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**Characterization of acid mine drainage at the Holden mine,
Chelan County, Washington**

By

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This report is preliminary and has not been reviewed for conformity with U.S. Geological Survey editorial standards and stratigraphic nomenclature. Any use of trade names is for descriptive purposes only and does not imply endorsement by the U.S. Geological Survey.

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Abstract—The Holden orebody is a relatively low-grade, Cu-Zn-Ag-Au, Kuroko-type volcanogenic massive sulfide deposit (VMS) located within the crystalline core of the northern Cascade Range, north-central Washington. The abandoned mine and related workings lie adjacent to Railroad Creek, a major tributary of Lake Chelan (a large fjord lake) some 12 mi. to the east. Because of their pyrite-and sulfide-rich nature, massive sulfide deposits such as Holden have an unusually high acid-generating capacity. Under oxidizing conditions, water draining these deposits can react with the sulfides to form acidic, metal-rich waters that represent potentially significant sources of acid and metal- loading in the environment, jeopardizing not only local water quality but neighboring aqueous and terrestrial ecosystems as well. Three sources of contaminated water discharging directly into nearby Railroad Creek were identified at the Holden site, including: (1) highly acidic, Fe-dominant seeps at the base of the tailings impoundment; (2) acidic, Cu and Zn-rich, Fe-poor seepage that surfaces immediately west of the tailings pile and below the abandoned mill; and (3) weakly acidic, flocculent-rich effluent that exits the main portal of the mine. In addition, a potential and less obvious source of contamination shows up at the base of the tailings and in the dismantled mill in the form of various soluble secondary sulfate minerals that store acid and metals in the solid phase. The dissolution and aqueous dispersion of these encrustations, caused by precipitation or seasonal runoff, could prove harmful to the local environment by causing short-term spikes or increases in the acidity and metal content of Railroad Creek and adjacent areas. Measurable effects of acid mine drainage on the water chemistry of Railroad Creek are most evident within relatively unagitated mixing zones and eddys opposite seepage and portal water inflow, where the influx of dissolved metals form spatially transient hydrogeochemical anomalies. Conversely, compositions of water samples taken from turbulent and rapidly flowing creek water above and below the mill tailings showed little chemical variance and compared favorably with background levels noted elsewhere along Railroad Creek and its tributaries. Given the relatively low discharge volumes from seeps and portal, coupled with the high runoff in Railroad Creek, it appears that metal concentrations and pH in the contaminated waters are quickly diluted to background levels and the metals are precipitated. The impact of seasonal variation, however, was not addressed and could be significant.

INTRODUCTION

Each mine site is unique, yet environmental hazards associated with acid-mine drainage remain a common and disturbing factor in past and present mineral development. In recent years, reliable accounts linking contaminated mine water with declines in aquatic insect populations (Arnekleiv and Storset, 1995) periodic fish kills, and even cattle deaths (Webster and others, 1994) has provoked considerable public sentiment regarding the nations water quality and stability of its aquatic ecosystems. In this regard, the United States and other industrialized countries have made a concerted effort to curb mining-related pollution by encouraging modern mining methods and enacting strict environmental codes or regulations to oversee active and future mining endeavors. Nevertheless, the plight of acid mine drainage persists, at a magnitude greater than once believed, in the form of what Allan (1995) termed "historical pollution" associated with inactive or abandoned mine sites. Of particular concern are

volcanogenic massive sulfide deposits such as Holden, a deposit type that has produced some of the most acidic, metalliferous mine drainage on record (Alpers and Nordstrom, 1991) (see figure 5). Although the amount and severity of contaminated discharge may vary considerably between individual deposits (depending on such factors as local hydrology, climate, and the acid-buffering capacity of enclosing host rocks), an intrinsic quality common to all massive sulfides is the abundance of pyrite and other sulfide minerals; the dominant source of acid-mine drainage. Under oxidizing conditions, water draining waste piles, underground workings, and unmined ore zones of such deposits may acquire high concentrations of acid and dissolved metals and represent potential sources of acid and metal loading in the environment.

The U.S. Geological Survey (USGS), in cooperation with the U.S. Forest Service, is currently conducting geochemical and mineralogical studies at the Holden mine to (1) characterize the behavior of a massive sulfide deposit as it undergoes weathering in a temperate environment typical of north-central Washington and (2) provide the Forest Service with information on the nature and extent of acid drainage and the degree of resultant metal contamination in local creeks and streams. Prior to the current investigation, the Forest Service launched a reclamation-restoration program to remedy obvious environmental concerns associated with the inactive mine complex. Restoration efforts focused on reestablishing landscapes and habitats that would mirror the surrounding undisturbed terrain. This included stabilizing the tailings piles, rechanneling stream and seasonal runoff, and establishing specialized nurseries to explore revegetation possibilities. These endeavors, however, did not address the problem of acid-mine drainage. In this regard, the USGS completed a geochemical reconnaissance study in and around the Holden mine in July 1994 to rapidly identify, at a relatively low cost, the probable sources and general character of acidic waters draining the abandoned mine site (Kilburn and others 1994; Kilburn and others, 1995 a,b). Detailed or follow-up studies, and the subject of this report, were undertaken the following summer (July 1995) in order to assess the extent and further characterize the contamination earmarked by the earlier investigation.

The Holden orebody is a relatively low-grade, copper-zinc-silver-gold volcanogenic massive sulfide deposit (VMS) located near Lake Chelan in north-central Washington state (see figure 1). The deposit, which has survived the impact of high-grade metamorphism (Nold, 1983), is a Kuroko-type VMS, exhaled in an island-arc setting associated with late Triassic extensional tectonism (Dragovitch and Derkey, 1994). The mine, which began production in 1938, ceased operations in 1957 because of high production costs and a drop in the copper market. While operating, over 212 million pounds of copper, 40 million pounds of zinc, 2 million ounces of silver, and 600,000 ounces of gold were extracted from 10 million tons of ore (McWilliams, 1958). At present, the mine site consists largely of mill tailings, waste dumps, portals and shafts, a dismantled mill and other surface structures.

Two sources of contaminated water flowing directly into neighboring Railroad Creek were identified during the 1994 reconnaissance study. One source was a series of low-volume, acidic to highly acidic, Fe-dominant seeps emerging from the base of the tailings impoundment and the other source was weakly acidic, metal-rich effluent (characterized by abundant flocculated metal hydroxides) that issued from the main portal of the mine. A third chemically discriminate (Fe-poor, Cu-Zn rich) seep discharging into Railroad Creek was identified

immediately west of the tailings and below the dismantled mill during the course of the 1995 follow-up study. In addition, a potential source of contamination shows up at the base of the tailings and in the abandoned mill in the form of various soluble salts derived from sulfide weathering and related acid-generation. The dissolution of exposed surface salts and flushing of similar accumulations within the tailings and related waste dumps following unseasonably heavy rain the day and evening preceding 1995 field work undoubtedly altered local water chemistry by increasing acidity and dissolved metal levels; a circumstance easily recognized when comparing 1995 data with findings from the 1994 reconnaissance.

Field observations and analytical data outwardly indicate a rapid neutralization of the acidic discharge and dilution and/or precipitation of accompanying dissolved solids upon entering and mixing with waters of Railroad Creek. However, the long-term environmental ramifications associated with the contaminated effluents (as well as other mining and ore processing wastes found at the Holden site) remains problematic, and is left to more integrated or multidisciplinary approaches to decipher.

Site Description and Mining History

The Holden VMS deposit is sheltered in a glacially modified valley located immediately east of the divide that forms the precipitous crest of the northern Cascade Range of north-central Washington state. The mine and related workings lie adjacent to Railroad Creek, one of the larger watercourses that feeds Lake Chelan, a sizable landlocked fjord situated some 12 mi east of the orebody (figure 1). Topographic relief is great in the Holden area (approximately 8,400 ft) with the mine surrounded by towering peaks and deep valleys. The region displays evidence of prolonged and extensive glaciation, with Railroad Creek draining a steep-sided, U-shaped valley characterized by hanging valleys and glacial lakes. In some of the higher basins and cirques, small glaciers persist and mark the headwaters of Railroad Creek's major tributaries, including Copper Creek, Big Creek, and Holden Creek. The valley floor is covered by a deep overburden (mostly glacial material and talus) that is largely hidden by thick underbrush and scattered stands of timber consisting of fir, cedar, spruce, and balsam. Most of the valley walls are abrupt, with rock exposures generally replacing timber above 4,000 ft (especially on the north side of the valley). The climate is temperate and typified by warm dry summers and cold wet winters with an average annual snowfall of 320 in. At the higher elevations snow cover may endure well into summer. Because of its remote locale, access to the Holden site is limited to regularly scheduled boat service out of Chelan or by floatplane to the Forest Service ranger station at Lucerne, a former resort community on Lake Chelan. From Lucerne, a graded dirt road negotiates the steep Railroad Creek valley to the mine.

Mining possibilities in the Railroad Creek region were first recognized in the summer of 1887, when a location engineer in search of potential routes for the Great Northern Railroad reported and described the weathered, rust-colored gossan marking the eventual site of the Holden mine. Accounts of these altered rocks soon spread, setting in motion wholesale prospecting efforts, with initial claims being staked in the Railroad Creek valley in 1892. Over the next 36 years a number of individuals and syndicates held options on the Holden deposit, although efforts to develop the claims proved ineffectual. In 1928 the Britannia Mining and Smelting Co., a subsidiary of the Howe Sound Co. acquired the property. Administration of the

claims and authority to conduct further exploration was soon passed to another subsidiary, the Chelan Copper Mining Co. In 1937 the subsidiary relationship was dissolved and the Howe Sound Co. took possession of the property and began active development. This encompassed not only the requisite tunneling and sinking of shafts (with underground workings, including drifts and cross-cuts, eventually extending almost 40 mi), but also erection of a mill to concentrate the ore and construction of the community of Holden to accommodate the miners and their families (Youngberg and Wilson, 1952; McWilliams, 1958). The mine, which began production in 1938, discontinued operations in 1957 because of escalating production costs and a decline in the copper market. Although the ore was of a relatively low tenor (averaging roughly 1.1 percent Cu, 0.2 percent Zn, 0.2 oz/short ton Ag, and 0.06 oz/short ton Au) (Nold, 1983) over 212 million pounds of copper, 40 million pounds of Zn, 2 million ounces of Ag, and 600 thousand ounces of Au were extracted from 10 million tons of ore (McWilliams, 1958). Today, residual evidence of mining and milling operations at the Holden site include massive tailings piles, scattered dumps, and dilapidated surface structures dominated by the dismantled mill. However, the town of Holden, located on the north side of Railroad Creek opposite the mine complex, remains quite active and serves as a mountain retreat sponsored by the Lutheran church.

Geologic Setting

The Holden mine lies within the crystalline core of the northern Cascade Range, a region characterized by three major northwest-trending tectonostratigraphic units: the Nason, the Swakane, and the Chelan Mountains terranes. The Holden orebody is located in the Chelan Block of the Chelan Mountains terrane (Dragovitch and Derkey, 1994). The oldest metamorphic rocks exposed in the region, the Swakane Biotite Gneiss, is considered early Paleozoic or older based on zircon age dating. This unit consists primarily of biotite gneiss interbedded locally with hornblende schist and gneiss, clinozoisite-epidote gneiss, and quartzite (Cater, 1982). Overlying the Swakane Biotite Gneiss is a complex series of upper Paleozoic metamorphic rocks referred to as "younger gneissic rocks of the Holden area" by Cater and Crowder (1967). This highly folded sequence includes schistic and gneissic rocks of varying compositions along with intercalated quartzite and marble lenses. Unconformably overlying the metamorphic units are shale, arkosic sandstone, and conglomerate of the Eocene Swauk Formation (Cater, 1982).

Igneous rocks in the northern Cascade Range vary considerably in age and composition. Pre-Tertiary ultramafic rocks of uncertain age mainly occur as small masses consisting of gabbro, hornblendite, and peridotite that are locally altered to serpentine. In addition, ultramafic rocks of probable Eocene age outcrop on the surface and in underground workings of the Holden mine. These younger ultramafic rocks are composed of larger masses of hornblendite and hornblende peridotite and hornblende gabbro (Cater, 1982). Regionally, the most common igneous rocks are Mesozoic metamorphosed granitic intrusives (orthogneisses) (Nold, 1983) including the Triassic Dumbell Mountain plutons (the oldest granitoid rocks in the region with a radiometric date of about 220 m.y.) which form a narrow belt of northwest trending rocks of gneissic hornblende-quartz diorite and quartz diorite gneiss. Tertiary intrusions ranging in age from early Eocene to Miocene are also common to the region. These Tertiary intrusives are largely granodiorite in composition, but can range from gabbro to quartz monzonite in a single mass (Cater, 1982).

The Holden orebody is interpreted as a metamorphosed, Kuroko-type, VMS deposit exhaled in a late Triassic island arc setting (Dragovitch and Derkey, 1994). The deposit is stratabound within a sequence of steeply dipping, high-grade metamorphic rocks, largely consisting of calc-silicate gneisses and amphibolites. These rocks are more or less andesitic in chemical makeup, suggesting andesitic volcanics and related volcanoclastic sedimentary rocks as likely protoliths. The immediate host of the orebody is a pyritic, sericite-quartz schist sequence within the high-grade metamorphic rocks. Exposures of the ore-bearing schist, which ranges from 300 to 600 ft in thickness, can be traced for at least three miles on the surface. The deposit is stratiform within the schist unit and displays the well developed zoning typical of VMS deposits, with a lower or original copper-rich footwall and a zinc-rich upper or original hanging wall. This primary zoning has endured the ravages of high-grade metamorphism as well as intense deformation, which has overturned the deposit, resulting in a copper-rich zone structurally above the zinc-rich zone (Nold, 1983). Principal ore and ore-related minerals encountered at Holden include pyrite, pyrrhotite, chalcopyrite, sphalerite, and native gold. Galena, magnetite, and molybdenite are also present but are merely considered accessories. Gold is mostly linked to chalcopyrite in the structural hanging wall, whereas silver is associated with sphalerite in the structural footwall (McWilliams, 1958). Mineralization is for the most part disseminated, although massive ores are found locally in the zinc-rich zone (Nold, 1983).

Field and Laboratory Methods

Sample media for 1995 investigation included mine and mine related effluents, creek water collected adjacent to solid mine waste and above the Holden mine complex (where exposure to mining and milling activity is minimal), secondary sulfate minerals, hydrous metal oxide precipitates, and mill tailings.

Water samples were collected from within, above, and below the mine workings in polypropylene bottles previously rinsed with 10% HNO₃. At each site a 60-mL sample, filtered through a 0.45 µm acetate membrane filter and acidified with concentrated HNO₃ as well as an untreated 250-mL sample were collected. On-site measurements of pH, specific conductance, and water temperature were also taken. The untreated water samples were analyzed for selected anions (F⁻, Cl⁻, SO₄²⁻, and NO₃⁻) by the method of Fishman and Pyen (1979) using a Dionex model 2120i ion chromatograph. Detection was by suppressed conductivity using peak height for quantification. Filtered and acidified water samples were analyzed for 55 major, minor, and trace elements by an unpublished inductively coupled plasma-mass spectrometry (ICP-MS) method (A.L. Meier, written commun., 1995). Elemental concentrations were determined without preconcentration or dilution, with detection limits for most cations in the sub-ppb range. In addition, unfiltered and filtered water samples (0.45 µm) were collected at randomly selected sites for Hg analysis. The samples were stored in 250 mL glass bottles and stabilized in the field by a potassium dichromate and nitric acid solution. Subsequent analysis was by the continuous flow-cold vapor atomic absorption method of O'Leary and others (1990).

Two dissimilar types of precipitates were collected at the Holden site. One is comprised of metal hydroxides (mostly Al) that appear as clot-like flocculent masses in water draining the main portal (1500 level) of the mine. The other type consists of secondary sulfate salts that develop as heterogeneous efflorescences within the abandoned mill and around the base of the

mill tailings. The flocculent material (3 sites) was collected by simply spooning (plastic spoon) the substance into a 250 mL polypropylene bottle that was rinsed on site with portal effluent prior to sampling. Eleven sulfate samples were gathered in the mill with the aid of a plastic knife and stored in individual plastic zip-lock bags to reduce contact with ambient air and curb possible dehydration and/or hydration reactions. The sulfates were processed for subsequent chemical and X-ray diffraction analysis by merely grinding the samples to a fine powder with an agate mortar and pestle. The metal hydroxide samples were prepared for analysis by first filtering the sample through coarse filter paper (25 μm), and splitting the residue (raw hydroxide) into two fractions. One split (raw hydroxide) was saved for analysis and the other subjected to a 3-step sequential extraction process to separate the hydroxide from sediment impurities (mostly silicates). The first extraction was from a solution of 0.01 N HCl followed by progressively harsher digestions of 0.1 N and 0.6 N HCl. The sulfate and raw hydroxide samples were analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES) using the 40-element procedure of Briggs (1990) and the 10-element method of Motooka (1990). The individual sequential extractions were only analyzed by the 40-element technique which is a complete digestion following multiacid sample decomposition. The 10-element process, which is a partial digestion and organic extraction approach, preferentially dissolves and analyzes environmentally significant minerals such as sulfides and sulfates and affords enhanced sensitivity. Analytical results are generally biased low when compared to the 40-element procedure. Standard X-ray powder diffraction (XRD) techniques (Klug and Alexander, 1974) were employed to determine the mineralogical composition of the sulfate and raw hydroxide precipitates. Packed powder samples were prepared for analysis by back loading a conventional cavity-type diffraction mount and analyzed on a Philips APD-3720 diffractometer using Cu K_{α} radiation, a step size of $0.03^{\circ} 2\Theta$, and a count time of 4 seconds.

Seven grab samples of shallow mill tailings material were collected intermittently along the length of the tailings impoundment. These samples were similarly analyzed by the ICP-AES methods of Briggs (1990) and Motooka (1990) and by routine XRD procedures. In addition, the tailings were analyzed by the flame atomic absorption spectrophotometry (FAAS) procedure of O'Leary and Meier (1990) for low-level gold following sample digestion with hydrobromic acid-bromine and solvent extraction.

Tables 1-2 and 5-7 record the analytical results for each of the geochemical samples collected during the 1995 field season. The mineralogy of secondary sulfate minerals identified at the Holden site in 1994 and 1995 is found in tables 3 and 4, respectively. Data column identifiers in tables 1-2 and 5-7 (with the exception of pH and conductivity in table 1) consist of two lines, the upper giving the elemental symbol and units of measurement (% , $\mu\text{g/L}$, etc.) and the lower specifying a code for the analytical method employed defined as:

FAAS...flame atomic absorption spectrophotometry

IC...ion-chromatography

ICP-MS...inductively coupled plasma-mass spectrometry

ICP-40...40 element inductively coupled plasma-atomic emission spectrometry

ICP-10...10 element inductively coupled plasma-atomic emission spectrometry

AA...cold vapor atomic absorption spectrophotometry

In the data tables (tables 1-2, 5-7), if a specific element was analyzed for but not detected, a "less than" symbol (<) was entered in front of the lower limit of determination. On the other hand, if an element was measured above the highest reporting value, a "greater than" symbol (>) was entered in the tables in front of the upper limit of determination. A triple asterisk symbol "***" in the data column signifies that no analysis was performed for this element. Analytical interference is indicated by "int" in the data column.

A complete listing of analytical results, sample locality maps, and description of analytical methods for samples collected in the 1994 field season are given in Kilburn and others (1994).

RESULTS AND DISCUSSION

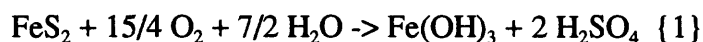
In order to provide a systematic reference for seep and drainage water sampled, this report occasionally relies on the pH-metal classification scheme of Ficklin and others (1992), whereby mine and natural drainage water can be quickly categorized and compared according to pH and the sum of base metals (Cu+Zn+Cd+Co+Ni+Zn) in solution (figures 5 and 6). In addition, Hg, a natural constituent of some massive sulfide deposits in the form of cinnabar (HgS) and derivative secondary minerals (Boyle, 1994) or artificially introduced on site as an ore processing agent (gold amalgamation), was not detected in randomly sampled creek water or mine effluents (lower limits of determination <0.10 ppb) and will not be considered further.

Three chemically distinct sources of contaminated water flowing directly into nearby Railroad Creek were identified (figure 2). The first consists of a series of acidic to highly acidic, Fe-dominant seeps located along the base of the mill tailings. Water from these seeps (1) issues immediately into Railroad Creek, (2) accumulates in numerous standing ponds below the eastern fringe of the tailings impoundment, or (3) forms small pools near the confluence of Railroad Creek and Copper Creek. The second source is weakly acidic, metal-rich water emerging from the main portal (1500 level) of the mine. The portal water, which is characterized by a profusion of suspended Al and to a lesser extent, Fe hydroxides (floc), flows into Railroad Creek roughly 300 m upstream (west) from the mine workings. The third source of contaminated discharge stems from a solitary Fe-poor, Cu-Zn rich seep located near the western edge of the tailings pile below the dismantled mill and related waste dumps. The origin of this effluent is unclear, although its location and chemical makeup suggest an indirect connection with sulfates, discarded ore material, and waste piles in the vicinity of the mill complex. In addition to acid-mine drainage, a potential source of contamination is found at the base of tailings and in the abandoned mill in the form of various soluble efflorescent salts derived from sulfide weathering (figure 2). These encrustations or secondary sulfate salts can host exceedingly high concentrations of metals and acid in the solid form. During the course of hydrologic events such as rain or seasonal snowmelt the soluble salts can readily dissolve, releasing their toxic

constituents to the environment. In light of these solubility properties, it is logical to expect that local water chemistry was altered to some extent (e.g. increased dissolved solid content) by the dissolution of exposed surface salts and flushing of like material in the tailings as an aftereffect of unseasonably heavy rains which drenched the Holden area the day and evening preceding 1995 field work.

Oxidation of Pyrite

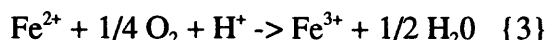
The primary mechanism controlling acid-mine drainage and subsequent growth of related secondary sulfates at the Holden site is the oxidation of pyrite. This is a complex biogeochemical process not thoroughly understood in natural settings, involving a number of oxidation-reduction reactions enhanced by bacterial catalysis. This subject, which has been investigated by numerous researchers, was comprehensively reviewed by Nordstrom (1982) and will not be covered in detail, although an overview of essential reactions is warranted. The overall pyrite oxidation process is frequently expressed by the following generic equation:



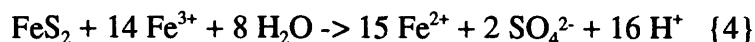
in which insoluble ferric hydroxide and sulfuric acid are produced by the reaction of pyrite and water, in the presence of oxygen. This is somewhat misleading as the reaction does not proceed as directly or as simply as the equation suggests, involving a number of intermediate steps as summarized by:



in which pyrite is initially oxidized by oxygen, liberating S^0 that is then oxidized to sulfate, creating an acidic ferrous sulfate solution. The reduced or ferrous iron (Fe^{2+}) in reaction {2} may then be oxidized to ferric iron (Fe^{3+}) as expressed by:

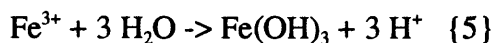


Ferric iron produced in reaction {3}, may now act as an oxidant, perpetuating and intensifying the oxidation of pyrite (Garrels and Thompson, 1960; Smith and Shumate, 1970) as indicated by the following equation:

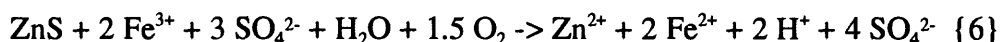


Reaction {4} is rapid (Alpers and Nordstrom) but is limited by conditions imposed on the rate determining step, reaction {3} (ferrous to ferric oxidation). Under weakly acidic and alkaline conditions most of the ferric iron produced by reaction {3} is lost by precipitation of insoluble ferric hydroxide and oxygen remains the dominant oxidizer of pyrite. In more acidic environments the rate of iron hydrolysis drops, and at $\text{pH} < 3$ ferric iron is the principle oxidant of pyrite. Oxidation of ferrous iron by oxygen proceeds very slowly at this point, with pyrite (reaction 4) reducing ferric iron faster than it can be replenished. If enough pyrite is present, all

the ferric iron will be reduced and reaction {4} abruptly terminated (Nordstrom, 1982). However, acidophilic, iron-oxidizing bacteria (*Thiobacillus ferrooxidans*) may act as catalysts and increase the ferrous oxidation rate up to six orders of magnitude (Lacey and Lawson 1970; Singer and Stumm, 1970), so that the regeneration rate of ferric iron is greater than its reduction by pyrite, making oxidation of pyrite under these conditions (reaction 4) a self-sustaining process. When the pyrite is completely weathered or oxidized, the remaining ferric iron is quickly hydrolyzed, yielding insoluble iron hydroxide:



The chemical weathering of pyrite generates large amounts of sulfuric acid and ferric sulfate, strong solvents that not only perpetuate the oxidation of pyrite, but that may also leach and accelerate the oxidation of other metal sulfides such as sphalerite (Guilbert and Park, 1986):



Reaction {6} takes place or is inferred at the Holden site and is considered a prominent factor in determining the composition of the area's mine drainage waters.

Fe-dominant Tailings Seepage

In 1995, a total of 15 seeps and 5 ephemeral ponds were sampled along the base of the mill tailings (figures 3 and 4). Most of the effluent seepage was collected west of Copper Creek from sites comparatively free of obstructing riprap and marked by actively forming ferricrete deposits (a ferric oxide and hydroxide cemented conglomerate composed of tailings material, gravel, and river rock). All the pond samples were gathered east of Copper Creek, either from a boggy swale adjacent to Railroad Creek or from furrow-like depressions at the extreme eastern periphery of the impoundment.

The Holden tailings impoundment extends nearly 1.5 km along the south bank of Railroad Creek, sloping upwards some 40 m above the creek bed at its highest point. The surface tailings are weathered a distinct yellow-ocher color and consist primarily of discarded gangue material (quartz, feldspar, and ferromagnesian silicates), and lesser amounts of secondary Fe-hydroxides (goethite) and hydroxysulfates (jarosite). The conspicuous absence of ore and ore-related minerals such as chalcopyrite and pyrite is predictable, and is merely an indication of near surface oxidizing processes. Another manifestation of surface weathering, which may pique mining interests and facilitate mitigation efforts, is the widespread enrichment of Au in the oxidized tailings (ranging from 0.43 to 1.7 ppm). The impoundment is unequally divided into two discrete piles by a small north-south tributary (Copper Creek) of Railroad Creek, with roughly 2/3 of the tailings situated east of this partitioning creek. Both piles are capped by a veneer of granitic gravel to control persistent wind blown contamination and a string of nurseries to propagate and restore native plant populations. The larger tailings pile east of Copper Creek is confined by an extensive network of basal riprap that forms a barrier against erosion or "flow slides" of unstable mill waste into Railroad Creek. The riprap, which is pervasively coated with rapidly precipitating red-brown Fe-oxides, greatly impaired the identification and sampling of

effluent seepage. The smaller tailings pile west of Copper Creek was only partially hedged by this stabilizing material and simplified the search for active seep water.

Although findings of the earlier 1994 study were minimized by constraints commonly attached to reconnaissance surveys (such as time and sampling limitations), the data proved informative and initial impressions were subsequently detailed (Kilburn and others, 1994; Kilburn and others, 1995a,b). As expected, basal tailings seepage was found to be highly acidic (pH 2.9), Fe-dominant (50,000 µg/L Fe), yet failed to exhibit the extreme metal chemistry anticipated. Of particular interest were the comparatively low concentrations of Cu (53 µg/L) and Zn (3,800 µg/L); a significant departure from the chemical properties frequently ascribed to waters derived from weathering VMS mines and deposits (figure 5). Applying the pH-metal classification scheme of Ficklin and others (1992), the 1994 tailings seepage was interpreted as a high-acid, high metal solution, with the high metal classification based almost entirely on the Zn content. The 1995 follow-up hydrogeochemical studies generally corroborated the 1994 findings (acidic, Fe-dominant tailings seepage) despite sampling in the wake of heavy rainfall which intensified tailings seepage flow, regenerated inactive seeps (especially evident west of Copper Creek) and more importantly, enhanced the dissolved metal content of effluent seepage through dissolution and flushing mechanisms. A further perusal of the 1995 seepage data also reveals a wide range of seep chemistry and underscores the chemical and mineralogical heterogeneity of the tailings pile. This may have important implications for evaluating acid drainage based on deposit type.

Seepage and Pond Water East of Copper Creek

Only two seeps were identified and sampled east of Copper Creek in 1995, although additional seepage was undoubtedly concealed beneath the ubiquitous riprap. The first, site 506 (figures 3 and 4), emerges from the eastern base of the tailings and passes slowly into a string of small, interconnected pools or ponds located in a low-lying area (furrows) next to the impoundment. The seep had a pH of 3.29, conductivity of 2,100 µS/cm and contained dissolved concentrations (in µg/L) of >10,000 Al, 15 Cd, 890 Cu, 100,000 Fe, 1,200 Zn, and 730 mg/L SO₄. The Fe and SO₄ levels were much lower than anticipated and suggest a local scarcity of oxidizing pyrite. No secondary sulfates, which were prevalent in this area in 1994 (Kilburn and others, 1994), were in evidence due to the recent rainfall; however, abundant Fe-oxide precipitates were noted. The second seep (site 511, figures 3 and 4), which discharges into Railroad Creek about 600 m upstream from site 506, was associated with a small ferrirete deposit protruding from beneath oxide coated riprap. The sample registered a pH of 2.87, specific conductance of 4,420 µS/cm, and contained (in µg/L) 8,400 Al, 5.9 Cd, 200 Cu, and 1,000 Zn. Aqueous Fe and SO₄ concentrations were again less than expected at 270,000 µg/L and 1,400 mg/L, respectively.

Two pond samples (sites 508 and 509, figures 3 and 4) were collected from shallow, furrow-like depressions near seep site 506 at the eastern foot of the tailings. Of the two, site 508 was slightly more acidic (pH 3.63 vs. 3.74 for site 509) and posted the higher conductivity (2,320 µS/cm), SO₄ (520 mg/L) and dissolved metal readings (including (in µg/L) 9,000 Al, 4.9 Cd, 310 Cu, 52,000 Fe, and 730 Zn). Three additional ponds were sampled (sites 541-543,

figures 3 and 4) from a marshy swale on the north side of the impoundment facing Railroad Creek. Water from site 542 was the most degraded, with a pH of 2.98, specific conductance of 1860 $\mu\text{S}/\text{cm}$, and SO_4 content of 570 mg/L. Major and base metal concentrations included (in $\mu\text{g}/\text{L}$) 6,500 Al, 7.4 Cd, 310 Cu, 10,000 Fe, and 800 Zn.

Ponds at the Holden site have various origins including seep, ground, and rain water, and may well have developed elevated acid and metal levels due to dissolution of secondary salts. These conditions, likely augmented by modifying processes such as dilution, oxidation, and evaporation make interpretation a risky and possibly misleading endeavor when used to accurately gauge or estimate the compositions of tailings-related discharge. The environmental ramifications, however, are unequivocal and best exemplified by the eastern base of the tailings, a sterile, oxide-stained tract, blemished by numerous stagnant ponds (sample sites 508 and 509, figure 3) and metal-bearing salts; a harsh contrast with the surrounding native terrain. The extended environmental impacts of the pond waters are primarily contingent on their migrating capacity, generally relying on groundwater flow, the scouring effects of heavy surface runoff, or the aqueous dissolution of soluble sulfates (formed during episodes of extreme evaporation) as dispersal mechanisms. Evaporation processes also provide an additional avenue for increasing pond or drainage acidity and metal content by concentrating ferric iron, an effective oxidant of pyrite under acidic conditions.

The rather modest dissolved Fe load of the foregoing seep and pond water is of some interest and may help explain the absence of a discrete Fe phase in the composite secondary sulfate suite (consisting of Mg, Al, and Ca sulfates) identified along the eastern base of the tailings in 1994 (Kilburn and others, 1994). It is conceivable that a shortage or exhaustion of available pyrite has caused the Fe deficiency, a supposition compatible with the relatively low SO_4 values. A different, but complementary scenario, in keeping with field observations, involves the rapid oxidation of Fe^{2+} to Fe^{3+} and ensuing precipitation of Fe (III) solids (oxides and hydroxides), thereby tempering aqueous Fe concentrations and impeding the local development of Fe^{2+} sulfates in favor of divalent Mg and Ca phases.

Seepage West of Copper Creek

In most cases, the tailings effluents sampled in 1995 west of Copper Creek (figures 3 and 4) surfaced in three localized zones consisting of three or more closely aligned or coalescing seeps. These discrete zones were invariably associated with substantial accumulations of ferric oxide precipitates, either as a thick coating on basal tailings material or as ferricrete conglomerates. A total of eleven seeps were sampled from the multiple or closely aligned seepage areas, and two other samples were collected from isolated localities. The general chemical properties of the effluent seepage, reported in terms of pH, conductivity, SO_4 content, and selected heavy metal concentrations, are given beginning at Copper Creek, moving progressively upstream (west) in the direction of the mill. All the seeps flow into Railroad Creek.

Three seeps (sites 515-16, 518) were sampled from a series of small seeps that exit the base of the tailings onto a small, flat-lying bench immediately above the confluence of Railroad Creek and Copper Creek. The bench, which is coated with a thick Fe-oxide crust, contained abundant sulfate salts (Mg, Ca, and Al phases) but only traces of seepage in the dry summer of

1994 (no salts were noticed in the 1995 field season). The seeps (1995) were highly acidic (pH 2.47-3.07), high-ionic strength solutions (with a conductivity range of 7,360-9,160 $\mu\text{S}/\text{cm}$), and contained dissolved metal concentrations of up to (in $\mu\text{g}/\text{L}$) >10,000 Al, 19 Cd, 780 Cu, >500,000 Fe, and 7,300 Zn. Sulfate levels (ranging from 3,200 to 4,400 mg/L) were consistent with the high Fe and conductivity values, and collectively suggest a high degree of local pyrite weathering. These waters are distinct from other tailings-related effluents by their relatively high U (up to 31 $\mu\text{g}/\text{L}$) and collective lanthanide or rare earth element (REE) content (478 $\mu\text{g}/\text{L}$), indicating reaction with and at least partial dissolution of altered wall rock material (such as complex aluminosilicates and rare earth phosphates). Uranium is typically immobile under reducing conditions and its presence, possibly as soluble hexavalent uranium ions or as sulfate complexes, demonstrates the oxidizing nature of the local seepage.

A second series of seeps (sites 520-521, 523-524) were sampled below oxide stained riprap approximately 100 m upstream from Copper Creek. The samples, associated with small, intermittent, ferricrete deposits, were Fe-dominant (>500,000 $\mu\text{g}/\text{L}$), highly acidic (pH 2.55, site 521) to moderately acidic (pH 3.17-4.22) solutions, with comparatively low Cu (ranging from 4 to 200 $\mu\text{g}/\text{L}$) and moderate Zn (ranging from 1,200 to 2,600 $\mu\text{g}/\text{L}$) and Cd (ranging from 2 to 13 $\mu\text{g}/\text{L}$) concentrations. Aluminum varied from >10,000 $\mu\text{g}/\text{L}$ in the more acidic solutions (pH <3.18), to relatively nominal levels (2,600-4,800 $\mu\text{g}/\text{L}$) in the higher pH effluents. Conductivity (up to 8980 $\mu\text{S}/\text{cm}$) and SO_4 levels (up to 3,900 mg/L) were similar to the last series of seeps (Copper Creek-Railroad Creek confluence) and, when interpreted with the Fe data, indicate the continuing oxidation of large volumes of pyrite. Tailings piles are notoriously heterogeneous bodies and the generally unimpressive Cu, Zn, and Cd concentrations may simply imply a lack of base-metal sulfides in this part of the impoundment, although some Cu has no doubt been lost from solution as a result of sorption onto solid phase Fe-oxides and hydroxides in the higher pH seepage. Attenuation of Zn and Cd through similar metal-partitioning reactions, however, can probably be dismissed, as both remain generally conservative in solution (nonreacting) at the measured pH values.

The final series of seeps sampled in 1995 (sites 525, 527-529) surfaced along a ferricrete terrace or ledge (about 30 m in length) some 250 m upstream from Copper Creek. The seeps tested highly acidic (pH 2.82-3.07) to moderately acidic (pH 3.85, site 525) with consistently high levels of Al (>10,000) and variable Fe (110,000->500,000 $\mu\text{g}/\text{L}$), Cd (13-28 $\mu\text{g}/\text{L}$), and base-metal concentrations (ranging from 140-330 $\mu\text{g}/\text{L}$ Cu and 4,800-6,000 $\mu\text{g}/\text{L}$ Zn). This represents a notable increase in dissolved metals when compared with seep water collected from this same terrace during the 1994 reconnaissance, when aqueous Fe, Cd, Cu, and Zn levels were measured at (in $\mu\text{g}/\text{L}$) 50,000, 6.8, 53, and 3,800, respectively (Kilburn and others, 1994); a circumstance no doubt reflecting the flushing effects of recent rainfall. Specific conductance (ranging from 2,680-6060 $\mu\text{S}/\text{cm}$), and SO_4 concentrations (ranging from 860-2,300 mg/L) measured in the 1995 terrace samples are for the most part lower than the two previous series of seeps described above, and when interpreted with the associated, generally moderate Fe levels, indicate a perceptible drop in oxidizing pyrite along this stretch of the tailings impoundment. However, base-metal levels as well as Cd concentrations are, for the most part higher than the last series of seeps (sites 520-521, 523-524) suggesting a slight enrichment of ore material in the

tailings and/or possible ancillary source of metal-rich discharge progressively closer to the western part of the impoundment and mill area. A continuance of this trend (lower Fe/Cu-Zn-Cd ratios) is seen in moderately acidic seepage (pH 3.66) sampled (site 536) about 80 m upstream from site 529. The seep, which surfaced roughly 10 m from the base of the tailings amid white coated river rock (likely Al hydroxides), contained (in µg/L) 29 Cd, 410 Cu, and 6,200 Zn. Fe was again somewhat depleted (160,000 µg/L) and Al remained at >10,000 µg/L. Sulfate (1,000 mg/L) and conductivity (3040 uS/cm) readings are analogous to the dissolved Fe, and further indicate a decline in the pyrite content of the tailings as you near the western part of the impoundment (mill area).

The last seep (site 538) sampled along Railroad Creek in 1995 emerges from composite creek bank material consisting of sand, tailings, and lesser amounts of decomposed organic matter (humus). Because of the seeps unique chemical makeup (Fe-poor, Cu-Zn-rich) and location (just west of the impoundment, down-drainage from the mill) its relationship with the tailings and corresponding Fe-dominant seepage appears marginal, and is discussed later in the report. However, it further corroborates the pattern of heightened base-metal rich seepage near the mill and may be related to the ancillary or secondary source of effluents hypothesized above and is discussed in the subsequent section on sulfates.

The geologic, geochemical, and external controls for high-acid, extreme metal drainage discussed by Plumlee and others (1992; 1993) are clearly in place at the Holden deposit where mining of massive sulfide ore has afforded oxygenated water easy access to tremendous volumes of highly permeable, fine grained, sulfide-rich tailings with little inherent buffering capacity (the tailings contain a high proportion of chemically resistate felsic minerals such as quartz and feldspar). This susceptibility for generating severe seepage chemistry may also be enhanced by local climatic conditions. Oxidation-mobility studies (Boyle, 1994) suggest that massive sulfide tailings located in temperate climates similar to that at Holden are capable of oxidizing at a rate estimated to be 200 times or more greater than natural or unmined massive sulfide orebodies. Under these circumstances, highly acidic, Fe-dominant seepage below the Holden tailings impoundment was quite predictable; the relatively low concentrations of accompanying base-metals, considering the nature of the deposit and source of the samples (base of the tailings) was not. Although merely conjecture, its possible that impermeable layers ("hardpans") within the tailings pile have contributed to the unimpressive Cu and Zn levels by forming local pH or oxidation boundaries that can effectively restrict the mobility of dissolved metals. However, similar metal-partitioning solubility and sorption reactions, which are pH-dependent and can effectively drive aqueous metal concentrations to the solid phase, do not appear to control dissolved metal species (other than Fe) in the sampled surface tailings effluents. The pH is far too low for significant sorption reactions to take place (Smith and others, 1994), and chemical analysis of ferricrete precipitates (mostly goethite) associated with actively flowing seep water contained, not surprisingly, 32 percent Fe, but only modest concentrations of 160 ppm Cu and 130 ppm Zn (Kilburn and others, 1994).

The preponderance of Fe detected in the seepage and ferricrete precipitates is consistent with a pyrite dominated system, while the rather low Cu and Zn concentrations indicate a lack of chalcopyrite and sphalerite in the tailings, apparently evidence of efficient milling procedures at the Holden mine. Analytical data for the oxidized mill tailings (sites 500-504, 505A,B) collected

along the length of the impoundment superficially upholds this inference, showing total concentrations of 4.5 to 7.4 percent Fe, 0.43 to 1.7 ppm Au, and only moderate total concentrations of Cu (86-330 ppm) and Zn (200-270 ppm). Interpretation of the tailings in this manner, however, should be viewed with some caution, since the data is derived from only seven grab samples collected at the surface and cannot be considered representative. In addition, surface tailings would be the first material to face dissolution by oxidation and weathering processes, liberating and dispersing major and trace metals and concentrating the immobile Au.

Seepage flow near the western edge of the tailings impoundment (mill area) was characterized by slightly elevated dissolved Cu, Zn, and Cd concentrations coupled with generally declining Fe, SO_4 , and conductivity levels. This can perhaps be attributed to a modest increase in the base-metal sulfide content of the tailings pile (a possible giveaway of ore processing activity) matched by diminishing pyrite accumulations, although analysis of tailings material also proved inconclusive in this regard. This inferred enrichment may also be augmented by the infiltration of contaminated effluents derived from the abandoned mill and surrounding area, where limited exploration and sampling in 1995 revealed a point source of intense sulfide weathering and sulfate dissolution; a circumstance, when interpreted with other data detailed later in this report, suggest a likely source of migrating acid drainage from the mill area.

From the data at hand, it remains uncertain what impacts the acidic, metalliferous seep waters might have on the general water quality of Railroad Creek. The influence of tailings discharge was naturally most pronounced in shallow, relatively unagitated mixing zones and eddys immediately adjacent to seepage inflow. This consistent observation was most evident near the confluence of Railroad and Copper Creeks (site 517) where the pH of Railroad Creek was measured at 3.91, with coinciding metal levels reaching (in $\mu\text{g/L}$) 3,000 Al, 1 Cd, 48 Cu, 35,000 Fe, and 690 Zn. Conversely, turbulent, free-flowing creek water appears to have been only slightly effected by seepage contamination. Creek water collected immediately below the mill tailings in 1994 proved somewhat enriched in dissolved Fe (320 $\mu\text{g/L}$) in contrast to samples gathered above the impoundment (<100 $\mu\text{g/L}$) but otherwise showed little chemical variance and compared favorably with background levels noted elsewhere along Railroad Creek (Kilburn and others, 1994). These findings were generally substantiated in 1995, although dissolved Fe was somewhat elevated (up to 1,200 $\mu\text{g/L}$) adjacent to and immediately below the tailings; no doubt a chemical manifestation of the recent rainfall. Given the relatively low discharge volumes from the acidic seeps and high runoff in Railroad Creek, it seems that metal concentrations and pH are quickly diluted to background levels and the metals are precipitated. The impact of seasonal variation, however, was not addressed and could be significant.

Portal Water

Effluent, approximate in volume to a small creek, emerges from the main portal (1500 level) of the mine and rapidly flows downhill nearly a quarter of a mile before discharging directly into Railroad Creek. Suspended in the water or adhering to rocks and debris the length of the drainage is a thick, tan-white, flocculent substance subsequently identified chemically as amorphous Al hydroxides intermixed with lesser amounts of Fe hydroxide precipitates. Water collected at the portal (site 534, figure 4)) had a pH of 5.07, specific conductance of 840 $\mu\text{S/cm}$,

and contained dissolved concentrations (in $\mu\text{g/L}$) of 2,400 Al, 29 Cd, 900 Cu, 940 Fe, 22 Pb, 6,000 Zn, and 340 mg/L SO_4 . As the portal water descended the hillside above Railroad Creek, these chemical properties remained remarkably uniform. A sample of the mine discharge (site 535, figure 4) collected about midway between the portal and Railroad Creek (some 250 m from the mine entrance) registered a pH of 5.0, conductivity of 840 $\mu\text{S/cm}$, and carried in solution (in $\mu\text{g/L}$) 2,200 Al, 29 Cd, 910 Cu, 430 Fe, 19 Pb, 6,000 Zn, and 340 mg/L SO_4 . A third sample of the portal effluent, taken just above its convergence with Railroad Creek (site 533, figure 4), had a pH of 5.01, conductivity of 820 $\mu\text{S/cm}$, and included dissolved concentrations (in $\mu\text{g/L}$) of 2,200 Al, 28 Cd, 940 Cu, 250 Fe, 19 Pb, 6,200 Zn, and 330 mg/L SO_4 . The only appreciable downstream variance in mine water chemistry was the steady decline in dissolved Fe (also reflected in the 1994 analytical results), a phenomenon attributed to the continued hydrolysis of Fe. Also of some interest is the relatively high levels of Pb (infrequently detected in Holden mine waters) and Cu remaining in solution. Normally, waters at this pH (5.0) would be expected to lose the greater proportion of these cations (Pb and Cu) to adsorption onto solid phase metal hydroxides (Smith and Macalady, 1991; Smith and others, 1994) or, considering the nature of the waters (acid-sulfate), precipitation of insoluble sulfates such as anglesite (PbSO_4) (Alpers and others, 1994). In reference to the classification of Ficklin and others (1992), the portal effluent equates to a slightly acidic, high metal solution; the high metal designation strongly enhanced by the elevated Zn content. This is not surprising since Zn, which is commonly the major base-metal constituent in acid-mine drainage, is highly mobile and resists sorption reactions within the limited pH range (5.0-5.1) of the Holden portal waters (Plumlee and others, 1993; Smith and others, 1994).

Samples of the ubiquitous flocculent material (floc) were collected at each portal effluent site. These clotlike masses, consisting of coalesced Al- and to some extent Fe-hydroxides, probably precipitated as a result of pH-dependent solubility reactions (Smith and others, 1989). The natural attenuating and/or mediating effects of metal hydroxides in aqueous systems is universally recognized and their development and impact on the portal discharge and ultimately Railroad Creek cannot be minimized. In this respect, the portal floc was instrumental in controlling not only dissolved Fe and Al concentrations, but also served as an effective sink for trace metals by immobilizing many dissolved ionic species (normally the most toxic form) through coprecipitation and adsorption reactions. Although sorption processes are not fully understood, it is apparent that the metal hydroxides capacity to effectively scavenge dissolved metals is directly linked to the net surface charge of the hydroxide, which in turn is a function of pH. As a rule, metal hydroxides sustain a net positive charge in highly acidic solutions, and become progressively more negatively charged (by losing protons) as the pH approaches neutral values. Sorption of cations therefore intensifies as pH increases, with bonding to solid phase hydroxides occurring over a narrow pH range (adsorption edge) that is unique to individual metals (Smith and others, 1991). How long trace metals remain immobile under sorptive conditions is subject to the scavenging metal hydroxides capacity to resist dissolution (Smith and others, 1993). Other variables affecting this metal partitioning reaction include the variety and abundance of metal hydroxides, the presence of competing ligands such as dissolved organic carbon and sulfate, and the concentration and speciation of dissolved metals. These scavenging properties are best illustrated at the Holden site by the base-metal composition of the portal

water hydroxides (sites 533-535), which displayed concentration ranges (in ppm) of 500-1,100 Cu, 81-210 Pb, and 200-400 Zn. Outwardly, this range of sorbed base-metals may appear incompatible with the water data, which indicates a fairly stable system from portal to Railroad Creek. The location of the sample sites, however may explain this inconsistency. Floc sampled at the mine entrance (site 534) contained the higher base-metal concentrations (roughly double the levels determined in metal-hydroxides collected further down drainage) and may reflect a more complex and reactive aqueous environment within the recesses of the mine. In contrast, the two floc samples (sites 533 and 535) gathered some distance from the mine entrance exhibited comparable (and lower) base-metal concentrations and more accurately depict the conservative nature (nonreacting) of the surface portal waters. In order to gain a better perspective or insight concerning sorption processes at Holden, a three-step sequential extraction procedure was devised to separate the metal hydroxides from minor mineral impurities that may have biased the original total chemical analyses. These results, which proved inconclusive, are included in the accompanying data tables (table 7).

The dynamic evolution of the weakly acidic, metal-rich portal discharge and related metal hydroxides is dependent on many complex and sometimes indistinct geochemical and geologic mechanisms (Plumlee and others, 1992). These interacting processes or controls are unique to each deposit, yet certain general inferences can be made regarding the development of the Holden portal effluent.

Ground water flowing along easily accessed conduits within the underground workings of the mine (e.g. drifts and crosscuts) or as confined seepage in faults, fractures, and other permeable zones, readily oxidizes and dissolves pyrite and other sulfides, liberating H^+ , Fe^{2+} , SO_4^{2-} , trace metals (such as Zn, Cu, Pb, and Cd) and high concentrations of acid to the migrating waters. The ensuing acidic solutions are highly corrosive and aggressively attack not only sulfides but the enclosing wallrock as well, prompting acid reactions with and partial dissolution of resistate minerals such as the aluminosilicates (releasing to solution major elements including Al, Ca, K, Na, and Mg) while consuming acid in the process. Influenced by various buffering reactions such as the wallrock interaction described above and/or dilution by divergent mine and ground waters, the pH of the oxidizing solutions rises, resulting in the precipitation of Fe and Al hydroxides (possibly in concert with relatively insoluble sulfate phases), and sorption or coprecipitation of compatible dissolved trace metals (depending on pH) with these same hydrous metal oxides (Smith and others, 1994). Because the first hydrolysis reaction of Fe^{3+} occurs at a much lower pH than Al (Alpers and others, 1994), most of the dissolved Fe precipitates prior to passing through the adit portal and explains the relatively low aqueous concentrations of Fe and corresponding scarcity of Fe hydroxides found in sampled portal effluent.

To what extent the portal discharge impacts Railroad Creek or jeopardizes the stability of local ecosystems remains open to question. As summarized above, a variety of naturally occurring buffering and metal-partitioning reactions have played an active role in substantially moderating the acidity and dissolved metal content of the portal effluent prior to its intersection with Railroad Creek. With much of the potentially harmful contaminants essentially removed or immobilized, it is likely that the balance of the dissolved metals as well as the particulate load (including floc) of the portal discharge is quickly attenuated by various physical and chemical processes associated with the high-flowing creek runoff. This view is consistent with field

observations and subsequent water analysis. At the point where the mine water enters Railroad Creek (mixing zone), and elongate plume of light colored metal hydroxides (presumably, a mixture of portal water floc and freshly precipitated metal hydroxide colloids) extends for about 20 m down drainage before quickly dispersing in the creek runoff. Analysis of mixing zone water (site 532, figure 4) found dissolved Al and Fe levels already in the ambient range, indicating immediate hydrolysis of these metals resulting from interaction with oxygenated, near neutral creek water (pH 7.12); yet relatively high concentrations of dissolved Cd (5.0 µg/L), Zn (1,200 µg/L), and surprisingly Cu (160 µg/L) persisted in the mixing zone. This hydrogeochemical anomaly, which is probably enhanced by incomplete mixing of creek and portal waters, suggests that rapidly precipitating metal hydroxides are not actively sorbing and controlling dissolved metals at this juncture. In any case, the chemistry of creek water (site 530, figure 4) collected about 250 m below the confluence of the hydroxide-rich portal discharge and Railroad Creek (mixing zone) was comparable with background levels noted elsewhere upstream and above the tailings impoundment (where the influence of mining activity on water quality is minimal), demonstrating an overall attenuation of not only portal effluent, but any intervening low-volume seeps and flows.

Secondary Sulfate Salts and Cu-Zn-rich Seep Water

As effluents or seepage at the base of the tailings and inside the abandoned mill evaporates during cycles of dry weather, a potential source of contamination is introduced at the Holden site in the form of various soluble salts derived from sulfide weathering and related acid-generation. These secondary sulfates, which store acid and metals in the solid phase, occur as a thin efflorescent veneer on basal tailings material and other debris or precipitate as stalactites and coat muck piles and wall surfaces in the former mill complex. The dissolution and aqueous dispersion of these salts, caused by precipitation or seasonal runoff, may adversely impact the local environment by causing short-term spikes or increases in the acidity and metal content of nearby Railroad Creek and adjacent areas. Furthermore, the solubilization of ferric sulfates could amplify local oxidizing processes by liberating Fe^{3+} , a strong oxidant of pyrite under acidic conditions. During the 1994 summer reconnaissance (Kilburn and others, 1994; Kilburn and others, 1995a,b), which was characterized by seasonably hot and dry weather, efflorescing salts were easily identified and collected from the base of the mill tailings. Unfortunately summer field work in 1995 was hampered by uncommonly heavy rains that effectively dissolved and dispersed the basal tailings salts, making resampling of these specific sites impossible. However, a primary target of the 1995 field effort, the dismantled mill complex, was partially explored and large sulfate growths and related seepage were sampled.

In July 1994, sulfate rich-coatings were collected along the periphery of the tailings pile near the base (figure 2). X-ray diffraction analysis of the salts revealed an extremely complex mineralogy, accommodating numerous interrelated secondary sulfates as well as minor amounts of relict primary minerals. Magnesium-, Ca-, and Al-sulfates were the common constituents in all the samples, with crusts gathered along the western fringe of the tailings exhibiting the most complex sulfate suites (table 3), including Fe, Cu, and Zn phases. Most of the salts displayed a wide-range of metal concentrations, with some notable enrichments in Cd (3 to 63 ppm), Cu (94 to 5,800 ppm), and Zn (320 to 15,000 ppm). Especially high metal accumulations, however,

were detected in coatings from the western lip of the tailings pile where metal levels reached (in ppm) 13 Ag, 370 Cd, 43,000 Cu, 280 Mo, 120 Pb, 40,000 Zn, and 8.3 % Fe (Kilburn and others, 1994). These extreme metal concentrations are associated with the multiple or complex sulfate phases alluded to above (table 3) and include such common Fe^{II} salts as siderotil ($\text{Fe}^{\text{II}}\text{SO}_4 \cdot 5\text{H}_2\text{O}$), melanterite ($\text{Fe}^{\text{II}}\text{SO}_4 \cdot 7\text{H}_2\text{O}$), and rozenite ($\text{Fe}^{\text{II}}\text{SO}_4 \cdot 4\text{H}_2\text{O}$) as well as their base-metal analogues chalcantite ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), bonattite ($\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$), and gunningite ($\text{ZnSO}_4 \cdot \text{H}_2\text{O}$). It is important to stress the close proximity (about 30 m) of these complex, high-metal sulfates with acidic (pH 3.92), Cu- and Zn-rich (1,700 and 1,800 $\mu\text{g/L}$, respectively), Fe-poor (650 $\mu\text{g/L}$) seepage (site 538, figures 3 and 4) mentioned earlier in connection with a possible secondary source of metalliferous tailings discharge (see section on Fe-dominant seeps).

The underlying cause regarding the segregated growth of efflorescent sulfate minerals in company with exceptionally high metal concentrations is obvious: a local reservoir of highly-acidic water transporting in solution high to extreme levels of Fe, Al, Cu, Zn, and other metals. The details, however, remain problematic. Perhaps the anomalous sulfate assemblage indirectly reflects the precipitation of laterally discontinuous, metal scavenging, "hardpans" elsewhere in the tailings (thereby impeding the wide-spread growth of exotic sulfates by controlling the mobility of dissolved metals) (Blowes and others, 1991), or simply exposes the heterogeneous nature of the impoundment or both. A more compelling scenario likely stems from the location of the high-metal sulfates (as well as the nearby Cu-Zn-rich seepage); positioned immediately below the mill and related waste dumps where sulfide weathering and related acid-mine drainage were identified.

In July 1995, because of hazardous circumstances, the abandoned mill was only given a cursory examination and secondary sulfate and water samples hastily collected (figure 4). Nevertheless, abundant sulfate minerals were observed in part of the old workings believed to be located beneath the former ore processing area, where apparatus such as ball mills and flotation cells were used to produce the ore concentrate. The sulfates occur as intricate stalactite aggregates (up to 30 cm in length) affixed to what appeared to be ore storage bins or chutes, as equally complex crusts atop oxide cemented muck piles (up to 1.5 m in height) located directly below the stalactites, and as gypsum wall coatings. The stalactites are a hybrid mixture of Fe^{2+} , Fe^{3+} , Mg, Cu, Zn, and Ca sulfates (see table 4), an assemblage that could be indicative of solutions low or depleted in Fe^{2+} ; since Cu, Zn, and Mg tend to be incorporated as solid solution constituents in Fe^{2+} -sulfates prior to forming their own distinct phases (Alpers and others, 1994). In this instance, the precipitation of Fe^{2+} sulfates such as rozenite ($\text{Fe}^{\text{II}}\text{SO}_4 \cdot 4\text{H}_2\text{O}$) and coinciding oxidation of Fe^{2+} to Fe^{3+} (as evidenced by the formation of hydroxysulfates such as xitieshanite [$\text{Fe}^{\text{III}}(\text{SO}_4)(\text{OH}) \cdot 7\text{H}_2\text{O}$]) has effectively consumed divalent Fe to the point that discrete Mg, Cu, and Zn sulfates have developed (including starkeyite [$\text{MgSO}_4 \cdot 4\text{H}_2\text{O}$], chalcantite [$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$], and gunningite [$\text{ZnSO}_4 \cdot \text{H}_2\text{O}$]). Owing to the recent rainfall, the stalactites were observed in an active dissolution cycle, with drippings forming a colorful array of efflorescing salts on waste piles and scattered floor refuse. As expected, analysis of acidic drip water (sites 549A,B) collected from the dissolving stalactites revealed extremely high metal concentrations, with 549B registering the lowest pH (2.79) and highest conductivity (37,500 $\mu\text{S/cm}$) and dissolved solid content including (in $\mu\text{g/L}$) 5.7 Ag, >10,000 Al, 2,300 Cd, 970 Co, >40,000 Cu, >500,000 Fe, >100,000 Mg, 180 Ni, 600 U, 140,000 Zn, and 39,700 mg/L SO_4 . Salts formed

from the stalactite drippings, not surprisingly, display a similar mineralogy as the propagating sulfates (including Fe and base-metal phases) (table 4), although evidence for the oxidation of Fe^{2+} to Fe^{3+} is more pronounced with the precipitation of butlerite [$\text{Fe}^{\text{III}}(\text{OH})\text{SO}_4 \cdot 2\text{H}_2\text{O}$], the extremely rare Fe^{2+} - Fe^{3+} sulfate bilinite [$\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}$] (Alpers and others, 1994) and the more evolved and relatively insoluble Na-, NH_4 -, and H_3O -jarosites. The chemical composition of the sulfate assemblage closely parallels the mineralogy, dominated by Fe and Cu concentrations of up to 23% and 11.8%, respectively (table 5). Lesser amounts of Zn (up to 19,000 ppm), Cd (up to 140 ppm) and As (up to 49 ppm) were also detected. Although minor sulfide and oxide impurities in the samples skew the sulfate analysis somewhat, the comparatively small amount of Zn in relation to Cu is interesting and may indicate and abundance of Cu ore and concentrate remain in the mill area (in relation to Zn). This discrepancy would concur with mine production data (McWilliams, 1958) and moreover, suggest that the stalactite drip water may contain considerably more Cu than the $>40,000 \mu\text{g/L}$ determined. Another factor which could magnify the Cu/Zn ratio involves the incorporation of Cu in preference to Zn as a solid solution replacement for Fe^{II} within the crystal structure of Fe^{II} sulfates. This partitioning phenomenon was documented by Alpers and others (1994) in experimental studies involving melanterite ($\text{Fe}^{\text{II}}\text{SO}_4 \cdot 7\text{H}_2\text{O}$) precipitated from mine waters collected at Iron Mountain, California. Although XRD studies failed to detect melanterite in the Holden mill sulfate assemblage, siderotil ($\text{Fe}^{\text{II}}\text{SO}_4 \cdot 5\text{H}_2\text{O}$), a dehydration product of Cu-bearing melanterite (Alpers and others, 1994), was identified in the mill stalactites and may contribute to the Cu enrichment.

The Fe-poor, Cu-Zn-rich seepage and adjoining complex sulfate mineral suite (Fe, Cu, and Zn phases) found below the mill and adjacent to Railroad Creek represent a significant departure from the Fe-dominate seeps and rather modest sulfate assemblages (Mg and Al) identified elsewhere at Holden (figure 2). Its reasonable to assume tailings in the vicinity of the mill would retain a relatively high proportion of ore and ore-related material, and at least partially trigger these unique salt and seepage anomalies (although tangible evidence for this is lacking). An alternative or complementary interpretation, for which there is some substance, stems from the gravitational migration of acidic, metalliferous ground water introduced at or in the vicinity of the mill by the oxidation of Fe and base-metal sulfides and subsequent growth and continued recycling of high-metal sulfates. A fairly sizable seep (20-25 m in length) was sampled (site 548, figure 4) at a break in slope west of the tailings pile and 50 m below the mill (at roughly the same elevation and 120 m south of Railroad Creek). The seepage proved moderately acidic (pH 4.55) and registered a specific conductance of $960 \mu\text{S/cm}$. Dissolved metals included (in $\mu\text{g/L}$) 62 Cd, 3,000 Cu, and 6,500 Zn. Iron was not detected ($<20 \mu\text{g/L}$). Water (pH 4.45) with similar chemical properties (Fe-poor, Cu-Zn rich) was also sampled (site 547, figure 4) from an excavation site (holding pond ?) that presumably contained a high measure of groundwater about 30 m north of site 548 and 90 m from Railroad Creek. Both water samples are akin (chemically) to the Fe-depleted, Cu-Zn rich discharge found below the mill (site 538) and clearly illustrate a downward and horizontal migration of metal-rich subsurface water in the direction of Railroad Creek and away from the mill area. The low Fe and moderate acidity that accompany the seepage and groundwater probably reflect favorable oxidizing

(access to ambient O₂) and buffering (high percentage of rock debris) conditions within the shallow, moist, mountain soil.

It is possible, or even likely, that as this greatly modified subsurface effluent moves downward and laterally away from the mill area, it may eventually emerge as Fe-poor, Cu-Zn-rich seepage along the banks of Railroad Creek (site 538) or pass beneath the western perimeter of the mill tailings, mixing with and enhancing the base-metal content of Fe-rich tailing solutions, an enrichment previously described in connection with basal tailings seepage. In the latter instance, the migrating water may in part move upward in response to drying conditions and resultant capillary forces to evaporate on the surface, precipitating high-metal, Fe-Cu-Zn-salts in the process. This capillary/evaporation effect was observed in the area of high-metal sulfates during the 1995 field season when salts, which had been dissolved during heavy rains, were replaced by small sulfate disseminations following a week of dry weather.

CONCLUSIONS

Inactive or abandoned mine sites associated with volcanogenic massive sulfide (VMS) deposits have yielded some of the most acidic, metalliferous, mine drainage on record, and are of particular environmental concern. With this in mind, the U.S. Geological Survey is currently conducting geochemical studies at the Holden mine, a relatively low-grade, Kuroko-type VMS deposit, in order to assess the character, origin, and extent of contaminated waters derived from this erstwhile producer of base- and precious-metal ore. Pyrite, the primary control of most acid-mine drainage, is inherently abundant in VMS deposits and is considered the major contributing factor of degraded mine water found at the Holden site.

Three sources of contaminated water flowing directly into nearby Railroad Creek were identified at the inactive Holden mine and milling complex. The first source includes a series of intermittent, moderate to highly acidic, Fe-dominant seeps emerging from the base of the mill tailings. These generally low-volume seeps flow into Railroad Creek or accumulate in numerous standing ponds or pools at the base of the tailings impoundment. The high acidity and preponderance of Fe associated with the seepage is consistent with a pyrite-dominated system, while comparatively low Cu and Zn concentrations suggest a lack of significant chalcopyrite and sphalerite in the tailings, apparently an indication of efficient milling procedures. The second source involves weakly acidic, metal-rich effluent exiting the main portal (1500 level) of the mine. This discharge is much more evolved than the tailings seepage and is partially mediated by natural buffering and metal-partitioning reactions (precipitation and sorption) prior to intersecting Railroad Creek. The last source of contaminated water stems from a solitary Fe-poor, Cu-Zn-rich seep that surfaces near the western edge of the tailings pile below the dismantled mill and related waste dumps. The origin of this seepage is unclear, although its location and chemical makeup suggest an indirect linkage with sulfates, discarded ore material, and muck piles in the area of the mill complex.

Presently, not enough information is available to adequately define or characterize the long-term impact of acid-mine drainage on nearby Railroad Creek and related ecosystems; an enduring topic left to more detailed multidisciplinary studies. Nevertheless, sporadic manifestations of mine engendered discharge occur in Railroad Creek along relatively unagitated mixing zones adjacent to seepage and portal water inflow, where the influx of dissolved metals

form spatially transient hydrogeochemical anomalies. Conversely, contaminated effluents appear to be quickly assimilated by the greater volume of creek water a short distance from their point of introduction by natural physical and chemical processes. Seasonal variations, which can have a profound effect on the volume and composition of acid-mine drainage, were not addressed and could prove significant.

In addition to acid-mine drainage, another by-product of sulfide weathering and potential source of contamination is found at the base of the tailings and in the abandoned mill in the form of various soluble sulfates that store acid and metals in the solid phase. The dissolution and aqueous dispersion of these salts could adversely impact the local environment by causing short-term spikes or increases in the acidity and metal content of Railroad Creek and adjoining areas.

In contrast to most VMS deposits, the Holden orebody was relatively enriched in Au (Derkey, 1994), with a recorded production of 600,000 ounces. This property is presently reflected in the oxidized tailings, which consistently display ore-grade levels (up to 1.7 ppm) along the length (approximately 1.5 km) of the impoundment; a factor that may encourage mining interests and facilitate remediation efforts.

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Table 1. Analytical data for untreated water samples collected at the Holden mine, July 1995
(Source of water samples identified in table as follows: 1=seep; 2=creek; 3=pond; 4=portal effluent; and
5=sulfate drip water)

Sample	Temp C	pH	Cond μ S/cm	SO ₄ mg/L	F mg/L	Cl mg/L	NO ₃ mg/L	Hg μ g/L
				IC	IC	IC	IC	AA
506 1	5	3.29	2100	730	1	<1	<0.2	<0.10
507 2	3.5	4.65	260	60	int	0.3	<0.2	***
508 3	5	3.63	2320	520	1	<1	<0.2	<0.10
509 3	7	3.74	740	260	0.4	0.4	<0.2	<0.10
510 2	4.5	7.03	140	5	0.2	0.3	<0.2	***
511 1	15	2.87	4420	1400	1	int	<0.2	***
512 2	3	7.06	100	3	0.2	0.2	<0.2	***
513 2	5	7.16	160	6	0.1	0.8	<0.2	***
514 2	2	7.46	80	3	0.2	0.2	<0.2	***
515 1	10	3.07	9160	4400	6	int	<0.2	<0.10
516 1	15	2.93	8000	3200	3	int	<0.2	<0.10
517 2	7.5	3.91	400	80	int	0.3	0.3	***
518 1	11.5	2.47	7360	3200	3	int	<0.2	<0.10
519 2	4.5	4.97	340	60	int	0.4	0.3	***
520 1	10	4.22	7400	2900	3	int	<0.2	***
521 1	9.5	2.55	7360	2600	2	int	<0.2	***
522 2	4.5	6.59	240	40	0.2	0.4	<0.2	***
523 1	11	3.63	8520	3800	3	int	<0.2	***
524 1	5	3.17	8980	3900	4	int	<0.2	***
525 1	6.5	3.85	5540	1600	1	1	<0.2	<0.10
526 2	6	6.70	140	16	0.2	0.4	<0.2	***
527 1	6.5	2.82	6060	2300	2	int	<0.2	***
528 1	8	2.92	5600	1700	2	2	<0.2	***
529 1	5	3.07	2680	860	1	3	<0.2	***
530 2	3	7.07	80	4	0.2	0.4	<0.2	***
531 2	3	7.12	80	3	0.2	0.3	<0.2	***
532 2	3	6.38	240	60	int	1.2	<0.2	***
533 4	5	5.01	820	330	0.8	3	<0.2	***
534 4	4.5	5.07	840	340	0.6	3	<0.2	<0.10
535 4	6.5	5.0	840	340	0.8	3	<0.2	***
536 1	11	3.66	3040	1000	1.2	3	<0.2	***
537 3	10.5	4.48	860	240	0.4	1.2	<0.2	***
538 1	6	3.92	420	120	0.3	0.4	<0.2	***
539 1	5.5	5.67	100	6	0.1	0.9	1.5	***
540 2	4	6.88	80	6	0.1	0.3	<0.2	***
541 3	18	4.13	300	97	int	0.5	<0.2	***
542 3	22.5	2.98	1860	570	1	1	<0.2	<0.10
543 3	22.5	3.39	1020	250	0.2	0.6	<0.2	***
544 2	6.5	6.86	140	6	0.2	0.3	<0.2	***
545 2	7	7.02	170	6	0.1	0.3	<0.2	***
546 2	4	7.17	100	3	0.1	0.3	<0.2	<0.10
547 3	14	4.45	540	190	int	1.7	<0.2	***
548 1	3	4.55	960	340	0.7	1.7	<0.2	***
549A 5	16	3.12	16000	12000	7	int	<0.2	***
549B 5	18	2.79	37500	39700	60	int	<0.2	***

Table 2. Analytical results for filtered and acidified water samples collected at the Holden mine, July 1995
(Source of water samples indentified in table as follows: 1= seep; 2= creek; 3= pond; 4=portal effluent;
and 5= sulfate drip water)

Sample	Ag µg/L ICP-MS	Al µg/L ICP-MS	As µg/L ICP-MS	Au µg/L ICP-MS	Ba µg/L ICP-MS	Be µg/L ICP-MS	Bi µg/L ICP-MS	Ca µg/L ICP-MS
506 1	0.1	>10000	<1	<0.1	12	0.4	<0.4	110000
507 2	<0.1	1300	<1	<0.1	47	<0.3	<0.4	13000
508 3	<0.1	9000	<1	<0.1	8.8	0.3	<0.4	66000
509 3	<0.1	5300	<1	<0.1	12	<0.3	<0.4	40000
510 2	<0.1	30	<1	<0.1	4.1	<0.3	<0.4	4900
511 1	<0.1	8400	<1	<0.1	3.5	<0.3	<0.4	130000
512 2	<0.1	10	<1	<0.1	4.6	<0.3	<0.4	3500
513 2	<0.1	51	<1	<0.1	4.3	<0.3	<0.4	5400
514 2	<0.1	<10	<1	<0.1	4.7	<0.3	<0.4	5300
515 1	<0.1	>10000	<1	<0.1	0.62	0.5	<0.4	130000
516 1	<0.1	>10000	<1	<0.1	4.0	0.8	<0.4	99000
517 2	<0.1	3000	<1	<0.1	3.9	<0.3	<0.4	11000
518 1	<0.1	>10000	<1	<0.1	2.6	1.2	<0.4	190000
519 2	<0.1	86	<1	<0.1	4.1	<0.3	<0.4	6400
520 1	<0.1	2600	4.8	<0.1	11	<0.3	<0.4	110000
521 1	<0.1	>10000	<1	<0.1	5.6	<0.3	<0.4	140000
522 2	<0.1	40	<1	<0.1	4.1	<0.3	<0.4	7300
523 1	<0.1	4800	5.4	<0.1	9.5	<0.3	<0.4	130000
524 1	<0.1	>10000	<1	<0.1	6.1	<0.3	<0.4	130000
525 1	<0.1	>10000	<1	<0.1	5.4	0.4	<0.4	130000
526 2	<0.1	40	<1	<0.1	4.4	<0.3	<0.4	5000
527 1	<0.1	>10000	<1	<0.1	0.52	0.90	<0.4	140000
528 1	<0.1	>10000	<1	<0.1	2.1	0.8	<0.4	130000
529 1	<0.1	>10000	<1	<0.1	6.0	0.8	<0.4	84000
530 2	<0.1	40	<1	<0.1	4.4	<0.3	<0.4	3600
531 2	<0.1	10	<1	<0.1	4.0	<0.3	<0.4	3600
532 2	<0.1	61	1	<0.1	4.6	<0.3	<0.4	20000
533 4	<0.1	2200	<1	<0.1	10	<0.3	<0.4	99000
534 4	<0.1	2400	<1	<0.1	12	<0.3	<0.4	94000
535 4	<0.1	2200	<1	<0.1	11	<0.3	<0.4	97000
536 1	<0.1	>10000	<1	<0.1	10	0.91	<0.4	80000
537 3	<0.1	>10000	<1	<0.1	10	<0.3	<0.4	46000
538 1	<0.1	3800	<1	<0.1	18	0.3	<0.4	21000
539 1	<0.1	40	<1	<0.1	14	<0.3	<0.4	3600
540 2	<0.1	20	<1	<0.1	4.3	<0.3	<0.4	4200
541 3	<0.1	540	<1	<0.1	24	<0.3	<0.4	24000
542 3	<0.1	6500	<1	<0.1	23	<0.3	<0.4	120000
543 3	<0.1	2100	<1	<0.1	26	<0.3	<0.4	47000
544 2	<0.1	30	<1	<0.1	4.3	<0.3	<0.4	4000
545 2	<0.1	30	<1	<0.1	4.0	<0.3	<0.4	4400
546 2	<0.1	20	<1	<0.1	3.8	<0.3	<0.4	3900
547 3	<0.1	1200	<1	<0.1	22	<0.3	<0.4	41000
548 1	<0.1	2200	1	<0.1	11	<0.3	<0.4	78000
549A 5	1.5	>10000	1	<0.1	6.4	2.6	<0.4	160000
549B 5	5.7	>10000	1	<0.1	2.8	3.2	<0.4	130000

Table 2. Analytical results for filtered and acidified water samples collected at the Holden mine, 1995 cont.

Sample	Cd µg/L ICP-MS	Ce µg/L ICP-MS	Co µg/L ICP-MS	Cr µg/L ICP-MS	Cs µg/L ICP-MS	Cu µg/L ICP-MS	Dy µg/L ICP-MS	Er µg/L ICP-MS
506 1	15	16	32	<0.9	0.4	890	3.5	1.6
507 2	2	2.3	13	<0.9	0.2	48	0.5	<0.1
508 3	4.9	6.0	10	<0.9	0.2	310	1.6	0.7
509 3	2	3.0	5.3	<0.9	0.1	350	0.7	<0.1
510 2	<1	<0.1	<0.2	<0.9	<0.1	3	<0.1	<0.1
511 1	5.9	27	9.8	<0.9	0.4	200	4.3	1.7
512 2	<1	<0.1	<0.2	<0.9	<0.1	<2	<0.1	<0.1
513 2	<1	<0.1	<0.2	<0.9	<0.1	4	<0.1	<0.1
514 2	<1	<0.1	<0.2	<0.9	<0.1	<2	<0.1	<0.1
515 1	8.1	120	66	2	0.7	270	17	8.2
516 1	11	82	58	2	0.5	410	12	6.0
517 2	1	3.9	3.7	<0.9	<0.1	48	0.5	<0.1
518 1	19	160	34	6.1	0.6	780	23	12
519 2	<1	0.5	0.4	<0.9	<0.1	5	<0.1	<0.1
520 1	2	16	11	<0.9	0.3	4	1.9	0.8
521 1	2	63	15	1	0.2	59	9.1	4.7
522 2	<1	0.2	0.4	<0.9	<0.1	3	<0.1	<0.1
523 1	2	21	11	<0.9	0.4	36	3.2	1.3
524 1	13	54	14	2	0.5	200	9.4	4.1
525 1	22	38	20	1	0.5	140	5.6	2.9
526 2	<1	0.1	0.2	<0.9	0.1	4	<0.1	<0.1
527 1	13	50	25	2	1.2	170	8.1	3.7
528 1	22	48	27	2	1.0	330	8.1	4.0
529 1	28	24	25	2	0.7	300	4.1	2.1
530 2	<1	<0.1	<0.2	<0.9	<0.1	7.4	<0.1	<0.1
531 2	<1	<0.1	<0.2	<0.9	<0.1	4	<0.1	<0.1
532 2	5.0	0.3	1.2	<0.9	0.1	160	<0.1	<0.1
533 4	28	1.9	5.6	<0.9	0.3	940	0.8	0.2
534 4	29	2.0	5.6	<0.9	0.4	900	0.7	0.3
535 4	29	1.9	5.8	<0.9	0.3	910	0.8	0.4
536 1	29	32	25	1	0.7	410	5.7	2.3
537 3	17	16	14	<0.9	0.4	160	3.0	1.4
538 1	20	1.9	7.1	<0.9	0.1	1700	0.4	<0.1
539 1	<1	<0.1	<0.2	<0.9	<0.1	9.4	<0.1	<0.1
540 2	<1	<0.1	<0.2	<0.9	<0.1	3	<0.1	<0.1
541 3	2	2.7	2.9	<0.9	0.1	46	0.3	<0.1
542 3	7.4	38	17	<0.9	0.6	310	6.4	3.1
543 3	4.1	7.6	7.5	<0.9	0.2	130	1.2	0.2
544 2	<1	<0.1	<0.2	<0.9	<0.1	3	<0.1	<0.1
545 2	<1	<0.1	<0.2	<0.9	<0.1	3	<0.1	<0.1
546 2	<1	<0.1	<0.2	<0.9	<0.1	3	<0.1	<0.1
547 3	24	1.7	3.6	<0.9	0.1	2300	0.3	<0.1
548 1	62	4.2	27	<0.9	0.7	3000	1.1	<0.1
549A 5	1500	110	510	31	3.9	>40000	34	14
549B 5	2300	170	970	120	5.2	>40000	62	29

Table 2. Analytical results for filtered and acidified water samples collected at the Holden mine, 1995 cont.

Sample	Eu µg/L ICP-MS	Fe µg/L ICP-MS	Ga µg/L ICP-MS	Gd µg/L ICP-MS	Ge µg/L ICP-MS	Hf µg/L ICP-MS	Ho µg/L ICP-MS	La µg/L ICP-MS
506 1	0.6	100000	0.1	3.8	<0.2	<0.1	0.8	8.2
507 2	<0.1	100	0.3	0.7	<0.2	<0.1	0.1	2.5
508 3	0.2	52000	<0.1	1.6	<0.2	<0.1	0.4	2.8
509 3	<0.1	6000	0.1	0.6	<0.2	<0.1	0.1	1.6
510 2	<0.1	560	<0.1	<0.1	<0.2	<0.1	<0.1	<0.1
511 1	0.7	270000	<0.1	5.1	<0.2	<0.1	0.8	9.8
512 2	<0.1	230	<0.1	<0.1	<0.2	<0.1	<0.1	<0.1
513 2	<0.1	1200	<0.1	<0.1	<0.2	<0.1	<0.1	<0.1
514 2	<0.1	<20	<0.1	<0.1	<0.2	<0.1	<0.1	<0.1
515 1	4.2	>500000	0.4	18	1.1	<0.1	3.7	35
516 1	3.0	>500000	0.2	12	0.9	<0.1	2.3	25
517 2	0.1	35000	<0.1	0.6	<0.2	<0.1	0.1	1.2
518 1	4.6	340000	0.5	26	0.2	<0.1	4.9	55
519 2	<0.1	13000	<0.1	<0.1	<0.2	<0.1	<0.1	0.3
520 1	0.4	>500000	0.1	2.2	0.65	<0.1	0.5	8.0
521 1	1.1	>500000	0.3	10	0.4	<0.1	1.9	20
522 2	<0.1	20000	<0.1	<0.1	<0.2	<0.1	<0.1	<0.1
523 1	0.5	>500000	<0.1	3.1	0.73	<0.1	0.7	9.2
524 1	2.1	>500000	<0.1	10	0.89	<0.1	2.1	21
525 1	1.2	480000	0.2	6.9	0.3	<0.1	1.3	17
526 2	<0.1	3200	<0.1	<0.1	<0.2	<0.1	<0.1	<0.1
527 1	1.6	>500000	0.2	8.8	<0.2	<0.1	1.7	21
528 1	1.6	390000	0.2	8.9	0.5	<0.1	1.7	19
529 1	0.9	110000	<0.1	4.2	<0.2	<0.1	0.9	10
530 2	<0.1	140	<0.1	<0.1	<0.2	<0.1	<0.1	<0.1
531 2	<0.1	240	<0.1	<0.1	<0.2	<0.1	<0.1	<0.1
532 2	<0.1	30	<0.1	<0.1	<0.2	<0.1	<0.1	0.1
533 4	0.2	250	<0.1	0.8	<0.2	<0.1	0.2	0.7
534 4	0.2	940	<0.1	1.0	<0.2	<0.1	0.2	0.7
535 4	0.2	430	<0.1	0.9	<0.2	<0.1	0.2	0.6
536 1	1.2	160000	0.2	6.6	<0.2	<0.1	1.2	14
537 3	0.7	110000	0.2	3.2	<0.2	<0.1	0.7	6.4
538 1	0.1	650	<0.1	0.4	<0.2	<0.1	0.1	1.5
539 1	<0.1	400	<0.1	<0.1	<0.2	<0.1	<0.1	<0.1
540 2	<0.1	600	<0.1	<0.1	<0.2	<0.1	<0.1	<0.1
541 3	<0.1	1900	<0.1	0.4	<0.2	<0.1	<0.1	1.3
542 3	0.7	10000	0.1	8.2	<0.2	<0.1	1.3	19
543 3	0.1	5400	<0.1	1.5	<0.2	<0.1	0.2	4.0
544 2	<0.1	680	<0.1	<0.1	<0.2	<0.1	<0.1	<0.1
545 2	<0.1	760	<0.1	<0.1	<0.2	<0.1	<0.1	<0.1
546 2	<0.1	40	<0.1	<0.1	<0.2	<0.1	<0.1	<0.1
547 3	<0.1	190	<0.1	0.4	<0.2	<0.1	0.1	1.8
548 1	0.2	<20	<0.1	1.7	<0.2	<0.1	0.3	5.5
549A 5	9.5	440000	1.3	38	1.3	0.2	6.6	27
549B 5	16	>500000	11	58	1.2	0.3	12	35

Table 2. Analytical results for filtered and acidified water samples collected at the Holden mine, 1995 cont.

Sample	Li µg/L ICP-MS	Mg µg/L ICP-MS	Mn µg/L ICP-MS	Mo µg/L ICP-MS	Na µg/L ICP-MS	Nb µg/L ICP-MS	Nd µg/L ICP-MS	Ni µg/L ICP-MS
506 1	30	15000	1800	<0.1	4300	<0.7	11	27
507 2	<4	1700	370	<0.1	1000	<0.7	2.8	9.8
508 3	26	13000	590	<0.1	3700	<0.7	4.4	9.7
509 3	13	7000	300	<0.1	2700	<0.7	2.5	6.9
510 2	<4	390	6.4	0.3	580	<0.7	<0.1	0.3
511 1	35	27000	2100	<0.1	6700	<0.7	18	11
512 2	<4	340	2.6	0.2	570	<0.7	<0.1	0.4
513 2	<4	490	9.7	0.3	700	<0.7	<0.1	0.7
514 2	<4	460	0.4	0.2	780	<0.7	<0.1	0.3
515 1	36	70000	5100	<0.1	9900	<0.7	68	100
516 1	33	47000	3800	<0.1	8500	1	50	75
517 2	<4	4000	240	<0.1	1200	<0.7	2.2	4.8
518 1	91	51000	3900	<0.1	9200	<0.7	120	43
519 2	<4	1200	68	0.2	650	<0.7	0.3	1.0
520 1	8	39000	3500	0.1	6800	<0.7	8.6	12
521 1	19	47000	4100	<0.1	8100	<0.7	40	15
522 2	<4	1600	88	0.2	780	<0.7	<0.1	0.5
523 1	12	51000	4500	0.2	7800	<0.7	12	13
524 1	32	50000	4400	<0.1	8900	<0.7	36	15
525 1	31	47000	2900	<0.1	>10000	<0.7	22	26
526 2	<4	620	19	0.2	660	<0.7	<0.1	0.5
527 1	39	50000	3300	<0.1	>10000	<0.7	32	25
528 1	41	44000	2700	<0.1	>10000	<0.7	30	28
529 1	35	28000	1500	<0.1	9000	<0.7	17	23
530 2	<4	290	3.5	0.2	470	<0.7	<0.1	0.3
531 2	<4	260	2.4	0.4	480	<0.7	<0.1	0.4
532 2	4	1800	59	0.2	2900	<0.7	0.1	1.2
533 4	26	9100	330	0.3	>10000	<0.7	2.2	6.3
534 4	24	8800	320	0.4	>10000	<0.7	2.6	7.2
535 4	23	8800	330	0.2	>10000	<0.7	2.1	6.5
536 1	55	30000	1400	<0.1	7300	<0.7	22	18
537 3	27	17000	780	<0.1	4300	<0.7	12	13
538 1	13	2400	120	<0.1	1500	<0.7	1.5	6.8
539 1	<4	390	6.8	<0.1	600	<0.7	<0.1	0.5
540 2	<4	380	6.2	0.3	520	<0.7	<0.1	0.4
541 3	<4	4200	180	<0.1	2000	<0.7	1.7	2.4
542 3	16	24000	1000	<0.1	6500	<0.7	26	14
543 3	6	9600	410	<0.1	3000	<0.7	4.8	7.5
544 2	<4	390	7.3	0.2	510	<0.7	<0.1	0.3
545 2	<4	420	7.6	<0.1	540	<0.7	<0.1	0.8
546 2	<4	280	1.6	0.3	500	<0.7	<0.1	0.5
547 3	9	4400	50	<0.1	5500	<0.7	2.4	10
548 1	27	9600	320	<0.1	5800	<0.7	6.3	78
549A 5	320	>100000	>6000	<0.1	6000	1	110	150
549B 5	780	>100000	>6000	<0.1	9200	2	160	180

Table 2. Analytical results for filtered and acidified water samples collected at the Holden mine, 1995 cont.

Sample	Pb µg/L ICP-MS	Pr µg/L ICP-MS	Rb µg/L ICP-MS	Re µg/L ICP-MS	Sb µg/L ICP-MS	Sc µg/L ICP-MS	Sm µg/L ICP-MS	Sn µg/L ICP-MS
506 1	0.6	2.8	11	<0.1	<0.2	16	2.5	<0.4
507 2	0.4	0.7	3.3	<0.1	<0.2	6.1	0.7	<0.4
508 3	0.3	1.1	5.7	<0.1	<0.2	8.8	1.2	<0.4
509 3	0.9	0.5	4.5	<0.1	<0.2	11	0.6	<0.4
510 2	<0.3	<0.1	0.5	<0.1	<0.2	2	<0.1	<0.4
511 1	<0.3	4.2	26	<0.1	<0.2	12	4.3	<0.4
512 2	<0.3	<0.1	0.5	<0.1	<0.2	2	<0.1	<0.4
513 2	<0.3	<0.1	0.6	<0.1	<0.2	2	<0.1	<0.4
514 2	<0.3	<0.1	0.6	<0.1	<0.2	3	<0.1	<0.4
515 1	<0.3	17	14	<0.1	<0.2	23	16	<0.4
516 1	<0.3	12	12	<0.1	<0.2	24	11	<0.4
517 2	<0.3	0.6	1.2	<0.1	<0.2	3	0.6	<0.4
518 1	0.3	26	17	<0.1	<0.2	39	30	<0.4
519 2	<0.3	<0.1	0.6	<0.1	<0.2	2	<0.1	<0.4
520 1	0.5	2.2	23	<0.1	<0.2	7.5	1.2	<0.4
521 1	4.6	8.8	28	<0.1	<0.2	17	7.7	<0.4
522 2	<0.3	<0.1	0.8	<0.1	<0.2	3	<0.1	<0.4
523 1	0.6	3.0	29	<0.1	<0.2	7.7	2.7	<0.4
524 1	0.9	8.6	26	<0.1	<0.2	13	9.0	<0.4
525 1	<0.3	5.5	12	<0.1	<0.2	18	4.8	<0.4
526 2	<0.3	<0.1	0.6	<0.1	<0.2	2	<0.1	<0.4
527 1	<0.3	7.9	15	<0.1	<0.2	22	6.6	<0.4
528 1	<0.3	7.4	11	<0.1	<0.2	24	7.1	<0.4
529 1	<0.3	3.9	8.0	<0.1	<0.2	23	3.5	<0.4
530 2	<0.3	<0.1	0.3	<0.1	<0.2	2	<0.1	<0.4
531 2	<0.3	<0.1	0.4	<0.1	<0.2	2	<0.1	<0.4
532 2	2.0	<0.1	1.4	<0.1	<0.2	3	<0.1	<0.4
533 4	19	0.3	5.8	<0.1	<0.2	7.1	0.7	<0.4
534 4	22	0.5	6.2	<0.1	<0.2	7.2	0.9	<0.4
535 4	19	0.4	6.1	<0.1	<0.2	7.7	0.6	<0.4
536 1	1.7	5.0	14	<0.1	<0.2	24	5.6	<0.4
537 3	0.4	2.6	7.2	<0.1	<0.2	12	2.6	<0.4
538 1	0.3	0.4	5.8	<0.1	<0.2	17	0.4	<0.4
539 1	<0.3	<0.1	1.8	<0.1	<0.2	2	<0.1	<0.4
540 2	<0.3	<0.1	0.5	<0.1	<0.2	2	<0.1	<0.4
541 3	0.3	0.4	2.8	<0.1	<0.2	5.9	0.4	<0.4
542 3	2.7	6.3	14	<0.1	<0.2	18	6.2	<0.4
543 3	1.0	1.2	5.0	<0.1	<0.2	6.9	1.0	<0.4
544 2	<0.3	<0.1	0.5	<0.1	<0.2	2	<0.1	<0.4
545 2	<0.3	<0.1	0.5	<0.1	<0.2	2	<0.1	<0.4
546 2	<0.3	<0.1	0.5	<0.1	<0.2	2	<0.1	<0.4
547 3	7.9	0.5	6.0	<0.1	<0.2	7.0	0.3	<0.4
548 1	0.6	1.6	6.7	<0.1	<0.2	8.6	0.9	<0.4
549A 5	26	20	14	0.6	<0.2	59	38	<0.4
549B 5	23	30	5.8	1.2	0.99	110	57	<0.4

Table 2. Analytical results for filtered and acidified water samples collected at the Holden mine, 1995 cont.

Sample	Sr $\mu\text{g/L}$ ICP-MS	Ta $\mu\text{g/L}$ ICP-MS	Tb $\mu\text{g/L}$ ICP-MS	Te $\mu\text{g/L}$ ICP-MS	Th $\mu\text{g/L}$ ICP-MS	Ti $\mu\text{g/L}$ ICP-MS	Tl $\mu\text{g/L}$ ICP-MS	Tm $\mu\text{g/L}$ ICP-MS
506 1	270	<0.1	0.6	<1	<0.5	16	<0.6	0.2
507 2	79	<0.1	0.1	<1	<0.5	<2	<0.6	<0.1
508 3	210	<0.1	0.3	<1	<0.5	10	<0.6	0.1
509 3	160	<0.1	0.2	<1	<0.5	4	<0.6	<0.1
510 2	17	<0.1	<0.1	<1	<0.5	<2	<0.6	<0.1
511 1	440	<0.1	0.8	<1	2	26	<0.6	0.3
512 2	12	<0.1	<0.1	<1	<0.5	<2	<0.6	<0.1
513 2	18	<0.1	<0.1	<1	<0.5	<2	<0.6	<0.1
514 2	14	<0.1	<0.1	<1	<0.5	<2	<0.6	<0.1
515 1	380	<0.1	3.0	<1	2	54	<0.6	1.2
516 1	300	<0.1	2.2	<1	1	30	<0.6	0.9
517 2	33	<0.1	0.1	<1	<0.5	2	<0.6	<0.1
518 1	460	<0.1	4.3	<1	22	51	<0.6	1.6
519 2	23	<0.1	<0.1	<1	<0.5	<2	<0.6	<0.1
520 1	410	<0.1	0.4	<1	0.6	28	<0.6	0.1
521 1	470	<0.1	1.6	<1	27	30	<0.6	0.7
522 2	24	<0.1	<0.1	<1	<0.5	<2	<0.6	<0.1
523 1	440	<0.1	0.5	<1	2	41	<0.6	0.2
524 1	490	<0.1	1.5	<1	2.4	37	<0.6	0.6
525 1	460	<0.1	1.0	<1	<0.5	35	<0.6	0.3
526 2	19	<0.1	<0.1	<1	<0.5	<2	<0.6	<0.1
527 1	440	<0.1	1.4	<1	<0.5	35	<0.6	0.5
528 1	400	<0.1	1.4	<1	<0.5	31	<0.6	0.5
529 1	300	<0.1	0.8	<1	<0.5	20	<0.6	0.3
530 2	18	<0.1	<0.1	<1	<0.5	<2	<0.6	<0.1
531 2	16	<0.1	<0.1	<1	<0.5	<2	<0.6	<0.1
532 2	75	<0.1	<0.1	<1	<0.5	<2	<0.6	<0.1
533 4	370	<0.1	0.1	<1	<0.5	6	<0.6	<0.1
534 4	360	<0.1	0.2	<1	<0.5	8.4	<0.6	<0.1
535 4	370	<0.1	0.1	<1	<0.5	8.0	<0.6	<0.1
536 1	250	<0.1	1.0	<1	<0.5	22	<0.6	0.4
537 3	160	<0.1	0.6	<1	<0.5	11	<0.6	0.3
538 1	98	<0.1	<0.1	<1	<0.5	2	<0.6	<0.1
539 1	18	<0.1	<0.1	<1	<0.5	<2	<0.6	<0.1
540 2	18	<0.1	<0.1	<1	<0.5	<2	<0.6	<0.1
541 3	110	<0.1	<0.1	<1	<0.5	3	<0.6	<0.1
542 3	490	<0.1	1.3	<1	<0.5	12	<0.6	0.4
543 3	200	<0.1	0.3	<1	<0.5	7	<0.6	0.1
544 2	18	<0.1	<0.1	<1	<0.5	<2	<0.6	<0.1
545 2	19	<0.1	<0.1	<1	<0.5	<2	<0.6	<0.1
546 2	17	<0.1	<0.1	<1	<0.5	<2	<0.6	<0.1
547 3	250	<0.1	<0.1	<1	<0.5	3	<0.6	<0.1
548 1	340	<0.1	0.2	<1	<0.5	5	<0.6	<0.1
549A 5	260	<0.1	6.5	<1	10	54	0.6	2.4
549B 5	190	0.2	10	<1	35	88	0.6	4.3

Table 2. Analytical results for filtered and acidified water samples collected at the Holden mine, 1995 cont.

	U µg/L ICP-MS	V µg/L ICP-MS	W µg/L ICP-MS	Y µg/L ICP-MS	Yb µg/L ICP-MS	Zn µg/L ICP-MS	Zr µg/L ICP-MS	Hg ppb AA
506 1	1.3	<0.3	<0.2	16	1.5	1200	0.1	<0.1
507 2	0.2	<0.3	<0.2	3.5	<0.1	170	<0.1	***
508 3	1.1	<0.3	<0.2	7.4	0.6	730	<0.1	<0.1
509 3	0.7	<0.3	<0.2	3.7	0.2	160	<0.1	<0.1
510 2	<0.1	<0.3	<0.2	<0.1	<0.1	22	<0.1	***
511 1	3.2	0.6	<0.2	16	1.5	1000	<0.1	***
512 2	<0.1	<0.3	<0.2	<0.1	<0.1	<3	<0.1	***
513 2	<0.1	<0.3	<0.2	<0.1	<0.1	25	<0.1	***
514 2	<0.1	<0.3	<0.2	<0.1	<0.1	<3	<0.1	***
515 1	23	2.4	<0.2	59	7.3	7300	0.5	<0.1
516 1	14	2.4	<0.2	44	5.3	7200	0.3	<0.1
517 2	0.6	<0.3	<0.2	2.4	0.2	690	<0.1	***
518 1	31	3.1	<0.2	74	11	4000	<0.1	<0.1
519 2	<0.1	<0.3	<0.2	0.4	<0.1	91	<0.1	***
520 1	1.1	1.5	<0.2	12	0.4	1200	0.3	***
521 1	8.8	1.4	<0.2	37	4.5	1700	0.2	***
522 2	<0.1	<0.3	<0.2	0.3	<0.1	63	<0.1	***
523 1	1.3	2.1	<0.2	16	0.9	1400	<0.1	***
524 1	6.7	9.8	<0.2	40	3.2	2600	0.2	***
525 1	2.0	0.9	<0.2	33	2.2	4900	<0.1	<0.1
526 2	<0.1	<0.3	<0.2	0.1	<0.1	62	<0.1	***
527 1	1.8	1.1	<0.2	41	2.8	5300	<0.1	***
528 1	2.9	0.8	<0.2	37	3.0	6000	0.1	***
529 1	2.2	<0.3	<0.2	20	1.9	4800	<0.1	***
530 2	<0.1	<0.3	<0.2	<0.1	<0.1	31	<0.1	***
531 2	<0.1	<0.3	<0.2	<0.1	<0.1	7	<0.1	***
532 2	0.1	<0.3	<0.2	0.5	<0.1	1200	<0.1	***
533 4	2.6	<0.3	<0.2	3.9	0.3	6200	<0.1	***
534 4	2.5	<0.3	<0.2	4.1	0.3	6000	<0.1	<0.1
535 4	2.4	<0.3	<0.2	3.8	0.3	6000	5.3	***
536 1	5.8	<0.3	<0.2	23	2.8	6200	0.2	***
537 3	3.5	<0.3	<0.2	13	1.3	3800	<0.1	***
538 1	1.1	<0.3	<0.2	2.4	0.1	1800	<0.1	***
539 1	<0.1	<0.3	<0.2	<0.1	<0.1	30	<0.1	***
540 2	<0.1	<0.3	<0.2	<0.1	<0.1	22	<0.1	***
541 3	0.2	<0.3	<0.2	1.6	<0.1	120	<0.1	***
542 3	1.9	<0.3	<0.2	27	2.8	800	<0.1	<0.1
543 3	0.5	<0.3	<0.2	5.2	0.4	500	<0.1	***
544 2	<0.1	<0.3	<0.2	<0.1	<0.1	24	<0.1	***
545 2	<0.1	<0.3	<0.2	<0.1	<0.1	20	<0.1	***
546 2	<0.1	<0.3	<0.2	<0.1	<0.1	5	<0.1	<0.1
547 3	0.4	<0.3	<0.2	2.6	<0.1	2700	<0.1	***
548 1	0.7	<0.3	<0.2	8.3	0.3	6500	<0.1	***
549A 5	210	0.5	<0.2	75	15	81000	<0.1	***
549B 5	600	2.3	0.3	140	29	140000	0.3	***

Table 3. Secondary sulfate minerals identified at the western base of the tailings impoundment, 1994.

<u>MINERAL</u>	<u>FORMULA</u>
Pickeringite	$\text{MgAl}_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}$
Hexahydrite	$\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$
Alunogen	$\text{Al}_2(\text{SO}_4)_3 \cdot 17\text{H}_2\text{O}$
Halotrichite	$\text{Fe}^{\text{II}}\text{Al}_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}$
Siderotil	$\text{Fe}^{\text{II}}\text{SO}_4 \cdot 5\text{H}_2\text{O}$
Melanterite	$\text{Fe}^{\text{II}}\text{SO}_4 \cdot 7\text{H}_2\text{O}$
Rozenite	$\text{Fe}^{\text{II}}\text{SO}_4 \cdot 4\text{H}_2\text{O}$
Romerite	$\text{Fe}^{\text{II}}\text{Fe}_2^{\text{III}}(\text{SO}_4)_4 \cdot 14\text{H}_2\text{O}$
Jarosite	$\text{KFe}_3^{\text{III}}(\text{SO}_4)_2(\text{OH})_6$
Antlerite	$\text{Cu}_3(\text{SO}_4)(\text{OH})_4$
Chalcanthite	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
Bonattite	$\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$
Dietrichite	$\text{ZnAl}_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}$
Gunningite	$\text{ZnSO}_4 \cdot \text{H}_2\text{O}$
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$

Table 4. Secondary sulfate minerals identified in the abandoned Holden mill, July 1995

<u>MINERAL</u>	<u>FORMULA</u>
Starkeyite	$\text{MgSO}_4 \cdot 4\text{H}_2\text{O}$
Alunogen	$\text{Al}_2(\text{SO}_4)_3 \cdot 17\text{H}_2\text{O}$
Siderotil	$\text{Fe}^{\text{II}}\text{SO}_4 \cdot 5\text{H}_2\text{O}$
Rozenite	$\text{Fe}^{\text{II}}\text{SO}_4 \cdot 4\text{H}_2\text{O}$
Bilinite	$\text{Fe}^{\text{II}}\text{Fe}_2^{\text{III}}(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}$
Hydronium Jarosite	$(\text{H}_3\text{O})\text{Fe}_3^{\text{III}}(\text{SO}_4)_2(\text{OH})_6$
Natrojarosite	$\text{NaFe}_3^{\text{III}}(\text{SO}_4)_2(\text{OH})_6$
Ammoniojarosite	$(\text{NH}_4)\text{Fe}^{\text{III}}(\text{SO}_4)_2(\text{OH})_6$
Butlerite	$\text{Fe}^{\text{III}}(\text{SO}_4)(\text{OH}) \cdot 2\text{H}_2\text{O}$
Xitieshanite	$\text{Fe}^{\text{III}}(\text{SO}_4)(\text{OH}) \cdot 7\text{H}_2\text{O}$
Antlerite	$\text{Cu}_3(\text{SO}_4)(\text{OH})_4$
Chalcanthite	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
Bonattite	$\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$
Gunningite	$\text{ZnSO}_4 \cdot \text{H}_2\text{O}$
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$

Table 5. Analytical results for salt and hydroxide precipitates collected at the Holden mine, July 1995.

Sample	Al% ICP-40	Ca% ICP-40	Fe% ICP-40	K% ICP-40	Mg% ICP-40	Na% ICP-40	P% ICP-40	Ti% ICP-40
550A	0.63	0.26	22	0.03	1.4	0.03	0.005	0.006
550B	2.1	0.32	19	0.08	1.4	0.10	0.28	0.02
550C	1.8	0.18	16	<0.01	1.6	0.02	0.04	<0.005
550D	1.7	3.8	17	0.21	1.0	0.33	0.06	0.04
551A	0.66	17	4.9	0.41	0.11	0.31	0.01	0.01
551AA	1.0	15	7.2	0.57	0.16	0.30	0.02	0.03
551B	1.4	14	5.5	0.25	0.47	0.52	0.03	0.03
552A	4.8	0.20	2.8	0.03	2.0	0.07	0.24	0.02
552B	2.2	1.4	4.2	0.14	2.6	0.18	0.19	0.03
552C	5.3	0.37	2.8	0.14	1.9	0.12	0.09	0.009
553	1.7	0.86	23	0.01	0.84	0.05	0.06	<0.005
533HO	12	2.5	5.6	0.66	1.6	1.3	0.05	0.41
534HO	12	1.6	5.6	0.49	0.71	1.2	0.06	0.19
535HO	12	2.1	4.7	0.63	0.94	1.5	0.05	0.27

Sample	Ag ppm ICP-40	As ppm ICP-40	Au ppm ICP-40	Ba ppm ICP-40	Be ppm ICP-40	B ppmi ICP-40	Cd ppm ICP-40	Ce ppm ICP-40
550A	<2	<10	<8	28	<1	<10	27	<4
550B	<2	49	<8	54	<1	44	50	<4
550C	<2	<10	<8	1	<1	<10	37	<4
550D	4	11	<8	140	<1	<10	46	<4
551A	10	<10	<8	74	<1	<10	13	7
551AA	6	20	<8	94	<1	<10	9	<4
551B	4	20	<8	660	<1	<10	26	7
552A	<2	12	<8	24	<1	<10	120	<4
552B	<2	<10	<8	120	<1	<10	52	<4
552C	<2	<10	<8	88	<1	10	140	<4
553	<2	18	<8	5	<1	<10	60	<4
533HO	<2	<10	<8	300	1	<10	<2	19
534HO	<2	<10	<8	230	1	<10	<2	16
535HO	<2	<10	<8	280	1	<10	<2	16

Sample	Co ppm ICP-40	Cr ppm ICP-40	Cu ppm ICP-40	Eu ppm ICP-40	Ga ppm ICP-40	Ho ppm ICP-40	La ppm ICP-40	Li ppm ICP-40
550A	58	25	1900	<2	<4	<4	<2	8
550B	90	82	118000	<2	<4	<4	<2	12
550C	54	12	16000	<2	<4	<4	<2	25
550D	46	34	22000	<2	5	<4	3	12
551A	6	4	1200	<2	<4	<4	3	8
551AA	4	6	1600	<2	<4	<4	3	8
551B	15	8	3900	<2	<4	<4	4	12
552A	48	16	79000	<2	<4	<4	<2	56
552B	150	29	66000	<2	<4	<4	<2	13
552C	41	22	35000	<2	<4	<4	<2	62
553	52	69	24000	<2	4	<4	<2	11
533HO	17	67	500	<2	11	<4	9	18
534HO	8	30	1100	<2	8	<4	7	12
535HO	11	32	520	<2	10	<4	7	15

Table 5. Analytical results for salt and hydroxide precipitates collected at the Holden mine, July 1995..cont.

Sample	Mn ppm ICP-40	Mo ppm ICP-40	Nb ppm ICP-40	Nd ppm ICP-40	Ni ppm ICP-40	Pb ppm ICP-40	Sc ppm ICP-40	Sn ppm ICP-40
550A	960	<2	<4	<4	19	6	2	<5
550B	1600	3	6	<4	110	<4	6	10
550C	1200	<2	<4	<4	15	<4	4	<5
550D	850	2	<4	<4	34	33	4	6
551A	85	<2	<4	<4	2	14	2	<5
551AA	93	<2	<4	<4	<2	28	3	<5
551B	330	<2	<4	<4	7	860	4	<5
552A	1200	<2	11	<4	43	<4	5	<5
552B	930	2	7	<4	58	32	4	8
552C	1100	<2	6	<4	38	13	5	<5
553	1200	<2	<4	<4	72	<4	3	12
533HO	600	7	13	10	22	81	18	<5
534HO	350	8	9	11	10	210	13	<5
535HO	510	10	12	7	10	100	14	<5

Sample	Sr ppm ICP-40	Ta ppm ICP-40	Th ppm ICP-40	U ppm ICP-40	V ppm ICP-40	Y ppm ICP-40	Yb ppm ICP-40	Zn ppm ICP-40
550A	7	<40	4	<100	3	<2	<1	12000
550B	14	<40	4	<100	4	2	<1	11000
550C	2	<40	5	<100	<2	3	<1	12000
550D	51	<40	4	<100	19	3	<1	9800
551A	210	<40	<4	<100	9	2	<1	1600
551AA	300	<40	<4	<100	16	2	<1	940
551B	200	<40	4	<100	12	6	<1	14000
552A	6	<40	<4	<100	31	8	<1	15000
552B	19	<40	<4	<100	23	<2	<1	19000
552C	9	<40	<4	<100	8	8	<1	15000
553	6	<40	<4	<100	<2	<2	<1	17000
533HO	210	<40	5	<100	120	11	<1	230
534HO	190	<40	4	<100	77	11	1	400
535HO	240	<40	5	<100	88	9	<1	200

Sample	Ag ppm ICP-10	As ppm ICP-10	Au ppm ICP-10	Bi ppm ICP-10	Cd ppm ICP-10	Cu ppm ICP-10	Mo ppm ICP-10	Pb ppm ICP-10
550A	0.50	<1.5	<0.15	<1.5	38	2000	5.8	38
550B	<0.12	44	<0.15	<1.5	61	99000	14	100
550C	<0.12	<1.5	<0.15	<1.5	42	40000	4.5	<1.5
550D	4.5	<1.5	<0.15	<1.5	55	22000	6.3	71
551A	7.9	<1.5	<0.15	<1.5	13	1100	1.2	32
551AA	6.8	<1.5	<0.15	<1.5	10	1300	1.6	56
551B	3.6	<1.5	<0.15	<1.5	26	3600	5.3	860
552A	<0.12	<1.5	<0.15	<1.5	130	48000	6.7	45
552B	<0.12	<1.5	<0.15	<1.5	50	61000	9.3	74
552C	0.34	<1.5	<0.15	<1.5	140	30000	7.0	<1.5
553	<0.12	14	<0.15	42	80	19000	10	27
533HO	2.3	<1.5	<0.15	<1.5	0.45	360	10	84
534HO	2.6	<1.5	<0.15	1.5	0.82	780	9.3	190
535HO	1.5	<1.5	<0.15	<1.5	0.41	530	14	130

Table 5. Analytical results for salt and hydroxide precipitates collected at the Holden mine, July 1995..cont

Sample	Sb ppm ICP-10	Zn ppm ICP-10
550A	<1.5	9900
550B	<1.5	11000
550C	<1.5	12000
550D	77	11000
551A	<1.5	1400
551AA	<1.5	830
551B	<1.5	9900
552A	<1.5	15000
552B	<1.5	17000
552C	<1.5	14000
553	28	16000
533HO	<1.5	150
534HO	<1.5	310
535HO	<1.5	210

Table 6. Analytical results for mill tailings collected at the Holden mine, July 1995.

Sample	Al%	Ca%	Fe%	K%	Mg%	Na%	P%	Ti%
	ICP-40	ICP-40	ICP-40	ICP-40	ICP-40	ICP-40	ICP-40	ICP-40
500T	4.4	1.6	5.0	0.71	0.89	1.4	0.03	0.21
501T	4.3	1.4	4.5	0.75	0.77	1.3	0.02	0.13
502T	3.8	1.1	5.4	0.81	1.1	1.0	0.04	0.14
503T	3.9	1.2	6.2	0.88	0.98	1.1	0.04	0.17
504T	3.2	1.1	7.4	0.73	0.71	1.0	0.04	0.18
505TA	3.7	1.1	7.3	0.81	0.84	1.1	0.04	0.17
505TB	3.7	1.1	5.9	0.80	0.76	1.1	0.03	0.15

Sample	Ag ppm	As ppm	Au ppm	Ba ppm	Be ppm	Bi ppm	Cd ppm	Ce ppm
	ICP-40	ICP-40	ICP-40	ICP-40	ICP-40	ICP-40	ICP-40	ICP-40
500T	<2	<10	<8	900	<1	<10	<2	14
501T	<2	<10	<8	680	<1	<10	<2	9
502T	<2	<10	<8	1200	<1	<10	<2	7
503T	2	<10	<8	860	<1	<10	<2	11
504T	3	<10	<8	790	<1	<10	<2	9
505TA	2	<10	<8	780	<1	<10	<2	8
505TB	2	<10	<8	850	<1	<10	<2	11

Sample	Co ppm	Cr ppm	Cu ppm	Eu ppm	Ga ppm	Ho ppm	La ppm	Li ppm
	ICP-40	ICP-40	ICP-40	ICP-40	ICP-40	ICP-40	ICP-40	ICP-40
500T	4	24	110	<2	12	<4	6	12
501T	3	19	86	<2	12	<4	6	12
502T	2	8	250	<2	12	<4	4	18
503T	2	13	260	<2	13	<4	5	16
504T	4	10	230	<2	12	<4	4	8
505TA	2	12	330	<2	11	<4	4	13
505TB	2	10	240	<2	11	<4	6	12

Sample	Mn ppm	Mo ppm	Nb ppm	Nd ppm	N ppm	Pb ppm	Sc ppm	Sn ppm
	ICP-40	ICP-40	ICP-40	ICP-40	ICP-40	ICP-40	ICP-40	ICP-40
500T	500	23	6	7	4	76	8	<5
501T	390	16	4	5	3	74	7	<5
502T	430	8	4	<4	<2	83	8	<5
503T	470	26	4	5	<2	97	10	<5
504T	420	25	4	5	<2	140	7	<5
505TA	460	30	4	4	<2	100	7	<5
505TB	420	25	4	6	<2	100	7	<5

Sample	Sr ppm	Ta ppm	Th ppm	U ppm	V ppm	Y ppm	Yb ppm	Zn ppm
	ICP-40	ICP-40	ICP-40	ICP-40	ICP-40	ICP-40	ICP-40	ICP-40
500T	180	<40	<4	<100	96	6	<1	210
501T	160	<40	<4	<100	66	4	<1	200
502T	130	<40	<4	<100	76	4	<1	270
503T	140	<40	<4	<100	94	4	<1	260
504T	130	<40	<4	<100	99	4	<1	200
505TA	130	<40	<4	<100	90	3	<1	200
505TB	140	<40	<4	<100	80	4	<1	220

Table 6. Analytical results for mill tailings collected at the Holden mine, July 1995...cont.

Sample	Ag	As	Au	Bi	Cd	Cu	Mo	Pb
	ICP-10	ICP-10	ICP-10	ICP-10	ICP-10	ICP-10	ICP-10	ICP-10
500T	1.1	<1.5	0.50	<1.5	<0.08	91	5.8	41
501T	1.0	<1.5	0.35	<1.5	<0.08	76	5.8	34
502T	1.2	<1.5	0.35	<1.5	<0.08	140	5.8	52
503T	2.4	3.2	0.61	3.2	0.14	210	13	66
504T	3.4	6.5	1.5	5.7	<0.08	210	16	110
505TA	2.8	3.1	0.96	3.6	<0.08	320	14	71
505TB	2.3	2.6	0.75	2.7	<0.08	210	11	66

Sample	Sb	Zn	Au
	ICP-10	ICP-10	FAAS
500T	<1.5	160	0.70
501T	<1.5	150	0.70
502T	<1.5	190	0.43
503T	<1.5	200	0.96
504T	<1.5	150	1.7
505TA	<1.5	160	1.1
505TB	<1.5	160	1.1

Table 7. Analytical results for hydroxide samples following progressive sequential extractions in solutions of .01 N, .1 N and .6 N HCl, Holden mine, 1995.

Sample	Extraction	Al % ICP-40	Ca % ICP-40	Fe % ICP-40	K % ICP-40	Mg % ICP-40	Na % ICP-40	P % ICP-40	Ti % ICP-40
533	.01 N	0.38	0.09	0.07	0.04	0.03	0.04	<0.005	<0.005
534	.01 N	0.45	0.08	0.14	0.01	0.01	0.02	<0.005	<0.005
535	.01 N	0.49	0.02	0.06	<0.01	0.005	0.01	<0.005	<0.005
533	.1 N	6.8	0.03	0.40	0.04	0.008	0.01	<0.005	<0.005
534	.1 N	6.7	0.02	0.74	0.01	0.005	0.007	0.006	<0.005
535	.1 N	4.3	0.03	0.90	0.01	0.005	0.005	0.01	<0.005
533	.6 N	3.5	0.24	3.3	0.13	0.58	0.05	0.06	0.06
534	.6 N	2.7	0.16	3.4	0.04	0.21	0.05	0.05	0.03
535	.6 N	0.60	0.10	1.0	0.03	0.14	0.04	0.02	0.02

Sample	Extraction	Ag ppm ICP-40	As ppm ICP-40	Au ppm ICP-40	Ba ppm ICP-40	Bi ppm ICP-40	Cd ppm ICP-40	Ce ppm ICP-40	Co ppm ICP-40
533	.01 N	<2	<10	<8	16	<10	<2	<4	1
534	.01 N	<2	<10	<8	11	<10	<2	<4	<1
535	.01 N	<2	<10	<8	7	<10	<2	<4	<1
533	.1 N	<2	<10	<8	15	<10	<2	<4	1
534	.1 N	<2	<10	<8	6	<10	<2	<4	2
535	.1 N	<2	<10	<8	6	<10	<2	<4	2
533	.6 N	19	<10	<8	84	<10	<2	7	16
534	.6 N	12	<10	<8	33	<10	<2	4	10
535	.6 N	6	<10	<8	28	<10	<2	<4	4

Sample	Extraction	Cr ppm ICP-40	Cu ppm ICP-40	Eu ppm ICP-40	Ga ppm ICP-40	Ho ppm ICP-40	La ppm ICP-40	Li ppm ICP-40	Mn ppm ICP-40
533	.01 N	<1	310	<2	<4	<4	<2	2	39
534	.01 N	<1	690	<2	<4	<4	<2	<2	22
535	.01 N	<1	260	<2	<4	<4	<2	<2	25
533	.1 N	2	200	<2	<4	<4	<2	<2	25
534	.1 N	2	460	<2	<4	<4	<2	<2	13
535	.1 N	2	200	<2	<4	<4	<2	<2	44
533	.6 N	14	1100	<2	<4	<4	<2	9	130
534	.6 N	10	850	<2	<4	<4	<2	4	68
535	.6 N	5	270	<2	<4	<4	<2	4	43

Sample	Extraction	Mo ppm ICP-40	Nb ppm ICP-40	Nd ppm ICP-40	Ni ppm ICP-40	Pb ppm ICP-40	Sc ppm ICP-40	Sn ppm ICP-40	Sr ppm ICP-40
533	.01 N	<2	<4	<4	23	44	<2	<5	12
534	.01 N	<2	<4	4	16	100	<2	<5	7
535	.01 N	<2	<4	<4	11	49	<2	<5	<2
533	.1 N	<2	9	<4	74	62	4	<5	3
534	.1 N	<2	8	<4	69	150	3	<5	<2
535	.1 N	<2	5	<4	130	63	2	<5	<2
533	.6 N	7	4	<4	1000	170	4	5	18
534	.6 N	8	<4	4	700	230	3	9	15
535	.6 N	5	<4	<4	250	150	<2	<5	12

Table 7. Analytical results for hydroxide samples following progressive sequential extractions in solutions of .01 N, .1 N. and .6 N HCl, Holden mine, 1995...cont

Sample	Extraction	Ta ppm ICP-40	Th ppm ICP-40	U ppm ICP-40	V ppm ICP-40	Y ppm ICP-40	Yb ppm ICP-40	Zn ppm ICP-40
533	.01 N	<40	<4	<100	<2	<2	<1	140
534	.01 N	<40	<4	<100	<2	3	<1	240
535	.01 N	<40	<4	<100	<2	<2	<1	89
533	.1 N	<40	<4	<100	<2	<2	<1	110
534	.1 N	<40	<4	<100	2	3	<1	250
535	.1 N	<40	<4	<100	6	<2	<1	320
533	.6 N	<40	<4	<100	35	3	<1	1900
534	.6 N	<40	<4	<100	26	<2	<1	820
535	.6 N	<40	<4	<100	13	<2	<1	300

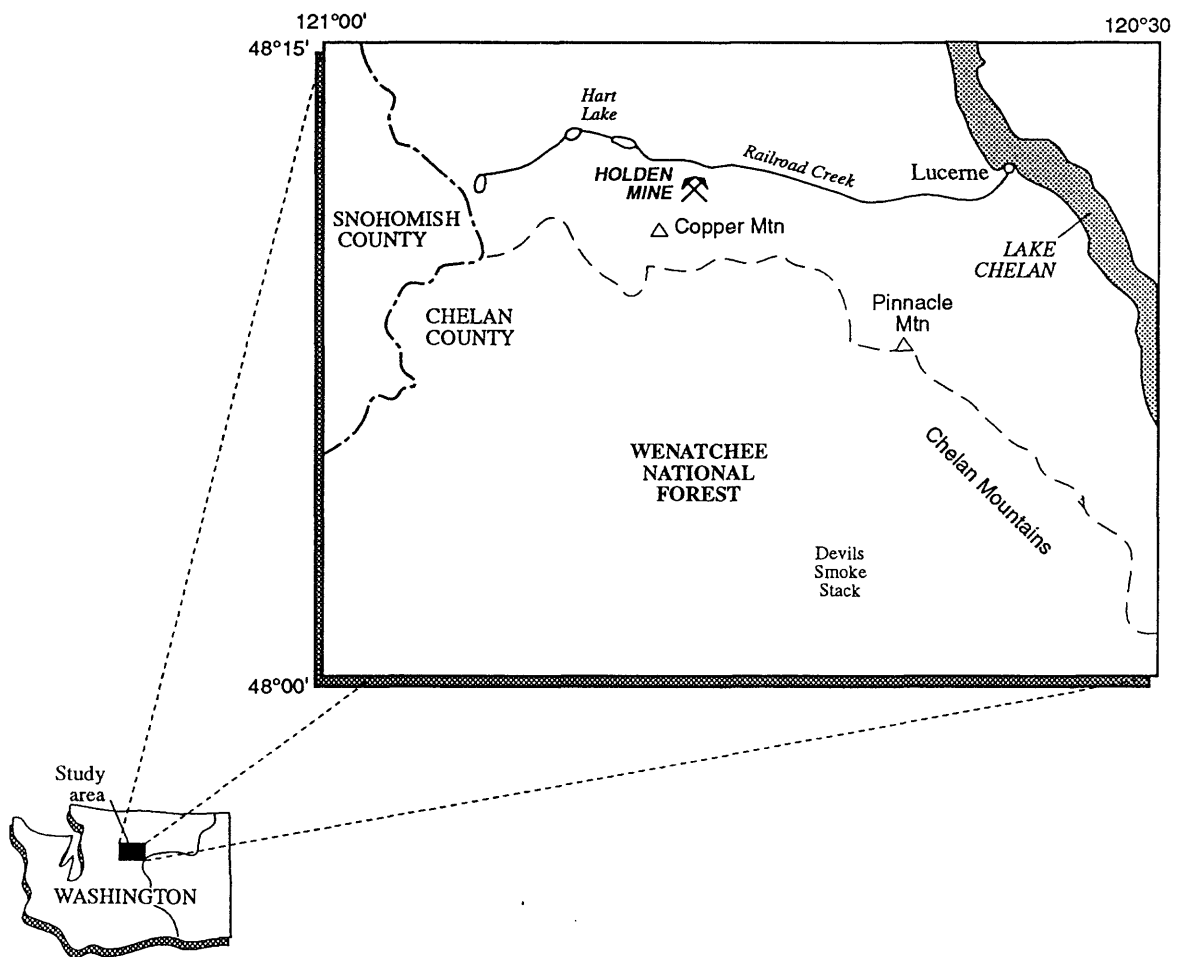


Figure 1. Location of the Holden Mine, Chelan County, Washington

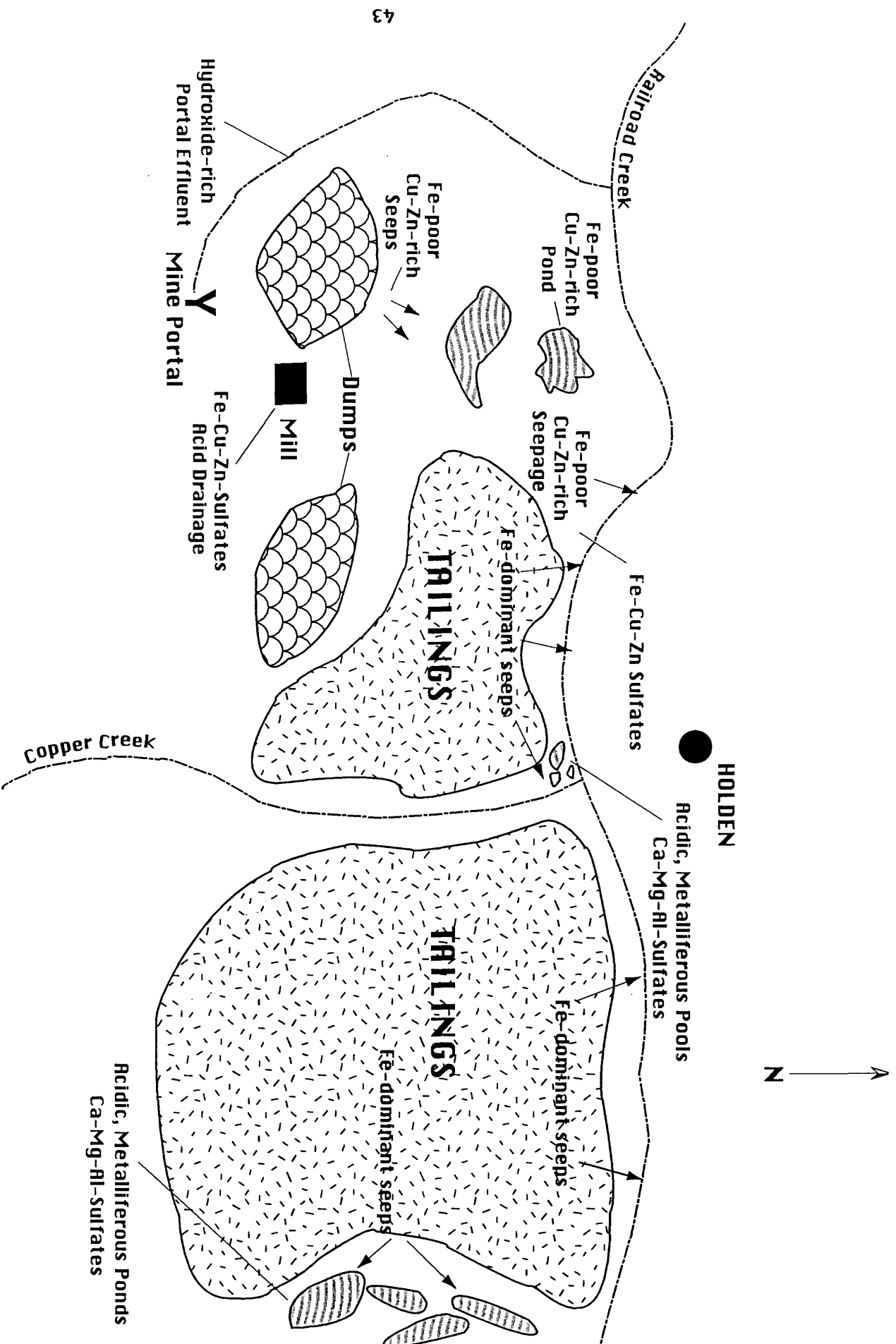


Figure 2. Schematic map showing the relative locations of acid drainage and secondary sulfate minerals at the Holden mine, Chelan County, Washington. NOT TO SCALE

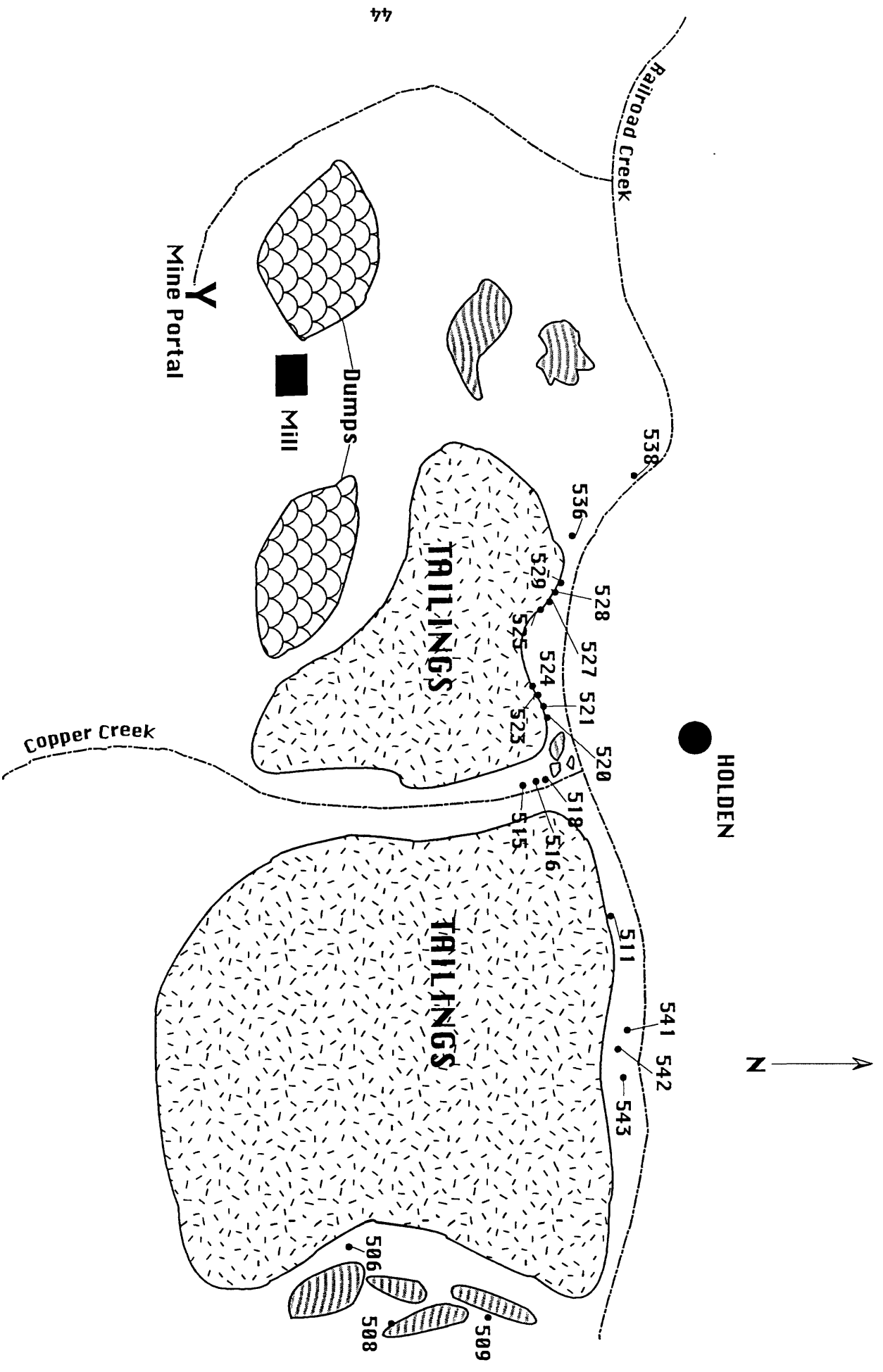


Figure 3. Schematic map showing the relative sample localities of seepage and pond waters collected at the base of the Holden mine tailings impoundment, Chelan County, Washington. NOT TO SCALE

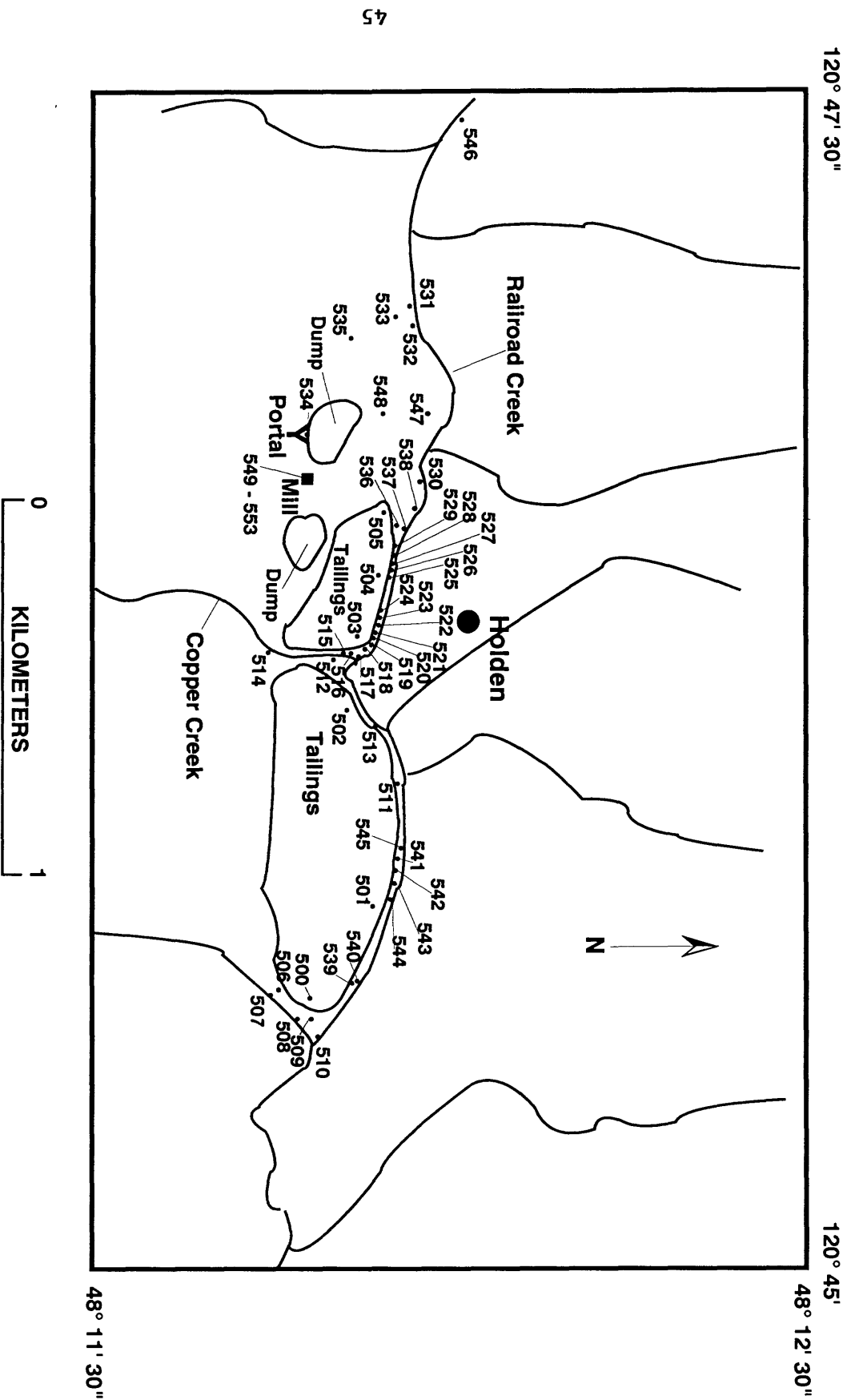


Figure 4. Map showing the location of water, secondary sulfate, and tailing samples collected at the Holden mine and milling complex, Chelan County, Washington, July 1995.

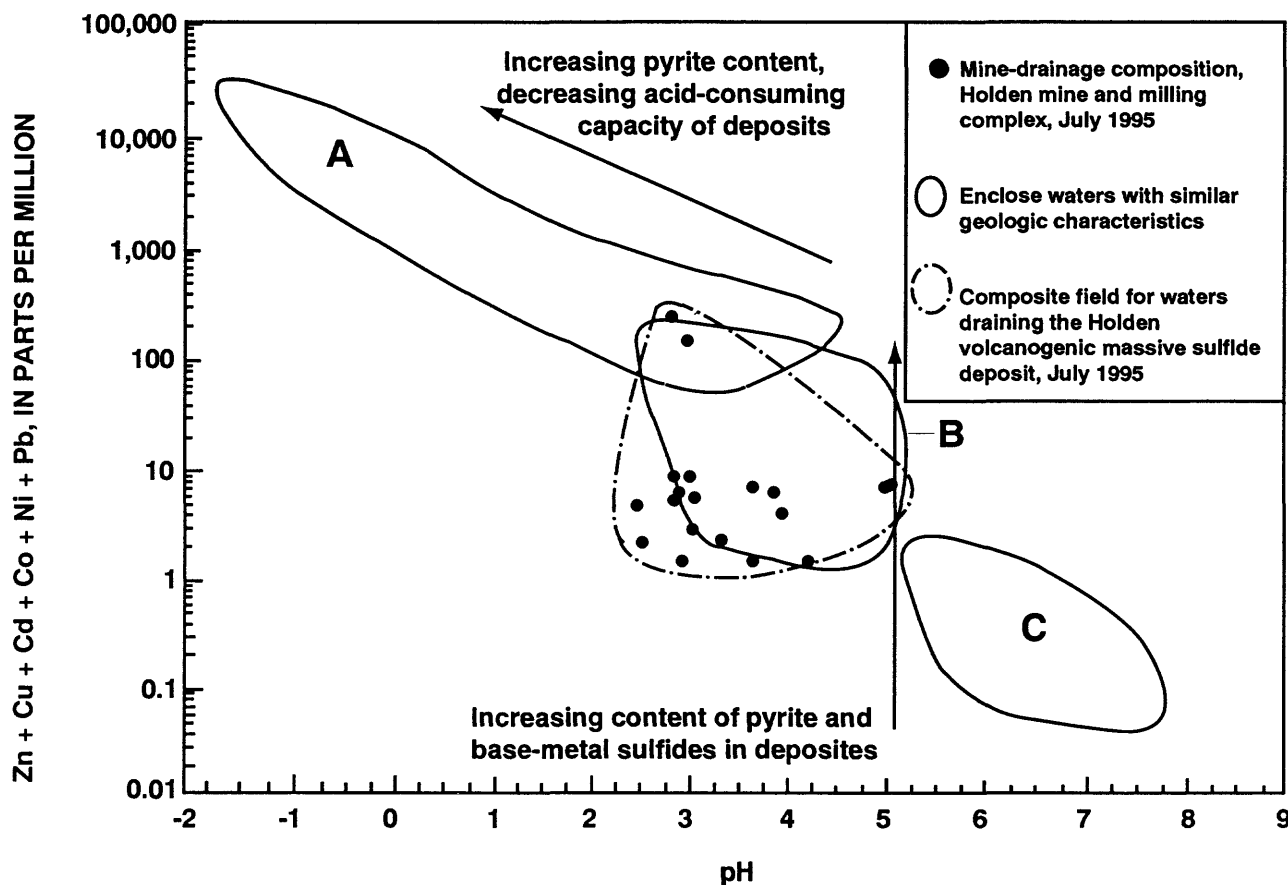


Figure 5. Ficklin diagram plotting pH versus dissolved base metal content of mine-drainage waters. Fields A, B, and C, from Plumlee and others (1994), define fields for the West Shasta district VMS deposits, sulfide-rich vein deposits in rocks with low-buffering capacity, and sulfide-rich vein deposits in carbonate host rocks, respectively. The diagram illustrates that mine waters sampled from the Holden mine and milling complex in July 1995 are generally less acidic and metalliferous than those draining VMS deposits of the West Shasta district.

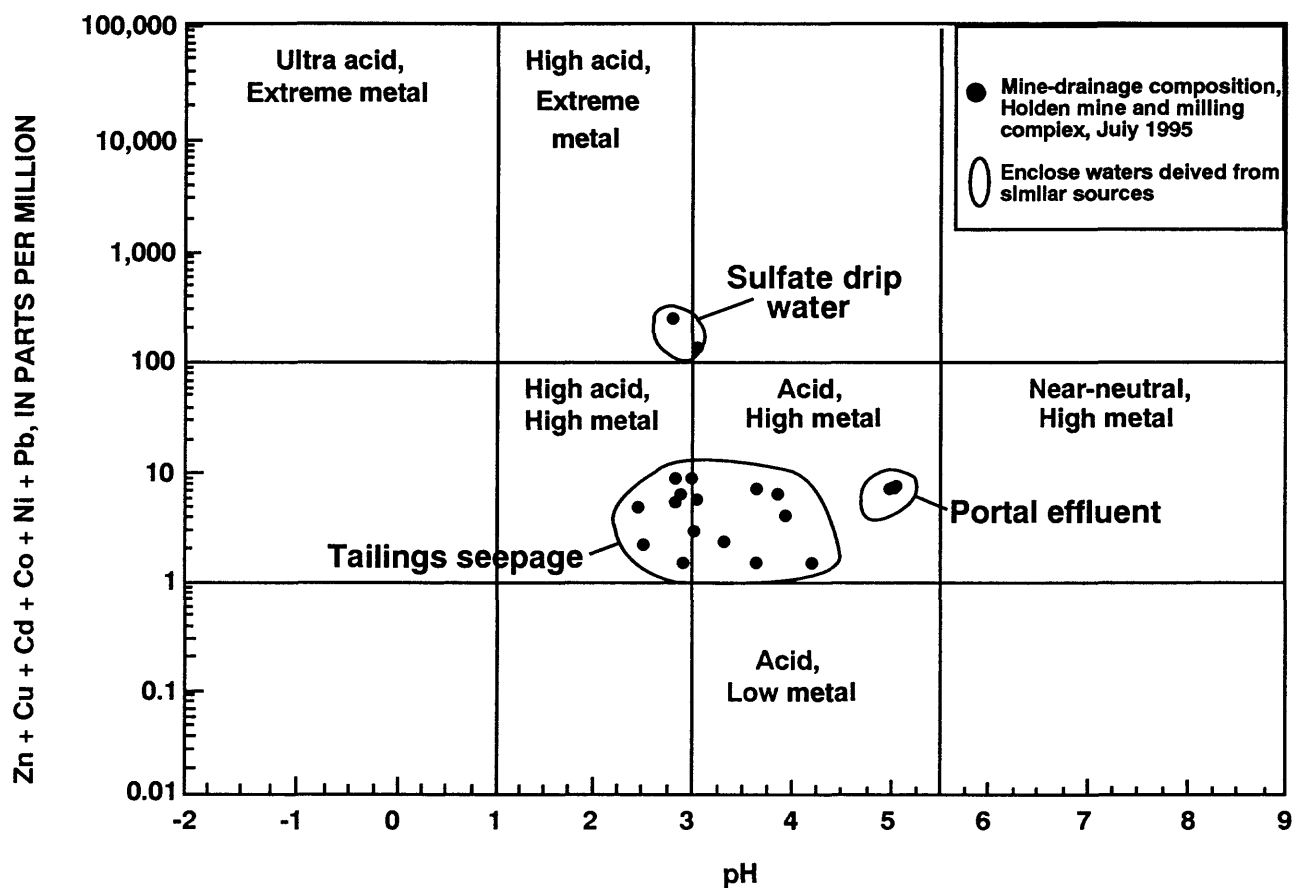


Figure 6. Ficklin diagram plotting pH versus dissolved base metal content of diverse mine-drainage waters collected at the Holden mine, July 1995. The diagram illustrates the wide-range of water compositions associated with various effluent sources. Copper in sulfate drip water exceeds the upper determination limit (> 40 ppm) for the ICP-MS method used; actual dissolved metal content of drip water higher than displayed on the diagram.