12-2017

A Geochemical Investigation and Comparison between Organic-rich Black Shales and Mississippi Valley-Type Pb-Zn Ores in the Southern Ozarks Region

Bryan Michael Bottoms
University of Arkansas, Fayetteville

Citation

Bottoms, B. M. (2017). A Geochemical Investigation and Comparison between Organic-rich Black Shales and Mississippi Valley-Type Pb-Zn Ores in the Southern Ozarks Region. *Graduate Theses and Dissertations* Retrieved from https://scholarworks.uark.edu/etd/2576

A Geochemical Investigation and Comparison between Organic-rich Black Shales and Mississippi Valley-Type Pb-Zn ores in the Southern Ozarks Region

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

by

Bryan Bottoms
University of Arkansas
Bachelor of Science in Geology, 2012

December 2017
University of Arkansas

This thesis is approved for recommendation to the Graduate Council.

Adriana Potra, Ph.D.
Thesis Director

Phil Hays, Ph.D. Committee Member	Chris Liner, Ph.D. Committee Member	Thomas McGilvery, Ph.D. Committee Member

Abstract

Mississippi Valley-type (MVT) deposits are base metal sulfide deposits that are important economic sources of both Pb and Zn, accounting for 24% of the global Pb and Zn reserves. They are found all over the world, often hosted in platform carbonates on the flanks of sedimentary basins, and often in proximity to hydrocarbons. They are epigenetic, not related to igneous activity, and thought to be sourced from low temperature, highly saline basinal brines that are expelled from sedimentary basins during compaction and/or in conjunction with an orogenic event. The basinal lithologies responsible for providing the metals for the ores are still a matter of debate. The ores are highly enriched in radiogenic Pb and thus potential sources must also share this same isotopic signature. Shales have been hypothesized to represent the original source of the metals due to their radioactive nature, the large volumes of connate fluid associated with their sediments before compaction, and their association with hydrocarbons.

The Pb isotopic compositions of 20 sphalerite samples from the Northern Arkansas and the Tri-State MVT mining districts, 23 shales from the Chattanooga and Fayetteville formations, and 2 granitic basement rocks from the southern Ozarks have been analyzed and compared in order to evaluate the potential source(s) of the metals. The granites and most of the shales do not match the isotopic signature of the ores and thus may not represent a viable metal source. However, one sample taken from the base of the Chattanooga shale has similar Pb isotopic ratios to the ores, suggesting that the shale may have provided the metals. The depositional environment of the aforementioned shale sample explains the isotopic signature and sheds some light on the origin of the ore deposits.

Acknowledgements

First and foremost, I would like to thank Dr. Adriana Potra for her relentless support, guidance, and friendship throughout this entire endeavor. She continuously motivated me to do my very best and become a better all-around geologist. I owe everything I know about geochemistry and effectively navigating through graduate school to her. I’d like to thank all of my committee members, Dr. Phil Hays, Dr. Chris Liner, and Dr. T. A. “Mac” McGilvery, for the additional insight they provided along the way. Additionally, I’d like to thank Dr. Chris Liner for making the connection between Dr. Potra and I, which ultimately led to the following research. I’d like to thank the entire University of Arkansas Geoscience Department for their continuous support throughout graduate school, without which, none of this would have been possible. Lastly, I would like to thank my good friends Riley Dickson and Francisco Rusconi for their provided friendship and company over the previous years. Graduate school wouldn’t have been the same without them.

Dedication

I’d like to dedicate this thesis to Selina Matthews. Without her constant love, support, and understanding, none of this would be possible. Additionally, I’d like to dedicate this thesis to my parents, Mike and Monica Bottoms, who have always been there for me and have always encouraged me to do my absolute best.

Table of Contents

List of Tables

List of Figures

1. Introduction

1.1 General Characteristics of the Mississippi Valley-Type Deposits

Mississippi Valley-type (MVT) deposits are important economic sources for both Pb and Zn. They account for 38% of the global tonnage of all sediment hosted Pb and Zn deposits (Leach et al., 2010) and 24% of the global Pb and Zn reserves. On average, Zn tonnage outweighs the Pb by 10:1; however, deposits can vary widely with some mineral districts only yielding Zn and others being dominated by Pb deposits (Leach et al., 2010). MVT deposits are found all over the world (Figure 1) but they owe their name to the fact that many of the largest and first researched deposits occur within the Mississippi River drainage of North America (Leach et al., 2010). The type locality is represented by the sedimentary basins of the midcontinent United States. Nearly all of the deposits are hosted in platform carbonates (mostly limestone and dolostone) and rarely sandstone, on the flanks of Phanerozoic sedimentary basins or near basement highs within the basins (Ridley, 2013; Leach, 2010). Many of the basins owe their development to foreland basin formation during compressional orogenic events that occur as a result of major tectonic plate collisions (Bradley and Leach, 2003).

The deposits are locally controlled by both structural and stratigraphic features such as faults, basement highs, and lithological transitions. Although they are associated with large scale crustal contraction events, the deposits are structurally confined to extensional faults that formed as a result of lithospheric flexure related to the compressional orogenic events (Bradley and Leach, 2003). The fundamental control on the location of the MVT ores is represented by lithologic transitions that provide drastic changes in both vertical and lateral permeability of the rocks (Leach, 2005). These lithologic transitions are often from shales to limestones, limestones to dolostones and, because the deposits are hosted in platform carbonates, by facies changes associated with carbonate reefs and barrier complexes.

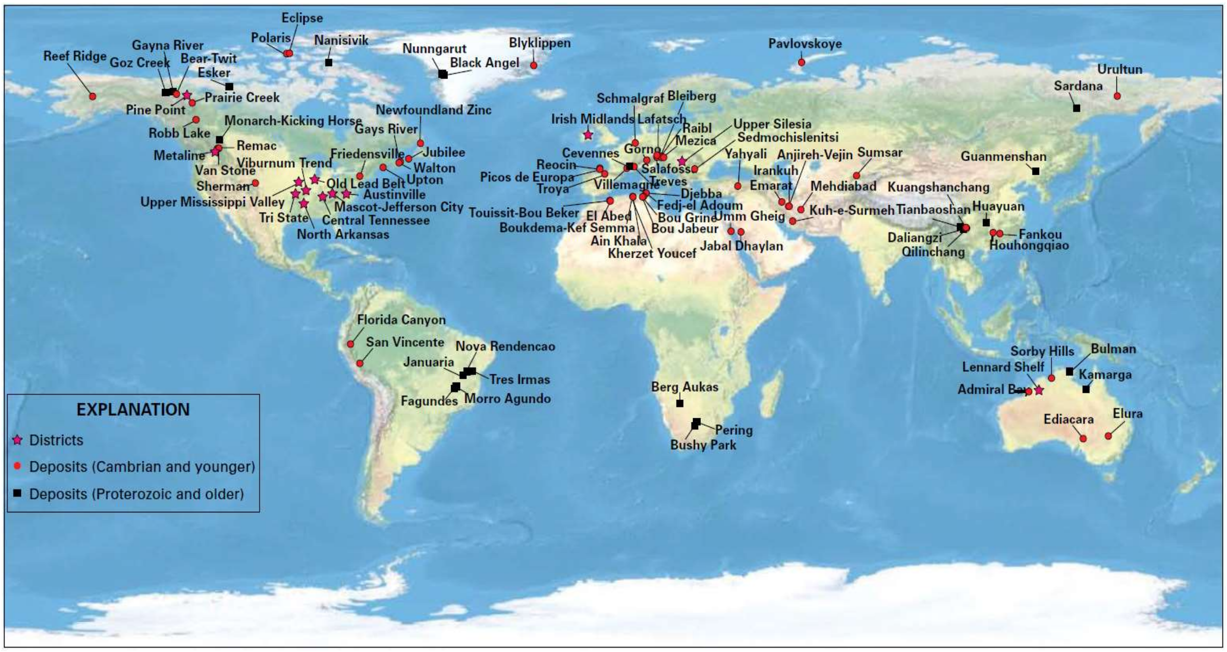


Figure 1. Global distribution of Mississippi Valley-Type lead-zinc deposits and districts (Leach et al., 2010).

Other important characteristics of the MVT deposits are: (1) they are epigenetic (deposited after the host rock); (2) they are not related to igneous activity; (3) the mineralization often occurs in large districts; (4) the mineralizing fluids are considered to be basinal brines with a composition of 10-30% weight salts and are referred to, colloquially, as oilfield brines; (5) the source of both the metals and sulfur is generally considered to be crustal in origin; (6) the temperatures of the mineralizing fluids are relatively low and range from 75°C-200°C; (7) the ores range from coarsely crystalline to fine grained, and vary from massive to disseminated within the host rock; (8) the sulfide mineralization occurs mainly as replacement of carbonate host rocks and, to a lesser extent, as void space fill; (9) the country rock is often altered through dolomitization, dissolution, or brecciation (Leach, 2005). The ores are often stratabound and locally stratiform in nature and the dominant minerals are sphalerite, galena, pyrite, marcasite, dolomite, and calcite, with minor barite and rare fluorite occurrences.

The ore deposits are generally found in close proximity to hydrocarbons and occasionally contain hydrocarbon fluid inclusions (Schutter, 2015). In addition, they are often located where organic rich shales of the sedimentary basins pinch out against platform carbonate deposits on the flanks of the sedimentary basins (Figure 2). The shales usually represent great hydrocarbon source rocks within the basins and thus there may be some relation to both hydrocarbon maturation and migration.

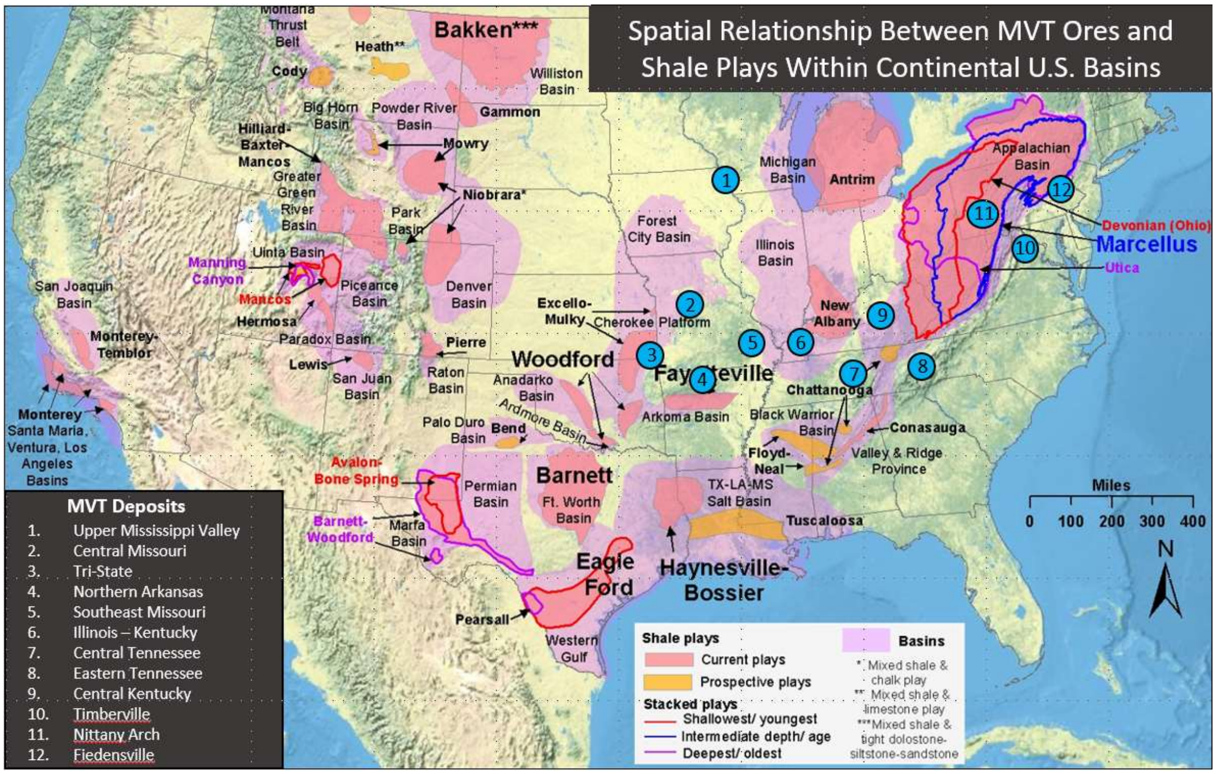


Figure 2. Spatial relationship between North American MVT deposits, sedimentary basins, and current organic rich, hydrocarbon producing shale plays in the Continental United States. (Modified from Energy Administration Information: May 9, 2011).

1.2 How do Mississippi Valley-Type Deposits Form?

Historical Explanations

The origin of Mississippi Valley-Type deposits has long been a subject of debate. Various mechanisms have been proposed to explain their origin, including artesian circulation of groundwater, hydrothermal activity associated with igneous activity, and large-scale fluid flow out from a foreland basin during an orogenic event. Explanations for the original source of the metals have also varied widely with limestones, dolostones, granitic basement rock, shales, and seawater all being called upon as the initial source of the metals.

As these deposits have been economically important resources for a long time, their study started quite some time ago. The following studies pertain to the ore deposits of the Southern Ozarks, which are also the focus of this study. Schmidt and Leonhard (1873-1874) were the first geologists to study the ore deposits in the Southern Ozarks. They concluded that the ores were deposited contemporaneously with the dolomitization of the Mississippian aged rocks in the area by laterally moving fluids. Jenney (1894), later supported by E. M. Shepard (1898), suggested that the ores were derived from fluids circulating through fractures and fissures of unknown extent in the pre-Cambrian crystalline basement rocks and precipitated out as the moderate to normal temperature fluids cooled during their long journey upwards.

Many authors concluded that shales might have been the source of the metals in the ores. F. L. Clerc (1887) proposed the idea that the ores were leached from sink-hole shale patches of Pennsylvanian age which dotted the region and may have been more laterally continuous in the past. Haworth (1904) suggested that the shales provided the source of the metals, and that the metals were carried down and concentrated in the underlying Mississippian limestones and cherts. Buckley and Buehler (1906) concluded that the metals were derived from the overlying

Pennsylvanian aged shales. During the erosion of the shales, the metals were oxidized, taken into solution, carried downward into the Mississippian limestones, and concentrated by the mixing of oxidizing and reducing solutions. Buckley and Buehler (1906) also suggested that ascending solutions carrying the metals likely mixed with H_2S gas associated with the organic matter in the shales. This input of sulfur played a role in the precipitation of the minerals.

Using geochemical analysis, Winslow (1894) showed that large volumes of Pb and Zn were disseminated in the Archean, Cambrian, Ordovician, and Mississippian rocks of the Ozark dome. He proposed that as these rocks eroded, they supplied metals for the younger rocks. He suggested that organic matter deposited during the Pennsylvanian period played a very important role in precipitating the ores. He stated that the margins of the Pennsylvanian sea posed the most favorable conditions for precipitation of the ores.

Siebenthal (1915) proposed that an artesian circulation of groundwater flowing outwards from the core of the Ozark dome was responsible for carrying the metals. He claimed that the metals were sourced from the Cambrian and Ordovician limestones and dolomites. Emmons (1929), Ridge (1936), and Garrels (1941) concluded that the ores were sourced from hydrothermal solutions associated with igneous activity. White (1958) proposed the connate-brine fluid theory as an explanation for ore formation. He concluded that the metals were initially disseminated in sedimentary rocks and later were concentrated and deposited in their present locales by warm, upward-moving fluids. The fluids were heated either by deep burial or by proximity to an intrusive igneous body.

Ohle (1959) reviewed the various competing theories on the origins of the MVT ores worldwide and favored the theory associated with igneous activity, yet cautioned ruling out the other options as viable alternate possibilities.

Hall and Friedman (1963) also called upon White's (1958) connate-hydrothermal theory to explain MVT ore deposits in the Upper Mississippi Valley districts. Whereas much of the early hypotheses explaining the genesis of the deposits were somewhat speculative in nature, the connate-hydrothermal fluid theory utilized fluid inclusion studies of the ores and noted similar composition to the saline, deep basinal brines. However, sodium chloride (NaCl), the main dissolved component of these brines, is also a major constituent of magmatic fluids.

Fischer and McKnight (1970) performed an intensive review of the ore deposits of the Picher Field in the Tri-State Mining District and concluded that the magmatic fluid hypothesis was the most plausible one. They stated that "the resemblance of the fluid inclusions from Tri-State sulfides to oil-field brines is believed to be superficial and of no genetic significance." They also objected to the feasibility of transporting hydrothermal fluids expelled from the Ouachita orogeny laterally hundreds of km to the north to the location of the ore deposits.

Modern Explanation

In most recent years, the connate-hydrothermal fluid theory has become the most widely accepted explanation for the ore formation. The theory postulates that saline basinal fluids are responsible for transporting the metals (Ridley, 2013, and references therein). The saline fluids are mobilized and expelled out of a sedimentary basin, often during an orogenic event (Figure 3). The fluids may flow hundreds of km through the basin before precipitating the ores (Oliver, 1986; Robb, 2005). Many articles have been published on the relation between the ores and the foreland basins formed during orogenies (Garven, 1985; Mitchell, 1985; Leach and Rowan, 1986; Oliver, 1986; Bradley and Leach, 2003). Advances in isotopic geochronology have constrained the timing relation between the two (Bradley and Leach, 2003).

However, the origins of the metals are still a subject of debate. Almost every unit in the stratigraphic columns of the different districts, including the metamorphic and igneous basement, has been proposed as the original source of the metals now found in the MVT deposits. Goldhaber et al. (1995) proposed a supracrustal origin for the metals. Leach et al. (2005) concluded that the metals came from a basement source, or rocks derived from the basement, due to their enrichment in radiogenic Pb isotopes. Schutter (2015) proposed that organic rich shales are the likely source for the metals. Shales may very well represent the source of the metals. They are often enriched in metals and radioactive elements and the ores are enriched in the radiogenic end members of those radioactive elements. Metals are often adsorbed onto the surface of clay sediments which make up significant portions of the shales or adsorbed to organic matter which is often preserved in black shales (Algeo and Maynard, 2004). In addition, shales are known to expel large volumes of fluids, both hydrocarbons and connate fluids.

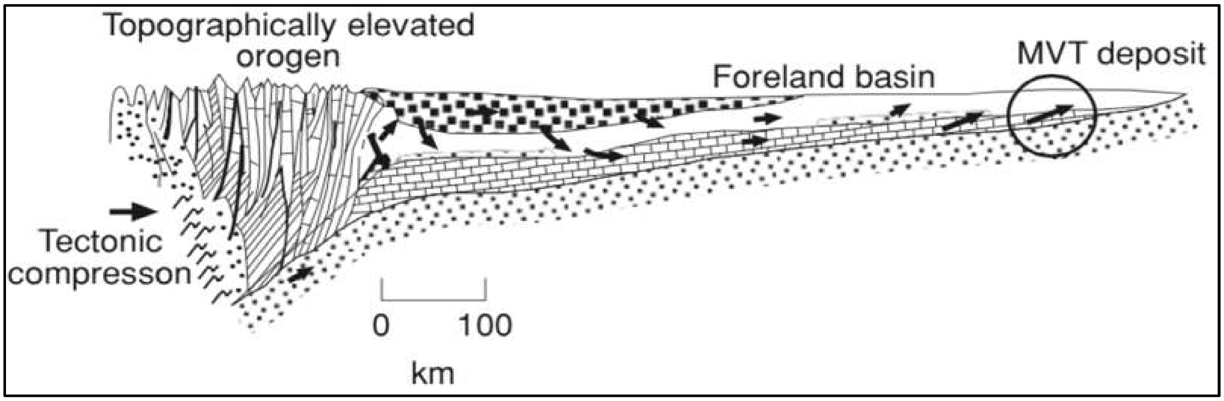


Figure 3. Diagram illustrating the concept of hydrological continuity between a compressional orogenic belt and a foreland sedimentary basin through which orogenically and topographically driven fluids flow; and within which MVT Zn-Pb deposits form (Robb, 2005).

1.3 Nature of Mineralizing Fluids

Fluid inclusion studies starting with Hall and Friedman (1963) revealed that the fluids responsible for transporting the metals were highly saline basinal brines. The brines typically consist of 10-30 weight % sodium-calcium-chloride salts (Leach et al., 2010; Ridley, 2013) and are also often found in deep sedimentary basins in conjunction with hydrocarbons. Hydrocarbon fluid inclusions are sometimes found within the brine fluid inclusions of the ore minerals (Ridley, 2013). The similarity to oil-field brines has led to widespread acceptance of a basin generated origin for the fluids (Leach et al., 2010).

Fluid salinity is an important control on metal transport, especially in regards to the base metals Pb, Zn, and Cu (Ridley, 2013). These metals form strong chloride complexes in low temperature fluids that can effectively transport the metals in solution. The following equation expresses this relationship between salinity and Zn solubility:

$$ZnS_{(sphalerite)} + 2NaCl_{(aq)} + 2H^{+}_{(aq)} \leftrightarrow ZnCl_{2\,(aq)} + H_2S_{(aq)} + 2Na^{+}_{(aq)}$$

The above equation demonstrates that Zn preferentially bonds with the Cl^- and forms a chloride complex that facilitates the transport of the metals. The higher the salinity, the higher the concentration of the metals that can be transported. Once the chloride complex comes in contact with a source of reduced sulfur, the Zn is precipitated as a sulfide mineral. As the ores are only stable under reducing conditions (Ridley, 2013), this input of reduced sulfur is an important control on ore deposition. Reduced sulfur can come from one of two possible sources 1) sulfides released directly into solution from the decay of organic matter, such as during oil maturation, or 2) derived from a sulfate that has reacted with a reductant such as organic matter (Ridley, 2013). Therefore, the distribution of organic matter plays an important role in ore deposition.

The equation above depicts the fluids as being slightly acidic, which helps dissolve the carbonates that host the deposits and creates the void spaces into which the ores precipitate. Dissolution of the limestone neutralizes the hydrothermal fluids, destabilizing the chloride complexes and contributing to the precipitation of the minerals. The following equation shows the dissolution of the carbonate host rocks:

$$CaCO_3 + 2H^+ \leftrightarrow Ca^{2+} + H_2CO_3$$

Temperatures gathered from fluid inclusion studies range from 50°C to 250°C (Leach et al, 2005). However, they commonly vary between 75°C and 150°C. The temperatures of the ore fluids responsible for generating the Tri-State and the Northern Arkansas mining districts range from 80°C to 120°C and from 90°C to 130°C, respectively (Leach et al., 2005). The above values correspond well with the "oil-window" (50°C-150°C) temperatures, the temperatures at which organic matter is converted to liquid hydrocarbons (Figure 4).

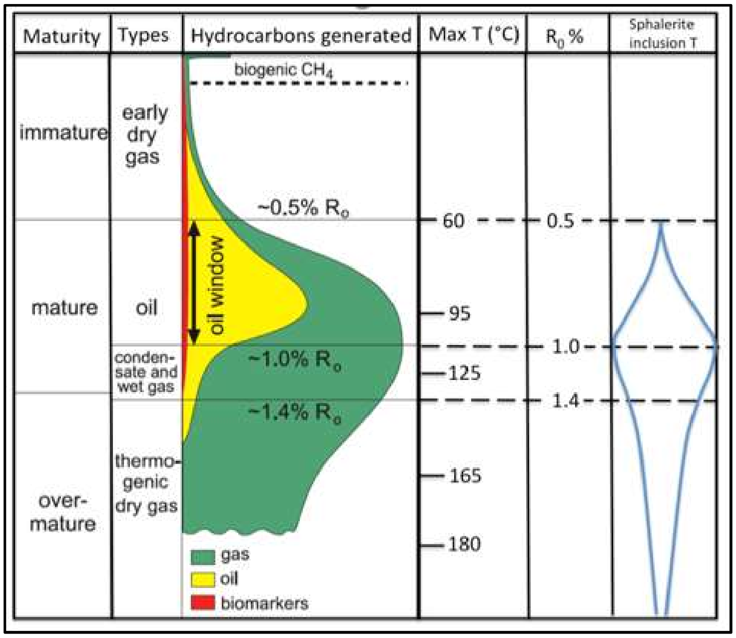


Figure 4. Relationship between hydrocarbon maturity, temperature, and vitrinite reflectance. Also shown is the temperature range of the fluids in MVT deposits, as indicated by sphalerite fluid inclusion temperature (from Mastalerz et al., 2013; Schutter, 2015).

1.4 Relation of Ores to Hydrocarbons

Many authors have commented on the coexistence and potential relationship between hydrocarbons and MVT ores. Veatch (1899) described sphalerite and galena found in conjunction with gas and oil at the crest of anticlinal salt mounds in Louisiana. Siebenthal (1915), in his review of the ore deposits around Joplin, MO, described heavy oil residue in contact with the base of the Pennsylvanian shales and in close proximity to the ore deposits. He interpreted this residue as evidence for ascending mineralizing fluids migrating with the bitumen. Schutter (2015) comments that MVT ores are known for the “ubiquitous” presence of hydrocarbons.

This phenomenon is not limited to North America. Hydrocarbons have been found in conjunction with Pb/Zn deposits in Sweden (Rickard et al. 1975), England (Parnell, 1990), Canada and Australia (Ridley, 2013). Oliver (1986) hypothesized that fluids mobilized from orogenies play a key role in the migration of both hydrocarbons and Pb/Zn metals (Figure 5). He notes the widespread similarity in their distribution patterns around the United States (Figure 2 and Figure 6). The proximal relation between both the ores and the hydrocarbons could be coincidental. The basins that host the mineral deposits are often known hydrocarbon-producing basins, and it is expected that the mineralizing fluids would follow similar flow paths to the hydrocarbons sourced from the basin. Moreover, besides being found in close proximity to one another, many times the ores contain hydrocarbon and brine fluid inclusions. This suggests that the hydrothermal fluids and hydrocarbons were present together at the same time, implying both, a spatial and a temporal relationship. The presence of mature hydrocarbons within the fluid inclusions, despite the fact that the host rock itself is not thermally mature, implies that the hydrocarbons migrated from deeper in the basin and were not matured locally (Schutter, 2015).

The aforementioned similarity between the fluid inclusion temperatures and the oil window is an intriguing piece of evidence supporting the relationship between the ores and hydrocarbons. Eisenlohr et al. (1989) linked the maturation and migration of hydrocarbons to the migration of mineralizing fluids responsible for the MVT ores in the Canning Basin of Australia.

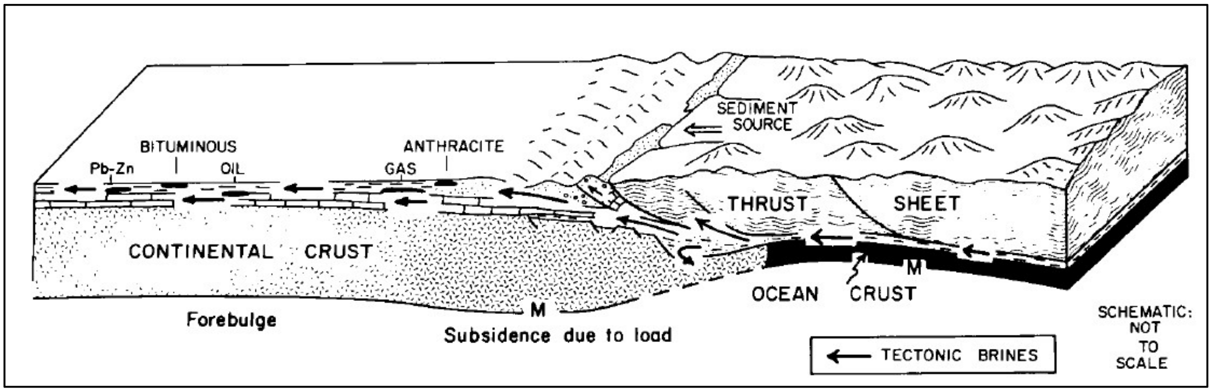


Figure 5. Block diagram of tectonic brines expelled from buried sediments during an orogeny and their relation to Pb-Zn deposits, oil, gas, and coals (Oliver, 1986).

Another pertinent fact is that the ores often occur on the flanks of sedimentary basins where organic rich shales pinch out along platform carbonates. These same organic rich shales are often the hydrocarbon producing source rocks of the adjacent sedimentary basins (Schutter, 2015). As stated earlier, the distribution of organic matter is an important control on the source of reduced sulfur needed for precipitation of the minerals.

1.5 Statement of the Problem

Little is known about the source(s) of metals in the MVT deposits from the Northern Arkansas and the Tri-State mining districts. An essential, still unanswered, question is whether the metal-bearing fluids required specific host-rock lithologies or rocks with high concentrations of metals Pb and Zn. The purpose of this study is to identify metal-contributing source rocks for MVT deposits from the Southern Ozarks region and elucidate what role, if any, organic rich shales and the maturation of hydrocarbons, play in the formation of MVT deposits. The competing theories of where the metals in the Southern Ozarks were sourced from were evaluated by performing whole-rock Pb isotope analyses on organic rich shales and granitic basement rocks. The Pb isotopic ratios of the whole rock samples represented by shales and granites were compared with the Pb isotopic ratios of the ores from the Northern Arkansas and the Tri-State mining districts, and the metal sources will be evaluated.

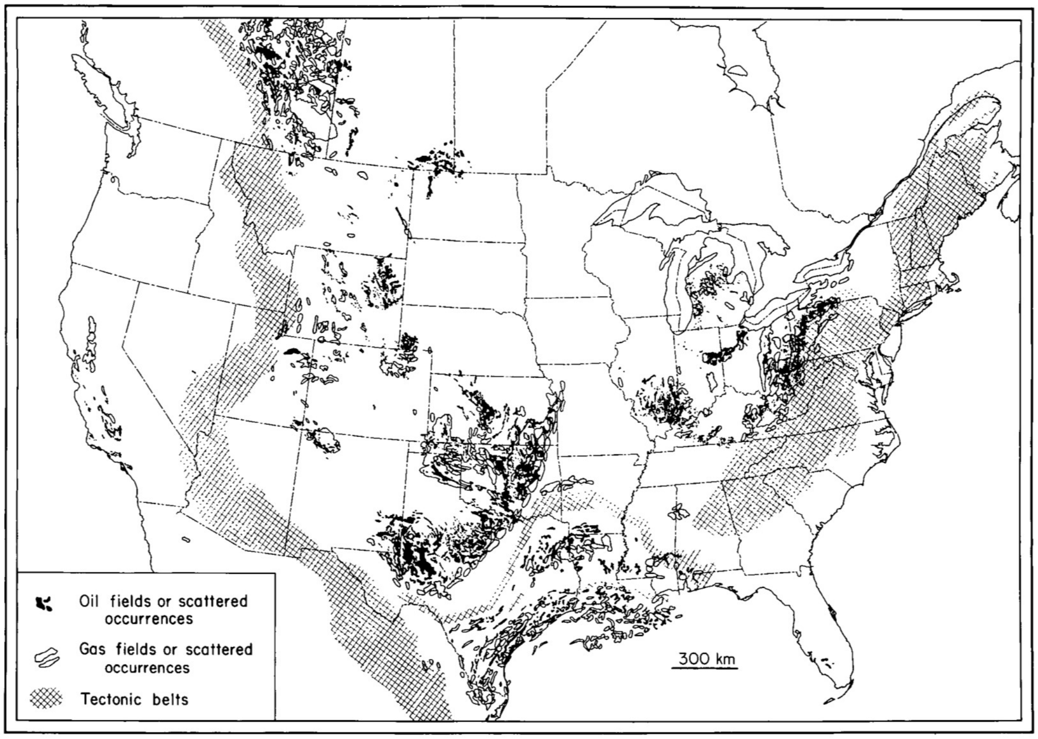


Figure 6. Distribution of Oil and Gas fields in relation to tectonic belts across continental United States (From: Wilkerson, 1982; Oliver, 1986).

2. Regional Geology

The Northern Arkansas and Tri-State mining districts are situated on the southern edge of the Ozark Dome. The Arkoma Basin, a deep sedimentary foreland basin that was formed as a result of the Ouachita orogeny, is located south of the aforementioned districts. (Figure 7 and Figure 8). The Ozark Dome is a Pre-Cambrian (1.4Ga) igneous cored uplift, with the core being exposed in the St. Francois mountains of southeastern Missouri (Guccione, 1993). Paleozoic sedimentary rocks lie unconformably atop the older igneous rocks and dip away in all directions from this igneous core.

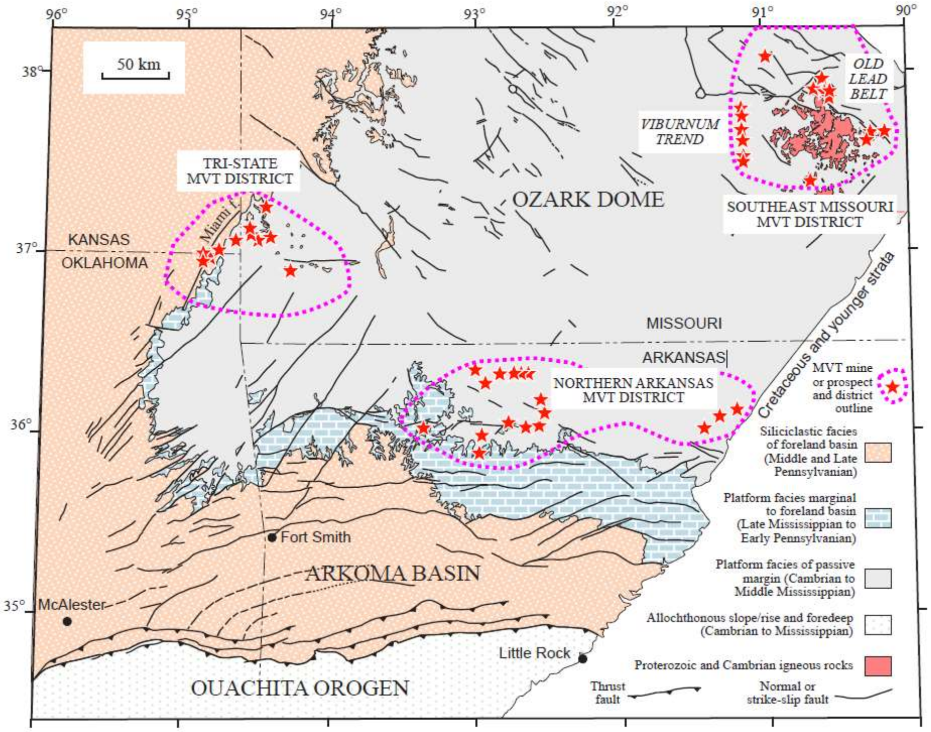


Figure 7. Location of Northern Arkansas and Tri-State mining districts in relation to structural and geographic elements of the area (From: Bradley and Leach, 2003).

From Cambrian to Middle Mississippian time, the southern Ozarks were a vast stable shelf on the edge of the North American continent. The shallow water passive margin allowed for the deposition of platform carbonates on the shelf. Black shales and cherts were deposited further to the south, in a deeper water setting (Byrnes and Lawyer, 1999). Carbonate deposition on the shelf was only interrupted by an influx of clastic sediments from the northeast during the middle Ordovician. Sea level fluctuation across the shallow shelf is responsible for multiple disconformities between formations and erosion of earlier strata in some locations.

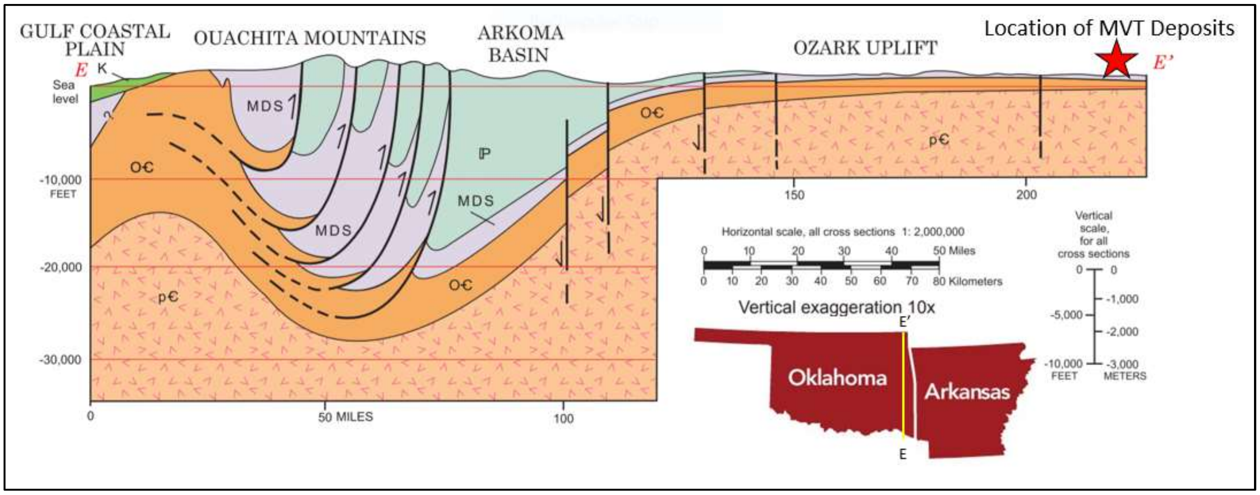


Figure 8. Cross section of Arkoma Basin from South to North with general location of MVT deposits in relation to the structure of the Arkoma Basin (Modified from Johnson et al., 1972). Notice the similarity between this figure and Figure 3.

By the late Paleozoic, the ocean basin to the south was closing as another landmass, Llanoria, was approaching form the south (Guccione, 1993). Beginning in the Middle Mississippian, subduction of the North American plate to the south caused the stable shelf along the southern edge of North America to begin subsiding. The developing Arkoma foreland basin subsided as the load of thrust sheets advancing from the south increased (Arbenz,1989). Sediments sourced from the uplifted Ouachitas to the south as well as from areas to the northeast began to fill the basin from east to west (Arbenz, 1989). On the shelf to the north, terrigenous sediments sourced from the Illinois Basin area were deposited. By the Pennsylvanian, subduction-related flexural bulging caused extensive normal faulting in the southern Ozarks, breaking down the once stable shelf and forming the northern flank of the modern Arkoma basin

(Houseknecht, 1986; Arbenz, 1989). Thick sections of clastics sourced from the uplifted Ouachita mountains filled the basin. By the end of the middle Atokan, major fault movement had stopped and prograding deltaic systems filled the basin from East to West (Sutherland; 1989). The Ouachita orogeny ended in the late Pennsylvanian/early Permian (Arbenz; 1989) and this time corresponds with the emplacement of the MVT ores in both districts.

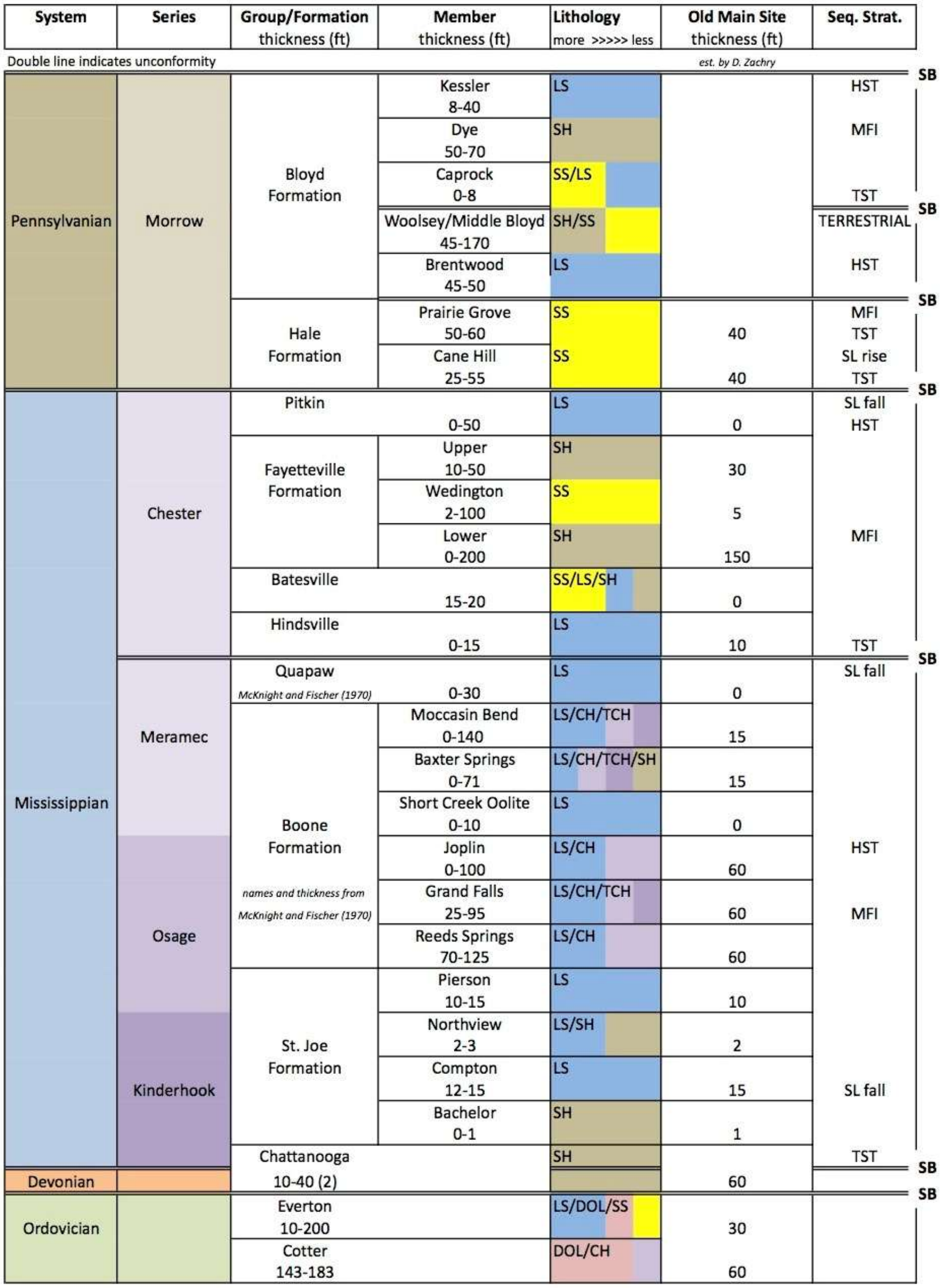
2.1. Organic-rich shales of the southern Ozarks region

Fayetteville Shale

The Fayetteville Shale is a Late Mississippian black shale (Figure 9) that is a known source rock and producer of hydrocarbons within the Arkoma Basin (Ratchford and Bridges, 2006). The Fayetteville shale represents a basinal deposit corresponding with a northward encroachment of the basin (Frezon and Glick, 1959). The shale can be divided into the Upper Fayetteville and Lower Fayetteville, split by the Wedington Sandstone member in western Arkansas (Frezon and Glick, 1959). The Upper Fayetteville is a black to grey shale with low organic content. The Lower Fayetteville has a much higher organic content compared to the upper Fayetteville (Ratchford and Bridges, 2006). Septarian concretions and fossils are plentiful within many intervals of the formation. The formation is thermally mature and produces dry gas across much of the Arkansas portion of the northern Arkoma Basin (Ratchford and Bridges, 2006).

Chattanooga/Woodford Shale

The Chattanooga Shale, also known as the Woodford in Oklahoma, is a Late Devonian to Early Mississippian black shale (Figure 9) that is present across a wide swath of the North American continent from Oklahoma to Tennessee. The shale corresponds with a large transgression across much of the area (Byrnes and Lawyer; 1999). The formation is very high in organic content, ranging between 2 and 12% TOC, and has long been regarded as an excellent hydrocarbon source rock in the Arkoma basin, as well as other basins around Oklahoma (Byrnes and Lawyer, 1999 and references therein).



System	Series	Group/Formation thickness (ft)	Member thickness (ft)	Lithology more >>>>> less	Old Main Site thickness (ft)	Seq. Strat.	
Pennsylvanian	Morrow	Bloyd Formation	Kessler 8-40	LS		HST	SB
			Dye 50-70	SH		MFI	
			Caprock 0-8	SS/LS		TST	
			Woolsey/Middle Bloyd 45-170	SH/SS		TERRESTRIAL	SB
			Brentwood 45-50	LS		HST	
		Hale Formation	Prairie Grove 50-60	SS	40	MFI TST	SB
			Cane Hill 25-55	SS	40	SL rise TST	
Mississippian	Chester	Pitkin	0-50	LS	0	SL fall HST	SB
		Fayetteville Formation	Upper 10-50	SH	30		
			Wedington 2-100	SS	5		
			Lower 0-200	SH	150	MFI	
		Batesville	15-20	SS/LS/SH	0		
		Hindsville	0-15	LS	10	TST	
	Meramec	Quapaw McKnight and Fischer (1970)	0-30	LS	0	SL fall	SB
		Boone Formation names and thickness from McKnight and Fischer (1970)	Moccasin Bend 0-140	LS/CH/TCH	15		
			Baxter Springs 0-71	LS/CH/TCH/SH	15		
			Short Creek Oolite 0-10	LS	0		
	Osage		Joplin 0-100	LS/CH	60	HST	
			Grand Falls 25-95	LS/CH/TCH	60	MFI	
			Reeds Springs 70-125	LS/CH	60		
		St. Joe Formation	Pierson 10-15	LS	10		
	Kinderhook		Northview 2-3	LS/SH	2		
			Compton 12-15	LS	15	SL fall	
			Bachelor 0-1	SH	1		
		Chattanooga		SH		TST	
Devonian		10-40 (2)			60		SB
Ordovician		Everton 10-200		LS/DOL/SS	30		SB
		Cotter 143-183		DOL/CH	60		

Double line indicates unconformity

est. by D. Zachry

Figure 9. Stratigraphy of southern Ozarks. (From Liner, 2013)

More recently the Chattanooga shale has become a target for unconventional resources. The shale contains the oil prone Type II kerogen (Carr, 1989). Like many other organic rich, black shales, the Chattanooga/Woodford is very radioactive. It was even considered as a potential source of uranium ore (Glover, 1959; Swanson and Landis, 1962).

3. Ore Districts of the southern Ozarks region

3.1 The Tri-State Mining District

The following description is mainly based on McKnight's study (1970) on the ore deposits from the Tri-State mining district. The aforementioned district is located in northeast Oklahoma, southeast Kansas, and southwest Missouri (Figure 2 and Figure 7). The mineralized region covers a large area, around125 miles by 50 miles, and contains many scattered deposits of Pb and Zn ores. The deposits were first discovered in 1901. Rapid development of the resources occurred during World War I and peak production was reached in 1925. Production remained at a high level well into the late 1950's, followed by a quick decline and demise.

The chief ore minerals are sphalerite (ZnS) and galena (PbS), with sphalerite being more prevalent than the galena by a ratio of 4.1:1. More than 7,283,000 tons of Zn ore and 1,766,00 tons of Pb ore were recovered from the area. Other common minerals associated with the deposits are dolomite, jasperoid, chalcopyrite, barite, enargite, luzonite, marcasite, and pyrite.

The ore is hosted in the Mississippian Boone Formation, which is a light-gray, crinoidal, finely crystalline limestone that contains significant and variable proportions (20-60%) of chert occurring in both beds or nodules (Frezon and Glick, 1959). Every stratigraphic horizon of the Boone Formation has been mineralized to some extent but the most productive intervals occur in the Joplin Member at the top of the Osagean series (Figure 9). The ore bodies occur in tabular masses that are much more widespread in extent than they are vertically and are typically confined locally to a stratigraphic interval.

Structurally, the rocks are not very deformed within the area and are typically flat lying or very gently folded. There is a gentle regional dip to the northwest. The two main structural features within the area are the Miami trough trending northeast in the western portion of the district and the Bendelari monocline trending northeast. The ore bodies do not seem to be greatly influenced by structural features and instead seem to be more influenced by lithologic parameters. Shattered zones of rock are the most abundant host areas for the ores (Figure 10). The shattered zones are areas of rock that have a favorable amount of brittleness and responded to pre-ore precipitation stresses by breaking rather than deforming in a ductile manner. The shattered zones create areas of excellent permeability and porosity, where mineralizing fluids later deposited the ores.

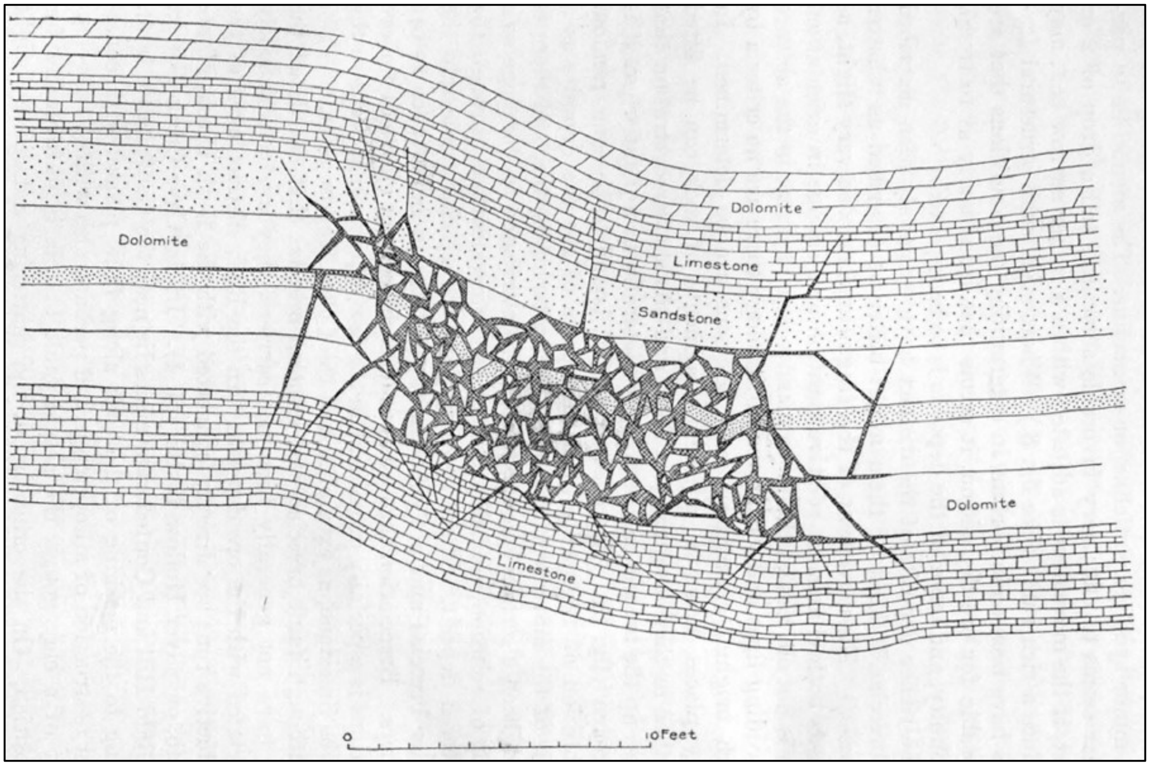


Figure 10. Shattered zones as a result of brittle response to flexure, hosting ore deposits. (From McKnight, 1935).

Even though a pure limestone provides a more favorable condition for precipitation of the ores, due to the aforementioned chemical aspects of carbonates, this is often offset by a lack of fracturing due to a pure limestone's tendency to respond more plastically to deformation.

Because of the importance of brittleness, a mixed lithology of both chert and limestone has often provided a more favorable location for ore precipitation. Normal faults are present in the area but are not a necessary control on ore locales, although fractured zones bordering the faults are important hosts for the ores. Many of the structural features within the area are related to long lived, deep seated faults in the Precambrian basement rock that have been reactivated through time. Other equally important controls on ore locations are facies changes. The fringes of dolomite-cored areas are often a host for mineralization. Bedding planes are another important host of mineralization.

Sphalerite, the principal ore mineral of the area, typically occurs in massive to coarse-grained crystals ranging from a 0.125 to 4 or 5 inches across, although crystals larger than a foot have been reported. The smaller crystals are typically well formed and the larger ones are much more likely to be imperfect and irregularly twinned. The sphalerite samples range in color from yellow to red to black. Galena is not as abundant as sphalerite but is still widely dispersed through the area. The crystals are often coarser in size than the sphalerite samples with sizes ranging between 0.25 and 1 inch, and some larger samples ranging from 6 to 8 inches. Crystals disseminated within the host rock are often smaller than crystals hosted in open spaces. Octahedron shaped galena is less abundant and typically smaller in size than the cubic variety.

3.2 The Northern Arkansas Mining District

The following description is mainly based on McKnight's study (1935) on the ore deposits from the Northern Arkansas mining district. The aforementioned mining district (Figure 2 and Figure 7) is located in north-central Arkansas. Although Zn is much more common than Pb in the area, Pb ore was of more importance historically and thus was reported and mined first. The first reports of Pb ore occurred in 1818 and Pb remained an important commodity locally for use as bullets throughout the 1800s, though it was never mined on an industrial scale. Zn was not recognized for its importance until later, and Zn mining reached its peak between 1914 and 1917, before quickly tapering off. The Northern Arkansas mining district was never as prolific as the Tri-State district and the tonnage of ore recovered was significantly less. 1,900 tons of PbS, 11,500 tons of ZnS, and 51,300 tons of $ZnCO_3$ and Zn silicates were recovered from the area.

The ore deposits are hosted in the Ordovician Everton, Powell, and Cotter formations, and the Mississippian Boone and Batesville formations (Figure 9). The Cotter is a lower Ordovician dolomite containing some chert, sandstone, and green shale. The Powell is a compact gray argillaceous dolomite of Lower Ordovician age. The Everton is a blue-gray limestone interbedded with sandy limestone, sandstone, and sandy dolomite, also of Lower Ordovician age. The Mississippian Boone is a massive gray crystalline crinoidal limestone containing significant amounts of chert. The Mississippian Batesville Sandstone is a gray limy sandstone with some sandy limestone and sandy shale beds. The richest deposits occur in the Everton and Boone formations. Although the Boone has fewer deposits than the Everton, deposits in the Boone are on average more productive than those in the Everton.

Similar to the Tri-State district, the rocks of the Northern Arkansas district are not highly deformed or structurally complex. The rocks are relatively flat lying with some minor folding occurring locally. Structural deformation is more pronounced in the older formations suggesting deformation has been recurrent through time and has accentuated previous features. Overall there is a low regional dip to the South. Some East-West trending normal faults traverse the area, sometimes in pairs, forming grabens. The faults are thought to have occurred during the Pennsylvanian. Faults do play a role in localizing ore bodies in some of the more productive mines; however, the shattered rock breccias near the fault host the ores rather than the fault plane itself. Ores fill the shattered rock fractures that provide porosity and permeability for the mineralizing fluids and replace country rock outwards from these shatter cracks along bedding planes and permeable zones.

The chief ore minerals of the Northern Arkansas district are sphalerite, galena, and various zinc oxides. Coarsely crystalline sphalerite is widespread throughout the region with crystals ranging on average between 0.25” and 1” and occasionally reaching sizes up to 6”. Galena is not nearly as widespread throughout the region but where present, crystals average in size from 0.5” to 1”, occasionally getting up to 3” in size. Chalcopyrite occurs throughout the region but never in commercial abundances. Unlike the Tri-State district, oxidized varieties of Zn are common and have provided the greatest commercial production of all the ores in the district. Smithsonite ($ZnCO_3$) and calamine ($Zn_4Si_2O_7(OH)_2 \cdot H_2O$) are the most important secondary minerals.

4. Methods

4.1 Chemical processing of mineral samples

The chemical processing of the rock and mineral samples was done in the University of Arkansas's class 100 Radiogenic Isotope Clean Laboratory. Twenty-one sphalerite ore samples (11 from the Northern Arkansas mining district and 10 from the Tri-State mining district) were analyzed for their Pb isotopic compositions. Sphalerite ore samples were collected in the field from chat piles in the Tri-State Mining district near Picher, Oklahoma (Figure 11).

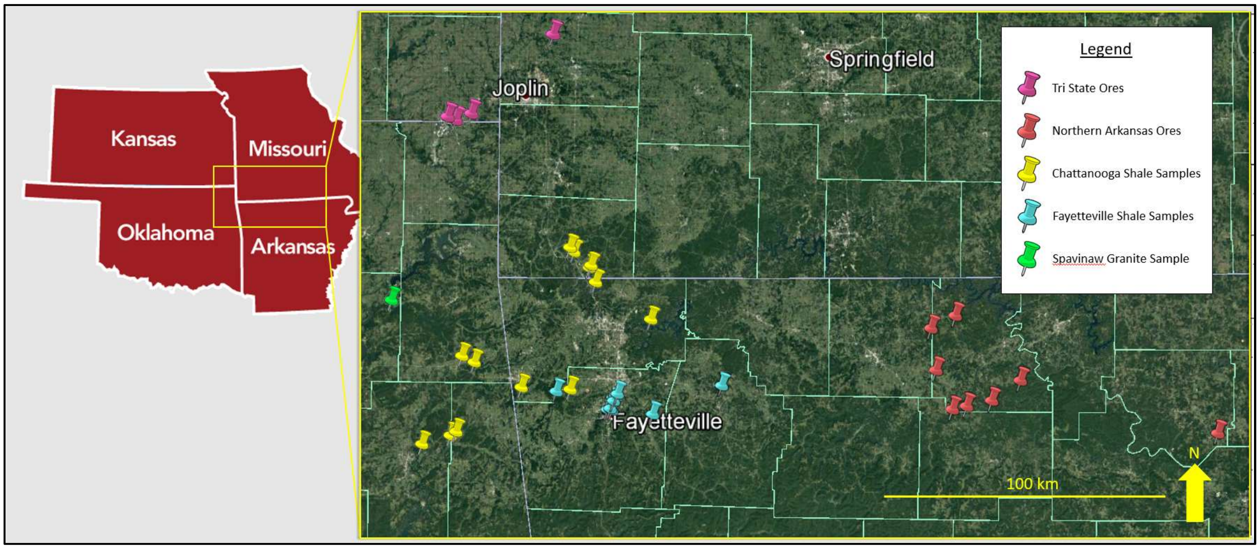


Figure 11. Location of analyzed samples.

Three other samples from the Tri-State Mining district and the sphalerites from the Northern Arkansas district were donated by D.L. Leach and M.S. Appold. Photographs were taken of each specimen prior to analysis (Figure 12). Fresh sphalerite crystals were handpicked from the ores and soaked for 30 minutes in nitric acid. The samples were rinsed with triple-distilled water and dried on a hot plate. 150 mg of each sample was weighed out. 2 mL of 8N HNO_3 was added to the samples and they were allowed to dissolve for 2 days. Samples were then heated at 150ºC and dried down on a hot plate within the laminar flow hood. Full digestion of undissolved samples was achieved by successive additions of 1 mL of 8N HBr and 1 mL of 8N HNO_3. The samples were dried down at 150ºC. 2 mL of 1N HBr was added to each sample and dried down.

Figure 12. Sphalerite ore from the Tri-State district hosted in carbonate breccia (left) and Chattanooga shale sample collected from the southern Ozarks (right).

This step was repeated two more times. 500 µL of 1N HBr was added to each sample to re-dissolve them. Each sample was centrifuged in a HNO_3 leached centrifuge tube for 10 minutes, rotated 180º and centrifuged for an additional 10 minutes. The samples were transferred to a 3 ml cation exchange column. Lead was separated and purified following the method by Manhes et al. (1978). The column had 0.1 ml of Dowex AG1-8X, 200-400 mesh resin with PTFE frits; the resin was precleaned by mixing it with 6N HCl and rinsing with 0.5N HNO3 and triple-distilled water. The sample was washed with three successive additions of 1 ml 1N

HBr, eluted using 1 ml of 20% HNO_3 into a 5 ml PTFE container, and dried in a laminar flow hood.

4.2 Chemical processing of sedimentary rocks

Thirteen Chattanooga shales and ten Fayetteville shales were analyzed for their Pb, Sr, and Nd isotopic compositions. Shale samples were collected in the field from outcrops in Arkansas, Oklahoma, and Missouri (Figure 11). Care was taken at the outcrop to dig back and collect as fresh and unaltered specimens as possible. Granite samples were collected from an outcrop in Spavinaw, Oklahoma. Each specimen was rinsed in de-ionized (DI) water and allowed to dry. Photographs of each sample were taken and each sample was described prior to being pulverized. The samples were wrapped in paper towels and aluminum foil, placed in plastic bags, and crushed with a hammer. Fresh, unaltered chips of rock were collected from the crushed rock samples. The selected chips were powdered using a Spex SamplePrep ShatterBox. Between each sample, the alumina ceramic grinding container was cleaned with DI water, double distilled (DDI) water, and methanol to avoid cross-contamination. A small amount of pure quartz sand that had been previously acid cleaned in nitric acid was added to the container and powdered in order to aid the cleaning process. The vessel was cleaned one more time with DI water, DDI water, and methanol. Some samples required multiple rounds of pure quartz sand powdering and cleaning before the vessel was clean. The vessel was self-contaminated by adding a few rock chips, powdering them, and then discarding the powdered sample. Once self-contaminated, the remainder of the sample was powdered and 250 mg of each rock sample was weighed out for isotopic analysis.

A high-purity high-strength mixture of 5mL of HF, 3 mL of HNO_3, and 1 mL of HCl was added to each shale sample in accordance with the clay dissolution method outlined in the

MARS laboratory microwave procedures. The shale samples were then heated in a MARS laboratory microwave. The temperature was ramped up to 200°C over a span of 15 minutes and then held at 200°C for 10 minutes. The shales were still not fully digested, therefore they were heated again, this time ramping the temperature to 200°C over 15 minutes and holding it at 200°C for 45 minutes. The samples failed to fully digest, with the highly refractory minerals and elements that formed insoluble fluorides (e.g., Al, Ba, Ca, and Mg) remaining undissolved. However, the current study does not focus on analyzing the aforementioned elements, and therefore the process outlined above is reliable for the scope of the current research. Following the dissolution procedure, the shale samples were dried down and transferred to cation exchange columns. Pb, Sr, and Nd were separated and purified following the method by Pin et al. (2014).

4.3 Chemical processing of igneous rocks

Two granite samples were analyzed for their isotopic ratios. 4 mL of 7 N HNO_3 and 3 mL of HF were added to the granite and co-processed blank sample and placed on a hot plate, with the caps on the beakers until digested. Once digested, the caps were removed and the samples were dried down. Successive additions of 0.5 ml 6N HCl + 0.5 ml 7N HNO_3, 2 ml of HNO_3, and 1 mL of HNO_3 ensured full digestion of the igneous rock samples. Between each addition, the sample solutions were dried down. 2 mL of 1N HNO_3 were added to the final dried samples, centrifuged for 15 minutes, rotated 180°, and centrifuged for an additional 15 minutes. The samples were transferred to cation exchange columns and Pb, Sr, and Nd were separated and purified following the method by Pin et al. (2014).

4.4 Isotopic analyses of processed samples

Lead, Sr, and Nd isotope ratios were determined by inductively coupled plasma mass spectrometry using the University of Arkansas's Nu Plasma MC-ICP Mass Spectrometer. The dried samples were redissolved in 2% HNO_3 prior to analysis. The sample was introduced into the plasma by an uptake system with a rate of 40 µl/min. The aerosol from the nebulizer is injected into the center region of the plasma, desolvated, and ionized.

The samples analyzed for Pb isotopic compositions were diluted with 2% HNO_3 containing 4 ppb Thallium (Tl) prior to analysis. Tl was used to correct for internal mass fractionation, since Pb does not have two stable non-radiogenic isotopes, unlike Sr (^{86}Sr, ^{88}Sr) and Nd (^{144}Nd, ^{146}Nd). The Pb-Tl mixtures were normalized using the Tl normalization technique for mass bias correction, following the procedure of Kamenov et al. (2004). The data collected for each sample represented averages of 60 ratio measurements each. The average standard errors on the analyzed samples were 0.000254% for ^{206}Pb/^{204}Pb, 0.000245% for ^{207}Pb/^{204}Pb, and 0.000641% for ^{208}Pb/^{204}Pb (Appendix 2.2). The readings were corrected for instrumental fractionation by comparison with replicate analyses of the National Bureau of standards common Pb standard NBS 981. Measured average values of 47 analyses of this standard are as follows: 16.9312 for ^{206}Pb/^{204}Pb, 15.4847 for ^{207}Pb/^{204}Pb, and 36.6772 for ^{208}Pb/^{204}Pb. Four duplicates FS1L, FS6L, FS8UU, and FS10L were prepared and analyzed to evaluate the accuracy and reproducibility of the measurements. The total procedural blanks level for Pb was less than 10 pg.

The data collected for Sr and Nd isotopic compositions represented averages of 50 ratio measurements each. The readings were corrected for instrumental fractionation by comparison with replicate sample analyses of the National Bureau of Standards common Sr and Nd standards NBS 987 (Sr) and JNdi 1 (Nd). Measured average values of 28 Nd analyses of this standard were 0.512 with an average error of 3.963×10^{-6} % (Appendix 2.6). Measured average values of 55 Sr analyses of this standard were 0.710 with an average error of 6.859 x 10^{-6} % (Appendix 2.7). Sr and Nd isotopic data collected in the current study will be used in future tracer studies.

4.5 Total Organic Carbon

TOC (total organic carbon) analysis was performed on select shales at the University of Arkansas Stable Isotope Laboratory. Samples were dried and weighed into tin capsules containing around 100 µg of carbon. The samples were analyzed using a Carlo Erba NC2500 elemental analyzer (EA). Samples were combusted at 100C in a stream of helium to quantitatively produce CO_2. The combustion gases were separated on a 4 M C/N column. The EA was interfaced with a delta plus isotope ratio mass spectrometer (MS) via a conflo II interface. The MS simultaneously monitored masses 44, 45, and 46 during the analysis. A pure gas CO_2 reference pulse was admitted to the MS after the sample peak to generate the raw instrumental results. The raw results were normalized using standards to the VPDB scale.

5. Results

A total of 10 sphalerite ores from multiple mines within the Northern Arkansas mining district, 10 sphalerite ores from chat piles near the Picher, Oklahoma area of the Tri-State mining district, 13 Chattanooga shale samples and 10 Fayetteville shale samples collected from multiple outcrops around the southern Ozarks, and 2 granitic basement samples from an outcrop near Spavinaw, Oklahoma were analyzed for their Pb isotope ratios. The results are compiled in tables 1, 2, and 3. The Pb isotope ratios of the shales have also been corrected to show their isotopic ratios at the time of mineralization (250 Ma) in order to more accurately constrain their potential as source of the metals. Age corrections were made by subtracting out the portion of radiogenic Pb that would have come after the mineralization of the ores using the equation: [Current Values – (the standard concentration of U or Th in shales averaged from multiple shales worldwide) x e^((the decay constant of U or Th x 250 my) – 1)]. Present day Pb isotope ratios are plotted on covariation diagrams in Figure 14. The age corrected Pb isotope ratios of the shales are plotted with the Pb isotope ratios of the ores and granites on covariation diagrams in Figure 15. The detailed analyses of the data acquired for all samples in this study can be found in Appendices 2.1 -2.8.

The $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, and $^{208}Pb/^{204}Pb$ ratios of ores from the Northern Arkansas district range between 20.1030 and 22.639, 15.776 and 16.723, and between 39.101 and 43.463, respectively (Table 1). The $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, and $^{208}Pb/^{204}Pb$ ratios from the Tri-State ores vary between 21.075 and 22.766, 15.833 and 16.105, and between 40.479 and 41.632, respectively (Table 1). Present day $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, and $^{208}Pb/^{204}Pb$ ratios of the Chattanooga shale samples range from 19.197 to 25.685, 15.675 to 16.031, and from 38.769 to 40.813, respectively (Table 2). Present day $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, and $^{208}Pb/^{204}Pb$ ratios of the

Fayetteville shale samples range from 18.730 to 21.897, 15.621 to 15.830, and from 38.877 to 39.487, respectively (Table 2).

Age corrected (250 Ma) $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, and $^{208}Pb/^{204}Pb$ ratios for the Chattanooga shale samples range from 18.760 to 24.880, 15.637 to 15.989, and from 38.214 to 40.272, respectively (Table 3). Age corrected $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, and $^{208}Pb/^{204}Pb$ ratios for the Fayetteville shale samples vary between 17.996 and 21.003, 15.598 and 15.787, and between 38.214 and 40.272, respectively (Table 3). $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, and $^{208}Pb/^{204}Pb$ ratios for the Spavinaw granite samples range from 19.734 to 19.742, 15.632 to 15.639, and 39.889, respectively (Table 2). Error bars (2σ) are plotted on each diagram; however, due to the high precision of the analyzed standard samples, the error bars are hardly noticeable. The values for the calculated error bars are 0.0028, 0.0023, and 0.0097 for $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, and $^{208}Pb/^{204}Pb$, respectively.

The TOC values for the Chattanooga shale samples ranged from 2.16 – 7.51 % (Table 3). Values for the Fayetteville shale samples range from 0.09 % TOC in the uppermost section of the formation to 7.48 % TOC in the lower section (Table 3). One sample from the lower member of the Fayetteville shale (13.46% TOC) was just outside the calibration curve and should thus be considered skeptically.

Table 4 records the $^{87}Sr / ^{86}Sr$ ratios for the Chattanooga shale samples, with values ranging from 0.753823 to 0.780325. The $^{87}Sr / ^{86}Sr$ values for the Fayetteville shale samples vary from 0.717474 to 0.733074, and for the Spavinaw granite samples from 0.756187 to 0.756263. The $^{143}Nd / ^{144}Nd$ values for the Chattanooga and Fayetteville shale samples range from 0.511848 to 0.511978, and from 0.511823 to 0.511994, respectively. The $^{143}Nd / ^{144}Nd$ values for the Spavinaw granite samples ranged from 0.511849 to 0.511966.

Sample Name	Location	^{206}Pb / ^{204}Pb	^{207}Pb / ^{204}Pb	^{208}Pb / ^{204}Pb
Northern Arkansas Ores				
NA 1	36° 2'25.98"N 92°49'25.86"W	20.150	15.843	39.301
NA 2	36° 7'49.86"N 92°33'5.46"W	21.508	15.915	40.765
NA 3	36°20'25.87"N 92°48'30.42"W	N/A	N/A	N/A
NA 4	36° 9'59.04"N 92°53'16.08"W	20.700	15.834	39.950
NA 5	36°18'2.20"N 92°54'22.00"W	22.639	16.723	43.463
NA 7	35°56'58.26"N 91°45'45.52"W	20.319	15.810	39.521
NA 8	N/A	21.829	15.919	41.042
NA 9	N/A	20.919	15.864	40.180
NA 10	N/A	20.103	15.776	39.101
NA Davy Crockett	36° 2'60.00"N 92°46'1.20"W	20.197	15.794	39.303
NA Red Bird	36° 4'1.20"N 92°40'1.20"W	21.626	15.914	40.867
Tri-State Ores				
TS 2	36°58'28.19"N 94°50'33.39"W	22.170	15.934	41.236
TS 3	36°58'28.19"N 94°50'33.39"W	22.094	15.925	41.182
TS 4	36°58'28.19"N 94°50'33.39"W	21.270	15.860	40.568
TS 5	36°58'28.19"N 94°50'33.39"W	22.107	15.930	41.184
TS 6	36°58'28.19"N 94°50'33.39"W	22.338	15.975	41.432
TS 7	36°58'28.19"N 94°50'33.39"W	22.049	15.932	41.168
TS 8	36°58'28.19"N 94°50'33.39"W	21.075	15.833	40.479
TS AB 1-1	37°14'31.13"N 94°25'15.67"W	22.766	16.105	41.632
TS BS 1-7	36°59'6.14"N 94°44'49.27"W	22.223	16.040	41.524
TS PC 2-1	36°57'51.05"N 94°48'37.66"W	21.768	15.900	40.883

Table 1. Pb isotope ratios of sphalerite ores analyzed in this study.

Sample Name	**Location**	**^{206}Pb / ^{204}Pb**	**^{207}Pb / ^{204}Pb**	**^{208}Pb / ^{204}Pb**
Chattanooga Shale		Present Day	Present Day	Present Day
CS1	35°55'34.65"N 94°55'38.68"W	25.685	16.031	38.769
CS2	35°57'18.90"N 94°48'51.25"W	21.453	15.795	38.883
CS3	35°58'3.60"N 94°47'30.20"W	22.130	15.837	39.047
CS4	36°12'39.97"N 94°46'15.90"W	21.087	15.779	39.112
CS5	36°11'27.50"N 94°43'16.55"W	20.322	15.730	38.938
CS6	36° 6'44.32"N 94°31'59.96"W	20.059	15.727	38.822
CS7	36° 6'23.95"N 94°20'20.85"W	23.756	15.907	38.853
CS8	36°33'40.76"N 94°20'36.97"W	19.658	15.702	39.140
CS9	36°32'48.16"N 94°19'39.37"W	19.197	15.675	38.801
CS10B	36°30'14.66"N 94°15'31.95"W	21.877	15.898	40.813
CS11	36°29'48.48"N 94°15'55.44"W	19.501	15.692	38.845
CS12	36°27'1.44"N 94°14'25.08"W	19.623	15.698	38.889
CS13	36°19'54.61"N 94° 1'12.05"W	19.765	15.704	39.204
Fayetteville Shale				
FS1L	36° 5'57.76"N 94°23'42.44"W	20.193	15.726	39.205
FS1L Duplicate	36° 5'57.76"N 94°23'42.44"W	20.115	15.722	39.321
FS2U	36° 2'32.64"N 94°11'28.32"W	18.730	15.634	38.877
FS3	36° 2'44.80"N 94°10'49.27"W	19.792	15.689	39.270
FS4	36° 2'27.00"N 94°10'28.30"W	18.872	15.621	39.002
FS6L	36° 5'33.31"N 94° 9'7.57"W	21.774	15.821	39.447
FS6L Duplicate	36° 5'33.31"N 94° 9'7.57"W	21.897	15.830	39.487
FS7L	36° 1'40.08"N 94° 0'45.72"W	20.526	15.756	39.477
FS8UU	36° 7'10.89"N 93°44'24.26"W	18.993	15.650	38.901
FS8UU Duplicate	36° 7'10.89"N 93°44'24.26"W	18.955	15.649	38.976
FS9LU	36° 7'10.99"N 93°44'23.94"W	18.799	15.637	38.988
FS10L	36° 7'11.50"N 93°44'21.79"W	18.747	15.636	38.923
FS10L Duplicate	36° 7'11.50"N 93°44'21.79"W	18.794	15.639	39.030
FS11	36° 4'12.98"N 94°10'1.30"W	20.594	15.755	38.892
Spavinaw Granites				
SG1	36°23'14.68"N 95° 3'22.79"W	19.734	15.632	39.889
SG2	36°23'14.68"N 95° 3'22.79"W	19.742	15.639	39.889

Table 2. Present day Pb isotope ratios of rocks analyzed in this study.

Sample Name	**^{206}Pb / ^{204}Pb**	**^{207}Pb / ^{204}Pb**	**^{208}Pb / ^{204}Pb**	**% TOC**
Chattanooga Shale	Age Corrected 250MY	Age Corrected 250MY	Age Corrected 250MY	
CS1	24.880	15.989	38.214	7.51
CS2	20.691	15.756	38.358	4.17
CS3	21.359	15.797	38.516	3.8
CS4	20.326	15.740	38.588	N/A
CS5	19.570	15.692	38.421	4.19
CS6	19.312	15.689	38.308	3.01
CS7	22.970	15.867	38.312	5.35
CS8	18.911	15.664	38.626	2.48
CS9	18.459	15.637	38.293	2.37
CS10B	21.090	15.858	40.272	3.87
CS11	18.760	15.654	38.334	3.23
CS12	18.879	15.660	38.377	2.84
CS13	19.017	15.665	38.689	2.16
Fayetteville Shale				
FS1L	19.441	15.687	38.687	13.46*
FS2U	17.996	15.597	38.372	1.19
FS3	19.043	15.651	38.754	3.8
FS4	18.135	15.583	38.495	2.02
FS6L	21.003	15.781	38.916	6.31
FS7L	19.767	15.717	38.955	7.48
FS8UU	18.256	15.612	38.394	0.09
FS9LU	18.063	15.600	38.482	0.27
FS10L	18.012	15.598	38.417	N/A
FS11	19.840	15.716	38.373	N/A
				*Just outside Calibration curve

Table 3. Pb isotope values (age corrected to 250 Ma) and TOC results from shales analyzed in this study.

Sample Name	**87 Sr / 86 Sr**	**143 Nd / 144 Nd**
Chattanooga Shale		
CS1	0.769558	0.511902
CS2	0.763639	0.511960
CS3	0.757829	0.511889
CS4	0.765359	0.511904
CS5	0.767123	0.511907
CS6	0.747974	0.511982
CS7	0.765623	0.511978
CS8	0.764009	0.511919
CS9	0.753823	0.511869
CS10B	0.780325	0.511876
CS11	0.767107	0.511861
CS12	0.767114	0.511848
CS13	0.757944	0.511939
Fayetteville Shales		
FS1L	0.730208	0.511950
FS2U	0.728390	0.511962
FS3	0.723788	0.511953
FS4	0.729967	0.511823
FS6L	0.717662	0.511994
FS7L	0.732811	0.511905
FS8UU	0.717474	0.511931
FS9LU	0.733074	0.511979
FS10L	0.726412	0.511825
FS11	0.720928	0.511980
Spavinaw Granites		
SG1	0.756187	0.511849
SG2	0.756263	0.511966

Table 4. Sr and Nd isotope values for rocks analyzed in this study.

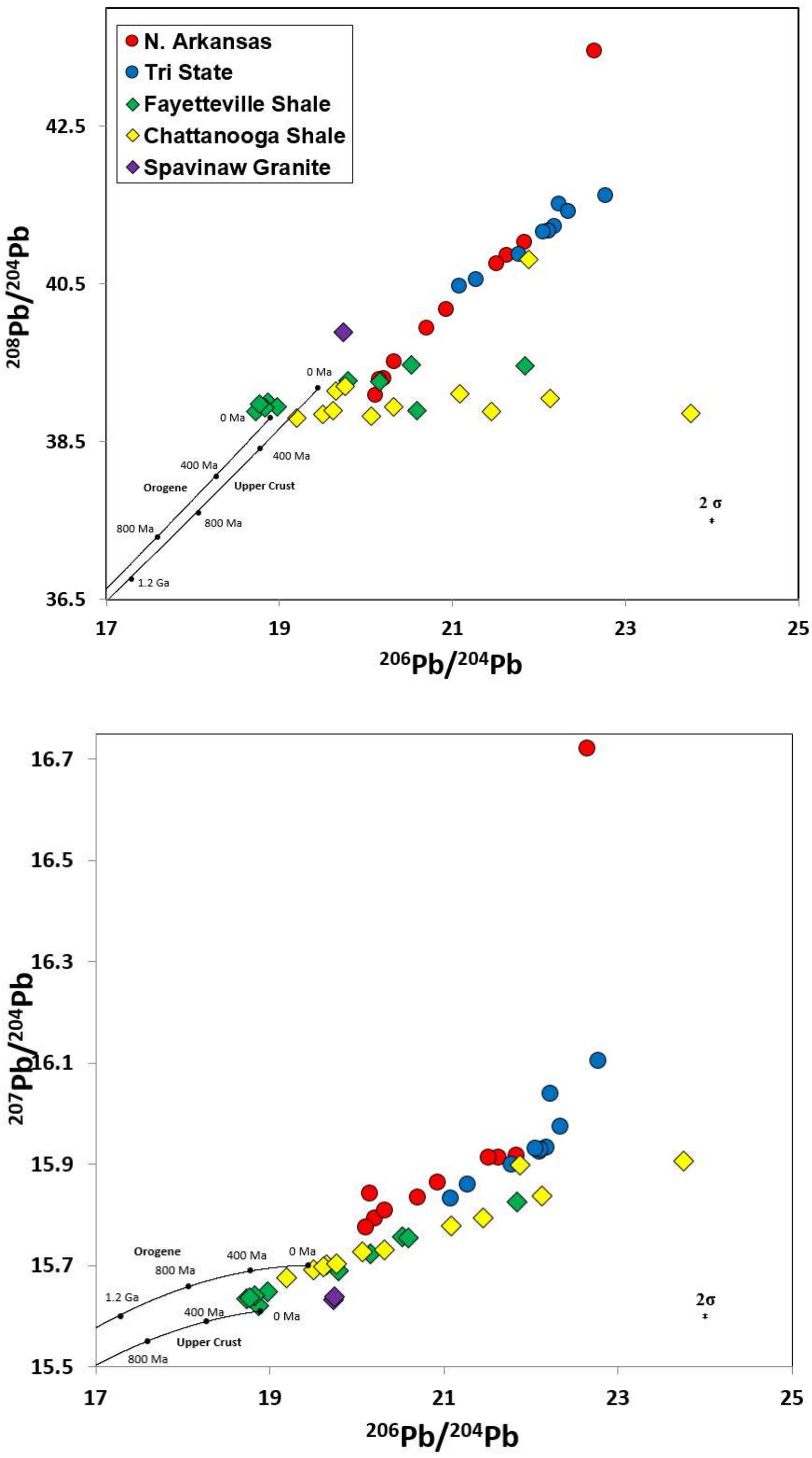


Figure 13. Covariation diagrams for all samples with present day isotope values for the shales. The samples are plotted in conjunction with Zartman and Doe's (1981) model for upper crust and orogene development curves.

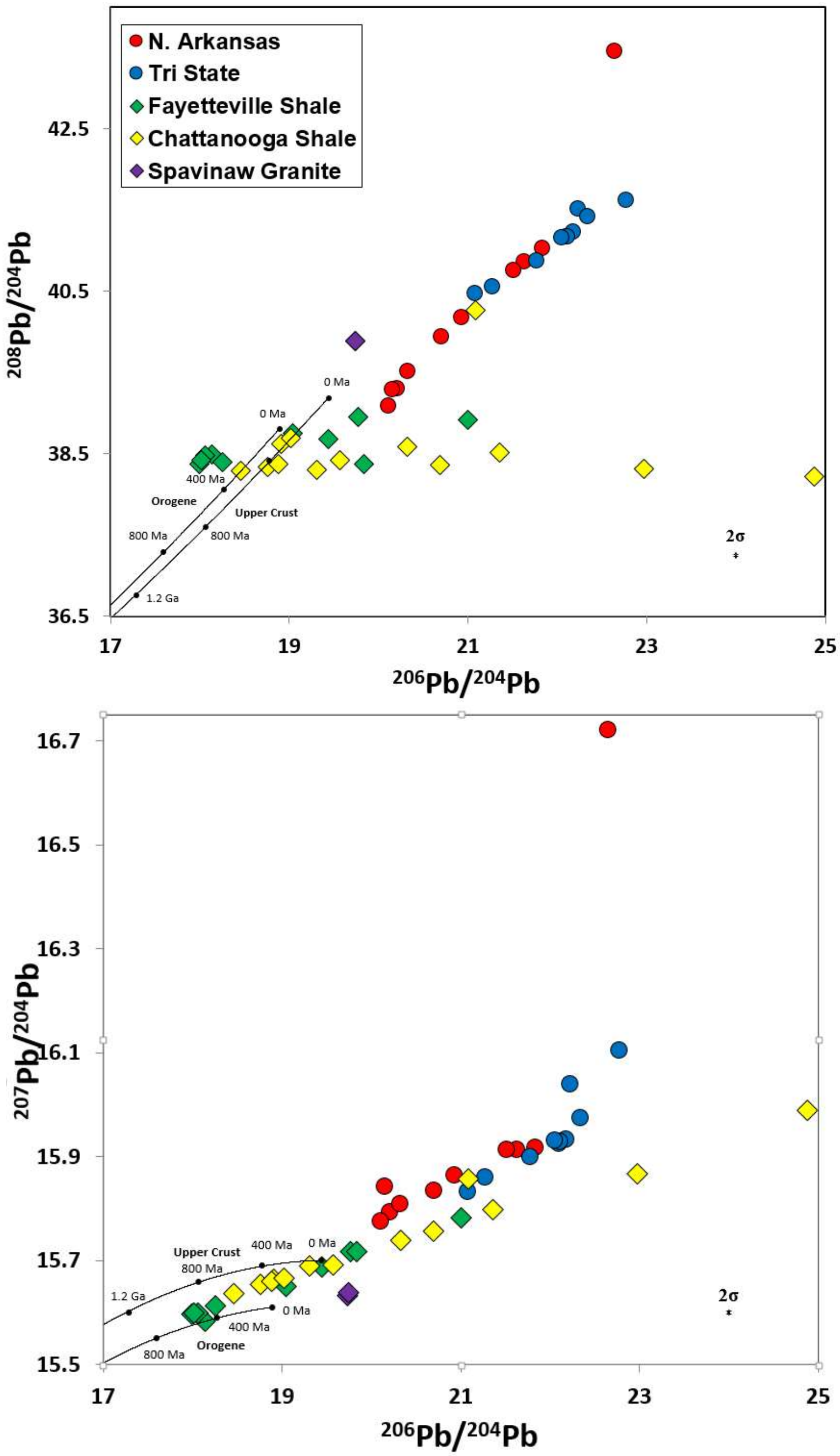


Figure 14. Covariation diagrams for all samples with age corrected (250my) isotope values for the shales. The samples are plotted in conjunction with Zartman and Doe's (1981) model for upper crust and orogene development curves.

6. Discussion

The Pb isotope ratios collected in this study have been plotted on Pb covariation diagrams alongside growth curves of both the upper crust and orogene outlined in Zartman and Doe (1981) (Figure 13 and Figure 14). These growth curves represent the Pb isotope composition of both the upper crust and orogenic regions throughout Earth's history. As noticed in Figures 13 and 14, these two reservoirs become more enriched in radiogenic Pb isotopes through time as the radioactive parents ^{238}U, ^{235}U, and ^{232}Th decay into their corresponding radiogenic daughters ^{206}Pb, ^{207}Pb, and ^{208}Pb, respectively. The MVT ores analyzed from both the Tri-State and Northern Arkansas districts are enriched well beyond the present day values of the growth curves, plotting to the right of the 0 Ma value of the aforementioned reservoirs (Fig. 13 and Fig. 14). As a group, the Tri-State ores are more enriched in the radiogenic products than the Northern Arkansas district ores, although there is a considerable amount of overlap between the two groups. The overlap may suggest that the metals in ores from both districts may share some common source. The isotopic signatures of both ore districts also display a wide range of compositions along a linear trend, which is indicative of a two end member mixed fluid source. This observation falls in line with the proposed theories outlined earlier, which suggest that the MVT ores may originate from the mixing of fluids from multiple sources. It is the mixing of fluids that often times causes rapid changes in fluid chemistry, triggering metal precipitation out of solution. The mixing of fluids also occurs in zones of high porosity and high permeability, like the breccias, which often host the ore deposits. This wide swath of isotopic signatures may also suggest that the ores have been sourced from multiple different lithologies. If the ores were sourced from only one lithology or brine, the isotopic signatures would plot in a much tighter group. The linear trend of the data is seen in Pb isotope data from many other MVT districts in

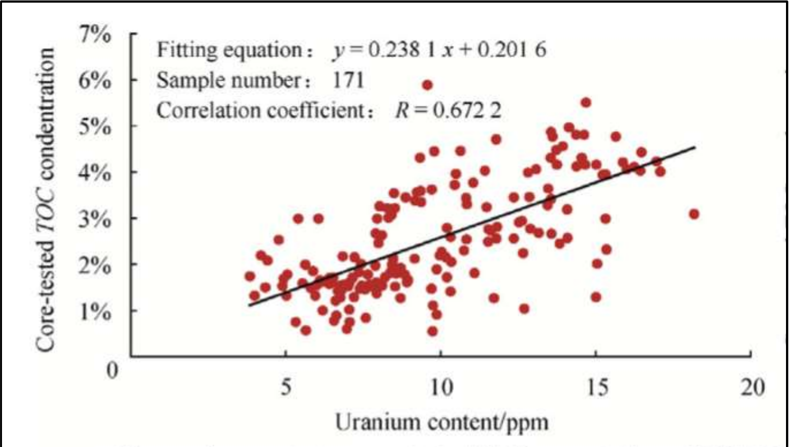
North America and other authors have attributed this linearity in their data to a few different possibilities besides a two end member mixing model. Heyl et al. (1966) and Kessler et al. (1994) suggest that a linear trend could be achieved by having a heterogeneous source of Pb with varying isotopic compositions. Kessler et al (1994) also suggest the possibility of a homogenous source of Pb that changed in isotopic composition over time, although this possibility can likely ruled out because it is unlikely the ores formed over a long enough time period to display such a wide array of isotopic compositions.

The TOC analysis performed on the shales indicates that most samples have a high TOC content, with the exception of the samples from the upper member of the Fayetteville shale. Table 5 shows the petroleum potential of source rocks according to their TOC content, suggesting that most of the analyzed shale samples have potential for being great hydrocarbon source rocks.

Generation Potential	Wt % TOC
Poor	0 – 0.5
Fair	0.5 – 1.0
Good	1.0 – 2.0
Very Good	2.0 – 4.0
Excellent	>4

Table 5. Geochemical parameters describing the petroleum potential of source rocks. (Peters & Cassa, 1994)

The Fayetteville shales are not nearly as enriched in radiogenic Pb as the ores and thus do not pose a potential source for the metals. Many of the age-corrected (250 Ma) Pb isotopic ratios of the Fayetteville shales plot to the left of the upper crust Pb growth curve (Fig. 14). Only three of the analyzed Fayetteville shales are enriched in ^{206}Pb and ^{207}Pb, which are the daughter products of ^{238}U and ^{235}U, respectively, but are not enriched in ^{208}Pb, which is the ^{232}Th decay product. The samples that are enriched in U radiogenic products also have the highest TOC content (Table 3). This can be explained by elevated U levels associated with increased preservation of organic matter in an anoxic depositional environment. Many authors have commented on the correlation between elevated uranium content and elevated TOC in a shale. Figure 15 displays this relationship graphically. In the petroleum industry, uranium radioactivity content from a spectral gamma ray log is often used as a proxy for organic content of the rock (Luening and Kolonic, 2003; Gonzalez et al. 2013, Renchun et al., 2015). The elevated uranium content is a result of reduced uranium being much less soluble than oxidized uranium. Because organic matter acts as a powerful reductant, anoxic environments elevate uranium concentrations in sediments by preventing the oxidation of uranium, and preserving organic matter which helps to reduce the uranium and deposit it in the sediments. The isotopically heavier ^{238}U is also preferentially preserved during anoxic conditions (Brennecka et al., 2011) and this can be seen in the Fayetteville shale samples, which are more enriched in ^{206}Pb compared to ^{207}Pb in relation to the growth curves (Fig. 14).



a. The uranium content vs. core-tested *TOC* concentrations of Well Y1

Figure 15. The relationship between TOC and uranium content from a shale core in the Sichuan Basin, China. (Renchun et al., 2015)

As a group, the Chattanooga shale samples are more enriched in radiogenic Pb than the Fayetteville shale samples, especially with respect to the uranium daughter products. On both, the thorogenic and uranogenic diagrams, some samples plot between the orogene and the upper crust growth curves, and some samples plot to the right of the Zartmans and Doe's (1981) growth curves. Like the Fayetteville shale samples, there is a relationship between %TOC and radiogenic Pb enrichment, although it is not as clear. All of the Chattanooga samples have %TOC values higher than 2, indicating that all samples would be good hydrocarbon source rocks. This is no surprise as the Chattanooga is known as one of the most prolific source rocks for hydrocarbons in both the Arkoma Basin and Anadarko Basin. While the majority of the Chattanooga shale samples are as enriched as the ores in ^{206}Pb and ^{207}Pb, the radiogenic end members of ^{238}U and ^{235}U, they are less radiogenic in terms of, ^{208}Pb, the ^{232}Th decay product. Therefore, the Chattanooga shales may not be a viable source of metals for the MVT ores. However, one sample from the Chattanooga shale has Pb isotopic ratios that plot within the field defined by ores from the Tri-State and Northern Arkansas districts and could thus pose as a potential source of the metals. Unfortunately, this sample is the only one from the base of the Chattanooga shale analyzed in this study, while the others were all collected from the uppermost portion of the formation. This anomaly and the potential for this stratigraphic interval to be the source of the metals will be discussed further below.

The Spavinaw granite samples are enriched in ^{208}Pb, plotting to the right of the growth curves on the thorogenic diagram. In contrast, the granite samples have lower ^{207}Pb/^{204}Pb ratios than most of the analyzed shale and ore samples and plot below the orogene growth curve (Fig. 14). The nonradiogenic ^{207}Pb/^{204}Pb values may be related to the loss of U during the Ouachita orogeny. The Pb isotopic ratios of the granite samples, as compared to the ore samples from the

Tri-State and the Northern Arkansas mining districts, preclude them from representing a potential source of the metals.

The fact that the one lone sample from the base of the Chattanooga shale matched the isotopic signature of the ores is an interesting point that must be examined further. Stratigraphic variability within the Chattanooga shale may be responsible for the difference in isotopic signatures between the set of samples from the uppermost portion of the formation and the sample from the base. In order to elucidate the differences between the base of the Chattanooga and the top, a sequence stratigraphy approach will be used.

With the increased interest over the past decade from the petroleum industry in organic rich shales, both as hydrocarbon source rocks and reservoirs, many valuable studies have been published, including many on the Chattanooga shale and its stratigraphic equivalent in Oklahoma, the Woodford. Many authors have studied the stratigraphic variability from a geochemical perspective and tied their findings to the sequence stratigraphy responsible for the deposition of the shales.

According to Slatt (2013), the Chattanooga/Woodford shale consists of a 2nd order depositional sequence made up of multiple 3rd and 4th order parasequences. The Chattanooga/Woodford shale can be subdivided into three informal members: the lower, middle, and upper, each differing on their depositional environments and lithological properties. As the Chattanooga/Woodford was deposited atop an unconformity, the lower and middle members represent a transgressive system tract as sea level rose. The upper member of the formation represents a highstand to regressive system tract as the maximum flooding surface was reached and the shoreline began to prograde seaward (Figures 16 and 17).

Although the Chattanooga sample from the base of the formation analyzed in this study was collected just above the unconformity, it likely represents the middle member of the formation, as the lower member is much more limited in geographical extent and has only been deposited in the deepest part of the basin as the transgressive sequence commenced. This sample was collected farther up on the shelf and not from the deep part of the basin itself.

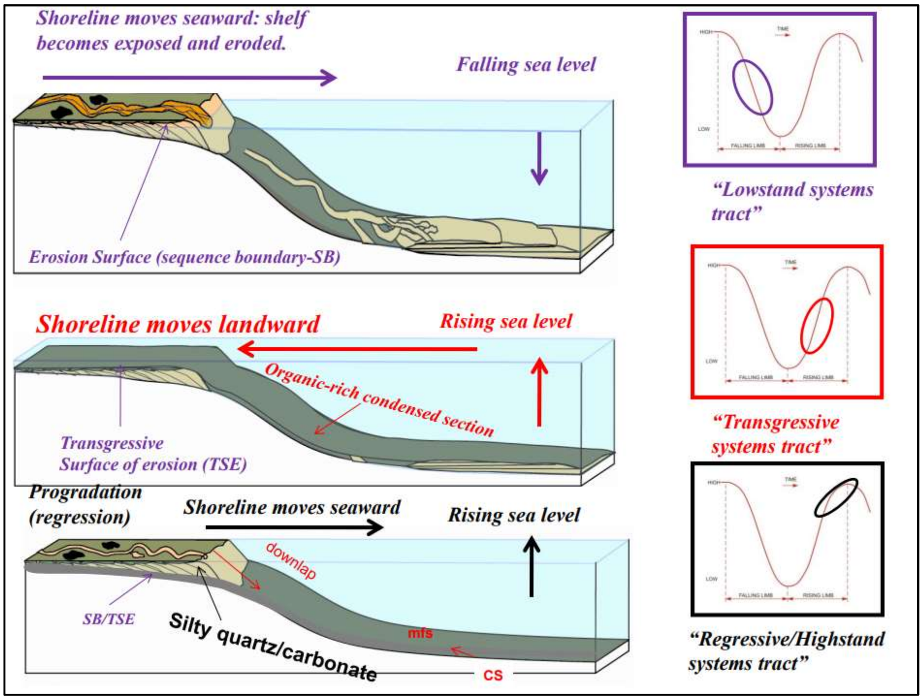


Figure 16. A depositional sequence from a lowstand systems tract to highstand systems tract explained. (Slatt, 2013)

Biomarker studies have also been utilized by many to assess the paleo-depositional environments of each member. *Chlorobiaceae*, or green sulfur bacteria, are indicative of euxinic depositional environments and a stratified water column. The bacteria require light and euxinic water conditions to live (Frigaard and Dahl, 2008). Evidence for these bacteria have been found in both the lower and middle members of the Chattanooga/Woodford shale. The lower Chattanooga/Woodford was characterized by sporadic photic zone euxinia (PZE) and the middle

Woodford was deposited during persistent PZE (Connock et al., 2017). This is significant because it implies that euxinic conditions (anoxic and sulfidic) could have persisted during the deposition of the basal Chattanooga sample and allowed for sulfide minerals to be initially precipitated in the shale. As referenced earlier, Zn dissolved in saltwater precipitates as sphalerite when exposed to a source of reduced sulfur (H_2S), according to the following equation.

$$ZnS_{(sphalerite)} + 2NaCl_{(aq)} + 2H^{+}_{(aq)} \leftrightarrow ZnCl_{2\,(aq)} + H_2S_{(aq)} + 2Na^{+}_{(aq)}$$

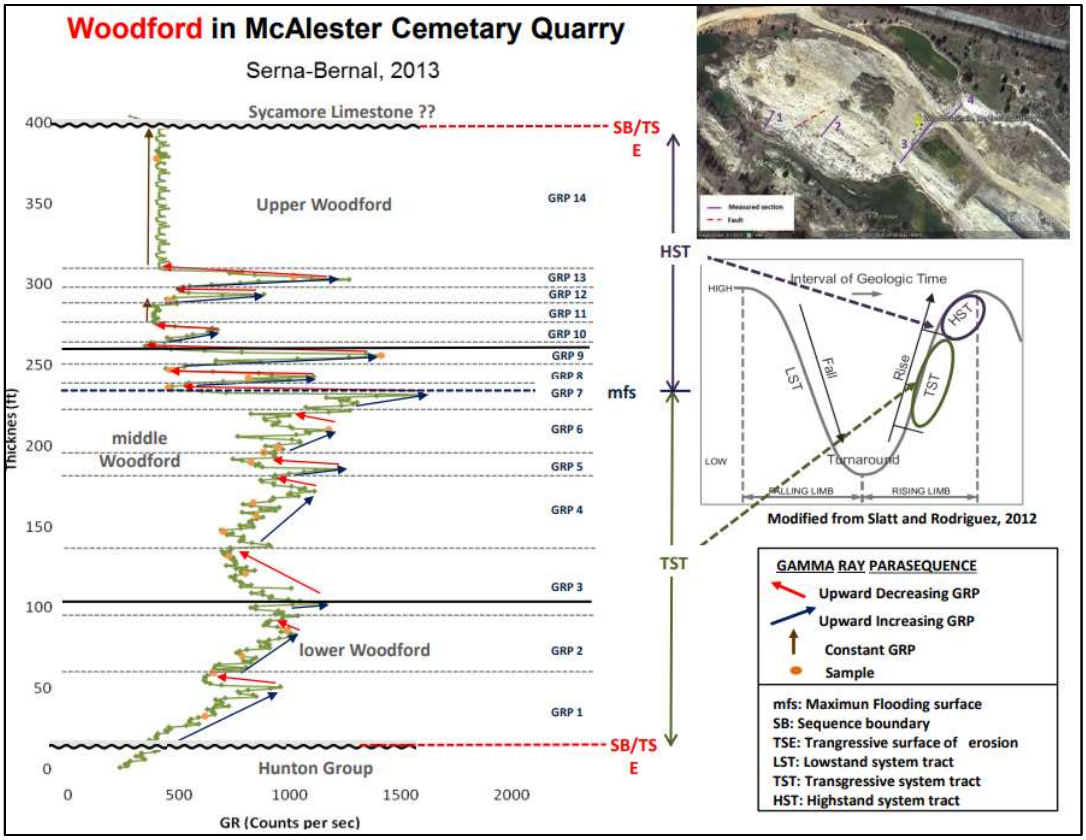
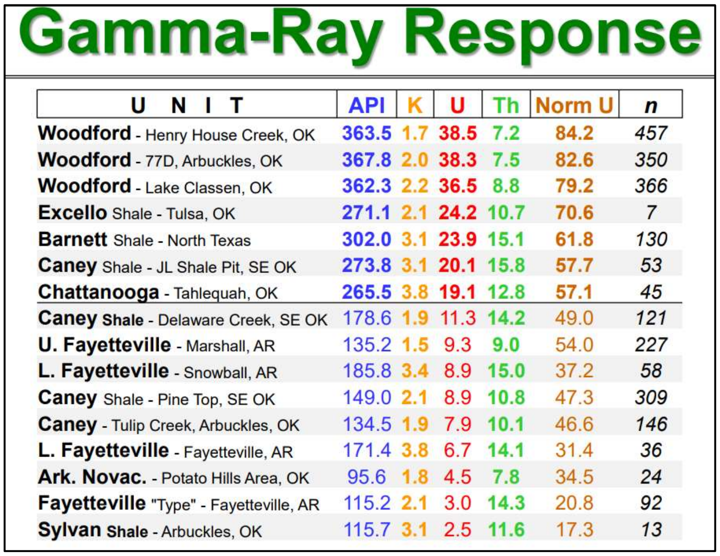


Figure 17. Sequence stratigraphy of a complete Chattanooga/Woodford outcrop in McAlester, Oklahoma explained using a gamma ray profile. (Serna-Bernal, 2013)

The euxinic waters would have created the prime conditions to disseminate the ores in the shales initially, since abundant reduced sulfur in the form of H_2S would have been present in the waters. Euxinic conditions have been responsible for the deposition of the famous Kupferschiefer Cu ores in the black shales of Europe (Jowett, 1992). It should be noted that Schutter (2015) also alluded to the Kupferschiefer as an example in his claim that shales could potentially pose as the source of the metals in MVT deposits. The euxinic conditions would have preserved abundant organic matter, causing an increase in U concentrations within the sediments and therefore an increase in the radiogenic isotopes ^{206}Pb and ^{207}Pb, as seen in the analyzed Chattanooga shale samples. These conditions would result in sediments enriched in both organic matter and substantial quantities of sulfide minerals. The Fayetteville shale was deposited under anoxic conditions and not euxinic conditions like the lower members of the Chattanooga/Woodford.

The ores are not only enriched in the uranogenic isotopes, but also in the thorogenic isotopes, so any potential source must account for this portion of radiogenic Pb as well. Adams and Weaver (1958) found that Th was more abundant in sediments deposited further offshore than sediments deposited closer to shore. Sediments from oxic environments also show lower Th levels than those from dysoxic or anoxic settings (Peters, 2005). The aforementioned evidence suggests that the Chattanooga shale may be a good sink for Th. As the Fayetteville shale was deposited on the shelf of the Arkoma basin, the lower members of the Chattanooga would have been deposited further offshore, suggesting that the latter samples should be more enriched in Th than the Fayetteville samples. The Wedington sandstone member of the middle Fayetteville also confirms this proximity to the shoreline as it represents a deltaic deposit. Paxton et al. (2008) performed spectral gamma ray analysis on both the Chattanooga/Woodford and Fayetteville shales and found the Fayetteville shale to be more enriched in Th than the Chattanooga / Woodford shales (Figure 18). However, the difference in Th concentrations between the

Chattanooga and the lower Fayetteville shales is minimal, 12.8 ppm Th and 15 ppm Th, respectively (Figure 18). Moreover, the aforementioned study did not subdivide the Chattanooga formation into different members. The finding of more Th in the lower Fayetteville outcrops than the Chattanooga/Woodford outcrops certainly poses a quandary in any of the aforementioned explanations of more elevated levels of thorogenic Pb in the basal Chattanooga sample than the Fayetteville samples. Overall, however, the Fayetteville samples analyzed in this study seem to have a slightly higher thorogenic component than the upper Chattanooga samples (Figure 14) and are in alignment with the gamma ray response levels observed by Paxton et. al. (2008). The Fayetteville samples with the elevated thorogenic Pb are represented by the lower member of the formation (Table 3). Elevated thorium levels are found in many igneous rocks and minerals derived from them, including many clay minerals. It is possible that the analyzed Chattanooga sample contained elevated levels of thorogenic Pb as a result of abundant clay minerals.



Gamma-Ray Response

UNIT	API	K	U	Th	Norm U	*n*
Woodford - Henry House Creek, OK	**363.5**	**1.7**	**38.5**	**7.2**	**84.2**	*457*
Woodford - 77D, Arbuckles, OK	**367.8**	**2.0**	**38.3**	**7.5**	**82.6**	*350*
Woodford - Lake Classen, OK	**362.3**	**2.2**	**36.5**	**8.8**	**79.2**	*366*
Excello Shale - Tulsa, OK	**271.1**	**2.1**	**24.2**	**10.7**	**70.6**	*7*
Barnett Shale - North Texas	**302.0**	**3.1**	**23.9**	**15.1**	**61.8**	*130*
Caney Shale - JL Shale Pit, SE OK	**273.8**	**3.1**	**20.1**	**15.8**	**57.7**	*53*
Chattanooga - Tahlequah, OK	**265.5**	**3.8**	**19.1**	**12.8**	**57.1**	*45*
Caney Shale - Delaware Creek, SE OK	178.6	**1.9**	11.3	**14.2**	49.0	*121*
U. Fayetteville - Marshall, AR	135.2	**1.5**	9.3	**9.0**	54.0	*227*
L. Fayetteville - Snowball, AR	185.8	**3.4**	8.9	**15.0**	37.2	*58*
Caney Shale - Pine Top, SE OK	149.0	**2.1**	8.9	**10.8**	47.3	*309*
Caney - Tulip Creek, Arbuckles, OK	134.5	**1.9**	7.9	**10.1**	46.6	*146*
L. Fayetteville - Fayetteville, AR	171.4	**3.8**	6.7	**14.1**	31.4	*36*
Ark. Novac. - Potato Hills Area, OK	95.6	**1.8**	4.5	**7.8**	34.5	*24*
Fayetteville "Type" - Fayetteville, AR	115.2	**2.1**	3.0	**14.3**	20.8	*92*
Sylvan Shale - Arbuckles, OK	115.7	**3.1**	2.5	**11.6**	17.3	*13*

Figure 18. Gamma ray response broken down by K, U, and Th components on select shales. (Paxton et. al., 2008)

The Arkansas Novaculite, which is the stratigraphic equivalent to the Chattanooga / Woodford deeper in the basin, does display elevated Th levels (7.8 ppm) in comparison to U levels (4.5 ppm) (Figure 18). This is expected, considering the depositional environment of the novaculite, further offshore. Recent research done by Philbrick et al. (2016) suggests a volcanic source of the silica within the formation, implying that igneous activity was occurring in proximity to the Chattanooga formation, as the shales were being deposited. As igneous rocks are known to be enriched in Th, this could explain the elevated Th levels observed in our sample.

Given the euxinic conditions persistent during deposition of the lower members of the Chattanooga shales and their Pb isotopic signatures, there is still a possibility for them to pose as a source of the metals. If metals were disseminated in the shale upon deposition of the sediments, they could have subsequently been driven outward and updip upon compaction or even expelled and mobilized along with other fluids released from the shales such as hydrocarbons. High salinity fluids would be required to mobilize the metals. Magara (1978) states that connate fluid salinity increases with compaction of sediments and thus it is possible that as the sediments compacted and connate fluids were expelled, the fluids eventually reached a point when their salinity was high enough to leach and mobilize the metals. These fluids were then orogenically and topographically mobilized updip, out of the basin, due to uplift of the foreland thrust belt during the Ouachita orogeny. The metal-carrying solutions may have migrated up to a few hundreds of kilometers through the sedimentary basin (Jebrak and Marcoux, 2015). It is likely that mixing of fluids caused a decrease in metal solubility, triggering ore precipitation. The fractured zones where the ores occur are great potential zones of mixing due to their high permeability and porosity. Another potential explanation for ore precipitation is neutralization of the fluids by the limestones. The aforementioned explanations would still require an input of reduced sulfur, and this is where the role of hydrocarbons may have come into play. The organic matter may have acted as a reductant and reduced sulfur from sulfate ions, or H_2S from the maturation of hydrocarbons may have come in contact with the fluids. Given that these shales are great hydrocarbon source rocks, and that the ores are often found in proximity to hydrocarbons, it is possible that the hydrocarbons and the hydrothermal fluids migrated in conjunction with one another.

7. Conclusions

The MVT ores in the Northern Arkansas and the Tri-State mining districts are highly enriched in both uranogenic and thorogenic components of Pb. The Fayetteville and Chattanooga shales are enriched in the uranogenic component of Pb. Although the Chattanooga shales may represent the original source of the metals responsible for the formation of the ores, the Pb isotopic compositions of most of the shales analyzed in this study do not correlate with the Pb isotopic compositions of the ores. The isotopic signatures of Spavinaw granite basement rocks preclude them from representing a viable source of metals.

Euxinic water conditions during deposition of the Chattanooga shales may provide the environment to disseminate metals within the sediments. The metals may later be mobilized as connate fluids become more saline with burial and subsequent compaction, and may be drawn out of the basin due to compressional forces associated with the Ouachita orogenic event. The mobilized fluids precipitate the ores in their present locations, due to solubility decrease of the metals associated with changes in fluid chemistry. Carbonate rocks provide a key environment for precipitation of the ores, both from a chemical and fluid mixing standpoint. As the slightly acidic fluids dissolve the carbonate rocks, the fluids are neutralized and the ores precipitate out of solution. The void spaces created by the dissolution also serve as host spaces for the ores and provide zones of fluid mixing that further assist with precipitation of the ores. Organic matter, potentially in the form of hydrocarbons, may provide the input of reduced sulfur required for the precipitation of the ores.

8. Future Directions

The anomaly of the sample from the base of the Chattanooga should be examined further. In order to confirm or reject the observed relationship between the shale and ores, additional Chattanooga sample from the base of the formation should be collected and analyzed. Moreover, in order to evaluate other stratigraphic intervals as potential sources of the metals, shales from other formations should also be analyzed, especially samples from deeper in the Arkoma and Anadarko Basins, as well as samples of lower Paleozoic shales from the core of the Ouachita Mountains. It is possible that more than one stratigraphic interval is responsible for providing an input of metals.

References

Adams, J. A. S., and Weaver, C. E. (1958). Thorium-to-uranium ratios as indicators of sedimentary processes; example of concept of geochemical facies. *Bulletin of the American Association of Petroleum Geologists, 42*(2), 387-430.

Alase, A. O. (2012). Gamma spectrometry and geochemical investigation of the mississippian (chesterian) fayetteville shale and imo shale, arkoma basin, arkansas. (Master's thesis, Oklahoma State). Retrieved from https://shareok.org/bitstream/handle/11244/7989/Alase_okstate_0664M_11287.pdf?sequence=1

Algeo, T. J., & Maynard, J. B. (2004). Trace-element behavior and redox facies in core shales of upper pennsylvanian kansas-type cyclothems. *Chemical Geology, 206*(3-4), 289-318.

Arbenz, J. K. (1989). In Bally A. W., Palmer A. R. (Eds.), *The ouachita system,* Geologic Society of America, Boulder, CO.

Bernal, A. S. *Geological characterization of the woodford shale, McAlister cemetery quarry, criner hills, ardmore basin, oklahoma* Available from GeoRef. (1673367662; 2015-034134).

Bradley, Dwight and L. Leach, David. (2003). Tectonic controls of Mississippi Valley-type lead–zinc mineralization in orogenic forelands. Mineralium Deposita. 38. 652-667. 10.1007/s00126-003-0355-2.

Brennecka, G. A., Herrmann, A. D., Algeo, T. J., and Anbar, A. D. (2011). Rapid expansion of oceanic anoxia immediately before the end-permian mass extinction. *Proceedings of the National Academy of Sciences of the United States of America, 108*(43), 17631-17634.

Buckley, E. R., and Buehler, H. A. (1906). The geology of the granby area. *Missouri Bureau of Geology and Mines, 2nd Series, 4*, 120.

Byrnes, A. P., and Lawyer, G. (1999). Burial, maturation, and petroleum generation history of the arkoma basin and ouachita foldbelt, oklahoma and arkansas.*Natural Resources Research (New York, N.Y.), 8*(1), 3-26.

Carr, J.L., III, 1987, The thermal maturity of the chattanooga formation along a transect from the ozark uplift to the arkoma basin. *Shale Shaker, v. 38*, p. 32-40.

Clerc, F. L. (1887). The lead and zinc ores of southwest missouri. *Engineering and Mining Journal (1869),* 397-398.

Connock, G. T., Nguyen, T. X., Philp, R. P. (2017). The development and extent of photic zone euxinia concomitant with woodford shale deposition. (in press; preliminary version published online ahead of print 21 August 2017) *AAPG Bulletin.*

Emmons, W. H. (1929). The origin of the deposits of sulphide ores of the mississippi valley. *Economic Geology, 24*(3), 221-271.

Frezon, S. E., Glick, E. E., and Frezon, W. E. (1959). Pre-atoka rocks of northern arkansas. *U.S.Geological Survey Professional Paper,* 171-189.

Frigaard, N.U. Dahl, C. (2009). Sulfur metabolism in phototrophic sulfur bacteria. *Advanced Microbial Physiology*, 54: 103-200.

Garrels, R. M. (1941). The mississippi valley type lead-zinc deposits and the problem of mineral zoning. *Economic Geology and the Bulletin of the Society of Economic Geologists, 36*(7), 729-744.

Garven, G. (1985). The role of regional fluid flow in the genesis of the pine point deposit, western canada sedimentary basin. *Economic Geology and the Bulletin of the Society of Economic Geologists, 80*(2), 307-324.

Glover,Lynn, I.,II. (1959). Stratigraphy and uranium content of the chattanooga shale in northeastern alabama, northwestern georgia, and eastern tennessee.*U.S.Geological Survey Bulletin,* 133-168.

Goldhaber, M. B., Church, S. E., Doe, B. R., Aleinikoff, J. N., Brannon, J. C., Podosek, F. A., . . . Gent, C. A. (1995). Lead and sulfur isotope investigation of paleozoic sedimentary rocks from the southern midcontinent of the united states; implications for paleohydrology and ore genesis of the southeast missouri lead belts. *Economic Geology and the Bulletin of the Society of Economic Geologists, 90*(7), 1875-1910.

Gonzalez, J., Lewis, R., Hemingway, J., Grau, J., Rylander, E., and Schmitt, R. (2013, January 1). Determination of Formation Organic Carbon Content Using a New Neutron-Induced Gamma Ray Spectroscopy Service that Directly Measures Carbon. Society of Petrophysicists and Well-Log Analysts.

Guccione, M. J. (1993). Geologic history of arkansas through time and space. *Arkansas and Regional Studies Center,* 1-63.

Hall, W. E., and Friedman, I. (1963). Composition of fluid inclusions, cave-in-rock fluorite district, illinois, and upper mississippi valley zinc-lead district. *Economic Geology and the Bulletin of the Society of Economic Geologists, 58*(6), 886-911.

Haworth, E. (1904). History, geography, geology, and metallurgy of galena-joplin lead and zinc. *Kans.Geol.Surv., 8*, 1-126.

Heyl, A. V., Delevaux, M. H., Zartman, R. E., & Brock, M. R. (1966). Isotopic study of galenas from the upper mississippi valley, the illinois-kentucky, and some appalachian valley mineral districts. *Economic Geology and the Bulletin of the Society of Economic Geologists, 61*(5), 933-961.

Jebrak, M., and Marcoux, E. (2015). Geology of mineral resources. Geological Society of Canada, 668 p.

Jenney, W. P., Blake, W. P., Nason, F. L., and Winslow, A. (1894). The lead and zinc deposits of the mississippi valley (with discussion by W. P. blake, arthur winslow, and F. L. nason). *Transactions of the Society of Mining Engineers of American Institute of Mining, Metallurgical and Petroleum Engineers, Incorporated (AIME),* , 171-225.

Johnson, K. S., Branson, C. C., Curtis,Neville M.,,Jr, Ham, W. E., Marcher, M. V., and Roberts, J. F. (1972). Geology and earth resources of oklahoma; an atlas of maps and cross sections. *Educational Publication - Oklahoma Geological Survey, 1*, 8.

Jowett, E. C. (1992). Role of organics and methane in sulfide ore formation, exemplified by kupferschiefer cu-ag deposits, poland. *Chemical Geology, 99*(1-3), 51-63.

Kamenov, G. D., Mueller, P. A., Perfit, M. R. (2004). Optimization of mixed Pb-Tl solutions for high precision isotopic analyses by MC-ICP-MS. *Journal of Analytical Spectrometry*, *19,* 1262-1267.

Kesler, S. E., Appold, M. S., Cumming, G. L., & Krstic, D. (1994). Lead isotope geochemistry of mississippi valley-type mineralization in the central appalachians. *Abstracts with Programs - Geological Society of America, 26*(7), 382.

Leach, D. L., and Rowan, E. L. (1986). Genetic link between ouachita foldbelt tectonism and the mississippi valley-type lead-zinc deposits of the ozarks. *Geology (Boulder), 14*(11), 931-935.

Leach, D. L., Sangster, D. F., Kelley, K. D., Large, R. R., Garven, G., Allen, C. R.,Walters, S. (2005). In Hedenquist J. W., Thompson J. F. H., Goldfarb R. J. and Richards J. P. (Eds.), *Sediment-hosted lead-zinc deposits; a global perspective.* Society of Economic Geologists, Littleton, CO.

Leach, D. L., Taylor, R. D., Fey, D. L., Diehl, S. F., and Saltus, R. W. (2010). A deposit model for mississippi valley-type lead-zinc ores. *Scientific Investigations Report,* 52.

Liner, Prof. Christopher L "Seismos." *Mathematica Strat Column*, 14 Mar. 2013, seismosblog.blogspot.com/2013/02/mathematica-strat-column.html

Luening, S., and Kolonic, S. (2003). Uranium spectral gamma-ray response as a proxy for organic richness in black shales; applicability and limitations. *Journal of Petroleum Geology, 26*(2), 153-174.

Magara, K. (1978). *Compaction and fluid migration; practical petroleum geology*Elsevier Sci. Publ., Amsterdam.

Manhes, G., Minster, J. F., and Allegre, C. J. (1978). Comparative uranium-thorium-lead and rubidium-strontium study of the saint severin amphoterite; consequences for early solar system chronology. *Earth and Planetary Science Letters, 39*(1), 14-24.

Mastalerz, M., Schimmelmann, A., Drobniak, A., and Chen, Y. (2013). Porosity of devonian and mississippian new albany shale across a maturation gradient; insights from organic petrology, gas adsorption, and mercury intrusion.*Abstracts with Programs - Geological Society of America, 45*(7), 174.

McKnight, E. T. (1935). Zinc and lead deposits of northern arkansas. *U.S.Geological Survey Bulletin,* 311.

McKnight, E. T., Fischer, R. P., and Mc Knight, E.T. (1970). Geology and ore deposits of the picher field, oklahoma and kansas. *U.S.Geological Survey Professional Paper,* , 165.
Mitchell, A. H. G. (1985). Mineral deposits related to tectonic events accompanying arc-continent collision. *Transactions - Institution of Mining and Metallurgy.Section B: Applied Earth Science, 94*, B115-B125.

Ohle, Ernest Linwood,,Jr. (1959). Some considerations in determining the origin of ore deposits of the mississippi valley type. *Economic Geology and the Bulletin of the Society of Economic Geologists, 54*(5), 769-789.

Oliver, J. (1986). Fluids expelled tectonically from orogenic belts; their role in hydrocarbon migration and other geologic phenomena. *Geology (Boulder), 14*(2), 99-102.

Parnell, J., and Swainbank, I. (1990). Pb-pb dating of hydrocarbon migration into a bitumen-bearing ore deposit, north wales. *Geology (Boulder), 18*(10), 1028-1030.

Paxton, S. T., Aufill, M., Kamann, P., and Krystyniak, A. (2008). Spectral gamma ray response of oklahoma shales in outcrop [PowerPoint slides]. Retrieved from http://ogs.ou.edu/docs/meetings/OGS-workshop-gas_shales_2008-paxton.pdf

Peters, K. E., and Cassa, M. R. (1994). Applied source rock geochemistry. *AAPG Memoir, 60*, 93-120.

Peters, K. E., Walters, C. C., and Moldowan, J. M. (2005). *The biomarker guide; I, biomarkers and isotopes in the environment and human history.* Cambridge University Press, Cambridge.

Philbrick, J.; Pollock, E.; and Potra, A. (2016) "Comparison of the Elemental Geochemistry of the Arkansas Novaculite and the Boone Chert in their Type Regions, Arkansas," *Journal of the Arkansas Academy of Science*: Vol. 70, Article 31.

Pin, C., Gannoun, A., and Dupont, A. (2014). Rapid, simultaneous separation of Sr, Pb, and Nd by extraction chromatography prior to isotope ratios determination by tims and mc-icp-ms. *Journal of Analytical Atomic Spectrometry, 29.* 1858-1870.

Ratchford, M. E., and Bridges, L. C. (2006). Geochemistry and thermal maturity of the upper mississippian fayetteville shale formation, eastern arkoma basin and mississippi embayment regions, arkansas. *Transactions - Gulf Coast Association of Geological Societies, 56*, 717-721.

Rickard, D. T., Willden, M., Marde, Y., and Ryhage, R. (1975). Hydrocarbons associated with lead-zinc ores at laisvall, sweden. *Nature (London), 255*(5504), 131-133.

Ridge, J. D. (1936). The genesis of the tri-state zinc and lead ores. *Economic Geology and the Bulletin of the Society of Economic Geologists, 31*(3), 298-313.

Ridley, J. (2013). *Ore Deposit Geology*. Cambridge: Cambridge University Press. doi:10.1017/CBO9781139135528

Robb, L. (2005). *Introduction to ore-forming processes* Blackwell Publishing, Malden, MA.

Schmidt, A., and Leonhard, A. (1874). The lead and zinc regions of southwest missouri. *Missouri Geological Survey,* , 1873-4.

Schutter, Stephen, 2015, Lead-zinc mineralization as an indicator of unconventional resources: *Houston Geological Society Bulletin*, v. 57, no. 5, p. 33-49

Siebenthal, C. E. (1915). Origin of the zinc and lead deposits of the joplin region, missouri, kansas, and oklahoma. *U.S.Geological Survey Bulletin,* 283.

Shepard, E. M. (1898). A report on greene county. *Missouri Bureau of Geology and Mines, 2nd Series,* 13-245

Slatt, R., (2013). Sequence stratigraphy of the woodford shale and application to drilling and production. *AAPG Search and Discovery*, Article #50792.

Sutherland, P. K. (1988). Late mississippian and pennsylvanian depositional history in the arkoma basin area, oklahoma and arkansas. *Geological Society of America Bulletin, 100*(11), 1787-1802.

Swanson, V. E., and Landis, E. R. (1962). Geology of a uranium-bearing black shale of late devonian age in north-central arkansas. *Information Circular - State of Arkansas, Arkansas Geological and Conservation Commission,* 16.

Tanaka, T., Togashi, S., Kamioka, H., Amakawa, H., Kagami, H., Hamamoto, T., Dragusanu, C. (2000). JNdi-1; a neodymium isotopic reference in consistency with LaJolla neodymium. *Chemical Geology, 168*(3-4), 279-281.

Veatch, A. C. (1899). The Five Islands: Louisiana Geol. Survey Kept, for 1899, p. 227, 248.

White, D. E. (1958). Liquid of inclusions in sulfides from tri-state (missouri-kansas-oklahoma) is probably connate in origin. *Economic Geology and the Bulletin of the Society of Economic Geologists, 53*(7), 929.

Wilkerson, R. M. (1982). Oil and gas fields of the U.S., *PennWell Publishing Company (Tulsa).* 1 p. map.

Winslow, A. (1894). Lead and zinc deposits. *Missouri Bureau of Geology and Mines, 2nd Series,*763.

Zartman, R. E., and Doe, B. R. (1981). Plumbotectonics—the model. *Tectonophysics*, *75*(1), 135-162.

Appendix 1.1

Sphalerite Dissolution Procedures:

1. Break samples to reveal fresh crystal faces.
2. Sort through broken rock and crystals, extracting only clean, pure sphalerite crystals and shards.
3. Rinse samples with 0.5N $HNO_3$and let rest for 30 minutes.
4. Rinse samples of nitric acid with triple-distilled water and dry.
5. Measure 150 mg of each sample
6. 2 mL of 8N HNO_3 added to each sample to digest. (Allowed to digest for 2 days)
7. Samples heated to 150°C and dried down.
8. Some samples still not completely digested, so 1 mL of concentrated HBr (8.84N) added to isotope samples.
9. 1 mL of 8N HNO_3 added to all samples to further digestion.
10. Heated samples to 150° C and dried.
11. Add 2 mL 1N HBr to isotope samples, heat on low and dry down.
12. Repeat Step 11 two more times.
13. Add 500 µL 1 N HBr to samples to get them back in solution.
14. Heated samples up to help get them back in solution.
15. Not all samples back in solution, so 1 mL 1N HBr added to samples to aid them back into solution.
16. Centrifuge isotope samples for 10 minutes, rotate 180°, and centrifuge samples for an additional 10 minutes.

17. Samples added to columns and followed column chemistry procedures outlined in Manhes et al., 1978.

Appendix 1.2

Rock Dissolution procedures:

1. Shales rinsed in DI and allowed to dry
2. Shales broken with hammer to reveal fresh chips.
3. Fresh, unaltered chips selected from interior of collected shale block.
4. Chips were powdered.
5. 250 mg of each sample weighed out for analysis.
6. 5ml of HF, 3 ml of HNO3, and 1 ml of HCl added to each sample (other than granites and blank) to dissolve according to clay method dissolution method from MARS machine.
7. Samples microwaved according to MARS method. Ramp to 200 degrees C for 15:00 and then held at 200 C for 10 minutes. – samples still not dissolved.
8. Samples microwaved again using MARS 6 machine using altered method. Ramp to 200 C for 15:00 and then held for 45:00 minutes at 200 C. – Still not dissolved completely.
9. Added additional 5ml of conc. HNO3 – ultra grade (same as used before) – to samples but CS3.
10. Repeated step 8. – samples still not fully dissolved.
11. Transferred samples to smaller beakers and dried down on hot plate.
12. Granites and blank followed steps 1-5 as above and then skipped to this point.
13. Added 4 ml 7N HNO3 and 3 ml HF. Placed sample beakers on hot plate with caps on until dissolved. Removed lids and dried down.
14. Added 0.5 ml 6N HCl + 0.5 ml 7N HNO3, placed sample beakers on hot plate with caps on until dissolved. Removed lids and dried down.

15. Shale samples and standards skipped steps 13 and 14 because plenty of HCl, HF, and HNO3 had been added previously. Granites and blank continue from above, shales and standards resume here. - Added 2ml of concentrated HNO3, placed sample beakers on hot plate with caps on until dissolved. Removed lids and dried down.
16. Add 1of concentrated HNO3, placed sample beakers on hot plate with caps on until dissolved. Removed lids and dried down.
17. Added 2 ml of 1N HNO3, placed sample beakers on hot plate with caps on until dissolved.
18. Transferred to centrifuge tubes and centrifuged 15 minutes, rotated 180 degrees and centrifuged again.
19. Samples added to columns and followed column chemistry procedures outlined in Pin et. al . 2014.

Sample Name	Weight of sample (mg)	Location (Lat/Long)	206 Pb / 204 Pb Present Day	% Error	207 Pb / 204 Pb Present Day	% Error	208 Pb / 204 Pb Present Day	% Error
Northern Arkansas Ores								
NA 1	150.02	36° 2'25.98"N 92°49'25.86"W	20.150	1.710E-03	15.843	1.950E-03	39.301	6.440E-03
NA 2	146.69	36° 7'49.86"N 92°33'5.46"W	21.508	1.590E-03	15.915	1.720E-03	40.765	5.800E-03
NA 4	150.04	36° 9'59.04"N 92°53'16.08"W	20.700	2.910E-03	15.834	2.740E-03	39.950	8.000E-03
NA 5	150.34	36°18'2.20"N 92°54'22.00"W	22.639	7.990E-03	16.723	1.020E-02	43.463	2.680E-02
NA 7	150.25	35°56'58.26"N 91°45'45.52"W	20.319	2.790E-03	15.810	3.240E-03	39.521	1.080E-02
NA 8	150.31	N/A	21.829	3.570E-03	15.919	3.030E-03	41.042	8.800E-03
NA 9	68.56	N/A	20.919	1.980E-03	15.864	2.090E-03	40.180	7.490E-03
NA 10	150.74	N/A	20.103	1.930E-03	15.776	2.17E-03	39.101	7.11E-03
NA Davy Crockett	147.5	36° 2'60.00"N 92°46'1.20"W	20.197	1.550E-03	15.794	1.730E-03	39.303	5.700E-03
NA Red Bird	84.51	36° 4'1.20"N 92°40'1.20"W	21.626	2.660E-04	15.914	2.980E-03	40.867	1.020E-02
Tri-State Ores								
TS 2	150.02	36°58'28.19"N 94°50'33.39"W	22.170	6.920E-04	15.934	7.160E-04	41.236	2.310E-03
TS 3	150.18	36°58'28.19"N 94°50'33.39"W	22.094	6.900E-04	15.925	6.910E-04	41.182	2.350E-03
TS 4	150.03	36°58'28.19"N 94°50'33.39"W	21.270	7.300E-04	15.860	7.210E-04	40.568	2.430E-03
TS 5	150.4	36°58'28.19"N 94°50'33.39"W	22.107	1.610E-03	15.930	1.720E-03	41.184	5.680E-03
TS 6	150.09	36°58'28.19"N 94°50'33.39"W	22.338	2.550E-03	15.975	2.620E-03	41.432	8.990E-03
TS 7	150.28	36°58'28.19"N 94°50'33.39"W	22.049	1.630E-03	15.932	1.690E-03	41.168	5.740E-03
TS 8	131.81	36°58'28.19"N 94°50'33.39"W	21.075	1.900E-03	15.833	2.160E-03	40.479	7.270E-03
TS AB 1-1	119.11	37°14'31.13"N 94°25'15.67"W	22.766	1.940E-03	16.105	1.840E-03	41.632	5.790E-03
TS BS 1-7	95.05	36°59'6.14"N 94°44'49.27"W	22.223	1.430E-03	16.040	1.480E-03	41.524	5.120E-03
TS PC 2-1	97.12	36°57'51.05"N 94°48'37.66"W	21.768	1.740E-03	15.900	1.870E-03	40.883	6.270E-03

Appendix 2.1: Detailed Pb isotope measurements of sphalerite ores.

Sample Name	Location	^{206}Pb / ^{204}Pb	% Error	^{207}Pb / ^{204}Pb	% Error	^{208}Pb / ^{204}Pb	% Error
Chattanooga Shale		Present Day		Present Day		Present Day	
CS1	35°55'34.65"N 94°55'38.68"W	25.685	4.520E-04	16.031	3.290E-04	38.769	8.750E-04
CS2	35°57'18.90"N 94°48'51.25"W	21.453	4.400E-04	15.795	3.460E-04	38.883	9.220E-04
CS3	35°58'3.60"N 94°47'30.20"W	22.130	3.590E-04	15.837	2.600E-04	39.047	6.160E-04
CS4	36°12'39.97"N 94°46'15.90"W	21.087	3.610E-04	15.779	2.960E-04	39.112	7.430E-04
CS5	36°11'27.50"N 94°43'16.55"W	20.322	2.750E-04	15.730	2.270E-04	38.938	5.700E-04
CS6	36° 6'44.32"N 94°31'59.96"W	20.059	2.310E-04	15.727	2.210E-04	38.822	6.160E-04
CS7	36° 6'23.95"N 94°20'20.85"W	23.756	2.850E-04	15.907	2.060E-04	38.853	5.540E-04
CS8	36°33'40.76"N 94°20'36.97"W	19.658	1.960E-04	15.702	1.780E-04	39.140	4.560E-04
CS9	36°32'48.16"N 94°19'39.37"W	19.197	2.980E-04	15.675	2.540E-04	38.801	6.670E-04
CS10B	36°30'14.66"N 94°15'31.95"W	21.877	2.660E-04	15.898	2.000E-04	40.813	6.480E-04
CS11	36°29'48.48"N 94°15'55.44"W	19.501	2.310E-04	15.692	2.040E-04	38.845	5.680E-04
CS12	36°27'1.44"N 94°14'25.08"W	19.623	2.930E-04	15.698	1.960E-04	38.889	6.270E-04
CS13	36°19'54.61"N 94° 1'12.05"W	19.765	1.510E-03	15.704	1.010E-03	39.204	2.560E-03

Appendix 2.2: Detailed Pb isotope measurments of Chattanooga shale samples.

Sample Name	**Location**	**^{206}Pb / ^{204}Pb**	**% Error**	**^{207}Pb / ^{204}Pb**	**% Error**	**^{208}Pb / ^{204}Pb**	**% Error**
Fayetteville Shale		Present Day		Present Day		Present Day	
FS1L	36° 5'57.76"N 94°23'42.44"W	20.193	2.270E-04	15.726	1.780E-04	39.205	4.810E-04
FS1L Duplicate	36° 5'57.76"N 94°23'42.44"W	20.115	2.480E-04	15.722	2.440E-04	39.321	7.880E-04
FS2U	36° 2'32.64"N 94°11'28.32"W	18.730	2.860E-04	15.634	2.650E-04	38.877	7.960E-04
FS3	36° 2'44.80"N 94°10'49.27"W	19.792	2.480E-04	15.689	2.080E-04	39.270	5.540E-04
FS4	36° 2'27.00"N 94°10'28.30"W	18.872	3.150E-04	15.621	2.490E-04	39.002	6.520E-04
FS6L	36° 5'33.31"N 94° 9'7.57"W	21.774	2.420E-04	15.821	1.650E-04	39.447	4.390E-04
FS6L Duplicate	36° 5'33.31"N 94° 9'7.57"W	21.897	3.680E-04	15.830	2.820E-04	39.487	7.750E-04
FS7L	36° 1'40.08"N 94° 0'45.72"W	20.526	4.530E-04	15.756	3.910E-04	39.477	9.490E-04
FS8UU	36° 7'10.89"N 93°44'24.26"W	18.993	7.060E-04	15.650	5.800E-04	38.901	1.540E-03
FS8UU Duplicate	36° 7'10.89"N 93°44'24.26"W	18.955	4.450E-04	15.649	3.450E-04	38.977	9.640E-04
FS9LU	36° 7'10.99"N 93°44'23.94"W	18.799	2.740E-04	15.637	2.770E-04	38.988	7.270E-04
FS10L	36° 7'11.50"N 93°44'21.79"W	18.747	6.620E-04	15.636	5.660E-04	38.923	1.350E-03
FS10L Duplicate	36° 7'11.50"N 93°44'21.79"W	18.794	4.850E-04	15.639	4.570E-04	39.030	1.310E-03
FS11	36° 4'12.98"N 94°10'1.30"W	20.594	5.710E-04	15.755	4.630E-04	38.892	1.230E-03

Appendix 2.3: Detailed Pb isotope measurements of Fayetteville shale samples.

Granites	Location (Lat/Long)	206 Pb / 204 Pb Present Day	% Error	207 Pb / 204 Pb Present Day	% Error	208 Pb / 204 Pb Present Day	% Error
SG1	36°23'14.68"N 95° 3'22.79"W	19.734	2.720E-04	15.632	2.240E-04	39.889	6.150E-04
SG2	36°23'14.68"N 95° 3'22.79"W	19.742	7.290E-04	15.639	5.870E-04	39.889	1.570E-03

Appendix 2.4: Detailed Pb isotope measurements of Spavinaw granite samples.

Standard	208 Pb / 204 Pb	% Error	207 Pb / 204 Pb	% Error	206 Pb / 204 Pb	% Error
NBS 981 - 35ppb	36.670	9.020E-04	15.483	3.540E-04	16.929	3.460E-04
NBS 981 - 35ppb	36.663	1.120E-03	15.481	4.340E-04	16.926	4.230E-04
NBS 981 - 35ppb	36.671	9.680E-04	15.484	3.540E-04	16.930	3.670E-04
NBS 981 - 80ppb	36.677	5.990E-04	15.485	2.200E-04	16.931	2.000E-04
NBS 981 - 80ppb	36.675	6.350E-04	15.484	2.410E-04	16.931	2.580E-04
NBS 981 - 80ppb	36.679	4.880E-04	15.485	1.810E-04	16.932	2.140E-04
NBS 981 - 80ppb	36.676	6.230E-04	15.485	2.390E-04	16.931	2.650E-04
NBS 981 - 80ppb	36.676	6.870E-04	15.485	2.700E-04	16.931	2.480E-04
NBS 981 - 80ppb	36.674	5.490E-04	15.484	2.070E-04	16.931	2.410E-04
NBS 981 - 80ppb	36.677	6.140E-04	15.485	2.150E-04	16.932	2.200E-04
NBS 981 - 35ppb	36.672	1.100E-03	15.484	4.170E-04	16.930	4.550E-04
NBS 981 - 80ppb	36.678	6.120E-04	15.485	2.330E-04	16.932	2.400E-04
NBS 981 - 80ppb	36.675	5.670E-04	15.484	2.270E-04	16.933	2.690E-04
NBS 981 - 80ppb	36.675	6.000E-04	15.484	2.360E-04	16.931	2.570E-04
NBS 981 - 80ppb	36.672	5.060E-04	15.483	1.990E-04	16.930	2.150E-04
NBS 981 - 80ppb	36.669	5.410E-04	15.482	1.990E-04	16.929	2.070E-04
NBS 981 - 80ppb	36.670	4.200E-04	15.483	1.870E-04	16.928	1.890E-04
NBS 981 - 80ppb	36.674	4.790E-04	15.484	1.980E-04	16.930	1.870E-04
NBS 981 - 80ppb	36.671	4.860E-04	15.483	1.950E-04	16.929	2.130E-04
NBS 981 - 80ppb	36.667	4.480E-04	15.482	1.960E-04	16.929	2.110E-04
NBS 981 - 100ppb	36.679	5.300E-04	15.485	1.940E-04	16.932	2.140E-04
NBS 981 - 100ppb	36.677	6.180E-04	15.485	2.250E-04	16.931	2.440E-04
NBS 981 - 100ppb	36.679	6.100E-04	15.485	2.250E-04	16.931	1.970E-04
NBS 981 - 100ppb	36.680	6.180E-04	15.485	2.340E-04	16.932	2.260E-04
NBS 981 - 100ppb	36.680	5.820E-04	15.485	2.120E-04	16.932	2.210E-04
NBS 981 - 100ppb	36.679	6.260E-04	15.485	2.420E-04	16.932	2.720E-04
NBS 981 - 100ppb	36.680	6.170E-04	15.485	2.330E-04	16.932	2.100E-04
NBS 981 - 100ppb	36.679	7.820E-04	15.485	3.030E-04	16.932	2.750E-04
NBS 981 - 100ppb	36.681	5.130E-04	15.486	1.930E-04	16.932	2.060E-04
NBS 981 - 100ppb	36.680	6.090E-04	15.485	2.310E-04	16.932	2.510E-04
NBS 981 - 100ppb	36.680	5.630E-04	15.485	2.070E-04	16.932	2.310E-04
NBS 981 - 100ppb	36.680	7.000E-04	15.485	2.670E-04	16.931	2.660E-04
NBS 981 - 100ppb	36.679	6.800E-04	15.485	2.540E-04	16.932	2.940E-04
NBS 981 - 100ppb	36.680	7.670E-04	15.485	2.880E-04	16.932	3.080E-04
NBS 981 - 100ppb	36.679	6.440E-04	15.485	2.350E-04	16.932	2.510E-04
NBS 981 - 100ppb	36.681	6.510E-04	15.485	2.670E-04	16.932	2.540E-04
NBS 981 - 100ppb	36.679	6.270E-04	15.485	2.520E-04	16.932	2.430E-04
NBS 981 - 100ppb	36.680	6.010E-04	15.485	2.380E-04	16.932	2.290E-04
NBS 981 - 100ppb	36.680	6.210E-04	15.485	2.270E-04	16.932	2.310E-04
NBS 981 - 100ppb	36.680	5.800E-04	15.485	2.240E-04	16.932	2.290E-04
NBS 981 - 100ppb	36.678	6.820E-04	15.485	2.570E-04	16.932	2.790E-04
NBS 981 - 100ppb	36.680	6.070E-04	15.485	2.240E-04	16.932	2.030E-04
NBS 981 - 100ppb	36.681	5.720E-04	15.485	1.970E-04	16.932	2.170E-04
NBS 981 - 100ppb	36.678	7.740E-04	15.485	3.010E-04	16.931	3.300E-04
NBS 981 - 100ppb	36.685	6.520E-04	15.487	2.400E-04	16.933	2.400E-04
NBS 981 - 100ppb	36.680	8.020E-04	15.485	3.060E-04	16.932	3.150E-04
NBS 981 - 100ppb	36.691	5.730E-04	15.488	2.460E-04	16.934	2.560E-04
Average	36.677	6.414E-04	15.485	2.452E-04	16.931	2.536E-04
Todt et al. 1996	36.701		15.485		16.936	

Appendix 2.5 Detailed Pb isotope measurement data of standards.

Sample Name	87 Sr / 86 Sr	% Error	143 Nd / 144 Nd	% Error
Chattanooga Shale				
CS1	0.769558	5.890E-06	0.511902	4.930E-06
CS2	0.763639	7.910E-06	0.511960	5.970E-06
CS3	0.757829	7.830E-06	0.511889	4.040E-06
CS4	0.765359	8.920E-06	0.511904	5.850E-06
CS5	0.767123	8.260E-06	0.511907	4.780E-06
CS6	0.747974	9.430E-06	0.511982	6.670E-06
CS7	0.765623	7.000E-06	0.511978	3.830E-06
CS8	0.764009	5.300E-06	0.511919	5.620E-06
CS9	0.753823	5.500E-06	0.511869	6.880E-06
CS10B	0.780325	9.700E-06	0.511876	9.920E-06
CS11	0.767107	6.240E-06	0.511861	5.860E-06
CS12	0.767114	5.610E-06	0.511848	4.390E-06
CS13	0.757944	9.100E-06	0.511939	5.570E-06
Fayetteville Shales				
FS1L	0.730208	8.120E-06	0.511950	3.410E-06
FS2U	0.728390	4.560E-06	0.511962	3.550E-06
FS3	0.723788	7.980E-06	0.511953	5.370E-06
FS4	0.729967	8.250E-06	0.511823	1.470E-05
FS6L	0.717662	5.440E-06	0.511994	6.600E-06
FS7L	0.732811	5.800E-06	0.511905	1.060E-05
FS8UU	0.717474	7.680E-06	0.511931	3.720E-06
FS9LU	0.733074	1.320E-05	0.511979	3.490E-06
FS10L	0.726412	6.100E-06	0.511825	4.960E-06
FS11	0.720928	7.900E-06	0.511980	5.360E-06
Spavinaw Granites				
SG1	0.756187	5.550E-06	0.511849	4.210E-06

Appendix 2.6 Detailed Sr and Nd data for rocks analyzed.

Standard	**143 Nd / 144 Nd**	**% Error**
JNdi 1- 200 ppb	0.512084	3.370E-06
JNdi 1- 200 ppb	0.512081	2.690E-06
JNdi 1- 200 ppb	0.512081	2.880E-06
JNdi 1- 200 ppb	0.512088	3.140E-06
JNdi 1- 200 ppb	0.512087	3.200E-06
JNdi 1- 200 ppb	0.512078	3.450E-06
JNdi 1- 200 ppb	0.512079	2.780E-06
JNdi 1- 200 ppb	0.512075	3.570E-06
JNdi 1- 200 ppb	0.512083	3.050E-06
JNdi 1- 200 ppb	0.512080	2.650E-06
JNdi 1- 200 ppb	0.512083	2.810E-06
JNdi 1- 200 ppb	0.512081	3.170E-06
JNdi 1- 80 ppb	0.512081	5.140E-06
JNdi 1- 80 ppb	0.512069	5.860E-06
JNdi 1- 80 ppb	0.512079	4.640E-06
JNdi 1- 80 ppb	0.512078	3.830E-06
JNdi 1- 80 ppb	0.512070	4.910E-06
JNdi 1- 80 ppb	0.512083	4.290E-06
JNdi 1- 80 ppb	0.512083	5.440E-06
JNdi 1- 80 ppb	0.512069	4.890E-06
JNdi 1- 80 ppb	0.512078	4.180E-06
JNdi 1- 80 ppb	0.512077	3.670E-06
JNdi 1- 80 ppb	0.512086	4.850E-06
JNdi 1- 80 ppb	0.512070	3.770E-06
JNdi 1- 80 ppb	0.512078	5.290E-06
JNdi 1- 80 ppb	0.512061	3.820E-06
JNdi 1- 80 ppb	0.512073	5.220E-06
JNdi 1- 80 ppb	0.512069	4.400E-06
Average	0.512000	3.963E-06
JNdi standard Tanaka et al., 2000	0.512115	

Appendix 2.7: Detailed Nd isotope data of standards.

Standard	**87 Sr / 86 Sr**	**% Error**
NBS 987 100ppb	0.710316	4.710E-06
NBS 987 100ppb	0.710274	5.530E-06
NBS 987 100ppb	0.710247	4.910E-06
NBS 987 100ppb	0.710259	6.170E-06
NBS 987 100ppb	0.710265	4.900E-06
NBS 987 100ppb	0.710272	5.940E-06
NBS 987 100ppb	0.710263	6.150E-06
NBS 987 100ppb	0.710267	5.600E-06
NBS 987 100ppb	0.710276	5.740E-06
NBS 987 100ppb	0.710267	6.370E-06
NBS 987 100ppb	0.710269	6.110E-06
NBS 987 100ppb	0.710263	5.210E-06
NBS 987 100ppb	0.710266	4.520E-06
NBS 987 100ppb	0.710316	4.710E-06
NBS 987 100ppb	0.710274	5.530E-06
NBS 987 100ppb	0.710247	4.910E-06
NBS 987 100ppb	0.710259	6.170E-06
NBS 987 100ppb	0.710265	4.900E-06
NBS 987 100ppb	0.710272	5.940E-06
NBS 987 100ppb	0.710263	6.150E-06
NBS 987 100ppb	0.710267	5.600E-06
NBS 987 100ppb	0.710276	5.740E-06
NBS 987 100ppb	0.710267	6.370E-06
NBS 987 100ppb	0.710269	6.110E-06
NBS 987 100ppb	0.710263	5.210E-06
NBS 987 100ppb	0.710266	4.520E-06
NBS 987 100ppb	0.710282	5.960E-06
NBS 987 100ppb	0.710248	5.500E-06
NBS 987 100ppb	0.710234	4.460E-06
NBS 987 100ppb	0.710237	5.700E-06
NBS 987 100ppb	0.710237	6.100E-06
NBS 987 100ppb	0.710233	5.400E-06
NBS 987 100ppb	0.710240	6.100E-06
NBS 987 100ppb	0.710237	5.480E-06
NBS 987 100ppb	0.710240	5.600E-06
NBS 987 100ppb	0.710244	5.070E-06
NBS 987 100ppb	0.710226	6.020E-06
NBS 987 100ppb	0.710231	5.260E-06
NBS 987 100ppb	0.710242	5.460E-06
NBS 987 100ppb	0.710221	5.940E-06
NBS 987 100ppb	0.710258	6.740E-05
NBS 987 100ppb	0.710220	5.380E-06
NBS 987 100ppb	0.710243	6.370E-06
NBS 987 100ppb	0.710246	6.110E-06
NBS 987 100ppb	0.710239	4.970E-06
NBS 987 100ppb	0.710240	4.450E-06
NBS 987 100ppb	0.710218	6.330E-06
NBS 987 100ppb	0.710213	1.090E-05
NBS 987 100ppb	0.710229	5.830E-06
NBS 987 100ppb	0.710218	6.000E-06
NBS 987 100ppb	0.710244	7.820E-06
NBS 987 100ppb	0.710251	5.900E-06
NBS 987 100ppb	0.710247	5.360E-06
NBS 987 100ppb	0.710229	7.190E-06
NBS 987 100ppb	0.710241	5.470E-06
Average	0.710253	6.859E-06
SRM 987 standard	0.7102550	

Appendix 2.8: Detailed Sr isotope measurements of standards.