

## Lead isotope trends and metal sources in the Mississippi Valley-type districts from the mid-continent United States

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### ABSTRACT

This study identifies metal-contributing source regions for Mississippi Valley-type (MVT) ore deposits in the Northern Arkansas district, the Tri-State district, and the Burkesville deposit in the Central Kentucky district. The Pb isotope ratios of sphalerite ores from the Tri-State district ( $^{208}\text{Pb}/^{204}\text{Pb}$  between 40.7443 and 41.2626;  $^{207}\text{Pb}/^{204}\text{Pb}$  between 15.8633 and 15.9571;  $^{206}\text{Pb}/^{204}\text{Pb}$  between 21.8373 and 22.1956) are congruent with the Pb isotope ratios defined by samples from the Central Missouri district, suggesting similar Pb sources. The ores from the Tri-State district plot in a narrow field and have higher  $^{208}\text{Pb}/^{204}\text{Pb}$  values than samples from the Southeast Missouri district (Viburnum Trend and Old Lead Belt). The sphalerite samples from the Northern Arkansas district yield lower Pb isotope values ( $^{208}\text{Pb}/^{204}\text{Pb}$  between 39.4633 and 40.8863;  $^{207}\text{Pb}/^{204}\text{Pb}$  between 15.8216 and 15.9176;  $^{206}\text{Pb}/^{204}\text{Pb}$  between 20.2396 and 21.6438) than the Tri-State district ores and overlap the Southeast Missouri ores. The Northern Arkansas samples show a wide range of isotopic ratios with a linear trend, suggesting mixing of two end-member components. Age-corrected (250 Ma) Pb isotope ratios of Devonian-Mississippian Chattanooga shales from the Arkoma basin analyzed in this study plot close to the non-radiogenic end of the Northern Arkansas ores, implying that the shales may represent the non-radiogenic end-member that contributed Pb to the ores. The slope of the linear Pb isotope trend for the Northern Arkansas ores corresponds to an age of about 1.23 Ga, suggesting that the radiogenic Precambrian igneous basement may have supplied some of the ore Pb. Therefore, current data may indicate that the linear trend defined by Northern Arkansas ores may be the result of mixing of two end-members: the radiogenic basement rocks and the non-radiogenic shales.

Pb isotope values of sphalerite from the Burkesville deposit are lower ( $^{208}\text{Pb}/^{204}\text{Pb}$  between 39.294 and 39.583;  $^{207}\text{Pb}/^{204}\text{Pb}$  between 15.709 and 15.806;  $^{206}\text{Pb}/^{204}\text{Pb}$  between 19.639 and 19.803) than those from the Northern Arkansas and Tri-State districts. The Pb isotope ratios of the Burkesville ores are similar to the Pb isotope values of the Central Tennessee (Elmwood deposit) and East Tennessee (Young deposit) ores and show evidence, the first of its kind for the region, of fluid mixing between the Illinois and Appalachian basins along the Cincinnati Arch that divides them.

On the  $^{208}\text{Pb}/^{204}\text{Pb}$  vs.  $^{206}\text{Pb}/^{204}\text{Pb}$  diagram, the Pb isotope values of MVT ore samples from districts within the mid-continent US show two collinear, parallel trends, suggesting a different Th/U trend: (1) Tri-State and Central Missouri ore samples are collinear with Southeast Missouri and Northern Arkansas district samples; (2) Upper Mississippi Valley and Illinois-Kentucky ores are collinear with the Central Appalachian, Southern Appalachian (including East Tennessee), Central Tennessee, and Burkesville (Central Kentucky) ores.

### 1. Introduction

Sediment-hosted Pb-Zn deposits have been the world's most important Pb and Zn resources (Leach et al., 2005; Leach et al., 2010).

Many Mississippi Valley-type (MVT) deposits, a subtype of sediment-hosted Pb-Zn deposits, formed between the Devonian and Permian periods and are related to the tectonic assimilation of Pangea (Leach et al., 2010). A second important period of MVT deposit formation was

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from the Cretaceous to Tertiary, coinciding with microplate assimilation along the western margin of North America and Africa-Eurasia (Leach et al., 2010). The world's largest MVT Pb-Zn deposits are found in North America, where they are hosted primarily by Middle Cambrian through Lower Ordovician and Mississippian carbonate rocks. Important tectonic events that coincide with the formation of these MVT deposits include the Acadian orogeny (Late Devonian to Early Mississippian), the Alleghanian orogeny (Pennsylvanian to Permian), the Ouachita orogeny (Pennsylvanian – Permian), and the Laramide orogeny (Late Cretaceous – early Tertiary) (Gregg and Shelton, 2012). The early mineralization in the Appalachian Mountain region is associated with the Acadian orogeny, the later mineralization in the Appalachian and midcontinent regions are associated with the Alleghanian – Ouachita orogeny, and the Laramide orogeny generated the mineralization in the Cordilleran region (Gregg and Shelton, 2012).

The MVT deposits in the midcontinent U.S. formed from very large hydrothermal systems in which the fluid drive was caused by deformation of foredeeps and uplift of foreland thrust belts during collisional tectonics (Leach and Rowan, 1986). The regional hydrothermal system is most accurately modeled as a topographically driven fluid flow in which groundwater, recharged mainly in the elevated foreland in front of the fold-and-thrust belt, migrates through deep portions of the basin, acquires heat and dissolved components, and discharges along the shallow margins of the basin and adjacent continental platform (Bethke and Marshak, 1990; Garven et al., 1993; Appold and Garven, 1999; Appold and Nunn, 2005). The saline ore fluids are inferred to be “oil-field” brines because MVT deposits are commonly associated with oil and because the composition of MVT ore fluids resembles the known composition of modern-day oil field brines (White, 1958; Hanor, 1979; Leach et al., 2010). Reduced sulfur content is the major control on the concentration of metals in MVT ore fluids; therefore, low reduced-sulfur sedimentary brines will have greater potential to extract metals from a variety of lithologies. The metals, especially base metals, are considered to be transported as metal chloride complexes in MVT ore fluids (Leach et al., 2010). Several precipitation mechanisms have been proposed to explain the formation of ore-grade MVT sulfide deposits, including fluid mixing, cooling, changes in pH through wall-rock alteration, and various sulfate reduction processes (Sverjensky, 1981; Viets and Leach, 1990; Anderson and Price, 1991; Plumlee et al., 1994; Goldhaber et al., 1995; Shelton et al., 2009; Appold and Wenz, 2011). A common characteristic of Pb from galenas in nearly all of the post-Precambrian lead, zinc, fluorite, and barite mineral deposits in the Mississippi Valley is the radiogenic Pb (Heyl et al., 1966; Delouie et al., 1986; Crocetti et al., 1988; Kesler et al., 1994a, 1994b; Goldhaber et al., 1995), called “J-type anomalous Pb” after Joplin, MO, in the Tri-State Mining District. J-type Pb, as first described by Nier (1938), is considered exceptional Pb because of its enriched abundances of radiogenic isotopes relative to ordinary lead. The Pb isotope ratios of this anomalous Pb do not fit the single-stage model of Pb evolution and correspond to future Pb-Pb ages.

The source of metals in these deposits is still a matter of debate. In the case of the Central Kentucky and Central Tennessee districts (Fig. 1), Anderson and Price (1991) and Baird and Dennen (1985) suggest that the Zn and Pb were carried into the district by migrating oil-field brines from the Appalachian basin. The authors propose that the Taconian orogeny (the first period of major convergence in the Appalachian region; 470–435 Ma) and downward bending of the Appalachian basin were responsible for westward migration of basinal fluids, rich in metals and hydrocarbons, that were expelled during basin subsidence and traversed the Appalachian basin until arriving at the Cincinnati Arch. The Central Kentucky and Central Tennessee districts are situated on or near the crest of the arch, which is a regional anticlinal structure that divides the Illinois Basin to the northwest from the Appalachian basin to the east. The systematic decrease in maximum temperature of homogenization from Eastern Tennessee to Central Tennessee and Central Kentucky led Hoagland (1976) and Anderson

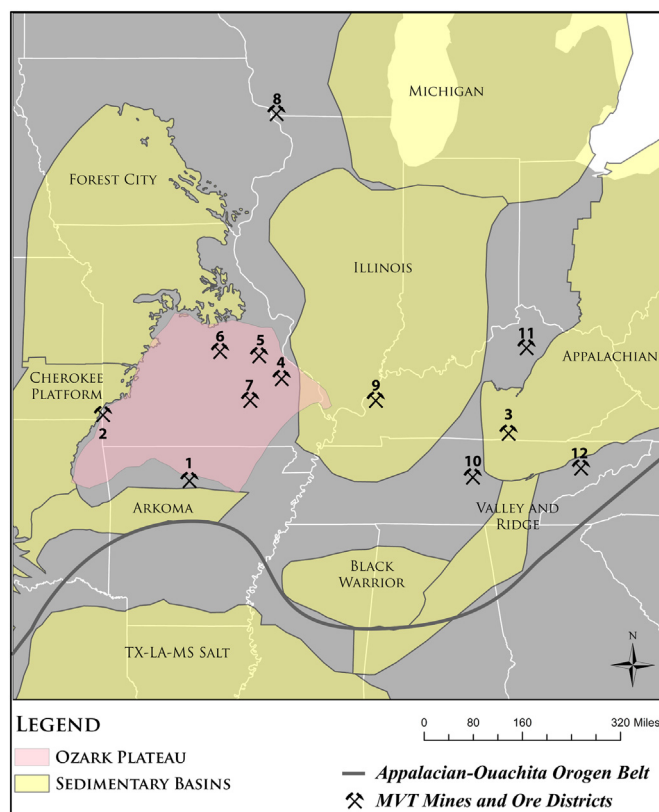


Fig. 1. Map of the US midcontinent region showing the locations of MVT mining districts and deposits (1 through 12), sedimentary basins, and the Ozark Plateau. (1) Northern Arkansas, (2) Tri-State, (3) Burkesville deposit, (4) Old Lead Belt, (5) Southeast Missouri Barite, (6) Central Missouri Barite, (7) Viburnum Trend, (8) Upper Mississippi Valley, (9) Illinois-Kentucky Fluorspar, (10) Central Tennessee, (11) Central Kentucky, and (12) Eastern Tennessee. Modified from Garven et al. (1993). For drawing the basemap: <https://www.eia.gov/maps/maps.htm>; <https://water.usgs.gov/GIS/metadata/usgswrd/XML/physio.xml>

and Price (1991) to conclude that the Appalachian basin was the source of the metal-rich fluids in the aforementioned MVT districts.

Unusually high concentrations of Ga and Ge in sphalerite samples in the Central Kentucky and Central Tennessee districts relative to concentrations of these elements in sphalerite from MVT deposits in the Appalachian basin (e.g., East Tennessee district) led Bonnet (2013) to conclude that mineralization in the Central Kentucky and Central Tennessee districts is a product of brines originating from the Illinois basin rather than the Appalachian basin. For Central Tennessee, Jolly and Heyl (1968) reported average Ga and Ge concentrations of 116 ppm and 266 ppm, respectively; for East Tennessee, the average Ga and Ge concentrations were 20 ppm and 38 ppm, respectively. Bonnet (2013) conducted a similar study on samples from the Cumberland, Gordonsville and Elmwood mines in Central Tennessee and reported average concentrations of Ga (536 ppm) and Ge (307 ppm). The same study reported 105 ppm Ga and 11 ppm Ge in samples from the Coy, Young, and Immel mines in the East Tennessee district. Although the reported concentrations for the same elements in the aforementioned studies vary substantially, perhaps due to the technological advances, both studies agree that Ga and Ge concentrations in the Central Tennessee deposits far exceeded the concentrations of Ga and Ge in the East Tennessee deposits. For Central and South-Central Kentucky ores, Jolly and Heyl (1968) reported average Ga and Ge concentrations of 164 ppm and 525 ppm, respectively, similar to the Central Tennessee concentrations. For the Illinois-Kentucky ores in the Illinois basin, the aforementioned study reported average Ga and Ge concentrations of

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