

U.S. Department of the Interior U.S. Geological Survey

Environmental Geochemical Studies of Selected Mineral Deposits in Wrangell–St. Elias National Park and Preserve, Alaska

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National Park Service, Wrangell–St. Elias National Park and Preserve, Alaska

Cover photographs. Lower right: Altered bedrock in the Orange Hill area, Alaska. Orange, red, and yellow hues are principally the result of oxidation of pyrite, resulting in iron oxide and soluble sulfate minerals. Left: USGS scientist getting pH reading from acidic, metalliferous water derived from seasonal snow melt draining the Nabesna mill tailings. Upper right: Naturally acidic, metalliferous stream water draining altered bedrock in the Orange Hill area, Alaska. Note rock hammer in stream for scale.

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By Robert G. Eppinger, Paul H. Briggs, Danny Rosenkrans, and Vanessa Ballestrazze

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Prepared in cooperation with the National Park Service, Wrangell–St. Elias National Park and Preserve, Alaska

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Environmental Geochemical Studies of Selected Mineral Deposits in Wrangell–St. Elias National Park and Preserve, Alaska

By Robert G. Eppinger,¹ Paul H. Briggs, Danny Rosenkrans,² and Vanessa Ballestrazze

Abstract

Environmental geochemical investigations took place in Wrangell–St. Elias National Park and Preserve (WRST), Alaska, between 1994 and 1997. Areas studied include the historic Kennecott stratabound copper mines and mill area; the historic mines and mill in the Bremner district, where gold was produced from polymetallic veins; the sporadically active gold placer mines at Gold Hill; the undisturbed, unmined porphyry copper-molybdenum deposits at Orange Hill and Bond Creek; and the historic mines and mill at Nabesna, where gold-bearing iron skarn deposits were exploited. The cooperative study between the U.S. Geological Survey and the National Park Service focused on identifying and characterizing geochemical signatures associated with these mineralized areas. Sample media included surface water, bedload sediment, rock, mine waste, and mill tailings samples.

Predominant influences on the variation in water and sediment chemistry are the deposit type and local geology. At Kennecott surface waters are near neutral in pH and of the calciumbicarbonate type. Most waters have relatively low conductivities (105 to 188 microsiemens per centimeter). With respect to drinking water standards, none of the significant inorganic parameters listed by the Alaska Department of Environmental Conservation and U.S. Environmental Protection Agency (pH, Ag, Al, As, Ba, Be, Cd, Cl⁻, Cr, Cu, F⁻, Fe, Hg, Mn, Na, Ni, NO_3^- , Pb, Se, SO_4^{2-} , Tl, and Zn) exceed established maximum contaminant levels. The dominant sulfide minerals in the Kennecott deposits, chalcocite and djurleite, are relatively stable in the surficial environment. These geochemical data suggest that Kennecott-type deposits are relatively benign to the environment, due to the large amount of carbonate rocks present, the resulting high buffering capacity of waters, the absence of acidgenerating minerals, and the scarcity of metals that could be mobilized at higher pH values.

Waters in the Bremner district have pH values ranging from 6.3 to 7.9 and are classified as calcium type and sulfate

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² Wrangell-St. Elias National Park and Preserve, Alaska; <Danny_Rosenkrans@nps.gov>. type. Conductivities range from 86 to 220 microsiemens per centimeter, and alkalinities range from < 10 to 26 parts per million (as calcium carbonate). In two instances, manganese concentrations are slightly above and pH is slightly below maximum contaminant level guidelines. In waters, the low alkalinities, predominance of sulfate over bicarbonate, near neutral pH values, and low dissolved metal contents are the result of the geologic setting-pyrite- and calcite-bearing quartz veins that cut carbonate-poor slates of the Cretaceous Valdez Group. Variation in leachate chemistry from mine waste and mill tailings samples is probably due to the relatively higher pyrite content compared to calcite in the mill tailings, a result of concentrating gold-bearing, pyrite-rich ore for milling. Highly anomalous mercury, used historically to amalgamate gold at the abandoned mill, is found in tailings at the Lucky Girl mill, and native mercury and gold-mercury amalgam were panned from mill products. Slightly anomalous mercury is found in two stream sediments directly below the mill. However, all water samples from the Bremner area, including those collected below the mill tailings, have mercury concentrations two orders of magnitude below the maximum contaminant level of 2 parts per billion.

Baseline geochemical data were collected at Gold Hill when placer mining activities were idle. Water samples are calcium-bicarbonate-dominant, and probably reflect the common presence of calcite veinlets in the area, which is underlain by marine, volcanic, and intrusive rocks. Waters are near neutral (pH 7.3 to 8.5), with conductivities ranging from 52 to 416 microsiemens per centimeter and alkalinities from 16 to 150 parts per million; metal contents are below established maximum contaminant levels. Significantly, however, these data suggest that waters in the Big Eldorado basin have less acid-neutralizing capability than waters elsewhere in the Gold Hill area, a characteristic that should be considered if the Big Eldorado Creek area is disrupted. Surface waters in the Gold Hill area contain the highest mercury concentrations found in the study, but even these are two orders of magnitude below the maximum contaminant level of 2 parts per billion.

The natural conditions at Orange Hill and Bond Creek demonstrate that mines and mills are not the sole sources of acidic, metalliferous waters in the environment. Bedrock is predominantly bleached, iron-stained, clay-altered granodiorite. Chalcopyrite, molybdenite, and pyrite and its alteration products are common. Surface water samples are calcium- and particularly sulfate-dominant, and they have total dissolved solids generally above 2,000 parts per million, values for pH ranging from 3.5 to 8.4, and conductivities from 192 to 3,080 microsiemens per centimeter. In nearly every sample, maximum contaminant levels are exceeded for sulfate, aluminum, iron, and manganese, and total dissolved solids. In several samples maximum contaminant levels are exceeded for cadmium, copper, nickel, antimony, and zinc. Other elements that are found in relatively high concentrations in waters include cobalt, molybdenum, strontium and the rare-earth elements. Sediments and rocks contain anomalously high levels of most of the elements listed herein. The low pH values, high sulfate, and high metal contents in many surface waters at Orange Hill and Bond Creek are due to the abundance of pyrite and associated sulfate minerals in altered rocks, and the absence of acid-consuming minerals. Leachate chemistry from samples of disaggregated, clay-altered bedrock indicates that during wet periods, initial waters flowing over the widespread altered bedrock would be acidic and metalliferous.

Nabesna was repeatedly sampled during a range of climatic conditions including summer periods of dry weather, intermittent rain, and extended rain, and during spring breakup. Major ion composition varied considerably in water samples from the Nabesna area. Calcium is the major cation, due to the dissolution of abundant carbonates. Anion composition varies from sulfate-dominant proximal to mines and the mill, to bicarbonatedominant at distal sites. High sulfate reflects the dissolution of pyrite and, to a lesser degree, pyrrhotite. Total dissolved solids and alkalinities vary considerably over more than two orders of magnitude, pH varies from 2.2 to 8.6, and conductivities range from 58 to > 4,500 microsiemens per centimeter. Maximum contaminant levels are exceeded for aluminum, arsenic, cadmium, copper, fluoride, iron, manganese, lead, sulfate, zinc, and total dissolved solids for samples collected during the spring breakup and summer rain events. Manganese and sulfate exceed maximum contaminant levels in samples collected during all sampling periods. Other elements found in high concentrations include cobalt, molybdenum, and the rare-earth elements. Leachates from sulfate-rich mill tailings samples have pH values from 2.2 to 8, high conductivities in the thousands of microsiemens per centimeter, and high concentrations of the elements listed herein as well as several additional ones. Stream sediments and rocks are anomalous in most of these elements. The season and surface flow conditions are important controlling factors on the major- and trace-element compositions of surface waters at Nabesna.

Introduction

Environmental geochemical investigations were carried out between 1994 and 1997 at several areas in Wrangell–St. Elias National Park and Preserve (WRST), Alaska. Surface water, bedload sediment, rock, mine waste, and mill tailings were collected from several mineralized areas: (1) the historic Kennecott copper mill and nearby Bonanza, Erie, Glacier, and Jumbo mines; (2) the historic mill and gold mines in the Bremner district; (3) the historic and active gold placer mines at Gold Hill; (4) the large, extensively altered, unmined copper-molybdenum deposits at Orange Hill and Bond Creek; and (5) the historic Nabesna gold mine/mill and surrounding areas (fig. 1). The purpose of the study was to characterize the geochemistry of these mineralized areas, to identify potential environmental geochemical hazards, and to determine baseline levels for selected elements. In this report, we focus on the hydrogeochemical media, the principal avenue for movement of metals from rocks and sediments into the aquatic biota. Results of solid media sampling are discussed as they pertain to the water samples.

In this cooperative effort between the U.S. Geological Survey (USGS) and the National Park Service (NPS), we addressed specific WRST land-management concerns in the different areas studied. Although our methodology did not vary from area to area, the land-management questions varied considerably. Specifically, (1) at Kennecott, a site recently acquired by the NPS, are there geoenvironmental hazards related to the mines and mill? (2) At Bremner, is mercury, once used for gold extraction at the now-abandoned mill, present in water at levels posing a hazard to visitors? (3) At Gold Hill, what are baseline metal concentrations in surface water during periods of placer mining inactivity? This is important in any attempt to measure environmental effects from active placer operations at Gold Hill. (4) At the Orange Hill and nearby Bond Creek deposits, what are natural background metal concentrations in surface waters at these unmined areas where active claims are held? Finally, (5) at Nabesna, what is the extent of metal dispersion in surface waters downstream from the mill site and what are the metals involved? The Environmental Protection Agency (EPA) initiated a site investigation (SI) at Nabesna to evaluate the site's potential for inclusion on the National Priorities List. However, the SI process did not include an extensive or complete site characterization (Environmental Protection Agency, 1995a).

Deposits at Nabesna, Kennecott, Gold Hill, Orange Hill, and Bond Creek are found within the allochthonous Wrangellia terrane (Jones and others, 1977), one of the accretionary terranes that constitute the geology of southern Alaska. Wrangellia originated at low paleolatitudes in the proto-Pacific region and probably was sutured to southern Alaska in the Late Cretaceous (Plafker and Berg, 1994). The Bremner district and surrounding Chugach Mountains lie within the Chugach terrane, part of a large subduction-related accretionary complex. Accretion of the Chugach terrane to southern Alaska began in the latest Triassic, but occurred mainly in latest Cretaceous to earliest Tertiary time. Subsequently, the Chugach terrane was intruded by numerous Tertiary granitoid plutons (Plafker and others, 1994). Rocks of the Tertiary to Quaternary Wrangell Lava volcanic field and unconsolidated glacial and fluvial deposits locally cap the accretionary rocks.

The Kennecott mill and its associated copper deposits (fig. 2A) are located in the central part of the McCarthy $1^{\circ} \times 3^{\circ}$ quadrangle. The Kennecott mill complex lies at the base of Bonanza Peak (2,128 m), along the margin of the Kennicott Glacier, at about 610 m in elevation, whereas the mines that supplied the mill are located more than 1,500 m higher on the steep slopes of Bonanza Peak (fig. 1). Present access to the Kennecott mill and associated mines is via foot or hired van from McCarthy. The Bremner mines and mill (fig. 2*B*) are located in the southwestern



Figure 1. Locations of areas studied in Wrangell–St. Elias National Park and Preserve, Alaska.

part of the McCarthy $1^{\circ} \times 3^{\circ}$ quadrangle. Elevation varies from about 1,070 m in the valley of Golconda Creek, to more than 1,830 m in the surrounding mountains. The area is accessible only by bush plane to a remote airstrip at Bremner. Gold Hill (fig. 2C) is located in the Chisana mining district in the southeastern part of the Nabesna $1^{\circ} \times 3^{\circ}$ quadrangle, about 9.6 km northeast of the remote community of Chisana. Elevation in this relatively hilly area varies from about 1,220 m near the base of Gold Hill, to 1,811 m at the summit of Gold Hill. The area is accessible by foot from Chisana, or by bush plane to a remote airstrip at Gold Hill. The Orange Hill deposit (fig. 2D) is located in the south-central part of the Nabesna $1^{\circ} \times 3^{\circ}$ quadrangle, about 21 km southeast of the Nabesna mine, near the terminus of the Nabesna Glacier. The Bond Creek deposit (fig. 2E) is about 6.4 km east of Orange Hill. Topography is subdued near the valley bottom at the base of Orange Hill (about 900 m in elevation)

but climbs steeply into rugged mountains rising to more than 2,440 m immediately east of Orange Hill and throughout the Bond Creek area. Both areas are accessible only by bush plane to a remote airstrip at Orange Hill. The Nabesna gold mine and mill (fig. 2*F*) are located in the south-central part of the Nabesna $1^{\circ} \times 3^{\circ}$ quadrangle, along the north edge of WRST. Topography varies from relatively subdued near the confluence of Cabin and Jack Creeks (about 854 m in elevation), 6.4 km below the Nabesna mill, to the steep slopes and cliffs of White Mountain (about 1,860 m) immediately to the west of the mill. The Nabesna and nearby Rambler mines are located on the eastern flank of White Mountain. The area is accessible to four-wheel drive vehicles over an unmaintained State right-of-way at the end of the Nabesna road.

Not surprisingly, variation in water and sediment chemistry is widespread across the different areas, and is dependent



Figure 2. Present-day setting of areas studied in Wrangell–St. Elias National Park and Preserve, Alaska. *A*, Kennecott mill; closest building is ammonia leaching plant, glacial debris in immediate background, Mt. Blackburn in far background. Mines were located along contact of dark rocks (Nikolai Greenstone) and overlying light rocks (Chitistone Limestone), as seen above mill. *B*, Bremner district, collapsed mill at Lucky Girl mine. *C*, Gold Hill, breached placer dam and flume, Coarse Money Creek. *D*, Orange Hill area, hydrothermally altered bedrock along Nikonda Creek; Harq Creek is leftmost creek, horizontal distance across photo is approximately 1 km. *E*, Bond Creek area, unnamed glacier-fed stream flowing through altered bedrock into Bond Creek in distance, stream pH 5.4, conductivity 1,550 µS/cm; note geologist D. Rosenkrans for scale. *F*, Nabesna mill with pyrite-rich mill tailings in foreground. Mines were located on White Mountain above the mill.

predominantly on the deposit type and local geology. Thus, for each area studied, the geologic setting, results, and interpretations are described separately, following an overview of methodology.

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Methods

This description of sample collection, preparation, and analysis is distilled from Eppinger and others (1999). Samples were collected at Kennecott in August of 1994 (dry period; no precipitation), at Bremner and Orange Hill in August of 1996 (dry period, no precipitation), and at Gold Hill and Bond Creek in August of 1997 (mostly dry, intermittent rain). The Nabesna site was repeatedly sampled during these same periods and also in April-May 1997 (spring breakup, an annual period of very wet conditions during which extensive melting of snow and ice occurs), and in September 1997 (following an extended 3-week rainy period).

The principal sample medium was surface water, but rock, mine waste, mill tailings, bedload stream-sediment, heavymineral concentrate, and precipitate samples were also collected (table 1). Elements determined, methods used, and details on sample collection and preparation are given in table 2. Sample localities are shown in figures 3, 4, 5, 6, and 7 for the Kennecott, Bremner, Gold Hill, Orange Hill/Bond Creek, and Nabesna areas, respectively. Although not discussed in this report, we also collected willow samples from 32 sites around and below the Nabesna mill tailings (Eppinger and others, 1999).

Water samples were collected from available natural water sources, principally from flowing streams, but also from seeps, springs, and ponds. Water samples collected include (1) an unacidified, filtered raw water sample for anion analysis, (2) an acidified, unfiltered sample for trace and major cation analysis of both dissolved and suspended species, (3) an acidified, filtered sample for trace and major cation analysis of dissolved species, (4) an acidified, filtered sample for ferrous iron content, and (5) a preserved, filtered sample for mercury content. The unacidified samples were kept cool prior to analysis. Samples were filtered and acidified to pH < 2 with ultra-pure acid to prevent precipitation of metals and bacterial growth (table 2). Other water data collected and recorded on-site include temperature, pH, conductivity (a measure of electrical conductance; the more ions a solution contains, the higher its conductivity), dissolved oxygen content, an estimate of the water flow rate, total acidity (a measure of water's base-consuming capacity; only for 1997 samples with pH < 7), and total alkalinity (a measure of water's acid-consuming capacity; for all samples with pH > 4.5). These data are given in Eppinger and others (1999).

Bedload stream sediments were collected below mines and mills and from nearby unmined areas, at water-sample sites where sufficient sediment was present. A few pond and spring sediments were also collected. Mineralized and unmineralized rock samples were collected generally as composite chip samples from outcrop, alluvium, mine waste, and mill tailings. A few precipitate samples were collected at Nabesna and Orange Hill, as flocs precipitating out of metalliferous waters onto the underlying substrates. The precipitates were analyzed chemically and mineralogically by X-ray diffraction. Because elements related to mineral deposits are commonly found in heavy minerals, pan concentrates were collected to provide chemical and mineralogical information. Most pan concentrate samples were collected from the same active alluvium as sediment samples. Some samples were also collected from mill tailings and mine waste.

Several mine waste, mill tailings, and mineralized bedrock samples were collected for leaching, using a synthetic meteoric water leach test. A modification of the EPA Synthetic Precipitation Leaching Procedure 1312 (Environmental Protection Agency, 1994) was used. This method is used to determine mobility of inorganic analytes present in samples of soils, wastes, and waste waters. For dry samples from mine waste and mill tailings, leachate composition can be used to mimic initial meteoric waters flowing off tailings, prior to dilution by adjacent surface flow and streams. Prior to leaching, splits of the solid samples were made for mineralogical analysis by X-ray diffraction.

Table 1.	Sample media	a collected at	t study areas ir	n Wrangell–St. Elia:	s National Park and F	Preserve, Alaska.

No. of samples	Total	Nabesna	Kennecott	Gold Hill	Orange Hill	Bond Creek	Bremner
Water	101	51	11	15	7	8	9
Site dupes	10	4	2	1	1	1	1
Anal. dupes	1	1					
Sediment	70	22	11	15	6	8	8
Site dupes	9	3	2	1	1	1	1
Anal. dupes	1						1
Leach	18	12			2	1	3
Anal. dupes	3	1			1		1
Rock	56	24	10	7	3	7	5
Anal. dupes	2	1				1	
Concentrate	51	11	7	14	5	5	9
Anal. dupes	1				1		
Precipitate	7	2			5		

[Site dupes, quality control sample site duplicates; anal. dupes, quality control analytical duplicates split from sample in laboratory]

Table 2. Elements determined, analytical methods, and collection/preparation procedures used.

[MW, water by inductively coupled plasma-mass spectrometry; EW, water by inductively coupled plasma-atomic emission spectrometry; ET, solid by total-extraction inductively coupled plasma-atomic emission spectrometry; EP, solid by partial-extraction inductively coupled plasma-atomic emission spectrometry; HY, hydride generation atomic absorption; GF, graphite-furnace atomic absorption; CV, cold-vapor atomic absorption; AF, atomic fluorescence; AA, atomic absorption; IE, specific-ion-electrode atomic absorption; ES, semiquantita-tive emission spectrography; IC, ion chromatography; CO, colorimetry; Arbogast, 1996; Eppinger and others, 1999]

Sample media	Method	Elements determined
¹ Water, filtered/ acidified	MW	Ag, Al, As, Au, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ge, Hf, Ho, In, Ir, K, La, Li, Lu, Mg, Mn, Mo, Na, Nb, Nd, Ni, Os, P, Pb, Pd, Pr, Pt, Rb, Re, Rh, Ru, Sb, Sc, Se, SiO ₂ , Sm, Sn, Sr, Ta, Tb, Te, Th, Ti, Tl, Tm, U, V, W, Y, Yb,
	EW	Zn, Zr Al, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Si, Sr, Ti, V, Zn
	CO	Fe ²⁺
	CV	Hg
	AF	Hg
Water, filtered/not acidified	IC	Cl ⁻ , F ⁻ , NO ₃ ⁻ , SO ₄ ²⁻
^{1,5} Leachates, filtered/ acidified	MW EW	Same as above, but omitting Ir, Lu, Os, Pd, Pt, and Rh Same as above, but also including Ag, As, Sb, and Sn
² Sediments,	ET	Ag, Al, As, Au, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cu, Eu, Fe, Ga, Ho, K, La, Li, Mg, Mn, Mo, Na, Nb, Nd, Ni, P, Pb, Sc, Sn, Sr, Ta, Th, Ti, U, V, Y, Yb, Zn
TOCKS	EP	Ag, As, Au, Bi, Cd, Cu, Mo, Pb, Sb, Zn
	HY	As, Sb, Se
	GF	Au
	CV	Hg
	AA	Tl
	IE	W
³ Precipitates	ET	Ag, Al, As, Au, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cu, Eu, Fe, Ga, Ho, K, La, Li, Mg, Mn, Mo, Na, Nb, Nd, Ni, P, Pb, Sc, Sn, Sr, Ta, Th, Ti, U, V, Y, Yb, Zn
	EP	Ag, As, Au, Bi, Cd, Cu, Mo, Pb, Sb, Zn
⁴ Concentrates	ES	Ag, As, Au, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, Ge, La, Mg, Mn, Mo, Na, Nb, Ni, P, Pb, Pd, Pt, Sb, Sc, Sn, Sr, Th, Ti, V, W, Y, Zn, Zr

¹ Water samples and leachates were filtered at 0.45 μ m, collected in acid-rinsed polypropylene bottles, and acidified with ultrapure nitric acid. Water samples for Hg analysis were filtered as above, collected in acid-rinsed glass bottles with Teflon lids; and preserved with potassium dichromate/nitric acid. Water samples for Fe²⁺ analysis were filtered as above, collected in opaque darkbrown polypropylene bottles, and acidified with ultra-pure hydrochloric acid.

² Stream sediments were composited 1-kg samples from active alluvium. In the laboratory, samples were air dried, sieved to minus-80 mesh (0.177 mm), and pulverized for chemical analysis. Clean quartz sand was pulverized between samples to reduce risk of contamination. Composited rock chip samples were coarsely crushed to pea-sized pieces, split with a Jones splitter, and pulverized as described for sediments.

³ Precipitates were composited from wet areas on alluvium or mill tailings and placed in sealed plastic bags. In the laboratory the precipitates were dried, hand ground with a mortar and pestle, and split for chemical and mineralogical analysis by X-ray diffraction. Clean quartz sand was hand ground between samples.

⁴ Pan concentrate samples (about 7 kg) were collected as grab samples in areas where heavy minerals tend to accumulate, and panned until 1 to 3 percent of the original sample remained. In the laboratory, the samples were sieved to minus-20 mesh (0.84 mm), gravity separated using bromoform (specific gravity about 2.85), and then separated into magnetic, weakly magnetic, and non-magnetic fractions. The nonmagnetic fraction, which commonly contains ore-related minerals such as sulfides, gold, and other native metals, was hand ground as described for precipitates.

⁵ Composite 1-kg samples for leaching were collected from the upper 2.5 cm of the surface layer. In the laboratory, samples were dried and sieved to minus-0.375 mesh (9.5 mm). Deionized water used for leaching was acidified with sulfuric acid/nitric acid (60/40 weight percent mixture) to a pH of 4.20. Using a ratio of 20:1 water to sample, 1 liter of water was added to 50 g of sample and the mixture was rotated at 30 ± 2 rpm for 18 ± 2 hours (Environmental Protection Agency, 1994). Following rotation, pH, conductivity, temperature, oxygen content, and alkalinity were determined on the leachates. The leachates were then filtered at 0.45 μ m, collected into polypropylene bottles, and acidified with ultra-pure nitric acid.

A large number of chemical elements were determined using a variety of quantitative and semiquantitative analytical techniques (table 2). Descriptions and quality assurance/quality control (QA/QC) protocol for most of the analytical methods are found in Arbogast (1996). Throughout the study, QA/QC concerns were addressed through the use of internal reference standards, field blanks, sample site duplicates, and analytical duplicates. QA/QC samples constituted 19 percent of the total number of samples analyzed. Reference standards were interspersed with batches of samples, and the analyses of the standards were checked to assure that reported values were within ± 20 percent of the accepted values. Chemical and mineralogical data are found in Eppinger and others (1999).

In subsequent sections of this report, water classifications, based on relative amounts of major cations and anions, follow those of Piper (1944), Hem (1985), and Drever (1997, fig. 2 of Appendix 1). For water samples where carbonate (CO_3^{2-}) and bicarbonate (HCO3⁻) are present, bicarbonate is overwhelmingly dominant. Thus, the term "bicarbonate" is used exclusively when discussing these species. Carbonate and bicarbonate concentrations were determined from measured pH and total alkalinity, following equations of Deutsch (1997, p. 13-14). These equations assume that carbonate alkalinity \cong total alkalinity, a reasonable assumption for most natural waters (Hem, 1985, p. 106; Drever, 1997, p. 46). In discussing water chemistry, emphasis is given to the following significant inorganic parameters listed by the Alaska Department of Environmental Conservation (AKDEC) drinking water standards (Alaska Department of Environmental Conservation, 1994) and by the U.S. Environmental Protection Agency (Environmental Protection Agency, 1995b): pH, Ag, Al, As, Ba, Be, Cd, Cl⁻, Cr, Cu, F⁻, Fe, Hg, Mn, Na, Ni, NO_3^- , Pb, Se, SO_4^{2-} , Tl, and Zn. Thallium was not found in concentrations exceeding 0.4 ppb (parts per billion) in any of the surface water samples collected and will not be discussed further. The AKDEC primary maximum contaminant level (MCL) for Tl is 2 ppb (Alaska Department of Environmental Conservation, 1994). Primary MCL values are regulatory waterquality action levels established by the AKDEC, whereas secondary MCL values are nonregulated recommended water-quality goals. In general, differences in metal concentration between filtered/acidified and unfiltered/acidified water samples are minimal, indicating that most metals are present as dissolved species; therefore the unfiltered/acidified samples will not be discussed further.

The subjective term "anomalous" and its synonyms are used as relative terms with respect to average crustal abundance values of Fortescue (1992), to background data for various sample media provided by Rose and others (1979), and to examination of data distributions for samples collected in this study.

Kennecott

Geology, Deposit Setting, and Mining History

Stratabound copper deposits in the Kennecott area are found in the lower part of the Upper Triassic Chitistone Limestone, near the disconformable contact with the underlying Middle to Upper Triassic Nikolai Greenstone (fig. 3). Basalt flows of the Nikolai Greenstone are mainly tholeiitic, have a high background copper content of around 150 ppm (parts per million), and are more than 2,740 m thick in the Kennecott region (MacKevett and others, 1997). The Chitistone Limestone grades upward into the Upper Triassic Nizina Limestone. The carbonate rocks represent a deepening-upward succession; the lower part of the Chitistone accumulated in an intertidal-supratidal, locally sabkha setting, whereas the Nizina was deposited in a moderately deep water marine environment (MacKevett and others, 1997). In the McCarthy quadrangle, the maximum thickness of the Chitistone Limestone is about 600 m and the maximum thickness of the Nizina Limestone is about 500 m (MacKevett, 1978).

The Kennecott deposits were mined for their spectacularly high grade copper ore, which locally exceeded 70 percent copper. MacKevett and others (1997) suggested that the Kennecott deposits formed through the following sequence: (1) copperenriched Nikolai Greenstone was extruded during the Middle or Late Triassic; (2) carbonate sediments (Chitistone Limestone) were deposited in a Late Triassic marine embayment on the Nikolai Greenstone; (3) sabkha-facies deposits, rich in sulfates and organic matter, formed locally in the embayment and restricted circulation, leading to evaporation that resulted in brine development; (4) karst features developed in exposed parts of the lower Chitistone Limestone following marine regression; (5) the Chitistone was buried by as much as 3,050 m of marine limestone, black shale, and other sedimentary rocks of the Nizina Limestone and the McCarthy, Nizina Mountain, and Root Glacier Formations; (6) the section was folded, faulted, and uplifted during the Late Jurassic to Early Cretaceous; (7) uplift and folding provided hydrologic head that caused brine circulation and leaching of copper from the Nikolai Greenstone; and (8) large orebodies formed in fissures and breccias in the lower Chitistone Limestone when migrating copper-rich brines mixed with reduced fluids derived from gypsum-organic matter mixtures in the sabkha horizons. The copper ore was mainly chalcocite and djurleite, with lesser chalcopyrite, bornite, covellite, digenite, anilite, luzonite, idaite, malachite, azurite, chalcanthite, and orpiment (Bateman and McLaughlin, 1920; MacKevett and others, 1997). More than 536,000 t (metric tons) of copper and around 100 t of silver were produced from 1911 to 1938, the major period of mining activity (MacKevett and others, 1997). Average grade of the ore was about 13 percent copper from 4.02 million t of ore.

Early Russian explorers reported implements of copper used by Copper River native peoples at the mouth of the Copper River (Douglass, 1964). Prospecting in the region in the late 1890's probably was stimulated by the Klondike gold rush. The first Kennecott-type deposit was found by prospectors in 1900, who located extensive copper-stained outcrops crowning the Bonanza deposit, high above the Kennicott Glacier (Douglass, 1964; Hunt, 1996). The other principal deposits were located within the next few years. The first ore was shipped in 1911, but the peak of mining activity was from 1915 to 1929. Copper sulfide ore was gravity-concentrated and shipped directly to Washington State for processing. Copper was stripped from carbonate ore (malachite and azurite) at the mill using a Kennecott-developed ammonia leach process, and then it was shipped for further refining. The mines ceased



Figure 3 (above and facing page). Generalized geology and site locations for samples collected in Kennecott mine area, Alaska. Geology generalized from MacKevett (1970, 1972, 1974) and MacKevett and Smith (1972). Base from U.S. Geological Survey 1:63,360 McCarthy B-5 (1970), B-6 (1959), and C-6 (1959). Contour interval 500 ft.

EXPLANATION

- Ou Surficial deposits (Quaternary)—Undivided alluvial, colluvial, and glacial deposits
- Tif Dacite and dacite porphyry (Tertiary)—Dikes and sills
- Ks Schulze Formation (Upper Cretaceous)—Siliceous shale with uncommon sandstone and siltstone
- Kc Chititu Formation (Cretaceous)—Dominantly mudstone and shale with lesser siltstone and limestone. Includes metamorphosed Chititu Formation (Kch) of MacKevett (1974) and MacKevett and Smith (1972)
- JTm McCarthy Formation (Lower Jurassic? and Upper Triassic)— Impure limestone, chert, shale, and minor siltstone. Includes both upper member (JTmu) and lower member (JTml) of MacKevett (1970, 1972, 1974) and MacKevett and Smith (1972)
- knz Nizina Limestone (Upper Triassic)—Limestone with layered and nodular chert
- Fc
 Chitistone Limestone (Upper Triassic)—Limestone, dolomite, and minor nodular chert. Contains local solution pits and caverns
- Fin
 Nikolai Greenstone (Upper to Middle Triassic)—Subaerial amygdaloidal basalt flows
- Contact, approximately located
- --- Fault contact, approximately located—Dotted where concealed
- ✓ Adit
- 🛠 Mine

production in 1938 because of low reserves, low copper prices, and labor problems (MacKevett and others, 1997). Presently, the mill area remains intact (fig. 2*A*), and carbonate-rich mine-waste rock remains below caved adits high above the mill on Bonanza Ridge.

Results of Study

Thirteen surface water samples were collected from below the Bonanza mine, from a rainwater pool below the Kennecott mill, from a small spring flowing from Kennecott mill tailings, from National Creek above and below the mill, and from several additional creeks distal to the mines and mill (fig. 3). At the time of sampling, no water was observed flowing from mine adits. Samples collected both proximal and distal to mines and the mill have similar chemistries. All 13 waters collected in the Kennecott area are classified as calcium-bicarbonate type waters (fig. 8*A*). With respect to other major cations and anions, there are only slight concentrations of sulfate, very low chloride, and low concentrations of magnesium, sodium, and potassium. All waters are near neutral, with pH values ranging from 7.7 to 8.2, and conductivities ranging from 105 to 188 μ S/cm (microsiemens per centimeter), except for a spring sample flowing from the base of the Kennecott mill tailings, with a value of $436 \,\mu\text{S}/$ cm (fig. 8*B*). Alkalinities range from 45 to 80 ppm (as calcium carbonate), except for the same spring sample with a value of 230 ppm. This spring sample also has the highest copper concentration from the area (67 ppb copper), well below the AKDEC secondary MCL of 1,000 ppb (fig. 8*C*). None of the AKDEC significant inorganic parameters having primary or secondary MCL values are found to exceed established limits (fig. 8*B*,*C*).

A perusal of sediment, rock, and concentrate data reveals anomalous concentrations for several elements (see Appendix) (Eppinger and others, 1997, 1999). Many of the stream sediments collected at water sample sites contain anomalous concentrations of arsenic, copper, and mercury and weakly anomalous concentrations of Ag, Au, Cd, Pb, Sb, and Zn. Rock samples exhibit an anomalous metal suite similar to that found in sediments. Alluvial heavy-mineral concentrates are variably anomalous in Ag, As, Bi, Cd, Cu, Pb, Sn, and V.

Interpretation

Surface water samples from the Kennecott area have low metal concentrations that are generally comparable to worldwide average surface water concentrations (Eppinger and others, 1997, table 4). Only slight differences in cation and anion content are found between samples proximal and distal to the mines and mill. The low metal concentrations are due primarily to two geologic controls, the widespread host carbonate rocks and the absence of unstable sulfide minerals. Chitistone Limestone hosts the deposits and is widespread throughout the area. The limestone greatly increases the buffering capacity of surface waters and results in near neutral pH values, reducing metal mobility. Kennecott-type deposits lack unstable sulfide minerals, such as pyrite, whose weathering commonly results in formation of acidic waters. Further, minerals containing elements such as zinc or uranium, which could be mobilized in neutral or higher pH waters, are uncommon in Kennecott-type deposits. The dominant sulfide minerals in the Kennecott deposits are chalcocite and djurleite, both copper sulfides that are relatively stable in the surficial environment. Although sediment, rock, and concentrate data indicate that high concentrations of potentially toxic elements such as arsenic, cadmium, copper, and mercury are found in mill and mine-waste piles, these metals are not mobilized because of the absence of acid-generating minerals in Kennecott-type deposits and the waste piles and mill tailings derived from them.

The geologic controls just described are also responsible for the calcium and bicarbonate composition of the waters. Both ions are likely derived from the abundant carbonate bedrock in the area. The absence of acid-generating minerals precludes consumption of the bicarbonate ion. The sparse sulfate in the waters is surprising, as gypsum from sabkha horizons is an integral part of the genesis of the deposits (MacKevett and others, 1997). Perhaps the gypsum was completely consumed during formation of chalcocite and djurleite. Alternatively, perhaps the gypsum-rich rocks are peripheral to the deposits themselves, beyond areas sampled in this study.



EXPLANATION

- Qu Surficial deposits (Quaternary)—Undivided alluvial, colluvial, and glacial deposits
- Ti Intrusive rocks (Tertiary)—Granodiorite and tonalite with subordinate hypabyssal rocks
- Kv Valdez Group (Cretaceous)—Flysch deposits, commonly metamorphosed to greenschist facies
- Contact, approximately located
- Glacier or ice
- Rock glacier
- Lake
- ✓ Adit
- ☆ Mine or prospect



The spring sample below the Kennecott mill that contains relatively elevated copper and alkalinity concentrations also contains the highest total dissolved solids (TDS, a calculated estimate of all dissolved constituents) (fig. 8*A*) and elevated nitrate (11 ppm as NO₃⁻). Although still below the AKDEC primary MCL of 44 ppm for nitrate, the nitrate concentration from the spring is the second highest concentration found in all water samples collected throughout this WRST study. The spring flows from the base of mill tailings on Nikolai Greenstone and is located below the abandoned ammonia leaching plant at the Kennecott mill (fig. 2*A*). X-ray diffraction of a pervasive red stain that coats the basalt in wet areas reveals an amorphous, likely organic, compound. White crusts rimming the water's edge are calcite, likely accounting for the higher conductivity and TDS at the site. It is unclear whether the nitrate in the water is related to the breakdown of ammonia (NH₃) used in the leaching process or to nearby pit toilets used by private land-owners higher up on the tailings piles.

Anomalous concentrations of mercury are found in rock samples (as much as 520 ppm mercury in chalcocite ore) and in sediments (as much as 3 ppm mercury) at Kennecott (Eppinger and others, 1997, 1999). The only form of mercury identified is cinnabar, a mercury-sulfide mineral that is very stable in the surficial environment. The most important aspect when evaluating the effect of mercury to surrounding aquatic systems is not total mercury concentrations, but conversion to bioavailable, organic mercury compounds, such as methylmercury, which is water soluble and highly toxic to all organisms (Gray and others, 1996). Although at Kennecott we have not analyzed mercury in water or studied mercury speciation, the likelihood of significant mercury present in the water column or of conversion to methylmercury is low, because the form of mercury (cinnabar) is highly stable, and the surface water is oxidized and has relatively high pH values (pH 7.7–8.2) (J.E. Gray, written commun., 1999).

A specific WRST management concern at Kennecott is whether geoenvironmental hazards related to the mines and mill exist. Geochemical data collected in this study suggest that Kennecott-type deposits are relatively benign to the environment, owing to the large amount of carbonate rocks present, the resulting high buffering capacity of waters, the absence of acidgenerating minerals, and the scarcity of metals that could be mobilized at higher pH values.

Bremner

Geology, Deposit Setting, and Mining History

The most recent geologic maps of the Bremner area are the 1:250,000-scale reconnaissance maps of the McCarthy quadrangle by MacKevett (1978) and the Bering Glacier quadrangle by George Plafker (unpub. mapping, 1998), the sources of the following summary. Outcrops in the mountainous region around the Bremner gold deposits are predominantly of the Cretaceous Valdez Group, and intervening valleys are filled with unconsolidated Quaternary alluvial, colluvial, and glacial deposits (fig. 4). The flysch deposits of the Valdez Group are at least several thousand meters thick; are composed of interlayered metagraywacke and argillite, and minor schist, slate, and phyllite; and are turbidite deposits that formed as extensive deep-sea fans. Rocks of the Valdez Group in the Bremner area have been variably metamorphosed to chlorite- or biotite-grade greenschist facies and have northwest-striking foliation and lineaments. Hypabyssal, hornblende-rich, early to middle Tertiary granodiorite and tonalite plutons, and dacite dikes and sills cut the Valdez Group in the study area. Large Tertiary intrusions cutting rocks of the Valdez Group are found about 13 km northeast and 8 km south of the Bremner deposits. During our study of the Bremner deposits, individual as well as swarms of granodiorite and dacite dikes were observed, all generally less than 2 m thick. We also noted pervasive thin quartz veins and veinlets cutting the Valdez Group metasediments.

Although gold can be panned from most streams in the area, paying placers were limited to (in order of increasing importance) parts of the Bremner River, the Little Bremner River, and Golconda Creek (Moffit, 1914). The Golconda Creek basin is where most placer and nearly all lode mining took place. Alluvial gravels along Golconda Creek were generally less than 3 m thick and were interpreted by Moffit as reworked bench gravels. The fluvial reworking of the bench gravels reconcentrated the gold accumulated within the bench deposits, making the deposits profitable (Moffit, 1914). Little lode prospecting had been done along Golconda Creek prior to Moffit's (1914) study, although he noted the presence of numerous dikes and locally mineralized calcite-bearing quartz veins. Moffit (1914) believed the placer gold to be derived from the quartz veins; subsequent discovery of gold-bearing quartz veins in the basin supports his theory. At the Lucky Girl mine (mislabeled as the Yellowband mine on the USGS McCarthy A-7 quadrangle), we found adits at three levels following a northwest-trending, near-vertical, pyrite-rich, banded white quartz vein cutting slate. Brecciated portions of the vein are as thick as 2 m, vuggy, and iron oxide rich. Ore at the adjacent mill site consists of white quartz cobbles with sericite, chlorite, iron oxide as clots and pseudomorphs after pyrite, calcite; and lesser galena, arsenopyrite, sphalerite, and free gold. At the Yellowband mine, located about 4 km south of the Lucky Girl mine, we found a gold-bearing, pyritic, iron-stained quartz vein containing sparse sericite and chlorite and following a granodiorite dike swarm. Biotite in the granodiorite dikes has been altered to chlorite. Vein quartz from the Sheriff mine, located about 3.2 km southeast of the Lucky Girl mine, contains iron-oxide clots, pyrite, chlorite, sericite, free gold, calcite, and probably arsenopyrite. Although production records from the Bremner district are scant, MacKevett (1976) listed placer gold production at between 2,000 and 3,000 oz (56,700 and 85,000 g) and lode gold production at about 750 oz (21,300 g).

The gold placers along the Little Bremner River were discovered in 1901 by two parties of prospectors, and placer claims were staked on Golconda Creek in that year (Moffit, 1914). Initial placer mining was by pick and hammer, but by 1911, hydraulic giants were in use, with associated ditch lines and flumes (Moffit, 1914). By the early 1930's, both lode mine development and placer prospecting were underway at Bremner, aided by construction of an airstrip in 1931 (Stewart, 1933). Placer activity was apparently considerably reduced from that reported by Moffit (1914), consisting of prospecting at the mouth of Standard Creek and on Golconda Creek along a 4-km stretch both above and below Standard Creek (Stewart, 1933). Lodes at the Lucky Girl, Yellowband, and Sheriff were apparently being exploited, and a small mill utilizing mercury amalgamation was constructed at the Lucky Girl mine. Mining activities at Bremner ceased during World War II and never resumed (Hunt, 1996). Presently, the mill and mine buildings have collapsed (fig. 2B), but several cabins remain standing. Mill tailings and mine waste piles are evident at the mill and lode mines. Extensive hand-stacked boulder piles and an abandoned backhoe remain along Golconda Creek as evidence of the previous placer operations.

Results of Study

Ten surface waters were collected from nine sites, including mine drainage flowing from the Lucky Girl mine, a stream below the Lucky Girl mill, a stream below the Yellowband mine,



Figure 5 (above and facing page). Generalized geology and site locations for samples collected in Gold Hill mine area, Alaska. Geology generalized from Richter and Jones (1973). Base from U.S. Geological Survey 1:63,360 Nabesna A-2 (1960). Contour interval 500 ft.

a stream flowing from the base of a rock glacier north of the Yellowband mine, and several streams more distal to the mines and mill (fig. 4). All the waters are classified as calcium- and sulfate-type waters (fig. 9A). Calcium is overwhelmingly the dominant major cation and sulfate is the major anion, followed by bicarbonate. Chloride, magnesium, sodium, and potassium are negligible components. Values for pH range from 6.3 to 7.9 (fig. 9B), with the lowest value from water below the Lucky Girl mill (site 6BR006, fig. 4). The pH values for mine drainage flowing from both the Lucky Girl mine (site 6BR001) and from the stream below the Yellowband mine (site 6BR010) are both 7.9. Conductivities range from 86 to 160 μ S/cm, except for the Lucky Girl mine drainage sample, which has a value of 220 μ S/ cm. Alkalinities (as calcium carbonate) range from < 10 ppm (from a site on Golconda Creek upstream of mining activity) to 26 ppm (from the Lucky Girl mine adit). With respect to the significant inorganic parameters for drinking water-pH, Ag, Al, As, Ba, Be, Cd, Cl⁻, Cr, Cu, F⁻, Fe, Hg, Mn, Na, Ni, NO₃⁻, Pb, Se, SO₄²⁻, Tl, and Zn—only pH and manganese exceed established AKDEC MCL values (fig. 9B, C). Water flowing from below the Lucky Girl mill, at pH 6.3, is slightly below the pH 6.5 secondary MCL. Water flowing from the base of the rock glacier north of the Yellowband mine (fig. 4, site 6BR011) is slightly high in manganese, with a value of 53 ppb (sample site

duplicate was 61 ppb Mn). The secondary MCL for manganese is 50 ppb. All other water samples contain < 10 ppb manganese.

Stream sediments collected at water sample sites contain anomalous arsenic and copper, and slightly anomalous silver, gold, bismuth, selenium, and zinc (see Appendix) (Eppinger and others, 1999). Rock samples contain anomalous concentrations of these same elements, plus cadmium, molybdenum, and lead. Alluvial heavy-mineral concentrates are variably anomalous in Ag, As, Au, Cu, Pb, and W. Leachates from mine waste (two sites) contain high aluminum and relatively elevated tungsten, whereas a leachate from mill tailings contains high concentrations of arsenic, iron, and manganese, and relatively elevated gold, lead, and zinc. The mill tailings leachate pH is 4.2, and the waste leachates are pH 8.3 and 8.7. Conductivities of the leachates are all 100 μ S/cm or less. Alkalinities on the leachates with pH exceeding 4.5 are 35 and 50 ppm (as calcium carbonate).

Interpretation

For waters at Bremner, alkalinities are all relatively low, sulfate is the predominant anion over bicarbonate, pH is near neutral, and dissolved metal contents are low. These features

EXPLANATION

- Qu Surficial deposits (Quaternary)—Undivided alluvial, colluvial, and glacial deposits
- Qa Alluvium (Quaternary)—Fan, cone, and flood plain deposits; includes Qal and Qaf of Richter and Jones (1973)
- Qc Colluvial deposits (Quaternary)—Undifferentiated colluvium and landslide deposits; includes Qcu and Qcl of Richter and Jones (1973)
- Org Rock glacier deposits (Quaternary)—Includes active and recently active rock glaciers
- Qw Glacial drift (Quaternary)—Undifferentiated glacial and fluvioglacial deposit of Wisconsin age
- Qog Glacial drift (Quaternary)—Undifferentiated older glacial deposits
- Qs Solifluction deposits (Quaternary)—Chiefly bedrock rubble but may include older glacial drift deposits
- QTg **Boulder and gravel deposits (Quaternary to Tertiary)**—Weakly consolidated and poorly sorted fluvioglacial(?) deposits locally interbedded with volcanic ash. On Gold Hill gravels contain disseminated native gold (Moffit, 1954) and may be in part source of Bonanza gold placers
- QTw Wrangell Lava (Pleistocene, Pliocene, Miocene)—Chiefly and esitic to basaltic flows and associated volcanic rocks
- TKp Andesite porphyry (Tertiary to Cretaceous)—Massive porphyry with conspicuous phenocrysts of altered plagioclase
- TKd Porphyritic diorite (Tertiary to Cretaceous)—Intrusive masses of augite-hornblende diorite
- TKdm **Pyroxene diorite-monzonite (Tertiary to Cretaceous)**—Gradational from pyroxene diorite west of Red Hill Creek to potassic pyroxene diorite, pyroxene monzonite, and hornblende monzonite east of Red Hill Creek. Pyroxene largely altered to actinolite and chlorite
- Tku Undifferentiated intrusive rocks (Tertiary to Cretaceous)—Dikes and sills of andesitic and basaltic composition and irregular bodies of feldspar porphyry
- Ks Continental sedimentary rocks (Cretaceous)—Conglomerate, coarse-grained sandstone, siltstone, and mudstone
- Kc **Chisana Formation (Cretaceous)**—Marine and subaerial volcanic andesite flows, volcaniclastic lahars and avalanche deposits, volcanic sandstone and siltstone, and lenses of marine sedimentary rock; unconformably overlain by Ks
- KJa Argillite and mudstone (Cretaceous to Jurassic)—Interbedded with graywacke, locally calcareous sandstone, pebble conglomerate, pebble mudstone, pelecypod coquina, and silty limestone
- Jg Graywacke-argillite (Jurassic)—Rhythmically interbedded argillite-siltstone-graywacke; metamorphosed to hornfels near larger intrusive bodies
- Contact, approximately located
- Dike
- --- Fault contact, approximately located—Dotted where concealed
- Thrust fault, approximately located—Dotted where concealed; sawteeth on upper plate
- Lake or pond
- ✓ Adit
- ☆ Prospect
- Cabin

are explained by the geologic setting of the deposits—pyriteand calcite-bearing quartz veins (generally) following granitic dikes that cut predominant, carbonate-poor slates. The predominant ions in the waters, calcium, sulfate, and lesser bicarbonate, are the result of weathering of the pyrite (producing acid and sulfate) and by vein calcite dissolution (producing calcium and bicarbonate). The acid is consumed by the bicarbonate, keeping pH values near neutral and metal mobility to a minimum. However, alkalinities are naturally low in waters both distal and proximal to mining and milling activities. The low alkalinities and minor bicarbonate suggest that most of the available carbonate is being consumed by the neutralization process. Disturbing mine waste or mill tailings, whether by human-induced or natural means, would probably disrupt this naturally established equilibrium and might necessitate further active treatment.

Minor sphalerite, observed in ore at the Lucky Girl mine, is probably the source of the slightly elevated zinc in the waters. The highest concentration found in Bremner waters is 10 ppb zinc, which, curiously, is from the sample containing relatively high manganese described previously. This sample (6BR011)



EXPLANATION

- Qu Surficial deposits (Quaternary)—Undivided alluvial, colluvial, and glacial deposits
- QTw Wrangell Lava (Pleistocene, Pliocene, Miocene)—Chiefly andesitic to basaltic flows and associated volcanic rocks
- Tp Hornblende-plagioclase porphyry (Tertiary)—Dikes, sills, and small bodies of andesite to latite composition
- Kg Nabesna batholith (Cretaceous)—Undifferentiated plutonic rocks; chiefly biotite-hornblende granodiorite
- FI Limestone (Triassic)—Micritic, nonfossiliferous limestone; locally converted to magnetite-calc-silicate tactite near plutons
- kn Nikolai Greenstone (Middle to Late Triassic)—Subaerial amygdaloidal basalt flows; near plutons metamorphosed to massive amphibolite
- kPa
 Argillite (Triassic to Permian)—Chiefly argillite with calcareous siltstone, chert, and carbonaceous, limy shale
- FPg Gabbro (Triassic to Permian)—Dikes, sills, and irregular bodies of augite gabbro
- PI **Limestone (Permian)**—Fossiliferous limestone; locally converted to calc-silicate tactite near plutons
- PPv Volcanic rocks (Permian and Pennsylvanian)— Undifferentiated andesitic flows, tuffs, and volcaniclastic rocks; locally contains siderite, barite, pyrite, and quartz-pyritechalcopyrite veins
 - Altered rocks (age uncertain)—Limonite stained and hydrothermally altered rocks
 - Contact, approximately located
 - Fault contact, approximately located—Dashed where inferred, dotted where concealed
-) Glacier or ice
- 🛠 Prospect
- Cabin

contains the highest cobalt (6 ppb), copper (18 ppb), and nickel (12 ppb) found in waters at Bremner, including those draining the mines and mill. Although these metal concentrations are all well below the AKDEC MCL values, their combined presence in the sample is noteworthy. Stream sediment from the site contains the highest arsenic, copper, and zinc (see Appendix) found in Bremner area sediments, including those draining the mines and mill. The rock glacier from which the water and sediment are derived is distal from known deposits, but the metals in the water and sediment suggest that the rock glacier or the basin above may contain mineralized rocks. These metal concentrations are apparently natural and unrelated to historic mining activity.

The low element content in leachates from mine waste is a result of the associated high pH values. Curiously, pH values of the waste leachates are higher than those found in surface waters in the area. This feature is probably due to the presence of calcite in the mineralized veins and associated dumps, but the general absence of carbonate elsewhere in bedrock. Leachate data suggest that the mine waste would not be expected to generate acidic, metalliferous waters during wet periods. However, the acidic, metal-bearing mill tailings leachate suggests that initial waters flowing from the finely ground tailings pile during rain events or spring breakup would likely be acidic and metalliferous. The overall minor volume of mill tailings present at the Lucky Girl mill, and rapid dilution by adjacent streams, would reduce the downstream impact in this event. Metals in leachates, found in excess of the AKDEC primary and secondary MCL's, include aluminum, arsenic, iron, manganese, and zinc (see Appendix). We reemphasize here that the metals in leachates mimic initial waters flowing off tailings, prior to dilution by adjacent surface flow and streams. However, surface flow from the mill tailings probably contributes to overall metal loading of the stream and associated sediment. The differences in behavior of leachates from mill tailings compared to those from mine waste are probably due to the relatively higher pyrite content compared to calcite in the mill tailings, a result of the selective concentration of gold-bearing, pyrite-rich ore for milling.

WRST resource staff were concerned whether mercury, used historically to amalgamate gold at the abandoned Bremner mill, was present in waters at levels posing a hazard to visitors. Mine waste and ore samples from the Bremner area do not contain mercury exceeding the 0.02 ppm analytical detection limit. However, 170 ppm mercury is found in tailings at the Lucky Girl mill, and native mercury and gold-mercury amalgam were panned from mill product samples. Anomalous mercury in stream sediments is found at two sites (both 1 ppm mercury) directly below the mill, but not elsewhere in the Bremner area. These data support, and historical records confirm, the presence of anthropogenic mercury in tailings and sediment at the Lucky Girl mill. However, all 10 water samples from the Bremner area, including water flowing from the Lucky Girl mine adit and water from below the mill, contain less than 0.025 ppb mercury—well below the AKDEC MCL of 2 ppb. This suggests that mercury was not being mobilized in surface water during the dry summer sampling period in 1996. Whether mercury is mobilized during wet periods or spring breakup is unknown. Leachate samples were not analyzed for mercury.

Gold Hill

Geology, Deposit Setting, and Mining History

The following description of the geology of the Gold Hill area is extracted from Richter and Jones (1973). Bedrock in the Gold Hill area is predominantly marine and subaerial volcanic and volcaniclastic rocks of the Lower Cretaceous Chisana Formation (fig. 5). The 3,000-m-thick Chisana Formation consists of andesitic volcanic flows; volcanic conglomerate; tuffs; fragmental volcanic units (probably lahars and avalanche deposits); volcanic sandstone and siltstone; and, in the lower part of the section, thin lenses of marine argillite, graywacke, pebble conglomerate, and tuffaceous mudstone. Jurassic to Cretaceous argillite and mudstone deposits are found locally. North of Gold Hill are extensive deposits of rhythmically interbedded Jurassic



Figure 7 (above and facing page). Generalized geology and site locations for samples collected in Nabesna mine area, Alaska. *A*, Geology generalized from Richter (1971) and Lowe and others (1982). *B*, Detailed site locations for samples collected at Nabesna mill. Base from U.S. Geological Survey 1:63,360 Nabesna B-4 (1970) and B-5 (1960). Contour interval 500 ft.

deposits of graywacke, siltstone, and argillite. Small bodies and dikes of Tertiary to Cretaceous andesite porphyry and porphyritic diorite are scattered throughout the placered area. A large intrusion of pyroxene-diorite monzonite is exposed just west of Gold Hill. Quaternary to Tertiary unconsolidated gravels and isolated patches of Wrangell Lava are present locally. Most of the bedrock underlying Gold Hill is concealed by Quaternary glacial gravel and sand deposits, fluvioglacial(?) deposits, solifluction deposits, and alluvial deposits.

The gold-bearing placer gravels are Quaternary to Tertiary, and lie near or on volcanic and sedimentary rocks of the Chisana Formation (Richter and Matson, 1972). All placer





- Qu Surficial deposits (Quaternary)—Undivided alluvial, colluvial, and glacial deposits
- QTw Wrangell Lava (Pleistocene, Pliocene, Miocene)—Chiefly and esitic to basaltic flows and associated volcanic rocks
- TKd Diorite (Tertiary to Cretaceous)—Small diorite bodies
- Kg Granodiorite to quartz diorite (Cretaceous)—Stocks and dikes
- Kc Chisana Formation (Cretaceous)—Basaltic to andesitic flows, breccias, and interbedded volcaniclastic rocks
- Ks Continental sedimentary rocks (Cretaceous)—Arkosic sandstone, siltstone, and shale
- KJs Nutzotin Mountain Sequence (Lower Cretaceous and Upper Jurassic)—Calcareous argillite, siltstone, and graywacke
- **Limestone (Upper Triassic)**—Includes thin-bedded (**k**tl) and massive (**k**ml) limestone units of Lowe and others (1982)
- Fin
 Nikolai Greenstone (Middle to Late Triassic)—Subaerial amygdaloidal basalt flows. Includes units Fin of Lowe and others (1982) and FPb of Richter (1971)
- Pm Mankomen Group (Lower Permian)—Argillite and subordinate interbedded calcareous siltstone and grit
- PPt Tetelna Volcanics (Permian and Pennsylvanian)-Interbedded andesitic flows, lahars, tuffs, and volcaniclastic rocks
- Contact, approximately located
- ---- Fault contact, approximately located—Dotted where concealed
- 🛠 Mine

mines in the district are found in an area 8 km in diameter, centered on Gold Hill; they include Little Eldorado Creek (some of the richest ground), Bonanza Creek and its tributaries, Coarse Money Creek (fig. 2C), Gold Run Creek, and Big Eldorado Creek (Capps, 1915; Moffit, 1943). Other heavy minerals found in the placer deposits include native copper, native silver, galena, cinnabar, and molybdenite (Nokleberg and others, 1987). Total gold production from the placers is about 1.4 million g (Nokleberg and others, 1987). Scattered about Gold Hill are pyritic, iron-oxide-stained outcrops of andesite(?) and a few prospects that explore gold- and silver-bearing base metal lodes. Several areas of iron-oxide-stained, sulfate-bearing, altered bedrock are found near the junction of Bonanza and Chathenda Creeks (Richter and others, 1975). One of the lodes visited in this study, on N.P. Nelson Hill, is a galena-sphalerite-chalcopyritecalcite-quartz vein breccia containing malachite and limonite. The vuggy vein cuts feldspar-andesite porphyry. Other small gold-bearing veins of similar character are described briefly by Capps (1915), Stewart (1931), Moffit (1943), and Richter and

others (1975). No production has been reported from the lode deposits. Capps (1915) believed that the gold-bearing lodes were the source of the placer gold deposits. The placer deposits produced about 50,000 oz (1.4 million g) of gold (Nokleberg and others, 1987).

Placer gold was discovered at Gold Hill in May 1913, resulting in initial claims on Bonanza Creek, where 200 oz of gold was recovered in 2 days (Bleakley, 1996). A gold rush ensued. Several thousand stampeders were in the Chisana district by October 1913, when Chisana City was founded, and all available sites had been claimed by July 1914. However, the boom was short lived, the district was in decline by 1915, and by 1920 only eight mines remained, employing fewer than 20 men (Bleakley, 1996; Hunt, 1996). Small-scale placer mining has been fairly continuous in the district since then and continues into the present on unpatented claims located prior to formation of the national park and preserve in 1980. Currently, a few scattered cabins are occupied sporadically during summer months, when small-scale sluicing and suction-dredge activities take place (fig. 2*C*).



Figure 8 (above and facing page). Geochemical data from 13 water samples, Kennecott area. *A*, Piper diagram showing major ion composition (Piper, 1944). Square, sample collected below mines or mill; triangle, sample collected distal to mines and mill; radius of open circles represents relative total dissolved solids in parts per million; values for ions are given as percent milli-equivalents per liter. *B*, *C*, Box and whisker diagrams showing summary statistics for selected ions and field parameters. *B*, Major cations, anions, pH, conductivity, dissolved oxygen, and alkalinity; *C*, Trace cations. Abbreviations used: Cond, conductivity; D_02, dissolved oxygen; Alk, alkalinity; TDS, total dissolved solids; μ S/cm, microsiemens per centimeter; MCL, maximum contaminant level; REE, sum of rare-earth elements. R indicates that qualified values were replaced with one-half of the qualified value prior to calculating statistics. See text (p. 7) for explanation of primary and secondary MCL values.

Results of Study

The Gold Hill area was visited during a relatively dry summer period in 1997. No activity was underway at any of the 27 placer claims, none of which had been worked since the previous summer. This provided the opportunity to collect baseline geochemical data during a period of relative quiescence. Sixteen surface water samples were collected at 15 sites upstream and downstream of active placer claims and also from sites distal to placer activities (fig. 5).

Intermediate volcanic, volcaniclastic, and marine sedimentary rocks crop out in the Gold Hill area. Calcite veinlets are common in all areas, except for Big Eldorado Creek and upper Gold Run Creek, and iron-rich sedimentary carbonate rocks were observed locally. Near the confluence of Little Eldorado and Bonanza Creeks, outcrops of propylitically altered andesite and lithic tuff are found, both containing chlorite, disseminated pyrite, and calcite veinlets. In most areas sampled, pyrite, gold, and epidote are common in alluvial heavy-mineral concentrates, and cinnabar is found locally. The only lode deposit observed was a prospect consisting of calcite-quartz vein breccia, with galena, sphalerite, chalcopyrite, siderite, and cerussite. A rock sample from the prospect contains highly anomalous Ag, Au, Cd, Cu, Hg, Pb, Sb, and Zn; and slightly anomalous Mn and Mo (site 7GH007, Eppinger and others, 1999).

The surface waters at Gold Hill are calcium-bicarbonatedominant, with minor contributions of sulfate, magnesium, sodium, and potassium (fig. 10*A*). Values for pH range from 7.3 to 8.5. The lowest pH values are found along Big Eldorado Creek, in both the active placer area and upstream of areas of placer activity. Conductivities range from 52 to 416 μ S/cm, and average 250 μ S/cm; the highest values are from sites along Bonanza Creek and the lowest values from sites along Big Eldorado Creek. Alkalinities range from 16 to 150 ppm (as calcium carbonate), with the lowest values from sites along Big Eldorado Creek (fig. 10*B*). None of the significant inorganic parameters for drinking water—pH, Ag, Al, As, Ba, Be, Cd, Cl⁻, Cr, Cu, F⁻,



Fe, Hg, Mn, Na, Ni, NO_3^- , Pb, Se, SO_4^{2-} , Tl, and Zn—are found exceeding the AKDEC MCL values (fig. 10*B*, *C*). Waters at three sites along Bonanza Creek have pH values of 8.5, matching the AKDEC secondary MCL upper limit for pH.

A review of sediment, rock, and concentrate data in Eppinger and others (1999) reveals elevated concentrations for several elements (see Appendix). Stream sediment and rock samples collected at water sample sites contain anomalous gold and slight to moderately anomalous concentrations of As, Bi, Hg, Sb, Se, Sn, and Zn. In addition, rock samples contain anomalous concentrations of Ag, Cd, Co, Cu, Mo, Pb, and V. Alluvial heavy-mineral concentrates are variably anomalous in Ag, As, Au, B, Ba, Bi, Cd, Cu, Pb, and Zn.

Interpretation

The predominant calcium-bicarbonate composition of surface waters is likely related to the common presence of calcite in bedrock and alluvium in the Gold Hill area. Chemical breakdown of disseminated and vein pyrite probably accounts for the minor concentrations of sulfate in waters. The predominance of



Figure 9 (above and facing page). Geochemical data from 10 water samples, Bremner area. *A*, Piper diagram showing major ion composition (Piper, 1944). Square, sample collected below mines or mill; triangle, sample collected distal to mines and mill; radius of open circles represents relative total dissolved solids in parts per million; values for ions are given as percent milli-equivalents per liter. *B*, *C*, Box and whisker diagrams showing summary statistics for selected ions and field parameters. *B*, Major cations, anions, pH, conductivity, dissolved oxygen, and alkalinity; *C*, Trace cations. Abbreviations used: Cond, conductivity; D_02, dissolved oxygen; Alk, alkalinity; TDS, total dissolved solids; μ S/cm, microsiemens per centimeter; MCL, maximum contaminant level; REE, sum of rare-earth elements. R indicates that qualified values were replaced with one-half of the qualified value prior to calculating statistics. See text (p. 7) for explanation of primary and secondary MCL values.

calcite over pyrite results in pH values above neutral. Minor magnesium, sodium, and potassium components in the surface waters may be related to locally altered intermediate igneous rocks in the area.

Surface waters from Big Eldorado Creek have the lowest pH and alkalinity values in waters from the Gold Hill area. Along Big Eldorado Creek, green diorite is predominant in outcrop and alluvium; carbonate was not observed. Although presently concealed by recent alluvial deposits, relatively recent lode exploration and placer operations along Big Eldorado Creek exposed a pyrite-rich vein underlying the active channel between the sampled water sites 7GH013 and 7GH015 (fig. 5). Present physical evidence of the pyrite-rich vein consists of a pile of disaggregated quartz-, kaolinite-, and pyrite-rich rubble adjacent to the creek bottom at site 7GH014. Geochemical analysis of the vein material reveals 0.48 ppm gold, 14 ppm bismuth, and 7 ppm antimony, but no other anomalous metal concentrations. A small amount of ore was found at a cabin at site 7GH013, but the source of the ore is undetermined. The ore contains pyrite, chalcopyrite, galena, and idaite (Cu₃FeS₄), and

is highly anomalous in Ag, As, Au, Bi, Co, Cu, Pb, Sb, and Zn (Eppinger and others, 1999). Weathering of pyrite-rich cobbles from veins underlying the Big Eldorado drainage basin could be the reason for stream waters there having slightly lower pH (7.3) and alkalinity (16 ppm as calcium carbonate), compared to elsewhere in the area (mean alkalinity, 91 ppm; median, 100 ppm; all Gold Hill water samples). Flow of chemically dissimilar ground water through pyritic or altered bedrock, and subsequent mixing with surface waters could also result in the slightly lower pH and alkalinity. The low alkalinity and absence of visible carbonate minerals suggest that water in the Big Eldorado basin has less acid-neutralizing capability than water elsewhere in the Gold Hill area. This characteristic, along with the known presence of pyritic rocks in the drainage, suggests that water quality should be monitored if the naturally reestablished equilibrium along Big Eldorado Creek is disrupted, either by human-induced or natural means.

Relatively low pH (7.3) and alkalinity (16 ppm as calcium carbonate) from site 7GH015, collected above placered areas along Big Eldorado Creek, suggest that mineralized (pyritic?)



veins like that at site 7GH014 may be present higher in the drainage. Stream sediment and concentrate data support this hypothesis. Site 7GH015 contains the highest gold (2.1 ppm) found in sediments from the Gold Hill area, as well as anomalous tin and zinc. Anomalous silver, gold, bismuth, and cadmium are also found in an alluvial heavy-mineral concentrate from the site. The Big Eldorado drainage lies within the eastern part of an area with potential for porphyry copper±molybdenum deposits (Richter and others, 1975), and the sulfide-bearing veins and chemically distinct ground water may be manifestations of the larger mineralizing system.

Cinnabar was observed in alluvial heavy-mineral concentrates from sites along upper Bonanza Creek above the confluence with Little Eldorado Creek. Highly anomalous mercury and antimony (both 120 ppm) are found in a rock sample from a prospect in the same area. Several rock and sediment samples collected elsewhere in the Gold Hill area contain elevated concentrations of mercury and antimony (Eppinger and others, 1999). Surface waters in the Gold Hill area contain the highest mercury concentrations found in the WRST study. Two of these comparatively high values, 0.054 ppb and 0.036 ppb mercury, are from sites along Bonanza Creek. Relatively high mercury



Figure 10 (above and facing page). Geochemical data from 16 water samples, Gold Hill area. *A*, Piper diagram showing major ion composition (Piper, 1944). Square, sample collected below mines or mill; triangle, sample collected distal to mines and mill; radius of open circles represents relative total dissolved solids in parts per million; values for ions are given as percent milli-equivalents per liter. *B*, *C*, Box and whisker diagrams showing summary statistics for selected ions and field parameters. *B*, Major cations, anions, pH, conductivity, dissolved oxygen, and alkalinity; *C*, Trace cations. Abbreviations used: Cond, conductivity; D_02, dissolved oxygen; Alk, alkalinity; TDS, total dissolved solids; μ S/cm, microsiemens per centimeter; MCL, maximum contaminant level; REE, sum of rare-earth elements. R indicates that qualified values were replaced with one-half of the qualified value prior to calculating statistics. See text (p. 7) for explanation of primary and secondary MCL values.

values are also found in waters from upper Gold Run (0.035 ppb) and upper Big Eldorado (0.033 ppb) Creeks. Water from the latter site also contains a comparatively high (relative to all WRST samples) concentration of antimony (0.2 ppb). We stress that although unusual in the context of all waters sampled from WRST, these mercury concentrations in water are two orders of magnitude below the AKDEC primary MCL of 2 ppb for mercury. Nevertheless, the presence of (1) cinnabar in concentrates, (2) anomalous mercury in rocks, and (3) high antimony in rocks, sediments, and waters is interesting and probably indicates a high-level epithermal setting for lode deposits in the area. However, the presence of mercury alone in sediments and water may result from dual origins: natural mercury related to the epithermal deposits, or anthropogenic mercury related to gold recovery during historic placer operations. (Modern-day suction dredge operators report that they periodically recover native mercury that has accumulated in stream beds).

At Gold Hill, a WRST resource management question was, "What are baseline metal concentrations in surface waters

during periods of placer inactivity?" Data on baseline conditions during quiescent periods are necessary to measure environmental changes resulting from active placer operations. Our data show that during the dry summer 1997 sampling period, none of the significant inorganic parameters for drinking water listed by the AKDEC were found in concentrations exceeding established primary or secondary MCL's. However, some of the parameters measured were found at levels equal to (pH) or just below (aluminum and TDS) the secondary MCL's for these parameters (fig. 10B). Trace elements were all found in concentrations at least one order of magnitude below established MCL values (fig. 10C). Whether these parameters exceed established limits during high-flow periods such as rain events and spring breakup, or during periods of placer mining activity, is unknown. The combined minimum, maximum, median, 25th, and 75th percentile values listed in figure 10B and 10C provide ranges of values expected for baseline conditions for surface waters during quiescent, latesummer, dry conditions.



Orange Hill and Bond Creek

Geology, Deposit Setting, and Mining History

Rocks in the vicinity of the unmined Orange Hill and Bond Creek porphyry copper-molybdenum deposits are composed predominantly of a variety of intrusive rocks of the Cretaceous Nabesna batholith, a quartz-diorite to granodiorite pluton dated at 105 Ma (Newberry and others, 1997). Less extensive are Pennsylvanian to Permian volcanic and volcaniclastic rocks, and lesser Triassic Nikolai Greenstone (fig. 6). Volumetrically minor thin bodies of Permian limestone are present locally (Richter, 1973). In both areas, quartz diorite and granodiorite of the Nabesna pluton are intruded by slightly younger hornblende-plagioclase porphyry (Nokleberg and others, 1994; Richter, 1973). Limonite staining and hydrothermally altered rocks are extensive (fig. 2*D*, *E*). Suites of alteration minerals include biotite-quartz, quartzsericite, and late-stage chlorite-sericite-epidote (Richter, 1973; Nokleberg and others, 1987; Nokleberg and others, 1994). Hydrothermally altered rock occupies an area of 1×3 km at Orange Hill and 2×3 km at Bond Creek (Richter and others, 1975).

Mineralization products consist of pyrite, chalcopyrite, and minor molybdenite in potassic and sericitic quartz veins and as disseminations, commonly found along altered granite porphyry dikes (Richter and others, 1975; Nokleberg and others, 1994). Magnetite and anhydrite are locally abundant. Associated with the porphyry deposits at Orange Hill are minor gold-poor skarns, found near limestone contacts. The skarn deposits consist of red, brown, and green garnet; vesuvianite; pyroxene; epidote; diopside; wollastonite; hematite; magnetite; and the sulfides pyrite, chalcopyrite, bornite, covellite, massive pyrrhotite, sphalerite, and minor molybdenite (Van Alstine and Black, 1946; Linn, 1973; Nokleberg and others, 1994; Newberry and others, 1997). The Orange Hill deposit contains 100-320 million t grading 0.30–0.35 percent copper and 0.02–0.03 percent molybdenum. The Bond Creek deposit contains an estimated 500 million t grading 0.15-0.40 percent copper and 0.02 percent molybdenum (Young and others, 1997).

Neither Orange Hill nor Bond Creek has been mined, although both have been explored in the past and patented mining claims are still held at Orange Hill. Early reports of ground staking at Orange Hill were for gold, although only negligible quantities were found (Moffit and Knopf, 1910; Moffit, 1943). By the early 1930's, several copper lode claims were held at Orange Hill and several hundred meters of drill core had been obtained (Stewart, 1931; Van Alstine and Black, 1946). Sporadic exploration in the 1960's and 1970's included mapping and drilling at Orange Hill (Linn, 1973) and Bond Creek (Gillespie, 1970). Exploration activity ceased around 1980, when the areas were included in the newly established national park and preserve. In 1996, only a few prospects, scattered drill core, and a cabin remained at Orange Hill. Evidence of exploration activity at Bond Creek in 1997 consisted of three small wooden drilling platforms and associated debris.

Results of Study

Stream and spring water samples collected include eight samples from seven sites at Orange Hill and nine samples from eight sites at Bond Creek (fig. 6). Most samples were collected from drainages underlain by hydrothermally altered rocks. Bedrock is predominantly bleached, iron-stained, clay-altered granodiorite. Quartz stockwork containing chalcopyrite and lesser molybdenite is common. Pyrite and iron-oxide pseudomorphs after pyrite were observed both in the stockwork and disseminated in the granodiorite, and pyrite is abundant in alluvial heavy-mineral concentrates. Other minerals identified in outcrop and alluvium include azurite, chlorite, epidote, gypsum, jarosite, potassium feldspar, malachite, montmorillonite, sepiolite, sericite, and silica. Ferricrete deposits cementing alluvium (as thick as several meters) were observed locally along drainage bottoms. At Bond Creek, magnetite, derived from alteration of mafic minerals (hornblende?), was observed. Calcite was noted only in unaltered areas.

Waters in the area are calcium- and particularly sulfate-dominant (fig. 11*A*). Bicarbonate is a minor component in four water samples, all from the Orange Hill area. Three of the waters containing bicarbonate were collected outside the areas of hydrothermal alteration. The fourth sample containing bicarbonate was collected along California Creek from a site where malachite and azurite were observed in alluvium. Magnesium is a minor component in the waters and is highest in samples from highly altered areas. Total dissolved solids exceed 2,000 ppm in most of the water samples. Values for pH range from 3.5 to 8.4 (pH mean, 6.1; median, 5.4) (fig. 11*B*). Conductivities range from 192 to 3,080 μ S/cm (conductivity mean, 1,361 μ S/cm; median, 1,292 μ S/cm). In general, pH values are lower and conductivities are higher in samples from Bond Creek than in those at Orange Hill. Alkalinities range from < 10 to 125 ppm (as calcium carbonate). Only four samples have alkalinities exceeding 50 ppm, and all were from the Orange Hill area. Acidities, calculated only on seven Bond Creek samples with pH values below 7, range from 40 to 540 ppm (as calcium carbonate).

For the major ions, the AKDEC MCL is exceeded in several samples for fluoride and iron. In nearly every sample collected, secondary MCL's are exceeded for sulfate, aluminum, manganese, and TDS (fig. 11*B*). Water from eight sites has pH values below 5.5, well below the AKDEC lower secondary MCL of pH 6.5. Trace cations are also found in relatively high concentrations (fig. 11*C*). In several samples, primary MCL's are exceeded for cadmium, nickel, and antimony; and secondary MCL's are exceeded for zinc. Nearly half the samples collected exceed the secondary MCL of 1,000 ppb for copper. Other elements not having established MCL values, but found in relatively high concentrations relative to worldwide averages (Hem, 1985; Martin and Whitfield, 1983), include cobalt, molybdenum, strontium, and the rare-earth elements (REE).

A perusal of sediment, rock, concentrate, and leachate data in Eppinger and others (1999) reveals anomalous concentrations for numerous elements (see Appendix). Many of the stream sediments collected at water sample sites contain very high concentrations of copper, molybdenum, and zinc, and moderately high concentrations of Ag, As, Au, Ba, Cd, Fe, Hg, Mn, Pb, Sb, Se, and V. Rock samples exhibit an anomalous metal suite similar to that found in sediments. Alluvial heavy-mineral concentrates are variably anomalous in Ag, Ba, Co, Cu, Fe, Mo, Pb, Sr, W, and Zn. Leachates from three sites in disaggregated, clayaltered bedrock contain high concentrations of Al, Co, Cu, Fe, Mn, REE, $SO_4^{2^-}$, and Zn. The leachate pH ranges from 3.2 to 3.6, and conductivities range from 1,260 to 2,340 µS/cm.

Interpretation

The low pH values and high sulfate in many surface waters at Orange Hill and Bond Creek are due to the abundance of pyrite and associated sulfate minerals present in altered rocks, and the sparse carbonate minerals. Outside the areas of alteration, carbonate minerals are more common, and waters have higher pH values and alkalinity concentrations. This situation is well illustrated at Orange Hill along Harq Creek (fig. 6). The lower 1 km reach of the creek is underlain entirely by pyritic, sulfate-rich, clay-altered bedrock. Along this lower reach, pH ranges from 3.6 (site 6OH006) to 4.6 (6OH003) and alkalinities are nil. Estimated flow at its mouth is 1,860 L/min (500 gal/ min). Immediately above the area of alteration, the pH is 7.7 (site 6OH007) and alkalinity is 42 ppm (as calcium carbonate). Carbonate sedimentary rocks are present in the basin above site 6OH007. Calcium is the dominant cation in the surface waters. In unaltered areas, where alkalinities and pH values are higher, the source of calcium is likely carbonate minerals. However, carbonate is scarce in areas of altered bedrock. In these areas, the source of the calcium may be gypsum and clay-altered plagioclase feldspar. Altered feldspar could also be the source of elevated REE in the surface waters. The higher magnesium found in acidic waters from highly altered areas could be due to alteration of mafic minerals (hornblende?). The high TDS and high conductivity in many of the water samples are due to the abundant major- and trace-ion content found in the samples (fig. 11*B*, *C*). High acidities, ranging from 180 to 540 ppm (as calcium carbonate), found in four water samples at Bond Creek indicate that the base-consuming potential of these waters is high.

Leachates derived from disaggregated, clay-altered bedrock have low pH values, high conductivities, and high content of several anions and cations—commonly found in concentrations exceeding AKDEC MCL's. This indicates that during rainstorms and spring breakup, initial waters flowing over the widespread altered bedrock would likely be acidic and metalliferous.

The specific WRST land-management question regarding Orange Hill and Bond Creek was, "What are the natural background metal concentrations in surface waters?" During the August 1996 and 1997 sampling periods, many of the significant inorganic parameters for drinking water listed by the AKDEC were found in concentrations well above established primary and secondary MCL's (fig. 11*B*, *C*). Leach data suggest that many of these parameters would also exceed established limits during wet periods such as rain events and spring breakup. The wide ranges of values listed in figure 11*B* and 11*C* illustrate the varied natural background composition of surface waters at Orange Hill and Bond Creek.

Porphyry copper-molybdenum deposits are typically the result of extensive hydrothermal mineralizing systems that can affect many square kilometers of land. Orange Hill and Bond Creek are no exception, having haloes of hydrothermally altered rocks that cover approximately 3 km² and 6 km², respectively (Richter and others, 1975). The subarctic climate, high relief, and presence of permanent and transient snowfields in the heads of minor valleys and glaciers in the upper parts of major valleys provide a continuous source of water that passes through and over the altered bedrock (fig. 2E). During rain events and spring breakup, the amount of surface flow (and probably associated ground-water flow) is greatly increased. These features, coupled with the fact that pyrite and its alteration products are widespread in the altered rocks whereas carbonate or other neutralizing minerals are volumetrically insignificant, result in the common presence of acidic, metalliferous surface waters in these otherwise pristine areas. Orange Hill and Bond Creek are excellent examples that demonstrate that mines and mills are not the sole sources of acidic, metalliferous waters in the environment. The present erosional level of the mineralized rocks at Orange Hill and Bond Creek indicates that the natural background conditions have probably been acidic and metalliferous for several tens of thousands of years.

Our data show that water quality is significantly degraded in altered areas at Orange Hill and Bond Creek. However, for the parameters we measured, water quality is generally good outside the areas of alteration. Because of the physiographic setting, downstream effects from the naturally acidic, metalliferous waters are minimal. The waters at Orange Hill flow into the high-volume, glacier-fed Nikonda Creek immediately above its juncture with the huge glacier-fed Nabesna River—the major river in the region. Similarly, degraded waters flow into Bond Creek, another high-volume, glacier-fed creek, immediately above its juncture with the Nabesna River. Turbidity is high in Nikonda Creek, Bond Creek, and the Nabesna River, due to the abundance of suspended glacial flour; and high alkalinities would be expected. Through mixing, neutralization of the acid and precipitation of the metals onto colloidal iron- and aluminum-oxides would be expected, followed by rapid dilution by the high-volume rivers. In fact, these processes were all observed at the junction of Harq Creek with Nikonda Creek, along a distance of about 50 m.

The water quality concerns discussed here relate primarily to drinking water standards of the AKDEC and EPA. However, the naturally occurring metalliferous, low pH waters found at Orange Hill and Bond Creek are not necessarily detrimental. These waters and the surrounding soils and bedrock create unique ecosystems that certain biota can thrive on. Low pH soils can, for example, provide habitat for rare plant life or serve as mineral licks for animals. At Orange Hill and Bond Creek, the acidic, metalliferous waters, soils, sediments, and rocks are critical components of a larger, naturally functioning ecosystem.

Nabesna

Geology, Deposit Setting, and Mining History

Rocks exposed near the Nabesna mine are predominantly Upper Triassic limestone; lesser underlying Nikolai Greenstone, a subaerial amygdaloidal basalt of Middle to Late Triassic age; and lesser overlying calcareous argillite and siltstone of the Upper Jurassic and Lower Cretaceous Nutzotin Mountain Sequence (Moffit, 1943; Wayland, 1943; Lowe and others, 1982; Newberry, 1986) (fig. 7). The limestone, referred to as Chitistone Limestone by Wayland (1943), consists of about 366 m of massive limestone, overlain by about 244 m of thin-bedded limestone (Wayland, 1943). It is intruded by Early Cretaceous stocks and dikes of granodiorite and quartz diorite (Wayland, 1943; Lowe and others, 1982; Newberry, 1986; Weglarz, 1991) that have potassium-argon hornblende and biotite ages respectively of 109 and 114 Ma (Nokleberg and others, 1994). The Triassic to Cretaceous rocks are overlain unconformably by andesitic and basaltic lavas of the Tertiary to Quaternary Wrangell Lava (Lowe and others, 1982).

The intrusion of granodiorite into the carbonate sequence recrystallized some limestone and formed gold-bearing, ironrich skarn bodies. These skarns were exploited at the Nabesna and Rambler mines. Principal ore minerals are pyrite, pyrrhotite, magnetite, and chalcopyrite, with minor galena, sphalerite, arsenopyrite, and stibnite. Gangue minerals include garnet, wollastonite, vesuvianite, epidote, actinolite, hornblende, chlorite, scapolite, apatite, serpentine, and quartz (Wayland, 1943; Newberry, 1986; Weglarz, 1991). The main gold ores were pyrite veins along crosscutting fractures in limestone and



Figure 11 (above and facing page). Geochemical data from 17 water samples, Orange Hill and Bond Creek areas. *A*, Piper diagram showing major ion composition (Piper, 1944). Square, sample collected from Orange Hill; triangle, sample collected from Bond Creek; radius of open circles represents relative total dissolved solids in parts per million; values for ions are given as percent milli-equivalents per liter. *B*, *C*, Box and whisker diagrams showing summary statistics for selected ions and field parameters. B, Major cations, anions, pH, conductivity, dissolved oxygen, and alkalinity; *C*, Trace cations. Abbreviations used: Cond, conductivity; D_O2, dissolved oxygen; Alk, alkalinity; TDS, total dissolved solids; μ S/cm, microsiemens per centimeter; MCL, maximum contaminant level; REE, sum of rare-earth elements. R indicates that qualified values were replaced with one-half of the qualified value prior to calculating statistics. See text (p. 7) for explanation of primary and secondary MCL values.

sulfide-silica-rich bodies (Nokleberg and others, 1994). Minor gold was produced from massive magnetite and pyrrhotite bodies (Wayland, 1943). Total gold production is listed in Theodore and others (1991) as 0.08 million t of ore at 25 g/t gold. Wayland (1943) also reported unquantified, but small production of silver and copper. As noted by Newberry and others (1997), classification of the deposits, based on production records, has been problematic. The Nabesna skarn deposit has been classified as an iron skarn with byproduct gold (Theodore and others, 1991, table 3; Nokleberg and others, 1994), and as a gold-rich copper skarn (Newberry and others, 1997). Similarly, the Rambler deposit has been classified as an iron skarn (Nokleberg and others, 1994) and as a gold skarn (Newberry and others, 1997).

Gold was first panned at the foot of White Mountain in 1899 (Wayland, 1943). The earliest claims were located in the Nabesna mine area between 1903 and 1905, and sporadic work continued into the 1920's. In 1929, the Nabesna Mining

Corporation was formed and mine development was accelerated (Hunt, 1996). By 1935, the operation was running year-round, and a stamp mill was processing 54 t of ore per day. In the 1930's both mercury amalgamation and cyanide treatment were attempted to recover gold (Holdsworth, 1937; Wayland, 1943). By 1940, the deposits at the Nabesna mine were exhausted. However, the discovery in 1941 of a nearby gold-bearing pyrrhotite skarn body (probably the Rambler orebody) prompted small-scale exploration and mining (Moffit, 1944). Sporadic exploration and drilling continued at Nabesna into the 1980's. Presently, the Nabesna mill and associated buildings are standing but in disrepair. A small amount of stockpiled ore remains near the old tram, and mine-waste rock remains near the mill and on slopes below caved adits high on White Mountain. A thin (less than 1 m thick) veneer of finely ground, pyriterich and iron-oxide-rich mill tailings is present over a severalthousand-square-meter area below the mill (fig. 2F).



Results of Study

Over three field seasons, 55 surface water samples were collected at Nabesna during a range of climatic conditions including summer periods of dry weather, intermittent rain, and extended rain; and during the snow and ice melt at spring breakup. Several sites were repeatedly sampled during these periods, including sites upstream of the mine and mill, at the base of the mill tailings, along a 2.5 km reach of Cabin Creek downstream of the mill tailings, and sites outside the influence of the mines and mill (fig. 7). Surface water samples were also collected on the mill tailings during wet periods.

Major ion composition of the waters varied considerably (fig. 12*A*). In all water samples collected, calcium is the major cation. Magnesium is also a major component, but only in samples from sites distal to the mines and mill. Major anion composition varies from sulfate- to bicarbonate-dominant. Chloride content is negligible. Total dissolved solids vary considerably from 63 to 7,100 ppm (TDS mean, 722 ppm; median, 361 ppm). Values for pH vary from 2.2 to 8.6 (pH mean, 6.7; median, 7.4) (fig. 12*B*). Conductivities range from 58 to more than 4,500 μ S/cm (conductivity mean, 743 μ S/cm; median, 492 μ S/cm). Lowest pH and highest conductivity values are found in waters collected directly on finely ground mill tailings during wet periods.



Figure 12 (above and facing page). Geochemical data from 55 water samples, Nabesna area. *A*, Piper diagram showing major ion composition (Piper, 1944). Square, sample collected below mines or mill; triangle, sample collected distal to mines and mill; radius of open circles represents relative total dissolved solids in parts per million; values for ions are given as percent milli-equivalents per liter. *B*, *C*, Box and whisker diagrams showing summary statistics for selected ions and field parameters. *B*, Major cations, anions, pH, conductivity, dissolved oxygen, and alkalinity; *C*, Trace cations. Abbreviations used: Cond, conductivity; D_02, dissolved oxygen; Alk, alkalinity; TDS, total dissolved solids; μ S/cm, microsiemens per centimeter; MCL, maximum contaminant level; REE, sum of rare-earth elements. R indicates that qualified values were replaced with one-half of the qualified value prior to calculating statistics. See text (p. 7) for explanation of primary and secondary MCL values.

Alkalinities, calculated on the 47 samples with pH above 4.5, range from < 50 to 350 ppm (mean, 116 ppm; median, 100 ppm, all as calcium carbonate). Acidities, determined on three 1997 samples with pH values below 7, range from 60 to 220 ppm (as calcium carbonate).

For the major ions, the AKDEC primary MCL is exceeded in two spring run-off samples for fluoride. Secondary MCL's are exceeded for sulfate, aluminum, iron, manganese, and TDS (fig. 12*B*). Trace ions vary widely. Primary MCL's are exceeded for arsenic, cadmium, and lead, and secondary MCL's are exceeded for copper and zinc (fig. 12*C*). Most samples exceeding AKDEC MCL's were collected during the spring breakup and extended summer rain sampling periods. Other elements not having established MCL values, but found in relatively high concentrations relative to worldwide averages (Hem, 1985; Martin and Whitfield, 1983), include cobalt and, to a lesser degree, molybdenum and the REE.

A review of sediment, rock, and concentrate data reveals anomalous concentrations for several elements (see Appendix) (Eppinger and others, 1997, 1999). Stream sediments collected near the mill and mines contain anomalous As, Au, Cu, Pb, and Zn, and slightly anomalous Bi, Cd, Co, Mo, Sb, and Se. Sediments collected distal to the mill and mines are variably anomalous in these same elements plus silver and iron. Weakly anomalous mercury is found in stream sediments below the Nabesna mill tailings. Rock samples from mill tailings, stockpiled ore, mine waste, mineralized outcrop, and mineralized alluvial cobbles contain variably anomalous concentrations of the preceding elements, plus manganese and tungsten. Anomalous mercury is found only in the mill tailings samples. Alluvial heavy-mineral concentrates near the mill and mines are variably anomalous in Ag, As, Au, Ba, Cu, Fe, and Pb. Concentrates distal to the mill and mines contain anomalous concentrations of Ag, As, Au, Cd, Co, Cu, Fe, Pb,





conductivities. Calcite was the dominant mineral identified by X-ray diffraction in the solid phases of these two samples prior to leaching. Numerous secondary minerals were also identified by X-ray diffraction in the solid phases of the tailings, waste, and outcrop samples prior to leaching: gypsum (CaSO₄2H₂O), rozenite (FeSO₄4H₂O), natrojarosite (NaFe₃(SO₄)₂(OH)₆), kalinite (KAl(SO₄)₂11H₂O), copiapite (Fe₁₄O₃(SO₄)₁₈63H₂O), magnesiocopiapite (MgFe₄(SO₄)₆(OH)₂20H₂O), butlerite (Fe(OH)SO₄2H₂O), rostite (Al(SO₄)(OH)5H₂O), starkeyite (MgSO₄4H₂O), aplowite (CoSO₄4H₂O), jarosite (KFe₃(SO₄)₂(OH)₆), hydronium jarosite ((K,H₃O)Fe₃(SO₄)₂(OH)₆), aluminocopiapite ((Mg,Al)(Fe,Al)₄(SO₄)₆(OH)₂20H₂O), fibroferrite (Fe(OH)SO₄5H₂O), ferrian sepiolite ((Mg,Fe)₄Si₆O₁₅(OH)₂6H₂O), cacoxenite (Fe₄(PO₄)₃(OH)₃12H₂O), and carbonate hydroxylapatite (Ca₁₀(PO₄)₅CO₃(OH)F) (Eppinger and others, 1997, table 8). The presence of soluble sulfate minerals in solid phases corresponded well with leachates having low pH values and relatively high metal content (Eppinger and others, 1997).

Interpretation

Major ions found in surface water samples are principally controlled by the geologic substrate. Upper Triassic limestones are predominant, followed by Triassic amygdaloidal Nikolai Basalt, and Jurassic to Cretaceous calcareous

argillite and siltstone. Cretaceous granitic bodies intrude these rocks. Tertiary to Quaternary andesitic and basaltic Wrangell Lava caps the older rocks. Carbonate minerals are abundant in the sedimentary rocks and locally fill amygdules in the basalt. Dissolution of carbonate accounts for the high calcium and bicarbonate in the waters (fig. 12A). Although less certain, the relatively higher magnesium present in some of the samples (all distal to the mines and mill) is probably due to the greater abundance of Wrangell Lava and Nikolai Basalt relative to other rock types in these areas. A close look at figure 12A reveals that nearly all sulfate-dominant water samples are from sites proximal to mines and the mill, whereas

conditions at spring breakup (sites 7NA040, 7NA044, 7NA049). In contrast, three water samples proximal to mines and the mill plot in the bicarbonate field in figure 12A. These three samples contain higher bicarbonate relative to sulfate because they were collected during an intermittent rain event, when the well-buffered Cabin Creek water flow was relatively high, but no runoff water was observed flowing from the tailings pile.

Element content in surface waters at Nabesna varies widely (fig. 12*B*, *C*). The season and surface flow conditions are important controlling factors for the major- and traceelement compositions of the surface waters. Downstream of the mill, this feature was largely a function of the relative amount of surface flow, whether waters were actively flowing over and through the mill tailings piles (as found during the spring breakup), or whether the piles were dry (typical during summer months). For example, analysis of samples collected from the same site at the base of the mill tailings (fig. 7) produced these results:

[mod, moderate/moderately; µS/cm, microsiemens per centimeter; ppb, parts per billion; ppm, parts per million]

Sample No.	рН	Conductivity (µS/cm)	Sulfate:bicarbonate ratio	Trace-element content
¹ 4NA011	near-neutral (7.1)	mod high (582)	1:1 (sulfate 180 ppm; bicarbonate 180 ppm)	mod (sum 1,600 ppb)
² 7NA036	low (2.8)	high (1,620)	high sulfate; no bicar- bonate (sulfate 970 ppm; bicarbonate 0)	extremely high (sum 190,000 ppb)
³ 7NA061	near-neutral (7.3)	low (58)	0.17 (sulfate 5 ppm; bicarbonate 30 ppm)	low (sum 79 ppb)

¹ Dry summer; no flow from mill tailings.

 2 Spring breakup, with flow from mill tailings.

³ Short summer rain event; no flow from mill tailings.

bicarbonate-dominant waters are from distal sites. This feature reflects the dissolution of pyrite and, to a lesser degree, pyrrhotite, both common sulfide minerals in the mine waste and mill tailings. The lower pH values, higher conductivities, higher TDS, and higher metal content of waters proximal to the mines and mill are directly related to dissolution of pyrite. In the mill tailings, dissolution of pyrite is further enhanced because the pyritic ore was ground to fine particle size during milling practices.

The few distal water samples in figure 12A containing relatively high sulfate content are from sites where pyrite was observed in alluvial heavy-mineral concentrates (site 4NA013) or where sulfate-rich water plumes from the mill tailings advanced farther down Cabin Creek during high-flow WRST resource staff requested data on the seasonal variation and extent of metal dispersion downstream from the mill site in surface waters. Figure 13 shows the arsenic and manganese content in surface waters collected along Cabin Creek during four different sampling periods: dry summers of 1994 and 1996, the April-May spring breakup in 1997, and an extended 3-week rainy period in late summer 1997. During the dry summer periods, arsenic content was consistently low (less than 3 ppb) throughout the sampled reach of Cabin Creek. There was no surface flow from the mill tailings during these dry periods. In contrast, arsenic was found in excess of the AKDEC MCL of 50 ppb at water sample sites on the mill tailings and at the base of the



Figure 13. Sketch map and distribution of arsenic and manganese in water along Cabin Creek above, on, and below Nabesna mill tailings piles. Patterns similar to that for As were observed for Ag, Al, Be, Cd, Cr, Co, Cu, F⁻, Fe, Pb, Mo, Ni, SO₄²⁻, and Zn. AKDEC MCL, Alaska Department of Environmental Conservation maximum contaminant level. See text (p. 7) for explanation of primary and secondary MCL values. Numbers in figures refer to sample field numbers. D, site duplicate. Note that sketch map is distorted for simplification and has two scale breaks.

tailings during the spring breakup and extended summer wet periods. However, the arsenic concentrations during these wet sampling periods fell to levels similar to those found during dry sampling periods within about 500 m downstream of the lowermost tailings. Similar patterns were observed for Ag, Al, Be, Cd, Cr, Co, Cu, F⁻, Fe, Pb, Mo, Ni, and Zn. Fluoride, aluminum, copper, iron, and zinc were found in concentrations in excess of established AKDEC MCL's only in waters collected on or near the base of the mill tailings. For these five ions, the concentrations fell below established MCL's within 850 m of the lowermost mill tailings. In contrast, manganese and sulfate were the only ions found to exceed AKDEC MCL's in samples collected during all sampling periods. Manganese (fig. 13) was found in low concentrations (10 ppb or less) above the mill, but climbed to levels exceeding the AKDEC secondary MCL of 50 ppb in samples collected on and below the mill. During wet periods, manganese concentrations remained above the MCL throughout most of the sampled reach of Cabin Creek. During dry periods manganese concentrations paralleled those found during wet periods, but at lower concentration levels. However, in all periods manganese concentrations were below the MCL's prior to reaching the mouth of Cabin Creek, about 2.5 km below the lowermost mill tailings pile. Sulfate concentrations fell to background levels in a much shorter interval, within about 1,300 m below the lowermost tailings pile.

During spring breakup and extended rainy periods, acidic, metal-bearing, sulfate-rich waters derived from the mill tailings piles are mixed with and diluted by well-buffered, high-pH, bicarbonate-rich surface and ground water derived from surrounding carbonate-rich bedrock. The mixing raises the pH, which initiates precipitation of ferri-hydroxides. Most metals are co-precipitated with the ferri-hydroxides. Metalliferous, rusty-red ferri-hydroxide precipitates are common along Cabin Creek from the base of the mill tailings to the Jacksina trail crossing at site 6NA028 (figs. 7, 13) (Eppinger and others, 1999). Downstream of this point, ferri-hydroxides are more sporadically distributed. Elements such as manganese remain in solution at the higher pH levels, so manganese concentrations remain high. Dilution alone appears to be the controlling factor on manganese concentration downstream from the mill tailings. Zinc, which can respond similarly to manganese at higher pH values, was found in concentrations below the AKDEC MCL of 5,000 ppb in all water samples except three, from sites directly on the mill tailings piles. The minor abundance of zinc in waters downstream of the mill tailings is most likely a reflection of the low zinc content in the skarn deposits at Nabesna.

Samples collected in 1994 contain anomalous mercury in Nabesna mill tailings (several samples, as much as 1.5 ppm mercury) and slightly anomalous mercury in stream sediment from Cabin Creek directly below the tailings (site 4NA011, 0.4 ppm)(Eppinger and others, 1997). However, anomalous mercury is not found in mine waste, ore rocks, or other sediments from sites peripheral to the mill tailings. Water samples collected in 1994 were not analyzed for mercury. Stream sediment samples collected in 1996 and 1997 along Cabin Creek confirmed slightly anomalous mercury in sediments below the mill tailings (6NA025, 6NA029, 7NA058, 0.5 to 1.3 ppm mercury). Mercury was determined in 15 water samples collected on mill tailings and along Cabin Creek to the junction of Jack Creek about 2.5 km downstream, during spring breakup, summer rain, and dry periods of 1996 and 1997. None of the water samples contain high concentrations of mercury. Values for mercury range from 0.013 to 0.032 ppb, well below the AKDEC MCL of 2 ppb. The multi-season water sampling at Nabesna indicates that mercury is not mobilized during wet periods or spring breakup. An anthropogenic origin for the mercury in mill tailings and related sediments, ascribed by Eppinger and others (1997) to a short-lived, unsuccessful attempt to recover gold (Wayland, 1943, p. 193), is still believed to be the most likely origin for the anomalous mercury. The possibility of higher mercury concentrations at depth in the mill tailings should be considered prior to any disturbance of the mill tailings.

Discussion

As illustrated in figure 13, conclusions drawn on water sample data can vary considerably, depending on the water flow conditions and season when a water sample is collected. Unless mine adits are continuously draining (a feature not found at most sites visited in WRST), timing can hamper the collection of mine drainage samples. For example, at Nabesna water flows over mine waste and mill tailings for only short periods throughout the year; the area is completely dry or frozen the majority of the time. Our data show that, in the absence of surface water, leachates of mine waste and mill tailings provide an approximation of expected metal content and pH. Water data derived from the Nabesna mill tailings, collected during spring breakup and extended wet summer periods, are in the "high acid/high metal" portion of the Ficklin plot, a diagram that shows pH versus the sum of selected dissolved metals (fig. 14A) (Plumlee and others, 1994). Data from Nabesna mill tailings leachates plot in this same field. Data from two other Nabesna mill leachates plot in the "near neutral/low metal" field. Both of these samples contain abundant calcite, which raises the pH and inhibits metals going into solution. Data for all other water samples from the Nabesna area plot in the "near neutral/low metal" field.

The acidic, metal-rich water samples from the Nabesna mill area are similar to several water samples collected from the unmined Orange Hill and Bond Creek areas (fig. 14*A*). The Orange Hill/Bond Creek water samples in the "moderate acid/ high metal" field are derived from highly altered areas. Data from leachates from samples of sulfate-rich, altered, disaggregated bedrock plot in the same field, and in the "moderate acid/ low metal" field. In the absence of water, the leachates from Nabesna and Orange Hill/Bond Creek would have provided good estimates of initial waters prior to dilution and buffering by adjacent surface flow and streams.

Figure 14*B* shows pH versus dissolved metal content for the Bremner, Kennecott, and Gold Hill waters. Data from all surface waters plot in the "near neutral/low metal" field. Data from samples from Kennecott and Gold Hill plot in this field because of the abundant carbonate minerals and attendant high alkalinity of waters from these areas, features that inhibit mobility of most metals. Mine drainage from the Lucky Girl mine at Bremner has high pH and low metal content because of the calcite gangue minerals present in the veins. The two leachates from Bremner having data that plot in this same field



Figure 14. Ficklin diagrams of pH versus dissolved metal content in water samples collected from Nabesna, Orange Hill and Bond Creek (*A*); and Kennecott, Bremner, and Gold Hill (*B*). Small + symbols are values for minedrainage waters from diverse mineral deposits for purposes of comparison (data from Plumlee and others, 1994).

are from mine waste piles at the Lucky Girl and Yellowband mines (fig. 4). Calcite gangue, present in the mine waste, results in the high pH/low metal character of the leachates. However, one Bremner leachate sample plots in the "moderate acid/low metal" field. This sample is from the Lucky Girl mill tailings pile. The tailings pile probably produces more acidic waters because sulfide minerals (chiefly pyrite) were pulverized and concentrated in the piles by milling practices. Free gold was observed in iron-oxide pseudomorphs after pyrite in hand specimens at the Lucky Girl mill—a reflection of the spatial association of gold with pyrite that the early miners recognized. At Nabesna, waters flowing from the mill tailings piles, and leachates of the tailings material, are very acidic and metal-rich. However, springs emanating from the tailings are not present throughout most of the year. Water coming from the tailings piles is derived from snow/ice buildup during winter months, and from summer rain. During the spring breakup and extended rainy periods, we observed alkaline, near neutral pH, low-conductivity surface water (derived from areas above the mill tailings) flowing down the Nabesna road between the upper and lower tailings piles (figs. 7*B*, 13). This water flows onto the lower mill tailings, increasing the volume of subsequently degraded water. Construction of berms and ditches adjacent to the tailings piles to divert and control surface flow from these "uncontaminated, off-site" sources would reduce total discharge off the tailings piles and reduce down-drainage impacts.

Orange Hill and Bond Creek are two members of a group of porphyry deposits found in a metallogenic belt that crosses the northeastern portion of WRST from Chistochina to Baultoff (fig. 1). Other porphyry systems, all smaller than Orange Hill and Bond Creek, include Baultoff, Horsfeld, Carl Creek, and Johnson Creek (Richter and others, 1975; Nokleberg and others, 1995). An obvious question is, "Are these unmined deposits affecting water quality, as was found at Orange Hill and Bond Creek?" The geologic setting, style of alteration present, and size of areas of altered rocks allow for speculation. The porphyry deposits exhibit variably sized haloes of altered rocks consisting principally of iron oxide and sulfate minerals resulting from weathering of iron sulfides (Richter and others, 1975). Other alteration minerals include chlorite, sericite, albite, pyrite, and actinolite (Nokleberg and others, 1995). Host granitoid rocks are part of the Klein Creek pluton. The largest deposits are Baultoff, which has a 2 km² area of altered rock, and Horsfeld, which has a 1.2 km² area of altered rock. The other named deposits have areas of altered rock of 0.3 km² or less, and numerous unnamed areas of alteration are also present (Richter and others, 1975). Altered rocks at Baultoff are underlain entirely by Cretaceous diorite (Richter, 1976). Horsfeld and Carl Creek are underlain by near-equal amounts of Cretaceous diorite and Cretaceous marine sedimentary and volcanic rocks. Johnson Creek is underlain almost completely by Cretaceous marine sedimentary rocks, and the area of altered rocks is just 0.005 km² (Richter, 1976; Richter and others, 1975). Based on the size of altered bedrock areas and on the mapped geologic units, one would expect rocks at Baultoff to be carbonate poor. If so, surface waters draining the altered areas at Baultoff probably are similar in pH and composition to those at Orange Hill and Bond Creek. Based on the descriptions of mapped geologic units, carbonate minerals are likely present at Horsfeld, Carl Creek, and particularly at Johnson Creek. If so, surface waters draining these areas are probably higher in pH and not as metalliferous as those at Orange Hill and Bond Creek.

Conclusions

Results from this study demonstrate that bedrock geology and mineral deposit type are critical aspects that must be considered in evaluating environmental geochemical effects of historic or active mine areas. Although this connection is intuitively obvious to most earth scientists, it is commonly overlooked in the environmental and regulatory arenas. For example, the large stratabound Kennecott copper deposits are relatively benign to the environment because of the predominance of carbonate rocks, the resulting high buffering capacity of waters, the absence of acid-generating minerals, and the absence of metals that could be mobilized at higher pH values. In contrast, pyrite-rich deposits, such as those at Nabesna, Orange Hill, and Bond Creek, can generate acidic, metalliferous waters. At the Nabesna skarn deposits, where carbonate rocks are widespread and fundamental to the formation of the deposits, waters surrounding deposits are well buffered and help to reduce overall downstream effects. However, at the Orange Hill and Bond Creek Cu-Mo porphyry deposits, surface and ground waters become acidic and metalliferous as they flow through large areas of sulfate-rich, altered bedrock, generally without the natural remediating effects of carbonate rocks.

Orange Hill and Bond Creek are naturally occurring, unmined, mineralized areas that demonstrate that mines and mills are not the sole sources of acidic, metalliferous waters in the environment-another commonly overlooked fact in the environmental and regulatory arenas. Established water quality standards for numerous inorganic parameters are exceeded at Orange Hill and Bond Creek under completely natural conditions. Natural background conditions at Orange Hill and Bond Creek have probably been acidic and metalliferous for several tens of thousands of years. However, the naturally occurring metalliferous, low pH waters found at Orange Hill and Bond Creek are not necessarily detrimental. They create unique ecosystems that certain biota can thrive on. Orange Hill and Bond Creek may be useful as unmined analogs to previously mined porphyry Cu-Mo deposits elsewhere, where premining background data are lacking for water and sediment quality.

Weather conditions and season when water sampling is undertaken can strongly influence the resulting geochemical signatures and associated interpretations. At Nabesna, results of sampling during dry summer periods downstream of the mill indicated minimal overall effects: waters were near neutral in pH and metal concentrations were low to moderate. However, samples collected at the same sites during the snow and ice melt at spring breakup and following extended summer rainy periods were very acidic and metalliferous.

In the absence of active mine drainage, surface flow, or springs at mine waste and mill tailings piles, leachates of composited waste and tailings can provide data that approximate the pH and metal composition for initial meteoric waters flowing from the piles, prior to dilution by adjacent surface flow and streams. Leachates from mill tailings at Nabesna have pH and metal contents similar to those found from surface runoff collected on the tailings. Similarly, leachates from disaggregated altered bedrock at Orange Hill and Bond Creek mimic adjacent stream waters in pH and metal content. For mine- and mill-related geoenvironmental sampling, leachates should be considered as a sample medium under those circumstances when repeated sampling during wet and dry seasons is not possible.

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Appendix. Basic Statistics for Sediments, Rocks, Alluvial Heavy Mineral Concentrates, and Leachates for Samples from All Areas Studied in Wrangell-St. Elias National Park and Preserve, Alaska

[Only data for elements considered anomalous in each area are shown; average crustal abundance values from Fortescue, 1992; Sediment, minus-80-mesh stream sediment; Concentrate, alluvial heavy-mineral concentrate; Leach, leachate following EPA 1312 leach procedure; # unqualified, number of samples not qualified by ">"; NA, not applicable; sediment, rock, and concentrate are all in parts per million, except Fe (percent); leachates are all in parts per billion, except SO²₄ (parts per million)]

	Ag	AI	As	Au	В	Ва	Bi	Cd	Co	Cu	Fe	Hg
Average crustal abundance	0.08	83600	1.8	0.004	9	390	0.0082	0.16	29	68	62200	0.086
Sodimont n = 12	1			Ke	nnecot	t						
seument, n = 15	6		10	10				10		12		10
	0		13	0.000				0.12		13		0.02
minimum			11	0.002				0.13		75		0.02
maximum	3		230	0.3				9.5		5000		3.1
mean	2		73	0.033				2.4		1500		0.69
standard deviation	0.89		74	0.09				3.7		2000		1.1
Rock, n = 10												
# unqualified	4		2	7				4		8		9
minimum	9		24	0.002				4		4		0.08
maximum	640		7900	0.1				73		380000		520
mean	270		2600	0.017				23		49000		59
standard deviation	270		3100	0.037				33		130000		170
Concentrate, n = 7												
# unqualified	7		4				1	2		4		
minimum	1		500				70	50		1500		
maximum	300		10000				70	300		>50000		
mean	87		4400				NA	180		14000		
standard deviation	110		4200				NA	180		24000		
				B	remner							
Sediment, $n = 9$												
# unqualified	4		7	7			2			9		7
minimum	0.1		26	0.003			14			31		0.023
maximum	0.7		240	0.18			17			1300		1.3
mean	0.45		140	0.05			15			320		0.38
standard deviation	0.3		87	0.07			21			500		0.6
$R_{ock} n = 5$												
# unqualified	5		4	5			3	2		5		
minimum	2		10	22			14	3		21		
maximum	19		810	2.2			60	3		1500		
maximum	70		200	5.0			209	25		500		
niedii	1.0		300	5.9			33	0.74		500		
	0.0		380					0.71		000		
Concentrate, $n = 4$												
# unqualmed	3		3	1						4		
minimum	1		500	300						150		
maximum	300		700	300						300		
mean	100		630	NA						230		
standard deviation	170		120	NA						87		
Leach, $n = 3$												
# unqualified		3	3	3							3	
minimum		99	0.4	0.03							57	
maximum		390	1700	0.05							480	
mean		240	570	0.037							210	
median		150	980	0.012							240	
				G	old Hill							
Sediment, $n = 16$												
# unqualified			11	10			14					16
minimum			16	0.005			11					0.03
maximum			250	2.1			20					0.2
mean			50	0.22			14					0.09
standard deviation			68	0.66			2.9					0.05
Rock, n = 7					+	+	+		+	+	+ +	
# unqualified	6		6	7			3	2	7	7		7
minimum	0.1		12	0.007			14	2	6	35		0.02
maximum	390		3300	59			3000	980	210	49000		120
mean	87		590	85			1000	490	50	7300		17
standard deviation	160		1300	22			1700	690	74	18000		45
	1 .00								, i T			.5

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	Ag	Al	As	Au	В	Ва	Bi	Cd	Со	Cu	Fe	Hg
Concentrate, $n = 14$												
# unqualified	8		2	4	10	6	2	3		13		
minimum	3		700	70	30	200	30	50		15		
maximum	1000		1000	>1000	>2000	>10000	>2000	200		2000		
mean	410		850	130	530	1900	65	120		220		
standard deviation	490		210	57	720	4000	49	76		540		
			0	range H	ill/Bond	l Creek						
Sediment, n = 16				angen								
# unqualified	7		12	16		16		12		16	16	16
minimum	2		17	0.006		89		0.06		120	4.7	0.02
maximum	23		110	0.99		2200		4.8		4600	9	0.39
mean	6.6		57	0.15		670		1.6		1100	6.4	0.079
standard deviation	7.4		29	0.27		480		1.5		1300	1.3	0.087
R_{ock} , $n = 10$										+		
# unqualified	10		6	10				6		q	10	
minimum	0.3		11	0.008				0.05		53	0.62	
maximum	73		79	2				4 7		13000	16	
mean	10		/3	0.20				1.7		1700	65	
standard deviation	22		40	0.29				1.2		4200	6.3	
				0.02				1.0		4200		
Concentrate, n = 9												
# unquaimed	9					8			9	9	9	
minimum	2					1000			50	50	2	
maximum	15					>10000			150	7000	30	
mean						5600			88	1500	12	
standard deviation	5					4000			32	2200	8.4	
Leach, $n = 3$												
# unqualified		3							3	3	3	
minimum		4600							2.4	13	480	
maximum		140000							380	6500	3000	
mean		51000							140	4100	1400	
standard deviation		77000							210	3600	1400	
				N	abesna							
Sediment, n = 25												
# unqualified	9		18	4			5	11	25	25	25	16
minimum	2		11	1			14	1	9	27	1.6	0.02
maximum	31		2100	5			70	32	120	910	25	1.3
mean	12		400	2.5			37	4.5	23	180	7	0.24
standard deviation	12		620	1.7			23	9.2	21	240	5.1	0.36
Rock, n = 24								[[[·	[
# unqualified	18		22	24			18	15	23	24	24	17
minimum	7		23	0.006			10	4	2	72	1.1	0.02
maximum	110		3100	32			310	95	130	12000	49	1.5
mean	30		800	6.1			89	19	46	2400	21	0.42
standard deviation	24		730	7.8			73	27	37	2600	13	0.46
Concentrate, n = 7										+		
# unqualified	5		2	2		7		1	7	7	7	
minimum	1.5		700	20		50		50	20	10	1	
maximum	20		1000	100		10000		50	1000	5000	15	
mean	7.3		850	60		1600		NA	200	1300	6.4	
standard deviation	7.9		210	57		3700		NA	360	1800	5.4	
Leach, n = 12	+	+ +						+ ·	+	+	+	+
# unqualified	9	11	12	2	4		9	11	12	12	11	
minimum	0.02	8.1	0.5	1	200		0.02	6	0.3	8	1	
maximum	27	130000	4000	11	400		27	200	1000	87000	900000	
mean	5.3	20000	540	6	250		7.5	40	370	18000	84000	
standard deviation	9.6	37000	1200	7.1	100		11	58	390	25000	270000	
	0.0							00				

	Mn	Мо	Pb	REE	Sb	Se	SO42-	Sn	Sr	W	V	Zn
Average crustal abundance	1060	1.2	13		0.2	0.05		2.1	384	1.2	136	76
0 // /0				Ke	ennecot	t				1		
Sediment, $n = 13$			_									
# unqualified			1		13							13
minimum			4		0.4							35
maximum			46		3.3							130
mean			27		1.2							79
standard deviation			15		0.91				L			30
<i>Rock, n</i> = 10												
# unqualified					7	8					5	9
minimum					0.5	0.1					85	14
maximum					2.4	1					390	260
mean					1	0.44					280	85
standard deviation					0.73	0.37					130	77
Concentrate, n = 7						+			+	+		
# unqualified			5					3			7	
minimum			300					70			30	
maximum			10000					150			500	
mean			2600					98			250	
standard deviation			4200					46			150	
			1200	D	romnor						100	
Sediment, $n = 9$				D	renner							
# unqualified						9						9
minimum						0.12						70
maximum						1.5						170
maan						0.40						110
niean						0.49						110
						0.45				+		
Rock, $n = 5$			-			_						_
# unqualified		1	5			5						5
minimum		10	65			0.14						35
maximum		10	860			3.9						610
mean		NA	420			0.95						230
standard deviation		NA	310			1.6						240
Concentrate, $n = 4$									T	T		
# unqualified			3							4		
minimum			30							100		
maximum			200							200		
mean			100							140		
standard deviation			89							48		
Leach, n = 3	+				+	+			+ '	+		
# unqualified	3		3							2		3
minimum	2.4		0.73							0.2		0.6
maximum	72		87							7.1		57
mean	26		30							37		20
median	40		50							49		32
	+0		50	C						4.0		
Sediment, n = 16				G								
# unqualified					2	11		16				16
minimum					2	0.2		36				86
maximum					7	0.2		100				120
mean					л с Л с	0.0		7				110
standard doviation					4.0	0.34		4/				110
					3.5	0.17			4	+		
$ROCK, \ \Pi = I$			_			-		-			_	-
# unqualified		3	7		4	6		3	'		7	7
minimum		2	16		3	0.2		11			38	45
maximum		16	46000		120	9.9		22			230	160000
mean		7	6700		35	3.3		15			140	23000
standard deviation		7.8	17000		57	3.6		6.3			67	60000

	Mn	Мо	Pb	REE	Sb	Se	SO42-	Sn	Sr	W	V	Zn
Concentrate, $n = 14$												
# unqualified			13									4
minimum			50									700
maximum			10000									15000
mean			3100									5400
standard deviation			3700									6800
			0,00	rango U	ill/Bond	Crook						
Orange Hill/Bond Creek Sediment, n = 16 I												
# unqualified	16	14	16		13	16					16	16
minimum	470	5	11		1	0.32					110	56
maximum	2500	320	1200		0	0.52					200	2800
maximum	1200	320	1200		3	9.5					200	2000
mean	1300	100	130		3.1	2.7					150	500
	600	100	300		2.4	2.3						
Rock, $n = 10$					_							
# unqualified	10	8	9		5	10					10	10
minimum	21	6	6		1	0.11					12	25
maximum	3200	800	230		5	24					220	870
mean	750	160	52		2.6	5.5					91	310
standard deviation	1100	270	75		1.5	9.7					58	340
Concentrate, n = 9												
# unqualified		2	8						7	2		7
minimum		20	20						200	50		500
maximum		50	700						2000	100		2000
mean		35	240						990	75		910
standard deviation		21	290						540	35		520
Leach, n = 3												
# unqualified	3			3			3					3
minimum	100			32			790					110
maximum	4200			490			3900					600
mean	2400			190			2000					360
standard deviation	2100			260			1700					250
	2100			200			1700					230
Sediment $n = 25$				IN a	apesna							
# unqualified	25	5	23		6	13						25
minimum	330	2	4		3	1						31
maximum	5000	16	2500		1/	3						1600
moon	1100	70	2000		62	17						230
atenderd deviation	000	7.2 5.0	570		0.2	0.62						230
	990	5.0			4.2	0.03						
$ROCK, \Pi = 24$		40	04		04	00				45		0.1
# unqualified	24	18	21		21	22				15		24
minimum	37	1.6	11		0.7	0.1				1.4		20
maximum	6100	70	6500		17	4.1				22		7300
mean	1300	15	1200		7.2	1.9				7.5		920
standard deviation	1600	19	1700		5.1	1.2				6.5		1500
Concentrate, $n = 7$												
# unqualified			6									1
minimum			20									1500
maximum			500									1500
mean			160									NA
standard deviation			200									NA
Leach, n = 12												
# unqualified	12	5	12	10			4		12		6	11
minimum	8.2	0.63	0.51	5.6			48		14		0.4	100
maximum	12000	35	3000	84			5100		700		29	10000
mean	2300	9.9	750	29			2300		290		9.1	3500
standard deviation	3200	14	1200	29			2100		180		11	3400
				_					-			

Additional anomalous elements for Nabesna leachates: Ca, Ce, Cr, Mg, Ni, Te, Th, Ti, TI, and U.