

Geochemistry of Flooded Underground Mine Workings Influenced by Bacterial Sulfate Reduction

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Abstract Unlike the majority of the water in the flooded mine complex of Butte Montana, which includes the highly acidic Berkeley pit lake, groundwater in the flooded West Camp underground mine workings has a circum-neutral pH and contains at least 8 μM aqueous sulfide. This article examines the geochemistry and stable isotope composition of this unusual H_2S -rich mine water, and also discusses problems related to the colorimetric analysis of sulfide in waters that contain $\text{FeS}_{(\text{aq})}$ cluster compounds. The West Camp mine pool is maintained at a constant elevation by continuous pumping, with discharge water that contains elevated Mn (90 μM), Fe (16 μM), and As (1.3 μM) but otherwise low metal concentrations. Dissolved inorganic carbon in the mine water is in chemical and isotopic equilibrium with rhodochrosite in the mineralized veins. The mine water is under-saturated with mackinawite and amorphous FeS , but is supersaturated with Cu- and Zn-sulfides. However, voltammetry studies show that much of the dissolved sulfide and ferrous iron are present as $\text{FeS}_{(\text{aq})}$ cluster molecules: as a result, the free $\text{H}_2\text{S} + \text{HS}^-$ concentration of the West Camp water is poorly constrained. Concentrations of dissolved sulfide determined by colorimetry were lower than gravimetric assays obtained by AgNO_3 addition, implying that the $\text{FeS}_{(\text{aq})}$ clusters are not completely extracted by the Methylene Blue reagent. In contrast, the clusters are quantitatively extracted as Ag_2S after addition of AgNO_3 . Isotopic analysis of co-existing aqueous sulfide

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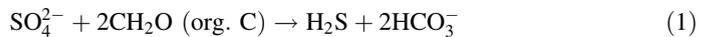
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and sulfate confirms that the sulfide was produced by sulfate-reducing bacteria (SRB). The H₂S-rich mine water is not confined to the immediate vicinity of the extraction well, but is also present in flooded mine shafts up to 3 km away, and in samples bailed from mine shafts at depths up to 300 m below static water level. This illustrates that SRB are well established throughout the southwestern portion of the extensive (>15 km³) Butte flooded mine complex.

Keywords Mine water · Hydrogen sulfide · Iron sulfide clusters · Bacterial sulfate reduction · Geochemistry · Arsenic · Rhodochrosite

1 Introduction

Mine waters pose a significant threat to the environment, because they are often highly acidic and can contain concentrations of dissolved metals that are toxic to aquatic or human health (Nordstrom and Alpers 1999; Blowes et al. 2004; Jambor et al. 2003). Since it was first proposed by Tuttle et al. (1969), production of H₂S by bacterial sulfate reduction has emerged as a viable and inexpensive technology for remediating metals-contaminated mine water (Ledin and Pedersen 1996; Cole 1998). The reactions of interest are often written as follows:



where M is any divalent metal (Zn, Cu, Fe, etc.). Reaction (1) is extremely slow inorganically, but is accelerated in the presence of heterotrophic bacteria that use SO₄²⁻ as a terminal electron acceptor (Postgate 1994). Reaction (2) proceeds instantaneously to form nanometer-scaled amorphous sulfide precipitates that slowly transform into more stable crystalline compounds with time (Moreau et al. 2004).

Although a number of engineered techniques based on bacterial sulfate reduction have been developed to remediate mine waters (Machemer and Wildeman 1992; Cauty 2000; Zaluski et al. 2000; Gammons and Frandsen 2001; Benner et al. 2002), there have been very few studies focusing on mine waters that are *naturally* enriched in H₂S. Sulfidic waters have been reported in the monimolimnion and underlying sediment of pit lakes formed in abandoned lignite mines in eastern Germany (Asmussen and Strauch 1998; Knöller et al. 2004). As for flooded underground mine workings, our literature search uncovered only two instances, where direct or indirect evidence of bacterial sulfate reduction has been documented. These include biofilms of sulfate-reducing bacteria in an underground Pb–Zn mine in Wisconsin (Moreau et al. 2004; Labrenz et al. 2000; Druschel et al. 2002), and a flooded underground mine in California with indirect stable isotopic evidence of bacterial sulfate reduction (Hamlin and Alpers 1996).

In a preliminary study (Gammons et al. 2003a), our group summarized the general geochemical and isotopic characteristics of an H₂S-rich mine water in Butte, Montana, and hypothesized that the sulfide was bacterial in origin. The main purpose of the present study was to collect additional data on the geochemistry and stable isotope composition of the sulfidic mine waters of Butte, and to draw conclusions regarding the dominant

biogeochemical processes responsible for the chemical and isotopic evolution of these waters. An additional objective was to document and describe the occurrence of $\text{FeS}_{(\text{aq})}$ cluster compounds in the Butte mine waters.

1.1 Site Description

The world class polymetallic mineral deposits of Butte, Montana have been mined almost continuously since the 1860's and have produced over 1×10^{10} , 2.2×10^9 , 1.7×10^9 , 3.9×10^8 , 1.5×10^8 , 2.3×10^7 , and 0.9×10^4 kg of Cu, Zn, Mn, Pb, Mo, Ag, and Au, respectively (Duaiame et al. 2004). Most of the early mine workings were underground, and it is estimated that the city of Butte is underlain by 67 km of vertical shafts up to 1.5 km deep, as well as 16,000 km of interconnected, horizontal tunnels and stopes spread over a surface area of roughly 18 km^2 (Duaiame et al. 2004; Duaiame et al. 1988; Gammons et al. 2006a). In the late 1950s concrete bulkheads were installed to isolate active versus inactive portions of the underground mines, thereby reducing the volume of mine openings that required ventilation and groundwater pumping. The inactive Travona, Emma and Ophir Mines, collectively referred as the West Camp, were hydraulically separated from the much more extensive underground workings of the East Camp (Fig. 1). East Camp groundwater drains into the Berkeley Pit, an abandoned open-pit copper mine, which now contains over 100 billion l of highly acidic (pH 2.5) and metal-rich water. Whereas the

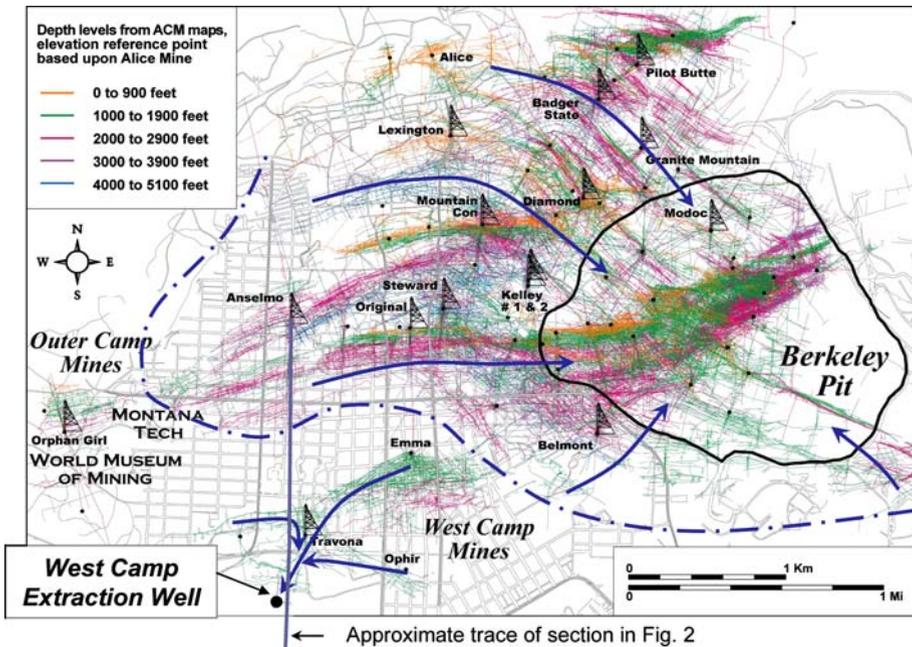


Fig. 1 Map of abandoned underground mines in Butte, color-coded for depth below the Alice Mine portal (modified from Duaiame et al. 2004). The broken line is a groundwater divide that separates “East Camp” mine water that currently flows to the Berkeley Pit from “West Camp” water that drains to the West Camp Extraction Well, and from “Outer Camp” water that is isolated from both systems. Blue arrows show the approximate direction of groundwater flow

geochemistry of the Berkeley 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. 2003b; Madison et al. 2003; Pellicori et al. 2005; Gammons and Duaiame 2006), relatively little attention has been paid to the West Camp groundwater system, which is the focus of the present study.

Once the West Camp workings were cut off from the mine dewatering system in the late 1950s, water levels began to rise and basement flooding of local dwellings occurred (Duaiame et al. 1988). The US Environmental Protection Agency (EPA) eventually ruled that water levels in the Travona shaft should be maintained below an elevation of 5435 ft (1656 m). From 1989 to 1998, West Camp water was pumped directly from the Travona shaft and treated at a local sewage treatment plant. In 1998, the pumping activities were relocated to the West Camp Extraction Well (WCEW), which was drilled into the Travona mine workings at a depth of 160 m below surface. The WCEW currently pumps at an approximate rate of 500–750 l min⁻¹, and has been in continuous operation since October 1998. Up to date, roughly 6 billion l of groundwater have been pumped and treated from the West Camp mine workings.

1.2 Geology and Hydrogeologic Setting

The major West Camp mine workings consist of approximately 110 km of horizontal tunnels serviced by the Emma, Ophir, and Travona mine shafts (Fig. 1). Collectively, these mines accounted for most of the manganese production from the Butte District, estimated at over 1.6 billion kg. The principal ore mineral was rhodochrosite, which occurred as a single large “bonanza” vein up to 30 m in width (Meyer et al. 1968), as well as smaller offshoots. Other minerals in the West Camp veins include abundant quartz and sphalerite, as well as common, but less ubiquitous pyrite, galena, calcite, dolomite, and rhodonite (Meyer et al. 1968). Copper sulfide minerals, being very abundant in the East Camp mines, are relatively rare in the West Camp veins. The veins are hosted by hydrothermally altered Butte Quartz Monzonite (BQM). When fresh, the BQM contains 36–40% plagioclase, 20–25% quartz, 20–25% orthoclase, and 15–20% biotite and hornblende. The BQM experienced several different episodes of hydrothermal alteration, including K-silicate (potassic) alteration associated with an early porphyry-style Cu–Mo event with formation of secondary biotite, K-feldspar, and anhydrite, and later muscovite-rich (phyllic) alteration associated with an overprinting epithermal event that formed the so-called “Main Stage” veins that made Butte famous. In the West Camp, both styles of alteration are present, with phyllic alteration being more abundant immediately adjacent to the quartz-rhodochrosite veins.

Figure 2 is a N–S cross-section from the Anselmo Mine to Silver Bow Creek showing the approximate location of the water table in the mine workings and adjacent fractured bedrock. The water levels in all three West Camp shafts are nearly identical at any one sampling time, suggesting the presence of a well-connected “mine pool” whose elevation is largely controlled by the rate of pumping from the West Camp extraction well. Supporting this hypothesis, the Emma, Ophir, and Travona mine shafts all contain water with a similar major and trace element composition to the WCEW (Gammons et al. 2006a). Over the past 10 years, the West Camp mine pool has been maintained at an elevation roughly 5–10 m below the elevation of the nearby Silver Bow Creek. Groundwater enters the WCEW through a screen at a depth of 155–160 m below surface. Toward the northeast, a groundwater divide separates the West Camp mine pool from the much larger East Camp

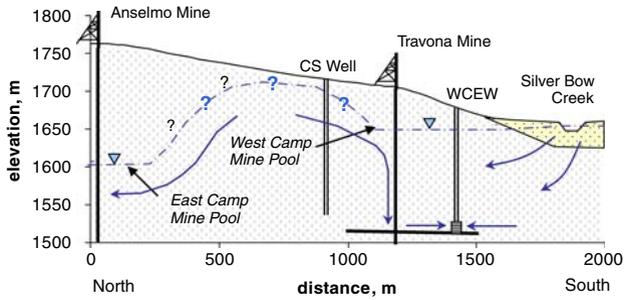


Fig. 2 N–S cross-section from the Anselmo mine to Silver Bow Creek. The approximate location of the water table is shown by the dashed line. Water enters the West Camp Extraction Well (WCEW) at a depth of ~160 m below surface. The stippled pattern represents shallow alluvial sediments. The rest of the geology consists of fractured granitic bedrock of the Butte Quartz Monzonite. CS Well = Chester Steele bedrock monitoring well

mine pool, which is represented in Fig. 2 by the Anselmo shaft. The East Camp system presently drains in the opposite direction to the Berkeley pit lake.

Recharge to the West Camp mine pool occurs via groundwater seepage from the north and northwest, by infiltration from the surface, and via shallow groundwater flow from Silver Bow Creek and its surrounding alluvial aquifer to the south. The relative contributions to the total recharge from these three sources are not known. However, the persistence of a relatively high hydraulic head in the West Camp mine pool despite continuous pumping at a rate of 1 million l day⁻¹ suggests a connection between the mines and the alluvial aquifer of Silver Bow Creek. Shallow groundwater along this reach of Silver Bow Creek has a near-neutral pH, but is chronically elevated in arsenic and heavy metals including Cd, Cu, Fe, Mn, and Zn (Gammons and Madison 2006).

1.3 Metal Sulfide Clusters

In several mineral systems, polynuclear clusters form as metastable intermediates that can persist for extended periods of time. Examples include Al-keggin-type structures (such as $\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12(\text{aq})}^{7+}$), silica polymeric fragments, uranyl clusters, iron and chromium polymeric clusters, calcium phosphate “Posner’s clusters,” and iron sulfide clusters (Rozañ et al. 2000; Luther et al. 1999; Luther et al. 2002; Furrer et al. 2002; Navrotsky 2004). These aqueous clusters represent the precursor steps for their respective mineral precipitation reactions. For many chemical systems—such as Fe–S, $\text{Al}_2\text{O}_3\text{–H}_2\text{O}$, or $\text{SiO}_2\text{–H}_2\text{O}$ —the concentrations of aqueous clusters can dominate the aqueous speciation for a specific set of conditions. Iron sulfide clusters are often abbreviated $\text{FeS}_{(\text{aq})}$ (after Theberge and Luther 1997), although it is important to realize that this notation represents a continuum of polynuclear species of differing stoichiometry and charge. Iron sulfide clusters are known to exist in a number of marine and freshwater environments (Theberge and Luther 1997; DeVitre et al. 1988; Davison et al. 1999; Luther et al. 2003), and are thought to play a significant role in the precipitation of iron sulfide minerals (Druschel et al. 2004; Rickard and Luther 1997; Butler et al. 2004). Although often overlooked, the presence of $\text{FeS}_{(\text{aq})}$ clusters in an environmental sample may complicate traditional methods of analysis for total dissolved sulfide, as well as geochemical modeling of sulfidic waters. This study investigates these complications using the West Camp water as a natural laboratory.

2 Methods

2.1 Field Methods

Water temperature, pH, specific conductance (SC), oxidation–reduction potential (ORP), and dissolved oxygen (DO) readings were collected once a month from the West Camp Extraction Well between November 2003 and November 2004 using two WTW 340i portable multimeters, calibrated on the morning of the sampling as per the manufacturer's recommendations. Since the well is continuously pumped, it was not necessary to purge the well casing. The pumping rate, which can be observed in a control room on site, was also recorded each month. The ORP electrode was calibrated in the field using ZoBell's solution maintained at the same temperature as the samples. DO concentrations of the West Camp water were below the practical quantifiable limit of the electrode (roughly 0.5 mg/l O₂). Turbidity was measured using a Hach model 2100P portable turbidity meter. The concentration of sulfide was determined in the field using the Methylene Blue method and a Hach Model 2010 portable spectrophotometer. The procedure followed Hach method 8131, which is equivalent to EPA method 376.2. Due to the potential loss of H₂S to oxidation or volatilization after sampling, it was essential to perform the sulfide analyses as quickly as possible after sampling. All sulfide measurements reported in this article are the average of triplicate analyses, which typically agreed within 10%.

Groundwater samples were collected in acid-washed high-density polyethylene bottles. Filtered unacidified samples were used for analysis of anions, nutrients, and alkalinity, as well as preparation of samples for stable isotopic analysis. Filtered acidified and raw acidified samples were preserved with 1% v/v HNO₃ (Fisher Optima), and were used for analysis of dissolved and total (acid-available) metals, respectively. Filtered samples acidified to 1% v/v HCl were used for speciation of Fe(II)/Fe(III) and As(III)/As(V). The samples for Fe and As speciation were filtered and immediately acidified in the field, and sealed with no headspace. Sample filtration used a peristaltic pump and disposable 142 mm cellulose–ester filter membranes with nominal pore size of 0.10 μm; prior to April, 2004, 0.45 μm cellulose–ester filter membranes were used. In order to test for the presence of fine colloids, a few ultra-filtered samples were collected using a Minitan tangential flow filter, with a nominal pore diameter of 0.001 μm. Field blanks and field duplicates were collected during each sampling event for each sample type.

2.2 Analytical Methods

Filtered samples were analyzed for major anions with a Dionex 500 or Dionex ICS 2500 ion chromatograph, following EPA method 300.0. Alkalinity measurements were performed in triplicate by gran titration within 48 h of sample collection. Concentrations of soluble reactive phosphorous (SRP) were measured within 24 h of sample collection following Hach method 8048 (similar to EPA method 365.2), which is based on addition of molybdate and ascorbic acid. Dissolved nitrate + nitrite and ammonium concentrations were near or below their respective practical quantification limits using Hach colorimetric procedures (0.01 mg/l and 0.05 mg/l as N, respectively). Dissolved Fe was speciated between Fe(II) and Fe(III) within 48 h of sample collection using the FerroZine method (To et al. 1999). Dissolved As was speciated between As(III) and As(V) at HKM Laboratory (Butte, Montana) within 7 days of sample collection by column separation followed by hydride atomic absorption spectroscopy.

All raw and filtered samples were collected in duplicate and analyzed for major and minor metals by inductively coupled plasma optical emission spectroscopy (ICP-OES) at HKM Laboratory (Butte, Montana) using EPA Method 200.7, or at the Murdock Environmental Laboratory at the University of Montana (Missoula, Montana) following EPA Method 200.15. Split samples were also analyzed at HKM Laboratory for a suite of trace metals using inductively coupled plasma mass spectroscopy (ICP-MS), following EPA Method 200.8. Early in the project, samples were analyzed by ICP-MS for the following elements: Ag, Al, Bi, Cd, Ce, Cu, Mo, Ni, Pb, Sb, Se, Tl, U, and Zn. Out of this list, only Cu, Mo, Ni, Pb, U, and Zn had concentrations above the analytical detection limit.

2.3 Stable Isotope Methods

Preparation of samples for S isotopic analysis of dissolved sulfide and sulfate followed the procedures developed by the US Geological Survey (Carmody et al. 1998). Aqueous sulfide was collected by precipitation of Ag_2S by direct addition of AgNO_3 solution in the field to a 50 l carboy that was filled with unfiltered WCEW groundwater. A black colloidal suspension of Ag_2S formed within 5–10 min, and was filtered back in the laboratory. The fine Ag_2S precipitate was rinsed with 10% NH_4OH to dissolve any AgCl solid that may have formed after addition of AgNO_3 to the field sample. Samples for $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ analysis of dissolved sulfate were obtained by addition of BaCl_2 to form a BaSO_4 precipitate (Carmody et al. 1998). The pH of the samples was adjusted to <3 prior to addition of BaCl_2 , to avoid precipitation of BaCO_3 . Preparation of samples for $\delta^{13}\text{C}$ analysis of dissolved inorganic carbon (DIC) entailed adjustment of pH to >10 , followed by addition of SrCl_2 to form a SrCO_3 precipitate (Friedman 1970).

All stable isotope analyses were performed at the University of Nevada-Reno. Oxygen isotope analyses of water samples were performed using the CO_2 equilibration technique (Epstein and Mayeda 1953) and analyzed using a Micromass Aquaprep device interfaced to a dual inlet Micromass Isoprime stable isotope ratio mass spectrometer. All other stable isotope analyses were performed using a Eurovector elemental analyzer interfaced to a Micromass IsoPrime stable isotope ratio mass spectrometer. Hydrogen isotope analyses of water samples were performed using the technique of Morrison et al. (2001). 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 BaSO_4 samples as a pyrolysis aid. Carbon isotope analyses were performed after the method of Harris et al. (1997). NIST standard NBS-127 BaSO_4 was used as an isotope standard for sulfate- $\delta^{18}\text{O}$ analyses, using the NIST-certified value of $\delta^{18}\text{O} = +9.3\text{‰}$. Stable isotope values are reported in the usual δ notation in units of ‰ (per mil, or parts per thousand), versus VCDT for sulfur, versus VSMOW for oxygen and hydrogen, and versus VPDB for carbon. Analytical uncertainties are $\pm 0.2\text{‰}$ for $\delta^{34}\text{S}_{\text{sulfide}}$ and $\delta^{34}\text{S}_{\text{sulfate}}$, $\pm 0.4\text{‰}$ for $\delta^{18}\text{O}_{\text{sulfate}}$, $\pm 0.1\text{‰}$ for $\delta^{18}\text{O}_{\text{water}}$, and $\pm 2\text{‰}$ for $\delta\text{D}_{\text{water}}$ and $\pm 0.2\text{‰}$ for $\delta^{13}\text{C}$.

2.4 Bacteria Counts

Duplicate samples for sulfate reducing bacteria-most probable number (SRB-MPN), direct total microbial count (DTMC) and heterotrophic plate count (HPC) were collected in the

field three times during the duration of the project. The SRB-MPN and HPC samples were collected in sterile 1 l sample bottles by rinsing with sample water three times and filling completely to the top (no headspace). SRB were enumerated following the American Petroleum Institute Recommended Practice 38. HPC analyses were performed by the spread plate method using R2A agar (Difco), following serial dilution with sterile buffered water (Standard Method 9215 C; APHA 1995). Colony forming units on the plates were enumerated after one week of incubation at room temperature. DTMC samples were collected in 50 ml tubes that already contained formalin (37% formaldehyde). DTMC populations were enumerated by epifluorescent direct count (Standard Method 9216 B; APHA 1995). Groundwater samples were preserved with formaldehyde (final concentration 4.7%) immediately after collection and stored at 4°C for no more than three weeks. Samples were diluted as necessary with filter-sterilized deionized water, filtered using 0.22 µm black polycarbonate filters, and stained with a 10 µg/ml solution of 4',6-diamidino-2-phenylindole (DAPI) (Kepner and Pratt 1994). For each filter, cells were counted in at least 10 randomly selected microscopic fields until approximately 300 total cells were counted.

2.5 Voltammetry

Cyclic voltammetry scans generate voltammograms which plot current (amps) versus potential (volts, versus a Ag/AgCl electrode). Voltammograms identify the specific potential at which a particular electrochemical reaction involving redox species in solution occurs at the surface of the working electrode. The value of the potential and the response of the redox species to how that potential is manipulated is used to identify specific reactions, which can then be quantified by the current response.

Electrochemical measurements were carried out in situ and in real time at the WCEW field site by employing a sealed polytetrafluoroethylene (PTFE) flow-through vessel (designed and built at the University of Vermont) which includes gas- and water-tight fittings to seal 3 electrodes into the system in order to make measurements without exposing the water to the atmosphere. Electrochemical measurements in the field were carried out using an Analytical Instruments, Inc. (AIS) DLK-60 Potentiostat and 3 solid state electrodes (100 µm-diameter Au-amalgam working electrode, Pt counter electrode, and Ag/AgCl reference electrode) constructed after Brendel and Luther (1995) operated with a computer controller using AIS software and powered by a 12 V battery.

Additional experiments to confirm the peak position of $\text{FeS}_{(\text{aq})}$ were carried out with a sample of West Camp water that had been allowed to oxidize and was subsequently filtered. Other experiments were performed using a 0.1 M KCl matrix buffered to pH 6.8 using PIPES (Piperazine-1,4-bis(2-ethanesulfonic acid)) buffer, which does not strongly interact with the metals or $\text{FeS}_{(\text{aq})}$ complexes. Stock solutions of sodium sulfide were made from $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ salts and ultra-high purity (UHP) N_2 -purged 18 MΩ water. Experiments to test the effect of iron sulfide clusters on colorimetric dissolved sulfide determinations were prepared in a glove box kept under positive pressure of UHP N_2 (first passed through a high-capacity Restek O_2 scrubber) and during preparation and execution of the experiments CampyPak H_2 -generating packs were used to further rid the experiments of molecular oxygen. Solutions were prepared in the glove box and 125 ml glass septum bottles were filled and sealed with a rubber cap and crimped aluminum seal without headspace until a sample was withdrawn using a gas tight syringe and 16-gauge needle. An experiment to determine if sulfide present as $\text{FeS}_{(\text{aq})}$ could be recovered using the

Methylene Blue colorimetric test was performed using 0.1 M KCl solution buffered to pH 6.8 in which 40 μM FeCl_2 + 40 μM $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ were added in parallel with a control sample containing 40 μM Na_2S and no Fe(II). The samples were contained in the glove box for the duration of the experiment and sample aliquots were withdrawn at 5 min, 1, 2, and 4 h for analysis. These samples and a set of sulfide standards were then transferred to a cuvette where sulfide was determined using the same colorimetric test as above (Hach method 8131 with a Hach 810 portable colorimeter), all inside the glove box system. In a separate experiment, excess AgNO_3 solution was added to 0.1 M KCl PIPES buffered matrix that had been purged and spiked with 40 μM FeCl_2 and 40 μM $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ in a 10 ml volume Hanging Mercury Drop electrode (HMDE) cell. Scans were performed immediately and at 1 min intervals to document the consumption of sulfide in the sample as Ag_2S precipitated.

2.6 Geochemical Modeling

The aqueous speciation and saturation states of selected minerals were calculated using the geochemical program Visual MINTEQ, Version 2.32 (here abbreviated V-MINTEQ), a recent variant of the original MINTEQ program (Allison et al. 1991). Chemical data for filtered anions, metals, and field measurements were input as their respective one-year averages (Tables 1, 2). Initially, an Eh value of -165 mV was calculated by V-MINTEQ assuming equilibrium with the $\text{HS}^-/\text{SO}_4^{2-}$ redox couple. This value was then used to calculate the speciation of other redox-sensitive elements, including Fe, Cu, Mn, U, and As. The V-MINTEQ database was updated with the Cu_2S solubility product and Cu(I) bisulfide stability constants given by Mountain and Seward (1999), the orpiment solubility product of Webster (1990), the amorphous ZnS solubility product of Gubeli and Ste-Marie

Table 1 Field parameters

Sample date	Flow (l s^{-1})	pH	Temp. ($^{\circ}\text{C}$)	SC (mS/cm)	Alkalinity (meq l^{-1})	ΣS^{2-} ($\mu\text{mol l}^{-1}$)	Eh (mV)
11/25/03	11.4	6.77	12.6	1.28	5.50	7.2	n/a
1/13/04	9.5	6.83	12.7	1.28	5.40	7.8	144
2/19/04	11.4	6.91	12.4	1.27	5.50	8.1	110
3/30/04	9.5	6.96	12.6	1.23	5.22	8.4	157
4/30/04	8.8	6.74	12.5	1.25	5.68	7.8	n/a
6/4/04	8.8	6.76	13.4	1.31	5.64	9.0	6.8
6/29/04	9.5	6.88	12.6	1.27	5.76	8.7	13.7
7/29/04	11.4	6.88	12.8	1.30	5.72	8.7	149
9/1/04	12.3	6.92	12.8	1.29	5.78	9.0	29.8
9/30/04	12.6	6.90	11.8	1.30	5.76	8.4	-87.3
10/27/04	13.9	6.85	11.9	1.30	5.80	8.7	-42.3
11/24/04	12.6	6.60	12.1	1.29	5.74	8.4	111
12-months avg.	11.0	6.83	12.5	1.28	5.62	8.4	53.8
rsd	16%	1%	3%	2%	3%	7%	128%

Table 2 Major and trace element concentrations

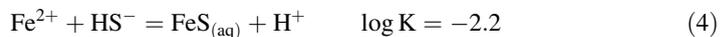
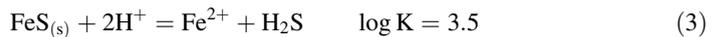
	Major solutes (mmol l ⁻¹)								
	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻	PO ₄ ³⁻	Ca	K	Mg	Na	Si
12-months avg.	1.24	4.06	5.61	0.0018	4.24	0.15	1.97	1.87	0.31
No. of samples	6	6	12	12	6	6	6	6	6
rsd	10%	9%	4%	11%	3%	5%	3%	4%	6%
	Trace solutes (μmol l ⁻¹)								
	As	Ba	Cu- <i>t</i>	Cu- <i>d</i>	Fe	Li	Mn	Mo	
12-months avg.	1.29	0.19	0.024	0.007	16	4.76	90	0.016	
No. of samples	6	6	6	6	6	6	6	2	
rsd	10%	0%	153%	55%	11%	0%	4%	14%	
	Ni	Pb- <i>t</i>	Pb- <i>d</i>	Sr	U	Zn- <i>t</i>	Zn- <i>d</i>		
	12-months avg.	0.12	0.0017	<0.0005	19	0.11	0.17	0.058	
No. of samples	6	6	6	6	2	6	6		
rsd	44%	29%	n/a	6%	3%	48%	25%		

All samples filtered to 0.1 μm unless otherwise noted

t = total (unfiltered) concentration; *d* = dissolved concentration

(1967), and stability constants for aqueous Cu(I), Cu(II), and Zn(II) sulfide clusters given by Thompson and Helz (1994) and Luther et al. (1996, 1999).

The fact that the size, stoichiometry, charge, and activity coefficients for aqueous Fe–S clusters are still poorly known complicates efforts to quantify their thermodynamic stability in solution. However, as a starting point, we used the following equilibrium constants for the dissolution of nano-crystalline mackinawite and formation of polynuclear iron–sulfur molecules (after Rickard 2006):



Although stability constants for other cluster species such as Fe₂(HS)³⁺ and Fe₃(HS)⁵⁺ are available (Rickard and Luther 2006), Rickard (2006) has shown that FeS_(s) solubility at low temperature is adequately explained over a large pH range with a simple, two-species model including Fe²⁺ and FeS_(aq).

3 Results

3.1 Water Quality Parameters

The chemistry of the West Camp mine water showed very few changes during the one-year study (Tables 1, 2). The total range in water temperature was less than 0.4°C, and concentrations of pH, alkalinity, and total dissolved sulfide were likewise nearly constant. The only measured parameter that showed large differences between visits was Eh. Eh measurements were problematic throughout the study, and were prone to unstable readings

and continuous drift, usually downwards. These difficulties are believed to have been caused either by redox dis-equilibrium, or to the fact that the redox state of the West Camp waters is “poorly poised” (Langmuir 1997) with respect to any redox couple, such as Fe(II)/Fe(III) or $\text{SO}_4/\text{H}_2\text{S}$. In the first case, concentrations of aqueous Fe(III) are vanishingly small compared to Fe(II); in the latter case, aqueous sulfide concentrations are much lower than sulfate. As a further complication, subsequent voltammetry work showed that much of the dissolved sulfide was tied up in aqueous $\text{FeS}_{(\text{aq})}$ cluster complexes (see below), leaving the concentration of “free” H_2S poorly constrained. Furthermore, it has been shown that field redox measurements of H_2S -rich waters often yield Eh values that are much higher than thermodynamic calculations based on the concentrations of co-existing aqueous sulfide and sulfate (Lindberg and Runnells 1984).

In terms of its major ions (Table 2), the WCEW groundwater is a Ca-bicarbonate-sulfate water. Based on a comparison of filtered (0.1 or 0.45 μm), ultrafiltered (0.001 μm) and non-filtered samples, most of the solutes analyzed were primarily (>90%) present in dissolved form. Exceptions included Cu, Pb, and Zn. Owing to the elevated concentrations of dissolved sulfide, the particulate forms of these base metals were probably fine-grained sulfides. Total dissolved Fe concentrations were consistently near 16 μM , and FerroZine analyses of monthly samples showed that essentially all of this iron was Fe(II). Concentrations of Mn (90 μM) and As (1.3 μM) were notably elevated, reflecting the high Mn and As content of the mineralized veins. An additional source of As in the mine waters is the timber that was used to support the underground tunnels and shafts, some of which was treated with As_2O_3 (a byproduct of the milling and smelting process) as a preservative. The majority of the dissolved As was found to be in the reduced As(III) valence, although minor (<10%) contributions of As(V) cannot be discounted.

Although dissolved H_2S is not a parameter that is routinely collected during the semi-annual inventory of Butte mine waters by the Montana Bureau of Mines and Geology (MBMG), a scattering of additional data (all collected by colorimetry) exist with which to compare to this study. The concentration of total dissolved sulfide in a sample bailed from 30 m below static water level in the Travona Shaft on 12/27/00 was 6.9 μM . This value is similar to the results from the WCEW (Table 1), which is not surprising considering that a direct connection exists between the extraction well and the Travona mine workings. Similarly, concentrations of dissolved sulfide measured by the MBMG during a 28 day pumping test of the Travona Shaft in 1989 ranged from <3 to 47 μM , with an average of 18 μM (Duaine et al. 1989). Higher sulfide concentrations of 56 and 270 μM were recently obtained for samples pumped from the Orphan Girl and Orphan Boy shafts, respectively, in 2006. These two shafts are located in the so-called “Outer Camp” at the extreme western edge of the Butte mine complex (Fig. 1), and are not connected by underground workings to the West Camp.

3.2 Stable Isotopes

Results of stable isotopic analyses from the West Camp extraction well (Table 3) once again showed negligible variation with time of year. Table 3 includes data for two other West Camp mine shafts—the Emma and Travona shafts—which were sampled in 2004 and analyzed for $\delta^{34}\text{S}_{\text{H}_2\text{S}}$, $\delta^{34}\text{S}_{\text{SO}_4}$, and $\delta^{18}\text{O}_{\text{SO}_4}$, as well as some early data reported by our group for the WCEW (Gammons et al. 2003a). The lack of any seasonal variation in the stable isotopic composition of the West Camp groundwater suggests a subsurface residence time long enough to allow for mixing of recharge water whose isotopic composition would

Table 3 Stable isotope results

Sample date	Site	$\delta^{34}\text{S}_{\text{H}_2\text{S}}$	$\delta^{34}\text{S}_{\text{SO}_4}$	$\Delta\delta^{34}\text{S}^{\text{a}}$	$\delta^{18}\text{O}_{\text{SO}_4}$	$\delta^{18}\text{O}_{\text{w}}$	$\delta\text{D}_{\text{w}}$	$\delta^{13}\text{C}_{\text{DIC}}$
2/19/04	WCEW	-34.7	11.3	46.0	-2.9	-17.3	-134	-15.9
3/30/04	WCEW	-35.1	11.5	46.5	-3.5	-17.3	-135	-13.1
6/4/04	WCEW	-34.0	11.4	45.4	-3.2	-17.3	-134	-13.9
7/26/04	WCEW	-35.2	12.9	48.1	-4.7	-17.3	-134	-13.9
9/30/04	WCEW	-35.2	11.5	46.7	-3.7	-17.3	-135	-12.9
11/24/04	WCEW	-30.4	11.4	41.8	-5.2	-17.3	-135	-13.0
2004 avg.		-34.3	11.6	45.9	-3.9	-17.3	-134	-13.4
10/26/00 ^b	WCEW	-32.4	9.5	41.9	-	-	-	-
11/13/00 ^b	WCEW	-35.1	9.5	44.6	-	-	-	-
6/21/01 ^b	WCEW	-	-	-	-	-17.5	-136	-
4/23/04	Emma	-24.7	18.0	42.6	0.2	-	-	-
4/23/04	Travona	-34.8	11.6	46.4	-3.5	-	-	-

All measurements in ‰ (per mil)

^a $\Delta\delta^{34}\text{S} = \delta^{34}\text{S}_{\text{SO}_4} - \delta^{34}\text{S}_{\text{H}_2\text{S}}$

^b Data from Gammons et al. (2003a)

have varied seasonally (Clark and Fritz 1997). Mixing of water occurs as groundwater makes its way through the labyrinth of underground mine workings, or closer to the extraction well itself, where water from opposite directions is mixed in the well bore. The implications of the stable isotope results are discussed in further detail below.

3.3 Bacteria Counts

Numbers of total (TDC) and heterotrophic (HPC) bacteria were both quite low (5.5×10^4 – 1×10^5 cells ml^{-1} and 10–130 CFU ml^{-1} , respectively), and concentrations of sulfate-reducing bacteria were near the lower limit of quantification (MPN of 1–3 per 10 ml). Such low levels of bacteria are not unusual for groundwater with low nutrient and organic C content (Garth James, MSE-Bozeman, pers. commun., 10-04). Given the high clarity of the West Camp water (turbidity < 1.0 Nephelometric Turbidity Units) and the fact that it has been pumped continuously for more than 7 years, it is likely that most of the bacteria in the mine workings are present as biofilms coating exposed mineral or wood surfaces. The latter include ubiquitous timbers and beams used by the underground miners for structural support.

3.4 $\text{FeS}_{(\text{aq})}$ Clusters

Voltammetry scans of water from the West Camp site distinctively show the presence of significant amounts of iron sulfide molecular clusters, $\text{FeS}_{(\text{aq})}$ (Fig. 3). In these scans, the current response of the $\text{FeS}_{(\text{aq})}$ molecular cluster is indicated by the signal at a potential of -1.15 V (versus Ag/AgCl) (Theberge and Luther 1997; Luther et al. 2003; Druschel et al. 2004), while signals for Fe^{3+} , HS^- , Fe^{2+} and Mn^{2+} can also be determined at their specific

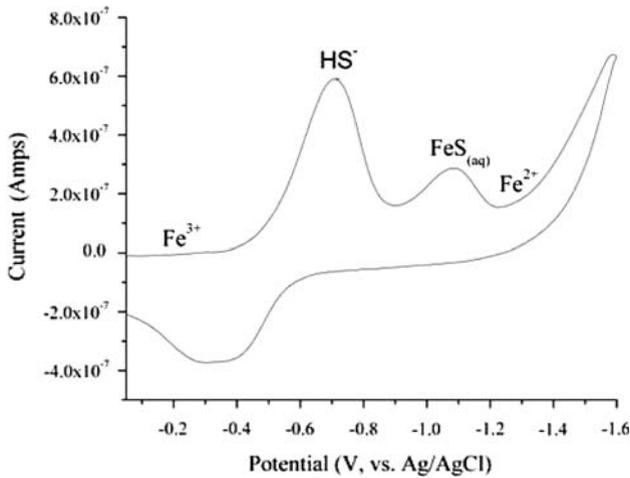


Fig. 3 Solid state Au-amalgam microelectrode voltammetric scan collected on site in a sealed flow-through chamber. Note the predominance of the $\text{FeS}_{(\text{aq})}$ peak at -1.15 V versus Ag/AgCl, very low amounts of free Fe^{2+} at -1.4 V versus Ag/AgCl, and the absence of Fe^{3+} at -0.3 V versus Ag/AgCl in this voltammogram

potentials. It is key to note that the majority of iron in this system is present as $\text{FeS}_{(\text{aq})}$ molecular clusters; very little monomeric Fe(II), present either as hydrated Fe^{2+} or as monomeric bisulfide or chloride species, was detected in these samples. Multiple scans were collected at different speeds and using different wave forms with similar results; replicate reproducibility was approximately $\pm 20\%$, likely due to chaotic hydrodynamic flow patterns in the flow-through cell employed on site.

In order to determine if $\text{FeS}_{(\text{aq})}$ clusters potentially affect the analytical results of colorimetric sulfide analyses performed in the field, we conducted a series of experiments to determine sulfide recovery from iron sulfide solutions over time. The results (Fig. 4) indicate that over 4 h the sulfide recovery dropped by approximately 30% relative to the sulfide blank. This implies that the $\text{FeS}_{(\text{aq})}$ clusters became more resistant to dissociation and subsequent complexation by the Methylene Blue reagent with time. Follow-up experiments showed that addition of AgNO_3 to solutions containing a mixture of free aqueous sulfide and $\text{FeS}_{(\text{aq})}$ completely extracted the sulfide from both forms (Fig. 5). Besides silver, Zn and Cu are also known to quantitatively precipitate dissolved sulfide from solution as ZnS or CuS (Luther and Rickard 2005).

The above laboratory results have obvious implications to the field data discussed above. Given the fact that Methylene Blue is unable to completely extract sulfide tied up in aged $\text{FeS}_{(\text{aq})}$ cluster compounds, it is very likely that the sulfide measurements in Table 1 underestimated the true concentration of total dissolved sulfide in the water samples. In order to test this hypothesis, a subsequent field sampling was conducted in January 2006 to directly compare the results of field colorimetry with a gravimetric analysis based on AgNO_3 addition to a 50 l sample of West Camp water. The results of the colorimetric analysis indicated a dissolved sulfide concentration of $7.5 \mu\text{M}$, which compared to a result of $23 \mu\text{M}$ obtained after purifying (with repeated NH_4OH rinses to dissolve AgCl) and weighing the Ag_2S precipitate. These results suggest that as much as 67% of the total dissolved sulfide in the West Camp groundwater is present as $\text{FeS}_{(\text{aq})}$ cluster compounds that are not detectable by standard colorimetric methods. In contrast, because the isotopic

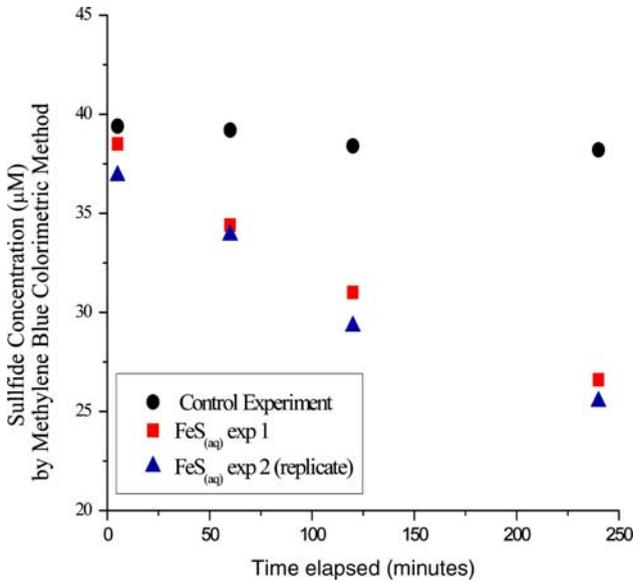


Fig. 4 Results of sulfide recovery using the methylene blue colorimetric method in solution containing $\text{FeS}_{(\text{aq})}$ versus a control solution containing only H_2S . Since $\text{FeS}_{(\text{aq})}$ takes time to form and because the likely structure of the cluster changes with time these results can only be used in a qualitative sense concerning the chemistry of field samples from the West Camp Extraction Well

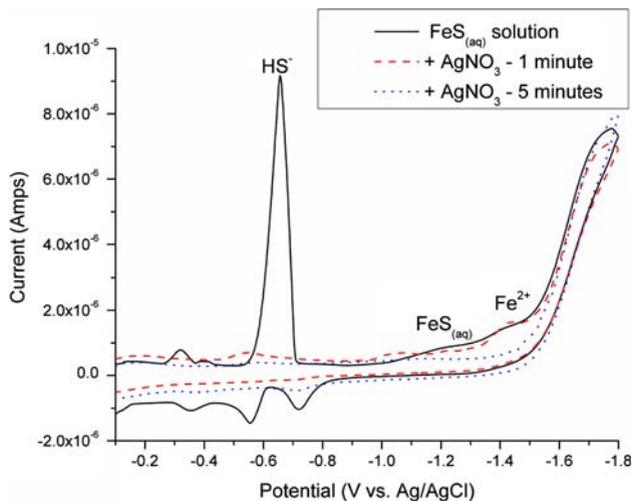


Fig. 5 Scans of a 0.1 m KCl, PIPES buffered solution with 40 μM FeCl_2 and 40 μM $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ before, then 1 and 5 min after addition of excess AgNO_3 . Note that all sulfide is recovered from both the free sulfide and $\text{FeS}_{(\text{aq})}$ forms using the AgNO_3 after 5 min

analysis of dissolved sulfide was performed on Ag_2S precipitates formed by AgNO_3 addition, the $\delta^{34}\text{S}$ results of this study should be representative of the total dissolved sulfide in the environmental samples. Also, the fact that total dissolved Fe concentrations deter-

mined by colorimetry agreed with Fe concentrations from ICP-AES indicates that the Fe(II) in the $\text{FeS}_{(\text{aq})}$ species was completely extracted by the FerroZine reagent.

4 Discussion

4.1 Groundwater Geochemistry

Based on V-MINTEQ modeling, the West Camp groundwaters are predicted to be close to equilibrium saturation with calcite and crystalline or amorphous MnCO_3 (Table 4). Equilibration with MnCO_3 is not surprising, as rhodochrosite was an abundant mineral in the West Camp mines, which at one time were the only domestic suppliers of Mn ore in the United States. The groundwater is also close to saturation with barite and hydroxyapatite. Dissolution of apatite, a common accessory mineral in the granitic rock hosting the Butte veins (Meyer et al. 1968), provides a potentially renewable source of P for microbes in the flooded mine workings.

For compounds containing ferrous iron or sulfide, the calculation of aqueous speciation and mineral saturation indices was complicated by the uncertainty in the concentration of dissolved sulfide, as well as the presence of the aforementioned $\text{FeS}_{(\text{aq})}$ clusters. Following the model of Rickard (2006), V-MINTEQ was run with $\text{FeS}_{(\text{aq})}$ in the database, and using estimates of total dissolved sulfide concentration obtained either colorimetrically (12-months average = 8.1 μM) or by AgNO_3 addition (23 μM). The WCEW water was found to be either slightly undersaturated (S.I. = -0.47) or near equilibrium (S.I. = -0.03) with nano-crystalline mackinawite, depending on the choice of total sulfide concentration. The water is predicted to be strongly supersaturated with Zn and Cu(I) sulfides, and

Table 4 Saturation indices (S.I.) for selected solids in West Camp water, assuming a computed Eh of -165 mV

		S.I.			S.I.
<i>Carbonates</i>			<i>Phosphates</i>		
Rhodochrosite	MnCO_3	0.59	Hydroxyapatite	$\text{Ca}_5(\text{PO}_4)_3(\text{OH})$	-0.37 ^b
$\text{MnCO}_3(\text{am})^{\text{a}}$	MnCO_3	0.10	Strengite	$\text{FePO}_4 \cdot 2\text{H}_2\text{O}$	-10.0
Calcite	CaCO_3	-0.27	Vivianite	$\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$	-3.1 ^c
Dolomite	$\text{CaMg}(\text{CO}_3)_2$	-0.90	Ningyoite	$\text{CaU}(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$	-9.2
Magnesite	MgCO_3	-1.40	<i>Oxides/hydroxides</i>		
Strontianite	SrCO_3	-3.73	Quartz	SiO_2	0.64
Smithsonite	ZnCO_3	-2.31	Chalcedony	SiO_2	0.17
Witherite	BaCO_3	-4.45	SiO_2 (am) ^a	SiO_2	-0.67
<i>Sulfates</i>			Uraninite	UO_2 (am)	-2.74
Barite	BaSO_4	0.34	<i>Other</i>		
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	-0.84	Metallic Cu	Cu	-1.07
Celestite	SrSO_4	-3.13			
Melanterite	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	-7.34			

^a am = amorphous solid

^b Adjusted to 1 Ca in unit formula

^c Adjusted to 1 Fe in unit formula

undersaturated with MnS or As₂S₃. The latter result underscores the relatively high mobility of Mn and As in sulfidic waters. It is possible that Mn and As concentrations are limited instead by co-precipitation with other secondary sulfide minerals, such as ZnS (Gammons and Frandsen 2001).

Table 5 includes S.I. values for several ferric compounds, including ferrihydrite, “aged” ferrihydrite, and goethite. Since the concentration of dissolved Fe(III) was below the detection limit of the Ferrozine method, these S.I. values had to be estimated from the measured or calculated Eh of the WCEW water. The former (+65 mV) was taken as the average of the 12-months field data, whereas the latter (−165 mV) was computed by V-MINTEQ based on the measured sulfide and sulfate concentrations. Using the higher of the two Eh estimates, the WCEW water is predicted to have an aqueous Fe(III) concentration that is intermediate between equilibrium saturation with ferrihydrite and “aged” ferrihydrite. However, based on the more realistic Eh estimate of −165 mV, the WCEW water is strongly undersaturated with any Fe(III) phase.

Regardless of the choice of sulfide concentration, the modeling results (Table 5) suggest that less than 10% of the dissolved Fe(II) and S(-II) should be present as FeS_(aq) clusters, and that Fe²⁺ should be the dominant ferrous aqueous Fe(II) species. This prediction is in contrast to the results of the aforementioned voltammetric scans, which indicate that essentially all of the dissolved Fe in the WCEW water was present as FeS_(aq). The reason for this discrepancy is not known, but it may reflect a difference between the formation of

Table 5 Influence of ΣS(-II) and Eh on aqueous speciation and saturation indices

Speciation scheme	Using Rickard (2006) model	
	I	II
Concentration of ΣS(-II), μmol l ⁻¹	8.1	23
% ΣS(-II) as HS ⁻ or H ₂ S	78.1%	81.2%
% ΣS(-II) as FeS(aq)	8.6%	8.4%
% ΣFe as Fe ²⁺	77.6%	73.1%
% ΣFe as FeS(aq)	3.2%	8.9%
S.I. of mackinawite	-0.47	-0.03
S.I. of ZnS(am)	4.7	5.0
S.I. of chalcocite	4.0 ^a	3.6 ^a
S.I. of MnS(green)	-3.6	-3.1
S.I. of orpiment	-0.80 ^b	-0.69 ^b
S.I. of siderite	-0.46	-0.49
S.I. of ferrihydrite (Eh = +65)	-0.72	-0.75
S.I. of aged ferrihydrite (Eh = +65)	0.52	0.50
S.I. of goethite (Eh = +65)	2.28	2.25
S.I. of ferrihydrite (Eh = -165)	-4.77	-4.80
S.I. of aged ferrihydrite (Eh = -165)	-3.53	-3.55
S.I. of goethite (Eh = -165)	-1.77	-1.80
Calculated m _{HS-}	2.0E-06	6.0E-06
Calculated m _{Fe²⁺}	1.7E-05	1.6E-05

^a Normalized to 1 Cu atom

^b Normalized to 1 As atom

FeS_(aq) from an equilibrium with nanocrystalline mackinawite (Rickard 2006) versus the formation of metastable concentrations of FeS_(aq) from dissolved Fe²⁺ and H₂S generated by microorganisms in low temperature settings. There are many other possible differences, including the much more complex water chemistry of the natural mine water samples as compared to the experimental system, as well as the fact that Rickard's (2006) experiments were performed for an ideal 1:1 Fe:S system.

Figure 6 is an Eh–pH diagram for the Fe–S–C–H₂O system drawn for the conditions of the West Camp groundwater. The stable Fe-oxides (hematite, goethite) were suppressed from the calculations, as these phases typically do not react quickly enough to influence the Eh and Fe concentrations of low temperature waters (Nordstrom and Alpers 1999; Langmuir 1997). The West Camp groundwaters plot close to the Fe²⁺/siderite pH boundary, whereas the Eh values range between those corresponding to saturation with amorphous ferric hydroxide and amorphous FeS. The Eh and pH of selected East Camp mine waters are shown for comparison, based on data in Pellicori et al. (2005). From this figure, it is clear that groundwater in the West Camp is significantly more reducing and higher in pH than the Berkeley pit lake and adjacent groundwaters in the East Camp flooded mine workings.

4.2 Origin of Sulfide and Sulfate

Dissolved sulfide in the WCEW and the West Camp mine shafts (Emma, Travona) is isotopically light, with δ³⁴S falling in a range of –24.7 to –35.4‰ (Table 3, Fig. 7). In contrast, the δ³⁴S of coexisting dissolved sulfate ranges from +11.3 to +18.0‰. The resultant isotopic separation values (Δ³⁴S_{SO₄–H₂S}) range from 41.8 to 46.9‰. This magnitude of isotopic separation is indicative of bacterial sulfate reduction (Canfield 2001). Although H₂S can also form during bacterial disproportionation of intermediate S compounds such as elemental sulfur, the magnitude of δ³⁴S separation between dissolved sulfide and sulfate formed by this pathway is typically in the range of 7–25‰ (Canfield

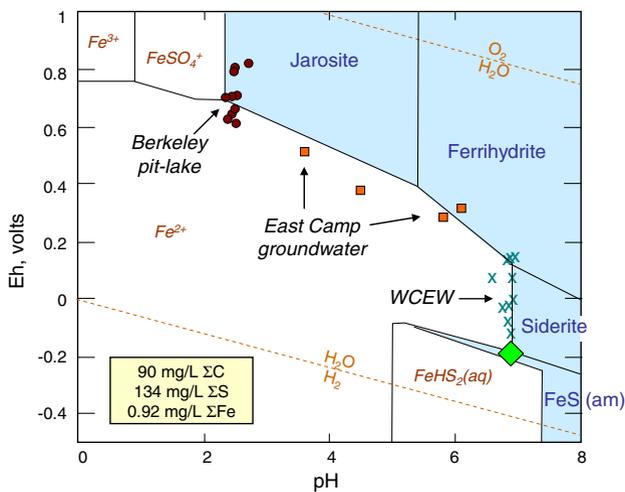


Fig. 6 Eh–pH diagram for West Camp groundwater, calculated for a temperature of 12.5°C. x = WCEW field data; ◇ = Eh calculated from S^{2–}/SO₄^{2–}; □ = East Camp groundwater; ● = Berkeley pit lake

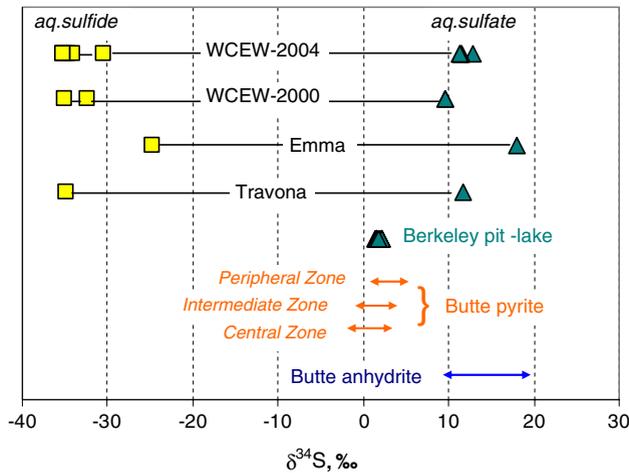


Fig. 7 S isotopic composition of coexisting aqueous sulfide (\square) and sulfate (\blacktriangle) from the West Camp groundwaters. Also shown are data for aqueous sulfate from the Berkeley pit lake (Pellicori et al. 2005), and pyrite and anhydrite from the Butte ore bodies (Field et al. 2005)

et al. 1998; Sørensen and Canfield 2004) and is, therefore, much less than the observed $\delta^{34}\text{S}$ separation in the West Camp mine water. Nor could the H_2S have been generated abiotically by dissolution of hydrothermal sulfide minerals such as ZnS under anaerobic, initially acidic conditions, as this process would have produced H_2S with an isotopic composition similar to that of the precursor sulfide minerals. Published values for $\delta^{34}\text{S}$ of pyrite and other sulfide minerals from the Butte ore bodies were recently compiled and discussed by Field et al. (2005). These data, summarized in Fig. 7, show a narrow range in $\delta^{34}\text{S}$ between -1 and $+4\text{‰}$, which is much heavier than the aqueous sulfide from the WCEW.

The stable isotope results can also be used to place constraints on the origin of dissolved sulfate in the West Camp groundwater. Oxidation of pyrite to sulfate results in minimal fractionation of S isotopes (Seal 2003). Thus, sulfate derived via oxidation of Butte pyrite should have $\delta^{34}\text{S}$ between -1 and $+4\text{‰}$. The WCEW sulfate is isotopically much heavier than this, with $\delta^{34}\text{S}$ of $+9.5$ to $+18.0\text{‰}$ (Table 3). Although bacterial sulfate reduction enriches the residual sulfate in ^{34}S (Canfield 2001; Seal 2003), it is unlikely that this process could explain a more than 10‰ increase in $\delta^{34}\text{S}$ of sulfate, as this would require a large percentage of the total initial reservoir of aqueous sulfate to be reduced, which is inconsistent with the low levels of dissolved sulfide that have been measured from the West Camp waters. A more reasonable explanation is that some of the isotopically heavy sulfate in the West Camp was sourced by dissolution of hydrothermal anhydrite (CaSO_4) from the early porphyry-style alteration of the Butte Quartz Monzonite. As shown in Fig. 7, the $\delta^{34}\text{S}$ of Butte anhydrite is generally heavier than that of sulfate from the West Camp waters, although there is some overlap.

The oxygen isotopic composition of aqueous sulfate (Fig. 8) is also compatible with a model in which the West Camp sulfate was derived from a mixture of pyrite oxidation and anhydrite dissolution. Aqueous sulfate from the West Camp has $\delta^{18}\text{O}$ of -5.2 to $+0.2\text{‰}$, which compares to $\delta^{18}\text{O} = -17.3\text{‰}$ for the West Camp groundwater, $\sim -12\text{‰}$ for sulfate in the acidic Berkeley pit lake, and $+7$ to $+9.5\text{‰}$ for anhydrite from the Butte ore bodies

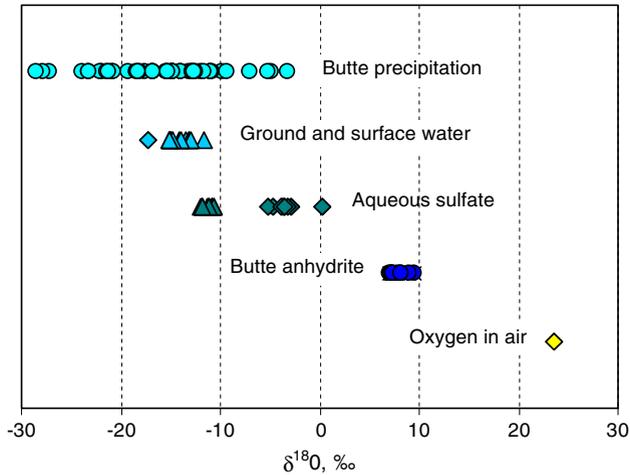


Fig. 8 Oxygen isotopic composition of selected compounds of interest. ○ = Butte precipitation (Gammons et al. 2006b); ◆ = WCEW water or WCEW aqueous sulfate (this study), △ = Berkeley pit lake water or aqueous sulfate (Pellicori et al. 2005), □ = Butte anhydrite (Field et al. 2005); ◇ = average isotopic composition of O₂ in air (Horibe et al. 1973)

(Field et al. 2005). Thus, the West Camp sulfate has an O-isotopic signature that is intermediate between that of hydrothermal anhydrite and that of sulfate in the pit lake. As shown by Pellicori et al. (2005), the $\delta^{34}\text{S}$ of sulfate in the Berkeley pit lake is nearly identical to that of pyrite from the Central Zone of the ore body (Fig. 7), implying that most of the dissolved sulfate was derived from oxidation of pyrite on the mine walls or surrounding underground workings. The so-called Central Zone of the Butte ore body, which surrounds the Berkeley Pit, was strongly overprinted by a younger alteration event that deposited copious pyrite and effectively destroyed the early anhydrite-rich alteration (Field et al. 2005). The similarity between the $\delta^{18}\text{O}$ of sulfate and water in the pit lake is consistent with pyrite oxidation under predominantly anaerobic conditions where all of the oxygen molecules in the sulfate come from water (Pellicori et al. 2005). However, it has also been demonstrated that rapid exchange of oxygen isotopes with water can occur during intermediate steps in the oxidation of sulfide to sulfate, causing the isotopic composition of sulfate to approach that of the surrounding water irrespective of whether pyrite oxidation was initially aerobic or anaerobic (Seal 2003). In contrast to the Berkeley pit lake, the heavier $\delta^{18}\text{O}$ and $\delta^{34}\text{S}$ values of West Camp sulfate suggest mixing of SO₄ derived through pyrite oxidation with SO₄ derived from dissolution of hydrothermal anhydrite (Pellicori et al. 2005).

4.3 Isotopic Composition of Water and Dissolved Inorganic Carbon

The H and O isotopic composition of groundwater from the West Camp deviates slightly from the global meteoric water line (Craig 1961) but plots very close to the local meteoric water line based on a one-year record of precipitation in Butte (Gammons et al. 2006b) (Fig. 9). Based on these results, it can be concluded that West Camp groundwater is of local meteoric origin and underwent minimal evaporation prior to its infiltration into the mine workings.

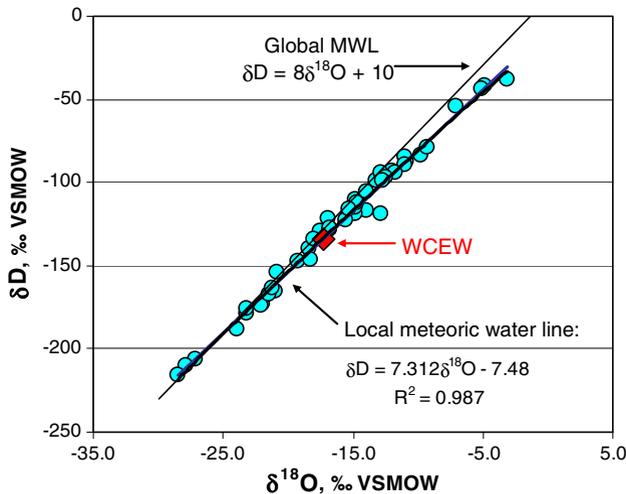


Fig. 9 δD versus $\delta^{18}O$ of Butte precipitation (Gammons et al. 2006b), the West Camp groundwater (this study), and the global meteoric water line of Craig (1961)

The isotopic composition of dissolved inorganic carbon (DIC) from the WCEW ($\delta^{13}C = -13.4 \pm 1.4\text{‰}$) is intermediate between that of atmospheric CO_2 (-7‰) and that of biogenic CO_2 in soil and shallow groundwater (-20 to -30‰) (isotopic ranges from Deines 2004). However, our calculations suggest that the DIC in the West Camp has re-equilibrated with carbonates (e.g., calcite, rhodochrosite) in the mine workings, making it impossible to tell its initial source. Rhodochrosite from the West Camp mines has a range in $\delta^{13}C$ of -7.2 to -7.8‰ (Garlick and Epstein 1966). Using published equilibrium C isotope fractionation factors for rhodochrosite-calcite (Deines 2004), and for calcite- CO_2 - HCO_3^- (Clark and Fritz 1997), the isotopic composition of HCO_3^- coexisting with rhodochrosite at $12.5^\circ C$ is predicted to be -11.9‰ . From V-MINTEQ, roughly 75% of the DIC in the West Camp is bicarbonate ion, and 25% is carbonic acid. Following these constraints, the calculated values of $\delta^{13}C$ - HCO_3^- and $\delta^{13}C$ - H_2CO_3 for the West Camp waters are -10.8‰ and -21.2‰ , respectively. The value so derived for $\delta^{13}C$ - HCO_3^- is close to what was predicted assuming equilibrium with rhodochrosite (-11.9‰), which is not surprising given the abundance of this phase in the mineralized veins.

4.4 Importance of Metal Sulfide Clusters

As shown above, a significant and possibly dominant fraction of dissolved sulfide and iron in the West Camp groundwater is present as $FeS_{(aq)}$. The $FeS_{(aq)}$ compounds represent a continuum of polynuclear species of varying age, stoichiometry, and mass. These species most likely formed in the flooded mine workings by combination of Fe^{2+} and dissolved sulfide liberated by separate microbial processes. Given the large isotopic separation between $\delta^{34}S_{H_2S}$ and $\delta^{34}S_{SO_4}$ noted above, there is little doubt that the sulfide in the WCEW water (as either H_2S , HS^- , $FeS_{(aq)}$ or other form) is biogenic. However, we note that no experimental work has been completed to date concerning possible isotopic fractionation between aqueous sulfide and $FeS_{(aq)}$.

Our results demonstrate the value of cyclic voltammetry to sort out detailed, in situ speciation of dissolved sulfide and metals in sulfidic waters, and also demonstrate potential problems with more commonly used methods for investigating aqueous sulfide chemistry in the field. In the case of the West Camp groundwater, higher total dissolved sulfide measurements were obtained gravimetrically as opposed to colorimetrically, and this discrepancy has been traced to the formation of $\text{FeS}_{(\text{aq})}$ clusters that are not completely dissociated by the Methylene Blue reagent. In lieu of voltammetric work, it is recommended that *both* colorimetric and gravimetric analysis of dissolved sulfide be performed in future studies of sulfidic waters, especially in cases where the ratio of dissolved sulfide to dissolved heavy metal (Fe + Zn + Cu) is low or approaching unity, as in the West Camp waters of this study. In such cases, the gravimetric analysis may be closer to the concentration of *total* dissolved sulfide in the water sample, whereas the colorimetric analysis may be a better approximation of the “free” sulfide (i.e., sum of H_2S , HS^- , and simple, mononuclear metal-sulfide complexes). Until more work is completed to further investigate these relationships, it may be wise to refer to dissolved sulfide measurements obtained colorimetrically as “methylene blue sulfide.” The existence of $\text{FeS}_{(\text{aq})}$ species also complicates the determination of metal sulfide solubility products and may account for at least part of the significant spread observed in field-based calculations of ion activity products for $\text{FeS}_{(\text{s})}$ recently reported by Chen and Liu (2005).

4.5 Implications to Mine Water Remediation

Compared to the Berkeley pit lake and flooded East Camp mine shafts (Pellicori et al. 2005), the water quality of the West Camp mine water of Butte is relatively benign. Concentrations of dissolved heavy metals such as Cu, Zn, and Pb are well below regulatory standards for aquatic life or human health, and levels of dissolved As, while above the new US EPA drinking water standard of 10 $\mu\text{g}/\text{l}$, are still much lower than in the pit lake and surrounding groundwaters. The main contaminant in the West Camp water that represents a possible health hazard is the very same compound that is directly responsible for its low trace metal concentrations, i.e., dissolved sulfide. The unforeseen establishment of sulfate reducing bacteria in the West Camp mine workings has resulted in precipitation of dissolved metal as metal sulfide minerals in the underground passageways, and as a result the contained groundwaters have much lower concentrations of toxic metals compared to the other mine waters in the Butte district. The colonization and spread of sulfate-reducing bacteria through the West Camp has occurred despite low concentrations of nutrients such as nitrate and phosphate, and in the absence of any obvious organic carbon source, other than the timber used to reinforce the underground mine workings.

An interesting question is to speculate whether sulfate-reducing bacteria may be present in the flooded mine complex of the East Camp, and if not then why not. Up to date, no water samples with detectable quantities of dissolved sulfide have been obtained from any of the East Camp shafts. With the exception of the Kelley Mine shaft (Fig. 1), which was the location of the main dewatering pumps in the Butte district, all of the flooded mine shafts of the East Camp have pH values above 5.5 (Gammons et al. 2006a; Metesh and Duaiame, 2000), and are, therefore, amenable to SRB growth. All of the East Camp mine waters are also anoxic, at least below a depth of $\sim 10\text{--}30$ m, and have moderately reducing Eh, with essentially all dissolved Fe in the ferrous state (Pellicori et al. 2005). It is possible that SRB exist at depth in the East Camp, but that their presence has not been detected because whatever small amounts of H_2S that are produced are rapidly consumed by

precipitation of less soluble Zn or Cu sulfides, by conversion of ferric hydroxide or hydroxy-sulfate minerals to FeS, or by production of aqueous metal clusters that are not detectable by colorimetric methods. Since the underground workings of the East Camp were dewatered for a longer period of time than the West Camp, it is reasonable to assume that they contain a greater proportion of pyrite oxidation products such as jarosite, schwertmannite, or ferric hydroxide (ferrihydrite). Heterotrophic bacteria will reduce Fe(III) before SO_4^{2-} and, therefore, as long as the supply of Fe(III) minerals lasts it is unlikely that sulfate-reducing bacteria can compete with Fe-reducing bacteria for the limited supply of nutrients and dissolved organic carbon in the flooded mine workings.

Ultimately, the matter of SRB establishment in the East Camp may be less a question of “if” as one of “when.” It is very possible that the deep groundwaters will become sulfidic in the future, once bacterial reduction of Fe(III) to Fe(II) eliminates all residual oxidation products that accumulated in the years when the workings were de-watered. This concept has important implications to future management of mine waters in Butte, as well as other flooded underground mine workings with a water chemistry that is favorable for bacterial sulfate reduction.

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