



Lead and sulfur isotope composition of trace occurrences of Mississippi Valley-type mineralization in the U.S. midcontinent



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ABSTRACT

Mississippi Valley-type (MVT) Zn-Pb mineralization in the U.S. mid-continent has formed in numerous widely dispersed trace occurrences and in a few large ore deposits that have been mined. Based on similarly high fluid inclusion salinities and high homogenization temperatures relative to inferred burial depth, the trace MVT occurrences and MVT ore deposits may be genetically related by having precipitated from the same regional groundwater flow system mobilized by Pennsylvanian-Permian tectonism. The purpose of the present study was to test the robustness of this inferred genetic relationship by characterizing the Pb and S isotope composition of trace MVT occurrences in light of the much more thoroughly studied MVT ore deposits.

Lead and sulfur isotope compositions have been obtained for trace MVT occurrences from three broad regions of the U.S. mid-continent: the Forest City basin (FCB), the Illinois basin (ILB), and the Greater Upper Mississippi Valley (GUMV) region. Lead isotope compositions of trace MVT occurrences from each of these three areas define discrete linear trends that are similarly oriented but not strictly collinear with one another or with the Pb isotope trends of MVT ore deposits, suggesting that trace MVT occurrences in each of these three regions derived their Pb from separate pairs of end-member Pb sources. An exception is the GUMV trace MVT occurrences and the Upper Mississippi (UMV) district ores, which appear to have collinear Pb isotope trends and thus may be the most closely related genetically with respect to sources of Pb. All of the trace MVT occurrences have radiogenic Pb suggesting derivation from Precambrian igneous basement rocks and not from the formations that host trace MVT mineralization. Trace MVT occurrences tend to have less radiogenic Pb than the MVT ore deposits, although trace MVT occurrences from the GUMV region are the most heterogeneous and can have Pb that is as radiogenic as the MVT ore deposits. Regionally, Pb isotope compositions of trace MVT occurrences tend to become less radiogenic southwestward and southward, but do not correlate with host rock age, and by proxy, distance from the Precambrian basement.

The sulfur isotope compositions of sphalerite and galena from the trace MVT occurrences are light compared to the MVT ore deposits and likely reflect incomplete reduction of marine sulfate reservoirs or derivation from organic matter. The Pb and S isotope compositions of the trace MVT occurrences do not correlate well, suggesting that Pb and S were not transported together in the same fluid.

1. Introduction

Mississippi Valley-type (MVT) Zn-Pb mineralization is widely distributed in the Paleozoic carbonate rocks of the North American mid-continent (Fig. 1). Most of this mineralization consists of no more than a few grams of Zn and Pb sulfide, but rare ore deposits may contain millions of tons of these metals. The great contrasts in scale of mineralization raise the question of whether fundamentally different genetic processes and sources of Pb and S were involved in the formation of trace and ore-scale mineralization, or whether trace and ore-scale

mineralization are different expressions of essentially the same genetic processes and sources of Pb and sulfur. This assessment has so far been difficult to make because little information about the trace occurrences of MVT mineralization has been available to compare to the much more thoroughly studied MVT ore deposits.

Much of the previous work on mid-continent trace MVT occurrences has focused on fluid inclusion microthermometry, which has shown that trace MVT occurrences tend to have homogenization temperatures ranging between about 55 and 129 °C and salinities between about 15 and 25 equivalent weight (eq. wt.) % NaCl (Coveney and Goebel, 1983;

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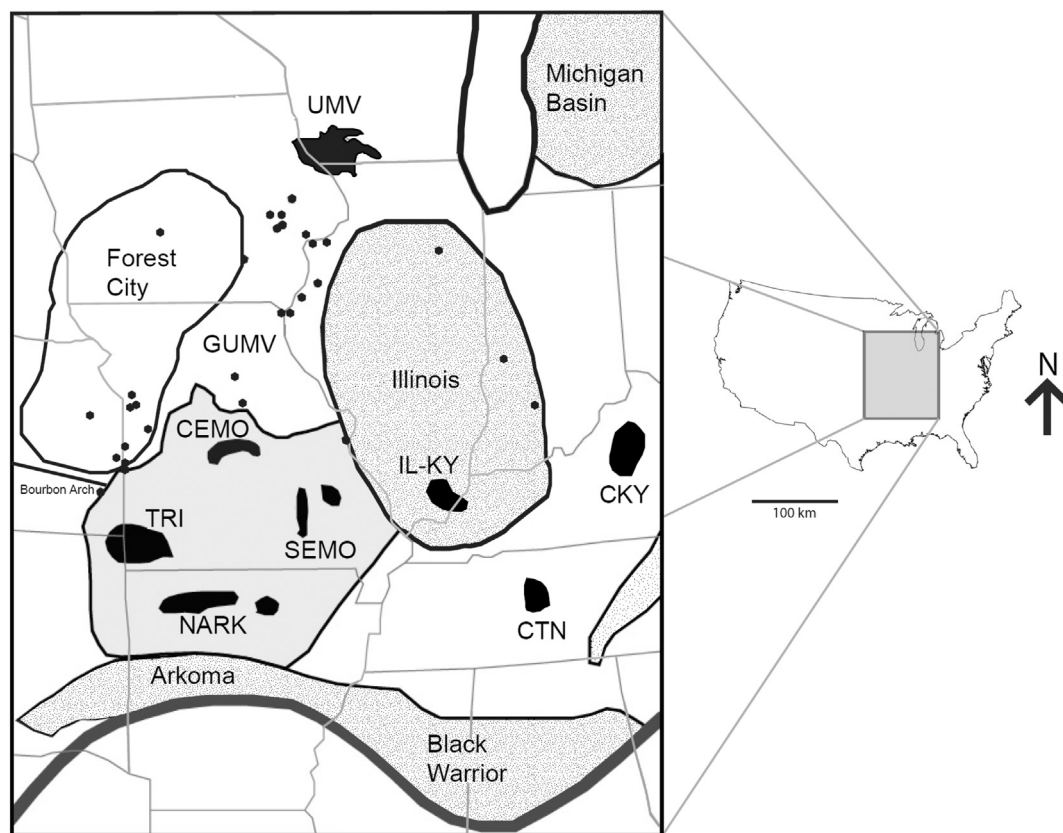


Fig. 1. Map of the U.S. midcontinent showing the locations of trace MVT occurrences analyzed in this study, which are represented by black circles. MVT ore districts are shown as black polygons. Sedimentary basins are represented by a stippled pattern, the Ouachita orogeny is shown in dark gray, and the Ozark Plateau is shown in gray. Abbreviations for MVT ore districts: TRI = Tri-State, NARK = Northern Arkansas, CEMO = Central Missouri, SEMO = Southeast Missouri, IL-KY = Illinois-Kentucky, CKY = Central Kentucky, CTN = Central Tennessee, UMV = Upper Mississippi Valley.

Coveney et al., 1987; Blasch and Coveney, 1988; Kutz and Spry, 1989; Ragan, 1994; Ragan et al., 1996). These values are slightly lower than the homogenization temperatures and salinities found for mid-continent MVT ore deposits, which range primarily between 85 and 135 °C and 22 and 26 eq. wt% NaCl, respectively (Viets and Leach, 1990; Stoffell et al., 2008; Wenz et al., 2012; Pelch et al., 2015).

The ages of trace MVT occurrences have been difficult to determine, due to the lack of good dating methods for sphalerite or galena, and because the genetic relationship of sphalerite and galena to associated datable minerals is typically unclear. Ore-stage calcite from a minor MVT occurrence, the Jumbo deposit, has been dated at 251 ± 11 Ma using the $^{232}\text{Th}/^{208}\text{Pb}$ and $^{238}\text{U}/^{206}\text{Pb}$ methods (Brannon et al., 1996). This age is consistent with a Pennsylvanian-Permian age of formation for the major mid-continent MVT ore deposits, suggesting that the Jumbo deposit was formed from the same regional groundwater flow event initiated by the Alleghanian orogeny (Wisniowiecki et al., 1983; Pan et al., 1990; Symons and Sangster, 1991; Chesley et al., 1994; Coveney et al., 2000; Pannalal et al., 2004). Ragan et al. (1996) suggested this genetic relationship to include trace and minor MVT occurrences in eastern Kansas and western Missouri based on their similarities to the Tri-State ores in oil inclusion abundance, and salinities and homogenization temperatures of aqueous fluid inclusions. In addition, Ragan et al. (1996) suggested that the highly radiogenic though distinct Pb isotope compositions of a trace MVT occurrence in Mound City, Kansas, the minor Jumbo deposit, and the Tri-State ore district may provide further support for a genetic relationship between the Tri-State ore district and trace and minor MVT occurrences generally in eastern Kansas and western Missouri.

Cathodoluminescence has yielded insights into the origin of some trace MVT occurrences. Garvin (2003) found that some of the trace

MVT occurrences fringing the Upper Mississippi Valley (UMV) ore district may be genetically related to the UMV ores in that they have in common a jasperoid phase showing a characteristic brown cathodoluminescence, whereas quartz from other trace MVT occurrences in the region shows blue cathodoluminescence and are thought to be diagenetic in origin.

Some previous stable isotope work has been performed on mid-continent trace MVT occurrences. Trace coal-hosted sulfide minerals from the northern Forest City basin (FCB) display $\delta^{34}\text{S}$ values similar to those of sulfide minerals in the UMV district. In contrast, trace sulfide minerals from the southern Forest City basin and Illinois basin have $\delta^{34}\text{S}$ values that more closely resemble sulfide minerals in high-sulfur coals rather than in nearby MVT ore deposits (Whelan et al., 1988). Kutz and Spry (1989) and Garvin and Ludvigson (1988) analyzed the stable isotope composition of trace MVT occurrences surrounding the UMV ore district in Iowa, Wisconsin, and Illinois. They found calcite from the trace MVT occurrences to have higher $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values (−9 to 5‰; 21 to 29‰) than calcite from the UMV district (−13 to −2‰; 17 to 23‰). The range of $\delta^{34}\text{S}$ values for sulfides from the trace MVT occurrences is wider (−22 to 36‰) than the range for sulfides from the UMV district (5.4 to 29.9‰). Fluid inclusions in the trace MVT occurrences have $\delta^{18}\text{O}$ values similar to those in the UMV district (−8 to 6‰ vs. −5 to 6‰) but have on the whole lower δD values than those in the UMV district (−95 to −20‰ vs. −47 to 2‰). They concluded that trace MVT occurrences that more closely resemble the UMV ore compositionally and paragenetically formed from the same regional mineralizing fluids, whereas the trace MVT occurrences that differ strongly from the UMV ores probably were formed from local diagenesis and multiple fluids.

Kessen et al. (1981) measured $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in gangue minerals

from trace MVT occurrences in Kentucky, Ohio, and Virginia. They interpreted their data to indicate that trace MVT occurrences formed from multiple fluids and included mixing between a metal-rich fluid and reduced sulfur derived from limestones, evaporites, or oil field brines.

Although the Pb isotope compositions of the major mid-continent MVT ore deposits have been well characterized (Heyl et al., 1966; Cannon and Pierce, 1969; Sverjensky et al., 1979; Hart et al., 1981; Deloule et al., 1986; Ludvigson and Millen, 1988; Viets and Leach, 1990; Goldhaber et al., 1995), comparatively little work on the Pb isotope compositions of mid-continent trace MVT occurrences has so far been done. Heyl et al. (1966) analyzed several trace galena occurrences in a broad study of MVT mineralization in the mid-continent and Appalachian region. They found trace galena occurrences in northeast Iowa and in the Rose Dome granite in southeastern Kansas to have highly radiogenic Pb and trace galena occurrences in siderite and coal in southeastern Kansas and central Illinois, respectively, to have much less radiogenic Pb. They also found the Pb isotope composition of ore galena within the UMV district to become more radiogenic northeastward. Millen et al. (1995) expanded the work of Heyl et al. (1966) to include trace and minor galena occurrences surrounding the UMV district. They found the isotopic trend, identified by Heyl et al. (1966), to continue to these surrounding locations, and identified a second vector of increasing radiogenic Pb from south to north in northern Illinois. Luczaj (2000) analyzed trace MVT occurrences in southern Wisconsin and found them to continue the northeastward trend of increasingly radiogenic Pb. Angino et al. (1971) studied the Jumbo deposit and several trace MVT occurrences in southeastern and northwestern Kansas, and southeastern Colorado. All of their samples had radiogenic “J-type” Pb including samples from the Jumbo deposit. Some of these occurrences were reanalyzed by Ragan et al. (1996) and as noted above, along with fluid inclusion data, were used to suggest a genetic relationship between the Jumbo deposit, trace MVT occurrences in eastern Kansas and western Missouri, and the Tri-State ore district.

Thus, previous studies provide some insights into the origin of trace MVT occurrences in the U.S. mid-continent and their relationship to mid-continent MVT ore districts. The MVT ore districts, including the minor Jumbo deposit, are likely genetically related in that they formed from the same regional physical groundwater flow system mobilized by the Alleghanian-Ouachita orogeny during the Pennsylvanian-Permian periods (Bethke, 1986; Leach and Rowan, 1986; Bethke and Marshak, 1990; Symons and Sangster, 1991; Jones et al., 1992; Spry and Fuhrmann, 1994). Though none of the trace MVT occurrences in the present study has been directly dated, and though their fluid inclusion homogenization temperatures and salinities on average are slightly lower than those of the MVT ore districts, nonetheless, the elevated fluid inclusion homogenization temperatures of the trace MVT occurrences relative to expected burial temperatures suggests that the trace MVT occurrences too may have precipitated from this same regional groundwater flow system that transported heat from deep in the Arkoma, Black Warrior, and Illinois basins (Leach et al., 1975; Leach, 1979; Coveney and Goebel, 1983; Coveney et al., 1987; Blasch and Coveney, 1988). This is because the Alleghanian-Ouachita orogeny is the Phanerozoic hydrologic event that likely was most capable of producing the pervasive thermal anomaly across the mid-continent observed in MVT occurrences and paragenetically related diagenetic cements (Voss and Hagni, 1985; Frank and Lohmann, 1986; Farr, 1989; Voss et al., 1989; Gregg and Shelton, 1990; Wojcik et al., 1992, 1994, 1997; Keller et al., 2000; Shelton et al., 2009; King and Goldstein, 2016). In addition, some of the trace MVT occurrences may have been derived from similar sources of mineralizing constituents as the respectively nearby UMV and Tri-State district, based on geochemical and isotopic similarities.

The purpose of the present study was to extend the Pb and S isotope characterization of trace MVT occurrences in the U.S. mid-continent in order to look for further evidence of genetic relationships among them

and with mid-continent MVT ore deposits, possible sources of Pb and S, and controls on the scale of mineralization.

2. Geologic background

The U.S. mid-continent borders and slightly overlaps the southern edge of the Precambrian igneous and metamorphic rocks of the Canadian Shield. Within most of the mid-continent, Phanerozoic sediments have been deposited unconformably upon Precambrian basement rock and have remained largely unaffected structurally by tectonic events, except in the Black Warrior and Arkoma foreland basins associated with the Pennsylvanian-Permian Alleghanian-Ouachita orogeny.

The Alleghanian-Ouachita orogeny appears to have had a pervasive hydrologic effect on the mid-continent, including the formation of MVT ore deposits. Dolomite cements possessing the characteristic cathodoluminescent microstratigraphy observed in gangue dolomite in the Southeast Missouri district are found in much of northern Arkansas and southern Missouri, indicating derivation from the same regional groundwater flow system (Rickman, 1981; Voss and Hagni, 1985; Frank and Lohmann, 1986; Rowan, 1986; Farr, 1989; Voss et al., 1989; Gregg and Shelton, 1990; Leach, 1997; Keller et al., 2000; Shelton et al., 2009). Furthermore, the predominantly Pennsylvanian-Permian dates that have been obtained for the mid-continent MVT ore deposits link this regional groundwater flow system with the Alleghanian-Ouachita orogeny (Wisniewiecki et al., 1983; Pan et al., 1990; Symons and Sangster, 1991; Brannon et al., 1992; Coveney et al., 2000; Chesley et al., 1994). Numerical models of groundwater flow show that uplift of the Arkoma basin during the waning stages of the Alleghanian-Ouachita orogeny could have driven brines out of the basin at rates sufficient to account for MVT ore deposit formation in the Ozark Plateau (Bethke and Marshak, 1990; Garven et al., 1993; Appold and Garven, 1999; Rowan and Marsily, 2001; Appold and Nunn, 2005). This regional groundwater flow system may also have precipitated many of the trace MVT occurrences in the mid-continent based on their elevated fluid inclusion salinities and homogenization temperatures, though none of these trace occurrences has so far been directly dated.

In addition to serving as the likely driver for the regional flow system, the Alleghanian-Ouachita orogeny also developed and reactivated faults and fractures that may have facilitated the ascent of fluid from depth to shallower ore-hosting formations (Clendenin and Duane, 1990; Leach and Sangster, 1993; Clendenin et al., 1994; Cox, 2009; Leach and Taylor, 2009). Faults and fractures may also have facilitated the formation of some of the trace occurrences of MVT mineralization. The host formations for MVT mineralization in the U.S. mid-continent are principally carbonate rocks, particularly local zones of elevated porosity and permeability in these rocks, such as breccias, oolitic beds, and reef facies, or dissolution cavities.

Trace MVT mineralization is found over a wide range of stratigraphic horizons from the Cambrian to the Pennsylvanian. Mineralization occurs primarily as veins, fracture linings, and vug-filling masses, and is always associated with gangue minerals (calcite, dolomite, barite, or pyrite). Some minor MVT occurrences, larger than trace occurrences that briefly attracted commercial interest are also known in the U.S. mid-continent, such as the Jumbo deposit, which produced about 35 tons of Pb in the mid to late 19th century (Schoewe, 1959).

3. Methodology

3.1. Sample acquisition

Samples for the present study were acquired from three broad geographical sub-regions within the U.S. mid-continent: the Forest City basin (FCB), the Illinois basin (ILB), and the Greater Upper Mississippi Valley (GUMV) region (Fig. 1). Many of the samples were collected in the field by the authors. Additional samples were acquired from the

collections of Paul Garvin (Cornell College), the Iowa Geological Survey, and the Illinois State Geological Survey. Most trace MVT samples acquired for the study consist of sphalerite with varying amounts of associated gangue minerals. Galena is much less common than sphalerite, and only four galena samples were included in the present study. At some trace MVT occurrences, samples of barren host rock were collected several meters away from where sphalerite or galena had been recovered.

Sulfide mineral samples selected for isotopic analysis were manually separated from their host rock matrix and inspected under a binocular microscope to ensure that they did not have adhesions of other minerals. Most of the sulfide mineral samples consisted of single crystals. Some Pb isotope analyses were performed on composites of up to three sphalerite crystals from a rock sample if the crystals were individually small so as to ensure that detectable quantities of Pb were obtained. In several samples, mineralization occurred as veins and/or fracture-linings so that picking individual crystals was not possible. In these samples, irregular masses of mineralization were separated from the host rock for isotopic analysis. Lead concentrations in 15 samples of sphalerite were determined by LA-ICP-MS analysis at the Virginia Tech Fluids Research Laboratory in order to help gauge the mass of sphalerite needed to obtain detectable quantities of Pb for isotopic analysis. The Pb concentrations were found to vary between about 0.1 and 580 ppm, with a median value of about 3 ppm.

3.2. Lead isotope analysis

Samples of sphalerite, galena, and carbonate host rock were analyzed for Pb isotope composition at the University of Missouri—Columbia and the University of Washington. Most of the samples were prepared and analyzed at the University of Missouri—Columbia according to the following procedure.

Sphalerite samples were pulverized using an agate mortar and pestle. Limestone samples were pulverized in ceramic jars using a mixer/mill. The resultant powders were dried at 105 °C for 24 h.

Sphalerite powders were digested in a mixture of 4 mL of 14 N HNO₃, 2 mL of 6 N HCl, and 1 mL of 24 N HF in closed Savillex® PFA vials over 48 h at 130 °C on a hot plate. The solutions were then evaporated at 90 °C. Next, the dry residues were dissolved in 3 mL of 14 N HNO₃ over 48 h at 120 °C on a hot plate. Solutions were then evaporated at 90 °C. After evaporation was complete, the resultant dry residues were digested in 3 mL of 6 N HCl over 48 h at 120 °C on a hot plate. The solutions were then evaporated at 90 °C.

Galena samples were digested in a mixture of 1 mL of 6 N HCl, 3 mL of 14 N HNO₃, 2 mL of 24 N HF, and 2 mL of mQ water in polypropylene tubes placed in a warming block at 105 °C for 24 h. An aliquot of the solution was evaporated at 90 °C in a Savillex® PFA vial, redigested in 6 N HCl, and evaporated.

Limestone powders were digested in a mixture of 5.5 mL of 6 N HCl and 0.5 mL of 24 N HF heated in a microwave oven for 25 min to a temperature of 190 °C. After the limestone powders had fully dissolved in the acid solutions, the solutions were evaporated at 90 °C. The resultant dry residues were then digested in 3 mL of 6 N HCl at 130 °C for 24 h in closed Savillex® PFA vials, after which the solutions were evaporated at atmospheric pressure at 90 °C.

Blanks were included in sphalerite and galena sets of samples to evaluate the amount of Pb introduced in the samples during the entire preparation (digestion and separation). Total procedure blank values were 0.015 ng for the sphalerite set and 0.13 ng for the galena set.

Lead isotope compositions were measured using a Nu Plasma II (Nu Instruments) multi-collector - inductively coupled plasma - mass spectrometer (MC-ICP-MS) at the University of Missouri—Columbia Research Reactor (MURR). The MC-ICP-MS was optimized daily for ²⁰⁸Pb maximum intensity and a minimum of 100 mV in the Axial (²⁰⁴Pb). Most samples were analyzed in wet plasma. Some samples had lower Pb concentrations and were analyzed using a Nu Instruments

DSN-100 desolvation nebulizer system to introduce the sample into the mass spectrometer.

The samples and standard were spiked using a Tl solution to monitor and correct for mass fractionation. Lead concentrations varied among samples so sample solutions were prepared to obtain Pb and Tl concentrations similar to those of the NIST SRM 981 solution (approximately 200 ng g⁻¹ Pb and 50 ng g⁻¹ Tl in wet plasma, and approximately 20 ng g⁻¹ Pb and 5 ng g⁻¹ Tl in dry plasma).

The NIST SRM 981 standard was measured several times before each analytical session and after every two samples. Values were corrected for mass fractionation using a 2.38714 value for ²⁰⁵Tl/²⁰³Tl natural ratio. A correction for mercury isobaric interference at mass 204 was also applied using a 0.229883 value for ²⁰⁴Hg/²⁰²Hg natural ratio. The mean ²⁰⁸Pb/²⁰⁴Pb, ²⁰⁷Pb/²⁰⁴Pb and ²⁰⁶Pb/²⁰⁴Pb ratios obtained for the SRM981 in wet plasma (n = 87) are 36.694 ± 0.012 (2SD), 15.490 ± 0.004 (2SD), and 16.937 ± 0.003 (2SD), respectively, where 2SD represents two standard deviations from the mean. The mean ²⁰⁸Pb/²⁰⁴Pb, ²⁰⁷Pb/²⁰⁴Pb and ²⁰⁶Pb/²⁰⁴Pb ratios obtained for the SRM981 in dry plasma (n = 19) are 36.665 ± 0.021 (2SD), 15.488 ± 0.002 (2SD) and 16.934 ± 0.002 (2SD), respectively. These values are in good agreement with the NIST values and with the long-term values obtained at MURR on the Nu Plasma II MC-ICP-MS. To eliminate error caused by instrumental drift, the sample results were corrected using the sample-standard bracketing method (White et al., 2000; Weis et al., 2006) using values published by Todt et al. (1996). Three duplicates (i.e. entire procedure applied twice to the same sample) and four replicates (i.e. second analysis of the same solution) were measured to evaluate the reproducibility of measurements.

Seven Pb isotope analyses were performed at the University of Washington Department of Earth and Space Sciences (Table 1) on a Nu Plasma mass spectrometer, preceded by the sample preparation procedure described in Harkins et al. (2008). Seven of these analyses were repeated at the University of Missouri—Columbia to assess the reproducibility of the measurements obtained in the two laboratories.

3.3. Sulfur isotope analysis

Sulfur isotope analyses were performed in the Stable Isotope Research Facility in the Department of Earth and Atmospheric Sciences at Indiana University. Analyses were performed on 3 to 5 g samples of sphalerite and galena mineral separates. The mineral separates were crushed into powder using an agate mortar and pestle. Next, a Kiba reagent (Kiba et al., 1957), consisting of pure tin (II)-strong phosphoric acid, was produced, beginning by dehydrating reagent grade phosphoric acid by heating it to 250 °C. Tin (II) chloride was added to the dehydrated phosphoric acid at a mass ratio of 1:100. The resultant mixture was heated to 280 °C and exposed to a nitrogen stream to remove HCl and any remaining H₂O, leaving behind pure tin (II)-strong phosphoric acid. The sample sulfide powders were measured into tin capsules such that the total sample contained 20 mg or less total sulfur. Next, 10 mL of the Kiba reagent and 40 mL of zinc acetate were added to the tin capsules and heated to 280 °C. The sulfide powders then produced H₂S, which reacted with the zinc acetate to form zinc sulfide.

Next, the zinc sulfide was collected and converted to Ag₂S through reaction with 1 M AgNO₃ solution. The resultant Ag₂S was placed in tin capsules with ~2 mg vanadium pentoxide at a ratio of ~10:1 sulfide to oxide by weight. The capsules were then heated in an ECS 4010 Costech Elemental Analyzer at 990 °C and at an oxygen pressure of 100 kPa, which oxidized the Ag₂S to SO₂ gas. The SO₂ gas was then transported via a helium stream into a 0.8 m long Costech teflon gas chromatograph (GC) column heated to 100 °C. The gas flowed from the GC column into a Thermo Scientific ConFlo IV for dilution and subsequent injection into a Thermo Scientific Delta V Plus mass spectrometer for analysis. International Atomic Energy Agency (IAEA) standards were used to ensure measurement accuracy. Results are given as delta (δ) values in per mil (‰) notation relative to Vienna Canyon Diabolo Troilite (VCDT).

Table 1
Lead isotope ratios and $\delta^{34}\text{S}$ values of trace MVT occurrence sulfides analyzed in the present study.

Sample	Region	Host formation	Host rock age	Latitude	Longitude	Analytical lab, Pb	Analytical lab, S	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$	$\delta^{34}\text{S}$ sph	$\delta^{34}\text{S}$ gn
1F-S6	GUMV	Little Cedar	Dev	41.86	-91.79	UW	IU	20.055	15.843	39.696	13.43	
BG-5	GUMV	Burlington	Miss	40.85	-90.86	UW	IU	18.765	15.658	38.441	-25.20	
BW-1*	GUMV	Maquoketa	Ord	42.12	-91.36	MURR	IU	22.197	16.015	42.097	14.19	2.69
BW-1*	GUMV	Maquoketa	Ord	42.12	-91.36	UW		22.182	16.006	42.060		
Core	FCB			41.61	-93.99	MURR	IU	21.485	15.937	40.741	-3.00	
CQ-25	GUMV	Davenport	Dev	41.70	-91.55	MURR	IU	18.758	15.655	38.522	-5.84	
CQ-25 Dupl	GUMV	Davenport	Dev	41.70	-91.55	MURR		19.271	15.715	38.945		
DA-4	GUMV	Burlington	Miss	40.64	-91.17	MURR	IU	19.062	15.670	38.578	-24.19	
DA-4	GUMV	Burlington	Miss	40.64	-91.17	UW		19.714	15.721	39.150		
Geode	GUMV	Warsaw	Miss	40.39	-91.58	MURR	IU	19.734	15.748	39.091	-15.37	
Geode	GUMV	Warsaw	Miss	40.39	-91.58	UW		19.901	15.946	39.841		
Iakeo	GUMV	Warsaw	Miss	40.40	-91.40	MURR	IU	19.107	15.674	38.718	-15.49	
Ialyle Repl	GUMV	St. Genevieve	Miss	41.22	-92.31	MURR		22.063	15.957	41.137		
Ialyle	GUMV	St. Genevieve	Miss	41.22	-92.31	MURR	IU	22.063	15.958	41.140	-6.64	
Iless	GUMV	Burlington	Miss	40.85	-90.86	MURR	IU	18.552	15.637	38.343	-6.636	
Inhar	ILB	Harrodsburg	Miss	39.01	-86.54	MURR	IU	19.143	15.671	38.858	-19.37	
Jum	FCB	Pleasanton	Penn	38.16	-94.69	MURR	IU	22.582	16.013	41.627	-1.07	-4.24
Jum*	FCB	Pleasanton	Penn	38.16	-94.69	UW		22.585	16.006	41.593		
Jum Dupl*	FCB	Pleasanton	Penn	38.16	-94.69	MURR		22.527	16.010	41.634		
KCo435	FCB	Winterset	Penn	38.98	-94.51	MURR	IU	18.568	15.639	38.358	-14.86	
KL-1	GUMV	Little Cedar	Dev	41.68	-91.62	MURR	IU	19.953	15.764	39.314	-18.94	
KL-1	GUMV	Little Cedar	Dev	41.68	-91.62	UW		19.108	15.688	38.652		
Ksjingo	FCB	Winterset	Penn	38.40	-94.70	MURR	IU	18.579	15.635	38.351	-17.02	
Kslone	FCB			38.84	-95.38	MURR		18.398	15.627	38.342		
Kslone*	FCB			38.84	-95.38	MURR		18.397	15.626	38.338		
LNC4	GUMV	Wapsipinicon	Dev	41.47	-90.69	MURR	IU	18.661	15.649	38.483	1.44	
LNC4 Dupl	GUMV	Wapsipinicon	Dev	41.47	-90.69	MURR		19.198	15.709	38.920		
LNGT	GUMV	Wapsipinicon	Dev	41.47	-90.69	MURR	IU	20.041	15.786	39.626	-7.29	
LNGT Dupl	GUMV	Wapsipinicon	Dev	41.47	-90.69	MURR		20.053	15.788	39.639		
LNGT Repl	GUMV	Wapsipinicon	Dev	41.47	-90.69	MURR		20.041	15.786	39.626		
Mbus	ILB	Warsaw	Miss	38.48	-90.28	MURR	IU	20.444	15.810	39.828	-9.56	
Mbus	ILB	Warsaw	Miss	38.48	-90.28	UW		20.643	15.826	39.927		
Mlq	ILB	Logan Quarry	Penn	39.70	-87.14	UW	IU	18.612	15.653	38.460	-16.60	
MM6	GUMV	Gower	Sil	41.87	-91.59	MURR	IU	21.225	15.937	40.550	13.13	
MM6	GUMV	Gower	Sil	41.87	-91.59	UW		21.239	15.937	40.565		
MM6 Repl	GUMV	Gower	Sil	41.87	-91.59	MURR		21.226	15.939	40.553		
Mmc	ILB	Francis Creek	Penn	41.32	-88.43	UW	IU	18.819	15.662	38.653	-3.18	
MO-8	GUMV	Wapsipinicon	Dev	41.58	-91.11	MURR	IU	20.932	15.907	40.336	13.127	
Mocass	FCB	Winterset	Penn	38.65	-94.24	MURR	IU	18.515	15.641	38.405	-7.99	
Momccl	FCB	Westerville	Penn	39.01	-94.49	MURR	IU	18.537	15.633	38.377	-7.99	
Morand	FCB	Winterset	Penn	39.16	-94.50	MURR		18.799	15.654	38.427		
Nfar	FCB	Bethany Falls	Penn	38.23	-94.85	UW	IU	18.724	15.649	38.455	-26.13	
Pres	FCB	Pleasanton	Penn	38.06	-94.70	UW	IU	22.486	15.997	41.602	-1.77	-5.37
R-4	GUMV	Davenport	Dev	41.70	-91.55	UW	IU	19.834	15.767	39.559	17.26	
Stark	FCB	Bethany Falls	Penn	37.71	-95.16	MURR	IU	19.614	15.694	38.479	-7.06	
Stark Dupl	FCB	Bethany Falls	Penn	37.71	-95.16	MURR		18.930	15.657	38.454		
West	FCB	Westerville	Penn	39.01	-94.49	MURR	IU	18.655	15.634	38.399	-15.58	
WY-1	GUMV	Caseyville	Penn	41.44	-90.95	MURR	IU	19.662	15.743	39.001	3.53	

An asterisks (*) next to a sample name indicates that the Pb isotope compositions shown are for galena, whereas the absence of an asterisk next to a sample name indicates that the Pb isotope compositions shown are for sphalerite.

Repl = replicate.

Dupl = duplicate.

sph = sphalerite.

gn = galena.

Measurements used in this study had precision of better than $\pm 0.05\%$.

4. Results

4.1. Pb isotopes

The Pb isotope compositions of the trace and minor MVT occurrences, the host rocks of trace MVT occurrences, and mid-continent MVT ore districts data are shown in Figs. 2–6. Some heterogeneity in isotopic composition within samples is evident. It is possible that this is due to differences in labs and lab procedures between UW and MURR, but the consistency of the majority of isotopic compositions as measured at both labs suggests that most of the heterogeneity is caused by genuine, albeit minor, isotopic variation. Samples exhibiting isotopic

heterogeneity show uniform variation such that all values lie on the regional (i.e. FCB, GUMV, or ILB) trends. One sample (Geode) is an exception. The analysis performed at MURR plots on the GUMV regional trend but the analysis performed at UW is highly enriched in ^{207}Pb and, to a lesser extent, ^{208}Pb . This may be caused by contamination, either during the analysis or by small inclusions of pyrite that formed from a different fluid(s) than the sphalerite.

Despite their diverse geographic and stratigraphic locations, the Pb isotope compositions of the trace MVT occurrences plot in relatively linear trends in both $^{207}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ space and in $^{208}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ space. The Pb isotope compositions of mid-continent trace MVT occurrences span most of the ranges of $^{208}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{206}\text{Pb}/^{204}\text{Pb}$ values reported for the major mid-continent MVT ore districts, but tend toward the lower, less

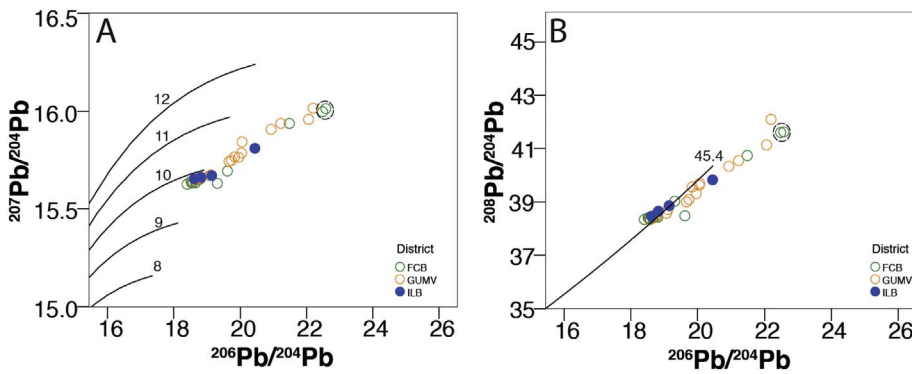


Fig. 2. Diagram showing A) $^{207}\text{Pb}/^{204}\text{Pb}$ vs $^{206}\text{Pb}/^{204}\text{Pb}$ and B) $^{208}\text{Pb}/^{204}\text{Pb}$ vs $^{206}\text{Pb}/^{204}\text{Pb}$ ratios in sphalerite and galena matrices from MVT trace occurrences. The black reference curves in panel A represent Stacey-Kramers Pb isotope growth curves for present-day μ values of 8, 9, 10, 11, and 12 from bottom to top, respectively. The black reference curve in panel B represents the Stacey-Kramers Pb isotope growth curve for a present-day ω value of 45.4. Circled points correspond to values obtained from the Jumbo and Prescott mines and as such are considered minor MVT occurrences rather than trace occurrences.

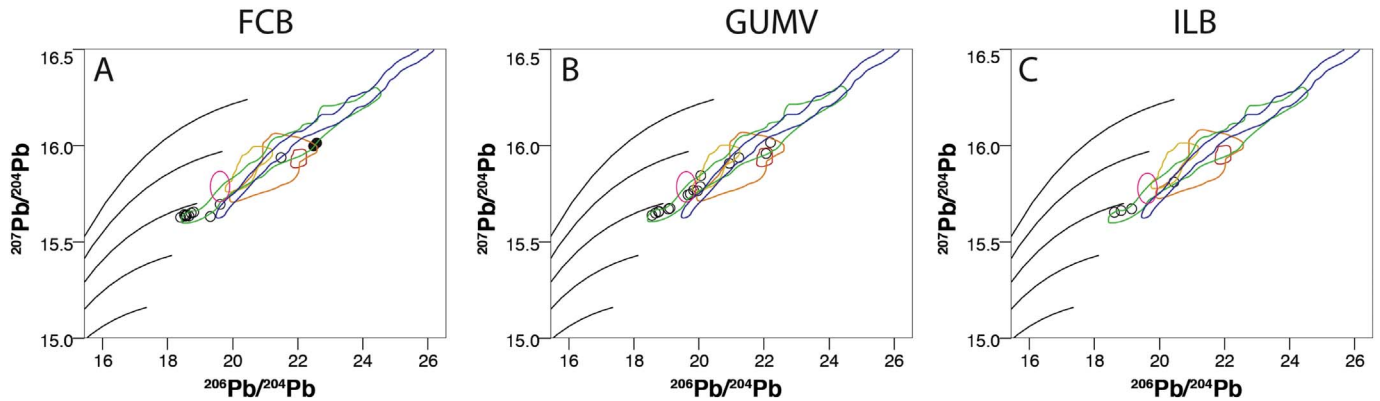


Fig. 3. Plots comparing the $^{207}\text{Pb}/^{204}\text{Pb}$ vs $^{206}\text{Pb}/^{204}\text{Pb}$ values of trace MVT occurrences in the (A) Forest City basin (FCB), (B) Greater Upper Mississippi Valley region (GUMV), and (C) Illinois basin (ILB) with those of MVT ores in the Central Missouri and Tri-State (red outline), Southeast Missouri, (orange outline), Illinois-Kentucky (yellow outline), Upper Mississippi Valley districts (green outline), and the Central Tennessee district (pink outline), and the trace MVT occurrences in north-eastern Wisconsin studied by Luczaj (2000) (blue outline). Black-filled points represent values obtained for the Jumbo and Prescott mines, which are considered minor rather than trace occurrences. Pb isotope values for the Tri-State and Central Missouri districts were similar enough to be combined as one field in all of the plots. The circles represent the Pb isotope compositions of the trace MVT occurrences indicated by the column label. The black reference curves represent Stacey-Kramers Pb isotope growth curves for present-day μ values of 8, 9, 10, 11, and 12 from bottom to top, respectively. Ore district and Wisconsin trace occurrence data were obtained from Heyl et al. (1966), Hart et al. (1981), Deloule et al. (1986), Goldhaber et al. (1995), Millen et al. (1995), Misra et al. (1997) and Luczaj (2000). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

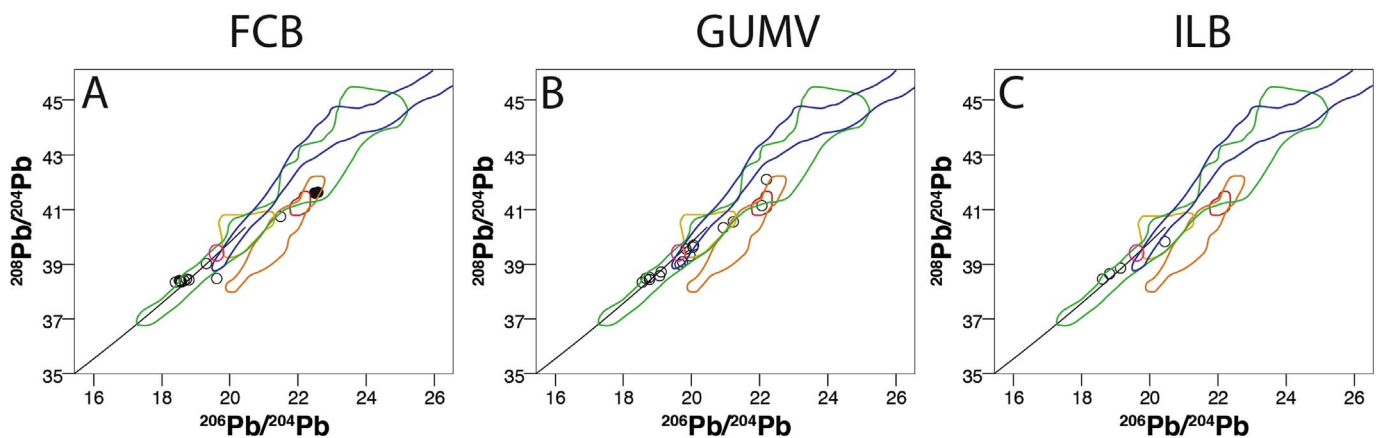


Fig. 4. Plots comparing the $^{208}\text{Pb}/^{204}\text{Pb}$ vs $^{206}\text{Pb}/^{204}\text{Pb}$ isotope values of trace MVT occurrences in the FCB, GUMV region, and ILB with Central Missouri and Tri-State (red outline), Southeast Missouri, (orange outline), Illinois-Kentucky (yellow outline), Upper Mississippi Valley districts (green outline), and the Central Tennessee district (pink outline), and the trace MVT occurrences in north-eastern Wisconsin studied by Luczaj (2000) (blue outline). Black-filled points represent values obtained for the Jumbo and Prescott mines, which are considered minor rather than trace occurrences. As in Fig. 2, Pb isotope values for the Tri-State and Central Missouri districts were similar enough to be combined as one field in all of the plots. The circles represent the Pb isotope compositions of the trace MVT occurrences indicated by the column label. The black reference curve represents the Stacey-Kramers Pb isotope growth curve for a present-day ω value of 45.4. Ore district and Wisconsin trace occurrence data were obtained from Heyl et al. (1966), Hart et al. (1981), Deloule et al. (1986), Goldhaber et al. (1995), Millen et al. (1995), Misra et al. (1997) and Luczaj (2000). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

radiogenic values than samples from other locations. The FCB and ILB occurrences have the least radiogenic Pb, where the three most radiogenic FCB samples are from the Jumbo and Prescott deposits, which are not true trace occurrences but small ore deposits, and thus better

classified as minor occurrences. Lead in true trace occurrences from the FCB and ILB is less radiogenic than most of the Pb from the major mid-continent MVT ore districts, with the exception of some of the Pb in the UMV district. Lead isotope compositions of trace MVT occurrences in

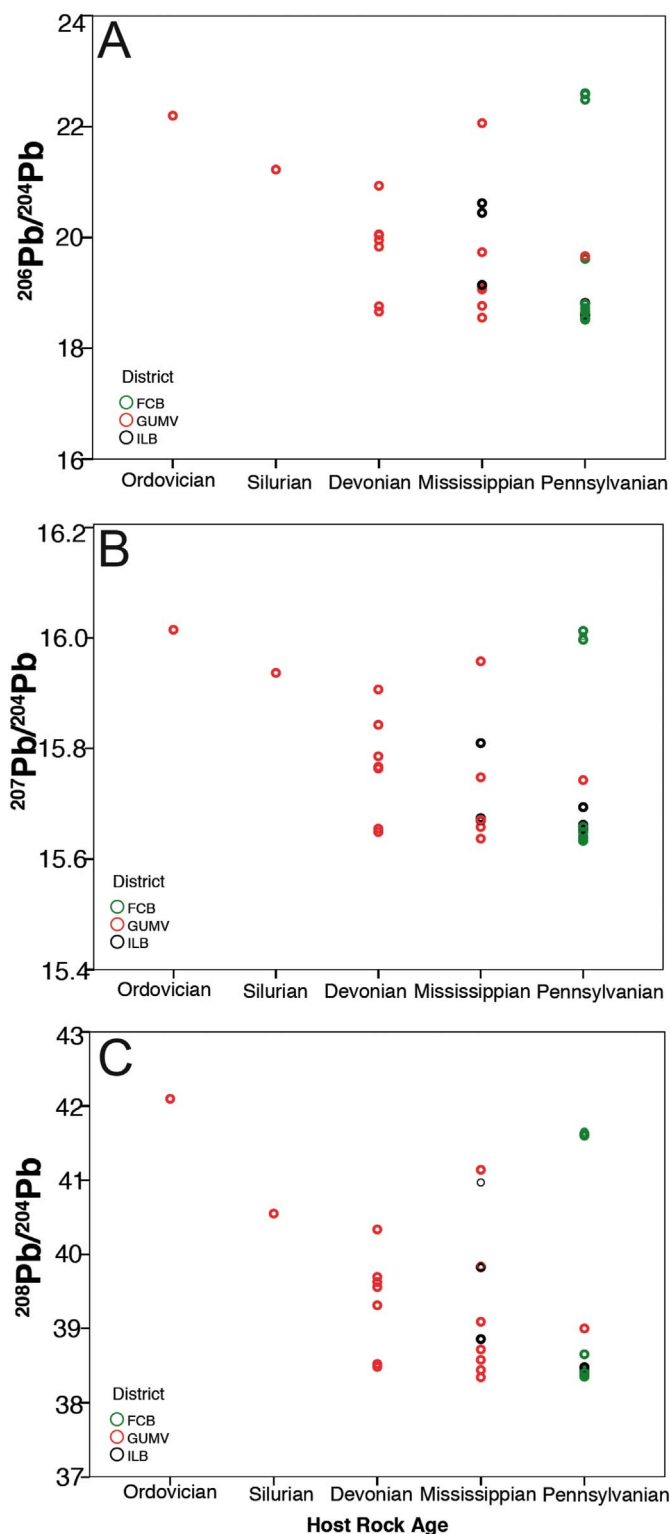


Fig. 5. Lead isotope ratios (A) $^{206}\text{Pb}/^{204}\text{Pb}$, (B) $^{207}\text{Pb}/^{204}\text{Pb}$, and (C) $^{208}\text{Pb}/^{204}\text{Pb}$ of all trace MVT occurrences included in this study plotted versus the age of their host rocks. The trace MVT occurrences are color coded as shown in the legends.

the GUMV region are much more heterogeneous than those of trace MVT occurrences in the FCB and ILB, and resemble the wide range of Pb isotope compositions of MVT ore in the UMV district.

Lead isotope composition of trace MVT occurrences does not correlate well with host rock age (Fig. 5). If host rock age is a proxy for stratigraphic distance from the igneous basement, then these results

suggest that either the trace MVT occurrences did not acquire much of their Pb from the basement (a widely held source of the radiogenic Pb in the mid-continent MVT ore deposits, e.g. Cannon and Pierce, 1969; Angino et al., 1971; Doe and Delevaux, 1972; Goldhaber et al., 1995; Ragan et al., 1996), or more likely, that mechanisms of upward transport of Pb from the basement varied widely in efficiency and not systematically as a function of distance from the basement.

Another possible source for Pb in the trace MVT occurrences is their respective host rocks. This possibility is considered in Fig. 6, which compares the Pb isotope compositions of trace MVT occurrences with those of their host rocks. The results show that the Pb isotope compositions of the host rocks do not lie on the respective Pb isotope composition trends of the trace mineralization contained within them. This suggests that the trace MVT occurrences did not acquire most of their Pb locally from their respective host rocks.

Trace occurrences of MVT mineralization in the GUMV region and FCB that were analyzed in the present study have Pb isotope compositions that generally decrease in radiogenic character southwestward, extending the pattern found by Heyl et al. (1966), Millen et al. (1995), Luczaj (2000), and Luczaj (2007) for trace MVT occurrences in the UMV district and southern Wisconsin (Figs. 7–9). This trend is best defined for $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$, and is weakly defined for $^{207}\text{Pb}/^{204}\text{Pb}$. Heyl et al. (1966), Millen et al. (1995), Luczaj (2000) and Luczaj (2007) interpreted the trend in Pb isotope compositions to reflect regional fluid flow paths, though Luczaj (2000) also raised the possibility that the Pb isotope compositions may reflect isotopic variability in the sandstone aquifers underlying the MVT mineralization. Among the MVT occurrences in the southern FCB, the Prescott and Jumbo deposits, consisting of vertical pipes, have markedly more radiogenic Pb than the trace MVT occurrences that more closely resembles the Pb in the major MVT ore districts. This suggests that the fluids that formed the Jumbo and Prescott deposits may have had more contact with the Precambrian basement than the fluids that formed the bona fide trace MVT occurrences in the southern FCB. It is conceivable that these two ore pipes may extend all the way to the Precambrian basement.

Most of the trace MVT occurrences in the U.S. mid-continent, like MVT ore deposits in the U.S. mid-continent, have “anomalous” Pb isotope compositions in that they yield future Pb isotope dates because they contain excess amounts of radiogenic Pb (Faure and Mensing, 2009). The Pb isotope compositions of trace MVT occurrences in the three geographic regions studied (FCB, ILB, and GUMV) form discrete trends that are similarly oriented but not strictly collinear. These trends may represent mixing between less radiogenic Pb withdrawn from the second stage of the Stacey-Kramers Pb evolution model with a more radiogenic Pb. Calculated model withdrawal dates for the less radiogenic Pb component in $^{207}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ space are 337.5 Ma (Middle Mississippian) for the FCB, 227.8 Ma (Upper Triassic) for the GUMV region, and 268.9 Ma (Middle Permian) for the ILB, assuming the standard μ value of 9.735 for the second stage of Pb evolution in the Stacey-Kramers model. Ages of the withdrawal of the more radiogenic Pb component from source rocks calculated using the instantaneous and continuous models also yield disparate ages, including two future ages (see Table 2). Whether these different model Pb withdrawal dates correlate to actual geological events is unclear, however, the differences in model dates suggest that the trace MVT occurrences in the FCB, GUMV region, and ILB acquired both their less radiogenic Pb and more radiogenic Pb components from different sources and did not incorporate mixtures of varying proportions of the same two end member Pb components.

The Pb isotope trends for trace MVT occurrences from the FCB, ILB, and GUMV region are for the most part not collinear with the Pb isotope trends of the mid-continent MVT ore districts. The exception is the GUMV region trace occurrences and the UMV ore district, which appear collinear, suggesting that the GUMV trace MVT occurrences and UMV ores acquired their Pb from the same end member sources.

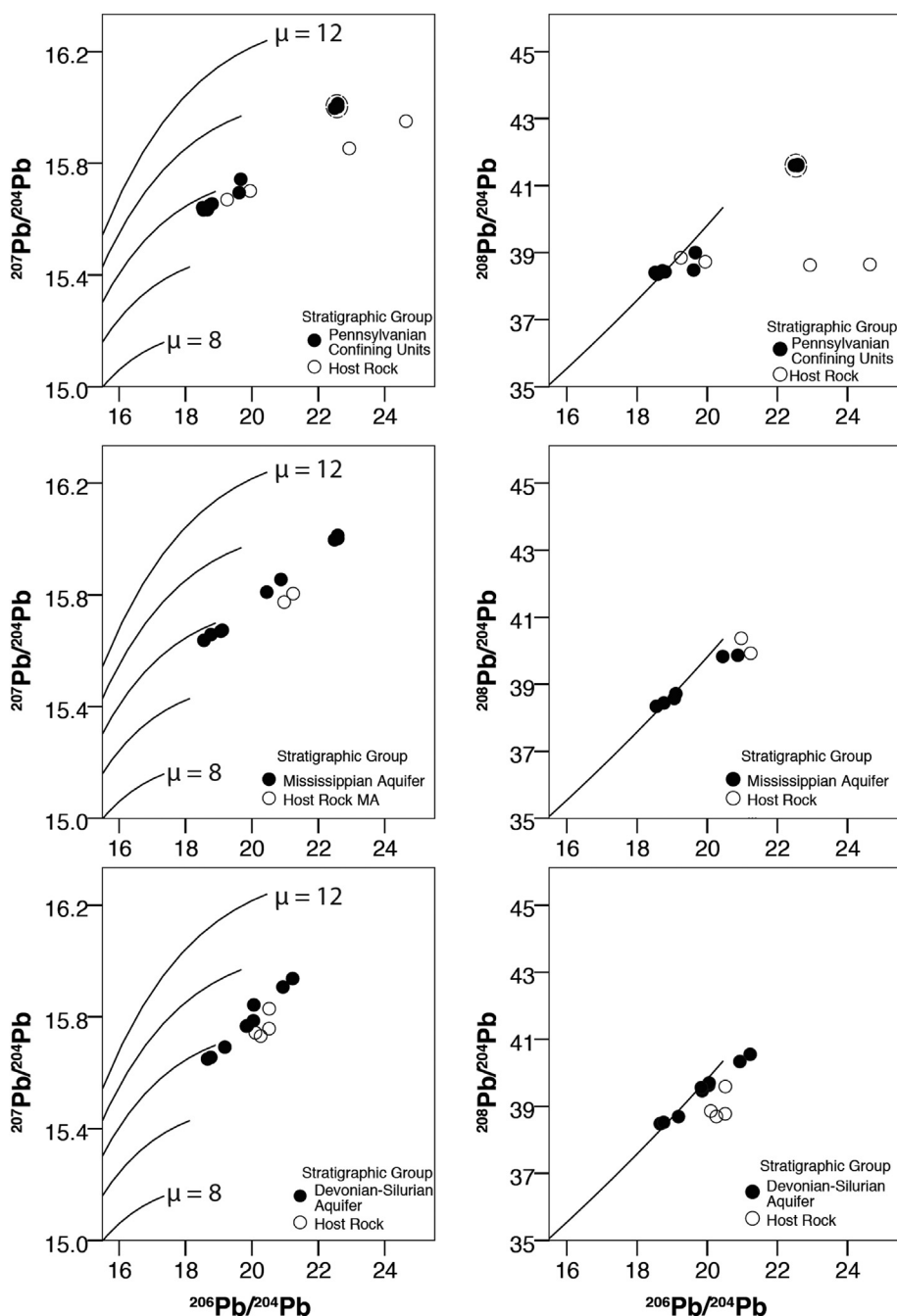


Fig. 6. Trace occurrences grouped by hydrostratigraphic unit rather than by region. The rows show the Pb isotopic compositions of trace occurrences hosted by Pennsylvanian strata, followed by Mississippian, and then Devonian-Silurian stratigraphic units. The left column plots are $^{206}\text{Pb}/^{204}\text{Pb}$ versus $^{207}\text{Pb}/^{204}\text{Pb}$ and the right column plots are $^{206}\text{Pb}/^{204}\text{Pb}$ versus $^{208}\text{Pb}/^{204}\text{Pb}$. Closed symbols are sulfide data, and open symbols are host rock. Circled data points represent samples from mineralization that may be considered “minor” occurrences rather than true trace occurrences.

4.2. Sulfur isotopes

The sulfur isotope compositions of trace MVT occurrences analyzed in the present study are shown in Fig. 10 and in Table 1. The $\delta^{34}\text{S}$ values vary widely, with the total range extending from -26.13 to $+17.26\text{‰}$. However, most of the $\delta^{34}\text{S}$ values are concentrated in a range from about -18 to $+2\text{‰}$, with median values for the FCB, GUMV, and ILB ranges equaling -7.5 , -6.6 , and -12.6‰ , respectively. The $\delta^{34}\text{S}$ values of sulfide minerals in trace MVT occurrences tend to be lower than those of sulfide minerals in the Southeast Missouri, Illinois-Kentucky, Central Kentucky, and UMV ore districts. The ranges of $\delta^{34}\text{S}$ values of trace MVT occurrences encompass those of the Tri-State, Central Missouri, and Central Tennessee districts, which consist of much lower but also much fewer numbers of analyses than the other three MVT ore districts. The sulfur isotope compositions of the trace MVT occurrences are likely a product of incomplete reduction of marine

sulfate reservoirs. This sulfate reduction could have been accomplished by bacteria, particularly for the occurrences with the lowest $\delta^{34}\text{S}$ values, with thermochemical (abiological) sulfate reduction becoming progressively more possible with increasing $\delta^{34}\text{S}$ value of the occurrences (Meshoulam et al., 2016). After its formation from marine sulfate, this reduced sulfur may have been directly incorporated into sphalerite or galena, or may have first temporarily resided in petroleum, coal, or diagenetic pyrite, which all have wide-ranging $\delta^{34}\text{S}$ values (Faure and Mensing, 2009), before being remobilized and incorporated into sphalerite or galena. Among the GUMV trace MVT occurrences, those with positive $\delta^{34}\text{S}$ values are located near the UMV district, which has $\delta^{34}\text{S}$ values ranging from 8.8‰ to 18.1‰ in sphalerite and from 5.4‰ to 13.9‰ in galena (Pinckney and Rafter, 1972; McLimans, 1977). Thus, as previously suggested by Kutz and Spry (1989), the isotopically heavier trace MVT occurrences in the GUMV region are more likely to be genetically related to MVT ore in the UMV

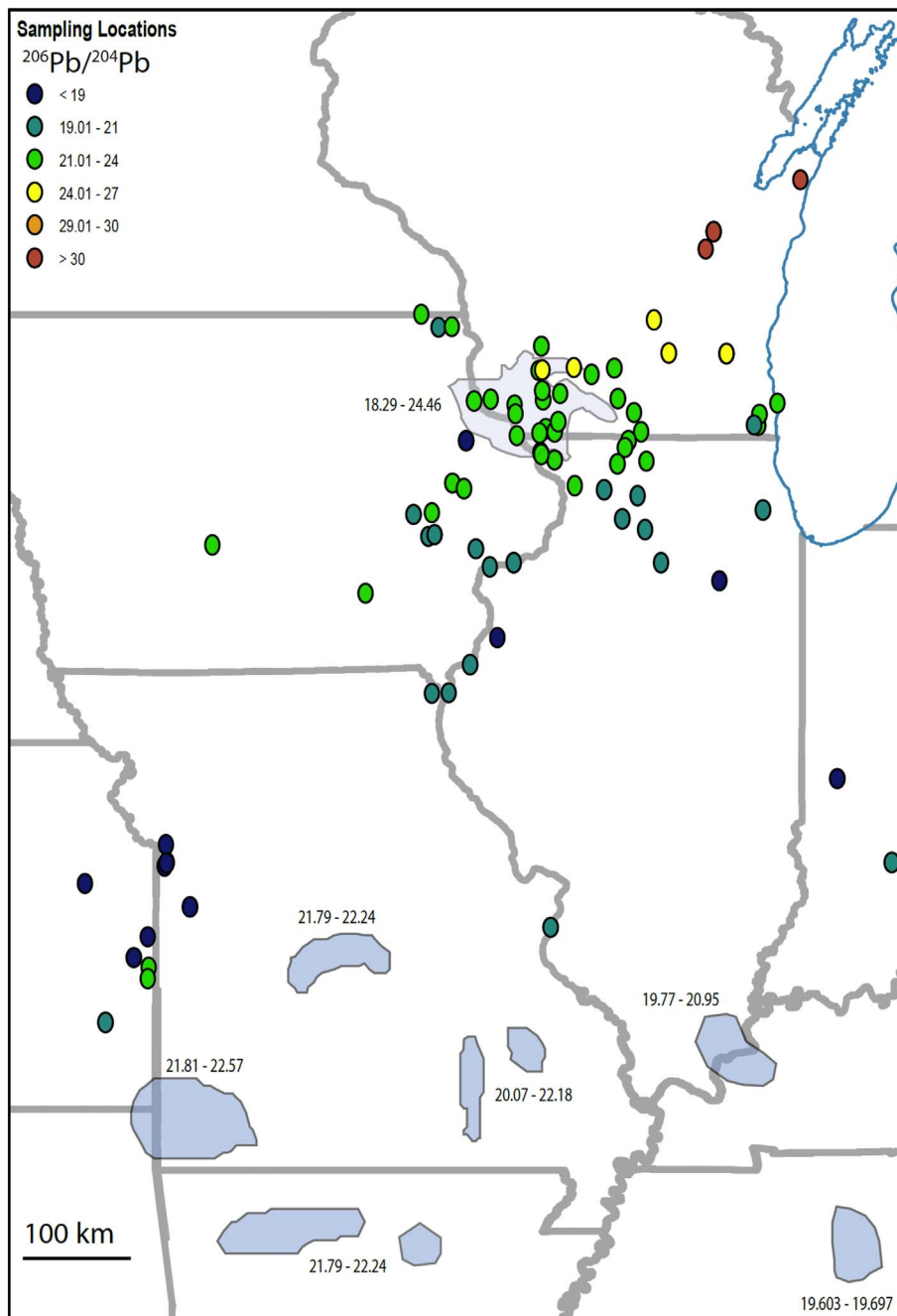


Fig. 7. Map showing the $^{206}\text{Pb}/^{204}\text{Pb}$ ratio of trace MVT occurrences and MVT ore deposits in the U.S. mid-continent. Data are from the present study and from Heyl et al. (1966), Goldhaber et al. (1995), Millen et al. (1995), Luczaj (2000) and Luczaj et al. (2007). Filled circles represent trace MVT occurrences, where the color of the fill is scaled according to $^{206}\text{Pb}/^{204}\text{Pb}$ value (see legend). Gray shaded areas represent MVT ore districts. Numerical ranges next to each district represent the range of published $^{206}\text{Pb}/^{204}\text{Pb}$ values for that district. Data for the Central Missouri and Northern Arkansas districts were obtained from Goldhaber et al. (1995) and were not differentiated by district. Thus, the data ranges for these two districts are identical in the present figure. Ore district data were obtained from Heyl et al. (1966), Hart et al. (1981), Deloule et al. (1986), Goldhaber et al. (1995), Millen et al. (1995), Misra et al. (1997), and Luczaj (2000).

district than the isotopically lighter occurrences, in that the isotopically heavier trace occurrences may have derived their sulfur from the same source as the UMV ore. The range of $\delta^{34}\text{S}$ values for trace MVT occurrences in the FCB encompasses the ranges of limited $\delta^{34}\text{S}$ sulfide values for the two nearest ore districts, the Tri-State and Central Missouri districts, which are -12‰ to -6.3‰ and -5.4‰ to 1.7‰ , respectively (Deloule et al., 1986; Burstein et al., 1993; Goldhaber et al., 1995). However, the $\delta^{34}\text{S}$ values of trace MVT sulfide occurrences in the FCB region, including the Prescott and Jumbo minor occurrences, do not appear to vary systematically with distance from either the Tri-State or Central Missouri districts (Fig. 11), although the existing data are very limited. In the ILB, trace MVT sulfide mineral occurrences analyzed in this study have substantially lower $\delta^{34}\text{S}$ values than sulfide minerals in the surrounding Illinois-Kentucky, Central Kentucky, Southeast Missouri, and UMV districts, and overlap the lowermost end of the range of $\delta^{34}\text{S}$ values for the Central Tennessee district. Thus, trace

MVT occurrences in the ILB do not have a clear genetic relationship to any of the surrounding MVT ore districts with respect to sulfur source. Sulfur and lead isotope compositions of trace MVT sulfide minerals do not correlate well (Fig. 12). Thus, a mineralizing fluid containing Pb of a particular isotopic composition could have encountered sulfide of a variety of isotopic compositions and vice versa. This is in contrast to the Southeast Missouri and Tri-State districts, where Pb and S isotope compositions of sulfide minerals co-vary strongly, suggesting that either mineralization formed from a succession of fluids each carrying isotopically distinct Pb and S together in solution, or that the mineralization formed from mixing of two fluids containing isotopically distinct Pb and S in high enough concentrations such that variable degrees of mixing could have led to recognizably variable Pb and S isotopic compositions in the precipitated sulfide minerals (Sverjensky et al., 1979; Hart et al., 1981; Goldhaber et al., 1995; Appold, 1998).

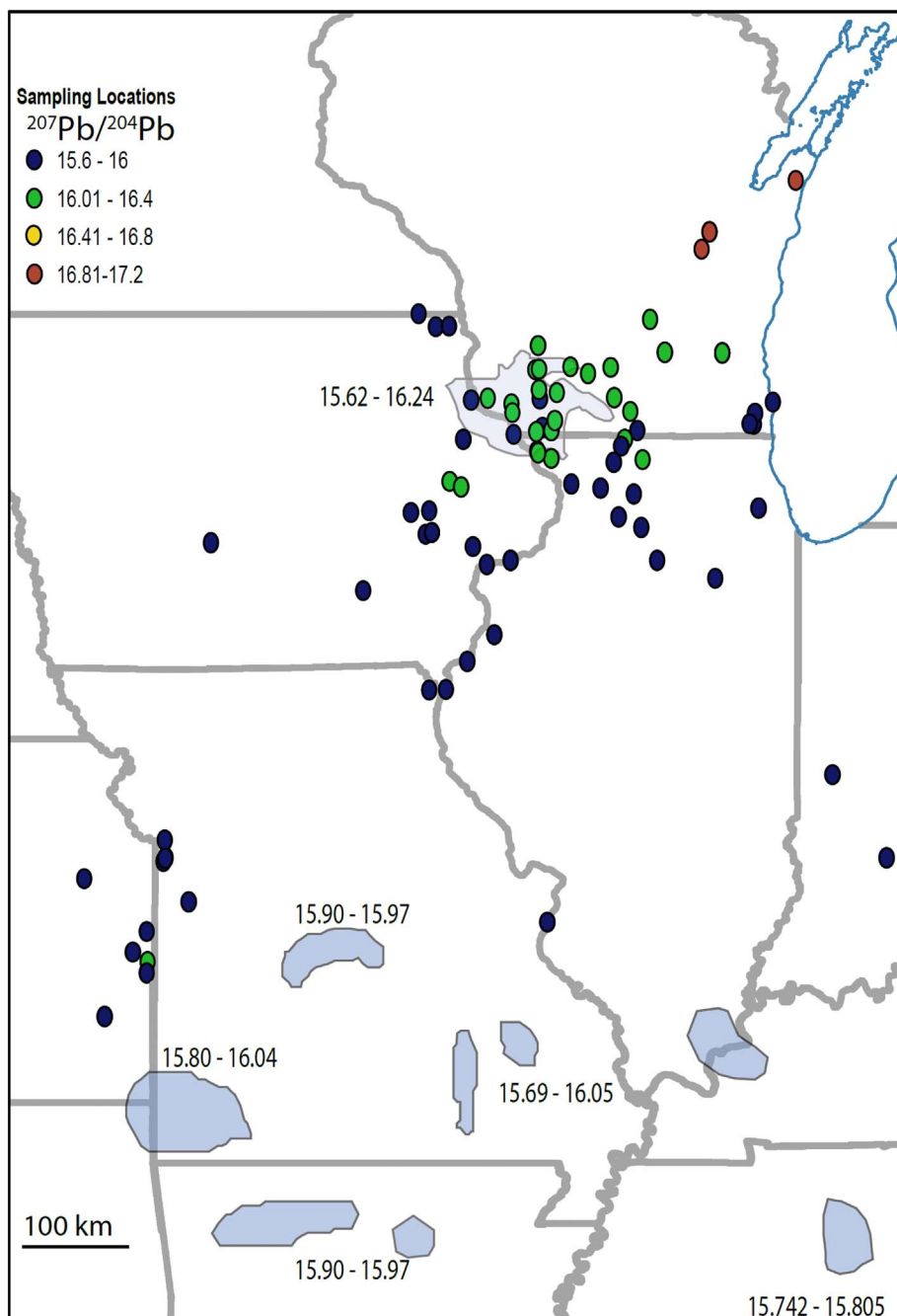


Fig. 8. Map showing the $^{207}\text{Pb}/^{204}\text{Pb}$ ratio of trace MVT occurrences and MVT ore deposits in the U.S. mid-continent. Data sources, symbols, and notation are the same as in Fig. 6.

5. Discussion

If the trace MVT occurrences in the mid-continent formed from the same northward-flowing physical groundwater system as the large MVT ore districts, then they generally do not appear to have formed from strictly the same sources of Pb. Trace MVT Pb isotope compositions from the FCB, ILB, and GUMV region form distinct trends that are not collinear with one another or with the trends defined by most of the major ore districts, thus indicating mixtures of different sources of Pb (Figs. 2–4). The most likely exception is the GUMV trace MVT occurrences and UMV ores, which appear to have collinear Pb isotope trends. Nonetheless, at least one component in each of these Pb mixtures was very radiogenic, consistent with derivation from a U-Th-rich Precambrian granitic basement or basement-derived sediment source, as has been widely previously suggested for the Ozark MVT ore deposits (Heyl et al., 1974; Doe et al., 1983; Deloule et al., 1986; Goldhaber

et al., 1995; Sicree and Barnes, 1999). The Precambrian granitic basement must have been heterogeneous with respect to its U and Th content and Pb isotope composition to account for the different radiogenic Pb end member compositions indicated by the different regional Pb isotope trends. In addition, the amount of radiogenic Pb captured by various occurrences of MVT mineralization varied widely.

All of the mid-continent MVT ore districts have very radiogenic Pb. In the case of the Southeast Missouri district, radiogenic basement Pb could easily have become incorporated into the ores because the ores are hosted by Cambrian rocks that are in close stratigraphic proximity to the Precambrian basement. This may also have been true for trace MVT occurrences near the Southeast Missouri district analyzed by Goldhaber et al. (1995), which have similar Pb isotope compositions to the Southeast Missouri ore. In the UMV district, ore is hosted principally in Ordovician rocks, though significant mineralization also occurs in Cambrian and Silurian rocks (Heyl, 1968), suggesting a strong

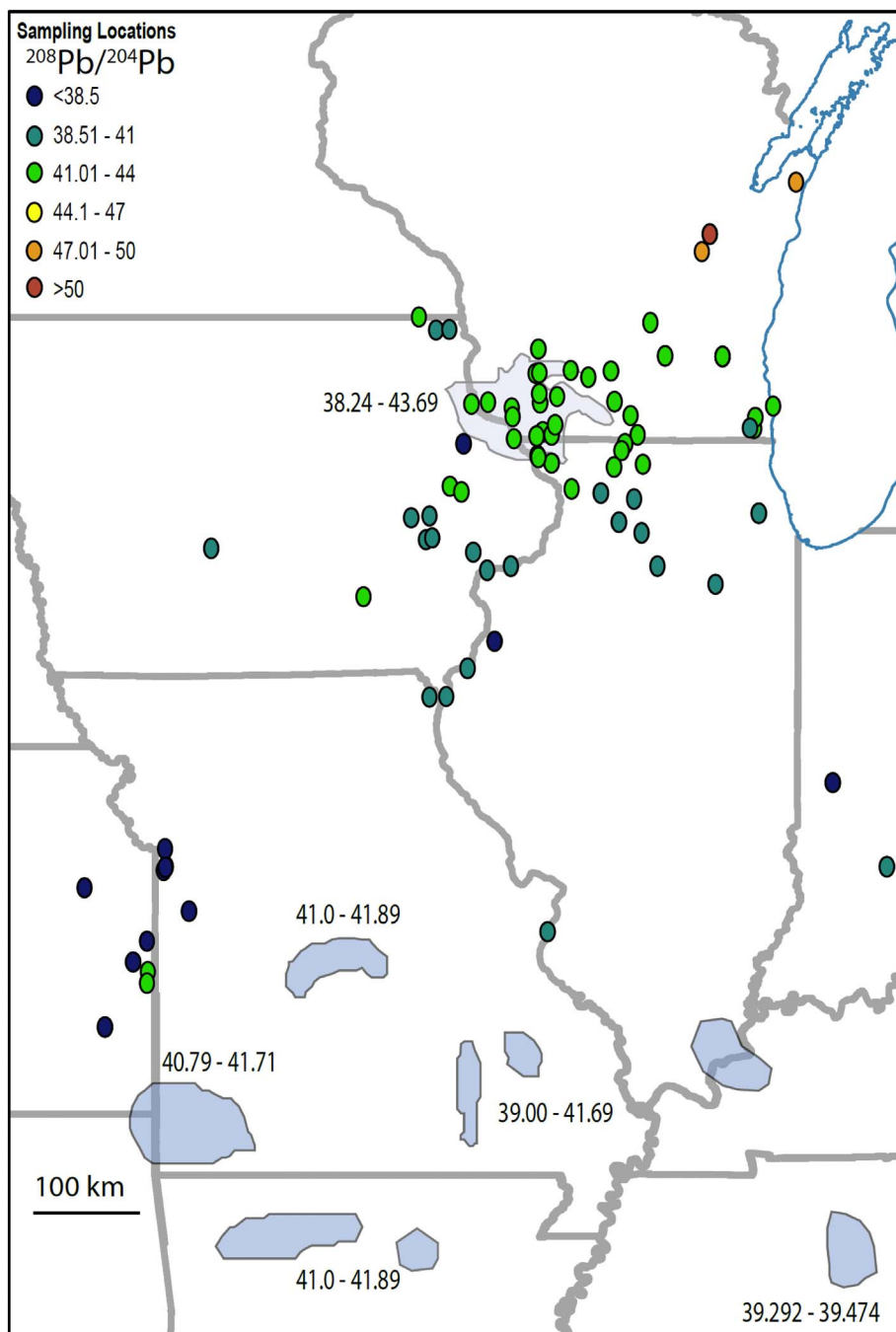


Fig. 9. Map showing the $^{208}\text{Pb}/^{204}\text{Pb}$ ratio of trace MVT occurrences and MVT ore deposits in the U.S. mid-continent. Data sources, symbols, and notation are the same as in Fig. 7.

Table 2

Calculated ages (in years) of withdrawal of the more radiogenic Pb component in hypothetical Pb isotope mixing trends for trace MVT occurrences in the FCB, GUMV, and ILB regions based on the instantaneous and continuous models of Faure and Mensing (2009).

Region	t (instantaneous)	t (continuous)
FCB	8.41E + 08	- 2.42E + 09
GUMV	9.83E + 08	4.15E + 08
ILB	7.94E + 08	- 1.56E + 09

Ages were calculated assuming the standard μ value of 9.735 for the second stage of Pb evolution in the Stacey-Kramers model.

vertical component to the flow of the ore fluids in the district (Arnold et al., 1996) and possible interaction of the ore fluids with Precambrian basement rock. MVT ores in the Northern Arkansas, Central Tennessee,

and Central Missouri districts are also hosted principally by Ordovician rocks, though a small amount of Northern Arkansas mineralization is hosted by Mississippian rocks. As in the UMV district, the wide stratigraphic interval in the Northern Arkansas district over which mineralization occurs and its close proximity to faults suggest a strong vertical component to the flow of the ore fluids and possible interaction with Precambrian basement rock. In the Central Missouri and Central Tennessee districts, conduits for vertical fluid flow that could have connected Precambrian basement rock to MVT ore hosting formations are not as apparent. MVT ores in these districts are associated with solution collapse features, though the distribution of these features may have been guided by faults in Central Tennessee (Misra et al., 1997) and the crests of northwest-trending folds and flexures in Central Missouri (Clark, 1970; Leach, 1980). The Tri-State and Illinois-Kentucky ores are hosted primarily by Mississippian beds. In both districts, mineralization

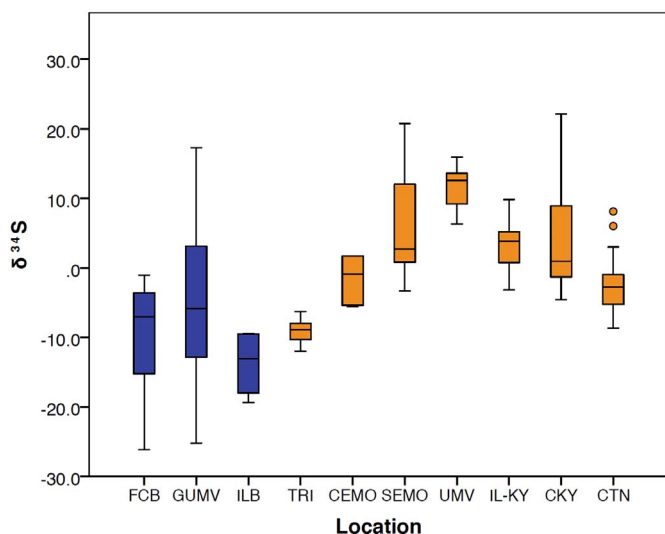


Fig. 10. Boxplot of $\delta^{34}\text{S}$ values of sphalerite and galena from trace MVT occurrences (blue boxes) and MVT ore deposits (orange boxes) in the U.S. mid-continent. Data for the trace MVT occurrences are from the present study (Table 1). Data for the MVT ore deposits are from Ault and Kulp (1960), McLimans (1977), Sverjensky et al. (1979), Deloule et al. (1986), Kesler et al. (1994), and Goldhaber et al. (1995). The upper and lower portions of the boxes represent the 75th and 25th percentile, respectively (interquartile range). The bold horizontal line within each box represents the median of the data. The horizontal lines at the end of each whisker (vertical line extending up or down from the box) represent the highest and lowest values that lie within a factor of 1.5 outside the interquartile range. Open circles that lie beyond the whiskers represent outliers that exceed the interquartile range by a factor of 1.5 to 3. Abbreviations: FCB = Forest City basin, GUMV = Greater Upper Mississippi Valley region, ILB = Illinois basin, TRI = Tri-State district, CEMO = Central Missouri district, SEMO = Southeast Missouri district, UMV = Upper Mississippi Valley district, IL-KY = Illinois-Kentucky district, CKY = Central Kentucky district, CTN = Central Tennessee district. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

is strongly associated with faults, some of which penetrate as deeply as the Precambrian basement (Brockie et al., 1933; Potter et al., 1992) and may have enabled ore fluids to transport radiogenic basement-derived Pb to the much shallower ore-hosting formations.

Trace MVT occurrences in the FCB and ILB generally contain less radiogenic Pb than the mid-continent MVT ore deposits. This suggests that the fluids that formed the trace MVT occurrences there had less interaction with Precambrian basement rocks. Although all of the MVT occurrences in the mid-continent, both trace and ore, may have formed from the same physical groundwater flow system, this flow system may have been stratified according to the hydrogeologic formations present (Garven et al., 1993; Appold and Garven, 1999; Appold and Nunn, 2005), leading to corresponding stratification in Pb isotope composition. Thus, fluids that flowed through or along the Precambrian basement would have acquired much more radiogenic Pb than the fluids that flowed through the younger overlying hydrogeologic formations. As suggested by Fig. 5, however, the isotopic composition of Pb in fluids in this stratified flow system need not necessarily have varied monotonically with depth (i.e. stratigraphic age of the host rock). In particular, Pb isotope ratios do not decrease monotonically with decreasing depth (i.e. decreasing stratigraphic age of the host rock). This is because the age and composition of the source rocks from which the host rock sediments were derived may not have correlated with the age of the host rock sediments themselves, through which fluid was flowing and leaching Pb. The fluid and Pb isotope stratification would have been perturbed in discharge zones and vertical structures that would have promoted cross-formational flow and mixing. Judging from their less radiogenic Pb isotope compositions, the trace MVT occurrences in the FCB and ILB analyzed in the present study appear to be products of lesser degrees of cross-formational flow delivering radiogenic Pb from the Precambrian basement compared to their ore deposit counterparts.

However, enough cross-formational fluid flow must have occurred at the trace MVT occurrences to prevent their having acquired the Pb isotope signature of their host rocks. The difference in radiogenic character between ore and trace occurrences could possibly be a useful exploration guide for MVT ore deposits in the FCB and ILB (Cannon and Pierce, 1969; Angino et al., 1971).

A high vertical fluid flux delivering radiogenic Pb from the Precambrian basement may account for the highly radiogenic Pb isotope compositions of the Jumbo and Prescott deposits (Fig. 2), minor and briefly commercial MVT occurrences that are located near trace MVT occurrences that have much less radiogenic Pb. Evidence for the existence of vertical structures connecting the basement to MVT mineralization in the Jumbo and Prescott deposits has not been clearly established, though MVT mineralization in the Jumbo deposit occurs in a breccia pipe that extends to a depth of at least 100 m (Blasch and Coveny, 1988).

The ores of the UMV district have the most variable Pb isotope compositions of the mid-continent MVT ore districts, including values that are more radiogenic and others that are less radiogenic than found in any of the other ore districts. On average, though, the UMV ores contain Pb that is more radiogenic than Pb in the other mid-continent MVT ore districts. Trace MVT occurrences in the GUMV region mirror the Pb isotope patterns in the UMV district in that they vary over a wider range than in trace occurrences from the ILB and FCB and on average are more radiogenic. MVT occurrences in the UMV district and surrounding GUMV region also show a clear gradient in Pb isotope composition in which radiogenic character increases from the south to the northeast (Figs. 7–9). Luczaj (2000) interpreted this pattern to record the intersection of two temporally unrelated regional groundwater flow systems. The first groundwater system flowed from the northeast, possibly out of the Michigan basin, and carried highly radiogenic Pb that it had leached from basement, which became diluted by less radiogenic Pb as the groundwater flowed southwestward. Luczaj (2000) believed this flow system to have been active during the Devonian to Early Mississippian, based on authigenic K-feldspar of this age in the GUMV region (Hay et al., 1988; Matthews, 1988; Girard and Barnes, 1995; Liu et al., 1995; Liu, 1997) containing highly radiogenic Pb. The second groundwater system flowed from the south and carried less radiogenic Pb. Luczaj (2000) believed this flow system to have been active during the Permian based on a subset of Permian authigenic K-feldspar in the GUMV region (Hay et al., 1988) and a Permian date for the UMV ore (Brannon et al., 1992; Pannalal et al., 2004). Thus, the trace MVT occurrences containing less radiogenic Pb in the southern GUMV region would have formed from the same physical groundwater flow system that formed MVT mineralization in the FCB, ILB, and Ozark Plateau. The fact that the UMV ore also has highly radiogenic Pb compared to MVT occurrences further south suggests that the groundwater system flowing toward it from the northeast may also have been activated during the Permian, rather than during the Devonian-Mississippian. If so, groundwater flow must have been set in motion by some mechanism other than the topographic uplift associated with the Alleghanian-Ouachita orogeny.

The sulfur isotope compositions of trace MVT occurrences largely overlap those of MVT ore deposits in the mid-continent, though the trace MVT occurrences tend to have lower $\delta^{34}\text{S}$ values. Also, many of the trace MVT occurrences have lower $\delta^{34}\text{S}$ values than the minimum value reached by the MVT ore deposits. Low $\delta^{34}\text{S}$ values in sulfide minerals may indicate incomplete reduction of a seawater sulfate source to sulfide, and the more complete the reduction of sulfate, the higher the $\delta^{34}\text{S}$ of the resultant sulfide. Thus, low $\delta^{34}\text{S}$ values in trace MVT occurrences may indicate low local availability of aqueous sulfide for sulfide mineral precipitation, which limited the trace occurrences' growth. However, the relationship between $\delta^{34}\text{S}$ value and size of MVT occurrence is not consistent. Large sources of isotopically light sulfur are potentially available from abundant organic matter in MVT ore deposits, such as in the Tri-State and Central Tennessee districts.

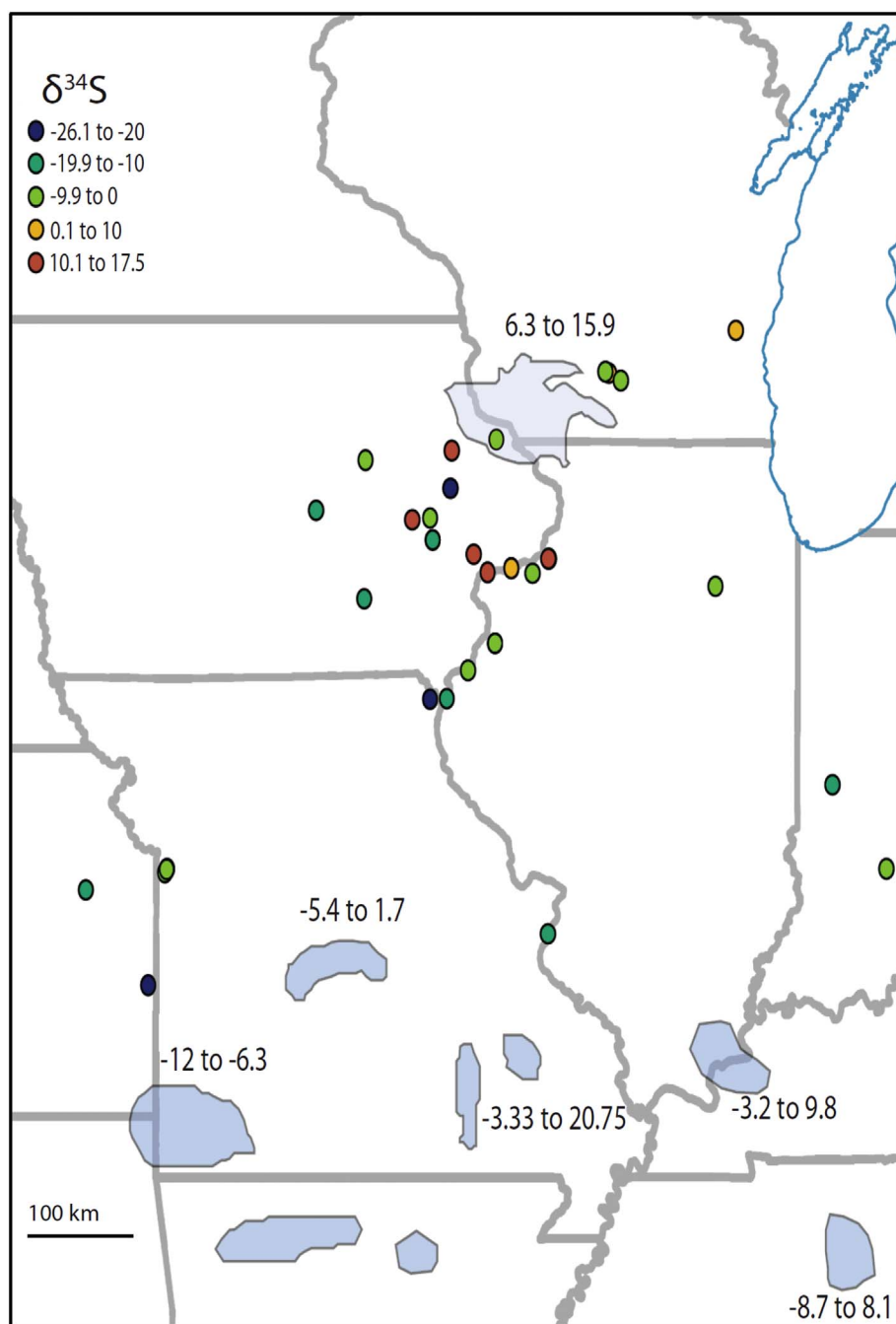


Fig. 11. Map showing $\delta^{34}\text{S}$ values of trace MVT occurrences (filled circles) and MVT ore deposits (gray regions) in the U.S. mid-continent. Data for trace MVT occurrences are from the present study (Table 1) and from Kutz and Spry (1989) and Luczaj (2000). The color of the filled circles is scaled according to $\delta^{34}\text{S}$ value (see legend). The $\delta^{34}\text{S}$ ranges shown for each ore district were obtained from Ault and Kulp (1960), McLimans (1977), Sverjensky et al. (1979), Deloule et al. (1986), Kesler et al. (1994), and Goldhaber et al. (1995). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Conversely, small reservoirs of seawater sulfate can potentially be completely reduced to sulfide, leading to small MVT occurrences that have isotopically heavy sulfur.

6. Conclusions

Trace MVT occurrences in the U.S. mid-continent contain radiogenic Pb that forms distinct linear trends within the three geographic regions defined in the present study, the Forest City basin (FCB), the Illinois basin (ILB), and the Greater Upper Mississippi Valley (GUMV) region. Though the trends have generally similar orientations, they are not strictly collinear with one another or with trace MVT occurrences in northeastern Wisconsin studied by Luczaj (2000) and Luczaj et al. (2007), indicating that trace MVT occurrences in each of these geographic regions acquired their Pb from different pairs of end member sources. Trace MVT occurrences from the FCB, ILB, and GUMV region

form Pb isotope trends that are also generally distinct from the mid-continent MVT ore districts. An exception is the GUMV trace MVT occurrences and UMV ore district, which appear to have collinear Pb isotope trends. Although their Pb isotope trends are not collinear, the highly radiogenic character of the trace MVT occurrences in the mid-continent likely indicates a high degree of derivation from the Precambrian granitic basement with little if any derivation from the sedimentary rocks that host the trace MVT occurrences. The efficiency with which radiogenic Pb was transported vertically from the basement must have been highly variable, based on the lack of correlation of Pb isotope composition with age of host rock of mineralization. The Pb isotope composition of the basement across the mid-continent must also have been heterogeneous to account for the different Pb isotope trends observed. The Pb isotope compositions found for trace MVT occurrences in the present study fit the previously observed trend of decreasing radiogenic character from northeast to south and southwest.

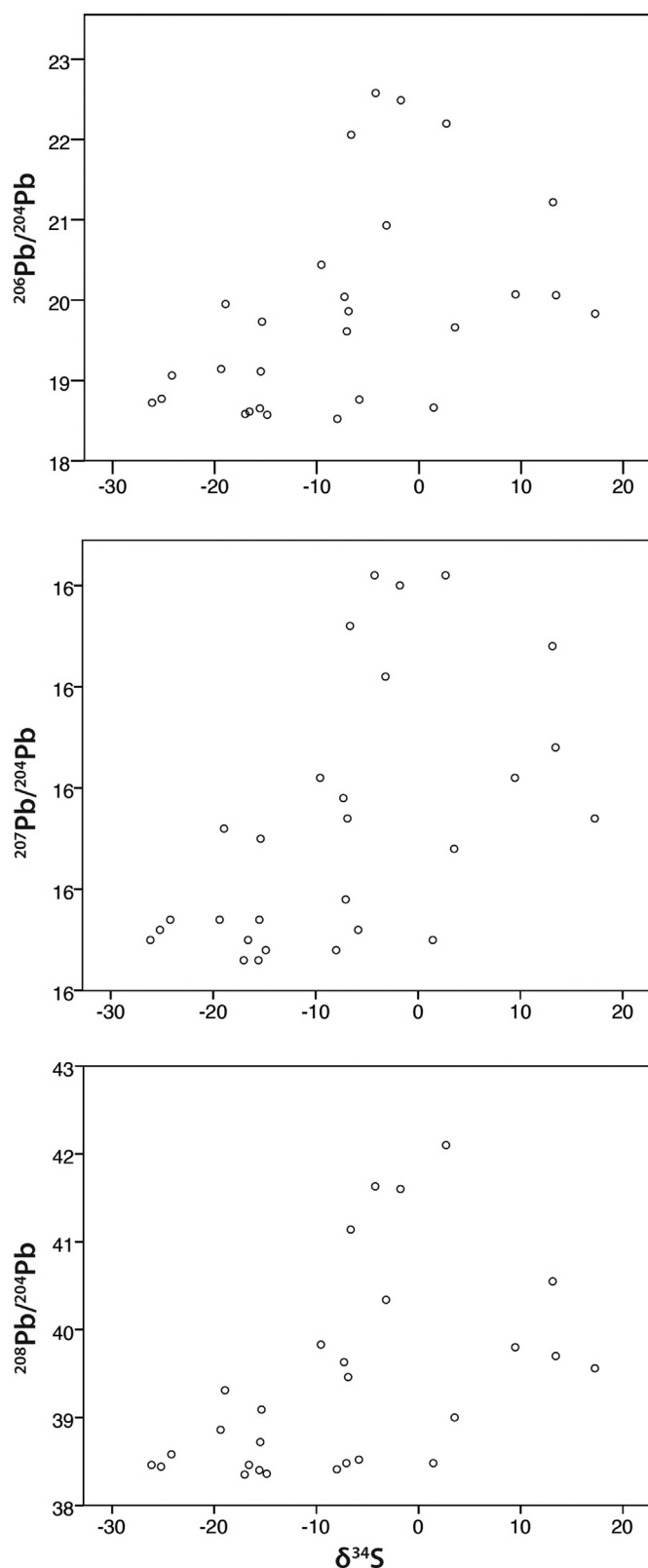


Fig. 12. Lead isotope ratio (A) $^{206}\text{Pb}/^{204}\text{Pb}$, (B) $^{207}\text{Pb}/^{204}\text{Pb}$, (C) $^{208}\text{Pb}/^{204}\text{Pb}$ plotted versus $\delta^{34}\text{S}$ value for trace MVT occurrences in the U.S. mid-continent analyzed in the present study.

The S isotope compositions of trace MVT occurrences are generally light compared to mid-continent MVT ore deposits. This suggests that the S in trace MVT occurrences was derived from the incomplete reduction of seawater sulfate reservoirs or from organic matter. Sulfur

and Pb isotope composition do not correlate well in trace MVT occurrences, suggesting that Pb and S were not transported together within the same fluid(s) to the sites of trace MVT mineralization.

The results of the present study suggest that if trace MVT occurrences and MVT ore deposits in the U.S. mid-continent were precipitated from the same regional physical groundwater flow system, then they must have formed from heterogeneous sources of Pb. However, the Pb was probably largely derived from the Precambrian igneous basement diluted to varying degrees by less radiogenic Pb, and from sources of sulfur that were isotopically lighter than seawater sulfate.

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