

Chapter E

ENVIRONMENTAL GEOCHEMISTRY OF PLATFORM CARBONATE-HOSTED SULFIDE DEPOSITS

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INTRODUCTION

Current efforts to develop geoenvironmental models for specific mineral deposit types are based on a foundation comprising geology, mineralogy, and environmental characteristics. This chapter will provide an overview of critical environmental issues that are common to many carbonate-hosted deposit types and distinguish aspects of geology, mineralogy, and geochemistry that lead to unique environmental concerns. More than any other factor, the geologic classification of ore deposits has provided the framework on which observations regarding environmental behavior have been based (e.g., Rytuba, 2002, Tuttle and others, 2002). The relatively recent developments of comprehensive models of environmental behavior of carbonate-hosted mineral deposits employ this geologic framework to evaluate the relative contribution of external conditions such as topography, rainfall, and temperature.

Geoenvironmental models are compilations of geologic, geochemical, and hydrologic information that describe pre- and post-mining environmental signatures of mineral deposits. The environmental behavior of carbonate-hosted deposits varies according to deposit type and this study considered two major groupings of carbonate-hosted deposits: (1) metallic ores deposited by the reaction of low temperature, basinal brines with platform carbonate host rocks and (2) metallic ores deposited by the reaction of higher temperature fluids with carbonate host rocks. The general category of carbonate-hosted deposits can be divided into distinct types on the basis of variability of host-rock types, and metal associations—for the purposes of this paper we've limited the discussions to platform carbonate or Mississippi Valley type deposits. For the purposes of this short course, we examined a broad class of platform carbonate hosted deposits consisting of sulfide ore including Pb-Zn, Zn-rich, Pb-rich, Pb-Zn-Cu and Cu-Pb-Zn. Under the category of polymetallic replacement and skarn deposits, Hammarstrom (this volume) includes manto or Leadville-type deposits and skarns of the W, Sn, Au, Pb-Zn, and Fe variety. A number of deposit types that are hosted by carbonate-bearing rocks including carbonatite, asbestos, Carlin-type Au, solution-collapse breccia pipe U, and some sedimentary Fe and Mn deposits, are outside the scope of this study. Silica-carbonate Hg deposits are covered by Rytuba (2002) in another chapter in this volume.

Environmental Considerations

All of the deposits considered in this review are hosted by rock packages that contain considerable amounts of carbonate minerals both in the rock itself and in veins and massive sulfide bodies that formed by mineralizing processes. In addition to Fe and Al, metals and metalloids most commonly associated with these deposits are Cu, Mn, Zn, Cd, Ge, Co, Ni, Pb, As, and Tl. This geochemical suite reflects the primary character of the ores (e.g., Cox and Singer, 1986). In general, the potential for deleterious effects can be related to genetic classification in terms of acid-generating potential, associated heavy metal suites, acid-buffering capacity of host rocks, weathering products, and natural, pre-mining background characteristics of associated waters and rocks, among other characteristics (du Bray, 1995, and references therein). Carbonate-hosted deposits as a group have some of the lowest probabilities for adverse environmental impacts because their potential for generating acid and heavy metal contents due to their sulfide content, is balanced by the high acid-neutralizing potential of the carbonate host rocks.

The purpose of this course is to present a brief overview of the genetic classification of carbonate-hosted deposits, and to identify specific geologic, mineralogical and chemical characteristics of the group that relate to the potential environmental behavior of these types of mineral deposits when disturbed by mining. The obvious links between genetic classification and environmental behavior have been established through the compilation of data from site-specific studies throughout North America (Leach and others, 1995; Hammarstrom and others, 1995a, b, c; Plumlee and others, 1999). On-going studies by the USGS are generating data to refine these links and make them more site-specific (D. Leach and J.

Viets, personal communications, 2000). This paper presents a summary of past developments in this area of research and some refinements of previous geoenvironmental models created for these carbonate-hosted deposits (du Bray, 1995, and references therein).

Geological Characteristics

Carbonate-hosted deposits can be expected to share many common aspects of environmental behavior due to their general geological and mineralogical similarities. However, significant differences can also be expected due to specific geochemical characteristics of the rock and mineral hosts that relate to their genetic classification. In 1985, Cox and Singer published a valuable compilation of the general descriptive characteristics of a wide variety of carbonate-hosted deposits models (e.g., specific references). Deposits of this type are classified by host rock, ore type, and thermal, chemical, and physical environment of ore deposition.

For the deposit models considered in this course, the thermal and chemical environment of ore deposition is probably the most distinguishing genetic criteria. Carbonate-hosted deposits can be subdivided into two groupings based on the temperature and chemistry of the mineralizing fluid. Polymetallic and skarn deposits form by reaction of hydrothermal fluids ($>>250^{\circ}\text{C}$) generated in high temperature igneous (e.g., porphyry) environments with carbonate-bearing sequences. These fluids can be of low to high salinity and may contain CO_2 and other gaseous components. In contrast, platform carbonate deposits form by the interaction of low to moderate temperature (generally $<200^{\circ}\text{C}$), high salinity (10-30 equivalent weight percent NaCl) basinal brines with carbonate-bearing sequences. The resulting ore and gangue mineralogies in each grouping of deposits reflect (1) the ability of the two distinct fluid types to leach metals from the original source rocks and transport them to the depositional sites and (2) the interaction of the fluids and host rocks at the site of deposition.

Genetic models that incorporate process-related information have been published for polymetallic replacement, carbonate-skarn and Mississippi Valley type deposits (e.g., Cox and Singer, 1986, and references therein). The following is a summary of specific geological and geochemical characteristics that comprise platform carbonate-type deposits.

PLATFORM CARBONATE-HOSTED DEPOSITS

In general, carbonate-hosted deposits are zinc-, lead, or copper-rich ores that are hosted predominantly by dolostones, with lesser amounts of limestone, sandstone and other siliciclastic units that formed within continental basins. Most of these deposits are found in rocks of Cambrian, Ordovician, Devonian, Carboniferous, and Triassic ages; Proterozoic examples also are found. MVT deposits occur throughout the world (Figure 1a); the largest and most important economically are located in North America. Predominantly lead-rich deposits include the Viburnum Trend and Old Lead Belt (within the Southeast Missouri lead district). Zinc-rich types include Tri-State (Missouri-Kansas-Oklahoma) district, Austinville-Ivanhoe (Virginia); Upper Mississippi Valley (Wisconsin), Central Tennessee, East Tennessee (Mascot - Jefferson and Copper Ridge subdistricts) in the United States and Pine Point, Polaris, Daniel's Harbor, Gays River, and Nanisivik in Canada. Table 1 lists general geologic characteristics of Mississippi Valley type deposits. Kipushi deposits generally are smaller although they also cluster in districts. The Apex mine, Utah, and Ruby Creek, Alaska, are North American examples.

Related Deposit Types

Deposits hosted by carbonate rocks are part of a broad spectrum of deposits hosted by sedimentary rocks (Cox and Singer, 1986; Sangster and Leach, 1995) that includes sedimentary exhalative lead-zinc-barite deposits (Model 31a), carbonate-hosted fluorite deposits (for example, Illinois- Kentucky fluorite deposits), MVT deposits (Model 32a), carbonate-platform deposits (for example, Mt. Isa and HYC, Australia; Balmat-Edwards, NY), Kipushi copper deposits (model 32c) and sandstone lead deposits (Model 30a) (for example Laisvall, Sweden and Largentiere, France). Another group of deposits to be included in this spectrum are siliciclastic-hosted deposits such as the Irish type Zn-Pb-Cu-Ag (Lion Hill, Vt; Silvermines, Navan, Ireland).



Figure 1. Distribution of carbonate-hosted Zn-Pb deposits occurring throughout the world. Figure from Leach and others (1995). Locations shown: 1, Polaris; 2, Eclipse; 3, Nanisivik; 4, Gayna; 5, Bear-Twit; 6, Godlin; 7, Pine Point district; 8, Lake Monte; 9, Nancy Island; 10, Ruby Lake; 11, Robb Lake; 12, Monarch-Kicking Horse; 13, Giant; 14, Silver Basin; 15, Gays River; 16, Daniels Harbour; 17, Metaline district; 18, Upper Mississippi Valley district; 19, southeast Missouri district (Old Lead Belt, Viburnum Trend, Indian Creek); 20, central Missouri district; 21, tri-State district; 22, northern Arkansas district; 23, Austinville-Ivanhoe district; 24, Friedensville; 25, central Tennessee district; 26, east Tennessee district; 27, San Vicente; 28, Vazante; 29, Harberton Bridge; 30, Silesian district; 31, Alpine district; 32, Pering; 33, Sorby Hills; 34, Coxco; 35-37, Lennard Shelf district (Cadjebut, Blendvale, Twelve Minle Bore); 38, El-Abad-Mekta district. (Adapted from Sangster, 1990).

Deposit Size

Platform carbonate deposits typically occur in districts covering hundreds, or even thousands, of square kilometers. Although individual ore zones may be small, these zones tend to cluster into districts that constitute world-class sources of lead and zinc. Leach and others (1995) compiled data for deposits versus districts. District totals for metals may represent several dozen individual deposits; for example, the Pine Point and Upper Mississippi Valley districts contain more than 80 and nearly 400 deposits, respectively. Individual deposits are generally small; most yield less than ten million tons of ore. An analysis of the Pine Point district, for example, showed that most deposits contained between 0.2 and 2 million tons of ore, and the largest had nearly 18 million tons (Sangster, 1990). For the Upper Mississippi Valley district, Heyl and others (1959) reported that the average deposit size was between 0.1 and 0.5 million tons, although a few contained as much as 3 million tons of ore.

Combined lead plus zinc grades in MVT deposits (districts) seldom exceed 10 percent. The Polaris deposit, in the Canadian Arctic Archipelago, is not only unusually large (22 million tonnes), but is anomalously high grade as well (18 percent lead plus zinc). A majority (about 85 percent) of deposits (districts) are zinc-rich relative to lead and have $Zn/(Zn+Pb)$ values between 0.5 and 1.0, with a distinct mode at 0.8. A smaller group, consisting of the entire Southeast Missouri district plus a few other small deposits, has a modal value of about 0.05 and is distinctly anomalous in this regard.

Table 1. Critical geological characteristics of MVT deposits (Leach and Sangster, 1993; Leach and others, 1995).

1.	Most deposits are hosted by dolostone; less commonly in limestone or sandstone
2.	Ores are epigenetic and stratabound
3.	Deposits are not associated with igneous activity
4.	Deposits are at shallow depths at the flanks of basins
5.	Deposits are in platform carbonate sequences, either located in relatively undeformed rocks bordering foreland deeps or in foreland thrust belts.
6.	Many deposits are in districts that cover hundreds of square kilometers; some districts form metallogenic provinces.
7.	Deposits form districts that are localized by geologic features, including breccias, depositional margins of shale units, facies tracts, faults, and basement highs that permit upward migration of ore fluids.
8.	Ore-deposition temperatures are low (50°C-200°C), but typically higher than those attributable to local basement-controlled thermal gradients; mineralization is in thermal equilibrium with respect to common host rocks.
9.	Deposits are mineralogically simple; dominant minerals are sphalerite, galena, pyrite, marcasite, chalcopyrite, dolomite, calcite, and quartz.
10.	Alteration associated with mineralization consists mainly of dolomitization, brecciation, host-rock dissolution, and dissolution/recrystallization of feldspar and clay.
11.	Evidence of carbonate rock dissolution is common and expressed as slumping, collapse, brecciation, or some combination of these.
12.	Ore fluids were dense basinal brines, typically containing 10-30 weight percent salt.
13.	Isotopic data indicate crustal sources for both metal and reduced sulfur.
14.	Sulfide mineral textures are varied, nature of the ore can range from coarsely crystalline to fine-grained, and massive to disseminated.

Table 2. Classification of selected deposits hosted by siliciclastic and carbonate-bearing rock sequences

Metal Suite	Clastic sedimentary \geq Carbonate	Carbonate > Clastic sedimentary
Pb-Zn-Cu-(Ag)	Irish type Silvermines, Ireland Navan, Ireland Lion Hill, Vt	MVType Southeast Missouri Upper Mississippi Valley
Cu-Pb-Zn	Sediment-hosted Cu type Kupferschiefer, Germany White Pine, MI Kamoto, Zaire	Brushy mine, SE MO Kipushi type Ruby Creek, AK Apex, UT Kipushi, Zaire
Zn-rich Pb-poor	Balmat-Edwards, NY	Appalachian type Austinville, VA, Copper Ridge, TN
Pb-rich	Laisvall type Laisvall, Sweden Largentierre, France	MVType Viburnum Trend, SE MO Old Lead Belt, SE MO

Host Rocks

Classic MVT deposits are hosted by dolostones and contain Zn-rich and Pb-Zn ores. Deposits hosted by rock sequences that predominantly consist of sandstone (e.g., the Pb-rich Laisvall district, Sweden) are lead-rich. Mixed carbonate-siliciclastic rocks contain deposits (e.g., the Lion Hill deposit, Vermont; Silvermines district, Ireland) comprised of the suite Zn-Pb-Cu-(Ag). Kipushi deposits formed in dolomite breccias with a shale component are characterized by Cu-Pb-Zn (Kipushi, Zaire).

Surrounding Geologic Terrane

MVT deposits commonly are at shallow depths along basin flanks (Figure 2). They form in platform carbonate sequences, located either in relatively undeformed rocks bordering foredeeps or in foreland thrust belts. Some deposits are associated with salt diapirs (for example, Bou Grine in Tunisia). Most deposits are surrounded by carbonate rocks with high acid buffering capacity.

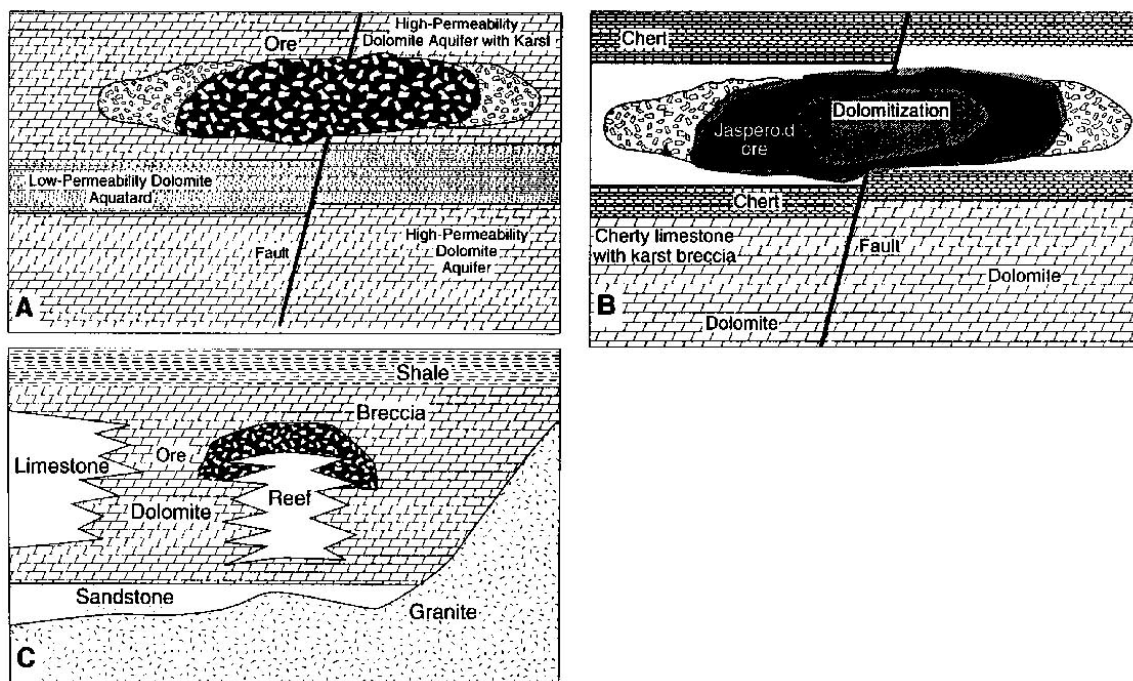


Figure 2. Schematic cross-sections showing geologic features of various platform carbonate deposits, from Plumlee and others (1999). The cross sections reflect concepts presented by Leach and Sangster (1983) and references therein: A. Central Missouri district, B. Tri-State district, and C. Viburnum Trend.

The deposits typically occur in undeformed, orogenic foreland carbonate platform environments. Some occur in carbonate sequences in foreland thrust belts bordering foredeeps and a few are associated with rift zones. Others, such as Kipishi-type deposits form in carbonaceous laminated stromatolitic dolomites where high fluid flow occurs along tabular or pipe-like fault or karst (?) breccia zones.

Wall-Rock Alteration

Dissolution, recrystallization, and hydrothermal brecciation of host carbonate rocks within and peripheral to mineralized rock is common to virtually all the deposits. These effects may develop in conjunction with silicification and dolomitization and constitute the major form of wall-rock alteration in most districts. Ore-related silicification of host rocks limits the buffering capacity of rocks near ore deposits and therefore influences the extent of metal-bearing water dispersion in some districts (for example, Tri-State). Hydrothermal dolomite may be pre-, syn-, or post-ore and has commonly replaced pre-ore carbonate host rocks to form distinctive alteration halos around deposits (for example, the East Tennessee and Tri-State districts). Formation of authigenic clay and feldspar minerals and destruction of detrital potassium-silicate minerals are recognized in some districts.

Nature of Ore

Platform carbonate ore is extremely varied in both character and form. Orebodies range in nature from massive replacement zones to open space layered fillings of fractures and coatings on breccias to disseminated clusters of crystals that occupy intergranular pore space. Crystal size ranges from

cryptocrystalline to museum quality specimens as much as a meter or more in length (e.g., "crystal caverns" in the Tri-State and Central Tennessee districts). In some districts, notably Pine Point, Silesia, Polaris, and Cadjebut, much of the ore occurs as extremely fine-grained, laminated aggregates of botryoidal (colloform) sphalerite which is commonly intergrown with dendritic or skeletal galena. Most platform carbonate deposits show clear evidence that open space deposition was accompanied by dissolution and replacement of host carbonate rocks. Carbonate host rock replacement can be nearly total (e.g., massive sulfide zones at Nanisivik and Polaris) or selective (zebra rock facies at Austinville, VA). Ore-hosting structures are most commonly zones of highly brecciated dolomite; in some instances (for example, Pine Point and Daniels Harbour) these zones are arranged in linear patterns suggesting a tectonic control, although faults of large displacement are never present. Faults that reflect reactivated basement structures are the most important ore control in some districts, notably Upper Silesia and Ireland. In other cases, more localized structures, such as breccia pipes in stromatolitic dolostone, focused mineralization.

Mining and Ore Processing Methods

Current mining methods use underground room-and pillar or longwall mining technologies. Ore is processed by pulverizing and flotation, and the concentrates are usually shipped to smelters.

Deposit Trace Element Geochemistry

Zinc, lead, and copper are the primary commodities produced in deposits of this kind, and constitute the dominant metal suite (Table 3). Variability in the dominant metallogeny of the districts has been suggested to result from controls imposed on bulk chemistry by the impact of large-scale fluid-flow regimes on regional lithotectonic setting (craton-Pb, basinal-Zn-Pb, and platform-Zn). Although the general deposit type can have a diverse metallogeny, typically individual districts have a more limited suite of associated metals (Table 3).

Carbonate-hosted deposits can contain a minor but complex suite of trace minerals and elements (Table 3). Other commodities reportedly produced at some deposits of this type include, silver, copper, cadmium, germanium, barite, fluorite, and nickel. Minor and trace minerals may include arsenate minerals, arsenopyrite, barite, bravoite, bornite, chalcopyrite, carrollite, celestite, chalcocite, covellite, digenite, djurleite, enargite, gallite, germanite, galena, greenockite, linnaeite, marcasite, millerite, molybdenite, pyrrhotite, renierite, siegenite, tennantite, and tungstenite and vaesite (co-sulfide). Some of these phases are present in trace amounts in many deposits, however only a few deposits (examples in Table 3) can be expected to contain the entire suite. Southeast Missouri deposits contain relatively abundant Ni and Co sulfides, whereas the Silesian deposits contain strong enrichments of arsenic and thallium in sphalerite and marcasite (Viets and others, 1996).

Primary Mineralogy and Zonation

The simple sulfide mineral assemblages of these deposits consist of galena, sphalerite, pyrite, marcasite, and chalcopyrite; trace amounts of other sulfide and sulfosalt minerals make up the balance. Within a given district, individual deposit mineralogy may be quite variable, although this is atypical for MVT deposits. The Viburnum Trend is one of the best studied, and most variable deposits in North America. For example, Pb-Zn-Cu deposits occurring within the Southeast Missouri district contain substantial pyrite, marcasite, and chalcopyrite although the amounts vary considerably from mine to mine. The mineralogical paragenesis of the Viburnum Trend subdistrict Number 28 mine is dominated by late marcasite and pyrite, whereas, the Brushy mine contains large amounts of chalcopyrite, lesser pyrite, and negligible marcasite (Horrall and others, 1983). In contrast, the deposits at East Tennessee almost uniformly consist of coarse yellow sphalerite and calcite. Chalcopyrite-rich types typically have a more diverse trace element geochemistry (e.g., Table 3).

Iron sulfide content is clearly the most important consideration for platform carbonate deposits (Leach and others, 1995). Most deposits of this type contain less than 5% iron sulfide by volume. For example, the Austinville-Ivanhoe district contains only trace to minor amounts of iron sulfide. A rare exception, the sulfide mineral assemblage at Nanisivik is dominated by pyrite. The most critical aspect of the iron sulfide mineralogy is that it generally occurs in fairly reactive forms. Anisotropic pyrite and marcasite are common. For example, the Silesian MVT district contains a late-stage of botryoidal marcasite that occurs in some deposits and is absent in others (Sutley and others, 1999). Sutley and others (1999) demonstrates that forms salts and release of trace metals. For example, Plumlee and others (1999) of iron sulfide

Table 3. Mineralogical and metal associations of MVT and associated deposits types

Deposit	General MVT	Viburnum Trend, SE MO	Ruby Creek* Apex*	East Tenn	Tri-state	Austin -ville	Upper Silesia, Poland	Nanisivik* Pine Point*
Major metals	Zn, Pb, Fe	Pb, Zn, Fe	Cu, Zn, Pb, As,	Zn	Zn, Pb	Zn, Pb, Fe	Fe, Zn, Pb, S	Zn, Pb, Fe
Minor and trace metals	Cu, Ba, Cd, Ag, Ge, Ga, Co, Ni, As	Cu, Co, Ni, Cd, Ag, In, Ge, Ga, Sb, Bi, As, Mo, Sn, Au	Co, Ag, Ge, Ga, Mo, W, Sn, Bi, U, V		Fe, Cu, Cd, Ba, Ag, Ge, Ga, Co, Ni, In, Sb, Bi	Cu, Cd, Ge, Ga, F, Ba, As	Zn, Cd, Fe, Pb, As, Ag, Tl, Cd	Ba, Cd, Ag, As, Ni, Ge
Dominant Fe sulfide	Py	Py, mc	Py	Py	Py	Py (aniso)	Mc	Py
Major ore sulfides	Sp, gn	Gn, sp, cp, py, mc	Py, bo, ch, gn, cp, ca, sp, tn, mc, as	Sp, py	Sp, gn	Sp, gn	Sp, gn, mc	Py, sp, gn
Minor sulfides	Py, mc, cp, as, br	Si, bo, tn, br, dg, cv, ar, po, as, ml, dj, ch, en	Co-py, ln, ge, re, ga, tu, mo, mc	Gn, cp	Cp, mc, br	Py, mc, cp, as	Gn	As, br
Primary sulfate	Ba	Ba			Ba	Ba,		Ba
Major carbonate	Do	Do	Do	Do	Do	Do	Ara	Do
Minor carb	Sm, cc, cr, cs	Cc	Cc	Cc	Cc	Cc, do, sm	Sm	Cc
Secondary oxides, arsenates, sulfates, oxy-hydroxide etc.	gr, an, cl, go, ep, gy, ma, me, sz, co, di, Fe-ox, hm		Co-ox, Co-ar, ja, ma, az, Fe-ox			an, cr, gy, ag, ce	Fe-ox, hm, an, he, li, pa, lo, hyzn, cr, gy, ja	

Abbreviations: an-anhydrite, ag-anglesite, ar-arsenate, ara-aragonite, as-arsenopyrite, ba-barite, az-azurite, br-bravoite, py-pyrite, bo-bornite, cp-chalcopyrite, ca-carrollite, cc-calcite, ce-celestite, ch-chalcocite, cl-calamine, co-copiatite, cr-cerrusite, cs-carphosiderite, cv-covellite, dg-digenite, di-diadochite, dj-djurleite, do-dolomite, en-enargite, ep-epsomite, ga-gallite, ge-germanite, gn-galena, go-goslarite, gr-greenockite, gy-gypsum, hyzn-hydrozincite, hm-hematite, he-hemimorphite, ja-jarosite, li-litharge, ln-linnaeite, lo-lollingite, ma-malachite, me-melanterite, mc-marcasite, ml-millerite, mo-molybdenite, ox-oxide, pa-parabutlerite, po-pyrrhotite, re-renierite, si-siegenite, sm-smithsonite, sp-sphalerite, sz-szomolnokite, tn-tennantite, tu-tungstenite, zn-carb.

may contain the bulk of the trace metals, which are readily released as the iron sulfide weathers. Mixtures of reactive iron sulfide and other sulfide may accelerate the formation of secondary have noted that

underground workings of the Viburnum trend that contain bornite intergrown with marcasite weather extensively to secondary copper sulfate salts whereas bornite alone is generally unreactive.

Recrystallized dolomite is the most common gangue mineral. Alteration haloes of dolomite surround many MVT and Kipushi deposits; they are particularly well-developed at East Tennessee and in the Tri-state district. The primary form of carbonate intergrown with ore in these deposits is hydrothermal dolomite. Dolomite is less reactive than simple carbonates such as calcite. Smithsonite is also present in many of these deposits, and was the primary source of the zinc ore in some deposits during early mining years. Hydrothermal calcite occur in many deposits of this type, but is generally much less abundant than dolomite. Jasperoid and botryoidal forms of quartz also occur as gangue material.

Secondary Mineralogy

Secondary minerals consist of smithsonite, calamine, anglesite, cerussite, celestite, malachite, sulfur, goslarite, epsomite, gypsum, melanterite, szomolnokite, copiatite, carphosiderite, diadochite, hydrous iron oxide minerals, hematite, and greenockite. Malachite and azurite are reported in copper-rich deposits. Jarosite, has also been reported rarely. ADD Sutley

Soil and Sediment Signatures

Many MVT deposits are thought to have essentially no geochemical signature outside of the zone of wall rock alteration because of limited primary dispersion of ore related elements into the surrounding carbonate rocks (Lavery and others, 1994), except along structures that acted as fluid conduits. However, in some districts where ore-bearing zones have been weathered, soil contains anomalous concentrations of lead and zinc. Soil geochemistry in the Irish district (Hitzman and others, 1992) and in the Newfoundland zinc district (Davenport and others, 1975) are effectively used in exploration.

Although MVT deposits are hosted by carbonate rocks, residual soil overlying some deposits can be acidic; it can have moderate to high permeability, medium to high erosion potential, and moderate to high water capacity. These factors can influence the mobility of metals into the environment. In the area of the Austinville-Ivanhoe, Va., district background carbonate rocks typically contain about 20 ppm zinc and 9 ppm lead. However, extensive volumes of rock containing dolomite cement are widely peripheral to mineralized zones (for example, Wythe County, Va.; Barnaby, 1989); replacement dolomite and late calcite have considerably elevated abundances of some trace metals, including as much as 9,300 ppm iron, 200 ppm strontium, 1,500 ppm lead, 1,000 ppm manganese, and 10,000 ppm zinc.

In the region of the East Tennessee district, readily detectable zinc, iron, and locally lead anomalies are found in residual soil and stream sediment. For example, NURE data for stream sediment indicate that over 100 samples from the Bluefield 1 x2 quadrangle (Va., W. Va., Tenn., and N.C.) have anomalous lead and zinc abundances (>20 ppm zinc and >10 ppm lead) that may be attributable to lead and zinc deposits in the region. Proctor and others (1981) conducted a survey of the acid soluble lead content of 416 stream sediment samples collected from active streams throughout a 7,000 square mile area that includes much of the Southeast Missouri lead district. Samples from areas underlain by Paleozoic carbonate rock and considered to be largely non-mineralized have a mean lead content of 25 ppm, whereas samples from areas of active mining and milling contain an average of 393 ppm lead. The specific residence of lead was not identified but Proctor and others (1981) considered metal from insoluble rock residues, primary dispersion halos, secondary dispersion of primary mineralization, and recent dispersion due to mining and milling and smelting activities as possible lead sources.

Topography and Physiography

Most platform-carbonate deposits are located in flat-lying carbonate sequences. However, some deposits are located in thrust and fold belts (for example, Monarch-Kicking Horse, British Columbia; Alpine district in Europe). The deposits typically occur in undeformed, orogenic foreland carbonate platform environments. Some occur in carbonate sequences in foreland thrust belts bordering foredeeps and a few are associated with rift zones. Others form in carbonaceous laminated stromatolitic dolomites along tabular or pipe-like fault or karst (?) breccia zones and in zones of higher permeability due to structural effects such as block faulting and caving due to carbonate dissolution.

Hydrology

Platform-carbonate deposits originally form as a result of the interaction of large-scale fluid-flow regimes that leach extensive sedimentary rock sequences and deposit metals when the fluids reach carbonate rocks. The ores in MVT deposits form from heated basinal brines that migrate regionally away from mountain uplift and compressional collision zones on basin edges. The brines deposit small amounts of sulfide minerals (iron sulfides, sphalerite, galena) regionally in the sedimentary aquifers through which they flow. Ore-grade mineral deposits form where fluids from different aquifers intersect zones of higher permeability due to structural effects such as block faulting and caving due to carbonate dissolution. Precipitation of minerals may occur by mixing of brines from different aquifers or by a change in the chemistry of the fluid that might result from flow of a brine from one aquifer to another. An example of this might be flow of fluid from a dolostone aquifer to a chemically more reactive limestone aquifer. Kipishi deposit form in dolomites where high fluid flow occurs along tabular or pipe-like breccia zones. Thus, high fluid transmissivity is a dominant characteristic of all platform-carbonate deposits and most districts have some spatial connection to major aquifers, karsts, breccia pipes, or faults occurring within the geologic record. Post-mineralization events such as tectonism, uplift, weathering, and metamorphism have altered the present-day hydrological setting.

Drainage Signatures

Metal mobility away from platform-carbonate deposits is limited by the abundance of carbonate rock associated with these deposits; carbonate rock consumes acid mine drainage and inhibits aqueous metal mobility (Figure 1c). Heavy metals abundances were determined at four seepage sites related to mine wastes in the Old Lead Belt (Smith and Schumacher, 1991). Maximum concentrations measured were: 850 mg/l SO₄, less than 10 g/l copper, 80 g/l lead, 18,000 g/l zinc, and 28 g/l cadmium. During two years of monitoring at the four sites, pH of the seeps ranged from 6.23 to 8.61. A lead-zinc ratio of 5 for Old Lead Belt ore (Snyder and Gerdman, 1968) indicates that zinc is clearly more mobile than lead or cadmium in water leaching waste materials; these relative mobilities also appear to apply to Big River water. The presence of Pb-sulfate in some of the districts (e.g., Austinville, VA) indicates that Pb can be sequestered in an insoluble sulfate form. Near-neutral waters having elevated concentrations of dissolved Zn (as high as 100 mg/l) and Pb and Cd have been reported in mine workings with high iron sulfide contents (Plumlee and others, 1999). Near-neutral zinc-bearing river waters are also reported for low iron sulfide districts (Austinville, VA). In this case, other factors besides iron sulfide content are working to increase the zinc contents of mine drainage waters, these include reactivity of the iron sulfide form and zinc mineralogy (Foley, 2001).

Ground water. Water from a depleted part of one mine in the Viburnum Trend is used as the municipal water supply for Viburnum, Mo. This water meets all U.S. Environmental Protection Agency water quality standards with the exception of that for sulfate (Missouri Department of Natural Resources, 1991). Reported sulfate content is 436 mg/l, whereas the accepted water quality standard is 250 mg/l. Other parameters are pH=7; alkalinity=260; 0.18 mg/l iron; 5.7 mg/l sodium; 72 mg/l magnesium; 0.24 mg/l fluorine; 856 mg/l total dissolved solids; and lead, zinc, and cadmium abundances are in the g/l range. In addition, several communities in Upper Silesia, Poland, use water from underground lead-zinc mines as their only domestic water supply. The sulfate content of this water is variable but is commonly in the 400 to 800 mg/l range and lead is present in the g/l range.

Surface water. The Big River flows through the Old Lead Belt and near many waste piles. Water quality data (Smith and Schumacher, 1991) for a site about 15 km above mining and smelting activity reflect background water parameters: SO₄ <24 mg/l, lead <10 g/l, cadmium <2 g/l, and zinc <27 g/l. During its flow through the district, carbonate buffering causes water pH (6.6-8.5) to be virtually unchanged. However, SO₄, lead, and zinc abundances increase due to inputs primarily from surface mine wastes. At a site 5 km below the district, the water contains 40-140 mg/l SO₄, 10 g/l lead, <1 g/l cadmium, and 110-160 g/l zinc.

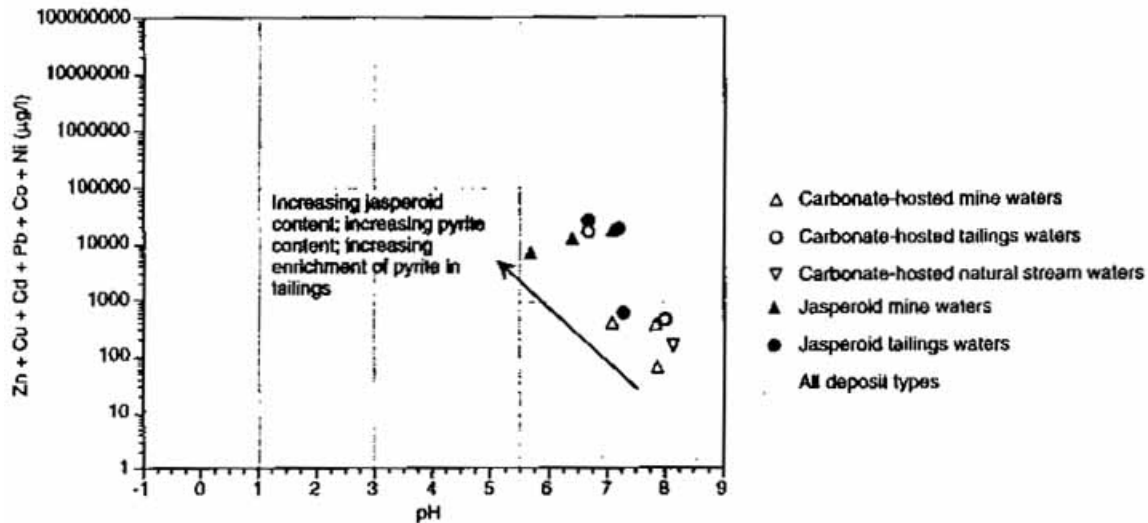


Figure 3. Ficklin plot showing some compositions of mine waters, tailing waters, and a natural water draining carbonate-hosted and jasperoid-rich MVT deposits. The plot is used to compare the sum of dissolved base metals (Zn, Cu, Cd, Pb, Co, and Ni) to pH and illustrate how mine drainage chemistry can vary as a function of the mineral deposit type. Figure is from Plumlee and others (1999).

Climatic Effects

Climate is extremely critical in assessing the environmental concerns associated with this deposit type. Current climatic setting can be as varied as Sahara conditions in North African deposits to permafrost conditions at the Polaris mine (Leach and others, 1995). Many North American deposits occur in humid temperate, and dry temperate regimes (e.g., Bailey, 1996). Potential acid-mine drainage problems related to MVT deposits in relatively dry climate settings are much less than those of deposits in warm, wet climates. Acid-rain aggravates potential environmental problems in the mid-Atlantic and northeastern United States, especially the Appalachians. Small MVT deposits are present throughout the Appalachians in Cambrian to Mississippian carbonate rock sequences (for example, Shady Dolomite and Knox Dolomite). The Austinville-Ivanhoe, Va., deposit is a prime example of how climatic conditions and soil properties interact to increase potential environmental problems. For example, in Wythe County, Va., soil is moderately to very strongly acidic (pH 5.6 to <4.5) although as much as 30 percent of the surface may consist of dolomitic limestone outcrops; the soil has moderate permeability, medium to high erosion potential, and moderate water capacity. Much of the soil is deemed suitable for cultivated crops (legumes), hay, or pasture and much is prime farmland (corn, vegetables, small grain, and strawberries) (U.S. Department of Agriculture, 1992). Most of the area is in the drainage basin of the New River, which has water quality problems including excessive concentrations of trace metals such as zinc, copper, lead, iron, and locally acidification caused by mining activities (Virginia Water Control Board, 1990a,b). Prime farmlands of the valley and ridges within and adjacent to the Appalachian Mountains (near historic lead and zinc mines) may be affected by metal contamination attributable to past releases of lead and zinc into soil and ground water as a result of environmental conditions specific to the region.

In contrast to the Appalachian deposits, the Polaris deposit is in a region of permafrost with little opportunity for dispersion into the environment from surface or ground water. Likewise, deposits in arid regions such as Bou Grine in Tunisia, have little opportunity for metal mobility in water.

Potential Environmental Concerns

Mine sites. Most modern underground carbonate hosted zinc-lead mining operations return a significant amount of mine waste and mill tailings to underground workings as fill. In the case of the Polaris mine in the Canadian Arctic, waste slurries are used to fill mining voids in their modified room and long pillar galleries. Once frozen, waste supports the roof and long pillars are mined so that essentially the entire deposit is mined. In Upper Silesia, Poland, surface disposal of iron sulfide-mineral-rich-tailings presents a potentially serious environmental problem in the district. Surface mill tailings pose the major

potential environmental concern associated with MVT deposits. Although modern processing facilities carefully monitor water draining from processing sites, some water, with elevated concentrations of lead, zinc, cadmium, arsenic, thallium, and a variety of trace elements characteristic of the ore deposit, may escape. Airborne dust from tailing ponds can potentially contribute ore particulates.

Smelter signatures. Studies of the effects of airborne smelter effluent in the Viburnum Trend of southeast Missouri by Bornstein and Bolter (1991) indicate that soil pH at distances of as much as 6.4 km from the smelter source and as deep as 15 cm are significantly reduced, ranging from 4.4 at 15 cm to 5.1 at 5 cm depths. At 9.6 km, pH ranged from 6.8 to 7.0. The sulfur content of the soil correlates with the pattern of pH depletion. Lead, zinc, copper, cadmium, cobalt and nickel contents of leaf litter and underlying soil decrease with distance from the point source and depth below surface. The extent of heavy metal enrichment was about half that of the area affected by sulfur enrichment suggesting that SO₂ is the principal sulfur species. Palmer and Kucera (1980) conducted a similar study for lead, by sampling both sycamore leaves and twigs and soil, around four smelter sites in southeast Missouri. Their results were very similar to those of Bornstein and Bolter (1991) and indicate that dominant wind directions and degree of lead enrichment are correlated.

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