Reconnaissance of Acid Drainage Sources and Preliminary Evaluation of Remedial Alternatives at the Copper Bluff Mine, Hoopa Valley Reservation, California

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Conversion Factors

Multiply	By	To obtain
foot (ft)	0.3048	meter
gallon (gal)	3.785	liter
gallon per minute (gal/min)	0.004546	cubic meter per minute
gallon per minute (gal/min)	448.831	cubic foot per second (ft^3/s)
gallon per minute (gal/min)	0.06309	liter per second
inch (in.)	25.4	millimeter
mile (mi)	1.609	kilometer
ounce per (short) ton (oz/ton)	0.028	milligram per kilogram
(short) ton	2000	pound
pound (lb)	0.45454	kilogram

Temperature is given in degrees Celsius (×C), which can be converted to degrees Fahrenheit (°F) by the following equation:

$$°F = 1.8\ (°C) + 32.$$

Water-Quality Information

Chemical concentrations in water are given in milligrams per liter (mg/L) or micrograms per liter (µg/L). One thousand micrograms per liter is equivalent to 1 milligram per liter. For concentrations less than about 7,000 mg/L, milligrams per liter is equivalent to “parts per million” and micrograms per liter is equivalent to “parts per billion.”

Vertical Datum

Sea level: In this report, “sea level” refers to the National Geodetic Vertical Datum of 1929—a geodetic datum derived from a general adjustment of the first-order level nets of the United States and Canada, formerly called Sea Level Datum of 1929.

Abbreviations and Chemical Notations

ft^3/s, cubic foot per second
km, kilometer
kV, kilovolt
L, liter
m, meter
mg/L milligram per liter
mL, milliliter
mm, millimeter
mV, millivolt
nA, nanoampere
s, second
µg/l, microgram per liter
µm, micrometer
µS/cm, microsiemens per centimeter

AMD, acid mine drainage
CERCLA, Comprehensive Environmental Response, Compensation, and Liability Act
DHS, Department of Health Services (State of California)
DMEA, Defense Minerals Exploration Administration
HFO, hydrous ferric oxide
ICP, inductively coupled plasma
NPL, National Priorities List
NWQL, National Water Quality Laboratory (USGS)
SI, saturation index
USEPA, United States Environmental Protection Agency
USGS, United States Geological Survey
UV-vis, ultraviolet-visible (spectroscopy)

Eh, Oxidation-reduction potential, referenced to the standard hydrogen electrode
pE, Oxidation-reduction potential, expressed as the negative logarithm of the activity of a hypothetical aqueous electron
redox, oxidation-reduction

Ag, silver
Al, aluminum
Al^{oct}, octahedral aluminum
Al^{tet}, tetrahedral aluminum
As, arsenic
Ca, calcium
Cd, cadmium
Cr, chromium
Cu, copper
Fe, iron
Fe^{II}, ferrous iron
Fe^{III}, ferric iron
Fe^{II}-Fe^{III}, ferrous-ferric redox couple
K, potassium
Mg, magnesium
Mn, manganese
Na, sodium
S, sulfur
Sb, antimony
Si, silicon
Ti, titanium
Zn, zinc
Zn/Cu, zinc to copper ratio

Al_2O_3, aluminum oxide
CaO, calcium oxide
Cr_2O_3, chromium oxide
FeO, ferrous oxide
Fe_2O_3, ferric oxide
H_2O, water
K_2O, potassium oxide
MgO, magnesium oxide
MnO, manganese oxide
Na_2O, sodium oxide

SiO_2, silica (or quartz)
TiO_2, titanium oxide

$CaAl_2Si_2O_8$, anorthite
$CaCO_3$, calcium carbonate; calcite (or aragonite)
$Fe(OH)_3$, ferric hydroxide
$KAlSi_3O_8$, orthoclase
$NaAlSi_3O_8$, albite

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ABSTRACT

Acidic drainage from the inactive Copper Bluff mine cascades down a steep embankment into the Trinity River, on the Hoopa Valley Reservation in northern California. The Copper Bluff mine produced about 100,000 tons of sulfide-bearing copper-zinc-gold-silver ore during 1957–1962. This report summarizes the results of a water-resources investigation begun by the U.S. Geological Survey in 1994 with the overall objective of gathering sufficient geochemical, hydrologic, and geologic information so that a sound remediation strategy for the Copper Bluff mine could be selected and implemented by the Hoopa Valley Tribe. This study had the following specific objectives: (1) monitor the quality and quantity of the mine discharge, (2) determine seasonal variability of metal concentrations and loads, (3) map and sample the underground mine workings to determine sources of flow and suitability of mine plugging options, and (4) analyze the likely consequences of various remediation and treatment options.

Analysis of weekly water samples of adit discharge over parts of two wet seasons (January to July 1995 and October 1995 to May 1996) shows that dissolved copper (Cu) and zinc (Zn) concentrations (in samples filtered with 0.20-micrometer membranes) varied systematically in a seasonal pattern. Metal concentrations increased dramatically in response to the first increase in discharge, or first flush, early in the wet season. The value of Zn/Cu in the adit discharge exhibited systematic seasonal variations; an annual Zn/Cu cycle was observed, beginning with values between 3 and 5 during the main part of the wet season, rising to values between 6 and 10 during the period of lowest discharge late in the dry season, and then dropping dramatically to values less than 3 during the first-flush period. Values of pH were fairly constant in the range of 3.1 to 3.8 throughout the wet season and into the beginning of the dry season, but rose to values between 4.5 and 5.6 during the period of lowest discharge, from October to early December 1995.

Underground reconnaissance was conducted once during dry-season conditions (September 1995) and twice during wet-season conditions (March 1995 and March 1996). The main tunnel was accessed to a distance of about 600 feet from the portal entrance. Water samples were collected at nine locations along the floor of the main tunnel and from several ore shoots to evaluate the contributions of water and dissolved constituents from different portions of the mine. Values of pH ranged from 2.5 to 6.4 at different underground locations, concentrations of copper ranged from 0.020 to 44 mg/L (milligram per liter), zinc from 6.3 to 160 mg/L, and cadmium from 0.010 to 0.47 mg/L. Discharge from the ore shoots ranged from less than 1 gallon per minute to more than 30 gallons per minute and was always a small component of the total mine flow compared with the tunnel floor drainage. During March 1996, the main flow originated in the northernmost portion of the underground workings (inaccessible) and mixed with an unknown quantity of water upwelling from flooded lower workings.

High-water marks observed on the tunnel walls indicate that past blockages impounded more than 100,000 gallons of water. Sudden release of a large volume of metal-rich water could have serious effects on fish and other aquatic resources in the Trinity River.

Because of the hydrogeologic setting, mine plugging is not likely to offer an effective long-term solution to the problem of acid mine drainage at the Copper Bluff mine. The underground workings are close to a state highway and underlie a 500-foot-high bluff with highly fractured rocks that seep during the wet season. Total plugging likely would result in additional uncontrolled seepage and could potentially destabilize the highway. Partial plugging to restrict flow during periods of highest discharge may provide benefits in terms of reduced risk of catastrophic release without the additional risks associated with total plugging. Passive water treatment methods such as wetlands or anoxic limestone drains are unlikely to succeed at the Copper Bluff mine because of the lack of available space. A covered conveyance for the discharge directly from the mine portal to the Trinity River is a low-cost remedial alternative that would not reduce metal loadings to the Trinity River, but would reduce pathways of metal exposure to humans and wildlife. Lime neutralization or innovative, active water treatment methods such as bioreactors represent high-cost remedial alternatives that likely would be successful if sufficient resources were available for adequate design, testing, construction, long-term maintenance, and sludge disposal.

INTRODUCTION

Mining History

The Copper Bluff mine is an inactive copper-zinc-gold mine on the Hoopa Valley Reservation in northeastern Humboldt County, California (figs. 1 and 2). The mine is located about 275 ft above and on the east side of the Trinity River approximately 4 mi north of the town of Hoopa and about 12.5 mi upstream of the confluence of the Trinity and Klamath Rivers (fig. 2). The mine was discovered and first worked for gold in 1928. Mining activity at the Copper Bluff mine prior to 1957 consisted mainly of exploration and development of the ore bodies. The mine was initially developed by several cuts into the vein and a 25-ft-long tunnel into sulfide mineralization 100 ft above State Highway 96. A tunnel 15 ft below present State Highway 96 was the main exploration tunnel (fig. 3). A total reserve of 100,000 tons of sulfide ore had been identified by 1957 (Bailey and others, 1979) with economic concentrations of copper, 3 percent; zinc, 3.5 percent; gold, 0.1 oz/ton; and silver, 2.0 oz/ton. The mine was operated from 1957 to 1962 under lease from the Bureau of Indian Affairs, acting in the role of trustee for the Hoopa Valley Tribe. The mine had a total production value of at least $460,000 between 1928 and 1962 (Bailey and others, 1979).

The Copper Bluff mine has several hundred feet of tunnels and crosscuts and several known levels. Waste rock and low-grade sulfide-bearing ore were discharged on the steep embankment outside the main tunnel along the east bank of the Trinity River. Sulfide ore was trucked about 0.9 mi upstream to the Celtor Chemical Works mill site (fig. 2), where it was milled and concentrated. Metals were recovered from the sulfide concentrates by smelting offsite.

Regulatory and Environmental Concerns

Acid drainage from inactive and abandoned mines is commonly referred to as acid mine drainage (AMD). Oxidation of sulfide minerals such as pyrite (iron sulfide, FeS_2), chalcopyrite (iron-copper sulfide, $CuFeS_2$), and sphalerite (zinc sulfide, ZnS) results in the formation of metal-rich, sulfuric acid solutions. Before mining, natural weathering processes caused oxidation of these minerals where there was access to a sustained supply of atmospheric oxygen, generally in the unsaturated zone. The oxidation process is greatly accelerated by the increase in mineral surface area, permeability, porosity, and exposure to oxygen caused by mining and milling activity. Seasonal wetting and drying of sulfide minerals and a sustained flow of atmospheric oxygen through an underground mine in which most mine workings are not flooded, such as the Copper Bluff mine, will contribute to rapid sulfide oxidation and accelerated generation of concentrated AMD. The higher solubility of metals such as copper

(Cu), zinc (Zn), and cadmium (Cd) in acidic solutions allows these metals to occur in concentrations above regulatory limits that may be toxic to humans and wildlife.

The mill site known as the Celtor Chemical Works (fig. 2) was placed on the National Priorities List (NPL) by the United States Environmental Protection Agency (USEPA) in September 1983. In 1986, under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA or “Superfund”), the mill was dismantled and the site was remediated. This was in response to an uncontrolled discharge into the Trinity River of metal-rich mill tailings from the Celtor Chemical Works settling ponds. The California Department of Fish and Game subsequently cited the Celtor Chemical Corporation for pollution and fish kills (United States Environmental Protection Agency, 1993). Prior to cleanup of the site in 1986, some mill tailings were stockpiled in the mill-site area (Morgan, 1985). The USEPA noted acidic surface water runoff at the site before removal of topsoil. Hoopa Valley tribal members reported that the floods of 1964 removed evidence of mill tailings prior to the cleanup by the USEPA. However, the USEPA found elevated metal concentrations of arsenic, cadmium, copper, lead, and zinc throughout the soils of the mill site (Morgan, 1985). The California Department of Health Services (DHS) performed sampling and confirmed these hazardous materials at the site in July 1981 (Morgan, 1985).

Figure 1. Location of study area, Humboldt County, California.

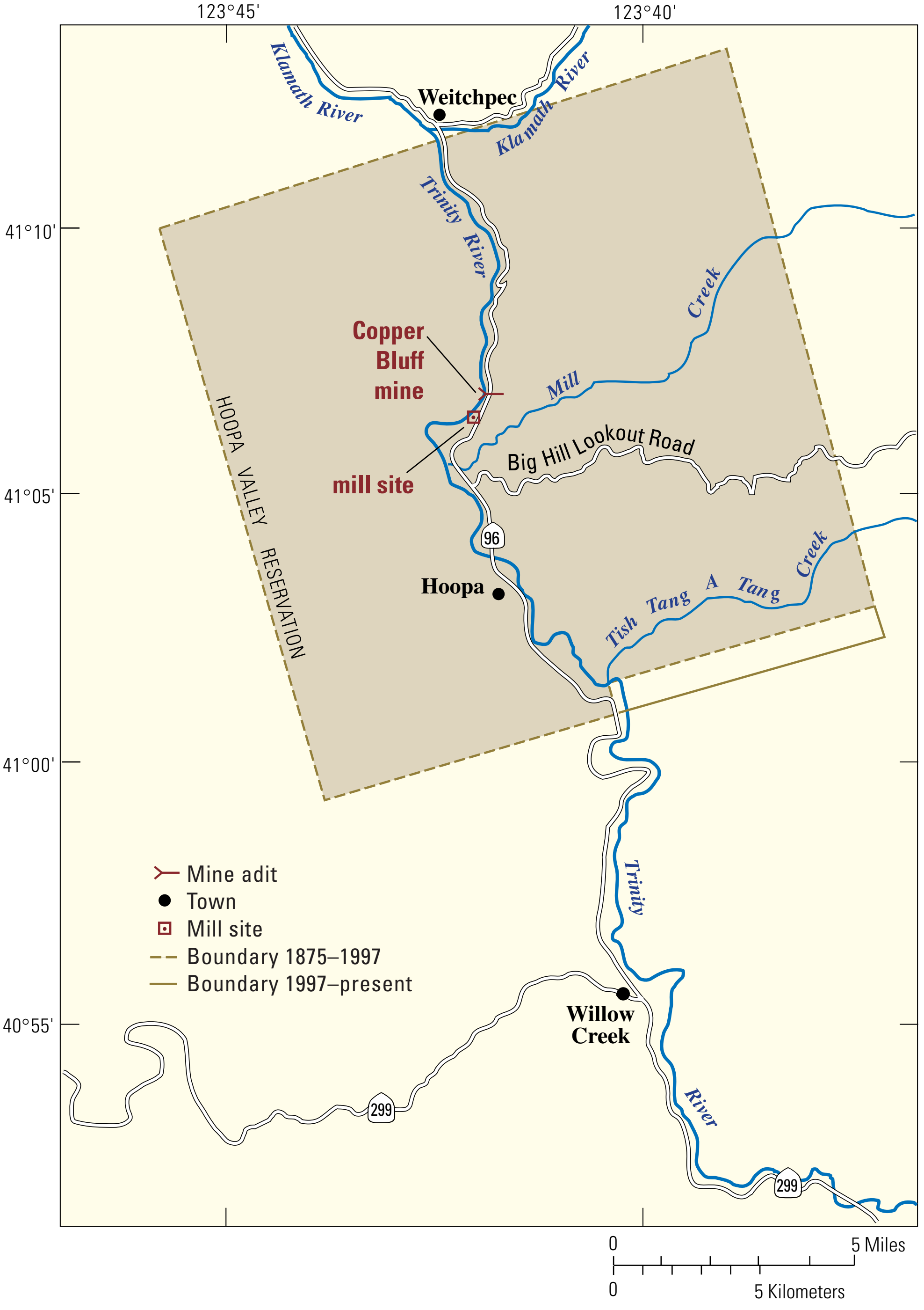

Figure 2. Location of the Copper Bluff mine in relation to the Trinity River.

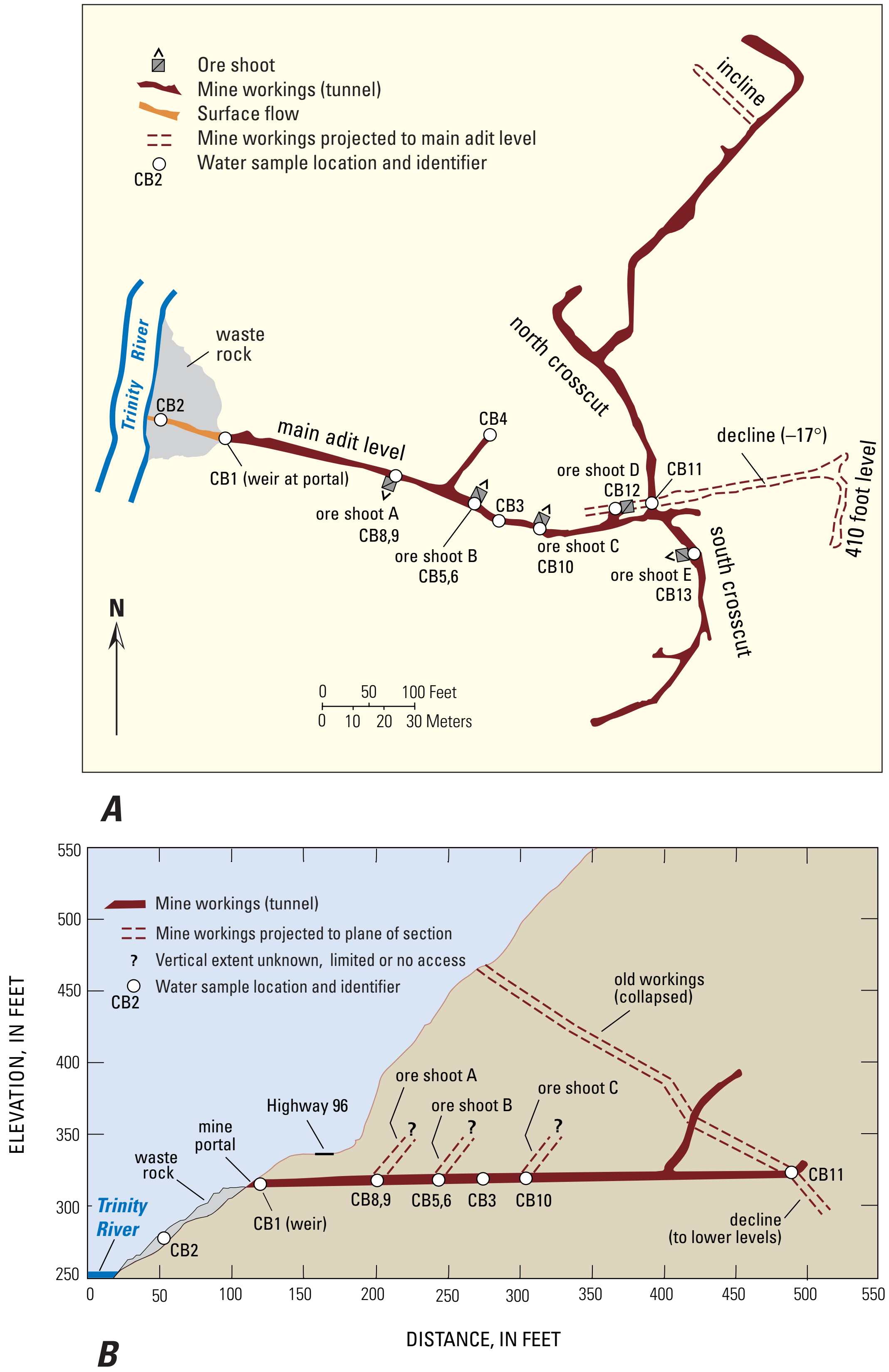

Figure 3. Plan view ***(A)*** and cross section ***(B)*** of the underground workings of the Copper Bluff mine.

At the Copper Bluff mine, an undetermined amount of sulfide-bearing waste rock was placed on the hill slope below the mine portal, on the east bank of the Trinity River (fig. 3). Acidic, metal-laden water discharges from the mine portal and cascades over and through the waste rock, eroding a drainage path to the Trinity River below. Potential chemical hazards to humans and wildlife exist in the contaminated soils and in the surface water having elevated concentrations of heavy metals and low pH; in addition, there are physical hazards from unstable waste-rock pile. Although no fish kills in the Trinity River have been documented as resulting from portal discharge from the Copper Bluff mine, there is concern that dissolved and particulate metals in the mine discharge are having an adverse effect on the aquatic resources in the Trinity and Klamath Rivers. Fishing for several species of salmon and trout, including steelhead, is an important source of food, tourism, and recreation for several native American tribes and other residents in the Trinity-Klamath watershed.

Study Objectives

Concerns regarding the acidic, metal-laden discharge from the portal of the main tunnel at the Copper Bluff mine were brought to the attention of the United States Geological Survey (USGS) in early 1994. An interagency agreement implemented in August 1994 between the USGS and the Hoopa Valley Tribe formed the basis for an investigation by the USGS with the overall objective of gathering sufficient geochemical, hydrologic, and geologic information so that a sound remediation strategy for the Copper Bluff mine could be selected and implemented by the Hoopa Valley Tribe.

The first phase of the USGS investigation involved site characterization and data collection. The quantity and quality of mine portal discharge was monitored by the Hoopa Valley Tribe, using methods developed in conjunction with the USGS, over two wet seasons and one dry season beginning in September 1994 and concluding in May 1996. Three reconnaissance inspections and sampling events in the underground mine workings were conducted by the USGS to investigate the origins of mine drainage, to determine flow pathways, and to assess the stability of the mine workings and their suitability to plugging. One of the underground visits was made during the dry season (September 1994), and two visits were made during the wet season (March 1995 and March 1996). Results of water-quality sampling, mineral geochemistry, and geological mapping from these underground reconnaissance visits are described in this report. Water-quality data for surface-water samples collected near the mine portal in March 1995 also are described.

The objective of the second phase of the study was to analyze the likely consequences of various remedial alternatives and treatment options and to report on their chances for success. Preliminary results from that analysis are presented in this report. It is expected that analysis of the cost and feasibility of remedial options for the Copper Bluff mine will continue, using the scientific results of this study as a basis for development of an environmentally sound, long-term remedial solution for the hazards at the Copper Bluff mine.

Acknowledgments

The authors are grateful to Larry Oetker and Robert Ulibarri, Hoopa Valley Tribe Department of Land Management, without whose support and dedication this study would not have been possible. The USGS also thanks the tribal personnel who collected samples and made field measurements for this study, including Forest Blake, Chip McCovey, and Ken Norton. The authors would also like to thank Rick Humphreys, California State Water Resources Control Board, for assisting with field work and Kirk Christman for doing an underground safety inspection at the Copper Bluff Mine and for providing underground safety training. The authors also wish to thank Peter Schiffman, University of California, Davis, Department of Geology, for doing the electron microprobe analyses. Susan Bird (USGS, Sacramento, Calif.) contributed to the study by performing the iron redox determinations.

REGIONAL AND LOCAL GEOLOGIC SETTING

The Copper Bluff deposit is hosted by rocks of the Western Jurassic Belt (Irwin, 1966). The deposit is in a metamorphosed belt of marine sedimentary and volcaniclastic rocks that are shown on the geological map of the Weed quadrangle (Wagner and Saucedo, 1987) as belonging to the Galice Formation. This belt of rocks also contains the Grey Eagle massive sulfide deposit, which has many geological similarities to the Copper Bluff deposit (Gronewald, 1983). The Grey Eagle deposit is located in Siskiyou County, about 60 mi northeast of Hoopa.

Published information on the Copper Bluff deposit is limited. Background information on the geology and mine workings was obtained from a draft of a Defense Minerals Exploration Administration (DMEA) report (Robertson and Holmes, 1953). These authors described the deposit as a 3-to-5-ft-thick layer of massive sulfide striking north and dipping 15° to 20° east. The country rocks are described as quartz-chlorite and quartz-sericite schists. Robertson and Holmes (1953) identified a bed of black carbonaceous phyllite greater than 5 ft in thickness that comprises the footwall to the sulfide-bearing unit and is separated from the massive sulfide layer by a fault that is parallel to bedding. Samples of the host rocks, including the carbonaceous phyllite, were taken in the mine workings for study of their mineralogy and petrography, which are described in the “Results” section of this report.

Robertson and Holmes (1953) interpreted the structure of the area as a generally homoclinal sequence of metasedimentary rocks with a shallow dip to the east. They interpreted the pervasive foliation in these rocks as predominantly parallel to the original bedding, but noted that the foliation is locally folded and discordant with the overall structural trends. These authors also interpreted the deposit as a blanket replacement deposit in which a particular stratigraphic horizon was selectively replaced by sulfide minerals.

On the basis of analogy with massive sulfide deposits world wide, the Copper Bluff deposit is reinterpreted in the present study to belong to the general class of volcanic-associated massive sulfide deposits that form contemporaneously with their host rocks. The present form of the deposit is interpreted as having resulted from the same deformational events that affected the country rocks, resulting in a deposit that is highly attenuated by flattening in an orientation perpendicular to the foliation plane. Neither the Copper Bluff nor the Grey Eagle deposit fit neatly into the common subcategories of volcanic-associated massive sulfide deposits, but these deposits are most similar to the Besshi-type massive sulfide deposits defined by Slack (1993). Deposits of this type typically are hosted by metasedimentary rocks having a volcaniclastic component and generally are thought to have formed in response to hydrothermal circulation related to synsedimentary igneous activity, which commonly results in basaltic sills intruded into the sedimentary sequences. A similar setting for the formation of the Copper Bluff deposit is probable; however, structural disruption, metamorphism, and a lack of detailed mapping in the area of the deposit preclude a more definitive description of deposit genesis.

REGIONAL AND LOCAL HYDROLOGIC SETTING

Trinity River Flows

The Trinity River and its tributaries are the primary water resources in the Hoopa Valley. The Trinity River enters the valley about 3.7 mi south of Hoopa, the major population center in the valley. The river meanders through alluvial terraces in the Hoopa Valley before exiting into a steep, narrow canyon about 0.6 mi upstream of the Copper Bluff mine. Acidic drainage from the Copper Bluff mine enters the Trinity River 5 mi upstream of the confluence with the Klamath River at Weitchepec (fig. 2). Trinity River flows are controlled by releases from Lewiston Dam, which is operated by the Bureau of Reclamation. Flow data for the Trinity River at Hoopa during the study period are shown in figure 4*A*. Between July 1, 1994, and June 30, 1996, the discharge of the Trinity River at Hoopa varied from 474 to 82,700 ft^3/s.

Climate

The climate in the Hoopa Valley generally is temperate. The mean annual temperature is 57°F. Recorded temperature extremes range from 7°F to 118°F (Hoopa Valley Tribe, 1997). The average annual rainfall is 57 in.; more than 90 percent of the rain falls from October to April. A complete daily rainfall record during the study period is available for Willow Creek (fig. 4*B*), located about 8 mi south of Hoopa. The rainfall data for Willow Creek correlate reasonably well with the discharge data for the Trinity River during the study period. Rainfall data for Hoopa, California, are unavailable for most of the 1995–96 wet season. During the 1994–95 wet season, the rainfall data from Hoopa and Willow Creek correlate reasonably well with each other and with the variations in Trinity River discharge.

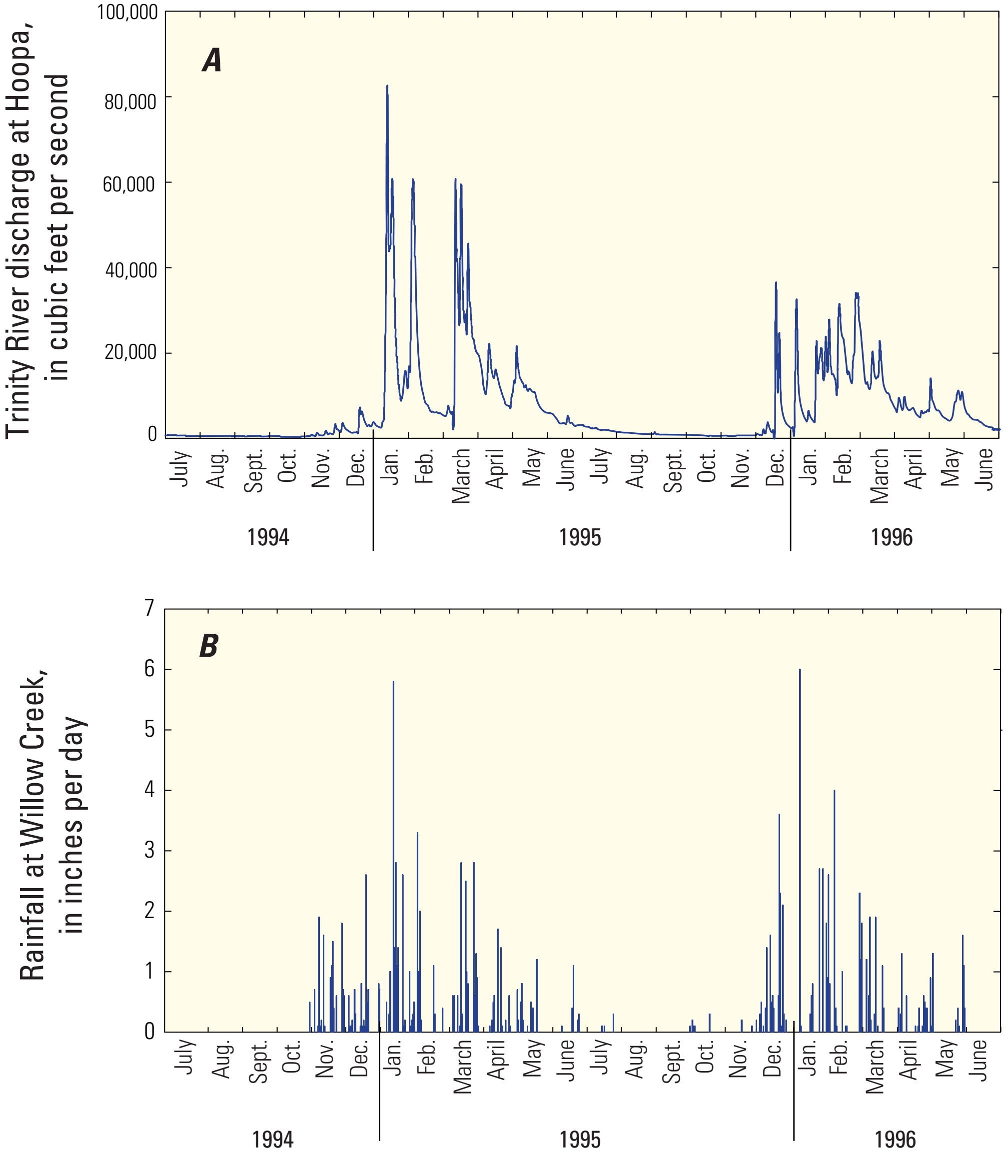

Figure 4. Hydrologic conditions in and near the Hoopa Valley, July 1994 through June 1996. (***A***) Trinity River discharge at Hoopa, California. (***B***) Rainfall at Willow Creek, California.

METHODS

Underground Mapping and Sampling

The underground workings of the Copper Bluff mine were entered on three occasions (September 1994, March 1995, and March 1996) for reconnaissance to determine the origin(s) of mine discharge. During the first underground visit on September 20 and 21, 1994, safety conditions were assessed and the accessible parts of the main tunnel were measured by steel tape and marked off in 100-ft intervals. Tunnel orientations were determined by Brunton compass. Principal features of the accessible underground workings are shown in figure 3*A* on the basis of underground mapping by the USGS and maps provided by the Eagle Picher Mining Company (Robert C. Brittain, written commun. 1996). During September 1994, the underground mine workings accessible on the main adit level (identified as the “476 level” on historic maps) generally were in good condition, except for some fallen timbers at site CB3, about 315 ft from the portal entrance (fig. 3*A*). Ponding of drainage at this point to a depth greater than 3 ft prevented further access.

During reentry of the mine on March 14 and 15, 1995, the ponding at the point of the fallen timbers (site CB3) was reduced. This allowed access to an additional 85 ft in the main tunnel, bringing the total distance mapped to 400 ft from the portal entrance. By the time of final reconnaissance on March 12 and 13, 1996, conditions had improved further, and the main tunnel was mapped an additional 200 ft for a total distance of 600 ft from the portal entrance. Also, 100 ft of crosscutting tunnels and raises were mapped at the intersection of the main tunnel and an inclined shaft. Five ore shoots (referred to as “A” through “E”) were found to intersect the main tunnel, raising up into the ore body to the north and south (fig. 3*A*). Ore shoot A was entered and mapped for a distance of about 75 ft; however, the other ore shoots were inaccessible. Rock samples, representative of wallrock and ores, were taken at several places in the mine workings and from a pile of sulfide-rich ore within ore shoot A.

Discharge from the five ore shoots ranged from less than 1 gallon per minute to more than 30 gallons per minute and was always a small component of the total mine flow compared with the tunnel floor drainage. During March 1996, the main flow originated in the northernmost portion of the underground workings (inaccessible) and mixed with an unknown quantity of water upwelling from flooded lower workings. High-water marks observed on the tunnel walls indicate that past blockages impounded a volume of water in excess of 100,000 gallons.

Water samples were collected at several locations in the underground mine workings (fig. 3) and in the immediate vicinity during each of the three reconnaissance visits. Water samples were collected using a 15-L polyethylene churn. The churn was acid washed with a 1-percent nitric acid solution between samples, and then rinsed three or more times with deionized water. During September 1994, water samples were taken at sites CB1 (at weir near portal entrance), CB2 (100 ft below portal entrance, near Trinity River), CB3 (main tunnel at caved area), CB4 (at face of dead-end drift), and CB5 (ore shoot B); duplicate samples were taken at sites CB1 and CB5 (labeled CB6). A field blank (labeled CB7) also was taken in September 1994 by processing deionized water in a manner identical to that for the other samples. During the second underground visit in March 1995, water samples were taken at sites CB1, CB3, CB5 (ore shoot B), CB8 (ore shoot A), and CB10 (ore shoot C); a duplicate sample (labeled CB9) was taken at site CB8. A field blank was also taken at site CB8. During the third and final underground visit in March 1996, water samples were taken at sites CB1, CB8, CB10, CB11 (floor in north crosscut), CB12 (floor in decline near ore shoot D), and CB13 (floor in south crosscut, near ore shoot E) (fig. 3*A*).

Unstable water-quality properties were determined in the field, including pH, specific conductance, temperature, and oxidation-reduction (redox) potential. Values of pH were determined using an Orion 250A or 290A meter with a gel-filled combination Triode electrode with automatic temperature compensation. Standard pH buffers 4 and 7 were checked before and after each measurement, and the calibration was accepted if readings on standard buffers were reproducible within 0.03 pH units. Redox measurements were made with an Orion combination platinum electrode and an Orion 250A or 290A meter. Redox buffers were prepared using hydroquinone mixed with pH 4 and 7 buffers. Values of redox potential for these two buffers were measured at the beginning and end of each field day and were used to convert redox potentials measured in water samples to values of Eh and pE, the negative logarithm of the activity of a hypothetical aqueous electron (Thorstenson, 1984), using the method described by Makita and Fujii (1992). Although the temperature dependence of these hydroquinone redox buffers is unknown, the temperature range encountered in this study was small and the errors introduced are likely insignificant.

Water samples were filtered in the field using disposable filters operated using a hand vacuum pump. Cellulose acetate membranes of 47 mm diameter and a pore size of 0.20 µm (micrometer) were used. One of the duplicate samples (site CB1 on September 19, 1994) was filtered using a 142-mm-diameter plate-filter assembly with a 0.20 µm pore-diameter membrane and a peristaltic pump, for comparison with the disposable, hand-pumped filtration processing. Filtered splits for anion analysis were stored in 125-mL, clear polyethylene bottles. Filtered splits for analysis of major cations and metals were preserved with concentrated nitric acid (2 mL) in 125-mL, acid-washed, clear polyethylene bottles. Filtered splits for iron speciation analysis were preserved with hydrochloric acid (2 mL) in 125-mL, acid-washed, amber polyethylene bottles and refrigerated. Archive splits were collected for the anions (filtered, nonacidified) and cations (filtered, acidified using nitric acid).

Surface-Water Sampling

On March 15, 1995, six surface-water samples were collected along the east side of State Highway 96 from a 500-ft-high bluff composed of highly fractured metamorphic rocks that seep during the wet season. Open joints and fractures in the face of the outcrop were examined for seepage. Surface-water samples were collected at five locations along the base of the bluff near the mine workings and from a sixth location several hundred feet to the south.

Weekly Sampling and Flow Monitoring at Portal

Variations in the chemistry and discharge rate of water exiting the Copper Bluff mine at the portal were evaluated during two wet seasons by weekly monitoring conducted by Hoopa Valley Tribe personnel. Water-quality samples were collected, filtered, and preserved according to USGS protocols, and unstable properties including pH, temperature, and specific conductance were measured in the field by Hoopa Valley tribal personnel, as described in the earlier subsection “Underground Mapping and Sampling.” Samples were shipped in refrigerated containers from Hoopa to Sacramento and analyzed for iron species. Sample splits for major cations, trace metals, and anions were then submitted by USGS personnel to the USGS National Water Quality Laboratory (NWQL) in Denver, Colo., for analysis.

Discharge measurements for the waters exiting the Copper Bluff mine portal were made on several occasions by Hoopa Valley tribal personnel. A concrete weir consisting of a stainless steel v-notch plate was constructed by tribal personnel about 6 m into the tunnel. A pygmy flow meter was used by tribal personnel to measure flow in a channelized part of the tunnel, downstream from the weir. Estimates of flow at the weir by tribal personnel were made on the basis of the theoretical design characteristics. Comparison of estimates from the weir correlated well with flow measurements from the pygmy meter on most occasions; however, a rating curve was not calibrated, nor was the weir maintained by the USGS. The flow data from the pygmy meter measurements are considered more reliable than the weir data, and it is the former data that are presented and discussed later in this report.

Geochemical Analyses

Chemical analyses for most constituents were performed at the NWQL. Two major cations (calcium and magnesium) and several trace metals (aluminum, cadmium, chromium, copper, iron, lead, manganese, nickel, silver, and zinc) were determined by inductively coupled plasma (ICP) atomic emission spectrometry. Two other major cations (potassium and sodium) were determined by flame atomic absorption spectroscopy. Silica was determined by a colorimetric method using molybdate blue. Major anions (chloride, fluoride, and sulfate) were determined by ion chromatography. Iron redox determinations (ferrous and total iron) were made at the USGS laboratory in Sacramento, Calif., using a colorimetric method with ferrozine as the complexing agent (Stookey, 1970). The water samples taken weekly at site CB1 during the period January 1995 to May 1996 were analyzed for fewer constituents than the surface-water samples and the samples taken during underground reconnaissance, as described later in this report.

Silicate minerals were analyzed by electron microprobe to determine their major and trace element contents. The analyses were performed using a CAMECA SX-50 microprobe at the University of California, Davis, Department of Geology (Peter Schiffman, analyst). Silicate analyses were made with a rastered 2-µm electron beam, with an accelerating voltage of 15 kV and a sample current of 10 nA or less.

Compositional data were converted from weight percentage to atomic (or molar) percentages using CAMECA software and spreadsheets (Peter Schiffman, University of California, Davis, written commun., 1997). After correction for structural oxygen and hydrogen, individual point analyses were rejected if weight percentage totals were in excess of 101 percent or below 98 percent. In some silicate minerals, aluminum can occur in both octahedral and tetrahedral crystallographic sites. The proportions of octahedral and tetrahedral aluminum were determined by allocating silicon and aluminum to fill tetrahedral sites, then using excess aluminum to fill octahedral sites. Iron was assumed to occur exclusively as Fe^{III} (ferric iron) in epidote, and exclusively as Fe^{II} (ferrous iron) in chlorite, mica, and stilpnomelane. In amphibole, iron commonly occurs as both Fe^{II} and Fe^{III}; relative proportions were estimated using a spreadsheet routine that maximizes mineral stoichiometry and oxide weight totals (Peter Schiffman, oral commun., 1997).

Geochemical Modeling

The computer program PHREEQC (Parkhurst, 1995) was used to compute aqueous speciation and mineral saturation indices for water samples collected during the underground reconnaissance visits in September 1994, March 1995, and March 1996. Version 1.5 of program PHREEQC (David Parkhurst, written commun., 1997) was used with the data base from the program WATEQ4F (Ball and Nordstrom, 1991). [Note that version 1.5 of PHREEQC has been superseded by version 2.0 (Parkhurst and Appelo, 1999).]

Analytical determinations of ferrous and total iron in filtered water samples were used as input to program PHREEQC to compute a value of Eh representing the ferrous-ferric (Fe^{II}-Fe^{III}) redox couple for each water sample. The Eh values were used to compute values of pE, defined as the negative logarithm of the activity of a hypothetical aqueous electron. The concept of pE is analogous in a theoretical sense to that of pH, which represents the negative logarithm of the activity of the aqueous hydrogen ion (Thorstenson, 1984). Values of Eh and pE for each water sample also were derived independently using field measurements taken using a platinum electrode. The saturation index of amorphous ferric hydroxide [$Fe(OH)_3$] was computed using the PHREEQC program in two different ways for each water sample with iron redox data. One method used the total (ferrous plus ferric) iron determination from the filtered water sample together with the field pE value to compute the saturation index. The other method used the ferrous and total iron determinations to compute dissolved ferric iron by difference, and then to compute the saturation index without regard to the field pE. A comparison of these two approaches appears in a later section of this report.

RESULTS

Geochemistry of Mine Drainage

Copper Bluff Mine Portal

Weekly water samples were taken of the Copper Bluff mine discharge at the weir in the main tunnel (site CB1) during the latter part of the 1994–95 wet season and into the beginning of the dry season (January to July 1995) and during the entire 1995–96 wet season (late October 1995 to May 1996). Chemical data for these water samples are given in appendix 1, and discharge data for the mine portal effluent are given in appendix 2. Time-series plots of various water-quality constituents and discharge (fig. 5) reveal a dramatic increase in metal concentrations in response to the first increase in discharge, or first flush, at the start of the 1995–96 wet season. Between December 6 and 19, 1995, mine discharge increased from 6 to 35 gal/min (fig. 5*A*; appendix 2), copper concentrations jumped from 2.6 to 77 mg/L, and zinc concentrations rose from 22 to 170 mg/L (fig 5*A*; appendix 1). As mine discharge continued to increase to a maximum of 486 gal/min in mid-January 1996, aqueous concentrations of copper and zinc declined to 17 and 50 mg/L, respectively, and continued to decline with decreasing flows over the next several months (fig. 5*A*; appendix 1).

The ratio of zinc to copper (Zn/Cu) in the adit discharge exhibited a systematic annual cycle, shown in the time-series plot (fig. 5*A*) and a plot of Zn/Cu versus discharge (fig. 6). Zn/Cu values were between about 3 and 5 during the main part of the 1994–1995 wet season (February 17 to April 12, 1995), rose to between 4 and 7 during the latter part of the wet season and into the dry season (April 19 to July 5, 1995), continued to rise to between 6 and 10 during the period of lowest discharge late in the dry season (October 30 to December 6, 1995), and then dropped dramatically to less than 3 in response to the first-flush period (December 13, 1995 to January 10, 1996). The annual cycle of Zn/Cu values in the adit discharge was repeated in 1996, with values between 3 and 5 during the main part of the wet season (February 1 to March 12, 1996) and rising values between 5 and 7 during the latter part of the wet season (April 16 to May 17, 1996). Five different stages in the annual cycle are identified by color on figures 5 and 6: I. First flush (orange); II. Maximum discharge (yellow); III. Main wet season (green); IV. Transition to dry season (blue), and V. Dry season (pink).

A similar overall relation between the Zn to Cu ratio and the discharge rate has been observed in the drainage from other massive sulfide deposits (for example, the Richmond Mine at Iron Mountain; Alpers and others, 1994b). The data from Copper Bluff mine are exceptional in that they clearly show the effect of the first flush on metal concentrations during the first increase in flow rates (December 13, 1995, to January 10, 1996) prior to the maximum observed flow (January 24, 1996).

A plot of zinc in relation to copper concentrations for samples of the adit discharge (site CB1) shows a strong, positive correlation (fig. 7*A*). A linear least-squares regression of the data for the CB1 site gives a line with the equation [Zn] = 1.98 [Cu] + 15.6, where [Zn] and [Cu] represent concentrations of zinc and copper, respectively, in units of milligrams per liter. The value of the square of the residuals (R^2) for this regression is 0.99. The plot on fig. 7*A* shows the 95 percent prediction interval (3σ) for the data population from site CB1, describing the computed range where the data values would fall 95 percent of the time for repeated measurements (Ulrich and others, 1995).

The strong, linear distribution of data in figure 7*A* suggests that seasonal variations in Zn/Cu (figs. 5 and 6) may be explained by mixing of two types of water: one relatively high in zinc and low in copper, having a Zn/Cu value greater than 8 (referred to as type-A water), and the other relatively high in both zinc and copper, having a Zn/Cu value of about 2.2 (referred to as type-B water). Type-A water would dominate the flow regime in the adit discharge during low-flow periods and would be mixed with variable amounts of type-B water during periods of higher flow.

Four hypotheses regarding the hydrogeochemical processes causing the systematic seasonal variations of Zn/Cu in the mine effluent are as follows: (1) formation of highly soluble, efflorescent sulfate salts that favor copper relative to zinc during periods of declining flow, followed by rapid dissolution of these salts during the first-flush period; (2) preferential sorption of copper relative to zinc by hydrous iron oxides during periods of declining flow and rising pH, followed by desorption of copper relative to zinc as pH values decline in response to accelerated sulfide oxidation rates at the start of the wet season; (3) changes in the relative kinetic rates of oxidation of sphalerite (ZnS) and chalcopyrite ($CuFeS_2$) caused by factors such as temperature, pH, availability of water and oxygen, and (or) reactive surface area; and (4) mixing of two major water types distinguished by very different Zn to Cu ratios (Type A ~ 8 and Type B ~ 2). Hypothesis 4 suggests that preferential flow paths within the mine workings discharge at different relative rates in response to varying hydrologic conditions.

Hypothesis 1 is difficult to evaluate at the Copper Bluff mine owing to the limited access to mine workings. No efflorescent salts were observed in the accessible part of the mine workings during any of three reconnaissance mapping and sampling visits. However, only the main adit level was visited, so it is possible that such salts form and dissolve in the upper, inaccessible parts of the mine. The increase in sulfate concentration during the first flush (December 13, 1995, to January 10, 1996; appendix 1) would be consistent with the rapid dissolution of soluble sulfate minerals during this period.

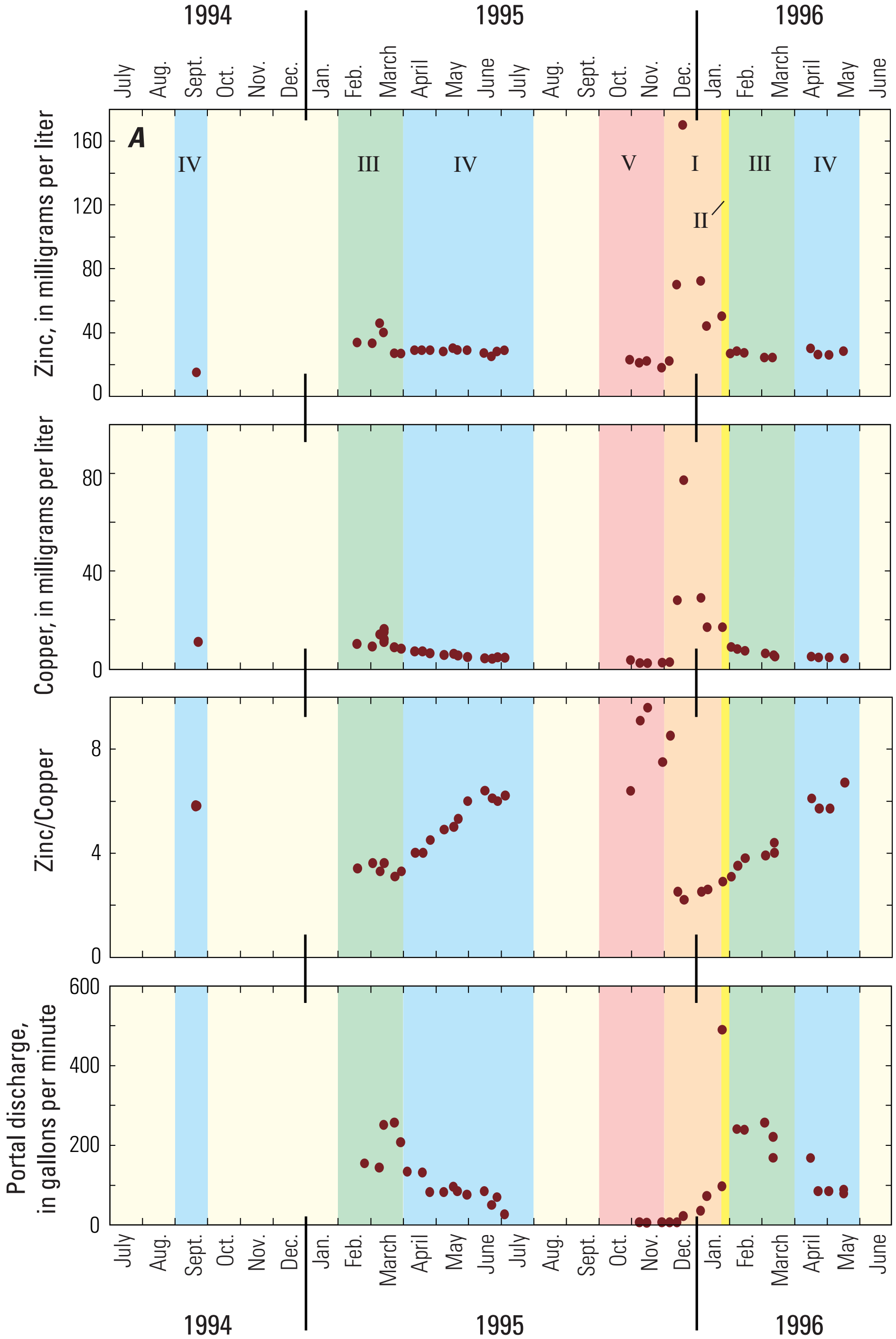

Figure 5. ***(A)*** Dissolved concentrations of zinc and copper, the ratio of zinc to copper, and the discharge rate at the Copper Bluff mine portal, September 1994–May 1996.

Stages in seasonal cycle: I, first flush; II, maximum discharge; III, main wet season; IV, transition to dry season; V, dry season; pale yellow indicates no data.

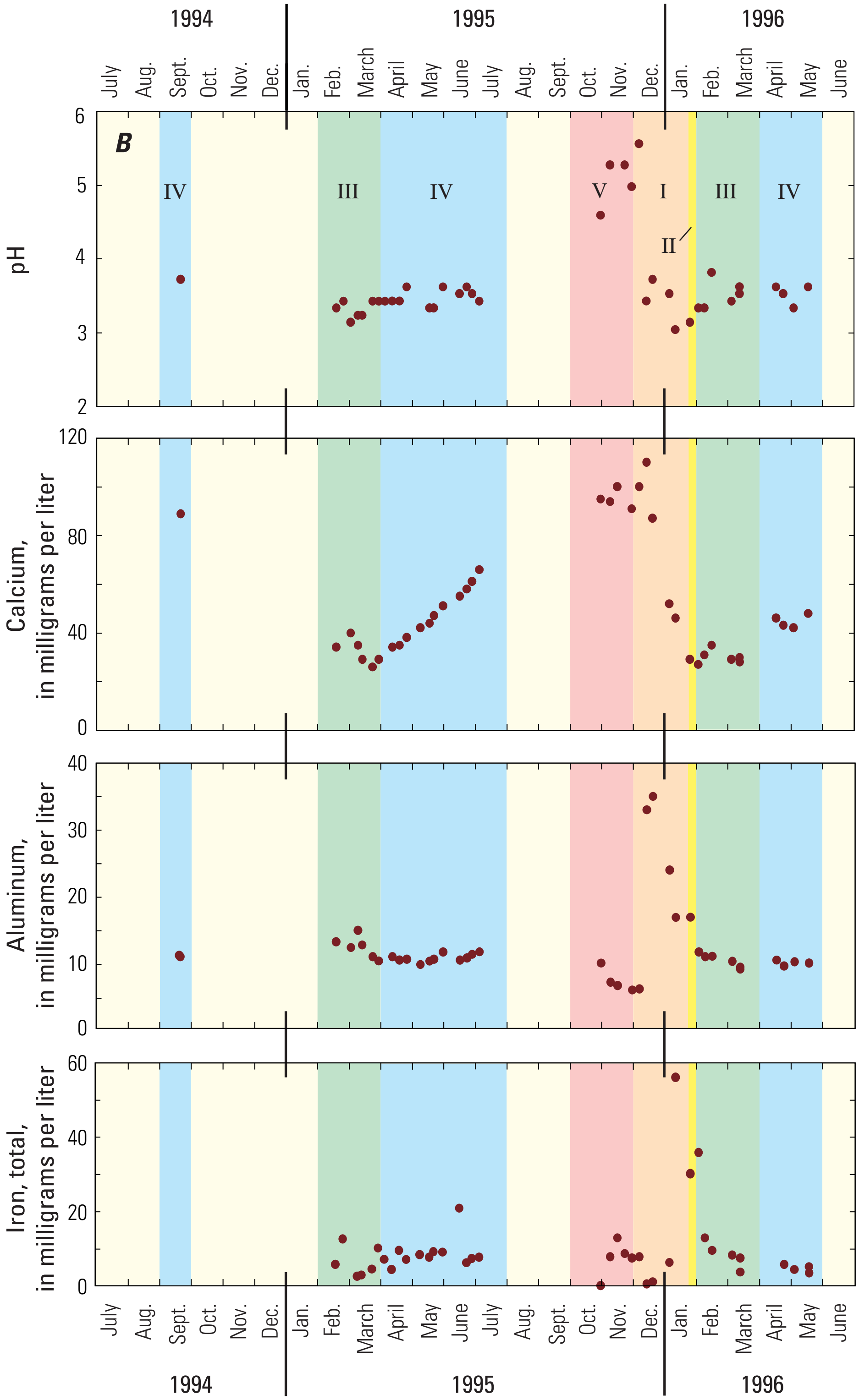

Figure 5.—Continued. ***(B)*** Values of pH and dissolved concentrations of calcium, aluminum, and iron at the Copper Bluff mine portal, September 1994–May 1996.

Hypothesis 2 also may explain certain aspects of the first-flush chemistry, as there was a change in pH from 5.6 at the end of the dry season (December 6, 1995) to 3.0–3.7 during the first-flush period (December 13, 1995, to January 10, 1996; appendix 1) accompanying the dramatic increase in metal concentrations in early December 1995. However, the pH of the mine portal effluent stayed relatively constant (3.1 to 3.8) for the periods between January and July 1995 and between January and May 1996 (appendix 1), during which time there were systematic increases in the Zn to Cu ratio. Although copper sorption in this pH range usually is minimal (Dzombak and Morel, 1990), it is possible that some copper sorption can take place below pH 4 in the presence of abundant hydrous iron oxides with high surface area, based on experiments using sediments from Keswick Reservoir, California (Jennifer Coston, written commun., 1998). Variations in aluminum (fig. 5*B*, appendix 1) and sulfate concentrations at site CB1 (appendix 1) are also consistent with temporal changes in pH. During low flow, as pH rose to values around 4.5, hydrous aluminum oxides formed, decreasing the concentration of soluble aluminum. Decreasing pH values can cause the dissolution of sulfate-bearing hydrous iron oxides such as schwertmannite, releasing sulfate to solution. Other changes in major ion composition, such as dissolved calcium, are not fully explained by this hypothesis.

The third hypothesis is problematic because changing hydrogeological and geochemical conditions throughout the year should affect the oxidation rates of sphalerite and chalcopyrite to an equal degree. However, little is known about microbial effects in these systems, as well as galvanic interactions between intergrown sulfide grains that could affect relative reaction rates.

The fourth hypothesis, mixing of two dominant water types in different proportions within the Copper Bluff deposit, may play a role, especially during low-flow conditions. The geochemistry of the adit discharge during the period of lowest flow (October 30 to December 6, 1995) was characterized by relatively high pH (4.6 to 5.6) and relatively low copper concentrations (2.3 to 3.6 mg/L, compared with 4.1 to 77 mg/L at other times during the period January 1995 through May 1996). It is likely that the hydrogeology and the distribution of host rock lithologies play a role in determining the flow paths that drain the mine workings at lowest flow. The flow paths that appear to be operative during this condition may involve contact with rocks having more neutralizing capacity, and (or) a higher Zn to Cu ratio, and (or) a lower sulfide content. In contrast, the rocks and mine workings in contact with flow paths operative during higher flows could have relatively less neutralizing capacity and (or) a lower Zn to Cu ratio and (or) a higher sulfide content.

Therefore, none of the hypotheses can be ruled out entirely, and all may contribute to some degree. The first hypothesis (efflorescent salt formation and dissolution) is spatially limited to the upper, undersaturated part of the mine workings. The second hypothesis (adsorption and desorption reactions) would require places where pH is greater than about 4, conditions under which significant copper sorption can occur. The third hypothesis (variable reaction rates of sulfide oxidation) is limited with regard to unknown biogeochemical processes that may favor sphalerite oxidation relative to chalcopyrite during drying-out conditions and that may favor chalcopyrite oxidation during relatively wet or lower-pH conditions. The last hypothesis (mixing of water types) depends on flow paths through different host rocks and (or) types of mineralization and wall-rock alteration.

Time-series plots of aluminum and iron (fig. 5*B*) show patterns similar to those for zinc and copper (fig. 5*A*) with regard to dramatic increases in concentration beginning in mid-December 1995 as part of the first-flush period. The positive correlation of these constituents as well as sulfate (not shown) with copper and zinc is an indication that hypothesis 1—dissolution of soluble salts—is a viable explanation, as many of the more common evaporite minerals formed from mine waters are iron and aluminum sulfates (Alpers and others, 1994a; Nordstrom and Alpers, 1999; Jambor and others, 2000). Apparently, if there was a first-flush period in the 1994–1995 wet season, it occurred prior to the onset of weekly sampling in January 1995.

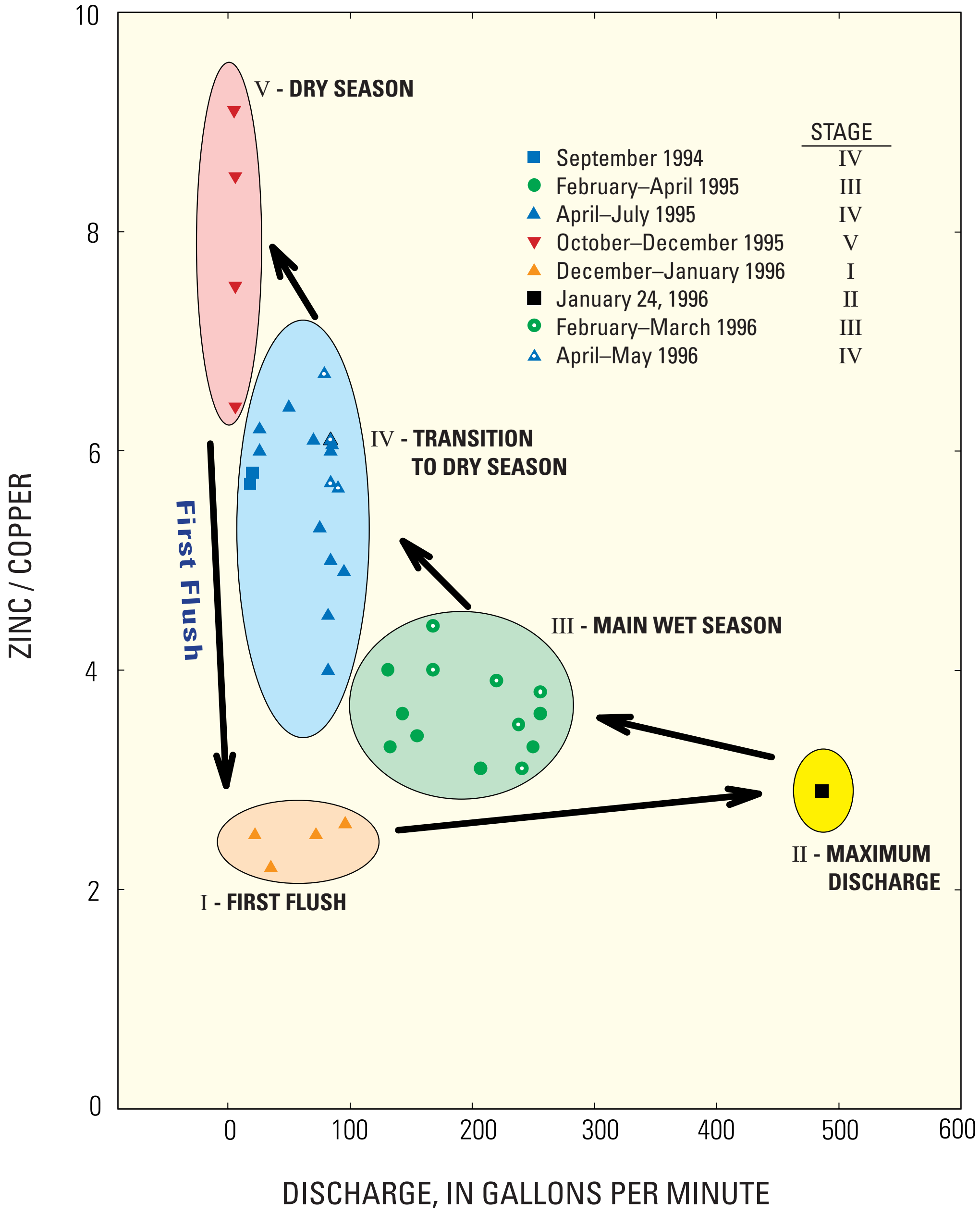

Figure 6. Ratio of dissolved zinc concentration to dissolved copper concentration versus rate of discharge at the Copper Bluff mine portal.

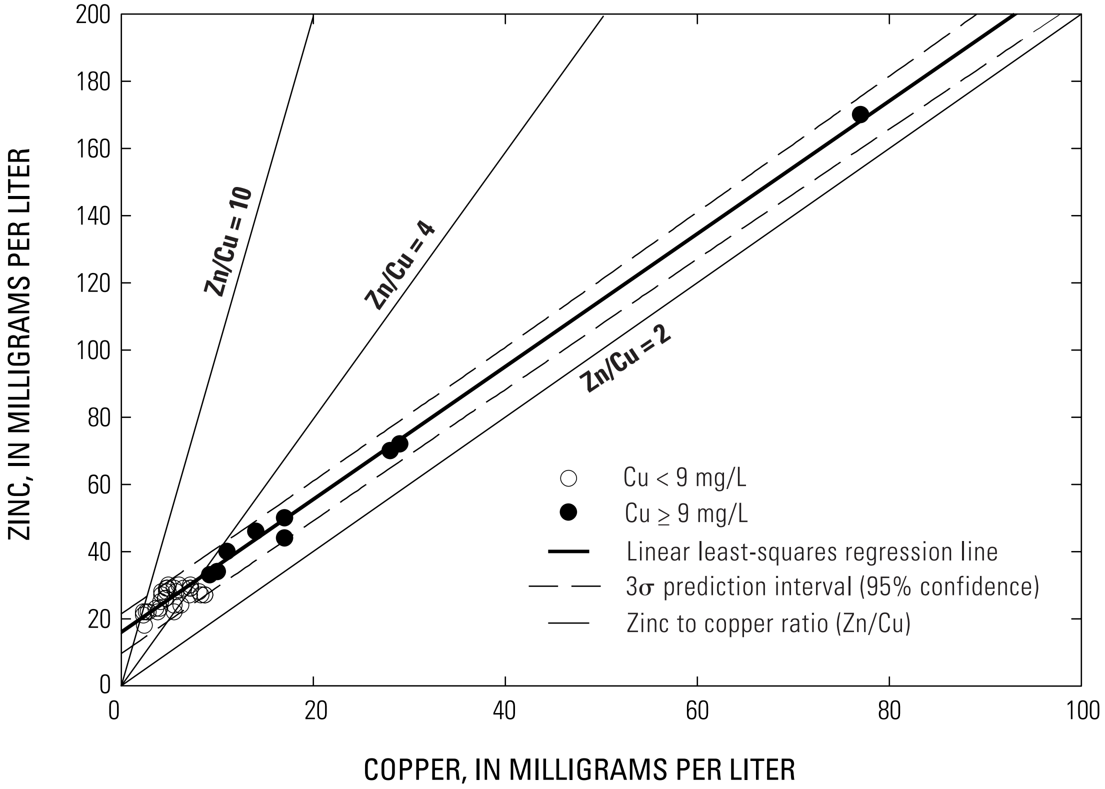

Figure 7. Correlations of dissolved constituents in the Copper Bluff mine waters. (***A)*** Copper (Cu) versus zinc (Zn), site CB1, linear scale. Linear least-squares regression applied to all data. mg/L, milligram per liter; <, less than; ≥, greater than or equal to.

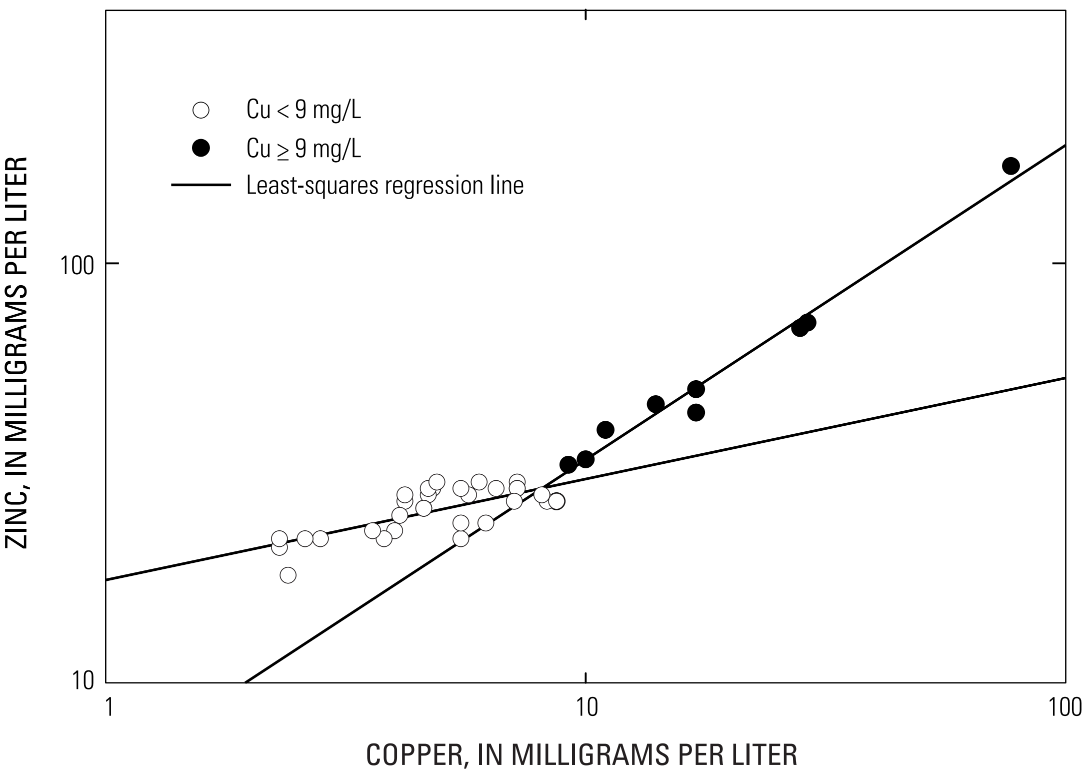

Figure 7—Continued. ***B.*** Copper versus zinc, site CB1, logarithmic scale. Two least-squares regressions applied separately to subsets of the data.

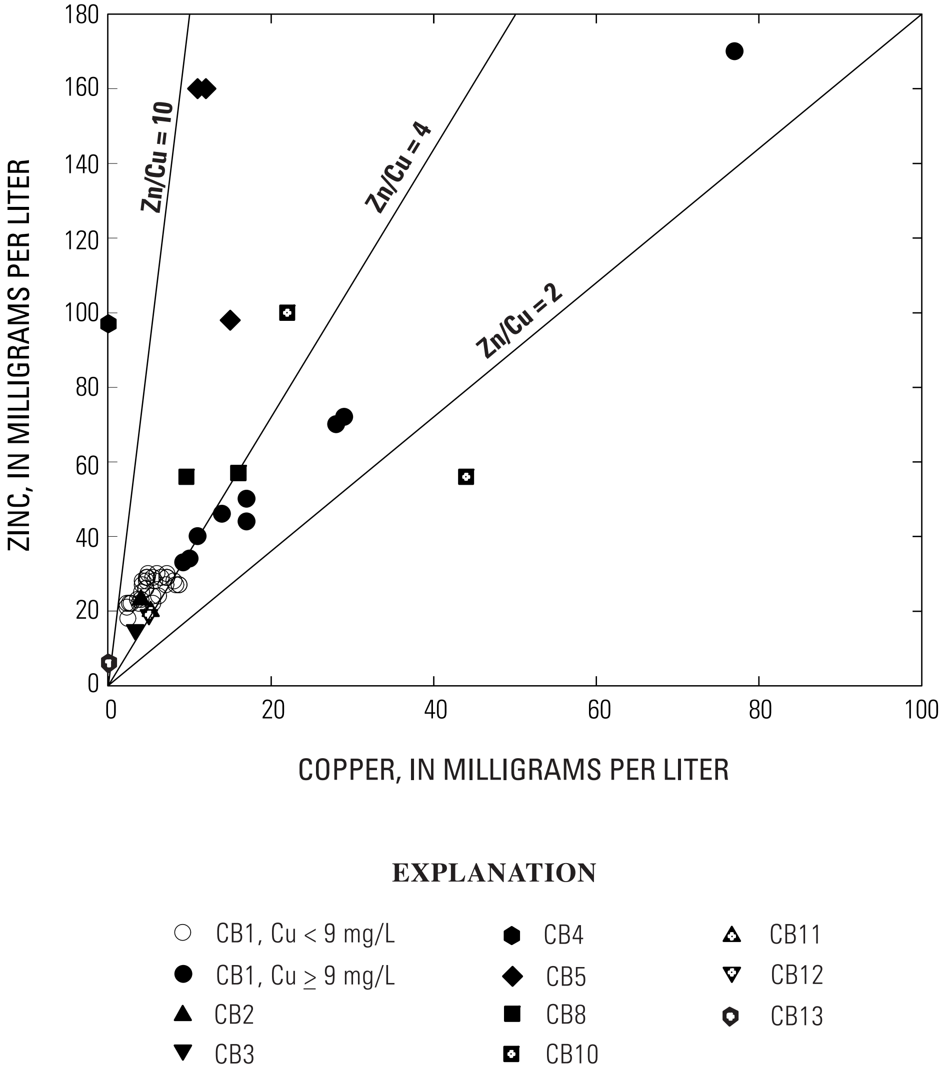

Figure 7—Continued***.*** ***C.*** Copper versus zinc, all mine sites.

Concentrations of sodium and calcium decreased or stayed nearly constant during the first-flush period in mid-December 1995 to early January 1996, in contrast with dramatic increases in concentrations of constituents such as iron, copper, zinc, and sulfate that are more directly associated with sulfate mineral oxidation. Sodium and calcium are contributed to solution by the dissolution of silicate and carbonate gangue (non-sulfide) minerals, for which dissolution rates are faster at lower pH, so their concentration is indirectly tied to sulfide oxidation and its effect on lowering pH. Nevertheless, the lack of dramatic increase in the concentrations of these elements during the first-flush period indicates that the effect of dilution is apparently stronger than that of increased gangue mineral hydrolysis.

Magnesium concentrations increased during the first two weeks of the first-flush period. The increase in magnesium concentrations may have been caused in part by the dissolution of common soluble salts such as epsomite ($MgSO_4 \cdot 7H_2O$) during the first-flush period.

Underground Reconnaissance

Water quality data for samples taken during the three underground reconnaissance visits are presented in table 1. The lowest pH values were from sites CB5 (ore shoot B), CB8 (ore shoot A), and CB10 (ore shoot C) (fig. 3). The highest concentrations of cadmium and copper were found at site CB10, whereas the highest concentrations of nickel and zinc were at site CB5. The flow rates from these ore shoots were relatively small, generally less than 1 percent of the total adit discharge, so these sources did not represent a significant part of the overall metals contained in the adit drainage at the time of sampling.

Water samples taken from the floor of the main tunnel near ore shoot B (site CB5) and farther back in the mine workings near the intersection of the north-south crosscut and the decline/winze (sites CB11 and CB12) had compositions similar to that of the overall drainage sampled at site CB1 (fig. 3*A*). Relatively dilute water in the south crosscut was sampled at site CB13. Water upwelling from lower levels of the mine was included in the sample taken at site CB11, although the sample also probably included some water flowing along the main adit level from the north crosscut area. Sample CB12 was taken nearby, and also likely represents a mixture of the upwelling water and the water from the north crosscut. Comparison of the chemistry of the water samples from sites CB11 and CB12 (table 1) indicates that these two samples have very similar composition with regard to major and trace elements. This result implies that water upwelling from lower levels of the mine is of similar quality to the overall drainage from the north crosscut. Because of limited access, it remains unknown whether the drainage from the north crosscut is primarily from the upper mine workings or perhaps from another upwelling zone.

Comparison of samples from CB11 and CB12 with the overall adit discharge at site CB1 indicates that mixing with more acidic waters from ore shoots at sites CB5, CB8, and CB10 causes a lowering of pH from about 4.0 to about 3.5 (based on data from samples collected in March 1996). Concentrations of copper and zinc are not appreciably different; however, other trace elements show variations in concentration along the flow path between sites CB11 and CB12 and site CB1; manganese varied from about 300 to 800 µg/L, and total iron from about 1 mg/L to more than 3 mg/L (table 1). These data suggest that the mixing of several different water types is involved and that there may be a wider range of iron and manganese concentrations than of copper and zinc concentrations among the water types.

The water sample taken in September 1994 at site CB4 (table 1), from drips at the end of a north-facing drift about 200 ft from the portal entrance, was unusual in that it had a relatively high pH of 5.7 and the highest concentration of dissolved iron encountered in the study. Although agreement between the two laboratories for the iron analysis of this split sample was poor, the reported iron concentrations of 250 and 430 mg/L are higher than even the most acidic samples from the ore shoots (for example, site CB5 in September 1994, 205 to 230 mg/L). The relatively high zinc concentration (97 mg/L) and extremely low copper (0.020 mg/L), plus the observation that site CB4 was actively seeping in September 1994 at a time of relatively low flow, indicate that the water from site CB4 is perhaps related to the end-member type-A water discussed in a previous section. However, the high iron content of the sample from site CB4 contrasts with the relatively low iron content of water samples taken at site CB1 at low flow.

Table 1. Water-quality data for samples from the Copper Bluff mine workings and nearby surface waters

[Eh, oxidation-reduction potential; ICP, inductively coupled plasma; UV-vis, ultraviolet-visible spectroscopy; $CaCO_3$, calcium carbonate; m/d/y, date format in month/day/year; µS/cm, microsiemens per centimeter; mV, millivolt; °C, degrees Celsius; mg/L, milligram per liter; µg/L, microgram per liter; dup, duplicate sample; —, no data]

Site	Date (m/d/y)	Time	Specific conductance (µS/cm)	pH, field	Eh, field (mV)	Temperature (°C)	Calcium, dissolved (mg/L)	Magnesium, dissolved (mg/L)	Sodium, dissolved (mg/L)	Potassium, dissolved (mg/L)
Mine waters										
CB1	9/19/94	1900	940	3.7	—	13.2	92	37	14	1.0
(dup)	9/19/94	1905	940	3.7	—	13.2	89	36	13	1.0
	9/20/94	1000	910	3.7	640	13.0	88	35	13	0.9
	3/14/95	1135	780	3.2	720	12.5	29	17	4.3	0.7
	3/12/96	1400	510	3.6	660	13.0	28	12	4.5	—
(dup)	3/12/96	1410	510	3.5	660	12.3	30	13	4.3	0.7
CB2	9/20/94	1117	950	3.6	640	15.4	92	37	13	1.0
CB3	9/20/94	1510	4,300	4.5	450	14.4	78	25	13	0.9
	3/14/95	1440	560	3.1	690	12.4	28	14	4.2	0.7
CB4	9/20/94	1143	4,200	5.7	190	13.0	630	180	16	1.3
CB5	9/21/94	1400	4,200	2.7	650	13.0	460	230	15	1.5
(dup)	9/21/94	1405	4,200	2.7	650	13.0	390	190	17	1.4
	3/14/95	1400	2,800	2.7	690	12.2	190	100	7.6	0.8
CB8	3/14/95	1300	1,400	2.8	720	13.0	28	41	4.0	0.2
(dup)	3/14/95	1305	1,400	2.8	720	11.6	28	41	4.0	0.7
	3/13/96	1100	1,200	3.0	680	11.3	39	41	4.8	0.5
CB10	3/14/95	1700	2,800	2.5	690	13.0	140	160	5.7	0.1
	3/13/96	1200	2,900	2.6	770	13.0	180	130	5.9	0.1
CB11	3/13/96	1340	400	3.8	650	12.5	26	9.4	4.2	0.7
CB12	3/13/96	1400	410	4.0	610	12.5	26	9.3	4.2	0.6
CB13	3/13/96	1620	360	6.4	350	13.7	40	14	7.5	0.6
Surface waters										
CBSWA	3/15/95	1225	320	4.9	—	—	17	9.3	3.3	—
CBSWB	3/15/95	1240	550	4.2	—	—	26	24	3.5	—
CBSWC	3/15/95	1340	410	4.0	—	—	17	15	4.2	—
CBSWD	3/15/95	1315	520	4.1	—	—	24	20	3.5	—
CBSWE	3/15/95	1405	520	4.0	—	—	24	20	3.6	—
CBSWF	3/15/95	1135	150	7.3	—	—	12	7.8	3.7	—
Field blanks										
	9/21/94	1600	6	—	—	—	0.09	<0.01	<0.2	0.1
	3/15/95	1430	50	—	—	—	0.08	<0.01	<0.2	—

Table 1. Water-quality data for samples from the Copper Bluff mine workings and nearby surface waters—Continued

Site	Date (m/d/y)	Time	Sulfate, dissolved (mg/L)	Chloride, dissolved (mg/L)	Fluoride, dissolved (mg/L)	Bromide, dissolved (mg/L)	Silica, dissolved (mg/L)	Aluminum, dissolved (mg/L)	Cadmium, dissolved (μg/L)	Chromium, dissolved (μg/L)	Copper, dissolved (mg/L)
Mine waters											
CB1	9/19/94	1900	540	2.9	0.3	0.06	30	6.3	60	< 1	4.0
(dup)	9/19/94	1905	510	2.6	0.3	0.09	29	6.4	60	< 1	3.8
	9/20/94	1000	500	2.4	0.3	0.09	30	6.1	60	< 1	3.8
	3/14/95	1135	290	3.2	0.2	—	21	7.9	160	3.3	11
	3/12/96	1400	240	—	—	—	19	4.3	80	—	5.5
(dup)	3/12/96	1410	—	—	0.1	—	20	4.6	87	1.5	5.5
CB2	9/20/94	1117	530	2.7	0.3	0.03	30	6.3	70	< 1	4.0
CB3	9/20/94	1510	380	2.6	0.4	0.09	27	2.1	60	2.6	3.3
	3/14/95	1440	330	3.6	0.2	—	—	—	—	—	—
CB4	9/20/94	1143	3,500	4.1	0.1	0.5	27	0.020	10	< 1	0.020
CB5	9/21/94	1400	3,300	1.7	0.1	0.9	56	42	210	13	11
(dup)	9/21/94	1405	3,300	2.1	0.1	0.9	57	42	250	13	12
	3/14/95	1400	1,700	5.0	0.1	—	63	27	240	10	15
CB8	3/14/95	1300	860	3.1	0.3	—	30	25	240	12	16
(dup)	3/14/95	1305	860	4.0	0.2	—	29	25	230	12	16
	3/13/96	1100	640	2.9	0.4	—	32	16	160	7.1	9.6
CB10	3/14/95	1700	3,100	6.8	0.1	—	66	81	470	25	44
	3/13/96	1200	2,100	2.9	0.7	—	59	59	280	18	22
CB11	3/13/96	1340	160	2.5	0.1	—	19	3.1	84	< 1	5.2
CB12	3/13/96	1400	160	2.7	0.1	—	18	2.9	77	< 1	5.0
CB13	3/13/96	1620	140	2.1	0.2	—	17	0.034	24	< 1	0.11
Surface waters											
CBSWA	3/15/95	1225	150	—	—	—	26	1.6	—	—	8.9
CBSWB	3/15/95	1240	280	—	—	—	31	12	—	—	9.0
CBSWC	3/15/95	1340	180	—	—	—	32	8.4	—	—	7.1
CBSWD	3/15/95	1315	240	—	—	—	31	8.8	—	—	10
CBSWE	3/15/95	1405	240	—	—	—	32	8.3	—	—	11
CBSWF	3/15/95	1135	4.7	—	—	—	17	0.030	—	—	0.010
Field blanks											
	9/21/94	1600	1.4	.20	.10	< 0.01	30	0.010	10	< 1	0.010
	3/15/95	1430	0.1	—	—	—	< 0.01	< 0.010	—	< 10	—

Table 1. Water-quality data for samples from the Copper Bluff mine workings and nearby surface waters—Continued

Site	Date (m/d/y)	Time	Iron, dissolved, ICP (mg/L)	Iron, dissolved, UV-vis (mg/L)	Iron, ferrous, dissolved, UV-vis (mg/L)	Lead, dissolved (µg/L)	Manganese, dissolved (µg/L)	Nickel, dissolved (µg/L)	Zinc, dissolved (mg/L)	Alkalinity (as mg/L $CaCO_3$)
Mine waters										
CB1	9/19/94	1900	5.2	4.86	4.31	11	2,400	60	23	0
(dup)	9/19/94	1905	4.7	5.77	4.28	9	2,300	59	22	0
	9/20/94	1000	6.5	12.6	2.77	10	2,200	60	22	0
	3/14/95	1135	14	4.61	2.69	26	770	40	40	0
	3/12/96	1400	3.4	3.80	1.80	—	800	—	22	0
(dup)	3/12/96	1410	3.0	3.30	1.90	19	840	38	24	0
CB2	9/20/94	1117	2.7	3.06	2.0	11	2,400	63	23	0
CB3	9/20/94	1510	2.9	3.06	2.60	5	1,200	30	15	—
	3/14/95	1440	9.9	9.15	0.800	31	480	25	40	0
CB4	9/20/94	1143	250	430	430	1	3,000	300	97	—
CB5	9/21/94	1400	230	206	72.0	5	34,000	890	160	0
(dup)	9/21/94	1405	220	205	70.0	5	34,000	870	160	0
	3/14/95	1400	—	101	25.7	6	13,000	370	98	0
CB8	3/14/95	1300	59	60.8	7.55	6	2,600	160	57	0
(dup)	3/14/95	1305	58	60.6	7.62	6	2,600	150	57	0
	3/13/96	1100	60	54.0	21.0	10	5,600	260	56	0
CB10	3/14/95	1700	44	256	1.66	4	9,500	420	56	0
	3/13/96	1200	190	190	1.60	5	9,900	340	100	0
CB11	3/13/96	1340	0.94	1.2	0.540	17	290	13	20	0
CB12	3/13/96	1400	0.83	1.1	0.570	16	300	13	19	0
CB13	3/13/96	1620	0.012	<0.010	<0.010	1	140	11	6.3	—
Surface waters										
CBSWA	3/15/95	1225	0.003	<0.010	<0.010	—	430	—	16	—
CBSWB	3/15/95	1240	0.022	0.018	0.014	—	520	—	8.2	—
CBSWC	3/15/95	1340	0.34	0.379	0.204	—	410	—	2.6	—
CBSWD	3/15/95	1315	0.096	0.108	0.054	—	690	—	11	—
CBSWE	3/15/95	1405	0.12	0.128	0.064	—	710	—	11	—
CBSWF	3/15/95	1135	0.003	<0.010	<0.010	—	6	—	0.11	64
Field blanks										
	9/21/94	1600	0.011	—	—	< 1	< 1	< 1	0.006	—
	3/15/95	1430	< 0.003	—	—	—	—	—	< 0.003	—

Surface Waters

Six surface-water samples were taken on March 15, 1995, from runoff associated with seeps along the 500-ft-high bluff along State Highway 96, above the main tunnel to the Copper Bluff mine. The runoff from the bluff flowed into a ditch along the east side of the road and into a culvert that passed under the road and discharged toward the Trinity River. Five samples taken in the mineralized zone had pH values ranging from 4.0 to 4.9, specific conductance from 320 to 550 µS/cm, sulfate concentrations from 150 to 280 mg/L, copper concentrations from 7.1 to 11.0 mg/L, and zinc concentrations from 2.6 to 16 mg/L. The sixth sample, taken from a less mineralized area several hundred feet to the south, had a pH of 7.3, a specific conductance of 150 µS/cm, a sulfate concentration of 4.7 mg/L, a copper concentration 0.010 mg/L, and a zinc concentration of 0.11 mg/L (table 1).

The elevated copper concentrations in the surface runoff from this area were displayed by the partial replacement of steel bars on a culvert drain screen by native copper. Metallic copper also was observed on the galvanized (zinc-coated) steel culvert pipe as a replacement deposit. Samples CBSWD and CBSWE were taken at upstream and downstream ends of the culvert pipe, respectively, in an attempt to determine if copper attenuation could be detected and if mobilization of zinc was occurring from the galvanized pipe. Comparison of the dissolved metal data for these two samples indicates that zinc concentrations were identical at the two ends of the pipe, and copper showed an apparent slight increase flowing through the pipe, but within the expected uncertainty of such analytical data. Therefore, it is concluded that the galvanized pipe in this culvert had no measurable effect on water quality during the sampling period.

Impact of Copper Bluff Mine Effluent on the Trinity River

The impact of the Copper Bluff mine effluent on water quality in the Trinity River can be evaluated by examining the relative flows of these two surface waters. Mean daily values for the discharge of the Trinity River at Hoopa from the gage maintained by the U.S. Geological Survey are compiled in appendix 2 for 37 dates on which there are discharge data for the Copper Bluff mine portal effluent from February 17, 1995, through May 17, 1996. The discharge ratio (or dilution factor) of these flows (Trinity River flow divided by Copper Bluff flow) during this period ranged from 18,100 to 509,000. Ninety percent (33 of 37) of the discharge ratios were between 20,000 and 82,000.

The water sample from site CB1 on December 19, 1995, had by far the highest concentrations of copper (77 mg/L), zinc (170 mg/L), and cadmium (0.84 mg/L) encountered during this study (appendix 1). The discharge ratio on that day was 67,100 (appendix 2). Assuming perfect mixing with the metal staying in the dissolved form, the incremental rise in metal concentrations in the Trinity River would have been as follows: copper, 0.0011 mg/L; zinc, 0.0025 mg/L; and cadmium 0.000012 mg/L. These incremental increases probably did not cause the Trinity River to exceed water-quality criteria designed for the protection of aquatic life because the river upstream of the Copper Bluff mine is not known to be close to the regulatory limits for these metals (for example, copper, 0.0056 mg/L).

A somewhat worse scenario than the situation in December 1995 might involve discharge of the typical first flush from the Copper Bluff mine at a time when the dilution ratio of the Trinity River was at a minimum. Assuming a discharge ratio of 18,100 (the minimum value during the period of study; appendix 2) instead of 67,100 (the value for December 1995) results in increasing the potential impact of the Copper Bluff mine on water quality in the Trinity River by a factor of 3.7, yielding the following potential increases in metal concentration: copper, 0.0043 mg/L; zinc, 0.0094 mg/L; and cadmium 0.000046 mg/L. Such increases are more likely if there is significantly more rain in the Hoopa Valley area than in the eastern part of the Trinity River watershed, perhaps following a prolonged drought causing low water levels in Trinity Lake. Flows are subject to change at any time because, to a large degree, flow in the Trinity River is determined by releases from Lewiston Dam, a facility operated by the Bureau of Reclamation.

A worst-case scenario would involve a catastrophic release of metal-rich water and sediment from the Copper Bluff mine during a time of relatively low flow in the Trinity River. High-water marks observed at a height of 3 to 4 ft above the floor on the tunnel walls during underground reconnaissance indicate that past blockages, caused by movement of mine waste in the ore chutes and (or) collapse of mine timbers and rock, impounded more than

100,000 gallons of water. Sudden release of a large volume of metal-rich water caused by breaching of a temporary blockage in the mine (or by catastrophic failure of an engineered mine plug) could have serious effects on fish and other aquatic resources in the Trinity River, especially if it occurred during a time of relatively low flow in the river.

Mineralogy and Geochemistry of Ores and Host Rocks

Samples of mineralized and unmineralized rocks collected near the Copper Bluff deposit were examined by transmitted and reflected light petrography to determine the mineralogy and to describe the geologic history of the area. The mineralogy of the rocks provides some constraints on geochemical reactions that influence the composition of waters draining the mine. In addition, the petrographic relationships between the minerals help to determine the geological events that control the mineralogy, grain size, and distribution of lithologies.

On the basis of preliminary identification of minerals using the petrographic microscope, samples were prepared for electron microprobe analysis. The formulas of minerals encountered in rock samples from the Copper Bluff mine are given in table 2. Formulas in table 2 with decimal compositions are based on electron microprobe determinations detailed in appendix 3.

Table 2. Composition of minerals observed in rock samples from the Copper Bluff mine

[Formulas for gangue minerals based on electron microprobe data in Appendix 3; formulas for ore minerals based on unpublished electron microprobe data. Fe^{II}, ferrous iron; Fe^{III}, ferric iron; Al^{oct}, octahedral aluminum; Al^{tet}, tetrahedral aluminum]

Gangue minerals

Mineral	Formula
Quartz	SiO_2
Calcite	$CaCO_3$
Feldspar (albite)	$Na_{0.987}Ca_{0.009}K_{0.004}Al_{1.009}Si_{2.991}O_8$
Epidote	$Ca_2\,(Fe^{III}_{0.73}Al^{oct}_{0.44})Al^{tet}_2Si_3O_{12}(OH)$
Amphibole	$Ca_2(Mg,Fe^{II},Fe^{III})Si_8O_{22}(OH)_2$
Chlorite	$(Mg_{3.94}Fe^{II}_{5.60}Mn_{0.11}Al^{oct}_{2.39})(Al^{tet}_{2.47}Si_{5.53})O_{20}(OH)_{16}$
Mica	$K_{1.80}Na_{0.09}(Mg_{0.70}Fe^{II}_{0.41}Ca_{0.01}Mn_{0.01}Al^{oct}_{3.09})(Al^{tet}_{1.50}Si_{6.50})O_{10}(OH)_2$
Stilpnomelane	$K_{0.14}Na_{0.01}Ca_{0.01}(Mg_{1.38}Fe^{II}_{4.02}Al^{oct}_{0.37})(Al^{tet}_{0.76}Si_{7.24})O_{10}(OH)_2(H_2O)_n$
Barite	$BaSO_4 \cdot 2H_2O$

Ore minerals

Mineral	Formula
Pyrite	FeS_2
Chalcopyrite	$CuFeS_2$
Sphalerite	$(Zn_{0.982}Fe_{0.013}Cd_{0.003}Cu_{0.002})S$
Tennantite	$(Cu_{9.856}Ag_{0.145})(As_{4.118}Sb_{0.658})(Zn_{1.051}Fe_{0.993}Cd_{0.007}Mn_{0.003})S_{13}$
Arsenopyrite	$FeAsS$
Galena	PbS
Bornite	Cu_5FeS_4
Gold	Au

Petrographic observations—host rocks

Two samples of the footwall schist (94RS704, 94RS705) were collected from the main adit. The protolith for these metamorphic rocks probably was a fine-grained clastic sediment with a significant component of material derived from mafic volcanic source rocks. The rocks have been metamorphosed to moderately foliated, fine-grained, quartz-albite-chlorite schists intergrown with fine-grained muscovite, acicular actinolite, and sphene. Fine-grained, subhedral epidote is abundant in these rocks and occurs as disseminated grains dispersed along the more mafic foliation bands. The textural relationships suggest that epidote nucleation and growth occurred after development of the foliation. Minor amounts of fine-grained biotite also occur in these rocks. Biotite typically occurs in radiating splays that cross-cut foliation at random angles. These textural relationships are consistent with a phase of metamorphic recrystallization of the rocks that post-dates the major deformation. Intrusion of igneous rocks into the metamorphic sequence is one possible explanation for what appears to be a post-deformational increase in metamorphic grade of these rocks, but further study, including detailed mapping of the surrounding area, would be required to substantiate this suggestion. No carbonate minerals were observed in the thin sections examined. There is minor veining of these rocks by late stage quartz and (or) epidote. Only trace amounts of sulfides are present as disseminated grains of chalcopyrite and as less abundant pyrite and sphalerite.

One sample of the black carbonaceous phyllite (CB-R2) that forms the immediate footwall to the sulfide horizon was examined. This rock is very fine-grained and has a strong foliation that is enhanced by styolitic dissolution of quartz. The rock is composed predominantly of quartz, amphibole (actinolite), mica (muscovite), and sphene. The presence of albite is suspected, but difficult to confirm because of the fine grain size. Trace amounts of disseminated pyrite and chalcopyrite occur along the foliation. Minor amounts (less than 1 percent) of carbonate occur as late-stage veins cutting across the foliation.

One rock sample was taken from the south crosscut on the east side of a fault that apparently marks the eastern continuation of the mineralized horizon in the upper mine workings (CB-R1). According to the structural interpretation of Robertson and Holmes (1953), these rocks are in the hanging wall of the sulfide zone. This sample is a quartz-muscovite-albite schist and differs from the footwall schist in that the mafic minerals—chlorite, actinolite, and epidote—are much less abundant. This rock also contains significant quantities (approximately 5-to-10 volume percent) of calcite, which tend to be concentrated in the quartz-rich bands. The presence of carbonate gives this rock considerably more acid-neutralizing capacity than other rocks examined in this study. However, it is important to note that the interpreted stratigraphic position of this rock unit or its distribution in the mine working was not determined as part of this investigation, so the potential importance of this rock unit for neutralizing acid mine water is presently unknown.

Petrographic observations—mineralized rocks

The only samples of in situ massive sulfide collected for this study were from the back at the north crosscut (CB-R11). Massive sulfide at this location is very pyrite-rich and contains only minor amounts of base-metal sulfide minerals. Pyrite is relatively coarse-grained (up to 1 mm), subhedral to euhedral, but heavily fractured. Minor amounts of chalcopyrite are present, with rare grains of sphalerite and trace amounts of tennantite. The gangue is predominantly coarse-grained, subhedral-to-euhedral albite and muscovite with only minor amounts of quartz. Most quartz occurs in late-stage veins, some of which contain coarse barite. Abundant disseminated, fine-grained rutile and (or) sphene suggest that massive sulfide at this site formed by precipitation in or replacement of sedimentary host-rock.

A massive sulfide sample collected from ore shoot E (CB-R13) is more enriched in base metals. Chalcopyrite is the dominant mineral, followed by pyrite and sphalerite. Galena occurs in minor amounts. All of the sulfide phases show textural evidence of deformation and recrystallization. The gangue is predominantly a post-deformational quartz vein with chlorite. The quartz contains muscovite-rich fragments with folded foliation. Barite is abundant in the sulfide-rich parts of the sample, which also contains minor amounts of euhedral sphene. Rare fine needles of actinolite and locally abundant coarse-grained biotite cut the massive sulfide in random orientations, indicating crystallization after the final phase of deformation.

Most of the massive sulfide samples examined were collected from rubble in ore shoot A (fig. 3*A*) and are assumed to be generally representative of the material mined (94RS708, 94RS708A, CB-R8B, CB-R8D, CB-R8F). The samples contain subequal amounts of sphalerite, pyrite, and chalcopyrite. No original depositional textures remain in these rocks; all have been deformed and are recrystallized. The textures reflect the relative strength of the different sulfides as well as the extent of recrystallization after deformation has ceased. Sphalerite also tends to be massive in these samples, often forming the matrix to the other sulfides. Sphalerite tends to be colorless to light yellow in transmitted light, but is generally only semitransparent because of the abundance of very fine-grained, crystallographically oriented inclusions of chalcopyrite (chalcopyrite disease of Barton and Bethke, 1987). Chalcopyrite ranges from massive to elongate wispy stringers that parallel the foliation plane. Pyrite tends to be subhedral to euhedral, but is often fractured because it undergoes brittle deformation at temperatures where sphalerite and chalcopyrite can deform plastically (Vokes, 1969). Pyrite often has atoll textures caused by large inclusions of other sulfide minerals or gangue minerals. Galena is the next most abundant sulfide and ranges from minor to common in these samples. Tennantite generally is less abundant than galena, but is relatively abundant in some samples. Arsenopyrite also is present in most samples, but is generally less abundant than tennantite. One grain, tentatively identified as enargite, was observed as an inclusion in chalcopyrite. Examination of some of the samples in reflected light, using a 100X oil immersion lens, revealed rare grains of gold as microscopic (1-to-6 μm) inclusions in arsenopyrite, tennantite, and chalcopyrite.

Gangue (non-sulfide) minerals in the mineralized samples are predominantly barite, albite, and quartz, which occur in variable amounts in the samples. Muscovite is a relatively common phase in most samples, and several samples contain chlorite, which tends to display anomalous brown and purple interference colors with cross-polarized light. Minor amounts of sphene are observed in many of the massive sulfide samples. Calcite occurs in very minor amounts in a few samples as late-stage, cross-cutting veinlets, insufficient to have a significant effect on acid buffering in these rocks. Fluid inclusions are abundant in much of the barite and quartz and in some albite. The overwhelming majority of inclusions are secondary in origin and are related to deformation. Most inclusions are two-phase vapor-liquid; no daughter minerals were observed.

Mineral geochemistry—silicates

Electron microprobe analysis was used to determine the composition of various silicate minerals in the host rocks and ores of the Copper Bluff mine. Detailed results of the analyses are given in appendix 3, grouped by mineral. The data are summarized in table 2 as average compositions for the following individual silicate phases: feldspar, epidote, amphibole, chlorite, mica (muscovite/phengite), and stilpnomelane (an iron-rich phyllosilicate similar to talc).

The feldspar grains encountered are nearly pure albite ($NaAlSi_3O_8$), with a small amount of substitution of potassium and calcium (plus aluminum) for sodium (plus silicon) (appendix 3*A*). The average feldspar composition given in table 2 is based on 14 point analyses showing minimal variation. The six epidote analyses (appendix 3*B*) indicate that the mineral is fairly homogeneous, yielding an average Fe^{III} to Al ratio of 0.73:0.44 on the octahedral site (table 2). Analyses of amphibole (appendix 3*C*) show that it is rich in Ca and Mg, indicating actinolite composition. Analyses of chlorite (appendix 3*D*) indicate a fairly homogeneous composition corresponding to that of ripidolite. The three distinct compositions of mica detected vary primarily with respect to Fe and Mg, and range from muscovite to phengite. The mica composition given in table 2 is based on averaging all 27 points in appendix 3*E*. The stilpnomelane formula in table 2 is based eight point analyses (Appendix 3*F)* that indicate a fairly homogeneous composition.

Mineral geochemistry—sulfides

Sphalerite in base-metal-rich massive sulfide samples from the Copper Bluff mine workings is very rich in zinc when compared with samples from other localities where the zinc can be replaced to a large degree by iron, manganese, and cadmium, and to a lesser extent by silver and mercury. The average composition of sphalerite from the Copper Bluff mine workings is $(Zn_{0.982}Fe_{0.013}Cd_{0.003}Cu_{0.002})S$, on the basis of 37 points (data not shown). Five points with elevated iron and copper contents (sample CB-R11) were excluded from this average because they probably represent inclusions of other sulfide minerals such as chalcopyrite and pyrite, a well known texture in sphalerites described as chalcopyrite disease (Barton and Bethke, 1987). Sphalerite is the dominant cadmium-bearing phase encountered; cadmium contents range from about 0.2 to 0.4 weight percent (corresponding to 0.1 to 0.3 mole percent), with the exception of sample CB-R11, which had 1.39 to 1.67 weight percent cadmium (1.2 to 1.4 mole percent). Antimony, manganese, and silver contents of sphalerite were about or below 0.05 weight percent, with the exception of a single analysis of a sphalerite grain encapsulated in pyrite, which gave about 0.07 weight percent silver.

Chalcopyrite in the massive sulfide samples shows near ideal stoichiometry and contains insignificant quantities of trace elements (data not shown). Tennantite in the massive sulfide displays a relatively narrow range of compositions with most grains containing 16–19 weight percent arsenic and 3–6 weight percent antimony. Tennantite is the major silver-bearing phase in these samples with silver contents ranging from 0.7 to 1.3 weight percent.

Geochemistry of Iron Redox Speciation

Oxidation-reduction potential

Laboratory determinations of ferrous and total iron in filtered samples from the underground mine workings were used to compute values of redox potential on the basis of the ferrous-ferric couple. These calculations were done as part of aqueous speciation calculations using the program PHREEQC (Parkhurst, 1995), as described earlier (see "Methods"). The computed values of redox potential, expressed as pE, are compared in table 3 and in figure 8 with field measurements of pE made with a platinum electrode. The correlation between field and laboratory (Fe^{II}-Fe^{III}) pE values is positive, but is far from a perfect correspondence. For most of the samples, the agreement is within one unit of pE; however, it must be recognized that pE is a logarithmic scale, so differences greater than one represent more than a 10-fold difference in electron activity. All but one of the pE values computed from the laboratory iron data are larger than the corresponding field pE value. Despite these differences, the data indicate that the platinum electrode was, in most cases, responding to the iron redox couple.

A possible source of uncertainty in the aqueous speciation calculations of redox potential is analytical uncertainty in the Fe(ferrous) and Fe(total) measurements. Electrical charge imbalance values in the PHREEQC output provide a measure of analytical uncertainty and can help identify biased or incomplete data. Comparing charge imbalance values computed using field pE with those computed using laboratory (Fe^{II}-Fe^{III}) pE shows that charge imbalance is slightly better for eight of ten samples when laboratory (Fe^{II}-Fe^{III}) pE is used. This indicates that analytical bias in either Fe(ferrous) or Fe(total) measurements is not the likely source of the variations in pE shown on Figure 8.

Ferric iron activity and mineral saturation

Values of the activity of ferric iron were calculated as part of the aqueous speciation calculations for samples for which concentrations of both ferrous and total iron were determined. A plot of ferric iron activity in relation to pH (fig. 9) shows a strong negative correlation, indicating that ferric iron solubility is controlled by a solid phase. This is not surprising, given the abundance of hydrous ferric oxide (HFO) in the Copper Bluff mine tunnel. The aqueous speciation analysis is the first step toward a thermodynamic analysis of the properties of the phase that controls ferric iron solubility. The slope of the line defined by the points in figure 9 indicates the stoichiometry of the solubility-controlling phase (Alpers and Nordstrom, 1999). A linear regression through the points in figure 9 indicates a slope of –1.95. A slope of –2.4 was previously found for similar data from the Leviathan / Bryant Creek watershed in Alpine County, California, by Nordstrom (1991).

Table 3. Oxidation-reduction potential and saturation indices for ferric hydroxide in water samples from the Copper Bluff mine

[m/d/y, date format as month-day-year; pE, oxidation-reduction potential; Fe^{II}-Fe^{III}, ferrous-ferric oxide couple; $Fe(OH)_3$, ferric hydroxide; n.d., not determined.]

Site	Date (m/d/y)	Time	pE, field	pE[1], from Fe^{II}-Fe^{III}	Saturation index[1], $Fe(OH)_3$, field pE	Saturation index[1], $Fe(OH)_3$, pE from Fe^{II}-Fe^{III}
CB1	9/19/1994	1900	n.d.	10.8	n.d.	–0.58
CB1	9/20/1994	1000	11.0	11.5	–0.34	0.02
CB2	9/20/1994	1117	11.2	11.4	–0.82	–0.65
CB3	9/20/1994	1510	7.9	9.8	–1.30	0.52
CB4	9/20/1994	1143	3.3	n.d.	–0.49	n.d.
CB5	9/21/1994	1400	11.5	12.1	–1.66	–1.35
CB1	3/14/1995	1135	12.7	12.0	–0.89	–1.17
CB3	3/14/1995	1440	12.1	13.2	–1.12	–0.84
CB5	3/14/1995	1400	12.2	12.4	–1.54	–1.48
CB8	3/14/1995	1300	12.7	12.9	–1.16	–1.13
CB10	3/14/1995	1700	12.1	14.0	–1.97	–1.73
CB1	3/12/1996	1400	11.6	11.9	–0.37	–0.19
CB8	3/13/1996	1100	12.0	12.3	–0.82	–0.66
CB10	3/13/1996	1200	13.5	14.0	–1.40	–1.39
CB11	3/13/1996	1340	11.4	11.8	–0.44	–0.22
CB12	3/13/1996	1400	10.9	11.4	–0.31	0.01
CB13	3/13/1996	1620	6.2	n.d.	0.26	n.d.

[1] Calculated using PHREEQC computer program (Parkhurst, 1995), version 1.5 (David Parkhurst, written commun., 1997)

The plots in figure 10 show the saturation indices (SI) for HFO from the PHREEQC speciation runs, computed using values of pE determined by both field and laboratory (Fe redox) methods (table 3), plotted as a function of pH. Figure 10*A* shows SI values computed using laboratory iron data and figure 10*B* shows SI values computed using field pE measurements. If an HFO solid phase with the stoichiometry $Fe(OH)_3$ were controlling solubility, the trends in figure 10 would be close to horizontal. Figure 10*B* more closely approximates the expected pattern, suggesting some inaccuracies in the Fe^{II} and (or) Fe(total) determinations. The slope of the line defined by the data in figure 9 and distribution of data points in figures 10*A* and 10*B* indicate that the phase controlling ferric iron solubility has a ratio of hydroxide to ferric iron [$(OH):Fe^{III}$] less than 3 to 1.

Several recent studies have shown that sulfate (SO_4^{2-}) substitutes for hydroxyl [$(OH)_2^{2-}$] in HFOs formed from sulfate-rich solutions in the pH range of 3 to 4 (Bigham and others, 1990, 1994, 1996; Bigham, 1994; Murad and others, 1994; Bigham and Nordstrom, 2000). A newly described mineral, schwertmannite, has the formula $Fe_8O_8(OH)_6(SO_4)$. If such a phase is controlling iron solubility at the Copper Bluff mine, it would have a more sulfate-rich composition than the schwertmannite formula reported by Bigham and coworkers.

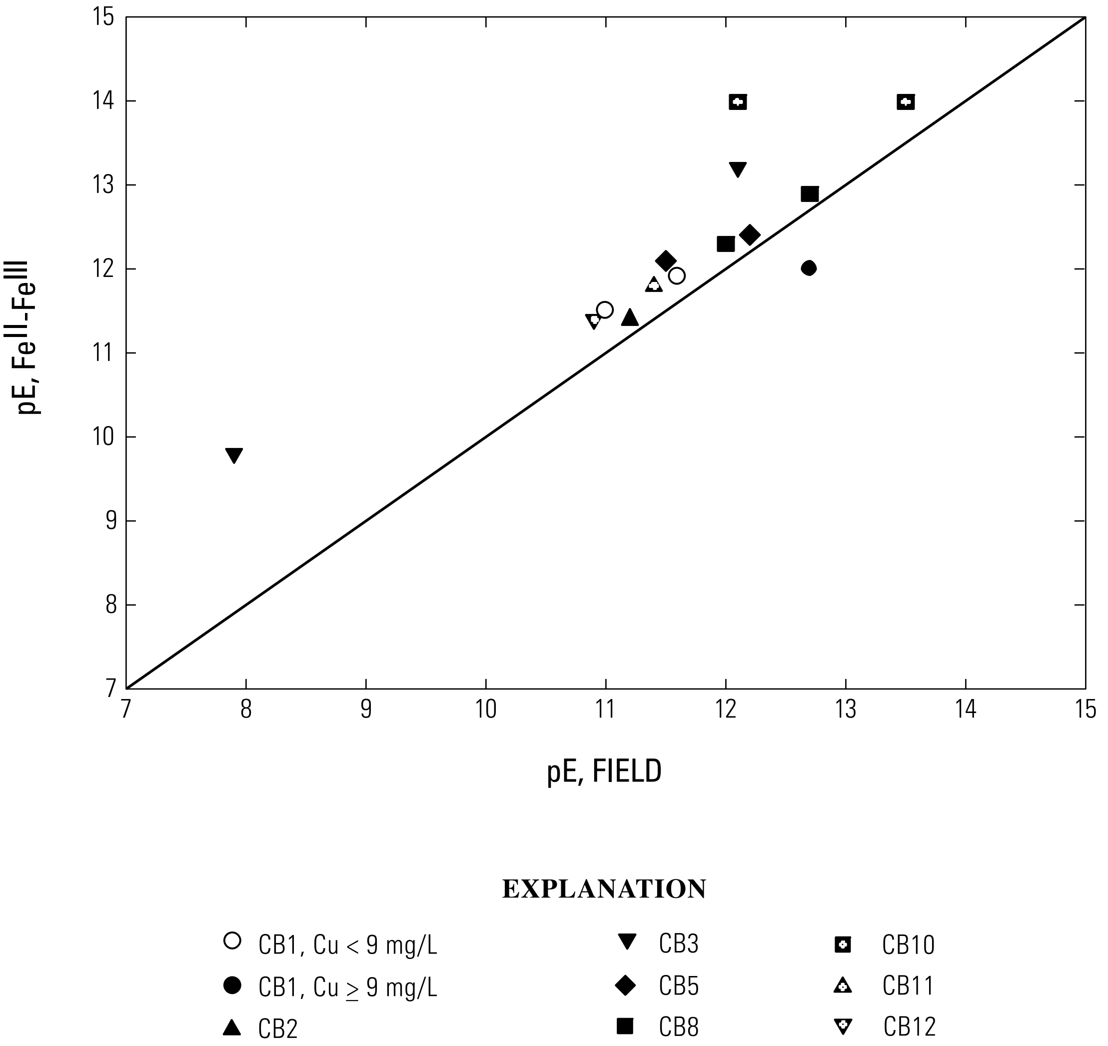

Figure 8. Relation of field pE values to pE values computed from dissolved iron concentrations for water samples from the underground mine workings, Copper Bluff mine.

pE, oxidation-reduction potential; Fe^{II}-Fe^{III}, ferrous-ferric oxidation-reduction couple; Cu, copper; mg/L, milligram per liter; <, less than; ≥, greater than or equal to.

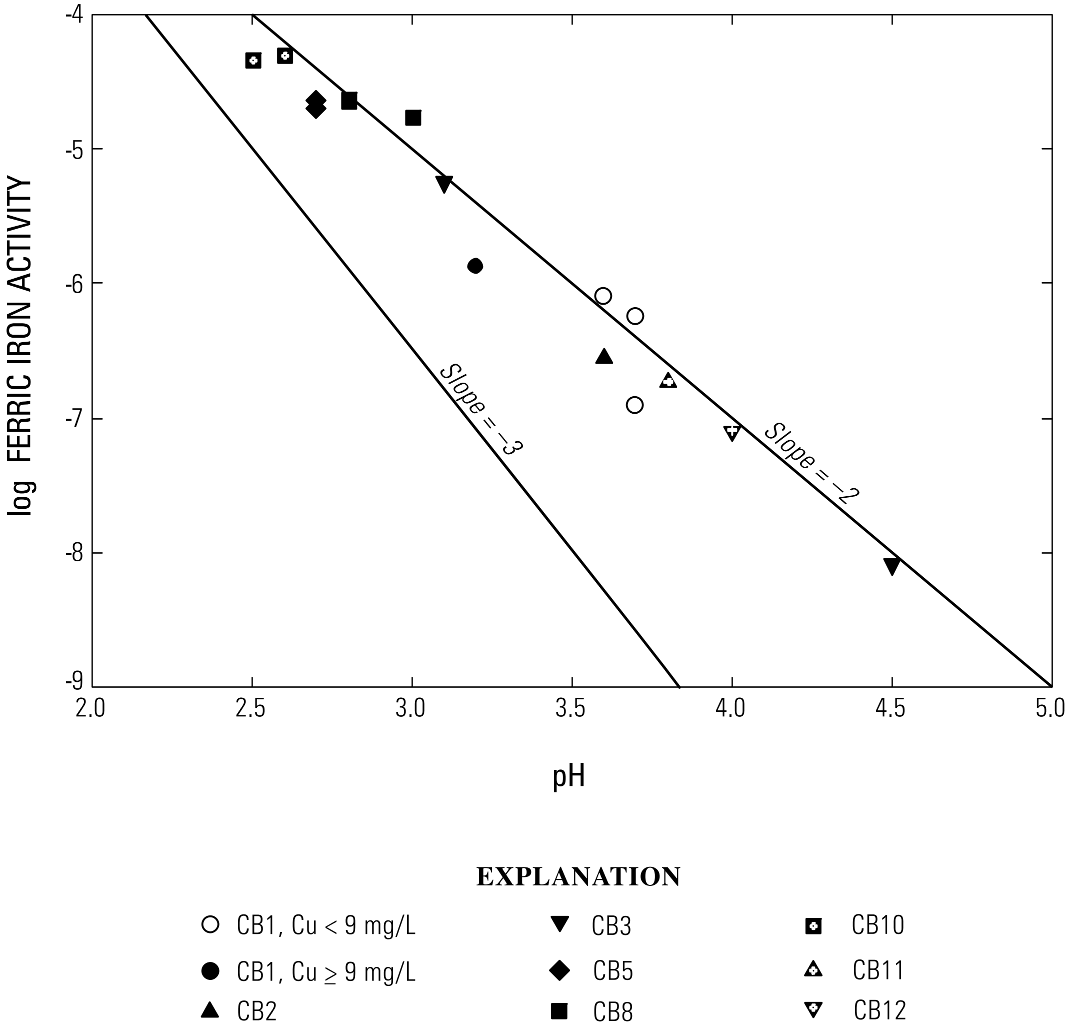

Figure 9. Relation of field pH to the logarithm of the activity of aqueous ferric iron for water samples from the underground mine workings, Copper Bluff mine.

Cu, copper; mg/L, milligram per liter; <, less than; ≥, greater than or equal to.

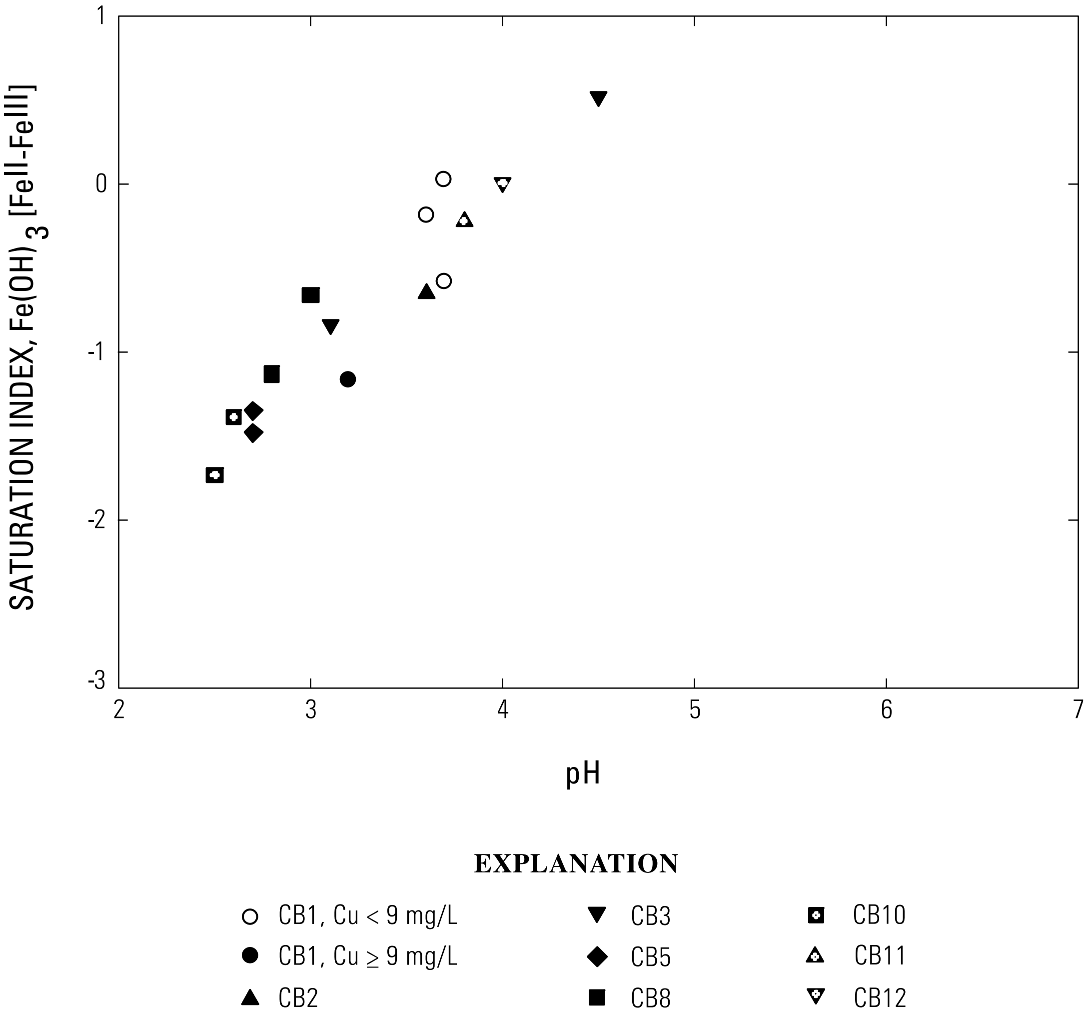

Figure 10. Relation of pH to saturation index of ferric hydroxide calculated using the geochemical model PHREEQC for the underground mine workings, Copper Bluff mine.

A. Saturation index computed using Fe^{II}-Fe^{III} (ferric-ferrous oxidation-reduction couple). $Fe(OH)_3$, ferric hydroxide; Cu, copper; mg/L; milligram per liter; <, less than; ≥, greater than or equal to

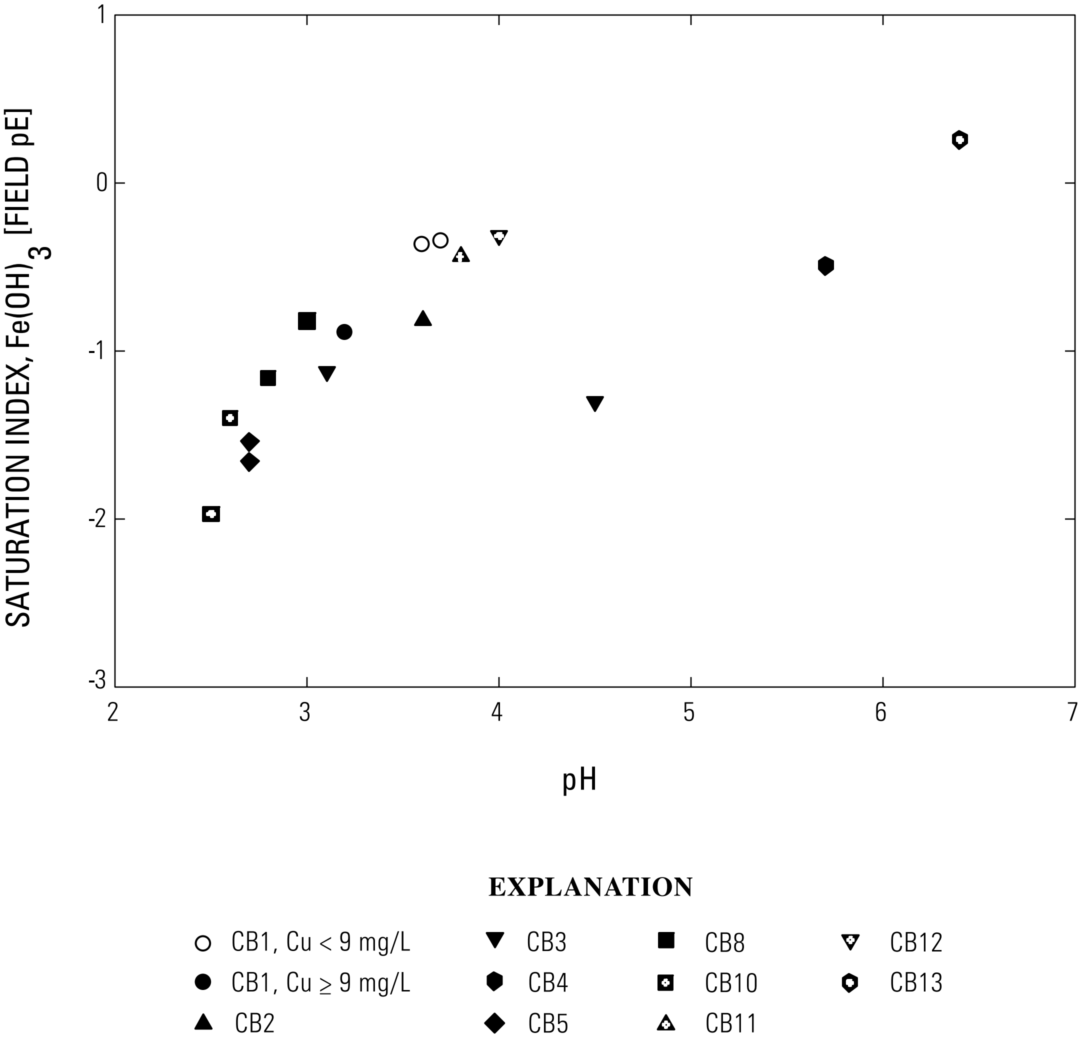

Figure 10.—Continued. **B**. Saturation index computed using field pE (oxidation-reduction potential).

IMPLICATIONS FOR REMEDIATION

Various remediation alternatives for the Copper Bluff mine acid discharge have been proposed by the Hoopa Valley Tribe, including conventional solutions such as mine plugging, piping the discharge directly to the Trinity River without treatment, and chemical treatment of the entire discharge by lime neutralization. Other, more innovative remediation alternatives also have been discussed, such as water treatment using microbial bioreactors and treatment of partial flows during periods of highest risk to the Trinity River ecosystem. In this section, the likely consequences of these remediation options are discussed in light of the improved understanding of mine hydrogeology and geochemistry resulting from the USGS underground reconnaissance investigations. The alternatives are discussed in approximate order of increasing relative cost of remediation. Table 4 summarizes the likely consequences of the various remediation alternatives considered.

No Action

If no remedial actions are taken at the Copper Bluff mine site, there is a low to medium risk of catastrophic release of acidic, metal-rich water to the Trinity River. Such a release could be caused by temporary blockage of water flow within the mine workings followed by a sudden breach. A scenario of this kind could conceivably contribute to slope failure above the mine tunnel if the blockage causes the water table to rise significantly in the area of the mine workings. Overall impacts on aquatic resources of the Trinity River are probably minimal because of adequate dilution; however, it is possible that water-quality problems associated with acute or chronic toxicity to aquatic life could result if Trinity River flows are insufficient at a time of high flow from the Copper Bluff mine portal. Even without such a catastrophic release, there may be ongoing environmental exposure risks for humans and wildlife that may come in contact with the portal effluent and associated chemical precipitates in the cascade area between the mine portal and the Trinity River.

Table 4. Summary of remedial alternatives for mine drainage at Copper Bluff mine, relative costs, and likely consequences

[N/A, not applicable]

Remedial alternative	Relative cost	Reduction in metals loading	Sufficient space	Risk of catastrophic release	Risk of slope failure	Long-term maintenance
No action	None	None	N/A	Some	Minor	None
Covered conveyance of adit flow to Trinity River	Low	None	Yes	Some	Minor	None
Wetlands	Low	Some	No	N/A	N/A	Yes
Limestone drain	Medium	Some	Yes	Some	Minor	Yes
Mine plugging	Medium	Possibly	Yes	Higher[1]	Major	Some
Partial plugging—flow restriction	Medium	None	Yes	Lower[1]	Possibly higher[1]	Yes
Partial capping	Medium	Possibly	Yes	Some	Possibly lower[1]	Some
Water treatment—bioreactor	High	Large	Maybe	Some	Minor	Yes
Water treatment—lime neutralization	Very high	Optimal	No (possibly at Celtor site)	Some	Minor	Yes

[1] Compared with no action.

Covered Conveyance of Adit Flow to Trinity River

Piping the adit discharge from the Copper Bluff mine directly to the Trinity River would reduce exposure of humans and animals to the concentrated mine drainage and associated metal-rich chemical precipitates. Although no metals would be removed from the system by this action, dilution by the Trinity River is apparently adequate under most conditions to result in only minimal increases in dissolved copper, zinc, and cadmium concentrations once the adit discharge has fully mixed with the Trinity River. Possible impacts to the aquatic life in the mixing zone immediately downstream of the discharge point could be addressed by monitoring water quality, sediment chemistry, and metal bioaccumulation at different trophic levels in the food web.

Water Treatment—Passive Methods

Passive methods of water treatment offer considerable cost savings over active methods such as lime neutralization and bioreactors. Wetlands, both natural and constructed, have been used to treat effluent water from hundreds of coal mines in the eastern United States, with resulting decreased costs and improved water quality (Kleinmann and others, 1991). The application of wetlands to treatment of metal-laden mine waters from hard rock metal mines has been attempted in a few pilot tests (for example, Emerick and others, 1994). However, these tests have been done at low-flow conditions, generally less than 1 gal/min. A relatively large area for either a natural or a constructed wetland would be necessary, given the metal concentrations and discharge rates from the Copper Bluff mine, and the geometry of such a system is clearly incompatible with the steep topography in this part of the Hoopa Valley.

Another passive treatment system that has been tried elsewhere with limited success is the limestone drain (Hedin and others, 1994). These systems use crushed limestone (calcium carbonate) to neutralize acid mine drainage, causing metal precipitation by reactions similar to those in a lime neutralization plant. A common problem with these systems is that hydrous iron and aluminum oxides tend to precipitate on the limestone fragments, diminishing their neutralizing capacity. Efforts to make the drains anoxic can reduce the amount of iron oxidation and precipitation (for example, Skousen, 1991; Skousen and Faulker, 1992). However, hydrous aluminum oxides still accumulate on the limestone surfaces, and the effectiveness of the drains has been less than expected (Charles Cravotta, U.S. Geological Survey, written commun., 1997).

Mine Plugging

Plugging has been used as a potentially low-cost remedial measure to control surface-water pollution from underground coal and metal mines that have perennial or seasonal discharge. A principal goal of mine plugging is to cause an increase in static water level in the mine, flooding the mine workings with water and thus slowing down the rate of sulfide oxidation by reducing the access of oxygen to sulfide surfaces (Chekan, 1985). Unfortunately, numerous hydrologic and geochemical factors complicate the potential success of this approach. Very few case studies have documented whether or not plugs have been successful in reducing overall rates of metal flux in surface waters, and the published studies are mostly of underground coal mines (for example, Maksimovic and Maynard, 1983; Adams and Lipscomb, 1984; Ladwig and others, 1984) rather than of hard-rock metal mines. In some cases, plugs have leaked or failed catastrophically (for example, Cogan and Kintzer, 1987), and in other cases, successful plugs have led to seepage of poor-quality water from connected mine workings (for example: Summitville Mine, Colorado [Plumlee and others, 1995]; Mammoth Mine, California, Dennis Heiman, California Regional Water Quality Control Board, Central Valley Region, oral commun., 1997).

In most hydrogeologic settings, the water impounded behind a mine plug finds other pathways by which to seep or flow from the mine workings, effectively converting a point source of pollution to a non-point, more diffuse source. There is some potential for water quality to stratify within the mine workings after an underground mine is plugged. Under favorable hydrogeologic conditions, this could lead to seepage of water of better quality from the mine area compared with the pre-plugging condition. A case study of the Lökken Mine in Norway (Smith and others, 1991) indicates that such stratified conditions developed over several years after the mine was plugged in 1984; however, the long-term benefits of plugging have not been demonstrated.

The hydrogeologic setting at the Copper Bluff mine is not consistent with permanent mine plugging as an effective long-term solution to the acid mine drainage problem. The underground workings of the Copper Bluff mine are close to a state highway and underlie a 500-ft-high bluff with highly fractured rocks that seep metal-bearing water during the wet season (as described in an earlier section). Effective plugging of the main tunnel would result in an elevated water level inside the mine that likely would lead to an increase in uncontrolled seepage from the cliff face above the highway. An additional complication from plugging that might arise is potential destabilization of State Highway 96. A considerable effort has been made by the California Department of Transportation in the past several years to stabilize the hillside and road bed near the Copper Bluff mine portal. Prior to plugging, extensive geotechnical studies would be required to ensure the stability of the cliff face and the state highway.

Mine plugging would significantly increase the risk of catastrophic release of acidic, metal-rich water and sediment from the Copper Bluff mine. As described previously in the "No Action" section, a catastrophic release of more than 100,000 gallons of mine water would likely exceed the dilution capacity of the Trinity River and therefore would probably result in adverse effects to the aquatic system.

Partial Plugging—Flow Restriction

The principal risk to aquatic resources in the Trinity River posed by the Copper Bluff mine is the worst-case scenario described in an earlier section of this report, in which a high rate of discharge of metal-rich water mixes with the Trinity River at low-flow condition. A partial plug restricting flow from the mine to a maximum rate of about 200 gal/min could mitigate such a potential situation. The flow restriction could consist of a partially plugged opening with a pipe or other outlet designed to permit the desired maximum discharge. Such a system should be constructed with a bulkhead allowing access to the area behind the partial plug for maintenance, which would be required to ensure that complete plugging did not occur, for reasons discussed in the previous sections.

Other types of partial plugging, such as plugging certain ore shoots or the upwelling zone within the mine, are not considered useful alternatives on the basis of the underground reconnaissance data collected. The plugging of these sources would provide only minimal benefit in terms of a temporary, minor reduction in discharge rate and metal loading, and could eventually lead to destabilization of the mine workings and, in the case of the ore shoots, an increased risk of catastrophic release of a large volume of poor-quality water.

Partial Capping

One way in which to reduce or eliminate flows from an underground mine is to intercept and (or) divert the recharge of ground water so that it does not flow through the mine workings. Capping mine openings where surface water infiltrates into the mine is potentially a cost-effective manner by which to reduce flows through the underground workings. Experience at other mine sites hosted in fractured rock, such as Iron Mountain, California (Richard Sugarek, U.S. Environmental Protection Agency, oral commun., 1997), indicates that such capping is very unlikely to be fully successful in eliminating all recharge to the mine; however, some reductions in infiltration may be achievable. A reduction in the amount of water flowing through the mine may not necessarily result in lower loads of metals because metal concentrations may increase in conjunction with reduced dilution flows.

Water Treatment—Bioreactors

Bioreactors, consisting of tanks containing organic matter through with the acid drainage is pumped (for example, Dvorak and others, 1991, 1992), are an innovative, relatively low-cost treatment alterative for certain acid mine waters. The bioreactors are designed to create an environment in which bacterial sulfate reduction can cause precipitation of metals as relatively insoluble sulfides, resulting in removal of more than 95 percent of dissolved metal from solutions having concentrations of dissolved iron, zinc, and aluminum comparable to the Copper Bluff effluent (Dvorak and others, 1991, 1992). The strong seasonal variations in the rate of discharge from the Copper Bluff mine would make use of bioreactors as a treatment method for all flow problematic. A large storage tank and a large bank of bioreactors would be required to equalize the flow over many months and to satisfy the necessary residence-time requirements for the sulfate reduction reaction to occur.

Although the bioreactor is potentially a lower cost treatment method than lime neutralization, some pH adjustment may be necessary (Dvorak and others, 1991, 1992), and a source of organic carbon must be found. Mushroom compost (Dvorak and others, 1991) and cottage cheese whey (Borek and others, 1995) have been used as carbon sources in pilot studies. In areas of limited space, such as the Copper Bluff mine, installation of a series of bioreactors in elongated pipes in a mine tunnel is possible in theory (Kleinmann and others, 1991); however, no examples of this have been demonstrated.

Water Treatment—Lime Neutralization

Lime neutralization is generally acknowledged as the most effective method for removing metals from acid mine drainage. Negative factors are relatively high costs for construction and for ongoing operation and maintenance of a neutralization plant and the high cost of disposal of resulting metal-rich sludge. At the Copper Bluff mine, there is limited space available near the portal entrance for a neutralization plant and no available space for the necessary clarification ponds. The Celtor Chemical Works site could provide a feasible site for such a plant and associated ponds. The negatives aspects of this scenario are the relatively high cost of conveying the acid mine water to the site (a distance of about 1 to 2 km) and the fact that the Celtor site sits in the floodplain of the Trinity River and has been inundated on at least two occasions in the past 40 years (1964 and 1997).

Summary of Remedial Alternatives and Consequences

As summarized in table 4, a variety of remedial alternatives has been considered for the Copper Bluff mine adit drainage. Of the relatively low-cost alternatives, a covered conveyance of adit flow to the Trinity River would reduce exposure of humans and animals to the acid drainage with minimal adverse impacts. Wetland treatment, either natural or constructed, appears to be infeasible because of space limitations.

Of the remedial alternatives considered to be of medium relative cost, a partial plug to achieve flow restriction at times of highest discharge appears to provide the most benefit with the least additional risk. The partial plug could be combined with the covered conveyance of adit flow described earlier to provide additional benefits in terms of reduced exposure of humans and wildlife to the mine effluent. Total plugging is likely to cause additional seepage from the cliff face and may cause instability of the slope and the adjacent state highway. Construction of a limestone drain, either oxic or anoxic, is unlikely to provide significant benefit after a short period of time because of precipitation of hydrous aluminum and iron oxides, armoring the limestone surfaces. Partial capping of open mine workings might reduce infiltration to the mine but might not have much effect on total metal loads.

Two relatively high-cost alternatives involving active water treatment are considered to have significant potential for success; however, space limitations in the mine and the adjacent lands would cause significantly higher costs than comparable installations elsewhere. A conventional lime neutralization plant could be constructed at the Celtor Chemical mill site (fig. 2), and the adit discharge conveyed by gravity-flow pipeline. A more innovative system involving bioreactors inducing metal precipitation by sulfate reduction also would have excellent potential for success. However, the extreme seasonality of the discharge rate from the mine indicates the need for a relatively large storage capacity so that flow to a treatment plant could be equalized, avoiding the need to bypass the treatment plant during times of highest mine discharge.

SUMMARY AND CONCLUSIONS

Geochemical, hydrologic, and geologic information related to the acid drainage problems at the Copper Bluff mine have been gathered by the U.S. Geological Survey so that a sound remediation strategy can be selected and implemented by the Hoopa Valley Tribe. Weekly monitoring of the quality and quantity of the mine portal discharge over parts of two wet seasons (1994–1995 and 1995–1996) was used to determine the seasonal variability of mine drainage chemistry and of metal loading to the Trinity River.

The results of the weekly sampling indicate the importance of sampling at this level of frequency so that the impact and extent of the first increase in discharge, or first flush, early in the wet season can be assessed.

Dissolved copper and zinc concentrations from the Copper Bluff mine portal discharge (filtered with 0.20-µm membranes) follow a systematic seasonal pattern. The pattern is characterized by a dramatic increase in metal concentrations in response to the first-flush period. The Zn to Cu ratio in the adit discharge also exhibited systematic seasonal variations; an annual Zn/Cu cycle was observed, beginning with values between 3 and 5 during the main part of the wet season, rising to values between 4 and 7 during the latter part of the wet season, continuing to rise to values between 6 and 10 during the period of lowest discharge late in the dry season, and then dropping dramatically to values less than 3 during the first-flush period and rising back to values between 3 and 5 as the wet season progressed.

Underground reconnaissance conducted both during dry-season conditions (September 1995) and wet-season conditions (March 1995 and March 1996) included the examination of approximately 600 linear feet of underground tunnels, crosscuts, and ore shoots. Discharge from the five ore shoots ranged from less than 1 gal/min to more than 30 gal/min and was always a relatively small component of the total mine flow compared with the tunnel floor drainage. During March 1996, the main flow originated in the northernmost portion of the underground workings (inaccessible) and mixed with an unknown quantity of water upwelling from flooded lower workings. High-water marks observed on the tunnel walls indicate that past blockages impounded more than 100,000 gallons of water. Sudden release of a large volume of metal-rich water could have serious effects on fish and other aquatic resources in the Trinity River.

Mineralogic and petrographic analyses indicate that the host rocks consist mostly of silicate minerals that have low capacity for the neutralization of acid mine drainage. Carbonate minerals such as calcite may provide a small amount of neutralizing capacity; however, such minerals probably react quickly along flow paths. Analysis of iron redox chemistry and aqueous speciation indicates that mine waters are saturated or slightly supersaturated with respect to amorphous or poorly crystalline hydrous ferric oxide (HFO). The identity of the HFO was not determined, but it is likely to be the mineral schwertmannite, a sulfate-bearing HFO that has a ratio of (OH) to Fe^{III} less than the 3 to 1 ratio corresponding to $Fe(OH)_3$.

Because of the hydrogeologic setting, mine plugging is not likely to offer an effective long-term solution to the acid mine drainage problem at the Copper Bluff mine. The underground workings are close to a state highway and underlie a 500-ft-high bluff with highly fractured rocks that seep during the wet season. Total plugging likely would result in additional uncontrolled seepage and could potentially destabilize the highway. Partial plugging to achieve flow restriction during periods of highest discharge may provide benefits in terms of reduced risk of catastrophic release without the additional risks associated with total plugging. Partial capping of open mine workings might reduce the volume and flow rate of water moving through the mine but might not have much effect on total metal loads based on results at other mine sites. Passive water treatment methods such as wetlands or anoxic limestone drains are unlikely to succeed at the Copper Bluff mine because of the lack of available ground with level topography between the mine portal and the Trinity River. A covered conveyance for the discharge directly from the mine portal to the Trinity River is a low-cost remedial alternative that does not reduce metal loadings to the Trinity River, but that would reduce pathways of metal exposure to humans and animals. Active water treatment of the adit discharge by lime neutralization or innovative methods such as bioreactors are relatively high-cost remedial alternatives that likely would be successful if sufficient resources are available for adequate design, testing, construction, long-term maintenance, and sludge disposal.

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APPENDIXES

Appendix 1. Chemical data for water samples from the Copper Bluff Mine portal, site CB1

[Eh, oxidation-reduction potential; ICP, inductively coupled plasma spectroscopy; UV-vis, ultraviolet-visible spectroscopy; m/d/y, date format as month/day/year; µS/cm, microsiemens per centimeter; mV, millivolt; °C, degrees Celsius; mg/L, milligram per liter; µg/L, microgram per liter; dup, duplicate sample; —, no data]

Date (m/d/y)	Time	Specific conductance (µS/cm)	pH, field	Eh, field (mV)	Temperature (°C)	Calcium, dissolved (mg/L)	Magnesium, dissolved (mg/L)	Sodium, dissolved (mg/L)	Potassium, dissolved (mg/L)
9/19/94	1900	940	3.7	—	13.2	92	37	14	1.0
9/19/94	1905 (dup)	940	3.7	—	13.2	89	36	13	1.0
9/20/94	1000	910	3.7	640	13.0	92	37	13	0.9
1/27/95	1545	1010	3.2	—	11.6	—	—	—	—
2/3/95	—	880	3.1	—	12.3	—	—	—	—
2/8/95	—	750	3.2	—	12.5	—	—	—	—
2/17/95	1202	790	3.3	—	11.7	34	19	4.7	—
2/24/95	1415	790	3.4	—	12.4	—	—	—	—
3/3/95	1530	740	3.1	—	11.6	40	21	5.4	—
3/10/95	1242	920	3.2	—	12.2	35	22	4.6	—
3/14/95	1135	780	3.2	—	12.5	29	17	4.3	0.7
3/24/95	1414	630	3.4	—	11.7	26	15	4.1	—
3/30/95	1440	610	3.4	—	12.0	29	16	4.7	—
4/5/95	1550	660	3.4	680	12.2	35	17	5.2	—
4/12/95	1445	650	3.4	670	—	34	18	4.9	—
4/19/95	1520	620	3.4	670	—	35	18	5.0	—
4/26/95	1445	630	3.6	680	—	38	19	5.3	—
5/9/95	1445	640	3.6	670	—	42	20	5.7	—
5/18/95	1130	680	3.3	680	—	44	21	5.8	—
5/22/95	1509	690	3.3	650	—	47	22	6.0	—
5/31/95	1545	620	3.6	690	—	51	24	6.4	—
6/16/95	1400	600	3.5	670	—	55	25	6.9	—
6/23/95	1530	730	3.6	650	13.0	58	23	7.2	—
6/28/95	1400	620	3.5	690	—	61	26	7.6	—
7/5/95	1530	630	3.4	590	13.0	66	28	8.2	—
10/30/95	1030	290	4.6	470	12.2	95	37	11	—
11/8/95	1500	160	5.3	400	11.4	94	36	12	—
11/15/95	1315	—	—	700	—	100	33	11	—
11/22/95	1030	170	5.3	380	14.0	97	33	11	—
11/29/95	1200	150	5.0	418	11.7	91	12	12	—
12/6/95	1330	160	5.6	390	14.5	100	32	10	—
12/13/95	1400	290	3.4	725	11.3	110	53	8.6	—
12/19/95	1130	340	3.7	690	13.7	87	42	6.4	—
1/4/96	0830	1,500	3.5	750	11.9	52	29	5.6	—
1/10/96	1100	1,000	3.0	690	11.9	46	24	5.4	—
1/24/96	1300	580	3.1	720	12.2	29	20	3.7	—
2/1/96	1400	660	3.3	690	12.9	27	14	3.9	—
2/7/96	1445	620	3.3	710	13.0	31	14	4.3	—
2/14/96	1300	650	3.8	700	12.1	35	16	4.6	—
3/4/96	1400	580	3.4	672	12.7	29	13	4.4	—
3/12/96	1400	510	3.6	660	13.0	28	12	4.5	—
3/12/96	1410	600	3.5	660	12.3	30	13	4.3	0.7
4/3/96	—	—	—	—	—	—	—	—	—
4/9/96	—	—	—	—	—	—	—	—	—
4/16/96	1200	650	3.6	600	—	46	19	5.3	—
4/23/96	1230	580	3.5	540	—	43	18	5.3	—
5/3/96	1030	590	3.4	822	—	42	18	5.1	—
5/17/96	1330	600	3.6	690	11.4	48	19	5.5	—

Appendix 1. Chemical data for water samples from the Copper Bluff Mine portal, site CB1—Continued

Date (m/d/y)	Time	Sulfate, dissolved (mg/L)	Chloride, dissolved (mg/L)	Fluoride, dissolved (mg/L)	Silica, dissolved (mg/L)	Aluminum, dissolved (μg/L)	Cadmium, dissolved (μg/L)	Copper, dissolved (μg/L)
9/19/94	1900	540	2.9	0.3	30	6,300	60	4,000
9/19/94	1905	510	2.6	0.3	29	6,400	60	3,800
9/20/94	1000	500	2.4	0.3	30	6,100	60	3,800
1/27/95	1545	—	—	—	—	—	—	—
2/3/95	—	—	—	—	—	—	—	—
2/8/95	—	—	—	—	—	—	—	—
2/17/95	1202	460	—	—	21	8,300	—	10,000
2/24/95	1415	—	—	—	—	—	—	—
3/3/95	1530	440	—	—	22	7,500	—	9,200
3/10/95	1242	510	—	—	23	10,000	—	14,000
3/14/95	1135	290	3.2	0.2	21	7,900	160	11,000
3/24/95	1414	280	—	—	18	6,100	—	8,700
3/30/95	1440	280	—	—	19	5,500	—	8,300
4/5/95	1550	300	—	—	19	5,900	—	7,200
4/12/95	1445	310	—	—	20	6,100	—	7,200
4/19/95	1520	300	—	—	20	5,600	—	7,200
4/26/95	1445	320	—	—	21	5,700	—	6,500
5/9/95	1445	310	—	—	21	5,000	—	5,700
5/18/95	1130	340	—	—	22	5,500	—	6,000
5/22/95	1509	380	—	—	22	5,700	—	5,500
5/31/95	1545	410	—	—	23	6,800	—	4,800
6/16/95	1400	390	—	—	22	5,600	—	4,200
6/23/95	1530	410	—	—	23	5,900	—	4,100
6/28/95	1400	440	—	—	22	6,500	—	4,700
7/5/95	1530	450	—	—	23	6,900	—	4,700
10/30/95	1030	530	—	—	26	5,200	—	3,600
11/8/95	1500	500	—	—	26	2,300	—	2,300
11/15/95	1315	540	—	—	28	1,800	50	2,300
11/22/95	1030	500	—	—	28	2,100	50	2,800
11/29/95	1200	410	—	—	27	1,200	50	2,400
12/6/95	1330	540	—	—	28	1,300	50	2,600
12/13/95	1400	1,300	—	—	39	28,000	340	28,000
12/19/95	1130	1,600	—	—	47	30,000	840	77,000
1/4/96	0830	820	—	—	31	19,000	270	29,000
1/10/96	1100	570	—	—	27	12,000	170	17,000
1/24/96	1300	560	—	—	22	12,000	210	17,000
2/1/96	1400	360	—	—	20	6,800	110	8,700
2/7/96	1445	360	—	—	21	6,100	100	8,100
2/14/96	1300	360	—	—	22	6,200	100	7,100
3/4/96	1400	320	—	—	20	5,400	90	6,200
3/12/96	1400	240	—	—	19	4,300	80	5,500
3/12/96	1410	—	—	0.1	20	4,620	87	5,500
4/3/96	—	—	—	—	—	—	—	—
4/9/96	—	—	—	—	—	—	—	—
4/16/96	1200	290	—	—	24	5,640	80	4,900
4/23/96	1230	270	—	—	23	4,700	80	4,600
5/3/96	1030	280	—	—	23	5,350	80	4,600
5/17/96	1330	290	—	—	23	5,160	80	4,200

Appendix 1. Chemical data for water samples from the Copper Bluff Mine portal, site CB1—Continued

Date (m/d/y)	Time	Iron, dissolved, ICP (μg/L)	Iron, dissolved, UV-vis (μg/L)	Iron, ferrous, dissolved (μg/L)	Lead, dissolved (μg/L)	Manganese, dissolved (μg/L)	Nickel, dissolved (μg/L)	Zinc, dissolved (μg/L)
9/19/94	1900	5,200	4,860	4,310	11	2,400	60	23,000
9/19/94	1905	4,700	5,770	4,280	9	2,300	59	22,000
9/20/94	1000	6,500	6,600	4,350	10	2,200	60	22,000
1/27/95	1545	—	—	—	—	—	—	—
2/3/95	—	—	—	—	—	—	—	—
2/8/95	—	—	—	—	—	—	—	—
2/17/95	1202	11,000	12,600	2,770	—	1,000	—	34,000
2/24/95	1415	—	—	—	—	—	—	—
3/3/95	1530	10,000	2,580	1,890	—	1,200	—	33,000
3/10/95	1242	20,000	3,010	1,510	—	1,000	—	46,000
3/14/95	1135	14,000	4,610	2,690	26	770	40	40,000
3/24/95	1414	9,600	10,300	2,020	—	770	—	27,000
3/30/95	1440	6,400	7,210	2,910	—	1,000	—	27,000
4/5/95	1550	6,400	4,440	3,380	—	1,300	—	30,000
4/12/95	1445	8,200	9,560	3,080	—	1,300	—	29,000
4/19/95	1422	6,700	7,210	2,940	—	1,300	—	29,000
4/26/95	1445	7,800	8,410	3,370	—	1,500	—	29,000
5/9/95	1445	7,300	7,760	3,850	—	1,500	—	28,000
5/18/95	1130	8,600	9,210	3,360	—	1,600	—	30,000
5/22/95	1509	8,600	9,160	4,050	—	1,700	—	29,000
5/31/95	1545	20,000	21,000	3,510	—	1,900	—	29,000
6/16/95	1400	6,000	6,320	3,100	—	2,000	—	27,000
6/23/95	1530	6,800	7,400	3,400	—	2,000	—	25,000
6/28/95	1400	8,400	7,700	3,580	—	2,300	—	28,000
7/5/95	1530	11,000	12,300	4,350	—	2,600	—	29,000
10/30/95	1030	7,000	7,800	6,700	—	2,600	—	23,000
11/8/95	1500	—	13,000	10,000	—	2,600	—	21,000
11/15/95	1315	10,000	[1]8,800	7,500	—	2,700	—	22,000
11/22/95	1030	8,700	7,500	5,400	—	2,600	—	22,000
11/29/95	1200	7,600	7,800	6,100	—	2,400	—	18,000
12/6/95	1330	7,500	7,500	6,400	—	2,500	—	22,000
12/13/95	1400	93,000	—	—	—	4,400	—	70,000
12/19/95	1130	110,000	—	—	—	2,300	—	170,000
1/4/96	0830	52,000	56,000	2,800	—	1,400	—	72,000
1/10/96	1100	28,000	30,000	1,900	—	1,000	—	44,000
1/24/96	1300	35,000	36,000	1,300	—	800	—	50,000
2/1/96	1400	12,000	13,000	1,200	—	580	—	27,000
2/7/96	1445	9,300	9,600	1,300	—	690	—	28,000
2/14/96	1300	7,700	8,300	1,600	—	910	—	27,000
3/4/96	1400	7,100	7,500	1,600	—	820	—	24,000
3/12/96	1400	3,400	3,800	1,800	—	800	—	22,000
3/12/96	1410	3,000	—	—	—	840	—	24,000
4/3/96	—	—	5,600	2,200	—	—	—	—
4/9/96	—	—	6,300	2,100	—	—	—	—
4/16/96	1200	5,500	5,800	2,200	—	1,500	—	30,000
4/23/96	1230	4,100	4,500	1,900	—	1,300	—	26,000
5/3/96	1030	4,800	5,300	2,000	—	1,300	—	26,000
5/17/96	1330	5,600	3,500	2,100	—	1,500	—	28,000

[1] Minimum value for total iron, interference detected.

Appendix 2. Discharge data for the Trinity River at Hoopa and the Copper Bluff mine portal

[Discharge data for Trinity River at Hoopa from U.S. Geological Survey Water Data Reports CA-94-2, CA-95-2, and CA-96-2; discharge data for Copper Bluff mine portal from Larry Oetker, Hoopa Valley Tribe, written commun., 1994–96. m/d/y, date format in month/day/year; ft^3/s, cubic foot per second; gal/min, gallon per minute; —, no data]

Date	Trinity River at Hoopa (ft^3/s)	Trinity River at Hoopa (gal/min)	Copper Bluff mine portal (gal/min)	Discharge ratio: Trinity River/Copper Bluff mine portal
9/19/94	599	269,000	—	—
2/17/95	6,230	2,800,000	155	18,100
2/24/95	6,050	2,720,000	—	—
3/3/95	7,210	3,240,000	143	22,700
3/10/95	45,600	20,500,000	250	82,000
3/14/95	42,200	18,900,000	256	73,800
3/24/95	25,200	11,300,000	207	54,600
3/30/95	19,400	8,710,000	133	65,500
4/5/95	10,600	4,758,000	—	—
4/12/95	14,100	6,330,000	131	48,300
4/19/95	10,400	4,670,000	82	57,000
4/26/95	7,520	3,380,000	82	41,200
5/9/95	12,300	5,520,000	95	58,100
5/18/95	10,700	4,800,000	84	57,100
5/22/95	7,500	3,370,000	75	44,900
5/31/95	6,030	2,710,000	84	32,300
6/16/95	4,570	2,050,000	50	41,000
6/23/95	3,080	1,380,000	70	19,700
6/28/95	3,230	1,450,000	26	55,800
7/5/95	2,450	1,100,000	26	42,300
7/15/95	2,030	911,000	—	—
10/30/95	712	320,000	6	53,300
11/8/95	701	315,000	5	63,000
11/15/95	721	324,000	—	—
11/22/95	762	342,000	6	57,000
11/29/95	868	390,000	6	65,000
12/6/95	3,730	1,670,000	6	278,000
12/13/95	25,000	11,200,000	22	509,000
12/19/95	5,230	2,350,000	35	67,100
1/4/96	6,680	3,000,000	72	41,700
1/10/96	6,320	2,840,000	96	29,600
1/24/96	21,800	9,780,000	486	20,100
2/1/96	14,500	6,510,000	241	27,000
2/7/96	25,900	11,600,000	238	48,700
2/14/96	15,100	6,780,000	256	26,500
3/4/96	14,500	6,510,000	220	29,600
3/12/96	21,000	9,430,000	168	56,100
3/12/96	21,000	9,430,000	168	56,100
4/16/96	5,550	2,490,000	84	29,600
4/23/96	6,420	2,880,000	84	34,300
5/3/96	5,960	2,680,000	89	30,100
5/17/96	9,510	4,270,000	79	54,100

Appendix 3. Electron microprobe data for minerals from the Copper Bluff mine, Hoopa Valley Reservation

A. Feldspar

[Chemical notation defined in front matter. Sum Ox%, sum of oxide weight percentage data; Sum Cat #, sum of cation coefficients. Ab, albite; An, anorthite; Or, orthoclase; n, number of data points]

	Oxides (weight percent)						Sum Ox%
Point	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**CaO**	**Na_2O**	**K_2O**	
#1	67.60	19.26	0.21	0.02	11.46	0.04	98.59
#2	68.14	19.72	0.12	0.12	11.39	0.09	99.58
#3	67.79	19.24	0.06	0.13	11.41	0.04	98.67
#4	67.94	19.50	0.09	0.09	11.16	0.02	98.80
#5	66.82	19.53	0.06	0.30	11.16	0.07	97.94
#7	67.46	19.57	0.28	0.11	11.57	0.06	99.05
#8	67.35	19.68	0.14	0.14	11.31	0.04	98.66
#9	67.33	19.60	0.22	0.45	11.24	0.07	98.91
#11	67.73	19.84	0.39	0.28	11.64	0.04	99.92
#12	67.09	19.23	0.16	0.37	11.18	0.06	98.09
#1	66.05	19.87	0.00	0.23	11.40	0.08	97.63
#2	64.85	19.67	0.10	0.10	11.49	0.08	96.29
#3	65.31	19.80	0.13	0.18	11.35	0.08	96.85
#4	65.22	19.65	0.18	0.11	11.03	0.10	96.29
Average (n = 14)	66.91	19.58	0.15	0.19	11.34	0.06	98.23
Standard deviation	1.10	0.21	0.10	0.12	0.17	0.02	1.13

	Molar ratios (based on 8 moles of oxygen)						Sum Cat #	Components (in percent)		
Point	**Si**	**Al**	**Fe^{III}**	**Ca**	**Na**	**K**		**Ab**	**An**	**Or**
#1	2.994	1.005	0.007	0.001	0.984	0.002	4.993	99.709	0.089	0.203
#2	2.987	1.019	0.004	0.006	0.968	0.005	4.989	98.906	0.600	0.494
#3	2.998	1.003	0.002	0.006	0.978	0.002	4.989	99.147	0.639	0.214
#4	2.997	1.014	0.003	0.004	0.954	0.001	4.973	99.428	0.434	0.138
#5	2.979	1.026	0.002	0.014	0.965	0.004	4.990	98.159	1.443	0.398
#7	2.978	1.018	0.009	0.005	0.990	0.004	5.004	99.130	0.504	0.365
#8	2.980	1.027	0.005	0.007	0.970	0.002	4.991	99.108	0.665	0.227
#9	2.976	1.021	0.007	0.021	0.963	0.004	4.992	97.440	2.168	0.392
#11	2.968	1.024	0.013	0.013	0.988	0.002	5.008	98.451	1.331	0.219
#12	2.988	1.009	0.006	0.018	0.965	0.003	4.989	97.857	1.804	0.339
#1	2.959	1.049	0.000	0.011	0.990	0.005	5.014	98.411	1.115	0.473
#2	2.950	1.054	0.003	0.005	1.013	0.005	5.030	99.074	0.468	0.457
#3	2.952	1.055	0.004	0.009	0.995	0.005	5.020	98.672	0.856	0.472
#4	2.960	1.051	0.006	0.005	0.971	0.006	4.999	98.872	0.538	0.591
Average (n = 14)	2.976	1.027	0.005	0.009	0.978	0.004	4.999	98.740	0.904	0.356
Standard deviation	0.016	0.018	0.003	0.006	0.016	0.002	0.061	0.622	0.589	0.136

Appendix 3. Electron microprobe data for minerals from the Copper Bluff mine, Hoopa Valley Reservation—continued

B. Epidote

[Chemical notation defined in front matter. Sum Ox%, sum of oxide weight perentage data; Sum Cat #, sum of cation coefficients; n, number of data points]

Point	Oxides (weight percent)									Sum Ox%
	SiO_2	TiO_2	Al_2O_3	Cr_2O_3	Fe_2O_3	MnO	MgO	CaO	H_2O(c)	
#14	38.11	0.14	25.08	0.04	10.94	0.11	0.00	23.54	1.86	99.82
#23	36.82	0.05	23.73	0.01	12.53	0.15	0.01	23.26	1.81	98.37
#24	37.45	0.07	23.80	0.02	12.02	0.13	0.00	23.33	1.83	98.65
#25	37.37	0.01	26.12	0.03	9.83	0.20	0.00	23.83	1.86	99.25
#13	37.05	0.09	27.27	0.11	9.93	0.18	0.07	23.55	1.88	100.13
#14	36.78	0.25	27.13	0.05	9.57	0.15	0.02	23.57	1.86	99.38
Average (n = 6)	37.26	0.10	25.52	0.04	10.80	0.15	0.02	23.51	1.85	99.27
Standard deviation	0.50	0.08	1.57	0.04	1.24	0.03	0.03	0.20	0.03	0.67

Point	Molar ratios (based on 13 moles of oxygen)								Sum Cat #
	Si	Ti	Al	Cr	Fe^{II}	Mn	Mg	Ca	
#14	3.07	0.01	2.38	0.00	0.74	0.01	0.00	2.03	8.23
#23	3.04	0.00	2.31	0.00	0.87	0.01	0.00	2.06	8.30
#24	3.08	0.00	2.30	0.00	0.83	0.01	0.00	2.05	8.27
#25	3.02	0.00	2.49	0.00	0.66	0.01	0.00	2.06	8.24
#13	2.96	0.04	2.57	0.01	0.66	0.01	0.01	2.02	8.25
#14	2.96	0.02	2.57	0.00	0.64	0.01	0.00	2.03	8.24
Average (n = 6)	3.02	0.01	2.44	0.00	0.73	0.01	0.00	2.04	8.25
Standard deviation	0.05	0.01	0.12	0.00	0.09	0.00	0.00	0.02	0.02

Appendix 3. Electron microprobe data for minerals from the Copper Bluff mine, Hoopa Valley Reservation—continued

C. Amphibole

[Chemical notation defined in front matter.Sum Ox%, sum of oxide weight percentage data; Sum Cat #, sum of cation coefficients; c, calculated; n, number of data points]

Point	Oxides (weight percent)												Sum Ox%
	SiO_2	TiO_2	Al_2O_3	Cr_2O_3	Fe_2O_3 (c)	FeO (c)	MnO	MgO	CaO	Na_2O	K_2O	H_2O(c)	
#1	55.38	0.02	1.30	0.01	3.18	7.26	0.24	18.06	12.48	0.38	0.12	2.13	100.56
#2	54.61	0.07	2.07	0.00	3.59	10.47	0.18	15.29	11.50	0.77	0.13	2.11	100.79
#3	54.70	0.00	1.71	0.00	4.02	8.06	0.19	17.03	12.13	0.55	0.07	2.12	100.58
#4	53.21	0.00	1.82	0.03	3.51	12.50	0.28	14.27	12.02	0.70	0.07	2.08	100.49
#5	56.06	0.00	1.17	0.04	3.98	8.50	0.22	17.13	12.18	0.43	0.06	2.15	101.92
#6	53.39	0.04	2.22	0.00	5.01	11.46	0.25	14.00	11.30	0.85	0.08	2.09	100.69
Average (n = 6)	54.56	0.02	1.72	0.01	3.88	9.71	0.23	15.96	11.94	0.61	0.09	2.11	100.84
Standard deviation	1.11	0.03	0.42	0.02	0.64	2.08	0.04	1.68	0.45	0.19	0.03	0.03	0.53

Point	Molar ratios (based on 24 moles of oxygen)										Sum Cat #
	Si	Ti	Al	Cr	Fe^{III}	Fe^{II}	Mn	Mg	Ca	Na	K	
#1	7.78	0.00	0.22	0.00	0.34	0.85	0.03	3.78	1.88	0.10	0.02	15.00
#2	7.76	0.01	0.24	0.11	0.00	0.38	1.24	0.02	3.24	1.75	0.21	14.96
#3	7.73	0.00	0.27	0.01	0.00	0.43	0.95	0.02	3.59	1.84	0.15	14.99
#4	7.69	0.00	0.31	0.00	0.38	1.51	0.03	3.07	1.86	0.20	0.01	15.07
#5	7.81	0.00	0.19	0.00	0.00	0.42	0.99	0.03	3.56	1.82	0.12	14.93
#6	7.67	0.00	0.33	0.05	0.00	0.54	1.38	0.03	3.00	1.74	0.24	14.98
Average (n = 6)	7.74	0.00	0.26	0.03	0.12	0.69	0.77	1.16	2.85	1.24	0.13	14.99
Standard deviation	0.05	0.00	0.05	0.04	0.19	0.44	0.59	1.77	0.79	0.85	0.09	0.04

Appendix 3. Electron microprobe data for minerals from the Copper Bluff mine, Hoopa Valley Reservation—continued

D. Chlorite

[Chemical notation defined in front matter. Al^{tet}, tetrahedral aluminum; Al^{oct}, octahedral aluminum; c, calculated; Sum Ox%, sum of oxide weight percentage data; Sum Cat #, sum of cation coefficients; n, number of data points]

Point	Oxides (weight percent)											Sum Ox%
	SiO_2	TiO_2	Al_2O_3	Cr_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	H_2O(c)	
#7	26.71	0.00	18.54	0.03	33.44	0.96	9.07	0.15	0.01	0.01	11.03	99.95
#9	30.11	0.00	16.60	0.06	32.95	0.89	5.75	0.21	0.06	0.06	10.86	97.54
#10	26.18	0.00	18.38	0.07	33.40	1.01	8.78	0.12	0.02	0.03	10.88	98.88
#11	25.24	0.04	19.62	0.00	31.87	0.52	12.43	0.07	0.00	0.01	11.22	101.03
#12	25.07	0.14	20.07	0.02	31.84	0.51	12.24	0.01	0.02	0.00	11.24	101.15
#13	25.02	0.02	20.28	0.00	31.79	0.59	12.29	0.00	0.03	0.00	11.25	101.29
#20	25.37	0.02	19.91	0.00	31.74	0.53	12.46	0.04	0.00	0.00	11.27	101.36
#21	27.12	0.00	16.75	0.00	31.08	0.26	13.49	0.03	0.01	0.00	11.15	99.90
#22	25.27	0.07	19.86	0.00	31.73	0.34	12.41	0.00	0.01	0.00	11.23	100.93
#5	25.22	0.12	19.49	0.01	28.99	0.62	14.48	0.01	0.03	0.00	11.26	100.24
#6	25.14	0.09	19.40	0.03	28.77	0.66	14.14	0.07	0.01	0.03	11.18	99.53
#7	25.84	0.13	19.26	0.00	28.96	0.61	14.11	0.05	0.02	0.00	11.29	100.27
#8	25.56	0.07	19.26	0.01	28.59	0.71	13.59	0.08	0.03	0.00	11.15	99.04
#1	24.19	0.05	19.71	0.03	31.04	0.53	12.08	0.04	0.03	0.00	10.95	98.65
#9	24.94	0.04	19.79	0.05	30.85	0.48	13.32	0.03	0.01	0.00	11.23	100.74
#10	25.22	0.01	18.97	0.04	30.20	0.49	13.45	0.05	0.01	0.01	11.12	99.56
#11	25.03	0.00	19.25	0.00	30.83	0.49	13.68	0.00	0.00	0.00	11.20	100.48
#12	25.17	0.00	19.20	0.00	30.54	0.51	13.52	0.04	0.03	0.00	11.18	100.18
Average (n = 18)	25.69	0.04	19.13	0.02	31.03	0.60	12.29	0.06	0.02	0.01	11.15	100.04
Standard deviation	1.29	0.05	1.02	0.02	1.51	0.20	2.25	0.06	0.02	0.02	0.13	1.03

Point	Molar ratios (based on 36 moles of oxygen)											Sum Cat #
	Si	Ti	Al^{tet}	Al^{oct}	Cr	Fe^{II}	Mn	Mg	Ca	Na	K	
#7	5.81	0.00	2.19	2.56	0.01	6.08	0.18	2.94	0.04	0.01	0.00	19.81
#9	6.65	0.00	1.35	2.97	0.01	6.08	0.17	1.89	0.05	0.03	0.02	19.21
#10	5.77	0.00	2.23	2.55	0.01	6.16	0.19	2.89	0.03	0.01	0.01	19.84
#11	5.40	0.01	2.60	2.34	0.00	5.70	0.09	3.96	0.02	0.00	0.00	20.13
#12	5.35	0.02	2.65	2.40	0.00	5.68	0.09	3.89	0.00	0.01	0.00	20.10
#13	5.33	0.00	2.67	2.43	0.00	5.67	0.11	3.91	0.00	0.01	0.00	20.12
#20	5.40	0.00	2.60	2.39	0.00	5.65	0.10	3.95	0.01	0.00	0.00	20.10
#21	5.83	0.00	2.17	2.08	0.00	5.59	0.05	4.32	0.01	0.00	0.00	20.05
#22	5.40	0.01	2.60	2.40	0.00	5.67	0.06	3.95	0.00	0.00	0.00	20.09
#5	5.37	0.02	2.63	2.26	0.00	5.16	0.11	4.60	0.00	0.01	0.00	20.17
#6	5.39	0.02	2.61	2.30	0.01	5.16	0.12	4.52	0.02	0.00	0.01	20.14
#7	5.49	0.02	2.51	2.32	0.00	5.15	0.11	4.47	0.01	0.01	0.00	20.08
#8	5.50	0.01	2.50	2.38	0.00	5.14	0.13	4.36	0.02	0.01	0.00	20.05
#1	5.30	0.01	2.70	2.39	0.01	5.69	0.10	3.94	0.01	0.02	0.00	20.15
#9	5.33	0.01	2.67	2.31	0.01	5.51	0.09	4.24	0.01	0.01	0.00	20.17
#10	5.44	0.00	2.56	2.26	0.01	5.45	0.09	4.32	0.01	0.00	0.00	20.15
#11	5.36	0.00	2.64	2.23	0.00	5.52	0.09	4.37	0.00	0.00	0.00	20.20
#12	5.40	0.00	2.60	2.26	0.00	5.48	0.09	4.33	0.01	0.01	0.00	20.18
Average (n = 18)	5.53	0.01	2.47	2.38	0.00	5.59	0.11	3.94	0.01	0.01	0.00	20.04
Standard deviation	0.32	0.01	0.32	0.19	0.00	0.31	0.04	0.70	0.01	0.01	0.00	0.23

Appendix 3. Electron microprobe data for minerals from the Copper Bluff mine, Hoopa Valley Reservation—continued

E. Mica

[Chemical notation defined in front matter. c, calculated; Sum Ox%, sum of oxide weight percentage data; Sum Cat #, sum of cation coefficients; Al^{tet}, tetrahedral aluminum; Al^{oct}, octahedral aluminum]

Point	Oxides (weight percent)											Sum Ox%
	SiO_2	TiO_2	Al_2O_3	Cr_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	H_2O(c)	
Mica-1												
#1	45.04	0.09	25.02	0.01	6.45	0.03	3.81	0.06	0.17	9.75	4.14	94.57
#2	43.43	0.16	24.11	0.00	8.74	0.10	4.38	0.11	0.16	8.56	4.07	93.82
#3	43.44	0.12	24.43	0.00	8.67	0.13	4.35	0.05	0.19	8.64	4.08	94.10
#4	40.41	0.07	23.65	0.00	9.84	0.15	4.37	0.18	0.23	7.97	3.90	90.77
#1	47.00	0.94	24.93	0.00	4.64	0.00	2.74	0.63	0.07	10.43	4.22	95.60
#2	51.17	0.07	23.27	0.05	7.72	0.01	3.40	0.11	3.50	6.26	4.43	99.99
#3	48.17	0.31	25.26	0.04	5.14	0.07	2.93	0.25	0.23	10.55	4.29	97.24
#4	41.22	0.18	24.50	0.00	14.18	0.12	5.97	0.05	0.16	7.26	4.14	97.78
Average (n = 8)	44.99	0.24	24.40	0.01	8.17	0.08	3.99	0.18	0.59	8.68	4.16	95.48
Standard deviation	3.63	0.29	0.69	0.02	3.03	0.06	1.03	0.19	1.18	1.52	0.16	2.84
Mica-2												
#9	45.18	0.11	28.51	0.00	1.60	0.03	3.05	0.04	0.21	10.13	4.19	93.05
#10	44.96	0.12	28.22	0.08	1.46	0.05	2.68	0.04	0.15	10.23	4.14	92.13
#11	44.61	0.16	30.28	0.00	1.26	0.00	2.40	0.02	0.24	10.16	4.21	93.34
#12	44.78	0.15	29.38	0.00	1.05	0.00	2.45	0.09	0.27	10.12	4.17	92.46
#13	45.06	0.07	27.85	0.00	1.78	0.06	3.07	0.00	0.14	10.16	4.15	92.34
#14	44.44	0.19	28.58	0.00	1.38	0.06	2.94	0.04	0.24	10.19	4.15	92.21
#15	44.45	0.17	27.70	0.02	1.46	0.00	2.78	0.01	0.23	10.30	4.10	91.22
#16	45.16	0.16	27.69	0.00	1.76	0.00	3.11	0.04	0.17	9.95	4.15	92.19
#17	46.62	0.38	29.33	0.00	0.43	0.03	3.05	0.00	0.29	10.81	4.30	95.24
#18	46.30	0.25	29.66	0.08	0.52	0.00	2.97	0.00	0.26	10.69	4.29	95.02
#19	46.09	0.28	29.86	0.00	0.60	0.07	2.72	0.00	0.28	10.87	4.29	95.06
#20	46.46	0.29	29.89	0.02	0.65	0.05	2.87	0.01	0.25	11.15	4.32	95.96
#21	46.66	0.57	28.76	0.00	0.46	0.08	3.14	0.05	0.27	10.72	4.29	95.00
#22	45.78	0.46	28.96	0.02	0.59	0.06	3.20	0.00	0.22	10.91	4.25	94.45
#23	46.53	0.39	26.80	0.01	0.67	0.00	3.82	0.04	0.16	10.75	4.21	93.38
#24	46.46	0.64	29.56	0.00	0.58	0.01	2.83	0.02	0.26	10.72	4.31	95.39
Average (n = 16)	45.60	0.27	28.81	0.01	1.02	0.03	2.94	0.03	0.23	10.49	4.22	93.65
Standard deviation	0.84	0.17	0.98	0.03	0.50	0.03	0.33	0.03	0.05	0.37	0.07	1.49
Mica-3												
#5	48.37	0.10	26.85	0.00	3.43	0.00	3.14	0.00	0.16	10.44	4.33	96.82
#6	47.61	0.12	27.81	0.00	2.96	0.00	2.99	0.03	0.19	10.37	4.32	96.40
#7	48.79	0.00	26.81	0.00	3.08	0.01	3.44	0.00	0.13	10.35	4.35	96.96
Average (n=3)	48.26	0.07	27.16	0.00	3.16	0.00	3.19	0.01	0.16	10.39	4.33	96.73
Standard deviation	0.60	0.06	0.57	0.00	0.24	0.01	0.23	0.02	0.03	0.05	0.02	0.29
All Micas (weighted averages of Mica-1, Mica-2, and Mica-3)												
Average (n = 27)	45.71	0.24	27.32	0.01	3.37	0.04	3.28	0.07	0.33	9.94	4.21	94.54
Standard deviation	2.22	0.21	2.17	0.02	3.62	0.04	0.76	0.13	0.64	1.18	0.11	2.18

E. Mica—continued

	Molar ratios (based on 12 moles of oxygen)											**Sum Cat #**
Point	**Si**	**Ti**	**Al^{tet}**	**Al^{oct}**	**Cr**	**Fe^{II}**	**Mn**	**Mg**	**Ca**	**Na**	**K**	
Mica-1												
#1	6.52	0.01	1.48	2.79	0.00	0.78	0.00	0.82	0.01	0.05	1.80	14.26
#2	6.40	0.02	1.60	2.58	0.00	1.08	0.01	0.96	0.02	0.05	1.61	14.32
#3	6.38	0.01	1.62	2.61	0.00	1.07	0.02	0.95	0.01	0.06	1.62	14.33
#4	6.21	0.01	1.79	2.50	0.00	1.27	0.02	1.00	0.03	0.07	1.56	14.45
#1	6.68	0.10	1.32	2.85	0.00	0.55	0.00	0.58	0.10	0.02	1.89	14.09
#2	6.92	0.01	1.08	2.63	0.01	0.87	0.00	0.69	0.02	0.92	1.08	14.21
#3	6.73	0.03	1.27	2.89	0.01	0.60	0.01	0.61	0.04	0.06	1.88	14.13
#4	5.98	0.02	2.02	2.16	0.00	1.72	0.02	1.29	0.01	0.04	1.34	14.60
Average (n = 8)	6.48	0.03	1.52	2.63	0.00	0.99	0.01	0.86	0.03	0.16	1.60	14.30
Standard deviation	0.30	0.03	0.30	0.23	0.00	0.38	0.01	0.24	0.03	0.31	0.28	0.17
Mica-2												
#9	6.47	0.01	1.53	3.29	0.00	0.19	0.00	0.65	0.01	0.06	1.85	14.06
#10	6.51	0.01	1.49	3.32	0.01	0.18	0.01	0.58	0.01	0.04	1.89	14.04
#11	6.36	0.02	1.64	3.44	0.00	0.15	0.00	0.51	0.00	0.07	1.85	14.04
#12	6.44	0.02	1.56	3.41	0.00	0.13	0.00	0.52	0.01	0.08	1.86	14.02
#13	6.51	0.01	1.49	3.26	0.00	0.22	0.01	0.66	0.00	0.04	1.87	14.06
#14	6.43	0.02	1.57	3.30	0.00	0.17	0.01	0.64	0.01	0.07	1.88	14.09
#15	6.51	0.02	1.49	3.28	0.00	0.18	0.00	0.61	0.00	0.07	1.92	14.08
#16	6.53	0.02	1.47	3.25	0.00	0.21	0.00	0.67	0.01	0.05	1.84	14.04
#17	6.50	0.04	1.50	3.32	0.00	0.05	0.00	0.63	0.00	0.08	1.92	14.05
#18	6.47	0.03	1.53	3.36	0.01	0.06	0.00	0.62	0.00	0.07	1.91	14.05
#19	6.45	0.03	1.55	3.37	0.00	0.07	0.01	0.57	0.00	0.08	1.94	14.06
#20	6.45	0.03	1.55	3.34	0.00	0.08	0.01	0.59	0.00	0.07	1.97	14.09
#21	6.53	0.06	1.47	3.27	0.00	0.05	0.01	0.65	0.01	0.07	1.91	14.04
#22	6.46	0.05	1.54	3.27	0.00	0.07	0.01	0.67	0.00	0.06	1.96	14.10
#23	6.63	0.04	1.37	3.14	0.00	0.08	0.00	0.81	0.01	0.05	1.95	14.08
#24	6.47	0.07	1.53	3.32	0.00	0.07	0.00	0.59	0.00	0.07	1.91	14.03
Average (n = 16)	6.48	0.03	1.52	3.31	0.00	0.12	0.00	0.62	0.00	0.06	1.90	14.06
Standard deviation	0.06	0.02	0.06	0.07	0.00	0.06	0.00	0.07	0.00	0.01	0.04	0.02
Mica-3												
#5	6.71	0.01	1.30	3.09	0.00	0.40	0.00	0.65	0.00	0.04	1.85	14.03
#6	6.62	0.01	1.39	3.17	0.00	0.34	0.00	0.62	0.00	0.05	1.84	14.04
#7	6.73	0.00	1.27	3.09	0.00	0.36	0.00	0.71	0.00	0.03	1.82	14.01
Average (n = 3)	6.68	0.01	1.32	3.12	0.00	0.37	0.00	0.66	0.00	0.04	1.84	14.03
Standard deviation	0.06	0.01	0.06	0.04	0.00	0.03	0.00	0.05	0.00	0.01	0.01	0.01
All Micas (weighted averages of Mica-1, Mica-2, and Mica-3)												
Average (n = 27)	6.50	0.03	1.50	3.09	0.00	0.41	0.01	0.70	0.01	0.09	1.80	14.13
Standard deviation	0.18	0.02	0.18	0.34	0.00	0.44	0.01	0.17	0.02	0.17	0.20	0.15

Appendix 3. Electron microprobe data for minerals from the Copper Bluff mine, Hoopa Valley Reservation—continued

F. Stilpnomelane

[Chemical notation defined in front matter. c, calculated; Sum Ox%, sum of oxide weight percentage data; Sum Cat #, sum of cation coefficients; Al^{tet}, tetrahedral aluminum; Al^{oct}, octahedral aluminum]

Point	Oxides (weight percent)											Sum Ox%
	SiO_2	TiO_2	Al_2O_3	Cr_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	H_2O(c)	
#1	45.88	0.00	5.69	0.00	29.13	2.43	5.89	0.06	0.02	0.95	3.75	93.80
#2	44.98	0.00	5.70	0.00	29.99	2.15	5.59	0.05	0.05	0.86	3.71	93.08
#3	44.21	0.03	5.44	0.00	29.60	2.53	5.56	0.10	0.04	0.48	3.65	91.64
#4	43.76	0.00	6.28	0.00	28.55	2.56	5.35	0.12	0.05	0.74	3.63	91.04
#5	44.80	0.04	5.51	0.00	29.80	2.26	6.05	0.08	0.03	0.62	3.70	92.89
#6	43.55	0.00	6.42	0.02	29.53	2.27	5.71	0.14	0.09	0.51	3.66	91.90
#7	43.02	0.00	5.47	0.00	28.99	2.32	5.46	0.02	0.00	0.52	3.56	89.36
#8	43.54	0.00	6.18	0.02	29.09	2.35	5.56	0.07	0.06	0.52	3.63	91.02
Average (n = 8)	44.22	0.01	5.84	0.01	29.34	2.36	5.65	0.08	0.04	0.65	3.66	91.84
Standard deviation	0.94	0.02	0.40	0.01	0.48	0.14	0.23	0.04	0.03	0.18	0.06	1.41

Point	Molar ratios (based on 12 moles of oxygen)											Sum Cat #
	Si	Ti	Al^{tet}	Al^{oct}	Cr	Fe^{II}	Mn	Mg	Ca	Na	K	
#1	7.33	0.00	0.67	0.40	0.00	3.89	0.33	1.40	0.01	0.01	0.19	14.24
#2	7.28	0.00	0.72	0.37	0.00	4.06	0.30	1.35	0.01	0.02	0.18	14.27
#3	7.27	0.00	0.73	0.33	0.00	4.07	0.35	1.36	0.02	0.01	0.10	14.25
#4	7.22	0.00	0.78	0.44	0.00	3.94	0.36	1.32	0.02	0.02	0.16	14.25
#5	7.26	0.01	0.74	0.31	0.00	4.04	0.31	1.46	0.01	0.01	0.13	14.28
#6	7.14	0.00	0.86	0.38	0.00	4.05	0.32	1.40	0.02	0.03	0.11	14.31
#7	7.26	0.00	0.74	0.34	0.00	4.09	0.33	1.37	0.00	0.00	0.11	14.26
#8	7.20	0.00	0.81	0.40	0.00	4.02	0.33	1.37	0.01	0.02	0.11	14.27
Average (n = 8)	7.24	0.00	0.76	0.37	0.00	4.02	0.33	1.38	0.01	0.01	0.14	14.26
Standard deviation	0.06	0.00	0.06	0.04	0.00	0.07	0.02	0.04	0.01	0.01	0.04	0.02