GEOCHEMICAL CHARACTERIZATION OF MINE WASTE FROM THE PIKE HILL SUPERFUND SITE IN VERMONT, USA[1]

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Abstract. The Pike Hill mines Superfund site consists of a group of mines that worked copper-rich Besshi-type massive sulfide deposits. The site contains the abandoned Smith, Eureka, and Union mines and was listed in 2004 as a Superfund site due to aquatic ecosystem impacts. This study is part of a larger project that includes mine waste characterization, surface-water geochemical studies, and documentation of downstream impacts on biota. It is intended to be a precursor to a formal remedial investigation by the U.S. Environmental Protection Agency (USEPA). The goal of this paper is to provide a relative comparison of the various waste piles through characterization of bulk geochemistry, mineralogy, paste pH, acid-base accounting, and metal leachability. In addition, results were compared to similar studies of mine waste from the nearby Ely and Elizabeth Superfund sites. Mine-waste samples at the Pike Hill mines include flotation-mill tailings and waste rock that is composed of fine-grained to boulder-sized host rock and mineralized rock. The waste is primarily composed of silicates, oxides, sulfates, and sulfides, including pyrrhotite, pyrite, chalcopyrite, and sphalerite. Samples locally contain native sulfur and calcite; efflorescent sulfate salts have been observed on waste piles and adit walls. Composite mine-waste samples contain concentrations of Cd, Cu, and Fe that exceed USEPA Preliminary Remediation Goals (PRGs). The concentrations of Se are elevated relative to the average composition of eastern U.S. soils. All mine-waste samples, except the processed flotation-mill tailings, which contain calcite, have paste pH values of 4 or less and negative net-neutralization potentials indicating the samples are acid generating. Twenty-four-hour leachate tests, which use a solution that approximates eastern U.S. precipitation, indicate that potentially toxic trace elements and acidity can be released under simulated weathering conditions. Mine waste at Pike Hill mines is chemically and mineralogically similar to that at the Elizabeth and Ely mines. Also, metals are leached and acid produced in comparable concentrations. Based on the results of this study, mine waste at the Pike Hill Superfund site contaminates soils, is acid generating, and may release potentially toxic metals to streams.

Additional Key Words: cadmium, copper, leachate, massive sulfide, metals, sulfides, Superfund, tailings, toxicity, zinc.

Introduction

The Pike Hill Superfund site, which includes the Smith (formerly named Bicknell), Eureka (formerly named Corinth), and Union mines, is located in the Vermont copper belt and was placed on the U.S. Environmental Protection Agency (USEPA) National Priorities List in July, 2004 due to aquatic ecosystem impacts. The Elizabeth and Ely mines in the Vermont copper belt are also listed on the National Priorities List. This report focuses on the Pike Hill mines site located primarily on the summit and northeast slope of Pike Hill in Corinth, Vermont (Fig. 1). The site encompasses about 87.4 hectares (216 acres) and contains approximately 18,000 metric tons (20,000 U.S. tons) of mill and mine dumps, averaging 1.6% Cu (U.S. Environmental Protection Agency, 2004a). The underground mines operated intermittently between 1847 and 1919 and were the only site in the Vermont copper belt where magnetic ore separation was successful. Mine elevations range from approximately 1,640 feet above mean sea level (MSL), at the Smith mine, to approximately 1,965 feet above MSL, at the Eureka and Union mines (USEPA, 2004a). The mines contributed an estimated 3,900,000 kg of Cu, which represents about six percent of known production from the Vermont copper belt (Kierstead, 2001). The area contains open mine cuts, trenches, shafts, adits, waste-rock piles including piles of mill tailings, foundations and the remains of an ore cobbing house, a blacksmith shop, the flotation/magnetic separation mill, and a tramway.

Several limited geochemical investigations have been carried out in the Pike Hill area. Gold and anomalous concentrations of Co, Cu, and Zn were found in stream sediments proximal to the site (Slack et al., 1984, 1990). Massive sulfide ore contains high amounts of Cd, Co, Cu, Mn, Se, and Zn (Slack et al., 2001). Leaves of several birch species collected at the site contain anomalous amounts of Cu and Zn (Power and Milton, 1990). Macro-invertebrate and fish populations in surface water downstream of the site have been significantly impaired due to acid mine drainage (U.S. Environmental Protection Agency, 2004a). Thesis projects by two students from Middlebury College in Vermont included geochemical and mineralogical analyses of waste-rock material (Wierscinski, 1999) and iron-oxide precipitates (Totten, 1999).

The USEPA is interested in assessing the potential threats to the aquatic ecosystem and water supplies, and any human health risks associated with the Pike Hill Superfund site as a precursor to a formal remedial investigation. Drainage from the Pike Hill mines site make up the headwaters of Pike Hill Brook, which drains into the Waits River and eventually the Connecticut River. The Waits and Connecticut rivers are used for recreational purposes and contain fisheries. The Elizabeth and Ely mines are in the same mining district and potential threats from these sites are also being evaluated. A preliminary study of the mine waste at Pike Hill was conducted in order to understand better one of the several potential sources of contamination. The goal is to provide a relative comparison and ranking of the various waste piles at the site by investigating the spatial distribution, mineralogy, bulk geochemistry, paste pH, and acid-generating potential of the mine waste as well as the leachability of metals. The results are then compared to studies of mine waste from the Elizabeth and Ely mines. If chemical similarities exist among the sites, remediation schemes developed by the USEPA for one site may be applied to the others.
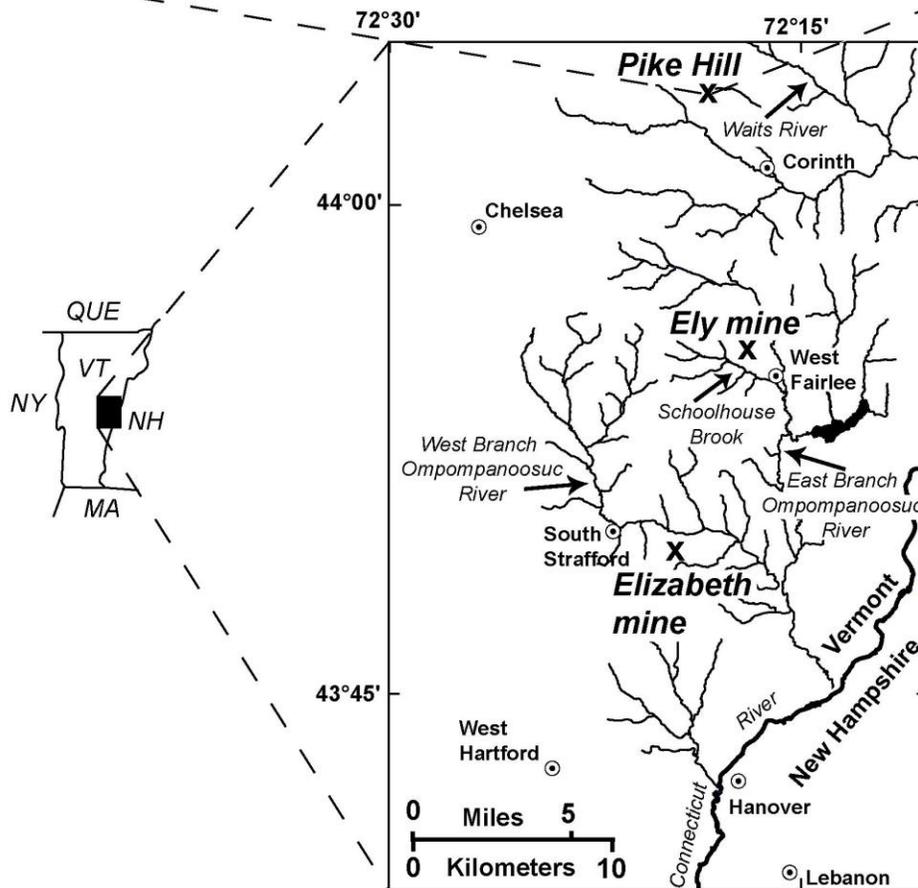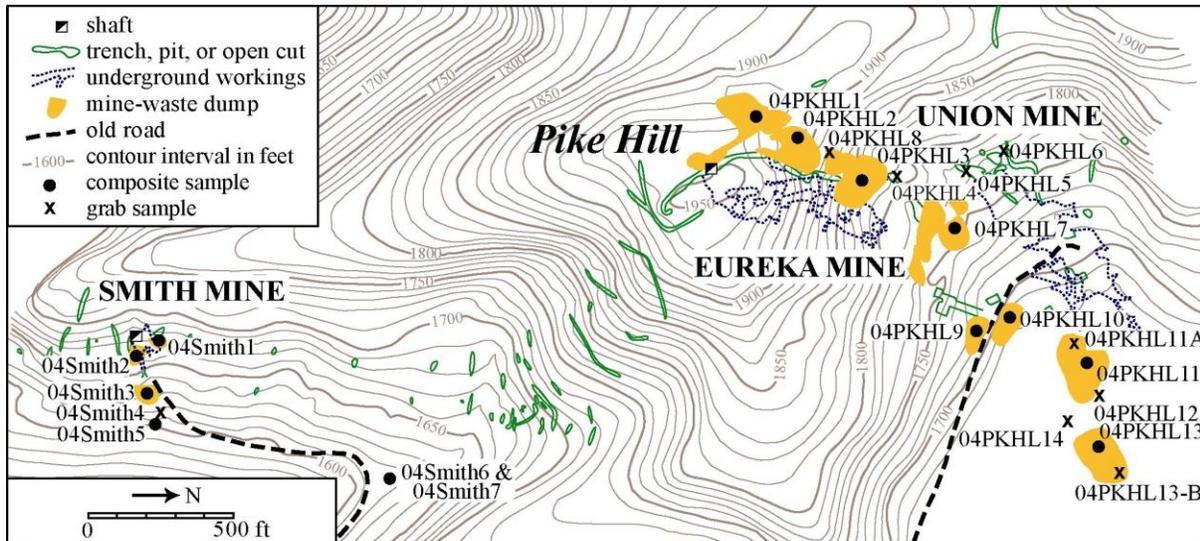
Figure 1. Upper map is the Pike Hill mines showing locations of composite and grab samples collected in October of 2004. Shafts, open cuts, underground workings and mine-waste piles are also shown. Modified from White and Eric (1944). Lower figures show regional locations of Pike, Ely, and Elizabeth mines.

Geologic Setting

The Vermont copper belt contains the Elizabeth, the Ely, and the Pike Hill mines and several other smaller mines and prospects. All three Superfund sites were mined for Besshi-type massive sulfide deposits that are stratabound and generally stratiform and contain massive sulfide ores composed of pyrrhotite, chalcopyrite, and minor sphalerite and pyrite within metasedimentary and minor mafic metavolcanic rocks of Silurian and Devonian age (Slack et al., 1993). The massive sulfides are generally closely associated with amphibolite. The deposits and host rocks were deformed during several stages of folding and amphibolite-grade metamorphism (Slack et al., 1993).

Mining of the Pike Hill area exploited a sheet-like ore zone that strikes a few degrees west of north and dips about 30° east (White and Eric, 1944). The deposits occur in the Silurian Waits River Formation, which consists of calcareous pelite, pelite, minor quartzose metalimestone and metadolostone and sparse calcite marble. In contrast, the Ely and Elizabeth deposits occur in the Early Devonian Gile Mountain Formation, which is characterized by siliciclastic rocks including graphitic pelite and quartzose granofels, and lesser micaceous quartzite, calcareous pelite, hornblende schist, and amphibolite (Slack et al., 1993). The host rock of the Pike Hill deposits contains significant amounts of carbonate minerals and thus has a greater acid-neutralizing capacity when compared to those of the Ely and Elizabeth deposits.

Methods

Samples from mine-waste piles at the Pike Hill mines site were divided based on variations in waste type, color, and geographic location. Eleven surface composites of waste-pile material were collected with a minimum of 30 equal sample increments over a measured area divided into a grid. Surface composites of background and downslope soils consist of three to ten increments. Composite samples were several kilograms in weight. Increments were homogenized, stored in plastic bags, air dried, dry-sieved to <2 mm (soil-size fraction), and split into aliquots by fractional shoveling (Pitard, 1993). The composite sampling protocol was developed by the U.S. Geological Survey (USGS) as a "toolkit" for the rapid screening and characterization of historical mine-waste piles (Smith et al., 2002). The use of the <2 mm size fraction may provide a worst-case scenario because it is likely the most reactive material. This size fraction choice has been shown to reduce the sampling error and reduce the sample size to one reasonable for field collection (Smith et al., 2002). Samples of ferricrete and hardpan were also air dried, sieved to <2 mm, and split. Grab samples collected for mineral-identification purposes only were either stored in plastic bags or sealed plastic vials until analysis.

Bulk geochemical composition

The bulk chemical composition of solid samples was determined using inductively coupled plasma-atomic emission spectrometry (ICP-AES) and inductively coupled plasma-mass spectrometry (ICP-MS) following acid-digestion by a mixture of HCl-HNO_3-$HClO_4$-HF in USGS laboratories in Denver, Colorado (Briggs, 2002a; Briggs and Meier, 2002). The samples were analyzed for Se using hydride-generation atomic absorption spectrometry (HG-AAS) after digestion with a mixture of HNO_3-HF-$HClO_4$ by XRAL Laboratories in Ontario, Canada (Hageman et al., 2002). NIST certified reference materials were analyzed to monitor accuracy and precision.

Mineralogy

Minerals were identified by X-ray diffraction analysis (XRD) in USGS laboratories in Reston, Virginia. The powder patterns were collected using a Scintag X1 automated powder diffractometer equipped with a Peltier detector with CuKα radiation. The XRD patterns were analyzed using Material Data Inc.'s JADE software and standard reference patterns. The relative amount of phases in each pattern was estimated using the Siroquant computer program that utilizes the full XRD profile in a Rietveld refinement (Taylor and Clapp, 1992). Amorphous content was determined using Siroquant on patterns of samples spiked with 15 wt% Al_2O_3. The analytical uncertainty of the Siroquant results is approximately ± 5 wt%.

Evidence for readily soluble salts was evaluated by filtering mine-waste leachates (see below) and evaporating to dryness. Also, 2.0 g of mine waste was mixed with 40 mL of deionized water, shaken, and centrifuged. Water was then decanted and the pH measured. The procedure was repeated on the solid sample with fresh deionized water each day for eight days. The decanted waters were evaporated. Leachate evaporates from both experiments were evaluated using XRD.

Acid-base accounting and paste pH

Acid-base accounting (ABA) is designed to estimate the inherent capacity of a material to produce or to neutralize acid (Sobek et al., 1978). Paste pH provides a quick measure of the relative acid-generation or acid-neutralizing potential of a material. The paste pH method is based on that of Price et al. (1997) and was determined by the USGS laboratories in Reston, Virginia, and the Vizon SciTec. Inc., Vancouver, British Columbia. ABA is numerically quantified as the net-neutralization potential (NNP), which is the difference between the neutralization potential (NP) and the acid-generating potential (AP), and was determined by Vizon SciTec, Inc., using a combination of the Sobek method to determine NP and the modified Sobek method to determine AP (Sobek et al., 1978; White et al., 1999). For this study, NNP less than zero and paste pH less than 4.0 were considered potentially acid-generating (Sobek et al., 1978).

Leach test

The field-leach test developed by Hageman and Briggs (2000) was done on splits of the samples in USGS laboratories in Reston, Virginia. Splits of the <2 mm size fraction were used because this represents the most chemically reactive material in weathered mine waste (Hageman and Briggs, 2000). This size fraction choice may slightly overestimate the leachability of the waste material, but does not appear to "miss" any readily leachable phases (Smith et al., 2002). According to Hageman and Briggs (2000), this procedure is comparable to the EPA Method 1312 (SPLP) and "provides indication of the potential chemical composition of runoff from the weathered surface of [mine-waste] piles." The sample was combined with a solution that approximates eastern United States precipitation (ESP) at a solution to sample ratio of 20:1. A mixture of sulfuric acid and nitric acid was added to deionized water to adjust the pH to 4.2 ± 0.1 to produce the ESP solution (U.S. Environmental Protection Agency, 1994). The mixtures were shaken for five minutes and after 24 hours the pH, specific conductivity, dissolved oxygen (DO), temperature, and oxidation-reduction potential (ORP) were measured on unfiltered splits. The leachates were then filtered through 0.45 μm pore-size nitrocellulose filters and analyzed for cations by ICP-MS and ICP-AES, and for anions (Cl^-, F^-, NO_3^-, and SO_4^{-2}) by ion chromatography (IC) in USGS laboratories in Denver, Colorado. ICP-MS, ICP-AES, and IC

analyses were done according to USGS methods outlined in Lamothe et al. (2002), Briggs (2002b), and Theodorakos et al. (2002). Dissolved total iron and ferrous iron concentrations were determined using colorimetric kits containing 1,10 phenanthroline indicator with a Hach DR/2000 spectrophotometer.

Sample Descriptions

Sample locations are shown on Fig. 1 and sample descriptions are given in Table 1. The three mine-waste piles sampled at the Smith mine are generally leaf-covered and sandy (Fig. 2), and locally contain oxidized ore having rinds of melanterite (Fig. 3), and areas of jarosite-rich soil (see Table 1 for grab sample mineralogy). A hardpan layer and a 3-increment composite of a red-brown soil horizon below the leaf litter were also collected from the Smith mine (Table 1). Two composite baseline soil samples are from locations not impacted by mining (Fig. 1; Table 1). The majority of mine-waste samples are from the landscape surrounding the Eureka and Union mines near the top of Pike Hill (Fig. 1). Mine-waste piles sampled in this area are generally barren of vegetation and strewn with boulders as shown in Fig. 4, and locally contain clots or coatings of jarosite and weathered pyrrhotite and chalcopyrite having melanterite rinds (see Table 1 for details). Mine-waste piles that differ from the majority include the partially burnt flotation-mill tailings (Fig. 5). This area was burnt in 1993 when spontaneous oxidation and combustion of reactive sulfides apparently caused this mine waste to smolder.

A 30-increment composite and grab samples of red-burnt, of black, and of yellow jarositic soils were collected (Table 1). Other unique samples are the composite of the sandy, quartz-rich processed flotation-mill tailings (Fig. 6) and the grab sample of a localized concentration of black flotation tailings (Table 1). The description and mineralogy of secondary precipitates and grab samples collected from Eureka and Union mine adits are given in Table 1. Examples of white and blue amorphous precipitates from one adit are shown in Fig. 7. Also, two samples of ferricretes were collected at seeps emerging from the base of waste piles at the Eureka and Union mines (Fig. 8).

Figure 2. Composite mine-waste sample 04Smith3 of lowermost waste dump at the Smith mine. Pink flag marks base of dump.

Figure 3. Melanterite salts (04Smith1-1) on weathered ore of the uppermost waste dump (04Smith1) at the Smith Mine.

Table 1. Descriptions for mine-waste, soils, and mineral samples collected from the Pike Hill mines site.

Sample	Mine	Sample type	Location	Description
04Smith1	Smith	composite waste	Uppermost dump at the Smith mine.	Orange, sandy soil with weathering sulfidic ore.
04Smith1-1	Smith	mineral	Same as above	Salts of melanterite[1] and gypsum[1] on weathered ore.
04Smith 1-2	Smith	mineral	Same as above	Local yellow soil of jarosite[1] and goethite[1].
04Smith2	Smith	composite waste	Middle dump near main Smith adit.	Orange-brown sandy soil and oxidized ore boulders.
04Smith3	Smith	composite waste	Lowermost dump below main Smith adit.	Orange-brown sandy soil and oxidized ore boulders, locally clots of jarosite.
04Smith4	Smith	hardpan	Swampy area in woods downslope from lowermost mine-waste dump.	Ochre hardpan below yellow jarositic layer.
04Smith5	Smith	composite soil	Series of holes dug downslope from lowermost mine-waste dump.	Red-brown soil samples below organic horizon. Composite of this horizon from 3 holes.
04Smith6	Smith	composite soil	Background soil sample.	Upslope sample away from mining-impacted area.
04Smith7	Smith	composite soil	Background soil sample.	Upslope sample away from mining-impacted area.
04PKHL1	Eureka	composite waste	Mine-waste dump at top of Pike Hill.	Barren, sandy, orange-brown-yellow mine-waste dump.
04PKHL2	Eureka	composite waste	Mine waste along snowmobile trail just downslope from 04PKHL1.	Same character as 04PKHL1, locally contains an ore pile.
04PKHL2-1	Eureka	rock	Same as above	Oxidized ore containing pyrrhotite[1], chalcopyrite[1], sulfur[1], and goethite[1] from small ore pile.
04PKHL3	Eureka	composite waste	Series of N-S trending mine-waste piles just above main Eureka mine adit.	Sandy, orange soil with yellow clots.
04PKHL3-1	Eureka	mineral	Same as above	Yellowish-green jarosite[1] coating.
04PKHL4-A	Eureka	mineral	Main Eureka mine adit.	Ferrihydrite[1] floc in mine pool at adit.
04PKHL4-B	Eureka	mineral	Same as above	Ferrihydrite[1] stalactites from drips along entryway.
04PKHL4-C	Eureka	mineral	Same as above	Bright blue amorphous[1] slime on wet rock face.
04PKHL4-D	Eureka	mineral	Same as above	White amorphous[1] slime on wet rock face.
04PKHL4-E	Eureka	mineral	Same as above	Ferrihydrite[1] just above waterline of adit pool.
04PKHL4-F	Eureka	mineral	Same as above	Calcite-rich[1] host rock to white slime.
04PKHL5-A	Union	mineral	Adit in wooded area north of main Eureka adit. Western-most opening for the Union mine.	White amorphous[1] foam floating on top of and lining the bottom of mine pool.

[1] Phases identified by X-ray diffraction analysis. Quantitative estimates of mineralogy of other samples given in Table 4.

Table 1. Descriptions for mine-waste, soils, and mineral samples collected from the Pike Hill mines site (continued).

Sample	Mine	Sample type	Location	Description
04PKHL5-B	Union	mineral	Same as above	Thick blue amorphous[1] slime along decline to adit pool.
04PKHL5-C	Union	mineral	Same as above	Blue weakly crystalline glaucocerinite[1].
04PKHL6	Union	mineral	Adit in wooded area adjacent to long, narrow engineered haulageway.	Starburst sprays of delicate white gypsum[1] growing from adit ceiling.
04PKHL7	Eureka and Union	composite waste	Large unvegetated area of mine-waste dumps below the Eureka and Union mines adits and above the road.	Sandy, orange mine-waste soil with cobbles and locally, weathering ore boulders.
04PKHL8	Eureka	mineral	Adit directly upslope of the Eureka adit.	Blue chalcanthite[1] and white gypsum[1] on adit ceiling.
04PKHL9	Eureka & Union	composite waste	Partially burnt flotation-tailings pile above the mine road.	Locally red where burned. Deep gullies expose black tailings. Pile is thin (~<1 m).
04PKHL9-A	Eureka & Union	tailings	Same as above	Red, hematite-rich tailings.
04PKHL9-B	Eureka & Union	tailings	Same as above	Black tailings dug from gully area.
04PKHL9-C	Eureka & Union	mineral	Same as above	Sample containing jarosite[1], goethite[1], chalcopyrite[1], quartz[1], and muscovite[1] above black tailings.
04PKHL10	Eureka & Union	composite waste	Tailings piles below the road.	Sandy, quartz-rich processed tailings; no vegetation or ore.
04PKHL11	Eureka & Union	composite waste	Large area of barren mine waste below the mine access road.	Mine-waste dumps with local concentrations of weathering ore boulders. Snowball salts observed.
04PKHL11-A	Eureka & Union	tailings	Same as above	Local concentration of black flotation tailings.
04PKHL11-1 snowballs	Eureka & Union	rock	Same as above	Melanterite[1] coating upper surfaces of weathering ore cobbles on mine-waste dump. Temperature 8.8°C, relative humidity 59.4%.
04PKHL12	Eureka & Union	ferricrete	Seep area below mine-waste piles 04PKHL11.	Flat ferricrete terrace forming at seeps from base of mine-waste pile.
04PKHL13	Eureka & Union	composite waste	Lowermost mine-waste piles at Pike Hill.	Mine-waste piles with clots of yellow jarosite and weathered ore boulders.
04PKHL13-A	Eureka & Union	rocks	Same as above	Thin yellowish-green jarosite[1] coatings on rock chips from dry seep area.
04PKHL13-B	Eureka & Union	ferricrete	Same as above	Ferricrete developed in dry seep area.
04PKHL14	Eureka & Union	mineral	Mine waste below the mine access road.	Jarosite-rich[1] clot in mine waste.

Figure 4. Composite mine-waste sample site 04PKHL3 from Eureka mine area.

Figure 5. Composite sample site of partially burnt tailings (04PKHL9).

Figure 6. Composite sample site of quartz-rich processed tailings (04PKHL10).

Figure 7. White (04PKHL5-A) and blue (-B & -C) amorphous or weakly crystalline glaucocerinite precipitates along decline to perched adit pool in Union mine workings.

Figure 8. Ferricrete (04PKHL12) forming at
a seep at the base of pile PKHL11.
Green area is filamentous algae.

Results and Discussion

Bulk geochemistry

The concentrations of elements in the mine-waste piles were evaluated by examining variations among piles, by comparing values to USEPA Preliminary Remediation Goals (PRGs), and by relating to concentrations of elements in mine waste from the Elizabeth and Ely mines. The concentrations of selected metals and the PRGs for residential and industrial soils are given in Table 2, with PRG exceedances shown in bold. PRGs are guidelines, not legally enforceable standards, used for initial evaluations of potentially contaminated sites. The concentrations of several elements are also compared to a range or average concentration in eastern United States soils reported by Shacklette and Boerngen (1984), which approximate a regional geochemical background level for a given element.

Mine-waste samples contain significant concentrations of Fe. Most samples exceed the PRG for residential soils of 2.3 wt% Fe; background soils contain 2.4 to 2.6 wt% Fe but black tailings (04PKHL11-A) contain only 0.65 wt% Fe (Fig. 9). The concentrations of Fe in the composite mine-waste samples range from 18 to 27 wt%, except for the quartz-rich flotation-mill tailings (04PKHL10) with 3.6 wt%. The ferricretes and hardpan material exceed the PRG for industrial soils with concentrations between 40 and 47 wt% Fe (Fig. 9).

The most abundant trace element in most mine-waste samples is Cu. The concentrations of Cu in all samples, except the background soils (04Smith6 and 04Smith7) and the downslope soil at the Smith mine (04Smith5), exceed the maximum concentration of 700 mg/kg for eastern United States soils (Shacklette and Boerngen, 1984). Seven of the composite mine-waste samples also exceed the PRG for Cu for residential soils with concentrations reaching 9,200 mg/kg for the partially-burnt tailings (Fig. 9). The concentrations of both Fe and Cu in mine-waste samples from the Pike Hill mines site generally fall within the range of concentrations for these metals in mine waste from the Ely and Elizabeth mines (Fig. 9).

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Table 2. Concentrations of selected metals in mine waste from the Pike Hill mines site. Values in bold exceed Preliminary Remediation Goals (PRGs).

Sample	Sample type	Ag mg/kg	Al wt%	As mg/kg	Cd mg/kg	Co mg/kg	Cr mg/kg	Cu mg/kg	Fe wt%	Mn mg/kg	Mo mg/kg	Ni mg/kg	Pb mg/kg	Se mg/kg	Tl mg/kg	V mg/kg	Zn mg/kg
PRG-residential[1]		390	7.6	22	37	1,400	210	3,100	2.3	1,800	390	1,600	400	390	5.2	78	23,000
PRG-industrial[1]		5,100	9.2	260	450	13,000	450	41,000	31	19,000	5,100	20,000	800	5,100	67	1,000	310,000
04Smith1	mine waste	5.89	4.6	1	0.63	39.4	85.1	1,800	**19**	1,370	4.6	15	69.9	20.1	0.61	**137**	614
04Smith2	mine waste	5.49	3.5	0.6	0.29	28.4	40.8	1,530	**21**	865	4	10	115	22.7	0.88	**138**	315
04Smith3	mine waste	6.6	3.2	1	0.22	31.7	28.2	1,380	**25**	609	16.2	9.9	83.2	24.8	1.1	**125**	344
04Smith4	hardpan	<3	0.16	0.6	0.1	1.3	23.1	1,120	**47**	39	0.2	1.4	22.2	2.1	0.2	32.9	55
04Smith5	downslope soil	<3	3	0.6	0.49	14	38.7	559	**14**	807	1.4	25.4	9.8	0.8	0.2	61.7	521
04Smith6	background soil	<3	4.7	0.5	0.13	10.7	52.8	19	**2.6**	1,120	0.36	27.3	14.1	0.3	0.3	63.5	66
04Smith7	background soil	<3	3.9	0.8	0.11	9.8	45.4	18	**2.4**	606	0.46	23	14.2	0.4	0.3	55.6	46
04PKHL1	mine waste	10.3	3	6.3	0.59	35	24.9	**4,410**	**20**	166	37.4	7.2	89.2	48.9	1.3	**83.8**	246
04PKHL2	mine waste	6.26	4.7	3.1	0.27	29.1	37	3,000	**18**	218	32.2	7	58.9	47	1.6	**82.2**	213
04PKHL3	mine waste	11.9	4.1	3.3	0.35	47.9	41.2	**3,240**	**19**	238	18.5	7.9	85.7	47.6	1.6	**89**	354
04PKHL7	mine waste	11.4	3.3	8.5	2.5	50.7	31.8	**8,060**	**19**	302	21.6	9.6	238	52	1.2	67	593
04PKHL9	burnt tailings	27.8	2	9.7	2	103	20	**9,200**	**27**	223	44.5	13.6	182	124.2	0.83	47.6	640
04PKHL10	processed tailings	3	3.7	57	**91.8**	122	42.3	**7,200**	**3.6**	1,360	4.1	8.9	103	7.4	0.78	60.4	16,000
04PKHL11	mine waste	7.63	2.8	3.2	0.64	36.2	24.3	**6,400**	**19**	159	19.4	7.1	78.3	60.7	1	63.1	233
04PKHL11-A	black tailings	<3	3.4	0.3	0.06	1.1	54.8	2,370	0.65	196	0.62	6.8	14	9.2	0.3	42.5	24
04PKHL12	ferricrete	<3	0.77	0.2	0.41	8	11.9	1,610	**40**	32	4.9	1.1	15.4	11.2	0.2	24.7	88
04PKHL13	mine waste	12.9	3.7	6.6	0.29	34.4	32.1	**3,670**	**20**	234	34.5	7.4	102	53.9	2.3	72.5	218
04PKHL13-B	ferricrete	<3	0.27	0.5	0.1	3.6	17.8	874	**46**	22	1.9	<1	29.4	7.1	0.2	**138**	32

[1] PRGs for metals are residential (chronic, noncarcinogenic, combined) and industrial (chronic, noncarcinogenic, combined) (Cr is cancer risk combined, not chronic) from "PRG Intercalc Tables: Soils" at http://www.epa.gov/region09/waste/sfund/prg/files/04soils.pdf (USEPA, 2004b) except Lead (noncarcinogenic) from "Region 9 PRG Table" at http://www.epa.gov/region09/waste/sfund/prg/files/04prgtable.pdf (USEPA, 2004c)
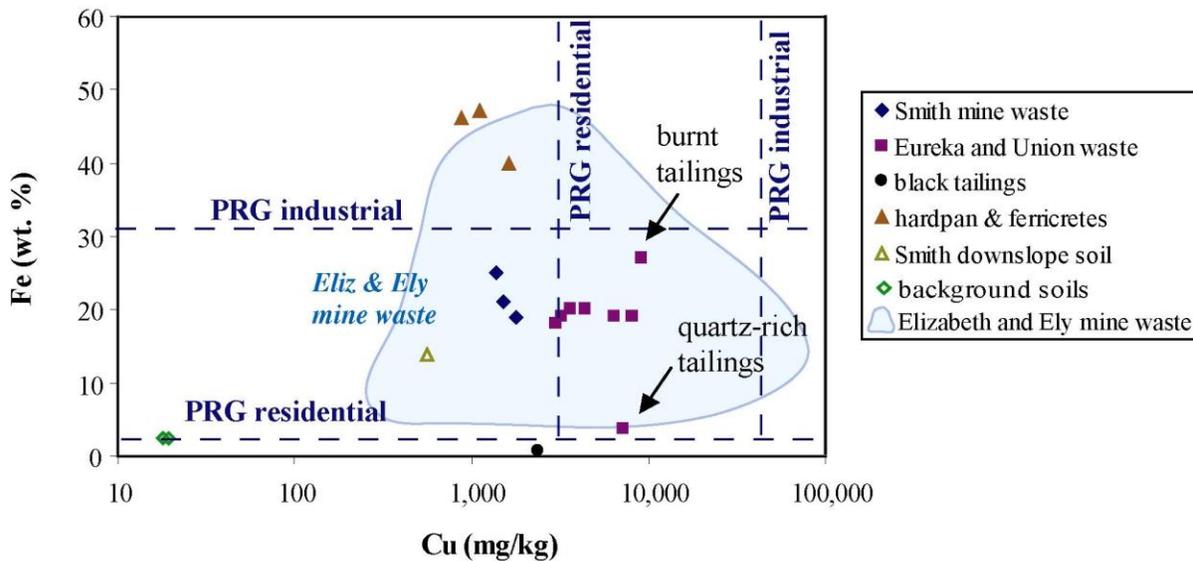
Figure 9. Concentrations of Fe and Cu in solid samples collected from the Pike Hill mines site. The composition of mine waste including waste rock and unoxidized tailings from the Elizabeth (Eliz) and Ely mines are shown as the blue colored area in the background (Hammarstrom et al., 2001, 2003; Piatak et al., 2004). PRGs for residential and industrial soils are from U.S. Environmental Protection Agency (2004b).

The concentrations of Zn in most mine waste are significantly higher than the mean concentration of 40 mg/kg for soils in the eastern United States (Shacklette and Boerngen, 1984) but do not exceed the PRG for residential soil (Table 2). The highest concentration of Zn was found in the processed flotation-mill tailings (04PKHL10) containing 16,000 mg/kg Zn and approximately 1 wt% sphalerite. This sample also contains the highest concentration of Cd (91.8 mg/kg) in exceedance of the PRG of 37 mg/kg Cd for residential soils (Fig. 10). The black tailings (04PKHL11-A) contain the lowest concentrations of Zn (24 mg/kg) and Cd (0.06 mg/kg), which fall below the concentrations of these elements in the background soils (Fig. 10). This material also contains concentrations of Fe, Mo, and Se less than or equivalent to background levels. It is unclear why the mining process created a flotation-mill tailings containing elevated concentrations of Cu, but not Cd, Fe, Mo, Se, or Zn when compared to baseline samples. The concentrations of Zn and Cd in the composite mine-waste samples are within the range for these elements at the other mine sites in the Vermont copper belt (Fig. 10). Note the positive correlation between Zn and Cd concentrations in Fig. 10. These elements occur together due to Cd substituting for Zn in the structure of sphalerite, the dominant Zn-bearing mineral found at the site.

The concentrations of Se range from 0.3 and 0.4 mg/kg in the background soil samples to 124.2 mg/kg in the partially burnt flotation-mill tailings (Table 2). The concentrations of Se correlate with the concentrations of S due to the substitution of Se for S in sulfide and SO_4^{-2} minerals (Fig. 11). All samples except the background soils, the downslope soil at the Smith mine (04Smith5), and the hardpan (04Smith4) contain elevated concentrations of Se when compared to the range of <0.1 to 3.9 mg/kg for soils in the eastern United States (Shacklette and Boerngen, 1984). In general, the ferricretes (04PKHL12 and 04PKHL13-B), quartz-rich

flotation-mill tailings (04PKHL10), and black tailings (04PKHL11-A) contain less (7.1 to 11.2 wt%) Se than the remaining composite mine-waste samples. Composites from the Smith mine average 22 mg/kg Se whereas samples from the Eureka and Union mines range from 47 to 124.2 mg/kg Se (Fig. 11). The anomalous concentration of Se in the partially-burnt flotation-mill tailings (04PKHL9) is consistent with anomalously high Se concentrations in partially-roasted waste rock at the Elizabeth mine (Hammarstrom et al., 1999). This sample also contains the highest concentration of S.
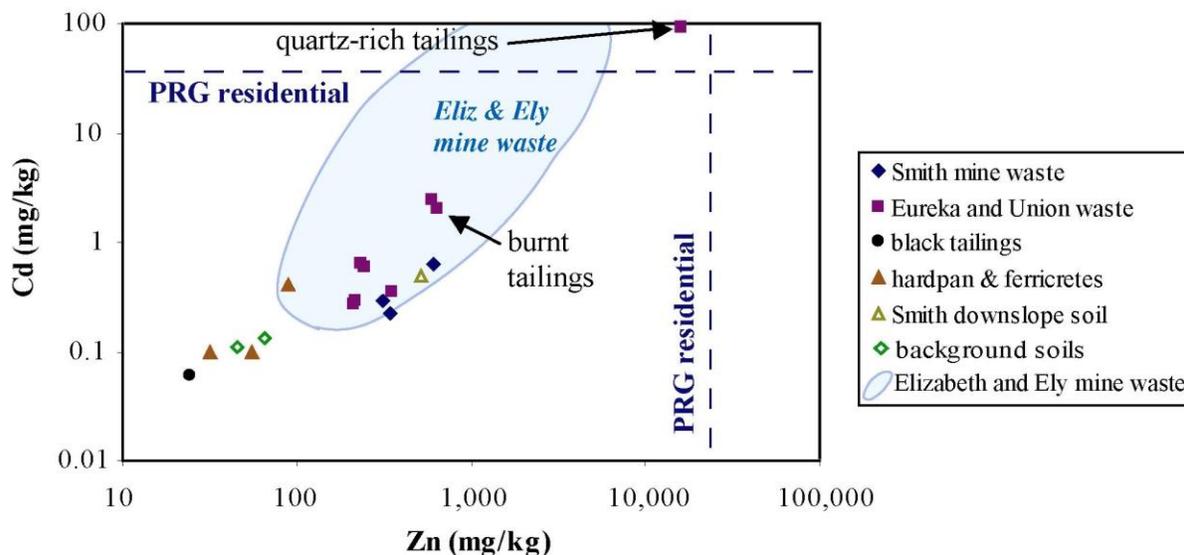
Figure 10. Concentrations of Cd and Zn in solid samples collected from the Pike Hill mines site. The composition of mine waste including waste rock and unoxidized tailings from the Elizabeth (Eliz) and Ely mines are shown as the blue colored area in the background (Hammarstrom et al., 2001, 2003; Piatak et al., 2004). PRGs for residential soils are from U.S. Environmental Protection Agency (2004b).

Mineralogy

Table 3 shows semi-quantitative mineralogy results for composites and several grab samples from Siroquant analysis of XRD patterns. Mineral percentages sum to 100 wt% and are for the crystalline part of the sample. The amorphous content determined on spiked splits are also reported in Table 3.

Sulfates and sulfides. The dominant SO_4^{-2} mineral in the mine-waste samples is jarosite (~18 wt% in sample 04Smith2, Table 3). The exception is sample 04PKHL9-B, black tailings from the partially-burnt area. This sample contains 19.1 wt% native S, trace (<1 wt%) jarosite and gypsum, and ~16 wt% sulfides, mostly present as chalcopyrite. This sample was collected as a mineralogically unique subset sample in order to understand variation within pile 04PKHL9, which contains the highest concentration of Cu based on bulk chemistry. In contrast to 04PKHL9-B, black tailings 04PKHL11-A contains no detectable sulfides. Overall, composite mine-waste samples contain sulfides in concentrations ranging from <1 to ~4 wt% (Table 3). Sulfides present include chalcopyrite, pyrite, pyrrhotite, and sphalerite. Generally, the samples containing the highest concentrations of Cu are samples with detectable chalcopyrite. The

composite sample of the quartz-rich flotation-mill tailings (04PKHL10) contains more sulfides (~4 wt%) and calcite (~2 wt%) when compared with the other composites. This sample also contains the highest concentrations of As, Cd, Co, and Zn. As the samples containing sulfides weather, they may generate acid and leach metals of environmental concern. Also, sulfide minerals define the acid-generating potential of the samples for acid-base accounting purposes. The background soils and downslope soil at the Smith mine do not contain detectable sulfides (~1 wt%) because these soils developed from un-mineralized rock.
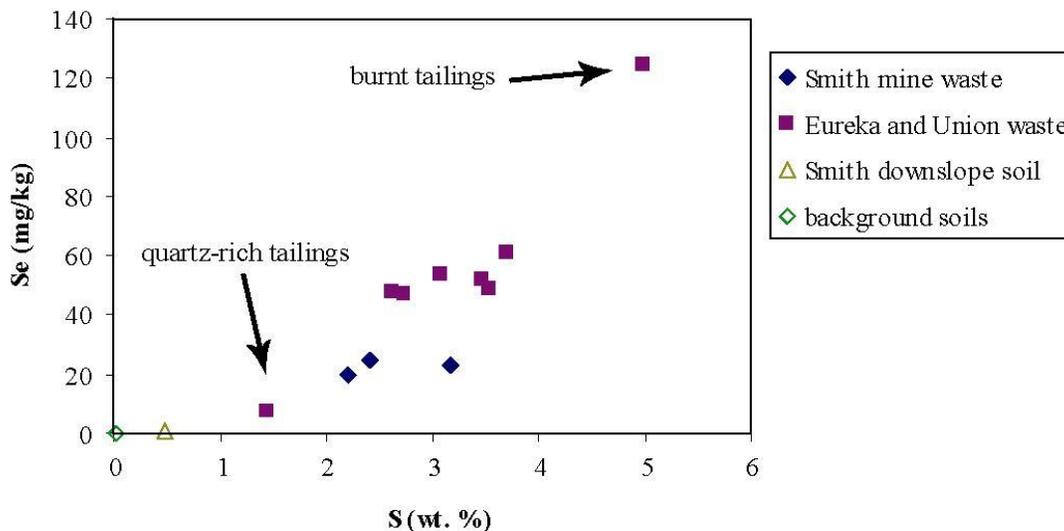
Figure 11. Concentrations of Se and S in solid samples collected from the Pike Hill mines site. Values for S were determined by LECO furnace; Se by hydride generation. Concentrations of Se for the Smith downslope soil (04Smith4), the black tailings (04PKHL11-A), and ferricretes (04PKHL-12 and 04PKHL-13-B) are not shown because samples not analyzed for S.

Iron oxides and amorphous material. The highest concentrations of Fe from chemistry results are found in the hardpan (04Smith4) and ferricretes (04PKHL12 and 04PKHL13-B). The mineralogy of these samples is consistent with the chemistry in that they contain significant amounts of goethite. Ferricretes contain 34 to 61 wt% goethite, whereas the hardpan contains 86 wt% goethite. These values are not normalized with respect to amorphous content given in Table 3. These samples also contain the highest concentrations of amorphous material ranging from 65.8 to 68.4 wt%. Other samples contain between 10.5 and 32.7 wt% amorphous material. This material likely consists of Al-hydroxides, Fe-hydroxides, or SiO_2 compounds. Al- and Fe-hydroxides are known to sorb selectively metals as a function of pH (Smith, 1999).

Table 3. Estimates of mineral abundances (wt%) based on Rietveld refinement of powder X-ray diffraction patterns using Siroquant.

	Ideal formula	Average error[1]	04Smith1	04Smith2	04Smith3	04Smith4	04Smith5	04Smith6	04Smith7	04PKHL1	04PKHL2	04PKHL3
chi-square[2]			4.24	4.2	4.22	3.08	4.55	5.44	5.17	4.48	5.48	4.9
PRIMARY MINERALS												
Albite	$NaAlSi_3O_8$	0.9	7.2	7.7	8.6	n.d.[3]	5.7	3.7	5.5	6.3	14.3	4.2
Anorthite	$CaAl_2Si_2O_8$	1.2	0.0	0.0	0.0	n.d.	0.0	0.0	0.0	0.9	2.3	0.0
Biotite	$K(Mg, Fe)_3(AlSi_3O_{10})(OH)_2$	0.4	0.5	0.0	0.0	n.d.	0.0	0.0	0.0	0.0	0.0	0.0
Calcite	$CaCO_3$	0.5	0.4	1.2	0.0	n.d.	0.6	0.7	0.1	0.0	0.0	0.0
Chalcopyrite	$CuFeS_2$	0.2	0.0	0.0	0.1	n.d.	0.0	0.0	0.0	1.5	0.3	0.8
Chlorite	$(Mg,Fe^{2+})_5Al(Si_3Al)O_{10}(OH)_8$	0.6	1.7	0.8	4.9	n.d.	3.2	3.5	1.6	1.6	2.6	0.0
Labradorite	$(Ca,Na)(Si,Al)_4O_8$	1.1	5.6	9.1	9.9	n.d.	7.5	8.0	0.3	3.9	6.6	5.1
Muscovite	$KAl_2(AlSi_3O_{10})(OH)_2$	0.6	6.2	6.6	7.4	n.d.	10.4	8.8	13.3	11.0	14.1	18.8
Pyrite	FeS_2	0.2	0.0	0.4	1.4	n.d.	0.1	0.0	0.0	0.8	0.5	0.4
Pyrrhotite	$Fe_{1-x}S$	0.2	0.0	0.0	0.0	n.d.	0.1	0.2	0.2	0.0	0.0	0.0
Quartz	SiO_2	1.2	26.8	33.0	29.5	5.1	63.4	72.0	77.8	39.4	25.0	28.8
Rutile	TiO_2	0.2	n.d.	0.0	1.0	n.d.	0.3	0.4	0.8	1.4	1.0	0.8
Sphalerite	ZnS	0.1	0.0	0.2	0.1	n.d.	0.1	0.0	0.0	0.1	0.0	0.1
Tremolite	$Ca_2Mg_5Si_8O_{22}(OH)_2$	0.9	0.5	0.0	0.0	n.d.	0.0	0.2	0.0	1.1	0.5	0.4
SECONDARY MINERALS												
Alunogen	$Al_2(SO_4)_3 \cdot 17H2O$	0.8	0.0	0.0	0.0	n.d.	0.0	0.5	0.0	0.7	0.0	0.0
Copiapite	$Fe^{2+}Fe^{3+}_4(SO_4)_6(OH)_2 \cdot 20H_2O$	0.4	0.4	1.1	0.4	n.d.	0.6	0.0	0.0	0.2	0.0	1.4
Goethite	$FeO(OH)$	0.5	21.4	15.7	12.6	85.8	4.1	0.5	0.0	10.0	8.4	7.6
Gypsum	$CaSO_4 \cdot 2H_2O$	0.3	0.4	0.0	0.3	n.d.	0.0	0.0	0.0	2.2	0.1	0.1
Hematite	Fe_2O_3	0.7	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Jarosite	$K_2Fe_6^{3+}(SO_4)_4(OH)_{12}$	0.4	14.9	17.7	12.5	9.1	0.3	0.2	0.1	15.1	13.1	15.4
Kaolinite	$Al_2Si_2O_5(OH)_4$	0.6	1.0	0.4	1.6	n.d.	1.7	0.0	0.0	1.3	0.7	2.5
Lepidocrocite	$FeO(OH)$	0.2	0.4	0.3	1.0	n.d.	0.0	0.0	0.0	0.0	0.7	0.8
Melanterite	$FeSO_4 \cdot 7H_2O$	0.4	0.0	0.2	0.8	n.d.	1.4	1.0	0.3	0.7	0.0	0.3
Rozenite	$FeSO_4 \cdot 4H_2O$	0.5	0.0	0.0	0.0	n.d.	0.0	0.1	0.0	0.0	0.0	0.0
Sepiolite	$Mg_4(OH)_2Si_6O_{15} \cdot 6H_2O$	0.5	12.5	5.5	7.6	n.d.	0.2	0.1	0.0	1.9	9.6	12.5
Sulfur	S	0.4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Amorphous		2.5	20.4	17.5	14.6	65.8	32.3	22.3	10.5	10.9	25.8	32.7

[1] Errors are estimated standard deviations (calculated by Siroquant based on square roots of diagonal elements of least-squares variance-covariance matrix).

[2] Chi-square is a computed statistical residual to measure the fit of refinement. Chi-square = 1 for perfect correspondence between least-squares model and observed data. Values below 6 are considered reasonable fits for these complex mine wastes due to systematic errors and imperfect physical corrections.

[3] n.d. indicates not determined.

Table 3. Estimates of mineral abundances (wt%) based on Rietveld refinement of powder X-ray diffraction patterns using Siroquant (continued).

	04PKHL7	04PKHL9	04PKHL9A	04PKHL9B	04PKHL10	04PKHL11	05PKHL11-D	04PKHL11A	04PKHL12	04PKHL13	04PKHL13B
chi-square ^{2}	3.86	4.76	2.85	4.75	6.88	4.06	4.81	4.44	2.85	4.53	3.00
PRIMARY MINERALS											
Albite	2.9	2.2	0.0	1.9	0.0	4.5	7.3	6.2	0.0	6.7	0.5
Anorthite	1.3	0.9	0.1	0.0	2.3	0.0	0.3	0.0	6.2	0.0	n.d.
Biotite	2.7	0.0	0.0	3.0	3.8	0.0	0	0.0	0.0	0.0	n.d.
Calcite	0.0	0.8	0.0	0.0	2.4	0.2	0.8	0.0	0.0	0.0	n.d.
Chalcopyrite	3.0	1.8	1.3	14.7	0.8	1.8	1.9	0.0	2.5	0.6	n.d.
Chlorite	3.5	0.6	0.6	0.5	1.1	0.0	1.3	3.3	0.0	0.0	n.d.
Labradorite	3.7	0.0	0.8	4.2	11.4	7.8	2.1	2.8	3.7	6.1	n.d.
Muscovite	11.1	3.6	0.8	15.7	7.1	8.8	7.3	11.5	8.3	11.2	18.0
Pyrite	0.6	0.0	1.2	0.7	1.8	0.1	0.5	0.0	0.0	0.0	n.d.
Pyrrhotite	0.0	0.0	0.5	0.1	0.5	0.0	0	0.0	0.3	0.0	n.d.
Quartz	39.8	33.0	9.3	36.1	65.2	38.2	38	68.7	23.1	30.9	9.5
Rutile	0.3	0.0	0.4	0.5	0.1	0.1	0.8	1.2	0.0	1.0	0.7
Sphalerite	0.0	0.8	0.0	0.3	1.0	0.2	n.d.	0.0	0.0	0.3	n.d.
Tremolite	1.6	4.6	3.4	0.3	0.8	0.4	1.8	3.9	n.d.	0.0	n.d.
SECONDARY MINERALS											
Alunogen	0.0	0.0	0.6	0.0	0.0	0.0	0	0.0	0.5	0.0	n.d.
Copiapite	0.0	0.2	0.5	0.3	0.0	0.6	0.4	0.2	0.6	0.0	n.d.
Goethite	7.7	27.3	2.2	0.0	0.0	8.7	13.6	0.0	33.5	15.6	60.5
Gypsum	1.3	2.4	1.0	0.5	0.0	3.0	4	0.0	1.2	1.7	n.d.
Hematite	n.d.	6.8	72.1	1.6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Jarosite	13.6	7.5	4.0	0.1	0.0	13.6	13.4	0.3	13.1	13.0	10.7
Kaolinite	2.1	2.3	0.9	0.5	0.9	2.1	2.8	0.3	1.8	0.7	n.d.
Lepidocrocite	0.0	0.0	0.2	0.0	0.0	0.0	0.6	0.2	2.0	0.6	n.d.
Melanterite	0.1	0.0	0.0	0.0	0.7	0.2	0.5	1.2	1.9	0.0	n.d.
Rozenite	0.0	0.0	0.0	0.0	0.0	0.0	0	0.0	1.0	0.0	n.d.
Sepiolite	4.7	5.0	0.2	0.1	0.0	9.4	2.4	0.0	0.3	11.5	n.d.
Sulfur	n.d.	n.d.	n.d.	19.1	0.1	n.d.	n.d.	0.1	n.d.	n.d.	n.d.
Amorphous	26.4	25.4	n.d.	27.5	11.9	21.5	n.d.	28.9	67.2	22.5	68.4

Efflorescent salts and pH. Efflorescent SO_4^{-2} salts are commonly present in amounts too small to detect with XRD although semi-quantitative mineralogy suggests up to 4 wt% salts for samples from Pike Hill. These salts include copiapite and melanterite with lesser amount of alunogen and rozenite. In order to verify the presence of these salts, three splits of mine waste were rinsed repeatedly with deionized water; the rinse pH was determined and then the rinse water was evaporated. Also, leachate water was filtered and evaporated. The pH of the rinse water is shown in Fig. 12. The pH values of <3.8 in Fig. 12 for the first few days are less than the equilibrium pH for the stoichiometric dissolution of jarosite (Langmuir, 1997). This suggests the dissolution of efflorescent SO_4^{-2} salts at the beginning of the experiment. The evaporates produced by the rinse water and leachate solutions are Ca-sulfate and hydrated Fe-sulfate salts, thus confirming the presence of these salts. Melanterite and chalcanthite identified in grab samples 04PKHL11-1 and 04PKHL8, respectively, verify the presence of these salts at the site (Table 1). Efflorescent SO_4^{-2} salts likely play a significant role in acid generation and metal sequestration. During rain events, these highly soluble salts dissolve and contribute acid and metals to the receiving waters at mine sites.
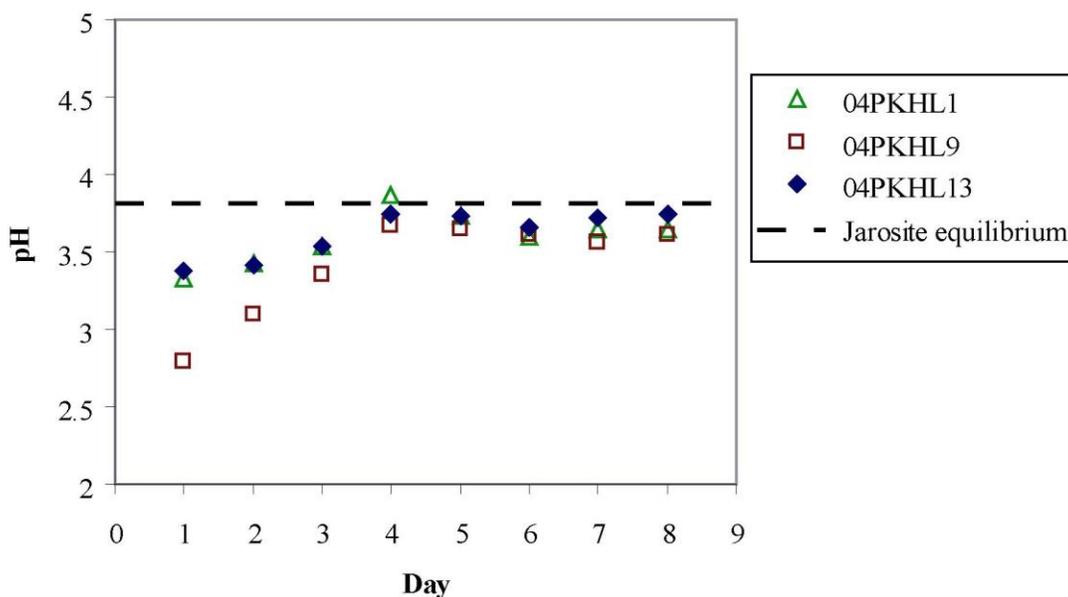
Figure 12. Effects of repeatedly washing three mine-waste samples with deionized water on leachate pH. Black dashed line represents nominal pH (3.8) for jarosite equilibrium (Langmuir, 1997). Lower pH values likely indicate dissolution of efflorescent SO_4^{-2} salts.

Acid-base accounting and paste pH

   Paste pH and acid-base accounting results (Table 4 and Fig. 13) indicate that most mine-waste samples from the Pike Hill mines site are net acid-generating. The paste pH of ferricretes 04PKHL12 and 04PKHL13-B (not analyzed by ABA) are <4 and therefore potentially acidic (Table 4). Figure 13 indicates that the paste pH and NNP of the background soils (04Smith6 and 04Smith7) plot within the non-acid generating field. The only other sample in this category is the processed flotation-mill tailings (04PKHL10) containing a neutral paste pH and NNP of 47.5

kg $CaCO_3$/t. This sample contains the highest concentrations of several metals including Zn and Cd (likely from sphalerite), but also contains significant carbonate (estimated to be 2.4 wt% calcite). For this sample only, the acid-neutralizing capacity from calcite is greater than the acid-generating potential from sulfides and sulfates.

Table 4. Paste pH and acid-base accounting results for samples from the Pike Hill mines site.

	Paste pH (USGS)	Paste pH (Vizon[1])	Total sulfur (wt%)	Sulfate sulfur (wt%)	Sulfide sulfur (wt%)	Maximum Potential Acidity (AP) (kg $CaCO_3$/t)	Neutralization Potential (NP) (kg $CaCO_3$/t)	Net Neutralization Potential (NNP) (kg $CaCO_3$/t)	Fizz
04Smith1	3.1	3.1	2.20	1.65	0.55	17.2	-4.5	-21.7	none
04Smith2	2.8	3.1	3.17	2.31	0.86	26.9	-6.7 *(-7.0)*	-33.6	none
04Smith3	2.7	2.7	2.41	1.87	0.54	16.9	-9.0	-25.9	none
04Smith 5	2.8	3.1	0.48	0.42	0.06	1.9	-0.7	-2.6	none
04Smith6	5.7	6.1	0.02	0.02	<0.01	<0.3	7.2	7.2	none
04Smith7	5.4	5.7	0.03 *(0.03)*[3]	0.02 *(0.02)*	0.01	0.3	-0.2	-0.5	none
04PKHL1	2.7	2.6	3.55	2.4 *(2.10)*	1.15	35.9	-7.5	-43.4	none
04PKHL2	2.7	2.9	2.74	1.93	0.81	25.3	-8.0	-33.3	none
04PKHL3	2.8	2.9	2.63	1.82	0.81	25.3	-8.7	-34.0	none
04PKHL7	3.1	4.1	3.48	1.77	1.71	53.4	-3.7	-57.1	none
04PKHL9	2.3	2.3	4.99	1.70	3.29	102.8	-10.0	-112.8	none
04PKHL10	7.0	7.5	1.44	0.09	1.35	42.2	90 *(88.8)*	47.5	moderate
04PKHL11	2.5	2.4	3.70	2.42	1.28	40.0	-5.0	-45.0	none
04PKHL12	2.5	n.a.[2]	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
04PKHL13	2.7	2.7	3.07 *(3.10)*	2.01	1.06	33.1	-5.5	-38.6	none
04PKHL13-b	2.4	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.

[1] Vizon SciTec, Inc.
[2] not analyzed.
[3] Italic numbers in parentheses are duplicates.

The paste pH values of <4 and negative NNP for all other mine-waste samples indicate the material is potentially acid-generating. The composite mine-waste samples from the Smith mine have a paste pH of approximately 3 and NNP values ranging from –21.7 to –33.6 kg $CaCO_3$/t (Fig. 13 and Table 4). The downslope soil at this mine (04Smith5) has a paste pH of 2.8 and slightly negative NNP (-2.6 kg $CaCO_3$/t). The lowest paste pH of 2.3 and most negative NNP of –112.8 kg $CaCO_3$/t in Figure 13 are for the partially burnt flotation-mill tailings. The remaining composites from the Eureka and Union mines are potentially acid-toxic with paste pH values of less than 4 and NNP ranging from –33.3 to –57.1 kg $CaCO_3$/t.

The range in paste pH and NNP values results from the complex mixture of minerals in the mine-waste samples. Sulfur-bearing minerals, and carbonates and silicates are the dominant acid generators and acid neutralizers, respectively, in these samples. In most samples from the Pike Hill mines site, sulfur has been oxidized to SO_4^{-2} and thus SO_4^{-2} sulfur is significantly greater than sulfide sulfur based on ABA results in Table 4. Samples 04PKHL7, 04PKHL9, and 04PKHL10 are the exceptions.
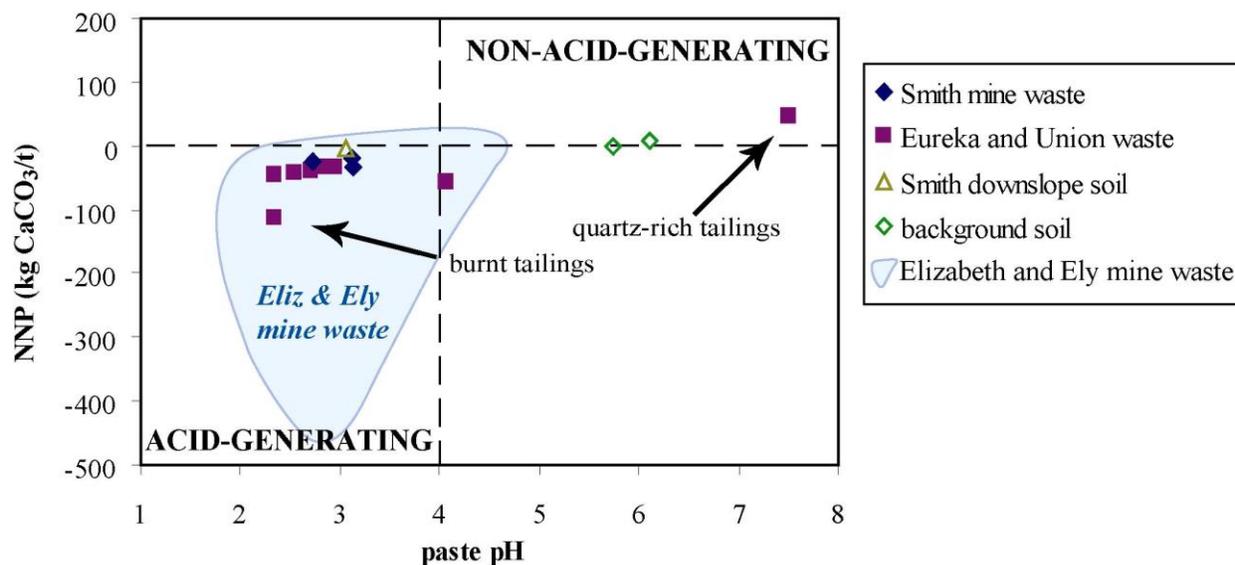
Figure 13. Acid-base accounting results for samples from the Pike Hill mines site. Data for the Elizabeth (Eliz) and Ely mines from Hammarstrom et al. (2003) and Piatak et al. (2004) are shown as the blue colored area in the background. Mine-waste samples from the Elizabeth mine do not include samples containing the underlying carbonate-rich till unit, which increases NNP and paste pH.

Acid-base accounting results for mine-waste piles at the Elizabeth and Ely mines are shown as the blue colored region in Fig. 13 (Hammarstrom et al., 2003; Piatak et al., 2004). Subeconomic mineralized rock and waste rock at the Elizabeth mine overly a carbonate-rich till, which increases the paste pH and NNP for samples containing this material. Samples of this till or waste rock mixed with till are not included in Figure 13. Most mine-waste samples collected from the Pike Hill mines fall within the range of paste pH and NNP for mine-waste from the Elizabeth and Ely mines in Fig. 13. The lowest NNP of approximately -420 kg $CaCO_3$/t for samples from these mines is for unoxidized pyrrhotite-rich black tailings from the Ely mine (Piatak et al., 2004). Acid generation in samples from the Pike Hill area does not reach this extreme.

Leachate

Leaching tests modified from Hageman and Briggs (2000) were performed on mine-waste samples sieved to <2 mm in diameter using a solution that approximates eastern United States precipitation. The results indicate that significant concentrations of metals can be released from these samples (Table 5). These tests provide an indication of the potential chemical composition of run-off (Hageman and Briggs, 2000). The results of the leaching tests were compared with USEPA water-quality guidelines for the protection of aquatic life and drinking water standards (U.S. Environmental Protection Agency, 2002; 2004d). Concentrations of metals exceeding criteria are shown in bold in Table 5. Water quality-guidelines for Cd, Cu, Ni, Pb, and Zn are hardness-dependent and were calculated based on a hardness of 100 mg/L $CaCO_3$. This is a

realistic approximation because the hardness of waters receiving drainage from the mines range from 85 to 110 mg/L $CaCO_3$.

The major anion in all samples is SO_4^{-2} and Al, Ca, Cu, Fe, K, Mg, and Si dominate the cations; Mn and Zn contents are significant in some samples. Elements and compounds in exceedance of water-quality guidelines in the leachate waters are Cd, Co, Cu, Fe, Mn, Se, SO_4^{-2}, and Zn (Table 5). Copper is generally the most abundant trace metal in the leachates. The only samples with leach Cu concentrations less than the acute toxicity guideline of 13 µg/L are the background soils and the quartz-rich flotation-mill tailings (04PKHL10); all other leachates exceed this criterion as shown in Fig. 14. The concentration of Cu in composite sample 04PKHL10 is the third highest based on bulk chemistry, but leachate tests suggest it is not readily leached from this material. In contrast, the highest concentration of Cu (17,000 µg/L) in the leachates is from the partially-burnt flotation tailings (04PKHL9), which also contain the highest concentration of Cu (9,200 mg/kg) reported for the solid samples. The amount of Cu in the sample does not consistently correlate with the amount of Cu leached from the sample. This is likely due to mineralogical variations. Leachates from 04PKHL9 as well as 04PKHL7 (2,270 µg/L Cu) and 04PKHL11 (2,240 µg/L Cu) exceed the drinking water standard of 1,300 µg/L Cu and leachates from the samples of ferricrete contain less Cu than that of composite mine-waste samples as shown in Fig. 14.

The next most abundant trace element in the leachates is Zn. The concentrations of Zn in leachate from the background soils are significantly less than in leachate from mine waste (Figure 14). Leachate concentrations that do not exceed the acute aquatic toxicity guideline are from waste pile 04Smith3 at the Smith mine, and the three uppermost waste piles (04PKHL1, 04PKHL2, and 04PKHL3), one ferricrete (04PKHL12), and the lowermost waste pile (04PKHL13) at the Eureka and Union mines. These samples do not necessarily have the lowest concentrations of Zn based on the bulk chemistry. For example, sample 04Smith3 contains 344 mg/kg Zn with a leachate concentration of 77.9 µg/L, which is well below the toxicity guideline. In contrast, sample 02Smith2 contains comparable Zn at 315 mg/kg, but the leachate concentration is 205 µg/L and exceeds the criteria. Also, the quartz-rich flotation-mill tailings (04PKHL10) contain anomalous Zn at 16,000 mg/kg and leaches only 700 µg/L Zn. The lack of consistent correlations between bulk and leachate chemistry suggest that other factors, such as mineralogy, affect the leachability of metals in the samples from the Pike Hill mines site. For example, Zn present in sphalerite is less likely to leach than Zn in highly soluble efflorescent SO_4^{-2} salts.

Other elements and compounds of concern in the leachates include Cd, Co, Fe, Mn, and SO_4^{-2}. The concentrations of Cd in leachates from seven composite mine-waste samples and one ferricrete sample exceed the acute toxicity guideline for aquatic life as shown in Fig. 14. The three highest concentrations also exceed the drinking water standard. USEPA does not have toxicity standards for Co, but when the composition of the leachates is compared to the New York water criterion of 5 µg/L for Co, most exceed this standard (Table 5; New York Department of Environmental Conservation, 1999). The concentration of Fe in the leachates reaches 5,020 µg/L, the highest values being from the ferricretes and the partially-burnt tailings.

Table 5. Select analytical results of leachate tests on solid samples from the Pike Hill mines site. Values in bold exceed criteria.

Parameter/Element	pH	sp. cond. μS/cm	D.O. mg/L	O.R.P. mV	Fe^{2+}/Fe$_{total}$	Al μg/L	Cd μg/L	Co μg/L	Cu μg/L	Fe μg/L	Mn μg/L	Ni μg/L	Pb μg/L	Se μg/L	sulfate mg/L	V μg/L	Zn μg/L
Units Methods[1]					Hach	AES	MS	MS	MS	AES	MS	MS	MS	MS	IC	MS	MS
aquatic toxicity[2]	-	-	-	-	-	750	2.0	-	13	1,000	-	470	65	4.6	-	-	120
drinking water[3]	-	-	-	-	-	50-200	5	-	1,300	300	50	-	15	50	250	-	5,000
04Smith1	3.6	225	8	509	0.8	**2,010**	**3.44**	41.9	**754**	**467**	**900**	10.2	0.1	< 1	110	<0.5	**710**
04Smith2	3.4	244	8	497	0.7	126	**2.03**	64.2	**698**	207	**221**	15.2	<0.05	< 1	117	<0.5	**205**
04Smith3	3.2	304	7	444	0.3	79.9	0.39	4.64	**534**	98.7	**66.4**	1.5	0.4	< 1	167	<0.5	77.9
04Smith5	3.3	295	8	411	n.d.[4]	**577**	1.19	20.2	**479**	75	**898**	9.3	0.5	< 1	142	<0.5	**380**
04Smith6	5.9	17.6	8	283	n.d.	<50	<0.02	0.07	<0.5	<20	42.5	<0.4	<0.05	< 1	4	<0.5	0.6
04Smith7	5.9	13.3	8	277	n.d.	<50	<0.02	0.09	<0.5	<20	28.6	<0.4	<0.05	< 1	3.5	<0.5	0.7
04PKHL1	3.1	577	8	390	0.7	**630**	1.23	7.89	**1,280**	252	**66.1**	0.8	1	2.6	**350**	<0.5	**146**
04PKHL2	3.2	314	8	373	0.8	92.4	0.66	11.1	**695**	128	33	1.4	<0.05	1.5	175	<0.5	82.6
04PKHL3	3.2	315	8	581	0.8	62.8	0.66	3.53	**844**	76.8	24.8	0.7	0.2	1	160	<0.5	86.5
04PKHL7	3.7	260	8	571	0.7	125	**22.1**	81	**2,270**	63	**1,020**	23.9	2.2	2	142	<0.5	**3,340**
04PKHL9	2.9	967	8	564	0.1	**8,090**	**10.2**	1,020	**17,000**	**3,130**	251	44	0.72	**9.1**	**690**	<0.5	**955**
04PKHL10	7.1	206	6	374	n.d.	<50	**23**	1.06	6.2	<20	38.5	<0.4	<0.05	< 1	91	<0.5	**700**
04PKHL11	3.1	934	8	470	0.5	**1,520**	**3.5**	53.7	**2,240**	308	**95.7**	3.6	1.2	**5.8**	**718**	<0.5	**318**
04PKHL12	2.9	583	8	537	0.4	**339**	0.6	30.8	**53.3**	**3,090**	42.2	5.8	1.8	< 1	**261**	<0.5	79.9
04PKHL13	3.3	525	8	567	0.6	**497**	**2.41**	6.45	**999**	83.2	**52.6**	0.5	0.87	2.2	**329**	<0.5	110
04PKHL13-B	2.8	737	8	537	0.3	**461**	**2.53**	46.9	**262**	**5,020**	**56.5**	7.5	0.76	< 1	**312**	<0.5	**263**

[1] Hach: colorimetric method using Hach spectrophotometer; IC: ion chromatography; AES: inductively coupled plasma-atomic emission spectrometry; MS: inductively coupled plasma-mass spectrometry.

[2] Toxicity standards are for freshwater Criteria Maximum Concentrations (acute), except Fe and Se for Criterion Continuous Concentration (chronic exposure). Values from USEPA (2004d). Calculated on a hardness of 100 mg/L for hardness-dependent criteria. Standard for Al based on total metals, not dissolved.

[3] Drinking water standards from USEPA (2002). Standards for Al, Fe, Mn, sulfate, and zinc are secondary standards.

[4] n.d. = not determined.
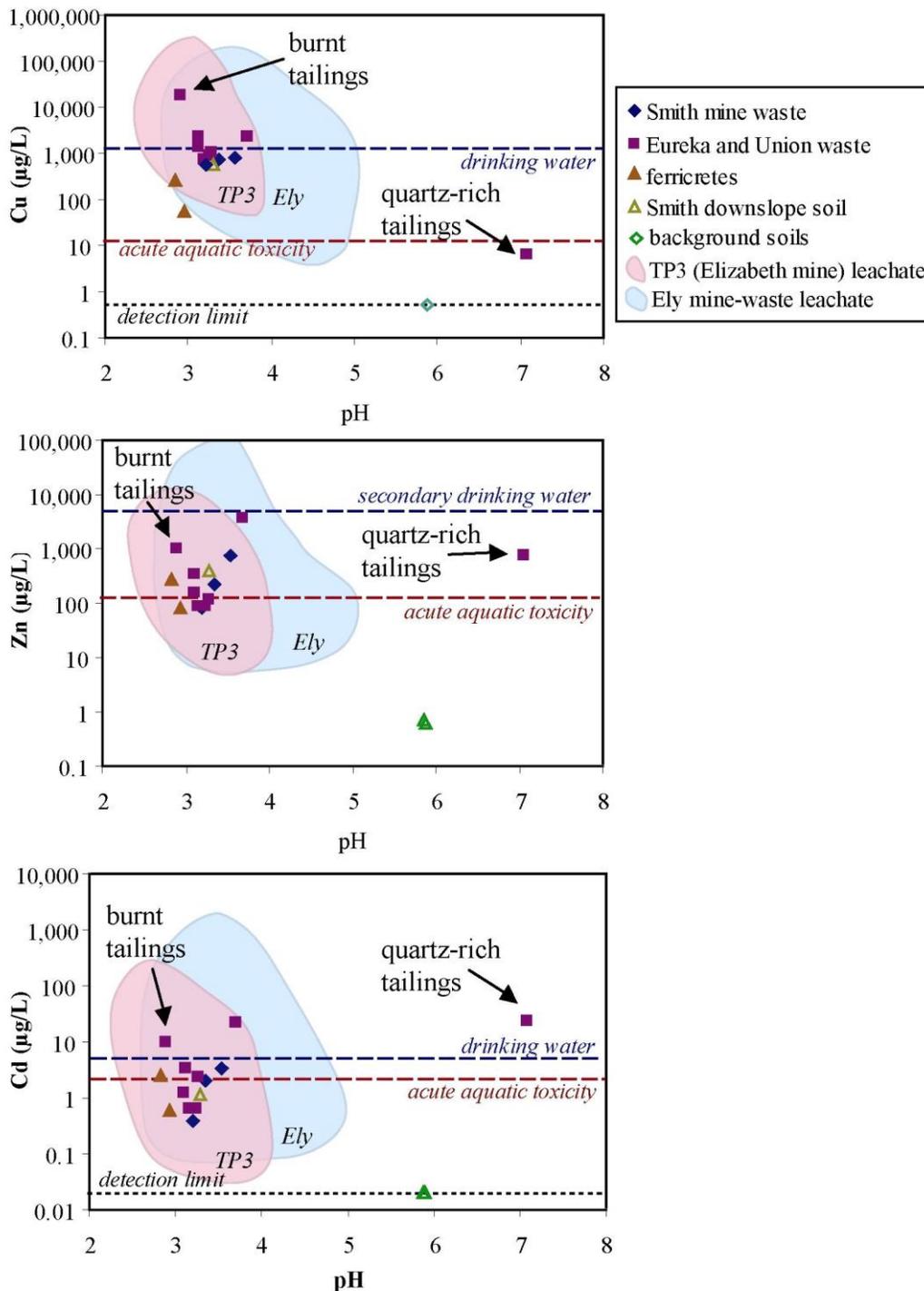
Figure 14. Dissolved metal concentrations in leachate as a function of pH. Shaded fields labeled TP3 and Ely represent the composition of leachate from the historic mine-waste pile (TP3) at the Elizabeth mine and mine waste at the Ely mine. Drinking water standards from U.S. Environmental Protection Agency (2002). Aquatic toxicity standards are based on a hardness of 100 mg/L $CaCO_3$ (U.S. Environmental Protection Agency, 2004d).

For these samples, the concentrations of Fe in the leachate exceed the chronic toxicity guideline for aquatic life. The concentrations of Mn in the leachates from most mine-waste samples exceed the secondary drinking water standard of 50 µg/L (Table 5). The two waste piles that contain the highest concentrations of Se leach Se in concentrations in exceedance of the acute toxicity standard. Four waste piles and two ferricrete samples from the Eureka and Union mines area leach SO_4^{-2} in concentrations that are greater than the secondary drinking water standard of 250 mg/L.

The pH of leachate from all mine-waste samples except the quartz-rich processed flotation-mill tailings, which contains calcite, is less than 4.2, the pH of the ESP solution. This decrease in leachate pH implies that precipitation interacting with most mine-waste at the site will produce acidic runoff.

The concentrations of Cd, Cu, and Zn in leachate from the historic mine waste at the Elizabeth mine (TP3) and mine waste from the Ely mine (Ely) are shown as shaded regions in Fig. 14. The same leachate procedures were preformed on all samples and data are from Hammarstrom et al. (2003) and Piatak et al. (2004). Concentrations of Cd, Cu, and Zn in leachate from most Pike Hill samples are within the compositional range of samples from the Elizabeth and Ely mines (Fig. 14). The pH of the leachate from the quartz-rich flotation-mill tailings (04PKHL10) is higher than leachates from the other mines sites; the concentration of Cu is low but the concentrations of Zn and Cd fall within the ranges of the other leachates (Fig. 14). In general, runoff from the Pike Hill mines site is expected to be similar in composition to that from the historic waste piles at the Elizabeth and Ely mines based on the results of leaching experiments. The pH of the runoff at Pike Hill may be higher due to the higher percentage of carbonate in the host rock compared to the Elizabeth and Ely mines.

Summary

Mine waste at the Pike Hill Superfund site was characterized in terms of bulk geochemistry, mineralogy, paste pH, acid-base accounting, and leachability of metals to provide a relative ranking of environmental impact and to serve as a basis for comparison to other mine waste at the nearby Elizabeth and Ely Superfund sites. The ultimate goal of this study, in conjunction with companion studies on surface water quality and downstream biologic impacts, is to serve as the foundation for a formal remedial investigation at the Pike Hill mines site. Results indicate that background soil samples, used as a baseline for comparison purposes, contain low concentrations of most metals; these concentrations of metals overlap background levels for metals in soils in the eastern U.S. The downslope soil at Smith mine contains slightly elevated concentrations of a few metals when compared to the background samples. These samples contain higher percentages of silicates than most mine-waste samples and their net-neutralization potentials are near zero. Leachate waters from background soils contain low concentrations of metals, which are below water-quality criteria.

All but two of the composite mine-waste samples at Pike Hill exhibit similar environmental signatures. The majority of mine-waste samples contain concentrations of Cu and Fe that exceed the PRGs for residential soils and concentrations of Se and Zn are significantly higher than mean concentrations for soils in the eastern United States. The low paste pH values and negative net-neutralization potentials indicate most material is potentially acid generating. Leachate tests indicate Cd, Co, Cu, Mn, and Zn are leached in concentrations higher than water-quality criteria

for the majority of composite mine-waste samples. The composite samples from the Smith mine generally have lower or comparable concentrations of metals, slightly lower acid-generating potentials, and comparable but not the maximum concentrations of metals in leachates relative to the composite samples from the Eureka and Union mines.

The two anomalous composite mine-waste samples are the quartz-rich processed flotation-mill tailings and the partially burnt flotation-mill tailings. First, the quartz-rich processed flotation-mill tailings contain concentrations of Zn and Cd that are over an order of magnitude higher than those found in the other samples. This sample also contains high As, Co and Mn. The high metal content is consistent with high sulfide content (~4 wt%), approximately 1 wt% of which is sphalerite. Despite the high concentrations of metals, this sample has a neutral paste pH and positive net-neutralization potential due to the presence of carbonate (~2 wt% calcite). This sample leaches Cu in concentrations that are below, but leaches Zn and Cd in concentrations above acute toxicity guidelines for aquatic life.

The second anomalous sample is the partially-burnt flotation-mill tailings that contain high concentrations of Ag, Cu, Mo, Se, and S when compared to the other mine-waste samples. The high Se is consistent with the anomalous concentration of Se in roasted waste rock from the Elizabeth mine. Besides high metal concentrations, this sample also has the lowest paste pH and net-neutralization potential and leaches Cd, Co, Cu, Fe, Mn, SO_4^{-2}, and Zn in excess of toxicity or drinking water criteria. These factors suggest that this material may be some of the most deleterious material on the site.

Based on the results of this study, mine waste at the Pike Hill Superfund site contaminates soils, is acid generating, and may release potentially toxic metals to streams. The environmental impacts of two other Superfund sites (the Ely and Elizabeth mines) are being evaluated along with the Pike Hill Superfund site. Mine waste at Pike Hill is chemically and mineralogically similar to that at the Elizabeth and Ely mines. Also, metals are leached and acid produced in comparable concentrations. However, in contrast to the Elizabeth and Ely mines, the host rock of the Pike Hill deposits contains significant amounts of carbonate minerals and thus has a greater acid-neutralizing capacity. Thus, deleterious effects to waters downstream of the Pike Hill mines site may be less or not as far-reaching due to metal-laden acidic waters interacting with alkaline waters in the receiving watershed. The formal remedial investigation will include at depth characterization of waste piles, assessments of metal loadings to surface water from individual piles, ground water impacts, and ecosystem and human health risk assessments.

Acknowledgments and Disclaimer

Literature Cited

Briggs, P.H. 2002a. The determination of forty elements in geological and botanical samples by inductively coupled plasma-atomic emission spectrometry. *In* J.E. Taggart, Jr. (ed). Analytical methods for chemical analysis of geologic and other materials. U.S. Geological Survey Open-File Report 02-0223, p. G1-G18.

Briggs, P.H. 2002b. The determination of twenty-seven elements in aqueous samples by inductively coupled plasma-atomic emission spectrometry. *In* J.E. Taggart, Jr. (ed). Analytical methods for chemical analysis of geologic and other materials. U.S. Geological Survey Open-File Report 02-0223, p. F1-F11.

Briggs, P.H. and A.L. Meier. 2002. The determination of forty-two elements in geological materials by inductively coupled plasma- mass spectrometry. *In* J.E. Taggart, Jr. (eds.). Analytical methods for chemical analysis of geologic and other materials. U.S. Geological Survey Open-File Report 02-0223, p. I1-I14.

Hageman, P.L., and P.H. Briggs. 2000. A simple field leach test for rapid screening and qualitative characterization of mine waste dump material on abandoned mine lands. ICARD 2000, Proceedings from the Fifth International Conference on Acid Rock Drainage II, p. 1463-1475.

Hageman, P.L., Z.A. Brown, and E. Welsch. 2002. Arsenic and selenium by flow injection or continuous flow-hydride generation-atomic absorption spectrophotometry. *In* J.E. Taggart, Jr. (ed). Analytical methods for chemical analysis of geologic and other materials. U.S. Geological Survey Open-File Report 02-0223, p. L1-L7.

Hammarstrom, J.M., A.L. Meier, J.C. Jackson, R. Barden, P.J. Wormington, J.D. Wormington, and R.R. Seal II. 1999. Characterization of mine waste at the Elizabeth copper mine, Orange County, Vermont. U.S. Geological Survey Open-File Report 99-564, 74 p.

Hammarstrom, J.M., R.R. Seal II, A.P. Ouimette, and S.A. Foster. 2001. Sources of metals and acidity at the Elizabeth and Ely mines. Society of Economic Geologists Guidebook Series, v. 35, p. 213-248.

Hammarstrom, J.M., N.M. Piatak, R.R. Seal II, P.H. Briggs, A.L. Meier, and T.L. Muzik. 2003. Geochemical characteristics of TP3 mine wastes at the Elizabeth copper Superfund site, Orange, Co., Vermont. U.S. Geological Survey Open-File Report 03-431, 40 p.

Kierstead, M.A. 2001. History and historical resources of the Vermont copper belt. Society of Economic Geologists Guidebook Series, v. 35, p. 165-191.

Lamothe, P.J., A.L. Meier, and S. Wilson. 2002. The determination of forty-four elements in aqueous samples in inductively coupled plasma-mass spectrometry, *In* J.E. Taggart, Jr. (ed). Analytical methods for chemical analysis of geologic and other materials. U.S. Geological Survey Open-File Report 02-0223, p. H1-H11.

Langmuir, D. 1997. Aqueous Environmental Geochemistry: Prentice-Hall Inc., New Jersey.

New York Department of Environmental Conservation. 1999. Water quality regulations: Surface water and groundwater classifications and standards. New York State codes, rules, and regulations, Title 6, Chapter X, Parts 700-706.

Piatak, N.M., J.M. Hammarstrom, R.R. Seal II, P.H. Briggs, A.L. Meier, T.L. Muzik, and J.C. Jackson. 2004. Geochemical characterization of mine waste at the Ely copper mine Superfund site, Orange County, Vermont. U.S. Geological Survey Open-File Report 2004-1248, 56 p.

Pitard, F.F. 1993. Pierre Gy's sampling theory and sampling practice – heterogeneity, sampling correctness, and statistical process control, 2nd ed. Boca Raton, FL. CRC Press, 488 p.

Power, M.S., and N.M. Milton. 1990. Detection of geobotanical anomalies associated with mineralization in the Glens Falls 1° x 2° quadrangle. *In* J.F. Slack (ed.). Summary results of the Glens Falls CUSMAP project, New York, Vermont, and New Hampshire: U.S. Geological Survey Bulletin 1887, p. I1-I8.

Price, W.A., K. Morin, and N. Hutt. 1997. Guidelines for the prediction of acid rock drainage and metal leaching for mines in British Columbia: Part II. Recommended procedures for static and kinetic testing. ICARD 1997, Proceeding from the 4th International Conference on Acid Rock Drainage, Vancouver, S.C., p. 15-30.

Shacklette, H.T., and J.G. Boerngen. 1984. Element concentrations in soils and other surficial materials of the conterminous United States. U.S. Geological Survey Professional Paper 1270, 105 p.

Slack, J.F., J.W. Whitlow, and M.P. Annis. 1984. Gold in stream sediments from the Orange County copper district, east-central Vermont. U.S. Geological Survey Open-File Report 84-889, 21 p.

Slack, J.F., P.J. Atelsek, and J.W. Whitlow. 1990. Geochemistry of stream sediments and heavy-mineral concentrates from the Orange County copper district, east-central Vermont. *In* J.F. Slack (ed.). Summary results of the Glens Falls CUSMAP project, New York, Vermont, and New Hampshire. U.S. Geological Survey Bulletin 1887, p. Q1-Q21.

Slack, J.F., T.W. Offield, W. C. Shanks III, and L.G. Woodruff. 1993. Besshi-type massive sulfide deposits of the Vermont copper belt. *In* J.F. Slack and T.W. Offield (eds.). Massive sulfide deposits of the Vermont copper belt. Society of Economic Geologists Guidebook Series, v. 17, Part II, p. 32-73.

Slack, J.F., T.W. Offield, L.G. Woodruff, and W.C. Shanks III. 2001. Geology and geochemistry of Besshi-type massive sulfide deposits of the Vermont copper belt. Society of Economic Geologists Guidebook Series, v. 35, p. 193-211.

Smith, K.S., 1999. Metal sorption on mineral surfaces: an overview with examples relating to mineral deposits. In G.S. Plumlee and M.J. Logsdon (eds.). The environmental geochemistry of mineral deposits, Part A. Society of Economic Geologists, Reviews in Economic Geology, v. 6A. p. 161-182

Smith, K.S., D.L. Campbell, G.A. Desborough, P.L. Hageman, R.W. Leinz, M.R. Stanton, S.J. Sutley, G.A. Swayze, and D.B. Yager. 2002. Toolkit for the rapid screening and characterization of waste piles at abandoned mine lands. *In* R.R. Seal II and N.K. Foley (eds.). Progress on geoenvironmental models for selected mineral deposit types. U.S. Geological Survey Open-File Report 02-195, Chapter C, p. 55-64.

Sobek, A.A., W.A. Schuller, J.R. Freeman, and R.M. Smith. 1978. Field and laboratory methods applicable to overburden and minesoils. EPA 600/2-78-054, 203 p.

Taylor, J.C., and R.A. Clapp. 1992. New features and advanced applications of Siroquant: A personal computer XRD full profile quantitative analysis software package. Advances in X-ray Analysis, v. 35, p. 49-55.

Theodorakos, P.M., W.M. d'Angelo, and W. H. Ficklin. 2002. Fluoride, chloride, nitrate, and sulfate in aqueous solution utilizing AutoSuppression chemically suppressed ion chromatography. *In* J.E. Taggart, Jr. (ed.). Analytical methods for chemical analysis of geologic and other materials. U.S. Geological Survey Open-File Report 02-0223, p. V1-V7.

Totten, B. 1999. Analysis of iron oxide coating that have formed as a result of acid mine drainage from the Pike Hill copper mine in northeastern Vermont. The Vermont Geological Society's spring meeting, presentation of student papers: The Green Mountain Geologist, v. 26, n. 2, p. 13-14.

U.S. Environmental Protection Agency. 1994. Test methods for evaluating solid waste, physical/chemical methods (SW-846), 3rd Edition, update 2B. Environmental Protection Agency National Center for Environmental Publications, Cincinnati, Ohio.

U.S. Environmental Protection Agency. 2002. List of Contaminants and their MCLs. EPA 816-F-02-013, July 2002. http://www.epa.gov/safewater/mcl.html#mcls.

U.S. Environmental Protection Agency. 2004a. Pike Hill Copper Mine, last updated December 17th, 2004. http://www.epa.gov/region1/superfund/sites/pikehill.

U.S. Environmental Protection Agency. 2004b. PRG Intercalc Tables, Soil. http://www.epa.gov/region09/waste/sfund/prg/files/04soils.pdf

U.S. Environmental Protection Agency. 2004c. USEPA Region 9, PRG Intercalc Table- Soils. http://www.epa.gov/region09/waste/sfund/prg/files/04prgtable.pdf

U.S. Environmental Protection Agency. 2004d. National Recommended Water Quality Criteria. http://epa.gov/waterscience/criteria/nrwqc-2004.pdf

White, W.S., and J.H. Eric. 1944. Preliminary report; geology of Orange County copper district, Vermont. U.S. Geological Survey Open-File Report 44-0019.

White, W.W., III, K.A. Lapakko, and R.L. Cox. 1999. Static-test methods most commonly used to predict acid-mine drainage: Practical guidelines for use and interpretation. *In* G.S. Plumlee and M.J. Logsdon (eds.). The environmental geochemistry of mineral deposits, Part A: Processes, techniques, and health issues. Society of Economic Geologists, Inc., Reviews in Economic Geology, v. 6A, p. 325-338.

Wiercinski, S. 1999. Geochemical and mineralogical analysis of the Pike Hill mine tailings, Corinth, Vermont. The Vermont Geological Society's spring meeting, presentation of student papers: The Green Mountain Geologist, v. 26, n. 2, p. 14-15.