Organic rich, black shales are known to act as sources of hydrocarbons, but they may also act as a source of Mississippi Valley Type (MVT) Pb/Zn ore deposits. MVT deposits are often found in close proximity to hydrocarbons and their presence may in fact be related. MVT deposits occur along the peripheries of sedimentary basins and are typically hosted within carbonate rocks. Very dense, chloride rich, basinal brines, known as “oilfield” brines due to their occurrence with oil in many basins, carry the mobilized metals. The brines responsible for creating the ores are sourced from the adjacent sedimentary basin, are of low temperature (around 60ºC – 150ºC), and may flow hundreds of km through the basin before precipitating the ores. The hydrocarbons are often concentrated in different areas of the host basins than the ores; however, ores in some deposits are characterized by hydrocarbon and brine fluid inclusions. Fluids expelled from the shales, both hydrocarbons and mineralizing fluids, are likely traveling along the same pathways, perhaps even simultaneously.

MVT ores from the Tri-State (TS) and Northern Arkansas (NA) mining district are of Permian age and are hosted in platform carbonates ranging from Ordovician and Mississippian in age for the NA district and Mississippian in age for the TS district. Sphalerite (ZnS) ores and black shales from the late Devonian age Chattanooga Shale and Mississippian age Fayetteville Shale were collected from strategic locations within and nearby the TS and NA mining districts. Mineral separates and whole rock shale samples were analyzed for their trace element concentrations and Pb isotopic ratios in order to compare and contrast them and evaluate the source of the metals. The analyses were conducted on a Thermo Scientific ICAP Q ICPMS for their elemental concentrations and a high resolution Nu Plasma MCICPMS for their Pb isotope ratios at the University of Arkansas.

Current results indicate that there is a genetic link between the organic rich, black shales and nearby MVT deposits. Organic rich, black shales may represent the source of the metals due to their anomalously high metal content and radioactive nature, in addition to the fact that shales have the most connate fluid associated with sediments before compaction. The mineralizing fluids may have been expelled from the shales in the Arkoma Basin during the Ouachita orogeny.
References Cited


Mississippi Valley-Type (MVT) deposits are epigenetic Pb-Zn deposits hosted within carbonate rocks on the flanks of sedimentary basins, often found in close proximity to hydrocarbons. Organic rich, black shales may represent the original source of the metals. The maturation of hydrocarbons likely plays a role in the precipitation of the minerals.

**Introduction**

MVT Deposits

**Why could shales be the source of metals?**

- Anomalously high metal content when compared with other basinal strata, especially with regards to Zn.
- Shales are very radioactive (enriched in Th, U, and K are gamma ray log below) and the ores are very radiogenic (enriched in radiogenic Pb which is the decay products of Th and U).
- Shales are known to expel significant volumes of hydrocarbons which occur in proximity and even in conjunction with the ore deposits. They also expel adsorbed water during burial.
- Fluids forming ores correspond to same temp as hydrocarbon maturation.
- Have most connate fluid of sediments before compaction. Connate fluids are responsible for mineralizing fluids.
- Black shales (precursors to black shales) contain up to 90% connate fluid.
- Shape of sediments have high surface area in contact with fluids and thus have a larger reactionary surface to potentially leach metals into solution.

**Objectives of Study**

- Determine feasibility of shales providing the source of the metals by testing the theory using Pb isotopes in the Southern Ozarks.
- Analyze sphalerite ores from the Tri-State and Northern Arkansas mining districts, along with hydrocarbon producing, organic rich, shales (Fayetteville Shale & Chattanooga/Woodford Shale) within the Arkoma Basin, and a sample of granitic basement for their Pb isotope ratios.
- Similar isotopic signatures between the shales and the ores would indicate a link (Pb isotopes are used as a tracer).
- If link is found between the shales and the ores, this type of mineralization could be used as an indicator for unconventional, hydrocarbon potential down dip, particularly in frontier basins.

**Model for MVT development**

**Spatial Relationship Between MVT Ores and Shale Plays Within Continental U.S. Basins**

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

**Figure 2**: Distribution of MVT ores in relation to shale plays of U.S. modified from U.S. DOE

**Figure 3**: Calcite (common gangue mineral associated with MVT ores) containing hydrocarbon fluid inclusions (Elmwood Mine, Central Tennessee District; Mississippi Valley-Type deposits, as indicated by sphalerite fluid inclusion temperature and H. Sphalerite fluid inclusion temperature

**Figure 4**: Mudlog depicting radioactivity (GR) of carbonaceous shale.

**Figure 5**: Relationship between hydrocarbon maturity, temperature, and vitrinite reflectance. Also shown is the temperature range of the fluids in MVT deposits, as indicated by sphalerite fluid inclusion temperature (from Mastalerz et al., 2013; Schutter, 2015).

**Figure 6**: Notice similarity between cross section of Arkoma Basin and Model for MVT development. The Southern Ozarks are the perfect place to test this theory. Only one major tectonic event influences the structure (Ouachita Orogeny) and no subsequent deformation complicates matters.
Could Organic Rich, Black Shales Be A Source For MVT Deposits?

Bryan Bottoms & Adriana Potra
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The Northern Arkansas mining district and the Tri-State mining district of NE Oklahoma, SE Kansas, & SW Missouri occur on the Northern flank of the Arkoma Basin. Deposits occur near where organic rich, black shales of the Arkoma Basin pinch out against the carbonate shelf deposits of the Ozark Dome. The Late Pennsylvania/Early Permian age deposits are hosted in carbonate rocks of Mississippian age for the Tri-State district and Ordovician and Mississippian age for the Northern Arkansas District. The Late Paleozoic Ouachita orogeny is thought to have mobilized the mineralizing fluids, expelling them northward out of the basin.

**Geologic Setting**

The Northern Arkansas mining district and the Tri-State mining district of NE Oklahoma, SE Kansas, & SW Missouri occur on the Northern flank of the Arkoma Basin. Deposits occur near where organic rich, black shales of the Arkoma Basin pinch out against the carbonate shelf deposits of the Ozark Dome. The Late Pennsylvania/Early Permian age deposits are hosted in carbonate rocks of Mississippian age for the Tri-State district and Ordovician and Mississippian age for the Northern Arkansas District. The Late Paleozoic Ouachita orogeny is thought to have mobilized the mineralizing fluids, expelling them northward out of the basin.

**Locations of Ore Deposits**

**Study Area**

**Results Explained**

- **Pb isotopes** from sphalerite ores, organic rich shales, and local granitic basement samples, plotted with previously published data of MVT ores from the mid continent. Previous published data plotted as fields.
- **Ores** are enriched in all radiogenic Pb isotopes. Tri state ores are on average more radiogenic than Northern Arkansas ores.
- **Shales** also enriched in radiogenic Pb but not as much as ores, especially in regards to Th²³² and Th²³⁸ decay components.

- 1 lone shale sample from base of Chattanooga/Woodford seems to match signature of ores. All other Chattanooga samples are from top.
- Sample of granitic basement (Spavinaw Granite) is enriched in Th²³² component of radiogenic Pb, but not so much in U components.

**Discussion**

- If shales are sourcing the metals, the mineralizing fluids are likely travelling along the same fluid pathways as the hydrocarbons being sourced from the shales, and could potentially be migrating in conjunction with one another.
- If link is found, MVT deposits could be used as a preliminary indicator of hydrocarbon potential down dip, particularly in frontier basins. (Would indicate a thermally mature shale of sufficient volume and organic content, to potentially be an unconventional reservoir).
- Lone sample from the base of the Chattanooga/Woodford seems to match the isotopic signature of the ores closely. Stratigraphic variability within this section should be examined further.

**Future Work**

- Analyze other shales and lithologies within the basin with a particular focus be putting on shales from deeper within the basin and shales that outcrop in the Ouachita thrust belt.
- Core samples or cuttings from deeper could provide better answer.
- Sample more of the base of the Chattanooga.
- Obtain a spectral gamma ray log through the basin and see if that may provide any additional insight or leads for future sampling.
- Spectral gamma ray log that breaks down radioactive components into U, Th, & K components, may help to identify source intervals.

**Acknowledgments**

Thank you to John Samuelson for his help analyzing the samples on the mass spectrometer, Thomas Liner, John Gist, and Lara Hardisty for their aid in collection of samples, and the Univ. of Arkansas for all of their support. An additional thank you is extended to AAPG for hosting this event.

**References**


**Geological Map**

Map showing the locations of ore deposits and the major geological provinces in the study area.

**Results**

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**Methods**

Fresh shale sample of Chattanooga/Woodford Shale, Pb fraction isolated using column chromatography. Work was done in a “Class 100” clean lab at the Univ. of Arkansas’s Radiogenic Isotope Laboratory.

**Results Explained**

- Radiogenic Pb isotopes (206, 207, & 208) are plotted against a stable Pb isotope (204).
- As radioactive decay occurs, the earth becomes more radiogenic in radiogenic Pb isotopes.
- The bulk composition of earth’s radiogenic isotopes through time is represented by the line with points and corresponding dates.

**Pb Isotopes Explained**

- Lead fraction analyzed on a high-resolution Nu Plasma MC-ICP-MS at University of Arkansas.

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