

Environmental Controls on Water Quality: Case Studies from Battle Mountain Mining District, North-Central Nevada

By Michele L.W. Tuttle, Richard B. Wanty, and Byron R. Berger

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Chapter A of

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Preface

Northern Nevada is one of the world's foremost regions of gold production. The Humboldt River Basin (HRB) covers 43,500 km² in northern Nevada (Crompton, 1995), and it is home to approximately 18 active gold and silver mines (Driesner and Coyner, 2001) among at least 55 significant metallic mineral deposits (Long and others, 1998). Many of the gold mines are along the Carlin trend in the east-central portion of the HRB, and together they have produced 50 million ounces of gold from 1962 (when the Carlin mine first opened) through April 2002 (Nevada Mining Association, 2002). Mining is not new to the region, however. Beginning in 1849, mining has taken place in numerous districts that cover 39 percent of the land area in the HRB (Tingley, 1998). In addition to gold and silver, As, Ba, Cu, Fe, Hg, Li, Mn, Mo, Pb, S, Sb, V, W, Zn, and industrial commodities such as barite, limestone, fluorite, sand and gravel, gypsum, gemstones, pumice, zeolites, and building stone, have been extracted from the HRB (McFaul and others, 2000).

Due to the large amount of historical and recent mining in the HRB, the Bureau of Land Management (BLM) in Nevada asked the U.S. Geological Survey (USGS) Mineral Resources Program to conduct a series of mineral-deposit-related environmental studies in the HRB. BLM required data and geoenvironmental interpretations regarding (1) the chemical composition of water, soil, sediment, and mine waste in the HRB, (2) the natural background chemistry of these materials, and (3) how mining activities may have altered their chemistry. The paper that follows describes one of the studies conducted by the USGS Minerals Program to answer these and similar questions.

All papers within this series of investigations can be found as lettered chapters of USGS Bulletin 2210, *Geoenvironmental Investigations of the Humboldt River Basin, Northern Nevada*. Each chapter is available separately online.

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Abstract

The environmental controls on water quality were the focus of our study in a portion of the Battle Mountain mining district, north-central Nevada. Samples representing areas outside known mineralized areas, in undisturbed mineralized areas, and in mined areas were chemically and isotopically analyzed. The results are related to geologic, hydrologic, and climatic data.

Streams in background areas outside the mineralized zones reflect normal weathering of volcanically derived rocks. The waters are generally dilute, slightly alkaline in pH, and very low in metals. As these streams flow into mineralized zones, their character changes. In undisturbed mineralized areas, discharge into streams of ground water through hydrologically conductive fractures can be traced with chemistry and, even more effectively, with sulfur isotopic composition of dissolved sulfate. Generally, these tracers are much more subtle than in those areas where mining has produced adits and mine-waste piles. The influence of drainage from these mining relicts on water quality is often dramatic, especially in unusually wet conditions.

In one heavily mined area, we were able to show that the unusually wet weather in the winter and spring greatly degraded water quality. Addition of calcite to the acid, metalrich mine drainage raised the stream pH and nearly quantitatively removed the metals through coprecipitation and (or) adsorption onto oxyhydroxides.

This paper is divided into four case studies used to demonstrate our results. Each addresses the role of geology, hydrology, mining activity and (or) local climate on water quality. Collectively, they provide a comprehensive look at the important factors affecting water quality in this portion of the Battle Mountain mining district.

Introduction

In 1998, the U.S. Geological Survey initiated a study in the Humboldt River basin to access the effect of mineral deposits on surface-water quality. The drainages discussed in this paper are within the Battle Mountain mining district, specifically on the north side of Battle Mountain (Elder Creek) and on the east side (Long, Little Cottonwood, and Galena Canyons) (fig. 1). The goals of the Battle Mountain study are:

- Establish background concentrations of metals in streams flowing through undisturbed mineralized deposits,
- Describe geochemical characteristics of waters in undisturbed and mined drainages,
- 3. Identify the important geochemical processes that control these characteristics (e.g., ore oxidation, metal adsorption, and mineral precipitation),
- Determine the appropriate sampling density needed to recognize diagnostic geochemical characteristics to assess water quality near to and downstream from deposits,
- Understand how local climate variability affects water composition, and
- 6. Integrate geochemical data with geology and hydrology within the drainage basins.

Studies in each of the drainages addressed different goals. Data from the entire study area were used to accomplish the first two goals. The Elder Creek study documented the role of fracture flow in the Battle Mountain drainages and the effect of this type of flow on water quality. The Long Canyon—Licking Creek study focused on the environmental behavior of a low-fluorine molybdenum porphyry system. The Galena Canyon study presented an opportunity to access water quality in a drainage with tributaries affected by different deposit types, various degrees of mining, and an unusually wet spring. Because only three samples were collected in Little Cottonwood Creek, data for the drainage are not discussed in this report but are included in the appendixes.

Background Information

Geology

The Battle Mountain area is geologically complex and reflects multiple episodes of deformation. A mixture of Paleo-



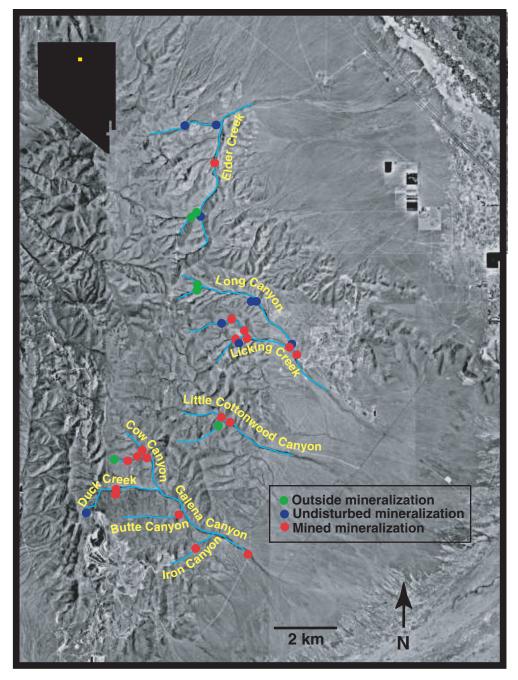


Figure 1. Aerial photo showing stream reaches sampled, sample locations, and mine disturbance upstream from Butte and Iron Canyons. Index map shows location of Battle Mountain study area.

zoic basinal-, slope-, and shelf-sedimentary rocks were structurally juxtaposed during the compressional late Paleozoic Antler and late Paleozoic to early Mesozoic Sonoma orogenies along generally east-verging thrust-fault systems (Roberts, 1964). Structural relations in the Buffalo Mountain range immediately west of the Battle Mountain range suggest that, at least by the Late Jurassic, transpressional tectonics probably dominated the regional structural geology. At this time, many thrust and related faults were reactivated as parts of northweststriking, right-lateral strike-slip systems. Strike-slip tectonics

and related extension dominated in the region from the Jurassic until the late Tertiary. Basin-and-Range extensional tectonics were superimposed on the far-field compression sometime during the Neogene.

Copper, molybdenum, lead, zinc, and silver mineral deposits in the Battle Mountain range are structurally controlled and related to emplacement of igneous intrusions. The oldest intrusive rocks in the Battle Mountain range are Late Cretaceous granodiorites and monzogranites (Theodore, 2000), and the Buckingham porphyry molybdenum deposit

is related to one of the Cretaceous intrusive centers. During the middle Tertiary, there was renewed granodioritic intrusive activity in the range. This period of igneous activity spawned copper-gold porphyry, gold-skarn, and polymetallic vein deposits. The Elder Creek porphyry copper deposit and related skarn are associated with this period of hydrothermal activity, as were the polymetallic vein deposits in the Galena, Butte, and Iron Canyon drainages.

Hydrology

Hydrology of the Battle Mountain area is characterized by mostly ephemeral surface runoff, superimposed on a fracture-controlled ground-water system (Tuttle and others, 2000). Streams flow in the spring and early summer months during snowmelt and periods of thunderstorms. Low annual precipitation (<10 inches in low-elevation valleys and 10–15 inches at higher elevation) (Western Regional Climate Center, 2001) results in overall sparse vegetation, with lush growth only within a few meters of perennial streams or in seep areas. Our samples were collected in May 1998, following an unusually wet spring (10-20 percent above average, see case study IV). Sample locations are shown in figure 1. Estimated stream discharges ranged from 1 L/min to approximately 2,000 L/min, based on visual estimates. Gaining and losing stream reaches were detected with a "sniffer.1" Surface-water runoff is confined to deeply incised canyons in this high-relief region. Typical stream gradients are in the range of 6 percent to greater than 11 percent. During peak spring flows, the filled channels are typically less than a few meters wide and tens of centimeters deep.

No completed wells were available for sampling on Battle Mountain at the time of our sampling. However, several "ground-water" samples were collected from springs distributed around Battle Mountain at a variety of elevations. A spring alongside Long Creek may be an uncompleted exploration well drilled into the outer portion of the Buckingham stock. Other springs sampled in the area include a seep from mineralized rock. Because the aquifers on Battle Mountain are characterized by fracture flow, it is reasonable to assume a geologic-structural control on the location of springs and gaining stream reaches.

Methods

Field Methods

Water samples were collected in the field in May 1998. We attempted to collect stream samples in June of 2000, but most drainages were dry. Field sampling methods included geochemical and hydrologic techniques. At each sampling

site, measurements were made for temperature, specific conductivity, and pH of the waters, using methods cited in Wood (1976). The pH of each sample was measured using a portable pH meter with automatic temperature compensation. The pH meter was calibrated each morning using three standard buffers with nominal pH values of 7.00, 4.01, and 10.00 at 25°C. Calibration slopes were always within 5 percent of ideal Nernstian behavior. At each subsequent stop during the day, the pH calibration was checked by measuring the pH of one of the standard buffers. Resulting values were always within ±0.05 pH units of the accepted value. The accuracy of each sample pH measurement is probably also within this range. Temperature was measured using a NIST-traceable electronic thermistor, accurate to within ±0.1°C. The stainless steel housing of the temperature sensor allowed temperature measurements to be made in the stream itself, as well as in the stream bed by inserting the sensor into the bed. In most cases, temperature differences of several degrees Celsius were observed. Specific conductivity (SpC) was measured using a portable temperature-compensated probe, sensitive to within ± 10 microsiemens/cm (μ S/cm) and accurate to within $\pm 20 \mu$ S/cm.

Samples were collected in the field for later laboratory analyses of major and trace cations, anions, alkalinity, and mercury. Anion samples were filtered through 0.45-µm-nominalpore-diameter cellulose acetate filters and refrigerated with no further treatment. Cation samples were filtered through the same 0.45-um filter and acidified by adding 0.5 mL of concentrated ultra high purity nitric acid to each 30-mL sample. Samples for alkalinity analyses were collected by filling a 125mL bottle, without filtering or acidification—samples were then refrigerated. Mercury samples were filtered with the same 0.45-µm filter into a 60-mL glass bottle. Bottles for mercury analyses were acid-washed prior to sampling, and mercury was preserved with a solution of nitric acid and sodium dichromate (O'Leary and others, 1996). For sulfur isotopes, samples were collected into 1-L high-density polyethylene bottles and refrigerated. The samples were filtered through 0.45-µm filters within 2 weeks of sample collection. For every sample type except alkalinity and sulfur isotopes, field blanks were collected using deionized water that was brought from the laboratory and treated as a sample in the field. This procedure helped assure the purity of reagents used for sample preservation, as well as assuring that the samples were not contaminated during collection. In every case, analyses of field blanks showed below detection concentrations for all constituents.

Laboratory Methods

Upon completion of field work, samples were transported back to the U.S. Geological Survey laboratories in Denver, Colo. Anion and alkalinity samples were kept cool during transport in insulated containers. Cation analyses were performed by inductively coupled plasma, atomic emission spectroscopy (ICP-AES; Briggs, 1996) and by ICP-mass spectrometry (ICP-MS; Lamothe and others, 1996). The ICP-

¹ The "sniffer" is a simple device devised to measure relative head differences (in inches) above or below stream level (Wanty and Winter, 2000).

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AES results are preferred for major cations (Mg, Ca, Na, K) and Fe, Al, and Si. The ICP-MS results are preferred for all other constituents, including first- and second-row transition elements, rare earths, and some actinides.

Anion analyses were conducted on a Dionex DX-500 ion chromatography (IC) system. The chromatography columns used were the AG-14 and AS-14 guard and separator columns, with a CO₃/HCO₃ eluent. Using this method, good analytical separations were made for fluoride, chloride, nitrate, phosphate, and sulfate. The IC was calibrated each day with a minimum of six standards. The accuracy and precision of the IC was checked by running standards as unknowns in at least 10 percent of the IC runs and by running duplicate analyses of 5 to 10 percent of all samples.

Alkalinity was determined by titrating a 50-mL aliquot of sample with standardized sulfuric acid (Papp and others, 1996). An Orion model 960 automatic titrator was used for these analyses. This instrument includes a 15-sample carousel in which to load samples and standards. For each set of 15 analyses, at least two standards were run to check for accuracy and precision.

Samples collected for mercury analyses were filtered in the field through 0.45-µm filters and stored in glass bottles that had been previously washed with nitric acid and dried. The samples were preserved with a mixture of nitric acid and sodium dichromate (O'Leary and others, 1996). Total mercury in these waters was determined using a cold vapor flow injection—atomic fluorescence spectrometry method modified from the method given in O'Leary and others (1996).

Sulfate was precipitated as BaSO₄ from 0.45-µm-filtered samples for isotope analysis. Approximately 0.7 mg of BaSO₄ was combusted with V_2O_5 in an elemental analyzer. The SO_2 gas released was analyzed by mass spectrometry with a reproducibility of $\pm 0.2\%$ (Kester and others, 2001). Isotope values are reported relative to the Cañon Diablo Troilite standard.

Case Study I— Comparative Chemistry of Surface Water Among Drainages Variably Affected by Mineralization and Mining

We established geochemical characteristics of surface water throughout the entire Battle Mountain study area. These characteristics represent baselines for the spring of 1998. Additional sampling was attempted in June of 2000, but all drainages were dry (see Galena Canyon case study).

Sample Distribution

Stream samples were collected to maximize our coverage and springs sampled where ever found (sample locations

in fig 1). At many of the confluences, three samples were taken—one above each tributary and one downstream of the confluence. For a description of sample sites, see Appendix I. The chemical and sulfur isotopic data for all samples collected in 1998 are in Appendix II. The different populations being compared are "outside mineralization" (background samples collected in areas outside of and unaffected by mineralization), "unmined mineralization" (samples collected from drainages crossing unmined mineralized areas), or "mined mineralization" (samples collected from drainages affected by mining).

Comparative Chemistry Among "Background," "Undisturbed," and "Mined" Samples

Box plots in figure 2 graphically show the distribution of chemical data for selected elements split by population (outside mineralization (background), undisturbed mineralization, and mined mineralization). Both stream and seep data are included. Current drinking water standards are shown in table 1 for comparison. Although the median value for some characteristics is not significantly different among populations, the range is always much larger for the "mined mineralization" population (note logarithmic scale on most plots). Many of the samples from the "mined mineralization" population have higher conductivity, lower pH and higher SO₄/Cl ratios. "Outside mineralization" samples are at the head of the drainage; therefore, one might argue that their lower conductivities are due to less rock/water interaction than those samples downstream. The lower SO_4^{2-}/Cl^- ratios (and $\delta^{34}S$ values for dissolved SO₄ in case study III) indicate, however, that the lower conductivity is not due just to less rock/water interaction alone.

Table 1. Current drinking water standards.

[From EPA, 2000. MCL, maximum contaminant level that is enforceable. MCLG, maximum contaminate level goal that is not enforceable. SDWR, secondary drinking water regulation that is not enforceable]

| Chemical | MCL | MCLG | SDWR |
|---------------|-------|------|---------|
| pН | | | 6.5-8.5 |
| As (mg/L) | 0.005 | | |
| Cd (mg/L) | 0.005 | | |
| Cu (mg/L) | | 1.3 | 1.0 |
| Fe (mg/L) | | | 0.3 |
| Pb (mg/L) | | zero | |
| $SO_4 (mg/L)$ | | | 250 |
| Zn (mg/L) | | | 5 |
| | | | |

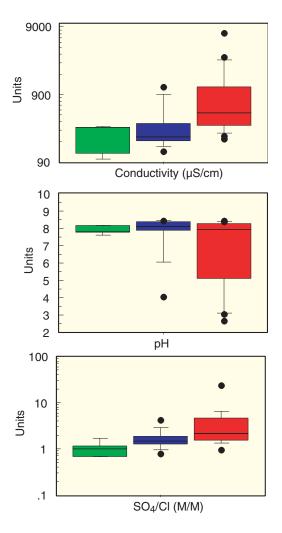
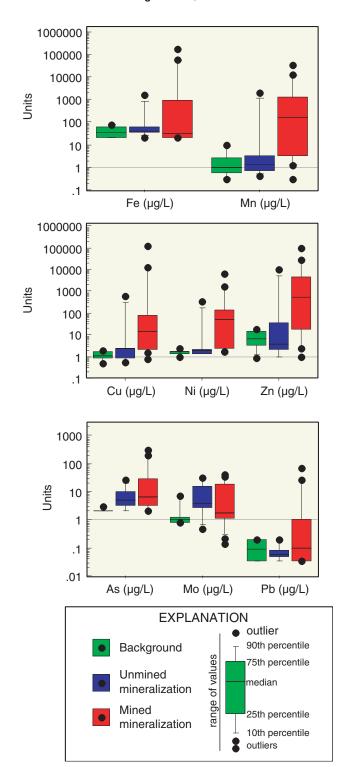


Figure 2 (above and facing column). Box plots showing the range; median; 10th, 25th, 75th, and 90th percentile, and outliers for selected chemical parameters. Data are separated into stream samples from areas outside mineralization, within unmined mineralized, and within mined mineralization.

The trend of larger ranges in the "mined" population is even more evident in the trace-metal plots and is consistent with ore minerals in adits and waste piles weathering and contributing products to the streams. The median and range of trace-metal values for the "unmined mineralization" population is generally intermediate between the "outside mineralization" and "mined mineralization" populations.

Conclusions

Results from this study illustrate that the presence of mineralization, whether mined or undisturbed, affects surfacewater quality. As ground water in contact with mineralization at depth enters the stream through fractures, water quality degrades (see Elder Creek and Long Canyon case studies).



In many drainages, mining activities increase the magnitude of this degradation process by increasing the surface area of reactive minerals in contact with the water. The extent of mining seems to play a role on the amount of weathering products entering the streams, and, in unusually wet years, areas affected by large mining operations can have serious waterquality problems (see Galena Creek case study).

Case Study II— Geological and Structural Controls of Fracture-Dominated Ground-Water Flow at a Variety of Spatial Scales— Elder Creek

An understanding of geologic structures and fracture networks aids the understanding of fracture-controlled flow at a variety of spatial scales, as demonstrated by many studies from throughout the Western United States (Berger and others, 2001). The Elder Creek study documents the interactions between ground water and surface water exhibited throughout the Battle Mountain area as springs, seeps, and gaining and losing stream reaches. Winter and others (1998) have shown that these connections between ground and surface water and their effect on water quality are too numerous to be ignored.

Fracture Control on Water Quality

The fracture system in Elder Creek illustrates the effect of fractures on water quality associated with mineralization in the area. Changes in surface-water flow at Battle Mountain are attributable to ground-water discharge and recharge that occurs in locations where regional-scale (tens of kilometers) throughgoing fractures cross stream drainages. Local-scale fractures (tens to hundreds of meters) are also important. Figure 3 shows a boulder approximately 1 m wide. Nitrophilous lichens grow along those fractures that are hydraulically conductive. The lichens depend on the conductive fractures for a supply of water and nutrients. The nonconductive fractures do not support a lichen community, indicating that not all fractures in this boulder, and by extension in this drainage, are conductive. The question remains as to whether we can explain, using geologic models, which fracture orientations might be more hydraulically conductive than others.

Elder Creek is on the north side of Battle Mountain and flows to the north and east (see fig. 1). In particular, we are interested in the unnamed tributary that flows west to east toward Elder Creek (fig. 4). Dashed-line sections of the stream in figure 4 show stream reaches over which no surface water was observed. At point "a," the stream reemerged with a conductivity of 130 µS/cm. Conductivity consistently increased from point "a" to point "b" as did concentrations of many elements (table 2). A known but undeveloped Cu-porphyry deposit is located in this area as shown by the pink fill in figure 4 between points "a" and "b." Interaction of this mineralized rock with ground water, and subsequent ground-water discharge into the stream, could explain observed increases in concentrations of individual dissolved constituents. The stream disappears again at point "b," at a location that coincides with the projected subcrop of a swarm of fractures observed in the outcrop at point "c." Vectors originating at point "c" on figure



Figure 3. Boulder above Elder Creek demonstrates that not all fractures are hydraulically conductive at the sub-meter scale. The orange patches are nitrophilous lichens, which grow only along those fractures that are hydraulically conductive.

4 show the orientations of observed fractures in outcrop. These fractures are likely hydraulically conductive, as suggested by the presence of a species of wild rye (fig. 5), which requires more moisture than is normally available in this arid region. The decrease in Elder Creek conductivity from south (310 $\mu\text{S/cm})$ to north (270 $\mu\text{S/cm})$ is evidence of hydraulic conductivity of fractures, as more dilute water from the unnamed tributary probably enters Elder Creek from below and mixes with the more conductive waters of Elder Creek.

Conclusions

In Elder Creek we have shown the importance of understanding the fracture network as a means to understanding the hydrologic and geochemical behavior of a drainage system. In this case, the hydrology of the unnamed tributary is controlled by the presence of fractures that cross the stream bed and by

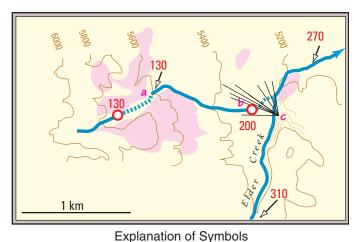




Figure 4. Map of Elder Creek and tributary showing water sample sites and conductivity, orientations of fractures, and outcrop of mineralized porphyry. Dashed blue lines indicate areas along streams where no surface water was observed. Points "a," "b," and "c" are explained in the text.

Table 2. Chemical parameters and concentrations for samples at points "a" and "b" along tributary to Elder Creek (see fig. 4).

| Element | Point "a" (site 33) | Point "b" (site 34) |
|-----------------------------------|---------------------|---------------------|
| pН | 8.14 | 7.85 |
| Conductivity (µS/cm) | 130 | 200 |
| As (μg/L) | 7.2 | 11 |
| Ca (mg/L) | 16 | 20 |
| K (mg/L) | 1.7 | 2.0 |
| Mg (mg/L) | 4.3 | 5.2 |
| Mo (μg/L) | 5.0 | 16 |
| Na (mg/L) | 15 | 20 |
| Si (mg/L) | 8.4 | 11 |
| SO ₄ (mg/L) | 42 | 59 |
| Sr (µg/L) | 100 | 130 |
| V (µg/L) | 2 | 3 |
| W (µg/L) | 0.10 | 0.26 |
| Zn (µg/L) | 3.0 | 20 |
| SO ₄ /Cl (molal basis) | 4.2 | 5.4 |

the fractures that connect the porphyry deposit to the surface. The geochemistry of the stream water is affected by mixing with discharging ground water as the stream crosses over the porphyry deposit. Similarly, the water in Elder Creek proper is diluted somewhat by the reemergent water from the tributary.



Figure 5. Species of wild rye growing in fractured rock above Elder Creek.

Case Study III— Environmental Behavior of a Molybdenum Porphyry System on Battle Mountain— Licking Creek and Long Canyon

This study compiles geological, hydrological, and geochemical data required to understand the environmental behavior of metals associated with a molybdenum (Mo) porphyry system on Battle Mountain. The porphyry is the Buckingham stockwork molybdenum deposit, a low-fluorine, granodiorite molybdenum system (deposit type described in Cox and Singer, 1985). The water quality of streams, natural springs, mine discharge, and ground water from springs was assessed in the region of the Buckingham deposit. In addition, the geology and controls on the hydrology were used to establish a framework for water-quality data.

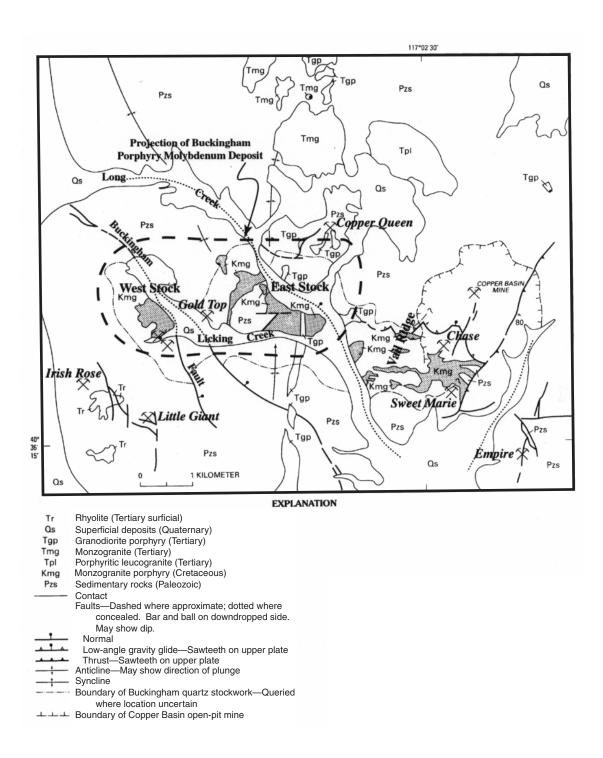


Figure 6. Generalized geologic map of the Late Cretaceous Buckingham porphyry molybdenum deposit, Battle Mountain, Nevada (Theodore and others, 1992). Bold dashed line indicates projection of outer boundary of the molybdenum deposit. Some major Late Cretaceous and early Tertiary polymetallic vein and skarn deposits are indicated in italic.

Geology of the Buckingham Porphyry Molybdenum Deposit

The study site is the location of an unmined, largely buried porphyry molybdenum deposit and associated veins (fig. 6). The deposit is related to a ≅86-Ma composite, porphyritic intrusive into feldspathic sandstone, quartz arenite, and shale of the Upper Cambrian Harmony Formation (Theodore and others, 1992).

Lithology

The Paleozoic Harmony Formation in the Battle Mountain range consists of interbedded quartz arenite, subarkose, arkose, pebbly quartz arenite, shale, and minor limestone (Roberts, 1964). In the Buckingham area, the Harmony consists predominantly of graded sandstone, including quartz arenite, arkose, subarkose, and litharenite with minor amounts of shale, calcareous shale, and greenstone (Theodore and others, 1992). According to Roberts (1964), the mineralogy of the sandstones is quite variable, but generally consists of quartz (60–80 percent), feldspar (≅20 percent), mica (2–5 percent), and matrix cement. The feldspars are a mix of orthoclase, microcline, and sodic plagioclase in proportions that regionally average ≅65 percent potassium feldspar and ≅35 percent oligoclase to sodic andesine. The matrix cements variably consist of clays, calcite, and quartz. Compaction, diagenetic clay growth, and hydrothermal metasomatism have reduced porosity in the Harmony Formation to less than 1 percent (Theodore and others, 1992). Ranges of whole-rock chemical analyses of the Harmony Formation from Theodore and others (1992) are in table 3.

Table 3. Ranges of analytical data (in weight-percent) for the Upper Cambrian Harmony Formation in the Buckingham Camp region, Nevada.

[From Theodore and others, 1992]

| SiO_2 | 57.8-88.3 |
|-------------------|------------|
| Al_2O_3 | 5.48-19.6 |
| Fe_2O_3 | 0.76–2.55 |
| FeO | 0.12-5.5 |
| MgO | 0.45-3.03 |
| CaO | 0.16-8.26 |
| Na ₂ O | 0.53-2.05 |
| K ₂ O | 1.17-5.83 |
| TiO_2 | 0.38-1.03 |
| P_2O_5 | <0.05-0.11 |
| MnO | <0.02-0.08 |
| CO_2 | 0.01-6.3 |
| F | 0.02-0.05 |
| _ | |

Intrusive igneous rocks in the Buckingham area range from Late Cretaceous monzogranite to Eocene monzogranite to early Oligocene(?) rhyolite, porphyritic leucogranite, and granodiorite porphyry (fig. 6). The porphyry molybdenum deposit is genetically related to \cong 86-Ma monzogranites that occur in a generally east-west zone that may be divided into three groups—West stock, East stock, and Vail Ridge dikes and plugs (cf. Theodore and others, 1992). There are four main compositional groups of monzogranitic rocks: (1) monzogranite porphyry, (2) megacrystic monzogranite porphyry, (3) aplite, and (4) a late-stage breccia pipe.

The Cretaceous intrusive phases show variable degrees of hydrothermal alteration. The West stock contains quartz, K-feldspar and clay (or white-mica-altered plagioclase) that is less abundant than in the East stock, and white-mica- or chlorite-altered biotite phenocrysts. The groundmass consists predominantly of fine-grained white mica and disseminated pyrite. Locally, the white mica is intergrown with molybdenite. Stockwork quartz or quartz-sericite veins characterize the West stock and can comprise as much as 40 to 50 volume percent of the rock locally (Theodore and others, 1992). Pyrite occurs in the veins as well as molybdenite. The East stock is similar to the West stock, but there is early-stage potassic alteration, and pervasive clay alteration of plagioclase is more common. The Vail Ridge intrusions consist of narrow dikes and small equant masses and are located east of the porphyry molybdenum deposit. Nevertheless, phyllic to argillic hydrothermal alteration is intense, and there is disseminated molybdenite. Megacrystic monzogranite is most abundant in the East stock, and it is inferred to intrude the porphyritic monzogranite. Aplite is a minor component of the intrusive system. The breccia pipe is located in the East stock and is interpreted to be part of the latest stage of porphyry molybdenum deposit formation.

Between about 39 and 37 Ma, numerous dikes and plutons were emplaced in the Buckingham area (Theodore and others, 1992). The main loci are north of the Buckingham porphyry molybdenum deposit just north of the Copper Queen mine (fig. 6) and south of Buckingham in the vicinity of the Little Giant mine (fig. 6). These rocks include a diverse variety of compositions such as biotite-hornblende monzogranite, porphyritic leucogranite, rhyolite, granodiorite, and minor diorite. Ranges of analytical data for some of these rock types are given in table 4.

Structural Geology

The Battle Mountain range is bounded on the north and south by regional, northwest- southeast-striking right-lateral strike-slip faults (T. Hildenbrand, unpub. data, 2000). The faults within the range form a system of faults linking these two strike-slip fault zones. This duplex of faults provided the permeability and structural control for Cretaceous to Pliocene igneous intrusions and related hydrothermal activity.

Veins within and adjacent to the Buckingham Creta-

Table 4. Ranges (in weight percent) of analyses for late Eocene to early Oligocene intrusive rocks in the Buckingham Camp region, Nevada.

| [Column 2 shows data from biotite-hornblende monzogranite, column 3 from porphyritic leucogranite, and |
|--|
| column 4 from rhyolite. From Theodore and others, 1992] |

| | Monzogranite | Leucogranite | Rhyolite |
|---------------------------|--------------|--------------|---------------|
| SiO_2 | 66.0–70.25 | 61.52–69.3 | 72.82–76.9 |
| Al_2O_3 | 13.46-15.73 | 14.1-16.48 | 12.7-13.27 |
| Fe_2O_3 | 0.62-4.29 | 0.05-1.83 | 0.03-1.48 |
| FeO | 1.8-2.73 | 0.58-3.82 | 0.12-1.11 |
| MgO | 1.14-2.84 | 1.9-2.8 | <0.01-0.39 |
| CaO | 2.32-5.38 | 4.41-7.64 | 0.55-1.14 |
| Na ₂ O | 2.02-3.75 | 2.55-3.9 | 2.3-3.55 |
| K ₂ O | 2.73-4.88 | 0.47 - 3.77 | 4.3-5.73 |
| $\overline{\text{TiO}}_2$ | 0.33-0.54 | 0.37-0.73 | 0.08-0.28 |
| P_2O_5 | 0.12-0.19 | 0.11-0.25 | 0.02-0.07 |
| MnO | 0.02-0.08 | <0.02-0.08 | 0.01-0.06 |
| CO_2 | 0.03-0.13 | 0.04-0.64 | 0.03-0.08 |
| F | 0.09 | 0.02-0.08 | 0.01-0.02 |
| Cl | | | 0.0012-0.0055 |

ceous monzogranites parallel the east-west trend of the intrusions, although the most strongly developed vein sets strike from east-west to N. 60° W. (Theodore and others, 1992). In the molybdenum orebodies in the east and west stocks, post-mineralization faults that strike N. 25° W. crosscut the orebodies and are interpreted to be normal-oblique faults by T. Loucks and C. Johnson (in Theodore and others, 1992). These faults consist of significant gouge and breccia zones, but the amount of rotation along these faults is unknown. One of them, the Buckingham fault, is estimated by Loucks and Johnson (in Theodore and others, 1992) to be 100–225 m thick and to have had 520 m of dip slip and 175 m of right-lateral slip.

Mineral Deposits

The Late Cretaceous Buckingham porphyry molybdenum deposit is a composite of seven mineralizing events (cf. Loucks and Johnson in Theodore and others, 1992). The molybdenum deposit encompasses five events related to two phases of intrusion in the West stock and three in the East stock. Some events form conical zones of veins localized at the apices of monzogranitic intrusions. The highest grades are developed where mineralization events overlap. Accompanying stockwork and disseminated pyrite-molybdenite mineralization are chalcopyrite, scheelite, and tetrahedrite. Some chalcopyrite occurs in the quartz-pyrite-molybdenite veinlets. However, copper concentrations tend to be highest in the peripheral parts of the molybdenum orebodies, occurring in chalcopyrite and freibergite. Low-grade, disseminated chal-

copyrite, pyrrhotite, tetrahedrite, and pyrite are found in latestage dikes that crosscut the molybdenum mineralization (cf. Loucks and Johnson in Theodore and others, 1992).

High-grade, late Eocene to early Oligocene polymetallic veins crosscut the Buckingham porphyry orebodies and also crosscut early Tertiary intrusive rocks (Theodore and others, 1992). Examples include the Little Giant and Irish Rose mines (fig. 6). Veins in the Little Giant mine occur along faults that strike N. 20° W. to N. 65° W. in the Harmony Formation (Roberts and Arnold, 1965). Oxide ores consist of iron oxides, jarosite, cerussite, anglesite, and pyrargyrite with some remnant argentite and polybasite. Primary ore minerals include pyrite, arsenopyrite, galena, sphalerite, and minor tetrahedrite. The Irish Rose mine ores were mined from veins that strike N. 20° W. to N. 10° E. in the Harmony Formation. The primary ores consist of arsenopyrite, pyrite, sphalerite, galena, chalcopyrite, and minor stibnite in a gangue of quartz and calcite (Roberts and Arnold, 1965).

Historic Mining Activity

Long Canyon and Licking Creek cross the Buckingham stockwork molybdenum deposit (fig. 6). There are very few mines in the Long Canyon drainage. The lower portion of the canyon represents an "undisturbed" mineralized area with its upper reaches well outside the mineralized area. Samples from the upper reaches of the stream provide valuable data to assess the water quality attributed to the unmineralized host rock in the area. A small spring (perhaps an uncompleted

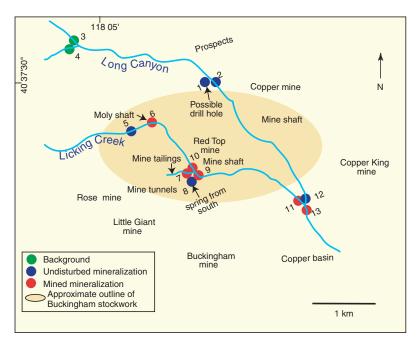


Figure 7. Map showing sample locations and mining activities in Long Canyon and Licking Creek. Outline of Buckingham stockwork from Theodore and others (1992).

drill hole; sample site 1) just outside the molybdenum deposit produces water that may be in contact with the molybdenum-mineralized stockwork at depth. From its chemistry, we have interpreted this spring water to be a natural "deposit drainage" into Long Canyon.

All samples collected along Licking Creek were within the boundary of the Buckingham stockwork molybdenum deposit (fig. 7). As mines and their dumps (some described above) are common throughout the drainage, we have characterized Licking Creek as a "mined" mineralized area. Camp Creek, a tributary to Licking Creek, was a site of the Buckingham Camp where ore was processed. Water from Camp Creek, a small tributary into Licking Creek, represents drainage from mines and processing dumps. Along the Buckingham fault at the confluence where Camp Creek enters Licking Creek, a hillside spring discharges water with high trace-metal content. We interpret this spring water as "deposit drainage" and, although natural and above stream base, is geochemically similar to water in Camp Creek.

Surface-Water/Ground-Water Interactions

In Long and Licking Creeks, numerous gaining and losing stream reaches were observed. These hydraulic data are supported by the chemical measurements of major and trace elements. For example, sites 3 and 4 (sample locations shown in fig. 7) combine near the headwaters of Long Creek; site 2 is below the confluence. Based on the major-element chemistry of those samples, the water at site 2 must also include at least

one other water source. The cation composition of these samples, as shown in a Piper diagram (fig. 8), shows sites 3 and 4, with site 2 shifted slightly toward the composition of site 1. The rare-earth-element (REE) compositions (fig. 9) suggest an input of a water similar to sample 1 to the stream at site 2, consistent with the major cation compositions. Flow at site 2 was greater than the sum of sites 3 and 4, and a large positive vertical hydraulic gradient was observed at site 1, supporting the possibility of ground-water discharge in the vicinity of site 2. Sites 1 and 2 are located along Long Canyon just below the intersection of north- to northwest-striking faults with the Long Canyon fault (Theodore and others, 1992). Site 12 is approximately 2 km downstream from site 2, and its major and REE compositions are close to those for site 2, suggesting no further ground-water discharge but not precluding the possibility of ground-water recharge.

In Licking Creek drainage, the chemistry of the surface water also infers some areas of ground-water discharge. For example, sites 5, 6, and 10 occur along a continuous reach of stream with no other surface-water tributaries. The major anion and cation compositions for sites 5 and 6 are indistinguishable, but sample 10 has higher concentrations of many major and trace elements but lower concentrations of others. This observation suggests an additional input of ground-water discharge between sites 6 and 10 (approximately 1-km stream reach). Similarly, sites 7 (stream) and 8 (spring) are adjacent to each other and appear similar from the Piper diagram (fig. 7). The concentrations of many trace elements and rare earth elements are significantly higher in sample 8 than 7, but the REE concentration ratios of most of those elements for the two

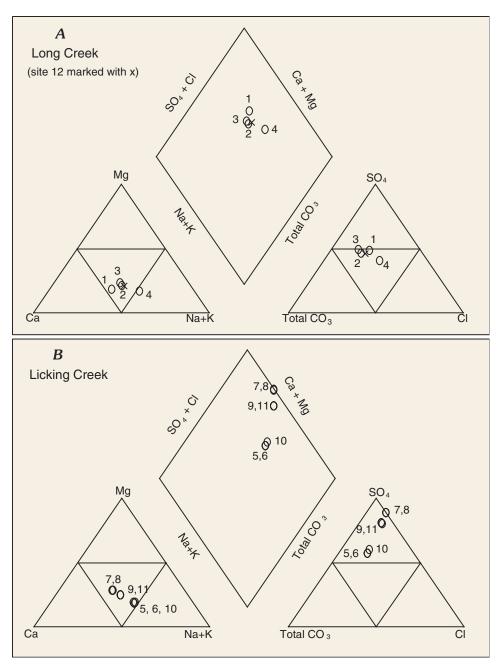


Figure 8. Piper diagrams for samples collected from *A*, Long Canyon; and *B*, Licking Creek.

samples lie within a very narrow range (2.5 to 3.0, fig. 9). A likely scenario explaining this narrow range of variation would be discharge of a ground water with a chemical composition similar to that of site 8 into a slightly more dilute, metal-poor stream to produce the observed chemistry at site 7. In support of this hypothesis, site 8 is a typical acidic, metal-rich drainage (pH 4.0; conductivity >1,100 $\mu\text{S/cm}$; SO₄ >600 ppm; and Al, Mn, and Zn at ppm levels). The other end-member must have major elements similar in concentration to that at site 7 but with low metals and REE concentrations. A ground-water discharge scenario also makes sense, based on the observation

that sites 7 and 8 are within a few meters of each other and the fact that the hydraulic head of the ground water is sufficiently high to create seeps at site 8.

Farther downstream on Licking Creek there is some evidence for ground-water discharge, but most of the changes are attributable to normal water-rock interactions. The primary change in water chemistry between sites 9 and 11 (approximately 2 km) is an increase in pH from approximately 7 to 8. This unit increase in pH appears to drive the adsorption or precipitation of metals such as Zn, Cu, Mn, Ni, Co, Cd, and REEs, and the desorption or dissolution of oxyanion spe-

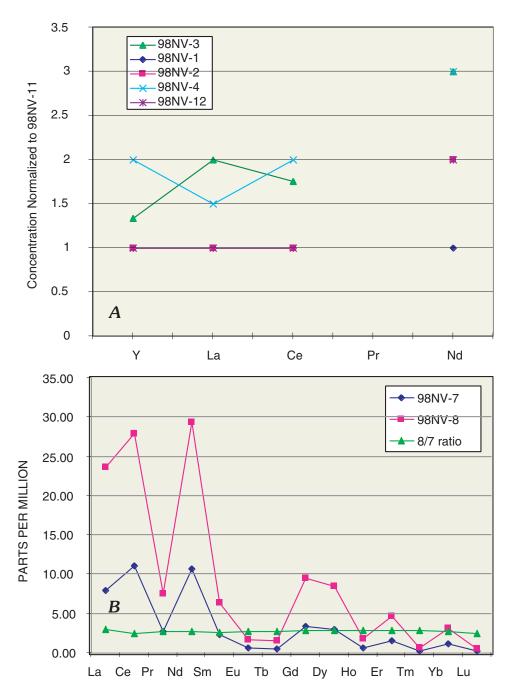


Figure 9. Rare-earth-element distribution in samples from A, Long Canyon; and B, Licking Creek.

cies such as As, Mo, V, and Sb. Aluminum concentrations increased slightly, consistent with a slightly increased solubility of gibbsite from pH 7 to 8. No appreciable change was observed in the major cation and anion concentrations.

Characteristics of Deposit Drainage

Waters thought to be in contact with the Buckingham deposit were collected (compositions are in table 5). The

Buckingham "deposit" sample was collected from the seep flowing from the Buckingham fault zone within the boundary of the Buckingham stockwork molybdenum deposit (site 8). This water has a pH of 4.0 and contains relatively little iron, although iron oxyhydroxides are found around the seep. Zinc accounts for 90 percent of the metal load. The sulfur isotopic composition of the sulfate ($\delta^{34}S_{SO_4}$) in the water is +5.1‰; the value of the sulfur in molybdenite (MoS) in the deposit is +4.3‰ to +5.2‰ (T.G. Theodore as cited in Theodore and others, 1992).

Table 5. Chemical and isotopic composition of dissolved constituents in "deposit" drainage in Long Canyon and Licking Creek.

[Numbers in italic are the proportion of the metal (μ moles/L) relative to the metal load] 1

| | Buckingham (site 8) | Long Canyon (site 1) |
|------------------------------|---------------------|----------------------|
| pH | 4.0 | 7.4 |
| Conductivity (µmho/cm) | 1,150 | 710 |
| Al (μg/L) | 9,880 | 7.2 |
| As (μg/L) | 4.8 | 5.3 |
| | 0.00042 | 0.41 |
| *Cd (µg/L) | 120 | 0.014 |
| | 0.011 | 0.001 |
| *Co (µg/L) | 52 | 0.24 |
| | 0.0050 | 0.018 |
| *Cu (µg/L) | 613 | 0.56 |
| | 0.054 | 0.043 |
| Fe (μg/L) | 40 | 1,640 |
| *Mo (μg/L) | 0.45 | 2.8 |
| | 0.00004 | 0.22 |
| *Ni (μg/L) | 352 | 3.0 |
| | 0.031 | 0.23 |
| *Pb (μg/L) | 0.20 | 0.08 |
| | 0.00001 | 0.006 |
| *Zn (µg/L) | 10,300 | 1.0 |
| | 0.90 | 0.077 |
| SO ₄ (mg/L) | 628 | 135 |
| $^{34}{ m S}_{ m SO_4}(\%o)$ | 5.1 | 5.2 |
| F:Cl molar ratio | 0.04 | 0.02 |

¹ Metal load is defined in this paper as the sum of metals, excluding iron, on a molal basis.

The Long Canyon "deposit" sample was collected from a seep near the deposit boundary on the inferred Long Canyon fault (site 1 on fig. 7). The water has a pH of 7.4 and was weakly effervescent (the likely gas is carbon dioxide). The dominant metal in this water is iron; however, arsenic (41 percent), nickel (23 percent), and Mo (22 percent) account for 96 percent of the metal load as defined previously. The sulfur isotopic composition of the sulfate ($\delta^{34}S_{SO_4}$) in the water is +5.2%. Both the Long Canyon and Buckingham waters have very low fluoride to chloride molar ratios (F:Cl ratio, 0.02 and 0.04 respectively), consistent with the Buckingham stock hosting a low-fluorine-type molybdenum deposit.

Concentrations of Dissolved Metal in Stream Drainages

Figures 10 and 11 graphically show how the log of the elemental concentrations in stream water spatially change relative to concentrations in the "deposit samples.²" In Long Canyon (fig. 10), the mineralized, undisturbed site, only pH

and Mo are consistently higher than in the deposit sample. Stream pH values are between 7.6 and 8.4; these alkaline values represent weathering of the volcaniclastic country rocks (Tuttle and others, 2000), with possible contributions by removal of CO₂ by algal growth. High pH enhances the mobility of Mo by several possible mechanisms: inhibiting adsorption to iron oxides, favoring desorption of Mo from iron oxides, or by increasing the solubility of molybdenum minerals. The dissolved iron (Fe) concentrations remain nearly constant throughout the stream and are very similar to those in the "deposit" sample. The relatively high pH of the stream and deposit drainage would favor precipitation of a mineral phase (goethite or amorphous Fe(OH)₃), thus controlling the concentration of Fe. Concentrations of most other metals in stream water are less than 1 percent of the concentration in the "deposit" sample and do not significantly change concentrations until Licking Creek enters the drainage (fig. 10).

In comparison to Long Canyon, the base-metal load in Licking Creek (mineralized, mined site) increases substantially after the "deposit" sample enters the stream (fig. 11), possibly due to contribution from weathering of mine waste in the near vicinity (fig. 7). Iron is similar in concentration to that in the deposit sample due to precipitation of oxyhydroxides. Molybdenum and As are higher in the stream water than in the deposit sample, consistent with the higher pH in the stream limiting adsorption onto freshly precipitated iron oxyhydroxides. Most metal concentrations decrease slightly when Licking Creek mixes with the more dilute Long Canyon; however, the relative metal concentrations are consistent with values ascribed to the "deposit" sample.

Figures 10 and 11, show that the composition of the "deposit" sample is preserved downstream in Licking Creek, the drainage that has been mined. In contrast, the overall composition of stream water in Long Canyon is not significantly changed by the mineralization that occurs lower in the drainage. These relations suggest that Long Canyon receives a smaller input of deposit drainage relative to its flow when compared to Licking Creek.

Trends in Sulfur Isotopic Composition of Stream Sulfate

To better understand the extent to which the molybdenum porphyry affects water quality in Long Canyon, sulfur isotopes were investigated. Figure 12 shows the sulfur isotopic composition ($\delta^{34}S_{SO_4}$, ‰) of sulfate in the stream water and of molybdenum porphyry "deposit" samples for both Licking Creek and Long Canyon.

² Log (variable in stream sample / variable in "deposit" sample). Samples that plot on the zero line have the same value as that of the "deposit" sample in the drainage. Samples with negative values have smaller values, and those with positive values have larger values than the "deposit" sample.

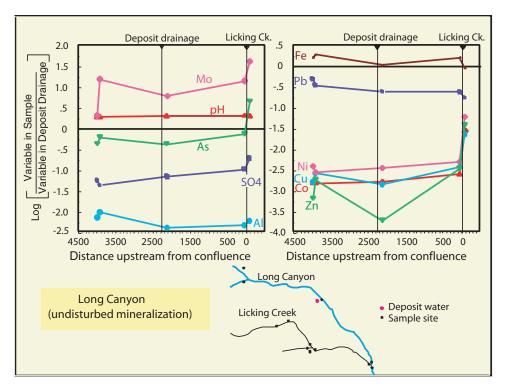


Figure 10. Log of ratio of variables in Long Canyon samples to those in the "deposit" sample plotted against the distance upstream from the confluence of Long Canyon and Licking Creek.

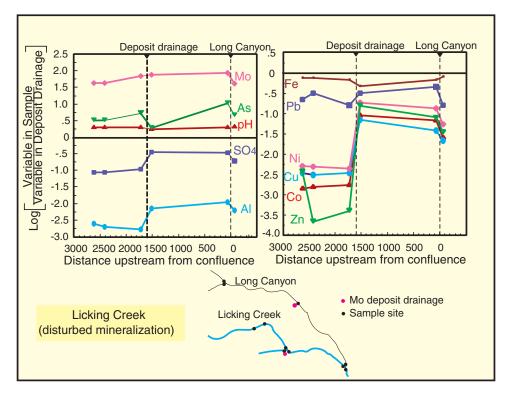


Figure 11. Log of ratio of variables in Licking Creek samples to those in the "deposit" sample plotted against the distance upstream from the confluence of Long Canyon and Licking Creek.

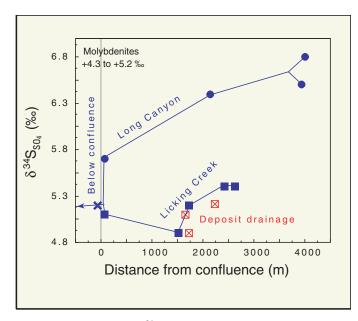


Figure 12. Distribution of δ^{34} S values in sulfate from Licking Creek and Long Canyon versus distance from their confluence. Isotopic values for molybdenites from Theodore and others (1992).

The $\delta^{34}S_{SO_4}$ values in Long Canyon decrease from near 6.8% outside the mineralized zone to 6.4% after mixing with the deposit drainage to 5.7% just before mixing with Licking Creek. The decrease from 6.4% to 5.7% suggests that some water associated with the molybdenum porphyry deposit besides the "deposit" seep sampled is entering Long Canyon, consistent with the major-element chemistry discussed above. Values in Licking Creek, although decreasing downstream, are never above 5.4% (just above the value for sulfur in the molybdenites). This general decrease likely reflects a continuous input of sulfur from mineralization to the stream as it flows across the molybdenum porphyry system.

Conclusions

Integration of chemistry, hydrology, and regional geology provides a comprehensive understanding of the environmental behavior of the Buckingham porphyry molybdenum deposit in areas that have been mined (Licking Creek) and that have not been mined (Long Canyon). In both drainages, fracture flow—controlled by local hydraulic head and regional stresses—affects the streams. As Long Canyon stream enters the mineralized area, the metal signature of deposit drainage is dampened, with the exception of Mo, which is mobile as an anion at higher pH. Conversely, in Licking Creek, the deposit-drainage signature persists downstream even though the stream pH is similar to that in Long Canyon and may, in part, reflect the availability of materials in waste piles to surface weathering. In Long Canyon, the progressive input of deposit

drainage can be monitored by sulfur-isotope data, which is more sensitive than chemical concentration in this drainage that has not been disturbed by mining.

Case Study IV— Metal Mobility in Galena Creek During an Unusually Wet Spring

Climate is thought to be an important control on the environmental behavior of metals. Even local climatic variability can affect water quality, especially in areas where mineralization has been disturbed during mining. This was particularly evident in Galena Canyon during the spring of 1998.

The surface elevations of our sites in Galena Canyon are 1,506 m (4,940 ft) to 1,926 m (6,320 ft). The town of Battle Mountain (elevation 1,383 m), some 10 km to the north of the deposit, receives 19 cm of precipitation per year and has a mean annual temperature of 9.5°C. Average annual evapotranspiration, as calculated by Shevenell (1996), is between 60 and 120 cm and depends strongly on elevation.

During the spring of 1998, precipitation in the Humboldt River basin was above average (fig. 13). In addition, the snowpack in May and June was more than 150 percent of average, indicating late runoff. Our sampling trip in mid May corresponded with this unusually wet period. A second sampling trip was attempted in June 2000, but Galena Creek and its tributaries were dry. Figure 13 shows that the precipitation and snowpack for that spring and the preceding winter were well below average, resulting in the lack of surface-water flow in June.

Sampling

Sample sites in Galena Canyon and tributaries are shown in figures 1 and 14. Samples below the confluence of tributaries with Galena Canyon were not obtained, but flows and chemistry were estimated during geochemical modeling. Solid material (treatment) was being added to the water below the sample site (24) in Iron Creek before the tributary entered the main stream. The suspected solid was calcite, although samples of the solid could not be obtained for positive identification. Upstream from both Butte and Iron Canyon sample sites is a large mining complex (fig. 1). Smaller historic mine sites are found in Cow Canyon and Duck Creek. Stream-flow measurements were not made in the field, although flow was estimated visually where possible.

Modeling Results

Water quality from Butte and Iron Creek, the two tributaries that have a large mining complex upstream, is substan-

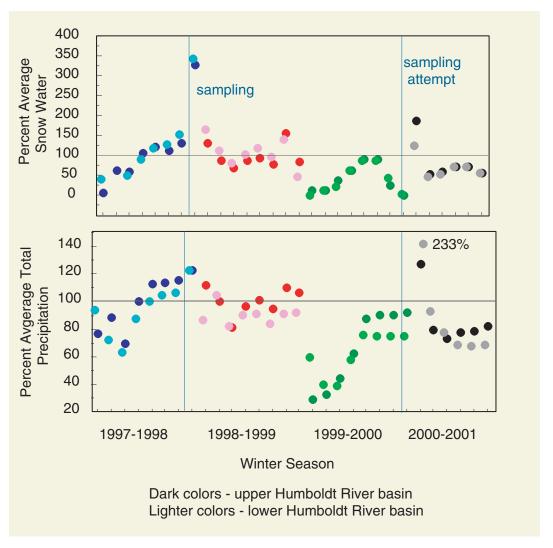


Figure 13. Plots showing the percent of average total precipitation and snow water for November through June for the season 1997–1998 through 2000–2001 in the upper and lower Humboldt River basins (data from Natural Resource Conservation Service; www.wcc.nrcs.usda.gov). Sampling dates designated by vertical lines.

tially different from that in Cow Canyon, Duck Creek, and Galena Canyon (fig. 15). The low pH values, elevated metal and sulfate concentrations, and sulfur isotopes from Butte and Iron Creek indicate that the unusually wet period in the Humboldt River basin resulted in acid mine drainage (AMD) in the two creeks with substantial historic mining activity upstream. Drainage from Butte and Iron Canyons into Galena Canyon might be expected to radically influence the composition of water in the main stream. However, the water composition from site 25, downstream of Butte and Iron Canyons, shows only minor elevations in concentrations of metals, and the pH is not affected at all (fig. 15). The relatively elevated concentration of sulfate and sulfur isotopes at site 25 versus values from Cow Canyon and Duck Creek (fig. 15) bear evidence that acid mine drainage from Butte and Iron Creek has impacted the main stream. The most severe impacts from metals and

low pH, however, have been mitigated, probably as a result of the solids addition in Iron Canyon.

A computer program (Geochemist's Workbench, Bethke, 1994; Berger and others, 2000) estimated mixing ratios, tested possible solids added to treat the stream, and assessed the change in pH and amounts of major elements during treatment. Lack of samples at each confluence, and "treatment" of water in Iron Canyon just above the confluence with Galena Creek complicated calculation of mixing ratios using element concentrations. Visual estimates of flow guided initial estimates of tributary contributions at various points in the main stream. A 50:50 mixture of Cow Canyon and Duck Creek water represented the composition in the main stream prior to addition of water from Butte and Iron Canyons. Water from Butte Canyon was mixed with Iron Canyon water in a 2:1 ratio to represent the input from the two tributaries producing

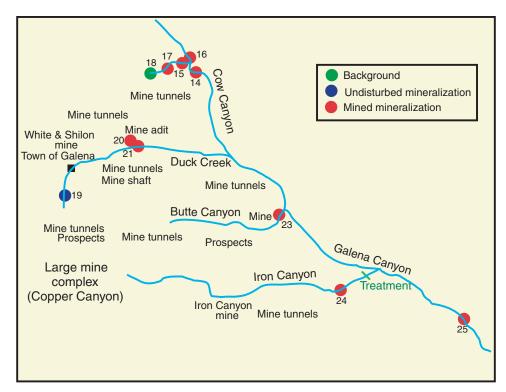


Figure 14. Map showing the location of sample sites in Galena, Iron, Butte, and Cow Canyons and Duck Creek.

AMD. Mineral precipitation was suppressed during mixing and speciation of the waters. The mixed water from Butte and Iron Canyons was treated with varying amounts of two solids, lime and calcite, to test the effects of these solids on water composition before entering the main stream. Precipitation was allowed to occur during treatment, but minerals believed to be inhibited from precipitating in nature (dolomite, hematite, quartz, and polymorphs) were suppressed. To achieve the final solution that was compared to measured values at site 25, the mixed water from Cow Canyon and Duck Creek was mixed with the treated water from Iron and Butte Canyons. Minor adjustments to mixing ratios were made during the course of modeling to achieve a water close in composition to that measured at site 25.

Calculations indicate that about 83 percent of the flow is from Cow Canyon and Duck Creek combined; 12 percent is from Butte Canyon; and 5 percent is from Iron Canyon. Flow calculations and sulfate concentrations were used to show that 88 percent of the sulfate in Galena Creek comes from Butte and Iron Canyons, and 12 percent comes from Cow Canyon and Duck Creek. Mass-balance calculations using sulfur isotopes of dissolved sulfate agreed with these percentages. Sulfur isotopes are a good variable to use for testing calculated results because they are not fractionated or altered during pH changes or mineral precipitation/dissolution.

Modeling results indicate that calcite was the likely solid being added to the stream at the mouth of Iron Canyon. About 1.35 g calcite per kilogram of water would be sufficient to bring the pH to 7.6, close to the pH of 7.76 at site 25 downstream (figs. 15 and 16A). The chemistry of the stream was modified radically by the treatment due to processes such as increases in pH, mineral precipitation and (or) adsorption of metals. These processes continued to occur after water in Iron Canyon mixed with that in Galena Canyon because AMD input from Butte Canyon was also modified by the treatment to Iron Canyon. Some of the minerals predicted to precipitate after addition of the calcite are gypsum, gibbsite, and goethite (fig. 16B). Precipitation of gypsum would remove about 20 percent of the sulfate that was added from the Butte and Iron Creek tributaries (fig. 15). Along with the gypsum, gibbsite and goethite³ would form, coprecipitating or adsorbing trace metals and removing them from the stream. Metal-load data show that essentially all the metals come from Butte and Iron Canyons (59 percent and 41 percent, respectively).

Alunite is predicted to form after addition of 0.3 g of calcite and redissolve after addition of 1.2 g because of the increase in pH (fig. 16*B*); however, due to precipitation kinetics, it may never actually form. Calcite in excess of the amount needed to neutralize acidic water from Iron and Butte Canyons would accumulate (fig. 16*B*) and likely be carried downstream

 $^{^{\}rm 3}$ Due to kinetics, iron oxyhydroxides would likely form first and then convert to goethite.

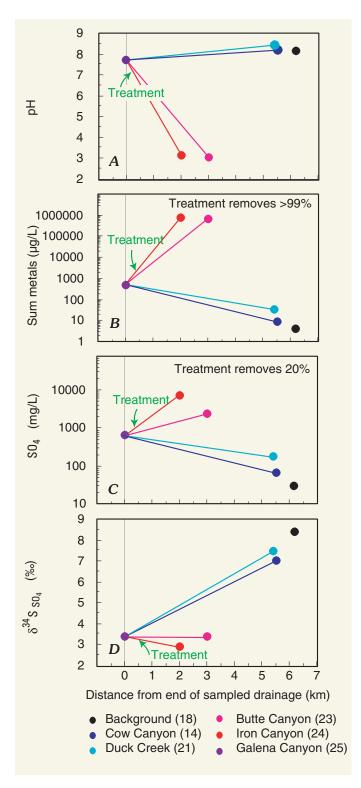


Figure 15. Cross plots of A, pH; B, sum of metals (µg/L, log scale); C, sulfate (mg/L, log scale); and D. $\delta^{34} S_{SO_4}$ (‰) versus distance from the end of sampled drainage (km). Points upstream from Galena Canyon are the most downstream sample in each tributary. Site numbers in parentheses behind drainage name.

along with any other minerals formed during treatment. A "stream" of white precipitate was observed in Galena Creek downstream of the input from Iron Canyon. The final mixture of Iron and Butte Canyon treated water with the mixture of water from Cow Canyon and Duck Creek produced a composition with concentrations of major constituents similar to that sampled at site 25 (table 6). The difference between measured and calculated fluoride is likely due to the kinetics of fluoride precipitation. Fluorite and fluorapatite are oversaturated and precipitated in the modeling run but, in fact, may not have time to form between mixing and site 25.

Table 6. Measured concentrations of major constituents in Galena Creek at site 25 and modeled concentrations after mixing of Cow, Duck, Iron, and Butte Creeks and addition of calcite.

| Element | Measured | Calculated |
|--------------------------|----------|------------|
| рН | 7.76 | 7.58 |
| HCO ₃ (mg/kg) | 76 | 72 |
| Ca (mg/kg) | 180 | 167 |
| F (mg/kg) | 0.87 | 0.21 |
| K (mg/kg) | 4 | 5 |
| Mg (mg/kg) | 67 | 76 |
| Na (mg/kg) | 64 | 49 |
| SO ₄ (mg/kg) | 650 | 669 |
| Sr (mg/kg) | 0.69 | 0.48 |

Although trace-metal precipitation and adsorption were not modeled, the amount of metal removed from the stream during treatment can be estimated as the difference between the actual measured and calculated concentrations in table 7. Calculated concentrations represent those from mixing of Cow, Duck, Iron, and Butte Creeks, assuming that no precipitation or adsorption occurred.

Table 7. Measured concentrations of metals in Galena Canyon at site 25 after mixing and treatment of Cow, Duck, Iron, and Butte Creeks and calculated estimates assuming no precipitation or adsorption.

| Metal | Measured | Calculated |
|-----------|----------|------------|
| As (μg/L) | 4.9 | 42 |
| Cd (µg/L) | 58 | 370 |
| Co (µg/L) | 69 | 330 |
| Cu (µg/L) | 66 | 6,200 |
| Ni (μg/L) | 130 | 530 |
| Zn (µg/L) | 570 | 8,300 |

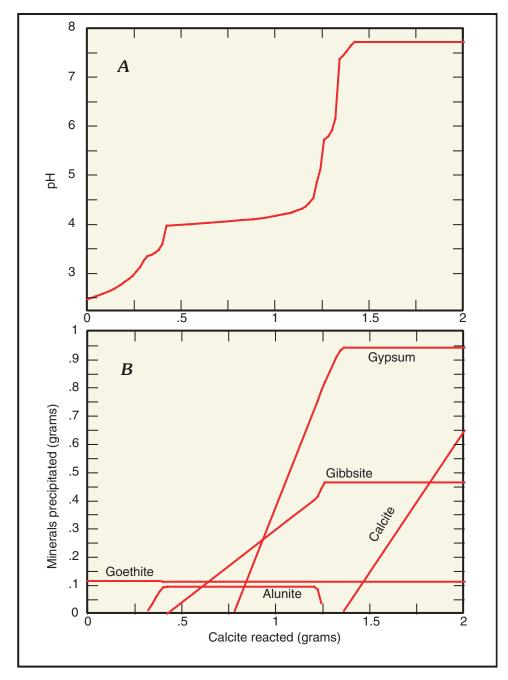


Figure 16. Plots showing *A*, pH; and *B*, mineral precipitation and dissolution as a function of calcite (in grams) added to the Iron Canyon—Butte Canyon mixture.

Conclusions

Geochemical processes such as metal adsorption and coprecipitation occur in all tributaries to Galena Creek, but, in heavily mined areas, these natural processes do not attenuate all trace metals mobilized. Exceptionally wet years in this otherwise arid region mobilized high concentrations of acid and metals in mined drainages and, if left untreated, would lower stream pH and increase metal concentrations. Addition of cal-

cite to the acidic, metal-rich streams entering Galena Canyon raised the pH sufficiently to precipitate minerals and nearly quantitatively remove most trace metals. This process was successfully modeled. Modeling results help estimate mixing ratios and identify the geochemical processes that occurred when calcite was added to acidic, metal-rich streams within the Galena Canyon drainage. Although trace-metal precipitation and adsorption were not modeled, mass-balance calculations estimated how much metal was removed during these geochemical processes.

Summary of Battle Mountain Studies

This study investigated the environmental controls on water quality in a portion of the Battle Mountain mining district, north-central Nevada. With a number of case studies, we were able to demonstrate that the geology, hydrology, degree of mining, and local climate were key factors in determining water quality in our study area.

Streams in background areas outside mineralized zones reflect normal weathering of unmineralized rocks. The waters are generally dilute, slightly alkaline in pH, and very low in metals. As these streams flow into mineralized zones, their character changes. In unmined areas, ground water influenced by mineralization discharges into streams through hydrologically conductive fractures, affecting water quality, but this effect is much more subtle than in areas were mining has produced adits and mine-waste piles. The influence of drainage from these mining relicts on water quality is often dramatic, especially in unusually wet conditions. The addition of calcite to the acidic, metal-rich mine drainage raises the pH and removes almost all of the metals through coprecipitation and (or) adsorption onto oxyhydroxides.

In many cases, the chemical composition of the stream was useful as a tracer of ground-water discharge into, or mixing of, "deposit drainage" with the stream. In some cases, however, the isotopic composition of dissolved sulfate was much more sensitive for indicating input of water influenced by mineralization, especially in areas where the amount of input was small or the weathering rate of ore minerals was slow.

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Appendix I— Description of Sample Sites

Green denotes outside deposit (background); blue, unmined mineralized areas (undisturbed), and red, mined areas. Sniffer measurements are cm of positive or negative head in the stream channel. Positive head indicates a gaining stream and negative head a losing stream.

Long Canyon and Licking and Camp Creeks

Long Canyon (Upper to Lower)

- Site 3 North fork of Long Canyon just above confluence with the South fork (site 4). Stream flow approximately 500 to 850 L/min with sniffer showing no head difference. The site is above influence from mining and is outside the Buckingham stockwork molybdenum deposit and the quartz stockwork zone (deposit boundaries from geologic and structural map in Theodore and others, 1992). Site is located on Harmony Formation. There are no mines in this drainage
- Site 4 South fork of Long Canyon just above confluence with the north fork (site 3). Estimated flow is 180 to 360 L/min. Geographic and geologic data same as for site 3.
- Site 1 Spring (possible uncompleted drill hole) in middle of road next to stream at site 2 in Long Canyon. Site sits directly on inferred Long Canyon fault. Water flowing "out of the road" from 20-cm-diameter hole with episodically spurting bubbles (CO₂?). Immediately downstream is Fe-oxide staining. Sniffer shows 25–28 cm of positive head. Site on Quaternary alluvium underlain by Cambrian Harmony Fm. and is about 150 m from a zone of pyritic alteration and 315 m outside inferred boundary of Buckingham stockwork molybdenum deposit and the quartz stockwork zone.
- Site 2 Stream about 30 m NE. from spring at site 1. The flow rate is estimated 1,700 L/min. The sniffer shows about 2.5 to 5 cm positive head. Geology and geography are the same as at site 1.
- Site 12 Stream above confluence with Licking Creek (site 11). The site sits on inferred Long Canyon fault. The site is on older Quaternary alluvium and underlain by either Harmony Fm., Tertiary quartz latite porphyry, or Cretaceous quartz monzonite porphyry. Site is within the quartz stockwork zone, but outside the Buckingham stockwork molybdenum deposit. Unnamed mine dumps are in the vicinity but do not flow into the stream above the site.
- Site 13 Stream 30–40 m below confluence with Licking Creek site along inferred Long Canyon fault. Site sits on younger Quaternary alluvium that is underlain by

formations as noted in site 12 description. Site is below several unnamed mine dumps and is within the quartz stockwork zone but outside the Buckingham stockwork molybdenum deposit.

Licking Creek (Upper To Lower)

- Site 5 Site sits on normal fault and on boundary of quartz stockwork and Buckingham stockwork molybdenum deposit. It is above Miss Nevada mine, on Harmony Fm., and near a sliver of Tertiary hornblende porphyry. Flow is approximately 500 to 850 L/min.
- Site 6 Site sits on same fault as site 5, with stream-flow rate about that of site 5. Site is within the Buckingham stockwork molybdenum deposit and quartz stockwork zone. The site is below several dogholes and is within 100 m of several mine dumps with pyrite, calcite, molybdenite, and quartz. Some efflorescent salts occur on the dumps. The site is on the boundary between the older Quaternary alluvium and the Cambrian Harmony Fm. and is very near a zone of alteration in outcrop.
- Site 10 Stream 8 m above confluence with Camp Creek. The site is in the vicinity of pyrite alteration visible in outcrop (about 150 m away) and within the quartz stockwork zone and the Buckingham stockwork molybdenum deposit. The site is not directly in the vicinity of mine dumps (Gold Top and Red Top mines are above the site, but their water enters the stream just below site). The site is very close to inferred fault that runs up Licking and Camp Creeks and is located in a swarm of short faults. It sits on older Quaternary alluvium; Harmony Formation underlies the alluvium.
- Site 9 Stream 10 m below confluence with Camp Creek. The site is in the vicinity of pyrite alteration visible in outcrop (about 150 m away) and is within the Buckingham stockwork molybdenum deposit and quartz stockwork zone. There is Al₂O₃ on rocks in stream bed. Site sits on Quaternary alluvium very near boundary of Buckingham fault zone. Underlying is the Harmony Fm.
- Site 11 The site is about 30 m above the confluence of Licking and Long Creeks and is between the boundary of younger Quaternary alluvium and a Quaternary fanglomerate deposit. Either Harmony Fm., Tertiary quartz latite porphyry, or Cretaceous quartz monzonite porphyry underlies the alluvium/fanglomerate deposits. Site is within the quartz stockwork zone but outside the Buckingham stockwork molybdenum deposit. There are no mine dumps immediately upstream; however, the site is influenced by mine drainage (see site 9).

Camp Creek (Lower)

Site 7 Site is on Camp Creek, which drains a heavily mined catchment (Midland, Hardy, Northland mines

and Buckingham Camp with ore sulfides in quartz veins plus oxides). Site is in vicinity of pyrite alteration (about 150 m away), within the Buckingham stockwork molybdenum deposit and quartz stockwork zone, and is on Quaternary alluvium near the contact with the Harmony Fm.

Site 8 Spring entering Camp Creek below site 7. The site is in the Harmony Formation and on the Buckingham fault zone contact. It is in the vicinity of pyrite alteration (about 150 m away) and within the Buckingham stockwork molybdenum deposit and quartz stockwork zone. Al₂O₃ precipitates from water upon entering Camp Creek.

Cow and Duck Creeks, and Butte, Iron, and Galena Canyons⁴

Cow Creek (Upper To Lower)

- Site 18 Site is above Moonlight mine dumps on south fork of Cow Creek. Flow is approximately 60 L/min. The site sits on the Cambrian Harmony Formation just east of the Trinity fault. It is very near or on a short fault running parallel to the Trinity.
- Site 17 Moonlight mine dump (Au, Ag, Cu, Pb, Zn, plus minor As and Sb)—we observed pyrite, quartz, and minor stibnite. The site is situated in the Trinity fault zone, which drops the Cambrian Harmony against the Cambrian Scott Canyon Formation. Pyrite is the principal sulfide mineral in the shear zone, with minor galena, sphalerite, and chalcopyrite. The water flows from the base of the dump at <1 L/min. The stream bed is orange to gray below the dump.
- Site 15 South fork of Cow Creek below site 17. The site sits on the boundary between Cambrian Scott Canyon Formation and Quaternary alluvium. The rocks in the stream are stained red. Flow is about 60 L/min.
- Site 16 North fork of Cow Creek above confluence with the south fork. The site is below the Eagle mine (not visited), which is situated in Trinity fault zone. Elements and gangue minerals are similar to those at site 17. The site is located on Quaternary alluvium underlain by the contact between the Scott Canyon and Harmony Formations. The site lies on a fault that is parallel to the stream that then intersects the Trinity fault near the mine to the north. The flow is about 500-850 L/min.
- Site 14 Cow Creek below confluence of north and south forks. The site sits on alluvium overlying the contact between Scott Canyon and Harmony Formations along a Mississippian thrust fault. There are no mines in the

⁴ Geology and structures from Roberts and Arnold (1965) unless noted otherwise.

immediate area.

Duck Creek (Upper to Lower)

- (Background/mineralized?) Very low flow in drainage near Blossom mine (Au, Ag, Pb with calcite/quartz gangue). The orebodies replace calcareous shale, limestone, and conglomerate of Permian Edna Mountain Formation along the Virgin fault. The site is on the contact between the Edna and Pumpernickel Formations. The influence of the mine on this site, if any, is not readily apparent.
- Site 20 Water issuing from covered adit at several L/min. The site is at the Trinity mine located on the intersection of the Trinity fault zone and the Plumas fault. The main metals mined are Au, Ag, Cu, Pb, and Zn in galena, sphalerite, pyrite and chalcopyrite plus minor stibnite—gangue minerals include calcite and quartz. Most of the mined rock is oxidized ore with pods of galena near the bottom of the oxidized zone. The site sits on alluvium underlain by the contact between the Harmony and Scott Canyon Formations. Limestone crops out 1.3 km to the west.
- Site 21 This site is on Duck Creek near an old homestead 50 m south of and above site 20. The geology is the same as at site 20. Upstream from this site are six Pb, Zn, Ag mines.

Butte Canyon (Lower)

Stream at mouth of Butte Canyon before entering Site 23 Galena Canyon. The site sits on Quaternary alluvium underlain by Scott Canyon Formation on an inferred Mississippian thrust fault. Upstream are the Butte and Post mines along the Butte fault. Ore minerals are oxidized pyrite, cerussite, CuO_x, Au, and minor arsenic and antimony minerals. A 15-stamp mill, started in 1871, is at the mouth of the canyon above the site.

Iron Canyon (Lower)

Site 24 This site is at the mouth of Iron Canyon on alluvium underlain by Scott Canyon Fm. The head of the canyon intersects the outer area of the contact-metamorphic zone and is very close to the Copper Canyon works. There are two mines in the canyon—the Iron Canyon mine and the Iron Canyon placer. Iron Canyon mine ore includes some pyrrhotite, arsenopyrite, sphalerite, galena, and chalcopyrite along with pyrite. Some of the ore is massive sulfide, and some of the sulfides are intercalated with shaly/cherty layers. Limestone units occur in the mine. Most ore mined consists of oxides with sulfide ores occurring at depth. A solid substance

(likely calcite) mixes into stream water at the confluence of Iron Canyon and Galena Creek. Galena Creek ran milky white for some distance through the Wilson Ranch.

Galena Canyon (Lower)

Site 25 Duck Creek where it crosses the old haulage road at the base of the mountain. The site is on young Quaternary alluvium past the mouth of Galena Canyon toward Reese Valley.

Little Cottonwood Creek— North and South Forks⁵

- Site 26 Site on north fork of Little Cottonwood Creek. Flow is about 1,700 L/min. Site sits on alluvium underlain by Scott Canyon Formation. Farther up drainage are the Antimony King mine (on Scott Canyon/Harmony contact—stibnite is the principal ore, with minor Sboxides; quartz and pyrite are gangue minerals) and Fuller Group mine (on Harmony Fm. cut by quartz monzonite porphyry dikes, with pyrite gold ores). The drainage parallels a Mississippian thrust fault and contact-metamorphic zone.
- Site 27 South fork of Little Cottonwood Creek with flow about 850 L/min. The site sits on alluvium underlain by Scott Canyon Formation and is very near a fault that cuts across the drainage. There are no mines in the drainage.
- Site 28 The site is some 60 m below sites 26 and 27. The conductivity suggests that the majority of flow is more like that at site 27 than 26 (contrary to estimated flow rates). The stream may be gaining waters similar to site 27, but we have no data to test this hypothesis. Site sits on alluvium above Scott Canyon Fm. No mines are in the vicinity of the site.

Elder Creek and Tributary⁶

Elder Creek (Upper to Lower)

Site 32 South fork of Elder Creek above site 30. Flow is about 800 L/min and there is about 4 inches of negative head in the stream bottom. The site sits on Harmony

- Fm. near a small granodiorite intrusion. There are no faults or mines in the vicinity, but site is likely in an area of mineralization.
- Site 30 North fork of Elder Creek, upstream from a zone of springs along both banks. Conductance of springs is 310–490 μ S/cm. Sniffer measures \cong 3 inches of negative head. Site sits on Harmony Formation. There are no faults or mines in vicinity.
- Site 31 North fork of Elder Creek, 200 m downstream from site 30. The sniffer measured ≅4 inches negative head. The site sits on Harmony Formation. There are no faults or mines in the vicinity.
- Site 29 Elder Creek below site 31. The flow is about 850 L/min. The site sits on alluvium underlain by the Harmony Formation and may be influenced by nearby pyritic Cu, Au, Ag mines (Gracie, Big Pay, and (or) Ridge mines). Ore is mostly sulfides in veins. Several faults intersect just upstream from this site.

Tributary (Upper to Lower)

- Site 33 Unnamed ephemeral tributary on the west side of Elder Canyon below site 29. The site sits on alluvium underlain by Harmony Formation or its contact with granodiorite. There are claim markers near the site, and the Dewitt thrust fault (Mississippian) is at the head of this drainage. There are no mines in the vicinity, but the site is within mineralization.
- Site 34 This site is downstream from site 33, about 100–200 m before joining Elder Creek. The stream disappears as it hits a series of fractures above and just below this site. The site sits on the contact of alluvium and Harmony Formation. Several granodiorite intrusives are in the immediate vicinity. There are no mines in the vicinity or up the drainage, but the site is within mineralization.

Appendix II— Geochemical Data

The following methods were used to analyze the water samples (see text for details).

- Cations: Inductively coupled plasma–atomic emission spectrophotometry (ICP-AES) and inductively coupled plasma–mass spectrometry (ICP-MS),
- Anions: Ion chromatography,
- Sulfur isotopes: Mass spectrometry,
- Mercury: Mercury analyzer.

The number of samples with concentrations below the limit of detection is given in table 8 (censored values). Elements with greater than 1/3 of samples censored are not reported. For those elements reported, censored values were

 $^{^{5}}$ Geology and structures from Roberts and Arnold (1965) unless noted otherwise.

 $^{^{\}rm 6}$ Geology and structures from Roberts and Arnold (1965) unless noted otherwise.

replaced with 0.7 times the limit of detection for the method of determination (Miesch, 1976) (table 9).

 Table 8.
 Detection limits for elements with censored values.

| As | 3 | (µg/L) |
|----|-------|--------|
| Cd | 0.02 | (μg/L) |
| Ce | 0.01 | (µg/L) |
| Fe | 30 | (μg/L) |
| La | 0.01 | (μg/L) |
| Mo | 0.20 | (μg/L) |
| P | 0.01 | (mg/L) |
| Pb | 0.05 | (μg/L) |
| Sc | 10 | (μg/L) |
| Si | 20 | (mg/L) |
| Th | 0.005 | (μg/L) |
| V | 0.10 | (μg/L) |
| | | |

Table 9. Chemical and sulfur isotopic data for all samples collected in 1998.

[ND, not determined. Num. censored, number of censored values (replaced with 0.7 detection limit)]

| Site no. | Description | Drainage system | Population | Latitude (°N) | Longitude (°W) | рН | Conductivity (µS/cm) | Alkalinity (mg/L as HCO ₃) | Hg (µg/L) |
|-------------|---|-----------------------|-------------|------------------|-------------------|------|-------------------------|---|--------------|
| 1 | Spring at Long Canyon | Long/Licking Ck. | Undisturbed | 40.625 | 117.064 | 7.43 | 710 | 102 | 0.016 |
| 2 | Stream at Long Canyon | Long/Licking Ck. | Undisturbed | 40.625 | 117.064 | 8.28 | 220 | 43 | 0.006 |
| 3 | N. Fork, Long Canyon | Long/Licking Ck. | Background | 40.629 | 117.083 | 7.62 | 130 | 31 | 0.006 |
| 4 | S. Fork, Long Canyon | Long/Licking Ck. | Background | 40.629 | 117.083 | 7.86 | 100 | 22 | 0.005 |
| 5 | Licking Creek | Long/Licking Ck. | Undisturbed | 40.618 | 117.078 | 8.11 | 170 | 31 | 0.008 |
| 6 | Licking Creek | Long/Licking Ck. | Mined | 40.619 | 117.075 | 8.24 | 200 | 31 | 0.005 |
| 7 | Tributary to Licking Creek | Long/Licking Ck. | Mined | 40.613 | 117.067 | 5.14 | 1,100 | ND | 0.007 |
| 8 | Springs at site 7 | Long/Licking Ck. | Undisturbed | 40.613 | 117.067 | 4.03 | 1,200 | ND | 0.007 |
| 9 | Licking Creek Below confluence with site 7 | Long/Licking Ck. | Mined | 40.612 | 117.066 | 7.08 | 520 | 21 | 0.006 |
| 10 | Licking Creek above confluence with site 7 | Long/Licking Ck. | Undisturbed | 40.612 | 117.066 | 8.03 | 210 | 31 | 0.006 |
| 11 | Licking Creek above confluence w/ Long Canyon | Long/Licking Ck. | Mined | 40.609 | 117.049 | 7.95 | 470 | 21 | 0.006 |
| 12 | Long Canyon above confluence w/ Licking Creek | Long/Licking Ck. | Undisturbed | 40.609 | 117.049 | 8.44 | 300 | 52 | 0.010 |
| 13 | Confluence of sites 11 and 12 | Long/Licking Ck. | Mined | 40.609 | 117.049 | 8.31 | 400 | 38 | 0.006 |
| 14 | Cow Creek below mine effluent | Galena Canyon | Mined | 40.575 | 117.112 | 8.24 | 400 | 92 | 0.005 |
| 15 | Mine effluent before it enters Cow Creek | Galena Canyon | Mined | 40.575 | 117.111 | 5.11 | 530 | ND | 0.007 |
| 16 | Cow Creek above confluence w/ mine effluent | Galena Canyon | Mined | 40.575 | 117.111 | 8.40 | 340 | 100 | 0.005 |
| 17 | Drainage from pyrite-rich dump | Galena Canyon | Mined | 40.575 | 117.114 | 2.65 | 310 | ND | 0.008 |
| 18 | Natural drainage above site 17 | Galena Canyon | Background | 40.574 | 117.116 | 8.18 | 300 | 88 | 0.007 |
| 19 | Duck Creek Headwaters above Galena townsite | Galena Canyon | Undisturbed | 40.560 | 117.131 | 8.42 | 180 | 52 | 0.007 |
| 20 | Caved adit | Galena Canyon | Mined | 40.566 | 117.120 | 6.71 | 1,400 | 154 | 0.007 |
| 21 | Duck Creek | Galena Canyon | Mined | 40.566 | 117.120 | 8.43 | 670 | 79 | 0.005 |
| 23 | Butte Canyon | Galena Canyon | Mined | 40.557 | 117.096 | 3.08 | 3,200 | 1 | 0.015 |
| 24 | Iron Canyon | Galena Canyon | Mined | 40.548 | 117.086 | 3.17 | 7,300 | 1 | 0.012 |
| 25 | Galena Canyon at old haulage road | Galena Canyon | Mined | 40.544 | 117.067 | 7.76 | 1,300 | 76 | 0.010 |
| 26 | Little Cottonwood Creek | Little Cottonwood Ck. | Mined | 40.589 | 117.079 | 8.25 | 220 | 54 | 0.006 |
| 27 | Tributary to Little Cottonwood Creek | Little Cottonwood Ck. | Background | 40.588 | 117.080 | 8.41 | 350 | 93 | 0.006 |
| 28 | Confluence of sites 26 and 27 | Little Cottonwood Ck. | Mined | 40.588 | 117.079 | 8.37 | 310 | 68 | 0.006 |
| 29 | Elder Creek | Elder Ck. | Mined | 40.670 | 117.083 | 8.02 | 310 | 71 | 0.006 |
| 30 | North fork of Elder Creek | Elder Ck. | Background | 40.653 | 117.089 | 8.16 | 290 | 73 | 0.006 |
| 31 | North fork of Elder Creek | Elder Ck. | Background | 40.653 | 117.088 | 7.80 | 290 | 74 | 0.006 |
| 32 | South fork of Elder Creek | Elder Ck. | Undisturbed | 40.654 | 117.087 | 8.00 | 210 | 49 | 0.006 |
| 33 | Unnamed tributary-west side Elder Creek | Elder Ck. | Undisturbed | 40.680 | 117.096 | 8.14 | 130 | 21 | 0.007 |
| 34 | Same tributary, downstream of site 33 | Elder Ck. | Undisturbed | 40.682 | 117.079 | 7.85 | 200 | 25 | 0.006 |
| Num. censor | • ' | | | | | 0 | 0 | 0 | 0 |

 Table 9. Chemical and sulfur isotopic data for all samples collected in 1998—Continued.

| Site no. | ³⁴ S (sulfate) (‰) | S04 (mg/L) | F ppm (mg/L) | CI ppm (mg/L) | SO ₄ /CI (M/M) | Al (μg/L) | As (μg/L) | Ba (µg/L) | Ca (mg/L) | Cd (µg/L) | Ce (µg/L) | Co (µg/L) | Cu (µg/L) |
|--------------|----------------------------------|---------------|-----------------|------------------|------------------------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|
| 1 | 5.2 | 135 | 0.44 | 46 | 3.2 | 7.2 | 5.3 | 11 | 72 | 0.014 | 0.04 | 0.24 | 0.56 |
| 2 | 6.4 | 46 | 0.32 | 13 | 3.8 | 41 | 2.1 | 14 | 22 | 0.014 | 0.04 | 0.09 | 0.90 |
| 3 | 6.8 | 37 | 0.32 | 8.0 | 5.1 | 75 | 2.1 | 8.7 | 16 | 0.27 | 0.07 | 0.08 | 1.0 |
| 4 | 6.5 | 28 | 0.21 | 15 | 2.1 | 100 | 3.0 | 7.8 | 9.4 | 0.05 | 0.08 | 0.08 | 1.7 |
| 5 | 5.4 | 55 | 0.30 | 11 | 5.4 | 25 | 16 | 11 | 17 | 0.12 | 0.03 | 0.08 | 2.3 |
| 6 | 5.4 | 56 | 0.30 | 12 | 5.4 | 20 | 15 | 11 | 17 | 0.08 | 0.03 | 0.09 | 2.1 |
| 7 | 4.9 | 560 | 0.60 | 50 | 13 | 3,200 | 4.0 | 15 | 110 | 57 | 11 | 20 | 280 |
| 8 | 5.1 | 628 | 0.89 | 55 | 13 | 9,900 | 4.8 | 16 | 120 | 120 | 28 | 52 | 610 |
| 9 | 4.9 | 225 | 0.38 | 24 | 10 | 73 | 9.2 | 14 | 51 | 15 | 1.5 | 5.2 | 48 |
| 10 | 5.2 | 68 | 0.37 | 12 | 6.2 | 17 | 25 | 13 | 20 | 0.13 | 0.02 | 0.10 | 2.3 |
| 11 | 5.1 | 218 | 0.40 | 25 | 9.6 | 109 | 51 | 15 | 49 | 11 | 0.23 | 3.8 | 26 |
| 12 | 5.7 | 67 | 0.38 | 19 | 3.8 | 48 | 3.6 | 18 | 31 | 0.06 | 0.04 | 0.13 | 2.3 |
| 13 | 5.2 | 125 | 0.35 | 21 | 6.5 | 63 | 22 | 17 | 38 | 3.8 | 0.12 | 1.5 | 15 |
| 14 | 7.0 | 67 | 0.24 | 14 | 5.3 | 92 | 2.1 | 46 | 52 | 0.90 | 0.007 | 0.91 | 1.7 |
| 15 | 6.6 | 287 | 0.49 | 17 | 19 | 3,200 | 2.1 | 42 | 59 | 37 | 5.5 | 19 | 43 |
| 16 | 7.3 | 50 | 0.20 | 14 | 4.0 | 15 | 2.1 | 53 | 52 | 0.48 | 0.01 | 0.14 | 1.5 |
| 17 | 6.5 | 606 | 0.81 | 9.4 | 71 | 38,000 | 6.3 | 16 | 74 | 93 | 30 | 50 | 130 |
| 18 | 8.4 | 30 | 0.32 | 16 | 2.1 | 20 | 2.1 | 80 | 39 | 0.02 | 0.02 | 0.13 | 1.2 |
| 19 | 5.6 | 23 | 0.20 | 5.3 | 4.8 | 56 | 9.6 | 150 | 24 | 0.06 | 0.06 | 0.15 | 4.3 |
| 20 | 1.9 | 581 | 0.34 | 45 | 14 | 9.9 | 6.5 | 29 | 180 | 61 | 0.05 | 40 | 1.7 |
| 21 | 7.5 | 177 | 0.32 | 45 | 4.3 | 90 | 48 | 130 | 78 | 1.6 | 0.08 | 0.96 | 4.1 |
| 23 | 3.4 | 2,400 | ND | ND | | 73,000 | 200 | 26 | 300 | 1,000 | 140 | 720 | 13,000 |
| 24 | 2.9 | 7,300 | ND | ND | | 360,000 | 290 | 33 | 550 | 4,900 | 350 | 4,800 | 120,000 |
| 25 | 3.4 | 653 | 0.87 | 40 | 18 | 76 | 4.9 | 43 | 180 | 58 | 0.07 | 69 | 66 |
| 26 | 5.3 | 48 | 0.22 | 11 | 4.9 | 22 | 3.5 | 23 | 30 | 0.04 | 0.02 | 0.12 | 2.6 |
| 27 | 6.5 | 53 | 0.24 | 16 | 3.8 | 7.5 | 2.1 | 39 | 46 | 0.06 | 0.02 | 0.16 | 1.8 |
| 28 | 5.7 | 50 | 0.21 | 12 | 4.5 | 20 | 2.1 | 29 | 35 | 0.07 | 0.02 | 0.13 | 2.1 |
| 29 | 6.9 | 47 | 0.24 | 18 | 2.9 | 4.6 | 5.4 | 23 | 36 | 0.014 | 0.007 | 0.08 | 0.77 |
| 30 | 7.5 | 38 | 0.23 | 14 | 3.0 | 4.9 | 2.1 | 17 | 35 | 0.014 | 0.007 | 0.08 | 0.51 |
| 31 | 7.5 | 39 | 0.23 | 15 | 2.9 | 7.9 | 2.1 | 18 | 35 | 0.014 | 0.007 | 0.08 | 0.82 |
| 32 | 6.8 | 30 | 0.18 | 14 | 2.3 | 32 | 2.1 | 21 | 23 | 0.014 | 0.02 | 0.07 | 0.66 |
| 33 | 4.5 | 42 | 0.22 | 11 | 4.4 | 72 | 3.1 | 47 | 16 | 0.08 | 0.04 | 0.07 | 2.2 |
| 34 | 4.3 | 59 | 0.27 | 12 | 5.6 | 15 | 7.2 | 50 | 20 | 0.09 | 0.01 | 0.07 | 2.3 |
| ım. censored | - | 0 | 0 | 0 | | 0 | 11 | 0 | 0 | 6 | 4 | 0 | 0 |

 Table 9. Chemical and sulfur isotopic data for all samples collected in 1998—Continued.

| Site no. | Fe (µg/L) | K (mg/L) | La (µg/L) | Li (μg/L) | Mg (mg/L) | Mn (μg/L) | Mo (μg/L) | Na (mg/L) | Ni (μg/L) | P (mg/L) | Pb (μg/L) | Rb (μg/L) | Sb (µg/L) |
|--------------|--------------|-------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|-------------|--------------|--------------|--------------|
| 1 | 1,600 | 2.9 | 0.02 | 17 | 17 | 250 | 2.8 | 57 | 3.0 | 0.03 | 0.08 | 4.8 | 0.20 |
| 2 | 43 | 1.7 | 0.02 | 8.0 | 7.6 | 1.7 | 2.8 | 24 | 1.3 | 0.03 | 0.05 | 0.30 | 0.62 |
| 3 | 64 | 1.6 | 0.04 | 7.6 | 5.9 | 1.2 | 0.95 | 17 | 1.4 | 0.02 | 0.10 | 0.45 | 0.56 |
| 4 | 77 | 1.4 | 0.03 | 3.4 | 3.3 | 0.7 | 7.2 | 17 | 1.0 | 0.05 | 0.07 | 0.48 | 0.22 |
| 5 | 34 | 2.1 | 0.02 | 7.8 | 5.9 | 0.8 | 20 | 25 | 2.0 | 0.06 | 0.05 | 1.6 | 0.44 |
| 6 | 34 | 2.0 | 0.02 | 7.6 | 5.9 | 1.2 | 20 | 25 | 1.9 | 0.06 | 0.07 | 1.5 | 0.94 |
| 7 | 37 | 8.6 | 8.0 | 87 | 40 | 750 | 18 | 79 | 250 | 0.01 | 0.52 | 14 | 0.67 |
| 8 | 40 | 10 | 24 | 110 | 42 | 2,000 | 0.45 | 80 | 350 | 0.05 | 0.20 | 15 | 0.20 |
| 9 | 21 | 4.7 | 1.4 | 33 | 18 | 210 | 34 | 48 | 72 | 0.007 | 0.07 | 5.0 | 0.62 |
| 10 | 30 | 2.4 | 0.02 | 9.1 | 6.6 | 1.7 | 32 | 29 | 1.7 | 0.06 | 0.04 | 0.97 | 0.47 |
| 11 | 30 | 4.5 | 0.24 | 32 | 17 | 160 | 40 | 48 | 52 | 0.02 | 0.10 | 4.4 | 2.2 |
| 12 | 64 | 2.6 | 0.02 | 11 | 9.5 | 3.1 | 6.4 | 32 | 1.8 | 0.04 | 0.05 | 1.3 | 0.48 |
| 13 | 36 | 3.4 | 0.09 | 19 | 13 | 61 | 19 | 38 | 21 | 0.03 | 0.04 | 2.5 | 1.3 |
| 14 | 21 | 1.9 | 0.01 | 13 | 18 | 41 | 1.0 | 23 | 5.6 | 0.007 | 0.04 | 1.1 | 0.41 |
| 15 | 21 | 2.4 | 2.2 | 43 | 19 | 710 | 0.14 | 33 | 71 | 0.007 | 1.0 | 1.7 | 0.39 |
| 16 | 21 | 1.8 | 0.007 | 12 | 17 | 3.9 | 0.73 | 22 | 2.5 | 0.01 | 0.04 | 1.1 | 0.34 |
| 17 | 20,000 | 3.3 | 11 | 120 | 24 | 2,400 | 0.21 | 28 | 170 | 0.04 | 66 | 2.6 | 1.1 |
| 18 | 53 | 2.6 | 0.02 | 11 | 11 | 9.2 | 1.2 | 33 | 1.7 | 0.04 | 0.20 | 1.2 | 0.20 |
| 19 | 61 | 5.6 | 0.06 | 7.0 | 5.3 | 1.1 | 2.6 | 19 | 2.2 | 0.40 | 0.20 | 0.55 | 0.54 |
| 20 | 3,300 | 3.6 | 0.02 | 46 | 79 | 4,800 | 1.2 | 55 | 56 | 0.007 | 0.10 | 9.1 | 0.20 |
| 21 | 130 | 7.2 | 0.07 | 17 | 22 | 21 | 1.7 | 43 | 7.9 | 0.30 | 1.2 | 1.5 | 3.2 |
| 23 | 58,000 | 4.8 | 66 | 62 | 200 | 13,000 | 14 | 76 | 1,700 | 0.70 | 25 | 6.8 | ND |
| 24 | 170,000 | 19 | 170 | 300 | 670 | 33,000 | 14 | 240 | 6,400 | 1.3 | 7.8 | 7.1 | ND |
| 25 | 21 | 4.0 | 0.05 | 25 | 67 | 910 | 1.7 | 64 | 130 | 0.01 | 0.30 | 1.2 | 0.65 |
| 26 | 33 | 1.6 | 0.02 | 8.1 | 9.2 | 1.8 | 1.6 | 22 | 1.7 | 0.03 | 0.10 | 0.60 | 3.6 |
| 27 | 21 | 1.9 | 0.02 | 10 | 16 | 2.7 | 1.2 | 25 | 2.4 | 0.02 | 0.20 | 0.70 | 0.50 |
| 28 | 31 | 1.5 | 0.007 | 8.5 | 12 | 1.8 | 1.4 | 23 | 1.9 | 0.03 | 0.04 | 0.62 | 2.5 |
| 29 | 21 | 1.6 | 0.007 | 12 | 12 | 0.3 | 1.2 | 29 | 1.6 | 0.02 | 0.04 | 0.26 | 0.20 |
| 30 | 21 | 1.5 | 0.01 | 9.9 | 11 | 0.3 | 0.80 | 23 | 1.6 | 0.02 | 0.04 | 0.24 | 0.10 |
| 32 | 21 | 1.4 | 0.007 | 10 | 11 | 0.6 | 0.79 | 23 | 1.6 | 0.02 | 0.04 | 0.25 | 0.20 |
| 32 | 37 | 1.2 | 0.02 | 7.4 | 7.4 | 0.6 | 0.87 | 20 | 1.3 | 0.02 | 0.08 | 0.24 | 0.20 |
| 33 | 65 | 1.7 | 0.03 | 3.6 | 4.3 | 0.7 | 5.0 | 15 | 1.8 | 0.10 | 0.06 | 0.59 | 0.61 |
| 34 | 21 | 2.0 | 0.01 | 3.5 | 5.2 | 0.4 | 16 | 20 | 1.3 | 0.10 | 0.04 | 0.42 | 0.59 |
| um. censored | 10 | 0 | 4 | 0 | 0 | 0 | 1 | 0 | 0 | 4 | 9 | 0 | 0 |

 Table 9. Chemical and sulfur isotopic data for all samples collected in 1998—Continued.

| Site no. | Sc (µg/L) | Si (mg/L) | Sr (μg/L) | Ta (μg/L) | Th (μg/L) | Ti (μg/L) | U (µg/L) | V (µg/L) | W (µg/L) | Y (µg/L) | Zn (μg/L) | Zr (µg/L) | metals (µg/L) |
|---------------|--------------|--------------|--------------|--------------|--------------|--------------|-------------|-------------|-------------|-------------|--------------|--------------|------------------|
| 1 | 3.5 | 11 | 385 | 0.10 | 0.26 | 2.8 | 0.23 | 0.07 | 2.4 | 0.03 | 1.0 | 1.2 | 4 |
| 2 | 3.1 | 11 | 155 | 0.10 | 0.10 | 1.7 | 0.44 | 0.8 | 0.27 | 0.03 | 2.0 | 0.59 | 2 |
| 3 | 2.8 | 10 | 115 | 0.10 | 0.06 | 2.2 | 0.10 | 0.7 | 0.20 | 0.04 | 6.7 | 0.40 | 3 |
| 4 | 3.2 | 11 | 77 | 0.10 | 0.05 | 2.3 | 0.02 | 0.8 | 0.21 | 0.06 | 19 | 0.30 | 4 |
| 5 | 3.3 | 11 | 115 | 0.09 | 0.05 | 1.5 | 0.04 | 1 | 0.21 | 0.04 | 42 | 0.30 | 7 |
| 6 | 3.1 | 11 | 115 | 0.09 | 0.04 | 1.5 | 0.03 | 0.8 | 0.20 | 0.03 | 2.4 | 0.20 | 4 |
| 7 | 6.2 | 21 | 455 | 0.09 | 0.07 | 11 | 0.73 | 0.4 | 0.21 | 22 | 6,400 | 0.20 | 3,900 |
| 8 | 7.6 | 25 | 465 | 0.09 | 0.06 | 12 | 1.4 | 0.4 | 0.22 | 66 | 10,300 | 0.20 | 3,200 |
| 9 | 4.4 | 14 | 225 | 0.07 | 0.03 | 4.3 | 0.13 | 0.8 | 0.20 | 2.4 | 1,800 | 0.10 | 260 |
| 10 | 3.3 | 12 | 125 | 0.06 | 0.02 | 1.7 | 0.05 | 1 | 0.20 | 0.03 | 4.5 | 0.10 | 4 |
| 11 | 4.3 | 14 | 220 | 0.08 | 0.03 | 4.4 | 0.13 | 1 | 0.20 | 0.46 | 910 | 0.10 | 180 |
| 12 | 3.3 | 12 | 195 | 0.06 | 0.01 | 2.3 | 0.53 | 1 | 0.29 | 0.03 | 35 | 0.20 | 6 |
| 13 | 3.6 | 13 | 210 | 0.07 | 0.02 | 3.0 | 0.38 | 1 | 0.20 | 0.30 | 390 | 0.10 | 54 |
| 14 | 2.2 | 7.2 | 260 | 0.06 | 0.01 | 1.4 | 0.80 | 0.2 | 0.10 | 0.02 | 18 | 0.08 | 10 |
| 15 | 3.2 | 10 | 265 | 0.05 | 0.02 | 5.2 | 0.69 | 0.07 | 0.10 | 5.5 | 2,200 | 0.05 | 2,400 |
| 16 | 2.4 | 7.2 | 260 | 0.05 | 0.02 | 1.0 | 0.82 | 0.4 | 0.10 | 0.03 | 33 | 0.09 | 6 |
| 17 | 15 | 22 | 280 | 0.05 | 2.5 | 12 | 2.6 | 0.4 | 0.10 | 31 | 4,100 | 0.20 | 271,000 |
| 18 | 3.0 | 10 | 240 | 0.06 | 0.10 | 1.1 | 1.1 | 1 | 0.09 | 0.03 | 6.7 | 0.20 | 4 |
| 19 | 3.9 | 13 | 180 | 0.07 | 0.03 | 1.9 | 0.42 | 3 | 0.22 | 0.18 | 2.5 | 1.7 | 7 |
| 20 | 2.9 | 8.6 | 1,000 | 0.05 | 0.05 | 11 | 2.2 | 0.07 | 0.09 | 0.57 | 5,500 | 0.20 | 700 |
| 21 | 4.5 | 13 | 385 | 0.06 | 0.06 | 5.0 | 1.1 | 4 | 0.47 | 0.13 | 18 | 0.50 | 36 |
| 23 | 7.0 | 14 | 1,100 | 2.8 | 1.9 | 41 | 26 | ND | 2.6 | 160 | 28,000 | ND | 708,000 |
| 24 | 26 | 31 | 2,400 | 3.7 | 16 | 110 | 120 | 40 | 2.6 | 830 | 98,000 | ND | 898,000 |
| 25 | 3.1 | 8.8 | 690 | 0.05 | 0.11 | 13 | 2.6 | 0.5 | 0.10 | 0.29 | 570 | 0.20 | 500 |
| 26 | 2.6 | 9.1 | 165 | 0.04 | 0.02 | 1.4 | 0.22 | 0.6 | 0.06 | 0.02 | 2.8 | 0.09 | 5 |
| 27 | 2.4 | 7.8 | 250 | 0.04 | 0.009 | 1.3 | 0.97 | 0.9 | 0.06 | 0.02 | 3.4 | 0.10 | 5 |
| 28 | 2.4 | 8.6 | 195 | 0.03 | 0.006 | 1.3 | 0.48 | 0.9 | 0.06 | 0.02 | 21 | 0.06 | 5 |
| 29 | 2.3 | 8.6 | 255 | 0.04 | 0.007 | 0.90 | 0.95 | 0.8 | 0.08 | 0.01 | 1.0 | 0.07 | 2 |
| 30 | 2.1 | 7.8 | 260 | 0.03 | 0.004 | 0.80 | 0.52 | 0.5 | 0.05 | 0.01 | 0.90 | 0.10 | 3 |
| 31 | 2.1 | 7.8 | 260 | 0.04 | 0.004 | 0.80 | 0.50 | 0.7 | 0.06 | 0.01 | 14 | 0.06 | 4 |
| 32 | 2.0 | 7.7 | 150 | 0.04 | 0.004 | 1.4 | 0.33 | 0.8 | 0.06 | 0.02 | 1.0 | 0.07 | 2 |
| 33 | 2.2 | 8.4 | 100 | 0.03 | 0.005 | 2.2 | 0.02 | 2 | 0.10 | 0.04 | 3.0 | 0.10 | 4 |
| 34 | 3.0 | 11 | 130 | 0.03 | 0.006 | 1.2 | 0.03 | 3 | 0.26 | 0.02 | 20 | 0.06 | 4 |
| Num. censored | 1 | 1 | 0 | 0 | 3 | 0 | 0 | 3 | 0 | 0 | 0 | 0 | _ |