Predicting Water Contamination from Metal Mines and Mining Wastes

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Workshop 2
International Land Reclamation and Mine Drainage Conference
and the
Third International Conference on the Abatement of Acidic Drainage
April 24, 1994
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FOREWORD

This report contains copies of slides used for a half-day workshop presented at the International Land Reclamation and Mine Drainage Conference and the Third International Conference on the Abatement of Acidic Drainage, Pittsburgh, Pennsylvania, on April 24, 1994. It consists of six sections. The Introduction lays out our geologic and geochemical approach to the prediction of mine-drainage composition and gives several examples of mine-drainage compositions from geologically diverse sites.

In the second section, Fundamentals of Mine-Drainage Formation and Geochemistry, we discuss the chemical reactions and factors that control pH and metal concentrations in mine-drainage systems. We also describe the resistance of different minerals to weathering reactions and the importance of carbonate minerals in pH buffering compared with other rock types. Finally, we introduce and define the term "geoavailability."

In the third section, Geologic Controls on Mine-Drainage Composition, we detail the geologic controls that dictate pH and metal concentrations in mine-drainage systems. In particular, we discuss mineralogic controls, host rock controls, and physical characteristics of mineral deposits that are important in determining mine-drainage composition.

In the fourth section, Geochemical Mobility of Metals in Mine-Drainage Systems: Prediction of Metal Transport, we describe several processes and interactions that influence metal mobility and transport in natural systems. We consider metal-sorption processes in detail and present examples of our predictive-modeling approach to sorption reactions in mine-drainage systems.

In the fifth section, An Empirical Study of Mine-Drainage Composition and Implications for Prediction, we present case studies that illustrate the importance of geologic controls on the composition of mine-drainage systems. We introduce the "Ficklin Plot," which illustrates the importance of pyrite and metal-sulfide content and acid-buffering capacity of the rock on mine-drainage composition. We give several examples that relate mine-drainage composition to geologic characteristics at particular mined sites.

In the final section, Geoenvironmental Models of Mineral Deposits and Their Applications, we outline a predictive approach for the weathering behavior of diverse mineral-deposit types based on the behavior of mineralogic zones. This approach is an extension of the case studies presented in the previous section. We give examples of how to apply this type of information to prioritize abandoned mine sites for cleanup, provide geologically and geochemically valid baselines for cleanup, and predict the degree of possible contamination at a site prior to mining.
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* Deceased October 11, 1993.
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Materials handed out during the workshop


Introduction
Introduction:
A geologic and geochemical approach

Issues

• Identifying and remediating of environmentally hazardous historic mine sites on public lands

• Predicting and mitigating the environmental effects of future mineral-resource development

• Determining natural baseline conditions
  • that existed prior to mining
  • that exist in drainage basins affected by mining
Examples of mine-drainage compositions

- Summitville, Solomon, Wellington, and Dauntless mines, Colorado (Plumlee et al., 1993)
- Broad spectrum of pH, metal contents
- Reflect importance of geologic controls on drainage composition

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<th>pH</th>
<th>SO4</th>
<th>Fe</th>
<th>Al</th>
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<td></td>
<td>mg/L</td>
<td>ppm</td>
<td>ppm</td>
<td>ppm</td>
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<td>1.8</td>
<td>128,000</td>
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1990,1991 data filtered 0.1 μm
### Summitville Mine Drainages

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<thead>
<tr>
<th></th>
<th>Zn (ppm)</th>
<th>Cu (ppm)</th>
<th>Cd (ppm)</th>
<th>Pb (ppm)</th>
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<tbody>
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<td>170</td>
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<tr>
<td>Reynolds</td>
<td>18</td>
<td>93</td>
<td>0.2</td>
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1990,1991 data, filtered 0.1 μm

### Summitville Mine Drainages

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<thead>
<tr>
<th></th>
<th>U (ppb)</th>
<th>Cr (ppb)</th>
<th>La (ppb)</th>
<th>Au (ppt)</th>
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<tr>
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<td>0.01</td>
<td>0.04</td>
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</table>

1990,1991 data, filtered 0.1 μm
Reynolds adit, Summitville
Changes in water composition over time

- Long-term changes reflect progressive exposure of sulfides by open-pit mining and resulting weathering
  - Predictable, based on deposit geology
- Spikes in spring most likely reflect flush of soluble secondary salts
  - Must understand secondary mineralogy in addition to primary sulfide mineralogy

Copper in Reynolds Tunnel Outflow
(modified from Golder Assoc., 1993)
<table>
<thead>
<tr>
<th></th>
<th>pH</th>
<th>SO$_4$</th>
<th>Fe</th>
<th>Al</th>
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<tr>
<td></td>
<td></td>
<td>mg/L</td>
<td>ppm</td>
<td>ppm</td>
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<tr>
<td>Solomon</td>
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<td>310</td>
<td>0.4</td>
<td>1.2</td>
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<tr>
<td>Mine</td>
<td>Zn</td>
<td>Cu</td>
<td>Cd</td>
<td>Pb</td>
</tr>
<tr>
<td>Drainage</td>
<td>ppm</td>
<td>ppm</td>
<td>ppm</td>
<td>ppm</td>
</tr>
<tr>
<td>Wellington</td>
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<td>87</td>
<td>0.2</td>
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<td>Pb</td>
</tr>
<tr>
<td>Drainage</td>
<td>ppm</td>
<td>ppm</td>
<td>ppm</td>
<td>ppm</td>
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<tr>
<td></td>
<td>170</td>
<td>0.3</td>
<td>0.1</td>
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</table>

filtered 0.1 $\mu$m
Dauntless Mine Drainage

<table>
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<tr>
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<th>pH</th>
<th>SO₄</th>
<th>Fe</th>
<th>Al</th>
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<td>.009</td>
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</table>

<table>
<thead>
<tr>
<th></th>
<th>Zn</th>
<th>Cu</th>
<th>Cd</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>ppb</td>
<td>27</td>
<td>1</td>
<td>0.4</td>
<td>1.5</td>
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</table>

filtered 0.1 μm

Water Contamination from Metal Mine Sites

A PREDICTABLE FUNCTION OF:

- Geochemical, biogeochemical processes**
  
  ** a fundamental control

- Mineral-deposit geology **
  
  ** a fundamental control

- Climate

- Mining method used

- Mineral processing method used
Fundamentals of Mine-Drainage Formation and Geochemistry
pH of Mine Drainage is a Function of:

- Balance between acid-producing and acid-consuming reactions that are part of weathering
- Relative rates of these reactions
- Accessibility of minerals that contribute to these reactions

Concentration of a Chemical Element in Mine Drainage is a Function of:

- Presence and concentration of that element in ore or host-rock minerals
- Accessibility of these minerals (mining method, porosity, grain size, climatic conditions, etc.)
- Susceptibility of these minerals to weathering
- Mobility of that element under surface or near-surface conditions
Acid-Producing Reactions

- Oxidation of pyrite and some other sulfide minerals releases Fe, \( \text{SO}_4^{2-} \), trace metals
- Hydrolysis of metal cations
- Precipitation of hydrous metal-oxide minerals

Generation of Acidic Drainage--Oxidation Reactions
(From Singer and Stumm, 1970; Forstner and Wittmann, 1979)

Initiator Reaction:

\[
\text{FeS}_2 + 3.5 \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + 2\text{SO}_4^{2-} + 2\text{H}^+ \quad \text{(Acidity)}
\]

Propagation Cycle:

\[
\begin{align*}
\text{Fe}^{2+} + 0.25 \text{O}_2 + \text{H}^+ & \xrightarrow{\text{Bacteria}} 0.5 \text{H}_2\text{O} + \text{Fe}^{3+} \\
14 \text{Fe}^{3+} + \text{FeS}_2 + 8 \text{H}_2\text{O} & \rightarrow 15 \text{Fe}^{2+} + 2\text{SO}_4^{2-} + 16\text{H}^+ \quad \text{(Acidity)}
\end{align*}
\]
Oxidation of Pyrite

\[
\begin{align*}
\text{Fe (II)} + S_2^{2-} + O_2 & \rightarrow \text{FeS}_2 + O_2 \\
\text{FeS}_2 + O_2 & \rightarrow \text{SO}_4^{2-} + \text{Fe (II)} \\
\text{Fe (II)} + O_2 & \rightarrow \text{Fe (III)} \\
\text{Fe (III)} & \rightarrow \text{Fe (OH)}_3 (s)
\end{align*}
\]

(from Stumm and Morgan, 1981)

Sources of Fe \(^{3+}\)

- Microbially-catalyzed oxidation of Fe (II)
  10\(^6\) times faster than abiotic (Singer and Stumm, 1970)

- Secondary iron-sulfate minerals
  Can form on surface of oxidizing FeS\(_2\)
  (Nordstrom, 1982; Cravotta, 1994)

Romerite
\[
\text{Fe (II)}\text{Fe}_{2(III)}\text{(SO}_4\text{)}_4 \cdot 14\text{H}_2\text{O}
\]

Coquimbite
\[
\text{Fe}_{2(III)}\text{(SO}_4\text{)}_3 \cdot 9\text{H}_2\text{O}
\]

Copiapite
\[
\text{Fe (II)}\text{Fe}_{4(III)}\text{(SO}_4\text{)}_6\text{(OH)}_2 \cdot 20\text{H}_2\text{O}
\]
Weathering of Other Sulfides

\[ \text{PbS} + 8 \text{Fe}^{3+} + 4 \text{H}_2\text{O} \rightarrow \text{Pb}^{2+} + \text{SO}_4^{2-} + 8 \text{Fe}^{2+} + 8 \text{H}^+ \]

versus

\[ \text{PbS} + 2 \text{O}_2 \rightarrow \text{Pb}^{2+} + \text{SO}_4^{2-} \]

Microbial Oxidation of Other Sulfides

Chalcopyrite - separate metal and S attack:

\[ \text{CuFeS}_2 + 4.25\text{O}_2 + \text{H}^+ \rightarrow \text{Cu}^{2+} + \text{Fe}^{3+} + 2\text{SO}_4^{2-} + 0.5\text{H}_2\text{O} \]

(+) hydrolysis

\[ \text{Fe}^{3+} + 3\text{H}_2\text{O} \rightarrow \text{Fe(OH)}_3 + 3\text{H}^+ \]

\[ \text{CuFeS}_2 + 4.25\text{O}_2 + 2.5\text{H}_2\text{O} \rightarrow \text{Cu}^{2+} + 2\text{SO}_4^{2-} + \text{Fe(OH)}_3 + 2\text{H}^+ \]

Chalcocite - microbial oxidation of S:

\[ \text{CuS} + 0.5\text{O}_2 + 2\text{H}^+ \rightarrow \text{Cu}^{2+} + \text{S}^0 + \text{H}_2\text{O} \]

\[ \text{S}^0 + 1.5\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + 2\text{H}^+ \]

\[ \text{CuS} + 2\text{O}_2 \rightarrow \text{Cu}^{2+} + \text{SO}_4^{2-} \]
Acid-Producing Reactions

Hydrolysis of metal cations

\[
\begin{align*}
Fe^{3+} + 3H_2O & \rightarrow Fe(OH)_3 + 3H^+ \\
Al^{3+} + 3H_2O & \rightarrow Al(OH)_3 + 3H^+
\end{align*}
\]

Acid-Producing Reactions

Precipitation of hydrous-oxide minerals

\[
\begin{align*}
Fe^{2+} + 0.25O_2 + 2.5H_2O & \rightarrow Fe(OH)_3(s) + 2H^+ \\
Fe^{3+} + 3H_2O & \rightarrow Fe(OH)_3(s) + 3H^+ \\
Al^{3+} + 3H_2O & \rightarrow Al(OH)_3(s) + 3H^+
\end{align*}
\]
Acid-Consuming (Buffering) Reactions

- Dissolution of carbonate minerals
  releases Ca, Mg, $H_2CO_3^\circ$ or $HCO_3^-$ or $CO_3^{2-}$

- Dissolution of aluminosilicate minerals
  releases Al, Ca, Fe, K, Mg, Mn, Na, Si

- Dissolution of hydrous Fe- and Al- oxide minerals
  releases Fe, Al, adsorbed elements

- Adsorption of $H^+$ onto mineral surfaces
  releases desorbed or ion-exchanged elements

Acid-Consuming (Buffering) Reactions

Most weathering reactions consume protons (acidity)
(Written in order of decreasing ease of weathering)

$$CaCO_3 + 2H^+ \rightarrow Ca^{2+} + H_2CO_3$$
calcite

$$KAISi_3O_8 + H^+ + 7H_2O \rightarrow K^+ + 3H_4SiO_4 + Al(OH)_3$$
K-feldspar

$$KAl_3Si_3O_{10}(OH)_2 + H^+ + 9H_2O \rightarrow K^+ + 3H_4SiO_4 + 3Al(OH)_3$$
muscovite
Acid-Consuming (Buffering) Reactions

Dissolution of silica does not consume protons

\[ \text{SiO}_2 + 2\text{H}_2\text{O} \rightarrow \text{H}_4\text{SiO}_4 \]

quartz

Resistance of Minerals to Weathering

- Olivine
- Augite
- Hornblende
- Biotite
- Potash feldspar
- Muscovite
- Quartz

Calcic plagioclase
Calc-alkalic plagioclase
Alkali-calcic plagioclase
Alkaline plagioclase

Increasing Stability

(from Goldich, 1938; Rose et al., 1979)
Acid-Consuming (Buffering) Reactions

Dissolution of silicate minerals can result in the formation of less reactive solid phases

\[
\text{CaAl}_2\text{Si}_2\text{O}_8 + 2\text{H}^+ + \text{H}_2\text{O} \rightarrow \text{Ca}^{2+} + \text{Al}_2\text{Si}_2\text{O}_6(\text{OH})_4
\]

\text{plagioclase} \quad \text{kaolinite}

Weathering
(from Rose et al., 1979)

Jackson's Series
Gypsum (halite, etc.)
Calcite (dolomite, aragonite, etc.)
Olivine-hornblende (diopside, etc.)
Biotite (glaucnite, chlorite, etc.)
Albite (anorthite, microcline, etc.)
Quartz
Illite (muscovite, sericite, etc.)
Intermediate hydrous micas
Montmorillonite
Kaolinite (halloysite)
Gibbsite (boehmite, etc.)
Hematite (goethite, limonite, etc.)
Anatase (rutilite, ilmenite, etc.)

Increasing stability
The Carbonate System

\[
\text{CO}_2(g) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_2\text{CO}_3(aq)
\]

\[
\text{H}_2\text{CO}_3 \rightleftharpoons \text{HCO}_3^- + \text{H}^+
\]

\[
\text{HCO}_3^- \rightleftharpoons \text{CO}_3^{2-} + \text{H}^+
\]

- Important pH buffering system in natural waters
- Usually responsible for alkalinity

Solubility of Carbonate Minerals

for MeCO$_3$ = Me$^{2+}$ + CO$_3^{2-}$ at 25°C

Nesquehonite (MgCO$_3$ · 3H$_2$O)
Magnesite (MgCO$_3$)
Aragonite (CaCO$_3$)
Calcite (CaCO$_3$)
Strontianite (SrCO$_3$)
Rhodochrosite (MnCO$_3$)
Smithsonite (ZnCO$_3$)
Siderite (FeCO$_3$)
Cerussite (PbCO$_3$)
Dolomite (Ca Mg (CO$_3$)$_2$)

Increasing Solubility

most
least
Classification of Bedrock Types
(from Glass et al., 1982)

- Type I - Low or no buffering capacity, overlying waters very sensitive to acidification
  (Granite/syenite, granitic gneisses, quartz sandstones)

- Type II - Medium-to-low buffering capacity, acidification restricted to 1st- and 2nd-order streams and small lakes
  (Sandstones, shales, conglomerates, high-grade metamorphic to intermediate volcanic rock, intermediate igneous rocks, calc-silicate gneisses)

Classification of Bedrock Types, continued
(from Glass et al., 1982)

- Type III - High-to-medium buffering capacity, no acidification except in cases of overland runoff
  (Slightly calcareous, low grade intermediate to mafic volcanic, ultramafic, glassy volcanic rocks)

- Type IV - “Infinite” buffering capacity
  (Highly calcareous sediments or metamorphic equivalents, limestones, dolomites)
Geoavailability

• That portion of an element’s or a compound’s total content in an earth material that can be liberated to the environment (or biosphere) through mechanical, chemical, or biological processes

• Related to the susceptibility and availability of the resident mineral phase(s) to mechanical, chemical, and biological processes

(from Smith and Huyck (1994; in press))
(Word coined by Warren Day and originally defined by Geoffrey Plumlee)

(modified from Smith and Huyck (1994; in press))
Geologic Controls on Mine-Drainage Composition
Geologic Controls on Mine-Drainage Composition: A Predictive Approach

Geologic Controls

- Pyrite (FeS$_2$) content
- Other sulfide content
- Host rock
- Wallrock alteration
- Gangue mineralogy
- Mineral textures, trace element content
- Nature of deposit
  - vein, massive, disseminated
- Structure, permeability
- Trace element content (deposit, host rocks)

Many sulfides generate acid

Control rate of weathering

Can consume acid

Control access of weathering agents
Mineral-deposit geochemistry

- Major/trace element composition of mineralization, host rocks, wallrock alteration
- Different deposit types can have quite different, distinctive geochemical characteristics
  - Function of plate tectonic setting, magma composition, host rock composition, mineralizing processes, etc.
- Mineral-deposit geochemistry reflected in mine-drainage compositions

Mineralogic Controls

Minerals as sources for major elements
- Si, Al, Ca, K, Na, Mg: From aluminosilicates, quartz, carbonates
- Fe: From pyrite, iron oxides (hematite, magnetite), aluminosilicates (Fe-clays, chlorites), carbonates (siderite)
- Mn: From carbonates, oxides, some aluminosilicates (i.e. MnSiO₃ or solid solutions in chlorite), etc.

Minerals as sources for trace elements
- Zn, Cu, Cd, Pb, As, Sb: Often from sulfides or sulfosalts, but are other sources
- U, Th, Rare earth elements: From uraninite, thorite, monazite, other “uncommon” minerals
Mineralologic controls

• Acid-generating primary minerals
  Pyrite, marcasite (FeS₂)  Pyrrhotite (FeS)
  Chalcopyrite (CuFeS₂)  Arsenopyrite (FeAsS)
  Enargite (Cu₃AsS₄)  Tennantite (Cu₁₂As₄S₁₃)
  Other sulfides (not all)  Siderite (FeCO₃) - if Fe(OH)₃ ppts.

Amount of acid generated depends on metal/sulfur ratio of sulfides, oxidant (O₂ vs Fe⁺⁺), and precipitates formed.

• Acid-consuming minerals
  • Carbonates, aluminosilicates, hydrous oxides

Mineral Resistance to Oxidation

• Important control on relative rates of acid production

<table>
<thead>
<tr>
<th>Mineralogy</th>
<th>Grain size</th>
<th>Texture</th>
<th>Trace elements</th>
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<tbody>
<tr>
<td>Pyrrhotite</td>
<td>Fine</td>
<td>Framboidal</td>
<td>High</td>
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<td>Chalcocite</td>
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<td>Enargite</td>
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<td>Molybdenite</td>
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Increasing resistance to oxidation
Mineralogic controls

Mineral deposits are mineralogically variable in time and space
- Strong influence on element mobility
- Encapsulation of earlier minerals by later minerals
- Mineral zoning on many scales
  - Within an ore shoot
  - Within a vein or ore body
  - Across a district

---

[Diagram showing mineral deposits and zones]

- **Central Zone**: High-pyrite quartz veins
- **Intermediate Zone**: Pyrite-quartz veins with base metal sulfides
- **Peripheral Zone**: Galena-sphalerite-quartz-carbonate veins
Mineralogic controls

Secondary minerals

- Form as a result of weathering of mineral deposits and mine wastes
- Mineralogy depends on:
  - Primary mineralogy
  - Climate (temperature, humidity, amount of water, etc.)
- Some are readily soluble, and form by evaporation
- Depending upon mineralogy, can either generate or consume acid during weathering.

From Plumlee and Whitehouse-Veaux (in press)
## Mineralogic controls

Examples of secondary minerals (Nordstrom and Alpers, in press)

- Ferrihydrite—$\text{Fe}_5\text{HO}_8\cdot4\text{H}_2\text{O}$ ($\Rightarrow$ goethite, hematite over time)
- Schwertmannite—$\text{Fe}^{III}\text{O}_6(\text{SO}_4)(\text{OH})_6$
- Jarosite—$\text{KFe}^{III}(\text{SO}_4)_2(\text{OH})_6$
- Chalcanthite*—$\text{CuSO}_4\cdot5\text{H}_2\text{O}$  
  * soluble
- Copiapite*—$\text{Fe}^{II}\text{Fe}^{III}(\text{SO}_4)_6(\text{OH})_2\cdot2\text{H}_2\text{O}$
- Melanterite*—$(\text{Fe}^{II},\text{Zn},\text{Cu})\text{SO}_4\cdot7\text{H}_2\text{O}$
- Rhomboclase*—$(\text{H}_3\text{O})\text{Fe}^{III}(\text{SO}_4)_2\cdot3\text{H}_2\text{O}$
- Scorodite—$\text{Fe}^{III}(\text{AsO}_4)\cdot2\text{H}_2\text{O}$
- Hinsdalite—$(\text{Pb},\text{Sr})\text{Al}_3(\text{PO}_4)(\text{SO}_4)(\text{OH})_6$

## Host rocks - chemical controls

**Host rock lithology**

- Ability to consume acid (function of mineralogy, reactivity):
  - i.e., carbonates$>$glassy volcanics$>$coarse igneous
- May produce acid: (i.e. sulfidic schists)
- Source of major, trace elements

**Host rock alteration**

- Can increase or decrease ability to consume acid:
  - acid-sulfate (silica, alunite, kaolinite) — low ability
  - propylitic (carbonate, epidote, chlorite, $\pm$pyrite) — higher ability
    - “Green is Good!”
Physical characteristics of mineral deposits

- Influence extent of water-mineralization interactions, access of groundwaters, rates of weathering
- Type of mineralization
  - Massive lenses of sulfides
  - Veins
  - Stockworks or disseminated
- Permeability
  - Structural (e.g., throughgoing fracture systems, etc.)
  - Lithologic (e.g. sedimentary aquifers, karst channels, aquitards, aquicludes)
Geochemical Mobility of Metals in Mine-Drainage Systems: Prediction of Metal Transport
Trace Elements in Natural Waters

Regardless of their source, high concentrations of dissolved trace elements generally do not persist as they are transported through aquatic systems.

Some Possible Reactions

- Precipitation
- Sorption
- Oxidation / reduction
- Hydrolysis
- Dilution
- Dispersion
- Microbial transformation
Trace Elements

Chemistry and mobility in water are dominated by:

- Complexation reactions
- Precipitation reactions
- Sorption reactions
- Particulate transport
- Biological uptake and transformation

Observed Degree of Mobility of Trace Elements

Smith et al. (1992)
Cd = Ni > Zn > Cu > Pb > As

Blowes and Jambor (1990)
Fe = Mn ≥ Zn > Ni ≥ Co > Pb > Cu

Dubrovsky (1986)
Co = Ni > Zn > Pb > Cu

Mann (1983)
Zn > Cu > Pb
Goldschmidt’s general geochemical classification of the elements in the periodic table (from Levinson, 1980). The geochemical character of a chemical element, and its position in the periodic table, can be correlated with the type of bonding it prefers.

**Lithophile** - Elements concentrated in the Earth’s crust as silicates

**Chalcophile** - Elements associated with sulfur and concentrated in sulfides

**Atmophile** - Elements present as gases

**Siderophile** - Elements associated with iron in the Earth’s core
Mobility of chemical elements in the surficial environment as a function of ionic charge and ionic radius. (Data from Whittaker and Muntus, 1970.) Ionic potential is the ionic charge divided by the ionic radius. Elements with low ionic potential (such as Ca and Na) are soluble as simple cations; those with very high ionic potential attract oxygen ions and form soluble oxyanions (such as SO$_4^{2-}$). Elements with intermediate ionic potential generally have low-solubility and strong-adsorption tendencies and hence are relatively immobile.

from Rose et al (1979)
Some Mobility Controls

- Abundance and geoavailability
- Redox conditions
- Aqueous speciation
  - pH, complexation (inorganic and organic), etc.
- Precipitation / dissolution
  - Solubility of secondary mineral phases
  - Provides an upper limit
- Sorption / desorption
  - (also coprecipitation and ion exchange reactions)
- Salinity
- Uptake and biotransformation
- Colloids / flocculation

(modified from Smith and Huyck (1994; in press))
Redox Conditions

Oxidation-reduction (redox) reactions can be considered as:

- Reactions involving transfer of oxygen
  or
- Reactions involving transfer of electrons

Redox Conditions

- Usually determined by the balance between supply of atmospheric oxygen and microbial consumption of oxygen
- Changes in redox conditions can have a large effect on the solubility and mobility of many metals
  
  Oxidizing conditions can mobilize Cr, Se, and U
  
  Reducing conditions can mobilize As, Fe, and Mn
The Eh (oxidation/reduction potential) and pH conditions of some natural environments. The parallel slanting lines are the limits of water stability.
Some Redox-Sensitive Elements

Fe  Mn  S
As  Cr  Cu  Hg
Mo  Se  U  V

Aqueous Speciation

- Difficult to measure directly
  Need complete chemical analysis to run
  chemical speciation computer programs
- Affects sorption / desorption reactions
- Biological uptake of trace elements is related to
  chemical speciation
  Complexation can reduce uptake and toxicity
  and can induce deficiency
  Bioavailability and toxicity of many trace elements
  is related to their free concentration
  rather than their total concentration
Precipitation / Dissolution

- Often fairly slow when compared with hydrologic residence times
- Solid initially precipitated often is not the most thermodynamically stable solid
- Metastable solids are often nonstoichiometric and typically contain impurities
- Provide an upper limit on trace element concentrations in aqueous systems

Thermodynamics vs Kinetics

Thermodynamics
- Determines overall energetics of a chemical system
- At equilibrium, free energy of the system is at its minimum value

Kinetics
- Rate at which a chemical reaction proceeds
- Depends on the molecular-level details of the chemical reaction
Figure 14. Fields of stability for solid and dissolved forms of iron as a function of Eh and pH at 25°C and 1 atmosphere pressure. Activity of sulfur species 96 mg/L as SO$_4$$^2^-$, carbon dioxide species 61 mg/L as HCO$_3^-$, and dissolved iron 56 µg/L.

(from Hem, 1989)
pH Range of Initial Hydrous Oxide Precipitation

<table>
<thead>
<tr>
<th>Metal</th>
<th>pH Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti $^{4+}$</td>
<td>1.4 - 1.6</td>
</tr>
<tr>
<td>Fe $^{3+}$</td>
<td>2.2 - 3.2</td>
</tr>
<tr>
<td>Sn $^{2+}$</td>
<td>2.3 - 3.2</td>
</tr>
<tr>
<td>Al $^{3+}$</td>
<td>3.8 - 4.8</td>
</tr>
<tr>
<td>Cr $^{3+}$</td>
<td>4.6 - 5.6</td>
</tr>
<tr>
<td>Fe $^{2+}$</td>
<td>5.1 - 5.5</td>
</tr>
<tr>
<td>Zn $^{2+}$</td>
<td>5.2 - 8.3</td>
</tr>
<tr>
<td>Cu $^{2+}$</td>
<td>5.4 - 6.9</td>
</tr>
<tr>
<td>Ni $^{2+}$</td>
<td>6.7 - 8.2</td>
</tr>
<tr>
<td>Co $^{2+}$</td>
<td>7.2 - 8.7</td>
</tr>
<tr>
<td>Pb $^{2+}$</td>
<td>7.2 - 8.7</td>
</tr>
<tr>
<td>Mn $^{2+}$</td>
<td>7.9 - 9.4</td>
</tr>
<tr>
<td>Cd $^{2+}$</td>
<td>8.0 - 9.5</td>
</tr>
</tbody>
</table>

Solid-Solution Substitutions and Replacement Reactions

Favored for metals that have relatively insoluble sulfides and relatively soluble secondary minerals such as Ag, Cu, and Ni

Covellite (CuS) replacement of pyrrhotite and sphalerite is often observed

\[
\begin{align*}
\text{Cu}^{2+} + \text{FeS} & \rightarrow \text{Fe}^{2+} + \text{CuS} \\
\text{Cu}^{2+} + \text{ZnS} & \rightarrow \text{Zn}^{2+} + \text{CuS}
\end{align*}
\]
Precipitation of Efflorescent Salts

Melanterite  
(Fe\(^{II}\), Zn, Cu) \(\text{SO}_4 \cdot 7\text{H}_2\text{O}\)  
Iron Mountain, CA  
(Alpers et al., 1994)

Chalcanthite  
\(\text{CuSO}_4 \cdot 5\text{H}_2\text{O}\)  
Summitville, CO  
(Plumlee et al., (in prep.))

- Soluble

- Transient storage/source for metals and acid

- Can influence mine-drainage composition  
  (related to seasonal wet/dry cycles)

Sorption / Desorption

What factors affect partitioning of trace elements between water and sediment?

Can partitioning reactions  
(and transport)  
be predicted?
Why do we care about sorption?

- Often maintains trace-element concentrations below the solubility limits of mineral phases
- An important control of element mobility
- Influences speciation and bioavailability of solutes and the electrostatic properties and reactivity of surfaces

Definitions
(from Sposito, 1986)

**Adsorption** - accumulation at the solid/water interface

**Absorption** - diffusion into a solid phase

**Sorption** - general term

**Precipitation** - growth of a 3-D solid phase
Model sorption curves showing relative placement of adsorption edges of selected cations and anions for sorption onto hydrous iron oxide (from Smith, 1991).
Sorption Summary

- pH is a master variable
  pH-dependent sorption edge

- Solid phases can serve as a sink or a source for trace elements

- Metal-sorption reactions can be predicted in many iron-rich systems

Important Adsorbent Properties

- Large binding capacity and intensity
- Abundance
- High specific surface area
- Large adsorption capacity
- High ion-exchange capacity
- High chemical reactivity
Important Adsorbents

- Hydrous-oxide minerals (of Fe, Mn, Al, Si)
- Clay minerals
- Organic Matter

(all are potentially important adsorbents even in low abundance)

Divalent Cation Adsorption on Hydrous Metal Oxide Minerals

Adsorption varies with:
- pH of solution
- Particular cation
- Particular solid
- Solid:solution ratio
- Properties of the solid
- Cation concentration
- Cation speciation
- Presence and concentration of other aqueous species
- Solution composition and redox state
- Presence of coatings
**Metal Adsorption Affinities**

**Different Hydrous Metal Oxides:**

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Cation Order</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amorphous Iron Oxide</td>
<td>Zn $^{2+}$ &gt; Ni $^{2+}$ &gt; Co $^{2+}$ &gt; Sr $^{2+}$ &gt; Mg $^{2+}$</td>
</tr>
<tr>
<td>Manganese Dioxide</td>
<td>Co $^{2+}$ &gt; Zn $^{2+}$ &gt; Ni $^{2+}$ &gt; Sr $^{2+}$ &gt; Mg $^{2+}$</td>
</tr>
<tr>
<td>Amorphous Aluminum Oxide</td>
<td>Zn $^{2+}$ &gt; Ni $^{2+}$ &gt; Co $^{2+}$ &gt; Mg $^{2+}$ &gt; Sr $^{2+}$</td>
</tr>
</tbody>
</table>

(after Kinniburgh et al. (1976) and Murray (1975))

**Divalent Cation Adsorption on Hydrous Iron and Aluminum Oxides**

(after Kinniburgh and Jackson, 1981)

<table>
<thead>
<tr>
<th>Cation</th>
<th>Critical pH Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu $^{2+}$, Pb $^{2+}$, Hg $^{2+}$</td>
<td>3 - 5</td>
</tr>
<tr>
<td>Zn $^{2+}$, Co $^{2+}$, Ni $^{2+}$, Cd $^{2+}$</td>
<td>5 - 6.5</td>
</tr>
<tr>
<td>Mn $^{2+}$</td>
<td>6.5 - 7.5</td>
</tr>
<tr>
<td>Mg $^{2+}$, Ca $^{2+}$, Sr $^{2+}$</td>
<td>6.5 - 9</td>
</tr>
</tbody>
</table>

(Generally higher pH's for silica and lower pH's for manganese oxides)
Anion Adsorption on Hydrous Oxides

• Adsorption favored by low pH  
  (opposite of cation adsorption behavior)

For hydrous iron oxide:
• Strongly-adsorbed anions - phosphate, selenite
• Weakly-adsorbed anions - chromate, selenate

Adsorption Inhibition in Carbonate Systems
(from Smith and Langmuir, 1987)

• Weak adsorption of metal-carbonate complexes
• Competition of $\text{HCO}_3^-$ and $\text{CO}_3^{2-}$ for surface sites
Figure 3. Distribution diagram for copper species as a function of pH for the Cu$^{2+}$-H$_2$O-CO$_2$ system for 10$^{-4}$ M (6,354 ppb) total copper, I = 0.01 M (as KNO$_3$ or KHCO$_3$), 25°C, and P$_{CO_2}$ = 10$^{-3.5}$ atm. (solid lines) and C$_T$ = 10$^{-2}$ M (dashed lines).

(from Smith and Langmuir, 1987)
Effect of Redox and Complexation on Sorption
(from Davis et al., 1993)

<table>
<thead>
<tr>
<th>Strongly sorbed solutes</th>
<th>Weakly sorbed solutes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn$^{2+}$</td>
<td>ZnEDTA$^{2-}$</td>
</tr>
<tr>
<td>Cr$^{3+}$</td>
<td>CrO$_4^{2-}$</td>
</tr>
<tr>
<td>SeO$_3^{2-}$</td>
<td>CrEDTA$^-$</td>
</tr>
<tr>
<td>Se$^0$</td>
<td>SeO$_4^{2-}$</td>
</tr>
</tbody>
</table>

complexation

redox

Adsorption Modeling

Distribution coefficient

\[ K_d = \frac{c_{\text{solid}}}{c_{\text{solution}}} \]

- Only for those conditions under which it was measured
- Only for a steady-state case
Adsorption Modeling

Need to account for

- Abundance
- Adsorption capacity
- Binding intensity

Computer-Simulation Method
(from Smith, 1991; Smith et al., 1992, 1993)

MINTEQA2 (USEPA; Allison et al., 1991)
+ Generalized Two-Layer Sorption Model
(Dzombak and Morel, 1990)

- Simultaneously compute sorption reactions and solution equilibria
- Predict sorption behavior over a wide range of pH and water composition
Computer-Simulation Method
(from Smith, 1991; Smith et al., 1992, 1993)

Input:

- Complete analytical information on water composition
- Sorption parameters from model
- No fitting parameters are used in modeling
  (this is a predictive method)

Assumptions:

- Sorption only onto hydrous ferric oxide
- Equilibrium conditions
- Validity of approach
Model Predictions

versus

Empirical Data

(from Smith, 1991)
Comparison of experimental metal-partitioning data (symbols) with model predictions (curves) for sorption onto hydrous iron oxide (from Smith, 1991).
Computer-Simulation Summary
(from Smith, 1991)

- Metal partitioning to the sediment is dominated by iron phases in the sediment
- Metal partitioning is consistent with simple laboratory experiments using synthetic hydrous iron oxide
- Metal partitioning can be predictively modeled
- Model requires very little characterization work
Metal and arsenic partitioning between water and suspended sediment at mine-drainage sites in diverse geologic settings

Kathleen S. Smith, Walter H. Ficklin, Geoffrey S. Plumlee, and Allen L. Meier

Seventh International Symposium on Water-Rock Interaction
Park City, Utah, July 13-18, 1992
Figure 1. Map of western Colorado showing the location of drainage sites sampled relative to the Colorado Mineral Belt and the San Juan volcanic field.

Figure 2. Variations in aqueous base metal concentrations (given as the sum of base metals Zn, Cu, Cd, Co, Ni, and Pb) as a function of pH for waters draining diverse ore deposit types in Colorado. Proposed classes for these waters are bounded by heavy lines and labeled with bold text.

(from Ficklin et al., 1992)
Site Selection Criteria for Adsorption Study
(from Smith et al., 1992)

- Presence of iron-rich bottom sediment
- Drainage in contact with iron-rich bottom sediment
- Presence of abundant dissolved oxygen
- At least 0.5 mg/L Fe present in suspended-particulate fraction

Selected Sites
(from Smith et al., 1992)

- pH ranges from 3.8 to 7.7
- Fe in suspended-particulate fraction ranges from 0.5 to 10 mg/L
- Diverse geological and geochemical settings
Model predictions of metal and arsenic sorption onto hydrous ferric oxide (HFO) as a function of pH for two different concentrations of HFO (A and B) (from Smith et al., 1992).

Suspended-sediment fraction of metals and arsenic computed in mine-drainage waters containing suspended iron particulates. Data points represent results from ten different mine-drainage sites. Values for pH are field measurements at the time of sampling. Cd and Ni suspended-sediment fractions are not shown because all values were less than 0.1 (from Smith et al., 1992).

\[
\text{Suspended Particulate Fraction} = \frac{(\text{Unfiltered Concentration} - \text{Filtered Concentration})}{\text{Unfiltered Concentration}}
\]
General Observations
(from Smith et al., 1992)

- Most attenuation takes place where iron-rich suspended particulates are formed (e.g., at mixing zones or confluences)
- If assume that sorption takes place only on suspended iron-rich particulates, can predict trends in downstream metal attenuation
- At pH > 5, most Pb and some As and Cu are sorbed
- Zn, Cd, and Ni tend to remain mostly dissolved throughout the pH range 3.8 to 7.7
- Because Zn is abundant and does not sorb, Zn is the major base metal in most mine-drainage streams

Sorption Reactions in Mine Drainage
(from Smith et al., 1992)

Waters appear to be equilibrated with suspended particulates rather than bed sediment

Potential Causes:
- Hydrologic controls
- Stagnant liquid film
- Proximity of suspended sediment
- Differences in sorption properties
Remediation Implications
(from Smith et al., 1992, 1993)

Contact between mine-drainage waters and suspended iron-rich particulates should be maximized to enhance sorption of trace metals.
Computer simulations of the influence of suspended iron-rich particulates on trace metal removal from mine-drainage waters

Kathleen S. Smith, Walter H. Ficklin, Geoffrey S. Plumlee, and Allen L. Meier

1993 Mined Land Reclamation Symposium, Billings, Montana, March 21-27, 1993
Cropsy Waste Dump, Summitville, CO

Very low pH, extreme trace-metal concentrations, extreme dissolved-iron concentration

Water Analysis (filtered 0.1 μm)

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>2.3</td>
</tr>
<tr>
<td>Fe (ppm)</td>
<td>5,000</td>
</tr>
<tr>
<td>As (ppb)</td>
<td>4,000</td>
</tr>
<tr>
<td>Cd (ppb)</td>
<td>1,000</td>
</tr>
<tr>
<td>Cu (ppb)</td>
<td>220,000</td>
</tr>
<tr>
<td>Ni (ppb)</td>
<td>10,000</td>
</tr>
<tr>
<td>Pb (ppb)</td>
<td>12</td>
</tr>
<tr>
<td>Zn (ppb)</td>
<td>170,000</td>
</tr>
</tbody>
</table>

Computer simulation of trace-metal sorption onto hydrous ferric oxide for water composition from the Cropsy Waste Dump, Summitville, Colorado.
Argo Tunnel, Idaho Springs, CO

Very low pH, high trace-metal concentrations, moderate/high dissolved-iron concentration

**Water Analysis (filtered 0.1 μm)**

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>2.9</td>
</tr>
<tr>
<td>Fe (ppm)</td>
<td>120</td>
</tr>
<tr>
<td>As (ppb)</td>
<td>90</td>
</tr>
<tr>
<td>Cd (ppb)</td>
<td>130</td>
</tr>
<tr>
<td>Cu (ppb)</td>
<td>4,500</td>
</tr>
<tr>
<td>Ni (ppb)</td>
<td>120</td>
</tr>
<tr>
<td>Pb (ppb)</td>
<td>40</td>
</tr>
<tr>
<td>Zn (ppb)</td>
<td>30,000</td>
</tr>
</tbody>
</table>

*Computer simulation of trace-metal sorption onto hydrous ferric oxide for water composition from the Argo Tunnel, Idaho Springs, Colorado (from Smith et al., 1993).*
Reynold's Tunnel, Summitville, CO

Very low pH, extreme trace-metal concentrations, high dissolved-iron concentration

Water Analysis (filtered 0.1 μm)

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>2.9</td>
</tr>
<tr>
<td>Fe (ppm)</td>
<td>310</td>
</tr>
<tr>
<td>As (ppb)</td>
<td>400</td>
</tr>
<tr>
<td>Ni (ppb)</td>
<td>800</td>
</tr>
<tr>
<td>Cd (ppb)</td>
<td>200</td>
</tr>
<tr>
<td>Pb (ppb)</td>
<td>320</td>
</tr>
<tr>
<td>Cu (ppb)</td>
<td>120,000</td>
</tr>
<tr>
<td>Zn (ppb)</td>
<td>20,000</td>
</tr>
</tbody>
</table>

Computer simulation of trace-metal sorption onto hydrous ferric oxide for water composition from the Reynolds Tunnel, Summitville, Colorado (from Smith et al., 1993).
Yak Tunnel, Leadville, CO

Low pH, high trace-metal concentrations, moderate/low dissolved-iron concentration

**Water Analysis (filtered 0.1 μm)**

- pH = 4.4
- Fe (ppm) 2.4
- As (ppb) < Ni (ppb) 40
- Cd (ppb) 290 Pb (ppb) 10
- Cu (ppb) 2,400 Zn (ppb) 69,000

Computer simulation of trace-metal sorption onto hydrous ferric oxide for water composition from the Yak Tunnel near Leadville, Colorado (from Smith et al., 1993).
Observations
(from Smith et al., 1993)

For moderate particulate:trace-metal ratio at neutral pH:
- As, Pb, and Cu tend to be predominantly sorbed
- Zn, Cd, and Ni tend to remain dissolved

For large particulate:trace-metal ratio at neutral pH:
- As, Pb, Cu, Zn, Ni, and Cd all tend to be predominantly sorbed

Affinity sequence
As > Pb > Cu > Zn > Ni > Cd

Possible Applications of this Method
(from Smith et al., 1993)

- Predict metal-removal efficiency
- Provide guidance in remediation and planning
- Estimate pH and optimal conditions for removal of a particular metal (selective recovery)
- Predict metal mobility
On-site Measurements for Water Sampling and Modeling

- pH
- Dissolved oxygen
- Redox-sensitive species of interest
- Specific conductivity
- Temperature
- Alkalinity / acidity

Additional Measurements for Water Sampling and Modeling

- Complete water analysis
  Major, minor, and trace species
  Cations and anions
- Isotopes
An Empirical Study of Mine-Drainage Composition and Implications for Prediction
Empirical study of mine-drainage compositions in diverse deposit types

Study Objectives

- Empirical study of natural and mine-drainage waters from diverse ore-deposit types
  - Initial focus on Colorado, now expanding to other states, countries
- Interpret drainage chemistries in terms of ore deposit geology, mining method, climate, geochemical processes
- Develop predictive techniques for drainage compositions based upon deposit geologic characteristics
- Study natural metal attenuation, and implications for low-cost remediation
## Water Sampling

- Measurements taken on site:
  - Water, air temperature
  - pH
  - Specific conductance
  - Dissolved oxygen
  - Alkalinity, acidity where appropriate
  - Fe(II), Fe(total)
- Observations of weather conditions, drainage flow rates

## Water Sampling

<table>
<thead>
<tr>
<th>Sample</th>
<th>Use</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unfiltered, acidified-nitric</td>
<td>Dissolved and particulate cations</td>
</tr>
<tr>
<td>Unfiltered, glass bottle</td>
<td>H-O isotope studies</td>
</tr>
<tr>
<td>Filtered, acidified-nitric</td>
<td>Dissolved cations</td>
</tr>
<tr>
<td>Filtered, un-acidified</td>
<td>Anions (stored on ice in cooler)</td>
</tr>
<tr>
<td>Filtered, acidified HCl</td>
<td>Fe(II), Fe(tot), Radiogenic isotopes</td>
</tr>
<tr>
<td>Filtered 0.1 ( \mu )m, pH 4</td>
<td>Sulfate isotopes</td>
</tr>
<tr>
<td>Glass-filtered, glass bottle</td>
<td>Dissolved organic carbon</td>
</tr>
</tbody>
</table>
- Filtered samples collected at some sites for 0.45\( \mu \)m, 0.1\( \mu \)m, 10,000 daltons to assess colloids, particle size
Water Sampling

- Laboratory analyses performed:

<table>
<thead>
<tr>
<th>Technique</th>
<th>Element</th>
</tr>
</thead>
<tbody>
<tr>
<td>ICP-AES</td>
<td>Ca, Mg, Na, K, Fe, Al, Si, P, B, Sr, Ti</td>
</tr>
<tr>
<td></td>
<td>Zn, Cu, Cd, Co, Ni, Cr</td>
</tr>
<tr>
<td>Flame or GF AA</td>
<td>Fe, Al, Mn, Cu, Zn</td>
</tr>
<tr>
<td>ICP-MS</td>
<td>Zn, Cu, As, Pb, Cd, Co, Cr, Ni,</td>
</tr>
<tr>
<td></td>
<td>U, Th, REE, Te, Ti</td>
</tr>
<tr>
<td>Cold vapor AA</td>
<td>Hg</td>
</tr>
<tr>
<td>Colorimetric</td>
<td>Fe(II)</td>
</tr>
<tr>
<td>IC</td>
<td>Sulfate, chloride, fluoride, nitrate</td>
</tr>
</tbody>
</table>

Data Sources

- This study (mine and natural drainages in Colorado and Utah; Plumlee et al., 1994b, 1993, 1992; Ficklin et al., 1992).
- Alpers and Nordstrom, 1991 (Iron Mtn., CA)
- Ball and Nordstrom, 1989 (Leviathan, CA)
- Davis and Ashenberg, 1989 (Butte, MT)
- Eychaner, 1988 (Globe, AZ)
- Kwong, Y. T. J., 1991 (Mt. Washington, B.C.)
- McHugh et al., 1987 (Blackbird, ID)
- W. R. Miller, unpub. data (Natural drainages in Alaska)
Geologic controls on mine-drainage composition

Increasing pyrite content, decreasing acid buffering capacity

Symbols depict waters draining deposits with similar geologic characteristics

G. Plumlee, K. S. Smith, W. H. Ficklin, unpub. data (all samples filtered)
Legend

- Massive pyrite, sphalerite, galena, chalcopyrite
- Cobalt-rich massive sulfides
- Massive pyrite-sphalerite-galena in black shales
- Pyrite-enargite-chalcocite-covellite ores in acid-altered rocks
- Pyrite-native sulfur in acid altered wallrocks
- Molybenite-quartz-fluorite veins, disseminations in U-rich igneous intrusions
- Pyrite-chalcopyrite disseminations in quartz-sericite-pyrite altered igneous rocks
- Pyrite-sphalerite-galena-chalcopyrite in carbonate-poor rocks
- Pyrite veins and disseminations with low base metals in carbonate-poor rocks
- Pyrite-sphalerite-galena-chalcopyrite veins, replacements in carbonate-rich sediments
- Pyrite-sphalerite-galena-chalcopyrite veins with high carbonates or in rocks altered to contain carbonates
- Pyrite-poor gold-telluride veins, breccias with high carbonates
- Pyrite-poor sphalerite-galena veins, replacements in carbonate sediments

Geologic controls on mine-drainage composition

G. Plumlee, K. S. Smith, W. H. Ficklin, unpub. data
Geologic controls on mine-drainage composition

**Iron (filtered)**

- pH > 5, Decreasing dissolved oxygen

**Zinc (filtered)**

G. Plumlee, K. S. Smith, W. H. Ficklin, unpub. data
Geologic controls on mine-drainage composition

**Uranium (filtered)**

G. Plumlee, K. S. Smith, W. H. Ficklin, unpub. data

**Lanthanum (filtered)**

G. Plumlee, K. S. Smith, W. H. Ficklin, unpub. data

75
Massive Pyrite-Chalcopyrite-Sphalerite-Galena Ores

- Ore occurs in massive lenses:
  - lenses can focus ground-water flow, limit interactions with wallrocks

EXAMPLE: Iron Mountain, CA;
- Data from Alpers and Nordstrom (1991)
Pyrite-Enargite-Covellite-Chalcocite Ores in Acid-Altered Rocks

- Extreme acid leaching of host rocks prior to mineralization:
  - vuggy silica, quartz-alunite, quartz-kaolinite, clay alteration
- Later mineralization:
  - pyrite, marcasite, enargite, native sulfur, covellite, chalcopyrite, tennantite, barite

EXAMPLES: Summitville, Colorado; Red Mountain Pass, Colorado; Butte, Montana
Pyrite-sphalerite-galena-chalcopyrite veins and replacements in carbonate-rich sediments

- Open-space filling and replacement of host carbonates and other sedimentary rocks
- Pyrite, marcasite, sphalerite, galena, chalcopyrite, sulfosalts, rhodochrosite, barite

EXAMPLES: Leadville, CO; Breckenridge, CO; Kokomo, CO; Bandora, CO
Pyrite-sphalerite-galena-chalcopyrite veins and disseminations in carbonate-poor rock

- Open-space filling in igneous and metamorphic rocks
- Pyrite, marcasite, sphalerite, galena, chalcopyrite, sulfosalts, rhodochrosite, barite

EXAMPLES: Central City, CO; Leadville, CO; Creede, CO; Globe, AZ
Pyrite-sphalerite-galena-chalcopyrite veins with high carbonates, or in rocks altered to carbonates

- Open-space filling in igneous rocks
- Some occur in igneous rocks propylitically altered to contain carbonates (green is good!)
- Not all veins may have high carbonate contents
- Pyrite, marcasite, sphalerite, galena, chalcopyrite, sulfosalts, calcite, rhodochrosite, Mn-silicates, barite

EXAMPLES: Bonanza, CO; Sunnyside, CO
Molybdenite-pyrite-topaz-fluorite veinlets and disseminations in uranium-enriched granite

- Cores of Climax-type porphyry molybdenum systems
- Molybdenite, pyrite, quartz, topaz, fluorite; some late rhodochrosite
- Potassium - feldspar or quartz - sericite (a fine-grained mica) - pyrite alteration of host rock

EXAMPLES: Climax, Henderson, Mt. Emmons, CO

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Molybdenite-pyrite-topaz-fluorite veinlets and disseminations in uranium-enriched granite
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<th>2</th>
<th>3</th>
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<td>Zn + Cu + Cd + Pb + Co + Ni (ppm)</td>
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<tr>
<td>700 mg/L F; Fe, Al &gt; Zn, Cu, U (10 ppm)</td>
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Examples: Climax, CO Henderson, CO Mt. Emmons, CO
Pyrite-poor, sphalerite-galena replacements in carbonate-rich sediments

- Open-space filling and replacement of host carbonates and other sedimentary rocks
- Sphalerite, galena, sulfosalts, barite
- Pyrite generally low

EXAMPLES: Dauntless, CO; Ruby, CO
Conclusions

- Mine-drainage chemistry is readily-predictable, given a good knowledge of:
  - ore deposit geology
  - mining method used
  - relevant geochemical processes
- Empirical studies allow prediction of:
  - likely ranges of pH, concs. of heavy metals, etc.
  - conc. ranges of other previously un-quantified elements such as F, U, REE, Cr, etc.

Project Work in Progress

- Continue sampling more drainages
- Extend study to new deposit types not in Colorado
  - Literature survey
  - New sampling
- Develop expert-system computer program to predict drainage chemistry
Geoenvironmental Models of Mineral Deposits and Their Applications
Geoenvironmental models of mineral deposits

Geoenvironmental Models of Mineral Deposits

- For a given ore deposit type, characterize environmental behavior for all mineralogic zones:
  - Prior to mining (soils, waters, sediments)
  - Resulting from mining or mineral processing
    - Solid mine wastes (dumps, etc.)
    - Mine waters
    - Tailings solids, waters
    - Heap leach solutions
  - Resulting from smelting
    - Slag, airborne particulates
Geoenvironmental Models of Mineral Deposits

- Based on empirical studies of diverse deposit types
- Empirical data lacking for some deposit types
  - For these deposit types, models are extrapolated from geologically similar deposit types for which data are available

Zoned Polymetallic Vein Systems

Central City, Colorado, as an example
- Core quartz-pyrite veins, ± chalcopyrite, ± enargite, ± uraninite
- Intermediate quartz-pyrite-sphalerite-galena
- Fringe sphalerite-galena-carbonates
  - Mine drainage data from Wildeman et al. (1974), this study
Quartz-Alunite Epithermal Deposits

Hydrothermal Cu-As-Au in acid-altered volcanic domes

ALTERATION, MINERALIZATION

- Extreme acid leaching of host rocks prior to mineralization by magmatic gas condensates: shallow vuggy silica, quartz alunite, quartz kaolinite, clay alteration
- Quartz-sericite-pyrite alteration of intrusive rocks at depth
- Later hydrothermal fluids deposited: pyrite, marcasite, enargite, native sulfur, covellite, chalcopyrite, tennantite, barite

GEOCHEMICAL SIGNATURES: Cu, As, Au, Ag in ore

EXAMPLES: Summitville, Colorado; Red Mountain Pass, Colorado
SIMPLIFIED CROSS SECTION
SUMMITVILLE DISTRICT
(after Enders and Coolbaugh, 1987)

South Mountain Dome

Elev. (ft.)
12000
11000
10000
9000

Clay alteration
Weak propylitic alteration
Quartz-sericite-pyrite alteration

Acid Sulfate Alteration
Monzonite Intrusion

SCHEMATIC ALTERATION ZONING
SUMMITVILLE
(After Rye et al., 1990)

Vuggy Silica
(oxide ore)

Quartz-Kaolinite

Montmorillonitic clay-rich
Illitic clay-rich
Quartz-Alunite

Fracture in wallrock

Decreasing permeability
Decreasing sulfide oxidation
Quartz-Alunite Epithermal Deposits

ENVIRONMENTAL MODEL

Lack of acid buffering capacity in core acid sulfate zone
- Can potentially generate highly acid waters with extreme Fe, Al, Cu, Zn, and As
- Due to rock dissolution, drainage waters can also contain high contents (up to 10's ppm) of Cr, Co, Ni, U, Th, REE.

Deposit permeability highly variable
- Vuggy silica zones promote groundwater flow—allow deep pre-mining oxidation
- Clay zones inhibit groundwater flow and allow sulfide minerals to persist near surface
Polymetallic Replacement Deposits

- Sulfide-rich deposits hosted by carbonate rocks, other sedimentary rocks, and associated igneous rocks
- Formed by fluids expelled from crystallizing magmas

ALTERATION, MINERALIZATION

- Open-space filling and replacement of host carbonates and other sedimentary rocks
- Polymetallic veins in associated intrusives
- Pyrite, marcasite, sphalerite, galena, chalcopyrite, sulfosalts, rhodochrosite, barite

GEOCHEMICAL SIGNATURES: Zn, Pb, Cu, Ag, As, ± Mo

EXAMPLES: Leadville, Colorado; Gilman, Colorado
Polymetallic Replacement Deposits

ENVIRONMENTAL MODEL
- Mine-drainage waters in sediment-hosted ores:
  - often not acidic; however, can carry high concentrations of zinc
  - can be acidic, metal-rich if limited contact with carbonates
- Mine-drainage waters in igneous-hosted ores:
  - typically acidic, with high concentrations of zinc, copper, arsenic, lead, other metals
- Smelter signatures have high Pb, Zn, ± Mo
Geology-based mineral-environmental assessments of public lands

USGS Mineral-Environmental Assessments

- Integrated with mineral-resource assessments
- Designed to provide land managers, industry, and regulators with:
  - information on the past, present, and future environmental character of public lands
  - information needed for balanced land-use decisions
  - information needed to help identify and prioritize for cleanup abandoned mine sites on public lands
USGS Mineral-Environmental Assessments

COMPONENTS:
- Compilation of data on mining districts:
  - location, boundaries, size, commodities
  - MILS (Bureau of Mines), MRDS (USGS), State databases
- Compilation of regional data:
  - climate, ecosystems, regional geochemistry, etc.
- Geologic characterization:
  - ore deposit types, environmental geology terranes, etc.
- Environmental geology models of deposit types.
- Environmental assessment.

USGS Mineral-Environmental Assessments

PROTOTYPES:
- State of Colorado
  - In cooperation with: Colorado Geological Survey, Colorado Division of Minerals and Geology; U. S Bureau of Land Management
- San Juan National Forest
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- USGS: Tom Nash, Alan Wallace, Steve Ludington, Greg Green, Dick Tripp
- State of Colorado: Randy Streufert, Matt Sares, Jim Herron, Bob Kirkham
- BLM: Rob Robinson
Colorado Streams Affected by Metals

Modified from Colorado Water Quality Control Division, 1989 Colorado Nonpoint Assessment Report

River affected by heavy metals
- Mining district
- Mining town
- Pueblo

Town or city

Colorado Average Annual Precipitation, 1951-1980

Modified from Colorado Climate Center map, 1984

Mean annual precipitation greater than:
- 20 inches/year
- 30 inches/year
- 50 inches/year

Metal district
- Uranium dist.
- Mining town
- Pueblo

Town or city

0 50 mi
0 60 km
Lead in Stream Sediments of Colorado

NURE data contained within the USGS National Geochemical Database.
Compiled by S. Smith

Colorado Smelters

Smelter locations from Fell (1979)
Quartz-alunite Epithermal Deposits in Colorado

Environmental Geology Model

Waters draining acid sulfate ores: Extremely acidic; extreme Fe, Al, Cu, Zn, As, Co, Ni, REE, U, Th

Waters draining deep sericite-pyrite zone: Acidic with high Fe, Al; variable Zn, Cu

Waters draining propylitic fringes: Near neutral to acidic, depending on carbonate content of ores and rocks; Near neutral waters high in Zn.
Environmental Geology Model

Waters draining sediment-hosted ores:
- Mostly near-neutral, with high Zn.

Waters draining associated igneous-hosted ores:
- Acidic with high Fe, Al, Zn, Cu, As, ± Pb

Waters draining mine dumps, tailings:
- Near neutral to acidic;
- Acidic waters high in Fe, Al, Zn, Cu

Smelter signatures:
Pb, Zn, Cu, As, ±Mo

Known deposit or prospect

Mean precip > 20 in/yr

Mining District

Waters draining core molybdenite zone:
- Highly acidic; extreme Fe, Al, F;
- high U; moderate Zn, Cu

Waters draining intermediate pyritic halo:
- Acidic with high Fe, Al; variable Zn, Cu

Waters draining propylitic fringes:
- Near neutral to acidic, depending on carbonate content of ores and rocks;
- Near neutral waters high in Zn.

Mine or proposed mine

Prospect

Mean precip > 20 in/yr

Mining District
Streams Affected by Metals
San Juan National Forest, SW Colorado

Land tracts with potential for the occurrence of undiscovered mineral deposits of the following types:

- Quartz-alunite gold-copper deposits (e.g. Summitville)
- Lead-zinc-silver skarn / replacement deposits
- Porphyry copper deposits
- Epithermal gold-silver-lead-zinc vein deposits
- Porphyry molybdenum deposits
- Uranium deposits
- Gold-telluride deposits

Compiled by Tosh, R. VanLoenen, N. Foley.
Lithoenvironmental Terrane Map, San Juan National Forest

Very Effective Acid Neutralizers: Rocks altered to contain carbonate

Carbonate-rich sedimentary rocks

Potential Acid Generators:

Intrusive rocks

Ineffective Acid Neutralizers:

Volcanic rocks

Other carbonate-poor rocks

Geologic map units compiled by G. Green

Acidity of Surface Waters
San Juan National Forest, SW Colorado

Acidities of surface waters, including major streams shown in blue, are denoted by the following map colors:

- Acidic
- Near-neutral
- Near-neutral to alkaline

Areas affected by, or potentially at risk from:

- Highly acidic waters with extreme metal concs.
- Acidic waters with high metal concs.
- Near-neutral waters with high metal concs.
Applications

Prediction and Mitigation

• Anticipate and plan for environmental effects resulting from mining of particular deposit types
  • “Ounce of prevention is worth pound of cure”

Industry:
• Factor likely environmental consequences into exploration; i.e., explore for quartz-alunite deposits in arid climates?

Land-use management:
• Incorporate geologically realistic environmental information into land-use decisions
Establishment of Realistic Remediation Standards

- Identify extent of and natural sources for metal contamination and acidity in the watershed containing a mine site under remediation
  - Provide realistic limits on the extent of remediation needed at a given site, considering the site's relative impact on its watershed
- Provide geologically and geochemically valid baselines for given deposit types and climates
  - Can be used to help establish realistic remediation standards for specific sites

Hazardous Mine Site Identification

- Land management agencies must identify and prioritize for remediation all hazardous mine sites on public lands

Mineral environmental assessments allow:

- Prioritization of districts for inventory, based on likely environmental hazards:
  - inventory first those districts with highest geologic potential for severe acid rock drainage or other environmental problems
- Further classification of sites identified in inventories:
  - use environmental models to estimate metals likely present in mine drainages, given a knowledge of site geology, drainage pH, and drainage conductivity
“Drainage Happens...”

Walt Ficklin
ACKNOWLEDGMENTS

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