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Chapter 2

AN OVERVIEW OF THE ABUNDANCE, RELATIVE MOBILITY, BIOAVAILABILITY, AND HUMAN TOXICITY OF METALS

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> *"All things are poisonous and yet there is nothing that is poisonous; it is only the dose that makes a thing poisonous."*—P.A. Paracelsus (1493?–1541)

INTRODUCTION

A major reason for considering the environmental geochemistry of mineral deposits is the environmental impact from such deposits on human, animal, and plant life. Some human activities may perturb or alter natural cycles of metals in the environment leading to accumulation of many potentially toxic metals in the food chain. To adequately assess the impact of human activities on metals in the environment, one must approach the issue from both a geological/geochemical/physical viewpoint and a biological/biochemical/toxicological perspective.

This chapter provides a geochemical and a biological context for chapters in this volume that discuss specifics of environmental geochemistry of mineral deposits. We alternate between the geological/geochemical/physical and biological/biochemical/toxicological aspects of selected metals. Because the emphasis of this volume is the environmental geochemistry of mineral deposits, we present examples that relate to metals or mineral deposits rather than provide a review of the literature. We also place emphasis on geological, geochemical, and chemical factors that affect metal bioavailability and toxicity to highlight connections between the earth and biological sciences. Radioactive materials are beyond the scope of this chapter.

Definitions

In this chapter, we use the term "metal" in a general sense to mean an element that, in aqueous solution, displays cationic behavior or that has an oxide that is soluble in acids (Parish, 1977). By this definition, elements that are non-metals include hydrogen, the rare gases, boron, carbon, silicon, nitrogen, phosphorus, arsenic, oxygen, sulfur, selenium, tellurium, polonium, fluorine, chlorine, bromine, iodine, and astatine. In our compilations, we may include some of the non-metals under a heading of "metals" in order to provide as much of the available information as possible. McKinney and Rogers (1992) state that the elements of major interest to the U.S. Environmental Protection Agency (U.S. EPA) include aluminum, antimony, arsenic, barium, beryllium, cadmium, chromium, cobalt, copper, lead, manganese, mercury, molybdenum, nickel, selenium, silver, sodium, thallium, vanadium, and zinc.

To understand toxicity of metals in humans, one must define various terms. "Toxicology" is the study of adverse effects of chemicals on living organisms. "Ecotoxicology" is the study of potentially harmful substances in the environment and involves the disciplines of environmental chemistry, toxicology, and ecology. "Toxicity" of an element or a chemical compound is the capacity of the material to adversely affect any biological function. A "toxicant" is a toxic material of non-biological origin whereas a "toxin" is a toxic material of biological origin.

Our definition for "bioavailability" is based upon Newman and Jagoe (1994): "Bioavailability is the degree to which a contaminant in a potential source is free for uptake (movement into or onto an organism)." Thus, we use the term bioavailability in a broad sense. Some definitions of bioavailability further imply that the toxicant must affect the organism. In environmental toxicity studies, the definition of bioavailability varies with the toxicant under study, the method of determining amount of toxicant absorbed, and the target organism (e.g., see Davis et al., 1992). In the field of toxicology, the term bioavailability is often used to compare resulting blood concentrations from a one-time oral dose with the same dose administered intravenously. Dickson et al. (1994) discuss various definitions of bioavailability and state that the term eludes a consensus definition. The term "bioaccessibility" refers to the amount of contaminant liberated under a specified set of test conditions (Ruby et al., 1993).

The term "geoavailability" (coined by W. Day, verbal commun., U.S. Geological Survey, 1993) was initially defined in Plumlee (1994). Geoavailability is that portion of a chemical element's or a compound's total content in an earth material that can be liberated to the surficial or near-surface environment (or biosphere) through mechanical, chemical, or biological processes. The geoavailability of a chemical element or a compound is related to the susceptibility and availability of its resident mineral phase(s) to alteration and weathering reactions.

PATHWAYS FROM TOTAL METAL CONTENT THROUGH TOXICITY

Figure 2.1 illustrates pathways and relationships between total metal content in an earth material and potential toxicity to an organism. Total metal is the abundance of a given metal in an earth material and geoavailability is a function of the total metal content, access to weathering, and susceptibility to weathering.

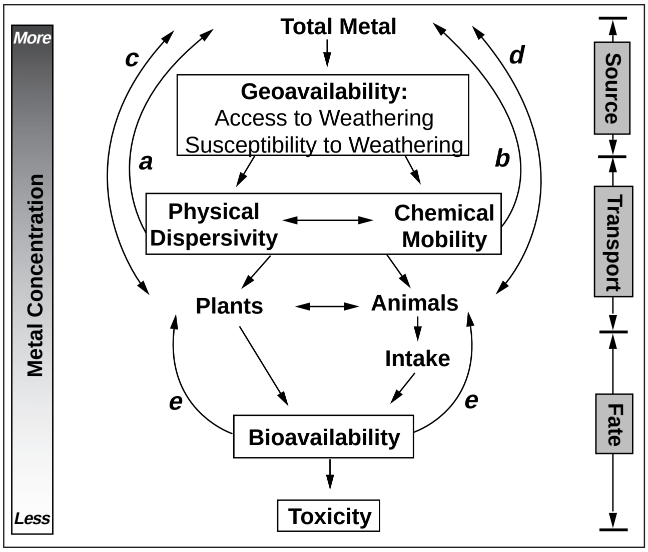

FIGURE 2.1—Diagram showing the pathways and relationships between total metal in an earth material and toxicity. As a metal or toxicant moves from one stage to another, generally less than 100% is transferred; not all of the total metal content in an earth material is usually geoavailable, bioavailable, or toxic. The gray scale on Figure 2.1 portrays this concept. Loops "a" and "b" signify transport and deposition of metals into another earth material (e.g., from weathering rocks to soil or sediment). Loops "c" and "d" denote direct uptake of the earth material by plants or animals (e.g., pica by children) and possible redeposition of metals by decay or excretion. Loops "e" illustrate biomagnification (see text).

"Dispersivity" refers to physical processes, or the ability to scatter via non-chemical means. Dispersion may occur via processes such as movement of bedload or suspended-sediment load in streams or as transport through air (e.g., smelter emissions, wind erosion). Mobility refers to chemical processes, which include chemical interactions with the surficial or near-surface environment, and the capacity for movement within fluids after dissolution. Mobility embodies the physicochemical characteristics and speciation of elements in aqueous systems.

Controls on geoavailability, dispersivity, and mobility incorporate both source characteristics and processes that interact with those characteristics, as summarized in Table 2.1. Plumlee (1999) discusses many of these characteristics and processes in detail; we note them here only in relation to controls on geoavailability, dispersivity, and mobility.

On Figure 2.1, we make a distinction between plants and animals because bioavailability is generally a prerequisite for uptake in plants, whereas animals may intake (ingest, inhale, etc.) toxicants that subsequently pass through their bodies without any systemic uptake. For animals, two levels of bioavailability distinguish (1) systemic uptake (e.g., into the bloodstream) from (2) uptake into target organs, where toxicants can accumulate and create specific toxicity symptoms (after Valberg et al., 1994; not shown on Fig. 2.1). For plants, metals can be either directly absorbed from the environment and stored by plant organs at the point of absorption (e.g., roots and leaves) or translocated and accumulated within plant tissues.

Bioavailability is a function of geoavailability, dispersivity, mobility, mode and pathway of exposure, biological specificity, and individual susceptibility of an organism. In this chapter, we use a broad definition for bioavailability based upon Newman and Jagoe (1994) (see definition above). Bioavailability is generally less than 100% of the amount of a chemical element or compound to which an organism is exposed (by ingestion, breathing, etc.), and may be far less than the total content of that element or compound in an earth material. Bioavailability is a prerequisite for toxicity but does not necessarily result in toxicity; toxicity requires an adverse effect on an organism. Toxicity is discussed in detail in later sections of this chapter.

TABLE 2.1—Outline of the controls on geoavailability, dispersivity, and mobility of chemical elements.

I. Controls on Geoavailability
    A. Abundance (total metal content)
    B. Access of weathering agents and degree of weathering
        1. Climate
        2. Porosity and permeability
            a. Structural and lithologic factors
            b. Surface exposure
        3. Topographic relief
    C. Susceptibility of source mineral phases in earth materials to weathering
        1. Mineral properties
            a. Mineral type
            b. Solubility
            c. Grain size, texture, and structure
            d. Impurities
        2. Geochemical conditions
            a. Aqueous concentration and speciation
            b. pH and redox conditions
            c. Kinetic constraints
II. Controls on Dispersivity (Physical Processes)
    A. Abundance and geoavailability
    B. Grain characteristics
        1. Size
        2. Shape
        3. Density
    C. Access of erosional agents
        1. Climate
        2. Topographic relief
    D. Access to transporting or retaining agents
        1. Movement through air
        2. Movement with or settling in water
            a. Particle properties
            b. Stream or river or aquifer hydrologic characteristics
            c. Pond or lake characteristics
            d. Aquifer characteristics
III. Controls on Mobility (Chemical Processes)
    A. Abundance and geoavailability
    B. Speciation
    C. Solubility product of primary and secondary minerals
        1. Aqueous concentration and speciation
        2. pH and redox conditions
        3. Kinetic constraints
        4. Temperature
        5. Climate
    D. Sorption, coprecipitation, or ion exchange reactions
        1. Aqueous concentration and speciation
        2. pH and redox conditions
        3. Soil properties and mineralogic characteristics
        4. Abundance of sorbent material
        5. Accessibility of sorbent material
    E. Redox conditions
    F. Photolysis
    G. Tendency for volatilization
    H. Tendency for biotransformation

Each stage from total metal content in an earth material through toxicity in the surficial environment on Figure 2.1 is a reservoir with a distinct "half-life." As a metal or toxicant moves from one stage to another, generally less than 100% is transferred. Therefore, not all of the total metal content in an earth material is usually geoavailable, bioavailable, or toxic. The gray scale on Figure 2.1 portrays this concept. Total metal content and geoavailability constitute the "source" factors; dispersivity and mobility comprise the "transport" factors; and intake, bioavailability, and toxicity constitute the "fate" of metals or toxicants. Biomagnification links the fate and transport segments of the diagram (as depicted by loops labeled "e" on Fig. 2.1). An example of biomagnification is the accumulation of mercury in marine biota.

HEALTH, TOXICITY, AND REGULATIONS

Metals can be essential to health and they also can be toxic. This section covers dietary requirements, essential effects, and toxic effects of metals. Huheey et al. (1993, Chapter 19) provide a detailed discussion of the inorganic chemistry of biological systems. Regulations and guidelines for metal concentrations in water also are discussed in this section.

Minimum human dietary requirements of "minerals" and electrolytes

Human health requires ingestion of many metals on a daily basis. Many people are aware of the need to consume sufficient iron, for example, to maintain hemoglobin in the blood. Relatively recently, dietary requirements have begun to emphasize other metals, e.g., zinc, as being necessary for maintaining health. Table 2.2A summarizes U.S. Recommended Daily Allowances (USRDAs) and estimated safe and adequate daily dietary intakes for adults (National Research Council, 1989). Among the elements listed in Table 2.2A, fluorine is the only element that is not considered to be essential for human health. However, its usefulness in preventing tooth decay garners the designation of "beneficial element" for human health (National Research Council, 1989). Table 2.2B lists other metals that some researchers consider to be essential for good health, but whose roles have not been sufficiently defined by scientific research to list under USRDAs.

Some other elements are also considered by some researchers to be potentially important to human health, although clinical studies are equivocal. These elements are: bromine, lead, and tin (Ensminger et al., 1994; Nielsen, 1994). Some of these elements are important to plant health; deficiencies of others cause problems for laboratory animals in one or two studies. Further research

TABLE 2.2A—U.S. Recommended Daily Allowances (USRDAs) and biological roles of elements that the National Research Council (1989) lists as essential to health.

Element	USRDA(2)	Biological role(4)
Calcium (Ca)	800 –1200 mg	Needed to build strong bones and teeth; for blood clotting, neural transmission, and muscle function
Chlorine/Chloride (Cl)	[750 –3600 mg]	Needed to maintain water balance, osmotic pressure, and acid-base balance, for digestive acid
Chromium (Cr)	50 –200 µg	Needed for glucose metabolism
Copper (Cu)	1.5 –3 mg	Respiratory and red blood cell function; present in oxidative enzymes
Fluorine/Fluoride (F)(1)	1.5 –4 mg	As fluoride, prevents tooth decay or disease
Iodine (I)	150 µg(3)	Needed for thyroid hormones, to control body temperature, metabolism, reproduction, and growth
Iron (Fe)	10 –15 mg(3)	Needed for hemoglobin in blood, energy production, and a healthy immune system
Magnesium (Mg)	280 –350 mg(3)	Needed for healthy bones and blood vessels, muscle function, nerve transmission, and energy formation
Manganese (Mn)	2 –5 mg	Promotes growth, development, and cell function; cofactor in a number of enzymatic reactions
Molybdenum (Mo)	75 –250 µg	Promotes growth, development, and cell function; essential cofactor in certain enzymes
Phosphorous (P)	800 –1200 mg(3)	Essential for healthy bones and energy production; present in almost every chemical reaction within the body
Potassium (K)	[2000 –3500 mg]	Regulates body fluid balance; aids muscle contraction and neural transmission
Selenium (Se)	55 –70 µg(3)	Prevents cardiovascular disease and cancer; detoxifies several major pollutants, especially oxidants and free radicals
Sodium (Na)	[500 –2400 mg]	Aids muscle contraction and neural transmission; maintains blood pressure
Zinc (Zn)	12 –15 mg	Maintains senses of taste and smell, and healthy immune system and growth; protects liver from chemical damage

(1) Although fluorine is not essential to health, the National Research Council (1989) considers it to have sufficient value to be included in this listing.

(2) [ ]: lower number is estimated minimum requirement for adults; upper limit is based upon text (National Research Council, 1989).

(3) Indicates USRDAs; all others are "estimated safe and adequate daily dietary intakes," which are less well defined. All values are listed for adults >18 years old (excluding pregnant or lactating women).

(4) After Griffith (1988), National Research Council (1989), Christian and Greger (1991), and Nielsen (1994).

TABLE 2.2B—Biological roles of metals that may be vital to human health.(1) (2)

Element	Biological Role
Boron (B)	Affects metabolism of some essential elements
Cobalt (Co)(3)	Constituent in vitamin B_{12} and a factor in formation of red blood cells
Lithium (Li)	May be essential for slow respiration on intracellular level
Nickel (Ni)	Important in critical enzymes
Silicon (Si)	Important in metabolism, maintaining bone tissue
Sulfur (S)(3)	Enables storage and release of energy; promotes enzyme reactions, aids in detoxification of body; constituent in thiamine, biotin, and required proteins
Vanadium (V)	May play a role in metabolism of bones and teeth

(1)Elements listed in this table were noted as being potentially vital to humans in at least two sources.
Sources: Venugopal and Luckey (1978); Griffith (1988); National Research Council (1989); Goyer (1991); Ensminger et al. (1994); Nielsen (1994).

(2)Tin has no known biological role, but deficiency has been produced in experimental animals and thus tin may be essential in humans (Ensminger et al., 1994) and is noted as a possible nutrient or nutrient under special conditions in Luckey and Venugopal (1977). Similarly, arsenic's role is not well defined, but deficiency in experimental animals resulted in depressed growth and abnormal reproduction (Ensminger et al., 1994; Nielsen, 1994).

(3)Although National Research Council (1989) does not specifically list cobalt and sulfur as essential, Christian and Greger (1991) and Ensminger et al. (1994) note that each is a constituent of vitamins or proteins for which U.S. Recommended Daily Allowances (USRDAs) have been established.

is necessary to define their benefits (or lack thereof) to humans. According to Robert Benson (U.S. EPA, personal commun., 1996), there are no credible data suggesting that lead is an essential element for humans; in fact, lead appears to have adverse effects on developing nervous systems at the lowest exposures that can be quantified. Figure 2.2 summarizes the current status of nutrients considered to be essential to mammalian health.

Toxicity of metals

Gossel and Bricker (1984), Hayes (1989), and Goyer (1991, 1995) provide useful reviews of metal toxicity in humans, and Gough et al. (1979) review element concentrations toxic to plants, animals, and humans. Many metals are essential to life in small amounts and such metals become toxic only when absorbed in excessive amounts. However, the level of toxicity for metals is commonly only a few to several times the level necessary to sustain life in humans. For example, while the recommended daily ingestion of zinc for humans is 12–15 mg, researchers have found that daily intakes of as low as 18.5 or 25 mg zinc cause decreased retention of copper (an essential metal) in adult males (Festa et al., 1985; Fischer et al., 1984). Types of toxicity commonly encountered in ecotoxicology are summarized in Table 2.3. Definitions of "acute" and "chronic" exposure vary with source and target. For aquatic species, the time limits of acute and chronic exposure are one hour and four days, respectively; time limits are longer for humans.

Toxic effects

Tables 2.4A and 2.4B summarize the human pathways of metal absorption and the organs in which the metals concentrate or

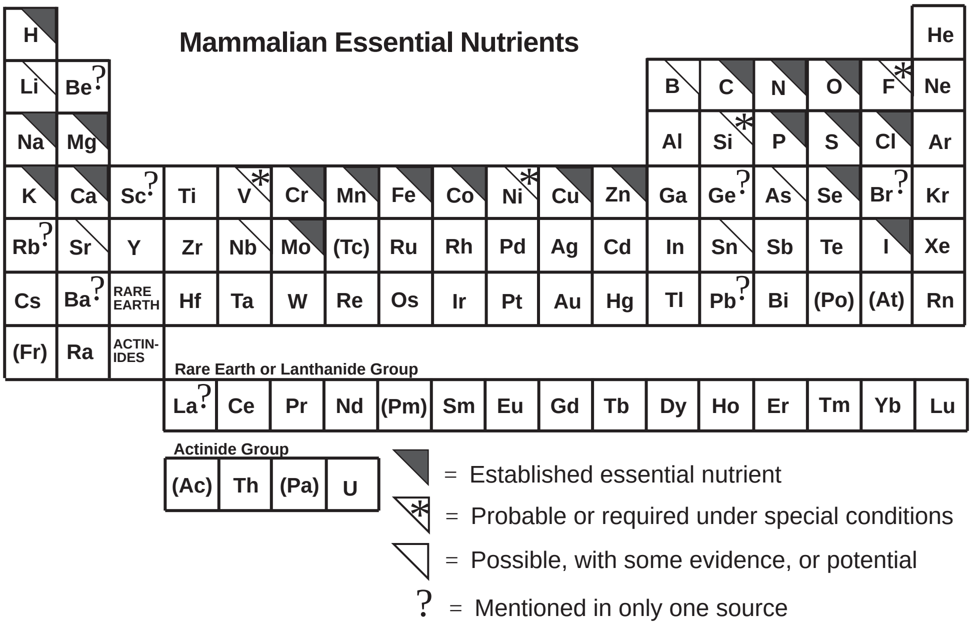

FIGURE 2.2—Periodic table of essential mammalian nutrients. Such nutrients are considered to be essential nutrients to humans, although many studies are based upon experiments on laboratory animals. Based on Luckey and Venugopal (1977), with modifications from National Research Council (1989), Griffith (1988), Nielsen (1994), and Ensminger et al. (1994). Lack of notation for rare earth and actinide group elements is due to lack of information about those elements.

TABLE 2.3—Types of toxicity (modified from Luckey and Venugopal, 1977; U.S. EPA, 1986; Hoffman, 1991; Klaassen and Eaton, 1991; Agency for Toxic Substances and Disease Registry (ATSDR), 1992).

Acute Exposure: (1) exposure to a toxic agent for 24 hours or less (Klaassen and Eaton, 1991); (2) exposure to a toxic agent for 14 days or less (ATSDR, 1992, Glossary); (3) exposure of aquatic life to a toxic agent for one hour (U.S. EPA, 1986, for setting water pollution standards)(1).

Acute Toxicity: adverse biological effects caused by a single dose or repeated doses over a short period of time (acute exposure).

Carcinogen: a biologic, chemical, or physical agent capable of producing uncontrolled cell proliferation in organs and tissues, or to induce cancer. Carcinogenicity depends on routes and times of exposure, dose, physical state of the agent, and host-specific factors.

Chronic Exposure: (1) exposure to a toxic agent for more than three months (Klaassen and Eaton, 1991); (2) exposure to a toxic agent for 365 days or more (ATSDR, 1992, Glossary); (3) exposure of aquatic life to a toxic agent for four days (U.S. EPA, 1986, for setting water pollution standards)(1).

Chronic Toxicity: (1) also called "cumulative poisoning" or "distal toxicity," adverse biological effects caused by long and continuous exposure (chronic exposure).

Mutagen: (1) A substance that causes mutations. A mutation is a change in the genetic material of a body cell. Mutations can lead to birth defects, miscarriages, or cancer (ASTDR, 1992, Glossary). (2) Any agent that causes mutation [by mutagenesis]. Mutagenesis includes the induction of DNA damage and all kinds of genetic alterations, ranging from changes in one DNA base pair to gross changes in chromosome structure or in chromosome number (Hoffman, 1991).

Teratogen: a biological, chemical, or physical agent that interferes with growth and development of an embryo or a fetus, creating growth retardation, and functional or structural defects in the fetus.

(1) See Table 2.7 for further clarification of definition (3). For purposes of setting water standards to protect aquatic life, the "acute" and "chronic" levels of toxicant concentrations may be reached on average only once every three years (U.S. EPA, 1986).

which the metals most strongly affect. This table is broken into two sets—metals that are "characteristically hazardous," as defined by U.S. EPA (see below), and other metals that may be hazardous. The main pathways of exposure to metals are inhalation and ingestion. Ingestion by humans occurs dominantly via eating contaminated plants or animals or by drinking contaminated water. The pathway of exposure can influence which organs are targets for toxic interactions.

Figure 2.3 and Table 2.5 summarize toxic effects of elements on mammals (and presumably on humans). Rare earth elements and actinides are excluded from this summary. Figure 2.3 focuses on carcinogens, teratogens, or embryocides (see Table 2.3 for definitions). Toxicity may result in pathologies that are not related to any of these. Table 2.5 lists "toxic" metals, defined as those that have strong toxic effects aside from (or in addition to) carcinogenicity or reproductive effects. Selection of elements is based on Goyer (1991). Venugopal and Luckey (1978) consider antimony, arsenic, lead, mercury, selenium, tellurium, thallium, and tin to be particularly toxic. When metals that may create toxic side effects (e.g., aluminum, bismuth, gold, lithium, and platinum) are used in the treatment of illnesses, these metals are considered to be special cases. For example, the association of long-term ingestion of lithium with central nervous system disorders is a special case.

The Agency for Toxic Substances and Disease Registry (ATSDR) publishes reports on toxicological profiles for various metals. A variety of information also is available through the ATSDR web site:

(http://atsdr1.atsdr.cdc.gov:8080/atsdrhome.html).

Regulatory response to metal toxicity

Within this chapter, we focus on regulations under the Resource Conservation and Recovery Act (RCRA), the Clean Water Act (CWA), and the Safe Drinking Water Act (SDWA). For an in-depth discussion of these regulations and their impact on mining, refer to Marcus (1997). Under the RCRA legislation (which regulates landfills and land-disposal sites), U.S. EPA distinguishes arsenic, barium, cadmium, chromium, lead, mercury, selenium, and silver as being sufficiently toxic to humans to warrant special regulation as "characteristically hazardous" metals. Based upon toxicity studies, the U.S. EPA set minimum extractable levels for metals in solid wastes for defining characteristically hazardous wastes under RCRA regulation (Table 2.6). The currently approved extraction method, "Toxicity Characteristic Leaching Procedure," or TCLP (U.S. EPA Method 1311), involves leaching of solids by dilute acetic acid for 18 hours. The resulting leachate is used to define materials as hazardous, with the assumption that the test simulates leaching in a mixed organic/metal landfill. Whereas this test is an improvement over simply using total metal content in solid materials, it does not account for other factors affecting geoavailability or, ultimately, bioavailability. Additional leaching methods exist, such as the "Synthetic Precipitation Leaching Procedure" (SPLP; U.S. EPA Method 1312, which involves leaching of solids with a very dilute mixture of sulfuric and nitric acid), but none of these other methods is currently approved for use by U.S. EPA. Under RCRA, the Bevill Amendment temporarily exempts the regulation of mining wastes derived from extraction or beneficiation (referred to as "Bevill Wastes") from regulation under Subtitle C (hazardous wastes). Instead, they are regulated under Subtitle D (solid wastes). This exemption defers the "cradle-to-grave" documentation and handling required under Subtitle C for mining wastes. In 1997, U.S. EPA proposed new restrictions on the Bevill Amendment for mining wastes. Information can be obtained from the internet at the following U.S. EPA sites:

http://earth1.epa.gov/OSWRCRA/hazwaste/data/
http://www.epa.gov/epaoswer/other/mining.htm

The Federal Water Pollution Control Act, along with its amendments, is commonly known as the Clean Water Act (CWA). The stated purpose of the CWA is to "restore and maintain the chemical, physical, and biological integrity of the nation's waters." This legislation includes regulations that set maximum allowable concentrations of toxicants in discharges and receiving waters, and establishes the National Pollutant Discharge Elimination System (NPDES) permit program. (As this paper goes to press, the CWA has not yet been reauthorized. New legislation may change regulations in the future.)

The Safe Drinking Water Act (SDWA; 1974, amended 1977, 1986, and 1996) establishes a federal regulatory system to ensure the safety of public drinking water, but applies only to drinking water facilities of a certain size. Under the SDWA, U.S. EPA must set "at-the-tap" maximum permissible levels for contaminants in water delivered by a public water system. A contaminant is defined in the Act as "any physical, chemical, biological, or radiological substance or matter in water." For each contaminant, U.S. EPA must set a Maximum Contaminant Level Goal (MCLG) and

TABLE 2.4A—Toxicity of "characteristically hazardous" metals (after Goyer, 1991; National Research Council, 1989).

Element	Class(1)	Nutrient(2)	Major forms of absorption(3)	Organs toxicologically affected
Arsenic (As)	H	P	Ingestion Inhalation	Nervous System Liver Vascular Skin, Lungs (c)(4)
Barium (Ba)	H	?	Inhalation Ingestion	Pulmonary Muscular
Cadmium (Cd)	S	No	Ingestion Inhalation	Renal Skeletal Cardiovascular Lungs (c)
Chromium (Cr)	H	Yes	Ingestion (Inhalation)	Renal (Nasal) Lungs (c) Skin
Lead (Pb)	B	?	Inhalation (<0.5 µm size) Ingestion	Nervous System Blood Lungs, Renal (c) Reproductive
Mercury (Hg)	S	No	Inhalation (Ingestion)	Nervous System (Gastrointestinal) Renal
Selenium (Se)	--	Yes	Ingestion (Inhalation)	Muscular Nervous System Skin(5)
Silver (Ag)	S	No	Ingestion	Gastrointestinal Skin

(1) H = hard acid, S = soft acid, B = borderline acid (metal classification after Huheey et al., 1993), -- = insufficient information. See Figure 2.9.
(2) Yes = essential or probable nutrient, P = possible nutrient, ? = noted as a potential nutrient in only one source, No = not an essential nutrient.
(3) Parentheses indicate lower occurrence rate, lower toxicity, or less common route of absorption.
(4) Although U.S. EPA and the World Health Organization consider arsenic to be a well-established carcinogen (Goyer, 1991), association of arsenic with cancer is considered by some authors to be equivocal (Nielsen, 1994; Frost, 1978). Petito and Beck (1990) provide evidence that the threshold for ingested arsenic to cause skin cancer is significantly higher than originally thought.
(5) Selenium tests for carcinogenesis are conflicting. Human epidemiological studies indicate that, in some cases, selenium actually protects against cancer (Goyer, 1991).
(c) Well-established carcinogen in humans or lab animals. Based on varying mixes of laboratory animal studies and human epidemiological studies. Commonly, these are contradictory. Carcinogen designation is based on evidence from either laboratory animal studies or human epidemiological studies.

a Maximum Contaminant Level (MCL). The MCLG is a nonenforceable health goal set solely on the basis of human health effects. The MCL is the enforceable drinking water standard and is set as close to the MCLG as is technologically or economically feasible. Upon authorization, states may adopt the federal MCLs or establish independent ones that are the same or more stringent. Under the SDWA, contaminants are regulated as either primary or secondary drinking water standards. Primary standards regulate contaminants that may cause adverse human health effects whereas secondary standards, which are federally unenforceable, are limited to contaminants that may adversely affect public welfare (for example, contaminants that may affect the odor or appearance of drinking water; see below for associated contaminant limits). U.S. EPA procedures for setting drinking water standards are contained in 56 FR 3526–3597 (Jan. 30, 1991 Federal Register) and in 57 FR 31776–31849 (July 17, 1992 Federal Register). The SDWA drinking water standards are often used to set remedial standards for actions under RCRA and the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA, also known as Superfund).

Risk assessment

The topic of risk assessment for metals is essential to the regulatory process. However, because it is a very broad topic, we do not discuss risk assessment in detail. Beck et al. (1995) provide a comprehensive introduction to health-based risk assessment for metals. They build their discussions around the "red book," "Risk Assessment in the Federal Government: Managing the Process" (NRC, 1983), and on the report "Science and Judgment in Risk Assessment" (NRC, 1994). Davis and Elias (1996) also discuss risk assessment of metals and contrast key features of the U.S. EPA risk assessments for lead and manganese. Fan (1996) describes the process of risk assessment used for setting permissible levels in drinking water. The U.S. EPA report, "A Framework for Ecological Risk Assessment," (U.S. EPA, 1992) develops guidelines and basic principles, and provides definitions of key terms for ecological risk assessment. Bartell et al. (1992), Suter (1993), and Landis and Yu (1995) discuss various aspects of ecological risk assessment.

Risk assessment includes hazard identification, dose-response

TABLE 2.4B—Toxicity of selected “other” metals (after Goyer, 1991; National Research Council, 1989; and Venugopal and Luckey, 1978).

Element	Class(1)	Nutrient(2)	Major forms of absorption(3)	Organs toxicologically affected
Aluminum (Al)	H	No	(Ingestion of large amounts; dialysis or P deficiency)	(Nervous system, bone, gastrointestinal)
Antimony (Sb)	B	No	Ingestion	Gastrointestinal (acute);
			Inhalation	Cardiac and liver (chronic)
Beryllium (Be)	H	?	Inhalation	Lungs, air passages (c)
			Dermal	Skin lesions
			(Ingestion)	(Bone, liver)
Cobalt (Co)	H/B	Yes	Ingestion	Muscle, liver, heart
			Inhalation	Lungs
			Dermal	Allergic on skin
			(Injection)	(c)
Copper (Cu)	S/B	Yes	Ingestion	Liver, bone marrow
			(Dermal-burn treatment)	(Blood-anemia)
Iodine (I)	--	Yes	Ingestion	Thyroid (either excess or deficiency)
Iron (Fe)	H/B	Yes	Ingestion	Liver, pancreas, endocrine system, heart
			Intravenously	
			(Inhalation)	(Lungs)
Lithium (Li)	H	P	Ingestion	Gastrointestinal, central nervous system, renal, cardiovascular, endocrine
Manganese (Mn)	H	Yes	Inhalation	Lungs/respiratory system (acute), central nervous system, liver (chronic)
Molybdenum (Mo)	--	Yes	Ingestion	Renal, adrenal
			(Inhalation)	Bone, mucous membranes
Nickel (Ni)	B	Yes	Inhalation	Lungs (kidneys, liver, brain) (c)
			Dermal	Allergic on skin
Thallium (Tl)	S	No	Ingestion	Gastrointestinal, renal
			Dermal	Nervous system, lungs
			Inhalation	Hair, bone, reproductive
Vanadium (V)	--	Yes	Inhalation	Respiratory
			(Dermal)	Cardiovascular
			(Ingestion)	Central nervous system, gastrointestinal
Zinc (Zn)	B	Yes	(Inhalation)	(Lungs—chills/fever, weakness (acute))

(1)H = hard acid, S = soft acid, B = borderline acid (metal classification after Huheey et al., 1993), -- = insufficient information. See Figure 2.9.

(2)Yes = essential or probable nutrient, P = possible nutrient, ? = noted as a potential nutrient in only one source, No = not an essential nutrient.

(3)Parentheses indicate lower occurrence rate, lower toxicity, or less common route of absorption.

(c) Well-established carcinogen in humans or lab animals. Based on varying mixes of laboratory animal studies and human epidemiological studies. Commonly, these are contradictory. Carcinogen designation is based on evidence from either laboratory animal studies or human epidemiological studies.

assessment, exposure assessment, and risk characterization. NRC (1994) recommends an iterative approach with initial conservative assumptions to protect human health in the risk assessment process. Risk is usually inferred from epidemiological investigations or calculated from models. Ginevan and Splitstone (1997) discuss methods for modeling spatial distribution of risk.

Contaminant levels in water

Tables 2.7A and 2.7B summarize U.S. EPA guidelines for concentrations of a number of metals, sulfate, fluoride, and cyanide for protection of freshwater aquatic life and of human life, respectively. These guidelines are general, and state agencies or U.S. EPA should be contacted for information on specific water-quality criteria. In addition, many states publish standards for pH. (A typical secondary MCL for drinking water pH is 6.5–8.5.) State regulations may vary among states and within states with respect to specific bodies of water and their classifications. For example, the state of Colorado has adopted one-day (not one-hour) standards for “acute” aquatic life criteria and a 30-day average (not 4-hour average) for “chronic” aquatic life criteria (W. Wuerthele, U.S. EPA, personal commun., 1995; refer to Table 2.3 for definitions).

For situations in which humans may ingest water and fish, the “published” column in Table 2.7B shows water-quality criteria for human health published by U.S. EPA in 1980 (U.S. EPA, 1980). U.S. EPA has published a more recent water quality criteria document since this paper entered copy editing (U.S. EPA, 1998). The “updated” column is based upon more recent toxicity information in U.S. EPA’s “Integrated Risk Information System,” (IRIS) database (U.S. EPA, 1993a). This database is constantly changing, based upon new studies on carcinogenicity or other toxicity of chemicals, and revised thresholds for triggering toxicities. These are national guidelines, although states may define other local levels for specific waterway segments. States commonly incorporate these updated numbers in their triennial reviews of regulations based upon the CWA. The best way to decide what regulations currently apply to a particular mine site is to contact the appropriate state agency.

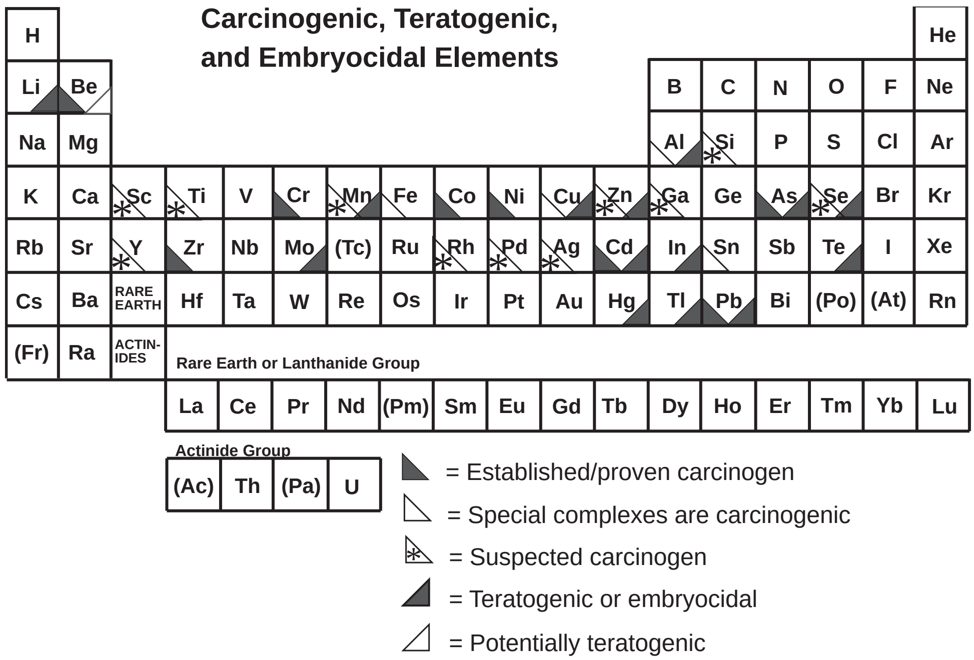

FIGURE 2.3—Periodic table of carcinogenic, teratogenic, and embryocidal elements, based upon epidemiological studies of humans and laboratory studies of humans and mammals. Based upon Luckey and Venugopal (1977), with modifications from Venugopal and Luckey (1978) and Goyer (1991). Lack of notation for rare earth and actinide group elements is due to lack of studies and should not be construed as meaning that these elements are not potentially toxic. This figure does not include toxic effects related to radioactivity.

TABLE 2.5—Summary of potential health-related effects of metals and other selected elements (after Luckey and Venugopal, 1977; Venugopal and Luckey, 1978; Griffith, 1988; National Research Council, 1989; Goyer, 1991; Ensminger et al., 1994; and Nielsen, 1994).

Element	Essential for human health	Toxicity	Carcinogenic	Teratogenic
Aluminum (Al)		S	S	P/E
Antimony (Sb)		t		
Arsenic (As)	P	T	Y	Y/E
Barium (Ba)	?	t		
Beryllium (Be)	?	T	Y(1) (2)	P
Bismuth (Bi)		S		
Boron (B)	P			
Bromine (Br)	?			
Cadmium (Cd)		T	Y(1)	Y/E
Calcium (Ca)	Y			
Chromium (Cr)	Y	T	Y(1) (3)	
Cobalt (Co)	Y	t	Y	
Copper (Cu)	Y	t	S	E
Fluorine (F)	H			
Gallium (Ga)		S	P	
Gold (Au)		S		
Iodine (I)	Y			
Iron (Fe)	Y	t	S	
Lanthanum (La)	?			
Lead (Pb)	?	T	Y	Y/E
Lithium (Li)	P	S		Y/E
Magnesium (Mg)	Y	t		
Manganese (Mn)	Y	t	P	E
Mercury (Hg)		T		Y/E
Molybdenum (Mo)	Y	t		Y
Nickel (Ni)	P	T	Y	
Niobium (Nb)	P			
Palladium (Pd)			P	
Phosphorus (P)	Y			
Platinum (Pt)		S		
Potassium (K)	Y			
Rhenium (Rh)			P	
Selenium (Se)	Y	t	P(4)	Y/E
Silver (Ag)		t	P	
Strontium (Sr)	P			
Sulfur (S)	Y			
Tellurium (Te)		t		Y/E
Thallium (Tl)		t		Y/E
Tin (Sn)	P	t	S(5)	
Titanium (Ti)		t	P	
Vanadium (V)	P	t		
Yttrium (Y)			P	
Zinc (Zn)	Y	t	P	Y/E
Zirconium (Zr)			Y	

Y = proven or established. For nutrients, "Y" is based solely on National Research Council (1989). Cobalt and sulfur are included as "Y" because they are constituents of vitamins or proteins considered to be essential by the National Research Council.
P = possible or suspected, plus probable for nutrients.
H = although fluorine is not essential to health, the National Research Council (1989) considers it to have sufficient value to be included in its USRDA listing.
? = nutrient cited in one source only.
S = special complex or special conditions required.
E = embryocidal.
T = toxic metals with multiple effects (after Goyer, 1991).
t = metals with potential for toxicity (after Goyer, 1991).
(1)Carcinogenic to humans by inhalation only.
(2)Although beryllium has been implicated as a human carcinogen by inhalation, epidemiological studies are conflicting. U.S. EPA considers evidence for carcinogenicity to be sufficient in animals (which includes by injection), but limited in humans (Goyer, 1991).
(3)Cr(VI) is considered to be carcinogenic, whereas Cr(III) is not.
(4)Although laboratory studies of rats indicate carcinogenicity, some human epidemiological studies indicate that selenium can inhibit cancer.
(5)Carcinogenic as organic form only.

TABLE 2.6—Hazardous levels of constituent concentrations in waste extract (Toxicity Characteristic Leaching Procedure, TCLP), as listed in the Resource Conservation and Recovery Act (RCRA) regulations for characteristically hazardous metals. See Table 2.4A for toxicity characteristics. The EPA number refers to regulatory identification numbers; "D" is the designation for characteristically hazardous wastes (U.S. EPA, 1996).

EPA No.	Constituent	Regulatory level (mg/l)
D004	Arsenic	5.0
D005	Barium	100
D006	Cadmium	1.0
D007	Chromium	5.0
D008	Lead	5.0
D009	Mercury	0.20
D010	Selenium	1.0
D011	Silver	5.0

TABLE 2.7A—Water-quality guidelines for metals and cyanide for which water-quality standards or lowest observed effect levels (L.O.E.L.s) have been established for protection of aquatic life.(1)

Constituent	Hardness-Dependent Criteria?(2)	Published Section 304(a) Freshwater Criteria(3) (H=100 mg/l $CaCO_3$) Acute (µg/l)	Chronic (µg/l)	Hardness-based equation for calculation of freshwater aquatic-life criteria(2, 5) (µg/l)
Cyanide (total)		22	5.2	
Aluminum (pH 6.5—9.0 only)		750	87	
Antimony		9000(4)	1600(4)	
Arsenic		360	190	
Arsenic (V)		850(4)	48(4)	
Arsenic (III)		44(4)	40(4)	
Beryllium		130(4)	5.3(4)	
Cadmium	Yes	3.9		e (1.128 [ln (hardness)] - 3.828) (a)
			1.1	e (0.7852 [ln (hardness)] - 3.490) (b)
Chromium (III)	Yes	1700		e (0.8190 [ln (hardness)] + 3.688) (a)
			210	e (0.8190 [ln (hardness)] + 1.561) (b)
Chromium (VI)		16	11	
Copper	Yes	18		e (0.9422 [ln (hardness)] - 1.464) (a)
			12	e (0.8545 [ln (hardness)] - 1.465) (b)
Iron			1000	
Lead	Yes	82		e (1.273 [ln (hardness)] - 1.460) (a)
			3.2	e (1.273 [ln (hardness)] - 4.705) (b)
Mercury		2.4	0.012	
Nickel	Yes	1400		e (0.8460 [ln (hardness)] + 3.3612) (a)
			160	e (0.8460 [ln (hardness)] + 1.1645) (b)
Selenium		20	5	
Silver	Yes	4.1	0.12(4)	e (1.72 [ln (hardness)] - 6.52) (a)
Thallium		1400(4)	40 (4)	
Zinc	Yes	120		e (0.8473 [ln (hardness)] + 0.8604) (a)
			110	e (0.8473 [ln (hardness)] + 0.7614) (b)

(1) Values are based on the Updated Version of EPA Region VIII Clean Water Act Section 304(a) Criteria Chart (U.S. EPA, 1993b). U.S. EPA has published guidelines for a different set of water-quality standards for specific river segments in the following locations: Arkansas, California, District of Columbia, Florida, Kansas, Michigan, New Jersey, Puerto Rico, Rhode Island, and Vermont (U.S. EPA, 1994). The values in this table should be used only as guidelines. Individual states and U.S. EPA should be contacted for updated and local water-quality criteria.

(2) Some freshwater criteria vary with water hardness. There is generally an inverse relationship between hardness and toxicity for a given metal concentration. Hardness is defined as the amount of polyvalent metal ions (primarily Ca^{2+} and Mg^{2+}; U.S. EPA, 1986), and is expressed as mg/l calcium carbonate ($CaCO_3$).

(3) In the case of hardness-dependent criteria, a water hardness (H) of 100 mg/l $CaCO_3$ is used. Unless otherwise noted, "acute" means a 1-hour average and "chronic" means a 4-day average. These definitions of acute and chronic are specifically for aquatic life and differ from those that refer to human life (see Table 2.3; U.S. EPA, 1986; ATSDR, 1992; U.S. EPA, 1993b). Streams are considered to be protective of aquatic life if the criterion is not exceeded more than once in 3 years.

(4) Values represent established L.O.E.L.s, which do not meet sufficient standards to be considered as water-quality criteria for aquatic life. A L.O.E.L. (lowest observed effect level) is the lowest contaminant level at which target aquatic species exhibit negative effects. Although these are not U.S. EPA criteria, they are included as guidelines according to U.S. EPA (1986).

(5) These equations are in the form $e^{(x\ [\ln\ (\text{hardness})]\ \pm\ y)}$ and are used to calculate hardness-dependent freshwater aquatic-life criteria for a given water-hardness value. (a) = 1-hour average, or acute; (b) = 4-day average, or chronic.

TABLE 2.7B—Water-quality criteria for metals, cyanide, sulfate, and fluoride for which water-quality standards and maximum contaminant levels (MCLs) have been established for protection of human life.(1)

	Water + Fish Ingestion(2)		Drinking water
Constituent	Published	Updated	MCLG and MCL (mg/l)(3)
Cyanide (total)	200 µg/l (m)	700 µg/l	0.2 (g); 0.2 (f)
Sulfate			500 (g); 500 (p); 250 (s)
Aluminum			0.05—0.2 (s, l)
Antimony	146 µg/l	14 µg/l (r)	0.006 (g); 0.006 (f)
Arsenic	2 ng/l	18 ng/l	0.05 (d)
Barium	1 mg/l (m)	1 mg/l (m)	2 (g); 2 (f)
Beryllium	3.7 ng/l	7.7 ng/l	0.004 (g); 0.004 (d)
Cadmium	10 µg/l (m); 29 µg/l (tx)	14 µg/l (r)	0.005 (g); 0.005 (f)
Chromium			0.1 (g); 0.1 (f)
Chromium (III)	50 µg/l (m); 170 mg/l (tx)	3.3 mg/l (r)	
Chromium (VI)	50 µg/l (m)	170 µg/l (r)	
Copper	1.0 mg/l (s)	1.3 mg/l	1.3 (g, tt); 1.0 (s)
Fluoride			4 (g); 4 (f); 2 (s)
Iron	0.3 mg/l (m)	0.3 mg/l (m)	0.3 (s)
Lead	50 µg/l (m)	— (r)	0 (g); 0.015 (tt)
Manganese	0.05 mg/l (m)	0.05 mg/l (m)	0.05 (s, l)(4)
Mercury	144 ng/l	140 ng/l	0.002 (g); 0.002 (f)
Nickel	13.4 µg/l	610 µg/l (r)	0.1 (g, rr); 0.1 (f, rr)
Selenium	10 µg/l (m)	170 µg/l (r)	0.05 (g); 0.05 (f)
Silver	50 µg/l (m)	170 µg/l	0.1 (s)
Thallium	13 µg/l	1.7 µg/l	0.0005 (g); 0.002 (f)
Zinc	5 mg/l (s)	9.1 mg/l	5 (s, l)

(1) After U.S. EPA (1993b; 1995). U.S. EPA (1993b) was used to define published and updated values. U.S. EPA (1995) was used to define drinking water MCLGs and MCLs. The values in this table should be used only as guidelines. Individual states and U.S. EPA should be contacted for updated and local water-quality criteria.

(2) These water-quality values apply to situations in which humans may ingest both water and fish. Values are based on the Updated Version of EPA Region VIII Clean Water Act Section 304(a) Criteria Chart (U.S. EPA, 1993b). Human-health criteria for ingestion of water + fish occur in two forms. The "published" criteria are those that have been officially published by U.S. EPA in Clean Water Act Section 304(a) criteria documents. The "updated" values (as of July 1993) are based upon the Integrated Risk Information System (IRIS), which is constantly changing, and which the states use for their triennial updates of water-quality regulations. Access to current versions of IRIS are available by commercial services. (m) = criteria based on drinking water MCL (after U.S. EPA, 1993b), (tx) = the calculated Section 304(a) toxicity-based value, if any, (r) = a more stringent final MCL has been issued by U.S. EPA under the Safe Drinking Water Act, and (s) = secondary criteria based on taste and odor.

(3) These MCLG and MCL values are published under the Safe Drinking Water Act (U.S. EPA, 1995). The MCLs are at various stages of regulatory development. (f) = final, (rr) = being remanded, (l) = listed for regulation as a primary MCL, (d) = draft, under review as a primary MCL, (p) = proposed as a primary MCL, and (s) = secondary MCL. All secondary MCLs are set for look, taste, or odor, and are final. In addition to having secondary MCLs, aluminum, manganese, and zinc are listed for regulation as primary MCLs. (g) = MCLG; (tt) = "treatment technique." Since in-house plumbing and soil characteristics can affect copper and lead contents of water, "action levels" (shown for copper and lead) are set under the treatment technique guideline. For example, if drinking water exceeds these action levels in a particular area, the water provider must initiate a variety of technical improvements to comply with each action level. These include corrosion controls and education of local residents. If the water provider implements all required technical improvements and still does not achieve action levels, it will not be sued to force compliance. For MCLs, however, the provider must be in compliance at the end user.

(4) A primary MCL for manganese is being considered at 0.8 mg/l (H. Fliniau, U.S. EPA, personal commun., 1997).

Metals for which MCL criteria are listed exist mainly for protection of human health (U.S. EPA, 1995). A few metals—iron and manganese—have levels that are mainly aesthetic to minimize taste, odor, or color problems in drinking water. [U.S. EPA is considering regulating manganese in the future; at continuous and long-term exposure to high levels it may adversely affect the human brain (R. Benson, U.S. EPA, personal commun., 1996)]. Zinc and copper are considered to be pollutants in water because of their high toxicity to aquatic life, despite their relatively low toxicity to humans.

ABUNDANCES OF ELEMENTS

Introduction

This section provides tables and figures that present generalizations about the abundances of elements in earth materials, water, and vegetation. This section can stand alone and is not essential to understanding the remainder of this chapter. The purpose of this section is to assemble element-abundance data in one place, with minimal explanation. These data are intended to serve only as a rough guide when evaluating the concentrations of chemical elements in the environment. Many of these types of data are still evolving as analytical-chemistry techniques are developed and refined. A standardized world geochemical atlas and global geochemical database are being prepared by the International Geological Correlation Program (IGCP, 1995; http://www.unesco.org/general/eng/programmes/science/programme/environ/igcp/index.html). The Geochemical Earth Reference Model (GERM) initiative is establishing a consensus on chemical characterization of the Earth (http://www-ep.es.llnl.gov/germ/germ-home.html).

Crustal abundance

There are numerous compilations of estimates of the average abundance of elements within the Earth's crust (see Rickwood, 1983). These compilations tend to vary due to the different approaches, methods, and assumptions used to derive estimates of crustal abundance. Our knowledge of the crustal abundance of most rock types (and hence their associated elements) is inadequate because the Earth's crust is so variable and so poorly exposed.

Table 2.8 lists approximate (order of magnitude) consensus values of various published estimates of crustal abundance and the range of these estimates (Rickwood, 1983). Clarke values, which refer to the average abundance of a particular element in the lithosphere, are also given in Table 2.8 (Fortescue, 1992); Clarke values are synonymous with crustal abundances. The "Clarke of Concentration" (KK), an expression for the relative abundance of an element in a given sample or set of samples, is the abundance of an element in the sample(s) divided by its Clarke value. The KK is used to delineate materials that are enriched or depleted in an element relative to average values.

Table 2.8 also includes the abundance of minor and trace elements in two different rock types, basalt and granite (Levinson, 1980). These data illustrate how the abundances of most minor and trace elements vary from mafic to granitic rocks, which in turn reflect magmatic differentiation. Figure 2.4 illustrates the range of minor and trace elements in rocks and the relationship between typical abundances (Rose et al., 1979). The trace-element content of specific rock types is the major control on background levels in soils, sediments, and waters.

Soil

Soils form from chemically and mechanically weathering rocks under the influence of climatic and topographic controls, microbiological processes, the abundance of an element in the parent rock, the nature and duration of the weathering processes operating on the parent rock, gains and losses by physical processes (e.g., wind transport), the solubility of the primary and secondary mineral phases present in the parent rock and in the soil (geoavailability), the type of vegetation, and the type and amount of organic matter in the soil. Solubility and kinetic reactions, and pore-water composition control the ability of solid phases to replenish an element as it is depleted from the soil's interstitial water. These factors are all related to geoavailability (see Table 2.1).

Soils normally contain different layers, which are referred to as soil horizons. These horizons commonly have very different properties and elemental distributions, and may range from a few millimeters to meters in thickness. When comparing the composition of different soils, it is important to be consistent in the soil horizon being considered.

Table 2.9 lists average concentrations and ranges of elements in soils compiled by different authors. Soil samples from the western and eastern United States (Shacklette and Boerngen, 1984) were collected from a depth of 20 cm. This depth was chosen because it is a depth below the plow zone that would include parts of the zone of illuviation (i.e., accumulation of dissolved or suspended soil materials as a result of transport) in most well-developed zonal soils (Shacklette and Boerngen, 1984). The selected average of Lindsay (1979) is an arbitrary reference level for elements in soils. Figure 2.5 compares minor and trace-element concentrations in topsoils to their abundance in the lithosphere (Kabata-Pendias and Pendias, 1992).

Vegetation

The ability of plants to absorb minor and trace elements is highly variable depending on the species, soil conditions, climate, and season. However, on average, this ability exhibits some general trends for particular elements, as illustrated on Figure 2.6 (Kabata-Pendias and Pendias, 1992). Table 2.10 lists concentration ranges of elements in plant leaf tissue as a function of typically measured range, deficiency, and toxicity. These ranges are only approximations. It is important to note that the typical range of concentrations of some elements in plant leaf tissue can be close to or even overlapping with excessive or toxic concentrations (e.g., boron, copper, and zinc). Markert (1994) has published the trace element content of a "reference plant" which represents the trace element content of plants in general (Table 2.10).

Dissolved and suspended riverine materials

Factors affecting the chemical composition of most surface waters are climate (especially intensity and frequency of rainfall), lithology, geoavailability of elements, vegetation, topography, biological activity, and time. It is difficult to predict which of these factors will be most important for a given situation. However, the composition of water is most often controlled by interactions with earth materials through which the water flows. For surface waters, these interactions generally take place in the soil zone. The composition of uncontaminated surface waters varies by several orders of magnitude depending on environmental conditions (Meybeck and Helmer, 1989), analytical techniques, and possible contamination.

Concentrations of trace elements in surface waters are still a matter of debate and uncertainty because water samples can be easily contaminated during collection or analysis, analytical detection limits are sometimes greater than the natural concentrations and few pristine surface waters have been analyzed cleanly for trace elements (Martin et al., 1980). Table 2.11 lists concentrations of dissolved constituents in surface waters compiled by various authors. The values listed in this table are meant only as a rough guide for element concentrations in surface water.

As a first approximation, the composition of suspended matter in rivers may be assumed to be that of proximal surficial rocks in the drainage basin (Whitfield and Turner, 1979; Martin and Whitfield, 1983). However, the degree of chemical weathering and individual element behavior will affect the ultimate element concentrations in suspended matter.

FACTORS AFFECTING METAL MOBILITY AND DISPERSIVITY

Chemical and physical properties of elements

Elements have certain inherent chemical and physical properties that influence their behavior in the environment (see Nordstrom, 1999). The chemistry of the elements is determined by how atoms exchange, interchange, and share the electrons that occupy their "outermost orbits" (the valence electrons). The term "electronegativity" refers to the relative tendency of an atom to acquire negative charge. Listings of electronegativities are common in most inorganic or physical chemistry textbooks (e.g.,

TABLE 2.8—Estimates of the crustal abundance of selected chemical elements by various authors, and the abundance of minor and trace elements in two different types of rocks. Data are as ppm; significant figures reflect those reported by the source.

	Estimates of crustal abundance (ppm)			Abundance in rocks (ppm)	
Element	Approximate consensus(1)	Consensus range(2)	Clarke value(3)	Basalt(4)	Granite(4)
Aluminum (Al)	80,000	74,500–88,649	83,600		
Antimony (Sb)		0.15–1	0.20	0.2	0.2
Arsenic (As)	2	1.7–5	1.80	2	1.5
Barium (Ba)	430	179–1070	390	250	600
Beryllium (Be)	3	1.3–10	2.00	0.5	5
Bismuth (Bi)	0.2	0.0029–0.2	0.0082(3)	0.15	0.1
Boron (B)	10	3–50	9.00	5	15
Bromine (Br)	3	0.26–10	2.50	3.6	2.9
Cadmium (Cd)	0.18	0.1–5	0.16	0.2	0.2
Calcium (Ca)	30,000	16,438–62,894	46,600		
Carbon (C)		200–4902	180		
Cerium (Ce)	45	29–96	66.4	35	46
Cesium (Cs)	3	1–10	2.60	1	5
Chlorine (Cl)	500(?)	100–2000	126	60	165
Chromium (Cr)	200	70–330	122	200	4
Cobalt (Co)	25	12–100	29.0	50	1
Copper (Cu)	60(?)	14–100	68.0	100	10
Dysprosium (Dy)	4.5	3–7.5	5.00	3	0.5
Europium (Eu)	1.2	0.2–1.4	2.14	1.27	
Fluorine (F)	500	270–800	544	400	735
Gadolinium (Gd)	7	5–10	6.14	4.7	2
Gallium (Ga)	17	1–19	19.0	12	18
Germanium (Ge)	15(?)	1.3–7	1.50	1.5	1.5
Gold (Au)	0.004	0.001–0.005	0.0040	0.004	0.004
Indium (In)	0.1	0.05–0.25	0.24	0.1	0.1
Iodine (I)	0.5	0.05–10	0.46	0.5	0.5
Iridium (Ir)	0.001	0.001–0.01	0.000002		
Iron (Fe)	50,000	30,888–64,668	62,200		
Lanthanum (La)		6.5–100	34.6	10.5	25
Lead (Pb)	16	12–20	13.0	5	20
Lithium (Li)	30	18–65	18.0	10	30
Lutetium (Lu)	0.9	0.27–1.7	0.54	0.2	0.01
Magnesium (Mg)	21,000	10,191–33,770	27,640		
Manganese (Mn)	900	155–1549	1,060	2200	500
Mercury (Hg)	0.08	0.03–0.5	0.086	0.08	0.08
Molybdenum (Mo)	2	1–15	1.20	1	2
Neodymium (Nd)	25	17–37	39.6	17.8	18
Nickel (Ni)	80	23–200	99.0	150	0.5
Niobium (Nb)	20	0.32–24	20.0	20	20
Nitrogen (N)	20(?)	15–400	19.0		
Oxygen (O)	470,000	452,341–495,200	456,000		
Palladium (Pd)	0.01	0.0084–0.05	0.015	0.02	0.002
Phosphorus (P)	1000	480–1309	1,120		
Platinum (Pt)	0.005	0.005–0.2	0.0005	0.02	0.008
Potassium (K)	26,000	15,773–32,625	18,400		
Rhenium (Re)	0.001	0.00042–0.001	0.0007	0.0005	0.0005
Rubidium (Rb)	120	78–310	78.0	30	150
Samarium (Sm)	7	6.5–8	7.02	4.2	3
Scandium (Sc)		5–22	25.0	38	5
Selenium (Se)	0.09	0.05–0.8	0.050	0.05	0.05
Silicon (Si)	270,000	257,500–315,896	273,000		
Silver (Ag)	0.07	0.02–0.1	0.080	0.1	0.04
Sodium (Na)	24,000	15,208–28,500	22,700		
Strontium (Sr)	350	150–480	384	465	285
Sulfur (S)	500	260–1200	340		
Tantalum (Ta)	2	0.24–3.4	1.70	0.5	3.5
Tellurium (Te)		0.00036–0.01	0.0040	0.001	0.001
Thallium (Tl)	1	0.1–3	0.72	0.1	0.75
Thorium (Th)	10	5.8–20	8.10	2.2	17
Tin (Sn)	2.5	2–80	2.10	1	3
Titanium (Ti)	5000	2458–9592	6320	9000	2300

TABLE 2.8—Continued

	Estimates of crustal abundance (ppm)			Abundance in rocks (ppm)	
Element	Approximate consensus[(1)]	Consensus range[(2)]	Clarke value[(3)]	Basalt[(4)]	Granite[(4)]
Tungsten (W)	1	0.4–70	1.20	1	2
Uranium (U)	3	1.7–80	2.30	0.6	4.8
Vanadium (V)	150	53–200	136	250	20
Ytterbium (Yb)	3	0.33–8	3.10	1.11	0.06
Yttrium (Y)	30	19–50	31.0	25	40
Zinc (Zn)	70	40–200	76.0	100	40
Zirconium (Zr)	160	130–400	162	150	180

(1)Data are from Rickwood (1983, table A-II) and represent an approximate consensus (within an order of magnitude) of published estimates of crustal abundance.
(2)Data are from Rickwood (1983, table A-II) and give the range of the published estimates of crustal abundance used to compile the approximate consensus values in the previous column.
(3)Data are from Fortescue (1992, table 4). According to the author, the value for Bi appears to be too low.
(4)Data are from Levinson (1980, table 2-1) for two different types of rocks.

Huheey et al., 1993). Elements that have low electronegativity, such as metals, are relatively easily ionized and tend to combine with non-metallic elements of high electronegativity. Hence, electronegativity is indicative of the types of compounds and the types of chemical bonds that a given element will form.

The oxidation state (also referred to as oxidation number) represents the charge that an atom "appears" to have when electrons are counted. Oxidation states are used to track electrons in oxidation-reduction reactions. Ionic radii generally decrease with increasing oxidation state. Also, for a given element, the preferred geometry varies with different oxidation states. For example, the electronic structure of Co^{2+} is such that tetrahedral or octahedral coordination is energetically favored; in contrast, trigonal bipyramidal coordination is most stable for Co^+ (Cotton and Wilkinson, 1988). Finally, elements with variable oxidation states, such as iron and copper, can take part in oxidation-reductions reactions. Consequently, oxidation state can influence binding sites and chemical reactions for a given element.

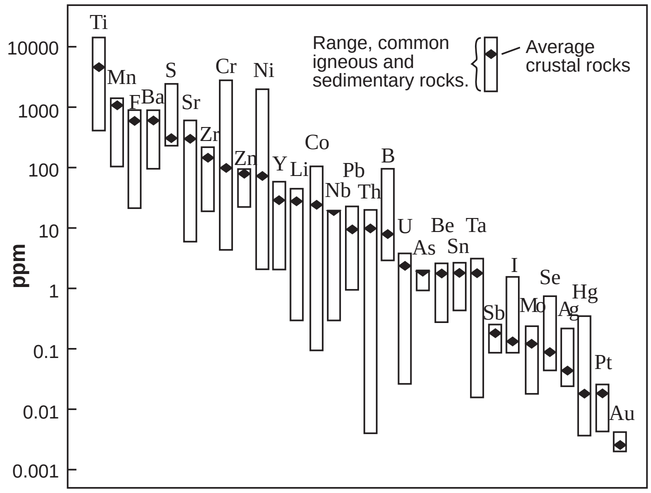

FIGURE 2.4—Average concentrations and ranges of trace elements in rocks. After Rose et al. (1979).

The size of an ion primarily depends on its oxidation state. The ionic radius of an element is important in determining if it can take part in particular biochemical reactions. Also, elements with similar ionic radii and charge can sometimes substitute for one another. For example, Cd^{2+} can substitute for Ca^{2+} in many geochemical and biological systems.

Ionic potential (the ratio of oxidation number to ionic radius) of elements has been related to their mobility (see Rose et al., 1979). Figure 2.7 shows the mobility of various elements as a function of ionic potential. Elements with low ionic potential are generally mobile in the aquatic environment as simple cations (e.g., Na^+, Ca^{2+}) and elements with high ionic potential are generally mobile as oxyanions (i.e., elements that combine with oxygen to form an anionic species in aqueous systems; e.g., SO_4^{2-}, MoO_4^{2-}). Elements with high ionic potential tend to form covalent bonds rather than ionic bonds. Elements with intermediate ionic potential have a tendency to strongly sorb or hydrolyze and exhibit low solubility; therefore, these elements are fairly immobile (Rose et al., 1979). The concept of ionic potential is useful in explaining how elements with apparently different chemical properties behave similarly during migration in the environment.

Classification systems

Goldschmidt's geochemical classification of the elements

Goldschmidt (1954) studied the distribution of elements in the Earth, meteorites, and smelter products. He grouped the elements into those that tend to occur with native iron and which are probably concentrated in the Earth's core (siderophile elements), those concentrated in sulfides and characteristic of sulfide ore deposits (chalcophile elements), those that generally occur with silica (lithophile elements), and those that exist in gaseous form (atmophile elements). Figure 2.8 shows Goldschmidt's groupings of the elements in the context of the periodic table. Elements of each group generally exhibit similar geologic behavior. However, some elements have characteristics common to two groups. Although rough, the terminology of Goldschmidt's classification system is still used, and this system has provided the foundation for other more recent geochemical classification systems (e.g., Beus and Grigorian, 1977).

TABLE 2.9—Means and ranges of elemental concentrations in soils. Data are as ppm; significant figures reflect those reported by the source.

	Western United States(1)		Eastern United States(2)		Lindsay (1979)
Element	Mean(3)	Range(4)	Mean(3)	Range(4)	Average(5)
Aluminum (Al)	58,000	5,000–>100,000	33,000	7,000–>100,000	71,000
Antimony (Sb)	0.47	<1–2.6	0.52	<1–8.8	
Arsenic (As)	5.5	<0.10–97	4.8	<0.1–73	5
Barium (Ba)	580	70–5,000	290	10–1,500	430
Beryllium (Be)	0.68	<1–15	0.55	<1–7	6
Boron (B)	23	<20–300	31	<20–150	10
Bromine (Br)	0.52	<0.5–11	0.62	<0.5–5.3	5
Cadmium (Cd)					0.06
Calcium (Ca)	18,000	600–320,000	3,400	100–280,000	13,700
Carbon (C)	17,000	1,600–100,000	15,000	600–370,000	20,000
Cerium (Ce)	65	<150–300	63	<150–300	
Cesium (Cs)					6
Chlorine (Cl)					100
Chromium (Cr)	41	3–2,000	33	1–1,000	100
Cobalt (Co)	7.1	<3–50	5.9	<0.3–70	8
Copper (Cu)	21	2–300	13	<1–700	30
Fluorine (F)	280	<10–1,900	130	<10–3,700	200
Gallium (Ga)	16	<5–70	9.3	<5–70	14
Germanium (Ge)	1.2	0.58–2.5	1.1	<0.1–2.0	1
Iodine (I)	0.79	<0.5–9.6	0.68	<0.5–7.0	5
Iron (Fe)	21,000	1,000–>100,000	14,000	100–>100,000	38,000
Lanthanum (La)	30	<30–200	29	<30–200	30
Lead (Pb)	17	<10–700	14	<10–300	10
Lithium (Li)	22	5–130	17	<5–140	20
Magnesium (Mg)	7,400	300–>100,000	2,100	50–50,000	5,000
Manganese (Mn)	380	30–5,000	260	<2–7,000	600
Mercury (Hg)	0.046	<0.01–4.6	0.081	0.01–3.4	0.03
Molybdenum (Mo)	0.85	<3–7	0.32	<3–15	2
Neodymium (Nd)	36	<70–300	46	<70–300	
Nickel (Ni)	15	<5–700	11	<5–700	40
Niobium (Nb)	8.7	<10–100	10	<10–50	
Nitrogen (N)					1,400
Oxygen (O)					490,000
Phosphorus (P)	320	40–4,500	200	<20–6,800	600
Potassium (K)	18,000	1,900–63,000	12,000	50–37,000	8,300
Rubidium (Rb)	69	<20–210	43	<20–160	10
Scandium (Sc)	8.2	<5–50	6.5	<5–30	7
Selenium (Se)	0.23	<0.1–4.3	0.30	<0.1–3.9	0.3
Silicon (Si)	300,000	150,000–440,000	340,000	17,000–450,000	320,000
Silver (Ag)					0.05
Sodium (Na)	9,700	500–100,000	2,500	<500–50,000	6,300
Strontium (Sr)	200	10–3,000	53	<5–700	200
Sulfur (S)	1,300	<800–48,000	1,000	<800–3,100	700
Thorium (Th)	9.1	2.4–31	7.7	2.2–23	
Tin (Sn)	0.90	<0.1–7.4	0.86	<0.1–10	10
Titanium (Ti)	2,200	500–20,000	2,800	70–15,000	4,000
Uranium (U)	2.5	0.68–7.9	2.1	0.29–11	
Vanadium (V)	70	7–500	43	<7–300	100
Ytterbium (Yb)	2.6	<1–20	2.6	<1–50	
Yttrium (Y)	22	<10–150	20	<10–200	50
Zinc (Zn)	55	10–2,100	40	<5–2,900	50
Zirconium (Zr)	160	<20–1,500	220	<20–2,000	300

(1) Values observed in the western United States, west of the 96th meridian. Samples were collected at a depth of approximately 20 cm. Data are from Shacklette and Boerngen (1984, table 2).

(2) Values observed in the eastern United States, east of the 96th meridian. Samples were collected at a depth of approximately 20 cm. Data are from Shacklette and Boerngen (1984, table 2).

(3) Means are geometric means except for K and Si, which are arithmetic means.

(4) Ranges are those observed from the study. Data are from Shacklette and Boerngen (1984, table 2).

(5) Selected average for soils from Lindsay (1979, table 1.1; no information on depth or type of average).

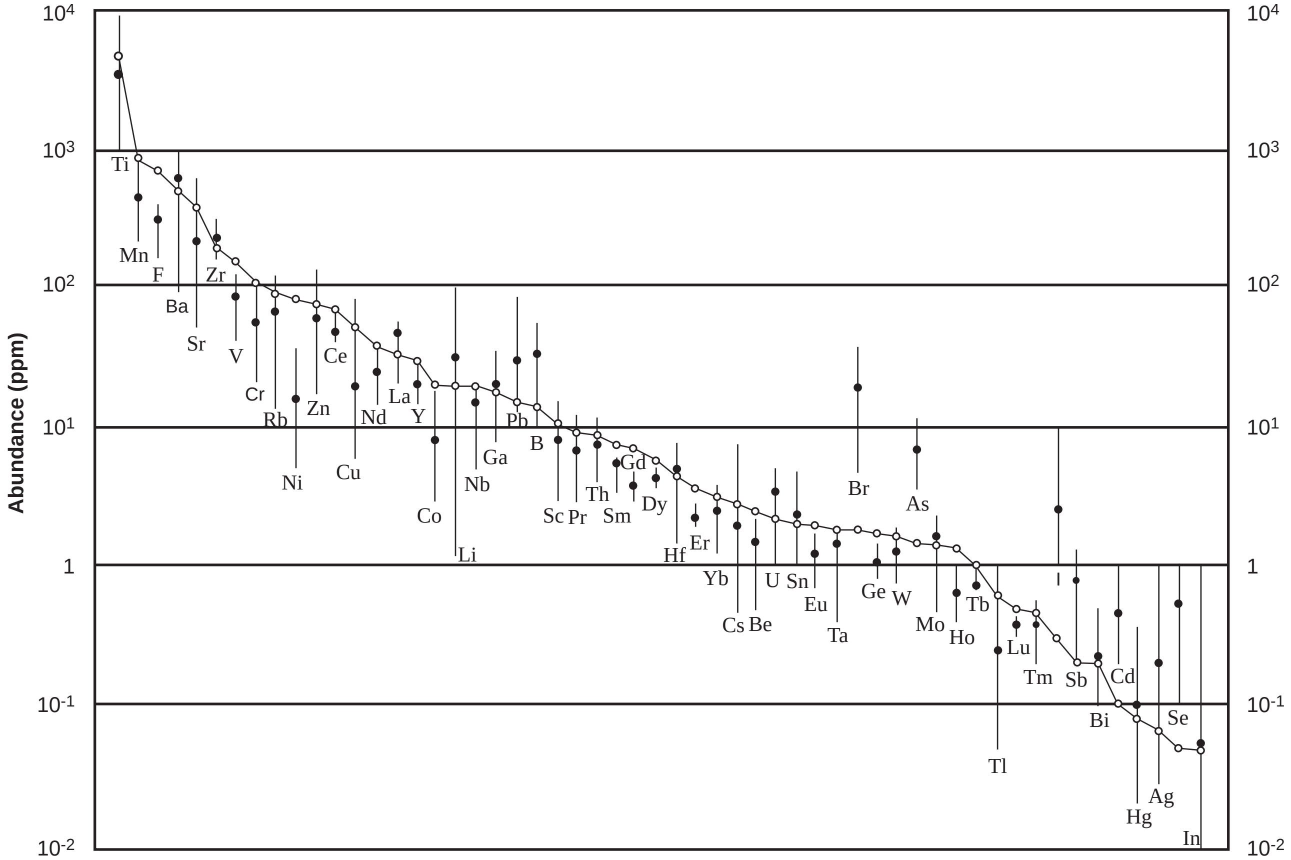

FIGURE 2.5—Abundance of trace elements in soils compared to their abundance in the lithosphere. Open circles are the mean content in the lithosphere. Filled circles are the mean content in topsoils and vertical lines indicate the range of values commonly found in topsoils. After Kabata-Pendias and Pendias (1992).

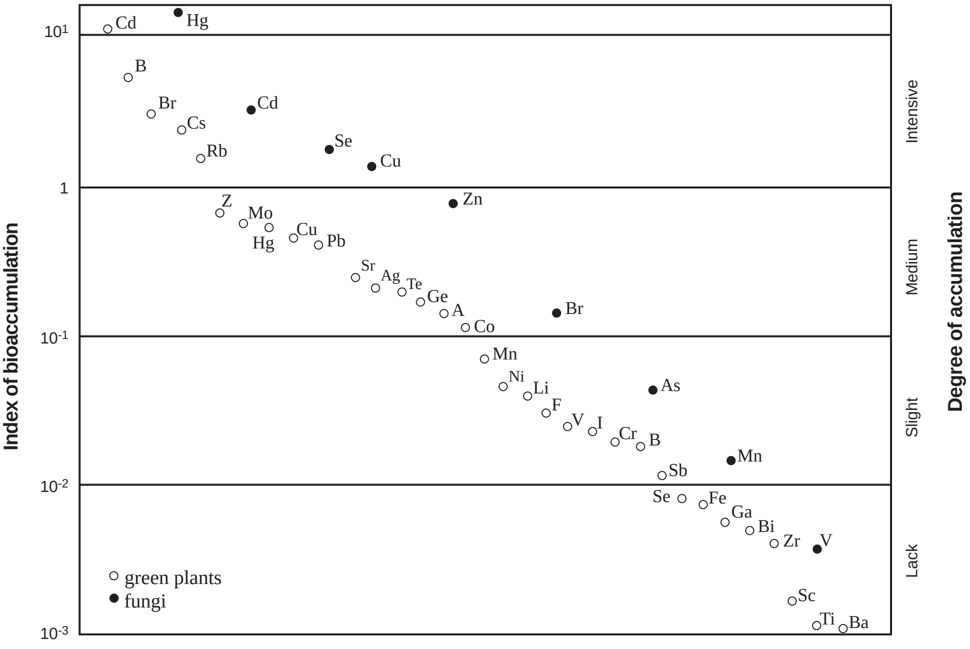

FIGURE 2.6—Generalized bioaccumulation of elements by plants from soils. Bioaccumulation by individual plants is highly variable and depends upon plant species, soil, climate, etc. The index of bioaccumulation is the ratio of the element concentration in plants to the concentration in soils. After Kabata-Pendias and Pendias (1992).

TABLE 2.10—Generalized concentration ranges of chemical elements in mature plant leaf tissue (as ppm on a dry-weight basis). Sensitive or highly tolerant species are not included. Significant figures reflect those reported by the source.

Element	Typical range[(1)]	Deficient[(1)]	Excessive or toxic[(1)]	Reference plant[(2)]
Antimony (Sb)	7–50		150	0.1
Arsenic (As)	1–1.7		5–20	0.1
Barium (Ba)			500	40
Beryllium (Be)	<1–7		10–50	0.001
Boron (B)	10–200	5–30	50–200	40
Cadmium (Cd)	0.05–0.2		5–30	0.05
Chromium (Cr)	0.1–0.5		5–30	1.5
Cobalt (Co)	0.02–1		15–50	0.2
Copper (Cu)	5–30	2–5	20–100	10
Fluorine (F)	5–30		50–500	2.0
Lead (Pb)	5–10		30–300	1.0
Lithium (Li)	3		5–50	
Manganese (Mn)	20–300	15–25	300–500	200
Mercury (Hg)			1–3	0.1
Molybdenum (Mo)	0.2–1	0.1–0.3	10–50	0.5
Nickel (Ni)	0.1–5		10–100	1.5
Selenium (Se)	0.001–2		5–30	0.02
Silver (Ag)	0.5		5–10	0.2
Thallium (Tl)			20	0.05
Tin (Sn)			60	0.2
Titanium (Ti)	0.5–2.0	0.2–0.5	50–200	5.0
Vanadium (V)	0.2–1.5		5–10	0.5
Zinc (Zn)	27–150	10–20	100–400	50
Zirconium (Zr)	0.5–2.0	0.2–0.5	15	

(1)Data are from Kabata-Pendias and Pendias (1992) with revisions by Pais and Jones (1997).

(2)Data are from Markert (1994). Represents the trace element content of plants in general.

Classifications of metals

Metals can be classified into groups based on their capacity for binding to different anions. Several classification systems have developed through the years (e.g., Whitfield and Turner, 1983), but the foundation is often built upon the empirical system of Ahrland et al. (1958). They divided metal ions into Classes A and B, depending on whether the metal ions formed their most stable complexes with ligands of the first row of groups V, VI, or VII of the periodic table (i.e., nitrogen, oxygen, and fluorine, respectively), or with heavier lower-row ligands of those groups (i.e., phosphorus, sulfur, and iodine). Stable complexes are formed depending on the number of valence electrons of the metal ion.

Class A metal cations preferentially form aqueous complexes with fluoride and with ligands having oxygen as the electron donor (e.g., carboxyl groups (COOH) and PO_4^{3-}). Water is strongly attracted to these metals, and no sulfides (complexes or precipitates) are formed by these ions in aqueous solution. Class A metals tend to form relatively insoluble precipitates with OH^-, CO_3^{2-}, and PO_4^{3-} (Stumm and Morgan, 1996). The stability of a Class A metal cation complex with a given ligand generally increases with an increase in charge on the metal ion, and ions with the smallest radii usually form the most stable complexes.

Class B metal cations form complexes preferentially with ligands containing iodine, sulfur, or nitrogen as donor atoms. These metal cations may bind ammonia more strongly than water, and CN^- in preference to OH^-. Class B metal cations form insoluble sulfides and soluble complexes with S^{2-} and HS^- (Stumm and Morgan, 1996). It is difficult to generalize about stability sequences for complexes in this class.

Pearson (1963, 1968a, 1968b) introduced the terms "hard" and "soft" acid and base to describe Class A and B metals and ligands. A "hard acid" is a Class A metal ion, a "soft acid" is a Class B metal ion, a "hard base" is a Class A ligand, and a "soft base" is a Class B ligand. Hard acids tend to bind to hard bases, and soft acids tend to bind to soft bases. The terms "hard" and "soft" are relative, and there are borderline cases between hard and soft for both acids and bases. Also, within each grouping, some acids are harder or softer than others and will behave accordingly. Figure 2.9 shows the periodic table with acids classified by the hard-soft-acid-base (HSAB) system according to Huheey et al. (1993); Table 2.12 lists the bases by this classification. Some of these classifications are mixed due to multiple common oxidation states of some elements. Generalizations about the speciation, behavior, and mobility of elements in aqueous systems can be made based on this type of classification system.

Transition-metal cations have a reasonably well-established rule for the sequence of complex stability based on empirical observation—the Irving-Williams order. According to this rule, the stability of complexes follows the order:

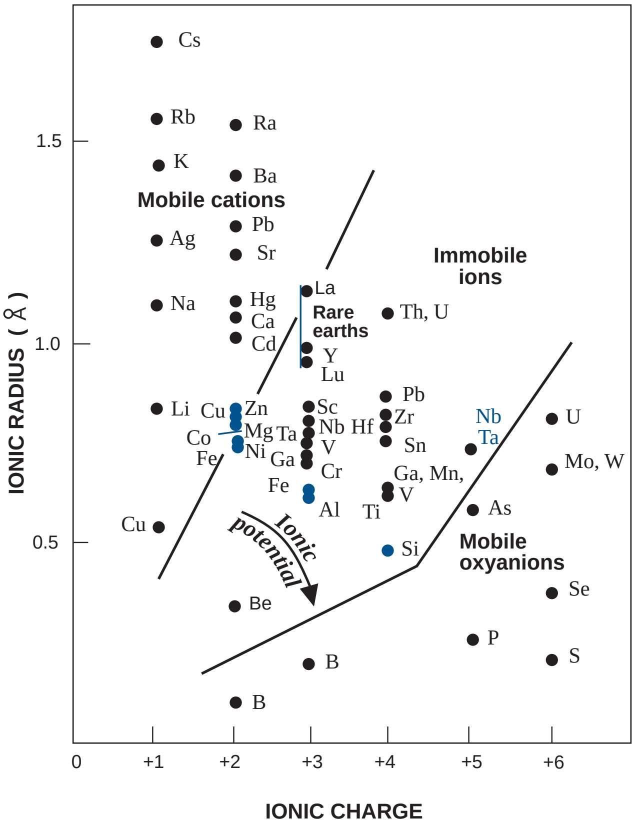

FIGURE 2.7—Mobility of chemical elements in the surficial environment as a function of ionic potential. After Rose et al. (1979).

TABLE 2.11—Summary of the average elemental composition of dissolved and suspended matter in surface water from a variety of sources and various authors.

	Martin and Whitfield (1983)		Meybeck (1988)	Hem (1985)
Element	Dissolved(1) (µg/l)	Suspended(1) (µg/g)	Dissolved(2) (µg/l)	Dissolved(3) (µg/l)
Aluminum (Al)	50	94,000	40 ± 20	
Antimony (Sb)	1	2.5		0.1–1s
Arsenic (As)	1.7	5	1 ± 0.5	0.1–1s
Barium (Ba)	60	600		10s
Beryllium (Be)				0.1s
Boron (B)	18	70	30 ± 20	
Bromine (Br)	20	5		
Cadmium (Cd)	0.02	(1)		0.1–1s
Calcium (Ca)	13,300	21,500		
Cerium (Ce)	0.08	95		
Cesium (Cs)	0.035	6	0.05 ± 0.03	
Chromium (Cr)	1	100	0.8 ± 0.3	0.1–1s
Cobalt (Co)	0.2	20	0.1 ± 0.05	0.1s
Copper (Cu)	1.5	100	2 ± 1	1–10s
Erbium (Er)	0.004	(3)		
Europium (Eu)	0.001	1.5		
Fluorine (F)			100 ± 20	
Gadolinium (Gd)	0.008	(5)		
Gallium (Ga)	0.09	25		
Gold (Au)	0.002	0.05		
Hafnium (Hf)	0.01	6		
Holmium (Ho)	0.001	(1)		
Iron (Fe)	40	48,000	50 ± 30	
Lanthanum (La)	0.05	45		
Lead (Pb)	0.1	100		0.1–1s
Lithium (Li)	12	25		
Lutetium (Lu)	0.001	0.5		
Magnesium (Mg)	3,100	11,800		
Manganese (Mn)	8.2	1,050	10 ± 5	
Mercury (Hg)				0.1s
Molybdenum (Mo)	0.5	3	0.8 ± 0.4	0.1–1s
Neodymium (Nd)	0.04	35		
Nickel (Ni)	0.5	90	0.4 ± 0.3	0.1–1s
Phosphorus (P)	115	1,150		
Potassium (K)	1,500	20,000		
Praseodymium (Pr)	0.007	(8)		
Rubidium (Rb)	1.5	100		
Samarium (Sm)	0.008	7		
Scandium (Sc)	0.004	18		
Selenium (Se)				0.1s
Silicon (Si)	5,000	285,000		
Silver (Ag)	0.3	0.07	0.4 ± 0.2	0.1s
Sodium (Na)	5,300	7,100		
Strontium (Sr)	60	150		
Tantalum (Ta)	<0.002	1.25		
Terbium (Tb)	0.001	1.0		
Thorium (Th)	0.1	14		0.01–0.1s
Thulium (Tm)	0.001	(0.4)		
Titanium (Ti)	10	5,600		
Uranium (U)	0.24	3	0.26	0.1–1s
Vanadium (V)	1	170		1s
Ytterbium (Yb)	0.004	3.5		
Yttrium (Y)		30		
Zinc (Zn)	30	250	10 ± 5	1–10s

(1) Data are from Martin and Whitfield (1983, Table 4). Values are based on analytical results from world rivers.
(2) Data are from Meybeck (1988, p. 262). Ranges are based on more than ten rivers and represent an estimate of world averages.
(3) Data are from Hem (1985). Values are based on a variety of literature citations for element concentrations in a variety of water sources, including ground water.

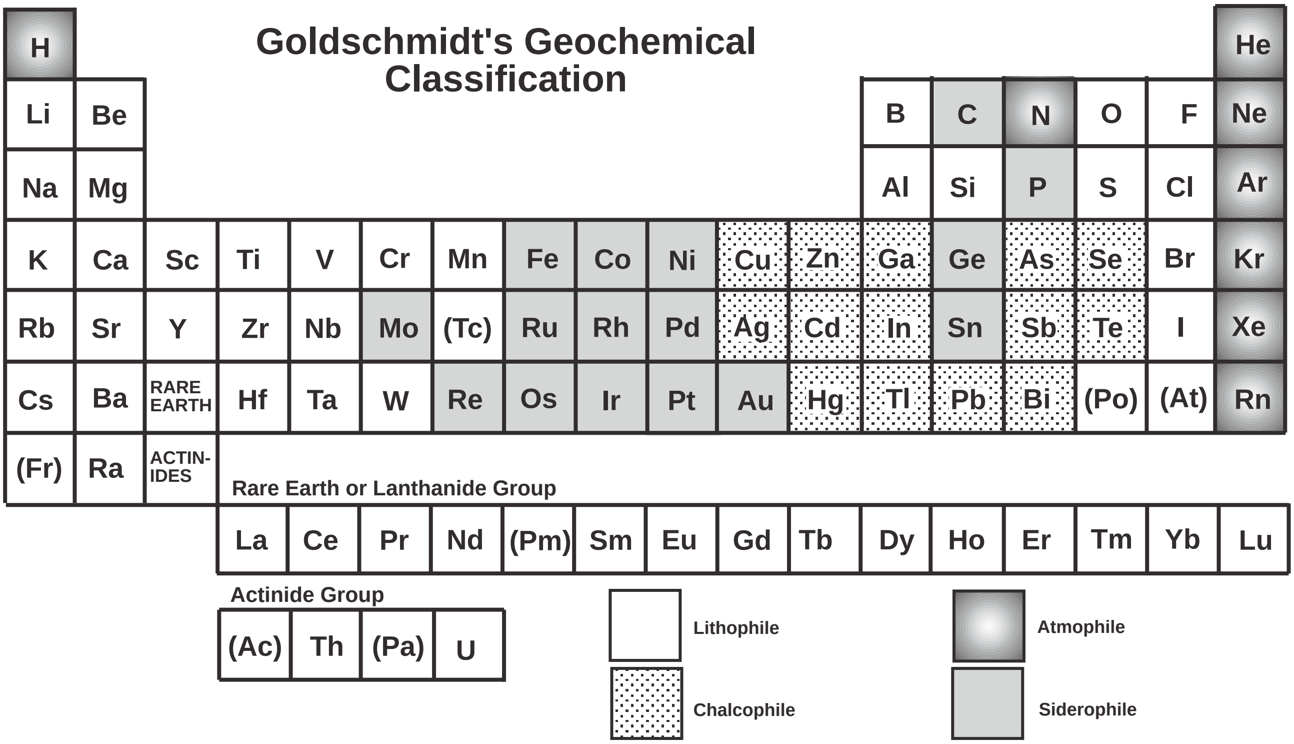

FIGURE 2.8—Periodic table showing Goldschmidt's geochemical classification of the elements. Siderophilic elements occur with native iron and are likely concentrated in the Earth's core, chalcophilic elements are concentrated in sulfides, lithophilic elements commonly occur with silica, and atmophilic elements exist as gases. After Levinson (1980).

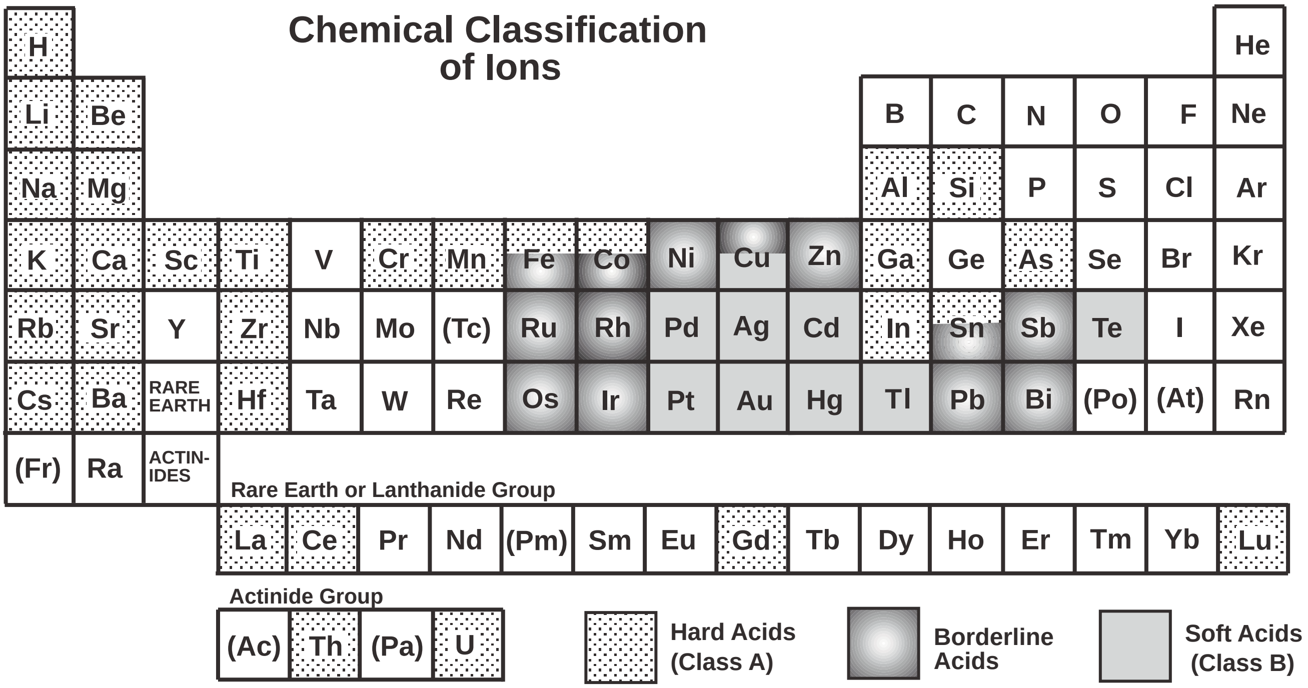

FIGURE 2.9—Periodic table showing the chemical classification of metal ions. Lack of shading or pattern is due to lack of information for that element or to its classification as a base. Information is from Huheey et al. (1993, table 9.7). Hybrid classifications are due to different valence states.

$$Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$$

This sequence is the same sequence as the elements are located in the periodic table. Note that copper forms the most stable complexes with ligands in this series of metals.

TABLE 2.12—List of hard, borderline, and soft bases (after Huheey et al., 1993; "R" refers to an organic molecule).

Hard Bases
NH_3, RNH_2, N_2H_4
H_2O, OH^-, O^{2-}, ROH, RO^-, R_2O
CH_3COO^-, CO_3^{2-}, NO_3^-, PO_4^{3-}, SO_4^{2-}, ClO_4^-
F^-, (Cl^-)

Borderline Bases
$C_6H_5NH_2$, C_5H_5N, N_3^-, N_2
NO_2^-, SO_3^{2-}
Br^-

Soft Bases
H^-
R^-, C_2H_4, C_6H_6, CN^-, RNC, CO
SCN^-, R_3P, $(RO)_3P$, R_3As
R_2S, RSH, RS^-, $S_2O_3^{2-}$
I^-

General characteristics of elements in aqueous systems

A general overview of the characteristics of trace elements is given by Pais and Jones (1997). Mobility encompasses the general characteristics and speciation of elements in aqueous systems. Table 2.13 lists several elements that exist as cations or anions in aqueous systems. The behavior of cations and anions is quite different in aqueous systems. Dissolved metals do not normally occur only as free ions, but rather combine with other atoms into different aqueous complexes. Cations are generally more mobile under acidic conditions whereas anions are generally less mobile. This characteristic can have an effect on bioavailability. For example, aluminum, a cation which may be toxic to aquatic life, is fairly soluble at low pH but is relatively insoluble at circumneutral pH. Another example is elements that tend to form oxyanions in water (e.g., arsenic, boron, chromium, molybdenum, selenium, and vanadium) are often transported through living cell membranes by diffusion-controlled processes; the membranes generally do not provide a barrier to these oxyanionic species (Wood, 1988).

Elements sensitive to oxidation-reduction (redox) conditions are also tabulated in Table 2.13. A redox-sensitive element will generally undergo a change in mobility at oxidizing or reducing geochemical barriers. For example, chromium dissolves as it is oxidized to chromium (VI) and precipitates on reduction to chromium (III); this is important because chromium (VI) is much more toxic than is chromium (III). Similarly, uranium is immobile under reducing conditions but can be mobile under oxidizing conditions. On the other hand, iron and manganese may be soluble under reducing conditions; consequently, metals sorbed onto hydrous iron and manganese oxides can be released under reducing conditions.

TABLE 2.13—General characteristics of some chemical elements in simple surface or near-surface aqueous systems.(1)(2)

Element	Anionic(3)	Cationic	Redox-sensitive(4)
Aluminum (Al)		X	
Antimony (Sb)	X		X
Arsenic (As)	X		X
Barium (Ba)		X	
Beryllium (Be)		X	
Boron (B)	X		
Cadmium (Cd)		X	
Chromium (Cr)	X	X	X
Cobalt (Co)		X	
Copper (Cu)		X	X
Iron (Fe)		X	X
Lead (Pb)		X	(X(6))
Lithium (Li)		X	
Manganese (Mn)		X	X
Mercury (Hg)		X	X
Molybdenum (Mo)	X	X(5)	X
Nickel (Ni)		X	
Selenium (Se)	X		X
Silver (Ag)		X	
Thorium (Th)		X	(X(6))
Uranium (U)	X	X	X
Vanadium (V)	X	X	X
Zinc (Zn)		X	

(1) This table is meant as a simple guide for element behavior under normal surface or near-surface aqueous conditions.
(2) This table does not include complexes with other elements.
(3) Anionic species exist as oxyanions.
(4) Elements that change oxidation state and oftentimes exhibit different behavior under different oxidation-reduction (redox) conditions.
(5) Cationic species exist for Mo but are rare and usually ignored in aqueous systems.
(6) Some of the elements, such as Pb and Th, are redox sensitive only under extreme conditions.

General geochemical concepts

Stability of minerals in the surficial environment

Minerals in the Earth's crust are the ultimate source of metals. Metals are neither created nor destroyed in the environment, but are redistributed by several different kinds of mechanisms. Consequently, metals are not distributed uniformly in the Earth's crust or among the various earth materials (e.g., rocks, soils, sediments).

There are two geochemical environments, (1) the deep-seated environment, which is not subject to surficial or near-surface processes, and (2) the surficial environment, which is subject to surficial or near-surface processes. Minerals formed in the deep-seated environment are unstable to varying degrees in the surficial environment, and elements contained in these minerals may be released, transported, and redistributed in the surficial environment. Table 2.14 lists some minor and trace elements found in common rock-forming minerals. When these minerals weather, the listed minor and trace elements may be expected to be released from the mineral matrix. From this type of information one may crudely predict which elements may be most readily remobilized in the surficial environment (geoavailability) based on the ease of weathering of the minerals in which they occur.

Bowen's reaction series, illustrated on Figure 2.10, schematically depicts the magma differentiation process in the deep-seated

TABLE 2.14—Minor and trace elements found in common rock-forming minerals and relative stability of those minerals in the surficial environment. Characteristically hazardous metals, as defined by the Resource Conservation and Recovery Act (RCRA), are in bold (see Table 2.6 and text). Information is from Levinson (1980, Table 2-2.).

	Range of concentration in crystal structure				
Mineral	X%	0.X%	0.0X%	0.00X% or less	Stability
Olivine	--	Ni, Mn	Ca, Al, **Cr**, Ti, P, Co	Zn, V, Cu, Sc	
Pyroxene	--	Ti, Na, Mn, K	**Cr**, V, Ni, Cl, Sr	P, Cu, Co, Zn, Li, Rb, **Ba**	
Plagioclase	K	Sr	**Ba**, Rb, Ti, Mn	P, Ga, V, Zn, Ni, **Pb**, Cu, Li	More Easily Weathered
Amphibole (e.g., hornblende)	--	Ti, F, K, Mn, Cl, Rb	Zn, **Cr**, V, Sr, Ni	**Ba**, Cu, P, Co, Ga, **Pb**, Li, B	
Biotite	Ti, F	Ca, Na, **Ba**, Mn, Rb	Cl, Zn, V, **Cr**, Li, Ni	Cu, Sn, Sr, Co, P, **Pb**, Ga	
Potash Feldspar	Na	Ca, **Ba**, Sr	Rb, Ti	**Pb**, Ga, V, Zn, Ni, Cu, Li	
Muscovite	--	Ti, Na, Fe, **Ba**, Rb, Li	**Cr**, Mn, V, Cs, Ga	Zn, Sn, Cu, B, Nb	
Quartz	--	--	--	Fe, Mg, Al, Ti, Na, B, Ga, Ge, Mn, Zn	More Stable

environment. As a magma cools some elements in the magma are depleted as minerals form. Minerals crystallized at higher temperatures are less stable in the surficial environment and minerals formed at lower temperatures are more stable in the surficial environment. (An important exception to this generalization is calcite, which can be a late magmatic mineral phase and which is soluble in the surficial environment.)

Element cycles

A holistic approach is required to adequately understand and assess the environmental impacts of mineral development. Elements cycle through the Earth's lithosphere, atmosphere, hydrosphere, and biosphere. Human activities, such as mining, can perturb these natural cycles and change the distribution, flux, and residence time of elements in various reservoirs (see Nriagu and Pacyna, 1988, and Nriagu, 1990, for world-wide inventories of industrial/municipal discharges of trace metals into air, soils, and aquatic ecosystems; Meybeck et al., 1989). To anticipate and assess the extent and degree of any perturbation one must understand and account for the various processes that control the distribution, flux, and residence times of elements in natural systems. There is a complex web of interrelationships between factors involved in the flow of elements through a system, in the resulting environmental quality, and in the degree of reversible or irreversible effects on the environment or on human health. Many of these interrelationships are poorly understood and much work remains to be done to define and assess these factors. One also must try to determine metal budgets in contaminated systems (Merrington and Alloway, 1994). One can then place the situation into a broader perspective (e.g., watershed impact) and, if necessary, devise ways to eliminate, minimize, mitigate, or remediate the perturbation.

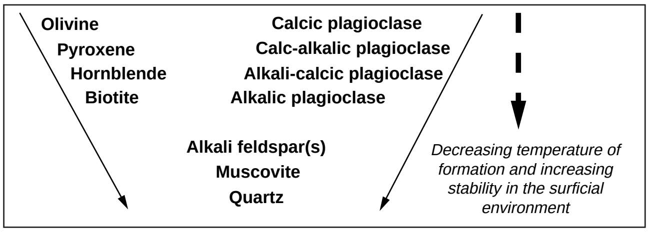

FIGURE 2.10—Bowen's reaction series showing the sequence of mineralogical differentiation starting with a basaltic magma in the deep-seated environment. Minerals at the top of the series tend to be unstable in the surficial environment and subject to higher geoavailability.

Landscape geochemistry

Landscape geochemistry can be applied to the understanding of metal distributions in the environment. Landscape geochemistry focuses on the interaction of the lithosphere with the hydrosphere, biosphere, and atmosphere, and links exploration geochemistry with environmental science (Fortescue, 1980). Landscape geochemistry is an holistic approach to the study of the geochemistry of the environment in that it involves element cycles and may involve local, regional, and global studies. Fortescue (1992) reviews the development of landscape geochemistry and provides the foundation of how it relates to environmental science.

Fortescue (1992) proposes the establishment of a discipline of "Global Landscape Geochemistry" (GLG), which may provide the foundation for future developments in applied and environmental geochemistry and which is necessary to adequately address current geoenvironmental problems. GLG regional geochemical mapping can be used to delineate geochemical provinces, identify local geochemical enrichments in mineral deposits, determine baseline environmental geochemistry, monitor environmental changes in soil and water geochemistry in response to human activities, evaluate the nutritional status of plants and animals, and study human health. Fortescue (1992) notes that there is a need to map geochemical landscapes as an essential preliminary step to the study of environmental geochemistry. Geochemical maps based on the analysis of rocks, soils, sediments, waters, and vegetation, originally compiled for mineral exploration purposes, may be extended to multi-purpose geochemical surveys that have applications in agriculture, pollution studies, and human health (Webb, 1964). However, geochemical analyses for mineral exploration purposes have generally been designed to be cost effective; consequently, the quality of the geochemical data often is inadequate for many environmental applications. Geochemical atlases have been prepared for Northern Ireland (Webb et al., 1973), England and Wales (Webb et al., 1978), the United Kingdom (Plant and Thornton, 1985), and several other countries. Darnley (1990) and IGCP (1995) discuss the International Geochemical Mapping Project, which proposes to produce geochemical maps of the world. A geology-based map of potential metal-mine drainage hazards in Colorado has been compiled by Plumlee et al. (1995).

Geochemical associations and pathfinder elements

Knowledge of geochemical associations and common pathfinder elements from the geochemical-exploration literature can be used for environmental purposes to determine which elements may be mobilized from a mined site for a given type of ore deposit. Ordinarily, a suite of elements is concentrated in a particular deposit. Geochemical exploration utilizes empirical knowledge of element associations that can serve as pathfinders for particular mineral deposit types. Boyle (1974), Beus and Grigorian (1977), Rose et al. (1979), Levinson (1980), Cox and Singer (1986), and du Bray (1995) compiled elemental associations for a variety of deposits. Table 2.15 lists geochemical signatures for selected types of mineral deposits. This information is useful for predicting element mobility and dispersivity in soils, sediments, water, and air from mined lands. For example, Li and Thornton (1993) report that the multi-element contamination of soils and plants in historical lead-zinc mining and smelting areas of the United Kingdom reflects the geochemical associations of the lead-zinc mineralization. Ficklin et al. (1992), Plumlee et al. (1992, 1993, 1999), and Ripley et al. (1996) relate the composition of mine-drainage waters to the geology of diverse mineral deposit types and discuss the environmental effects of mining various mineral deposit types. This topic is also discussed in Plumlee (1999).

Pathfinder elements are elements associated with a mineral deposit type that are used to explore for ore bodies. Elements enriched in an ore deposit will have different relative mobilities in surrounding wall rocks and in the weathering environment. The most useful pathfinder elements commonly are more easily analyzed or detected or are more mobile in the surficial environment than are the primary elements of the ore deposit. Additional elements may have been introduced at the ore deposit if ore processing occurred onsite. For example, if mercury has been used in gold amalgamation, this may be an element of concern during site characterization and remediation.

Geochemical gradients and barriers

As an outgrowth of landscape geochemistry, Perel'man (1977) discusses the importance of geochemical gradients, which describe gradual changes of a landscape, and geochemical barriers, which describe abrupt changes. An example of a geochemical gradient might be the vertical and horizontal distribution of certain elements away from a mineral deposit within a constant lithology; for a given element an anomalous concentration eventually declines to a background concentration at some distance away from the deposit. Another example of a geochemical gradient is the concentration plume for some elements downwind from a smelter. Perel'man (1986) defines geochemical barriers as zones of the Earth's crust with sharp physical or chemical gradients that are commonly associated with accumulation of elements. Geochemical barriers represent abrupt changes in physical or chemical environments in the path of migration of elements causing the precipitation of certain elements from solution. Geochemical barriers include mechanical, physicochemical, biochemical, and anthropogenic (or technogenic) types. This chapter discusses physicochemical barriers including acidic, alkaline, reducing, oxidizing, evaporation, adsorption, and thermodynamic barriers. Complex barriers may be created when two or more barrier types are superimposed. Nordstrom and Alpers (1999) discuss the geochemistry of several physicochemical barriers.

Acidic barriers develop when pH drops. Under these conditions, elements that form anions (such as molybdenum) as well as certain complexes, generally become less mobile, whereas many metals that form cations (such as copper) generally become more mobile (see Table 2.13). Solubility relationships can play an important role. For example, aluminum is usually fairly mobile below a pH of about 4, but will precipitate between a pH of about 5 and 9. On the other hand, silicon (as SiO_2) is relatively insoluble at low pH and becomes more soluble at high pH. One of the most important effects of developing low-pH environments is the destruction of the carbonate-bicarbonate buffering system, a feedback mechanism that controls the extent of pH change in an aqueous system. Below a pH of about 4.5, carbonate and bicarbonate are converted to carbonic acid. Upon such acidification, the water loses its capacity to buffer changes in pH, and many photosynthetic organisms that use bicarbonate as their inorganic carbon source become stressed or die. Once damaged, the acid buffering capacity of a natural system may take significant time to recover, even if no further acid is added to the system. The carbonate-bicarbonate system may have both a direct and an indirect effect on the mobility of several elements.

Alkaline barriers develop where acidic waters encounter alkaline conditions over a short distance (e.g., oxidation zones of pyrite in limestone host rock). This type of barrier mostly retains those elements that migrate easily under acidic conditions and precipitate as hydroxides or carbonates under alkaline conditions (such as iron, aluminum, copper, nickel, and cobalt). During the shift to alkaline conditions, hydrous iron, aluminum, and manganese oxides may sorb trace metals and create an alkaline/adsorption complex barrier.

Reducing conditions develop in the absence of free oxygen (or other electron acceptors). They may result from inorganic or organic chemical reactions that are frequently mediated by microorganisms. Figure 2.11 illustrates the chemical-reaction sequence for oxidation-reduction reactions. This redox sequence is biologically mediated by a succession of microorganisms (see Stumm and Morgan, 1996). Reducing barriers can be divided into those that contain hydrogen sulfide and those that do not (referred to as "reducing gley" environments; Perel'man, 1986). Reducing hydrogen sulfide barriers develop where oxidizing or reducing

TABLE 2.15—Geochemical signatures for selected types of mineral deposits.(1)(2)

Mineral deposit type	Model number(s)(3)	Examples	Geochemical signature
Magmatic sulfide (Ni, Cu, PGE)	1; 2b; 5a, b; 6a, b; 7a	Noril'sk, Merensky Reef, Stillwater, Kambalda, Duluth	Ag, As, Au, Bi, Co, Cu, Cr, Fe, Hg, Mg, Ni, Pb, Sb, Se, Te, Ti, Zn, PGE (± Cd, Ga, In, Sn)
Carbonatite	10	Oka, Mountain Pass, Phalaborwa	Ba, Cu, F, Mn, Mo, Na, Nb, P, Pb, Th, Ti, U, V, Y, Zn, Zr, REE (B, Be, Hf, Li, Sn, Ta, W are rare)
Rare-metal pegmatite(4)	13a, b	Petaca district, Black Hills district	B, Be, Cs, F, Li, Nb, Rb, Sn, Ta, Th, U, W, REE
Tin and (or) tungsten skarn replacement	14a-c	Pine Creek, Moina, Renison Bell	Ag, As, B, Be, Bi, Cs, Cu, F, Fe, Li, Mn, Mo, Pb, Rb, Re, Sn, W, Zn
Vein and greisen tin and tungsten	15a-c	Cornwall, Erzgebirge	Ag, As, B, Be, Bi, Cs, Cu, F, Li, Mo, Nb, P, Pb, Rb, Re, Rn, Sb, Sn, Ta, Th, U, W, Zn, REE
Climax molybdenum	16	Climax, Henderson, Questa	Al, Be, Cs, Cu, F, Fe, Li, Mo, Nb, Pb, Rb, Sn, Ta, Th, U, W, Zn
Porphyry copper	17	Bingham, El Salvador	Ag, As, Au, B, Ba, Bi, Cd, Co, Cr, Cs, Cu, F, Fe, Hg, K, La, Li, Mg, Mn, Mo, Na, Ni, Pb, Rb, Re, Sb, Se, Sr, Te, Tl, U, V, W, Zn
Copper, gold, and zinc-lead skarn	18b, c	Carr Fork, Fortitude, Bismark, New World	Ag, Al, As, Au, Be, Bi, Cd, Co, Cu F, Fe, Mn, Mo, Pb, Sb, Se, Sn, Te, W, Zn (± Cr, Hg)
Polymetallic vein and replacement	19a; 22c	Leadville, New World, Park City, Eureka	Ag, Al, As, Au, Ba, Bi, Cu, F, Fe, Hg, Mn, Mo, P, Pb, Sb, Zn
Gold-silver-tellurium vein	22b	Sulpherets, Zortman-Landusky, Porgera	Ag, As, Au, Ba, Bi, Cu, F, Fe, Hg, Mn, Mo, Ni, Pb, Sb, Te, V, Zn, PGE (± Cd, Sc)
Volcanic-associated massive sulfide	24a, b; 28a	Cyprus, Kuroko, Besshi, Skouriotissa, Kidd Creek	Ag, As, Au, Ba, Bi, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Sb, Se, Sn, Zn (± Al, Mo)
Epithermal vein	25b-d	Creede, Comstock, Sado	Ag, Al, As, Au, Ba, Bi, Cu, Fe, Hg, Mn, Pb, Sb, Se, Te, U, W, Zn
Epithermal quartz-alunite	25e	Summitville, Julcani	Al, As, Au, Ba, Be, Bi, Co, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Sb, Se, Sn, Te, Th, Tl, U, W, Zn, REE
Epithermal manganese	25g	Talamantes, Sardegna	Ag, As, Au, Ba, Cu, Fe, Mn, Mo, P, Pb, Sb, Sr, Tl, W, Zn
Rhyolite-hosted tin	25h	"Mexican-type" in the states of Durango and Zacatecas; Black Range, NM	As, Be, Bi, F, Fe, Li, Mo, Nb, Pb, Sb, Sn, Th, U, Zn, REE (± Ti, Y, Zr)
Low titanium iron oxide copper-uranium-REE	25i, 29b	Olympic Dam, Kiruna, Bayan Obo	Ag, As, Au, B, Ba, Bi, Cl, Co, Cu, F, Fe, K, Mn, Mo, Na, Nb, Ni, P, Te, U, V, REE
Sediment-hosted gold (Carlin type)	26a	Carlin, Jerritt Canyon, Mercur	Ag, As, Au, Ba, F, Hg, Mo, Sb, Se, Tl, W (± Cd, Cr, Cu, Ni, Pb, Zn)
Hot spring gold-silver or mercury(4)	25a; 27a	McLaughlin, Round Mountain, McDermitt, Sulfur Bank	Ag, As, Au, Hg, Sb, Tl, W
Almaden mercury	27b	Almaden, Las Cuevas	As, Fe, Hg, Sb (± Cu, Ni, Pb, Zn, Zr)
Stibnite-quartz	27d, e; 36c	Lake George, Xiguanshan	As, Au, Ba, Cu, Fe, Hg, Pb, Sb, U, Zn (± Ag, W)
Algoma iron	28b	Sherman, Wadi Sawanin, Vermillion Iron Formation	Au, Fe
Sediment-hosted copper	30b	Kupferschiefer, African copper belt, Nacimiento, Spar Lake, White Pine	Ag, As, Au, B, Ba, Bi, Cd, Co, Cr, Cu, Ge, Hg, Mo, Ni, Pb, Sc, Se, Sn, Sr, U, V, Zn, PGE
Sandstone uranium(4)	30c	Grants district, Colorado Plateau	Ag, Cu, Mo, Pb, Rn, Se, U, V
Sedimentary exhalative zinc-lead-silver	31a	Sullivan, Red Dog, Rammelsberg, McArthur River, Tynagh, Broken Hill	Ag, Al, As, Au, B, Ba, Cd, Co, Cu, Fe, Hg, Mn, Ni, Pb, Sb, Zn
Mississippi Valley type lead-zinc	32a	Viburnum Trend, Mascot-Jefferson, Pine Point, Polaris, Silesian District, Lennard Shelf District	Ag, As, Au, Ba, Bi, Cd, Co, Cu, F, Fe, Ga, Ge, Hg, In, Mg, Mo, Ni, Pb, Sb, Sn, Zn
Solution-collapse breccia pipe uranium	32e	Arizona breccia pipe district, Tsumeb	Ag, As, Ba, Cd, Co, Cr, Cu, Hg, Mo, Ni, Pb, Rn, Sb, Se, Sr, U, V, Y, Zn
Superior iron	34a	Mesabi and Marquette iron ranges, Minas Gerais	Fe, P
Sedimentary manganese	34b	Molango, Nikopol, Groote Eylandt, Kalahari, Imini	Ba, Mn, P, Pb
Low sulfide gold quartz veins	36a	Yilgarn block, Abitibi belt, Mother Lode, Muruntau	Ag, As, Au, Bi, Cu, Fe, Hg, Mo, P, Pb, Sb, Te, W, Zn
Stratabound gold in iron formations	36b	Homestake, Lupine, Cuiaba, Champion	Ag, As, Au, B, Bi, Cu, Fe, Hg, Mo, Pb, Sb, Zn, PGE

(1)Listings include enriched elements within or adjacent to mineral deposits. Groupings are based on du Bray (1995) unless otherwise noted. Examples and geochemical signatures are from du Bray (1995), Boyle (1974), Cox and Singer (1986), Beus and Grigorian (1977, adapted from Table 57), Rose et al., (1979, adapted from Table 4.2), and Levinson (1980, adapted from Table 2–3). Elements are listed alphabetically and not in order of abundance.

(2)Sulfur is present in many mineral deposits. However, due to variations within deposit types and within alteration types, sulfur may or may not be of environmental significance. Refer to du Bray (1995) for discussions relating to sulfur content of mineral deposits.

(3)Model numbers are based on Cox and Singer (1986). (4)Grouping is based on Cox and Singer (1986).

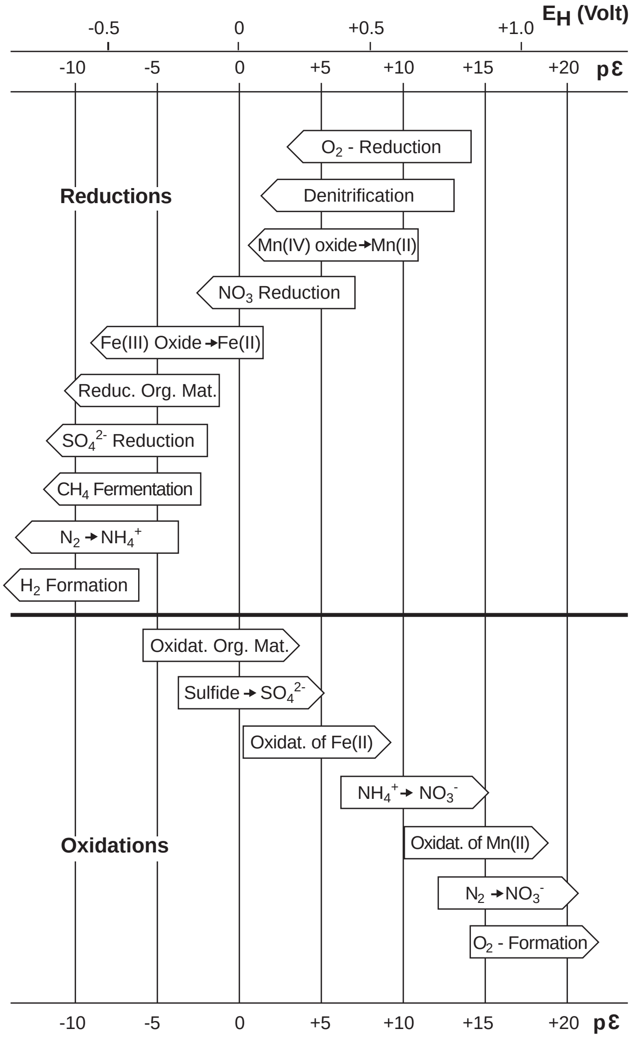

FIGURE 2.11—Sequence of microbially mediated oxidation-reduction reactions. This sequence is often observed in natural systems and represents the thermodynamic order of reactions. Modified from Stumm and Morgan (1996).

gley waters come into contact with a reducing hydrogen sulfide environment or with sulfide minerals, or where deoxygenated sulfate-rich water encounters an accumulation of organic matter. Insoluble sulfides of elements such as iron, copper, zinc, lead, cobalt, nickel, and silver may precipitate at reducing barriers that contain hydrogen sulfide. Reducing gley barriers can form where water infiltrates soil and the weathering crust, and free oxygen is lost or consumed. Depending on the pH, reducing gley waters are usually favorable for the transport of many ore-forming elements; additionally, elements such as selenium, copper, uranium, molybdenum, rhenium, vanadium, chromium, silver, and arsenic are known to accumulate at some reducing gley barriers (Perel'man, 1986). For example, roll-front-type uranium deposits may form under such conditions. See Table 2.13 for a list of redox-sensitive elements.

Oxidizing barriers occur where oxygen is introduced into anoxic waters or when anoxic ground water is discharged to the surficial environment. Iron, and possibly manganese, may precipitate at these barriers (see Fig. 2.11). Since hydrous iron and manganese oxides are good sorbents for metals (such as copper and cobalt), a complex barrier may form by combining an oxidizing barrier with an adsorption barrier.

Figure 2.12 illustrates the ranges of pH and Eh (oxidizing-reducing conditions) of water commonly found in different natural environments. Nordstrom and Alpers (1999) discuss Eh-pH diagrams in more detail. This type of diagram helps distinguish the types of natural environments where geochemical barriers may be formed. The shaded area on Figure 2.12 represents the approximate conditions reported by Plumlee et al. (1999) for geologically and geochemically diverse mine-drainage waters; conditions are approximate because dissolved oxygen, rather than Eh, was determined in many of the waters. There is a wider range of pH in mine waters than shown on Figure 2.12. The pH of mine waters can range from -3.5 to >12 (D.K. Nordstrom, USGS, personal commun., 1997).

Evaporation barriers are often indicated by the presence of salt crusts or efflorescent salts. Sodium, magnesium, calcium, chlorine, sulfur, and carbonate salts may precipitate at these barriers. Evaporation barriers may be temporary and related to changing

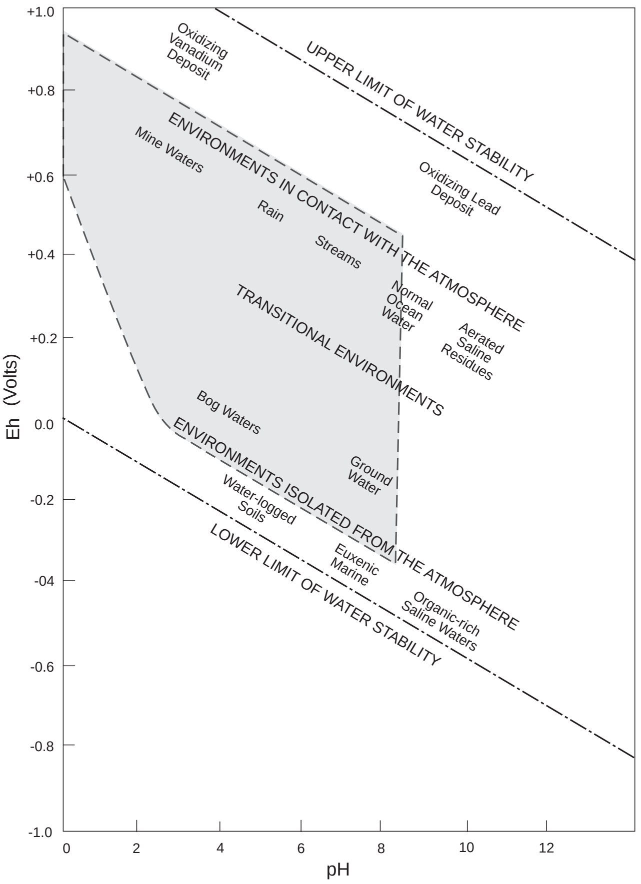

FIGURE 2.12—Eh-pH regimes of some natural near-surface environments. The shaded area represents the approximate conditions reported in Plumlee et al. (1999) for geologically and geochemically diverse mine-drainage waters (see text). Modified from Garrels and Christ (1965).

climatic conditions. For example, in some mine dumps efflorescent salts, enriched in elements such as iron, aluminum, copper, and sulfur, may form during the dry season. These salts will be flushed from the system during a subsequent wet period and may cause a brief spike in metal content and acidity of the stormwater runoff (see Nordstrom and Alpers, 1999).

Adsorption barriers are typically part of complex barriers. The most common sorbents (e.g., hydrous iron, aluminum, and manganese oxides; organic matter and clay minerals) have different affinities for elements under different geochemical conditions (see Smith, 1999). Adsorption reactions are known to control trace-metal concentrations in many natural systems.

Thermodynamic barriers are formed in areas with temperature and pressure variations. One example of such a barrier is the degassing of carbon-dioxide-rich ground water, as pressure drops, and subsequent deposition of carbonate minerals. Trace elements such as lead and cadmium can precipitate as carbonate minerals or coprecipitate with $CaCO_3$.

Perel'man (1977, 1986) gives a more in-depth discussion of geochemical barriers. This concept can help anticipate element distributions in the surficial environment and understand metal transport and mobility.

Metal mobility in the surficial environment

In this chapter, mobility refers to the capacity of an element to move within fluids after dissolution. It is difficult to predict element mobility quantitatively in surficial environments. Rather, mobility should be considered in a relative sense by empirically comparing the behavior of elements under changing environmental conditions such as at geochemical barriers. Figure 2.13 illustrates the generalized relative mobility of elements expected under a variety of geochemical conditions. This figure takes into account the tendency of the elements to sorb onto hydrous oxides or to precipitate. Criteria for mobility distinctions are scaled by element abundance rather than being based on absolute solubility; no quantitative information can be inferred from Figure 2.13. By comparing the periodic tables (Fig. 2.13a-e), one may make qualitative statements about the behavior of a given element under changing conditions such as at geochemical barriers. Data for Figure 2.13 are derived from a wide range of information about mine-drainage systems as well as from Vlasov (1966), Fuller (1977), Parish (1977), Perel'man (1977, 1986), Callahan et al. (1979), Lindsay (1979), Rose et al. (1979), Levinson (1980), Greenwood and Earnshaw (1984), Lukashev (1984, 1986), Adriano (1986), Cotton and Wilkinson (1988), Hem (1985), and Kabata-Pendias and Pendias (1992).

Figure 2.13a shows the generalized relative mobility of elements under oxidizing acidic (pH <3) conditions in aqueous systems and Figure 2.13b shows mobilities under circumneutral conditions. For redox-sensitive elements (see Table 2.13), the most oxidized form is assumed to be present. This is important because some redox-sensitive elements have different mobility and toxicity characteristics. For example, chromium (VI), the more toxic form, is more mobile in soils than chromium (III). By comparing data in these two periodic tables, it is possible to estimate the behavior of a given element at an acidic or alkaline geochemical barrier under oxidized conditions. For example, under acidic conditions iron remains dissolved, but it will precipitate when conditions become more alkaline. Figure 2.13c shows the generalized relative mobility of elements in the presence of such iron-rich precipitates and, when compared with Figures 2.13a and 2.13b, represents a complex alkaline and sorption geochemical barrier. Elements such as copper and arsenic become much less mobile under these conditions if sufficient iron-rich precipitates are present and if the pH for optimal sorption is attained (which is different for different elements and substrates; see Smith, 1999).

Figure 2.13d shows the generalized relative mobility of elements under reducing conditions without hydrogen sulfide (reducing gley environments) and Figure 2.13e shows mobilities in the presence of hydrogen sulfide. Comparing these two periodic tables illustrates the influence of sulfide-mineral formation. For example, copper and zinc become much less mobile when hydrogen sulfide is present because they form insoluble sulfide minerals.

It is also useful to compare the oxidizing-conditions periodic tables (Fig. 2.13a, b, and c) with the reducing-conditions periodic tables (Fig. 2.13d and e). For example, a reducing gley geochemical barrier could be simulated by comparing an initial condition with low-sulfate, oxidizing, circumneutral pH water (in the absence of abundant iron-rich particulates as on Fig. 2.13b) to the conditions represented on Figure 2.13d. In this situation, iron becomes more mobile and uranium will become less so. Another example is when sulfate-rich waters infiltrate a wetland system (e.g., passive mine-drainage treatment or natural systems; see Walton-Day, 1999), where it would be appropriate to compare Figures 2.13a or 2.13b with Figure 2.13e.

Figure 2.13 provides a general guide or first approximation to predict metal behavior in surficial environments. This approach does not substitute for in-depth field studies and topical research; there is no reliable "cookbook" approach. This approach may help to determine which elements could be mobile in a given environment and to anticipate the effects of various geochemical barriers. It should be kept in mind that there was a great degree of subjectivity in assigning the elements to the various categories on Figure 2.13. To use this approach in a natural setting, one must know something about the geochemical conditions. One must also have a good grasp of underlying chemical and geochemical principles (e.g., Garrels and Christ, 1965; Nordstrom and Munoz, 1994; Stumm and Morgan, 1996). Figure 2.13 should be used only in a relative sense and does not provide any information about absolute concentrations or quantitative data.

The rates of geochemical and biological reactions also can impact metal mobility; many reactions involving metals are kinetically controlled and biologically mediated. This rate dependence makes reactions extremely difficult to predict (e.g., Langmuir and Mahoney, 1984).

Success in estimating metal behavior in surficial environments also depends on scale. At a regional scale, generalizations often can be used to understand broad trends in metal mobility. As the scale becomes increasingly finer, however, estimating metal behavior usually becomes increasingly difficult. Many chemical interactions involve elements of interest as well as other elements and components such as acidity, rainfall, and factors that are involved in complicated synergisms or antagonisms. Once these other components are recognized and addressed, a more accurate assessment of metal mobility can be made.

It is often necessary to understand the mobility of major elements before data on the mobility of trace elements can be interpreted. For example, insoluble salts or solution complexes may form between trace metals and major elements, such as the formation of cadmium chloride complexes. Major or minor elements may modify the concentration or activity of a trace element. For example, cadmium and calcium compete to form chloro complex-

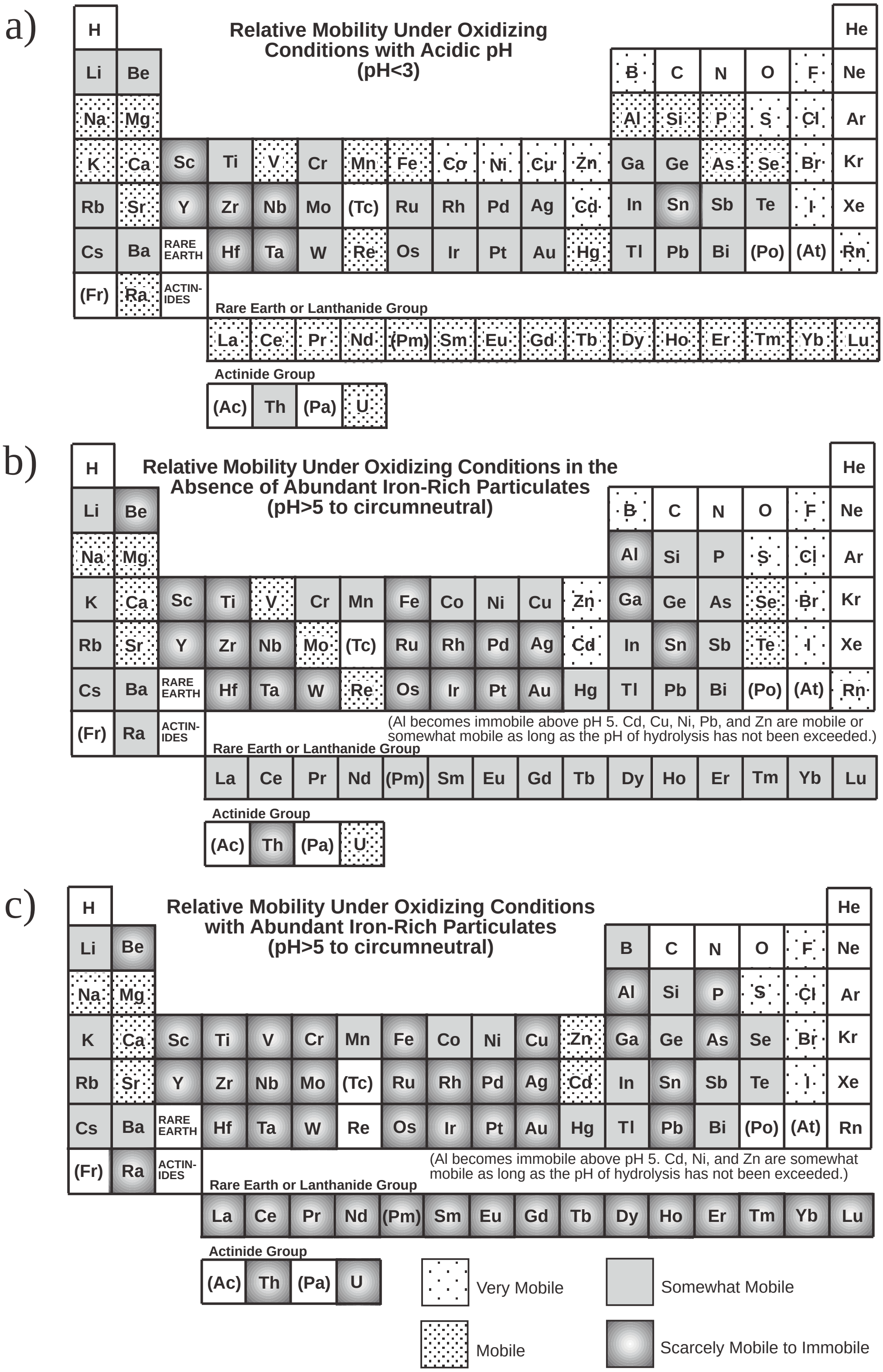

FIGURE 2.13a-c—Periodic tables of generalized relative mobility of chemical elements under different environmental conditions. For rare elements it is difficult to assign a mobility category due to their low abundance and lack of data. Lack of shading or pattern for some elements is due to either their existence in the gaseous state or a lack of information about that element.

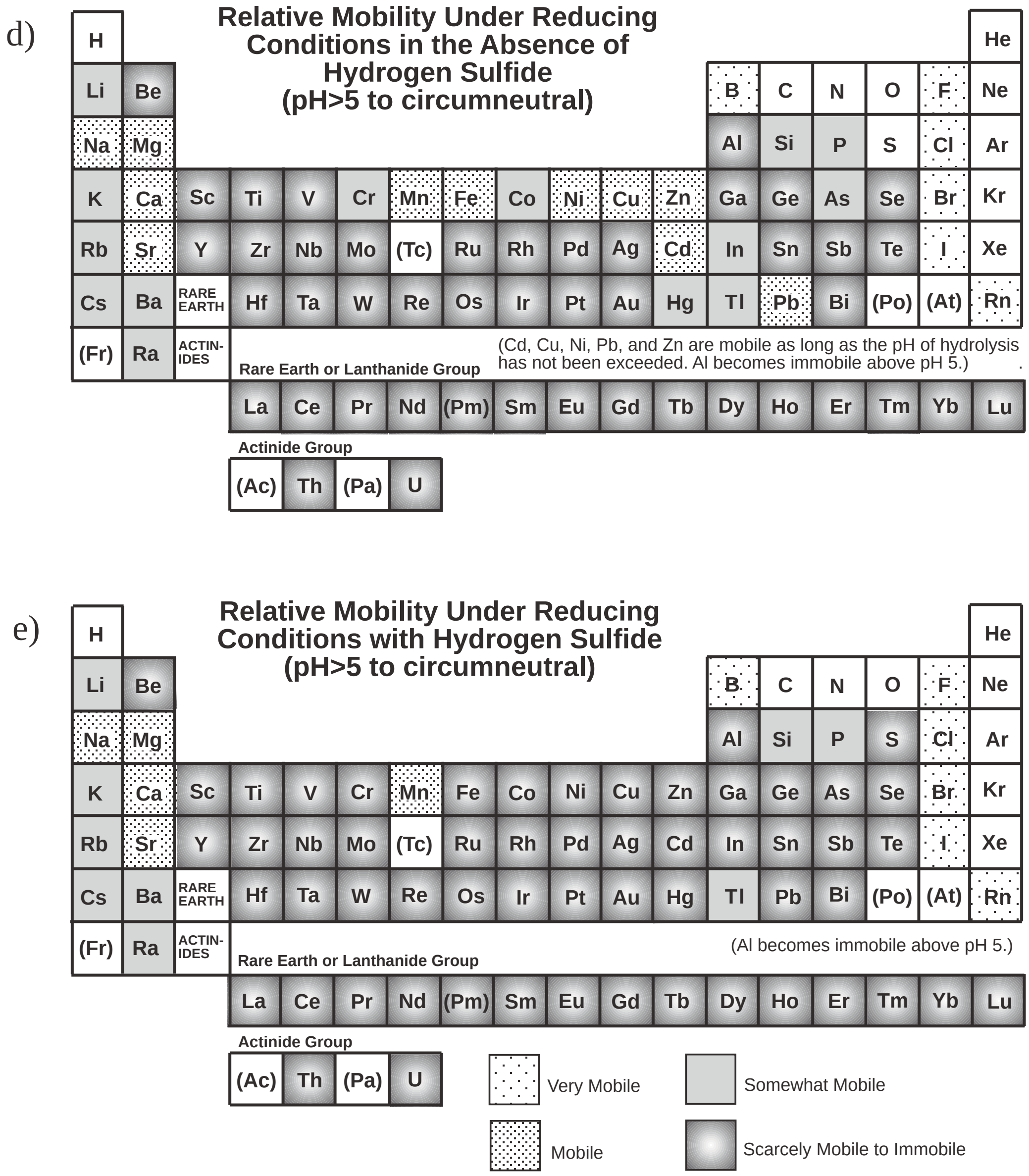

FIGURE 2.13d and e—Continued

es or insoluble carbonate and phosphate minerals. Another example is the iron system, where concentrations of many trace elements can be controlled by sorption onto iron-rich precipitates (see Smith, 1999; Smith et al., 1998).

Metal dispersivity in the surficial environment

Air

Atmospheric deposition of metals may impact the chemistry of soils, rivers, lakes, estuaries, and oceans. Metals enter the atmosphere as gases, vapors, aerosols, and particles originating from a variety of natural and anthropogenic sources. Tables 2.16A and 2.16B list estimates of some of these sources and their relative importance. According to Nriagu (1989), wind-borne soil particles generally account for more than half of the chromium, cobalt, manganese, and vanadium, and for one-third to one-half of the molybdenum, nickel, and zinc emitted from natural sources (although metals in wind-blown dust are often of industrial origin). Volcanoes account for more than half of the cadmium, and significant amounts of arsenic, chromium, copper, lead, mercury, and nickel. Biogenic sources are the leading contributors of mercury and selenium, and significant sources of arsenic (Table 2.16A; Nriagu, 1989). In Table 2.16B, nonferrous metal produc-

TABLE 2.16A—Estimates of worldwide trace-metal emissions into the atmosphere from natural sources (x 10^3 kg/yr). Data from Nriagu (1989, Table 1).

Source (median values)	As	Cd	Co	Cr	Cu	Hg	Mn
Wind-borne soil	2,600	210	4,100	27,000	8,000	50	221,000
Seasalt spray	1,700	60	70	70	3,600	20	860
Volcanoes	3,800	820	960	15,000	9,400	1,000	42,000
Forest fires	190	110	310	90	3,800	20	23,000
Biogenic							
Continental particulates	260	150	520	1,000	2,600	20	27,000
Continental volatiles	1,300	40	60	50	320	610	1,300
Marine	2,300	50	80	60	390	770	1,500
Total Natural Sources (Median value)	**12,000**	**1,300**	**6,100**	**44,000**	**28,000**	**2,500**	**317,000**

Source (median values)	Mo	Ni	Pb	Sb	Se	V	Zn
Wind-borne soil	1,300	11,000	3,900	780	180	16,000	19,000
Seasalt spray	220	1,300	1,400	560	550	3,100	440
Volcanoes	400	14,000	3,300	710	950	5,600	9,600
Forest fires	570	2,300	1,900	220	260	1,800	7,600
Biogenic							
Continental particulates	400	510	1,300	200	1,120	920	2,600
Continental volatiles	60	100	200	40	2,600	130	2,500
Marine	80	120	240	50	4,700	160	3,000
Total Natural Sources (Median value)	**3,000**	**30,000**	**12,000**	**2,400**	**9,300**	**28,000**	**45,000**

tion and use accounted for the largest fraction of lead (in addition to gasoline combustion), arsenic, cadmium, copper, and zinc emitted into the atmosphere in 1983 (Nriagu and Pacyna, 1988). Pacyna (1996) provides an in-depth discussion of trace metal emissions into the atmosphere. He states that trace metals emitted into the atmosphere can be transported a long distance and that atmospheric deposition is an important pathway for worldwide metal contamination of terrestrial and aquatic ecosystems.

Residence times of metals in the atmosphere are fairly short—generally on the order of days to weeks (Salomons and Forstner, 1984). However, volcanogenic particles can remain in the upper atmosphere for much longer periods of time. The distance of airborne transport depends on the source, size, shape, and density of the particles, on changes in particle characteristics during transport and on meteorological conditions. Particles in the atmosphere can undergo diffusion, coagulation, condensation, sedimentation, scavenging by precipitation, and reaction with atmospheric gases. Deposition varies with particle-size distribution, ground cover, and meteorological conditions.

Metals can be transported in different forms when associated with fly ash from urban waste incinerators. Fernandez et al. (1992) suggested that the behavior of elements in fly ash correlates with the following four classes originally suggested by Klein et al. (1975):

Class I: Elements that make up the matrix of the fly ash and are only minimally deposited on the fly-ash surface. These include Al, Ba, Be, Ca, Co, Fe, K, Mg, Mn, Si, Sr, and Ti.

Class II: Elements that volatilize during combustion and condense on the surface of fly-ash particles, forming soluble compounds. These elements also tend to be more enriched in smaller size fly ash particles (because of the particle's greater specific surface area) and include As, Cd, Cu, Ga, Pb, Sb, Se, and Zn.

Class III: Elements that volatilize but do not condense. These include Br, Cl, and Hg.

Class IV: Elements whose behavior is a combination of the above classes.

Several studies have examined metal contamination near smelters. The elements enriched in various smelter emissions are similar to the suite of elements enriched in fly ash, and are related to the ore deposit type. For example, Li and Thornton (1993) observed that lead, zinc, cadmium, antimony, and arsenic are enriched in a lead-zinc smelting area in England. Ragaini et al. (1977) found greater concentrations of cadmium, arsenic, lead, indium, scandium, antimony, zinc, silver, gold, nickel, and possibly copper in soils, grasses, and ambient aerosols near a lead smelting complex in Kellogg, Idaho. Small et al. (1981) studied emissions from five copper smelters in southeastern Arizona. They report that sulfur, copper, zinc, arsenic, selenium, silver, cadmium, indium, antimony, tungsten, gold, lead, and iodine are strongly enriched in the plumes relative to background, and that copper, arsenic, selenium, cadmium, and indium are enriched in the copper smelters far in excess of other sources. In a companion study, Germani et al. (1981) determined that variations in the elemental enrichments among plumes from the five copper smelters appear to be due to differences in the feed material, smelting conditions, and equipment used by the smelters. Researchers have also documented the distribution of smelter emissions (e.g., Gabriel and Patten, 1994) and the migration and mobility of metals in smelting areas (e.g., Scokart et al., 1983; Maskall et al., 1995).

Water

Physical transport of sediments is related to hydrologic and geomorphologic processes such as erosion, vertical and horizontal

TABLE 2.16B—Estimates of worldwide trace-metal emissions into the atmosphere in 1983 from anthropogenic sources (x 10^3 kg/yr). Data from Nriagu and Pacyna (1988, Table 2).

Source	Arsenic	Cadmium	Chromium	Copper
Pyrometallurgical nonferrous metal production				
Mining	40.0–80	0.6–3		160–800
Pb production	780–1,560	39–195		234–312
Cu–Ni production	8,500–12,750	1,700–3,400		14,450–30,600
Zn–Cd production	230–690	920–4,600		230–690
Secondary nonferrous metal production		2.3–3.6		55–165
Steel and iron mfg.	355–2,480	28–284	2,840–28,400	142–2,840
Coal combustion				
electric utilities	232–1,550	77–387	1,240–7,750	930–3,100
industry and domestic	198–1,980	99–495	1,680–11,880	1,390–4,950
Oil combustion				
electric utilities	5.8–29	23–174	87–580	348–2,320
industry and domestic	7.2–72	18–72	358–1,790	179–1,070
Wood combustion	60–300	60–180		600–1,200
Refuse incineration				
municipal	154–392	56–1,400	98–980	980–1,960
sewage sludge	15–60	3–36	150–450	30–180
Phosphate fertilizers		68–274		137–685
Cement production	178–890	8.9–534	890–1,780	
Miscellaneous	1,250–2,800			
Total 1983 Emissions	**12,000–25,630**	**3,100–12,040**	**7,340–53,610**	**19,860–50,870**
Median value	**18,820**	**7,570**	**30,480**	**35,370**

Source	Mercury	Indium	Manganese	Molybdenum
Pyrometallurgical nonferrous metal production				
Mining			415–830	
Pb production	7.8–16			
Cu–Ni production	37–207	8.5–34.0	850–4,250	
Zn–Cd production		2.3–4.6		
Secondary nonferrous metal production			1,065–28,400	
Coal combustion				
electric utilities	155–542		1,080–6,980	232–2,320
industry and domestic	495–2,970		1,485–11,880	396–2,480
Oil combustion				
electric utilities			58–580	58–406
industry and domestic			358–1,790	107–537
Wood combustion	60–300			
Refuse incineration				
municipal	140–2,100		252–1,260	
sewage sludge	15–60		5,000–10,000	
Total 1983 Emissions	**910–6,200**	**11–39**	**10,560–65,970**	**793–5,740**
Median value	**3,560**	**25**	**38,270**	**3,270**

TABLE 2.16B—Continued

Source	Nickel	Lead	Antimony	Selenium
Pyrometallurgical nonferrous metal production				
Mining	800	1,700–3,400	18–176	18–176
Pb production	331	11,700–31,200	195–390	195–390
Cu–Ni production	7,650	11,050–22,100	425–1,700	427–1,280
Zn–Cd production		5,520–11,500	46–92	92–230
Secondary nonferrous metal production		90–1,440	3.8–19	3.8–19
Steel and iron mfg.	36–7,100	1,065–14,200	3.6–7.1	0.8–2.2
Coal combustion				
electric utilities	1,395–9,300	775–4650	155–775	108–775
industry and domestic	1,980–14,850	990–9,900	198–1,480	792–1,980
Oil combustion				
electric utilities	3,840–14,500	232–1,740		35–290
industry and domestic	7,160–28,640	716–2,150		107–537
Wood combustion	600–1,800	1,200–3,000		
Refuse incineration				
municipal	98–420	1,400–2,800	420–840	28–70
sewage sludge	30–180	240–300	15–60	3–30
Phosphate fertilizers	137–685	55–274		0.4–1.2
Cement production	89–890	18–14,240		
Mobile sources		248,030		
Miscellaneous		3,900–5,100		
Total 1983 Emissions	**24,150–87,150**	**288,700–376,000**	**1,480–5,540**	**1,810–5,780**
Median value	**55,650**	**332,350**	**3,510**	**3,790**

Source	Tin	Thallium	Vanadium	Zinc
Pyrometallurgical nonferrous metal production				
Mining				310–620
Pb production				195–468
Cu–Ni production	425–1,700		43–85	4,250–8,500
Zn–Cd production				46,000–82,800
Secondary nonferrous metal production				270–1,440
Steel and iron mfg.			71–1,420	7,100–31,950
Coal combustion				
electric utilities	155–755	155–620	310–4,650	1,085–7,750
industry and domestic	99–990	495–990	990–9,900	1,485–11,880
Oil combustion				
electric utilities	348–2,320		6,960–52,200	174–1,280
industry and domestic	286–3,580		21,480–71,600	358–2,506
Wood combustion				1,200–6,000
Refuse incineration				
municipal	140–1,400			2,800–8,400
sewage sludge	15–60		300–2,000	150–450
Phosphate fertilizers				1,370–6,850
Cement production		2,670–5,340		1,780–17,800
Miscellaneous				1,724–4,783
Total 1983 Emissions	**1,470–10,810**	**3,320–6,950**	**30,150–141,860**	**70,250–193,500**
Median value	**6,140**	**5,140**	**86,000**	**131,880**

transport, sediment deposition, and compaction. In general, to transport sediment, flow rate of water must exceed a certain critical velocity, which depends on grain size and density; for deposition, the flow must decrease below another critical value. In rivers and estuaries, the sand- and gravel-size bedload fraction moves along the bottom by rolling or by a series of leaps. These particles usually are not transported long distances before deposition. Finer-grained sediments are carried in suspension and can be transported long distances before deposition (Horowitz, 1991). For example, Axtmann and Luoma (1991) document wide-scale fluvial distribution of fine-grained mining waste along the Clark Fork River in Montana.

In the water column, metals are commonly associated with suspended particulates. This suspended load can transport significant quantities of metals during spring runoff and storm events when the suspended load is highest. It is difficult to obtain a representative sample of suspended sediments and their associated metals (Horowitz et al., 1990).

Metals are not homogeneously distributed among the various grain-size fractions in sediments. Generally, the finer-grained clay-size fractions have the highest metal concentrations due to large specific surface areas and to the presence of metal-oxide and organic coatings on mineral surfaces that tend to sorb metals. In the silt and sand-size fractions, metal concentrations generally decrease due to the greater abundance of quartz and lower oxide and organic content. The coarse fractions either may increase in metal concentrations, if they include metal-containing minerals (e.g., sulfide minerals), or may decrease in metal concentrations. Filipek and Owen (1979) discuss the influence of grain size on metal distribution in lacustrine sediments.

Physical transport of particulates in ground water encompasses many of the factors involved in surface water plus such factors as complex flow paths and finite pore sizes. Ranville and Schmiermund (1999) provide a description of colloid transport in ground water.

FACTORS AFFECTING METAL BIOAVAILABILITY AND TOXICITY

Because the emphasis of this volume is the environmental geochemistry of mineral deposits, we place emphasis on geological, geochemical, and chemical factors that affect metal bioavailability and toxicity. We also present mining-related examples rather than provide a review of the literature. In doing so, we do not intend to overemphasize the importance of geological, geochemical, and chemical factors. Rather, we endeavor to familiarize earth scientists with some of the linkages that exist between the earth sciences and biological sciences.

Measurement of bioavailability

Because absorption pathways vary with metals, bioavailability for different hosts is measured differently for specific metals within specific biological systems. As noted in the discussion of Figure 2.1, bioavailability may be measured by systemic availability of a metal or by accumulation in organs. For example, the bioavailability of lead can be measured by dose response (or internal dose) of lead levels in blood. In contrast, cadmium levels in laboratory animals are measured by content in livers or kidneys; urine content is not considered to be a reliable indicator of cadmium in test animals because, unlike other metals, cadmium is generally stored in tissue rather than excreted. There are also measurement differences for the same metal. For example, the bioavailability of ingested lead, as measured in Davis et al. (1992), is based on the amount of lead absorbed by digestion. This is not equivalent to blood-lead measurements since lead is transported by the blood to soft tissues and bone. Krieger et al. (1999) discuss bioavailability of arsenic, cadmium, and lead.

Host-related factors

Biologically related factors, such as mode of exposure, cumulative residence time in the host, ability of the host to absorb a particular size or compound, presence of other metals in the host, genetics, host species, and age and development of the host, affect the bioavailability of a particular metal. Host-related factors are very important to metal bioavailability and toxicity, and are also very complex; we include only a brief discussion of these factors in this chapter. For more detailed discussions relating to metals, refer to Fergusson (1990), Goyer (1991), Goyer et al. (1995), and Chang (1996).

Mode of exposure significantly affects bioavailability. Natural modes of exposure to humans include inhalation, ingestion, and transfer through the skin. Potential for airborne exposure to metals in the workplace and in ambient air is significant. Inhaled metals may increase susceptibility to respiratory infection, may be related to immune suppression (Selgrade and Gardner, 1996), or may be associated with pulmonary carcinomas (Gordon, 1995). Ingestion of toxicants commonly takes place through food or water. Ingestion of soil is a significant mode of exposure of metals to children. The significance of this mode of exposure is related to behavioral characteristics of small children (i.e., the hand-to-mouth action of most small children; Beck et al., 1995). Gulson et al. (1994a) found that ingestion of soil and dust is the main source for elevated blood-lead levels in children from a mining community in Australia. Skin does a good job of keeping out water, particles, ionic inorganic species, and materials of high molecular weight. However, skin does not keep out lipid-soluble substances and therefore is susceptible to the absorption of organometallic compounds (Fergusson, 1990).

Cumulative residence time in the host is different for different metals and different hosts. For example, lead is particularly toxic to children, who absorb it much more readily than adults. Hemphill et al. (1991) report that absorption of ingested lead is <20% in adults, and <53% in children. In contrast to lead, cadmium accumulates gradually in the human body, and so becomes increasingly concentrated in adults. Thus, adults generally exhibit higher cadmium levels than children.

Airborne particles exist in fine (<2.5 µm) and coarse (>2.5 µm) sizes; particles from anthropogenic sources (e.g., smelters) are usually fine. In the case of lead, inhalation is much more dangerous if the particle size is fine. Goyer (1991) reports that, for particle sizes smaller than 0.5 µm, human lungs retain 90% of the particles and absorb almost 100% of the retained lead. Larger particles are generally swallowed. This may help to explain why people living in mining communities that once had smelters generally have greater blood-lead levels than those living in mining areas without smelters.

As previously mentioned, the toxicity of chromium depends on its oxidation state, with chromium (VI) being more toxic than chromium (III). The National Research Council (1989) notes that most dietary chromium is trivalent, which is relatively nontoxic; humans cannot oxidize this to chromium (VI). Toxicity of chromium has been associated with bronchial cancer related to occupational exposure to dust in chromium metallurgical, refinery, or manufacturing operations. This dust is generally a mixture of chromium (III) and chromium (VI). A 1972 study of German workers exposed for 20–25 years to chromium (III) in manufacturing reveals no lung cancer among the workers (Luckey and Venugopal, 1977). However, chromium (III) is the metabolically active form within humans, and may be toxic in some cases (Goyer, 1991). Klein (1996) states that the carcinogenic risk associated with human exposure to chromium seems to be most directly correlated with particular chromium oxidation states, with the greatest observed risks associated with exposure to chromium(VI) compounds such as chromates. Whether chromium causes cancer outside the respiratory tract is unclear.

Some metal compounds are known to be more bioavailable than others. A variety of metal-carbon compounds are lipid soluble, and hence presumably can penetrate lipid membranes. For example, methyl mercury, tributyl tin, and tetraethyl lead can dissolve in cell membranes. Pelletier (1995) provides an overview of the environmental chemistry of these organometallic compounds.

Interactions among elements in the host affect the bioavailability and the dose response in the host. For example, people with low intake of calcium, iron, or phosphorous can increase absorption of lead from their diet. As noted above, even slightly greater than optimal concentrations of zinc can diminish absorption of copper by humans; but zinc can provide protection against cadmium and lead toxicities (Sandstead, 1980, 1988; Hill, 1988). In another example, phosphate depletion, negative phosphorous balance, or problems with phosphorous reactions can create aluminum toxicity, even though ingested aluminum generally is not a toxic substance to humans (Luckey and Venugopal, 1977). Cattle with excess dietary exposure to molybdenum can be treated by addition of copper sulfate to their diet (Goyer, 1991) because high concentrations of copper in the body decrease uptake of molybdenum. Selenium uptake by alfalfa may be diminished by moderate sulfur concentrations in the soil (Severson et al., 1991; Severson and Gough, 1992).

Genetic effects on the susceptibility and tolerance to contaminants are documented for several types of organisms. For example, Bryan (1976) provides a review of metal tolerance in estuarine invertebrates, and metal tolerance in plants is discussed in Shaw (1990). The importance of genetic factors in human metal toxicity is not well known; a National Academy of Sciences report states that the role of genetic factors in susceptibility to lead toxicity has received little attention (NRC, 1993).

Different types of plants absorb elements at different rates under otherwise similar circumstances. Plants may be classified as accumulators or excluders of metals (Fergusson, 1990). In smelter-contaminated soils in New Mexico containing 2,000–10,000 ppm lead, rabbitbrush contained approximately 3 times the lead level of adjacent cactus or creosote (Austin et al., 1992). Selenium is absorbed to an unusual degree by a limited number of plant species, some of which serve as livestock feed (Erdman et al., 1991). For example, in parts of the arid west some species of *Astragalus* contain several thousand ppm selenium compared with grasses in the same soil that contain only a few ppm selenium (Thornton, 1982). Other plants, such as wheat, do not contain abnormal selenium even when grown in high-selenium soils. Selenium uptake in wheat requires "selenium converter plants" to change the soil selenium to a form that is absorbable by wheat (Ensminger et al., 1994).

Metal-tolerant plants avoid toxic effects in a variety of ways. Some species accumulate the metals in the roots and restrict access to shoots. Others may bind the metals in complexes that isolate them from sensitive sites (Thurman, 1982). Uptake from soil can be "passive" (due to diffusion based on concentration differences), "facilitated" (due to increased availability from chemical changes induced by roots), or "active" (due to metabolic selection and concentration by roots; Phipps, 1981). An example of facilitated uptake is organic-acid exudates from roots that are known to drop the pH of the rhizosphere, thus dissolving metal carbonates and freeing them for assimilation (Gough et al., 1980).

Age and development of the host play a role in bioavailability. For example, blood lead levels in humans appear to decrease during adolescence, evidently due to lead deposition in bone, and increase during menopause and osteoporosis, apparently due to demineralization of bone (Goyer, 1995). Many toxic metals exert their most serious adverse effects during fetal development. For example, lead and mercury can be transferred from the placenta to the fetus; however, the placenta selectively retains cadmium (Goyer, 1995).

Chemical, geochemical, and geological factors

Most metals cannot be considered solely detrimental because they commonly are also essential micronutrients for plants and animals. Uptake and accumulation of metals by organisms provides an essential link between the types, concentrations, forms, and species of metals in the environment and the effects that these have on living systems. Physical chemistry, geochemistry, and geology can significantly influence the bioavailability of metals to organisms. Kelly (1999) discusses toxic effects on aquatic biota of metals associated with mining activities.

Chemical factors

Chemical factors, such as water composition (e.g., pH, hardness) and chemical and physical properties of elements (e.g., oxidation state), can influence element bioavailability in aquatic systems. The pH of a system is often a master variable that governs reactions and processes in the system; this, in turn, will influence bioavailability. For example, the bioavailability of cationic metals to aquatic organisms is generally greater in the acidic pH range than in the alkaline range. A study of metal bioavailability in lakes showed that fish in lakes with lower pH usually had higher body or tissue burdens of aluminum, cadmium, lead, and mercury than fish in nearby lakes with higher pH (Spry and Weiner, 1991). These relationships largely are due to pH-dependent metal speciation (see discussion below). Frequently, amendments are used to alter the pH of a soil in order to control metal availability because pH is a major factor in determining the free metal ion activity in the soil interstitial water (e.g., Pierzynski and Schwab, 1993). Kabata-Pendias and Pendias (1992) state that to provide an effective evaluation of the pool of bioavailable trace elements, techniques based on both soil tests and plant analyses should be used together. For example, cadmium uptake by plants generally is inversely related to soil pH (Andersson and Nilsson, 1974). Alloway et al. (1988) report that cadmium concentrations in various crops are highest for crops grown on acidic soils, and Jackson and Alloway (1991) show that application of lime to soils amended with sewage sludge reduced cadmium bioavailability to cabbage and lettuce, but not to potatoes. Conversely, anionic metals, such as molybdenum, are usually more bioavailable in alkaline soils (e.g., Smith et al., 1997). This different behavior of cationic and anionic elements is due primarily to pH-dependent sorption reactions in the soils (see Smith, 1999).

Water hardness may affect the toxicity of some metals. Water hardness refers to the concentration of calcium and magnesium ions, as well as other polyvalent metals such as manganese, iron, and aluminum. In general, most metals are more toxic to aquatic life in soft (total hardness <75 mg/l) water rather than hard water (Zitko and Carson, 1976). According to Sprague (1985), heavy metals are an order of magnitude more toxic to aquatic life in very soft water than in very hard water; he attributed this increased toxicity to increased membrane permeability due low calcium concentrations. This toxicity-hardness relationship drives the hardness-based water quality criteria shown in Table 2.7A.

Oxidation state influences toxicity of metals. Molybdenum (VI) and chromium (VI), for example, are much more toxic than molybdenum (II) (commonly occurring as a sulfide mineral) or chromium (III). Similarly, toxicity of arsenic varies with oxidation state. Toxicity increases such that:

$$As^{o} < As^{5+} < As^{3+}$$

(Valberg et al., 1994).

Nieboer and Richardson (1980) modified existing systems of classification of metal ions, based upon those of Ahrland et al. (1958) and Pearson (1963, 1968a, 1968b) (discussed briefly in a previous section) and presented them in a more biological context (Fig. 2.14). According to Nieboer and Richardson's classification, Class A metals, which tend to seek oxygen-containing ligands, comprise all the macronutrient metals (such as potassium and calcium). Class B metals, which tend to seek nitrogen- and sulfur-containing groups, include many of the more toxic metals. Borderline metals, which have intermediate properties, include most of the common metals. As shown on Figure 2.14, there is a distinct break between Class A metals and the borderline group, but there is little distinction between the borderline group and Class B metals. This type of approach can provide a general set of criteria by which the actions of different metals can be compared. For example, Class B metals may displace borderline metals, such as zinc or copper, from enzymes. The toxicity of a borderline metal depends on its Class B character; it will be able to displace many Class A metals and, depending upon their relative affinities, other borderline metals. With the exception of barium, characteristically hazardous metals (see Table 2.6) are either class B or borderline based on Nieboer and Richardson's (1980) classification.

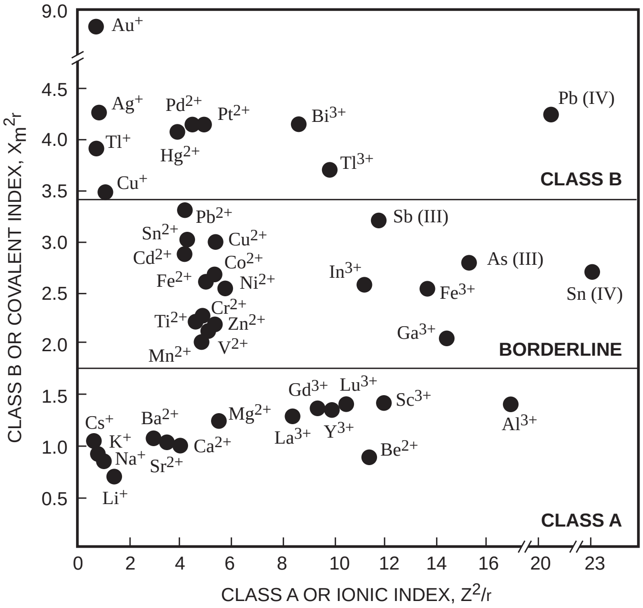

FIGURE 2.14—Chemical classification of metal ions according to Nieboer and Richardson (1980). X_m is the Pauling electronegativity, r is the effective ionic radius, and Z is the formal ion charge. Modified from Nieboer and Richardson (1980).

Geochemical and geological factors

Simple relationships between metal concentrations in organisms and total metal concentrations in the food, water, or sediment to which the organisms are exposed, are seldom found in natural systems (Jenne and Luoma, 1977). Consequently, it is not sufficient to determine total metal concentrations in earth materials if the ultimate goal is to estimate bioavailability of the metals. (However, the total metal concentrations do place an upper limit on metal bioavailability.) Luoma (1989, p. 380) states, "extensive trace metal analyses of sediment, water and biotic tissues through the last decade demonstrate that bioaccumulation by plants and animals may vary considerably from one environment to the next, independent of concentration in sediment or water." For example, Erdman et al. (1976) found no strong correlation between element concentrations in crops and associated soils in Missouri. Pascoe et al. (1994) performed a food-chain transfer analysis for resident small mammals in a wetland habitat to evaluate the impacts of mining wastes on bioaccumulation of metals at the Milltown Reservoir Sediments Superfund site in Montana. Although several metals are present in high concentrations in the mining wastes, Pascoe et al. (1994) found limited bioavailability of these metals and arsenic to resident small mammals. On the other hand, in a study of invertebrates and vegetation associated with mine tailings from base-metal rich gold veins in British Columbia, Azcue et al. (1995) found arsenic, lead, and cadmium to be highly bioavailable; however, the metals appeared to be less bioavailable to invertebrates in a lake ecosystem that receives and accumulates the tailings.

Aquatic organisms may accumulate metals from the dissolved phase, suspended particulates, bottom sediments, and prey or food sources. However, it is not clear if water, particulate material, or food source is the primary route of exposure in natural systems. Questions remain as to what environmental variables should be monitored and regulated. Luoma and Carter (1993, p. 793) state that "understanding of the actual toxicity of sediments in nature is constrained by inadequate knowledge of processes in ecosystems that contain contaminated sediments." Figure 2.15 summarizes some of the processes and geochemical conditions that can redistribute dissolved metal cations among various reservoirs. Several publications address biological and geochemical processes that affect metal bioavailability in surface-water systems (e.g., Luoma, 1983; Morel and Hudson, 1985; Brezonik et al., 1991; Tessier and Turner, 1995).

Mineralogy and mode of occurrence can affect bioavailability of metals. For example, Mahaffey (1978) notes that, all other things being equal, bioavailability of ingested lead in lab rats increases in the following order:

lead chromate, lead sulfide, lead molybdate < lead acetate
< lead oxalate, lead carbonate.

Preliminary results from a study of lead bioavailability in soils and other test materials using juvenile swine indicate that ingested lead carbonate has high relative bioavailability, lead oxide and lead phosphate have intermediate relative bioavailability, and lead sulfide, lead sulfate, and native lead have low relative bioavailability (U.S. EPA, 1997). This sequence may differ from the order of increasing geoavailability, dispersivity, or mobility.

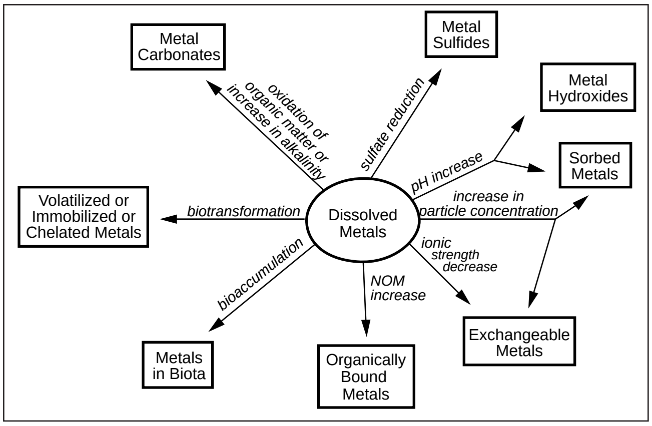

FIGURE 2.15—Some processes and geochemical conditions that can redistribute cationic dissolved metals in oxidizing, circumneutral-pH systems. Metals contained in each of the reservoirs (illustrated by boxes in the figure) also can be redistributed by geochemical or biological processes or by changing geochemical conditions. "NOM" refers to natural organic matter.

The bioavailability of soil-bound metals is related to the physicochemical form of the metal in the soil. Ingestion of soil by animals and humans can be an important route of exposure for metals. Generally, the more soluble a metal is, the more bioavailable it is (Sheppard et al., 1995). Ruby et al. (1992) demonstrate that dissolution kinetics must be considered when assessing metal availability from minerals or soils. The soluble metal salts often used in toxicological studies are not a good proxy for kinetically-controlled dissolution of minerals in the gut (Davis et al., 1992; Freeman et al., 1992; Ruby et al., 1992). Ruby et al. (1993) developed a screening method to evaluate the bioaccessibility of ingested lead. Wixson and Davies (1994) propose a protocol for decisions and guidelines concerning lead in soil.

Lead levels in blood provide an example of the variability in lead bioavailability from different sources. Recent studies of children living in and near inactive tailings or mill dumps in four Colorado areas—Leadville, Smuggler Mountain (Aspen), Telluride, and the Clear Creek-Black Hawk-Central City region—and in Park City, Utah, show relatively little enrichment of lead in blood compared to the national average, except for Leadville (Table 2.17). During the 1980s, the national average blood-lead level for children declined from 17 µg/dl to approximately 4–6 µg/dl (U.S. EPA, 1991). These statistics are for all children; Table 2.17 refers to children under 6 years of age. The first three studies shown in Table 2.17 are from blood samples taken in 1986–1987; the last three are from samples taken in 1990–1991. These are separated because the national blood-lead level of people continued to drop (to 2.9 µg/dl for people aged 1–74 years in 1989–1991) due to phasing out of leaded gasoline and lead solder in food containers (Univ. of Cincinnati, 1997). The current Centers for Disease Control "level of concern" for lead content in blood is 10 µg/dl. As Table 2.17 shows, only the 1987 blood samples for Leadville exhibit arithmetic mean blood-lead levels above 10 µg/dl; the more recent (and larger) study indicates that these levels have dropped even faster than the national trend and are within health safety ranges (Univ. of Cincinnati, 1997). It should be

TABLE 2.17—Blood-lead levels in children and soil-lead contents in mining towns. Sources: Colorado Dept. of Health (1990); Colorado Dept. of Health (1992); Colorado Dept. of Health (1993); Agency for Toxic Substances and Disease Registry (1988); Univ. of Cincinnati (1997). Means are arithmetic means unless otherwise noted.

Location	Blood sampling year	Mean blood lead in children(1) (µg/dl)	Soil range (ppm)	Soil mean (ppm)
Telluride, Colorado	1986	6.7(3); 7.4		641(3); 1370
Park City, Utah	1987	7.8(3)	16–5,840	
Leadville, Colorado	1987	8.7(3); 10.1		
front yard cores			49–15,100	1,108(3); 1,762
rear yard cores			10–27,800	915(3); 1,625
Leadville, Colorado(4)	1991	4.8(3); 5.53	118–15,403	812(3)
Aspen (Smuggler Mtn.), Colorado	1990	2.6(3); 3.0	135–11,676(2)	641(3); 1,370
Clear Creek/Central City, Colorado	1990	5.9(3); 6.3	10–2,590(2)	201(3); 375

(1) Blood levels shown for children less than 6 years of age.
(2) Soil values for households with children less than 6 years of age. In Smuggler Mt., soil samples for adults and children's yards range from 0–46,100 ppm Pb, with means of 505 ppm(3) and 1,155 ppm Pb (Colorado Dept. of Health, 1992).
(3) Geometric mean.
(4) Two studies of Leadville show a drop in mean blood level in children over 4 years' time (see text).

noted that some variation in the blood-lead levels of children may be due to differences in the studies; geometric mean soil contents for lead are slightly lower in the second study.

Blood-lead levels in children may depend partially on the geoavailability of the lead source. In a study at Butte, Montana, Davis et al. (1993) report that low blood-lead levels in young children are due to the low solubility of lead minerals in the soil and waste rock. Figure 2.16 shows that children living in the mining district of Butte, Montana, had lower blood-lead levels than children living in Cincinnati, urban Minnesota, or adjacent to smelters. Similar observations were noted in a study in a mining village in the United Kingdom where, although garden soils and household dust averaged 7,000 and 1,500 ppm lead, respectively, blood lead levels were within the normal range. The researchers found that the lead in lead-rich soils was primarily present as pyromorphite ($Pb_5(PO_4)_3Cl$), a relatively insoluble lead mineral. They attribute the lower-than-expected blood lead levels to the predominance of this mineral phase (Cotter-Howells and Thornton, 1991). Tingle et al. (1993) found that lead tends to be adsorbed onto mineral surfaces in tailings or soils with near-neutral pH. However, tailings with low-pH (pH~2) have little or no detectable surface-bound lead. Presence of surface-bound lead, and of smelter-impacted soils, may help to explain the higher blood-lead levels in children in the 1987 sampling at Leadville. Gulson et al. (1994b) applied mineral-exploration techniques to determine the sources and pathways of lead into children living in a zinc-lead mining district in Australia. They report some cases where elevated blood-lead levels in children appear to be derived from orebody lead, but they found other cases where lead appears to be derived from gasoline lead or paint.

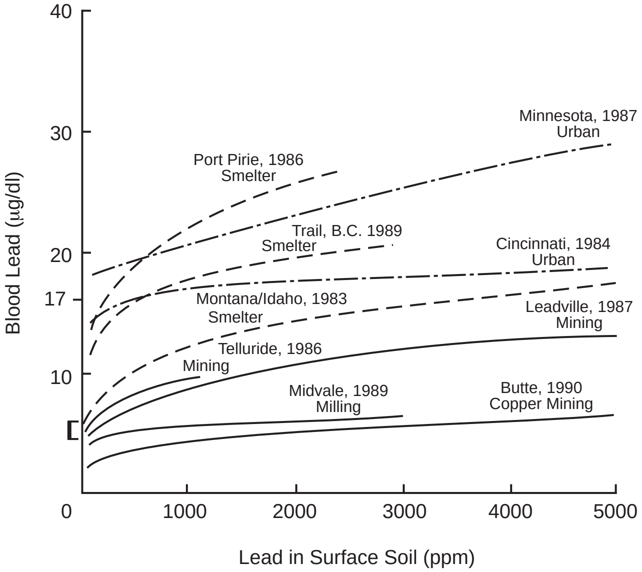

FIGURE 2.16—Blood-lead levels in children from mining (solid lines), smelter (dashed lines), and urban (dash-dot lines) sites in the United States. Modified from Gulson et al. (1994b, Fig. 12). During the 1980s, the national average blood-lead level for U.S. children declined from 17 µg/dl (noted) to approximately 4–6 µg/dl (bracket) (U.S. EPA, 1991). These ranges are shown because most of the studies were published in the 1980s. These averages are for all U.S. children under the age of 18 years.

Sediment texture can play a role in metal bioavailability. For example, Pesch and Morgan (1978) showed that a polychaete (a type of worm) exhibited greater bioaccumulation when exposed to metal-spiked water mixed with sandy sediment than when exposed to water mixed with fine-grained sediment. This is probably due to the higher metal-binding capacity of fine-grained sediment.

Metal speciation

Nieboer and Fletcher (1996) define speciation as "the occurrence of an element in separate, identifiable forms (i.e., chemical, physical, or morphological state)." The speciation of an element, rather than its total concentration, influences its effects on an organism. Factors that affect speciation include pH and redox conditions, the solubility of solid compounds, the oxidation state of the element, the availability and type of complexing agents, complex and ion-pair formation, sorption-desorption reactions, and biochemical processes.

The bioavailability and toxicity of metals may be strongly modified by the chemical partitioning of metals in food components (e.g., Luoma and Jenne, 1977), the speciation of metals in solution (e.g., Pagenkopf et al., 1974; Sunda and Guillard, 1976; Andrew et al., 1977; Driscoll et al., 1980), and the speciation of metals in sediments and soils (Luoma and Jenne, 1976, 1977). For example, Phipps (1981, p. 31) illustrates the importance of aqueous copper speciation on copper uptake by excised roots, with

$$[Cu(II)(OH_2)]^{2+} \sim [Cu(II)(en)_2]^{2+} > [Cu(II)(gly)_2]^o$$
$$>> [Cu(II)EDTA]^-,$$

where en, gly, and EDTA are organic ligands. This sequence of root uptake follows the overall charges of the copper complexes (Phipps, 1981).

Metal concentrations in soils and sediments are commonly several orders of magnitude greater than those found in associated waters. Metals can partition among various components of soils or sediments and may be (1) sorbed on hydrous metal oxides, organic matter, or clays, (2) present in the lattice of primary or secondary minerals, or (3) occluded in amorphous materials or remains of organisms. Salomons (1995) relates metal speciation to potential relative mobility with the following distinctions:

Exchangeable cations	High mobility
Metals associated with iron and manganese hydroxides	Medium mobility
Metals bound or fixed inside organic substances	Medium mobility
Metals bound or fixed inside mineral particles	Low mobility
Metals associated with a sulfidic phase	Strongly dependent on environmental conditions

In a study of the Amazon and Yukon rivers, Gibbs (1973) found that copper and chromium are mainly associated with mineral particles, manganese is present in oxide coatings, and iron, nickel, and cobalt are equally distributed between solids and coatings. Differences in metal bioavailability occur when metals are bound to different types of binding sites on particles (Luoma and Jenne, 1977; Campbell and Tessier, 1991). Luoma and Davis (1983, p. 161) state that "…with some exceptions, the metal particle reactions which are biologically most important in estuaries are those that affect metal distributions among the organic and inorganic components of fine-grained, oxidized sediments."

The composition of the suspended phase influences the physicochemical form in which a metal is transported, which in turn influences bioavailability (e.g., Luoma and Bryan, 1979). Bioavailability also can be affected by the preferential partitioning of metals to the suspended sediment and consequent removal from the dissolved phase since metals are generally more bioavailable when dissolved.

Geochemical methods to estimate metal speciation and bioavailability

In aqueous systems, the simplest speciation distinction is between what does and does not pass through a filter. The filter pore size determines what passes through a filtering unit (filtrate). The filtrate includes free ions and their complexes with various ligands and, perhaps, colloidal materials. Tanizaki et al. (1992) used filtration and ultrafiltration techniques to determine the physicochemical forms of several elements in river water (see Ranville and Schmiermund, 1999).

Generally, the free-ion concentrations of dissolved metals are the best indicator of bioavailability and toxic effects to aquatic organisms (O'Donnel et al., 1985) and crops (Kabata-Pendias and Pendias, 1992). Free metal ion concentrations in waters are determined either with specialized chemical and analytical techniques or with thermodynamically-based chemical-equilibrium calculations. These calculations are done with the aid of computer programs; when using these computer programs it is important to be aware of their limitations. Failure to (1) include all of the important species (e.g., major elements, organics), (2) consider all of the possible reactions (e.g., sorption), or (3) verify the validity of any inherent assumptions (e.g., thermodynamically versus kinetically-controlled reactions; reliability of stability constant data) may lead to erroneous conclusions. Hence, these models provide a qualitative estimate of the actual reactions and interrelationships between aqueous speciation and bioavailability. Turner (1995) provides a detailed discussion of problems in modeling trace metal speciation. An extension of the modeling approach is the free-ion activity model (FIAM; Morel, 1983), which was developed to link metal speciation with bioavailability in controlled laboratory studies, and has since been extrapolated to natural waters. Campbell (1995) describes and critiques the FIAM.

Quantification of metal speciation also requires specialized techniques. For example, it is necessary to distinguish the carcinogenic form of chromium (Cr(VI)) from the noncarcinogenic forms (Cr(III) and elemental chromium). Reliable analytical techniques, especially field techniques, have yet to be developed for many important speciation issues.

Predictions of metal bioavailability in soils and sediments have met with limited success. Metal speciation in soils and sediments can be determined by direct instrumental techniques (e.g., x-ray diffraction, electron microprobe, various spectroscopic methods), physical separation (e.g., size, density, magnetism), and chemical extractants. Partial chemical extractions or sequential extractions of soils and sediments are used to extract only the bioavailable fraction of metal (e.g., Pickering, 1981) or only the fraction associated with particular components of the soil or sediment (e.g., Tessier et al., 1979; Filipek et al., 1981; Luoma and Bryan, 1981; Chao, 1984). However, incomplete knowledge of the complicated chemistry of soils and sediments, coupled with the lack of selectivity of some reagents, can make interpretation difficult (e.g., Luoma, 1989; Filipek and Theobald, 1981; Papp et al., 1991). Despite the limitations, partial extractions remain a useful technique for the examination of metals associated with various components in soils and sediments that serve as controls of metal mobility (Gatehouse et al., 1977; Lion et al., 1982; Chao, 1984). Positive assessment of partial dissolution techniques by Tessier et al. (1979) includes information about the origin and mode of occurrence of metals, physicochemical availability, and mobility of trace elements in the environment. In soil/plant studies with diverse soil types, the correlation between estimates of metal bioavailability and plant uptake is marginal (e.g., Gough et al., 1980). However, in agriculture partial dissolution techniques are used successfully to determine nutrient availability from soils to crops (Westerman, 1990). A few studies have been conducted with aquatic sediments and several different extraction procedures have shown correlations with metal bioavailability (e.g., Diks and Allen, 1983; Luoma, 1983), but no single approach is consistently successful (e.g., Weimin et al., 1992). Predictive capabilities may be improved by the use of normalizing parameters, such as iron (Luoma and Bryan, 1981), organic matter (Langston, 1982), or H^+/iron oxyhydroxide (Tessier et al., 1984).

ENVIRONMENTAL GEOCHEMISTRY AND HEALTH

The field of environmental geochemistry and health involves the application of geochemistry, in particular geochemical mapping, to studies of plant, animal, and human health (Lag, 1983; Thornton, 1993; Cotter-Howells, 1996). This requires combining the disciplines of geochemistry, geology, chemistry, soil science, botany, zoology, microbiology, animal husbandry, veterinary science, epidemiology, and public health. Links between geochemistry and human health are usually difficult to establish. Warren (1989) provides an overview of potential health implications of exposure to Al, As, Au, Cd, Cu, Hg, I, Pt, Se, and Zn in the environment.

Geochemical maps have been used to correlate areas of trace-element deficiency or excess with problems in crops and animal nutrition (e.g., Thornton, 1983), and to identify areas where the population may be exposed to unusually great concentrations of metals (e.g., Morgan, 1988). A reconnaissance geochemical survey of Missouri by the U.S. Geological Survey provided information to epidemiologists in search of relationships between geochemistry of the environment and human health (see Miesch, 1976). Geochemical atlases have been generated for various European countries (e.g., Webb et al., 1978); they provide the geochemical basis for studies that seek links between geochemistry and health. Simpson (1995) describes the Geochemical Baseline Survey of the Environment (G-BASE) for the United Kingdom. Examples of other studies include Piispanen (1989), who compared disease maps with geochemical maps in Finland, and Irvine et al. (1988), who proposed a link between multiple sclerosis clusters in Saskatchewan and excess lead, nickel, and zinc in the soil. These types of studies do not demonstrate a direct association between trace elements and disease, but they do show that trace elements may influence health. Accordingly, public-health measures can be taken to reduce exposure to trace elements in problem areas. Shaper (1979) and Thornton (1987) outline some of the potential problems associated with this approach.

There are several well-known correlations between health and trace elements. For example, iodine deficiency can result in enlargement of the thyroid gland, iron deficiency can cause anemia, fluoride deficiency has been associated with high rates of dental caries, and Keshan Disease in China has responded to treatment with selenium (McLaren, 1994).

The relationship between the environment and human health is illustrated by the mercury incident in Minamata Bay, Japan. In the 1930s a chemical plant began discharging mercury into Minamata Bay. The mercury was converted to methylmercury by microorganisms (Zakrzewski, 1991). In the 1960s, local residents began to show symptoms such as sensory impairment and approximately 6% of the infants born near Minamata had cerebral palsy (Eisler, 1987). By 1982, methylmercury poisoning was diagnosed in some local residents, more than 50 people died, and 700 were left permanently paralyzed (Kudo and Miyahara, 1984). The methylmercury accumulated in fish and birds, and because fish was a staple in the diet of the local residents, ingestion of the mercury-contaminated fish led to what has become known as Minamata disease.

Another example is a bone disease, known as itai-itai ("ouch-ouch") disease, found in people in Japan exposed to large amounts of cadmium in food during the later part of World War II. Itai-itai disease occurred in people living downstream from a lead-zinc mine who used contaminated river water for drinking and irrigation of rice paddies. The relationship between itai-itai disease and cadmium is based on increased disease prevalence in areas of highest cadmium exposure, concomitant kidney disease that corresponds to cadmium-related kidney disease in industrial workers, and high cadmium concentrations in blood, urine, and organs (Bhattacharyya et al., 1995).

Chronic thallium poisoning was reported in a rural area of Southwest Guizhou Province, China, in the 1960s and 1970s. Weathering of waste slag from coal and mercury mining released thallium to overlying soil, and the thallium accumulated in vegetables that were ingested by humans (Zhou and Liu, 1985).

CONCLUDING REMARKS

Metals can be both essential and toxic to humans (Maugh, 1973; Mertz, 1981). Unlike some organic contaminants, metals do not break down in the environment; they are neither created nor destroyed by human activities. However, human activities can perturb the natural cycles of metals and redistribute them throughout the various reservoirs of natural systems (Nriagu and Pacyna, 1988; Nriagu, 1990). Contamination associated with mineral extraction has prompted controversies about human-health issues (Moore and Luoma, 1990).

The metal content of biota is often influenced by the geochemical nature of their habitat. This reflects a general pattern of metal transfer from the terrestrial to the biotic environment (Chang and Page, 1996). There is considerable evidence that the bioavailability and toxicity of metals are influenced by the speciation and physicochemical forms in which metals are present in waters, sediments, and soils (Jenne and Luoma, 1977; Allen et al., 1980). The speciation of metals in the environment is controlled by an interrelated web of chemical, geochemical, and biological processes that control the behavior and mobility of metals in the surficial environment. A first approximation of metal behavior and mobility often can be made based on a knowledge of the physicochemical properties of metals, and on empirical observations.

It is important to combine physicochemical, geochemical, geological, and biological information in the study of metal bioavailability and toxicity. Much remains to be learned about interactions and interferences among metals and their combined effects on physiology. However, it is clear that a holistic approach is required to adequately understand and assess the environmental impacts of metals on human health.

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REFERENCES

Adriano, D.C., 1986, Trace elements in the terrestrial environment: Springer-Verlag, New York, 533 pp.

Agency for Toxic Substances and Disease Registry, 1988, The Silver Creek mine tailings exposure study: Final report, technical assistance to the Summit City/County, Utah, Health Dept., 48 pp.

Agency for Toxic Substances and Disease Registry, 1992, Toxicological profile for aluminum: U.S. Dept. of Health and Human Services, TP-91/01, 136 pp.

Agency for Toxic Substances and Disease Registry, 1993, Toxicological profile for arsenic: U.S. Dept. of Health and Human Services, TP-92/02, 175 pp.

Ahrland, S., Chatt, J., and Davies, N.R., 1958, The relative affinities of ligand atoms for acceptor molecules and ions: Quarterly Reviews Chemical Society, v. 12, pp. 265–276.

Allen, H.E., Hall, R.H., and Brisbin, T.D., 1980, Metal speciation effects on aquatic toxicity: Environmental Science and Technology, v. 14, pp. 441–443.

Alloway, B.J., Thornton, I., Smart, G.A., Sherlock, J.C., and Quinn, M.J., 1988, Metal availability: Science of the Total Environment, v. 75, pp. 41–69.

Andersson, A., and Nilsson, K.O., 1974, Influence of lime and soil pH on Cd availability to plants: Ambio, v. 3, pp. 198–200.

Andrew, R.W., Biesinger, K.E., and Glass, G.E., 1977, Effects of inorganic complexing on the toxicity of copper to Daphnia magna: Water Research, v. 11, pp. 309–315.

Austin, G.S., Branduold, L.A., Hawley, J.W., and Renault, J., 1992, Lead contamination at old smelter sites in the West—The Socorro, New Mexico case history: Society for Mining, Metallurgy, and Exploration, Inc., Preprint No. 92–99, 13 pp.

Axtmann, E.V., and Luoma, S.N., 1991, Large scale distribution of metal contamination in fine-grained sediments of the Clark Fork River, Montana, USA: Applied Geochemistry, v. 6, pp. 75–88.

Azcue, J.M., Mudroch, A., Rosa, F., Hall, G.E.M., Jackson, T.A., and Reynoldson, T., 1995, Trace elements in water, sediments, porewater, and biota polluted by tailings from an abandoned gold mine in British Columbia, Canada: Journal of Geochemical Exploration, v. 52, pp. 25–34.

Bartell, S.M., Gardner, R.H., and O'Neill, R.V., 1992, Ecological risk estimation: Lewis Publishers, Chelsea, Mich., 252 pp.

Beck, B.D., Rudel, R, Hook, G.C., and Bowers, T.S., 1995, Risk assessment; *in* Goyer, R.A., Klaassen, C.D., and Waalkes, M.P. (eds.), Metal Toxicology: Academic Press, San Diego, Calif., pp. 141–185.

Beus, A.A., and Grigorian, S.V., 1977, Geochemical exploration methods for mineral deposits: Applied Publishing Ltd., Wilmette, Ill., 287 pp.

Bhattacharyya, M.H., Wilson, A.K., Silbergeld, E.K., Watson, L., and Jeffery, E., 1995, Metal-induced osteotoxicities; *in* Goyer, R.A., Klaassen, C.D., and Waalkes, M.P. (eds.), Metal Toxicology: Academic Press, San Diego, Calif., pp. 465–510.

Boyle, R.W., 1974, Elemental associations in mineral deposits and indicator elements of interest in geochemical prospecting: Geological Survey of Canada Paper 74–45, 40 pp.

Brezonik, P.L., King, S.O., and Mach, C.E., 1991, The influence of water chemistry on trace metal bioavailability and toxicity to aquatic organisms; *in* Newman, M.C., and McIntosh, A.W. (eds.), Metal Ecotoxicology, Concepts and Applications: Lewis Publishers, Chelsea, Mich., pp. 1–31.

Bryan, G., 1976, Some aspects of heavy metal tolerance in aquatic organisms; *in* Lockwood A. (ed.), Effects of Pollutants on Aquatic Organisms: Cambridge Univ. Press, Cambridge, Mass., pp. 7–34.

Callahan, M.A., Slimak, M.W., Gabel, N.W., May, I.P., Fowler, C.F., Freed, J.R., Jennings, P., Durfee, R.L., Whitmore, F.C., Maestri, B., Mabey, W.R., Holt, B.R., and Gould, C., 1979, Water-related environmental fate of 129 priority pollutants, Vol. I, Introduction and technical background, metals and inorganics, pesticides and PCB's: U.S. Environmental Protection Agency, EPA-440/4–79–029a.

Campbell, P.G.C., 1995, Interactions between trace metals and aquatic organisms—A critique of the free-ion activity model; *in* Tessier, A., and Turner, D.R. (eds.), Metal Speciation and Bioavailability in Aquatic Systems: John Wiley and Sons, New York, pp. 45–102.

Campbell, P.G.C., and Tessier, Andre, 1991, Biological availability of metals in sediments—Analytical approaches; *in* Vernet, J.-P. (ed.), Heavy Metals in the Environment: Elsevier, N.Y., pp. 161–173.

Chang, A.C., and Page, A.L., 1996, Assessment of ecological and health effects of soil-borne trace elements and metals; *in* Chang, L.W. (ed)., Toxicology of Metals: CRC Press, Boca Raton, Fla., pp. 29–38.

Chang, L.W. (ed.), 1996, Toxicology of metals: CRC Press, Inc., Boca Raton, Fla., 1198 pp.

Chao, T.T., 1984, Use of partial dissolution techniques in geochemical exploration: Journal of Geochemical Exploration, v. 20, pp. 101–135.

Christian, J.L., and Greger, J.L., 1991, Nutrition for living, 3rd ed.: Benjamin/Cummings Pub. Co., Inc., Redwood City, Calif., 651 pp.

Colorado Dept. of Health, 1990, Leadville metals exposure study: Colorado Dept. of Health, Denver, 89 pp.

Colorado Dept. of Health, 1992, Final report, Clear Creek/Central City mine waste exposure study, Part I. Smuggler Mountain Site: Colorado Dept. of Health, Denver, 267 pp.

Colorado Dept. of Health, 1993, Clear Creek/Central City mine waste exposure study, Part II. Clear Creek/Central City Mine Sites: Colorado Dept. of Health, Denver, 90 pp.

Cotter-Howells, J., 1996, Environmental geochemistry and health: Mineralogical Society Bulletin, Sept. 1996, pp. 3–6.

Cotter-Howells, J., and Thornton, I., 1991, Sources and pathways of environmental lead to children in a Derbyshire mining village: Environmental Geochemistry and Health, v. 13, pp. 127–135.

Cotton, F.A., and Wilkinson, Geoffrey, 1988, Advanced inorganic chemistry, 5th ed.: John Wiley and Sons, New York, 1455 pp.

Cox, D.P., and Singer, D.A., 1986, Mineral deposit models: U.S. Geological Survey Bulletin 1693, 379 pp.

Darnley, A.G., 1990, International geochemical mapping—A new global project: Journal of Geochemical Exploration, v. 39, pp. 1–13.

Davis, A., Ruby, M.V., and Bergstrom, P.D., 1992, Bioavailability of arsenic and lead in soils from the Butte, Montana, mining district: Environmental Science and Technology, v. 26, pp. 461–468.

Davis, A., Drexler, J.W., Ruby, M.V., and Nicholson, A., 1993, Micromineralogy of mine wastes in relation to lead bioavailability, Butte, Montana: Environmental Science and Technology, v. 27, pp. 1415–1425.

Davis, J.M., and Elias, R.W., 1996, Risk assessment of metals; *in* Chang, L.W. (ed.), Toxicology of Metals: CRC Press, Inc., Boca Raton, Fla., pp. 55–67.

Dickson, K.L., Giesy, J.P., Parrish, R., and Wolfe, L., 1994, Closing remarks—summary and conclusions; *in* Hamelink, J.L., Landrum, P.F., Bergman, H.L., and Benson W.H. (eds.), Bioavailability—Physical, Chemical, and Biological Interactions, SETAC Spec. Pub. Series: CRC Press, Inc., Boca Raton, Fla., pp. 221–230.

Diks, D.M., and Allen, H.E., 1983, Correlation of copper distribution in a freshwater-sediment system to bioavailability: Bulletin of Environmental Contamination and Toxicology, v. 30, pp. 37–43.

Driscoll, C.T., Baker, J.P., Bisogni, J.J., and Schofield, C.L., 1980, Effect of aluminum speciation on fish in dilute acidified waters: Nature, v. 284, pp. 161–164.

du Bray, E.A. (ed.), 1995, Preliminary compilation of descriptive geoenvironmental mineral deposit models: U.S. Geological Survey Open-File Report 95–831, 272 pp.

Eisler, R., 1987, Mercury hazards to fish, wildlife, and invertebrates—A synoptic review: Biological Report 85(1.10), U.S. Dept. of the Interior, Fish and Wildlife Service, Laurel, Md.

Ensminger, A.H., Ensminger, M.E., Konlande, J.E., and Robson, J.R., 1994, Nutrition encyclopedia, 2nd ed.: CRC Press, Ann Arbor, Mich., 2415 pp. (2 vols.).

Erdman, J.A., Shacklette, H.T., and Keith, J.R., 1976, Elemental composition of corn grains, soybean seeds, pasture grasses, and associated soils from selected areas in Missouri: U.S. Geological Survey Professional Paper 954–D, 23 pp.

Erdman, J.A., Severson, R.C., Crock, J.G., Harms, T.F., and Mayland, H.F., 1991, Selenium in soils and plants from native and irrigated lands at the Kendrick Reclamation Project Area, Wyoming; *in* Severson, R.C., Fisher, Jr., S.E., and Gough, L.P. (eds.), Proceedings of the 1990 Billings Land Reclamation Symposium on Selenium in Arid and Semiarid Environments, Western United States: U.S. Geological Survey Circular 1064, pp. 91–105.

Fan, A.M., 1996, Assessment of metals in drinking water with specific references to lead, copper, arsenic, and selenium; *in* Chang, L.W. (ed.), Toxicology of Metals: CRC Press, Inc., Boca Raton, Fla., pp. 39–53.

Fergusson, J.E., 1990, The heavy elements—chemistry, environmental impact and health effects: Pergamon Press, New York, 614 pp.

Fernandez, M.A., Martinez, L., Segarra, M., Garcia, J.C., and Espiell, F., 1992, Behavior of heavy metals in the combustion gases of urban waste incinerators: Environmental Science and Technology, v. 26, pp. 1040–1047.

Festa, M.D., Anderson, H.L., Dowdy, R.P., and Ellersieck, M.R., 1985, Effect of zinc intake on copper excretion and retention in men: The American Journal of Clinical Nutrition, v. 41, pp. 285–292.

Ficklin, W.H., Plumlee, G.S., Smith, K.S., and McHugh, J.B., 1992, Geochemical classification of mine drainages and natural drainages in mineralized areas; *in* Kharaka, Y.K., and Maest, A.S. (eds.), Water-Rock Interaction, v. 1, 7th Internatl Symposium on Water-Rock Interaction: A.A. Balkema, Rotterdam, pp. 381–384.

Filipek, L.H., and Owen, R.M., 1979, Geochemical associations and grain-size partitioning of heavy metals in lacustrine sediments: Chemical Geology, v. 26, pp. 105–117.

Filipek, L.H., and Theobald, P.K., Jr., 1981, Sequential extraction techniques applied to a porphyry copper deposit in the basin and range province: Journal of Geochemical Exploration, v. 14, pp. 155–174.

Filipek, L.H., Chao, T.T., and Carpenter, R.H., 1981, Factors affecting the partitioning of Cu, Zn and Pb in boulder coatings and stream sediments in the vicinity of a polymetallic sulfide deposit: Chemical Geology, v. 33, pp. 45–64.

Fischer, P.W.F., Giroux, A., and L'Abbé, M.R., 1984, Effect of zinc supplementation on copper status in adult men: The American Journal of Clinical Nutrition, v. 40, pp. 743–746.

Fortescue, J.A.C., 1980, Environmental geochemistry—a holistic approach: Springer-Verlag, New York, 347 pp.

Fortescue, J.A.C., 1992, Landscape geochemistry—Retrospect and prospect—1990: Applied Geochemistry, v. 7, pp. 1–53.

Freeman, G.B., Johnson, J.D., Killinger, J.M., Liao, S.C., Feder, P.I., Davis, A.O., Ruby, M.V., Chaney, R.L., Lovre, S.C., and Bergstrom, P.D., 1992, Relative bioavailability of lead from mining waste soil in rats: Fundamentals of Applied Toxicology, v. 19, pp. 388–398.

Frost, D.V., 1978, The arsenic problems; *in* Schrauzer, G.N. (ed.), Inorganic and Nutritional Aspects of Cancer: Plenum Press, New York, pp. 259–280.

Fuller, W.H., 1977, Movement of selected metals, asbestos, and cyanide in soil—Applications to waste disposal problems: U.S. Environmental Protection Agency, EPA-600/2–77–020, 242 pp.

Gabriel, I.E., and Patten, T., 1994, Distribution of copper smelter emissions in southeastern Arizona—using honey mesquite as a bioindicator: Water, Air, and Soil Pollution, v. 72, pp. 67–87.

Garrels, R.M., and Christ, C.L., 1965, Solutions, minerals, and equilibria: Freeman, Cooper and Company, San Francisco, Calif., 450 pp.

Gatehouse, S., Russell, D.W., and Van Moort, J.C., 1977, Sequential soil analysis in exploration geochemistry: Journal of Geochemical Exploration, v. 8, pp. 483–494.

Germani, M.S., Small, M., Zoller, W.H., and Moyers, J.L., 1981, Fractionation of elements during copper smelting: Environmental Science and Technology, v. 15, pp. 299–305.

Gibbs, R.J., 1973, Mechanisms of trace metal transport in rivers: Science, v. 180, pp. 71–73.

Ginevan, M.E., and Splitstone, D.E., 1997, Improving remediation decisions at hazardous waste sites with risk-based geostatistical analysis: Environ. Sci. Tech., v. 31, pp. 92A–96A.

Goldschmidt, V.M., 1954, Geochemistry: Oxford Univ. Press, Fair Lawn, N.J.

Gordon, T. 1995, Respiratory system; *in* Goyer, R.A., Klaassen, C.D., and Waalkes, M.P. (eds.), Metal Toxicology: Academic Press, San Diego, Calif., pp. 237–263.

Gossel, T.A., and Bricker, J.D., 1984, Metals; *in* Principles of Clinical Toxicology: Raven Press, New York, pp. 153–187.

Gough, L.P., Shacklette, H.T., and Case, A.A., 1979, Element concentrations toxic to plants, animals, and man: U.S. Geological Survey Bulletin 1466, 80 pp.

Gough, L.P., McNeal, J.M., and Severson, R.C., 1980, Predicting native plant copper, iron, manganese and zinc levels using DTPA and EDTA soil extractants, Northern Great Plains: Soil Science Society of America Journal, v. 44, pp. 1030–1035.

Goyer, R.A., 1991, Toxic effects of metals; *in* Amdur, M.O., Doull, J., and Klaassen, C.D. (eds.), Casarett and Doull's Toxicology, The Basic Science of Poisons, 4th ed.: Pergamon Press, New York, pp. 623–680.

Goyer, R.A., 1995, Factors influencing metal toxicity; *in* Goyer, R.A., Klaassen, C.D., and Waalkes, M.P. (eds.), Metal Toxicology: Academic Press, San Diego, Calif., pp. 31–45.

Goyer, R.A., Klaassen, C.D., and Waalkes, M.P. (eds.), 1995, Metal toxicology: Academic Press, San Diego, Calif., 525 pp.

Greenwood, N.N., and Earnshaw, A., 1984, Chemistry of the elements: Pergamon Press, New York, 1542 pp.

Griffith, W.H., 1988, Complete guide to vitamins, minerals and supplements: Fisher Books, Tucson, Ariz., 510 pp.

Gulson, B.L., Davis, J.J., Mizon, K.J., Korsch, M.J., Law, A.J., and Howarth, D., 1994a, Lead bioavailability in the environment of children—Blood lead levels in children can be elevated in a mining community: Archives of Environmental Health, v. 49, pp. 326–331.

Gulson, B.L., Mizon, K.J., Law, A.J., Korsch, M.J., Davis, J.J., and Howarth, D., 1994b, Source and pathways of lead in humans from the Broken Hill mining community—an alternative use of exploration methods: Economic Geology, v. 89, pp. 889–908.

Hayes, J.A., 1989, Metal toxicity; *in* Marquis, J.A. (ed.), A Guide to General Toxicology, 2nd ed.: Karger, New York, pp. 179–189.

Hem, J.D., 1985, Study and interpretation of the chemical characteristics of natural water, 3rd ed.: U.S. Geological Survey Water-Supply Paper 2254, 263 pp.

Hemphill, C.P., Ruby, M.V., Beck, B.D., Davis, A., and Bergstrom, P.D., 1991, The bioavailability of lead in mining wastes—physical/chemical considerations: Chemical Speciation and Bioavailability, v. 3, pp. 135–148.

Hill, C.H., 1988, Interactions among trace elements; *in* Prasad, A.S. (ed.), Essential and Toxic Trace Elements in Human Health and Disease: Alan R. Liss, Inc., New York, pp. 491–500.

Hoffman, G.R., 1991, Genetic toxicology; *in* Amdur, M.O., Doull, J., and Klaassen, C.D. (eds.), Casarett and Doull's Toxicology, the Basic Science of Poisons: Pergamon Press, New York, pp. 201–225.

Horowitz, A.J., 1991, A primer on sediment-trace element chemistry, 2nd ed.: Lewis Publishers, Chelsea, Mich., 136 pp.

Horowitz, A.J., Rinella, F.A., Lamothe, P., Miller, T.L., Edwards, T.K., Roche, R.L., and Rickert, D.A., 1990, Variations in suspended sediment and associated trace element concentrations in selected riverine cross sections: Environmental Science and Technology, v. 24, pp. 1313–1320.

Huheey, J.E., Keiter, E.A., and Keiter, R.L., 1993, Inorganic chemistry—principles of structure and reactivity, 4th ed.: Harper Collins College Publishers, New York, 964 pp.

IGCP, 1995, A global geochemical database for environmental and resource management, recommendations for international geochemical mapping, final report of the International Geological Correlation Programme (IGCP) Project 259, by A.G. Darnley, A. Bjorklund, B. Bolviken, N. Gustavsson, P.V. Koval, J.A. Plant, A. Steenfelt, M. Tauchid, and X. Xuejing: UNESCO Publishing, France, 122 pp.

Irvine, D.G., Schiefer, H.R., and Hader, W.J., 1988, Geotoxicology of multiple sclerosis—The Henribourg, Saskatchewan, cluster focus, II. The soil: Science of the Total Environment, v. 77, pp. 175–188.

Jackson, A.P., and Alloway, B.J., 1991, The transfer of cadmium from sewage sludge amended soils into the edible components of food crops: Water, Air, and Soil Pollution, v. 57–58, pp. 873–881.

Jenne, E.A., and Luoma, S.N., 1977, Forms of trace elements in soils, sediments and associated waters—An overview of their determination and biological availability; *in* Wildung, R.E., and Drucker, H. (eds.), Biological Implications of Metals in the Environment: Technical Information Center, Energy Research and Development Administration Symposium Series 42, NTIS, Springfield, Va., CONF-750929, pp. 110–143.

Kabata-Pendias, A., and Pendias, H., 1992, Trace elements in soils and plants, 2nd ed.: CRC Press, Inc., Boca Raton, Fla., 342 pp.

Kelly, M.G., 1999, Effects of heavy metals on the aquatic biota; *in* Plumlee, G.S., and Logsdon, M.J. (eds.), The Environmental Geochemistry of Mineral Deposits, Part A. Processes, Techniques, and Health Issues: Society of Economic Geologists, Reviews in Economic Geology, v. 6A, pp. 363–371.

Klaassen, C.D., and Eaton, D.L., 1991, Principles of toxicology; *in* Amdur, M.O., Doull, J., and Klaassen, C.D. (eds.), Casarett and Doull's Toxicology, The Basic Science of Poisons: Pergamon Press, New York, pp. 12–49.

Klein, C.B., 1996, Carcinogenicity and genotoxicity of chromium; *in* Chang, L.W. (ed.), Toxicology of Metals: CRC Press, Inc., Boca Raton, Fla., pp. 205–219.

Klein, D.H., Andren, A.W., Carter, J.A., Emery, J.F., Feldman, C., Fulkerson, W., Lyon, W.S., Ogle, J.C., Talmi, Y., Van Hook, R.I., and Bolton, N., 1975, Pathways of thirty-seven elements through coal-fired power plant: Environmental Science and Technology, v. 9, pp. 973–979.

Krieger, G.R., Hattemer-Frey, H.A., and Kester, J.E., 1999, Bioavailability of metals in the environment—Implications for health risk assessment; *in* Plumlee, G.S., and Logsdon, M.J. (eds.), The Environmental Geochemistry of Mineral Deposits, Part A. Processes, Techniques, and Health Issues: Society of Economic Geologists, Reviews in Economic Geology, v. 6A, pp. 357–361.

Kudo, A., and Miyahara, S., 1984, Mercury dispersion from Minamata Bay to the Yatsushiro Sea during 1975–1980: Ecotoxicol. Environ. Safety, v. 8, pp. 507–510.

Lag, J., 1983, Geomedicine in Scandinavia; *in* Thornton, I. (ed.), Applied Environmental Geochemistry: Academic Press, London, pp. 335–353.

Landis, W.G., and Yu, M–H., 1995, Introduction to environmental toxicology: CRC Press, Inc., Boca Raton, Fla., 328 pp.

Langmuir, D., and Mahoney, J.J., 1984, Chemical equilibrium and kinetics of geochemical processes in ground water studies; *in* Hitchon, B., and Wallick, E. (eds.), Practical Applications of Ground Water Geochemistry: National Water Well Association, Dublin, Ohio, pp. 69–95.

Langston, W.J., 1982, Distribution of mercury in British estuarine sediments and its availability to deposit-feeding bivalves: J. Mar. Biol. Assoc. U.K., v. 62, pp. 667–684.

Levinson, A.A., 1980, Introduction to exploration geochemistry, 2nd ed.: Applied Publishing Ltd., Wilmette, Ill., 924 pp.

Li, X., and Thornton, I., 1993, Multi-element contamination of soils and plants in old mining areas, U.K.: Applied Geochemistry, Suppl. Issue no. 2, pp. 51–56.

Lindsay, W.L., 1979, Chemical equilibria in soils: John Wiley and Sons, New York, 449 pp.

Lion, L.W., Altmann, R.S., and Leckie, J.O., 1982, Trace-metal adsorption characteristics of estuarine particulate matter: evaluation of contributions of Fe/Mn oxide and organic surface coatings: Environmental Science and Technology, v. 16, pp. 660–666.

Luckey, T.D., and Venugopal, B., 1977, Metal toxicity in mammals, Vol. 1, Physiologic and chemical basis for metal toxicity: Plenum Press, New York, 238 pp.

Lukashev, V.K., 1984, Mode of occurrence of elements in secondary environments: Journal of Geochemical Exploration, v. 21, pp. 73–87.

Lukashev, V.K., 1986, Some scientific and applied problems of supergene geochemistry in the U.S.S.R.: Applied Geochemistry, v. 1, pp. 441–449.

Luoma, S.N., 1983, Bioavailability of trace metals to aquatic organisms—a review: Science of the Total Environment, v. 28, pp. 1–22.

Luoma, S.N., 1989, Can we determine the biological availability of sediment bound trace elements?: Hydrobiologia, v. 176/177, pp. 379–396.

Luoma, S.N., and Bryan, G.W., 1979, Trace metal bioavailability—modeling chemical and biological interactions of sediment-bound zinc; *in* Jenne, E.A. (ed.), Chemical Modeling in Aqueous Systems—Speciation, Sorption, Solubility, and Kinetics, ACS Symposium Series 93: American Chemical Society, Washington, D.C., pp. 577–609.

Luoma, S.N., and Bryan, G.W., 1981, A statistical assessment of the form of trace metals in oxidized estuarine sediments employing chemical extractants: Science of the Total Environment, v. 17, pp. 165–196.

Luoma, S.N., and Carter, J.L., 1993, Understanding the toxicity of contaminants in sediments—beyond the bioassay-based paradigm: Environmental Toxicology and Chemistry, v. 12, pp. 793–796.

Luoma, S.N., and Davis, J.A., 1983, Requirements for modeling trace metal partitioning in oxidized estuarine sediments: Marine Chemistry, v. 12, pp. 159–181.

Luoma, S.N., and Jenne, E.A., 1976, Estimating bioavailability of sediment-bound trace metals with chemical extractants; *in* Hemphill, D.D. (ed.), Trace Substances in Environmental Health: Univ. of Missouri Press, Columbia, pp. 343–353.

Luoma, S.N., and Jenne, E.A., 1977, The availability of sediment-bound cobalt, silver and zinc to a deposit-feeding clam; *in* Wildung, R.E., and Drucker, H. (eds.), The Biological Implications of Metals in the Environment: Technical Information Center, Energy Research and Development Administration Symposium Series 42, NTIS, Springfield, Va., CONF-750929, pp. 213–230.

Mahaffey, K.R., 1978, Environmental exposure to lead; *in* Nriagu, J.O. (ed.), The Biogeochemistry of Lead in the Environment, Part B. Biological Effects: Elsevier/North-Holland Biomedical Press, New York, pp. 1–36.

Marcus, J.J. (ed.), 1997, Mining environmental handbook: Imperial College Press, London, 785 pp.

Markert, B., 1994, Plants as biomonitors—potential advantages and problems; *in* Adriano, D.C., Chen, Z.S., and Yang, S.S. (eds.), Biogeochemistry of Trace Elements: Science and Technology Letters, Northwood, N.W., pp. 601–613.

Martin, J.H., Knauer, G.A., and Flegal, A.R., 1980, Distribution of zinc in natural waters; *in* Nriagu, J.O. (ed.), Zinc in the Environment, Part I. Ecological Cycling: John Wiley and Sons, New York, pp. 193–197.

Martin, J-M., and Whitfield, M., 1983, The significance of the river input of chemical elements to the ocean; *in* Wong, C.S., Boyle, E., Bruland, K.W., Burton, J.D., and Goldberg, E.D. (eds.), Trace Metals in Sea Water: Plenum Press, New York, pp. 265–296.

Maskall, J., Whitehead, K., and Thornton, I., 1995, Heavy metal migration in soils and rocks at historical smelting sites: Environmental Geochemistry and Health, v. 17, pp. 127–138.

Maugh, T.H., II, 1973, Trace elements—a growing appreciation of their effects on man: Science, v. 181, pp. 253–254.

McKinney, J.D., and Rogers, R., 1992, Metal bioavailability—EPA workshop identified research needs: Environmental Science and Technology, v. 26, pp. 1298–1299.

McLaren, D.S., 1994, Clinical manifestations of human vitamin and mineral disorders—a resume; *in* Shils, M.E., Olsen, J.A., and Shike, M. (eds.), Modern Nutritional Health and Disease, 8th ed., vol. 1: Lea and Febeger, Philadelphia, Pa., pp. 909–923.

Merrington, G., and Alloway, B.J., 1994, The transfer and fate of Cd, Cu, Pb and Zn from two historic metalliferous mine sites in the U.K.: Applied Geochemistry, v. 9, pp. 677–687.

Mertz, W., 1981, The essential trace elements: Science, v. 213, pp. 1332–1338.

Meybeck, M., 1988, How to establish and use world budgets of riverine materials; *in* Lerman, A., and Meybeck, M. (eds.), Physical and Chemical Weathering in Geochemical Cycles: Kluwer Academic Publishers, Dordrecht, pp. 247–272.

Meybeck, M., and Helmer, R., 1989, The quality of rivers—From pristine stage to global pollution: Paleogeography, Paleoclimatology, Paleoecology, Global and Planetary Change Section, v. 75, pp. 283–309.

Meybeck, M., Chapman, D.V., and Helmer, R. (eds.), 1989, Global freshwater quality—a first assessment: Published on behalf of the World Health Organization and the United Nations Environment Programme by Blackwell Reference, Oxford, 300 pp.

Miesch, A.T., 1976, Geochemical survey of Missouri—methods of sampling, laboratory analysis, and statistical reduction of data: U.S. Geological Survey Professional Paper 954–A, 39 pp.

Moore, J.N., and Luoma, S.N., 1990, Hazardous wastes from large-scale metal extraction: Environmental Science and Technology, v. 24, pp. 1278–1285.

Morel, F.M.M., 1983, Principles of aquatic chemistry: Wiley Interscience, New York, 301 pp.

Morel, F.M.M., and Hudson, R.J.M., 1985, The geobiological cycle of trace elements in aquatic systems—Redfield revisited; *in* Stumm, W. (ed.), Chemical Processes in Lakes: John Wiley and Sons, New York, pp. 251–281.

Morgan, H. (ed.), 1988, The Shipham report—an investigation into cadmium contamination and its implications for human health: The Science of the Total Environment, v. 75, pp. 41–69.

National Research Council, 1983, Risk assessment in the federal government—Managing the process: National Academy of Sciences, National Academy Press, Washington, D.C.

National Research Council, 1989, Recommended dietary allowances, 10th ed.: National Academy of Sciences, National Academy Press, Washington, D.C., 284 pp.

National Research Council, 1993, Measuring lead exposure in infants, children, and other sensitive populations: National Academy of Sciences, National Academy Press, Washington, D.C.

National Research Council, 1994, Science and judgment in risk assessment: National Academy of Sciences, National Academy Press, Washington, D.C.

Navarra, T., and Lipkowilz, M.A., 1996, Encyclopedia of vitamins, minerals, and supplements: Facts on File, Inc., New York, 281 pp.

Newman, M.C., and Jagoe, C.H., 1994, Inorganic toxicants—ligands and the bioavailability of metals in aquatic environments; *in* Hamelink, J.L., Landrum, P.F., Bergman, H.L., and Benson, W.H. (eds.), Bioavailability—Physical, Chemical, and Biological Interactions, SETAC Spec. Pub. Series: CRC Press, Inc., Boca Raton, Fla., pp. 39–61.

Nieboer, E., and Fletcher, G.G., 1996, Determinants of reactivity in metal toxicology; *in* Chang, L.W. (ed.), Toxicology of Metals: CRC Press, Boca Ragon, Fla., pp. 113–132.

Nieboer, E., and Richardson, D.H.S., 1980, The replacement of the nondescript term "heavy metals" by a biologically and chemically significant classification of metal ions: Environmental Pollution, Series B, v. 1, pp. 3–26.

Nielsen, F.H., 1994, Ultratrace minerals; *in* Shils, M.E., Olson, J.A., and Shike, M. (eds.), Modern Nutrition in Health and Disease, 8th ed., Vol. 1: Lea and Febeger, Philadelphia, Pa., pp. 269–296.

Nordstrom, D.K., 1999, Some fundamentals of aqueous geochemistry; *in* Plumlee, G.S., and Logsdon, J.J. (eds.), The Environmental Geochemistry of Mineral Deposits, Part A. Processes, Techniques, and Health Issues: Society of Economic Geologists, Reviews in Economic Geology, v. 6A, pp. 117–123.

Nordstrom, D.K., and Alpers, C.N., 1999, Geochemistry of acid mine waters; *in* Plumlee, G.S., and Logsdon, J.J. (eds.), The Environmental Geochemistry of Mineral Deposits, Part A. Processes, Techniques, and Health Issues: Society of Economic Geologists, Reviews in Economic Geology, v. 6A, pp. 133–160.

Nordstrom, D.K., and Munoz, J.L., 1994, Geochemical thermodynamics, 2nd ed.: Blackwell Science, 493 pp.

Nriagu, J.O., 1989, A global assessment of natural sources of atmospheric trace metals: Nature, v. 338, pp. 47–49.

Nriagu, J.O., 1990, Global metal pollution: Environment, v. 32, no. 7, pp. 6–11, 28–33.

Nriagu, J.O., and Pacyna, J.M., 1988, Quantitative assessment of worldwide contamination of air, water and soils by trace metals: Nature, v. 333, pp. 134–139.

O'Donnel, J.R., Kaplan, B.M., and Allen, H.E., 1985, Bioavailability of trace metals in natural waters; *in* Cardwell, R.D., Purdy, R., and Bahner, R.C. (eds.), Aquatic Toxicology and Hazard Assessment, 7th Symposium, ASTM Spec. Tech. Pub. No. 854: American Society for Testing and Materials, Philadelphia, Pa., pp. 485–501.

Pacyna, J.M., 1996, Monitoring and assessment of metal contaminants in the air; *in* Chang, L.W. (ed.), Toxicology of Metals: CRC Press, Inc., Boca Raton, Fla., pp. 9–28.

Pagenkopf, G.K., Russo, R.C., and Thurston, R.V., 1974, Effect of complexation on toxicity of copper to fishes: J. Fish Res. Bd. Can., v. 31, pp. 462–465.

Pais, I., and Jones, J.B., Jr., 1997, The handbook of trace elements: St. Lucie Press, Boca Raton, Fla., 223 pp.

Papp, C.S.E., Filipek, L.H., and Smith, K.S., 1991, Selectivity and effectiveness of extractants used to release metals associated with organic matter: Applied Geochemistry, v. 6, pp. 349–353.

Parish, R.V., 1977, The metallic elements: Longman Inc., New York, 254 pp.

Pascoe, G.A., Blanchet, R.J., and Linder, G., 1994, Bioavailability of metals and arsenic to small mammals at a mining waste-contaminated wetland: Arch. Environ. Contam. Toxicol., v. 27, pp. 44–50.

Pearson, R.G., 1963, Hard and soft acids and bases: Journal of the American Chemical Society, v. 85, pp. 3533–3539.

Pearson, R.G., 1968a, Hard and soft acids and bases, HSAB, Part I. Fundamental principles: Journal of Chemical Education, v. 45, pp. 581–587.

Pearson, R.G., 1968b, Hard and soft acids and bases, HSAB, Part II. Underlying theories: Journal of Chemical Education, v. 45, pp. 643–648.

Pelletier, E. 1995, Environmental organometallic chemistry of mercury, tin, and lead—present status and perspectives; *in* Tessier, A., and Turner, D.R. (eds.), Metal Speciation and Bioavailability in Aquatic Systems: John Wiley and Sons, New York, pp. 103–148.

Perel'man, A.I., 1977, Geochemistry of elements in the supergene zone (translated from Russian): Keter Publishing House Ltd., Jerusalem, 266 pp.

Perel'man, A.I., 1986, Geochemical barriers—theory and practical applications: Applied Geochemistry, v. 1, pp. 669–680.

Pesch, C.E., and Morgan, D., 1978, Influence of sediment in copper toxicity tests with the polychaete Neathes arenaceodentata: Water Research, v. 12, pp. 747–751.

Petito, C.T., and Beck, B.D., 1990, Evaluation of evidence of nonlinearities in the dose-response curve for arsenic carcinogenesis: Trace Substances in Environmental Health, v. 24, pp. 143–176.

Phipps, D.A., 1981, Chemistry and biochemistry of trace metals in biological systems; *in* Lepp, N.W. (ed.), Effect of Heavy Metal Pollution on Plants, Vol. 1, Effects of Trace Metals on Plant Function: Applied Science Publishers, London, pp. 1–54.

Pickering, W.F., 1981, Selective chemical extraction of soil components and bound metal species: CRC Critical Reviews in Analytical Chemistry, v. 12, pp. 233–266.

Pierzynski, G.M., and Schwab, A.P., 1993, Bioavailability of zinc, cadmium, and lead in a metal-contaminated alluvial soil: Journal of Environmental Quality, v. 22, pp. 247–254.

Piispanen, R., 1989, Geochemical interpretation of cancer maps of Finland: Environmental Geochemistry and Health, v. 11, pp. 145–147.

Plant, J.A., and Thornton, I., 1985, Geochemistry and health in the United Kingdom; *in* Thornton, I. (ed.), Proceedings of the 1st Internatl Symposium on Geochemistry and Health: Science Reviews, Northwood, pp. 1–15.

Plumlee, G., 1994, Environmental geology models of mineral deposits: SEG Newsletter, January 1994, no. 16, pp. 5–6.

Plumlee, G.S., 1999, The environmental geology of mineral deposits; *in* Plumlee, G.S., and Logsdon, M.J. (eds.), The Environmental Geochemistry of Mineral Deposits, Part A. Processes, Techniques, and Health Issues: Society of Economic Geologists, Reviews in Economic Geology, v. 6A, pp. 71–116.

Plumlee, G.S., Smith, K.S., Ficklin, W.H., and Briggs, P.H., 1992, Geological and geochemical controls on the composition of mine drainages and natural drainages in mineralized areas; *in* Kharaka, Y.K., and Maest, A.S. (eds.), Water-Rock Interaction, Vol. 1, 7th Internatl Symposium on Water-Rock Interaction: A.A. Balkema, Rotterdam, pp. 419–422.

Plumlee, G.S., Smith, K.S., Ficklin, W.H., Briggs, P.H., and McHugh, J.B., 1993, Empirical studies of diverse mine drainages in Colorado—Implications for the prediction of mine-drainage chemistry, Proceedings, Vol. 1: 1993 Mined Land Reclamation Symposium, Billings, Mont., pp. 176–186.

Plumlee, G.S., Streufert, R.K., Smith, K.S., Smith, S.M., Wallace, A.R., Toth, M., Nash, J.T., Robinson, R., Ficklin, W.H., and Lee, G.K., 1995, Geology-based map of potential metal-mine drainage hazards in Colorado: U.S. Geological Survey Open-File Report 95–26.

Plumlee, G.S., Smith, K.S., Montour, M.R., Mosier, E.L., and Ficklin, W.H., 1999, Geologic controls on the composition of natural waters and mine waters draining diverse mineral-deposit types; *in* Filipek, L.H., and Plumlee, G.S. (eds.), The Environmental Geochemistry of Mineral Deposits, Part B, Case Studies and Research Topics: Society of Economic Geologists, Reviews in Economic Geology, v. 6B, pp. 373–432.

Purcell, K.F., and Kotz, J.C., 1980, An introduction to inorganic chemistry: Saunders College, Philadelphia, Pa., 637 pp.

Ragaini, R.C., Ralston, H.R., and Roberts, N., 1977, Environmental trace metal contamination in Kellogg, Idaho, near a lead smelting complex: Environmental Science and Technology, v. 11, pp. 773–781.

Ranville, J.F., and Schmiermund, R.L., 1999, General aspects of aquatic colloids in environmental geochemistry; *in* Plumlee, G.S., and Logsdon, M.J. (eds.), The Environmental Geochemistry of Mineral Deposits, Part A. Processes, Techniques, and Health Issues: Society of Economic Geologists, Reviews in Economic Geology, v. 6A, pp. 183–199.

Rickwood, P.C., 1983, Crustal abundance, distribution, and crystal chemistry of the elements; *in* Govett, G.J.S., Handbook of Exploration Geochemistry, Vol. 3, Rock Geochemistry in Mineral Exploration: Elsevier Scientific Publishing Company, Amsterdam, pp. 347–387.

Ripley, E.A., Redmann, R.E., and Crowder, A.A., 1996, Environmental effects of mining: St. Lucie Press, Delray Beach, Fla., 356 pp.

Rose, A.W., Hawkes, H.E., and Webb, J.S., 1979, Geochemistry in mineral exploration, 2nd ed.: Academic Press, New York, 657 pp.

Ruby, M.V., Davis, Andy, Kempton, J.H., Drexler, J.W., and Bergstrom, P.D., 1992, Lead bioavailability—Dissolution kinetics under simulated gastric conditions: Environmental Science and Technology, v. 26, pp. 1242–1248.

Ruby, M.V., Davis, A., Link, T.E., School, R., Chaney, R.L., Freeman, G.B., and Bergstrom, P., 1993, Development of an in vitro screening test to evaluate the in vivo bioaccessibility of ingested mine-waste lead: Environmental Science and Technology, v. 27, pp. 2870–2877.

Salomons, W., 1995, Environmental impact of metals derived from mining activities—processes, predictions, prevention: Journal of Geochemical Exploration, v. 52, pp. 5–23.

Salomons, W., and Forstner, U., 1984, Metals in the hydrocycle: Springer-Verlag, Berlin, 349 pp.

Sandstead, H.H., 1980, Interactions of toxic elements with essential elements—Introduction: Ann. N.Y. Acad. Sci., v. 355, pp. 282–284.

Sandstead, H.H., 1988, Interactions that influence bioavailability of essential metals to humans; *in* Kramer, J.R., and Allen, H.E. (eds.), Metal Speciation—Theory, Analysis and Application: Lewis Publishers, Chelsea, Mich., pp. 315–332.

Scokart, P.O., Meeus-Verdinne, K., and de Borger, R., 1983, Mobility of heavy metals in polluted soils near zinc smelters: Water, Air, and Soil Pollution, v. 20, pp. 451–463.

Selgrade, M.J.K., and Gardner, D.E., 1996, Altered host defenses and resistance to respiratory infections following exposure to airborne metals; *in* Chang, L.W. (ed.), Toxicology of Metals: CRC Press, Inc., Boca Raton, Fla., pp. 853–860.

Severson, R.C., and Gough, L.P., 1992, Selenium and sulfur relationships in alfalfa and soil under field conditions, San Joaquin Valley, California: Journal of Environmental Quality, v. 21, pp. 353–358.

Severson, R.C., Gough, L.P., Crock, J.G., Fey, D.L., Hageman, P.L., Love, A.H., and Peacock, T.R., 1991, Uptake and physiological antagonism of selenium and sulfur in alfalfa and wheat under field conditions, San Joaquin Valley, California: U.S. Geological Survey Open-File Report 91–16, 42 pp.

Shacklette, H.T., and Boerngen, J.G., 1984, Element concentrations in soils and other surficial materials of the conterminous United States: U.S. Geological Survey Professional Paper 1270, 105 pp.

Shaper, A.G., 1979, Epidemiology for geochemists: Phil. Trans. R. Soc. London B, v. 288, pp. 127–136.

Shaw, A.J. (ed.), 1990, Heavy metal tolerance in plants—evolutionary aspects: CRC Press, Boca Raton, Fla.

Sheppard, S.C., Evenden, W.G., and Schwartz, W.J., 1995, Ingested soil—bioavailability of sorbed lead, cadmium, cesium, iodine, and mercury: Journal of Environmental Quality, v. 24, pp. 498–505.

Simpson, P.R., 1995, Geochemical baselines for sustainable development: Mineralogical Society Bulletin, no. 109, Dec. 1995, pp. 21–26.

Small, M., Germani, M.S., Small, A.M., Zoller, W.H., and Moyers, J.L., 1981, Airborne plume study of emissions from the processing of copper ores in southeastern Arizona: Environmental Science and Technology, v. 15, pp. 293–299.

Smith, K.S., 1999, Metal sorption on mineral surfaces—An overview of examples relating to mineral deposits; *in* Plumlee, G.S., and Logsdon, M.J. (eds.), The Environmental Geochemistry of Mineral Deposits, Part A. Processes, Techniques, and Health Issues: Society of Economic Geologists, Reviews in Economic Geology, v. 6A, pp. 161–182.

Smith, K.S., Balistrieri, L.S., Smith, S.M., and Severson, R.C., 1997, Distribution and mobility of molybdenum in the terrestrial environment; *in* Gupta, U.C. (ed.), Molybdenum in Agriculture, Ch. 3: Cambridge Univ. Press, Cambridge, Mass., pp. 23–46.

Smith, K.S., Ranville, J.F., Plumlee, G.S., and Macalady, D.L., 1998, Predictive double-layer modeling of metal sorption in mine-drainage systems; *in* Jenne, E.A. (ed.), Adsorption of Metals by Geomedia: Academic Press, San Diego, Calif., pp. 521–547.

Sprague, J.B., 1985, Factors that modify toxicity; *in* Rand, G.M., and Petrocelli, S.R. (eds.), Fundamentals of Aquatic Toxicology: Hemisphere, Washington, D.C., pp. 123–163.

Spry, D.J., and Weiner, J.G., 1991, Metal bioavailability and toxicity to fish in low-alkalinity lakes: a critical review: Environmental Pollution, v. 71, pp. 243–304.

Stumm, W., and Morgan, J.J., 1996, Aquatic chemistry—chemical equilibria and rates in natural waters, 3rd ed.: John Wiley and Sons, New York, 1022 pp.

Sunda, W.G., and Guillard, R.R., 1976, The relationship between cupric-ion activity and the toxicity of copper to phytoplankton: Journal of Marine Research, v. 34, pp. 511–529.

Suter, G.W., II, 1993, Ecological risk assessment: Lewis Publishers, Chelsea, Mich., 538 pp.

Tanizaki, Y., Shimokawa, T., and Nakamura, M., 1992, Physicochemical speciation of trace elements in river waters by size fractionation: Environmental Science and Technology, v. 26, pp. 1433–1444.

Tessier, A., and Turner, D.R. (eds.), 1995, Metal speciation and bioavailability in aquatic sediments, IUPAC Series on Analytical and Physical Chemistry of Environmental Systems, Vol. 3: John Wiley and Sons, New York, 679 pp.

Tessier, A., Campbell, P.G.C., and Bisson, M., 1979, Sequential extraction procedure for the speciation of particulate trace metals: Analytical Chemistry, v. 51, pp. 844–851.

Tessier, A., Campbell, P.G.C., Anclair, J.C., and Bisson, M., 1984, Relationships between the partitioning of trace metals in sediments and their accumulation in the tissues of the freshwater mollusk Elliptio comlanata in a mining area: Can. J. Fish. Aquat. Sci., v. 41, pp. 1463–1472.

Thornton, I., 1982, Geochemical aspects of the distribution and forms of heavy metals in soils; *in* Lepp, N.W. (ed.), Effect of Heavy Metal Pollution on Plants, Vol. 2, Metals in the Environment: Applied Science Publishers, London, pp. 1–33.

Thornton, I., 1983, Geochemistry applied to agriculture; *in* Thornton, I. (ed.), Applied Environmental Geochemistry: Academic Press, London, pp. 231–266.

Thornton, I., 1987, Mapping of trace elements in relation to human disease: Clinical Nutrition, v. 6, pp. 97–104.

Thornton, I., 1993, Environmental geochemistry and health in the 1990's—A global perspective: Applied Geochemistry, Suppl. Issue No. 2, pp. 203–210.

Thurman, D.A., 1982, Mechanism of metal tolerance in higher plants; *in* Lepp, N.W. (ed.), Effect of Heavy Metal Pollution on Plants, Vol. 2, Metals in the Environment: Applied Science Publishers, London, pp. 239–249.

Tingle, T.N., Borch, R.S., Hochella, M.F., Jr., Becker, C.H., and Walker, W.J., 1993, Characterization of lead on mineral surfaces in soils contaminated by mining and smelting: Applied Surface Science, v. 72, pp. 301–306.

Turner, D.R., 1995, Problems in trace metal speciation modeling; *in* Tessier, A., and Turner, D.R. (eds.), Metal Speciation and Bioavailability in Aquatic Systems: John Wiley and Sons, New York, pp. 149–203.

University of Cincinnati, 1997, Leadville/Lake County environmental health lead study, final report: Dept. of Environmental Health, 82 pp. and 17 appendices.

U.S. EPA, 1980, Notice of availability, ambient water quality criteria documents (64 documents), Office of Water Regulations and Standards, Criterion Standards Division: U.S. Environmental Protection Agency, Federal Register, v. 45, pp. 79,318–79,379.

U.S. EPA, 1986, Quality criteria for water 1986, U.S. Environmental Protection Agency, EPA 440/5–86–001: U.S. Government Printing Office, Washington, D.C.

U.S. EPA, 1989, Risk assessment guidance for Superfund, I. Human health evaluation manual, Part A, U.S. Environmental Protection Agency, EPA

540/1–89–002: U.S. Government Printing Office, Washington, D.C.

U.S. EPA, 1991, Comprehensive review of lead in the environment under TSCA: U.S. Environmental Protection Agency, Federal Register, v. 56, pp. 22,096–22,098.

U.S. EPA, 1992, A framework for ecological risk assessment, Risk Assessment Forum, February, 1992: U.S. Environmental Protection Agency, EPA 630/R–92/001, 56 pp.

U.S. EPA, 1993a, Integrated Risk Information Service (IRIS) on-line database: U.S. Environmental Protection Agency, Washington, D.C.

U.S. EPA, 1993b, EPA Region VIII Clean Water Act Section 304(a) criteria chart, July 1, 1993: U.S. Environmental Protection Agency, 12 pp.

U.S. EPA, 1994, Code of Federal Regulations, Title 40, Part 131, July 1, 1994 edition, pp. 335–369.

U.S. EPA, 1995, Drinking water regulations and health advisories, May 1995: U.S. Environmental Protection Agency, Office of Water, 11 pp.

U.S. EPA, 1996, Code of Federal Regulations, Title 40, Sec. 261.24, July 1, 1996 edition., p. 52.

U.S. EPA, 1997, Measurement of lead bioavailability in soils and other test materials using juvenile swine; June 1997 Working Draft by S.W. Casteel, L.D. Brown, M.E. Dunsmore, C.P. Weis, G.M. Henningsen, E. Hoffman, W.J. Brattin, and T.L. Hammon: U.S. Environmental Protection Agency, Region VIII, Denver, Colo.

U.S. EPA, 1998, National recommended water quality criteria: U.S. Environmental Protection Agency, Federal Register, v. 63, pp. 68,354–68,364.

Valberg, P., Boardman, P., Bowers, T., and Beck, B., 1994, Arsenic health risks in the mining environment—current controversies, National Western Mining Conference, March 23–25, 1994: Denver Region Exploration Geologists Society, reprint, 11 pp.

Venugopal, B., and Luckey, T.D., 1978, Metal toxicity in mammals, Vol. 2, Chemical toxicity of metals and metalloids: Plenum Press, New York, 409 pp.

Vlasov, K.A. (ed.), 1966, Geochemistry and mineralogy of rare elements and genetic types of their deposits, Vol. 1, Geochemistry of rare elements (translated from Russian): Israel Program for Scientific Translations Ltd., Jerusalem, 688 pp.

Walton-Day, K., 1999, Geochemistry of the processes that attenuate acid mine drainage in wetlands; *in* Plumlee, G.S., and Logsdon, M.J. (eds.), The Environmental Geochemistry of Mineral Deposits, Part A. Processes, Techniques, and Health Issues: Society of Economic Geologists, Reviews in Economic Geology, v. 6A, pp. 215–228.

Warren, H.V., 1989, Geology, trace elements and health: Soc. Sci. Med., v. 8, pp. 923–926.

Webb, J.S., 1964, Geochemistry and life: New Scientist, v. 23, pp. 504–507.

Webb, J.S., Nichol, I., Foster, R., Lowenstein, P.L., and Howarth, R.J., 1973, Provisional geochemical atlas of Northern Ireland: Applied Geochemistry Research Group, Imperial College of Science and Technology, London.

Webb, J.S., Thornton, I., Thompson, M., Howarth, R.J., and Lowenstein, P.L., 1978, The Wolfson geochemical atlas of England and Wales: Oxford Univ. Press.

Weimin, Y., Batley, G.E., and Ahsanullah, M., 1992, The ability of sediment extractants to measure the bioavailability of metals to three marine invertebrates: The Science of the Total Environment, v. 125, pp. 67–84.

Westerman, R.L. (ed.), 1990, Soil testing and plant analysis, 3rd ed.: Soil Science Society of America, 784 pp.

Whitfield, M., and Turner, D.R., 1979, Water-rock partition coefficients and the composition of sea water and river water: Nature, v. 278, pp. 132–137.

Whitfield, M., and Turner, D.R., 1983, Chemical periodicity and the speciation and cycling of the elements; *in* Wong, C.S., Boyle, E., Bruland, K.W., Burton, J.D., and Goldberg, E.D. (eds.), Trace Metals in Sea Water: Plenum Press, New York, pp. 719–750.

Wixson, B.G., and Davies, B.E., 1994, Guidelines for lead in soil: Environmental Science and Technology, v. 28, pp. 26A–31A.

Wood, J.M., 1988, Transport, bioaccumulation, and toxicity of metals and metalloids in microorganisms under environmental stress; *in* Kramer, J.R., and Allen, H.E. (eds.), Metal Speciation—Theory, Analysis and Application: Lewis Publishers, Chelsea, Mich., pp. 295–314.

Zakrzewski, S.F., 1991, Principles of environmental toxicology: American Chemical Society, Washington, D.C., pp. 270.

Zhou, D., and Liu, D., 1985, Chronic thallium poisoning in a rural area of Guizhou Province, China: Journal of Environmental Health, v. 48, pp. 14–18.

Zitko, V., and Carson, W.G., 1976, A mechanism of the effects of water hardness on the lethality of heavy metals to fish: Chemosphere, v. 5, pp. 299–303.