ICARD 2000

PROCEEDINGS FROM THE FIFTH INTERNATIONAL CONFERENCE ON ACID ROCK DRAINAGE

VOLUME I

Published by the Society for Mining,
Metallurgy, and Exploration, Inc.

5th International
ICARD

281104/ bibOK

Estimation of pre-mining conditions for trace metal mobility in mineralized areas: An overview

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ABSTRACT

A variety of approaches have been used in the recent literature for the estimation of pre-mining (or natural background) metal concentrations in areas affected by mining. The following is a list of some of these approaches: (1) historical and anecdotal data, (2) remote analogues (other similarly mineralized areas), (3) proximal analogues (nearby mineralized areas), (4) sediment sampling (streambeds, lakes, estuaries, floodplain deposits, and soil profiles), (5) stable isotopes (hydrogen, oxygen, sulfur, and carbon), (6) geochemical modeling (forward, equilibrium-based), (7) geochemical modeling (forward, kinetic- and transport-based, and inverse), (8) statistical analyses, (9) mass balance on oxygen flux, (10) mass balance with age determination of weathered material. Examples of each approach are described, and the strengths and limitations of each approach are discussed.

INTRODUCTION

Establishing the pre-mining concentrations and loads for trace metals in water and sediment in mined mineralized areas is a challenging task, yet it represents an important aspect of mine-site remediation. Such estimates are needed to establish realistic clean-up goals. It is unreasonable to spend large sums of money cleaning up streams whose metal content is largely caused by natural weathering of mineralized areas. Alternatively, determination of pre-mining conditions may be important to demonstrate that mining has caused large and detrimental increases in metal mobility. Determining the difference, between mining-related and pre-mining metal mobility, usually requires estimation, because a careful pre-mining studies that incorporate natural hydrochemical variability have generally not been done. This report summarizes a number of approaches to the estimation of pre-mining conditions that have been described in the recent literature and that are being used in ongoing investigations. Because of the highly uncertain nature of this kind of estimation, multiple approaches are recommended to document uncertainties and to establish a reasonable range of values for a given site.

Because pre-mining conditions are largely controlled by bedrock geology, it is important to understand the geologic setting of different mineral deposits. Conceptual models for ore formation (e.g. Cox and Singer 1986; Barnes 1997) and "geo-environmental models" or compilations describing the environmental geology of mineral deposits (du Bray 1995;, Plumlee 1999) provide a useful context for discussing the mineralogical and geochemical controls on trace-metal distribution in mineralized areas. Different deposit types contain different suites of minerals and characteristic trace-element signatures in associated soils, sediments, and waters (Langmuir 1997). For example, different kinds of gold deposits, such as epithermal hot springs (McLaughlin-type), sediment-hosted (Carlin-type), and low-sulfide gold-quartz veins (Mother-Lode-type), have widely varying, naturally occurring amounts of associated arsenic, lead, mercury, thallium, and other metals of environmental concern (du Bray 1995; Plumlee 1999).

The best approach to understanding the pre-mining conditions in a mineralized area would be to take baseline samples at the future mine site prior to any disturbance. However, the opportunity for such direct sampling was lost many decades ago in most of North America, Europe, and other relatively developed areas. Instead, a variety of indirect approaches to estimation of pre-mining background conditions have been used, as summarized below.

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SUMMARY OF APPROACHES

There are several approaches to the estimation of pre-mining conditions that have been described in the recent literature (Nordstrom et al. 1996). The purpose of this paper is to summarize the various methods used and to describe, in a general sense, the strengths and limitations of each method. A summary of methods, with references and comments, is provided in Table 1.

Table 1. Summary of methods used to estimate natural background in mineralized areas.

Method	References	Comments
1. *Historical and anecdotal data*	Runnels et al. 1992	Qualitative and subjective, but a useful start
2. *Remote analogues*: Natural analogues in other mineralized areas or mining districts	Runnels et al. 1992 USGS 1995 Kelley and Taylor 1997 Engle et al. 1998 Miller and McHugh 1999	Geological and hydrological similarity essential for comparison; Climate variations also may be a factor
3. *Proximal analogues*: Empirical comparison of chemical loads and concentrations of springs, seeps, and ground waters unaffected by mining with mine-influenced waters in the same mineralized region or mining district	Miller and McHugh 1994, 1999 Sibbick and Laurus 1995 Chermak et al. 1998 Will 1998 Bove et al. 2000 Mast et al. 2000 Posey et al. 2000 Yager et al. 2000	Mined areas likely to have been more extensively mineralized than unmined areas; Zoned alteration must be considered; Springs near mined areas may be affected by mining-related changes in elevation of water table and flow path of ground water
4. *Sediment sampling*: streambeds, lakes, estuaries, floodplain deposits, and soil profiles	Prusty et al. 1994 Schuck 1995 Helgen and Moore 1996 Kliza 1997 Hornberger et al. 1999 McMartin et al. 1999 Church et al. 2000	Dating with ^{210}Pb and ^{137}Cs may help to quantify age of sediment; Provides no information on water chemistry; May be affected by post-depositional changes
5. *Stable isotopes* (SO_4, H_2O)	Alpers et al. 1994b, 1999a Finley et al. 1997 Wright and Nordstrom 1999	Strong evaporative signal from H_2O; Processes controlling oxygen isotopes in sulfate are complex
6. *Geochemical modeling* (forward, equilibrium-based)	Runnels et al. 1992 Lichtner and Waber 1992 Miller et al. 1999 Miller and McHugh 1999	Assumes equilibrium conditions are applicable and that initial (or final) conditions are known
7. *Geochemical modeling* (forward, with kinetics) (forward, with fluid transport) (inverse, with or without kinetics)	Alpers et al. 1992 Lichtner and Waber 1992 Alpers and Nordstrom 1999 Mast et al. 2000	Several assumptions are needed depending on available data; Knowledge of modeler a key factor
8. *Statistical analysis* (multivariate methods)	Selinus and Esbensen 1995 Runnells et al. 1996, 1997, 1998 Bruxvoort et al. 1997 Salminen and Tarvainen 1997 Zhang and Selinus 1998	May be applied to sediment or water-quality data; Interpretations problematic in areas with more than two sources
9. *Mass balance on O_2 flux*	Nordstrom and Alpers, written communication, 1990	Requires site-specific knowledge of water table levels before and after mining as well as estimates of annual rainfall, infiltration, and water balance
10. *Mass balance with age determination of weathered material*	Alpers et al. 1999b	Long-term average metal fluxes; Minimum ages yield maximum fluxes; Geologic reconstruction of maximum deposit size needed

Historical and Anecdotal Data

Historical accounts may be available describing naturally occurring, metal-rich water and affected biological systems in mineralized areas prior to mining, as described by Runnells et al. (1992). Geographic names such as Alum Creek, Sulfur Creek, Iron Creek, and Bitter Creek are common in mineralized areas, indicating probable natural effects on water-quality. Mining history and the evolution of its operations can provide valuable information on environmental changes. However, such information tends to be qualitative and subjective and therefore is of only limited use in reconstructing pre-mining conditions. Nevertheless, in the absence of quantitative pre-mining baseline data, it can provide a context suggesting that some degree of metal mobility may have been taking place prior to mining activity.

Remote Analogues

This method uses data on water quality and sediment chemistry from unmined mineralized areas that are somewhat distant from the area where natural background information is needed. Runnells et al. (1992) compiled published information on water chemistry from several reportedly unmined, mineralized areas. Much of the data was gathered for the purposes of mineral exploration and was published in journals such as the *Journal of Geochemical Exploration*. An important limitation to the application of such data to the estimation of natural-background conditions at a given mine site is limited information on the geology, hydrology, and mineralogy at the analogue sites. Another common problem with data from earlier geochemical literature is the general lack of information on sample collection and preservation methods and on quality assurance and quality control. Such information is needed to assess the possibility of sample contamination or metal loss by iron precipitation.

Detailed hydrogeochemical characterization of mineralized watersheds with minimal mining activity (e.g. Miller et al. 1999) provide a useful database on which to draw for baseline data and background estimates. The "geoenvironmental model" approach described by du Bray (1995) and Plumlee (1999) stresses the importance of determining the type of mineralization at both the mine site, for which background information is needed, and at the unmined analogue sites, so that proper analogies can be made. For example, as pointed out in this volume by Seal et al. (2000), it would be inappropriate to use baseline water chemistry data from a sedimentary-exhalative deposit such as Red Dog, Alaska, as an indication of premining conditions at a Noranda-type volcanic-hosted massive sulfide deposit such as Iron Mountain, California. Climate and hydrologic setting are additional variables that can make comparisons from remote settings problematic; however, in some cases the closest geologic analogues are in very different climatic settings (e.g., Miller and McHugh 1999). Anthropogenic activities not related to mining (non-mining road construction, timber harvesting, dam construction, or residential and industrial development) may be complicating factors in some areas.

Proximal Analogues

This method is based on empirical comparisons of water chemistry from the same or nearby mineralized areas. There are a few localities in the world where the mineralization is so widespread that both mining-affected and unmined watersheds are weathering within the same climate, geology, and biology. This circumstance makes it possible to collect water samples and discharge measurements from watersheds with the same general geochemical characteristics and directly compare and contrast unmined or natural contributions to metal concentrations and loads with those from mined contributions. The advantage of this approach is that a direct comparison can be made today with most other aspects, such as bedrock geology and climate being kept constant or at least comparable. For large mineralized systems, such as copper porphyry deposits, zoned alteration assemblages need to be taken into account. The weakness of this approach is that the mined areas were generally the sites of most extensive ore mineralization and most widespread hydrothermal alteration, and were likely to have made greater natural contributions to metal concentrations than current unmined analogues. The greater abundance and surface exposure of the areas that became mining sites might well have caused more rapid weathering rates than unmined sites under pre-mining conditions. Hence, background conditions tend to be underestimated.

The San Juan Mountains, in southwestern Colorado, are underlain by one of the thickest and most extensive volcanic fields in the world, which has been subject to extensive hydrothermal alteration and mineralization. Numerous "natural" mineralized springs with low pH and high metal concentrations as well as natural ferricrete deposits can be found throughout the area. Several geochemical comparisons between mined and unmined areas in the upper Animas River Basin, a major drainage of the San Juan Mountains, are reported in this volume (Bove et al. 2000; Mast et al. 2000; Yager et al. 2000). Comparisons between mined and unmined areas for the Summitville area, a drainage of the Rio Grande, were reported by Miller and McHugh (1994, 1999) and by Posey et al. (2000). The main conclusion that appears in these reports is that weathering from "natural" or unmined areas can contribute a significant proportion of metal mobility in these watersheds.

Some studies have attempted to separate natural from mining-related sources of metals in watersheds using novel methods such as diverting a creek to expose base-flow seeps from bedrock (Hall and Ekoniak 1997). Other studies have used water-balance methods to divide partially mined watersheds into unmined and mined sub-basins in attempts to separate natural from mine-related sources (e.g. Will 1998). Such efforts are prone to significant uncertainty and error if they fail to take into account the effects of mining activities on the water table both during and after mining. Mineralized wall rocks that have become unsaturated by the changes in water table elevation from underground mining excavations are susceptible to increased oxidation rates. Also, in areas that were unsaturated during mining but are now once again saturated, residual oxidation products such as ferric sulfate salts can cause continuing oxidation in the absence of dissolved oxygen (Alpers et al. 1994a).

Sediment Sampling: Streambeds, lakes, estuaries, floodplain deposits, and soil profiles

Sediments can provide useful records of pre-mining conditions for sediment contamination, in certain depositional settings, if pre-mining sediments are preserved by sediments deposited during and after mining. If it can be determined that the chemistry of the sediments has not been altered by processes such as diagenesis, interaction with ground-water, bioturbation, or other disturbances, then the pre-mining sediment layers can provide potentially useful information regarding pre-mining conditions.

An excellent example of using sediment sampling to assess pre-mining conditions is the work of Hornberger et al. (1999) in San Francisco Bay, California. Large-scale hydraulic mining of placer gold deposits in the Sierra Nevada caused massive amounts of sediment to be mobilized during the California Gold Rush. It has been estimated that more than 1.4×10^9 tons of gravel were mined by hydraulic methods (Gilbert 1917) and the majority of the fine-grained sediment was transported to the San Francisco Bay. Elemental mercury was used extensively in the processing of placer gold ores, and many thousands of tons of mercury were lost to environment (Hunerlach et al. 1999). Hornberger et al. (1999) analyzed several sediment cores from San Francisco Bay and determined trace metal profiles. Radiometric methods (primarily ^{137}Cs and ^{210}Pb) were used to date the sediment profiles, resulting in the conclusion that pre-mining mercury background levels were less than 0.1 mg/kg whereas mercury in syn- and post-mining sediments ranged from 0.3 to 0.95 mg/kg.

Examples of sediment profile studies in lakes adjacent to mining areas include the Master's theses by Schuck (1995) in Arrowhead Lake, Vermont, and by Kliza (1997) in southeastern Ontario. Overbank deposits in the Clark Fork basin downstream of Butte, Montana were studied by Helgen and Moore (1996). Streambed sediments associated with zinc mining in India were described by Prusty et al. (1994). Church et al. (2000) report in this volume on streambed sediments from the upper Animas River Basin, an area with considerable natural background metal concentrations caused by erosion of aerially extensive zones of mineralization and alteration. In each of these sediment studies, an effort was made to sample vertical profiles that penetrated into a pre-mining horizon.

It is important in the interpretation of such data that one can rule out the possible disturbances to the profiles as described above, especially the possible migration of contaminants via ground water or pore waters from a mining-affected zone into a sediment layer that was deposited prior to mining. An example of a problematic sampling environment would be ferricrete deposits in the streambed of an acidic stream affected by mining. Even if the ferricretes were deposited prior to mining, their composition may have been affected by metals in the stream system that were derived from mining wastes."

Stable Isotopes

The stable isotopes of hydrogen, oxygen, sulfur, and carbon can be very useful as environmental tracers (Clark and Fritz 1997). In ground-water studies of areas affected by mining, hydrogen and oxygen isotopes in water, expressed as δ^2H and δ^{18}O, respectively, can help distinguish recharge sources. Tailings ponds and other impoundments tend to promote extensive evaporation, which leaves a distinct isotope signature – a slope of 3 to 6 on plots of δ^2H and δ^{18}O as opposed to a slope of 8 which is the typical line for meteoric waters.

Alpers et al. (1994b; 1999a, and references therein) used stable isotopes along with metals, sulfate, pH, tritium, and chlorofluorocarbons to delineate a ground-water plume affected by acidic drainage from an unlined impoundment downstream of sulfidic mine-waste piles at the Penn Mine, California, a Kuroko-type volcanogenic massive sulfide deposit. The stable isotopes helped to establish a clear mixing relationship between unevaporated natural background groundwaters, the highly evaporated, acidic impoundment waters, and Camanche Lake waters. The lake waters were unevaporated but isotopically lighter than local ground water because the lake waters originate from snowmelt at higher elevations in the watershed. Finley et al.

(1997) used stable isotopes of hydrogen, oxygen, sulfur, and carbon to delineate water types affecting an acidic, metal-rich ground-water plume near Bingham Canyon, Utah, the site of a large porphyry copper deposit.

Wright and Nordstrom (1999) proposed that oxygen isotopes in aqueous sulfate may provide a tool for distinguishing natural from mining-related sources of sulfate in mined areas. The principles on which this hypothesis is based involve determining whether the source of oxygen is primarily oxygen from the atmosphere (gaseous or dissolved O_2) or oxygen from water (H_2O). The former is generally incorporated in sulfide oxidation reactions at higher pH where the oxidant is O_2, whereas the latter is thought to predominate in more acidic condition where aqueous Fe^{3+} is the primary oxidant (Taylor and Wheeler 1994, and references therein). Because there are several other factors that may affect oxygen isotopes in sulfates, the utility of oxygen isotopes in sulfate as a tool for distinguishing natural background from mining sources remains to be clearly established. Such an application will depend on site-specific conditions.

Geochemical Modeling: Forward (equilibrium-based)

One approach to geochemical modeling is to start with a known (or assumed) mineral assemblage and other boundary conditions such as gas pressures and oxidation-reduction state and to compute the composition of water in equilibrium with the desired configuration. This approach was taken by Runnells et al. (1992), who used three different sets of assumptions to describe possible geochemical controls on surface waters in the area of the Galena mining district, in the Tri-State Pb-Zn mining district of southeastern Kansas, using the program PHREEQE (Parkhurst et al. 1980). Because some of the simulations produced concentrations of trace metals and major elements in the approximate range of a surface water sample taken downstream of the mining district, Runnells et al. (1992) concluded that *"...the concentrations of metals and other components in contaminated sections of Short Creek could certainly result from natural weathering of a variety of assemblages of ore minerals of the Tri-State Mining District..."* However, Runnells et al. (1992) also pointed out, in reference to ground and surface waters from Red Dog, Alaska, that ground waters tend to have higher concentrations than surface waters, *"probably...from the longer time that the groundwaters have had to approach equilibrium with the ore minerals."* Hence, kinetics, mineral surface areas, and contact time can play an important role in determining surface water compositions, and the relatively simple equilibrium-based geochemical models do not take such factors into account.

Miller and McHugh (1999) used PHREEQE to simulate the mixing of waters from mineralized and unmineralized areas in the vicinity of the Summitville acid-sulfate epithermal Au-Ag-Cu system in Colorado. Estimates of the proportions of mineralized and unmineralized areas in the Wightman Fork basin were used in combination with water quality data from unmined sites in both mineralized and unmineralized areas. One of the more sensitive variables in the modeling turned out to be the amount of iron and aluminum that were allowed to hydrolyze and precipitate, reactions that lead to a lowering of pH.

Another application of equilibrium-based geochemical modeling to natural background studies in mining environments is to compute mineral saturation indices for water samples from mineralized watersheds that have minimal mining impacts (e.g., Miller et al. 1999). This type of study provides useful empirical data on minerals that may control solubility and metal mobility in undisturbed settings.

Geochemical Modeling: Forward (kinetics- or transport-based) and Inverse

The following three additional types of geochemical models are considered: (1) forward models that incorporate the kinetics of mineral dissolution and/or precipitation, (2) forward models that incorporate fluid transport, and (3) inverse models that use mass balance and the stoichiometry of minerals to deduce the water-rock and water-mixing reactions that may have caused changes in water chemistry along a flow path. These types of models (as well as equilibrium-based models) and their application in mining environments were described by Alpers and Nordstrom (1999).

Lichtner and Waber (1992) applied a reactive-transport model with kinetic rate laws for mineral dissolution and precipitation and advective transport of ground water to the natural weathering of a pyritic uranium deposit in Brazil containing a redox front for a 500,000 year time period. A quasi-stationary state approximation was used and solution speciation equilibria were assumed. The results were in agreement with the detailed mineralogical assemblages and they were found to be insensitive to the kinetic rate constants. The evolution of both mineralogy and water chemistry with time were output in this modeling example of natural sulfidic weathering.

There are very few examples of mass balances applied to mined or unmined mineralized areas. Alpers et al. (1992) tried several methods to determine whether the Richmond Mine at Iron Mountain, California was hydraulically connected to the Hornet Mine for which mine working connections were shown on mine maps. If there was a significant hydraulic connection then plugging was a cost-effective remediation but if they were not hydraulically connected then additional mine water treatment would be required. The inverse method of mass balancing was the only method that could definitively demonstrate there was no significant hydraulic connection between the two mines. Although this example does not address the question of natural or baseline conditions, it does show the usefulness of the approach in a mining environment. Mast et al. (2000) and Bove et al. (2000) applied similar mass-balancing calculations to natural acid springs occurring in the upper Animas River basin, Colorado to look at mineral dissolution/precipitation signatures as a function of the degree of rock alteration. They showed that differences in water-rock interaction could be demonstrated with this approach. This method is the preferred approach for integrating and quantifying geological and water quality data for mined and unmined sites.

The main limitation of geochemical modeling is that a lot of high quality information on both hydrology and geochemistry of a site is often needed to produce useful and reliable results. With poorer quality data and less information generally available, more assumptions with greater uncertainties are required.

Statistical Analysis

Multivariate statistics have long been used by geochemical explorationists and others as a means of identifying regional background levels so that anomalous values of indicator elements can be identified (Runnells 1998). Papers by Selinus and Esbensen (1995), Salminen and Tarvainen (1997), and Zhang and Selinus (1998) address the issues of statistical methods in distingiushing regional baseline trends.

The application of statistical methods to multivariate data sets from mining environments as a means for distinguishing natural background from mining-related impacts is discussed by Bruxvoort et al., (1997) and by Runnells et al. (1996; 1997; 1998). These studies used probability distribution diagrams in an attempt to distinguish between natural concentrations of metals and those influenced by anthropogenic activities, including mining, milling, and smelting. As with some other approaches, if there are more than 2 or 3 sources of chemical input it is not clear that probability distribution functions can distinguish these features. Cluster analysis, factor analysis, or multidimensional scaling can still be helpful under these conditions.

Mass Balance on Oxygen Flux

The diffusion rate of oxygen gas (O_2) through air is several orders of magnitude faster than its diffusion rate through water. Therefore, in saturated conditions below the water table, sulfide oxidation is generally limited by the supply of the oxidant, most commonly either $O_{2(aq)}$ or $Fe^{3+}_{(aq)}$. At Iron Mountain, California, the massive sulfide ore in the Richmond Mine was mostly below the water table prior to mining, with a small amount of gossan formation at the top. The deposit is tabular and sub-horizontal, with approximate dimensions of 60 m high by 60 m wide and 500 m long and is U-shaped in cross-section; the gossan development was in the upper parts of the limbs defining the "U" (Kinkel et al. 1956). The Richmond tunnel on the main haulage level from the Richmond Mine (2,600 foot level) has served as an effective drain for the mine since the mid-1940s. The Richmond tunnel currently produces some of the most concentrated acid mine drainage recorded anywhere, with pH values typically around 0.5, sulfate concentrations of more than 100 g/L, iron concentrations of about 20 g/L, and zinc of about 2 g/L (Nordstrom and Alpers 1999a,b). Mass balance analysis using iron, sulfate, and other major elements in the Richmond Mine effluent and weekly discharge data from 1990 indicate that about 2,500 tons per year of pyrite are oxidizing, so there is enough pyrite remaining in the mine workings to fuel the reaction for about 3,000 years (Nordstrom and Alpers 1999a).

A relatively simple mass balance on oxygen flux was made by Nordstrom and Alpers (written communication, 1990). The result was used to compare the present pyrite oxidation rate to the rate likely to have occurred prior to mining when the deposit was largely below the water table. With an average infiltration of 50 inches/yr for a 45 acre site and an average concentration of 10 mg/L of oxygen in rainwater, the potential oxygen flux would be about 72,000 moles/yr. If this value is converted into the stoichiometric amount of pyrite oxidized, the result would be about 2.5 tons/yr for the whole Iron Mountain site or 1,000 times slower than the current post-mining weathering rates in just the Richmond mine area. A limitation in applying this approach is that detailed information is needed on the location of the water table prior to mining. It cannot always be assumed that the oxide-sulfide transition in the rock corresponds to the position of the water table at a particular point in time. Also, fluctuations in ground-water levels on annual and multi-year drought cycles, which may be up to tens of feet per year in some climates, and other sources of oxygen infiltration such as barometric pumping and convection in the unsaturated zone, must be considered in any detailed analyses. At least this approach gives some constraints on the weathering of pyrite.

Mass Balance with Age Determination of Weathered Material

Metal loads in surface waters are measurements of mass per unit time, such as kilograms per day or tons per year of a constituent passing through a specific stream cross-section. Long-term metal fluxes can also be estimated over geologic time frames if limits can be placed on the mass weathered over a known time interval. An application of this approach was described by Alpers et al. (1999b). They used evidence for a paleomagnetic reversal in some samples of gossan (weathered massive sulfide) at Iron Mountain, California, to determine that weathering began at least 780,000 years before present, the time of the last full reversal of the Earth's magnetic field. Mass balance computations were made to estimate the amount of massive sulfide ore (approximately 15 tons) needed to produce the pre-mining amount of gossan (approximately 10 tons). Despite their Devonian age, the massive sulfide deposits at Iron Mountain are relatively undeformed, which allows reasonable estimates to be made of the mass that could have been eroded prior to mining. Using various assumptions for the copper and zinc grades of the sulfide that was eroded and that turned into gossan, maximum long-term flux rates for copper and zinc removal from the site were calculated and were found to be 2-3 orders of magnitude less than present rates of chemical weathering (Alpers et al. 1999b). This result is consistent with the mass balance approach on oxygen and provides a confirmation that the oxygen mass flux is reasonable.

The approach taken by Alpers et al. (1999b) can also be used with other dating methods for weathering processes. K-Ar and $^{40}Ar/^{39}Ar$ are well established dating methods that can be used with supergene alunite, jarosite, and potassium-bearing manganese oxide minerals (Vasconcelos et al. 1994). A variety of other radiogenic and cosmogenic isotope dating methods may also be applied. Maximum estimates of metal mass removed divided by minimum ages yield maximum long-term metal flux rates. A limitation of this approach is that the long-term rates are averages, and geologic history may be quite episodic, such that the rates may have been considerably higher (and lower) than the long-term average for certain periods in Earth history.

CONCLUDING REMARKS

This report summarizes ten approaches to the estimation of natural background concentrations of water and sediment in mined areas. These approaches and their limitations are: (1) historical data, a qualitative but helpful approach when any other data is lacking, (2) remote analogues, made difficult because comparisons between geology, hydrology, and climate are never quite the same, (3) proximal analogues, made difficult because differences in mineralogy and hydrogeology between adjacent mined and unmined sites can complicate the comparisons, (4) sediment sampling, made difficult because it provides no information on water chemistry and it is affected by post-depositional changes, (5) stable isotopes, tends to be semi-quantitative because of complexities and mixing, (6) equilibrium-based geochemical modeling, assumes equilibrium conditions for strongly irreversible processes, (7) geochemical modeling as mass balancing or with kinetics and transport, dependent upon several assumptions for input data and puts large responsibility on user and the quality of data for interpretation, (8) statistical multivariate methods, puts large responsibility on user for interpretation, which can be problematic in areas of more than two apparent sources, (9) oxygen mass balance, requires knowledge of water balance and basic hydrogeology of site, (10) mass balance on weathered deposit with age determination for beginning of weathering, assumes an average weathering rate and assumes a size and an average composition of the original deposit. Because of the high level of uncertainty associated with these types of estimation, it is recommended that multiple methods be applied wherever possible.

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US Geological Survey, *Provided funding specifically for the proceedings*

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ISBN 0-87335-182-7