

Geochemistry and stable isotope composition of the Berkeley pit lake and surrounding mine waters, Butte, Montana

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Abstract

Samples of mine water from Butte, Montana were collected for paired geochemical and stable isotopic analysis. The samples included two sets of depth profiles from the acidic Berkeley pit lake, deep groundwater from several mine shafts in the adjacent flooded underground mine workings, and the acidic Horseshoe Bend Spring. Beginning in July-2000, the spring was a major surface water input into the Berkeley pit lake. Vertical trends in major ions and heavy metals in the pit lake show major changes across a chemocline at 10–20 m depth. The chemocline most likely represents the boundary between pre-2000 and post-2000 lake water, with lower salinity, modified Horseshoe Bend Spring water on top of higher salinity lake water below. Based on stable isotope results, the deep pit lake has lost approximately 12% of its initial water to evaporation, while the shallow lake is up to 25% evaporated. The stable isotopic composition of SO₄ in the pit lake is similar to that of Horseshoe Bend Spring, but differs markedly from SO₄ in the surrounding flooded mine shafts. The latter is heavier in both δ³⁴S and δ¹⁸O, which may be due to dissolution of hypogene SO₄ minerals (anhydrite, gypsum, barite) in the ore deposit. The isotopic and geochemical evidence suggests that much of the SO₄ and dissolved heavy metals in the deep Berkeley pit lake were generated in situ, either by leaching of soluble salts from the weathered pit walls as the lake waters rose, or by subaqueous oxidation of pyrite on the submerged mine walls by dissolved Fe(III). Laboratory experiments were performed to contrast the isotopic composition of SO₄ formed by aerobic leaching of weathered wallrock vs. SO₄ from anaerobic pyrite oxidation. The results suggest that both processes were likely important in the evolution of the Berkeley pit lake.

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1. Introduction

In the latter half of the 20th century, a shift in the dominant method of hard rock mining occurred from selective underground stoping to bulk tonnage open pit mining. As the open pit mines reach the end of their life many will be flooded upon closure to create pit lakes. The hydrogeochemistry of the resulting pit lakes involves a multitude of processes

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(Miller et al., 1996; Eary, 1999), and therefore the prediction of their chemistry prior to flooding presents a significant challenge to environmental scientists and engineers (Eary, 1998, 1999; Fennemore et al., 1998; Shevenell et al., 1999; Tempel et al., 2000; Kempton et al., 2000). In this respect, much can be learned from detailed studies of existing pit lakes. Amongst the world's mining pit lakes, the Berkeley Pit in Butte, Montana is well known both for its size and for the poor quality of the water contained therein. Over 100 billion L of acidic, metal-rich water (pH \sim 2.6, Fe > 1000 mg/L, Zn > 600 mg/L, Cu > 150 mg/L) fill the former open pit Cu mine (Davis and Ashenberg, 1989; Gammons et al., 2003a; www.pitwatch.org). Unlike younger pit lakes, the Berkeley Pit and surrounding underground mine waters have been flooding since 1983, and consequently the pit lake is in a relatively mature state.

Most models for predicting pit lake chemistry use a chemical mass balance approach, in which the bulk chemistry of a lake water is computed by the weighted sum of the chemistry of each input water, is corrected for evaporative losses, and is speciated to allow precipitation of supersaturated minerals or adsorption of trace metals (Miller et al., 1996; Lewis, 1999). In the case of the Berkeley pit lake, use of a simple chemical mass balance approach would give a poor approximation of the existing pit lake chemistry. As discussed below, the water quality of the Berkeley pit lake is much worse than any of its influent waters, implying that reactions between water in the pit and surrounding wallrock must have had a profound influence on the lake chemistry. Newbrough and Gammons (2002) showed that interaction of distilled water with weathered wallrock from the Berkeley Pit is capable of producing a leachate with a chemical composition similar to the Berkeley pit lake. Maest et al. (2004) used mass balance calculations to conclude that much of the Cu in the Berkeley pit lake must have been derived by wallrock leaching. Furthermore, Madison et al. (2003) argued that continued degradation of water quality is possible in the deep pit lake due to sub-aqueous oxidation of pyrite and other sulfide minerals by dissolved Fe(III).

The focus of the present study was to re-evaluate the processes responsible for the poor quality of water within the Berkeley pit lake by collecting a set of water samples for paired geochemical and stable isotopic analysis. The basic geochemical data reported in this study are important in that very little

information of this type is available in the peer-reviewed literature for the Berkeley pit lake, other than the early study of Davis and Ashenberg (1989), and a recent detailed investigation of U and rare earth elements in the pit lake (Gammons et al., 2003a). The only stable isotope data for the Butte mine waters are two preliminary studies reported by the present research group (Gammons et al., 2003b; Madison et al., 2003). The authors are not aware of a detailed stable isotopic study of any mining pit lake, which is surprising, considering the widespread use of stable isotopes in investigations of the hydrogeochemistry of natural lakes (Gat, 1981; Gonfiantini, 1986). The present study demonstrates how stable isotopes can be used to help identify sources of water and dissolved SO₄ to a pit lake, to quantify evapo-concentration effects, to recognize the presence or absence of lake mixing/turnover events, and to place constraints on the mechanisms of pyrite oxidation (e.g., aerobic vs. anaerobic) leading to water quality degradation.

1.1. Site description

The Berkeley pit lake (Fig. 1) is one of the most notorious bodies of water in the world, due to the widespread negative publicity it has attracted (Dobb, 1996; Langewiesche, 2001), and its location at the head of the largest (in terms of aerial extent) Superfund complex in the US. The world class polymetallic mineral deposits of Butte, Montana (Meyer et al., 1968; Miller, 1973) have been mined nearly continuously from the 1870s to the present day. Mining prior to 1953 was mainly by underground stoping methods, and focused on high grade Cu–Zn–Pb–Ag–Mn veins. Several dozen shafts were constructed for underground access, and it is estimated that over 10,000 km of interconnected mine workings underlie Butte Hill (Duaine et al., 1995). Beginning in 1953, the focus shifted to open pit mining of a lower grade, porphyry Cu-style deposit in the center of the Butte District. Approximately 320 million tons of ore and >700 million tons of waste rock were mined from the Berkeley Pit before closure in May of 1982, at which point dewatering pumps in a nearby underground shaft (the Kelley Mine) were shut down and the pit began filling with acidic water. A portion of the huge amount of waste mined out of the pit was used to construct the Yankee Doodle tailings impoundment, which stands over 200 m tall to the north of the pit (Fig. 1). Low grade waste was also piled into heap-leach

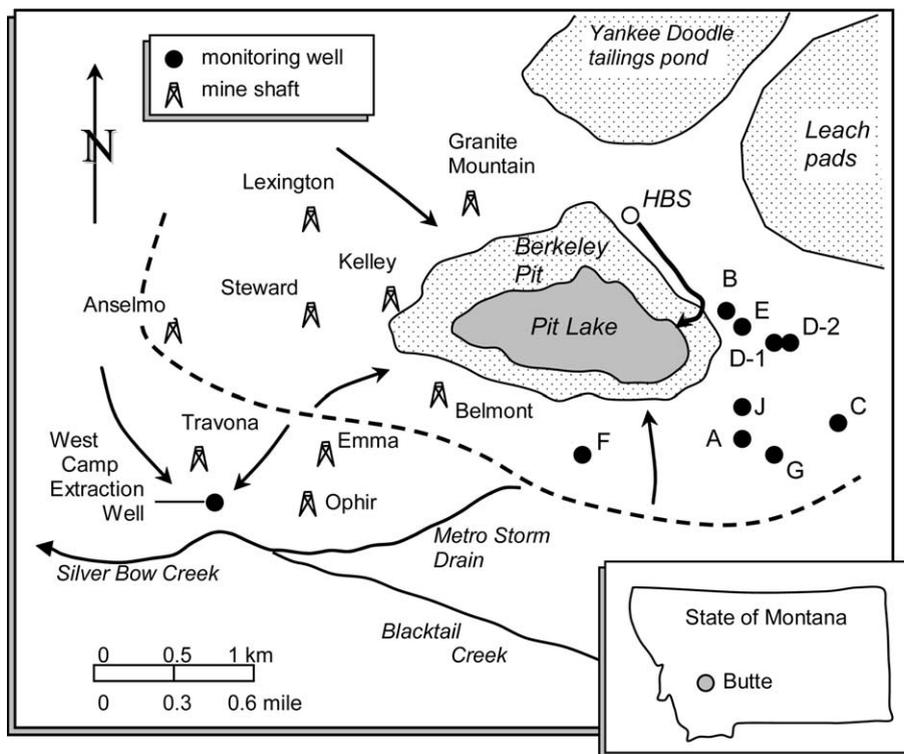


Fig. 1. Map of the Berkeley Pit area. The dashed line is a groundwater divide that separates water that flows towards the Berkeley Pit from water that flows towards Silver Bow Creek or the West Camp Extraction Well. HBS, Horseshoe Bend Spring.

pads NE of the Berkeley Pit. Copper was recovered from this material by percolating dilute H_2SO_4 through the heaps, recovering the leachate, and then passing it over scrap Fe to cement out the Cu. The cementation facility is located adjacent to Horseshoe Bend, at the toe of the tailings impoundment.

As of March 30, 2001, the Berkeley pit lake contained $>1.1 \times 10^{11}$ (110 billion) L of acidic mine water, was 220 m deep, with a surface elevation of 1585 m above sea level. As the pit lake occupies a cone of depression in the regional water table, the only output of water from the lake is direct evaporation. The two main inputs into the pit lake are groundwater seepage and the Horseshoe Bend spring (HBS), a large, acidic (pH 3–3.5) discharge near the base of a nearby tailings dam (Fig. 1). Over most of the period of mine flooding, the spring has been allowed to dump into the Berkeley Pit, at a rate of 8–11 million L/day. Based on an extensive groundwater monitoring network and water balance calculations, it is known that roughly the same quantity of deep groundwater enters the pit each day (Duaiame et al., 1998). During the period 1995–2000, the Horseshoe Bend Spring was diverted

away from the pit, and co-disposed with mill tailings. Most of the data reported by Robins et al. (1997), Jonas (2000) and Madison et al. (2003) were collected at this time. The samples from the present study were collected between April and October of 2003, when the spring had been dumping into the pit lake for more than two years. Beginning in November of 2003, the spring was again diverted away from the pit and is now passed through a new lime treatment facility before being recycled by the active mining operation.

From the onset of mine flooding, the Berkeley pit lake has consistently given pH readings in the range 2.20–2.95, with a 15-a mean of 2.63 (Metesh and Duaiame, 2000). The concentration of metals such as Cu and Zn in the deeper portions of the lake have also remained essentially constant in the past 10 a of monitoring (Table 1). In contrast, the chemistry of deep groundwater in most of the surrounding shafts and bedrock monitoring wells has improved since mine flooding began (Metesh and Duaiame, 2000). Between 1990 and 2000, the average pH of flooded shafts and bedrock monitoring wells surrounding the Berkeley Pit was >5.5 for 12 of 13 stations

Table 1
pH, SC, and Cu concentration of selected groundwater and surface water bodies in the Butte area, 1990–2000

	pH			SC ($\mu\text{S}/\text{cm}$)			Cu (mg/L)			#
	Low	High	Mean	Low	High	Mean	Low	High	Mean	
<i>Flooded mine shafts</i>										
Anselmo	6.10	8.32	7.08	1555	2110	1880	0.004	0.050	0.025	6
Belmont	5.52	6.21	5.93	1310	1460	1370	0.110	0.810	0.420	9
Granite Mtn	5.16	6.03	5.54	2430	3480	3040	0.090	1.59	0.500	9
Kelley	3.53	5.60	4.86	3130	9850	5460	0.105	0.256	0.172	11
Lexington	6.34	6.38	6.36	2640	2640	2640	0.013	0.250	0.120	4
Steward	5.27	7.10	5.76	1800	3520	2930	0.017	9.60	4.17	8
<i>Bedrock monitoring wells</i>										
Well A	5.74	6.81	6.25	1380	1770	1650	<0.002	0.0024	<0.002	10
Well B	6.42	7.41	7.22	1190	1380	1315	<0.002	0.0075	<0.002	6
Well C	5.67	6.10	5.82	680	1030	743	<0.002	0.0096	<0.002	8
Well D-1	5.87	6.52	6.20	670	692	681	<0.002	0.0028	<0.002	2
Well E	6.38	6.76	6.63	790	816	801	<0.002	0.002	<0.002	3
Well F	7.25	7.68	7.51	1510	1690	1610	<0.002	<0.002	<0.002	3
Well G	5.75	8.69	6.46	730	1070	989	<0.002	0.0025	<0.002	9
<i>Surface water</i>										
Horseshoe Bend	2.79	3.34	3.10	4170	6090	5240	77	103	89.2	11
Berkeley Pit lake	2.20	2.95	2.63	5950	11600	7340	134	305	189	29

All data summarized from Metesh and Duaine (2000).

(Table 1). Dissolved metal concentrations were also much lower than in the Berkeley Pit. For example, the vast majority of groundwater samples collected since 1980 have had Cu concentrations less than 1 mg/L, as opposed to a 10-year average of 190 mg/L Cu in the pit lake (Table 1). The drastic difference between the water quality of the Berkeley pit lake and that of its influent waters has led to the hypothesis that much of the acidity and metal content of the lake is due to in situ processes, such as leaching of soluble salts and subaqueous oxidation of pyrite on the pit walls (Newbrough and Gammons, 2002; Madison et al., 2003; Maest et al., 2004). This hypothesis will be tested in the current study.

2. Methods

2.1. Field methods

All water samples described in this study were collected in 2003, with the exception of groundwater samples from bedrock monitoring wells, which were collected in 2000 and 2001. Samples of groundwater from the Anselmo, Steward, Kelley, Emma, and Ophir mine shafts were collected on 4/08/03. Water from each shaft was bailed from a depth 30 m below the static water level to the surface by a truck-

mounted winch. On 5/7/03, the Horseshoe Bend spring was sampled from the point where the largest of the springs issues from the ground to the spill-over point to the Berkeley Pit (Fig. 1). A depth profile of water samples from the Berkeley pit lake was collected by personnel from the Montana Bureau of Mines and Geology (MBMG) on 5/14/03 and again on 10/22/03. Samples of pit water at depths greater than 30 m were taken with a General Oceanics Model 1080 series GO-FLO non-metallic water-sampling bottle supported from a graduated nylon rope. For depths less than 30 m, samples were taken with a peristaltic pump and flexible 5/16-inch (8 mm) Teflon tubing. At least 4 L of water (~ 3 tube volumes at 30 m depth) were pumped into a bucket and discarded before each sample was collected. Also on 5/14/03, water samples of two prominent springs were collected at lake level, where the springs entered the south side of the Berkeley pit-lake. On 10/8/03, water samples for isotopic analysis were collected from two tributary streams entering the Yankee Doodle tailings impoundment from the north (Yankee Doodle Creek, and upper Silver Bow Creek), as well as 3 locations along the shore of the tailings pond itself.

Parameters measured in the field for most samples included pH, temperature (T), redox potential (Eh), specific conductance (SC), and dissolved

oxygen (DO). Field parameters were either collected with a WTW Multi 340i hand-held multimeter, or a Hydrolab Datasonde 4. In either case, all equipment was freshly calibrated via the manufacturer's recommendations immediately before use. All water samples were filtered in the field with a peristaltic pump and disposable in-line filters (0.45 μm). Samples were collected in high density polyethylene (HDPE) bottles and were kept in a cooler on ice for transport back to the laboratory refrigerator. Split samples were taken for ICP-OES metals analysis, Fe speciation, and stable isotope analysis. Samples for ICP analysis were preserved with 2% v/v HNO_3 in the laboratory, within 12 h of sample collection. No visible precipitation of Fe was noted prior to acidification. Samples for isotopic analysis were not preserved. Samples for Fe speciation were immediately filtered and acidified in the field to $\text{pH} \sim 1$ by addition of HCl (trace metal grade). The samples were stored in the dark in tightly-sealed plastic bottles with no head space at 4 °C. [To et al. \(1999\)](#) stated that samples preserved in this manner can be stored in the refrigerator for up to 6 months without significant changes in Fe redox distribution. All samples in this study were analyzed within two weeks of collection, usually within two days.

2.2. Laboratory methods

[Pellicori \(2004\)](#) performed a large number of laboratory experiments aimed at quantifying rates of pyrite oxidation in the Berkeley pit lake. Results from two experiments are reported here. The purpose of these experiments was to contrast the isotopic composition of SO_4 formed by leaching of weathered wallrock vs. SO_4 formed by anaerobic oxidation of pyrite by dissolved Fe(III). In the first experiment, 4 \times 1 kg samples of crushed and partially weathered rock collected from the north high-wall of the Berkeley Pit near lake level were placed in acrylic humidity cells. These samples were selected from bulk specimens previously characterized in more detail by [Newbrough and Gammons \(2002\)](#). The cells were partially filled with deionized water to completely saturate the crushed rock. The solution was allowed to sit for two days, at which point it was drained by gravity out the bottom of the cell, filtered (0.45 μm), and analyzed for pH, SC, Eh, and Fe speciation. Samples were collected for isotopic analysis of water and SO_4 .

In the second experiment, 2.5 g of crushed and size-fractionated (0.15–0.25 mm diameter) pyrite from

Butte were placed in a 3-necked glass flask with 750 mL of FeCl_3 solution containing 300 mg/L Fe(III). The reaction vessel was continuously stirred, and N_2 gas (99.999% pure) was bubbled through the solution to maintain anaerobic conditions. During the experiment, Fe(III) oxidized pyrite to form aqueous SO_4 (see [Pellicori, 2004](#) for details from additional experiments). After 14 days of reaction, the SO_4 and coexisting water were sampled for isotopic analysis.

2.3. Analytical methods

Acid-preserved samples were analyzed for a suite of 11 major and trace metals by ICP-OES at HKM Laboratories, Butte, Montana. EPA Method 200.7 was used to quantify the elements Al, As, Ca, Cu, Fe, Mg, Mn, K, Na, S, and Zn. Concentrations of SO_4 were derived from the ICP results for S, assuming that all dissolved S was present as SO_4 . The concentrations of Fe(II) and total Fe were determined using the Ferrozine spectrophotometric method ([To et al., 1999](#)) and a HACH DR/2010 portable spectrophotometer. Concentrations of Fe(III) were determined by difference.

Filtered, unacidified samples were collected for $\delta^{18}\text{O}$ and δD analysis of water and $\delta^{18}\text{O}$ and $\delta^{34}\text{S}$ analysis of dissolved SO_4 . The water analyses required no pre-treatment. SO_4 samples were prepared by precipitation of BaSO_4 , following the procedure of [Carmody et al. \(1998\)](#). To prevent formation of BaCO_3 , non-acidic samples were adjusted to $\text{pH} < 3$ with HCl prior to the addition of BaCl_2 . Stable isotope analyses were performed at the University of Nevada-Reno, using a Eurovector elemental analyzer interfaced to a Micromass IsoPrime stable isotope ratio mass spectrometer ($\delta\text{D}_{\text{water}}$, $\delta^{18}\text{O}_{\text{SO}_4}$, and $\delta^{34}\text{S}_{\text{SO}_4}$) or using a Micromass Aquaprep device interfaced to a Micromass dual inlet IsoPrime stable isotope ratio mass spectrometer ($\delta^{18}\text{O}_{\text{water}}$). Sulfur isotope analyses were performed using a method similar to that of [Giesemann et al. \(1994\)](#), with the modification that V_2O_5 was added to BaSO_4 samples as a combustion aid. O-isotope analyses of SO_4 followed a method similar to that of [Kornexl et al. \(1999\)](#), with the modifications that the analyses were performed at 1300 °C, and that nickelized graphite was added to BaSO_4 samples as a pyrolysis aid. Oxygen isotope analyses of water samples were performed using the CO_2 – H_2O equilibration method of [Epstein and Mayeda \(1953\)](#). Hydrogen isotope analyses of water

followed the procedure of Morrison et al. (2001). Stable isotope values are reported in the usual δ notation in units of ‰, vs. VCDT for S and vs. VSMOW for O and H. Analytical uncertainties are $\pm 0.2\text{‰}$ for $\delta^{34}\text{S}_{\text{sulfate}}$, $\pm 0.4\text{‰}$ for $\delta^{18}\text{O}_{\text{sulfate}}$, $\pm 0.1\text{‰}$ for $\delta^{18}\text{O}_{\text{water}}$, and $\pm 2\text{‰}$ for $\delta\text{D}_{\text{water}}$.

Rigid quality assurance (QA) protocols were followed throughout this study, including collection of field blanks and field duplicates, as well as submittal of split samples to different laboratories. The results showed no significant problems for any of the data reported in this study. Speciated charge imbalances were all within $\pm 6.3\%$, with an average imbalance of 3.1%. For samples from the Berkeley pit lake, the Eh measured in the field agreed within ± 20 mV with the theoretical Eh calculated from the Fe(II)/Fe(III) speciation results. A more detailed discussion of the QA results in this study is given in Pellicori (2004).

3. Results and discussion

3.1. Geochemistry of mine waters

3.1.1. Horseshoe Bend and South Side springs

During most of the period of mine flooding since 1983, the Horseshoe Bend spring (HBS) has been a major input into the Berkeley pit lake. This water originates at the base of the Yankee Doodle tailings impoundment as several large seeps that are channeled through a series of 3 ponds before cascading >100 m into the Berkeley Pit (Fig. 1).

Geochemical analyses obtained in this study (Tables 2 and 3) confirm that the Horseshoe Bend Spring is of poor quality, but still considerably better than the Berkeley pit lake itself. A number of changes in water chemistry occurred between the source (HBS-1) and mouth (HBS-6) of the Horseshoe Bend

Table 2
Field parameters and stable isotope results

	Sample date	Temp (°C)	pH	SC (mS/cm)	Eh (mV) SHE	$\delta^{18}\text{O}_w$ (‰)	δD_w (‰)	$\delta^{18}\text{O}_s$ (‰)	$\delta^{34}\text{S}_s$ (‰)
Anselmo	4/8/03	15.5	6.09	2.43	317	-17.0	-134	-7.0	7.0
Ophir	4/8/03	11.0	6.40	0.89	n.a.	-17.2	-135	-3.3	13.8
Kelley	4/8/03	30.8	4.48	7.8	377	-17.4	-139	-10.2	2.5
Emma	4/8/03	15.5	6.67	1.51	381	-17.0	-132	-8.0	4.2
Steward	4/8/03	20.4	5.8	3.75	291	-17.2	-135	-8.1	5.8
HBS-1	5/7/03	10.9	3.57	3.94	522	-15.2	-125	-11.3	2.3
HBS-6	5/7/03	10.5	3.13	4.42	728	-15.0	-124	-11.3	2.3
SS-1	5/14/03	14.0	5.92	1.27	204	-17.5	-137	-10.5	1.9
SS-2	5/14/03	13.0	6.58	0.92	193	-16.8	-133	-8.4	2.2
YDC	10/8/03	10.8	7.68	0.22	624	-16.3	-133	n.a.	n.a.
SBC	10/8/03	10.8	7.40	0.27	594	-17.7	-141	n.a.	n.a.
YDP-1	10/8/03	13.5	7.53	2.94	667	-6.7	-85	-10.8	2.5
YDP-2	10/8/03	14.1	8.26	2.96	639	-5.3	-75	-10.8	2.6
YDP-3	10/8/03	n.a.	n.a.	n.a.	n.a.	-7.4	-88	-10.8	2.6
<i>Depth (m) Berkeley pit lake, Spring, 2003</i>									
0.2	5/14/03	14.0	2.71	4.65	831	-13.4	-117	-11.2	2.1
3.0	5/14/03	4.3	2.50	5.75	722	-13.2	-115	-10.8	2.1
7.6	5/14/03	4.6	2.50	6.00	693	-13.2	-116	-11.1	2.0
15.2	5/14/03	6.1	2.38	7.48	680	-14.2	-121	-10.8	1.5
30.5	5/14/03	6.5	2.43	7.88	650	-15.0	-125	-10.7	1.4
61.0	5/14/03	6.5	2.42	7.92	650	-15.1	-125	-10.8	1.6
216.4	5/14/03	8.3	2.44	7.87	651	-14.9	-125	-10.7	1.4
<i>Depth (m) Berkeley pit lake, Fall, 2003</i>									
0.2	10/22/03	11.9	2.47	5.45	815	-11.7	-111	-11.4	2.2
7.6	10/22/03	7.2	2.47	6.77	670	-13.0	-115	-11.9	2.1
15.2	10/22/03	6.2	2.37	7.32	662	-14.0	-118	-11.9	1.6
30.5	10/22/03	6.7	2.46	7.90	623	-14.8	-127	-11.1	1.6
61.0	10/22/03	6.8	2.50	7.96	619	-15.1	-123	-12.0	1.6
216.4	10/22/03	n.a.	n.a.	n.a.	n.a.	-15.1	-124	-11.8	1.7

HBS-1, Horseshoe Bend Spring source; HBS-6, point where HBS empties into Berkeley Pit; SS, South Side Spring; YDC, Yankee Doodle Creek; SBC, upper Silver Bow Creek; YDP, Yankee Doodle tailings pond. The subscripts w and s refer to water and dissolved sulfate, respectively.

Table 3
Solute concentrations for samples shown in Table 2

	Al	As	Ca	Cu	Fe(T)	Fe(II)	Fe(III)	Mg	Mn	K	Na	Zn	Cl ⁻	SO ₄	HCO ₃ ⁻	SiO ₂
Anselmo	0.2	0.001	382	0.008	37	35	2	113	33.8	15	48	35	30	1420	215	19
Steward	0.85	3.08	553	0.092	272	272	n.d.	173	35.9	43	50	84	39	2560	77	46
Kelley	41.2	13.4	485	0.006	2029	2029	n.d.	414	208	72	85	348	n.a.	7560	n.a.	68
Ophir	<0.03	0.003	110	0.005	0.2	0.2	n.d.	29.2	11.2	4.6	24	1.8	39	240	218	18
Emma	<0.15	<.005	194	0.056	0.2	0.2	n.d.	57.5	22.6	7.2	38	20	40	552	383	16
HBS-1	66.3	<.001	469	44.6	104	98.4	15.8	169	79.7	16	87	146	n.a.	3090	n.a.	n.a.
HBS-6	116	<.001	492	54.4	141	0.8	140.2	219	97.9	13	86	183	n.a.	3750	n.a.	n.a.
SS-1	<0.03	<.001	164	9.7	0.15	n.a.	0.15	63.5	3.6	8.1	35	18.2	n.a.	753	n.a.	n.a.
SS-2	0.03	<.001	123	1.0	n.a.	n.a.	<0.01	30.5	11.7	6.4	27	11.9	n.a.	453	n.a.	n.a.
<i>Depth (m) Berkeley pit lake, Spring, 2003</i>																
0.2	134	.38	420	64.8	264	1	263	302	161	14	70	275	19	4530	n.a.	64
3.0	165	.76	476	78.9	373	30	342	380	202	16	81	348	n.a.	5520	n.a.	n.a.
7.6	188	1.48	509	89.1	462	111	350	424	230	18	84	408	n.a.	6300	n.a.	n.a.
15.2	286	.35	466	121	753	243	510	512	242	5.9	79	613	n.a.	8040	n.a.	98
30.5	297	.74	458	173	1050	719	332	508	248	7.3	77	652	n.a.	8610	n.a.	n.a.
61.0	280	1.00	426	169	1062	779	283	486	237	7.0	75	603	27	8220	n.a.	103
216.4	278	.93	422	167	1066	771	295	483	233	7.0	75	596	27	8160	n.a.	105
<i>Depth (m) Berkeley pit lake, Fall, 2003</i>																
0.2	141	.42	484	69.7	283	0	283	331	170	16	78	293	n.a.	5100	n.a.	75
7.6	180	1.00	478	84.9	431	122	309	398	209	17	81	370	n.a.	6030	n.a.	n.a.
15.2	284	.47	469	122	683	249	434	504	248	5.4	80	577	n.a.	7980	n.a.	99
30.5	290	.77	444	165	1007	718	289	494	238	6.5	75	606	n.a.	8340	n.a.	n.a.
61.0	295	.99	453	174	1065	788	277	501	245	6.7	75	622	n.a.	8580	n.a.	107
216.4	294	1.00	447	173	1054	798	256	501	240	6.8	77	612	n.a.	8520	n.a.	106

All data are from Pellicori (2004) except for Ophir and Emma shafts (GWIC, 2004), and Cl⁻, HCO₃⁻, and SiO₂ (GWIC, 2004). All units are mg/L. n.d., non detected; n.a., not analyzed.

spring, including a drop in pH, an increase in SC, a rise in Eh, an increase in total dissolved metals, and an increase in the aqueous Fe(III)/Fe(II) ratio (Table 3). These changes are attributed to oxidation of ferrous iron, coupled with an influx of acidic drainage of the old Cu heap leach pads to the east, which joins the Horseshoe Bend flow prior to the point where it discharges to the Berkeley pit. The much smaller South Side springs (SS-1, SS-2), which discharge from an alluvial aquifer exposed on the SE highwall of the Berkeley Pit, were found to be only mildly acidic and had relatively low metal content on the date sampled (Tables 2 and 3). These springs likely represent a negligible source of metal and acidity loading to the Berkeley pit lake.

3.1.2. Flooded mine shafts

The Anselmo, Steward and Kelley mine shafts are located in the “East Camp” flooded workings of Butte, and are roughly on a W–E line that represents the inferred flow path of groundwater heading towards the Berkeley Pit (Fig. 1). Groundwater

from the flooded East Camp mine complex is thought to be the main water input into the deep Berkeley pit lake, and is estimated at ~2–3 million gallons (7.6–11.4 × 10⁶ L)/day (Metesh and Duaiame, 2000). At first glance, the results suggest that the quality of the East Camp mine water deteriorates as it travels from the Anselmo to the Steward to the Kelley mines (Tables 2 and 3). However, this conclusion is most likely erroneous, as the Kelley mine is singularly worse than all other flooded mine shafts and bedrock wells monitored by the MBMG (e.g., compare to data in Table 1). The reason for the poor water quality of the Kelley mine may be that the Kelley shaft was the former location of the main dewatering pumps for the Butte mines; it has therefore had the largest vertical extent of pyrite exposed to oxidation for the longest period of time. Kelley Mine water is also anomalous in its high temperature (31 °C, compared to 15 °C at the Anselmo and 20 °C at the Steward). The unusually high temperature could be the result of pyrite oxidation, an exothermic reaction that is capable of heating mine waters.

The Emma and Ophir shafts lie within the “West Camp” flooded mine workings, which are physically separated from the East Camp waters by a series of bulkheads and a groundwater divide. Groundwater in the Emma and Ophir shafts flows in a southwesterly direction (away from the Berkeley Pit), and is eventually pumped to the surface at the West Camp Extraction Well (Fig. 1). Groundwater in the West Camp is notable for the presence of elevated levels of H_2S , and – with the exception of As – very low trace metal content. A preliminary stable isotope investigation showed that the H_2S in the West Camp water is most likely sourced from bacterial reduction of SO_4 (Gammons et al., 2003b). Additional geochemical and stable isotopic investigations

of the West Camp waters are in progress (Roesler, 2005), and will be reported elsewhere.

As shown in Table 3, nearly all of the dissolved Fe sampled from the flooded shafts was present in the Fe(II) form, consistent with the relatively low Eh values measured. Also evident from Table 3 is the extremely high dissolved As concentration of some of the mine shaft waters, particularly the Kelley and Steward shafts (13 and 3 mg/L As, respectively).

3.1.3. The Berkeley pit lake

Variations in field parameters and dissolved Fe speciation with depth in the Berkeley pit lake are plotted in Figs. 2 and 3, respectively. Depth in the

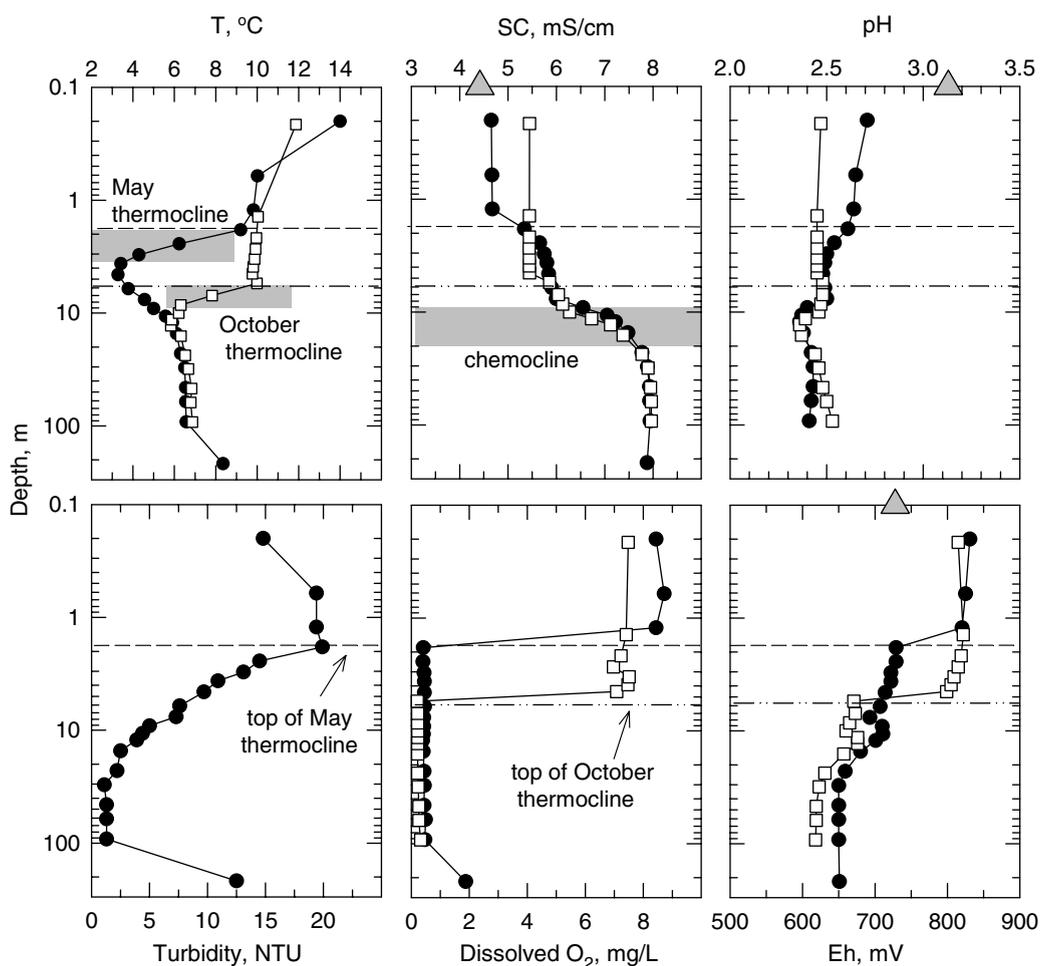


Fig. 2. Depth profiles for temperature (T), specific conductance (SC), pH, turbidity, dissolved O_2 , and Eh from the Berkeley pit lake on May 14, 2003 (filled circles) and Oct. 22, 2003 (open squares). Note the logarithmic y-axis scale. No turbidity data were gathered in the fall. The upper and lower dashed lines show the top of the May and October thermoclines, respectively. The SC, pH and Eh of Horseshoe Bend Springs is shown for comparison (gray triangle).

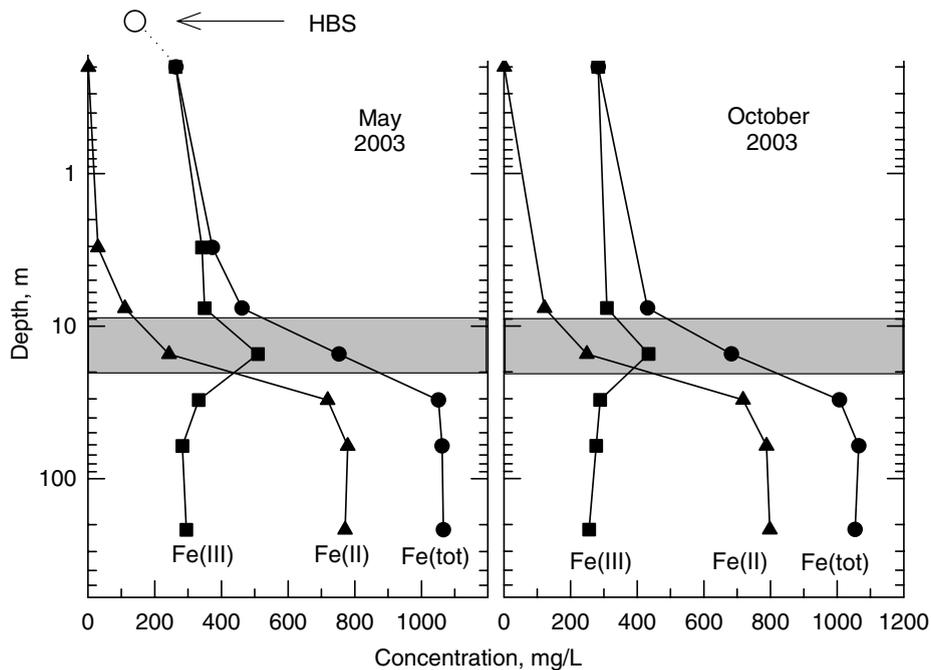


Fig. 3. Depth profiles for Fe speciation in the Berkeley pit lake, for May and October, 2003. The shaded regions represent the chemocline during both sampling periods. The total Fe concentration of Horseshoe Bend Spring (HBS) in May is shown by the open circle. Essentially all of the dissolved Fe at the outlet of HBS was Fe(III) on this date.

lake is shown on a logarithmic scale to accentuate features in the top 10 m of the water column. In May of 2003, chemical and/or physical discontinuities were present at depths of 2–3 m, and 10–20 m. At this time, water at the surface of the pit lake had a specific conductance (SC) similar to that of Horseshoe Bend Spring, consistent with the latter being the dominant input to the shallow pit lake. The discontinuity at 2–3 m coincided with the position of the May thermocline. Changes with depth across this interface included a rapid drop in temperature, a slight drop in pH, a step-like increase in SC, a drop in DO to levels below the detection limit, a step-like drop in Eh, and a decline in turbidity. In October of 2003, the top of the thermocline had shifted to a depth of 6 m, although changes in field parameters were similar to the Spring. In comparing the data in Figs. 2 and 3 from one season to another, it is important to note that the lake level rose approximately 2 m between the spring and fall samplings due to continued mine flooding and inputs from Horseshoe Bend. The rise in lake level is partly responsible for the fact that some of the chemical discontinuities were shifted to greater depth between the two sampling periods.

Both sampling events showed a sharp increase in SC at a depth of 10–20 m, as well as an increase in total Fe and a shift in Fe(II)/Fe(III) ratio from Fe(III)-dominant (above 10 m depth) to Fe(II)-dominant (below 20 m depth). Bearing in mind that the Horseshoe Bend Spring was diverted into the pit in mid-2000, and assuming a typical rate of lake level rise of ~ 0.5 m per month, it is probable that the 10–20 m discontinuity – here referred to as the *chemocline* – represents the boundary between pre-2000 Berkeley pit water at depth, and post-2000 modified Horseshoe Bend Spring water at shallower levels. The fact that the SC gradient is spread over a broad depth interval (Fig. 2) is explained by 3 years of aqueous diffusion of solutes, as well as mixing and entrainment of the chemocline during shallow lake turnover events.

Fig. 3 shows that a substantial amount of dissolved Fe(III) (>250 mg/L) was present throughout the entire depth of the pit lake on both sampling events. The influence of the Horseshoe Bend Spring is clearly seen, as total Fe values in the shallow pit-lake are roughly a quarter of those at depth. Essentially all of the Fe at the lake surface was Fe(III) on both dates. With depth, both the declining O_2 con-

tent (Fig. 2) and the hypothesized transition to pre-HBS water through the chemocline are responsible for the increase in Fe(II). Both the May and October profiles show an anomalously high Fe(III) content at a depth of 15 m. This depth corresponds to the elevation of the 2000 lake surface before Horseshoe Bend Spring water was allowed to contribute to the shallow pit-lake. Prior to these inputs, the Fe(III) concentration of shallow Berkeley pit lake water was extremely high (Jonas, 2000), owing to oxidation of the vast reservoir of Fe(II) at shallow depth.

Diagrams showing vertical changes in the concentration of common ions and trace elements in the Berkeley pit lake in May, 2003 are given in Figs. 4 and 5, respectively. Berkeley pit water is elevated in Ca^{2+} and Mg^{2+} relative to Na^+ and K^+ , whereas the anions are completely dominated by SO_4 . The Horseshoe Bend Spring had a diluting or concentrating effect on the chemistry of the shallow pit lake, depending on the analyte: concentrations of SO_4 and Ca^{2+} decreased above the chemocline, K^+ increased, and Na^+ and Mg^{2+} remained essentially unchanged. The concentrations of all of the metallic elements (Al, Cu, Mn, Zn) in Horseshoe Bend were much lower than in the deep pit lake, resulting in sharp drops in these solutes above the chemocline (Fig. 5). Arsenic had an unusual vertical profile, with a minimum value near the bottom of

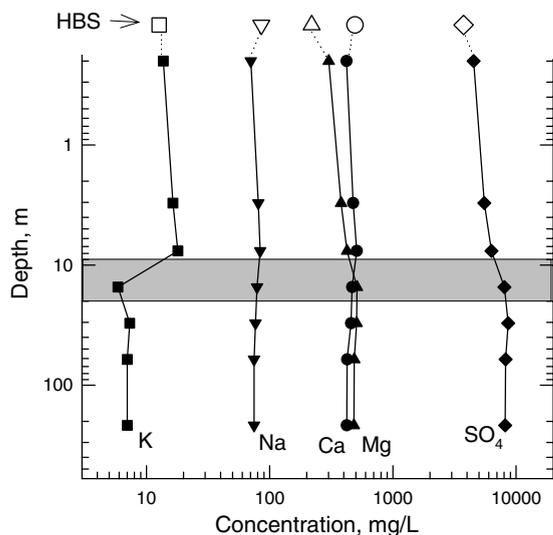


Fig. 4. Depth profiles for K, Na, Ca, Mg and SO_4 from the Berkeley pit lake on May 14, 2003. The composition of Horseshoe Bend Spring is shown for comparison (open symbols). The shaded region represents the chemocline.

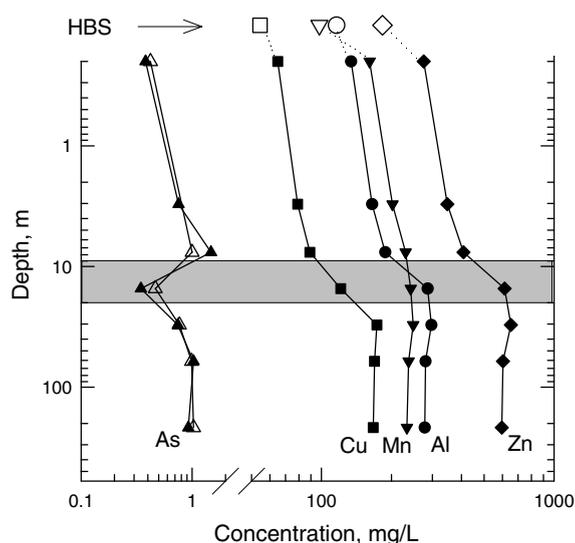


Fig. 5. Depth profiles for As, Cu, Mn, Al and Zn from the Berkeley pit lake on May 14, 2003. The composition of HBS in May is shown for comparison at the top of the diagram. Also shown are results for As from Oct. 22, 2003 (open triangles). The shaded region represents the chemocline.

the chemocline and a maximum value near the top of the chemocline. Although it would be tempting to discard these results as an artifact of analytical error, a similar pattern was shown for the October sampling event (Fig. 5). In fact, the decrease in As concentration near 15 m depth is consistent with historical data (Jonas, 2000) which showed that, prior to 2000, As levels decreased towards the top of the pit lake due to co-precipitation of As with secondary Fe(III) minerals. The increase in As at the top of the chemocline is more difficult to explain. Additional samples at closer spaced depth intervals would be necessary to sort out the details in the As concentration profiles. Although there are no As(III)/As(V) speciation data, it is likely that all of the dissolved As in the Berkeley pit lake is As(V), given the presence of elevated concentrations of dissolved Fe(III).

3.1.4. Mineral saturation indices

Mineral saturation indices (defined as \log_{10} of the ratio of the ion activity quotient divided by the equilibrium constant) were computed for each mine water sample using Visual MINTEQ, and selected results are summarized in Table 4. The MINTEQ database was supplemented with thermodynamic data for schwertmannite and 6-line ferrihydrite from Majzlan et al. (2004), and hydroxy- and

Table 4
Calculated saturation indices for selected Butte mine waters

	Gyp	Fer	Goe	Sch ^a	KJ ^a	GR ^a	AHS	Cal	Sid	MnC	ZnC
Anselmo	-0.23	3.10	5.88	2.70	2.59	2.76	-0.74	-0.98	-0.15	-0.07	0.12
Steward	-0.01	2.93	5.67	2.63	2.87	2.83	-0.03	-1.60	0.04	-0.84	-0.31
Kelley	0.02	1.58	4.24	1.73	2.91	0.94	0.20	-	-	-	-
Ophir	-1.12	-	-	-	-	-	-	-1.01	-1.78	-0.04	-0.63
Emma	-0.71	2.13	4.90	1.47	0.73	0.65	-	-0.30	-3.13	0.70	0.85
HBS-1	-0.01	0.59	3.40	1.08	2.84	-1.07	0.22	-	-	-	-
HBS-6	0.02	0.73	3.54	1.38	3.41	-3.01	0.02	-	-	-	-
<i>Depth (m)</i>	<i>Berkeley pit-lake (Spring, 2003)</i>										
0.2	-0.06	0.01	2.80	0.79	3.06	-3.82	-0.45	-	-	-	-
3.0	0.04	-0.86	2.01	0.04	2.65	-3.25	-0.36	-	-	-	-
12.2	0.05	-1.09	1.76	-0.14	2.41	-2.95	-0.36	-	-	-	-
30.5	0.05	-1.14	1.71	-0.21	2.35	-2.60	-0.26	-	-	-	-
61	0.01	-1.09	1.74	-0.18	2.33	-2.59	-0.38	-	-	-	-
216	0.01	-1.09	1.74	-0.18	2.35	-2.58	-0.38	-	-	-	-

See text for details.

Abbreviations: Gyp, gypsum; Fer, ferrihydrite; Goe, goethite; Sch, schwertmannite; KJ, K-jarosite; GR, hydroxy green rust; AHS, AlOHSO₄; Cal, calcite; Sid, siderite; MnC, amorphous MnCO₃; ZnC, amorphous ZnCO₃.

^a Saturation indices adjusted to 1 Fe atom per formula unit.

SO₄-green rusts from Bourrié et al. (1999). In Table 4, saturation indices for Fe-bearing minerals have been adjusted to one Fe atom per formula unit. This allows for a more equitable comparison of the relative saturation state of different solids formed from the same component.

The results of the Visual MINTEQ calculations show that all of the Berkeley pit lake samples were very close to equilibrium saturation with gypsum (Table 4). Similar results were obtained for the Fall, 2003 Berkeley Pit samples (data not shown in Table 4). Of the various Fe(III)-bearing solids that could impart a solubility control in the lake, schwertmannite was predicted to be the phase closest to equilibrium saturation. Previous workers have concluded that schwertmannite is a dominant constituent of suspended solids in the pit lake, based on geochemical modeling (Robins et al., 1997), scanning electron microscopy (SEM) of sediment collected by in situ samplers (Johnnie Moore, Univ. of Montana, pers. commun.), as well as SEM examination of precipitates formed upon aging and oxidation of Berkeley Pit water in the laboratory (Newbrough and Gammons, 2002; Gammons et al., 2003a). Other more crystalline Fe(III) solids, such as goethite and K-jarosite, were supersaturated in the pit lake, whereas ferrihydrite was undersaturated in all but the topmost portion of the water column. The aluminous phase that was closest to equilibrium saturation in the pit lake was AlOHSO₄ (i.e., the mineral jurbanite).

Saturation indices for the two Horseshoe Bend samples suggest equilibrium with gypsum and AlOHSO₄, and supersaturation with respect to all Fe(III) phases. The apparent supersaturation with Fe(III) precipitates is not surprising, considering that the spring had highly elevated concentrations of Fe(II) that rapidly oxidized to Fe(III) upon discharge to the surface.

Saturation indices for the mine shafts gave varied results. All 3 of the East Camp shafts were close to equilibrium with gypsum, whereas the West Camp shafts were undersaturated with this phase. Jurbanite (AlOHSO₄) was near saturation for the Kelley and Steward shafts, and was undersaturated for the Anselmo, whereas dissolved Al was non-detected for the West Camp shaft samples. With the exception of the acidic Kelley Mine, each of the mine shaft samples was near equilibrium saturation with at least one carbonate mineral. Calcite was near saturation for Emma; siderite for Anselmo and Steward, amorphous MnCO₃ for Anselmo, Ophir and Emma, and amorphous ZnCO₃ for Anselmo and Steward. All of the Fe(III) phases were predicted to be supersaturated in the mine shaft waters. However, because concentrations of dissolved Fe(III) were below the practical quantifiable limit, the saturation indices for Fe(III) minerals had to rely on the measured Eh values of each water. Because this type of calculation is prone to large error (due to both instrumental and non-equilibrium problems), the saturation indices in Table 4 for

the Fe(III) minerals in mine shaft water should be treated with skepticism. Nevertheless, it is interesting to speculate that hydroxy green rust (here defined as $\text{Fe(II)}_2\text{Fe(III)(OH)}_7$) may be present in some of the flooded mine shafts, and may be imparting a solubility control for dissolved Fe in both the Fe(III) and Fe(II) oxidation states.

The fact that all of the mine waters of the East Camp (including the Berkeley pit lake) were saturated with CaSO_4 is significant, as it indicates that gypsum (or anhydrite) is ubiquitous in the East Camp mine workings, and also implies that aqueous transport of Ca^{2+} and SO_4^{2-} may locally be non-conservative. Likewise, Mn^{2+} and Zn^{2+} appear to have solubility-controls as carbonate minerals in the West Camp and portions of the East Camp. The apparent saturation with MnCO_3 is not surprising, as rhodochrosite is an abundant gangue mineral in the veins of Butte (Meyer et al., 1968; Miller, 1973), and rhodochrosite-rich veins of the West Camp were once mined for Mn ore. In contrast, there appears to be no direct solubility control for Mn, Zn or Cu in the more acidic East Camp waters, including the Kelley Mine, Horseshoe Bend and the Berkeley pit lake. The concentrations of these metals in the acidic waters may be controlled by the rate of weathering and dissolution of source minerals, or perhaps by adsorption or co-precipitation with other phases, such as schwertmannite or jarosite.

3.2. Stable isotope results

Results of stable isotope analyses of water ($\delta^{18}\text{O}_w$ and δD_w) and aqueous SO_4 ($\delta^{18}\text{O}_s$ and $\delta^{34}\text{S}_s$) for all field samples collected in this study are summarized in Tables 2 and 5.

3.2.1. $\delta^{18}\text{O}$ and δD of mine waters

Trends in δD and $\delta^{18}\text{O}$ of water vs. depth (Fig. 6) illustrate that the shallow Berkeley pit lake was enriched in both ^2H and ^{18}O with respect to the deep lake in 2003. These trends are most easily explained by evaporation of HBS-derived shallow lake water (e.g., see Clark and Fritz, 1997). Similar trends were obtained for both sampling events, although the degree of isotopic enrichment at the surface of the lake was more pronounced in the Fall as compared to the Spring. The sharp gradient in isotopic composition in the top 30 m of the pit lake supports the theory that the shallow lake had not mixed with the deep lake since the Horseshoe Bend Spring was allowed to empty into the pit in mid-2000. Although no samples were collected between 70 and 210 m depth, it is probable that the pit lake is more or less isotopically homogenous below a depth of 30 m. Coincidentally (or perhaps not, see below), deep Berkeley pit lake water has a very similar isotopic composition to Horseshoe Bend water. In contrast, groundwater in the flooded mine shafts is isotopically lighter than either the pit lake or Horseshoe Bend.

Fig. 7 plots the isotopic composition of all the waters sampled in this study in comparison to the global meteoric water line of Craig (1961), as well as the local meteoric water line, which is based on one full year of precipitation data for Butte, Montana (Gammons et al., in review). Direct precipitation in Butte has a very large range in isotopic composition ($\delta\text{D} = -38$ to -207‰ ; $\delta^{18}\text{O} = -3.2$ to -27.2‰) with weighted averages of $\delta^{18}\text{O} = -15.3\text{‰}$ and $\delta\text{D} = -118\text{‰}$ for the 2004 calendar year (Gammons et al., in review). The fact that groundwater on Butte Hill is isotopically lighter than the yearly average for Butte precipitation

Table 5
Field parameters and isotope results for bedrock monitoring wells

Location	Total depth (m)	Date	T ($^{\circ}\text{C}$)	pH	SC (mS/cm)	Eh (mV)	$\delta^{18}\text{O}_s$ (‰)	$\delta^{34}\text{S}_s$ (‰)
Well A	227	12/19/00	18.8	5.70	1.65	102	+2.0	16.8
Well B	195	12/27/00	15.7	7.32	1.28	28	-8.6	4.2
Well C	244	12/21/00	17.6	6.19	0.69	138	-10.8	3.6
Well D1	194	1/25/01	14.2	6.93	0.74	175	-6.4	9.6
Well D2	236	1/3/01	16.4	6.34	1.42	159	-6.1	8.3
Well E	108	12/27/00	13.7	6.77	0.78	17	-5.4	7.9
Well F	195	12/28/00	16.0	6.96	1.54	-126	-0.7	14.7
Well G	294	12/26/00	18.2	6.41	0.98	55	+0.3	10.6
Well J	210	12/19/00	23.2	4.01	3.15	193	-10.0	3.7

Total depth refers to the depth below the land surface where the groundwater samples were taken.

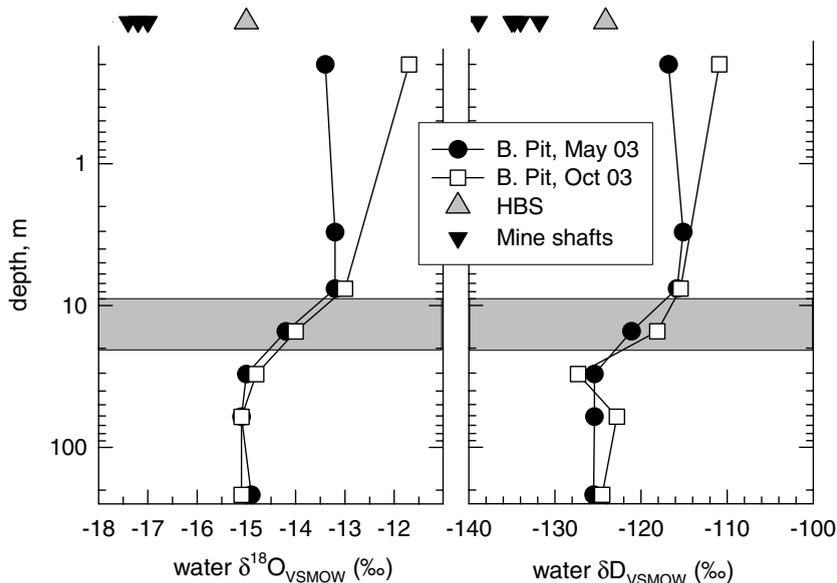


Fig. 6. Depth profiles for $\delta^{18}\text{O}_w$ and δD_w in the Berkeley pit lake on May 14, 2003 (filled circles) and Oct. 22, 2003 (open squares) (results in ‰). The isotopic compositions of Horseshoe Bend Spring and the flooded mine shafts are shown for comparison. The shaded region represents the chemocline.

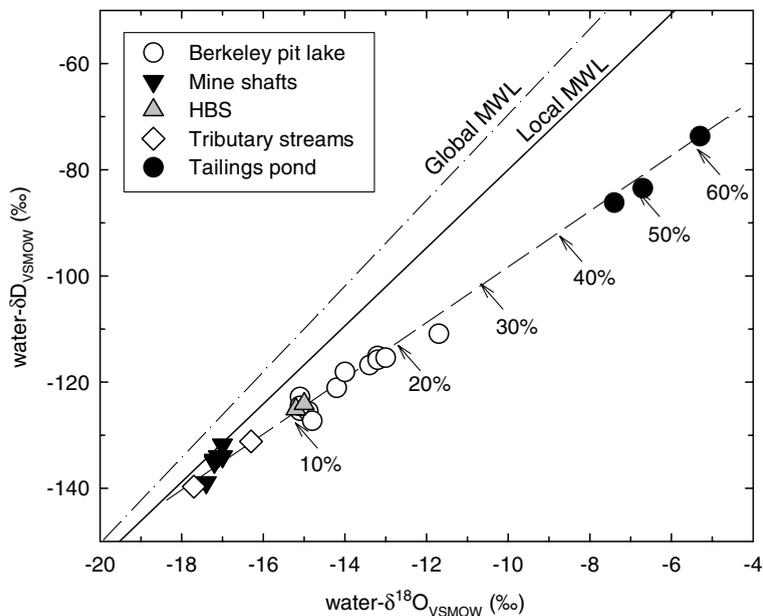


Fig. 7. The δD and $\delta^{18}\text{O}$ composition of Butte mine waters. The global and local meteoric water lines (MWL) are shown for reference. The Butte mine waters show progressive deviation from the MWL, an indication of evaporative isotope enrichment. Estimates of the percentage of water evaporated (at 15 °C and 65% relative humidity) to cause the observed deviations are given by the arrows. Data for the global MWL are from Craig (1961). Data for the local MWL and the % evaporation estimates are from Gammons et al., in review.

implies that most of the groundwater recharge to the flooded mine complex occurs during the cooler months from snowmelt and rain.

As shown in Fig. 7, the Butte mine waters do not plot directly on the local MWL, but are rather shifted to the right along an evaporation trend

(Seal, 2003). During evaporation, ^{16}O is fractionated into the vapor phase to a greater extent than ^1H , such that the residual water follows a slope on a δD vs. $\delta^{18}\text{O}$ diagram that deviates from the MWL. The greater the degree of evaporation, the further the water will plot off of the MWL. Also, the lower the relative humidity, the greater the angle of deviation between the MWL and the evaporation line (Clark and Fritz, 1997; Seal, 2003). The estimated percent evaporation needed to generate a given isotopic deviation from average Butte recharge water is shown by the arrows in Fig. 7. These calculations were made assuming a constant temperature of $15\text{ }^\circ\text{C}$, and 65% relative humidity (see Gammons et al., in review, for details). Horseshoe Bend water and deep Berkeley pit lake water have nearly identical isotopic signatures, and show intermediate degrees of evaporation (approximately 12% water loss). Water in the shallow Berkeley pit lake shows up to 25% evaporation, whereas surface water from the Yankee Doodle tailings pond was even more fractionated (up to 60% water loss). The high degree of evaporation in the tailings pond is due to the fact that this shallow water body had no surface outlet during the study period. At the opposite end of the spectrum, the mine shaft waters and small tributary streams entering the Yankee Doodle tailings pond from the north are isotopically light and plot relatively close to the local MWL, indicating that minor amounts of evaporation (<10%) occurred in their history. Of the two tributary streams, Yankee Doodle Creek (YDC) shows more evidence of evaporation than upper Silver Bow Creek (SBC), which is explained by the existence of two drinking water reservoirs near its headwaters.

The difference in isotopic composition of water in the flooded mine shafts and the deep Berkeley pit lake is somewhat difficult to reconcile with the widely held belief that East Camp groundwater is the primary input into the deep pit lake. Two possible explanations are: (1) deep pit lake water is indeed East Camp groundwater that has subsequently undergone an evaporation cycle at some time during the history of pit filling; and (2) the primary influx of deep groundwater is coming from a different direction, for example, from the general vicinity of the tailings dam and heap leach pads. The first hypothesis is possible, but would require periodic “top to bottom” lake turnover events to thoroughly mix the O and H isotopes in the deep Berkeley pit lake. Such events are believed to have occurred prior to 2000 (Jonas, 2000; Madison

et al., 2003), and this helps to explain the nearly homogenous chemistry and isotopic composition of the pit lake below the chemocline (Figs. 2–6). The second hypothesis goes against conventional thinking about the primary groundwater inputs into the lake, and would require a substantial groundwater underflow from the north or NE (Fig. 1). Supporting this theory is the fact that the hydraulic gradient of the cone of depression surrounding the Berkeley Pit is much steeper towards the north than in any other direction. Approximately 300 m difference in hydraulic head exists between the spigot point on the Yankee Doodle tailings dam and the Berkeley pit lake. At the moment it is impossible to validate this hypothesis, as there are no deep groundwater monitoring wells north of the Berkeley Pit (Fig. 1). Finally, it is also possible that both hypotheses are valid, but that the dominant source of water to the pit lake has changed with time. In the early years of pit flooding, seepage from the East Camp may have been the dominant influx of water. However, the subsequent rise in the lake level would have lowered the gradient of the water table towards the west, such that the primary influx of deep groundwater to the Berkeley Pit may have shifted to the north. Evidence in support of this hypothesis includes the fact that the water quality of the Kelley Shaft declined sharply during the period 2000–2005 (GWIC, 2004, and John Metesh, pers. commun., 2005), suggesting a possible change in direction of groundwater flow in the mine workings closest to the Berkeley Pit.

3.2.2. $\delta^{18}\text{O}$ and $\delta^{34}\text{S}$ of aqueous SO_4

The isotopic composition of aqueous SO_4 from various Butte mine waters are summarized in Fig. 8. This figure includes data for bedrock monitoring wells briefly discussed in the preliminary study of Madison et al. (2003), and reported here in Tables 5 and 6. The $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ results again show a distinct similarity between the Berkeley pit lake and the Horseshoe Bend Spring, implying a similar source of SO_4 for the two water bodies. In addition, only minor variation in $\delta^{34}\text{S}_{\text{SO}_4}$ occurred with depth in the pit lake (Table 2). Because negligible fractionation of S isotopes occurs during oxidative weathering of pyrite (Field, 1966; Seal, 2003), the $\delta^{34}\text{S}$ signature of dissolved SO_4 in the pit lake should be similar to that of pyrite (the most abundant sulfide mineral) in the surrounding ore body. Lange and Cheney (1971) noted that pyrite in the Butte district had a relatively narrow range in $\delta^{34}\text{S}$

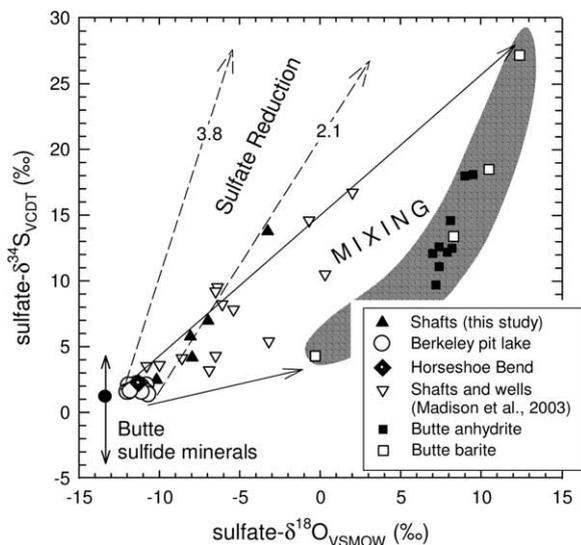


Fig. 8. The $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ isotopic composition of aqueous SO_4 from Butte mine waters. Well and shaft data from Madison et al. (2003) (inverted triangles) have been added to the results of this study. Also shown is the range (solid arrow) and average (black dot) of $\delta^{34}\text{S}$ of hydrothermal sulfide minerals from the Butte ore body (Lange and Cheney, 1971; Field et al., 2005). The dashed lines labeled 2.1 and 3.8 show the range in trajectories of S and O isotopes that would be expected for bacterial SO_4 reduction, beginning with SO_4 with a similar composition to the Berkeley pit lake. Data for hydrothermal barite and anhydrite (shaded region) from the Butte ore body are from Field et al. (2005).

(-1.8 to $+4.8\text{‰}$), with slightly lower values in the central zone of the ore body (near the Berkeley Pit), and slightly higher values in veins from the outer parts of the district. Pyrite samples from the immediate vicinity of the Berkeley Pit had an average $\delta^{34}\text{S}$ value of $+1.7\text{‰}$ ($n = 3$) (Lange and Cheney, 1971). More recently, Field et al. (2005) reviewed all available S isotope data for sulfide minerals from the Butte district, including a large number of new analyses of their own, and found a total range in $\delta^{34}\text{S}$ of -3.7 to $+4.8$, very similar to the

earlier study of Lange and Cheney (1971). Field et al. (2005) reported an average value for all Butte sulfides of $+1.4\text{‰}$ ($n = 281$), which is very close to the average $\delta^{34}\text{S}$ value of the pit lake sulfates analyzed in this study ($+1.8 \pm 0.3\text{‰}$, $n = 14$). The fact that the S isotopic composition of SO_4 from Horseshoe Bend is also similar to that of hydrothermal pyrite from Butte is not surprising, considering that the spring discharges near the base of the Yankee Doodle tailings dam, and that all of the waste rock used to construct the dam – as well as the impounded mine tailings – came from the Butte ore body.

In comparison to the Berkeley pit lake and Horseshoe Bend, the $\delta^{34}\text{S}$ values of SO_4 in the flooded mine shafts and bedrock monitoring wells vary over a much larger range, and are isotopically heavier in both S and O (Fig. 8). Taken together, the data show a probable mixing trend between SO_4 derived from oxidation of hydrothermal sulfide minerals and isotopically-heavy SO_4 from another source or sources. Potential sources of heavy SO_4 include dissolution of primary or secondary SO_4 minerals (e.g., anhydrite, gypsum, barite) in the mineralized veins, altered wallrock, or overlying stratum, and inputs from human activities (e.g., drilling fluids, concrete used for grout or stabilization of mine workings, pollution from the city of Butte). Field et al. (2005) recently reported $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ for a number of hydrothermal barite and anhydrite samples from the Butte District, which are also plotted in Fig. 8. The hydrothermal SO_4 minerals are highly enriched in ^{34}S relative to coexisting sulfide minerals, and also contain very heavy O_2 with $\delta^{18}\text{O} \sim +7$ to $+12\text{‰}$. This reinforces the hypothesis that SO_4 in the shaft waters and bedrock monitoring wells is a mixture of SO_4 derived from pyrite oxidation and leaching of hypogene SO_4 minerals from the altered granitic wallrock (see also Nordstrom et al., 2005).

Table 6
Solute concentrations for samples shown in Table 5

	Al	As	Ca	Cu	Fe	Mg	Mn	K	Na	Zn	SO_4^{2-}	HCO_3^-	SiO_2
Well A	<0.3	0.060	206	<0.02	18.6	54	4.9	21	112	114	967	51.2	53.6
Well B	<0.03	0.011	180	<0.002	1.45	46	2.1	9.9	66	5.0	647	124	30.6
Well D1	<0.3	0.013	79	<0.002	7.83	21	1.3	12	22	1.1	310	80.5	62.7
Well D2	0.15	0.037	180	<0.002	44.5	65	5.3	17	42	3.9	871	n.a.	69.1
Well G	<0.3	0.008	145	<0.002	12.2	32	1.9	14	20	86	520	63.8	55.8
Well J	42.7	0.75	337	13.4	311	83	6.5	52	132	34	2546	n.a.	79.6

All data are from GWIC (2004). No data are available for Wells C, E, and F on the dates that the isotopic samples were collected. All units are mg/L. n.a., not analyzed.

It is also possible that fractionation of S and O isotopes of SO_4 occurred in some of the West Camp mine waters (which includes the Emma and Ophir shaft samples of this study) where bacterial SO_4 reduction is known to occur (Gammons et al., 2003b). Bacterial SO_4 reduction fractionates the isotopes of both S and O, and enriches the remaining SO_4 in the heavy isotopes (Seal, 2003). The dashed lines in Fig. 8 show the range in evolution trends in SO_4 (based on data reviewed by Seal, 2003) that would be expected if bacterial SO_4 reduction was an important process in the flooded mine workings, and if the initial SO_4 had an isotopic composition similar to SO_4 in the Berkeley pit lake. The slopes of the enrichment lines vary from 2.1 to 3.8, and in general are steeper than the spread in the field data. This result, combined with the lack of direct evidence for SO_4 reduction in any of the East Camp waters, makes SO_4 reduction a less likely mechanism to explain the isotopically-enriched sulfates in the Butte mine waters.

Perhaps the most important point to take from the data in Fig. 8 is that SO_4 in the Berkeley pit lake is isotopically distinct from that in the surrounding flooded mine waters. This observation implies that most of the SO_4 (and by implication, the acid and heavy metals) in the lake must have been derived by in situ interaction with pit wallrock, combined with inputs from the Horseshoe Bend Spring. By comparison, inputs of SO_4 from the flooded mine complex may have been minor or negligible. These ideas are further illustrated in Fig. 9, which plots the $\delta^{34}\text{S}$ composition of SO_4 for all of the Butte mine water samples vs. dissolved SO_4 concentration (Fig. 9A) and vs. pH (Fig. 9C). On both diagrams, a mixing trend is displayed between the Berkeley pit lake and Horseshoe Bend, whereas the mine shafts and bedrock monitoring wells define a trend that is more or less consistent with mixing of SO_4 from pyrite oxidation and SO_4 from dissolution of gypsum/anhydrite. In general, the $\delta^{34}\text{S}$ values of SO_4 increase as dissolved SO_4 concentration decreases, and as pH increases. The tailings pond is an exception to the latter observation (Fig. 9C), as its low $\delta^{34}\text{S}$ values are more similar to the pit lake, and are therefore indicative of SO_4 sourced from pyrite oxidation. In Fig. 9B, the concentrations of Ca and SO_4 are plotted against each other. The arrow denotes the trend that would be expected if all dissolved SO_4 was sourced from stoichiometric dissolution of anhydrite or gypsum. With the exception of the West Camp mine shafts and several of the bed-

rock monitoring wells, most of the mine waters in this study plot well to the right of the gypsum dissolution trend, implying derivation of a high percentage of aqueous SO_4 from oxidation of sulfide minerals. The shaded region in Fig. 9B encloses those samples that were predicted from Visual MINTEQ to be very close to equilibrium saturation with gypsum. This region extends from a theoretical endpoint corresponding to 15 mmol Ca^{2+} and 15 mmol SO_4^{2-} (for dissolution of gypsum in pure water), and extending to the right with a slightly negative slope, in a manner similar to that recently demonstrated by Naus et al. (2005) in a study of SO_4 in the Red River valley, New Mexico.

3.2.3. Results of laboratory experiments

Previous experiments in which crushed and weathered samples of pyrite-bearing wallrock from the Berkeley Pit were leached with de-ionized water showed that the resultant solutions had a pH and metal chemistry similar to the Berkeley pit lake (Newbrough and Gammons, 2002). In the present study, the conditions of the experiments performed by Newbrough and Gammons (2002) were repeated, and the leachates were analyzed for their isotopic composition of water and dissolved SO_4 . The results (Table 7) show the following: (1) there was no change in the O and H isotopic composition of water between the beginning and end of the experiment; (2) all of the samples had $\delta^{34}\text{S}$ of SO_4 that fell within the range of pyrite from the central zone of the Butte ore body (Lange and Cheney, 1971); and (3) the O_2 isotopic composition of SO_4 in all of the leachate samples was significantly heavier (by 7.6–12.6‰) than the water used in the experiment. The Fe leached out of the weathered Berkeley pit wallrock was a mixture of both Fe(II) and Fe(III), with $\text{Fe(II)} > \text{Fe(III)}$. However, the shallow pit lake profiles of May and October (Fig. 3) show the presence of very little Fe(II) in the shallow water, suggesting that any Fe(II) leached from the pit walls as the lake level rises and reacts with wall rock is catalytically oxidized to Fe(III) by microbes in the presence of O_2 in the oxidized, shallow lake.

The results of the 14 day anaerobic pyrite oxidation experiment (Table 7) showed the following: (1) water at the end of the experiment was significantly heavier than the initial water, due to evaporation caused by passage of $\text{N}_2(\text{g})$ through the reaction chamber; (2) the $\delta^{34}\text{S}$ of the dissolved SO_4 formed by anaerobic pyrite oxidation was similar to that of the starting pyrite material; and (3) the $\delta^{18}\text{O}$ of

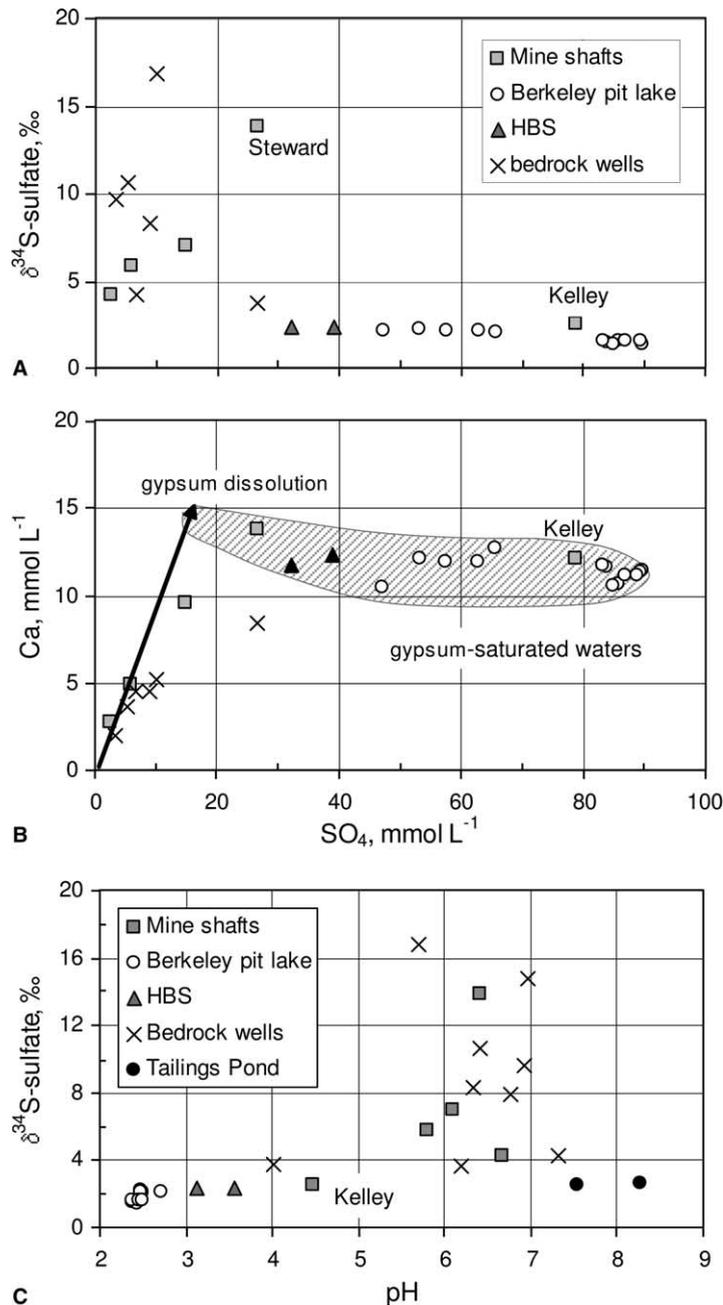


Fig. 9. Trends in selected parameters for Butte mine waters: (A) $\delta^{34}\text{S}$ of dissolved SO_4 vs. SO_4 concentration; (B) Ca concentration vs. SO_4 concentration; (C) $\delta^{34}\text{S}$ of dissolved SO_4 vs. pH. The arrow in B shows the expected trend for stoichiometric dissolution of anhydrite or gypsum, while the shaded region encircles mine water samples that are very close to equilibrium saturation with gypsum.

the aqueous SO_4 was similar to that of the co-existing water. The average of the initial and final $\delta^{18}\text{O}_{\text{water}}$ values was -16‰ whereas the $\delta^{18}\text{O}$ sulfate value was -14.2‰ . Thus, the O isotopic composition of SO_4 formed from anaerobic pyrite oxidation was closer to that of coexisting water than was SO_4

formed by aerobic leaching of the wallrock. The significance of this result is discussed below.

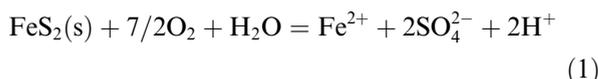
3.2.4. Mechanism of pyrite oxidation in the pit lake
Beginning with Taylor et al. (1984a,b), numerous investigators have attempted to use O isotopes of

Table 7
Stable isotope results for wallrock leachate and anaerobic pyrite oxidation experiments

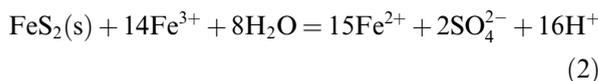
Sample	$\delta^{18}\text{O}_{\text{water}}$	$\delta\text{D}_{\text{water}}$	$\delta^{34}\text{S}_{\text{sulfate}}$	$\delta^{18}\text{O}_{\text{sulfate}}$
<i>Wallrock leachate experiments</i>				
Laboratory water	-18.8	-141	n.a.	n.a.
Leachate BP-1	-18.6	-141	2.1	-9.6
Leachate BP-2	-18.5	-141	0.4	-10.9
Leachate BP-4	-18.5	-141	2.7	-5.9
<i>Anaerobic pyrite oxidation experiment</i>				
Laboratory water	-18.0	-142	n.a.	n.a.
Unreacted pyrite	n.a.	n.a.	2.9	n.a.
Final solution	-13.9	-108	1.9	-14.2

All results in ‰, n.a., not analyzed.

mine water sulfates to elucidate the mechanisms of pyrite oxidation. The oxidation of pyrite is traditionally written with molecular O_2 as the electron acceptor, as follows:

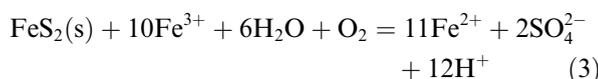


However, oxidation of pyrite by dissolved Fe(III) can take place at a rapid rate in acidic waters, even in the complete absence of O_2 or bacteria (Garrels and Thompson, 1960; Singer and Stumm, 1970; Moses et al., 1987; Nordstrom and Alpers, 1999). The reaction may be written as follows:



Oxidation of pyrite by Fe^{3+} in the absence of O_2 should produce SO_4 ions in which 100% of the oxygen atoms were derived from the surrounding water. In this case, the $\delta^{18}\text{O}$ composition of the SO_4 should be similar to that of the water, assuming that the oxidation reaction is accompanied by a small or negligible isotope fractionation effect, which has been demonstrated (Lloyd, 1968; Taylor et al., 1984a,b; Van Everdingen and Krouse, 1988). In contrast, because reaction (1) takes place in the presence of molecular O_2 , there is a possibility that some O_2 atoms of atmospheric origin will be incorporated into the SO_4 produced. Oxygen in air ($\delta^{18}\text{O} = +23\text{‰}$, Horibe et al., 1973) is much heavier than oxygen in Butte meteoric H_2O . However, a number of studies (Seal, 2003, and references therein; Usher et al., 2004) have shown that, even in the presence of molecular O_2 , the majority of the O atoms in SO_4 formed during pyrite oxidation are inherited from water. As reviewed by Seal (2003),

pyrite oxidation often involves the generation of sulfite as a reactive intermediate species. Whereas the isotopic exchange of water and SO_4 is extremely slow at the pH conditions of the Berkeley pit lake (the exchange reaction has a half-life of approximately 1 Ka, based on Fig. 8 of Seal, 2003), sulfite and water exchange their isotopes very quickly (Van Stempvoort and Krouse, 1994). However, in the presence of molecular O_2 , there is still the possibility that some atmospheric O_2 could be incorporated into the SO_4 molecule in the final oxidation of sulfite to SO_4 . Seal (2003) suggested the following end-member reaction for the oxidation of pyrite under aerobic conditions:



In this reaction, 75% of the O molecules in the SO_4 are derived from water, and 25% from atmospheric O_2 . As shown by Seal (2003), the majority of mine waters investigated to date have isotopic compositions that are intermediate between what one would expect from the stoichiometries of reactions (2) and (3). However, it should be stressed that dissolution of gypsum and anhydrite may have been an important source of SO_4 in many of the systems studied, which complicates the interpretation of the SO_4 stable isotopes.

Fig. 10 plots $\delta^{18}\text{O}_{\text{SO}_4}$ vs. $\delta^{18}\text{O}_{\text{water}}$ for field samples collected in this study, as well as the results of the laboratory experiments. Superimposed on the data are dashed lines showing the percentage of incorporation of atmospheric O_2 during the formation of SO_4 from pyrite oxidation via reactions (2) and/or (3), assuming no isotopic fractionation between oxygen in SO_4 and O_2 . The line labeled 0% is the theoretical limit for reaction (2), whereas the line labeled 25% is the limit defined by reaction (3). Sulfates from Horseshoe Bend and the Berkeley pit lake show relatively little evidence of incorporation of atmospheric O_2 , as does SO_4 from the anaerobic pyrite oxidation experiment. However, this situation is complicated by the aforementioned evaporation effect, which enriches the residual water in ^{18}O , but has no effect on the isotopic composition of SO_4 . This is best seen for the highly evaporated samples from the Yankee Doodle tailings pond, which have $\delta^{18}\text{O}_{\text{sulfate}} \ll \delta^{18}\text{O}_{\text{water}}$. In contrast, SO_4 from the flooded mine shafts plots well into the aerobic field, indicating significant incorporation of atmospheric O_2 . Similar results were obtained for the aerobic leach experiments. This

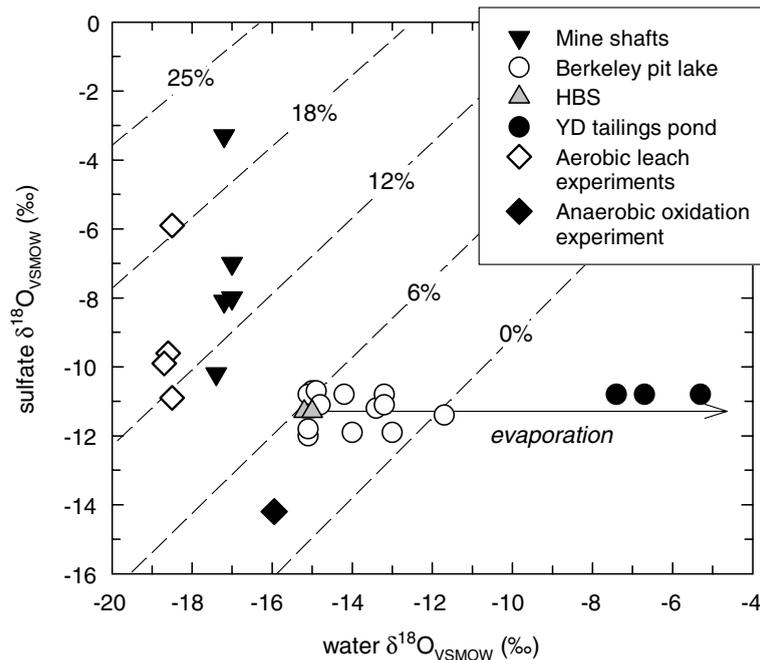


Fig. 10. Diagram comparing the $\delta^{18}\text{O}$ composition of aqueous SO_4 and coexisting water for samples collected in this study. The dashed lines indicate the proportion of O_2 atoms in aqueous SO_4 inherited from atmospheric O_2 (see text). Also shown are data from the aerobic wallrock leach and anaerobic pyrite oxidation experiments of this study.

result suggests that SO_4 in the flooded mine shafts may have been primarily derived by leaching of soluble salts as the mine waters rose. However, as discussed above, it is also possible that SO_4 in the mine shafts was partly derived from a source other than pyrite oxidation, such as primary or secondary SO_4 minerals in the surrounding bedrock and overlying soil or alluvial sediment, urban pollution, or exotic materials in the mine workings themselves.

Although a detailed SO_4 and water mass balance for the Berkeley pit lake would seem to be a logical next step, this would be a very daunting task due to the complexity of the system. Possible sources of SO_4 to the pit lake include: (1) the Horseshoe Bend Spring; (2) dissolved SO_4 in influent deep groundwater; (3) dissolution of hydrothermal SO_4 minerals (anhydrite, barite) from mineralized bedrock; (4) flushing of soluble salts from the mine walls during precipitation events; (5) dissolution of soluble salts from the mine walls as the lake level rises; (6) anaerobic oxidation of pyrite by Fe^{3+} dissolved in non-evaporated water; and (7) anaerobic oxidation of pyrite by Fe^{3+} dissolved in water that has been partially evaporated. Each of these end-member situations could result in different combinations of $\delta^{18}\text{O}_{\text{sulfate}}$ and $\delta^{18}\text{O}_{\text{water}}$. With the exception of

HBS, the position (i.e., isotopic composition) of each of these end members can only be roughly approximated from the various results reported in this study. For example, although the flooded mine shafts all have $\delta^{18}\text{O}_{\text{water}}$ close to average recharge water for the Butte area, the average $\delta^{18}\text{O}_{\text{sulfate}}$ of groundwater entering the pit is not known, owing to the large range in the shafts and wells sampled (Fig. 8). Conversely, whereas soluble salts flushed from the pit walls during storms are likely to have $\delta^{18}\text{O}_{\text{sulfate}}$ close to $+10\text{‰}$ (based on data in Table 6), the $\delta^{18}\text{O}_{\text{water}}$ could vary over a huge range, depending on the time of year and meteorological conditions. For these reasons, it is not possible to attempt a quantitative isotopic mass balance for the pit lake at this time.

4. Conclusions

The following is a list of some of the more important conclusions of this study:

- (1) In terms of pH and metal concentration, the chemistry of the Berkeley pit lake is considerably worse than all of its known influent waters.

- (2) In 2003, the Berkeley pit lake was stratified, with relatively low salinity water in the top 10 m, reflecting more than two years of influx of the Horseshoe Bend Spring to the shallow lake.
- (3) Based on vertical gradients in field parameters, metal concentrations, and isotopic composition, there has been no large scale (top to bottom) lake turnover event since July of 2000, when Horseshoe Bend Spring was diverted into the lake.
- (4) All of the mine waters in the East Camp flooded mine workings are in equilibrium with gypsum. Many of these waters are also close to equilibrium saturation with Al and Fe(III) hydroxy-SO₄ minerals (schwertmannite, jurbanite). Groundwater samples from the West Camp are undersaturated with gypsum but close to equilibrium with MnCO₃, whereas waters in the Anselmo and Steward shafts of the East Camp are saturated with siderite and ZnCO₃.
- (5) The isotopic composition of mine waters in Butte plot along an evaporation trend that deviates from the meteoric water line (precipitation line).
- (6) Water near the surface of the pit lake and in a nearby tailings dam show the largest extent of evaporation, whereas small tributary streams and groundwater in the flooded mine shafts are relatively non-evaporated; water in the deep Berkeley pit lake is isotopically indistinguishable from Horseshoe Bend Spring, and shows intermediate degrees of evaporation.
- (7) Sulfate in the Berkeley pit lake is isotopically similar to SO₄ in Horseshoe Bend, but is very different from SO₄ in the surrounding flooded mine shafts and bedrock monitoring wells. This implies that the flooded mine complex has been a minor contributor of SO₄ to the pit lake.
- (8) The O₂ isotopic composition of SO₄ in the Berkeley pit lake and Horseshoe Bend Spring is intermediate between what would be expected for oxidation of pyrite under subaqueous, anaerobic conditions and for oxidation of pyrite under subaerial, aerobic conditions.
- (9) The S and O isotopic composition of SO₄ in the flooded underground mine workings is consistent with derivation from a mixture of pyrite oxidation and dissolution of primary

SO₄ minerals in the mineralized rock, coupled with some fractionation during bacterial SO₄ reduction, the latter being important mainly in the West Camp mine workings.

- (10) Although leaching of soluble SO₄ salts (by rising lake waters or pitwall runoff during storms) and subaqueous oxidation of pyrite by Fe³⁺ are both believed to be important factors controlling the poor water quality of the Berkeley pit lake, the relative importance of these two mechanisms cannot be quantified at this time.

Finally, the results of this study underscore the usefulness of stable isotopes in pit lake studies, but also illustrate some of the difficulties in applying isotopic data to a system as large and complex as the Butte flooded mine complex.

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