

# **Comparison of geochemical characteristics of modern-style mine wastes from a variety of mineral deposit types for insights into environmental challenges associated with future mining<sup>1</sup>**

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## **ABSTRACT**

Geoenvironmental mineral-deposit models based on characteristics of modern-style mine wastes provide a means of anticipating potential challenges associated with ore deposits at every stage throughout the life cycle of a mine especially exploration and permitting. These models present a means of quantitatively comparing, at least in a relative sense, the environmental challenges associated with specific deposit types in terms of potential acid generation, and ecosystem and human-health effects associated with metals and related compounds. Acid-base accounting and various leaching protocols normalized to relevant environmental standards are useful in this regard. However, variations in behavior due to climate must be evaluated on a local or regional basis. During exploration, geoenvironmental models highlight those deposit types that may pose significant challenges, the mitigation of which may affect profitability. During permitting, models can focus attention on the highest priority issues most likely to be associated with a deposit type (acid generation, potentially toxic elements in various media such as ground water, surface water, and dusts), and place less-likely concerns in an appropriate perspective.

Additional Key Words: acid-base accounting, arsenic, cadmium, copper, lead, zinc

## **INTRODUCTION**

Environmental challenges are an inescapable part of modern mining and they affect multiple facets of the viability of all potential mines including their permitting, profitability, and successful closure. Geoenvironmental models based on genetic mineral-deposit classifications provide a means of anticipating potential challenges associated with ore deposits at every stage throughout the life cycle of a mine especially exploration and permitting. However, perspectives based on the characteristics of historical, abandoned mines may not provide an accurate prediction of the environmental behavior of current and future mines because commodities of economic interest, mining methods, and ore processing methods change due to economic and technological motivations. For example, studies of abandoned mines that include mine wastes produced from modern-style mining and ore-processing practices as well as from historical mine wastes derived from practices no longer used demonstrate that historical mine sites may not be representative of modern operations (Seal et al., 2001). For example, the Elizabeth mine includes modern-style tailings produced from a copper flotation circuit that ceased operation in 1958, and historical waste-rock piles from the early 19<sup>th</sup> century resulting from copperas production and hand sorting of copper ore for smelting on site. Copperas ( $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ ) is a commodity of

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<sup>1</sup> Paper presented at Securing the Future and 8th ICARD, June 23-26, 2009, Skellefteå, Sweden.

limited modern use that is no longer produced by the methods used at Elizabeth. Seeps draining from the base of the historical waste-rock piles have low pH and high concentrations of Fe and Cu, among other metals, and sulfate. In contrast, seeps draining from the base of the modern-style tailings piles have near neutral pH and high concentrations of Fe and sulfate, but low concentrations of Cu and other metals. Because of these differences in the environmental behavior of historical mine waste and modern-style mine waste, historical abandoned mines probably do not represent reasonable analogues for the environmental behavior of future mines.

A means of quantitatively comparing the environmental characteristics of various deposit types would be useful for identifying potentially problematic elements from the perspective of human and ecosystem health. Such insights can be valuable to a wide audience focused on all steps of mine development including exploration, permitting, production, and closure. This paper presents preliminary results from an approach being developed by the US Geological Survey (USGS) to evaluate potential environmental challenges associated with future mining of undiscovered mineral resources. The approach is being designed to benefit all stakeholders, including land-use managers, regulators, the mining industry and its contractors, and the general public, by focusing attention on specific elements or compounds of concern on a deposit type by deposit type basis. It concentrates on the geochemical characteristics of modern-style mine wastes. The geochemical characterization of the mine waste samples includes bulk mineralogy, bulk geochemistry, acid-base accounting, and a synthetic precipitation leaching procedure.

## **METHODS**

### **Samples**

Preliminary results are from a diverse suite of modern-style mine waste and are from a spectrum of deposits assembled to capture a variety of deposit types. These types span a range of mineralogical and geochemical compositions and a range of acid-generating potentials and reactivities during leaching experiments. “Modern-style” mine wastes are meant to include material, specifically flotation tailings and leach-pad wastes, from recent or current mines that produced wastes that are similar to modern operations. Waste rock is currently excluded because of the difficulty in getting a representative sample of coarse-grained material. The current suite of samples includes samples from the United States, Canada, and New Zealand. Deposit types include orogenic Au deposits (n = 5); low sulfidation epithermal deposits (n = 1), Kuroko-type massive sulfide deposits (n = 5), Besshi-type massive sulfide deposits (n = 2), sedimentary-exhalative Zn-Pb deposits (n = 1), carbonate-hosted Pb-Zn-Ag deposits (n = 4), ultramafic-hosted asbestos deposits (n = 4), magmatic Ni-Cu sulfide deposits (n = 4), porphyry Cu deposits (n = 1), and U deposits (n = 4). Some of the samples are Natural Resources Canada reference materials. Therefore, their grain sizes are smaller than typical mine waste because of grinding associated with preparation of the reference materials. All other samples were sieved to less than 2 mm.

### **Analytical Methods**

Samples were characterized by a variety of means. The mineralogy was determined by X-ray diffraction using a PANalytical X'Pert PRO automated powder diffractometer. The bulk geochemistry was determined by wavelength dispersive X-ray fluorescence spectroscopy (XRF), inductively coupled plasma-atomic emission spectrometry (ICP-AES), and inductively coupled plasma-mass spectrometry (ICP-MS). The acid-base accounting included paste pH, acid-generating potential (AP) based on total and sulfate sulfur, and neutralizing potential (NP) by the Old Lawrence Back Titration method. The leaching protocol was the synthetic precipitation leaching procedure (SPLP; USEPA Method 1312; USEPA, 1994) using a solution that approximates western United States precipitation (pH 5.0) at a solution-to-sample ratio of 1:20

(mass basis). Filtered (0.45 µm nitrocellulose filter) acidified splits of leachates were analyzed for cations by ICP-MS and ICP-AES and filtered splits for anions by ion chromatography (IC). Also, specific conductance and pH were measured using a YSI multi-parameter meter and alkalinity was determined by titration.

### **Interpretative Methods**

The bulk and leachate geochemical results provide useful information about the concentrations of various elements in these media, but more meaningful interpretation of the results can be obtained by comparing the concentrations in the two media to relevant environmental standards. The bulk geochemical data from the mine wastes can be compared to soil standards. The US Environmental Protection Agency (USEPA) lists a Preliminary Remediation Goal (PRG) for various contaminants in both end-use residential and industrial soils, which are used to assess human-health risks (USEPA, 2008). The leachate results can be compared either to drinking water standards or aquatic ecosystems standards. The USEPA and the World Health Organization (WHO) provide drinking water standards for a variety of trace element contaminants (USEPA, 2003; WHO, 2006). Both sets of standards are similar to one another, but the WHO covers more contaminants. The USEPA has both acute and chronic water-quality standards for the protection of aquatic ecosystems, many of which vary on the basis of water hardness (USEPA, 2006). Thus, the comparison of leachate data with environmental standards for these metals requires that a representative hardness value be chosen arbitrarily. For the purposes of this paper, a hardness value of 100 mg/L CaCO<sub>3</sub> was selected.

The comparison of the concentration of an element in a sample with an appropriate environmental standard is easily accomplished through the use of a hazard quotient (HQ), which is simply the ratio of the concentration of an element in the sample (C) to the environmental standard (S) or  $HQ = C/S$ . Thus, a quotient greater than unity can be interpreted as being potentially problematic, whereas one less than unity would not.

The acid-generating potential is considered in terms of a net-neutralization potential (NNP). The NNP is the difference between the NP and AP ( $NNP = NP - AP$ ) and is expressed as kilograms of CaCO<sub>3</sub> per tonne of waste material. Thus, a negative NNP represents a net potentially acid-generating material, whereas a positive NNP represents a net potentially acid-neutralizing material.

## **RESULTS AND DISCUSSION**

The comparison bulk mine-waste or leachate geochemical characteristics with relevant environmental standards provides useful insights for a given deposit type and among different deposit types. From the perspective of individual deposit types, this approach enables potentially problematic elements and their likely deleterious pathways to be identified. For example, Figure 1 illustrates these points for representative examples of three different deposit types: Kuroko-type volcanic-associated massive sulfide deposits, which are important economic sources of Zn, Pb, Cu, Ag, and Au, but are notorious for their high acid-generating potential (Seal and Hammarstrom, 2003); orogenic Au deposits, also known as “Mother Lode” or “shear-zone hosted” Au deposits, which are a major source of Au globally (Kerrich et al., 2000); and ultramafic-hosted asbestos deposits, which are the primary sources of chrysotile asbestos (Van Gosen, 2007), but may also represent a reasonable proxy for diamondiferous kimberlites. Hazard quotients based on the ratio of the concentrations of various elements in mine waste to USEPA residential soil PRGs, and the concentrations of various elements in leachate to WHO or USEPA drinking water standards, indicate which elements and pathways may pose significant mitigation or remediation challenges associated with the mining of these deposit types. Elements for which

regulatory guidance for soil and drinking water are available include As, Cd, Cu, Ni, Pb, Se, U, and Zn. For Kuroko-type massive sulfide deposits, Cu, Pb, and Zn in mine waste relative to soil guidelines are likely to present challenges as indicated by hazard quotients greater than one, whereas Cd, Pb, and Zn may pose problems in drinking water supplies around waste piles in the absence of mitigation or remediation measures (Figure 1a). Elements, such as As, Ni, Se, and U, are not likely to be concerns. For orogenic Au deposits, this approach highlights As as the primary element of concern in both mine waste relative to soil guidelines and associated waters with the other elements not likely to be problematic (Figure 1b). For ultramafic-hosted asbestos deposits, Ni and As are the only elements that are likely to warrant a significant level of scrutiny (Figure 1c).

Comparisons among deposit types on an element-by-element basis for various pathways of deleterious effects are useful for contrasting suites of elements that pose particular challenges for specific deposit types. Figure 2 presents results for three contrasting elements for three different pathways. The elements are: Zn, a micronutrient for humans, and to a lesser extent aquatic organisms; Cd, an element that is geochemically similar to Zn, but is toxic to all organisms; and As, an element that commonly forms oxyanions upon weathering and is toxic to all organisms. The pathways include human ingestion of mine-waste solids, human ingestion of water, and chronic exposure of aquatic ecosystems. For Zn, the deposit types that this approach identifies as consistently being potentially problematic by any pathway include sedimentary-exhalative massive sulfide deposits, Kuroko-type massive sulfide deposits, Besshi-type massive sulfide deposits, and carbonate replacement Pb-Zn-Ag deposits (Figure 2a). All of these deposit types are economic sources of Zn. The prominence of Zn as an environmental concern is a reflection of the importance of sphalerite in these deposit types. Potential risks to aquatic organisms are greater than those to humans via drinking water because of differences in the environmental standards, which reflect the fact that Zn is a micronutrient for humans, and less so for aquatic organisms. For deposit types for which Zn is an issue, the pathway of concern depends upon the acid-generating potential of the mine waste. Sedimentary-exhalative, Kuroko-type, and Besshi-type deposits all have significant acid-generating potential, whereas carbonate replacement deposits have significant acid-neutralizing potential. From the perspective of the hazard quotients, the aqueous phase is of greater concern for the high acid-generating potential deposits, whereas the solids are more problematic for the high acid-neutralizing mine wastes. This observation reflects the pH dependence of Zn mobility. With the exception of one

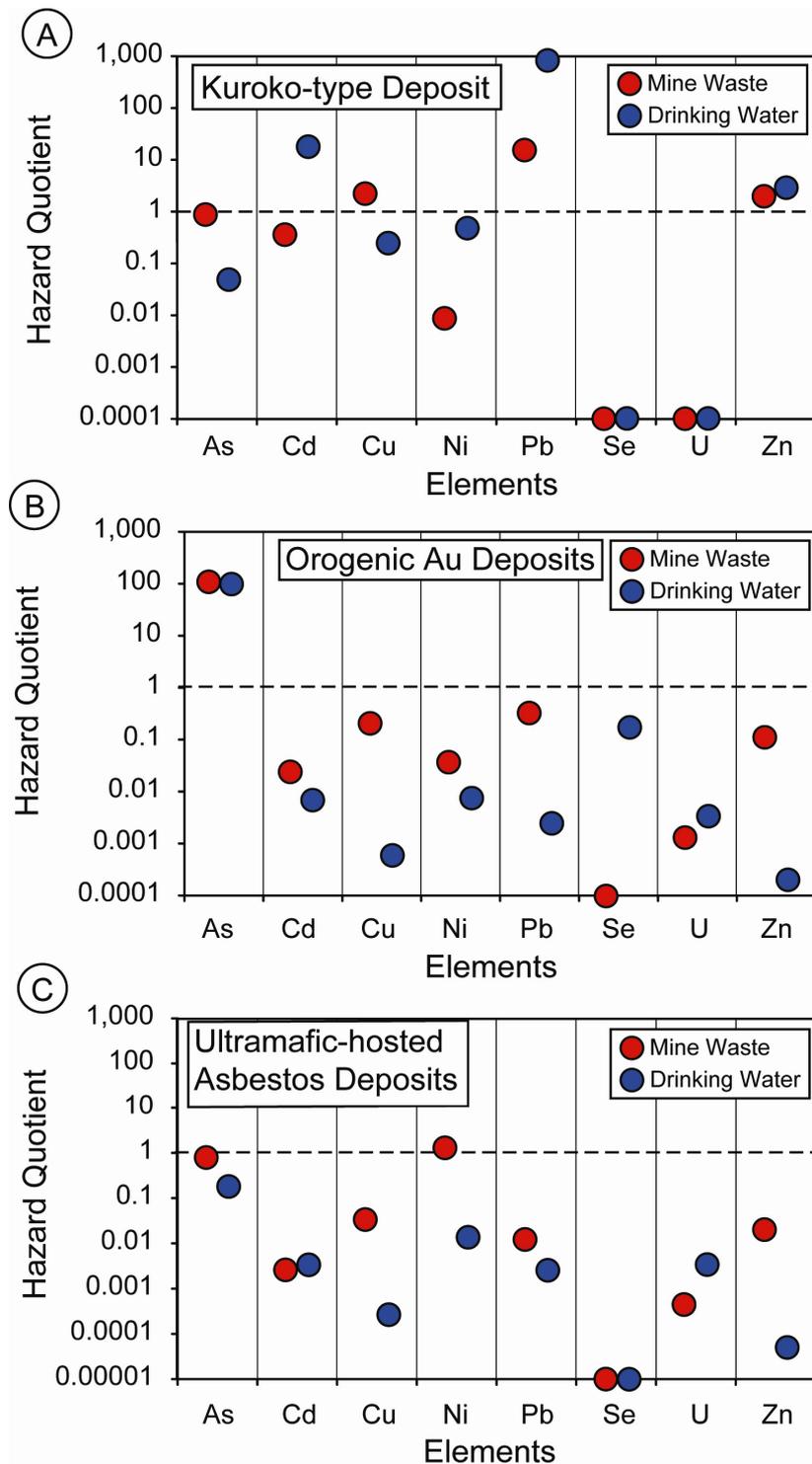


Figure 1. Hazard quotients for selected elements in mine wastes and leachates for representative samples from selected deposit types. The hazard quotients for mine waste solids are relative to USEPA residential soil PRGs (USEPA, 2008). The hazard quotients for SPLP leachates are relative to WHO (2006) drinking water standards, except for Zn, which is from USEPA (2003). Values above unity highlight elements that require greater scrutiny in mine planning. A. Kuroko-type massive sulfide deposits; B. Orogenic Au deposits; C. Ultramafic-hosted asbestos deposits.

anomalous sample from a magmatic Ni-Cu deposit, all other deposit types do not have Zn as a potentially significant environmental challenge. On a deposit type by deposit type basis, Cd is

identical to Zn despite being toxic to all organisms. However, the difference in the aqueous threat to humans and aquatic organisms is not as great for Cd as it is for Zn (Figure 2b).

In contrast, the geochemical affinities of As on a deposit type by deposit type basis are distinctly different than those for Zn and Cd (Figure 2c). Orogenic Au deposits, sedimentary-exhalative deposits, Kuroko-type massive sulfide deposits, carbonate replacement deposits, and ultramafic-hosted asbestos deposits potentially represent the greatest challenges with respect to As. Humans are the most vulnerable bioreceptor through ingestion of solids or drinking water. For orogenic Au deposits, solids and water are both pathways of greatest concern, whereas ingestion and inhalation of dusts are the dominant pathways of concern for the carbonate replacement and asbestos deposits. The environmental significance of As associated with these deposit types is a direct reflection of their mineralogy. Orogenic Au deposits commonly contain arsenian pyrite or arsenopyrite in minor, but important amounts. The carbonate replacement Pb-Zn-Ag deposits contain As-bearing sulfosalt minerals, and arsenide minerals can occur in ultramafic rocks in trace amounts.

The combination of hazard quotients for specific elements and specific pathways with acid-base accounting data for the mine waste provides additional information about potential challenges associated with future mining of undiscovered resources on a deposit type basis (Figure 3). A plot of net-neutralization potential (NNP) and the hazard quotient for the leachates relative to the chronic aquatic toxicity standard for Cu shows a crude negative correlation, which is consistent with increased mobility of Cu under acidic conditions (Figure 3a). Data from individual deposit types tend to cluster together, although some do more than others. Deposit types for which Cu is a commodity of economic interest tend to have higher hazard quotients for chronic Cu toxicity to aquatic ecosystems than for those deposit types for which Cu is not of economic interest. Likewise, those deposit types for which carbonate minerals are an important part of the host rock or alteration assemblage tend to have the higher NNP values. Thus, the economic geology of these mineral-deposit types is manifested in their environmental characteristics.

The variations of hazard quotients of As in leachates relative to drinking water standards and the net-neutralization potential of the mine wastes are significantly different from the patterns seen for Cu relative to aquatic ecosystems (Figure 3b). Orogenic Au deposits alone have high hazard quotients, but at high NNP values. An important implication of this result is that the mitigation or remediation of As mobility from mine wastes from this deposit type will not be able to take advantage of commonly used technology that relies on the passive sorption of As onto hydrated ferric oxides during neutralization. This is because this deposit type will likely not produce iron-rich acid drainage. Instead, strategies will need to be developed independent of acid neutralization.

Hazard quotients for Pb in mine waste relative to residential soil guidelines compared to net-neutralization potentials provide different insights (Figure 3c). The hazard quotients vary according to the primary character of the ores from which they were derived. Lead-rich mineral deposits have mine wastes with the highest hazard quotients, but the NNP values reflect the carbonate content of the host rocks or alteration

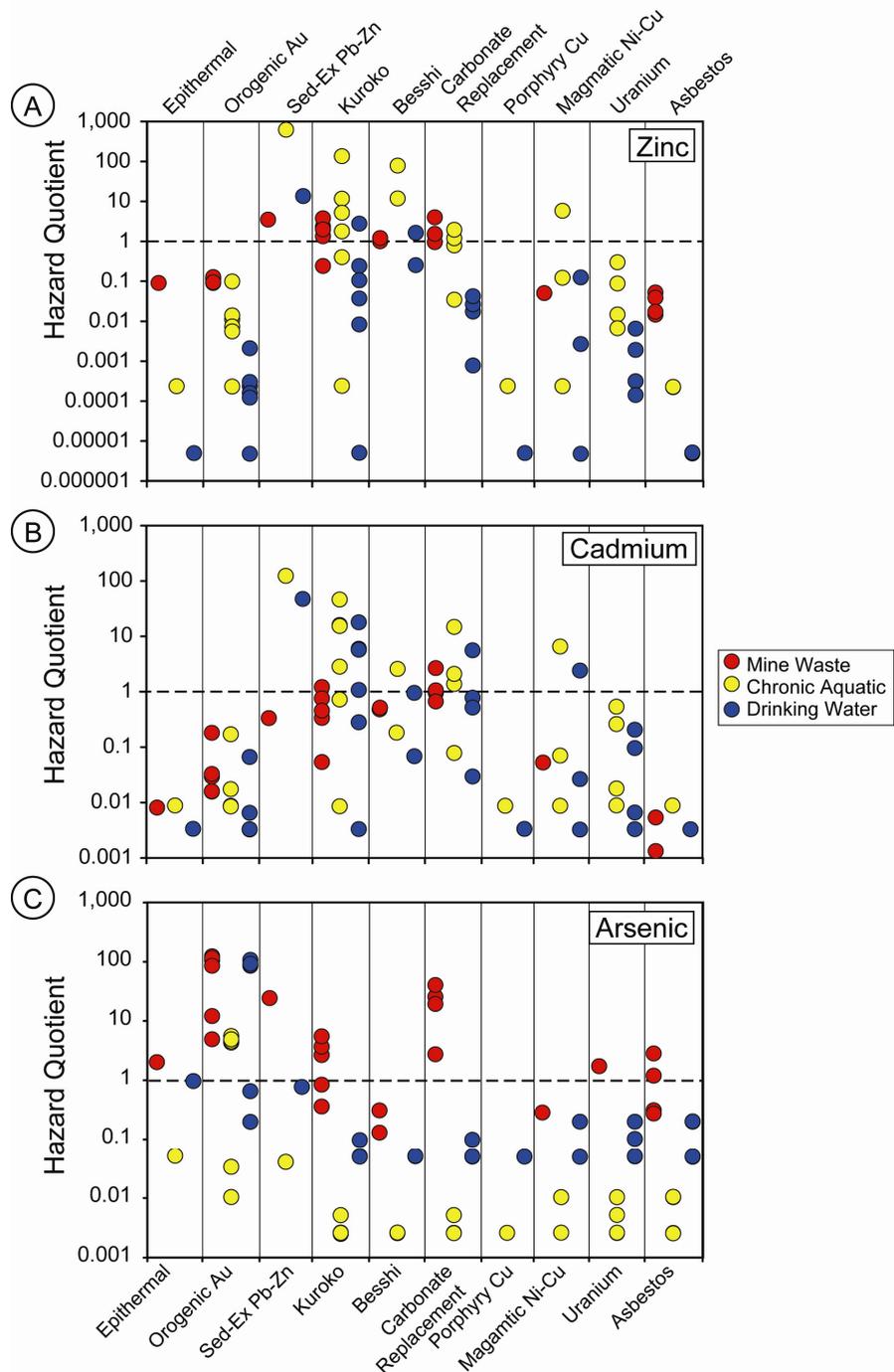


Figure 2. Hazard quotients for selected elements in mine wastes and leachates for representative samples from selected deposit types on an element-by-element basis. The hazard quotients for mine-waste solids are relative to USEPA residential soil PRGs (USEPA, 2008). The hazard quotients for SPLP leachates relative to chronic aquatic toxicity of Zn and Cd are from USEPA (2006) and based on a hardness of 100 mg/L CaCO<sub>3</sub>. The hazard quotients for SPLP leachates relative to drinking water standards are from WHO (2006), except for Zn, which is from USEPA (2003). Values above unity highlight elements that require greater scrutiny in mine planning. A. Zn; B. Cd; C. As.

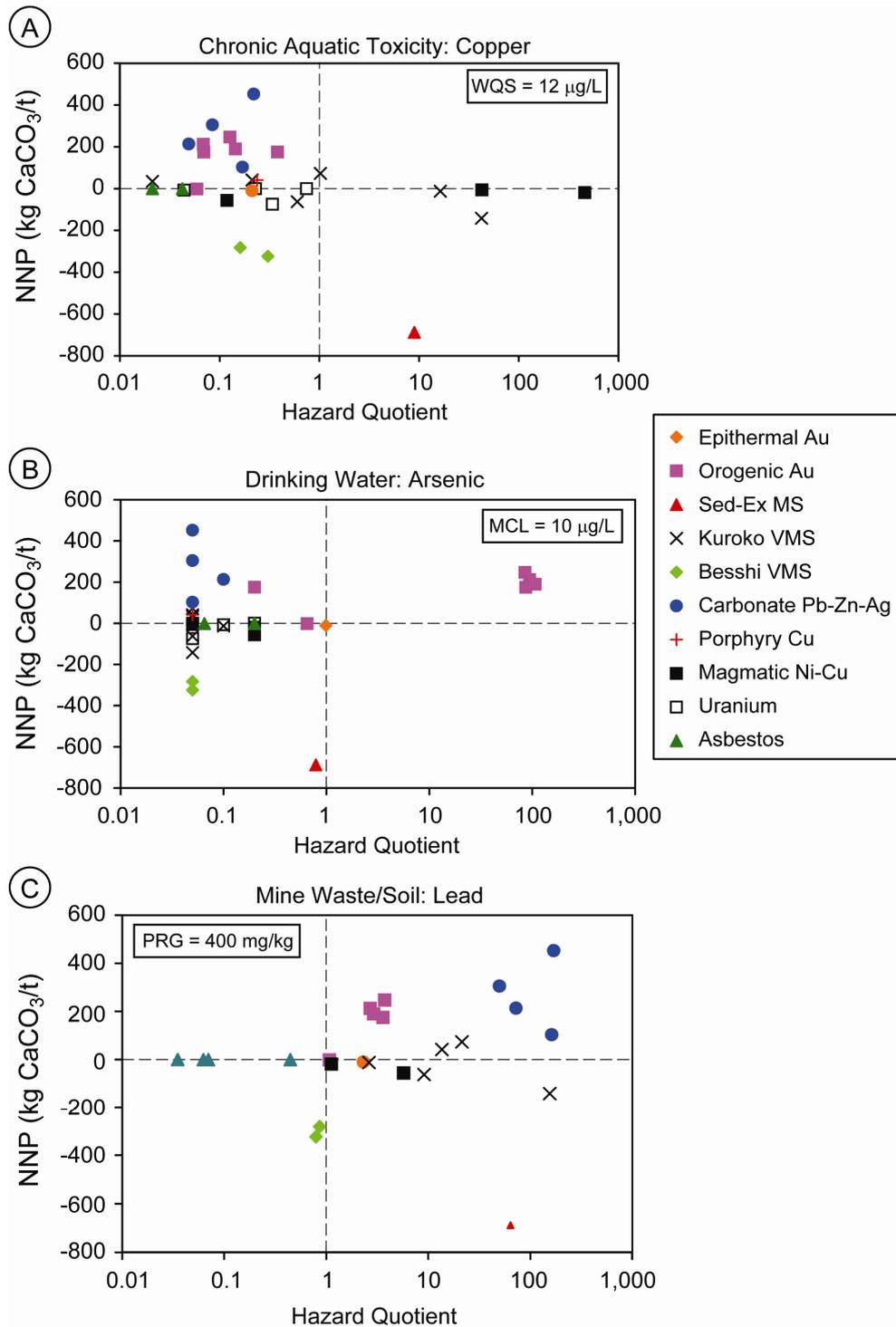


Figure 3. Scatter diagrams showing the variations of net-neutralization potential and hazards quotients for selected elements in selected media. Net-neutralization potential (NNP) values greater than zero are net alkaline, whereas those below zero are net acid. A. Chronic Cu toxicity in aquatic ecosystems. The hazard quotients for SPLP leachates are relative to the chronic aquatic toxicity water quality standard (WQS) for Cu, which is from USEPA (2006); B. As in drinking water. The hazard quotients for SPLP leachates are relative to drinking water standard (maximum contaminant limit; MCL), which is from WHO (2006); C. Pb in mine wastes. The hazard quotients for mine waste solids are relative to the USEPA residential soil preliminary remediation goal (PRG) for Pb (USEPA, 2008).

assemblages. An important aspect of potential challenges associated with Pb in mine wastes is that the bioavailability of Pb in the digestive track of mammals is strongly dependent upon the mineralogy of Pb. Blood Pb levels in juvenile swine fed with mine waste containing different Pb minerals demonstrates that Pb carbonate (cerussite) is more bioavailable than either Pb sulfate (anglesite) or Pb sulfide (galena) (USEPA, 1999). Thus, the weathering of galena in mine wastes from carbonate-hosted ores such as carbonate replacement deposits is more likely to produce a more bioavailable form of Pb than the weathering of silicate-hosted ores such as Kuroko-type deposits. This difference underscores the importance of linking the mineralogy of mine wastes to their environmental signatures.

This general approach enables the proactive anticipation of environmental issues associated with specific deposit types at all stages in the life cycle of a mine. The general clustering of environmental signatures according to deposit type in the context of various pathways of potential environmental effects, for instance the comparison of the geochemical characteristics of mine wastes and leachates derived from mine wastes to relevant solid and water environmental standards, confirms the validity of a geology-based strategy. The geology-based approach focuses attention on specific elements and other characteristics of specific deposit types, such as acid-generating potential, that pose potential environmental challenges to development and closure. The ability to anticipate environmental issues prior to discovery means that exploration companies should be able to rate and rank prospects more effectively with respect to future environmental costs, and factor those considerations in to assessing necessary grade and tonnage characteristics of exploration targets needed for profitability. At the permitting stage, this approach identifies specific elements that may potentially pose environmental challenges such that more effective mitigation and remediation strategies can be designed on an element- or compound-specific basis. Furthermore, the early identification of potential problematic elements will insure that their distributions are adequately characterized during baseline studies. Despite the numerous strengths of this approach, these insights are not meant to take the place of site specific studies for deposits under consideration.

## **CONCLUSIONS**

This approach has a number of advantages and several limitations. The main advantage is that it permits a quantitative geochemical comparison of various mine-waste samples on a deposit type by deposit type basis independent of local factors such as climatic and hydrologic setting. Nevertheless, this approach does provide a starting point from which to consider the role of these variables. This method is also independent of any local environmental mitigation or remediation practices implemented at the mines, such as capping or water treatment, and thus does not reflect the site-specific behavior of these materials. Another advantage is the amenability to use environmental guidelines from a variety of regulatory organizations (state, federal, or foreign governments). The greatest limitation is the need for a large collection of representative mine-waste samples from a broad range of deposit types. The assembly of this larger suite of samples will require expanded cooperation and collaboration with domestic and foreign land-use managers, regulators, mining companies, and other government agencies.

## **ACKNOWLEDGEMENTS**

This research was funded by the Mineral Resources Program of the USGS. The paper benefited from reviews by Larry Gough and Harvey Belkin, and discussions with Carol Russell. Any use of trade, product, or firm names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

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