[PS]Could Organic Rich, Black Shales Be A Source For MVT Deposits?*

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Search and Discovery Article #80615 (2017)**
Posted October 30, 2017

*Adapted from poster presentation given at AAPG 2017 Mid-Continent Section Meeting, Oklahoma City, Oklahoma, September 30 – October 3, 2017

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Abstract

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.

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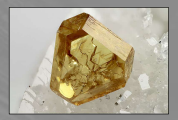
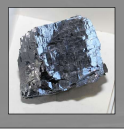
Introduction

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.





Sphalerite (ZnS) pictured on left. Galena (PbS) pictured on right. Main economic minerals of MVT deposits.

What is known about MVT Deposits?

- Low temperature fluids (60°C-150°C) are responsible for their formation.
- Fluids are sourced from sedimentary basin adjacent to deposits and may flow hundreds of km before precipitating the ores.
- Ores are highly enriched in radiogenic Pb.
- Often found in proximity to hydrocarbons and even with hydrocarbon fluid inclusions, yet host rocks are not thermally mature themselves.
- Often found in proximity to where hydrocarbon producing, organic rich shales pinch out against flanks of sedimentary basins.
- Timing of formation often coincides with orogenic event.

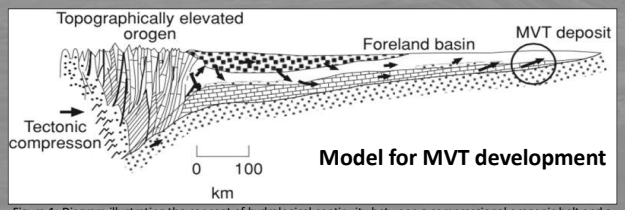


Figure 1: Diagram illustrating the concept of hydrological continuity between a compressional orogenic belt and a foreland sedimentary basin through which orogenically and topographically driven fluids flow; and within which MVT Zn-Pb deposits form. (Robb, 2005)

$$ZnCl_2\ (aq) + H_2S\ (aq) + 2Na^+(aq) <-> ZnS\ (sphalerite) + 2NaCl\ (aq) + 2H^+(aq)$$

$$CaCO_3(solid) + 2H^+ <-> Ca^{2+} + H_2CO_3(aq)$$

Above equations depict how metals are mobilized as chloride complexes and precipitated out when in contact with source of reduced sulfur (H_2S). 2nd Equation depicts carbonate dissolution by acidic waters. Using up H+ ions in carbonate dissolution pushes first equation to the right, further destabilizing chloride complexes and driving precipitation of sulfides.

How Metals Are Mobilized and Precipitated

Saline "oilfield" brines transport the metals as strong chloride complexes. Fluids are acidic and dissolve host limestones creating voids. Neutralization of acidic brines by limestone destabilizes choloride complexes.

Source of Reduced Sulfur is required to precipitate the metals out of solution.

- Could come from maturation of hydrocarbons in form of H_2S.
- Could be derived from a sulfate, through a reaction with a reductant, such as organic matter.

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 see 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 oozes (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.

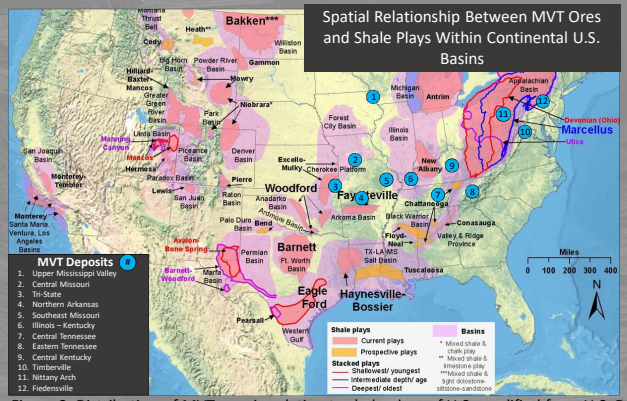


Figure 2: Distribution of MVT ores in relation to shale plays of U.S; modified from U.S. DOE

Figure 3: Calcite (common gangue mineral associated with MVT ores) containing hydrocarbon fluid inclusions (Elmwood Mine, Central Tennessee District).

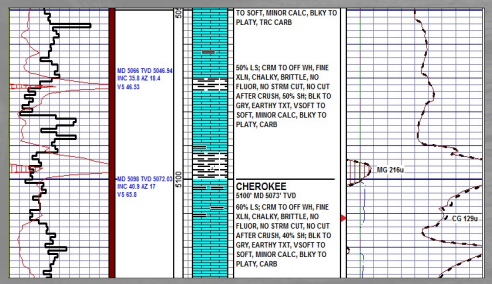


Figure 4: Mudlog depicting radioactivity (GR) of carbonaceous shale.

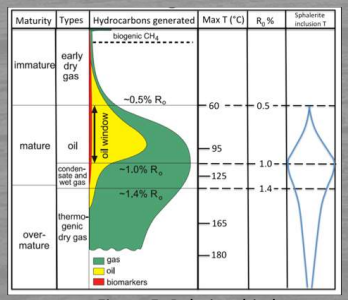


Figure 5: Relationship between hydrocarbon maturity, temperature, and vitrinite reflectance. Also shown is the temperature range of the fluids in MVT deposits, as indicated by sphalerite fluid inclusion temperature (from Mastalerz et al., 2013; Schutter, 2015).

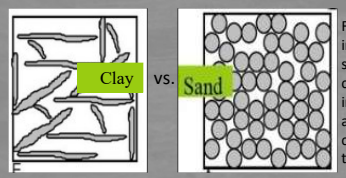


Figure 6: Physical difference in shape between clay and sand grains. Difference causes more connate fluid in mud rocks and provides a larger surface area in contact with connate fluid to potentially leach metals.

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.

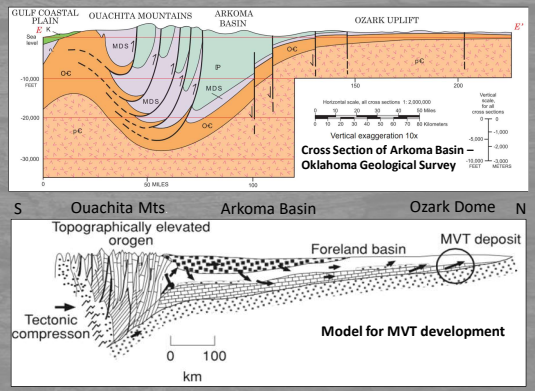


Figure 6: Notice similarity between cross section of Arkoma Basin and Model for MVT development. The Southern Ozarks are the perfect place to test this theory. Only one major tectonic event influences the structure (Ouachita Orogeny) and no subsequent deformation complicates matters.

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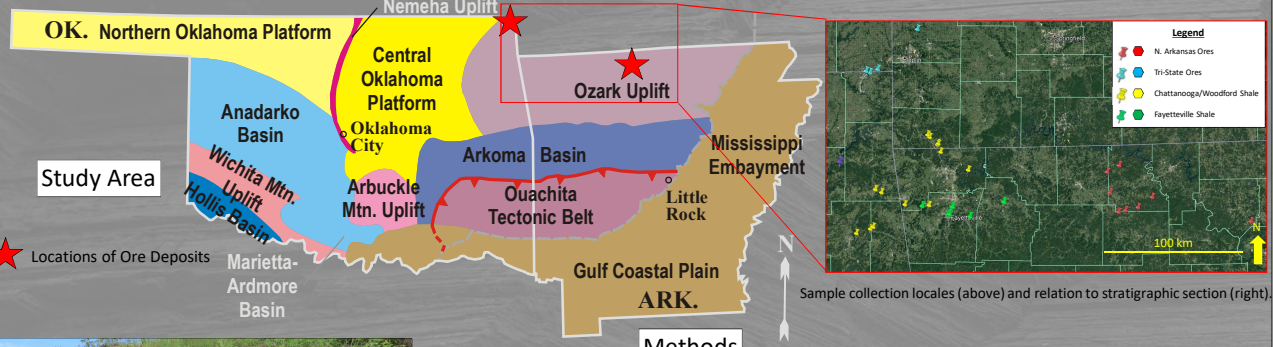
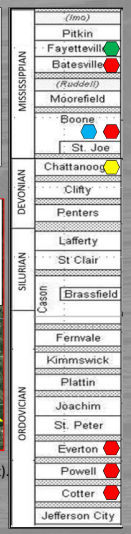
Geologic Setting

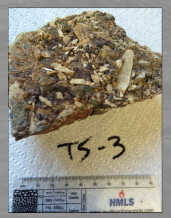
The Northern Arkansas mining district and the Tri-State mining district of NE Oklahoma, SE Kansas, & SW Missouri occur on the Northern flank of the Arkoma Basin. Deposits occur near where organic rich, black shales of the Arkoma Basin pinch out against the carbonate shelf deposits of the Ozark Dome. The Late Pennsylvanian/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.





Sample collection locales (above) and relation to stratigraphic section (right).

Collecting shale sample from upper Fayetteville shale near Huntsville, AR.



Sphalerite ore sample hosted in carbonate breccia from Tri-State-mining district.

Methods

Fresh shale sample of Chattanooga/Woodford Shale.

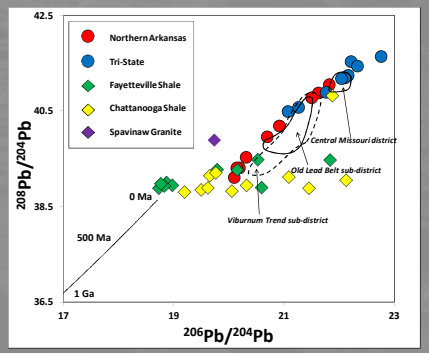
Pb fraction isolated using column chromatography. Work was done in a "class 100" clean lab at the Univ. of Arkansas's Radiogenic Isotope Laboratory.

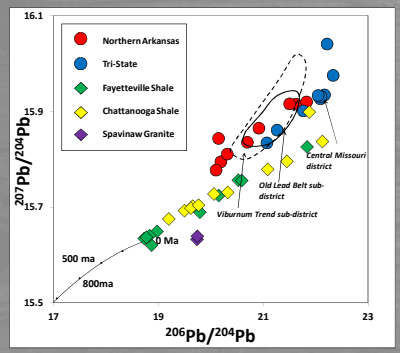
Pb fraction analyzed on a high-resolution Nu Plasma MC-ICP-MS at University of Arkansas.

Results

TOC analysis of shales reported below.

Chattanooga / Woodford Shales	%TOC	Fayetteville Shales	%TOC
CS1	7.5	FS2 - Upper	1.2
CS2	4.2	FS3	3.8
CS3	3.8	FS4	2.0
CS5	4.2	FS6 - Lower	6.3
CS6	3.0	FS7L - Lower	7.5
CS7	5.3	FS8UU - Upper part of Upper	0.1
CS8	2.5	FS9LU - Lower part of Upper	0.3
CS9	2.4	FS10L - Lower	0.9
CS10 - Base	3.9		
CS11	3.2	FS1L – Lower	13.5*
CS12	2.8		
CS13	2.2	*just outside calibration curve	





Results Explained

- Radiogenic Pb isotopes (206,207,&208) are plotted against a stable Pb isotope (204).
- As radioactive isotopes decay over time, the earth becomes more enriched 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

^{204}Pb	^{206}Pb	^{207}Pb	^{208}Pb
203.97302	205.97444	206.97588	207.97663
1.40%	24.10%	22.10%	52.40%
Stable	Radiogenic	Radiogenic	Radiogenic
Decay Product of:	U^{238}	U^{235}	Th^{232}

Explanation of Results (Continued)

- Pb isotope data 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 U^{235} and Th^{232} 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 Th^{232} 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 being put 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 Lura 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.

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