Geologic and Environmental Characteristics of Porphyry Copper Deposits with Emphasis on Potential Future Development in the Bristol Bay Watershed, Alaska

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Introduction

This report is prepared in cooperation with the Bristol Bay Watershed Assessment being conducted by the U.S. Environmental Protection Agency. The goal of the assessment is to help understand how future large-scale development in this watershed may affect water quality and the salmon fishery. Mining has been identified as a potential source of future large scale development in the region, especially because of the advanced stage of activity at the Pebble prospect. The goal of this report is to summarize the geologic and environmental characteristics of porphyry copper deposits in general, largely on the basis of literature review. Data reported in the Pebble Project Environmental Baseline Document, released by the Pebble Limited Partnership in 2011, are used to enhance the relevance of this report to the Bristol Bay watershed.

The geologic characteristics of mineral deposits are paramount to determining their geochemical signatures in the environment. The geologic characteristics of mineral deposits are reflected in the mineralogy of the mineralization and alteration assemblages; geochemical associations of elements, including the commodities being sought; the grade and tonnage of the deposit; the likely mining and ore-processing methods used; the environmental attributes of the deposit, such as acid-generating and acid-neutralizing potentials of geologic materials; and the susceptibility of the surrounding ecosystem to various stressors related to the deposit and its mining, among other features (Seal and Hammarstrom, 2003). Within the Bristol Bay watershed, or more specifically the Nushagak and Kvichak watersheds, the geologic setting is permissive for the occurrence of several mineral deposit types that are amenable for large-scale development. Of these deposit types, porphyry copper deposits (e.g., Pebble) and intrusion-related gold deposits (e.g., Shotgun) are the most important on the basis of the current maturity of exploration activities by the mining industry. The Pebble deposit sits astride the drainage divide between the Nushagak and Kvichak watersheds, whereas the Humble, Big Chunk, and Shotgun deposits are within the Nushagak watershed. The Humble and Big Chunk prospects are geophysical anomalies that exhibit some characteristics similar to those found at Pebble. Humble was drilled previously in 1958 and 1959 as an iron prospect on the basis of an airborne magnetic anomaly. Humble is approximately 85 miles (137 km) west of

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Pebble; Big Chunk is approximately 30 miles (48 km) north-northwest of Pebble; and Shotgun is approximately 110 miles (177 km) northwest of Pebble. The H and D Block prospects, west of Pebble, represent additional porphyry copper exploration targets in the watershed.

Geologic Characteristics of Porphyry Copper Deposits

Geologic Setting of the Bristol Bay Watershed

The Nushagak and Kvichak watersheds are characterized by a complex geologic history. The history, going back at least 100 million years, has been dominated by northward movement and subduction of the oceanic crust beneath the Alaskan continental landmass, which continues today. The northward subduction of oceanic crust led to the accretion of island land masses to the Alaskan mainland. The divide between the Nushagak and Kvichak watersheds is near the geologic boundary between the Peninsular Terrane to the southeast and the Kahiltna Terrane to the northwest (Decker and others, 1994; Nokleberg and others, 1994). The Peninsular Terrane consists of Permian limestone, Triassic limestone, chert, and volcanic rocks, Jurassic volcanic and plutonic rocks, and Jurassic to Cretaceous clastic sedimentary rocks.

The Pebble porphyry copper deposit and the Humble and Big Chunk prospects are located within the southern Kahiltna Terrane (Fig. 1). The southern Kahiltna Terrane consists of a deformed sequence of Triassic to Jurassic basalt, andesite, tuff, chert, and minor limestone of the Chilikadrotna Greenstone, which is overlain by the Jurassic to Cretaceous Koksetna River sequence comprising turbiditic sandstones, siltstone, and shales (Wallace and others, 1989). The area was intruded by Cretaceous to Tertiary plutons, which include those associated with the Pebble deposit. The area also was partially covered by Tertiary to Quaternary volcanic rocks and varying thicknesses of glacial deposits (Detterman and Reed, 1980; Bouley and others, 1995).

The underlying geology can exert a significant influence on water chemistry, and therefore the possible toxicity of trace elements to aquatic organisms. The presence or absence of carbonate minerals and pyrite is the most significant influences on water chemistry in terms of pH, hardness, and alkalinity. Carbonate minerals such as calcite – the main constituent of limestone – can raise the pH and increase water hardness and alkalinity. Limestone, dolomite, and siltstone with abundant calcareous concretions are the most common hosts of carbonate minerals and are most abundant in Kvichak watershed in the vicinity of Lake Clark (Detterman and Reed, 1980; Bouley and others, 1995). Pyrite, a potential source of acid, can be a minor constituent of turbiditic sediments such those found in the Koksetna River sequence, northeast of Pebble. Hydrothermal activity associated with the formation of mineral deposits, discussed below, also can introduce significant amounts of both pyrite and carbonate minerals.

Mineral Resource Potential of the Nushagak and Kvichak Watersheds

The geologic setting of the Nushagak and Kvichak watersheds has characteristics that indicate that the region is favorable for several different mineral-deposit types (Schmidt and others, 2007). These deposit types include porphyry copper deposits, copper and iron skarn deposits, intrusion-related gold deposits, epithermal gold-silver vein deposits, hot spring mercury deposits, placer gold deposits, and sand and gravel deposits (Table 1). Of these deposit types, porphyry copper deposits and intrusion-related gold deposits are represented by prospects within the area that could prompt large-scale development. Copper skarn deposits hold less potential, in the absence of infrastructure from other mine development in the region, because of their typical smaller size (John and others, 2010). Significant exploration activity associated with porphyry copper deposits is currently being done at the Pebble prospect, and to a lesser extent the Humble and Big Chunk prospects. Several other porphyry copper prospects are immediately adjacent to Pebble, including the H Block and D Block prospects. Notable exploration also is being done in the watershed at several gold properties including Shotgun, Kisa, and Bonanza Hills.

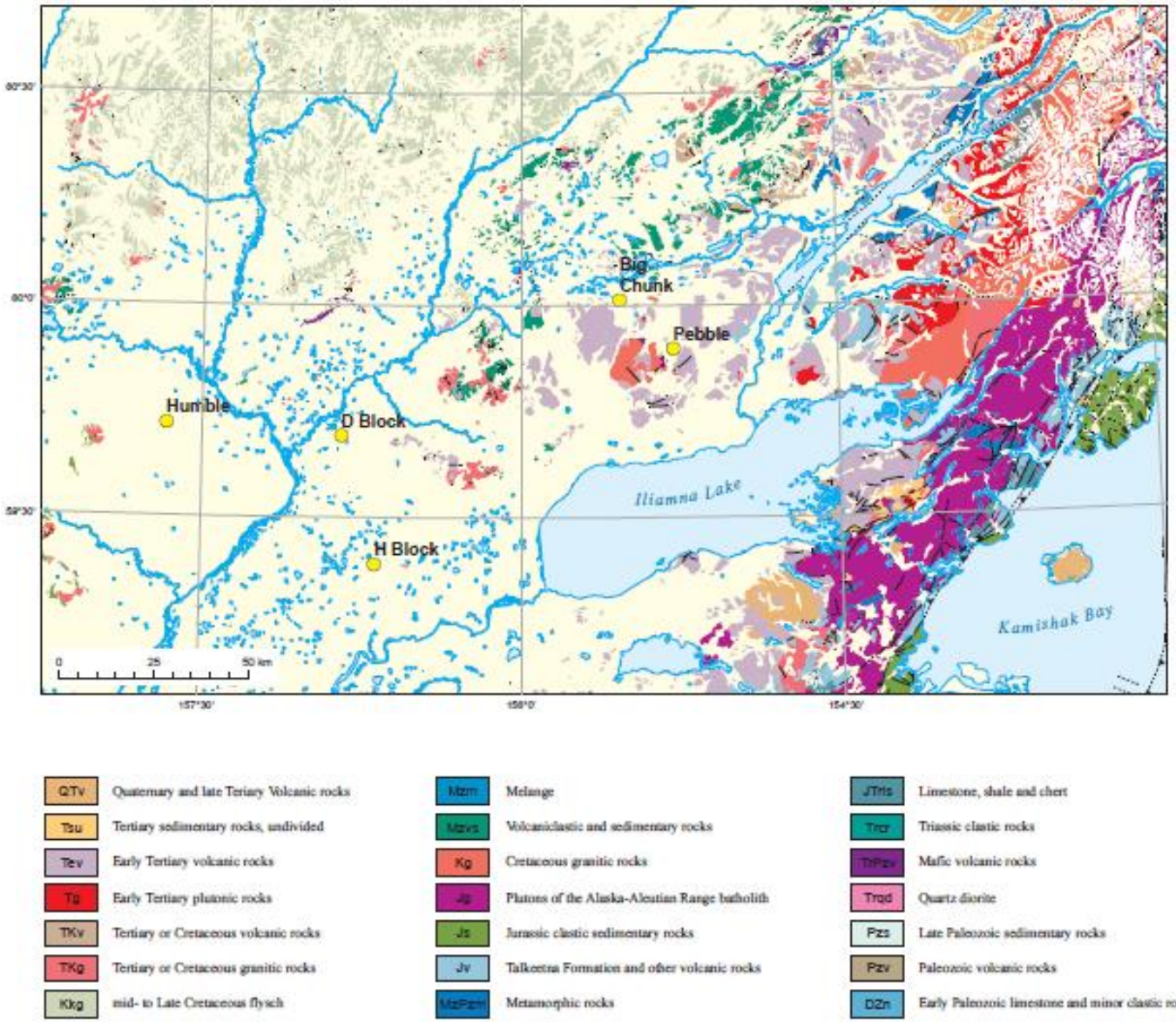

Figure 1. Generalized geologic map of the central part of the Bristol Bay watershed showing the general locations of the Pebble, Humble, and Big Chunk prospects. Adapted from Wilson and others (2006). Map was made by Keith Labay (USGS).

The Pebble deposit is the most advanced among the mining prospects in the Bristol Bay watershed in terms of exploration and preparation for the submission of mine permit applications. Therefore, the potential for large-scale mining development within the watershed in the near future is greatest for porphyry copper deposits. Accordingly, the remainder of the report will focus exclusively on this deposit type – porphyry copper deposits.

Table 1. Deposit types with significant resource potential for large-scale mining in the Nushagak and Kvichak watersheds.

Deposit type	Commodities	Examples	References
Porphyry copper	Cu, Mo, Au, Ag	Pebble, Big Chunk, Kijik River	Schmidt and others (2007); Bouley and others (1995)
Intrusion-related gold	Au, Ag	Shotgun/Winchester. Kisa, Bonanza Hills	Schmidt and others (2007); Rombach and Newberry (2001)
Copper(-iron-gold) skarn	Cu, Au, Fe	Kasna Creek, Lake Clark Cu, Iliamna Fe, Lake Clark	Schmidt and others (2007), Newberry and others (1997)

General Characteristics of Porphyry Copper Deposits

Geologic Features:

The geological characteristics of porphyry copper deposits recently have been reviewed by John and others (2010), Sinclair (2007), and Seedorff and others (2005). Therefore, only salient features are summarized here. Porphyry copper deposits are found around the world, most commonly in areas with active or ancient volcanism (Fig. 2). The economic viability of porphyry copper deposits is dictated by the economy of scale – they typically are low grade (average 0.44 % copper in 2008), large tonnage (typically hundreds of millions to billions of metric tonnes of ore) deposits that are exploited by bulk mining techniques (John and others, 2010). Because of their large size, their mine lives typically span decades.

Primary (hypogene) ore minerals found in porphyry copper deposits are structurally controlled and genetically associated with felsic to intermediate composition, porphyritic intrusions that typically were emplaced at shallow levels in the crust. Mineralization typically forms both within the associated intrusions and in the surrounding wall rocks. The distribution of primary minerals is structurally controlled, filling veins, veinlets, stockworks and breccias. Pyrite (FeS_2) is typically the most abundant sulfide mineral. The main copper sulfide ore minerals are chalcopyrite ($CuFeS_2$) and bornite (Cu_5FeS_4). A number of other minor copper sulfide minerals are commonly found; most notable from an environmental perspective is the arsenic-bearing mineral enargite (Cu_3AsS_4). Molybdenite (MoS_2) is the main molybdenum mineral. Gold in porphyry copper deposits can be associated in appreciable amounts with bornite, chalcopyrite, and pyrite; the gold may occur as a trace element within these sulfide minerals or as micrometer-scale grains of native gold (Kesler and others, 2002).

Hydrothermal mineralization events produce hydrothermal alteration haloes that are much larger than the actual ore deposit. The classic alteration zonation includes a potassium feldspar-biotite rich core, surrounded by a muscovite/illite sericitic (phyllic) alteration zone, which is surrounded by a clay-rich argillic alteration zone and finally by a chlorite-epidote rich propylitic zone (Fig. 3; Lowell and Gilbert, 1970). The ore zones generally coincide with the potassic and sericitic alteration zones. From an environmental perspective, the importance of these alteration

zones is that the sericitic and argillic alteration tends to destroy the acid-neutralizing potential of the rock, while enhancing the acid-generating potential through the addition of pyrite. In contrast, the outer portion of the propylitic zone tends to have enhanced acid-neutralizing potential due to the introduction of trace amounts of carbonate minerals.

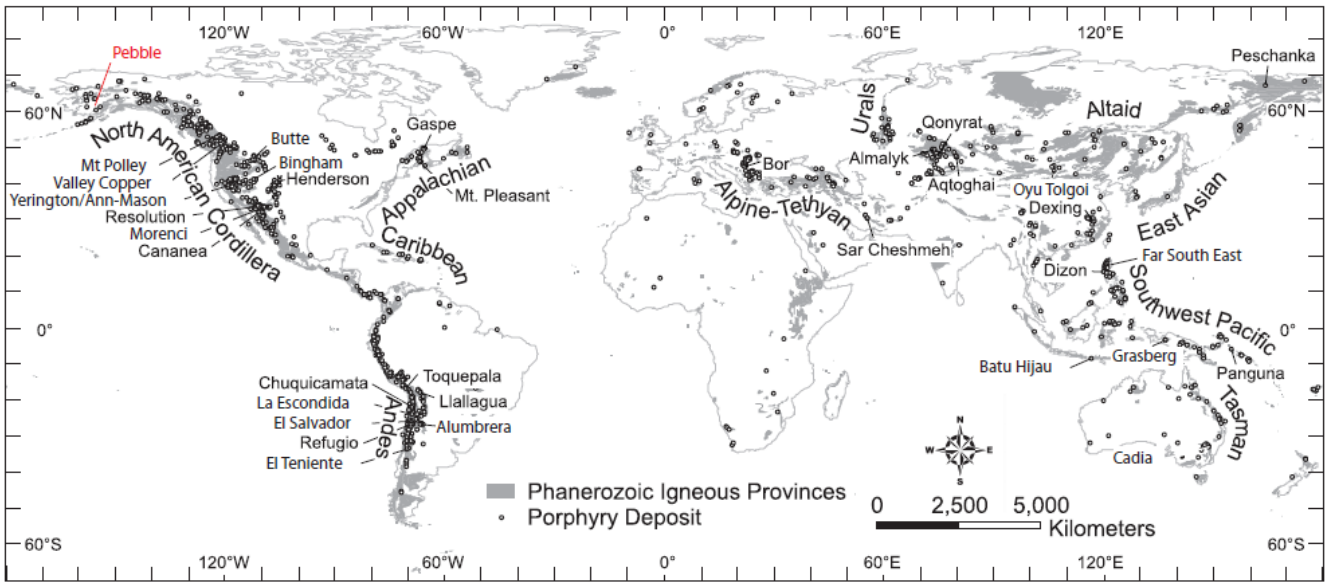

Figure 2. Map showing location of Phanerozoic porphyry deposits with representative deposits labeled. Modified from Seedorff and others (2005) and John and others (2010).

Supergene (weathering) processes, which occur long after the initial hydrothermal mineralizing events, can lead to zones of supergene enrichment near the tops of these deposits (John and others, 2010). The supergene enrichment zones can be either oxide- or sulfide-dominated depending on the prevailing oxidation state at the site of formation, the depth of the water table, and climate. Mined material from the oxide enrichment zone is amenable to a heap-leaching method of ore processing known as "solvent-extraction – electrowinning" (SX-EW; Jergensen, 1999). However, supergene ores are likely to be minor in Alaska due to recent glaciation.

Porphyry copper deposits can be divided into three subtypes on the basis of Au (g/t)/Mo (%) ratios: porphyry Cu, porphyry Cu-Mo, and porphyry Cu-Au deposits, where Cu-Au deposits have Au/Mo ratios greater than or equal to 30, Cu-Mo deposits have Au/Mo ratios less than or equal to 3, and Cu deposits are all other deposits not within these bounds (Sinclair, 2007; Singer and others, 2008). On the basis of these criteria, the Pebble deposit would be classified as a porphyry Cu deposit.

Economic Characteristics:

Porphyry copper deposits are important sources of copper, molybdenum, gold, and silver; they also can supply significant amounts of byproduct rhenium, tellurium, and platinum group elements. Porphyry copper deposits supply over 60 percent of the copper for global copper production and together with porphyry molybdenum deposits, account for over 95 percent of the molybdenum production (Sinclair, 2007; John and others, 2010). In 2010, the United States consumed 1,730,000 tonnes of copper, of which 30 percent was imported, chiefly from Chile, Canada, and Peru. In the same year, the United States consumed 48,000 tonnes of molybdenum, and was a net exporter. In 2010, the United States consumed 380 tonnes of gold of which 33 percent was imported,

primarily from Canada, Mexico, Peru, and Chile. These commodities serve myriad uses (U.S. Geological Survey, 2011). Copper is used primarily in building construction (wiring and pipes; 49 %), electric and electronic products (20 %), vehicles (12 %), consumer products (10 %), and industrial machinery and equipment (9 %). Molybdenum is primarily used as a steel alloy (75 %). Gold is used mainly for jewelry (69 %), and electrical and electronic products (9 %). Silver is used for a variety of applications including industrial and medical uses, electronics, coins and silverware, and photography (albeit a declining application). Rhenium is principally used as an alloy in turbine engines (70 %) and for petroleum refining (20 %). Tellurium is primarily used as an alloy with steel, iron, and lead, but increasingly is being used in solar cells. Platinum-groups metals (platinum, palladium, rhodium, ruthenium, iridium, and osmium) principally are used in vehicle catalytic converters, as catalysts for chemical manufacturing, in electronics and in emerging applications to fuel cells.

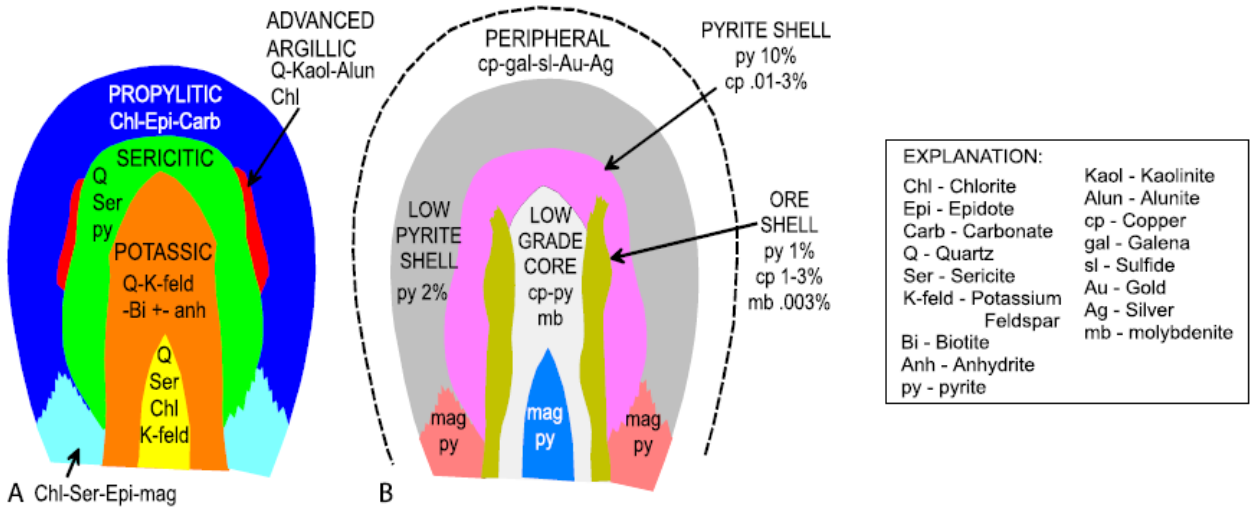

Figure 3. Idealized cross section through a porphyry copper deposit showing the relationship of the ore zone to various alteration types. A. Distribution of alteration types; B. Distribution of ore mineral assemblages. The causative intrusion corresponds to the potassic alteration zone. From John and others (2010) and modified from Lowell and Guilbert (1970).

The grade and tonnage of porphyry copper deposits vary widely (Singer and others, 2008). Summary statistics compiled for 256 porphyry copper deposits are presented in Table 2, and in Figure 4. For total tonnage of ore, Pebble is in the upper 5th percentile, lower 50th percentile for copper grade, upper 10th percentile for molybdenum grade, and upper 10th percentile for gold grade. The amount of metal contained in the Pebble deposit corresponds to a 21-year supply of copper for the United States, a 53-year supply of molybdenum, and a 9-year supply of gold, based on 2010 consumption statistics (Table 3). From the perspective of future discoveries in the watershed, it is therefore highly unlikely that new deposits will approach the size of Pebble, but instead will be considerably smaller.

Geology of Bristol Bay Porphyry Copper Deposits:

Several porphyry copper prospects within the Bristol Bay watershed are being explored, and include Pebble, Humble, and Big Chunk. The Pebble deposit is the only one with a significant published description of its geology (Bouley and others, 1995; Kelley and others, 2010). The deposit is controlled by the Pebble Limited Partnership – a joint venture between Northern Dynasty Minerals, Ltd., and Anglo American. The Pebble deposit may be viewed

as consisting of two contiguous ore bodies: Pebble West and Pebble East, with the buried Pebble East having the higher ore grades. Pebble West was discovered in 1989 at the surface, and delineation drilling in 2005 resulted in discovery of Pebble East beneath a 300 to 600 m thick cover of Tertiary volcanic rocks. The deposit has been explored extensively with more than 1,150 drill holes that total greater than 949,000 feet (289,250 m) (Northern Dynasty Minerals, 2011).

Table 2. Global grade and tonnage summary statistics for porphyry copper deposits (n = 256; Model 17, Singer and others, 2008) compared to the Pebble deposit.

Parameter	10th Percentile	50th Percentile	90th Percentile	Pebble[1]
Tonnage (Mt)	1,400	250	30	10,777
Cu grade (%)	0.73	0.44	0.26	0.34
Mo grade (%)	0.023	0.004	0.0	0.023
Ag grade (g/t)	3.0	0.0	0.0	unknown
Au grade (g/t)	0.20	0.0	0.0	0.31

Sources: [1]PLP (0.3 % Cu cut-off grade), includes measured, indicated, and inferred resources (*http://www.pebblepartnership.com/*)

Table 3. Annual consumption of copper, molybdenum and gold compared to the Pebble deposit.

Commodity	US Annual Consumption (2010)[1]	Pebble Resource[2]	Years of 2010 Consumption
Copper (tonnes)	1,730,000	36,636,364	21
Molybdenum (tonnes)	48,000	2,531,818	53
Gold (tonnes)	380	3,337	9

Sources: [1]U.S. Geological Survey (2011); [2]PLP (0.3 % Cu cut-off grade), includes measured, indicated, and inferred resources (*http://www.pebblepartnership.com/*)

The oldest rocks in the vicinity of the deposit are Jurassic to Cretaceous (ca. 150 Ma) clastic sedimentary rocks (i.e., mudstone, siltstone, and sandstone), which were intruded by dominantly granitic plutons from 100 to 90 Ma; granodiorite stocks and sills, spatially and genetically related to the Cu-Au-Mo mineralization, were intruded about 90 Ma (Kelley and others, 2010). Intrusion of these granodiorite bodies resulted in hydrothermal activity that produced the mineralization and associated alteration of the intrusions and surrounding rocks. The Pebble West deposit extends from the surface to a depth of about 500 m and encompasses roughly 6 square kilometers on the surface. Pebble East is covered by a wedge of post-mineralization Tertiary volcanic rocks that exceeds 600 m in thickness towards the east. The eastern end of the deposit is truncated by a high-angle fault that offsets the deposit 600 to 900 m down to the east (Kelley and others, 2010). Early copper mineralization was dominated by pyrite, chalcopyrite, and gold, which was overprinted by pyrite, bornite, digenite, covellite, and minor enargite, followed by quartz-molybdenite veinlets (Bouley and others, 1995; Kelley and others, 2010).

Geologic information on the Humble prospect (previously known as Kemuk) is limited to the details found on the Millrock Resources, Inc. website (*http://www.millrockresources.com/projects/humble/*). The prospect is covered by glacio-fluvial gravels and sands 30 to greater than 140 m thick. The site was identified on the basis of the presence of an airborne geophysical (magnetic) anomaly and the presence of igneous rocks similar to those found at Pebble. The Humble Oil Company drilled the property in 1958 and 1959 as an iron prospect. No mention is made of Cu-Au-Mo mineralization from the 1950s drilling, and there are no recent data available. Information on the Big Chunk Super project is limited to details on the Liberty Start Uranium and Metals Corporation website

(*http://www.libertystaruranium.com/www/projects/big-chunk-super-project*). Current exploration efforts are focused on six to seven airborne electromagnetic geophysical anomalies from data collected in 2009 that are consistent with porphyry-style mineralization. Although exploratory drilling is mentioned on the web site, no results are discussed.

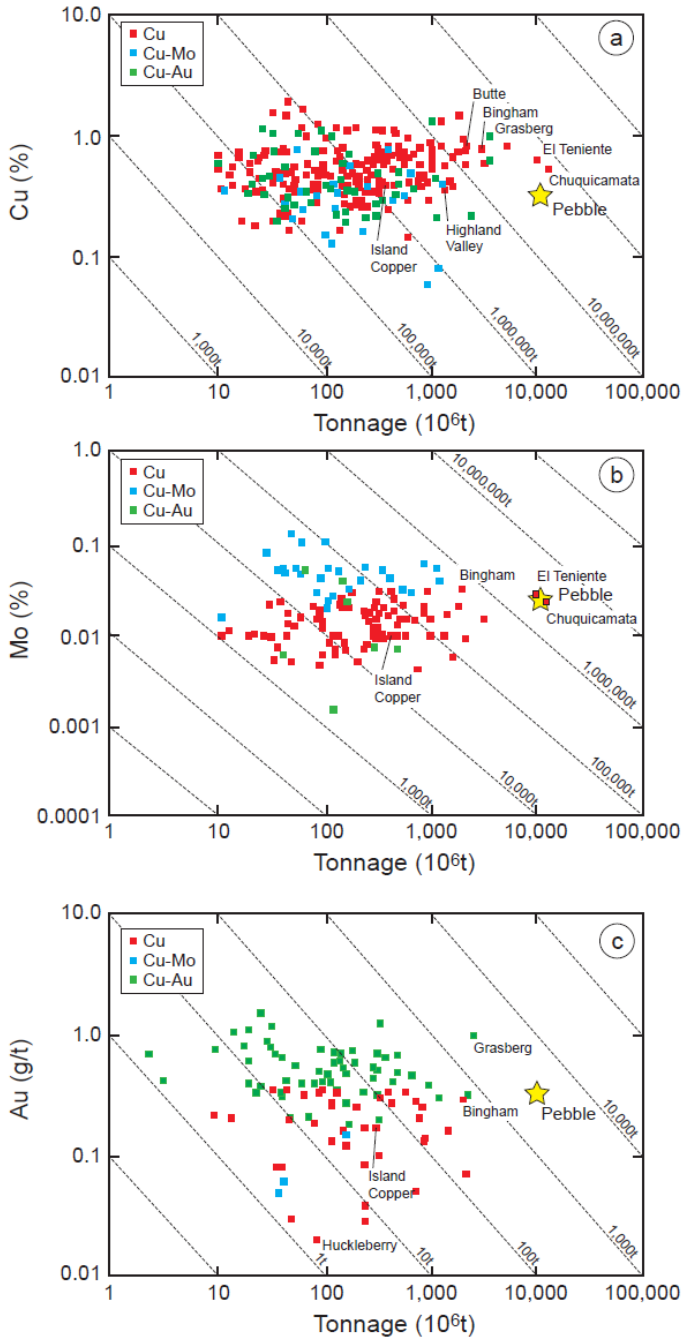

Figure 4. Grade-tonnage characteristics of the Pebble deposit compared to other porphyry-type deposits. A. Copper; B. Molybdenum; C. Gold. The Pebble deposit is shown as the yellow star. Selected, noteworthy deposits are labeled. Pebble is classified as a porphyry Cu deposit (red squares). The dashed diagonal lines represent the total contained metal. Modified from Sinclair (2007).

Mining and Beneficiation Considerations:

Mining and ore-processing methods can vary based on whether or not parts of the ore are weathered, and on the commodities being extracted. Due to their large size and low grades, porphyry copper deposits are mined by bulk mining methods such as open-pit mining for deposits near the surface, and block caving for deposits at depth. Because the copper ore grades are generally less than 2 percent, greater than 98 percent of the material mined ends up as waste. The beneficiation of the ore is distinctly different between hypogene (primary) sulfide ores and supergene (secondary) oxide ores. Mining begins with the removal of waste rock, which may or may not be acid-generating. Country rocks that host the mineralization are commonly acid-generating due to the presence of hydrothermal pyrite formed during the mineralizing event. These rocks may be classified as subeconomic ore and may be stockpiled separately from barren waste rock. The processing of subeconomic ore commonly is prompted by either an increase in metal prices making the material economically viable, or if a high-grade zone is encountered during mining, the subeconomic ore may be mixed with high-grade ore to ensure that an appropriate grade of material is being fed to the mill. In either case, subeconomic ore generally is handled in a similar fashion to that of waste rock during mine operations because of its acid-generating potential.

The primary (hypogene) sulfide ore is crushed to sand or silt size prior to ore concentrate separation using the froth flotation method (Fuerstenau and others, 2007). For porphyry copper deposits, such as Pebble, separate concentrates for copper and molybdenum generally are produced. The gold in porphyry copper deposits can be partitioned variably among the copper-sulfide minerals (chalcopyrite, bornite, chalcocite, digenite, and covellite), pyrite, and free gold (Kesler and others, 2002). Gold associated with the copper minerals remains with the copper concentrate and is recovered at an off-site smelter. Gold associated with pyrite will end up in the tailings, unless a separate pyrite concentrate is produced. Pyrite concentrates can be produced during the froth flotation process for the recovery of gold or to more effectively manage the high acid-generating potential of this material. Gold commonly is recovered by cyanidation, but gold recovery from sulfide-rich material is poor (Marsden and House, 2006). To improve gold recovery, pyritic material typically is oxidized by various means including high-temperature (pyrometallurgical) roasting; low-temperature, pressurized autoclaving; or bio-oxidation using bacteria. Following oxidation, the material then is leached with cyanide, typically in a vat to recover gold (Marsden and House, 2006). The resulting spent iron oxides generally are disposed with the tailings. Autoclaving is probably the most likely option in southwest Alaska because cyanide can be managed effectively in a vat-leaching operation. High-temperature roasting is energy intensive and presents additional challenges with respect to stack emissions. Bioleaching may be more difficult because of the cold climate and slow biotic oxidation rates at lower temperatures.

Tellurium generally is recovered from the copper anode slimes at the refinery (John and others, 2010). Rhenium is recovered as a byproduct of the roasting of the molybdenum concentrate at the refinery (U.S. Geological Survey, 2011). The platinum-group metals generally are associated with copper concentrates (Tarkian and Stribrny, 1999) and thus, would not be recovered on site at Pebble. Thus, the recovery of tellurium and platinum-group elements from Pebble or other porphyry copper deposits in the watershed would likely be an activity conducted off-site when ore concentrates are further processed.

Supergene (secondary) oxide ores commonly are beneficiated using a heap-leach method known as solvent extraction-electrowinning (SX-EW). This process involves placing coarsely crushed ore on a lined pad and applying sulfuric acid to leach copper from the ore. The pregnant leach solution is collected and the copper is removed from the leachate electrolytically (Jergensen, 1999). The supergene enrichment zone at Pebble is poorly developed and dominated by the secondary copper sulfide minerals covellite (CuS), digenite ($Cu_{1-x}S$), and chalcocite (Cu_2S), in part due to recent glaciation (Bouley and others, 1995). Therefore, processing of oxide ore is unlikely at Pebble or geologically similar deposits within the watershed.

Environmental Characteristics of Porphyry Copper Deposits

Overview

Porphyry copper deposits can pose geochemical risks to aquatic and terrestrial ecosystems, and to human health. The risks can range from nil to significant and depend upon a variety of factors. Factors that influence the environmental characteristics of mineral deposits range from geologic setting (both local and regional), hydrologic setting, climatic settings, and mining methods, to ore beneficiation methods. The sources of the risk can be considered in the broad categories of acid-generating potential, trace element associations, mining and ore beneficiation methods, and waste disposal practices. The significance of these sources of risk will vary from deposit to deposit, but some generalizations can be made for porphyry copper deposits as a whole.

Acid-Generating Potential

Acid generation can be considered a "master variable" for aqueous risks. Metals and other cations are more soluble at low pH as compared to neutral or high pH. Therefore, the acid-generating or acid-neutralizing potentials of the waste rock, tailings, and mine walls are of prime importance in identifying the potential environmental risks associated with mining and ore beneficiation.

The acid-generating or acid-neutralizing character of a rock or mine waste material is evaluated in terms of an "acid-base account". Acid-base accounting uses static tests to assess maximum acid-generating potential. Static tests are based on a single analysis of waste material and therefore are independent of rates of reactions. In contrast to static tests, kinetic tests expose mine waste samples for weeks, months, or years. Most proposed mining projects take a staged approach to evaluating acid-generating potential starting with acid-base accounting data to screen numerous samples, which are followed by the more laborious kinetic testing process on fewer, carefully selected samples.

The acid-generating potential of rocks and mine waste samples can be evaluated using a variety of techniques (Price, 2009; INAP, 2011). In North America, one of the most common techniques investigates the difference or ratio of the acid-generating and acid-neutralizing potential of the sample. Theoretically, a sample with an acid-neutralizing potential (NP) equal to its acid-generating potential (AP) is "net neutral", meaning that its acid-neutralizing potential (NP) should theoretically cancel (or neutralize) its acid-generating potential (AP). Numerically, this is expressed as a "net neutralizing potential" (NNP) of zero, where

$$NNP = NP - AP$$

Values for AP, NP, and NNP are typically expressed in the units of kilograms of calcium carbonate per tonne of waste material (kg $CaCO_3$/t), such that the amount of calcium carbonate amendment that would be needed to achieve "net neutrality" is readily apparent. The AP values are generally based on an analysis of the sulfide-sulfur content of the sample, and the NP values are based on either an analysis of the carbonate content of the sample or by leaching of the sample followed by a wet chemical titration of the resulting leachate. NNP values that are greater than zero are "net alkaline" and those below zero are "net acidic". Alternatively, the acid-base account of a sample also can be expressed in terms of its neutralizing potential ratio (NPR), which is simply the ratio of its NP to its AP:

$$NPR = NP/AP$$

Thus, a sample with a NPR equal to one is net neutral, greater than one is net alkaline, and less than one is net acidic. Current industry standards generally divide rocks and mine waste samples into three distinct categories based on the NPR values: potentially acidic drainage generating (PAG) for NPR less than 1; uncertain (possibly)

acidic drainage generating for NPR between 1 and 2; and non-potentially acidic drainage generating (non-PAG)(INAP, 2011). Note that the requirement that non-PAG material have a NPR value greater than 2 represents twice the amount of alkalinity needed for net neutrality under equilibrium conditions. In practice, kinetic considerations are important, which is why a NPR greater than 2 is desirable.

The rocks associated with porphyry copper deposits, in general, tend to straddle the boundary between being "net acidic" and "net alkaline". This aspect is illustrated well by the study of Borden (2003) on the Bingham porphyry copper deposit in Utah (Figures 5 and 6), which shares many similar geologic features with the Pebble deposit. The AP values for porphyry copper deposits approximately reflect the distribution of pyrite. The distribution of acid-generating and non-acid-generating material in plan view at the Bingham mine matches well with the idealized cross section of porphyry copper deposits shown in Figure 3B. The pyrite-poor, low-grade core corresponds to the central part of the Bingham Canyon deposit where NNP values are greater than 0. The progression out to the ore shell and pyrite shell with their increasing abundance of pyrite in these areas is reflected in the progressively more negative NNP values.

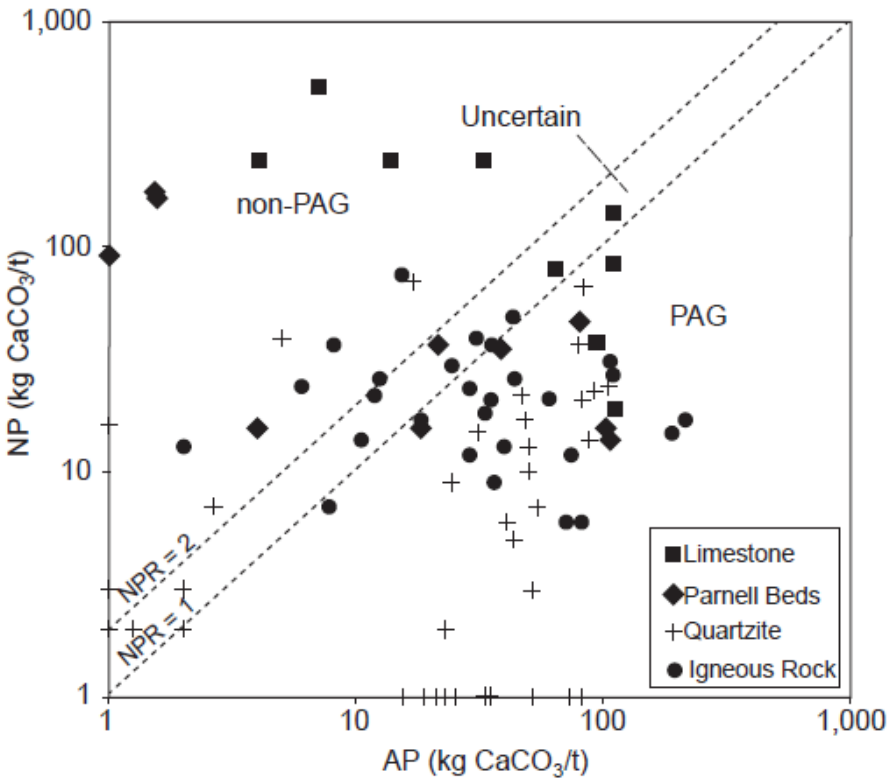

Figure 5. Plot of neutralizing potential (NP) and acid-generating potential (AP) for mineralized rock types at the Bingham Canyon porphyry copper deposit, Utah. Modified from Borden (2003).

During mining of porphyry copper deposits, a variety of materials with differing NNP values may be encountered. The low NNP, largely barren pyrite shell likely represents waste rock that may need to be removed to access the ore (Fig. 3B). The boundary between the ore shell and the pyrite shell is cryptic and typically is defined operationally on the basis of a cut-off copper grade. Therefore, some of the "waste" material with significant, subeconomic copper grades could be stockpiled for potential future beneficiation. The intrusions that produce

porphyry copper deposits can intrude any rock type. Therefore, the NNP values of the country rock of undiscovered deposits cannot be predicted reliably. Likewise, geologic events following ore formation could juxtapose a variety of rock types against an ore deposit, which can have a range of NNP values. In the case of Pebble, subsequent volcanic activity after mineralization covered the eastern part of the deposit with material that lacks acid-generating potential (Kelley and others, 2010; Pebble Partnership, 2011).

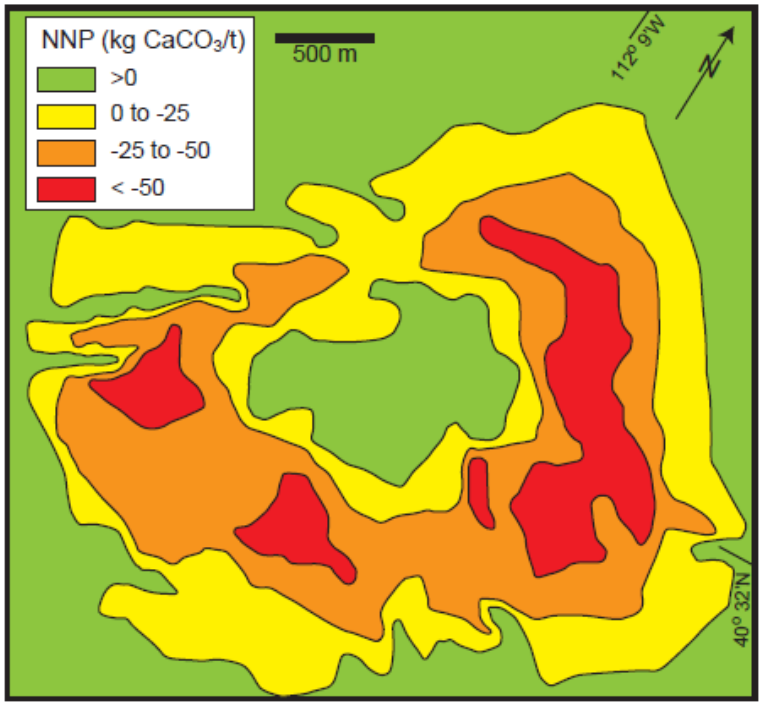

Figure 6. Plan view of the distribution of net neutralizinig potential (NNP) values at the Bingham Canyon porphyry copper deposit, Utah. NNP values above zero are "net alkaline"; those below zero are "net acid". Modified from Borden (2003).

The mining method will influence the amount of waste rock removed. Open pit mining can require the removal of large volumes of potentially acid-generating material. A waste-to-ore ratio of 2:1, meaning that two tonnes of waste are removed for each tonne of ore, is not uncommon for porphyry copper deposits (Porter and Bleiwas, 2003). Underground block caving of ore requires that a shaft or decline be sunk to facilitate mining. The amount of waste rock removed for block caving is much less than that removed in a typical open pit operation. In the specific case of Pebble, the volcanic rocks overlaying Pebble East are devoid of pyrite and are generally classified as non-PAG material, which would not require special handling to mitigate acidic drainage (Pebble Partnership, 2011). In fact, this material could be used for a variety of construction projects on site (e.g., road fill, tailings dam construction). In contrast, the pre-Tertiary rocks at Pebble are generally classified as PAG, with some samples having uncertain potential for generating acid and fewer with no potential for generating acid (non-PAG). During mining, some of this rock will be waste rock removed to access the ore, and some of it will be ore that will be processed to extract mineral concentrates.

The most profound influence that beneficiation of ore can have on mine tailings derived from froth flotation centers on the fate of pyrite (Fuerstenau and others, 2007). At many porphyry copper mines, the pyrite is discharged with the waste tailings, thereby contributing to the acid-generating potential of the tailings. However,

the option exists to produce a pyrite concentrate to manage more effectively the acid-generation risks associated with tailings, to extract gold associated with the pyrite, or both. The production of a pyrite concentrate will decrease the acid-generating potential of the tailings.

Waste Rock

Waste rock associated with porphyry copper deposits reflects the geologic history of the deposit. Because porphyry copper deposits are associated with igneous rocks intruded into shallow levels of the Earth's crust, the geochemical properties of the country rocks can vary widely, particularly in terms of their acid-base accounting properties and their trace element compositions. The hydrothermal activity that forms the ore deposits introduces sulfur, which commonly forms sulfide minerals such as pyrite, and a variety of trace elements. Introduced sulfur may also occur as the sulfate minerals anhydrite ($CaSO_4$), or barite ($BaSO_4$), which are environmentally benign with respect to acid-generating potential. In fact, for acid-base accounting, the portion of sulfur that occurs as sulfate should be subtracted from the total amount of sulfur present to accurately estimate acid-generating potential (Price, 2009). The hydrothermal alteration haloes around these deposits are significantly more extensive than the ores themselves (Fig. 3) and commonly represent waste rock with significant associated environmental risks. Rocks that form after the mineralization event, and not affected by supergene processes, are devoid of these hydrothermal overprints of sulfur and trace elements.

An early step in mining is to remove the waste rock to access the ore. For open pit mines, waste to ore (stripping) ratios commonly can exceed 2:1 (Porter and Bleiwas, 2003). As discussed in the previous section, the acid-generating potential of the waste rock can span the range from potentially acid-drainage generating (PAG) to non-PAG. The ability of leachate generated from waste rock to mobilize metals and oxyanions will vary, depending in part, on the pH of the resulting solution, which largely is a function of the pyrite content of the waste rock.

The primary environmental risk associated with waste rock is through the oxidation of waste-rock material, which may result in contamination of either groundwater or surface water. The oxidation of sulfide minerals such as pyrite produce sulfuric acid, which then can dissolve metals and related elements from associated sulfide, silicate, and carbonate minerals. The magnitude of this risk will depend upon waste management practices and whether or not drainage is treated.

The geochemical characteristics of waste-rock dump drainage have been investigated by several studies. Day and Rees (2006) conducted a study of dump seepage associated with several operating or recently closed porphyry copper and porphyry molybdenum mines in British Columbia, many of which are located in the Fraser River watershed. Porphyry copper mines included in their study were Gibraltar, Huckleberry, Island Copper, and Mount Polley; the data from Huckleberry were from laboratory column tests only. These deposits fell into two groups: those that produced low pH drainage and those that did not. The pH of waste-dump drainage from Gibraltar and Huckleberry ranged from neutral down to approximately 2, whereas drainage from Island Copper only reached a low of approximately 4.5. In contrast, the pH of waste-rock drainage at Mount Polley ranged between 7 and 8.5. The concentrations of sulfate and metals were negatively correlated with pH. The maximum concentrations of sulfate (<30,000 mg/L), Al (< 1,000 mg/L), Mn (< 100 mg/L), and Cu (< 1,000 mg/L) were all highest from Gibraltar; the highest concentrations of Zn (< 100 mg/L) were found in the Huckleberry column tests (Day and Rees, 2006). For comparison, Lister and others (1993) found that 41 percent of the NPR values for waste rock at Island Copper were below 1, 23 percent were between 1 and 3, and 36 percent were above 3, which is consistent with the range of pH values, from 4.5 to 8, observed by Day and Rees (2003). Khorasanipour and others (2011) found similar geochemical trends, but in a more arid environment, for drainage associated with waste-rock dumps at the Sarcheshmeh mine in southeastern Iran. The pH ranged between 3.1 and 6.3, specific conductance between 0.72 and 2.25 mS/cm, sulfate between 365 and 1,590 g/L, Al between < 0.05 and 60 mg/L, Mn between 14.6 and 95.8 mg/L, Cu between 2.15 and 70 mg/L, and Zn between 2.4 and 27.4 mg/L.

In the vicinity of the proposed Pebble mine, the best insights into the potential behavior of waste rock come from the humidity-cell tests being conducted by the Pebble Limited Partnership, and its contractors (Pebble Partnership, 2011). Management of waste rock during mine operation typically involves placing waste rock in subaerial piles on site. This configuration is similar to the conditions of humidity-cell tests where samples are exposed to a weathering protocol under unsaturated conditions (Price, 2009). Standard procedures require that rock be crushed to less than 6 mm, placed in cylinders, cycled through moist and dry air for six days, and leached on the seventh day, all at room temperature. This requirement produces a material that has significantly more surface area than waste rock produced during mining, which makes the test material more reactive than the actual material. As such, this approach does not incorporate the temperature and precipitation variations encountered on site, or the heterogeneous grain size of typical waste rock. "Barrel" kinetic tests were conducted also, where rather than weathering samples in the laboratory, larger volumes of material were placed in barrels in the field and the samples were exposed to site conditions. The goal of barrel testing is to scale-up laboratory results to conditions that are more representative of the site in terms of amount and seasonality of precipitation and temperature variations. The barrel test results are not discussed in this report. However, despite these caveats, the humidity-cell results presented by the Pebble Partnership (2011) provide relevant information.

Pebble Partnership (2011) has divided material at the site into several different groups, for both Pebble West and Pebble East: pre-Tertiary sedimentary and volcano-sedimentary units, Pre-Tertiary plutonic units, and Tertiary volcanic units. In general, results from the pre-Tertiary rocks from Pebble West and Pebble East were not significantly different. The pre-Tertiary rocks were present at the time of mineralization and therefore have the potential to be significantly mineralized. The Tertiary volcanic rocks were deposited after mineralization, and therefore should be lacking sulfide minerals as a source of acidity and metals.

The results of the Pebble Partnership (2011) humidity-cell tests are summarized in Table 4. Table 4 presents the mean composition of leachate from these tests divided into three groups: Tertiary rocks, hydrothermally altered pre-Tertiary rocks (undifferentiated) from Pebble West, and hydrothermally altered pre-Tertiary rocks (undifferentiated) from Pebble East. The results from the variety of pre-Tertiary rock types were grouped together here with the assumption that individual waste-rock types would not be selectively removed during mining. The concentration of constituents in the leachate was calculated from the average release rate data presented by the Pebble Partnership using the formula:

Concentration (mg/L) = [Release (mg/kg/week) x Mass of Sample (kg)]/Leachate Recovered (L),

where the average release rate, the mass of the solid sample, and amount of leachate recovered are provided in the Pebble Partnership (2011) report. The results from Pebble include a number of parameters (Pebble Partnership, 2011): pH, conductivity, acidity, alkalinity, total dissolved solids, hardness, F, Cl, SO_4, Al, Sb, As, Ba, Be, Bi, B, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Hg, Mo, Ni, K, Se, SiO_2, Ag, Na, Tl, Sn, V, and Zn. The present discussion focuses on pH, sulfate, Cu, Mo, As, and Zn. The pH of a solution is a master variable that controls the solubility of most elements. Sulfate is a proxy for pyrite oxidation, which produces the acid in acid-mine drainage. Copper is a cationic species, and the most likely inorganic ecologic stressor expected at the site, especially for aquatic organisms. Zinc commonly occurs in base-metal hydrothermal systems, but typically not in economic concentrations in porphyry copper deposits. Arsenic and molybdenum are oxyanion species; arsenic is a potentially significant stressor, especially with respect to drinking water contamination, whereas molybdenum is an important ore constituent with less potential to be an environmental stressor.

Table 4. Summary of geochemical results from humidity-cell tests on waste-rock samples conducted by the Pebble Partnership (2011).

Parameter	Units	Tertiary Waste Rock		Pebble West Pre-Tertiary Waste Rock		Pebble East Pre-Tertiary Waste Rock	
		Mean	Standard Deviation	Mean	Standard Deviation	Mean	Standard Deviation
Pebble Partnership (2011) Source		Table 11-31 (calc); Appendix 11C (pH)	Table 11-31 (calc); Appendix 11C (pH)	Table 11-21 (calc); Appendix 11C (pH)	Table 11-21 (calc); Appendix 11C (pH)	Table 11-21 (calc); Appendix 11C (pH)	Table 11-21 (calc); Appendix 11C (pH)
pH	S.U.	7.2	1.3	6.6	1.7	4.8	1.9
Alkalinity	mg/L $CaCO_3$	65.9	51.0	18.5	16.4	9.9	14.1
Hardness	mg/L $CaCO_3$	74.0	88.1	59.2	51.9	21.9	23.1
Cl	mg/L	0.53	0.11	0.52	0.01	0.91	0.91
F	mg/L	0.06	0.09	0.12	0.12	0.11	0.16
SO_4	mg/L	28.0	83.8	60.8	68.4	51.9	52.0
Ag	mg/L	0.000011	0.000003	0.000027	0.000044	0.000019	0.000013
Al	mg/L	0.08	0.21	0.32	0.85	0.38	0.58
As	mg/L	0.0027	0.0042	0.0015	0.0018	0.0080	0.0189
B	mg/L	0.0177	0.0122	0.0159	0.0085	0.0125	0.0052
Ba	mg/L	0.0572	0.0824	0.0136	0.0087	0.0045	0.0056
Be	mg/L	0.0003	0.0005	0.0003	0.0003	0.0006	0.0006
Bi	mg/L	0.0005	0.0002	0.0007	0.0004	0.0006	0.0003
Ca	mg/L	21.3	31.6	12.7	8.9	6.3	5.3
Cd	mg/L	0.0002	0.0006	0.0004	0.0007	0.0032	0.0083
Co	mg/L	0.0039	0.0157	0.0070	0.0146	0.0097	0.0120
Cr	mg/L	0.0006	0.0002	0.0007	0.0004	0.0016	0.0023
Cu	mg/L	0.0032	0.0061	1.5989	3.2469	1.4162	2.1609
Fe	mg/L	0.140	0.484	1.671	6.042	10.195	16.051
Hg	mg/L	0.000010	0.000001	0.000011	0.000002	0.000010	0.000001
K	mg/L	1.85	2.24	1.41	0.72	0.96	0.69
Mg	mg/L	5.06	7.49	6.69	8.68	1.50	3.40
Mn	mg/L	0.1015	0.3990	0.7289	1.5653	0.3386	1.0745
Mo	mg/L	0.0063	0.0138	0.0018	0.0018	0.0043	0.0070
Na	mg/L	7.21	12.46	2.05	0.03	2.07	0.06
Ni	mg/L	0.0044	0.0165	0.0068	0.0143	0.0105	0.0168
Pb	mg/L	0.0001	0.0002	0.0002	0.0003	0.0004	0.0004
Sb	mg/L	0.0021	0.0019	0.0031	0.0018	0.0008	0.0018
Se	mg/L	0.0019	0.0020	0.0038	0.0057	0.0032	0.0024
Sn	mg/L	0.0013	0.0015	0.0001	0.0001	0.0019	0.0022
Tl	mg/L	0.00007	0.00003	0.00041	0.00098	0.00009	0.00010
V	mg/L	0.0018	0.0022	0.0007	0.0004	0.0024	0.0056
Zn	mg/L	0.0159	0.0500	0.0556	0.1080	0.4786	1.3618

The pre-Tertiary rocks show a range of responses in the humidity-cell tests as reflected by the significant standard deviations associated with their mean leachate concentrations (Table 4). The leachates from the pre-Tertiary rocks are characterized by neutral to acidic pH values. As expected from the role of pyrite oxidation in acid generation, the samples that generated the lowest pH values had the higher sulfate concentrations and lower alkalinity values. For example, the mean pH for humidity-cell leachates for Pebble East was 4.8 ± 1.9 compared to 6.6 ± 1.7 for Pebble West, presumably reflecting the higher grade and pyrite content of Pebble East. The pH of the samples correlated negatively with the alkalinity of the leachates. Copper concentrations generally correlate with sulfate concentrations and low pH, as would be expected from the higher solubility of metals with acidic pH conditions. The mean concentrations of copper in humidity-cell leachates from both Pebble West and Pebble East were high compared to other metals and exceeded 1 mg/L. The mean zinc concentration reached 0.5 mg/L. In contrast, the highest mean molybdenum concentration was less than 0.005 mg/L and the highest mean arsenic concentration was 0.008 mg/L. The high standard deviations associated with all parameters in the leachate chemistry from pre-Tertiary waste-rock types underscore the challenges associated with predicting waste-rock seepage chemistry with a high level of confidence. At an operating mine, the drainage from waste-rock piles will be a mixture of direct leachates from the waste rock and local ambient surface water and precipitation. The relative proportion of these sources will depend upon local climatic conditions, the natural topography, alterations to the natural topography made during mine construction, and engineering controls put in place during mine construction to manage surface water. The range of potential compositions of seepage is shown in Figure 7.

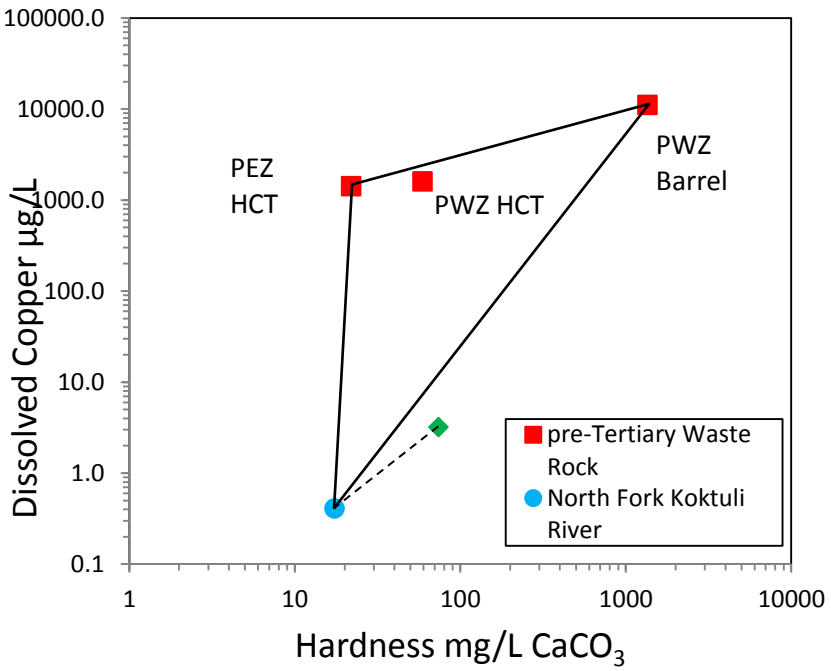

Figure 7. Dissolved copper concentrations and water hardness values for various potential end-member waters around the Pebble site in the Bristol Bay watershed associated with waste-rock piles. The humidity-cell test concentrations are from Table 4. The barrel-test results and the mean concentration for the North Fork of the Koktuli River are from Pebble Partnership (2011). The triangle represents the range of potential compositions that could be expected for seepage from Pebble West and Pebble East waste rock piles and the dashed line represents the range of potential compositions that could be expected from piles of Tertiary waste rock (see text). Abbreviations: PWZ, Pebble West Zone; PEZ, Pebble East Zone; HCT, Humidity-Cell Test.

The humidity-cell test results for the Tertiary volcanic rocks yielded more coherent results than did the pre-Tertiary rocks discussed above. Invariably, the humidity-cell test results show no ability to generate acid with all pH values ranging between 7 and 9 with a mean pH 7.2 ± 1.3. Sulfate concentrations generally range between 1 and 100 mg/L with a mean concentration of 28.0 mg/L, but the lack of correlation with pH suggests that the resulting sulfate may be derived from benign sulfate minerals rather than acid-generating iron sulfide minerals. Copper concentrations were low and generally correlated with sulfate concentrations.

Tailings

Mill tailings are the waste products from froth flotation, a process used to produce concentrates of economic minerals. The specific minerals separated greatly influence the character of the waste material. For porphyry copper deposits, it is typical to separate the copper-sulfide minerals [chalcopyrite ($CuFeS_2$) and bornite (Cu_5FeS_4)] as a copper concentrate, and the molybdenum-sulfide mineral, molybdenite (MoS_2) as a molybdenum concentrate (Fuerstenau and others, 2007). Gold commonly is associated with the copper sulfide minerals or pyrite. The gold associated with the copper concentrate will be recovered during smelting, typically conducted off-site. Gold associated with pyrite will require additional processing commonly on-site, as described above, to recover the gold. Thus, pyrite, the main source of acid-mine drainage, can be disposed with the tailings or it can be separated as a concentrate to either recover gold or to more effectively manage acid-generation risks. Therefore, the acid-generating potential and mobility of trace metals will be affected by whether or not pyrite is separated from tailings prior to disposal.

A greater number of environmental risks are associated with tailings due to their finer grain size compared to waste rock. Like waste rock, tailings can weather and the associated leachate can contaminate surface water and groundwater (Stollenwerk, 1994; Brown and others, 1998; Khorasanipour and others, 2011). Furthermore, because of the sand to silt size grains, tailings are prone to be transported by waters, especially in the case of tailings dam failure, and wind. Thus, they present additional potential risks to aquatic organisms through sediment contamination.

A compilation of geochemical analyses of “pristine”, unoxidized tailings from porphyry copper deposits is presented in Table 5. These data include analyses of tailings from the Aitik mine, Sweden (R. Seal, unpublished data), the El Teniente mine, Chile (Smuda and others, 2008; Dold and Fontboté, 2001), the Andina mine, Chile (Dold and Fontboté, 2001), the El Salvador mine, Chile (Dold and Fontboté, 2001), and the Sarcheshmeh mine, Iran (Khorasanipour and others, 2011). It is important to note that none of these tailings had a pyrite concentrate removed.

A summary of the geochemistry of tailings derived from metallurgical testing of drill core from the Pebble deposit is summarized in Table 6 from the PLP Environmental Baseline Document (Pebble Partnership, 2011). That report presents data from three sample sets, 2004, 2005, and 2008, which were used in the humidity-cell tests described below. The 2004 and 2005 samples were from Pebble West. The 2008 samples were from Pebble West and Pebble East. The analyses for all sets included acid-base accounting analyses. The analyses for the 2004 and 2005 samples focused on a more restricted group of analytes, limited mostly to elements for which regulatory guidance exists (Ag, As, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Sb, Se, Tl, and Zn). The analyses for the 2008 samples included a larger group of analytes (Ag, Al, As, Au, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Fe, Ga, Ge, Hf, Hg, In, K, La, Li, Mg, Mn, Mo, Na, Nb, Ni, P, Pb, Rb, Re, S, Sb, Sc, Se, Sn, Sr, Ta, Te, Th, Ti, Tl, U, V, W, Y, Zn, and Zr. The table includes average values, the standard deviation for the average, and the low and high values. For the entire dataset, paste pH values are near neutral, ranging from 6.6 to 8.9. The NP/AP ratio ranges from 0.1 to 9.0, corresponding to probably acidic drainage generating values (PAG; net acidic) to not probably acidic drainage generating (non-PAG; net alkaline), with the average being 2.7 (non-PAG; net alkaline). None of

Table 5. Geochemical composition of porphyry copper tailing samples from the literature and unpublished USGS studies.

Mine	Unit	Aitik	El Teniente	El Teniente	Cauquenes-Teniente	Piquenes-Andina	El Salvador	Sarcheshmeh
Country		Sweden	Chile	Chile	Chile	Chile	Chile	Iran
Sample No.		Aitik 1	Channel average	Sediment average	T1 average	A2 average	E2 average	S6/S7 average
Source		1	2	2	3	3	3	4
Al_2O_3	%	15.65						
CaO	%	3.425						
Fe_2O_3	%	10.3						
K_2O	%	4.775						
MgO	%	2.185						
MnO	%	0.32						
Na_2O	%	2.36						
P_2O_5	%	0.64						
SiO_2	%	54.4						
TiO_2	%	0.74						
As	mg/kg	3.50	33.0	36.0	92.9	62.0	136.3	18.5
Ba	mg/kg	930.5	382	384	470.3	721.3	418.3	
Be	mg/kg	1.55						
Bi	mg/kg	1.505						
Cd	mg/kg	<0.01						
Co	mg/kg	61.45						27.6
Cr	mg/kg	20	67	64	29.4	14.4	8.5	53
Cu	mg/kg	478	1035	921	3037	2515.2	5091.2	1205
Mn	mg/kg	2165	358	376	334.5	592.3	67.3	700.5
Mo	mg/kg	11.75	89	101	108.5	53	234.6	96.7
Ni	mg/kg	14.15	23	23				40
Pb	mg/kg	9.85			20	36.9	22.5	46.0
Sb	mg/kg	2.77						
U	mg/kg	4.45						
V	mg/kg	155.5	243	230	208.9	125.5	139.9	
Zn	mg/kg	74	62	58	92.94	208.98	42.9	210
S	%	2.64	3.62	3.43				
Carbonate C	%	0.01						
Total C	%	0.01						
LOI	%	3.55						
NNP	kg $CaCO_3$/t	-74.3			-18.2	-28.3	-101.6	

Sources: 1. This study; 2. Smuda and others (2008); 3. Dold and Fonboté (2001); 4. Khorasanipour and others (2011)

the tailing samples presented in Table 5 had pyrite separated; all of their NNP values are negative, indicating a net acidic character, unlike the Pebble tailings, which had pyrite removed. Otherwise, the overall chemistry of the tailing samples in Tables 5 and 6 compares favorably in terms of the range of values. It is worth noting that the 2005 LT C2 Combined Pre-Cleaner Tailings sample (Table 11-46 of the Pebble Project Environmental Baseline Document) has a copper concentration (2,050 mg/kg) that is 68 percent of the 0.3 percent cut-off grade, a molybdenum concentration (188 mg/kg) that 80 percent of the published resource molybdenum grade, and one of the lowest NNP values (-30 kg$CaCO_3$/t). Further metallurgical testing presumably will seek to improve copper and

molybdenum recovery, which also will improve the separation of sulfide minerals and increase NNP of the resulting tailings.

Table 6. Geochemical composition of test tailings samples from the Pebble deposit from the Pebble Project Environmental Baseline Document. Summary statistics include all samples presented in Tables 11-46 and 11-47 in Pebble Partnership (2011).

Parameter	Units	Average	Standard Deviation	Low	High
Ag	mg/kg	0.7	0.5	0.23	2.17
As	mg/kg	25.2	31.6	4.2	169
Ba	mg/kg	30.0	10.6	20	50
Be	mg/kg	0.3	0.1	0.18	0.64
Bi	mg/kg	0.6	0.5	0.2	1.98
Cd	mg/kg	0.1	0.1	0.03	0.4
Co	mg/kg	8.1	10.2	2.2	45.9
Cr	mg/kg	149.9	177.3	6	748
Cu	mg/kg	682.9	414.0	142	2050
Hg	mg/kg	0.1	0.1	< 0.01	0.56
Mn	mg/kg	359.9	201.4	84	880
Mo	mg/kg	51.9	35.1	10.5	188
Ni	mg/kg	67.7	111.6	6.3	452
Pb	mg/kg	15.0	16.6	3.3	88.4
Sb	mg/kg	1.0	1.0	0.2	5.41
Se	mg/kg	1.8	2.0	0.4	8.8
Tl	mg/kg	0.3	0.2	0.07	1.2
U	mg/kg	0.4	0.2	0.17	0.87
V	mg/kg	87.3	36.0	36	149
Zn	mg/kg	87.4	66.3	29	267
Paste pH	Standard Unit	8.2	0.4	6.6	8.9
Total S	%	0.5	0.9	0.09	4.19
Sulfate	%	0.0	0.0	-0.01	0.2
Sulfide	%	0.5	0.9	0.05	4.12
AP	kg $CaCO_3$/t	14.2	27.8	1.56	128.8
TIC	%	0.3	0.2	0.05	0.75
TIC	kg $CaCO_3$/t	22.6	15.5	4.5	62.5
NP (Modified)	kg $CaCO_3$/t	13.5	6.9	4.6	25.9
NP/AP	ratio	2.7	1.9	0.1	9
NNP	kg $CaCO_3$/t	-0.5	27.2	-110.2	22.4

Additional insights into aquatic risks associated with tailings can be found in case studies from mines. The geochemical characteristics of tailings seepage have been investigated by several studies. Smuda and others

(2008) investigated the geochemical environment associated with tailings at the El Teniente porphyry copper deposit, Chile. They found a range of values for various water-quality parameters associated with the tailings pond. These parameters included pH (7.2-10.2), sulfate (1556-5574 mg/L), Fe (1.44-8.59 mg/L), Al (below detection - 0.886 mg/L), Mn (0.001-20.1 mg/L), Ni (0.008-0.393 mg/L), Cu (0.003-0.250 mg/L), Zn (0.007-130 mg/L), Mo (0.033-13.2 mg/L), and As (below detection – 0.345 mg/L). Khorasanipour and others (2011) studied the geochemical environment associated with tailings at the Sarcheshmeh mine, Iran. They too found a range of values for water-quality parameters such as pH (3.6-7.9),sulfate (1348-4479 mg/L), Fe (<0.01-19.3 mg/L), Al (<0.5-154 mg/L), Mn (5.6-73.7 mg/L), Ni (0.088-1.74 mg/L), Cu (< 0.002-149.9 mg/L), Zn (0.094-20.3 mg/L), Mo (0.027-2.9 mg/L), and As (< 0.005-0.04 mg/L).

Morin and Hutt (2001) compared predictions for tailing leachate chemistry with actual drainage chemistry at the Bell mine in British Columbia on the basis of samples collected seven years after closure. The predictions indicated that drainage from the tailing piles would start at near neutral pH conditions, but would turn acidic over the course of several decades. Their post-closure sampling results indicated that acid generation is roughly 100 times less than predicted. The authors attributed this discrepancy to basing prediction on an insufficient number of humidity-cell tests and incorrect assumptions about the rate of sulfide oxidation. Weibel and others (2011) found similar results in studies of a porphyry copper mine in Chile.

As with the waste rock at Pebble, the best insights into the potential behavior of mill tailings come from the humidity-cell tests being conducted by the Pebble Limited Partnership and its contractors (Pebble Partnership, 2011). The Pebble Partnership initiated two sets of humidity-cell tests on tailings derived from preliminary metallurgical testing: one set in 2005 and one set in 2008 (Pebble Partnership, 2011). Humidity-cell tests represent one of the best predictors of long-term weathering of tailings in an aerobic environment (Price, 2009). The test conditions are most representative of unsaturated tailings exposed at the surface of a pile. The geochemical environment found at depth in the saturated zone is typically quite different (Blowes and others, 2003). The 2005 tailings samples originated from a relatively simple set of metallurgical methods, whereas the 2008 samples originated from a greater variety of metallurgical processing methods. The humidity-cell tests for the tailings samples were conducted using standard procedures, as described above for the waste-rock samples (Price, 2009). However, the grain size of the tailings is well below the 6 mm maximum size of waste-rock samples, which means that the tailings should be more reactive than were the waste-rock samples in humidity-cell tests. The results included the same set of parameters as with the waste-rock testing. As for the waste-rock samples, the following discussion focuses on pH, sulfate, copper, zinc, molybdenum, and arsenic.

The humidity-cell results were similar for both the 2005 and 2008 sets of tailings (Pebble Partnership, 2011). Both sets had pH values ranging between 7 and 8.5 in experiments lasting up to 5 years for the 2005 samples and for more than one year for the 2008 samples (Table 7). Sulfate concentrations for both sets generally are below 40 mg/L after the initial flush of soluble sulfate salts. The mean sulfate release concentration was 17.4 ± 8.0 mg/L. The mean copper (5.3 ± 2.2 µg/L), and zinc (3.2 ± 1.7 µg/L) concentrations were less than those from the waste-rock samples, whereas the molybdenum (33.5 ± 23.7 µg/L), and arsenic (5.5 ± 8.4 µg/L) concentrations were higher (Table 4).

The chemical composition of the pond on top of the tailing impoundment is difficult to estimate, but bounds can be placed on its composition. During mine operation, the water should represent a mixture of the supernatant solution from the mill that is pumped with the tailings slurry to the impoundment, solutes derived from aerobic leaching of the tailings material, which can be limited by the average humidity-cell results from tailings, and ambient surface water and precipitation, which can be approximated by the mean composition of the North Fork of the Koktuli River. The range of potential compositions is shown in Figure 8 by the triangle, which limits the range from these three sources in terms of dissolved copper concentration and water hardness. The supernatant solution has the highest copper concentration and water hardness of the three end members.

Table 7. Summary of geochemical results from humidity-cell tests on tailing samples and the supernatant solution from metallurgical testing conducted by the Pebble Partnership (2011)

Parameter	Units	Tailings Humidity Cell		Supernatant	
		Average	Standard Deviation	Average	Standard Deviation
Pebble Partnership (2011) Source		Table 11-49 (calc); Appendix 11L (pH)	Table 11-49 (calc); Appendix 11L (pH)	Table 11-48	Table 11-48
pH	S.U.	7.8	0.2	7.9	0.3
Alkalinity	mg/L $CaCO_3$	59.7	15.5	74.8	20.4
Hardness	mg/L $CaCO_3$	66.8	13.6	322.8	254.8
Cl	mg/L	0.52	0.08	nr	nr
F	mg/L	0.451	0.440	nr	nr
SO_4	mg/L	17.4	8.0	318.7	372.1
Thiosalts (S_2O_3)	mg/L	nr	nr	44.1	156.1
Ag	mg/L	0.00001	0.00000	0.00002	0.00025
Al	mg/L	0.02	0.03	0.07	0.08
As	mg/L	0.0055	0.0084	0.0172	0.0212
B	mg/L	0.0107	0.0010	nr	nr
Ba	mg/L	0.0092	0.0050	nr	nr
Be	mg/L	0.0002	0.0000	nr	nr
Bi	mg/L	0.0005	0.0000	nr	nr
Ca	mg/L	22.6	3.9	116.0	101.2
Cd	mg/L	0.00001	0.00000	-0.00008	0.00018
Co	mg/L	0.0002	0.0002	-0.0001	0.0004
Cr	mg/L	0.0005	0.0000	-0.0010	0.0012
Cu	mg/L	0.0053	0.0022	0.0078	0.0049
Fe	mg/L	0.03	0.00	0.02	0.32
Hg	mg/L	0.000010	0.000000	-0.000037	0.000103
K	mg/L	4.02	1.69	25.95	8.16
Mg	mg/L	2.55	2.07	8.00	5.53
Mn	mg/L	0.0441	0.0224	0.0719	0.0631
Mo	mg/L	0.0335	0.0237	0.0697	0.0560
Na	mg/L	2.10	0.26	43.78	132.40
Ni	mg/L	0.0005	0.0001	-0.0008	0.0018
Pb	mg/L	0.00006	0.00001	0.00023	0.00062
Sb	mg/L	0.0018	0.0017	0.0060	0.0058
Se	mg/L	0.0015	0.0006	0.0076	0.0062
Sn	mg/L	0.0029	0.0040	nr	nr
Tl	mg/L	0.00005	0.00000	0.00002	0.00022
V	mg/L	0.0008	0.0008	nr	nr
Zn	mg/L	0.0032	0.0017	0.0043	0.0080

nr: not reported

The composition of water potentially seeping from the base of tailing piles is more problematic to estimate. At depth in the saturated zone in tailing piles, dissolved oxygen is rapidly removed by reaction with trace amounts of sulfide minerals, which limits the ability to generate acid during further interaction with tailings material. In these acid-limited environments, silicate minerals such as feldspars and trace amounts of carbonate minerals can effectively neutralize acid and restrict the ability of groundwater to dissolve additional metals and other trace elements (Blowes and others, 2003). Under these conditions, the chemical composition of seepage from a tailings pile should fall along the join between the average humidity-cell test composition and ambient surface water and groundwater (Figure 8).

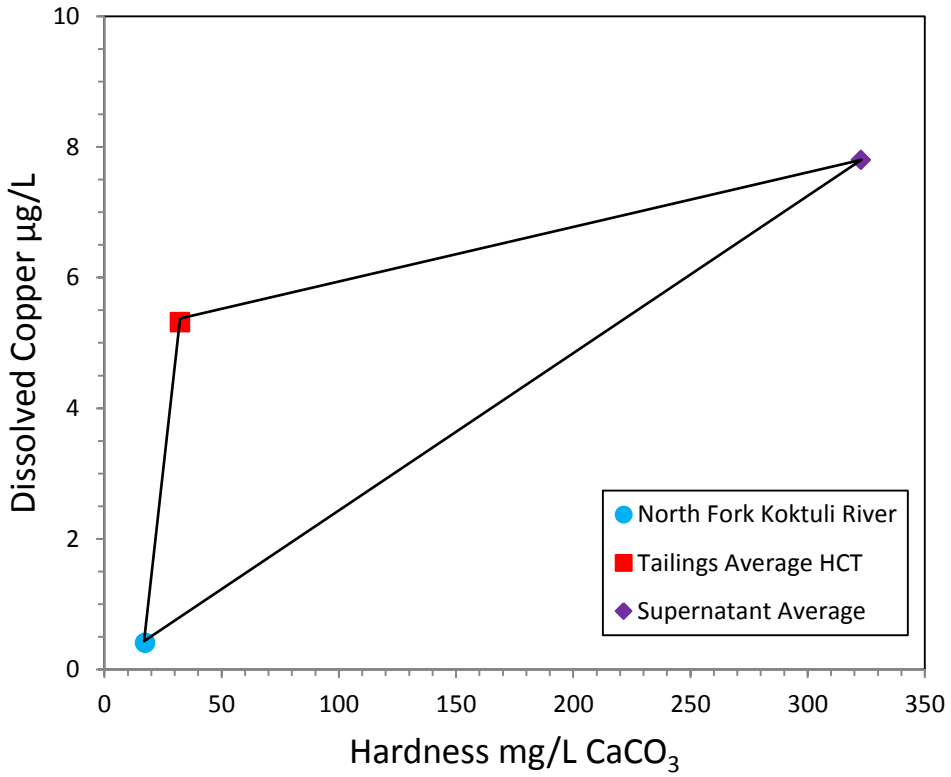

Figure 8. Dissolved copper concentrations and water hardness values for various potential end-member waters around the Pebble site in the Bristol Bay watershed associated with a tailings impoundment. The humidity-cell test concentrations are from Table 7. The mean concentrations for the North Fork of the Koktuli River are from Pebble Partnership (2011). The triangle represents the range of potential compositions that could be expected for a tailing pond during mine operation; after closure, once ore processing has ceased, the join between the North Fork and the Tailings Average HCT compositions may be more representative of the range of potential compositions (see text). Abbreviations: HCT, Humidity-Cell Test.

Copper Concentrate

Limited data are available on the geochemistry of copper concentrates from porphyry copper deposits. The geochemical analysis by USGS laboratories of a single sample of a copper concentrate from the Aitik porphyry copper deposit is presented in Table 8. X-ray diffraction analysis indicates that the sample is dominated by

chalcopyrite with trace amounts of pyrite, quartz, and possibly molybdenite. The ideal composition of chalcopyrite is 34.6 weight percent Cu, 30.4 weight percent Fe, and 34.9 weight percent S. For the analysis presented in Table 8, the Cu concentration is above the upper detection limit. However, the analyzed concentration of S (33.4 wt. %) indicates that the sample is greater than 95 percent chalcopyrite, whereas that of Fe (25.8 wt. %) indicates approximately 85 percent chalcopyrite. The most notable trace elements in this concentrate are Zn (2190 mg/kg), presumably reflecting the presence of minor sphalerite, Mo (1100 mg/kg), presumably reflecting the presence of molybdenite, and Mn (346 mg/kg), likely hosted by sphalerite or traces of the Fe-carbonate mineral siderite.

Table 8. Geochemical analysis of the copper concentrate (Aitik 2) from the Aitik porphyry copper mine, Sweden

Element	Units	Concentration
Al	%	0.98
Ca	%	0.32
Fe	%	25.8
K	%	0.49
Mg	%	0.11
Na	%	0.19
Ti	%	0.05
Ag	mg/kg	>10
As	mg/kg	12
Ba	mg/kg	59
Bi	mg/kg	44.9
Cd	mg/kg	2.4
Co	mg/kg	53.9
Cu	mg/kg	>10000
Ga	mg/kg	0.88
In	mg/kg	2.35
Mn	mg/kg	345
Mo	mg/kg	1100
Ni	mg/kg	72.1
Pb	mg/kg	64.9
Sb	mg/kg	43.4
Te	mg/kg	4.1
Th	mg/kg	1.5
Tl	mg/kg	0.2
U	mg/kg	2.2
V	mg/kg	23
Zn	mg/kg	2190
S	%	33.4

The solution chemistry associated with the transport of concentrate as a slurry in a pipeline can be assessed by conducting leaching experiments on the Aitik copper concentrate sample described above, which is mineralogically similar to copper concentrates from most porphyry copper mines. In flotation circuits, chalcopyrite is not especially sensitive to pH, but pH may be adjusted to alkaline values to separate molybdenite or pyrite (Fuerstenau and others, 2007).

The leachability of elements from copper concentrate was evaluated using the *Synthetic Precipitation Leaching Procedure* (USEPA Method 1312), and a modification of this protocol. The standard procedure reacts a sample in a 20:1 (solution: sample) ratio with a weak acidic solution (pH 5), made of a mixture of sulfuric and nitric acids, under continuous agitation for 18 hours, after which the solution is sampled. Additional leaching experiments were conducted in which the copper concentrate sample was leached following the same procedure except that the starting leaching solution was either distilled water + NaOH solutions (pH 6, 7, 8, 9), or distilled water + Na_2CO_3 solutions (pH 7, 9) adjusted to various starting pH values. The purpose of these experiments was to evaluate the range of starting pH values that may be associated with a copper-concentrate slurry discharged from a mill to a pipeline.

The results of the leaching experiments on the copper concentrate are presented in Table 9. Results from a copper tailings sample from Aitik are also presented in Table 9. One of the most striking features of these experiments using the copper concentrate is that regardless of the starting pH (pH = 5 to 9), the final pH after 18 hours for all experiments ended up between 4.1 and 4.2. Equally striking was the fact that dissolved copper concentrations in the leachate ranged between 15,300 and 16,800 µg/L, dissolved iron concentrations ranged between 5,480 and 10,200 µg/L, and dissolved sulfate ranged between 183.7 and 208.8 mg/L.

Summary

The Pebble deposit in the Bristol Bay watershed, southwestern Alaska, shares many geologic attributes with typical porphyry copper deposits throughout the world. These features include: (1) its spatial association with coeval granitic intrusions; (2) its large tonnage of ore and its low grade, although the size of Pebble places it in the upper 5 percent of porphyry copper deposits globally; (3) the association of copper, molybdenum, and gold; (4) the style of mineralization as veinlets, stockworks, and disseminations with igneous and sedimentary host rocks; and (5) its zoned ore-mineral and alteration assemblages. From an environmental perspective, the acid-generating potential of Pebble is similar to that found at other porphyry copper deposits: waste rock and tailings span the range from potentially acidic drainage generating to non-potentially acidic drainage generating due to the low contents of pyrite and other sulfide minerals as potential sources of acid, and the presence of silicate minerals such as feldspars and trace amounts of carbonate minerals to neutralize acid. Humidity-cell tests by Pebble Partnership (2011) indicate that drainage associated with pre-Tertiary waste rocks is likely to have higher concentrations of solutes and lower pH than drainage associated with mine tailings. Solutions associated with a copper concentrate slurry are likely to be weakly acidic and have high concentrations of dissolved copper and zinc.

Table 9. Geochemical analyses of dissolved constituents (< 0.45 µm) in leachates from tailings and copper concentrate from the Aitik Mine, Sweden, using USEPA Method 1312 and a modified leaching method.

Field No.	**Units**	**Tailings**	**Copper Concentrate**						
Base (Acid)		WSP*	WSP*	NaOH	NaOH	NaOH	NaOH	Na_2CO_3	Na_2CO_3
Starting pH	S.U.	5	5	6	7	8	9	7	9
Final pH	S.U.	7.3	4.2	4.2	4.2	4.2	4.1	4.2	4.2
Spec. Cond.	µS/cm	133	349	362	350	345	372	340	340
DO	mg/L	10							
T	°C	22.6							
Alkalinity	mg/L $CaCO_3$	9.3	0	0	0	0	0	0	0
Ag	µg/L	<1	<10	<10	<10	<10	<10	<10	<10
Al	µg/L	158	1,910	1,820	1,790	1,770	1,850	1,950	1,870
As	µg/L	<1	<10	<10	<10	<10	<10	<10	<10
Ba	µg/L	50.5	38.6	39.2	40	40.7	38.5	37.9	36.2
Ca	mg/L	16	30	28.9	29	28.5	28.7	28.2	28.3
Cd	µg/L	<0.02	6.3	6	5.9	5.9	6	6.3	6
Co	µg/L	0.43	157	151	152	151	151	154	152
Cr	µg/L	<1	<1	<1	<1	<1	<1	<1	<1
Cu	µg/L	0.8	16,500	16,300	15,400	15,300	16,800	16,300	15,600
Fe	µg/L	<50	7,940	9,190	7,440	7,070	10,200	5,560	5,480
K	mg/L	2.15	3.4	3.7	3.4	3.4	3.8	3	3.1
Mg	mg/L	0.38	5.5	5.2	5.3	5.3	5.2	5.5	5.4
Mn	µg/L	20	931	887	891	880	883	918	899
Mo	ug/L	< 2	< 20	< 20	< 20	< 20	< 20	< 20	< 20
Na	mg/L	4.67	0.41	0.52	0.84	0.89	1	0.87	1.5
Ni	µg/L	<0.4	634	607	613	609	607	620	612
Pb	µg/L	<0.05	6.16	6.93	6.15	6.08	7.92	5.36	5.55
Sb	µg/L	0.47	17.4	13.4	16.6	16.2	14.7	16.8	16.6
Se	µg/L	< 1	<10	<10	<10	<10	<10	<10	<10
SiO_2	mg/L	1.8	<2	<2	<2	<2	<2	<2	<2
U	µg/L	< 0.1	33.7	33.8	31.2	31.9	34	34.8	33
Zn	µg/L	0.6	2,040	1,920	1,950	1,940	1,940	2,040	1,980
Cl	mg/L	0.8	2.6	2.6	2.8	2.6	2.6	2.6	2.5
F	mg/L	0.2	1.4	1.5	1.5	1.5	1.5	1.6	1.5
NO_3	mg/L	0.7	0.4	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08
SO_4	mg/L	43.6	192.6	200.8	191.4	185.1	208.8	183.7	184.5

*WSP: Mixture of H_2SO_4 and HNO_3 with pH = 5.0 in accordance with EPA Method 1312.

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