A Deposit Model for Mississippi Valley-Type Lead-Zinc Ores

Chapter A of
Mineral Deposit Models for Resource Assessment

2 cm

Scientific Investigations Report 2010–5070–A

U.S. Department of the Interior
U.S. Geological Survey

COVER:
Sample of spheroidal sphalerite with dendritic sphalerite, galena, and iron sulfides (pyrite plus marcasite) from Pomorzany mine. Note the "up direction" is indicated by "snow-on-the-roof" texture of galena and sphalerite along colloform layers of light-colored sphalerite. Hydrothermal sulfide clasts in the left center of the sample are encrusted by sphalerite and iron sulfides. Size of sample is 20x13 centimeters. (Photograph by David L. Leach, U.S. Geological Survey.)

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U.S. Department of the Interior
KEN SALAZAR, Secretary

U.S. Geological Survey
Marcia K. McNutt, Director

U.S. Geological Survey, Reston, Virginia: 2010

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Conversion Factors

SI to Inch/Pound

Multiply	By	To obtain
Length		
centimeter (cm)	0.3937	inch (in.)
millimeter (mm)	0.03937	inch (in.)
Micrometer (μm)	0.00003937	inch (in.)
meter (m)	3.281	foot (ft)
kilometer (km)	0.6214	mile (mi)
Area		
square kilometer (km^2)	0.3861	square mile (mi^2)
Volume		
cubic meter (m^3)	6.290	barrel (petroleum, 1 barrel = 42 gal)
liter (L)	33.82	ounce, fluid (fl. oz)
liter (L)	2.113	pint (pt)
liter (L)	1.057	quart (qt)
liter (L)	0.2642	gallon (gal)
Mass		
gram (g)	0.03527	ounce, avoirdupois (oz)
microgram (μg)	0.00000003527	ounce, avoirdupois (oz)
milligram (mg)	0.00003527	ounce, avoirdupois (oz)
tonnes (t)	2204.6226	pound avoirdupois (lb)
tonnes (t)	1.1023	ton (US, short)
million tonnes (Mt)	1.1023	million tons (US, short)
kilogram (kg)	2.205	pound avoirdupois (lb)

Temperature in degrees Celsius (°C) may be converted to

degrees Fahrenheit (°F) as follows:

°F=(1.8×°C)+32

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Abstract

This report is a descriptive model of Mississippi Valley-Type (MVT) lead-zinc deposits that presents their geological, mineralogical and geochemical attributes and is part of an effort by the U.S. Geological Survey Mineral Resources Program to update existing models and develop new models that will be used for an upcoming national mineral resource assessment. This deposit modeling effort by the USGS is intended to supplement previously published models for use in mineral-resource and mineral-environmental assessments. Included in this report are geological, geophysical and geochemical assessment guides to assist in mineral resource estimation. The deposit attributes, including grade and tonnage of the deposits described in this report are based on a new mineral deposits data set of all known MVT deposits in the world.

Mississippi Valley-Type (MVT) lead-zinc deposits are found throughout the world but the largest, and more intensely researched deposits occur in North America. The ores consist mainly of sphalerite, galena, and generally lesser amounts of iron sulfides. Silver is commonly an important commodity, whereas Cu is generally low, but is economically important in some deposits. Gangue minerals may include carbonates (dolomite, siderite, ankerite, calcite), and typically minor barite. Silicification of the host rocks (or quartz gangue) is generally minor, but may be abundant in a few deposits. The deposits have a broad range of relationships with their host rocks that includes stratabound, and discordant ores; in some deposits, stratiform and vein ore are important.

The most important characteristics of MVT ore deposits are that they are hosted mainly by dolostone and limestone in platform carbonate sequences and usually located at flanks of basins, orogenic forelands, or foreland thrust belts inboard of the clastic rock-dominated passive margin sequences. They have no spatial or temporal relation to igneous rocks, which distinguishes them from skarn or other intrusive rock-related Pb-Zn ores. Abundant evidence has shown that the ore fluids were derived mainly from evaporated seawater and were driven within platform carbonates by large-scale tectonic events.

MVT deposits formed mainly during the Phanerozoic with more than 80 percent of the deposits hosted in Phanerozoic rocks and less than 20 percent in Precambrian rocks. Phanerozoic-hosted MVT deposits also account for 94 percent of total MVT ore, and 93 percent of total MVT lead and zinc metal. Many MVT deposits formed during Devonian to Permian time, corresponding to a series of intense tectonic events during assimilation of Pangea. The second most important period for MVT deposit genesis was Cretaceous to Tertiary time when microplate assimilation affected the western margin of North America and Africa-Eurasia.

Many subtypes or alternative classifications have been applied to MVT deposits. These alternative classifications reflect geographic and or specific geological features that some workers believe set them apart as unique (for example, Appalachian-, Alpine-, Reocin-, Irish-, Viburnum trend-types). However, we do not consider these alternative classifications or sub-types to be sufficiently different to warrant using them.

This report also describes the geoenvironmental characteristic of MVT deposits. The response of MVT ores in the supergene environment is buffered by their placement in carbonate host rocks which commonly results in near-neutral associated drainage water. The geoenvironmental features and anthropogenic mining effects presented in this report illustrates this important environmental aspect of MVT deposits which separates them from other deposit types (especially coal, VHMS, Cu-porphyry, SEDEX, acid-sulfate polymetallic vein).

Introduction

Mississippi Valley-Type (MVT) lead-zinc deposits are found throughout the world (fig. 1), but the largest, and more intensely researched deposits occur in North America where the deposit type was first recognized about 70 years ago (Bastin, 1939). MVT deposits owe their commonly accepted name to the fact that several classic districts are located in the drainage basin of the Mississippi River in the central U.S.

MVT deposits have a median size of 7 million tonnes (Mt) and grades of about 7.9 wt. percent lead (Pb) and zinc (Zn) metal. However, MVT deposits usually occur in
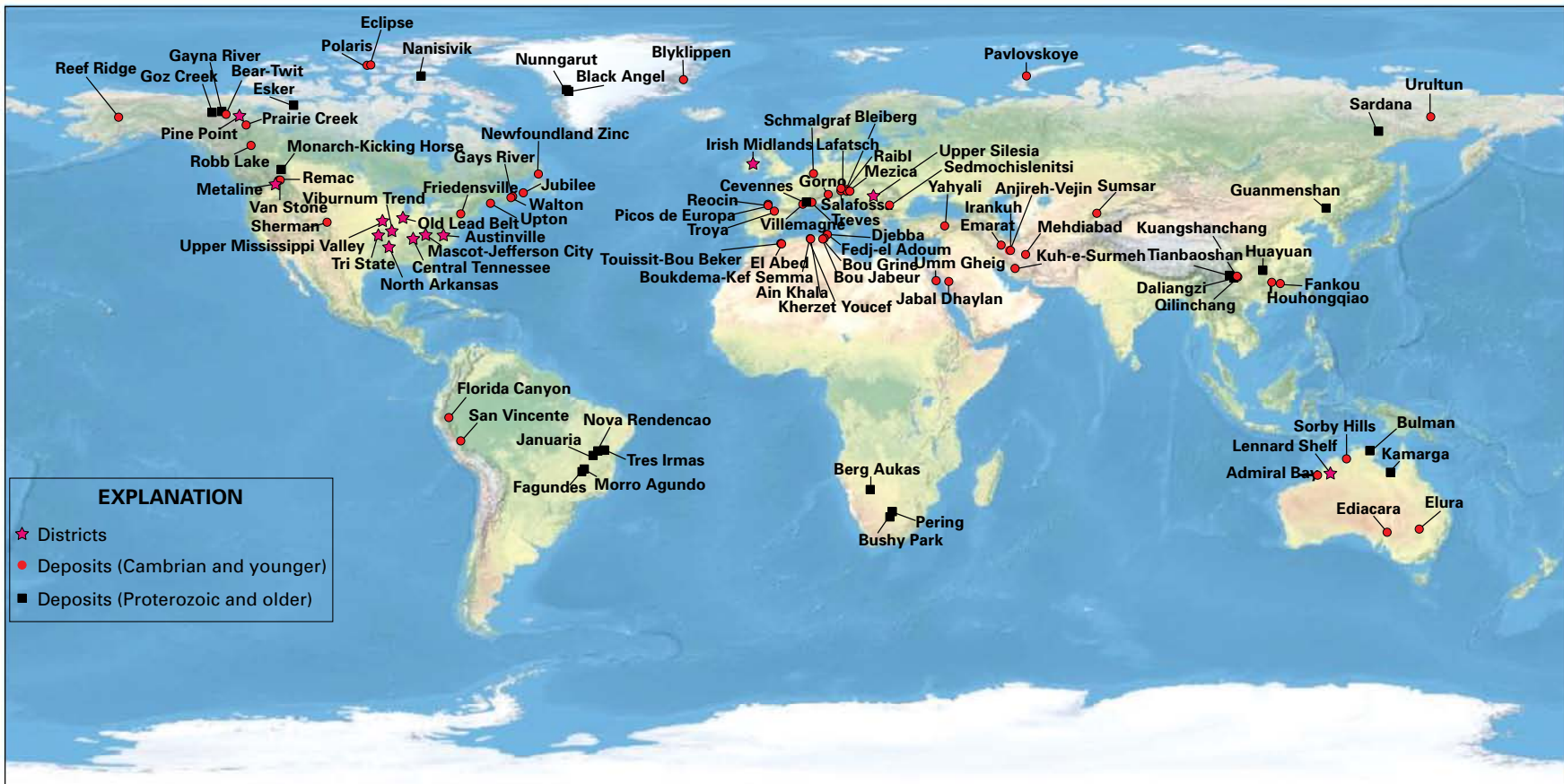
Figure 1.   Global distribution of Mississippi Valley-Type lead-zinc deposits and districts.

extensive districts consisting of several to as many as 400 deposits. Because of the large grain size, processing of the ores is easier than most sediment-hosted ores and the carbonate host-rocks mitigate many environmental issues.

This document draws extensively from Leach and others (2005) because it is the most comprehensive existing description of known MVT deposits. This USGS model of MVT deposits includes numerous references to tables, figures, and compilations in Leach and others (2005). Furthermore, Leach and others (2005) contains grade-tonnage data for all known sediment-hosted lead-zinc (Pb-Zn) deposits, including 110 MVT deposits and 8 districts and 129 sedimentary exhalative (SEDEX) deposits. Taylor and others (2009) provides an update of the grade-tonnage data from Leach and others (2005). Either data compilation can be used to construct grade-tonnage models for resource estimations.

Additional resources for users of this report are other reviews of MVT deposits including Ohle (1959; 1980), Callahan (1964), Brown (1967), Snyder (1967), Heyl and others (1974), Hoagland (1976), Anderson and Macqueen (1982), Kisvarsanyi and others (1983), Sangster (1983; 1986; 1990; 1996), Sverjensky (1986), Leach and Sangster (1993), Leach and others (2001), Bradley and Leach (2003), Paradis and others (2007), and Leach and others (2010).

Purpose and Scope

This report of MVT deposits is part of an effort by the U.S. Geological Survey Mineral Resources Program to update existing models and develop new descriptive mineral deposit models that will be used for an upcoming national mineral resource assessment. This deposit modeling effort by the USGS is intended to supplement previously published models for use in mineral-resource and mineral-environmental assessments.

Deposit Type and Associated Commodities

Name

Mississippi Valley-Type (MVT)

Synonyms

Numerous sub-types and alternative classifications applied to MVT include but not limited to: Viburnum Trend-, Alpine-, Silesia-, Irish-, Appalachian-, and Reocin-type. A discussion of these sub-types and classification issues is presented in Leach and others (2005).

Brief Description

Mississippi Valley-Type deposits account for 24 percent of the global resources for Pb and Zn in sediment- and volcanic-hosted deposits [MVT + volcanic hosted massive sulphide (VHMS) + sedimentary exhalative (SEDEX) + sandstone lead (ss-Pb)]. Relative to all sediment-hosted ore deposits (MVT + SEDEX + ss-Pb), MVT deposits account for 38 percent of the total Pb and Zn tonnage.

The most important characteristics of MVT deposits, modified from Leach and Sangster (1993) and taken from Leach and others (2005), are: (1) they are epigenetic; (2) they are not associated with igneous activity; (3) they are hosted mainly by dolostone and limestone, rarely in sandstone; (4) the dominant minerals are sphalerite, galena, pyrite, marcasite, dolomite, and calcite, whereas barite is typically minor to absent and fluorite is rare; (5) they occur in platform carbonate sequences commonly at flanks of basins or foreland thrust belts; (6) they are commonly stratabound but may be locally stratiform; (7) they typically occur in large districts; (8) the ore fluids were basinal brines with ~10 to 30 wt. percent salts; (9) they have crustal sources for metals and sulfur; (10) temperatures of ore deposition are typically 75°C to about 200°C; (11) the most important ore controls are faults and fractures, dissolution collapse breccias, and lithological transitions; (12) sulfides are coarsely crystalline to fine grained, massive to disseminated; (13) the sulfides occur mainly as replacement of carbonate rocks and to a lesser extent, open-space fill; and (14) alteration consists mainly of dolomitization, host-rock dissolution, and brecciation.

As noted by Sangster (1990) and discussed by Leach and others (2001; 2005) and Kesler and Reich (2006), most MVT deposits are hosted in Phanerozoic rocks and the ore type is significantly less common in Proterozoic rocks. Only one known deposit (Pering-Bushy Park) is contained in Neoarchean rocks.

MVT ores are in platform carbonate sequences in passive margin environments and commonly related to extensional domains inboard of Phanerozoic contractional tectonic belts (Leach and others, 2001; 2005). The exception to this general relation are the deposits in the platform carbonate sequence of the Canning Basin, Australia, where the ore deposition was controlled in part by extensional faulting along a late Paleozoic continental extensional basin transitional to a passive margin basin.

MVT deposits usually occur in extensive districts and, excluding district total metal endowments, the median parameters for individual MVT deposits are 7.0 Mt ore, 1.9 percent Pb, 6.0 percent Zn, 0.23 percent copper (Cu) and 32.5 grams per tonne (g/t) silver (Ag) (table 1).

Table 1. Summary statistics for select parameters of Mississippi Valley-Type deposits (data from Taylor and others, 2009).

[Min, minimum value; 10th, 10th percentile; 25th, 25th percentile; 75th, 75th percentile; 90th, 90th percentile; Max, maximum value; n, number of deposits with data for given parameter; (Mt), million tonnes; %, percent; (g/t), grams per tonne]

	Min	10th	25th	Median	75th	90th	Max	n
				MVT deposits (113 deposits)				
Size (Mt)	0.06	0.65	1.90	7.00	18.1	42.4	394	113
Pb (Mt)	<0.01	<0.01	0.02	0.11	0.36	0.98	6.30	108
Zn (Mt)	<0.01	0.03	0.11	0.33	0.95	2.44	16.6	108
Pb (%)	0.18	0.75	1.10	1.90	3.60	6.27	13.0	101
Zn (%)	0.11	1.89	3.56	6.00	9.94	12.5	24.0	107
Cu (%)	0.10	0.14	0.17	0.23	0.33	0.44	0.52	8
Ag (g/t)	3.40	10.2	17.8	32.5	54.8	88.0	485	34

Associated and Transitional Deposit Types

SEDEX

SEDEX (sedimentary exhalative) and MVT ores are the two most important types of sediment-hosted Pb-Zn ores. SEDEX ores are traditionally characterized as synsedimentary to early diagenetic based primarily on the presence of laminated ore textures and tabular morphology of the deposits. MVT deposits generally exhibit abundant evidence for an epigenetic and replacement nature to the ores. However, the distinction between some SEDEX and MVT deposits can be quite subjective because some SEDEX ores replaced sediments in an early or burial diagenetic environment whereas some MVT deposits formed in an early diagenetic environment and display laminated ore textures. Both sub-types formed from sedimentary brines at similar temperatures and ore depositional paths. As a consequence of the controversy over the inherent time factor built into the term "SEDEX", Leach and others (2010) proposed the term Clastic Dominated (CD) Pb-Zn ores as an alternative classification. However, for consistency with other USGS mineral assessment reports, we use the term SEDEX rather than CD.

The most significant difference between MVT and SEDEX deposits is their depositional environment, which is determined by their respective tectonic settings. The contrasting tectonic setting also dictates the fundamental deposit attributes that generally set them apart, such as host-rock lithology, deposit morphology, and ore textures.

Sandstone-Lead

Sandstone lead (ss-Pb) deposit classification was proposed as a distinct deposit type by Bjørlykke and Sangster (1981). The deposits contain disseminated galena in basal, quartzitic sandstones, typically deposited in transgressive sequences onto sialic basement.

Sandstone-Hosted Lead Deposits

Sandstone-hosted lead deposits are a poorly studied set of sediment-hosted ores that contain abundant lead but lack the geologic characteristics of Sandstone lead deposits.

Fracture Controlled Pb-Zn and Fluorite-Barite Deposits

(for example, Central Kentucky, Hansonburg, New Mexico, or the English Pennines).

Distal Pb-Zn Skarn and Igneous Related Pb-Zn Manto Deposits

(for example, El Mochito, Honduras and Nikolaevsky, Russia).

Primary Commodities

Zinc and lead are the primary commodities for most MVT deposits. On average, MVT deposits yield about a 10:1 mass ratio of Zn to Pb metal. Some deposits and districts yield only zinc (for example, East Tennessee, Central Tennessee) and others dominantly lead (for example, Viburnum Trend, Old Lead Belt, Beddiane, Sorby Hills).

Byproduct Commodities

Byproduct commodities include Ag, Cu, and indium (In) for some deposits. Silver is reported for 34 of 113 deposits in table 1, with a median value of 32.5 g/t and the 90th percentile value of 88.0 g/t. Total silver production can be substantial; for example, during the period 1960 to 1990, annual silver production from the Viburnum Trend averaged 45.9 tonnes. Historically, some deposits and districts yielded road aggregate and iron sulfides for sulfuric acid production.

Trace Constituents

Some deposits have recoverable economic levels of germanium (Ge), gallium (Ga), and cadmium (Cd). Cobalt (Co) is present in significant but sub-economic amounts at the Madison Mine in the Old Lead Belt, and Southeast Missouri.

Example Deposits

Leach and others (2005) reported metal endowment data for the grade and tonnage data for 248 known sediment-hosted deposits, including 110 MVT deposits and 8 districts. Included in the data compilations are the contents of Cu and Ag and key references to the geology of the deposits. The data compilations in Leach and others (2005) were based on efforts of D.F. Sangster in the World Minerals Geoscience Database Project (Sinclair and others, 1999). Taylor and others (2009) updated the MVT deposit data compilations and included tectonic classifications of the deposits. A summary of the statistics for selected parameters for the deposits from Taylor and others (2009) is given in table 1.

Mississippi Valley-Type deposits are characteristically distributed over hundreds of square kilometers (km^2) that define individual ore districts. Large MVT districts include Southeast Missouri (3,000 km^2), Tri-State (1,800 km^2), Pine Point (1,600 km^2), Alpine (10,000 km^2), Upper Silesia (2,800 km^2), Irish Midlands (8,000 km^2), and the Upper Mississippi Valley (7,800 km^2). Pine Point contains more than 80 deposits, and the Upper Mississippi Valley contains nearly 400 deposits. Individual deposits can be small in some districts. Most deposits in the Pine Point district contain between 0.2 and 2 Mt of ore, and the largest has nearly 18 Mt (Sangster, 1990). Heyl and others (1959) reported that the average deposit size in the Upper Mississippi Valley district was between 0.1 and 0.5 Mt, although a few contained as much as 3 Mt of ore. Deposits within districts usually have similar deposit attributes and ore controls whereas individual districts can be quite distinct. Some MVT hydrothermal events formed multiple districts in large areas defining huge metallogenic provinces. Examples of selected MVT provinces, districts, and important deposits are given below with general references to geological descriptions and illustrations.

MVT Metallogenic Provinces

Ozarks: Ohle, 1959; Leach, 1994; refer to Figures B3, B4 and table B1 in Leach and others (2005).

Appalachian province: Included in the Appalachian province are the East Tennessee district (including the Mascot-Jefferson City district), Newfoundland Zinc, Gays River and the Austinville-Ivanhoe district: Kesler (1996), refer to figures 4, 5 in Kesler (1996).

MVT Districts

Upper Silesia, Poland: Leach and others (1996); Leach and others (2003); refer to figure 4 in Leach and others (1996).

Viburnum Trend and Old Lead Belt, United States: Sverjensky (1981); Ohle (1996).

Irish Midlands, Ireland: Hitzman and Beaty (1996); Leach and others (2005) and references therein; refer to figures 3D and 3E and figures B12, B13, and B14 in Leach and others (2005).

Tri-State, United States: Newhouse (1933); Hagni and Grawe (1964); Brockie and others (1968).

East Tennessee, United States: Misra and Fulweiler (1995).

Pine Point, Canada: Rhodes and others (1984).

Upper Mississippi Valley, United States: Heyl and others (1959).

Important Deposits

Reocin, Spain: Velasco and others (2003); refer to figure 3C Leach and others (2005).

Metaline, United States: Dings and Whitebread (1965); refer to figure 3A Leach and others (2005).

Polaris, Canada: Randell and Anderson (1996).

Navan, Ireland: Ashton and others (1986).

Historical Evolution of Descriptive and Genetic Knowledge and Concepts

Early models for MVT ores called upon ore formation by dilute meteoric groundwater, magmatic, and connate fluids, and invoked processes that ranged from synsedimentary-exhalative to supergene activity involving meteoric water. Sharp divisions of opinion existed between geologists who believed the ores were syngenetic, early diagenetic, or epigenetic in origin. The syngenetic interpretations were mainly based on the stratiform nature of some ores and ore textures that are now known to be the result of host-rock replacement that mimic sedimentary features. Perspectives of this debate are summarized by Snyder (1967), Brown (1970), Ohle (1970) and Leach and others (2005).

Modern thoughts on the origin of MVT deposits began with fluid inclusion studies that showed the ore fluids were similar to oil-field brines (Newhouse, 1933; Hall and Friedman, 1963; Roedder and others, 1963; White, 1968). A major step in understanding their genesis was the suggestion that they formed by the mixing of multiple basinal fluids with contrasting reduced sulfur and metal content (for example, Dunham, 1966). Early models assumed that MVT deposits had no connection with tectonic processes. However, in the last 25-30 years, studies have noted the association of MVT

ore genesis to major crustal tectonic events (see Sharp, 1978; Garven, 1985; Oliver, 1986; Leach and Rowan 1986; Bethke and Marshak, 1990; Oliver, 1992; Leach and others, 2001). Furthermore, in the last 20 years, abundant evidence has shown that the ore fluids were derived mainly from evaporated seawater and were driven within platform carbonates by large-scale tectonic events. Perhaps the most significant achievements in understanding MVT ore genesis have been from advances in dating MVT ores (for example, Leach and others, 2001, and references therein).

Regional Environment

Geotectonic Environment

It is generally recognized that most MVT deposits have a temporal and spatial connection with orogenic forelands (Garven, 1985; Mitchell, 1985; Leach and Rowan, 1986; Oliver, 1986; Leach and others, 2001). Many MVT deposits formed during Devonian to Permian time, corresponding to a series of intense tectonic events during assimilation of Pangea resulting in approximately 61 percent of the Pb and Zn content in dated MVT deposits. The second most important period for MVT deposit genesis was Cretaceous to Tertiary time when microplate assimilation affected the western margin of North America and Africa-Eurasia and created approximately 36 percent of the Pb and Zn in dated deposits. Therefore, 97 percent of MVT Pb and Zn metal was generated within these two time periods. Based on the deposits that have been dated (Leach and others, 2001), it appears that few MVT deposits were formed during periods of major plate dispersal represented by the Neoproterozoic to early Paleozoic period or during the rapid breakup of Pangea in Triassic through Jurassic time.

Bradley and Leach (2003) examined the tectonic aspects of foreland evolution and concluded that the type of foreland is not a critical control on ore formation. MVT deposits are located in collisional (for example, the Ozark MVT province), Andean (for example, the Western Canada Basin deposits), and transpressional orogens (for example, the Cévennes district). Also associated with orogens are MVT deposits that occur in fold and thrust belts. Some deposits formed in flat-lying rocks or were later caught up in thrusting. Others formed synchronously with thrusting and others formed after burial by the thrusts.

Some MVT deposits clearly formed in a large-scale extensional environment. The best examples of these are the Lennard Shelf, Australia deposits. The age obtained for ore deposition (Christensen and others, 1995; Brannon and others, 1996a; Brannon and others, 1996b) coincides with crustal extension of the Fitzroy Trough.

Temporal (Secular) Relations

MVT deposits formed mainly during the Phanerozoic (Leach and others, 2001; 2005), with more than 80 percent of the deposits hosted in Phanerozoic rocks and less than 20 percent in Precambrian rocks. Phanerozoic-hosted MVT's also account for 94 percent of total MVT ore, and 93 percent of total MVT Pb+Zn metal (fig. 2). Recent papers on the secular distribution of MVT ores include Leach and others (2001; 2005; 2010) and Kesler and Reich (2006). Leach and others (2005; 2010) attribute the distribution to the increased recycling rate of carbonate rocks in passive margin environments and to a fundamental change in the nature and permeability of carbonate platform sequences beginning in the Neoproterozoic. Ancient carbonate platforms consisted primarily of stromatolites and sea-floor precipitates (Grotzinger and James, 2000). Synsedimentary lithification, early diagenetic dolomitization and silicification, lack of bioturbation, and coarse skeletal carbonate debris, render these platform carbonate successions impermeable (Grotzinger, 1989). Kesler and Reich (2006) and Leach and others (2010) suggested the lower contents of sulfate in Proterozoic seawater limited the production of oxidized evaporites that favor formation of MVT ores. However, Leach and others (2010) show that the genesis of MVT ores and the formation of most evaporites in the rock record are not coeval, suggesting that MVT ore fluids are sourced from preexisting brines in the carbonate platform sequences.

Duration of Magmatic-Hydrothermal System and/or Mineralizing Processes

The few studies that focused on the duration of MVT mineralizing events indicate the ore forming event was relatively short compared to the duration of the associated orogenic events. Rowan and Goldhaber (1995) used fluid inclusion data together with thermal alteration of biomarkers to calculate the duration of the ore-forming event in the Upper Mississippi Valley district. The best fit of the fluid inclusion data to the biomarkers yielded a probable duration of about 200 thousand years (kyr), consistent with the 250 kyr estimated from fluid-rock (mass transfer) arguments for the Upper Mississippi Valley district (Lavery and Barnes, 1971). Repetski and Narkiewicz (1996) used fluid inclusion data together with time-temperature dependent thermal alteration of conodonts in the Cracow-Silesia zinc-lead district in Poland. Their calculations indicate that the Polish ore-forming event could not have lasted for more than about 50 kyr. Symons and others (1998) used paleomagnetic techniques in the Viburnum Trend to determine that the time span between the deposition of main-stage (cube-octahedral galena) and late-stage (cubic galena) ore was between 5 and 12 million years (Myr). On the basis of transient numerical modeling of mass and energy transport by topographic gradients, Appold and Garven (1999) suggested the period of mineralization in Southeast Missouri

was relatively short (on the order of hundreds of thousands of years) compared to the lifetime of the gravity-flow system that could have persisted for tens of millions of years. Coveney and others (2000) found that hydrothermal calcite was deposited over hundreds of millions of years within the Tri-State district, with Zn mobilization occurring over periods of tens of millions of years based on dated samples.

Relation to Structures

Although MVT deposits typically formed during crustal-scale contractional events, the single most important tectonic controls at the deposit or district scale are extensional faults (normal, transtensional, and wrench faults) and associated fractures and dilatancy zones. This relation applies to most MVT districts, including the Ozark MVT province (for example, Clendenin and Duane, 1990). Bradley and Leach (2003) discussed MVT deposits that formed within extensional domains that developed due to lithospheric flexure (refer to figures 2, 3, 11 and 12, in Bradley and Leach, 2003) or in large dilational zones within bounding strike-slip faults during large-scale contractional events. Ordovician normal faults related to the Taconic collision controlled MVT mineralization in the Newfoundland Zinc district (Bradley, 1993). Far-field tectonic effects in the host rocks for MVT deposits commonly reflect reactivation of preexisting faults and fractures in the basement (for example, Ozark Province, Irish Midlands, and Cèvennes). Far-field extension inboard of orogenic belts can extend several hundred kilometers into the foreland and may explain districts such as those in the Western Canada Basin, Upper Mississippi Valley, and the Irish Midlands. The endowment of orogenic forelands with MVT deposits reflects the link between contractional events in orogenic zones, inboard extensional tectonic domains, and fluid flow. The extensional domains provide fluid drains for large regional aquifers (in other words, like the Ozark region) or focused pathways for the ascent of fluids in buoyancy-driven hydrothermal systems.

Relations to Igneous Rocks

Igneous rocks are not genetically associated with MVT deposits.

Relations to Sedimentary Rocks

Obviously MVT ores are related to carbonate rocks simply by definition of the ore type. However, the most fundamental control on where MVT ores are deposited is determined by lithology transitions, especially those which create dramatic changes in both the vertical and lateral permeability of the rocks in a carbonate platform sequences. The ore controls in figure 3 are mainly controls on the transmissivity of the ore-forming fluids which include facies transition (shale to carbonate, limestone to dolostone, and sandstone to
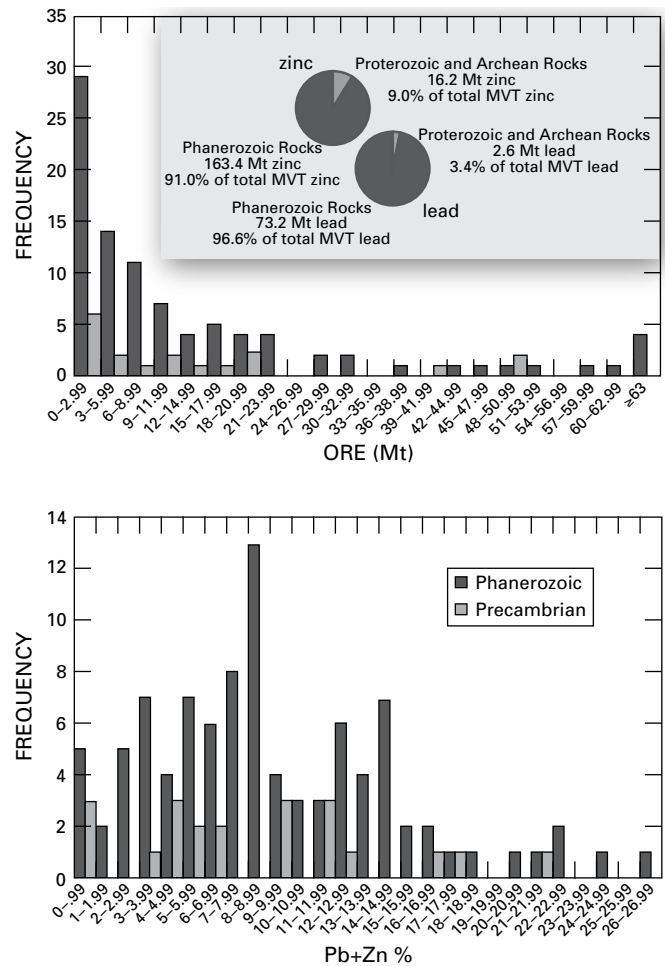
Figure 2. Comparison of metal content and size of Precambrian and Phanerozoic Mississippi Valley-Type (MVT) deposits. Phanerozoic MVT deposits greatly outnumber and contain a greater quantity of metal than Precambrian deposits.

carbonates), and the dramatic facies transitions common in reef and barrier complexes. Pre-ore dissolution collapse features are important ore controls in most MVT districts because they can provide extreme contrasting fluid transmissivity in carbonate platform sequences. Pre-ore dissolution collapse features are important sites for ore deposition and host-rock dissolution and hydrothermal-dissolution collapse. Carbonate rocks overlying fractured or faulted crystalline basement rocks also provide a contrast in the reactivity of the ore fluids. Some ore deposits are believed to have formed in part by the reaction of metalliferous fluids equilibrated with crystalline rocks with carbonate rocks through changes in pH and redox reactions.

Relations to Metamorphic Rocks

Metamorphic rocks are not genetically associated with MVT deposits.

DEPOSIT/DISTRICT	SHALE EDGES	LIMESTONE/DOLOSTONE	REEF AND BARRIER COMPLEX	SOLUTION COLLAPSE BRECCIAS	BASEMENT TOPOGRAPHY	FAULTS AND FRACTURES	PRE-ORE DISSOLUTION FEATURES
Viburnum Trend	●	●	●	●	●	●	
Old Lead Belt	●	●	●		●	●	
Tri-State	●	·	●	●		●	
North-Arkansas	●	·		●		●	
Cent. Tennessee		·		●		·	·
Mascot-Jefferson City (East Tenn.)		·		●		◐	
Austinville	·					●	
Gays River			●		◐	●	
Newfoundland Zn		●		·		●	●
Nanisivik				●		●	
Polaris	●	●		●			
Pine Point	●	●	●	●		·	·
Gayna				●			
Upper Mississippi Valley		·		·		●	
Alpine	●	·	●	●		●	
Robb Lake	●	·		●		·	
Monarch-Kicking Horse	●	·		·			
Upper Silesia	●	●		●	◐	●	·
Lennard Shelf	·	·		●	◐	●	·
Coxco				●			
Irish Midlands		·		·		●	·
Metaline	●	●		●		●	·
Cévennes		·		●	◐	●	·
Bushy Park				●		·	●
Pering				●		·	●
Reocin				●		●	·

● Major   ● Less important   · Minor
Ore controls in selected MVT districts

Figure 3. Summary of ore controls in selected Mississippi Valley-Type (MVT) deposits and districts (from Leach and others, 2005; modified from Leach and Sangster, 2003).

Physical Description of Deposits

Dimensions in Plan View

Plan views of MVT deposits are extremely variable in shape and reflect the large size of the ore-forming events and the diversity of district-scale geological features that controlled ore deposition. Therefore, there are no typical dimensions. Some examples of deposit dimensions are:

1. Deposits located in carbonate dissolution collapse breccias and associated features may take the form of individual collapse breccia bodies. In the Pine Point district for example, the plan views of the deposits are circular to oval expressions of collapse breccia bodies that are several tens to hundreds of meters in diameter (Skall, 1975; Hannigan, 2007). These individual ore breccias total 60 deposits in a 1,600 km² district.

2. Some MVT districts appear as an interconnected paleo-karst network that may extend for many kilometers. For example, the East Tennessee ore field connects multiple districts over a 15,000 km² area (Kesler and others, 1988).

3. MVT districts with mineralization controlled by carbonate reef and barrier facies such as the Southeast Missouri District which have plan views reflective of the reef complex (fig. 4) (Ohle, 1996; Leach and others, 2005). Economic, sub-economic, and trace mineralization define a nearly continuous belt that extends for more than 160 km.

4. MVT deposits that have a dominant fault control (for example, Raibl, Italy, and Irish Midlands) have plan views that trend along the strike projection of the ore control-ling fault system (fig. 5) (see Hitzman and Beaty, 1996 in Leach and others, 2005).

Size of Hydrothermal System Relative to Extent of Economically Mineralized Rock

A characteristic feature of most MVT deposits and ore districts is the enormous extent of the hydrothermal systems that produced widespread trace mineralization, prospects, and economic deposits. For example, the hydrothermal system for the Ozark Metallogenic province (includes Southeast Missouri and Tri-State districts) affected more than 350,000 km³ of rock in the late Paleozoic (Leach, 1994, and references therein). On the district-scale, trace mineralization and geochemical altera-tion is widespread throughout much of the districts; South-east Missouri (3,000 km²), Tri-State (1,800 km²), Pine Point (1,600 km²), Alpine (10,000 km²), Upper Silesia (2,800 km²), Irish Midlands (8,000 km²), and the Upper Mississippi Valley (7,800 km²).

Vertical Extent

The vertical extent of the ore deposits is also highly vari-able, although economic mineralization is usually on the order of a few to several tens of meters. Vertically stacked mineral-ized zones and minor to trace mineralization can extend for several hundred meters.

Form and Shape

MVT deposits are commonly discordant on a deposit scale but stratabound on a district scale. They can have exten-sive stratiform or stratabound replacement ores that continue for several kilometers (for example, Reocin, Spain, and the Yellowhead ore zone at Metaline, United States). The loca-tion and geometry of most MVT deposits reflect the interplay between faults, pre-ore carbonate dissolution features, and permeable stratigraphic units. In some deposits, extensive mineralized zones are stratiform in nature. One of the most characteristic morphologies of many MVT deposits is dis-solution collapse breccias. They vary from the prismatic breccias of Pine Point (Kyle, 1981; Rhodes and others, 1984)
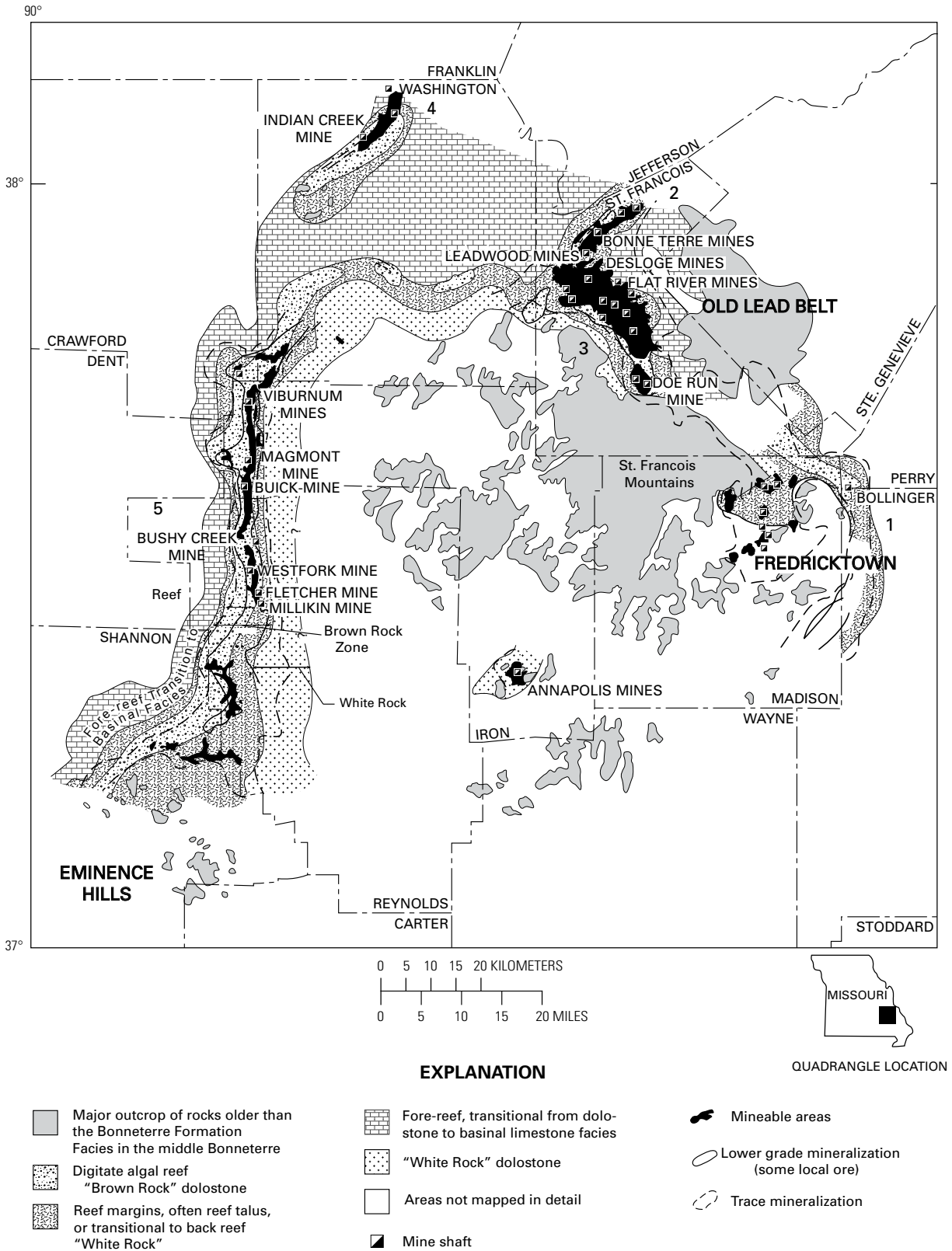
Figure 4.   Southeast Missouri mining district (from Leach and others, 2005; modified from Ohle, 1996).
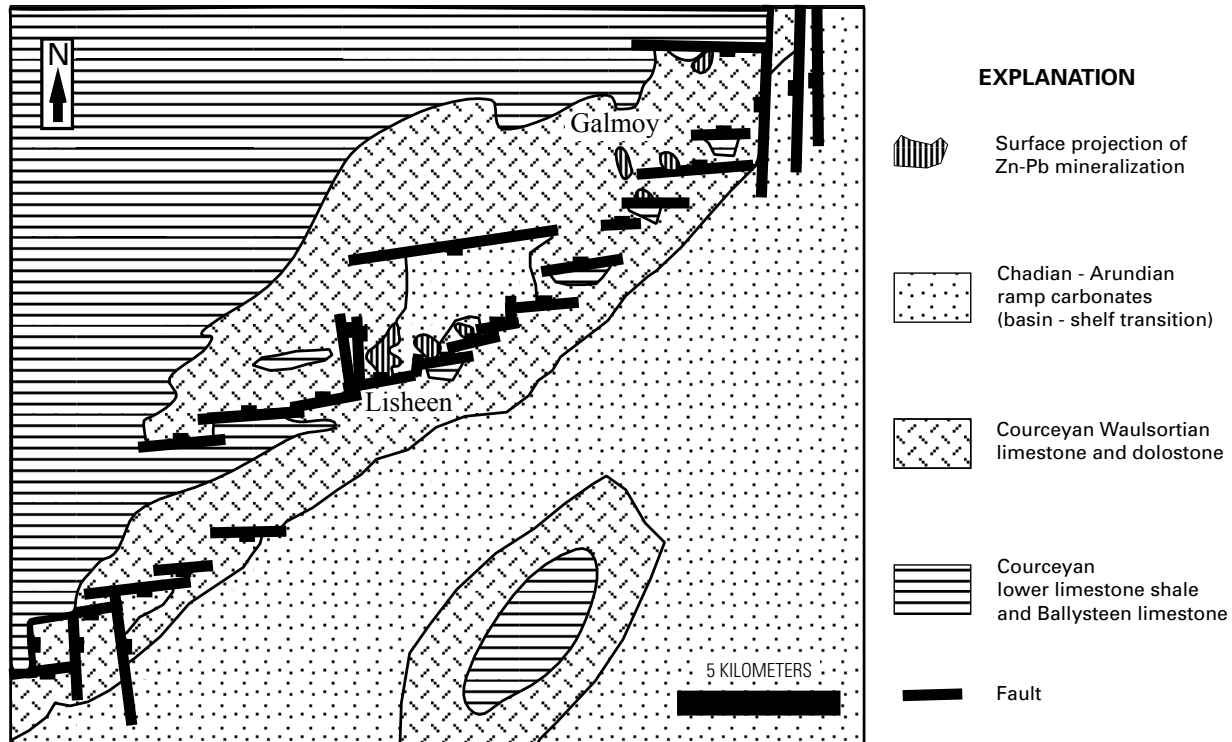
Figure 5.   Irish Midlands mining district displaying correlation of ores and faulting (from Leach and others, 2005; modified from Hitzman, 1999).

and columnar breccias of East Tennessee (Ohle, 1985) to the low domal breccias and stratiform breccias of the Tri-State and Upper Silesia districts. In plan view, some breccia-hosted deposits (East and Central Tennessee districts) appear as a reticulate pattern similar to karst cave systems. In contrast, the Viburnum Trend contains breccia-hosted ores that occur in narrow breccia trends related to a reef complex (less than several hundred meters wide but up to 10 km long).

Fault-controlled deposits vary significantly in shape and size, reflecting the influence of a variety of structural and lithological controls. Important variations on fault-controlled morphology range from the steeply dipping fracture-controlled ores of Raibl and the Irish Midlands districts, to the graben-controlled ores of Toussit Bou-Beker, Morocco (fig. 6a) (Leach and others, 2005), and Reocin deposit, Spain (fig. 6b) (Leach and others, 2005). Salt-dome environments provide a minor but interesting form of MVT ores. Sulfides are present in the cap-rock mineral assemblage, as fracture fill, and as replacement of carbonate host rocks. The most important deposits are the Fedj el Adoum and Bou Grine deposits in Tunisia (fig. 7) (Rouvier and others, 1985; Leach and others, 2005). Other significant but presently noneconomic occurrences are in the Gulf Coast of the United States (Kyle and Saunders, 1996).

Host Rocks

Coarse-grained carbonates are the most important host for MVT ores as well as reservoirs for hydrocarbons. Hydrocarbon traps and accumulations are favorable sites where oxidized metalliferous fluids can be reduced or mixed with reduced sulfur-rich gas to precipitate ore. Carbonate platforms with coarse-grained, fractured, or karsted carbonates with enhanced secondary porosity and permeability are highly favorable sites for sulfide deposition.

More MVT deposits are hosted in dolostone rather than limestone, and dolostone-hosted deposits are generally larger and contain higher Pb, Zn, and Ag grades than those in other host rocks (Leach and others, 2005). The preference for mineralization to be hosted by dolostone may be related to a higher transmissivity to fluid flow compared to limestone. An exception to this tendency is the large and high-grade Navan deposit in the Irish Midlands district that is hosted by limestone.

Structural Setting(s) and Controls

Faults and fractures are important ore controls in most MVT districts (fig. 3). The faults are usually unmineralized; rather, ore is localized in dilatancy zones associated with the faults. Ores located in dilatancy zones of normal faults include the deposits in the Irish Midlands district (fig. 5) (Hitzman
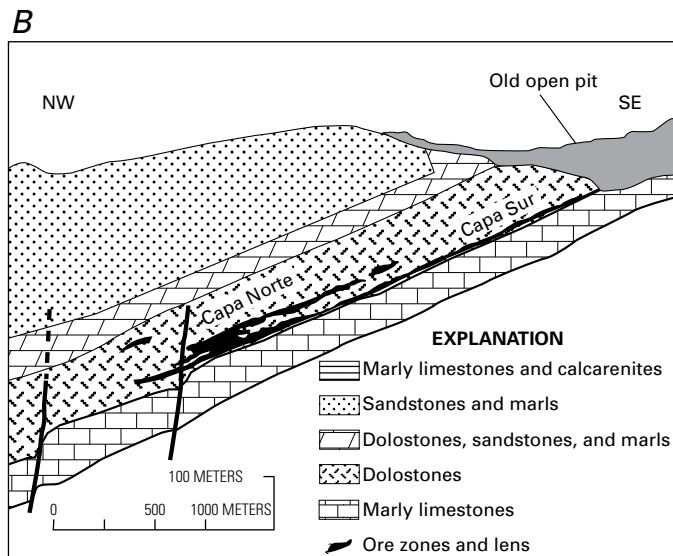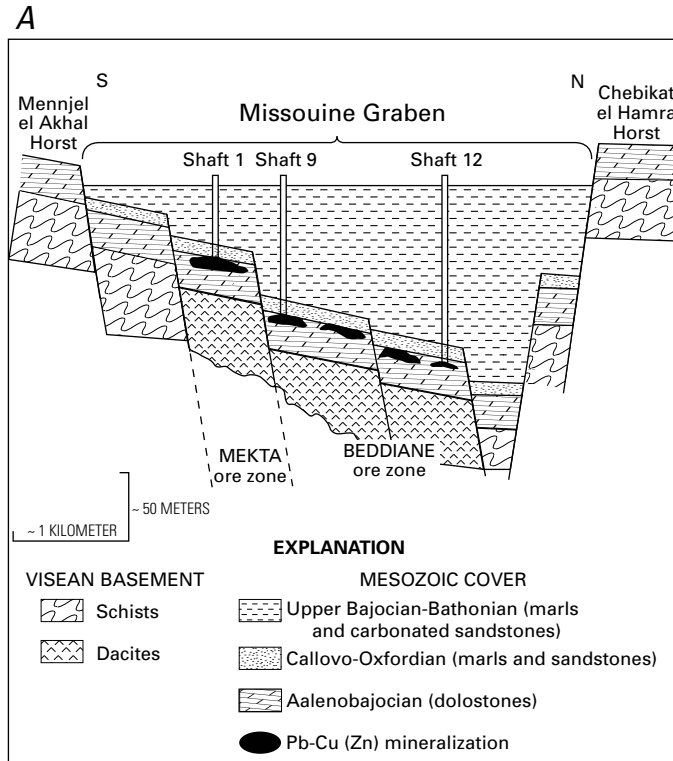
Figure 6.   Geology and mineralization in select Mississippi Valley-Type (MVT) deposits. (*A*) Generalized section showing piano keylike horst/graben structure of the Toussit-Bou Beker mining district, Morocco (from Bouabdella and others, 1996). (*B*) Cross section through the central part of the Reocin deposit, Spain, showing the relation of the ore lenses and the host dolostones (from Leach and others, 2005; modified from Velasco and others, 2003).
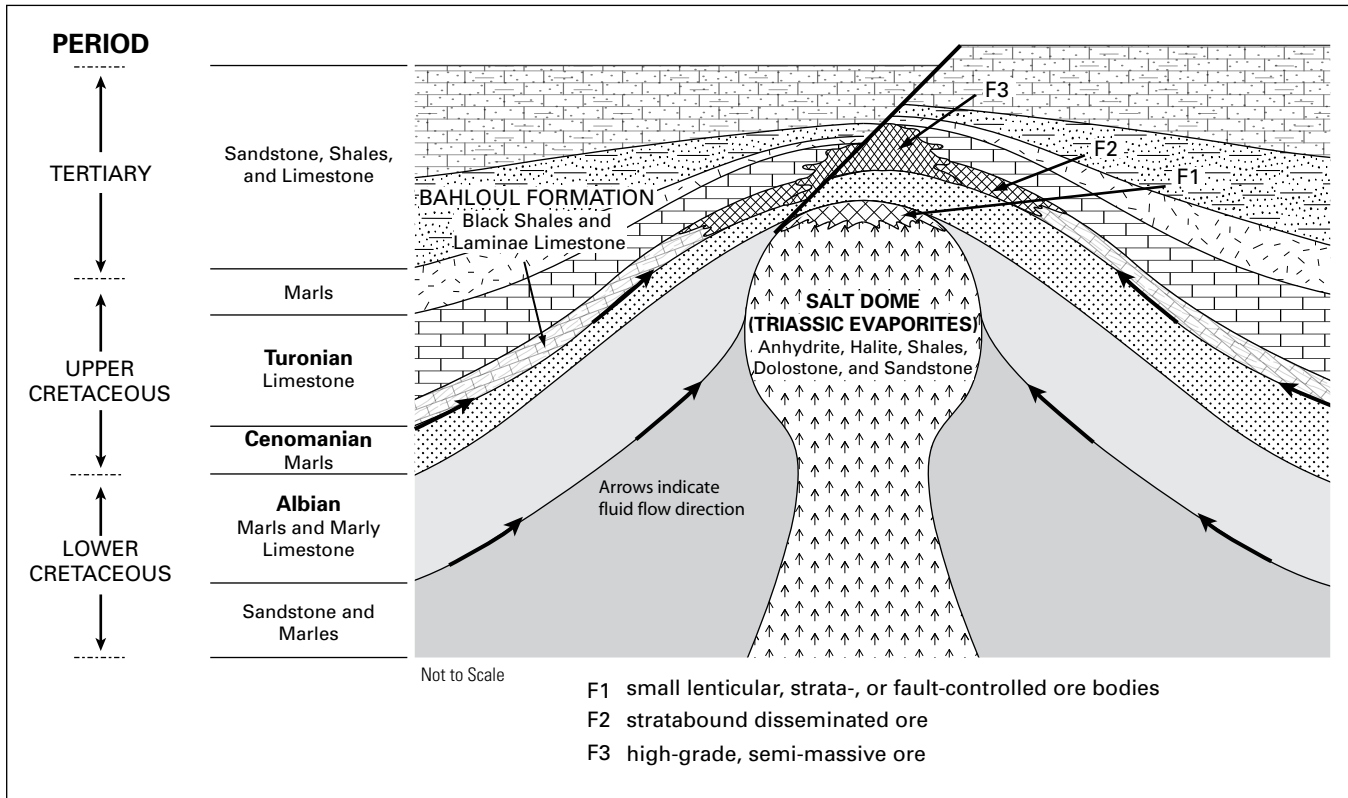
Figure 7.   Mississippi Valley-Type (MVT) deposit in Tunisia displaying the relation between MVT mineralization and a salt dome environment (modified from Leach and others, 2005).

and Beaty, 1996; Hitzman, 1999; Leach and others, 2005) and Upper Silesia district (Kibitlewski, 1991). Mineralization is localized in dilatancy zones associated with wrench faulting in the Viburnum Trend district (Clendenin, 1993; Clendenin and others, 1994). Transtensional faults are important in the Ozark MVT province (Hudson, 2000) and dilatancy zones between strike-slip faults are important ore controls in the Cévennes district. In some deposits, normal faults have juxtaposed different rock units, which provide for the focused ascent of metalliferous fluids into contrasting geochemical environments and sites of fluid mixing (Reocin, Spain; Upper Silesia, Poland; Toussit-Bou Becker, Morocco; and Irish Midlands, Ireland).

Use of Geophysics in Resource Assessment for Mississippi Valley-Type Deposits

A composite, multi-scale geophysical approach can assist in the assessment of the potential for Mississippi Valley-Type (MVT) deposits. Regional gravity and magnetic data, particularly when interpreted with drilling and/or seismic constraints, are useful for mapping basement depth and composition.

These data also are useful for delineating subsurface fault zones that may have provided pathways for ore fluids.

For the conterminous United States, regional-scale gravity, magnetic, and gamma-ray data are available for use in MVT assessment. Published regional scale interpretations (for example, Simpson and others, 1986 for gravity; Sims and others, 2008 for magnetic) provide good starting points for more specific interpretation relating to revised assessment study. On going work by Mickus and students (for example, Cosatt and Mickus, 2008) is focused on regional geophysical characterization of the historical MVT districts in the central United States.

Gravity and magnetic data are sensitive to sources and structures at a range of depths, whereas gamma ray surveys measure only surficial lithologic properties (for example, Broome and others, 1987). Regional gamma-ray element and ratio maps, in conjunction with surficial geochemistry, can provide characteristic lithologic properties of the cover geology and surficial processes. In areas with bedrock exposure, gamma-ray maps may directly aid in geologic mapping.

Direct geophysical detection of MVT deposits is possible with sufficiently detailed gravity data (because the ore is significantly denser than the surrounding carbonate rock) or with detailed induced polarization (IP) surveys, particularly if appropriate conductive sulfides such as pyrite, marcasite, and pyrrhotite are associated with a given deposit. For example, Siegel and others (1968) describe a combined IP/gravity

approach to the discovery of the Pyramid orebodies in the Northwest Territories of Canada. There are also reports that orebodies of the Polaris deposit of the Cornwallis District of Canada were drilled on the basis of gravity anomalies (Dewing and others, 2007; Ford and others, 2007). A summary of geophysical signatures contributing to MVT deposit favorability at the district scale is given by Paradis and others (2007) based on experience in Canada. We do not know of any cases of geophysical discovery of MVT deposits within the continental United States, although post discovery geophysical surveys have been conducted in several areas (for example, Jakosky and others, 1942; McMurry and Hoagland, 1956; Keller, 1960) to test possible exploration techniques (with limited success).

MVT exploration in modern industry practice, as documented in Canada by Ford and others (2007) and in Australia by a case study on the Lennard Shelf (Scott and others, 1994), relies on regional geology and geophysical studies followed up with detailed geochemistry, geophysics, and exploratory drilling. Because of the high cost of new detailed geophysical data collection and exploratory drilling, USGS MVT assessment will, by necessity, rely on regional reevaluation of existing regional geophysical data sets. The greatest opportunities for new insights will come from integrated interpretation of multiple data sets and incorporation of new and better genetic models into geophysical analysis. Table 2 lists deposits and features associated with MVT mineralization that has been explored through geophysical means.

Hypogene Ore Characteristics

Mineralogy and Mineral Assemblages

Most MVT deposits have a simple mineralogy, consisting primarily of sulfide minerals that are dominated by sphalerite, galena, and iron sulfides. With the exception of the Southeast Missouri district, all major MVT districts are sphalerite-rich relative to galena and have $Zn/(Zn+Pb)$ ratios greater than 0.5. By contrast, this metal ratio is less than 0.1 for the Southeast Missouri district. Some ores, such as those in the East Tennessee and Newfoundland Zinc districts, are essentially Pb-free. Wurtzite is reported in some districts (for example, Tri-State). However, it may be more common than reported because it is easily misidentified as sphalerite. Iron sulfide contents are quite variable and range from trace to the dominant sulfide (for example, Nanisivik). In some districts, iron sulfides are present as deposits spatially separate from lead and zinc sulfides (for example, Ozark Metallogenic Province). Chalcopyrite occurs in trace amounts in many MVT districts except for the Viburnum Trend district where it is the main source of byproduct copper and in the Cornwallis district, Canada (Randall and Anderson, 1996). Barite may be present in minor to trace amounts and fluorite is rare. Barite dominates over sulfides in a few smaller districts that include the Central

Missouri and Southeast Missouri barite districts (Leach, 1980) and the Sweetwater district in Tennessee (for example, Kesler, 1996). The Central Missouri and Southeast Missouri barite districts (Leach, 1980) are temporally distinct from the early sulfide event. The Viburnum Trend district has one of the most complex mineralogies, consisting of a variety of Cu, Co, nickel (Ni), iron (Fe), Ag, and antimony (Sb) sulfides and sulfosalts (for example, Heyl, 1983). Minor to trace minerals include arsenopyrite, bravoite, bornite, boulangerite, chalcocite, chalcopyrite, covellite, digenite, djurleite, enargite, gallite, germanite, millerite, molybdenite, pyrrhotite, siegenite, tennantite, and vaesite.

Paragenesis

Paragenesis varies from exceptionally simple to complex multi-stages that result from chemically complex and evolving systems. Paragenetically complex deposits or districts may be related to multiple ore-forming hydrothermal events (for example, the Viburnum Trend district). Among the most complex sulfide paragenesis observed is in the Viburnum Trend district (Heyl, 1983). It is common for deposits within a district to have very similar mineral paragenesis spread over thousands of square kilometers (for example, the Ozark Metallogenic province, Leach, 1994 and references therein; Upper Silesia district, Viets and others, 1996; Upper Mississippi Valley districts, Heyl, 1983; Tri-State district, Hagni and Grawe, 1964).

A highly generalized global paragenesis on the basis of the first author's experience is a trace element-rich early main stage sphalerite, followed by sphalerite ± galena, ± late galena. Iron sulfides, if present, frequently occur as discrete stages early, intermittently in the paragenesis, but more commonly in the late stages and commonly on the fringes of the deposits.

Zoning Patterns

Geochemical zoning in MVT deposits is generally not strongly developed and has been described only in a few areas (for example, in the Irish Midlands, Southeast Missouri, Pine Point, and Upper Mississippi Valley districts). Perhaps the best-developed zoning is for some deposits in the Irish Midlands district, where metal-bearing fluids were highly focused into limestone by steeply dipping basement-rooted faults. In the Irish Midlands district, the Navan deposit displays a vertical increase in Fe and Zn/Pb from the center of the deposit along with a lateral increase in Zn/Pb outward, while other Irish deposits display Pb-enrichment near the feeder zones with increasing Zn/Pb away from the feeder zones (Hitzman and Large, 1986). Deposits in the Southeast Missouri districts have chemical zoning patterns of Pb, Zn, Fe, Cu, Ni, and Co; however, these patterns are highly irregular along the trend of deposits (for example, Hagni, 1983; Mavrogenes and others, 1992, and references therein). At Pine Point, $Fe/(Fe+Zn+Pb)$ and $Zn/(Zn+Pb)$ ratios increase outward from prismatic breccia (high vertical-lateral aspect ratio) ore bodies (Kyle, 1981).

Table 2. Mississippi Valley-Type geophysical exploration table.

[mGal, milligal; MVT, Mississippi Valley-Type deposit]

District/deposit	Geophysical technique		Notes	Reference
Cornwallis/Pine Point (Canada)	Gravity	Post discovery	~+1 mGal anomalies, 11.7 percent combined lead/zinc	Siegel and others, 1968
Cornwallis/Pine Point (Canada)	Induced polarization	Post discovery	Marcasite and galena conductivity	Siegel and others, 1968
Cornwallis/Polaris (Canada)	Gravity	Discovery (+1 mGal anomaly)	Mentioned with reference to unpublished map from Teck Cominco	Ford and others, 2007; Dewing and others, 2007
Nanisivik (Canada)	Seismic reflection	Post discovery	Test method - success reported in ideal conditions	Hearst and others, 1994
Austinville (U.S.A.)	Direct Current (DC) applied potential	Post discovery	Electrodes lowered into ore body in discovery well	McMurry and Hoagland, 1956
Eastern Tennessee (U.S.A.)	Resistivity logging	Post discovery	Electrical logs in drill holes shows ore to be a conductive target	Keller, 1960
Illinois-Wisconsin (U.S.A.)				
Tri-State (U.S.A.)	Gravity	Post discovery	Subtle gravity lows thought to correlate with some deposits	Jakosky and others, 1942
Tri-State (U.S.A.)	Natural potential	Post discovery	Concluded that this method does not image the deposits	Jakosky and others, 1942
Tri-State (U.S.A.)	Resistivity survey	Post discovery	Found resistivity useful for structural mapping not deposit detection	Jakosky and others, 1942

Tectonic feature				
Precambrian basement (U.S.A.)	Regional magnetics	Regional Precambrian domains and faults	Define major basement faults	Sims and others, 2008
Midcontinent rift (U.S.A.)	Regional magnetics and gravity	Map buried structure	Map fault structure of northern midcontinent rift	Cannon, 2002;
Reelfoot rift (U.S.A.)	Seismicity; regional gravity and magnetics	Map extent and structure	Reelfoot rift provides tectonic control for U.S. MVTs	Hildenbrand, 1985; Hendricks 1988; Hildenbrand and Hendricks, 1995;
Arkoma basin	Magnetotelluric, seismic reflection/refraction, gravity	Map buried structure	Attempt to map concealed thrust faults	Mickus, 1999; Mickus and Keller, 1992
Illinois basin	Seismic reflection, regional gravity and magnetics	Define deep structure	Propose multi-stage history Proterozoic caldera + New Madrid rifting	McBride and others, 2003
Black Warrior basin	Seismic reflection, refraction and gravity	Map north-south whole crust transect	Map Laurentian continental margin transform zone	Harry, 2003
Forest City basin	Seismic refraction, gravity, magnetics	Map basin and crustal structure	Fault compartmentalization of basin	Harrison and Schultz, 2002
Michigan basin	Seismic reflection, regional gravity and magnetics	Regional mapping		Dickas and Mudrey, 2002
Boothia uplift (Canada)	Airborne gravity and magnetic surveys	Map extent and structure	Map faulted basement rocks beneath cover	Jober and others, 2007; Miles and others, 2000a,b

Textures, Structures, and Grain Size

Deposition of MVT ores involves an inextricable link between sulfide precipitation, dissolution, host-rock replacement, open-space filling, and solution-collapse brecciation. This interrelationship exists because sulfide precipitation is nearly always an acid-generating process. Ore textures from MVT deposits can be highly complex due to commonly inherited fabrics of the replaced host rock and the ore-forming processes. The ores can be extremely fine grained but in some districts crystals can be as large as a meter or more (for example, Tri-State and Central Tennessee districts).

The most important ore mineral textures include the following features. *Fine-grained banded ore*: Fine-scale banding (millimeter to micron scale bands) is common in individual crystals and in some deposits (for example, Upper Mississippi Valley district; McLimans and others, 1980). *Colloform and dendritic ores*: These are fine-scale (<1 mm) banded sulfides, spherulitic aggregates of colloform sphalerite, dark bands of fibrous aggregates of crystals (schalenblende), zones of dendritic galena, and iron sulfides in discrete bands or botryoidal masses. *Replacement ores*: Nearly complete replacement of host rock can produce massive sulfides (for example, Nanisivik) but replacement can be remarkably selective for a specific rock fabric. *Dissolution collapse breccias*: These are commonly multistage breccias that may include pre- and syn-ore breccias. Breccia clasts are characteristically polylithic reflecting the various lithology of the host rocks involved in the dissolution collapse. Textures in dissolution collapse bodies include rock-matrix breccias, crackle breccias, ore-matrix breccias, and hydrothermally altered and replaced breccias and internal sediments of stratified sand- to clay-size disaggregated wall rock. *Fault and sedimentary breccias*: Fault breccias consist of clasts of adjacent local host rocks in contrast to polylithic fragments in dissolution collapse breccias. *Sedimentary breccias*: Mineralized sedimentary breccias can show soft-sediment deformation. *Other textures* include:

1. snow-on-roof which typically consists of sulfides preferentially coating the tops of crystals or breccia clasts in open space;

2. pseudobreccia is a breccia-like fabric that is produced by the selective replacement of a particular host rock fabric;

3. zebra texture is usually gangue dolomite that formed by a variety of processes (for example, selective replacement of primary rock fabric, open-space filling of dilated bedding planes and fractures);

4. rhythmites consist of rhythmically banded ore containing distinct generations of sphalerite or gangue carbonate that usually develop from cycles of dissolution and open-space filling;

5. speoleothem-like sulfides consists of a variety of dripstone-like stalactites, stalagmites, curtains, and drape stones.

Hypogene Gangue Characteristics

Mineralogy and Mineral Assemblages

Dolomite, ferroan-dolomite, ankerite, siderite, and calcite are the most common gangue minerals in MVT deposits. Hydrothermal dolomite occurs as coarse to finely crystalline sparry dolomite and saddle dolomite in most MVT deposits. Hydrothermal dolomite is also present as cement in intergranular porosity and open-space fill and replacement of the host carbonates. Sparry dolomite forms a variety of textures including zebra textures (discussed previously), fracture fillings in brecciated rock and in the matrix of dissolution collapse breccias through coupled replacement and open space filling. Calcite is common in a few MVT districts (for example, Central Tennessee) and is more likely to be present in limestone-dominated lithologies (for example, Irish Midlands). Dolomite commonly forms intricate and complex compositional zoning, (see Rowan, 1986) which can provide constraints on MVT ore fluid pathways.

Quartz is present in most MVT deposits in generally minor to trace amounts depending on the relative importance of cooling and dilution of the ore fluid (Plumlee and others, 1994; Leach and others, 2006). Extensive silicification of the host-carbonate rocks is present in the Tri-State district, Northern Arkansas and Metaline district where silica forms alteration zones about the ores. Coarse quartz crystals also occur on ore minerals in places like the Viburnum Trend.

Barite occurs in minor to trace amounts in some ore deposits where it is generally late in the paragenetic sequence. Barite has never been reported in the Cambrian-hosted Southeast Missouri Lead districts. However, large deposits of post-sulfide barite are present in the overlying Upper Cambrian-Ordovician lead-zinc bearing deposits of the Southeast Missouri Barite district.

Organic matter occurs as degraded liquid hydrocarbons and bitumen in variable amounts and types in MVT deposits (Leventhal, 1990). However, its relation to ore genesis is usually equivocal. Studies of organic material from the Viburnum Trend district (for example, Leventhal, 1990) show that organic matter in the ore was thermally and compositionally altered by the ore fluids. Some districts contain abundant liquid hydrocarbons generally as late infilling of vugs and coatings on ore stage minerals (Tri-State district and Pine Point district). Liquid or solid petroleum-type organic matter has infrequently been observed in primary fluid inclusions in main-stage minerals. Ore-stage liquid hydrocarbon fluid inclusions have been observed in the Upper Silesia district (Kozlowski, 1996), Tri-State district (Coveney and others, 2000), Jumbo mine (Blasch and Coveney, 1988), and Polaris deposit ores (Randell and Anderson, 1996).

Paragenesis and Zoning Patterns

Hydrothermal dolomite may be pre-, syn-, or post-ore and form distinctive alteration halos around the deposits (for example, Irish Midlands, East Tennessee, and Tri-State districts). It is important to note that the carbonate gangue minerals generally do not co-precipitate with sulfides due to the acid generated as a consequence of sulfide deposition in MVT environments (Anderson, 1983). At Pine Point district, Krebs and Macqueen (1984) reported eight major paragenetic stages, within which there were at least seven periods of dolomite or calcite deposition. Hydrothermal dolomite cement, commonly associated with trace amounts of sulfides, may be present in barren carbonate rocks hundreds of kilometers from the ore deposits, reflecting the regional scale of some MVT ore events, such as in the Ozark region (for example, Rowan, 1986), Central and East Tennessee districts (for example, Montanez, 1996) and the Western Canada Basin (for example, Qing and Mountjoy, 1992). Dolomite forms at least 1-kilometer halos around the Polaris deposit (Randell and Anderson, 1996). At Pine Point, coarse-grained calcite forms halos around many of the orebodies (Hannigan, 2007). Although hydrothermal dolomite is usually associated with MVT mineralizing events, its complex relationship with sulfides and common widespread distribution without associated mineralization restricts its use in exploration. The Irish Midlands is an exception because specific types of hydrothermal dolomite (dolomite-matrix breccias) are usually associated with mineralization (Hitzman and others, 1992; Doyle and Bowden, 1995; Hitzman, 1996; Wilkinson and Earls, 2000).

Hydrothermal Alteration

Dissolution and Hydrothermal Brecciation

The most common host-rock modification associated with MVT deposits is dissolution and hydrothermal brecciation of the carbonate-host rocks that result from reactions of the ore fluid (Corbella and others, 2004) with the host-rocks or from acid-producing reactions commonly associated with fluid mixing (Anderson, 1983). Consequently, hydrothermal dissolution features and replacement halos are common in and about MVT deposits. The most significant acid production occurs as a consequence of the mixing of reduced sulfur-bearing fluids with a metal-bearing fluid and, to a lesser extent, by sulfate reduction in the ore zone.

Dolomite and Calcite Alteration

Dolomite or calcite alteration of the host-rocks is present in most MVT deposits. As discussed above, carbonate flooding of porosity about the deposits often forms envelopes that extend for meters to hundreds of meters. In many examples, the hydrothermal alteration produces a coarsely crystalline dolomite by recrystallization of the host carbonate rocks [for

example, gray coarse-grained early dolomite halos in Tri-State district (McKnight and Fischer, 1970)].

Silicification

Silicification of the host carbonate rocks is generally minor in most MVT deposits but is well developed in the Tri-State (Brockie and others, 1968) and the Northern Arkansas districts (McKnight, 1935). In both districts, the hydrothermal silicification and dolomitization form as alteration halos about the ore zones. Paradis and others (2007) note that in the Canadian MVT deposits (for example, Robb Lake, Esker, Prairie Creek, and Goz Creek), minor silicification may be present as small discontinuous zones of microcrystalline quartz both within and peripheral to sulfide ore.

Clay, Mica, and Feldspar Diagenesis

The formation or destruction of clay, mica, and feldspar minerals are recognized in a few deposits which can form subtle but possibly useful exploration guides. Authigenic K-silicates related to ore formation are reported in the Gays River deposit (Ravenhurst and others, 1987; Heroux and others, 1999), East Tennessee district (Hearn and others, 1987), Polaris deposit (Heroux and others, 1999), Newfoundland Zinc deposit (Hall and others, 1989), and Upper Mississippi Valley district (Hay and others, 1988). Alteration of feldspars has been observed in the basal sandstone of the Southeast Missouri lead district, both locally (Stormo and Sverjensky, 1983) and regionally (Diehl and others, 1989).

Supergene Ore and Gangue Characteristics

Mineral Assemblages

Fluctuation in the depth of water tables is an important factor that drives supergene alteration. Each rise and fall of the water table introduces oxygenated water to the primary sulfide body, driving oxidation reactions. In high precipitation environments water tables are generally less than tens of meters deep; therefore, supergene alteration in ore deposits is less extensive because there is a narrower vertical band of oxidation activity, and oxygen in the ground water tends to be consumed relatively quickly. Water table depths are much greater in arid climates. As a result, percolating surface water, charged with oxygen, traverses a greater rock thickness through the unsaturated (vadose) zone between the surface and water table. This setting provides for more frequent replenishment of oxygen to the primary sulfide body, resulting in both a larger degree and greater thickness of supergene alteration.

Supergene oxidation, or near-surface weathering, of primary carbonate-hosted Zn sulfide minerals results in

secondary minerals such as smithsonite ($ZnCO_3$), hydrozincite ($Zn_5(CO_3)_2(OH)_6$), or hemimorphite ($Zn_4Si2O_7(OH)2\cdot(H_2O)$), which were commonly the first minerals to be economically recovered (Boni and Large, 2003, and references therein). Weathering of galena produces cerrusite ($PbCO_3$), anglesite ($PbSO_4$), or rarely phosgenite ($Pb_2(CO_3)Cl_2$). In an editorial, Gilg, Boni, and Cook (2008) describe the contents of a special issue in *Ore Geology Reviews* devoted to nonsulfide Zn-Pb deposits. Examples of non-sulfide Zn ± Pb deposits include Upper Silesia district, Sardinia, Italy, Irish Midlands district, the Alpine district in Italy and Austria, La Calamine district, Belgium, and the Reocin deposit, Spain (Boni and Large, 2003). Large nonsulfide zinc deposits (Mehdiabad, Irankuh, and Kuh-e-Surmeh) also occur in Iran (Reichert and Borg, 2008).

Supergene gangue minerals consist of carbonates (calcite, aragonite), gypsum, minor quartz, and silicified host rocks. Hematite (Fe_2O_3) and goethite ($FeO(OH)$) are also common supergene gangue Fe-oxide products.

# Weathering/Supergene Processes

Mineralogical Reactions to Establish Process

The iron sulfide content of the deposits is an important control on the acid-producing potential of MVT ores (Leach and others, 1995). Iron sulfide content (pyrite plus marcasite) is generally low in MVTs (typically less than five percent) (Foley, 2002). Tri-State district (Southeast Kansas, Northeast Oklahoma, Southwest Missouri, United States) deposits have from a few tenths of a percent to several percent pyrite (Leach and others, 1995). East Tennessee and the Upper Mississippi districts are also low in iron sulfides. Nanisivik, Canada, and Cadjebut, Australia, and some Upper Silesian deposits in Poland are examples of high-iron-sulfide deposits. The iron sulfide content of the Olkusz, Poland deposit can be as high as 15 percent (Wirt and others, 2001). One deposit, the Pend Oreille mine in the Metaline district in northeast Washington State, contains both high- and low-sulfide ore (St. Marie and others, 2001).

The oxidation of pyrite and marcasite is responsible for the majority of mine-waste-acid production. The following equations describe the simplified reaction for pyrite and marcasite with water and oxygen (Stumm and Morgan, 1996):

$$FeS_2 + H_2O + (7/2)O_2 = Fe^{2+} + 2\ SO_4^{2-} + 2H^+ \quad (1)$$
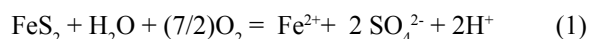
Bacterial activity (*Acidithiobacillus ferrooxidans*) will cause oxidation of ferrous iron to ferric iron; the ferric iron then oxidizes more pyrite or marcasite releasing more acid (Moses and others, 1987):

$$FeS_2 + 14\ Fe^{3+} + 8\ H_2O = 15\ Fe^{2+} + 2\ SO_4^{2-} + 16\ H^+ \quad (2)$$
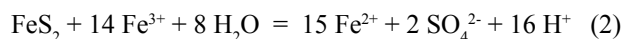
The sulfuric acid produced by the oxidation of iron sulfides attacks other sulfide minerals and country rocks in the deposit or waste material, releasing Zn, Pb, and their trace elements (TEs) into solution. The reaction rates for weathering and dissolution of marcasite are greater than those for pyrite. Trace elements contained in sulfides from various MVT districts are shown in table 3.

Rates of Reactions and Factors Controlling

The rate of formation of sulfuric acid depends on a number of factors. Iron sulfide oxidation and acid production is significantly affected by the accessibility of water and oxygen to the pyritic material; iron sulfide in a dry, compacted tailings-waste impoundment will react much more slowly than in a waste-rock pile with abundant pore space, which allows water and oxygen infiltration. The physical grain size of iron sulfides also affects reaction rates—fine-grained pyrite presents greater surface reaction area than coarse-grained pyrite. Trace impurities in the pyrite lattice also elevate its susceptibility to oxidation, thereby increasing its rate of weathering (Savage and others, 2000; Blanchard and others, 2007). Temperature also affects chemical reaction rates, from the initiation of iron sulfide oxidation to the dissolution of other sulfides by the resulting acid.

The release rate of trace metals is a function of the trace metal content, the mineral phase in which the trace element is present, and the pH of the mine outflow (Lapakko, 1992). As important as the iron sulfide content is to the formation of acid, so is the presence of the carbonate host-rock important to neutralizing the acid. MVT deposits and other carbonate-hosted deposits (for example, skarns) contain more buffering capacity for acid than any other deposit type, and the drainage from them is often circum-neutral in pH. Resulting drainage waters typically contain lower concentrations of deposit-related metals than those from other deposit types. Silicified carbonate rocks are less reactive than fresh carbonates, resulting in both lower capacity and rate for acid neutralization (Leach and others, 1995; Foley, 2002).

Geochemical Characteristics

Trace Elements and Element Associations

Trace elements and element associations include antimony, arsenic, barium, bismuth, cadmium, cobalt, copper, gallium, germanium, gold, indium, iron, manganese, mercury, molybdenum, nickel, silver, thallium and tin. Trace elements in selected MVT districts are summarized in table 3. Although primary sulfide mineralogy is fairly simple, minor minerals associated with MVT mineralization differ widely between individual districts; consequently minor and trace metals also vary (Lavery and others, 1994). This inconsistency diminishes the amount of universally useful geochemical exploration indicators.

Table 3.   Mineralogical and metal associations of select Mississippi Valley-Type deposits/districts.

[Sulfide abreviations: ar, arsenate; as, arsenopyrite; br, bravoite; bo, bornite; ce, celestite; ch, chalcocite; cp, chalcopyrite; cv, covellite; dg, digenite; dj, djurleite; en, enargite; gn, galena; gr, greenockite; mc, marcasite; ml, millerite; mo, molybdenite; po, pyrrhotite; py, pyrite; si, siegenite; sp, sphalerite; tn, tennantite. Data from Hannigan (2007), Krebs and Macqueen (1984), Kontak (1995), Lavery and others (1994), Leach and others (1995), Pannalal and others (2007), Park and Cannon (1943), Sicree and Barnes (1996), and St. Marie and Kesler (2000)]

	Viburnum Trend district	Eastern Tennessee district	Tri-State district	Austinville district	Upper Silesia district, Poland	Nanisivik district, Canada	Pine Point district, Canada	Metaline deposit	Upper Mississippi Valley district	Gays River deposit
Major metals	Pb, Zn, Fe	Zn	Zn, Pb	Zn, Pb, Fe	Fe, Zn, Pb, S	Zn, Pb, Fe	Zn, Pb, Fe	Zn, Pb, Fe	Zn, Pb, Fe	Zn, Pb
Minor and trace metals	Cu, Co, Ni Cd, Ag, In, Ge, Ga, Sb, Bi, As, Mo, Sn, Au			Fe, Cu, Cd, Ba, Ag, Ge, Ga, Co, Ni, In, Sb, Bi	Zn, Cd, Fe, Pb, As, Ag, Tl, Cd	Cd, Ag, As, Ni, Ge	Cu, Mn, Cd, Ag, As, Ni	Ag, Au, Cu, Mo, Cd	Cu, Ba, Cd, Ag, Ge, Ga, Co, Ni, In	Ag, Cd, Ni, Cu
Dominant Fe sulfide	py, mc	py	py	py (aniso)	mc, py	py	py, mc	py, mc	py, mc	py
Major ore sulfides	gn, sp, cp, py, mc	sp, py	sp, gn	sp, gn	sp, gn, mc	py, sp, gn	sp, gn	sp, gn, py	gn, sp	sp, gn
Minor sulfides	si, bo, tn, br, dg, cv, ar, po, as, mo, dj, ch, en	gn, cp	gn, cp	py, mc, cp, as	gn	as, br	mc, py, po, ce	mo, ch, gr, cp, po	cp, ml	py, cp, mc

Zoning Patterns

Primary dispersion halos of metals around MVT deposits are generally small—less than 50 to 75 m in the Upper Mississippi Valley district and less than 125 cm in Central Tennessee (Lavery and others, 1994, and references therein). Zones of Zn-bearing hydrothermal dolomite (Zn bound in the crystal lattice) extend 50 m from ore in the Viburnum Trend district (Viets, 1983) and several kilometers in the Upper Silesia district (B. Bak, written commun., 1986). Deposits in the Southeast Missouri district have minor element zoning patterns of Cu, Ni, and Co; however, these patterns are highly irregular along the trend of deposits (for example, Hagni, 1983; Mavrogenes and others, 1992). In the Ozark region, Erickson and others (1983) identified regional geochemical halos of trace elements in trace sulfides from insoluble residues of barren carbonate rocks that extend for several hundred kilometers from the MVT districts. Erickson and others (1983) also described a systematic change of increasing Zn/Pb from insoluble residues of barren carbonate from the lower-most to upper-most carbonates in the stratigraphic section in the region.

Fluid Inclusion Thermometry and Geochemistry

Temperature of the Ore Fluids

Fluid inclusion temperatures in MVT deposits range from about 50°C to 250°C; however, most of the temperatures are between 75°C and 200°C (fig. 8). These ranges are similar to values determined by Basuki and Spooner (2004). The highest fluid inclusion temperatures (~180°C to ~250°C) recorded are for the Irish Midlands district and Gays River deposit, ores that were relatively near each other during ore deposition but drifted apart during the opening of the Atlantic (Leach and others, 2001). In many districts (for example, the deposits in the Ozarks region in the Midcontinent United States, Irish Midlands, Upper Silesia, and Cèvennes districts), the fluid inclusion temperatures generally exceed values expected for geologically reasonable thermal gradients and estimated stratigraphic burial temperatures at the time of mineralization. Therefore, the temperatures observed for many ore deposits must be explained by unusually high geothermal gradients, advective heat transport from deeper parts of the basin (as with the Ozark MVT province), or the ascent of deeply circulating fluids in basement rocks beneath the deposits (for example, Upper Silesia and Irish Midlands).

Salinity of the Ore Fluids

The salinities of MVT fluids determined from fluid inclusions are typically 10 to 30 wt. percent NaCl equivalent (fig. 9). The compositional similarities between MVT inclusion fluids and oil-field brines are well established and have led to widespread acceptance of a basin-generated origin for MVT fluids

(for example, White, 1958; Hanor, 1979). The high salinity of sedimentary basin brines is explained by the dissolution of evaporites, incorporation of connate bittern brines, or through infiltration of evaporated surface waters (Hanor, 1979).

Composition of the Ore Fluids

The brine compositions measured from fluid inclusions in sphalerite from MVT districts are summarized in Leach and others (2005) (fig. 10). The measured compositions are similar to present-day brines that are formed mainly from subaerially evaporated seawater (Kesler and others, 1996; Viets and others, 1996). Fluid-rock reactions (dolomitization, and feldspar and clay-mineral diagenesis) account for the small shift of
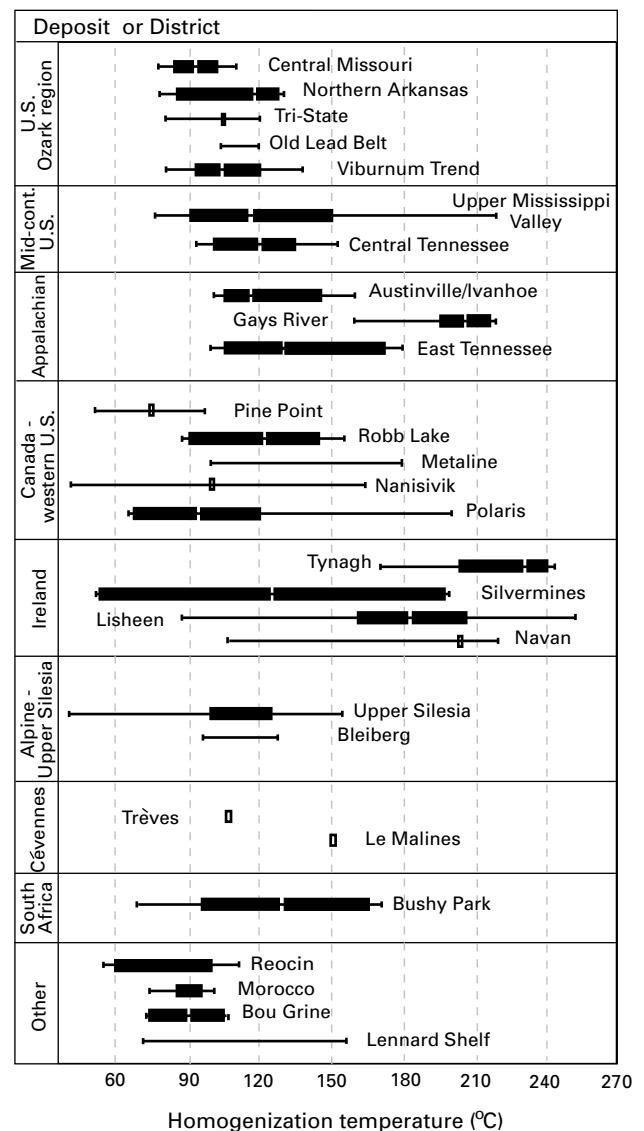

Figure 8. Summary of homogenization temperatures for sphalerite for selected Mississippi Valley-Type deposits based on fluid inclusion studies (from Leach and others, 2005).

the molar ratios away from the evaporated seawater trend, especially for Ca, Mg, and K which are attributed to fluid-rock reactions. Dolomitization increases the Ca concentration relative to Mg in the fluid inclusions, and K-silicate reactions shift the K content.

Metal Contents

Present-day oil-field brines with significant metal content include brines in the Arkansas and Gulf Coast region in the United States (Carpenter and others, 1974; Kharaka and others, 1987; Saunders and Rowan, 1990; Moldovanyi and Walter, 1992; Hanor, 1996), and Northern Alberta, Canada

Figure 9.   Summary of fluid inclusion salinity data from sphalerite for selected Mississippi Valley-Type deposits based on fluid inclusion studies (from Leach and others, 2005).

(Billings and others, 1969). The Pb and Zn content of these brines can reach several hundred parts per million and there is a pronounced inverse relation with reduced sulfur content. Recent calculations of Zn in sphalerite fluid inclusions are reported to be as great as 3,000 to 5,000 parts per million (ppm) (Wilkinson and others, 2009).

Stable Isotope Geochemistry

Sulfur Isotopes

Sulfur isotope values of MVT sulfides throughout the world are consistent with sulfur being derived from a variety of crustal sources (Sangster, 1990), that may include sulfate-bearing evaporites, connate seawater, diagenetic sulfides, sulfur-bearing organic material and H_2S reservoir gas. The ultimate source of the sulfur is most likely seawater sulfate contained by the sediments in various minerals and/or connate water that was subsequently reduced by one or more processes (Sangster, 1968; 1971; 1990). The $\delta^{34}S$ values for MVT sphalerite and galena are typically less than those for seawater contemporaneous in age with the host rocks (Sangster, 1968; 1971; 1990). The $\delta^{34}S$ values for many districts reflect mixing of sulfur from different sources, isotopic fractionation as a function of mineralogy, disequilibrium and kinetic effects between mineral pairs, and chemical environment. Given the complexities possible for sulfur isotope fractionation, extreme variations in the $\delta^{34}S$ values (fig. 11) are expected. Despite the variability of the data, some general observations are warranted. Biogenic sulfate reduction (BSR) is commonly invoked to explain the wide range in $\delta^{34}S$ values in MVT deposits and is the best explanation for the extreme negative values of $\delta^{34}S$ observed in some deposits.

Carbon and Oxygen Isotopes

Gangue carbonate minerals generally have distinct oxygen and carbon isotopes (lighter) when compared with MVT host rocks, indicative of infiltration of an external hydrothermal fluid during mineralization. At the Pine Point deposit, and applicable worldwide, Qing and Mountjoy (1994) noted that the oxygen isotopes indicated a higher temperature than would occur from geothermal heating from burial, so an external hydrothermal fluid invading the area is required to create the oxygen isotope signature. Because of the temperature-dependent fractionation of the oxygen isotopic system, direction of mineralizing fluid flow can be determined by cooling fluid temperatures shown by increasing $\delta^{18}O$ values. This pattern has been noted in Ireland (Hitzman and others, 1998) and in the Presqu'ile region of Canada (Paradis and others, 2006). Care must be taken with the interpretation of individual deposits, though, as different isotopic compositions of pore fluids may have a dramatic effect on the spatial patterns.

Since distinctive carbon isotope signatures exist between meteoric water, seawater, carbonates, and organic matter,
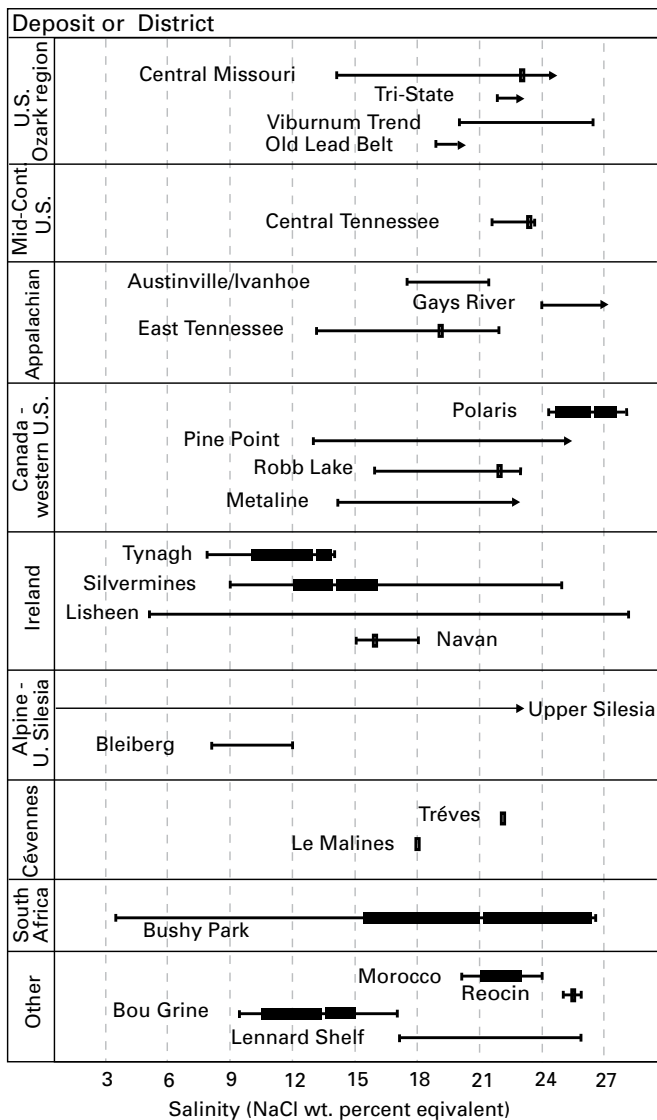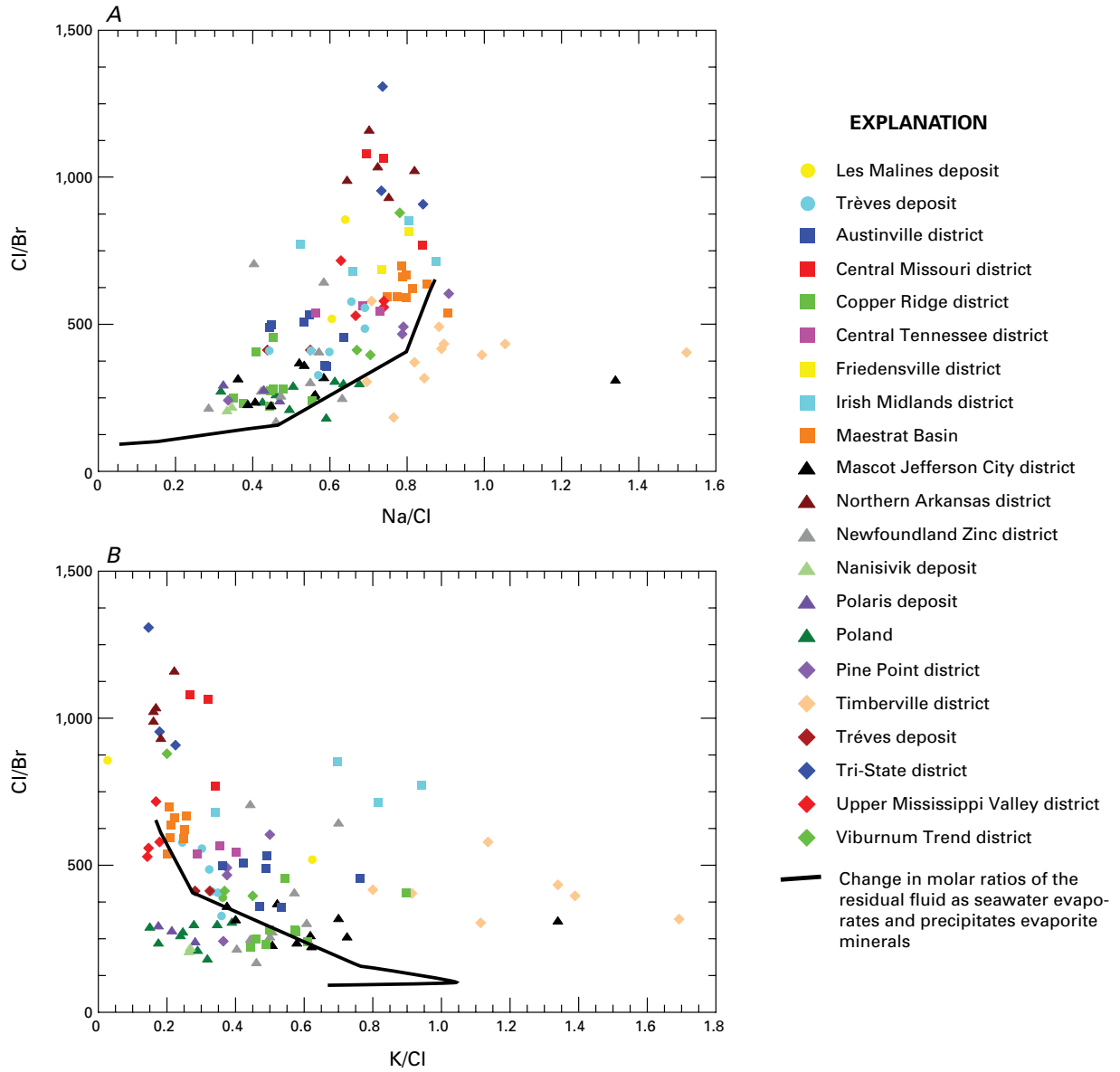
Figure 10. Brine compositions from fluid inclusion solutes in sphalerite from world Mississippi Valley-Type deposits (from Leach and others, 2005).
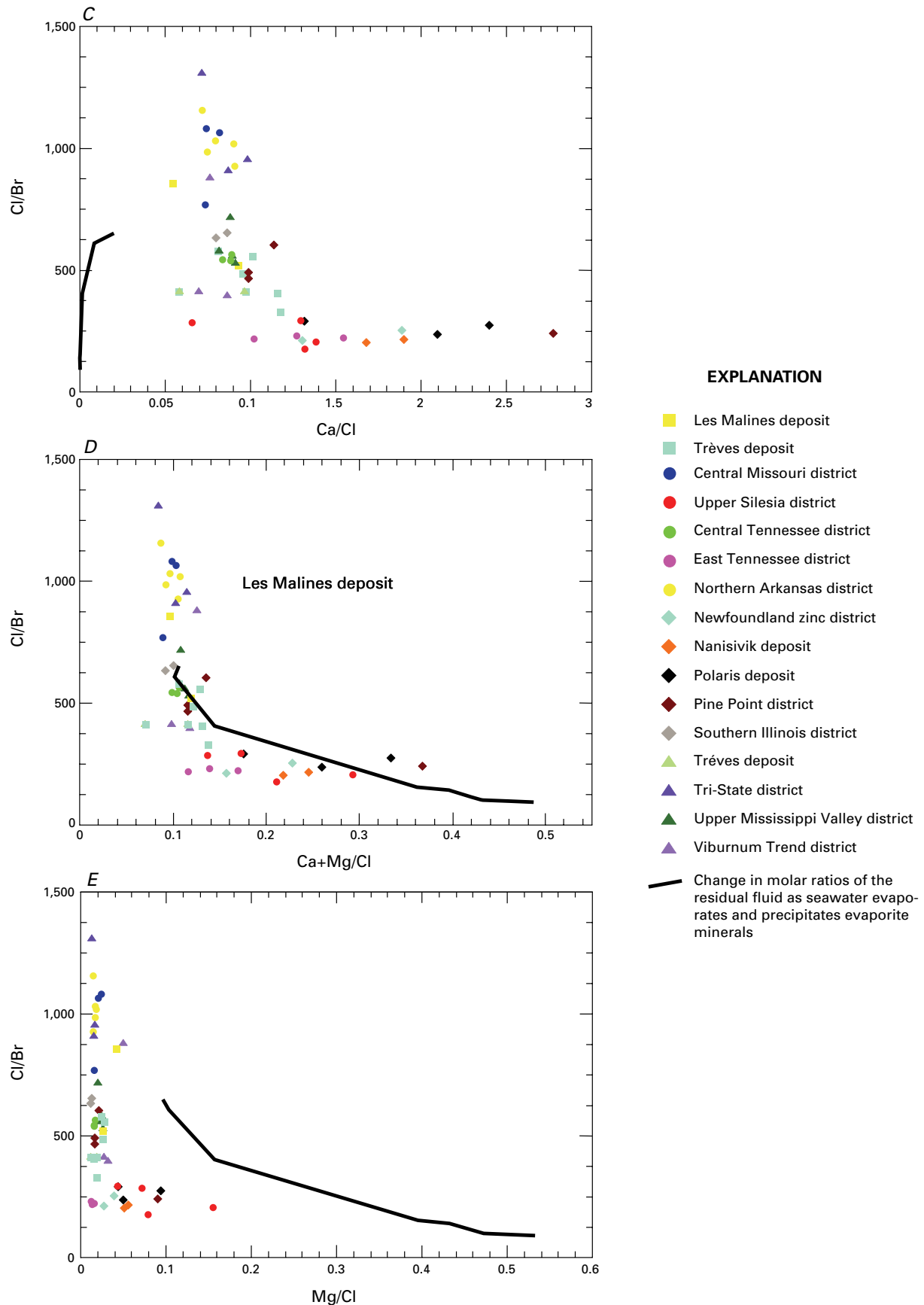
Figure 10.   Brine compositions from fluid inclusion solutes in sphalerite from world Mississippi Valley-Type deposits (from Leach and others, 2005).—Continued
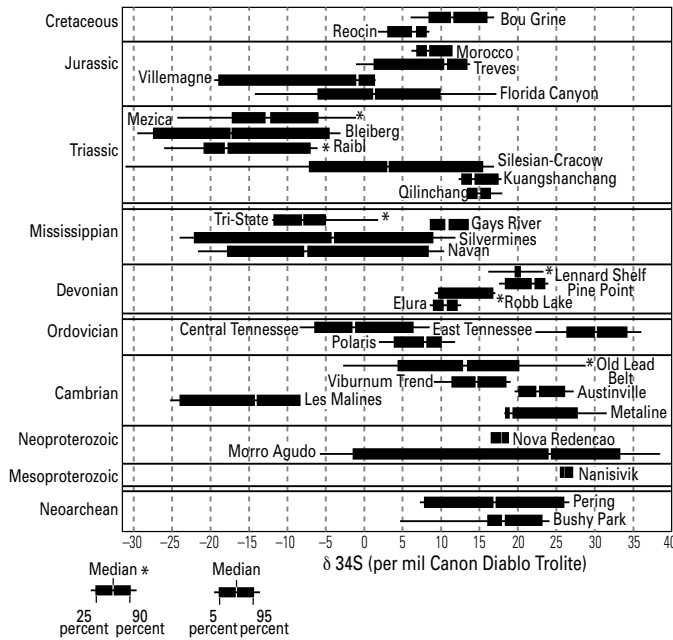
Figure 11. Distribution of sulfur isotope compositions from selected Mississippi Valley-Type deposits compared with host rock ages.

elucidation of the processes for sulfide mineralization and the source for reduced sulfur has commonly referred to carbon isotopes, unfortunately with mixed interpretations. The great depletion of ^{13}C found in the gangue dolomites of Nanisivik, Canada has been interpreted to be due to thermochemical sulfate reduction releasing isotopically light CO_2 from organic matter (Ghazban and others, 1991), as organic matter is commonly associated with MVT deposits. However, Savard and others (2000) prefer fluid mixing between metal-bearing and reduced sulfur-bearing fluids at the site of deposition at Polaris, Canada, because gangue carbonates have $\delta^{13}C$ values similar to those of the host rocks.

Radiogenic Isotope Geochemistry

Strontium Isotopes

Gangue dolomite has consistently more radiogenic strontium (higher $^{87}Sr/^{86}Sr$) than host dolostones and unaltered carbonates that were derived from seawater. This uniquely radiogenic strontium signature indicates that the responsible fluid interacted and flowed through rocks containing potassium-rich minerals such as potassium feldspar, muscovite, and clays. For individual deposits, this can be used to trace which sedimentary or metamorphic formation had interacting fluids that transported this signature to the site of ore deposition.

Systematic decreases in $^{87}Sr/^{86}Sr$ have been linked to fluid-flow direction (Hitzman and others, 1998; Paradis and others, 2006). Lower $^{87}Sr/^{86}Sr$ typically accompanies

increasing $\delta^{18}O$ down fluid-flow gradient. This change in strontium values is thought to occur by increasing dilution from formation waters, mixing with some other fluid, or increased interaction with a cool, nonradiogenic limestone.

Lead Isotopes

Leach and others (2005) provided a compilation of lead isotope data from global sediment-hosted Pb-Zn deposits (MVT and SEDEX) to provide insights into the possible sources of the metal and if the data could serve to distinguish between the two ore types. The following is a summary of their study. A basement source or sedimentary rocks derived from the basement is indicated for many MVT districts or deposits. Lead isotope data for Bushy Park deposit, Pering deposit, Gays River deposit, Walton deposit, Irish Midlands district, Lennard Shelf district, Upper Mississippi Valley district, Southeast Missouri district, and Tri-State district have all been interpreted in terms of a significant component from basement-derived lead. High μ ($^{238}U/^{204}Pb$) values for several districts also confirm a supracrustal origin for Pb (Goldhaber and others, 1995). The Newfoundland Zinc deposit is alone among the MVT deposits to indicate an anomalously low-μ source for lead. A comparison of MVT model-Pb ages show a very poor correlation with measured mineralization ages, suggesting strongly that the former should not be relied on to accurately date MVT mineralization.

The degree of within-deposit lead-isotopic homogeneity has commonly been cited as a distinguishing feature between SEDEX and MVT deposits. Sangster (1990) and Leach and others (2005) demonstrated the similarity in homogeneity between MVT and SEDEX, thus precluding the general use of within-deposit variation to distinguish between the two classes. Other observations include:

1. Pb appears to have been ultimately derived from crustal sources, in accord with their close association with sedimentary basins;

2. MVT deposits in the Midcontinent region of the United States contain very high abundances of radiogenic Pb, whereas no SEDEX deposits analyzed to date reveal such abundant radiogenic Pb;

3. model-Pb ages in SEDEX deposits are generally older than the ages of their host rocks. Mississippi Valley-Type model ages, in contrast, show little or no correlation with mineralization-age determinations; some MVT deposits yield future model ages while others show model ages significantly older than the host rocks

Petrology of Associated Igneous Rocks

Igneous rocks are not genetically associated with MVT deposits.

Petrology of Associated Sedimentary Rocks

The essential roles played by carbonate rocks in the genesis of MVT deposits are discussed in previous sections. The roles are those of basic controls on the gross permeability of the carbonate rock sequences and changes in permeability that determine where the ore forming fluids can efficiently migrate. At the petrographic scale, such features are difficult to assess. Nevertheless, some thin section features that may be useful include the following sections: Fracture Density and Permeability, Secondary Porosity, Hydrothermal Cement, Organic Matter, and Facies Transition.

Fracture Density and Permeability

Bulk or gross permeability is an important control on the transmissivity for MVT ore fluids. Increases in fracture density, especially in dolostones may contribute to the exploration for deposits within districts where faults and fractures are important controls.

Secondary Porosity

Dissolution of the host carbonates is an expected consequence of sulfide deposition. Therefore, increased secondary porosity may indicate proximity to ore depositional sites.

Hydrothermal Cement

As discussed in previous sections, hydrothermal calcite or dolomite may form halos around deposits or in some cases may be expressed as regional alterations of the aquifers for brine migration. Techniques such as cathodoluminescence (CL) or microstratigraphy (for example, Rowan, 1986) can delineate possible fluid pathways and small changes in the redox state of the ore fluid that control the intensity of cathodoluminescence.

Organic Matter

Increased abundance of organic matter in carbonate rocks or thermally altered organic matter may signal the effects of the passage of hot sedimentary brines.

Facies Transition

Facies transitions discussed previously are extremely important controls (for example, back reef to fore reef, limestone to dolomite, micrites to calcarenite). Therefore, fundamental carbonate facies studies can assist delineation of permissive areas for MVT mineralization.

Environment of Deposition

MVT ores are found in a variety of carbonate facies. However, the least favorable carbonates and their environments include the massive micritic and fine-grained deep-water carbonates, shaley back reef facies, chemical precipitates, and Archean to early Neoproterozoic carbonate platform sequences. The most favorable rocks and their depositional environments are the Phanerozoic passive margin sequences with dolomitized, carbonate platform sequences, and especially those sequences that were deposited in arid belts (Leach and others, 2010).

Petrology of Associated Metamorphic Rocks

Metamorphic rocks are not genetically associated with MVT deposits.

Theory of Deposit Formation

Ore Deposit System Affiliation

MVT deposits formed from sedimentary brines in platform carbonate sequences are a sub-type of a broader class of ores called "sediment-hosted Pb-Zn" deposits.

Sources of Metals

As discussed previously, the sources of the metals are a variety of crustal rocks. A conclusion from Leach and others (2005) was that no special rock type stood out as a preferred source. Information from Pb isotope data, discussed previously in this report, suggest a variety of crustal sources for MVT deposits that include basement rocks of various compositions, the weathered regolith and basal sandstones from the basement rocks, and carbonate aquifers. Given that reduced sulfur content is the dominant control on the concentration of metals in MVT ore fluids, low reduced-sulfur sedimentary brines will have greater potential to extract metals from a variety of lithologies. An important control on reduced sulfur content in basin brines is the presence of chemically reactive iron that can be sulfidized (Hunt, 1996). Rocks with high content of reactive iron (in other words, hematitic sandstone aquifers) may provide the means to help form metalliferous brines from a variety of host-rock lithologies.

Sources of Sulfur

The ultimate source of the sulfur is most likely seawater sulfate contained by the sediments in various minerals and or connate water that was subsequently reduced by one or more processes (Sangster, 1968; 1971; 1990). The immediate sources of sulfur for the ores include sulfate-bearing

evaporites, connate seawater, diagenetic sulfides, sulfur-bearing organic material and H_2S reservoir gas, and reduced sulfur in anoxic waters of stratified basins. Sulfate in the metalliferous fluid could be transported to the ore depositional site and reduced locally by reductants such as organic matter. Alternatively, the reduced sulfur could have been produced by bacteria or other processes and later mixed with the metalliferous fluid.

Sources of Ligands Involved in Ore Component Transport

Although metal-bisulfide and organometallic complexes have been proposed, only metal chloride complexes are considered likely base metal-transporting species for MVT ore fluids. Yardley (2005) has inferred that there is a chlorinity threshold of $\approx >10$ wt. percent in sedimentary brines for the presence of Zn and Pb in sedimentary fluids at MVT ore forming conditions. In addition, there are abundant thermodynamic calculations that show chloride complexing is the dominant metal ligand at MVT ore forming conditions. The chlorinity and other major solutes in the fluid inclusions of ore-stage minerals are derived mainly from the subaerial evaporation of seawater, and to a minor extent, from the dissolution of evaporate minerals (primarily halite) in the subsurface.

Sources of Fluids Involved in Ore Component Transport

As discussed elsewhere, the main sources of the ore fluids were sedimentary brines derived mainly from seawater evaporation. The evaporation may have occurred coeval with ore-fluid migration in coastal-evaporative areas or within closed marine basins or from residual brines stored in the basin sedimentary sequences or the crystalline basement. As discussed below, many ore deposits formed by the mixing of metalliferous brines with other fluids at the depositional site. Little is known about these "other fluids". However, they are likely fluids of various origins in the basin-sedimentary sequence (for example, meteoric, dehydration waters from diagenesis and metamorphism).

Chemical Transport and Transfer Processes

The primary controls for the extraction, transport, and deposition of Pb and Zn under MVT ore forming conditions are processes related to the redox state and concentration of sulfur species [SO_4 and H_2S]. As discussed previously, the reduced sulfur content is the dominant control on the concentration of metals in MVT ore fluids, thus low reduced-sulfur sedimentary brines will have greater potential to extract metals from a variety of lithologies. Therefore, geological and

geochemical features that buffer the redox state of aqueous sulfur species must be considered in resource assessments.

Most MVT ore fluids are believed to have been in equilibrium with carbonate-bearing lithologies which limits the pH values greater than ≈ 4.5 to 5 under most MVT pressures and temperatures. However if the fluids are in equilibrium with crystalline rocks, lower pH can be achieved and therefore, more reduced sulfur and higher metal contents are possible. In this case, sedimentary brines in crystalline basement rocks that ascend into carbonate cover rocks, can precipitate metal in sufficient quantities through cooling and change in pH.

Fluid-Drive Mechanisms

The fluid-drive mechanisms proposed for MVT deposits are numerous and include topography-driven, sediment compaction, orogenic squeezing, overpressured gas reservoirs, and thermal and density reflux drives. Leach and others (2001) considered the implications of fluid flow mechanisms from the perspective of the ages of MVT ore formation and concluded that no single mechanism can be applied to all districts. However, the most robust mechanism for many MVT districts is topography-driven fluid flow. Support for this comes from the ages of MVT ore genesis that often coincide with the time of orogenesis of adjacent uplifted margins of foreland and intracratonic basins. Furthermore, Garven and Raffensperger (1997) and Garven and others (1999) support that the flow patterns, rates of flow, and thermal effects generated by topography-driven hydrologic systems seem to provide optimal conditions for ore genesis, conditions that are not simulated in models of other fluid-flow processes, such as basin subsidence and compaction.

Nature of Traps and Geological Controls that Trigger Ore Precipitation

The ore controls recognized for selected MVT districts are shown in figure 3. The ore controls can be viewed as fundamental factors in fluid transmissivity, either at the district or mine scale, that allow the focusing of fluid flow and create opportunities for depositional processes to occur. These depositional processes are mainly fluid mixing, but also include, change in pH, temperature, and redox reactions of sulfate (table 4). Each ore-controlling feature typically has an unmineralized counterpart in each district, suggesting that the coincidence of several controls must have been important in localizing ore. The various controls are generally interrelated. For example, shale-depositional edges, limestone to dolostone transitions, and reef complexes are parts of sedimentary facies, all of which may be related to basement topography or faults.

Dissolution-Collapse Breccias

Dissolution collapse breccia is the most common host for MVT ores. Dissolution-collapse breccias are typically complex multistage breccias consisting of ore-stage hydrothermal dissolution with selective replacement textures that are superimposed on pre-ore breccias. The complex interplay between sulfide deposition, acid generation, and hydrothermal brecciation with pre-ore carbonate dissolution features is discussed by Leach and others (2003). In nearly all MVT districts, preexisting solution-collapse breccias and related carbonate-dissolution features provide high permeability zones that facilitate effective fluid mixing and ore deposition. These may be pre-ore solution-collapse features that are commonly located beneath an unconformity or disconformity, suggesting they originated by subaerial karstification. Alternatively the pre-ore dissolution features may be the result of hydrothermal dissolution independent of sulfide deposition. Corbella and others (2004) proposed that the initial ascent of mineralizing fluids into the ore zone, fluid mixing can produce carbonate dissolution. The distinction between a pre-ore karst (meteoric compared to hydrothermal) can be extremely useful in assessments for MVT resources. Nevertheless, the distinction between meteoric and hydrothermal karst is usually problematic. The lack of speleothems and other cave features in MVT ore breccias is commonly argued for hydrothermal dissolution brecciation. In reality, the absence of these features could reflect their destruction by mineralization or a pre-ore hydrothermal (non-sulfide occurence) in a preexisting meteoric karst. If the pre-ore karst breccia network (sulfide barren) is regionally extensive from the ore-bearing breccias or related to a regional unconformity, a meteoric origin is likely (like the East Tennessee district).

Faults and Fractures

Faults and fractures are important controls in most MVT districts. The faults are usually unmineralized; rather, ore is localized in dilatancy zones associated with the faults. Ores located in dilatancy zones of normal faults include the deposits in the Irish Midlands district (for example, Hitzman, 1999) and Upper Silesia district (Kibitlewski, 1991). Mineralization is localized in dilatancy zones associated with wrench faulting in the Viburnum Trend district (Clendenin, 1993; Clendenin and others, 1994). Transtensional faults are important in the Ozark MVT province (Hudson, 2000) and dilatancy zones between strike-slip faults are important ore controls in the Cévennes district.

Facies Transitions

Shales and shaley carbonate units that act as aquitards within a stratigraphic sequence provide an important control on fluid migration. The relation between a shale edge and location of MVT deposits in the Tri-State district is shown by the occurrence of ore only beyond the subcrop edge of the Chattanooga and Northview shales, both of which stratigraphically underlie the main ore-bearing carbonate units in the district (Siebenthal, 1916; Brockie and others, 1968). In the Viburnum Trend, ore deposits are restricted to a diagenetic dolostone located within a few kilometers of a facies transition to shaley limestone. MVT ore deposits typically occur near a limestone to dolostone transition (for example, Upper Silesia district, Viburnum Trend district, and Old Lead Belt of Southeast Missouri district) that may simply reflect contrasting permeability or solubility.

Table 4.   Important depositional models for Mississippi Valley-Type lead-zinc deposits.

Reduced sulfur model (one fluid model)
Metals and reduced sulfur transported together in acidic fluid at temperatures ≈>200°C
  Decrease in temperature
  Decrease in pressure
  Change in pH
  Dilution
  Wall-rock alteration
  Addition of reduced sulfur

Local sulfate reduction model (oxidized sulfur and metal fluid + local sulfate reduction)
Metals and sulfate carried in same solution to depositional site; sulfate locally reduced by reactions with methane or other organic matter
Metals and sulfate reducing agent (for example, methane) carried to sulfate at depositional site

Two fluid mixing model: metal-bearing fluid mixes with reduced sulfur fluid (two fluid model)
Metals carried by a fluid with low content of reduced sulfur fluid; this fluid mixes with fluids with abundant reduced sulfur
  Mixing of metal-rich fluid with reduced sulfur-rich fluid
  Mixing of metal-rich fluid with local hydrogen sulfide gas reservoir

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Reef and Barrier Complexes

The Viburnum Trend district, Old Lead Belt district, Pine Point district, Gays River deposit, and the Gayna River deposit are examples of ore related to carbonate reef complexes. In the Viburnum Trend district, little ore actually occurs within reef rock; rather, ore is located in permeable carbonate facies and sedimentary breccias that fringe the original reef. The Pine Point district ore bodies occur in solution-collapse breccias developed in a biohermal to bioclastic carbonate buildup (Rhodes and others, 1984). Both reef and carbonate barrier complexes are parts of a sequence in which abrupt changes in sedimentary facies produce dramatic permeability contrasts.

Basement Topography

Some deposits are situated above or near basement highs that controlled the development of sedimentary facies, brecciation, faulting, and pinchouts of sandstone aquifers (for example, Viburnum Trend and Old Lead Belt of the Southeast Missouri district, Pine Point district, Upper Silesia district, and Gays River deposit).

Geological Assessment Guides

Essential for Inclusion in Permissive Tracts

Platform carbonate sequences

Regional Scale Favorability

Neoproterozoic and Phanerozoic platform carbonate sequences located less than ≈600 km inboard of Phanerozoic orogenic belts, especially those related to faults and deformation features associated with Pangean and neocontinental supercontinent assembly in Devonian to Early Triassic and Cretaceous to Tertiary time, have the potential for MVT deposition. There is increased favorability in platform carbonate sequences deformed by oblique convergent orogens. Favorability also occurs in Phanerozoic-Neoproterozoic deformed intracratonic basins, with the presence of folds, swells and arches in platform sequences, and with the presence of trace sphalerite and galena in apparently unmineralized rock. There is a low potential on undeformed passive margin carbonate platforms, but it is permissive (Lennard Shelf model).

Consideration should be given to the fact that a single MVT deposit is unlikely to be the only one in the region because MVT deposits are the result of large regional occurrences.

Most common favorable factors include:
- Increasing fault density yields increasing favorability.
- Transtensional, wrench, strike-slip, and fore bulge normal faults are most favorable.
- Evidence of evaporative facies in regional carbonates (gypsum and salt casts). Bedded evaporite sequences.
- Presence of karstification (meteoric or hydrothermal).
- Widespread trace and minor occurrences of MVT mineralization.

Other favorable factors include:
- Presence of regional oxidized basal sandstones.
- Presence of regional aquifers, especially those having a hydrological connection to an orogenic front.
- Presence of reef and barrier facies.
- Presence of regional aquitards (regional fine-grained limestone and shales) with overlying and underlying aquifers.
- Rapid transition of basin sediment to basement contacts (in other words, basement relief) and rapid facies changes (in other words, shale to carbonate transitions, back reef to fore reef facies).
- Presence of regional sparry hydrothermal dolomite.
- Indicators of anomalous regional temperatures unrelated to igneous occurrences.

Within District (Undiscovered Deposits) Considerations

Figure 3 gives the main geological controls on deposits within districts as discussed previously in this report. Higher favorability should be associated with the greater number of geological controls present in an area.

Geochemical and Alteration Considerations

Most deposits have only limited lithogeochemical halos, but some have regional lithogeochemical zoning. Disseminated pyrite and marcasite may occur as 'blankets' around some deposits. Hydrothermal dolomitization may be present in some regions but only useful as a mineralization guide in a few districts. Silicification is uncommon. Districts may be characterized by widespread base metal anomalies in stream

sediment, soil, and rock-chip sampling. However, use of geochemistry can define or prioritize discrete drill targets.

Surficial Zn anomalies may be useful in exploration; however, care must be taken as not all Zn anomalies are associated with economic mineralization. For example, shales in the Western Canadian Sedimentary Basin have large background Zn contents that are similar to values associated with orebodies (Paradis and others, 2007). Anomalous Pb and Zn contents found through soil geochemistry, stream-sediment analysis, and boulder tracing have been successfully used as methods of discovery. The use of "zinc zap" may aid in the discovery of supergene Zn deposits; when this chemical mixture is sprayed, a vibrant scarlet color forms on secondary Zn-minerals (Hitzman and others, 2003). The Lisheen, Irish Midlands deposit was discovered in 1990 with the use of soil geochemistry, geologic mapping, and geophysics (Hitzman, 1992; Hitzman and others, 1992). Newfoundland Zinc was discovered in 1963 by means of a regional geochemical survey (Crossley and Lane, 1984). In the Ozark region, Erickson and others (1983) identified regional geochemical halos of trace elements in insoluble residues of barren carbonate rocks that extend for several hundred kilometers from the MVT districts. Other MVT deposits that were discovered by means of surficial geochemistry include numerous deposits in the Yukon, Canada.

Geophysics

Regional gravity and magnetics can be useful in defining basement highs and fundamental structures. In districts that have also been explored for petroleum, availability of regional seismic data can provide high-quality, three-dimensional resolution of structure and stratigraphy.

Geoenvironmental Features and Anthropogenic Mining Effects

Soil and Sediment Signatures Prior to Mining

Geochemical anomalies in stream sediment can be the result of the erosion of bedrock and soil anomalies, precipitation from the water column, and sequestration into bed sediment of dissolved metals released from an unmined deposit, or a combination thereof (Rose and others, 1979; Siegel, 1990). Primary geochemical zoning of metal deposition in MVT deposits is limited and has been described in only a few areas (Southeast Missouri, Pine Point, and Upper Mississippi Valley districts; Leach and others, 2005). Primary dispersion halos are small scale; most MVT deposits have minor geochemical signatures because of limited primary dispersion of elements into surrounding carbonate country rock (Lavery and others, 1994). In other studies, insoluble residue analyses of soils have been used to detect MVT mineralization (Proctor and

others, 1981). Stream sediment geochemistry and boulder tracing studies have been successful in the discovery of MVT deposits in Canada.

In general, the geochemical signature of unmined MVT deposits in soil and sediment media is limited in amplitude and areal extent. Environmental effects of unmined MVT deposits are consequently moderate, except where a highly fractured system may allow infiltration of oxygenated water to flow through dispersed sulfides and carry contaminants to underlying permeable aquifers (Leach and others, 1995).

Secondary Minerals

Sedimentary rock mine-waste piles cover hundreds of thousands of hectares in the United States. Mississippi Valley Type deposits were first mined in the United States prior to 1800. Mine-waste piles were abandoned over many years of evolving mining techniques, resulting in significant dissimilarity of sulfide content in waste material as mining and milling technology improved. Mine-waste piles are heterogeneous, composed of overburden of various lithologies, gangue minerals, and host rock—largely carbonates in the case of Pb-Zn MVT deposits—as well as acid-producing sulfide minerals.

As mentioned above, supergene oxidation of in place ore, and/or surface weathering of Pb-Zn sulfide minerals in waste material results in secondary minerals such as smithsonite ($ZnCO_3$), cerrusite ($PbCO_3$), hydrozincite (($Zn_5(CO_3)_2(OH)_6$), or hemimorphite ($Zn_4Si2O_7(OH)2 \cdot (H_2O)$)), cerrusite ($PbCO_3$), anglesite ($PbSO_4$), or rarely phosgenite (($Pb_2(CO_3)Cl_2$).

Efflorescent Minerals

Efflorescent secondary minerals form from the surficial weathering of sulfide minerals in mine-waste piles and tailings (fig. 12) (Hammarstrom and Smith, 2002) and sulfate-rich pore fluids. Evaporative soluble minerals, such as epsomite ($MgSO4 \cdot 7H_2O$), starkeyite ($MgSO_4 \cdot 4H_2O$), and/or gunningite (($Zn,Mn)SO_4 \cdot (H_2O)$)), form: (1) around seeps in mine-waste piles and the edges of remediation ponds (Diehl and others, 2007); (2) as surficial crusts on tailings ponds (fig. 12) (Lee and others, 2005); and (3) along stream banks containing acid-rock drainage (Romero and others, 2006). Minerals such as melanterite ($Fe^{2+}(SO_4) \cdot 7H_2O$), rozenite ($Fe^{2+}SO_4 \cdot 4H_2O$) or goslarite ($ZnSO_4 \cdot 7H_2O$), commonly form on pit walls or the mouths of adits (Hammarstrom and Smith, 2002).

Diehl and others (2007) observed a preferential sequence of precipitation of soluble salts, from an early formed Zn-rich starkeyite, to a later formed gunningite, which had a lower Zn content. Bulk chemical analysis showed a variety of metals stored in the salts, such as Cd, Co, and Ni. Gypsum ($CaSO_4 \cdot H_2O$) was the last evaporative mineral to form in the sequence. It is important to emphasize that because efflorescent salts dissolve rapidly, they are a source of acid and metals during every rainfall or snowmelt.
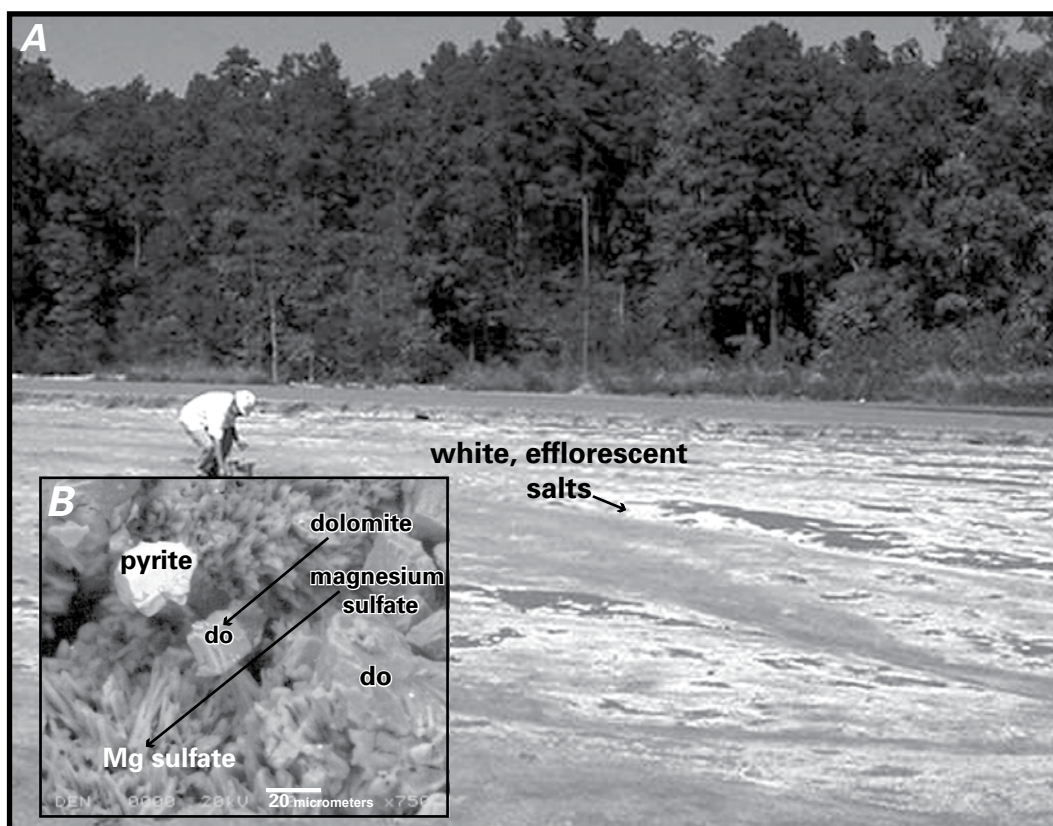
Figure 12. (*A*) White, efflorescent minerals formed at the top of drying tailings, Upper Fletcher/St. Joe tailings, Missouri (Photography by Philip Hageman, U.S. Geological Survey, date unknown). (*B*) Evaporative mineral crusts (arrow in *A*) contain Mg-sulfate minerals, remnant etched dolomite rhombs, and sulfide minerals consisting of etched pyrite grains from ≤ 20 microns and grains of galena, sphalerite, and nickel, copper sulfides ≤ 5 microns. Magnesium-sulfate minerals are poorly ordered, commonly have curved crystal faces, and are susceptible to rapid dissolution.

Drainage Signatures

An important environmental aspect of MVT deposits which separates them from other deposit types (especially coal, VHMS, Cu-porphyry, SEDEX, acid-sulfate polymetallic vein) is their placement in carbonate host-rocks. The acid neutralizing capacity afforded by this setting commonly results in near-neutral associated drainage waters. The municipal-water supply for the town of Viburnum, Missouri is taken from groundwater from one of the mines in the area (Foley, 2002).

In the assessment of acid-mine drainage, a useful diagram has been developed that compares the sum of the metals $\Sigma(Zn+Cu+Cd+Co+Ni+Pb)$ on the Y-axis with the pH on the X-axis. This is known as the Ficklin diagram, after the late Walter Ficklin of the USGS (Plumlee and others, 1999). When many drainage waters from all mineral deposit types are plotted on one diagram, each deposit type tends to plot in limited fields, with characteristic boundaries of pH and metal sum (Σ). The drainage signatures of MVT deposits, mines, and waste material generally have pH values of more than 6 and are dominated by aqueous Zn. The chemical nature of Zn

allows it to stay in solution and remain mobile at near-neutral pH (Smith, 1999). MVT drainage waters described by Plumlee and others (1999) and Wirt and others (2001) had average pH values between 6.6 and 7.4, and Ficklin sums up to 45,000 micrograms per liter (μg/L), with Zn contributing an average 92 percent of the total metals.

The iron sulfide content appears to have little effect on the pH of mine drainage and surface waters in MVT deposits. For example, in the Upper Silesia district, drainage pH from high-iron sulfide deposits (Olkusz) averaged 7.2, whereas drainage-mine seeps of low-iron sulfide deposits (Trzebionka) averaged 7.3 (Wirt and others, 2001). Similarly, bicarbonate concentrations did not differ markedly between the two classes of seeps.

Despite similar aqueous pH values, seeps and drainages from the high- and low- Fe-sulfide deposits had markedly different metal and sulfate concentrations. The Ficklin sum from the Olkusz seeps had a median value of 1,200 μg/L, which is 2.9 times higher than that from the Trzebionka seeps (median of 414 μg/L). The Zn concentration in the high-Fe-sulfide seeps was about three times higher than those from the

low-Fe-sulfide seeps. Sulfate is commonly the major anionic component in MVT drainage water. Smith and Schumacher (1991) reported a maximum concentration of 850 mg/L in Old Lead Belt mine-waste seeps. Wirt and others (2001) reported up to 11,000 mg/L sulfate, with a median of 360 mg/L from Upper Silesia district mine seeps.

There are several possible reasons for the higher metal and sulfate concentrations in the high-Fe-sulfide deposit seeps. First, the pyrite itself can contain high concentrations of trace elements such as As, Co, Ni, or Tl. In addition, the higher pyrite content generates greater amounts of sulfuric acid, and local low-pH conditions at mineral surfaces dissolve greater quantities of the primary sulfides and their contained trace elements. Galena can contain several percent As, whereas sphalerite can contain up to one percent Cd and up to 100 ppm Ge (Viets and others, 1996). Thus, despite overall bulk-fluid pH being buffered by carbonates to levels similar to that of low-Fe-sulfide ores, the high-Fe-sulfide ores can produce leachates or drainage with much higher major and trace-metal concentrations. Although the above discussion demonstrates that high-Fe deposits can and do produce high concentrations of metal (mostly Zn) in their drainages, since most MVT deposits are low in Fe-sulfides (five percent or less), they tend to release drainage lower in metal concentrations than other deposit types do.

Arsenic-bearing pyrite occurs in some MVT deposits. When deposit material is isolated from oxygenated groundwater, As does not typically release from the pyrite. However, if the deposit has a fracture system, or waste material is porous and permeable, atmospheric oxygen can reach the pyrite (and other As-bearing sulfides such as sphalerite) and release As into groundwater (Lee and Goldhaber, 2001). Released As can become sorbed or incorporated into Fe oxides and transferred to suspended or bottom sediment. Marcasite, which can be the dominant sulfide, can release As in anoxic waters. However, Lee and Goldhaber (2001) found no dissolved As concentrations greater than 10 μg/L in Ozark Plateau waters.

Climate Effects on Geoenvironmental Signatures

MVT deposits are located in diverse climatic settings, from deposits in arid African conditions (for example, Touissit-Bou Beker district, Morocco), to temperate deposits in the United States (for example, Viburnum Trend and Tri-State districts, Missouri), to permafrost conditions in northern Canada (for example, Polaris Mine) (Foley, 2002). Rates of erosion and leaching of metals from mine-waste piles in a humid climate are higher than in an arid environment (Hammarstrom and Smith, 2002).

Temperature has an effect on reaction rates of weathering and mineral transformations. Warmer temperatures increase rates of dehydration to transform minerals such as melanterite to rozenite, or epsomite to starkeyite. Warmer average temperatures in arid to semi-arid climates may affect internal conditions in mine-waste piles, increasing the potential for capillary

rise, thus leading to the precipitation of evaporative metal-bearing salts on the surfaces of waste material (Palumbo-Roe and others, 2007). Tailings ponds, which hold fine-grained material, may dry and be more susceptible to wind erosion. Metal-bearing dust is a human-health hazard from wind-blown tailings in the arid southwest United States and from U.S. Environmental Protection Agency (EPA) Superfund sites.

Climate changes, such as increase or decrease in precipitation, will affect flushing of metals from mine-waste piles into receiving streams. Decreasing precipitation may affect the ability of streams to dilute metal concentrations; increasing precipitation may result in episodes of rapid runoff and erosion, thereby increasing sediment and metal loads in streams.

Mining Methods

The current methods used for mining MVT deposits are room-and-pillar, or longwall techniques (Foley, 2002). The room-and-pillar method is suitable for stratiform deposits, the type which typifies MVTs. This method results in a checkerboard pattern of mined rooms, supported by pillars of unmined rock (Bateman, 1942). In the Old Lead Belt district, these pillars were 3 to 12 m (10 to 40 ft) in diameter, 6 to 18 m (20 to 50 ft) apart, and constituted 10 to 35 percent of the ore, which was not recovered (Lewis, 1948). Historically, the longwall method was applied to some deposits. The longwall method consists of developing a central shaft, and mining many faces, starting from a peripheral tunnel, towards the central shaft. This method essentially recovered all the ore, and allowed subsidence of the mined rooms as the faces retreated towards the central shaft (Bateman, 1942). In the past, open-pit methods were also used for some near-surface deposits.

Ore Processing Methods

Early ore processing consisted of crushing and grinding the ore, and using gravity separation techniques such as jigging or concentrator tables. One of the drawbacks of gravity techniques was incomplete removal of sulfides from coarse tailings and slimes. Slimes are very finely ground material, on the order of < 250 micrometers (μm), and are problematic to dispose of because gravity tailings contain unrecovered sulfides, and slimes fill in interstitial spaces in stream-bottom substrate, impairing aquatic habitat. Around 1915, flotation technology began to be applied throughout the United States to all mineral-deposit types (Jones, 2007). Through careful matching of frothing and floating reagents, larger metal recoveries were possible. Ore was typically ground with ball mills to finer size fractions for flotation separation; slime discharges remain as a legacy problem from early flotation mills. In addition, whereas increased recovery of metals led to lower metal concentrations in tailings, flotation milling allowed the mining of lower-grade rock, resulting in larger volumes of tailings.

Metal Mobility from Solid-Mine Waste

Metals released from primary and secondary phases are dispersed in a number of ways, including mass wasting, wind, and hydraulic processes. Mass wasting can introduce material into a waterway where contaminants are then transported as solids in bottom sediment, in suspension, or in the dissolved phase. Rainwater and snowmelt runoff can transport dissolved and suspended metals off of waste and tailings piles into nearby streams. Direct wind transport may occur from dried waste and tailings piles. Channel-bar deposits or overbank-flood deposits that include mine waste can also subsequently release contaminants to wind transport.

Whereas dissolved transport of metals in the water column can result in concentrations exceeding water-quality standards, often 90 percent or more of the total metal load is transported in the solid phase, either detritally as mineral grains, or sorbed to particle surfaces or as particle coatings (Miller, 1996). Lead and copper are examples of metals that travel predominantly in the solid phase. Zinc is likely to travel in the dissolved phase, and become incorporated into stream bottom or lake sediment at some distance. Downstream from the Tri-State district, Juracek (2006) showed extensive distributions of elevated concentrations of Zn, Cd, and Pb in the bottom sediments of Empire Lake, Kansas and nearby floodplain soils.

Volume and Footprint of Mine Waste and Tailings

The footprint of a mining operation is the areal extent of land that is physically impacted by mine waste, tailings impoundments, smelting operations, and associated contamination of surface and groundwater. Extensive piles of unmanaged mine-waste material, discarded through many years of mining activity, have changed landscapes globally.

Two examples of MVT mining localities that are located within EPA Superfund sites are the Tri-State district, in parts of Kansas, Oklahoma, and Missouri, and the Big River Mine and St. Joe tailings site, southeast Missouri. Mine-waste piles, chat (milled gravel-size remnant particles), and mill tailings cover tens of thousands of acres at these sites, with related metal-contaminated drainage. Long-term exposure to elevated metal content in soils and waters at these sites are a public health hazard.

The Tri-State mining district, located within the largest EPA Superfund site in the United States, extends approximately 1,800 km^2 in area, at the northwest edge of the Ozark Uplift. Waste-removal and clean-up operations have been ongoing, but millions of metric tons of surficial mine waste and chat remain (table 5) that contain Cd, Cu, Pb, and Zn.

The Big River Mine/St. Joe Tailings Superfund Site (BRMT) is in the Old Lead Belt district, Missouri. Areas and masses of mine waste and mill tailings from the Bonne Terre, Desloge, Elvins, Federal mine and mill complex (renamed the St. Joe State Park), Leadwood, National, Doe Run, and Hayden Creek mines are listed in table 6. Tailings dumped in and adjacent to the Big River have been subject to erosion by water during precipitation and by wind during dry periods, dispersing metals in sediments, surface waters, and dust. Metals of concern are As, Pb, Cd, and Zn. Before flotation milling, material from chat piles was used for railroad and highway ballast and substrate for concrete and asphalt (U.S. Fish and Wildlife Service, 2009); therefore, estimated tonnages of existing chat piles represents only a minimum of the actual amount produced.

New technologies are decreasing the volume and areal extent of mine waste in some modern mining operations, such as the development of dry-stack and paste tailings. Tailings are dewatered through large-capacity vacuum pumping and pressure filtering to a nonpumpable state, then spread and compacted to form dense-tailings stacks (Davies and Rice, 2001). In addition to reducing the areal extent of tailings

Table 5.   Estimates of tonnages of chat in Tri-State Superfund sites (data from U.S. Environmental Protection Agency Office of Solid Waste, 2006).

Site	City, State	Tonnage of chat		Surface area of chat	
		Short tons	**Metric tons**	**Acres**	**Hectares**
Cherokee County	Galena, Kansas	5,000,000	4,500,000	4,000	1,620
Oronogo-Duenweg Mining Belt	Joplin, Missouri and vicinity	7,200,000	6,500,000	2,321	940
Tar Creek	Picher, Cardin, North Miami, Quapaw, Commerce, Oklahoma	45,100,000 to 75,000,000	41,000,000 to 68,000,000	25,600	10,400
Total		≈100,000,000	≈91,000,000	32,000	12,960

Table 6.   Tailings and chat distribution in the Big River mine tailings Superfund (modified from U.S. Fish and Wildlife Service and Missouri Department of Natural Resources, 2008).

Site	Estimated tailings		Estimated chat		Estimated mass (chat)	
	Acres	Hectares	Acres	Hectares	Short tons	Metric tons
Desloge[1]	275	111	95	39	3,500,000	3,200,000
National[1]	108	44	44	18	9,000,000	8,200,000
Leadwood[1]	528	214	35	14	3,500,000	3,200,000
Elvins/Rivermines[1]	77	31	72	29	6,600,000	6,000,000
Bonne Terre[1]	306	124	39	16	3,600,000	3,300,000
Federal[1,2]	1,130	457	32	13	3,500,000	3,200,000
Doe Run[1]	0	0	9	4	NA[3]	NA[3]
Hayden Creek[1]	8	4	0	0	NA[3]	NA[3]

[1] Newfields, 2006; [2] USFWS and MDNR, 2008; [3] NA, not available.

storage, this process eliminates water impoundment, removing the risk of tailings-dam failures. This new technology is more expensive than conventional methods but may be economically advantageous in arid regions, where there is limited water, or in cold regions, where freezing water during winter makes it difficult to manage tailings dams.

Smelter Signatures

Emissions resulting from smelting of metals of any deposit type can affect widespread dispersal of metals contamination (Thornton and others, 1980; Dudka and others, 1995). Smelters processing MVT ores typically emit Pb, Zn, Cd, As, SO_4^{-2}, and trace metals contained within the ores. In the Upper Silesia district, Poland, Dudka and others (1995) reported extensive contamination of soils, mainly from smelter emissions, resulting in the contamination of cereal crops and potatoes. Sixty percent of arable land had concentrations of Cd and Zn above critical concentrations that resulted in plant intake of the contaminants. Studies of smelter signatures in southeast Missouri showed acidified soils related to sulfur deposition (soil pH was about 5 and 6.8 is normal) (Bornstein and Bolter, 1991), and Pb contamination of soils related to prevailing wind directions (Palmer and Kucera, 1980).

Potential Ecosystem Impacts

Environmental impacts resulting from past mining can be significant. Besser and Rabeni (1987) studied the effect of Pb, Cd, and Zn in leachates of Old Lead Belt mine waste on freshwater organisms and found that concentrations of these metals were positively correlated with whole-body burdens of

crayfish, mayflies, and midges, and negatively correlated with survival and growth. Besser and others (2009) tested for toxicity on amphipods and daphnids with Viburnum Trend district sediment and pore water. Toxic effects from both media were noted for Ni, Zn, Cd, and Pb.

Gale and Wixson (1986) conducted a study of Pb content of suckers and sunfish samples collected from streams in the Old Lead Belt district. These bottom-feeding species tend to ingest bottom sediments as they forage. Levels of Pb in muscle tissues of these fish commonly exceeded the suggested World Health Organization (WHO) dietary Pb standard [0.3 milligrams per kilogram (mg/kg)]. Other species, such as largemouth and smallmouth bass did not show such levels, probably because they do not tend to ingest sediment while feeding.

Beyer and others (2004) noted Zn and Pb poisoning in some free-flying wild birds in the Tri-State district such as American robins, northern cardinals and waterfowl. Allert and others (2008) applied in-place toxicity tests to crayfish in the Tri-State district. Significant negative effects were noted on percent survival of caged crayfish.

Subsidence of land surface over abandoned mine tunnels is a noted problem in some localities, such as Picher, Oklahoma, Galena, Kansas, and Dubuque, Iowa.

During mining operations, pumping typically keeps underground mines dewatered. After mines are closed or abandoned, underground workings typically flood, resulting in extensive water, oxygen, and sulfide contact. The effects of past MVT mining on surface and groundwater were discussed above. A good overview on the characterization of mine waste in general and its effects on water is contained in Hammarstrom and Smith (2002).

Acknowledgments

References

Alert, A.L., Fairchild, J.F., DiStefano, R.J., Schmitt, C.J., Brumbaugh, W.G., and Besser, J.M., 2008, Ecological effects of lead mining on Ozark streams: in-situ toxicity to woodland crayfish (*Orconectes hylas*): Ecotoxicology and Environmental Safety, v. 72, p. 1207–1219.

Anderson, G.M., 1983, Some geochemical aspects of sulfide precipitation in carbonate rocks, *in* Kisvarsanyi, Geza, Grant, S.K., Pratt, W.P., and Koenig, J.W., eds., 1983, International conference on Mississippi Valley-Type lead-zinc deposits; Proceedings Volume: Rolla, University of Missouri, p. 61–76.

Anderson, G.M., and Macqueen, R.W., 1982, Ore deposit models–6. Mississippi Valley-Type lead-zinc deposits: Geoscience Canada, v. 9, p. 107–117.

Appold, M.S., and Garven, Grant, 1999, The hydrology of ore formation in the Southeast Missouri district: numerical models of topography-driven fluid flow during the Ouachita orogeny: Economic Geology, v. 94, p. 913–936.

Ashton, J.H., Downing, D.T., and Finlay, S., 1986, The geology of the Navan Zn-Pb orebody, *in* Andrew, C.J., Crowe, R.W.A., Finlay, S., Pennell, W.M., and Pyne, J.F., eds., Geology and genesis of mineral deposits in Ireland: Irish Association for Economic Geology, p. 243–280.

Bastin, E.S., 1939, Theories of formation of ore deposits: Scientific American, v. 49, no. 6, p. 538–547.

Basuki, N.I., and Spooner, E.T.C., 2004, A review of fluid inclusion temperatures and salinities in Mississippi Valley-Type Zn-Pb deposits: identifying thresholds for metal transport: Exploration and Mining Geology, v. 11, p. 1–17.

Bateman, A.M., 1942, Economic Mineral Deposits: New York, John Wiley and Sons, Inc., 898 p.

Besser, J.M., Brumbaugh, W.G., Allert, A.L., Poulton, B.C., Schmitt, C.J., and Ingersoll, C.G., 2009, Ecological impacts of lead mining on Ozark streams: toxicity of sediment and pore water: Ecotoxicology and Environmental Safety, v. 72, p. 516–526.

Besser, J.M., and Rabeni, C.F., 1987, Bioavailability and toxicity of metals leached from lead-mine tailings to aquatic invertebrates: Environmental Toxicology and Chemistry, v. 6, p. 879–890.

Bethke, C.M., and Marshak, Stephen, 1990, Brine migrations across North America—the plate tectonics of groundwater: Annual Review of Earth and Planetary Science, v. 18, p. 287–315.

Beyer, W.N., Dalgarn, J., Dudding, S., French, J.B., Mateo, R., Miesner, J., Sileo, L., and Spann, J., 2004, Zinc and lead poisoning in wild birds in the Tri-State mining district (Oklahoma, Kansas, and Missouri): Archives Environmental Contamination and Toxicology, v. 48, p. 101–117.

Billings, G.K., Kesler, S.W., and Jackson, S.E., 1969, Relation of zinc-rich formation waters, northern Alberta, to the Pine Point ore deposit: Economic Geology, v. 64, p. 385–391.

Bjørlykke, A., and Sangster, D.F., 1981, An overview of sandstone lead deposits and their relation to red-bed copper and carbonate-hosted lead-zinc deposits: Economic Geology 75th anniversary volume, p. 179–213.

Blanchard, Marc, Alfredsson, Maria, Brodholt, John, Wright, Kate, and Catlow, C.R.A., 2007, Arsenic incorporation into FeS_2 pyrite and its influence on dissolution: a DFT study: Geochimica et Cosmochimica Acta, v. 71, p. 624–630.

Blasch, S.R., and Coveney, R.M., Jr., 1988, Goethite-bearing brine inclusions, petroleum inclusions, and the geochemical conditions of ore deposition at the Jumbo mine, Kansas: Geochimica et Cosmochimica Acta, v. 52, p. 1007–1017.

Boni, Maria, and Large, Duncan, 2003, Nonsulfide zinc mineralization in Europe—an overview: Economic Geology, v. 98, p. 715–729.

Bornstein, R.E., and Bolter, Ernst, 1991, Long-term effects of lead smelting in soils, *in* Beck, B.D., ed., Trace substances in environmental health XXV: Gradient Corporation, Cambridge, Mass., United States: Trace Substances in Environmental Health, v. 25, p. 71–83.

Bouabdellah, Mohammed, Brown, A.C., and Sangster, D.F., 1996, Mechanisms of formation of internal sediments at the Beddiane lead-zinc deposit, Toussit mining district, northeastern Morocco *in* Sangster, D.F., ed., Carbonate-hosted lead-zinc deposits: Society of Economic Geologists Special Publication 4, p. 356–363.

Bradley, D.C., 1993, Role of lithospheric flexure and plate convergence in the genesis of some Appalachian zinc deposits: U.S. Geological Survey Bulletin, v. 2039, p. 35–43.

Bradley, D.C., and Leach, D.L., 2003, Tectonic controls of Mississippi Valley-Type lead-zinc mineralization in orogenic forelands: Mineralium Deposita, v. 38, p. 652–667.

Brannon, J.C., Cole, S.C., Podosek, F.A., Ragan, V.M., Coveney, R.M., Jr., Wallace, M.W., and Bradley, A.J., 1996a, Th-Pb and U-Pb dating of ore-stage calcite and Paleozoic fluid flow: Science, v. 271, p. 491–493.

Brannon, J.C., Podosek, F.A., and Cole, S.C., 1996b, Radiometric dating of Mississippi Valley-Type ore deposits, *in* Sangster, D.F., ed., Carbonate-hosted lead-zinc deposits: Society of Economic Geologists Special Publication 4, p. 536–545.

Brockie, D.C., Hare, E.H., and Dingess, P.R., 1968, The geology and ore deposits of the Tri-State district of Missouri, Kansas, and Oklahoma, *in* Ridge, J.D., ed., Ore deposits in the United States 1933–1967: New York, American Institute of Mining, Metallurgical, and Petroleum Engineers, p. 400–430.

Broome, J., Carson, J.M., Grant, J.A., and Ford, K.L., 1987, A modified ternary radioelement mapping technique and its application to the south coast of Newfoundland: Geological Survey of Canada, Paper 87–14, scale 1:500,000.

Brown, J.S., 1967, Isotopic zoning of lead and sulfur in southeast Missouri: Economic Geology Monograph 3, p. 410–426.

Brown, J.S., 1970, Mississippi Valley-Type lead-zinc ores: a review and sequel to the Behre Symposium: Mineralium Deposita, v. 5, p. 103–119.

Callahan, J.S., 1964, Paleogeographic premises for prospecting for strata-bound base metal deposits in carbonate rocks: CENTO Symposium on mining geology and base metals, Ankara, Turkey, Proceedings, p. 191–248.

Cannon, W., 2002, Mapping Precambrian rift structures in the mid-continent: *in* Examples of the utility of magnetic anomaly data for geologic mapping, Finn, C.A., (ed.), U.S. Geological Survey Open-File Report 02–400, p. 5–7. (also available online at http://pubs.usgs.gov/of/2002/ofr-02-0400/).

Carpenter, A.B., Trout, M.L., and Pickett, E.E., 1974, Preliminary report on the origin and evolution of lead- and zinc-rich oil field brines in central Mississippi: Economic Geology, v. 69, p. 1191–1206.

Chapple, K., 2003, The Mehdiabad zinc deposit—Tethyan giant, *in* Eliopoulos, D.D., ed., Mineral exploration and sustainable development: Rotterdam, Millpress, p. 1149–1152.

Christensen, J.N., Halliday, A.N., Vearncombe, J.R., and Kesler, S.E., 1995, Testing models of large-scale crustal fluid flow using direct dating of sulfides: Rb-Sr evidence for early dewatering and formation of MVT deposits, Canning basin, Australia: Geology, v. 90, p. 877–884.

Clendenin, C.W., 1993, Faults, fluids, and Southeast Missouri MVT deposits: Geological Society of America Abstracts with Programs, v. 25, no. 3, p. 12.

Clendenin, C.W., and Duane, M.J., 1990, Focused fluid flow and Ozark Mississippi Valley-Type deposits: Geology, v. 18, p. 116–119.

Clendenin, C.W., Niewendrop, C.A., Duane, M.J., and Lowell, G.R., 1994, The paleohydrology of Southeast Missouri Mississippi Valley-Type deposits, interplay of faults, fluids, and adjoining lithologies: Economic Geology, v. 89, p. 322–332.

Corbella, M., Ayora, C., and Cardellach, E., 2004, Hydrothermal mixing, carbonate dissolution and sulfide precipitation in Mississippi Valley-Type deposits: Mineralium Deposita, v. 39, p. 344–357.

Cosatt, M., and Mickus, K.L., 2008, Preliminary gravity and magnetic study of the Tri-state mining district, Kansas, Missouri and Oklahoma: Abstracts with Programs–Geological Society of America, v. 40, no. 3, p. 31.

Coveney, R.M., Jr., Ragan, V.M., and Brannon, J.C., 2000, Temporal benchmarks for modeling Phanerozoic flow of basinal brines and hydrocarbons in the southern midcontinent based on radiometrically dated calcite: Geology, v. 28, p. 795–798.

Crossley, R.V., and Lane, T.E., 1984, A guide to the New-foundland Zinc Mines Limited ore bodies, Daniel's Harbour, *in* Mineral deposits of Newfoundland; a 1984 perspective: Report-Province of Newfoundland Department of Mines and Energy, v. 84–3, p. 45–51.

Davies, M.P., and Rice, Stephen, 2001, An alternative to conventional tailing management-"dry stack" filtered tailings, AMEC Earth & Environmental, Vancouver, Canada: 10.

Dewing, Keith, Turner, Elizabeth, and Harrison, J.C., 2007, Geological history, mineral occurrences and mineral potential of the sedimentary rocks of the Canadian Arctic Archipelago, *in* Goodfellow, W.D., ed., Mineral Deposits of Canada: A synthesis of major deposit-types, district metallogeny, the evolution of geological provinces, and exploration methods: Geological Association of Canada, Mineral Deposits Division, Special Publication No. 5, p. 733–753.

Dickas, A.B., and Mudrey, M.G., Jr., 2002, Regional-scale geologic interpretation of seismic reflection, gravity, and magnetic profiles collected along the western arm of the Midcontinent rift system, Upper Peninsula of Michigan, Wisconsin, Minnesota, and Iowa: Wisconsin Geological and Natural History Survey Open-File Report 2002–01, 1 disc.

Diehl, S.F., Koenig, A.E., Hageman, P.L., Smith, K.S., Fey, D.L., and Lowers, H.A., 2007, From the micro to the macro scale; A textural and chemical perspective of characterizing waste rock material: Society for Mining, Metallurgy, and Exploration, Inc. (SME) Annual Meeting, February 25–28, Denver, Colorado, 17 p., CD-ROM.

Diehl, S.F., Goldhaber, M.B., and Mosier, E.L., 1989, Regions of feldspar precipitation and dissolution in the Lamotte Sandstone, Missouri-implications for MVT ore genesis: U.S. Geological Survey Open-File Report 89–169, p. 5–7.

Dings, M.G., and Whitebread, D.H., 1965, Geology and ore deposits of the Metaline zinc-lead district, Pend Oreille County, Washington: U.S. Geological Survey Professional Paper 489, 109 p.

Doyle, E., and Bowden, A.A., 1995, Field guide to the Galmoy zinc-lead deposit: Society for Economic Geologists Guidebook Series, v. 21, p. 139–145.

Dudka, S., Piotrowska, A., and Witek, T., 1995, Trace metal contamination of soils and crop plants by the mining and smelters in Upper Silesia, Southern Poland: Journal of Exploration Geochemistry, v. 52, p. 237–250.

Dunham, K.C., 1966, Role of juvenile solutions, connate waters and evaporitic brines in the genesis of lead-zinc-fluorine-barium deposits: Transactions, Institution of Mining and Metallurgy, sec. B, v. 75, p. B226–B229.

Erickson, R.L., Mosier, E.L., Viets, J.G., Odland, S.K., and Erickson, M.S., 1983, Subsurface geochemical exploration in carbonate terrane-midcontinent United States, *in* Kisvarsanyi, Geva, Grant, S.K., Pratt, W.P., and Koenig, J.W., eds., Proceedings of international conference on Mississippi Valley-Type lead-zinc deposits: Rolla, University of Missouri, p. 575–583.

Foley, N.K., 2002, Environmental geochemistry of platform carbonate-hosted sulfide deposits, *in* Seal, R.R., and Foley, N.K., eds., Progress on geoenvironmental models for selected mineral deposit types: U.S. Geological Survey Open-File Report, 02–195, p. 87–100.

Ford, K., Keating, P., and Thomas, M.D., 2007, Overview of the geophysical signatures associated with Canadian ore deposits, *in* Goodfellow, W.D., ed., Mineral deposits of Canada: A synthesis of major deposit-types, district metallogeny, the evolution of geological provinces, and exploration methods: Geological Association of Canada, Mineral Deposits Division, Special Publication no. 5, p. 939–970.

Gale, N.L., and Wixson, B.G., 1986, Fish from Missouri's lead belt: to eat or not to eat: Environmental Geochemistry and Health, v. 8, p. 3–10.

Garven, Grant, 1985, The role of regional fluid flow in the genesis of the Pine Point deposit, Western Canada sedimentary basin: Economic Geology, v. 80, p. 307–324.

Garven, Grant, Appold, M.S., Toptygina, V.I., and Hazlett, T.J., 1999, Hydrogeologic modeling of the genesis of carbonate-hosted lead-zinc ores: Hydrogeology Journal, v. 7, p. 108–126.

Garven, Grant, and Raffensperger, J.P., 1997, Hydrogeology and geochemistry of ore genesis in sedimentary basins, *in* Barnes, H.L., ed., Geochemistry of Hydrothermal Ore Deposits, 3rd ed.: New York, John Wiley and Sons, p. 125–189.

Ghazban, F., Schwarcz, H.P., and Ford, D.C., 1991, Correlated strontium, carbon and oxygen isotopes in carbonate gangue at the Nanisivik zinc-lead deposits, northern Baffin Island, N.W.T. Canada: Chemical Geology (Isotope Geoscience Section), v. 87, p. 137–146.

Gilg, H.A., Boni, Maria, and Cooke, N.J., 2008, A special issue devoted to nonsulfide Zn-Pb deposits: Ore Geology Reviews, v. 33, p. 115–116.

Goldhaber, M.B., Church, S.E., Doe, B.R., Aleinikoff, J.N., Brannon, J.C., Podosek, F.A., Mosier, E.L., Taylor, C.D., and Gent, C.A., 1995, Lead and sulfur isotope investigation of Paleozoic sedimentary rocks from the southern midcontinent of the United States: implications for paleohydrology and ore genesis of the Southeast Missouri lead belts: Economic Geology, v. 90, p. 1875–1910.

Grotzinger, J.P., 1989, Facies and evolution of Precambrian depositional systems: emergence of the modern platform archetype: Society for Sedimentary Geology Special Publication 44, p. 79–106.

Grotzinger, J.P., and James, N.P., 2000, Precambrian carbonates: evolution of understanding: Society for Sedimentary Geology Special Publication 67, p. 3–20.

Guinness, E.A., Arvidson, R.E., Leff, C.E., Edwards, M.H., Bindschadler, D.L., 1983, Digital image processing applied to analysis of geophysical and geochemical data for southern Missouri: Economic Geology, v. 78, p. 654–663.

Hagni, R.D., 1983, Minor elements in Mississippi Valley-Type ore deposits, *in* Shanks, W.C., ed., Cameron volume on unconventional mineral deposits: Society of Economic Geology and Society of Mining Engineers, AIME, New York, p. 44–88.

Hagni, R.D., and Grawe, O.R., 1964, Mineral paragenesis in the Tri-State district, Missouri, Kansas, Oklahoma: Economic Geology, v. 59, p. 449–457.

Hall, W.E., and Friedman, Irving, 1963, Composition of fluid inclusions Cave-in-Rock fluorite district, Illinois, and Upper Mississippi Valley lead-zinc district: Economic Geology, v. 58, p. 886–911.

Hall, W.E., York, D., Saunders, C.M., and Strong, D.F., 1989, Laser $^{40}Ar/^{39}Ar$ dating of Mississippi Valley-Type mineralization from western Newfoundland: International Geological Congress, Abstracts-Congres Geologique Internationale, Resumes, v. 28, p. 2.10–2.11.

Hammarstrom, J.M., and Smith, K.S., 2002, Geochemical and mineralogical characterization of solids and their effects on waters in metal-mining environments, *in* Seal, R.R., II, and Foley, N.K., Progress on geoenvironmental models for selected mineral deposit types: U.S. Geological Survey Open-File Report 02–195, Chapter B, p. 8–54.

Hannigan, Peter, 2007, Metallogeny of the Pine Point Mississippi Valley-Type zinc-lead district, southern Northwest Territories, *in* Goodfellow, W.D., ed., Mineral deposits of Canada: A synthesis of major deposit-types, district metallogeny, the evolution of geological provinces, and exploration methods: Geological Association of Canada, Mineral Deposits Division, Special Publication no. 5, p. 609–632.

Hanor, J.S., 1979, The sedimentary genesis of hydrothermal fluids, *in* Barnes, H.L., ed,. Geochemistry of hydrothermal ore deposits: New York, Wiley-Interscience, p. 137–142.

Hanor, J.S., 1996, Controls on the solubilization of lead and zinc in basin brines, *in* Sangster, D.F., ed., Carbonate-hosted lead-zinc deposits: Society of Economic Geologists Special Publication 4, p. 483–500.

Harrison, R.W., and Schultz, Art, 2002, Tectonic framework of the southwestern margin of the Illinois Basin and its influence on neotectonism and seismicity: Seismological Research Letters, v. 73, p. 698–731.

Harry, D.L., 2003, Geophysical constraints on the structure of the Laurentian transform continental margin beneath the central Gulf of Mexico and southeastern USA coastal plain: Abstracts with Programs, Geological Society of America, v. 35, p. 344.

Hay, R.L., Lee, Mingchou, Kolata, D.R., Matthews, J.C., and Morton, J.P., 1988, Episodic potassic diagenesis of Ordovician tuffs in the Mississippi Valley area: Geology, v. 16, p. 743–747.

Hearn, P.P., Jr., Sutter, J.F., and Belkin, H.E., 1987, Evidence for late-Paleozoic brine migration in Cambrian carbonate rocks of the central and southern Appalachians: implications for Mississippi Valley-Type mineralization: Geochimica et Cosmochimica Acta, v. 51, p. 1323–1334.

Hearst, R.B., Morris, W.A., and Schieck, D.G., 1994, Reflection seismic profiling for massive sulphides in the high Arctic: 64th Annual International Meeting, Society of Exploration Geophysicists, p. 531–533.

Hendricks, J.D., 1988, Bouguer gravity of Arkansas: U.S. Geological Survey Professional Paper 1474.

Heroux, Yvon, Chagnon, Andre, Dewing, Keith, and Rose, H.R., 1999, The carbonate-hosted base-metal sulphide Polaris deposit in the Canadian Arctic: organic matter alteration and clay diagenesis, *in* Glikson, Miryam, and Mastalerz, Maria, eds., Organic matter and mineralisation: thermal alteration, hydrocarbon generation and role in metallogenesis: Kluwer Academic Publisher, p. 260–295.

Heyl, A.V., 1983, Geologic characteristics of three Mississippi Valley-Type districts, *in* Kisvarsanyi, Geva, Grant, S.K., Pratt, W.P., and Koenig, J.W., eds., Proceedings of International Conference on Mississippi Valley-Type lead-zinc deposits: Rolla, University of Missouri, p. 27–60.

Heyl, A.V., Agnew, A.F., Lyons, E.J., and Behre, C.H., 1959, The geology of the Upper Mississippi Valley zinc-lead district: U.S. Geological Survey Professional Paper 424–D, 310 p.

Heyl, A.V., Landis, G.P., and Zartman, R.E., 1974, Isotopic evidence for the origin of Mississippi Valley-Type mineral deposits: a review: Economic Geology, v. 69, p. 992–1006.

Hildenbrand, T.G., 1985, Rift structure of northern Mississippi Embayment from the analysis of gravity and magnetic data: Journal of Geophysical Research, v. 90, n. 12, p. 12,607–12,622.

Hildenbrand, T.G., and Hendricks, J.D., 1995, Geophysical setting of the Reelfoot rift and relations between rift structures and the New Madrid seismic zone: U.S. Geological Survey Professional Paper 1538–E.

Hitzman, M.W., 1992, Discovery of the Lisheen Zn-Pb-Ag deposit, Ireland: Society of Economic Geology Newsletter, April 1992, v. 9, p. 1, 12–15.

Hitzman, M.W., 1996, Hydrothermal alteration associated with Irish type zinc-lead-(silver) and carbonate-hosted copper deposits: Geological Society of America Abstracts with Programs, v. 28, no. 7, p. 23.

Hitzman, M.W., 1999, Extensional faults that localized syndiagenetic Zn-Pb deposits and reactivation during Variscan compression: Geological Society of London Special Publication 155, p. 233–245.

Hitzman, M.W., Allan, J.R., and Beaty, D.W., 1998, Regional dolomitization of the Waulsortian limestone in southeastern Ireland: evidence of large-scale fluid flow driven by the Hercynian orogeny: Geology, v. 26, p. 547–550.

Hitzman, M.W., and Beaty, D.W., 1996, The Irish Zn-Pb-(Ba) orefield, in Sangster, D.F., ed., Carbonate-hosted lead-zinc deposits: Society of Economic Geologists Special Publication 4, p. 112–143.

Hitzman, M.W., and Large, Duncan, 1986, A review and classification of the Irish carbonate-hosted base metal deposits, in Andrew, C.J., Crowe, R.W.A., Finlay, S., Pennell, W.M., and Pyne, J.F., eds., Geology and genesis of mineral deposits in Ireland: Irish Association for Economic Geology, p. 217–238.

Hitzman, M.W., O'Connor, P., Shearly, E., Schaffalitzky, C., Beaty, D.W., Allan, J.R., and Thompson, T., 1992, Discovery and geology of the Lisheen Zn-Pb-Ag prospect, Rathdowney Trend, Ireland, in Bowden, A.A., Earls, G., O'Connor, P.G., and Pyne, J.F., eds., The Irish minerals industry 1980–1990: Dublin, Irish Association for Economic Geology, p. 227–246.

Hitzman, M.W., Reynolds, N.A., Sangster, D.F., Allen, C.R., and Carman, C.E., 2003, Classification, genesis, and exploration guides for nonsulfide zinc deposits: Economic Geology, v. 98, p. 685–714.

Hoagland, A.D., 1976, Appalachian zinc-lead deposits, in Wolf, K.H. ed., Handbook of strata-bound and stratiform ore deposits: Amsterdam, Elsevier, v. 6, p. 495–534.

Hudson, M.R., 2000, Coordinated strike-slip and normal faulting in the southern Ozark dome of northern Arkansas: deformation in a late Paleozoic foreland: Geology, v. 28, p. 511–514.

Hunt, J.M., 1996, Petroleum geochemistry and geology: New York, Freeman, 743 p.

Jakosky, J.J., Dreyer, R.M., and Wilson, C.H., 1942, Geophysical investigations in the Tri-State zinc and lead mining district: Kansas Geological Survey Bulletin no. 44, 151 p.

Jober, S-A, Dewing, Keith, and White, J.C., 2007, Structural geology and Zn-Pb mineral occurrences of northeastern Cornwallis Island; implications for exploration of the Cornwallis fold belt, northern Nunavut: Bulletin of Canadian Petroleum Geology, v. 55, p. 138–159.

Jones, W.R., 2007, History of mining and milling practices and production in San Juan County, 1871–1991, in Church, S.E., von Guerard, Paul, and Finger, S.E., eds., Integrated investigations of environmental effects of historical mining in the Animas river watershed, San Juan County, Colorado. U.S. Geological Survey Professional Paper 1651, Chapter C, p. 39–86.

Juracek, K.E., 2006, Sedimentation and occurrence and trends of selected chemical constituents in bottom sediment, Empire Lake, Cherokee County, Kansas, 1905–2005, U.S. Geological Survey Scientific Investigations Report 2006–5307, 61 p.

Kalenich, A.P., Kryukov, V.D., Lastochkink A.V., Semenov, Y.P., Zubarev, B.M., volkov, B.K., Tsopanov, O.K., and Bur'yan, Y.I., 2002, New silver-bearing lead-zinc ore deposit in Novaya Zemlya: Razvedka I Okhrana Nedr, v. 2002, p. 20–23 (in Russian).

Keller, G.V., 1960, Electrical properties of zinc-bearing rocks in Jefferson County, Tennessee: U.S. Geological Survey Professional Paper P–0400–B, p. B128–B132.

Kesler, S.E., 1996, Appalachian Mississippi Valley-Type deposits: Paleoaquifers and brine provinces, in Sangster, D.F., ed., Carbonate-hosted lead-zinc deposits: Society of Economic Geologists Special Publication 4, p. 29–57.

Kesler, S.E., Jones, L.M., and Ruiz, Joaquin, 1988, Strontium isotopic geochemistry of Mississippi Valley-Type deposits, East Tennessee: implications for age and source of mineralizing brines: Geological Society of America Bulletin, v. 100, p. 1300–1307.

Kesler, S.E., Martini, A.M., Appold, M.S., Walter, L.M., Huston, T.J., and Furman, F.C., 1996, Na-Cl-Br systematics of fluid inclusions from Mississippi Valley-Type deposits, Appalachian basin: constraints on solute origin and migration paths: Geochimica et Cosmochimica Acta, v. 60, p. 225–233.

Kesler, S.E., and Reich, M.H., 2006, Precambrian Mississippi Valley-Type deposits; relation to changes in composition of the hydrosphere and atmosphere, in Kesler, S.E., and Ohmoto, Hiroshi, eds., Evolution of early Earth's atmosphere, hydrosphere, and biosphere; constraints from ore deposits: Geological Society of America Memoir, v. 198, p. 185–204.

Kharaka, Y.L., Maest, A.S., Carothers, W.W., Law, L.M., Lamothe, P.J., and Fries, T.L., 1987, Geochemistry of metal-rich brines from central Mississippi Salt Dome basin, U.S.A.: Applied Geochemistry, v. 2, p. 543–561.

Kibitlewski, Stanislaw, 1991, Tectonic control of the origin of the Zn-Pb deposits in the Chrzanow region, Poland: Geological Quarterly, v. 37, p. 229–240.

Kisvarsanyi, Geva, Grant, S.K., Pratt, W.P., and Koenig, J.W., eds., 1983, Proceedings of International Conference on Mississippi Valley-Type lead-zinc deposits: Rolla, University of Missouri, 603 p.

Kozlowski, Andrzej, 1996, Fluid inclusion studies of the Silesia-Cracow zinc-lead district, southern Poland: Society of Economic Geologists Special Publication No. 4, p. 144–170. Polish Geological Quarterly v. 37, p. 129–149.

Kontak, D.J., 1995, A study of fluid inclusions in sulfide and nonsulfide mineral phases from a carbonate-hosted Zn-Pb deposit, Gays River, Nova Scotia, Canada: Economic Geology, v. 93, p. 793–817.

Krebs, Wolfgang, and Macqueen, Roger, 1984, Sequence of diagenetic and mineralization events, Pine Point lead-zinc property, Northwest Territories, Canada: Canadian Petroleum Society Bulletin, v. 32, p. 434–464.

Kyle, J.R., 1981, Geology of the Pine Point lead-zinc district, *in* Wolf, K.H., ed., Handbook of strata-bound and stratiform ore deposits: New York, Elsevier, v. 9, p. 643–741.

Kyle, J.R., and Saunders, J.A., 1996, Metallic deposits of the Gulf Coast basin: diverse mineralization styles in a young sedimentary basin: Society of Economic Geologists Special Publication 4, p. 218–229.

Lapakko, K.A., 1992, Characterization and static testing of ten gold mine tailings: Proceedings of the American Society for Surface Mining and Reclamation Meeting, Duluth, Minnesota, June 14–18, 1992, p. 370–416. (also available at http://www.techtransfer.osmre.gov/nttmainsite/Library/proceed/asmr92/section_2b2.pdf.)

Lavery, N.G., and Barnes, H.L., 1971, Zinc dispersion in the Wisconsin zinc-lead district: Economic Geology, v. 66, p. 226–242.

Lavery, N.G., Leach, D.L., and Saunders, J.A., 1994, Lithogeochemical investigations applied to exploration for sediment-hosted lead-zinc deposits, *in* Fontboté, Lluis, and Boni, Maria, eds., Sediment-hosted Zn-Pb Ores: Society for Geology Applied to Mineral Deposits Special Publication 10, p. 393–428.

Leach, D.L., 1980, Nature of mineralizing fluids in the barite deposits of central and southeast Missouri: Economic Geology, v. 75, p. 1168–1180.

Leach, D.L., 1994, Genesis of the Ozark Mississippi Valley-Type metallogenic province, Missouri, Arkansas, Kansas, and Oklahoma, USA, 1994: Society for Geology Applied to Mineral Deposits Special Publication 10, p. 104–138.

Leach, D.L., Bechstadt, Thilo, Boni, Maria, and Zeeh, Stefan, 2003, Triassic-hosted MVT Zn-Pb ores of Poland, Austria, Slovenia and Italy, *in* Kelly, J.G., Andrew, J.H., Ashton, J.H., Boland, M.B., Earls, G., Fusciardi, L., and Stanley, G., eds., Europe's Major Base Metal Deposits: Irish Association for Economic Geology, p. 169–214.

Leach, D.L., Bradley, D.C., Huston, D., Pisarevsky, S.A., Taylor, R.D., and Gardoll, S.J., 2010, Sediment-hosted lead-zinc deposits in Earth history: Economic Geology, in press.

Leach, D.L., Bradley, D.C., Lewchuk, M.T., Symons, D.T.A., de Marsily, Ghislain, and Brannon, J.C., 2001, Mississippi Valley-Type lead-zinc deposits through geological time: implications from recent age-dating research: Mineralium Deposita, v. 36, p. 711–740.

Leach, D.L., Macquar, J.C., Lagneau, Vincent, Leventhal, Joel, Emsbo, Poul, and Premo, Wayne, 2006, Precipitation of lead-zinc ores in the Mississippi Valley-Type deposit at Treves, Cevennes region of southern France: Geofluids, v. 6, p. 24–44.

Leach, D.L., and Rowan, E.L., 1986, Genetic link between Ouachita foldbelt tectonics and the Mississippi Valley-Type lead-zinc deposits of the Ozarks: Geology, v. 14, p. 931–935.

Leach, D.L., and Sangster, D.F., 1993, Mississippi Valley-Type lead-zinc deposits: Geological Association of Canada Special Paper 40, p. 289–314.

Leach, D.L., Sangster, D.F., Kelley, K.D., Large, R.R., Garven, Grant, Allen, C.R., Gutzmer, Jens, and Walters, Steve, 2005, Sediment-hosted lead-zinc deposits: a global perspective: Society of Economic Geologists, Economic Geology One Hundredth Anniversary Volume, 1905–2005, p. 561–607.

Leach, D.L., Viets, J.B., Foley-Ayuso, N.K., and Klein, D.P., 1995, Mississippi Valley-Type Pb-Zn deposits (Models 32a, b; Briskey, 1986 a, b), *in* Du Bray, E. A., ed., Preliminary Compilation of Descriptive Geoenvironmental Mineral Deposit Models: U.S. Government Consulting Group, Open-File Report 95–831, p. 234–243.

Leach, D.L., Viets, J.G., Kozlowski, Andrzej, and Kibitlewski, Stanislaw, 1996, Geology, geochemistry, and genesis of the Silesia-Cracow zinc-lead district, southern Poland, *in* Sangster, D.F., ed., Carbonate-hosted lead-zinc deposits: Society of Economic Geologists Special Publication 4, p. 144–170.

Lee, R.L., and Goldhaber, M.B., 2001, The behavior of As in drinking-water aquifers containing Mississippi Valley-Type mineralization: A characterization of the Ozark Plateaus region of the U.S.: Abstract in USGS Workshop on Arsenic in the Environment, Denver, CO, February 2001, 2 p. (also available online at http://wwwbrr.cr.usgs.gov/Arsenic/Final-AbsPDF/lee.pdf.)

Lee, Lopaka, Hageman, P.L., Besser, John.., Brumbaugh, William, and Diehl, S.F., 2005, Geochemical and biological impacts of modern lead mining in the mid-continental USA: Geological Society of America, vol. 37, no. 7, p. 179.

Leventhal, J.S., 1990, Organic matter and thermochemical sulfate reduction in the Viburnum Trend, Southeast Missouri: Economic Geology, v. 85, p. 622–632.

Lewis, R. S., 1948, Elements of Mining (2nd ed.): New York, John Wiley and Sons, Inc. p. 609–632.

Mavrogenes, J.A., Hagni, R.D., and Dingess, P.R., 1992, Mineralogy, paragenesis, and mineral zoning of the West Fork mine, Viburnum Trend, Southeast Missouri: Economic Geology, v. 87, p. 113–124.

McBride, H.H., Kolata, D.R., and Hildenbrand, T.G., 2003, Geophysical constraints on understanding the origin of the Illinois basin and its underlying crust: Tectonophysics, v. 363, p. 45–78.

McKnight, E.T., 1935, Zinc and lead deposits of northern Arkansas: U.S. Geological Survey Bulletin 853, 311 p.

McKnight, E.T., and Fischer, R.P., 1970, Geology and ore deposits of the Picher Field, Oklahoma and Kansas: U.S. Geological Survey Professional Paper, Report P 0588, 165 p.

McLimans, R.K., Barnes, H.L., and Ohmoto, Hiroshi, 1980, Sphalerite stratigraphy of the Upper Mississippi Valley zinc-lead district: Economic Geology, v. 75, p. 351–361.

McMurry, H.V., and Hoagland, A.D., 1956, Three-dimensional applied potential studies at Austinville, Virginia: Geological Society of America Bulletin, v. 67, p. 683–696.

Mickus, K.L., 1999, Magnetotelluric observations in the western Ouachita Mountains, southeastern Oklahoma: Geophysics, v. 64, p. 1680–1688.

Mickus, K.L., and Keller, G.R., 1992, Lithospheric structure of the south-central United States: Geology, v. 20, p. 335–338.

Miles, W.F., Roest, W.R., and Vo, M.P., 2000a, Gravity anomaly map, Canada: Geological Survey of Canada, Open file 3830a, scale 1:7,500,000.

Miles, W.F., Roest, W.R., and Vo, M.P., 2000b, Magnetic anomaly map, Canada: Geological Survey of Canada, Open file 3829a, scale 1:7,500,000.

Miller, J.R., 1996, The role of fluvial geomorphic processes in the dispersal of heavy metals from mine sites: Journal of Geochemical Research, v. 58, p. 101–1108.

Mitchell, A.H.G., 1985, Mineral deposits related to tectonic events accompanying arc-continent collision: Transactions of the Institution of Mining and Metallurgy, sec. B, v. 94, p. B115–B125.

Misra, K.C., and Fulweiler, R.E., 1995, Zinc deposits of the Mascot-Jefferson City district, East Tennessee, in Misra, K.C. ed., Guidebook Series (Society of Economic Geologists (U.S.), vol. 22, p. 206–221.

Moldovanyi, E.P., and Walter, L.M., 1992, Regional trends in water chemistry, Smackover Formation, southwest Arkansas: geochemical and physical controls: American Association of Petroleum Geologists Bulletin, v. 76, p. 864–894.

Montanez, I., 1996, Application of cathodoluminescent cement stratigraphy for delineating regional diagenetic and fluid migration events associated with Mississippi Valley-Type mineralization in the southern Appalachians, in Sangster, D.F., ed., Carbonate-hosted lead-zinc deposits: Society of Economic Geologists Special Publication 4, p. 432–447.

Moses, C.O., Nordstrom, D.K., Herman, J.S., and Mills, A.L., 1987, Aqueous pyrite oxidation by dissolved oxygen and ferric iron: Geochimica et Cosmochimica Acta, vol. 51, issue 6 p. 1561–1571.

Newfields, Inc., 2006, Focused remedial investigation for mined areas in St. Francois County, Missouri. Prepared on behalf of the Doe Run Company in fulfillment of one of the requirements of the Administrative Order of Consent Docket number VIJI-97-F-002.

Newhouse, W.H., 1933, Temperature of formation of the Mississippi Valley lead-zinc deposits: Economic Geology, v. 28, p. 744–750.

Ohle, E.L., 1959, Some considerations in determining the origin of ore deposits of the Mississippi Valley-Type. Part I: Economic Geology, v. 54, p. 769–789.

Ohle, E.L., 1970, Mississippi Valley-Type ore deposits, a general review: Washington Division of Mines Bulletin, v. 61, p. 5–15.

Ohle, E.L., 1980, Some considerations in determining the origin of ore deposits of the Mississippi Valley-Type. Part II. Economic Geology, v. 75, p. 161–172.

Ohle, E.L., 1985, Breccias in Mississippi Valley-Type deposits: Economic Geology, v. 80, p. 1736–1752.

Ohle, E.L., 1996, Significant events in the geological understanding of the southeast Missouri lead district, *in* Sangster, D.F., ed., Carbonate-hosted lead-zinc deposits: Society of Economic Geologists Special Publication 4, p. 1–7.

Oliver, Jack, 1986, Fluids expelled tectonically from orogenic belts: their role in hydrocarbon migration and other geologic phenomena: Geology, v. 14, p. 99–102.

Oliver, Jack, 1992, The spots and stains of plate tectonics: Earth Science Reviews, v. 32, p. 77–106.

Palmer, K.T., and Kucera, C.L., 1980, Lead contamination of sycamore and soil from lead mining and smelting operations in eastern Missouri: Journal of Environmental Quality, v. 9, p. 106–110.

Palumbo-Roe, Barbara, Banks, Vanessa, Quigley, Sean, and Klinck, B.A., 2007, Sensitivity of mine spoil heaps from an abandoned lead mine in mid Wales (UK) to changes in pH of natural water systems in the context of climate change *in* Cidu, Rosa, and Frau, Franco, eds., IMWA Symposium: Water in Mining Environments, May 27–31, Cagliari, Italy, 5 p.

Pannalal, S.J., Symons, D.T.A., and Leach, D.L., 2007, Paleomagnetic and mineral magnetic constraints on Zn-Pb ore genesis in the Pend Oreille Mine, Metaline district, Washington, USA: Canadian Journal of Earth Sciences, v. 44, p. 1661–1673.

Paradis, Suzanne, Hannigan, Peter, and Dewing, Keith, 2007, Mississippi Valley-Type lead-zinc deposits, *in* Goodfellow, W.D., ed., Mineral deposits of Canada: A synthesis of major deposit-types, district metallogeny, the evolution of geological provinces, and exploration methods: Geological Association of Canada, Mineral Deposits Division, Special Publication no. 5, p. 185–203.

Paradis, Suzanne, Turner, W.A., Coniglio, Mario, Wilson, N., and Nelson, J.L., 2006, Stable and radiogenic isotopic signatures of mineralized Devonian carbonate rocks of the northern Rocky Mountains and the Western Canada Sedimentary Basin, *in* Hannigan, P.K., ed., Potential for Carbonate-Hosted Lead-Zinc Mississippi Valley-Type Mineralization in Northern Alberta and Southern Northwest Territories: Geological Survey of Canada, Bulletin 591, p. 75–103.

Park, C.F., and Cannon, R.S., 1943, Geology and ore deposits of the Metaline quadrangle, Washington: U.S. Geological Survey Professional Paper 202, 81 p.

Plumlee, G.S., Leach, D.L., Hofstra, A.H., Landis, G.P., Rowan, E.L., and Viets, J.G., 1994, Chemical reaction path modeling of ore deposition in Mississippi Valley-Type Pb-Zn deposits of the Ozark region, U.S. midcontinent: Economic Geology, v. 89, p. 1361–1383.

Plumlee, G.S., Smith, K.S., Montour, M.R, Ficklin, W.H., Mosier, E.L., 1999, Geological controls on the composition of natural waters and mine waters draining diverse mineral-deposit types, *in* Plumlee, G.S., and Filipek, L.H., eds., The environmental geochemistry of mineral deposits. Part B: Case studies and research topics, Reviews in Economic Geology, v. 6B: Littleton, Colorado. Society of Economic Geologists, Inc., p. 373–409.

Proctor, P.D., Afzali, B., Collins, S., Panhorst, T., and Sinha, B., 1981, Lead additions to stream sediments, Southeast Missouri: Abstracts with Programs, Geological Society of America, vol. 13, no. 5, p. 261.

Qing, Hairuo, and Mountjoy, E.W., 1992, Large-scale fluid flow in the Middle Devonian Presqu'ile barrier, Western Canada sedimentary basin: Geology, v. 20, p. 903–906.

Qing, Hairuo, and Mountjoy, E.W., 1994, Formation of coarsely crystalline, hydrothermal dolomite reservoirs in the Presqu'ile Barrier, Western Canada sedimentary basin: AAPG Bulletin, v. 78, p. 55–77.

Randell, R.N., and Anderson, G.M., 1996, Geology of the Polaris Zn-Pb deposit and surrounding area, Canadian Arctic Archipelago, *in* Sangster, D.F., ed., Carbonate-hosted lead-zinc deposits: Society of Economic Geologists Special Publication 4, p. 307–319.

Ravenhurst, C.E., Renolds, P.H., Zentili, M., and Akande, S.O., 1987, Isotopic constraints on the genesis of Zn-Pb mineralization at Gays River, Nova Scotia, Canada: Economic Geology, v. 82, p. 1294–1308.

Reichert, Jörg, and Borg, Gregor, 2008, Numerical simulation and a geochemical model of supergene carbonate-hosted non-sulphide zinc deposits: Ore Geology Reviews, v. 33, p. 134–151.

Repetski, J.E., and Narkiewicz, Marek, 1996, Conodont color and surface textural alteration in the Muschelkalk (Triassic) of the Silesian-Cracow Zn-Pb district, Poland, *in* Gorecka, Ewa, and Leach, D.L., eds., Carbonate-hosted zinc-lead deposits in the Silesian-Cracow area, Poland: Wydawnictwa Geologiczne, Warsaw, Poland, v. 154, p. 113–122.

Rhodes, D., Lantos, E.A., Lantos, J.A., Webb, R.J., and Owens, D.C., 1984, Pine Point orebodies and their relationship to the stratigraphy, structure, dolomitization, and karstification of the Middle Devonian barrier complex: Economic Geology, v. 79, p. 991–1055.

Roedder, Edwin, Ingram, Blanche, and Hall, W.E., 1963, Studies of fluid inclusions. III. Extraction and quantitative analysis of inclusions in the milligram range: Economic Geology, v. 58, p. 353–374.

Romero, Antonia, Gonzalez, Isabel, and Galan, Emilio, 2006, The role of efflorescent sulfates in the storage of trace elements in stream waters polluted by acid mine-drainage: the case of Pena Del Hierro, southwestern Spain: The Canadian Mineralogist, v. 44, no. 6, p. 1431–1446.

Rose, A.W., Hawkes, H.E. and Webb, J.S., 1979, Geochemistry in mineral exploration (Second Edition): New York, Academic Press.

Rouvier, H., Perthuisot, V., and Mansouri, A., 1985, Pb-Zn deposits and salt-bearing diapirs in southern Europe and North Africa: Economic Geology, v. 80, p. 666–687.

Rowan, E.L., 1986, Cathodoluminescent zonation in hydrothermal dolomite cements: relationship to Mississippi Valley-Type Pb-Zn mineralization in southern Missouri and northern Arkansas, *in* Hagni, R.D., ed., Process mineralogy VI: Warrendale, Pennsylvania: Metallurgical Society, p. 69–87.

Rowan, E.L., and Goldhaber, M.B., 1995, Duration of mineralization and fluid-flow history of the Upper Mississippi Valley zinc-lead district: Geology, v. 23, p. 609–612.

Sangster, D.F., 1968, Relative sulphur isotope abundances of ancient seas and stratabound sulphide deposits: Geological Association of Canada, Proceedings 19, p. 79–91.

Sangster, D.F., 1971, Sulphur isotopes, stratabound sulphide deposits, and ancient seas: Society of Mining Geologists of Japan, Special Issue 3 (Proceedings of the IMA-IAGOD meetings '70), p. 295–299.

Sangster, D.F., 1983, Mississippi Valley-Type deposits: a geological mélange, *in* Kisvarsanyi, Geza, Grant, S.K., Pratt, W.P. and Koenig, J.W., eds., Proceedings of international conference on Mississippi Valley-Type lead-zinc deposits: University of Missouri-Rolla Press, Rolla, Mo., p. 7–19.

Sangster, D.F., 1986, Age of mineralization in Mississippi Valley-Type (MVT) deposits: a critical requirement for genetic modeling, *in* Andrew, C.J., Crowe, R.W.A., Finlay, S., Pennell, W.M. and Pyne, J.F., eds., Geology and Genesis of Mineral Deposits in Ireland: Irish Association for Economic Geology, Dublin, Ireland, p. 625–634.

Sangster, D.F., 1990, Mississippi Valley-Type and sedex lead-zinc deposits: A comparative examination: Transactions of the Institution of Mining and Metallurgy, sec. B, v. 99, p. B21–B42.

Sangster, D.F., 1996, ed., Carbonate-hosted lead-zinc deposits: Society of Economic Geologists Special Publication 4, 664 p.

Saunders, J.A., and Rowan, E.L., 1990, Mineralogy and geochemistry of metallic well scale, Raleigh and Boykin Church oilfields, Mississippi, U.S.A.: Transactions, Institution of Mining and Metallurgy, sec. B, v. 99, p. 54–58.

Savage, K.S. Tingle, T.N., O'Day, P.A., Waychunas, G.A., and Bird, D.K., 2000, Arsenic speciation in pyrite and secondary weathering phases, Mother Lode Gold District, Tuolumne County, California, 2000: Applied Geochemistry, v. 15, no. 8, p. 1219–1244.

Savard, M.M., Chi, G., Sami, T., Williams-Jones, A.E., and Leigh, K., 2000, Fluid inclusion and carbon, oxygen, and strontium isotope study of the Polaris Mississippi Valley-Type Zn-Pb deposit, Canadian Arctic Archipelago: implications for ore genesis: Mineralium Deposita, v. 35, p. 495–510.

Scott, R.L., Whiting, T.H., and Turner, Richard, 1994, Role of geophysics in exploration for MVT lead-zinc deposits on the Lennard Shelf, western Australia: Geology Department and Extension Service, University of Western Australia (Publication 0156-9287), v. 26, p. 107–117.

Sicree, A.A., and Barnes, H.L., 1996, Upper Mississippi Valley district ore fluid model: the role of organic complexes: Ore Geology Reviews, v. 11, p. 105–131.

Siebenthal, C.E., 1916, Origin of the zinc and lead deposits of the Joplin region, Missouri, Kansas, and Oklahoma: U.S. Geological Survey Bulletin 606, 283 p.

Siegel, F.R., 1990, Exploration for Mississippi-Valley type stratabound Zn ores with stream suspensates and stream sediments, Virginia, U.S.A: Journal of Geochemical Exploration, vol. 38, p. 265–283.

Siegel, H.O., Hill, H.L., and Baird, J.G., 1968, Discovery case history of the Pyramid orebodies Pine Point, Northwest Territories, Canada: Geophysics, v. 33, p. 645–656.

Simpson, R.W., Jachens, R.C., Blakely, R.J., and Saltus, R.W., 1986, A new isostatic residual gravity map of the conterminous United States with a discussion on the significance of isostatic residual anomalies: Journal of Geophysical Research, v. 91, p. 8348–8372.

Sims, P.K., Saltus, R.W., and Anderson, E.D., 2008, Precambrian basement structure map of the continental United States—An interpretation of geologic and aeromagnetic data: U.S. Geological Survey Scientific Investigations Map 3012, scale: 1:8,000,000.

Sinclair, W.D., Chorlton, L.B., Laramee, R.M., Eckstrand, O.R., Kirkham, R.V., Dunne, K.P.E., and Good, D.J., 1999, World minerals geoscience database project: digital databases of generalized world geology and mineral deposits for mineral exploration and research, *in* Stanley, C.L., and others, eds., Mineral deposits: Processes to processing: Rotterdam, Balkema, p. 1435–1437.

Skall, H., 1975, The paleoenvironment of the Pine Point lead-zinc district: Economic Geology, v. 70, p. 22–47.

Smith, K.S., 1999, Metal sorption on mineral surfaces: an overview with examples relating to mineral deposits, *in* Plumlee, G.S., and Logsdon, M.J., eds., The environmental geochemistry of mineral deposits. Part A Society of Economic Geologists, Reviews in Economic Geology, vol. 6A, p. 161–182.

Smith, B.J. and Schumacher, J.G., 1991, Hydrochemical and sediment data for the Old Lead Belt, southeastern Missouri, 1988-89: U.S. Geological Survey Open-File Report 91–0211, 98 p.

Snyder, F.G., 1967, Genesis of strata-bound lead-zinc-barite-fluorite deposits in carbonate rocks: Economic Geology Monograph 3, p. 1–13.

St. Marie, J., and Kesler, S.E., 2000, Iron-rich and iron-poor Mississippi Valley-Type mineralization, Metaline district, Washington: Economic Geology, v. 95, p. 1091–1106.

Stormo, S., and Sverjensky, D.A., 1983, Silicate hydrothermal alteration in a Mississippi Valley-Type deposit-Viburnum Trend, southeast Missouri: Geological Society of America Abstracts with Programs, v. 15, p. 699.

Stumm, W., and Morgan, J.J., 1996, Aquatic chemistry: Chemical equilibria and rates in natural waters, 3rd edition, John Wiley and Sons, NY, 1022 p.

Sverjensky, D.A., 1981, The origin of a Mississippi Valley-Type deposit in the Viburnum Trend, southeast Missouri: Economic Geology, v. 76, p. 1848–1872.

Sverjensky, D.A., 1986, Genesis of Mississippi Valley-Type lead-zinc deposits: Annual Reviews of Earth and Planetary Sciences, v. 14, p. 177–199.

Symons, D.T.A., Lewchuk, M.T., and Leach, D.L., 1998, Age and duration of the Mississippi Valley-Type mineralizing fluid flow event in the Viburnum Trend, Southeast Missouri, USA, determined from paleomagnetism: Geological Society Special Publications, v. 144, p. 27–39.

Taylor, R.D., Leach, D.L., Bradley, D.C., and Pisarevsky, S.A., 2009, Compilation of mineral resource data for Mississippi Valley-Type and clastic-dominated sediment-hosted Pb-Zn deposits: U.S. Geological Survey Open-File Report 2009–1297, 46 p.

Thornton, I., Jong. S., Moorcroft, S., Watt, J., Strehlow, C.D., Baltrop, D., and Wells, J., 1980, Cadmium at Shipham – a unique example of environmental geochemistry and health, *in* Hemphill. D.D., ed., Trace substances in environmental health-XIV, Columbia, University of Missouri, p. 27–37.

U.S. Environmental Protection Agency Office of Solid Waste, 2006, Assessment of the potential cost benefits and other impacts of chat use in transportation projects: U.S. Environmental Protection Agency Office of Solid Waste, 81 p.

U.S. Fish and Wildlife Services, and Missouri Department of Natural Resources, 2008, Preassessment screen and determination—Big River mine tailings site, St. Francois County, Missouri, 20 p. (also available online at www.fws.gov/midwest/semonrda/documents/brmtPAS.pdf.)

U.S. Fish and Wildlife Service, 2009, Maximum chat utilization in asphalt paving at the Tar Creek superfund site, test road (also available online at http://www.crossroads.odl. state.ok.us/u?/stgovpub,9095.)

Velasco, Francisco, Herrero, J.M., Yusta, Iñaki, Alonso, J.A., Seebold, Ignacio, and Leach, D.L., 2003, Geology and geochemistry of the Reocin zinc-lead deposit, Basque-Cantabrian basin, northern Spain: Economic Geology, v. 98, p. 1371–1396.

Viets, J.G., 1983, Geochemical variations of major, minor, and trace elements in samples of the Bonneterre Formation from drill holes transecting the Viburnum Trend Pb-Zn district of Southeast Missouri, *in* Kisvarsaynyi, Geza, Grant, S.K., Pratt, W.P., and Koenig, J.W., eds., International Conference on Mississippi Valley-Type lead-zinc deposits: Proceedings volume: University of Missouri-Rolla, Rolla Press, p. 174–186.

Viets, J.G., Hofstra, A.H., Emsbo, Poul, and Kozlowski, Andrzej, 1996, The composition of fluid inclusions in ore and gangue minerals from Mississippi Valley-Type Zn-Pb deposits of the Cracow-Silesia region of southern Poland: genetic and environmental implications, *in* Gorecka, E., and Leach, D.L., eds., Carbonate-hosted zinc-lead deposits in the Silesian-Cracow area, Poland: Warsaw, Poland, Prace Panstwowego Instytuti Geologicznego, v. 154, p. 85–104.

White, D.E., 1958, Liquid inclusions in sulfides from Tri-State (Missouri, Kansas, and Oklahoma) are probably connate in origin: Geological Society of America Bulletin, v. 69, p. 1660–1661.

White, D.E., 1968, Environments of generation of some base metal ore deposits: Economic Geology, v. 63, p. 301–335.

Wilkinson, J.J., and Earls, G., 2000, A high-temperature hydrothermal origin for black dolomite matrix breccias in the Irish Zn-Pb orefield: Mineralogical Magazine, v. 64, p. 1017–1036.

Wilkinson, J.J., Stoffell, Barry, Wilkinson, C.C., Jeffries, T.E., and Appold, M.S., 2009, Anomalously metal-rich fluids form hydrothermal ore deposits: Science, v. 323, p. 764–767.

Wirt, Laurie, Motyka, Jacek, Leach, David, Sass-Gustkiewicz, Maria, Szuwarzynski, Marek, Adamczyk, Zbigniew, Briggs, Paul, and Meiers, Al, 2001, Water quality data at selected sites in the Mississippi Valley-Type Zn-Pb ore district of upper Silesia, Poland, 1995–97: U.S. Geological Survey Open-File Report 2001–283, 18 p.

Yardley, B.W.D., 2005, Metal concentrations in crustal fluids and their relationship to ore formation: Economic Geology, v. 100, p. 613–632.

Appendix

Grade and Tonnage

Mississippi Valley-Type deposits are characteristically distributed over hundreds of square kilometers that define individual ore districts. Because production and reserve data for MVT deposits, particularly in the U.S., are commonly presented only as district totals, the size, grade, and metal-ratio parameters for individual deposits are difficult to compile. For example, the Viburnum Trend and Old Lead Belt deposits in table A2 are effectively production units within a mineralized zone that is continuous for more than 120 km. Therefore, grade-tonnage models for MVT deposits must take into account the district scale of mineralization along with individual deposit data. Assessments based solely on deposit data may misrepresent the actual resource defined by MVT mineralization.

Grade-tonnage data for all known MVT deposits are available from Leach and others (2005) and Taylor and others (2009). The Taylor and others (2009) compilation is an updated version of Leach and others (2005) and contains resource data as of 2009 from newly published articles and from company data, along with newly classified MVT deposits and new mineralization age dates. Given the great diversity in MVT deposits, resource assessments can select subsets of deposit data for specific regions and known MVT deposit styles for regional specific grade-tonnage models.

The largest known MVT deposits are Mehdiabad, Iran, (Chapple, 2003; Reichert and Borg, 2008 and references cited within) with 394 Mt of ore and 22.9 Mt Pb+Zn, followed by Pavlovskoye, Russia, (Kalenich and others, 2002) with 128 Mt of ore and 7.0 Mt Pb+Zn, and Admiral Bay, Australia, with 120 Mt ore and 10.4 Mt Pb+Zn. The highest grade ores belong to Schmalgraf, Belgium with 26.1 percent Pb+Zn and 24 percent Zn, and Touissit-Bou Beker, Morocco with 13 percent Pb. The Navan, Ireland deposit (95.3 Mt at 2.1 percent Pb and 8.3 percent Zn) is the largest active mine associated with an MVT deposit, and a metal endowment larger than most districts.   The range of ore and metal tonnage extends from the above mentioned maximums down to less than 1 Mt, thus displaying a wide range of resource potential in MVT deposits.

The above data are summarized from a more complete dataset shown as figures A1-A5 and tables A1-A2 within Appendix A and in table 1 within the text.
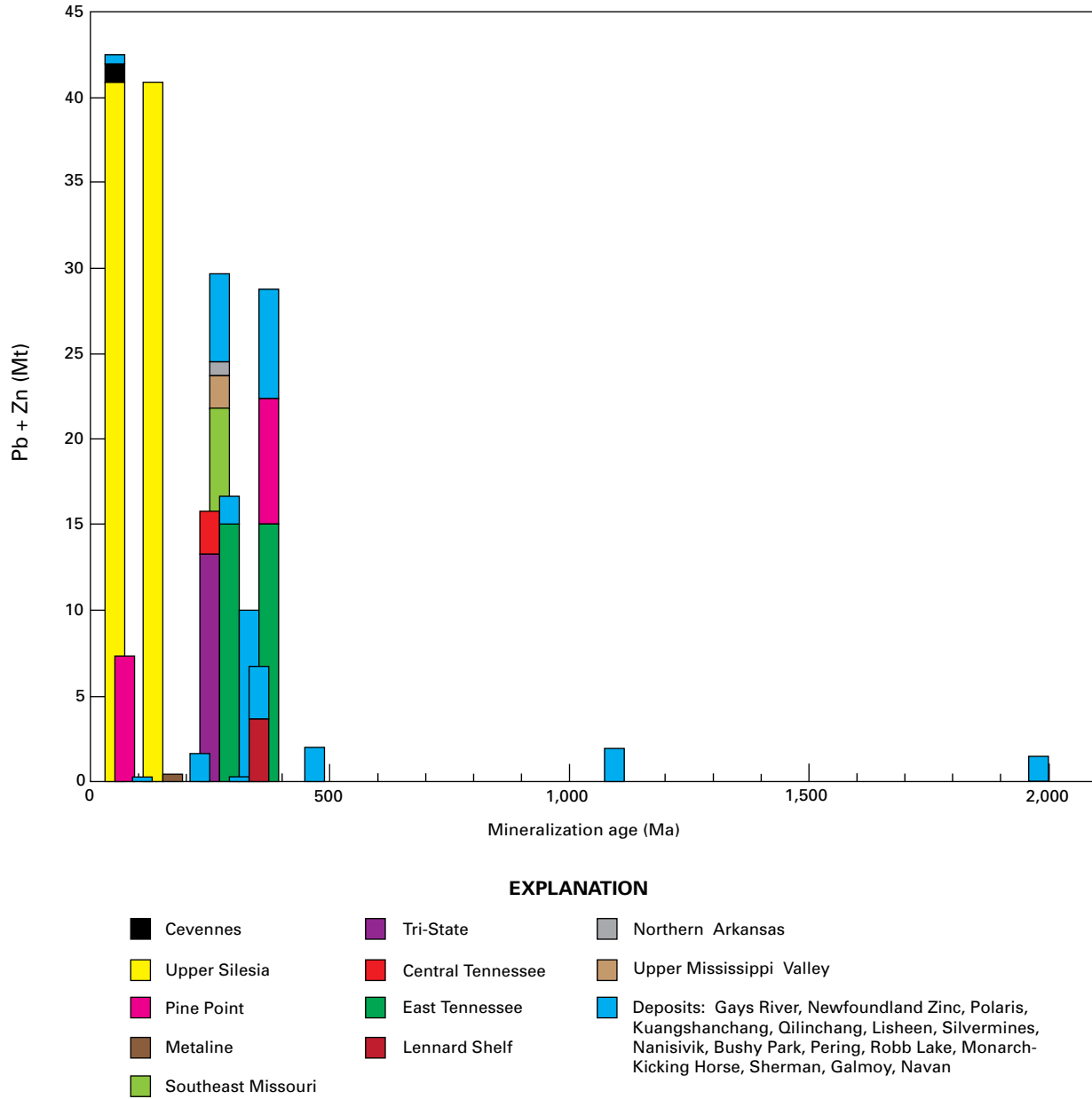
Figure A1. Secular distribution of Mississippi Valley-Type deposits and districts with paleomagnetic and/or radiometric ages of mineralization (data from Taylor and others, 2009).
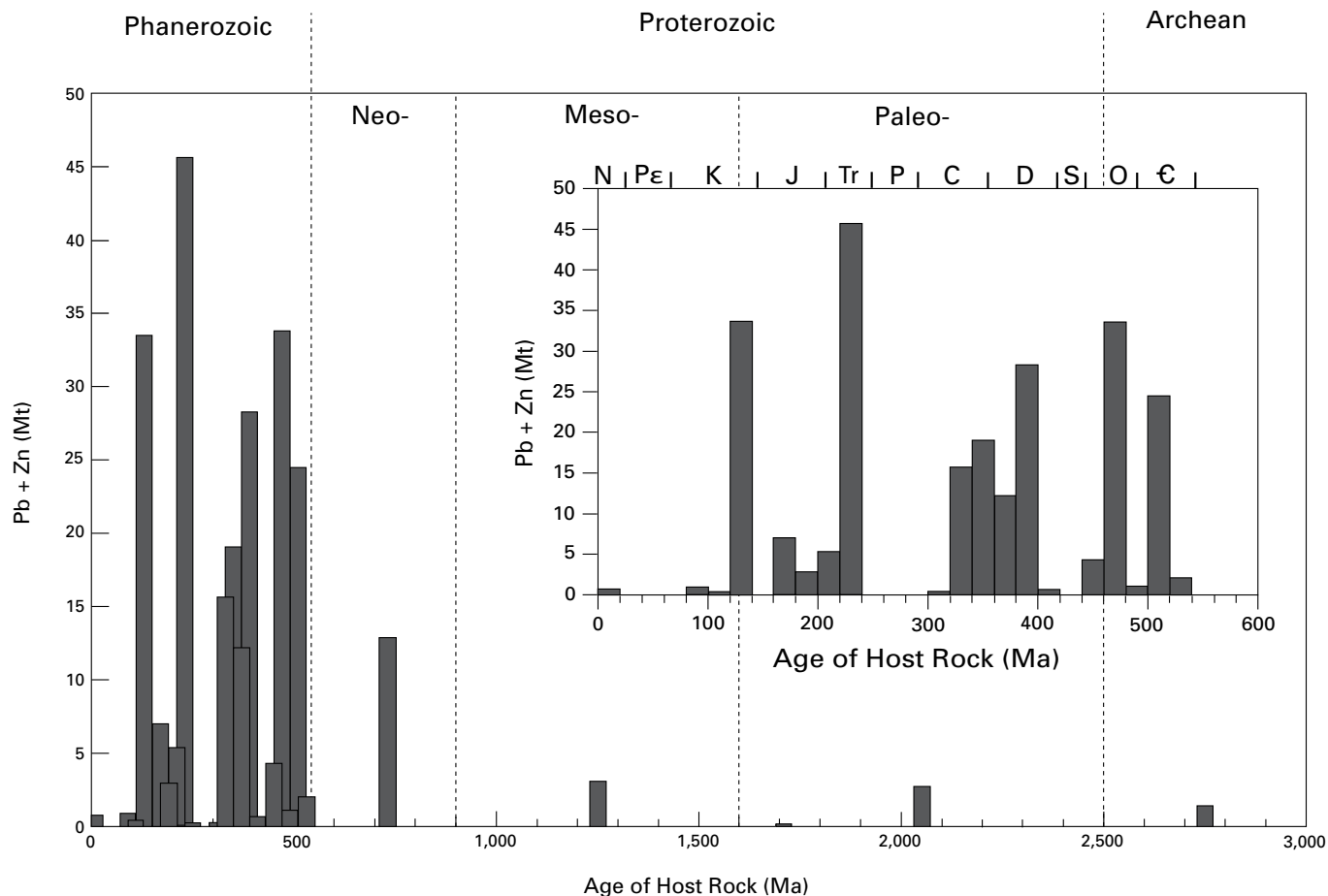
Figure A2.   Secular distribution of Missippi Valley-type metal and age of host rock. Data for more than 100 deposits and districts is summarized from the Neoproterozoic to present. Mesoproterozoic deposits include Bulman and Nanisivik. Paleoproterozoic deposits include Black Angel, Esker, and Nunngarut. Archean deposits include Bushy Park-Pering (data from Taylor and others, 2009).
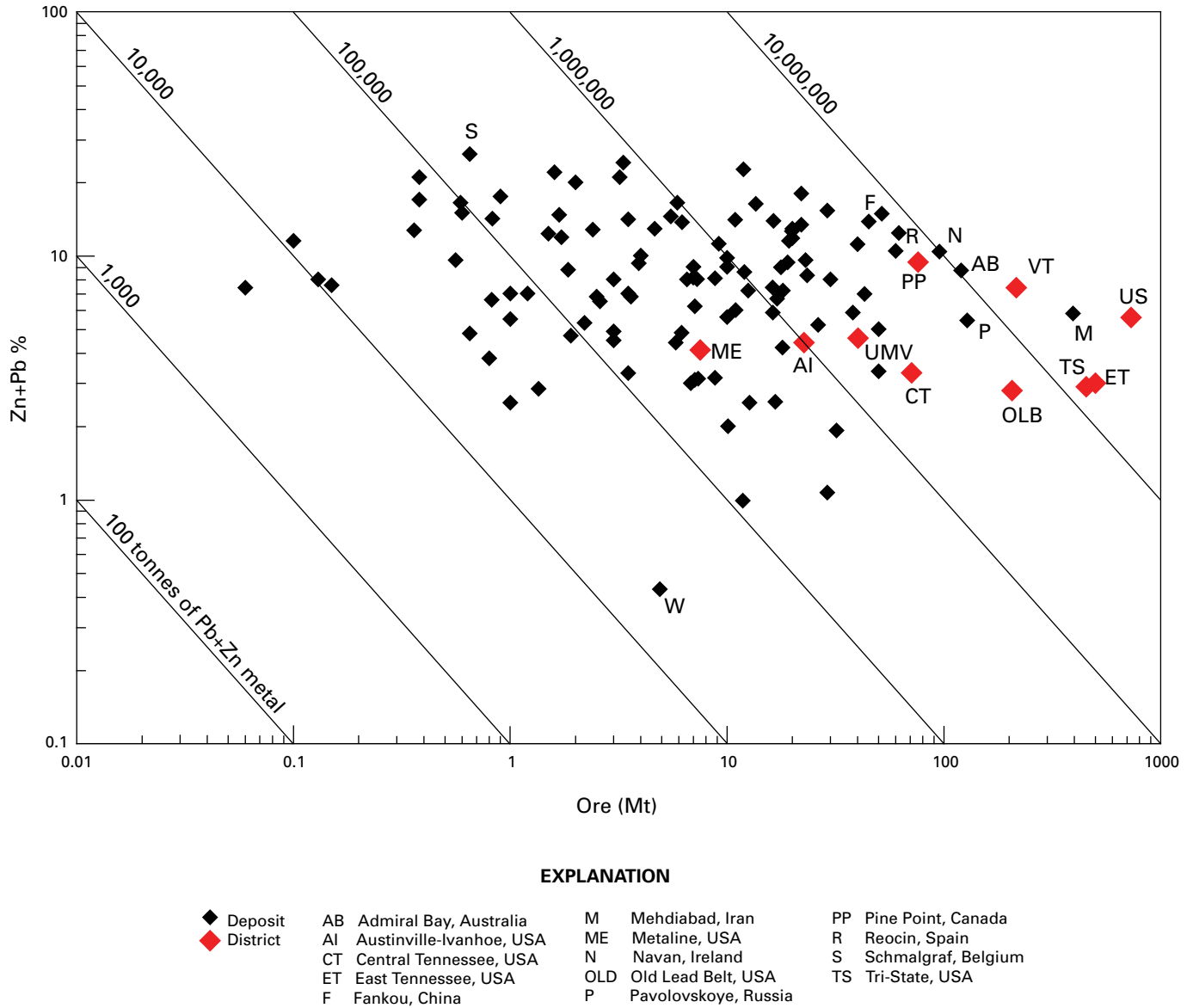
Figure A3.   Grade-tonnage for 113 Mississippi Valley-Type deposits and 10 districts. Diagonal lines represent tonnage of Pb and Zn metal (data from Taylor and others, 2009).

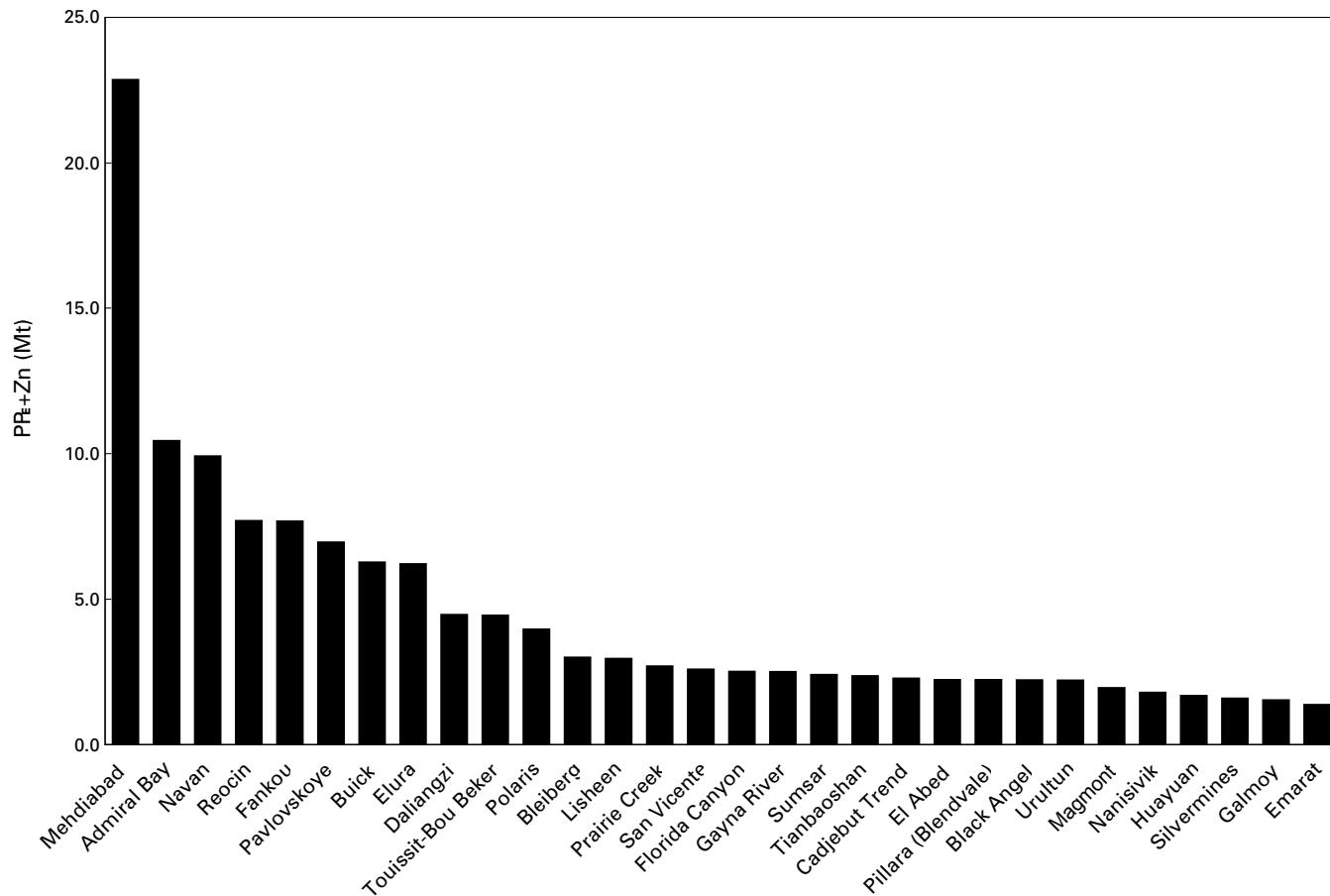**Figure A4**.   The largest 30 Mississippi Valley-Type deposits based on total lead and zinc content (Mt) (data from Taylor and others, 2009).
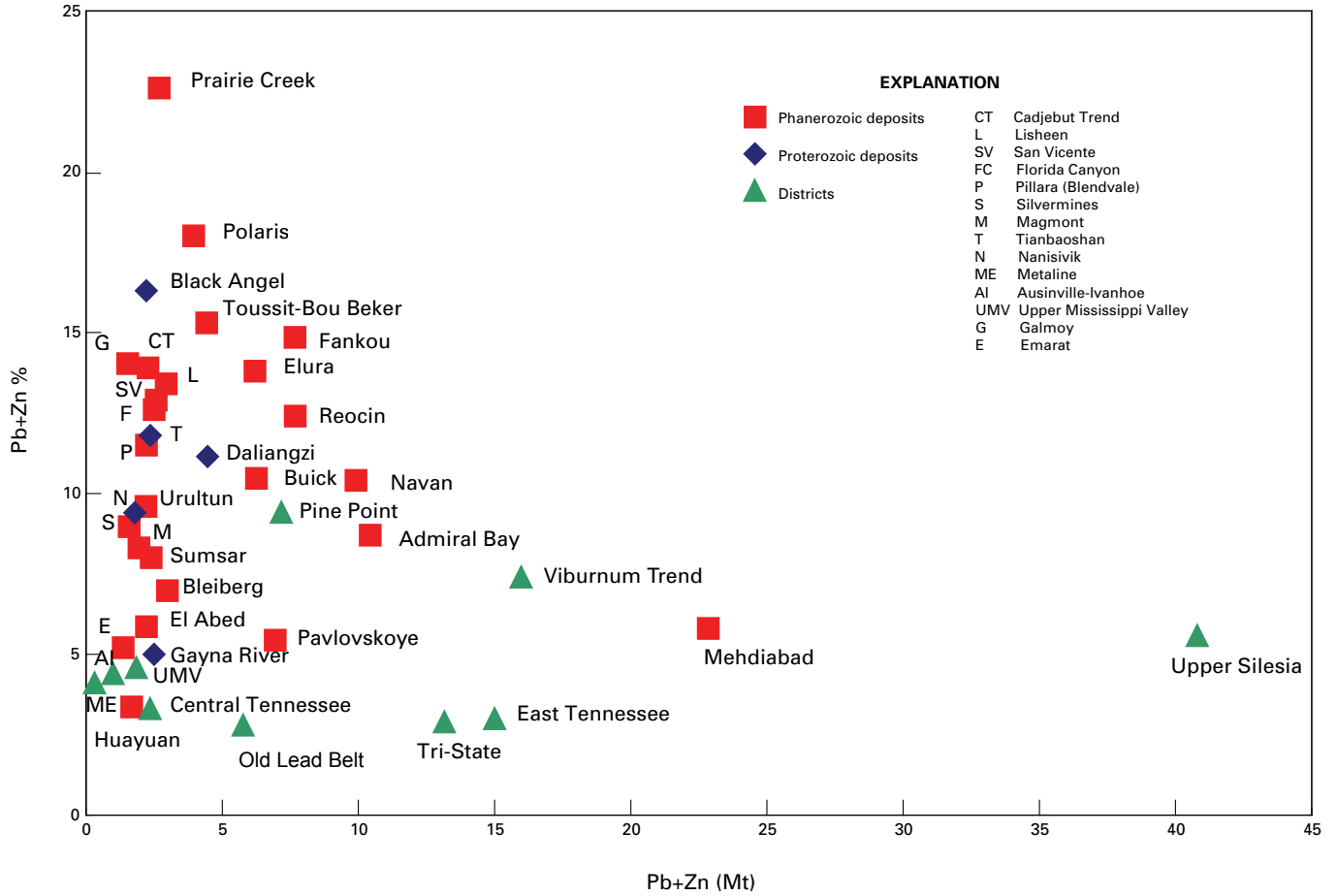
Figure A5. Metal endowment of the 30 largest Mississippi Valley-Type deposits in contained metal and the districts from Table A2. Deposits are separated by host rock age of Phanerozoic or Proterozoic (data from Taylor and others, 2009).

Table A1. Summary of characteristics of the 30 largest Mississippi Valley-Type deposits based on contained Pb+Zn metal [data from Taylor and others (2009)].

[Mt, Million tonnes; Pb, lead; Zn, zinc; %, percent; Cu, copper; Ag, silver; g/t, grams per tonne]

Deposit	Country	Size (Mt)	Pb (Mt)	Zn (Mt)	Pb+Zn (Mt)	Pb (%)	Zn (%)	Pb+Zn (%)	Cu (%)	Ag (g/t)	Host-rock age
Admiral Bay	Australia	120.00	2.8	7.7	10.4	2.3	6.4	8.7	--	32.0	Early Ordovician
Navan	Ireland	95.30	2.0	7.9	9.9	2.1	8.3	10.4	--	--	Early Mississippian
Reocin	Spain	62.00	0.9	6.8	7.7	1.4	11.0	12.4	--	--	Early Cretaceous
Fankou	China	51.68	2.5	5.2	7.7	4.9	10.0	14.9	--	102.0	Middle-Late Devonian
Pavlovskoye	Russia	128.00	2.0	5.0	7.0	1.5	3.9	5.4	--	--	Early Devonian
Buick	USA	59.87	4.9	1.3	6.3	8.2	2.2	10.5	--	--	Late Cambrian
Elura	Australia	45.00	2.4	3.8	6.2	5.3	8.5	13.8	--	69.0	Early Devonian
Daliangzi	China	40.00	0.3	4.2	4.5	0.8	10.4	11.2	--	43.0	Neoproterozoic
Touissit-Bou Beker	Morocco	29.00	3.8	0.7	4.4	13.0	2.3	15.3	--	--	Middle Jurassic
Polaris	Canada	22.00	0.9	3.1	4.0	4.0	14.0	18.0	--	--	Late Ordovician
Bleiberg	Austria	43.00	0.5	2.5	3.0	1.1	5.9	7.0	--	--	Middle to Late Triassic
Lisheen	Ireland	22.00	0.4	2.5	2.9	1.9	11.5	13.4	--	26.0	Early Mississippian
Prairie Creek	Canada	11.90	1.2	1.5	2.7	10.1	12.5	22.6	0.40	161.0	Early Ordovician
San Vicente	Peru	20.00	0.2	2.4	2.6	0.9	12.0	12.9	--	--	Early Jurassic
Florida Canyon	Peru	19.90	0.3	2.2	2.5	1.7	10.9	12.6	--	17.1	Late Triassic-Early Jurassic
Gayna River	Canada	50.00	0.2	2.4	2.5	0.3	4.7	5.0	--	--	Neoproterozoic
Sumsar	Kirghistan	30.00	1.5	0.9	2.4	5.0	3.0	8.0	--	--	Devonian
Tianbaoshan	China	20.00	0.3	2.1	2.4	1.4	10.4	11.8	--	93.6	Neoproterozoic
Cadjebut Trend	Australia	16.37	0.8	1.5	2.3	5.0	8.9	13.9	--	--	Middle Devonian
El Abed	Algeria	38.00	0.9	1.3	2.2	2.3	3.5	5.9	--	--	Middle Jurassic
Pillara (Blendvale)	Australia	19.31	0.5	1.7	2.2	2.6	8.9	11.5	--	17.0	Late Devonian
Black Angel	Greenland	13.56	0.5	1.7	2.2	4.0	12.3	16.3	--	32.0	Paleoproterozoic
Urultun	Russia	23.00	0.7	1.6	2.2	2.9	6.7	9.6	--	--	Early Devonian
Magmont	USA	23.40	1.7	0.2	1.9	7.3	1.0	8.3	0.26	10.6	Late Cambrian
Nanisivik	Canada	19.00	0.1	1.7	1.8	0.7	8.7	9.4	--	41.0	Mesoproterozoic
Huayuan	China	50.00	0.0	1.7	1.7	--	3.4	3.4	--	--	Early Cambrian
Silvermines	Ireland	17.69	0.4	1.1	1.6	2.5	6.4	9.0	--	24.2	Early Mississippian
Galmoy	Ireland	10.90	0.2	1.4	1.5	1.6	12.4	14.0	--	--	Early Mississippian
Emarat	Iran	26.30	0.8	0.6	1.4	3.1	2.1	5.2	--	--	Early Cretaceous

Table A2. Compilation of age and resource information for selected Mississippi Valley-Type districts [data from Leach and others (2005)].

[Ma, million years ago; Prod+Res (Mt), Production and resources in million tonnes; Mt, million tonnes; Pb, lead; Zn, zinc; %, percent; Th, thorium; Rb, rubidium; Sr, strontium]

District	Country	Host Rock Age	Mineralization Age (Ma) and Method	Prod+Res (Mt)	Pb%	Zn%	Zn metal (Mt)
Austinville-Ivanhoe	United States	Cambrian		22.63	0.70	3.70	0.84
Central Tennessee	United States	Early Ordovician	249 (Paleomagnetism); 260 (Th-Pb)	[1]71		3.31	2.35
East Tennessee (Mascot-Jefferson City)	United States	Early Ordovician	286 (Paleomagnetism); 347, 377 (Rb-Sr)	500		3.00	15.00
Metaline	United States	Middle Cambrian		7.52	1.34	2.77	0.21
Old Lead Belt	United States	Late Cambrian		206	2.80		
Tri-State	United States	Early to Late Mississippian	265 (Paleomagnetism); 251 (Th-Pb)	453.59	0.57	2.33	10.57
Upper Mississippi Valley	United States	Middle Ordovician	269 (Rb-Sr); 277 (Rb-Sr)	40.22	1.86	2.73	1.10
Upper Silesia	Poland	Middle Triassic	46 (Paleomagnetism); 135 (Rb-Sr)	731	1.34	4.24	30.98
Viburnum Trend	United States	Late Cambrian		215.91	6.47	0.93	2.01
Pine Point	Canada	Middle Devonian	71 (Paleomagnetism); 361 (Rb-Sr)	76.11	2.91	6.51	4.95
Northern Arkansas	United States	Ordovician; Mississippian	265 (Paleomagnetism)				0.65

[1]Note: Data for Central Tennessee represents production for 1975 to 1985, 1993 to 2003, and unmined resources as of 2003. Production data for the years 1986 to 1992 were not available at the time of compilation.