Cover. Leached ilmenite grain approximately 60 microns in diameter surrounded by quartz overgrowth in Lower Pennsylvanian sandstone in Indiana. Quartz overgrowths occlude much of the pore space in these rocks. Sample collected by Paula Hansley, U.S. Geological Survey.
Lead Isotopes from the Upper Mississippi Valley District—A Regional Perspective

By Timothy M. Millen, Robert E. Zartman, and Allen V. Heyl

EVOLUTION OF SEDIMENTARY BASINS—ILLINOIS BASIN
Jennie L. Ridgley, Project Coordinator

U.S. GEOLOGICAL SURVEY BULLETIN 2094–B

A multidisciplinary approach to research studies of sedimentary rocks and their constituents and the evolution of sedimentary basins, both ancient and modern

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LEAD ISOTOPES FROM THE UPPER MISSISSIPPI VALLEY DISTRICT—A REGIONAL PERSPECTIVE

By Timothy M. Millen,1 Robert E. Zartman,2 and Allen V. Heyl3

ABSTRACT

New lead isotopic data on galena from within and peripheral to the Upper Mississippi Valley lead-zinc district make it possible, by extending coverage to outlying locations, to trace the pathway traversed by the mineralizing fluids beyond the boundary of the main district. All but one of the samples exhibit elevated ratios of the radiogenic isotopes typical of the Upper Mississippi Valley ore deposits; \( \frac{^{206}Pb}{^{204}Pb} \) ranges from 19.38 to 24.46, \( \frac{^{207}Pb}{^{204}Pb} \) ranges from 15.73 to 16.24, and \( \frac{^{208}Pb}{^{204}Pb} \) ranges from 39.24 to 43.69. Galena from the Pints quarry near Waterloo, Iowa, has distinctly lower values of these ratios and may not be related paragenetically to the other samples. Otherwise, the lowest ratios are for samples in the southern part of the region in north-central Illinois, and the highest ratios are for samples to the northeast of the main district in the vicinity of Madison, Wisconsin. Thus, an isotopic pattern rather similar to that observed originally by Heyl and others (1966) prevails regionally, although the predominant fluid flow is now believed to have emanated from the Illinois Basin rather than from the Forest City Basin. Metal-bearing brines being driven northward out of the Illinois Basin probably played the key role in mineralization of the Upper Mississippi Valley district.

Both the new and the previously reported lead ratios for the Upper Mississippi Valley district are plotted on \( \frac{^{207}Pb}{^{204}Pb} \) and \( \frac{^{208}Pb}{^{204}Pb} \) versus \( \frac{^{206}Pb}{^{204}Pb} \) diagrams, which permit their comparison and the calculation of refined slopes for the expanded data set. A two-stage model age for the time of mineralization can be determined from the \( \frac{^{207}Pb}{^{204}Pb} \)-\( \frac{^{206}Pb}{^{204}Pb} \) slope, provided that the source age of the lead is known. With our limited knowledge of this source age, the time of mineralization cannot be tightly constrained but is permissive of a Permian or younger lateral secretion event, as suggested by other geochronological results.

INTRODUCTION

Previously, Heyl and others (1966) reported the lead isotopic composition of 17 galenas from the Upper Mississippi Valley lead-zinc district of southwestern Wisconsin, northwestern Illinois, and northeastern Iowa. Contouring of the \( \frac{^{206}Pb}{^{204}Pb} \) and \( \frac{^{208}Pb}{^{204}Pb} \) ratios across the district revealed a pattern of isotopic zonation in which lower ratios are on the western margin of the district and higher ratios are concentrated toward the northeast. The data of Heyl and others (1966) were reported as raw ratios uncorrected for mass fractionation (absolute standards were unavailable at that time), and they were later converted to absolute values and reinterpreted by Yonk (1970) and Richards and others (1972). The revised absolute ratios were not published, however, until more recently (Sangster, 1985) (see table 1). Aside from these adjustments—generally leading to a refinement in the linear regressions of the data and to a recalculation of secondary isochron ages—no other high-precision lead isotopic analyses have been reported for the Upper Mississippi Valley district since Heyl and others (1966).

The present study adds a significant number (22) of new galena isotopic analyses for the Upper Mississippi Valley district and vicinity that, hopefully, will renew interest in the source and transport mechanism of lead in this important mining region. Although a variety of new geologic research has been conducted on the Mississippi Valley deposits subsequent to Heyl and others (1966), this paper does not broadly discuss ore genesis in the Upper Mississippi Valley. The interested reader is referred to Heyl (1983) and Sverjensky (1986) for a review of some recent studies of Mississippi Valley-type zinc-lead deposits. Instead, we take this opportunity to revisit the Upper Mississippi Valley zinc-lead district and surrounding areas of Illinois, Wisconsin, Iowa, and Minnesota in order to draw more extensive regional lead

1Department of Geology, Northern Illinois University, DeKalb, Illinois 60115.
3P.O. Box 1052, Evergreen, Colorado 80439.
Table 1. Revised lead isotopic data for the Upper Mississippi Valley district from Heyl and others (1966).

<table>
<thead>
<tr>
<th>Locality number and name</th>
<th>$^{206}\text{Pb}/^{204}\text{Pb}$</th>
<th>$^{207}\text{Pb}/^{204}\text{Pb}$</th>
<th>$^{208}\text{Pb}/^{204}\text{Pb}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Waukon (Mineral Creek) mines</td>
<td>20.70 (20.83)</td>
<td>15.85 (15.96)</td>
<td>40.19 (40.45)</td>
</tr>
<tr>
<td>2. Captain Turner mine</td>
<td>21.22 (21.35)</td>
<td>15.99 (16.10)</td>
<td>40.83 (41.10)</td>
</tr>
<tr>
<td>3. Holmes mine</td>
<td>21.74 (21.88)</td>
<td>15.95 (16.06)</td>
<td>41.29 (41.57)</td>
</tr>
<tr>
<td>4. Skene mine</td>
<td>21.92 (22.07)</td>
<td>16.02 (16.13)</td>
<td>41.67 (41.96)</td>
</tr>
<tr>
<td>5. Amelia mine (average of 3 samples)</td>
<td>21.91 (22.06)</td>
<td>15.98 (16.09)</td>
<td>41.60 (41.89)</td>
</tr>
<tr>
<td>6. Rockville mine</td>
<td>21.89 (22.05)</td>
<td>16.01 (16.12)</td>
<td>41.44 (41.73)</td>
</tr>
<tr>
<td>7. Piquette mine</td>
<td>22.06 (22.20)</td>
<td>16.01 (16.12)</td>
<td>41.64 (41.92)</td>
</tr>
<tr>
<td>8. Bautsch mine</td>
<td>22.18 (22.33)</td>
<td>16.06 (16.17)</td>
<td>41.98 (42.27)</td>
</tr>
<tr>
<td>9. Nigger Jim mine</td>
<td>22.07 (22.22)</td>
<td>15.97 (16.08)</td>
<td>41.79 (42.07)</td>
</tr>
<tr>
<td>10. New Hoskins mine</td>
<td>22.17 (22.31)</td>
<td>15.98 (16.09)</td>
<td>42.09 (42.37)</td>
</tr>
<tr>
<td>11. Calumet mine (cubic crystal)</td>
<td>22.80 (22.95)</td>
<td>16.15 (16.25)</td>
<td>42.58 (42.86)</td>
</tr>
<tr>
<td>12. Calumet mine (octahedral crystal)</td>
<td>22.62 (22.77)</td>
<td>16.04 (16.15)</td>
<td>42.43 (42.72)</td>
</tr>
<tr>
<td>13. Ohlerking mine</td>
<td>23.18 (23.32)</td>
<td>16.10 (16.20)</td>
<td>42.40 (42.68)</td>
</tr>
<tr>
<td>14. Old Slack mine</td>
<td>23.48 (23.62)</td>
<td>16.14 (16.25)</td>
<td>42.93 (43.22)</td>
</tr>
<tr>
<td>15. Ivey mine</td>
<td>23.76 (23.91)</td>
<td>16.17 (16.28)</td>
<td>43.27 (43.55)</td>
</tr>
<tr>
<td>16. North Yellowstone mine</td>
<td>23.60 (23.76)</td>
<td>16.16 (16.27)</td>
<td>43.40 (43.71)</td>
</tr>
<tr>
<td>17. Demby-Weist mine</td>
<td>24.24 (24.44)</td>
<td>16.22 (16.33)</td>
<td>43.65 (43.95)</td>
</tr>
</tbody>
</table>

isotopic zonation maps and to calculate refined secondary isochron ages based on the expanded data set.

SAMPLE LOCALITIES

Minor occurrences of Mississippi Valley-type sulfide mineralization outside the main Upper Mississippi Valley district were located and described by Heyl and West (1982), who noted (p. 103) that “Epigenetic lead, zinc and copper sulfides have been found in old mines, prospects and other occurrences over a wide area on all sides of the Upper Mississippi district. These sulfides have the same crystal habits, trace elements, lead isotope patterns, and sequence of formation” within the main district and in the outlying areas surrounding the main productive district. Samples from several of these localities, together with those from other mineral occurrences previously unreported in the literature, were included in the present study. The new sites were chosen on the basis of availability of galena, Mississippi Valley-type paragenetic relationships, and geographic distribution peripheral to the main Upper Mississippi Valley district.

The location, host rock, and mode of occurrence for many of the samples included in this study are described in Heyl and others (1966) and Heyl and West (1982); otherwise, a brief description is given in the appendix. All but one of the nine previously unreported occurrences (sample 21) are quarries containing noneconomic concentrations of galena, sphalerite, and iron sulfides. Most, but not all, have associated calcite, and at one location (sample 38) substantial quantities of associated euhedral, acicular barite are present. Although galena has been reported in rocks ranging in age from Cambrian to Pennsylvanian (Heyl and others, 1966), the present study only includes galena in Cambrian to Devonian rocks. Because the bulk of the ore extracted from the Upper Mississippi Valley district was hosted in rocks of Ordovician age, effort was concentrated on obtaining samples from rocks of this age in order to expand the lateral isotopic pattern developed by Heyl and others (1966) for the main ore district. By restricting sampling mostly to this horizon, however, vertical isotopic variation was not investigated, and its contribution to the overall pattern remains indeterminate.

ANALYTICAL PROCEDURE

Lead isotopic analyses from localities 18, 21, 27, and 29–32 were initially conducted at Northern Illinois University on a 6-in.-radius, Nier-type solid-source mass spectrometer to determine approximate isotopic compositions of galenas from outlying locations and to establish the general nature of the isotopic anomaly pattern. The precision of these analyses (+1 percent) was insufficient, however, to compare them with previously reported data from the Upper Mississippi Valley district. These samples were then reanalyzed on a 12-in.-radius, solid-source mass spectrometer at the U.S. Geological Survey to obtain the desired precision. In addition, other samples that had been previously analyzed at
Table 2. New lead isotopic data for the Upper Mississippi Valley district and vicinity. [Sample localities are shown by number in figures 1 and 2 and are described in the appendix. Data are given as absolute values based on intercomparison with the NBS 981 lead standard]

<table>
<thead>
<tr>
<th>Locality number and name</th>
<th>$^{206}$Pb/$^{204}$Pb</th>
<th>$^{207}$Pb/$^{204}$Pb</th>
<th>$^{208}$Pb/$^{204}$Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>18. Spring Grove quarry</td>
<td>21.83</td>
<td>15.99</td>
<td>41.36</td>
</tr>
<tr>
<td>19. Pints quarry</td>
<td>18.29</td>
<td>15.62</td>
<td>38.24</td>
</tr>
<tr>
<td>20. Anamosa diggings</td>
<td>22.65</td>
<td>16.08</td>
<td>41.48</td>
</tr>
<tr>
<td>21. Fessler mine</td>
<td>22.06</td>
<td>15.99</td>
<td>41.91</td>
</tr>
<tr>
<td>22. Orion mine</td>
<td>22.77</td>
<td>16.06</td>
<td>42.24</td>
</tr>
<tr>
<td>23. Doylestown mines</td>
<td>24.46</td>
<td>16.24</td>
<td>43.25</td>
</tr>
<tr>
<td>24. Speedway roadcut</td>
<td>23.11</td>
<td>16.10</td>
<td>43.04</td>
</tr>
<tr>
<td>25. Blue Mounds mines</td>
<td>23.16</td>
<td>16.12</td>
<td>43.15</td>
</tr>
<tr>
<td>26. Exeter diggings</td>
<td>23.32</td>
<td>16.16</td>
<td>43.69</td>
</tr>
<tr>
<td>27. Brohead quarry</td>
<td>23.09</td>
<td>16.14</td>
<td>43.39</td>
</tr>
<tr>
<td>28. Avon lead-zinc occurrence</td>
<td>21.70</td>
<td>15.97</td>
<td>41.78</td>
</tr>
<tr>
<td>29. Vinegar Hill mine</td>
<td>22.30</td>
<td>16.03</td>
<td>42.25</td>
</tr>
<tr>
<td>30. Ten Strike mine</td>
<td>21.79</td>
<td>15.97</td>
<td>41.44</td>
</tr>
<tr>
<td>31. Morseville quarry</td>
<td>22.75</td>
<td>16.07</td>
<td>42.58</td>
</tr>
<tr>
<td>32. Mt. Carroll mines</td>
<td>21.80</td>
<td>15.99</td>
<td>41.66</td>
</tr>
<tr>
<td>33. Stebbins mine</td>
<td>22.12</td>
<td>16.00</td>
<td>42.30</td>
</tr>
<tr>
<td>34. Brookville quarry</td>
<td>20.47</td>
<td>15.87</td>
<td>40.50</td>
</tr>
<tr>
<td>35. Oregon East quarry</td>
<td>19.38</td>
<td>15.73</td>
<td>39.25</td>
</tr>
<tr>
<td>36. Dixon Southwest quarry</td>
<td>19.55</td>
<td>15.76</td>
<td>39.36</td>
</tr>
<tr>
<td>37. Butler quarry</td>
<td>19.64</td>
<td>15.78</td>
<td>39.39</td>
</tr>
<tr>
<td>38. Troy Grove quarry</td>
<td>19.57</td>
<td>15.75</td>
<td>39.24</td>
</tr>
<tr>
<td>39. Elmhurst quarry</td>
<td>20.81</td>
<td>15.88</td>
<td>40.22</td>
</tr>
</tbody>
</table>

The U.S. Geological Survey over the past decade (samples 20, 22–26, 28, and 33), but not reported, were incorporated into the data set.

Approximately 1–2 mg of galena powder or crystal fragments was converted to Pb(NO$_3$)$_2$ by dissolution in 30 mL of nitric acid (10 mL of 70 percent distilled HNO$_3$ and 20 mL ultrapure H$_2$O). From this 30-mL solution, a 10-μL aliquot was transferred to a 5-mL centrifuge tube to which 1 drop of ultrapure H$_3$PO$_4$ was added. After heating the sample almost to dryness, a single drop of ultrapure silica gel was added, and the total solution loaded onto a rhenium filament for mass spectrometric analysis. Samples were run alternately with the NBS 981 lead standard, and all new data were normalized to absolute values. Replicate measurements were made on about three-fourths of the samples, confirming a precision of ±0.1 percent or better (95 percent confidence level) for all ratios. The results of the new analyses are shown in table 2.

**DISCUSSION**

The $^{206}$Pb/$^{204}$Pb and $^{208}$Pb/$^{204}$Pb isotopic data in tables 1 and 2 were plotted and contoured on a base map of the Upper Mississippi Valley region (figs. 1 and 2, respectively). In order to minimize the effect of local isotopic scatter known to be present even in samples from a single mine (for example, compare samples 11 and 12 in table 1; also the Stillhouse 40 mine has a range in $^{206}$Pb/$^{204}$Pb of 21.45–22.10; T.M. Millen, unpublished data), some smoothing of the contours was allowed in the computer program used to construct the figures. Expectedly, comparison of these plots with those of Heyl and others (1966) shows the retention of a similar pattern, as well as the extension of the contours well outside the original study area.

Heyl and others (1966) suggested that this districtwide gradient reflects fluid flow paths of the ore solutions and discussed two possible mechanisms for generating the regional lead isotopic.

1. Ore fluids migrated up dip from adjacent source basins, depositing lead as they traversed the district. The increasingly radiogenic character of the galena across the Upper Mississippi Valley district was produced by additions of radiogenic lead to these migrating fluids. Left in doubt is whether the radiogenic lead was leached from the lower Paleozoic sedimentary rocks, which served as primary aquifers for the solutions, from underlying basement rocks, which also became involved in the hydrologic system, or from some combination of the two possible sources.

2. Ore fluids initially entered and migrated through basement rock at some structural high, such as along the
Wisconsin arch, where they became enriched in radiogenic lead. Subsequently, the metal-bearing fluids rose into overlying sedimentary rocks and then moved laterally toward the southwest. In this case, a less radiogenic lead component derived from the host rocks is required to contaminate the fluid as it migrated away from the site of upward flow.

Because of its geologic plausibility, the first model, which presumes that the fluids were derived by lateral secretion from, or, at least, flowed through, an adjacent sedimentary basin, seems preferable. The original contour map of Heyl and others (1966) appears to implicate the Forest City Basin, to the southwest in central Iowa, as the main ore-fluid source. Cathles and Smith (1983) and Bethke (1986), in their respective studies of compaction-driven fluid flow and of gravity-driven fluid flow as an ore-fluid forming process in sedimentary basins, assumed that the Illinois Basin, more than 12,000 ft thick in southern Illinois, was the source of the fluids for the Upper Mississippi Valley district. The Forest City Basin, which contains only about one-third the thickness of sediments, was deemed less favorable by Cathles and Smith (1983) and, by itself, unable to produce the ore-fluid temperatures observed in the Upper Mississippi Valley district. Cathles and Smith (1983, p. 998) and Bethke (1986) did not, however, preclude some involvement of the Forest City Basin as an ore-fluid source for the Upper Mississippi Valley district.

Our new isotopic contour maps, which extend sample coverage a considerable distance to the south and west (figs. 1, 2), are permissive of, but may not require, fluid flow originating from, or passing through, both of these basins. In particular, one might interpret the relatively high sample density between the Illinois River and Freeport to be the “tracks” of

Figure 1. Map showing galena sample localities (solid circles) and distribution of $^{206}\text{Pb}/^{204}\text{Pb}$, Upper Mississippi Valley district and vicinity. Contour interval 0.5; contours smoothing was allowed in computer program; dashed contours are controlled solely by Pints quarry sample (locality 19). Arrows indicate suggested flow paths for mineralizing fluids.
an isotopically evolving lead emerging from the Illinois Basin and flowing northward into southwestern Wisconsin. Much poorer control, anchored mainly by the low $^{206}\text{Pb}/^{204}\text{Pb}$ sample 19 from Pints quarry near Waterloo, serves to define a second possible flow path from the Forest City Basin. Paragenetic relationships and Late Devonian age of the limestone at Pints quarry are, however, the most dissimilar to the Upper Mississippi Valley occurrences of any sample included in this study (M. Goldhaber, written commun., 1993). Accordingly, those contours in figures 1 and 2 that are controlled solely by the Pints quarry sample are shown as dashed, and we interpret the Forest City Basin flow path with great caution. Evidence for an isotopic high separating the Illinois Basin and Forest City Basin flow regimes is provided almost entirely by sample 20 from the Anamosa diggings. Although an extensive field search was made for additional samples from east-central Iowa, we have, as yet, been unsuccessful in better defining this weakly mineralized area. Indeed, the presence or absence of trace galena in limestone quarries may be, in itself, an important clue to fluid paths.

Whether or not formation of these outlying occurrences of lead and zinc sulfides is related to deposition of ores in the main Upper Mississippi Valley district may be questioned. In order for the lead data from this study to be of significance to the study of the Upper Mississippi Valley district, these outlying occurrences must have been a result of the same mineralizing process. Interpretations of paragenetic, fluid inclusion, and stable isotopic studies of outlying and main district occurrences (Jenkins, 1968; Garvin and others, 1987; Millen and Ludvigson, 1987; Ludvigson and Millen, 1988; Kutz and Spry, 1989) do not unequivocally indicate a genetic

Figure 2. Map showing galena sample localities (solid circles) and distribution of $^{208}\text{Pb}/^{204}\text{Pb}$, Upper Mississippi Valley district and vicinity. Contour interval 0.5; contours smoothing was allowed in computer program; dashed contours are controlled solely by Pints quarry sample (locality 19). Arrows indicate suggested flow paths for mineralizing fluids.
relationship between the outlying occurrences of Upper Mississippi Valley-type mineralization and deposits of the main district. Although most geochemical and paragenetic studies on Upper Mississippi Valley mineralization within the district are on pitch-and-flat deposits, many studies of the outlying occurrences have been conducted on disseminated, gash-vein, karst-fill, replacement, and vug-fill deposits. Paragenetic similarities exist between many of these types of occurrences and the main ore district pitch-and-flat deposits (for example, Bradbury, 1961), but the full range of the paragenetic sequences in outlying mineralized zones is usually not present at a given location.

Sulfur isotopic studies show that most outlying occurrences are isotopically lighter than the deposits in the main district, although some overlap between pitch-and-flat deposits and outlying occurrences does exist (McLimans, 1977; Garvin and others, 1987; Millen and Ludvigson, 1987; Ludvigson and Millen, 1988; Kutz and Spry, 1989). Sulfur isotopic geothermometry and fluid inclusion studies on outlying occurrences (Ludvigson and Millen, 1988; Kutz and Spry, 1989) produce fluid temperatures similar to those that formed the Upper Mississippi Valley district; however, late-stage calcites from several localities exhibit higher salinities than is typical for the Upper Mississippi Valley district fluids (Kutz and Spry, 1989). The general conclusion from stable isotopic, paragenetic, and fluid inclusion studies is that the closer the outlying occurrence approximates values and relationships of the main Upper Mississippi Valley district deposits, the more likely it is genetically related. Of the new sites in this study, those within the historic mining district (samples 21, 29, 30, and 31) and those nearest the district (samples 22, 24–28, 32, and 33) are most likely genetically related to main district mineralization. Sites in this study least likely related to Upper Mississippi Valley mineralization are those farthest from the main district (samples 18, 19, and 36–39).

Lead isotopic studies seem, however, to support coprecipitation of most outlying occurrences and main district

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**Figure 3.** $^{206}$Pb/$^{204}$Pb versus $^{207}$Pb/$^{204}$Pb diagram for revised data of Heyl and others (1966) (solid circles) and data from this study (open squares). Slopes, $M$, and correlation coefficients, $R$, are based on least-squares regression.

<table>
<thead>
<tr>
<th>EXPLANATION</th>
<th>$M$</th>
<th>$R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heyl and others (1966)</td>
<td>0.0976</td>
<td>0.939</td>
</tr>
<tr>
<td>This study</td>
<td>0.1022</td>
<td>0.998</td>
</tr>
<tr>
<td>All data</td>
<td>0.1013</td>
<td>0.984</td>
</tr>
</tbody>
</table>
ores (Millen and Ludvigson, 1987; Ludvigson and Millen, 1988). \(^{207}\text{Pb}/^{204}\text{Pb}\) and \(^{208}\text{Pb}/^{204}\text{Pb}\) versus \(^{206}\text{Pb}/^{204}\text{Pb}\) diagrams plotting the combined revised Heyl and others (1966) data and the data from this study are shown in figures 3 and 4. There is good agreement between the slopes of the new data from outlying occurrences and those from the main Upper Mississippi Valley district proper, suggestive of a genetic relationship. As previously discussed, of course, more paragenetic, fluid inclusion, and isotopic work needs to be completed before some of these outlying occurrences can be definitely related to the main Upper Mississippi Valley mineralizing event.

Assigning an age of mineralization in the Upper Mississippi Valley district has long been problematic. Stratigraphically, galenas have been reported in rocks of Cambrian to Pennsylvanian age. Because no Permian to pre-Pleistocene rocks are present in the Upper Mississippi Valley, a minimum age cannot be determined by stratigraphic means. On the basis of structural evidence, Heyl and others (1970) suggested that mineralization occurred between the late Paleozoic and the end of the Mesozoic. Zimmermann (1986) interpreted “young”apatite fission-track ages determined on Precambrian granitic rock from a northern Illinois drill core and from exposed basement in Wisconsin and Michigan to indicate substantial post-Permian, possibly Cretaceous and early Tertiary, uplift of the region. He speculated that removal of several thousands of feet of cover rock at that time might have provided the hydrologic conditions for brine migration and lead-zinc mineralization. Doe and others (1983) and Peterman and others (1986) concurred, on the basis of disturbed whole-rock and zircon U-Pb systems, respectively, that middle to late Phanerozoic uplift had affected the rocks in the northern Illinois drill core—a conclusion also reached by Afifi and others (1984) in a study of the whole-rock U-Pb system in Early Proterozoic metavolcanic rocks of northern Wisconsin. More recently, Brannon and others (1992a, b) obtained Rb/Sr ages of ~270 Ma on sphalerite from main district ores. An episode of late Paleozoic brine migration through Cambrian carbonate rocks of the central and southern Appalachians, which may also have implications for contemporaneous Mississippi Valley-type mineralization in the continental interior, has been recorded by the growth of authigenic potassium feldspar (Hearn and others, 1987; however, also see Duffin and others, 1989, for evidence of both Devonian and Permian potassium diagenesis).

![Figure 4](image-url)

**Figure 4.** \(^{208}\text{Pb}/^{204}\text{Pb}\) versus \(^{206}\text{Pb}/^{204}\text{Pb}\) diagram for revised data of Heyl and others (1966) (solid circles) and data from this study (open squares). Slopes, \(M\), and correlation coefficients, \(R\), are based on least-squares regression.
Attempts at dating the time of ore deposition using a two-stage lead isotope model have been made by Heyl and others (1966), Yonk (1970), and Richards and others (1972) for the Upper Mississippi Valley. Whereas Heyl and others (1966) used a simple least-squares method to determine the \( ^{207}\text{Pb}/^{204}\text{Pb} - ^{206}\text{Pb}/^{204}\text{Pb} \) slope, \( M \), of the regression line, Yonk (1970) and Richards and others (1972) used variations of a more complex method, developed by York (1969), of determining best-fit lines. The first variant attributes all error in \( M \), to the \( Y \), or \( ^{207}\text{Pb}/^{204}\text{Pb} \), value, whereas the second variant takes into account systematic and related errors in both the \( Y \) and \( X \) variables, as would be the case if error is due mainly to mass fractionation or imprecision in measurements of the lesser abundant \( ^{204}\text{Pb} \). Both the simple least-squares method and the second variant of the York (1969) method of obtaining a slope are utilized for all the data available in tables 1 and 2. A comparison of values for \( M \) and \( t_2 \) (the time of mineralization) of Heyl and others (1966), Richards and others (1972), and this study is shown in table 3. Results determined by least-squares regression (\( M=0.1013\pm0.0056 \)) and those determined by using the York best-fit program (\( M=0.1005\pm0.0034 \)) show little difference, and use of either slope value does not alter the conclusions of our study.

In addition to a precise determination of \( M \), the ages of ore emplacement given in table 3 rely on the ability to define \( t_1 \) (age of the source of the lead; usually taken to be the age of the local midcontinent basement, although it could be a hybrid age arising from multiple sources or even an apparent age transferred to overlying sedimentary rock that was derived from the basement). Heyl and others (1966), Yonk (1970), and Richards and others (1972) used \( t_1=1,350 \) Ma, an average age of basement rocks in the Upper Mississippi Valley as determined by Kanasewich (1962), Tilton and others (1962), Goldich and others (1966), Muehlberger and others (1966), and Lidiak and others (1966). Subsequent studies indicate that this choice of \( t_1 \) might be too young. Doe and others (1983), in their whole-rock U-Pb study of granite from the northern Illinois deep drill core, determined an upper concordia intercept age of 1,416±20 Ma and a secondary isochron age of 1,451±19 Ma. Hoppe and others (1983) dated zircon by the U-Pb method from this same and adjacent cores and determined upper intercept ages of 1,461–1,509 Ma for the granitic basement underlying the Upper Mississippi Valley area. The estimated age of ore formation from Doe and others (1983) is 260±35 Ma, as suggested by the lower intercept on their concordia plot. If these older ages for the basement source rocks are more appropriate, then mineralization ages calculated from the slope of the secondary isochrons will be about 100–200 m.y. younger than if the source rocks are 1,350 Ma, as previously assumed. Thus, our new results are reconcilable with other recent efforts to establish mineralization ages for the Upper Mississippi Valley deposits, but, unfortunately, geologic uncertainties together with inherent scatter in the secondary isochrons prevent us from further resolving this important question.

**SUMMARY AND CONCLUSIONS**

On the basis of this and previous studies, it is likely that mineralization in the Upper Mississippi Valley was the result of lateral secretion of metal-rich basinal brines from the Illinois and, possibly, the Forest City basins. Extension of the lead isotopic pattern of Heyl and others (1966) further defines fluid paths within the region of northern Illinois, southern Wisconsin, northeastern Iowa, and southeastern Minnesota. Although isotopic data exhibit significant

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**Table 3.** Comparison of regression slope (\( M \)), source rock age (\( t_1 \)), and time of mineralization (\( t_2 \)), as determined by different authors and calculation methods. (Errors in slopes and ages are ±2σ values)

<table>
<thead>
<tr>
<th>Regression slope (( M ))</th>
<th>( t_1 ) (for ( t_2=0 ) Ma)</th>
<th>( t_2 ) (for ( t_1=1,350 ) Ma)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.088±0.0087 (^{12})</td>
<td>1,410±180 Ma</td>
<td>100±250 Ma</td>
<td>Heyl and others (1966).</td>
</tr>
<tr>
<td>0.093±0.0071 (^{3})</td>
<td>1,530+130/-160 Ma</td>
<td>285+215/-240 Ma</td>
<td>Richards and others (1972).</td>
</tr>
<tr>
<td>0.096±0.0070 (^{4})</td>
<td>1,570±140 Ma</td>
<td>365±200/-240 Ma</td>
<td>Richards and others (1972).</td>
</tr>
<tr>
<td>0.1013±0.0056 (^{1})</td>
<td>1,648+102/-108 Ma</td>
<td>479+142/-144 Ma</td>
<td>All data, this study.</td>
</tr>
<tr>
<td>0.1013±0.0056 (^{5})</td>
<td>378+148/-152 Ma</td>
<td>All data, this study.</td>
<td></td>
</tr>
<tr>
<td>0.1005±0.0034 (^{6})</td>
<td>1,633+57/-63 Ma</td>
<td>456+88/-92 Ma</td>
<td>All data, this study.</td>
</tr>
<tr>
<td></td>
<td>355+94/-97 Ma</td>
<td>All data, this study.</td>
<td></td>
</tr>
<tr>
<td>0.1005±0.0034 (^{6})</td>
<td>230+97/-99 Ma</td>
<td>All data, this study.</td>
<td></td>
</tr>
</tbody>
</table>

\(^{1}\)Slope determined by unweighted least-squares method.  
\(^{2}\)Calculated regression based on uncorrected lead values.  
\(^{3}\)Slope assigns all errors to \( Y \) value (York, 1969).  
\(^{4}\)Slope assigns errors to \( X \) and \( Y \) values (York, 1969).  
\(^{5}\)Assumes \( t_1=1,420 \) Ma.  
\(^{6}\)Assumes \( t_1=1,500 \) Ma.
variations in lead ratios within single mines and mining sub-districts ($^{206}\text{Pb}/^{204}\text{Pb}=20.69-22.10$ for the Mt. Carroll sub-district as a whole; T.M. Millen, unpublished data), averaged values for these regions plot well with respect to contours in the original study of Heyl and others (1966). The regional contour pattern defined by this study helps to define specific flow paths for mineralizing fluids, as shown in figures 1 and 2. On the basis of these plots, the Illinois Basin in particular and perhaps the Forest City Basin probably contributed to the development of the Upper Mississippi Valley district mineralization. Because the lead isotopic control in eastern Iowa is scant, the role of the Forest City Basin in Upper Mississippi Valley mineralization cannot be fully assessed.

Our data are nonetheless compatible with the following scenario. At the time of mineralization, dominantly northward flowing, metal-rich brines from the Illinois Basin—combined with eastward flow, if any, from the Forest City Basin—apparently were deflected to the northeast through the Upper Mississippi Valley district. If the flow path was mostly confined to a lower Paleozoic aquifer, such as the Cambrian Mount Simon or Ordovician St. Peter Sandstones, the lead isotope pattern is best explained by the regional mixing of a basinal brine component ($^{206}\text{Pb}/^{204}\text{Pb}=19.4$ and $18.3$ and $^{208}\text{Pb}/^{204}\text{Pb}=39.2$ and 38.2 where sampled in northeastern Illinois and northeastern Iowa, respectively) with a local, radiogenic-isotope-enriched component leached from the indigenous sedimentary rock. The proportion of the second component increased to the northeast because either the basinal brine component was being progressively spent or physicochemical conditions favored the leaching of radiogenic lead in that direction.

Alternatively, the flow path may have included excursions into, or intersection with fluids derived from, the underlying Precambrian basement from whence the radiogenic-isotope-enriched component was acquired. Precipitation of the galena and other sulfides took place when the mineralizing brine escaped through fractures and dissolution channels from the aquifers into the overlying carbonate rock, a phenomenon capturing the local lead isotopic composition and structurally focused in the main Upper Mississippi Valley district. Unfortunately, the isotopic characteristics of the underlying Precambrian basement are insufficiently known to predict the regional pattern in $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ that might emerge from such a local sourcing of the lead.

Two-stage model ages determined from these galena leads do not tightly constrain the time of mineralization but are permissive of a Permian or younger lateral secretion event. Such an age is in agreement with the time of mineralization suggested by Heyl and others (1966, 1970), Yonk (1970), Richards and others (1972), McLimans (1977), Doe and others (1983), and Bethke (1986). Recent efforts by Brannon and others (1992a, b) and Hearnd and others (1987) to date directly minerals from the Mississippi Valley para- genetic sequence undoubtedly represent a more definitive approach toward establishing the late Paleozoic as the time of mineralization.

REFERENCES CITED


Hearrn, P.P., Jr., Sutter, J.F., and Belkin, H.E., 1987, Evidence for Late-Paleozoic brine migration in Cambrian carbonate rocks of the central and southern Appalachians—Implications for


APPENDIX—SAMPLE DESCRIPTIONS AND LOCALITIES

[Samples are shown by number in figures 1 and 2. Descriptions and locations of samples 1–17 are summarized from Heyl and others (1966)]


7. Piquette mine. Cubic galena from bedded deposit in Decorah and basal Galena formations. 1 mi east of Tennyson, Wis., in center NE¼ sec. 36, T. 3 N., R. 3 W., lat 42°41'15" N., long 90°40'00" W., Potosi, Wis., 7½-minute quadrangle. Reference: Heyl and others (1959).


18. Spring Grove quarry (south pit). Near-vertical, 5-mm-wide veinlet in Middle Ordovician Platteville Formation. Cubic to cubo-octahedral galena, sphalerite, iron sulfides, and calcite noted on surface of veinlet. At former site of the CMSP&P railroad overpass on Minnesota State Highway 44, 3.2 mi west of Spring Grove, Minn., NW¼NE¼ sec. 20, T. 101 N.,


21. Fessler mine no. 2. Galena in Upper Ordovician Wise Lake Formation. Area lies within the main Upper Mississippi Valley district and was mapped and studied by Brown and Whitlow (1960). When examined by A.V. Heyl in 1946, sphalerite and smithsonite were found on the mine dumps, but galena was the only ore mineral noted during later visit by T.M. Millen. Along Catfish Creek in Mines of Spain Nature Preserve, 1.3 mi south of Dubuque, Iowa, SW¼NE¼ sec. 6, T. 88 N., R. 3 E., lat 42°30'20" N., long 90°39'10" W., Dubuque South, Iowa, 7½-minute quadrangle. Samples provided by J.C. Wright, Dubuque College. Reference: Ludvigson and others (1986).


24. Speedway roadcut. Galena in Middle Ordovician Platteville Formation. Roadcut 6 mi west of center of Madison, Wis., on County Road M near Pine Bluff, Wis., secs. 19 and 20, T. 7 N., R. 8 E., lat 43°03'40" N., long 89°35'00" W., Middleton, Wis., 7½-minute quadrangle. Sample collected by R.A. Jenkins. Reference: Jenkins (1968).


27. Brodhead quarry. Galena in Ordovician Shakopee Formation. 2 mi north of Brodhead, Wis., on east side of City Road G near conjunction of Rock, Green, and Dane Counties, Wis., NW¼SW¼ sec. 30, T. 30 N., R. 10 E., lat 42°41'40" N., long 89°22'05" W., Orfordville, Wis., 7½-minute quadrangle. New galena locality; sample collected by T.M. Millen.


31. Morseville quarry. Galena and oxidized iron sulfides collected from vugs in Upper Ordovician Wise Lake Formation. Major old lead mines are just east of Morseville. 0.5 mi south of Morseville (Plum River), Ill., SE¼SW¼NE¼ sec. 25, T. 27 N., R. 4 E., lat 42°17'50" N., long 89°13'45" W., Galena, Ill., 7½-minute quadrangle. Sample collected by T.M. Millen.

32. Mt. Carroll mines. Gash-vein and vug occurrences of cubic and cube-octahedral galena, sphalerite, dolomite, marcasite, and cubic to cube-octahedral pyrite. Primary host rocks are Upper Ordovician Wise Lake Formation and Silurian Gower Formation Vug-fill barite noted in Middle Ordovician Dubuque Formation. Major lead mines, quarries, and diggings west and northwest of Mt. Carroll, Ill., secs. 2, 3, and 10, T. 24 N., R. 4 E., lat 42°06'00" N., long 90°01'00" W., Wacker, Ill., 7½-minute quadrangle. Reference: Heyl
and West (1982); Ludvigson (1988); Ludvigson and Millen (1988).

33. Stebbins (Yellow Creek) mine. Gash-vein galena in middle strata of Upper Ordovician Dunleith Formation. Galena also noted as vug-fill in nearby quarries. 0.25 mi west of Springfield Road on old U.S. Route 20, 2.5 miles east of Freeport, Ill., NW¼SW¼SW¼ sec. 2, T. 26 N., R. 8 E., lat 42°16'40" N., long 89°33'10" W., Freeport East, Ill., 7½-minute quadrangle. Sample collected by A.V. Heyl and W.S. West. Reference: Heyl and West (1982).


36. Dixon Southwest quarry. Fracture-fill galena and vug-fill sphalerite in Upper Ordovician Dunleith Formation. 1.3 mi southwest of Dixon, Ill., on Hoyle Road, NW¼NE¼ sec. 7, T. 21 N., R. 9 E., lat 41°49'40" N., long 89°30'00" W., Dixon West, Ill., 7½-minute quadrangle. New galena locality; sample collected by T.M. Millen.

37. Butler quarry. Fracture- and vug-fill galena, sphalerite, and iron sulfides in Middle Ordovician Mifflin Formation. 1.5 mi southeast of Lee Center, Ill., center W½ sec. 9, T. 20 N., R. 11 E., lat 41°44'20" N., long 89°14'40" W., Sublette, Ill., 7½-minute quadrangle. New galena locality; sample collected by T.M. Millen.

38. Troy Grove quarry. Vug- and fracture-fill calcite, galena, sphalerite, and iron sulfides in Middle Ordovician Mifflin and Pecatonica Formations. East edge of Troy Grove, Ill., NE¼NE¼ sec. 35, T. 35 N., R. 1 E., lat 41°28'00" N., long 89°04'20" W., Troy Grove, Ill., 7½-minute quadrangle. Sphalerite and calcite noted by Buschbach (1970), but new galena locality; sample collected by T.M. Millen.

39. Elmhurst quarry. Octahedral galena, sphalerite, calcite, marcasite, and acicular barite in collapse breccias, vertical veinlets, and as disseminations in Upper Ordovician Wise Lake Formation. Underground limestone quarry 0.5 mi south of junction of Illinois Highways 83 and 64, SW¼NW¼ sec. 2, T. 39 N., R. 11 E., lat 41°54'00" N., long 87°57'30" W., Elmhurst, Ill., 7½-minute quadrangle. New galena locality; sample collected by T.M. Millen.