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Lead-isotopic characteristics of the Cracow-Silesia Zn-Pb ores, southern Poland

By

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Abstract

New lead-isotope analyses of a suite of samples of ore collected from a paragenetic sequence in the Cracow-Silesia MVT district show no lead-isotopic variation in carbonate-hosted ores and are in agreement with lead-isotopic results from previous work by Zartman *et al.* (1979). Two well-studied MVT districts in the world show uniform lead-isotopic compositions, the Cracow-Silesia and the Pine Point districts. The lead-isotopic data require that the saline hydrothermal fluids which formed these deposits be prevented from circulation through crystalline basement rocks. This requirement is met in both the Cracow-Silesia and Pine Point districts because thick sequences of Devonian shale and carbonate rocks containing shale aquacludes separate the aquifers from the basement in both basins.

We postulate two sources of lead which might account for such uniform lead-isotopic signatures. Hypothesis one would require that the ore lead is bound in iron-oxide phases in multicycle molasse sedimentary rocks. In this case, leaching of ore lead must have occurred shortly after deposition to prevent measurable contributions of radiogenic lead which would form because of radiogenic decay of uranium and thorium in the silicate components of the sediments, and which, upon leaching by the hydrothermal fluids, would result in a radiogenic lead-isotope array such as seen in most other MVT deposits. The time span between deposition and leaching would be limited by the mass balance between lead in the iron-oxide phases and the radiogenic lead in the silicate components. This hypothesis is supported by the lead-isotopic data from the Kozieglowy mine. Hypothesis two calls for leaching of lead from evaporite sequences in the Upper Silesia Basin. Concentrations of lead from the evaporite sequence in the Western Canada sedimentary basin average nearly 1 ppm in halite and 10 ppm in anhydrite (Thiede and Cameron, 1978). Dissolution of the evaporite sequences in the Upper Silesia Basin by meteoric recharge in the Pre-Carpathian Mountains would produce the necessary hydrodynamic fluid flow producing the highly saline brines currently present in the Upper Silesia Basin. Mixing of these saline brines with sulfur-rich waters would cause precipitation of the ores. Lead in the evaporites would be uniform in composition because it was homogenized in solution and precipitated along with the evaporites. Furthermore, lead would be decoupled from uranium and thorium so there would be no radiogenic growth of lead in the source rocks. Under these conditions, the 230 Ma model age of the lead in the Silesia-Cracow ores would reflect the age of the source rocks and provide <u>no</u> constraints on the time of formation of the ore deposits themselves, but does constrain the age of the source of lead. Further research is proposed to test these two hypotheses.

Introduction

This progress report of recent lead-isotopic studies of Mississippi Valley-type (MVT) deposits from the Cracow-Silesia district summarizes the constraints placed on the origin of these deposits. Leach and Viets (1992) have summarized the ore-deposit geology, paragenetic studies, and observations on the formation of the Cracow-Silesia ores, and have compared the basic features of the Cracow-Silesia district with various MVT districts throughout North America. Zartman *et al.* (1979) summarized previous lead-isotopic work in the Cracow-Silesia district and demonstrated, from a suite of ore samples collected throughout the Cracow-Silesia district, that the isotopic composition of lead in the deposits is uniform within analytical error. In the present study, we have analyzed the lead-isotopic composition of a suite of samples collected from several of the same deposits. However, this suite of samples was selected to evaluate the range of lead-isotopic variation throughout the paragenetic sequence of the Cracow-Silesia district.

Lead isotopes in MVT districts throughout the world give two basic types of lead-isotopic results: the classic MVT deposits in the central U.S. have highly variable and radiogenic lead-isotope compositions, and many form linear lead-isotope arrays. In contrast, the lead-isotopic data from the Cracow-Silesia and the Pine Point districts have uniform lead-isotopic compositions. In the Cracow-Silesia and Pine Point districts, molasse or evaporite sedimentary rocks may have been the source of the metals which formed the uniform lead-isotopic composition of the ore lead. By comparing the lead-isotopic data from the Cracow-Silesia district with other MVT and carbonate-hosted Zn-Pb deposits both within Europe and North America, we can provide some constraints on the source of the metals, suggest some restrictions on the hydrothermal flow regime, and provide limits on the time of formation of the ores in the Cracow-Silesia district.

Lead-isotopic data

Results from the previous work of Zartman *et al.* (1979) and the work of Ridge and Smolarska (1972) from the Cracow-Silesia district and from polymetallic veins from the Upper Silesia Basin are in table 1; results from our studies of ores from the Cracow-Silesia district are in table 2. Our results for carbonate-hosted ores (fig. 1) agree with the previous work summarized by Zartman *et al.* (1979). Both suites of lead-isotopic data give nearly identical results within analytical error. We conclude that there is no variation in lead-isotopic composition of the carbonate-hosted ores in the Cracow-Silesia district throughout the paragenetic sequence represented by this suite of samples. However, two samples from the Kozieglowy mine, one hosted by the Buntsandstein, have analytically distinct lead-isotopic compositions.

Our lead-isotopic data (table 2) were determined on small pieces of galena ore selected on the basis of the paragenetic sequence (Leach and Viets, 1992). About 3 mg of galena powder were sampled by scratching a tungsten-carbide tipped scribbing tool across the galena grain surfaces. These powders were transferred into 15 mL polypropylene test tubes and one mL of concentrated high-purity HNO_3 acid was added to the sample. The solutions were heated to 80°C in a water bath for 30 minutes. These solutions were diluted to 15 mL with ultrapure water and an aliquot taken for lead concentration analysis. The solutions were diluted to a concentration of 500 μg/mL and a 5 μg aliquot was evaporated to dryness in a clean 10 mL teflon beaker in a laminar-flow fume hood. All analyses were made using 2 μg of lead loaded on a single rhenium-filament using the silica gel method (e.g., Church and Tatsumoto, 1975). Analyses were done at 1250°C; replicate sets of data were taken within individual runs. Twenty-nine replicate analyses of the NBS lead standard SRM 981 have been made over the last 9 months. Within-run precision is better than 0.05 percent per mass unit, but reproducibility is limited to 0.05 percent per mass unit on the basis of replicate runs of SRM 981 as well as replicate analyses of samples from this study.

Table 1. Previously published lead-isotope data from Cracow-Silesia district, southern Poland#

Locality	$\frac{^{206}Pb}{^{204}Pb}$	$\frac{^{207}Pb}{^{204}Pb}$	$\frac{^{208}Pb}{^{204}Pb}$	Age of of Host
Cracow-Silesia district				
Boleslaw mine	18.422	15.609	38.412	Triassic
Chechlo mine	18.419	15.625	38.424	Devonian
Chorzow mine	18.444	15.619	38.418	Carboniferous
Marchlewski mine	18.406	15.599	38.410	Triassic
Matylda mine	18.423	15.613	38.424	Triassic
Nowy Dwor mine	18.438	15.615	38.434	Triassic
Olkusz mine	18.422	15.623	38.426	Triassic
Trzebionka mine	18.425	15.611	38.426	Triassic
Warynski mine	18.412	15.619	38.412	Triassic
Wiktor-Emanuel mine	18.415	15.627	38.421	Triassic
Expl DH ZNG-5	18.427	15.634	38.434	Triassic
Expl DH 72	18.412	15.633	38.419	Triassic
Average value	**18.422**	**15.619**	**38.422**	
Upper Silesia Basin				
Jastrzebie mine	18.289	15.617	38.291	Carboniferous
Expl. Hole 261 TN	18.331	15.628	38.372	Silurian

Data from Zartman *et al.* (table 2, 1979).

Table 2. New lead-isotope data for samples from the Cracow-Silesia District, southern Poland [#]

Locality	^{206}Pb/^{204}Pb	^{207}Pb/^{204}Pb	^{208}Pb/^{204}Pb	Lithology of Host	Formation	Age[§] of Host	Min. Form	Bore Hole (depth m)
Upper Silesia region								
Klucze prospect								
KLU-G1	18.410	15.621	38.393	dolostone	Muschelkalk-Olkusz Beds	mTr	gn	BK-290 (13m)
KLU-G7	18.434	15.634	38.424	dolostone	Muschelkalk-Gogolin Beds	Tr	oct. gn	BK-75 (101m)
KLU-G10	18.388	15.593	38.324	ss-dolomite	Rott	eTr	oct. gn	BK-288 (25m)
	18.401	15.599	38.326					
	18.413	15.611	38.386[*]					
KLU-G11	18.412	15.623	38.394	dolostone		eP	oct. gn	BK-286 (31m)
KLU-G12	18.413	15.615	38.373	dolostone		eP	oct. gn	BK-287 (35m)
KLU-G13	18.426	15.632	38.419	limestone		lD	oct. gn	BK-287 (136m)
KLU-G14	18.417	15.622	38.394	limestone		lD	oct. gn	BK-75 (129m)
KLU-G15	18.411	15.625	38.402	limestone		lD	gn	BK-288 (43m)
KLU-G54	18.427	15.633	38.433	limestone		lD	gn	BK-288 (69m)
Kozieglowy mine								
KOZ-2	18.351	15.625	38.340			eCarb	gn	
KOZ-72	18.379	15.620	38.348	sandstone	Buntsandstein	eTr	gn	
Olkusz mine								
OLK-91A	18.447	15.652	38.482	dolostone	Muschelkalk-Olkusz Beds	mTr	gn	
	18.399	15.602	38.327					
Average	18.423	15.627	38.405[*]					
Pomoreany mine								
POM 89-2X	18.392	15.593	38.299	dolostone	Muschelkalk	Tr	gn	
	18.400	15.604	38.337					
	18.404	15.606	38.345[*]					
POM 91-105	18.405	15.603	38.349[*]	dolostone	Muschelkalk-Gogolin Beds	Tr	cubic gn	
	18.392	15.590	38.301					
Trzebionka mine								
TRZ-89-13	18.441	15.631	38.476	dolostone	Muschelkalk	mTr	oct. gn	
	18.413	15.599	38.353					
	18.448	15.640	38.500					
	18.391	15.638	38.400					
	18.382	15.618	38.342					
Average	18.415	15.625	38.414[*]					
Warynski mine								
WAR-91A	18.416	15.616	38.410	dolostone	Muschelkalk	Tr	gn	
Zarkie region								
ZAR-53/1	18.414	15.616	38.350	ss-dolomite	Rott	eTr	cubic gn	
	18.416	15.625	38.372[*]					
Average value[+]	18.416	15.621	38.393					

[#] All analyses run using 2μg Pb on single Re-filament using silica gel-phosphoric acid emitter technique at 1250°C. Analyses done on an NBS 30.5 cm radius, 60° sector, solid-source mass spectrometer. All data are normalized to the value obtained for the NBS Pb-isotope standard SRM 981 (raw data: ^{206}Pb/^{204}Pb = 16.925, ^{207}Pb/^{204}Pb = 15.471, ^{208}Pb/^{204}Pb = 36.634; mean of 29 analyses run over a 9 month period; correction factor 1.005/mass unit).

[§] Age abbreviations: eTr, mTr, Early and Middle Triassic; eP, Early Permian; lD, Late Devonian; eCarb, Early Carboniferous.

[*] Replicate analyses were run on several outlier samples; the asterisk indicates the value used (replicate analysis) in plots.

[+] Average value does not include results from two samples from the Kozieglowy mine.

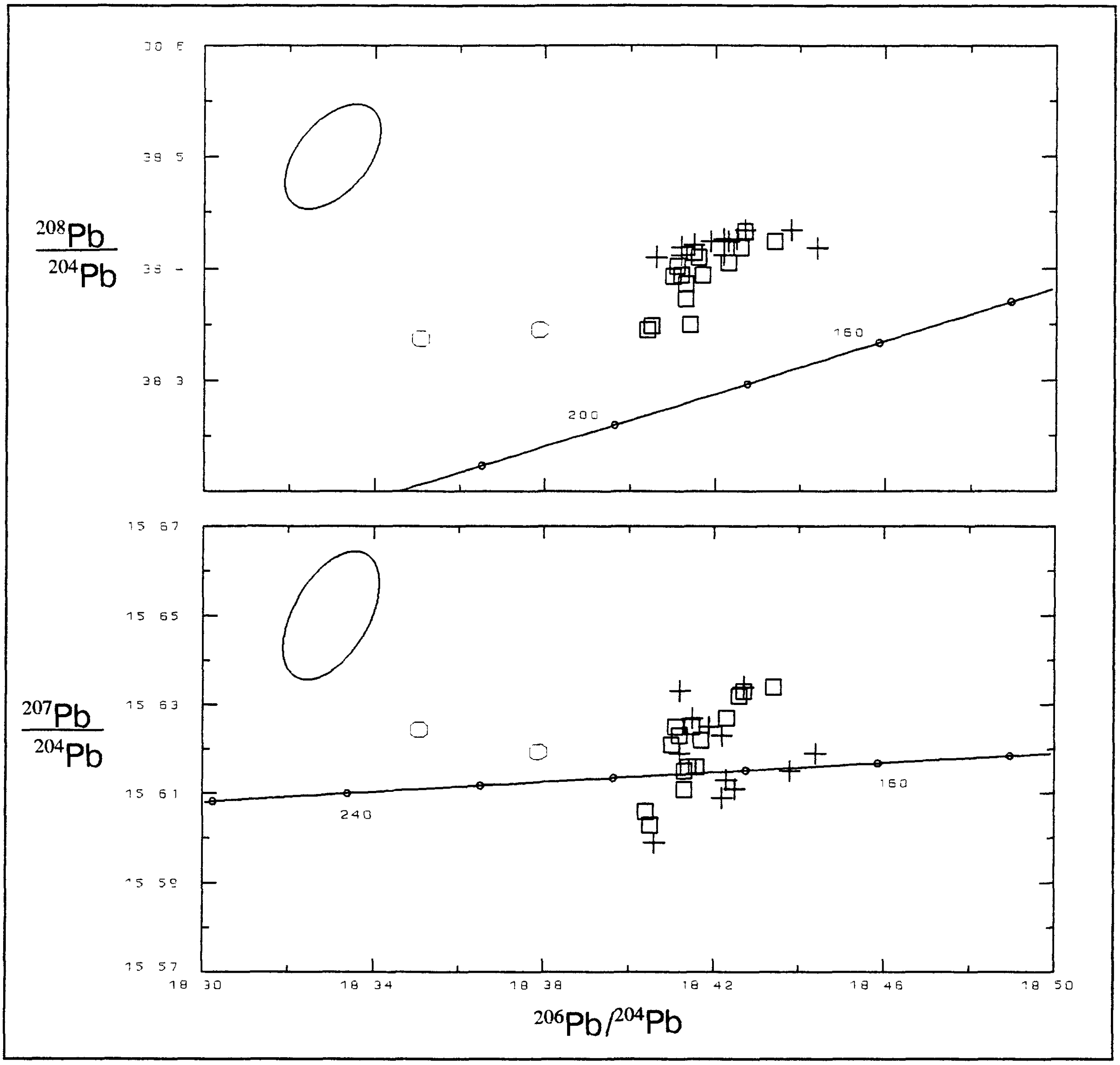

Figure 1. Lead-isotope diagram showing analyses from the Cracow-Silesia district (+, data from Zartman *et al.*, 1979; □, data from carbonate-hosted ores, table 2; ○, data from Kozieglowy mine, table 2). The Stacey-Kramers lead-isotope growth curve is shown for reference (μ = 9.74 and K = 3.8); the numbers are the model ages (in millions of years) for labeled points on the Stacey-Kramers growth curves; model ages are from the uncalibrated Stacey-Kramers growth curve. An error ellipse (0.05 percent) is shown in the upper left corner of each diagram.

Comparison of the lead-isotopic data from the Cracow-Silesian deposits with other carbonate-hosted deposits in Europe

The regional geologic setting of the Cracow-Silesia area is complex. However, the discussion of the basement geology and the development of the three different geologic provinces by Zartman *et al.* (1979) is sufficient for the purposes of this paper. To briefly summarize, three geologic provinces converge in southern Poland: 1) the Precambrian East-European Platform, 2) the Variscan Paleozoic orogenic terrane of central Europe, and 3) the Mesozoic and Cenozoic Alpine fold-and-thrust belt predominately located in southern Europe. Each of these areas contain carbonate-hosted Zn-Pb deposits having differing lead-isotopic characteristics.

In describing the evolution of lead and comparing lead-isotope data from diverse sources, such as rocks, ores, and sediments, we commonly use lead-isotope evolution models. These models are mathematical models which simulate the growth of lead in various lead-isotope reservoirs. In favorable cases, it is possible to date the time of formation of ore deposits using such models. In all figures, we have plotted the Stacey-Kramers model curve as a convenient frame of reference (Stacey and Kramers, 1979). Modern lead, according to the model, would have evolved in a homogeneous, closed system through time, and ore samples from this reservoir would plot along this growth curve. Model ages could then be determined by the position of the sample on these curves, and if the mathematical model were applicable, the geologic age and the model age of the deposit would agree. However, since the earth is a dynamic rather than a static body, mixing between various reservoirs for lead in the upper crust, the lower crust, and the mantle, caused by both tectonic and magmatic processes, results in a very complex process of lead-isotopic evolution. Our mathematical models are, by comparison, simple, and are only an approximation of the real dynamic process. For example, Doe and Zartman (1979) demonstrated that various portions of the crust and mantle have behaved very differently over the evolutionary history of the earth. Zartman *et al.* (1979) showed that the lead-isotopic data from the Cracow-Silesia district plotted very near the orogene curve which represents the average composition of lead in the tectonically-active upper crust. They also showed that lead from the Cracow-Silesia district cannot contain major contributions from either lower crustal or mantle rocks because both of those reservoirs contain lead of very different isotopic character.

In order to use the lead-isotopic growth curve to obtain model ages for deposits within the upper crust, one must first find a method to calibrate the growth curve for the local depositional basin (for example see Godwin and Sinclair, 1982; Godwin *et al.*, 1982; Church *et al.*, 1987). This calibration can best be achieved by using the lead-isotopic composition from independently dated syngenetic deposits which have been formed by hydrothermal circulation processes in the crust and calculating a growth curve which matches that lead-isotopic composition. Sedimentary exhalitive deposits (SEDEX) and Kuroko-volcanogenic massive sulfide deposits (K-VMS) are the most desirable deposit types for this exercise because the stratigraphy is usually adequately enough known to allow determination of a geologic age of the deposits. Deposits of both types are formed by large-scale hydrothermal circulation processes that provide an adequate sampling of the earth's crust in a sedimentary basin to provide a tie point on the local lead-isotope growth curve.

Klau and Mostler (1986) summarize the distribution of several major carbonate-hosted Zn-Pb deposits in central Europe. Lead-isotopic studies of carbonate-hosted Zn-Pb deposits in the

Alpine fold-and-thrust belt have been carried out by Köppel and Schroll (1983, 1985, 1988). Lead-isotopic studies of carbonate-hosted SEDEX Zn-Pb deposits in Ireland in the Paleozoic orogenic terrane of central Europe have been carried out by LeHuray *et al.* (1987). Lead-isotopic studies of carbonate Zn-Pb deposits in the Precambrian Eastern European and Baltic shield areas have been done, but will not be discussed in detail here. Fundamental differences in the lead-isotopic character of these deposits are shown in figure 2. Lead-isotopic data from deposits hosted in carbonate rocks in the Southern and Eastern Alps are generally characterized by higher values of μ ($^{238}U/^{204}Pb$) and K ($^{232}Th/^{238}U$) than are deposits from the Pennine, Northern Alps, or the Cracow-Silesia district (Köppel and Schroll, 1983). However, lead from the Plakalnitsa MVT deposit in Bulgaria lies on a lower set of μ and K curves (Zartman *et al.*, 1979). Similarly, some ore leads from deposits from southern Germany (Wedepohl *et al.*, 1978; Kober and Lippolt, 1985; Lippolt *et al.*, 1983; Höhndorf and Dill, 1986) generally lie within the lower lead-isotope field characteristic of the Variscan orogenic belt of central Europe. Deposits in rocks north of this zone (Kober and Lippolt, 1985; Lippolt *et al.*, 1983; Höhndorf and Dill, 1986) plot above this growth curve and reflect the Precambrian rocks of the Eastern European Platform. Lead from the carbonate-hosted (MVT?) occurrences in the Keuper Limestone in southwest Germany, (Lippolt *et al.*, 1983) also plot above this growth curve near the upper end of the 1700 Ma-250 Ma secondary isochron formed by the lead-isotope data from the Kupferschiefer (Wedepohl et al., 1978) and may reflect a lead-source from the evaporites in the Zechstein of southern Germany.

Calibration of the local upper crustal lead-isotope growth curves have been attempted in the Southern and Eastern Alps. Köppel and Schroll (1983) reported lead-isotopic data from the Lower Devonian VMS deposits of Graz in Austria and they calculated a lead-isotope evolution model in which the growth curves would intersect the lead-isotope data from these deposits at 390 Ma. Using this calibration point, the MVT deposits hosted in the Triassic rocks of the Southern Alps, which Köppel and Schroll (1985) call the Bleiberg-type lead, have model ages of about 100 Ma (fig. 3). Data from the Grödener Sandstone also plots in this field and probably represents the precipitation of sulfides from the fluids along the flow path rather than syngenetic deposition of galena in the Grödener Sandstone as suggested by Köppel and Schroll (1983). Köppel and Schroll (1983) reject the 100 Ma model age for the Bleiberg-type ores as unreasonable because they argue that the ores are syngenetic.

In a similar manner, we can calibrate the growth curves for the Variscan orogenic terrane of central Europe if we assume that the lead-isotope data from the synsedimentary Meggen and Rammelsberg deposits, both of Middle Devonian age, are representative of the crustal lead-isotope growth curve applicable to the Cracow-Silesia deposits. These data provide a similar tie point on this lead-isotope evolution curve at about 380 Ma. The lead-isotope data from the Kupferschiefer of Germany (Wedepohl *et al.*, 1978) provide an independent test point on this lead-isotope growth curve. They give a model age of about 250 Ma where the secondary isochron intersects this growth curve. This model age is in agreement with the stratigraphic age of the Kupferschiefer. It is slightly older than, but lies within the range of error of, the 240-230 Ma age of mineralization determined from paleomagnetic data (Jowett *et al.*, 1987). If we accept this calibration of the lead-isotope growth curve for the Cracow-Silesia MVT deposits,

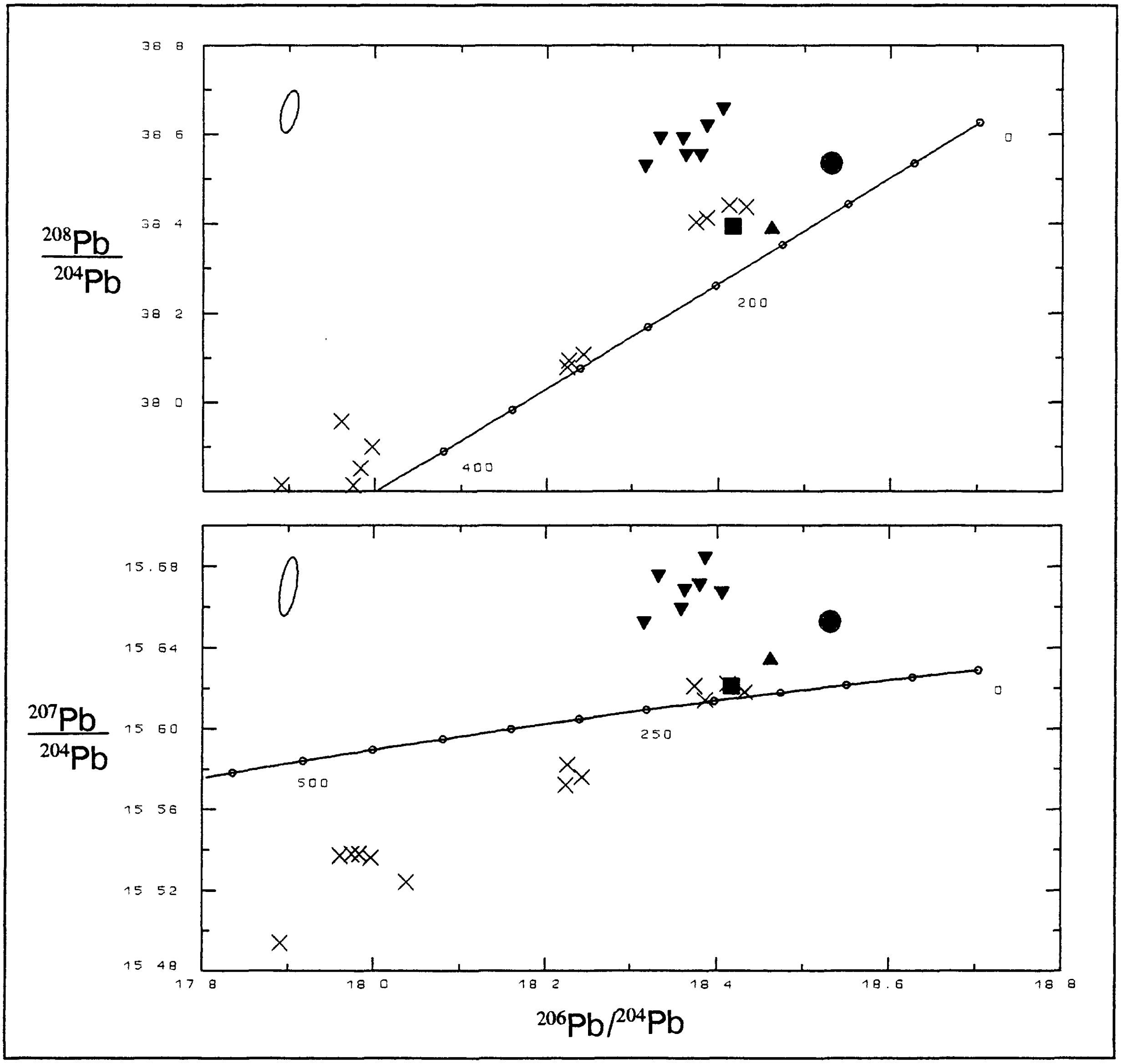

Figure 2. Lead-isotope diagram showing the data from MVT ores from the Cracow-Silesia district (■), the Bleiberg-type MVT ores (▼, Köppel and Schroll, 1983), the Plakalnitsa, Bulgaria MVT ores (▲, Zartman *et al.*, 1979), the average value for carbonate-hosted lead from the Keuper limestones in southwestern Germany (●, Lippolt *et al.*, 1983), and the SEDEX Carboniferous ores from Ireland (X, LeHuray *et al.*, 1987). The Stacy-Kramers Pb-isotope growth curve is shown for reference; model ages are from the uncalibrated Stacey-Kramers growth curve. An error ellipse (0.05 percent) is shown in the upper left corner of each diagram.

we derive a model age of the Cracow-Silesia MVT deposits of about 230 Ma, or Middle Triassic. This feature of the lead-isotope data lead Zartman *et al.* (1979) to support a syngenetic origin for the Cracow-Silesia deposits.

Additional evidence supporting this calibration of the lead-isotope growth curve comes from the lead-isotope analyses of polymetallic veins from the Holy Cross Mountains area (Góry Świetokrzyskie), Poland. Zartman *et al.* (1979) reported lead-isotope analyses from four samples, one from each of four different types of mineralization in the Holy Cross Mountains area. We report analyses from two additional samples and obtained very comparable lead-isotopic compositions (table 3). Three samples are from polymetallic veins exposed in deformed Paleozoic and Mesozoic rocks exposed in the Świetokrzyskie anticlinorium. The rocks are a part of the Variscan Paleozoic orogenic belt of central Europe. The absolute age of mineralization for these mineralization systems is not known. The sample from Miedzianka is of the copper-rich polymetallic vein type and is latest Variscan in age whereas the other veins are post Variscan (Rubinowski, 1971). Using this lead-isotope growth curve, the polymetallic veins would give model ages of about 290 Ma to 240 Ma suggesting that they are late Paleozoic to early Mesozoic in age.

The sample from Pierzchnica is hosted in Triassic carbonate rocks. The lead-isotopic composition matches that of the Cracow-Silesia ores within analytical error and also gives a model age of about 230 Ma. It may well represent the same mineralization event and process as found in the Cracow-Silesia MVT district. Two additional polymetallic vein samples from the Upper Silesia Basin (table 1, Zartman *et al.*, 1979) plot between the 380 Ma calibration point and the polymetallic veins from the Holy Cross Mountains indicating model ages in the 330 to 300 Ma range.

Constraints on models for the origin of the Cracow-Silesia MVT deposits

What constraints on the origin of these deposits do the lead-isotope data provide? Basically, the very limited range of lead-isotopic compositions of individual deposits in the Cracow-Silesia district and the Bleiberg-type ores suggest four limitations on the process of ore formation. First, the uniformity of the lead-isotopic data suggests that the process was a single event of short duration in geologic time, otherwise the radiogenic growth of lead from the decay of in situ uranium and thorium would produce radiogenic arrays rather than the tight field of lead-isotopic data in the ores. Second, the source of lead was from sedimentary rocks which were probably derived either from multiple cycles of erosion of sedimentary precursors that were well mixed by the erosion process to provide a uniform lead-isotopic composition, or they were derived from evaporite sequences present in the Upper Silesia Basin (Osika, 1986). Third, because these MVT deposits lack radiogenic lead-isotope arrays, leaching must have occurred not long after deposition of the source rocks if clastic rocks were the source of the lead. In this case, the composition of lead in the ores is constrained by the mass balance between labile and radiogenic lead in the source rocks. Molasse sediments are characterized by the presence of red beds; these iron- and manganese-oxides represent a substantial sink for lead in the weathering process. However, in marine sedimentation, these iron- and manganese-oxides are soluble and are recycled at the seawater-sediment interface to form manganese nodules on the sea floor. Flysch sediments generally contain lower concentrations of lead which are tied up in detrital silicate components (Church, 1976). In contrast, if the evaporites were the source of the lead, lead would be decoupled from uranium and thorium and the lead-isotopic data would place <u>no</u> constraints on the ore formation process unless the composition of lead in the evaporite sequences matches that of the Cracow-Silesia ores. There would be no radiogenic component of lead, and the hydrothermal solutions must have been isolated from contact with old crystalline basement rocks. We draw these conclusions on the basis of existing lead-isotope studies as well our

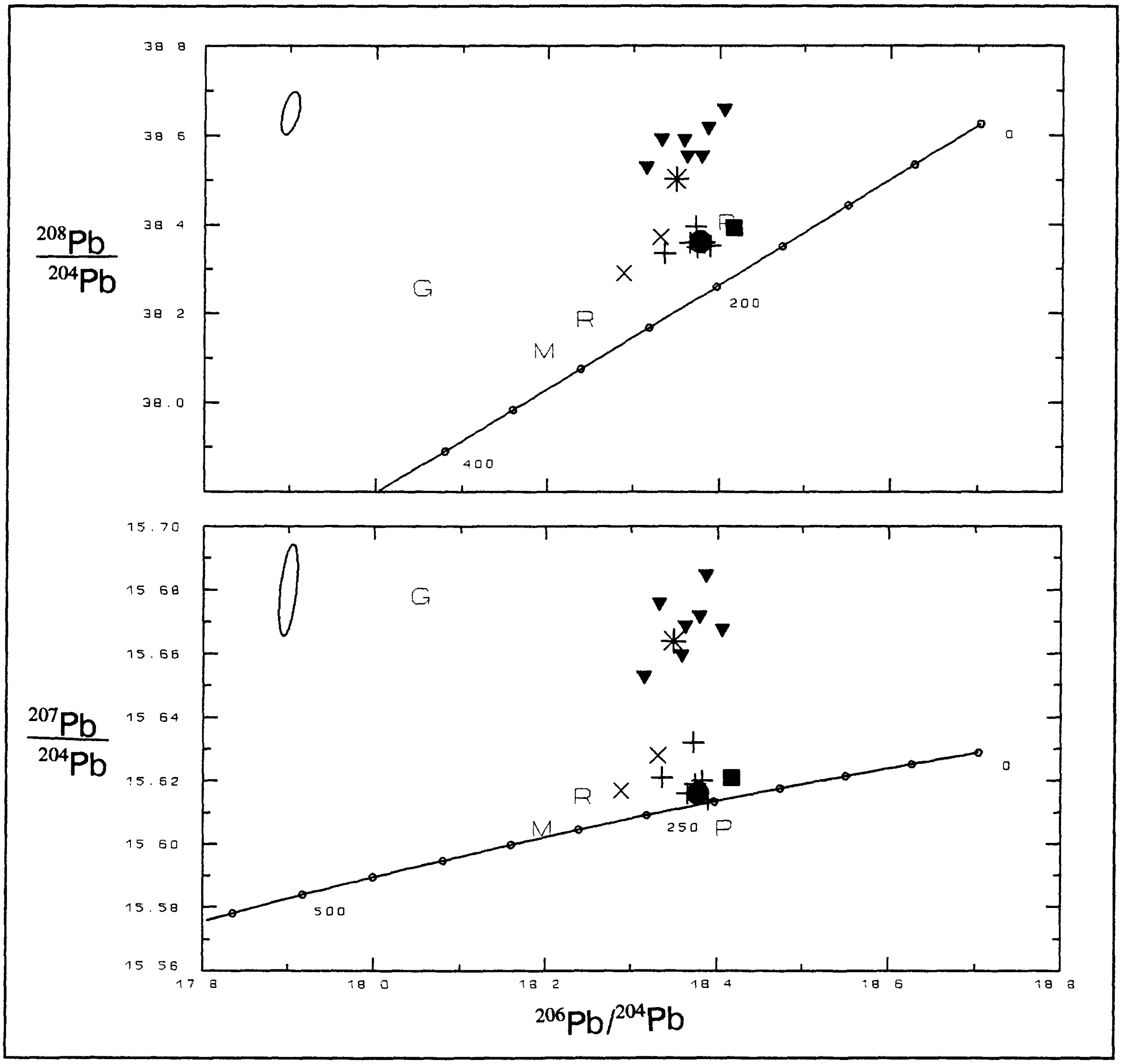

Figure 3. Figure caption on page 11.

ongoing studies of the process of formation of MVT ore deposits around the world. As mentioned above, lead-isotopic data from MVT deposits from around the world fall into two classes. Either they form some type of linear array indicating leaching of lead from a silicate source that contains sites of both common and radiogenic lead, or they have a uniform lead-isotopic composition. The Irish SEDEX deposits of Carboniferous age are a well studied ore district that demonstrates this formation of linear lead-isotope arrays caused by mixing of lead from two sources during leaching (fig. 2). The lead-isotopic data from the Irish SEDEX deposits plot along an array interpreted as a mixing line between sedimentary lead and Lewisian basement lead leached from the older crystalline rocks during the ore formation processes. LeHuray *et al.*

Table 3. Lead-isotope data from the Góry-Świetokrzyskie region, Poland

Locality	$\frac{^{206}\text{Pb}}{^{204}\text{Pb}}$	$\frac{^{207}\text{Pb}}{^{204}\text{Pb}}$	$\frac{^{208}\text{Pb}}{^{204}\text{Pb}}$	Lithology of Host	Age[§] of Host	Deposit Form
Miedzianka[#]	18.336	15.621	38.335	limestone	D	Cu-polymetallic vein
Bukowka[#]	18.372	15.632[*]	38.396	sandstone	eC	Pb-Zn-bar fissure vein
Kielce, góra Kadzielnia[+]	18.374	15.619	38.349	limestone	D	Pb-Zn-bar fissure vein
Mojcza[#]	18.382	15.620	38.360	limestone	O	Pb-Zn-bar vein on N-S Alpine fault
Szczukowskie Gorki[#]	18.365	15.616	38.359	sandstone	mTr	Pb-Zn-bar vein in clastic rocks
Zygmantówlia Quarry[+]	18.389	15.614	38.352	conglomerate	P	Pb-Zn-bar vein in clastic rocks
Pierzchnica[#]	18.408	15.606	38.412	limestone	mTr	stratiform sulfides

[§] Age abbreviations: eC, Early Cambrian; O, Ordovician; D, Devonian; P, Permian; mTr, Middle Triassic.

[#] Data from Zartman *et al.* (table 2, 1979).

[*] Value originally reported as 15.362; corrected data verified by R.E. Zartman (oral commun., 1992).

[+] Data from this study.

Figure 3. Lead-isotope diagram showing the Bleiberg-type ores (▼), the average value of the Graz VMS deposits (G, 390 Ma, Köppel, 1983), and the average value of galena from the Grödener Sandstone (*). These three data points lie in the upper μ and K fields of lead-isotope space and define the lead-isotope growth curve for the Bleiberg-type ore lead (Köppel and Schroll, 1985). In the lower μ and K fields of lead-isotope space applicable to the Cracow-Silesia ore lead, the lead-isotope data from the syngenetic Meggen (M) and Rammelsberg (R) deposits are shown which provide a tie point at 380 Ma on this growth curve, the value where the isochron formed by the lead-isotope data from the Kupferschiefer of Germany intersect the growth curve (●), and the average value of the Cracow-Silesia ore lead (■). The lead-isotope data from polymetallic veins (table 3) from the Upper Silesia Basin (X) and the Holy Cross Mountains area are also shown for comparison (+). Data from the Pierzchnica deposit is also shown (P, table 3, Zartman *et al.*, 1979). The Stacey-Kramers lead-isotope growth curve is shown for reference; model ages are from the uncalibrated Stacey-Kramers growth curve. An error ellipse (0.05 percent) is shown in the upper left corner of each diagram.

(1987) have demonstrated a regional change in the lead-isotope arrays and correlated these data with regional changes in the geology. The lead-isotopes of the ores become less radiogenic moving northwest in the ore district in Ireland.

Additional radiogenic lead-isotope arrays are found in many important MVT districts on the North American continent (Leach and Sangster, in press), which we interpret to reflect hydrothermal leaching of radiogenic lead from crystalline basement rocks during the formation of these ore deposits. However, the lead-isotopic character of both the Cracow-Silesia and the Pine Point districts are unique in that ores from these two districts have no measurable lead-isotopic variation within or between individual deposits within the districts. By comparing the Cracow-Silesia district with the data from recent studies of these deposits at Pine Point, we provide evidence for the constraints on the ore formation process as proposed above.

Studies of the fluid-flow paths in carbonate aquifers in the central U.S. were summarized by Leach and Rowen (1986). Tests of specific fluid-flow hypothesis were constrained by studies of the lead-isotopic composition of trace sulfides in core samples, bulk insoluble residues, and authigenic feldspar overgrowths in proposed flow paths in the midcontinent of North America (Goldhaber *et al.*, 1989; Aleinikoff *et al.*, in press). The presence of vuggy dolomite in the carbonate aquifers (Rowen, 1986; Leach and Rowen, 1986) and the absence of iron-oxides in the major red-bed sandstone aquifer (Mosier *et al.*, 1989) document the fluid pathways for the formation of the Mississippi Valley Zn-Pb deposits. Precipitation of these MVT ores resulted from the mixing of lead- and zinc-bearing fluids with sulfur-rich fluids along the pinch out zone of the various aquifers against the Precambrian high in the St. Francois Mountains causing rapid precipitation of much of the ore (Goldhaber *et al.*, 1989; Viets and Leach, 1990). A key to the modeling of these fluids is the observation that the metal-rich fluids were buffered to low H_2S values by the presence of iron-oxides in the sandstone aquifers. We proposed that the formation of the linear, radiogenic lead-isotope arrays in the Mississippi Valley deposits is caused by the leaching of radiogenic lead from iron-oxides and grain boundary sites within a continental red-bed and regolith composed of 1,400 Ma granitic components (Goldhaber *et al.*, 1989). Thus, a radiogenic lead-isotope array resulted not because of hydrothermal leaching of basement rocks, but because of leaching of red-bed arkose and regolith formed by the weathering of basement rocks deposited in a foreland basin.

Analysis of the fluid-flow path which resulted in the formation of the Pine Point deposit in the Western Canada sedimentary basin also provides constraints on the ore-formation process (Garven, 1985). Cumming *et al.* (1990) have shown that the isotopic composition of lead at Pine Point is very uniform ($^{206}Pb/^{204}Pb = 18.175$, $^{207}Pb/^{204}Pb = 15.574$, $^{208}Pb/^{204}Pb = 38.169$). The lead has a composition that places it on low μ and high K growth curves, very much unlike that of the Canadian Cordillera (Cumming *et al.*, 1990; Godwin and Sinclair, 1982; Godwin *et al.*, 1982). On the basis of feldspar lead data from the Churchill province of the Canadian shield (Sinha and Tilton, 1973), the lead in the Pine Point deposit was probably derived from sedimentary rocks formed by erosion of rocks from the Churchill province (Kyle, 1981). Model ages derived from the Pine Point lead-isotope data give ages of about 320 Ma, very near the age of the host rocks (Kyle, 1981). Qing and Mountjoy (1992) have shown that the Presqûile barrier reef was the aquifer through which hydrothermal solutions flowed during the Laramide orogeny in Late Cretaceous to early Tertiary time to form the Pine Point deposit. The probable source area for fluids was in the foothills of the Northern Rockies (Kyle, 1981; Garven, 1985). These rocks are a thick section of continental sediments (molasse), conglomerates, sandstones, and siltstones, derived largely from sedimentary rocks, deposited in a foreland basin. Fluid flow was isolated from the underlying continental shield and the sandstones directly overlying them by a thick section of Middle Devonian shale and carbonate rocks, and at the site of deposition, by anhydrite (Parsons, 1972; Kyle, 1981). We propose that the uniform isotopic composition of the lead in the Pine Point deposit is derived by leaching of sedimentary lead bound in these molasse sedimentary rocks or possibly from the Middle Devonian evaporites (Thiede and Cameron, 1978; Kyle, 1981). Perhaps more important however, is the isolation of the hydrothermal fluids from basement rocks allowing the fluids to migrate updip to form the Pine Point deposit and maintain the uniform lead-isotopic signature.

Discussion of the geologic development of the Upper Silesia (Wodzicki, 1987) indicates a similar geologic history of sedimentation in a foreland basin. The formation of thick flysch sedimentary section in Visean (Early Carboniferous) and of thick molasse sedimentary sections in both the Namurian and Westphalian (Early and Late Carboniferous) time in the central Upper Silesian Basin, separated from the Precambrian crystalline basement by thick sequences of earlier Devonian carbonate rocks, provide a similar source rock for lead which would have the same sedimentary source rock characteristic seen in both the Mississippi Valley and the Western Canada sedimentary basin. Różkowski *et al.* (1979) proposed a model whereby fluid flow would have originated along the front of the Pre-Carpathian Mountains. This fluid would leach metals from the multicycle sediments that make up the molasse and evaporite sequences in the Upper Silesian Basin. Fluid flow into the Upper Silesia Basin through these sandstones resulted in heating of the fluids and leaching of lead and zinc. Wodzicki (1987) has noted that the fluids present in these units (group 2 saline brines) in the Upper Silesia Basin have the correct light-stable isotopic and chemical composition to be possible ore fluids and are in probable equilibrium with the sediments. Fluid flow to the zone where the Cracow-Silesia deposits are today would occur through the Upper Silesia Basin and ascend to the surface along faults causing mixing with cooler sulfur-rich fluids forming the Cracow-Silesia MVT deposits. The timing of the fluid flow would be controlled by the tectonic process of uplift in the source area and is geologically limited by the presence of mineralization in the Klucze deposit. Here, MVT mineralization occurs in rocks of the Muschelkalk Formation which have been cut by Late Jurassic faulting. MVT ore cuts this fault indicating that deposition of the ore could have taken place only after this faulting event (Gorecka, 1991).

Suggestions for Further Research

Additional lead-isotopic work can be done to further constrain the proposed model. First, lead-isotopic analyses of additional stratabound and stratiform ores, such as the Ordovician deposits near Zawiercie (Wodzicki, 1987), could further constrain the lead-isotope evolution model and may provide an additional test of the calibration of the model age of deposits calculated from this curve. Second, lead-isotope and chemical analyses of samples from and inspection of cores of the Carboniferous molasse sequence in the Upper Silesian Basin would be essential to test for evidence of fluid flow, and to evaluate both the isotopic composition and the mass balance of lead in both the iron-oxide and silicate phases. Third, lead-isotope and chemical analyses of a selected sequence of samples from the Zechstein salt deposits and the Miocene

Rybnik salt deposit (Osika, 1986) may provide a test of the evaporite source rock model. Differences in the isotopic composition of lead in these two evaporite sequences will also provide time stratigraphic age constraints on the lead-isotope growth curve and allow a distinction between these two evaporite sequences as possible sources of lead. This study would also provide an independent test of the model proposed by Wodzicki (1987) who suggested that the group 2 formation waters (saline brines) may have provided the metals. However, analysis of samples of the salt beds themselves would eliminate the problem of collecting group 2 formation waters without contaminating them and would remove the uncertainty of the migration history of these formation waters.

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