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Geochemical Analysis and Numerical Modeling of Central and East Tennessee Mississippi Valley-Type Ore Districts: Constraints on Ore Genesis

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Geochemical Analysis and Numerical Modeling of Central and East Tennessee Mississippi

Valley-Type Ore Districts: Constraints on Ore Genesis

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Abstract

A simple two-way stochastic mixing model is presented for analysis of the lead (Pb) isotope compositions of the North American Mississippi Valley-Type (MVT) districts of East Tennessee, Central Tennessee, and Central Kentucky. Four distinct mixing scenarios were run to critically evaluate the stochastic model and examine different hypotheses regarding the genesis of Central Tennessee and Central Kentucky MVT deposits. Additionally, Pb isotope analysis was conducted on sphalerite samples from the Central and East Tennessee MVT districts. Model and sampling results suggest that Central Tennessee and Central Kentucky ores likely formed by mixing of three fluids. In contrast to conclusions from previous workers, our results suggests that Central Tennessee and Central Kentucky deposits may have formed via mixing between Appalachian Basin brines and a unique source that is distinct from the Upper Mississippi Valley and Illinois-Kentucky trend. The possible third source has a composition lying along the Ozark Pb isotope trend and may have also contributed metals to the Central Tennessee ores. Alternatively, Pb isotope observations can be explained if Upper Mississippi Valley ore metals were derived from a single fluid which evolved over time.

Although it is still unclear whether these model results can be relied on for analysis of MVT ore compositions, the methods employed here present a promising means for Pb isotope analysis of sulfide ores. Stochastic generation of hypothetical ore deposits as the result of mixing between different sources of Pb has the potential to allow researchers to test their hypotheses regarding the nature of the mineralizing fluids in a more rigorous and semiquantitative manner. Nonetheless, further sampling is required before confidence regarding the origin of Central Tennessee and Central Kentucky ores is warranted.

Introduction

1. Mississippi Valley-Type Pb-Zn-F-B deposits

Mississippi Valley-Type (MVT) ore deposits account for 38% of Earth's sediment-hosted lead (Pb) and zinc (Zn) resources, and 25% of all the world's resources of Pb (Leach et al., 2010). MVT deposits occur around the world, but the largest are in the North America. In the United States, the Central Tennessee and Central Kentucky MVT districts have been shown to have high concentrations of gallium (Ga), germanium (Ge), and cadmium (Cd) (Bonnet et al., 2016; Anderson, 1991). Gallium and germanium are "strategic metals," and are in high demand for a wide array of semiconductor and electronics applications. Previous work has shown that processed zinc recovered from Tennessee has economically viable Ga and Ge concentrations, with "…enough gallium and germanium to potentially supply the needs of the United States for many years." (Harbuck, 1992). The continued study of MVT deposits is therefore potentially important for resource assessment and discovery, especially as the United States seeks to reduce its reliance on foreign imports of key resources. Although North American MVT districts have been widely studied, Central Tennessee, East Tennessee, and Central Kentucky have received substantially less attention.

Researchers have long inferred important information about the nature of many MVT deposits using Pb isotope data (e.g., Heyl et al., 1966; Kesler et al., 1994a; Goldhaber et al., 1995). Heyl et al. (1966) compiled existing Pb isotope data for several North American districts and hypothesized that the strong linear relationship observed formed either by regional mixing of two fluids of differing compositions or by variations in the lead isotope composition of a single source. Others have noted two roughly parallel Pb isotope trends for North American MVT deposits and have speculated that these are related to the basins (and associated hydrothermal fluids) within

which each deposit is located. Importantly, ores associated with the Illinois Basin (e.g., Illinois-Kentucky, Upper Mississippi Valley) have consistently elevated $^{206}Pb/^{204}Pb$ values when compared with ores from the Ozark region (Goldhaber, 1995). Figure 1 provides an overview of important North American MVT deposits.
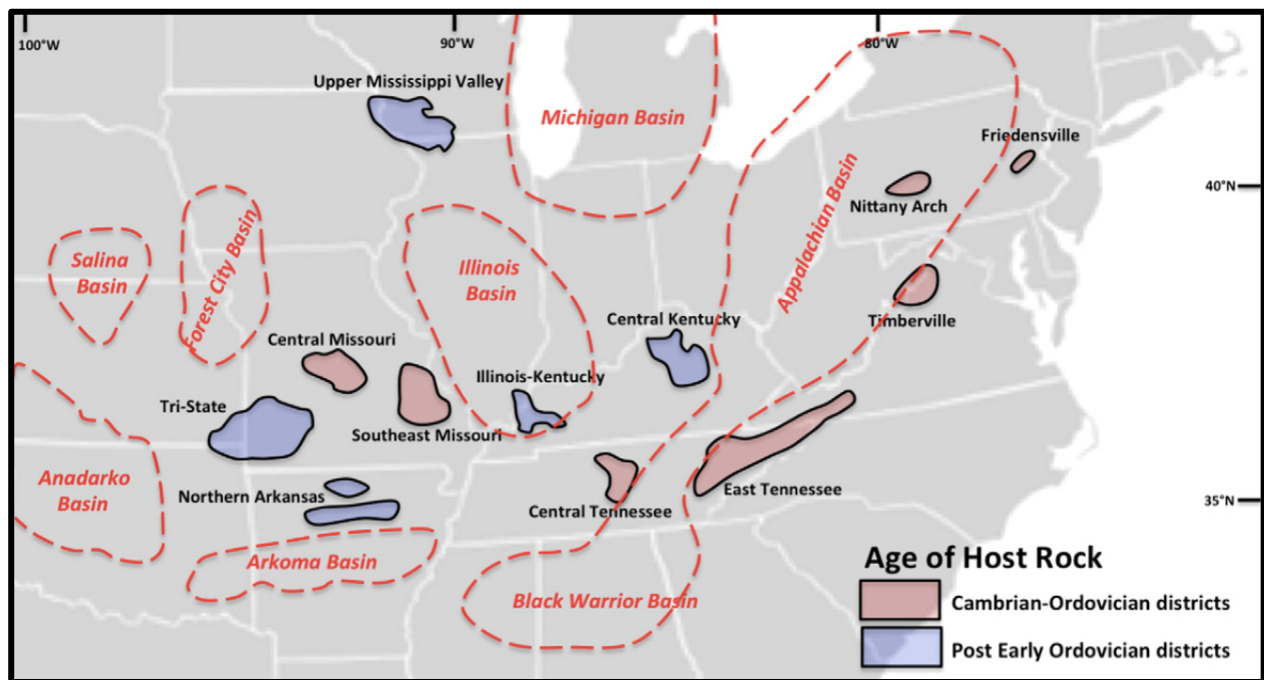
Figure 1. Map of North American MVT Deposits and the ages of their host rocks. Associated Basins are circled with red dashed lines. From Potra and Moyers (2017).

Bonnet et al. (2016) noted that isotopic characterization of Central Tennessee ores could aid in formulating hypotheses to explain their unique and potentially abundant resources of Ge and Ga. Misra et al. (1995) and Potra and Moyers (2017) sampled and compiled Pb isotope data for sphalerites from Central Tennessee, and Garmon (2016) obtained Pb isotope values for sphalerite samples taken from Burkesville in Central Kentucky. Each study concluded that ores in these districts formed as a product of mixing between fluids derived from the Appalachian and Illinois basins, suggesting that a large regional fluid migration or flow extended from the Upper

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Mississippi Valley and Illinois-Kentucky districts to Central Tennessee and Central Kentucky, which mixed with Appalachian Basin sources at these locations.

Kesler (1988) proposed that the Sevier Basin, located in the southern Appalachian region, provided the metalliferous fluids responsible for East Tennessee mineralization. Kesler et al. (1994a) suggested that East Tennessee MVT sulfide ore deposits had formed from two different sources based on distinct Pb isotope signatures within and among sphalerite samples from different East Tennessee districts. They further showed that fluorite and barite samples from various East Tennessee districts have a distinctly heterogeneous Pb isotope composition. They hypothesized that phosphorite from the Devonian Chattanooga shale or a similar lithology might have supplied the Pb for fluorite in this region in order to explain its distinct linear trend.

The present study seeks to further constrain the origin of Central Tennessee and Central Kentucky ore metals by comparing their Pb isotope compositions with Pb isotope data from other North American MVT districts. Previous work comparing the Pb isotope compositions of multiple ore districts has mainly utilized qualitative descriptions of their compositional ranges. Here, we model stochastic mixing of sources in order to bring clarity to the ongoing discussion surrounding the origin of ore metals in the East Tennessee, Central Tennessee, and Central Kentucky MVT districts.

2. Lead isotopes

Lead is useful for characterization of many ore deposits because of its abundance in sulfide minerals and its unique radiogenic signature. There are four common naturally occurring stable isotopes of Pb: ^{204}Pb, ^{206}Pb, ^{207}Pb, and ^{208}Pb. ^{204}Pb is a primordial nuclide while ^{206}Pb, ^{207}Pb, and ^{208}Pb are the radiogenic daughters of ^{238}U, ^{235}U, and ^{232}Th, respectively. Because these isotopes of U and Th have different half-lives and thus produce daughter nuclides at different rates, the relative

abundances of ^{206}Pb, ^{207}Pb, and ^{208}Pb will change over time due to radioactive decay. If a fluid extracts Pb and not U or Th from a rock at a particular time, the fluid will act as a "snapshot" of the Pb isotope composition of that rock and will not appreciably change unless contaminated by Pb from other sources.

Because MVT deposits form by mineralization from a hydrothermal fluid containing the associated ore metals, analysis of the Pb isotope composition of MVT ores may reveal whether two separate deposits share a common mineralizing fluid or mixture of fluids. For example, it is possible to constrain the sources of ore metals by comparing ore Pb isotope compositions to the Pb isotope compositions of lithologies which could have hosted the ore fluids. Additionally, one can infer relationships between MVT ore deposits by comparing their Pb isotope values.

In reality, accurate Pb isotope characterization of MVT deposits is made possible by a series of assumptions regarding the chemical behavior of U, Th, and Pb in solution. For example, both U and Th are insoluble under reducing conditions, and thus less willingly mobilized in a hydrothermal fluid. It is subsequently assumed that they are not present in solution with Pb when leaching occurs. Nonetheless, U and Th are in general excluded from the ore mineral phase, and mineralization timescales are short. The modern Pb isotope composition is therefore assumed to be very close to that of the fluid when mineralization occurred (Tosdal et al., 1999). Finally, because Pb behaves similarly to Zn (Tosdal et al., 1999; Bourcier and Barnes, 1987) and is likely to have been present in metalliferous fluids containing copper (Cu), gold (Au), and silver (Ag) (Henley et al., 1984), it is assumed that the ore fluid also contained these alternative metals.

3. Modeling

The only assumptions used in the stochastic model presented herein are that the Pb isotope composition of a particular source is comprised of many sampled points and that each point in a

single source undergoes mixing in stochastic proportions with a stochastically-generated point in each other source. Thus, model results are interpreted as a composite of all possible mixing scenarios between two distributions at a time. The density of the model points in a given location is an analog to the probability of drawing a point from that region out of all the generated model values. In other words, if two sources mix, an array of possible Pb isotope compositions will be generated between them. The denser portions of this array correspond to compositions with higher chances of being drawn from the distribution.

Twelve sphalerite samples were analyzed for the present study. Five of these samples were gathered from the Elmwood-Gordonsville mine in Central Tennessee and seven from the Young mine in East Tennessee. Pure sphalerite shards were collected from each sample and processed for analysis using mass spectrometry. In addition to the samples collected in the present study, existing Pb isotope data was compiled for several North American MVT districts, including (and most importantly) Central Tennessee, East Tennessee, Central Kentucky, and Central and Southeast Missouri.

Geological Setting

1. Overview

Mississippi Valley-Type (MVT) deposits are regionally extensive, carbonate-hosted, epigenetic base-metal ore deposits. They are dominantly composed of sphalerite (ZnS), galena (PbS), pyrite, and marcasite (FeS_2) (Leach et al., 2010; Gregg & Shelton, 2012). Dolomite and calcite are the most common gangue minerals, in addition to fluorite and barite in some deposits (Leach et al., 2010). MVT deposits occur within platform carbonate sequences along the edges of foreland basins or on the apexes of forebulges (Kyle 1976; Garvin et al., 1999; Appold and Garvin, 1999). Mineralization of ore metals from associated hydrothermal fluids occurs on timescales of

hundreds of thousands of years and is generally initiated tens of millions of years after the host carbonates are deposited (Leach et al., 2010). Ore mineralization temperatures are relatively cool, and generally range between 75° and 200° C (Leach et al., 2010).

Researchers have long understood that tectonic-induced topographic gradients are the major driver of fluid migration for most MVT deposits. The association between MVT districts and large tectonic events has been noted on the basis of fluid inclusion studies (Leach and Rowan, 1986) and radiometric and paleomagnetic dating techniques (Leach et al., 2001). Numerical models have indicated that tectonically generated topographic gradients create a region of high hydrologic potential from which groundwater can flow inland, and have suggested that orogenesis plays a dominant role in driving hydrothermal fluids responsible for ore mineralization (Garvin, 1985; Garvin et al., 1999). Although some have proposed alternative mechanisms for fluid migration such as sediment compaction and orogenic squeezing (Oliver, 1986), Ge and Garvin (1992) found that it is unlikely that these mechanisms could have resulted in fluid volumes required to form some MVT districts. Nonetheless, regional basin-scale fluid transport is a complex problem which may be shaped by alternative processes.

Importantly, good aquifer-forming lithologies – in particular dolomite, calcite, and sometimes sandstones – are required to facilitate and concentrate groundwater flow and react with metal-bearing hydrothermal fluids (Leach et al., 2010). In some cases, these lithologies act as lenses for fluid migration, as is the case with the Viburnum Trend in the Ozark Dome (Garvin et al., 1999). Faults, fractures, and karst features are also known to act as a primary control on ore concentrations as a result of improved secondary porosity (Leach et al., 2010).

The dominant control on base metal concentrations in hydrothermal fluids is reduced sulfur content (Leach et al., 2010). Thus, mineralization is thought to occur primarily as a result of mixing

of metalliferous fluids and fluids containing concentrated reduced sulfur. Other mechanisms have been proposed, including changing fluid temperature and redox reactions with carbonate host rocks. Although some studies have found these depositional processes to be insufficient for mineralization over appropriate timescales (Garvin et al., 1999), others have suggested that an array of processes must have occurred within a single district to explain the observed mineralization patterns (Plumlee et al., 1994). The sources of ore metals in many MVT districts, including the Southeast Missouri, Upper Mississippi Valley, and Tri-State districts, have been confirmed to be regional basement or supracrustal rocks (Goldhaber et al., 1995). However, the precise sources of ore metals have yet to be elucidated for several districts.

Eighty percent of MVT deposits occur in Phanerozoic rocks, with most forming from Devonian to Permian time as a result of the assimilation of Pangea and its associated tectonic activity (Leach et al., 2010). In North America, the Late Devonian to Early Mississippian Acadian Orogeny generated initial MVT deposits in the Appalachian region, with later deposits forming in the Appalachians and the mid-continent region as a result of the Alleghenian-Ouachita orogeny during Pennsylvanian to Permian time. In general, most North American deposits are found near the margins of the Appalachian-Ouachita foreland basins (e.g., Timberville, East Tennessee) and on the associated foreland uplifts (e.g., Central Kentucky, Central Tennessee, and Northern Arkansas) (Leach et al., 2010; Gregg and Shelton, 2012; Kyle, 1976).

2. Central Tennessee, East Tennessee, and Central Kentucky MVT districts

The Central Tennessee district is found at the apex of the Nashville Dome, the southernmost structural element of the Cincinnati Arch, a large regional anticline trending northeast (Kyle, 1976; Gaylord, 1995). Central Kentucky ores are also found on the Cincinnati Arch in a structure known as the Jessamine Dome. The two districts are separated by the

Cumberland Saddle, an intervening physiographic depression (Kesler et al., 1994c). Central

Tennessee hosts ore-grade deposits extending into southern Kentucky and Northern Tennessee

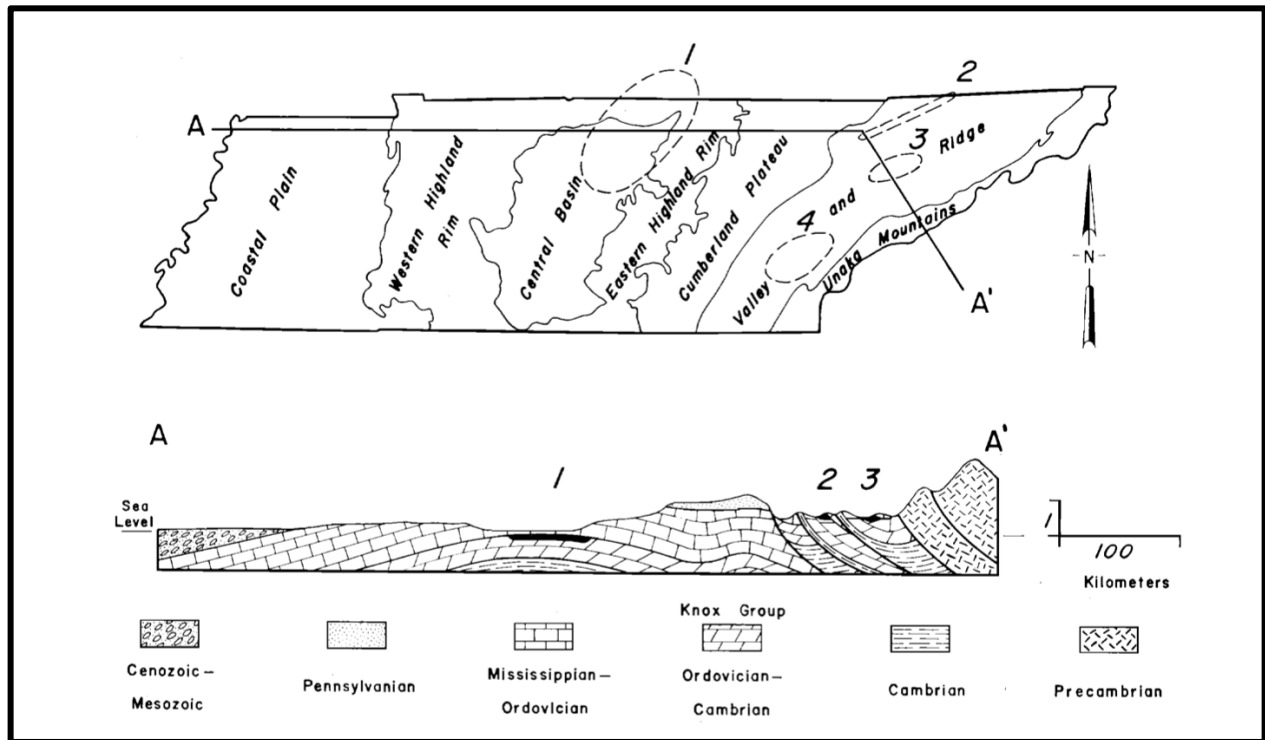(Kyle, 1976; Kesler et al, 1994c; Figure 2).

Figure 2. Figure from Kyle (1976) illustrating a stratigraphic cross-section of Tennessee. MVT districts are Central Tennessee (1), Copper Ridge (2), Mascot-Jefferson City (3), and Sweetwater (4), and colored black in the cross-section.

Both Central and East Tennessee deposits are hosted in the Knox Group, an Upper

Cambrian to Lower Ordovician shallow marine dolostone. In each district, mineralization occurs

primarily in the Mascot Dolomite, an altered limestone sequence at the top of the Knox Group,

which is separated by an erosional unconformity from overlying, deeper marine carbonates (Kyle,

1976). This period of erosion facilitated the development of a large regional karst system and

associated paleoaquifer within the Mascot Dolomite and underlying Kingsport Formation. Central

and East Tennessee ores are found within solution-collapse breccias and caverns associated with this paleoaquifer (Harris, 1971; Leach et al., 2010). Many North American MVT districts are believed to belong to either a Lower Cambrian or a Lower Ordovician paleoaquifer, which are named based on the ages of their respective host rocks (Leach et al, 1994; Goldhaber, 1995). Central and East Tennessee districts belong to the Lower Ordovician paleoaquifer while Central Kentucky and Northern Arkansas lie in Middle to Upper Ordovician carbonates. Illinois-Kentucky ores are associated with Devonian-Carboniferous carbonates and are found in proximity to igneous rocks and the Reelfoot Rift (Gregg & Shelton, 2012).

Central Tennessee ores have been dated to late Permian time (249-260 Ma) while East Tennessee ores have less constrained mineralization ages due to disagreement between paleomagnetism-based ages (286 Ma) and Rb-Sr isotopic ages (347 – 377 Ma), which place them between the Late Devonian to Early Permian periods. Northern Arkansas and Southeast Missouri ores have been dated to 265-283 Ma (Leach et al., 2001).

The major differences between Central and East Tennessee ores concern their color – Central Tennessee ores are a dark, reddish brown, while East Tennessee hosts pale yellow ores. Ores in Central Tennessee are believed to have mineralized after brecciation of the surrounding host rocks. Although East Tennessee ores were initially suspected to form simultaneously with brecciation (Hill et al., 1971), more recent studies have suggested that there was no relationship between ore mineralization and host rock dissolution for East Tennessee and that dolomitization likely resulted in observed brecciation for both East and Central Tennessee (Haynes and Kesler, 1994). East Tennessee gangue minerals are principally dolomite with minor to rare pyrite, marcasite, and calcite, while Central Tennessee ore bodies are mainly associated with calcite, but

occasionally abundant galena, barite, and fluorite (Kyle, 1976). Central Tennessee has abundant unmineralized open breccias while in East Tennessee these features are rare (Leach et al., 2010)

In the Sweetwater district of East Tennessee, fluorite and barite are the most abundant minerals. Cadmium, Ge, and Ga are present in high concentrations (~2500 ppm, ~300 ppm, and ~540 ppm, respectively) in Central Tennessee, while East Tennessee has only abundant Cd (concentrations are ~3680 ppm Cd, 11 ppm Ge, and 105 ppm Ga for East Tennessee) (Bonnet et al., 2016). Concentrations of Cd, Ge, and Ga as reported by Anderson (1991) for Central Kentucky are 11,950 ppm Cd, 366 ppm Ge, and 155 ppm Ga. Mine geologists in Kentucky have apparently recognized similarities between the strategic element concentrations in Central Tennessee and Kentucky (Garmon, 2016; Anderson, 1991), and these districts also share a similar structural environment and locations.

Overall, a genetic relationship between Central Tennessee, Central Kentucky, and East Tennessee has been assumed and supported by Pb isotope analysis (Garmon, 2016, Gaylord, 1995, Misra et al., 1997). A link between districts on the Cincinnati Arch (Central Tennessee and Central Kentucky) and deposits farther northwest (Illinois-Kentucky and Upper Mississippi Valley) has been suggested on the basis of the irregular and somewhat heterogeneous Pb isotope compositions of Central Tennessee and Central Kentucky ores. This hypothesis is further supported by the location of the Nashville Dome between the Illinois-Kentucky and East Tennessee districts (Figure 2).

Methods

1. Trace element concentration and Pb isotope analysis

All samples were processed in the class 100 Radiogenic Isotope Clean Laboratory and analyzed using a Multi-collector Inductively-coupled Plasma Mass Spectrometer (MC-ICP-MS)

at the University of Arkansas. Approximately 200 mg of clean sphalerite shards from each sample were separated and rinsed with a small quantity of 3.5 N HNO_3 and triple-distilled water and allowed to dry. Three mL of HCl and HNO_3 were added to each sample and to a single blank in clean acid-leached Teflon containers. Samples were subsequently heated at $175°$ C for 12 hours and allowed to dry. Two mL of 2% HNO_3 was added to each sample and heated at $175°$ C for 2 hours. One sample (E-7) did not digest entirely, so 2 mL HF was added, heated, and subsequently dried at $175°$ C. For this sample, the step of adding HNO_3 was repeated three times until only a residual powder remained after drying. At this point, each sample consisted of well-dissolved sphalerite in a solution of 2 mL 2% HNO_3.

Samples were subsequently centrifuged for 3 minutes. Separation of Pb was achieved using columns made of 3 mL syringe bodies with Teflon filters and a 250 μL resin in the narrow ends. Resin was pre-cleaned by rinsing three times with 3 mL of 6 N HCl and 0.05 N HNO_3. The column was pre-conditioned with 0.1 mL of 1 N HNO_3. After loading 1.5 mL of each sample into their associated columns, they were washed twice with 0.5 mL of 1N HNO_3. For each sample, strontium (Sr) was separated into a 2 mL solution of 0.05 N HNO_3 after two 1 mL additions of 7 N HNO_3 and one 0.5 mL addition of 2 N HNO_3 for each column. Pb was collected after rinsing the samples twice with 1 mL of 3 N HCl and was collected in 2 mL solutions of 6 N HCl.

2. Modeling

A simplistic stochastic mixing model was constructed in Python. In this model, field boundaries are defined based on the convex hulls of the ore data from each deposit. A fixed number of samples can then be randomly generated uniformly within these bounds. For artificially-generated East Tennessee fluorite, Upper Mississippi Valley, and Ozark (Southeast Missouri, Central Missouri, Tri-State, and Northern Arkansas districts) ore fields, points are generated with

a normal distribution around a specific point on the uranogenic ($^{207}Pb/^{204}Pb$ vs. $^{206}Pb/^{204}Pb$) and thorogenic ($^{208}Pb/^{204}Pb$ vs. $^{206}Pb/^{204}Pb$) diagrams. Fluid mixing is modeled stochastically by iterating over each point in a single field and calculating the vectors that separate each point from one random point in each of the other selected fields. A random factor between zero and one is multiplied by each vector, returning an "offset" from the initial point. By adding this offset to the point's initial coordinates, an artificial sample point may be generated at a random location between two points lying within two separate fields. Thus, by sampling a large number of points, a plot of expected mixing results can be generated for any arbitrary end-member scenario. For the present study, 10,000 points were assigned to each field.

Model-generated point density is calculated using Gaussian kernel density estimation (KDE), and points may be colored accordingly. Areas of high density represent fluid compositions that are likely to occur when selected at random because they result from multiple mixing scenarios. Note that dense portions of the model results do not necessarily represent locations where ores are likely to plot in reality. The model shows all possible mixing scenarios for a set of given source distributions. The dense portions of the model can be thought of as Pb isotope compositions to which various mixing scenarios converge. In reality, only a single set of Pb sources will be available at a given time, and this scenario may or may not conform to the convergent portions of each plot.

One major limitation of this method is that it is only capable of simulating mixing between two source composition areas at a time, and thus cannot truly model mixing of three or more fluids simultaneously. However, by generating an array of values between two points and then using the generated values as a model input along with a third source, one may effectively model the mixing of a linear Pb isotope trend and a third source. Furthermore, by modeling source areas rather than

specific points, these three-component systems may or may not be roughly approximated due to the range of compositions that can be found within each source. Finally, this method assumes that the measured ore compositions accurately reflect the shape, size, and location of their sources on the uranogenic and thorogenic covariation diagrams. Uncertainty in Pb isotope values for these ore deposits could negatively impact model accuracy.

In the first mixing scenario, the model was tested by simulating mixing between the upper and lower East Tennessee sulfide sources described by Kesler et al. (1994). These generated values were then mixed with the predicted fluorite source for East Tennessee, and the results were compared with the East Tennessee fluorite Pb isotope data.

In the second model, mixing was simulated between Central Kentucky, the East Tennessee upper and lower sulfide clusters, and a lower end-member on the Ozark MVT trend. This scenario examines the mixing results for known source compositions only, and does not include any hypothetical sources. Results are compared with the existing Pb isotope data for Central Tennessee to determine if mechanistic models including alternative sources are necessary.

The third model examines the conclusions of previous studies to determine if Central Tennessee and Central Kentucky could have formed via mixing between Appalachian Basin and Illinois-Kentucky (along the Upper Mississippi Valley trendline) metal sources. Mixing was first simulated between Central Kentucky and the upper sulfide cluster. These values were then mixed with the lower sulfide cluster, the same Ozark MVT end-member, and a hypothetical source lying on the Upper Mississippi Valley trendline.

The fourth model utilized a source which was placed on the Upper Mississippi Valley trendline in the uranogenic plot and the Northern Arkansas/Southeast Missouri trend in the

thorogenic plot, in order to examine the possibility that a source unrelated to the Upper Mississippi Valley trend could have contributed ore metals to Central Tennessee and Central Kentucky.

Results

The gathered Pb isotope values are generally consistent with existing Central and East Tennessee ore data (Table 1). Although the Pb isotope compositions for Central Tennessee have been found to be somewhat more sporadic and heterogeneous than other districts (Potra and Moyers, 2017; Gaylord, 1995; Misra et al., 1997), it is not entirely clear to what extent this heterogeneity represents actual variability within Central Tennessee ores, as opposed to analytical error on the part of previous research. The present study contains two samples from Central Tennessee, E-4 and E-6, with distinctly elevated $^{206}Pb/^{204}Pb$ ratios (Figure 1). All other samples plot within a reasonable range of existing data for both Central and East Tennessee.

East Tennessee Pb isotope data from the present study are in excellent agreement with those from Kesler et al. (1994a). In particular, the data lie squarely within the upper sulfide cluster from the aforementioned study. The outlier samples E-4 and E-6 were analyzed in a previous study (Potra and Moyers, 2017) but rejected due to their highly anomalous and radiogenic $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ ratios. Although their $^{206}Pb/^{204}Pb$ ratios were similar to those reported in this study, the high variability of these samples – in addition to a processing issue of the sample E-6 which caused it to be relatively dilute during isotopic analysis – were valid reasons for these values to not be included in the analysis of Central Tennessee ore compositions.

Sample	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$
E-2	19.5860	15.734	39.240
E-4	21.6629	15.756	39.352
E-6	21.3613	15.757	39.321
E-7	20.0156	15.750	39.192
E-8	19.8956	15.750	39.301
1-9215 A	19.4593	15.738	39.524
1-9215 B	19.4792	15.733	39.426
4-2248 A	19.3724	15.723	39.410
4-2248 B	19.4041	15.735	39.439
4-2248 C	19.3681	15.735	39.477
2-9922 A	19.3578	15.737	39.475
5-4338 B	19.4627	15.746	39.523

Table 1. Measured Pb isotope ratios for sphalerite samples from the Elmwood-Gordonsville mine in Central Tennessee (denoted with the letter "E") and the Young mine from East Tennessee (denoted with a number).
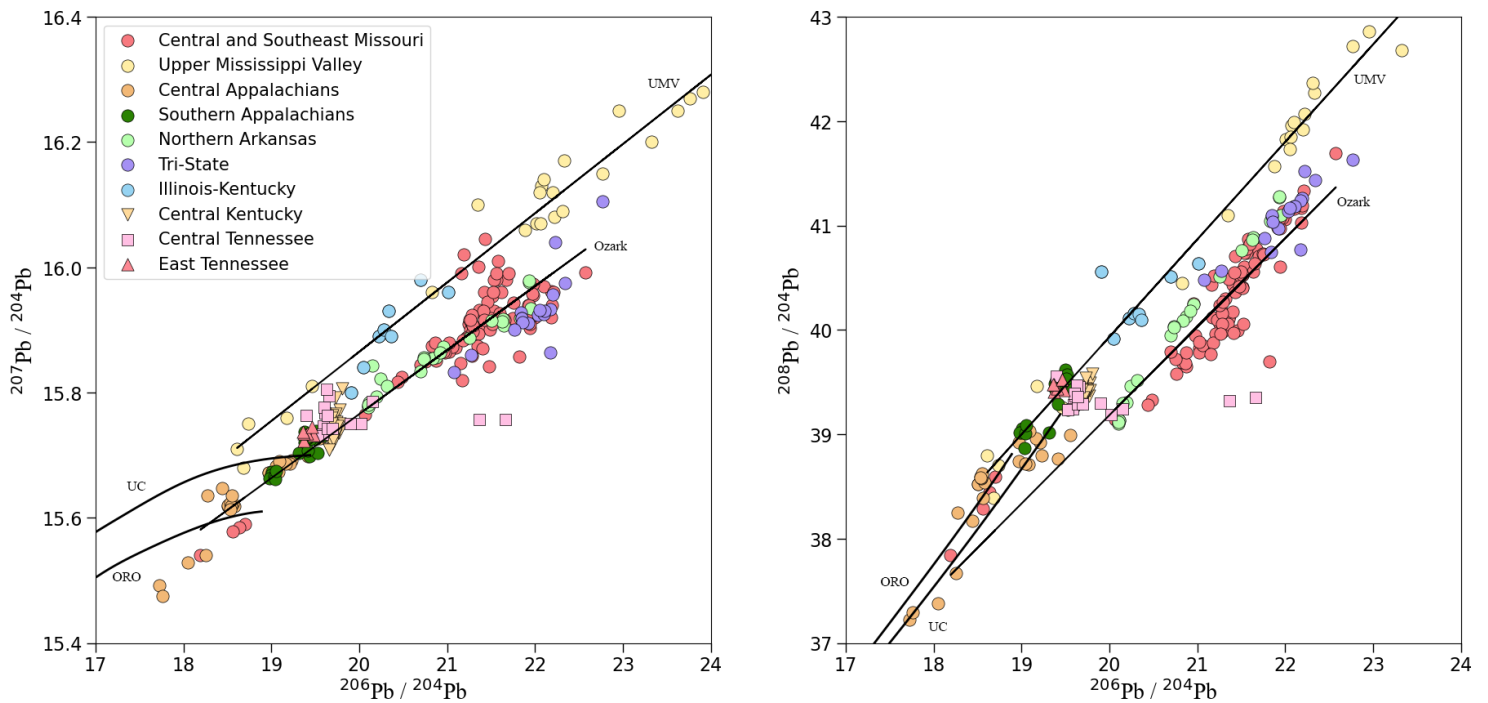
Figure 3. Uranogenic (left) and thorogenic (right) diagrams containing all data included in this study with the exception of East Tennessee fluorite and barite from Kesler (1994a). Publications for the compositions of each district are: Missouri (Goldhaber et al., 1995), Upper Mississippi Valley (Heyl et al., 1966), Central Appalachians (Kesler et al., 1994b), Southern Appalachians (Kesler et al., 1994a), Northern Arkansas (Bottoms et al., 2019), Tri-State (Bottoms et al., 2019), Illinois-Kentucky (Heyl et al., 1966), Central Kentucky (Garmon, 2016), Central Tennessee (Gaylord, 1995; Misra et al., 1997; Potra and Moyers, 2017; This Study), and East Tennessee (This Study). UC (Upper Crust) and ORO (Orogene) are model growth curves from Zartman and Doe (1981). UMV and Ozark are trendlines through the Upper Mississippi Valley and various Missouri and Northern Arkansas districts, respectively.
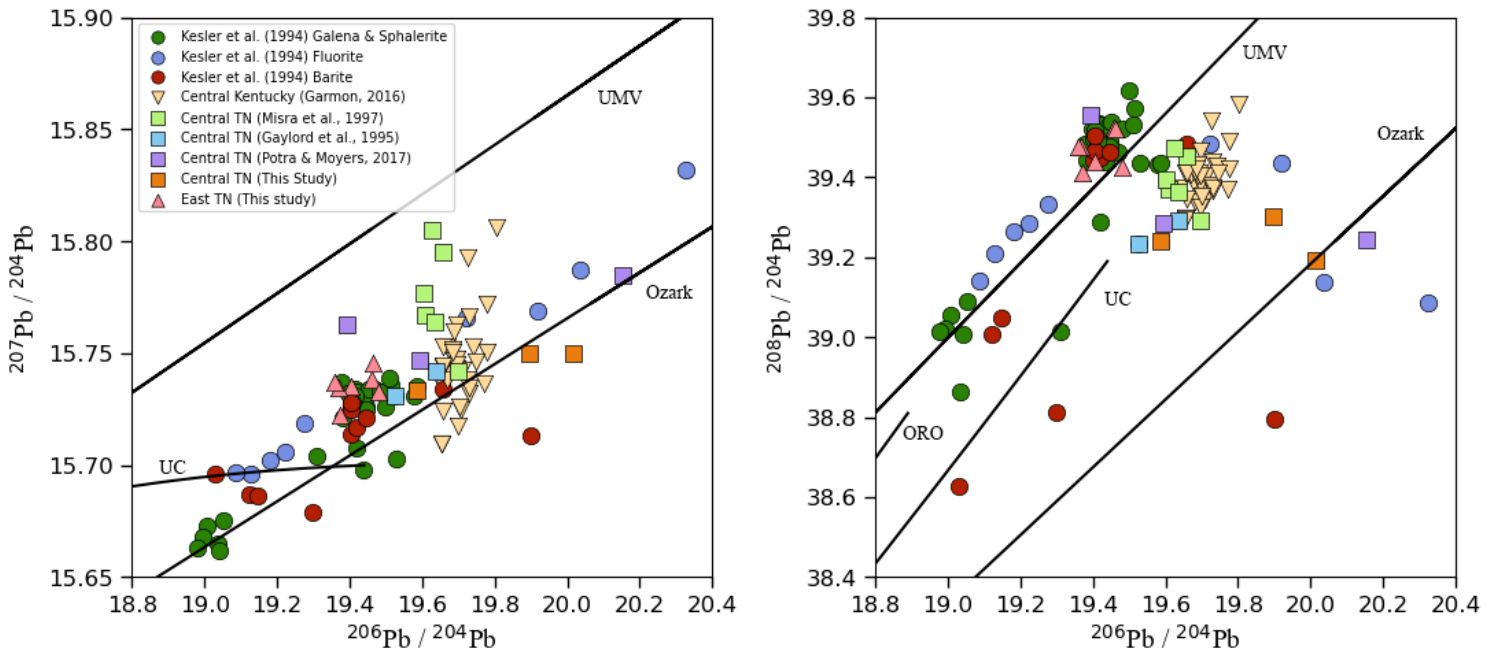
Figure 4. Enlarged view of Figure 3 with East Tennessee samples from Kesler et al. (1994a) colored based on the mineral type.

It is clear from Figure 3 and Figure 4 that Central Tennessee, Central Kentucky, and the upper and lower sulfide clusters from Kesler et al. (1994) are essentially bounded by the Upper Mississippi Valley/Illinois-Kentucky and Ozark trendlines identified by Goldhaber (1995).

The East Tennessee Pb isotope data from Kesler et al. (1994) are derived from the Mascot-Jefferson City, Copper Ridge, and Sweetwater districts. Sweetwater Pb isotope data are dominantly fluorite and barite, and these samples show significant deviation from the Pb isotope compositions of East Tennessee sphalerite and galena. On the thorogenic diagram ($^{208}Pb/^{204}Pb$ vs. $^{206}Pb/^{204}Pb$), the two outliers recorded in this study appear to fall within the field defined by the

Sweetwater fluorite, while on the uranogenic diagram (^{207}Pb/^{204}Pb vs. ^{206}Pb/^{204}Pb) the same samples plot well outside this trend (Figure 5).
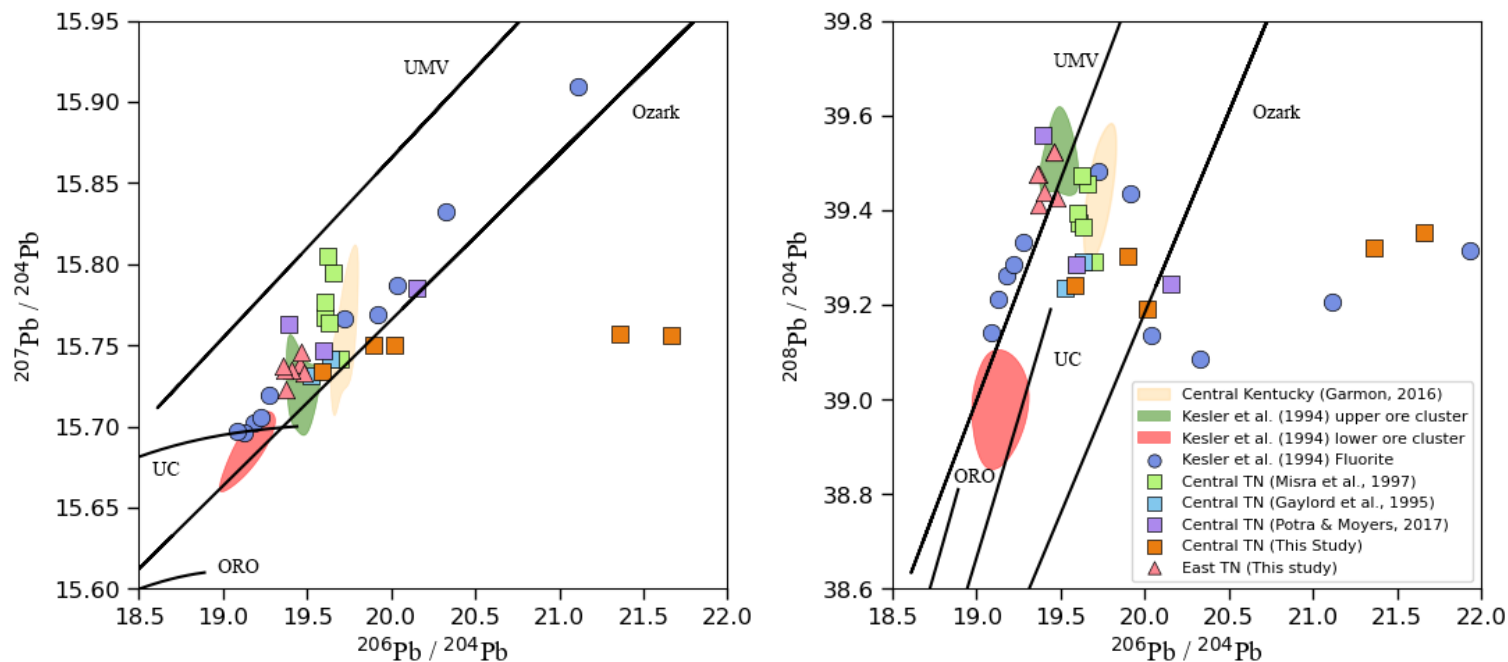

Figure 5. Lead isotope compositions of Central Tennessee sphalerites and East Tennessee fluorites overlaid on fields for the upper and lower sulfide clusters and Central Kentucky.

In the uranogenic plot, the Ozark trendline best describes the bulk Central Tennessee, Central Kentucky, and East Tennessee sulfide data, while on the thorogenic plot, the Upper Mississippi Valley/Illinois-Kentucky trendline better characterizes the bulk data (Figure 5).

In both plots, Central Tennessee data appear to conform to the bulk distribution of Central Kentucky and East Tennessee for the range of values displayed in Figure 4. Although Central Tennessee samples plot closely to Central Kentucky data, they appear to be significantly more heterogeneous with respect to their Pb isotope compositions.

An initial model scenario was run as an attempt to recreate the findings of Kesler et al. (1994) (Figure 6). This model was constructed by first generating mixing values between the upper

and lower sulfide clusters. These generated values were themselves mixed with a fluorite distribution centered at (23.5, 16.17) and (23.5, 39.2) for the uranogenic and thorogenic plots, respectively (Kesler et al., 1994a). These graphs clearly indicate that the East Tennessee fluorite ores fall within the upper sulfide, lower sulfide, and fluorite end-members. Figure 6 also overlays the generated upper and lower sulfide mixing data onto their associated fluorite source mixing values. It is clear from both the uranogenic and thorogenic plots that the model adequately accounts for virtually all East Tennessee fluorite data.
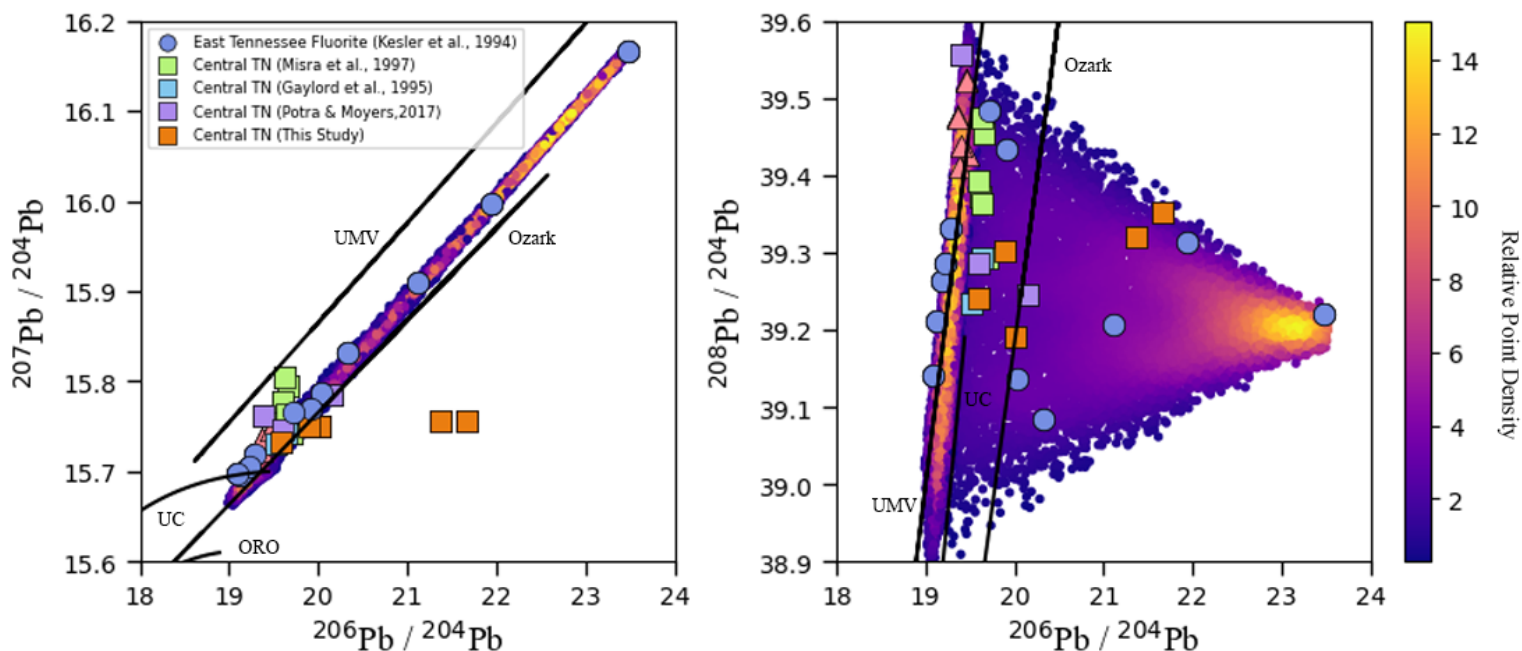

Figure 6. Model results for a three end-member scenario involving the upper sulfide cluster, lower sulfide cluster, and a fluorite source.

The thorogenic plot reveals that although Sweetwater fluorite plots significantly outside the Upper-MVT/Ozark-MVT bounding trendlines, Central Tennessee remains largely within these trends with the exception of the two outliers from this study.

The second model scenario involved mixing between the upper and lower sulfide clusters, Central Kentucky, and the lower end-member of the Ozark trendline (Figure 5). In the uranogenic diagram, three regions of particularly high mixing density are present, with the largest containing several samples from Central Tennessee. The thorogenic diagram exposes two distinct high-density regions which also contain several Central Tennessee samples. There are also several points lying outside the expected range for strict mixing between the given sources, indicating that a mechanistic approach with an alternate source composition is required.
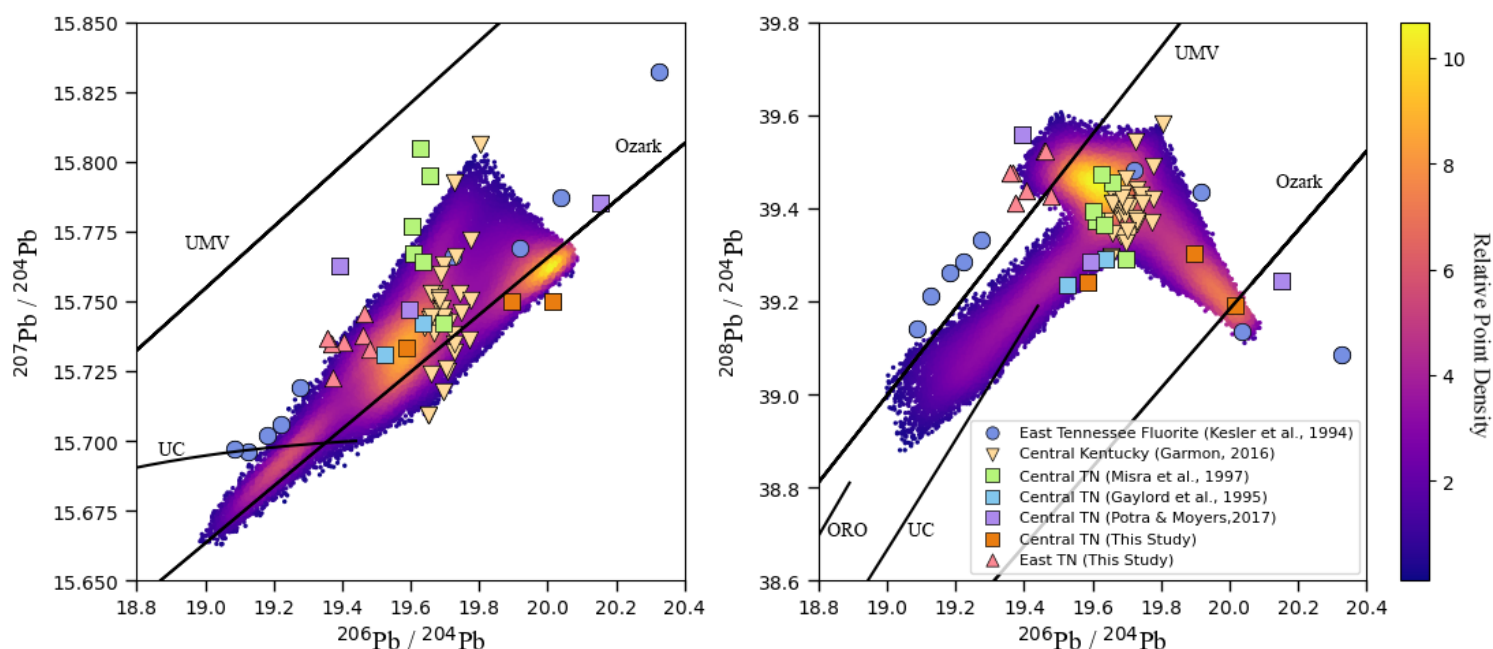

Figure 7. Model output for mixing between Central Kentucky and the upper sulfide cluster, lower sulfide cluster, and Ozark trendline source.

In Figure 7, Central Tennessee data lying within the densest portion of the uranogenic model appear in the thorogenic plot along the bottom portion of the mixing trend between Central Kentucky and the East Tennessee lower ore cluster. Similarly, Central Tennessee data from Misra et al. (1997) lie squarely within the dense portion of the thorogenic plot, while plotting near or beyond the top boundary of the uranogenic model.
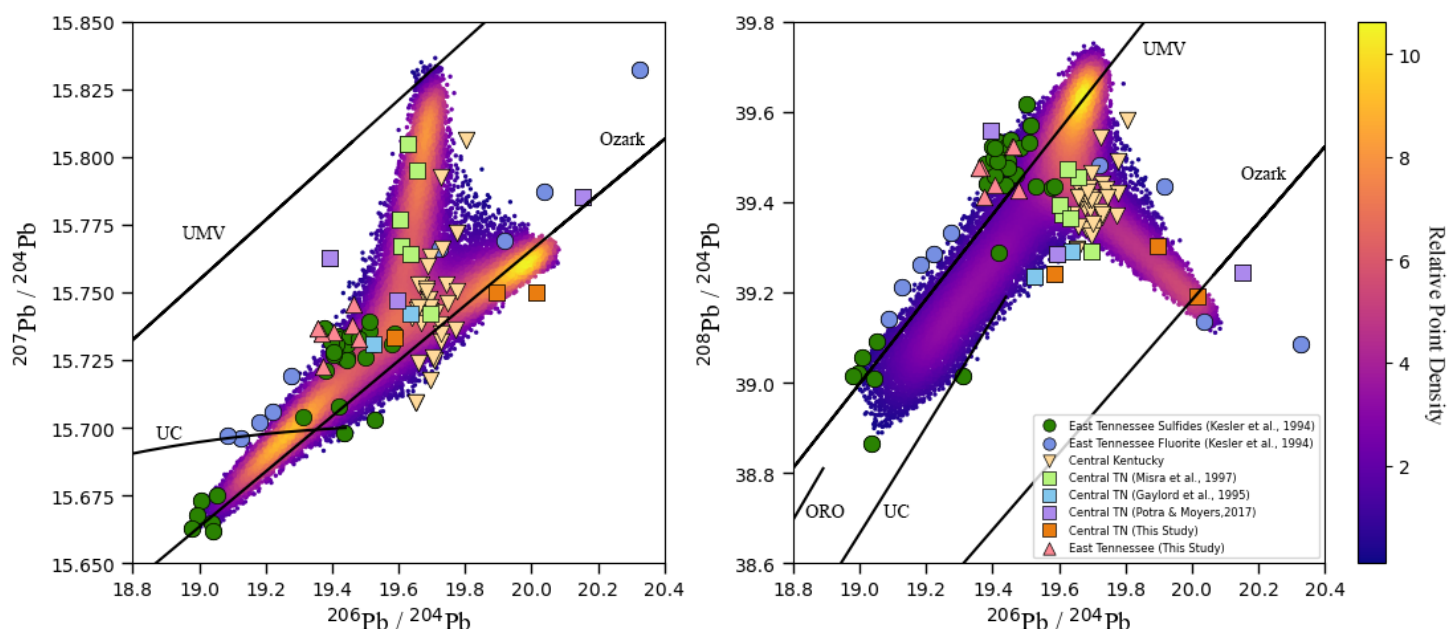

Figure 8. Model output for mixing between a combined upper sulfide/Central Kentucky source and an Upper Mississippi Valley/Illinois-Kentucky-type source, the lower sulfide cluster, and an Ozark trendline source.

A third model was constructed to illustrate a mixing scenario involving a potential source along the Upper Mississippi Valley trendline (Figure 8). Based on the vertical trend in the Central Tennessee and Central Kentucky data, a hypothetical source can be placed on the Upper-MVT trendline at $^{206}Pb/^{204}Pb = 19.6$. For this model, Central Kentucky and the upper sulfide clusters were first mixed. The generated values were then used as the central node in a four-way mixing model with the East Tennessee lower sulfide cluster, the hypothetical Upper Mississippi Valley trendline source, and the Ozark lower end-member source. The resulting simulation results

visually fit the available data better than any previous model scenario, most notably in the uranogenic diagram.

An alternative trend can explain the Central Tennessee/Central Kentucky data. Recall that the East Tennessee sources, which were likely derived from Appalachian sedimentary basin brines, resemble the Pb isotope compositions of the Ozark trendline in the uranogenic plot but the Upper Mississippi Valley trend in the thorogenic plot. A lithology or fluid which was distinct from the Upper Mississippi Valley trend could lie at the same $^{206}Pb/^{204}Pb$ ratio as the Cincinnati arch districts, but on different trendlines in each plot. To this end, a fourth model was constructed which accounted for this possibility (Figure 9).
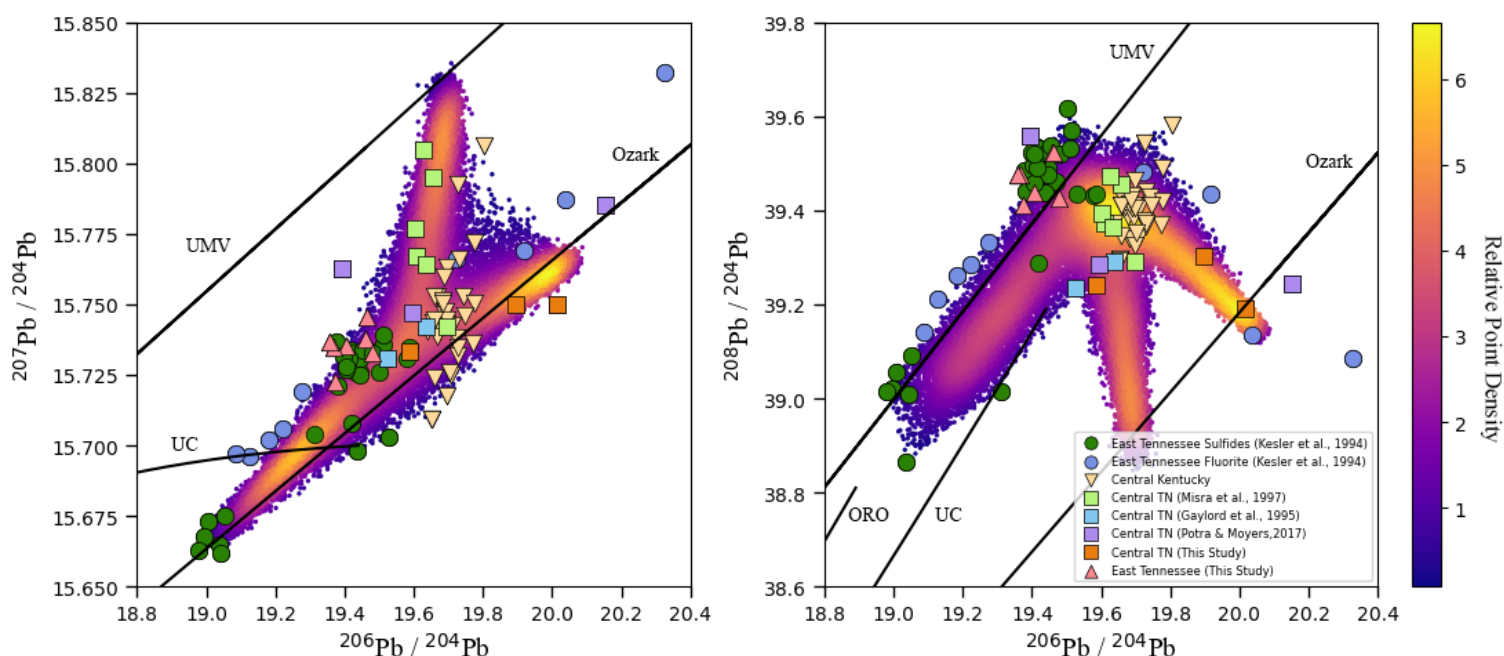

Figure 9. Model output for mixing between a combined upper sulfide/Central Kentucky source with a hypothetical source that lies along different trendlines in the uranogenic and thorogenic diagrams and an Ozark trendline source.

Results from this final simulation are promising. Visual inspection of the graphs suggests that the new hypothetical source describes both the uranogenic and thorogenic data well. Every existing Central Tennessee sample composition, with the exceptions of two points from Potra and Moyers (2017) and E-4 and E-6 from this study, plots within the model scenario's boundaries, most often within or near areas of high density. Furthermore, the lower sulfide cluster is no longer required to explain the distribution of the Central Tennessee and Central Kentucky Pb isotope compositions. Nonetheless, inclusion of the lower sulfide cluster allows this model to not only describe Central Tennessee and Kentucky data, but also East Tennessee fluorite for this narrow range.

Discussion

Agreement between the Pb isotope compositions of East Tennessee ores from this study and those from Kesler et al. (1994a) suggests that our Central Tennessee data are likely to accurately represent at least a subset of the overall Pb isotope composition of Central Tennessee ores, and that the East Tennessee data from Kesler et al. (1994a) are reliable. If samples E-4 and E-6 are included, an alternative source composition must be proposed to account for the resulting anomalous trend.

Model results indicate that the second simulated mixing scenario using East Tennessee, Central Kentucky, and Ozark sources marginally succeeds at encompassing Central Tennessee Pb isotope data in both the thorogenic and uranogenic plots. Initial models using only East Tennessee sources lack the fine-scale structures observable in the Central Tennessee thorogenic plot, but do adequately account for East Tennessee results and are in good agreement with predictions by Kesler et al. (1994a). The third model tests the hypothesis that mixing occurred with a source from the Upper Mississippi Valley/Illinois-Kentucky trendline, and shows the second greatest

correlation with Central Tennessee ore compositions, particularly in the uranogenic diagram. The final model is based on the hypothesis that a source bounded by but unrelated to either trendline could have supplied some of the ore metals. The implications of these models are that Central Tennessee and Central Kentucky were likely products of a similar mixing trend, as shown by the better model fit for both Central Tennessee and Central Kentucky in the "mechanistic" models using a hypothetical Illinois-Kentucky-type or Ozark-type source.

These model scenarios should not be construed as capable of providing definitive information regarding the origin of Central Tennessee and Central Kentucky ores. Instead, each model provides a means of comparing the measured Pb isotope distributions to the composition of an array of hypothetical deposits, formed as a result of mixing between multiple possible lead sources. Further study is needed regarding the Pb isotope composition of Central Tennessee ores as well as ores of other deposits before potential metal sources can be identified with a high degree of confidence. In particular, the model does not account for the possibility that geochemical factors may influence or enrich a source in certain Pb isotopes over time. It is nonetheless possible that the model can provide insight into the nature of prospective metal sources based on the model's preference for a "decoupled" source (i.e. separate from the Upper Mississippi Valley and Ozark trendlines).

Previous workers have suggested that Central Tennessee and Central Kentucky ores formed via mixing between Southern Appalachian sources and a source from the Illinois Basin (Misra et al., 1995; Potra and Moyers, 2017; Garmon, 2016). If this hypothesis is correct, then one might expect an end-member lying along the Upper Mississippi Valley/Illinois-Kentucky trendline for both the uranogenic and thorogenic diagrams. Although the appropriate model scenario (Figure 8) does fit the data well, the opposing model using a Th-depleted source distinct from both the

Upper Mississippi Valley and Ozark trendlines appears to be more capable of describing the measured distribution.

Figure 5 illustrates that Central Kentucky and the East Tennessee upper and lower sulfide clusters lie along the Upper Mississippi Valley trendline in the uranogenic diagram but the Ozark trendline in the thorogenic diagram, in a manner consistent with a preferentially Th-enriched mineralization fluid. Therefore, although the associated metal sources lie between the trendline boundaries, they most likely do not correspond to direct mixing between compositions along each trendline. For example, the Pb isotope composition of a single sample, formed as the result of mixing between sources A and B, will lie some fraction of the total distance away from its initial source, A. This fraction will be the same in both uranogenic and thorogenic diagrams if only mixing occurs. The established values, on the other hand, lie on entirely different trends. This observation lends support to the notion that Central Tennessee and Central Kentucky did not undergo mixing with an Illinois-Kentucky-type source composition, as has been previously proposed, and rather underwent mixing with an entirely decoupled and/or geochemically altered source composition.

Alternatively, it is possible that the Upper Mississippi Valley trend represents a single mineralizing fluid's evolution over time as hypothesized by Heyl et al. (1966). In this case, it is possible that some kind of geochemical anomaly or mixing event could have perturbed the evolution of this fluid at the time of Central Tennessee, Central Kentucky, and East Tennessee ore mineralization.

Essentially, Figure 8 assumes that mixing occurred between four sources; these included the upper and lower sulfide clusters from Kesler et al. (1994a), an Upper Mississippi Valley source, and an Ozark end-member. While the uranogenic plot for Figure 8 and Figure 9 are identical, the

thorogenic plot in Figure 8 places the hypothetical Upper Mississippi Valley source almost on top of the upper sulfide cluster. This results in Central Tennessee values which are not well-explained without the East Tennessee lower sulfide cluster. In contrast, Figure 9 suggests that only three sources are required; by allowing the hypothetical source to "wander" in the thorogenic plot, it can be placed at a location on the Ozark trendline similar to the behavior of the lower and upper sulfide clusters from Kesler et al. (1994a).

Finally, each model independently suggests that Central Tennessee and Central Kentucky ore fluids may have been the product of mixing with an additional source having a composition similar to that of the Ozark region's lower end-member. Both sets of districts range in age between 240-275 Ma and are located in tectonically similar environments. The origin of ore metals in the Ozark region is believed to be the Precambrian granitic basement rock (Goldhaber et al., 1995) or various Paleozoic shale lithologies (Bottoms et al., 2019; Simbo et al., 2019). Two basement reservoirs have been identified in North America (Rohs and Schmus, 2007), with the Eastern Granite-Rhyolite (EGR) extending over much of the southeast, including Tennessee, Kentucky, southeast Missouri, and northeast Arkansas, and the Southern Granite-Rhyolite (SGR), extending over Northern Arkansas, Oklahoma, and Texas. A genetic link between these two reservoirs has been established by previous workers (Rohs and Schmus, 2007). It is therefore possible that a common Precambrian-Cambrian basement source could have supplied metalliferous fluids to both Ozark and Jessamine Dome MVT deposits.

Conclusions

Figure 9 indicates that the last model scenario has the greatest probability of accurately describing the Central Tennessee and Central Kentucky Pb isotope data, based on the lower number of required sources and its ability to better predict the ore Pb isotope compositions of these

districts. Thus, the possible compositional sources most likely to represent the origin of anomalous Central Tennessee and Central Kentucky ores are the "decoupled" sources allowed to wander between the Upper Mississippi Valley and Ozark trendlines. If this is the case, then it is unlikely that Central Tennessee and Central Kentucky ores are the result of mixing between Appalachian Basin and Upper Mississippi Valley metal sources. Instead, a possible sedimentary or unique igneous source is implied by this model on the basis of an apparently basement-decoupled composition. Alternatively, a geochemical disturbance to the evolution of the Upper Mississippi Valley and/or Ozark brines could have occurred around the time and location of southern Appalachian and Jessamine Dome mineralization.

Based on comparisons of existing model results to Pb isotope data for Central Tennessee, Central Kentucky, and East Tennessee, it is likely that Central Tennessee and Central Kentucky ore fluids shared common metal sources, including the East Tennessee upper sulfide cluster, a potential Ozark-type source, and an unknown source which is geochemically distinct from the Upper Mississippi Valley and Illinois-Kentucky ores, but nonetheless may be derived from the Illinois Basin.

Although further research is necessary before accurate characterizations of Central Tennessee and Central Kentucky ores are possible, our model contradicts previous assumptions regarding the relationship between Cincinnati Arch districts and the Illinois-Kentucky district. Although still highly uncertain, this unique origin may explain the elevated strategic metal concentrations in Central Tennessee and Kentucky. Further supracrustal or basement Pb isotope research is required before specific Pb sources for Central Tennessee and Kentucky can be isolated.

Overall, our stochastic model provides an effective means of evaluating different mixing scenarios, and was able to verify the validity of compositions from Kesler et al. (1994a). The model produces results which are able to assume a wide range of morphologies depending on the input parameters. Researchers should exercise due diligence in examining the possible scenarios from multiple angles while acknowledging the inherent uncertainties with model results. Ultimately, the stochastic model should be regarded as a data-visualization tool with limited modeling capabilities in an early stage of development. It is nonetheless suggested that results from these models can inform sampling strategies regarding potential crustal metal sources.

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