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**Case study of the environmental signature of a recently abandoned,
carbonate-hosted replacement deposit: The Clayton Mine, Idaho**

by

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Figure 1. Mine waste dump piles at the Clayton mine. The buff to orange colored rock on the talus slope is dolomite.

Introduction

The Clayton mine (Fig. 1) is a silver-lead-zinc replacement deposit in the Bayhorse mining district in Custer County, Idaho. The deposit is hosted by dolomite and quartzite within a fault-bounded block of Paleozoic rocks east of the Idaho batholith. The mine was discovered in 1877, developed as an underground mine, and produced silver (218,692 kg), lead (39,358,903 kg), zinc (12,778,700 kg), copper (754,858 kg) and minor gold (Hillman, 1986). Cobalt is also reported. The mine operated from 1935 to 1986. The geology of the area and descriptions of the 1920's-era workings are given by Hobbs (1985a, 1985b), Hobbs and others (1991, 1995), Fisher (1985), Ross (1937, 1963), Hillman (1986), and Mitchell and others (1986).

The mine was last operated by Clayton Silver Mines, Inc. through 1986. The modern mill at the mine site is along Kinnikinic Creek, which drains into the Salmon River at Clayton, about 1.5 miles (2.4 km) downstream from the mine (Fig. 2). The mill produced a lead concentrate by selective flotation that contained 35 to 45 percent lead and 3,400 to 6,800 g/t silver (Hillman, 1986). Mill tailings were placed as terraces along steep slopes within the narrow stream valley, extending to the edge of creek. Prior to the most recent mining activity, a historic smelter, on the north bank of the Salmon River at the town of Clayton, processed ores from a number of mines in the district and dumped slag directly into the river. The smelter operated intermittently from the 1880s to 1902 (Wells, 1983). The U.S. Environmental Protection Agency (EPA) and the U.S. Bureau of Land Management (BLM) have been investigating environmental issues related to the abandoned mine site since the early 1990s (EPA, 2000a). In October, 2001, EPA completed a Time-Critical Removal Action to stabilize mine tailings to prevent erosion into

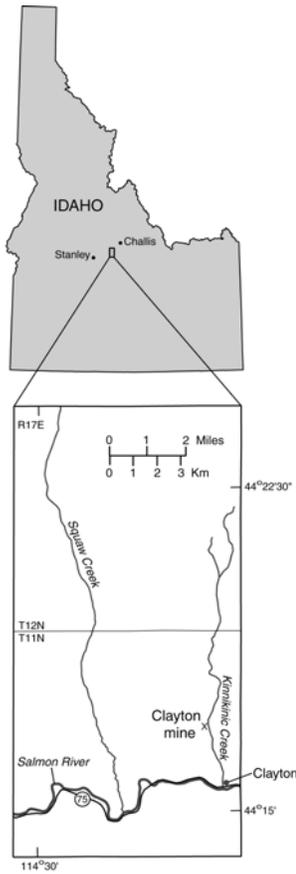


Figure 2. Index map showing the location of the Clayton mine.

Kinnikinic Creek, to control infiltration of water into tailings and seepage of water from tailings, and to minimize wind erosion (EPA 1999, 2001).

The Clayton Silver mine is located in sec. 13, T11N, R 15E on the Clayton 7.5' topographic quadrangle map. The mine site includes about 565 acres in and adjacent to Kinnikinic Creek (EPA, 2000a); the site encompasses private land as well as patented lode claims within lands under the jurisdiction of the U.S. Bureau of Land Management (BLM). Erosion of a 15-acre pile of fine-grained flotation mill tailings and other mine waste by wind and water threatens aquatic life in Kinnikinic Creek (bulltrout habitat) and the Salmon River (Chinook salmon, steelhead, and cutthroat trout habitat) and airborne particulates from mill tailings pose a potential inhalation hazard for humans (BLM, 2000). A 1994 study by the Agency for Toxic Substances and Disease Control identified elevated metal concentrations in soil contaminated with mill tailings in the town of Clayton. Local residents conducted a voluntary clean-up program to remove soil from an outdoor basketball court in the town that had previously served as a pad for mill concentrates. Contaminated soils were hauled to the mill site tailings pile. Follow-up human health studies of Clayton residents in 1995 by the Idaho Bureau of Environmental Health and Safety showed that blood lead levels and arsenic levels in hair and urine were within normal ranges (BLM, 2000). As part of an integrated site assessment in the 1990s, a variety of sample media were analyzed by the Idaho Department of Environmental Quality, the U.S. Forest Service, and the EPA. These data showed that metal concentrations in Kinnikinic Creek surface waters below the mine (during high flow) exceeded acute and chronic criteria for lead, zinc, and arsenic. Drinking water criteria were not exceeded in residential wells. Elevated metal concentrations (likely to impact most benthic species) were found in sediments in the creek and in the Salmon River downstream of the

confluence. In 1999, EPA inventoried and removed chemicals from the abandoned processing buildings on the site. In 2000, short-term stabilization of mill tailings was initiated under an EPA-financed, time-critical removal action. Geotechnical studies were undertaken to characterize the stability and moisture content of the tailings. Piezometers were installed and geophysical testing was initiated to characterize the tailings before implementation any earth moving in 2001. One of the main issues that led to the time-critical removal action was stabilization of the solids on the site, especially the large mill tailings pile that is subject to severe wind erosion. Elements of concern include arsenic, lead, zinc, and cadmium. The site is not a National Priorities List site; Kinnikinic Creek is included in the Idaho 303(d) listing for water quality limited streams (BLM, 2000). A number of federal and state agencies worked together to develop strategies to isolate the creek from contact with the mill tailings, to stabilize the pile, and to reduce wind erosion (EPA, 2000a). These include the U.S. Environmental Protection Agency (EPA), the Idaho office of the U.S. Bureau of Land Management (BLM), the Idaho Department of Environmental Quality, and the U.S. Fish and Wildlife Service. The BLM is addressing the site as part of their Idaho Abandoned Mine Lands Project. BLM data for maximum concentrations of metals in Kinnikinic Creek and in the Salmon River below the confluence (table 1) indicate elevated concentration of arsenic, lead, and zinc in sediments and surface water. Removal activities completed in 2001 include creek channel construction and diversion, stabilization of the top and side slopes of the tailings pile with a rock/soil cover, armoring the toe of the tailings with rip rap, and revegetation of the flood plain. See EPA (2001) for a summary of EPA site activities at Clayton, including photos of the site reclamation activities.

The USGS sampled solids and waters at the site in August, 1999 and repeated water sampling in August, 2000. Data for solids, surface waters, and leachates from composite mine waste and mill tailings are reported here, along with descriptive information from the literature, in the form of a geoenvironmental model for the deposit. Sample locations from global positioning system instruments (GPS) and laboratory numbers keyed to the National Geochemical Database (U.S. Geological Survey, 1997) are listed in Appendix A. Analytical methods and detection limits are given in the Appendix B.

Table 1. BLM data for metals in sediments and surface waters at Clayton (BLM, 2000). [ppm, parts per million; N.R., not reported]

Location	Kinnikinic Creek above mill tailings pile	Kinnikinic Creek below mill tailings pile	Salmon River below confluence with Kinnikinic Creek
Element	<u>Sediment concentrations</u>		
As (ppm)	9.6	470	320
Pb (ppm)	61	2,600	1,900
Zn (ppm)	127	4,700	5,500
	<u>Surface water concentrations</u>		
As (ppm)	0.001	0.035	N.R.
Pb (ppm)	0.001	0.4	N.R.
Zn (ppm)	0.005	0.2	N.R.

Deposit Geology

The deposit is localized on the eastern limb of an anticline in Ordovician Ella Dolomite (Hobbs and others, 1991). The underground workings show that the ore zone is irregular, in shaley dolomite sandwiched between two Ordovician quartzites (Hillman, 1986). Middle Ordovician Kinnikinic Quartzite overlies the Ella Dolomite and a Lower Ordovician or older feldspathic quartzite, known as the Clayton Mine Quartzite, underlies the mineralized dolomite. Buff-colored Ella Dolomite forms talus slopes along the west side of Kinnikinic Creek, just north of the mine area (Fig. 1). Most of the underground workings trend northwesterly, following the average trend of bedding along the creek. Ore is partly controlled by fractures and bedding planes, but also is disseminated in dolomite host rock. Exploration and development focused on two mineralized shear zones: (1) the Clayton shear zone, which strikes N. 11° - 20° W. and dips 60° - 80° NE, is exposed at the surface for more than 1,000 m and is the locus of gossan zones and prospect pits and (2) a south shear that strikes S. 40° W. and dips 80° SE to vertical and truncates the Clayton shear zone (Hillman, 1986).

The ore minerals are galena, sphalerite, tetrahedrite, chalcopyrite, pyrargyrite, arsenopyrite, cerussite and covellite. Seal and others (1990) showed that Clayton tetrahedrite contains arsenic, as well as silver and zinc. By analogy with similar deposits elsewhere in the Bayhorse mining district, they concluded that the deposit formed at temperatures of about 300 °C. Siderite is the principal gangue mineral, along with dolomite, quartz, barite, calcite, fluorite, pyrite, chlorite, goethite, and garnet. The orebody is zoned. Galena and sphalerite decrease to the north as siderite and tetrahedrite increase; massive sphalerite occurs near the bottom of the ore shoots. The Clayton deposit, like other carbonate replacement deposits in the district, is related to Cretaceous-Tertiary igneous intrusions. Hydrothermal fluids interacted with sedimentary country rocks and deposited metals in fractured carbonate host rocks.

Site Description

In August of 1999, several wooden buildings full of mining equipment and chemicals remained on the site (workshop, tram, power plant, etc.). EPA inventoried the site in 1999 and removed potentially hazardous materials. The site includes a caved adit and head frame, mine waste dump piles, and a large dry flotation mill tailings pile about 18 m high that extends to the creek (Fig. 3). The toe of the flotation mill tailings pile extended along the creek for more than 350 m prior to the 2000 cleanup activities. The finely ground mill tailings were barren of vegetation and subject to wind erosion. Crusts of cemented, oxidized tailings and efflorescent salts coated parts of the mill tailings surface (Fig. 4). Laterally discontinuous crusts formed hardpan ledges on the slopes of the mill tailings (Fig. 5). The hardpans are hard, impervious layers typically cemented by iron- and manganese oxides, and indicate re-distribution of metals by sub-surface water flow within the pile. No flocculates or precipitates were observed in Kinnikinic Creek adjacent to, or downstream of the mill tailings. The creek water was colorless, odorless, had variable turbidity, and flowed at approximately 2 to 10 cubic feet per second (0.06 to 0.28 m³/s) at the times of our visits.

Solids Sampling

A variety of different types of solid samples were collected at the site. These include (1) ore and host rocks collected to characterize chemistry and mineralogy of ore and alteration assemblages, (2) composite weathered surface mine-waste dump and mill tailings (< 2 mm size fraction), (3) salt crusts on the mill tailings, (4) hardpan ledges observed on mill tailings slopes, (5) fine-grained (< 80 mesh, < 0.177 mm, size fraction) stream sediments from stream-water sample sites, and (6) a composite sample of slag at the historic smelter along the Salmon River at the town of Clayton. The <2 mm size fraction represents the soil-sized fraction of surface mine-waste dump material and flotation mill tailings. Samples were collected following the USGS protocols described by Smith and others (2000). Composite surface samples were collected by traversing the piles to collect samples using a randomly stratified grid (to the extent possible). Paste pH measurements made in the field (table 2) suggest that the mill tailings are relatively alkaline. Sample mineralogy was determined by optical microscopy, x-ray diffraction (XRD), and scanning electron microscopy (SEM). Splits of composite mine waste, mill tailings, and slag were subjected to a passive leach procedure (Hageman and Briggs, 2000).

Table 2. Field paste pH measurements of mine waste and mill tailings (<2 mm fraction).

<u>Sample number</u>	<u>Description</u>	<u>pH</u>
02JH99	Mine waste dump	7.5
05JH99	Top surface of mill tailings	7.7
07JH99	Salt crust on mill tailings	7.7



Figure 3. View south from the Clayton mine main adit showing gray mine waste dump (sample 02JH99) in the foreground and fine-grained tan mill tailings (sample 05JH99). The mill tailings extend down to Kinnikinic Creek.



Figure 4. Dry pond on mill tailings at the Clayton mine. Note fine-grained white powder crust (sample 06JH99) in the pond depression and film of white salts in the foreground.



Figure 5. Hardpan ledges (sample 09JH99) on the east bank of the mill tailings pile (~18 m high) along Kinnikinic Creek. The creek is in the lower foreground of the photo. Composite mill tailings sample 08JH99 was collected along the entire length of the mill tailings pile, about 5 m above the base, avoiding the hardpan ledges. Sample 05JH99 was collected along the entire pile near the top.

Water Sampling

Four water samples were collected from the area. Three sites were sampled in August, 1999 and resampled with an additional downstream site along Kinnikinic Creek in August 2000. Samples 99CH016 (Fig. 6) and 00CH53 were collected from Kinnikinic Creek just upstream of the mine site. Samples 99CH017 (Fig. 7) and 00CH55 are from Kinnikinic Creek immediately below the lowermost mill tailings pile. Samples 99CH015 (Fig. 8) and 00CH54 are from the main adit drainage sample at the mine site. Sample 00CH56 was collected from Kinnikinic Creek downstream from the mine workings, just upstream of an old wooden bridge across the creek.

Water samples were collected in clean 1 L polypropylene bottles. At the two stream sites, width-integrated samples were collected below riffles to obtain representative water samples. The adit-drainage samples were collected from a small steel- and concrete-lined mine drainage channel near the adit entrance.

Parameters measured in the field at each of the three sites include pH, conductivity, field alkalinity, turbidity, dissolved oxygen, acidity, an estimate of flow, water color, and water odor. Conductivity, pH, and turbidity meters were calibrated at each site. Field alkalinity and acidity were measured using portable titration kits available from CHEMetrics¹ and Hach, respectively.

¹ Any use of a trade product or firm name is for descriptive purposes only and does not imply endorsement by the U.S. Government.

Dissolved oxygen was measured using a portable colorimetric kit from CHEMetrics. Six separate water splits were collected at each site, and analyzed as follows:

(1) a filtered (0.45 micron disposable filter), acidified (HNO_3) sample for major and trace cation analysis, collected in a new, acid-rinsed (HNO_3) clear polypropylene bottle, analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES) and inductively coupled plasma-mass spectrometry (ICP-MS).

(2) an unfiltered, acidified (HNO_3) raw sample for major and trace cation analysis, collected in a new, acid-rinsed (HNO_3) clear polypropylene bottle, analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES) and inductively coupled plasma-mass spectrometry (ICP-MS).

(3) a filtered (0.45 micron disposable filter), acidified (HCl) sample for Fe^{2+} analysis, collected in a new, acid-rinsed (HCl) dark brown polypropylene bottle, protected from sunlight, analyzed by colorimetry.

(4) a filtered (0.45 micron disposable filter), preserved ($\text{KCrO}_2\text{-HNO}_3$) sample for Hg analysis, collected in an acid-rinsed (HNO_3) glass bottle with teflon lid, analyzed by atomic fluorescence.

(5) a filtered (0.45 micron disposable filter), unacidified sample (refrigerated) for anion analysis, analyzed by ion chromatography.

(6) an unfiltered, unacidified sample (refrigerated) for alkalinity analysis by laboratory titration.

Collection of samples (1) and (2) above allows for comparison of dissolved versus suspended chemical constituents. Mine-dump and mill-tailings samples were leached as described below in the Results section. Water samples collected from the leachate were processed by methods (1), (4), and (5).

Results

Results of multi-element geochemical analysis of host rock, ore, mine waste, flotation-mill tailings, slag, stream sediments, creek and adit waters, and leachates of mine waste and mill tailings, are presented in tables 3-7. Details for the analytical methods are reported along with detection limits in Appendix B.

Ore and host rock

The host-rock dolomite immediately adjacent to the orebody (sample 01BV99, table 3) is sulfide-poor ($< 0.05\%$ S), but contains higher concentrations of lead and zinc than typical carbonates, probably due to the alteration visible as iron staining along fractures. Ella Dolomite sampled from the talus slopes north of the mine workings (sample 43BV00, table 3) for background is also sulfide-poor. The Ella Dolomite is siliceous (38 wt. % SiO_2) and unremarkable in terms of concentrations of potentially hazardous elements. The talus slope dolomite might be suitable as convenient borrow material for any future site work, provided it meets geotechnical engineering criteria. The geochemical signature of the ore is defined by high concentrations of (in decreasing concentrations) $\text{Pb} > \text{Zn} > \text{Cu} > \text{Ag}$. Minor elements (As, Sb, Bi) are heterogeneously distributed among different types of ore. The most Zn-rich sample is also the richest in Cd. Seal and others (1990) showed that Clayton sphalerite incorporates as much as 0.35 wt. % Cd. Weathering of sphalerite releases cadmium as well as zinc to the environment, at Clayton and in other deposits where cadmium is sequestered in the mineral sphalerite (Seal and others, 2000).



Figure 6. Sample site for stream water and sediment collected along Kinnikinick Creek upstream of the Clayton mine site (site 99CH016). Stream water pH, 6.8; conductivity, 140 $\mu\text{S}/\text{cm}$; alkalinity 55 ppm (as CaCO_3); flow rate, approximately 10 cubic feet per second ($0.28 \text{ m}^3/\text{s}$).



Figure 7. Sample site for stream water and sediment along Kinnikinick Creek just downstream of the lowermost mill tailings pile (site 99CH017). The fine sediment infilling cobbles on the point bar above the water level (left side of the photograph) is composed largely of mill tailings. Stream water pH, 6.5; conductivity, 170 $\mu\text{S}/\text{cm}$; alkalinity 58 ppm (as CaCO_3); flow rate, approximately 3 cubic feet per second ($0.08 \text{ m}^3/\text{s}$).



Figure 8. Water sample site for adit drainage coming from the main portal of the Clayton mine. Water pH, 6.6; conductivity, 440 $\mu\text{S}/\text{cm}$; alkalinity, 130 ppm (as CaCO_3); flow rate, calculated at 0.4 cubic feet per second ($0.001\text{m}^3/\text{s}$).

Mine waste and mill tailings

Composited mine dump waste rock (littered with ore) and finer-grained mill tailings samples (table 4) contain elevated concentrations of Ag, As, Cd, Mn, Pb, Sb, and Zn. Total sulfur concentrations range from 0.5 to 1.2% and total carbon (2 to 8%) exceeds total sulfur. The hardpan ledges (Fig. 5) on the slope of the 15-acre flotation mill-tailings pile (sample 09JH99) are enriched in iron (16% Fe), manganese (1.8% Mn), and arsenic (880 ppm As) relative to other tailings materials sampled. This suggests that arsenic is locally mobilized by groundwater flowing through the pile and subsequently sorbed on secondary iron oxyhydroxide minerals. Siderite is ubiquitous in the mill tailings. Samples 05JH99 and 08JH99 are from the upper and lower parts of the mill tailings pile, respectively. The lower sample, collected about 5 meters above the creek, is elevated in lead and zinc, and depleted in arsenic relative to the sample collected near the top of the mill tailings. The two mill tailings samples are similar in mineralogy and total iron, sulfur, and carbon content (table 4). The metals may be present in trace sulfide minerals (near or below XRD detection limits) or in poorly crystalline or amorphous iron oxyhydroxides. White salts on the margins of the dry pond on the mill tailings pile (Fig. 3) were identified by XRD and SEM as starkeyite, $\text{MgSO}_4 \cdot 4\text{H}_2\text{O}$.

Mine waste and mill tailings are not natural soils; they represent processed materials that contain soil-size particles (<2 mm) and are subject to wind and water erosion. Both mine waste and mill tailings were barren of vegetation during sampling. Comparison of measured concentrations of potentially toxic elements with EPA preliminary remediation goals (PRGs) for

evaluating soils at contaminated sites (EPA, 2000b) indicates that lead and arsenic in surface mine waste and tailings at the Clayton mine exceed PRGs for both residential and industrial soils (table 4). In some samples, copper and zinc exceed residential soil PRGs but fall below the PRG concentration for industrial soils. The PRG values listed in table 4 are generic, are focused on human health, and do not consider ecological impacts of contamination or replace site-specific toxicity studies. Ecological soil screening level guidelines are complicated by the numbers of species and ecotoxicological differences among species that can be affected by soils (EPA, 2000b), and methods to address toxicity in soils are an ongoing research topic. A number of countries have developed critical limits for selected heavy metals (Pb, Cd, Cu, Zn, Ni, Cr, and Hg) in soils as a screening tool for further investigation. Compared with the ecological soil criteria used in Canada, for example, the Clayton materials (table 4) exceed critical limits for Cd, Cu, Cr, Hg, Pb, and Zn (Ecological Planning and Toxicology, Inc., 1999). In addition, observed metal concentrations for As, Mn, Pb, and Zn exceed critical values above which soil toxicity to plants is considered possible (Alloway, 1995).

Table 3. Geochemical data for host rock and ore at the Clayton mine.

Field No. ¹			01BV99	02BV99	03BV99	04BV99	05BV99	40BV00	42BV00	43BV00
Element	Units ²	Method ³								
As	ppm	Hydride	9.1	13	1,200	93	1,800	52	13	7
Au	ppm	Fire Assay	0.012	0.012	0.15	0.099	0.67	0.01	<0.01	<0.01
Hg	ppm	Cold Vapor	0.07	0.42	1.7	1.6	0.8	0.68	0.03	0.04
Al	%	ICP-AES	0.59	0.99	0.62	0.54	0.17	0.66	0.23	0.98
Ca	%	ICP-AES	18	0.31	1.3	2.7	0.047	0.89	0.17	14
Fe	%	ICP-AES	1.3	16	14	16	16	20	25	0.94
K	%	ICP-AES	0.28	0.47	0.21	0.26	<0.01	0.28	0.15	0.58
Mg	%	ICP-AES	11	6.4	3.1	6.2	1.8	6	0.35	8.2
Na	%	ICP-AES	0.018	0.009	0.009	0.009	0.014	0.01	0.01	0.01
P	%	ICP-AES	0.005	<0.005	<0.005	<0.005	<0.005	0.01	0.01	0.01
Ti	%	ICP-AES	0.006	0.006	0.006	0.006	<0.005	0.01	0.01	0.02
Ag	ppm	ICP-AES	<2	15	500	560	190	89	16	<2
As	ppm	ICP-AES	<10	<10	1,100	103	1,800	52	13	7
Ba	ppm	ICP-AES	57	63	25	37	7	29	310	56
Bi	ppm	ICP-AES	<50	<50	78	<50	53	<50	<50	<50
Cd	ppm	ICP-AES	6	23	51	13	40	13	4	<2
Ce	ppm	ICP-AES	<5	<5	8	8	8	37	14	<5
Co	ppm	ICP-AES	3	7	9	12	6	4	<2	<2
Cr	ppm	ICP-AES	13	56	52	56	45	<2	<2	3
Cu	ppm	ICP-AES	32	44	1,800	2,000	1,500	370	<2	17
Li	ppm	ICP-AES	3	3	3	3	<2	3	<2	6
Mn	ppm	ICP-AES	1,200	19,000	12,000	18,000	8,700	28,000	39,000	590
Mo	ppm	ICP-AES	<2	2	3	<2	4	<2	3	<2
Pb	ppm	ICP-AES	1,500	10,000	71,000	7,700	4,700	1,800	3,700	34
Sr	ppm	ICP-AES	77	2	8	13	<2	7	39	72
Th	ppm	ICP-AES	<6	6	<6	6	<6	<6	<6	<6
U	ppm	ICP-AES	<100	101	<100	<100	<100	<100	<100	<100
V	ppm	ICP-AES	11	33	29	30	24	<2	<2	12
Y	ppm	ICP-AES	2	4	<2	3	<2	3	3	3
Zn	ppm	ICP-AES	660	5600	7,000	1,000	3,200	2,300	1,400	28
Sb	ppm	Hydride	1.9	4.6	490	1,200	130	220	4.6	3
Se	ppm	Hydride	<0.2	<0.2	<0.2	0.3	1.1	<0.2	1.1	<0.2
Te	ppm	Fire Assay	<0.1	0.1	<0.1	<0.1	<0.1	0.2	0.2	<0.1
C _{Total}	%	LECO	11	7.7	4.3	8.0	2.6	8.5	0.16	9.2
S _{Total}	%	LECO	<0.05	0.51	7.1	0.61	13	0.57	0.22	<0.05

01BV99 Dolomite host rock with Fe-oxide minerals on fractures

02BV99 Galena-rich ore in dolomite with veinlets of siderite; traces of pyrite

03BV99 Galena-rich ore with chalcopyrite and pyrite in dolomite

04BV99 Siderite-rich vein in dolomite

05BV99 Ore in dolomite and quartzite, with siderite and with sulfide, Fe-oxide (goethite), and Mn-oxide minerals; contains pyrite, galena, chalcopyrite, tetrahedrite, cerussite, and covellite.

40BV00 Dark brown, siderite-rich replacement ore.

42BV00 Dark brown, siderite-rich replacement ore with abundant sulfides.

43BV00 Siliceous dolomite from talus slope 0.3 mi N of Clayton mine sampled for background. XRF data for this sample show that it contains 38 wt. % SiO₂.

¹See Appendix A for sample locations.

²Units: ppm, parts per million; %, percent.

³See Appendix B for explanation of methods and detection limits. Elements sought, but below detection limits for all samples: Be, Eu, Ga, Ho, La, Nb, Nd, Ni, Sc, Sn, Ta, Yb, and Tl.

Table 4. Geochemical and mineralogical data for solid mine waste and mill tailings, Clayton silver mine.

Field No. ¹		02JH99 05JH99 06JH99 08JH99 09JH99					PRGs ²		
Element	Units ³	Method ⁴						Residential soil	Industrial soil
<u>Major elements</u>									
Al	%	ICP-AES	1.3	0.59	3.8	0.56	0.36		
Ca	%	ICP-AES	10	7.5	16	4.1	0.88		
Fe	%	ICP-AES	7.2	11	6.2	14	17		
K	%	ICP-AES	0.38	0.19	0.72	0.21	0.07		
Mg	%	ICP-AES	7.6	7.4	2.7	6.1	5.2		
Na	%	ICP-AES	0.03	0.04	0.46	0.01	0.01		
P	%	ICP-AES	0.01	0.01	0.07	0.005	0.005		
Ti	%	ICP-AES	0.02	0.01	0.3	0.006	0.006		
C _{Total}	%	LECO	8.2	8.3	2.1	7.6	6.7		
S _{Total}	%	LECO	0.79	1.1	0.52	1.1	1.2		
<u>Minor and trace elements</u>									
Ag	ppm	ICP-AES	100	17	24	22	20		
As	ppm	Hydride	430	910	61	560	880	22	440
As	ppm	ICP-AES	410	990	73	580	910		
Au	ppm	Fire Assay	0.055	0.046	0.012	0.047	0.038		
Ba	ppm	ICP-AES	59	82	940	50	151		
Be	ppm	ICP-AES	<1	<1	2	<1	<1		
Bi	ppm	ICP-AES	<50	<50	110	<50	<50		
Cd	ppm	ICP-AES	25	40	100	35	25	37	810
Ce	ppm	ICP-AES	14	5	37	8	<5		
Co	ppm	ICP-AES	9	6	11	8	9	4,700	100,000
Cr	ppm	ICP-AES	60	51	67	62	55		
Cu	ppm	ICP-AES	406	89	120	104	85	290	7,600
Ga	ppm	ICP-AES	<4	<4	9	<4	<4		
Hg	ppm	Cold Vapor	0.79	0.7	0.2	0.51	0.38	23	610
La	ppm	ICP-AES	4	<2	21	<2	<2		
Li	ppm	ICP-AES	6	4	18	3	2		
Mn	ppm	ICP-AES	7,000	11,000	11,000	15,000	18,000	1,800	32,000
Mo	ppm	ICP-AES	<2	8	12	3	3		
Nd	ppm	ICP-AES	<9	<9	13	<9	<9		
Ni	ppm	ICP-AES	4	<3	19	<3	<3		
Pb	ppm	ICP-AES	6,800	2,000	6,500	2,900	1,900	400	750
Sb	ppm	Hydride	150	28	18	30	40	31	820
Sc	ppm	ICP-AES	<2	<2	7	<2	<2		
Se	ppm	Hydride	<0.2	<0.2	2.4	<0.2	<0.2	390	10,000
Sn	ppm	ICP-AES	<50	<50	54	<50	<50		
Sr	ppm	ICP-AES	47	42	230	17	6		
Te	ppm	Fire Assay	0.1	<0.1	0.5	0.2	0.2		
Th	ppm	ICP-AES	<6	<6	8	<6	<6		

Field No. ¹			02JH99	05JH99	06JH99	08JH99	09JH99	PRGs ²	
Tl	ppm	Fire Assay	<0.1	<0.1	0.3	<0.1	<0.1	5.2	130
V	ppm	ICP-AES	21	27	127	27	30		
Y	ppm	ICP-AES	3	2	17	<2	<2		
Yb	ppm	ICP-AES	<1	<1	2	<1	<1		
Zn	ppm	ICP-AES	3,600	3,400	9,200	4,700	2,300	2,300	100,000

Field number	Description and XRD mineralogy
02JH99	Composite of <2 mm-size fraction from mine dump surface waste Dolomite, quartz, siderite, muscovite, sphalerite, kaolinite, galena(?)
05JH99	Composite of <2 mm size fraction from upper mill tailings pile surface Quartz, dolomite, siderite, sphalerite, K-feldspar
06JH99	Fine white powder crust in center of dry pond on mill tailings. Calcite, garnet, pyroxene, quartz, sphalerite, albite, kaolinite, K-feldspar, dolomite
08JH99	Composite of <2 mm size fraction of lower (near creek) mill tailings pile surface Dolomite, siderite, quartz, sphalerite
09JH99	Red-brown hardpan ledge on east slope of mill tailings Siderite, quartz, dolomite, pyrite

¹ See Appendix A for sample locations. Samples are composites of 30 increments.

² PRGs are EPA preliminary remediation goals for soils (EPA, 2000b); these are generic risk-based concentrations used for site screening. Chemical concentrations above the PRG suggest that further evaluation of potential risks to human health posed by site contaminants is warranted, but concentrations in excess of these values do not necessarily indicate that a site is contaminated. PRGs do not address potential ecological impacts.

³Units: ppm, parts per million; %, weight percent.

⁴ See Appendix B for methods and detection limits. Elements sought, but below detection limits for all samples: Eu, Ho, Ta, and U.

Slag

A 30-ton smelter along the Salmon River processed lead-silver ore from the Clayton mine and from other mines in the Bayhorse district until 1902 (West, 1983). The smelter is located at the Clayton town site, 2.4 km from the mine, and a few meters downstream from the confluence of Kinnikinic Creek with the Salmon River (Fig. 9). Geochemical analysis of a composite sample of slag (table 5) shows that the slag contains extremely high concentrations of lead (5.3 wt. %) and relatively high concentrations of some other metals (Zn, Cu, As, Sb, Fe, and Mn).



Figure 9. Slag pile along the bank of the Salmon River just downstream from the confluence with Kinnikinnic Creek at the town of Clayton, 2.4 km downstream from the Clayton silver mine.



Figure 10. Panned heavy minerals from Kinnikinnic Creek stream sediment just below the lowermost mill-tailings pile (site 99CH017). As identified by X-ray diffraction, the abundant gray minerals are dominantly galena (PbS) and cerussite (PbCO_3); trace amounts of mendipite ($\text{Pb}_3\text{O}_2\text{Cl}_2$) were also identified.

Table 5. Geochemical data for a composite sample (45BV00) of slag along the Salmon River.

Element	Units	Method	45BV00	Element	Units	Method	45BV00
Ag	ppm	ICP-AES	92	Mn	ppm	ICP-AES	22,000
Al	%	ICP-AES	1.6	Mo	ppm	ICP-AES	23
As	ppm	Hydride	570	Na	%	ICP-AES	0.10
Au	ppm	Fire Assay	<0.005	Nb	ppm	ICP-AES	<4
Ba	ppm	ICP-AES	310	Nd	ppm	ICP-AES	11
Be	ppm	ICP-AES	<1	Ni	ppm	ICP-AES	25
Bi	ppm	ICP-AES	<50	P	%	ICP-AES	0.21
C _{Total}	%	LECO	0.02	Pb	ppm	ICP-AES	53,000
CO ₂	%	LECO	0.04	S	%	LECO	0.85
Ca	%	ICP-AES	6.2	Sb	ppm	Hydride	2,400
Cd	ppm	ICP-AES	<2	Sc	ppm	ICP-AES	<2
Ce	ppm	ICP-AES	47	Se	ppm	Hydride	4.7
Co	ppm	ICP-AES	6	Sn	ppm	ICP-AES	140
Cr	ppm	ICP-AES	8	Sr	ppm	ICP-AES	480
Cu	ppm	ICP-AES	4,000	Ta	ppm	ICP-AES	<40
Eu	ppm	ICP-AES	<2	Te	ppm	Hydride	0.3
Fe	%	ICP-AES	25	Th	ppm	ICP-AES	<6
Ga	ppm	ICP-AES	15	Ti	%	ICP-AES	0.07
Hg	ppm	Cold Vapor	0.03	Tl	ppm	Hydride	<0.1
Ho	ppm	ICP-AES	<4	U	ppm	ICP-AES	<100
K	%	ICP-AES	0.46	V	ppm	ICP-AES	41
La	ppm	ICP-AES	19	Y	ppm	ICP-AES	13
Li	ppm	ICP-AES	11	Yb	ppm	ICP-AES	2
Mg	%	ICP-AES	0.86	Zn	ppm	ICP-AES	15,000

¹ppm, parts per million; %, percent; see Appendix B for explanation of methods and detection limit]

Stream sediments

Stream sediment collected below the Clayton mine and mill site (site 99CH017, Fig. 10, table 6) contains elevated concentrations of Ag, As, total C, Cd, Cu, Fe, Hg, Mn, Mg, Pb, S, Sb, and Zn relative to the sediment collected upstream (site 99CH016). Probable-effects concentration stream-sediment guidelines are exceeded for As, Cd, Pb, and Zn (MacDonald and others, 2000) in the downstream sample. These data suggest that stream sediments below the mine have some metal concentrations in the range where harmful effects to freshwater ecosystems are possible.

Table 6. Geochemical data for < 80-mesh (< 0.177 mm) stream sediments in Kinnikinic Creek at the Clayton silver mine.

Sample			99CH016	99CH017	PEC ¹
			upstream	downstream	
<u>Element</u>	<u>Units</u>	<u>Method</u>			
Ag	ppm	ICP-AES	<2	44	
Al	%	ICP-AES	8	0.73	
As	ppm	ICP-AES	16	1,000	33
As	ppm	Hydride	45	1,100	33
Au	ppm	Fire Assay	<0.005	0.055	
Ba	ppm	ICP-AES	1,400	120	
Be	ppm	ICP-AES	2	<1	
C _{total}	%	LECO	1.4	8.1	
Ca	%	ICP-AES	1.6	3.5	
Cd	ppm	ICP-AES	<2	31	4.98
Ce	ppm	ICP-AES	92	<5	
Co	ppm	ICP-AES	12	12	
Cr	ppm	ICP-AES	110	48	111
Cu	ppm	ICP-AES	21	140	149
Fe	%	ICP-AES	3	16	
Ga	ppm	ICP-AES	17	<4	
Hg	ppm	Cold Vapor	0.1	0.40	1.06
K	%	ICP-AES	2.2	0.26	
La	ppm	ICP-AES	47	<2	
Li	ppm	ICP-AES	24	3	
Mg	%	ICP-AES	0.77	6.2	
Mn	ppm	ICP-AES	560	20,000	
Mo	ppm	ICP-AES	3	2	
Na	%	ICP-AES	1.2	0.055	
Nb	ppm	ICP-AES	20	<4	
Nd	ppm	ICP-AES	42	<9	
Ni	ppm	ICP-AES	32	<3	48.6
P	%	ICP-AES	0.068	0.011	
Pb	ppm	ICP-AES	57	4,300	128
S _{total}	%	LECO	<0.05	1.5	
Sb	ppm	Hydride	5.1	49	
Sc	ppm	ICP-AES	10	<2	
Se	ppm	Hydride	0.3	<0.2	
Sr	ppm	ICP-AES	330	28	
Th	ppm	ICP-AES	13	<6	
Ti	%	ICP-AES	0.48	0.02	
Tl	ppm	Hydride	0.4	0.1	
V	ppm	ICP-AES	71	46	
Y	ppm	ICP-AES	12	2	
Yb	ppm	ICP-AES	2	<1	
Zn	ppm	ICP-AES	97	4,100	459

¹PEC, Consensus-based probable effects concentrations for stream sediments above which harmful effects to freshwater ecosystems are likely to occur (MacDonald and others, 2000); ppm, parts per million; %, percent; see Appendix B for explanation of methods and detection limits.

Waters and leachates

Waters at all sampling sites are near-neutral (pH = 6.5 to 8.4), including water draining the mine adit (table 7). Alkalinity ranges from 50 to 130 ppm CaCO₃. Hardness for creek waters is in the range 60 to 90 mg/L CaCO₃ equivalent. Water flowing from the mine adit has higher hardness values (225, 239 mg/L CaCO₃ equivalent). Higher conductivities in the adit water reflect higher metal concentrations. Adit water is elevated in Zn, Mo, and Mn relative to stream waters. Lead concentrations in adit water and downstream surface waters are comparable (1.2 and 1.1 parts per billion, ppb) whereas the upstream water sample contained <0.05 ppb Pb. Comparison of filtered and unfiltered water compositions (table 7b) provides a qualitative measure of the role of sorption processes (Seal and others, 1998) because the unfiltered samples includes particulates as well as dissolved constituents of the waters. For most elements, the filtered (<0.45 micron) and unfiltered water analyses are comparable (within an analytical error of $\pm 10\%$). However, for Al, Fe, Pb, and Zn, the unfiltered concentrations exceed the filtered concentrations. This suggests that some lead and zinc may be carried as sorbed metals on hydrous ferric oxides. For example, the 1999 downstream Kinnikinic Creek water sample contains 22 ppb dissolved iron (filtered) and 220 ppb total iron (unfiltered). The 1999 water samples were collected when winds were calm; higher element variation would be expected between filtered (table 7C) and unfiltered samples (table 7d) if winds were present, blowing mill tailings dust into the creek and increasing stream water turbidity. These variations are especially apparent in the 2000 data set, which was collected at the same time of year (August), but on a windy day. The 2000 downstream Kinnikinic Creek sample contains <50 ppb dissolved iron whereas the unfiltered sample contains 8,400 ppb total iron. Unfiltered downstream water samples collected in 2000 also contain elevated concentrations of Al and Mn relative to the 1999 water samples, as well as elevated concentrations of a number of potentially toxic elements including lead, zinc, copper, arsenic, and antimony. The difference in sediment/colloid load at this site from one sampling event to another is also reflected in a change in measured turbidity (table 7A). Turbidity at the downstream site measured 3.1 FTU in 1999; turbidity measured 42 FTU in 2000.

The simple field leaching protocol adopted for this study is a passive leach procedure that provides an indication of the potential chemical composition of meteoric water runoff from weathered surfaces of mine waste or mill tailings piles (Hageman and Briggs, 2000). This method produces results that are comparable to EPA-1312 (EPA, 1994) for leachate pH and dissolved metal concentration trends; however, the more rigorous leaching procedure used in EPA-1312 tends to produce higher absolute concentrations (Hageman and Briggs, 2000). The passive leach is less labor-intensive than EPA-1312, and may more realistically simulate natural precipitation and snowmelt (Hageman and Briggs, 2000). All of the mine waste and mill tailings leachates (table 8) have measurable, but low alkalinities implying that there is not much acid-consuming capability left in the mine waste and mill tailings piles. Leachate metal concentrations for mine waste and mill tailings are unremarkable, with the exception of sporadic elevated concentrations of Ba, Pb, Sb, and Zn; Zn concentrations are greater than Pb concentrations in all but one of the leachates. The slag leachate contains elevated lead (1,200 ppb) relative to the lead concentrations leached from the tailings (≤ 30 ppb). The slag leachate is also elevated in arsenic, copper, and manganese relative to the tailings leachates, but contains similar or lower concentrations of dissolved sulfate, cadmium, and zinc.

Table 7. Field measurements and geochemical data for water samples.

A. Field data and alkalinity ¹							
Site	<u>1</u>		<u>2</u>		<u>3</u>		<u>4</u>
Site description	Strong flow from the main Clayton mine adit (in shade)		Kinnikinic Creek upstream from the Clayton mine; flowing stream in a sunny area		Kinnikinic Creek downstream from the Clayton mine; flowing stream in a sunny area. Water loss compared to upstream site due to water diversion into 18" steel flume next to stream. Higher pH values for 2000 samples (compared to 1999) could be due to carbonate-rich, wind-blown tailings.		Kinnikinic Creek downstream from the Clayton mine; flow is higher and turbidity lower here than at 00CH055 because water is not running in the flume.
Channel bed description	Steel/wood ditch and flume with slimy green algae in flat-bottomed areas; salts immediately above water line		Turbulent cascading stream with abundant moss and algae		Minor iron oxide staining and brown algae on cobbles and boulders; mossy and heavily vegetated banks (willow, grass, bushes, trees); alluvial boulders with mill tailings fines		Moderate iron- and manganese oxide coatings on boulders; boulders are interspersed with silt from the tailings pile
Samples	99CH015	00CH54	99CH016	00CH53	99CH017	00CH55	00CH56
Sampling date	8/15/99	8/7/2000	8/15/99	8/7/2000	8/26/99	8/7/2000	8/7/2000
Temperature	13 ° C	13 ° C	9.6 ° C	9.2 ° C	6.3 ° C	13 ° C	13 ° C
Flow rate	640 L/minute	650 L/minute	10 cubic ft/sec	8 cubic ft/sec	3 cubic ft/sec	2 cubic ft/sec	8 cubic ft/sec
Flow method	calculated	estimated	estimated	estimated	estimated	estimated	estimated
Water color	none	none	none	none	none	none	none
Water odor	none	none	none	none	none	none	none
pH	6.6	7.7	6.8	8.3	6.5	8.4	8.4
Conductivity (µS/cm)	440	427	140	141	170	181	175
Turbidity (FTU)	0.28	0.8	2.3	2.5	3.1	42	9.3
Dissolved oxygen (ppm)	2	2.5	7	7	7	8	8
Alkalinity (ppm, on-site CHEMetrics kit)	130	60	55	50	58	60	50
Acidity (ppm)	<20	n.d.	<20	0	<20	0	0

¹µS/cm, microsiemens per centimeter; ppm, parts per million; FTU, formazine turbidity unit (identical to the NTU, nephelometric turbidity unit), n.d., not determined; See Appendix B for explanation of methods and detection limits.

B. Laboratory measurements¹

<u>Site</u>		<u>1</u>		<u>2</u>		<u>3</u>		<u>4</u>
<u>Samples</u>		99CH015	00CH54	99CH016	00CH53	99CH017	00CH55	00CH56
<u>Parameter</u>	<u>Method</u>							
Hardness (mg/L CaCO ₃ equivalent)	C	225	239	60	70	70	90	88
Alkalinity (ppm, lab titration)	TI	150	n.d.	65	n.d.	69	n.d.	n.d.
F ⁻ (ppm)	IC	0.2	0.2	0.1	0.1	0.1	0.1	0.1
Cl ⁻ (ppm)	IC	1	0.9	0.6	0.6	0.6	0.6	0.7
SO ₄ ²⁻ (ppm)	IC	92	88	6.5	5.7	12	18	17
NO ₃ ⁻ (ppm)	IC	<0.1	<0.08	<0.1	<0.08	<0.1	<0.08	<0.08
Fe ²⁺ (ppm)	CO	0.07	n.d.	0.03	n.d.	0.0	n.d.	n.d.

¹All measurements made on unfiltered waters except for Fe²⁺, which is measured on filtered, acidified water. ppm, parts per million; See Appendix B for explanation of methods and detections limits.

C. Multi-element geochemical analyses for filtered (dissolved) element concentrations in waters¹.

Sample site			<u>1</u>		<u>2</u>		<u>3</u>		<u>4</u>
Element	Units	Method	99CH015	00CH54	99CH016	00CH53	99CH017	00CH55	00CH56
Ag	ppb	ICP-MS	0.3	<0.01	<0.01	<0.01	0.1	<0.01	<0.01
Al	ppb	ICP-MS	<0.01	<0.4	<1	0.8	<1	<0.4	<0.4
As	ppb	ICP-MS	7	6	0.3	<0.2	0.6	2	1
Ba	ppb	ICP-MS	31	32	56	55	53	49	51
Ca	ppm	ICP-AES	44	48	14	14	16	18	17
Cd	ppb	ICP-MS	<0.02	<0.02	<0.02	<0.02	0.06	0.4	0.2
Ce	ppb	ICP-MS	<0.01	<0.01	<0.01	0.02	<0.01	0.01	<0.01
Co	ppb	ICP-MS	1.3	1.3	<0.02	<0.02	0.03	0.03	0.05
Cs	ppb	ICP-MS	0.1	0.2	<0.02	0.01	<0.02	0.02	0.02
Cu	ppb	ICP-MS	0.5	0.5	<0.5	<0.5	<0.5	1	0.7
Fe	ppb	ICP-AES	62	77	22	<50	22	<50	<50
Hg	ppb	AF	0.006	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
K	ppm	ICP-AES	0.91	0.93	0.57	0.5	0.57	0.58	0.59
La	ppb	ICP-MS	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	<0.01
Li	ppb	ICP-MS	0.8	<0.5	1	<0.5	1	<0.5	<0.5
Mg	ppm	ICP-AES	28	29	8.1	8.6	9.6	11	11
Mn	ppb	ICP-MS	550	430	0.57	0.37	28	19	29
Mo	ppb	ICP-MS	3	2.5	0.2	0.2	0.2	0.3	0.3
Na	ppm	ICP-AES	1.7	1.8	1.9	1.8	1.9	1.8	1.9
Nd	ppb	ICP-MS	<0.01	<0.01	0.02	0.01	0.01	<0.01	<0.01
Ni	ppb	ICP-MS	0.5	1.1	<0.1	<0.1	<0.1	<0.1	<0.1
P	ppb	ICP-MS	2	<3	13	8	11	<3	3
Pb	ppb	ICP-MS	1.2	0.88	<0.05	<0.05	1.1	8.8	4.2
Rb	ppb	ICP-MS	1.8	2	0.73	0.72	0.7	0.89	0.85
Re	ppb	ICP-MS	0.04	0.03	<0.02	<0.02	<0.02	<0.02	<0.02
Sb	ppb	ICP-MS	2.5	1.8	<0.03	0.04	0.18	0.4	0.4
Si	ppm	ICP-AES	3	3.2	4	4	4	3.9	3.8
Sr	ppb	ICP-MS	70	70	100	94	100	91	92
Th	ppb	ICP-MS	0.04	<0.007	<0.03	<0.007	<0.03	<0.007	<0.007
U	ppb	ICP-MS	0.31	0.34	0.11	0.12	0.12	0.12	0.15
V	ppb	ICP-MS	0.2	<0.2	0.2	<0.2	<0.1	<0.2	<0.2
W	ppb	ICP-MS	0.1	0.02	0.05	<0.02	0.02	<0.02	<0.02
Y	ppb	ICP-MS	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	<0.01
Zn	ppb	ICP-MS	190	190	<0.5	<0.5	22	63	38

¹Filtered (< 0.45 micron)/acidified waters. ppb, parts per billion; ppm, parts per million; see Appendix B for explanation of methods; NA, not applicable. Elements sought, but below detection limits for all samples: Au, B, Be, Bi, Cr, Dy, Er, Eu, Ga, Gd, Ge, Ho, In, Pr, Se, Sm, Tb, Ti, Tl, Tm, and Yb

D. Multi-element geochemical analyses for unfiltered (total) element concentrations in waters.

Sample site			<u>1</u>		<u>2</u>		<u>3</u>		<u>4</u>
Element	Units	Method	99CH015	00CH54	99CH016	00CH53	99CH017	00CH55	00CH56
Ag	ppb	ICP-MS	0.2	<0.01	<0.01	<0.01	0.2	0.3	0.01
Al	ppb	ICP-MS	<0.01	<0.4	31	41	26	76	20
As	ppb	ICP-MS	9	6.8	0.3	0.2	1	23	2
Ba	ppb	ICP-MS	30	32	57	55	53	54	21
Bi	ppb	ICP-MS	0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Ca	ppm	ICP-AES	47	47	14	14	16	20	6.8
Cd	ppb	ICP-MS	0.1	0.1	<0.02	<0.02	0.1	2.1	0.2
Ce	ppb	ICP-MS	<0.01	<0.01	0.1	0.1	0.1	0.2	0.04
Co	ppb	ICP-MS	1.2	1.3	0.05	0.03	0.1	0.4	0.06
Cs	ppb	ICP-MS	0.1	0.2	0.03	0.03	0.03	0.04	0.01
Cu	ppb	ICP-MS	0.5	<0.5	<0.5	<0.5	0.9	10	1
Dy	ppb	ICP-MS	<0.005	<0.005	<0.005	0.007	<0.005	0.03	<0.005
Er	ppb	ICP-MS	<0.005	<0.005	0.007	<0.005	<0.005	0.01	<0.005
Eu	ppb	ICP-MS	<0.005	<0.005	0.006	<0.005	<0.005	0.007	<0.005
Fe	ppb	ICP-AES	110	120	81	120	220	8,400	490
Ga	ppb	ICP-MS	<0.02	<0.02	<0.02	<0.02	<0.02	0.02	<0.02
Gd	ppb	ICP-MS	<0.005	<0.005	0.02	0.01	0.009	0.05	0.005
In	ppb	ICP-MS	<0.01	<0.01	<0.01	<0.01	<0.01	0.2	<0.01
K	ppm	ICP-AES	0.95	0.92	0.62	0.49	0.57	0.57	0.23
La	ppb	ICP-MS	<0.01	<0.01	0.05	0.06	0.05	0.09	0.02
Li	ppb	ICP-MS	0.9	<0.5	1	<0.5	1	<0.5	<0.5
Mg	ppm	ICP-AES	28	28	8.1	8.6	9.6	14	4.4
Mn	ppb	ICP-MS	550	460	4.2	5.7	43	830	68
Mo	ppb	ICP-MS	2.4	2.7	0.2	0.2	0.2	0.09	0.07
Na	ppm	ICP-AES	1.8	1.7	2	1.8	2	1.7	0.67
Nd	ppb	ICP-MS	<0.01	<0.01	0.06	0.06	0.04	0.1	0.02
Ni	ppb	ICP-MS	0.5	0.9	<0.1	<0.1	<0.1	0.8	0.4
P	ppb	ICP-MS	<1	<3	19	16	16	15	<3
Pb	ppb	ICP-MS	18	18	0.3	0.2	7.9	280	20
Pr	ppb	ICP-MS	<0.01	<0.01	<0.01	0.01	0.01	0.03	<0.01
Rb	ppb	ICP-MS	1.8	1.9	0.83	0.83	0.74	0.98	0.4
Re	ppb	ICP-MS	0.05	0.03	<0.02	<0.02	<0.02	<0.02	<0.02
Sb	ppb	ICP-MS	2.4	1.9	<0.03	0.04	0.22	1.8	0.3
Se	ppb	ICP-MS	0.3	<0.4	<0.8	<0.4	<0.8	<0.4	<0.4
Si	ppm	ICP-AES	3.1	3.1	4.2	4	4.10	3.9	1.5
Sm	ppm	ICP-MS	<0.01	<0.01	<0.01	<0.01	<0.01	0.02	<0.01
Sr	ppb	ICP-MS	70	71	100	96	97	97	37
Th	ppb	ICP-MS	<0.005	<0.007	<0.03	<0.007	<0.03	0.02	<0.007
Ti	ppb	ICP-MS	0.2	n.d.	<0.05	n.d.	<0.05	n.d.	n.d.
Tl	ppb	ICP-MS	0.2	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
U	ppb	ICP-MS	0.29	0.33	0.13	0.13	0.13	0.14	0.06
V	ppb	ICP-MS	0.1	<0.2	0.3	<0.2	0.1	0.2	<0.2
W	ppb	ICP-MS	0.2	0.03	0.03	<0.02	<0.02	<0.02	<0.02
Y	ppb	ICP-MS	<0.01	<0.01	0.04	0.06	0.03	0.2	0.03
Yb	ppb	ICP-MS	<0.01	<0.01	<0.01	<0.01	<0.01	0.02	<0.01
Zn	ppb	ICP-MS	240	220	0.9	0.8	31	480	45

¹Unfiltered, acidified waters. ppb, parts per billion; ppm, parts per million; see Appendix B for explanation of methods; NA, not applicable. Elements sought, but below detection limits for all samples: Au, B, Be, Cr, Ge, In, Tb, and Tm.

Table 8. Geochemical data for leachates of mine waste, mill tailings, and slag.¹

Sample	02JH99	05JH99	06JH99	08JH99	09JH99	45BV00		
Final leach pH	8.7	8.6	8.5	8.5	8.0	6.0		
Conductivity (µS/cm)	250	480	410	170	240	6.9		
	<u>Units</u>	<u>Method</u>	<u>Leachate chemistry</u>					
Alk	ppm	TI	32	30	23	19	11	0
F ⁻	ppm	IC	<0.08	0.2	0.4	<0.08	<0.08	n.d.
Cl ⁻	ppm	IC	0.09	0.1	0.09	<0.08	<0.08	0.1
SO ₄ ²⁻	ppm	IC	100	250	190	66	110	1.7
NO ₃ ⁻	ppm	IC	0.5	<0.08	<0.08	<0.08	<0.08	n.d.
Al	ppb	ICP-MS	1.9	1.6	0.75	0.5	0.3	2.1
As	ppb	ICP-MS	0.6	0.9	0.6	0.5	0.7	4.6
B	ppb	ICP-AES	<5	<5	<5	<5	7.7	n.d.
Ba	ppb	ICP-MS	7.6	4	41	2	3	12
Bi	ppb	ICP-MS	<0.1	<0.1	0.2	<0.1	<0.1	<0.01
Ca	ppm	ICP-AES	19	21	74	10	5.1	0.6
Cd	ppb	ICP-MS	0.2	1.2	6.3	1.2	0.1	0.5
Cs	ppb	ICP-MS	<0.01	0.01	1.2	<0.01	<0.01	0.01
Co	ppb	ICP-MS	0.02	<0.02	<0.02	<0.02	<0.02	0.04
Cu	ppb	ICP-MS	0.7	0.6	0.9	<0.5	<0.5	7
Fe	ppb	ICP-MS	16	20	n.d.	8.2	10	5.9
Ge	ppb	ICP-MS	<0.02	<0.02	0.03	<0.02	<0.02	<0.02
K	ppm	ICP-AES	0.36	0.29	0.89	0.12	<0.1	0.076
Li	ppb	ICP-MS	<0.1	0.2	<0.1	0.2	<0.1	<0.2
Mg	ppm	ICP-AES	18	48	2.8	11	26	0.05
Mn	ppb	ICP-MS	<0.03	19	11	14	3.6	78
Mo	ppb	ICP-MS	<1	1	1	<1	<1	0.05
Na	ppm	ICP-AES	<0.1	0.15	0.24	<0.1	<0.1	0.03
Pb	ppb	ICP-MS	1.5	0.85	30	1.2	1.2	1,200
Rb	ppb	ICP-MS	0.3	0.3	4.4	0.1	0.1	0.2
Sb	ppb	ICP-MS	2.8	0.96	0.87	0.6	0.83	58
Se	ppb	ICP-MS	<0.5	<0.5	4	<0.5	<0.5	<0.2
Si	ppm	ICP-AES	<0.1	<0.1	0.46	<0.1	<0.1	n.d.
Sr	ppb	ICP-MS	32	21	69	5.8	3.9	12
U	ppb	ICP-MS	<0.005	<0.005	0.007	<0.005	<0.005	0.01
Zn	ppb	ICP-MS	4	27	20	58	4	46

¹Hageman field leach method (Hageman and Briggs, 2000). Results are for filtered (0.45 micron), acidified water samples. Alk, alkalinity; µS/cm, microsiemens per centimeter; ppb, parts per billion; ppm, parts per million; n.d., not determined; see Appendix for explanation of methods and detection limits. Refer to table 4 for sample descriptions. Elements sought, but below detection limits for all samples: Ag, Au, Be, Ce, Cr, Dy, Er, Eu, Ga, Gd, Hg, Ho, In, La, Nd, Ni, P, Pr, Re, Sm, Tb, Th, Tl, Tm, V, W, Y, and Yb.

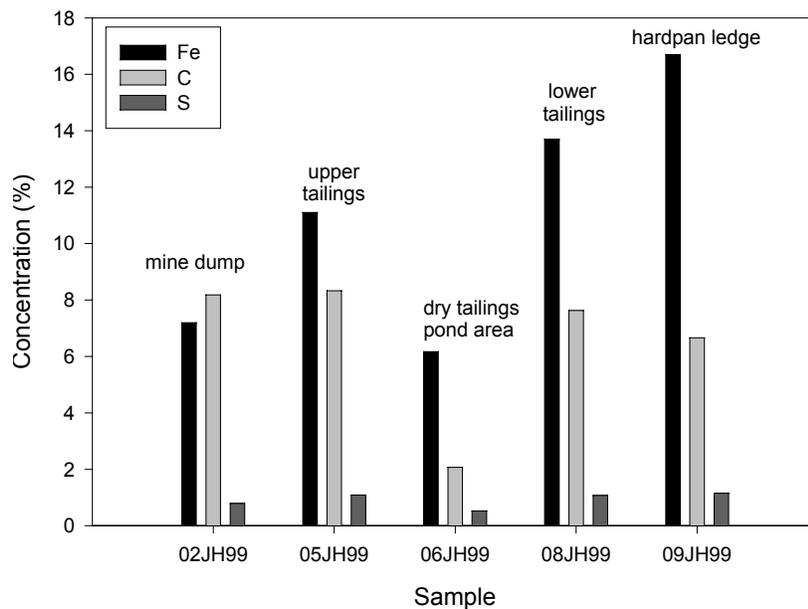
Discussion

The Clayton mine represents a polymetallic, carbonate-hosted replacement deposit (Foley and others, 2000; Plumlee and others, 1995). Mine waste and mill tailings reflect the chemistry and mineralogy of the deposit. For example, although the solid mine wastes and mill tailings are somewhat heterogeneous (Fig. 11, table 3), total carbon exceeds total sulfur in all of the samples and lead and zinc dominate the base-metal suite (Fig. 11B). Pyrite is identified in some of the mine waste material and is reported as a dominant gangue mineral (Hillman, 1986), but siderite is ubiquitous and accounts for much of the total iron. Hillman (1986) showed that the siderite is Mg-rich, rather than end-member FeCO_3 . Siderite can generate acid if hydrous oxides are formed, and complicate acid-base accounting by contributing a false indication of neutralization potential by some accounting methods (White and others, 1999). The primary ore minerals at Clayton, galena and sphalerite, are monosulfide minerals that typically do not produce acid when oxidized by oxygen (Plumlee, 1999), although they may be acid-generating when oxidized by ferric iron. All of the observed pH measurements (paste pH measurement on mine waste and mill tailings, adit water, surface water in Kinnikinic Creek, and leachates) are near-neutral, and the acid-neutralizing minerals dolomite and calcite are ubiquitous in the mine waste, mill tailings, and in host rock. Any acidity generated by oxidation of pyrite or other sulfide minerals appears to be readily neutralized, and therefore, acid mine drainage is not a concern at this site. However, some metals, such as zinc or manganese, can have enhanced mobilities at near-neutral pH resulting in elevated dissolved metal concentrations in waters associated with some carbonate-hosted polymetallic replacement deposits (Fig. 12).

Lead exceeds zinc in the mine waste dump composite (02JH99); in all of the surface samples from the flotation mill tailings, zinc exceeds lead (Fig. 11). Similarly, the unprocessed mine dump waste (02JH99) contains more silver than the other composite samples (table 3). This probably reflects efficient removal of lead and silver during ore processing, leaving relatively zinc-rich, lead-poor mill tailings. The elevated lead concentration of the composite mine waste dump sample should be factored into any plans to move mine waste (Fig. 3) or to use it to cap finer-grained adjacent mill tailings. The concentration of readily leachable lead from the mine waste dump sample (1.5 ppb) is lower than the leachable lead from the dry pond on mill tailings (30 ppb), but greater than all of the other mill tailings samples. Fine-grained (<80 mesh, < 0.77 mm) fractions of sediments in Kinnikinic Creek downstream from the mine contain 75 times as much lead and 40 times as much zinc, and more than 10 times as much arsenic and antimony as sediments upstream (background sample site) of the mine area (table 4).

The Clayton adit drainage plots in the near-neutral, low-metal field on a Ficklin diagram (pH versus dissolved base metals, Fig. 12). The Clayton adit drainage signature is similar to drainages from other carbonate-hosted, pyrite-poor polymetallic replacement deposits (Plumlee and others, 1999). Waters associated with pyrite-rich, carbonate-hosted deposits, such as those at Leadville, CO, typically plot in the near-neutral, high- or extreme-metals fields (Fig. 12). Comparison of our 1999-2000 Clayton adit discharge data with data reported by EPA (1999) for samples taken in August 1985 indicate that the adit discharge chemistry has changed dramatically over time. The 1985 samples were collected when the mine was still active and the lower levels were being de-watered. Underground flooding associated with the 1983 Borah Peak earthquake necessitated increased pumping during the last years of the mine life. Unfiltered adit waters from 1985 contained as much as 2,390 $\mu\text{g/L}$ zinc, 4,490 $\mu\text{g/L}$ lead, 290 $\mu\text{g/L}$ copper, and 9.5 $\mu\text{g/L}$ cadmium. Unfiltered adit discharge data for 1999 and 2000 (table 7D, sample site 1)

A



B

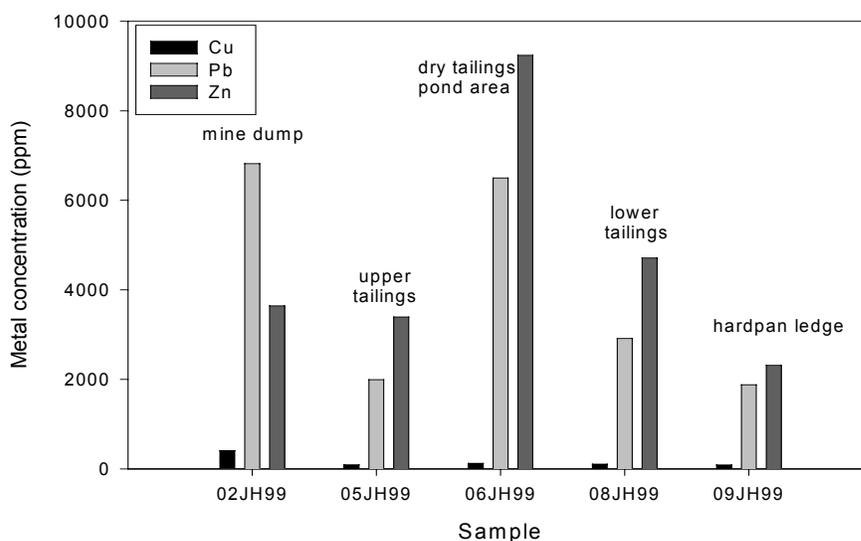


Figure 11. Bar graphs showing metal concentration in composite mine waste dump material and mill tailings (< 2 mm fraction). A, Iron, total carbon, and total sulfur (wt. %), B, Copper, lead, and zinc in parts per million (ppm).

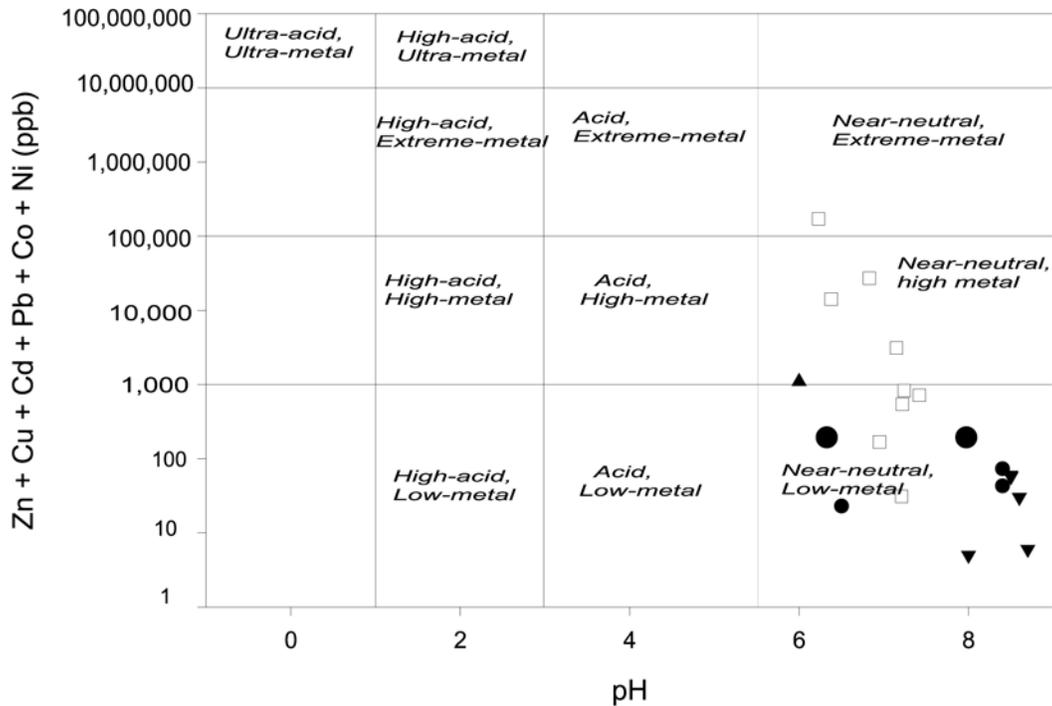


Figure 12. Ficklin diagram showing the sum of dissolved base-metal concentrations in Clayton adit drainage (large filled circles), Kinnikinic Creek surface water downstream from the Clayton mine (small filled circles), mine waste and mill tailings leachates (inverted triangles), and slag leachate (upright triangle) as a function of pH. Water data from the literature on other carbonate-hosted polymetallic replacement deposits (open squares) are shown for comparison (Plumlee and others, 1999). Boundaries and names of fields are from Plumlee and others (1992). Parts per billion (ppb) and micrograms per liter ($\mu\text{g/L}$) are equivalent concentration units.

show that concentrations for these metals are 1 to 2 orders of magnitude lower than the metal concentrations reported from 1985.

Kinnikinic Creek water downstream from the mine site has about the same pH, but lower total dissolved metals than the adit water. The upstream sample concentrations for this suite of metals were all below the detection limits and are not plotted on figure 12. Leachates from mine waste and mill tailings (Fig. 12) are all more alkaline than the adit and creek waters. Leachate from smelter slag along the Salmon River had the lowest pH and highest base-metal concentrations of any of the water samples or leachates. Kinnikinic Creek is near-neutral above and below the Clayton mine site; acid-mine drainage is not a problem at Clayton. Wind erosion caused fine-grained mill tailings dunes to migrate along the Kinnikinic Creek valley (Fig. 13). In the 1990s, potential health threats to the Clayton residents were evaluated and a playground area that had previously served as a pad for storing ore concentrates was cleaned up (BLM, 2000). Prior to EPA's completion of a time-critical removal action in 2001, the solid materials on the site posed the biggest environmental concern. Removal activities implemented in 2001 were designed to mitigate continued erosion and stabilize tailings. The ecosystem effects of the smelter and the influx of sediment from the Clayton mine have not yet been fully evaluated, but may be factor in the success of any future attempts to restore fish habitat along the Salmon River.



Figure 13. Wind blowing fine mill tailings from lowermost mill tailings pile, Clayton mine. Photograph taken in late afternoon on August 7, 2000; view is to the northwest from Kinnikinic Creek at site 99CH017. Water in Kinnikinic Creek was murky and tan-colored (turbidity 42 FTU, a value 14 times higher than the 1999 turbidity value of 3.1 FTU, collected under calm conditions, Table 7).

Data presented in this report, along with data collected by EPA and BLM in developing site mitigation plan (EPA 1999, 2000a, 200b, 2001; BLM, 2000) provide baseline data on the post-mining, pre-reclamation environmental signature of a carbonate-hosted polymetallic base-metal replacement deposit that was mined in modern times. These types of deposits are significant sources of lead, zinc, and silver worldwide. Waters associated with such replacement deposits tend to be near-neutral and contain relatively low concentrations of base metals compared to waters associated with many other types of mineral deposits. Erosion of solid mine wastes and mill tailings associated with carbonate-hosted polymetallic base metal replacement deposits however, can contribute sediment and airborne particles that impact aquatic and terrestrial ecosystems and pose potential human health threats.

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APPENDIX A: Sample locations¹

Field sample number	Laboratory number	Sample media	Location/Description	Latitude	Longitude
99CH015	C-137522	water	Clayton mine adit drainage	44° 16' 51.9"	114° 24' 36.7"
99CH016	C-137552	water, sediment	Kinnikinic Creek upstream of Clayton mine	44° 16' 57.9"	114° 24' 37.9"
99CH017	C-137555	water, sediment	Kinnikinic Creek downstream of Clayton mine and mill	44° 16' 27.8"	114° 24' 28.8"
00CH53	C-176670	water	Kinnikinic Creek upstream of Clayton mine	44° 16' 57.9"	114° 24' 37.9"
00CH54	C-176686	water	Clayton mine adit drainage	44° 16' 51.9"	114° 24' 36.7"
00CH55	C-176676	water	Kinnikinic Creek downstream of Clayton mine and mill	44° 16' 27.8"	114° 24' 28.8"
00CH56	C-176675	water	Kinnikinic Creek downstream of Clayton mine and mill	44° 16' 5.9"	114° 24' 14.4"
01JH99	None	mineral	White salts on mine waste dump; location given is for the top of the dump	44° 16' 48.9"	114° 24' 35.1"
02JH99	C-153096	mine waste, leachate	Mine waste dump; location given is for the top of the dump	44° 16' 48.9"	114° 24' 35.1"
05JH99	C-153109	mill tailings, leachate	Upper part of mill tailings pile	44° 16' 34.2"	114° 24' 30.2"
06JH99	C-153100	mill tailings, leachate	White crust in dry pond on top of mill tailings pile	44° 16' 34.2"	114° 24' 30.2"
07JH99	None	mineral	Salt crust on top surface of mill tailings pile	44° 16' 34.2"	114° 24' 30.2"
08JH99	C-153091	mill tailings, leachate	Lower part of mill tailings pile	44° 16' 34.2"	114° 24' 30.2"
09JH99	C-153095	hardpan, leachate	Hardpan ledge on east slope of the mill tailings pile above Kinnikinic Creek	44° 16' 34.2"	114° 24' 30.2"
01BV99	C-137991	rock	Host rock adjacent to mine workings	44° 16' 51.6"	114° 24' 44.5"
02BV99	C-137992	rock	Clayton mine ore	44° 16' 48"	114° 24' 36.2"
03BV99	C-137993	rock	Clayton mine ore	44° 16' 48"	114° 24' 36.2"
04BV99	C-137994	rock	Clayton mine ore	44° 16' 48"	114° 24' 36.2"
05BV99	C-137995	rock	Clayton mine ore	44° 16' 48"	114° 24' 36.2"
40BV00	C-175672	rock	Clayton mine ore	44° 16' 48"	114° 24' 36.2"
42BV00	C-175673	rock	Clayton mine ore	44° 16' 48"	114° 24' 36.2"
43BV00	C-175674	rock	Ella Dolomite on talus slope 0.3 mi N of Clayton mine site	44° 17' 5.8"	114° 24' 43.2"
45BV00	C-175676	slag, leachate	Slag pile along the Salmon River at the town of Clayton	44° 15' 29.4"	114° 24' 7.7"

¹Mine waste and mill tailings represent composite samples; see tables in text for additional sample information. Latitude and longitude by GPS referenced to WGS84 datum. Laboratory numbers refer to samples submitted for geochemical analysis and entered into the National Geochemical Database.

APPENDIX B: Summary of Analytical Methods

In this study, Quality Assurance/Quality Control concerns for solid media were addressed through the use of blind reference materials (accuracy) and analytical duplicates (precision). Reference standards were interspersed with batches of samples and the analyses of the reference standards were checked to assure that the reported values were within ± 20 percent of accepted values. Analytical duplicates were interspersed with batches of samples and the analyses of the duplicates were checked to assure that the relative standard deviation (RSD) between duplicates was no greater than ± 20 percent.

Chemical analyses of the stream sediment and mine dump materials were performed by XRAL Laboratories of Don Mills, Ontario, Canada, under a contract with the USGS following analytical methods described in Arbogast (1996). The analytical methods and techniques that were used are described below. In the discussion below and the attached data files:

- “ppm” signifies parts per million,
- “ppb” is parts per billion,
- “%” is weight percent of the sample, and
- “<” represents a less than value below the specified lower limit of determination.

METHODS USED ON SOLID MEDIA (ROCK, MINE WASTE, AND SEDIMENTS)

40 Element ICP-AES

Forty major, minor, and trace elements were determined in geological materials by inductively coupled plasma-atomic emission spectrometry (ICP-AES). The sample (0.2 g) is decomposed using a mixture of hydrochloric, nitric, perchloric, and hydrofluoric acids at low temperature. The digested sample is aspirated into the ICP-AES discharge where the elemental emission signal is measured simultaneously for the forty elements. Calibration is performed by standardizing with digested rock reference materials and with a series of multi-element solution standards. Upper and lower determination limits for this method are listed below in table A1.

Analytical Performance: Data were deemed acceptable if recovery for all 40 elements was $\pm 15\%$ at five times the Lower Limit of Determination (LOD) and the calculated Relative Standard Deviation (RSD) of duplicate samples was no greater than 15%.

Table B1. Reporting limits for 40 elements by ICP-AES:

Element	Lower Determination Limit	Upper Determination Limit
Weight Percent		
Al	0.005	50
Ca	0.005	50
Fe	0.02	25
K	0.01	50
Mg	0.005	5
Na	0.005	50
P	0.005	50
Ti	0.005	25
Parts Per Million		
Ag	2	10,000
As	10	50,000
Au	8	50,000
Ba	1	35,000
Be	1	5,000
Bi	10	50,000
Cd	2	25,000
Ce	5	50,000
Co	2	25,000
Cr	2	25,000
Cu	2	15,000
Eu	2	5,000
Ga	4	50,000
Ho	4	5,000
La	2	50,000
Li	2	50,000
Mn	4	50,000
Mo	2	50,000
Nb	4	50,000
Nd	9	50,000
Ni	3	50,000
Pb	4	50,000
Sc	2	50,000
Sn	5	50,000
Sr	2	15,000
Ta	40	50,000
Th	6	50,000
U	100	100,000
V	2	30,000
Y	2	25,000
Yb	1	5,000
Zn	2	15,000

Hydride Generation AA for As, Sb, Se, Te, and Tl

Arsenic, antimony, and thallium are determined by weighing 0.1 g of sample into a zirconium crucible. Approximately 0.75 g of sodium peroxide is added and mixed. The mixture is heated in a muffle furnace set at 750°C for four minutes. The sample is cooled, then 15 ml of water and 5 ml of concentrated HCl is added. The mixture is shaken and 0.25 ml of an ascorbic acid KI solution is added, then diluted with 20% HCl and let to stand overnight. Arsenic, selenium, and thallium are then measured using hydride generation atomic absorption spectrometry (Hydride AA). The optimum concentration ranges without sample dilution for these elements in various solid phase sample media are: As—0.6 ppm to 20 ppm, Sb—0.6 ppm to 20 ppm, and thallium—0.1 ppm to 10 ppm.

Selenium and tellurium are determined by weighing 0.25 g of sample into a test tube, adding a mixture of nitric and perchloric acids and heating. After the solution is cooled, hydrochloric and nitric are added, heated again and cooled. The samples are diluted and analyzed using hydride generation atomic absorption spectrometry. The expected analytical range for selenium is 0.2 to 4 ppm, and the lower reporting limit for tellurium is 0.1 ppm.

Analytical Performance: Data were deemed acceptable if recovery of As and Sb was $\pm 20\%$ at five times the LOD and the calculated percent RSD of duplicate samples was no greater than 20%. Data for selenium were deemed acceptable if recovery of that element was $\pm 20\%$ at five times the LOD and the calculated percent RSD of duplicate samples was no greater than 20%. Data for tellurium were deemed acceptable if recovery of that element was $\pm 15\%$ at five times the LOD and the calculated percent RSD of duplicate samples was no greater than 15%.

Gold by Fire Assay

Gold was determined by DCP or atomic absorption spectrophotometry after collection by fire assay. An assay fusion consists of heating a 15 g mixture of the finely pulverized sample with about three parts of a flux until the product is molten. One of the ingredients of the flux is a lead compound, which is reduced by other constituents of the flux or sample to metallic lead. The latter collects all the gold, together with silver, platinum metals, and small quantities of certain base metals present in the sample and falls to the bottom of the crucible to form a lead button. The gangue of the ore is converted by the flux into a slag sufficiently fluid so that all particles of lead may fall readily through the molten mass. The choice of a suitable flux depends on the character of the ore. The lead button is cupelled to oxidize the lead, leaving behind a dore bead containing the precious metals. The dore bead is then transferred to a test tube, dissolved with aqua regia, diluted to a specific volume and determined by DCP or atomic absorption spectrophotometry. The lower reporting level for a 15 g sample charge is 5 ppb by DCP and atomic absorption. The upper reporting limit is 10,000 ppb.

Analytical Performance: Data were deemed acceptable if recovery of gold was $\pm 20\%$ at five times the LOD and the calculated percent RSD of duplicate samples was no greater than 20%.

Hg Analyses of Separated Cold Vapor (Cold Vapor Hg)

Mercury was determined by weighing out 0.1 g of sample, which was digested with a mixture of sulfuric acid, nitric acid, 5% potassium permanganate, and 5% potassium peroxydisulfate in a water bath for one hour. The excess of potassium permanganate is reduced with hydroxylamine sulfate solution and then Hg (II) is reduced with stannous chloride. The Hg vapor is separated and measured using a LEEMAN PS200 automated mercury analyzer. The

technique offers a lower reporting limit of 0.02 ppm mercury in solid-phase samples. Samples exceeding the working range of 0.02 - 1.8 ppm mercury require dilution.

Analytical Performance: Data were deemed acceptable if recovery of mercury was $\pm 20\%$ at five times the LOD and the calculated percent RSD of duplicate samples was no greater than 20%.

Total Carbon Analyses

Total carbon was determined by the use of an automated carbon analyzer. A weighed sample (0.25 g sample used) is combusted in an oxygen atmosphere at 1370°C to oxidize carbon to carbon dioxide. Moisture and dust are removed and the carbon dioxide gas is measured by a solid state infrared detector. The operating range for total carbon is from 0.05% to about 30%.

Analytical Performance: Data were deemed acceptable if recovery of total carbon was $\pm 15\%$ at five times the LOD and the calculated percent RSD of duplicate samples was no greater than 15%.

Total Sulfur Analyses (LECO)

Total sulfur was determined by using an automated sulfur analyzer. Approximately 0.25 g of sample is mixed with iron chips and LECOCEL and is heated in a combustion tube in a stream of oxygen at high temperature. Sulfur is oxidized to sulfur dioxide. Moisture and dust are removed and then the sulfur dioxide gas is measured with a CS-244 infrared detector. The reporting range for total sulfur is from 0.05% to about 35%.

Analytical Performance: Data were deemed acceptable if recovery of total sulfur was $\pm 15\%$ at five times the LOD and the calculated percent RSD of duplicate samples was no greater than 15%.

METHODS USED ON WATER AND LEACHATE SAMPLES

In this study, Quality Assurance/Quality Control concerns for water samples were addressed through the use of internal reference standards, field blanks, site duplicates, and analytical duplicates. Reference standards were interspersed with batches of samples and the analyses of the reference standards were checked to assure that reported values were within ± 20 percent of the accepted values. Water samples included field blanks of de-ionized water, used to check for contamination from sampling equipment and preservatives. Field blanks were collected following the same procedures as those used for normal water samples. For all analytical methods used on water samples listed below, data were deemed acceptable if recovery was $\pm 20\%$ at five times the LOD and the calculated percent RSD of duplicate samples was no greater than 20%.

27 Elements by inductively coupled plasma-atomic emission spectrometry (ICP-AES)

Acidified water samples were analyzed for major (Al, Ca, Fe, K, Mg, Na, and Si) and selected trace elements following the inductively coupled plasma-atomic emission spectrometry (ICP-AES) method of Briggs and Fey (1996). Water samples were aspirated into a plasma and element concentrations were determined directly by ICP-AES. Limits of determination for the multi-element ICP-AES method for water samples are shown in the table A2.

Table B2. Reporting limits for the multi-element ICP-AES method for water samples.

Element	Lower Determination Limit	Upper Determination Limit
Parts Per Million		
Al	0.01	1,000
Ca	1	1,000
Fe	0.02	1,000
K	1	1,000
Mg	1	1,000
Na	1	1,000
P	0.1	1,000
Si	1	1,000
Parts Per Billion		
Ag	10	10,000
As	100	10,000
B	5	10,000
Ba	5	10,000
Be	5	10,000
Cd	5	10,000
Cr	10	10,000
Co	10	10,000
Cu	10	10,000
Li	10	10,000
Mn	10	10,000
Mo	20	10,000
Ni	10	10,000
Pb	50	10,000
Sb	50	10,000
Sr	1	10,000
Ti	50	10,000
V	10	10,000
Zn	10	10,000

Ion Chromatography (IC)

The anions Cl^- , F^- , NO_3^- , and SO_4^{2-} were determined sequentially by ion chromatography on unfiltered, unacidified water samples following a modification (d'Angelo and Ficklin, 1996) of the procedure of Fishman and Pyen (1979). The raw water samples were kept cool from the time of collection until they were analyzed. The samples were injected into a chromatograph where ions of interest separate along an ion exchange separator column at different rates, depending on the affinity of each species for the ion-exchange resin. Samples then passed into a flow-through conductivity cell where the anions were detected and their peak heights were recorded. Unknown samples were compared with peak heights of reference standards to

determine sample concentrations. Limits of determination for anions in raw water samples are shown in the table B3.

Table B3. Reporting limits for anions in raw water samples by sequential ion chromatography.

Anion	Lower Determination Limit	Upper Determination Limit ¹
Parts Per Million		
Cl ⁻	0.1	4
F ⁻	0.05	2
NO ₃ ⁻	0.1	10
SO ₄ ²⁻	0.5	20

Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)

Acidified-filtered and acidified-unfiltered waters, and leachates were analyzed to determine 52 elements by ICP-MS using a method developed by the U.S. Geological Survey (A.L. Meier, personal commun., 1995; Meier and others, 1994). The method is used to determine numerous elements directly in the water sample without the need for preconcentration or dilution. Element detection limits are in the sub-part-per-billion range and the working linear range is six orders of magnitude or more. By using derived response curves, percent of ionization, and natural isotopic abundances, estimates of concentrations for the elements can be determined in samples without the need of a calibration standard for every element. The method is most useful for trace elements in the parts-per-billion range; analyses for major elements in the parts-per-million range are less accurate and ICP-AES data should be used. Limits of determination for elements by ICP-MS are shown in the table B4.

Mercury by Cold Vapor Atomic Absorption (CVAC)

Mercury was measured in water samples using the cold-vapor AAS technique of O'Leary and others (1996). Preserved water samples were analyzed directly. Mercury (II) was reduced in the solutions to elemental mercury gas with hydroxylamine hydrochloride and stannous chloride in a continuous flow system, releasing mercury into the quartz cell of an atomic absorption spectrophotometer where the mercury concentration was determined. Limits of determination are shown in the table B5.

Ferrous Iron by Colorimetry (IC)

Ferrous iron was determined by colorimetry, using a microprocessor-controlled, single beam Hach spectrophotometer. Samples were introduced into an AccuVac Ampul and mixed quickly. Phenanthroline in the ampul reacts with ferrous iron in the sample to form an orange color in proportion to the ferrous iron concentration. Ferric iron does not react. The ampul was then placed into the spectrophotometer and concentration was measured. For concentrations higher than 3 ppm, solutions were diluted and re-analyzed. Limits of determination are shown in the table B5.

Table B4. Limits of determination for elements in water samples by the ICP-MS method.

Element	Lower Determination Limit ¹	Element	Lower Determination Limit ¹
Parts per million (ppm)		Parts per billion (ppb)	
Ca	0.05	K	0.30
Mg	0.01	La	0.01
Na	0.01	Li	0.10
Si	0.25	Mn	0.01
Parts per billion (ppb)		Mo	0.02
Ag	0.01	Nd	0.01
Al	0.01	Ni	0.10
As	0.20	P	1
Au	0.01	Pb	0.05
Ba	0.02	Pr	0.01
Be	0.05	Rb	0.01
Bi	0.01	Re	0.02
Cd	0.02	Sb	0.03
Ce	0.01	Se	0.8
Co	0.02	Sm	0.01
Cr	1.0	Sr	0.02
Cs	0.02	Tb	0.005
Cu	0.50	Th	0.03
Dy	0.005	Ti	0.05
Er	0.005	Tl	0.05
Eu	0.005	Tm	0.005
Fe	30	U	0.01
Ga	0.02	V	0.10
Gd	0.005	W	0.02
Ge	0.02	Y	0.01
Ho	0.005	Yb	0.01
In	0.01	Zn	0.50

Alkalinity by Titration (TI)

On-site alkalinity tests were done on all samples collected throughout the study, using a field-portable CHEMetrics titration kit. For comparison, water samples were also collected for laboratory alkalinity determination. For the laboratory alkalinity, an Orion 960 Autochemistry System was used for endpoint titration analysis. The titrant was added to 50 ml of sample until a pH of 4.5 was achieved. Alkalinity was then calculated and reported in units of ppm as CaCO₃. Limits of determination are shown in the table B5.

Table B5. Lower and upper determination limits for mercury by the cold-vapor AAS techniques, ferrous iron by colorimetry, and alkalinity by titration.

Element	Method	Lower Determination Limit	Upper Determination Limit
Hg	CV	0.1 ppb	None ¹
Fe ²⁺	CO	0.01 ppm	None ¹
Alkalinity	TI	1.0 ppm	None ¹

¹ Samples with high concentrations were diluted and re-analyzed.