POLYMETALLIC VEIN AND REPLACEMENT DEPOSITS
(MODELS 19a and 22c; Morris, 1986; Cox, 1986)

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SUMMARY OF RELEVANT GEOLOGIC, GEOENVIRONMENTAL, AND GEOPHYSICAL INFORMATION
Deposit geology
Deposits consist of massive lenses and (or) pipes, known as mantos or replacement orebodies, and veins of iron, lead, zinc, and copper sulfide minerals that are hosted by and replace limestone, dolomite, or other sedimentary rocks; most massive ore contains more than 50 percent sulfide minerals. Sediment-hosted ore commonly is intimately associated with igneous intrusions in the sedimentary rocks. Emplacement of these intrusions triggered ore formation and they host polymetallic veins and disseminations that contain iron, lead, zinc, and copper sulfide minerals. Some polymetallic replacement deposits are associated with skarn deposits in which host carbonate rocks are replaced by calc-silicate±iron oxide mineral assemblages. Most polymetallic vein and replacement deposits are zoned such that copper-gold ore is proximal to intrusions, whereas lead-zinc-silver ore is laterally and vertically distal to intrusions.

Examples
Leadville, Gilman, and Breckenridge districts, Bandora Mine, Colo.; Park City, Utah, district; Eureka, Nev., district; New World, Mont., district.

Spatially and (or) genetically related deposit types
Related deposit types (Cox and Singer, 1986) include Climax molybdenum (Model 16); porphyry molybdenum, low fluorine (Model 21b); porphyry copper (Model 17); porphyry copper-gold (Model 20c); porphyry copper-olybdenum (Model 21a); base metal skarns (Models 18a-d).

Potential environmental considerations
(1) Many polymetallic vein and replacement deposits are hosted in carbonate-rich sedimentary rocks that consume acid and inhibit metal transport. However, mine water that drains deposits not hosted by carbonate-bearing rocks tends to be acidic to extremely acidic and contain elevated abundances of iron, aluminum, zinc, and copper and moderate abundances of lead, cadmium, and arsenic.
(2) Water draining pyrite-rich, tailings and waste dumps can be acidic to highly acidic, and can contain high to extreme abundances of iron and aluminum, and very high abundances of zinc and copper.
(3) Karst, where present, can impose significant control on the local hydrologic regime because of its ability to channelize ground water for long distances from mine sites.
(4) Slag produced by smelting may contain elevated abundances of lead, zinc, and copper, and lesser amounts of other metals; the mobility of metals from slag varies as a function of how slag cooled.
(5) Soil downwind from smelters can contain elevated abundances of Pb, Zn, Cu, As, Sb, Mo, Hg, and Au.
        Mitigation and remediation strategies for potential environmental concerns presented above are described in the section below entitled "Guidelines for mitigation and remediation."

Exploration geophysics
Most massive sulfide replacement bodies have high density, low resistivity, are electrically chargeable when excited by induced polarization, have high magnetic susceptibility when magnetite or pyrrhotite are present, and may generate negative self-potential voltages (Ward, 1966; Buselli, 1980; Frischknecht and others, 1991; Fallon and Busuttil, 1992; Thomas and others, 1992). Consequently, these deposits often can be identified by detailed electrical, gravity, magnetic, and self-potential surveys. Specifics of particular geophysical responses are controlled by sulfide mineralogy, concentration, and continuity; hydrologic conditions; and by host and country rock characteristics and geometry. Airborne or ground-based electromagnetic, direct current resistivity, and induced polarization surveys can identify low-resistivity and chargeable sulfide masses, high-resistivity silicified-carbonitized zones, and pyritic alteration assemblages (Ward, 1966; Zonge and Hughes, 1991; Shalley and Harvey, 1992; Thomas and others, 1992). Anomalies initially identified by airborne electromagnetic and magnetic surveys can be further studied by ground-based geophysical surveys coupled with geologic and geochemical investigations. Targets for detailed exploration can also be selected using remote sensing data. Large (several hundred meters long) gossans can be identified on satellite-derived Thematic Mapper remote sensing images; smaller gossans may be detected using airborne imagery,

including aerial photography (Watson and Knepper, 1994), or AVIRIS imagery. Regional magnetic and gravity surveys may identify anomalies related to fault zones or intrusions that may control ore distribution or indicate prospective terrane (Fallon and Busuttil, 1992; Shalley and Harvey, 1992).

References
Geology: Lovering and others (1978), Beaty and others (1990), Titley (1993).
Environmental: Chaffee (1980; 1987), Plumlee and others (1993), Montour (1994), Smith and others (1994).

GEOLOGIC FACTORS THAT INFLUENCE POTENTIAL ENVIRONMENTAL EFFECTS
Deposit size
Deposits are small (10,000 tonnes) to very large (as much as 30-40 million tonnes).

Host rocks
These deposits are principally hosted by sedimentary rocks (dolomite, limestone, sandstone, and shale) that have been intruded by intermediate- to felsic-composition igneous stocks, dikes, and sills (figs. 1 and 2).

Surrounding geologic terrane
These deposits are in sedimentary rock sequences that host local igneous intrusions.

Wall-rock alteration
Carbonate-hosted replacement ore: Host carbonate rocks are commonly recrystallized, dolomitized, bleached, and (or) sanded (the process whereby carbonate cement is removed from sedimentary rocks). Alteration of carbonate rocks to silica-rich jasperoid is common locally in some districts. In some districts, carbonate minerals have been replaced by calc-silicate skarn minerals (epidote, amphibole, garnet, pyroxene, and iron oxide minerals) near their contacts with igneous intrusions (fig. 1).
Igneous-hosted ore: In the central, hottest parts of mineralized systems, igneous host rocks are altered to quartz-sericite-pyrite and quartz-clay (argillic) assemblages that grade into distal propylitic (epidote, chlorite, pyrite, carbonate) alteration assemblages.

Nature of ore
Ore is present in massive lenses (mantos), pipes (chimneys), and veins of iron, lead, zinc, and copper sulfide minerals that are hosted by and replace limestone, dolomite, or other sedimentary rocks; most massive ore contains >50 percent sulfide minerals. A given district or mine may contain a single, massive orebody or a series of orebodies aligned along structural features such as fractures, joints, fold limbs, stratigraphic features such as karst openings, or lithologic discontinuities (such as shale pinchouts) that control fluid movement (fig. 1). Manto and chimney ore is compact and can be relatively impermeable. Some ore replaces carbonate clasts in karst breccias, and may fill interstices between clasts.

Deposit trace element geochemistry
Polymetallic vein and replacement deposits are characterized by elevated abundances of Pb-Zn±Cu±Au±Ag±Mo±As±Bi±Sb. In some districts, ore proximal to igneous intrusions is copper and gold rich, and grades laterally (and sometimes vertically) into lead-zinc-silver-rich ore. A distal, manganese-enriched zone is present in some districts.

Ore and gangue mineralogy and zonation
Minerals listed in approximate decreasing order of abundance. Potentially acid-generating minerals are underlined; those that are acid-generating when oxidized by aqueous ferric iron are denoted by *.
Carbonate replacement ore: Pyrite, sphalerite*, galena*, siderite, quartz, marcasite, rhodochrosite, dolomite, chalcopyrite, pyrrhotite, tetrahedrite, digenite*, argentite, electrum, ± enargite, ± bornite, ± arsenopyrite, ±Bi-Te-Hg-Au-Ag minerals (hessite, petzite, pyrargyrite, etc.), ± barite, ± fluorite. Most deposits are pyrite-rich; however, a few (rare?) deposits are pyrite-poor and are dominated by sphalerite and galena.
Igneous-hosted vein ore: Quartz, pyrite, chalcopyrite, sphalerite*, galena*, sericite, acanthite, gold/electrum, ± molybdenite, ± wolframite, ± scheelite.
Skarn ore: Magnetite, epidote, amphibole, pyroxene, ± serpentinite.
Zoning: In many deposits, ore grades from copper sulfide mineral-rich (chalcopyrite, enargite, bornite) within and near igneous intrusions, to sphalerite- and galena-rich away from intrusions, to sphalerite- and manganese carbonate-
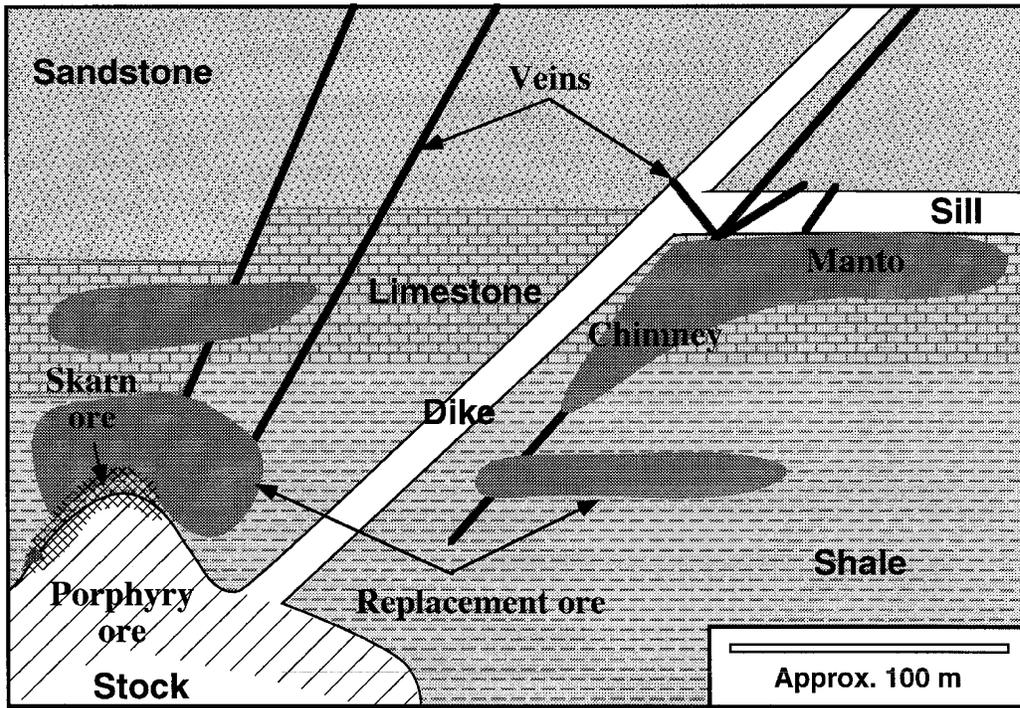
Figure 1. Schematic vertical section through a polymetallic replacement deposit showing distribution of ore types and host rocks.
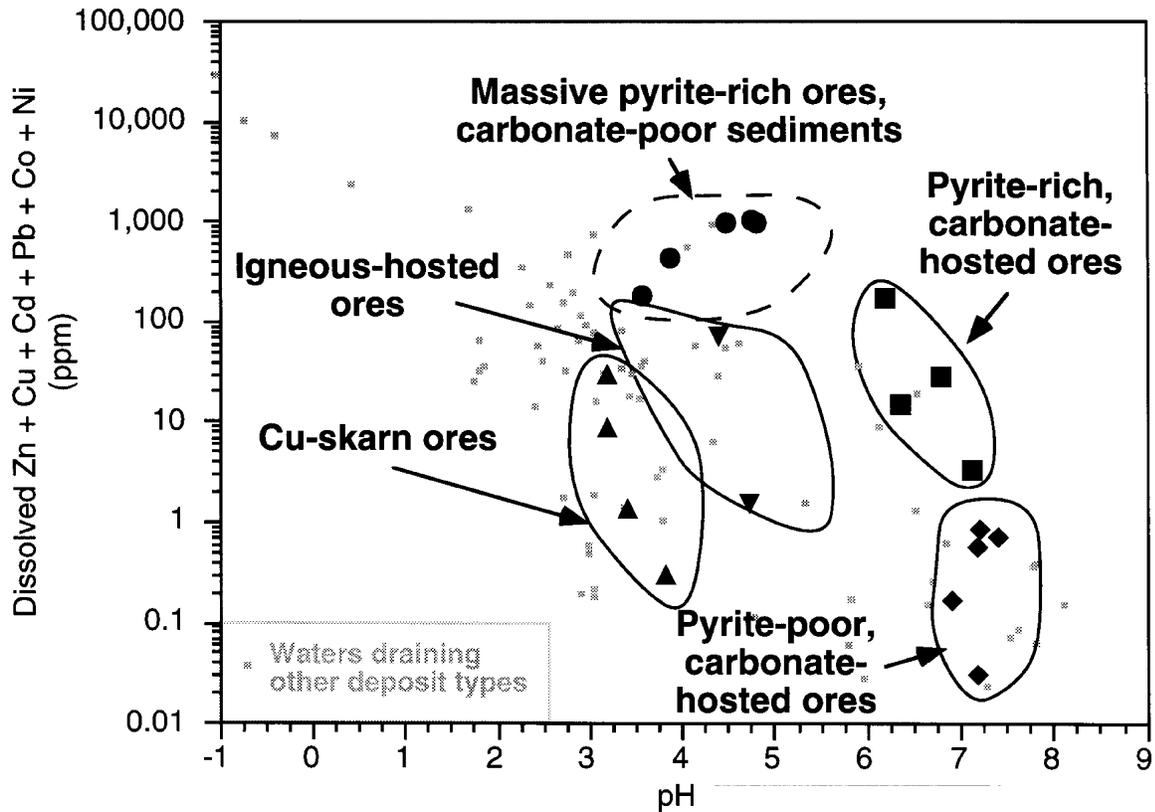

Figure 2. Ficklin plot showing pH versus the sum of dissolved base metals Zn, Cu, Cd, Co, Ni, and Pb in mine and natural water draining polymetallic replacement ore types.

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bearing distal ore. Most skarn ore is near the intrusion-sedimentary rock contact.

Mineral characteristics
Textures: Mineral grains are typically medium to coarse grained (0.5 to >1 cm), and range in texture from euhedral to massive interlocking grains.
Trace element contents: In many deposits, sphalerite typically has very high iron contents (5-20 mol percent) and cadmium (several tenths to 1 mol percent) and minor amounts of other trace elements such as silver. Galena can contain silver and bismuth (generally <1 mol percent).
General rates of weathering: Euhedral to massive, interlocking sul fides weather at very slow rates. Samples exposed on mine dumps for >100 years are fresh and unweathered. Marcasite may weather at faster rates than pyrite, sphalerite, and galena. Fine-grained sulfide minerals weather more rapidly than those that are coarse-grained.

Secondary mineralogy
Readily soluble minerals underlined.
Minerals formed by weathering prior to mining: Carbonate ore— These minerals, including anglesite, cerussite, smithsonite, hemimorphite, hydrozincite, hemimorphite, manganese oxide minerals (psilomelane, pyrolusite, braunite), iron oxide minerals (limonite), cerargyrite, and jarosite, tend to be relatively insoluble and indicative of deposition from relatively high-pH water. Igneous ore—native gold, cerargyrite, and iron oxide minerals.
Minerals formed by recent weathering after the onset of mining: These minerals are primarily soluble sulfate minerals indicative of deposition from locally highly acidic water. Zinc sulfate minerals include goslarite, which grades to magnesium-rich epsomite. Iron sulfate minerals include copiapite, coquimbite, melanterite, szomolnokite, fibroferrite and roemerite. Chalcanthite is the dominant copper sulfate mineral although others may also be present.

Topography, physiography
Silica-rich orebodies in sedimentary and igneous rocks may form topographic highs.

Hydrology
Natural ground water flow in the vicinity of these deposits is dominantly along fractures and faults or through karst systems in carbonate rocks; mine workings enhance ground-water permeability. Karst, where present, can impose significant control on the local hydrologic regime because of its a bility to channelize ground water for long distances from mine sites. Some flow may also occur in sedimentary rock aquifers, including sandstone and fractured carbonate rocks. Pre-mining discharge points may in some ca ses be determined by mapping surficial iron-hydroxide (ferricrete) deposits.

Mining and milling methods
Historic: Processing typically involved milling to produce zinc-, lead-, and (or) copper-rich concentrates that were subsequently smelted.
Modern: Processing typically involves milling; resulting concentrates are smelted. Stopes are backfilled by coarse tailings and fine t ailings are stored in surface impoundments. Some copper-rich ore is currently being processed by sulfuric acid leaching and subsequent solvent extraction electrowinning.

ENVIRONMENTAL SIGNATURES
Drainage signatures
Mine-drainage data (figs. 2 and 3): Data for Leadville, Kokomo, Breckenridge, and Bandora, Colo., from Plumlee and others (1993) and Smith and others (1994); data for New World, Mont., from Montana Department of State Lands (1994); data for Eagle, Colo., mine from Engineering Science, Inc. (1985).
(1) Mine water draining orebodies in carbonate-rich sedimentary rocks tends to be slightly acidic to near-neutral, pH 5.5 to 7.5; water draining pyrite-rich orebodies tends to contain tens to low hundreds of mg/l dissolved zinc. Water that drains copper-rich proximal ore can have several mg/l dissolved copper. Water with low dissolved oxygen content, such as tha t draining collapsed adits, can contain several tens of mg/l dissolved iron; as this water becomes oxygenated, oxidatio n and precipitation of iron can lead to significant pH decreases away from the drainage source.
(2) Water draining igneous-hosted ore, ore i n carbonate-poor sedimentary rock, and massive ore (in which water has limited interaction with host carbonate rocks) tends to be acidic (pH 3.5 to 5), contain several tens of mg/l iron and aluminum, tens to low hundreds of mg/l zinc, several to several tens of mg/l copper, and several hundred µg/l lead,
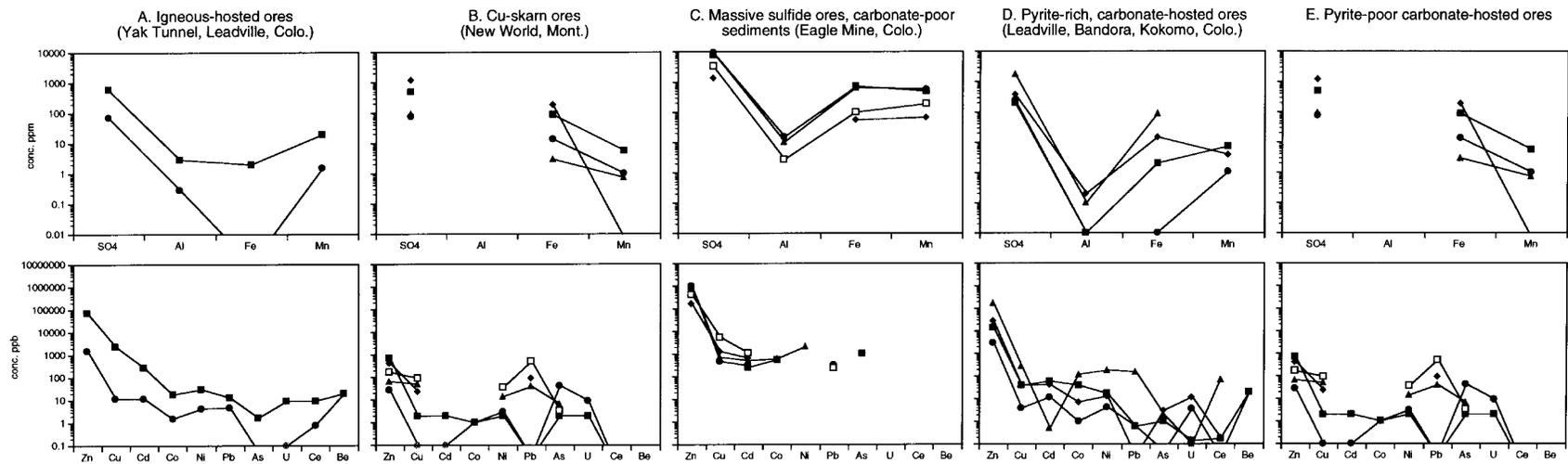
Figure 3. Dissolved concentrations of sulfate and major metals and various trace elements in mine water draining polymetallic replacement ore types. Data from Plumlee and others (1993), Smith and others (1994), Engineering Science, Inc. (1985), and Montana Department of State Lands (1994).

cadmium, and arsenic.

(3) Water draining pyrite-rich, carbonate-poor tailings and waste dumps tends to be acidic to highly acidic (pH 2 to 5), contains hundreds to several thousand s of mg/l iron and aluminum, and tens to several hundreds of mg/l zinc and copper.

Natural-drainage data: Not available. However, anecdotal accounts indica te that cerussite, a lead carbonate mineral, was abundant in stream sediments downstream from Leadville, Colo.; the presence of cerussite indicates that associated stream water was not acidic. Cerussite was probably transported physically as eroded fragments of mineralized rock; however, the possibility that some lead was transported as an aqueous phase, and subsequently precipitated in stream sediments, cannot be ruled out entirely. Mine-water data suggest that pre-mining pH values at Leadville were near neutral (pH 6 to 7.5); this water may have contained as much as several mg/l zinc and several tens of µg/l lead.

Potentially economically recoverable elements: Zinc extraction may become economically viable if aqueous extraction technologies continue to evolve.

Metal mobility from solid mine wastes

Metal mobility is greatest from mine dumps having the highest pyrite and lowest carbonate mineral contents. Metals and acid are readily liberated from pyrite-rich mine wastes and intermittently wet/dry mine workings due to the rapid dissolution of soluble secondary salts. In above-water-table settings, soluble salts form coatings on mine wastes, fracture fillings, and coatings on mine workings. The rate of salt dissolution (and resulting acid and metal generation) is much more rapid than acid consumption by carbonate minerals in the dumps or rocks surrounding the mine workings. Dumps with high carbonate mineral contents and low pyrite contents produce limited amounts of secondary salts; associated runoff has near neutral pH and low dissolved metal contents. In contrast, pyrite-rich, carbonate-poor dumps and mi ll tailings contain abundant secondary salts and down-gradient vegetation is adversely effected by acid, metal-rich drainage.

Storm water samples: No data available. However, extensive vegetation kill zones downhill from pyrite-rich mine dumps indicate that highly acidic, metalliferous water can be generated in spite   of the presence of carbonate-mineral-rich rocks on the mine dumps.

Results of water-rock leaching experiments: Dilute sulfuric acid leaches of mine waste from Leadville, Colo., (Montour, 1994) using U.S. Environmental Protection Agency Method 1312 (20:1 water-rock ratio) yielded water with pH values mostly between 2 and 3; however, the pH of two samples was about 4 and several had pH values near 8. These leach samples also contained elevate d metal abundances, including as much as 350 mg/l iron, 16 mg/l manganese, as much as 22 mg/l aluminum, as much as 250 mg/l zinc, and as much as 2,500 mg/l sulfate.

        Dilute sulfuric acid leaches of smelter slag and soil affected by smelter particulates generally yielded much lower (<1 mg/l) abundances of lead and other metals than mine wastes (Montour, 1994). Mobility of metals from slag is a function of the way in which slag was cooled; metals in slag poured onto the ground generally are less readily liberated into the environment tha n those from slag cooled by frothing into the air (John Drexler, oral comm. to M. Montour, 1993).

Bioavailability studies: Results of bioavailability studies at Aspen, Colo., document the importance of particle mineralogy and size on lead bioavailability (Andy Davis, PTI Environmental, oral presentation, 1993). Lead in galena from mine wastes may be signi ficantly less bioavailable than lead in smelter particulates and auto emissions.

Soil, sediment signatures prior to mining

Soil: Arid climate- Geochemical data for soil in the vicinity of polymetallic replacement deposits   in the Eureka, Nev., district are presented by Chaffee (1980; 1987). Fine-gr ained fractions (<0.063 mm) of soil samples uncontaminated by smelter emissions c ontain elevated metal abundances, including as much as 10,000 ppm lead, as much as 30,000 ppm zinc, as much as 50 ppm cadmium, as much as 500 ppm copper, as much as 30 ppm molybdenum, as much as 100 ppm bismuth, as much as 400 ppm antimony, as much as 200 ppm tin, and as much as 30 ppm silver.

Temperate climate- Limited soil geochemistry data (Montour, 1994) were obtained for samples collected beneath an historic residence in Leadville, Colo.; data for samples from these particular sample sites are presumed to reflect baseline metal abundances in soil unaffected by smelter contamination. This soil contains <100 ppm lead and <5 ppm cadmium. This soil is derived from unmineralized glacial o utwash; its geochemistry should not be extrapolated to soil developed on mineralized bedrock, which probably contained substantially higher metal abundances.

Stream sediments: Very high lead concentrations identified in downstream sediment prior to mining at Leadville, Colo., probably reflect the abundance of cerussite.

Potential environmental concerns associated with mineral processing
Historic processing typically involved milling to produce zinc-, lead-, and (or) copper-rich concentrates that were smelted. Pyrite-rich tailings produced as a milling by-product have high potential for generation of highly acidic, metal-bearing water, especially if the water is evaporatively concentrated. Storm-related flushing of soluble secondary salts may also lead to periodic degradation of downstream surface water quality.

Modern processing typically involves milling followed by concentrate smelting; stopes are backfilled with coarse tailings materials and fine tailings are stored in surface impounds. If pyritic tailings are backfilled, potential detrimental environmental effects can be largely avoided. In modern operations, gold-rich ore is increasingly recovered using a cyanide-free flotation system. Copper-rich ore may be treated using flotation. Some copper-mining operations use sulfuric acid heap leaching, followed by solvent extraction-electrowinning, to extract copper. The primary drawback of the acid-leach method for copper recovery is generation of potentially large volumes of acidic, iron- and aluminum-rich waste water that must be treated.

Smelter signatures
Chaffee (1980) demonstrated that soil geochemistry data effectively discriminates samples contaminated by smelter emissions from uncontaminated samples.
Leadville (Montour, 1994): Slag contains 1,500 to 3,400 ppm lead and 5 to 15 ppm cadmium; mineralogical studies indicate that most of the lead is present in sulfide minerals that survived smelting. Residential soil downwind from smelters contains more than 2,700 ppm lead and 5 to 37 ppm cadmium.
Eureka, Nev. (Chaffee, 1980; 1987): Soil in the vicinity of two smelters contains >1,000 ppm lead, >500 ppm arsenic and zinc, >100 ppm antimony and copper, >200 ppm tin, and >15 ppm molybdenum.

Climate effects on environmental signatures
Currently available data for mine water pertain to moderately wet, seasonally temperate climates. Evaporation of acid water during dry periods increases metal abundances and decreases pH. No data are available concerning evaporation of near-neutral water draining carbonate-hosted ore; evaporation of iron-poor water probably causes pH to increase.

Potential environmental effects:
Potential downstream effects of mine-drainage water associated with polymetallic replacement deposits are probably significantly less than those associated with other deposit types because of the abundance of near-neutral mine water and carbonate sedimentary rocks surrounding these deposits. Water draining carbonate rock terranes is highly alkaline and can effectively buffer acid generated by deposits or resulting from the formation of hydrous ferric and aluminum oxide particulates. In these situations, zinc and manganese are the elements most likely to remain mobile either in solution or as colloids (Kimball and others, 1995) for appreciable distances downstream.

The greatest potential for deleterious downstream environmental effects of mine-drainage water is associated with deposits principally composed of igneous or skarn ore; copper, zinc, manganese, and cadmium, to a lesser extent, can remain mobile for considerable distances downstream. In addition, deposits that contain abundant massive-sulfide ore in carbonate-poor sedimentary rocks, or carbonate-hosted massive sulfide ore in which drainage water does not interact with carbonate-rich sediments pose significant potential for environmental degradation. These ore types generate acidic, metal-rich water (figs. 2 and 3). Deposits that drain into geologic terranes with low acid-buffering capacity, such as those with low amounts of carbonate-bearing rocks, may also pose significant environmental hazards.

The most deleterious historic environmental effects associated with this deposit type are related to mining operations that released significant large volumes of fine-grained pyritic tailings into rivers or streams; these tailings have become part of accumulated sedimentary deposits, especially in low-velocity reaches of drainages. Oxidation of these tailings results in long-term release of metals and acid from sediments into overlying stream water resulting in water quality degradation; these downstream effects can be extensive.

Geoenvironmental geophysics
Distributions of conductive acid water can be delineated using electromagnetic and direct current resistivity surveys, and in some cases, ground penetrating radar (King and Pesowski, 1993; King, 1995; Paterson, 1995). Local hydrologic conditions, including permeable fault zones, bedrock channels, shallow caves, sandy flow channels, and clay aquitards, may be investigated using ground electrical, radar, seismic, magnetic, and gravity surveys. The same

methods can help define structural relations in tailing heaps (Paterson, 1995). Induced polarization can be utilized to estimate pyrite concentrations in tailings heaps (Paterson, 1995). Remote sensing imagery (Watson and Knepper, 1994; King, 1995) can help identify tailings distributions; bedrock lithologies, including acid-buffering carbonate rocks; and important structures that may control fluid flow.

Guidelines for mitigation and remediation:

(1) Acid water draining igneous and skarn ore, some massive sulfide lenses, and tailings can be remediated successfully using lime addition and sodium-bisulfide precipitation of metals; this process yields a potentially acid-generating sludge. Lime addition to iron-rich drainage water may generate a quantity of suspended particulates, onto which a major fraction of dissolved arsenic, lead, and copper can sorb, sufficient to reduce or eliminate the need for sodium bisulfide addition; this particulate sludge is non-acid-generating.

(2) Dilution of low-oxygen, near-neutral mine-drainage water by fresh water from carbonate aquifers may provide a low-cost remedial option, if sufficient dissolved iron is present to sorb metals.

(3) The utility of carbonate sedimentary host rocks should be considered in acid drainage mitigation. For example, acid water could be channeled through artificially or naturally fractured carbonate rocks, away from orebodies, to help reduce acidity.

(4) Careful fracture and karst mapping is required to adequately characterize site hydrology.

(5) Isolation of pyrite-rich waste dumps from weathering and formation of soluble secondary salts is crucial to prevent storm- and snowmelt-related pulses of acid and metals into surface water. High carbonate mineral content of dump material is not sufficient to prevent acid pulses because secondary salt dissolution generates acid and metals much faster than the carbonates can react with and consume acid.

(6) Backfilling the acid-generating, pyritic part of mill tailings into workings below the post-mining water table should be considered as a mitigative measure in modern milling operations to help avoid accidental downstream releases.

(7) Future advances in aqueous zinc extraction technologies may render mine water draining these deposits a potentially economic zinc resource that can be used to help defray mitigation and remediation costs.

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