U.S. DEPARTMENT OF THE INTERIOR

U.S. GEOLOGICAL SURVEY

PREDICTING WATER CONTAMINATION FROM METAL MINES AND MINING WASTES

NOTES FROM A WORKSHOP PRESENTED AT THE INTERNATIONAL LAND RECLAMATION AND MINE DRAINAGE CONFERENCE AND THE THIRD INTERNATIONAL CONFERENCE ON THE ABATEMENT OF ACIDIC DRAINAGE, PITTSBURGH, PENNSYLVANIA, APRIL 24, 1994

By

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Open-File Report 94-264

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Predicting Water Contamination from Metal Mines and Mining Wastes

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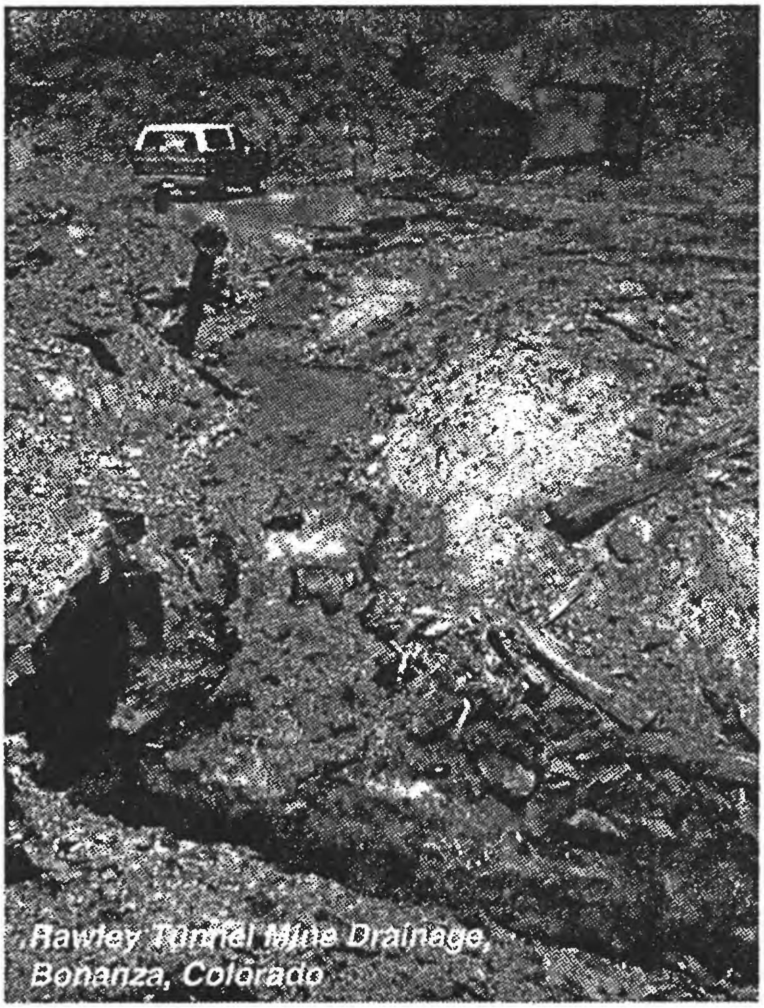
Rawley Tunnel Mine Drainage, Bonanza, Colorado

Workshop 2

International Land Reclamation and
Mine Drainage Conference

and the

Third International Conference on the
Abatement of Acidic Drainage

April 24, 1994

Predicting Water Contamination from Metal Mines and Mining Wastes

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.

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
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Pittsburgh, Pennsylvania

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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

Summitville Mine Drainages

	pH	SO_4 mg/L	Fe ppm	Al ppm
Blackstrap	1.8	128,000	30,000	7,100
Cropsy	2.3	27,000	4,500	200
Reynolds	2.9	1,920	280	130

1990,1991 data filtered 0.1 µm

Summitville Mine Drainages

	Zn ppm	Cu ppm	Cd ppm	Pb ppm
Blackstrap	700	500	4.4	0.9
Cropsy	160	170	0.9	0.1
Reynolds	18	93	0.2	0.3

1990,1991 data filtered 0.1 µm

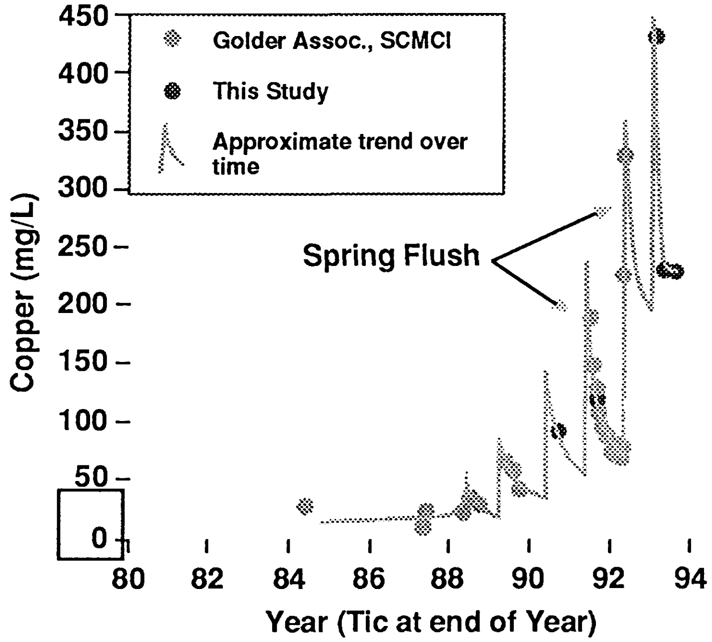
Summitville Mine Drainages

	U ppb	Cr ppb	La ppb	Au ppt
Blackstrap	5.8	3.6	3.1	55
Cropsy	0.9	1.3	0.8	48
Reynolds	0.05	0.01	0.04	1

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)

Solomon Mine Drainage

pH	SO_4 mg/L	Fe ppm	Al ppm
4.45	310	0.4	1.2

Zn ppm	Cu ppm	Cd ppm	Pb ppm
26	0.03	0.1	1.0

filtered 0.1 μm

Wellington Mine Drainage

pH	SO_4 mg/L	Fe ppm	Al ppm
6.4	1800	87	0.2

Zn ppm	Cu ppm	Cd ppm	Pb ppm
170	0.3	0.1	0.1

filtered 0.1 μm

Dauntless Mine Drainage

pH	SO_4 mg/L	Fe ppm	Al ppm
7.86	2.3	<0.01	.009

Zn ppb	Cu ppb	Cd ppb	Pb ppb
27	1	0.4	1.5

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, SO_4^{2-}, trace metals
- Hydrolysis of metal cations
- Precipitation of hydrous metal-oxide minerals

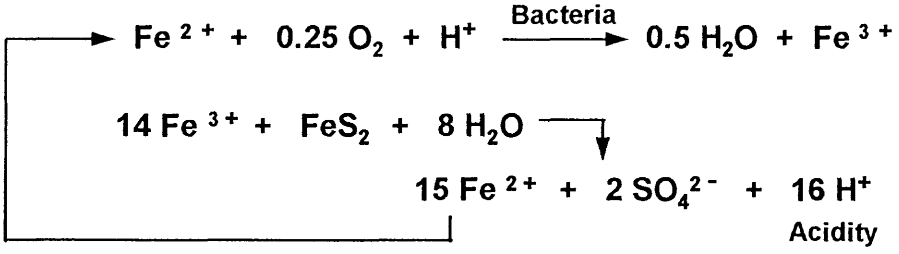
Generation of Acidic Drainage--Oxidation Reactions

(from Singer and Stumm, 1970; Forstner and Wittmann, 1979)

Initiator Reaction:

$$\underset{\text{Pyrite}}{FeS_2} + 3.5\,O_2 + H_2O \rightarrow Fe^{2+} + 2\,SO_4^{2-} + \underset{\text{Acidity}}{2\,H^+}$$

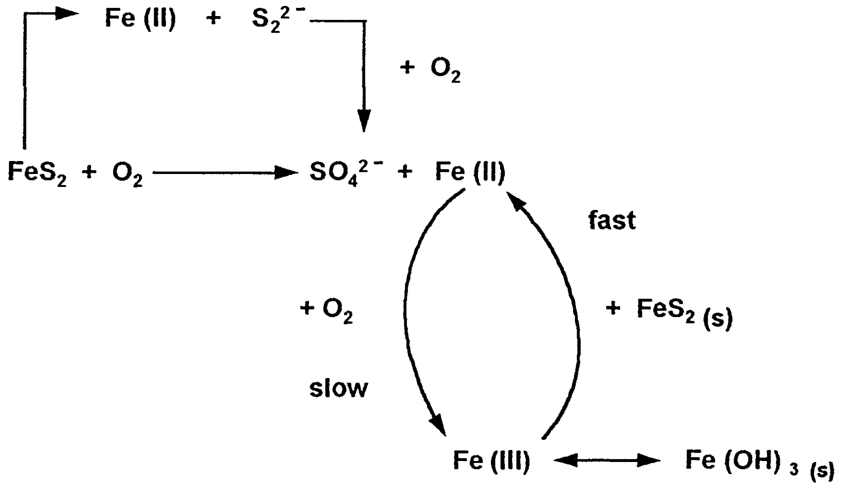
Propagation Cycle:



$$Fe^{2+} + 0.25\,O_2 + H^+ \xrightarrow{\text{Bacteria}} 0.5\,H_2O + Fe^{3+}$$

$$14\,Fe^{3+} + FeS_2 + 8\,H_2O \rightarrow 15\,Fe^{2+} + 2\,SO_4^{2-} + \underset{\text{Acidity}}{16\,H^+}$$

Oxidation of Pyrite



(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
$Fe^{(II)} Fe_2^{(III)} (SO_4)_4 \cdot 14H_2O$

Coquimbite
$Fe_2^{(III)} (SO_4)_3 \cdot 9H_2O$

Copiapite
$Fe^{(II)} Fe_4^{(III)} (SO_4)_6 (OH)_2 \cdot 20H_2O$

Weathering of Other Sulfides

$$PbS + 8\,Fe^{3+} + 4\,H_2O \rightarrow Pb^{2+} + SO_4^{2-} + 8\,Fe^{2+} + 8\,H^+$$

versus

$$PbS + 2\,O_2 \longrightarrow Pb^{2+} + SO_4^{2-}$$

Microbial Oxidation of Other Sulfides

Chalcopyrite - separate metal and S attack:

$$\begin{array}{ll}
 & CuFeS_2 + 4.25O_2 + H^+ \rightarrow Cu^{2+} + Fe^{3+} + 2SO_4^{2-} + 0.5H_2O \\
\text{(+ hydrolysis)} & Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+ \\
\hline
 & CuFeS_2 + 4.25O_2 + 2.5H_2O \rightarrow Cu^{2+} + 2SO_4^{2-} + Fe(OH)_3 + 2H^+
\end{array}$$

Chalcocite - microbial oxidation of S:

$$\begin{array}{l}
CuS + 0.5O_2 + \cancel{2H^+} \rightarrow Cu^{2+} + S^o + H_2O \\
S^o + 1.5O_2 + H_2O \rightarrow SO_4^{2-} + \cancel{2H^+} \\
\hline
CuS + 2O_2 \rightarrow Cu^{2+} + SO_4^{2-}
\end{array}$$

Acid-Producing Reactions

Hydrolysis of metal cations

$$Fe^{3+} + 3H_2O \longrightarrow Fe(OH)_3 + 3H^+$$

$$Al^{3+} + 3H_2O \longrightarrow Al(OH)_3 + 3H^+$$

Acid-Producing Reactions

Precipitation of hydrous-oxide minerals

$$Fe^{2+} + 0.25O_2 + 2.5H_2O \longrightarrow Fe(OH)_{3\,(s)} + 2H^+$$

$$Fe^{3+} + 3H_2O \longrightarrow Fe(OH)_{3\,(s)} + 3H^+$$

$$Al^{3+} + 3H_2O \longrightarrow Al(OH)_{3\,(s)} + 3H^+$$

Acid-Consuming (Buffering) Reactions

- Dissolution of carbonate minerals
  releases Ca, Mg, $H_2CO_3^o$ 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)

$$\underset{\text{calcite}}{CaCO_3} + 2H^+ \longrightarrow Ca^{2+} + H_2CO_3$$

$$\underset{\text{K-feldspar}}{KAlSi_3O_8} + H^+ + 7H_2O \longrightarrow K^+ + 3H_4SiO_4 + Al(OH)_3$$

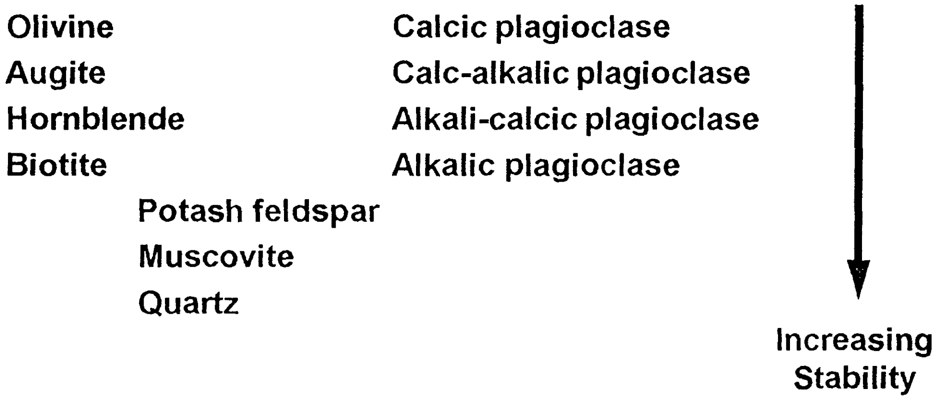
$$\underset{\text{muscovite}}{KAl_3Si_3O_{10}(OH)_2} + H^+ + 9H_2O \longrightarrow K^+ + 3H_4SiO_4 + 3Al(OH)_3$$

Acid-Consuming (Buffering) Reactions

Dissolution of silica does not consume protons

$$\underset{\text{quartz}}{SiO_2} + 2H_2O \longrightarrow H_4SiO_4$$

Resistance of Minerals to Weathering



Olivine
Augite
Hornblende
Biotite

Calcic plagioclase
Calc-alkalic plagioclase
Alkali-calcic plagioclase
Alkalic plagioclase

Potash feldspar
Muscovite
Quartz

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

$$\underset{\text{plagioclase}}{CaAl_2Si_2O_8} + 2H^+ + H_2O \longrightarrow Ca^{2+} + \underset{\text{kaolinite}}{Al_2Si_2O_5(OH)_4}$$

Weathering

(from Rose et al., 1979)

Jackson's Series

Gypsum (halite, etc.)
Calcite (dolomite, aragonite, etc.)
Olivine-hornblende (diopside, etc.)
Biotite (glauconite, 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 (rutile, ilmenite, etc.)

↓ **Increasing stability**

The Carbonate System

$$CO_{2\,(g)} + H_2O_{(l)} \longleftrightarrow H_2CO_{3\,(aq)}$$

$$H_2CO_3 \longleftrightarrow HCO_3^- + H^+$$

$$HCO_3^- \longleftrightarrow CO_3^{2-} + H^+$$

- 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 ($MgCO_3 \cdot 3H_2O$)
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 ($CaMg(CO_3)_2$)

↑ most

least

Increasing Solubility

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)

Continued

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)

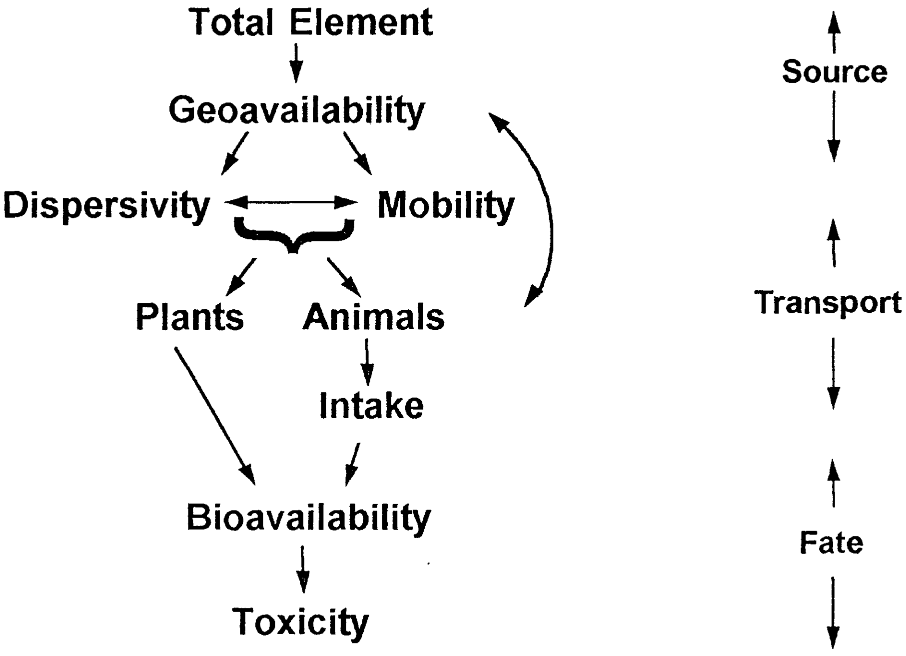
- Type IV - "Infinite" buffering capacity

  (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

Many sulfides generate acid

- Host rock
- Wallrock alteration
- Gangue mineralogy

Can consume acid

- Mineral textures, trace element content

Control rate of weathering

- Nature of deposit
  vein, massive, disseminated
- Structure, permeability

Control access of weathering agents

- Trace element content (deposit, host rocks)

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. $MnSiO_3$ 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

Mineralogic controls

- **Acid-generating primary minerals**

Pyrite, marcasite (FeS_2)
Chalcopyrite ($CuFeS_2$)
Enargite (Cu_3AsS_4)
Other sulfides (not all)
Pyrrhotite (FeS)
Arsenopyrite ($FeAsS$)
Tennantite ($Cu_{12}As_4S_{13}$)
Siderite ($FeCO_3$) - if $Fe(OH)_3$ ppts.

Amount of acid generated depends on metal/sulfur ratio of sulfides, oxidant (O_2 vs Fe^{+++}), and precipitates formed.

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

Mineral Resistance to Oxidation

- Important control on relative rates of acid production

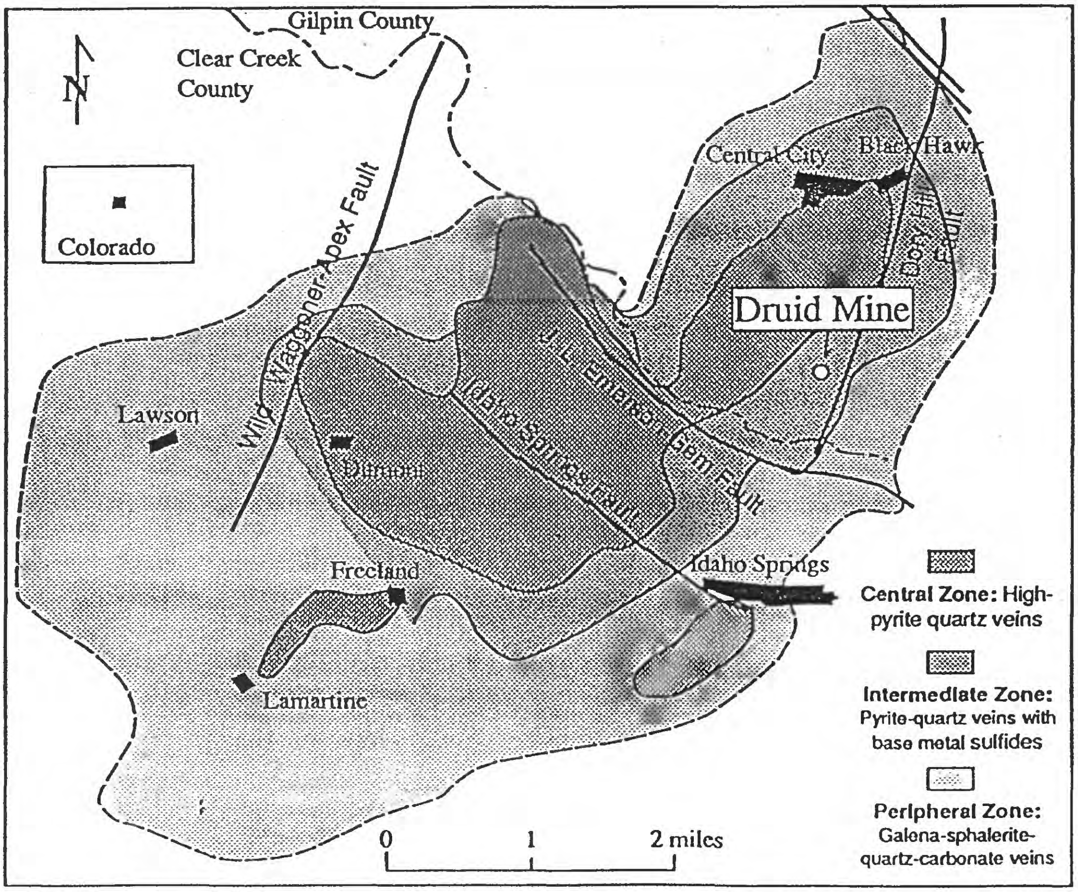
Mineralogy (Brock, 1979)	Grain size	Texture	Trace elements
Pyrrhotite	Fine	Framboidal	High
Chalcocite		Colloform	
Galena			
Sphalerite		Massive	
Pyrite	Medium		
Enargite			
Marcasite			
Chalcopyrite			
Molybdenite	Coarse	Euhedral	Low

Increasing resistance to oxidation ↓

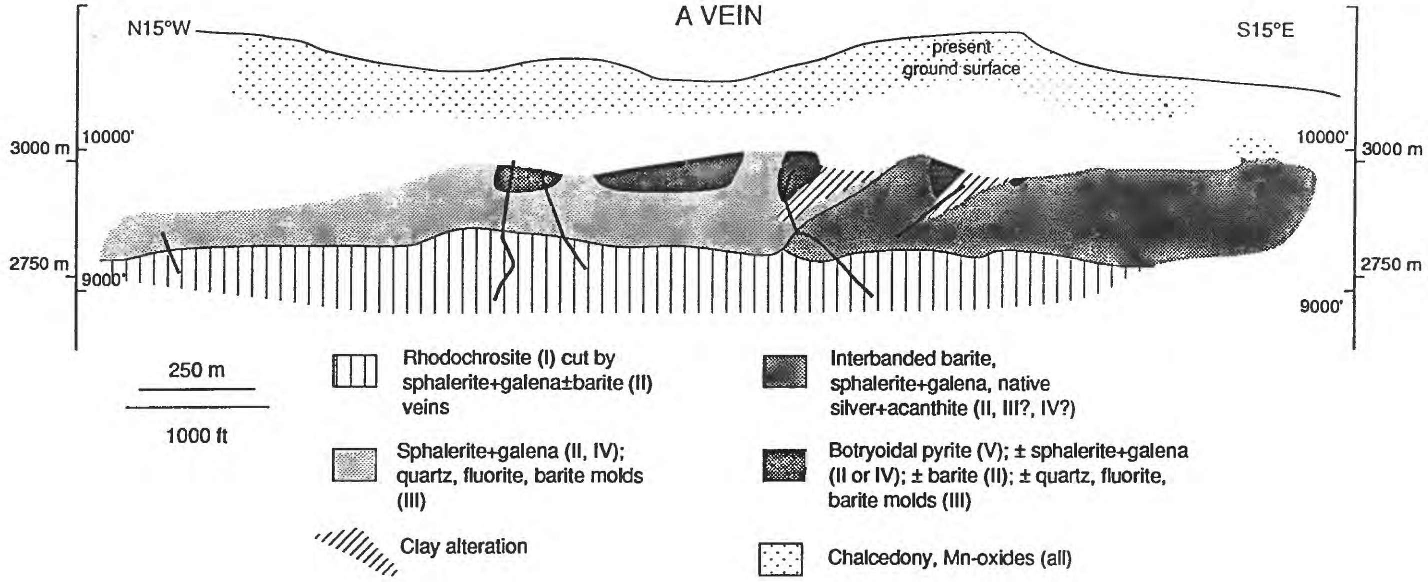
Mineralogic controls

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**



BULLDOG MOUNTAIN VEIN SYSTEM
COMPOSITE MINERAL DISTRIBUTION
A VEIN



From Plumlee and Whitehouse-Veaux (in press)

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.

Mineralogic controls

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

- Ferrihydrite—$Fe_5HO_8 \cdot 4H_2O$ (⇛ goethite, hematite over time)
- Schwertmannite—$Fe^{III}O_8(SO_4)(OH)_6$
- Jarosite—$KFe^{III}(SO_4)_2(OH)_6$
- Chalcanthite*—$CuSO_4 \cdot 5H_2O$
- Copiapite*—$Fe^{II}Fe^{III}(SO_4)_6(OH)_2 \cdot 20H_2O$
- Melanterite*—$(Fe^{II},Zn,Cu)SO_4 \cdot 7H_2O$
- Rhomboclase*—$(H_3O)Fe^{III}(SO_4)_2 \cdot 3H_2O$
- Scorodite—$Fe^{III}(AsO_4) \cdot 2H_2O$
- Hinsdalite—$(Pb,Sr)Al_3(PO_4)(SO_4)(OH)_6$

* soluble

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, ±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

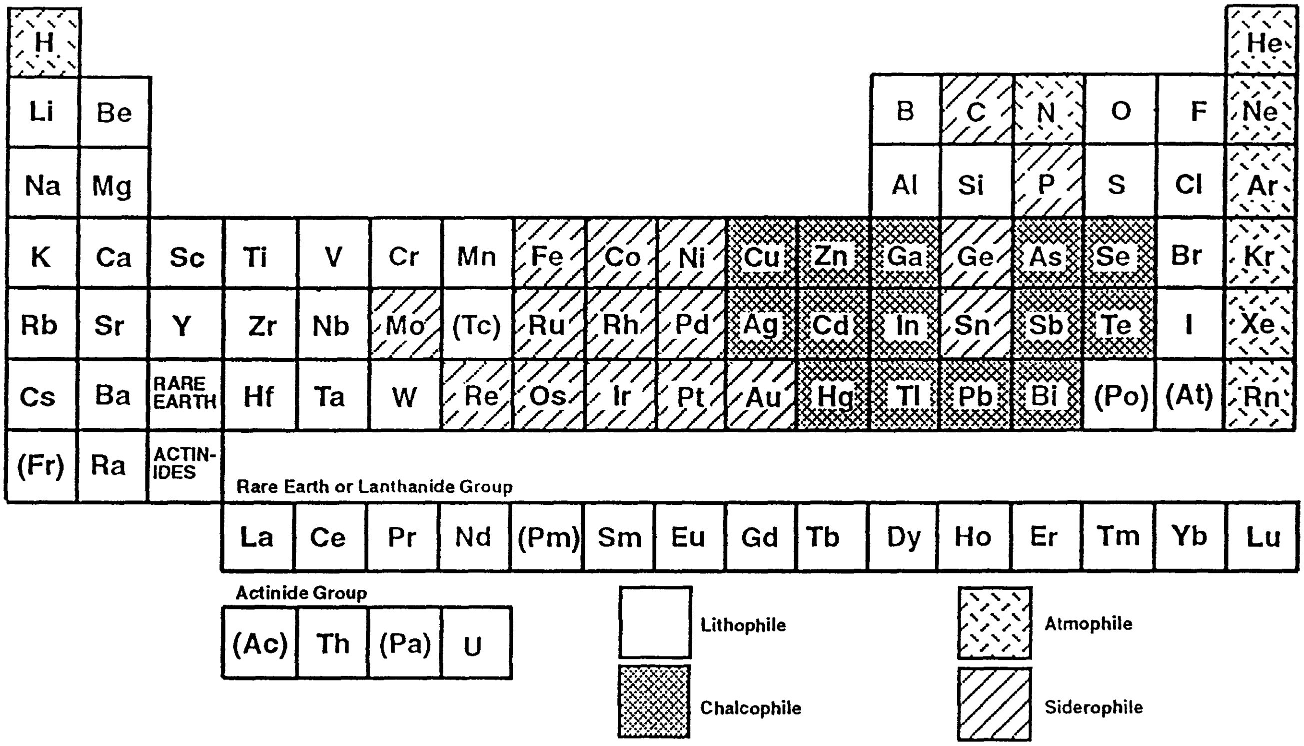
Observed Degree of Mobility of Trace Elements

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



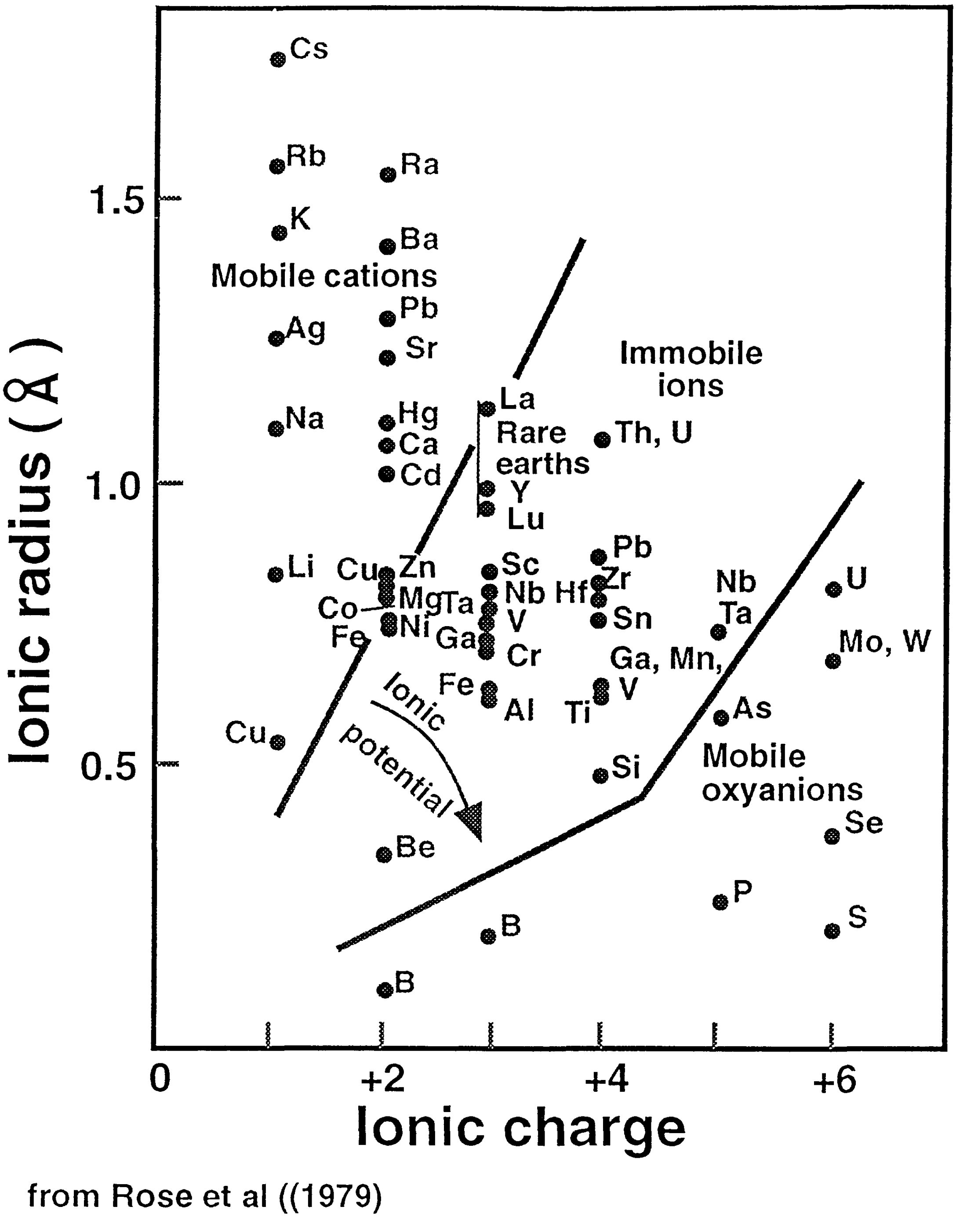
Goldschmidt's general geochemical classification of the elements in the periodic table (from Levinson, 1980). The geochemical character of a chemical element, and its position in the periodic table, can be correlated with the type of bonding it prefers.

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

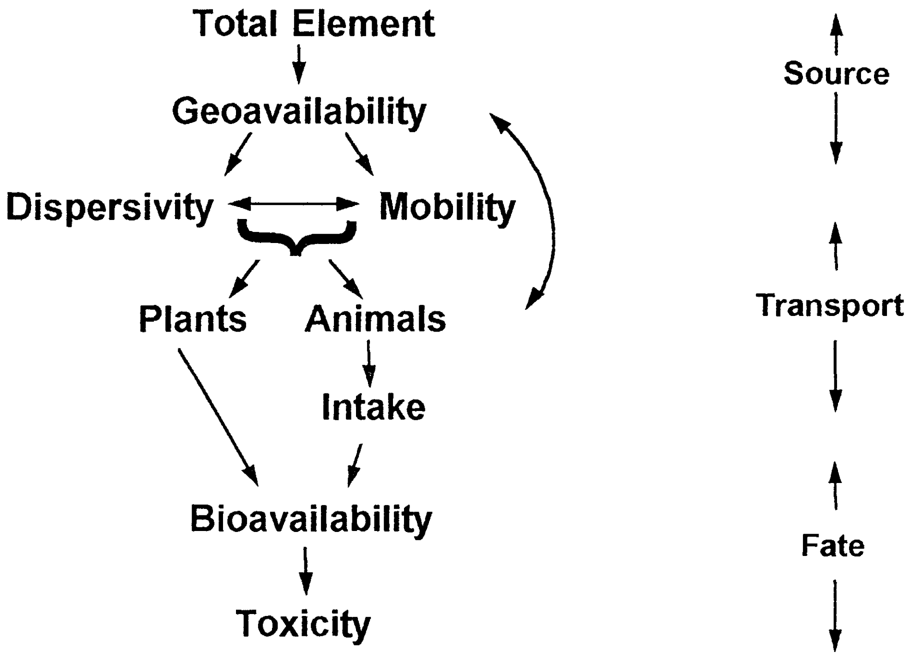


from Rose et al ((1979)

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.

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



Total Element

Geoavailability

Dispersivity

Mobility

Plants

Animals

Intake

Bioavailability

Toxicity

Source

Transport

Fate

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

Redox Conditions

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

- Reactions involving transfer of oxygen

or

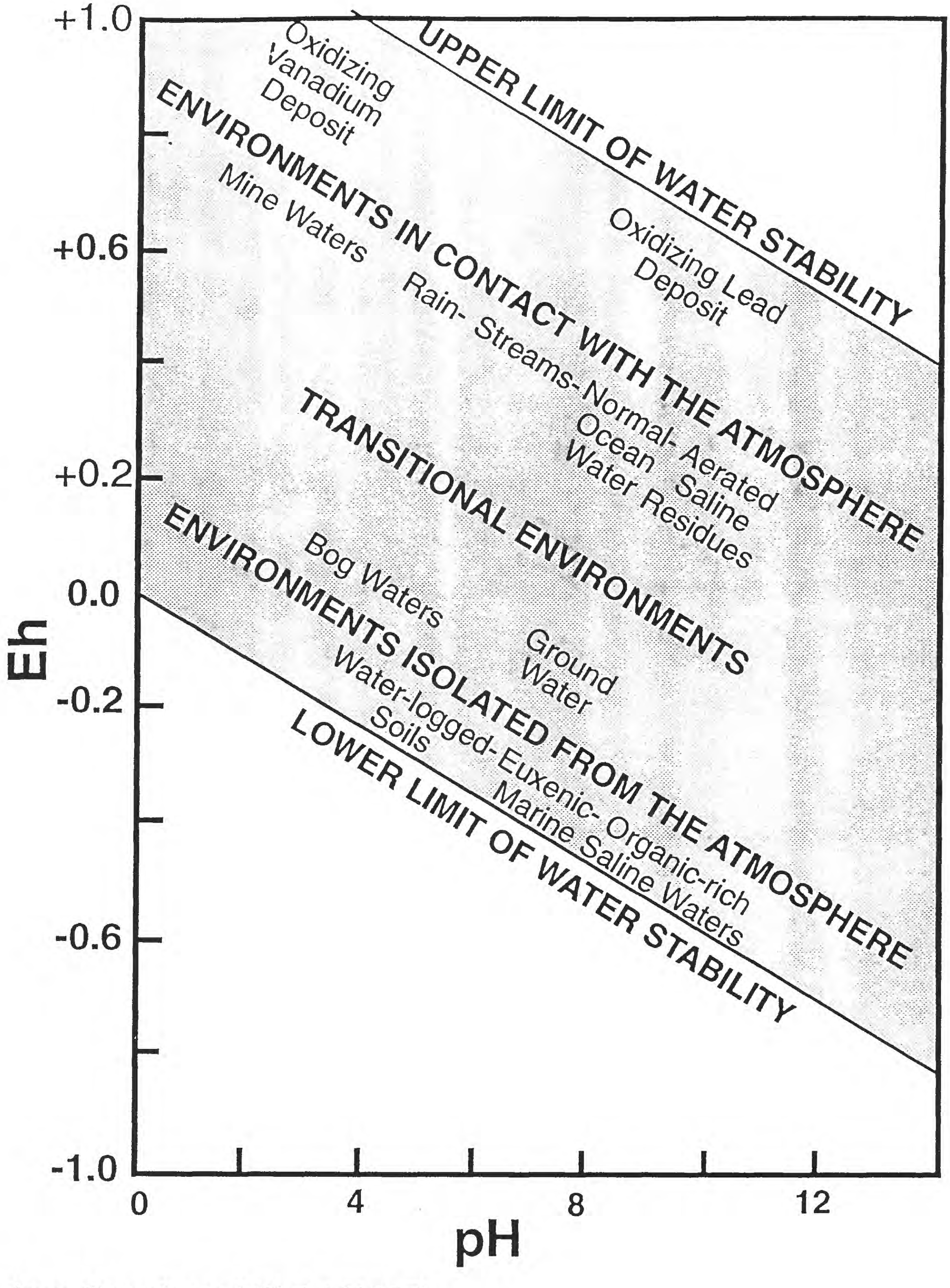
- Reactions involving transfer of electrons

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



from Garrels and Christ (1965)

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

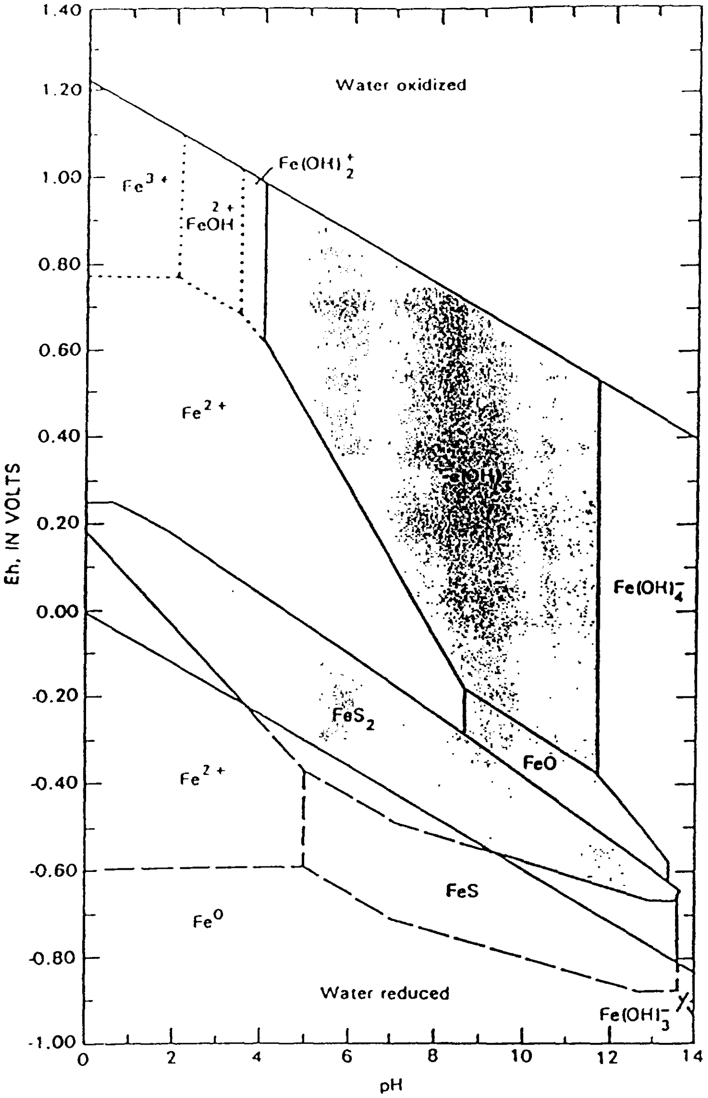


Figure 14. Fields of stability for solid and dissolved forms of iron as a function of Eh and pH at 25°C and 1 atmosphere pressure. Activity of sulfur species 96 mg/L as SO_4^{2-}, carbon dioxide species 61 mg/L as HCO_3^-, and dissolved iron 56 μg/L.

(from Hem, 1989)

pH Range of Initial Hydrous Oxide Precipitation

Ti^{4+}	1.4 - 1.6
Fe^{3+}	2.2 - 3.2
Sn^{2+}	2.3 - 3.2
Al^{3+}	3.8 - 4.8
Cr^{3+}	4.6 - 5.6
Fe^{2+}	5.1 - 5.5
Zn^{2+}	5.2 - 8.3
Cu^{2+}	5.4 - 6.9
Ni^{2+}	6.7 - 8.2
Co^{2+}	7.2 - 8.7
Pb^{2+}	7.2 - 8.7
Mn^{2+}	7.9 - 9.4
Cd^{2+}	8.0 - 9.5

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

$$Cu^{2+} + FeS \longrightarrow Fe^{2+} + CuS$$

$$Cu^{2+} + ZnS \longrightarrow Zn^{2+} + CuS$$

Precipitation of Efflorescent Salts

Melanterite	Chalcanthite
$(Fe^{II}, Zn, Cu)\,SO_4 \cdot 7H_2O$	$CuSO_4 \cdot 5H_2O$
Iron Mountain, CA	Summitville, CO
(Alpers et al., 1994)	(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

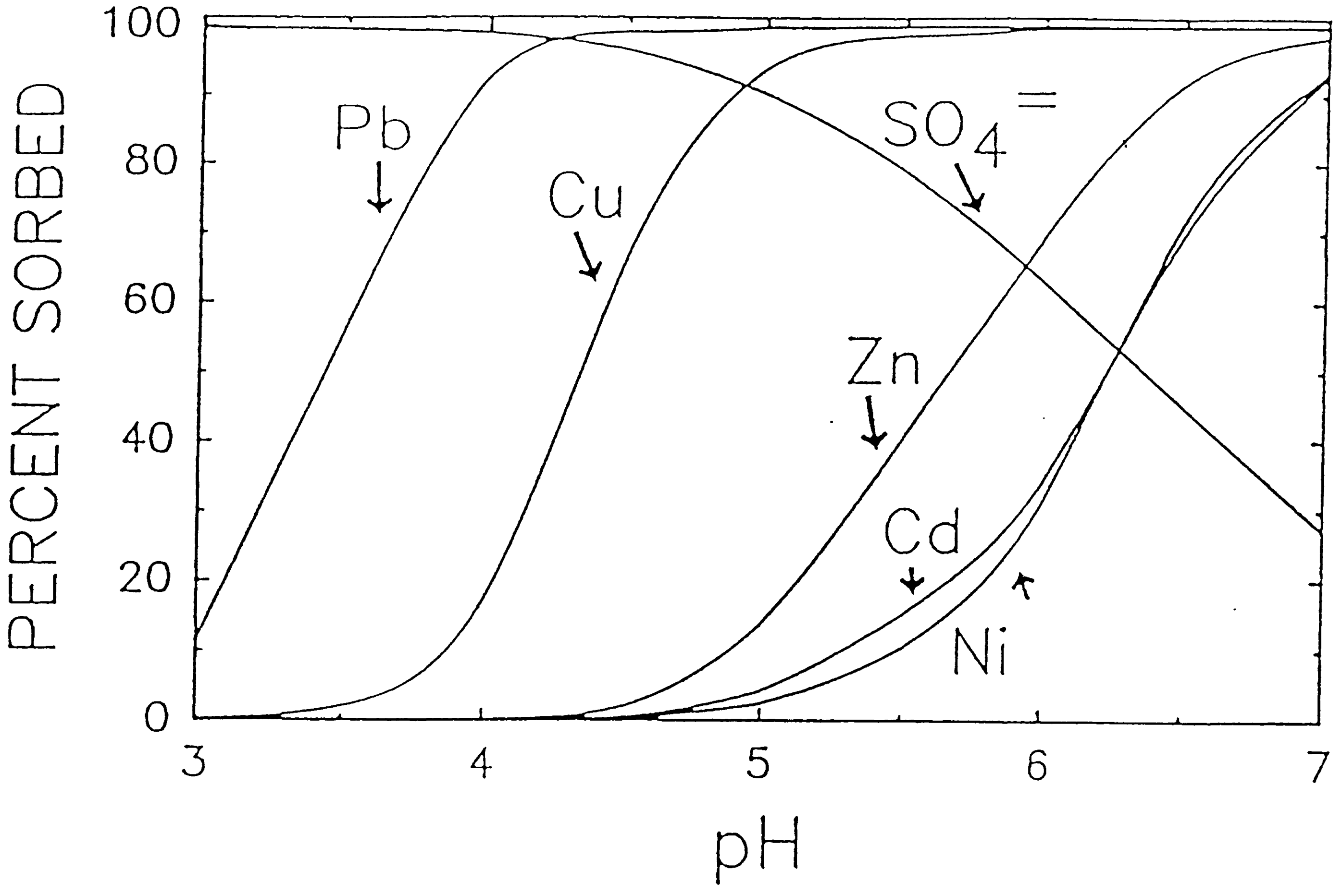
(from Sposito, 1986)

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:

Amorphous Iron Oxide	$Zn^{2+} > Ni^{2+} > Co^{2+} > Sr^{2+} > Mg^{2+}$
Manganese Dioxide	$Co^{2+} > Zn^{2+} > Ni^{2+} > Sr^{2+} > Mg^{2+}$
Amorphous Aluminum Oxide	$Zn^{2+} > Ni^{2+} > Co^{2+} > Mg^{2+} > Sr^{2+}$

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

Divalent Cation Adsorption on Hydrous Iron and Aluminum Oxides

(after Kinniburgh and Jackson, 1981)

Cation	Critical pH Range
Cu^{2+}, Pb^{2+}, Hg^{2+}	3 - 5
Zn^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}	5 - 6.5
Mn^{2+}	6.5 - 7.5
Mg^{2+}, Ca^{2+}, Sr^{2+}	6.5 - 9

(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 HCO_3^- and CO_3^{2-} for surface sites

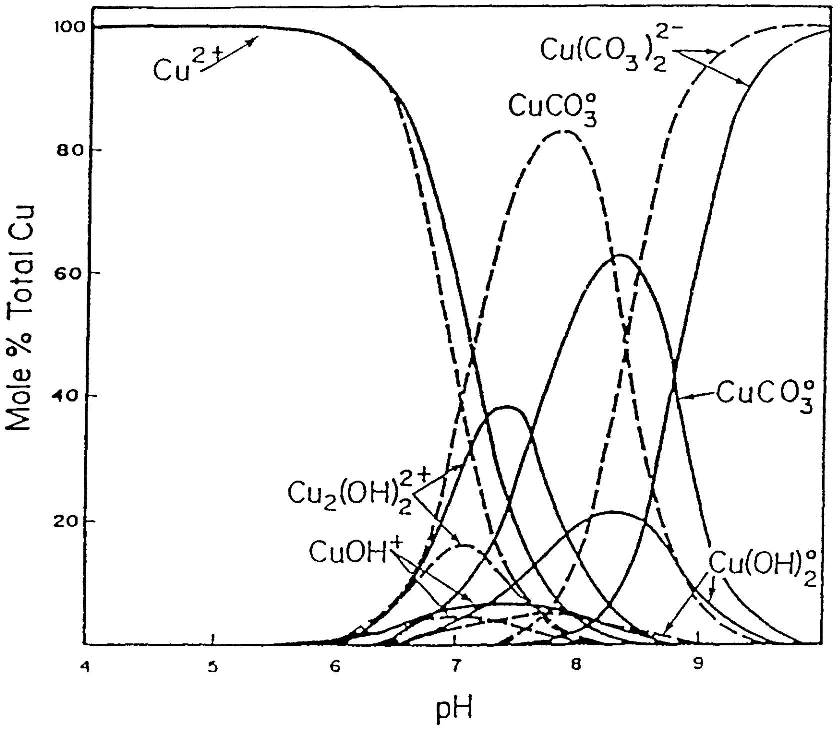
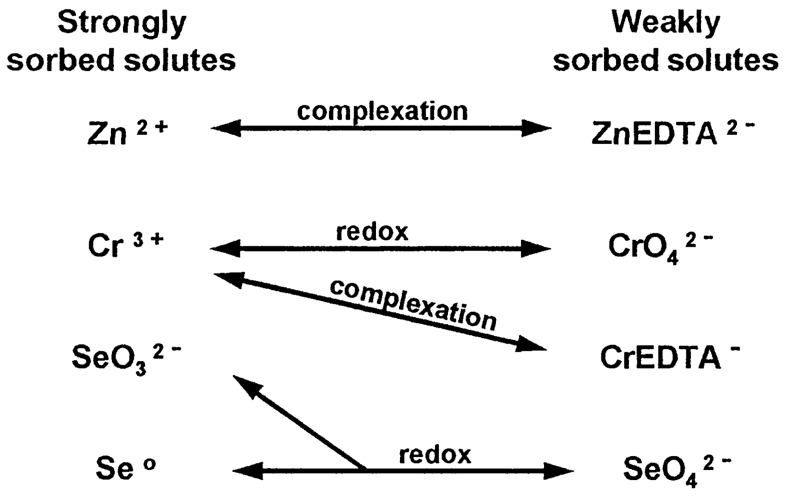


Figure 3. Distribution diagram for copper species as a function of pH for the Cu^{2+}-H_2O-CO_2 system for 10^{-4} *M* (6,354 ppb) total copper, I = 0.01 *M* (as KNO_3 or $KHCO_3$), 25°C, and $P_{CO_2} = 10^{-3.5}$ atm. (solid lines) and $C_T = 10^{-2}$ *M* (dashed lines).

(from Smith and Langmuir, 1987)

Effect of Redox and Complexation on Sorption

(from Davis et al., 1993)



Strongly sorbed solutes

Weakly sorbed solutes

Zn^{2+} complexation $ZnEDTA^{2-}$

Cr^{3+} redox CrO_4^{2-}

complexation $CrEDTA^{-}$

SeO_3^{2-}

Se^{o} redox SeO_4^{2-}

Adsorption Modeling

Distribution coefficient

$$K_d = C_{solid} / C_{solution}$$

- 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)

Computer-Simulation Method

(from Smith, 1991; Smith et al., 1992, 1993)

Assumptions:

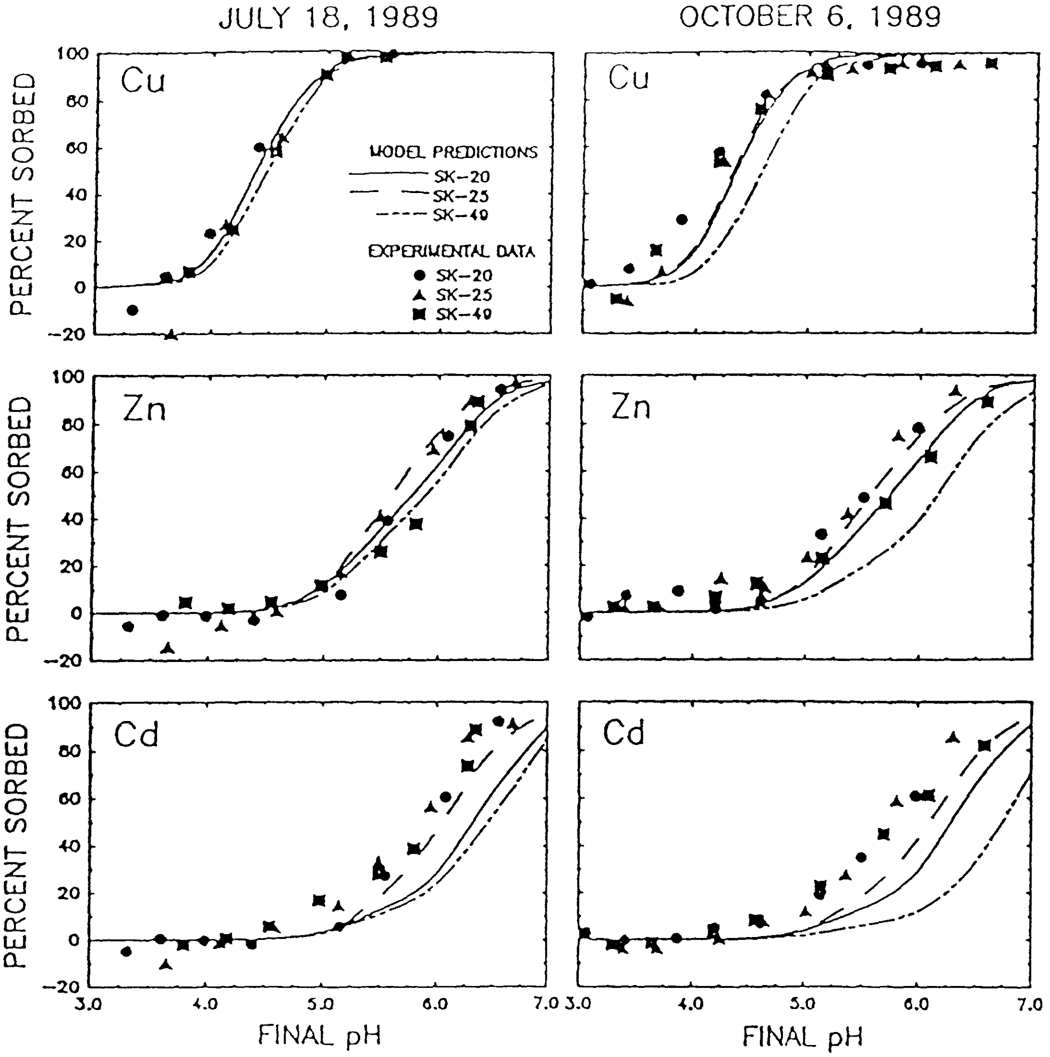
- Sorption only onto hydrous ferric oxide
- Equilibrium conditions
- Validity of approach

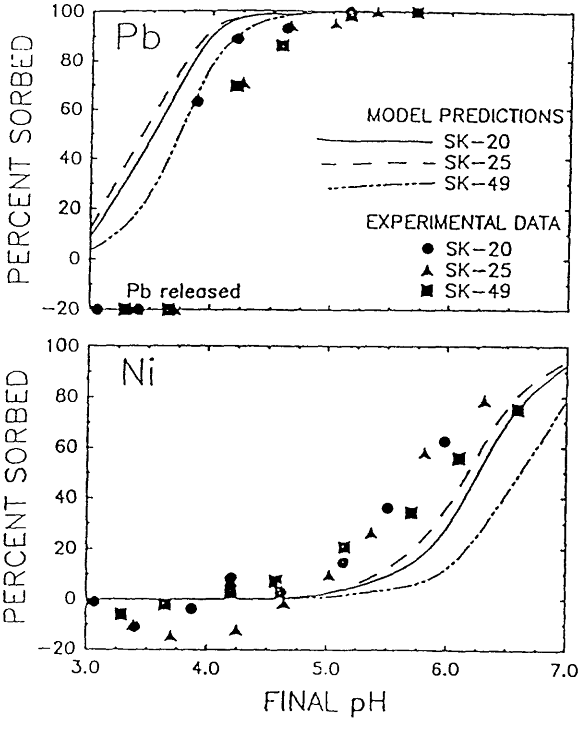
Model Predictions

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

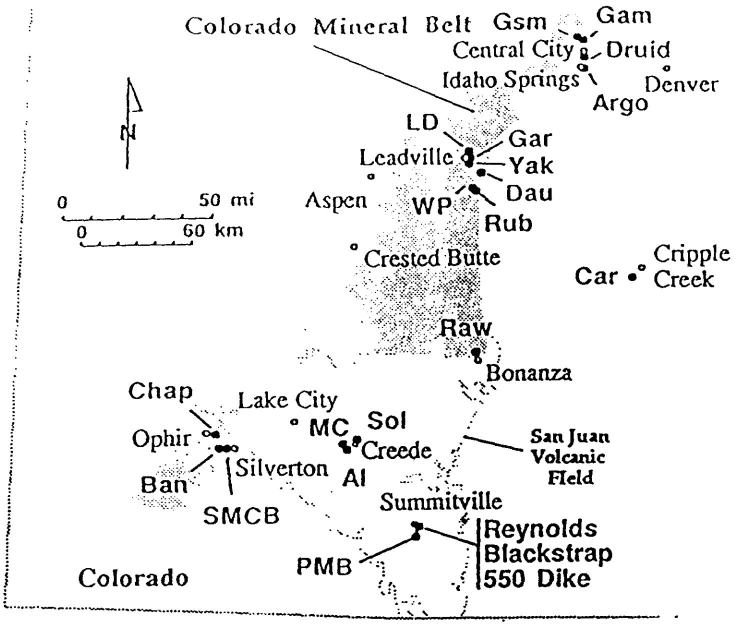


Figure 1. Map of western Colorado showing the location of drainage sites sampled relative to the Colorado Mineral Belt and the San Juan volcanic field.

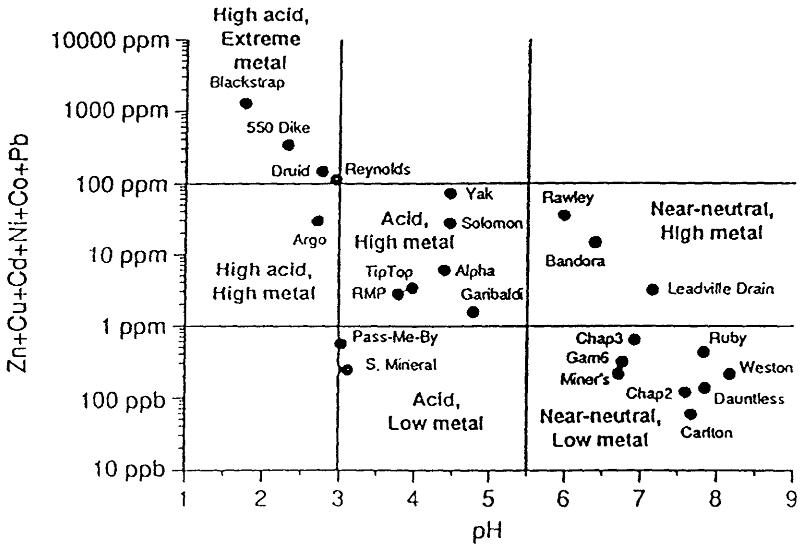


Figure 2. Variations in aqueous base metal concentrations (given as the sum of base metals Zn, Cu, Cd, Co, Ni, and Pb) as a function of pH for waters draining diverse ore deposit types in Colorado. Proposed classes for these waters are bounded by heavy lines and labeled with bold text.

(from Ficklin *et al.*, 1992)

Site Selection Criteria for Adsorption Study

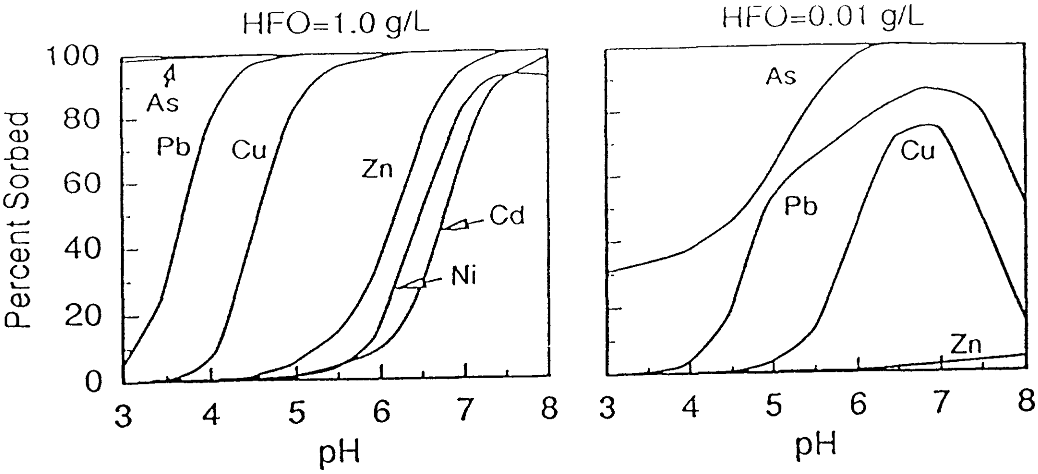
(from Smith et al., 1992)

- 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

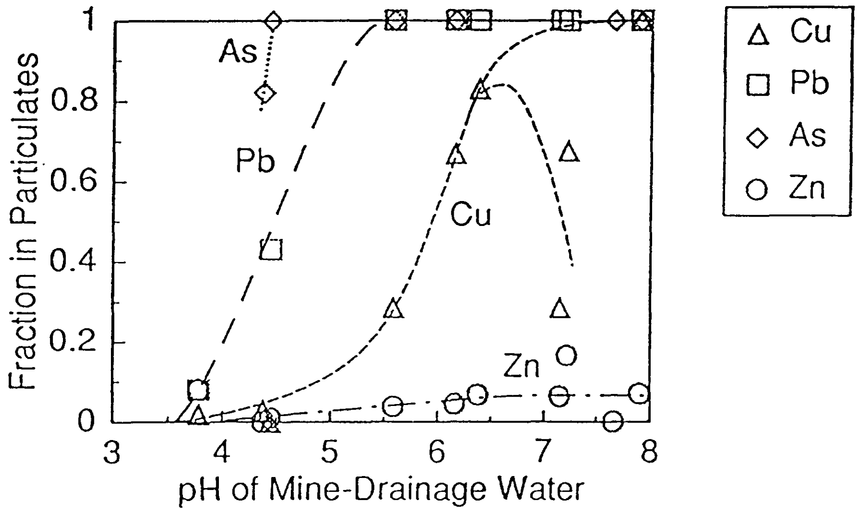
Selected Sites

(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).

$$\text{Suspended Particulate Fraction} = \frac{\text{(Unfiltered - Filtered Concentration)}}{\text{Unfiltered Concentration}}$$

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

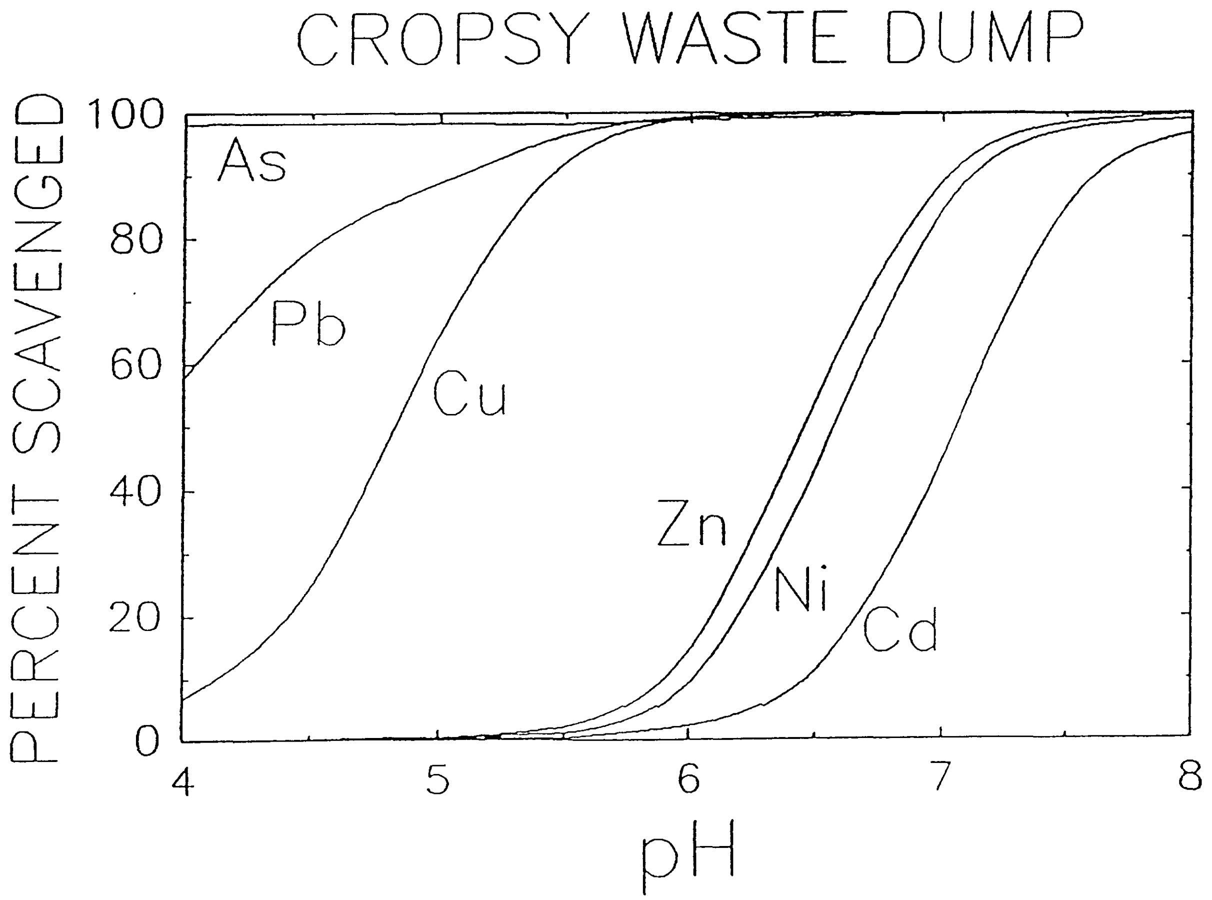
Very low pH, extreme trace-metal concentrations, extreme dissolved-iron concentration

Water Analysis (filtered 0.1 μm)

pH = 2.3

Fe (ppm) 5,000

As (ppb)	4,000	**Ni (ppb)**	10,000
Cd (ppb)	1,000	**Pb (ppb)**	12
Cu (ppb)	220,000	**Zn (ppb)**	170,000



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

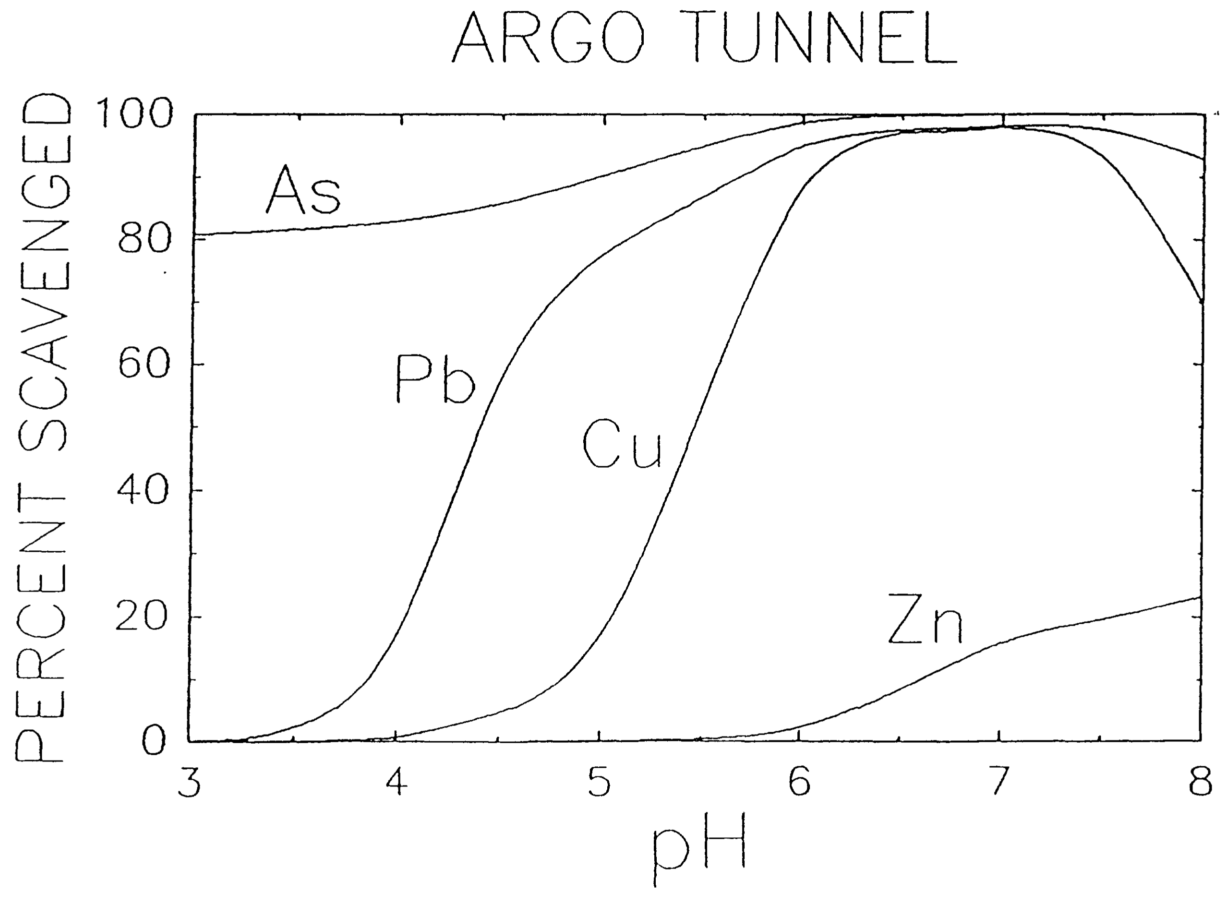
Very low pH, high trace-metal concentrations, moderate/high dissolved-iron concentration

Water Analysis (filtered 0.1 μm)

pH = 2.9

Fe (ppm) 120

As (ppb)	90	Ni (ppb)	120
Cd (ppb)	130	Pb (ppb)	40
Cu (ppb)	4,500	Zn (ppb)	30,000



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

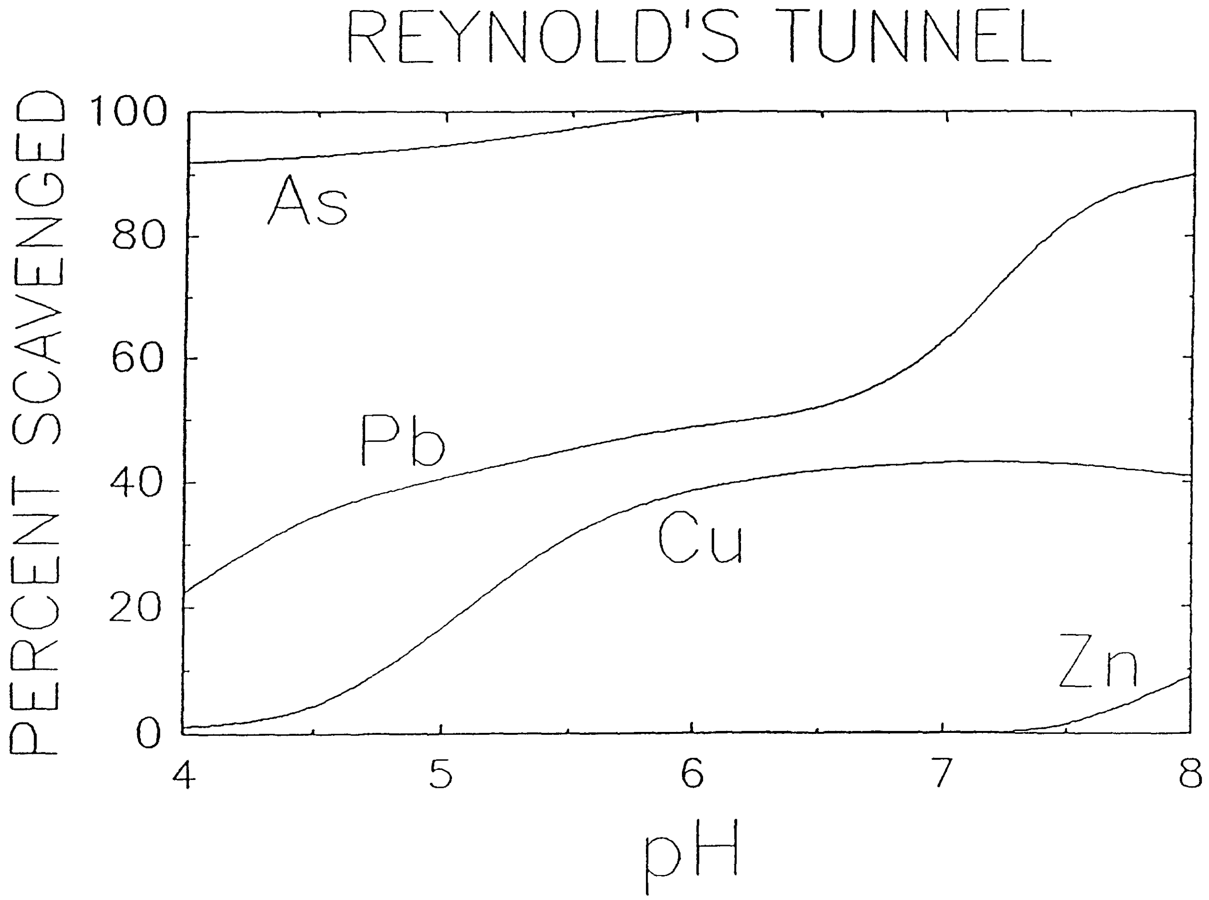
Very low pH, extreme trace-metal concentrations, high dissolved-iron concentration

Water Analysis (filtered 0.1 μm)

pH = 2.9

Fe (ppm) 310

As (ppb)	**400**	**Ni (ppb)**	**800**
Cd (ppb)	**200**	**Pb (ppb)**	**320**
Cu (ppb)	**120,000**	**Zn (ppb)**	**20,000**



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

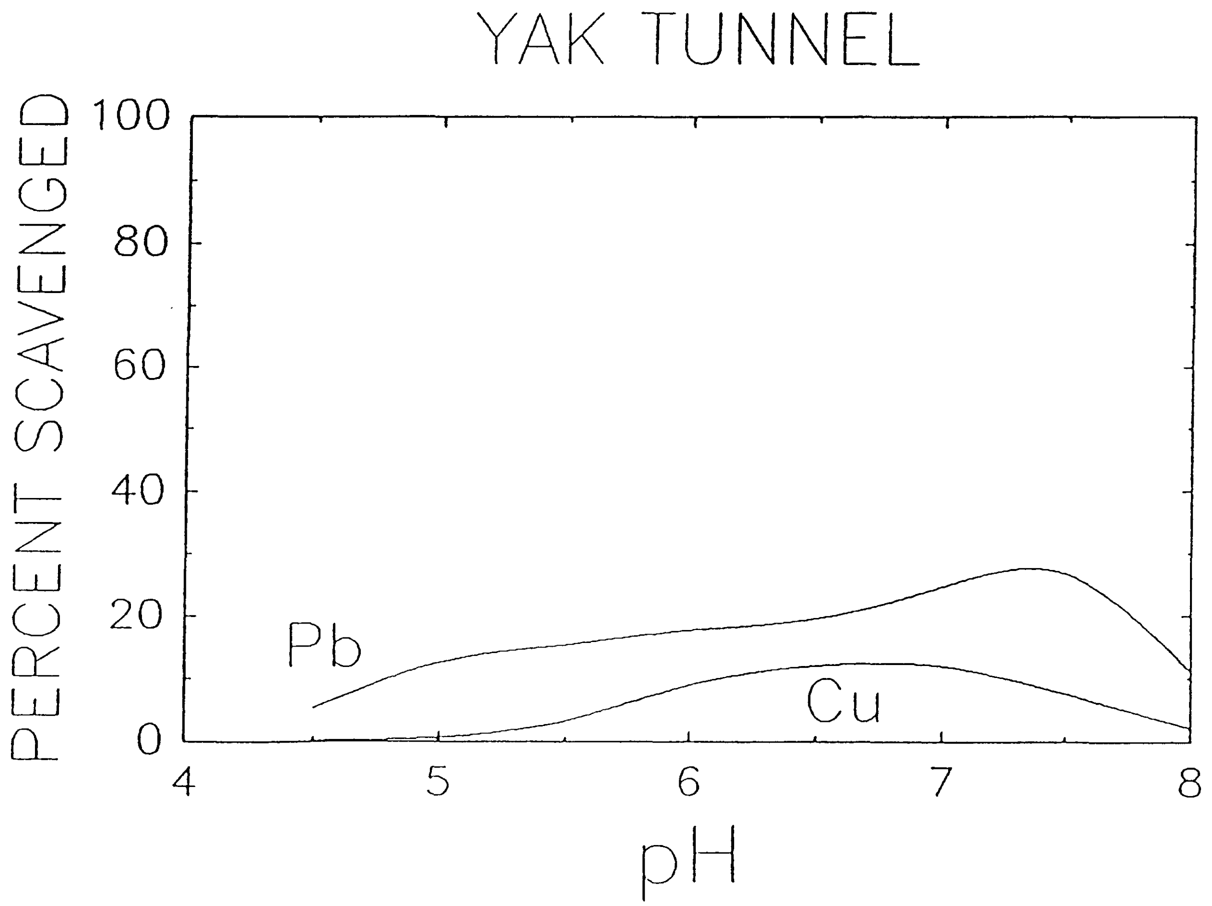
Low pH, high trace-metal concentrations, moderate/low dissolved-iron concentration

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

- Samples collected:

Sample	Use
Unfiltered, acidified-nitric	Dissolved and particulate cations
Unfiltered, glass bottle	H-O isotope studies
Filtered, acidified-nitric	Dissolved cations
Filtered, un-acidified	Anions (stored on ice in cooler)
Filtered, acidified HCl	Fe(II), Fe(tot), Radiogenic isotopes
Filtered 0.1 μm, pH 4	Sulfate isotopes
Glass-filtered, glass bottle	Dissolved organic carbon

- Filtered samples collected at some sites for 0.45μm, 0.1μm, 10,000 daltons to assess colloids, particle size

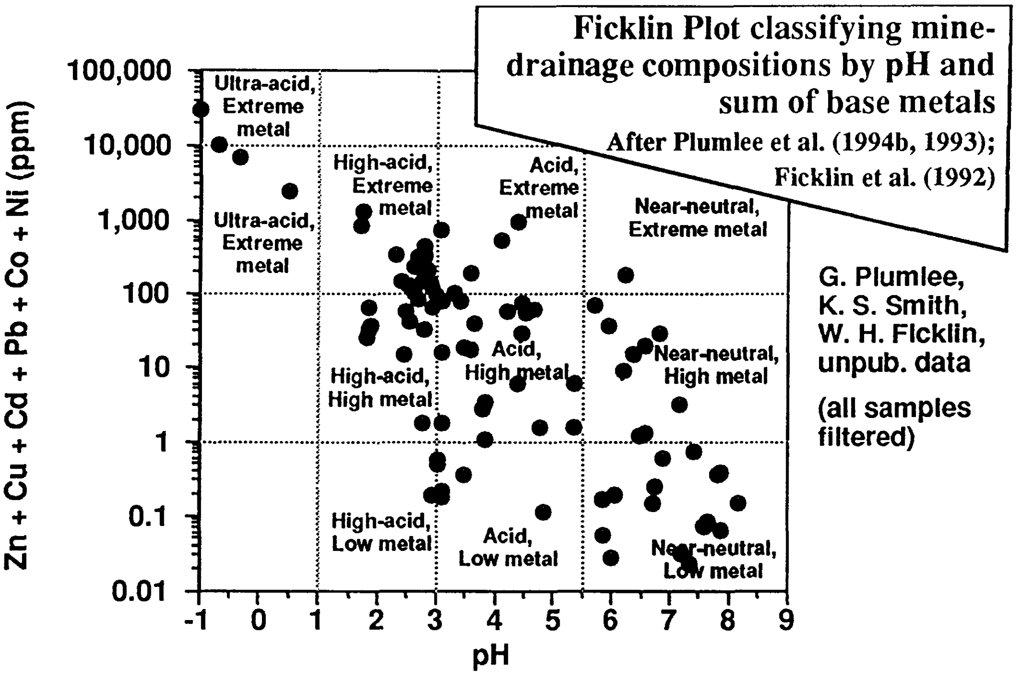
Water Sampling

- Laboratory analyses performed:

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

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)



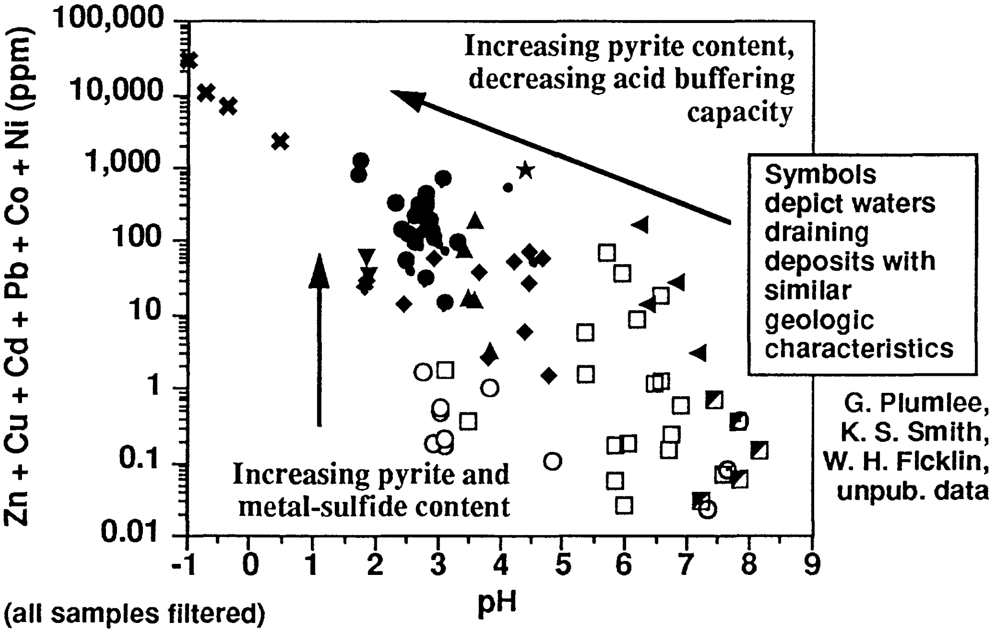
Ficklin Plot classifying mine-drainage compositions by pH and sum of base metals

After Plumlee et al. (1994b, 1993); Ficklin et al. (1992)

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

(all samples filtered)

Geologic controls on mine-drainage composition



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

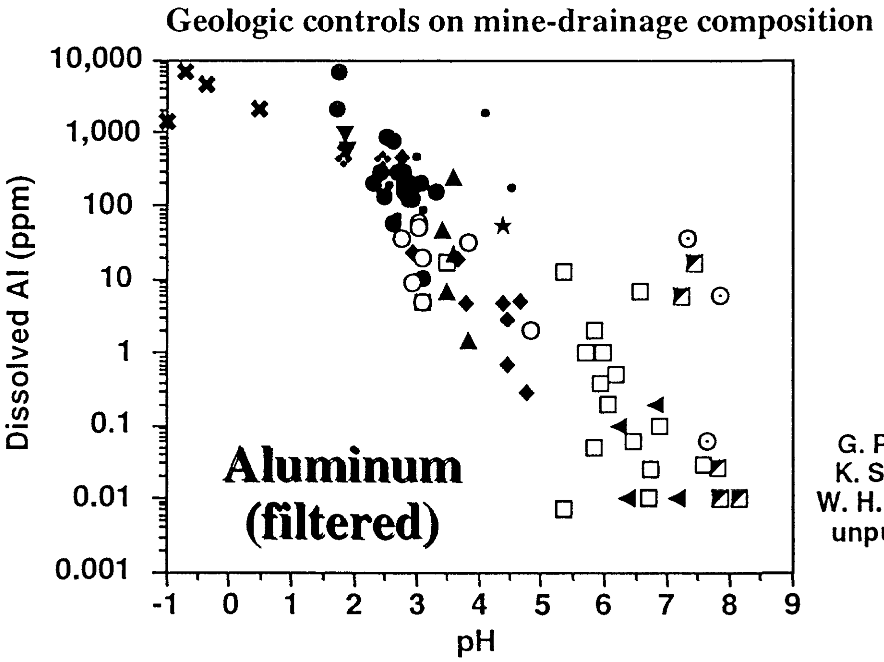
O Pyrite veins and disseminations with low base metals in carbonate-poor rocks

◀ Pyrite-sphalerite-galena-chalcopyrite veins, replacements in carbonate-rich sediments

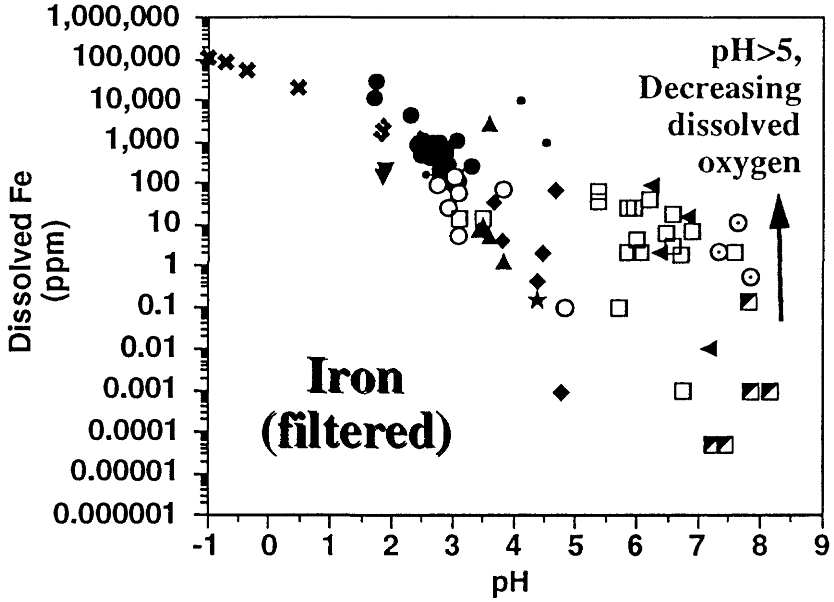
□ Pyrite-sphalerite-galena-chalcopyrite veins with high carbonates
or in rocks altered to contain carbonates

⊙ Pyrite-poor gold-telluride veins, breccias with high carbonates

◪ Pyrite-poor sphalerite-galena veins, replacements in carbonate sediments

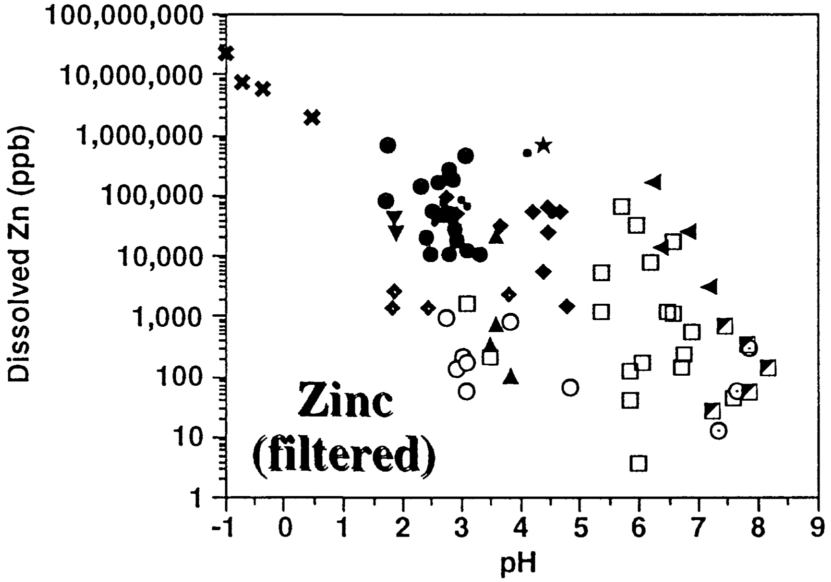

Geologic controls on mine-drainage composition

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



Geologic controls on mine-drainage composition

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



Geologic controls on mine-drainage composition

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W. H. Ficklin,
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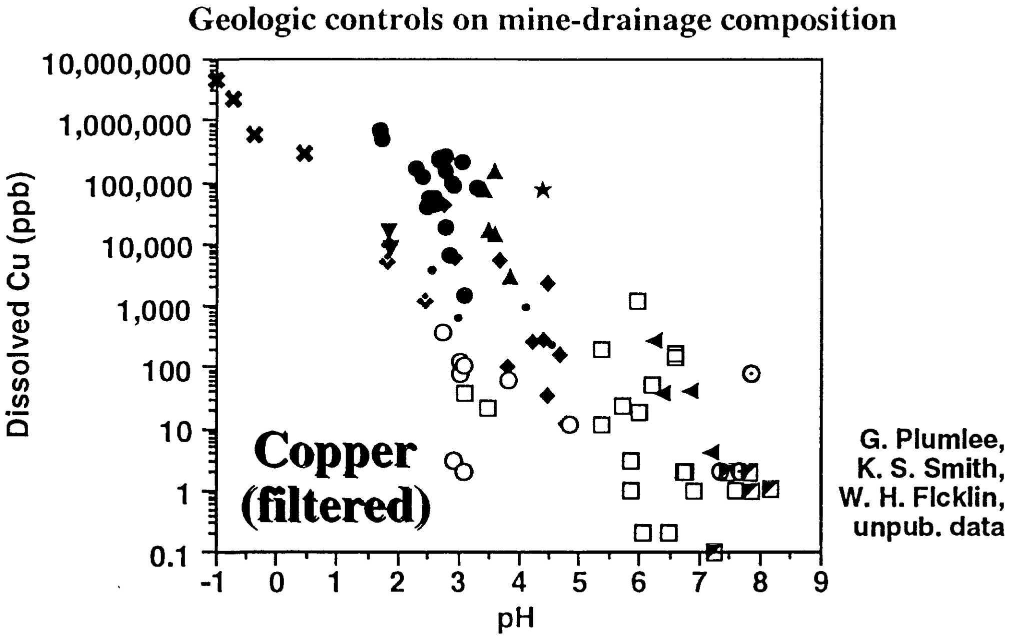
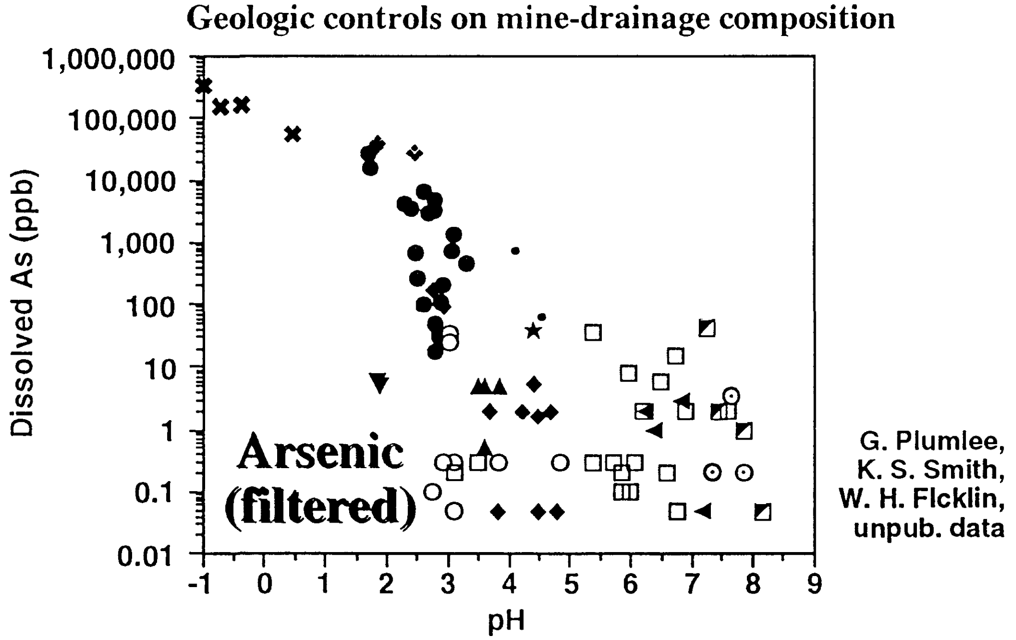

Geologic controls on mine-drainage composition
10,000,000
1,000,000
100,000
10,000
1,000
100
10
1
0.1
Dissolved Cu (ppb)
Copper
(filtered)
-1
0
1
2
3
4
5
6
7
8
9
pH
G. Plumlee,
K. S. Smith,
W. H. Ficklin,
unpub. data


Geologic controls on mine-drainage composition
1,000,000
100,000
10,000
1,000
100
10
1
0.1
0.01
Dissolved As (ppb)
Arsenic
(filtered)
-1
0
1
2
3
4
5
6
7
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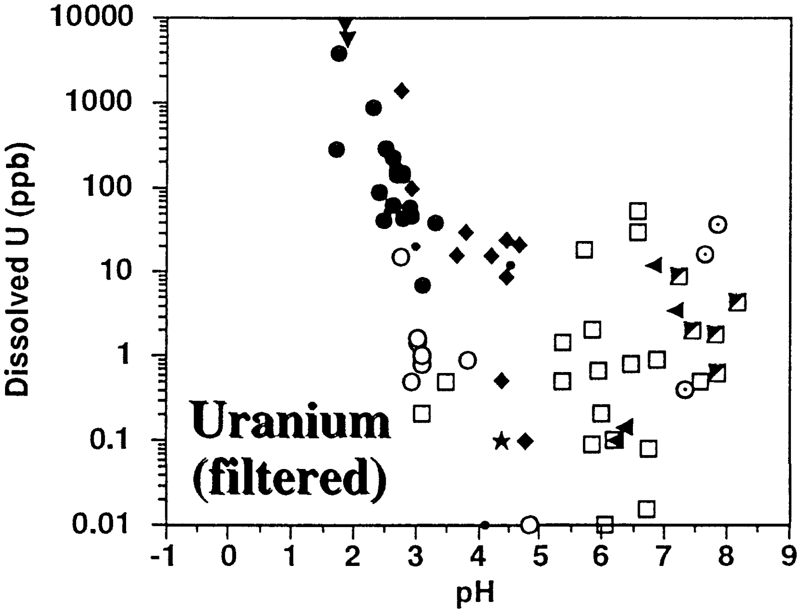
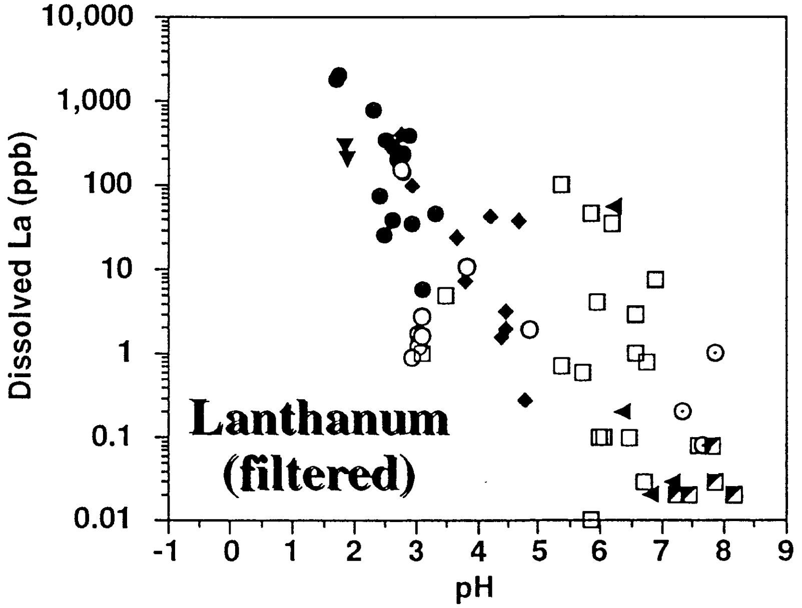
pH
G. Plumlee,
K. S. Smith,
W. H. Ficklin,
unpub. data

Geologic controls on mine-drainage composition



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

Geologic controls on mine-drainage composition



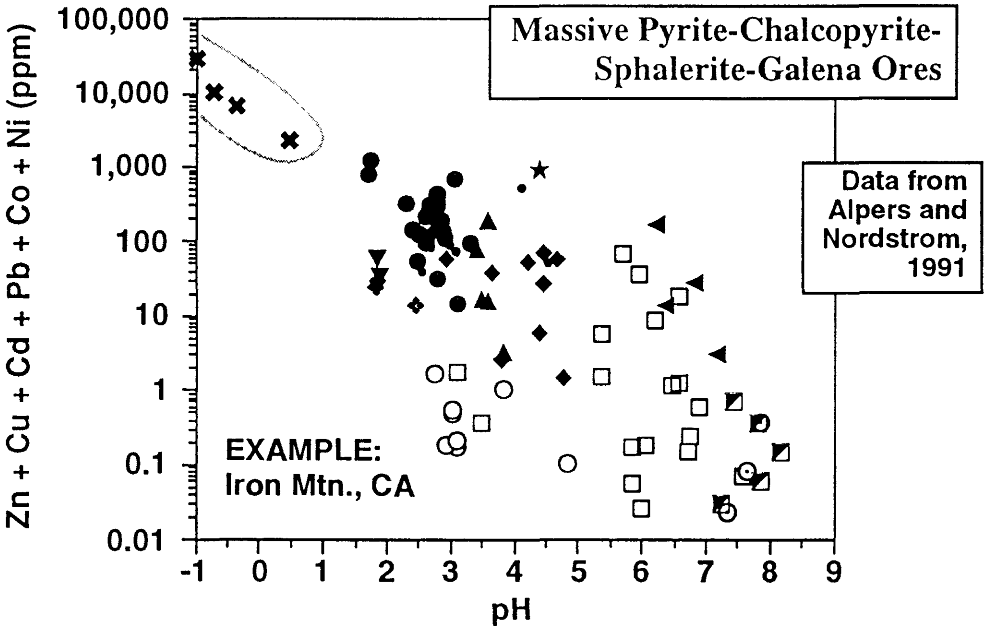
G. Plumlee,
K. S. Smith,
W. H. Ficklin,
unpub. data

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;

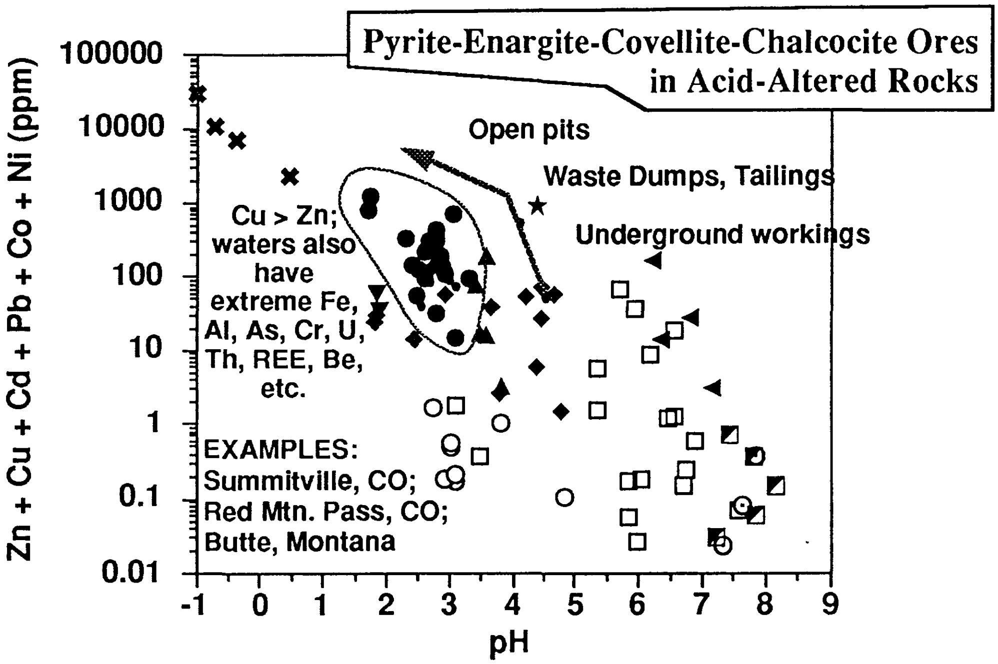
- **Data from Alpers and Nordstrom (1991)**



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**

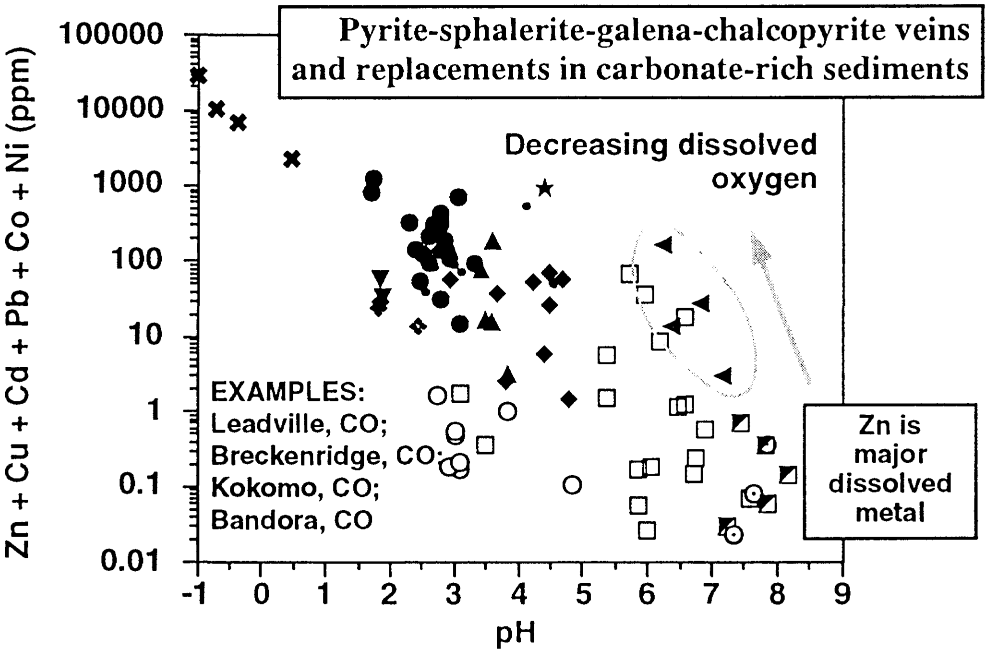
EXAMPLES: Summitville, Colorado; Red Mountain Pass, Colorado; Butte, Montana



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

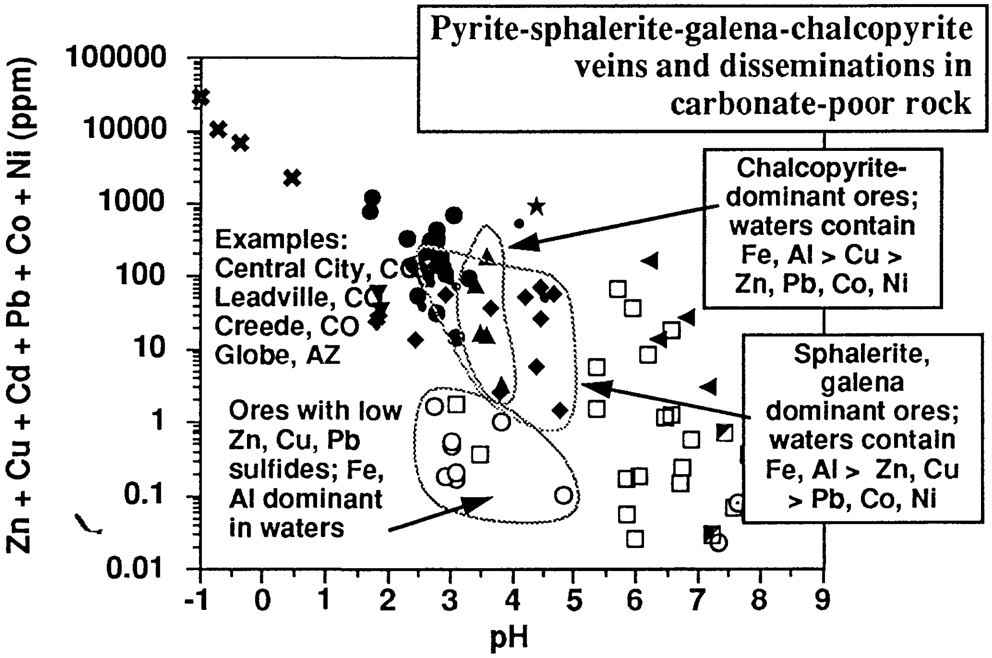
EXAMPLES: Leadville, CO; Breckenridge, CO; Kokomo, CO; Bandora, CO



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**

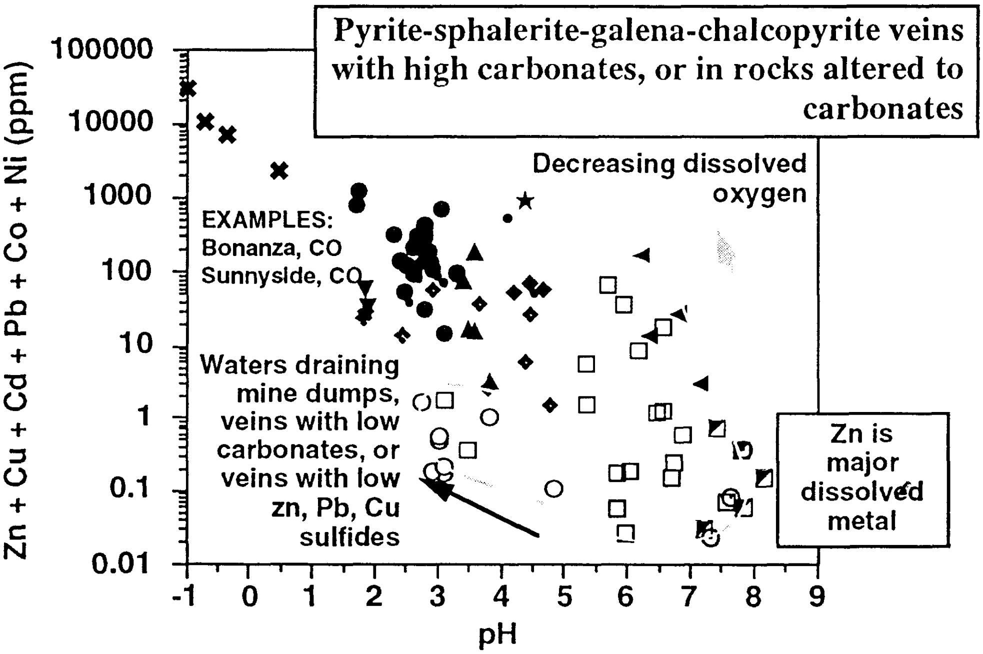
EXAMPLES: Central City, CO; Leadville, CO; Creede, CO; Globe, AZ



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

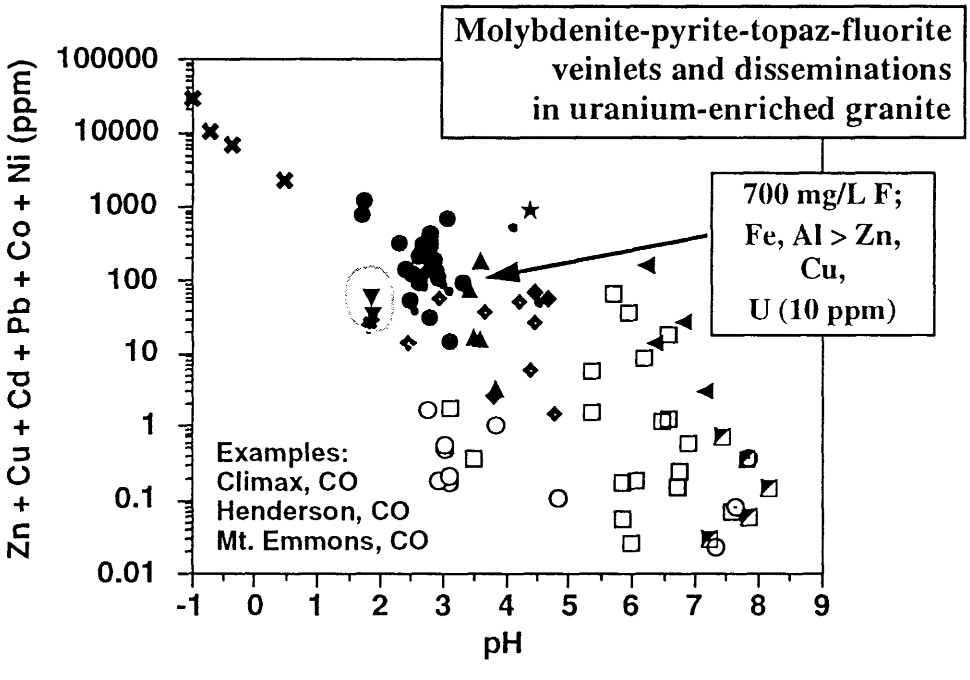
EXAMPLES: Bonanza, CO; Sunnyside, CO



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

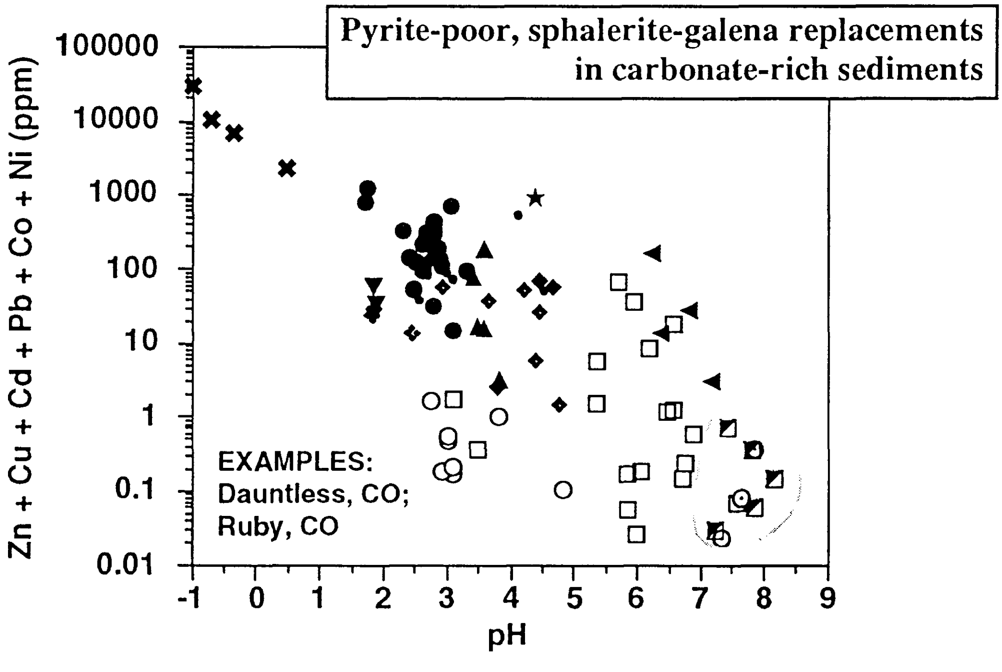
EXAMPLES: Climax, Henderson, Mt. Emmons, CO



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

Geonvironmental 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

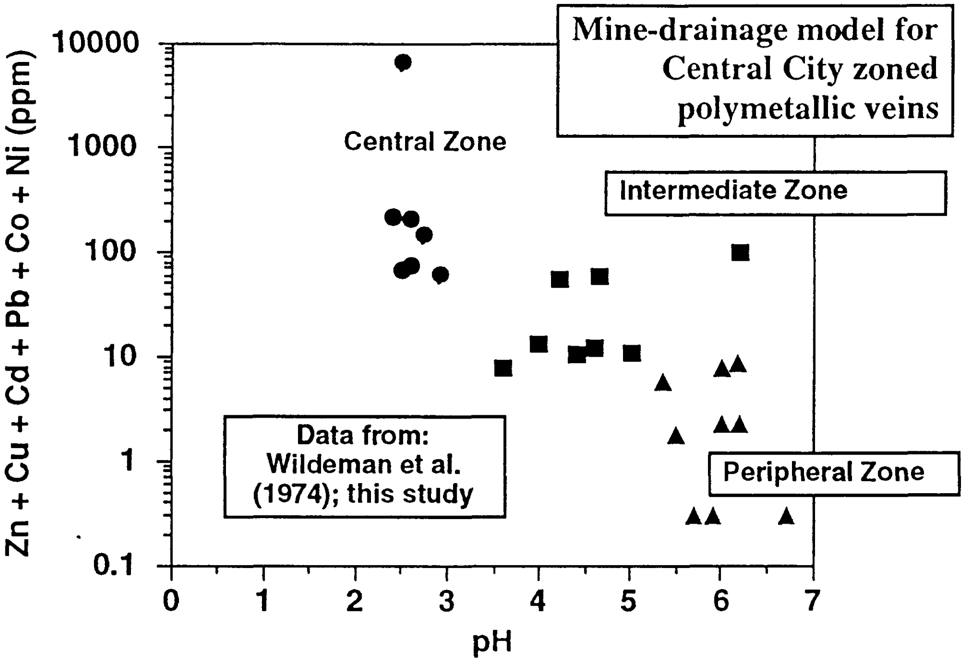
Geoenvironmental Models of Mineral Deposits

- 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

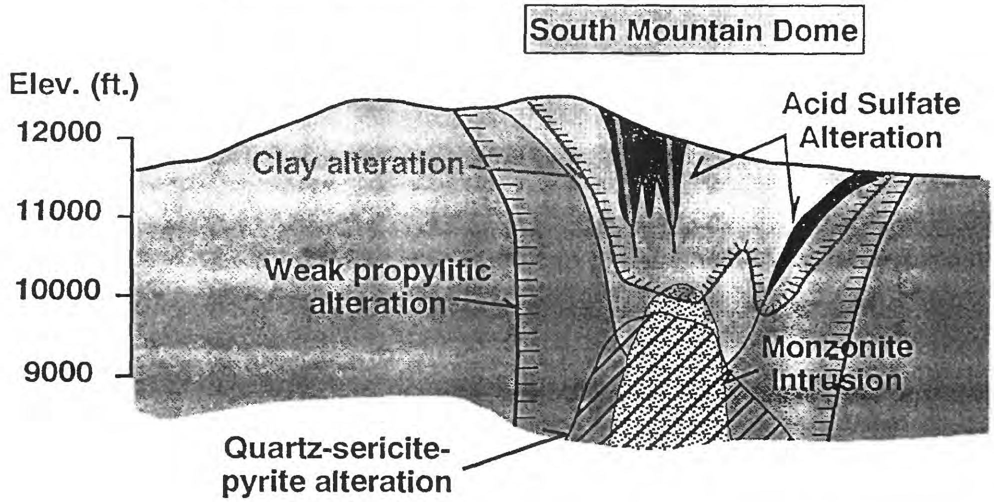
ALTERATION, MINERALIZATION

- 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

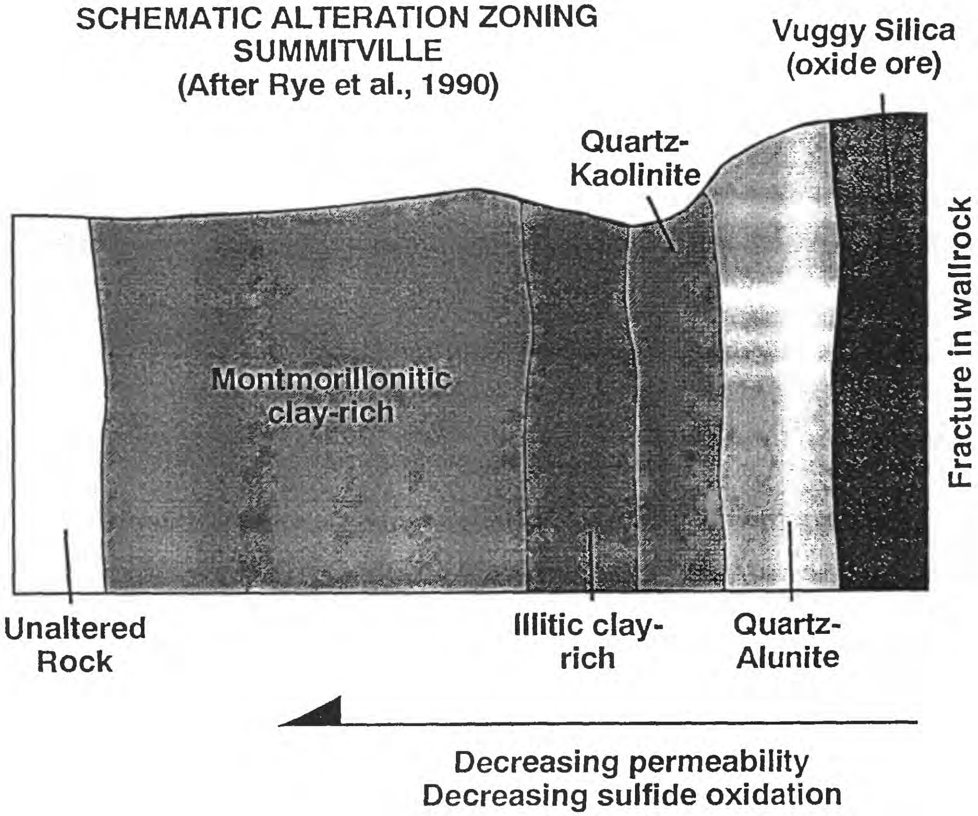
GEOCHEMICAL SIGNATURES: Cu, As, Au, Ag in ore

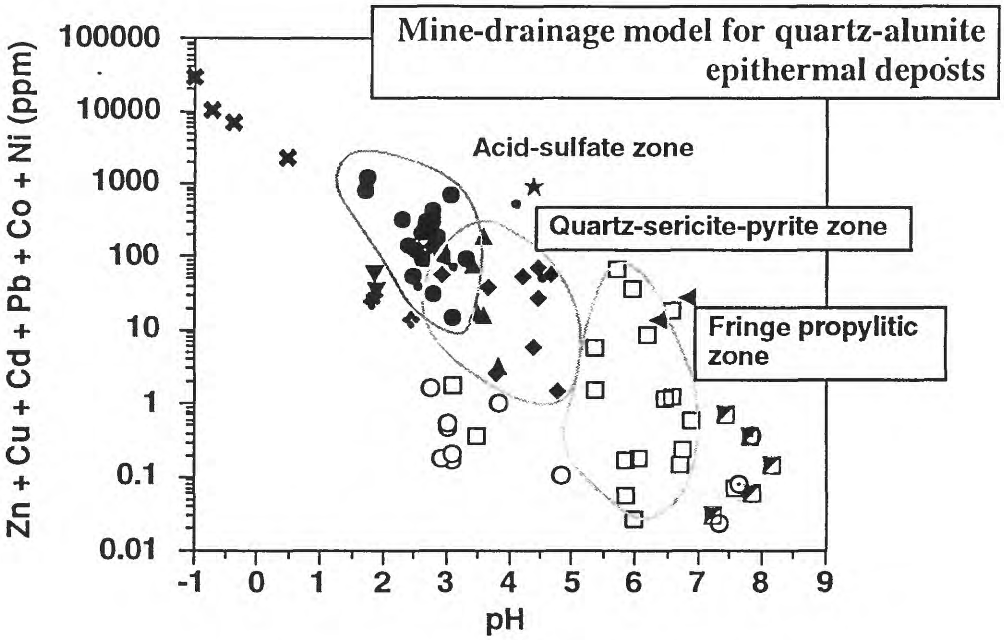
EXAMPLES: Summitville, Colorado; Red Mountain Pass, Colorado

SIMPLIFIED CROSS SECTION
SUMMITVILLE DISTRICT
(after Enders and Coolbaugh, 1987)



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





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

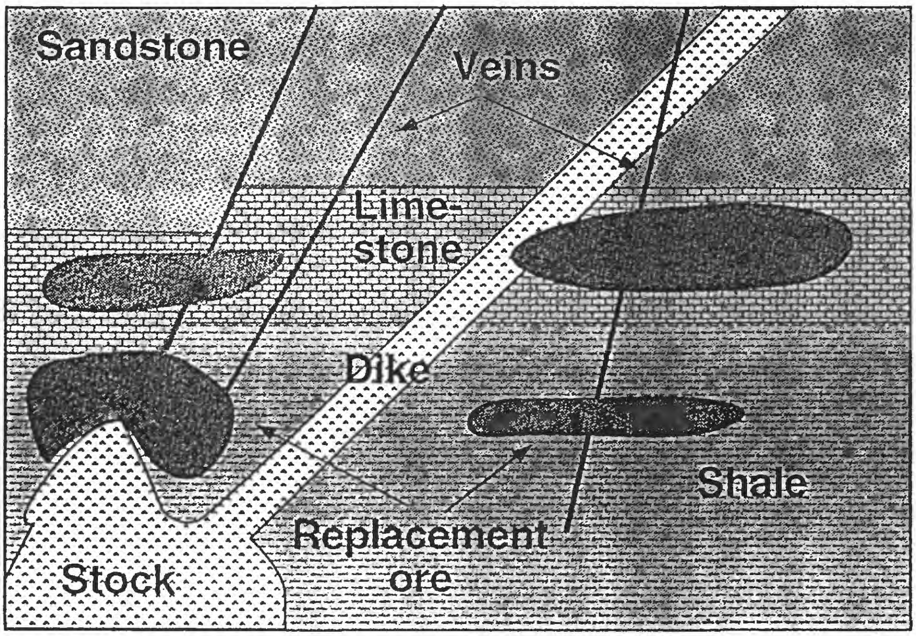
ALTERATION, MINERALIZATION

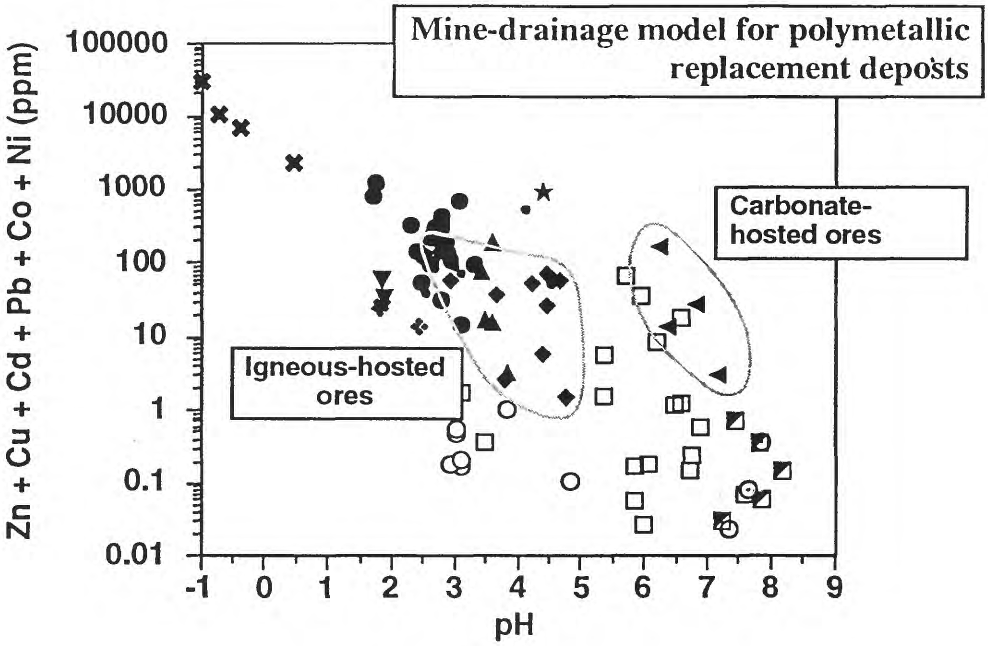
- Open-space filling and replacement of host carbonates and other sedimentary rocks
- Polymetallic veins in associated intrusives
- Pyrite, marcasite, sphalerite, galena, chalcopyrite, sulfosalts, rhodochrosite, barite

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

EXAMPLES: Leadville, Colorado; Gilman, Colorado

Schematic Cross Section, Polymetallic Replacement Deposits and Veins Associated with Igneous Stocks and Dikes





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.

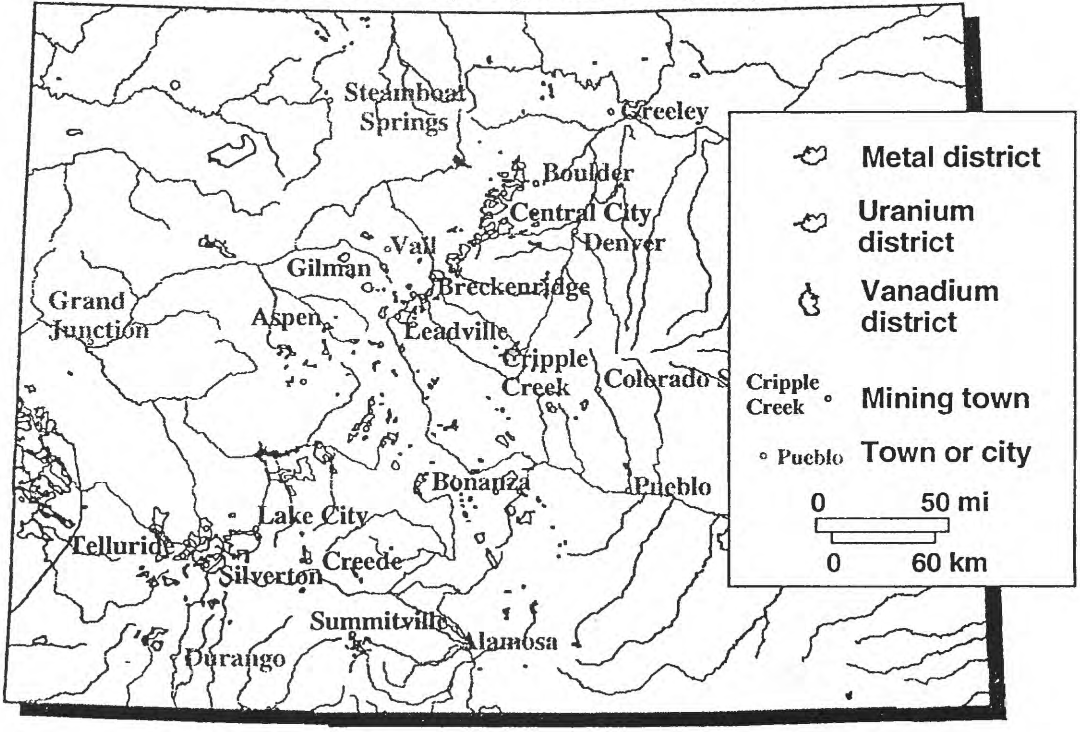
USGS Mineral-Environmental Assessments

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

Acknowledgments

- 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

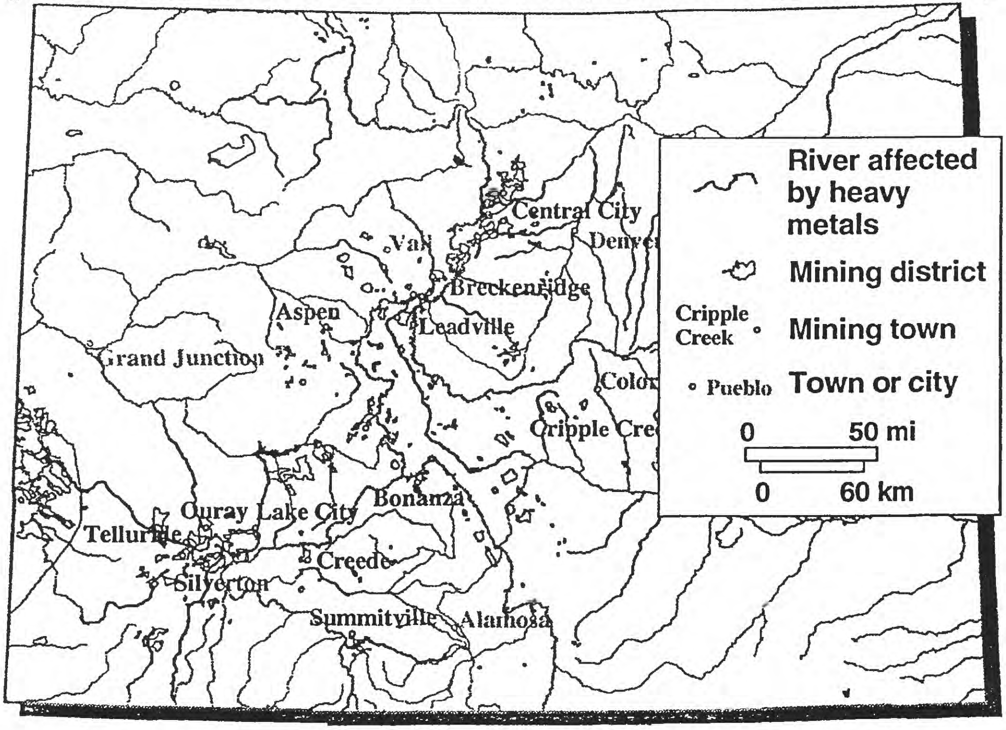


Colorado Mining Districts

Data from Streufert and Davis (1990), Beach et al. (1990), USGS sources

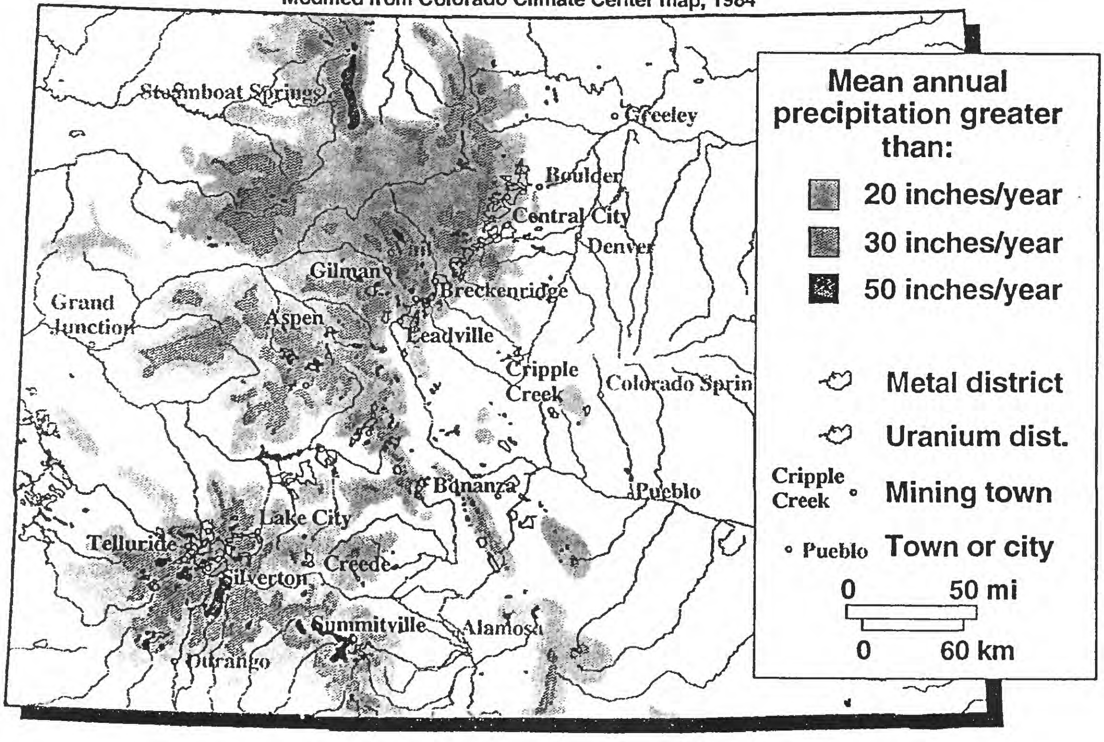
Colorado Streams Affected by Metals

Figure Modified From Colorado Water Quality Control Division, 1989 Colorado Nonpoint Assessment Report

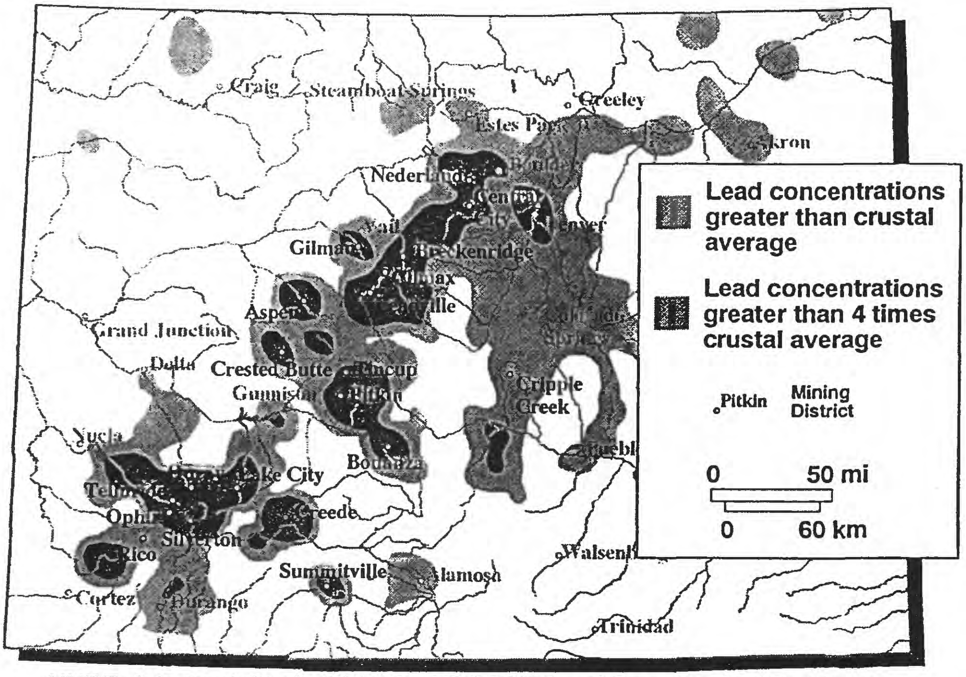


Colorado Average Annual Precipitation, 1951-1980

Modified from Colorado Climate Center map, 1984

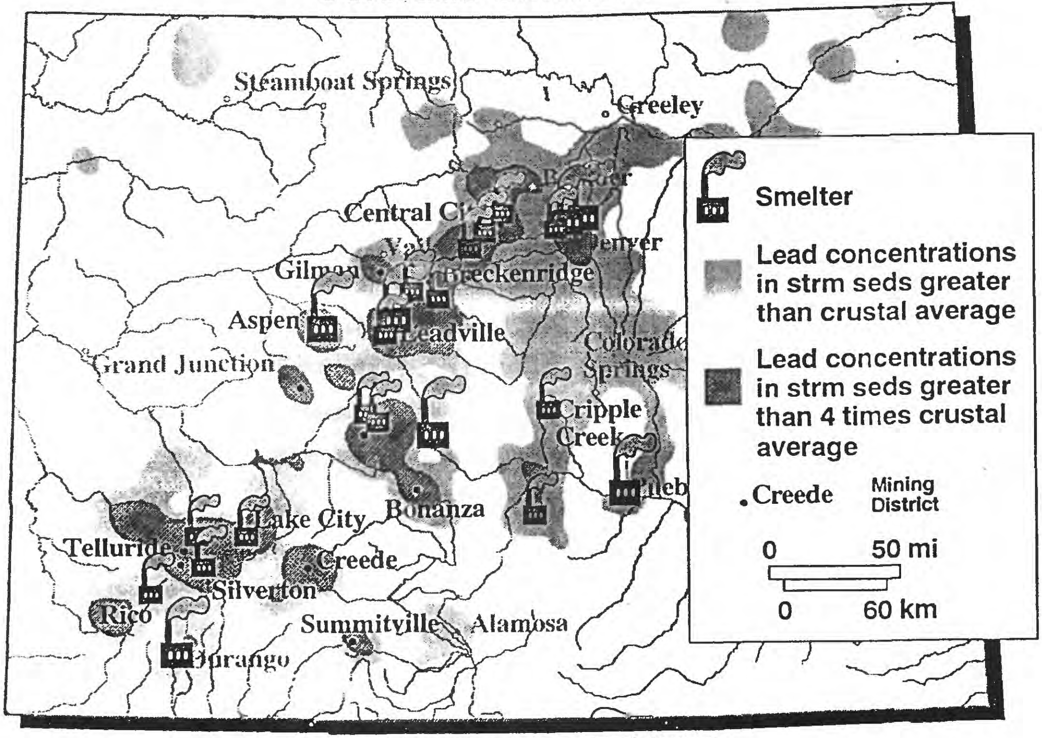


Lead in Stream Sediments of Colorado



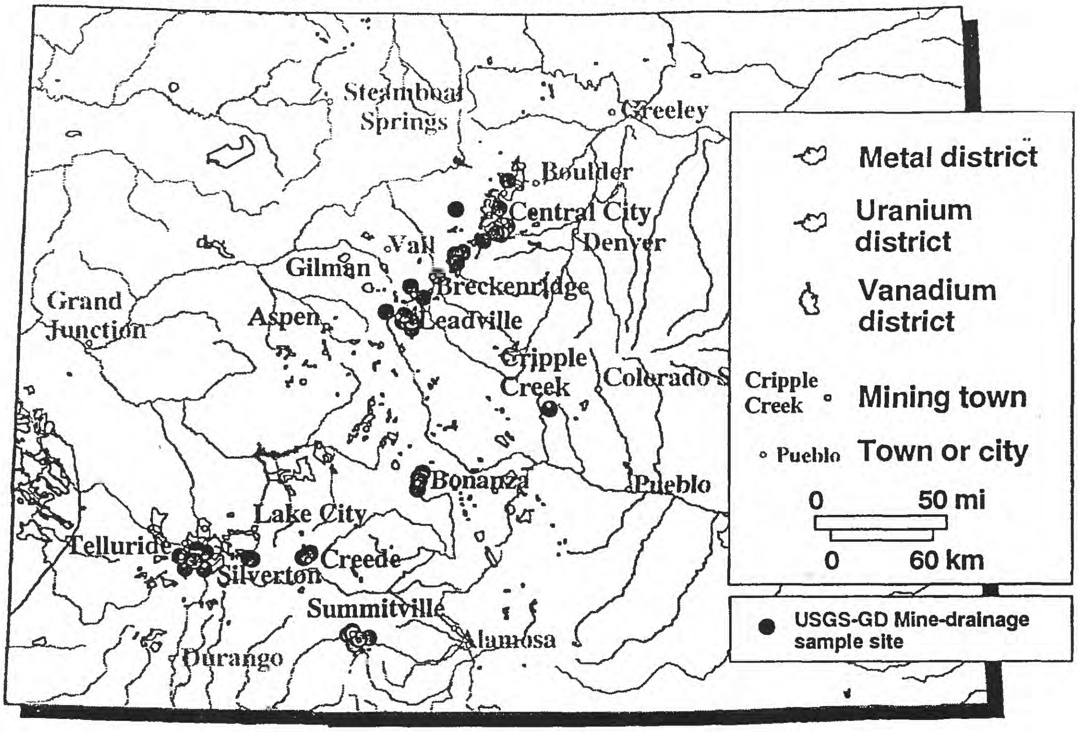
NURE data contained within the USGS National Geochemical Database.
Compiled by S. Smith

Colorado Smelters

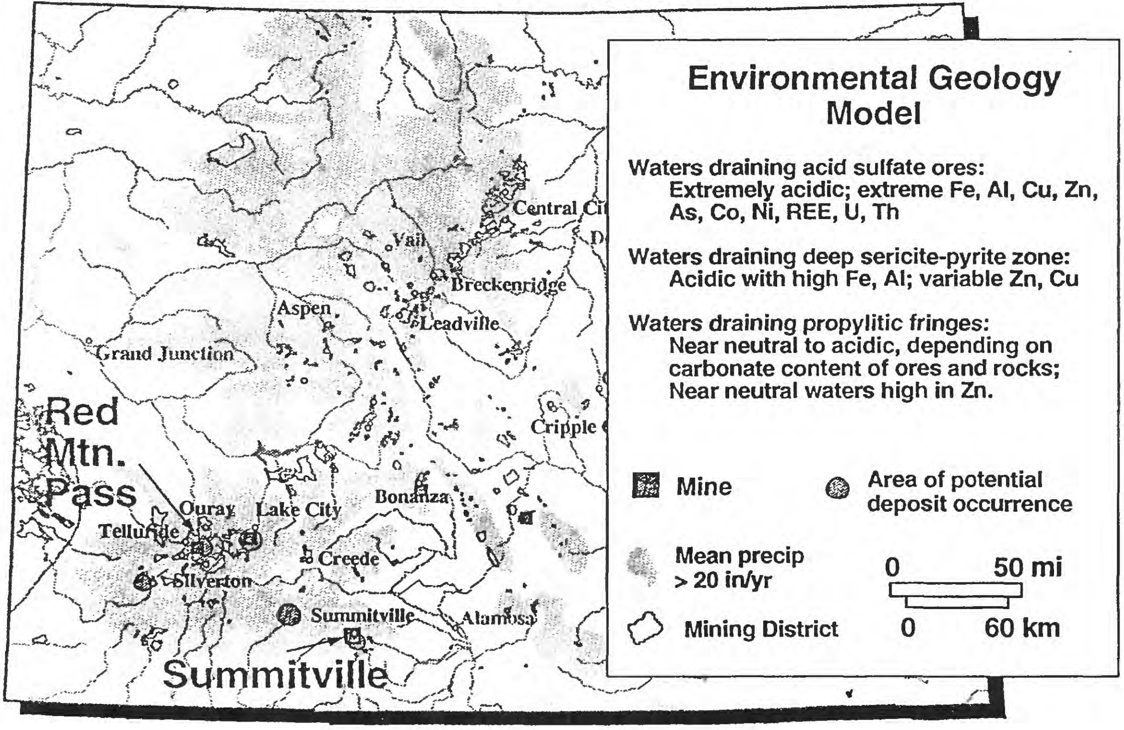


Smelter locations from Fell (1979)

USGS-Geologic Division Mine-Drainage Sample Sites



Quartz-alunite Epithermal Deposits in Colorado

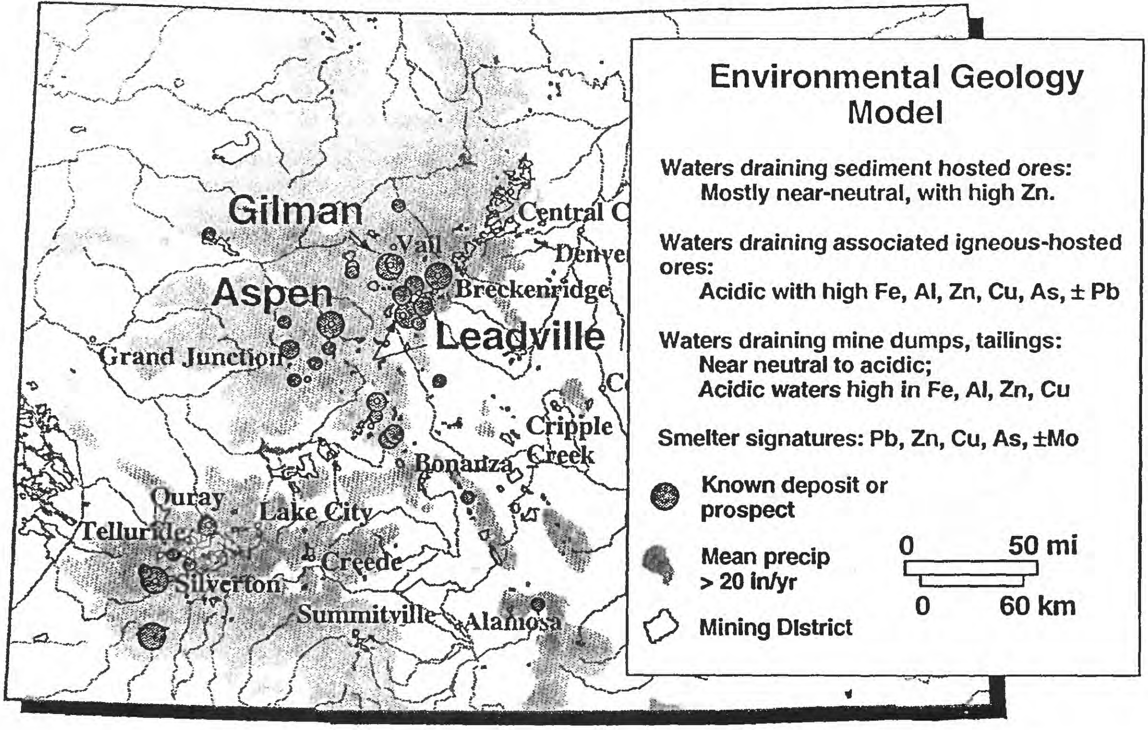


Waters draining acid sulfate ores:
Extremely acidic; extreme Fe, Al, Cu, Zn, As, Co, Ni, REE, U, Th

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.

Sediment-hosted Vein and Replacment Deposits of Colorado



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

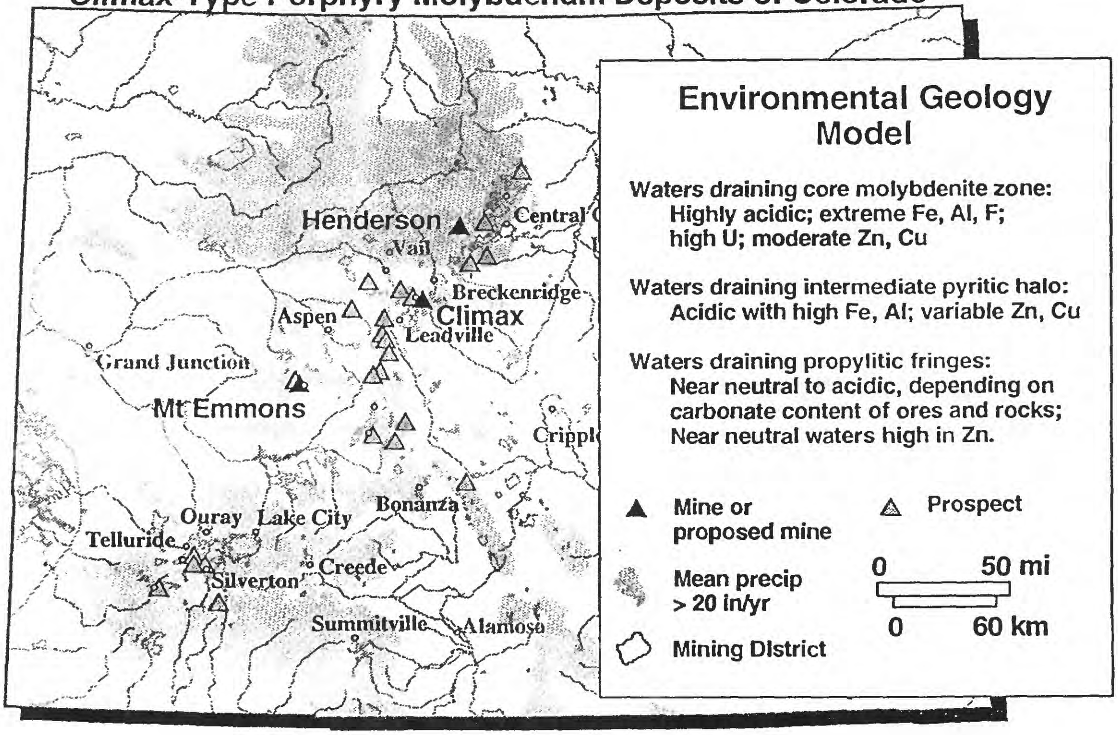
Smelter signatures: Pb, Zn, Cu, As, ±Mo

● Known deposit or prospect

▨ Mean precip > 20 in/yr

○ Mining District

Climax-Type Porphyry Molybdenum Deposits of Colorado



Environmental Geology Model

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.

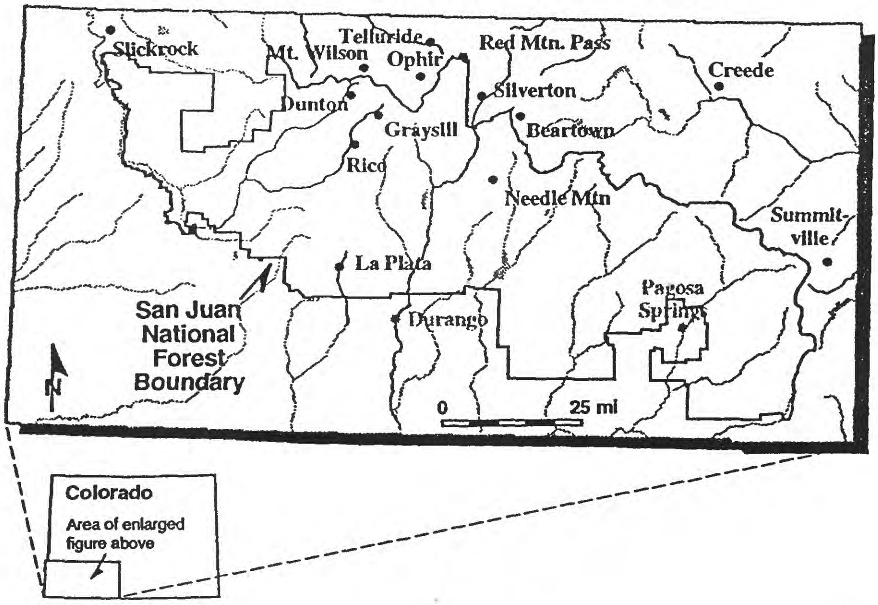
▲ Mine or proposed mine

△ Prospect

▨ Mean precip > 20 in/yr

○ Mining District

Streams Affected by Metals
San Juan National Forest, SW Colorado



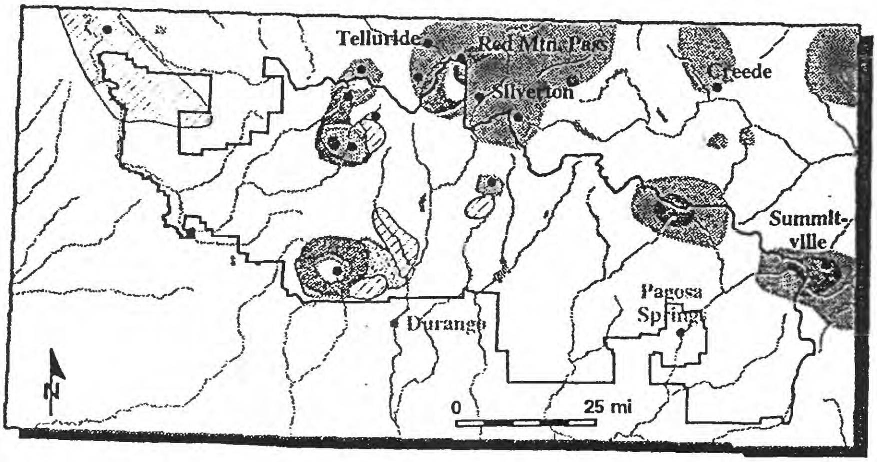
Telluride• Mining District

• Durango Major Town or City

◡ Stream affected by metals

Modified from Colorado 1989
Non-Point Assessment Report.

Mineral-Resource Assessment Map
San Juan National Forest, SW Colorado



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

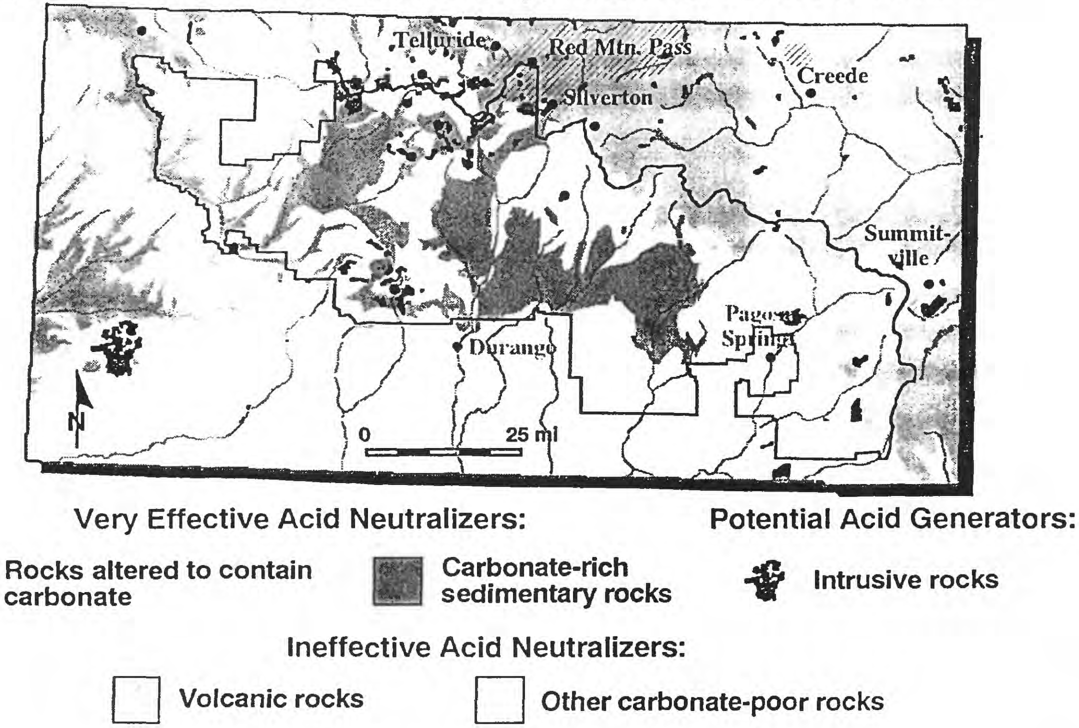
- ● Quartz-alunite gold-copper deposits (e.g. Summitville)
- ▨ Lead-zinc-silver skarn / replacement deposits
- ○ Porphyry copper deposits
- ▨ Epithermal gold-silver-lead-zinc vein deposits
- ▨ Porphyry molybdenum deposits
- ▨ Uranium deposits
- ▨ Gold-telluride deposits

• Mining District

• Durango Town

Compiled by T. Nash, R. VanLoenen, N. Foley.

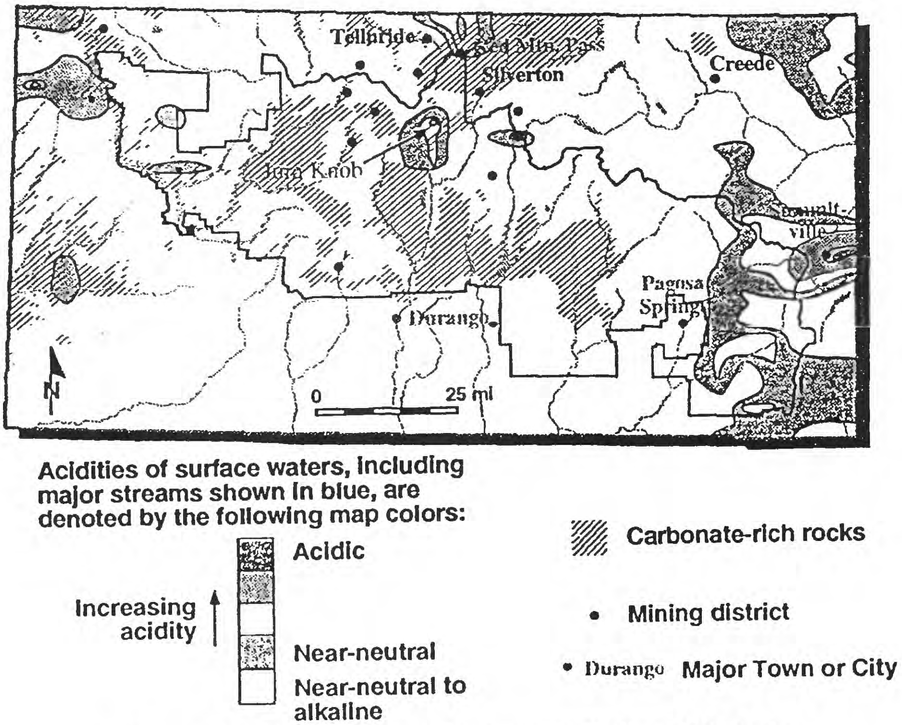
Lithoenvironmental Terrane Map, San Juan National Forest



Geologic map units compiled by G. Green

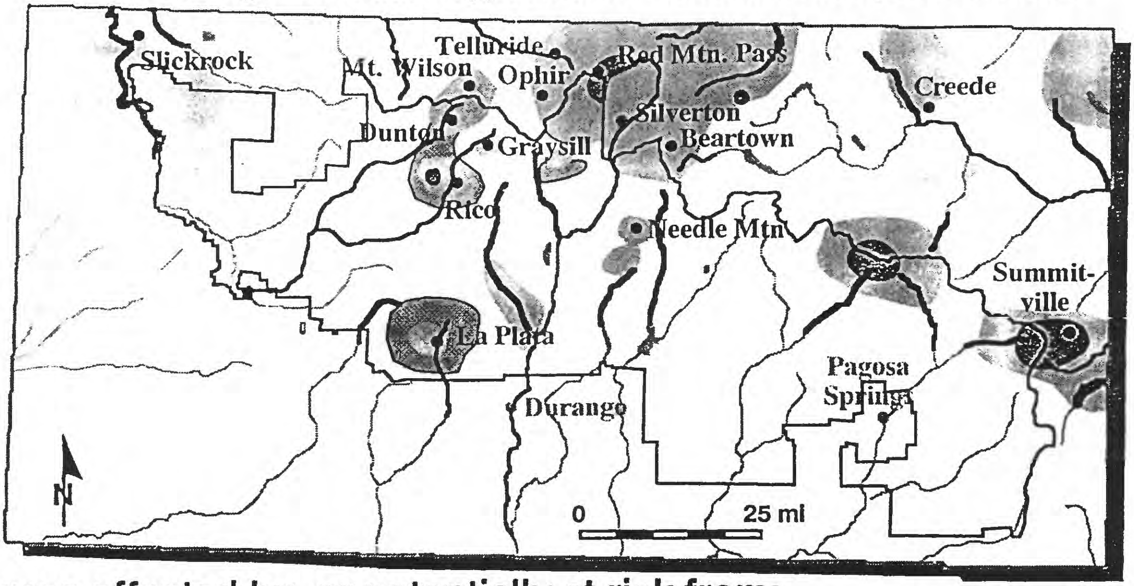
Acidity of Surface Waters

San Juan National Forest, SW Colorado



Data source: National Uranium Resource Evaluation (NURE) data, collected 1976, USGS National Geochemical Database.

Mine-Drainage Potential Map, San Juan National Forest, SW Colorado



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.

Affected stream

Potentially Affected stream

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

This workshop is dedicated to the memory of Walter H. Ficklin. Walt's input to this work has been significant, and his presence will be greatly missed. Analytical chemistry assistance was provided by Cate Ball, Paul Briggs, Joe Christie, David Fey, Phil Hageman, Mollie Malcolm, John McHugh, Al Meier, and George Riddle. Field assistance was provided by Maria Montour, Cate Ball, Steve Kulinski, Phil Hageman, Amy Berger, and Christene Albanese. We thank Jim Herron, Bruce Stover, Bob Kirkham, and Julie Lake of the Colorado Division of Minerals and Geology for their assistance in locating mines and mine owners. We gratefully acknowledge the mine owners who allowed us access to sample their mines. Steve Smith, Margo Toth, and Sherm Marsh were co-investigators in the mineral-environmental assessments of Colorado and the San Juan National Forest. Geologic and mineral resource information used in the prototype environmental assessments was compiled by Steve Ludington, Alan Wallace, Tom Nash, Nora Foley, Rich Van Loenen, Barry Moring, and Greg Green. Graphical assistance was provided by Dick Walker. We thank George Breit and Dave Zimbelman for their helpful reviews of these notes. We also thank Lori Filipek and Tom Wildeman for their helpful comments during the preparation of this workshop.

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