

Sulfide oxidation and distribution of metals near abandoned copper mines in coastal environments, Prince William Sound, Alaska, USA

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Abstract

The oxidation of sulfide-rich rocks, mostly leftover debris from Cu mining in the early 20th century, is contributing to metal contamination of local coastal environments in Prince William Sound, Alaska. Analyses of sulfide, water, sediment, precipitate and biological samples from the Beatson, Ellamar, and Threeman mine sites show that acidic surface waters generated from sulfide weathering are pathways for redistribution of environmentally important elements into and beyond the intertidal zone at each site. Volcanogenic massive sulfide deposits composed of pyrrhotite and (or) pyrite + chalcopyrite + sphalerite with subordinate galena, arsenopyrite, and cobaltite represent potent sources of Cu, Zn, Pb, As, Co, Cd, and Hg. The resistance to oxidation among the major sulfides increases in the order pyrrhotite $\ll$ sphalerite $<$ chalcopyrite $\leq$ pyrite; thus, pyrrhotite-rich rocks are typically more oxidized than those dominated by pyrite. The pervasive alteration of pyrrhotite begins with rim replacement by marcasite followed by replacement of the core by sulfur, Fe sulfate, and Fe–Al sulfate. The oxidation of chalcopyrite and pyrite involves an encroachment by colloform Fe oxyhydroxides at grain margins and along crosscutting cracks that gradually consumes the entire grain. The complete oxidation of sulfide-rich samples results in a porous aggregate of goethite, lepidocrocite and amorphous Fe-oxyhydroxide enclosing hydrothermal and sedimentary silicates. An inverse correlation between pH and metal concentrations is evident in water data from all three sites. Among all waters sampled, pore waters from Ellamar beach gravels have the lowest pH (~ 3) and highest concentrations of base metals (to $\sim 25,000$ $\mu\text{g/L}$), which result from oxidation of abundant sulfide-rich debris in the sediment. High levels of dissolved Hg (to 4100 ng/L) in the pore waters probably result from oxidation of sphalerite-rich rocks. The low-pH and high concentrations of dissolved Fe, Al, and SO_4 are conducive to precipitation of interstitial jarosite in the intertidal gravels. Although pore waters from the intertidal zone at the Threeman mine site have circumneutral pH values, small amounts of dissolved Fe^{2+} in the pore waters are oxidized during mixing with seawater, resulting in precipitation of Fe-oxyhydroxide flocs along the beach–seawater interface. At the Beatson site, surface waters funneled through the underground mine workings and discharged across the waste dumps have near-neutral pH (6.7–7.3) and a relatively small base-metal load; however, these streams probably play a role in the physical transport of metalliferous particulates into

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intertidal and offshore areas during storm events. Somewhat more acidic fluids, to pH 5.3, occur in stagnant seeps and small streams emerging from the Beatson waste dumps. Amorphous Fe precipitates in stagnant waters at Beatson have high Cu (5.2 wt%) and Zn (2.3 wt%) concentrations that probably reflect adsorption onto the extremely high surface area of colloidal particles. Conversely, crystalline precipitates composed of ferrihydrite and schwertmannite that formed in the active flow of small streams have lower metal contents, which are attributed to their smaller surface area and, therefore, fewer reactive sorption sites. Seeps containing precipitates with high metal contents may contribute contaminants to the marine environment during storm-induced periods of high runoff. Preliminary chemical data for mussels (*Mytilus edulis*) collected from Beatson, Ellamar, and Threeman indicate that bioaccumulation of base metals is occurring in the marine environment at all three sites.

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1. Introduction

Between 1897 and 1930, approximately 6.4 million metric tons of Cu ore were mined from deposits of volcanogenic massive sulfide (VMS) located along shorelines of fjords and islands in Prince William Sound, Alaska (Fig. 1; Jansons et al., 1984). A large proportion of the total production was derived from the Beatson (~94%) and Ellamar (~5%) mines, although several other mines reported the shipment of small amounts of ore. Most of the mines occur on steep slopes within a few hundred meters of the ocean, except at Ellamar where the

orebody was mined offshore from a shaft protected by a cofferdam. Both underground and open-pit mining were conducted at the Beatson deposit. At all sites, piles of sulfide-rich rock accumulated along shorelines near the mines, milling operations and dock facilities. Although mining activity in Prince William Sound ceased in 1930, considerable ore-grade reserves remain unmined (Jansons et al., 1984).

Although some of the ore and waste material has been reworked by anthropogenic activity and natural erosion since 1930, much of the original mine-related debris remains in place along the Prince

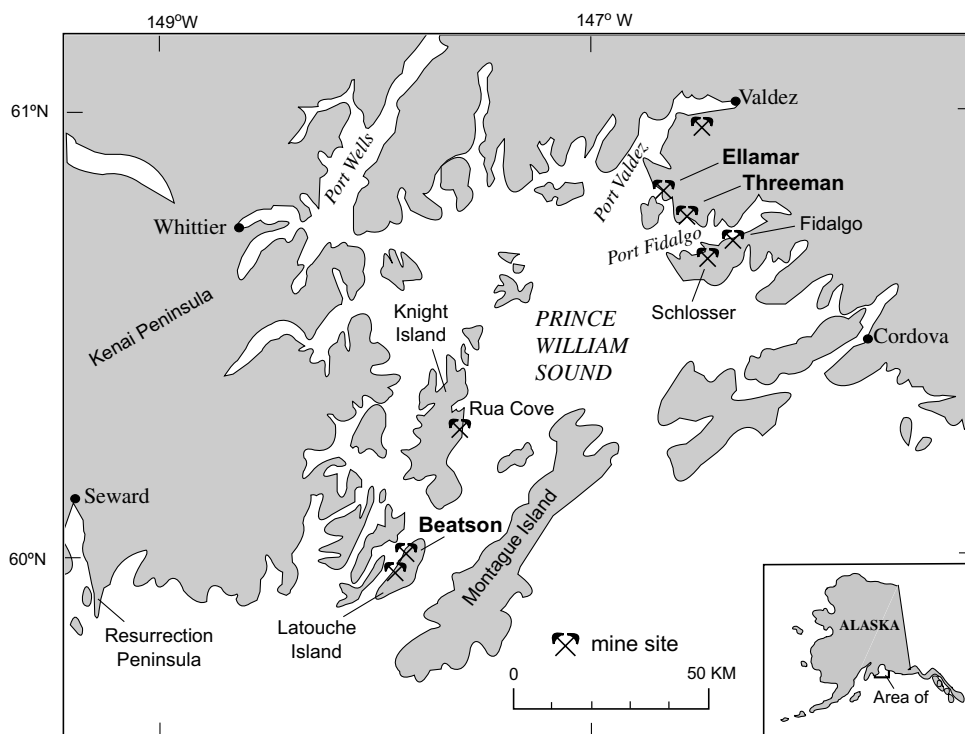


Fig. 1. Regional map showing locations of Cu mines in Prince William Sound, Alaska.

William Sound coastline. Thus, diverse sulfide-bearing material present in outcrops, underground and surface mines, mine talus, and remnant ore and waste piles has been exposed to surface weathering and oxidation for more than 70 a. Because of the wet subarctic climate of Prince William Sound (average precipitation 250–350 cm a⁻¹) and steep slopes, considerable surface water flows from high elevations along pathways over and through mine-related debris into the ocean. Flooded mine workings contribute to this flow. Earlier workers (Goldfarb et al., 1996; Gray and Sanzalone, 1996; Munk et al., 2003) identified the conditions of acid-mine drainage related to several massive sulfide deposits in Prince William Sound. Recent field investigations revealed that acidic metal-rich fluids extend into intertidal gravels at the Ellamar and Threeman mine sites (Koski et al., 2003; Shanks et al., 2003). This overview paper is the first of several reports that present new data and interpretations regarding the oxidation of source rocks (massive sulfides) and mobilization of environmentally important elements along fluid pathways at the Beatson, Ellamar, and Threeman mine sites. Companion papers will address seasonal variations in flow rates and metal fluxes at the Beatson site (Stillings et al., 2008), and microbiological communities and toxicity of water and sediments in specific mine-site environments (Foster et al., 2008). Additional chemical data for rock, sediment, water, precipitate, and biological samples are presented in Koski and Munk (2007).

1.1. Regional geology and origin of VMS deposits

Most of the VMS deposits in Prince William Sound are hosted by the Orca Group, a steeply dipping sequence of marine sandstone, siltstone, argillite, and greenstone of early Tertiary age. The sedimentary rocks represent turbiditic fan deposits formed in trench settings; greenstones intercalated with the sedimentary rocks indicate sedimentation near an ocean ridge. Within the Orca Group, more extensive fragments of oceanic crust occur in the ophiolites of Knight Island and the Resurrection Peninsula (Fig. 1). The deformed belt of trench deposits and oceanic crust fragments exposed around Prince William Sound records the early Tertiary history of continental collision involving ridge subduction along the southern Alaska continental margin (Haeussler et al., 1995; Bradley et al., 2003; Madsen et al., 2006).

The VMS deposits of Prince William Sound are by-products of sea-floor spreading and volcanic eruptions along a northern Pacific Ocean ridge prior to ridge subduction at the North American plate margin. Analogous mineral deposits on the sea floor of modern ocean ridges are formed at zones of focused high-temperature (250–350 °C) hydrothermal discharge in the neovolcanic zone along the ridge axis (Hannington et al., 1995). The eruption of lavas and fluid circulation at ridges are related to emplacement of magma bodies into the upper oceanic crust during sea-floor spreading.

At present-day ocean ridges distal from continental margins, the host rocks for VMS deposits are entirely volcanic rocks; these mineral deposits are analogous to ophiolite-hosted deposits on land, such as the Rua Cove deposit on Knight Island (Fig. 1; Crowe et al., 1992). In contrast, ocean ridges evolving near continental margins are subjected to sedimentation from terrigenous sources, and in this environment VMS deposits commonly have sediment substrates (Koski et al., 1993; Goodfellow et al., 1999). Owing to water–rock interactions during circulation of hydrothermal fluids, the mineralogy and chemistry of hydrothermal deposits at ocean ridges are, to an extent, influenced by the substrate composition. For example, the abundance of pyrrhotite and enrichments of Pb, As, Se, Bi, and other elements in massive sulfide deposits from the southern Gorda Ridge (offshore northern California) reflect interaction between fluids and continentally derived sediment covering the ridge axis (Koski et al., 1994). The Prince William Sound VMS deposits described in this paper formed in a sediment-dominated paleoridge environment (Crowe et al., 1992).

1.2. Nature of copper orebodies in the Orca Group

Orebodies within the Orca Group occur as multiple layers and lenses of massive sulfide (mainly pyrrhotite, pyrite, chalcopyrite, and sphalerite) or semi-massive sulfide (sulfide plus variable amounts of quartz, calcite, chlorite, and muscovite) that are conformable with sedimentary beds. Greenstones interlayered with sandstone and shale typically have a small volume compared with sedimentary rocks (Moffit and Fellows, 1951). The sedimentary and volcanic strata, along with the contained massive sulfide bodies, typically are steeply dipping throughout the region; variable amounts of shearing, foliation in massive sulfides, and slaty cleavage in shaly

beds are the result of transpressional tectonics during accretion of the Orca Group strata to the continental margin in the early Tertiary (Kusky et al., 1997; Bradley et al., 2003). Along strike, massive sulfides grade into semi-massive sulfides, disseminated sulfide, and finally, barren sedimentary rock. The largest individual deposit in Prince William Sound, mined at Beatson, was approximately 300 m in length and 120 m in width (Bateman, 1924).

1.3. Site descriptions

Along the northwestern coast of Latouche Island, the Beatson and Blackbird VMS deposits occur along a NE-trending zone of semicontinuous sulfide mineralization. The mining of nearly 6 million tons of Cu ore at Beatson resulted in extensive underground workings, an open pit, and large mine dumps around the pit perimeter and at lower elevations along the shoreline of Latou-

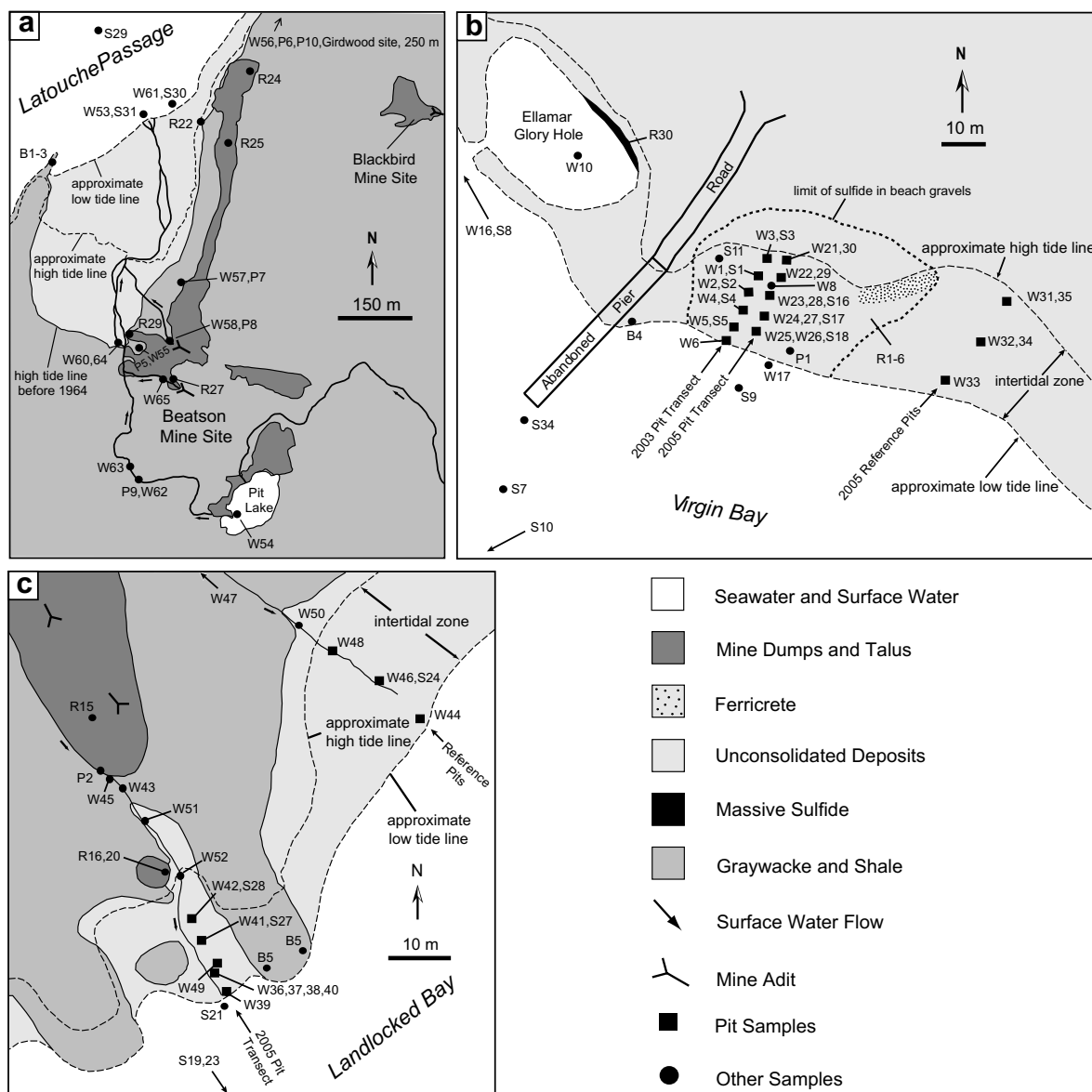


Fig. 2. Sketch maps showing geologic and anthropogenic features and sample sites at the (a) Beatson, (b) Ellamar, and (c) Threeman mine sites in Prince William Sound. Labels of sample sites correspond to map numbers in data tables. In sample numbers, W: water, R: rock, P: precipitate, S: sediment, and B: biological.

che Passage (Figs. 2a and 3a). A stream eroding through the higher elevation waste dumps has filled the open pit, and water from this pit lake currently flows through the mine workings and discharges from the southernmost adit. Goldfarb et al. (1996) measured the flow rate from this adit at $\sim 0.3 \text{ m}^3 \text{ s}^{-1}$. This discharge has incised through

the lower dump and merges with other small creeks, one of which emanates from the base of the upper dump. The combined drainage results in a braided stream that flows onto beach deposits at lower elevations (Fig. 3a). Relatively minor volumes of water were seeping from the base of shoreline dumps during field work in June, 2005.



Fig. 3. Photographs of features related to sulfide oxidation at the three mine sites. (a) View to west across debris of Beatson waste dumps, braided stream carrying discharge from underground mine, and wide beach area uplifted by 1964 earthquake. (b) View to SE from abandoned pier showing low mound of sulfide-rich debris in beach gravels at Ellamar mine site. (c) Fe oxyhydroxide precipitates covering beach gravels at the Threeman mine site. (d) Yellowish-green jarosite precipitation surrounding partly oxidized sulfide clast in pit excavated in beach gravels at the Ellamar mine site. (e) Precipitates composed of ferrihydrite and schwertmannite in bed of small stream below upper mine dumps and pit lake at the Beatson mine site.

These seepages formed shallow stagnant ponds in flat areas, and rills on steeper slopes; all were sites of Fe-oxyhydroxide precipitation. Approximately 0.5 km NE of the main Beatson drainage, a stagnant pool containing abundant Fe precipitates extends from a mine adit onto beach gravels containing mine wastes (Girdwood site; Fig. 2a). Deformation during the 1964 earthquake raised the land surface in the Beatson mine area approximately 3 m relative to sea level. This uplift increased the distance between the lower Beatson mine dumps and the high-tide line by as much as 150 m (Fig. 2a).

Mining of the Ellamar deposit largely was conducted below sea level, through access from a large shaft excavated behind a cofferdam. Approximately 536,000 tons of ore were produced. The mine, now marked by a “glory hole” flooded with seawater (Fig. 2b), was developed to a depth of about 180 m below sea level (Moffit and Fellows, 1951). Massive sulfide is exposed around the edge of the glory hole at low tide. Much of the mine waste was backfilled into the mine, and consequently, little of the original waste rock is apparent on the surface. Today, a low reddish mound of massive sulfide rubble mixed with sedimentary detritus extends across the intertidal zone into Virgin Bay (Figs. 2b and 3b). Part of this mound has been indurated owing to precipitation of Fe-oxyhydroxide cement in the interstices between lithic and sulfide clasts, and is referred to as ferricrete in this study (Fig. 2b). This sulfide-bearing debris is the remains of a large accumulation of ore bunkered next to the loading dock prior to shipping in the early 1900s.

At the Threeman mine (Fig. 2c), about 6000 tons of ore were recovered from several adits that follow a steeply dipping zone of mineralization on the north shore of Landlocked Bay. Ore was trammed down the steep slope to sea level for temporary storage in bunkers before loading onto steamships docked nearby. Today, aprons of sulfide-bearing talus cover the slope below each adit, and talus from the lowest adit extends nearly to the level of unconsolidated beach deposits (Fig. 2c). A small volume of water flows from the base of the lowest talus pile and drains into the intertidal zone. A deeply weathered, 5-m-wide mound of sulfide rubble lies on bedrock adjacent to the drainage and near the high-tide line. Below the point where this drainage enters the intertidal zone, flocculent red precipitates cover the beach gravels (Fig. 3c).

2. Sampling and analytical methods

2.1. Field approach

During field activities in 2003 and 2005, sulfide-rich rock samples exhibiting various degrees of weathering were collected from surface and underground mine workings, mine talus, ore bunkers, ore and waste dumps, and beach gravels. Water samples were collected from streams above and below mine dumps, seepages below mine dumps and adits, the pit lake at Beatson, and offshore (seawater). Pore waters were also collected from pits excavated into beach gravels at the Ellamar and Threeman sites. Measurements of pH, dissolved O₂, conductivity, temperature, and alkalinity were made in the field. Precipitates were collected from seeps and drainages below mine dumps at the Threeman and Beatson (including the nearby Blackbird and Girdwood sites) deposits, and from unconsolidated beach sediment at Ellamar. In 2005, mussels were collected at all three sites for analyses of trace elements. Sketch maps showing geologic and anthropogenic features and sample sites were prepared for the Ellamar, Threeman, and Beatson mine areas (Fig. 2).

All field activities in 2003 and 2005 were supported by the research vessel *Auklet*. Submarine samples of unconsolidated sediment were collected by gravity core and dredge. In 2005, a remotely operated vehicle (ROV) designed by Eastern Oceanics was deployed from the *Auklet* to sample seawater, precipitates, and sediment in intertidal and subtidal areas.

2.2. Analyses of solids

Samples of sulfide-rich rocks, ferricrete, unconsolidated marine sediment (mud and sand fractions), precipitates, and mussel tissue were analyzed by inductively coupled plasma-mass spectrometry (ICP-MS) following multi-acid (HCl–HNO₃–HClO₄–HF) digestion in USGS laboratories, Denver, CO (Briggs and Meier, 2002). Mercury was determined by continuous-flow cold-vapor atomic absorption spectroscopy (CV-AAS; Brown et al., 2002), and total S was determined by standard combustion techniques. Mussel samples were frozen shortly after collection. Tissue was hand picked from shell material and freeze dried before grinding and analysis.

Initial textural and mineral investigations of sulfide-bearing and ferricrete samples were obtained

by reflected-light microscopy of doubly polished thin sections. X-ray diffraction (XRD) analyses of sediments, precipitates, and mineralized rocks were performed on powdered samples (<200 mesh) by S. Sutley of the USGS. The diffractometer is equipped with a Philips automated goniometer and utilizes Cu $K\alpha$ radiation; power settings were 40 kV and 25 mA. XRD patterns were interpreted using the Materials Data Inc. Jade + S/M software (v.7.1) in conjunction with the latest International Centre for Diffraction Data (ICDD) database. Additional mineralogical and chemical data for solids and precipitates were obtained from C-coated thin sections using scanning electron microscopy (SEM) and electron microprobe (EM) at the USGS microbeam facility in Menlo Park, California. The SEM is equipped with backscattered and secondary electron detectors and coupled with an energy-dispersion X-ray spectrometer (EDS). Concentrations of 13 elements in sulfide minerals were determined by wavelength-dispersion analysis using a Jeol 8900 Superprobe equipped with five spectrometers. The instrument conditions were 30 kV accelerating potential, 30 nA beam current, focused beam width 5 μ m, and 20 s counts per analysis. Standard reference materials include natural pyrite for calibration of Fe and S; chalcopyrite for Cu and S; galena for Pb; skutterudite for As and Co; pentlandite for Ni; cinnabar for Hg; synthetic ZnS for Zn; Ag₂S for Ag; CdS for Cd; Mn₂O₃ for Mn; and elemental Se for Se. X-ray intensities were converted to concentrations utilizing the standard ZAF correction method.

2.3. Analyses of waters

Surface water, pore water, and seawater were collected with sterile plastic syringes and stored in HDPE bottles. Samples for analysis of total acid-recoverable metal content (unfiltered and acidified) and analysis of dissolved metal content (<0.45 μ m filter and acidified) were taken at each site. Water samples were preserved with ultra-pure trace metal-grade HNO₃. In addition, at each site a water sample for anion determination was also collected in a HDPE bottle and kept cold until analysis in the laboratory. Elemental concentrations were analyzed by ICP-AES/MS in laboratories of the USGS in Denver, CO (Briggs, 2002; Lamothe et al., 2002). Mercury was analyzed by flow-injection cold-vapor atomic fluorescence spectrometry (Hageman, 2002). Anions, including Cl and SO₄ were analyzed by ion chromatography (Theodorakos et al., 2002) and

alkalinity that were not reliably measured in the field were rechecked in the laboratory by automatic titration. Analytical accuracy was assessed through the submission of internal standards obtained from NIST and commercial chemical suppliers (SpexCerti-Prep™). As an additional check for accuracy, precision, and agreement between sample batches, a sample collected in 2003 was resubmitted for analysis along with the 2005 samples.

3. Results

3.1. Composition of sulfide-rich samples

3.1.1. Mineralogy

The mineralogy of 31 sulfide-rich samples collected at the Beatson, Ellamar, Threeman, Fidalgo, and Schlosser mine sites is summarized in Table 1. Nearly all of the samples fall into two categories based on the dominant Fe-sulfide mineral. Pyrite-dominant samples consist of pyrite $\pm$ chalcopyrite $\pm$ sphalerite $\pm$ pyrrhotite, whereas pyrrhotite-dominant samples contain pyrrhotite + chalcopyrite + sphalerite $\pm$ pyrite. Samples obtained from beach gravels and outcropping massive sulfide at Ellamar are predominantly the pyrite-dominant type, whereas samples from the Threeman, Schlosser, and Fidalgo mine sites are pyrrhotite-dominant. Samples from the Beatson mine dumps include both pyrite- and pyrrhotite-dominant types. Texturally, the pyrite-dominant samples (pyrite may comprise up to 95% of total sulfide) range from compact and nearly monomineralic aggregates of subhedral to euhedral pyrite crystals to loose aggregates of clastic pyrite with variable amounts of interstitial chalcopyrite and sphalerite. In pyrite-dominant samples, pyrrhotite is a minor phase or absent. Pyrrhotite-dominant samples (pyrrhotite up to 50% of the total sulfide) from the Threeman and Beatson sites have a very different texture in which clusters of pyrrhotite and sphalerite grains are embedded in a semicontinuous matrix of chalcopyrite. Clusters of subhedral pyrite are present in a few pyrrhotite-dominant samples, and absent in others. The ratio of chalcopyrite to total sulfides in ore-grade samples is generally >0.5, with modal amounts of chalcopyrite up to 90% of total sulfide. Although cubanite has been reported from the Beatson and Ellamar deposits (Bateman, 1924; Crowe et al., 1992), it was not identified in this study. Sphalerite with Fe contents between 6.5 and 10.5 wt% (see sulfide mineral chemistry) is ubiquitous in sulfide-rich samples;

Table 1
Relative abundances of primary and secondary minerals in sulfide-rich samples

Major		Minor		Trace	
<i>Primary minerals</i>					
Pyrrhotite	$Fe_{1-x}S$	Arsenopyrite	$FeAsS$	Barite	$BaSO_4$
Pyrite	FeS_2	Cobaltite	$CoAsS$	Cassiterite	SnO_2
Chalcopyrite	$CuFeS_2$	Galena	PbS	Bismuthinite	Bi_2S_3
Sphalerite	$(Zn, Fe)S$	Calcite	$CaCO_3$	Hedleyite	Bi_7Te_3
Quartz	SiO_2	Dolomite	$CaMg(CO_3)_2$	Hessite	Ag_2Te
Albite	$NaAlSi_3O_8$			Stibnite	Sb_2S_3
Chlorite (clinochlore)	$(MgFe)_5Al(Si_3Al)O_{10}(OH)_8$			Brannerite	UTi_2O_6
Muscovite	$KAl_2(Si_3Al)O_{10}(OH)_2$			Gold	$Au(Ag)$
Talc	$Mg_3Si_4O_{10}(OH)_2$			Monazite-(Ce)	$(Ce, La)PO_4$
				Rutile	TiO_2
				Apatite	$Ca_5(PO_4)_3(OH)$
<i>Weathering products</i>					
Goethite	$\alpha-FeO(OH)$	Lepidocrocite	$\gamma-FeO(OH)$	Jarosite	$KFe_3(SO_4)_2(OH)_6$
Fe oxyhydroxide	(amorphous)	Covellite	CuS		
Marcasite	FeS_2	Fe–Al sulfate ^a			
Sulfur	S				
Fe sulfate ^a					

^a Mineral name and formula uncertain.

modal amounts of sphalerite range from 5% to 30% of total sulfide.

Arsenopyrite and galena are present in minor amounts in nearly all sulfide-rich samples; typically, arsenopyrite and galena together comprise <1% of the total sulfide content. Arsenopyrite is locally concentrated in massive sulfide as subhedral crystals, up to 0.25 mm across, intergrown with the major sulfide minerals. Arsenopyrite is somewhat more abundant in pyrite-dominant massive sulfide. In one pyrrhotite-dominant sample from the Threeman deposit, cobaltite intergrown with galena is present as inclusions in chalcopyrite. Galena typically forms small euhedral to irregular inclusions (<30 μ m) in other sulfides in both pyrite- and pyrrhotite-dominant samples. Barite, cassiterite, bismuthinite, stibnite, brannerite, gold, rutile, apatite, and monazite-(Ce) are present in trace amounts in pyrite-dominant samples, usually as tiny crystals along pyrite–pyrite grain boundaries. The telluride minerals hedleyite and hessite occur as elongate binary inclusions in chalcopyrite grains within pyrrhotite-dominant samples.

Mineralized rock samples viewed in thin section commonly have domains with clastic textures preserved from the original sand and silt turbidites. Regionally, the Orca Group sandstones of Prince William Sound are quartz rich (>50%) with moderate feldspar (25–30%) and lithic (to 25%) contents (Dumoulin, 1987, 1988). Detrital phyllosilicate

grains including chlorite, muscovite and biotite, comprise <10% of total sand grains. Volcanic grains comprise about 1/3 of the total lithic fraction.

At scales ranging from hand samples to individual thin sections, there is a complete gradation from unmineralized quartzo-feldspathic sandstone to clast-dominated textures with interstitial sulfide to massive sulfide devoid of a detrital component. Quartz and phyllosilicate minerals of hydrothermal origin can be distinguished from detrital material. Hydrothermal quartz is relatively clear and forms interpenetrating intergrowths with all major sulfide minerals. Hydrothermal chlorite (clinochlore) and muscovite are coarse-grained relative to detrital phyllosilicates, and are also intimately intergrown with sulfides. Chlorite and talc also occur as massive replacements of sand-size grains, most likely mafic volcanic clasts in the original sediment. Patches of fine-grained muscovite may also represent replacement of original feldspathic grains in the sediment. Interstitial calcite and dolomite are present in many pyrite- and pyrrhotite-dominant samples, and based on textural considerations, formation of these carbonate minerals was contemporaneous with sulfide deposition. The identification of albite in sulfide-rich samples by XRD may reflect the presence of hydrothermally altered detrital feldspar grains.

Sulfide-rich samples from all sites show signs of deformation related to post-mineralization tectonic events along the plate margin. These features

include anastomosing fractures healed by sulfides, quartz, and calcite, brecciation and granulation of pyrite, curved mica plates and calcite cleavages, and pressure fringes of quartz, calcite, and mica around pyrite grains. Vein-like masses of coarse-grained calcite associated with massive sulfide at the Ellamar deposit also appear to postdate seafloor mineralization.

Weathering and exposure to oxygenated surface waters has resulted in the widespread degradation of sulfide-rich rocks and formation of secondary minerals at all mine sites. The weathering products include goethite, amorphous Fe-oxyhydroxide, lepidocrocite, marcasite, sulfur, covellite, jarosite and unidentified Fe and Fe–Al sulfates (Table 1). The occurrence of secondary minerals is described in greater detail in Section 4.1.

3.1.2. Chemistry of whole-rock sulfide samples

Chemical data for 20 samples of sulfide-rich rock from five separate Cu deposits are presented in Table 2. The highest S contents near 50 wt% are obtained from pyritic massive sulfide, whereas S contents <20 wt% are derived from oxidized pyrrhotite-rich samples. One pyrite-dominant sample (the sample of Cu ore collected at Busby Reef) contains 15 wt% Cu; however, samples dominated by pyrrhotite or pyrrhotite + pyrite are generally enriched in chalcopyrite and have high Cu concentrations (11 samples average 8.7 wt%). In comparison, six pyrite-dominant samples collected from the beach at Ellamar average 2.3 wt% Cu, and three samples (as well as a pyrite-dominant sample from the Schlosser mine) contain <0.5 wt% Cu. The Zn contents of samples from all five mine sites are generally <1 wt%, but two sphalerite-rich samples from the Ellamar and Beatson sites have 17 and 5.7 wt% Zn, respectively.

The distribution of trace elements from sample to sample can be related to the observed mineralogy, most notably the high Cd (477 mg/kg) concentration in a sphalerite-rich Ellamar sample (03R-8A3) and high As (9100 mg/kg) and Pb (4150 mg/kg) concentrations in a Beatson sample (05B007Rb) containing relatively abundant arsenopyrite and galena. High Co contents (>300 mg/kg) occur in both pyrite-dominant and pyrrhotite-dominant samples from the Ellamar and Threeman sites, but the highest Co (854 mg/kg) value was obtained from the Threeman sample (03R-3A) containing cobaltite. Other notable metal enrichments at specific mine sites include the three highest Ni values and

three of the four highest Cr values in pyrrhotite-dominant sulfide samples from the Threeman deposit, high Ag values in samples from the Beatson deposit, and relatively high U in samples from Ellamar. The elevated U in Ellamar samples (to 4.9 mg/kg) is probably related to the occurrence of the U–Ti oxide mineral brannerite.

3.1.3. Sulfide-mineral chemistry

Electron microprobe analyses for sulfides from the Beatson, Ellamar, and Threeman deposits provide additional detail about the distribution of environmentally important trace elements at the scale of individual minerals (Table 3). Although concentrations of many trace elements in the major sulfide minerals are typically at or below their detection levels (~0.01 wt%), elements with average concentrations in the range from ~0.1 to ~0.2 wt% include Pb in pyrite, pyrrhotite, chalcopyrite and sphalerite, Co in pyrite and pyrrhotite, and Cd in sphalerite. Pyrite grains in one sample have an average As content of 0.15 wt%. Sphalerite grains in nine samples average 7.8 wt% Fe and 0.32 wt% Cu, and individual grains in sample 05PWSB004Ra are enriched in multiple trace elements, including Pb (to 0.47 wt%), Co (to 0.18 wt%), Ni (to 0.10 wt%), Se (to 0.10 wt%), Ag (to 0.13 wt%), Mn (to 0.15 wt%), Cd (to 0.31 wt%), and Hg (to 0.18 wt%).

3.2. Composition of sediments and precipitates

Sediment samples collected in offshore and intertidal environments and precipitate samples from seeps and drainages below mine dumps were analyzed to characterize more fully the distribution of metals at the Ellamar, Threeman, and Beatson mine sites (Table 4). One precipitate sample from Ellamar (05PWSE201P) was collected in the intertidal zone. Mud samples dredged offshore from the three mine sites are generally low in Fe (<5 wt%) and other metals with the exception of the sample dredged offshore of Beatson (depth 33 m) which contains 1590 mg/kg Cu and 684 mg/kg Zn. Two sediment samples from the seaward margin of the intertidal zone at Beatson also have high Cu concentrations (>1000 mg/kg). Sandy sediment collected in shallow water offshore at Ellamar is enriched in Cu and Zn compared with sediments sampled in deeper water of Virgin Bay.

Compared with samples recovered offshore, the sand fraction of sediment samples from the intertidal zone at Ellamar are considerably enriched in

Table 2
Whole-rock chemical data for sulfide-rich samples

Map no. ^a	Sample no.	Mine site	Location	Mineralogy ^b	S wt%	Fe wt%	Cu wt%	Zn wt%	Ag mg/kg	As mg/kg	Cd mg/kg	Co mg/kg	Cr mg/kg	Hg mg/kg	Mn mg/kg	Ni mg/kg	Pb mg/kg	Se mg/kg	U mg/kg
R1	03–100	Ellamar	Intertidal	py	n.a. ^c	38	0.78	0.19	n.a.	380	5.9	26	3.4	n.a.	68	8.2	93	n.a.	0.26
R2	03R-1	Ellamar	Intertidal	py	n.a.	23	6.7	0.18	n.a.	75	5.8	416	17	n.a.	638	29	23	n.a.	2.1
R3	05E006R	Ellamar	Intertidal	py	52	41	0.14	0.068	26	280	2.7	14	2.8	7.2	6.3	4.6	258	140	0.97
R4	03R-8A2	Ellamar	Intertidal	po-py	35	26	12	0.37	27	88	9.8	786	1.6	0.64	334	1.5	23	200	4.6
	05BR001Ra	Ellamar	Busby Reef ^d	py	34	24	15	0.10	12	250	3.6	529	2.6	0.48	14	3.4	32	440	0.16
R5	03R-8A3	Ellamar	Intertidal	py	38	28	0.20	17	28	1000	477	7.7	1.6	61	359	4.8	325	7.2	4.9
R6	03R-8C	Ellamar	Intertidal	py	36	30	5.8	0.25	21	120	7.4	435	0.8	0.05	453	2.6	42	170	2.8
R30	03R-9	Ellamar	Outcrop	py	50	42	0.31	0.77	17	320	18	62	0.4	4.4	255	1.7	185	17	1.7
	03R-3A	Threeman	Bunker ^e	po	n.a.	33	2.4	0.24	n.a.	800	6.4	854	34	n.a.	228	82	1570	n.a.	0.16
R15	03R-4A	Threeman	Mine talus	po	n.a.	20	10	0.48	n.a.	98	17	323	47	n.a.	337	130	15	n.a.	0.08
R16	03R-5A	Threeman	Ore pile	po	35	44	3.6	0.13	7.5	8.7	5.1	580	0.3	0.04	72.8	129	5.1	380	0.05
R20	05T003R	Threeman	Ore pile	po-ox	14	40	2.7	0.071	4.8	13	1.8	97	49	0.04	380	18.5	4.7	170	1.8
R22	05B002R	Beatson	Dump	po	32	22	16	0.77	54	22	24	143	<0.2	0.06	132	45	27	200	0.04
R24	05B004Rb	Beatson	Dump	po	20	21	9.6	0.35	45	24	13	114	5.9	0.02	184	5.0	52	210	1.3
R25	05B005R	Beatson	Dump	po	22	16	15	0.24	64	9.5	7.3	52	2.2	<0.02	128	17	404	280	0.13
R27	05B007Rb	Beatson	Dump	po-py	24	23	7.4	5.7	47	9100	153	70	1.2	<0.02	1350	17	4150	78	0.04
R27	05B007Ra	Beatson	Dump	po-py	30	19	11	0.48	64	340	14	268	4.5	<0.02	114	12	559	210	0.14
R29	05B011R	Beatson	Dump	po-py-ox	3.6	14	1.0	0.12	7.7	66	3.1	18	69	2.9	1450	12	69	16	0.71
	03R-2C	Fidalgo	Bunker	po	n.a.	26	8.4	0.094	n.a.	17	4.5	109	11	n.a.	344	15	22	n.a.	0.48
	SM-1	Schlosser	Mine	py	n.a.	38	0.20	0.051	n.a.	160	1.5	31	<0.2	n.a.	11	<1	53	n.a.	0.25

^a Map numbers refer to locations in Fig. 2.

^b Mineralogy: py, pyrite dominant; po, pyrrhotite dominant; po-py, pyrrhotite + pyrite; ox, oxidized.

^c Not analyzed.

^d Ore sample from Ellamar recovered from site of sunken ship on Busby Reef, Prince William Sound.

^e Ore sample from bunker near Threeman.

Table 3

Average electron microprobe analyses of sulfide minerals from Beatson, Ellamar, and Threeman mine sites (Concentrations reported in wt%)

Mineral	Mine site	Sample no.	<i>n</i> ^a	Fe	Cu	Zn	Pb	As	Co	Ni	Se	Ag	Mn	Cd	Hg	S	Total
Pyrite	Beatson	05PWSB007Rb	20	47.29	0.01	0.03	0.14	0.04	0.16	0.01	0.02	0.01	0.00	0.00	0.00	53.11	100.82
	Beatson	05PWSB001R	20	47.65	0.02	0.06	0.16	0.15	0.07	0.01	0.00	0.01	0.00	0.00	0.00	52.08	100.21
	Ellamar	PWS03R-8C1	9	47.25	0.05	0.02	0.15	0.01	0.09	0.01	0.00	0.01	0.00	0.01	0.00	53.67	101.27
	Ellamar	PWS03R-8A2	11	46.91	0.34	0.07	0.14	0.01	0.24	0.01	0.01	0.01	0.01	0.00	0.01	53.83	101.58
	Ellamar	PWS03-100	16	47.01	0.01	0.04	0.14	0.02	0.05	0.00	0.01	0.00	0.03	0.00	0.00	53.93	101.24
	Ellamar	PWS03R-8A3	7	47.32	0.01	0.04	0.15	0.07	0.05	0.00	0.00	0.01	0.02	0.00	0.00	53.78	101.45
Pyrrhotite	Beatson	05PWSB004Ra	18	60.38	0.01	0.05	0.11	0.00	0.09	0.01	0.02	0.01	0.00	0.01	0.00	38.32	99.00
	Beatson	05PWSB007Rb	5	61.11	0.01	0.07	0.12	0.01	0.08	0.01	0.02	0.01	0.00	0.01	0.00	39.18	100.63
	Beatson	05PWB002R	20	60.63	0.02	0.02	0.09	0.00	0.14	0.02	0.03	0.00	0.01	0.01	0.00	36.70	97.67
	Ellamar	PWS03R-8C1	10	60.80	0.03	0.08	0.00	0.01	0.06	0.00	0.03	0.00	0.00	0.00	0.00	38.90	99.90
	Threeman	PWS03R-4A	14	61.03	0.00	0.01	0.09	0.00	0.18	0.05	0.04	0.00	0.01	0.01	0.00	39.07	100.49
	Threeman	PWS03R-3A	10	61.39	0.00	0.03	0.08	0.00	0.19	0.02	0.04	0.00	0.00	0.00	0.00	39.14	100.9
	Threeman	PWS03R-5A	9	61.31	0.01	0.03	0.08	0.00	0.14	0.02	0.03	0.02	0.01	0.01	0.00	38.91	100.57
Altered pyrrhotite	Beatson	05PWSB004Ra	8	45.10	0.02	0.03	0.16	0.01	0.11	0.01	0.03	0.00	0.01	0.00	0.00	50.61	96.66
	Beatson	05PWSB002R	19	44.83	0.06	0.04	0.10	0.00	0.14	0.03	0.03	0.01	0.00	0.01	0.00	48.71	94.58
	Ellamar	PWS03R-8C1	6	50.93	0.02	0.02	0.00	0.00	0.02	0.00	0.02	0.00	0.00	0.00	0.00	43.42	94.49
	Threeman	PWS03R-5A	6	50.12	0.05	0.01	0.10	0.01	0.14	0.01	0.03	0.02	0.00	0.00	0.00	43.96	94.95
Chalcopyrite	Beatson	05PWSB004Ra	15	30.80	34.99	0.04	0.08	0.00	0.04	0.00	0.02	0.02	0.01	0.00	0.00	34.24	100.25
	Beatson	05PWSB007Rb	10	30.72	34.94	0.14	0.10	0.00	0.03	0.00	0.00	0.02	0.01	0.01	0.00	34.57	100.54
	Beatson	05PWSB002R	10	31.00	33.69	0.09	0.08	0.00	0.03	0.01	0.01	0.03	0.01	0.00	0.00	32.98	97.94
	Ellamar	PWS03R-8C1	12	30.91	34.62	0.06	0.11	0.00	0.03	0.00	0.02	0.02	0.00	0.00	0.00	35.21	100.98
	Ellamar	PWS03R-8A2	7	31.09	34.16	0.03	0.07	0.00	0.04	0.00	0.02	0.02	0.01	0.00	0.00	35.69	101.13
	Threeman	PWS03R-4A	7	30.75	34.94	0.03	0.08	0.01	0.03	0.01	0.04	0.01	0.01	0.00	0.00	35.33	101.24
	Threeman	PWS03R-4B	12	31.11	34.44	0.10	0.11	0.00	0.04	0.01	0.03	0.02	0.01	0.00	0.00	35.17	101.04
	Threeman	PWS03R-3A	13	31.01	34.48	0.11	0.08	0.00	0.07	0.00	0.02	0.01	0.01	0.00	0.00	35.36	101.15
	Threeman	PWS03R-5A	8	30.91	34.44	0.11	0.08	0.00	0.02	0.00	0.04	0.02	0.01	0.01	0.00	35.42	101.04
Sphalerite	Beatson	05PWSB004Ra	9	6.93	0.24	60.00	0.24	0.01	0.08	0.07	0.05	0.08	0.08	0.22	0.08	32.60	100.68
	Beatson	05PWSB007Rb	10	6.65	0.23	60.42	0.09	0.00	0.01	0.01	0.01	0.00	0.02	0.18	0.00	33.15	100.77
	Beatson	05PWSB002R	5	6.96	0.43	59.54	0.07	0.01	0.02	0.00	0.00	0.00	0.05	0.18	0.00	31.16	98.43
	Ellamar	PWS03R-8C1	7	7.70	0.24	58.63	0.08	0.00	0.02	0.01	0.04	0.01	0.00	0.17	0.00	33.77	100.67
	Ellamar	PWS03R-8A2	5	7.39	0.52	59.57	0.08	0.00	0.02	0.01	0.02	0.01	0.01	0.17	0.02	33.91	101.73
	Ellamar	PWS03R-8A3	11	8.76	0.31	57.57	0.09	0.01	0.02	0.01	0.00	0.02	0.02	0.17	0.00	33.92	100.90
	Threeman	PWS03R-4A	4	10.55	0.34	55.67	0.05	0.01	0.06	0.00	0.04	0.01	0.14	0.15	0.00	34.30	101.32
	Threeman	PWS03R-4B	3	8.37	0.52	57.95	0.08	0.01	0.13	0.00	0.05	0.01	0.06	0.19	0.00	33.76	101.13
	Threeman	PWS-3R-3A	1	9.89	0.00	56.84	0.12	0.00	0.04	0.00	0.03	0.02	0.11	0.13	0.00	33.73	100.91

^a Number of grains analyzed.

Table 4
Chemical data for sediment and precipitate samples from the Ellamar, Threeman, and Beatson mine sites

Map no. ^a	Sample number	Sample description, location	Al %	Fe %	Cu mg/kg	Zn mg/kg	Ag mg/kg	As mg/kg	Cd mg/kg	Co mg/kg	Cr mg/kg	Hg mg/kg	Mn mg/kg	Ni mg/kg	Pb mg/kg
Sediment, offshore															
<i>Ellamar</i>															
S7	05PWSE008S	olive–brown mud, 6 m water depth	6.6	3.4	41	86	<3	7.1	0.33	8	94	0.06	502	26	13
S10	05PWSE112S	Gray mud and sand, 5 m water depth	6.9	3.6	61	87	<3	11	0.22	7.9	103	0.13	469	27	16
S34	PWS03SELL-4	Fine sand near end of pier	5.8	5.9	294	198	0.50	23	<0.01	14	81	n.a. ^b	554	32	149
S9	05PWSE111S	Black mud and sand below low tide line	6.6	5.1	487	260	<3	31	0.45	13	99	0.76	523	31	66
S8	05PWSE108S	Fine sand near glory hole	4.4	4.5	498	154	<3	34	0.43	8.9	68	0.66	359	21	56
<i>Threeman</i>															
S19	05PWST115S	Olive–brown mud, 14 m water depth	8.5	4.0	89	113	<3	9	0.55	10	89	0.05	830	29	15
S23	05PWST120S	Olive–brown mud, 3 m water depth	8.2	4.3	114	132	<3	11	1.3	13	94	0.04	854	35	17
<i>Beatson</i>															
S29	05PWSE010S	Dark–gray mud, 33 m water depth	n.r. ^c	5.8	1590	684	<3	38	1.4	19	94	0.19	611	26	63
Sediment, intertidal zone															
<i>Ellamar</i>															
S11	05PWSE301Pa	Brown sand above low tide line	5.6	15	3220	909	3.6	140	<0.003	17	63	1.5	234	11	385
S17	05PWSE207S	Brown sand, beach pit 7(2005)	4.7	18	2120	854	7.9	170	1.3	38	57	2.6	232	16	143
S16	05PWSE208S	Brown sand, beach pit 8(2005)	1.7	34	3090	820	12	380	4.4	187	24	3.2	115	7.9	116
S18	05PWSE308MP	Course sand, beach pit 6(2005)	4.9	18	2660	1250	6.2	150	1.6	29	56	2.2	228	15	235
S5	03PWS Ellamar 5	Jarosite-rich sand, beach pit 5(2003)	3.0	19	4400	512	62	284	1.4	50	38	n.a.	106	12	1480
S4	03PWS Ellamar 4	Jarosite-rich sand, beach pit 4(2003)	0.65	41	2240	356	5.5	346	0.38	68	9.8	n.a.	64	3.6	297
S3	03PWS Ellamar 3	Jarosite-rich sand, beach pit 3(2003)	5.4	19	1310	105	2.5	191	0.06	7.5	66	n.a.	161	7.8	139
S2	03PWS Ellamar 2	Jarosite-rich sand, beach pit 2(2003)	3.7	25	2450	861	12	196	3.4	14	35	n.a.	34	6	581
S1	03PWS Ellamar 1	Jarosite-rich sand, beach pit 1(2003)	4.2	19	1440	37	1.0	43	0.031	11	38	n.a.	8.5	1	33

<i>Threeman</i>															
S24	05PWST304S(#1)	Beach sand, reference pit 11	10	4.8	377	139	<3	9.1	0.05	14	105	0.03	951	31	24
S27	05PWST305SM(#1)	Sand with orange precipitate, beach pit 3	10	9.9	870	289	<3	7.9	0.16	27	280	0.02	2010	65	22
S28	05PWST306SM(#2)	Dark gray sand, beach pit 4	7.1	7.6	4690	938	<3	9.7	1.4	28	192	0.11	1650	40	7.8
S21	05PWST118S	Sand with orange precipitate, low tide line	5.1	18	1300	260	<3	67	0.38	12	98	0.14	888	25	30
<i>Beatson</i>															
S30	05PWSB101S	Sand-silt, shallow water near old pier	n.r.	5.1	1010	233	<3	24	0.08	11	105	0.12	528	29	59
S31	05PWSB104S	Sand in delta, low tide line	7.2	6.1	2580	350	<3	50	0.12	16	92	0.16	738	25	98
Precipitates															
<i>Ellamar</i>															
P1	05PWSE201P	Green and orange crust near low tide line	n.r.	12	26,900	3260	<3	73	0.53	17	38	0.41	105	9.2	143
<i>Threeman</i>															
P2	05PWST310PM	Red–brown precipitate below mine talus	12	3.7	4750	529	<3	5.7	1.3	113	94	0.27	1360	56	8.9
<i>Beatson</i>															
P5	05PWSB201P	Brown precipitate, seep below lower dump	6.7	16	10,700	704	3.1	110	2.1	30	76	1.0	2140	28	917
P7	05PWSB203P	Red–brown precipitate, seep below lower dump	3.1	20	8000	332	4.8	74	0.46	5	42	0.56	365	9.1	909
P8	05PWSB204P	Brown precipitate, seep below lower dump	5.7	8.9	7240	762	5.9	110	1.3	9	76	0.67	583	12	365
P9	05PWSB306P	Orange precipitate, drainage below upper dump	3.4	44	2000	185	3.6	9.4	0.14	0.39	118	0.09	13	1.2	309
P6	05PWSB202P	Yellow–brown precipitate, Girdwood seep	n.r.	11	52,300	23,400	<3	26	31	141	8.3	n.a.	12,000	47	3770
P10	BBM-5S	Yellow–brown precipitate, Girdwood seep	0.96	20	82,600	16,700	0.4	52	8.8	120	11	n.a.	10,900	48	5020

^a Map numbers correspond to locations in Fig. 2.

^b n.a., not analyzed.

^c n.r., not reported.

Table 5
Chemistry (pH and dissolved elements) for water samples from Ellamar, Threeman, and Beatson mine sites

Map no. ^a	Field no.	Sample type, location	pH	Al (µg/ L)	Fe (µg/ L)	Cu (µg/ L)	Zn (µg/ L)	Cd (µg/ L)	Co (µg/ L)	Cr (µg/ L)	Mn (µg/ L)	Ni (µg/ L)	Pb (µg/ L)	Hg (ng/ L)	Cl (mg/ L)	SO ₄ (mg/ L)
<i>Ellamar</i>																
W8	PWS03WEL100.2	Pore water, auger hole	3.8	6800	8100	1000	440	1.5	15	2.3	180	<0.1	360	50	16,000	2200
W1	PWS03WELLP1	Pore water, pit 1 (2003 transect)	4.9	70	74	260	100	0.34	6.7	<1	32	1.4	0.47	50	1600	380
W2	PWS03WELLP2	Pore water, pit 2 (2003 transect)	3.4	1000	9700	1100	920	2.5	17	1.0	90	2.8	44	2000	2900	600
W3	PWS03WELLP3	Pore water, pit 3 (2003 transect)	5.5	130	67	130	190	0.71	9.9	<1	78	3.1	0.083	1100	1500	400
W4	PWS03WELLP4	Pore water, pit 4 (2003 transect)	4.1	160	5200	270	500	0.9	7.5	<1	86	<0.1	2.1	65	3700	670
W5	PWS03WELLP5	Pore water, pit 5 (2003 transect)	3.9	12,000	39,000	1900	3500	20	45	3.7	580	70	240	110	10,000	1600
W6	PWS03WELLP6	Pore water, pit 6 (2003 transect)	4.4	16,000	48,000	23	1900	4.3	49	2.0	800	15	24	n.a. ^b	11,000	1600
W31	05PWSE401aW	Pore water, reference pit 1	6.7	13	<50	48	32	0.14	2.4	1.2	24	3.4	0.63	n.a.	4761	1015
W32	05PWSE402aW	Pore water, reference pit 2	7.5	27	<50	23	28	0.2	1.7	1.6	27	8.6	1.8	n.a.	11,744	1759
W33	05PWSE403aW	Pore water, reference pit 3	6.8	9	9060	9.1	13	<0.02	0.9	1.6	46	10	<0.05	145	16,266	2123
W34	05PWSE405bW	Pore water, reference pit 5	6.6	30	218	86	72	0.26	3.6	1.2	32	4.3	0.2	35	4237	892
W35	05PWSE406W	Pore water, reference pit 6	6.2	109	724	6.2	21	0.040	0.3	<1	21	0.8	2.4	n.a.	<0.08	<1.6
W21	05PWSE201aW	Pore water, pit 1 (2005 transect)	3.7	2850	1640	7030	1610	2.3	51	6.2	124	18	189	4100	12,947	1864
W22	05PWSE202W	Pore water, pit 2 (2005 transect)	3.1	8370	25,900	18,400	6980	12	231	7.9	485	29	44	680	12,798	2066
W23	05PWSE203aW	Pore water, pit 3 (2005 transect)	3.0	10,900	31,500	10,000	6730	7.7	154	11	641	35	39	1400	13,916	2180
W24	05PWSE204W	Pore water, pit 4 (2005 transect)	3.6	14,300	1900	5030	6550	9.3	67	9.0	421	35	20	270	12,500	1952
W25	05PWSE205W	Pore water, pit 5 (2005 transect)	5.0	3660	15,400	1420	3970	18	64	6.6	519	34	242	27	10,650	1700
W26	05PWSE206W	Pore water, pit 6 (2005 transect)	6.8	26	11,600	12.8	23	0.05	1.2	6.7	100	12	0.3	<15	17,446	2260
W27	05PWSE207W	Pore water, pit 7 (2005 transect)	5.8	508	32,000	11.9	1110	1.5	37	3.8	842	26	4.6	<15	7173	1350
W28	05PWSE208W	Pore water, pit 8 (2005 transect)	3.9	14,900	21,700	3570	4050	11	62	8.6	460	30	186	46	11,673	1892
W29	05PWSE209W	Pore water, pit 9 (2005 transect)	3.4	15,400	14,000	2950	2590	6.2	64	7.9	393	37	47	74	10,495	1816
W30	05PWSE210W	Pore water, pit 10 (2005 transect)	2.9	7850	28,300	8480	3290	8.2	101	9.1	439	27	2020	3700	11,341	2298
W17	05PWSE111W	Seawater, offshore, depth 0.5 m	8.4	18	431	13	19	0.070	0.81	6.9	3.6	13	0.06	<15	16,552	2157

W16	05PWSE108W	Seawater, near glory hole	8.3	28	452	13	20	0.25	0.88	6.8	4.4	12	0.1	<15	16,352	2115
W10	PWS03WE3-8	Seawater, depth 8 m in glory hole	7.8	14	660	15	70	0.24	<0.02	1.9	33	<0.1	<0.05	n.a.	16,000	2100
<i>Threeman</i>																
W49	PWS03W3M105	Pore water, pit (2003)	7.2	7.3	2500	15	6.5	<0.02	0.78	1.3	28	1.1	<0.05	n.a.	4700	740
W45	05PWST205W	Seep below mine talus	n.a.	26	86	4.0	2.0	<0.02	0.16	1.1	27	1.0	<0.05	<15	1100	293
W43	05PWST206W	Stream, 5 m below mine talus	7.5	31	<50	168	35	0.07	2.2	1.2	13	3.1	<0.05	<15	1126	241
W51	PWS03W3M102	Stream, 10 m below mine talus	6.5	39	54	170	20	0.031	0.97	<1	11	1.2	0.053	n.a.	270	73
W52	PWS03W3M103	Stream, 30 m below mine talus	6.6	21	170	160	31	0.054	2	<1	15	1.8	0.059	n.a.	1800	270
W47	PWS03W3M106	Stream, below mine talus, E side	8.0	35	42	130	66	0.19	2.4	<1	8.2	3.4	<0.05	n.a.	2.1	23
W50	05PWST404W	Stream, above reference pits	7.2	23	<50	144	103	0.3	3.6	<1	7.7	5.5	<0.05	<15	2.2	33
W44	05PWST401aW	Pore water, reference pit 1	7.3	20	357	7.7	20	<0.02	0.68	5.3	8.8	8.5	<0.05	<15	10,864	1517
W46	05PWST402aW	Pore water, reference pit 2	7.7	19	<50	29	8.2	<0.02	0.41	1.1	1	1	0.3	<15	10,481	1490
W48	05PWST403bW	Pore water, reference pit 3	7.1	20	<50	61	16	0.02	0.58	<1	1	1.1	0.1	<15	n.a.	n.a.
W39	05PWST201W	Pore water, pit 1	6.8	14	1910	6.2	7	<0.02	0.37	3.6	54	4.6	<0.05	<15	5427	1111
W40	05PWST202W	Pore water, pit 2	6.7	21	11400	3.3	4.9	<0.02	0.65	3.2	77	2.6	<0.05	<15	3858	626
W41	05PWST203W	Pore water, pit 3	7.2	32	108	100	44	0.33	2.6	4.3	24	10	0.1	<15	10,057	1436
W42	05PWST204W	Pore water, pit 4	8.3	41	575	24	85	0.3	8.6	4.0	192	6.8	<0.05	<15	4000	787
W36	05PWST116W	Seawater, pit 2, ROV ^c sample	7.8	3	<50	6.5	8.4	0.070	0.59	2.0	1.7	6.5	<0.05	<15	16,103	2091
W37	05PWST117W	Seawater, pit 2, ROV sample	8.0	4.8	<50	7.9	8.7	0.1	0.70	2.2	4.3	7.0	<0.05	<15	16,079	2118
W38	05PWST118W	Seawater, pit 2, ROV sample	8.3	4.5	<50	8.5	9.3	0.060	0.67	2.1	1.8	7	<0.05	<15	16,060	2121
<i>Beatson</i>																
W54	05PWSB106W	Beatson pit lake	7.5	15	<50	21	15	0.040	0.17	<1	3.3	0.6	0.4	<15	<0.08	<1.6
W62	05PWSB306W	Stream below upper dump and pit lake	5.3	1670	1140	794	1360	3.1	7.4	<1	318	24	5	<15	<0.08	431
W63	05PWSB008W	Stream below upper dump and pit lake	5.5	774	1160	776	1880	3.6	8.7	<1	426	28	1.8	<15	<0.08	<1.6
W60	05PWSB206W	Stream, base of lower mine dump	6.7	23	192	32	88	0.18	0.29	<1	32	0.9	1.1	<15	<0.08	296
W64	AS1	Stream, base of lower mine dump (auto sampler)	7.0	26	142	26	83	0.17	0.29	0.0	31	0.8	1.0	48	0.0	177
W65	AS2	Stream, below main adit (auto sampler)	7.3	19	136	22	78	0.16	0.24	0.0	29	0.7	1.1	<15	0.0	285
W55	05PWSB201W	Seep below main waste dump	5.8	25	<50	388	393	0.89	1.8	<1	43	2.4	1.4	<15	<0.08	289
W57	05PWSB203W	Seep below house	6.6	15	15,000	138	68	0.11	2.8	<1	325	2.6	8.7	<15	<0.08	285

(continued on next page)

Table 5 (continued)

Map no. ^a	Field no.	Sample type, location	pH	Al (μg/L)	Fe (μg/L)	Cu (μg/L)	Zn (μg/L)	Cd (μg/L)	Co (μg/L)	Cr (μg/L)	Mn (μg/L)	Ni (μg/L)	Pb (μg/L)	Hg (ng/L)	Cl (mg/L)	SO ₄ (mg/L)
W58	05PWSB204W	Seep near foundation	6.1	20	251	37	132	0.25	0.30	<1	36	0.9	2.4	<15	<0.08	283
W56	05PWSB202W	Seep Girdwood site	7.6	12	<50	225	1400	2.5	5.8	2.0	539	11	0.77	15	<0.08	373
W61	05PWSB101W	Seawater, nearshore below pier	8.4	18	<50	14	23	1.1	0.84	2.5	3.2	10	0.89	<15	16394	2206
W53	05PWSB104W	Seawater, delta area, low tide	8.5	4.9	<50	10	15	0.33	0.74	1.9	2.1	7	0.090	<15	15,312	2075

^a Map numbers correspond to sample locations in Fig. 2.^b Not analyzed.^c Remotely operated vehicle.

Fe, Cu, Zn, Ag, As, Cd, Co, Hg, and Pb. This enrichment reflects (1) a significant amount of massive sulfide particles in the beach detritus and (2) the presence of abundant jarosite and Fe oxyhydroxide in samples obtained from shallow pits excavated in the beach sediment (Fig. 3d). An XRD analysis of a beach pit sample (03PWS Ellamar 4) with the highest Fe content (40.6 wt%) revealed the following mineralogy: pyrite, jarosite, quartz, and goethite with minor calcite, muscovite, albite, and kaolinite. The average Pb concentration for nine Ellamar sand samples (380 mg/kg) is slightly higher than the maximum value for Pb obtained from sulfide-rich rock samples from the same locality (325 mg/kg; Table 2).

Sediment samples excavated from shallow pits in the intertidal zone at the Threeman mine site contain lesser amounts of clastic sulfide debris, but are characterized by elevated levels of Fe, Cu, Zn, As, Cr, Ni, and Mn compared with a reference beach-sand sample collected nearby, and with mud samples from deeper water localities offshore. The Cr and Ni contents are consistent with higher values for these metals in massive sulfide samples from Threeman, whereas the low Pb contents reflect the generally low Pb levels of Threeman sulfide samples (Table 2). The high Fe concentrations (to 18 wt%) in Threeman sediment samples mainly reflect the presence of Fe-oxyhydroxide precipitates.

The seven precipitates in Table 5 are orange–red to yellow–brown flocculent suspensions and coatings sampled in stagnant and actively flowing waters emanating from mine dumps, except for the Ellamar sample, which was a green and orange laminated crust exposed on the beach surface at low tide. In two of the Beatson samples, crystalline Fe-oxyhydroxide minerals were determined by XRD. Schwertmannite is abundant in the red–brown precipitate (sample 05PWSB203P) collected below the lower mine dump, and ferrihydrite (6-line type) and schwertmannite comprise the fluffy orange precipitate (sample 05PWSB306P) coating the bed of a small stream emanating from the base of the upper mine dumps (Fig. 3e). In the other precipitate samples, the Fe oxyhydroxides are amorphous. All but two of the samples (05PWSB202P and 05PWSB306P) contain quartz, albite, muscovite, and clinocllore, indicating a small amount of detrital contamination. The precipitates contain no XRD-detectable sulfide minerals.

The precipitate sample from the intertidal zone at Ellamar is notable for high Cu (2.7 wt%) and Zn (0.33 wt%) concentrations. The Threeman precipi-

tate, collected from a stagnant seep at the base of the mine talus, has a low Fe content (3.7 wt%), an Al/Fe mass ratio >3 and the highest Ni value (56 mg/kg) among all precipitate samples. Compared with other precipitate samples, flocculent material from the Girdwood drainage is highly enriched in Cu, Zn, Mn, Pb, Cd and Co. Interestingly, the most Fe-rich (44 wt%) precipitate sample from Beatson (05PWSB306P) contains relatively low amounts of other metals except Cr.

3.3. Chemistry of mine and surface waters

Fluid samples from the Ellamar, Threeman, and Beatson mine sites (Table 5) include stream and seep waters (Threeman and Beatson), pore waters from intertidal zone sediments (Ellamar and Threeman), pit-lake water (Beatson), and nearshore seawater (all sites). Pore waters in beach gravels were collected from rows of shallow pits excavated along transects perpendicular to the beach at Ellamar in 2003 and 2005 and at Threeman in 2005 (Fig. 2b and c). Data for stream water below the southern Beatson adit (AS1 and AS2 in Table 5) are from samples collected with an autosampler over a period of 60 days in June, July and August, 2005. Temporal variations in discharge and chemistry for waters discharging from the Beatson adit are presented by Stillings et al. (2007, 2008).

Chemical data for dissolved (filtered through 0.45 μm and acidified) elements are reported in Table 5. Waters at the Ellamar site ranged from pH 2.9 (pore water in intertidal beach gravel) to 8.2 (nearshore seawater). The average pH for pore water measured in 17 pits within sulfide-rich sediment was 4.2, whereas five pore waters in a series of background reference pits away from the sulfide rubble averaged 6.8 (Fig. 2b). Waters at the Threeman site had pH values in the range 6.5 (stream below mine talus) to 8.3 (seawater). Unlike Ellamar, however, the average pH of pore waters (7.2) in pits dug in sulfide-bearing gravels of the intertidal zone at Threeman is about the same as the pH for pore water in a nearby series of background reference pits (Fig. 2c). Waters at the Beatson site had a pH range between 5.3 (stream flowing from the base of the upper waste dump) and 8.5 (nearshore seawater), but most pH values were circumneutral.

Among all water samples analyzed, pore waters in sulfide-bearing gravels at Ellamar have the highest metal concentrations. Iron in pore waters from

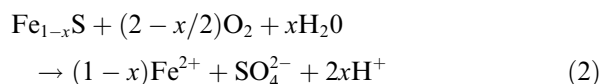
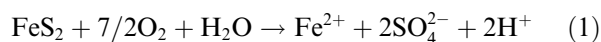
Threeman beach sediment, and Fe, Al, Mn, Cu, and Zn in streams and seeps below Beatson waste dumps are concentrated to a lesser extent. Mercury concentrations in water samples are generally below detection limits at the Threeman and Beatson sites. At the Ellamar site, however, Hg concentrations are as high as 4100 ng/L in beach pore waters.

High levels of Cl and SO_4 in the metal-rich porewaters at the Ellamar and Threeman sites indicate a substantial seawater component in the fluid. The concentrations of Cl (to ~ 16000 mg/L) and SO_4 (to ~ 2200 mg/L) in seawater samples from all 3 sites are somewhat below normal values for these anions in seawater ($\sim 19,000$ and ~ 2700 mg/L, respectively). This result probably reflects a dilution effect related to the influx of surface waters along shorelines in Prince William Sound. Although somewhat diluted, the seawater samples at Ellamar are strongly enriched in trace metals such as Fe (to 660 $\mu\text{g/L}$), Al (to 28 $\mu\text{g/L}$), and Mn (to 33 $\mu\text{g/L}$) compared to values for northern Pacific Ocean water (Donat and Bruland, 1995). The metal loading in seawater at Ellamar is apparently influenced by migration of porewaters from the local beach gravels and contamination from the flooded Ellamar glory hole.

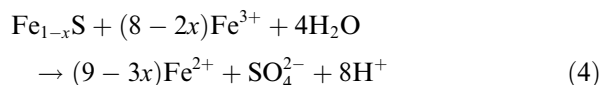
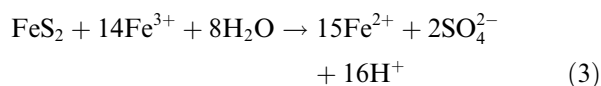
4. Discussion

The Cu mining environment of Prince William Sound is conducive to the development of acid-mine drainage and transport of environmentally sensitive elements because (1) the VMS deposits have high concentrations of polymetallic sulfides, including pyrite and pyrrhotite, all of which are susceptible to attack by oxygenated fluids; (2) mining activity has increased the surface area of sulfide-rich rocks exposed to weathering in mine talus, mine dumps, milled ore and waste piles, bunkers, and beach deposits; (3) oxidation of this material is accelerated by the wet subarctic climate of Prince William Sound, where annual precipitation exceeds 250 cm a^{-1} ; (4) much of this precipitation accumulates in thick winter snow packs on steep slopes, and runoff during summer months contributes to continuous supply of water in the vadose zone surrounding the mine sites; and (5) the absence of limestone and predominance of quartzose sedimentary rocks in the Orca Group flysch (Nelson et al., 1985; Dumoulin, 1988) limit the natural buffering capacity for acid solutions in the environment of oxidizing massive sulfides.

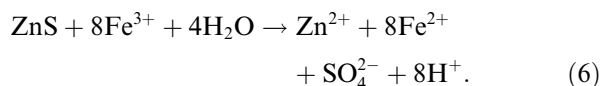
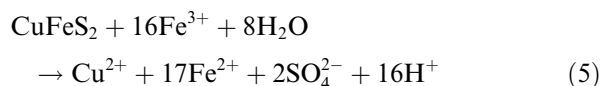
The generation and composition of acidic, metal-enriched waters at Ellamar, Threeman, and Beatson mine sites can largely be attributed to the oxidation of pyrite, pyrrhotite, chalcopyrite, and sphalerite, the major sulfide minerals. The oxidation reactions for these sulfides in aqueous fluids have been studied in numerous laboratory experiments over the past 25 a (see reviews of Nordstrom and Southam, 1997; Nordstrom and Alpers, 1999; Belzile et al., 2004). It is well established that molecular O₂ dissolved in ground waters can oxidize pyrite and pyrrhotite according to the reactions



which in either case, results in the formation of small amounts of H₂SO₄. Whereas reactions (1) and (2) proceed under circumneutral conditions, lower pH values (<4) permit stabilization of dissolved Fe as Fe³⁺, which can also oxidize pyrite and pyrrhotite as follows:



resulting in significantly greater acidity. Furthermore, Fe³⁺ is a more effective oxidant than O₂ for chalcopyrite and sphalerite (Rimstidt et al., 1994; Plumlee, 1999):



It is important to note that the oxidation of Fe²⁺ to Fe³⁺ tends to be sluggish under acidic conditions, and it is unlikely that reactions (3)–(6) proceed abiotically. Therefore, catalysis of Fe oxidation by acidophilic bacteria such as *Acidithiobacillus ferrooxidans* is a key component of acid generation (Nordstrom and Alpers, 1999).

4.1. Differential weathering of sulfide minerals

The degree of weathering (oxidation) of sulfide-rich samples varies considerably among the different

environments at the mine sites. Limited weathering (usually in the form of thin oxidation layers or films) of the exterior and fracture surfaces are typical of samples from mine workings at all sites as well as coarse sulfide debris on the surface of intertidal gravels at Ellamar. More advanced, penetrative oxidation is evident in sulfide-rich rock fragments embedded or buried in mine dumps at Threeman and Beatson, the bunker near Threeman, and intertidal beach gravels at Ellamar and Threeman. It is important to note, however, that even samples of the most intensely oxidized material, such as the ferricrete at Ellamar and the small pyrrhotite-rich ore pile at Threeman, contain some residual sulfide, usually chalcopyrite, pyrite, or both.

Weathering patterns and rates also vary according to sulfide mineralogy. Key factors in acid generation at the Prince William Sound mine sites are the abundance of Fe sulfides and whether the dominant Fe sulfide is pyrite or pyrrhotite. Petrographic observations indicate that the resistance to oxidation among the major sulfide minerals increases in the order pyrrhotite ≪ sphalerite < chalcopyrite ≦ pyrite. Thus, pyrrhotite-rich rocks are the most readily oxidized in any given mine-site environment. The relatively rapid alteration of pyrrhotite in Prince William Sound samples is in accord with laboratory experiments, indicating that abiotic dissolution rates for pyrrhotite (with either O₂ or Fe³⁺ as the oxidant, pH values 2–6) are one to two orders of magnitude higher than for pyrite (Nicholson and Scharer, 1994). Higher reaction rates for pyrrhotite have been attributed to mineral-specific controls on permeability such as fracturing along cleavage planes (Janzen et al., 2000) and site vacancies related to missing Fe atoms in the crystal lattice (Jambor, 2003).

In a temporal sense, the oxidative alteration of Prince William Sound massive sulfides can be described as a series of overlapping steps beginning with destruction of pyrrhotite. In the earliest stage of sulfide weathering, the edges of pyrrhotite grains are replaced by a fibrous sulfide mineral with color and optical anisotropy similar to marcasite (Fig. 4a). Electron microprobe analyses reveal that unaltered pyrrhotites have compositions close to Fe_{0.9}S, whereas the altered rims have compositions ranging from FeS₂ to Fe₂S₃ (Table 3). These analytical data confirm the alteration of pyrrhotite to marcasite, which has been recognized elsewhere in waste dumps and mine tailings (Jambor, 1994, 2003; Hammarstrom et al., 2001). Although the Fe₂S₃ compo-

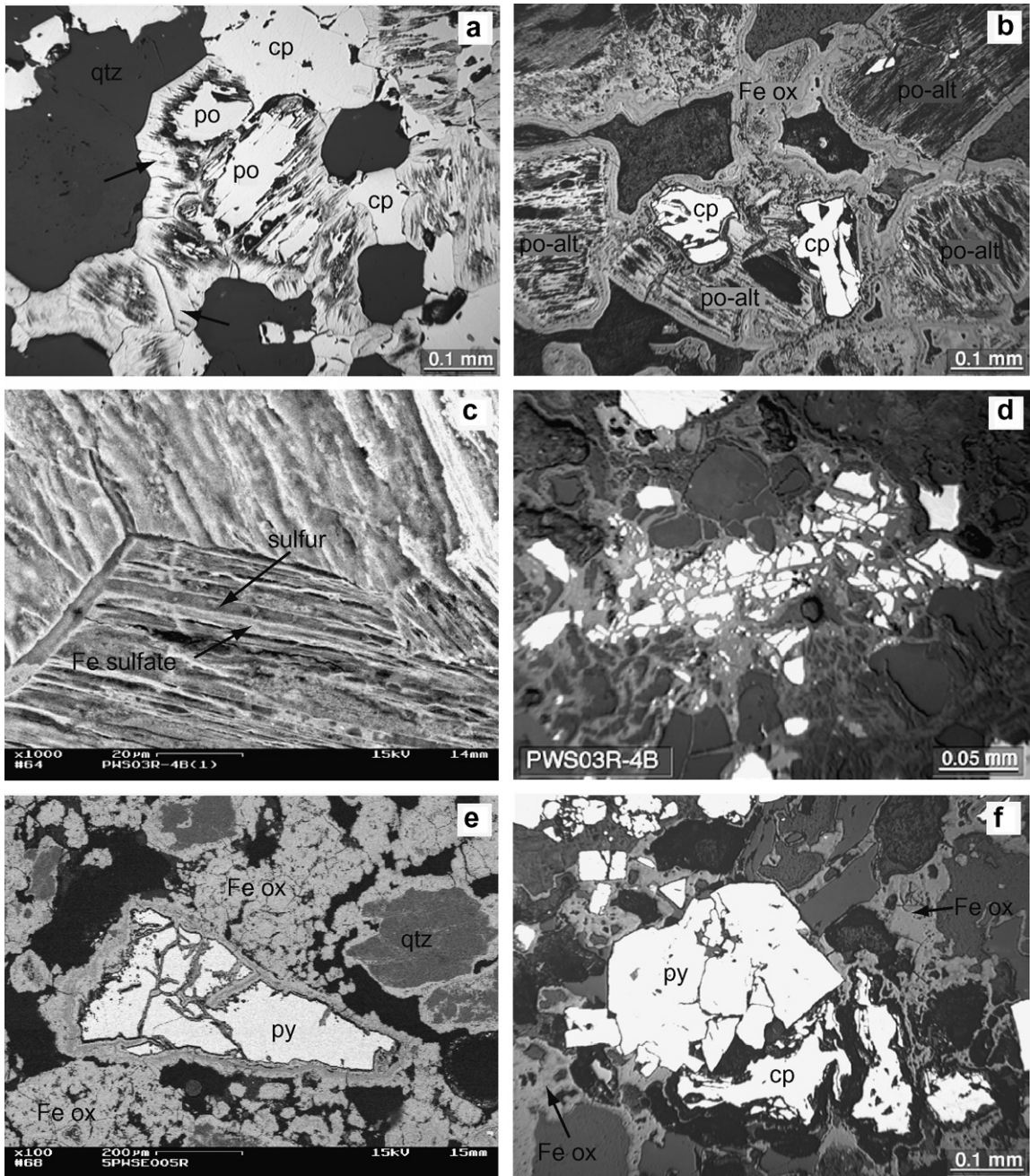


Fig. 4. Paragenetic aspects of sulfide oxidation. (a) Photomicrograph showing marcasite (arrows) at pyrrhotite grain margins and along contacts between pyrrhotite grains. Cores of pyrrhotite grains (po) are unaltered. Other grains are chalcopyrite (cp) and quartz (qtz). (b) Photomicrograph showing more advanced alteration in which pyrrhotite grains are replaced by a mixture of sulfur and Fe sulfate (po-alt) and coated by Fe oxyhydroxide, probably goethite (Fe ox). Grains of chalcopyrite (cp) are relatively unaltered. (c) SEM backscattered electron image at higher magnification showing alternating laminae of sulfur and Fe sulfate in core of original pyrrhotite grain. (d) Photomicrograph showing weblike replacement of chalcopyrite (bright reflectivity) by Fe oxyhydroxide. Medium-gray grains are detrital quartz. (e) SEM backscattered electron image shows corrosion of pyrite grain (py) and replacement by Fe oxyhydroxide (Fe ox) along grain margins and cracks. Quartz (qtz) grains also show signs of dissolution along grain edges. (f) Photomicrograph illustrates more advanced corrosion of chalcopyrite (cp) grains relative to pyrite (py). Fe ox = Fe oxyhydroxide.

sition is somewhat problematic, Jones et al. (1992) identified a secondary Fe_2S_3 phase in pyrrhotite oxidation experiments, and Pratt et al. (1994) and Mycroft et al. (1995) have used X-ray spectroscopic data to model the formation of both FeS_2 and Fe_2S_3 during near-surface oxidation experiments of pyrrhotite.

With increasing oxidation, the secondary marcasite and remaining pyrrhotite are partly to completely replaced by mixtures of sulfur, Fe sulfate and, less commonly, Fe–Al sulfate (Fig. 4b). At high magnification, the sulfur and sulfate minerals appear to occur in laminar intergrowths that in aggregate form rough, corrugated surfaces in the plane of the thin section (Fig. 4c). The loss of Fe during breakdown of pyrrhotite and marcasite results in precipitation of Fe-oxyhydroxide minerals along fracture surfaces and grain boundaries, and in void spaces in the rock. SEM and XRD analyses indicate that pyrrhotite is ultimately pseudomorphed by mixtures of goethite, lepidocrocite, and amorphous Fe-oxyhydroxide.

The style of oxidation for pyrite and chalcopyrite is distinct from the alteration pattern for pyrrhotite. Pyrite and chalcopyrite are replaced by goethite and amorphous Fe-oxyhydroxide in the form of colloform overgrowths that encroach on grain margins and veinlets that follow preexisting fractures across grains (Fig. 4d and e). With increasing volume of Fe oxyhydroxides, the corrosion of chalcopyrite and pyrite advances inward from grain surfaces and fractures resulting in aggregates of angular mineral fragments within the space occupied by the original grains. Chalcopyrite and pyrite are more resistant to oxidation than other sulfides in all of the Prince William Sound mine environments, but in deeply weathered samples containing remnants of both minerals (e.g., ferricrete at Ellamar), the dissolution of chalcopyrite by corrosion along grain edges and cracks generally appears to be more advanced (Fig. 4f).

The placement of sphalerite in the alteration sequence is problematic in that its alteration products are difficult to recognize in thin section. Because of its occurrence as intergrowths and inclusions in pyrite and chalcopyrite, a portion of the sphalerite in most samples tends to be chemically isolated from the oxidation process. In a few samples of pyritic massive sulfide, however, the margins of sphalerite crystals in contact with Fe oxyhydroxide appear more corroded than edges of adjacent pyrite cubes. Furthermore, sphalerite appears to

be completely absent in pyrite- and chalcopyrite-bearing clasts in deeply weathered samples from Threeman and Ellamar. Thus, sphalerite is considered to be more susceptible to oxidation than either pyrite or chalcopyrite. Sphalerite has an appreciable Fe content (Table 3; average 7.8 wt%, $n = 55$), and is an abundant phase in many samples from Prince William Sound. The dissolution of sphalerite contributes to the supply of Fe^{3+} oxidant for reaction with pyrite and chalcopyrite.

4.2. Sources, pathways, and sinks for environmentally important elements

The flux of environmentally important elements at the three mine sites occurs within three distinctive systems comprised of mineralized sources, fluid pathways, and repositories. The sources are sulfide-rich rocks exposed in mines, mine talus, ore and waste piles, and unconsolidated sedimentary deposits. The fluid pathways include mine drainage, streams, seeps, pit water, pore water, and seawater. The principal repositories include sulfide oxidation products, precipitates and bioreceptors. Although the three mine sites have differing physical attributes, the mobilization and redistribution of elements from source rocks to biota are recognized as variations on a theme.

4.2.1. VMS as a metal-rich source rock

The supply of potentially toxic elements from weathering of sulfide-rich rocks depends on the abundance and proportion of sulfide minerals and the distribution of major and trace elements among sulfide minerals (Table 3). The dissolution of pyrrhotite, pyrite, chalcopyrite, and sphalerite should result in the release of considerable quantities of Fe, Cu, and Zn and much smaller amounts of Pb, As, Co, Cd, and other elements to the ambient fluid phase. The low concentrations of Pb and As in the major sulfides indicate that galena and arsenopyrite represent the principal source of these elements in solution. This is especially true for alteration of rock material represented by sample 05PWSB007Rb from the Beatson mine site which contains unusually high modal abundances of galena and arsenopyrite (approximately 5% of total sulfide combined). Although a large proportion of the Co in fluids should be derived from the dissolution of pyrite and pyrrhotite, the presence of cobaltite (e.g., at the Threeman site) represents an additional Co source. According to the mineral analyses in

Table 3, sphalerite in sulfide-rich rocks is probably the principal source for Cd and Hg released during weathering.

4.2.2. Chemical variations in surface waters

Plots of dissolved element concentrations (Fe, Al, Cu, and SO_4) versus pH at Ellamar (Fig. 5) and cumulative base metals ($\text{Zn} + \text{Cu} + \text{Cd} + \text{Pb} + \text{Co} + \text{Ni}$) versus pH at all three sites (Fig. 6) illustrate variations in surface water chemistry. Data for dissolved base metals in waters of the Beatson mine area (including the Girdwood and Blackbird seeps) have been added to Fig. 6 from previous work by Goldfarb et al. (1996) and Munk et al. (2003). Among all water samples analyzed, Ellamar pore waters have the lowest pH values (to ~ 3) and highest concentrations of dissolved base metals (to $\sim 25,000 \mu\text{g/L}$). High dissolved Fe, Al and SO_4 concentrations in the Ellamar pore fluids (Table 5, Fig. 5) contribute to the precipitation of jarosite in the shallow subsurface where seawater mixes with terrestrial surface water during the tidal cycle (Fig. 3d). Decreases in Fe and Al with increasing pH probably reflect removal from solution by precipitation of oxyhydroxide phases. These trends for Fe and Al are expected because the solubility of Fe and Al oxyhydroxides is significantly reduced in oxidizing, near neutral fluids. At all sites, the concentrations of dissolved base metals generally are

inversely correlated with pH because of reduced mobility and increased sorption of these metals at near-neutral or higher pH (Smith and Huyck, 1999; Smith, 1999). This trend is especially well illustrated for Cu at Ellamar where the waters have a wider range in pH (Fig. 5).

The Ficklin-type diagram in Fig. 6 allows further comparison of water compositions among the three mine sites. The overall trend in concentrations illustrates the correlation between decreasing pH and increasing dissolved-metal load. The acidic and metal-rich pore waters from the Ellamar mine site reflect oxidation of abundant sulfide-rich debris in the intertidal gravels. In contrast, pore waters from a similar intertidal environment at the Threeman mine site have circumneutral pH values and very low concentrations of base metals, probably because oxidation of a much smaller volume of sulfides in the gravels generates less acidity. Despite the relative paucity of sulfide-rich detritus, some oxidation of sulfides is evident in the shallow pits dug in the narrow beach surface; oxidation probably occurs during reaction with slightly acid surface waters flowing down slope from the mine talus and pyrrhotite-rich ore pile. A small amount of dissolved Fe^{2+} in the pore waters at Threeman is rapidly oxidized and precipitated as Fe-oxyhydroxide flocculent along the beach–seawater interface (Fig. 3c). The high pH values (≥ 6.5) for pore waters

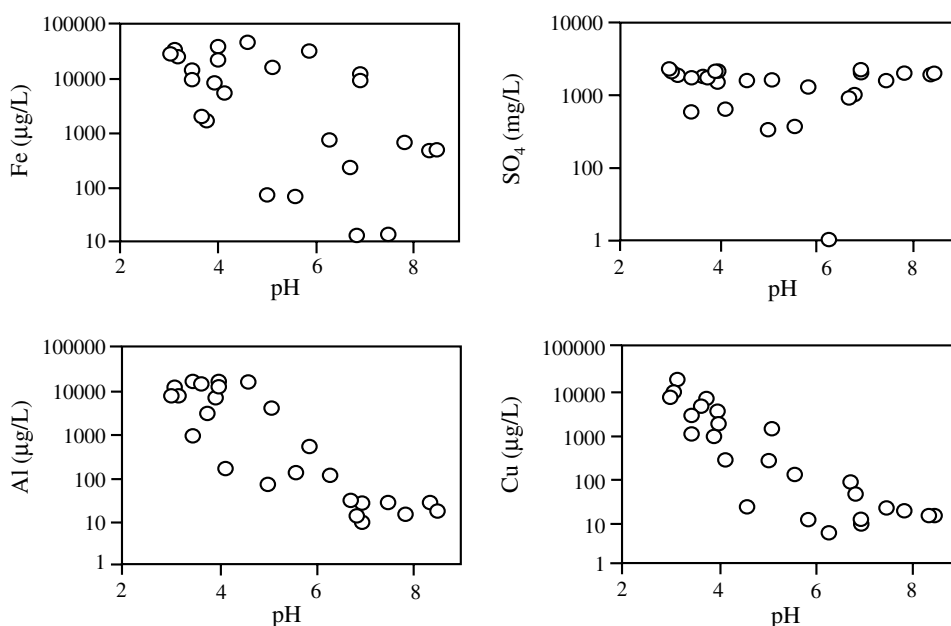


Fig. 5. Diagrams for Ellamar water samples showing dissolved concentrations of Fe, Al, SO_4 , and Cu plotted against pH.

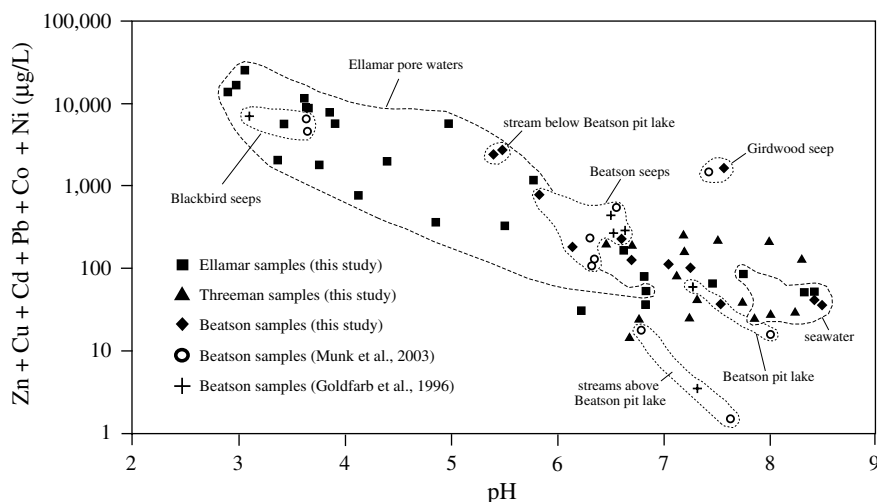


Fig. 6. Ficklin-type diagram (Plumlee, 1999) showing total dissolved base metals (Zn + Cu + Cd + Pb + Co + Ni) plotted against pH for water samples collected in 2003 and 2005 from the Ellamar, Beatson, and Threeman mine sites. Chemical data for water samples from the Beatson mine area, reported by Munk et al. (2003) and Goldfarb et al. (1996), are also plotted.

in the Threeman beach gravels preclude the deposition of jarosite.

In pore waters from the Ellamar and Threeman sites, the total base-metal concentrations for water samples (L. Munk, unpublished data) exceed their dissolved equivalents. This occurs because, in the pH range of most samples, these elements tend to sorb onto Fe oxyhydroxide and hydroxysulfate precipitates that become part of the suspended load or deposits on the stream bed. This affinity is especially evident for Pb (Fig. 7), which commonly is the most efficiently adsorbed of the base metals at any given pH (Dzombak and Morel, 1990). From the dissolved and total base-metal concentrations obtained for Prince William Sound samples, the observed trend of sorption efficiency among the base metals (Pb > Cu > Zn) is consistent with trends found in other weathering environments for massive sulfides where hydrous ferric oxides are formed (Dzombak and Morel, 1990; Munk et al., 2002).

At the Beatson mine site, snow- and rain-fed streams entering the pit lake have pH and metal contents typical of fresh waters in the subarctic environment of Prince William Sound (Fig. 6). Water in the pit lake has a pH near 7.5 and a low metal content. Goldfarb et al. (1996) suggested that the surprisingly high pH and low content of dissolved metals (<50 µg/L) of this pit lake result from “consolidation” (and thus lowered reactivity) of debris in the pit walls, as well as from extensive dilution by

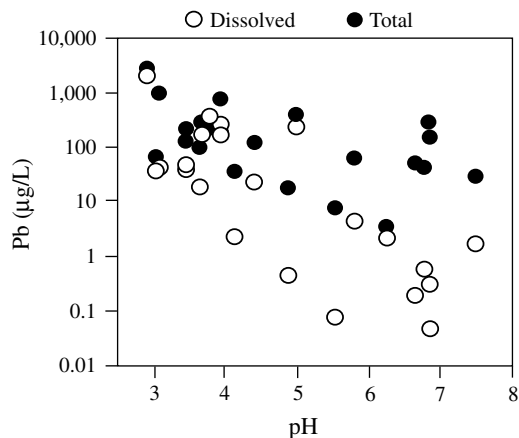


Fig. 7. Plot of dissolved and total concentrations for Pb versus pH in Ellamar pore waters. Consistently higher values for total concentrations reflect adsorption of Pb onto Fe-oxyhydroxide precipitates.

the stream entering the lake. The data in Table 5 as well as additional data cited by Stillings et al. (2007, 2008) indicate a slight decrease in pH and increase in metal content of waters that have entered the underground workings from the bottom of the pit lake, circulated through the underground mine, and discharged from the southern adit before flowing across the mine waste and onto the wide exposure of gravel deposits along the shoreline. Seeps emanating from the lower Beatson mine dumps have lower pH (5.8–6.6) and higher content of total dissolved base metals (to 800 µg/L). However, sam-

ples from the small stream flowing from the base of the dump adjacent to the pit lake have the lowest pH (~5.4) and the highest concentrations of dissolved base metals (2200–2700 µg/L) among all Beatson water samples (Fig. 6). Zinc concentrations in this stream are increased by two orders of magnitude relative to Zn in the pit lake. Water collected from a seep immediately above the high tide line at the Girdwood site (Fig. 2a) also has high base-metal contents (e.g., Zn to 1400 µg/L) despite the high fluid pH (~7.5). These Zn-rich water compositions at Girdwood are consistent with the reported mobility of Zn in circumneutral solutions in which Fe-rich precipitates are present (Smith, 1999). The compositions of seeps associated with the Blackbird mine dump (Goldfarb et al., 1996; Munk et al., 2003) shown in Fig. 6 suggest the potential for acidity and metal loading in seep waters throughout the Beatson mine area. The Beatson, Girdwood, and Blackbird seeps may also play a role in the physical dispersion of metals into the intertidal environment during periods of high runoff.

The levels of dissolved Hg (to 4100 ng/L) in pore waters in the beach gravels at the Ellamar site are very high compared to values typically reported (<0.1 ng/L) for mine drainage associated with VMS-type deposits (Rytuba, 2003). The source for Hg is probably sphalerite-rich massive sulfide, samples of which have Hg concentrations up to 61 mg/kg (sample 03R-8A3, Table 2). Electron microprobe analyses reveal that sphalerite grains from the Prince William Sound mine sites contain as much as 0.18 wt% Hg (R.A. Koski, unpublished data). Thus, Hg enrichment in the pit waters at Ellamar is likely derived from oxidation of sphalerite, although Hg from an anthropogenic source cannot be discounted.

4.2.3. *The role of precipitates in the distribution of metals*

Jarosite is abundantly precipitated in the low pH, oxidizing environment of the Ellamar beach gravels. However, the mixture of jarosite with Fe oxyhydroxide and remnant sulfide in the sediment precludes a quantitative assessment of partitioning of base metals and other elements based on bulk-sample chemistry. Here, the precipitates composed of Fe oxyhydroxides (ferrihydrite, schwertmannite, and amorphous Fe-oxyhydroxide) precipitating from weakly acid to weakly alkaline solutions at the Beatson mine site, including the nearby Girdwood seep, are emphasized. Based on samples ana-

lyzed for both chemistry and mineralogy, the precipitates dominated by amorphous Fe-oxyhydroxides (e.g., 05PWSB201P and 05PWSB202P from Beatson, BBM-5S from Girdwood) are sinks for base metals. The enrichment of Mn to >1 wt% indicates that a small amount of Mn oxyhydroxide may also be present in these precipitates. The amorphous Fe-oxyhydroxide crust (sample 05PWSE201P) from the sediment surface in the intertidal zone at Ellamar is enriched in Cu and Zn at a similar scale.

In contrast, two samples composed of crystalline precipitates (schwertmannite in 05PWSB203P and ferrihydrite plus schwertmannite in 05PWSB306P) from the Beatson site contain lower concentrations of these elements. Furthermore, the crystalline precipitate with the lowest base-metal content (05PWSB306P), sampled from the stream below the upper waste dump, is in contact with water that has the highest level of dissolved base metals at Beatson (Table 5). The approximately equivalent concentrations of total and dissolved base metals in those water samples are consistent with a lack of partitioning between the water and solid phases at this site.

The base-metal enrichments in the amorphous Fe-rich precipitates are in accordance with well defined, pH-dependent sorption edges for Cu, Zn, and Pb at oxide surfaces (Dzombak and Morel, 1990; Bigham and Nordstrom, 2000). The relatively low base-metal concentrations in the crystalline precipitates, especially in comparison with the amorphous Beatson precipitates, are somewhat puzzling. There is considerable field and experimental evidence that ferrihydrite and schwertmannite are effective sorbents for heavy metals under a range of conditions for acid-mine drainage (Webster et al., 1998; Jambor and Dutrizac, 1998; Dinelli et al., 2001; Swedlund and Webster, 2001). One explanation for the apparently anomalous compositions of the crystalline Beatson precipitates is related to the kind of flow regime at the site of sampling. In the stagnant waters of the Girdwood seep, for example, the metal-rich “amorphous” precipitates may be dominated by colloidal particles either suspended in the water or attached to microbial sheaths and plant matter. Their exceptionally high metal contents are then a function of enhanced sorption onto extremely large surface areas (Ranville and Schmiermund, 1999). The effective adsorption of base metals onto Fe oxyhydroxide colloids under mildly acid to near-neutral conditions has been

demonstrated at other sites of acid-mine drainage (e.g., Schemel et al., 2000). On the other hand, crystalline precipitates collected from bodies of moving water flowing from the lower and upper mine dumps at Beatson are likely to have less colloidal particles, and therefore, less surface area available for sorption. Thus, the composition of precipitates containing schwertmannite and ferrihydrite may be more representative of precipitates deposited in stable, actively flowing channel ways.

At Ellamar, another factor may contribute to the enrichment of Cu and Zn in the amorphous surface crust. With lowering tide, a rapid neutralization of acidic pore water advected to the beach surface may induce nearly instantaneous precipitation of amorphous Fe-oxyhydroxides. Base metals in solution can then be rapidly adsorbed at this mixing interface between pore water and seawater. It is relevant that the pit waters at Ellamar have the highest dissolved Cu and Zn concentrations analyzed in this study (Table 5).

4.2.4. Evidence for bioaccumulation in the marine environment

Systematic analysis to examine the influence of metals on marine organisms is beyond the scope of this study. However, preliminary analysis of a marine invertebrate common to each site, blue mussels (*Mytilus edulis*), suggests the importance of further biological and ecological investigations. Metal data for mussel tissue from specimens collected in three places along the rocky point across from the Beatson mine site, from pilings below the old pier at Ellamar, and from outcrops of sedimentary rock between the pit transects at Threeman are presented in Table 6. A survey of the literature and the NOAA Mussel Watch website permits a comparison with data for mussels of similar species from other locations in Prince Williams Sound, southeastern Alaska, and other U.S. coastal areas (Table 6). Mussels from the Beatson, Ellamar, and Threeman sites are clearly enriched (>7X) in Cu compared to mussels from uncontaminated sites in Prince Wil-

Table 6

Metal concentrations (in mg/kg dry weight) in mussels (*Mytilus edulis*) from three mine sites in Prince William Sound and mussels from other locations in Prince William Sound, southern and southeastern Alaska, and mainland U.S. coastal areas

Map No. ^a	Field no.	Location	Cu	Zn	Pb	Cd	Cr	Ni	As	Hg
B1	05PWS204B	Beatson	86	177	2.4	3.4	2.9	<1	7.0	0.04
B2	05PWS204Bm	Beatson	67	174	3.0	3.6	3.3	1.2	5.6	0.08
B3	05PWS203Bm	Beatson	58	304	2.9	3.2	2.7	1.2	6.9	0.08
B4	05PWSE201m	Ellamar	45	117	0.95	3.0	2.0	1.0	5.8	0.07
B5	05PWST2	Threeman	74	117	0.92	5.9	2.6	1.4	9.7	0.07
Average for three mine sites			66	178	2.0	3.8	2.7	1.2	7.0	0.07
Data for uncontaminated sites in southern Alaska (NOAA Center for Coastal Monitoring and Assessment Mussel Watch Project web site ^b):										
Prince William Sound, Sleepy Bay (1995 data)			9.4	82	0.74	3.1	2.4	1.6	8.5	0.10
Prince William Sound, Disk Island (1995 data)			8.5	116	0.78	3.3	2.3	1.9	9.4	0.10
Prince William Sound, Knowles Head (1995 data)			8.8	74	0.57	2.4	1.4	1.9	9.2	0.10
Prince William Sound, Sheep Bay (1995 data)			8.0	86	0.67	2.7	1.7	2.6	9.1	0.07
Port Valdez, Mineral Creek Flats (2003 data)			7.7	75	0.95	4.0	1.1	2.3	17	0.07
Ketchikan, Mountain Point (2003 data)			7.6	100	0.26	4.6	0.59	0.83	9.0	0.12
SE Alaska, uncontaminated site, Kensington mine site baseline study (Rudis, 2001) ^c			6.2	53	0.68	9.7	1.1	0.95	9.2	0.07
SE Alaska, Misty Fjords, range for multiple uncontaminated sites, 1981–1982 (Franson et al., 1995)			4.8–8.7	52–86	<0.1–4.0	3.4–9.6	1.8–6.5	n.a. ^e	<0.05–0.8	n.a.
U.S. coastal, 1986–1996, average (O'Connor, 1998) ^d			9.0	126	0.79	2.5	na	1.8	9.1	0.11
Howe Sound, British Columbia, range attributed to acid mine drainage from abandoned copper mine (Grout and Levings, 2001)			15–115	117–192						

^a Map numbers refer to locations in Fig. 2.

^b http://www8.nos.noaa.gov/cit/nsandt/download/mw_monitoring.aspx.

^c Species *Mytilus trossulus*.

^d Species include *Mytilus edulis* and *Mytilus californianus*.

^e n.a., not analyzed.

liam Sound and other coastal locations. A smaller 2-fold to 3-fold enrichment for Zn and Pb is evident in specimens from Beatson when compared to other mussel specimens from Prince Williams Sound. The Cu and Zn values fall within the range of Cu and Zn concentrations for mussels affected by acid-mine drainage from an abandoned Cu mine in British Columbia (Grout and Levings, 2001). Additional chemical data for mussels as well as data for other marine organisms collected near the mine sites are presented in Munk and Koski (2007). The limited database obtained thus far indicates local bioaccumulation of base metals in the marine environment at all three Prince William Sound mine sites.

5. Conclusions

The weathering of sulfide-rich mine wastes distributed in near-shore settings has a measurable impact on local coastal environments in Prince William Sound. At the Beatson, Ellamar, and Threeman mine sites, sulfide oxidation generates acidic surface waters that mobilize environmentally important elements into fluid pathways that reach into the marine environment. Most sulfide-rich rock samples are dominated by pyrrhotite or pyrite. Chalcopyrite and sphalerite are the other major sulfide minerals and, together with the Fe sulfides, represent a potent source for Fe, Cu, and Zn at all three sites. Volumetrically minor galena, arsenopyrite, and cobaltite are the major sources for Pb, As, and Co, but the presence of these as enriched trace elements in the major sulfide minerals adds to the supply. Sphalerite is the principal source for Cd in all locations and probably represents the primary source of Hg in pore waters at Ellamar. Oxidation of sulfides is most advanced in samples embedded or buried in mine dumps and in sulfide-bearing beach gravels at Threeman and Ellamar. Among the major sulfide minerals, the resistance to oxidation increases in the order pyrrhotite $\ll$ sphalerite $<$ chalcopyrite $\leq$ pyrite. Thus, pyrrhotite-rich material at any mine site typically exhibits the most advanced stages of alteration. Progressive alteration of pyrrhotite grains is pervasive and involves the development of marcasite along grain edges followed by replacement of the core by sulfur, Fe sulfate and Fe–Al sulfate. The oxidation patterns for chalcopyrite and pyrite involve a gradual replacement by colloform Fe oxyhydroxides at grain margins and along crosscutting

cracks that ultimately coalesce to consume the sulfide crystal. The end product of sulfide oxidation is an ochreous aggregate of goethite + lepidocrocite + amorphous Fe-oxyhydroxide mixed with detrital and hydrothermal silicate minerals.

An inverse correlation between pH and metal concentrations is evident in the water data from all three sites. The waters of lowest pH (~ 3) and highest concentrations of dissolved base metals (to $\sim 25,000$ $\mu\text{g/L}$) in gravels at the Ellamar mine site reflect the oxidation of abundant sulfide-rich debris. The low pH and high dissolved Fe, Al and SO_4 contents of these pore waters are conducive to the precipitation of jarosite in the intertidal zone. Pore waters from the intertidal zone at the Threeman mine site have circumneutral pH values and low base-metal concentrations, probably because the much smaller volume of sulfide-rich detritus in the gravels cannot generate sufficient acidity. However, small amounts of dissolved Fe^{2+} in the pore waters are oxidized during mixing with seawater and are precipitated as Fe-oxyhydroxide flocs at the beach–seawater interface.

At the Beatson site, water from melting snow and rain enters the pit lake and then flows through the underground mine workings before discharging across the waste dumps. This circumneutral water carries a relatively small base-metal load into the marine environments (Stillings et al., 2008), but stream waters crossing waste piles may also play a significant role in transport of metalliferous particulates into offshore areas during storm events. More acidic fluids (to pH 5.3) are present in seeps and small streams that emerge from the Beatson waste dumps. Amorphous Fe precipitates formed in stagnant seeps may be predominantly colloidal; thus, their high concentrations of Cu and Zn probably reflect adsorption onto extremely high surface areas. Conversely, crystalline precipitates composed of ferrihydrite and schwertmannite, more abundant in bodies of moving water, have comparatively low metal contents attributed to the reduced surface area of crystalline Fe oxyhydroxides. The physical dispersion of precipitates during storm-induced runoff may contribute metals to intertidal and subtidal environments near the mine sites.

Limited chemical data for mussels (*Mytilus edulis*) collected from the intertidal zone at Beatson, Ellamar, and Threeman indicate that bioaccumulation of base metals is occurring in the marine environment at all three sites.

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