MAJOR AND TRACE-ELEMENT ANALYSES OF ACID MINE WATERS IN THE LEVIATHAN MINE DRAINAGE BASIN, CALIFORNIA/NEVADA--OCTOBER, 1981 TO OCTOBER, 1982

By James W. Ball and D. Kirk Nordstrom

U.S. GEOLOGICAL SURVEY

Water-Resources Investigations Report 85-4169

Prepared in cooperation with

CALIFORNIA REGIONAL WATER QUALITY CONTROL BOARD

Menlo Park, California

1985

UNITED STATES DEPARTMENT OF THE INTERIOR

DONALD PAUL HODEL, Secretary

GEOLOGICAL SURVEY

Dallas L. Peck, Director

For additional information
write to:

Regional Hydrologist, WR
U.S. Geological Survey
345 Middlefield Road
Menlo Park, California 94025

Copies of this report can
be purchased from:

Open-File Services Section
Western Distribution Branch
U.S. Geological Survey
Box 25425, Federal Center
Denver, Colorado 80225
(Telephone: (303) 234-5888)

CONTENTS

ILLUSTRATIONS

TABLES

CONVERSION FACTORS AND ABBREVIATIONS

The metric system of units is used in this report. For readers who prefer inch-pound units, the conversion factors for the terms used in this report are listed below.

Multiply	By	To obtain
m^3 sec^{-1} (cubic meters per second)	35.31	ft^3 sec^{-1} (cubic feet per second)
kg cm^{-2} (kilograms per square centimeter)	14.29	psi (pounds per square inch)
µm (micrometer)	3.937×10^{-5}	in (inch)
mm (millimeter)	0.03937	in (inch)
mL (milliliter)	0.03382	fl oz (fluid oz)
L (liter)	0.2642	gal (gallon)
µg (microgram)	3.520×10^{-8}	oz (ounce)
mg (milligram)	3.520×10^{-5}	oz (ounce)
g (gram)	0.03520	oz (ounce)
hectare (10,000 square meters)	2.471	acre

Explanation of abbreviations:

M (Molar, moles per liter)
N (Normal, equivalents per liter)
mg L^{-1} (milligrams per liter)
nm (nanometer)
µg L^{-1} (micrograms per liter)

MAJOR AND TRACE-ELEMENT ANALYSES OF ACID MINE WATERS IN THE LEVIATHAN MINE DRAINAGE BASIN, CALIFORNIA/NEVADA--OCTOBER, 1981 to OCTOBER, 1982

By James W. Ball and D. Kirk Nordstrom

ABSTRACT

Water issuing from the inactive Leviathan open-pit sulfur mine has caused serious degradation of the water quality in the Leviathan/Bryant Creek drainage basin which drains into the East Fork of the Carson River. As part of a pollution abatement project of the California Regional Water Quality Control Board, the U.S. Geological Survey collected hydrologic and water quality data for the basin during 1981-82. During this period a comprehensive sampling survey was completed to provide information on trace metal attenuation during downstream transport and to provide data for interpreting geochemical processes. This report presents the analytical results from this sampling survey. Sixty-seven water samples were filtered and preserved on-site at 45 locations and at 3 different times. Temperature, discharge, pH, Eh and specific conductance were measured on-site. Concentrations of 37 major and trace constituents were determined later in the laboratory on preserved samples. The quality of the analyses was checked by using two or more techniques to determine the concentrations including d.c.-argon plasma emission spectrometry (DCP), flame and flameless atomic absorption spectrophotometry, UV-visible spectrophotometry, hydride-generation atomic absorption spectrophotometry and ion chromatography. Additional quality control was obtained by comparing measured to calculated conductance, comparing measured to calculated Eh (from Fe^{2+}/Fe^{3+} determinations), charge balance calculations and mass balance calculations for conservative constituents at confluence points.

Leviathan acid mine waters contain mg L^{-1} concentrations of As, Cr, Co, Cu, Mn, Ni, Tl, V and Zn, and hundreds to thousands of mg L^{-1} concentrations of Al, Fe, and SO_4 at pH values as low as 1.8. Other elements including Ba, B, Be, Bi, Cd, Mo, Sb, Se and Te are elevated above normal background concentrations and fall in the μg L^{-1} range.

The chemical and $^{34}S/^{32}S$ isotopic analyses demonstrate that these acid waters are derived from pyrite oxidation and not from the oxidation of elemental sulfur.

INTRODUCTION

The Leviathan Mine is an inactive open-pit sulfur mine located near Markleeville in Alpine County, California (Figure 1). Open-pit operations began about 1951. To access the sulfur ore body, overburden waste above it was removed and dumped at expedient locations around the mine site. This overburden contained significant quantities of sulfide minerals, and the waste covered areas are still largely devoid of vegetation because of the resultant acidity.

The excavation resulted in a large open pit occupying an area of approximately 20.2 hectares (see Hammermeister and Walmsley (1985) for a map of the area). Some of the underground mine workings still remain beneath the southern end of the pit. One tunnel (tunnel 5), with a blocked portal located near the "throat" of the open pit, discharges acidic water year-around and appears to serve as a drain for the southern portion of the pit. See Figures 1, 2A, and 2B for locations of various features of the area.

In addition to the open pit and tunnel network, there are a number of other important features in the mine area. To the north of the pit, there is a large active landslide partially covered by native vegetation (13.8 hectares). An additional 28.3 hectares adjacent to the open pit is covered by overburden and mining waste.

Leviathan Creek flows directly through portions of mine waste material and becomes contaminated from direct contact with waste, numerous acidic seeps, surface discharges from the open pit and tunnel 5, and sediment from the active landslide on the northern part of the site which continually encroaches on the creek. Aspen Creek, which flows into Leviathan Creek, becomes contaminated to a lesser degree from seeps as it travels along the edge of the waste material near the northern boundary of the mine site. Leviathan Creek above the mine site supports a population of fish and other aquatic life typical of unpolluted streams in the eastern Sierra Nevada. However, from a point near where Leviathan Creek enters the mine to the point where the Leviathan/Bryant Creek system enters the East Fork of the Carson River approximately 16 km downstream, the water quality is severely degraded and the creek does not support fish or other aquatic life. Furthermore, other beneficial uses such as irrigation and stock and wildlife watering have severely deteriorated.

As part of a pollution abatement project undertaken by the California Regional Water Quality Control Board, the U.S. Geological Survey has collected basic hydrologic and water quality data for the drainage basin (Hammermeister and Walmsley, 1985). One aspect of the program involved sampling of the water to provide data for geochemical characterization and to elucidate downdrainage attenuation of pollutants under different flow conditions. This report presents the analytical results of three sample-collecting trips, taken in October, 1981; June, 1982; and October, 1982. Only four samples were collected in October, 1981, to obtain preliminary information on the range of water composition in the drainage basin and to test analytical methods.

SAMPLE COLLECTION AND PRESERVATION METHODS

Unique problems are encountered in the sampling, preservation, and analysis of acid mine effluent because of the instability and/or high concentrations of some constituents. Arsenic^{+3}, iron^{+2} and other variable valence ions may be rapidly oxidized and/or precipitated upon aeration, precluding valence species determinations.

To maximize cost effectiveness and analytical precision and accuracy, analyses were done on site for only those constituents which could not be preserved for laboratory analysis. pH, Eh, specific conductance, and temperature

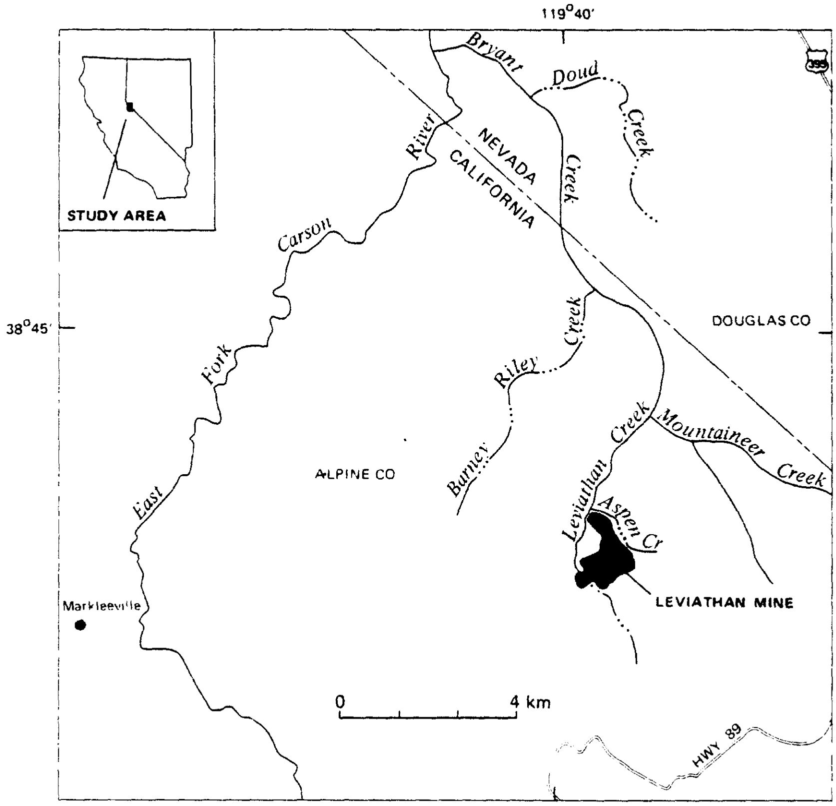

FIGURE 1.--Location of Leviathan Mine.
(from Hammermeister and Walmsley, 1985)

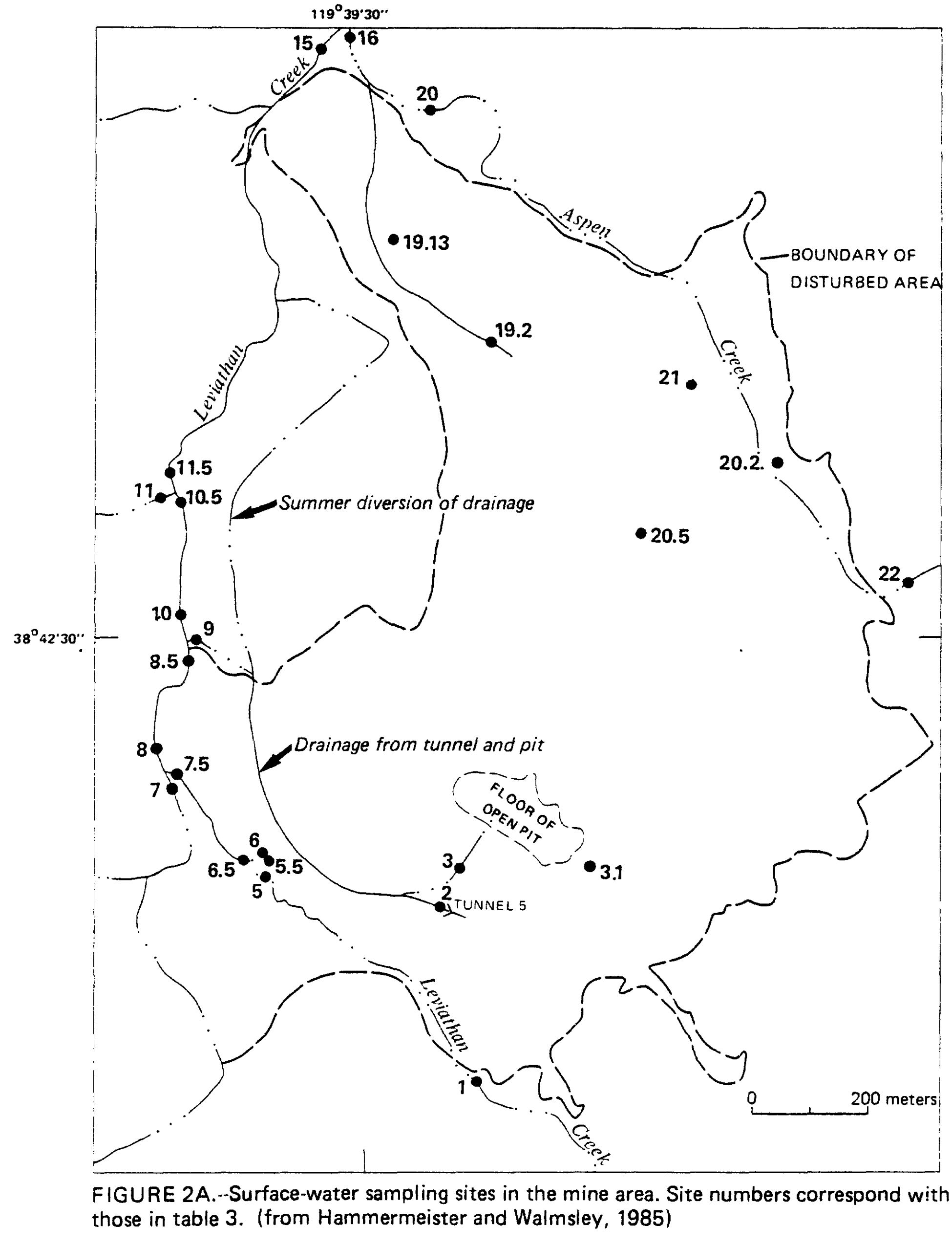

FIGURE 2A.--Surface-water sampling sites in the mine area. Site numbers correspond with those in table 3. (from Hammermeister and Walmsley, 1985)

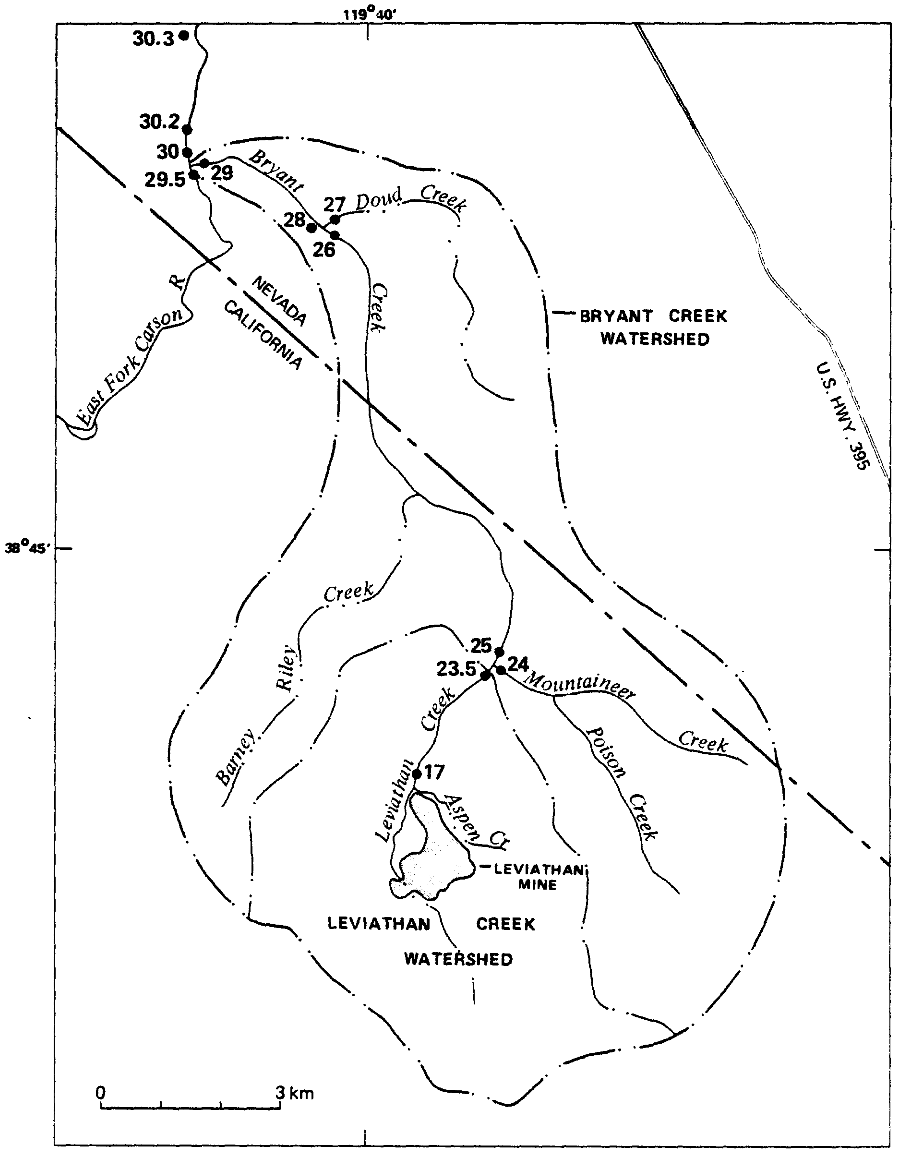

FIGURE 2B.--Surface-water sampling sites downstream from the mine area. Site numbers correspond with those in table 3. (from Hammermeister and Walmsley, 1985) were determined on site. Because the non-carbonate alkalinity was not significant, carbonate-bicarbonate alkalinity was determined later and the pH was also remeasured (Ellis and others, 1968; A. H. Truesdell, unpub. data).

Due to the instability of the dissolved constituents in these waters, samples were filtered immediately. The high concentration of trace elements in the surrounding area mandated stringent precautions to avoid water sample contamination. During a sampling day, the filter assembly was used first for waters of lowest metal concentrations and last for waters of highest concentrations. At the end of a day the assembly was rinsed out with dilute acid followed by deionized or distilled water.

On-Site Measurements

Determination of pH and Eh was accomplished by pumping sample fluid (slowly for pH, rapidly for Eh) through an acrylic plastic cell containing pH, redox, and temperature probes, and test tubes of standard pH buffer solution. The probes were of rugged, high-impact plastic construction, glass electrode membranes were well protected, and liquid junctions were of a type highly resistant to clogging and fouling. A meter with compatible electrodes was used to measure both pH and Eh. The meter was calibrated before and after each measurement with buffer solutions of pH values that bracketed the sample pH at the temperature of the sample. Eh values were calculated later from the measured emf value, the half-cell potential of the reference cell and the temperature.

Sampling Methods

Due to remoteness of some sampling sites, compact, lightweight equipment was transported, along with the samples taken, in two backpacks (weight >20 kg each). The portable pump, used to pump sample water through the flow-through pH-Eh cell and the filter apparatus, was capable of delivering the sample fluid from a depth of at least 3 m to the apparatus with a head of at least 1.4 kg cm^{-2} for four continuous hours or more.

The filtration assembly consisted of a 0.1-μm, 142-mm Millipore VCWP membrane sealed between two acrylic plastic discs sealed with a viton or silicone rubber o-ring. To facilitate homogeneous water and particulate loading of the membrane, air was released at the start of filtration using an integral valve. The assembly was supported by three polyvinyl chloride legs threaded into the underside of the the bottom disc. The two discs were secured together by integral, swing-away nylon bolts and nuts hinged in the bottom plate.

Sample fluid was pumped from the source through the filter assembly into all-linear- or conventional-polyethylene or Teflon collection bottles. Field cleaning of the filtration assembly consisted of wiping the inside of the filter with tissue if necessary, rinsing with distilled water, and changing the filter membrane. Sample water from the new site was used to thoroughly flush the sampling line during pH and Eh measurements. The sampling line was then attached to the filtration assembly. At least 1000 mL of sample were pumped through the membrane before collection of the portion used for trace-element determinations.

Samples were collected after on-site measurements were completed. Samples for major anions (500 mL) were collected first; then samples for iron (II/III) and arsenic (III/V) (500 mL); then samples for major cations and trace elements (250 mL). Duplicate samples were sometimes taken for trace constituents.

Samples to be analyzed for Hg were pumped through the filter assembly into a 1000-mL borosilicate glass reagent bottle.

The operator and all equipment fit on a 3-meter square polyethylene ground sheet, used to avoid contamination of the sample water by surrounding oxide-coated rocks and other surficial deposits.

Sample Preservation Methods

Samples for Fe and As determinations were acidified with 4 mL of ultrapure hydrochloric acid per 500 mL of sample; samples for major and the remaining trace metals were acidified with 2 mL of ultrapure nitric acid per 250 mL of sample. Hydrochloric acid is used to minimize possible oxidation of reduced Fe and As species in the former sample (Stauffer and others, 1980). The pH of some acidified samples was checked at the end of the day to assure that a pH of <1.5 had been reached. The above preservatives were transported to the field in their original borosilicate glass ampules, minimizing the risk of contamination or total loss associated with open-container transport. The acids were transferred to Teflon bottles upon initial arrival at the sampling area, and dispensed with piston pipets into the sample bottles immediately prior to sample collection. Samples for Hg analysis were preserved by adding 10-mL increments of 5% $KMnO_4$ solution until the sample remained purple for several hours. No preservative was added to the samples for anion analysis.

ANALYTICAL METHODS

A number of techniques were employed to chemically analyze the samples. They include: (1) Direct current plasma/multielement atomic emission spectrometry for the determination of Al, As, Ba, B, Be, Cd, Ca, Cr, Co, total Fe, Cu, Pb, Mg, Mn, Mo, Ni, K, Si, Na, Sr, Tl, V, Zn. (2) The ferrozine colorimetric method (Gibbs, 1976; Stookey, 1970) for the determination of Fe(II) and total Fe. (3) Graphite furnace atomic absorption for the determination of Tl. (4) Molybdate-blue colorimetry for the determination of As. (5) Hydride generation/atomic absorption for the determination of As, Sb, Bi, and Se. (6) Cold-vapor flameless atomic absorption using a preliminary separation/concentration step (Harsanyi and others, 1973) for the determination of Hg. (7) Flame atomic absorption for the determination of Li, and for selected samples, Na and K. (8) Ion chromatography for the determination of Cl, F, and SO_4. These techniques are specifically discussed in the following sections.

Digestion of Elemental Sulfur Samples

Clean fragments of elemental sulfur were readily obtained by partially breaking a large hand specimen and brushing off contaminating particles. These fragments were ground in a sapphire mortar and then 0.1 g triplicate aliquots were weighed out to the nearest 0.01 mg into Teflon Parr bomb cups. Four mL of aqua regia was added to each, the cups were sealed in steel casings and then placed in an oven at 110°C for 2 hours and then in the freezer for about 2 hours. The cooled digests were quantitatively transferred to 25 mL volumetric flasks and diluted to volume with distilled water. The solution was then analyzed for As, Sb, Bi and Se by both d.c.-argon plasma spectrometer and by hydride generation/atomic absorption.

Analysis by d.c.-argon Plasma Spectrometry

Samples were analyzed using a Spectraspan IIIB d.c.-argon plasma emission spectrometer having a Spectrajet III torch (Spectrametrics, Inc., Andover, Mass.). A set of working standards for each of two groups of elements was prepared by making 1 N HNO_3 dilutions of the respective multielement standard solution containing 14 and 15 elements, respectively, in 1 N HNO_3. A solution of 0.1 N HNO_3 was used as a blank and was prepared by diluting the ultrapure HNO_3 with distilled water. The multielement solution was composed of alkali and alkaline earth salts of purity 99.99 percent or better and other metal salts, acids, and commercially prepared solutions of purity 99.999 percent or better. The readout and photomultiplier modules were optimized with respect to voltage and gain compatibility to achieve the best combination of sensitivity and stability.

Standards were interspersed among samples during analysis. A calibration curve for each element was constructed using data from four standard solutions and the 0.1 N HNO_3 blank. To increase thermal contact between the plasma and the measuring zone, located directly below the plasma (Johnson and others, 1979, p. 204), a Li solution was mixed at approximately a 1:11 ratio with the sample just prior to nebulization, such that a total concentration of 2270 mg L^{-1} of Li was generated in the sample (Ball and others, 1978).

Two groups of elements were determined, using interchangeable cassettes. Cassette 1 contained slits designed to pass to the photomultiplier tubes the emission lines of the following elements: B, Mn, Cu, Zn, Si, Be, Mn, Sr, Ca, Fe, Ba, K, Na, and Al. The elements determined using cassette 2 were: As, Se, Bi, Zn, Cd, Sb, Cu, Ni, Mo, Co, Cr, Fe, V, Tl, and Pb. Analytical wavelengths are listed in Table 1. The Zr, Ag, Ti, and Rb channels (cassette 1) and the Sn, Hg, and Li channels (cassette 2) were not used because either a stable multielement solution did not result from a mixture containing these elements, or the levels present in these samples were below detection limits. Neither the background nor the internal standard channels (channels 3 and 6, respectively, on cassette 1, and channels 17 and 1, respectively, on cassette 2) were used with either cassette. They were found by prior experiment to make inaccurate concentration adjustments for some elements.

Data Collection and Processing

The emission data were collected on a magnetic tape storage device and simultaneously displayed on the screen of a CRT terminal. Sample dilutions of 1/10, 1/100, 1/1000, and 1/5000 were also analyzed as necessary to bring all elemental concentrations within the measuring range of the instrument. The machine-readable data were subsequently converted to concentration values, which were stored on a flexible disk storage medium. When data for all elements were available, sample concentrations were corrected for interelement

Table 1. Analytical wavelengths for the elements

Cassette 1			Cassette 2		
Channel	Element	Wavelength, nm	Channel	Element	Wavelength, nm
1	B	249.773	1	Not used	265.118
2	Mn	257.610	2	As	193.696
3	Not used	237.1	3	Se	196.026
4	Cu	324.754	4	Bi	223.061
5	Zn	213.856	5	Zn	213.856
6	Not used	265.118	6	Cd	214.438
7	Si	251.611	7	Sb	206.833
8	Zr not used	339.198	8	Cu	324.754
9	Be	313.061	9	Sn not used	283.999
10	Mg	279.553	10	Ni	341.476
11	Ag not used	328.068	11	Hg not used	253.652
12	Sr	421.552	12	Mo	379.825
13	Ti not used	334.941	13	Co	345.350
14	Ca	393.366	14	Cr	425.435
15	Fe	371.994	15	Fe	371.994
16	Ba	455.403	16	V	437.924
17	K	766.490	17	Not used	300.6
18	Na	589.592	18	Tl	535.046
19	Rb not used	780.023	19	Li not used	670.784
20	Al	396.152	20	Pb	405.783

spectral effects, which are due to the presence of concomitant major elements and are observed when measuring concentrations of minor elements. This correction required collection of apparent concentration data for a representative concentration range of suspected interferent in the absence of analyte at the appropriate wavelengths. The resulting apparent analyte concentration values were fitted to various types of linear and exponential simple regression equations, and the selected fit parameters were recorded. The concentration of the concomitant element in an unknown sample was combined with the fit parameters to yield a numerical value for its interference which was subtracted from the apparent concentration of the analyte. The resulting data were stored in a master data set, to which data from other sources were added later.

The above interelement interference correction technique was used to correct for the effects of Ca, Mg, Si, K, Na, and Fe on the apparent concentrations of B, Mn, Cu, Zn, Fe, Al, As, Se, Bi, Cd, Sb, Ni, Co, Mo, Cr, V, Tl, and Pb. No effects of Ca, Mg, Si, K, Na, or Fe at their upper concentration limits (490, 110, 110, 33, 39, and 2510 mg L^{-1}, respectively) were observed on the apparent concentrations of Si, Be, Mg, Ca, Fe, Sr, Ba, K or Na. The effect of Ca was the most serious, followed by the effect of Fe, for the analysis of acid mine effluent. Al, Ti, and Pb are elements upon which Ca, frequently present at levels exceeding 100 mg L^{-1}, interferes due to stray light effects (Johnson and others, 1979). The effect of Ca on the apparent concentration of Al or Pb is significant at Ca concentrations as low as 10 mg L^{-1}. The effect can be as high as 1 µg L^{-1} Al or Pb per 1 mg L^{-1} Ca. Aluminum, present at concentrations up to 620 mg L^{-1}, also qualifies as a potential interferent, but data do not presently exist to enable corrections to be made, if any apply.

Colorimetric Iron and Arsenic Redox Species Determinations

Iron redox species were determined with a colorimetric method employing ferrozine as the color-producing reagent (Stookey, 1970; Gibbs, 1976). A sample aliquot of 0.01-20 mL (HCl acidified sample) containing up to 40 µg Fe, was placed in a 25-mL volumetric flask. Ten percent (w/v) hydroxylamine hydrochloride (0.25 mL) was added, then 0.5 mL of 0.25% (w/v) ferrozine in water solution, then 1.25 mL of 15.4% (w/v) CH_3COONH_4 buffer solution. After mixing and dilution to volume, the 562-nm absorbance of the solution was measured within one hour using a Bausch & Lomb Spectronic 710 spectrophotometer equipped with 1-cm cells for the 1-40 µg range, and 5-cm cells for the 0.1-1 µg range. For the determination of Fe^{+2}, the hydroxylamine hydrochloride reductant addition was omitted. A calibration curve was mathematically constructed from the absorbances of concurrently prepared standards, and Fe^{+2} or total Fe concentration was calculated using the fit parameters, the sample absorbance, and the volume of sample taken for analysis. Ferric iron was calculated from the difference between total Fe and Fe^{+2}.

Arsenic redox species were determined by the molybdate-blue technique of Stauffer and others (1980). The composition of the acid mine effluent precluded the accurate estimation of As redox species concentrations in all samples except those having the highest As concentrations. Therefore, total As was also determined by a hydride generation/atomic absorption technique.

Atomic Absorption Determinations for Selected Elements

Two hydride generation techniques, coupled with atomic absorption measurement, were employed for the determination of As, Sb, Bi, Se, and Te. In the first, an aliquot of sample made 1.5 M in HCl was injected into a reaction vessel containing $NaBH_4$ solution. The resulting gas mixture was purged, using helium, into a quartz cuvette which was placed in the light beam of an atomic absorption spectrophotometer and externally heated by an air-acetylene flame. In the second, the hydride generated in the above reaction was purged into a cold trap consisting of a borosilicate glass U-tube half-filled with glass beads and immersed in liquid nitrogen. Following a suitable preconcentration time, the liquid nitrogen was removed and the U-tube was heated to drive off the hydrides, which were purged into the argon-hydrogen flame of the spectrophotometer. A calibration curve was constructed from the absorbances of similarly prepared and analyzed standards.

Graphite furnace atomic absorption was used to determine Tl. Flame atomic absorption was used to determine Li, and to check a selected subset of the d.c.-argon plasma determinations of Na and K.

Ion Chromatographic Determinations of Cl, F, and SO_4

A Model 16 ion chromatograph (Dionex Corp., Sunnyvale, Calif.) with standard-run separator (#30170) and suppressor (#30064) columns was used for Cl and F determinations. Standard- and fast-run (#30985) separator columns were used in the determination of SO_4. The eluent was 0.003 M $NaHCO_3$/0.0024 M Na_2CO_3 in double-distilled H_2O. Prior to analyses, the eluent was pumped through the columns for 1-2 hours to condition the separator and stabilize the suppressor. High standards were first injected to clear out complexes and verify retention times for ions. Injections of double-distilled H_2O were run to clear the columns of residual high standards and to stabilize the baseline.

Samples were arranged in order of projected increasing concentration, determined either from prior rapid analysis of a 1/10 dilution of the samples, or by association with the field conductivity measurement. Dual-ion working standards, for F and Cl, or for Br and SO_4, were interspersed with the samples. Two or more levels of each standard at each full-scale setting were run each day. Scales 10 and 100 were used to determine SO_4, and scales 1, 3, and 10 were used for F and Cl. A 2-mL aliquot of sample or standard was injected by plastic syringe to flush and load the 100-μL injection loop. Samples were diluted, if necessary, with double-distilled H_2O, using piston pipets, just before injection. A calibration curve was constructed from the conductance responses of similarly prepared and analyzed standards.

RESULTS AND DISCUSSION

Several critical factors can adversely affect the quality of the data. One such factor is an increase in concentration of the analyte, due to evaporation of the sample or to possible contamination of a dilute sample, either during collection or in the laboratory when subsampling for a particular analysis. A second factor is possible loss of a constituent from solution between the time a sample is removed from its source and the time it is analyzed. This can occur by valence change, precipitation, sorption onto surfaces, vaporization, or a combination of these factors. Preservation of a sample's dissolved constituents and their original oxidation state is difficult, especially when the array of solutes is large, the concentrations of interest range from fractional $\mu g\ L^{-1}$ to percent concentrations, and the sample is equilibrating rapidly at the time of collection. The approach used for this study was to collect several subsamples, appropriately preserved to stabilize the various constituents, and to analyze all subsamples as soon as possible after collection. Priority was assigned to constituents that are the most likely to change in concentration, such as redox species or solutes that precipitate or volatilize readily. Examples of these kinds of problems are the oxidation or reduction of Fe, As and S species, or vaporization or sorption of Hg or the "hydride" elements, such as Sb or Se. Constituents which constitute a major proportion of total dissolved solids (e.g., SO_4 in these samples) must be determined extremely precisely, because even small percentages of error in the concentration estimate can result in significant errors in aqueous geochemical calculations and interpretations.

Plasma Analyses

Accuracy of analysis is variable between elements. The four elements B, Ca, Ba, and Sr have been investigated in detail and give precision and accuracy better than ±5%. Changes in sensitivity, or slope of the calibration curve, due to movement of either the plasma or the grating, greatly affect the precision of the analyses. Table 2 illustrates the magnitude of this effect. The values shown are indicative of typical changes in the relative intensity seen over short time periods during a run in which the instrument has been carefully standardized and optimized. Generally, the magnitude of these variations is acceptably low for most elements; however, note the difference for Cd (+6.6 percent) on cassette 2, only 10 minutes after standardization. Effects such as these are reduced considerably by interspersing the samples and standards, which provides a means of time averaging the sensitivity changes. Sensitivity is known to change as a function of concentration as well. For example, self-absorption of Na emission causes a reduction in the slope of the calibration curve at the 20 mg L^{-1} upper measuring limit. Use of the second-order, multipoint standardization, which is part of the data reduction technique, permits closer calibration over the entire analytical range.

Table 2. Drift of instrument response with time

Element	Relative intensity		Magnitude of change (Percent)	Element	Relative intensity		Magnitude of change (Percent)
	Initial	After 10 min			Initial	After 10 min	
As	20.3	20.3	0	Mn	520	527	+1.3
Se	20.1	21.0	+4.5	Cu	526	544	+3.4
Bi	10.1	10.3	+2.0	Zn	515	524	+1.7
Zn	498	510	+2.4	Si	21.1	22.2	+0.5
Cd	1014	1081	+6.6	Zr	523	523	0
Sb	19.9	21.0	+5.5	Be	205	210	+2.4
Cu	199	197	-1.0	Mb	20.8	21.5	+3.4
Ni	496	478	-3.6	Sr	1056	1087	+2.9
Hg	4.02	4.19	+4.2	Ti	525	531	+1.1
Mo	492	464	-5.7	Ca	21.1	21.1	0
Co	990	968	-2.2	Fe	2124	2243	+5.6
Cr	495	485	-2.0	Ba	1058	1075	+1.6
Fe	9.93	9.60	-3.3	K	21.1	21.5	+1.9
V	979	924	-5.6	Na	21.0	21.4	+1.9
Tl	490	470	-4.1	Rb	2124	2290	+7.8
Pb	3.97	3.81	-4.0	Al	529	546	+3.2
B	1030	1052	+2.1				

Physical measurements and concentration values for chemical constituents are shown in Table 3. The data are arranged in order of site number, with

Table 3. Physical measurements and chemical analyses of water collected from the Leviathan/Bryant Creek drainage basin

	Site#1		Site#2	
	Sample Code Number			
	82WA117	82WA170	81WA132C	82WA118
	Date Collected			
	6/16/82	10/6/82	10/9/81	6/16/82
Determination				
Discharge, m^3 sec^{-1}	0.025	0.0031	0.001	0.001
Temperature, ^{o}C	12.5	6.0	12.5	12.0
Specific Conductance,				
field, uS cm^{-1}	105	150	6,250	9,300
lab, uS cm^{-1}	113	138	4,150	8,040
pH, field	8.10	7.50	2.45	1.80
lab	8.27	8.34	2.60	2.00
Eh, volts	0.380	0.279	0.463	0.465
Alkalinity, mg L^{-1} as HCO_3^-	60.4	82.4	------	------
Aluminum	<0.01	<0.01	440	430
Antimony	<0.0005	------	0.002	0.002
Arsenic	0.003	0.0007	27	30
Barium	0.071	0.064	0.007	0.007
Beryllium	<0.002	<0.002	0.01	0.01
Bismuth	<0.0005	------	0.003	0.067
Boron	<0.02	<0.02	<0.02	0.1
Cadmium	<0.01	<0.01	0.15	0.21
Calcium	11	12	110	140
Chloride	1	1.1	------	8.4
Chromium	0.01	0.01	1.8	2.6
Cobalt	0.01	<0.005	3.3	4.9
Copper	<0.003	<0.003	1.2	5.3
Fluoride	0.054	0.063	------	3.4
Iron(Fe^{2+})	0.0076	0.0005	1,100	1,440
Iron(total)	0.0088	0.0041	1,160	1,570
Lead	0.02	0.04	<0.02	0.22
Lithium	0.0021	0.0018	0.0815	0.0935
Magnesium	3.2	4.4	42	56
Manganese	0.02	<0.01	7.6	11
Molybdenum	0.01	0.02	<0.003	0.02
Nickel	0.005	<0.004	8.0	12
Potassium	3	4.0	13	17
Selenium	<0.002	------	0.01	<0.002
Silica	39	42	100	110
Sodium	7.3	9.6	26	29
Strontium	0.21	0.25	2.4	2.7
Sulfate	5.3	7.2	5,400	7,500
Thallium	0.001	0.002	0.81	2.0
Vanadium	0.005	0.006	0.76	1.1
Zinc	<0.006	<0.006	1.4	1.4
Charge Balance, %	5.08	-2.98	-5.05	-2.63

Table 3. Physical measurements and chemical analyses of water collected from the Leviathan/Bryant Creek drainage basin--Continued

	Site#2	Site#3	Site#3.1	Site#5
	Sample Code Number			
	82WA169	82WA119	82WA120	82WA166
	Date Collected			
	10/6/82	6/16/82	6/16/82	10/6/82
Determination				
Discharge, m^3 sec^{-1}	0.001	0.0009	<0.0003	0.003
Temperature, ^{o}C	12.0	14.0	10.5	8.2
Specific Conductance,				
field, uS cm^{-1}	5,900	12,900	2,200	315
lab, uS cm^{-1}	5,690	7,530	2,070	376
pH, field	2.28	1.85	2.50	5.08
lab	2.14	2.10	2.38	3.64
Eh, volts	0.494	0.543	0.756	0.437
Alkalinity,				
mg L^{-1} as HCO_3^-	------	------	------	------
Aluminum	420	620	22	2.2
Antimony	------	0.002	<0.0005	------
Arsenic	34	40	0.002	0.001
Barium	0.009	0.01	<0.005	0.065
Beryllium	0.01	0.01	0.004	<0.002
Bismuth	------	0.041	<0.0005	------
Boron	0.09	0.35	0.1	<0.02
Cadmium	0.16	0.27	<0.01	<0.01
Calcium	110	270	60	24
Chloride	6.9	9.2	0.9	1.3
Chromium	2.3	3.5	0.070	0.004
Cobalt	4.0	4.7	0.10	0.068
Copper	1.5	9.7	0.52	0.03
Fluoride	3.6	5.1	1.5	0.27
Iron(Fe^{2+})	1,240	2,150	4.46	11.1
Iron(total)	1,270	2,510	60.6	11.4
Lead	0.2	0.18	0.05	0.04
Lithium	0.101	0.163	0.0368	0.0055
Magnesium	39	75	14	7.4
Manganese	8.1	9.5	2.6	0.77
Molybdenum	0.073	0.066	0.035	0.02
Nickel	10	13	0.19	0.16
Potassium	16	33	2	3.9
Selenium	------	<0.002	<0.002	------
Silica	99	110	70	43
Sodium	25	39	4.0	9.3
Strontium	2.3	3.3	0.11	0.28
Sulfate	5,700	11,000	680	140
Thallium	1.1	0.82	0.007	0.002
Vanadium	1.0	1.6	<0.005	<0.005
Zinc	1.0	2.5	0.27	0.03
Charge Balance, %	-6.46	-5.30	-0.749	-2.43

Table 3. Physical measurements and chemical analyses of water collected from the Leviathan/Bryant Creek drainage basin--Continued

	Site#5.5	Site#6	Site#6.5	Site#7
	Sample Code Number			
	82WA167	82WA168	82WA165	82WA121
	Date Collected			
	10/6/82	10/6/82	10/6/82	6/17/82
Determination				
Discharge, m^3 sec^{-1}	0.003	0.002	0.0031	0.0037
Temperature, ^{o}C	7.9	7.9	7.8	18.0
Specific Conductance,				
field, uS cm^{-1}	4,050	3,500	1,800	750
lab, uS cm^{-1}	5,270	5,060	2,460	690
pH, field	2.97	3.28	3.78	6.85
lab	2.10	2.05	2.75	8.18
Eh, volts	0.563	0.528	0.547	0.238
Alkalinity,				
mg L^{-1} as HCO_3^-	------	------	------	146
Aluminum	110	110	52	0.10
Antimony	------	------	------	<0.0005
Arsenic	0.53	0.42	0.021	0.001
Barium	0.02	0.008	0.04	0.076
Beryllium	0.01	0.01	0.007	<0.002
Bismuth	------	------	------	<0.0005
Boron	0.2	0.2	0.08	0.03
Cadmium	0.01	0.02	<0.01	<0.01
Calcium	300	310	160	110
Chloride	4.6	4.4	1.6	0.9
Chromium	0.14	0.13	0.069	<0.003
Cobalt	2.0	2.0	0.85	0.03
Copper	0.085	0.50	0.23	<0.003
Fluoride	5.1	4.9	2.4	0.22
Iron(Fe^{2+})	626	606	278	6.03
Iron(total)	631	621	280	6.38
Lead	0.19	0.19	0.16	0.05
Lithium	0.0735	0.0741	0.0365	0.0060
Magnesium	83	84	40	24
Manganese	22	22	12	2.1
Molybdenum	0.11	0.11	0.088	0.048
Nickel	3.8	3.7	1.8	0.077
Potassium	20	20	10	3
Selenium	------	------	------	<0.002
Silica	54	51	46	25
Sodium	25	24	15	14
Strontium	1.6	1.5	0.87	1.0
Sulfate	2,900	2,800	1,400	280
Thallium	0.037	0.099	0.067	0.002
Vanadium	0.18	0.18	0.04	<0.005
Zinc	0.67	0.64	0.36	0.02
Charge Balance, %	3.51	4.42	-6.50	1.21

Table 3. Physical measurements and chemical analyses of water collected from the Leviathan/Bryant Creek drainage basin--Continued

	Site#7	Site#7.5		Site#8
	Sample Code Number			
	82WA162	82WA129	82WA164	82WA122
	Date Collected			
Determination	10/5/82	6/17/82	10/5/82	6/17/82
Discharge, m^3 sec^{-1}	0.0003	0.021	0.0057	0.032
Temperature, ^{o}C	14.3	18.0	11.5	18.0
Specific Conductance,				
field, uS cm^{-1}	1,870	875	2,240	920
lab, uS cm^{-1}	1,870	1,610	3,550	1,520
pH, field	6.00	4.18	3.43	4.50
lab	7.29	2.68	2.23	2.68
Eh, volts	0.263	0.488	0.574	0.471
Alkalinity,				
mg L^{-1} as HCO_3^-	37.6	------	------	------
Aluminum	0.28	17	54	15
Antimony	<0.0005	<0.0005	<0.0005	<0.0005
Arsenic	0.005	0.005	0.032	0.005
Barium	0.04	0.055	0.05	0.065
Beryllium	<0.002	<0.002	0.007	<0.002
Bismuth	<0.0005	<0.0005	<0.0005	<0.0005
Boron	0.05	0.04	0.09	0.03
Cadmium	<0.01	<0.01	<0.01	<0.01
Calcium	350	49	180	72
Chloride	1.4	1.3	2.3	1.0
Chromium	<0.003	0.004	0.083	<0.003
Cobalt	0.19	0.37	1.0	0.33
Copper	<0.003	0.20	0.29	0.18
Fluoride	0.72	0.69	2.8	0.55
Iron(Fe^{2+})	37.6	90.0	299	77.8
Iron(total)	38.1	91.1	308	80.0
Lead	0.20	0.05	0.1	<0.02
Lithium	0.0162	0.0154	0.0426	0.0142
Magnesium	70	18	46	20
Manganese	12	3.8	12	3.8
Molybdenum	0.10	0.048	0.077	0.032
Nickel	0.40	0.67	1.9	0.62
Potassium	4.2	4.7	12	4.9
Selenium	<0.002	<0.002	<0.002	<0.002
Silica	23	45	48	44
Sodium	22	8.7	16	11
Strontium	2.3	0.37	0.90	0.56
Sulfate	1,200	520	1,600	500
Thallium	0.004	0.029	0.070	0.024
Vanadium	0.02	<0.005	0.086	<0.005
Zinc	0.05	0.25	0.38	0.15
Charge Balance, %	3.92	-12.0	-3.82	0.383

Table 3. Physical measurements and chemical analyses of water collected from the Leviathan/Bryant Creek drainage basin--Continued

Determination	Site#8	Site#8.5	Site#9	Site#10
Sample Code Number	82WA163	82WA130	82WA132	82WA131
Date Collected	10/5/82	6/17/82	6/17/82	6/17/82
Discharge, m^3 sec^{-1}	0.0082	0.032	0.003	0.031
Temperature, °C	12.0	18.0	18.0	18.0
Specific Conductance,				
field, uS cm^{-1}	2,160	900	7,280	1,340
lab, uS cm^{-1}	3,450	1,550	5,180	2,390
pH, field	3.78	4.58	2.10	3.40
lab	2.24	2.72	2.27	2.41
Eh, volts	0.555	0.461	0.601	0.591
Alkalinity,				
mg L^{-1} as HCO_3^-	------	------	------	------
Aluminum	44	14	310	36
Antimony	<0.0005	<0.0005	0.002	<0.0005
Arsenic	0.017	0.005	27	1.4
Barium	0.04	0.058	0.01	0.053
Beryllium	0.007	<0.002	0.01	0.002
Bismuth	<0.0005	<0.0005	0.015	<0.0005
Boron	0.09	0.04	0.2	0.05
Cadmium	<0.01	<0.01	0.16	<0.01
Calcium	210	76	240	88
Chloride	2.3	1.4	7.7	1.2
Chromium	0.067	<0.003	1.9	0.16
Cobalt	0.91	0.32	3.7	0.53
Copper	0.24	0.17	5.4	0.54
Fluoride	2.9	0.60	3.9	1.3
Iron(Fe^{2+})	264	79.4	1,070	142
Iron(total)	266	81.3	1,210	150
Lead	0.2	0.05	0.24	0.1
Lithium	0.0386	0.0148	0.0924	0.0193
Magnesium	47	22	75	25
Manganese	13	4.3	15	4.9
Molybdenum	0.092	0.044	0.089	0.055
Nickel	1.7	0.58	8.7	1.1
Potassium	10	5.1	15	5.2
Selenium	<0.002	<0.002	<0.002	<0.002
Silica	46	45	92	49
Sodium	16	11	29	11
Strontium	1.1	0.61	2.7	0.76
Sulfate	1,500	530	5,700	830
Thallium	0.057	0.023	1.1	0.093
Vanadium	0.04	<0.005	0.84	0.067
Zinc	0.35	0.15	1.3	0.21
Charge Balance, %	-6.70	-2.68	-0.746	-1.62

Table 3. Physical measurements and chemical analyses of water collected from the Leviathan/Bryant Creek drainage basin--Continued

Determination	Site#10.5		Site#11	
	Sample Code Number			
	82WA116	82WA161	82WA114	82WA159
	Date Collected			
	6/16/82	10/5/82	6/16/82	10/5/82
Discharge, m^3 sec^{-1}	0.041	0.0079	0.0045	0.002
Temperature, ^{o}C	18.5	9.1	13.5	4.0
Specific Conductance,				
field, uS cm^{-1}	1,300	2,620	240	415
lab, uS cm^{-1}	2,390	3,840	231	394
pH, field	3.32	3.10	8.00	7.15
lab	2.36	2.24	8.20	8.03
Eh, volts	0.622	0.612	0.384	0.463
Alkalinity,				
mg L^{-1} as HCO_3^-	------	------	73.4	75.7
Aluminum	33	51	0.12	0.04
Antimony	<0.0005	<0.0005	<0.0005	<0.0005
Arsenic	0.88	0.032	0.005	0.001
Barium	0.052	0.04	0.084	0.090
Beryllium	0.002	0.008	<0.002	<0.002
Bismuth	<0.0005	<0.0005	<0.0005	<0.0005
Boron	0.05	0.07	<0.02	<0.02
Cadmium	<0.01	<0.01	<0.01	<0.01
Calcium	89	250	26	41
Chloride	1.8	2.4	1.1	1.0
Chromium	0.14	0.11	0.009	0.009
Cobalt	0.54	0.93	0.006	0.009
Copper	0.40	0.33	<0.003	<0.003
Fluoride	1.3	2.8	0.15	0.23
Iron(Fe^{2+})	123	254	0.0081	0.0053
Iron(total)	141	277	0.0091	0.0127
Lead	0.1	0.2	0.03	0.10
Lithium	0.0207	0.0483	0.0041	0.0072
Magnesium	26	65	7.0	12
Manganese	5.2	15	0.02	0.01
Molybdenum	0.052	0.089	0.02	0.034
Nickel	1.1	1.9	<0.004	0.007
Potassium	5.2	9.6	3.2	3.7
Selenium	<0.002	<0.002	<0.002	<0.002
Silica	49	51	43	36
Sodium	12	21	10	13
Strontium	0.79	1.4	0.37	0.63
Sulfate	790	1,600	57	130
Thallium	0.093	0.047	0.001	<0.001
Vanadium	0.03	0.05	<0.005	0.01
Zinc	0.19	0.40	<0.006	<0.006
Charge Balance, %	3.98	13.6	-1.16	-9.42

Table 3. Physical measurements and chemical analyses of water collected from the Leviathan/Bryant Creek drainage basin--Continued

Determination	Site#11.5		Site#15	
	Sample Code Number			
	82WA115	82WA160	82WA113	82WA152
	Date Collected			
	6/16/82	10/5/82	6/16/82	10/4/82
Discharge, m^3 sec^{-1}	0.031	0.011	0.040	0.010
Temperature, °C	18.0	6.0	14.5	7.0
Specific Conductance,				
field, uS cm^{-1}	1,200	2,260	1,050	2,230
lab, uS cm^{-1}	2,090	3,450	1,880	3,200
pH, field	3.58	3.52	3.31	3.11
lab	2.55	2.29	2.63	2.35
Eh, volts	0.612	0.607	0.644	0.658
Alkalinity,				
mg L^{-1} as HCO_3^-	------	------	------	------
Aluminum	30	46	26	44
Antimony	<0.0005	<0.0005	<0.0005	<0.0005
Arsenic	0.92	0.032	0.37	0.019
Barium	0.062	0.04	0.063	0.04
Beryllium	<0.002	0.007	<0.002	0.006
Bismuth	<0.0005	<0.0005	<0.0005	<0.0005
Boron	0.03	0.07	0.03	0.06
Cadmium	<0.01	<0.01	<0.01	<0.01
Calcium	83	220	79	220
Chloride	1.6	1.8	1.4	1.7
Chromium	0.11	0.094	0.092	0.080
Cobalt	0.44	0.79	0.40	0.80
Copper	0.35	0.27	0.33	0.25
Fluoride	0.89	2.5	0.81	2.2
Iron(Fe^{2+})	103	215	66.6	112
Iron(total)	117	233	83.3	174
Lead	0.09	0.2	0.10	0.2
Lithium	0.0179	0.0432	0.0165	0.0408
Magnesium	23	56	23	56
Manganese	4.1	13	3.7	12
Molybdenum	0.045	0.086	0.044	0.087
Nickel	0.91	1.6	0.86	1.5
Potassium	5.6	8.7	5.2	8.4
Selenium	<0.002	<0.002	<0.002	<0.002
Silica	50	48	50	47
Sodium	13	20	13	19
Strontium	0.76	1.3	0.78	1.3
Sulfate	690	1,500	630	1,500
Thallium	0.092	0.044	0.070	0.043
Vanadium	0.02	0.054	0.005	0.02
Zinc	0.19	0.35	0.19	0.32
Charge Balance, %	3.98	3.06	1.55	-3.80

Table 3. Physical measurements and chemical analyses of water collected from the Leviathan/Bryant Creek drainage basin--Continued

	Site#16		Site#17	
	Sample Code Number			
	82WA111	82WA150	81WA131C	82WA112
	Date Collected			
Determination	6/16/82	10/4/82	10/9/81	6/16/82
Discharge, m^3 sec^{-1}	0.018	0.014	------	0.070
Temperature, °C	13.0	11.9	12.5	14.0
Specific Conductance,				
field, uS cm^{-1}	610	610	1,710	880
lab, uS cm^{-1}	640	597	1,440	1,450
pH, field	7.98	7.62	3.62	3.68
lab	7.98	8.04	3.04	2.74
Eh, volts	0.304	0.235	0.641	0.628
Alkalinity,				
mg L^{-1} as HCO_3^-	50.8	59.6	------	------
Aluminum	0.09	0.10	13	20
Antimony	<0.0005	<0.0005	<0.0005	<0.0005
Arsenic	0.003	0.004	0.0080	0.31
Barium	0.03	0.03	0.04	0.052
Beryllium	<0.002	<0.002	<0.002	0.003
Bismuth	<0.0005	<0.0005	<0.0005	<0.0005
Boron	0.03	<0.02	0.04	0.03
Cadmium	<0.01	<0.01	<0.01	<0.01
Calcium	83	76	150	80
Chloride	1.2	1.3	2.8	1.4
Chromium	<0.003	0.02	0.009	0.03
Cobalt	<0.005	0.03	0.29	0.28
Copper	0.01	<0.003	0.10	0.28
Fluoride	0.38	0.35	------	0.58
Iron(Fe^{2+})	0.0177	0.0045	30.0	47.9
Iron(total)	0.0207	0.0123	39.0	55.7
Lead	<0.02	0.2	<0.02	0.03
Lithium	0.0114	0.0075	0.118	0.0145
Magnesium	21	20	42	23
Manganese	1.2	0.92	6.2	3.0
Molybdenum	<0.003	0.057	<0.003	0.036
Nickel	0.03	0.03	0.61	0.60
Potassium	3.9	4.2	4.9	4.3
Selenium	<0.002	<0.002	<0.002	<0.002
Silica	23	25	31	35
Sodium	11	13	15	11
Strontium	0.63	0.62	1.1	0.69
Sulfate	280	240	760	560
Thallium	0.002	<0.001	0.012	0.053
Vanadium	<0.005	0.02	<0.005	<0.005
Zinc	<0.006	<0.006	0.11	0.11
Charge Balance, %	-4.33	0.271	-4.82	-8.68

Table 3. Physical measurements and chemical analyses of water collected from the Leviathan/Bryant Creek drainage basin--Continued

	Site#17	Site#19.13		Site#19.2
	Sample Code Number			
	82WA151	82WA128	82WA158	82WA127
	Date Collected			
Determination	10/4/82	6/17/82	10/5/82	6/17/82
Discharge, $m^3\ sec^{-1}$	0.024	<0.0003	0.0003	<0.0003
Temperature, °C	7.8	17.0	14.0	15.0
Specific Conductance,				
field, $uS\ cm^{-1}$	1,290	2,200	2,780	2,100
lab, $uS\ cm^{-1}$	1,560	2,490	2,440	2,420
pH, field	3.55	7.44	7.75	3.65
lab	2.84	7.81	6.80	3.75
Eh, volts	------	0.521	0.463	0.667
Alkalinity,				
$mg\ L^{-1}$ as HCO_3^-	------	34.9	106	------
Aluminum	18	0.37	0.12	47
Antimony	<0.0005	<0.0005	<0.0005	<0.0005
Arsenic	0.0070	0.002	0.0008	0.0080
Barium	0.04	0.02	0.02	0.01
Beryllium	0.003	<0.002	<0.002	0.007
Bismuth	<0.0005	<0.0005	<0.0005	<0.0005
Boron	0.04	0.1	0.1	0.1
Cadmium	<0.01	<0.01	<0.01	<0.01
Calcium	150	490	460	370
Chloride	1.6	1.7	1.6	1.9
Chromium	0.03	<0.003	<0.003	<0.003
Cobalt	0.31	0.085	<0.005	0.39
Copper	0.12	0.01	0.008	0.76
Fluoride	1.1	1.1	1.5	4.4
Iron(Fe^{2+})	45.6	0.0055	0.0058	1.08
Iron(total)	56.2	0.0056	0.0124	1.90
Lead	0.1	0.27	0.18	0.26
Lithium	0.0223	0.0297	0.0262	0.0580
Magnesium	35	100	100	91
Manganese	5.5	5.1	1.9	17
Molybdenum	0.065	0.33	0.11	0.11
Nickel	0.59	0.13	0.04	0.52
Potassium	5.2	7.5	8.3	8.4
Selenium	<0.002	<0.002	<0.002	<0.002
Silica	32	16	17	55
Sodium	14	26	25	24
Strontium	0.96	1.8	2.1	1.0
Sulfate	760	1,600	1,600	1,600
Thallium	0.016	0.004	0.003	0.018
Vanadium	0.01	0.04	0.01	0.03
Zinc	0.13	0.05	0.008	0.52
Charge Balance, %	-3.12	-2.15	-7.26	-0.489

Table 3. Physical measurements and chemical analyses of water collected from the Leviathan/Bryant Creek drainage basin--Continued

	Site#19.2	Site#20	Site#20.2	Site#20.5
	Sample Code Number			
	82WA157	82WA126	82WA155	82WA124
	Date Collected			
Determination	10/5/82	6/17/82	10/5/82	6/17/82
Discharge, m^3 sec^{-1}	<0.0003	0.012	0.0009	0.003
Temperature, ^{o}C	12.8	13.5	8.6	15.5
Specific Conductance,				
field, uS cm^{-1}	2,670	418	758	1,680
lab, uS cm^{-1}	2,490	447	736	1,550
pH, field	3.78	7.73	4.19	3.65
lab	3.66	7.66	3.99	3.83
Eh, volts	0.669	0.385	0.497	0.602
Alkalinity, mg L^{-1} as HCO_3^-	------	39.2	------	------
Aluminum	51	0.12	6.5	30
Antimony	<0.0005	<0.0005	<0.0005	<0.0005
Arsenic	0.012	0.003	0.021	0.001
Barium	0.009	0.04	<0.005	0.02
Beryllium	0.009	<0.002	<0.002	0.007
Bismuth	<0.0005	<0.0005	<0.0005	<0.0005
Boron	0.1	0.02	0.04	0.10
Cadmium	<0.01	<0.01	<0.01	<0.01
Calcium	380	53	89	200
Chloride	2.0	1	1.4	2.1
Chromium	<0.003	<0.003	0.009	<0.003
Cobalt	0.38	0.009	0.04	0.18
Copper	0.89	0.005	0.38	0.53
Fluoride	4.4	0.39	0.61	1.7
Iron(Fe^{2+})	0.500	0.0147	0.0089	1.86
Iron(total)	1.29	0.0154	0.0336	2.27
Lead	0.19	0.02	0.16	0.1
Lithium	0.0650	0.0102	0.0161	0.0413
Magnesium	96	14	22	49
Manganese	20	1.2	3.1	8.7
Molybdenum	0.10	0.02	0.057	0.071
Nickel	0.52	0.04	0.10	0.33
Potassium	9.5	3.6	7.7	12
Selenium	<0.002	<0.002	<0.002	<0.002
Silica	49	23	34	46
Sodium	23	9.7	11	14
Strontium	0.99	0.34	0.39	0.85
Sulfate	1,700	190	360	910
Thallium	0.016	0.002	0.003	0.008
Vanadium	0.01	<0.005	0.02	<0.005
Zinc	0.60	<0.006	0.15	0.45
Charge Balance, %	0.466	-7.48	2.68	0.355

Table 3. Physical measurements and chemical analyses of water collected from the Leviathan/Bryant Creek drainage basin--Continued

Determination	Site#20.5	Site#21		Site#22
	Sample Code Number			
	82WA154	82WA125	82WA156	82WA123
	Date Collected			
	10/5/82	6/17/82	10/5/82	6/17/82
Discharge, m^3 sec^{-1}	0.0005	0.003	0.003	0.003
Temperature, ^{o}C	11.2	15.5	14.0	19.0
Specific Conductance,				
field, uS cm^{-1}	183	2,900	3,000	200
lab, uS cm^{-1}	122	4,160	3,360	198
pH, field	7.60	3.19	3.35	8.10
lab	7.66	2.38	2.27	8.29
Eh, volts	0.396	0.622	0.618	0.328
Alkalinity, mg L^{-1} as HCO_3^-	107	------	------	131
Aluminum	0.02	73	57	0.02
Antimony	<0.0005	<0.0005	<0.0005	<0.0005
Arsenic	0.0009	0.001	0.001	0.003
Barium	<0.005	0.006	<0.005	0.03
Beryllium	<0.002	0.01	0.01	<0.002
Bismuth	<0.0005	<0.0005	<0.0005	<0.0005
Boron	<0.02	0.30	0.27	<0.02
Cadmium	<0.01	<0.01	<0.01	<0.01
Calcium	20	420	380	24
Chloride	0.8	2.0	2.0	0.8
Chromium	0.01	<0.003	<0.003	<0.003
Cobalt	<0.005	0.63	0.42	<0.005
Copper	<0.003	1.9	1.6	<0.003
Fluoride	0.02	5.9	5.2	0.03
Iron(Fe^{2+})	0.0010	173	167	0.0461
Iron(total)	0.0040	196	190	0.0569
Lead	0.05	0.24	0.18	<0.02
Lithium	0.0018	0.0704	0.0714	<0.0010
Magnesium	4.8	110	95	6.1
Manganese	<0.01	23	22	<0.01
Molybdenum	0.02	0.35	0.11	0.007
Nickel	<0.004	0.77	0.65	<0.004
Potassium	0.7	22	28	1
Selenium	<0.002	<0.002	<0.002	<0.002
Silica	22	46	33	26
Sodium	9.3	22	22	10
Strontium	0.29	0.57	0.56	0.34
Sulfate	1.3	2,300	2,000	1.1
Thallium	<0.001	0.013	0.012	0.002
Vanadium	0.009	0.05	0.03	<0.005
Zinc	<0.006	0.79	0.80	<0.006
Charge Balance, %	0.381	-1.55	3.22	-1.35

Table 3. Physical measurements and chemical analyses of water collected from the Leviathan/Bryant Creek drainage basin--Continued

	Site#22	Site#23.5		Site#24
	Sample Code Number			
	82WA153	82WA110	82WA149	82WA108
	Date Collected			
Determination	10/5/82	6/15/82	10/4/82	6/15/82
Discharge, m^3 sec^{-1}	0.0037	0.071	0.040	0.091
Temperature, °C	7.3	19.5	8.3	12.5
Specific Conductance,				
field, uS cm^{-1}	209	1,000	1,350	150
lab, uS cm^{-1}	179	1,260	1,600	143
pH, field	8.25	3.25	------	8.85
lab	8.20	2.90	2.84	8.24
Eh, volts	0.399	0.689	0.662	0.379
Alkalinity,				
mg L^{-1} as HCO_3^-	125	------	------	94.3
Aluminum	0.02	19	20	0.03
Antimony	<0.0005	<0.0005	<0.0005	<0.0005
Arsenic	0.001	0.010	0.0082	0.001
Barium	0.005	0.056	0.04	0.04
Beryllium	<0.002	<0.002	0.003	<0.002
Bismuth	<0.0005	<0.0005	<0.0005	<0.0005
Boron	<0.02	0.02	0.03	<0.02
Cadmium	<0.01	<0.01	<0.01	<0.01
Calcium	22	77	140	14
Chloride	0.9	1.1	1.4	1
Chromium	0.02	0.037	0.032	0.02
Cobalt	0.01	0.27	0.31	0.03
Copper	<0.003	0.26	0.13	<0.003
Fluoride	0.02	0.52	1.2	0.04
Iron(Fe^{2+})	0.0035	9.01	23.6	0.0086
Iron(total)	0.0058	18.4	35.5	0.0099
Lead	0.09	0.08	0.2	<0.02
Lithium	0.0016	0.0145	0.0208	0.0024
Magnesium	5.8	22	35	5.6
Manganese	<0.01	2.9	5.4	0.03
Molybdenum	0.03	0.044	0.071	0.01
Nickel	0.01	0.55	0.57	0.02
Potassium	0.9	4.6	5.0	3
Selenium	<0.002	<0.002	<0.002	<0.002
Silica	24	46	33	35
Sodium	10	12	14	7.1
Strontium	0.33	0.72	1.0	0.23
Sulfate	1.3	480	720	1.9
Thallium	<0.001	0.033	0.017	<0.001
Vanadium	0.02	<0.005	0.02	<0.005
Zinc	<0.006	0.18	0.13	0.56
Charge Balance, %	-2.81	-1.77	4.31	-3.82

Table 3. Physical measurements and chemical analyses of water collected from the Leviathan/Bryant Creek drainage basin--Continued

	Site#24	Site#25		
	Sample Code Number			
	82WA147	81WA130C	82WA109	82WA148
	Date Collected			
Determination	10/4/82	10/9/81	6/15/82	10/4/82
Discharge, m^3 sec^{-1}	0.057	------	0.16	0.091
Temperature, ^{o}C	7.0	5.0	16.0	7.0
Specific Conductance,				
field, uS cm^{-1}	162	455	435	500
lab, uS cm^{-1}	151	407	477	467
pH, field	8.20	6.70	4.90	5.53
lab	8.14	6.84	3.87	4.34
Eh, volts	0.344	0.303	0.692	0.370
Alkalinity,				
mg L^{-1} as HCO_3^-	95.5	------	------	------
Aluminum	0.02	0.11	4.8	0.39
Antimony	<0.0005	<0.0005	<0.0005	<0.0005
Arsenic	0.002	<0.0005	0.005	0.003
Barium	0.03	0.03	0.05	0.04
Beryllium	<0.002	<0.002	<0.002	<0.002
Bismuth	<0.0005	<0.0005	<0.0005	<0.0005
Boron	<0.02	<0.02	<0.02	<0.02
Cadmium	<0.01	<0.01	<0.01	<0.01
Calcium	15	52	42	51
Chloride	1.1	------	1	1.1
Chromium	0.02	<0.003	<0.003	<0.003
Cobalt	0.02	0.067	0.11	0.090
Copper	<0.003	0.005	0.11	0.02
Fluoride	0.04	------	0.30	0.21
Iron(Fe^{2+})	0.0059	3.60	4.44	6.94
Iron(total)	0.0110	3.70	4.72	7.00
Lead	0.07	<0.02	<0.02	0.07
Lithium	0.0021	<0.0010	0.0073	0.0084
Magnesium	6.0	15	13	15
Manganese	<0.01	1.5	1.2	1.5
Molybdenum	0.02	<0.003	0.007	0.03
Nickel	0.01	0.14	0.23	0.19
Potassium	3	3.1	3.6	3.8
Selenium	<0.002	<0.002	<0.002	<0.002
Silica	33	29	36	32
Sodium	7.4	9.6	9.0	9.9
Strontium	0.25	0.44	0.41	0.46
Sulfate	1.3	0.2	210	220
Thallium	<0.001	0.002	0.017	0.005
Vanadium	0.02	<0.005	<0.005	<0.005
Zinc	<0.006	<0.006	0.04	0.03
Charge Balance, %	-0.787	------	0.741	2.13

Table 3. Physical measurements and chemical analyses of water collected from the Leviathan/Bryant Creek drainage basin--Continued

Determination	Site#26		Site#27	
	Sample Code Number			
	82WA107	82WA146	82WA105	82WA144
	Date Collected			
	6/15/82	10/4/82	6/15/82	10/4/82
Discharge, m^3 sec^{-1}	0.22	0.11	0.0085	0.0057
Temperature, $^{\circ}C$	21.0	12.7	17.5	12.2
Specific Conductance, field, uS cm^{-1}	390	412	350	369
lab, uS cm^{-1}	445	396	345	355
pH, field	5.30	7.69	8.41	8.20
lab	3.76	7.53	8.36	8.40
Eh, volts	0.398	0.404	0.340	0.439
Alkalinity, mg L^{-1} as HCO_3^-	------	33.8	168	173
Aluminum	0.48	0.05	0.03	0.03
Antimony	<0.0005	<0.0005	<0.0005	<0.0005
Arsenic	0.003	0.001	0.003	0.002
Barium	0.05	0.03	0.05	0.04
Beryllium	<0.002	<0.002	<0.002	<0.002
Bismuth	<0.0005	<0.0005	<0.0005	<0.0005
Boron	<0.02	<0.02	<0.02	<0.02
Cadmium	<0.01	<0.01	<0.01	<0.01
Calcium	39	41	31	31
Chloride	1.2	1.2	4.0	4.1
Chromium	<0.003	0.02	<0.003	0.009
Cobalt	0.084	0.059	<0.005	<0.005
Copper	0.071	<0.003	<0.003	<0.003
Fluoride	<0.002	0.22	0.069	0.008
Iron(Fe^{2+})	5.12	0.0018	0.0236	0.0155
Iron(total)	5.52	0.0091	0.0242	0.0389
Lead	<0.02	0.1	<0.02	0.07
Lithium	0.0067	0.0078	0.0044	0.0047
Magnesium	13	14	15	16
Manganese	1.0	0.98	0.01	<0.01
Molybdenum	0.010	0.035	0.01	0.03
Nickel	0.19	0.11	<0.004	<0.004
Potassium	4.0	4.3	5.3	5.6
Selenium	<0.002	<0.002	<0.002	<0.002
Silica	46	32	56	54
Sodium	9.5	9.7	15	15
Strontium	0.38	0.38	0.30	0.33
Sulfate	190	150	39	45
Thallium	0.013	0.003	0.001	<0.001
Vanadium	<0.005	0.01	<0.005	0.01
Zinc	0.03	<0.006	<0.006	<0.006
Charge Balance, %	-4.78	1.27	-1.65	-6.08

Table 3. Physical measurements and chemical analyses of water collected from the Leviathan/Bryant Creek drainage basin--Continued

	Site#28		Site#29	
	Sample Code Number			
	82WA106	82WA145	82WA104	82WA143
	Date Collected			
Determination	6/15/82	10/4/82	6/14/82	10/4/82
Discharge, m^3 sec^{-1}	0.24	0.11	0.071	0.11
Temperature, $^{\circ}C$	20.0	13.5	23.0	14.0
Specific Conductance,				
field, uS cm^{-1}	350	406	430	442
lab, uS cm^{-1}	431	396	452	416
pH, field	5.88	7.78	5.50	7.80
lab	3.86	7.45	3.83	7.80
Eh, volts	0.338	0.394	0.392	0.423
Alkalinity,				
mg L^{-1} as HCO_3^-	2.65	39.7	------	39.2
Aluminum	0.14	0.06	0.32	0.14
Antimony	<0.0005	<0.0005	<0.0005	<0.0005
Arsenic	0.003	0.001	0.001	0.001
Barium	0.05	0.03	0.05	0.03
Beryllium	<0.002	<0.002	<0.002	<0.002
Bismuth	<0.0005	<0.0005	<0.0005	<0.0005
Boron	<0.02	<0.02	0.02	<0.02
Cadmium	<0.01	<0.01	<0.01	<0.01
Calcium	39	41	41	39
Chloride	1.3	0.9	1.3	1.6
Chromium	<0.003	0.009	<0.003	0.02
Cobalt	0.084	0.05	0.077	0.05
Copper	0.045	0.03	0.051	<0.003
Fluoride	0.11	<0.002	0.20	0.22
Iron(Fe^{2+})	4.84	0.0013	4.29	0.0019
Iron(total)	5.17	0.0033	4.59	0.0066
Lead	<0.02	0.08	<0.02	0.1
Lithium	0.0079	0.0075	0.0070	0.0081
Magnesium	12	15	13	15
Manganese	1.0	0.95	0.99	0.87
Molybdenum	0.01	0.032	0.010	0.037
Nickel	0.19	0.10	0.41	0.088
Potassium	4.1	4.6	4.2	4.9
Selenium	<0.002	<0.002	<0.002	<0.002
Silica	45	34	47	35
Sodium	9.9	10	11	12
Strontium	0.38	0.38	0.39	0.41
Sulfate	180	160	190	160
Thallium	0.013	0.003	0.014	0.003
Vanadium	<0.005	0.007	<0.005	0.02
Zinc	0.03	<0.006	0.03	<0.006
Charge Balance, %	-2.42	-2.56	-0.048	-2.23

Table 3. Physical measurements and chemical analyses of water collected from the Leviathan/Bryant Creek drainage basin--Continued

	Site#29.5		Site#30	
	Sample Code Number			
	82WA101	82WA142	81WA129N	82WA103
	Date Collected			
Determination	6/14/82	10/4/82	10/8/81	6/14/82
Discharge, m^3 sec^{-1}	40	5.6	------	40
Temperature, ^{o}C	10.0	11.5	13.0	12.8
Specific Conductance,				
field, uS cm^{-1}	65.0	126	233	80.0
lab, uS cm^{-1}	53.0	113	195	60.0
pH, field	7.65	8.18	8.72	7.60
lab	7.79	6.92	8.05	7.72
Eh, volts	0.347	0.379	0.302	0.239
Alkalinity,				
mg L^{-1} as HCO_3^-	27.6	52.6	------	29.2
Aluminum	0.04	0.04	<0.01	0.06
Antimony	<0.0005	<0.0005	<0.0005	<0.0005
Arsenic	0.002	0.004	0.0080	0.002
Barium	0.02	0.02	0.03	0.02
Beryllium	<0.002	<0.002	<0.002	<0.002
Bismuth	<0.0005	<0.0005	<0.0005	<0.0005
Boron	0.02	0.09	0.22	0.02
Cadmium	<0.01	<0.01	<0.01	<0.01
Calcium	5.6	9.8	18	6.6
Chloride	0.6	2.8	8.3	0.7
Chromium	0.02	0.02	<0.003	0.03
Cobalt	0.02	0.01	<0.005	0.02
Copper	<0.003	<0.003	0.003	<0.003
Fluoride	0.05	0.074	------	0.05
Iron(Fe^{2+})	0.0162	0.0152	0.0130	0.0076
Iron(total)	0.0239	0.0426	0.0260	0.0087
Lead	0.03	0.05	<0.02	0.05
Lithium	0.0047	0.0158	<0.0010	0.0041
Magnesium	1.6	3.1	4.9	2.0
Manganese	<0.01	<0.01	0.01	0.04
Molybdenum	0.01	0.02	<0.003	0.02
Nickel	0.007	0.007	<0.004	0.01
Potassium	0.7	2	2	0.9
Selenium	<0.002	<0.002	<0.002	<0.002
Silica	13	21	21	14
Sodium	2.9	9.0	16	3.3
Strontium	0.085	0.19	0.26	0.098
Sulfate	2.9	10	27	8.2
Thallium	<0.001	<0.001	<0.001	<0.001
Vanadium	0.008	0.008	<0.005	0.01
Zinc	<0.006	0.01	<0.006	<0.006
Charge Balance, %	4.96	2.13	------	-0.416

Table 3. Physical measurements and chemical analyses of water collected from the Leviathan/Bryant Creek drainage basin--Continued

	Site#30	Site#30.2	Site#30.3
		Sample Code Number	
	82WA141	82WA102	82WA100
		Date Collected	
	10/4/82	6/14/82	6/14/82
Determination			
Discharge, m^3 sec^{-1}	5.6	40	40
Temperature, °C	9.2	10.4	8.0
Specific Conductance, field, uS cm^{-1}	144	69.1	56.0
lab, uS cm^{-1}	137	55.0	51.0
pH, field	8.05	7.60	8.20
lab	8.11	7.73	7.59
Eh, volts	0.421	0.300	0.352
Alkalinity, mg L^{-1} as HCO_3^-	49.1	28.6	32.3
Aluminum	0.02	0.05	0.04
Antimony	<0.0005	<0.0005	<0.0005
Arsenic	0.004	0.002	0.003
Barium	0.02	0.02	0.02
Beryllium	<0.002	<0.002	<0.002
Bismuth	<0.0005	<0.0005	<0.0005
Boron	0.08	0.03	0.03
Cadmium	<0.01	<0.01	<0.01
Calcium	12	5.9	5.6
Chloride	3.0	0.6	0.6
Chromium	0.02	0.03	0.02
Cobalt	0.01	0.02	0.02
Copper	<0.003	<0.003	<0.003
Fluoride	0.090	0.051	0.04
Iron(Fe^{2+})	0.0040	0.0309	0.0167
Iron(total)	0.0089	0.0394	0.0207
Lead	0.05	0.06	0.03
Lithium	0.0158	0.0038	0.0047
Magnesium	3.8	1.8	1.6
Manganese	0.07	0.02	<0.01
Molybdenum	0.02	0.02	0.02
Nickel	0.01	0.01	0.007
Potassium	2	0.7	0.7
Selenium	<0.002	<0.002	<0.002
Silica	22	13	13
Sodium	9.5	2.9	2.9
Strontium	0.21	0.088	0.084
Sulfate	20	5.4	2.4
Thallium	<0.001	<0.001	<0.001
Vanadium	0.008	0.02	0.007
Zinc	<0.006	<0.006	0.007
Charge Balance, %	5.85	-1.20	-6.65

earlier samples preceding later ones at a given site. Figures 2A and 2B show locations of all sites from which water samples were collected. Unless specified in the table, the units are mg L^{-1}. Temperature is reported to the nearest 0.1°C; pH is reported to the nearest 0.01 unit; Eh to the nearest 0.001 volt. Specific conductance, alkalinity, Fe^{+2}, Fe^{total}, Li, and charge balance are reported to three significant figures. All remaining data are reported to two significant figures. For the latter two categories, one significant figure is dropped if the reported value is less than or equal to ten times the detection limit for that determination. Charge balances (%) are those calculated from WATEQ3 (Ball and others, 1981) after speciation according to the equation

$$\text{Charge Balance (\%)} = \frac{200(\Sigma\text{meq } L^{-1} \text{ cations} - \Sigma\text{meq } L^{-1} \text{ anions})}{\Sigma\text{meq } L^{-1} \text{ cations} + \Sigma\text{meq } L^{-1} \text{ anions}} \qquad (1)$$

Cu and Zn are determined using either cassette. In constructing Table 3, if a value greater than the detection limit occurred for each cassette, the values were averaged. If not, the cassette 2 value was taken, because analysis for Cu and Zn using cassette 2 has been determined to be more precise than using cassette 1. One exception to this is the Zn value for sample 82WA148, an instance in which the cassette 2 data appeared upon closer examination to have been underestimated.

Hg and Te Determinations on a Limited Subset of Samples

Three sites were sampled during October, 1981 for Hg. During hydride methodology testing, samples from the four sites sampled during October, 1981 were analyzed for Te. All three of the Hg samples contained less than the detection limit of 0.1 μg L^{-1} Hg. Sample 81WA132C was found to contain 4±0.5 μg L^{-1} Te; the three remaining samples contained less than the detection limit of 0.5 μg L^{-1} Te.

Arsenic Redox Species Determination

Sample 82WA169 was analyzed by molybdate-blue colorimetry for As(V) and total As. The total As concentration was 28±1 mg L^{-1}, and the As(V) was 26±1 mg L^{-1}. By difference, the As(III) concentration was 2±1 mg L^{-1}.

Comparison of Data Obtained by Alternate Methods

Tl was analyzed by both d.c. plasma emission (DCP) and graphite furnace atomic absorption spectrometry (GFAAS). Figure 3 compares the concentrations estimated by these two techniques. The scatter at the lower concentrations indicates that the actual DCP detection limit for Tl in acid mine water is about 50 μg L^{-1}. The slight slope deviation below a Tl concentration of about 1 mg L^{-1} suggests the possibility that a small, uncorrected interference on the DCP determination of Tl may be present.

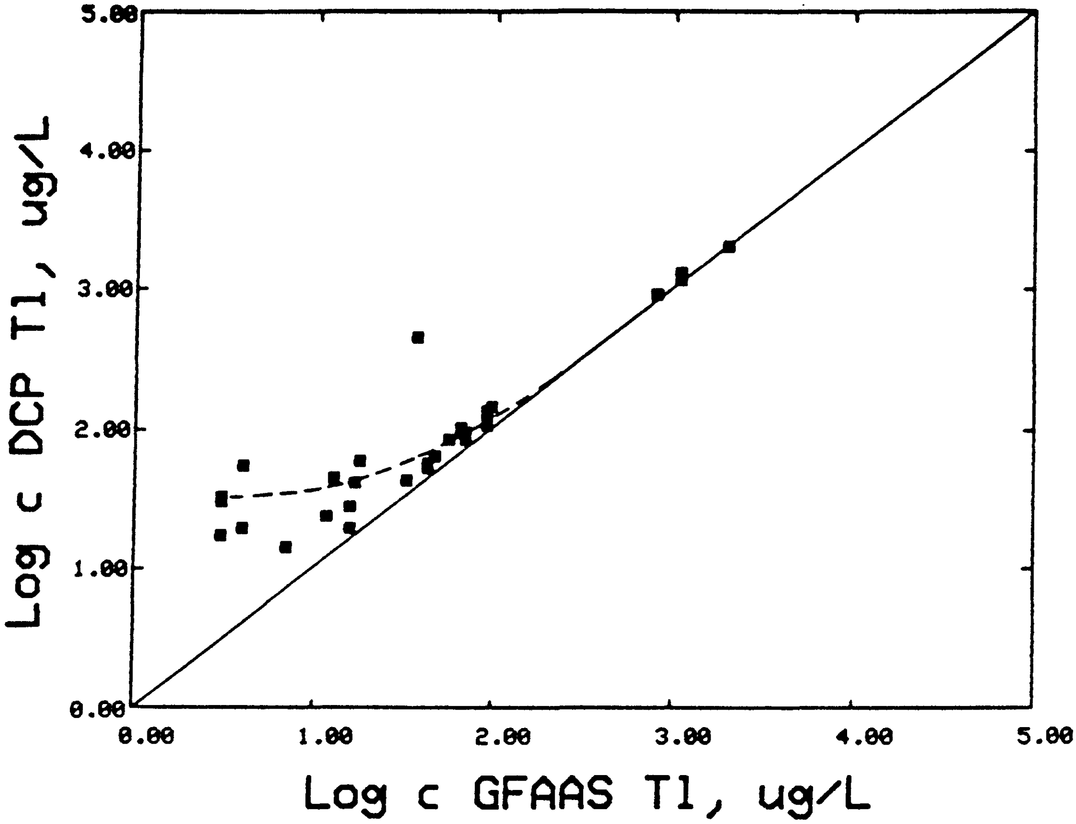

Figure 3. Comparison of Tl by GFAAS to Tl by d.c. plasma.

Arsenic was analyzed by five different techniques: (1) d.c. plasma with direct nebulization of the sample solution, (2) d.c. plasma following hydride generation and cold-trap preconcentration, (3) molybdate-blue colorimetry, and (4) atomic absorption following hydride generation, with and (5) without cold-trap preconcentration. The hydride generation-d.c. plasma technique was investigated in an effort to achieve simultaneous multielement analysis of the hydride elements. This approach appeared promising, but further method development is necessary. Its implementation has therefore been deferred as of this writing. Figure 4 shows a comparison of total As analyzed by molybdate-blue versus hydride/AA. Only the most concentrated samples were determined by the molybdate-blue technique because of a reaction between the sample and the color reagent that appeared to destroy the color reagent's blue response to As. The agreement between the two methods is very good, especially above 0.1 mg L^{-1}. At low concentrations the effect of some positive interference in the colorimetric technique may be indicated. Figure 5 shows the comparison of total As analyzed by DCP to that by hydride/AA. Most samples contained too little As to be detected by the DCP technique. The agreement between the higher level values is quite good, but is poor at the lower levels because the detection limit for the DCP determinations was about 1 mg L^{-1} As in these particular samples.

Selected samples were analyzed for Na by flame atomic absorption spectrometry. Figure 6 illustrates marked disagreement between Na values estimated using the two measurement techniques above about 15 mg L^{-1}. The DCP results for several dilutions of a given sample are markedly imprecise, and are therefore the ones that are suspect. In fact, if DCP values at alternate sample dilutions are substituted (Figure 7), the disagreement is reduced significantly. However, since the disagreements all occur in the highly concentrated acid waters, where Na is a relatively minor constituent, errors of the magnitude illustrated have little effect on the interpretation of the water chemistry.

Specific conductance was measured both in the field at the time of sample collection, and about 2 years later in the laboratory. Specific conductance was also calculated by the method of Laxen (1977) using data obtained by analysis of the samples for the major constituents Ca, Mg, Na, K, Cl, SO_4, HCO_3, NO_3, H, and OH. Figures 8 and 9 compare calculated and laboratory conductance, respectively, to field conductance. The greater scatter of the lab versus field conductance plot, compared to the calculated versus field conductance plot, reflects the chemical changes that have occurred in the samples over the 2-year interval. The closeness of approximation to a straight line of the calculated versus field conductances suggests that both the solute concentration determinations and the field conductance measurements are accurate. Since ion-specific conductance parameters are not available for Fe and Al, their effect on the conductance cannot be calculated, nor evaluated.

Nordstrom and others (1979) have demonstrated that the measured Eh values of acid mine waters are sometimes strongly correlated to their Fe redox chemistry. Emf of the sample water was measured in the field with a Pt electrode and converted to Eh, and the Eh was computed by WATEQ3 (Ball and others, 1981) using measured concentration data for Fe(II) and Fe(III). Figure 10 is a plot of calculated versus measured Eh of the samples. The data points represented by circles are for samples which contain <0.06 mg L^{-1} total Fe; the remaining

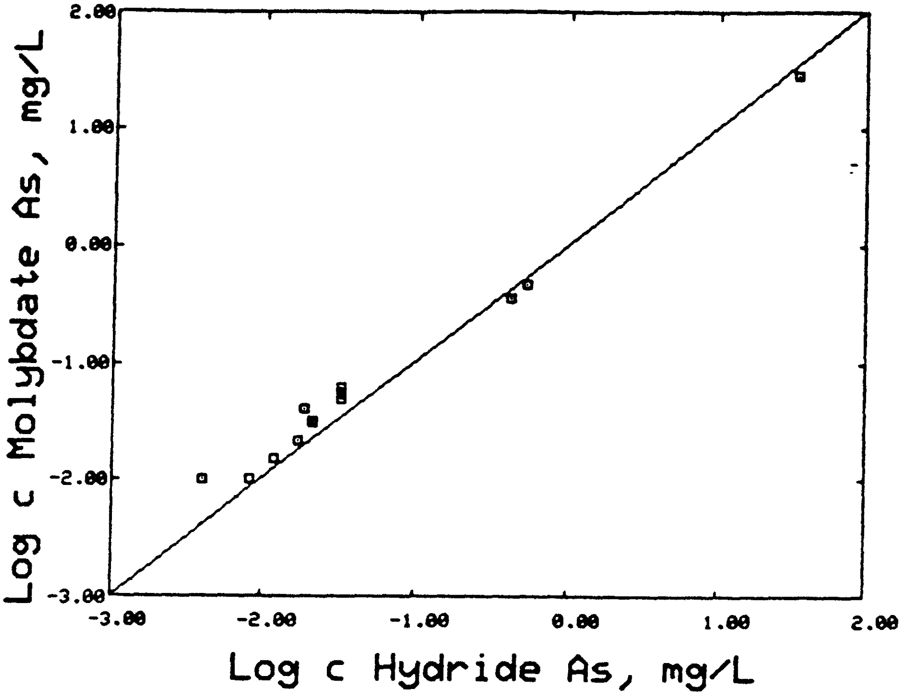

Figure 4. Comparison of As by molybdate-blue to As by hydride-atomic absorption.

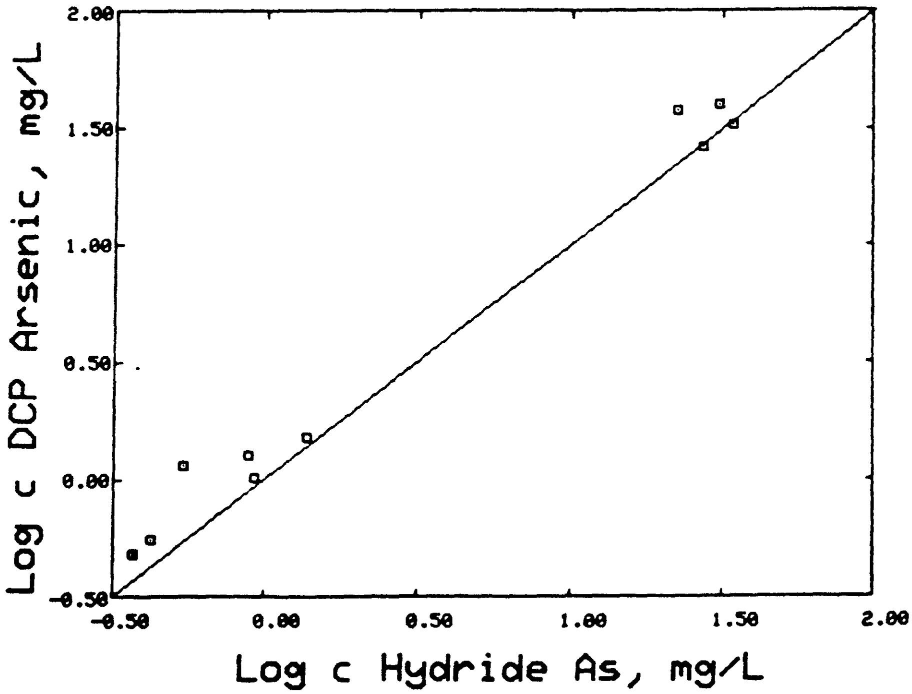

Figure 5. Comparison of As by d.c. plasma to As by hydride-atomic absorption.

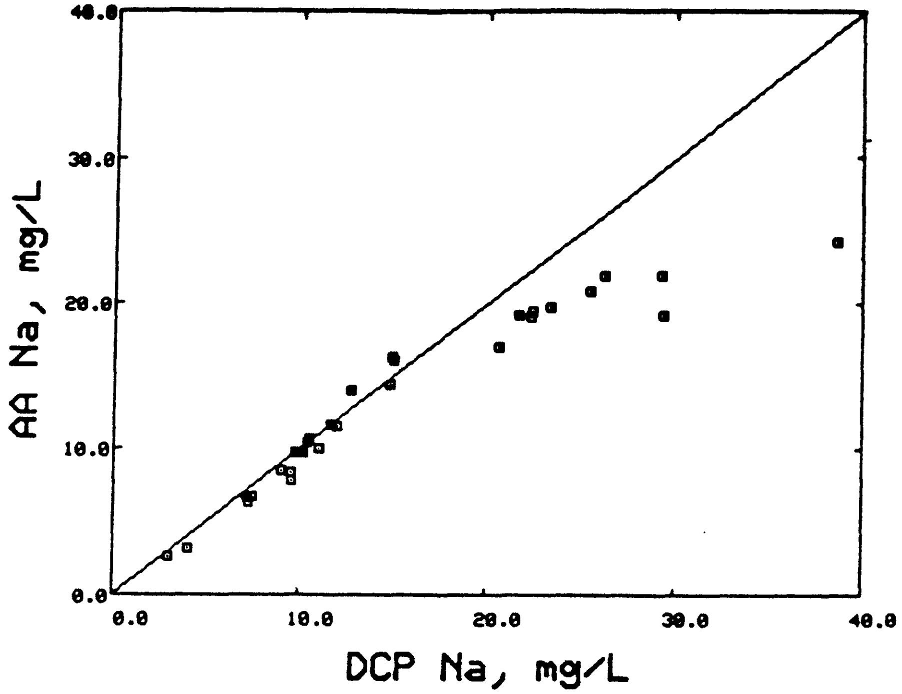

Figure 6. Comparison of Na by flame atomic absorption to Na by d.c. plasma.

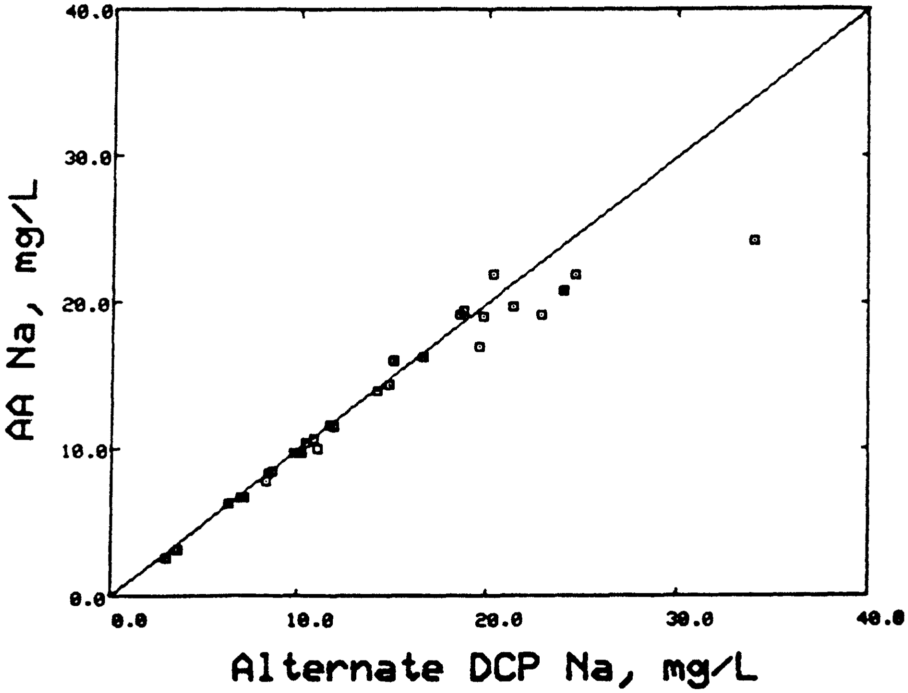

Figure 7. Comparison of Na by flame atomic absorption to selected alternate d.c. plasma Na values.

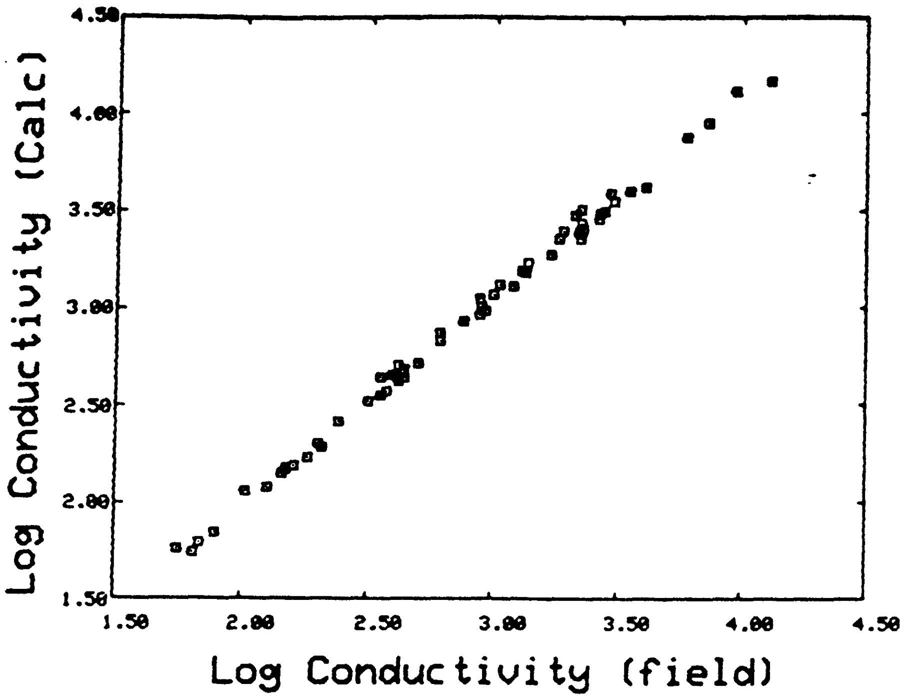

Figure 8. Comparison of calculated to field conductance.

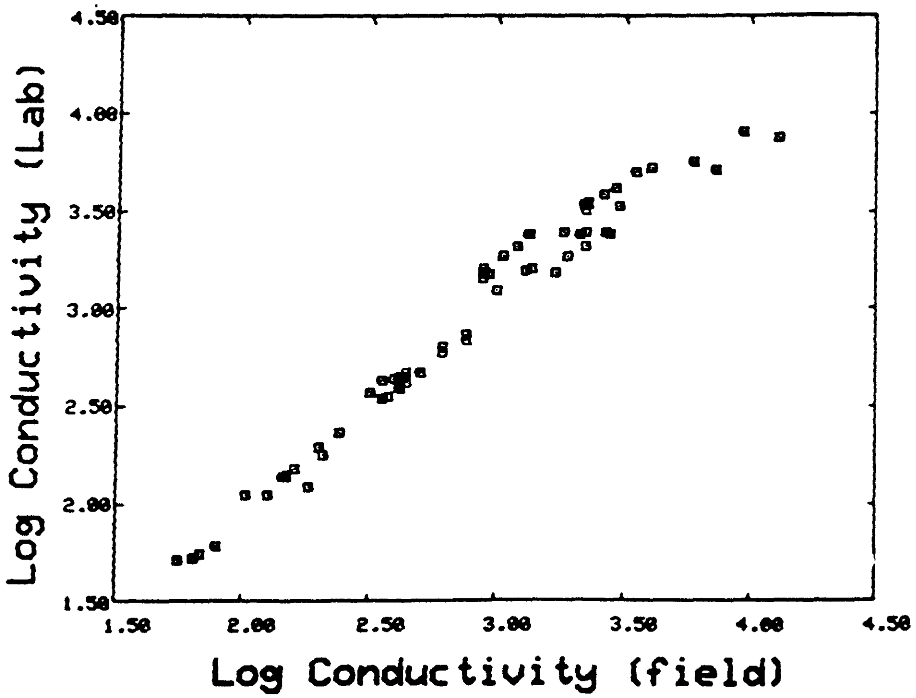

Figure 9. Comparison of conductance measured 2 years later in the laboratory to field conductance.

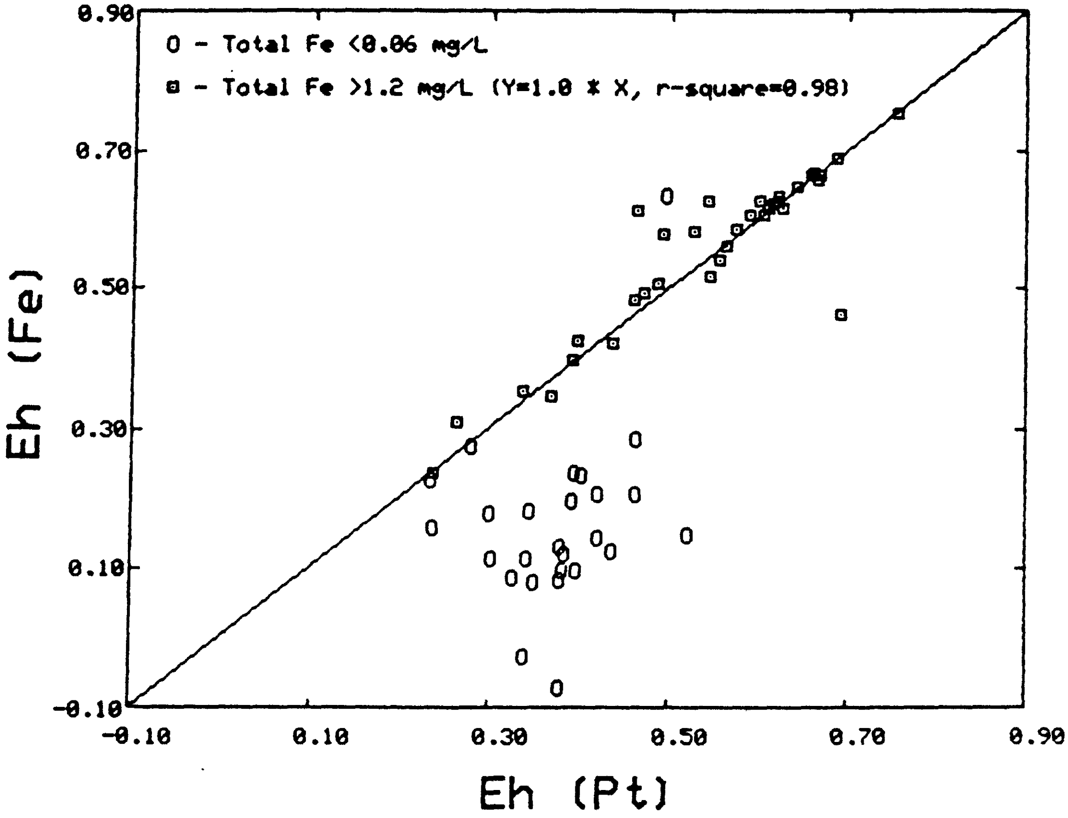

Figure 10. Comparison of Eh calculated from $Fe^{2/3}$ activity ratio to Eh measured with a platinum electrode.

samples, represented by squares, all contain >1.2 mg L^{-1} Fe. The one outlying data point below and to the right of the slope=1 line is for a measurement taken in a turbulent mixing zone where differential precipitation of Fe and Al oxides was occurring, and stable pH and emf readings could not be obtained. The three most outlying high-Fe points above the line near the lone "O" contain >20 mg L^{-1} As. Under these conditions, As redox chemistry may be affecting the emf that was measured with the Pt electrode. The lone "O" sample is from a spring with a strong H_2S odor, suggesting that S redox chemistry may be causing the measured emf to be low. A simple linear regression of the remaining data points yields a slope of 1.0 and an r-square of 0.98. This correlation demonstrates that at Fe concentrations above 1.2 mg L^{-1}, and in the absence of significant concentrations of other redox couples, the measured redox electrode potential is in equilibrium with the Fe redox chemistry of these waters. The absence of samples containing Fe in the 0.06 to 1.2 mg L^{-1} range precludes speculation regarding further reduction of the lower Fe concentration limit; however, such reduction may, in fact, prove to be possible.

In addition to the ferrozine technique, Fe was analyzed by d.c. plasma using both of the cassettes. Figures 11 and 12 illustrate the agreement between DCP, cassettes 1 and 2, respectively, with ferrozine data, above 0.3 mg L^{-1} Fe. The upward scatter in DCP values below this level is very likely due to memory in the DCP aerosol introduction device. The six-order-of-magnitude range of Fe concentrations in the samples of this set was a secondary reason for utilizing the ferrozine technique to measure ferrous and total Fe.

Evaluation of Sulfate Data and Selection of Best Values

The SO_4 concentrations are of critical importance in the accuracy of chemical speciation and mineral equilibrium calculations because SO_4 is the only major anion and it therefore contributes substantially to the charge balance. In several cases, the cations Fe and Al approach but do not equal SO_4 in concentration. Precision of the Fe data is good to excellent. Comparable Al data from d.c. plasma analyses run at alternative dilutions, but not selected, closely approximate the selected concentration estimates. Replicate SO_4 values frequently had less-than-acceptable precision. This was due to temperature fluctuations during analysis, undiagnosed failure of instrumental electronics, analyses performed with conditions optimized for another constituent, changing of separator and suppressor columns at irregular intervals, and sample aging. When SO_4 values obtained under these differing analytical conditions were compared, sometimes the values which had been previously judged suboptimal seemed to be the more logical choice when assessed in conjunction with knowledge of charge balance and confluence mass-balance results.

For the above reasons, SO_4 concentration estimates were recalculated using only peak area measurements. This alternative set of values was tested against the values estimated using peak height measurements to determine which data set appeared to give a more coherent interpretation of the hydrogeochemistry of the drainage basin.

Due to a higher level of inconsistency in analyses performed later than June, 1983, all data gathered after that time were omitted from further consideration. Where several values for a single sample were in good agreement,

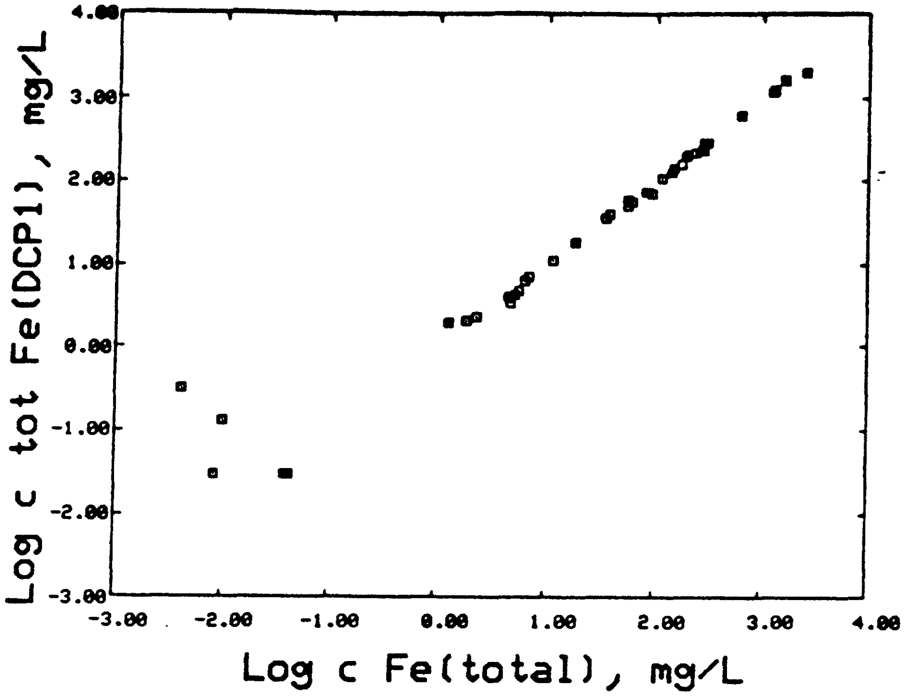

Figure 11. Comparison of d.c. plasma cassette 1 Fe to ferrozine Fe.

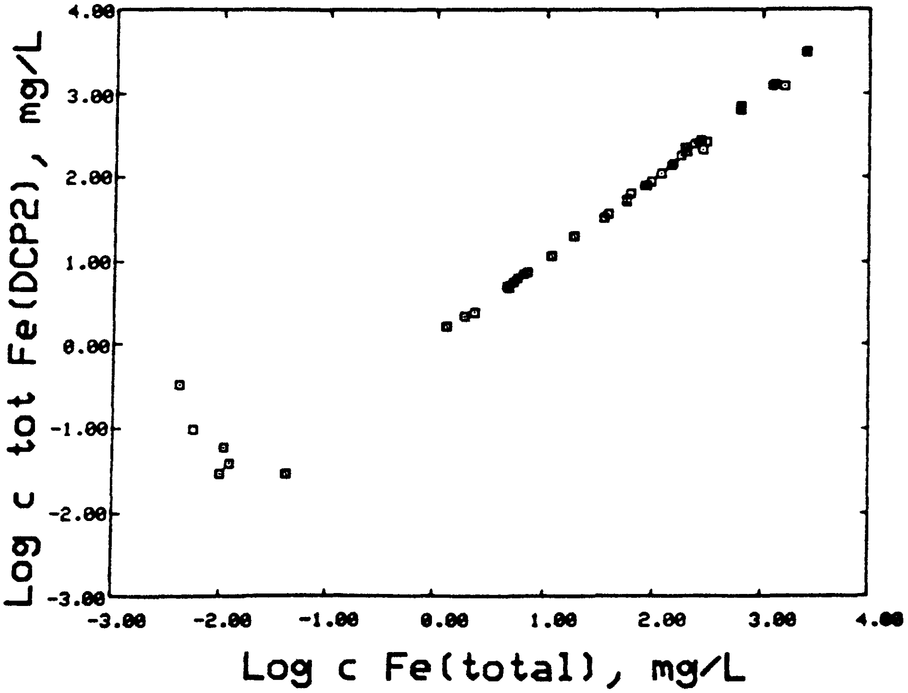

Figure 12. Comparison of d.c. plasma cassette 2 Fe to ferrozine Fe.

they were averaged. If agreement between replicates was poor, individual analytical runs were scrutinized to determine their overall desirability in terms of linearity, goodness of fit of several standards to the curve, and detector response of the sample relative to the standards. If an alternate value was available, responses which were either very low or above the top standard were not considered. For a small subset of samples, there was no clearly defined criterion for selecting one divergent concentration estimate over another. In these instances, the values were used to perform WATEQ charge-balance calculations. If the charge balance difference calculated from the mean value was less than ±10%, the mean value was retained; if not, the individual values which did yield reasonable balances were retained. Most values are simply the mean of all analyses done during 1982 and the first 6 months of 1983. The imbalances fall fairly regularly into individual analytical runs, and are quite randomly distributed among sample types and sources. It, therefore, seems unlikely that an unanalyzed cation or anion is responsible for the sometimes large charge imbalances calculated.

The histogram plots in Figures 13A to 13D illustrate the improvement in distribution of the charge balances using peak area versus peak height SO_4 concentrations. Since the ionic valences in the input concentration data cannot reflect the actual charge distribution of all the solute species, scattering of the input charge balances is expected, particularly for samples of low pH where significant protonation occurs. After speciation calculations, the scatter in the charge balances should be reduced. A comparison of Figures 13A and 13B reveals that, in fact, the scattering is greater, whereas the desired trend is apparent in a comparison of Figures 13C and 13D. This comparison suggests that combining the peak area data with the critical selection discussed above results in a more reliable overall set of data.

ANALYSIS OF ELEMENTAL SULFUR AND STABLE ISOTOPES: ORIGIN OF ACID MINE WATERS AT LEVIATHAN

The ore body at the Leviathan mine was primarily composed of thick veins of elemental sulfur, large amounts of which can be found scattered throughout the waste dumps. Hence, it was thought that most of the acid mine water was produced from the oxidation of sulfur even though occurrences of pyrite, marcasite and chalcopyrite have been reported (Evans, 1977). Very few specimens of pyrite could be found after extensive searching on waste piles. Both pyrite and sulfur samples were submitted for $^{34}S/^{32}S$ isotope analysis, and the sulfur was also analyzed for As, Sb, Se and Bi to compare with the sulfur-isotope composition and trace-element composition of the tunnel 5 effluent. If there is any fractionation of isotopes or trace elements between the pyrite and the sulfur, then the composition of the most acid water should reflect the mineral being oxidized most rapidly and possibly the proportion of pyrite- versus sulfur-derived SO_4.

The results of the analysis of the elemental sulfur and the tunnel 5 effluent are reported in Table 4 in $\mu g\ g^{-1}$ of sulfur for column 1. Since the sample was solid sulfur, these values are equivalent to the elemental ratios relative to sulfur, and can be directly compared to the ratios of dissolved elements to sulfur (in SO_4) in the acid mine effluent. The high

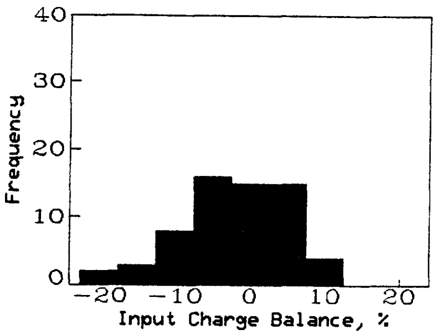

Figure 13A. Frequency plot of input charge balance(initial data)

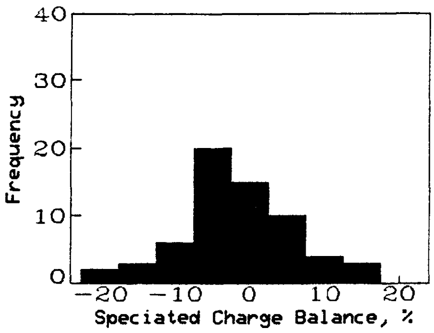

Figure 13B. Frequency plot of speciated charge balance(initial data)

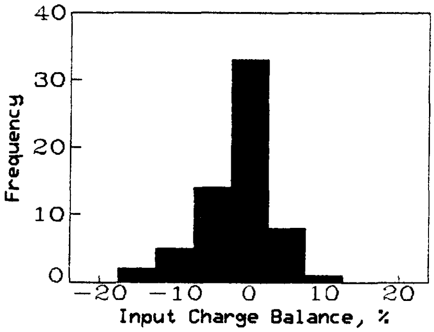

Figure 13C. Frequency plot of input charge balance(revised data)

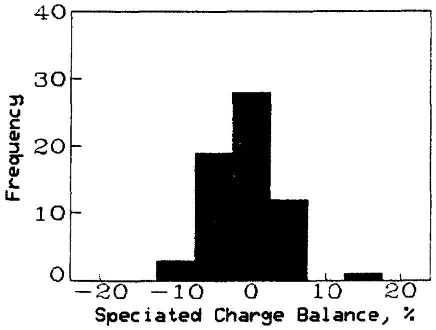

Figure 13D. Frequency plot of speciated charge balance(revised data)

Table 4. Weight ratios of selected elements relative to sulfur in elemental sulfur and acid mine water

	Elemental sulfur	Tunnel 5 effluent
As/S	$<0.4 \times 10^{-6}$	0.5×10^{-3}
Sb/S	$<0.5 \times 10^{-6}$	$<2 \times 10^{-7}$
Bi/S	0.18×10^{-6}	0.6×10^{-6}
Se/S	500×10^{-6}	2×10^{-6}

concentration of Se in the sulfur is to be expected because Se has very similar chemical properties to sulfur, and should have a strong geochemical association. The most striking aspect of this comparison is that the As/S ratio for native sulfur is three orders of magnitude lower than that in the water, whereas the Se/S ratio is more than two orders of magnitude greater than that found for the water. Assuming that all of the Se in the effluent comes from sulfur, and that no chemical fractionation takes place, then only about 0.4% of the dissolved SO_4 in the tunnel 5 effluent is due to the oxidation of elemental sulfur. Chemical fractionation of Se, such as adsorption or precipitation, is highly unlikely due to the strong protonation of the SeO_3 and SeO_4 ions in these acid waters and the strong competition from SO_4 and AsO_3/AsO_4 which are present in much higher concentrations. The remaining dissolved SO_4 must be a byproduct of the oxidation of pyrite, and that pyrite must have a high As content.

Isotopic analyses confirm that little sulfur is oxidizing. Negligible fractionation of $^{34}S/^{32}S$ occurs when pyrite or sulfur is oxidized to SO_4 under acidic conditions (Field, 1966; Taylor and others, 1984). Therefore, the isotopic composition of sulfur in the dissolved SO_4 should be identical to that in the pyrite. The isotope analyses given in Table 5 demonstrate that this is correct. Unfortunately, pure pyrite was not analyzed, and all whole-rock sulfur isotope determinations were contaminated with some sulfur. Nevertheless, Table 5 shows that the sulfur isotope signature does not agree with the elemental sulfur and agrees much better with rock samples containing pyrite.

This conclusion raises an important question: where is the pyrite? Almost no identifiable pyrite can be found in hand specimens in surface outcrop or waste dumps, whereas native sulfur is found everywhere. The answer was given by Pabst (1940), who gives a description of pyrite from Leviathan, including X-ray, optical and spectrographic data. The pyrite commonly occurs as a soft, black, friable, and cryptocrystalline material dispersed through the altered tuff, sometimes imparting a grayish color to the rock. This form of pyrite would make hand-specimen identification extremely difficult, and it would suggest that pyrite is abundant throughout the whole rock. The qualitative emission-spectrographic data show that

Table 5. $\delta^{34}S$ values for sulfur-containing phases

Sample	$\delta^{34}S$ (CD)*
Tunnel 5 aqueous SO_4^{2-}	-17.5, -17.6
Open pit aqueous SO_4^{2-}	-17.6
Whole-rock sulfur (containing variable pyrite)	-15.3 (average of 7 determinations)
Elemental sulfur	-12.1, -12.7, -11.8

*Relative to the Canyon Diablo troilite standard.

the pyrite has high concentrations of Ni, As, and Cr with traces of Cu and V. These results correlate well with the composition of the tunnel 5 and open pit drainages which consistently contain high concentrations of As, Ni, and Cr and slightly lower concentrations of Cu and V. The pyrite is easily oxidized since it is very fine-grained, an observation also made by Pabst (1940). Efflorescences of soluble sulfate salts can grow within a day or two after samples of this pyrite are briefly rinsed in water.

Therefore, the acid mine waters issuing from the Leviathan mine are being produced by the oxidation of abundant fine-grained pyrite occurring throughout the rock. The overall reaction is:

$$FeS_2 + 15/4\ O_2 + 7/2\ H_2O \rightarrow Fe(OH)_3 + 2H_2SO_4 \qquad (2)$$

However, when the pH drops below 4.0, significant amounts of dissolved ferric iron are produced that increase the oxidation of pyrite by the following reaction:

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \qquad (3)$$

Reactions (2) and (3) can both be catalyzed by the iron-oxidizing bacterium, Thiobacillus ferrooxidans. Further details of this process can be found in a review by Nordstrom (1982). Evidence for microbial catalysis at Leviathan has been obtained by bacterial examination of 2 water samples from the tunnel 5 effluent. These samples were found to contain high concentrations of Thiobacillus ferrooxidans and Thiobacillus thiooxidans (Aaron Mills, written comm., 1982).

SUMMARY

The inactive Leviathan open-pit sulfur mine became the subject of a pollution abatement project of the California Regional Water Quality Control Board about 1980. The U.S. Geological Survey has collected basic hydrologic and water quality data for the drainage basin. One aspect of the data collection effort was to study the aqueous geochemistry of the major and trace constituents of the water.

Water collected from the sampling sites was filtered and preserved as it was collected, to minimize the effects of oxidation, precipitation, adsorption, and vaporization. Temperature, pH, Eh, and specific conductance were measured at the time and place of sampling. Concentrations of solute species were determined later in the laboratory on the preserved samples. Al, Ba, B, Be, Cd, Ca, Cr, Co, Cu, Pb, Mg, Mn, Mo, Ni, K, Si, Na, Sr, V, and Zn were determined by d.c.-argon plasma emission spectrometry (DCP). Fe was determined by DCP and the ferrozine colorimetric technique. Tl was determined by DCP and by graphite furnace atomic absorption spectrophotometry. As was determined by DCP, molybdate-blue colorimetry, and hydride generation/atomic absorption. Sb, Bi, Se, and Te were determined by hydride generation/atomic absorption. Hg was determined by cold-vapor flameless atomic absorption. Li was determined by flame atomic absorption. Selected samples were also analyzed for Na and K by flame atomic absorption. F, Cl, and SO_4 were determined by ion chromatography.

Several approaches were utilized to check the quality of the analyses. Many solutes were analyzed by two or more techniques, as mentioned above. Conductance was calculated using concentrations of major solutes and compared to the on-site measurements. Eh was calculated from the Fe^{2+}/Fe^{3+} activity ratio for comparison to the Eh determined using a Pt electrode. Solution charge balance was calculated both before and after equilibrium geochemical speciation calculations, and material balances for solutes were calculated for the three members of all the confluences that were sampled. Corrections suggested by one quality control check were often consistent with other checks, and all techniques were needed to adequately appraise data quality. Large charge balance differences (up to 20%) did occur in the most acid samples before WATEQ3 speciation, due to the necessity for redistribution of H^+ among previously unprotonated input species. The charge balances reported are those calculated following speciation.

The method of choice for low-level Tl determinations is GFAAS. For As, hydride generation-atomic absorption was best for the lowest levels, but not clearly so at elevated concentrations. For the alkali metals, flame atomic absorption may be slightly better, but its routine use as a procedure separate from plasma emission is questionable in view of the added time consumption. Comparison of calculated to measured conductance tended to reinforce accuracy of both measured conductance and measured concentrations of major ions. Comparisons of measured to calculated Eh tended to verify accuracy of both field Eh measurements and colorimetric Fe determinations. Solution charge balance and confluence material balance calculations were both helpful in estimating total SO_4 concentrations.

The water issuing from the mine area was found to contain mg L^{-1} concentrations of As, Cr, Co, Cu, Mn, Ni, Tl, V, and Zn, and hundreds to thousands of mg L^{-1} concentrations of Al, Fe, and SO_4, at pH values as low as 1.8.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the valuable contributions of the following persons: Alan Welch and Dale Hammermeister, whose efforts made this study possible; Kenneth Bencala, Alan Welch, Steven Walmsley, Dale Hammermeister, and Kent Standley for their assistance in water sampling; Gary Zellweger for his assistance in sampling and for performing the GFAAS Tl determinations; Jo Burchard for much support in preparation for field sampling and for performing the Cl, F, and SO_4 determinations; and Mark Wheeler and Bruce Taylor for performing the sulfur isotopic determinations.

REFERENCES

Ball, J. W., Jenne, E. A., and Cantrell, M. W., 1981, WATEQ3--A geochemical model with uranium added: U.S. Geological Survey Open-File Report 81-1183, 81 p.

Ball, J. W., Thompson, J. M., and Jenne, E. A., 1978, Determination of dissolved boron in fresh, estuarine and geothermal waters by d.c. argon-plasma emission spectrometry: Analytica Chimica Acta, v. 98, p. 67-75.

Ellis, A. J., Mahon, W. A. J., and Ritchie, J. A., 1968, Methods of collection and analysis of geothermal fluids, 2nd edition: Chemistry Division, New Zealand Department of Scientific and Industrial Research Report CD 2103, 51 p.

Evans, J. R., 1977, Leviathan mine, in Clark, W. B., ed., Mines and mineral resources of Alpine County, California: Sacramento, California Division of Mines and Geology, County Report 8, p. 35-39.

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

Gibbs, C. R., 1976, Characterization and application of ferrozine iron reagent as a ferrous iron indicator: Analytical Chemistry, v. 48, no. 8, p. 1197-1200.

Hammermeister, D. P., and Walmsley, S., 1985, Hydrologic data for Leviathan Mine and vicinity, Alpine County, California, 1981-83: U.S. Geological Survey Open-File Report 85-160, 120 p.

Harsanyi, E., Polos, L., and Pungor, E., 1973, Enhancement of sensitivity for the determination of mercury in waters: Analytica Chimica Acta, v. 67, p. 229-233.

Johnson, G. W., Taylor, H. E., and Skogerboe, R. K., 1979, Determination of trace elements in natural waters by the d.c. argon plasma multi-element atomic emission spectrometer (DCP-MAES) technique: Spectrochimica Acta, v. 34B, p. 197-212.

Laxen, D. P. H., 1977, A specific conductance method for quality control in waters: Water Research, v. 11, p. 91-94.

Nordstrom, D. K., Jenne, E. A., and Ball, J. W., 1979, Redox equilibria of iron in acid mine waters, in Jenne, E. A., ed., Chemical modeling in aqueous systems: speciation, sorption, solubility, and kinetics: Washington, D. C., American Chemical Society, p. 51-79.

Nordstrom, D. K., 1982, Aqueous pyrite oxidation and the consequent formation of secondary iron minerals, in Kittrick, J. A., Fanning, D. S., and Hossner, L. R., eds., Acid sulfate weathering: Madison, Soil Science Society of America, p. 37-56.

Pabst, A., 1940, Cryptocrystalline pyrite from Alpine County, California: American Mineralogist, v. 25, p. 425-431.

Stauffer, R. E., Jenne, E. A., and Ball, J. W., 1980, Chemical studies of selected trace elements in hot-spring drainages of Yellowstone National Park: U.S. Geological Survey Professional Paper 1044-F, 20 p.

Stookey, L. L., 1970, Ferrozine--a new spectrophotometric reagent for iron: Analytical Chemistry, v. 42, no. 7, p. 779-781.

Taylor, B. E., Wheeler, M. C., and Nordstrom, D. K., 1984, Isotope composition of sulphate in acid mine drainage as a measure of bacterial oxidation: Nature, v. 308, p. 538-541.