

Bacterial sulfate reduction (BSR) occurs in anaerobic environments where decaying organic matter and SO_4^{2-} are present, such as marine, estuary, or lake sediments, natural wetlands, or anoxic groundwater (Postgate 1994). In recent decades, engineered BSR systems, such as bioreactors and constructed wetlands, have emerged as viable technologies for the remediation of metal-contaminated waters related to mining activities (Wildeman et al. 1993; Cole 1998). The BSR reaction lowers sulfate concentrations, produces alkalinity (thereby raising pH), and also lowers the concentrations of many dissolved metals by precipitation of insoluble sulfide minerals. Despite the great interest in *artificial* BSR systems to treat mine drainage, there have been very few documented cases of sulfate-reducing bacteria establishing themselves naturally in a flooded mine environment. We are aware of only two references to this phenomenon (Hamlin and Alpers 1996; Druschel et al. 2002). In the more recent study, Druschel et al. report the formation of ZnS-rich biofilms dominated by sulfate-reducing bacteria in flooded mine workings of an abandoned carbonate-hosted Pb-Zn deposit in Wisconsin. This paper presents new chemical and stable isotopic evidence for BSR in flooded underground workings, and discusses the geochemistry of the sulfidic mine waters.

Site Background

The water samples investigated in this study were collected from the West Camp pumping well, an extraction well that drains flooded workings in the southwest portion of the Butte mining district, Montana (Figure 1). Butte is better known amongst environmental scientists for the Berkeley Pit, an open pit copper mine flooded with over 100 billion L of highly acidic and metal-rich mine water. Whereas the geochemistry of this pit lake has been the focus of numerous investigations (Davis and Ashenberg 1989; Robins et al. 1997; Jonas 2000; Newbrough and Gammons 2002; Gammons et al. 2003; Madison et al. 2003), relatively little attention has been paid to the West Camp groundwater system. The results of a pumping test of the Travona Mine shaft, as well as recent reviews of the history of mine flooding and water quality monitoring in the Butte district, are available through the Montana Bureau of Mines and Geology (MBMG) (Duaime et al. 1989, 1998; Metesh and Duaime 2000) and at www.pitwatch.org.

The world class mineral deposits of Butte have been mined nearly continuously since the 1860s, and have produced over $9x10^9$, $2.2x10^9$, $3.8x10^8$, $2.2x10^7$ and $1.2x10^5$ kg of copper, zinc, lead, silver, and gold, respectively (Miller 1973). Most of the early mine workings were underground, and it is estimated that the city of Butte in underlain by more than 10,000 km of interconnected shafts, tunnels, and stopes, spread over a surface area of > 10 km^2 (Duaime et al. 1995). The Anaconda Company began open-pit mining in

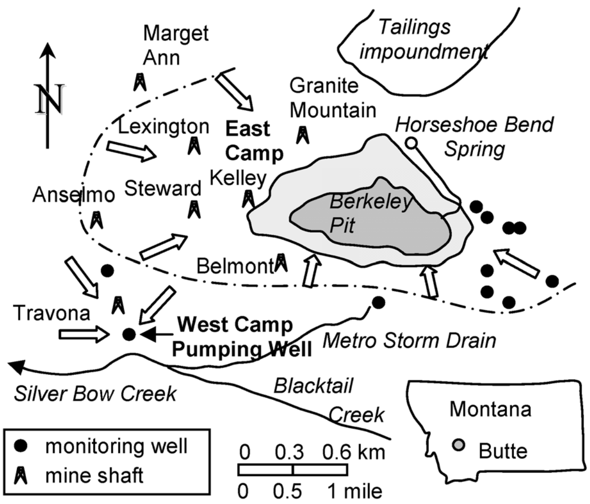

Figure 1. Map of Butte, showing the location of the West Camp pumping well, the Berkeley Pit, and selected mine shafts and bedrock monitoring wells. The dashed curve shows the approximate location of the groundwater divide between the West Camp and East Camp flooded mine workings.

the Berkeley Pit in 1955. In the late 1950's and early 1960's, concrete bulkheads were installed to isolate active vs. inactive portions of the underground mines, thereby reducing the volume of mine openings that required ventilation and groundwater pumping. The Travona, Emma, and Ophir Mines, primarily manganese producers, were isolated from the rest; collectively, these mines and their workings are referred to as the West Camp System.

Once the West Camp System was isolated from the remainder of the mines on Butte Hill, water levels began to rise to the point where surface seeps and flooding basements occurred (Duaime et al. 1998). To alleviate these problems, the Anaconda Company drilled a well into the 800 ft (244 m) level of the Travona Mine. A 28-day pumping test was conducted (Duaime et al. 1989) to test the feasibility of controlling the rate of flooding in the West Camp, and to help with the design of treatment options. Pumping began in 1989, and continues to the present day at an approximate rate of 12.6 L/sec (200 gpm). Water pumped from the West Camp is currently sent to the Butte-Metro sewage treatment plant, prior to discharge to Silver Bow Creek. The groundwater is pre-treated aerobically to co-precipitate arsenic and Fe-oxide, and also to reduce H_2S concentrations. To date, over 3 billion L of water has been pumped and treated from the West Camp System.

Methods

Groundwater from the West Camp extraction well was sampled in 2000 on Sept 28, Oct 26, Nov 13, Dec 20, and in 2001 on June 21. Because this well is continuously pumped, it was not necessary to purge the well casing. Instead, a sample was collected directly from a spigot at the wellhead. A complete set of field parameters (temperature, pH, SC, Eh, turbidity, alkalinity) was collected on Sept 28, 2000, using freshly calibrated and temperature-compensated electrodes. Also on this date, 2 x 250mL filtered (0.45 µm) samples were collected for analysis of a complete suite of major and trace elements, at the analytical laboratory of the MBMG. Equipment used in these analyses included a TJA Iris Advantage ICP-AES, a Perkin-Elmer SCIEX Elan 5000 ICP-MS, and two Dionex ion chromatographs (DX-100 and -300).

On Sept 28, 2000, the concentration of total dissolved sulfide ($H_2S + HS^-$) was determined in the laboratory on a filtered sample 30 minutes after collection, using a HACH Model 2100 portable spectrophotometer. Readings conducted over the next hour showed a slow and steady decline in concentration, from a high of 0.116 to a low of 0.075 mg/L total dissolved sulfide. Clearly, some loss of H_2S occurred after sampling, due to oxidation and/or volatilization. On Nov 13, 2000, the sulfide analysis was repeated on-site, immediately after sampling. A total dissolved sulfide concentration of 0.249 mg/L was obtained. Both of these readings may be slightly low, due to the possibility of loss of H_2S in the well bore. During all visits, the water being sampled was effervescing slightly. The identity of the exsolved gas is not known, but is speculated to be a mixture of N_2 and CO_2. Although the computed partial pressure of H_2S for the West Camp groundwater is many log units below saturation, it is possible that some H_2S could partition into the gas bubbles evolved during pumping of the deep water to the surface. For this reason, the H_2S measurements obtained in this study should be considered minimum estimates of the true groundwater conditions.

Stable isotope analyses

Groundwater samples from the West Camp extraction well were collected for analysis of $\delta^{34}S_{sulfide}$ and $\delta^{34}S_{sulfate}$ on Oct 26 and Nov 13, 2000, for $\delta^{34}S_{sulfate}$ and $\delta^{18}O_{sulfate}$ on Dec 20, 2000, and for δD_{water} and $\delta^{18}O_{water}$ on June 21, 2001. Sample preparation for stable isotope analysis of sulfide and sulfate followed established procedures (Carmody et al. 1998). Dissolved sulfide ($H_2S + HS^-$) was extracted by direct and immediate addition of $AgNO_3$ solution to a sample of filtered West Camp water. A black colloidal suspension of Ag_2S formed within 2 minutes. After 10 minutes, this precipitate was filtered with a peristaltic pump through a 0.45 µm filter membrane. The precipitate on the membrane was recovered, rinsed several times with 18 mΩ water and centrifuged, and then dried at 40°C. Dissolved sulfate was extracted by addition of $BaCl_2$, after adjusting the pH of the water samples to 3 with HCl (to avoid precipitation of $BaCO_3$). The white $BaSO_4$ precipitate was centrifuged and rinsed several times with 18 mΩ water, and dried at 40°C. No preparation was necessary for analysis of δD and $\delta^{18}O$ of water, other than field filtering to 0.45 µm.

Stable isotope analyses were performed using a Eurovector elemental analyzer interfaced to a Micromass IsoPrime stable isotope ratio mass spectrometer. Sulfur isotope analyses were performed using a method similar to that of Giesemann et al. (1994), with the modification that V_2O_5 was added to $BaSO_4$ samples as a combustion aid. Oxygen isotope analyses of sulfate followed a method similar to that of Kornexl et al. (1999), with the modifications that the analyses were performed at 1300°C, and that nickelized graphite was added to BaSO4 samples as a pyrolysis aid. Oxygen isotope analyses of water samples were performed using the CO_2-H_2O equilibration method (Epstein et al. 1953). Hydrogen isotope analyses of water followed the procedure of Morrison et al. (2001). Stable isotope values are reported in the usual δ notation in units of ‰, vs. VCDT for sulfur and vs. VSMOW for oxygen and hydrogen. Analytical uncertainties are ±0.2‰ for $\delta^{34}S_{sulfide}$ and $\delta^{34}S_{sulfate}$, ±0.4‰ for $\delta^{18}O_{sulfate}$, ±0.1‰ for $\delta^{18}O_{water}$, and ±2‰ for δD_{water}.

Results and Discussion

Water chemistry

Table 1 gives a complete chemical analysis of water collected from the West Camp Pumping Well (GWIC ID #184133) on Sept 28, 2000. The West Camp groundwater is a Ca-HCO_3-SO_4 water, with moderately high TDS, but relatively low metal concentrations. Of the various solutes analyzed, only arsenic consistently exceeds current regulatory standards for human or aquatic health.

Based on long-term monitoring by the MBMG, the West Camp Pumping Well chemistry has changed very little with time. For the 7 samples collected in 2000 and 2001, the measured SC ranged from a low of 1186 to a high of 1238 µS/cm, a variation of only 4.2%. Most individual analytes likewise showed little variation. For example, As concentrations ranged between 109 and 115 µg/L, and Fe ranged from 1.15 to 1.24 mg/L. Although dissolved sulfide is not routinely monitored at the West Camp Pumping Well, the distinct odor of H_2S has been ubiquitous for years, and has necessitated an aerobic treatment circuit. It is probable that the H_2S concentration varies somewhat over time, in response to subtle variations in pH, H_2S partial pressure, or the rate of pumping (which in turn affects the degree of exsolution of gases in the well bore). Assuming typical total dissolved sulfide and arsenic concentrations of 0.1 mg/L, and a typical pumping rate of 12.6 L/sec, the flux of H_2S and As pumped out of the West Camp is each estimated to be roughly 0.1 kg/day.

Mineral Saturation Indices

Table 2 gives a summary of saturation indices for selected minerals and amorphous solids in the West Camp groundwater, calculated by MINTEQ (Allison et al. 1991), based on the analysis given in Table 1. Saturation indices for additional minerals were calculated using a separate spreadsheet (see footnotes to Table 2) in cases where thermodynamic data in MINTEQ were missing or suspect. The results show that West Camp groundwater is close to saturation with the carbonate minerals calcite, siderite, and rhodocrosite, the sulfate minerals gypsum and barite, and amorphous or chalcedonic SiO_2. These results are

Table 1. Chemical analysis, West Camp Pumping Well

Parameters Measured in the Field

T = 13.2°C
alkalinity = 270 mg/L, as $CaCO_3$
pH = 6.81
Σ dissolved sulfide = 0.093 mg/L
SC = 1296 µS/cm
turbidity = 0.78 NTU
Eh = +65 mV [a], -180mV [b]
flow rate ~ 760 L/min

Parameters Measured in the Laboratory

analyte	mg/L	analyte	µg/L
Ca	167	Ag	<
Mg	48.3	Al	< 30
Na	45.8	As	109
K	6.91	B	225
Fe	1.21	Ba	24.3
Mn	4.64	Be	< 2
SiO_2	17.9	Cd	< 2
H_2CO_3	88.2 [c]	Co	< 2
HCO_3^-	326 [c]	Cu	< 2
CO_3^{2-}	0.11 [c]	Li	34.7
SO_4	391	Ni	5.58
Cl	40.8	Pb	< 2
NO_3 - N	< 0.5	Sb	< 2
PO_4 - P	< 0.5	Se	< 12
H_2S	0.059 [d]	Sr	1790
HS^-	0.034 [d]	Zn	9.07

sum cations = 12.73 mmol/L, sum anions = 12.69 mmol/L, charge imbalance = 0.18%; [a] measured Eh (corrected to SHE); [b] calculated Eh (based on H_2S/SO_4^{2-}); [c] calculated from pH, temperature, and alkalinity, using MINTEQ; [d]calculated from pH, temperature, and total S^{2-}, using MINTEQ

Table 2. Saturation indices (S.I.) for selected solids in West Camp water

Carbonate Minerals		S.I.	Oxides/Hydroxides		S.I.
Calcite	$CaCO_3$	-0.27	Quartz	SiO_2	0.67
Siderite	$FeCO_3$	-0.56	Chalcedony	SiO_2	0.14
Rhodocrosite	$MnCO_3$	-0.03	SiO_2(Am)	SiO_2	-0.37
Magnesite	$MgCO_3$	-1.16	Goethite	FeOOH	4.54[b], 0.25[c]
Strontionite	$SrCO_3$	-1.68	Ferric Hydroxide	$Fe(OH)_3$	-1.35[b], -5.6[c]
Smithsonite	$ZnCO_3$	-5.79			
Hydrozincite	$Zn(CO_3)_{0.36}(OH)_{1.28}$	-7.12[a]	Sulfides		
Dolomite	$CaMg(CO_3)_2$	-0.94	FeS (Am)	FeS	-0.30
Ankerite	$CaFe(CO_3)_2$		Mackinawite	FeS	0.43
Witherite	$BaCO_3$	-4.38	ZnS (Am)	ZnS	0.24
			Sphalerite	ZnS	2.94
Sulfate Minerals			Wurtzite	ZnS	0.91
Gypsum	$CaSO_4{\cdot}2H_2O$	-0.59	Orpiment	As_2S_3	-2.03[d]
Barite	$BasO_4$	0.42	As_2S_3 (Am)	As_2S_3	-2.58[e]
Celestite	$SrSO_4$	-1.23	Millerite	NiS	0.83
Melanterite	$FeSO_4{\cdot}7H_2O$	-5.16	Alabandite	MnS	-7.62

All data were computed from the MINTEQ database except: [a] calculated from log K_{sp} = -14.42 (Mann and Deutscher 1980); [b] calculated using measured Eh and thermodynamic data in Drever (1997); [c] calculated using Eh estimated from SO_4^{2-}/H_2S couple; [d] calculated from solubility data of Webster (1990);[e] calculated from solubility data of Eary (1992); [f] based on chemical analysis of water sample collected on Sept. 28, 2000.

consistent with the abundance of calcite, rhodocrosite, and lesser amounts of barite in the mineralized veins of the West Camp (Meyer et al. 1968; Miller 1973). In addition, siderite, gypsum and amorphous silica are common by-products of the weathering of pyrite-rich ore deposits (Nordstrom and Alpers 1999).

Of the various sulfides investigated, West Camp waters are closest to equilibrium saturation with amorphous FeS, amorphous ZnS, and millerite (NiS). At the pH and total dissolved sulfide concentrations measured, the predicted solubility of simple sulfides of Ag(I), Cu(I), Cu(II), Pb(II) and Cd(II) are all below the analytical detection limits, which is consistent with the information in Table 1. In contrast, orpiment, amorphous As_2S_3, and alabandite (MnS) are calculated to be significantly under-saturated in the West Camp waters. It is possible that the mobility of dissolved arsenic (assumed to be trivalent H_3AsO_3) is limited by co-precipitation or adsorption onto amorphous FeS or ZnS (Rittle et al. 1995). Although Mn^{2+} can also partition into freshly formed ZnS particles (Gammons and Frandsen 2001), manganese concentrations appear instead to be buffered by rhodocrosite ($MnCO_3$).

Based on the measured Eh value (+65mV), West Camp waters are calculated to be supersaturated with respect to goethite, but undersaturated with respect to ferric hydroxide. However, it is very common for natural waters to give field Eh measurements that are in apparent disequilibrium with respect to different redox couples (e.g., Fe^{2+}/Fe^{3+} vs. SO_4^{2-}/H_2S) (Lindberg and Runnells 1984; Langmuir 1997). Using thermodynamic data in Drever (1997), an Eh of –180mV was calculated for the West Camp waters, based on the measured concentrations of sulfate and sulfide listed in Table 1. If this lower Eh value is used, West Camp water is found to be very close to equilibrium saturation with goethite (SI = +0.25), as well as siderite and amorphous FeS. It is probable that the co-existence of these three Fe-rich phases is exerting a major effect on buffering the chemistry of the mine waters. At an Eh of –180 mV, essentially all dissolved arsenic is predicted to be in the arsenite (+III) valence. Although arsenic was not speciated in this study, As(III)/As(V) results collected during the pumping test of 1989 (Duaime et al. 1989) did indicate a predominance of As(III) over As(V).

Stable isotopes

The results of stable isotope analysis of West Camp water are summarized in Table 3. Dissolved sulfide from the pumping well is isotopically very light, with $\delta^{34}S$ falling in a narrow range of –32.4 to –35.1‰. In contrast, the $\delta^{34}S$ of coexisting dissolved sulfate ranges from +4.4 to +9.5‰. The resultant values of $\Delta^{34}S_{SO4-H2S}$ fall between +41.9 and +44.6‰. Such large values of $\Delta^{34}S_{SO4-H2S}$ are consistent with sulfur isotope fractionation associated with bacterial sulfate reduction (Canfield 2001), and are compelling evidence that the H_2S in the flooded West Camp mine workings is of biological origin. This also refutes the hypothesis that H_2S could have been generated

Table 3. Stable isotope results

sample date	$\delta^{34}S_{H2S}$	$\delta^{34}S_{SO4}$	$\Delta_{SO4-H2S}$	$\delta^{18}O_{SO4}$	$\delta^{18}O_{W}$	δD_{W}
West Camp Pumping Well						
10-26-00, A	-32.8‰	-	-	-	-	-
10-26-00, B	-32.4‰	+9.5‰	41.9‰	-	-	-
11-13-00	-35.1‰	+9.5‰	44.6‰	-	-	-
12-20-00	-	+4.4‰	-	-6.9‰	-	-
6-21-01	-	-	-	-	-17.5‰	-136‰
pyrite from Travona Mine drill core	+4.8‰	-	-	-	-	-

abiotically by dissolution of hypogene (hydrothermal) pyrite or other primary metal sulfide minerals under anaerobic, initially acidic conditions, as this process would produce H_2S with an isotopic composition very similar to the value for hydrothermal pyrite $\delta^{34}S$ of 0 to +5‰ (see below).

Oxidation of sulfide minerals, whether or not it is assisted by microbes, typically results in small or negligible fractionation of S isotopes (Field 1966; Taylor et al. 1984a). As a consequence, S in sulfate from mine drainage is usually isotopically similar to S in pyrite from the original ore deposit (Taylor and Wheeler 1994). Lange and Cheney (1971) found that hydrothermal pyrite in the Butte district is isotopically zoned, with $\delta^{34}S$ values averaging +0.7‰ in the Central Zone (which includes the Berkeley Pit), increasing outwards to an average of +3.6‰ in the Peripheral Zone (which includes the West Camp workings). A single pyrite specimen from the Travona Mine (Peripheral Zone) analyzed in this study gave $\delta^{34}S$ = +4.8‰ (Table 3), consistent with the trend of slightly heavier pyrite with distance from the Berkeley Pit. The $\delta^{34}S$ composition of dissolved sulfate in the West Camp overlaps this range in $\delta^{34}S$, but extends to heavier values of +9.5‰. The heavier values could be explained by BSR, since sulfur isotope fractionation during BSR will result in residual sulfate that is isotopically heavy. However, mass balance calculations indicate that roughly 10% of the initial sulfate would need to be reduced to H_2S, assuming an example fractionation factor of 44‰, in order to raise the $\delta^{34}S_{sulfate}$ from +4.8 to +9.5‰. For this hypothesis to be true, there must be a tremendous sink for H_2S in the flooded mine workings, since the molal concentration of total dissolved sulfide measured at the well head was only 0.07% of the sulfate concentration. It is possible that H_2S is being lost to precipitation of metal sulfides from contaminated water, as well as sulfidation of secondary iron oxides and iron carbonates in the flooded mines. However, it is also possible that a component of the isotopically heavy sulfate comes from a different and as yet unidentified source (Wright and Nordstrom 1999), such as man-made materials in the mine workings (concrete, plaster, drilling mud, etc.), overlying alluvial sediment, or urban pollution.

Empirically, it has been shown that oxygen in sulfate from mine waters tends to be isotopically heavier than coexisting water (Taylor and Wheeler 1994). This may be due to incorporation of atmospheric O_2 ($\delta^{18}O$ = +23‰, Horibe et al. 1973) into the SO_4^{2-} molecule (Taylor et al. 1984b), although the processes involved are by no means straightforward (Van Stempvoort and Krouse 1994; Krouse and Mayer 2000). In any event, a single $\delta^{18}O$ analysis of –6.9‰ was obtained for dissolved sulfate from the West Camp pumping well, which compares with –17.5‰ for West Camp groundwater (Table 3). The 10.6‰ fractionation between $\delta^{18}O_{sulfate}$ and $\delta^{18}O_{water}$ is typical of mine waters from the Northern Rockies (Taylor and Wheeler 1994). Also, the $\delta^{18}O$ and δD results for West Camp water are typical of meteoric water in Montana.

Comparison of West Camp vs. other Butte mine waters

The geochemistry of groundwater in the flooded West Camp is completely different from that in the Berkeley pit lake (Figure 2). The pit waters are very acidic and moderately oxidized, while the groundwater in the West Camp is near-neutral and strongly reducing. As discussed previously, it is probable that the West Camp groundwater is buffered by the coexistence of goethite, siderite, and amorphous FeS. In contrast, Berkeley Pit water is buffered near the aqueous Fe(III)/Fe(II) boundary, and is closer to saturation with ferric hydroxy-sulfate minerals such as jarosite or schwertmannite (Robins et al. 1997; Gammons et al. 2003). Further differences in the chemistry of the Berkeley Pit and West Camp waters are shown in Figure 3. Compared to the Berkeley Pit water, West Camp water has lower concentrations for most of the elements analyzed, especially Al, Cd, Cu, Fe, Ni, Pb, and Zn. The only solutes that are more concentrated in West Camp water include inorganic carbon (as H_2CO_3 and HCO_3^-), Sr^{2+}, and chloride ion.

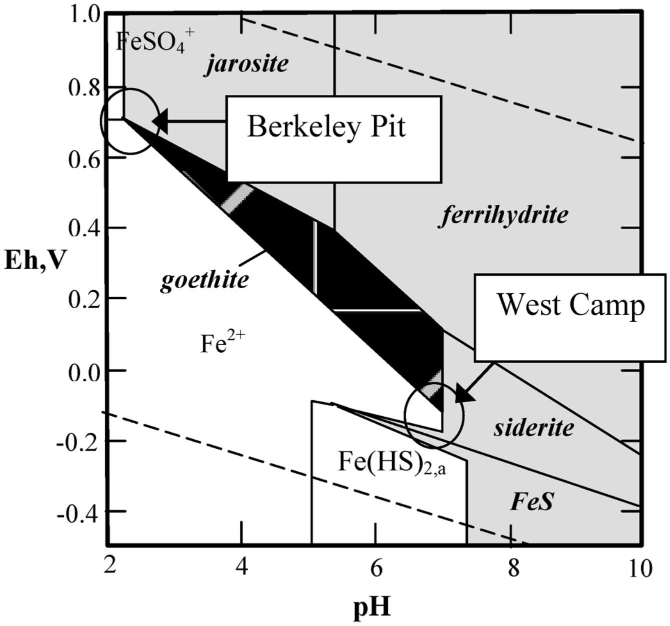

Figure 2. Eh-pH diagram showing the approximate conditions of West Camp and Berkeley Pit waters, for $\Sigma S = 4.1 \times 10^{-3}$ molal, $\Sigma Fe = 2.2 \times 10^{-5}$ molal, and $\Sigma C = 6.6 \times 10^{-3}$ molal (see Table 1). Areas in solid shading show the stability fields of ferric hydroxide, H-jarosite, siderite, and amorphous FeS. The central area in diagonal shading shows a portion of the much larger stability field of goethite. As discussed in the text, it is possible that deep West Camp waters have an Eh, pH, and Fe^{2+} concentration that is buffered near the triple point between goethite, siderite, and amorphous FeS. The program STABCAL (Huang 1998) was used to draw this diagram, using the MINTEQA2 (Allison 1991) thermodynamic database.

The profound differences in chemistry between the East Camp and West Camp waters are due to a number of factors. Granitic bedrock exposed in the Berkeley Pit and surrounding underground workings is very highly altered, with very high pyrite content and essentially no acid-neutralizing ability (Newbrough and Gammons 2002). Towards the periphery of the Butte mineralized complex, the alteration style was less intense, with abundant carbonate minerals (calcite, rhodocrosite) in veins, as well as disseminated through the altered rock (Meyer et al. 1968; Miller 1973). Massive pods and veins of rhodocrosite and rhodonite were mined as a source of Mn metal in the Travona Mine, which is located near the West Camp pumping well (Figure 1). Superimposed on this contrasting geology are mining-related factors that led to a further degradation in water quality of the East Camp in general, and in the Berkeley Pit, specifically. These include the fact that the East Camp was dewatered for a much longer period of time, and the fact that the open mine walls of the Berkeley Pit allow for much greater ingress of atmospheric oxygen.

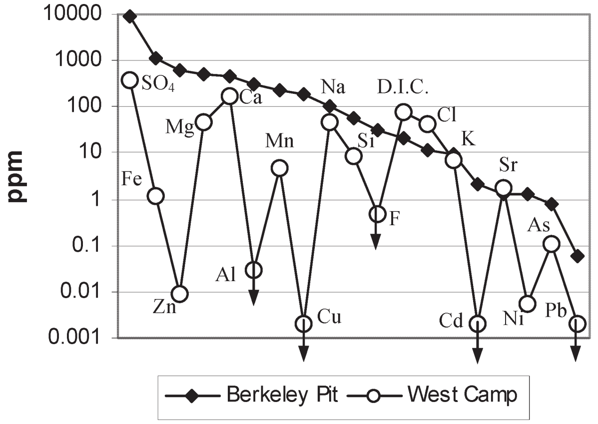

Figure 3. Comparison of the chemistry of the Berkeley Pit lake vs. groundwater from the West Camp. Data for the Berkeley Pit were collected in May-1998 (Jonas 2000), from a depth of 15 m below the surface. Data for the West Camp are from this study (Sept-2000). Data points with arrows indicate analyses that were below the detection limit.

Differences in microbiology between the flooded systems have also influenced water chemistry. The natural inoculation and proliferation of sulfate-reducing bacteria in the West Camp has fortuitously resulted in a dramatic drop in the concentration of toxic metals that form insoluble sulfide minerals, including Cd, Cu, Pb, and Zn. Although some of this decrease is no doubt due to the higher pH of West Camp water, it is worth noting that the concentration of metals such as Zn and Cd is generally lower in the West Camp than in flooded mine workings in the East Camp that have similar pH values but are devoid of H_2S (Metesh and Duaime 2000).

One question regarding the evolution of mine waters in the West Camp is the potential source of organic carbon necessary to initiate BSR. Many possible sources of carbon exist in a flooded mine environment, including rotting timbers, waste gasoline, diesel and other petroleum products. The importance of decaying wood should not be overlooked, as most of the 10,000 km of underground workings were originally framed with timber. Although most of the timber used for permanent man-ways was treated with preservative (including As_2O_3, a possible source for elevated As in the West Camp mine waters), wood used for temporary support of stopes and drifts while ore was being excavated was untreated. These old timbers provide a virtually inexhaustible supply of organic carbon, although not necessarily in an easily biodegradable form.

Willett (2001) measured levels of non-purgeable dissolved organic carbon (NPOC) in the Berkeley Pit lake, as well as selected bedrock monitoring wells and shafts. An average NPOC concentration of 2.2 ± 1.1 mg C/L was obtained from 17 analyses of 9 different shaft and well locations. The total range was 0.6 to 4.5 mg C/L, and included a single analysis of 2.4 mg C/L from the Marget Ann shaft, which is located in the West Camp groundwater system. Although these levels of organic carbon are not particularly high, they are roughly an order of magnitude greater than the concentration of dissolved sulfide in the West Camp mine waters. It is probable that the organic carbon concentrations reflect a balance between production by fermentative bacteria, fungi, etc., and consumption by heterotrophic bacteria (such as Fe- or S-reducing bacteria). Further work is in progress that will attempt to characterize in more detail the biological complexity of the flooded mine workings of the Butte mining district.

Acknowledgment

Much of this work was performed by AH, through the Montana Tech Undergraduate Research Program, funded by grants from NSF and NASA. Funding for stable isotope analysis was provided by the MBMG through a contract with the MT Dept of Environmental Quality. The authors thank the Atlantic Richfield Co., Montana Resources, and the U.S. EPA for their support.

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