Isotopic Identification of Multiple Contributors of Metal Ions in Mississippi Valley-Type Ore Deposits Along the Cincinnati Arch in South-Central Kentucky

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Isotopic Identification of Multiple Contributors of Metal Ions in Mississippi Valley-Type Ore Deposits Along the Cincinnati Arch in South-Central Kentucky

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

by

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Abstract

Mississippi Valley-Type (MVT) ores are economically-viable deposits of sulfide minerals, often dominated by sphalerite (zinc-sulfide) in carbonate facies, and galena (lead-sulfide) in siliciclastic facies. MVT ores precipitate from migrating fluids, which carry base metals often complexed with chlorine ions within a basinal brine. This study identifies metal-contributing source-regions of the Burkesville MVT deposit using Pb-isotope ratios within sphalerite samples collected from the Burkesville deposit. The deposit is found in south-central Kentucky within the Middle-Tennessee ore district along the crest of the Cincinnati Arch, which is the anticlinal divide between the Appalachian Basin and the Illinois Basin. Competing theories argue that MVT ores along the Cincinnati Arch were precipitated from either Appalachian or Illinois Basin brines that were mobilized during orogenic events within the Appalachian Mountains, Oachita Mountains, and/or Ozark Plateau. The orogenic events were considered concurrent with sulfide mineralization, dolomitization, and petroleum brine migration throughout the region. Ratios for $^{206}\text{Pb}/^{204}\text{Pb}$ ranged from 19.639 to 19.803, ratios for $^{207}\text{Pb}/^{204}\text{Pb}$ ranged from 15.709 to 15.806, and ratios for $^{208}\text{Pb}/^{204}\text{Pb}$ ranged from 39.294 to 39.583. Results from this study of Pb-isotopes imply that the Burkesville deposit correlates strongly with the southern Appalachian Basin, but also suggest that there were some contributions from the Illinois Basin due to brine mixing or multiple paragenetic events. Isotopic ratios were obtained via analysis with a Nu-Plasma MC-ICP-MS. These results provide an explanation to the contradictory works of previous researchers, who sought to constrain the contributing basin of the Middle Tennessee district via trace-element, crystallographic, and fluid-inclusion analyses. The current research has produced a new model for MVT ore formation near the Cincinnati Arch, in which the majority of the ore minerals precipitated from brines from the
southern Appalachian Basin, but which either mixed with or were later altered by a higher-
temperature brine originating from the Illinois Basin which contributed the higher concentrations
of Cd, Cu, Ge, and Ga observed in the district today.
Acknowledgements

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Additionally, thanks are extended to Fred Smith and Derrik Unger of NyrStar for their assistance in sample collection and for taking the time to provide mine and facility tours. Walter Graupner, Erik Pollock, and Lindsey Conaway of the University of Arkansas are thanked for their technical assistance and support with analyses over the course of the project. Del Harper and Bob Dunn are also thanked for taking an interest in the project, and for their consultations and interviews. Finally, friends and co-workers John Samuelsen, Lauren Williams, Austin Moyers, Jason Dodd, and Kaelin Groom are sincerely thanked for their assistance and provision of sanity over the last couple of years.
Dedication

This thesis is dedicated to my parents, Charles and Crystal, and to my grandparents, Jimmy and Verna-Jean. Without their encouragement and support, this endeavor would not have been possible. Thank you for everything.
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Introduction

MVT ores form when hydrothermal brines carry metal ions complexed with chlorine into sedimentary strata, and interact with aqueous S ions to precipitate sulfide minerals such as sphalerite and galena. The brines are particularly sensitive to changes in pH and temperature, with variance in either property determining the mobility of numerous metals that will form either soluble chlorine complexes or insoluble S complexes (Heinrich, 2007). Common mineral assemblages found in MVT districts include sphalerite (ZnS), galena (PbS), pyrite (FeS), fluorite (CaF₂), barite (BaSO₄), calcite (CaCO₃), aragonite (CaCO₃), dolomite (CaMg(CO₃)₂), quartz (SiO₂), and chert (SiO₂); and rarely covellite (CuS), and chalcopyrite (CuFeS₂), with trace amounts of metals such as Cu, Cd, Ga, Ge, Ag, and Fe present within the metal-bearing minerals. Less common minerals found associated with supergenetically altered MVT deposits include anglesite (PbSO₄), cerussite (PbCO₃), and hydrozincite (Zn₅(CO₃)₂(OH)₆). MVT deposits hosted within carbonate units are typically dominated by sphalerite, with Zn levels greater than Pb levels greater than Cu levels. MVT deposits hosted within siliciclastic units are typically dominated by galena, with Pb levels greater than Zn levels greater than Cu levels (Robb, 2005).

MVT deposits form at relatively low-temperature (typically less than approximately 120°C, though potentially up to 250°C) that occur in permeable sedimentary units at the point where two or more hydrothermal fluids mix (Robb, 2005; Gregg and Shelton, 2012). It is this mixing of fluids which is critical to the formation of MVT deposits. Under the low temperature conditions in which Zn and Pb are mobile with Cl in these environments, mixing with an anoxic (reduced) acidic S-rich fluid results in the breaking of the Zn-Cl and Pb-Cl bonds, and the forming of Zn-S and Pb-S bonds (Heinrich, 2007). Upon the formation of these new sulfide
bonds, the new complex is no longer soluble under the existing conditions, and precipitation of metal sulfide ores ensues (Audetat et al., 1998; Heinrich, 2007; Susak and Crerar, 1982).

The south-central KY, north-central TN, and other prominent MVT deposits throughout the central United States are often found along the margins of regional dolomitization fronts (Anderson, 1991). The process of dolomitization, whereby Mg ions from basinal brines substitute into the crystal structure of calcite is a reaction which in turn mobilizes Zn ions (Baird and Dennen, 1985; Moreira et al., 2004; Harper and Borrock, 2007; Merino and Canals, 2011; Gregg and Shelton, 2012). The Zn ions are most mobile along this diagenetic/dolomitizing front in the presence of the Mg for Ca replacement reaction, with little mobility existing in the unaltered limestone, and little unmobilized Zn remaining in the altered dolomite regime (Merino and Canals, 2011). Thus, the dolomitization reaction may be likened to a “snow plow” which pushes Zn out of a basin, and concentrates it along the “edge” of the diagenetic reaction as the brines migrate. Since the Zn is only mobilized along the edge of the front where the Mg for Ca replacement reaction is taking place, and since no sphalerite precipitation occurs until the brine encounters mobilized S, the process of dolomitization is a concentrating mechanism in which aqueous Zn is focused into a narrow band at the edge of a dolomite for calcite replacement reaction in a permeable unit.

The process of dolomitization enhances both porosity and permeability (Ohle, 1951; Baird and Dennen, 1985; Harper and Borrock, 2007; Bojiang et al., 2010; Merino and Canals, 2011). The substitution of the smaller Mg ions (approximately 0.66 Å) for the larger Ca ions (approximately 0.99 Å) distorts the crystal structure and yields newly created void spaces (a result of the loss of volume from the calcite) in which fluids may flow (Merino and Canals, 2011). This enhanced porosity is typically interconnected throughout the dolomitized region,
and is thus a permeability enhancement as well. The result is that subsequent brine pulses follow not only the pre-existing structural features such as faults and fractures, but are also able to flow through previously dolomitized units with greater ease and speed.

Gregg and Shelton (2012) describe these metal-mobilizing and MVT-precipitating fluids as being concentrated seawater that leaches metals from sedimentary units and basement rocks throughout a basin. This process has been hypothesized to be related to petroleum production and migration, and the presence of liquid petroleum and bitumen within these metal-rich basinal brines is supportive of that hypothesis (Anderson, 1991; Kessler et al., 1994; Gregg and Shelton, 2012). Along the Cincinnati Arch in south-central KY and north-central TN, paleokarst development within the upper Knox Dolostone led to the formation of solution-collapse breccia pipes, followed by a porosity-enhancing dolomitization of the carbonate host, followed by one or more periods of sulfide mineralization, roughly concurrent with the uplift of the Appalachian and Oachita Mountains, as well as karstification, brecciation, and sulfide mineralization in the southern Appalachian district (Gregg and Shelton, 2012).

The south-central Kentucky MVT ore district is primarily constrained to the upper Knox formation, which is a carbonate unit of late-Cambrian to Ordovician age. The upper Knox is partially dolomitized, with ore deposits frequently found near the contact between primary calcite and secondary dolomite throughout the unit (Anderson, 1991). Stromatolites and algal mounds are frequent throughout the unit, and are often silicified and bounded by low levels of sphalerite and pyrite (Anderson, 1991). The ore district lies near the crest of the Cincinnati Arch, which is the anticlinal divide separating the Appalachian Basin to the east from the Illinois Basin to the northwest. Furthermore, the deposits are found in the Cumberland Saddle region of the Cincinnati Arch, which is a structural low that intersects the arch roughly perpendicularly.
At the surface, the region has been heavily incised by the Cumberland River, producing a topography of steep-walled, tall valleys and narrow floodplains which tend to follow fracture patterns along the arch. In contrast, the surrounding regions to the north, west, and east form a relatively flat, well-developed karst plane that is approximately 150-200 ft. higher in elevation. The most concentrated volumes of ore within the south-central Kentucky district are found within vein-fills and solution-collapse breccia pipes, the latter of which are vertical paleokarst structures (Anderson, 1991).

The primary difference between the south-central Kentucky and north-central Tennessee deposits is the relative grade of sphalerite within the most prominent ore horizons. Both districts host all three of the primary horizons, as well as several deeper horizons, but the north-central TN mines have focused extraction efforts on the top two horizons, while the Burkesville mine in south-central KY was intended to extract from the lowest of the primary horizons. The north-central Tennessee deposits (sometimes referred to as the “Middle Tennessee District” or the “Central Tennessee District”) are mostly located within the Upper Mascot, Middle Mascot, and Lower Mascot subdivisions of the Upper Knox (Lower Ordovician) units. As illustrated in Figures 1 and 2, the south-central Kentucky MVT deposits at the Burkesville and Fountain Run sites both lie near the edge of the regional dolomitization front within the Knox Dolostone. Both sites host ore deposits that correlate stratigraphically with the rest of the north-central TN district (Anderson, 1991). In south-central KY, the horizons are identified as “A,” “B,” and “C,” with A being the shallowest horizon (Upper Mascot) and C being the deepest (Lower Mascot). In north-central TN, these same horizons are identified as the “Elmwood Horizon,” the “Gordonsville Horizon” (Middle Mascot), and the “Burkesville Horizon,” respectively. Deeper deposits within the lower units of the Kingsport Dolostone have been located via coring in both the south-central
KY and north-central TN districts, which stratigraphically correlate to MVT deposits within the east-Tennessee district of the Appalachian Basin (Anderson, 1991; F. Smith, personal communication). The Fountain Run deposit is one of the stratigraphically deeper mineralized zones.

The purpose of this study was to identify the contributing unit(s) of the metals found within the Burkesville MVT ore deposit via isotopic investigations and characterization of the bulk-geochemistry of the sphalerites. Measurements of isotopic ratios of metals such as Pb allows for a clear identification of the major contributing source region(s) for that metal, and can be considered to be a geochemical “fingerprint.” Bulk-geochemical analyses were compared to contradictory interpretations by Anderson (1991) and Bonnet (2013) on the contributing source region(s) for the district. Based on atomic absorption and spectrographic analyses on samples taken from the Burkesville mine in south-central Kentucky, Anderson (1991) concluded the metals were likely mobilized from the Appalachian Basin during the orogenic events which uplifted the Appalachian Mountains. This interpretation has been endorsed by several current workers in the north-central Tennessee district as well. A similar study by Bonnet (2013) on samples from the Gordonsville and Elmwood mines in north-central Tennessee suggested that the anomalous high levels of Ga, and Ge did not correspond to observed levels in the Appalachian Basin, and instead suggested that the ores along the Cincinnati Arch were more likely products of Illinois Basin brines. The conclusions of Bonnet (2013) are more in line with the hypotheses held by former industry workers from the Burkesville mining operations, who correlated the bulk geochemistry of the south-central Kentucky deposits with the Illinois Basin deposits.
Why Pb Isotopes?

Pb was chosen to be studied in detail due to the geochemical nature and behavior of Pb ions in MVT-forming hydrothermal solutions closely imitating that Zn and Cu. Due to its relatively large atomic mass, Pb isotopes are not significantly fractionated under the temperature, pressure, and pH conditions typical of MVT deposit formation, implying that $^{204}\text{Pb}$, $^{206}\text{Pb}$, $^{207}\text{Pb}$, and $^{208}\text{Pb}$ will all exhibit near-identical chemical behavior under these conditions (MacFarlane, 1989; Tosdal et al., 1999). In addition, numerous studies by Heyl et al. (1966), Kessler et al. (1994), and Goldhaber et al. (1995) have characterized the distinct isotopic signatures of Pb in MVT sites across the central United States. Analyses of four isotopes of Pb were performed ($^{204}\text{Pb}$, $^{206}\text{Pb}$, $^{207}\text{Pb}$, and $^{208}\text{Pb}$). $^{204}\text{Pb}$ has an average isotopic abundance of 1.4%, and is not a decay product of any radionuclides. $^{206}\text{Pb}$ has an isotopic abundance of 24.1%, and is an end-result daughter-product of the $^{238}\text{U}$ Uranium/Radium-series decay. $^{207}\text{Pb}$ has an isotopic abundance of 22.1%, and is an end-result daughter-product of the $^{235}\text{U}$ Actinium-series decay. $^{208}\text{Pb}$ has an isotopic abundance of 52.4% and is an end-result daughter-product of the $^{232}\text{Th}$ Thorium-series decay.

Zn ions in a sphalerite crystal occupy a 4-coordinated (tetrahedral) site, forming bonds of 1.84 Å in length with neighboring S ions (Klein and Dutrow, 2008). Common ions found in solid solution with Zn in sphalerite include Fe, Mn, Cd, Cu, Ga, Ge, Pb, and Ag. Pb has an ionic radius of 1.19 Å, while Zn has an ionic radius of 1.39 Å. Zn is more favorable in the tetrahedral sphalerite structure, while Pb is more favorable in the cubic galena structure, due to the small differences in their ionic radii, though both display solid solution with each other in both minerals (Klein and Dutrow, 2008). Coupled with their highly similar geochemical behaviors in
solution, as discussed in MacFarlane (1989) and Tosdal et al. (1999), the solid solution of Pb for Zn in sphalerite makes it an ideal tracer for studies of metal provenance in MVT ores.

The $^{235}$U Actinium-series decay is a lengthy chain-reaction of multiple alpha ($^4$He$^{2+}$) and beta ($e^-$) particle decays that reduces the radioactive $^{235}$U to a stable $^{207}$Pb. A similar process occurs for the production of $^{206}$Pb and $^{208}$Pb from $^{238}$U and $^{232}$Th, respectively. Figures 3, 4, and 5 depict these decay processes. $^{204}$Pb is considered primordial, with current levels of the isotope reflecting levels that were present at the Earth's formation. However, due to $^{206}$Pb, $^{207}$Pb, and $^{208}$Pb being radioactive decay products, the concentration of these isotopes within the crust has been slowly increasing since the Earth was born. Doe and Zartman (1979) proposed a model for three distinct global source-regions for each of the initial parent products of $^{206}$Pb, $^{207}$Pb, and $^{208}$Pb. They proposed that $^{238}$U, $^{235}$U, and $^{232}$Th were primarily sourced from the upper crust, lower crust, and upper mantle, with periodic tectonic processes beginning four billion years ago driving cycling from one reservoir to another. In the Doe and Zartman (1979) model, radiogenic Pb is produced in situ within igneous and sedimentary units, as $^{238}$U, $^{235}$U, and $^{232}$Th undergo various stages of decay, leading to production of $^{206}$Pb, $^{207}$Pb, and $^{208}$Pb. The older the source unit(s), the higher the levels of Pb due to additional half-lives leading to higher levels of the daughter-products. The Doe and Zartman (1979) model further explains the high levels of $^{238}$U to $^{204}$Pb in the upper crust compared to the lower crust, as the younger continental materials have not yet undergone many half-lives for the $^{238}$U. Doe and Zartman (1979) further describe a dichotomy in $^{206}$Pb and $^{207}$Pb between oceanic and continental crust, with tholeiitic basalts containing noticeably lower levels of both isotopes when compared to crust with a dominantly granitic composition, implying that continuous recycling of the younger oceanic crust plays a role in redistributing radiogenically-produced Pb.
Geologic Setting

The carbonate-hosted MVT ores of the south-central Kentucky and north-central Tennessee ore districts are predominantly sphalerite (zinc sulfide) deposits hosted in the Knox Dolostone, which lie along the crest of the Cincinnati Arch (the anticlinal divide between the Illinois Basin to the northwest, and the Appalachian Basin to the east). MVT deposits are typically identified as being carbonate (limestone or dolostone) or siliciclastic (sandstone) hosted metal-sulfide deposits that form after the deposition of the host rock (epigenetically) due to diagenetic interactions between the host units and both metal-bearing and S-bearing basinal brines forced into the region by orogenic uplift. Two camps have emerged with differing opinions on the diagenesis in the region, as well as the source of the mineralizing brines. Current industry workers believe the north-central TN and south-central KY deposits formed from metal-bearing brine migration from the Appalachian Basin (D. Unger, F. Smith, personal communications), though former industry workers from the area believe a similar process occurred with brines migrating out of the Illinois Basin (R. Dingess, B. Dunn, D. Harper, personal communications).

The primary ore horizons of the central Kentucky and central Tennessee deposits are mostly hosted in within the Knox Dolostone, a predominantly secondary dolostone unit (Kyle, 1976; Churnet, et al., 1982; Montanez and Read, 1992; Lumsden and Caudel, 2001) of late Cambrian to late Ordovician age. Mineralization is associated with paleokarst solution-collapse breccias and cavities, and along partially to fully healed fault and fracture networks (Kyle, 1976; Anderson, 1991; R. Dingess, D. Harper, R. Dunn, and F. Smith, personal communications). Both ore districts are situated on or near the crest of a regional anticlinal structure known as the
Cincinnati Arch, which divides the Illinois Basin to the northwest from the Appalachian Basin to the East.

Mining and/or exploration sites considered to be within the north-central TN district by this study include the Gordonsville, Cumberland, Elmwood, and Stonewall mines in Tennessee, the Sugar Creek deposit in Tennessee, the Burkesville mine in Kentucky, and the Fountain Run deposit in Kentucky. All sites lie on or near the sharp dolomitization contact within the upper Knox units (Mascot and Kingsport Dolostones). Deposits found within south-central KY (Burkesville and Fountain Run) tend to be hosted within the secondary dolomite facies of the Upper Knox Dolostone, while north-central TN deposits (Gordonsville, Elmwood, Sugar Creek, Stonewall, and Cumberland) are predominantly hosted within the primary-calcite facies along the regional dolomitization front (Anderson, 1991). This is a generalization, however, and both carbonate minerals can be found at many listed sites at varying depths due to the stratigraphically intertonguing nature of the diagenetic replacement reaction. Aside from the carbonate mineralogy of the host rocks, all other factors appear to be similar between the five Tennessee and two Kentucky sites. The deposits are hosted in the same sedimentary units, correlate stratigraphically, and have similar trace metal compositions (R. Dingess, personal communication).

An exploratory basement core of 5400+ ft. deep taken by the NyrStar mining company near the Gordonsville deposit in the mid-90’s revealed trace levels of sphalerite mineralization (approximately 2%) in dolomite roughly 200 ft. from the contact with igneous basement. The basement rocks themselves are found to begin at approximately 4300 ft. depth, and are dominated by rhyolite breccias and pyroclastic flows, underlain by amygdaloidal basalts. When examined with the RAMAN Microscope at Western Kentucky University, the rhyolite breccias
were shown to be cemented with dolomite, and the basalts contained dolomite amygdules; perhaps suggesting deep-flow brine circulation between the shallower MVT mineralization zones and the igneous basement.

A previous geochemical study by Anderson (1991) suggested between four and seven different diagenetic events in the south-central KY district, likely linked to the four different Appalachian orogenies, which would have forced brines out of the Appalachian Basin (and which are also responsible for the formation of the Cincinnati Arch, as well as the prevalent fracturing in the district). Evidence for this multi-stage diagenesis is observable even in hand samples, as most sphalerite crystals collected from the Burkesville deposit are dark red in coloration (much akin to sphalerites found in MVT mineralization sites of the KY-IL Fluorspar district within the southern Illinois Basin), though yellow intergrowth bands can be seen in hand sample (similar to East-TN MVT sphalerite). Samples collected from the Gordonsville and Elmwood mines in north-central TN are similar, though the TN sphalerites are predominantly black.

The Upper Knox Dolostone is composed largely of secondary dolomite, with intertonguing units of primary dolomite, limestone, and shale. It has long been suspected that dolomitizing brines are also the primary carriers of metal ions into MVT districts, thus determining the temperature and general chemistry of these dolomitizing brines can provide insights into the source(s) of metal ions in MVT districts (Baird and Denned, 1985). Previous research performed by Misra et al. (1996) and by Lumsden and Caudel, 2001 utilized different approaches to determining the paleothermometry of the Upper Knox System throughout central TN. Both studies arrived at very different results. Lumsden and Caudel (2001) employed a stable isotope approach, measuring the $\delta^{18}O$ levels at varying depths throughout the Knox
Dolostone in an undeformed tectonically-stable district in east-central Tennessee. The study site was chosen due to the undeformed nature of the area, and was thought that the oxygen isotope ratios would be representative of those within the initial dolomitizing and depositional brines responsible for the conversion of calcite to dolomite in the system. The results from Lumsden and Caudel (2001) showed fairly consistent paleothermometry data throughout the dolostone, with values ranging from 70°C to 75°C.

The research of Misra et al. (1996) focused on fluid inclusion microthermometry to determine the temperature of the brines responsible for the sphalerite mineralization in the district. Their work was conducted on sphalerite samples from the Elmwood Mine, located just south of Carthage, TN, approximately 50 miles from the Burkesville, KY deposit site. Fluid inclusion analyses require the preparation of a doubly-polished thick section (approximately 100 microns thick, with a polish on both sides of the slab), which is then placed on a heating and cooling stage microscope. Fluid inclusions which contain vapor bubbles are heated until homogenized (single-phase fluid), and the temperature at which this occurs is recorded, and represents the minimum temperature at which the fluid had to have been for minerals to precipitate from it (in order for the fluid to be trapped in a mineral assemblage, and for a vapor bubble to separate from solution). The results of Misra et al. (1996) yielded a wide range of mineralization temperatures, some near agreement with the 2001 study by Lumsden and Caudel (approximately 80°C), and some in substantial excess (up to 156°C). Similar work was attempted on Burkesville sphalerites by the author at the University of Missouri – Columbia in 2014, but failed due to multiple instrument issues and a flawed methodology.

The Knox Dolostone is a prevalent carbonate unit that is found across much of the eastern continental United States, stretching from Minnesota, to Texas, to Georgia, to
Pennsylvania, and to Michigan. The Knox is primarily a dolostone and limestone assemblage of units of Cambrian and Ordovician age, with minor shale and sandstone units occurring at various depths; sediments were mostly deposited in a shallow marine reef environment (Churnet et al., 1982; Anderson, 1991; Montanez and Read, 1992; Glumac and Walker, 1997).

Although diagenetic events within the Knox are still a topic of great debate and dispute, a study performed by Montanez and Read (1992) on a core of undeformed Knox Dolostone from east-central Tennessee suggests that the Knox was mostly deposited as limestone, with minor bands of primary dolomite occurring as a result of fresh/saline fluid mixing in intertidal zones during deposition of the sediments. The Montanez and Read (1992) study further suggested that the Knox is representative of a period of roughly 20 million years of relatively stable climatic and tectonic conditions in the region, during which only minor transgression and regression cycles occurred. Numerous fossils are found throughout the units. Stromatolites and algal mounds are prevalent, and minor traces of pyrite, chalcopyrite, and sphalerite have been observed to form within the now silicified algal mound remains. Other biotic traces of note within the unit include crinoids, brachiopods, bryozoans, corals, and various echinoderms; with bryozoans, crinoids, stromatolites, and algal mounds being the dominant fossils within the unit.

The Knox is truncated on both the upper and lower boundaries by unconformities, which serve as hydrocarbon and brine traps, preventing upward migration and restricting fluid migration to lateral movement (Anderson, 1991). The Cincinnati Arch (which strikes northeast to southwest) is itself folded in central Kentucky (roughly striking west to east), to form the structural low known as the Cumberland Saddle. The additional folding resulted in a structural high near present-day central Kentucky, along which the crest of the arch has been eroded, and allows for fluids from lower units within the Knox to migrate directly into stratigraphically
higher and younger units such as the Wells Creek formation and Lexington Limestone (Baird and Dennen, 1985).

Figure 6 illustrates the stratigraphy of central Kentucky along the Cincinnati Arch. Not shown are the brecciated rhyolites and basalt flows observed in the Gordonsville basement core, which begin at a depth of approximately 4900 ft. The granite basement is mostly overlain by interbedded sandstones, basalt flows, and rhyolite flows which are potentially of relation to the CAMP large igneous province to the south and the St. Francois rhyolite province to the north (Ericksson et al., 2003; Bedel and van der Lee, 2006). The igneous and metamorphic basement is then overlain by predominantly carbonate units, with sandstone and shale interbedded of Cambrian and Ordovician ages (inclusive of the Knox Dolostone and two major unconformities). Atop the latter unconformity rests the Chattanooga Shale, which is a fluid trap that serves to isolate the brines and hydrocarbons within the Knox from overlying sediments, except in central Kentucky where this barrier has been mostly eroded away north of the Cumberland Saddle (Baird and Dennen, 1985; Anderson, 1991). The Chattanooga Shale is a potential S source for MVT deposits of the south-central KY and north-central TN districts, as it is an organic-rich black shale known for a high S content, as well as being a low-grade uranium ore. Further up into the stratigraphic column, one begins to encounter mostly limestone units, with some interbedded shale, rising up into the Mississippian and Pennsylvanian units which outcrop at the surface throughout both states. Of these units, the St. Louis, Ste. Genevieve, and Girkin are perhaps the most famous for cave formations such as Mammoth Cave and Lost River Cave. Although these particular units do not host economic mineralization, similar units within the Knox are also karstified, which has resulted in solution-collapse breccia features that are among the most productive mineralized zones within the Knox (Anderson, 1991). Within the
Pennsylvanian, coal beds begin to show up in the record, and above that most units have been eroded away or are exposed at the surface.

Each primary ore horizon within the south-central KY and north-central TN districts are dominated by solution-collapse breccia and vein-fill sphalerite mineralization. Smaller horizons do exist above, below, and between the primaries, and appear to be of varying genesis due to formational relics such as color, crystal size, and degree of “fracture healing” (F. Smith, personal communication). A core taken by the NyrStar mining company near the Gordonsville Mine operation to a depth of approximately 5400 feet revealed that MVT mineralization occurs even near the igneous basement, where a 20 foot interval of translucent yellow sphalerite can be found 200 ft. above the contact between a metamorphosed sandstone unit and a basalt flow. The NyrStar company currently only mines from the shallower, richer, and more voluminous Elmwood and Gordonsville horizons, though the Burkesville horizon has been explored in several sites (Anderson, 1991; D. Unger, F. Smith, D. Harper, personal communications). The Burkesville horizon was exclusively mined at the Burkesville, KY mine despite the present Elmwood and Gordonsville horizons having thicker, higher-grade ore reserves. The mine was jointly opened and operated by Cominco American and ASARCO in the 1970’s, but closed shortly after beginning operation with no commercial production (Anderson, 1991).

Most MVT deposits are a product of orogenic tectonic events, which increase the pressure head on a carbonate system and force interstitial brines carrying dissolved Zn and Pb (complexed with Cl) into adjacent basins (Robb, 2005). Though much work remains to be done in the south-central KY and north-central TN districts, and no extensive study of each known deposit and each ore horizon has been carried out, previous work by Anderson (1991), and by Baird and Dennen (1985) each suggest that the Zn and Pb within the north-central TN and south-
central KY deposits were carried into the region by migrating oil-field brines from the Appalachian Basin. Their models propose that the fluids were mobilized as a result of the four major Appalachian orogenic events. These models are consistent with the work of Anderson (1991), Montanez and Read (1992), and Lumsden and Caudel (2001), who each report between three and seven diagenetic events apparent within the Knox Group sediments. Additional work performed by Bonnet (2013) on sphalerites collected from the Gordonsville, Elmwood, and Cumberland mines found unusually high levels of Cd, Ga, and Ge within the north-central TN sphalerites, which did not align with values that would be expected based on current understanding of hydrothermal conditions which Pb to MVT deposit formation. Bonnet (2013) measured levels of Cd to be 2505.9 ppm, Ga to be 536.4 ppm, and Ge to be 307.8 ppm in sphalerite samples from the north-central Tennessee district. For Cd, with was a slight decrease from the eastern Tennessee district levels, but Ga and Ge levels were both highly elevated, comparable to levels in Illinois Basin sphalerite deposits.

Furthermore, these orogenic events coincide with the timing of the deposit formation and the creation of the Cincinnati Arch itself, which was also a relic of the continent-continent collisional events which uplifted the Appalachian Mountains and deformed the eastern edge of North America (Anderson, 1991). The folding associated with the arch is accredited with the heavy fracturing and mild faulting observed along and near the crest of the arch. It is along these structural weak points that much of the karst dissolution and ore mineralization is observed throughout the region. Vein-fills (sometimes referred to as “fracture heals”) are the 2nd most common form of ore mineralization in the region, and host the lesser ore horizons (Anderson, 1991).
In the case of the south-central KY and north-central TN districts, evidence suggests that subsequent pulses of fluids from the Appalachian Basin followed this exact trend, pushing aqueous Zn further out into the basin and ultimately to the Cincinnati Arch with each successive dolomitization event, with later pulses following and expanding the extent of the first, resulting in a progressive dolomitization front, and a region along the front highly concentrated in Zn (Baird and Dennen, 1985; Harper and Borrock, 1985; Anderson, 1991). Figure 2 illustrates the concentration of ore deposits along a dolomitization front in the Upper Knox formation along the Cincinnati Arch.
Methodologies

Samples were collected from the now-abandoned Burkesville mine site in south-central KY from tailings piles left on site after abandoned mining operations. All samples with visible sphalerite were collected. Only samples that were not visibly oxidized were further processed, due to potential fractionation of Zn, Cu, and Pb ions during alteration. Chosen samples were labeled and photographed before being mechanically separated/destroyed. To separate sphalerite grains, samples were wrapped in multiple layers of aluminum foil and paper towels, and struck with a hammer on a steel anvil. To reduce potential for contamination, the anvil was also layered with foil and paper towels, and wrappings were changed if they ripped during the separation process. Crushed samples were then sorted through, and “fresh” (non-oxidized, clean) samples of sphalerite were removed and stored in a clean, labeled envelope. Remaining sample material was stored for future use, if desired. 37 usable samples from the Burkesville deposit were separated in total, as well as two unknowns donated from a private collection but initially believed to be from the Burkesville mine. Figure 7 includes images of cleaned samples from the Burkesville mine tailings pile (as well as one unknown) used in this study.

Of the first batch of 12 samples, 400mg (+/- 1 mg) of sphalerite was weighed out for dissolution in the class-100 clean lab at the University of Arkansas. 13 more were weighed out for 200mg (+/- 1 mg) of material, when available. The final batch of 14 samples were also weighed out to be 200mg (+/- 1 mg) of material. These 39 samples were placed in labeled teflon vials, and dissolved using a mixture of 2mL 20% HNO₃(aq), 2mL 6N HCl(aq), and 2mL 1N HBr(aq). Different mixtures and concentrations of acids were attempted throughout the study, but the above mixture was found to be optimal. Initially, it was found that over-application of nitric acid would lead to the precipitation of a nitrate foam upon drying that inhibited further
dissolution. The foam is best dissolved by using a more dilute acid (adding additional triple-distilled water), particularly if little or no nitric acid is reapplied. It was also found that samples could be easily dissolved in concentrated nitric acid with no other additives if left for several days on the hot plate, but nitrate precipitation would still occur. Complete dissolution was not possible without the nitric acid, however. It was found that dissolution would occur quicker and more completely if vials were left capped while on the hot plate. Once the optimal acid mixture was applied to the samples, vials were left on a hot plate at 150-200°F for several days, until samples were mostly dissolved. It was not necessary to fully dissolve samples for isotopic analyses, as minimal fractionation of the ions of interest occurs during the dissolution process; therefore the isotopic ratios of Zn, Cu, and Pb in the product fluid should reflect the same ratios within the sphalerite crystals.

Following dissolution, the sample vials were dried completely, and the precipitate was redissolved with 2mL of 1N HBr(aq), then dried again, a total of three times to remove any excess nitric and hydrochloric acids. Afterward, the samples were again dissolved in 2mL of hydrobromic acid, and 1.5mL of solution was pipetted into centrifuge tubes, with effort being made to minimize particulate material being placed into the tubes. The tubes were placed in a centrifuge for 15 minutes, rotated 180°, and centrifuged for an additional 15 minutes. 1mL of solution was then pipetted out of the centrifuge tubes (with all sediment avoided, due to being concentrated at the bottom of the centrifuge tube) and loaded into ion exchange columns at the appropriate stage. The columns that were initially used for Pb-ion separation were 5mL syringes, with plungers removed. Custom-made teflon columns were produced and used for the final 14 samples. Porous teflon frits were cut and placed in the bottom of the columns to serve as a flow-control filter as the fluids loaded into the columns drained via gravity-drip. Prior to
loading of samples, columns were loaded with 130μL of Dowex 1X8 100-200 mesh ion-exchange organic resin, rinsed with triple-distilled water, and rinsed multiple times with 6N HCl(aq). Following the rinse, the sample solution was loaded into the columns and allowed to drip to completion. Clean teflon vials were placed beneath the columns to collect the residual fluid, known as “wash.” Sample was then rinsed further with three 1mL pulses of 1N HBr(aq). Wash has been collected, labeled, and stored for future metal (Zn and Cu) separation and isotopic analyses. A new clean teflon vial was then placed beneath the columns, and the columns were rinsed with 1mL of 20% HNO₃(aq) to collect the Pb ions from the resin. Collected Pb solution was then dried and stored in an air-tight container until ready for analysis.

For analyses, separated Pb fractions were dissolved in 2% nitric acid and spiked with a thallium internal standard. The solution was then analyzed using the University of Arkansas’s Nu-Plasma multi-collector inductively-coupled plasma mass spectrometer (MC-ICP-MS). Multiple runs of a pre-prepared standard were analyzed initially to “tune” the instrument to provide optimal results. Once properly tuned, samples were analyzed using a standard-sample-standard bracketing method, whereby the initial analysis is of a standard, followed by three analyses of samples, followed by another standard analysis. This is done to account for machine drift, and allow for retuning of the machine, should the need arise. The first 25 samples were analyzed for Pb isotopes over the course of two days, and all but the first two analyses were deemed usable (bracketed standard runs on the first two samples were outside the range of acceptable values). The final 14 samples were analyzed in a single day several weeks later, and no variance between the spread of the data points from day-to-day has been observed.

The only alteration in methodology that was performed for the final 14 Pb samples was a replacement of the polypropylene columns with custom-designed teflon columns. Excess
material from 12 of the samples, including one of the unknowns, has been dissolved for major, minor, and trace metal geochemistry, but has not been processed or analyzed. Bulk-geochemistry dissolution was performed by applying 2mL of concentrated nitric acid to each sample, capping the vial, and placing the vials on a hot plate at 150°C for 4 days. Bulk geochemical analyses were proposed to be carried out utilizing the quadrupole mass-spectrometer at the University of Arkansas, but were not completed due to technical difficulties and time constraints.

Additional samples collected from the Gordonsville and Elmwood sites are currently being analyzed by undergraduate researchers at Western Kentucky University under the direction of Dr. Andrew Wulff. Students at WKU are using non-destructive bulk geochemistry techniques such as RAMAN Microscopy and single-crystal X-Ray Diffractometry (XRD) to determine the trace metal assemblages of the sphalerites.

Once analyses were complete, the datasets were corrected by converting measured bracketing standards to the actual values, and applying the same correction factors to the bracketed sample runs. Values were plotted on scatter plots to display the ranges of values for the samples. Values from additional studies by, Heyl et al. (1966), Kesler et al. (1994), and Goldhaber et al. (1995) were also plotted, and generalized fields of expected values for each major ore district were determined. Standard deviation values were calculated from the bracketing standards that were utilized. Additionally, average Pb evolution curves were plotted using data from Stacey and Kramers (1975).
Results

The spread of Pb-isotope ranges from Burkesville sphalerite samples are shown in Figures 8 and 9. Approximate ratios for $^{206}\text{Pb}/^{204}\text{Pb}$ ranged from 19.639 to 19.803, approximate ratios for $^{207}\text{Pb}/^{204}\text{Pb}$ ranged from 15.709 to 15.806, and approximate ratios for $^{208}\text{Pb}/^{204}\text{Pb}$ ranged from 39.294 to 39.583. One outlier point exists within the current dataset, and represents the range of values from the sample Unknown #2. Both Unknown #1 and #2 were donated to the project from a private collection, and previously belonged to an individual that had worked at the Burkesville Mine during its brief period of operation.

Visible in Figures 10, 11, 12, and 13 are the average Pb evolution curves from Stacey and Kramers (1975). Figures 8 and 9 show only data from the Burkesville study, and exclude the one outlier point from Unknown #2. The error bars shown each represent two standard deviations, and illustrate the tight constraint of the current dataset.

As illustrated in Figures 10, 11, 12, and 13, samples from the Burkesville site are enriched with radiogenic Pb ($^{206}\text{Pb}$, $^{207}\text{Pb}$, and $^{208}\text{Pb}$) relative to the average abundances from Stacey and Kramers (1975). The $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ levels appear to be roughly in line with an extension of the average Pb growth curve from Stacey and Kramers (1975), with approximate enrichments of approximately +5% and +2%, respectively. However, the $^{207}\text{Pb}/^{204}\text{Pb}$ levels are enriched to a much greater degree than the Stacey and Kramers (1975) trend. Although the $^{207}\text{Pb}/^{204}\text{Pb}$ enrichment is only approximately +1%, the analytically-determined values for the Burkesville site show levels much greater than would be expected if the enrichment curves were to be extended. This is indicative of a $^{235}\text{U}$-rich source for the Pb found within the deposit, as $^{207}\text{Pb}$ is a daughter product of the $^{235}\text{U}$ Actinium-series decay.
Discussion

Previous studies of central Tennessee and central Kentucky deposits suggest that hydrocarbons accompanied by basinal brines bearing dissolved Zn, Pb, and other trace metals were mobilized by the Appalachian orogenies and traversed the Appalachian Basin until arriving at the Cincinnati Arch (Anderson, 1991; Baird and Dennen, 1985). Previous S isotope research has suggested that the S-rich brines originated from the Illinois Basin (Appold et al., 1995). All three ratios of Pb isotopes within sphalerites from the Burkesville ore deposit in south-central KY show that the district plots within the southern-Appalachian field. Figures 12 and 13 illustrate generalized ranges of values for multiple ore districts across central North America, based on data collected from numerous studies by Heyl et al. (1966), Kessler et al. (1994), and Goldhaber et al. (1995). Although clearly within the southern-Appalachian field, the samples seem to plot consistently near the edge of that field, with apparent shift toward the Illinois-Kentucky Fluorspar district (also possible would be the Old Lead Belt or Viburnum Trend districts). This result would seem to suggest a minor degree of mixing of fluids between the two basins along the dividing Cincinnati Arch. If isotopic signatures from all three metals (Pb, Cu, Zn) suggest the same conclusion once a more robust dataset for Cu and Zn isotopes in MVT deposits can be compiled, then concentrations of assorted metals at the major, minor, and trace levels should be usable as a tool for determining the percentage of contribution that each brine made to the overall sulfide complex (effectively, the extent of mixing between the basinal brines along the Cincinnati Arch).

Figures 10 and 11 include the data collected by Austin Moyers (2015) on Elmwood mine samples from north-central TN and Young mine samples from eastern TN. The samples from Moyers (2015) were prepared in the clean lab and analyzed with the MC-ICP-MS at the
University of Arkansas, using the same equipment and techniques implemented during this study. Moyers’s dataset from the Young mine samples showed a clear southern-Appalachian Basin signature, though the Elmwood mine samples showed considerable scatter. It is suspected that instrumentation error resulted in the scatter (Austin Moyers and Adriana Potra, personal communication, 2015). Of note is that if the Elmwood mine samples are geochemically and isotopically comparable to the Burkesville samples as is proposed in this study, then averaging the values from Moyers’s dataset yields values very close to the analytically-determined Burkesville ratios.

Potential regional sources of $^{235}\text{U}$ that could have produced enriched levels of $^{207}\text{Pb}$ include sedimentary basement units from either the Appalachian or Illinois basins, which would host brines hypothesized to be concentrated sea-waters (Swanson, 1961), basement rocks of granitic/rhyolitic composition which are genetically related to the St. Francois rhyolites of eastern MO (F. Smith, personal communication), or the overlying Chattanooga Shale (Glover, 1959; Swanson, 1961). The Chattanooga Shale is black shale and a low-grade uranium ore of Devonian age which overlies the bounding unconformity of the Knox Group in south-central Kentucky and north-central Tennessee. Unfortunately, the Pb-isotope ratios of the underlying rhyolite and overlying shale units have not yet been characterized, so a contributing source unit for the extra $^{207}\text{Pb}$ cannot currently be determined with certainty.

Although MVT deposits are typically not considered to be directly related to igneous source rocks (Robb, 2005), more recent studies have set a precedent for this possibility. Studies by Crocetti et al. (1988) and Goldhaber et al. (1995) on the Viburnum Trend galena ores bodies suggested that the MVT ore district within south-eastern MO appears to have been deposited by an oil field brine (as discussed in Robb, 2005), but also suggests that the Pb within the ores was
leached from igneous basement rocks of both felsic and mafic composition. Crocetti et al. (1988) names the nearby St. Francois rhyolite as the likely contributor, and describes the igneous basement of the region as being mostly felsic in composition, with both intrusive and extrusive bodies, and notes the presence of several mafic intrusions as well. Not only does the set a precedent for metallic contributions of igneous units to MVT deposits through leaching by oil-field brines, this sets a precedent for metallic contributions of the igneous St. Francois rhyolite to MVT deposits. This is of particular interest, as the St. Francois rhyolite has been observed underlying the north-central TN MVT district in the basement core taken by NyrStar near the Gordonsville Mine. Furthermore, the rhyolite was heavily brecciated and cemented with dolomite, adding to the evidence that dolomitizing and metal-bearing basinal brines did encounter and chemically interact with the underlying igneous units near the crest of the Cincinnati Arch.

It should be noted that preliminary results from an unpublished bulk-geochemical study by Garmon and Wulff using a laser-ablation inductively-coupled plasma mass-spectrometer (LA-ICP-MS) at the University of Missouri – Columbia on the Kentucky Geological Survey CA-225 core did not show any detectable levels of U in a sphalerite vein deposit. Since the Chattanooga Shale still contains trace levels of U in present-day, and due to its geochemical nature of mimicking the behavior of S, the non-detection of U in the Burkesville sphalerite ore deposit may indicate that the Chattanooga Shale contributed neither metals nor S to the MVT deposit. It is worth noting that even though the U levels within the Chattanooga Shale are “trace,” they are still substantially elevated over average crustal abundances, and it is thus considered a low-grade U ore.
Additional ions of interest identified in the unpublished 2014 study by Garmon and Wulff included, in order of greatest abundance, Zn, Cd, Cu, Ge, Pd, Ga, Fe, Al, Ag, and Pb. The relatively high abundance of Cd and Cu was of particular interest, due to the tendency of these ions to resist dissolution and mobilization in MVT regimes, except under relatively high temperature conditions. This result seems to be in agreement with the fluid inclusion works of Misra, Gratz, and Lu (1996), which identified mineralization temperatures in excess of 150°C within the north-central TN district.

The high levels of Ge and Ga are also of particular interest. In his 1991 Kentucky Geological Survey report, Anderson (1991) uses trace element analyses conducted via atomic absorption and spectrography on cores taken near the Burkesville mine of south-central KY, and identifies elevated levels of Cd (0.246%), Ga (0.016%), and Ge (0.019%). Anderson (1991) also levels of In at 79.6 ppm in one analyzed core, and observed lower levels of Cd in the same sample, concluding that In was substituting for Cd in solid-solution at that particular location. Bonnet (2013) performed a similar study on samples retrieved from the Gordonsville and Elmwood mines of north-central Tennessee and found levels of Cd to be 2505.9 ppm (approximately 0.251%), Ga to be 236.4 ppm (0.024%), and Ge to be 307.8 ppm (0.031%). Bonnet (2013) concluded that levels were similar to concentrations found in ores from the KY-IL Fluorspar district, which far exceeded levels found in the Appalachian Basin deposits. Bonnet (2013) also found that Fe levels were greatly suppressed in the north-central Tennessee district, as was shown in the unpublished Garmon and Wulff dataset. The deficit of Fe was an unexpected find, since sphalerite ores analyzed by Bonnet (2013) were mostly of a reddish coloration, and red sphalerites normally acquire their color through an Fe surplus. Bonnet’s 2013 findings and interpretations were in agreement with the opinions and findings of previous
industry workers in the south-central Kentucky district, who argued that the elevated levels of Ge, Ga, and other trace metals in MVT deposits along the Cincinnati Arch closely resembled those of the Illinois Basin deposits, and were indicative of a common origin (R. Dingess, personal communication).

However, the isotopic data gathered on the Pb from the Burkesville deposit does not wholly support this hypothesis. As illustrated in Figures 12 and 13, ores analyzed from the Burkesville mine of south-central Kentucky during this study, as well as the ores analyzed by Moyers (2015) from the Elmwood mine of north-central Tennesse exhibit much stronger correlation to the Appalachian Basin (particularly the southern Appalachian Basin) than to the Illinois Basin. Based on the results from Heyl et al. (1966), Kessler et al. (1994), and Goldhaber et al. (1995), Pb originating from the Appalachian Basin would exhibit isotopic ratio ranges of 17.722 to 21.933 for \(^{206}\text{Pb}/^{204}\text{Pb}\), 15.475 to 15.810 for \(^{207}\text{Pb}/^{204}\text{Pb}\), and 37.220 to 39.678 for \(^{208}\text{Pb}/^{204}\text{Pb}\). From the same studies by Heyl et al. (1966), Kessler et al. (1994), and Goldhaber et al. (1995), it has been determined that Illinois Basin and Ozark Plateau deposits (which include the KY-IL Fluorspar district, the Old Lead Belt, the Viburnum Trend, the Central Missouri district, and the Tri-State district) would have expected values of 19.910 to 22.576 for \(^{206}\text{Pb}/^{204}\text{Pb}\), 15.800 to 16.045 for \(^{207}\text{Pb}/^{204}\text{Pb}\), and 39.283 to 41.694 for \(^{208}\text{Pb}/^{204}\text{Pb}\). Actual values determined for the Burkesville deposit along the Cincinnati Arch (excluding the outlier values from Unknown #2) ranged from 19.639 to 19.803 for \(^{206}\text{Pb}/^{204}\text{Pb}\), 15.709 to 15.806 for \(^{207}\text{Pb}/^{204}\text{Pb}\), and 39.294 to 39.583 for \(^{208}\text{Pb}/^{204}\text{Pb}\). These values place the Burkesville deposit within the range of expected values for an Appalachian Basin source, not for the Illinois Basin or Ozark Plateau. However, it should be noted that some measured values from the Burkesville
samples plot near the extreme of known ranges for the Appalachian Basin source, and appear to demonstrate a shift toward either the Illinois Basin or Ozark Plateau ranges.

In addition to the broad source regions of the Appalachian Basin and Illinois Basin, six distinct regions were selected for comparison throughout this study. The Appalachian Basin was split into the Southern Appalachian and Central Appalachian fields. The Central Appalachian Field also included data from the Appalachian Valley. The Illinois Basin and Ozark Plateau was subdivided into the Old Pb Belt and Viburnum Trend, The KY-IL Fluorspar District, and the Central MO and Tri-State District. The Upper MVT District was defined as the region of ore deposits near the IA-WI-IL triple border. The studies of Heyl et al. (1966), Kessler et al. (1994), and Goldhaber et al. (1995) were combined to establish $^{206}\text{Pb}/^{204}\text{Pb}$ ranges of 18.501 to 21.933 for the Southern Appalachian District, 17.722 to 19.551 for the Central Appalachian District, 19.910 to 21.010 for the KY-IL Fluorspar District, 20.066 to 21.600 for the Old Pb Belt, 20.435 to 21.943 for the Viburnum Trend, 21.910 to 22.190 for the Central MO District, 21.901 to 22.210 for the Tri-State District, and 20.830 to 24.440 for the Upper MVT District. Heyl et al. (1966), Kessler et al. (1994), and Goldhaber et al. (1995) were also used to establish $^{207}\text{Pb}/^{204}\text{Pb}$ ranges of 15.644 to 15.832 for the Southern Appalachian District, 17.760 to 15.727 for the Central Appalachian District, 15.800 to 15.980 for the KY-IL Fluorspar District, 15.765 to 15.926 for the Old Pb Belt, 15.817 to 16.045 for the Viburnum Trend, 15.910 to 15.973 for the Central MO District, 15.920 to 15.960 for the Tri-State District, and 16.060 to 16.330 for the Upper MVT District. Finally, Heyl et al. (1966), Kessler et al. (1994), and Goldhaber et al. (1995) were used to define $^{208}\text{Pb}/^{204}\text{Pb}$ ranges of 37.985 to 39.618 for the Southern Appalachian District, 37.220 to 39.032 for the Central Appalachian District, 39.920 to 40.640 for the KY-IL Fluorspar District, 39.143 to 40.824 for the Old Pb Belt, 39.283 to 40.801 for the Viburnum
Trend, 40.970 to 40.190 for the Central MO District, 41.072 to 41.330 for the Tri-State District, and 40.450 to 43.950 for the Upper MVT District.

Outlier points from the Heyl et al. (1966), Kessler et al. (1994), and Goldhaber et al. (1995) were not included when defining ranges of values for the selected ore districts, as illustrated in Figures 12 and 13. Outliers were most common in the Southern Appalachian District dataset from Kesler et al. (1994), with $^{206}\text{Pb} / ^{204}\text{Pb}$ and $^{207}\text{Pb} / ^{204}\text{Pb}$ values as high as 23.472 and 16.166, respectively. The cause of multiple outlier points from the typically less-radiogenic Southern Appalachian District extending far into the highly-radiogenic Upper MVT District field is currently unknown.

If the outlier data point for Unknown-2 is omitted, the only range that the Burkesville dataset plots entirely within for all three ratios is the Southern Appalachian District. Values for $^{206}\text{Pb} / ^{204}\text{Pb}$, $^{207}\text{Pb} / ^{204}\text{Pb}$, and $^{208}\text{Pb} / ^{204}\text{Pb}$ for sample Unknown-2 were 20.155, 15.735, and 39.250, respectively. Interestingly, none of the defined fields fully satisfy the range of values observed in Unknown-2, though it does appear to correlate more strongly with the Old Pb Belt and Viburnum Trend districts than any other regions.

An additional oddity in the bulk geochemical data was the relatively high concentration of Pd observed in the Burkesville ores in the unpublished 2014 Garmon and Wulff study. Pd is a platinum-group element (PGE) commonly only observed in or near igneous bodies due to a lack of ionic mobility in relatively cool hydrothermal environments. Replication of the 2014 unpublished study by Garmon and Wulff using total dissolution methods and a quadrupole mass spectrometer at the University of Arkansas was sought to determine exact concentrations of major, minor, and trace metals within the Burkesville sphalerites, but has not been completed.
The LA-ICP-MS analyses performed at the University of Missouri were also capable of illustrating a qualitative difference between the different zones of the Burkesville sphalerites. A doubly-polished thick-section of a reddish-orange sphalerite exhibiting a prominent yellow intergrowth band was analyzed in the study, with a prominent chemical dichotomy emerging between the two zones of coloration. Ge levels were highly elevated in the orange zones, but sharply dropped off in the yellow intergrowth bands. The opposite was true for Ga, which was much more abundant in the yellow bands. A single black sphalerite crystal was analyzed, which had almost negligible levels of both Ga and Ge, but was slightly enriched with Fe with respect to any other analyzed locations. Cu levels were also slightly higher in the reddish-orange regions. Although primary and secondary fluid inclusions were observed throughout the section, they were most abundant within the yellow intergrowth band. The intergrowth band has been hypothesized to form from either a period of late-stage fluid mixing or from a “crystal poisoning” effect that occurred as the sphalerite crystals grew throughout the paragenetic process, but no conclusions have yet been drawn due to lack of additional data.
Conclusions

The south-central Kentucky and north-central Tennessee MVT ore deposits are complicated ore districts. The region has undergone numerous diagenetic events since the deposition of the Knox Group, including dolomitization and silicification events. Additionally, the formation of MVT deposits calls for the mixing of additional fluids, often including a metal-rich basinal brine or oil and a S-rich fluid (which would have interacted with the carbonate units via dissolution). That particular model assumes only a single source for the metal ions, though. The lack of high concentrations of Ga and Ge ions in the Appalachian Basin led former industry workers in the region (as well as current researchers such as Bonnet) to conclude that MVT deposits along the Cincinnati Arch were sourced from the Illinois Basin or Ozark Plateau during the uplift of the Ozark Plateau or during the Oachita Orogeny. The evidence for multi-stage diagenesis in the host units, the direction of propagation of the dolomitization of the Knox Group, the multiple pulses of fluid from the four major Appalachian orogenies, and crystallographic similarities with eastern Tennessee MVT ores has led current industry workers (and previous researchers such as Anderson) to argue in favor of an Appalachian Basin source for the metal ions now mineralized within the deposits.

Now equipped with isotopic data on the Pb ions present in the ore, a new hypothesis can be proposed for MVT paragenesis along the Cincinnati Arch that unifies the two previously competing hypotheses. Pb isotopes analyzed from sphalerite samples collected from the Burkesville mine confirm an Appalachian Basin source for the majority of Pb ions in the deposit. Due to the geochemical behaviors of Pb and Zn ions being largely comparable, it can be reasonably inferred that the Zn (the primary metallic constituent of the ore deposit) is also mostly derived from the Appalachian Basin (mobilized during orogenic events). However, the same
isotopic dataset does show some evidence of fluid mixing between the Illinois and Appalachian basins along the Cincinnati Arch that divides them. This evidence is the first of its kind for the region, and provides a potential mechanism of unifying the two the hypotheses. A new explanation emerges when the Pb-isotope results are combined with the bulk geochemical evidence of Misra, Gratz, and Lu (1996), Bonnet (2013), and previous industry workers such as Rick Dingess. Elevated levels of minor and trace elements such as Cd, Cu, Ge, and Ga not observed in the Appalachian Basin but prominent in the Illinois Basin and Ozark Plateau can now be explained by fluid-mixing between the two source regions, and/or by post-depositional higher-temperature hydrothermal alteration of an Appalachian Basin derived ore body via Illinois Basin or Ozark Plateau derived hydrothermal brines.

Furthermore, if completed, a published record of the Zn, Cd, Cu, Ge, Ga, Al, Fe, Ag, and Pb levels from the Burkesville deposit could be compared to the results of Bonnet (2013) to make the first quantitative case for either the reconciliation or division of the south-central Kentucky and north-central Tennessee districts. No hard argument has yet been made in the literature for either action due to the lack of published research done on the Burkesville MVT deposit, and the lumping or splitting of the two regions is often done at the discretion of the author (despite the same ore horizons occurring in the same stratigraphic units along the same structural and diagenetic features in a relatively small geographic area). A repetition of Moyers’s work on the Elmwood deposit (preferably with inclusion of samples from the Gordonsville deposit) would also be necessary, to ensure that isotopic data was also capable of being correlated between each site. Confirmation of the Pd anomaly within the Burkesville deposit would also be of extreme interest, as it would be a strong indication of ion exchange from the relatively shallow igneous basement and the Knox Group ore bodies along the
Cincinnati Arch (perhaps indicating three contributing source regions to the deposits, or replacing the Illinois Basin or Ozark Plateau source with an igneous basement source). The shallowest igneous body in the region is the St. Francois rhyolite, which is considered a potential ion source for MVT deposits in the Illinois Basin and Ozark Plateau. This would be in addition to the circumstantial evidence of dolomite cements within the fractured igneous basement, the higher-temperature formation of the north-central Tennessee and south-central Kentucky ores, and the high concentrations of Cd and Cu observed in and near deposits along the Cincinnati Arch.
Figure 1: Dolomitization fronts within the Knox Group carbonate and their relation to MVT ore districts (after Harper and Borrok, 2007). Shaded regions represent areas within the Knox that have undergone dolomite-for-calcite replacement. The specific study area of the current project is shown within the boxed region incorporating the north-central TN and south-central KY districts.
Figure 2: The south-central KY and north-central TN MVT ore districts in relation to the Knox dolomitization front (after Harper and Borrok, 2007). Dolomitized regions of the upper Knox are shown shaded. Prominent deposits (greater that 8% sphalerite), as determined by coring, are outlined with major deposits and mine shafts labeled.
Figure 3: $^{238}\text{U}$ to $^{206}\text{Pb}$ Uranium/Radium-series decay chain. Relevant atomic numbers and elemental symbols are shown along the x-axis, while the relevant atomic masses are shown within the markers. Alpha decays (emission of a $^4\text{He}^{2+}$ ion) are represented by an “α” symbol. Beta decays (emission of an e$^-$ particle) are represented by a “β” symbol.
Figure 4: $^{235}\text{U}$ to $^{207}\text{Pb}$ Actinium-series decay chain. Relevant atomic numbers and elemental symbols are shown along the x-axis, while the relevant atomic masses are shown within the markers. Alpha decays (emission of a $^4\text{He}^{2+}$ ion) are represented by an “α” symbol. Beta decays (emission of an $e^-$ particle) are represented by a “β” symbol.
Figure 5: $^{232}$Th to $^{208}$Pb Thorium-series decay chain. Relevant atomic numbers and elemental symbols are shown along the x-axis, while the relevant atomic masses are shown within the markers. Alpha decays (emission of a $^4\text{He}^{2+}$ ion) are represented by an “α” symbol. Beta decays (emission of an $\text{e}^-$ particle) are represented by a “β” symbol.
Figure 6: Generalized stratigraphy of ore-bearing horizons in the Upper Knox Dolostone in south-central KY (after Anderson, 1991). The A-horizon (Elmwood horizon) runs from the top of the Knox to the M-5 marker bed. The B-horizon (Gordonsville horizon) runs from the M-5 to the D-Wispy marker bed. The C-horizon (Burkesville horizon) begins at the D-Wispy marker and continues to the TR marker. Not pictured: The Fountain Run horizon found within the Kingsport Dolostone.
Figure 7: Select samples analyzed in the current study. Pictured are dolomite and calcite hosted sphalerite ore samples collected from tailings piles on-site at the Burkesville mine, as well as one unknown donated from a private collection thought to have originated from the site. Picture are samples BV-TP-2-1, BV-TP-2-3, BV-TP-2-5, and BV-Unknown-2. Following Pb-isotope ratio analyses, it has been determined that sample BV-Unknown-2 did not originate from the Burkesville mine, and is instead thought to have been collected from a mine in either the Old Pb Belt or Viburnum Trend within the Ozark Plateau.
Figure 8: $^{208}\text{Pb} / ^{204}\text{Pb}$ vs. $^{206}\text{Pb} / ^{204}\text{Pb}$ and $^{207}\text{Pb} / ^{204}\text{Pb}$ vs. $^{206}\text{Pb} / ^{204}\text{Pb}$ ratios measured for 36 samples collected from the Burkesville MVT deposit. Error bars illustrate two standard deviation ranges computed for the dataset.
Figure 9: $^{208}\text{Pb}/^{204}\text{Pb}$ vs. $^{207}\text{Pb}/^{204}\text{Pb}$ ratios measured for 36 samples collected from the Burkesville MVT deposit. Error bars illustrate two standard deviation ranges computed for the dataset.
Figure 10: Comparison of $^{208}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ ratios from the Burkesville, KY deposit to data from Moyers (2015) on the Young Mine in eastern TN (green) and Elmwood Mine in north-central TN (red). The outlier from the Burkesville dataset is
North-central TN data is thought to be scattered due to instrumentation error. The present-day average crustal Pb abundance from Stacey and Kramers (1975) is shown.

Figure 11: Comparison of $^{208}\text{Pb}/^{204}\text{Pb}$ vs. $^{207}\text{Pb}/^{204}\text{Pb}$ ratios from the Burkesville, KY deposit to data from Moyers (2015) on the Young Mine in eastern TN (green) and Elmwood Mine in north-central TN (red). The outlier from the Burkesville dataset is from Unknown-2. North-central TN data is thought to be scattered due to instrumentation error. The present-day average crustal Pb abundance from Stacey and Kramers (1975) is shown.
Figure 12: $^{208}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ data from the Burkesville, KY mine relative to the Elmwood and Young mines of TN (Moyers, 2015), as well as known values for deposits within the Southern Appalachian District, Central Appalachian District, KY-IL Fluorspar District, Upper MVT District, Central MO District, Tri-State District, Old Pb Belt, and Viburnum Trend (Heyl et al., 1966; Kessler et al., 1994; and Goldhaber et al., 1995).
Figure 13: $^{208}\text{Pb}^{204}\text{Pb}$ vs. $^{207}\text{Pb}^{204}\text{Pb}$ data from the Burkesville, KY mine relative to the Elmwood and Young mines of TN (Moyers, 2015), as well as known values for deposits within the Southern Appalachian District, Central Appalachian District, KY-IL Fluorspar District, Upper MVT District, Central MO District, Tri-State District, Old Pb Belt, and Viburnum Trend (Heyl et al., 1966; Kessler et al., 1994; and Goldhaber et al., 1995).
References


