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Geochemistry and Stable Isotopes of the Flooded Underground Mine Workings of Butte, Montana

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Abstract

Over a century of mining and smelting of the world-class porphyry lode ore deposit at Butte, Montana, has resulted in extensive environmental damage. In addition to its being the location of one of the world's largest and most acidic mining pit lakes, Butte is host to over 16,000 km of flooded underground mine workings. Of the more than 60 mine shafts that have historically operated in Butte, approximately one dozen are presently accessible for groundwater sampling. The geochemistry of the mine shaft waters is zoned and roughly coincides with a district-wide zonation in hydrothermal alteration and mineralization. Mine waters in the so-called "Central zone" of intense phyllic and advanced argillic alteration have lower pH and very high concentrations of As, Fe, Mn, and Zn, but very low concentrations of dissolved Cu. The scarcity of Cu is attributed to cementation onto scrap iron left in the mines, and/or to replacement of preexisting sulfide minerals below the water table in a manner analogous to supergene enrichment processes. At the other extreme, mine waters in the "Peripheral zone" of weakest alteration have near-neutral pH, low metal concentrations, and contain dissolved sulfide (H_2S, HS^-). These waters are close to equilibrium with calcite, siderite, crystalline or amorphous $MnCO_3$, and mackinawite (poorly crystalline FeS). A suite of deep groundwater monitoring wells completed in fractured and mineralized Butte Quartz Monzonite, unassociated with the mining complex, shows a similar range in groundwater chemistries to the mine shaft waters, suggesting a fundamental control of bedrock geology on water quality.

Based on its isotopic composition, aqueous sulfate in the Butte mine waters was sourced from a combination of pyrite oxidation and leaching of hydrothermal anhydrite associated with early, porphyry-style Cu-Mo mineralization. Aqueous sulfide in the Peripheral zone mine workings is 28 to 50 per mil depleted in ^{34}S relative to coexisting aqueous sulfate, consistent with microbial sulfate reduction. Dissolved inorganic carbon in the majority of the waters sampled appears to have isotopically equilibrated at low temperature with hydrothermal rhodochrosite, an abundant mineral at Butte. Waters with the highest H_2S concentrations also have unusually high dissolved inorganic carbon concentrations that are depleted in ^{13}C, consistent with an influx of CO_2 from microbial oxidation of organic carbon. The source of organic carbon is not known, but may include timbers used to reinforce the tunnels and stopes.

In contrast to the large horizontal gradients in mine water chemistry on a district scale, vertical gradients in chemistry and temperature within each individual shaft at Butte are negligible, possibly due to vertical water circulation. The circulation model is consistent with data on the local geothermal gradient in Butte, and explains why the deepest mine shafts tend to have the warmest water. The Kelley mine has an anomalously warm temperature (~35°C), and some of the excess heat in this mine shaft may have come from pyrite oxidation, a highly exothermic reaction. The flooded underground mine complex of Butte has potential for heat recovery using modern heat pump technology.

Introduction

THE STUDY of mine water geochemistry has relevance to economic geologists for a number of reasons. From an exploration point of view, the release of trace metals and other constituents during the natural weathering of mineral deposits often creates a geochemical anomaly which the discerning prospector can identify and interpret as a pathfinder to ore (Rose et al., 1979). The same processes occur during weathering of mined deposits, albeit at a greatly accelerated rate (e.g., Nordstrom and Alpers, 1999). During mine operations, management of water can be a major logistical issue and after closure, the quality of any groundwater and surface water leaving a mine site is typically subject to stringent and enforceable numerical standards. Therefore, better knowledge of the processes that control the chemistry of mine waters is of immediate value to the mining industry. Finally, acidic mine waters sometimes have concentrations of dissolved metals that are high enough to be extracted at a profit. This is certainly the case for active heap-leach copper mines, for example. However, in rare cases, it is also true of abandoned mine sites. The Berkeley pit lake of Butte, Montana, is one example, as will be shown below.

Besides being one of the world's largest and most extensively studied porphyry deposits, the mines of Butte, Montana, offer an unparalleled opportunity to examine the geologic and microbiological processes that control mine water chemistry. Contamination from mining and smelting of the Butte orebodies has created the largest Environmental Protection Agency (EPA) Superfund complex in the United States (Moore and Luoma, 1990; Frandsen, 2006), and remedial work is still ongoing at a

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Acronyms Used

BSR: bacterial sulfate reduction
DIC: dissolved inorganic carbon
DO: dissolved oxygen
LEL: local evaporation line
LMWL: local meteoric water line
S.C.: specific conductance
S.I.: saturation indices

very heavy cost. Butte's most famous landmark is the Berkeley pit lake (see http://www.pitwatch. org/), a huge manmade lake occupying a former open-pit copper mine, with strongly acidic pH and extremely high concentrations of Cu, Zn, Fe, and other dissolved metals. The geochemistry and limnology of the Berkeley pit lake are well documented (Davis and Ashenberg, 1989, Robins et al., 1997; Jonas, 2000; Gammons et al., 2003; Pellicori et al., 2005; Gammons and Duaime, 2006). Less well documented is the geochemistry of the extensive flooded underground mine network, perhaps the largest of its type in the world, that exists below and adjacent to the pit lake.

Gammons et al. (2006a) summarized historical data collected by the Montana Bureau of Mines and Geology (MBMG) on the geochemistry of the roughly one dozen flooded mine shafts in Butte that are accessible for collection of water samples. Metesh (2004, 2006) provided a detailed analysis of the history of flooding of the underground mines, and also performed geochemical modeling of the submerged mine workings. Roesler et al. (2007) conducted a detailed study of a pumping well that drains the southwestern portion of the underground mines of Butte, and presented stable isotopic and geochemical evidence for bacterial sulfate reduction in these flooded mine workings. The current paper builds on these previous works and provides the most comprehensive picture to date of horizontal and vertical gradients in mine-water chemistry and stable isotopic composition of the flooded underground mines of Butte. A number of geologic and microbial processes are discussed to explain the field observations, many of which are backed up by thermodynamic calculations.

Site Description

Geology and mineralization

The ore deposits of Butte, Montana, have a complex history of multiple mineralizing events that is still being unraveled today. Early works outlining the basic geology of Butte include Sales (1914) and Meyer et al. (1968, and references therein), as well as a compilation of papers published as a Butte field trip guide (Miller, 1973). George Brimhall and coworkers advanced our understanding of the genesis of the Butte deposits and porphyry copper deposits in general (Brimhall, 1977, 1979, 1980; Brimhall and Ghiorso, 1983; Brimhall et al., 1985; Ague and Brimhall, 1989). More recent contributions include the geochronological study of Lund et al. (2002), the stable isotope study of Field et al. (2005), and the fluid inclusion papers of Rusk et al. (2004, 2008). Much of the following description is synthesized from Meyer et al. (1968) and Rusk et al. (2008).

The predominant host rock in the Butte district is the Butte Quartz Monzonite (Fig. 1), dated at ~ 76 Ma (Lund et al.,

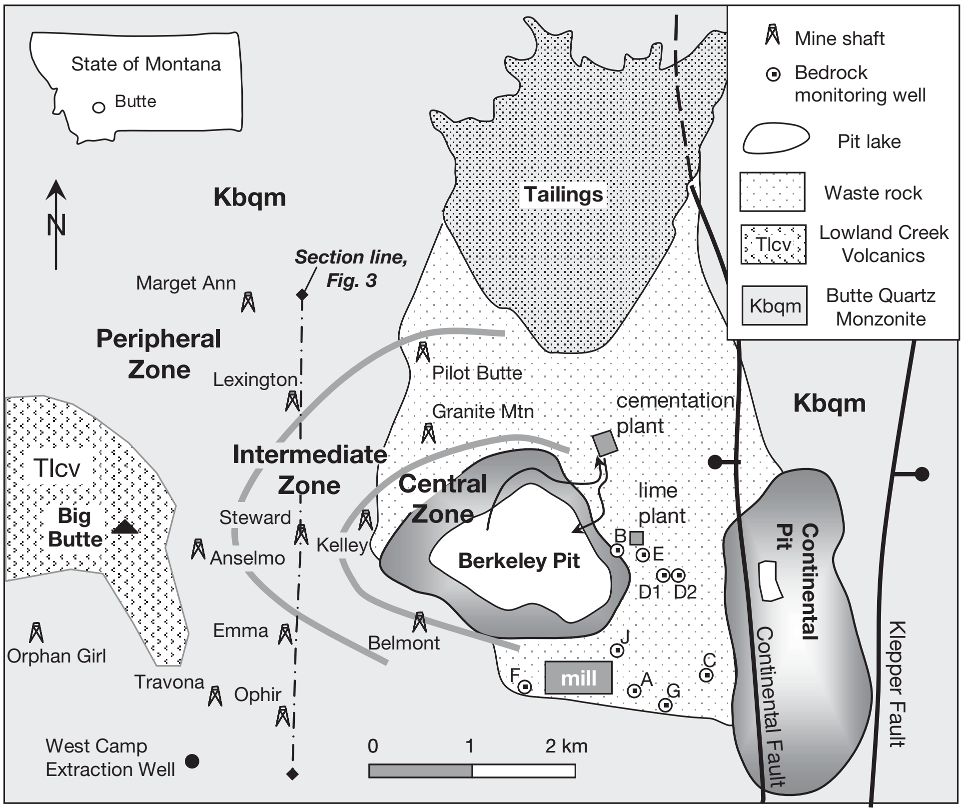

FIG. 1. Map of a portion of Butte, Montana, showing the location of the main geologic and mining features discussed in the text. Geology simplified from Rusk et al. (2008) and Meyer et al. (1968). The outlines of mining features were taken from a 2007 aerial photograph.

2002). The Butte Quartz Monzonite is the largest pluton within the late Cretaceous Boulder batholith, and has a borderline granite-to-quartz monzonite composition consisting of 35 to 40 vol percent plagioclase, 20 to 25 percent quartz, 20 to 25 percent K-feldspar, and 15 to 20 percent biotite + hornblende, with trace accessory minerals including apatite, magnetite, titanite, and ilmenite. The Butte Quartz Monzonite on Butte Hill is cut by a number of pegmatite and aplite dikes that are late differentiates of the parent Butte Quartz Monzonite magma. A distinctly younger set of quartz porphyry dikes dated at 66 ± 1 Ma are roughly coeval with "pre-Main stage" porphyry Cu-Mo mineralization at Butte. This event resulted in formation of a very large but low-grade porphyry deposit, with widespread potassic alteration reflected in conversion of hornblende to biotite and plagioclase to K-feldspar. Mo-rich veins are generally younger than Cu-rich veins, and occur as two large domes defined by disseminated molybdenite and an abundance of magnetite.

Superimposed on the porphyry Cu-Mo system is a younger set of subvertical, Cordilleran-style Main stage hydrothermal veins. Many of the Main stage veins were unusually thick (up to 10 m) and continuous, and were mined for strike lengths of >3 km and depths up to >1 km (Figs. 2, 3). Main stage mineralization was strongly zoned, with a Cu-rich Central zone centered more or less over the present-day Berkeley pit, grading outward into a Cu-Zn–rich Intermediate zone, and a Zn-Pb-Ag-Mn–rich Peripheral zone (Meyer et al., 1968; Figs. 1, 4). Hydrothermal alteration associated with the Main stage event was also zoned, with intense phyllic and advanced argillic alteration in the Central zone, grading outward into weaker phyllic, argillic, and propylitic alteration toward the Peripheral zone. Although detailed fluid inclusion studies are lacking, it appears that the Main stage event occurred at shallower depths and lower temperatures than the earlier porphyry system (Rusk et al., 2008). Within the Central zone, the Main stage veins share features in common with high-sulfidation epithermal deposits, including the abundance of high f_{S_2} minerals such as enargite, bornite, and hydrothermal chalcocite, as well as hypogene advanced argillic alteration. Brimhall (1979) stressed that the Main stage hydrothermal event was key in remobilizing metals from the low-grade porphyry protore into the large and unusually high grade Main stage veins that made Butte famous. Another important process was supergene enrichment, which resulted in leaching of hypogene Cu-(±Fe)-sulfides and reprecipitation of Cu as chalcocite (Cu_2S) below the water table (McClave, 1973; Brimhall et al., 1985; Ague and Brimhall, 1989).

Ignimbrite and dikes of rhyolitic composition belonging to the Eocene Lowland Creek Volcanics crop out to the west of the main zone of mineralization on Butte Hill (Fig. 1). These rocks, dated at 51.5 Ma, are essentially unmineralized. Two large normal faults—the Continental and Klepper faults—border the district to the east. The Continental fault is west-side-down, whereas the Klepper fault has the reverse sense of offset. The

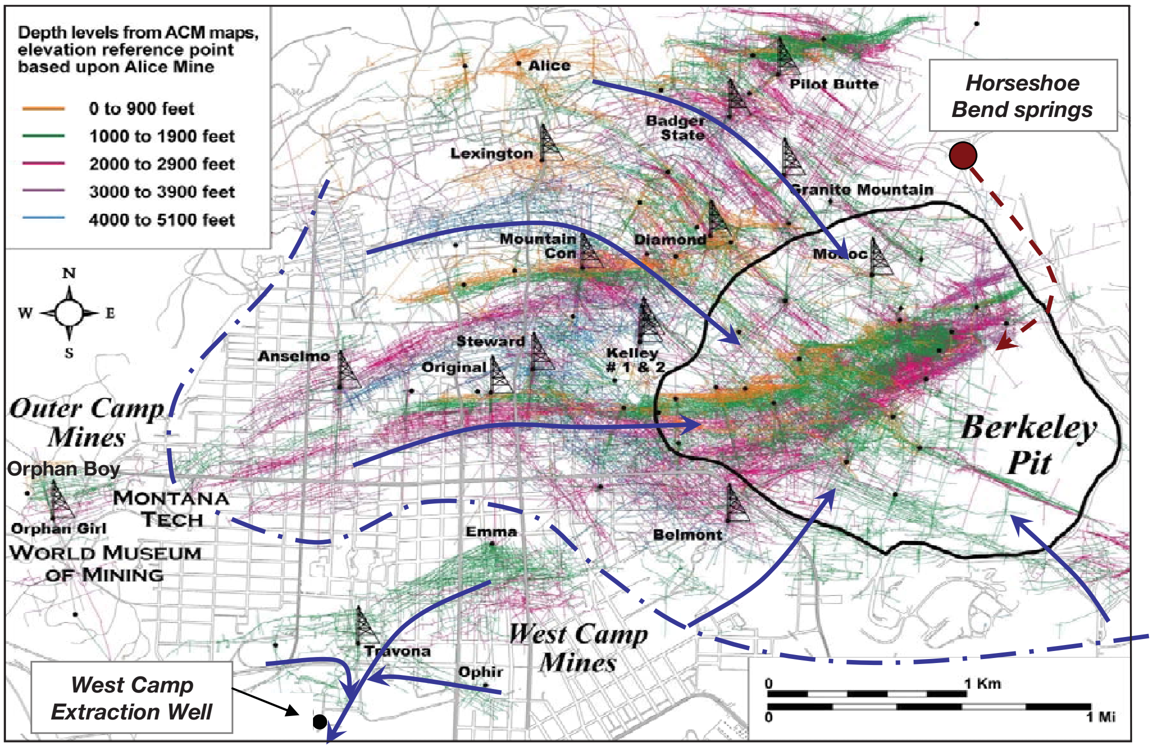

FIG. 2. Map showing the extent of major underground mine workings, color-coded for depth below the ground surface at the Alice mine (located near the top of the map). Black dots show the location of older mine shafts, most of which are no longer accessible. The blue arrows show the approximate direction of groundwater flow, and the dot-dashed line is a groundwater divide. The dashed brown arrow shows the location of the Horseshoe Bend springs which in the past was dumped into the Berkeley pit but is now diverted away from the pit and treated with lime. The gray overlay shows streets of the city of Butte. Modified from Duaime et al. (2004).

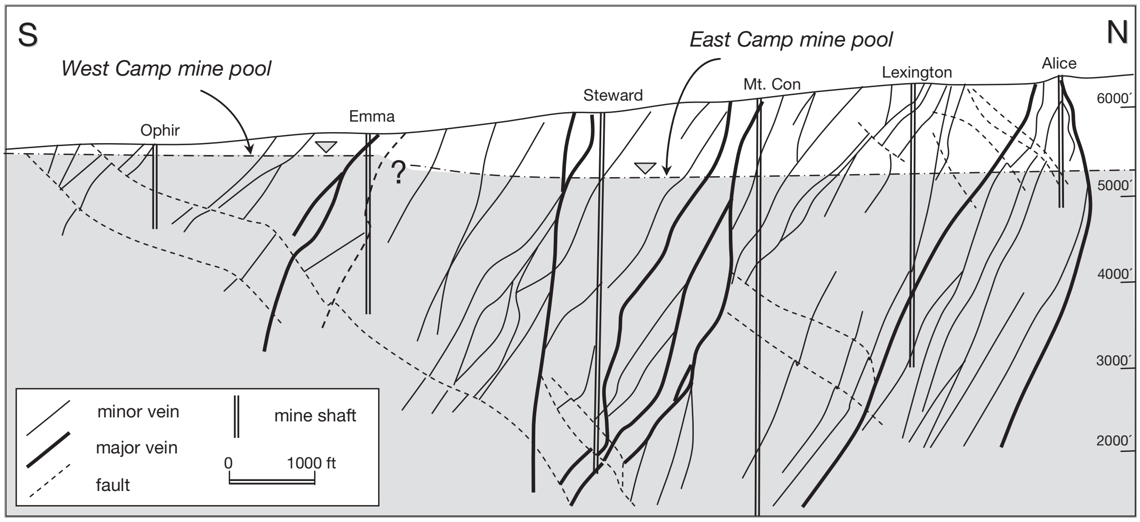

FIG. 3. Cross section along an approximately north-south transect showing the geometry of major Main stage veins and the location of the present water table (modified from Meyer et al., 1968). Refer to Figure 1 for location of this section.

Continental porphyry Cu-Mo deposit, which is the site of present-day mining in Butte (Czehura, 2006), resides in the horst formed between these two structures (Fig. 1). Based on geologic correlations, there has been at least 1,000 m of vertical offset along the Continental fault (Czehura, 2006). In terms of mine drainage chemistry, the Continental fault is important as it separates intensely altered, pyrite-rich rock with high acid generation potential to the west from weakly altered, low-pyrite rock with significant acid neutralization potential (in the form of disseminated calcite) to the east (Newbrough and Gammons, 2002). Thus, in contrast to the Berkeley pit lake, which is highly acidic and metal rich, a small lake in the Continental pit has near-neutral pH with relatively low dissolved metal concentrations (Table 1).

■ = abundant
▬ = common
─ = minor

		pre-Main Stage	Main Stage Central	Main Stage Intermed.	Main Stage Periph.
gangue minerals	quartz	■	■	■	■
	calcite	─	─	▬	■
	ankerite				▬
	rhodochrosite			─	■
	rhodonite			─	■
	anhydrite	■			
	K-feldspar	▬			
	magnetite	▬			
	rutile	─			
ore minerals	pyrite	▬	■	■	■
	chalcopyrite	■	▬	▬	─
	bornite		▬	■	─
	chalcocite		■	■	
	covellite		▬		
	digenite		▬		
	enargite		■	■	
	molybdenite	▬			
	sphalerite		─	▬	■
	galena		─	▬	■
	tennantite			▬	
	tetrahedrite				▬
	argentite				─

FIG. 4. Simplified vein mineral paragenesis for the Butte orebodies. Modified from Meyer et al. (1968), Czehura (2006) and Rusk et al. (2008). See Meyer et al. (1968) for a more complete listing of minerals in the Main stage veins.

History of mining and mine flooding

Hard-rock mining began in Butte during the 1870s and has continued with a few brief interruptions to the present day. Total production through 2003 is estimated at 1×10^{10} kg Cu, 2.2×10^9 kg Zn, 1.7×10^9 kg Mn, 3.9×10^8 kg Pb, 1.5×10^8 kg Mo, 2.3×10^7 kg Ag, and 0.9×10^4 kg Au (Duaime et al., 2004). Early mining concentrated on the high-grade Main stage veins and employed underground stoping methods. The vast underground mine complex (Fig. 2) was accessed by more than 75 km of vertical shafts and over 16,000 km of horizontal tunnels on levels that were spaced at 100 ft (30.5 m) intervals (Duaime et al., 2004). Between 1953 and 1963 the Anaconda Mining Company conducted a large underground block-caving operation to extract disseminated Cu ore in the vicinity of the Kelley mine shaft (Miller, 1973). However, Anaconda eventually shifted its focus to open-pit mining. The Berkeley pit was excavated between 1955 and 1982, and the nearby Continental pit broke ground in 1981. On April 23, 1982, Anaconda announced they were suspending all Butte operations, with the exception of the Continental pit, which was kept open for another year. Mining of the Continental pit resumed in 1986 under a different owner, and has continued—with one interruption from 2000 to 2003—to the present day (Czehura, 2006).

The main pumps used to dewater the underground mines and Berkeley pit were located at level 3900 (1,110 m below surface) of the Kelley mine (Figs. 1, 2). To lessen the quantity of water that needed to be pumped, a smaller network of underground mines, referred to as the West Camp (Fig. 2), were sealed off from the rest of the workings by bulkheads. To prevent flooding of residential basements, it later became necessary to install a pump to maintain a constant mine pool elevation within the West Camp. The pumping station was initially

TABLE 1. Representative Geochemical Data for Miscellaneous Mine Waters of Butte (all data are in mg/L unless otherwise noted)

	Sample depth (m)	Sample date	Data source[1]	Temp (°C)	pH (s.u.)	Eh (mV)	SC (mS/cm)	Al	As	Ca	Cu	Fe	K	Mg	Mn	Na	Ni	P	Sr	Zn	SiO_2	Cl^-	HCO_3^-	SO_4^{2-}	ΣS^{2-}
Pit lakes																									
Berkeley pit lake	Surface	5/14/03	a	14.0	2.71	630	4.65	134	0.38	420	64.8	254	14	302	161	71	n.a.	n.a.	n.a.	275	n.a.	n.a.	<0.1	4530	<0.004
Berkeley pit lake	220	5/14/03	a	6.6	2.41	450	7.92	278	0.93	422	167	973	7	483	233	75	n.a.	n.a.	n.a.	596	n.a.	n.a.	<0.1	8160	<0.004
Continental pit lake	Surface	Average[2]	b	10.9	7.20	n.a.	1.95	<0.2	<.01	420	0.57	0.1	10	36	3.1	37	0.03	n.a.	4.0	3.29	17	9.1	140	1208	<0.004
Bedrock monitoring wells																									
A	227	Average[2]	b,c	18.2	6.48	224	1.67	<0.2	0.06	193	<.01	14.8	23	54	4.9	118	0.01	n.a.	0.76	0.11	51	16	60.3	940	<0.004
B	195	Average[2]	b,c	15.2	7.31	51	1.45	<0.2	0.01	195	<.01	1.0	10	50	2.2	73	0.01	n.a.	0.84	0.01	32	25	126	709	0.010
C	244	Average[2]	b,c	16.6	5.96	200	0.70	0.4	<.01	84	<.01	7.1	10	17	1.7	25	0.01	n.a.	0.37	1.63	43	3.1	19.5	335	<0.004
D1	193	Average[2]	b,c	15.3	6.54	270	0.70	<0.2	0.01	72	<.01	6.5	12	21	1.3	22	0.01	n.a.	0.22	1.21	59	2.3	37.0	310	<0.004
D2	236	Average[2]	b,c	16.0	5.99	241	1.53	0.3	0.04	190	<.01	44.5	19	70	6.1	43	0.02	n.a.	0.45	6.00	70	5.0	22.2	954	<0.004
E	108	Average[2]	b,c	13.3	6.48	215	0.85	<0.2	0.03	95	<.01	2.5	12	30	2.0	28	<0.01	n.a.	0.68	0.03	60	4.9	47.7	399	0.018
F	195	Average[2]	b,c	16.1	7.36	121	1.57	<0.2	0.27	176	<.01	0.9	22	18	0.6	171	0.01	n.a.	4.4	0.10	21	16	163	792	0.004
G	294	Average[2]	b,c	18.7	6.33	200	0.99	<0.2	0.01	143	<.01	12.5	15	31	1.9	21	0.01	n.a.	0.52	0.11	57	1.9	29.5	534	0.006
J	210	Average[2]	b,c	22.9	3.74	417	3.54	47.1	1.18	374	23.7	345	51	98	11.6	125	0.18	n.a.	6.3	45.9	83	10	<0.01	2730	<0.004
Other																									
WCEW	153	2004	d	12.5	6.83	54	1.28	<0.2	0.10	170	<.01	0.9	6	48	5	43	0.01	0.06	1.7	<.01	19	44	342	390	0.27
HSB source	Surface	5/7/03	a	n.a.	3.57	522	3.94	66.3	<1	469	44.6	107	16	169	80	87	n.a.	n.a.	n.a.	146	n.a.	n.a.	<0.01	4120	<0.004
Precip. plant in	BPit-30	3/7/00	b	n.a.	3.13	n.a.	7.15	232	<1	422	188	942	8	501	202	80	1.3	n.a.	1.2	625	111	42	<0.01	9070	<0.004
Precip. plant out	Surface	3/7/00	b	n.a.	3.13	n.a.	7.15	227	<1	422	42	1200	7	520	202	79	1.3	n.a.	1.2	631	109	38	<0.01	9050	<0.004

Abbreviations: n.a. = not available, HSB = Horseshoe Bend, Precip. = precipitation, SC = specific conductance, WCEW = West Camp extraction well

[1] Sources of data: a = Pellicori et al. (2005); b = GWIC (2008); c = the S^{2-} measurements are from this study; d = Roesler et al. (2007)

[2] Data for bedrock monitoring wells represent the average of all analyses collected between 2000 and 2008

located at the Travona mine shaft (Figs. 1, 2), but was later moved to the present-day West Camp extraction well (WCEW), which is directly connected to the Travona mine workings at a depth of 160 m below surface (Roesler et al., 2007).

When the Berkeley pit was closed in 1982, the dewatering pumps in the Kelley mine were turned off, allowing the mine complex (with the exception of the Continental deposit) to begin flooding. Water levels in the underground mines quickly rebounded, and in November 1983 a lake began to form in the Berkeley pit (Metesh, 2006). The Berkeley pit is still flooding to this day from a combination of direct precipitation, runoff, and influent groundwater seepage from the East Camp mine workings. Prior to 2003, the rate of filling was augmented by the influx of 0.4 to 1 × 10^7 L/day of acidic seepage near the toe of the tailings dam referred to as the Horseshoe Bend springs (Fig. 2). The Horseshoe Bend seepage is presently diverted and treated with lime for re-use by the active mining operation. The Berkeley pit lake is now over 200 m deep and contains >100 billion L of water with pH <3.0, up to 150 mg/L Cu, and up to 550 mg/L Zn (Pellicori et al., 2005; Gammons and Duaime, 2006). Although highly publicized as an environmental disaster, the Berkeley pit lake is currently a source of revenue for the active mining company that is pumping water from depth and cementing the dissolved Cu onto scrap iron (Gammons and Duaime, 2006; Duaime and Tucci, 2008).

Sampling, Analytical, and Geochemical Modeling Methods

Methods are described here for samples collected from the Butte mine shafts and bedrock monitoring wells. Methods used in collection of samples from the Berkeley pit lake and West Camp extraction well have previously been published (Pellicori et al., 2005; Duaime and Metesh, 2007; Roesler et al., 2007; Duaime and Tucci, 2008).

Water samples were collected at different depths from the Anselmo, Granite Mountain, Kelley, Marget Ann, Orphan Girl, Steward, and Travona mine shafts by use of either an open bailer or a 2-L Kemmerer-type point sampler. Both devices were constructed of stainless steel. The bailer or point sampler was lowered into the shaft to the desired depth by hand or using a truck-mounted winch. Samples raised to the surface were filtered (to 0.45 μm) immediately into polyethylene bottles and preserved as needed for later chemical analysis. Although some of the mine shafts extend to depths >1,500 m, it was not possible to collect samples deeper than 500 m below ground surface owing to equipment limitations. Retrieval of deep samples proved difficult and time consuming, and gear was occasionally lost when it got hung up on debris in the shaft. Several other mine shafts, including the Emma, Ophir, and Orphan Boy shafts, are presently sealed, but could be sampled through monitoring wells with screens located approximately 9 m below the static water level in each shaft. These wells were purged at a rate of several L/s for 30 minutes prior to collection of water samples. A set of deep bedrock monitoring wells located to the southeast of the Berkeley pit (Fig. 1) were also sampled by MBMG hydrogeologists using this method, although in this case purging was allowed to continue for several hours (Duaime and Metesh, 2007; Duaime and Tucci, 2008). Although the Belmont shaft is permanently sealed, water samples can be withdrawn from a nearby well that penetrates to 600 ft (185 m) level of the mine. Sampling of the Belmont shaft in this study occurred during a 57-day pumping test of this well (see Petritz, 2008, for more details).

Field parameters including pH, temperature (T), redox potential (Eh), specific conductance (SC), and dissolved oxygen (DO) were measured in the field with a Hydrolab Minisonde MS-5 and an In-Situ Troll 9000 datasonde. The MS-5 was used to collect parameters for water samples hauled or pumped to the surface, whereas the Troll was used to collect in situ parameters in the top 100 m of the static water column in each shaft. Additional temperature data were obtained using a "Tidbit" temperature logger attached to the sampling devices that were sent to a depth >300 m below static water level. All Eh measurements were corrected to the Standard Hydrogen Electrode by calibration with ZoBells solution. Alkalinity was determined by pH titration soon after each sample was raised to the surface. Sulfidic waters were analyzed immediately for total S^{2-} (sum of H_2S + HS^-) using a portable spectrophotometer and the methylene blue colorimetric test. Filtered and HNO_3-preserved water samples were analyzed for a suite of major and trace metals by conventional ICP-AES analysis (EPA Method 200.7). Filtered and HCl-preserved samples were analyzed colorimetrically for Fe^{II}/Fe^{III} speciation using the Ferrozine procedure (Stookey, 1970). Filtered samples were speciated in the field following the method of Langner et al. (2001) for later As^{III}/As^{V} analysis. This method involves collection of two duplicate samples, one of which is immediately purged with N_2 + $NaBH_4$ to eliminate all dissolved As^{III} as arsine gas. The purged and nonpurged samples can then be stored indefinitely prior to analysis by conventional ICP-AES, which gives the As^{V} and total As concentrations, respectively.

Filtered samples for isotopic analysis of water were collected in a 10 mL glass vial with no head space. Preparation of samples for isotopic analysis of dissolved sulfide and sulfate followed the procedures of Carmody et al. (1998). Aqueous sulfide was extracted immediately after sample recovery as Ag_2S by direct addition of silver nitrate solution to a 1-L Nalgene bottle filled with unfiltered mine shaft water. This precipitate was later filtered and purified with NH_4OH to remove traces of AgCl. Aqueous sulfate was extracted as $BaSO_4$ by addition of $BaCl_2$ to a filtered water sample with pH adjusted to <3 to prevent formation of $BaCO_3$. Preparation of samples for isotopic analysis of dissolved inorganic carbon (DIC) followed a procedure adapted from Friedman (1970), in which DIC is extracted as $SrCO_3$.

All stable isotope analyses were performed at the University of Nevada-Reno using a Micromass IsoPrime stable isotope ratio mass spectrometer (IRMS). Water-$\delta^{18}O$ analyses were performed using a Micromass MultiPrep device interfaced to a dual inlet and the IRMS, and all other isotope analyses were performed using a Eurovector elemental analyzer interfaced to the IRMS. 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 versus VPDB for carbon. Sample preparation followed the method of Epstein and Mayeda (1953) for $\delta^{18}O_{water}$, Morrison et al. (2001) for δD_{water}, Giesemann et al. (1994) for $\delta^{34}S_{sulfide}$ and $\delta^{34}S_{sulfate}$, Kornexl et al. (1999) for $\delta^{18}O_{sulfate}$, and Harris et al. (1997) for $\delta^{13}C_{DIC}$. Analytical uncertainties are ±0.2 per mil for $\delta^{34}S_{sulfide}$ and $\delta^{34}S_{sulfate}$, ±0.4 per mil for $\delta^{18}O_{sulfate}$, ±0.1 per mil for $\delta^{18}O_{water}$, ±1 per mil for δD_{water} and ±0.4 per mil for $\delta^{13}C_{DIC}$.

The software package Visual Minteq (V-Minteq, version 2.32), a recent adaptation of the original Minteq program (Allison et al., 1991), was used to compute aqueous speciation and mineral saturation indices (S.I.) for selected water samples The V-Minteq database was supplemented with thermodynamic data for aqueous and solid As species given in Langmuir et al. (2006). Solubility products of 2-line and 6-line ferrihydrite were taken from Majzlan et al. (2004). For schwertmannite, parallel calculations were performed using thermodynamic data from Bigham et al. (1996) and Majzlan et al. (2004).

Gradients in Mine Water Chemistry

Horizontal gradients

Representative chemical analyses for all accessible mineshaft waters and bedrock monitoring wells in Butte are given in Tables 1 and 2, and Figure 5a summarizes regional zonation patterns in mine water chemistry. As defined in this paper, "type I" water is highly acidic and moderately oxidized (little or no dissolved O_2 present), with very high dissolved metal concentrations. Type I waters include the Berkeley pit

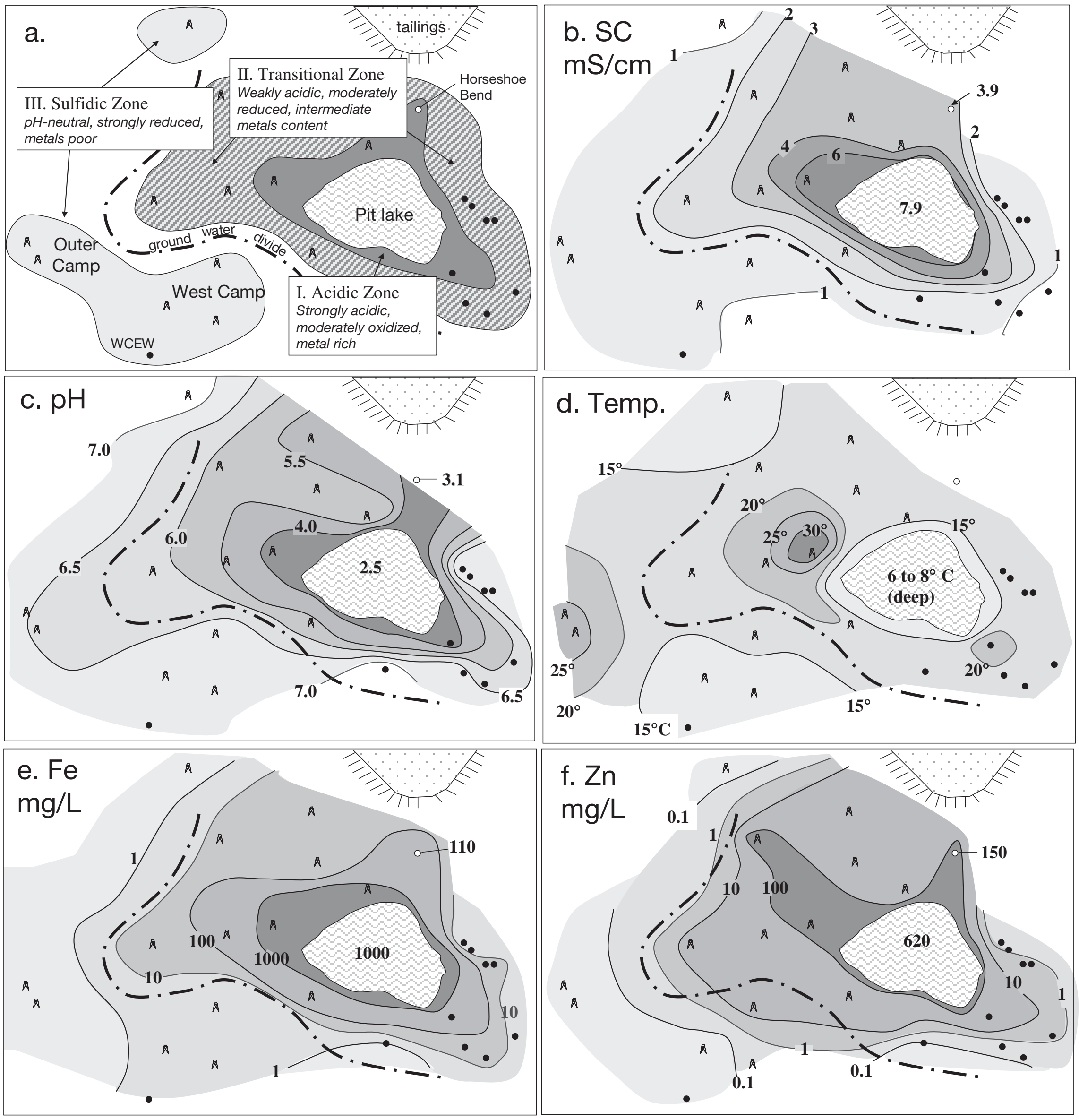

FIG. 5. Maps showing horizontal gradients in mine water chemistry: a) general zonation within the district; b) specific conductance (SC); c) pH; d) water temperature; e) Fe; f) Zn. The bold dot-dashed line is the approximate location of the groundwater divide between the East and West Camps.

TABLE 2. Representative Geochemical Data for Mine Shaft Waters of Butte[1] (all data are in mg/L unless otherwise noted)

	Sample Depth (m)	Shaft depth (m)	Sample date	Temp (°C)	pH (s.u.)	Eh (mV)	SC (mS/cm)	Al	As	Ca	Cu	Fe	K	Mg	Mn	Na	Ni	P	Sr	Zn	SiO_2	Cl^-	HCO_3^-	SO_4^{2-}	ΣS^{2-}
East Camp mine shafts																									
Anselmo	1	1311	4/20/06	17.5	5.58	242	2.22	<.2	<0.05	312	<0.01	29	14	88	18.6	38	0.02	<0.05	3.30	14.9	23	34	312	1030	<0.004
Anselmo	30	1311	4/20/06	17.5	6.25	163	2.23	<.2	<0.05	308	<0.01	30	13	88	18.5	38	0.02	<0.05	3.27	14.6	23	n.a.	314	1020	<0.004
Anselmo	137	1311	4/20/06	n.a.	n.a.	n.a.	n.a.	<.2	<0.05	302	<0.01	29	14	86	18.3	37	0.02	<0.05	3.24	14.5	23	n.a.	325	1010	<0.004
Granite Mountain	7.6	1001	9/14/06	15.5	5.82	356	3.32	0.6	<0.05	485	1.2	15	19	157	41.8	27	0.09	<0.06	4.85	17.8	20	12	n.a.	2000	<0.004
Granite Mountain	30	1001	9/14/06	15.4	5.82	324	3.31	0.4	<0.05	491	1.2	16	19	159	42.0	27	0.10	<0.06	4.92	17.9	20	n.a.	181	2020	<0.004
Granite Mountain	305	1001	9/14/06	n.a.	n.a.	n.a.	n.a.	0.5	0.03	497	1.2	16	19	163	42.2	28	0.09	<0.06	5.02	18.0	20	n.a.	155	2020	<0.004
Kelley	1	1473	5/5/06	34.6	4.37	328	7.45	31.3	10.9	432	n.a.	1530	60	307	145	72	0.40	0.06	0.63	192	82	25	11.0	5430	<0.004
Kelley	30	1473	5/5/06	34.9	4.05	285	7.38	30.7	10.7	421	0.05	1500	58	298	143	73	0.39	0.10	0.60	191	81	n.a.	6.1	5430	<0.004
Kelley	305	1473	5/5/06	n.a.	n.a.	n.a.	n.a.	42.7	11.0	366	0.05	1920	59	301	149	82	0.44	0.70	0.31	194	82	n.a.	9.8	5520	<0.004
Steward	1	1379	4/21/06	24.2	5.74	274	3.54	0.5	2.9	460	<0.01	235	32	142	26.4	42	0.04	<0.05	1.95	40.5	47	38	316	2020	<0.004
Steward	37	1379	4/21/06	24.5	5.47	230	3.52	0.6	3.0	448	<0.01	237	35	136	25.8	42	0.04	0.08	1.93	40.3	47	n.a.	320	1980	<0.004
Steward	341	1379	4/21/06	n.a.	n.a.	n.a.	n.a.	0.6	3.0	449	<0.01	235	33	138	26.0	41	0.04	<0.05	1.91	40.2	46	n.a.	310	1980	<0.004
Belmont	84	1153	2007	19.3	5.69	182	2.72	0.7	1.3	373	<0.01	179	19	112	21.0	52	<0.01	n.a.	n.a.	17.5	n.a.	30	193	1750	<0.004
Pilot Butte	9	838	2005	19.3	5.70	n.a.	3.73	0.4	0.36	502	<0.01	69.9	16	253	287	40	0.11	<0.05	6.57	55.9	35	13	35	3030	<0.004
Lexington	9	994	2000	15.6	5.76	n.a.	2.58	<.1	0.14	347	<0.01	22.1	7	104	107	49	0.08	<0.05	3.60	144	20	40	243	1570	<0.004
West Camp mine shafts																									
Emma	9	526	4/19/06	15.2	6.61	167	1.30	<.1	<0.05	181	<0.01	1.8	9	54	9.7	35	<0.01	0.06	1.48	0.15	21	41	394	390	0.37
Ophir	9	299	4/19/06	11.5	6.93	65	0.70	<.1	<0.05	88	<0.01	3.9	6	25	7.2	19	<0.01	<0.06	0.39	<0.01	14	35	231	168	0.15
Travona	1.5	434	7/20/06	13.1	6.23	70	1.28	<.2	0.09	175	<0.01	1.2	5	51	5.9	34	<0.01	<0.06	1.32	0.017	19	37	370	390	0.19
Travona	9	434	7/20/06	13.0	6.85	41	1.28	<.2	0.09	179	<0.01	1.4	8	51	6.1	36	<0.01	<0.06	1.37	0.025	20	n.a.	365	405	0.20
Travona	30	434	7/20/06	13.1	6.85	34	1.28	<.2	0.09	173	<0.01	1.3	10	48	5.9	35	<0.01	<0.06	1.31	0.028	20	n.a.	370	390	0.19
Travona	107	434	7/20/06	13.1	6.72	26	1.29	<.2	0.10	176	<0.01	1.2	6	50	5.9	34	<0.01	<0.06	1.31	0.014	19	n.a.	367	402	0.20
Travona	271	434	7/20/06	13.1	n.a.	n.a.	n.a.	<.2	0.10	175	<0.01	1.3	5	50	5.9	34	<0.01	<0.06	1.33	0.013	19	n.a.	372	393	0.40
Outer Camp mine shafts																									
Marget Ann	1.5	n.a.	8/22/06	9.7	4.59	115	0.92	<.2	<0.03	137	<0.01	0.7	6	24	1.8	12	<0.01	<0.06	2.67	0.149	8.1	18	242	264	0.008
Marget Ann	11	n.a.	8/22/06	8.9	7.24	26	0.90	<.2	<0.03	139	<0.01	<0.1	6	24	1.8	12	<0.01	<0.06	2.72	0.005	8.3	n.a.	220	267	0.230
Marget Ann	23	n.a.	8/22/06	8.6	7.50	–52	0.90	<.2	<0.03	135	<0.01	<0.1	3	24	1.7	12	<0.01	<0.06	2.67	0.005	8.1	n.a.	233	258	0.27
Marget Ann	36	n.a.	8/22/06	8.6	7.55	–74	0.90	<.2	<0.03	134	<0.01	0.1	5	23	1.7	12	<0.01	<0.06	2.61	0.004	7.9	n.a.	220	255	0.54
Orphan Girl	1	832	9/1/06	26.5	6.37	–89	1.82	<.2	<0.03	229	<0.01	0.2	9	62	5.1	113	<0.01	n/a	6.00	0.012	25	17	844	247	5.5
Orphan Girl	9	832	9/1/06	26.6	6.32	–114	1.82	<.2	<0.03	224	<0.01	0.1	9	60	5.0	112	<0.01	.17	5.92	0.009	25	n.a.	869	n.a.	6.8
Orphan Girl	30	832	9/1/06	26.6	6.30	–124	1.82	<.2	<0.03	226	<0.01	0.1	8	61	5.1	112	<0.01	.17	5.96	0.008	25	n.a.	869	n.a.	7.4
Orphan Girl	91	832	9/1/06	26.5	6.27	–130	1.82	<.2	<0.03	231	<0.01	0.2	8	63	5.1	114	<0.01	.18	5.77	0.008	25	n.a.	859	254	6.1
Orphan Girl	305	832	9/1/06	n.a.	n.a.	n.a.	n.a.	<.2	0.03	205	<0.01	0.5	10	54	4.6	104	<0.01	.17	5.34	0.081	23	n.a.	859	n.a.	5.9
Orphan Boy	9	154	4/19/06	25.7	6.63	–36	1.80	<.2	<0.05	210	<0.01	0.2	10	56	4.7	100	<0.01	.15	5.39	0.01	25	16	856	247	8.5

Abbreviations: n.a. = not available, SC = specific conductance

[1] All data are from this study except Belmont (Petritz, 2008), Pilot Butte (GWIC, 2008), and Lexington (GWIC, 2008); all data for Cl^- are from GWIC (2008)

lake, the Kelley mine shaft, and bedrock Well J. By contrast, "type III" waters have a near-neutral pH and low metal concentrations, are strongly reducing, and are characterized by the presence of reduced sulfur (H_2S, HS^-). All of the mine shafts in the West Camp and Outer Camp workings, including the West Camp extraction well, belong to type "III." Several of the deep bedrock monitoring wells to the southeast of the Berkeley pit also contain trace levels of H_2S, and have a chemistry similar to the West Camp waters. "Type II" waters have weakly acidic pH, intermediate concentrations of metals, and redox conditions that are moderately reducing (no H_2S present). Most of the mine shafts in the East Camp, with the exception of the Kelley mine, are type II. The boundary between type II and III waters is sharp, and corresponds to the groundwater divide shown in Figure 2. The boundary between type II and I waters is less well defined, and most likely is gradational.

District-wide trends in mine water chemistry are further summarized in Figure 5b-f, which shows contours in SC, pH, water temperature, and the concentrations of dissolved Fe and Zn. District-wide redox zonation is shown in an Eh-pH diagram for the Fe-S-H_2O-CO_2 system (Fig. 6). Based on data collected in this study and previous work (e.g., Pellicori et al., 2005; Roesler et al., 2007), all of the dissolved Fe in the mine shaft waters and bedrock monitoring wells is ferrous (Fe^{II}), whereas Fe in the Berkeley pit lake is present in both the Fe^{II} and Fe^{III} oxidation states (Pellicori et al., 2005). This is consistent with the measured Eh and pH conditions (Fig. 6). Based on a limited data set, dissolved As appears to be primarily in the As^{III} oxidation state in type III waters, but is a mixture of As^{III} and As^{V} in the East Camp mine shafts (Table 3). No data are available on the oxidation state of As in the Berkeley pit lake, although the presence of dissolved Fe^{III} suggests that As^{V} should be the dominant valence state. None of the mine shaft waters contain detectable DO, and DO levels typically drop to zero within the top 2 to 5 m of the Berkeley pit lake as well (Pellicori et al., 2005; Duaime and Metesh, 2007; Duaime and Tucci, 2008). As shown in Figure 5d, there are interesting district-wide trends in mine shaft temperature. Possible reasons for the temperature trends are discussed near the end of this paper.

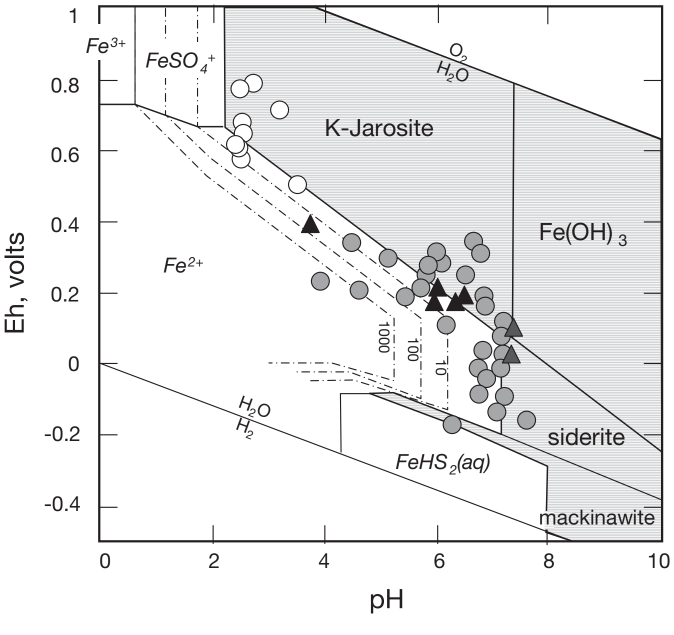

FIG. 6. Eh-pH diagram of Butte mine waters. The diagram was drawn for ΣS = 1,000 mg/L, ΣC = 100 mg/L, and ΣK = 15 mg/L. Boundaries between solids (shaded regions) and aqueous Fe species were drawn for 1 mg/L, and contours are shown for ΣFe = 10, 100, and 1,000 mg/L. Gray circles are flooded underground mine workings, solid triangles are bedrock monitoring wells, and white circles are the Berkeley pit lake and Horseshoe Bend springs. The stability fields of crystalline Fe minerals such as goethite, pyrite, and hematite have been suppressed.

All of the West and Outer Camp waters have measurable quantities of dissolved sulfide, ranging from 0.01 to 8.5 mg/L as S^{2-} (see last column in Tables 1 and 2). To the best of the authors' knowledge, the Butte district is the only location in the world where H_2S-rich water has been directly observed in an abandoned metal mine. Bacterial production of H_2S has been inferred to take place in a flooded Pb-Zn mine in Wisconsin (Labrenz et al., 2000; Druschel et al., 2002) and a Cu-Zn mine in California (Church et al., 2007) based on examinations of bacterial biofilm and sulfide precipitates coating submerged surfaces and sediment in those mines. The concentrations of H_2S in the Butte mine waters are high enough to produce a foul odor during sampling, and are a potential concern to human health, particularly in confined spaces such as mine shafts. To date, no microbial work has been published on these unique sulfidic waters.

Vertical gradients

Vertical changes in the chemistry of Butte mine shaft waters are summarized in Table 2 and Figure 7. Profiles of field parameters were collected in situ by lowering a datasonde down the top 100 m of water in each mine shaft (Fig. 7). All the shafts showed a trend of decreasing Eh with increase in depth below static water level, reaching a steady-state value at >30 m depth. These trends are predictable considering that O_2 must diffuse into the water from the overlying air column, whereas any reduced gases such as H_2S, H_2, CO, or CH_4

Table 3. Results of As^{III}/As^{V} Speciation of Mine Shaft Waters (all data in mg/L)

	Depth (m)	As(total)	As^{V}	As^{III}	%As^{III}
East camp					
Anselmo	1	0.059	b.d.	0.059	100
Anselmo	30	0.068	b.d.	0.068	100
Anselmo	137	b.d.	b.d.	b.d.	b.d.
Steward	1	1.93	1.17	0.76	39
Steward	37	1.98	1.11	0.87	44
Steward	341	2.30	1.08	1.22	53
Kelley	1	8.68	6.03	2.65	30
Kelley	30	8.54	5.84	2.70	32
Kelley	305	10.0	6.9	3.1	31
West Camp					
Ophir	9	0.059	b.d.	0.059	100
Emma	9	0.068	b.d.	0.068	100
Travona	1.5	0.076	b.d.	0.076	100
Travona	9	0.083	0.026	0.056	68
Travona	30	0.087	b.d.	0.087	100
Travona	107	0.088	b.d.	0.088	100
Travona	271	0.090	b.d.	0.090	100

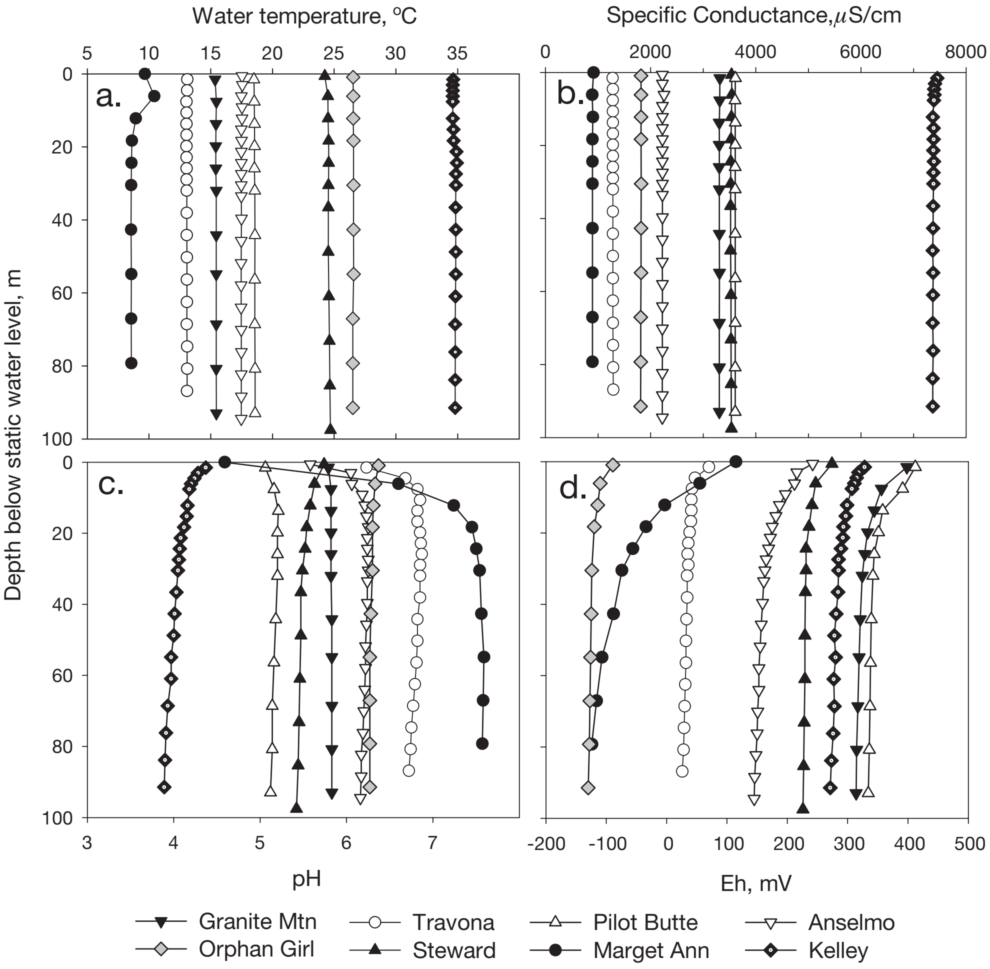

FIG. 7. Vertical changes in mine shaft chemistry: a) temperature, b) specific conductance, c) pH, d) Eh.

would be diffusing out of the water into the air. Vertical trends in pH varied from shaft to shaft. In the Marget Ann and Travona mines, pH decreased toward the surface of the water column, possibly due in part to oxidation of dissolved sulfide near the water surface:

$$H_2S + 2O_2 \rightarrow SO_4^{2-} + 2H^+ \quad (1)$$

This hypothesis is supported by the fact that dissolved sulfide concentrations in the Marget Ann mine decreased to near-zero levels at shallow depth (Table 2). In the Kelley and Steward mines, pH increased toward the water surface. This opposite trend is most likely due to evasion of dissolved CO_2. All the Butte mine shaft waters have calculated CO_2 partial pressures (Table 4) that are well above air-saturation values (~0.0003 atm at the elevation of Butte). This is particularly true of the Kelley and Steward mines, for which the calculated CO_2 partial pressures are 2.4 and 0.81 atm, respectively. Water bailed to the surface from depth in the Kelley mine was observed to effervesce, consistent with CO_2 partial pressures >1 atm. Dissolved CO_2 is the weak acid in the dissolved inorganic carbon system that—along with HCO_3^- ion—helps to buffer the pH of most groundwaters. Consequently, loss of CO_2 to the air results in an increase in pH. Consistent with this hypothesis, the pH of deep Kelley mine water measured after bailing to the surface was higher than the pH measured in situ using the submersible datasonde, sometimes by as much as 0.5 units.

In contrast to the vertical gradients in Eh and pH, the top 100 m of the water column in all of the mine shafts examined showed no gradients in either water temperature or SC (Fig. 7a, b). Data from the "Tidbit" temperature loggers also showed negligible changes in water temperature to depths as great as 300 m below static water level. Chemical analyses of samples retrieved from shallow (<3 m), intermediate (10–100 m) and deep (>100 m) locations within each shaft were likewise indistinguishable within the analytical error (with the exception of somewhat higher metal concentrations in the deep Kelley mine sample, Table 2). The absence of vertical gradients in temperature and chemical composition in the mine shaft waters implies that they continuously mix in a vertical direction. This possibility is explored in greater detail in a later section.

Changes in water chemistry with time

Although all of the data summarized in this paper were collected during the time period 2000 to 2007, flooding of the Butte underground mine workings began in 1982. The MBMG's Ground Water Information Center (GWIC) database includes chemical analyses of mine-shaft waters collected in

TABLE 4. Calculated Charge Balances, CO_2 Partial Pressures, Ionic Strengths, and Mineral Saturation Indices (S.I.) for Averaged Mine Shaft Water Compositions

				Saturation indices				
	Charge balance[1]	pCO_2 (bars)	Ionic st. (molal)	BAR	GYP	CAL	MNA	RDC
East Camp shafts								
Anselmo	0.9%(+)	0.15	0.036	*0.31*	*–0.39*	–0.71	*0.01*	*0.50*
Granite Mt.	4.6%(–)	0.21	0.057	*0.28*	*–0.05*	–1.30	*–0.40*	*0.09*
Kelley	7.8%(+)	2.41	0.125	–	*–0.13*	–4.35	–2.92	–2.41
Belmont	2.5%(–)	0.30	0.050	–	*–0.21*	–1.41	–0.72	*–0.23*
Steward	1.1%(+)	0.81	0.059	*–0.20*	*–0.15*	–1.27	–0.59	*–0.09*
Lexington	1.2%(+)	0.31	0.049	–	*–0.26*	–1.32	*0.13*	0.62
Pilot Butte	1.5%(–)	0.07	0.079	–	*–0.01*	–1.99	*–0.28*	*0.22*
West and Outer Camp shafts								
Travona	1.9%(+)	0.06	0.021	*0.39*	–0.83	*–0.31*	*0.16*	0.64
Orphan Girl	6.2%(+)	0.39	0.027	*0.41*	–1.02	*–0.08*	*0.13*	0.63
Orphan Boy	1.7%(+)	0.18	0.026	*0.37*	–1.01	*0.23*	*0.42*	0.92
Ophir	3.2%(+)	0.023	0.011	*–0.20*	–1.33	*–0.44*	*0.39*	0.88
Emma	4.3%(+)	0.076	0.021	*0.40*	–0.83	*–0.34*	*0.32*	0.81
M. Ann	1.7%(+)	0.01	0.014	*0.34*	–1.00	*–0.02*	*0.04*	0.52

	Saturation indices							
	SMS	SID	CHA	SIA	HAP[2]	MAC	SPH	PYR
East Camp Shafts								
Anselmo	*0.18*	*0.23*	*0.22*	–0.60	–	–	–	–
Granite Mt.	–0.52	–0.82	*0.20*	–0.63	–	–	–	–
Kelley	–2.53	–1.80	0.58	*–0.20*	–	–	–	–
Belmont	–0.54	*0.23*	–	–	–	–	–	–
Steward	*–0.13*	*0.40*	*0.44*	*–0.36*	–	–	–	–
Lexington	*0.52*	*–0.55*	*0.19*	–0.65				
Pilot Butte	–0.74	–0.89	*0.39*	*–0.44*	–	–	–	–
West and Outer Camp Shafts								
Travona	–1.60	*–0.44*	*0.20*	–0.64	*0.18*	–0.69	5.37	9.70
Orphan Girl	–2.25	–1.19	*0.14*	–0.66	*0.00*	*–0.58*	5.33	10.80
Orphan Boy	–2.64	–1.12	*0.14*	–0.66	*0.45*	*–0.08*	5.37	–
Ophir	–2.76	*0.16*	*0.03*	–0.81	–	*–0.04*	4.22	9.85
Emma	–1.26	*–0.38*	*0.20*	–0.64	*0.09*	*–0.42*	5.89	10.20
Marget Ann	–1.60	–0.64	*–0.12*	–0.98	–	*–0.36*	5.96	9.64

Values of S.I. in italics are considered to be close to equilibrium (within ±0.5 units of 0.0)

[1] A positive sign in parentheses indicates an excess of cations, a negative sign is an excess of anions [2] Saturation indices for hydroxyapatite were adjusted to 1 Ca atom per unit formula; Abbreviations: BAR = barite, CAL = calcite, CHA = chalcedony, GYP = gypsum, HAP = hydroxyapatite, MAC = mackinawite, PYR = pyrite, MNA = amorphous $MnCO_3$, RDC = rhodochrosite, SIA = amorphous SiO_2, SID = siderite, SMS = smithsonite, SPH = sphalerite

the 1980s and 1990s. Metesh (2004, 2006) pointed out that the water quality of several of the mine shafts during the first two years of flooding (1982–1984) was anomalously bad in terms of lower pH and higher metal and sulfate concentrations. This was especially true for mine shafts closer to the Berkeley pit, such as the Kelley, Steward, and Belmont mines. A major reason for this initially poor water quality was that the hydraulic gradients during the early period of mine flooding were such that acidic pit-wall runoff and diverted low-pH surface water (including the Horseshoe Bend seepage) entering the Berkeley open pit were percolating downward and outward into the underground mine complex (Metesh, 2004, 2006). By late 1983 the water levels in the mine shafts had rebounded to the extent that the gradients reversed and the open pit became a zone of groundwater capture. Once this occurred, water quality in the surrounding mine shafts quickly improved and reached a quasisteady state that is observed today.

Roesler et al. (2007) found no significant changes with time in any measurable parameter during a 12-month study in 2004 of the West Camp extraction well, which is pumped continuously at a rate of 500 to 750 L min^{-1}. This suggests that seasonal changes in chemistry of the flooded underground mine workings are likely to be small or nonexistent. In addition, an examination (Gammons et al., 2006a) of archived data collected by MBMG during 2000 to 2007 (GWIC, 2008) showed few long-term changes in the chemical compositions of the Butte mine-shaft waters, with the notable exception of the Kelley mine. Kelley mine water initially had poor water quality but made a definite improvement during the late

1980s, only to degrade again to lower pH and higher metal concentrations by the late 1990s. In the last 15 years there has also been a noticeable increase in the temperature of the Kelley shaft water, from the low 20s to the low- to mid-30s (°C). The reason for this increase in temperature is not known with confidence but may reflect an increase in the rate of pyrite oxidation (see below).

Thermodynamic Controls on Mine Water Chemistry

The average composition of water in each mine shaft or bedrock monitoring well was input into V-Minteq to calculate aqueous speciation and mineral S.I values. Selected results are summarized in Table 4 and Figure 8.

East Camp mine waters

The flooded East Camp mine workings include waters of type I (Kelley mine) and II (Anselmo, Belmont, Granite Mountain, Lexington, Pilot Butte, and Steward Mines). All of these waters are characterized by moderate to very high concentrations of dissolved Fe^{II}, Mn, Zn, and sulfate, with variable As concentrations (Table 2). Based on V-Minteq modeling, all of the East Camp waters are near equilibrium saturation with gypsum and barite. As discussed below, the most likely sources for the elevated dissolved SO_4 concentrations are the following: (1) weathering of pyrite and other sulfide minerals, and (2) dissolution of hydrothermal anhydrite. Although both type I and II waters are strongly undersaturated with calcite, all of the type II waters are close to equilibrium with at least one other carbonate mineral, including smithsonite ($ZnCO_3$), siderite ($FeCO_3$), rhodochrosite, or amorphous $MnCO_3$. It is likely that one or more of these metal-carbonate phases are present as secondary precipitates coating flooded mine walls, and that equilibrium between these carbonate minerals and dissolved inorganic carbon buffers the pH of the type II waters. The Kelley mine and Well J are highly undersaturated with all of the carbonate minerals, and the pH of these waters is most likely controlled by other reactions, such as equilibrium between CO_2(aq), dissolved Al^{3+}, and aluminous clay or hydroxysulfate minerals. Based on V-Minteq, Kelley water is close to equilibrium with kaolinite (S.I. = +0.12), alunite (S.I. = +0.95), and $AlOHSO_4$ (S.I. = –0.16). The apparent equilibrium with $AlOHSO_4$ (i.e., jurbanite) may be erroneous, as Bigham and Nordstrom (2000) point out that this phase rarely forms in mine waste settings in lieu of other Al-hydroxysulfate phases, such as basaluminite. Dissolved silica concentrations in East Camp waters generally decrease with increasing pH (Table 2). Type II waters are closest to equilibrium with chalcedony, whereas the Kelley mine waters are closer to saturation with amorphous SiO_2. The latter scenario is indicative of a greater extent of hydrolytic alteration which leaches cations such as Al^{3+} and K^+ out of feldspars and micas, leaving a relatively soluble, SiO_2-enriched "leached layer" behind (Helgeson, 1971; Casey et al., 1988).

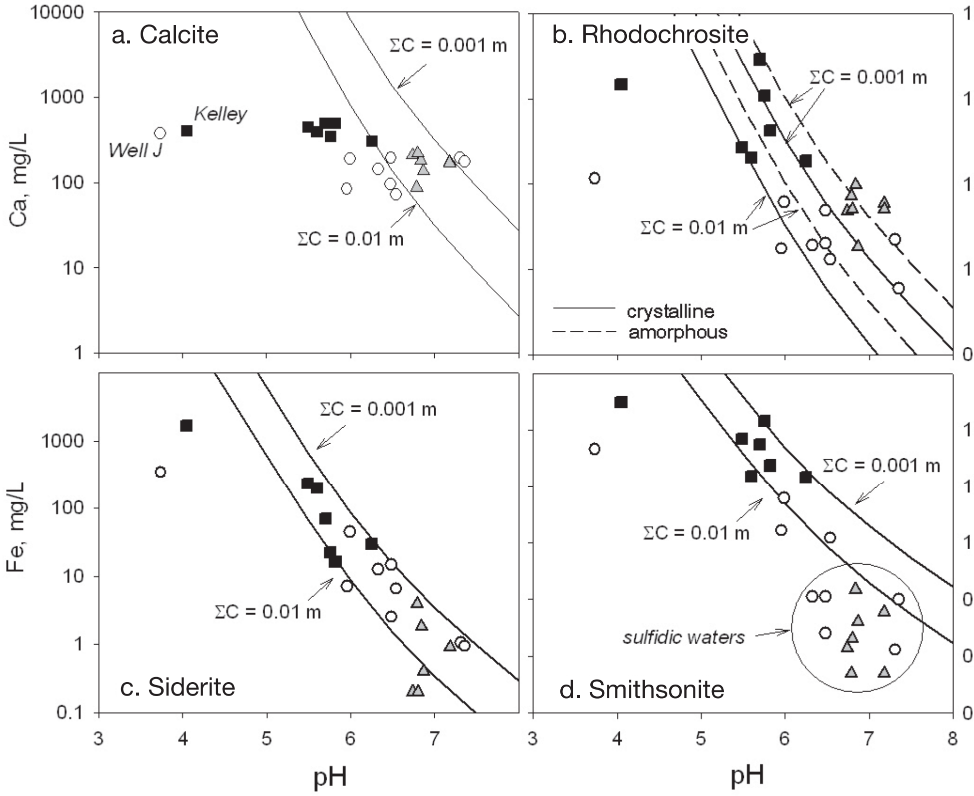

FIG. 8. Relationship between dissolved Ca, Mn, Fe, and Zn vs. pH. Filled squares are East Camp mine shafts, diamonds are West and Outer Camp waters, and circles are bedrock monitoring wells. Solubility curves for (a) calcite, (b) rhodochrosite, amorphous $MnCO_3$ (dashed lines in b), (c) siderite and (d) smithsonite are shown for comparison, assuming ΣC concentrations of 0.001 or 0.01 molal.

Because no detectable Fe^{III} was found in the East Camp mine waters, it is not possible to directly calculate the saturation state with respect to ferric minerals. However, this can be indirectly assessed by inputting the Eh measured at depth and assuming redox equilibrium between ferric solids and dissolved Fe^{II} species. The results suggest that Kelley water may be in redox equilibrium with goethite (S.I. = +0.69) and scorodite ($FeAsO_4$, S.I. = –0.18). The latter result is not surprising, given the very high concentration of dissolved As^{V} in this water (>10 mg/L, Table 3). Similar calculations (results not shown) suggest that type II waters are supersaturated with goethite and are closer to equilibrium with schwertmannite and/or ferrihydrite.

Explanation for low Cu^{2+} concentrations

Considering the fact that the East Camp mines of Butte were primarily worked for copper, it is interesting that most of their mine waters have dissolved Cu concentrations near or below analytical detection limits (Table 2). Based on V-Minteq modeling, all of the East Camp waters are strongly undersaturated with all Cu-bearing minerals in the thermodynamic database. However, it is possible that dissolved Cu concentrations are buffered by replacement reactions that occur at the surface of preexisting sulfide minerals. The replacement of pyrite by chalcocite and sphalerite by covellite can be written as follows:

$$5FeS_2(s) + 14Cu^{2+} + 12H_2O = 7Cu_2S(s) + 5Fe^{2+} + 3SO_4^{2-} + 24H^+ \quad (2)$$

$$ZnS(s) + Cu^{2+} = CuS(s) + Zn^{2+} \quad (3)$$

In both reactions, Cu^{2+} ions “scavenge” the reduced S that is present in the preexisting sulfide mineral. Reaction (2) is common in nature, and leads to coatings of chalcocite-after-pyrite that increase the average Cu grade of the orebody (McClave, 1973; Brimhall et al., 1985; Ague and Brimhall, 1989; Lichtner and Biino, 1992). Reaction (3) is less well documented in the economic geology literature but has been proposed based on detailed mineralogical studies of weathered mine tailings impoundments in Canada (Blowes and Jambor, 1990; Johnson et al., 2000). It is also possible that secondary Cu-sulfide minerals could form in the underground mine workings from direct precipitation as Cu_2S or CuS in the presence of H_2S. Such a reaction could be written as follows:

$$Cu^{2+} + H_2S = CuS(s) + 2H^+ \quad (4)$$

Although no H_2S was detected from any of the East Camp mine shafts (and no odor of H_2S was evident during sampling), it is possible that local environments of bacterial sulfate reduction exist. Because the solubility product of CuS is so much lower than that of FeS, ZnS, or MnS (e.g., Stumm and Morgan, 1996), any H_2S formed by microbial processes would likely be immediately scavenged by dissolved Cu^{2+}.

Using published free energies of formation (Faure, 1998), it is possible to place mathematical constraints on the dissolved Cu/Fe and Cu/Zn concentrations that would be present if local equilibrium were achieved with either reaction (2) or (3) above. The results of calculations for the replacement of pyrite by chalcocite (Fig. 9) suggest that reaction (2) may be buffering dissolved Cu concentrations in some type I waters, which include the Berkeley pit lake, the Kelley mine, and possibly Well J. This result should be of particular interest for the operating mine, as it implies that dissolved Cu concentrations in the pit lake may rebound to levels >100 mg/L after Cu removal by cementation, i.e., by dissolution of secondary chalcocite stored on the submerged mine walls. Based on thermodynamic data for reaction (3), the predicted Cu^{2+}/Zn^{2+} ratio for equilibrium between covellite and sphalerite is exceedingly low ($<10^{-11}$), indicating a very strong thermodynamic potential for sphalerite to be replaced by covellite in low-temperature, acidic mine waters. Sphalerite was an uncommon mineral in the Central zone of Butte, but was a major ore mineral in the Intermediate and Peripheral zones (Fig. 4).

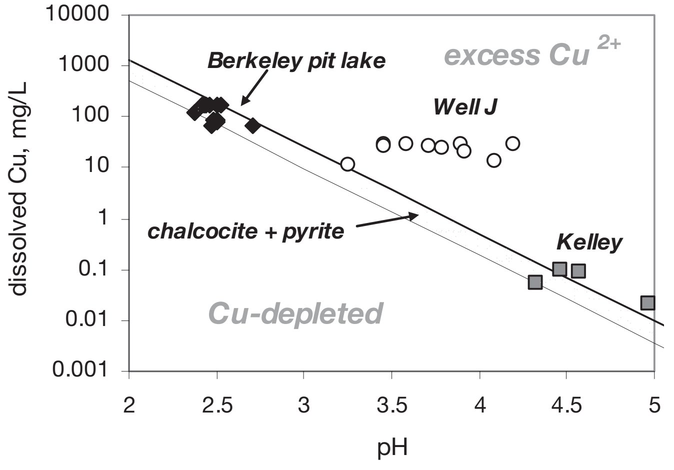

FIG. 9. The calculated concentrations of dissolved Cu in local equilibrium with the assemblage chalcocite + pyrite at different pH values. The shaded area denotes the range in uncertainty in the thermodynamic data. The calculations assume log αFe^{2+} = –2.5, and log αSO_4^{2-} = –1.9. All of the Berkeley pit lake and Kelley mine shaft waters plot near the binary assemblage buffer, whereas the Well J waters plot in the excess Cu^{2+} field. Most of the other mine shafts in the Butte district have Cu concentrations near or below the analytical detection limits. Data for Berkeley pit are from Pellicori et al. (2005); data for Well J and Kelley mine are from GWIC (2008).

An alternative explanation for the lack of dissolved Cu in the East Camp mine waters is that Cu^{2+} is cementing onto scrap iron (e.g., equipment, tools, cables, steel rails, reinforcement on mine walls and ceilings) left behind in the flooded mines. The reaction of interest can be written as follows:

$$Cu^{2+} + Fe(s) = Cu(s) + Fe^{2+} \quad (5)$$

Reaction (5) is rapid at low pH, and, as mentioned above, a large-scale project employing cementation onto scrap iron is currently being used to recover dissolved Cu from the Berkeley pit lake (Gammons and Duaime, 2006; Duaime and Tucci, 2008).

West and Outer Camp mine waters

All of the mine waters in the West and Outer Camps belong to type III, and are characterized by a near-neutral pH, strongly reducing conditions, and presence of aqueous sulfide. Unlike the East Camp waters, type III waters are undersaturated with gypsum, and are close to equilibrium with calcite. Most type III waters are also close to equilibrium with amorphous $MnCO_3$, barite, chalcedony, and hydroxyapatite (Table 4). Saturation with apatite is not surprising, given its presence as an accessory mineral in the Butte Quartz Monzonite. All of the West Camp shafts (Travona, Emma, Ophir) are near equilibrium with siderite, whereas the Outer Camp shafts are undersaturated with this phase. The latter result is most likely due to the higher concentrations of H_2S in the Outer Camp mines, which limits Fe mobility as Fe-sulfides. Likewise, because the presence of H_2S drastically reduces the solubility of Zn^{2+} by formation of ZnS(s), all of the type III waters are undersaturated with smithsonite (Table 4, Fig. 8).

Type III waters are close to equilibrium with mackinawite (i.e., crystalline FeS) but are strongly supersaturated with pyrite and sphalerite (Table 4). As is often the case in low-temperature waters, equilibrium is more quickly established with amorphous or poorly crystalline phases (such as mackinawite) as opposed to the thermodynamically stable compounds (pyrite, sphalerite). Nonetheless, pyrite framboids and individual pyrite octahedra were found attached to floating fragments of wood in the Orphan Girl shaft (Fig. 10). This shows that, given time, amorphous sulfide precipitates will convert to their crystalline counterparts. Another phenomenon that confounds attempts to thermodynamically model the sulfidic type III waters is the presence of aqueous metal-sulfide clusters. These molecules are polymeric aqueous species with a range in stoichiometry, such as Fe_xS_y, Zn_xS_y, etc., where the ratio of x/y is typically close to 1 (Luther and Rickard, 2005). For the sake of convenience, it has become customary to refer to metal-sulfide clusters by their simplified formulae, FeS(aq), ZnS(aq), etc… (Theberge and Luther, 1997). Roesler et al. (2007) recently showed that FeS(aq) clusters are the dominant form of dissolved Fe and sulfide-S in the West Camp extraction well of Butte. Similar clusters are probably present in the Outer Camp mine shafts as well.

Bedrock monitoring wells

Chemical data from the bedrock monitoring wells (Fig. 1) provide an interesting counterpart to the data collected from the flooded mine shafts. All of these wells were completed in fractured Butte Quartz Monzonite at depths ranging from 91 to 330 m below land surface. As shown in Table 1, the chemistry of the bedrock wells runs the gamut, from strongly acidic and metal rich (Well J) to pH neutral, weakly sulfidic, and metal poor (Wells B, E, F, G). Calculated Eh-pH conditions and mineral saturation indices for the bedrock wells overlap with the range of results from the mine shafts (Figs. 6, 8). This is strong evidence that the basic trends in mine water chemistry in Butte are fundamentally controlled by the

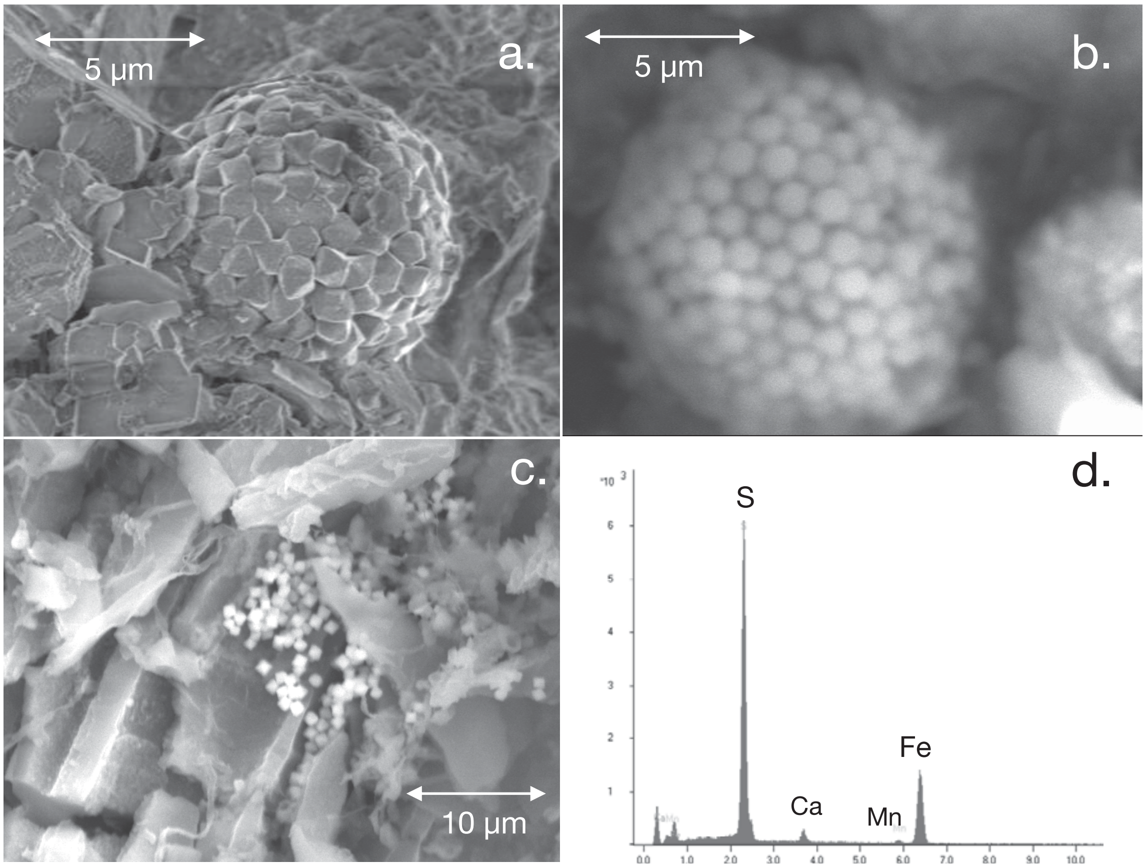

FIG. 10. Photographs of pyrite grains on wood from the Orphan Girl mine shaft. a) Field emission microscope (FEM) image of a pyrite framboid roughly 10 μm in diameter. The framboid is an aggregate of much smaller (<1 μm) pyrite octahedra. b) Scanning electron image (SEI) of a pyrite framboid. c) SEI image of individual pyrite octahedra (small white grains) scattered in the wood (blocky material in the background). d) EDS spectrum of a pyrite framboid. The Ca impurity may represent trace amounts of gypsum.

mineralogy of the surrounding hydrothermally altered rock, a point that was previously made by Metesh (2004). Following this train of thought, it is possible that the pH of some of the groundwaters in Butte (e.g., within the Central zone) could have been acidic prior to mining. As well, concentrations of dissolved metals such as As, Mn, Zn, and Fe were probably always elevated over background levels, a possibility that has implications to ongoing reclamation efforts on Butte Hill, as well as geochemical exploration for undiscovered, Butte-like porphyry deposits. This said, it is also obvious that mining has accelerated the rate of sulfide mineral oxidation and acid generation at Butte by creating a labyrinth of voids in which highly mineralized rock is exposed to weathering.

Stable Isotopes

Table 5 summarizes stable isotope data collected from mine shafts and bedrock monitoring wells in Butte. Isotopic data for the Berkeley pit lake and Horseshoe Bend springs can be found in Pellicori et al. (2005). Additional data for $\delta^{18}O$ and δD of local precipitation and miscellaneous surface waters are given in Gammons et al. (2006b).

O and H isotopes of water

A summary of the O and H isotope composition of Butte mine waters is given in Figure 11. The Butte local meteoric water line (LMWL) and local evaporation line (LEL) are taken from Gammons et al. (2006b). All of the Butte mine shafts and bedrock monitoring wells fall near the intersection of the LMWL and LEL. Since this point of intersection approximates the average isotopic composition of groundwater recharge on Butte Hill (Gammons et al., 2006b), it implies that the mine-shaft waters are of local meteoric origin and have not undergone significant evaporation prior to recharge to their respective mine pools. In contrast, the Berkeley pit

TABLE 5. Stable Isotope Data for Selected Butte Mine Waters

Date	Sample ID (depth)	$\delta^{18}O_{water}$	δD_{water}	$\delta^{34}S_{sulfate}$	$\delta^{18}O_{sulfate}$	$\delta^{34}S_{sulfide}$	$\delta^{13}C_{DIC}$
East Camp mine shafts							
2007[1]	Belmont (avg)[1]	–17.7	–136	4.9	–8.3	–	–11.9
2007[1]	Belmont (±1σ)[1]	± 0.0	± 1	± 0.7	± 0.7	–	± 2.3
5/5/2006	Kelley (1 m)	–17.5	–140	2.7	–9.9	–	–
5/5/2006	Kelley (96 m)	–17.6	–140	2.7	–8.7	–	–
5/5/2006	Kelley (305 m)	–17.7	–140	2.3	–9.4	–	–
4/8/2003	Kelley (30 m)	–17.4	–139	2.5	–10.2	–	–
9/14/2006	Granite Mt. (8 m)	–17.2	–135	3.7	–11.1	–	–14.4
9/14/2006	Granite (30 m)	–17.3	–136	3.8	–11.1	–	–13.8
9/14/2006	Granite (305 m)	–17.3	–136	3.9	–10.6	–	–14.6
4/8/2003	Steward (30 m)	–17.2	–135	5.8	–8.1	–	–
4/8/2003	Anselmo (30 m)	–17.0	–134	7.0	–7.0	–	–
West Camp and Outer Camp mine waters							
2004[2]	WCEW (avg)[2]	–17.3	–134	11.7	–3.9	–34.3	–13.8
2004[2]	WCEW (±1σ)[2]	± 0.0	± 0.5	± 0.6	± 0.8	± 1.8	± 1.4
4/19/2006	Orphan Boy	–17.6	–141	34.6	2.2	3.7	–
1/17/2006	Orphan Girl (10 m)	–	–	33.9	2.9	5.6	–
9/1/2006	Orphan Girl (2 m)	–17.7	–140	34.3	1.3	3.8	–21.2
9/1/2006	Orphan Girl (96 m)	–17.4	–139	34.0	1.2	4.7	–21.1
9/1/2006	Orphan Girl (305 m)	–17.7	–140	–	–	–	–20.9
4/19/2006	Emma	–17.4	–135	18.6	0.8	–20.9	–
4/23/2004	Emma	–	–	18.0	0.2	–24.7	–
7/19/2006	Travona	–17.3	–135	13.0	–2.9	–	–
4/23/2004	Travona	–	–	11.6	–3.5	–34.8	–
4/19/2006	Ophir	–17.5	–134	7.3	–3.1	–24.0	–
8/22/2006	Marget Ann (38 m)	–18.6	–146	15.8	–0.1	–34.6	–16.1
Bedrock monitoring wells							
12/19/2000	Well A	–	–	16.8	2.0	–	–
7/13/2001	Well A	–18.5	–150	–	–	–	–
12/27/2000	Well B	–	–	4.2	–8.6	–	–
12/21/2000	Well C	–	–	3.6	–10.8	–	–
7/17/2001	Well C	–18.6	–145	–	–	–	–
1/25/2001	Well D1	–	–	9.6	–6.4	–	–
1/3/2001	Well D2	–	–	8.3	–6.1	–	–
12/27/2000	Well E	–	–	7.9	–5.4	–	–
12/28/2000	Well F	–	–	14.7	–0.7	–	–
12/26/2000	Well G	–	–	10.6	0.3	–	–
12/19/2000	Well J	–	–	3.7	–10.0	–	–

WCEW = West Camp extraction well

[1] The values shown are the average and standard deviation of 10 isotope samples collected between July 6 and Sept. 5, 2007, during a continuous pumping test of the Belmont irrigation well (Petritz, 2008)

[2] The values shown are the average and standard deviation of 6 isotope samples taken every 2 months during 2004 (Roesler et al., 2007)

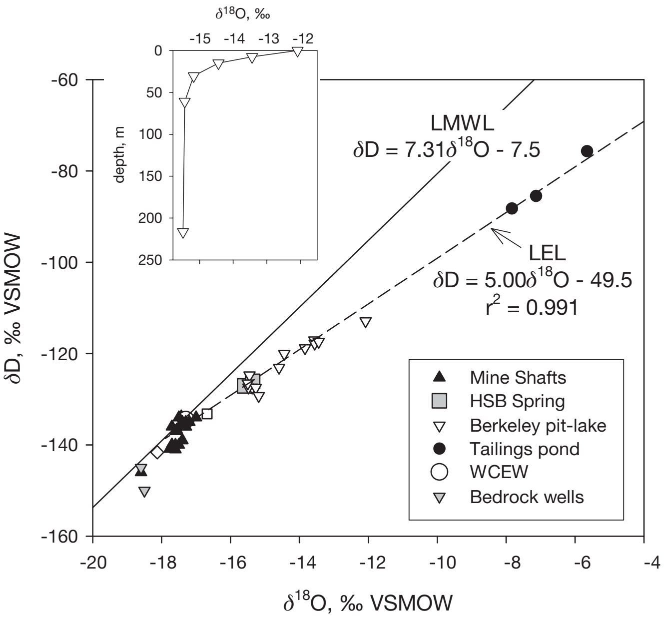

FIG. 11. Stable isotopic composition of mine waters from Butte. Data are from this study, Pellicori et al. (2005), and Gammons et al. (2006b). The inset shows vertical gradients in $\delta^{18}O$ of the Berkeley pit lake. Abbreviations: HSB = Horseshoe Bend, LEL = local evaporation line, LMWL = local meteoric water line, WCEW = West Camp extraction well. Diagram modified from Gammons et al. (2006b).

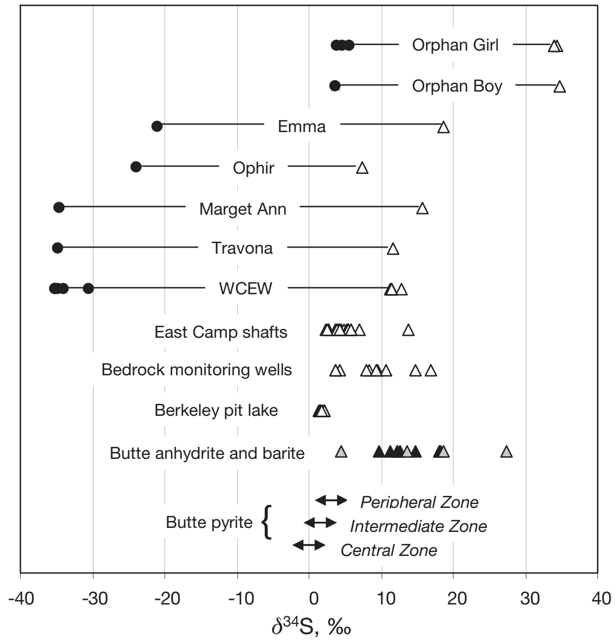

FIG. 12. S isotope data for Butte mine waters (Pellicori et al., 2005; Roesler et al., 2007; this study). Black circles are dissolved sulfide, and open triangles are dissolved sulfate. Also shown for comparison are mineral data (Field et al., 2005) for Butte anhydrite (gray triangles), barite (black triangles), and pyrite (arrows).

lake and Horseshoe Bend springs both have a distinct evaporation signature. Shallow water in the Berkeley pit lake is more enriched in $\delta^{18}O$ than deeper water (Fig. 11 inset), with up to 25 percent of the shallow water having been lost to evaporation based on isotope mass balance and kinetic enrichment calculations (Gonfiantini, 1986; Gammons et al., 2006b). Samples collected in 2003 from the tailings pond (Fig. 1) were even more strongly evaporated, with an estimated 50 to 60 percent water loss (Gammons et al. 2006b).

Significantly, the isotopic composition of Butte mine-shaft waters showed no discernable changes with depth below static water level (Table 5). This supports the idea that the mine shaft waters are vertically mixed.

S and O isotopes of dissolved S species

The $\delta^{34}S$ and $\delta^{18}O$ of dissolved sulfate from Butte mine waters and bedrock monitoring wells vary over a large range (Table 5, Figs. 12, 13). The observed variations are interpreted to be the result of three dominant processes: (1) oxidation of pyrite and other hydrothermal sulfide minerals, (2) dissolution of hydrothermal sulfate minerals, and (3) fractionation during bacterial sulfate reduction (BSR). Regarding the first process, previous workers (e.g., Field, 1966; Seal, 2003; Balci et al., 2007) have shown that oxidation of pyrite and other metal sulfides results in negligible fractionation of S isotopes, whether or not the oxidation process is microbially mediated. Thus, sulfate formed during weathering of sulfide minerals should have about the same $\delta^{34}S$ value as the precursor sulfides. Figure 12 provides $\delta^{34}S$ data (Field et al., 2005) for selected hypogene minerals from Butte, including pyrite, anhydrite, and barite. Dissolved sulfate in the Berkeley pit lake has a similar S isotope signature as Butte pyrite, supporting the hypothesis that most of the sulfate in the lake came from oxidation of pyrite (Pellicori et al., 2005). Dissolved sulfate from the Kelley mine and Well J also has $\delta^{34}S$ close to Butte pyrite, whereas sulfate from the other East Camp mine shafts is somewhat heavier. The West Camp and Outer Camp mine shafts have the heaviest sulfate (Table 5), with $\delta^{34}S$ ranging as high as +34.6 per mil (Orphan Boy shaft).

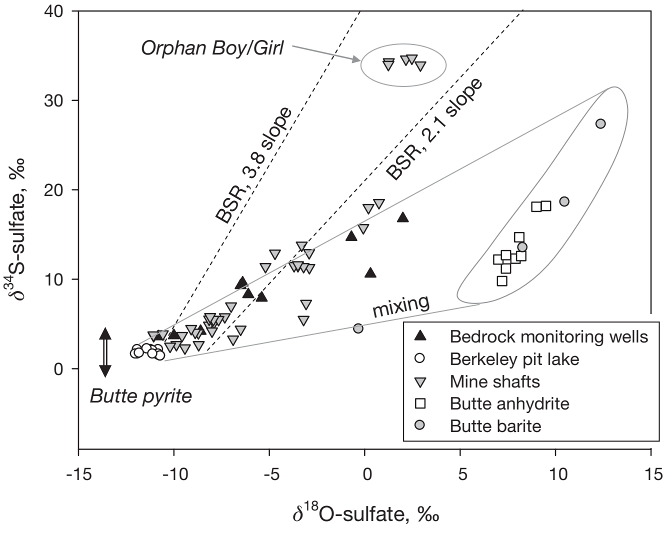

FIG. 13. $\delta^{34}S$-sulfate vs. $\delta^{18}O$-sulfate of Butte mine waters. Dashed lines show theoretical trajectories for bacterial sulfate reduction (BSR). Solid lines show approximate limits for mixing of sulfate formed by pyrite oxidation and sulfate formed by dissolution of hydrothermal sulfate minerals (anhydrite, barite). Data are from this study, Madison et al. (2003), Field et al. (2005), Pellicori et al. (2005), and Roesler et al. (2007).

The above isotopic trends can be partly explained by mixing of isotopically light sulfate derived from pyrite oxidation with isotopically heavy sulfate derived from dissolution of hydrothermal sulfate minerals, such as anhydrite or barite (Fig. 13). Waters with the lowest pH (e.g., Kelley Mine, Well J, Berkeley pit and Horseshoe Bend) predictably plot near the pyrite oxidation end member along this mixing line. The other waters most likely inherited some of their sulfate from sulfide mineral oxidation and some from sulfate mineral dissolution. Given its low solubility, it is unlikely that barite could contribute much to the total dissolved SO_4 pool. Anhydrite is a more likely source given its much higher solubility and its abundance as a pre-Main stage alteration mineral at Butte (Meyer et al., 1968; Rusk et al., 2008). Because of the intense hydrothermal overprint in the Central zone during Main stage mineralization, most of the original anhydrite was likely lost from the vicinity of the Berkeley pit and nearby Kelley mine. Preservation of anhydrite is more likely elsewhere in the district, and its abundance is furthermore known to increase with depth (John Dilles, pers. commun., 2006). Given the possibility that the mine shaft waters of Butte are circulating vertically, anhydrite may have been leached from potassically altered rock at deep levels in a given mine and then advected to shallower levels in the shaft. Once again, minimal differences were noted between the isotopic compositions of sulfate collected at different depths within a given mine shaft (Table 5).

The S isotope composition of dissolved sulfide ($\delta^{34}S_{sulfide}$) in Butte mine waters varied over a large range, from –34.6 (Marget Ann) to +5.6 per mil (Orphan Girl) (Table 5, Fig. 12). The measured isotopic separation ($\Delta^{34}S$) between coexisting sulfate and sulfide ranged from 28 to 50 per mil. Such large isotopic separation values are characteristic of bacterial sulfate reduction (Canfield, 2001), and support the conclusion of Roesler et al. (2007) that aqueous sulfide in the West Camp extraction well is of microbial origin. It is not known with confidence why some mine shaft waters have larger $\Delta^{34}S_{sulfate\text{-}sulfide}$ (e.g., Travona, Marget Ann) whereas others have lower isotopic separation values (e.g., Ophir, Orphan Boy, Orphan Girl). Considering that the Orphan waters are anomalously warm (Table 2), some of this variation could be due to temperature effects. Isotopic separation accompanying microbial sulfate reduction should decrease with increase in temperature (Canfield, 2001). However, it is also plausible that side reactions have occurred, such as loss of early-formed, isotopically depleted H_2S to sulfidation of weathered wall rock within the mine workings. As well, very little is known regarding the nature of the carbon substrate utilized by sulfate-reducing bacteria, which could vary from sample location to sample location within the district.

The dashed arrows in Figure 13 show the range in predicted trajectories for isotopic fractionation accompanying BSR (Seal et al., 2000; Seal, 2003). The Orphan samples plot squarely in the middle of these trends, and clearly these waters have been profoundly influenced by BSR. Some of the other West Camp and Outer Camp sulfates may also have been enriched by BSR (which would tend to shift their isotopes off the "mixing" line to the upper right), but not to the extent of the Orphan waters. BSR in the Orphan waters was further examined by computing trajectories of $\delta^{34}S_{sulfate}$ and $\delta^{34}S_{sulfide}$ as a function of f, the fraction of total initial sulfate reduced. These calculations assumed either a completely closed, equilibrium model or an open, Rayleigh distillation model (e.g., Clark and Fritz, 1997). The initial $\delta^{34}S_{sulfate}$ value was taken to be +5 per mil, based on interpolation of the Orphan Boy/Girl samples in Figure 13 back to the origin along the BSR enrichment trend lines, and a constant isotopic enrichment value ($\varepsilon_{sulfate\text{-}sulfide}$) of 30 per mil was assumed. The results (Fig. 14) indicate that near-complete reduction of sulfate to sulfide would be necessary to explain the measured $\delta^{34}S_{sulfate}$ and $\delta^{34}S_{sulfide}$ values of the Orphan shaft waters if an equilibrium, closed model applied. However, because BSR is a far from equilibrium process, these calculations are almost certainly erroneous. In addition, it is very likely that most of the H_2S formed by BSR was lost from the system, either through sulfidation reactions involving Fe and other transition metals stored on the weathered mine walls, or through volatilization to the atmosphere. (Regarding the second possibility, the water in the Orphan Girl mine shaft was observed to "burp" periodically during sampling, presumably due to evasion of H_2S, N_2, CO_2, and other gaseous compounds). Following the open system Rayleigh model, the measured isotopic compositions of the Orphan Boy and Orphan Girl waters correspond to an f value of ~0.62, i.e., > 60 percent reduction of the initial dissolved sulfate pool. Based on the current SO_4 concentrations in these waters, this means that ~4.2 mmol L^{-1} of sulfate reduction has occurred. The fact that less than 0.3 mmol L^{-1} of dissolved sulfide remains in the shaft water at the present time suggests that >90 percent of the H_2S that formed through BSR was lost to the aqueous system.

C isotopes of dissolved inorganic carbon

Although there are comparatively few analyses of $\delta^{13}C$ of DIC from Butte mine waters (Table 5), some general trends exist. The majority of samples analyzed have $\delta^{13}C_{DIC}$ between

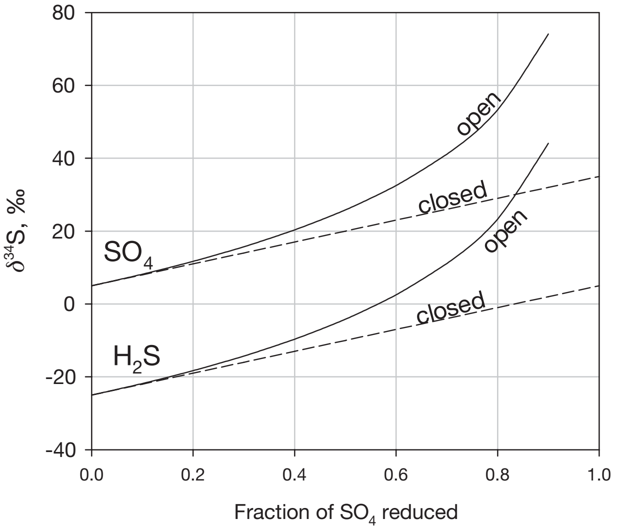

FIG. 14. Calculated trends in $\delta^{34}S$ of dissolved sulfate and sulfide as a function of the fraction of the total initial sulfate reduced for open and closed systems. The calculations assume an initial $\delta^{34}S$-sulfate of +5 per mil and a constant SO_4-H_2S enrichment factor of 30 per mil.

–17 and –12 per mil (Fig. 15). Roesler et al. (2007), attributed $\delta^{13}C_{DIC}$ values in this range from the West Camp extraction well to low-temperature isotopic equilibration with hydrothermal rhodochrosite ($\delta^{13}C$ = –7.2 to –7.8‰, Garlick and Epstein, 1966). Rhodochrosite was an abundant mineral in the Butte Main stage veins, especially in the Intermediate and Peripheral zones (Fig. 4). Indeed, some of the West Camp veins were mined primarily for Mn, and for many years Butte was an important U.S. domestic supplier of Mn ore.

Relative to the other mine waters, DIC in the Orphan Girl shaft is strongly isotopically depleted. Coincidently, the Orphan Girl and Orphan Boy waters also have much higher DIC concentrations than any of the other mine shaft waters in Butte. Given the aforementioned evidence for extensive bacterial sulfate reduction in the Orphan mine waters, it is logical to assume that the isotopically light DIC has a biogenic source. DIC is a byproduct of all heterotrophic microbial reactions, including sulfate reduction, as shown by the following example reaction which uses acetate as an organic carbon source:

$$SO_4^{2-} + CH_3COO^- + H^+ \rightarrow H_2S(aq) + 2HCO_3^- \qquad (6)$$

The ultimate source of organic carbon for sulfate-reducing bacteria in the Butte mine waters is not known with confidence, although it is logical to point to the millions of board-feet of timber that were used to reinforce the underground mine workings, some of which were treated with preservative (e.g., in major access tunnels), but much of which were not (e.g., in active stopes). Coniferous trees in temperate regions such as Montana typically have $\delta^{13}C$ in the range of –24 to –30 per mil (Clark and Fritz, 1997). Because sulfate-reducing bacteria require low molecular weight organic compounds for their energy source, they must coexist with fungi, fermenting bacteria, and other microorganisms that break down complex organic compounds (such as wood) into smaller organic molecules (such as acetate). Although few data exist, dissolved organic carbon concentrations in the Butte underground mine waters appear to be very low, in the 0 to 1 mg/L range (e.g., Roesler et al., 2007). Most likely the concentrations are maintained at a low level by the balance between slow DOC production (by fungi and fermenters) and relatively rapid DOC consumption (by S- and Fe-reducing bacteria, and other heterotrophs). If wood is the ultimate source of organic carbon for bacteria in the West and Outer Camp mine waters, then oxidation of this C should produce DIC with a similar isotopic composition, i.e., –24 to –30 per mil. Indeed, this overlaps with the observed $\delta^{13}C_{DIC}$ values in the Orphan Girl mine (Fig. 15).

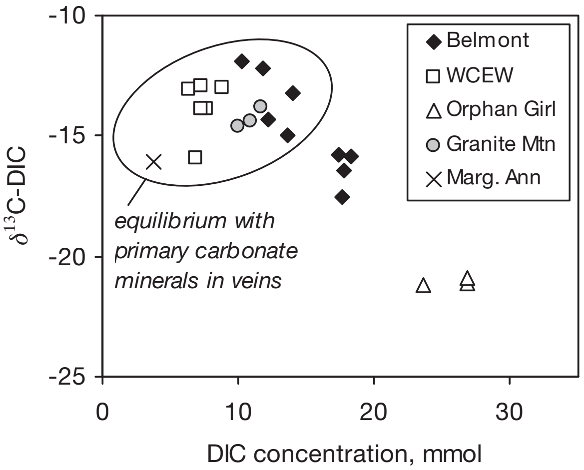

FIG. 15. Stable isotopic composition of dissolved inorganic carbon (DIC) in selected Butte mine waters. Most of the shafts plot in a cluster that is more or less in isotopic equilibrium with coexisting rhodochrosite and calcite in the veins, whereas much lighter dissolved inorganic carbon from the Orphan Girl shaft suggests the influx of biogenic CO_2.

As discussed in the preceding section, the S isotope data from the Orphan Girl and Orphan Boy shafts suggest that as much as 60 percent or more of the initial sulfate in the mine waters, or 4.2 mmol L^{-1}, may have been reduced to H_2S. By the stoichiometry of reaction (6), this means that 8.4 mmol L^{-1} of biogenic inorganic carbon would have been produced. Significantly, the observed HCO_3^- concentrations in the Orphan shaft waters are about 8.4 mmol L^{-1} (512 mg L^{-1}) higher than those in the nearby West Camp mine workings. Thus, the DIC concentration and isotopic data support the conclusion that a very high extent of microbial sulfate reduction has occurred in the Orphan Boy and Orphan Girl workings.

Temperature and Mine Water Convection

One possible explanation for the lack of vertical gradients in chemistry and temperature of the Butte mine waters is that the shaft waters are continuously circulating in a vertical direction. Direct evidence of vertical circulation in the Anselmo mine shaft was noted, via a submersible movie camera, by MBMG hydrogeologists in 2005. When the movie camera was held stationary, suspended particles in the water column were clearly shown to be moving upwards through the shaft (Mike Kerschen, MBMG, pers. commun., 2007).

A consideration of the local geothermal gradient on Butte Hill provides insight into likely mechanisms for mine water convection. Figure 16a shows changes in water temperature as a function of depth from several sources. The black triangles are data recorded in GWIC for the bedrock monitoring wells located to the south and east of the Berkeley pit lake (Fig. 1). Because these wells are purged for several hours prior to collection of field parameters and water samples, the water temperatures are believed to be representative of the conditions in the deep, fractured bedrock aquifer. Also shown are some temperature data collected by the Anaconda Company from two deep exploration drill holes (DDH #1, DDH#2). Finally, the arrows labeled "Kelley 4600 level" show the range in groundwater temperatures measured by Anaconda in freshly blasted drifts and stopes at the 4600-ft level of the Kelley mine during the period of active mining (from Blackwell and Robertson, 1973). Together, the data show a more-or-less consistent pattern (bedrock Well J falls off the trend, and will be discussed below), indicating a local geothermal gradient of between 30° and 35°C per km. This slope falls near the higher end of what is typically encountered in intracontinental settings lacking active volcanism and may be a result of relatively high concentrations of radioactive elements in the Butte Quartz Monzonite. For example, the concentrations of K, U, and Th in the Butte Quartz Monzonite are higher by a factor of roughly two than in the similarly-aged Idaho Batholith (Swanberg and Blackwell, 1973).

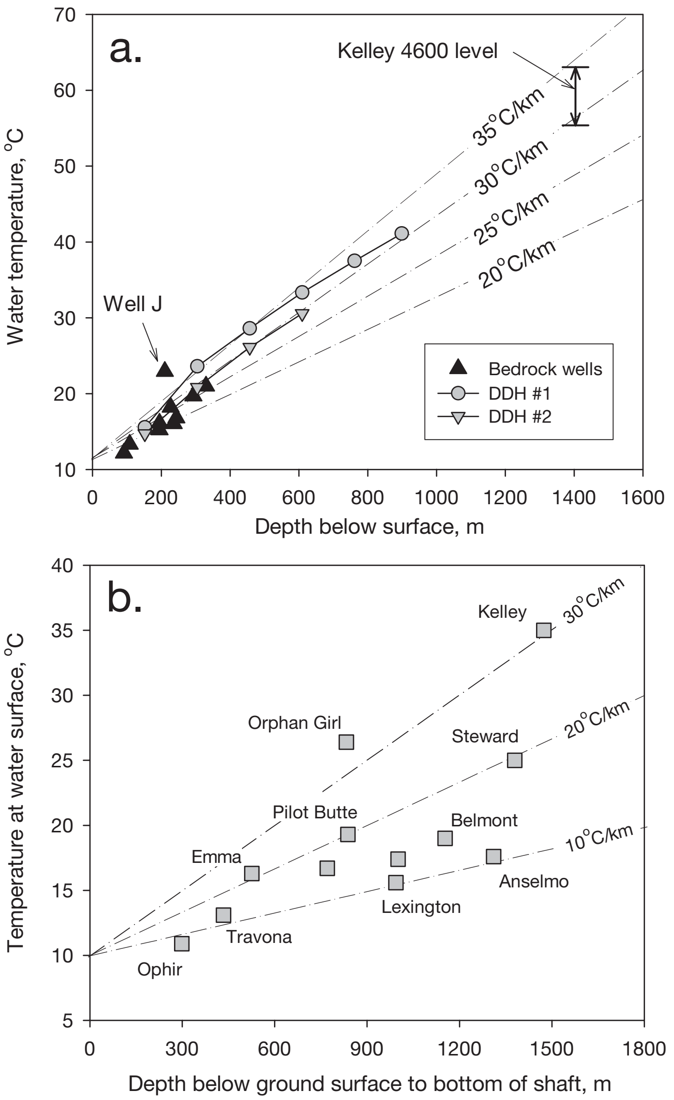

FIG. 16. Temperature gradients of Butte groundwater. a) In situ temperatures of groundwater measured in two deep drill holes (DDH) and numerous bedrock monitoring wells near the southeast side of the Berkeley pit. Also shown are rock temperatures measured on level 4600 of the Kelley mine during the period of active mining (from Blackwell and Robertson, 1973). With the exception of Well J, the data are consistent with a thermal gradient of around 30° to 35°C/km. b) Temperatures of near-surface water in mine shafts as a function of the total depth of each shaft. With the exception of the Orphan Girl and Kelley mines, most of the shaft waters fall on gradients between 10° and 20°C/km. These temperatures are most likely modified by vertical circulation within the flooded shafts.

Blackwell and Robertson (1973) estimated a heat production of 8.5×10^{-13} cal/cm^3/sec for the Butte Quartz Monzonite in Butte, which compares with an average value of only 2.6×10^{-13} cal/cm^3/sec (Swanberg and Blackwell, 1973) for the main phase of the Idaho batholith.

Figure 16b summarizes the average temperatures of mine shaft waters from Butte plotted against the total depth of each individual mine shaft. In general, mine water temperature increases with increasing mine shaft depth, and the data cluster between apparent thermal gradients of 10° to 20°C/km. (The Kelley and Orphan Girl shafts fall off this trend, and are discussed below). It is plausible that the majority of the mine shafts act as conduits for groundwater upflow, thereby advecting geothermal heat from depth. The exact position of a particular mine shaft in Figure 16b could reflect a number of confounding circumstances, including the following: (1) different rates of vertical water movement, (2) the presence or absence of obstructions in a given mine shaft that cut off circulation, (3) water entering the shaft horizontally from adjacent mine workings, and (4) the presence of ongoing chemical or biological reactions that are heating up the water. The latter explanation deserves special attention, as it may help to explain the anomalously warm water temperatures of the Kelley and Orphan Girl mines, as well as the Well J bedrock monitoring well.

The Kelley mine has by far the most acidic, Fe-rich, and sulfate-rich water of any of the flooded mine shafts of Butte. It is reasonable to assume that the source of the Fe and sulfate in this water is pyrite oxidation, and indeed the S isotope data support this hypothesis. The overall reaction can be written as follows:

$$\mathrm{FeS_2(s) + H_2O + 7/2O_2 \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+} \qquad (7)$$

Using thermodynamic data in Faure (1998), the calculated enthalpy change for reaction (7) is –1450 kJ/mol, indicating that the reaction is very strongly exothermic. If it is assumed that all of the dissolved Fe in the Kelley mine shaft (~0.032 mol/L) formed through reaction (7), then this would require oxidation of approximately 0.032 moles of pyrite, which would liberate 45.9 kJ of heat per liter of water. Assuming an average heat capacity of water of 4.187 kJ/kg/K, this much heat would raise the temperature of the water by roughly 11 K. This amount of warming is consistent with the observed temperature of the Kelley mine shaft in comparison to the surrounding mine waters (Fig. 16b). Using similar thermodynamic calculations for Well J, and basing the extent of reaction progress on sulfate concentration as opposed to Fe, a temperature rise of approximately 4 to 5 K is estimated. Again, this is roughly similar to the magnitude of the temperature anomaly for this well (see Fig. 16a). The reason for the anomalously warm temperatures in the Orphan Boy-Orphan Girl mine complex is less obvious. Given the near-neutral pH values, pyrite oxidation is unlikely to be a factor. Although it is possible that biological reactions (e.g., fermentation, sulfate reduction) are contributing to the warming trend, it is considered more likely that the elevated temperatures in these two shafts are due to local hydrologic conditions which allow more efficient advection of water and heat from deep portions of the mine to the near-surface.

Resource Recovery Potential

At the time of this writing, all of the flooded East Camp mine waters of Butte are slowly draining to the Berkeley pit, and therefore pose no threat to surrounding ground or surface water. Remediation of the East Camp mine pool to meet human health or aquatic life standards would require expensive treatment, and this idea has been written off by the U.S. EPA as being "technically impracticable" (EPA, 1994). Meanwhile, water in the West Camp mine workings is continuously pumped by the West Camp extraction well to a nearby water treatment facility where it is mixed with contaminated alluvial groundwater and treated with lime prior to discharge to the local stream (Silver Bow Creek). The combined discharge from the treatment facility must meet stringent standards for protection of aquatic life in Silver Bow Creek (see Department of Environmental Quality, 2008).

Given the unusual volume of the flooded underground mine complex at Butte, the question may well be raised as to whether a resource exists that could lead to a positive economic benefit. Although a large-scale copper recovery operation is currently taking place for the Berkeley pit lake, concentrations of Cu in the underground workings are far too low to be of economic interest. Zinc is much more abundant, with a range in concentration in the East Camp shafts of 10 to 200 mg/L (Table 2). Concentrations of this order of magnitude are often cited as being sufficient for an ore fluid to form an economic hydrothermal Zn deposit (e.g., Barnes, 1979) given enough time (tens to hundreds of thousands of years). However, such levels are currently noneconomic for direct recovery. In fact, Zn concentrations in the Berkeley pit lake are even higher (>500 mg/L, Table 1), and, as of this writing and despite considerable interest, there is still no demonstrated technology to recover Zn from the pit lake at a profit.

The city of Butte currently imports roughly half of its drinking water supply from a river located 45 km away, on the other side of the Continental Divide. Thus, the costs for consumptive use of city water are significant. Petritz (2008) evaluated the possibility of using Belmont mine water for irrigation of lawns on a nearby municipal property. As part of this study, a 57-day pumping test of the Belmont extraction well was conducted. Unfortunately, the quality of the extracted water quickly degraded during the first day of pumping, with dissolved Fe, Mn, Zn, and As levels exceeding proposed irrigation standards. Methods of inexpensively treating this water prior to irrigation are currently being evaluated.

Perhaps the most viable resource that the flooded mine waters of Butte have to offer is heat. The idea of using flooded mines as heat exchangers is gaining momentum worldwide, and a number of demonstration projects are in progress in Europe and North America (Arkay, 1992; Watzlaf and Ackman, 2006; NETL, 2006; Ghomshei, 2007; Minewater Project, 2007). With modern heat pump technology, it is now possible to heat buildings with water that has ambient temperatures of ~10° to 15°C. As shown above, many of the Butte mine waters are much warmer than this (e.g., ~25°C for the Steward and Orphan Girl mines, ~35°C for the Kelley mine), and the huge volume of these underground workings increases their potential for use as a heat reservoir.

Conclusions

The main intent of this paper is to describe the distribution of geochemical and stable isotopic constituents in time and space within the flooded underground mine complex of Butte, and to speculate as to the geologic and biological controls on the observed patterns. Horizontal, district-wide zonations in mine shaft chemistry are fundamentally controlled by zonation in the primary mineralization and hydrothermal alteration of the Butte orebody. Hence, mine water in the highly altered Central zone is acidic and metal rich, whereas water in the Intermediate and Peripheral zones has weakly acidic to near-neutral pH and is in equilibrium with one or more carbonate minerals. The latter observation is explained by the abundance of primary carbonate minerals (calcite, rhodochrosite) in the veins of the outer portions of the Butte district. The scarcity of copper in the Butte mine shaft waters could be due to present-day supergene enrichment processes, such as precipitation of chalcocite or covellite, or to cementation onto scrap iron left behind in the mines. In the outer portions of the district, the mine-water chemistries and S and C isotope signatures have been profoundly modified by bacterial sulfate reduction. The absence of vertical changes in mine shaft chemistry, coupled with observations on the temperatures of the mine waters, suggests that water in the shafts is circulating vertically. There is potential for economic recovery of heat from the mine shaft waters, and this may be an interesting legacy for the once-famous underground mines of Butte.

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REFERENCES

Ague, J. J., and Brimhall, G. H., 1989, Geochemical modeling of steady state fluid flow and chemical reaction during supergene enrichment of porphyry copper deposits: ECONOMIC GEOLOGY, v. 84, p. 506–528.

Allison, J.D., Brown, D.S., and Novo-Gradac, K.J., 1991, MINTEQA2/PRODEFA2, a geochemical assessment model for environmental systems: U.S. Environmental Protection Agency, EPA/600/3-91/021.

Arkay, K., 1992, Geothermal energy from abandoned mines: A methodology for an inventory, and inventory data for abandoned mines in Québec and Nova Scotia: Geological Survey of Canada, Open File Report 3825, 45 p.

Balci, N., Shanks, W.C., Mayer, B., and Mandernack, K.W., 2007, Oxygen and sulfur isotope systematics of sulfate produced by bacterial and abiotic oxidation of pyrite: Geochimica et Cosmochimica Acta, v. 71, p. 3796–3811.

Barnes, H.L, 1979, The solubilities of ore minerals, *in* Barnes, H.L., ed., Geochemistry of hydrothermal ore deposits, 2nd ed., Wiley & Sons, p. 404–460.

Bigham, J.M., and Nordstrom, D.K., 2000, Iron and aluminum hydroxysulfates from acid sulfate waters: Mineralogical Society of America, Reviews in Mineralogy and Geochemistry, v. 40, p. 351–403.

Bigham, J.M., Schwertmann, U., Traina, R.L., Winland, R.L., and Wolf, M., 1996, Schwertmannite and the chemical modeling of iron in acid sulfate waters: Geochimica et Cosmochimica Acta, v. 60, p. 2111–2121.

Blackwell, D.D., and Robertson, E.C., 1973, Thermal studies of the Boulder batholith and vicinity, Montana, *in* Miller, R.N., ed., Guidebook for the Butte field meeting of the Society of Economic Geologists, Butte, MT: Montana Bureau of Mines and Geology, August 18–21, 1973, p. D1–D21.

Blowes, D.W., and Jambor, J.L., 1990, The pore-water geochemistry and the mineralogy of the vadose zone of sulfide tailings, Waite Amulet, Quebec, Canada: Applied Geochemistry, v. 5, p. 327–346.

Brimhall, G.H, 1977, Early fracture-controlled disseminated mineralization at Butte, Montana: ECONOMIC GEOLOGY, v. 72, p. 37–59.

——1979, Lithologic determination of mass transfer mechanisms of multiple stage porphyry copper mineralization at Butte, Montana: Element recycling by hypogene leaching and enrichment of potassium-silicate protore: Economic Geology, v. 74, p. 556–589.

——1980, Deep hypogene oxidation of porphyry copper potassium-silicate protores: A theoretical evaluation of the copper remobilization hypothesis: Economic Geology, v. 75, p. 384–409.

Brimhall, G.H., and Ghiorso, M.S., 1983, Origin and ore-forming consequences of the advanced argillic alteration process in hypogene environments by magmatic gas contamination of meteoric fluids: Economic Geology, v. 78, p. 73–90.

Brimhall, G.H., Alpers, C., and Cunningham, A., 1985, Analysis of supergene ore-forming processes and ground water solute transport using mass balance principles: Economic Geology, v. 80, p. 1227–1256.

Canfield, D.E., 2001, Biogeochemistry of sulfur isotopes, *in* Valley, J.W., and Cole, D.R., eds., Stable isotope geochemistry: Mineralogical Society of America, Reviews in Mineralogy and Geochemistry, v. 43, p. 607–636.

Carmody, R.W., Plummer, L.N., Busenberg, E., and Coplen, T.B., 1998, Methods for collection of dissolved sulfate and sulfide and analysis of their sulfur isotopic composition: U.S. Geological Survey, Open File Report 997-234.

Casey, W.H., Westrich, H.R., and Arnold, G.W., 1988, Surface chemistry of labradorite feldspar reacted with aqueous solutions at pH = 2, 3, and 12–Geochimica et Cosmochimica Acta, v. 52, p. 2795–2807.

Church, C.D., Wilkin, R.T., Alpers, C.N., Rye, R.O., and McCleskey, R.B., 2007, Microbial sulfate reduction and metal attenuation in pH 4 acid mine water: Geochemical Transactions, v. 8(10), doi: 10.1186/1467-4866-8-10.

Clark, I.D., and Fritz, P., 1997, Environmental isotopes in hydrogeology: New York, Lewis Publishers.

Czehura, S.J., 2006, Butte: A world class ore deposit: Mining Engineering, v. 58(9), p. 14.

Davis, A., and Ashenberg, D., 1989, The aqueous geochemistry of the Berkeley pit, Butte, Montana, USA: Applied Geochemistry, v. 44, p. 23–36.

Department of Environmental Quality, 2008, Montana numeric water quality standards: Montana Department of Environmental Quality, Circular DEQ-7, http://deq.mt.gov/wqinfo/Standards/CompiledDEQ-7.pdf.

Druschel, G.K., Labrenz, M., Thomsen-Ebert, T., Fowle, D.A., and Banfield, J.F., 2002, Geochemical modeling of ZnS in biofilms: An example of ore depositional processes: Economic Geology, v. 97, p. 1319–1329.

Duaime, T.E., and Metesh, J.J., 2007, 2005 Consent decree update, water-level monitoring and water-quality sampling, Butte underground mines and Berkeley pit, Butte, Montana, 1982–2005: Montana Bureau of Mines and Geology, Open-File Report 549, 120 p.

Duaime, T.E., and Tucci, N.J., 2008, History of flooding of the Butte underground mines and Berkeley pit water-level monitoring and water-quality sampling 2006 consent decree update 1982–2006: Montana Bureau of Mines and Geology, Open-File Report 566, 165 p.

Duaime, T.E., Kennelly, P.J., Thale, P.R., 2004, Butte, Montana: Richest hill on Earth, 100 years of underground mining: Montana Bureau of Mines and Geology, Misc. Contribution, v. 19, unpaginated poster.

EPA, 1994, U.S. Environmental Protection Agency, Superfund record of decision, Silver Bow Creek/Butte Area, 1994, Butte, MT: http://www.epa.gov/superfund/sites/rods/fulltext/r0894102.pdf.

Epstein, S., and Mayeda, T., 1953, Variation of O-18 content of waters from natural sources: Geochimica et Cosmochimica Acta, v. 4, p. 213–224.

Faure, G., 1998, Principles and applications of geochemistry, 2nd edition: Upper Saddle River, N.J., Prentice Hall, 600 p.

Field, C.W., 1966, Sulfur isotope method for discriminating between sulfates of hypogene and supergene origin: Economic Geology, v. 61, p. 1428–1435.

Field, C.W., Zhang, L., Dilles, J.H., Rye, R.O, and Reed, M.H., 2005, Sulfur and oxygen isotopic record in sulfate and sulfide minerals of early, deep, pre-Main stage porphyry Cu-Mo and late Main stage base-metal mineral deposits, Butte district, Montana: Chemical Geology, v. 215, p. 61–93.

Frandsen, A., 2006, Mining megasite cleanup: The water report: Eugene, Oregon, Envirotech Publications, v. 26, p. 10–25.

Friedman, I., 1970, Some investigations of the deposition of travertine from hot springs—I. The isotope chemistry of a travertine depositing spring: Geochimica et Cosmochimica Acta, v. 34, p. 1303–1315.

Gammons, C.H., and Duaime, T.E., 2006, Long-term changes in the geochemistry and limnology of the Berkeley pit-lake, Butte, Montana: Mine Water and the Environment, v. 25, p. 76–85.

Gammons, C.H., Wood, S.A., Jonas, J.P., and Madison, J.P., 2003, Geochemistry of rare earth elements and uranium in the acidic Berkeley pit lake, Butte, Montana: Chemical Geology, v. 198, p. 269–288.

Gammons, C.H., Metesh, J.J., and Snyder, D.M., 2006a, A survey of the geochemistry of flooded mine shaft water in the Butte district, Montana: Mine Water and the Environment, v. 25, p. 100–107.

Gammons, C.H., Poulson, S.R., Pellicori, D.A., Roesler, A., Reed, P.J., and Petrescu, E.M., 2006b, The hydrogen and oxygen isotopic composition of precipitation, evaporated mine water, and river water in Montana, USA: Journal of Hydrology, v. 328, p. 319–330.

Garlick, G.D., and Epstein, S., 1966, The isotopic composition of oxygen and carbon in hydrothermal minerals at Butte, Montana: Economic Geology, v. 61, p. 1325–1335.

Ghomshei, M.M., 2007, Geothermal energy from Con mine for heating the city of Yellowknife, NWT: A concept study: Geothermal Study Final Report 6259. http://www.yellowknife.ca/__shared/assets/Geothermal_Study_Final_Report6259.pdf

Giesemann, A., Jager, H.J., Norman, A.L., Krouse, H.P., and Brand, W.A., 1994, On-line sulfur-isotope determination using an elemental analyzer coupled to a mass spectrometer: Analytical Chemistry, v. 66, p. 2816–2819.

Gonfiantini, R., 1986, Environmental isotopes in lake studies, *in* Fritz, P., and Fontes, J. Ch., eds., Handbook of environmental geochemistry, v. 2, p. 113–168.

GWIC, 2008, Montana Bureau of Mines and Geology, Groundwater Information Center: http://mbmggwic.mtech.edu/.

Harris, D., Porter, L.K., and Paul, E.A., 1997, Continuous flow isotope ratio mass spectrometry of carbon dioxide trapped as strontium carbonate: Communications in Soil Science and Plant Analysis, v. 28, p. 747–757.

Helgeson, H.C., 1971, Kinetics of mass transfer among silicates and aqueous solutions: Geochimica et Cosmochimica Acta, v. 35, p. 421–469.

Horibe, Y., Shigehara, K., and Takakuwa, Y., 1973, Isotope separation factor of carbon dioxide-water system and isotopic composition of atmospheric oxygen: Journal of Geophysical Research, v. 78, p. 2625–2629.

Jonas, J.P., 2000, Current seasonal limnology of the Berkeley pit lake: Society for Mining, Metallurgy, and Exploration, Proceedings of the 5th International Conference on Acid Rock Drainage, Denver, Colorado, p. 359–366.

Johnson, R.H., Blowes, D.W., Robertson, W.D., and Jambor, J.L., 2000, The hydrogeochemistry of the Nickel Rim mine tailings impoundment, Sudbury, Ontario: Journal of Contaminant Hydrology, v. 41, p. 49–80.

Kornexl, B.E., Gehre, M., Höffling, R., and Werner, R.A., 1999, On-line $\delta^{18}O$ measurement of organic and inorganic substances: Rapid Communications in Mass Spectrometry, v. 13, p. 1685–1693.

Labrenz, M., Druschel, G.K., Thomsen-Ebert, T., Gilbert, B., Welch, S.A., Kemner, K.M., Logan, G.A., Summons, R.E., De Staslo, G., Bond, P.L., Lai, B., Kelly, S.D., and Banfield, J.F., 2000, Formation of sphalerite (ZnS) deposits in natural biofilms of sulfate-reducing bacteria: Science, v. 290, p. 1744–1747.

Langmuir, D., Mahoney, J., and Rowson, J., 2006, Solubility products of amorphous ferric arsenate and crystalline scorodite ($FeAsO_4{\cdot}2H_2O$) and their application to arsenic behaviour in buried mine tailings: Geochimica et Cosmochimica Acta, v. 70, p. 2942–2956.

Langner, H.W., Jackson, C.R., McDermott, T.R., and Inskeep, W.P., 2001, Rapid oxidation of arsenite in a hot spring ecosystem, Yellowstone National Park: Environmental Science and Technology, v. 35, p. 3302–3309.

Lichtner, P.C., and Biino, G.G., 1992, A first principles approach to supergene enrichment of a porphyry copper protore: I. Cu-Fe-S subsystem: Geochimica et Cosmochimica Acta, v. 56, p. 3987–4013.

Lund, K., Aleinkoff, J., Kunk, M., Unruh, D., Zeihen, G., Hodges, W., Du Bray, E., and O'Neill, J., 2002, Shrimp U-Pb and $^{40}Ar/^{39}Ar$ age constraints for relating plutonism and mineralization in the Boulder batholith region, Montana: Economic Geology, v. 97, p. 241–267.

Luther, G.W., and Rickard, D., 2005, Metal sulfide cluster complexes and their biogeochemical importance in the environment: Journal of Nanoparticle Research, v. 7, p. 389–407.

Madison, J.P., Gammons, C.H., Poulson, S.R., and Jonas, J.P., 2003, Oxidation of pyrite by ferric iron in the acidic Berkeley pit lake, Montana, USA: Australasian Institute of Mining and Metallurgy (AusIMM) and the Australian Centre for Mining Environmental Research (ACMER): Proceedings of the 6th International Conference on Acid Rock Drainage, Cairns, Australia, p. 1073–1078.

Majzlan, J., Navrotsky, A., and Schwertmann, U., 2004, Thermodynamics of iron oxides; Part III, Enthalpies of formation and stability of ferrihydrite (~ $Fe(OH)_3$), schwertmannite (~ $FeO(OH)_{3/4}(SO_4)_{1/8}$), and ε-Fe_2O_3: Geochimica et Cosmochimica Acta, v. 68, p. 1049–1059.

McClave, M.A., 1973, Control and distribution of supergene enrichment in the Berkeley pit, Butte district, Montana: *in* Miller, R.N., ed., Guidebook for the Butte field meeting of the Society of Economic Geologists: Montana Bureau of Mines and Geology, Butte, MT: August 18–21, 1973, p. K1-K4.

Metesh, J.J., 2004, Geochemical evolution of flooding mine waters in a zoned, sulfide-hosted ore deposit: Summit Valley mining district, Butte, Montana: Unpublished Ph.D. dissertation, Missoula, MT, University of Montana, 157 p.

——2006, Using a water balance to determine the source of water in the flooding underground mine workings of Butte: Mine Water and the Environment, v. 25, p. 108–113.

Meyer, C., Shea E.P., and Goddard, C.C. Jr., 1968, Ore deposits at Butte, Montana: *in* Ridge, J.D., ed., Ore deposits of the United States, 1933–1967: American Institute of Mining, Metallurgy and Petroleum Engineering, p. 1373–1416.

Miller, R.N., 1973, Guidebook for the Butte field meeting of the Society of Economic Geologists, Butte, MT: Montana Bureau of Mines and Geology, Butte, MT, August 18–21, 1973.

Minewater Project, 2007, http://www.minewaterproject.info/, accessed December 2007.

Moore, J.N., and Luoma, S.N., 1990, Hazardous wastes from large-scale metal extraction: Environmental Science and Technology, v. 24, p. 1279–1285.

Morrison, J., Brockwell, T., Merren, T., Fourel, F., and Phillips, A.M., 2001, On-line high precision stable hydrogen isotopic analyses on nanoliter water samples: Analytical Chemistry, v. 73, p. 357–3575.

NETL, 2006, Underground mine water for heating and cooling using geothermal heat pump systems: National Energy Technology Laboratory, U.S. Department of Energy, http://www.netl.doe.gov/publications/factsheets/rd/R&D088.pdf.

Newbrough, P., and Gammons, C.H., 2002, Experimental investigation of water-rock interaction and acid mine drainage at Butte, Montana: Environmental Geology, v. 41, p. 705–719.

Nordstrom, D.K., and Alpers, C.N., 1999, Geochemistry of acid mine waters: Reviews in Economic Geology, v. 6A, p. 133–160.

Pellicori, D.A., Gammons, C.H., and Poulson, S.R., 2005, Geochemistry and stable isotope composition of the Berkeley pit lake and surrounding mine waters, Butte, Montana: Applied Geochemistry, v. 20, p. 2116–2137.

Petritz, K., 2008, Resource recovery of flooded underground mine workings—Butte, Montana: Unpublished MS thesis, Montana Tech, Butte, MT, 59701, 95 p.

Robins, R.G., Berg, R.B., Dysinger, D.K., Duaime, T.E., Metesh, J.J., Diebold, F.E., Twidwell, L.G., Mitman, G.G., Chatham, W.H., Huang, H.H., and Young, C.A., 1997, Chemical, physical and biological interaction at the Berkeley pit, Butte, Montana: Proceedings of Tailings and Mine Waste '97, Rotterdam, Balkema Press, p. 521–541.

Roesler, A.J., Gammons, C.H., Druschel, G.K., Oduro, H., and Poulson, S.R., 2007, Geochemistry of flooded underground mine workings influenced by bacterial sulfate reduction: Aquatic Geochemistry, v. 13, p. 211–235.

Rose, A.W., Hawkes, H.E., and Webb, J.S., 1979, Geochemistry in mineral exploration, 2nd edition: New York, Academic Press, 657 p.

Rusk, B., Reed, M., Dilles, J.H., Klemm, L., and Heinrich, C.A., 2004, Compositions of magmatic hydrothermal fluids determined by LA-ICP-MS of fluid inclusions from the porphyry copper-molybdenum deposit at Butte, Montana: Chemical Geology, v. 210, p. 173–199.

Rusk, B.G., Reed, M.H., and Dilles, J.H., 2008, Fluid inclusion evidence for magmatic-hydrothermal fluid evolution in the porphyry copper-molybdenum deposit at Butte, Montana: ECONOMIC GEOLOGY, v. 103, p. 307–334.

Sales, R.H., 1914, Ore deposits at Butte, Montana: American Institute of Mining and Metallurgical Engineers, Transactions, v. 46, p. 3–109.

Seal, R.R. II, 2003, Stable-isotope geochemistry of mine waters and related solids: Mineralogical Society of Canada, Short Course Series, v. 31, p. 303–334.

Seal, R.R. II, Alpers, C.N., and Rye, R.O., 2000, Stable isotope systematics of sulfate minerals: Reviews in Mineralogy and Geochemistry, v. 40, p. 541–602.

Stookey, L.L., 1970, Ferrozine—a new spectrophotometric reagent for iron: Analytical Chemistry, v. 42, p. 779–781.

Stumm, W., and Morgan, J.J., 1996, Aquatic Chemistry, 3rd ed. Wiley-Interscience, 1022 p.

Swanberg, C.A., and Blackwell, D.D., 1973, Areal distribution and geophysical significance of heat generation in the Idaho Batholith and adjacent intrusions in eastern Oregon and western Montana: Geological Society of America Bulletin, v. 84, p. 1261–1282.

Theberge, S.M., and Luther, G.W., 1997, Determination of the electrochemical properties of a soluble aqueous FeS species present in sulfidic solutions: Aquatic Geochemistry, v. 3, p. 191–211.

Watzlaf, G.R., and Ackman, T.E., 2006, Underground mine water for heating and cooling using geothermal heat pump systems: Mine Water and the Environment, v. 25, p. 1–14.