VERTICAL GRADIENTS IN GEOCHEMISTRY OF FLOODED MINE SHAFTS IN BUTTE, MONTANA

by

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Abstract

The flooded mines of Butte, Montana include over 15,000 km of vertical shafts, horizontal drifts and stopes, interconnected to each other in varying degrees. The main objective of this study is to document the presence or absence of vertical gradients in chemistry, temperature, and stable isotopic composition of mine water in the flooded shafts. Mine shafts that were successfully sampled for this thesis include the Anselmo, Steward, Kelley, Granite Mountain, and Pilot Butte shafts of the so-called "East Camp" mine workings, the Travona shaft of the "West Camp" mine workings, and the Orphan Girl and Marget Ann shafts of the "Outer Camp" mine workings. At each of the above shafts, a vertical profile of environmental parameters including temperature, SC, pH, and ORP was obtained by lowering a datasonde through the top 300 feet of the water column. Water samples at various depths to a maximum of 1200 ft below static water level (BSWL) were brought to the surface with either a bailer or a "Kemmerer" point sampler. The East and West Camps are hydrologically separated, and contain water with very different chemistry. Whereas the majority of the East Camp waters are slightly acidic with elevated heavy metal concentrations (including Fe, Mn, and Zn), the West Camp waters are pH-neutral and enriched in hydrogen sulfide (H_2S), with extremely low metal concentrations. Water in the Outer Camp is more similar to the West Camp in most respects. The Orphan Girl shaft contains the highest concentration of H_2S (up to 10 mg/L) of any of the mine waters of Butte.

The results of this study show surprisingly few changes in chemistry, temperature, and isotopic composition with depth BSWL in most of the mine shafts. Some of the shafts showed systematic changes in pH and Eh in the top 300 ft BSWL, but these changes can be explained by inwards diffusion of O_2 and outwards diffusion of CO_2 towards the top of the water column. Likewise, there were virtually no vertical changes in the stable isotopic composition of water or dissolved sulfate in any of the mines, however, horizontal changes were large... Horizontal variations in the stable isotopic composition of SO_4 are attributed to three processes: 1) oxidative dissolution of sulfide minerals, which produces SO_4 with a S isotopic composition similar to the precursor sulfides; 2) dissolution of hydrothermal sulfate minerals (gypsum, anhydrite) present in altered and mineralized bedrock; and 3) bacterial sulfate reduction,.

The lack of any discernible gradients in temperature and salinity (i.e., SC) in most of the mine shafts implies that the shaft waters are circulating in a vertical direction. The Kelley Mine is an exception to this rule, as it does show gradients in chemistry and temperature between 300 and 1200 ft BSWL. The Kelley mine water is anomalously warm (34°C) at the surface, and becomes even warmer (> 38°C) at depth. It is speculated that the high temperature of the Kelley Mine water is partly due to pyrite oxidation, a strongly exothermic reaction. This is consistent with the fact that the Kelley Mine has by far the lowest pH and highest dissolved Fe and SO_4 concentrations of any of the mine shafts in the Butte complex.

Keywords: mine water, geochemistry, stable isotope, bacterial sulfate reduction

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1. Introduction

1.1. Statement of Purpose

The main objective of this thesis was to examine changes as a function of depth in the geochemistry and stable isotope composition of mine shaft water in Butte, Montana. This study was an outgrowth of previous Montana Tech theses which focused on the geochemistry and stable isotope composition of mine water in the Berkeley pit lake, the Kelley, Anselmo and Steward shafts of the East Camp flooded mine workings (Pellicori, 2004; Pellicori et al., 2005), and the West Camp Extraction Well which drains the West Camp flooded mine workings (Roesler, 2005; Roesler et al., 2007) (see below for more site description). These previous theses, in conjunction with ongoing monitoring by the Montana Bureau of Mines and Geology (MBMG), have documented the incredible diversity in the chemistry of mine waters in the Butte district, as well as the various processes – both biological and geological – that have influenced these waters. However, whereas a good understanding exists of vertical changes in chemistry of the Berkeley pit lake, very little information exists on similar changes in chemistry or microbiology of the flooded mine shafts. Typically in the past, MBMG has collected samples of mine shaft water from a depth of 100 feet below static water level (BSWL). Little information is available at greater depths, despite the fact that the majority of the underground mine workings are at depths between 1000 and 5000 feet.

This thesis describes the results of Mine Waste Technology Program Project 40, which examined vertical gradients in mine water geochemistry in eight mine shafts within the Butte district. Besides reviewing the geochemical data obtained, some interesting new findings are reported on vertical and lateral changes in mine water temperature throughout the district.

1.2. Site Description and Previous Work

The flooded abandoned mine complex of Butte, Montana is the most extensive in the world, and contains over 16,000 km of underground mine workings (Duaime et al., 2004), forming a labyrinth of horizontal tunnels, partly backfilled stopes, and vertical shafts (Fig. 1). The mine workings extend to a depth of over 1600 m, and cover an area of > 15 km^2. Approximately 90% of the underground workings belong to the so-called East Camp, which drains to the Berkeley pit lake (Fig. 1). The latter is a very large (> 100 billion L), highly acidic (pH 2.6), and metal-rich artificial lake that is over 200m deep and 1.5 km by 1.0 km in aerial extent. The pit lake, which occupies the site of a former porphyry-style open pit Cu mine that closed in 1982, is still rising at the approximate rate of 2 to 3 m yr^{-1}. The conventional belief is that most of this gain in water, which amounts to roughly 6 to 10 million L day^{-1}, is from East Camp groundwater, represented by the arrows in Fig. 1. In the past, a significant amount of surface water was also added by diversion of a large acidic spring – called the Horseshoe Bend Spring (HSB) – into the pit lake, which roughly doubled the rate of rise of the lake level. At the current time, HSB is treated with lime and the majority of the water is recycled by the active mining operation, whereas the small amount of high-density sludge produced by the plant is dumped back into the pit lake. Separated by a groundwater divide are the so-called "West Camp" and "Outer Camp" flooded mine workings, which include the other 10% of the underground tunnel complex (Fig. 1). Groundwater in the West Camp is continuously pumped from the West Camp Extraction Well (WCEW) at a rate of ~ 500-750 L min^{-1}, is treated in a lagoon to remove As and H_2S, and is discharged to Silver Bow Creek.

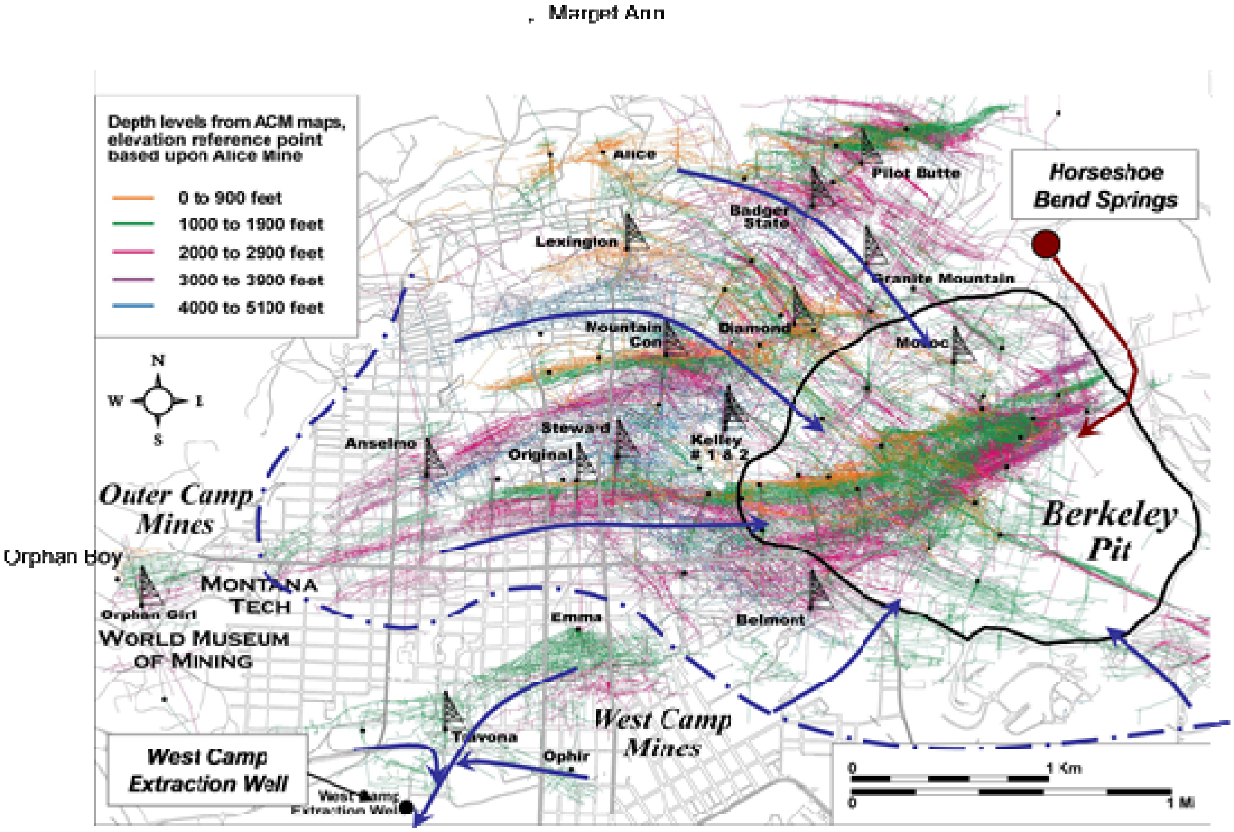


Figure 1: Map of the Butte mine workings (modified from Duaime et al., 2004) showing the location of some of the more important mine shafts and other features in the district.

The dashed blue line is a groundwater divide between the East and West Camps. Blue arrows approximate the direction of groundwater flow.

1.3. Bedrock Hydrogeology

Static water levels in mine shafts from this study and from deep wells and mine shafts located in the study area are plotted below for April 2006 (Figure 2). Data used in the interpolation is included in Table 26 in Appendix E. Criterion for inclusion into the interpolation of groundwater elevation is that the shaft or well had to be screened in Boulder Batholith which helped assure a contour map with a good representation of bedrock groundwater gradients. Estimated groundwater elevations in bedrock used the static water level at the time of drilling and were verified for correct location.

A key feature of the contour map is the west camp mine pool represented by mine shafts Emma, Travona, and Ophir (Figures 2 and 3). These mine shafts have groundwater elevations that are controlled by the effect of pumping the West Camp Extraction well and are within 1 foot of each other. The east camp mine pool is represented by the Kelley, Granite Mountain, Anselmo, and Steward Mine Shafts. Groundwater elevations in the Continental Pit, located east of the Berkeley Pit, are not included in the interpolation. Dashed contours are inferred due to sparse coverage of measurements in these areas.

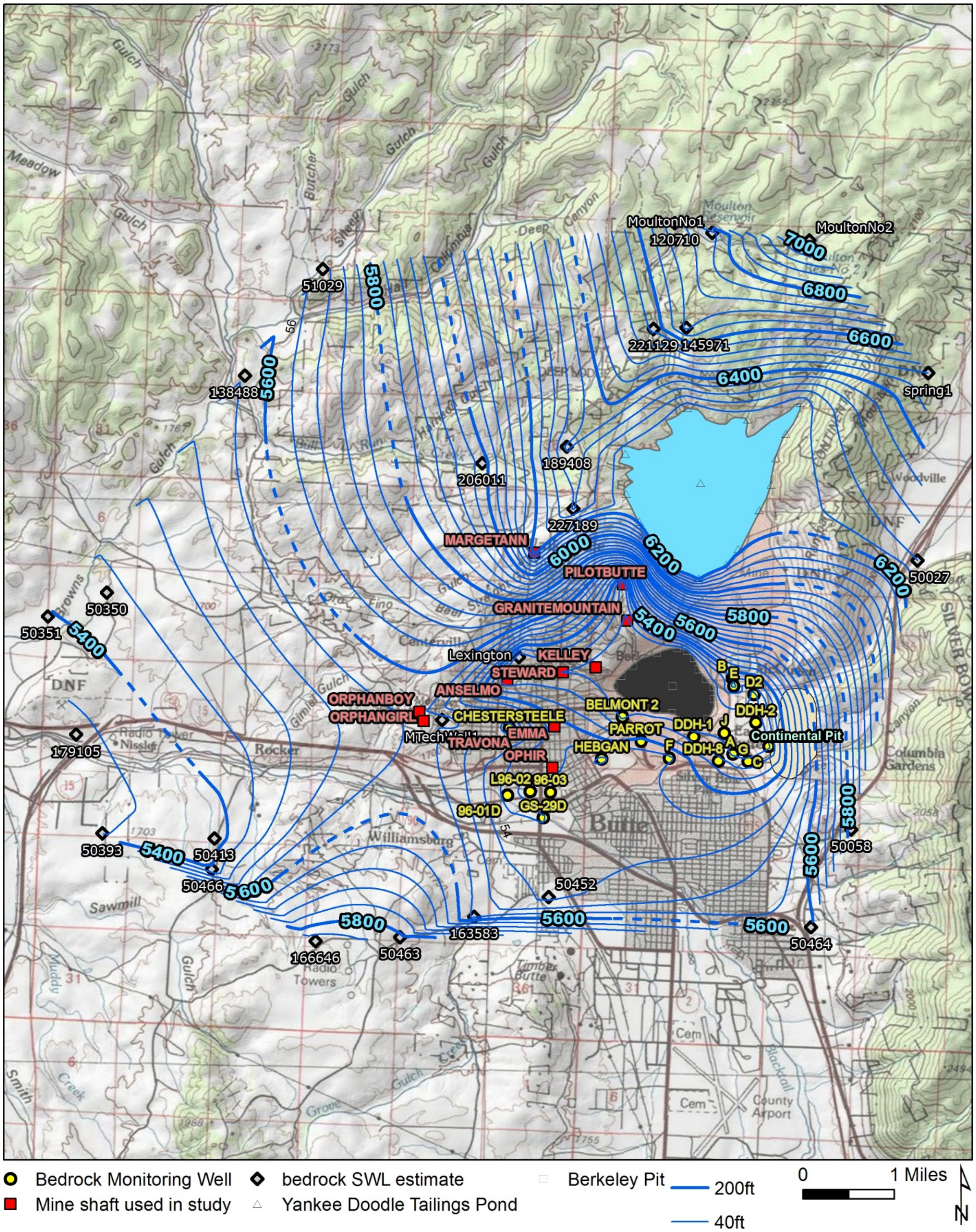


Figure 2 Static Water Table for the bedrock aquifer in the Butte Flooded Mine Complex and surrounding area. Only thick, 200 feet contours are dashed where inferred due to lack of data.

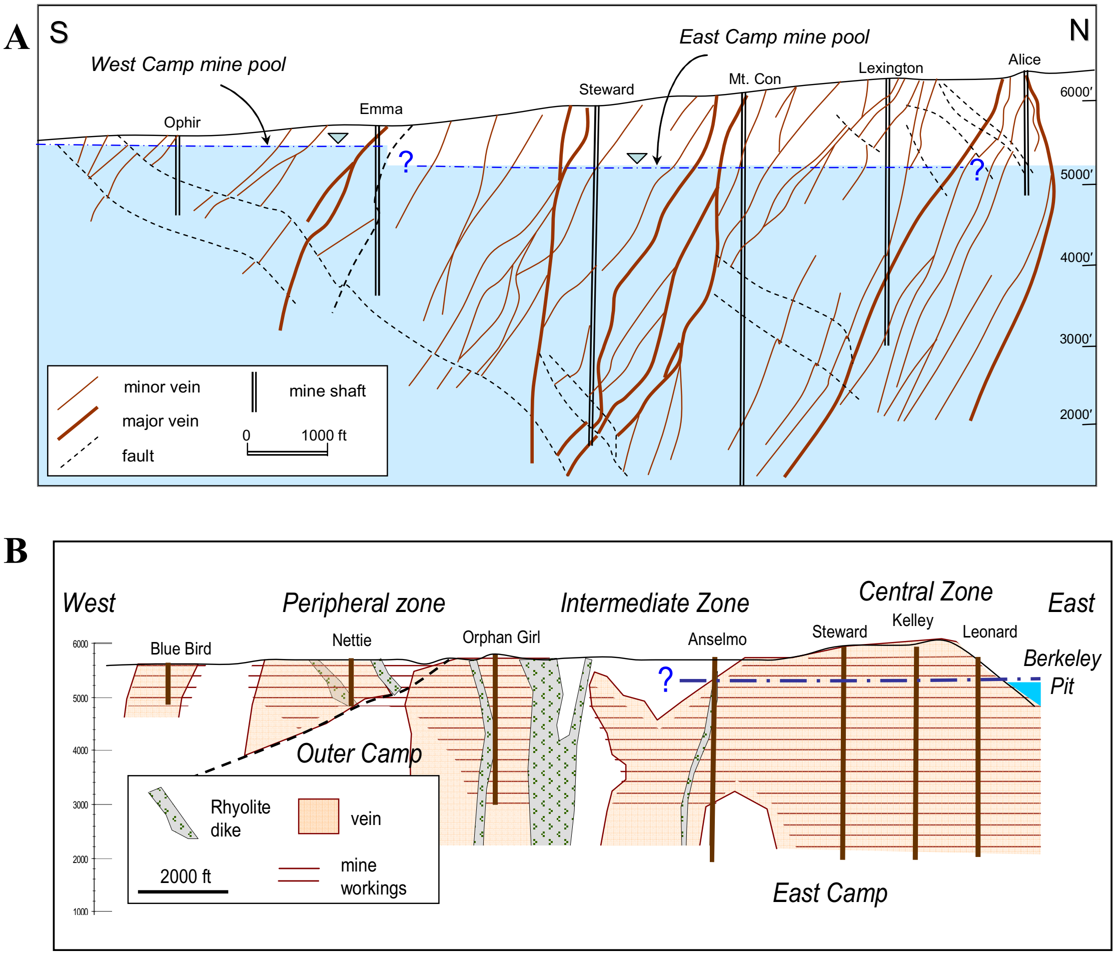


Figure 3 Cross sections showing geological features in the underground mine complex.

Cross sections showing geological features in the underground mine complex (modified from Meyer et al., 1968). A) Cross section along an approximately N-S transect. B) Longitudinal section along an approximately E-W transect parallel to the "Anaconda" Main Stage vein. Horizontal lines simulate levels in the mine, which in reality are spaced at 100 ft (30m) vertical intervals. Horizontal mine workings are omitted in "A" for clarity.

Hydrographs from periphery wells and shafts are compared to hydrographs of mine shafts closer to the Berkeley Pit (Figure 4). The hydrographs were produced by the Groundwater Information Center (GWIC) of the Montana Bureau of Mines and Geology in Butte, Montana and are available through the internet at http://mbmggwic.mtech.edu/. Figures are arranged in order of decreasing groundwater elevation from left to right. Periphery sites that include a MT Tech well, the Marget Ann, and Orphan Boy reflect seasonal fluctuations while shafts closer to the rising pit lake such as the Steward reflect the filling of the pit lake exclusively, with no seasonal fluctuations. Note the steps in the Orphan Boy and the MT Tech hydrographs representing aquifer recharge which resulted from above average annual precipitation for the three years between 1993 and 1997; also, the similar groundwater elevations of the Orphan Boy mine shaft, the MT Tech 01 well, and Chester Steele Park well. Sites in between such as the Chester Steele well and the Emma mine shaft show a rise in groundwater elevation associated with the recovery of the Berkeley Pit while also reacting to seasonal fluctuations, at least until about 1999 when rising groundwater elevations began dampening the response. The Chester Steele hydrograph rose in response to aquifer recharge of 1993 to 1997; however, it did not react to the drought from 1999 to around 2005 as the MT Tech well and Orphan Boy did as the effect on the Chester Steele well due to the rising pit lake increased.

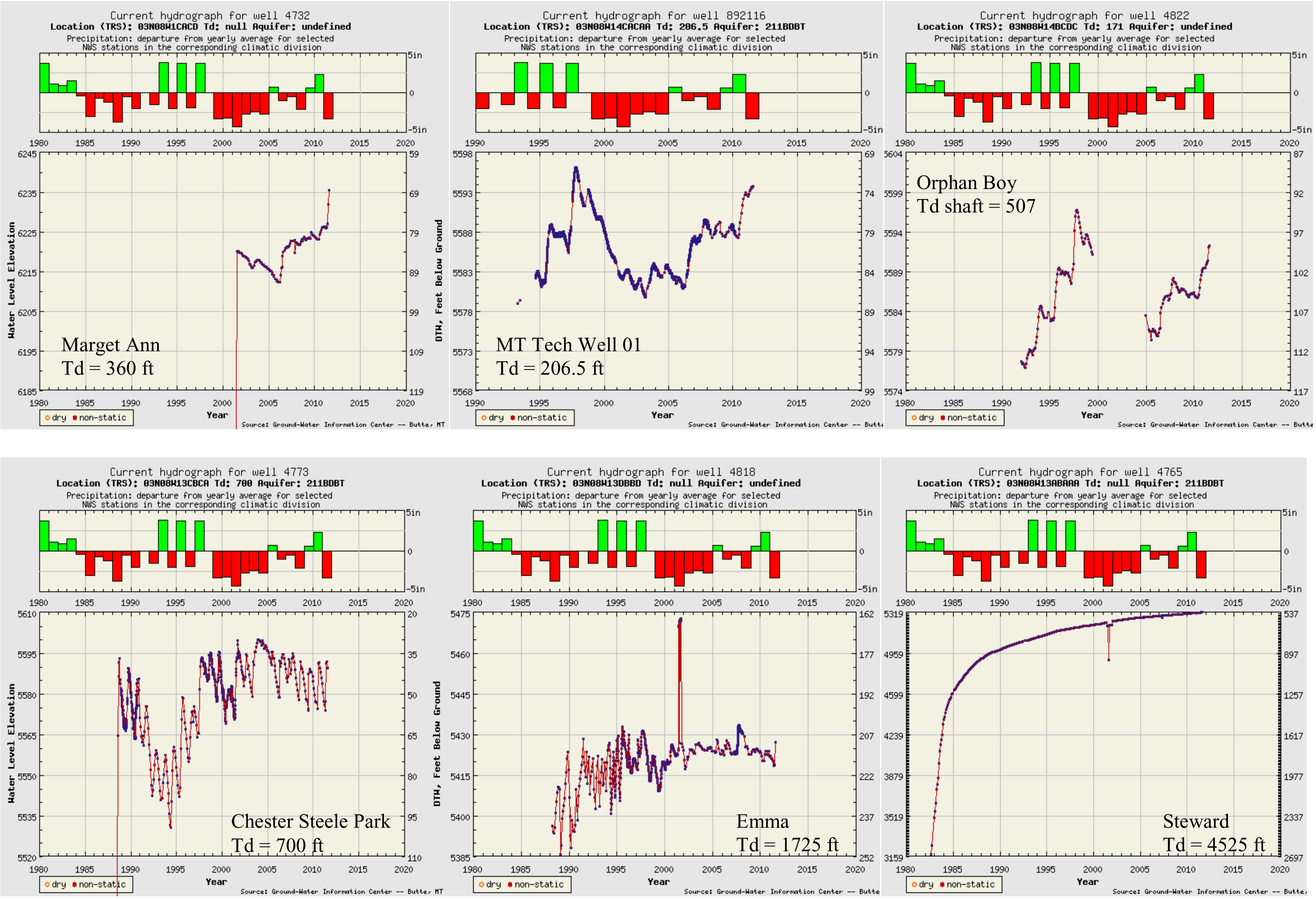
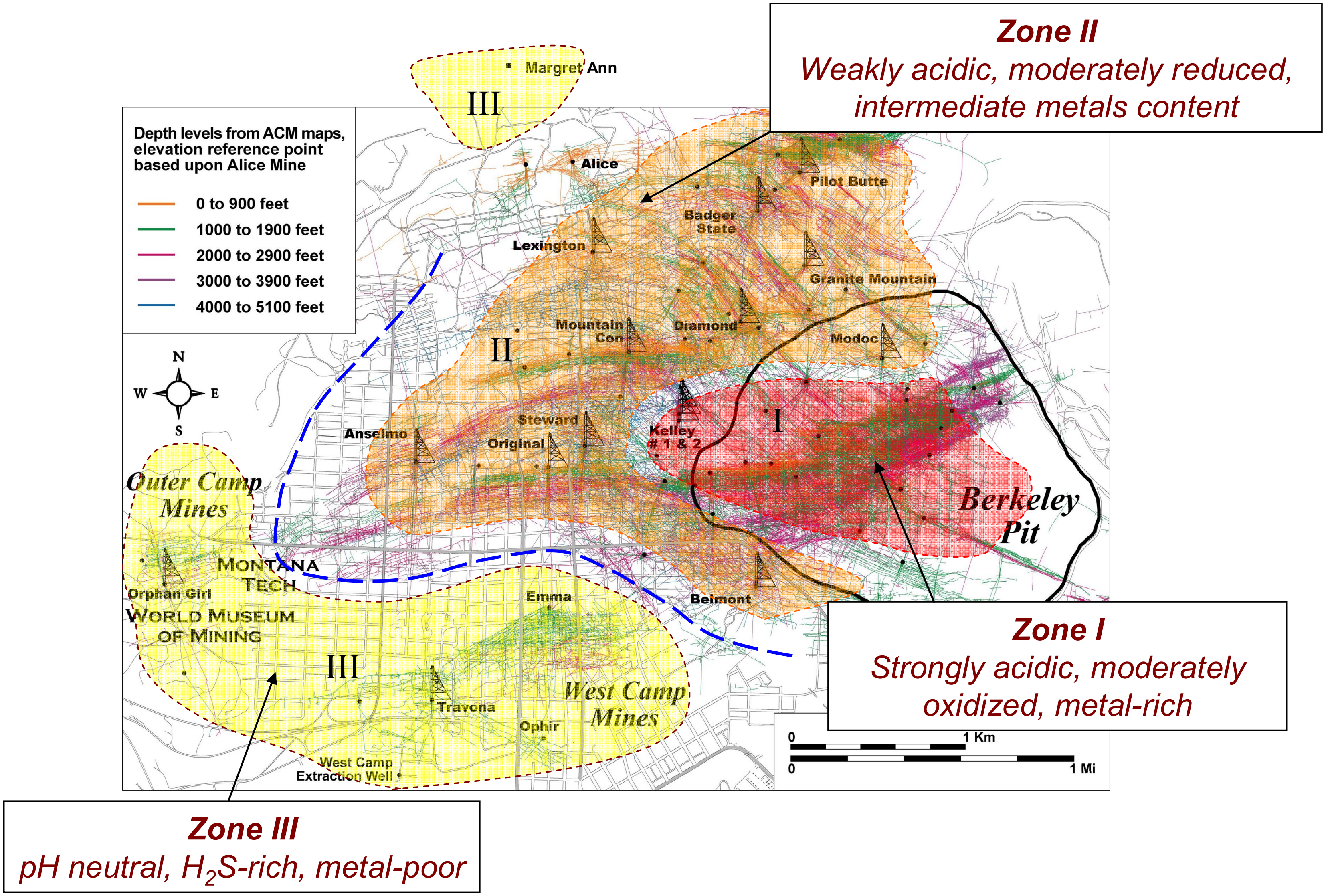


Figure 4 Hydrographs in bedrock in study area depicting effect of Berkeley Pit recovery depending on proximity to the pit.

Based on the cumulative work performed by previous investigations, a generalized view of the geochemical zonation of the Butte mine waters is given in Figure 5. The mine waters are divided into 3 zones: Zone 1 includes water that is highly acidic, relatively oxidized, and extremely rich in heavy metals (such as Fe, Mn, Zn), and includes the Berkeley pit lake as well as the Kelley mine shaft. Zone 3 includes the West Camp and Outer Camp mine waters, has a near-neutral pH, is enriched in hydrogen sulfide (H_2S) formed by bacterial sulfate reduction (Roesler et al., 2007), and contains very low levels of heavy metals. Zone 2 includes most of the East Camp mine shafts and is characterized by moderately reduced waters with slightly acidic pH and intermediate dissolved metal concentrations.



Zone II
Weakly acidic, moderately reduced, intermediate metals content

Zone I
Strongly acidic, moderately oxidized, metal-rich

Zone III
pH neutral, H_2S-rich, metal-poor

Figure 5: Generalized mineral and water quality zonation of the Butte mine waters (From Gammons et al., 2006
The dashed blue line is a groundwater divide between the East and West Camps.

1.4. Thesis Objectives

The main objective of this thesis was to characterize gradients with depth in the geochemistry and stable isotopic composition of groundwater in the Butte flooded underground mine complex. Specific objectives included:

a. To determine whether there are significant differences in the geochemistry of deep vs. shallow groundwater.

b. To compare and contrast the dominant solubility controls on the concentration of dissolved metals (including aluminum (Al), arsenic (As), copper (Cu), iron (Fe), manganese (Mn), zinc (Zn)).

c. To document vertical and lateral gradients in redox state that reflect regional-scale transitions in the dominant redox couples (e.g., O_2/H_2O, Mn^{3+}/Mn^{2+}, Fe^{3+}/Fe^{2+}, As^{5+}/As^{3+}, SO_4^{2-}/H_2S).

d. To use stable isotopes to determine whether there are changes in the source of water, dissolved sulfate, H_2S, or dissolved inorganic carbon in the flooded mine complex.

e. To examine in more detail the lateral and vertical changes in groundwater temperature in the flooded mine complex, which could provide information as to the location of pyrite oxidation hot spots, as well as providing clues to groundwater flow paths.

f. To determine if sulfate-reducing bacteria have established themselves in the deeper levels of the East Camp shafts.

2. Methods

2.1. Field Methods

2.1.1. Sample Collection

During the course of this thesis, three different methods were used to retrieve mine shaft water samples: a submersible pump, a bailer, and a point sampler (Table 1). The Emma, Ophir, and Orphan Boy shafts are permanently sealed by a concrete plug that is penetrated by a monitoring well that is capped at the bottom and screened approximately 30 feet below static water level (BSWL). Although it is not possible to get depth profiles in these shafts, a single sample was collected from each of the wells on 4/19/06 during the MBMG's semi-annual shaft sampling. This was done to collect a set of samples for inter-laboratory comparison of ICP results (see Appendix B). Each of the wells was purged for at least 30 minutes (over 3 well volumes) before field parameters and samples were collected.

The second method of sample retrieval was to use a bailer. For most of their deep mine shaft samples, the MBMG uses a 2-L capacity stainless steel bailer with a "ball" check valve in the bottom. The bailer is raised and lowered into the shaft with a truck-mounted winch. This method was used for mine shaft sampling on 4/20 and 4/21 of 2006 (Steward, Kelley, Anselmo, Travona mines). On 8/22/06, 2 x 1-L plastic bailers tied together were used to retrieve water (by hand) from the Marget Ann mine.

The third method of sample retrieval was to use a point sampler. A point sampler is a cylinder with spring-loaded endcaps that seal water inside when closed. The sampler is lowered to the desired depth on a cable or rope, and then a weighted "messenger" is sent down the line to trip the sampler and close the endcaps. The sealed sample is then raised to the surface. Two types of point sampler were used on this thesis, a 1-L stainless steel "Kemmerer" type sampler, and a 2-L plastic "Van Dorn" type sampler. Although the Kemmerer point sampler was considered the best of the various sampling methods, both the original sampler and – later – its replacement were lost in the mine shafts, when the samplers hung up on debris in the shaft.

2.1.2. Sample Filtration and Preservation

All field samples were filtered to 0.1 μm using a peristaltic pump and a GeoTech filter holder with disposable cellulose ester filter membranes. The tubing and filter housing were rinsed several times with distilled water between samples. At least 50 mL of sample were filtered to pre-rinse the equipment, and this water was then used to rinse the sample bottles to be filled. After rinsing, each bottle was filled with filtered water. Samples for ICP-AES analysis were preserved with 1% Trace Metal grade HNO_3 acid. Samples for Fe or As speciation were preserved with 1% HCl. Other details are given below.

Table 1 Shaft parameters, sampling dates, and information collected

Shaft and Date sampled	Shaft depth (feet)	Elevation at surface (feet)	Depth to SWL (feet)	Troll profile (ft BSWL)	"TidbiT" profile (ft BSWL)	Water samples (ft BSWL)	Sample retrieval method
Emma 4/19/06	1725	5702	211	none	none	35	Pump
Ophir 4/19/06	980	5587	108	none	none	30	Pump
Orphan Boy 4/19/06	507	5751	115	0 - 300	none	30	Pump
Anselmo 4/20/06	4301	5839	498	none	none	2, 100, 450	Bailer (steel)
Anselmo 7/19/06	"	"	"	0 – 300[a]	0 – 450[a]	none	none
Steward 4/21/06	4525	5912	579	none	none	2, 120, 1120	Bailer (steel)
Steward 7/19/06	"	"	"	0 - 300	0 - 1400	none	none
Kelley 4/21/06	4834	5969	642	none	none	2	Bailer (steel)
Kelley 5/5/06	"	"	"	none	none	2, 100, 1000	Point sampler
Kelley 7/18/06	"	"	"	0 - 300	0 - 1200	5, 1350	Point sampler
Gran. Mtn 8/18/06	3283	6107	~ 830	0 - 300	none	none	n/a
Gran. Mtn 9/14/06	"	"	"	none	none	25, 100, 1000	Point sampler
Pilot Butte 8/18/06	2748	6133	n/a	0 - 300	none	none	n/a
Travona 7/19/06	1424	5647	~ 165	0 - 300	0 - 890	none	n/a
Travona 7/20/06	"	"	"	none	none	5,30,100, 350,890	Point sampler
Orph. Girl 9/7/06	2731	5731	~ 250	0 - 300	0 - 1000	5,30,100, 300,1000	Point sampler
Marg. Ann 8/21/06	360	6330[b]	84	0 - 300	none	none	n/a
Marg. Ann 8/22/06	"	"	"	none	none	5, 35, 75, 120	Bailer (plastic)

2.1.3. Field Measurements

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, an In-Situ Troll 9000 datasonde, or a Geotech WTW 340i hand-held multi-meter. The MS-5 and WTW were 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 300 feet of the static water in each shaft. The MS-5 and WTW were used together initially but agreed so well that the MS-5 was used exclusively for the majority of the field visits.

All probes were freshly calibrated via the manufacturer's recommendations on the day of use. For Eh measurement, the Troll and the MS-5 were calibrated with ZoBell's solution, and were set up to read Eh directly (i.e., the redox potential of the water relative to the Standard Hydrogen Electrode). After calibration, the Troll was programmed to collect field measurements every minute. The Troll was then lowered down the shaft and was stopped at pre-determined depths for 2-3 minutes to collect a reading prior to advancing to the next depth. The depth of each measurement was then determined by calibrating the Troll's clock with a watch at the surface, and keeping track of the depth of the cable. *In situ* vertical profiles in water chemistry were collected via this method for the top 300 feet of water only. There was concern that we might lose or damage the Troll if we went deeper.

For samples bailed to the surface, the MS-5 was placed in the water as soon as possible. However, because of the small volume of each sample, it was not possible to use a flow cell or some other method that isolated the water from the atmosphere during the measurements. For this reason, the "bailed" field parameter measurements are considered less reliable than the "*in situ*" data collected from the Troll, especially for Eh and pH. This is discussed in more detail in the Results section.

In addition to the Troll data, *in situ* temperature profiles were collected for several of the mine shafts using a "TidbiT" temperature sensor. The TidbiT is a small, button-sized sensor that was attached to the bottom of the cable, and was programmed to collect temperature data every minute. The advantage of using the TidbiT was that we could get in-situ temperature readings over the entire depth of the water column while sampling with the bailer.

2.2. Analytical Methods

2.2.1. Major and Trace Metals

All filtered water samples collected in this study were analyzed for a suite of major and trace metals by conventional ICP-AES analysis at the Murdock Environmental Laboratory, University of Montana, Missoula. Elements included in the lab report were Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, P, S, Si, Sn, Sr, Ti, V, and Zn. Rigorous QC protocols were followed, according to EPA Method 200.7. Results of QC validation are included in Appendix A of this report. Interlaboratory comparisons were performed on several split samples collected early in the project when the MBMG were conducting their semi-annual mine shaft sampling. Parallel samples were collected in the field, and one set was sent to Murdock for ICP analysis, whereas the other set went through the MBMG laboratory. Results of the inter-laboratory analyses are also included in Appendix A of this report

2.2.2. Alkalinity

Alkalinity measurements were performed in the field within 20 minutes of sample collection. Exactly 100 mL of filtered water was transferred to an Erlenmeyer flask on a portable magnetic stirrer. The titration was performed using a HACH digital titrator and 0.16N or 1.6N H_2SO_4 cartridges. The pH endpoint for the titration was determined by addition of bromcresol green-methyl red indicator powder.

2.2.3. Major Anions

Although it is common to analyze for a suite of major anions by ion chromatography, this was not done in this study, mainly as a cost savings. Examination of historical data in the GWIC database showed that sulfate (SO_4^{2-}) and bicarbonate (HCO_3^-) are by far the dominant anions in the Butte mine shaft waters. The concentrations of dissolved bicarbonate for each sample were computed based on the measured water temperature, alkalinity, and pH. With the exception of the Orphan Boy and Orphan Girl samples, concentrations of sulfate were obtained by ICP-AES analysis of total dissolved S, assuming that SO_4^{2-} was the dominant form of dissolved S in all samples.

For the Orphan samples, it was not possible to use the ICP-AES results for S to approximate dissolved sulfate concentrations, because of a strong positive interference between H_2S and total S on the ICP-AES. Apparently, the presence of low mg/L levels of H_2S in the Orphan samples resulted in total S concentrations as determined by ICP-AES that were much too high, by a factor of about three. This problem was first noticed when it was discovered that both the Orphan Boy and Orphan Girl samples gave unrealistically poor charge balances, with a large excess of anions. Results for S based on ICP-AES from Orphan Boy were then compared to data in MBMG's GWIC database for a sample collected for the same shaft. The GWIC data for sulfate (based on ion chromatography) were much lower than the ICP-AES concentrations from the Murdock lab, and using the former data resulted in a much better charge balance. Next, the concentrations of sulfate in the Orphan Boy and Orphan Girl shafts were cross-checked vs. the mass of $BaSO_4$ produced during the stable isotope preparation steps (see 2.3.3, below). The sulfate concentrations based on $BaSO_4$ extraction agreed well with the data in GWIC. Therefore, it was concluded that the ICP-AES results for S for the Orphan Boy/Girl samples were inaccurate, and that the sulfate results based on the $BaSO_4$ assays should be used instead. A later email discussion with Heiko Langner at the U-Montana Murdock laboratory revealed that he also has noticed this unusual interference between H_2S and total S on the ICP-AES.

2.2.4. Fe(II)/Fe(III)

Iron speciation was performed in the field, immediately after sample collection, using a HACH 2010 spectrophotometer and the Ferrozine method (To et al., 1999). The instrument was calibrated with a freshly prepared standard in the range 0.1 to 1.0 mg/L Fe. In the Ferrozine procedure, the concentration of Fe(II) and total dissolved Fe are measured independently, and the concentration of Fe(III) is then determined by difference. Because most of the dissolved iron in the mine shaft waters sampled in this study was Fe(II), this meant that the Fe(III) analyses had a very large uncertainty.

2.2.5. As(III)/As(V)

Arsenic speciation was performed on selected samples to discriminate between the As(III) and As(V) valence states. Separation of the two valence states was performed in the field, following the method described by Langner et al. (2001). This method entailed collection of two 15 mL filtered samples to which an aliquot of TRIS buffer was added to adjust pH. One of these samples (labeled As(V)) was then treated with $NaBH_4$ (which produces a volatile As-hydride gas with trivalent arsenic) and was purged with a stream of N_2 gas from a portable gas bottle to eliminate the As(III) from the sample. The other sample (labeled Total As) was not pre-treated. Both bottles were then acidified with HCl to $pH < 2$, prior to analysis of As by ICP-AES. The concentration of As(III) was then determined by the difference between the Total As and As(V) concentrations. The advantage of this method over conventional As(III)/As(V) analysis is that the speciation of the two valence states is done in the field immediately upon sample collection. In this way, the samples can be stored for long periods before ICP analysis without fear of degradation.

2.2.6. Nutrients

Concentrations of soluble reactive phosphorous (SRP) were measured on a HACH 2010 portable spectrophotometer, following HACH Method 8048 (HACH, 1996), which is based on addition of molybdate and ascorbic acid, and corresponds to EPA Method 365.2. The estimated detection limit is 0.01 mg/L PO_4 (as PO_4). Calibration of the instrument was performed using freshly prepared standards in the range 0.1 to 1.0 mg/L PO_4(as P).

Although attempts were made early in the project to quantify nitrate and ammonium by HACH methods, this was discontinued after all samples were below detection for these analytes. In a detailed 12-month study of the West Camp extraction well, Roesler (2005) also found negligible concentrations of nitrate and ammonia. As well, the majority of Butte mine shaft waters in the GWIC database have concentrations of nitrate below the detection limit of the MBMG laboratory, which uses ion chromatography.

2.2.7. Aqueous Sulfide

The concentrations of total (unfiltered) and dissolved (filtered to 0.1 μm) sulfide were determined directly in the field using the Methylene Blue Method, and a HACH Model 2010 portable spectrophotometer. The procedure followed HACH Method 8131, which is equivalent to EPA method 376.2. The estimated detection limit of the H_2S analyses immediately upon sample collection for this method is 0.01 mg/L S^{2-} (HACH, 1996). Due to the potential loss of H_2S to oxidation or volatilization after sampling, it was essential to perform the H_2S analyses as quickly as possible after sampling. Because H_2S standards degrade quickly, it was not possible to perform calibrations in the field. Standards freshly prepared in the laboratory from Na_2S powder agreed with the HACH results within 20%.

2.3. Stable Isotope Analysis

All stable isotope analyses were performed by Dr. Simon Poulson, at the University of Nevada –Reno using a Eurovector elemental analyzer interfaced to a Micromass IsoPrime stable isotope ratio mass spectrometer (IRMS). Stable isotope values are reported in the usual δ notation in units of ‰ (per mil, or parts per thousand), versus VCDT for sulfur, versus VSMOW for oxygen and versus VPDB for carbon. Analytical uncertainties are ±0.2‰ for $\delta^{34}S_{sulfide}$ and $\delta^{34}S_{sulfate}$, ±0.4‰ for $\delta^{18}O_{sulfate}$, ±0.1‰ for $\delta^{18}O_{water}$, and ±2‰ for δD_{water} and ±0.4‰ for $\delta^{13}C_{DIC}$

2.3.1. δD and $\delta^{18}O$ of water

For isotopic analysis of water, a filtered sample was collected into a 10 mL glass vial with no head space. No refrigeration or preservation was required. Oxygen isotope analyses of water samples were performed at UNR using the CO_2-H_2O equilibration method (Epstein et al., 1953). Hydrogen isotope analyses were performed at UNR using the method of Morrison et al. (2001). Two split samples were sent to the University of Waterloo (Ontario, Canada) for $\delta^{18}O$ and δD analysis, as an additional QC check. Results from this interlaboratory comparison are included in Appendix A, as are results of internal IRMS laboratory calibrations and analyses of blind duplicate samples.

2.3.2. $\delta^{34}S$ of aqueous sulfide

Collection and preparation of samples for isotopic analysis of S of dissolved sulfide ($\delta^{34}S$-H_2S) followed the procedures developed by the U. S. Geological Survey (Carmody et al., 1998). Aqueous sulfide was extracted by precipitation of silver sulfide (Ag_2S). This was done in the field immediately after sample recovery by direct addition of silver nitrate ($AgNO_3$) solution to a 1-L Nalgene bottle filled with unfiltered mine shaft water. Within minutes a black colloidal suspension of Ag_2S formed. The suspension was filtered back in the laboratory. The filter membrane was scraped with a clean spatula and rinsed with water to transfer the fine Ag_2S precipitate into a 50mL beaker. NH_4OH was added to the beaker to make an approximate 10% NH_4OH solution. The precipitate was allowed to soak for at least 3 hours in order to dissolve any AgCl solid that may have formed after addition of $AgNO_3$ to the field sample. The remaining purified Ag_2S precipitate was then quantitatively transferred to a vacuum filtration flask, and collected onto a pre-weighed glass filter. The filtered solid was rinsed well with deionized water, dried, weighed (to determine the percent yield), transferred to a glass vial, labeled, and sent to the UNR for determination of $\delta^{34}S$ of sulfide.

2.3.3. $\delta^{34}S$ and $\delta^{18}O$ of aqueous sulfate

Samples for $\delta^{34}S$ and $\delta^{18}O$ of aqueous sulfate were first analyzed for the approximate dissolved sulfate concentration using a HACH 2010 spectrophotometer, and HACH Method 8051 (equivalent to EPA Method 375.4). Then the dissolved sulfate was extracted for isotopic analysis, following the detailed procedures of Carmody et al. (1998). This procedure entails the following steps:

1) Adjust pH to < 3 with addition of HCl (this step is to avoid precipitation of $BaCO_3$ when $BaCl_2$ is added).
2) Heat sample to > 50°C on a hot plate to increase the reaction rate and enlarge solids of $BaSO_4$ resulting in a more complete extraction of $BaSO_4$ precipitate when filtering.
3) Add 3 times excess of $BaCl_2$, with stirring, to 100mL of sample.
4) Stir for 10 minutes and cool to room temperature, to allow $BaSO_4$ precipitation to proceed to completion.
5) Collect the $BaSO_4$ precipitate on a pre-weighed filter paper and rinse several times with de-ionized water.
6) Dry at 40-50°C overnight.
7) Weigh the mass of $BaSO_4$ to determine the % yield
8) Transfer to a glass vial and label for shipment to Reno.

Sulfur isotope analyses were performed by Simon Poulson at the University of Nevada-Reno, using a method similar to that of Giesemann et al. (1994), with the modification that V_2O_5 was added to $BaSO_4$ samples as a combustion aid. Oxygen isotope analyses of sulfate followed a method similar to that of Kornexl et al. (1999), with the modifications that the analyses were performed at 1300°C, and that nickelized graphite was added to $BaSO_4$ samples as a pyrolysis aid.

2.3.4. $\delta^{13}C$ of dissolved inorganic carbon

Preparation of samples for $\delta^{13}C$ analysis of dissolved inorganic carbon followed a procedure adapted from Friedman (1970). A filtered (0.1 μm) sample was collected into a pre-weighed 250 mL glass bottle with a conical closure during field sampling. The bottle was filled with no head space and stored on ice or in the refrigerator until carbonate extraction, back in the laboratory. A $SrCO_3$ precipitate was formed by addition of 5 mL of 1.5 M + 6 M NH_4OH solution. The precipitate was filtered onto a pre-weighed filter paper using a vacuum flask and hand vacuum pump, and then was dried overnight at 50°C. The final precipitate was then weighed to determine the yield and transferred to a glass vial for shipment to Reno for isotopic analysis following the method of Harris et al. (1997).

3. Results

3.1. Field Parameters

Field parameters collected for each mine shaft water sample included pH, Eh, SC, temperature, and alkalinity. Results are summarized in Table 2 and are discussed in more detail below.

Table 2 Field parameters measured for each mine shaft sample.

Sample	feet bswl	pH (standard units)		Eh (mV)		SC (µS/cm)		T (°C)	alkalinity (mg/L $CaCO_3$)
		bail	*in-situ*	*bail*	*in-situ*	*bail*	*in-situ*	*in-situ*	*bailed*
Orp. Girl 1	5	6.81	6.37	-65	-89	1830	1820	26.5	692
Orp. Girl 4	30	6.80	6.32	-63	-114	1780	1820	26.5	712
Orp. Girl 5	100	6.83	6.30	-74	-124	1790	1820	26.6	712
Orp. Girl 2	300	6.90	6.27	-68	-130	1860	1810	26.5	704
Orp. Girl 6-D	300	6.81	6.27	-16	-130	1800	1810	26.5	717
Orp. Girl 3	1000	6.89	na	-36	na	1800	na	na	704
Orp. Boy	30	6.63	na	-127	na	1730	na	25.7	702
Mar. Ann 2	5	7.01	4.59	194	115	881	916	9.7	198
Mar. Ann 3	35	7.29	7.24	154	26	933	898	9.3	180
Mar. Ann 3D	35	7.29	7.24	154	26	933	898	9.3	184
Mar. Ann 4	75	7.41	7.50	134	-52	863	895	8.6	191
Mar. Ann 5	120	7.52	7.54	107	-74	835	897	8.6	180
Travona 2	5	6.50	6.23	40	70	1280	1280	13.1	297
Travona 3-D	5	6.58	6.23	40	70	1280	1280	13.1	303
Travona 4	30	6.47	6.83	67	41	1280	1280	13.0	299
Travona 5	100	6.40	6.85	66	34	1270	1280	13.0	303
Travona 7	350	6.81	6.72	64	26	1250	1290	na	301
Travona 8	890	6.78*	na	67	na	1310	na	na	305
Emma	34	6.73	na	167	na	1300	na	15.1	323
Ophir	30	6.95	6.93	65	na	701	na	11.5	189
Kelley A	2	4.13	4.37	367	328	7080	7450	34.6	0
Kelley B	100	3.79	4.05	347	285	7070	7380	34.9	0
Kelley C	1000	3.72	na	354	na	8240	na	na	0
Steward A	2	5.72	5.74	231	274	3470	3540	24.2	259
Steward B	120	5.93	5.47	193	230	3450	3520	24.5	262
Steward C	1120	5.84	na	201	na	3470	na	na	254
Gran. Mtn 1	25	5.58	5.82	363	356	3300	3320	15.4	138
Gran. Mtn 2	100	5.69	5.82	375	324	3260	3310	15.4	148
Gran. Mtn 3	1000	5.69	na	362	na	3300	na	na	127
Anselmo A	2	6.30	5.58	191	242	2170	2220	17.5	256
Anselmo C	100	6.39	6.25	180	163	2150	2230	17.5	257
Anselmo D	450	6.44	na	172	na	2110	na	na	266

See Table 1 for dates of sampling.

3.1.1. Water Temperature

Figure 6 shows *in situ* temperature results obtained from each mine shaft using the Troll 9000 datasonde. The most striking thing to note from this diagram is the lack of any appreciable temperature variations with depth for most of the shafts. The only possible exceptions are the Marget Ann shaft (which shows some small temperature variations in the top 50' of the water column) and the Kelley shaft (which shows a slight "step" in temperature at a depth of 70' BSWL). In contrast, there are very large variations in mine water temperature *between* shafts. The Marget Ann has the coldest water (~ 8 to 10°C), while the Kelley Mine has by far the warmest water (~ 35°C).

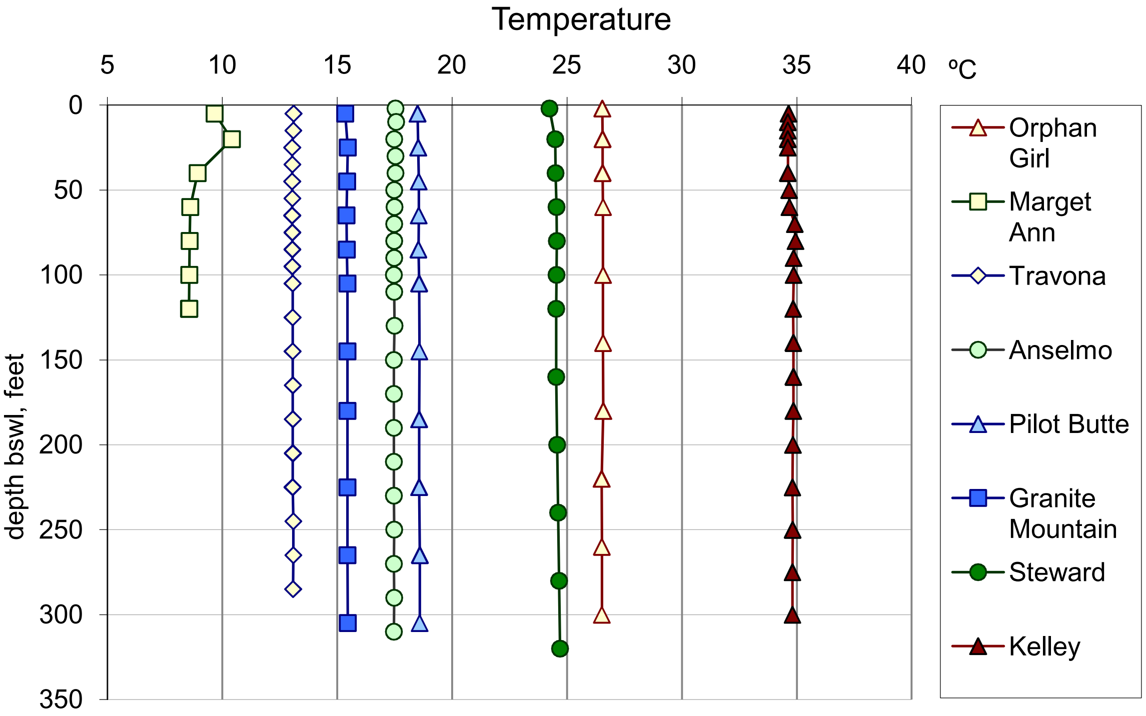


Figure 6 In situ temperature profiles for mine shafts collected by the Troll

Based on historical data in GWIC, the average water temperature of over 250 data entries for groundwater monitoring wells in Sections 19, 20, 29, and 39 of T3N R7W (the area of downtown Butte between the Metro Storm Drain and Blacktail Creek) was 10.2±1.8°C (error denotes 1 standard deviation). Thus, compared to shallow groundwater in alluvial sediments of the Butte valley, most of the mine shaft waters are warmer than surrounding groundwater. The only exceptions to this rule are the Marget Ann Mine and possibly the Travona Mine. Possible reasons for the elevated temperatures are presented in Section 4.

Figure 7 shows *in situ* temperature results for 4 of the mine shafts that were obtained using the "TidbiT" temperature recorders. These records extend to greater depths than the data from the datasonde. For the Anselmo, Steward and Travona shafts, there were no changes in water temperature to depths as great as 1000' BSWL. In contrast, the Kelley Mine data show an increase in temperature below 500' BSWL. The deepest location (1000' BSWL) in the Kelley had a temperature of 38.1°C.

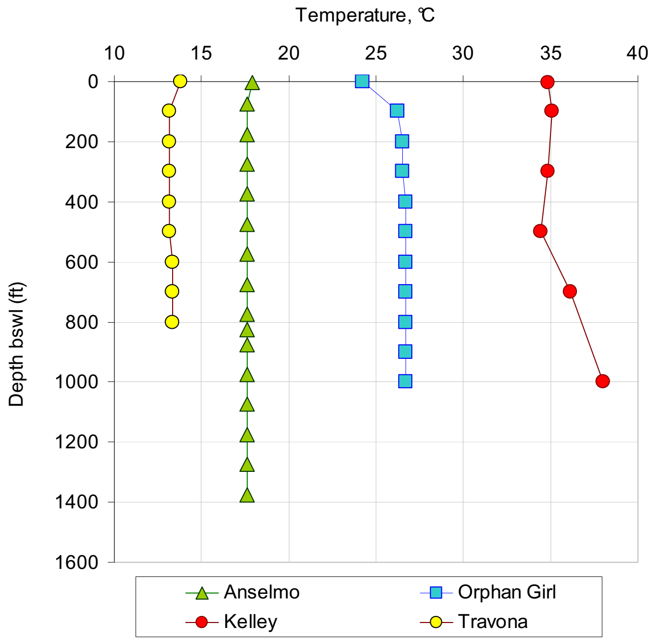


Figure 7 In situ temperature profile, obtained with a TidbiT temperature logger in July, 2006.

Another observation is relevant while on the topic of temperature. It was noted during the course of this project that the temperatures of mine shaft water samples bailed to the surface were often different than the *in situ* temperatures measured using the datasonde or TidbiT recorders. This was especially true for the Kelley Mine, where water cooled down as much as 5°C during the time it took to raise the water sample to the surface. This should not come as too much of a surprise, considering the fact that there is ~ 640 vertical feet of relatively cool air in the shaft between the static water level and the ground surface. It took as long as 10 minutes or more to raise the sample to the surface, even with the truck-mounted winch. Based on these observations, it is cautioned that temperatures for mine shaft water samples recorded in the GWIC database (which are routinely measured at the ground surface) may not necessarily reflect the true *in situ* temperatures of the mine waters.

The long term trend in Kelley Shaft temperature has steadily increased at a rate of 0.55°C/year since flooding began in 1982 (Figure 8).

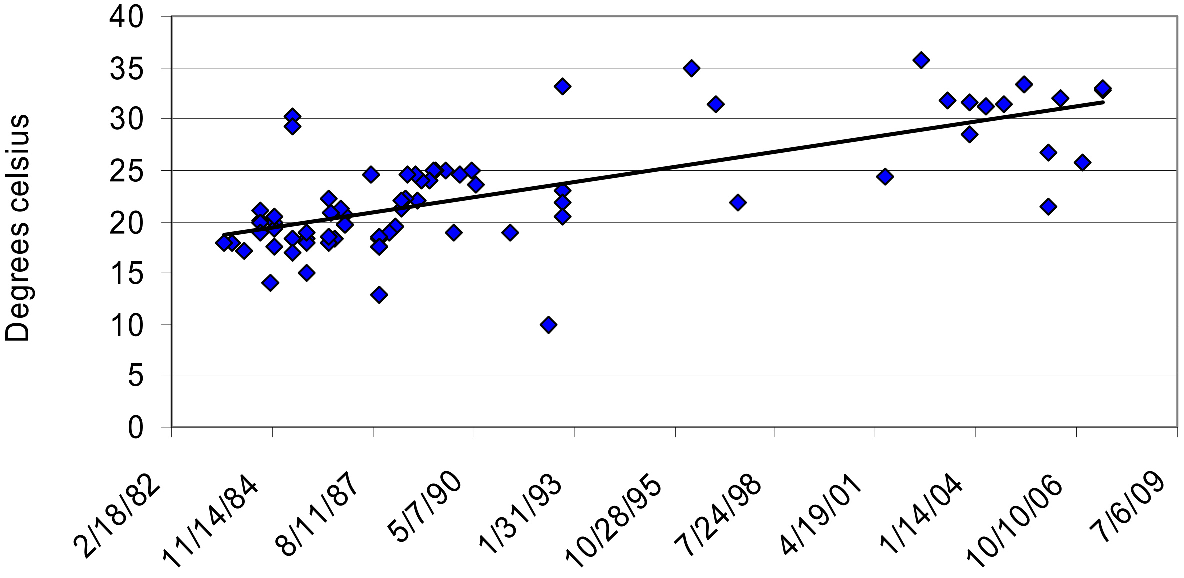


Figure 8 Long term trend in in temperature for the Kelley Mine Shaft. Trend line slope indicates a rise in temperature of 0.55°C/year

3.1.2. Specific Conductance

Vertical changes in specific conductance (SC) measured *in situ* by the Troll in the top 300 feet of each mine shaft are shown in Figure 9. Although each shaft had its own unique SC value, there were no apparent gradients in SC with depth. Furthermore, the SC of water samples brought to the surface also showed virtually no change with depth (Fig. 12). The only exception to this rule was the Kelley Mine, which had a significantly higher SC for a single sample bailed from depth on 5/5/06 (8240 µS/cm at 1000 ft. BWSL, compared to 7070 and 7080 µS/cm for samples recovered from 100 and 2 ft. BWSL, respectively). The higher SC sample from the Kelley Mine was collected from the same depth that had a significantly higher water temperature (Fig. 7). These observations suggest that water in the Kelley Mine shaft is not vertically-mixed, or is mixing very slowly.

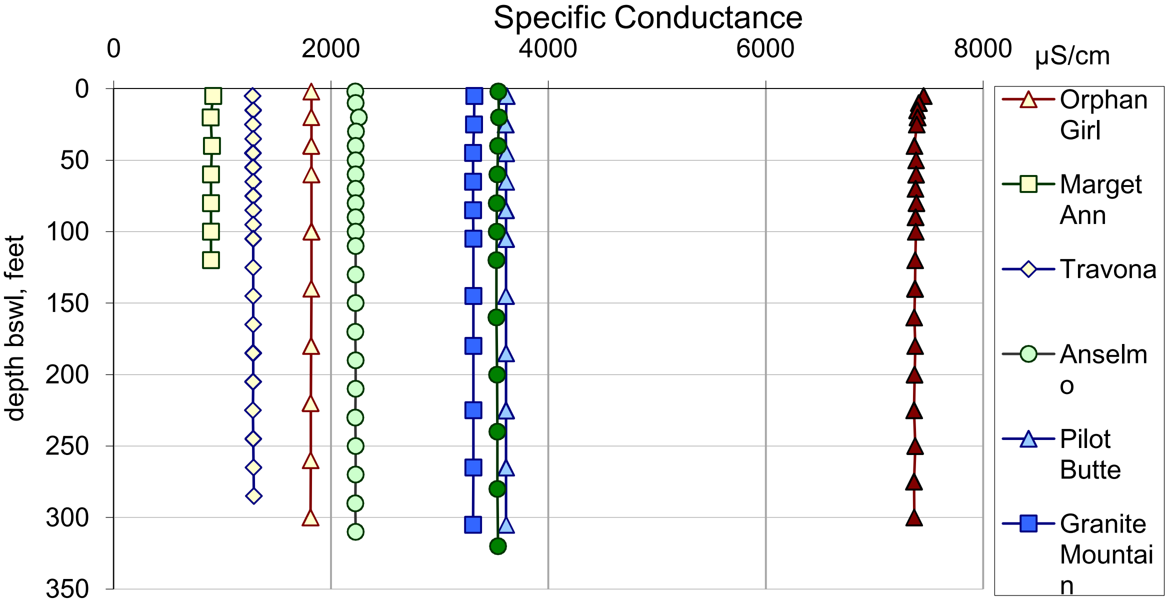


Figure 9 *In situ* specific conductance (SC) profiles for mine shafts collected by the datasonde.

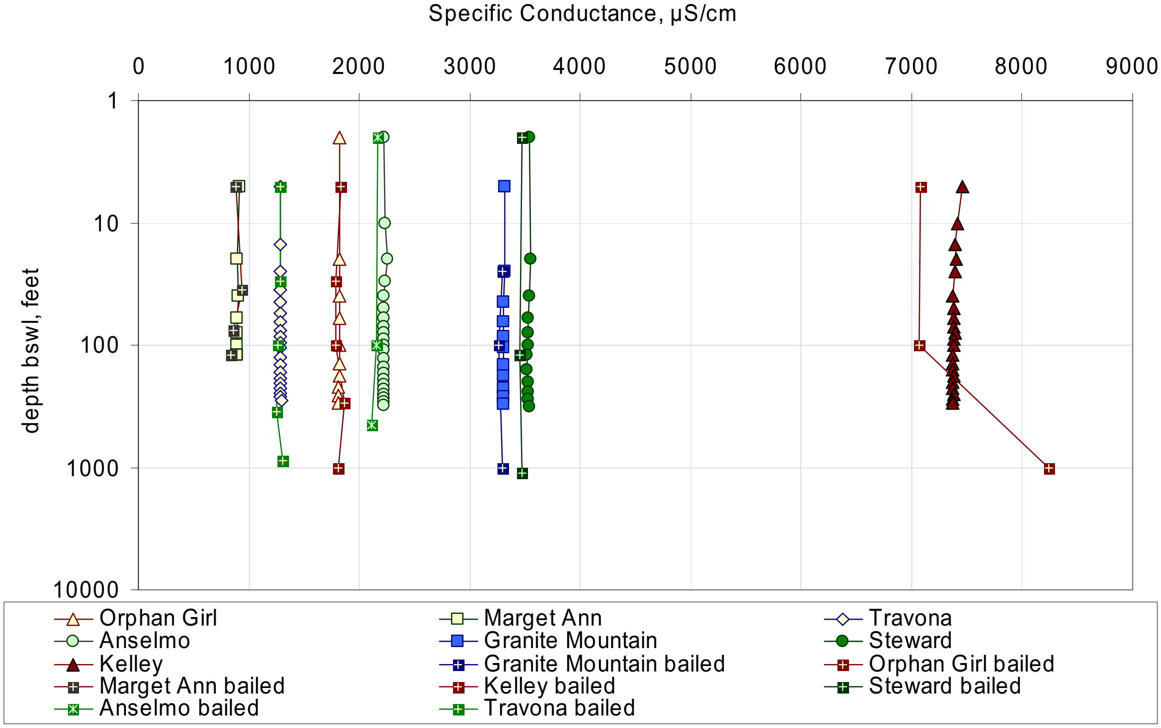


Figure 10 Comparison of in situ SC values with SC of samples bailed to the surface

3.1.3. pH

Vertical changes in pH measured *in situ* by the Troll in the top 300 feet of each mine shaft are shown in Figure 11. Several of the mine shafts showed significant (greater than ±0.1 units) changes in pH with depth, particularly in the top 100 ft. BSWL. For example, the Kelley and Steward shafts showed a 0.3 to 0.5 unit increase in pH towards the surface, whereas the Pilot Butte, Anselmo, Travona, and Marget Ann shafts all showed rather sharp decreases in pH towards the water surface. Given the fact that the SC profiles show no gradients with depth in the shallow water columns, the increase in pH towards the top of the Kelley and Steward shafts may be due to degassing of CO_2. Kelley mine water effervesced an odorless gas upon bailing to the surface, and this was almost certainly CO_2, or a mixture of CO_2 and N_2. This suggests that the partial pressure of CO_2 in the mine shaft water is very high, in which case there would be a continual diffusion of this solute upwards and into the air space of the shaft. Loss of dissolved CO_2 from the water would result in a rise in pH, by driving the following reaction to the right:

$$HCO_3^- + H^+ \rightarrow CO_2(aq) + H_2O \qquad (1)$$

A similar process may have occurred in the Steward Mine, although this water did not effervesce on sampling.

The decrease in pH near the surface of the Marget Ann and Travona shafts was most likely due to oxidation of H_2S, as shown by the following reaction:

$$H_2S(aq) + 2O_2 \rightarrow 2H^+ + SO_4^{2-} \qquad (2)$$

Both the Marget Ann and Travona mine waters are enriched in H_2S (Sect. 3.2.2). Interestingly, the Orphan Girl shaft did not show a similar decrease in pH at the top of its water column. This is odd considering that H_2S levels are much higher in the Orphan Girl compared to the Marget Ann and Travona mines. A possible explanation is that there could be very little O_2(g) in the air *immediately above* the static water level in the Orphan Girl mine. This is an important safety consideration in future visits to this site. Another possible factor to explain the lack of a pH change in the Orphan Girl is that this water has the highest alkalinity of any of the Butte shafts (Sect. 3.2.1), and therefore has a much higher pH-buffering ability.

Figure 12 compares the pH of water samples measured *in situ* (data in Table 2) with the pH's of individual water samples measured after the samples were brought to the surface. For the most part, the pH values obtained using both methods showed similar trends with depth, and agreed within ±0.2 units. Some of the pH differences shown in the diagram are probably real (due to escape of CO_2 or other reactions that could have occurred during sample retrieval), and some could be due to instrument calibration error. Another consideration is that – whereas the datasonde measures pH over a narrow depth interval (< 5 cm), a bailer or point sampler collects water over a larger depth interval (> 20 cm). This is the most likely explanation for the large difference in the near-surface pH measurements obtained from the Marget Ann mine.

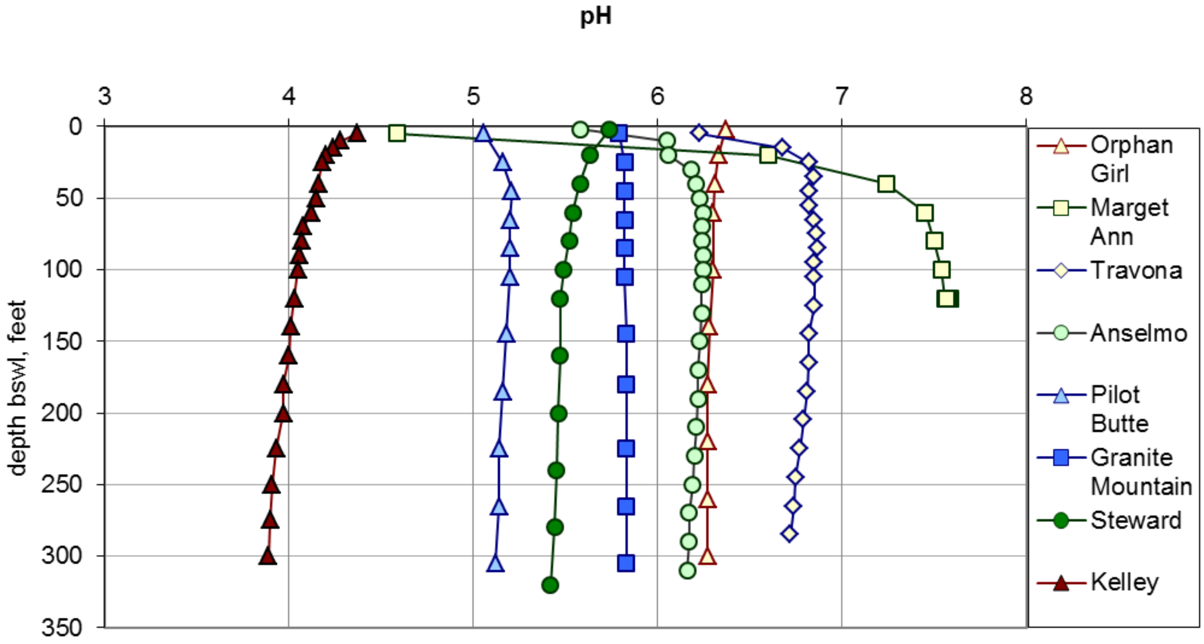


Figure 11 In situ pH profiles for mine shafts collected by the Troll

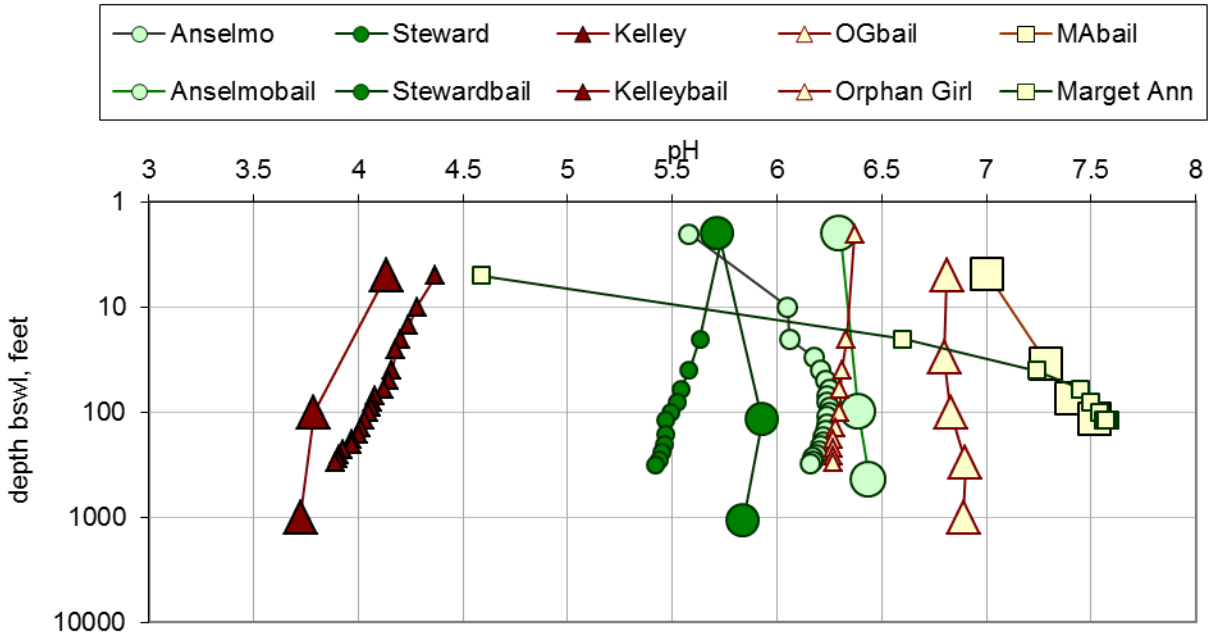


Figure 12 Comparison of *in situ* pH vs. pH of samples bailed to surface

3.1.4. Eh

Vertical changes in Eh measured in situ by the Troll in the top 300 feet of each mine shaft are shown in Figure 13. Water from the West Camp (Travona) and Outer Camp (Marget Ann, Orphan Girl) mines had lower Eh than water from the East Camp mines. This is to be expected, since the former waters have H_2S in them, whereas the East Camp waters do not. The Eh of all of the mine shafts increased towards the surface, which is also to be expected, given the likelihood that O_2 in the air column is diffusing into the shallow water samples, thereby raising the Eh. With the possible exception of Marget Ann, the *in situ* Eh values for all waters appeared to level off to a constant value below a depth of ~ 100 feet BSWL.

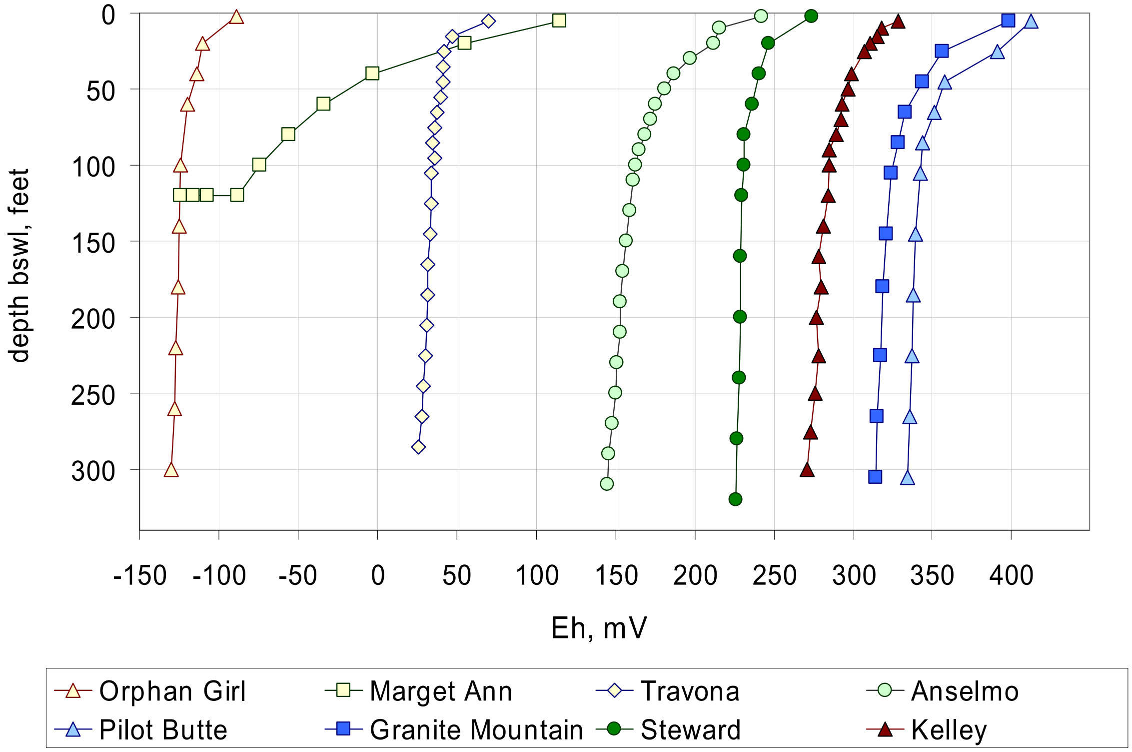


Figure 13 In situ Eh profiles for mine shafts collected by the Troll.
All Eh measurements are calibrated to the standard hydrogen electrode (SHE)

Figure 14 compares Eh values measured *in situ* (data from table 2) vs. measurements for samples brought to the surface. With the exception of the Steward mine samples, the surface measurements were higher (more positive) than the *in situ* measurements. This is to be expected, given the likelihood of oxidation reactions during the time it took to bring the water samples to the surface. For some reason the Steward mine samples showed the opposite trend, although in this case the *in situ* and surface Eh measurements were in relatively close agreement.

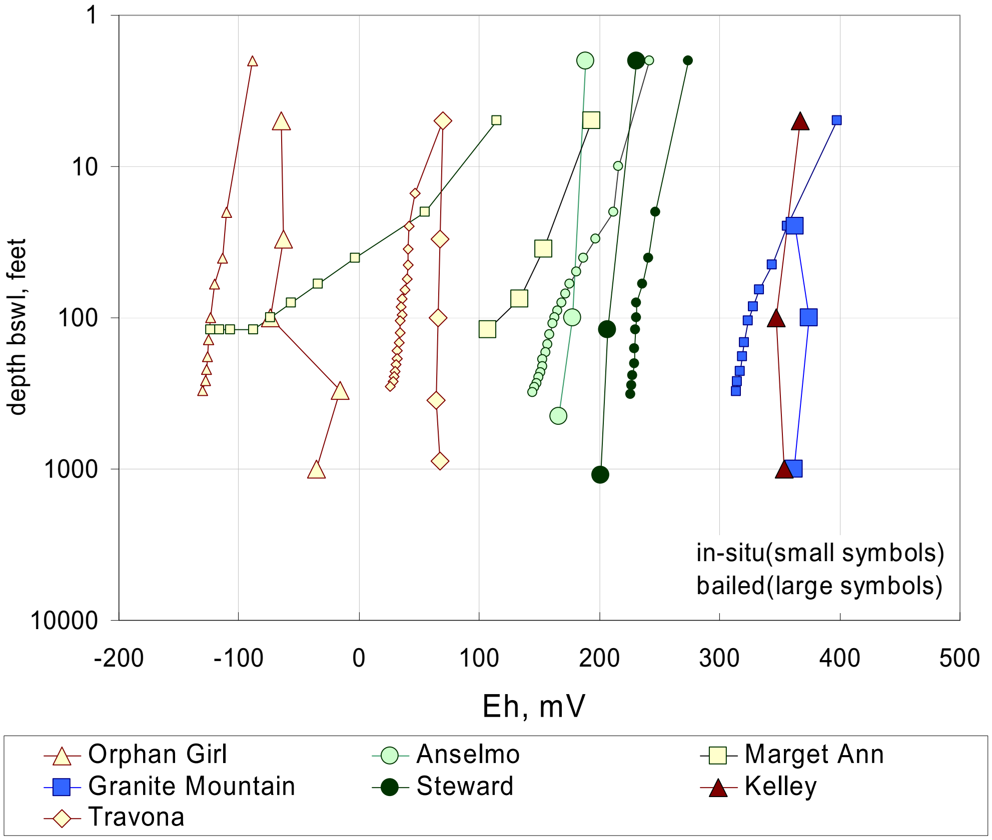


Figure 14 Comparison of in situ Eh with Eh of samples bailed to surface.

3.1.5. Dissolved Oxygen

All mine shaft waters examined in this study had dissolved oxygen (DO) concentrations near or below the practical detection limit of the datasonde. Example profiles for the Granite Mountain and Anselmo shafts are given in Figure 15. In some cases, DO profiles were collected in the air column of the shaft, as well as the underlying water. Interestingly, some of the mines (e.g., the Anselmo) showed a significant depletion in O_2 concentration in the shaft air relative to 100% saturation. In all shafts, DO levels fell rapidly to near-zero levels once the datasonde was submerged in water. Considering the elevated concentrations of dissolved Fe(II) and/or H_2S in all of the Butte mine waters, it is likely that there is NO dissolved oxygen present, especially below a depth of a foot or more. Oxidation of H_2S or Fe(II) by DO is rapid at the pH levels of most of the mine waters investigated, and therefore any dissolved O_2 molecules would be consumed quickly upon diffusion into the water column.

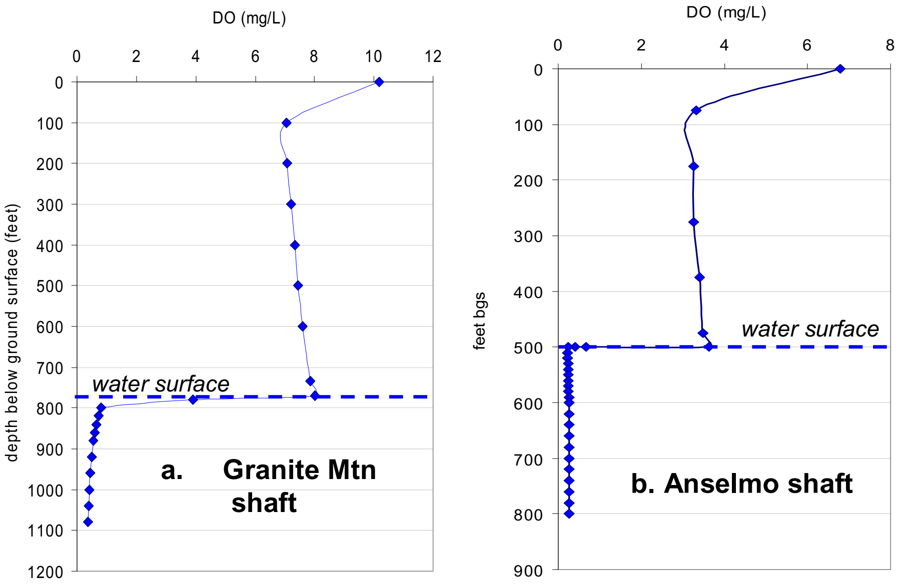


Figure 15 Vertical changes in dissolved oxygen (DO) in (a) Granite Mountain mine shaft and (b) Anselmo mine shaft.

3.2. Analytical results

3.2.1. Alkalinity

Vertical changes in alkalinity (measured at the surface immediately after sample retrieval) are given in Figure 16. Although there are large differences in alkalinity between shafts, none of the mines showed any clear vertical gradient in alkalinity with depth. The Orphan Boy and Orphan Girl mines had by far the highest alkalinity values of the waters sampled, whereas the Kelley Mine had the lowest. Alkalinity data from the Kelley have a high uncertainty, given the low pH of this water. Kelley water samples had a weak purple coloration when bromcresol green-methyl red powder was added, which then quickly turned bright pink upon titration with a few drops of dilute H_2SO_4. Based on these observations, it is likely that there is some bicarbonate alkalinity present in the Kelley waters, but the levels are close to the limit of quantification.

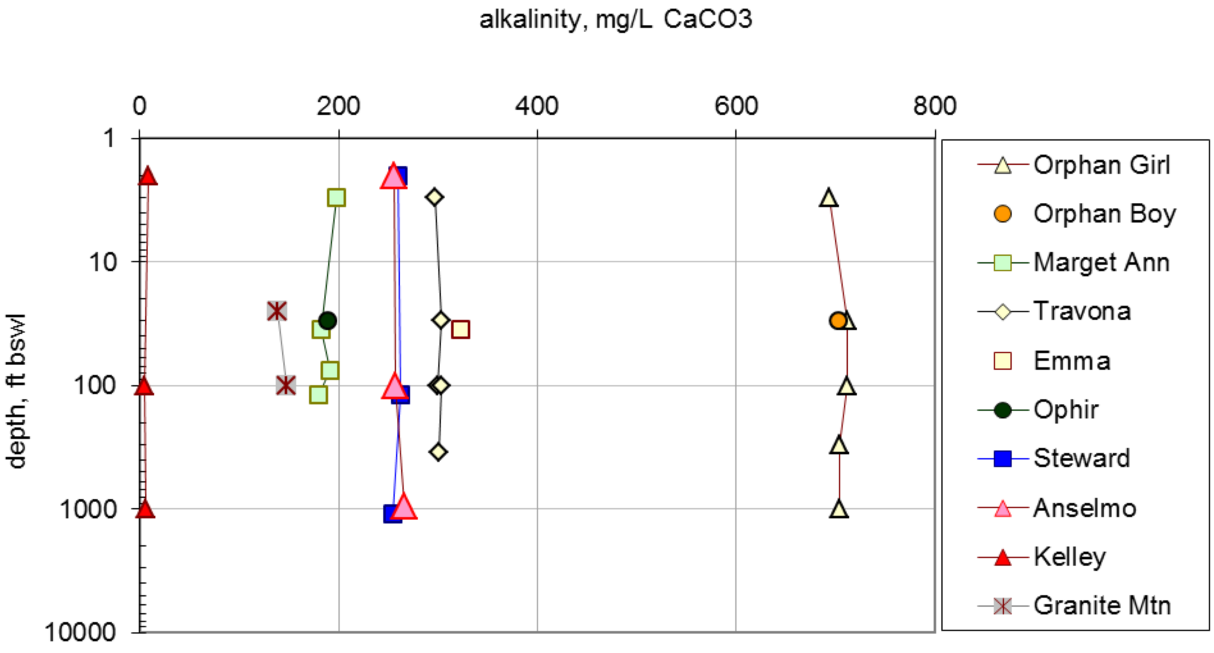


Figure 16 Vertical changes in alkalinity for selected mine shafts.

3.2.2. Sulfide

Concentrations of dissolved (filtered) and total (unfiltered) sulfide measured by colorimetry from mine shafts in the Outer Camp and West Camp are summarized in Table 3 and Figures 17 and 18. In most cases, the dissolved concentrations were lower than the total concentrations (e.g., see Fig. 18). This could reflect the presence of suspended particles of metal sulfide (e.g., very small FeS, ZnS, or FeS_2 particles). However, some of the discrepancy could also have been due to loss of H_2S during the filtration step, either through oxidation or volatilization to air. Because of these problems, plus the fact that the colorimetric analyses were un-calibrated, the dissolved sulfide measurements in this study have a relatively large uncertainty. Although field duplicate analyses typically agreed within 5%, the accuracy of the S^{2-} data reported in Table 3 is probably more like ±25%. Because of possible loss of H_2S, the true dissolved S^{2-} concentrations are probably somewhere between the data shown in the "total" and "dissolved" columns.

Table 3 Concentrations of dissolved and total sulfide (mg/L as S^{2-})

	feet bswl	S^{2-} (total)	S^{2-} (dissolved)
Outer Camp			
Orphan Boy	30	8.5	n.a.
Orphan Boy-D	30	8.5	n.a.
Orphan Girl 1	3	5.5	3.9
Orphan Girl 4	30	6.8	5.1
Orphan Girl 5	100	7.4	6.7
Orphan Girl 2	300	6.1	4.6
Orphan Girl 2-D	300	5.6	4.6
Orphan Girl 3	1000	5.9	3.3
Marget Ann 1	3	0.008	n.a.
Marget Ann 3	35	0.230	n.a.
Marget Ann 4	75	0.27	n.a.
Marget Ann 5	120	0.54	0.34
West Camp			
Ophir	30	0.15	0.065
Emma	34	0.37	0.01
Travona 2	5	0.20	0.01
Travona 3-D	5	0.19	0.15
Travona 4	30	0.20	0.16
Travona 5	100	0.19	0.15
Travona 6-D	100	0.20	0.16
Travona 7	350	0.20	0.13
Travona 8	890	0.40	0.16

As shown in Figures 17 and 18, there were no clear vertical gradients in H_2S concentration in any of the shafts, with the exceptions of the Marget Ann and Orphan Girl mines, The Marget Ann showed a decrease in H_2S towards the surface and the Orphan Girl mine may contain a region of relatively elevated sulfate reduction at the 100 foot level (Tables 3 and 4 and Fig. 18). Although several of the deeper waters from the East Camp (e.g., Anselmo, Steward shafts) were tested for H_2S, all results from these mines were below detection. This is consistent with the higher Eh values obtained from the East Camp shafts (Fig. 13).

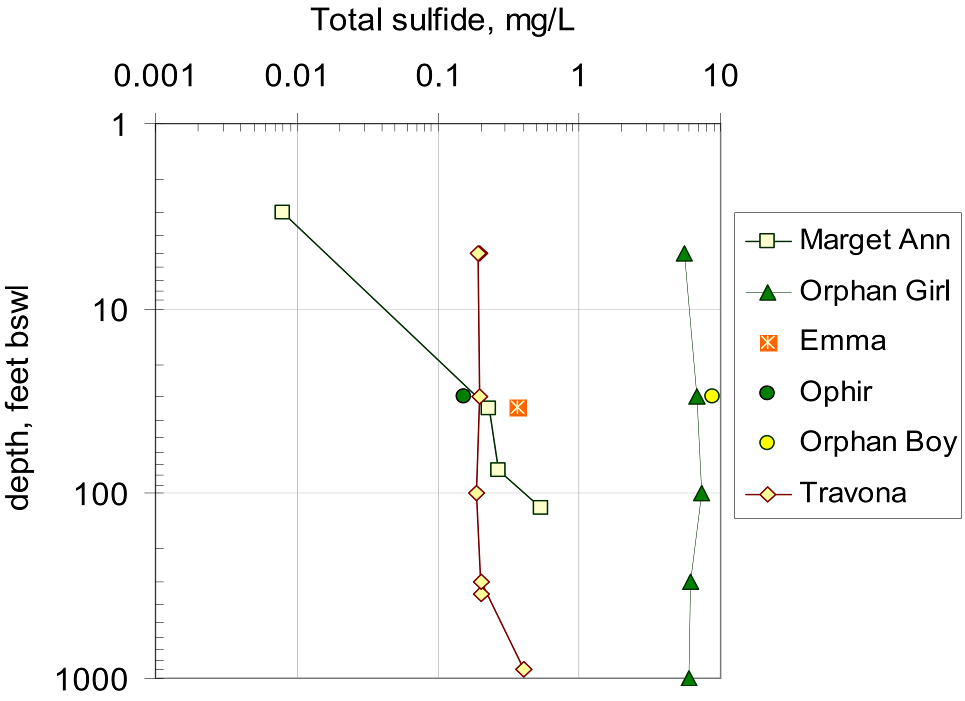


Figure 17 Vertical changes in total sulfide concentration in mine shafts. These data were collected using the methylene blue method on unfiltered samples.

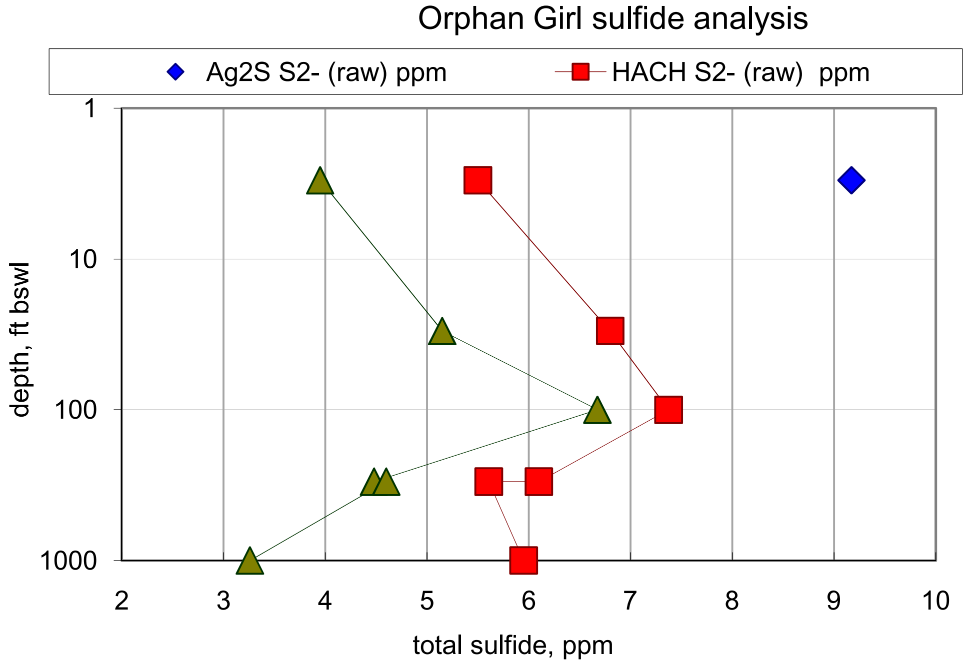


Figure 18 Vertical changes in the concentration of filtered and unfiltered sulfide (sum of $H_2S + HS^-$) in the Orphan Girl shaft determined by the Methylene Blue method. Compare to unfiltered extraction of sulphide by$AgNO_3$ that includes "free sulfide" clusters.

Table 4 Water quality parameters, sulfide, and iron concentrations for the Orphan Girl mine shaft.

Depth	Alkalinity	S^{2-} (raw)	S^{2-} (filtered)	Fe^{2+}	ΣFe	T	pH	SC	Eh	LDO	LDO
feet bswl	*mg/l $CaCO_3$*	*ppm*	*ppm*	*ppm*	*ppm*	*ºC*	*pH*	*uS/cm*	*mV*	*ppm*	*%sat*
5	693	5.5	3.95	0.139		26.13	6.81	1833	-65	0.2	3.1
30	712	6.8	5.15				6.8	1785	-63	1.37	
100	712	7.38	6.68				6.83	1786	-74	0.89	
300	704	6.1	4.48	0.205	0.161		6.9	1862	-16	1.6	21
1000	704	5.95	3.26	0.707			6.89	1804	-36	1.23	16.4
300	717	5.61	4.6				6.81	1803	-68	1.2	

3.2.3. Fe(II)/Fe(III)

As shown in Table 5, the vast majority of the dissolved Fe in all of the shafts was present in the reduced, Fe(II) valence state. Because Fe(III) concentrations were determined by the difference between two large numbers (i.e., Fe(Total) - Fe(II)), the Fe(III) data in Table 5 should be viewed with skepticism. Given the Eh-pH conditions of the mine waters, it is very likely that concentrations of Fe(III) were < 0.1 mg/L in all samples. Figure 19 is an Eh-pH diagram that summarizes the aqueous speciation of Fe. All of the waters sampled in this study (shown by the capital letters on the diagram) plot well into the field of predominance for Fe^{2+} (the dominant aqueous Fe(II) species), suggesting that concentrations of Fe(III) should have been negligible. Figure 20 is an Eh-pH diagram which combines data for this study, as well as previous work (Pellicori et al., 2005; Roesler et al., 2007) summarizing mine shafts, bedrock wells, and surface water relating to the Berkeley Pit. The diagram illustrates a control of Eh and pH caused by oxidation of reduced iron to various species of hydrous ferrous oxides or the iron-carbonate mineral siderite in the Outer and West Camp regions.

Table 5 Results of Fe(II)/Fe(III) analyses.

	Depth (ft bswl)	Fe(Total)	Fe(II)	Fe(III)	% Fe(II)
Emma	34	2.0	1.8	0.2	88%
Ophir	30	4.1	3.8	0.3	93%
Orphan Boy	30	0.21	0.20	0.01	98%
Anselmo A	2	30	26	4	88%
Anselmo C	100	31	30	1	98%
Anselmo D	450	30	30	0	100%
Steward A	2	250	250	0	100%
Steward B	120	260	230	30	90%
Steward C	1120	230	250	< 0	100%
Kelley A	2	1840	1830	10	99%
Kelley B	100	1710	1730	< 0	100%
Kelley B-D	100	1756	1763	< 0	100%
Kelley C	1000	2200	2180	20	99%
Granite Mtn 1	25	20.5	17.5	3.0	86%
Granite Mtn 2	100	17.8	15.0	2.8	84%
Granite Mtn 3	1000	18.0	16.6	1.4	92%
Marget Ann 1	3	0.04	0.04	0.00	100%
Marget Ann 3	35	0.10	0.10	0.00	100%
Marget Ann 4	75	0.06	0.06	0.00	100%
Marget Ann 5	120	0.13	0.13	< 0	100%
Orphan Girl 1	3	n.a.	0.14	n.a.	n.a.
Orphan Girl 2	300	0.16	0.20	< 0	100%
Orphan Girl 3	1000	n.a.	0.71	n.a.	n.a.
Kelley A	100	1500	1470	30	98%
Kelley B	1000	1540	1540	0	100%

Data are in mg/L.

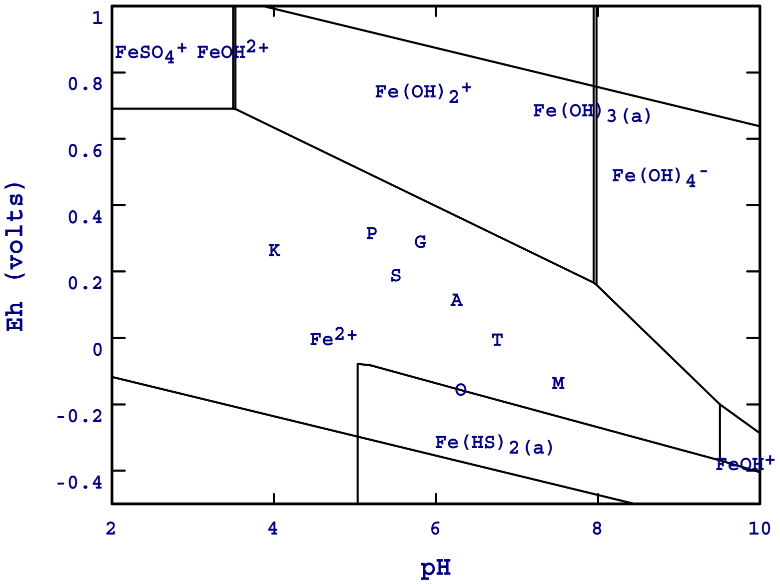


Figure 19 Eh-pH diagram for the Fe-S-H2O system

The diagram was drawn using the program STABCAL, and the MINTEQA2 thermodynamic database. The approximate Eh-pH conditions of the mine shafts investigated in this study are given by capital letters which correspond to the first letter of the mine. (K = Kelley Mine shaft; S = Steward Mine shaft; etc. Solid phases were suppressed from the calculations to more easily show the boundaries of the aqueous Fe species.

Figure 20 is an Eh-pH diagram which combines data for this study, as well as previous work (Pellicori et al., 2005; Roesler et al., 2007) summarizing mine shafts, bedrock wells, and surface water relating to the Berkeley Pit. The diagram illustrates a control of Eh and pH caused by oxidation of reduced iron to various species of hydrous ferrous oxides or the iron-carbonate mineral siderite in the Outer and West Camp regions

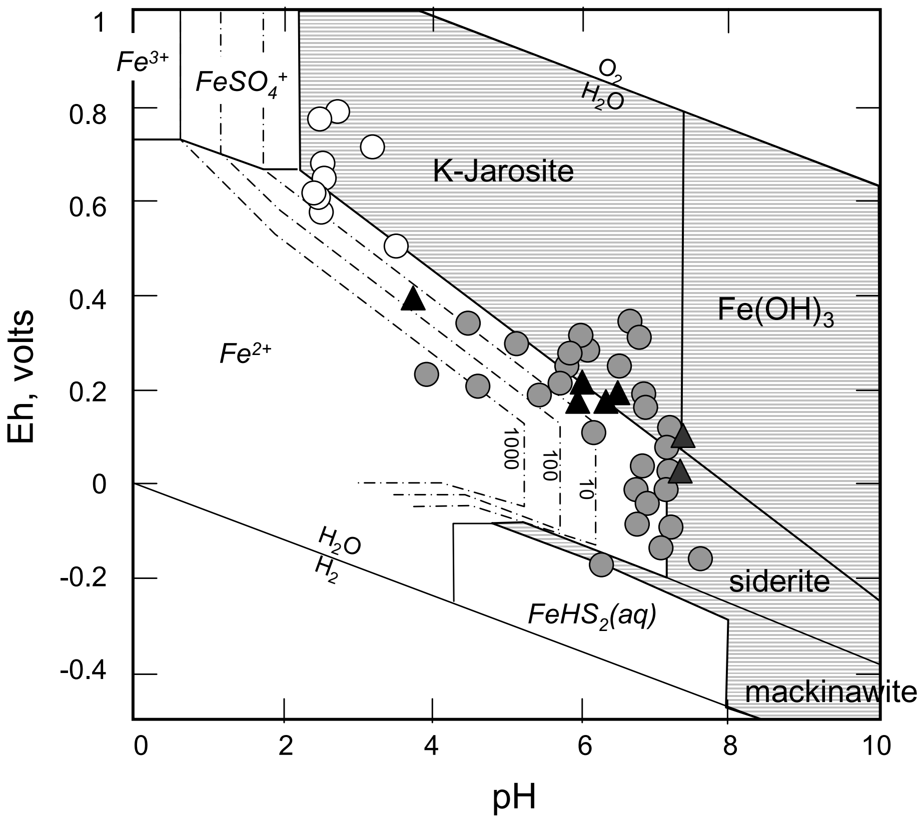


Figure 20 Eh-pH diagram of Butte mine waters.

The diagram was drawn for ΣS = 1000 mg/L, ΣC = 100 mg/L, and ΣK = 15 mg/L. Boundaries betweensolids (shaded regions) and aqueous Fe species were drawn for 1 mg/L, and contours are shown for ΣFe = 10, 100, and 1000 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.

3.2.4. As(III)/As(V)

Results for As(III)/As(V) speciation are given in Table 6. The data show some interesting trends which are, for the most part, explainable. Whereas the Steward and Kelley mine shafts apparently had a mixture of As(III) and As(V), essentially all of the dissolved arsenic in the Anselmo, Ophir, Emma, and Travona shafts was in the reduced, As(III) form. This is consistent with the higher Eh of the Steward and Kelley mines relative to the rest of the waters sampled (see Fig. 13). Figure 21 is an Eh-pH diagram for the As-S-H_2O system. The four mine shafts sampled for As speciation all had Eh-pH conditions near the dissolved As(III)/As(V) boundary. Thus, it would not be surprising to see a mixture of both valence states in any of these waters. The dominant As(III) species in the Butte mine waters is most likely H_3AsO_3(aq), whereas $HAsO_4^-$ and $H_2AsO_4^-$ are the probable As(V) species.

Table 6 Results of As(III)/As(V) speciation.

	depth(ft)	ΣAs(T)	As(V)	As(III)	%As(III)
East camp					
Anselmo A	2	0.059	b.d.	0.059	100%
Anselmo C	100	0.068	b.d.	0.068	100%
Anselmo D	450	b.d.	b.d.	b.d.	b.d.
Steward A	2	1.93	1.17	0.76	39%
Steward B	120	1.98	1.11	0.87	44%
Steward D	1120	2.30	1.08	1.22	53%
Kelley A	2	8.68	6.03	2.65	30%
Kelley B	100	8.54	5.84	2.70	32%
Kelley C	1000	10.0	6.9	3.1	31%
West Camp					
Ophir	30	0.059	b.d.	0.059	100%
Emma	34	0.068	b.d.	0.068	100%
Travona	5	0.076	b.d.	0.076	100%
Travona	30	0.083	0.026	0.056	68%
Travona	100	0.087	b.d.	0.087	100%
Travona	350	0.088	b.d.	0.088	100%
Travona	890	0.090	b.d.	0.090	100%

Data are in mg/L.

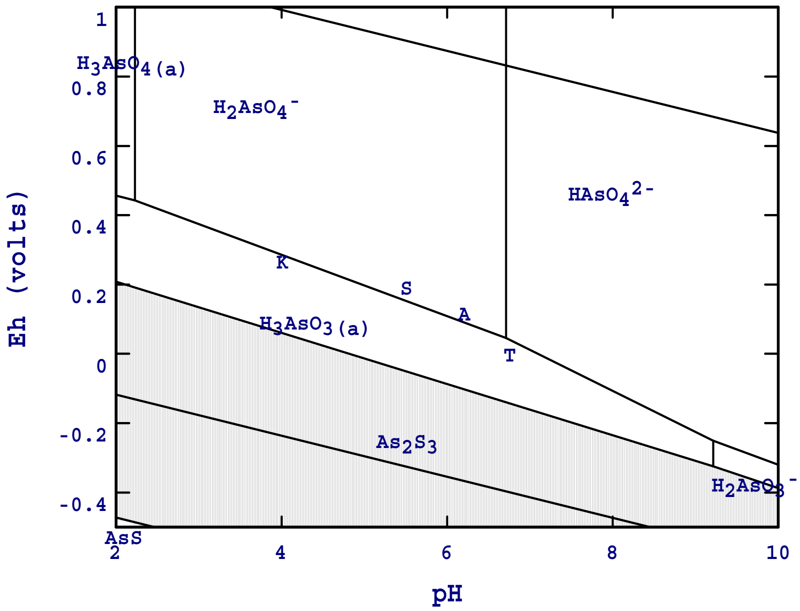


Figure 21 Eh-pH diagram for the As-S-H_2O system

The diagram was drawn using the program STABCAL, and the MINTEQA2 thermodynamic database. The approximate Eh-pH conditions of the Anselmo, Kelley, Steward, and Travona mine shafts are shown by the letters "A", "K", "S", and "T", respectively. The shaded region shows the area of stability of orpiment (As_2S_3), assuming 100 mg/L ΣS and 1 mg/L ΣAs.

3.2.5. ICP-AES Results

Results of ICP-AES analysis of selected major and trace elements are given in Appendix B. QA/QC considerations attached to these data are summarized in Appendix A of this document. Overall, the ICP-AES results reinforce observations noted above that there are very few clear differences in the geochemistry of the mine shaft waters with depth. Table 7 summarizes a statistical analysis of the data in Appendix B. The top row in Table 7 shows the average relative percent difference (rpd) in element concentration of 5 field duplicate samples collected during the course of the study. Subsequent rows show the average concentration and relative standard deviation (rsd) for samples collected from different depths in the each mine shaft. It was reasoned that if the rsd of samples from different depths was greater than 2 x the rpd of the field duplicate samples, then this would indicate a potentially significant change in solute concentration with depth. Following this line of reasoning, the only two shafts that show any significant changes in solute concentration with depth for more than one analyte are the Kelley and Orphan Girl shafts. In the case of the Kelley shaft, whereas the samples collected from 5' and 100' bswl had essentially identical chemistry, the deep sample (1000' bswl) had significantly higher Fe, Ca, Na, and Sr. The deep sample also had higher SC (Fig. 10) and a significantly warmer temperature (Fig. 6) than the overlying water column. For these reasons, it is concluded that the apparent variation in water chemistry in the Kelley mine at depth is real. The situation is less clear in the case of the Orphan Girl shaft. Vertical profiles in water temperature and SC through the Orphan Girl mine showed no vertical gradients (Fig. 6, 10). However, both the alkalinity (Fig. 16) and sulfide (Fig. 17) profiles showed higher concentrations at mid-depths, which is also the trend for several ICP analytes, including Ca, Mg, S, and Sr. It is concluded that the Orphan Girl may have some changes in chemistry with depth, but they are relatively small.

In contrast to the Kelley and Orphan Girl mines, vertical changes in chemistry for the other mine shafts were remarkably small. This is particularly true of the Steward, Anselmo, and Granite Mountain mines. Although both Marget Ann and Travona showed fairly large deviations in K concentration, the precision and accuracy of K via ICP-AES analysis is quite low, and therefore this could easily be an artifact of laboratory error, compounded by the relatively low K concentrations. Likewise, the very large rsd values for several of the West Camp and Outer Camp mines for Zn and Fe are almost certainly due to their concentrations being very low and near the detection limit for the diluted ICP-AES samples. Thus, these rsd anomalies (shown in green parentheses in Table 7) were not considered significant.

Table 7 Summary of the average (avg) and relative standard deviation (rsd) for solute concentrations from each mine shaft.

		Ca	Fe	K	Mg	Mn	Na	S	Si	Sr	Zn
Average rpd of duplicates		1.7%	11.6%	11.8%	2.8%	1.2%	2.8%	2.3%	2.1%	2.2%	49.4%
Anselmo	avg	307	29.3	14	87	18.5	38	340	10.7	3.27	14.7
	rsd	1.6%	2.0%	4.2%	1.3%	0.8%	1.5%	1.2%	0.5%	0.9%	1.4%
Granite Mtn	avg	495	16.3	19	162	42.3	28	677	9.5	4.99	18
	rsd	0.8%	3.5%	0.0%	1.4%	0.9%	2.1%	0.6%	1.6%	1.3%	0.6%
Kelley	avg	406	1650	59	302	146	76	1820	38.2	0.513	192.3
	rsd	8.7%	14.2%[1]	1.7%	1.5%	2.1%	7.3%	1.0%	0.5%	34.4%	0.8%
Marget Ann	avg	137	0.4	5.25	23.8	1.76	12.3	87	3.8	2.67	0.04
	rsd	1.9%	(106%)	32.5%	2.1%	3.3%	4.1%	2.1%	2.1%	2.0%	(177%)
Orphan Girl	avg	223	0.22	8.8	60	4.98	111	*206*	11.5	5.86	0.02
	rsd	4.7%	(74.7%)	9.5%	5.9%	4.5%	3.6%	16.8%	4.6%	5.1%	(136%)
Steward	avg	452	236	33	139	26.1	42	664	21.8	1.93	40.3
	rsd	1.5%	0.5%	4.6%	2.2%	1.1%	1.4%	1.2%	0.5%	1.0%	0.4%
Travona	avg	174.6	1.42	7.4	49.4	5.91	34.4	131.4	9.06	1.314	0.06
	rsd	1.9%	19.5%	26.3%	2.7%	2.1%	3.3%	2.4%	3.2%	3.3%	(149%)

3.2.6. Phosphate

Overall, results for phosphate and other nutrients collected in this study were problematic. All samples analyzed for nitrate or ammonia were below their respective analytical detection limits by HACH methods. In the case of phosphate, rapid precipitation of hydrous ferric oxide (HFO) for unpreserved samples collected from East Camp wells caused turbidity that interfered with the colorimetric determinations. This was not a problem for the Fe-poor Outer and West Camp wells, and some reasonable data were obtained from the Travona and Orphan Girl Shafts (Table 9). In fact, the agreement between the colorimetric results for phosphate (as P) vs. the ICP-AES results for total dissolved P was very good for the Orphan Girl samples (compare the last two columns in Table 9). Although the agreement was less good for the Travona mine, the colorimetric results indicate PO_4 levels were very close to the limit of detection via ICP. Furthermore, phosphate concentrations measured in this study from the Travona are similar to values reported by Roesler (2005) in her study of the West Camp extraction well, which drains water from the Travona mine workings.

Table 8 Phosphate concentrations (mg/L) for selected mine shafts.

	Depth, ft bswl	PO_4 as PO_4	PO_4 as P	P-ICP
Travona 3	5	0.22	0.07	<0.06
Travona 4	30	0.22	0.07	<0.06
Travona 5	100	0.29	0.09	<0.06
Travona 7	350	0.28	0.09	<0.06
Travona 8	890	0.29	0.09	<0.06
Orphan Girl 1	5	0.45	0.15	0.17
Orphan Girl 4	30	0.42	0.14	0.17
Orphan Girl 5	100	0.49	0.16	0.17
Orphan Girl 3	1000	0.44	0.14	0.17
Marget Ann 2	5	0.00	0.00	<0.06
Marget Ann 3	35	0.00	0.00	<0.06
Marget Ann 4	75	0.00	0.00	<0.06
Marget Ann 5	120	0.00	0.00	<0.06

3.3. Stable Isotope Results

All stable isotope results collected in this study from the UNR laboratory are summarized in Table 10. The results of inter-laboratory splits for isotopic analysis of two water samples are discussed in Appendix A.

The stable isotope results reinforce the field parameter and chemistry results presented above, and show a lack of any clear vertical gradients in any of the mine shafts sampled in this study. However, there are interesting differences between the different mine shafts, especially for $\delta^{34}S_{H2S}$, $\delta^{34}S_{SO4}$, $\delta^{18}O_{SO4}$ and $\delta^{13}C_{DIC}$. These are discussed in Section 4.

Table 9 Stable isotope results.

Sample ID	ft bswl	$\delta^{34}S_{H2S}$	$\delta^{34}S_{SO4}$	$\Delta\delta^{34}S$ [a]	$\delta^{18}O_{SO4}$	$\delta^{18}O_{H2O}$	δD_{H2O}	$\delta^{13}C_{DIC}$
Analytical error		± 0.2‰	± 0.2‰	± 0.4‰	± 0.4‰	± 0.1‰	± 1‰	± 0.4‰
Orphan Girl 1	5	3.8	34.3	30.5	1.3	-17.7	-140	-21.2
Orphan Girl 4	30	5.6	33.9	28.3	2.9	n.a.	n.a.	n.a.
Orphan Girl 2	300	4.7	34.0	29.3	1.2	-17.4	-139	-21.1
Orphan Girl 3	1000	n.a.	n.a.	n.a.	n.a.	-17.7	-140	-20.9
Orphan Boy	30	3.7	34.6	30.9	2.2	-17.6	-141	n.a.
Orphan Boy-D[b]	30	3.6	34.7	31.1	2.5	n.a.	n.a.	n.a.
Marg. Ann 2	5	-34.6	15.8	50.4	-0.1	-18.6	-146	n.a.
Marg. Ann 5	120	n.a.	n.a.	n.a.	n.a.	-18.6	-147	n.a.
Marg. Ann 5-D[b]	120	n.a.	n.a.	n.a.	n.a.	-18.3	-147	-16.1
Emma	34	-20.9	18.6	39.5	0.8	-17.4	-135	n.a.
Ophir	30	-24.0	7.3	31.3	-3.1	-17.5	-134	n.a.
Travona 2	5	n.a.	13.0	n.a.	-2.9	-17.3	-135	n.a.
Granite Mtn 1	25	n.a.	3.7	n.a.	-11.1	-17.2	-135	-14.4
Granite Mtn 2	100	n.a.	3.8	n.a.	-11.1	-17.3	-136	-13.8
Granite Mtn 3	1000	n.a.	3.9	n.a.	-10.6	-17.3	-136	-14.6
Kelley A	2	n.a.	2.7	n.a.	-9.9	-17.5	-140	n.a.
Kelley B	100	n.a.	2.7	n.a.	-8.7	-17.6	-140	n.a.
Kelley C	1000	n.a.	2.3	n.a.	-9.4	-17.7	-140	n.a.
Steward A	2	n.a.	n.a.	n.a.	n.a.	-17.4	-136	n.a.
Steward B	120	n.a.	n.a.	n.a.	n.a.	-17.5	-138	n.a.
Steward C	1120	n.a.	n.a.	n.a.	n.a.	-17.4	-137	n.a.
Anselmo A	2	n.a.	n.a.	n.a.	n.a.	-17.2	-133	n.a.
Anselmo C	100	n.a.	n.a.	n.a.	n.a.	-17.1	-135	n.a.
Anselmo D	450	n.a.	n.a.	n.a.	n.a.	-17.1	-135	n.a.

All measurements in ‰ (per mil). n.a. = not analyzed. [a] $\Delta\delta^{34}S = \delta^{34}S_{SO4} - \delta^{34}S_{H2S}$; [b] the suffix “D” denotes a field duplicate sample.

4. Discussion

4.1. Controls on geochemistry of mine shaft water

The average composition of water in each mine shaft was input into the program Visual MINTEQ (Allison et al., 1991) to calculate aqueous speciation and mineral saturation indices. Selected results are summarized in Table 8, from which the following observations are drawn:

- All of the waters had good to very good charge balance calculations.
- All of the shafts had calculated CO_2 partial pressures much greater than atmospheric saturation values (~ 0.0003 bars). The Kelley Mine had $PCO_2 > 1$ bar, consistent with the observation that this mine effervesced CO_2 during sampling.
- Most of the mine waters were near equilibrium or slightly supersaturated with barite. This is not surprising considering the low solubility of this mineral and the abundance of dissolved sulfate in the mine waters.
- All of the East Camp mine shaft waters were near equilibrium with gypsum ($CaSO_4 \cdot 2H_2O$), whereas all of the West and Outer Camp mine shafts were undersaturated with this mineral. Saturation with gypsum is probably a ubiquitous phenomenon in the East Camp waters, and is one reason for their higher salinity and ionic strength.
- All of the West and Outer Camp waters were near equilibrium with calcite ($CaCO_3$), whereas all of the East Camp waters were undersaturated with this mineral.
- With the exception of the Kelley mine, all of the waters investigated were near equilibrium with either amorphous or crystalline $MnCO_3$ (i.e., rhodochrosite). This is not

surprising, considering that rhodochrosite is an abundant mineral in the Butte ore bodies (Meyer et al., 1968).

- The Anselmo and Steward mines were near equilibrium with smithsonite ($ZnCO_3$), and the Granite Mountain mine was not far off. Probably smithsonite is helping to control dissolved Zn concentrations in many of the East Camp mine workings, with the exception of the Kelley mine. None of the carbonate minerals were near saturation in the Kelley mine, mainly because of its low pH.
- Several of the mine shafts were near equilibrium with siderite ($FeCO_3$), including the Anselmo, Steward, Emma, Ophir, and Travona mines. The Outer Camp mines were undersaturated with siderite, probably because their higher H_2S concentrations lowered the solubility of Fe as Fe-sulfide minerals.
- Most of the mine shafts had dissolved silica concentrations close to saturation with chalcedony (microcrystalline quartz). The Steward and Kelley mines had higher silica concentrations and were closer to equilibrium with amorphous silica.
- All of the mine waters with measurable concentrations of dissolved phosphate were found to be very close to equilibrium with hydroxyapatite ($Ca_5(PO_4)_3OH$). Apatite is a common accessory mineral in the Butte Quartz Monzonite (Meyer et al., 1968; Miller, 1973), and so it is not surprising that phosphate concentrations in the mine waters are buffered by this mineral.
- Several of the mine shafts with elevated H_2S were near equilibrium with mackinawite (FeS), but were 9 to 10 orders of magnitude supersaturated with pyrite. Although pyrite is the stable phase in H_2S-rich waters, mackinawite is the first Fe-sulfide phase to form

when Fe^{2+}-rich waters mix with H_2S, and the latter mineral is known to exert a stronger solubility control in low temperature sulfidic waters (e.g., Roesler et al., 2007).

- All of the mine waters with H_2S in them were strongly supersaturated with sphalerite (ZnS). It is possible that some of the "dissolved" Zn that passed through the filters used in this study was actually nano-crystalline particles of ZnS, or aqueous ZnS clusters.

Table 10 Calculated charge balances, CO2 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
Anselmo	0.9%(+)	0.15	0.036	0.31	-0.39	-0.71	0.01	0.50
Gran.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
M.Ann	1.7%(+)	0.01	0.014	0.34	-1.00	-0.02	0.04	0.52
Or Girl	6.2%(+)	0.39	0.027	0.41	-1.02	-0.08	0.13	0.63
Steward	1.1%(+)	0.81	0.059	-0.20	-0.15	-1.27	-0.59	-0.09
Travona	1.9%(+)	0.06	0.021	0.39	-0.83	-0.31	0.16	0.64
Or 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

	Saturation Indices							
	SMS	SID	CHA	SIA	HAP[2]	MAC	SPH	PYR
Anselmo	0.18	0.23	0.22	-0.60	-	-	-	-
Gran. Mt	-0.52	-0.82	0.20	-0.63	-	-	-	-
Kelley	-2.53	-1.80	0.58	-0.20	-	-	-	-
M.Ann	-1.60	-0.64	-0.12	-0.98	-	-0.36	5.96	9.64
Or Girl	-2.25	-1.19	0.14	-0.66	0.00	-0.58	5.33	10.80
Steward	-0.13	0.40	0.44	-0.36	-	-	-	-
Travona	-1.60	-0.44	0.20	-0.64	0.18	-0.69	5.37	9.70
Or 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

Values of S.I. in red 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 one Ca atom per unit formula. Abbreviations: BAR = barite ($BaSO_4$); GYP = gypsum ($CaSO_4.2H_2O$); CAL = calcite ($CaCO_3$); MNA = amorphous $MnCO_3$; RDC = rhodochrosite ($MnCO_3$); SMS = smithsonite ($ZnCO_3$); SID = siderite ($FeCO_3$); CHA = chalcedony (microcrystalline SiO_2); SIA = amorphous SiO_2; HAP = hydroxyapatite ($Ca_5(PO_4)_3OH$); MAC = mackinawite (FeS); SPH = sphalerite (ZnS); PYR = pyrite (FeS_2).

From the preceding discussion, it is apparent that a number of primary and secondary minerals are exerting a control on the chemistry of the Butte mine waters, and that there are definite trends when one compares the East Camp vs. the West and Outer Camp mine waters.

One puzzling aspect of the mine shaft waters of Butte is their very low dissolved Cu concentrations. Of all the mines sampled in this study, the only waters that had detectable Cu in them were from the Granite Mountain mine (Table 7). Considering the fact that the East Camp shafts were primarily mined for copper, an explanation is needed for the very low Cu concentrations in – for example – the Kelley, Anselmo, and Steward mines. Based on Visual-MINTEQ modeling, all of the East Camp waters are strongly undersaturated with all of the Cu-bearing minerals in the thermodynamic database, even when "dummy" Cu concentrations of 1 mg/L are added to the input files. Several hypotheses are advanced here to help explain the absence of copper:

1) Dissolved Cu^{2+} ions may be adsorbing strongly onto hydrous ferric oxide and other solid minerals in the mine workings.
2) Cu^{2+} may be precipitating onto the surfaces of pyrite as the mineral chalcocite (Cu_2S).
3) Cu^{2+} may be cementing onto scrap iron left behind in the mines.

Although the first explanation is possible, it is difficult to see how dissolved Zn^{2+} concentrations could be so high when Cu^{2+} is virtually non-existent, given the fact that both metals have a tendency to adsorb onto ferric precipitates. The second hypothesis is compelling, because it is analogous to the process known to economic geologists as "supergene enrichment" that takes place during natural weathering of porphyry copper ore deposits. The reaction can be written as follows:

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

When written in this way, the reaction can be thought of as a replacement reaction, wherein Cu^{2+} ions "scavenge" the reduced S that is present in the preexisting pyrite mineral. This reaction is very common in nature, and leads to coatings of chalcocite-after-pyrite that increase the average Cu grade of the ore body. Such a process played a key role in making the Berkeley Pit more economical to mine as a bulk-tonnage deposit (Miller, 1973). It is very possible that a similar process is taking place in the flooded Butte mine workings today.

The third hypothesis listed above is the familiar cementation reaction, and can be written:

$$Cu^{2+} + Fe(s) \rightarrow Fe^{2+} + Cu(s) \tag{4}$$

This reaction takes place at a rapid rate in low pH waters, and is being used at the time of this writing to "mine" copper from the Berkeley Pit lake. Given the large mass of scrap iron left behind in the mines (e.g., from rock bolts and sheets used in mine-wall stabilization, shaft cables, pipes, heavy equipment, etc…), it is possible that this process is happening in the flooded underground mine workings as well.

4.2. Discussion of Stable Isotopes

4.2.1. Stable Isotopes of Water

The O and H isotopic compositions of water in the shafts are typical of Butte groundwater. Figure 22 shows the data of this study on a δD_{H2O} vs $\delta^{18}O_{H2O}$ plot. The lines labeled LMWL and LEL refer to the local meteoric water line and local evaporation line, respectively, for Butte (Gammons et al., 2006b). All of the mine shaft waters plot very close to the LMWL, and this implies negligible evaporation prior to recharge to the water table. Interestingly, the

Marget Ann samples are significantly lighter (more negative $\delta^{18}O_{H2O}$ and δD_{H2O} values) then the rest of the samples. The most likely reason for this is that the Marget Ann mine sits alone on the outskirts of the district at a higher elevation (6330' above sea level) then the rest of the mine shafts (see Figure 1 and Table 1), and therefore it is most likely recharged by water that originates from higher elevations. As shown by Gammons et al. (2006b), rain and snow that falls at higher elevation in Butte is isotopically lighter than precipitation that falls in the valley.

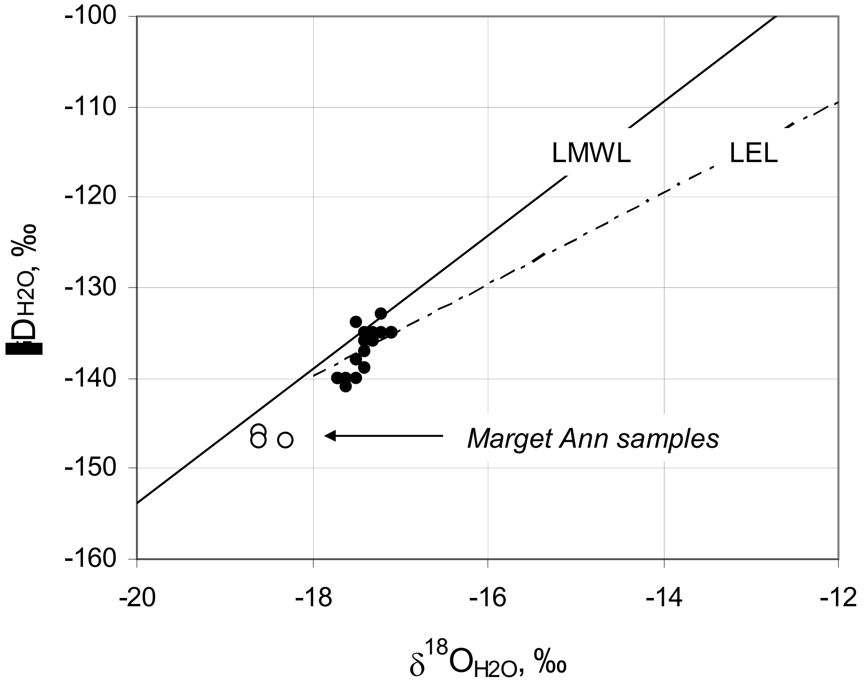


Figure 22 O and H isotopic composition of water samples collected in this study

LMWL and LEL are the local meteoric water line and local evaporation line, respectively, for Butte, Montana (Gammons et al., 2006b).

It is significant that the isotopic composition of water in the Kelley Mine is no different from that of the other East Camp shafts. One possible explanation (John Metesh, pers. comm., 2007) for the increasingly poor water quality of the Kelley Mine is that it may be hydrologically-connected to other sources of acidic water, such as the Berkeley Pit lake, the old Anaconda heap leach pads, or acidic groundwater beneath the Yankee Doodle tailings dam (e.g., Horseshoe Bend spring). However, Pellicori et al. (2005) showed that waters in the tailings pond, pit lake, and Horseshoe Bend springs were all strongly evaporated, and therefore have had their isotopic compositions shifted along the LEL to more positive values of $\delta^{18}O_{H2O}$ and δD_{H2O}. The fact that the Kelley Mine waters show no such evidence of evaporation suggests that the poor water quality of its water was probably caused by processes occurring *in situ*, and not due to mixing with water from some external source.

4.2.2. Stable Isotopes of Sulfide and Sulfate

As shown in Table 10, the S isotopic composition of dissolved sulfide ($\delta^{34}S$-H_2S) varied over a large range, from -34.6 ‰ (Marget Ann mine) to +5.6 ‰ (Orphan Girl). The S isotopic composition of dissolved sulfate ($\delta^{34}S$-SO_4) also varied over a large range, from +2.3 ‰ (Kelley) to +34.7 ‰ (Orphan Boy), and tended to be considerably heavier (more positive $\delta^{34}S$ values) than coexisting sulfide. These relationships are summarized in the S-isotope diagram of Figure 23, which includes stable isotope data from this study, as well as previous data given in Pellicori et al. (2005) and Roesler et al. (2007). In mine waters where both dissolved sulfide and sulfate are present, there is a consistent isotopic separation ($\Delta^{34}S$) between the two compounds, with sulfate 28 to 50 ‰ (i.e., 2.8 to 5.0 %) more enriched in the heavy ^{34}S isotope relative to sulfide (see 5th column ($\Delta\delta^{34}S^{a}$), of Table 9,). These large values of $\Delta^{34}S$ between sulfate and coexisting sulfide are characteristic of bacterial sulfate reduction (Canfield, 2001), and support the hypothesis of Roesler et al. (2007) that the H_2S in the flooded West and Outer Camps is of biological origin.

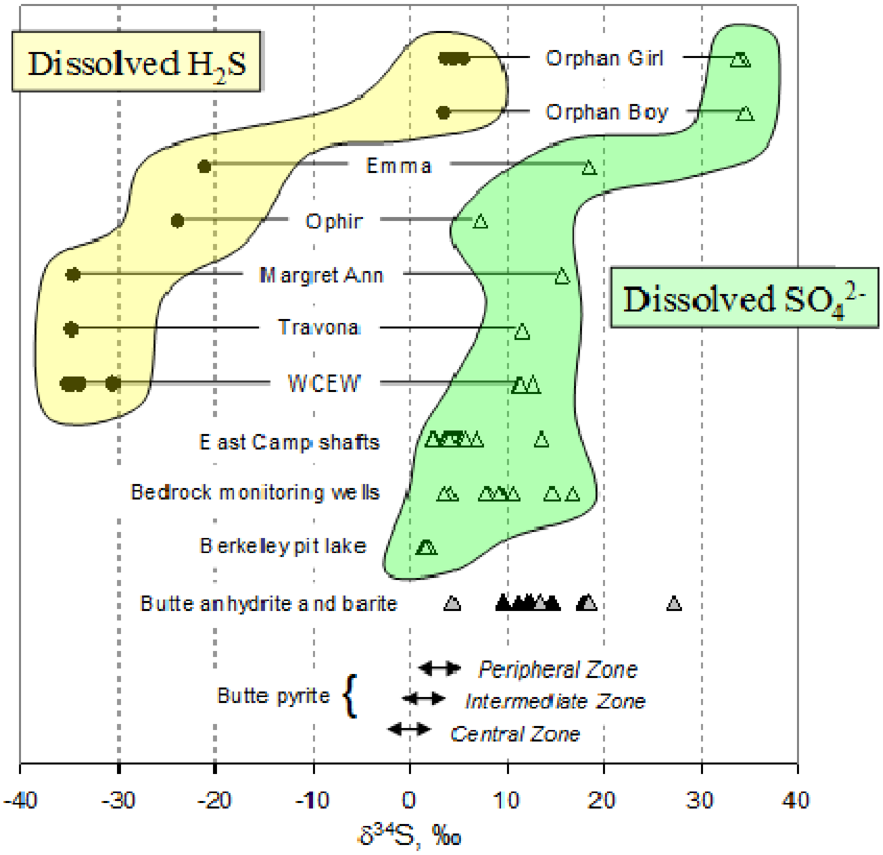


Figure 23 S isotopic composition of dissolved sulfide.

Dissolved sulfate(black circles, yellow shading) and sulfate (open triangles, green shading) from the Butte district. Data are from this study (Table 3.7), Pellicori et al. (2005), and Roesler et al. (2007). Also shown are S-isotope data (from Field et al., 2005) for the Butte minerals pyrite (arrows), anhydrite (black triangles) and barite (gray triangles).

The stable isotopic compositions of dissolved sulfate from the various mine waters of Butte are interpreted as having been derived from a combination of three processes: 1) oxidation of pyrite and other hydrothermal sulfide minerals from the Butte ore body; 2) dissolution of hydrothermal *sulfate* minerals from the Butte ore body; and 3) fractionation to heavier values of $\delta^{18}O$ and $\delta^{34}S$ during bacterial sulfate reduction. Figure 24 shows the isotopic compositions of some hydrothermal minerals from the Butte ore body (data from Field et al., 2005), including pyrite, anhydrite ($CaSO_4$), and barite ($BaSO_4$). 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 acidic lake came from oxidation of pyrite (Pellicori et al., 2005). Dissolved sulfates from the Kelley and Granite Mountain mines (this study, Table 10) also have an isotopic composition close to that of Butte pyrite. In contrast, most of the West Camp and Outer Camp mines have dissolved sulfates that are isotopically heavier (more positive values of $\delta^{34}S$). This could be due in part to dissolution of hydrothermal sulfate minerals that are also isotopically heavy (Figure 24). Anhydrite is a common alteration mineral in the early potassic-style hydrothermal alteration at Butte (Meyer et al., 1968), and it's abundance in the district should increase with an increase in depth. Since it is possible that the mine shaft waters of Butte are circulating vertically (see Section 4.3), it is also possible that these waters could have leached anhydrite – a highly soluble mineral – from the altered wallrock. However, it is also possible that some of the mine shafts have dissolved sulfate that has become enriched in ^{34}S and ^{18}O during bacterial sulfate reduction (BSR). As shown by the review article of Seal (2003), sulfate-reducing bacteria selectively metabolize sulfate molecules that contain ^{32}S and ^{16}O. This produces isotopically light H_2S, and leaves the remaining sulfate in the water enriched in ^{34}S and ^{18}O.

To help sort out the relative contributions of sulfate from the 3 processes listed above, it is necessary to plot $\delta^{34}S$-sulfate vs. $\delta^{18}O$-sulfate (Fig. 24). On this diagram, sulfate that is primarily derived from pyrite oxidation should have a S-isotopic composition similar to that of Butte pyrite, whereas sulfate derived from dissolution of anhydrite should have substantially heavier values of both $\delta^{34}S$ and $\delta^{18}O$. As seen in Figure 24, many of the mine shafts and bedrock monitoring wells have intermediate isotopic compositions that can be explained by mixing of sulfate from these two sources. The Orphan Boy and Orphan Girl mine shafts, however, fall off the mixing trend line and are anomalously enriched in ^{34}S relative to ^{18}O. The most likely explanation for this is that these sulfates have undergone extensive fractionation by bacterial sulfate reduction. The dashed lines in Fig. 24 show the range in predicted trajectories for fractionation accompanying BSR, according to Seal (2003). The Orphan samples plot square in the middle of these trends, consistent with bacterial fractionation. Some of the other West Camp and Outer Camp sulfates may have been affected 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 mines.

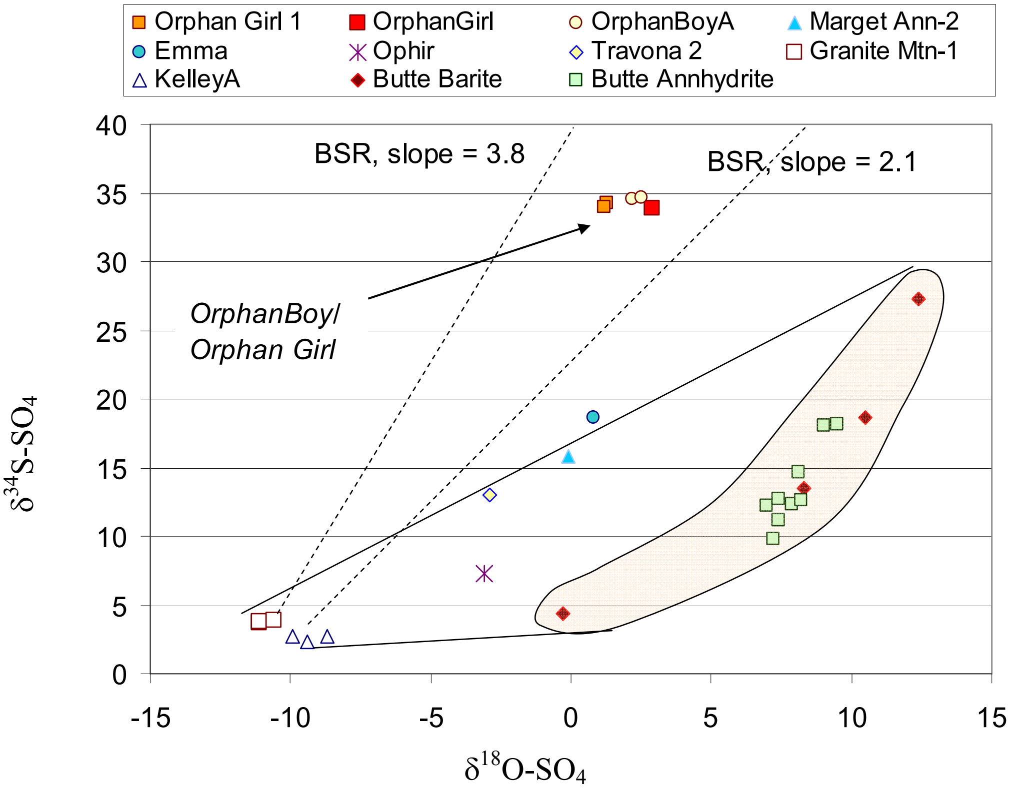


Figure 24. Stable isotopic composition of dissolved sulfate from Butte mine shafts and common sulfate containing minerals

4.2.3. Stable isotopes of dissolved inorganic carbon

This study did not generate as many new isotopic analyses of dissolved inorganic carbon (δ^{13}C-DIC) as was initially hoped. The main problem was that the East Camp mine waters produced an impure $SrCO_3$ precipitate during the isotope preparation step, which included adjustment of pH to > 8. Because the East Camp waters are all rich in dissolved Fe^{2+}, the precipitate was a mixture of $SrCO_3$ and Fe-bearing precipitates, which tended to be green immediately after filtering, but turned red after drying. Although this problem was insurmountable for the Kelley and Steward mines, samples were obtained for δ^{13}C -DIC analysis from the Granite Mountain shaft (Table 11). Additional samples were collected from the Orphan Girl and Marget Ann shafts. Samples were not collected from the West Camp mines, mainly because Roesler et al. (2007) already reported data for δ^{13}C-DIC from the West Camp waters.

The interpretation of δ^{13}C-DIC isotopes is complicated by the large isotopic fractionation that exists between the two dominant DIC species, H_2CO_3(aq) and HCO_3^-. To calculate δ^{13}C-H_2CO_3 and δ^{13}C- HCO_3^- one needs to know δ^{13}C-DIC (obtained from the laboratory) as well as the relative proportion of each species and the temperature-dependent isotopic separation between them at equilibrium. The DIC speciation was calculated for each mine shaft using the program Visual-MINTEQ, based on the measured temperature, pH, and ionic strength of each water sample. From this and a simple mass balance expression, the isotopic compositions of H_2CO_3(aq) and HCO_3^- were calculated using isotope fractionation factors given in Clark and Fritz (1997). The isotopic compositions of CO_2(g) that would be in equilibrium with each water were also computed. These results are summarized in the final 3 columns of Table 11. Also shown are C-isotope data collected by Roesler et al. (2007) from the West Camp extraction well (WCEW).

Table 11 Calculated speciation and isotopic composition of inorganic carbon for each shaft.

					isotopic composition ($\delta^{13}C$, ‰)			
		Temp	DIC speciation		measured	calculated		
shaft	**pH**	**°C**	**H_2CO_3**	**HCO_3^-**	**total DIC**	**HCO_3^-**	**H_2CO_3**	**CO_2,g**
Marget Ann	**7.5**	**9**	**8%**	**92%**	**-16.1**	**-15.2**	**-26.1**	**-25.0**
Orphan Girl	**6.3**	**27**	**49%**	**51%**	**-21.1**	**-16.8**	**-25.5**	**-24.5**
Granite Mtn	**5.8**	**15.5**	**77%**	**23%**	**-14.3**	**-6.5**	**-16.6**	**-15.5**
WCEW[a]	**6.8**	**12.5**	**75%**	**25%**	**-13.4**	**-10.8**	**-21.2**	**-20.1**

[a] data from Roesler et al. (2007)

As discussed in some length by Roesler et al. (2007), the C-isotopic composition of the West Camp mine water is consistent with isotopic equilibration between DIC and Butte rhodochrosite ($MnCO_3$), the latter having an average $\delta^{13}C$ value of approximately -7.2 ‰ (Garlick and Epstein, 1966). Rhodochrosite was extremely abundant in the West Camp veins of Butte, so it stands to reason that it would exert a major influence in the West Camp flooded mine workings. A similar analysis for the results from the Granite Mountain mine suggests that its waters are close to equilibrium with calcite, based on published data for this mineral from several East Camp mine shafts given by Garlick and Epstein (1966). In contrast, the Marget Ann and Orphan Girl mine shafts have DIC that is isotopically lighter than would be expected from equilibration with either Butte rhodochrosite or Butte calcite. The most likely explanation for the lower $\delta^{13}C$ values is input of DIC from biogenic reactions, such as bacterial sulfate reduction. Biogenic DIC typically has $\delta^{13}C$ in the range -20 to -30 ‰ (Clark and Fritz, 1997). Following this line of reasoning, it is significant that the Orphan Girl shaft has the lightest value of $\delta^{13}C$, as this mine also has the highest H_2S concentrations and largest degree of isotopic fractionation of

δ^{18}O-sulfate and δ^{34}S-sulfate of any of the waters in this study. Thus, the results from the various isotopic systems are in independent agreement, and indicate that the Orphan Boy/Girl water has been significantly modified by biological reactions, more so than the other mine waters of Butte.

4.3. Vertical convection of mine shaft waters

The lack of any substantial vertical gradients in chemistry of the Butte mine shaft waters was somewhat surprising, especially considering the very large gradients in chemistry that typically exist in the top 300' of the Berkeley pit lake (e.g., see Pellicori et al., 2005). One possible explanation for the lack of vertical gradients is that the shaft waters are continuously circulating in a vertical direction. Direct evidence of vertical circulation in one of the Butte shafts was noted via a submersible movie camera by MBMG hydrogeologists. When the movie camera was held stationary, suspended particles in the water column were clearly shown to be moving upwards through the shaft at a fairly rapid rate (Mike Kerschen, MBMG, pers. communication, 2007). Most of the Butte shafts were constructed with three vertical shaft compartments: two compartments were used for hauling ore and waste rock to the surface, and one compartment was used for people (Robin McCulloch, MBMG, pers. communication, 2007). Thus, it is very possible that water could rise towards the surface in one compartment, and sink down one of the other compartments, forming a semi-closed loop. This concept is illustrated on the right side of Figure 25.

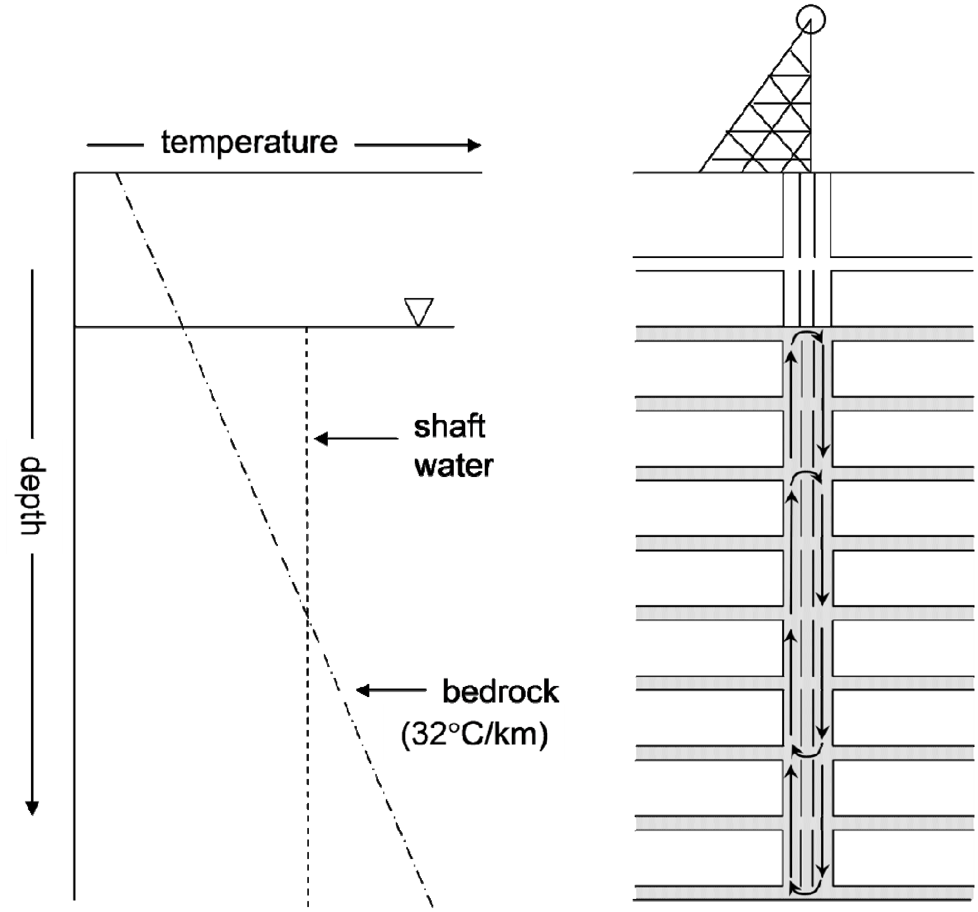


Figure 25 Schematic diagram summarizing the mine shaft convection model

A logical reason for the mine shaft convection hypothesis is afforded by a consideration of the local geothermal gradients on Butte Hill. Figure 26a shows changes in water temperature as a function of depth from several sources. The black triangles are data recorded in GWIC for deep bedrock monitoring wells located to the south and east of the Berkeley Pit lake. Because these wells are usually purged for several hours prior to collection of field parameters and water samples, the water temperatures are most likely representative of the conditions in the deep fractured bedrock aquifer. Also shown are some historical temperature data that were collected by Anaconda from two deep drill holes (DDH #1, DDH#2) (data from Ed Deal, MBMG, personal communication., 2007). 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, while it was actively being mined (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 type of geothermal gradient is typical of granite terrain in the continental US, and does not reflect any unusual geothermal inputs, e.g., from an active hydrothermal system.

Figure 26b plots average temperature of mine shaft waters from Butte collected from this study, supplemented by data in GWIC. Instead of plotting the data vs. the depth at which the water samples were collected, the data are plotted vs. the total depth of each individual mine shaft, based on MBMG records (mine elevation and depth data from Ted Duaime, MBMG, personal communication, 2007). Although the results are scattered, the data show a trend of increasing average temperature with increasing mine shaft depth, and cluster between geothermal gradients of 10 to 20°C/km. (The Kelley and Orphan Girl shafts fall off this trend, and are discussed below). The bold arrow labeled "convection" corresponds to a gradient of 16.5°C/km, which is one half of the geothermal gradient of 30-35°C/km shown in Fig. 26a. Here it was reasoned that a deep flooded mine shaft that is undergoing continuous vertical circulation would have an "evened out" temperature profile with a temperature that would be approximately the average of the corresponding rock temperatures (estimated by the 32.5°C/km geothermal gradient) at the top and bottom of the shaft (see diagram at left of Fig. 25). Indeed, with the exception of the Kelley and Orphan Girl mines, all of the mine shafts plot within 5 or 6°C of this ideal "convection" line. This is taken as strong supporting evidence in favor of the mine shaft convection hypothesis. The extent to which a particular mine water deviates from the ideal trend could reflect a number of confounding circumstances, including: 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.

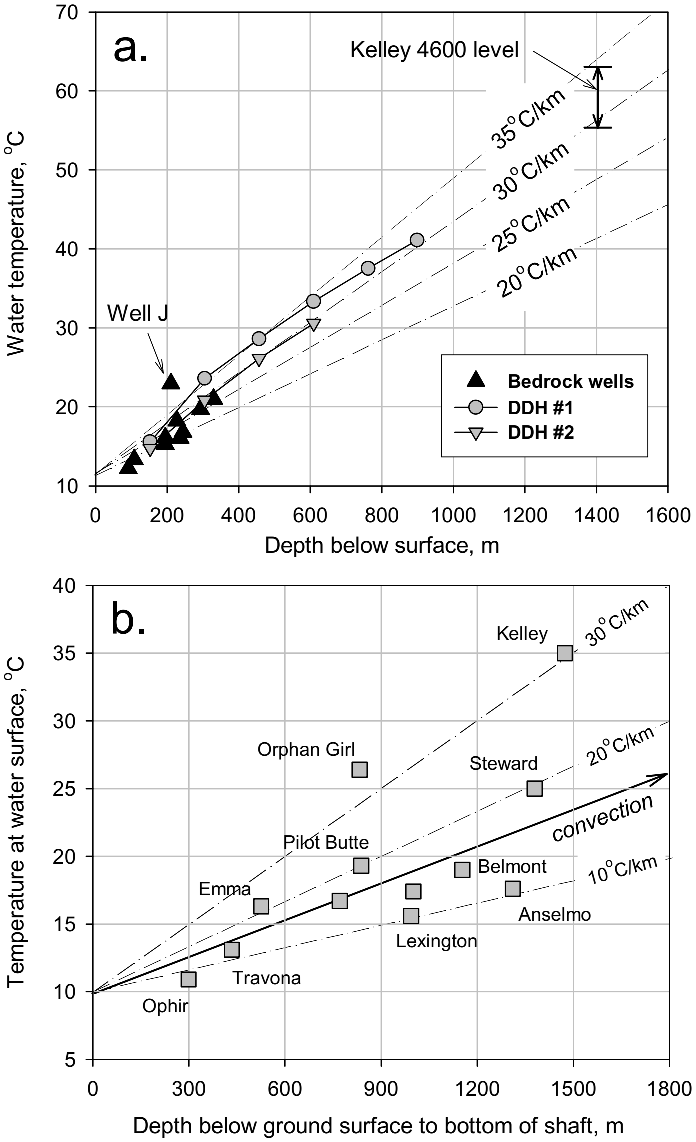


Figure 26 Temperature gradients in the Butte district.

a) Geothermal gradients based on temperatures from bedrock monitoring wells (GWIC database), temperature logs from two deep drill holes (DDH), and water temperatures measured at the 4600' level of the Kelley mine during active operation. b) Temperatures of mine shafts in the Butte district, plotted as a function of the total depth below ground surface of each shaft.

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 S-isotope data from Pellicori et al. (2005) and this study supports this hypothesis. The overall reaction can be written as follows:

$$FeS_2(s) + H_2O + 7/2O_2 \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \qquad (5)$$

Using thermodynamic data in Faure (1998), the calculated enthalpy change for reaction (5) 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 (5), 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 45.9/4.187, or ~ 11° (K or C, the units don't matter in this case). Interestingly, this amount of warming is consistent with the observed temperature of the Kelley mine shaft (Fig. 26b), after taking the total depth of the mine shaft into consideration. Although there are many assumptions and uncertainties implicit in this simple calculation, the good agreement between theory and observation lends plausibility to the hypothesis that pyrite oxidation is a major contributing factor for the warm water temperatures in the Kelley mine.

Following this train of thought, it should not be surprising that bedrock monitoring Well J has an anomalously warm temperature, given the fact that it is the only one of the bedrock wells that is strongly acidic and Fe-rich. Using similar thermodynamic calculations as above, and basing the extent of reaction progress on sulfate concentration as opposed to Fe, a temperature rise of approximately 4-5 degrees is estimated for Well J water, which is roughly similar to the magnitude of the temperature anomaly for this well (see Fig. 26a). Compared to the Kelley mine and Well J, all of the other mine shaft waters examined in this study have higher pH and lower dissolved Fe concentrations. The Steward mine is the only other flooded shaft whose temperature could be significantly impacted by pyrite oxidation. Based on data collected in this study, and using either dissolved Fe^{2+} or sulfate as the reaction progress variable, a temperature increase of only 1-2°C is estimated for the Steward mine.

Given the near-neutral pH of the Orphan Girl mine waters, it is doubtful that pyrite oxidation is the explanation for its anomalously warm temperature. A more likely hypothesis is that bacterial sulfate reduction is partly responsible. Like pyrite oxidation, bacterial sulfate reduction is exothermic, but only weakly so. For the following reaction:

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

.

the calculated ΔH is -28.5 kJ/mol, based on data in Faure (1998). For the same extent of reaction progress, sulfate reduction would produce about 50 x less heat than pyrite oxidation. It would take a very high rate of SRB activity to achieve even a 5°C warming of the mine water. Thus, although the Orphan Girl and Orphan Boy shafts have much higher HCO_3^- alkalinity and H_2S concentrations than any other mine water in Butte, the concentrations are probably too low to explain the temperature anomaly.

5. Conclusions and Recommendations

5.1. Conclusions

With the exception of the Kelley mine, there were no significant vertical gradients in temperature or specific conductivity in the flooded Butte mine shafts, to depths as great as 1400 feet below static water level (BSWL). All of the mine shafts showed increases in Eh towards the surface of the water column, consistent with oxidation by the overlying air in the shaft. Most shafts also showed gradients in pH in the top 100 feet of the water column. In some cases (e.g., Kelley mine) the pH increased towards the water surface, and in other cases (e.g., Travona, Marget Ann) the pH decreased. The former situation can be explained by loss of CO_2 as water pressure decreases, whereas the latter is explained by oxidation of H_2S near the air/water interface.

Vertical gradients in chemical composition were negligible for all of the mine shafts, with the exception of a single deep sample from the Kelley mine. This deep sample also had significantly higher temperature and SC then overlying waters, indicating the existence of vertical stratification in deeper parts of the Kelley mine shaft. The dominant valence state of dissolved Fe was Fe(II) for all of the waters examined in this study. Dissolved arsenic existed as both As(III) and As(V) for water from the Kelley and Steward mines, but was predominantly As(III) for the other mine shafts sampled.

All of the mines from the West and Outer Camps had elevated concentrations of dissolved sulfide. Concentrations of H_2S were particularly high in the Orphan Girl and Orphan Boy mines. In contrast, no H_2S has yet been detected in any of the East Camp mine shafts. This is consistent with the measured Eh values, which indicate conditions that are too oxidized to permit bacterial sulfate reduction in the East Camp shafts.

Thermodynamic calculations indicate that many of the East Camp mine shaft waters are near equilibrium with the minerals siderite ($FeCO_3$), rhodochrosite ($MnCO_3$), and smithsonite ($ZnCO_3$). West and Outer Camp mine waters are close to equilibrium with calcite ($CaCO_3$), rhodochrosite, and mackinawite (poorly crystalline FeS), and are supersaturated with sphalerite (ZnS) and pyrite (FeS_2). The very low concentrations of dissolved copper in the Butte mine waters – particularly those of the East Camp mine shafts –may be due to precipitation of chalcocite (Cu_2S) on pyrite, or elemental Cu onto scrap iron left behind in the mine workings. The former reaction is the same process that leads to supergene enrichment during weathering of porphyry Cu ore deposits, whereas the latter reaction is familiar to metallurgists as the "cementation" process for recovering Cu^{2+} from acid mine waters.

With the exception of the Marget Ann mine, the isotopic compositions of waters from the Butte mine shafts are similar to each other, and are consistent with local recharge from non-evaporated meteoric water. Water in the Marget Ann shaft is isotopically lighter than the other shafts, and this is explained by the fact that the Marget Ann is at the extreme north end of the district, and is probably recharged by precipitation that fell at a higher elevation.

The isotopic composition of H_2S in the West Camp and Outer Camp mine shafts is consistent with bacterial sulfate reduction (BSR). Based on stable isotope mass balance, the extent of BSR was much greater in the Orphan Boy/Orphan Girl shafts. The S and O isotopic composition of dissolved sulfate in the mine shafts is explained by three processes: 1) oxidation of pyrite and other primary metal sulfide minerals; 2) dissolution of hydrothermal sulfate minerals, such as gypsum and anhydrite; and 3) isotope fractionation during bacterial sulfate reduction. In general, sulfate from East Camp mine shafts is dominated by process #1, whereas processes #2 and #3 are more important for the West Camp and Outer Camp mines.

The isotopic composition of dissolved inorganic carbon (DIC) in the Granite Mountain and Marget Ann mines is similar to values reported by Roesler et al. (2007) for the West Camp mine workings, and is consistent with isotopic equilibration with hydrothermal rhodochrosite. DIC from the Orphan Girl mine is isotopically lighter, which may reflect a greater contribution of DIC from biogenic sources. This hypothesis is consistent with the higher rate of BSR in the Outer Camp compared to the other mine shafts of Butte.

A vertical circulation model is proposed for the Butte mine shafts. Because the Butte mines had three-compartment shafts, water can rise in one compartment and then sink in another compartment, forming a closed convective loop. This hypothesis explains: 1) the lack of temperature and chemistry gradients with depth for the majority of the mines; and 2) the fact that there is a correlation between shaft water temperature and the total depth of each mine. The vertical circulation of water is most likely driven by the local geothermal gradient in Butte (30-35°C/km), which is typical of granitic continental crust. The anomalously warm water temperatures of the Kelley mine, as well as bedrock monitoring Well J, are most likely due – at least in part – to pyrite oxidation, a strongly exothermic reaction. The warm water in the Orphan Boy/Orphan Girl mines is more difficult to explain, although bacterial sulfate reduction may be a contributing factor.

5.2. Recommendations for Future Work

Based on the results of this study, a number of recommendations are given for future work in the Butte mining district, and elsewhere.

Because of the aforementioned changes in pH and Eh in the top 100 feet of the water column in several of the Butte mine shafts, it is recommended that the MBMG continue to collect their shaft samples from a depth of 100 feet BSWL or greater. This will allow better comparability of results for long-term trend analysis. Also, although this study showed that vertical gradients in mine shaft water chemistry are for the most part negligible below a depth of ~ 100 feet BSWL, it is recommended that the MBMG continue to periodically collect samples at different depths (e.g., 100 ft and 1000 ft) to verify that no stratification exists. This is particularly true for the Kelley Mine, which was the only shaft in this study that showed any appreciable changes in temperature or water chemistry with depth.

The convective loop model proposed in this study for vertical mixing of water in the multi-compartment mine shafts could possibly be tested by injecting a conservative tracer into the top or bottom of the shaft, and then observing dispersion of this tracer with time. Also, given the very warm mine water temperatures in several of the mine shafts investigated (e.g., Orphan Girl, Steward, Kelley), it seems appropriate to investigate the possibility of heat recovery from these systems.

Finally, this study has demonstrated that deep mine shaft sampling is difficult, time-consuming, and frustrating. It is also expensive, given the high probability that equipment will be lost to obstructions in the shafts. This was definitely the case in the present study. The major problems encountered on this project trying to retrieve deep mine shaft samples could have been avoided if an effort had been made *prior to mine flooding* to permanently install tubing or pipe in the shafts that could later be used to collect water samples at different depths. Whereas this obviously was not possible in the present study, the opportunity to do this may exist at other underground mine sites that are approaching closure.

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Appendix A

6. Quality Assurance/Quality Control

This project was conducted to more fully understand the processes that control the geochemistry of the West Camp mine waters. The programmatic and regulatory setting in which the project quality assurance (QA) was conducted was Category IV. The project-specific quality assurance project plan (QAPP) complied with the requirements of a Category IV project plan. Category IV projects are those producing results for the purpose of assessing suppositions.

6.1. Quality Assurance Project Plan Objective

The QA/quality control (QC) objectives outlined for the project were specified to generate acceptable Category IV data. The QAPP is presented in detail elsewhere (MWTP-225). Briefly, the QAPP was designed to demonstrate:

- the intended measurements are appropriate for achieving project objectives;
- QC procedures are sufficient for obtaining data of known and adequate quality; and
- data are defensible if challenged technically.

6.2. Sampling Procedures

Collection of field samples and field measurements (pH, temperature, specific conductance, ORP, dissolved oxygen, alkalinity, H_2S) of water from the WCEW followed procedures outlined in the QAPP (MWTP)-225), and will not be elaborated here. Further details are given in the Methods section of this final report. A chain-of-custody sheet accompanied each set of samples shipped to the University of Nevada-Reno and the University of Waterloo for stable isotope analysis. All other laboratory procedures were conducted by graduate student Dean Snyder, under the supervision of PI Chris Gammons.

6.3. Analytical Procedures

6.3.1. Field Parameters

Table 12 summarizes relevant QC criteria and outcomes for collection of field and laboratory data in this study.

Table 12 Summary of QC criteria and outcomes.

Location	Matrix	Measurement	Sample Frequency	Acceptable QC Criteria	Criteria Met?
Mine Shafts	Water	Temp, pH, ORP, DO, SC	1 replicate per event	na	yes
Travona, Orphan Girl	Water	Alkalinity	1 replicate per event	±10% RPD	yes
Marget Ann	Water	Alkalinity	duplicate	±10% RPD	yes
Emma, Ophir, Orphan Boy, Anselmo, Steward, Kelley, Granite Mountain	Water	Alkalinity	1 per event	±10% RPD	Alkalinity varied ≤ 10% between depths in all shafts where a vertical profile was measured.
Orphan Boy, Orphan Girl, Emma, Travona, Ophir	Water	H_2S	1 per event, duplicate	±20% RPD	yes
Marget Ann	Water	H_2S	1 per event	n/a	yes
Steward, Kelley, Anselmo,Granite Mountain	Water	H_2S	1 per event	n/a	yes
All shafts	Water	Major/trace metals	Replicates (1 per event) Field Blank (1 per event) Laboratory splits (1 per 8 events)	Replicate (±20% RPD), Field Blank (< 2 x MDL), Splits (±40% RPD)	Yes
Marget Ann, Travona, Orphan Girl	Water	Phosphate	Replicate (1 per event) Field Blank (1 per event)	Replicate ±30% RPD Field Blank (< 2 x PQL)	Yes
All shafts	Water	Fe^{+3}/Fe^{+2} speciation	Replicate (1 per event) Field Blank (1 per event)	Replicate ±20% RPD Field Blank (< 2 x PQL)	No. Travona not speciated.
All shafts	Water	As^{+5}/As^{+3} speciation	Replicate (1 per event) Field Blank (1 per event)	Replicate ±30% RPD Field Blank (< 2 x PQL)	No. Orphan Girl and Granite Mountain not speciated
All shafts	Water	$\delta^{18}O$, δD of water	Replicates (2 per 10 events)	Replicate ±0.2‰ (O) ±2.0‰ (H)	No. Marget Ann had a replicate with difference of ±0.3‰ (O)
All shafts	Water	$\delta^{34}S$ and $\delta^{18}O$ of dissolved sulfate and sulfide	Replicates (2 per 10 events)	Replicate ±0.8 ‰ (O) ±0.4 ‰ (S)	No. Steward and Anselmo not analyzed.

6.3.2. ICP-AES analysis

A number of QA/QC checks were performed for the ICP-AES data collected in this study. These can be divided into field procedures:

- field blanks
- field duplicates
- interlaboratory splits

and laboratory procedures:

- lab blanks
- lab duplicates
- lab spikes
- instrument performance checks (IPC).

6.3.2.1. Field Blanks

Two ICP-AES analytical sessions were performed at the Murdock laboratory by graduate student Dean Snyder, on 5/26/06 and 9/27/06. During the May session, three field blanks were included in the sample list: one of these was a filtered-acidified (HNO_3) sample, and the other two were blanks that were carried through the same preparation steps used in the field for As(TOT) and As(V) speciation analysis. During the September session, two field blanks were included. One was a sample of laboratory deionized water that was allowed to soak inside the Kemmerer point sampler for several hours. This water was then filtered and acidified with HNO_3. The second sample was a conventional filtered-acidified (HNO_3) field blank. Table 13 summarizes instances where the concentration of a particular analyte in each blank sample exceeded its respective practical quantification limit (PQL). The two filtered-acidified (HNO_3) blanks had traces of S and K. The former were at concentrations far below those of the environmental samples, whereas the levels of K in the blanks indicate significant contamination from unknown sources. However, uncertainty in the accuracy of the K results has no bearing on any of the conclusions of this report. One of the filtered-acidified blanks had slightly elevated Si, which is not surprising, as Si is a common trace contaminant in ICP work (due to the nebulizer glassware). The "Kemmerer blank" was quite clean for most elements, with the exception of trace levels of Mn and Zn. The Mn contamination (0.003 mg/L over the PQL) is not a concern, as all of the environmental samples in this study had concentrations > 5 mg/L of Mn, i.e., much greater than the levels in the blank. The Zn contamination is a bigger concern, especially for samples that were collected from the West Camp and Outer Camp wells, all of which had very low Zn concentrations near the PQL. The presence of ppb levels of Zn in the Kemmerer blank lends a high degree of uncertainty to the Zn results for these mine shafts. On the other hand, Zn concentrations in the East Camp shafts were much higher, and should not be effected by this problem. As well, none of the conclusions in this study are compromised by the uncertainty in low-level Zn concentrations reported from the West Camp and Outer Camp mine waters.

Table 13 Summary of QA/QC results for field blank samples submitted for ICP-AES analysis

Lab ID	Explanation	Elements exceeding PQL (result/PQL, mg/L)
ICP-AES analyses of 5/26/2006		
Sny 02	Filtered-acidified (HNO_3) blank	K (1.3/0.8), S (0.9/0.1), Si (0.06/0.05)
Sny 03	As(TOT) blank	Ni (0.08/0.01), S (1.5/0.1), Si (0.07/0.05)
Sny 30	As(V) blank	B, Ba, Ca, Fe, K, Mg, Mn, Na, Ni, S, Si, Zn
ICP-AES analyses of 9/27/2006		
Sny 01	Kemmerer blank	Mn (0.007/0.004), Zn (0.006/0.004)
Sny 11	Filtered-acidified (HNO_3) blank	K (2.2/0.8), S (0.2/0.1)

Of the two As speciation blanks, the As(TOT) sample was clean, whereas the As(V) blank was very dirty. This is not surprising, because large amounts of reagent grade Na-borohydride were added to the As(V) samples during the As speciation preparation step. The only critical element that was quantified from the As(TOT) and As(V) samples was arsenic itself, and both blanks had no detectable As in them. Thus, the presence of impurities for other elements has no bearing on the results of this study.

6.3.2.2. Field Duplicates

A comparison of the ICP-AES results for 5 field duplicate samples collected in this study is given in Table 14. Overall, the agreement between results for duplicate samples was quite good. The high RPD values for Sn and Zn are largely due to these analytes being close to the detection limit. In the case of Zn, the possibility also exists of trace contamination from the Kemmerer sampler (see above). The Travona 2 and Travona 3 duplicate samples gave poor RPD for both K and Fe. However, no major problems were noted for the other duplicate pairs, including another pair collected from deeper in the Travona shaft. Overall, the results of field duplicate samples indicate good to very good reproducibility for the ICP-AES results of this study.

6.3.2.1. Inter-laboratory Comparisons

Table 15 gives results of inter-laboratory comparisons for 6 environmental samples that were collected at the same time and analyzed by ICP-AES at both the Murdock Laboratory (results reported in this study) and the MBMG laboratory. Overall, the results of inter-laboratory comparisons were quite good. The only analyte with an average RPD values > 25% was Se. Error in the Se analyses is not important, as no conclusions in this study are based on the Se results. The split sample from the Kelley mine had poor RPD for several analytes, including S (converted to SO_4 in Table 15) and Zn. The reason for this disagreement is not known, but is not really surprising considering that the Kelley mine water has the highest solute concentrations of all of the waters sampled, and therefore presented a challenge in terms of quantification by ICP-AES.

Table 14 Comparison of ICP-AES results for field duplicate samples.

Sample Name	Al	As	B	Ba	Be	Ca	Cd	Co	Cu	Fe	K	Li
Orphan Girl 2	<0.2	<0.025	0.01	0.088	<0.0005	231	<0.004	<0.005	<0.01	0.2	8	0.158
Orphan Girl 6-D	<0.2	<0.025	<0.01	0.084	<0.0005	219	<0.004	<0.005	<0.01	<0.1	8	0.149
RPD				4.7%		5.3%					0.0%	5.9%
Marget Ann 3	<0.2	<0.025	<0.01	0.025	<0.0005	139	<0.004	<0.005	<0.01	<0.1	6	0.013
Marget Ann 3-D	<0.2	<0.025	<0.01	0.025	<0.0005	140	<0.004	<0.005	<0.01	<0.1	7	0.014
RPD				0.0%		0.7%					15.4%	7.4%
Travona 2	<0.2	0.08	0.12	0.027	<0.0005	170	<0.004	<0.005	<0.01	1.9	8	0.031
Travona 3-D	<0.2	0.09	0.13	0.028	<0.0005	175	<0.004	<0.005	<0.01	1.2	5	0.032
RPD		11.8%	8.0%	3.6%		2.9%				45.2%	46.2%	3.2%
Travona 5	<0.2	0.09	0.12	0.026	<0.0005	173	<0.004	<0.005	<0.01	1.3	10	0.03
Travona 6-D	<0.2	0.09	0.12	0.028	<0.0005	174	<0.004	<0.005	<0.01	1.2	8	0.029
RPD		0.0%	0.0%	7.4%		0.6%				8.0%	22.2%	3.4%
Granite Mtn 1	0.6	0.03	<0.01	0.011	0.0008	498	0.024	0.042	1.3	17	19	0.057
Granite Mtn 1-D	0.6	<0.025	<0.01	0.01	0.0008	485	0.023	0.041	1.2	15	19	0.058
RPD	0.0%			9.5%	0.0%	2.6%	4.3%	2.4%	8.0%	12.5%	0.0%	1.7%
Average RPD	0.0%	5.9%	4.0%	5.0%	0.0%	2.4%	4.3%	2.4%	8.0%	21.9%	16.8%	4.3%

All data are in mg/L. Results are flagged if RPD > 25%.

Table 14 (Continued)

Sample Name	Mg	Mn	Na	Ni	P	S	Se	Si	Sn	Sr	Zn
Orphan Girl 2	63	5.13	114	<0.01	0.18	191	<0.08	11.9	0.02	6.08	0.008
Orphan Girl 6-D	58	5.01	108	<0.01	0.16	212	<0.08	11.3	0.03	5.77	0.009
RPD	8.3%	2.4%	5.4%		11.8%	10.4%		5.2%	40.0%	5.2%	11.8%
Marget Ann 3	24	1.76	12	<0.01	<0.06	89	<0.08	3.9	<0.02	2.72	<0.004
Marget Ann 3-D	24	1.77	13	<0.01	<0.06	89	<0.08	3.9	<0.02	2.74	0.005
RPD	0.0%	0.6%	8.0%			0.0%		0.0%		0.7%	
Travona 2	48	5.77	33	<0.01	<0.06	127	<0.08	8.6	<0.02	1.25	0.22
Travona 3-D	51	5.91	34	<0.01	<0.06	130	<0.08	9	<0.02	1.32	0.017
RPD	6.1%	2.4%	3.0%			2.3%		4.5%		5.4%	171.3%
Travona 5	48	5.86	35	<0.01	<0.06	130	<0.08	9.3	<0.02	1.31	0.028
Travona 6-D	49	5.92	35	<0.01	<0.06	132	<0.08	9.1	<0.02	1.31	0.01
RPD	2.1%	1.0%	0.0%			1.5%		2.2%		0.0%	94.7%
Granite Mtn 1	163	42.75	28	0.09	<0.06	681	0.26	9.7	0.03	5.04	18.1
Granite Mtn 1-D	157	41.79	27	0.09	<0.06	668	0.25	9.4	0.02	4.85	17.8
RPD	3.8%	2.3%	3.6%	0.0%		1.9%	3.9%	3.1%	40.0%	3.8%	1.7%
Average RPD	4.0%	1.7%	4.0%	0.0%	11.8%	3.2%	3.9%	3.0%	40.0%	3.1%	69.9%

Table 15 Inter-laboratory comparison of ICP-AES samples.

Sample	Lab	Al	As	B	Ba	Ca	Cd	Co	Cr	Cu	Fe
Ophir	Murdock	<0.04	<0.05	<0.01	0.012	88	<0.005	<0.005	<0.05	<0.01	3.9
4/19/2006	MBMG	<0.01	0.011	0.066	0.012	88.6	<0.001	<0.002	<0.002	<0.002	3.8
	RPD				0.0%	0.7%					2.6%
Emma	Murdock	<0.04	<0.05	<0.01	0.031	181	<0.005	<0.005	<0.05	<0.01	1.8
4/19/2006	MBMG	<0.01	0.024	0.11	0.033	189	<0.001	<0.002	<0.002	<0.002	1.78
	RPD				5.0%	4.3%					1.1%
O Boy	Murdock	<0.04	<0.05	<0.01	0.074	210	<0.005	<0.005	<0.05	<0.01	0.2
4/19/2006	MBMG	<0.01	0.005	0.04	0.083	223	<0.001	<0.002	0.008	<0.002	0.22
	RPD				11.5%	6.0%					9.5%
Anselmo	Murdock	<0.04	<0.05	<0.01	0.016	308	0.01	0.012	<0.05	<0.01	30
4/20/2006	MBMG	<0.01	0.026	0.06	0.019	341	0.011	0.012	<0.002	0.004	30.5
100' bswl	RPD				17.1%	10.2%	9.5%	0.0%			1.7%
Steward	Murdock	0.6	3	<0.01	0.005	448	<0.005	0.055	<0.05	<0.01	237
4/21/2006	MBMG	0.633	3.45	<0.15	0.012	509	<0.005	0.065	<0.10	0.028	256
100' bswl	RPD	5.4%	14.0%		82.4%	12.7%		16.7%			7.7%
Kelley	Murdock	30.7	10.7	<0.01	<.0030	421	<0.005	0.59	<0.05	<0.01	1500
4/21/2006	MBMG	32	12	<0.3	<0.02	491	0.02	0.733	<0.02	0.044	1640
100' bswl	RPD	4.1%	11.5%			15.4%		21.6%			8.9%
average	RPD	4.7%	12.7%	n.a.	23.2%	8.2%	9.5%	12.8%	n.a.	n.a.	5.3%

All data in mg/L. Data are flagged if the RPD is > 25%.

Table 15 (Continued)

Sample	Lab	K	Li	Mg	Mn	Mo	Na	Ni	P	Pb	SO_4[1]
Ophir	Murdock	6	0.013	25	7.18	<0.01	19	<0.01	<0.05	<0.04	168
4/19/2006	MBMG	4.2	0.012	24.9	6.6	<.01	21.5	<.002	<.25	<0.002	164
	RPD	35.3%	8.0%	0.4%	8.4%		12.3%				2.4%
Emma	Murdock	9	0.042	54	9.7	<0.01	35	<0.01	0.06	<0.04	390
4/19/2006	MBMG	6.93	0.044	55.7	9.53	<.01	38.9	<.002	<0.1	<0.002	402
	RPD	26.0%	4.7%	3.1%	1.8%		10.6%				3.0%
O Boy	Murdock	10	0.152	56	4.66	<0.01	100	<0.01	0.15	<0.04	n.a.
4/19/2006	MBMG	8.98	0.17	59.4	4.61	<.01	118	<.002	0.15	<0.002	260
	RPD	10.7%	11.2%	5.9%	1.1%		16.5%		0.0%		
Anselmo	Murdock	13	0.035	88	18.53	<0.01	38	0.02	<0.05	<0.04	1023
4/20/2006	MBMG	13.3	0.039	93.9	19.6	<0.01	42.9	0.014	<0.05	<0.002	1112
100' bswl	RPD	2.3%	10.8%	6.5%	5.6%		12.1%	35.3%			8.3%
Steward	Murdock	35	0.039	136	25.84	0.019	42	0.04	0.08	<0.04	1977
4/21/2006	MBMG	34.9	0.0435	159	30.8	<0.05	48.2	0.034	<0.25	<0.01	2388
100' bswl	RPD	0.3%	10.9%	15.6%	17.5%		13.7%	16.2%			18.8%
Kelley	Murdock	58	0.242	298	143	0.075	73	0.39	0.1	0.19	5430
4/21/2006	MBMG	66.4	0.288	394	172	<.1	85.5	0.48	<0.5	<0.02	7552
100' bswl	RPD	13.5%	17.4%	27.7%	18.4%		15.8%	20.7%			32.7%
average	RPD	14.7%	10.5%	9.9%	8.8%	n.a.	13.5%	24.1%	0.0%	n.a.	11.7%

[1] ICP-AES data for S from Murdock were converted to SO_4, assuming all S = SO_4. Data for SO_4 from MBMG were collected by ion chromatography.

Table 15 (Continued)

Sample	Lab	Sb	Se	Si	Sr	V	Zn	HCO_3^- [2]
Ophir	Murdock	<0.08	<0.08	6.4	0.39	<0.02	0.003	231
4/19/2006	MBMG	<0.002	<.001	5.9	0.475	<0.005	0.004	222
	RPD			8.3%	19.7%		28.6%	4.1%
Emma	Murdock	<0.08	<0.08	9.4	1.48	<0.02	0.154	379
4/19/2006	MBMG	<0.002	<.001	8.9	1.7	<0.005	0.139	395
	RPD			5.7%	13.8%		10.2%	4.0%
O Boy	Murdock	<0.08	<0.08	11.6	5.39	<0.02	0.012	817
4/19/2006	MBMG	<0.002	0.009	11.1	5.61	0.005	0.015	845
	RPD			4.2%	4.0%		22.2%	3.3%
Anselmo	Murdock	<0.08	0.11	10.7	3.27	<0.02	14.6	297
4/20/2006	MBMG	<0.002	0.002	10.6	3.86	<0.005	16.1	286
100' bswl	RPD		192.9%	1.3%	16.5%		9.8%	3.8%
Steward	Murdock	<0.08	0.2	21.9	1.93	<0.02	40.3	292
4/21/2006	MBMG	<0.10	0.006	21.6	2.5	<0.025	47.3	n.a.
100' bswl	RPD		188.3%	1.4%	25.7%		16.0%	
Kelley	Murdock	0.09	0.48	38	0.6	0.07	191	16
4/21/2006	MBMG	<0.02	0.02	35.9	0.913	<.05	303	n.a.
100' bswl	RPD		184.0%	5.7%	41.4%		45.3%	
average	RPD		188.4%	4.4%	20.2%		22.0%	3.8%

[2] HCO3- was calculated based on alkalinity, pH and temperature.

6.3.2.5. Laboratory QC checks

Table 16 summarizes QC criteria and results for the ICP-AES analyses at the Murdock Laboratory. Overall the QC results were good, with a few exceptions as noted in the last column. Problems with LDUPs (lab duplicates) were attributed to the fact that the samples that were used for two of the LDUPs had concentrations of several metals of importance (e.g., Zn, Cu) that were near their practical quantification limits. Problems with the LSPIKE (lab spike) for S were probably due to the large interference between dissolved H_2S and S, as discussed in Section 2.2.3.

Table 16 ICP-AES laboratory QA/QC Summary

QA/QC Check	Frequency	Frequency Met?	Criteria	Results
ICV(IPC4)	Initially	yes	+-10%	-8.9% to 5.8% +14.1%(B)
ICB(LBLANK)	Initially	yes	<2 * PQL	All<PQL except 1.17*PQL (K)
CCV	Every 10 samples	yes	+-10%	All -7.9% to 9.9% except -48.3% to -2.7% (B) -18% to 18.6%(K) -18.2% to 6.8%(S)
CCB(LRB)	Every 10 samples	yes	<2 * PQL	All<PQL except >2 * PQL (B) two sets >2 * PQL (Ca) one set >2 * PQL (S) one set
LRB	Initially	yes	<2 * PQL	All<PQL except <2 * PQL (K)
LDUP	Every 10 samples	yes	RPD+-10%	-36% to 24% (K) LDUP's with large ranges in differences (-34% to 348% Zn, P); (-21.9% to 26.6% Cu) are a result of duplicating samples that are near the PQL.
LSPIKE	Every 10 samples	no	75% to 125% recovery of spike	All <+- 25% except 2 of 6 are -90% , -32.2% (S), 1 of 6 is -48.5% (Na)

6.3.3 Stable Isotope Analyses

A number of QA/QC procedures were followed and validated with regards to stable isotope analysis, including:

- inter-laboratory comparisons
- field duplicate standards
- laboratory replicate analyses
- bracketing the analysis of unknowns with laboratory QA samples

The results of inter-laboratory comparisons of $\delta^{18}O$-H_2O and δD-H_2O for two water samples collected in this study are summarized in Table 17. One set was sent to the Univ. of Nevada-Reno (the lab that we used throughout the project, as well as previous MWTP projects), and the other was sent to the Univ. of Waterloo, Ontario, which is one of the largest commercial environmental isotope labs in the world. The analytical results agree very well, and are within the quoted analytical uncertainties. Although split samples were not sent for stable isotope analysis of sulfate or DIC, very good inter-laboratory agreement was shown between the UNR and Waterloo labs for $\delta^{34}S$-sulfate and $\delta^{13}C$-DIC during Project 32 (Roesler, 2005).

Table 17 Inter-laboratory comparison for stable isotope analyses.

	UNR lab		Waterloo lab	
Sample ID	$\delta^{18}O-H_2O$	$\delta D-H_2O$	$\delta^{18}O-H_2O$	$\delta D-H_2O$
Marget Ann 5	-18.6 ± 0.1	-147 ± 1	-18.5 ± 0.1	-145 ± 1
Granite Mountain 3	-17.3 ± 0.1	-136 ± 1	-17.2 ± 0.1	-137 ± 1

All results in ‰.

Two field duplicate samples were submitted to the UNR lab during the course of the project. Results are summarized in Table 18. The agreement between the duplicate samples was very good, being for the most part well within the limits of the laboratory error. The only exception was $\delta^{18}O-H_2O$ for the Marget Ann duplicates, where the disagreement was outside the laboratory error, but still well within the acceptable error for duplicate samples as specified in the QAPP for this project.

Table 18 Results for field duplicates of stable isotope analyses.

Sample ID	$\delta^{34}S-H_2S$	$\delta^{34}S-SO_4$	$\delta\ ^{18}O-SO_4$	$\delta^{18}O-H_2O$	$\delta D-H_2O$
Marg Ann 5	n.a.	n.a.	n.a.	-18.6 ± 0.1	-147 ± 0.1
Marg Ann 5D	n.a.	n.a.	n.a.	-18.3 ± 0.1	-147 ± 0.1
Orphan Boy	+3.7 ± 0.2	+34.6 ± 0.2	+2.2 ± 0.4	n.a.	n.a.
Orph. Boy D	+3.6 ± 0.2	+34.7 ± 0.2	+2.5 ± 0.4	n.a.	n.a.

All results in ‰.

Table 19 summarizes results of laboratory replicate samples for stable isotope analyses conducted at UNR. All of the sample replicates agreed within the quoted laboratory precisions, which are ± 0.1 ‰ for $\delta^{18}O-H_2O$, ± 1 ‰ for $\delta^{18}D-H_2O$, ± 0.2 ‰ for $\delta^{34}S-H_2S$ and $\delta^{34}S-SO_4$, and ± 0.4 ‰ for $\delta^{13}D$-DIC.

Table 19 Results for laboratory replicates of stable isotope analyses.

Water-H		Water-O		Sulfate-O		Sulfate-S		DIC-C	
11-13-06	δD	10-5-06	$\delta^{18}O$	1-3-07	$\delta^{18}O$	12-13-06	$\delta^{34}S$	10-13-06	$\Delta^{13}C$
MA5-1	-146	GM1-1	-17.2	K-A-1	-9.6	K-A-1	3.8	MT-1	-21.2
MA5-2	-147	GM1-2	-17.2	K-A-2	-10.0	K-A-2	3.8	MT-2	-21.3
MA5-3	-146	GM1-3	-17.2	K-A-3	-9.9	OG-1	2.7	GM-1	-14.7
OG2-1	-139	MA2-1	-18.6	EM-1	1.0	OG-2	2.7	GM-2	-14.5
OG2-2	-139	MA2-2	-18.6	EM-2	0.7				
OP-1	-134	S-A-1	-17.5	EM-3	0.5				
OP-2	-134	S-A-2	-17.4						
OP-3	-134	K-A-1	-17.5						
		K-A-2	-17.6						

All results in ‰.

Table 20 summarizes results of laboratory analyses of stable isotope standards. Each of the standards used (EVAP, INS5, NV2A, NBS127, GSL, MIC, ANU) has an optimal value that has been determined by inter-laboratory analysis by the Univ-Nevada Reno and other stable isotope labs throughout the world. The values for “R1, R2, R3…” are replicate analyses of these standards. As shown in the Table, all of the standards came back with results that were well within the quoted uncertainty in their respective optimal values.

Table 20 Results of laboratory analyses of stable isotope standards.

Isotopic standard	Optimal value	Measured values							
		R1	R2	R3	R4	R5	R6	R7	R8
$\delta D\text{-}H_2O$, ‰ (analyzed on 11-13-06)									
EVAP	15 ± 2	15	15	15	15	15	15	15	14
INS5	-395 ± 2	-395	-395	-395	-395	-395			
$\delta^{18}O\text{-}H_2O$, ‰ (analyzed on 10-5-06)									
EVAP	16.0 ± 0.2	15.9	15.9						
INS5	-50.5 ± 0.2	-50.6	-50.6						
NV2A	-15.2 ± 0.2	-15.1	-15.2	-15.1	-15.2	-15.1	-15.1	-15.1	
$\delta^{18}O\text{-}SO_4$, ‰ (analyzed on 1-3-07)									
NBS127	9.4 ± 0.8	9.1	9.3	9.3	9.8	9.0	9.5	9.6	9.6
$\delta^{34}S\text{-}SO_4$ and $\delta^{34}S\text{-}H_2S$, ‰ (analyzed on 12-13-06)									
GSL	-2.9 ± 0.4	-2.8	-2.9	-3.0					
MIC	17.9 ± 0.4	17.9	17.8	18.0					
$\delta^{13}C\text{-}DIC$, ‰ (analyzed on 10-13-06)									
ANU	10.5 ± 0.2	-10.4	-10.5	-10.5	-10.5	-10.4	-10.4	-10.6	

Appendix B: ICP-AES Results

Table 21 ICP-AES results.

Sample Name	feet bswl	Al	As	B	Ba	Be	Ca	Cd	Co	Cr	Cu	Fe
Outer Camp Shafts												
Orphan Girl 1	5	<0.2	<0.025	0.02	0.086	<0.0005	229	<0.004	<0.005	<0.01	<0.01	0.2
Orphan Girl 4	30	<0.2	<0.025	0.01	0.085	<0.0005	224	<0.004	<0.005	<0.01	<0.01	0.1
Orphan Girl 5	100	<0.2	<0.025	<0.01	0.086	<0.0005	226	<0.004	<0.005	<0.01	<0.01	0.1
Orphan Girl 2	300	<0.2	<0.025	0.01	0.088	<0.0005	231	<0.004	<0.005	<0.01	<0.01	0.2
Orphan Girl 6	300	<0.2	<0.025	<0.01	0.084	<0.0005	219	<0.004	<0.005	<0.01	<0.01	<0.1
Orphan Girl 3	1000	<0.2	0.03	<0.01	0.079	<0.0005	205	<0.004	<0.005	<0.01	<0.01	0.5
Marget Ann 2	5	<0.2	<0.025	<0.01	0.025	<0.0005	137	<0.004	<0.005	<0.01	<0.01	0.7
Marget Ann 3	35	<0.2	<0.025	<0.01	0.025	<0.0005	139	<0.004	<0.005	<0.01	<0.01	<0.1
Marget Ann 3	35	<0.2	<0.025	<0.01	0.025	<0.0005	140	<0.004	<0.005	<0.01	<0.01	<0.1
Marget Ann 4	75	<0.2	<0.025	<0.01	0.024	<0.0005	135	<0.004	<0.005	<0.01	<0.01	<0.1
Marget Ann 5	120	<0.2	<0.025	<0.01	0.024	<0.0005	134	<0.004	<0.005	<0.01	<0.01	0.1
Orphan Boy A	30	<0.04	<0.05	<0.01	0.074	<.001	210	<0.005	<0.005	<0.05	<0.01	0.2
West Camp Shafts												
Travona 2	5	<0.2	0.08	0.12	0.027	<0.0005	170	<0.004	<0.005	<0.01	<0.01	1.9
Travona 3	5	<0.2	0.09	0.13	0.028	<0.0005	175	<0.004	<0.005	<0.01	<0.01	1.2
Travona 4	30	<0.2	0.09	0.13	0.028	<0.0005	179	<0.004	<0.005	<0.01	<0.01	1.4
Travona 5	100	<0.2	0.09	0.12	0.026	<0.0005	173	<0.004	<0.005	<0.01	<0.01	1.3
Travona 6	100	<0.2	0.09	0.12	0.028	<0.0005	174	<0.004	<0.005	<0.01	<0.01	1.2
Travona 7	350	<0.2	0.10	0.12	0.028	<0.0005	176	<0.004	<0.005	<0.01	<0.01	1.2
Travona 8	890	<0.2	0.10	0.13	0.028	<0.0005	175	<0.004	<0.005	<0.01	<0.01	1.3
Emma	34	<0.04	<0.05	<0.01	0.031	<0.001	181	<0.005	<0.005	<0.05	<0.01	1.8
Ophir	30	<0.04	<0.05	<0.01	0.012	<0.001	88	<0.005	<0.005	<0.05	<0.01	3.9
East Camp Shafts												
Kelley A	2	31.3	10.9	<0.01	<.0030	0.0801	432	<0.005	0.601	<0.05	<0.01	1527
Kelley B	100	30.7	10.7	<0.01	<.0030	0.0760	421	<0.005	0.590	<0.05	<0.01	1501
Kelley C	1000	42.7	11.0	<0.01	<.0030	0.0843	366	<0.005	0.663	<0.05	<0.01	*1924*

Steward A	2	0.5	2.9	<0.01	0.006	0.0024	460	<0.005	0.055	<0.05	<0.01	235
Steward B	120	0.6	3.0	<0.01	0.005	0.0035	448	<0.005	0.055	<0.05	<0.01	237
Steward C	1120	0.6	3.0	<0.01	0.005	0.0031	449	<0.005	0.054	<0.05	<0.01	235
Granite Mountain 1	25	0.6	0.03	<0.01	0.011	0.0008	498	0.024	0.042	0.011	1.3	17
Granite Mountain 1	25	0.6	<0.025	<0.01	0.010	0.0008	485	0.023	0.041	<0.01	1.2	15
Granite Mountain 2	100	0.4	<0.025	<0.01	0.010	0.0007	491	0.023	0.041	0.013	1.2	16
Granite Mountain 3	1000	0.5	0.03	<0.01	0.010	0.0008	497	0.024	0.042	<0.01	1.2	16
Anselmo A	2	<0.04	<0.05	<0.01	0.017	<.001	312	0.011	0.012	<0.05	<0.01	29
Anselmo C	100	<0.04	<0.05	<0.01	0.016	<.001	308	0.010	0.012	<0.05	<0.01	30
Anselmo D	450	<0.04	<0.05	<0.01	0.016	<.001	302	0.010	0.012	<0.05	<0.01	29
	feet bswl	Al	As	B	Ba	Be	Ca	Cd	Co	Cr	Cu	Fe

	feet bswl	Hg	K	Li	Mg	Mn	Mo	Na	Ni	P	Pb	S
						Outer Camp Shafts						
Orphan Girl 1	5	<0.08	9	0.155	62	5.12	<0.005	113	<0.01	0.17	<0.08	174
Orphan Girl 4	30	<0.08	9	0.151	60	5.02	<0.005	112	0.01	0.17	<0.08	222
Orphan Girl 5	100	<0.08	8	0.152	61	5.06	<0.005	112	0.01	0.17	<0.08	259
Orphan Girl 2	300	<0.08	8	0.158	63	5.13	<0.005	114	<0.01	0.18	<0.08	191
Orphan Girl 6	300	<0.08	8	0.149	58	5.01	<0.005	108	<0.01	0.16	<0.08	212
Orphan Girl 3	1000	<0.08	10	0.139	54	4.59	<0.005	104	<0.01	0.17	<0.08	184
Marget Ann 2	5	<0.08	6	0.013	24	1.83	<0.005	12	<0.01	<0.06	<0.08	88
Marget Ann 3	35	<0.08	6	0.013	24	1.76	<0.005	12	<0.01	<0.06	<0.08	89
Marget Ann 3	35	<0.08	7	0.014	24	1.77	<0.005	13	<0.01	<0.06	<0.08	89
Marget Ann 4	75	<0.08	3	0.011	24	1.71	<0.005	12	<0.01	<0.06	<0.08	86
Marget Ann 5	120	<0.08	5	0.015	23	1.71	<0.005	12	<0.01	<0.06	<0.08	85
Orphan Boy A	30	<0.05	10	0.152	56	4.66	<0.01	100	<0.01	0.15	<0.04	269
						West Camp Shafts						
Travona 2	5	<0.08	8	0.031	48	5.77	<0.005	33	<0.01	<0.06	<0.08	127
Travona 3	5	<0.08	5	0.032	51	5.91	<0.005	34	<0.01	<0.06	<0.08	130
Travona 4	30	<0.08	8	0.032	51	6.10	<0.005	36	<0.01	<0.06	<0.08	135
Travona 5	100	<0.08	10	0.030	48	5.86	<0.005	35	<0.01	0.03	<0.08	130

Travona 6	100	<0.08	8	0.029	49	5.92	<0.005	35	<0.01	<0.06	<0.08	132
Travona 7	350	<0.08	6	0.031	50	5.93	<0.005	34	<0.01	<0.06	<0.08	134
Travona 8	890	<0.08	5	0.030	50	5.88	<0.005	34	<0.01	<0.06	<0.08	131
Emma	34	<0.05	9	0.042	54	9.70	<0.01	35	<0.01	0.06	<0.04	130
Ophir	30	<0.05	6	0.013	25	7.18	<0.01	19	<0.01	<0.05	<0.04	56
						East Camp Shafts						
Kelley A	2	<0.05	60	0.257	307	145	0.076	72	0.40	0.06	0.19	1813
Kelley B	100	<0.05	58	0.242	298	143	0.075	73	0.39	0.10	0.19	1814
Kelley C	1000	<0.05	59	0.282	301	149	0.075	82	0.44	0.70	0.20	1837
Steward A	2	<0.05	32	0.038	142	26.41	0.020	42	0.04	<0.05	<0.04	673
Steward B	120	<0.05	35	0.039	136	25.84	0.019	42	0.04	0.08	<0.04	659
Steward C	1120	<0.05	33	0.038	138	25.97	0.021	41	0.04	<0.05	<0.04	659
Granite Mountain 1	25	<0.08	19	0.057	163	42.75	<0.005	28	0.09	<0.06	<0.08	681
Granite Mountain 1	25	<0.08	19	0.058	157	41.79	<0.005	27	0.09	<0.06	<0.08	668
Granite Mountain 2	100	<0.08	19	0.058	159	41.99	<0.005	27	0.10	<0.06	<0.08	674
Granite Mountain 3	1000	<0.08	19	0.059	163	42.16	<0.005	28	0.09	<0.06	<0.08	675
Anselmo A	2	<0.05	14	0.036	88	18.57	<0.01	38	0.02	<0.05	<0.04	344
Anselmo C	100	<0.05	13	0.035	88	18.53	<0.01	38	0.02	<0.05	<0.04	341
Anselmo D	450	<0.05	14	0.035	86	18.30	<0.01	37	0.02	<0.05	<0.04	336
	feet bswl	Hg	K	Li	Mg	Mn	Mo	Na	Ni	P	Pb	S

	feet bswl	Sb	Se	Si	Sn	Sr	V	Zn	pH	pH	Eh (mV)	Eh (mV)
				Outer Camp Shafts					*bailed*	*in-situ*	*bailed*	*in-situ*
Orphan Girl 1	5	<0.08	<0.08	11.8	0.02	6.00	<0.02	0.012	6.81	6.35	-65	-89
Orphan Girl 4	30	<0.08	<0.08	11.6	0.03	5.92	<0.02	0.009	6.8	6.32	-63	-114
Orphan Girl 5	100	<0.08	0.09	11.7	0.03	5.96	<0.02	0.008	6.83	6.30	-74	-124
Orphan Girl 2	300	<0.08	<0.08	11.9	0.02	6.08	<0.02	0.008	6.9	6.27	-68	-130
Orphan Girl 6	300	<0.08	<0.08	11.3	0.03	5.77	<0.02	0.009	6.81	6.27	-16	-130
Orphan Girl 3	1000	<0.08	<0.08	10.6	0.02	5.34	<0.02	0.081	6.89	na	-36	na
Marget Ann 2	5	<0.08	<0.08	3.8	<0.02	2.67	<0.02	0.149	7.01	4.59	194	115
Marget Ann 3	35	<0.08	<0.08	3.9	<0.02	2.72	<0.02	<0.004	7.29	7.24	154	-3

Marget Ann 3	35	<0.08	<0.08	3.9	<0.02	2.74	<0.02	0.005	7.29	7.24	154	-3
Marget Ann 4	75	<0.08	<0.08	3.8	<0.02	2.67	<0.02	0.005	7.41	7.50	134	-56
Marget Ann 5	120	<0.08	<0.08	3.7	<0.02	2.61	<0.02	0.004	7.52	7.55	107	-81
Orphan Boy A	30	<0.08	<0.08	11.6	<0.03	5.39	<0.02	0.012	6.63	6.63	-127	-104
West Camp Shafts												
Travona 2	5	<0.08	<0.08	8.6	<0.02	1.25	<0.02	0.220	6.50	6.23	40	70
Travona 3	5	<0.08	<0.08	9.0	<0.02	1.32	<0.02	0.017	6.58	6.23	40	70
Travona 4	30	<0.08	<0.08	9.3	<0.02	1.37	<0.02	0.025	6.47	6.83	67	41
Travona 5	100	<0.08	<0.08	9.3	<0.02	1.31	<0.02	0.028	6.40	6.85	66	34
Travona 6	100	<0.08	<0.08	9.1	<0.02	1.31	<0.02	0.010	Enough sample for ICP only.			
Travona 7	350	<0.08	<0.08	9.1	<0.02	1.31	<0.02	0.014	6.81	6.72	64	26
Travona 8	890	<0.08	<0.08	9.0	<0.02	1.33	<0.02	0.013	6.78	na	67	na
Emma	34	<0.08	<0.08	9.4	<0.03	1.48	<0.02	0.154	6.73	6.38	167	106
Ophir	30	<0.08	<0.08	6.4	<0.03	0.39	<0.02	0.003	6.95	6.93	65	65
East Camp Shafts												
Kelley A	2	0.10	0.45	38.4	<0.03	0.63	0.07	192	4.13	4.37	367	328
Kelley B	100	0.09	0.48	38.0	<0.03	0.60	0.07	191	3.79	4.05	347	285
Kelley C	1000	0.10	0.46	38.2	<0.03	0.31	0.09	194	3.72	na	354	na
Steward A	2	<0.08	0.19	21.9	<0.03	1.95	<0.02	40.5	5.72	5.74	231	274
Steward B	120	<0.08	0.20	21.9	<0.03	1.93	<0.02	40.3	5.93	5.47	193	230
Steward C	1120	<0.08	0.20	21.7	<0.03	1.91	<0.02	40.2	5.84	na	201	na
Granite Mountain 1	25	<0.08	0.26	9.7	0.03	5.04	<0.02	18.1	5.58	5.82	363	356
Granite Mountain 1	25	<0.08	0.25	9.4	0.02	4.85	<0.02	17.8	5.58	5.82	363	356
Granite Mountain 2	100	<0.08	0.26	9.4	0.03	4.92	<0.02	17.9	5.69	5.82	375	324
Granite Mountain 3	1000	<0.08	0.26	9.5	0.03	5.02	<0.02	18.0	5.69	na	362	na
Anselmo A	2	<0.08	0.12	10.7	<0.03	3.30	<0.02	14.9	6.3	5.58	191	242
Anselmo C	100	<0.08	0.11	10.7	<0.03	3.27	<0.02	14.6	6.39	6.25	180	163
Anselmo D	450	<0.08	0.11	10.6	<0.03	3.24	<0.02	14.5	6.44	na	172	na
Sample Name	feet bswl	Sb	Se	Si	Sn	Sr	V	Zn	pH	pH	Eh (mV)	Eh (mV)

Values are in mg/l.

Table 22 Major cations and anions used in charge balance

Shaft	HACH/ MBMG	BaSO4 or $S_{(ICP)}$x3	MBMG	HACH/ MBMG	MBMG	MBMG	ICP	ICP	ICP	ICP	ICP	ICP	ICP
100 ft bswl	Cl^-	SO_4^{2-}	HCO_3^-	PO_4^{3-}	F^-	NO_3^-	Ca2+	K+	Fe2+	Mg2+	Mn2+	Na+	Si4+
Orphan Boy	20.0	269	835.0	0.00	0.828	0.0	210	10	0.2	56	4.66	100	11.6
Orphan Girl	30.0	275	780.0	0.45	0.929	0.0	226	8	0.1	61	5.06	112	11.7
Marget Ann	12.0	260	261.0	0.00	0.000	0.0	135	3	0.1	24	1.71	12	3.8
Emma	39.6	399	395.0	0.00	0.000	0.0	181	9	1.8	54	9.70	35	9.4
Ophir	22.1	166	222.0	0.00	0.482	0.0	88	6	3.9	25	7.18	19	6.4
Travona	40.8	367	362.7	0.14	0.000	0.0	174	8	1.2	49	5.92	35	9.1
Anselmo	32.0	1023	286.1	0.00	0.000	0.0	308	13	30	88	18.5	38	10.7
Steward	34.7	1977	160.0	0.00	0.000	0.0	448	35	237	136	25.8	42	21.9
Kelley	0.0	5442	0.0	0.00	26.4	0.0	421	58	1756	298	143	73	38.0
Granite Mtn	10.0	2021	102.0	0.00	1.777	0.0	491	19	18	159	42.0	27	9.4
Pilot Butte	8.5	2666	69.8	0.00	0.000	0.922	515	16	49.6	234	184	38	31.9

charge balance	Σcations *meq/L*	Σanions *meq/L*	% error
Orphan Boy	19.88	19.89	0.0%
Orphan Girl	21.61	19.42	5.3%
Marget Ann	9.38	10.03	-3.3%
Emma	15.69	15.90	-0.7%
Ophir	7.87	7.74	0.8%
Travona	14.69	14.74	-0.2%
Anselmo	26.29	26.89	-1.1%
Steward	45.71	44.76	1.0%
Kelley	118.30	114.69	1.5%
Granite Mtn	41.47	44.12	-3.1%
Pilot Butte	55.46	56.90	-1.3%

Appendix C: Table of values for potentiometric surface

Table 23 Data used to construct potentiometric surface of bedrock in the study area

GWIC ID	Label	Easting, feet	Northing, feet	Groundwater Elevation, feet above mean sea level	Site Name	Site Type
158230	BELMONT 2	1201519	657142	5270.93	BELMONT 2	Bedrock Monitoring Well
4773	CHESTERSTEEL	1194987	656483	5591.94	CHESTER STEELE PARK	Bedrock Monitoring Well
126152	GS-29D	1196952	651307	5438.00	GS-29D	Bedrock Monitoring Well
4644	HEBGAN	1200319	654717	5486.50	HEBGAN PARK	Bedrock Monitoring Well
4647	PARROT	1202609	655750	5414.81	PARROT PARK	Bedrock Monitoring Well
174134	J	1207406	656222	5265.39	WELL J	Bedrock Monitoring Well
158224	96-01D	1194873	652630	5424.30	WELL96-01D	Bedrock Monitoring Well
158226	L96-02	1196178	652835	5458.86	WELL96-02	Bedrock Monitoring Well
158231	96-03	1197371	652788	5457.54	WELL96-03	Bedrock Monitoring Well
123701	A	1207919	654999	5272.35	WELL A	Bedrock Monitoring Well
125710	B	1207883	659378	5350.21	WELL B	Bedrock Monitoring Well
122535	C	1209994	655430	5272.52	WELL C	Bedrock Monitoring Well
122536	D2	1209118	658455	5266.09	WELL D2	Bedrock Monitoring Well
155681	DDH-1	1205644	655998	5292.09	WELL DDH-1	Bedrock Monitoring Well
155683	DDH-2	1209233	656809	5267.15	WELL DDH-2	Bedrock Monitoring Well
4607	DDH-8	1207064	654594	5335.31	WELL DDH-8	Bedrock Monitoring Well
127293	E	1207955	658947	5374.38	WELL E	Bedrock Monitoring Well
128498	F	1204232	654770	5449.86	WELL F	Bedrock Monitoring Well
145674	G	1208792	654564	5283.43	WELL G	Bedrock Monitoring Well
120678	BerkeleyPit	1201010	658923	5259.12	Berkeley Pit	Berkeley Pit

GWIC ID	Label	Easting, feet	Northing, feet	Groundwater Elevation, feet above mean sea level	Site Name	Site Type
120678	BerkeleyPit	1201469	659526	5259.12	Berkeley Pit	Berkeley Pit
120678	BerkeleyPit	1202149	660109	5259.12	Berkeley Pit	Berkeley Pit
120678	BerkeleyPit	1202206	657956	5259.12	Berkeley Pit	Berkeley Pit
120678	BerkeleyPit	1203479	657334	5259.12	Berkeley Pit	Berkeley Pit
120678	BerkeleyPit	1203526	660855	5259.12	Berkeley Pit	Berkeley Pit
120678	BerkeleyPit	1204407	657354	5259.12	Berkeley Pit	Berkeley Pit
120678	BerkeleyPit	1204694	661133	5259.12	Berkeley Pit	Berkeley Pit
120678	BerkeleyPit	1205249	656875	5259.12	Berkeley Pit	Berkeley Pit
120678	BerkeleyPit	1205249	660961	5259.12	Berkeley Pit	Berkeley Pit
120678	BerkeleyPit	1205651	660540	5259.12	Berkeley Pit	Berkeley Pit
120678	BerkeleyPit	1205938	659889	5259.12	Berkeley Pit	Berkeley Pit
120678	BerkeleyPit	1206072	656760	5259.12	Berkeley Pit	Berkeley Pit
120678	BerkeleyPit	1206349	659315	5259.12	Berkeley Pit	Berkeley Pit
120678	BerkeleyPit	1206454	657038	5259.12	Berkeley Pit	Berkeley Pit
120678	BerkeleyPit	1206780	658875	5259.12	Berkeley Pit	Berkeley Pit
120678	BerkeleyPit	1206827	658176	5259.12	Berkeley Pit	Berkeley Pit
12067	BerkeleyPit	1204425	658923	5259.12	Berkeley Pit	Berkeley Pit
892116	MTECHWELL1	1191103	656973	5581.20	MTECH*WELL01	estimate
50393	50393	1171435	650407	5358.20		estimate
50464	50464	1212421	645005	5587.33		estimate
50463	50463	1188664	644417	5810.60		estimate
50413	50413	1177939	650126	5371.73		estimate
51029	51029	1184215	683038	5660.02		estimate
120710	120710	1204558	685687	6709.79	BSB WATER DEPT	estimate

GWIC ID	Label	Easting, feet	Northing, feet	Groundwater Elevation, feet above mean sea level	Site Name	Site Type
50058	50058	1214744	650640	5819.69		estimate
50350	50350	1171704	664340	5429.75		estimate
138488	138488	1179706	676885	5564.23		estimate
50452	50452	1197252	646728	5467.67		estimate
227189	227189	1198681	669180	6323.04		estimate
179105	179105	1169933	656124	5345.17		estimate
166646	166646	1183774	644191	5870.44		estimate
145971	145971	1205221	679636	6689.57		estimate
206011	206011	1193419	671819	5974.77		estimate
221129	221129	1203324	679580	6570.05		estimate
189408	189408	1198313	672769	6369.63		estimate
50466	50466	1177786	648342	5404.77		estimate
163583	163583	1192941	645602	5548.03		estimate
50351	50351	1168301	662955	5396.23		estimate
50027	50027	1218591	666190	6280.00		estimate
	MoultonNo.1	1206708	685131	6746.00	Moulton Reservoir No.1	estimate
	MoultonNo.2	1212334	684682	7040.00	Moulton Reservoir No.2	estimate
	Spring1	1219207	677020	6480.00	Spring1	estimate
4768	ANSELMO	1194867	659296	5284.42	ANSELMO	Mine shaft used in study
4818	EMMA	1197584	656601	5424.30	EMMA	Mine shaft used in study
4506	GRANITE MTN	1201810	662712	5274.83	GRANITE MOUNTAIN	Mine shaft used in study
4514	KELLEY	1199978	660010	5269.57	KELLEY	Mine shaft used in study
4732	MARGETANN	1196423	666641	6214.05	MARGET ANN	Mine shaft used in study
142793	OPHIR	1197491	654197	5424.28	OPHIR SHAFT	Mine shaft used in study

GWIC ID	Label	Easting, feet	Northing, feet	Groundwater Elevation, feet above mean sea level	Site Name	Site Type
4822	ORPHANBOY	1189788	657452	5572.47	ORPHAN BOY	Mine shaft used in study
202167	ORPHANGIRL	1190020	656905	5568.00	ORPHAN GIRL	Mine shaft used in study
139286	PILOTBUTTE	1201561	664801	5284.52	PILOT BUTTE	Mine shaft used in study
4765	STEWARD	1198088	659708	5279.16	STEWARD	Mine shaft used in study
4782	TRAVONA	1195409	654934	5425.26	TRAVONA	Mine shaft used in study
196519	YDT pond	1201686	672354	6210.00	Yankee Doodle Tailings Pond	Yankee Doodle Tailings Pond
196519	YDT pond	1201734	670023	6210.00	Yankee Doodle Tailings Pond	Yankee Doodle Tailings Pond
196519	YDT pond	1202496	668413	6210.00	Yankee Doodle Tailings Pond	Yankee Doodle Tailings Pond
196519	YDT pond	1203355	666943	6210.00	Yankee Doodle Tailings Pond	Yankee Doodle Tailings Pond
196519	YDT pond	1204407	665757	6210.00	Yankee Doodle Tailings Pond	Yankee Doodle Tailings Pond
196519	YDT pond	1205287	674987	6210.00	Yankee Doodle Tailings Pond	Yankee Doodle Tailings Pond
196519	YDT pond	1205925	665168	6210.00	Yankee Doodle Tailings Pond	Yankee Doodle Tailings Pond
196519	YDT pond	1207531	665935	6210.00	Yankee Doodle Tailings Pond	Yankee Doodle Tailings Pond
196519	YDT pond	1208216	666828	6210.00	Yankee Doodle Tailings Pond	Yankee Doodle Tailings Pond
196519	YDT pond	1208760	674321	6210.00	Yankee Doodle Tailings Pond	Yankee Doodle Tailings Pond
196519	YDT pond	1209442	669087	6210.00	Yankee Doodle Tailings Pond	Yankee Doodle Tailings Pond
196519	YDT pond	1210124	670562	6210.00	Yankee Doodle Tailings Pond	Yankee Doodle Tailings Pond
196519	YDT pond	1210410	672101	6210.00	Yankee Doodle Tailings Pond	Yankee Doodle Tailings Pond
196519	YDT pond	1210981	673512	6210.00	Yankee Doodle Tailings Pond	Yankee Doodle Tailings Pond
196519	YDT pond	1211805	675289	6210.00	Yankee Doodle Tailings Pond	Yankee Doodle Tailings Pond
196519	YDT pond	1206057	670659	6210.00	Yankee Doodle Tailings Pond	Yankee Doodle Tailings Pond

XY coordinate system = Montana State Plane, NAD83, feet

Appendix D: In-Situ Hydrolab data for vertical profiles

Table 24 Raw data from In-Situ Hydrolab MS-5 profiles

swl
497'

Anselmo Hydrolab Profile

depth *ft bgs*	depth *ft bswl*	Temperature *Celsius*	ORP *mV*	pH *pH*	Clark DO *mg/L*	Clark DO *%Sat*	Conductivity *µSiemens/cm*
0					6.8	92.7	
75					3.3	44.5	
175					3.3	43.7	
275					3.3	43.5	
375					3.4	44.5	
475					3.5	44.6	
500	2	17.53	242	5.58	3.6	45.9	2224
500	10	17.56	216	6.05	0.7	8.4	2228
510	20	17.48	212	6.06	0.4	5.3	2256
520	30	17.53	197	6.18	0.3	3.2	2228
530	40	17.53	187	6.21	0.2	2.9	2227
540	50	17.48	181	6.23	0.2	2.9	2226
550	60	17.49	175	6.25	0.2	3.1	2227
560	70	17.48	172	6.24	0.3	3.2	2226
570	80	17.48	169	6.24	0.3	3.2	2227
580	90	17.48	165	6.25	0.3	3.3	2227
590	100	17.47	163	6.25	0.3	3.3	2226
600	110	17.48	161	6.24	0.3	3.3	2227
620	130	17.49	159	6.24	0.3	3.3	2227
640	150	17.47	157	6.23	0.3	3.3	2226
660	170	17.46	155	6.22	0.3	3.3	2225
680	190	17.46	153	6.22	0.3	3.2	2227
700	210	17.46	153	6.21	0.3	3.3	2226
720	230	17.47	151	6.20	0.3	3.3	2225
740	250	17.48	150	6.19	0.3	3.3	2226
760	270	17.47	148	6.17	0.3	3.4	2225
780	290	17.48	146	6.17	0.3	3.3	2224
800	310	17.47	145	6.16	0.3	3.3	2226

swl
164'

Travona Hydrolab Profile

depth *ft bswl*	Temperature *Celsius*	ORP *mV*	pH *pH*	Clark DO *mg/L*	Clark DO *%Sat*	Conductivity *µSiemens/cm*
5	13.10	70	6.23	1.8	20.8	1279
15	13.09	47	6.68	0.4	4.7	1284
25	13.04	42	6.82	0.2	2.6	1281
35	13.05	41	6.85	0.2	2.0	1284
45	13.04	41	6.82	0.1	1.7	1283
55	13.05	40	6.82	0.1	1.5	1283
65	13.04	38	6.85	0.1	1.4	1284
75	13.05	36	6.86	0.1	1.4	1284
85	13.05	35	6.87	0.1	1.3	1284
95	13.05	36	6.85	0.1	1.4	1284
105	13.06	34	6.85	0.1	1.3	1284
125	13.06	34	6.85	0.1	1.4	1285
145	13.06	33	6.82	0.1	1.4	1284
165	13.07	32	6.82	0.1	1.5	1284
185	13.07	32	6.81	0.1	1.5	1284
205	13.07	31	6.79	0.1	1.5	1283
225	13.06	30	6.77	0.1	1.6	1282
245	13.09	29	6.75	0.1	1.6	1286
265	13.09	28	6.74	0.1	1.6	1288
285	13.08	26	6.72	0.1	1.6	1291

swl
771'

Pilot Butte Hydrolab Profile

depth ft bgs	depth ft bswl	Temperature Celsius	ORP mV	pH pH	Clark DO mg/L	Clark DO %Sat	Conductivity µSiemens/cm
135					7.7	103.7	
435					7.8	104.0	
535					8.0	105.3	
635					8.2	106.7	
735					8.4	108.3	
765					8.9	110.1	
775	5	18.50	412	5.06	7.2	98.1	3615
800	25	18.53	391	5.16	2.8	38.3	3607
820	45	18.55	358	5.21	0.5	6.2	3611
840	65	18.55	351	5.20	0.5	6.1	3611
860	85	18.54	344	5.20	0.5	6.1	3609
880	105	18.57	342	5.20	0.4	5.4	3609
920	145	18.58	339	5.18	0.4	4.8	3609
960	185	18.57	338	5.16	0.3	4.6	3610
1000	225	18.57	337	5.14	0.4	4.9	3609
1040	265	18.60	336	5.14	0.3	4.7	3610
1080	305	18.59	334	5.12	0.3	4.3	3610

swl 578'	Steward Hydrolab Profile					
depth ft bswl	Temperature Celsius	ORP mV	pH pH	Clark DO mg/L	Clark DO %Sat	Conductivity µSiemens/cm
2	24.24	274	5.74	1.0	14.4	3541
20	24.49	247	5.63	0.5	8.0	3546
40	24.50	241	5.58	0.5	7.9	3537
60	24.55	236	5.54	0.5	7.6	3530
80	24.56	231	5.52	0.5	7.5	3525
100	24.54	231	5.49	0.5	7.4	3524
120	24.53	230	5.47	0.5	7.5	3522
160	24.53	229	5.47	0.5	7.3	3522
200	24.57	229	5.46	0.5	7.2	3528
240	24.61	228	5.45	0.5	7.3	3530
280	24.65	227	5.44	0.5	7.2	3532
320	24.70	226	5.42	0.5	7.3	3536

swl 84'	Marget Ann Hydrolab Profile					
depth ft bswl	Temperature Celsius	ORP mV	pH pH	Clark DO mg/L	Clark DO %Sat	Conductivity µSiemens/cm
5	9.66	115	4.59	4.0	43.1	916
20	10.42	55	6.60	1.9	21.3	892
40	8.93	-3	7.24	1.1	11.7	904
60	8.61	-34	7.45	0.7	8.1	897
80	8.58	-56	7.50	0.6	6.8	895
100	8.56	-74	7.54	0.5	6.0	895
120	8.55	-88	7.56	0.5	5.4	896
120	8.57	-107	7.59	0.4	4.7	897
120	8.56	-116	7.58	0.4	4.4	897
120	8.57	-124	7.57	0.4	4.6	897

swl 775'	Granite Mountain Hydrolab Profile						
depth bgs	depth ft bswl	Temperature Celsius	ORP mV	pH pH	Clark DO mg/L	Clark DO %Sat	Conductivity µSiemens/cm
0					10.2	122.3	
100					7.1	84.2	
200					7.1	83.7	
300					7.2	84.4	
400					7.4	85.2	
500					7.5	85.9	
600					7.6	87.2	
735					7.9	89.2	
770					8.0	91.1	
780	5	15.35	398	5.79	3.9	49.4	3318
800	25	15.46	356	5.82	0.8	10.2	3316
820	45	15.43	344	5.82	0.7	9.1	3306
840	65	15.41	333	5.82	0.7	8.3	3307
860	85	15.42	328	5.82	0.6	7.5	3306
880	105	15.45	324	5.82	0.5	6.8	3309
920	145	15.45	321	5.83	0.5	6.1	3309
960	180	15.45	319	5.83	0.5	5.7	3311
1000	225	15.45	317	5.83	0.4	5.2	3309
1040	265	15.45	315	5.83	0.4	5.0	3309
1080	305	15.46	314	5.83	0.4	4.7	3308

swl 120'	Orphan Girl Hydrolab Profile					
depth ft bswl	Temperature Celsius	ORP mV	pH pH	Clark DO mg/L	Clark DO %Sat	Conductivity µSiemens/cm
2	26.54	-89	6.37	0.5	7.0	1819
20	26.55	-110	6.33	0.2	2.9	1819
40	26.55	-114	6.31	0.2	2.3	1819
60	26.57	-120	6.30	0.1	2.1	1820
100	26.57	-124	6.30	0.2	2.2	1821
140	26.57	-125	6.28	0.2	2.2	1819
180	26.58	-126	6.27	0.2	2.3	1818
220	26.51	-127	6.27	0.2	2.5	1813
260	26.52	-128	6.27	0.2	2.8	1814
300	26.52	-130	6.27	0.2	2.9	1813

swl 636'	Kelley Hydrolab Profile					
depth ft bswl	Temperature Celsius	ORP mV	pH pH	Clark DO mg/L	Clark DO %Sat	Conductivity µSiemens/cm
5	34.64	328	4.37	1.1	19.5	7454
10	34.61	318	4.28	1.2	21.5	7409
15	34.61	315	4.24	1.3	21.9	7394
20	34.61	311	4.20	1.2	21.7	7398
25	34.61	307	4.18	1.2	21.5	7390
40	34.61	299	4.16	1.2	21.3	7368
50	34.66	297	4.15	1.2	21.1	7384
60	34.68	293	4.12	1.2	21.3	7384
70	34.91	292	4.08	1.3	22.2	7379
80	34.94	289	4.07	1.3	22.5	7387
90	34.86	285	4.06	1.3	22.4	7380
100	34.86	285	4.05	1.3	22.2	7381
120	34.84	284	4.03	1.3	21.9	7375
140	34.85	281	4.01	1.3	21.7	7374
160	34.85	278	4.00	1.3	21.6	7366
180	34.85	280	3.97	1.3	21.8	7375
200	34.83	277	3.97	1.2	21.5	7370
225	34.81	278	3.93	1.2	21.5	7365
250	34.82	276	3.91	1.2	21.5	7375
275	34.81	273	3.90	1.3	21.8	7365
300	34.81	271	3.89	1.3	21.8	7367

Appendix E: Data for vertical profiles sampled using bailer

Table 25 Raw data for vertical profiles obtained with bailer

Orphan Girl Parameters

Depth	Alkalinity	S^{2-} (raw)	S^{2-} (filtered)	Fe^{2+}	ΣFe	T	pH	SC	Eh	LDO	LDO
feet bswl	mg/l $CaCO_3$	ppm	ppm	ppm	ppm	ºC	pH	uS/cm	mV	ppm	%sat
5	693	5.50	3.95	0.139		26.13	6.81	1833	-65	0.2	3.1
30	712	6.80	5.15				6.80	1785	-63	1.37	
100	712	7.38	6.68				6.83	1786	-74	0.89	
300	704	6.10	4.48	0.205	0.161		6.9	1862	-16	1.6	21
1000	704	5.95	3.26	0.707			6.89	1804	-36	1.23	16.4
300	717	5.61	4.60				6.81	1803	-68	1.2	

Marget Ann Parameters

Depth feet bswl	Alkalinity mg/l CaCO3	S2- (raw) ppm	S2- (filtered) ppm	Fe2+ ppm	ΣFe ppm	Cl- ppm	T ºC	pH pH	SC uS/cm	Eh mV	LDO ppm	LDO %sat
5	198	0.008		0.038	0.045	14.9	13.3	7.01	881	194	1.3	15.5
35	182	0.231		0.099	0.100	16.0	14.9	7.29	933	154	1.14	13.8
75	191	0.266		0.056	0.060	17.2		7.41	863	134	1.3	17.7
120	180	0.535	0.342	0.130	0.129	23.6		7.52	835	107	1.14	15.9

Kelley Parameters

	SWL	Depth	Alkalinity	Fe2+	ΣFe	%Fe2+	T	pH	SC	Eh
	feet	feet bswl	mg/l CaCO3	ppm	ppm		ºC	pH	uS/cm	mV
A	636	5	8.8	1830.24	1837.68	99.6%	29.4		7080	361
B		100	5	1763.28	1755.84	100.4%	30.1		7070	341
C		1000	5.3	2183.64	2196.66	99.4%	33.5		8240	348
Kelley A from 4/21/06		5		1726.08	1711.2	100.9%				

Steward Parameters

Steward	Depth feet bswl	Alkalinity mg/l CaCO3	Fe2+ ppm	ΣFe ppm	%Fe2+	T ºC	pH pH	SC uS/cm	Eh mV	SWL feet
A	2		254.355	251.565	101.1%	21.4	5.72	3470	231	578
B	120		232.035	255.75	90.7%	21.9	5.93	3450	193	
C	1100		250.17	228.315	109.6%	23.1	5.84	3470	201	

Travona Parameters

Depth feet bswl	Alkalinity mg/l CaCO3	S2- (raw) ppm	S2- (filtered) ppm	Cl- ppm	T ºC	pH pH	SC uS/cm	Eh mV	DO ppm
TR2-5	310,295	0.196	0.008	27.3,23.0	17.2	6.50	1284	228	3.06
TR3-5	241,297	0.192	0.151	21.1	16.6	6.58	1281	70	
TR4-30	303	0.198	0.155	18.8	18.0	6.47	1279	67	
TR5-100	299	0.187	0.153	20.4	18.8	6.40	1266	66	
TR7-350	301	0.205	0.164	22.2	26.1	6.81	1248	64	
300		0.203	0.127						
TR8-890	305	0.404	0.162	20.0		6.78	1306	67	

Anselmo Parameters

	Depth feet bswl	Alkalinity mg/l CaCO3	SO_4^{2-} ppm	Fe^{2+} ppm	ΣFe ppm	%Fe^{2+}	T ºC	pH pH	SC uS/cm	Eh mV
A	2		1000	26.3	30.0	87.8%	16.1	6.30	2170	191
C	100		1300	30.1	30.6	98.5%	15.1	6.39	2150	180
D	450	266	1200	29.6	30.1	98.1%	16.3	6.44	2110	172

Orphan Boy parameters

pH	SC, uS/cm	ORP mV	T ˚C	SO42- ppm	Fe(tot), ppm	Fe(II), ppm	%Fe2+	alkalinity mg/L CaCO3
6.63	1731	-104	25.7	320	1.0	0.2	19.5%	702

Table 26: Data used for Potentiometric surface in Figure 2

gwic	Site_name	Easting, ft	Northing, ft	Groundwater Elevation, feet AMSL, April 2006	site_type
158230	BELMONT 2	1201519.15	657142	5270.93	Bedrock Monitoring Well
4773	CHESTERSTEELEPARK	1194986.51	656483	5591.94	Bedrock Monitoring Well
126152	GS-29D	1196952.41	651307	5438	Bedrock Monitoring Well
4644	HEBGANPARK	1200318.51	654717	5486.5	Bedrock Monitoring Well
4647	PARROTPARK	1202609.32	655750	5414.81	Bedrock Monitoring Well
174134	WELL_J_MAY06	1207406.2	656222	5265.39	Bedrock Monitoring Well
158224	WELL96-01D	1194873.19	652630	5424.3	Bedrock Monitoring Well
158226	WELL96-02	1196177.76	652835	5458.86	Bedrock Monitoring Well
158231	WELL96-03	1197371.13	652788	5457.54	Bedrock Monitoring Well
123701	WELLA	1207918.59	654999	5272.35	Bedrock Monitoring Well
125710	WELLB	1207882.82	659378	5350.21	Bedrock Monitoring Well
122535	WELLC	1209994.04	655430	5272.52	Bedrock Monitoring Well
122536	WELLD2	1209118.27	658455	5266.09	Bedrock Monitoring Well
155681	WELLDDH-1	1205643.73	655998	5292.09	Bedrock Monitoring Well
155683	WELLDDH-2	1209233.3	656809	5267.15	Bedrock Monitoring Well
4607	WELLDDH-8	1207064.22	654594	5335.31	Bedrock Monitoring Well
127293	WELLE	1207954.51	658947	5374.38	Bedrock Monitoring Well
128498	WELLF	1204232.06	654770	5449.86	Bedrock Monitoring Well
145674	WELLG	1208791.67	654564	5283.43	Bedrock Monitoring Well
120678	BerkeleyPit	1201010.09	658923	5259.12	Berkeley Pit
120678	BerkeleyPit	1201469.35	659526	5259.12	Berkeley Pit
120678	BerkeleyPit	1202148.68	660109	5259.12	Berkeley Pit
120678	BerkeleyPit	1202206.09	657956	5259.12	Berkeley Pit
120678	BerkeleyPit	1203478.63	657334	5259.12	Berkeley Pit
120678	BerkeleyPit	1203526.47	660855	5259.12	Berkeley Pit
120678	BerkeleyPit	1204406.73	657354	5259.12	Berkeley Pit
120678	BerkeleyPit	1204693.77	661133	5259.12	Berkeley Pit
120678	BerkeleyPit	1205248.72	656875	5259.12	Berkeley Pit
120678	BerkeleyPit	1205248.72	660961	5259.12	Berkeley Pit
120678	BerkeleyPit	1205650.57	660540	5259.12	Berkeley Pit
120678	BerkeleyPit	1205937.61	659889	5259.12	Berkeley Pit
120678	BerkeleyPit	1206071.56	656760	5259.12	Berkeley Pit
120678	BerkeleyPit	1206349.04	659315	5259.12	Berkeley Pit
120678	BerkeleyPit	1206454.28	657038	5259.12	Berkeley Pit

120678	BerkeleyPit	1206779.6	658875	5259.12	Berkeley Pit
120678	BerkeleyPit	1206827.44	658176	5259.12	Berkeley Pit
12067	BerkeleyPit	1204425.25	658923	5259.12	Berkeley Pit
892116	MTECH*WELL01	1191103.13	656973	5581.2	estimate
50393	RICHENS, V.	1171435.01	650407	5358.2	estimate
50464	BLANKENSHIP JIM	1212420.72	645005	5587.33	estimate
50463	BRASIER FRANK	1188663.92	644417	5810.6	estimate
50413	DUNKS, TOM	1177938.59	650126	5371.73	estimate
51029	PIZZOLA DAN	1184214.77	683038	5660.02	estimate
120710	BUTTE SILVER BOW WATER DEPARTMENT	1204557.98	685687	6709.79	estimate
50058	RILEY RUSS 93-125	1214743.9	650640	5819.69	estimate
50350	UELAND, OLE M.	1171704.36	664340	5429.75	estimate
138488	HOCKADAY JEFF & DOROTHY	1179705.89	676885	5564.23	estimate
50452	REAP KENNETH 93-213	1197251.77	646728	5467.67	estimate
227189	METESH, JOHN J. AND YVONNE	1198681.37	669180	6323.04	estimate
179105	BLOMSTROM, KEITH / GRAHAM, GUY	1169932.99	656124	5345.17	estimate
166646	ZALUSKI, MAREK AND ELIZABETH	1183774.42	644191	5870.44	estimate
145971	MCCLOSKEY JAY	1205220.55	679636	6689.57	estimate
206011	MANNIX GARY	1193419.26	671819	5974.77	estimate
221129	MIHELICH, CHAD	1203324.37	679580	6570.05	estimate
189408	OKEEFE DAN	1198312.51	672769	6369.63	estimate
50466	ZELLER, KENNETH	1177786.48	648342	5404.77	estimate
163583	ZIMPEL ED	1192940.95	645602	5548.03	estimate
50351	UELAND, OLE	1168301.13	662955	5396.23	estimate
50027	Murphy, Dorothy	1218590.69	666190	6280	estimate
0		1206708	685131	6746	estimate
0		1212334.07	684682	7040	estimate
0		1219207.48	677020	6480	estimate
0		0	0	5281.52	estimate
4768	ANSELMO	1194867.26	659296	5284.42	Mine shaft used in study
4818	EMMA	1197583.83	656601	5424.3	Mine shaft used in study
4506	GRANITEMOUNTAIN	1201810.32	662712	5274.83	Mine shaft used in study
4514	KELLEY	1199977.93	660010	5269.57	Mine shaft used in study
4732	MARGETANN	1196423.48	666641	6214.05	Mine shaft used in study
142793	OPHIR	1197490.59	654197	5424.28	Mine shaft used in study
4822	ORPHANBOY	1189788.08	657452	5572.47	Mine shaft used in study
202167	ORPHANGIRL	1190020.33	656905	5568	Mine shaft used in study
139286	PILOTBUTTE	1201560.62	664801	5284.52	Mine shaft used in study
4765	STEWARD	1198088.08	659708	5279.16	Mine shaft used in study

4782	TRAVONA	1195409.25	654934	5425.26	Mine shaft used in study
196519	YDT pond	1201686.12	672354	6210	Yankee Doodle Tailings Pond
196519	YDT pond	1201733.71	670023	6210	Yankee Doodle Tailings Pond
196519	YDT pond	1202496.45	668413	6210	Yankee Doodle Tailings Pond
196519	YDT pond	1203355.18	666943	6210	Yankee Doodle Tailings Pond
196519	YDT pond	1204407.12	665757	6210	Yankee Doodle Tailings Pond
196519	YDT pond	1205286.59	674987	6210	Yankee Doodle Tailings Pond
196519	YDT pond	1205924.88	665168	6210	Yankee Doodle Tailings Pond
196519	YDT pond	1207531.43	665935	6210	Yankee Doodle Tailings Pond
196519	YDT pond	1208215.57	666828	6210	Yankee Doodle Tailings Pond
196519	YDT pond	1208760.16	674321	6210	Yankee Doodle Tailings Pond
196519	YDT pond	1209442.19	669087	6210	Yankee Doodle Tailings Pond
196519	YDT pond	1210124.21	670562	6210	Yankee Doodle Tailings Pond
196519	YDT pond	1210409.71	672101	6210	Yankee Doodle Tailings Pond
196519	YDT pond	1210980.71	673512	6210	Yankee Doodle Tailings Pond
196519	YDT pond	1211805.48	675289	6210	Yankee Doodle Tailings Pond
196519	YDT pond	1206057.2	670659	6210	Yankee Doodle Tailings Pond

SIGNATURE PAGE

This is to certify that the thesis prepared by Dean M. Snyder entitled "Vertical Gradients in Geochemistry of Flooded Mine Shafts in Butte, Montana" has been examined and approved for acceptance by the Department of Mining and Geology, Montana Tech of The University of Montana, on this 24th day of April, 2012.

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