

Chapter B

GEOCHEMICAL AND MINERALOGIC CHARACTERIZATION OF SOLIDS AND THEIR EFFECTS ON WATERS IN METAL-MINING ENVIRONMENTS

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THE ROLE OF MINERALOGY AND GEOCHEMISTRY OF SOLIDS IN GEOENVIRONMENTAL MODELS

The geologic characteristics (ore mineralogy, geochemistry, host rock lithology, etc.) that economic geologists use to classify mineral deposits are key to understanding their environmental signatures. Mineralogic characterization and chemical analysis are among the many scientific tools that can be applied to mining-environmental prediction, mitigation, and remediation (Plumlee and Logsdon, 1999a).

Mineralogy is important because (1) the primary ore and non-ore (gangue) minerals are sources of metals and other elements released into solution upon weathering, (2) these weathering reactions can produce or consume acidity (H^+), and (3) many secondary minerals that form during the weathering process can permanently or temporarily sequester metals, recycling them and generating or consuming acidity in reactions triggered by changes in moisture, temperature, or pH in the local environment. The pH of mine drainage varies depending on the balance between acid-producing and acid-consuming reactions that occur during weathering, the relative rates of these reactions, and the accessibility of minerals that contribute to these reactions (Smith and others, 1994). Thus, the chemical signature of waters and solids associated with a mineral deposit are intimately linked. Most mines are situated along streams and in many cases mine waste is deposited in or adjacent to streams (fig. 1), so surface runoff from and infiltration into mine waste is an important control of drainage water chemistry.

Static tests (acid-base accounting) used to predict acid-rock drainage (ARD) and develop remediation options such as lime requirements are based on assumptions about mineralogy that may or may not be appropriate. These tests are at best a screening tool and provide no information about reaction rates. However, these tests are relatively rapid and inexpensive compared to long-term kinetic tests and are a reality of modern mining and environmental regulation. Knowledge of the mineralogy of the mine waste provides a guide to choosing the most appropriate methods for acid-base accounting because results for different methods vary depending on the minerals that represent the sources of acid and the minerals that provide sources of neutralization. Mineralogic characterization provides information on (1) sources and identity of potential metals and acidity, (2) sources of neutralization, (3) presence of minerals that may contribute to laboratory-based neutralization potential calculations, but behave differently under field conditions, (4) soluble and insoluble constituents of earth materials, and (5) textures and grain sizes that can affect reactivity of different minerals (Price and others, 1997; Jambor and Blowes, 1998). Many active mine operations are starting to incorporate detailed mineralogic characterization in mitigation plans. Modified static tests have been developed to address some of the problems associated with static tests. For abandoned mines, knowledge of mineralogy gleaned from geoenvironmental models can assist with prioritization and choices of appropriate tests and remediation options for different types of mineral deposits, many of which can occur within a single watershed.

Typically, mineralogic characterization of solids includes microscopic examination, x-ray diffraction (XRD), scanning electron microscopy (SEM), and in some cases, electron probe microanalysis (EPMA). A variety of other techniques are available to mineralogists for characterization of individual mineral grains by x-ray diffraction methods and for chemical analysis of minerals (Jambor and Blowes, 1998). Chemical analysis is important because potentially toxic metals, such as cadmium and selenium, are typically sequestered as minor constituents in ore minerals such as sphalerite or galena and their presence may not be apparent from casual examination of ore mineral assemblages. Many secondary minerals (1) occur as very fine-grained or poorly crystalline materials that can sorb and desorb metals, depending on local conditions, (2) form complex solid solutions that incorporate metals, and (3) are transient because they can precipitate and dissolve in a matter of hours depending on changes in the local environment. Geochemical models use complete water chemistry analysis to compute saturation indices, predict what minerals should be stable under equilibrium conditions, and provide insights about the processes that control the release, transport, and fate of contaminants (Alpers and Nordstrom, 1999). However, most models are limited to equilibrium conditions and contain limited data for secondary minerals encountered in weathered mining systems. Mineralogic data can be used to constrain models, and model results provide clues to the presence of secondary minerals involved in precipitation and dissolution reactions. No single technique suffices to identify all the minerals that may be encountered and some combination or iterative use of different methods may be necessary to characterize the mineralogy of a site.

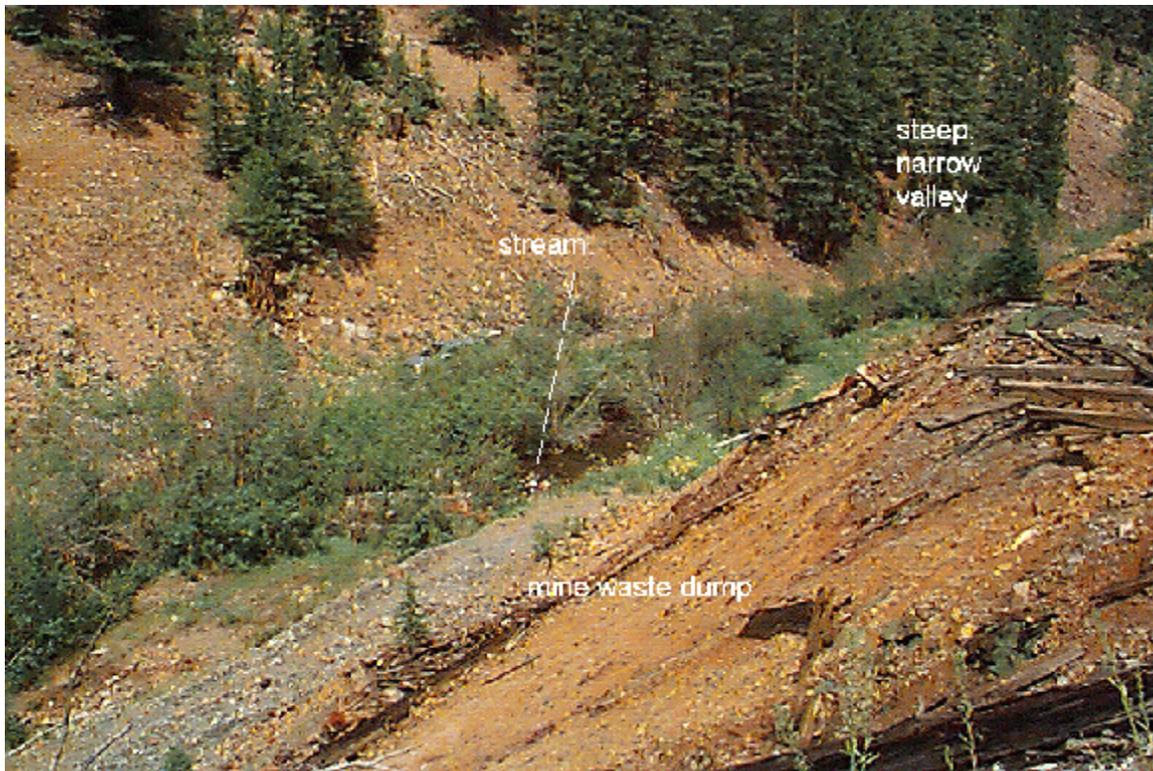


Figure 1. Typical abandoned mine waste dump in the Rocky Mountains of the western U.S. Oxidized ore and soil developed from mine waste material form a steep slope in a narrow valley drained by a perennial stream. Surface runoff from solids on the dump and infiltration through the dump contributes sediments and dissolved metals to the stream. The underground mine here exploited a tungsten skarn deposit that was last worked in 1955. Photo taken August 1999.

Chemical analysis of solid geologic materials (rocks, soils, sediments) provides information on sources and sinks for potentially toxic elements. Chemical data can be used to establish pre-mining backgrounds and baselines and evaluate post-mining or post-reclamation geochemical signatures. Recognition of natural high or low backgrounds or baselines in an area may be a factor in the economic viability of developing a mineral deposit and in setting realistic site remediation goals (Wanty and others, 1999; Wanty and others, in press). Coupled with leaching and sequential extractions, the chemistry of the solids becomes a powerful tool for documenting transport and fate of different elements in the environment and for predicting potential surface runoff problems. Although acid-base accounting techniques are based on assumptions about mineralogy, the values reported rely on chemical analyses of bulk samples for sulfur and carbon species. Multi-element chemical analysis can also provide information on the presence of unsuspected elements. For example, metals that could be detrimental to the environment may be detected that were not assayed for during the mine life or by older analytical techniques. In particular, mercury was used for gold amalgamation at many historic gold mines, especially at placer operations and may contribute to the geochemical signature at a site. Zinc tended to be under-reported in historic production data because of smelter penalties. Geochemical analysis can indicate elevated concentrations of metals that could be recovered by re-mining, establish the geochemical signature of different parts of a study site (hotspots or neutral zones), and provide a rapid and economical screening tool for ranking large numbers of sites and identifying areas for follow-up studies.

In this chapter, we (1) provide an overview of acid-base accounting, (2) outline tools available for characterizing solids, and (3) discuss different types of solid materials that can be sampled and the information they provide. Chapter C outlines a toolkit of methods, strategies, and approaches for rapid site characterization of metal-mining waste piles. We include examples from USGS efforts to develop uniform approaches to data collection to enhance the preliminary geoenvironmental models in du Bray (1995). These preliminary models were structured to add an environmental component to mineral deposit models used for mineral deposit classification for resource assessment (Cox and Singer, 1986). By developing a consistent data set for a variety of different deposit types in different ecoregions, the effects of climate, latitude, and altitude on the environmental signatures of deposits can be incorporated into models to enhance their predictive value. A number of recent publications discuss processes and

techniques relevant to solids chemistry and characterization as well as overviews of the behavior of metals in acid drainage environments, case studies, and useful reference tables (mineral resistance to weathering, possible reactions involving ore and gangue minerals, element distributions in different sample media, etc.). See for example, Plumlee and Logsdon, 1999b; Filipek and Plumlee, 1999; Cabri and Vaughn, 1998; Jambor and Blowes, 1994; Kwong, 1993; MEND, 2000, 1994, 1989). In addition, the InfoMine website (Robertson Info-Data, Inc.) subscription service provides access to EnviroMine, a reference library, resource, and forum for exchange of current information on mining-related environmental technology.

ACID-BASE ACCOUNTING

Static acid-base accounting (ABA) is a screening procedure to predict if a waste material will produce acid-rock drainage (ARD). It compares the acid production potential (AP, APP, or AGP) with the acid neutralization potential (NP or ANP) for a given waste material. ABA results are usually reported in tons CaCO₃ per 1,000 tons (ppt) of waste material. The net neutralization potential (NNP) is the difference between NP and AP.

$$\text{NNP} = \text{NP} - \text{AP}$$

The neutralization potential ratio (NPR) is the ratio of NP to AP.

$$\text{NPR} = \text{NP} / \text{AP}$$

The NNP and NPR are used to categorize the tested material into acid-producing or non-acid-producing material. An excellent discussion of ARD prediction, ABA test procedures, and an ABA overview can be found on the EnviroMine web site at:

<http://www.infomine.com/technology/enviromine/ard/welcome.htm>.

There is a great deal of controversy about how to interpret NNP and NPR calculations. NNP values in the range of -20 to 20 g CaCO₃ / kg are generally considered to be uncertain (e.g., Brady and Cravotta, 1992; Lapakko, 1992). NNP values less than -20 are typically taken to indicate acid producing potential while NNP values greater than 20 are usually interpreted to identify materials with little potential to produce net acidity. For NPR, when the ratio is less than one, the material is predicted to generate acidic drainage. However, diPretorio and Rauch (1988) found that materials with ratios less than about 2.4 often produce acidic drainage. Smith (1997, p. 291) states that "...a proponent should consider using a conservative 3:1 ANP/AGP ratio for determining, without further testing, that a waste rock will not be acid generating in the long term. Samples which have lower ANP/AGP ratios may not be acid generating; they merely require kinetic tests to establish their long-term behavior." Price (1997, p. 89) states that a NPR of 4 is "a conservative screening criteria selected to ensure the detection of all sites where there is an unfavorable balance between acid generation and neutralization reactions..." Table 1 provides an example of NPR screening criteria for the potential of a mine-waste material to produce ARD. The relative usefulness of NPP versus NPR is affected by the absolute amounts of sulfide sulfur and neutralization potential in the material in question. Very small values might be better evaluated by the ratio (NPR) than the difference (NNP) because of the potential impact of analytical uncertainty.

Many problems associated with NNP and NPR interpretations are directly attributable to the methods used to determine AP and NP. AP and NP determinations involve static procedures, which do not directly take into account rates of reactions. These procedures originally were developed for coal overburden and wastes. Several AP and NP procedures exist, and these procedures often yield different results. The Sobek method (Sobek and others, 1978), and modifications thereof (Coastech, 1989; Lawrence, 1990), is the most commonly used approach for determining ABA. Some guidelines have been developed by permitting and regulatory agencies (e.g., Price and Errington, 1998), but there is no standard procedure for conducting ABA. Furthermore, even methods that have been codified as ASTM or EPA methods with specific, detailed procedures are routinely modified by commercial analytical laboratories but not marketed as a "modified" method. Such methods may or may not be inferior to the standard method, but such variability makes comparisons among data sets unreliable. Price (1997) recommends the following analyses be performed for ABA determination:

1. Total sulfur, acid leachable sulfate sulfur, acid insoluble sulfate sulfur, sulfide sulfur, and organic sulfur
2. Bulk neutralization potential
3. Carbonate carbon
4. pH

Table 1. Neutralization potential ratio (NPR) screening criteria (from Price, 1997).

[ARD = acid-rock drainage; Note that these are screening criteria and that most sites require further characterization beyond the screening stage.]

| ARD Potential | NPR | Comments |
|---------------|-------|--|
| Likely | < 1 | Likely ARD generating unless sulfide minerals are non-reactive |
| Possibly | 1 - 2 | Possibly ARD generating if NP is insufficiently reactive or is depleted at a faster rate than sulfides |
| Low | 2 - 4 | Not potentially ARD generating unless significant preferential exposure of sulfides along fracture planes, or extremely reactive sulfides in combination with insufficiently reactive NP |
| None | > 4 | No further ARD testing required unless materials are to be used as a source of alkalinity |

Coastech (1989), Smith and others (1992), Kania (1998), White and others (1998, 1999), and the EnviroMine web site provide an overview of procedures to determine AP and NP. Generally, AP is determined by a sulfur assay (either total sulfur or sulfide sulfur). The form of sulfur used in AP determinations is an area of dispute. It is worth remembering that “sulfur forms” are analytically defined (e.g., “sulfide sulfur” is defined as nitric-acid-soluble sulfur even though not all sulfide minerals are soluble in nitric acid). Use of total sulfur in the AP calculation can overestimate AP, but use of other forms of sulfur can underestimate AP, especially if sulfides have been oxidized to sulfates prior to testing. Total sulfur is the most reproducible and verifiable approach to determine the maximum potential acidity (Brady and Smith, 1990). American Society for Testing and Materials (ASTM) methods for total sulfur include D4239-97e1 (Standard Test Methods for Sulfur in the Analysis Sample of Coal and Coke Using High Temperature Tube Furnace Combustion Methods) and D3177-89 (1997, Standard Test Methods for Total Sulfur in the Analysis Sample of Coal and Coke, Method A---Eschka, Method B---Bomb Washing Method). A standard C - S method is currently being developed under ASTM (Draft Test Method for the Analysis of Metal Bearing Ores and Related Materials by Combustion Infrared Absorption Spectrometry, updates are available through <<http://shell.rmi.net/~chb/chemist.html>>). Procedures for determining forms of sulfur are given in Sobek and others (1978), Coastech (1989), and Lawrence (1990).

There is a factor of 31.25 that is typically used to convert weight percent sulfur to standard units of AP (kg CaCO₃ / T rock). It is based on the assumption that all sulfide sulfur is present as pyrite and that all pyrite oxidizes according to a stoichiometry that results in two protons per mole of pyrite. Different sulfide minerals or different reaction paths necessarily mean that the 31.25 factor is incorrect.

Generally, NP is determined by acid digestion followed by titration with a base. The NP procedure usually begins with a fizz test. The fizz test is done by adding one-to-two drops of 25% hydrochloric acid to the sample (Sobek and others, 1978). The observer rates the extent of reaction and adjusts the amount and strength of acid used for sample digestion accordingly. Data reported by Evans and Skousen (1995) and Skousen and others (1997) indicate that there are problems with this subjective fizz test, and that the amount and strength of acid used to digest a given sample can affect the NP results. It should be noted that not all laboratories perform the fizz test and defer to only one concentration and volume of acid. Also, the presence of siderite in a sample can lead to erroneous NP results. Skousen and others (1997) suggest using a peroxide step in the procedure to address this problem. It is important to be aware of these types of issues when evaluating NP data.

Measurement of NP is often problematic because many common rock-forming minerals are able to neutralize acid but vary greatly in their neutralization capacity and reaction rates. Mineralogic composition controls the ability of a given material to produce or neutralize acid (see previous discussions in this chapter). Morin and Hutt (1994, 1997) make the distinction between effective NP and potential NP sources. Effective NP is the ability of a potential NP source to neutralize acid and maintain pH-neutral conditions, which is highly dependent on the rate of acid production and the rate of neutralization. Generally, carbonates dissolve relatively quickly whereas sulfides tend to oxidize more slowly. Hence, a mine-waste material may initially generate non-acidic drainage, but eventually may generate acidic drainage as the carbonates become depleted or armored with weathering products of pyrite oxidation (e.g., iron oxides). Conversely, aluminosilicate minerals tend to dissolve relatively slowly and can only effectively

neutralize acid if the acid production rate is also fairly slow. Hence, if non-carbonate minerals are a significant source of acid neutralization in laboratory tests, then kinetic testing is needed to predict the effective field NP (Price, 1997).

A phased approach to ARD prediction (e.g., simple static tests followed by kinetic testing when necessary) has been suggested by several sources. For example, the B.C. Research Confirmation Test is designed to follow the B.C. Research Initial Test when a test sample is found to be potentially acid producing (Bruynesteyn and Hackl, 1984). However, as noted above, there are no required standard procedures or approaches, and different approaches and different laboratories can generate disparate results.

A subset of ABA tests that are more easily performed in the field include the Net Acid Production (NAP, Coastech, 1989), Net Acid Generation (NAG, Miller and others, 1990), Acid Concentration Present (ACP, C. Bucknam, written communication; <<http://shell.rmi.net/~chb/chemist.html>>), and paste pH (see previous discussions in this chapter) tests. The NAP and NAG are based on addition of hydrogen peroxide to accelerate the oxidation of sulfide minerals. The resulting acid attacks potentially neutralizing minerals. The ACP test determines the presence of acidic material on mine-waste samples.

KINETIC TESTING

Kinetic tests have been developed to simulate or examine weathering of mine-waste material. These types of tests target the relative rates of reactions of acid producing and acid neutralizing constituents, and generally are used when static ABA tests determine that a test material is in the "gray area" for ARD production. Kinetic tests also can be used to examine the leachability of chemical constituents in the waste material as a function of time. Kinetic tests tend to be expensive and time consuming (varying from several weeks to over a year in duration). Common types of kinetic tests include humidity cells, lysimeters, Soxhlet extractions, column tests, shake-flask tests, biological tests, field-test pads, mine-wall washing, and examination of site drainage. This wide variety of tests measures different parameters, and the tests are not interchangeable (see table 2). Current common practice for obtaining laboratory kinetic data (e.g., humidity cell tests) generally does not allow for scaling up and extrapolating to field weathering rates. Also, common laboratory practice does not routinely quantify important experimental variables, such as temperature, relative humidity, and effects of freezing and thawing, grain size, surface area, and airflow. As a consequence, results may be difficult to compare. The interpretation of kinetic test results can be very complicated, depending upon the mineralogy of the samples tested, their origin, and their history. Valid interpretation depends upon solid knowledge of sample petrology and mineralogy, size distribution, and liberation characteristics (Price, 1997). Overviews of kinetic testing can be found in Coastech (1989), Perkins and others (1995), Hornberger and Brady (1998), and on the EnviroMine web site.

Humidity cell tests are the most commonly used laboratory kinetic tests. An American Society for Testing and Materials (ASTM) method has been adopted for humidity cell tests. The scope of this method (number D5744-96), titled *Standard Test Method for Accelerated Weathering of Solid Materials Using a Modified Humidity Cell*, states that "this test method covers a procedure that accelerates the natural weathering rate of a solid material sample so that diagnostic weathering products can be produced, collected, and quantified. Soluble weathering products are mobilized by a fixed-volume aqueous leach that is performed, collected, and analyzed weekly. When conducted in accordance with the following protocol, this laboratory test method has accelerated metal-mine waste-rock weathering rates by at least an order of magnitude greater than observed field rates."

A field procedure, termed Minewall, has been developed through the Canadian MEND Program and the British Columbia ARD Task Force (MEND, 1995). This procedure requires the cyclic irrigation of a small (1 m by 1 m), physically isolated, area of exposed pit wall or underground rock exposure, and the collection of leachate. This procedure is in its infancy but appears to provide an order of magnitude calculation of contributions from possible contaminant sources (Price, 1997).

LEACHING PROCEDURES

Although acid generation has received the most attention, leachable metals are a primary potential source of toxicity (Price and Errington, 1998). For many mine sites, metals are only mobile at fairly low pH (pH < about 5). However, some metals, such as zinc and manganese, can be mobile at circumneutral pH, and some metals are more mobile at higher pH (Smith and Huyck, 1999).

The U.S. Environmental Protection Agency (1994), state agencies, and industry often use the Toxicity Characteristic Leaching Procedure (TCLP, Method 1311) or the Synthetic Precipitation Leaching Procedure (SPLP, Method 1312). These tests were not designed for mining wastes; rather, the TCLP was designed to simulate leaching in a sanitary landfill. The TCLP involves leaching the test material with acetic acid, which preferentially binds lead due to a strong complex between lead and acetate. It is required under the Resource Conservation and

Recovery Act (RCRA) to define a hazardous waste. The SPLP comes closest to simulating conditions in a waste-rock dump (Smith, 1997). There is now a fairly sizable database of information about a variety of mine sites using these leaching methods. The SPLP has been designated an American Society for Testing and Materials (ASTM) method (D6234-98 Standard Test Method for Shake Extraction of Mining Waste by the Synthetic Precipitation Leaching Procedure).

Table 2. Test conditions for various kinetic tests (from Price, 1997). [Primary? = whether the measurement objective is primary mineral weathering or secondary mineral solubility]

| Test Procedure | Field or Lab | Scale | Primary? | Drainage Chemistry? |
|-----------------------|--------------|-------------------------|----------|--|
| Humidity cell | Lab | Bench, < 6 mm particles | Yes | With numerical geochemical models or site drainage |
| Column | Lab | Bench to pilot | No | Yes |
| Soxhlet extraction | Lab | Bench | Yes | No |
| Field test pads | Field | Pilot | No | Yes |
| Wall washing stations | Field | 1 m ² | Yes | With numerical geochemical models or site drainage |
| Site drainage | Field | Real | No | Yes |

Another commonly used test is the Nevada Meteoric Water Mobility Procedure (MWMP). Originally, the procedure was similar to the SPLP but recently has been substantially modified. The current procedure involves a much larger volume of rock with larger particle sizes and is conducted in six-inch-diameter columns. This procedure is currently being reviewed for ASTM codification.

A significant issue related to leaching tests is the interpretation. To what standards should the results be compared? The standards set by EPA for the TCLP results are apparently based on the assumption that a leachate would be diluted by clean water by 100-fold prior to being used as a drinking water source. It seems clear that the evaluation of leachability results requires an examination of the applicability of the test conditions to the site in question, an assessment of the dilution factors that might occur at the site upstream of a potential receptor, and the water-quality guidelines that should be applied (e.g., aquatic, agricultural, etc.).

GEOLOGIC MATERIALS THAT CONTRIBUTE TO ENVIRONMENTAL SIGNATURES

A variety of different types of geologic materials can be present on a site depending on the site history. At many historical mines, open-air roasting of sulfide minerals, on-site milling, smelting, and mineral processing occurred at different times and in different parts of the mine area. Older mine waste piles are more likely to contain elevated metal concentrations because of improvements in ore recovery over time. More modern tailings may be highly reactive because of their very fine grain size. On-site smelting may be represented by slag piles and may have contributed elevated metals concentrations to soils over a large area surrounding the smelter sites, depending on the prevailing winds. High-grade ore may remain on-site in stockpiles that were never processed. The following discussion gives an overview of terms encountered in studying solid materials.

Terms related to metals in the environment

Geoavailability: That portion of the total content of a chemical element or compound in an earth material that can be liberated to the surficial or near-surface environment through mechanical, chemical, or biological processes (Smith and Huyck, 1999). Characterization of the mineralogy and chemistry of solid earth materials provides information about geoavailability because geoavailability is a function of total metal content as well as access and susceptibility to weathering.

Bioavailability: The degree to which a contaminant in a potential source is free for uptake (movement into or onto an organism) (Newman and Jagoe, 1994). Bioavailability is a function of geoavailability as well as other factors such as mobility and biologic specificity (Smith and Huyck, 1999). Sequential extractions and leach studies on solid materials can contribute information about the potential bioavailability of elements.

Toxicity: The capacity of an element or a chemical compound to adversely affect any biological function (Smith and Huyck, 1999). In order for an element to be toxic to an organism, it must first be bioavailable. Characterization of solids can provide information about source and transport of potentially toxic materials and identify target areas or materials for follow-up toxicity studies, but does not in and of itself provide any information about toxicity.

Geologic materials related to mine sites

Tailings: Residue of raw material or waste separated out during the processing of crops or mineral ores (USEPA, 1997a). AGI (1997) includes the following definitions: (1) the gangue and other refuse material resulting from washing, concentration, or treatment of ground ore. (2) Those portions of washed ore or coal that are regarded as too poor to be treated further, as distinguished from the concentrates, or material of value. (3) The reject from froth flotation cells. Mill tailings are the waste remaining after physical or chemical extraction of the mineral of interest. Tailings are discharged into impoundments as a very fine-grained wet slurry. At many historical mines, tailings were discharged directly into streams or rivers. Tailings are finer-grained and mineralogically different from other mine waste materials; chemical reagents and solids formed in the flotation process become part of the tailings sediment along with primary minerals. A number of recent case studies of tailings at active and inactive mines document the mineralogy, chemistry, techniques for study, and processes that operate within tailings from different types of mineral deposits (e.g., Al and others, 1994; Dold, 1999; Blowes and Ptacek, 1994; Blowes and others, 1994).

Mine waste: Residue resulting from the extraction of raw materials from the earth. (USEPA, 1997a). Most of the dumps encountered at historic abandoned mines are designated as mine waste, which may include some comminuted material. Materials that are discarded as mine waste can vary over the life of a mine. Many of the massive sulfide mines in the eastern U.S. for example were worked at shallow levels to mine gossan for iron production or to mine pyrite for sulfuric acid production and then later worked by underground methods for base metals. Thus, the pyrite that comprised ore in the early days of mining became a waste product later on. Areas around ore bins and loading chutes may represent “hot spots” of metal concentrations due to weathering of exposed ores. We include hand-sorted ore piles that remain at many abandoned mines as mine waste. Most mine waste piles in the Rocky Mountain region, and many waste piles in other areas, resulted from exploration rather than from actual production.

Spoil: Dirt or rock removed from its original location – destroying the composition of the soil in the process - as in strip mining, dredging, or construction. (USEPA, 1997a). This term is commonly used in coal mining, but occasionally creeps into use for “mine waste” or “tailings” related to metal mining, especially in the eastern U.S.

Slag: The top layer of the multilayer melt formed during some smelting and refining operations. In smelting, slag contains the gangue minerals and the flux. (AGI, 1997; other definitions also). Slag is an impure residue, consisting largely of calcium, iron, aluminum, and magnesium silicate, derived during the process of pig iron and steel production and during the smelting of metals, such as copper, lead, and nickel. Slag from modern iron and steel production is environmentally benign and is used for aggregate, railroad ballast, soil conditioning, and a variety of other applications. Slag from historical metal mining however, can be a source of contamination in dust, soil, ground or surface water. For example, the Palmerton zinc pile site in Pennsylvania became a Superfund site due to lead, zinc, and cadmium contamination associated with 33 million tons of slag from a zinc smelting operation.

Stream sediments: Stream sediment sampling is a well-established tool in mineral exploration that also provides important information about the geoenvironmental signature of a mineral deposit. For regional-scale screening, national databases such as the National Uranium Resource Evaluation (NURE) and databases from past mineral exploration can highlight areas that may be anomalous in certain metals (Smith, 1997; Grossman, 1998). For on-line access to NURE data, see:

<http://greenwood.cr.usgs.gov/pub/open-file-reports/ofr-97-0492/>

Geochemical maps showing the distribution of copper, lead, and zinc in stream sediments in the upper Arkansas River basin in Colorado (Smith, 1994) allowed Church and others (1994) to identify ten metal sources in the basin that had anomalous lead in addition to the known source in the Leadville mining district. In another study, Church and others (1997) coupled bed sediment studies with water, and suspended colloid studies to identify large metal loads and to examine movement and partitioning of metals in the Animas River watershed in Colorado. The Animas

River drains three significant mineral districts (epithermal deposits, placer gold, unexposed porphyry molybdenum deposits). The synoptic study identified the particular drainage basin in the watershed that was the source area for metals in the river, and showed that metal partitioning among different phases depended on metal source, stream pH, and flow rate. Colloids (0.001 to 0.45 microns) carried most of the metal load in bed sediments in some parts of the watershed, where they formed aggregates and settled until flushed by high flow during snowmelt runoff.

Other sample media

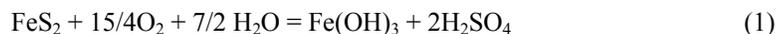
Other solid materials that may be sampled for mineralogy and chemistry to understand the concentrations of major and trace elements include soils and slag. Smith and Huyck (1999) discuss geoavailability and element concentration ranges in soils and vegetation. Analysis of plants and organisms, such as tissue sampling, provides information on bioavailability and metal distributions up the food chain. Such analyses are beyond the scope of this discussion; see Crock and others (1999) and references therein for additional information.

Environmental mineralogy

Primary minerals: For tailings, Jambor (1994) defined primary minerals as the ore and gangue minerals that were processed and deposited in an impoundment without any changes other than reduction in grain size by comminution. Primary ore and gangue mineral assemblages vary by deposit type. Thus, different types of copper deposits for example, can have very different mineral assemblages and consequently, very different environmental signatures. Recognition of different carbonate minerals is important because some carbonate minerals are effective at neutralizing acid (calcite, dolomite, ankerite) whereas iron- and manganese- carbonate minerals such as siderite and rhodochrosite are neutral or can actually produce acid. The “siderite” problem has been the focus of a number of modifications to acid-base accounting protocols to account for overestimates of neutralization potential obtained by assuming that all the carbonate in a sample is due to calcite (Skousen and others, 1997; Dold, 1999; White and others, 1999). Similarly, some silicate gangue minerals such as calcic feldspars, biotite, chlorite, amphibole, and pyroxene can contribute to acid-neutralization, albeit at much slower rates than calcite, and provide a source of aluminum, magnesium, and other elements that form secondary minerals.

Mineral assemblages for selected deposit types are listed in table 3, along with mineral formulas. Table 3 represents a generalized guide to minerals associated with different deposit types. Arsenopyrite, for example, would be expected in the ore mineral assemblages of most skarn or epithermal vein deposits but not in porphyry copper ores. Arsenic may be associated with other deposit types, but may be present as a trace element in pyrite rather than as a discrete, arsenic-rich mineral. Considerable mineralogic variations can exist within subtypes of these groups, as demonstrated by variations in pyrite: pyrrhotite among different classes of massive sulfide deposits.

The relative resistance of different sulfide ore minerals to weathering is variable, and depends on such factors as grain size, crystallinity, trace element content, and mineral assemblage (Kwong, 2000, 1993). The oxidation products formed depend on the type and composition of the mineral undergoing oxidation. Monosulfide minerals such as sphalerite and galena undergoing oxidation by oxygen do not release acidity (H^+) whereas disulfide minerals such as pyrite can release many moles of acid per mole of pyrite oxidized, depending on the oxidant (oxygen or ferric iron) and the reaction path (see for example, Plumlee, 1999, Table 3.2). Although a variety of different metal sulfide minerals contribute metals and sulfur to the environment upon weathering, it is the weathering of the iron sulfide minerals, especially pyrite, that leads to acid mine drainage. Fine-grained FeS_2 (pyrite or marcasite, especially the framboidal varieties commonly associated with coal or black shale) or finely-milled pyrite in tailings is especially reactive when subjected to wet-dry cycles and microbial oxidation; it is the mixture of air and water that leads to acid production. Pyrite (or marcasite) reacts with oxygen and water through a complex series of reactions (Nordstrom and Southam, 1997), which can be simplified in terms of overall reactants and products as:



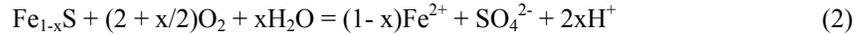
The actual oxidation paths are complex, and can involve oxidation by dissolved oxygen only, by ferric iron at low pH, and microbial catalysis of the aqueous oxidation of ferrous iron (Nordstrom and Southam, 1997; Nordstrom and Alpers, 1999). The ferric hydroxide oxidation product shown in equation (1) can include a variety of secondary oxyhydroxide or hydroxysulfate minerals such as goethite, ferrihydrite, schwertmannite, and jarosite that form oxidized zones on weathered tailings or mine waste dumps and precipitate along streams.

Trace elements in pyrite, which reduce its resistance to weathering and oxidation, typically include cobalt, nickel, selenium, or arsenic. As much as 6.5 weight percent As is present in arsenic-rich overgrowths on pyrite framboids in a sandstone aquifer in southeastern Michigan (Kolker and others, 1999a) and up to 4.5 weight percent

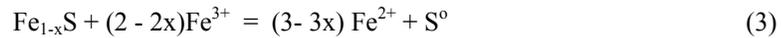
arsenic is reported in pyrite in coals in the Black Warrior Basin, Alabama (Kolker and others, 1999b).

Pyrrhotite oxidizes much more rapidly than pyrite (Robertson, 1994; Nicholson and Scharer, 1994). The amount of acid produced or consumed by pyrrhotite weathering depends on the particular oxidation path followed and the pyrrhotite composition. The general chemical formula for pyrrhotite is Fe_{1-x}S , where x can vary from 0.125 to 0. Reactions that have been proposed to describe pyrrhotite oxidation are as follows (from Jambor and Blowes, 1994):

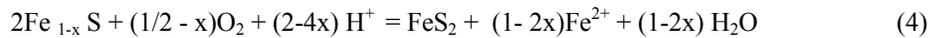
Complete reaction (amount of acid produced depends on pyrrhotite stoichiometry):



Partial reaction to produce native S:



Rapid oxidation to pyrite/marcasite (FeS_2) consumes acid:



Secondary minerals: Processes that can lead to precipitation include evaporation, oxidation, reduction, dilution, mixing, and neutralization (Alpers and others, 1994). Secondary minerals include efflorescent sulfate salts as well metal oxide, hydroxide, hydroxysulfate, and sulfide minerals. Dissolution and precipitation of secondary minerals is an important mechanism for recycling metals and acidity (H^+) in surficial environments. Based on studies of active mines and recent tailings impoundments, Jambor (1994) further distinguished tailings minerals as tertiary (crystallized from pore waters during drying) and quaternary (oxidation products that form during laboratory storage of dried samples). In some modern flotation plants, secondary materials formed by human activities may be precipitated as part of ore processing and end up as waste in tailings impoundments. For example, the zinc refining circuit at the Kidd Creek massive sulfide deposit operating in the 1980s produced natrojarosite, which formed 2.5% of the tailings solids (Al and others, 1994). Strictly speaking, “minerals” are naturally occurring or formed accidentally rather than through human intervention [see Jambor and Blowes (1998) for a detailed discussion]. For the purposes of this chapter, we use the term “secondary” to refer to all of the minerals that are not primary because the history and details of human intervention in many abandoned mines may be difficult to ascertain.

Secondary minerals found within a given deposit type can vary dramatically with climate. Many of the hydrated efflorescent salts, for example, are stable within only relatively narrow ranges of temperature and relative humidity. A study of porphyry copper mine tailings in different climate zones in Chile (Dold, 1999) showed that although the primary sulfide mineral assemblage of three different deposits was similar (pyrite, chalcopyrite, bornite, molybdenite, with minor magnetite and hematite), the secondary mineral assemblages that developed on the tailings surfaces differed markedly. In a hyper-arid climate with high rates of evaporation throughout the year (precipitation about 20mm/year), an evaporite zone formed at the top of the tailings pile containing the secondary mineral assemblage: jarosite, vermiculite, schwertmannite, gypsum, chalcantite, halotrichite, hexahydrite, bonattite, pickeringite, and magnesioauberite. In more humid climates (precipitation >540 mm/year), no evaporite zone was noted. In the more humid settings, oxidized tailings contained jarosite, vermiculite, schwertmannite, and gypsum and where evaporation is important during part of the year, the highly soluble mineral chalcantite was reported in the oxidized zone.

Some of the commonly encountered secondary minerals are listed in table 4, grouped by mineral type. This is not an exhaustive list. Different secondary minerals may appear at different times at the same deposit and in different parts of a site. Melanterite is one of the most commonly reported efflorescent salts from a variety of different deposit types. Gypsum, which does not contribute acidity, is ubiquitous if calcium and sulfate are available. Many of the sulfate minerals are highly soluble, and readily dissolve during rainstorms. Pure melanterite, for example, has a solubility of 15.65 grams/cc in cold water, whereas gypsum has a solubility of 0.241 grams/cc, and the ferric iron sulfate mineral coquimbite is extremely soluble, at 440 grams/cc cold water (Weast, 1986). Many of the minerals in table 4 are solid solutions. Element substitutions, as well as acid strength of solvents, can decrease solubility. See Jambor and others (2000) for a detailed discussion of solid solution ranges and stabilities of metal-sulfate salts formed from sulfide mineral oxidation.

Some of the minerals included as ore minerals (Table 3A) such as covellite and chalcocite are actually secondary minerals formed by supergene alteration (near-surface alteration by meteoric waters) of primary minerals.

Climate and topography affect the extent of weathering products that develop in mineral deposits. In deeply weathered deposits, any primary sulfide minerals that were once exposed at the surface are oxidized and decomposed and what remains is a surface cap of reddish-brown, iron-oxide-rich gossan. Gossan typically has an earthy or cellular texture and many ore deposits have been discovered by exploration for gossans. The unweathered primary sulfide minerals lie below the gossan, and as the primary sulfide minerals interact with groundwater, an intermediate zone of supergene enrichment can develop as the sulfide minerals at the surface dissolve and leach elements (such as copper) downward. Supergene zones can be tens of feet thick depending on water table fluctuations and weathering history of a deposit, and can constitute very high-grade ores. Secondary carbonate, sulfate, and silicate minerals may occur with secondary sulfides in supergene zones. Processes of alteration that form gossans are similar to processes that operate on mine dumps and tailings. Studies of the chemical, mineralogic, and textural changes in gossan provide clues to transport and fate of metals during weathering (Boyle, 1994). Some analogies can be drawn between gossan formation and the zones that develop in weathered tailings to the extent that both develop leached, sulfide-depleted caps enriched in iron oxides and hydroxides that overlie zones of precipitation of secondary minerals. However, tailings have much of the primary ore removed and are finely comminuted materials with lots of surface area available for oxidation reactions (Jambor, 1994). In addition, tailings may be very heterogeneous in mineralogy and texture both laterally and vertically, depending on how the tailings pile was constructed, and they may contain reaction products from addition of reagents, such as lime, during mineral processing.

Efflorescent salts

Efflorescent salts are secondary metal-sulfate minerals that form from the weathering of sulfide minerals. Many salts are highly soluble, hydrated solid solution minerals that react in changing weather conditions; salts exert an important control on metal mobility from mine wastes. Salts can form in open spaces in arid climates or during dry periods in normally humid climates, or can form under protected overhangs. During rainstorms or snow melt, the soluble salts dissolve and contribute metals and acidity to surface runoff. Capillary action draws waters to tailings, soil, rock, or wood surfaces where it evaporates to form salt crusts. Observations of storm runoff at the Sulfur massive sulfide mine in central Virginia (Dagenhart, 1980) demonstrated that dissolution of efflorescent salts from mine tailings can elevate the peak metal load in a nearby creek to as much as fifty times base-flow metal loads. Because salts can store acidity that can be released on dissolution, minor amounts of salts within tailings and mine dump soils contribute to low paste pH values. Many of the soluble efflorescent salt minerals are white or yellowish. Brightly colored salts (green, blue, purple) usually indicate a transition metal, such as iron or copper, and therefore provide a clue that metals are being sequestered. Salts can be tested in the field for dissolution and acidity generated with a little water and a pH indicator. Yellow efflorescent salts like copiapite are sometimes misidentified as elemental sulfur in the field. Although these minerals are characteristic of mine waste environments, they can occur on natural outcrops of sulfide-bearing rock away from mineralized areas and can contribute to acidity and metals. Fresh exposures of sulfide-bearing bedrock produced by road cuts, or landslides are especially prone to weathering that produces acid rock drainage. Acid rock drainage can form naturally or can be induced by human activity and can mimic acid mine drainage.

The presence of sulfate minerals is important to recognize because some sulfate minerals, such as barite, are relatively insoluble and therefore sequester barium from dissolution in surface waters whereas highly soluble minerals, such as melanterite or rozenite, are ready sources of iron. Furthermore, the acid-generating potential of a mine waste can be overestimated if one assumes that total sulfur equals sulfide sulfur when in fact much of the sulfur is present as sulfate in barite or gypsum (White and others, 1999). Nordstrom and Alpers (1999) identified ten different soluble iron sulfate salts in addition to gypsum and chalcantinite at the Richmond mine (Iron Mountain, CA massive sulfide deposit). They noted stalactites and stalagmites of rhomboclase in underground workings and other salts coating adit walls and ceilings. They used the chemical information provided by identification of the salts to estimate the mine pool composition that would develop if the mine was plugged and the large quantity of salts dissolved. Secondary ferric iron sulfate minerals, such as copiapite, romerite, and coquimbite (table 4), are commonly reported forming on coal mine wastes. Dissolution of these salts releases Fe^{3+} , which can promote acid generation by pyrite oxidation or hydrolysis (Cravotta, 1994).

Table 3. Mineralogy of selected deposit types. [Mineral formulas after Mandarino, 1999; X, major; x, minor; S, supergene]

A. Ore minerals.

| Class of deposits | | Massive sulfide deposits | | | Porphyry-related deposits | Carbonate-hosted deposits | Gold deposits | Epithermal vein deposits | Mercury deposits | | | | | | |
|------------------------|--|--------------------------|--------|--------|---------------------------|---------------------------|---------------|--------------------------|------------------------------------|-----|-----------------------------|---------------------------------|---------------|---------------------|---------|
| Deposit model | | Sed Ex | Kuroko | Besshi | Cyprus | Porphyry | Climax | Cu, Au, and Pb-Zn skarns | Sn and(or) W skarn and replacement | MVT | Low-sulfide Au-quartz veins | Creede-, Comstock and Sado-type | Hot-spring Hg | Silica-carbonate Hg | Almaden |
| acanthite | Ag ₂ S | X | S | X | | | | | | | | x | | | |
| arsenopyrite | FeAsS | x | | | | | | X | X | x | X | x | | | |
| Bi (native) | Bi ^o | | X | X | | | | | x | | x | | | | |
| bismuthinite | Bi ₂ S ₃ | x | | X | | | | x | | | | | | | |
| bornite | Cu ₅ FeS ₄ | | X | X | S | X | | X | x | x | | X | | | |
| boulangerite-boursaite | Pb ₅ (Sb,Bi) ₄ S ₁₁ | X | X | | | | | | | | | | | | |
| carrollite | Cu(Co,Ni) ₂ S ₄ | | | X | | | | | | | | | | | |
| cassiterite | SnO ₂ | x | X | | | | x | | X | | | | | | |
| chalcocite | Cu ₂ S | | S | S | | S | | S | | x | | | | | |
| cinnabar | HgS | | | | | | | | | | | | X | X | |
| chalcopyrite | CuFeS ₂ | x | X | X | X | X | | X | x | x | x | X | | | |
| cobaltite | CoAsS | x | | X | | | | x | | x | | | | | |
| corderoite | Hg ₃ S ₂ Cl ₂ | | | | | | | | | | | | X | | |
| covellite | CuS | | S | S | | S | | | | S | | | | | |
| Cu (native) | Cu | | | S | X | | | | | | | | | | |
| cubanite | CuFe ₂ S ₃ | | x | x | | | | | | | | | | | |
| cuprite | Cu ₂ O | | X | S | X | | | | | | | | | | |
| digenite | Cu ₉ S ₅ | | S | | S | | | | | | | | | | |
| djurleite | Cu ₃₁ S ₁₆ | | | | S | | | | | | | | | | |

| Class of deposits | | Massive sulfide deposits | | | | Porphyry-related deposits | | Carbonate-hosted deposits | | Gold deposits | Epithermal vein deposits | Mercury deposits | |
|--------------------|---|--------------------------|---|---|---|---------------------------|---|---------------------------|---|---------------|--------------------------|------------------|---|
| electrum | AuAg | | x | x | | x | | x | | X | x | | |
| enargite | Cu ₃ AsS ₄ | x | S | | | x | | x | | | | | |
| gahnite | ZnAl ₂ O ₄ | | X | | | | | | | | | | |
| galena | PbS | X | X | x | | x | | x | X | X | X | | x |
| hematite | α-Fe ₂ O ₃ | | x | | | | X | X | | | X | | |
| ilmenite | Fe ²⁺ TiO ₃ | | X | X | | | | X | | | | | |
| loellingite | FeAs ₂ | X | | X | | | | | | | | | |
| mackinawite | Fe ₉ S ₈ | | X | X | | | | | | | | | |
| magnetite | Fe ²⁺ Fe ³⁺ ₂ O ₄ | | X | X | | X | X | | x | | | | |
| marcasite | FeS ₂ | X | X | X | X | | | | | | x | | X |
| mercury (native) | Hg ⁰ | | | | | | | | | | | x | x |
| millerrite | NiS | x | | | | | | | | | | | X |
| molybdenite | MoS ₂ | x | X | X | | X | X | x | x | x | | | |
| pyrite | FeS ₂ | X | X | x | X | X | X | X | X | X | X | x | X |
| pyrrhotite | Fe _{1-x} S (x = 0 to 0.17) | X | x | X | x | | | X | X | x | X | | |
| rutile | TiO ₂ | | X | X | | | X | | | | | | |
| scheelite | CaWO ₄ | | | | | | | x | X | | | | |
| sphalerite | ZnS | X | X | X | X | x | | X | x | X | x | X | |
| stannite | Cu ₂ FeSnS ₄ | X | X | X | | | | x | | | | | |
| stibnite | Sb ₂ S ₃ | | | X | | | | | | | x | | |
| sulfosalts | variable (Ag,Sb,Cu,Fe,Pb) | x | x | x | | | | x | | | x | | |
| sulfur (native) | S ⁰ | | | | | | | | | | | | X |
| tetrahedrite group | (Cu,Fe,Ag,Zn) ₁₂ Sb ₄ S ₁₃ | x | x | x | | x | | x | | x | x | | |
| wolframite | (Fe,Mn)WO ₄ | | | | | | x | | x | | | | |

B. Gangue, alteration, and associated primary minerals.
 [* , generalized formula for mineral group]

| Class of deposits | | Massive sulfide deposits | | | Porphyry-related deposits | | Carbonate-hosted deposits | | | Gold deposits | Epithermal vein deposits | Mercury deposits | | |
|-------------------|---|--------------------------|--------|--------|---------------------------|-------------|---------------------------|--------------------------|------------------------------------|---------------|-----------------------------|----------------------------------|---------------|---------------------|
| | | Sed Ex | Kuroko | Besshi | Cyprus | Porphyry Cu | Climax Mo | Cu, Au, and Pb-Zn skarns | Sn and(or) W skarn and replacement | MVT | Low-sulfide Au-quartz veins | Creede-, Comstock, and Sado-type | Hot-spring Hg | Silica-carbonate Hg |
| adularia | KAlSi ₃ O ₈ | | | | | | | | x | | X | X | | |
| albite | NaAlSi ₃ O ₈ | X | X | X | | X | | | | X | | | | |
| alunite | K ₂ Al ₆ (SO ₄) ₄ (OH) ₁₂ | | | | | X | | | | | X | | | |
| amphibole* | Ca ₂ (Mg,Fe) ₅ Si ₈ O ₂₂ (OH) ₂ | | X | X | | X | | X | | | | | | |
| andalusite | Al ₂ SiO ₅ | | | | | x | | | | | | | | |
| anhydrite | CaSO ₄ | | x | | x | X | | | x | | | | | |
| ankerite | Ca(Fe,Mg,Mn)(CO ₃) ₂ | | | | | | | | | X | | | | |
| barite | BaSO ₄ | X | X | | | | | | X | | X | | | |
| biotite | K(Fe,Mg) ₂ Al ₃ Si ₂ O ₁₀ (OH) ₂ | | | | | X | | | | | | | | |
| calcite | CaCO ₃ | | | | x | x | | | | | X | | | X |
| chalcedony | SiO ₂ | | | | X | | | | | | X | | X | |
| chlorite* | (Mg,Fe) ₅ Al(Si ₃ Al)O ₁₀ (OH) ₈ | X | X | X | X | X | | X | | X | X | | | |
| clays* | variable | X | x | | X | X | | X | x | | X | X | | |
| dolomite | CaMg(CO ₃) ₂ | X | | | | | | | X | | | | X | |
| epidote | Ca ₂ (Fe ³⁺ ,Al) ₃ (SiO ₄) ₃ (OH) | | | | | X | | X | | | | | | |
| fluorite | CaF ₂ | | | | | | X | x | x | x | X | | | |

| Class of deposits | | Massive sulfide deposits | | | | Porphyry-related deposits | | Carbonate-hosted deposits | | | Gold deposits | Epithermal vein deposits | Mercury deposits | | | |
|-------------------|--|--------------------------|---|---|---|---------------------------|---|---------------------------|----------|---|---------------|--------------------------|------------------|---|---|---|
| garnet* | Ca ₃ Al ₂ (SiO ₄) ₃ | | | | | | | X | X | X | | | | | | |
| graphite | C | X | | | | | | | | | | | | | | |
| gypsum | CaSO ₄ .2H ₂ O | X | | | | | | | | x | | | | | | |
| kaolinite | Al ₂ Si ₂ O ₅ (OH) ₄ | | | | | | | | | | | X | | | | |
| muscovite | KAl ₃ Si ₃ O ₁₀ (OH) ₂ | X | X | | | | | | | | | X | | | | |
| pyrophyllite | Al ₂ Si ₄ O ₁₀ (OH) ₂ | | | | | | | | | | | X | | | | |
| pyroxene* | CaMgSi ₂ O ₆ | | | | | | | | | | | | | | | |
| quartz | SiO ₂ | X | X | X | X | X | X | X | X | X | X | X | X | X | X | X |
| rhodochrosite | MnCO ₃ | | | | | | | X | X(Pb-Zn) | | | X | | | | |
| rhodonite | (Mn,Fe,Mg,Ca)SiO ₃ | | | | | | | X | X(Pb-Zn) | | | | | | | |
| siderite | FeCO ₃ | | | | | | | | | | X | X | | | | |
| topaz | Al ₂ SiO ₄ (F,OH) ₂ | | | | | | | X | | | | | | | | |
| tourmaline | NaFe ₃ Al ₆ (BO ₃) ₃ Si ₆ O ₁₈ (OH) ₄ | X | X | X | | X | | | | X | | | | | | |
| vesuvianite | Ca ₁₀ Mg ₂ Al ₄ (SiO ₄) ₅ (Si ₂ O ₇) ₂ (OH) ₂ | | | | | | | | X | X | | | | | | |
| wollastonite | CaSiO ₃ | | | | | | | | X | X | | | | | | |

Table 4. Secondary minerals.

[*, highly soluble; !, relatively insoluble (mineral solubility depends on particle size and degree of crystallinity; mineral formulas from Mandarino, 1999)]

| | <u>Sulfate minerals</u> | | <u>Carbonate minerals</u> |
|-------------------|---|---------------------|---|
| alunogen* | $\text{Al}_2(\text{SO}_4)_3 \cdot 17\text{H}_2\text{O}$ | aurichalcite | $(\text{Zn}, \text{Cu})_5(\text{CO}_3)_2(\text{OH})_6$ |
| alunite | $\text{K}_2\text{Al}_6(\text{SO}_4)_4(\text{OH})_{12}$ | azurite | $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$ |
| anglesite! | PbSO_4 | cerussite | PbCO_3 |
| antlerite! | $\text{Cu}_3\text{SO}_4(\text{OH})_4$ | hydrozincite | $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ |
| argenobarrosite! | $\text{Ag}_2\text{Fe}^{3+}_6(\text{SO}_4)_4(\text{OH})_{12}$ | malachite! | $\text{Cu}_2\text{CO}_3(\text{OH})_2$ |
| barite! | BaSO_4 | smithsonite | ZnCO_3 |
| basaluminite | $\text{Al}_4(\text{SO}_4)(\text{OH})_{10} \cdot 5\text{H}_2\text{O}$ | | <u>Iron oxyhydroxide (ochre) minerals</u> |
| bassanite* | $2\text{CaSO}_4 \cdot \text{H}_2\text{O}$ | akageneite | $\beta\text{-Fe}^{3+}(\text{O}, \text{OH}, \text{Cl})$ |
| beaverite! | $\text{Pb}(\text{Cu}^{2+}, \text{Fe}^{3+}, \text{Al})_6(\text{SO}_4)_4(\text{OH})_{12}$ | bernalite | $\text{Fe}^{3+}(\text{OH})_3 \cdot n\text{H}_2\text{O}$ (n=0 to 0.25) |
| beudantite | $\text{PbFe}^{3+}_3(\text{AsO}_4)(\text{SO}_4)(\text{OH})_6$ | ferrihydrite | $5\text{Fe}^{3+}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$ |
| bianchite* | $(\text{Zn}, \text{Fe}^{2+})\text{SO}_4 \cdot 6\text{H}_2\text{O}$ | goethite | $\text{Fe}^{3+}\text{O}(\text{OH})$ |
| bilinite | $\text{Fe}^{2+}\text{Fe}^{3+}_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}$ | hematite | $\text{Fe}^{3+}_2\text{O}_3$ |
| brochantite! | $\text{Cu}_4(\text{SO}_4)(\text{OH})_6$ | lepidocrocite | $\text{Fe}^{3+}\text{O}(\text{OH})$ |
| chalcantinite* | $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ | maghemite | Fe_2O_3 |
| copiapite* | $\text{Fe}^{2+}\text{Fe}^{3+}_4(\text{SO}_4)_6(\text{OH})_2 \cdot 20\text{H}_2\text{O}$ | | <u>Other minerals</u> |
| coquimbite* | $\text{Fe}^{3+}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ | bindheimite | $\text{Pb}_2\text{Sb}_2\text{O}_6(\text{O}, \text{OH})$ |
| dietrichite* | $(\text{Zn}, \text{Fe}^{2+}, \text{Mn})\text{Al}_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}$ | chalcophanite | $(\text{Zn}, \text{Fe}^{2+}, \text{Mn}^{2+})\text{Mn}^{4+}_3\text{O}_7 \cdot 3\text{H}_2\text{O}$ |
| epsomite* | $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ | chlorargyrite group | $\text{Ag}(\text{Cl}, \text{Br})$ |
| ferricopiapite* | $\text{Fe}^{3+}_{2/3}\text{Fe}^{3+}_4(\text{SO}_4)_6(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ | chrysocolla | $(\text{Cu}^{2+}, \text{Al})_2\text{H}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot n\text{H}_2\text{O}$ |
| ferrohexahydrite* | $\text{FeSO}_4 \cdot 6\text{H}_2\text{O}$ | cinnabar | HgS |
| fibroferrite! | $\text{Fe}^{3+}(\text{SO}_4)(\text{OH}) \cdot 5\text{H}_2\text{O}$ | coronadite | $\text{Pb}(\text{Mn}^{4+}, \text{Mn}^{2+})_8\text{O}_{16}$ |
| goslarite* | $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ | ferrimolybdite | $\text{Fe}^{3+}_2(\text{Mo}^{6+}\text{O}_4)_3 \cdot 8\text{H}_2\text{O}(?)$ |
| gunningite* | $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$ | ilsemanite | $\text{Mo}_3\text{O}_8 \cdot n\text{H}_2\text{O}(?)$ |
| gypsum | $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ | litharge | PbO |
| hexahydrite* | $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ | luzonite | Cu_3AsS_4 |
| halothrichite* | $\text{FeAl}_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}$ | olivenite | $\text{Cu}_2(\text{AsO}_4)(\text{OH})$ |
| hinsdalite | $(\text{Pb}, \text{Sr})\text{Al}_3(\text{PO}_4)(\text{SO}_4)(\text{OH})_6$ | psilomelane group | $(\text{Ba}, \text{H}_2\text{O})_2(\text{Mn}^{4+}, \text{Mn}^{3+})\text{O}_{10}$ |
| jarosite! | $\text{KFe}^{3+}_3(\text{SO}_4)_2(\text{OH})_6$ | scorodite | $\text{Fe}^{3+}\text{AsO}_4 \cdot 2\text{H}_2\text{O}$ |
| jurbanite | $\text{Al}(\text{SO}_4)(\text{OH}) \cdot 5\text{H}_2\text{O}$ | | |
| kornelite | $\text{Fe}^{3+}_2(\text{SO}_4)_3 \cdot 7\text{H}_2\text{O}$ | | |
| leadhillite! | $\text{Pb}_4\text{SO}_4(\text{CO}_3)_2(\text{OH})_2$ | | |
| linarite! | $\text{PbCu}(\text{SO}_4)(\text{OH})_2$ | | |
| melanterite* | $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ | | |
| meta-aluminite | $\text{Al}_2(\text{SO}_4)(\text{OH})_4 \cdot 5\text{H}_2\text{O}$ | | |
| paracoquimbite* | $\text{Fe}^{3+}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ | | |
| pentahydrite | $\text{MgSO}_4 \cdot 5\text{H}_2\text{O}$ | | |
| pickeringite* | $\text{MgAl}_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}$ | | |
| plumbojarosite! | $\text{PbFe}^{3+}_6(\text{SO}_4)_4(\text{OH})_{12}$ | | |
| rhomboclase* | $(\text{H}_3\text{O})\text{Fe}^{3+}(\text{SO}_4)_2 \cdot 3\text{H}_2\text{O}$ | | |
| romerite* | $\text{Fe}^{2+}\text{Fe}^{3+}_2(\text{SO}_4)_4 \cdot 14\text{H}_2\text{O}$ | | |
| rozenite* | $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$ | | |
| schwertmannite | $\text{Fe}^{3+}_8\text{O}_8(\text{OH})_6(\text{SO}_4) \cdot n\text{H}_2\text{O}$ | | |
| serpierite! | $\text{Ca}(\text{Cu}, \text{Zn})_4(\text{SO}_4)_2(\text{OH})_6 \cdot 3\text{H}_2\text{O}$ | | |
| siderotil* | $\text{Fe}^{2+}\text{SO}_4 \cdot 5\text{H}_2\text{O}$ | | |
| szomolnokite* | $\text{Fe}^{2+}\text{SO}_4 \cdot \text{H}_2\text{O}$ | | |
| voltaite | $\text{K}_2\text{Fe}^{2+}_5\text{Fe}^{3+}_4(\text{SO}_4)_{12} \cdot 18\text{H}_2\text{O}$ | | |
| woodhouseite | $\text{CaAl}_3(\text{PO}_4)(\text{SO}_4)(\text{OH})_6$ | | |

Ochre deposits

Ochre deposits are concentrations of secondary iron minerals that form from the weathering and oxidation of iron sulfide minerals (Bigham, 1994). Ochres can include hardpan layers in and along streams, layers in tailings piles, soft crusts, and wet (typically slimy) precipitates and flocs that range from amorphous ferric hydroxide to well-crystallized minerals such as goethite and jarosite. “Yellowboy” in and along streams is a hallmark of acid mine drainage. Yellowboy is the informal name for the hydroxysulfate mineral schwertmannite (Bigham and others, 1994; Schwertmann and others, 1995), a poorly crystalline mineral that has only recently been characterized. Both schwertmannite and ferrihydrite (Chukrov and others, 1973), a very poorly crystalline oxyhydroxide mineral, are commonly referred to simply as “mine drainage minerals” (Bigham, 1994), especially in older literature. The exact formulas, solubilities, and the very existence of these minerals have been the subject of considerable debate (Yu and others, 1999).

Ochre minerals form by hydrolysis and precipitation of the iron available from sulfide oxidation reactions. Hydrous-oxide minerals form initially as polymers (nanometer size particles) that behave as amorphous solid phases (too poorly crystalline to produce an XRD pattern). These minerals can play a critical role in trace metal transport because they (1) produce acid on formation and (2) can adsorb metals at the solid-water interface, effectively removing them from contaminated waters. Furthermore, the hydrous-oxide minerals consume acid when they precipitate and release any adsorbed metals when they dissolve. All of these reactions are pH dependent. For example, iron and aluminum hydrous oxides adsorb Cu, Pb, and Hg in the pH range 3 to 5, and adsorb Zn, Co, Ni, and Cd at higher pH values (5 to 6.5). Desborough and others (2000) demonstrated that schwertmannite-rich ochre deposits dissolved and generated acid during passive serial leaching tests using deionized water. Within 24 hours, pH dropped from 5 to 3.5 in their 200:1 solute: solid ratio leaching experiment.

Ochres are typically iron-rich (up to 50 wt. %Fe) but highly variable in composition because they can incorporate other minerals (Winland and others, 1991). Because the iron-rich precipitates cement entrained debris, ochre hardpans (ferricrete) can contain significant Si, Al, and organic C as well as grains of ore minerals.

The self-mitigating capacity of mine waters (i.e., the ability of the water to clean itself up by removing dissolved metals from solution by metal sorption on freshly precipitated hydrous ferric oxides) is a function of the amount of dissolved iron and metals, the nature of the metals, and the ratio of available sites for binding to dissolved metals at a particular pH (Smith, 1999). Hammarstrom and others (1999a) found that Cu/Zn ratios in ochres precipitating from acidic waters were consistently lower than Cu/Zn ratios associated with near-neutral, reduced seeps at the same site. These data indicated that zinc, a metal that is generally difficult to remove in AMD settings, was locally sequestered in ochre deposits. The permanence of the ochres as sinks for various metals depends on the pH of the environment over time.

The particular ochre minerals that form vary as a function of pH, dissolved sulfate content, and availability of elements such as K, Na, or Si. Goethite is the most widespread mineral associated with acid drainage. Other ochre minerals are all transient relative to goethite as a stable end-product, following dissolution and reprecipitation of other minerals as conditions vary (Bigham, 1994). Low pH (3 to 4) and moderately high concentrations of dissolved sulfate (1,000 to 3,000 µg/L) favor schwertmannite formation. Schwertmannite and ferrihydrite, which are stable at higher pH and lower dissolved sulfate concentrations, are the two most common ochre precipitates associated with acid mine drainage (Yu and others, 1999). Ferrihydrite is commonly reported from coalmine drainage. Jarosite tends to form at lower pH (<3.0) and higher concentrations of dissolved sulfate. The jarosite crystal structure can incorporate K, Na, Pb, or H₃O⁺ resulting in the end-member minerals jarosite, natrojarosite, plumbojarosite, and hydronium jarosite, respectively. The spatial distribution of ochre minerals can be mapped using remote sensing tools such as imaging spectroscopy (Swayze and others, 2000) and spectral reflectance (Anderson and Robbins, 1998). Spectral techniques can be more effective than XRD for detecting small amounts of iron ochre minerals (Swayze and others, 2000) in surface materials.

TOOLS OF THE TRADE

Field observations and measurements

A number of different observations and measurements can be made in the field to assess the potential for acid mine drainage to develop and to evaluate abandoned mine sites. Kwong (1993) proposed a practical checklist for field measurements during the mineral exploration stage and emphasized the role that geologists can play in the prediction and prevention of acid rock drainage before mining commences. He noted, for example, that observations made on rock materials allow estimates of potential maximum acidity, neutralization capacity, and proportion of sulfide minerals susceptible to weathering. Such an approach allows industry to factor in mitigation up-front. Land managers faced with modern mineral development have the benefit of legally mandated environmental impact studies on which to base development decisions. However, when faced with thousands of

abandoned mines which were developed before modern state and federal regulations were enacted, land managers need quick and cost-effective tools for evaluation and prioritization of sites and allocation of money for clean-up. Given a watershed or national forest full of abandoned mine sites, where single sites may cover tens of acres, the task of characterizing and sampling solid materials is daunting. In table 5, we expand on Kwong's checklist for pre-mining field observations to include mine waste and tailings and additional site considerations. Maps, photos, and historical reports can be compiled beforehand to facilitate site visits - it can take a lot of time to find overgrown mine shafts and pits and identify the various parts of abandoned mine sites. GIS tools including mineral locality databases, smelter sites, etc., can be used to construct maps showing the location and nature of all known mining activities in an area to identify suitable areas for background or baseline sampling and to identify other sites that may have influenced the site of interest. Sometimes, older (15' or smaller scale) topographic maps are useful in historical mining districts because more mine-related features are shown than on newer maps. Short-term and seasonal weather variations that affect stream flow can also affect the distribution of solids materials. Efflorescent salts may be ubiquitous on a hot dry day and disappear following a rainstorm, so weather conditions before and during site visits should be noted. Highly soluble salts may be present even in very humid climates if there is a relatively protected place for them to form.

Field paste pH measurements provide a quick indication of readily available acidity or alkalinity in fine-grained mine waste materials. Like acid-base accounting, paste pH is a static procedure that provides no information about reaction rates. Paste pH procedures vary in amount of sample and standing time before measurement, but most methods use a 1:1 by weight solid: solution ratio on air dried material, distilled or deionized water, and a pH meter calibrated with pH 4.00 and pH 7.00 buffer solutions. The MEND (1990) method for metal mine paste pH determination is to mix 5 mL of deionized or distilled water with 10 grams of sieved (<60 mesh) sample and allow it to wet by capillary action without stirring. More water or sample is added as necessary to saturate the sample and a spatula is used to stir the sample to form a thin paste that just slides off the spatula. In the field, we modify this procedure by using the <2 mm fraction, weighing out 10 grams of sample in a disposable plastic beaker, adding 10 mL of water and stirring the paste gently with a disposable wooden coffee stirrer, and measuring the pH within 5 minutes with a calibrated pH meter equipped with an appropriate electrode for immersion in soil pastes. Our method is similar to ASTM method D4972-89, a laboratory method that calls for measurement on the <2 mm fraction in a 1:1 solid: solution ratio after the sample has been standing at room temperature for an hour. The recommended paste pH procedure used in British Columbia (Price, 1997) is a method described by Sobek and others (1978) and modified by Page and others (1982) that calls for 20 grams of solid and 20 mL of distilled water mixed for 5 seconds and allowed to stand for 10 minutes before measurement. Paste pH values < 5 suggest that the material contains acidity from prior acid generation whereas paste pH values >7 suggest the presence of reactive carbonate (Price, 1997). This test provides no mineralogic information, but can be a useful screening tool for identifying areas for further sampling. Paste pH measurements for a variety of mine waste materials from different types of mineral deposits are listed in table 4, along with total sulfur and total carbon determined on the same material. Paste pH measurements can vary by 2 or more pH units over a given mine site. The actual pH reading in the field is not especially significant - the important point is whether the pH goes acidic or neutral when the sample is wetted. As long as the field procedure is kept consistent, the results can be helpful in characterizing the distribution of readily available acidity on the site.

Useful field equipment

Pocket-type combination thermometer- hygrometers are handy for recording temperature and relative humidity in the field. Observations of water flow along outcrop fractures, ferricrete deposits, and seeps provide clues to the site hydrology. Color can provide clues about secondary minerals and pH. Munsell field soil color charts are useful for quantifying color variations and communicating color differences in a more or less objective manner. Dilute hydrochloric acid carried in a plastic dropper bottle is useful for identifying calcite (readily effervesces in cold HCl) and limestone in the field. Alizarin-red S is also useful because it stains calcite very bright red within 30 seconds of application (Desborough, written communication, 2000). Plastic gold pans are useful for panning heavy minerals to concentrate ore minerals. Pen-type magnets pick up magnetite and the magnetic form of pyrrhotite. Small shovels and augers can be used to determine the thickness of oxidized zones and expose profiles through tailings and mine waste dumps. Large syringes or turkey basters are practical for sampling wet precipitates and flocs in streams and seeps. Solder-free (lead-free) sieve screens are useful for field-sieving soil-size (<2 mm) fractions of mine waste and tailings and for sampling stream sediments. Note that the sieve opening is 2.00 mm for 10 mesh (USA ASTM standard), 9 mesh (Tyler mesh number), or 8 mesh (British standard). Portable battery-operated balances facilitate in-field paste pH measurements. Refillable epoxy pH electrodes are best suited to sludge and paste-type samples

and field use. Conductivity equipment can be used to identify inflows of mining effluent to streams. Alkalinity kits can be used to identify waters receiving acidic inflows or waters susceptible to acidic inflows.

Table 5. Field checklist for site assessment (modified from Kwong, 1993).

| <u>Type of material</u> | <u>Measurements and observations</u> |
|--|--|
| Rocks (ore, host rock, altered rock) | Lithology Mineralogy and texture Fizz test for carbonate Hand magnet (magnetite, some pyrrhotite) Ore minerals Nature and extent of weathering Fractures, joint density Water flow along fractures? Efflorescent salts (protected overhangs)? |
| Natural weathering products (gossan, soil, sediments) Mine waste Tailings | Mineralogy and texture Fizz test for carbonate Hand magnet (magnetite, some pyrrhotite) Ore and gangue minerals Panning and sieving Color (Munsell color charts) Moisture content Profile development (shovels, augers) Paste pH Presence and condition of vegetation Erosion Efflorescent salts Presence and distribution of hardpans Presence and distribution of seeps |
| Water bodies | pH, conductivity, alkalinity, dissolved oxygen Presence of secondary minerals Evidence of microbial activity (biofilms) |
| Other considerations | Weather (temperature, relative humidity, recent precipitation) Climate zone (weathering rate, metal transport) Ecozone Proximity of waste to an area of risk (stream, wetland) Site accessibility Topography Vegetation (natural wetlands, barren areas) |

Mineralogy

Instrumental techniques available for determinative mineralogy range from routine optical and scanning electron microscopy and x-ray diffraction to relatively recent microanalysis techniques that are largely used in mineralogic research (proton and ion microprobes, secondary ion mass spectrometry, etc.). Jambor and Blowes (1998) discuss theories and applications of mineralogy in environmental studies of sulfide-bearing mine-waste. Jambor (1994) describes sampling and methods for studying tailings and Bigham (1994) addresses methodologies applicable to ochre deposits. More sophisticated techniques are especially useful for determining trace element distributions and for studying mineral surfaces, but are beyond the scope of routine characterization of the solid phases. Therefore, we limit our discussion to the routine methods that we have applied to solids characterization in our development of geoenvironmental models. Interested readers are referred to Cabri and Vaughns' (1998) overview of modern approaches to ore and environmental mineralogy for an introduction to other techniques.

No one technique suffices to identify minerals. The very small grain size and complex intergrowths of secondary mineral assemblages can be extremely complicated to unravel. What appears to be a single phase under the optical microscope, such as a white efflorescent crust, may turn out to be a mixture of several phases with different compositions when examined by SEM. Qualitative x-ray energy dispersive spectra acquired by SEM and quantitative wavelength dispersive analysis by electron microprobe can identify most elements in a sample, but cannot distinguish ferrous from ferric iron, sulfide from sulfate sulfur, or provide quantitative data on water present.

Table 6. Paste pH values for mine waste (<2mm surface material) for different types of mineral deposits.

| Deposit type | Paste pH | Total sulfur (wt.%) | Total carbon (wt. %) |
|--|----------|---------------------|----------------------|
| Tungsten skarn | 2.6 | 7.7% | 0.23% |
| Polymetallic replacement (Carbonate-hosted) | | | |
| Dump | 7.5 | 0.79% | 8.18% |
| Mill tailings | 7.7 | 1.09% | 8.33% |
| Massive sulfide (Besshi-type) | | | |
| Dump | 2.1 | 3.77% | 0.1% |
| Flotation tailings | 3.0 | 1.04% | 0.2% |

X-ray diffraction (XRD)

X-ray diffraction has become an invaluable tool for characterizing solids because it provides a quick method for identifying minerals. Diffractograms represent a “fingerprint” of the minerals present in a sample that can be interpreted by comparison with standard reference patterns. Many automated search-match routines are available to access the JCPDS database of standard X-ray powder diffraction patterns (International Centre for Diffraction Data, 1997). Results of these programs must be interpreted with care and with some forehand knowledge of what minerals are likely (or unlikely) to be present. The number of different minerals present in mine waste and tailings can complicate interpretation of patterns. Furthermore, the presence of many of the secondary minerals (soluble, metastable, very poorly crystalline) typical of mine waste environments can pose problems in sample preparation and analysis. In addition to mineral identification, XRD can provide information about the relative abundance of a mineral in a mixture and the degree of crystallinity but not about composition. Amorphous can be a significant component of mine waste (see Chapter C). Materials that are not detected by XRD because they are amorphous or because they are present in concentrations too low to detect may still have a significant impact on surface runoff and infiltration waters. Therefore, chemical analysis and leach studies (Chapter C) as well as mineralogic studies are recommended for complete characterization of element mobility from mine wastes.

We routinely run splits of pulverized powders of mine waste chemistry samples as dry-mounted pressed powders in aluminum holders. Quartz is ubiquitous in many samples and serves as an internal standard; quartz or corundum or fluorite can be added to samples if necessary. Sample preparation is a critical step in x-ray powder diffraction because variables such as grinding, sample area, thickness, and packing can produce errors that complicate pattern interpretation (Bish and Reynolds, 1989). Pressed powder mounts have the advantage of providing an “infinite” sample thickness, but they require a fair amount (typically a gram or so) of sample. Small samples and minerals (hand picked under a binocular microscope or concentrated with heavy liquids) can be ground and mounted on glass or preferably zero-background quartz slides using toluene as a binder. Acetone and isopropyl alcohol are used as binders, but can affect metastable minerals. Metastable samples can be placed in capped plastic vials in the field (they make their own atmosphere) or in mineral oil to retard changes in hydration state during transport back to the lab. The mineral oil must be washed out, and grinding can dehydrate some hydrous minerals. In some cases, we have resorted to smearing the mush (a less than ideal sample surface) onto a quartz plate with a spatula to make a mount and running the pattern at a fast scan rate before it dehydrates. Environmental sample chambers are available for diffractometers that allow the sample to reside in a controlled atmosphere during the run; x-rays access the sample through a beryllium window in the sealed chamber. For very small samples, x-ray film techniques that use Debye-Scherrer or Guinier or Gandolfi cameras may be necessary for identification. Bish and Post (1989) provide a good reference for modern x-ray diffraction techniques.

Scanning electron microscopy

Scanning electron microscopy (SEM) can be used to determine crystal shape, size, and texture, obtain qualitative or semi-quantitative compositional information, and help identify minerals that are too small to be identified by other means. Scanning electron microscopes have been generally used as cameras for photographing specimens beyond the capabilities of ordinary optical microscopes. While the images obtained look like ordinary photographs, the apparent illumination is a function of emission of secondary electron (SE) particles detected with a SE detector and displayed on a scanning TV display. A bright image will be the result of high secondary electron emission, while the primary influence on high emission is the surface structure of the specimen. The end result therefore, is brightness associated with surface characteristics and an image, which looks very much like a normally illuminated subject. When the SEM is operated in backscattered mode, one can see differences in the images that reflect differences in composition. Backscattered electrons (BSE) are high energy electrons emitted from the specimen as a result of the high-energy electron beam's interaction within the specimen. BSE emission is the result of elastic events between primary electrons and other electrons within the specimen that are relatively tightly bound. BSE emission intensity is very much a function of the specimen's atomic number; i.e., the higher the atomic number (e.g., Fe(26) vs. Mg(12)), the brighter the image. Most SEMs are equipped with an energy-dispersive spectrometer (EDX) that provides a qualitative measure of the elements present in the sample in the form of a spectrum. Energy dispersive detectors (EDX) are quick and easy to use. Turn on the electron beam and the detector, and a display appears of all elements present. The disadvantages are relatively poor spectral resolution and low signal-to-noise, which results in many spectral interferences and poor sensitivity (relative to wavelength dispersive detectors used in electron microprobe analysis). Low-voltage and low-vacuum SEMs are available (generally referred to as "environmental" instruments) which accommodate samples with little or no sample prep such as hydrated or uncoated samples and biological materials.

Electron probe microanalysis (EPMA)

Electron probe microanalyzers (EPMA) are designed to analyze x-rays generated from the specimen when probed with an electron beam. The design considerations primarily accommodate three to six wave dispersive x-ray spectrometers, which are inherently large. Specimens prepared for x-ray microanalysis are generally flat and polished, and the microprobe analyzer is designed to allow only a considerable amount of x and y translation rather than the specimen manipulation which is typical of the SEM. In EPMA, wave dispersive technology is used to detect and count x-rays. These spectrometers are much more sensitive to low elemental concentrations than the energy dispersive detectors used in most SEM applications, and concentrations in the range of 100 ppm can generally be measured. EPMA is useful for obtaining quantitative chemical analyses of the major and minor elements in a mineral. Trace elements can be measured (Robinson and others, 1998), but a variety of other analysis methods such as ion probes, proton probes, or laser-ablation mass spectrometry are starting to be used in research studies of trace element distributions in earth materials. Limitations to EPMA are that not all specimens can be exposed to the high vacuum within the specimen chamber, elements lighter than atomic number 8 (oxygen) cannot be measured without reservations, and EPMA is not sensitive to many elements at concentrations below 100ppm. Analysis of hydrous minerals such as clays, iron oxyhydroxides, and efflorescent salts is possible but generally time-consuming because of the difficulty of obtaining good flat polished surfaces, suitable standards, and instability in both the vacuum and under the electron beam. Areas of samples can be mapped to show the distribution of various elements. X-ray element maps are powerful tools for monitoring chemical changes that accompany alteration and for identifying mineral grains or zones that contain elements of interest.

Geochemical analysis

A variety of different analytical techniques are available for geochemical analysis. The choice of method depends on the elements and detection limits sought, the amount and nature of the samples, and cost. Crock and others (1999) reviewed sample preparation and laboratory methods for total and partial analysis of major- minor- and trace elements in rock samples, soils, sediments, vegetation, and waters. Geologic materials can pose special problems for analysis because of matrix effects, extreme concentrations of a particular element such as iron, presence of refractory minerals, which are not readily dissolved in sample digestion, and elements that occur in different oxidation states. Methods developed within and (or) adopted by the USGS for analysis of geologic materials are described in detail in Arbogast (1990, 1996) and Baedecker (1987).

EPA test methods for evaluating solid waste are documented in SW-846, which includes information on quality control, choosing the correct procedure, and sampling considerations as well as protocols for physical and chemical analysis of inorganic and organic analytes. The EPA documents can be accessed on-line at:

The most commonly used multi-element methods are inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and inductively coupled plasma-mass spectrometry (ICP-MS). Detection limits by ICP-MS are orders of magnitude lower than detection limits for other methods, so very low concentrations of elements can be measured by this method and it is increasingly becoming the method of choice for trace element analysis of environmental samples. Crock and others (1999) evaluated relative advantages and disadvantages of different spectroscopic methods of analysis for environmental samples and discussed special methods of analysis for elements such as mercury, arsenic, selenium, and antimony. Total carbon and sulfur are typically analyzed by combustion- infrared spectrophotometers (LECO furnaces) using automated carbon and sulfur analyzers. For sulfur species (acid-soluble S, sulfide S, organic S), acid leaches and sequential extractions are conducted to obtain residues that are subtracted from total sulfur to obtain the different sulfur species by difference (Arbogast, 1996). Sobek and others (1978) describe a wet-chemical leach procedure for determining sulfur species. Similarly, carbonate carbon is determined by coulometric titration and subtracted from total carbon to get a value for total organic carbon by difference. Some acid-base accounting methods use total sulfur and assume that total sulfur equals sulfide sulfur. Many modifications to acid-base accounting have been developed (see above) to account for mineralogic variation in mine waste that can include insoluble (barite) and soluble sulfate minerals as well as sulfides.

Wavelength dispersive X-ray fluorescence spectroscopy (WD-XRF) is used for determination of major elements (reported as oxides) in geologic materials. XRF is commonly used to determine major element oxides (including silica) in rocks (Taggart and others, 1987) along with loss on ignition (LOI), which includes water and other volatile species released on sample ignition (Mee and others, 1996).

Thermal analysis techniques such as thermogravimetric analysis can be coupled with quadrupole mass spectrometry (QMS) or Fourier-transform infrared detectors (FTIR) to detect water, sulfur, carbon dioxide, and other volatile species released from samples undergoing controlled heating (Morgan and others, 1988). Hammack (1994) described an evolved-gas analysis for determining pyrite, marcasite, and alkaline-earth carbonates in coal overburden and for estimating oxidation rates for coal pyrite to improve the predictive capability of acid-base accounting.

Other techniques that may be needed in certain situations include ion selective electrodes for chlorine or fluorine, determination of redox-sensitive species (iron, arsenic), and instrumental neutron activation analysis (multi-element, rare-earth elements).

SAMPLING MEDIA, METHODS, AND EXAMPLES

Ore and gangue

The ore and associated gangue assemblages contain the primary minerals that represent the source of acid-generating and metal-bearing materials, and in some cases, a source of acid-neutralizing materials in a mineral deposit. The ore and gangue mineral assemblages are typically characteristic of a mineral deposit type. For most deposits that have been explored or developed, some information is available on the nature of the ore and gangue minerals. Worldwide databases such as the USGS Mineral Resources Data System (McFaul and others, 2000) and compilations of mines and prospects maintained by state and provincial geological surveys, contain mineralogic information and references to more detailed data that may be available for a given site. Weathered ore on mine dumps or gossan outcrops provides clues to the behavior particular metals on the site.

The composition and degree of alteration of sulfide minerals in weathered ore provide clues to element mobility. Some ore minerals tend to have ideal stoichiometry, such as chalcopyrite, whereas others, including pyrite and pyrrhotite incorporate trace amounts of other elements. Pyrrhotite generally weathers faster than pyrite, but produces less acid (see equations above). Typically, however, pyrrhotite alters to highly reactive marcasite/pyrite (Jambor, 1994), so the net effect on acid mine drainage can be comparable. Polished thin section study of oxidized ore and gossan can establish the relative degrees of alteration of different minerals and identify carbonate and secondary minerals as well as gangue minerals that may contribute to acid neutralization. Note that routine preparation of sections using water will dissolve any soluble secondary minerals. Alteration halos may extend well beyond "ore", so samples of country rock away from the orebody should be examined to assess the extent of element dispersion and distribution of alteration minerals (such as calcite veining, silica flooding, etc.).

Example

The Fontana copper mine is a Besshi-type massive sulfide deposit in Great Smoky Mountains National Park that ceased production in 1944. Most of the mine waste was removed from the site at closure and the mine area is heavily overgrown with vegetation that has erased most vestiges of mining. The National Park Service expressed

concern about drainage from underground workings and impacts on a small stream that drains the mine area and flows into Fontana Lake, a major recreational area. Seal and others (1998) reported on the water quality associated with the mine and showed that although mine waters were characterized by low pH and elevated metal concentrations, very little effluent is discharged from the underground workings, which are flooded at depth. Secondary copper minerals and drip terraces and stalactites of goethite, schwertmannite, and jarosite are observed along oxidized adit walls (figure 2a). The stream that flows past the mine workings is near neutral (pH>6) and locally exceeds acute toxicity standards for aquatic life for some elements, such as zinc, but not for others. Water in the lake, which receives the stream flow and sediment load from the mine area, showed no evidence of impact from mine drainage.

We used a number of tools to evaluate metal distributions in the solid materials that could affect water quality at the site. Although no waste piles are observed, some oxidized ore is scattered about the surface at the mine site. Back-scattered electron images (SEM) of an oxidized ore sample (fig. 2b) shows that pyrrhotite, the major sulfide mineral in the deposit, alters to marcasite. Petrography and XRD show that the ores also contain chalcopyrite, sphalerite, galena, cubanite, as primary ore minerals; biotite, chlorite, calcite, magnetite, and quartz as gangue minerals; and a secondary mineral assemblage of acanthite, anglesite, brochantite, chalcocite, covellite, ferrihydrite, goethite, gypsum, hematite, hinsdalite(?), jarosite, and malachite. Quartz is ubiquitous in most mineral deposits. The presence of quartz provides an internal standard for x-ray diffraction patterns, which is especially useful when evaluating XRD patterns for complex mineral mixtures (fig. 2c). Although thin section study revealed the pyrrhotite, it did not show up in the XRD pattern because of the extensive alteration to marcasite(pyrite) and goethite, both of which do appear as prominent mineral phases in the XRD pattern of the crushed rock. This illustrates the need to approach solid samples with a variety of techniques to document the mineralogy of solid materials that can potentially contribute to, or ameliorate, acid mine drainage.

Geochemical analysis of the bulk rock sample (table 7a) shows that ore contains trace amounts of arsenic, cadmium, selenium, and antimony. Note that none of these trace elements are present as major constituents of the ore mineral assemblage (table 3). Electron microprobe analysis of ore minerals (Tble 7b) shows these trace metals are present as minor constituents of the ore minerals. All pyrrhotite in the oxidized ores shows evidence of alteration but most chalcopyrite is intact. Sphalerite is iron-rich and less stable than chalcopyrite. Analysis of the iron oxyhydroxide minerals that form from the excess iron released by alteration of pyrrhotite to marcasite shows that they incorporate minor amounts of copper, zinc, silica, aluminum, or manganese, depending on which particular mineral is being replaced. For example, a goethite vein adjacent to sphalerite (Table 7b) contains elevated zinc (in this case about 4%). Although secondary copper minerals were observed in some of the oxidized ores, no secondary zinc minerals were noted suggesting that most of the zinc is removed from the system. Cadmium typically substitutes for zinc in sphalerite; in the Fontana mine samples, cadmium was not detected in sphalerite by microprobe. Geochemically, cadmium and zinc behave similarly, as shown by the smooth decrease in cadmium concentrations with decreasing zinc concentrations in both solids and waters associated with the Fontana mine. Ochres precipitated at groundwater seeps contain significant concentrations of zinc (1,000 ppm) whereas an ochre stalactite formed underground had about 100 ppm zinc. Groundwaters, which interact with oxidizing ore in adit walls, have higher zinc and cadmium concentrations than surface waters. Ochre deposits mark two near-neutral groundwater seeps adjacent to the stream that flows past the mine workings. Dissolved metal concentrations in the water from these seeps have copper/zinc <1 whereas the ochres precipitating from these waters have copper/zinc >>1 suggesting a natural process is at work to sequester copper, probably via sorption on iron oxyhydroxide minerals. Under the existing pH conditions at the site, zinc remains in solution and so the processes that are occurring between water and solids at the site explain the reason for the high (in excess of regulatory standards) dissolved zinc concentrations in the mine area. Water samples from the lake and from an adjacent stream unaffected by mining (background samples) contain <10 µg/L zinc. A number of factors contribute to the lack of acid drainage in the stream that drains the mine site. These include (1) the extremely high rate of precipitation in the Smokies (>800 mm/year) which dilutes any mine discharge and prevents efflorescent salts from forming, (2) the absence of significant amounts of ore and mine waste exposed to weathering at the site, and possibly, (3) the presence of carbonate in the alteration assemblage.

Host rock and alteration

The practical ability of host rocks to neutralize, or contribute to acid mine drainage is a subject of considerable interest. Alteration associated with hydrothermal alteration typically forms a halo around the actual orebody that may extend for centimeters to kilometers, depending on the deposit type and the local geologic setting. A series of experiments on fresh granitic rocks of the Boulder batholith in Montana showed that those particular granites have significant acid-neutralizing capacity (Desborough and others, 1998a,b). Minor amounts of calcite contribute to

short-term neutralization potential whereas some of the major rock-forming minerals (biotite, tremolite, and feldspars) contribute to long-term acid neutralization. The minor amount of calcite (<5 wt. % of the rock) was not detected in these rocks by x-ray diffraction; large, sawed rock slabs were stained for calcite with alizarin red-S (Dickson, 1965) and carbonate content was calculated from whole-rock analysis for total carbon (by coulometer) and assuming that all of the carbon was present in calcite. By reacting mine-waste leachate (pH3) from mineralized pyrite-rich quartz veins (hosted by the granite) with the pulverized calcite-bearing granite samples, Desborough and others (1998b) found that the acid-neutralizing potential of the rocks was higher than expected and higher than could be accounted for by calcite alone. A number of other studies also suggest that when reactive carbonates are absent or depleted, mafic silicates minerals, especially biotite, play a role in long-term acid consumption (Acker and Bricker, 1992; Stromberg and Banwart, 1994; Malmstrom and Banwart, 1997; Dold, 1999) because biotite can alter to vermiculite by rapid removal of potassium and consumption of H^+ . Vermiculite-type mixed layer minerals have been reported as secondary minerals forming in oxidized zones in sulfide-rich mine tailings associated with deposits that have biotite as a common gangue mineral such as porphyry copper deposits (Dold, 1999). Although a number of gangue minerals in ore or tailings can contribute to long-term acid neutralization (micas, pyroxenes, amphiboles, calcic plagioclase), the phyllosilicate minerals (biotite and chlorite) appear to weather fastest (Nesbitt and Jambor, 1998), probably due to physical properties of the mineral group that promote development of large reactive surface areas relative to other groups of minerals (e.g., layer structure, perfect basal cleavage, low hardness number). Although biotite, phlogopite, and chlorite are fast-weathering minerals, muscovite and illite are very resistant to dissolution.

Alternatively, host rocks may represent sources of natural acid drainage that has nothing to do with mining. Rocks of the regionally extensive Great Smoky Group of the Late Proterozoic Ocoee Supergroup of the southern Appalachians host the massive sulfide deposits at Ducktown and the deposits at the southern end of Great Smoky Mountains National Park, such as the Fontana mine described above (Southworth, 1995; King and others, 1968). Metamorphic pyrite and pyrrhotite occur throughout a number of slate, phyllite, and schist lithologies of the Great Smoky Group. Weathering of exposed outcrops of these rocks, especially where exacerbated by roadcuts or landslides, leads to acid rock drainage that can be severe enough to result in fish kills (Bacon and Maas, 1979) due to stream acidification and release of iron, aluminum, and manganese.

In protected areas, weathering of such rocks produces highly soluble efflorescent salt minerals that form via the same processes that result in salt formation on mine waste dumps (Flohr and others, 1995); these salts can contribute pulses of acidity and metals (Fe, Al, Mg) to surface runoff. In the parts of the southern Appalachians where such rocks crop out, special efforts are taken in road and powerline construction to mitigate potential acid rock drainage problems (Byerly, 1996; Schaeffer and Clawson, 1996). Seal and others (1997, 1998) showed that the pH of regional streams in the Fontana mine area draining pyritic rocks can be lower than the pH of stream waters draining the immediate mine area, but total dissolved base metals concentrations are much lower in the regional streams due to differences in geoavailability of metals in host rock versus ore. Consideration of these types of host rock controls on water quality can be important in setting realistic reclamation goals for treating acid mine drainage.

Mine waste and tailings

Mine waste dumps and tailings piles pose sampling problems because many types and textures of waste may be present at a site. The surface material is the most important contributor to runoff during rainstorm and snow melt. If waste dumps or tailings are to be moved during site remediation, it may be critical to understand the vertical heterogeneity of the piles by sampling at depth using augers or drills. The strategy for sampling such material depends on the information needed. To meet the need for a protocol for cost-effective, rapid screening of large numbers of abandoned mine-waste dumps for prioritization for cleanup, the USGS developed a statistically based sampling strategy (Smith and others, 2000). This protocol provides a representative composite sample for chemical and mineralogic analyses and for leach studies. The sampling protocol is described in Chapter C.

Example

The Elizabeth mine is an abandoned, Besshi-type massive sulfide deposit in east-central Vermont that was evaluated by EPA in 1999 and listed on EPA's National Priority List (Superfund) in December, 2000 as an ecological threat to the West Branch of the Ompompanoosuc River (Hammarstrom and others, 1999b). The mine was discovered in 1793 and developed for copperas (iron sulfate) production from pyrrhotite in the 1800s. From the 1830s until closure in 1958, the deposit was mined for copper from chalcopyrite. Three large mine-waste piles on the site (fig. 3a) contribute metals and acidity to surface runoff that form the headwaters of Copperas Brook which flows into the West Branch of the Ompompanoosuc River about a kilometer downstream from the mine site. The waste piles have been designated as TP1, TP2, and TP3 (fig. 3a). TP1 is a 30-acre, 30-meter high pile of fine-grained, pyrrhotite-rich

tailings from a flotation plant that operated on-site until 1958. The flat top surface of the pile is partly vegetated and contains a small pond that receives surface water drainage from the upper piles; water is decanted from the pond to a discharge point at the base of the pile and the decant water coalesces with seeps at the base of the tailings to form Copperas Brook. The north slope of TP1 above the seeps is deeply eroded and barren (fig. 3b). TP2 represents a 5-acre tailings pile from an older (early 1900s) phase of mining and is similar in texture and appearance to TP1, but has a thicker (60 cm as opposed to 6 cm) orange oxidized zone overlying black, unoxidized tailings. TP3 is a 6-acre area that includes a series of piles of mine waste from the early days of mining and copperas production. We arbitrarily divided TP3 into 6 subareas (A-F) based on differences in surface color and texture (fig. 3c,d). We sampled surface materials from each of the 6 subareas of TP3, as well as from the tops and steep, deeply eroded barren north slopes of TP1 and TP2. Paste pH of composite samples was measured in the field, and samples were returned to the lab for mineralogy and chemistry. Physical characteristics, paste pH, and dominant minerals determined by XRD are listed in table 8a. Colors were determined on dry materials by comparison with Munsell soil color charts. These data show that the red piles of the old workings (TP3), where open-ore roasting of ore and possibly smelting occurred, are hematite-rich and have slightly higher paste pH values than the adjacent jarosite-rich piles. Weathered ore and host rock litters the upper parts of TP3 and on dry days, white coatings of efflorescent salts look like snowballs on the dump (fig. 3e). These salts (melanterite, rozenite, a variety of copper-aluminum salts) disappear after a rainstorm. The oxidized surfaces of the more recent flotation tailings (TP2 and TP1) are dominated by jarosite and goethite. The partly vegetated tops of both of these piles are less acidic than the base, eroded slopes. Selected metal concentrations from geochemical analysis of these samples are listed in table 8b, along with reference soil values for normal ranges of metal concentrations in soils and critical values above which plant toxicity is considered to be possible. These data demonstrate a number of points that should be factored into reclamation plans:

- (1) Copper and zinc concentrations in all types of mine waste on the site are elevated and locally exceed critical values for acute toxicity for plants; these elevated metal concentration and the acidity of the surface material probably account for the lack of success of revegetation (planted or volunteers) and the stunted appearance of the vegetation that has established itself on parts of the flat tops of the flotation tailings.
- (2) Metal concentrations in the older waste piles (smaller volume of waste at the site) are an order of magnitude higher than in the more extensive flotation tailings. For any improvements to stream water quality in Copperas Brook, the continuing cycle of weathering of exposed ore, salt formation, salt dissolution, and release of metals and acidity to the surface materials and to surface runoff from these older dumps has to be broken by moving the problem material, or regrading and capping and diverting surface flow. Casual inspection of the site could lead one to conclude that the large tailings pile (TP1 and TP2) represent the major source of impact to Copperas Brook. Recognition of the presence and role of efflorescent salts at the site, and the elevated metal concentrations documented by this approach to sampling however, indicate that the older mine waste is a significant source of metals and acidity.
- (3) A number of potentially toxic metals such as mercury, lead, cadmium, and arsenic are present in low concentrations at this site, reflecting their low abundances in this particular type of mineral deposit.

Secondary minerals

Sampling of secondary minerals can be difficult, but can provide information on temporary metal sequestration and empirical data for comparison with solid phases predicted from saturation index computations based on water chemistry. Efflorescent salts are transient, so they may not be evident when the site is visited. Salts are best observed at times of the year when high evaporation rates prevail at the site, and may be preserved year round in protected areas (under rock overhangs such as shown in fig. 4a, in pipes or other structures on the site). Salts can change during the course of hours depending on the prevailing temperature and relative humidity conditions and can change during transport to the lab, and during grinding to prepare x-ray mounts. Tweezers and wood or plastic spatulas are good for sampling delicate salt encrustations (fig. 4b); storage in tightly capped plastic vials allows the salts to control the humidity in the vial. X-ray diffraction is useful for identifying mineral groups, but does not provide chemical information. We have found that an iterative approach using XRD and qualitative SEM analysis on hand-picked concentrates (by color, usually) is most effective for identifying efflorescent salts because these minerals typically form complex solid solutions, tend to be very-fine grained and intimately intergrown. For example, copper can substitute for iron in melanterite rather than form discrete secondary copper minerals. Minerals such as melanterite, a very commonly reported secondary salt, with 7 waters of hydration, can dehydrate to rozenite (4 waters of hydration) as relative humidity falls below about 60% at 20 °C (Chou and others, 1999).

A



B



C

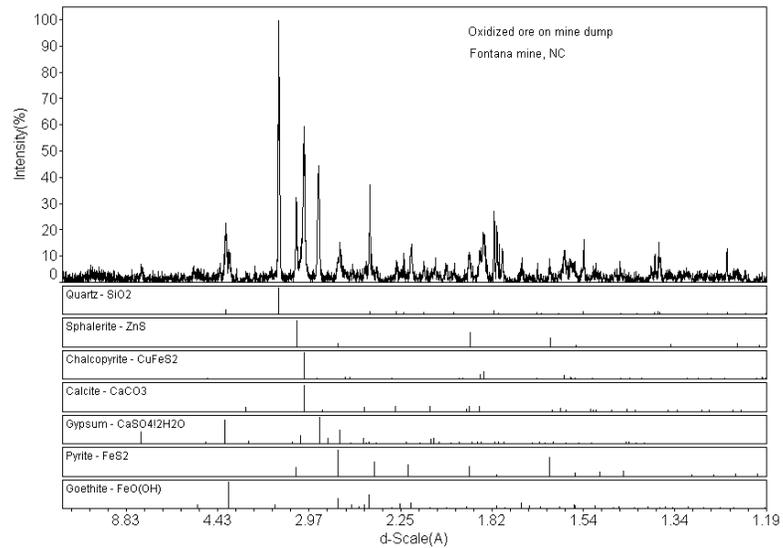


Figure 2. A, Secondary ochre minerals forming along adit walls at the Fontana mine, NC. Waters dripping from these stalactites (goethite, schwertmannite, jarosite) have a pH of 3 and over 900 mg/L dissolved sulfate (Seal and others, 1999). B, Back-scattered electron image of as polished thin section cut through oxidized massive sulfide ore. Marcasite replaces pyrrhotite; excess iron from the alteration forms a network of iron-oxyhydroxide minerals around the sulfides. Field of view about 600 microns. Fontana mine, NC, (sample FM-1B-96). C, X-ray diffractogram of oxidized ore to determine mineralogy (same sample as shown in B).

Table 7a. Selected geochemical data for oxidized copper ore shown in Figure 2.

| Element | Concentration | Element | Concentration |
|---------|---------------|-----------------|---------------|
| Fe | 20% | Sb | 2.6 ppm |
| Al | 0.2% | As | 0.8 ppm |
| Cu | 120,000 ppm | Cd | 44 ppm |
| Zn | 23,000 ppm | Se | 61 ppm |
| Pb | 580 ppm | S (total) | 14.7% |
| Mn | 1,900 ppm | CO ₂ | 9.3% |

Table 7b. Mineral chemistry of ore minerals in oxidized copper ore determined by electron microprobe for the sample shown in Figure 2b. [n, number of analyses averaged]

| Element (wt.%) | Pyrrhotite (n=4) | Marcasite (n=4) | Chalcopyrite (n=5) | Sphalerite (n=4) | Goethite vein |
|----------------|------------------|-----------------|--------------------|------------------|---------------|
| S | 38.1 | 51.6 | 34.3 | 33.2 | 2.23 |
| Fe | 61.2 | 46.1 | 30.2 | 7.2 | 53.7 |
| Cu | 0.05 | 0.32 | 34.4 | 0.26 | 0.08 |
| Zn | 0.02 | 0.02 | 0.05 | 58.6 | 4.17 |
| Co | 0.09 | 0.07 | 0.04 | 0.01 | 0.05 |
| Se | 0.02 | 0.02 | 0.01 | 0.02 | 0 |
| Mn | 0 | 0 | 0 | 0.02 | 0.06 |
| Total | 99.4 | 98.1 | 99.0 | 99.3 | 60.5 |

Example

The Mineral Belt of Central Virginia includes over 20 abandoned mines and prospects that worked Kuroko-type massive sulfide deposits. Despite the relatively humid climate of this region where precipitation (>1,000 mm/yr) exceeds evaporation, summer droughts occur (Bailey, 1995). During dry periods, efflorescent salts form where capillary action draws metal-rich solutions to the surface. Dagenhart (1980) documented over 20 different secondary sulfate salts associated with massive sulfide mine waste along Contrary Creek in Virginia, and showed that no other metal source could explain the rapid chemical response of the creek to rainfall. Recent (2000) visits to Contrary Creek confirm that salts continue to form in protected areas (fig. 4a) and in dry periods, on tailings surfaces that line the creek (fig. 4b). SEM and XRD show well-developed crystals of copiapite, melanterite, halotrichite (figs. 4 c and d) and other minerals that continue to form and impact the creek some twenty years after unsuccessful and limited attempts at reclamation along the creek.

The Valzinco mine, north of Contrary Creek and in a different watershed, was mined intermittently for lead, zinc, and minor copper from 1914 until the 1940s. Underground workings included five mine levels and more than 5,000 ft of workings (Grosh, 1949). Ore was processed on-site in a flotation plant. Fine-grained tailings from the 1940s mining operations were deposited in and along Knights Branch, a perennial stream (fig. 4e), resulting in an impacted area of about 10 acres. Tailings in and adjacent to Knights Branch and acid seeps from underground workings have impacted the stream. Oxidized tailings surfaces adjacent to the creek are highly acidic (fig. 4e) and Knights Branch is elevated in dissolved iron, lead, manganese, and zinc as it flows through the Valzinco mine site. The state of Virginia is currently implementing a project to restore Knights Branch and reclaim and revegetate more than 10 acres of disturbed lands (MVTechnologies Inc., 1998). Tailings were inspected (by Hammarstrom) during site visits to the Valzinco site in April, July, September, and December of 1999. In July, thick encrustations of

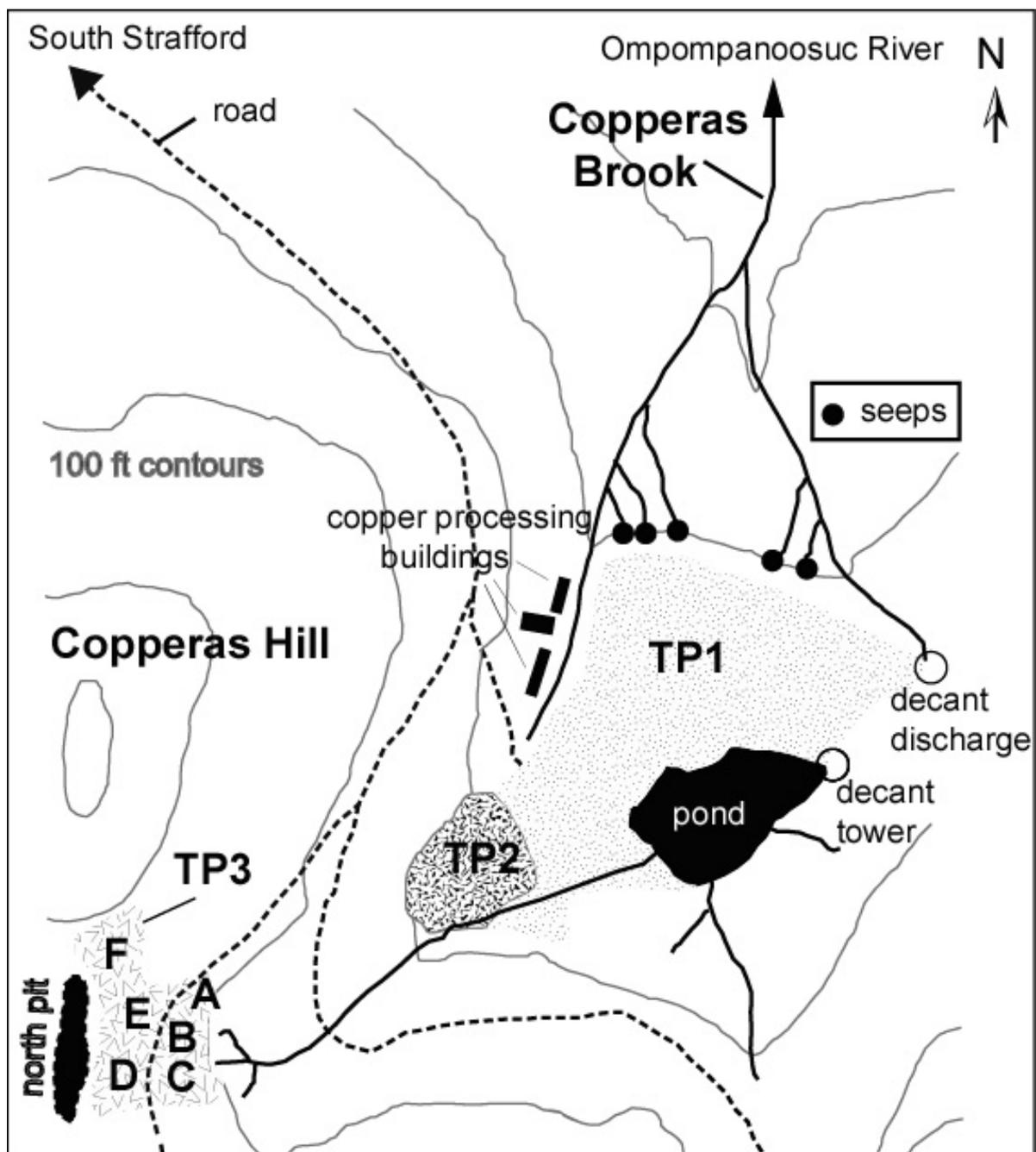


Figure 3. Mine waste and flotation tailings at the abandoned Elizabeth copper mine, VT. A. Site map showing the relative size and distribution of solid materials that impact Copperas Brook. TP1 and TP2 represent flotation tailings from 20th century mining. TP3 consists of heterogeneous piles of mine waste from 19th century mining and copperas processing. See table 8a for descriptions of individual piles.

B



C



D



E



Figure 3. B, Deeply eroded, bare north slope of TP1 above seeps. C, Ochres precipitating at seeps at base of TP1. D, TP3-D (yellow-brown pile in center of photo) and TP3-E (red pile in foreground). E, Close-up of melanterite-rozenite “snowballs” on weathered ore that litters TP3-F. Salts are observed on hot, dry days; they disappear when it rains.

white, yellow, and locally blue efflorescent salts coated tailings exposed in walls of a former settling pond adjacent to the flotation plant (fig. 4f, g). XRD, SEM, and EMP were used to identify the salts, which include halotrichite-pickeringite, goslarite, hexahydrate, and melanterite.

Composite 20-gram salt samples from two sites along Contrary Creek and from Valzinco were dissolved in 400 mL of deionized water overnight. The solution pH was measured after 30 minutes, 60 minutes, 12 hours, and 24 hours. The solutions were filtered through 0.45- micron nitrocellulose filters, and analyzed by inductively coupled plasma-mass spectrometry (ICP-MS) to characterize metal sequestration in readily soluble efflorescent salts. Results are listed in table 9. In all three samples, pH decreased (from the pH of 6.8 of the deionized water solvent) and conductivity increased over a 24-hour period. The most dramatic changes came in the first 30 minutes, attesting to the rapid kinetics of dissolution of these minerals. Significant concentrations of metals known to impact aquatic ecosystems such as iron, aluminum, copper, zinc, and cadmium are sequestered in these salts, as well as sulfate. Cadmium concentrations increase with increasing zinc. Dissolved lead is an order of magnitude lower than other base metals, even at Valzinco which was mined for lead and zinc, reflecting the relatively low mobility of lead and low solubility of secondary lead minerals. These data emphasize the need for turning off sources of metals and acidity by removal and(or) capping of exposed mine waste in addition to diverting or treating mine effluents and surface waters for effective site remediation even in relatively wet climates.

Ochres and other precipitates

Precipitates of iron, aluminum, or manganese provide clues to water chemistry. These precipitates can sequester metals by cation sorption processes and release sorbed metals as pH fluctuates. Flocculates and slimes of these

minerals can form a blanket of poorly crystalline very fine-grained sediment on stream beds and coat rocks and organic matter (twigs, leaves) along streams and seeps. Sampling is best accomplished using some sort of vacuum device or pump, such as a turkey baster or a large syringe because the material tends to float away as soon as it is disturbed. Repeated operations of the sampling device are usually necessary to obtain a large enough sample; sample increments can be placed in a large plastic bottle, allowed to settle, and then excess water can be decanted to concentrate the solid material. Alternatively, rocks coated with the material can be placed in a plastic container with native water, and the precipitates can then be shaken off, decanted, and air-dried. Samples are air dried at room temperature in the lab or freeze dried. In many cases, these materials are amorphous or very poorly crystalline and produce very poor x-ray diffraction patterns (especially ferrihydrite and schwertmannite). SEM is useful for confirming the presence or absence of sulfur and for identifying aluminum in oxyhydroxide and hydroxysulfate minerals.

Example

A variety of different precipitates are observed at the Elizabeth mine (Hammarstrom and others, 1999). Goethite-rich hardpan layers up to several cm thick within tailings represent paleosurfaces or in-situ development of cemented layers. Precipitates that range from slimes to protohardpans to hardpans form at seeps at the base of tailings and downstream along the length of Copperas Brook (Fig. 3a). Goethite, schwertmannite, and jarosite occur in these hardpans (Fig. 3c). XRD (fig. 5a) patterns show the diffuse, broad peaks typical of the iron-rich ochre minerals. Although the iron contents of these ochres remains nearly constant downstream from the mine working (about 40 wt. % Fe), base metal concentrations increase (fig. 5a). Jarosite is most prevalent near the seeps (but not necessarily precipitating from the seeps) where it locally forms a nearly pure, yellow muck at the base of the tailings pile. EDX spectra on jarosite analyzed by SEM confirm that the jarosite contains potassium. The seeps discharge near-neutral waters rich in ferrous iron and dissolved sulfate (>600 mg/L). Jarosite is stable under relatively narrow conditions of low pH and high dissolved sulfate, and should transform to ferric oxyhydroxide with increasing pH. Ferrous iron oxidizes and hydrolyzes rapidly as the waters emerge from the seeps, precipitating ochre minerals and causing stream pH to drop to values of about 3. Lime added to the flotation process and (or) chemical processes operating within the tailings may contribute to the neutral waters at the seeps; white slime precipitates collected on leaf litter in the area of the seeps dried to crystalline gypsum, indicating that calcium is mobile in this environment. Since lime, $\text{Ca}(\text{OH})_2$, is highly soluble in water, it has likely washed out of the tailings in the 40 years since the mine closed and lost any neutralization potential. The ochres were sampled in August during low flow and high evaporation. The metal load sequestered in these fine-grained sediments may vary over the course of a year.

Along the Ompompanoosuc River upstream from the confluence of Copperas Brook, a former mine ventilation shaft discharges groundwater (pH 5) from underground workings. The discharge pipe is grated, and the grate is encrusted with a thick coating of white and orange precipitate (fig. 5b). The white material is an essentially amorphous aluminum-rich material that is too poorly crystalline to characterize by XRD. EDX spectra document the aluminum-rich nature of the white slime, and show that it also contains minor silicon, iron, and sulfur (fig. 5c). The occurrence of aluminous precipitates at around pH 5 is consistent with other studies that note that aluminum minerals typically precipitate where acidic (pH<5) and near-neutral waters mix. We have observed such “white slimes” in a number of other locations where acidic tributaries or seeps discharge into near-neutral streams. Such precipitates are also known as “white death” because of their toxicity to fish (Witters and others, 1996). In some cases, we observe “white slimes” at the same location as ochrous precipitates, where they form separate layers but are difficult to sample as discrete phases. These situations probably indicate fluctuations in pH or other variables at the site over time. Geochemical analysis of a bulk sample of white vent precipitate confirms that it is Al-rich (4.5% Al), contains moderate Fe (14 wt. %), significant silicon (28 wt.%) and manganese (0.5 wt. %) and greater concentration of base metals (585 ppm) than the iron-rich ochres along Copperas Brook (fig. 5a). Iron-rich precipitates at the air vent are comparable to the stream ochres in iron content (44 wt. %), but have significantly higher concentrations of base metals (3,000 ppm). These data identify a source of metal-rich fine sediment that enters the river upstream of the confluence of the creek. Dissolution of precipitates will release sorbed metals as dissolved species in the river; dissolution and reprecipitation of these phases effectively recycle dissolved metals and depending on the extent of these processes over the course of a year, may produce pulses in metal loads that would be difficult to characterize unless water quality was monitored on a continuous basis. Although the creek that drains the mine workings is the most visible source of impact on the river, the air vent discharge also affects river water quality.

Table 8a. Characteristics of Elizabeth mine waste piles.

[Measurements are for 30-increment surface soil samples (<2 mm fraction) composited over the pile described; see fig. 3a for locations of piles]

| Sample | Description | Munsell color | Mineralogy | Paste pH |
|--------|--|--------------------------------|--|----------|
| TP3-A | Northernmost pile east of the road characterized by a yellow-brown soil color. | yellow 2.5Y 7/6 | jarosite + quartz | 2.4 |
| TP3-B | Central pile east of road; appears to be site of historic processing. Surface soil is very heterogeneous, local blue-green iridescent copper coatings on slag(?). Red to black soil on pile surface. | dark reddish brown 5 YR 3/2 | hematite + quartz | 2.6 |
| TP3-C | Southernmost pile east of the road. Surface runoff from this pile directly affects water sample site LIZM13. Red to orange soil with white salts. | reddish brown 2.5Y 4/4 | hematite + quartz + mica + feldspar | 2.6 |
| TP3-D | Southernmost pile west of the road. Yellow-brown soil similar to TP3-A. | brownish yellow 10YR 6/8 | jarosite + quartz | 2.1 |
| TP3-E | Central pile west of road. Red soil with some black material, but lacks the slag(?) noted on TP3-B. | red 2.5YR 4/6 | hematite + quartz + mica | 3.2 |
| TP3-F | Northernmost pile west of the road and adjacent to the north end of the north pit. Orange soil littered with salt-coated ("snowballs") loose pieces of weathered ore. | yellowish brown 10YR 5/6 | mica + quartz + jarosite + goethite | 2.2 |
| TP2-1 | Partially vegetated, flat top of tailings pile 2. | strong brown 7.5YR 5/8 | jarosite + quartz + mica + plagioclase feldspar | 5.5 |
| TP2-2 | Bare, eroded north slope of tailings pile 2. | strong brown 7.5YR 5/8 | jarosite + goethite + quartz + plagioclase feldspar + mica | 3.2 |
| TP1-1 | Bare area of flat top of tailings pile 1 adjacent to the pond. | strong brown 7.5YR 5/8 | quartz + mica + goethite + jarosite | 3 |
| TP1-2 | Vegetated area on flat top of tailings pile 1. | strong brown 7.5YR 5/8 | quartz + mica + goethite + jarosite | 5.9 |
| TP1-3 | Steep, bare eroded north slope of tailings pile 1 with seeps along the base. | strong brown 7.5YR 5/8 | quartz + mica + goethite + jarosite | 2.8 |

Table 8b. Heavy metals in Elizabeth mine waste piles (<2mm composite surface materials) in parts per million. [References values from Alloway, 1999. Critical values = total soil concentration ranges above which plant toxicity is considered to be possible. n.d., not determined. Values in excess of upper range values for both normal and critical concentrations are shown in boldface.]

| Element | Reference soil values (not near orebodies) | | Elizabeth mine pre-1958 tailings (oxidized surface material) | | | | |
|---------|--|-----------------|--|-------|-------|-------|-------|
| | Normal range in soils | Critical values | TP1-1 | TP1-2 | TP1-3 | TP2-1 | TP2-2 |
| Ag | 0.01-8 | 2 | 1.8 | 0.87 | 1.8 | 0.81 | 0.58 |
| As | 0.1-40 | 20-50 | 5.9 | 6.2 | 9.7 | 5.6 | 14 |
| Au | 0.001-0.02 | - | n.d. | n.d. | 0.014 | 0.16 | 0.029 |
| Cd | 0.01-2.0 | 3-8 | 0.4 | 0.2 | 0.2 | 0.2 | 0.3 |
| Co | 0.5-65 | 25-50 | 26 | 38 | 29 | 48 | 68 |
| Cr | 5-1,500 | 75-100 | 72 | 91 | 57 | 93 | 48 |
| Cu | 2-250 | 60-125 | 680 | 120 | 120 | 230 | 96 |
| Hg | 0.01-0.5 | 0.3-5 | 0.05 | 0.02 | 0.05 | 0.04 | 0.11 |
| Mn | 20-10,000 | 1,500-3,000 | 270 | 600 | 410 | 490 | 650 |
| Mo | 0.1-40 | 2-10 | 15 | 6.4 | 16 | n.d. | n.d. |
| Ni | 2-750 | 100 | 9 | 31 | 12 | 16 | 21 |
| Pb | 2-300 | 100-400 | 49 | 33 | 50 | 42 | 45 |
| Sb | 0.2-10 | 5-10 | <0.1 | <0.1 | 0.2 | <0.1 | 0.1 |
| Se | 0.1-5 | 5-10 | 22 | 11 | 31 | n.d. | n.d. |
| Sn | 1-200 | 50 | n.d. | n.d. | n.d. | n.d. | n.d. |
| Tl | 0.1-0.8 | 1 | <0.1 | <0.1 | 0.8 | 0.8 | 0.7 |
| U | 0.7-9 | - | 0.52 | 1.2 | 0.5 | n.d. | n.d. |
| V | 3-500 | 50-100 | 76 | 93 | 83 | 100 | 84 |
| W | 0.5-83 | - | n.d. | n.d. | n.d. | n.d. | n.d. |
| Zn | 1-900 | 70-400 | 300 | 320 | 380 | 370 | 450 |

Table 8b. (cont.)

| Reference soil values (not near orebodies) | | | Elizabeth mine older waste dumps (oxidized surface material) | | | | | |
|--|--------------------------|-----------------|--|-------|-------|-------|-------|-------|
| Element | Normal range in soils | Critical values | TP3-A | TP3-B | TP3-C | TP3-D | TP3-E | TP3-F |
| Ag | 0.01-8 | 2 | 3.3 | 8.9 | 24.2 | 7 | 11.8 | 10.7 |
| As | 0.1-40 | 20-50 | 4 | 10 | 25 | 8 | 20 | 16 |
| Au | 0.001-0.02 | - | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| Cd | 0.01-2.0 | 3-8 | 0.2 | 2 | 0.8 | 0.3 | 1.1 | 1.3 |
| Co | 0.5-65 | 25-50 | 5 | 100 | 30 | 9.2 | 41 | 22 |
| Cr | 5-1,500 | 75-100 | 100 | 41 | 81 | 65 | 68 | 62 |
| Cu | 2-250 | 60-125 | 1,800 | 2,100 | 1,100 | 3,200 | 850 | 6,600 |
| Hg | 0.01-0.5 | 0.3-5 | 0.23 | 0.08 | 0.51 | 0.17 | 0.35 | 0.24 |
| Mn | 20-10,000 | 1,500-3,000 | 170 | 65 | 220 | 230 | 170 | 83 |
| Mo | 0.1-40 | 2-10 | 27 | 34 | 100 | 47 | 67 | 56 |
| Ni | 2-750 | 100 | <2 | 26 | 8 | <2 | 9.2 | 3 |
| Pb | 2-300 | 100-400 | 87 | 51 | 120 | 61 | 84 | 76 |
| Sb | 0.2-10 | 5-10 | <0.1 | 0.1 | 0.2 | <0.1 | .1 | .2 |
| Se | 0.1-5 | 5-10 | 39 | 45 | 170 | 55 | 100 | 75 |
| Sn | 1-200 | 50 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| Tl | 0.1-0.8 | 1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 |
| U | 0.7-9 | - | 0.2 | 0.3 | 0.4 | 0.2 | 0.4 | 0.4 |
| V | 3-500 | 50-100 | 90 | 32 | 84 | 78 | 70 | 83 |
| W | 0.5-83 | - | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| Zn | 1-900 | 70-400 | 170 | 1,200 | 350 | 200 | 400 | 420 |

Stream sediments

Stream sediment samples are, by nature, composite samples. The statistical procedure outlined by Smith and others (2000) for sampling mine waste can also be applied to stream sediments (i.e., a 30-increment sample). In USGS geoenvironmental studies, stream sediments are collected by defining a stretch of the stream as the sampling area (typically 30 meters or less) and sampling the uppermost sediment from the sides and center of streams (where possible). Samples are collected with a plastic or stainless steel scoop, and wet sieved through a solder-free 10 mesh screen (<2 mm) into a gold pan. Excess water is drained off and the wet sediment is placed in a double thickness of plastic zip-lock bags for transport to the lab. In the lab, the sediment is spread out on a tray (plastic paint pans work well for this) and air-dried - a process that can take more than a week. The bulk sample is weighed, and the <80 mesh (<177 µm) material is sieved out, weighed, and pulverized for chemical analysis, typically by multi-element ICP-AES and other methods (for gold, mercury, etc.) as warranted by the study. The <80 mesh sample fraction is used because this is the sediment fraction most likely to include the fine-grained materials that can sorb metals, interact with benthic organisms, physically affect aquatic ecosystems by increasing turbidity, and be transported farthest downstream from source areas. Stream sediments reflect the geology of the drainage area. Mineral deposits can superimpose a suite of metals on the regional chemical signature. Many types of mineral deposits have distinctive geochemical signatures that can be manifested in associated altered rocks, soils, or stream sediments (Cox and Singer, 1986; du Bray, 1995). Geochemical backgrounds are difficult to establish, especially in areas that have been disturbed by human activities. Geochemical baselines (measured at a point in time) are what can usually be measured. Data from watersheds that drain the same lithology, but are not affected by mining (but may contain unexploited mineral deposits) can be used to approximate background. Acquisition of pre-mining baseline data can provide guidelines for establishing realistic post-mining reclamation goals for both water and sediments.

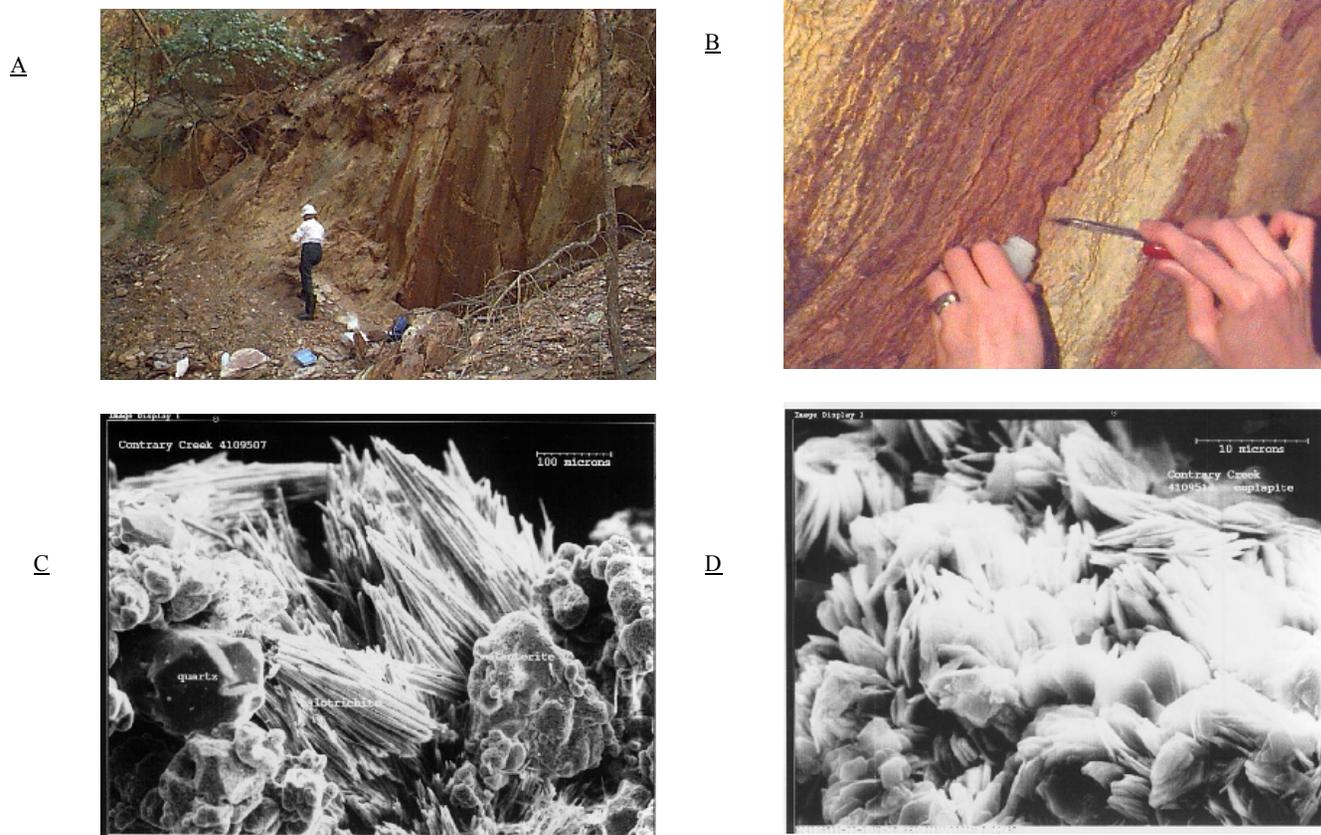


Figure 4. Efflorescent salt minerals along a pit wall. A, Salts form colored vertical bands on outcrops under a protected overhang. B, Sampling techniques. C, Secondary-electron SEM image showing needles of halotrichite intergrown with melanterite and quartz. D, Secondary-electron SEM image of copiapite crystals (yellow mineral shown in B).

E



F



G



Figure 4. E, Knights Branch decreases in pH from about 6 to 4 as it flows through sulfide-rich (pyrite, sphalerite, galena, chalcopyrite) Valzinco mine tailings. F, Efflorescent salt minerals coating flotation tailings in the process water pit area at Valzinco. These salts were present on a hot, dry day in April, 1999 but were not observed on subsequent visits during more humid periods. G, Close-up of salts on black, unoxidized tailings. Note pen for scale. XRD and SEM show that these salts include a variety of highly soluble hydrated Al, Mg, Fe, and Zn-bearing sulfate minerals including pickeringite and goslarite.

Table 9. Geochemical data for dissolved efflorescent salts collected at Kuroko-type massive sulfide deposits in Virginia.

[Solutions analyzed by ICP-MS; elements of particular environmental concern (Campbell and others, 1985) are highlighted in bold]

| | <u>Valzinco</u> | <u>Sulphur</u> | <u>Arminius</u> | | <u>Valzinco</u> | <u>Sulphur</u> | <u>Arminius</u> |
|--|---------------------|---------------------|--------------------|--|-----------------------|----------------|-----------------|
| <u>pH measurements</u> | | | | <u>conductivity measurements (mS/cm)</u> | | | |
| 0 mins | 3.69 | 2.28 | 3.40 | 0 mins | 9.2 | 1.5 | 3.4 |
| 30 mins | 3.18 | 2.34 | 3.13 | 30 mins | 12 | 7.1 | 7.5 |
| 1 hr | 3.18 | 2.42 | 3.03 | 1 hr | 12 | 7.9 | 7.4 |
| 12 hr | 3.09 | 2.21 | 3.00 | 12 hr | 12 | 8.9 | 7.6 |
| 24 hr | 3.07 | 2.20 | 2.98 | 24 hr | 12 | 9.1 | 7.6 |
| <u>Dissolved metal concentrations in 24 hour leachates</u> | | | | | | | |
| <u>Element (units)</u> | | | | <u>Element (units)</u> | | | |
| Ag µg/L | 0.1 | 0.03 | < 0.01 | Na mg/L | 0.12 | 0.16 | 0.22 |
| Al µg/L | > 30,000 | > 30,000 | > 30,000 | Nb µg/L | 0.2 | 0.2 | 0.58 |
| As µg/L | | 120 | < 0.2 | Nd µg/L | 510 | 1,400 | 500 |
| Au µg/L | < 0.01 | 0.01 | 0.05 | Ni µg/L | 970 | 110 | 160 |
| Ba µg/L | 9.7 | 22 | 11 | Pb µg/L | 460 | 5.2 | 7.4 |
| Be µg/L | 42 | 9.5 | 33 | Pr µg/L | 160 | 410 | 120 |
| Bi µg/L | 0.06 | 0.53 | < 0.01 | Rb µg/L | 2.7 | 3.7 | 1.8 |
| Ca mg/L | 36 | 13 | 120 | Re µg/L | 0.1 | 0.06 | 0.04 |
| Cd µg/L | 6,900 | 13 | 2,600 | Sb µg/L | 1.0 | 0.4 | 0.75 |
| Ce µg/L | 1,400 | 3,500 | 880 | Sc µg/L | 89 | 66 | 240 |
| Co µg/L | 2,700 | 660 | 250 | Se µg/L | 23 | < 0.2 | < 0.2 |
| Cr µg/L | 260 | 260 | 570 | SiO ₂ mg/L | 2 | < 0.5 | 2 |
| Cs µg/L | 0.05 | 0.30 | 0.47 | Sm µg/L | 110 | 300 | 150 |
| Cu µg/L | 59,000 | 4,400 | 88,000 | Sn µg/L | < 0.05 | 1 | 0.1 |
| Dy µg/L | 43 | 110 | 120 | SO₄ mg/L | 7,200 | 5,000 | 5,100 |
| Er µg/L | 20 | 42 | 58 | Sr µg/L | 11 | 8.1 | 82 |
| Eu µg/L | 20 | 65 | 79 | Ta µg/L | 0.1 | 0.2 | < 0.02 |
| Fe µg/L | > 200,000 | > 200,000 | 51,000 | Tb µg/L | 9.7 | 24 | 20 |
| Ga µg/L | < 0.02 | 21 | < 0.02 | Te µg/L | < 2 | < 2 | < 2 |
| Gd µg/L | 81 | 200 | 130 | Th µg/L | 260 | 860 | 160 |
| Ge µg/L | < 0.02 | < 0.02 | < 0.02 | Ti µg/L | 760 | 290 | 420 |
| Hf µg/L | < 0.05 | 0.76 | < 0.05 | Tl µg/L | < 0.05 | < 0.05 | 0.2 |
| Ho µg/L | 6.7 | 17 | 22 | Tm µg/L | 2.7 | 5.5 | 8.8 |
| In µg/L | 15 | 1.3 | 24 | U µg/L | 360 | 160 | 450 |
| K µg/L | 180 | 340 | 160 | V µg/L | 330 | 22 | 2 |
| La µg/L | 520 | 850 | 330 | W µg/L | 1.6 | 0.3 | < 0.02 |
| Li µg/L | 270 | 110 | 250 | Y µg/L | 180 | 350 | 490 |
| Mg mg/L | 600 | 250 | 460 | Yb µg/L | 20 | 37 | 52 |
| Mn µg/L | 77,000 | 23,000 | 35,000 | Zn µg/L | > 1,000,000 | 1,300 | 610,000 |
| Mo µg/L | 0.73 | 0.86 | 0.08 | Zr µg/L | 3.1 | 92 | 2.6 |

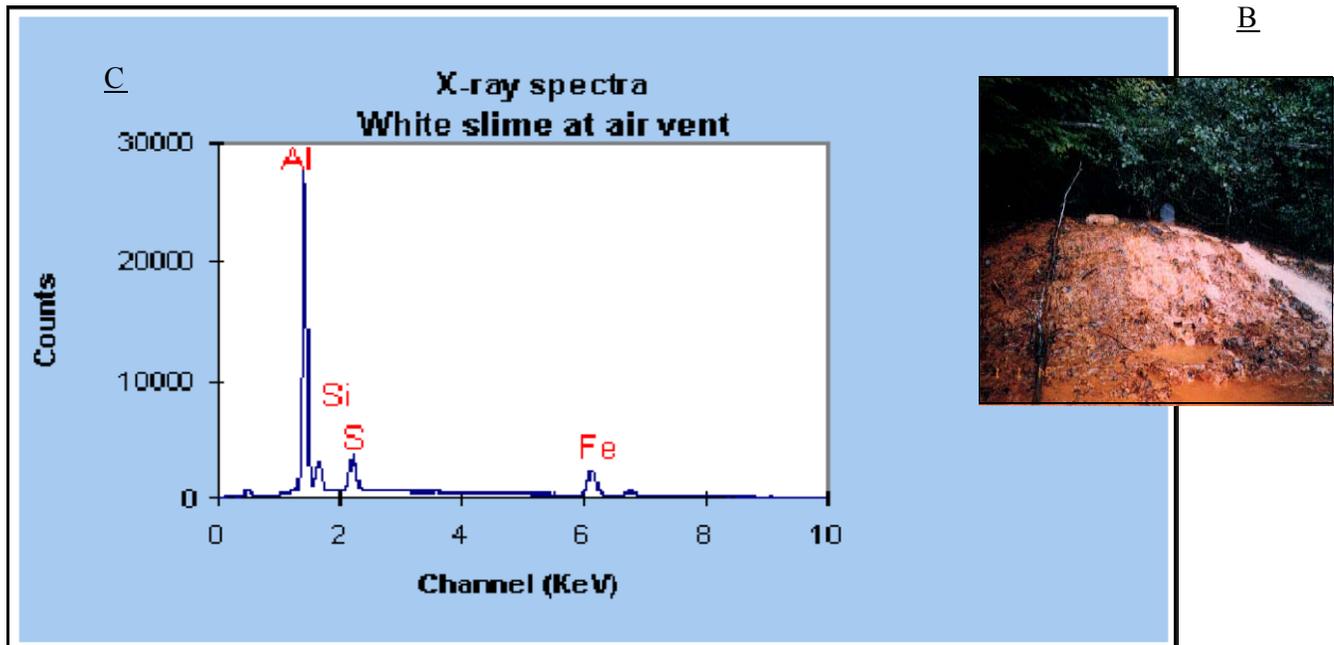
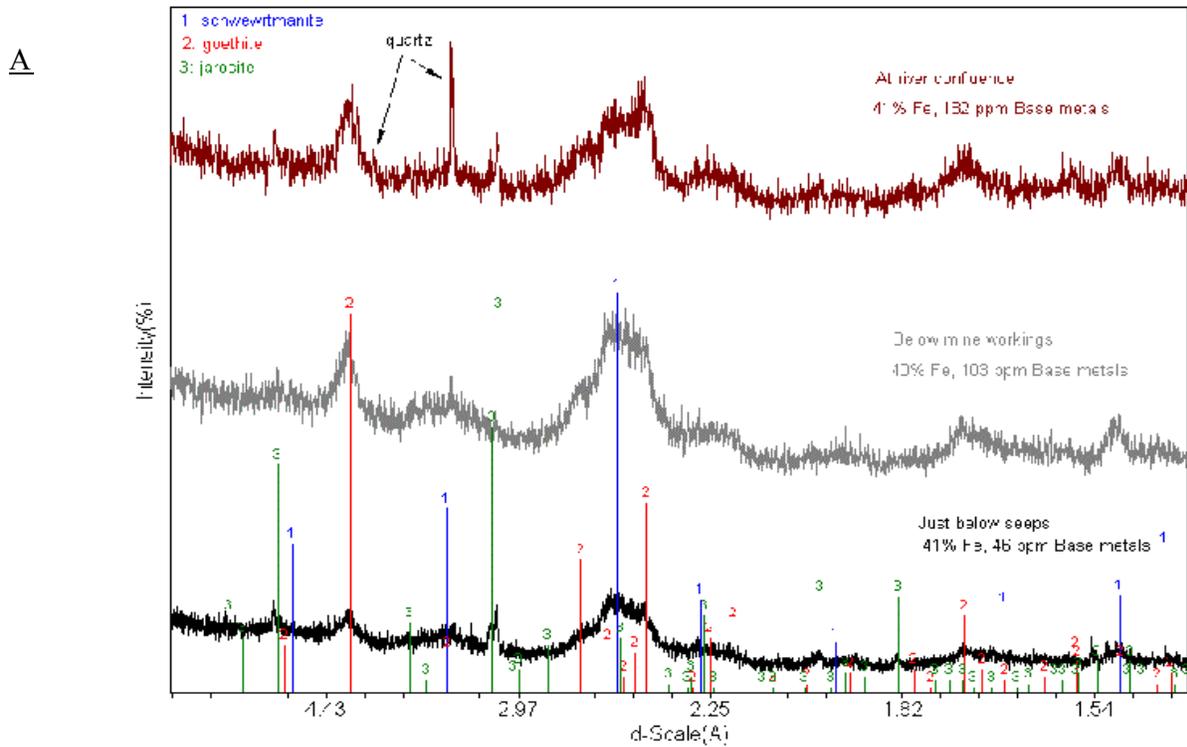


Figure 5. Ochre minerals. **A**, XRD patterns of iron-rich precipitates in Copperas Brook below the Elizabeth mine (fig. 3). Note that base metals incorporated in these ochres increase downstream from the mine workings. **B**, White slime at air vent, with a mound of white and red-orange precipitates that engulf leaf litter. **C**, Energy-dispersive spectrum of white slime analyzed by SEM shows that it is aluminum-rich, with minor silicon, iron, and sulfur.

Stream sediment data can also be compared with crustal abundance values (Fortescue, 1992) or with ranges of element concentrations typical of a particular lithology (Rose and others, 1979). Contaminated stream sediments can affect aquatic ecosystems and human health because of their potential toxicity to benthic organisms and to humans who ingest organisms exposed to contaminated sediments (USEPA, 1997b). Sediments can serve as sources and sinks as well as reservoirs for heavy metals. The use of stream sediment data for aquatic life toxicity assessment is controversial and cannot substitute for bioassay toxicity data; different sediments can represent different degrees of bioavailability for the same total concentration of a trace metal (Di Toro and others, 1990). Nevertheless, stream sediment data provide a useful screening tool to alert investigators to areas that may need further detailed sampling. EPA's National Stream Sediment Survey (USEPA, 1997b, Appendix B) provides a discussion of different stream sediment quality chemical guidelines developed by comparing dry weight sediment metal concentrations with biological effects data, and caveats about the use of chemical data to assess toxicity. More recently, consensus-based stream sediment quality guidelines for freshwater ecosystems have been proposed (MacDonald and others, 2000). Consensus-based guidelines for 28 metals and organic compounds, are based on guidelines previously developed from comparisons of sediment chemistry with toxicity data collected in field studies. Two consensus-based values are reported for each potential contaminant: (1) the threshold effect concentration (TEC) is the concentration below which harmful effects are unlikely to be observed and (2) the probable effects concentration (PEC) is the concentration above which harmful effects are likely to be observed. These values provide a screening tool for more costly and time-consuming field toxicity studies.

Example

Mining occurred from the early 1800's to the 1950's at several sites along an 8-mile stretch of Contrary Creek in central Virginia. The mines along Contrary Creek (fig. 6a) represent stratabound massive sulfide deposits of the regionally extensive Gold-Pyrite Belt of the Virginia Piedmont province. Early mining targeted near-surface gossan iron ore and pyrite, and the most recent mining produced copper, lead, and zinc from underground workings. Gold was mined from surface workings along the northern part of the creek, and the locality continues to be a popular site for recreational placer mining. Tailings and mine waste are present along creek banks and eastern tributaries. Despite reclamation efforts in the 1970's, the water quality has not improved and the area continues to be of concern to state regulators of environmental quality. The creek turns sharply east just north of the Rt. 522 bridge. The Tinder gold placer mine operated along the creek just north of the bridge. A number of small pyrite mines operated in the early 1900's between the Arminius Mine and the headwaters of the creek, but these workings are overgrown and do not appear to have impacted Contrary Creek (Dagenhart, 1980).

Geochemical analysis of the <80 mesh fraction of stream sediments collected along Contrary Creek shows that concentrations of copper and lead exceed PEC stream sediment quality guidelines (table 10) at all localities downstream of mine workings and that the streambed sediments at the Arminius mines, where tailings line the stream bank, are a significant source of copper, lead, zinc, and arsenic. Mercury is below PEC guideline concentrations at all localities and exceeds TEC guidelines at only one locality, although it does exceed the headwaters (proxy for background) concentration at all localities downstream. Mercury was probably used in the early placer gold operations (fig. 6a). The stream bank tailings at the Arminius mine develop efflorescent salts during the summer and salts form in protected areas year-round at the Sulfur mine (fig. 4a-d). An acidic (pH 2.9) side drainage from the Boyd Smith mine is a significant source of iron (fig. 6b) in the creek streambed sediments. We also observed a white aluminous precipitate at the point in the stream where the acidic drainage mixed with the main creek flow (pH 6.2). Just downstream of this confluence the creek pH measured 5.6. based probable effects concentration (above which harmful effects are likely to be observed) for metals in stream sediments in freshwater ecosystems (MacDonald and others, 2000).

Dagenhart (1980) identified the primary factors that affect stream water quality along Contrary Creek as (1) production of acid from oxidation of pyrite-rich tailings, (2) mobilization of heavy metals in the tailings, and (3) siltation from erosion of barren mine dumps. He concluded that without further reclamation activity or remining, water quality in Contrary Creek would continue to degrade for at least fifty years. Seal and others (1996) demonstrated that water quality at the Sulfur mine site has not improved in the twenty years since Dagenhart's (1980) study. Microbiological, remote sensing and mineralogic analysis of Contrary Creek flocculates and precipitates (Robbins and others, 1996; Anderson and Robbins, 1998) document extensive development of poorly

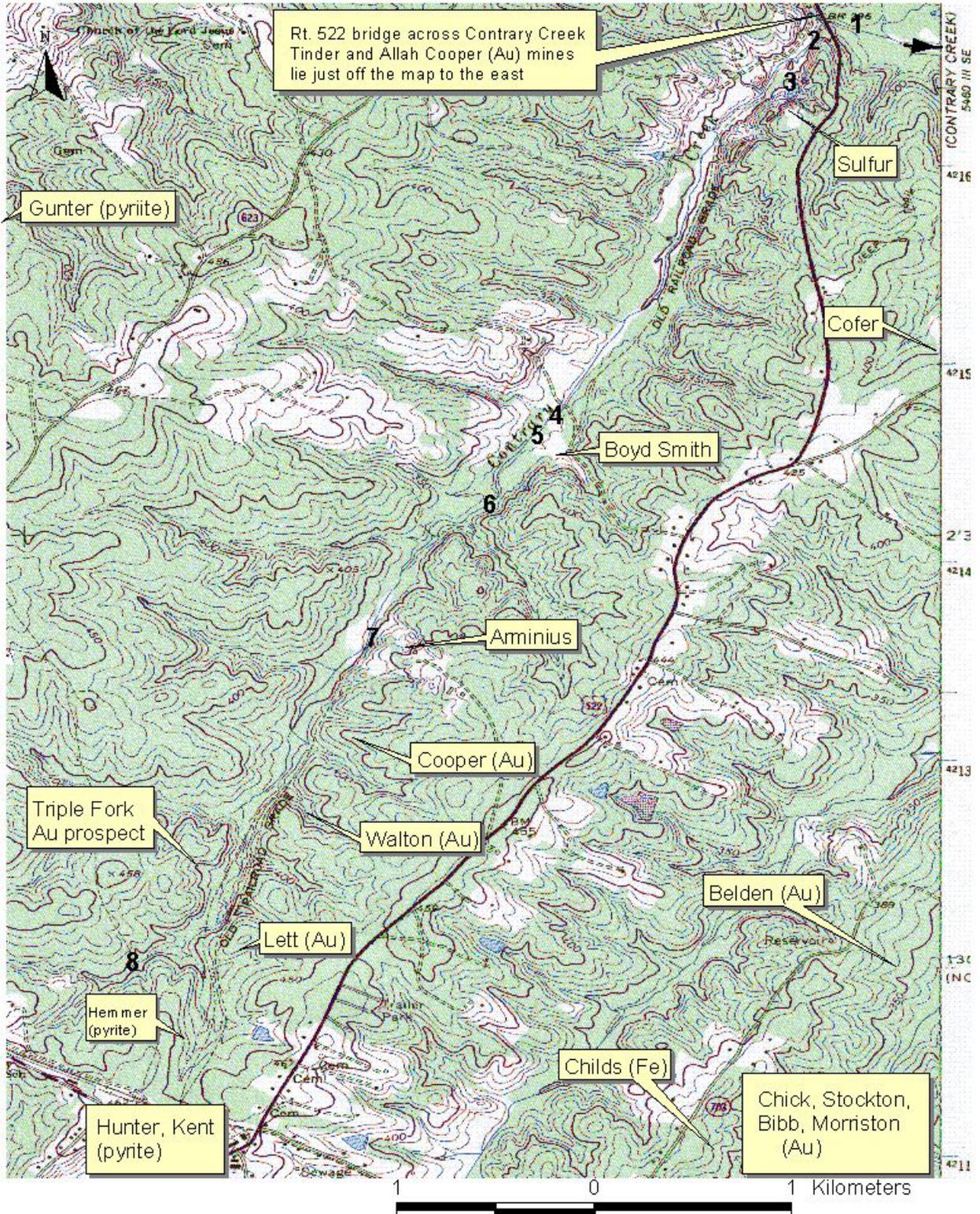


Figure 6a. Mines and prospects near Contrary Creek on the Mineral, VA 7.5' quadrangle. Stream sediments were sampled at localities 1-8.

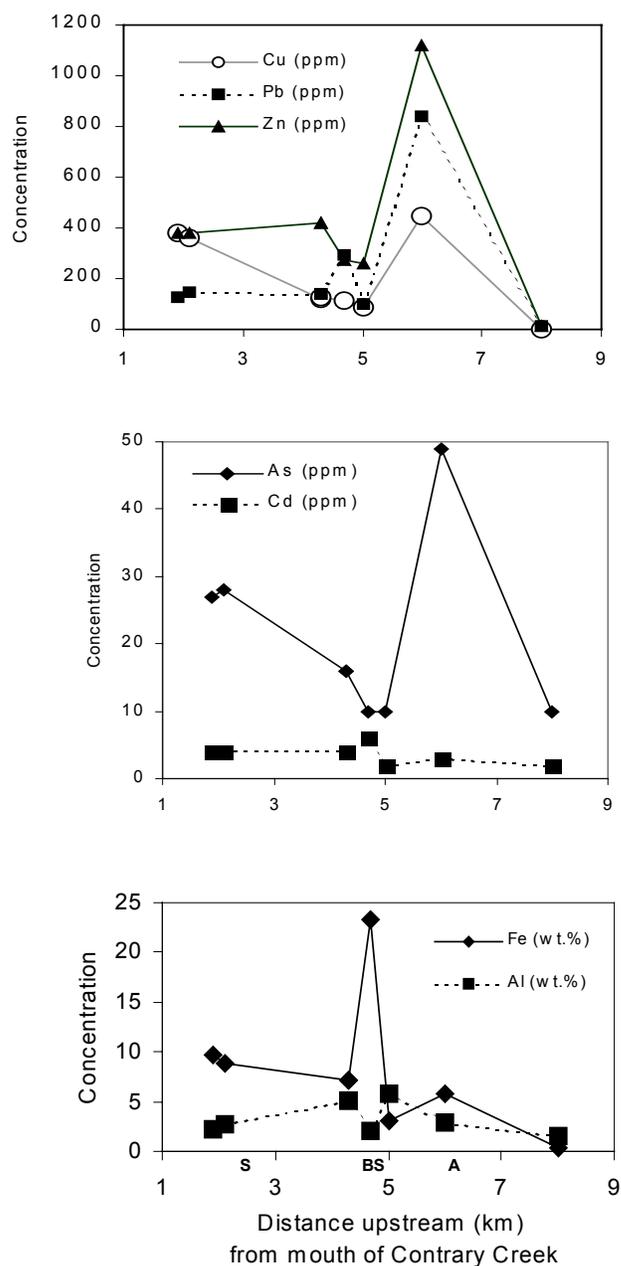


Figure 6. B. Metal concentrations in <80 mesh stream sediments along Contrary Creek as it flow past abandoned mines. See localities 1-8 on fig. 6A for sample locations. S, Sulfur mine; BS, Boyd Smith mine, A, Arminius mine. The Arminius mine near the headwaters of the creek (at 6 km) inputs significant amounts of base metals and arsenic; the Boyd Smith mine area contributes the most iron. Relative to the headwaters area above the mines, all metals increase downstream.

Table 10. Geochemical data for stream sediments (<80 mesh fraction) along Contrary Creek, VA.

| Locality | 1 | 2 | 4 | 4 | 5 | 6 | 7 | 8 | <u>Reference Values</u> | | | |
|-----------------------|-------|--|-------|-------|-------|-------|-------|-------|-------------------------|-----------|------------|------------|
| Element | Units | Localities numbered from north to south along Contrary Creek | | | | | | | | <u>CI</u> | <u>TEC</u> | <u>PEC</u> |
| <u>Major elements</u> | | | | | | | | | | | | |
| Al | % | 2.275 | 2.71 | 5.12 | 5.175 | 2.05 | 5.75 | 2.815 | 1.45 | 8.4 | | |
| Ca | % | 0.242 | 0.247 | 0.232 | 0.232 | 0.211 | 0.175 | 0.469 | 0.062 | 4.7 | | |
| Fe | % | 9.73 | 8.76 | 7.08 | 7.16 | 23.3 | 3 | 5.8 | 0.33 | 6.2 | | |
| K | % | 0.7 | 0.85 | 2.12 | 2.15 | 0.48 | 2.43 | 0.92 | 0.86 | 1.8 | | |
| Mg | % | 0.58 | 0.53 | 1.615 | 1.64 | 0.265 | 0.635 | 0.575 | 0.05 | 2.8 | | |
| Na | % | 0.361 | 0.447 | 0.67 | 0.679 | 0.152 | 0.556 | 0.442 | 0.247 | 2.3 | | |
| P | % | 0.02 | 0.02 | 0.015 | 0.015 | 0.015 | 0.01 | 0.11 | 0.005 | 0.1 | | |
| Ti | % | 0.684 | 0.78 | 0.636 | 0.642 | 1.656 | 0.348 | 0.384 | 0.168 | 0.6 | | |
| <u>Trace elements</u> | | | | | | | | | | | | |
| Ag | ppm | <2 | <2 | <2 | <2 | 3 | <2 | 6 | <2 | 0 | | |
| As | ppm | 27 | 28 | 16 | 16 | <10 | <10 | 49 | <10 | 2 | 9.79 | 33 |
| Au | ppm | 12 | 11 | <8 | <8 | 17 | <8 | <8 | <8 | 0 | | |
| Ba | ppm | 527 | 533 | 1,950 | 3,070 | 1,140 | 1,990 | 727 | 237 | 390 | | |
| Be | ppm | <1 | <1 | 2 | 2 | 1 | 2 | <1 | <1 | 2 | | |
| Bi | ppm | 28 | 20 | 30 | 25 | 61 | <10 | 16 | <10 | 0 | | |
| Cd | ppm | 4 | 4 | 4 | 4 | 6 | <2 | 3 | <2 | 0 | 0.99 | 5 |
| Ce | ppm | 16 | 20 | 47 | 52 | 13 | 52 | 18 | 10 | 66 | | |
| Co | ppm | 5 | 4 | 25 | 26 | <2 | 7 | <2 | <2 | 29 | | |
| Cr | ppm | 9 | 13 | 52 | 32 | 29 | 6 | 13 | <2 | 122 | 43.4 | 111 |
| Cu | ppm | 377 | 359 | 120 | 127 | 113 | 85 | 449 | <2 | 68 | 31.6 | 149 |
| Eu | ppm | <2 | <2 | <2 | <2 | <2 | <2 | <2 | <2 | 2 | | |
| Ga | ppm | 11 | 12 | 15 | 5 | 21 | 17 | 14 | 5 | 19 | | |
| Hg | ppm | 0.08 | 0.09 | 0.04 | 0.04 | 0.08 | 0.05 | 0.54 | <0.02 | 0.09 | 0.18 | 1.1 |
| Ho | ppm | <4 | <4 | <4 | <4 | <4 | <4 | <4 | <4 | 1 | | |
| La | ppm | 6 | 8 | 31 | 33 | 6 | 33 | 7 | 4 | 35 | | |
| Li | ppm | 3 | 4 | 8 | 8 | 3 | 5 | 4 | <2 | 18 | | |
| Mn | ppm | 464 | 452 | 2,220 | 2,050 | 1,030 | 685 | 301 | 71 | 1,060 | | |
| Mo | ppm | 4 | <2 | <2 | <2 | 3 | <2 | 4 | <2 | 1 | | |
| Nb | ppm | 8 | 10 | 10 | 10 | <4 | 9 | 12 | 6 | 20 | | |
| Nd | ppm | 22 | 20 | 35 | 36 | 40 | 26 | 14 | <9 | 40 | | |
| Ni | ppm | <3 | <3 | 27 | 28 | <3 | 12 | 3 | <3 | 99 | 22.7 | 49 |
| Pb | ppm | 128 | 144 | 141 | 142 | 292 | 103 | 841 | 11 | 13 | 35.8 | 128 |
| Sc | ppm | 7 | 6 | 18 | 19 | 8 | 12 | 6 | <2 | 25 | | |
| Sn | ppm | 7 | <5 | <5 | <5 | 13 | <5 | 11 | <5 | 2 | | |
| Sr | ppm | 36 | 40 | 65 | 66 | 130 | 42 | 74 | 15 | 384 | | |
| Ta | ppm | <40 | <40 | <40 | <40 | <40 | <40 | <40 | <40 | 2 | | |
| Th | ppm | 6 | <6 | 9 | 9 | 8 | 11 | <6 | <6 | 8 | | |
| U | ppm | <100 | <100 | <100 | <100 | <100 | <100 | <100 | <100 | 2 | | |
| V | ppm | 45 | 52 | 128 | 134 | 123 | 35 | 43 | 10 | 136 | | |
| Y | ppm | 5 | 5 | 11 | 12 | 5 | 12 | 6 | 3 | 31 | | |
| Yb | ppm | <1 | <1 | 1 | 1 | 1 | 2 | 2 | <1 | 3 | | |
| Zn | ppm | 377 | 381 | 417 | 421 | 273 | 259 | 1,120 | 14 | 76 | 121 | 459 |

Reference values: CI, Clarke Index value for crustal abundance from Fortescue (1992, table 4). TEC, Consensus-based threshold effects concentration (below which harmful effects are unlikely to occur) and PEC, Consensus-

crystalline ferrihydrite in the bed sediment. These studies, along with our new data on stream sediments, indicate that reclamation of an individual site along Contrary Creek is unlikely to significantly improve water quality and that the whole drainage poses a problem some fifty years after mining ceased. The limited reclamation that was done in the 1970s has had no measurable long-term effect.

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