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Effects of Landscape Disturbances on Autotrophic Processes Within Arkansas Ozark Streams

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Source Constraints of Ore Metals In Mississippi Valley-Type Deposits in Central and Eastern Tennessee Using Pb Isotopes

Source Constraints of Ore Metals In Mississippi Valley-Type Deposits in Central and Eastern Tennessee Using Pb Isotopes

A thesis submitted in partial fulfillment
of the requirements for the degree of
Master of Science in Geology

by

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Western Kentucky University
Bachelor of Science in Geology, 2010

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This thesis is approved for recommendation to the Graduate Council.

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Abstract

The Mississippi Valley-Type (MVT) Central and East Tennessee (TN) Districts contain economically significant lead-zinc deposits that occur in the Early Ordovician carbonates of the Knox Group. Although both districts share similar host rock, have similar temperatures of formation, and typically fill open spaces of collapse breccias or replace their host carbonates, previous studies may suggest that these ores did not form from the same mineralizing fluids and may have different Pb sources. Nu Plasma MC-ICP-MS Pb isotopic analyses on sulfides from Central and East TN were conducted and the metal sources evaluated. Results were plotted on covariation diagrams with respect to the average crustal growth curve from Stacy and Kramers (1975) and the orogene curve from Zartman and Doe (1981). Lead isotope data from both Central and East TN plot beyond the present day age (0 m.y. ago) indicative of a crustal source of Pb-Zn. Central TN $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, and $^{208}Pb/^{204}Pb$ ratios range from 19.334 – 20.128, 15.548 – 16.034, and 38.837 – 40.034 respectively. Eastern TN $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, and $^{208}Pb/^{204}Pb$ ratios range from 19.341 – 19.455, 15.638 – 15.789, and 39.045 – 39.591 respectively. Pb isotope ratios from the Young Mine in the East TN District plot within ranges defined by other East TN District samples from previous studies. Three Pb isotope ratios from the Elmwood Mine in the Central TN District plot near these East TN samples, while the remaining Elmwood samples remain suspect to analytical error as they plot away from any other recorded Central TN deposits. It appears that the thick, black, metal-rich shales of the Appalachian Basin have been the source of the Pb-Zn and ore fluids of MVT deposits that formed the East TN deposits. When East TN Pb data from this study are compared to Central TN Pb data from previous studies, Central TN Pb is commonly more radiogenic, suggestive of a

mineralizing fluid with different compositions. Further analysis of Central TN Pb deposits is needed to further constrain this source.

Acknowledgements

I would like to express my sincere gratitude to Dr. Adriana Potra who showed continuous support, patience, enthusiasm and guidance. I am forever grateful and appreciative as this would not have been possible without her. I’d like to thank my committee members Dr. Doy Zachry and Dr. Gregory Dumond for their additional input and critique. I’d also like to thank Walter Graupner for sharing his knowledge and expertise on University of Arkansas’ Nu Plasma MC ICP-MS, in addition to Derick Unger, Paul Brooks, and Joshua Gentry from Nyrstar Mining for leading the mine tours and providing the ore samples. I also owe thanks to Travis Garmon for his support and friendship. Lastly, I’d like to thank Western Kentucky University professor, Dr. Andrew Wulff, for lighting the spark and nudging me in the right direction.

Dedication

I dedicate this thesis to Brittanee Morgan Hunt for her constant support, love, and patience throughout the years. I can say with absolution I would not be where I am today if it weren’t for her.

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Introduction

Mississippi Valley Type (MVT) deposits host a large proportion of the Earth's economic lead and zinc. The most abundant minerals in MVT deposits are sphalerite, and galena (zinc and lead, respectively), in addition to barite, fluorite, calcite and dolomite. Often, the MVT deposits occur in *clusters*, forming Pb and Zn ore districts at the margins of sedimentary basins; most districts cover hundreds and in some cases, thousands of square miles (Misra, 1999).

MVT deposits are characterized by low temperature of formation (50°C to 200°C), epigenetic (formed after host) emplacement and stratabound (generally restricted to carbonates). As illustrated in Figure 1 (Robb, 2005), MVT deposits form from diagenetic interactions between the host carbonates and both metal-bearing and sulfur-bearing basinal brines forced into the region by orogenic uplift.

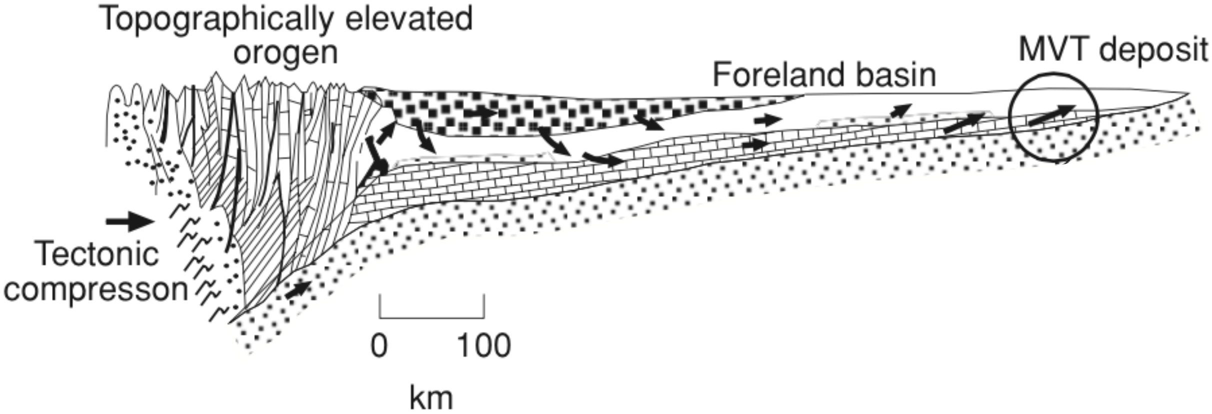

Figure 1: diagram illustrating the concept of hydrological continuity between a compressional orogenic belt and a foreland sedimentary basin through which orogenically and topographically driven fluids flow, and within which MVT Zn-Pb deposits form (Robb, 2005).

MVT Deposits are typically present at shallow depths on flanks of basins, have a relatively simple mineralogy (sphalerite, galena, pyrite, marcasite, dolomite, calcite, and quartz), and are not associated with igneous activity (with the exception of deposits from the Illinois-Kentucky District) (Leach and Sangster, 1993; Sangster, 1995; Misra, 1998; Leach et al., 2001). The global distribution of MVT deposits varies from continent to continent as illustrated in Figure 2 (Leach et al., 2010).

The world's largest MVT districts include Pine Point (Northwest Territories, Canada), the Irish Midlands (Ireland), Upper Silesia (Poland), the Viburnum Trend (also called the New Lead Belt), and Old Lead Belt (United States) and the Upper Mississippi Valley (United States) (Figure 1). Important MVT districts within the United States include the East Tennessee, Central Tennessee, and Tri-State (Kansas, Missouri, and Oklahoma) in addition to the aforementioned Viburnum Trend and Old Lead Belt (Arkansas and Missouri), Upper Mississippi Valley (Illinois, Iowa, and Wisconsin), and the Northern Arkansas Districts (Rakovan, 2006) (Figures 2 & 3).

Relatively little research has been published on MVT deposits specifically those of Central and Eastern TN resulting in a very limited understanding of both the origin of the hydrothermal fluid and of the Pb and Zn. This study is an attempt to contribute to the overall understanding of Central and Eastern TN MVT deposits through use of Pb isotope geochemistry. Since Pb is common in ore deposits, either as primary Pb or as minor/trace elements, Pb isotopes will be used to establish isotopic provinces/ranges for Central and Eastern TN from which the source of the Pb and Zn might be inferred (Kesler, et al., 1994). Lead, zinc, and commonly copper, share similar geochemical behavior in

Figure 2: Global distribution of MVT Lead-Zinc Deposits and Districts (Leach, 2010).

hydrothermal fluids, so measured Pb isotope compositions closely approximate the composition of the mineral and hydrothermal fluid at the time of crystallization (Tosdal, et al., 1999).

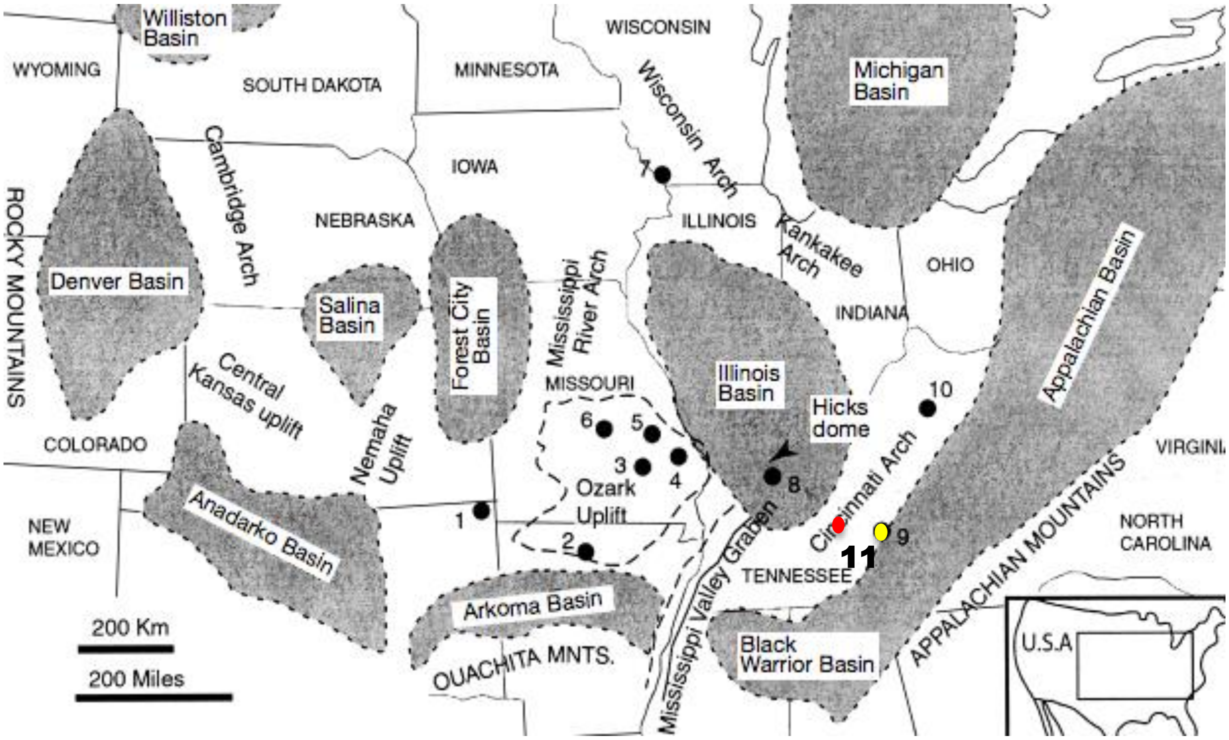

Figure 3: Tri-State District (1); Northern Arkansas Zn District (2); Viburnum Trend, Southeast MO (3); Upper Mississippi Valley District (7); Eastern Tennessee District (9); Central Tennessee District (11) (Modified after Kendrick and Burgess, 2002).

Objectives

The objectives of this study are to:

1) Obtain Pb isotope data from 14 sphalerite (Zn ore) samples collected from the Elwood Mine located in the Central TN District and the Young Mine located in the Mascot-Jefferson City District (East TN)
2) Establish the radiogenic nature of the ore. Are these samples ordinary or do they contain anomalous amounts of Pb similar to “J-type” MVT deposits?
3) Compare Pb isotope ratios from this study to Pb isotope ratios of East and Central TN ratios from previous studies
4) Compare Pb isotope ratios from this study to Pb isotope ratios of other districts in the US from previous studies
5) Establish the source/reservoir of the Pb/Zn abundant in MVT ore in Central and East TN
6) Contribute to the overall understanding of the nature and occurrence of MVT ore in Central and East TN

The Geology of the Central Tennessee District

The Central Tennessee District is comprised of the Gordonsville-Elmwood Mine located approximately 50 miles east of Nashville, TN in the northeastern corner of the Central Basin with the Eastern Highland Rim to the east and the Western Highland Rim to the west (figure 4). Structurally, the Central Basin is a broad anticlinal feature known as the Nashville Dome. Regional dip along the flanks of the dome is gentle (Misra et al., 1996). The burial depth of the Knox Group (zone of ore mineralization) reaches a minimum of about 300ft from the surface at the deeply eroded apex of the dome (Winslow and Hill, 1973).

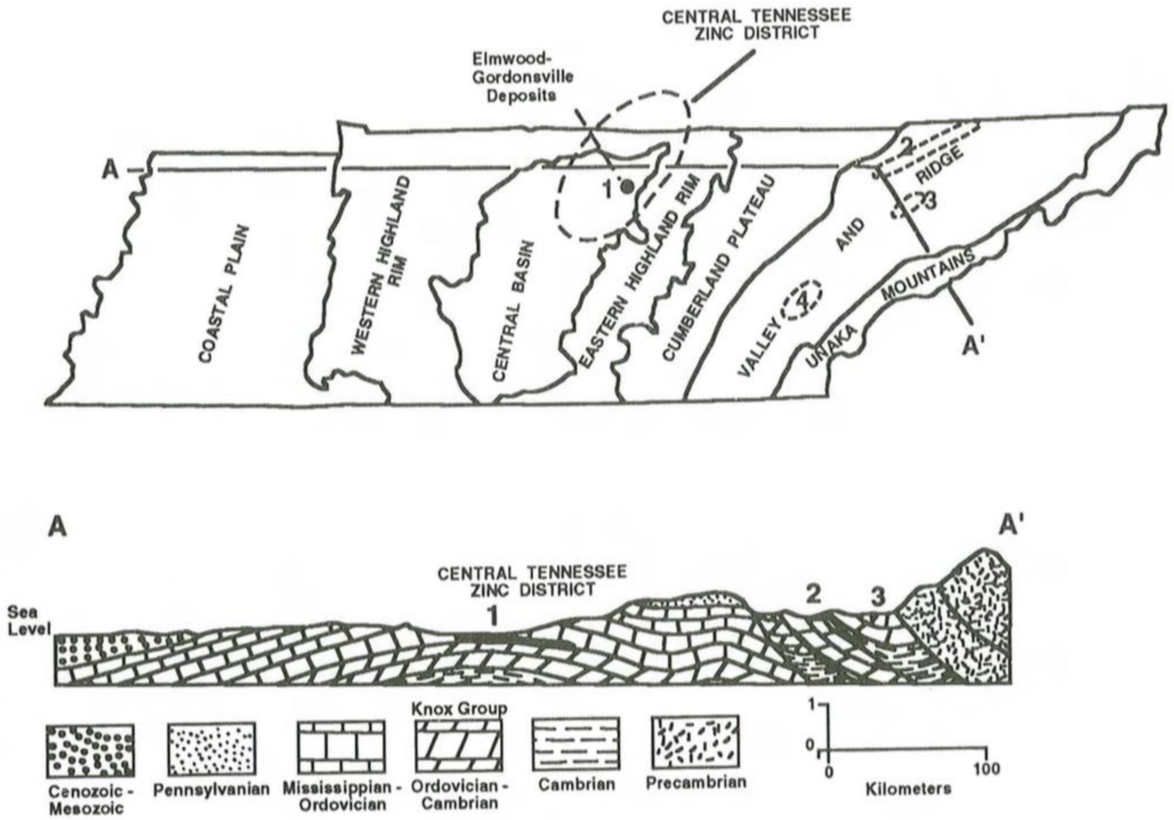

Figure 4: location of mineral districts in the Knox Group relative to major physiographic provinces and geologic structures in Tennessee. The Central Tennessee District (1) is in essentially horizontal strata in the subsurface along the axis of the Cincinnati Arch. The Copper Ridge (2), Mascot-Jefferson City (3), and Sweetwater (4) districts are in inclined strata exposed in the imbricate thrust fault belts of the Valley and Ridge province in East Tennessee. (From Kyle, 1976).

An extensive erosional unconformity separates the Upper Cambrian-Lower Ordovician Knox Group (interpreted as shallow-water marine dolostones) from the overlying Middle Ordovician limestones (deeper-water marine) (Figure 5). Rubble breccias mark paleosinkhole sites and are just below the unconformity and dissolution has been identified at more than 1600ft below the paleokarst surface (Gilbert and Hoagland, 1970). Most ore occurs in altered limestone beds in the lower and middle members of the Mascot Dolomite (uppermost formation in the Knox Group) within dissolution collapse breccias and caverns in a paleoaquifer system that are thought to have developed in the soluble limestone horizons related to karst development on the regional unconformity at the top of the Knox (Gaylord, 1995) (Figure 6).

Where the Mascot dolomite is the principle host to the ore, it is described as light-gray to brown, finely crystalline dolostone interbedded with ~20% limestone that is variably dolomitized and silicified. Many of the dolomites near altered and mineralized areas display reaction rims where sulfides have remobilized around breccia clasts (Gaylord, 1995). Throughout the Central TN District, limestone beds have been partially or completely replaced by dolostone and silica (crypto- and/or microcrystalline quartz). The dolomitization is well developed in areas of previous porosity and permeability enhancement through earlier dissolution activity related to the Knox paleoaquifer system (Gaylord, 1995).

Pb-Zn and S Source/Age of Mineralization

It has been suggested that the Pb and Zn were carried into the region by migrating oil-field brines from the Appalachian Basin (Anderson, 1991; Baird and Dennen, 1985), and that these Pb-Zn bearing oil-field brines and associated hydrocarbons were mobilized by Appalachian orogenies (Anderson, 1991). The source of these fluids likely originated from

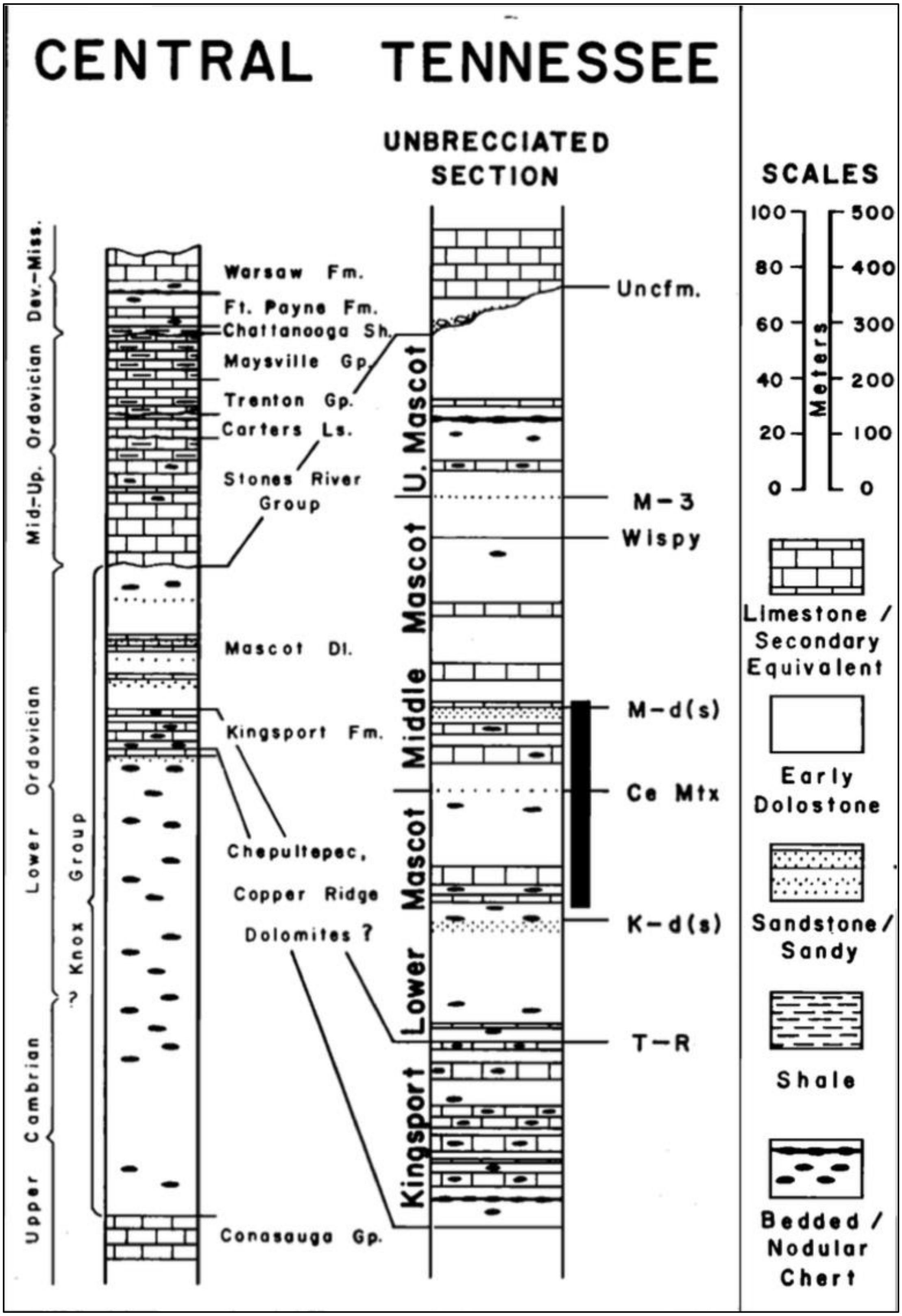

Figure 5: generalized stratigraphic section of the Central Tennessee zinc district (Modified from Crawford and Hoagland, 1968).

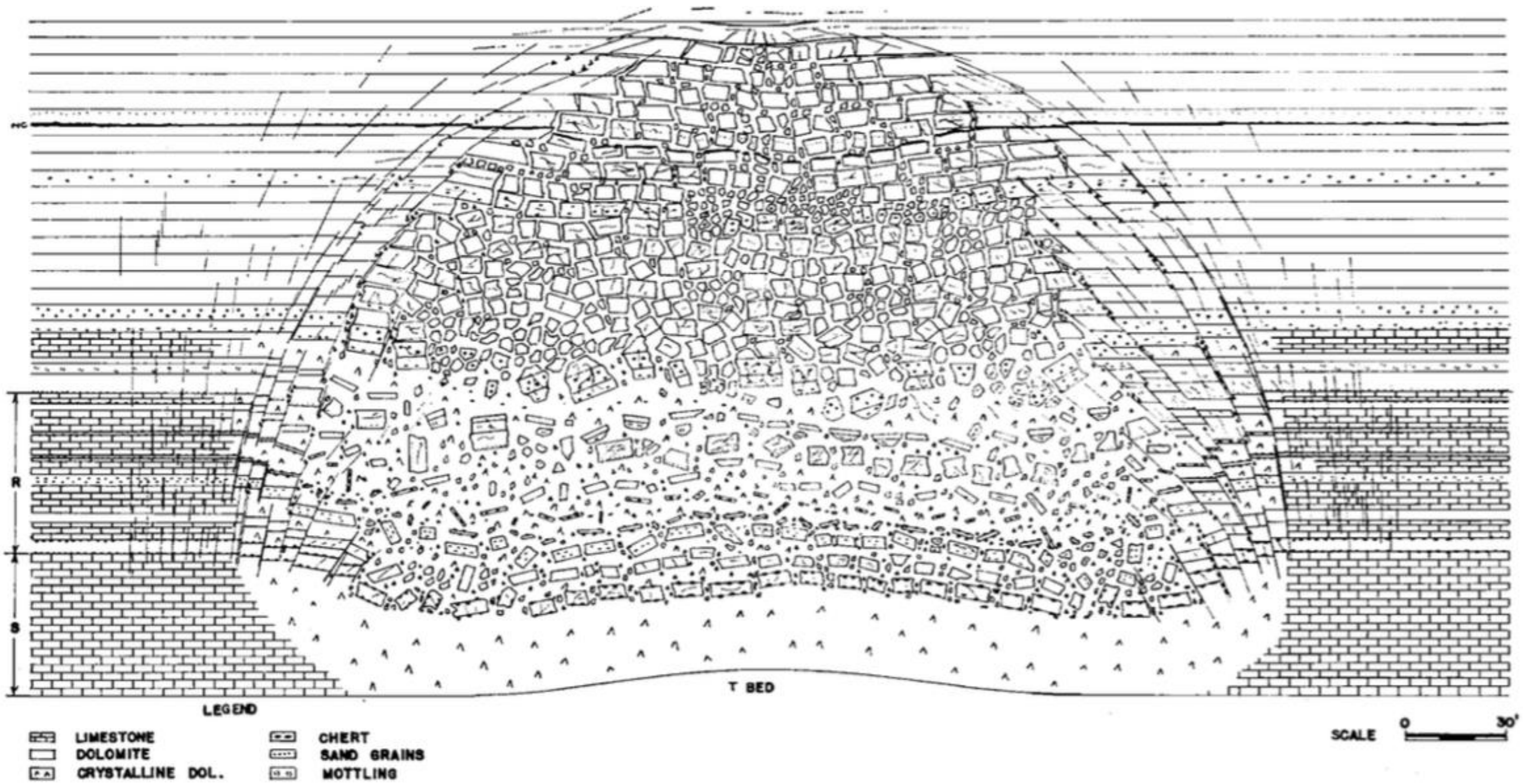

Figure 6: generalized high-domal ore structure depicting collapse structures created through dissolution from paleoaquifer system; common to Central and Eastern Tennessee MVT Districts (from McCormick et al., 1971).

evaporation of seawater or from the dissolution of evaporite minerals, like halite, in the subsurface. Sulfur sources obtained from sulfur isotope studies (Kesler et al., 1994) were ultimately derived from a seawater sulfate and that sulfide precipitation in Central TN involved the mixing of a metal-rich brine with reduced sulfur at the deposition site (Misra et al., 1996). Estimated salinities from fluid inclusion studies (Gratz and Misra, 1983) range from 21-23% weight equivalent NaCl and are similar to modern day oil-field brines.

Exact sources of Pb-Zn in the Central Tennessee District remains somewhat of a mystery but Leach et al. (2005) identified several potential crustal sources for all MVT deposits: basement rocks, weathered regolith, basal sandstones, and carbonate aquifers. Pb-Zn metal concentrations that are contained within the ore fluids/brines commonly transport via metal chloride complexing and are controlled by temperature, pH, and the activity of reduced sulfur (Leach et al., 2005). Misra at al. (1995) suggested the source of Central Tennessee Pb and Zn to at least be more radiogenic than Eastern Tennessee, as well as homogenous, suggesting a well mixed source, potentially from a young nearby sedimentary basin.

Based on field observations of Kyle (1976), the age of mineralization occurred in the Lower Mississippian. Paleomagnetic studies by Lewchuk and Symons (1993) suggested an age of MVT mineralization to be Late Permian and to have lasted an estimated 8 million years, suggesting strong correlation with the Alleghenian-Ouachita Orogeny (Lewchuk and Symons, 1995). Brannon et al. (1995) suggested an age of 260±42 million years for the main-stage calcite growth using Th-Pb age dating, and 35±14 million years for late-stage calcite using ^{238}U-^{206}Pb dating.

The Geology of the Eastern Tennessee District

The East Tennessee District is composed of the Mascot-Jefferson City, Copper Ridge, Embreeville, and Powell River areas; the major being Mascot-Jefferson City which is located approximately 20 miles northeast of Knoxville, TN. The Young Mine is located within the Mascot-Jefferson City district and in the central part of the valley of the Appalachian Valley and Ridge Province (Figure 4). The dominant structure of the valley is a series of sub-parallel sheets or belts of rocks, thrust up on southeast dipping faults. The Appalachian Plateau bounds the Valley and Ridge Province to the northwest and is comprised of a thick Paleozoic sequence which has been disrupted by a series of NE-SW-trending thrusts presumably during the Alleghenian Orogeny (Hatcher and Odom, 1980).

Locally, the Young Mine is located on top of a dome structure known as Hodges dome that has been displaced on the north flank by a high-angle, post-ore reverse fault with approximately 100ft of vertical displacement. This dome is situated between two low angle thrust faults knows as the Bays Mountain to the south and the Mill Spring to the north, both of which are thought to have occurred during the Appalachian Orogeny (McCormick et al., 1969).

The Kingsport and Mascot formations host the majority of the ore and were deposited in marine peritidal environments on a stable continental shelf (Churnet et al., 1982). Upward bending of the shelf from attempted subduction of the North American craton beneath volcanic arcs to the east (Shanmugam and Lash, 1982) resulted in the regionally extensive unconformity (post-Knox unconformity) that separates the Chicamauga Group (Middle Ordovician) from the upper part of the Knox Group (Lower Ordovician) (Harris, 1971) (Figure 7). Almost all pre-Chicamauga carbonates contain varying amounts of ore but the vast majority occurs within the Lower Ordovician Kingsport and Mascot formations. The ore-bearing structures are similar to that of Central Tennessee and are related to extensive dissolution and alteration of host carbonates through a paleoaquifer system. This volume loss due to dissolution of limestone resulted in re-crystalline dolomite that ultimately fractured and collapsed from overlying weight, forming collapse-breccia structures (Figure 6). Generally, these structures are irregular in shape and can range up to 900ft wide, 1,500ft long, and 100ft high (McCormick et al., 1969).

The host rock consists of one of two types of dolostone: fine-grained and medium- to coarse-grained. The fine-grained dolostone occurs as regionally persistent beds, indicative of primary or sedimentary origin. The medium- to coarse-grained dolostone formed through replacement, like much of Central Tennessee. Where ore exists in medium- to coarse-grained dolostone, the dolomitization must have occurred prior to cessation of sphalerite mineralization, because sphalerite partially replaced dolomite rhombs in dolomitized limestone (Matlock and Misra, 1992). An accepted general paragenetic sequence for the ore deposition in the Young mine is as follows: deposition of the Kingsport and Mascot formations; emergence of the Upper Knox (unconformity); karstification along the erosional surface; dolomitization and dissolution of limestones (alteration and solution resulting in loss of volume and ultimately formation of collapse breccias); multi-solution hydrothermal influx from a nearby basin resulting in deposition of ore; folding and thrust faulting from Appalachian Orogeny; erosion and exposure (Rasnick et al., 1992).

Pb-Zn and S Source/Age of Mineralization

Bachtadse et al. (1987) suggested through paleomagnetism that mineralization was Pennsylvanian in age. Kesler et al. (1988) proposed through use of Sr isotope ratios that the

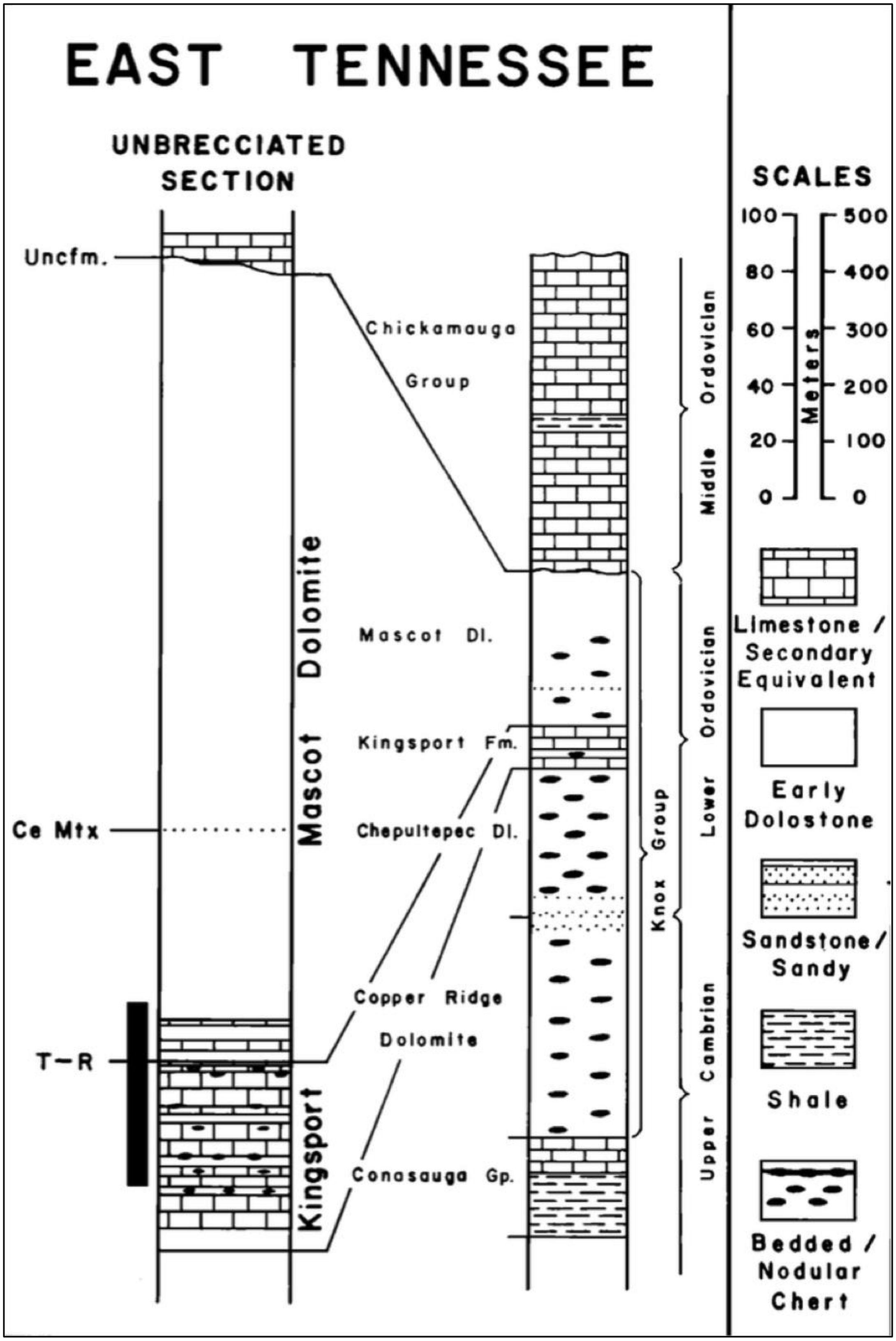

Figure 7: generalized stratigraphic section of the East Tennessee zinc district (Modified from Crawford and Hoagland, 1968).

the age of was 405±32 million years ago and occurred during the Alleghenian Orogeny. However, later studies by Nakai et al. (1990, 1993) suggested an earlier age of 347 million years ago and then 377±29 million years ago respectively, using Rb-Sr dating of the main-stage sphalerite. Nakai et al. (1990) suggested the hydrothermal fluids associated with the ore mineralization were expelled during thrusting through the Acadian Orogeny. Misra (1992) however doubted Nakai’s interpretation since thered was little evidence of the Acadian orogeny in the southern Appalachian Valley and Ridge Province.

Noble (1963) proposed the MVT deposits were formed from an expulsion of Pb-Zn rich fluid from the compaction of thick argillaceous sediments in adjacent basins, specifically the Appalachian basin adjacent to both East and Central TN districts. This thick sequence of shales compacted vast volumes of brines rich in metals that ultimately made its way into the Knox Group carbonates (Hoagland, 1976). Kesler (1988) used Sr isotope ratios to determine that the Ordovician Sevier basin and underlying Cambrian and Lower Ordovician sediments were a potential source for mineralizing fluids. Fluid inclusion studies suggest MVT deposits from East Tennessee formed from moderately hot (100° to 180°C) and highly saline brines (17 to 22% weight equivalent NaCl) indicating a disassociation with magmatic activity and that likely, the ore fluids were instead deep basinal and re-circulated meteoric water (Roedder, 1971).

Sulfur isotope studies by Jones et al. (1990) suggest seawater sulfate as the sulfur source, initially derived from evaporites or brines of Precambrian and early Cambrian age. Kesler et al. (1994) suggested through use of Pb isotope ratios that the most likely source of Pb originated from the North American Craton to the west, the Blue Ridge massif (which is exposed immediately adjacent to the Eastern Tennessee district), or sediment derived from the Mount Rogers formation.

Table 1 below is a compilation from a number of studies comparing Central and East Tennessee MVT districts from Misra et al. (1996) and references therein.

Table 1: Comparison of the Central Tennessee (Elmwood-Gordonsville) and East Tennessee (Mascot-Jefferson City) Mississippi Valley-Type zinc districts (Modified from Misra et al., 1996).

	Central Tennessee (Elmwood-Gordonsville Mines)	**East Tennessee (Mascot-Jefferson City District)**
Main Ore Interval	Upper Knox Group (Lower Ordovician) - middle member of the Mascot Dolomite	Upper Knox Group (Lower Ordovician) - Kingsport Formation and lowermost part of the Mascot Dolomite
Nature of Mineralization	Open-space filling chemical precipitates in strata-bound late mineral-matrix breccias at the peripheral parts of collapse breccia bodies; minor mineralization in semiconcordant dissoulution caverns and vugs in dolomitized limestone horizons, commonly with large euhedral crystals Abundant unfilled open space Early fine rock-matrix breccia is essentially unmineralized	Open-space filling chemical precipitates in strata-bound late mineral-matrix breccias at the peripheral parts of collapse breccia bodies; important cavity-filling and replacement mineralization in "bedded-ore structures" (strata-bound mantos) in dolomitized limestone horizons Rare unfilled open space Early fine rock-matrix breccia is essentially unmineralized
Ore-gangue mineralogy *Ore min.*	Low-Fe sphalerite	Low-Fe sphalerite
Main gangue min.	Sparry calcite	Sparry dolomite
Minor min.	Quartz, fluorite, barite, galena, dolomite	Quartz, pyrite/marcasite, calcite
Trace min.	Pyrite/marcasite, enargite, celestite	Fluorite, galena, chalcopyrite, anhydrite
Sphalerite composition	Fe (wt %) = 0.14 - 0.54 Cd (wt %) = <0.1 - 0.76 Relatively high Ge and Ga (~300 and ~600 ppm respectively; Hoagland, 1976)	Fe (wt %) = 0.03 - 0.48 Cd (wt %) = 0.10 - 0.79 Relatively low Ge and Ga (~80 and ~5 ppm respectively; Hoagland, 1976)

Table 1: Comparison of the Central Tennessee (Elmwood-Gordonsville) and East Tennessee (Mascot-Jefferson City) Mississippi Valley-Type zinc districts (Modified from Misra et al., 1996) (Cont.).

Fluid inclusion data	Misra and Gratz (1988); Misra and Lu (1992)	Taylor et al., (1983)
Main-stage min.	Sphalerite	Sphalerite
	Th = 93° - 153°C (Mean = 115±11°C)	Th = 90° - 200° C (Mean = 138°C)
	Tm = -24° - -14°C (Mean = -20.3°±3.1°C)	Tm = -8° - -40°C (Mean = -20°C)
Late-stage min.	Amber (to clear) calcite	Vug-fill fluorite
	Th = 59° - 116°C (Mean = 92±13°C)	Th = 114° - 116°C (Mean = 115±0.7°C)
	Tm = -20° - -2°C (Mean = -6.8±4.0°C)	Tm = -7.5° - -10°C (Mean = -9.3°±0.7°C)
S isotope ratios	Kesler et al. (1994); Misra and Torssander (1995) (Figure 9)	Jones (1993)
	δ^{34} (sulfides) = -8.44 - -0.4 permil	δ^{34} (sulfides) = 27.6 - 36.1 permil
	δ^{34} (barite) = 27.42 - 32.8 permil	
Pb isotope ratios	Galena	Sulfides (Kesler et al., 1994)
	206/204 = 19.603 - 19.697	206/204 = 19.378 - 19.469
	207/204 = 15.742 - 15.805	207/204 = 15.721 - 15.730
	208/204 = 39.292 - 39.474	208/204 = 39.441 - 39.538
Ore fluids and ore-stage precipitation	Mixing of metal-bearing basinal brines with H_2S derived from oil or other organic matter (Kesler et al., 1994c; this study)	Mixing of metal-bearing basinal brines with H_2S derived by thermochemical reduction of sulfate (Jones, 1993)
	Salinity of mineralizing fluids by dissolution of evaporite (Kesler et al., 1995)	Salinity of mineralizing fluids by seawater evaporation (Kesler et al., 1995)
Age of min.	Lower Mississippian (Field data; Kyle, 1976)	Pennsylvanian (Paleomagnetic; Bachtadse et al., 1987))
	Late Permian (Paleomagnetic; Lewchuk and Symons, 1993)	405±320 Ma (Rb-Sr; Kesler et al. 1988)
Age of min. (Cont)	260±42 Ma for main-stage calcite (Th-Pb; Brannon et al. 1995a)	377±29 Ma (Rb-Sr isochron for main-stage sphalerite; Nakai et al., 1990)
	35±14 Ma for late stage calcite (^{238}U-^{206}Pb method; Brannon et al, 1995a)	347±20 Ma (Rb-Sr isochron for main-stage sphalerite; Nakai et al. 1993)

Table 1: Comparison of the Central Tennessee (Elmwood-Gordonsville) and East Tennessee (Mascot-Jefferson City) Mississippi Valley-Type zinc districts (Modified from Misra et al., 1996) (Cont.).		
General ref.	Kyle (1976), Gaylord and Briskey (1983), Briskey et al. (1986), Gratz and Misra (1987)	Crawford and Hoagland (1968), Misra et al., (1983), Misra and Fulweiler (1995)

Why Pb Isotopes?

There are 4 stable isotopes of lead: ^{204}Pb, ^{206}Pb, ^{207}Pb, and ^{208}Pb. Of those, only ^{204}Pb is non-radiogenic and not the product of radioactive decay. The other three isotopes are the final products of three decay chains from uranium (U) and thorium (Th) and can be illustrated as follows:

$$^{238}\text{U} \rightarrow {}^{206}\text{Pb};\ {}^{235}\text{U} \rightarrow {}^{207}\text{Pb};\ {}^{232}\text{Th} \rightarrow {}^{208}\text{Pb}$$

The true decay chains of ^{206}Pb, ^{207}Pb, and ^{208}Pb are in fact much more complex, but usually ignored since each is short-lived. The overall abundances of daughter products of decay have grown throughout the 4.6 billion years of the Earth's existence (Figure 8).

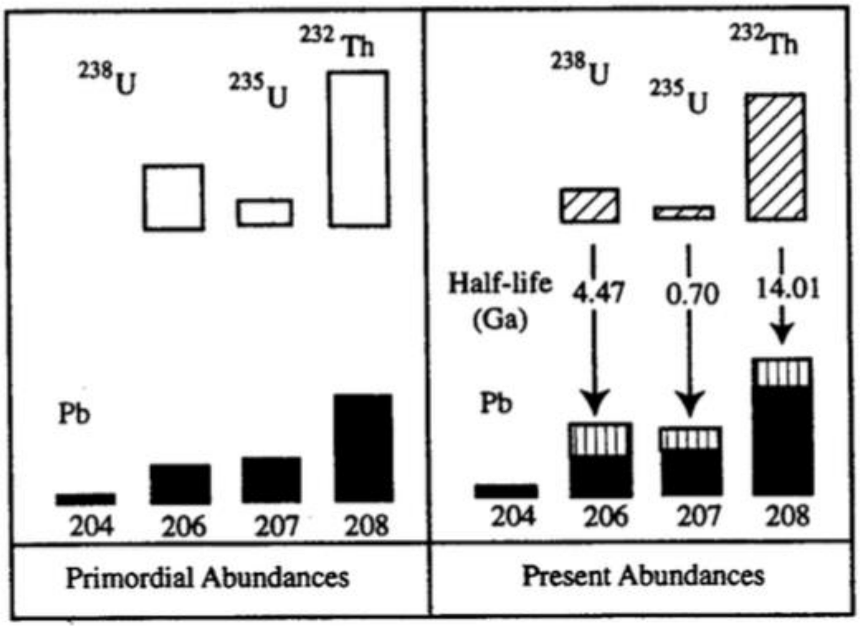

Figure 8: Relative primordial and present-day abundance of the isotopes of uranium (U), thorium (Th), and lead (Pb) showing half-lives in billion of years (Ga). Modified from Cannon et al. (1961) and Gulson (1986).

Time-integrated growth of Pb isotopes from a starting time of t_0, to an ending time of t_1, in a setting where no U, Th, and their daughter products have migrated can be described by the following equations:

$$({}^{206}Pb/{}^{204}Pb)t_1 = ({}^{206}Pb/{}^{204}Pb)t_0 + ({}^{238}U/{}^{204}Pb)(e^{\lambda t0} - e^{\lambda t1})$$

$$({}^{207}Pb/{}^{204}Pb)t_1 = ({}^{207}Pb/{}^{204}Pb)t_0 + ({}^{235}U/{}^{204}Pb)(e^{\lambda' t0} - e^{\lambda' t1})$$

$$({}^{208}Pb/{}^{204}Pb)t_1 = ({}^{208}Pb/{}^{204}Pb)t_0 + ({}^{232}Th/{}^{204}Pb)(e^{\lambda'' t0} - e^{\lambda'' t1})$$

where λ, λ’, and λ’’ are the decay constants of ^{238}U, ^{235}U, and ^{232}Th respectively. These constants and symbols are compiled in Table 2 for reference.

Symbol	Value	Explanation
λ	0.155125×10^{-9}/a	Decay constant of ^{238}U
$t^{1/2}$	4.47 Ga	Half-life of ^{238}U
λ'	0.98485×10^{-9}/a	Decay constant of ^{235}U
$t^{1/2}$	0.70 Ga	Half-life of ^{235}U
λ''	0.49475×10^{-9}/a	Decay constant of ^{232}Th
$t^{1/2}$	14.01 Ga	Half-life of ^{232}Th
μ	Variable	^{232}U/^{204}Pb
κ	Variable	^{232}Th/^{238}U

Table 2: constants and symbols critical to Pb Isotope Geochemistry (From Tosdal et al., 1999).

These equations show measured present-day Pb compositions are equal to the sum of the initial Pb compositions plus the radiogenic compositions added over time. Because ^{204}Pb is stable and fixed, and because the abundances of ^{206}Pb, ^{207}Pb, and ^{208}Pb change over time, Pb isotope data is examined as the ratio of ^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb, and ^{208}Pb/^{204}Pb (Tosdal et al., 1999). Common or ordinary Pb as described by Doe (1970) is Pb that has a low U/Pb and/or Th/Pb ratio in which no significant radiogenic lead has been generated in place, generally with a ^{206}Pb/^{204}Pb ratio less than 20. Because of the long-lived isotopes of U, and that each U parent decays into two separate Pb daughters, a time control is created. This time control occurs because at the time when Pb is isolated from U, the composition becomes a function of the U/Pb ratios of the sources and the respective resident times of the Pb in the sources. With different sources (the mantle, lower, and upper crust), each has a distinct U/Pb ratio, of which the isotopic composition of Pb reflects a particular source (Köppel and Saager, 1976)

The half-life of ^{235}U is 0.70 Ga where the half-life of ^{238}U is 4.47 Ga. During the earth's early history, the abundance of ^{207}Pb increased more rapidly than ^{206}Pb. The rate of ^{207}Pb growth diminishes with time as the parent, ^{238}U disappears. As result, ^{207}Pb growth over the last billion years has been negligible (Doe, 1970; Tosdal; 1999) (Figure 9).

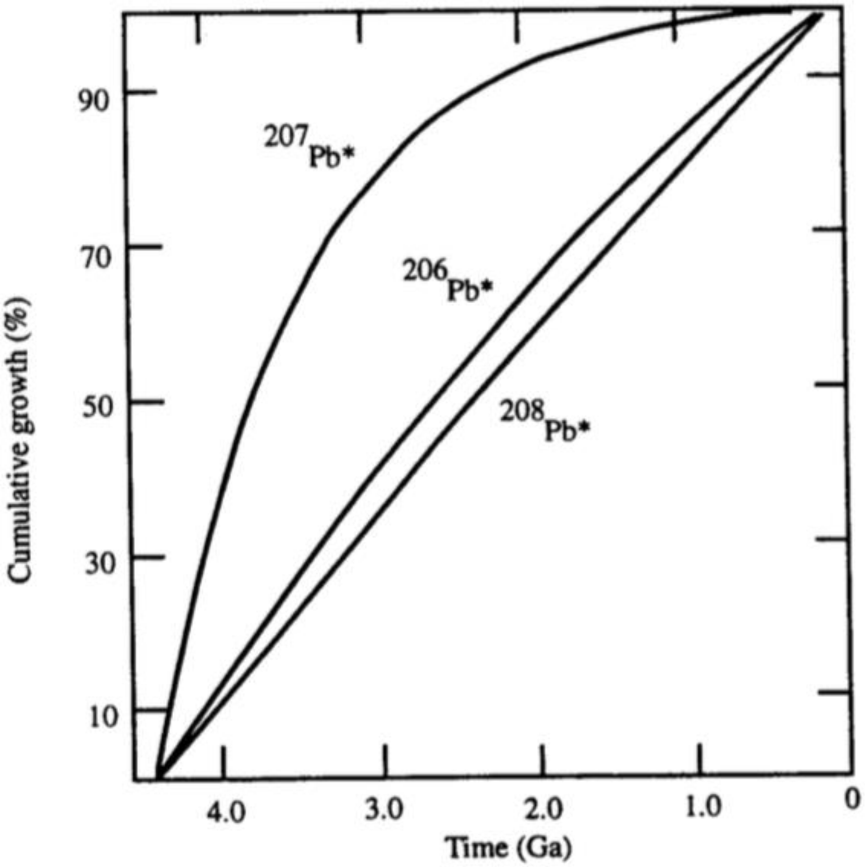

Figure 9: Growth of radiogenic Pb with time showing the rapid increase in ^{207}Pb in the early history of the earth because of the relative short half-life of ^{235}U (700 m.y.) followed by only limited growth in ^{207}Pb in the last 1 billion years (Ga). The limited growth of ^{207}Pb results from the fact that most ^{235}U has already decayed, and only a small fraction of the original primordial abundance is still present. Modified from Gariepy and Dupre (1991).

In order to understand Pb isotopic variations, two parameters, U/Pb and Th/U ratios are important, as a basic understanding of U, Th, and Pb geochemical properties (Faure, 1977). Both

U and Th have comparable geochemical properties. They act together and can substitute for each other in compounds. During partial melting and fractional crystallization, U and Th are concentrated in the liquid phase. In contact with aqueous fluid, however, Th is insoluble (Taylor and McLennan, 1985). Uranium, when present in oxidizing conditions, forms uranyl ions that are extremely soluble in aqueous fluids, and when in these conditions, can be significantly fractionated from Th. Lead is soluble at moderate to high temperatures often associated with hydrothermal, magmatic, or metamorphic environments. At low temperatures, however, it is generally not soluble and associated with organic matter. Lead is also a larger ion than either of its parents, U and Th, and will behave differently as a result during partial melting and/or metamorphism. The contrasting geochemical behavior of U, Th, and Pb is recorded in the Th/U (κ or ^{232}Th/^{238}U) and U/Pb (μ or ^{238}U/^{204}Pb), which can be directly measured as elemental concentrations, calculated using modern parameters, or inferred from Pb data (Tosdal et al., 1999) (Table 3).

	Bulk Earth	Depleted Mantle	Continental Crust
U (ppb)	21	3.5	1,200
Th (ppb)	88	8.5	5,800
Pb (ppb)	170	50	8,600
^{238}U/^{204}Pb	9.1	4.7-5.9	10.6-10.8
^{232}Th/^{238}U	4.2	2.3-2.5	4.6-4.7

Table 3: Present-day U-Th-Pb compositions of the Crust-Mantle system (modified from Allegre et al., 1988; Gariepy and Dupre, 1991).

Doe and Zartman (1979) developed the “plumbotectonics” model in which they formed a hypothetical model of the evolution of Pb on earth. This model consisted of three different Pb sources: the upper crust, lower crust and the mantle. They modeled orogenies at 400 million-year intervals based on evidence that continental accretion started around 4 billion years ago. During each orogenic event, portions of each of the sources (upper crust, lower crust and mantle) were converted into new upper and lower crust. Initially, all crustal material originated from the mantle. After, both the mantle and older crust contributed in the generation of newer crust through orogenic events. During each orogeny, Pb, U, and Th are extracted from the upper and lower crust, and mantle sources and chemically mixed and redistributed into newly formed upper and lower crust and some recycled in the mantle. The "plumbotectonics" model curves for each of the major sources were derived empirically and presented on two covariation diagrams: the Thorogenic diagram (Figure 10.A) which plots $^{208}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ or the radiogenic daughter of Th versus the radiogenic daughter of the most abundant U isotope and the Uranogenic diagram (Figure 10.B) which plots $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$, or the least abundant isotope of U versus the most abundant.

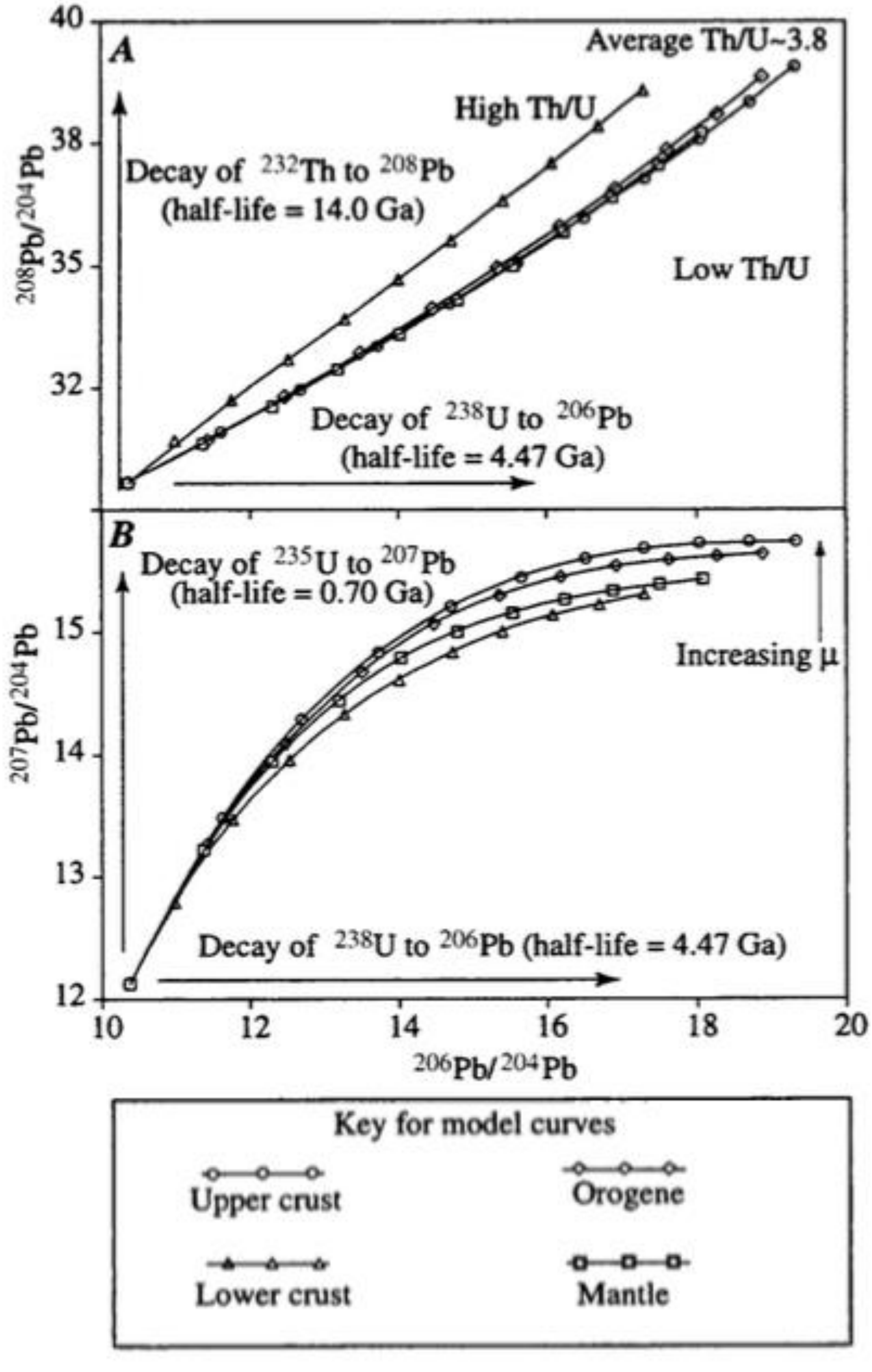

Figure 10: Thorogenic (A) and uranogenic (B) Pb isotope diagrams showing the plumbotectonic curves of Zartman and Doe (1981). Relative values of Th/U (κ or ^{232}Th/^{238}U) and U/Pb (μ or ^{238}U/^{204}Pb) are shown. Arrows denote radioactive decay of the parent U and Th isotopes to the respective daughter isotopes of Pb. Tick marks on curves represent 500 million years of growth (From Tosdal et al., 1999).

Since Pb is commonly found in ore deposits like galena and sphalerite in economic or trace amounts, Pb isotopes can more accurately be detected to as few as 1 part per billion (ppb) through improvement and development of more sensitive instrumentation (Billström, 2008). Because the concentrations of U with respect to Pb is low in ore minerals, growth in the Pb composition is minimal to negligible for minerals formed in the Phanerozoic, approximately 540 million years ago to present. For this reason, assuming a closed system, measured Pb isotopic composition approximates the composition of the mineral and fluid at the time of crystallization. For older minerals in Proterozoic and Archean, there has been enough time for sufficient growth of Pb through decay. In this instance, those minerals would need to be time-corrected to obtain initial concentrations (Tosdal et al., 1999).

Pb can also be used to determine the source of associated metals such as Zn, Cu, Au, and Ag but is limited by the assumption that the Pb was derived from the same source, transported, and the deposited by the same hydrothermal fluid (Tosdal et al., 1999). However, since Pb, Zn, and Cu have comparable geochemical behavior, this assumption is most likely true, particularly in base metal-rich magmatic hydrothermal systems, or Pb-rich deposits in sedimentary settings (Henley et al., 1984).

Historically, Pb type has been defined based on the ratios of $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, and $^{208}Pb/^{204}Pb$. Heyl (1974) initially summarized that there were two distinct types of lead: common or “ordinary” Pb that followed the hypothetical evolution of Pb through time, as related to the plumbotectonic model as described by Doe and Zartman (1979) and anomalous Pb. Common Pb is presumed to have a homogenous source from the mantle or lower crust through mixing of the upper crustal leads (Gaylord, 1992) and follows the hypothetical evolution of Pb. Anomalous Pb is Pb with isotopic ratios considerably different from ordinary Pb and likely the result of preferential concentration of radiogenic lead over a long period of time or a consequence of the mixing of radiogenic Pb and common Pb during a much shorter time (Gaylord, 1992).

Two growth curves are used in this study: the Stacy and Kramers (1975) average crustal growth curve and the Zartman and Doe (1981) orogene growth curve. Each of these curves represents Pb-isotope compositions of continental crust, mantle, and orogene based on U/Pb and Th/U ratios. Stacy and Kramers (1975) is based on two stages of evolution of Pb within the continental crust. The first stage begins 4.57 Ga ago with primordial isotope ratios that were recorded in troilite of an iron meteorite in Devils Canyon. (Tatsumoto et al., 1973). The second stage starts at 3.7 Ga and represents geochemical differentiation of the first reservoir (Table 4). The growth curves from Stacy and Kramers (1975) and Zartman and Doe (1981) are established through use of the equations described previously in this section where λ, λ’, and λ’’ are the decay constants of ^{238}U, ^{235}U, and ^{232}Th respectively; t_0 corresponds to the starting time of growth; t_1 corresponds to the ending time of growth; (^{206}Pb/^{204}Pb)t_1, (^{207}Pb/^{204}Pb)t_1, and (^{208}Pb/^{204}Pb)t_1 are the ratios at t_1; and (^{206}Pb/^{204}Pb)t_0, (^{206}Pb/^{204}Pb)t_0, and (^{206}Pb/^{204}Pb)t_0 are the initial ratios.

S&K (1975)	Time (b.y.)	^{206}Pb/^{204}Pb	^{207}Pb/^{204}Pb	^{208}Pb/^{204}Pb
Start 1st stage	4.6	9.307	10.294	29.487
Start 2nd Stage	3.7	11.152	12.998	31.210
Present Day	0.0	18.700	15.628	38.630

Table 4: Two-stage parameters for average Pb from continental crust (Stacy and Kramers, 1975).

Zartman and Doe (1981) begins at 4 Ga ago and continuously evolves throughout the earth’s history to present day (Table 5) (Tosdal et al., 1999).

Z&D (1981)	Time (b.y.)	^{206}Pb/^{204}Pb	^{207}Pb/^{204}Pb	^{208}Pb/^{204}Pb
Start	4.0	10.320	12.120	30.560
Present Day	0.0	18.890	15.610	38.810

Table 5: Single-stage or continuous parameters for average Pb from the orogene (Zartman and Doe, 1981).

Previous Investigations of Pb Isotopes Used In MVT Studies

Cannon et al. (1961) provided one of the first pioneering compilations of published and unpublished Pb isotope data on nearly 1,300 Pb samples from a number of academic and government sources from around the world. The main objective was to measure and study the variations of Pb, and from those variations, interpret the geologic environments in which the sample of Pb has evolved. They developed their analyses to be plotted on triangular diagrams where ^{206}Pb + ^{207}Pb + ^{208}Pb = 100 rather than the modern practice of using ratios of ^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb, and ^{208}Pb/^{204}Pb because methods were not precise to measure such low amounts of the invariant ^{204}Pb isotope.

Cannon et al. (1961) raised several questions in the investigations into Pb isotopes. From where did the ore originate? Was the Pb originally from a crustal source or much deeper in the mantle? When was the ore deposited and how long did mineralization progress? Cannon et al. (1961) established several variables that play into the hypothetical evolution of Pb throughout earth's history: the original amounts of Pb, Th, and U in the local environment, the time-span for which radioactive decay has occurred, the isotopic composition of Pb, and the geologic processes that have contributed to modern day Pb concentrations.

Several commonalities arose in Cannon et al. (1961). They established 4 classes of Pb types based on similar isotopic ratios: *ordinary lead, U-lead, Th-lead,* and *J-lead.* 83% of samples were considered *ordinary lead,* as these samples followed the hypothetical model of the evolution of lead through earth's history and had a ratio of ^{206}Pb/^{204}Pb less than 20. *Th-lead* is slightly enriched in ^{208}Pb relative to ordinary leads and *U-lead* is slightly enriched in ^{206}Pb and ^{207}Pb relative to ordinary leads. *J-leads,* or "Joplin type" leads (as first described by Nier (1938)) are considered exceptional leads because of their enriched abundances of radiogenic isotopes relative to *ordinary lead*. These leads do not follow the hypothetical model of lead evolution, and imply “impossible” Pb ratios. For that reason, J-leads have since attracted considerable attention and research due to their anomalous and mysterious nature.

Several genetic implications were derived from the compilation of the Pb isotope data. The simplest concept was that the original crustal source remained virtually a closed system and was unaltered by geochemical change through time, except for generating minor quantities of ore. Other hypotheses from Cannon et al. (1961) suggested that igneous and metamorphic processes geochemically mixed the radiogenic Pb with ordinary lead, disrupting the natural or hypothetical model of U and Th decay into Pb, producing the variability of Pb ratios that are were detected, and that all ratios were a reflection of either a closed system or an open system where sources of Pb were allowed to mix.

Heyl et al. (1966) conducted a regional study of the Pb isotopes of galena from the Upper Mississippi Valley, the Illinois-Kentucky, and the Appalachian Valley (East TN) districts. A total of 7 galena samples were collected (only two occurring in the East TN; the other five from New Jersey and Pennsylvania) and analyzed to determine their range in isotopic composition. The galenas from East TN were somewhat more radiogenic than those from the northern Appalachians (NJ and PA) showing slight enrichments in ^{206}Pb/^{204}Pb and ^{208}Pb/^{204}Pb. All the leads analyzed from the Appalachian Zn and Pb deposits were notably different in isotopic composition from those in the major Mississippi Valley districts. They concluded that the features of the deposits in the folded Appalachians are similar in many respects to those in the Mississippi Valley, but the Pb isotopic compositions suggest that at least the galenas have had a different origin than the J-Type leads of the Mississippi Valley, and they may be unrelated genetically (Heyl, et al., 1966).

Cannon and Pierce (1969) established that Pb in stratiform lead-zinc deposits were found to vary notably in isotopic composition, and those variations could be used as guideposts for geologists in search of major lead/zinc deposits. They noted that most deposits in the eastern hemisphere contained ordinary Pb of reasonable model age. In the western hemisphere however, particularly in the Mississippi Valley, the deposits contained the aforementioned J-Lead, which were relatively enriched in radiogenic ^{206}Pb, ^{207}Pb, and ^{208}Pb (Cannon and Pierce, 1969).

Nearly 10% of their analyzed samples fell within the “J-Lead” zone beyond the zero end of the best-fit curve (Figures 11-13). Most of those samples represented galenas from the major lead-zinc districts of the Mississippi Valley. Figure 11 shows the 3 distinct types of Pb ratios plotted in terms of ^{206}Pb + ^{207}Pb + ^{208}Pb = 100. Figure 12 is an enlargement of the small triangle found in the lower right side of figure 11 and illustrates the distribution of Pb isotopes of samples relative to the ordinary Pb evolution line. Figure 13 is an enlargement of the upper half of Figure 12, illustrating the majority of analyzed samples fell within the “J-lead” or anomalous range, and notably, samples from East TN were among the least radiogenic that plotted beyond the 0 m.y. age (Cannon and Pierce, 1969).

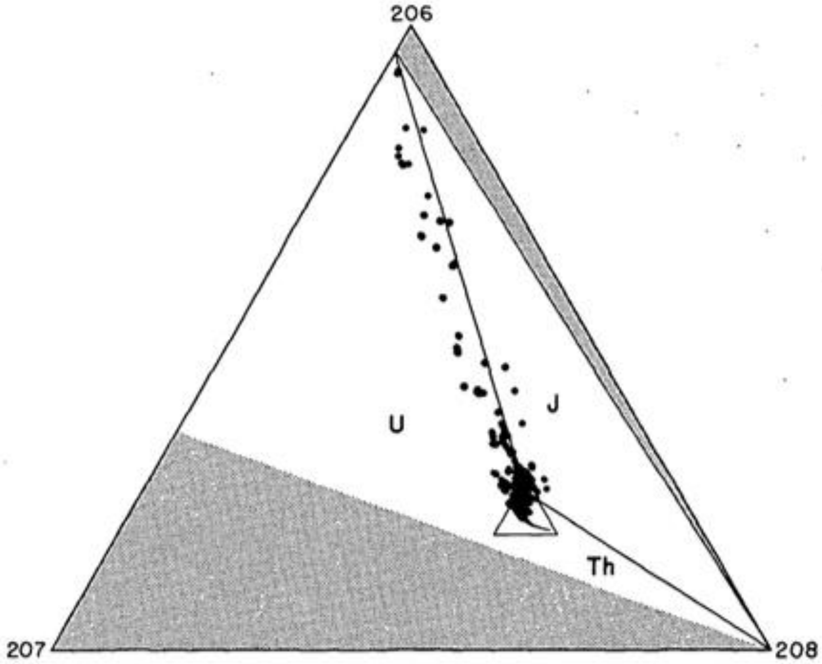

Figure 11: isotopic composition of Pb from 1,280 Pb ore minerals – plotted in terms of ^{206}Pb + ^{207}Pb + ^{208}Pb = 100. (Cannon et al., 1961).

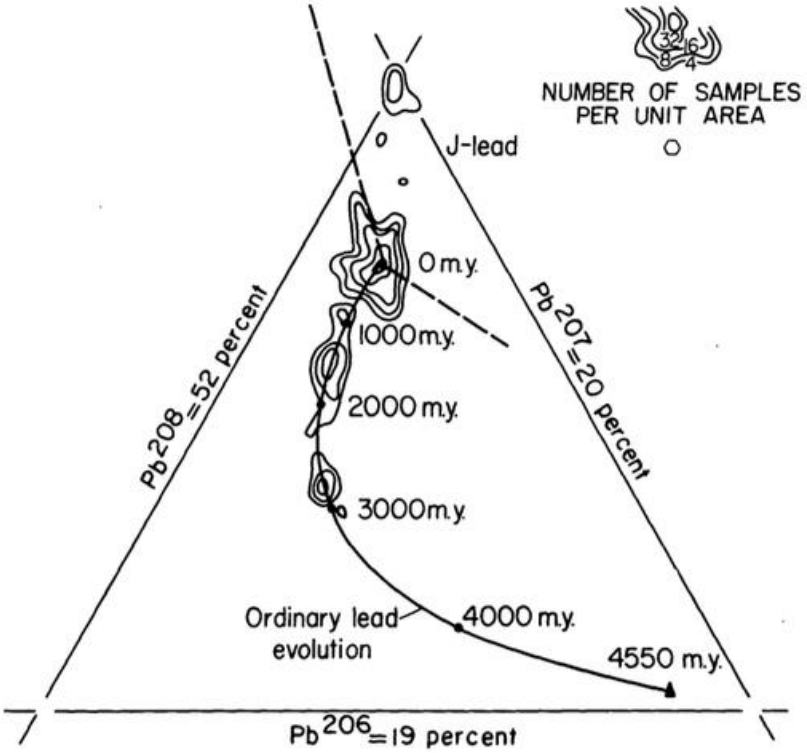

Figure 12: frequency distribution of Pb isotope analyses of worldwide ore-leads. Enlargement of triangle from figure 11 (Cannon and Pierce, 1967).

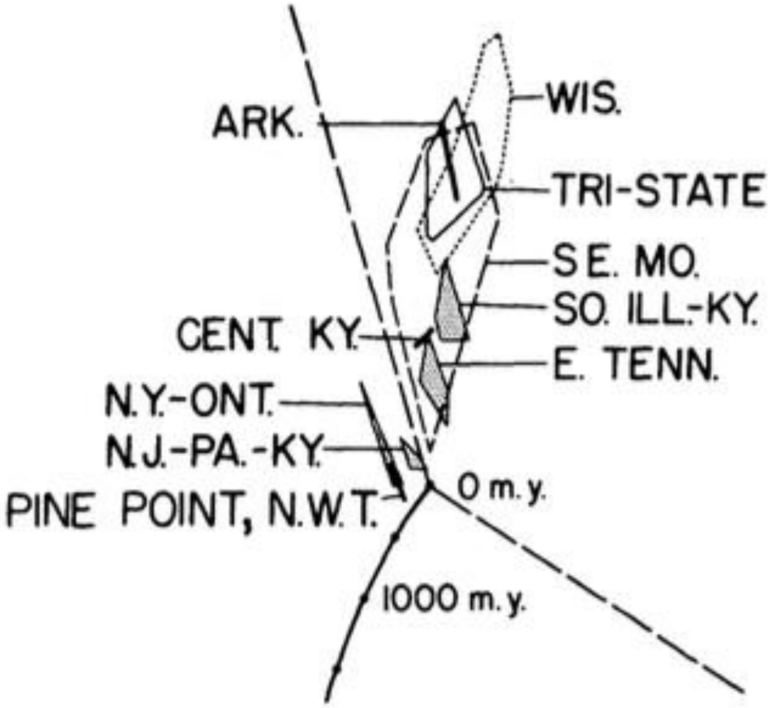

Figure 13: ore-leads in Phanerozoic stratiform lead-zinc deposits of North America (Cannon and Pierce, 1967). This area corresponds to the upper half of Figure 12.

Heyl et al. (1974) discussed only MVT deposits with the distinguishing characteristic of the "J-type" Pb. They stated that Pb in galena in all large deposits in the Mississippi Valley was appreciably enriched in radiogenic isotopes (with the exception of those deposits from the Appalachian Valley where their ratios were less than 20.0, only slightly radiogenic). This enrichment in most of the Mississippi Valley deposits was interpreted as signifying a shallow crustal source that likely came from a heated basinal brine that moved through the region. The Pb was likely derived from Precambrian basement and carbonate cements in sandstone aquifers and that within each ore district, Pb isotope patterns reflected solution flow direction and areas of major localized ore deposition (Heyl et al., 1974).

Kesler et al. (1994a) focused on a Pb isotopic analysis of MVT deposits in the Southern Appalachians (Eastern TN). From the spatial distribution of the Pb isotope compositions, it was hypothesized that there were at least two distinct mineralizing solutions represented by two Pb clusters (Figure 14): an “upper cluster” solution dominated the Lower Ordovician paleoaquifer whereas a “lower cluster” dominated the Lower Cambrian paleoaquifer, and the two solutions mixed in most areas except the Mascot-Jefferson City district, where Zn mineralization was the strongest.

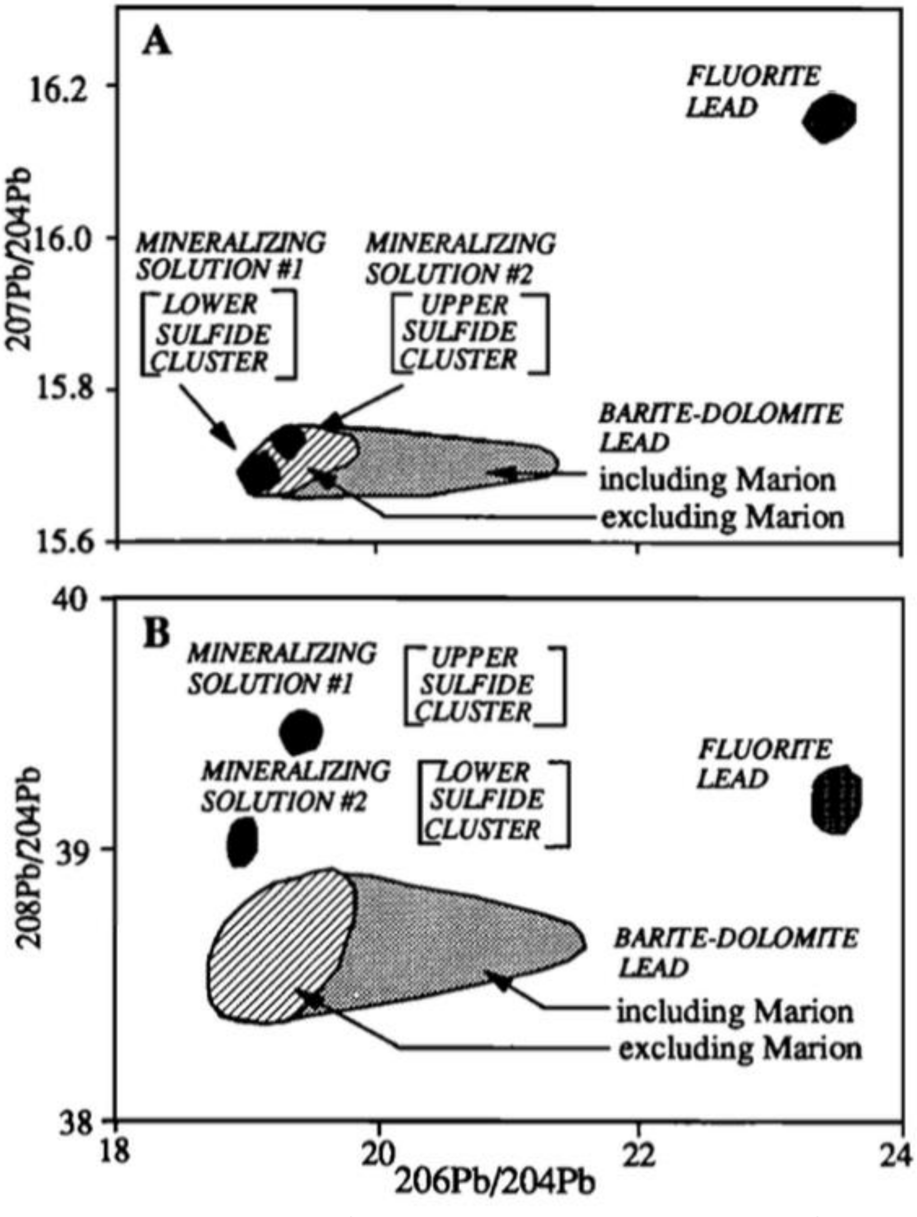

Figure 14: Approximate ranges of compositional groups that account for Pb-isotope compositions of MVT deposits in the southern Appalachians (Kesler et al., 1994).

Kesler stated that these two Pb clusters likely originated from relatively young, well-mixed sedimentary basins. Furthermore, the isotopic compositions of Pb in the Southern Appalachians (Eastern TN) differed significantly from those found in mid-continent deposits, suggesting a different source, confirming the previous studies of Heyl et al., (1974) and Cannon et al., (1961). Kesler et al. (1994a) suggested tectonic influences on the distribution of the ore deposits in the Southern Appalachians and that MVT mineralization likely occurred during the peak of Taconic and Acadian orogenies and associated metamorphism but before the Alleghenian orogeny.

Gaylord (1995) compiled Pb isotope data (Table 6) on samples taken from various locations in the Appalachians and Central TN districts in which he established three separate Pb isotope populations. As shown in Figures 15 and 16, samples from diagenetic and Canadian deposits and the small mines in Pennsylvania and New Jersey have common Pb isotope ratios falling near the "zero-age" isochron. The major Appalachian deposits are intermediate between those samples near the "zero-age" isochron and those of the strongly radiogenic "J-leads" of the Mississippi Valley. With the exception of the analyzed samples from Central TN, all the deposits defined a linear trend implying relations by a uniform process of Pb isotope evolution. Gaylord (1995) suggested that this relationship resulted from one of two scenarios: the interaction of two separate and isotopically different Pb sources, or from the physical/chemical processes operating on a single source material.

Location	**$^{206}Pb/^{204}Pb$**	**$^{207}Pb/^{204}Pb$**	**$^{208}Pb/^{204}Pb$**
Central TN, veins[1]	19.42	15.41	38.30
Central TN, Knox[1]	19.22	15.32	38.03
Mascot, TN[2]	19.56	15.77	39.66
Flat Gap, TN[3]	19.14	15.85	39.43
Flat Gap, TN[4]	19.17	15.76	39.46
Embreeville, VA[5]	19.46	15.81	39.26
Austinville, VA[6]	19.19	15.85	39.17
Friedensville, PA[2]	19.24	15.68	39.66
Bamford, PA[4]	18.74	15.75	38.70
Sinking Valley, PA[4]	18.61	15.71	38.80
Califon, NJ[4]	18.68	15.68	38.39
Pine Point, NWT, Canada[6]	18.47	15.84	38.54
Gays River, NS, Canada[6]	18.29	15.76	38.48
Central TN, Elmwood[7]	19.637	15.742	39.292
Central TN, Hartsville[7]	19.697	15.742	39.292

Table 6: Lead isotope ratios for Appalachian and other "Strata-bound" carbonate-hosted lead-zinc deposits. [1]Hoagland (1976). [2]Russell and Farquhar (1960). [3]Crawford and Hoagland (1968). [4]Heyl et al. (1966). [5]Brown and Weinberg (1968). [6]Brown (1962). [7]Unpublished data; permission to publish by B. R. Doe (Modified from Gaylord and Briskey, 1983).

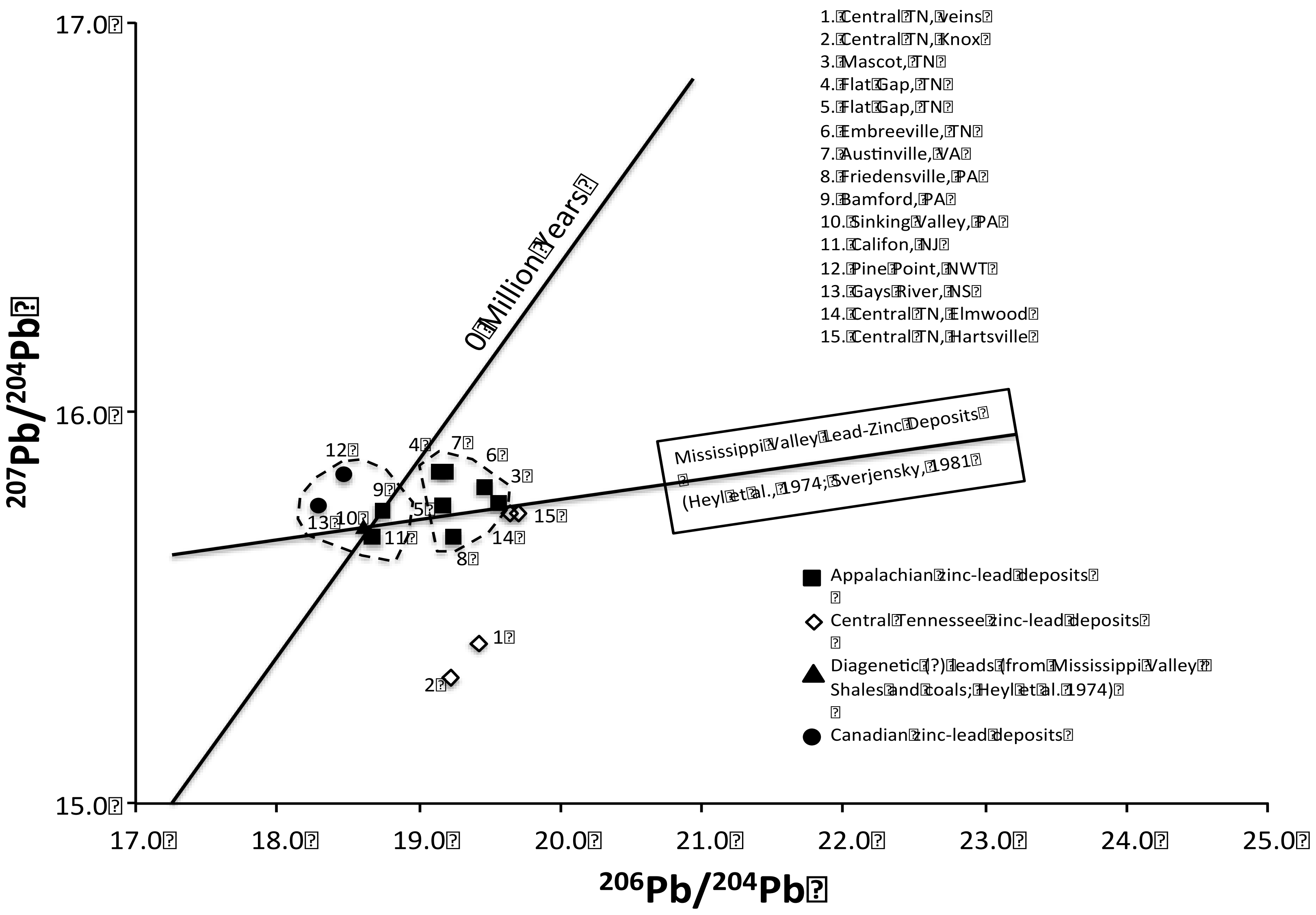

Figure 15: Plot of ratios ^{207}Pb/^{204}Pb versus ^{206}Pb/^{204}Pb for galenas from selected strata-bound carbonate-hosted zinc-lead deposits (after Gaylord and Briskey, 1983).

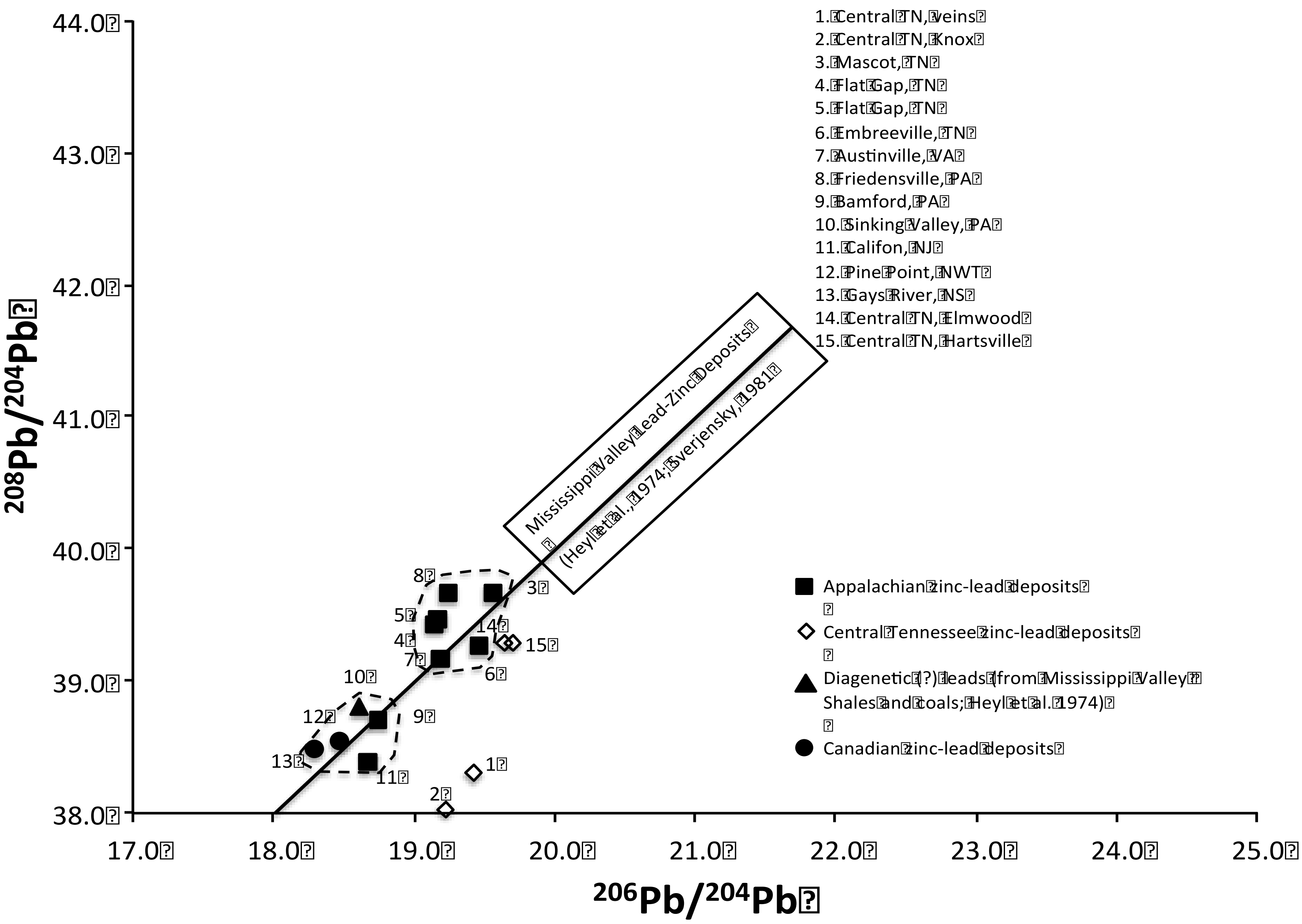

Figure 16: Plot of ratios ^{208}Pb/^{204}Pb versus ^{206}Pb/^{204}Pb for galenas from selected strata-bound carbonate-hosted zinc-lead deposits (after Gaylord and Briskey, 1983).

Misra et al. (1996) analyzed Pb from five galena samples taken from the Elmwood-Gordonsville mines in Central TN, confirming the well-established anomalous nature of this ore. Misra et al. (1996) also distinguished the notable feature of isotopic homogeneity, which contrasted sharply to other MVT deposits such as those in southeast Missouri, the Upper Mississippi Valley, and the Illinois-Kentucky District.

Figure 17 from Misra et al. (1996) shows three populations of Pb isotope ratios based on samples from Copper Ridge (C-R; East TN), Mascot-Jefferson City (M-J; East TN), and the Central TN (CT) District. Isotopic analysis shows that the CT deposits contain the most radiogenic Pb, and plot within a relatively narrow range away from East TN deposits. As proposed by Misra et al. (1996), this homogeneity is indicative of a well-mixed source, likely from relatively young sedimentary basin where local isotopic differences had not developed before MVT brines were expelled.

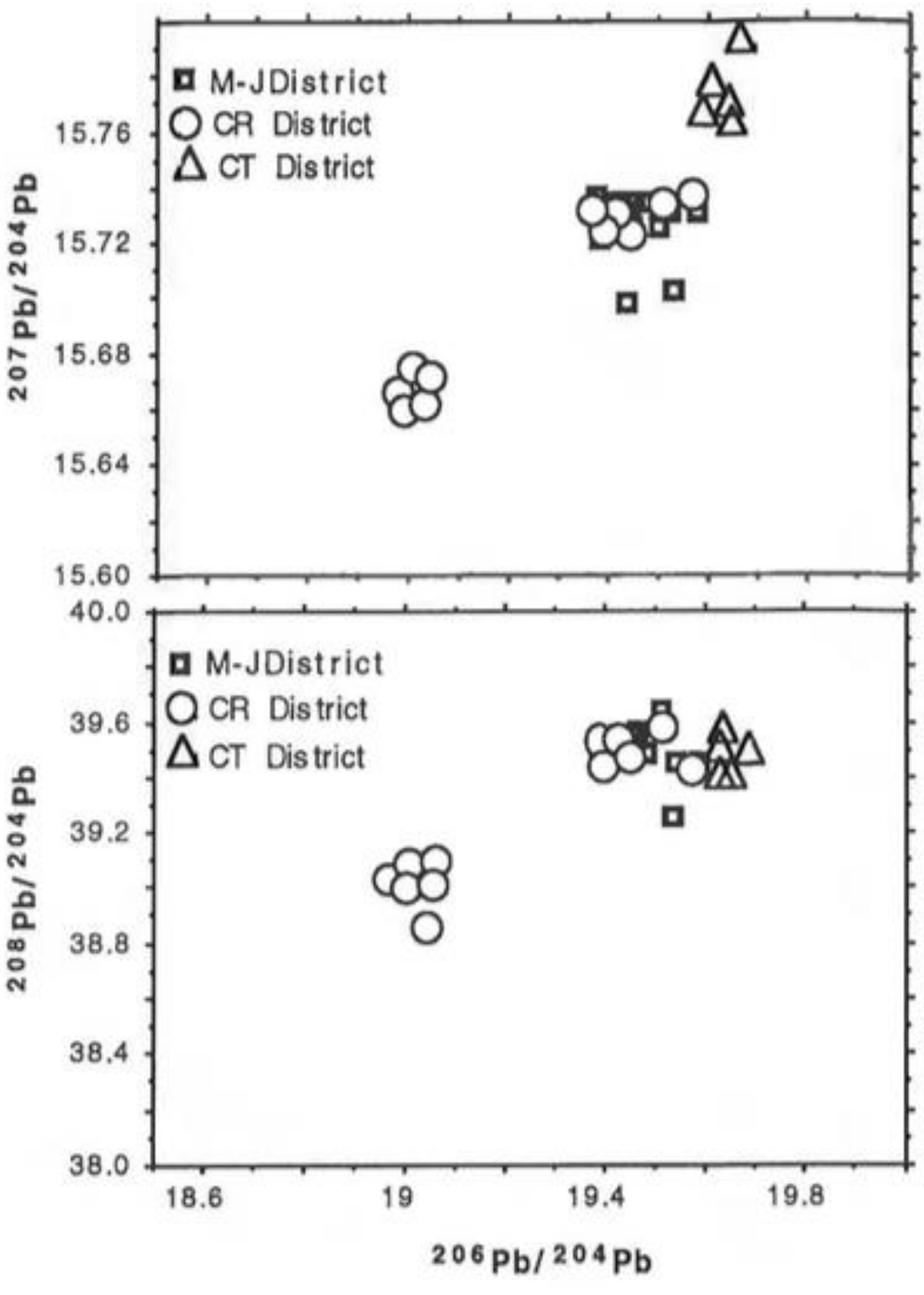

Figure 17: Pb isotope ratios of ore galena samples from the Central Tennessee (CT) district (Elmwood-Gordonsville mines) compared with those of sulfide samples from the Mascot-Jefferson City (M-J) district and Copper Ridge (CR) district reported by Kesler et al. (1994a) (From Misra et al., 1996).

Methods

Ore samples were collected by hand (with help of Nyrstar production geologists) in both the Elmwood Mine in Central Tennessee and the Young Mine in Eastern Tennessee. Each sample was photographed and wrapped in several layers of aluminum foil and plastic bags and broken into smaller pieces with a hammer. Around 0.1 grams of sphalerite from each of the crushed samples were handpicked, collected and transferred to clean, HNO_3- and HCl-leached Teflon containers. Sulfide minerals were chemically processed in the class 1,000 Radiogenic Isotope Clean Laboratory at University of Arkansas.

Teflon beakers used for dissolution and collection of final samples were soaked in cold aqua regia for no less than 48 hours. Beakers were then placed in boiling 1:1 HCl and 1:1 HNO_3 for no less than 30 minutes. After cooling from the boil, each beaker was then successively rinsed with purer water beginning with deionized, Milli-Q, and then finally two-bottle (2B) Teflon distilled water. The resin (Dowex AG1-8X, 200-400 mesh) used in Pb separation was mixed with 6N HCl and cleaned with 0.5N HNO_3 and 2B water. Three ml syringe bodies with filters (frits) attached at the narrow end were used as columns. These columns were stored in a 1:1 HCl bath between uses; before use, they were leached in 1:1 HNO_3 and rinsed successively with deionized, Milli-Q, and 2B water.

Approximately 100 mg of sphalerite sample were dissolved in 1 ml 1N HBr and then 1 ml 0.5N HNO_3 in Teflon containers, placed on a hotplate in the laminar flow hood, and allowed to sit overnight. The dried samples were re-dissolved in 1 ml 1N HBr and dried for a total of three times. One ml 1N HNO_3 was added to dissolve the remaining sample. One last addition of 1 ml 1N HBr was needed to collect the sample from the Teflon container. Each sample was transferred to HNO_3-leached 1.5 ml centrifuge tubes. Each loaded tube was placed into centrifuge for 15 minutes, rotated 180° and centrifuged for an additional 15 minutes. The centrifuging process separated the Pb-bearing HBr solution from any remaining suspended particles in the tube.

Lead was separated and purified using cation exchange columns and an HBr medium. After adding 2 ml of 2B water, resin was added to each exchange column. Each column was cleaned with 2 ml of 2B water, 2 ml of 0.5N HNO_3 and then conditioned successively with 2 ml of 2B water, and 2 ml of 6N HCl before loading each sample. The samples, contained in 0.2 ml of 1N HBr, were loaded in the columns and allowed to drain. The Pb was adsorbed on the clean resin while other elements passed through. Before sample collection, each sample was rinsed in 3 successive additions of 1 ml 1N HBr. For sample collection, a final addition of 1 ml 0.2N HNO_3 was added and collected in clean HNO_3- and HCl-leached Teflon containers, and placed on hot plate to dry. Dried samples were covered with lids, and removed from the laminar flow hood for analysis.

Lead isotope ratios were determined by inductively coupled plasma mass spectrometry on University of Arkansas' Nu Plasma II MC-ICP Mass Spectrometer. Four ml of 1N HNO_3 was added to each sample vial. The sample was introduced into the plasma by an uptake system with a rate of 40 microliters/min^{-1}. The aerosol from the nebulizer is injected into the center region of the plasma and desolvated and ionized. The data collected for each sample represented averages of 60 ratio measurements each. The average standard errors on the analyzed samples were 0.1020% for $^{208}Pb/^{204}Pb$, 0.0360% for $^{207}Pb/^{204}Pb$, and 0.0390% for $^{206}Pb/^{204}Pb$. The data were corrected for instrumental fractionation by comparison with replicate analyses of the National Bureau of Standards common Pb standard SRM-981. Measured average values of 9 analyses of this standard are as follows: $^{208}Pb/^{204}Pb$ = 36.650; $^{207}Pb/^{204}Pb$ = 15.474; and $^{206}Pb/^{204}Pb$ = 16.922.

Results

A total of 14 sphalerite samples were collected from two separate mines in Central and Eastern Tennessee representing two MVT districts. Nine samples were taken from the Young Mine located in New Market, TN, approximately 20 miles northeast of Knoxville, TN and five samples were taken from the Elmwood Mine located in Gordonsville, TN, approximately 50 miles east of Nashville, TN. The results of Pb-isotope analyses of samples from both this study and similar studies have been compiled in Table 5. Pb isotope ratios from this study have been plotted on conventional covariation diagrams and are shown in Figure 18. A compilation of all East and Central Tennessee samples from Appendix 2 has been plotted on covariation diagrams as shown in Figure 19, and a compilation of samples from Appendix 2 has been plotted on covariation diagrams as shown in Figure 20

From Table 7, ^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb and ^{208}Pb/^{204}Pb ratios of samples from the Elmwood Mine range from 19.334 – 20.128, 15.548 – 16.034, and 38.837 – 40.034 respectively, and ratios of samples from the Young Mine range from 19.341 – 19.455, 15.638 – 15.789, and 39.045 – 39.591 respectively. Samples can be categorized into two clusters: the first cluster contains all samples from the Young Mine (East Tennessee) in addition to 3 Elmwood Mine samples (Central Tennessee). The second cluster contains only Elmwood Mine samples and consists of a much wider range of Pb isotope data, arousing suspicion as to the analytical accuracy of these samples. Further evaluation and comparison of these samples can be seen in the *Discussion* section.

Table 7: Results of Pb Isotope analyses of this study

Sample	**Location/District**	**Mine**	**$^{206}Pb/^{204}Pb$**	**$^{207}Pb/^{204}Pb$**	**$^{208}Pb/^{204}Pb$**	**Sample Type**
E1[1]	Gordonsville, Central TN	Elmwood	19.334	15.698	39.329	Sphalerite
E1[1] (duplicate)	Gordonsville, Central TN	Elmwood	19.407	15.784	39.609	Sphalerite
E2[1]	Gordonsville, Central TN	Elmwood	20.128	15.763	39.174	Sphalerite
E3[1]	Gordonsville, Central TN	Elmwood	19.966	16.034	40.034	Sphalerite
E5[1]	Gordonsville, Central TN	Elmwood	19.414	15.748	39.475	Sphalerite
E8[1]	Gordonsville, Central TN	Elmwood	19.872	15.548	38.837	Sphalerite
1 9215A[1]	Mascot - Jefferson City	Young	19.417	15.682	39.340	Sphalerite
1 9215B[1]	Mascot - Jefferson City	Young	19.442	15.706	39.376	Sphalerite
2 9922A[1]	Mascot - Jefferson City	Young	19.341	15.713	39.395	Sphalerite
2 9922B[1]	Mascot - Jefferson City	Young	19.443	15.735	39.423	Sphalerite
2 9922C[1]	Mascot - Jefferson City	Young	19.455	15.638	39.045	Sphalerite
4 2248A[1]	Mascot - Jefferson City	Young	19.349	15.706	39.357	Sphalerite
4 2248B[1]	Mascot - Jefferson City	Young	19.437	15.789	39.591	Sphalerite

Table 7: Results of Pb Isotope analyses of this study

4 2248C[1]	Mascot - Jefferson City	Young	19.411	15.728	39.484	Sphalerite
5 4338B[1]	Mascot - Jefferson City	Young	19.407	15.692	39.332	Sphalerite

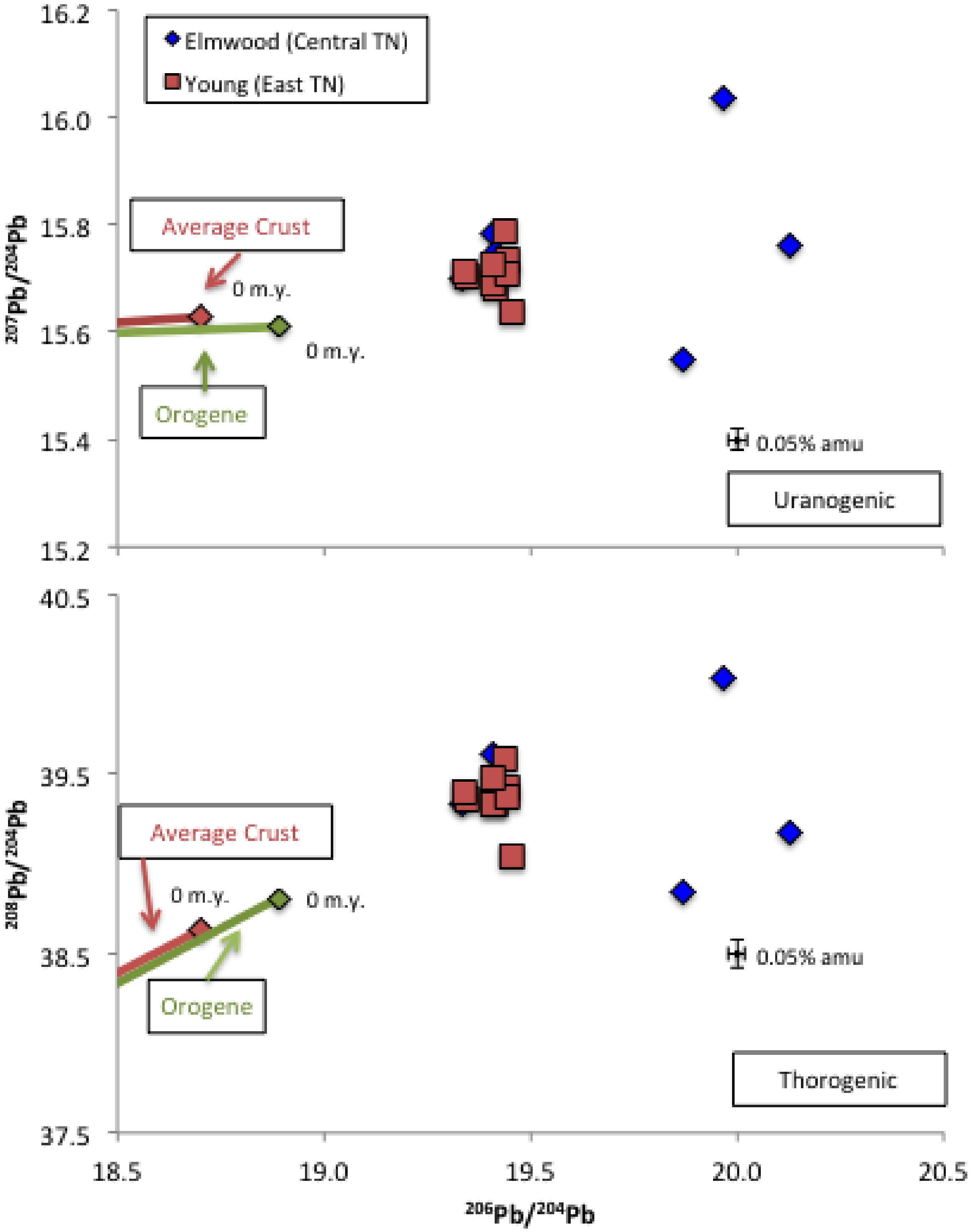

Figure 18: Pb-isotope data from this study displayed on uranogenic (top) and thorogenic (bottom) diagrams. Red curve represents the average crustal growth from Stacy and Kramers (1975). Green curve represents the orogene growth curve from Zartman and Doe (1981). Error bar indicates ±0.05% per atomic mass unit.

Discussion

The Pb isotopic data from this study (Table 7) were plotted on Pb covariation diagrams (Figures 18) with a crustal growth curve from Stacy and Kramers (1975) and an orogene curve from Zartman and Doe (1981) as already described in the aforementioned "Why Pb Isotopes" section. All Pb isotope ratios from samples taken from the Elmwood and Young Mines plot beyond the present day age ("0 m.y.") for both the Stacy and Kramers (1975) average growth curve and the Zartman and Doe (1981) orogene growth curve. With regard to the spatial distribution and isotopic variations of the Pb ratios, an examination of Figure 18 reveals approximately two groups defined by samples belonging to:

1) Young Mine + Elmwood Mine
2) Solely Elmwood Mine

The first group defined by the Young Mine samples + 3 Elmwood samples are relatively homogenous whereas the second group defined by the 3 outlying Elmwood samples are much more heterogeneous and are suspect to analytical error. All samples lie beyond and/or above the average crustal growth curve of Stacy and Kramers (1975) and the orogene growth curve of Zartman and Doe (1981) indicative of an upper crustal Pb source. The host rocks of both groups are Paleozoic (Ordovician) age and carbonates, which supports epigenetic mineralization of the ore. Three samples from the Elmwood Mine plot close to the field defined by samples from the Young Mine. This similarity could be due to ore deposition of a similar hydrothermal fluid but additional analysis of sulfides from Central TN is needed to confirm. The narrow range of East TN Pb data is indicative of a well-mixed source. Although ores from East and Central Tennessee are among the least radiogenic of the "MVT" class of ore deposits in the US, isotopic ratios from this study do confirm they are of the Mississippi Valley Type.

A comparison of Pb isotope ratios from this study has been made with the Pb isotope ratios from Kesler et al. (1994), Misra et al. (1994) and Gaylord (1995; and references therein) (Appendix 2), as shown in Figure 19 below. As with Figure 18, this compilation of Pb isotope data has been plotted on covariation diagrams with the average crustal growth curve from Stacy and Kramers (1975) and the orogene growth curve from Zartman and Doe (1981). With reference to spatial distribution and isotopic variation of all ore samples, there appears to be at least 3 major groups, one of which contains ores from both East and Central TN. Each group is defined by the following:

1) East TN samples from Kesler et al. (1994)
2) East TN samples from this study and Kesler et al. (1994) and Central TN samples from this study
3) Central TN samples from Misra et al. (1996) and Gaylord (1995)

Group 1, containing only East TN deposits, represents the least radiogenic of all samples from Table 7 and plots nearest (yet still beyond) the 0 m.y. age of both curves from Stacy and Kramers (1975) and Zartman and Doe (1981). Group 2 contains primarily ore samples from East TN, in addition to three Central TN samples from this study, and is slightly more radiogenic than group 1. Group 3 contains ore samples from Central TN, and is the most radiogenic ore of all East and Central TN deposits (Misra et al., 1996). Despite the relatively radiogenic nature of these Central TN deposits, they are still among the least radiogenic MVT deposits in the United States.

All East TN samples from this study plot within group 2 and are most similar to those of East TN deposits from the Copper Ridge and Mascot-Jefferson City Districts (Kesler et al., 1994). This is suggestive of a similar source of Pb brought in by hydrothermal fluid from the nearby Appalachian Basin. Three Central TN samples from this study also plot within group 2. The remaining three Central TN samples from this study all plot well beyond ranges defined by all three groups. As such, analytical accuracy of these three samples is suspect.

As suggested by Tosdal et al. (1999) MVT deposits are expected to be more heterogeneous in their sedimentary rock-hosted deposits where multiple fluids might have mixed at the site of ore deposition, and where fluids might have traveled through differing aquifers equilibrated with rocks of different chemical and isotopic compositions. Both of these factors could result in Pb isotopic compositions intermediate between multiple sources. The resultant variability in Pb isotopic ratios from both East and Central TN samples from this study can be attributed to this hypothesis, as already suggested by Kesler et al. (1994a-b) and Misra et al. (1996).

A further evaluation of Pb isotope compositions from this study in terms of their relationships to Pb isotope data from other well-studied MVT deposits found throughout the United States (Viburnum Trend a.k.a. the New-Lead Belt, Tri-State, Southeast Missouri a.k.a. the Old-Lead Belt, Illinois-Kentucky, and Central Appalachian districts) can be seen on Figure 20. Each polygon or outlined group in Figure 20 represents ranges of Pb isotope ratios of ore samples that define that particular district. A complete compilation of Pb isotope data used to define these groups can be found in Appendix 2.

Most samples (with the exception of the three outliers from the Elmwood Mine) plot nearest or within ranges defined by samples from the Central Appalachian, East TN, and Central TN districts. Pb isotope ratios of the Viburnum Trend, the Old-Lead Belt, the Tri-State, and the

IL-KY Districts plot further away from the 0 m.y. age implying more evolved Pb, but still of a crustal source. Since Pb isotope ratios of ore samples from this study are isolated to fields of their own (with the exception of Central Appalachian samples), the likely source of the hydrothermal fluid is from a differing basin. Data from this study as well as from Misra et al. (1996), Kesler et al. (1996), and Kesler et al. (1994) suggest the Appalachian Basin.

Samples defining the Central Appalachian deposits from Figure 20 are from the Austinville-Ivanhoe, Timberville, Friedensville and the Nittany Arch sub-districts. These sub-districts are located within the Appalachian Mountains from southern Virginia to as far north as Pennsylvania. Kesler et al. (1994b) suggested that Pb from the Nittany Arch and Timberville deposits originated from Paleozoic igneous rocks or sediments derived from them while the Pb from the Friedensville deposits came from underlying Grenville-age basements rocks. Only Pb data from the Timberville deposit compared similarly to Pb data from East TN suggesting a possible correlation. As summarized from Kesler et al. (1994b), this relationship indicates that although MVT brines in the Central Appalachians participated in significant cross-formational flow, they were not as regionally extensive as those in the Southern Appalachians (East TN). This might be a factor that accounts for the relative scarcity of larger MVT deposits found in the Central Appalachians, as opposed to the abundant MVT deposits found in the southern Appalachians (East TN) and in Central TN.

Lead isotopic data defining the Illinois-Kentucky (IL-KY) District are from deposits found in an area covering nearly 1,000 mi^2 in southern Illinois and western Kentucky (Yancey, 1995). Most ore deposits in this district are found within the thick carbonate sequences of Mississippian age, interbedded with thinner shales and sandstones. The age of these deposits contrasts with the Ordovician age (Knox Group) East and Central TN ore deposits. Origin of the

Pb and F found in the IL-KY district is still disputed but two scenarios have been suggested. Early workers (Currier, 1923; Grogan and Bradbury, 1968) attributed the Pb and F to that of an igneous source of hydrothermal fluids likely from, or associated with, the nearby Hicks Dome, composed of a system of ultramafic igneous dikes and diatremes. Additionally, alkalic elements present at Hicks Dome are uniquely associated with magmatic sources. It has been suggested that isotopic and trace-element analysis of galenas from the IL-KY district supports this magmatic-hydrothermal genesis.

Another scenario suggests the more commonly accepted basinal brine model where fluorine and metal rich fluids from a non-magmatic source (likely the Illinois Basin) migrated to the deposition site. This migration occurred through episodic basin compactional dewatering and gravity-driven flow to the site of deposition, in response to regional tectonic events. The uplift of the Appalachian fold-belt to the east and the Ouachitas to the south provided enough relief to cause large-scale flow (Lasemi, 2010). Hayes and Anderson (1992) suggested that such a large-scale, regionally extensive, and interconnected hydrothermal system was responsible for MVT mineralization in the IL-KY district and that this fluid extended into Central KY and Central TN. Additionally, based on the similar paragenetic sequences, hydrothermal carbonate minerals in both Central TN and Central KY appear to correlate with the IL-KY district, indicative of a similar hydrothermal source.

Lead isotope ratios from the IL-KY district from Figure 20 plot further away from crustal growth curve of Stacy and Kramers (1975) and the orogene growth curve of Zartman and Doe (1981) indicative of a more evolved Pb as compared to those Pb isotope ratios from East and Central TN. Although these two districts share very similar ore geneses, a comparison of Pb isotopes confirms separate hydrothermal sources.

Lead isotopic data defining the Viburnum Trend (“New-Lead Belt”) are from the western half of the much larger Southeast Missouri Pb district. The main host of the ore is the Upper Cambrian Bonneterre Formation that overlies the basal Lamotte Sandstone. The Lamotte Sandstone unconformably overlies the Precambrian basement. Crocetti et al. (1988) summarized from Pb isotopic analyses that the isotopic composition of the Pb can be explained by the mixing of two separate sources of Pb: the first source containing normal Pb derived from basinal brines (similar to the source responsible for those deposits found in Central TN, Central and Southern Appalachians), and the second source containing radiogenic Pb from the underlying Precambrian basement of Grenvillian age. This basinal brine as proposed by Rowan et al. (1984), Viets et al. (1984), and Leach and Rowan (1986), originated from the Arkoma-Ouachita basin and migrated north into southeast Missouri while leaching Pb from the Grenvillian basement during transportation.

Pb isotope ratios defining the Tri-state district are from an area covering nearly 2,000 mi^2 in southwest Missouri, northeast Oklahoma, and southeast Kansas. Nier (1938) first described these anomalous ore deposits from their extremely radiogenic Pb isotope compositions and called them “J-type” from their discovery site in Joplin, MO. Ore mineralization in the Tri-State occurs in the Ordovician through Pennsylvanian, but is primarily restricted to the Mississippian (Keokuk and Warsaw Formations) (Leach and Sangster, 1994). As summarized by Viets and Leach (1990), Pb isotope ratios from the Viburnum Trend are isotopically similar to those of the Tri-state, indicative of a common brine source, but much more radiogenic than East and Central TN deposits.

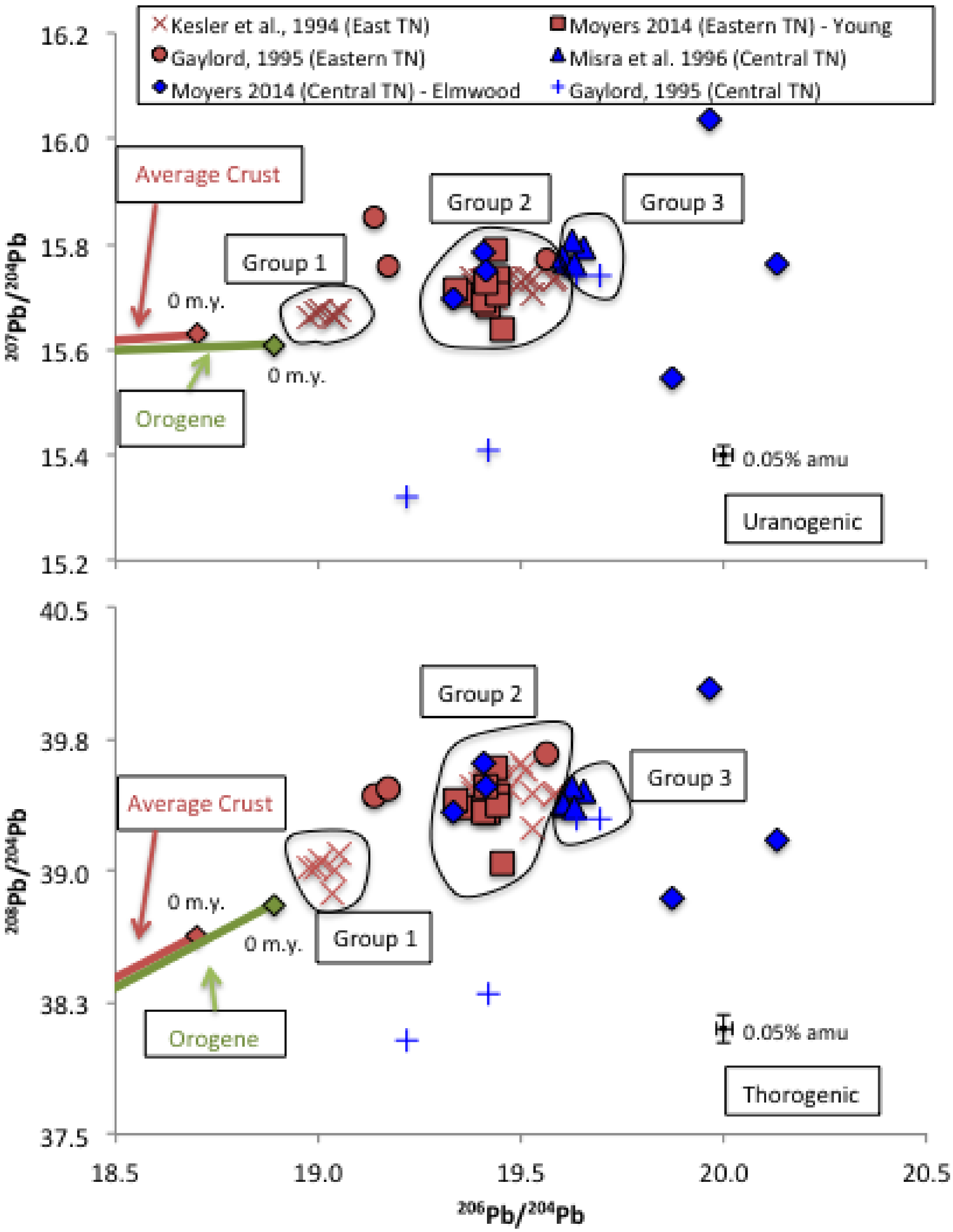

Figure 19: Pb isotopic compositions of ore samples from this study; Kesler et al., 1994; Misra et al, 1996; Heyl et al., 1966, plotted on uranogenic (top) and thorogenic (bottom) covariation diagrams. Red curve represents the average crustal growth curve from Stacy and Kramers (1975). Green curve represents the orogene growth curve from Zartman and Doe (1981). Error bar indicates ±0.05% per atomic mass unit.

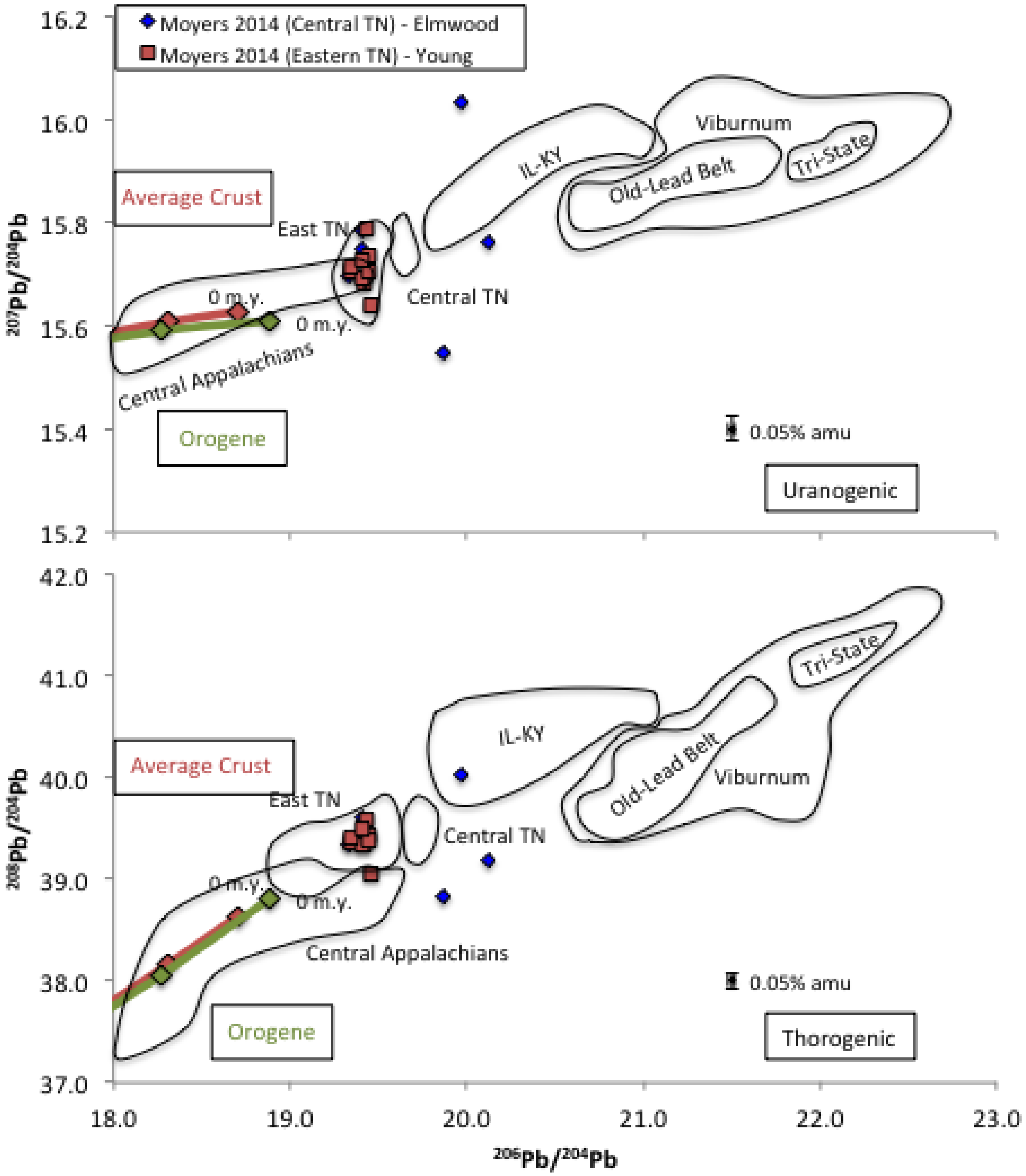

Figure 20: Pb isotopic compositions of ore samples from of this study; Kesler et al., 1994; Misra et al., 1996; Hoagland, 1976; Russell and Farquhar, 1960; Crawford and Hoagland, 1968; Heyl et al., 1966; Goldhaber et al., 1995; and Kesler et al., 1994b, plotted on uranogenic (top) and thorogenic (bottom) covariation diagrams. Red curve represents the average crustal growth curve from Stacy and Kramers (1975). Green curve represents the orogene growth curve from Zartman and Doe (1981). Each polygon is defined by a range of Pb isotope ratios from that particular district. Error bar indicates ±0.05% per atomic mass unit.

Conclusions

1) Pb isotope ratios of sulfides from this study can be divided into two separate groups:
    a) Young Mine + Elmwood Mine
    b) Elmwood Mine

2) All samples from this study (Figure 18) plot beyond both Stacy and Kramers' (1975) average crustal growth curve and Zartman and Doe's (1981) orogene growth curve, confirming an upper crustal source of Pb for both Central and East Tennessee districts.

3) Pb data from this study plot in similar fields defined by data from previous studies as shown in Figure 19 (Kesler et al. 1994; Misra et a., 1996; Gaylord, 1995). East Tennessee samples from this study are the least radiogenic, and plot in a relatively tight cluster. This is indicative of a well-mixed, homogenous source of hydrothermal fluid possibly derived from the nearby Appalachian Basin.

4) When comparing samples from this study to Central Appalachian deposits from Kesler et al. (1994b), several observations are made:
    a. Central Appalachian deposits contain the least radiogenic Pb of the samples compiled on Figure 20, slightly less radiogenic than Pb data from this study.
    b. Pb data from this study plot nearest the Timberville District deposits found in the Central Appalachians. Kesler et al (1994b) suggested the sources of all Pb in Central Appalachia originated from Paleozoic igneous rocks and sediments derived from them but an addition of a much younger, Triassic diabase Pb source was responsible for the distribution of Pb found specifically in Timberville District deposits.

5) East Tennessee deposits from this study plot in the same field as deposits specifically from the Mascot-Jefferson City and Copper Ridge Districts in East TN. Kesler et al. (1994a) suggested that there were two mineralizing solutions responsible for the spatial distribution and isotopic composition of ore found in East Tennessee. These two solutions were allowed to mix through a Lower Cambrian paleoaquifer that extended from Georgia to Virginia, and a Lower Ordovician paleoaquifer that extended from East Tennessee northward into Virginia. The spatial extent of these two paleoaquifers contributed to the range and variability of Pb ratios in ore deposits found in both East Tennessee and the Central Appalachians.

6) Pb isotope data from this study plot nearest but still beyond the average crustal growth curves. This confirms their less radiogenic nature as compared to the more anomalous and radiogenic “J-Type” leads found in the Tri-State and Southeast Missouri Districts.

7) The isotopic compositions of three samples from the Elmwood mine in Central Tennessee appear suspicious and may be subject to analytical error. As result, the compositions of these samples should be reanalyzed before any further interpretation is made.

8) Although both East and Central Tennessee deposits from this study share similar Pb isotopic ratios (with exception to the three spurious samples from Central TN), isotopic data from Misra et al. (1996) and Kesler (1994a) suggests these two districts did not mineralize from the same hydrothermal fluid and are not necessarily related genetically. Misra et al (1996) concludes that deposits from Central TN might be part of a much larger mid-Continent brine

province that could've originated from a basin similarly responsible for deposits in the Tri-State and Southeast Missouri Districts (such as the Arkoma-Ouachita). However, further analysis and comparison of Central TN Pb isotope data is needed.

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Appendix 1.1

Appendix 1.1: Detailed Pb isotope measurement data of the analyzed ore samples

Sample	^{208}Pb/^{204}Pb	% error	^{207}Pb/^{204}Pb	% error	^{206}Pb/^{204}Pb	% error
E1	39.329450	0.0408	15.698330	0.0124	19.334380	0.0107
E1 (duplicate)	39.608520	0.0436	15.783770	0.0133	19.407410	0.0114
E2	39.174120	0.2520	15.763180	0.1050	20.128300	0.1330
E3	40.034220	0.1950	16.034370	0.0784	19.966280	0.0943
E5	39.475160	0.0379	15.747670	0.0109	19.413730	0.0093
E8	38.837130	0.3020	15.547600	0.1150	19.871770	0.1420
1 9215A	39.339850	0.0437	15.681660	0.0130	19.417460	0.0117
1 9215B	39.376460	0.0348	15.706390	0.0106	19.441750	0.0103
2 9922A	39.394870	0.0468	15.712900	0.0142	19.340640	0.0111
2 9922B	39.423250	0.1380	15.735110	0.0422	19.443040	0.0386
2 9922C	39.044900	0.1190	15.638190	0.0388	19.455090	0.0352
4 2248A	39.356860	0.0775	15.705630	0.0239	19.348700	0.0206
4 2248B	39.591210	0.1220	15.789410	0.0381	19.436650	0.0339
4 2248C	39.483650	0.0456	15.728200	0.0147	19.411310	0.0149
5 4338B	39.332140	0.0317	15.692090	0.0099	19.406790	0.0084
Average (n = 15)	39.386786	0.1020	15.730967	0.0360	19.521553	0.0390

Appendix 1.2

Appendix 1.2: Detailed Pb isotope measurement data of standards

Lead Standard	^{208}Pb/^{204}Pb	% error	^{207}Pb/^{204}Pb	% error	^{206}Pb/^{204}Pb	% error
SRM-981	36.621470	0.0293	15.461380	0.0117	16.900750	0.0113
SRM-981	36.627290	0.0229	15.466770	0.0095	16.923870	0.0102
SRM-981	36.632370	0.0451	15.462870	0.0184	16.910260	0.0200
SRM-981	36.639770	0.0185	15.472150	0.0077	16.925270	0.0089
SRM-981	36.622240	0.0187	15.461200	0.0077	16.908300	0.0084
SRM-981	36.677020	0.0238	15.486240	0.0101	16.937000	0.0110
SRM-981	36.672560	0.0143	15.481660	0.0060	16.930190	0.0064
SRM-981	36.683730	0.0193	15.487970	0.0081	16.931460	0.0083
SRM-981	36.671890	0.0175	15.485360	0.0071	16.931450	0.0075
Average (n = 9)	36.649816	0.0233	15.473956	0.0096	16.922061	0.0102
Todt et al., 1996)	36.712000		15.484000		16.939000	

Appendix 2

Appendix 2: Compilation of Pb Isotope data: Pb Isotope analyses of this study[1]; Kesler et al., 1994[2]; Misra et al., 1996[3]; Hoagland, 1976[4]; Unpublished data from B. R. Doe[5]; Russell and Farquhar, 1960[6]; Crawford and Hoagland, 1968[7]; Heyl et al., 1966[8]; Goldhaber et al., 1995[9]; and Kesler et al., 1994b[10].

Sample	**Location/District**	**Mine**	**^{206}Pb/^{204}Pb**	**^{207}Pb/^{204}Pb**	**^{208}Pb/^{204}Pb**	**Sample Type**
E1[1]	Gordonsville, Central TN	Elmwood	19.334	15.698	39.329	Sphalerite
E1[1] (duplicate)	Gordonsville, Central TN	Elmwood	19.407	15.784	39.609	Sphalerite
E2[1]	Gordonsville, Central TN	Elmwood	20.128	15.763	39.174	Sphalerite
E3[1]	Gordonsville, Central TN	Elmwood	19.966	16.034	40.034	Sphalerite
E5[1]	Gordonsville, Central TN	Elmwood	19.414	15.748	39.475	Sphalerite
E8[1]	Gordonsville, Central TN	Elmwood	19.872	15.548	38.837	Sphalerite
1 9215A[1]	Mascot - Jefferson City	Young	19.417	15.682	39.340	Sphalerite
1 9215B[1]	Mascot - Jefferson City	Young	19.442	15.706	39.376	Sphalerite
2 9922A[1]	Mascot - Jefferson City	Young	19.341	15.713	39.395	Sphalerite
2 9922B[1]	Mascot - Jefferson City	Young	19.443	15.735	39.423	Sphalerite
2 9922C[1]	Mascot - Jefferson City	Young	19.455	15.638	39.045	Sphalerite

Appendix 2: Compilation of Pb Isotope data: Pb Isotope analyses of this study[1]; Kesler et al., 1994[2]; Misra et al., 1996[3]; Hoagland, 1976[4]; Unpublished data from B. R. Doe[5]; Russell and Farquhar, 1960[6]; Crawford and Hoagland, 1968[7]; Heyl et al., 1966[8]; Goldhaber et al., 1995[9]; and Kesler et al., 1994b[10] (Cont.).

4 2248A[1]	Mascot - Jefferson City	Young	19.349	15.706	39.357	Sphalerite
4 2248B[1]	Mascot - Jefferson City	Young	19.437	15.789	39.591	Sphalerite
4 2248C[1]	Mascot - Jefferson City	Young	19.411	15.728	39.484	Sphalerite
5 4338B[1]	Mascot - Jefferson City	Young	19.407	15.692	39.332	Sphalerite
Y-9[2]	Mascot - Jefferson City	Young	19.431	15.726	39.502	Sphalerite
Y-49[2]	Mascot - Jefferson City	Young	19.446	15.726	39.490	Sphalerite
Y-32[2]	Mascot - Jefferson City	Young	19.409	15.733	39.462	Sphalerite
Y-23[2]	Mascot - Jefferson City	Young	19.469	15.734	39.462	Sphalerite
Y-49[2]	Mascot - Jefferson City	Young	19.579	15.731	39.433	Sparry Dolomite
Y-23[2]	Mascot - Jefferson City	Young	19.437	15.698	39.438	Sparry Dolomite
Y-24[2]	Mascot - Jefferson City	Young	19.529	15.703	39.435	Sparry Dolomite
NW-44[2]	Mascot - Jefferson City	New Market	19.382	15.721	39.441	Sphalerite

Appendix 2: Compilation of Pb Isotope data: Pb Isotope analyses of this study[1]; Kesler et al., 1994[2]; Misra et al., 1996[3]; Hoagland, 1976[4]; Unpublished data from B. R. Doe[5]; Russell and Farquhar, 1960[6]; Crawford and Hoagland, 1968[7]; Heyl et al., 1966[8]; Goldhaber et al., 1995[9]; and Kesler et al., 1994b[10] (Cont.).

NW-44[2]	Mascot - Jefferson City	New Market	19.500	15.726	39.618	Sparry Dolomite
IMMEL-X[2]	Mascot - Jefferson City	Immel	19.415	15.734	39.534	Galena
IMMEL-X[2]	Mascot - Jefferson City	Immel	19.416	15.730	39.530	Pyrite
IMMEL-X[2]	Mascot - Jefferson City	Immel	19.418	15.733	39.532	Sphalerite
IMMEL[2]	Mascot - Jefferson City	Immel	19.414	15.729	39.507	Sphalerite
C-39[2]	Mascot - Jefferson City	Coy	19.378	15.737	39.485	Sphalerite
C-16-L[2]	Mascot - Jefferson City	Coy	19.444	15.731	39.527	Sphalerite
C-16-D[2]	Mascot - Jefferson City	Coy	19.452	15.734	39.538	Sphalerite
C-39[2]	Mascot - Jefferson City	Coy	19.526	15.731	39.235	Sparry Dolomite
CS-37-965.5[2]	Copper Ridge	Idol	19.401	15.732	39.497	Sphalerite
I-61-861[2]	Copper Ridge	Idol	19.007	15.673	39.055	Sphalerite
I-64-1079[2]	Copper Ridge	Idol	19.587	15.735	39.435	Sphalerite

Appendix 2: Compilation of Pb Isotope data: Pb Isotope analyses of this study[1]; Kesler et al., 1994[2]; Misra et al., 1996[3]; Hoagland, 1976[4]; Unpublished data from B. R. Doe[5]; Russell and Farquhar, 1960[6]; Crawford and Hoagland, 1968[7]; Heyl et al., 1966[8]; Goldhaber et al., 1995[9]; and Kesler et al., 1994b[10] (Cont.).

FG-33-370[2]	Copper Ridge	Flat Gap	18.994	15.668	39.020	Sphalerite
FG-71-338[2]	Copper Ridge	Flat Gap	19.445	15.725	39.476	Sphalerite
FG-65-12[2]	Copper Ridge	Flat Gap	18.979	15.663	39.015	Galena
FG-17-314-D[2]	Copper Ridge	Flat Gap	19.036	15.665	38.865	Sparry Dolomite
E-21-455[2]	Copper Ridge	Eidson	19.405	15.727	39.457	Sphalerite
IN-61-486[2]	Copper Ridge	Independence	19.513	15.736	39.571	Sphalerite
IN-61-496-D[2]	Copper Ridge	Independence	19.042	15.662	39.008	Sparry Dolomite
BW-2-326[2]	Copper Ridge	Big War Creek	19.053	15.675	39.090	Sphalerite
CR-24-194[2]	Copper Ridge	Shiloh	19.414	15.731	39.490	Sphalerite
Gal-1[3]	Gordonsville, Central TN	Elmwood-Gordonsville	19.609	15.767	39.372	Galena
Gal-2[3]	Gordonsville, Central TN	Elmwood-Gordonsville	19.657	15.795	39.454	Galena
Gal-3[3]	Gordonsville, Central TN	Elmwood-Gordonsville	19.626	15.805	39.474	Galena

Appendix 2: Compilation of Pb Isotope data: Pb Isotope analyses of this study[1]; Kesler et al., 1994[2]; Misra et al., 1996[3]; Hoagland, 1976[4]; Unpublished data from B. R. Doe[5]; Russell and Farquhar, 1960[6]; Crawford and Hoagland, 1968[7]; Heyl et al., 1966[8]; Goldhaber et al., 1995[9]; and Kesler et al., 1994b[10] (Cont.).

Gal-4[3]	Gordonsville, Central TN	Elmwood-Gordonsville	19.603	15.777	39.393	Galena
Gal-5[3]	Gordonsville, Central TN	Elmwood-Gordonsville	19.634	15.764	39.364	Galena
unnamed[4]	Gordonsville, Central TN	-	19.420	15.410	38.300	vein
unnamed[4]	Gordonsville, Central TN	-	19.220	15.320	38.030	Knox
unnamed[5]	Gordonsville, Central TN	Elmwood	19.637	15.742	39.292	-
unnamed[5]	Gordonsville, Central TN	Hartsville	19.697	15.742	39.292	-
unnamed[6]	Mascot - Jefferson City	Mascot	19.560	15.770	39.660	-
unnamed[7]	Copper Ridge	Flat Gap	19.140	15.850	39.430	-
unnamed[8]	Copper Ridge	Flat Gap	19.170	15.760	39.460	-
78BRD-3[9]	Viburnum Trend	Milliken	21.321	15.905	40.302	Disseminated Galena
&8BRD-4[9]	Viburnum Trend	Milliken	21.943	15.903	40.604	Cubic Galena
78BRD-7[9]	Viburnum Trend	Milliken	21.363	15.932	40.139	Disseminated Galena

Appendix 2: Compilation of Pb Isotope data: Pb Isotope analyses of this study[1]; Kesler et al., 1994[2]; Misra et al., 1996[3]; Hoagland, 1976[4]; Unpublished data from B. R. Doe[5]; Russell and Farquhar, 1960[6]; Crawford and Hoagland, 1968[7]; Heyl et al., 1966[8]; Goldhaber et al., 1995[9]; and Kesler et al., 1994b[10] (Cont.).

79RE-1[9]	Viburnum Trend	Milliken	21.510	15.954	40.526	Chalcopyrite
SWC[9]	Viburnum Trend	Milliken	21.420	15.960	40.515	Chalcopyrite
Dol-IISW[9]	Viburnum Trend	Milliken	21.179	15.820	40.120	Dolomite
Dol-IIISW[9]	Viburnum Trend	Milliken	21.401	15.905	40.430	Dolomite
75D-21[9]	Viburnum Trend	Fletcher	21.429	15.919	40.363	Disseminated Galena
75D-23[9]	Viburnum Trend	Fletcher	21.248	15.910	40.080	Disseminated Galena
FOGA[9]	Viburnum Trend	Fletcher	21.160	15.990	40.430	Octahedral Galena
FOGB[9]	Viburnum Trend	Fletcher	21.190	16.020	40.520	Octahedral Galena
FCG[9]	Viburnum Trend	Fletcher	21.620	15.960	40.801	Cubic Galena
FLCG[9]	Viburnum Trend	Fletcher	21.670	15.980	40.780	Cubic Galena
FCM1[9]	Viburnum Trend	Fletcher	21.490	15.900	40.520	Chalcopyrite
FCM2[9]	Viburnum Trend	Fletcher	21.580	16.010	40.870	Chalcopyrite
FCM3[9]	Viburnum Trend	Fletcher	21.530	15.930	40.605	Chalcopyrite
FCM4[9]	Viburnum Trend	Fletcher	21.560	15.980	40.740	Chalcopyrite

Appendix 2: Compilation of Pb Isotope data: Pb Isotope analyses of this study[1]; Kesler et al., 1994[2]; Misra et al., 1996[3]; Hoagland, 1976[4]; Unpublished data from B. R. Doe[5]; Russell and Farquhar, 1960[6]; Crawford and Hoagland, 1968[7]; Heyl et al., 1966[8]; Goldhaber et al., 1995[9]; and Kesler et al., 1994b[10] (Cont.).

FCM5[9]	Viburnum Trend	Fletcher	21.530	15.980	40.740	Chalcopyrite
FCM6[9]	Viburnum Trend	Fletcher	21.560	15.990	40.780	Chalcopyrite
FC[9]	Viburnum Trend	Fletcher	21.701	15.990	40.710	Chalcopyrite
77DR-2[9]	Viburnum Trend	Buick	21.258	15.901	40.058	Early Octa. Galena
77DR-2[9]	Viburnum Trend	Buick	21.020	15.869	39.821	Late Octa. Galena
77DR-3[9]	Viburnum Trend	Buick	21.360	15.894	40.103	Late Octa. Galena
77DR-3[9]	Viburnum Trend	Buick	21.631	15.917	40.559	Late Cubic Galena
C-1[9]	Viburnum Trend	Buick	21.512	15.914	40.412	Cubic Galena
C-4[9]	Viburnum Trend	Buick	21.510	15.914	40.529	Cubic Galena
37S-5[9]	Viburnum Trend	Buick	21.509	15.910	40.405	Cubic Galena
T-23[9]	Viburnum Trend	Magmont	21.207	15.886	39.961	Octahedral Galena
T-47[9]	Viburnum Trend	Magmont	21.820	15.858	39.700	Disseminated Galena
LDT-15[9]	Viburnum Trend	Magmont	21.286	15.898	39.976	Disseminated Galena
T-9[9]	Viburnum Trend	Magmont	21.058	15.873	39.851	Disseminated Galena

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MMC-1[9]	Viburnum Trend	Magmont	21.285	15.859	40.174	Octahedral Galena
MMB-1[9]	Viburnum Trend	Magmont	21.474	15.842	40.415	Octahedral Galena
MMB-2[9]	Viburnum Trend	Magmont	21.246	15.874	40.054	Disseminated Galena
MMB-3[9]	Viburnum Trend	Magmont	21.404	15.870	40.177	Disseminated Galena
KBH-V-5.21[9]	Viburnum Trend	Viburnum 28	22.576	15.992	41.694	Cubic Galena
KBH-V-5.21[9]	Viburnum Trend	Viburnum 28	21.182	15.883	39.874	Octahedral Galena
OG29-1A[9]	Viburnum Trend	Viburnum 29	21.460	15.945	39.995	Octahedral Galena
OG29-1B[9]	Viburnum Trend	Viburnum 29	21.410	15.930	39.970	Octahedral Galena
OG29-1A1[9]	Viburnum Trend	Viburnum 29	21.520	15.960	40.060	Octahedral Galena
CG29-1A[9]	Viburnum Trend	Viburnum 29	21.360	16.001	40.490	Cubic Galena
CG29-1B1[9]	Viburnum Trend	Viburnum 29	21.430	16.045	40.710	Cubic Galena
CG29-1A1[9]	Viburnum Trend	Viburnum 29	21.280	15.910	40.160	Cubic Galena
BS29-1A[9]	Viburnum Trend	Viburnum 29	20.870	15.860	39.650	Sphalerite
BS29-1A1[9]	Viburnum Trend	Viburnum 29	20.830	15.875	39.690	Sphalerite

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BS29-1B[9]	Viburnum Trend	Viburnum 29	20.860	15.880	39.680	Sphalerite
100.3997 [9]	Old Lead Belt	Derby-Doe Run	20.877	15.851	39.782	Galena
H-1[9]	Old Lead Belt	Hayden Creek	20.972	15.864	39.949	Galena
FM60-30[9]	Old Lead Belt	Madison	21.600	15.926	40.824	Galena
Pot60-1[9]	Old Lead Belt	Potosi Fm.	20.958	15.865	40.250	Galena
74-1 [9]	Old Lead Belt	Surface sample	21.251	15.916	40.240	Galena
G-11 [9]	Old Lead Belt		20.750	15.850	39.720	Galena
G-12	Tri-State	Weber	22.210	15.960	41.300	Cubic Galena
-	Tri-State	Blue Goose	21.942	15.920	41.076	Cubic Galena
-	Tri-State	Blue Goose	21.901	15.922	41.072	Cubic Galena
YORK-1.1[10]	Kinzers Fm.	York Quarry	19.078	15.674	38.709	Sphalerite
DOWN-1.1[10]	Ledgers Fm.	Downington	18.272	15.636	38.252	Sphalerite
AK-2.1[10]	Timberville	Armstrong-Kiser	19.233	15.692	38.794	Sphalerite
BC-9.1[10]	Timberville	Bowers-Cambell	19.211	15.686	38.923	Sphalerite

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BC-9.2[10]	Timberville	Bowers-Cambell	19.169	15.686	38.960	Sphalerite
BC-9.3[10]	Timberville	Bowers-Cambell	19.551	15.727	38.989	Sparry Dolomite
BC-29.1[10]	Timberville	Bowers-Cambell	18.973	15.672	38.925	Galena
MM-11.1[10]	Timberville	Martin	19.055	15.683	39.029	Galena
MM-11.3[10]	Timberville	Martin	19.090	15.691	39.032	Sparry Dolomite
MH-2.1[10]	Timberville	Mole Hill	18.441	15.647	38.169	Sphalerite
TW-7.1[10]	Timberville	Weatherholz	18.970	15.672	38.739	Sphalerite
VR-5.1[10]	Timberville	Vetter	19.042	15.674	38.717	Sphalerite
VR-5.2[10]	Timberville	Vetter	19.419	15.698	38.763	Sparry Dolomite
FRDMA-1[10]	Friedensville	New Hartman	17.722	15.942	37.220	Sphalerite
UB-3.1[10]	Friedensville	Ueberroth	17.760	15.475	37.293	Sphalerite
CL-5.1[10]	Friedensville	Ueberroth	18.049	15.529	37.383	Sphalerite
UB-8[10]	Friedensville	Correll	18.256	15.541	37.627	Sphalerite
CP-KY-4[10]	Nittany Arch	Keystone	18.510	15.619	38.526	Galena

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CB-KY-5[10]	Nittany Arch	Keystone	18.505	15.620	38.527	Galena
CP-SS-5[10]	Nittany Arch	Samuel Snyder	18.583	15.618	38.537	Galena
CP-SS-6[10]	Nittany Arch	Samuel Snyder	18.560	15.622	38.388	Galena
CP-SD-1[10]	Nittany Arch	Schad	18.540	15.619	38.579	Galena
CP-SD-3[10]	Nittany Arch	Schad	18.535	15.624	38.591	Sphalerite
CP-SD-5[10]	Nittany Arch	Schad	18.543	15.618	38.582	Galena
CP-SD-10[10]	Nittany Arch	Schad	18.554	15.635	38.623	Sphalerite
CP-SD-20[10]	Nittany Arch	Schad	18.534	15.614	38.585	Galena
18 [8]	IL-KY Fluorite	Fairview	20.050	15.840	39.920	Galena
19 [8]	IL-KY Fluorite	Deardor	20.220	15.890	40.110	Galena
20 [8]	IL-KY Fluorite	Hill	20.280	15.900	40.160	Galena
21 [8]	IL-KY Fluorite	Oxford	20.330	15.930	40.150	Galena
22 [8]	IL-KY Fluorite	Dyer Hill	20.360	15.890	40.100	Galena
23 [8]	IL-KY Fluorite	Rag Hill	21.010	15.960	40.640	Galena

Appendix 2: Compilation of Pb Isotope data: Pb Isotope analyses of this study[1]; Kesler et al., 1994[2]; Misra et al., 1996[3]; Hoagland, 1976[4]; Unpublished data from B. R. Doe[5]; Russell and Farquhar, 1960[6]; Crawford and Hoagland, 1968[7]; Heyl et al., 1966[8]; Goldhaber et al., 1995[9]; and Kesler et al., 1994b[10] (Cont.).

24 [8]	IL-KY Fluorite	Hicks Dome	19.910	15.800	40.560	Galena
25 [8]	IL-KY Fluorite	Dike Vein	20.700	15.980	40.510	Galena