

Rb-Sr dating of sphalerites from Mississippi Valley-type (MVT) ore deposits

SHUN'ICHI NAKAI,^{1,*} ALEX N. HALLIDAY,¹ STEPHEN E. KESLER,¹ HENRY D. JONES,¹
J. RICHARD KYLE,² and THOMAS E. LANE³

¹Department of Geological Sciences, University of Michigan, Ann Arbor, MI 48109-1063, USA

²Department of Geological Sciences, University of Texas, Austin, TX 78713-7909, USA

³Department of Earth Sciences, Memorial University of Newfoundland, St. John's, Newfoundland A1B 2X6, Canada

(Received October 24, 1991; accepted in revised form June 1, 1992)

Abstract—Mississippi Valley-type (MVT) ore deposits are epigenetic carbonate-hosted Pb-Zn deposits that contain galena, sphalerite, fluorite, barite, dolomite, calcite, and quartz. Although they are thought to form from basinal brines, their exact origins are still unclear, partly because of the scarcity of reliable geochronological data. Rb-Sr dating of sphalerites has recently been shown to be a promising technique for the direct dating of ore minerals in MVT deposits. This paper reports the results of a reconnaissance study of sphalerites, their fluid inclusions, and associated minerals from MVT deposits of North America. Sphalerites from Immel mine, Mascot-Jefferson City district, east Tennessee, define a Rb-Sr age of 347 ± 20 Ma consistent with a Rb-Sr age of 377 ± 29 Ma for sphalerites from Coy mine in the same district, but inconsistent with models that ascribe their genesis to the effects of the late Paleozoic Alleghenian orogeny. Rb-Sr isotopic analyses of K-feldspar from Immel mine preclude the possibility that the Rb-Sr data reflect feldspar inclusions. Sphalerites from the main ore zone of Daniel's Harbour mine, Newfoundland, do not form a linear isochron and open behavior of the Rb-Sr system is suspected. Sphalerites from the Pine Point district, Northwest Territories, Canada, define a Rb-Sr age of 361 ± 13 Ma, indicating that the mineralization took place shortly after the deposition of the middle Devonian host carbonate rocks. These results are not compatible with mineralization models based on regional fluid migration related to early Tertiary Cordilleran deformation. Sphalerites from northern Arkansas have very low Rb and Sr concentrations (less than 0.1 ppm). The Rb-Sr data do not form isochrons and the sphalerites have higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratios than expected, given their Rb/Sr ratios and reasonable constraints on their ages. The sphalerites are suspected to contain clay inclusions; and it is likely that the Sr isotopic compositions of these sphalerites, which have very low Sr concentrations, were affected by small amounts of inherited inclusions. Except for sphalerite from northern Arkansas, SEM studies and isotope dilution trace element measurements have so far failed to identify any suitable phases other than sphalerite that might be a host for the Sr.

INTRODUCTION

A VARIETY OF evidence suggests that large-scale fluid movements affected the upper crust of North America during the Phanerozoic, and that these migrations played an important role in the formation of certain types of metalliferous and hydrocarbon mineral deposits (OLIVER, 1986; BETHKE and MARSHAK, 1990). Mississippi Valley-type (MVT) deposits of North America are commonly regarded as the product of such large-scale brine migrations. These deposits formed from warm (50–200°C) and saline (10–30% TDS) basinal brines expelled from sedimentary basins, moving through upper crustal aquifers and precipitating ore in carbonate rocks several hundred kilometers from the original basins (WHITE, 1968; OHLE, 1980; SVERJENSKY, 1986). Although this generalized model has been widely accepted, the specific events that trigger the migration of basinal brines and their relation to tectonic events has been poorly constrained.

MVT deposits commonly comprise minerals generally considered unsuitable for direct isotopic dating, resulting in limited constraints on the timing of ore formation. One approach to solving this problem has been to date the effects

of hydrothermal overprinting of pre-existing minerals. Glauconites from southeast Missouri record Devonian and early Mississippian Rb-Sr ages inconsistent with a genetic link between ore formation in southeast Missouri and peak Ouachita-Appalachian orogeny during the Pennsylvanian (STEIN and KISH, 1985; 1991). However, it is uncertain whether the Rb-Sr system of the glauconites was reset by migration of the ore brines.

There have been several attempts to date phases found in MVT deposits directly. LANGE et al. (1983, 1985) applied the Rb-Sr method to galenas from the Viburnum mine in southeast Missouri and obtained an isochron that gives an age of 392 ± 21 Ma, although isotopic inhomogeneity of the ore fluid, which could cause a fortuitous isochron, was questioned by RUIZ et al. (1985). In addition, MEDFORD et al. (1983) carried out Rb-Sr analyses on sphalerites from the Pine Point district, Canada, and reported high and variable Rb/Sr ratios. HALLIDAY et al. (1990) showed that the variable Sm/Nd ratios of fluorites from the North Pennine orefield, U.K., could be used to place model age constraints on the timing of mineralization. Following this work, CHESLEY et al. (1991) reported high-precision Sm-Nd isochrons of fluorites from Sn-W orebodies in Cornwall, U.K., highlighting the hitherto unrealized potential of the technique for certain types of mineralization. SHEPHERD and DARBYSHIRE (1981)

* Present address: Laboratory for Earthquake Chemistry, Faculty of Science, The University of Tokyo, Tokyo 113, Japan.

demonstrated the feasibility of Rb-Sr isochrons for fluid inclusions in quartz. Following this success, SHEPHERD et al. (1982) attempted to date MVT mineralization in the North Pennine orefield and presented a Rb-Sr isochron age of 206 ± 9 Myr for inclusion fluids in quartz. NAKAI et al. (1990) dated sphalerites from Coy mine, Mascot-Jefferson City district, east Tennessee at 377 ± 29 Ma by the Rb-Sr method and demonstrated the viability of such an approach. BRANNON et al. (1991) reported Rb-Sr isotopic data for several ore and gangue minerals from Viburnum Trend, southeast Missouri and reported that Sr isotopic compositions in fluids varied during the mineralization. They also revealed that primary fluid inclusions in sulfide minerals have different Sr isotopic compositions from their host minerals. However, BRANNON et al. (1992) obtained a Permian Rb-Sr age for sphalerites from Upper Mississippi zinc-lead district, which reconfirm the usefulness of the method for dating sphalerites. This paper reports the results of Rb-Sr dating of sphalerites from a variety of MVT deposits from North America (Fig.

1), and is focused specifically on sphalerites from MVT districts in east Tennessee and northern Arkansas in the USA and Newfoundland and Pine Point in Canada.

TECHNIQUES

About 100 mg of hand-picked sphalerite were used for each analysis. The minerals were crushed in deionized water using a boron carbide mortar and pestle and leached with water to remove the fluid inclusions. The leachates were separated from wash residues by centrifugation; however, separation turned out to be imperfect (discussed in a later section). The wash residues of the sphalerites were dissolved with hot 6 M HCl. No visible solid residues under a microscope were observed after dissolution. Rb and Sr abundances were determined by isotope dilution using a mixed $^{87}\text{Rb}/^{84}\text{Sr}$ spike. K abundances were also determined by isotope dilution. The ^{84}Sr spike was highly enriched (>99%), enabling accurate Sr isotopic composition measurements on totally spiked samples. The mass of the fluid inclusions in the sphalerites could not be measured accurately, and reported elemental concentrations in Table 1a are based on the weight of the initial solid samples. The Rb/Sr ratios are accurate to better than 1%. Rb and Sr were separated by a conventional cation exchange

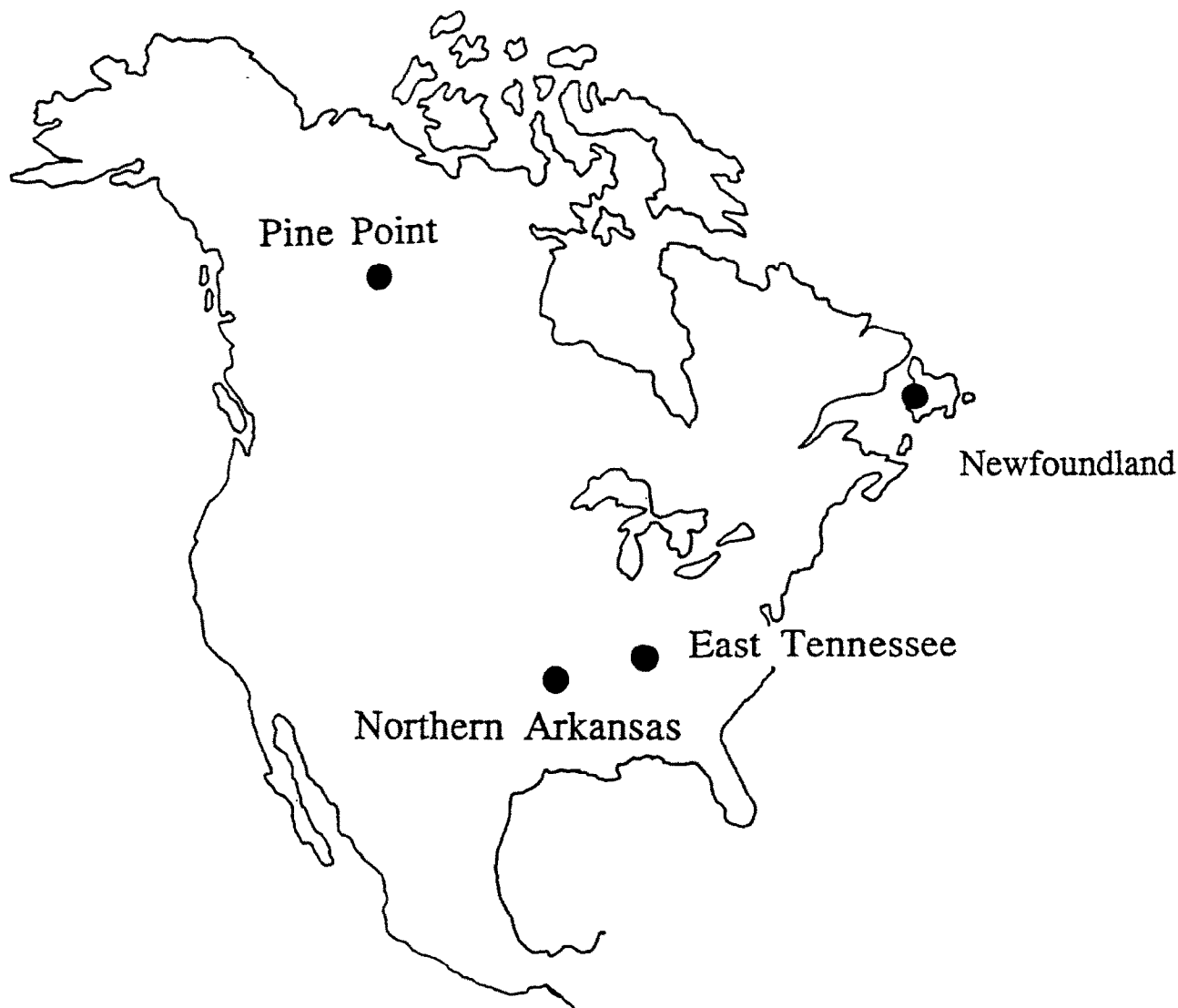


FIG. 1. Locations of the MVT deposits investigated in this study.

method using 3 mL of AG50W-X8 resin. Total procedure blanks for Rb and Sr were 20 pg and 50 pg, respectively, less than 1% of most of the samples. Blank corrections were made for data in Table 1a, using a $^{87}\text{Sr}/^{86}\text{Sr}$ of ratio of 0.709. A VG sector multi-collector thermal ionization mass spectrometer was used for all isotopic measurements. All isotopic measurements were made using Faraday cups. Rb was loaded on Ta triple filaments and Sr was loaded on Re or W single filaments with TaCl_5 and phosphoric acid. During this study, the average measured $^{87}\text{Sr}/^{86}\text{Sr}$ ratio for NBS987 standard was 0.710258 ± 6 (2σ mean, $N = 21$). Samples of K-feldspar from Immel mine were prepared by leaching host carbonate rocks with cold 1 M HCl. The feldspars were divided into two fractions. One fraction was leached with hot 6 M HCl to simulate the procedure adopted for sphalerite dissolution, and another was totally dissolved in HF. Rb, Sr abundances and Sr isotopic compositions were analyzed using the same procedures described above. Data were regressed using the program of LUDWIG (1990). As isochrons obtained in this study have rather large MSWD values (>100), age calculations were based on Model 2, which assigns equal weights and zero error-correlations to each point. The results of Model 1 calculation, which assumes that all scatter is due to analytical error, are also shown. The errors indicated for ages and initial isotopic ratios are expressed at the 95% confidence limits. The decay constant used for ^{87}Rb was $1.42 \times 10^{-11} \text{ yr}^{-1}$.

RESULTS AND DISCUSSION

Immel Mine, Mascot-Jefferson City District, East Tennessee

The MVT deposits in east Tennessee are hosted by the Lower Ordovician Kingsport Formation of the Knox Group. The top of the Knox Group is marked by an extensive Middle Ordovician unconformity and MVT ores occur in collapse breccias formed by karstification beneath this unconformity (HOAGLAND, 1976). There has been considerable debate about the timing of MVT mineralization in this district. KENDALL (1969), HOAGLAND et al. (1965), and CHURNET (1985) argued for early Paleozoic ages on the basis of geological observations. On the other hand, ^{40}Ar - ^{39}Ar ages of low-temperature K-feldspars in the southern Appalachians led HEARN et al. (1987) to conclude that mineralization took place in the late Paleozoic. From these results, it has been suggested that Appalachian MVT deposits formed from large-scale migration of basal brines during the late-Paleozoic Alleghenian Orogeny that took place 250–330 Ma (HEARN et al., 1987; OLIVER, 1986).

The three samples used in this study were collected from the same orebody within about a 100 m radius. A single sample was taken from specimen I-23, three from I-24, two from I-17, and four from an unnumbered specimen that had particularly well-developed layering. Rb and Sr abundances and Sr isotopic compositions of the sphalerites analyzed are indicated in Table 1a and Fig. 2a. Because the sphalerites from this district are known to have experienced deformation and to contain some secondary fluid inclusions, the leachate data were not used in calculating an isochron. The Rb-Sr isochron defines an age of 347 ± 20 Ma with an initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.7103 ± 3 (MSWD = 192) using Model II of the Ludwig program. If Model I is used, an age and an initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 346 ± 44 Ma and 0.7103 ± 3 , respectively, are obtained. If the leachates are included in the regression, an isochron gives an age of 343 ± 11 Ma with an initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.7104 ± 1 (Model II). Apparent Rb-Sr ages calculated for leachate-sphalerite pairs (Table 1a) show about

a 20% variation from the isochron age. It is accepted that the formation of MVT deposits may last 0.5–5 Myr (for example, GARVEN, 1985); that is, an order of magnitude longer than most mineral deposits related to igneous activity. It is doubtful that the initial isotopic ratios of the ore minerals were uniform (HART et al., 1981) over this time span, an interpretation supported by the variation, albeit limited, in initial $^{87}\text{Sr}/^{86}\text{Sr}$ of inclusion fluids at 347 Ma (0.7102 to 0.7106).

The 347 ± 20 Ma age agrees with the previously reported age of 377 ± 29 Ma for sphalerites from the Coy mine in the Mascot-Jefferson City district (NAKAI et al., 1990). It is certain that sphalerites from the two mines precipitated from brines with similar Sr isotopic compositions. The initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio for sphalerite from the Coy mine is 0.7107 ± 3 , which is higher, but similar to, the initial ratio for sphalerite from the Immel mine (0.7103 ± 3), which is 20 km to the west. The fluid inclusions in the sphalerites from the two mines can also be divided into two groups according to their Sr isotopic ratios. Initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of fluid inclusions range between 0.7102 and 0.7106 in the sphalerites from Immel mine and between 0.7104 and 0.7111 in the sphalerites from Coy mine. It can be seen from Fig. 2b that the Sr isotopic ratios of the inclusion fluids from Coy mine generally scatter above the best fit regression line determined for the respective sphalerite residues, while the Sr isotopic ratios of the inclusion fluids from Immel mine scatter around the isochron for the sphalerites' residues. These variations in initial ratio between two mines are hardly surprising, since by nature, hydrothermal fluids rarely equilibrate with all of the mineral assemblages with which they interact. This is supported by the observation that oil field brines from a single oil field show considerable variation in Sr isotopic compositions (CHAUDHURI, 1978; STUBER et al., 1984). A general inverse correlation between homogenization temperature and salinity, suggesting the existence of two different fluids, led TAYLOR et al. (1983) to conclude that mixing between evolved connate brines and fluids resident in the host limestone triggered precipitation of the ore. The difference in Sr isotopic compositions in fluid inclusions between the two mines might reflect different mixing ratios of the two fluids. KESSEN et al. (1981) and KESLER et al. (1988) reported that the gangue minerals precipitated from early (pre-ore) dolomite-forming brines had similar Sr isotopic ratios to their host rocks but later gangue minerals had Sr that was more radiogenic. The ore fluids contained more radiogenic Sr than their host carbonate rocks, whose $^{87}\text{Sr}/^{86}\text{Sr}$ ratio was between 0.709–0.710 (KESSEN et al., 1981; KESLER et al., 1988). Compared with reported $^{87}\text{Rb}/^{86}\text{Sr}$ values for fluid inclusions in ore minerals from MVT deposits (<0.02); (BRANNON et al., 1991, 1992), the values for leachate obtained in this study are high. As mentioned in the section on techniques, it is suspected that the separation of leachates from residues with centrifugation was not complete.

As TAYLOR et al. (1983) indicated, fluid mixing might have played an important role in ore precipitation. However, the question of isotopic homogeneity of the brine seems not to be a serious problem in this district. The variations in initial ratio (0.7102–0.7106) are limited in inclusion fluids of sphalerites from Immel mine. The rise in Sr ratio of the brine through the paragenetic sequence recorded in gangue

Table 1a Rb-Sr data for sphalerites and their fluid inclusions

Sample		Rb(ppm)	Sr(ppm)	$^{87}\text{Rb}/^{86}\text{Sr}$	$^{87}\text{Sr}/^{86}\text{Sr}$	Apparent sphalerite-fluid Age (Ma)
Immel Mine, East Tennessee						
1	r	0.129	0.177	2.09	0.72048 ± 3	347
	l	0.0315	1.08	0.158	0.71093 ± 3	
2	r	0.166	0.659	0.726	0.71381 ± 2	318
	l	0.0275	0.916	0.0657	0.71082 ± 2	
3	r	0.162	0.421	1.10	0.71565 ± 2	349
	l	0.0277	1.21	0.0865	0.71062 ± 2	
4	r	0.225	0.450	1.44	0.71779 ± 2	357
	l	0.0136	0.249	0.0833	0.71090 ± 2	
I17L	r	0.144	1.28	0.324	0.71176 ± 2	288
	l	0.0109	0.450	0.0701	0.71072 ± 2	
I17D	r	0.156	1.16	0.384	0.71219 ± 2	298
	l	0.0121	0.824	0.0422	0.71074 ± 1	
I23	r	0.136	0.834	0.470	0.71243 ± 2	309
	l	0.0180	0.509	0.102	0.71081 ± 2	
I24-1	r	0.138	1.14	0.350	0.71198 ± 2	329
	l	0.0285	0.620	0.132	0.71096 ± 2	
I24-2	r	0.148	1.12	0.379	0.71246 ± 2	338
	l	0.0266	1.01	0.0759	0.71100 ± 2	
I24-3	r	0.137	1.13	0.309	0.71216 ± 2	385
	l	0.0256	0.610	0.121	0.71113 ± 2	
Daniel's Harbour mine, Newfoundland						
DH1	r	0.226	1.91	0.341	0.71148 ± 1	370
	l	0.0183	1.89	0.0278	0.70983 ± 2	
DH2	r	0.137	0.309	1.27	0.71860 ± 1	487
	l	0.0109	0.391	0.0801	0.71034 ± 2	
DH3 I	r	0.0514	0.178	0.831	0.71484 ± 3	392
	l	0.00378	0.168	0.0649	0.71056 ± 17	
DH3 II	r	0.0162	0.0691	0.676	0.71459 ± 4	519
	l	0.0120	0.323	0.107	0.71038 ± 4	
DH4 I	r	0.0752	0.217	0.997	0.71635 ± 3	421
	l	0.00951	0.348	0.0788	0.71085 ± 2	
DH4 II	r	0.0819	0.214	1.10	0.71597 ± 5	361
	l	0.00734	0.203	0.105	0.71085 ± 4	
DH5	r	0.0827	0.210	1.13	0.71651 ± 4	451
	l	0.00954	0.590	0.0466	0.70955 ± 3	
DH6	r	0.0239	0.0784	0.864	0.71382 ± 3	393
	l	0.00307	0.130	0.0681	0.70937 ± 2	
Pine Point district						
zone3 D	r	0.573	0.197	8.40	0.75218 ± 10	
zone3 L	r	0.594	0.345	4.97	0.73409 ± 6	
zone3	r	0.361	0.334	3.11	0.72552 ± 2	
zone2	r	0.107	0.312	0.989	0.71447 ± 2	434
	l	0.00267	0.0708	0.109	0.70903 ± 3	
PP-N38	r	0.148	0.319	1.34	0.71521 ± 2	358
	l	0.0121	0.0391	0.0890	0.70884 ± 3	
PP	r	0.022	0.0697	1.04	0.71401 ± 5	373
	l	0.00102	0.132	0.0222	0.70860 ± 2	
PP J44	r	0.0118	0.0556	0.609	0.71119 ± 2	
O28-2L	r	0.162	0.0625	7.49	0.74647 ± 14	

Table 1a. (Continued)

Sample	Rb(ppm)	Sr(ppm)	$^{87}\text{Rb}/^{86}\text{Sr}$	$^{87}\text{Sr}/^{86}\text{Sr}$	Apparent sphalerite-fluid Age (Ma)
Monte Cristo mine, Northern Arkansas					
AR4-II r	0.0110	0.0126	2.53	0.73154±6	625
l	0.00146	0.0571	0.0735	0.70965±2	
AR4-III r	0.00534	0.00620	2.49	0.72855±9	551
l	0.00114	0.0448	0.0732	0.70957±3	
AR4-III1	0.0114	0.0347	0.0946	0.70966±4	

Footnote to Table 1a: The suffix "r" and "l" in the "Sample no." column denote residue and leachate, respectively. Uncertainties of Sr isotopic compositions are two sigma.

Rb and Sr concentrations of fluid inclusions were calculated based on total starting sample weight.

minerals in this district (KESSEN et al., 1981; KESLER et al., 1988) are also limited compared to the variations in Sr isotopic compositions of the sphalerite residues. In addition, a plot of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and $1/\text{Sr}$ does not show a linear relationship characteristic of two-component mixing.

The locations of Rb and Sr in sphalerite are uncertain (NAKAI et al., 1990; BRANNON et al., 1991). The Rb/Sr ratio of the sphalerites (>0.5) differs from that of carbonate, fluorite, and barite, but could be similar to K-feldspar or clay minerals. Hence, it is possible that such a phase is the real host for these elements. Scanning electron microscopy (SEM) revealed that sphalerites from this district contain only sparse K-feldspar or quartz inclusions, and that K-feldspar constitutes <0.1% of hand-picked sphalerite. Quartz would have a negligible effect on the Rb-Sr system in sphalerite. Low-temperature K-feldspars are distributed in both unmineralized carbonate rocks and ore zones. In order to assess further its possible contribution, Rb and Sr of K-feldspar from unmineralized carbonate rocks in the Immel mine were analyzed. The data are given in Table 2 and plotted in Fig. 3 along with the reference isochron for the sphalerites from Immel mine. The (6 M HCl) leachable portion of the K-feldspars had higher Rb/Sr ratios and more radiogenic Sr than the

bulk minerals dissolved in hydrofluoric acid. This result might be due to the outer part of the K-feldspars having a higher Rb/Sr ratio. These K-feldspars are mixtures of detrital cores and low-temperature overgrowths. Hence, the slope of the best fit line for the K-feldspars (580 Ma) has no geochronological significance. Since the HCl leach mimics the procedure adopted in dissolving sphalerite, it yields analyses that fall on the line delineated by total analyses, and it is clear that the sphalerite isochron is not an artifact of the leaching of alkali feldspar. All of the data for the K-feldspar plot well above the isochron for the sphalerites. It is concluded that mixing between K-feldspar and other components with a lower Rb/Sr ratio cannot have formed the observed sphalerite isochron. In addition, K concentrations were determined for four sphalerite samples of the unnumbered hand specimen (Table 1b). A plot of concentrations of K and Sr does not show the linear correlation characteristic of two-component mixtures.

The extensive work of BRANNON et al. (1991) failed to confirm a suitable phase which can host radiogenic Sr other than the sulfide mineral itself, including sphalerite. If the Rb and Sr are located in the sphalerite, it is uncertain what site the elements occupy. It is unlikely that Rb and Sr, whose

Table 1b. K data for sphalerites from Immel mine, East Tennessee

sample	K (ppm)
1r	19.4
1l	9.06
2r	26.9
2l	14.3
3r	25.6
3l	12.9
4r	38.5
4l	14.1

Concentrations determined by isotope dilution, based on total starting sample weight.

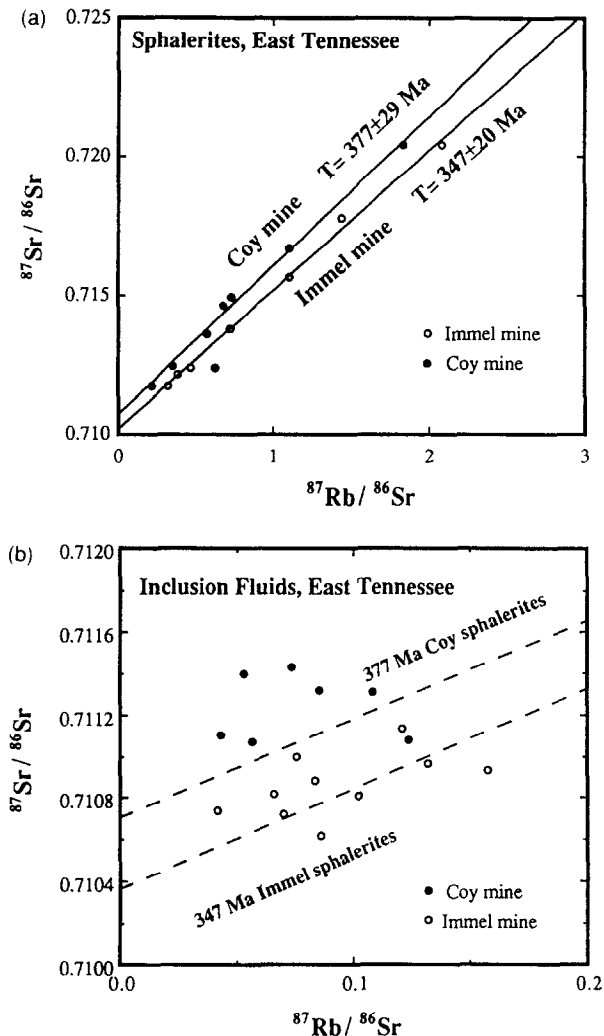


FIG. 2. (a) Rb-Sr isochrons of sphalerites from Coy mine and Immel mine, Mascot-Jefferson city district, east Tennessee. Open circles denote the sphalerites from the Immel mine. The isochron for sphalerites from the Immel mine gives an age of 347 ± 20 Ma with an initial $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.7103 ± 3 (MSWD = 192). The Rb-Sr isochron of sphalerites from the Coy mine is also shown. Data for the sphalerites from the Coy mine are taken from NAKAI et al. (1990) and the data points are shown as filled circles. The isochron gives an age of 377 ± 29 Ma with an initial $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.7107 ± 3 (MSWD = 62.6). (b) Rb-Sr diagram of fluid inclusions in sphalerites from Immel mine and Coy mine. Data for the sphalerites from the Coy mine are taken from NAKAI et al. (1990). Filled circles and open circles denote fluid inclusions of sphalerites from Coy mine and those from Immel mine, respectively. The two dashed lines are isochrons regressed for sphalerite residues from Coy mine and Immel mine.

ionic radii are 1.52 \AA and 1.18 \AA (SHANNON, 1976), can occupy a zinc site (0.60 \AA). It is possible that they are located in crystal defects; however, the mechanism required to generate high Rb/Sr ratios is uncertain. Variable $^{87}\text{Rb}/^{86}\text{Sr}$ ratios for the residues of the sphalerites obtained probably stem from the fact that samples were taken from different stages of deposition. Samples from a single hand specimen (two samples from I17 and three from I24) show a limited range in $^{87}\text{Rb}/^{86}\text{Sr}$ ratios.

The two ages for the sphalerites from Coy mine and Immel mine, 394 Ma and 357 Ma, respectively, indicate that ore

formation in east Tennessee took place in the Devonian and predated the Alleghenian Orogeny. These ages are coincident with the mid-Paleozoic Acadian Orogeny. The Acadian Orogeny has been thought to have had its strongest effect in the northeastern Appalachian Mountains (GLOVER et al., 1983). However, HATCHER and ODOM (1980) reported that thrusting took place during the Devonian in the southern Appalachian Blue Ridge located immediately to the southeast of the Mascot-Jefferson City district. In addition, recent faunal and geologic studies suggest that this area was the site of a Devonian-age foreland basin (UNRUG and UNRUG, 1990; TULL and GROSZOC, 1990). Devonian events have also been found in the midcontinent. The Rb-Sr systematics of glauconites from the Bonneterre formation, Missouri (STEIN and KISH, 1985, 1991) recorded late Devonian-early Mississippian fluid migration. Glauconites from Ohio, Indiana, and Missouri gave Devonian Rb-Sr ages concordant with K-Ar ages (GRANT et al., 1984). Finally, MACINTYRE (1986) reported K-Ar ages of K-feldspar in sediments from Ohio, Indiana, and Missouri of between 360 and 390 Ma which he related to the passage of MVT mineralizing fluids. There is therefore a reasonable body of evidence to support the view that the Devonian represented an important period of migration of hot brines and mineralization in the southeast USA (KESLER and VAN DER PLUIJM, 1990).

Daniel's Harbour Mine, Newfoundland

The Newfoundland Zinc Mine in western Newfoundland is the northernmost example of Appalachian-type sphalerite-rich MVT mineralization (HOAGLAND, 1976). Mineralization here consists almost entirely of sphalerite and sparry dolomite in porous, burrowed zones in the Lower Ordovician St. George Formation (COLLINS and SMITH, 1975; SWINDEN et al., 1988; LANE, 1989). KESLER and VAN DER PLUIJM (1990) have called attention to the strong similarities between MVT mineralization in this district and that hosted by Lower Ordovician carbonates in other parts of the Appalachians, including the Mascot-Jefferson City district. As they pointed out, this similarity could provide an important contribution to the definition of the age of MVT mineralization and its relation to Appalachian tectonic evolution because deformation was essentially complete in Newfoundland by the end of the Acadian (Devonian) Orogeny. Partial confirmation of this age was obtained by HALL et al. (1989), who reported $^{40}\text{Ar}/^{39}\text{Ar}$ ages of 350 to 370 Ma on authigenic feldspars associated with mineralization.

Six samples were chosen to represent the paragenetic and spatial range of mineralization for Rb-Sr analyses. These samples form two spatial groups and two paragenetic groups. In terms of paragenesis, samples 1, 2, and 3 represent early sphalerite, whereas samples 5 and 6 represent late sphalerite. Sample 4 is of uncertain paragenesis and could contain both stages of mineralization. In terms of location, samples 2, 3, 5, and 6 are from a single ore body and were deposited within less than 300 m of each other; sample 4 is from a distal part of this orebody about 600 m from the first group; sample 1 is from a completely distinct orebody almost 3 km from the other samples.

The results of Rb-Sr analyses of the sphalerites are given in Table 1a and plotted in Fig. 4. Data for the sphalerite

Table 2 Rb-Sr data for K-feldspars from Immel mine, East Tennessee

Sample	Rb(ppm)	Sr(ppm)	$^{87}\text{Rb}/^{86}\text{Sr}$	$^{87}\text{Sr}/^{86}\text{Sr}$
I12 HCl	30.5	2.10	43.4	1.09503±3
I12 HF	99.2	22.5	12.8	0.82828±2
I32 HCl	27.6	3.79	21.4	0.92452±3
I32 HF	78.2	28.1	8.10	0.79996±3
I34 HCl	35.6	4.58	22.8	0.89343±3
I34 HF	450	153	8.52	0.8022±10

Samples with "HCl" and "HF" were leached with hot 6M HCl and dissolved with HF, respectively. Rb and Sr concentrations of samples leached with HCl were calculated using whole sample weight. Uncertainties of Sr isotopic compositions are two sigma.

residues in Fig. 4 do not fall on a single line. Both the fluid inclusion leachate and the residue analyses appear to form two somewhat distinct populations. Inclusion leachates from samples 2 and 3 contain Sr that is more radiogenic than those in leachate samples 1, 5, and 6. Similarly, residues for samples 2, 3, and 4 contain Sr that is more radiogenic for the Rb/Sr ratio than those for samples 1, 5, and 6. Analyses of 2 residues from sample 4 are split between the two groups, consistent with the suspected presence of both stages of mineralization in this sample. Thus, with the exception of sample 1 (which is geographically remote from the others), the Sr isotopic data parallel the petrographic evidence in that early sphalerite is either distinctly older (by tens of millions of years) or was precipitated from fluids with Sr that was more radiogenic than that found in late sphalerite. No reliable age information is available from these data.

Pine Point District

The Pine Point district in the Northwest Territories, Canada is a major area of MVT mineralization (KYLE, 1981). The lead-zinc orebodies occur in a Middle Devonian carbonate barrier complex, the "Presqu'île Formation," that separated the MacKenzie shale basin to the northwest from the Elk Point evaporite basin to the southeast (SKALL, 1975; KYLE, 1981; RHODES et al., 1984). Like other MVT deposits, the age of mineralization in this district has been the subject of much controversy. The homogeneity and nonradiogenic lead isotope compositions of galena from this district are quite different from those of galena-rich mid-continent MVT deposits such as the Tri-State district. CUMMING et al. (1990) determined a late Pennsylvanian (290 Ma) model lead age based on the STACEY and KRAMERS (1975) model. GARVEN

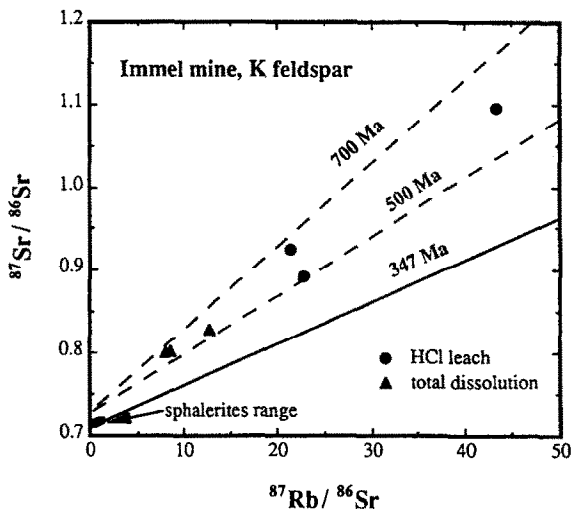


FIG. 3. Rb-Sr diagram of K-feldspars from Immel mine. Circles and triangles denote minerals treated with HCl and those totally dissolved, respectively. The solid line indicates an isochron for sphalerites from the same mine. Range of Rb/Sr ratios of the sphalerites from this mine is shown as a thick solid line.

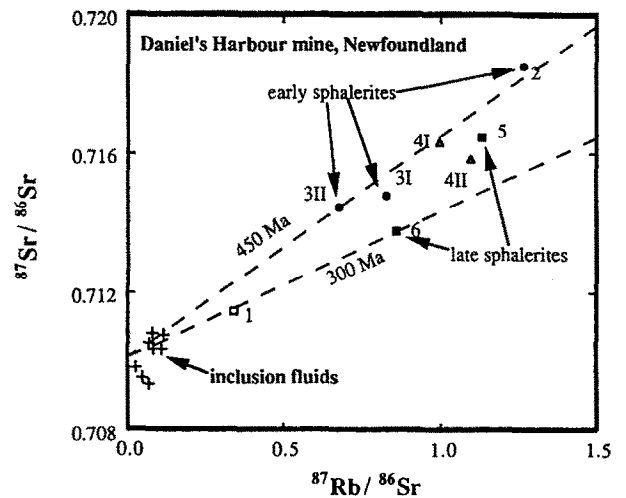


FIG. 4. Rb-Sr plot of sphalerites from Daniel's Harbour mine, Newfoundland. Filled circles and filled squares denote early and late sphalerites from a single orebody, respectively. Open triangles and open squares denote sphalerites from distal part of the same orebody and from distinct orebodies, respectively (see text). Crosses denote fluid inclusion leachates.

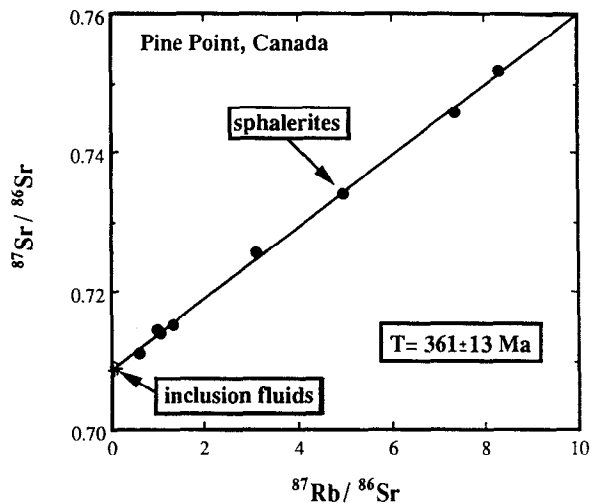


FIG. 5. Rb-Sr isochron of sphalerites from Pine Point district. Circles and crosses denote residues and leachates, respectively. The isochron gives an age of 361 ± 13 Ma with an initial $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.7087 ± 8 (MSWD = 116).

(1985) proposed a gravity-driven fluid migration model in which groundwater fluids were driven by hydraulic gradients and applied the model to the Pine Point district. He suggested that ore genesis took place in the Eocene when hydraulic gradients across the basin could have been greatest because of the uplift of the Rocky Mountains.

The results of Rb-Sr analyses of the sphalerites are indicated in Table 1a and a Rb-Sr diagram for the sphalerites is shown in Fig. 5. The isochron regressed on all eight sphalerite residues gives an age of 361 ± 13 Ma (MSWD = 116), with an initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.7087 ± 8 using Model II of the Ludwig program. Model I calculation gives an age of 361 ± 32 Ma, with an initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.7089 ± 7 . If the leachates are included in the regression, isochron gives an age of 363 ± 9 Ma with an initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.7086 ± 5 . This age suggests that ore formation took place shortly after deposition of the host carbonate rocks. Our result is not consistent with a model that ascribes the mineralization to regional fluid migration related to early Cenozoic Cordilleran deformation. Furthermore, the initial Sr ratio, 0.7086, is nearly as low as that of the host carbonate rocks (MEDFORD et al. 1983). SEM examination of sphalerite from this location demonstrated that the samples contain no inclusions other than galena. The Rb and Sr abundance data of galena from the Viburnum Trend, southeast Missouri reported by BRANNON et al. (1991) show that abundances of the two elements and Rb/Sr ratio of galena cannot be much higher than values for sphalerite. Therefore, it is unlikely that minute inclusions of galena affect Rb/Sr ratios of sphalerite, suggesting that the sphalerite itself has high and variable Rb/Sr ratios.

MVT Deposits in Northern Arkansas

The Monte Cristo mine in the north Arkansas MVT district is hosted by carbonate rocks of the Ordovician Everton Formation. The orebody consists of sphalerite and sparry dolomite that fill breccia porosity and replace favorable horizons (LONG et al., 1986). This mineralization is part of the ex-

tensive mid-continent MVT province. LEACH and ROWAN (1986) proposed that late Pennsylvanian-early Permian orogenesis in the Ouachita foldbelt expelled fluids from the Arkoma basin to form these MVT deposits. Sphalerites from the Monte Cristo mine were analyzed in this study.

The results of Rb-Sr analyses of the sphalerites are indicated in Table 1a and Rb-Sr diagrams for the sphalerites are shown in Fig. 6. Because of extremely low Sr concentrations, the requirement of more than one gram of sample for precise isotopic measurements made it difficult to obtain samples of sphalerites from a single generation. The two sphalerites analyzed have similar and high Rb/Sr ratios, whereas the fluid inclusions contain Sr that is considerably less radiogenic. The differences between the fluid inclusions and host sphalerite cannot be attributed solely to *in situ* radioactive decay since the data define an apparent age of approximately 600 Ma, that is, in excess of the age of the host rocks (Fig. 6). SEM analysis of a sample of AR-4 showed that the sphalerite was pure except for small pores. Although no actual solid inclusion was recognized, EDA responses for Ca-Al-Si were detected from these holes. Among all sphalerites examined, these are the only ones that may have clay inclusions. If the pits represent some clay inclusions that are detrital in origin, they could cause the erroneous old ages.

Figure 7 summarizes Sr concentrations for the sphalerites used in this study. There is a clear distinction between sphalerites that can be dated by Rb-Sr methods and those which cannot. Because the sphalerites from northern Arkansas contain very little Rb and Sr, it is likely that their Rb-Sr isotopic systematics have been dominated by minute amounts of inherited silicate inclusions such as clay minerals. BRANNON et al. (1991) reported that $^{87}\text{Sr}/^{86}\text{Sr}$ in solid sulfide minerals is commonly higher than the associated fluid inclusions. The cause of this is unclear but could be analogous to the effect observed for the Arkansas samples studied here.

MVT MINERALIZATION AND CONTINENT-SCALE FLUID FLOW MODELS

One of the most important aspects of this study is the discovery that some MVT mineralization in the Appalachian

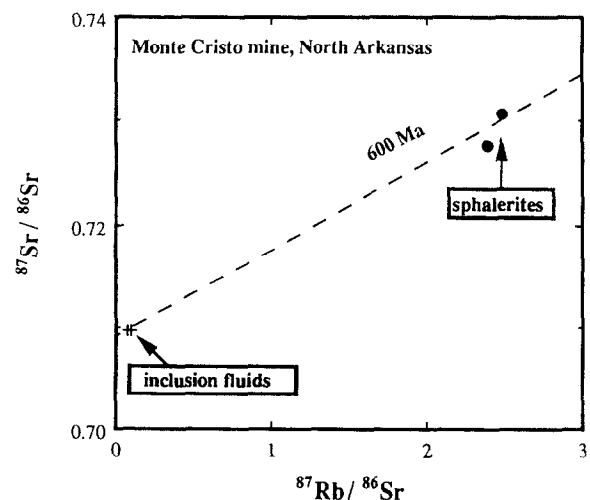


FIG. 6. Rb-Sr diagram of sphalerite from Northern Arkansas district. Circles and crosses denote residues and leachates, respectively.

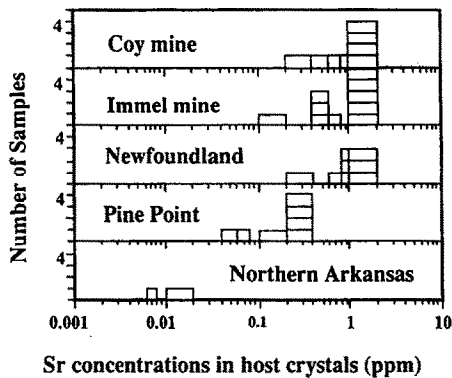


FIG. 7. Sr abundance histogram of sphalerites analyzed in this study.

orogen was not produced during the Permian Alleghenian/Ouachita Orogeny. In recent years there has been a tendency to emphasize very large-scale transport and the importance of global orogenic processes in consanguineous MVT mineralization, deformation, very low-grade metamorphism, and hydrocarbon migration triggered by a Permian event (BETHKE and MARSHAK, 1990; OLIVER, 1986; HEARN et al., 1987; ELLIOT and ARONSON, 1987; MCCABE et al., 1983; BACHTADSE et al., 1987; SUK et al., 1990). Permian Rb-Sr ages for sphalerites from the Upper Mississippi Valley by BRANNON et al. (1992) provide clear evidence that the uplift of the Pascola Arch initiated by the Alleghenian/Ouachita Orogeny triggered MVT ore formation in this area. However, our data implicate strongly proximal sedimentary basin evolution in Devonian time as the prime mechanism for generating MVT mineralization in east Tennessee. Multiple fluid migration was reported by HAY et al. (1988), who obtained a late Devonian K-Ar and Rb-Sr age for authigenic K-feldspar and Permian K-Ar age for illite-smectite clay from a single drill core sample from northeastern Missouri which indicated two periods of brine migration in the midcontinent. These lines of evidence suggest the possibility that Devonian events occurred on a continental scale.

This study has touched upon only a few MVT deposits in North America. It is clearly necessary to obtain meaningful absolute age information on many other North American MVT deposits before further general models can be considered. Some of these deposits may be amenable to Rb-Sr dating of sulfides as in this study and the study by BRANNON et al. (1992), Rb-Sr dating of quartz (SHEPHERD and DARBYSHIRE, 1981), U-Pb dating of carbonates (HOFF and JAMESON, 1989; DEWOLF and HALLIDAY, 1991), or Sm-Nd dating of fluorite (HALLIDAY et al., 1990; CHESLEY et al., 1991).

CONCLUSIONS

- 1) The results of this study confirm the general usefulness of the Rb-Sr method for dating sphalerites. The Rb-Sr dating of sphalerites can play a key role in elucidating the genesis of MVT and other types of ore deposits. Sphalerite is a common mineral in sedimentary basins; therefore this technique may be applied to determine the timing of fluid flow from sedimentary basins. Isotopic inhomogeneity of ore brines limits the accuracy of sphalerite dating.

Samples for dating should be taken from the same ore body, preferably from the same hand specimen. However, there is a tradeoff, since individual hand specimens may exhibit a rather limited spread in Rb/Sr ratio.

- 2) Pure sphalerites have reasonably high Rb/Sr ratios, much higher than their associated fluid inclusions, for example. The measured Rb and Sr appears to be primarily hosted in the sphalerite itself rather than in silicate inclusions. It appears that sphalerite fractionates Rb from Sr when it precipitates from mineralizing brines by excluding Sr more than Rb, although the details of the mechanism are unknown. It is not certain where Rb and Sr are located in sphalerites. These elements are too large to enter the site for Zn and are almost certainly associated with crystal defects.
- 3) The Rb-Sr age for the sphalerites from Immel mine, east Tennessee, agrees with the age for Coy mine mineralization reported previously, indicating that MVT deposits in the district formed between 350 and 380 Ma. These results suggest that the mineralization events are not related to the late Paleozoic Alleghenian Orogeny, but are more probably related to the mid-Paleozoic Acadian Orogeny.
- 4) Similarly, MVT mineralization at Pine Point took place at 360 Ma, shortly after deposition of the carbonate host rocks. These results suggest that mineralization was not associated with the regional fluid migration related to the early Tertiary Cordilleran deformation.
- 5) Sphalerites with very low Sr concentrations are difficult to date because their Sr isotopic compositions are easily affected by small amounts of silicate inclusions.

Acknowledgments—We are grateful to R. Keller and M. Johnson for technical assistance. This study was supported by NSF grants EAR-88-04072 and EAR-90-04413 to ANH, the University of Michigan Turner Fund, the Michigan Memorial Phoenix Project, the Office of the Vice-President for Research, and the Shell Foundation. We thank K. Mezger for discussion and criticism of the manuscript. The comments of J. Banner and an anonymous reviewer were particularly helpful for improving this manuscript.

Editorial handling: Scott Wood

REFERENCES

- BACHTADSE V., VAN DER VOO R., HAYNES F. M., and KESLER S. E. (1987) Late Paleozoic magnetization of mineralized and unmineralized Ordovician carbonate from East Tennessee: Evidence for a post-ore chemical event. *J. Geophys. Res.* **92B**, 165–176.
- BETHKE C. M. and MARSHAK S. (1990) Brine migrations across North America—The plate tectonics of groundwater. *Ann. Rev. Earth Planet. Sci.* **18**, 287–315.
- BRANNON J. C., PODOSEK F. A., VIETS J. G., LEACH D. L., GOLDHABER M., and ROWAN E. L. (1991) Strontium isotopic constraints on the origin of ore-forming fluids of the Viburnum Trend, southeast Missouri. *Geochim. Cosmochim. Acta* **55**, 1407–1419.
- BRANNON, J. C., PODOSEK, F. A., and MCLIMANS, R. K. (1992) A Permian Rb-Sr age for sphalerite from the Upper Mississippi zinc-lead district, Wisconsin. *Nature* **356**, 509–511.
- CHAUDHURI S. (1978) Strontium isotopic composition of several oilfield brines from Kansas and Colorado. *Geochim. Cosmochim. Acta.* **42**, 329–331.
- CHESLEY J. T., HALLIDAY A. N., and SCRIVENER R. C. (1991) Samarium-neodymium direct dating of fluorite mineralization. *Science* **252**, 949–951.

- CHURNET H. G. (1985) Fluid inclusion evidence for fluid mixing, Mascot-Jefferson City zinc district, Tennessee—A discussion. *Econ. Geol.* **80**, 1440–1443.
- COLLINS J. A. and SMITH L. (1975) Zinc deposits related to diagenesis and intrakarstic sedimentation in the lower Ordovician St. George Formation, western Newfoundland. *Bull. Canadian Petrol. Geol.* **23**, 393–427.
- CUMMING G. L., KYLE J. R., and SANGSTER D. F. (1990) Pine Point: A case history of lead isotope homogeneity in a Mississippi Valley-type district. *Econ. Geol.* **85**, 133–144.
- DEWOLF C. P. and HALLIDAY A. N. (1991) U-Pb dating of a remagnetized Paleozoic limestone. *Geophys. Res. Lett.* **18**, 1445–1448.
- ELLIOTT W. C. and ARONSON J. L. (1987) Alleghanian episode of K-bentonite illitization in the southern Appalachian basin. *Geology* **15**, 735–739.
- GARVEN G. (1985) The role of regional fluid flow in the genesis of the Pine Point deposits, Western Canada sedimentary basins. *Econ. Geol.* **80**, 307–324.
- GLOVER L., III, SPEER J. A., RUSSEL G. S., and FARRAR S. (1983) Ages of regional metamorphism and ductile deformation in the central and southern Appalachians. *Lithos* **16**, 223–245.
- GRANT N. K., LASKOWSKI T. E., and FOLAND K. A. (1984) Rb-Sr and K-Ar ages of Paleozoic glauconites from Ohio-Indiana and Missouri, U.S.A. *Isotope Geosci.* **2**, 217–239.
- HALL C. M., YORK D., SAUNDERS C. M., and STRONG D. F. (1989) Laser $^{40}\text{Ar}/^{39}\text{Ar}$ dating of Mississippi Valley-type mineralization in western Newfoundland. *International Geological Congress Abstract Volume*, 2–10.
- HALLIDAY A. N., SHEPHERD T. J., DICKIN A. P., and CHESLEY J. T. (1990) Sm-Nd evidence for the age and origin of Mississippi Valley Type ore deposits. *Nature* **344**, 54–56.
- HANOR J. S. (1979) The sedimentary genesis of hydrothermal fluids. In *Geochemistry of Hydrothermal Ore Deposits*, 2d ed. (ed. H. L. BARNES), pp. 137–142. Wiley-Interscience.
- HART S. R., SHIMIZU N., and SVERJENSKY D. A. (1981) Lead isotope zoning in galena: An ion microprobe study of a galena crystal from Buick Mine, Southeast Missouri. *Econ. Geol.* **76**, 1873–1878.
- HATCHER R. D. and ODOM A. L. (1980) Timing of thrusting in the southern Appalachians, USA: Model for orogeny? *J. Geol. Soc. London*. **137**, 321–327.
- HAY R. L., LEE M., KOLATA D. R., MATTHEWS J. C., and MORTON J. P. (1988) Episodic potassic diagenesis of Ordovician tuffs in the Mississippi Valley area. *Geology* **16**, 743–747.
- HEARN P. P., JR., SUTTER J. F., and BELKIN H. E. (1987) Evidence for Late-Paleozoic brine migration in Cambrian carbonate and southern Appalachians: Implications for Mississippi Valley-type sulfide mineralization. *Geochim. Cosmochim. Acta* **51**, 1323–1334.
- HOAGLAND A. D. (1976) Appalachian lead-zinc deposits. In *Handbook of Stratabound and Stratiform Ore Deposits*. (ed. K. H. WOLFE), Vol. 6, pp. 495–534. Elsevier.
- HOAGLAND A. D., HILL W. T., and FULWEILER R. E. (1965) Genesis of the Ordovician zinc deposits in East Tennessee. *Econ. Geol.* **60**, 693–714.
- HOFF J. A. and JAMESON J. (1989) Timing of uranium enrichment in dolostones from the Wahoo Formation, subsurface, Prudhoe Bay, Alaska. *Geol. Soc. Amer. Abstr. Prog.* **22**, 16.
- KENDALL D. L. (1969) Ore deposits and sedimentary features, Jefferson City Mine, Tennessee. *Econ. Geol.* **55**, 985–1003.
- KESLER S. E. and VAN DER PLUIJM B. (1990) Timing of Mississippi Valley-type mineralization: Relation to Appalachian orogenic events. *Geology* **18**, 1115–1118.
- KESLER S. E., JONES L. M., and RUIZ J. (1988) Strontium isotopic geochemistry of Mississippi Valley-type deposits, East Tennessee: Implications for age and source of mineralizing brines. *Geol. Soc. Amer. Bull.* **100**, 1300–1307.
- KESSEN K. M., WOODRUFF M. S., and GRANT N. K. (1981) Gangue mineral $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and the origin of Mississippi Valley-type mineralization. *Econ. Geol.* **76**, 913–920.
- KYLE J. R. (1981) Geology of the Pine Point lead-zinc district. In *Handbook of Stratabound and Stratiform Ore Deposits*. (ed. K. H. WOLFE), Vol. 9, pp. 643–741. Elsevier.
- LANE, T. (1989) Sphalerite/dolomite stratigraphy and the tectonic origin of MVT deposits, Daniels Harbour, Newfoundland, Canada. *Geol. Soc. Amer. Abstr. Prog.* **21**, 48.
- LANGE S., CHAUDHURI S., and CLAUER N. (1983) Strontium isotopic evidence for the origin of barites and sulfides from the Mississippi Valley-type ore deposits in Southeast Missouri. *Econ. Geol.* **78**, 1255–1261.
- LANGE S., CHAUDHURI S., and CLAUER N. (1985) Strontium isotopic evidence for the origin of barites and sulfides from the Mississippi Valley-type ore deposits in Southeast Missouri—A reply. *Econ. Geol.* **80**, 775–776.
- LEACH D. L. and ROWAN E. L. (1986) Genetic link between Ouachita foldbelt tectonism and the Mississippi Valley-type lead-zinc deposits of the Ozark. *Geology* **14**, 931–935.
- LONG K. L., KELLY W. C., OHLE E. L., and LOHMANN K. C. (1986) Ground preparation and zinc mineralization in bedded and breccia ores of the Monte Cristo Mine, North Arkansas. *Econ. Geol.* **81**, 809–830.
- LUDWIG K. R. (1990) ISOPLOT: A plotting and regression program for radiogenic-isotope data, for IBM-PC compatible computers, version 2.01. *USGS Open-file Rept.* 88-557.
- MACINTYRE R. M. (1986) K-Ar ages and MVT deposits (abstr.). *Terra Cognita* **6**, 227.
- MCCABE C., VAN DER VOO R., PEACOR D. R., SCOTSESE C. R., and FREEMAN R. (1983) Diagenetic magnetite carries ancient yet secondary remanence in some Paleozoic sedimentary carbonate. *Geology* **11**, 221–223.
- MEDFORD G. A., MAXWELL R. J., and ARMSTRONG R. L. (1983) $^{87}\text{Sr}/^{86}\text{Sr}$ ratio measurements on sulfides, carbonates, and fluid inclusions from Pine Point, Northwest Territories, Canada: An $^{87}\text{Sr}/^{86}\text{Sr}$ ratio increase accompanying the mineralizing process. *Econ. Geol.* **78**, 1375–1378.
- NAKAI S., HALLIDAY A. N., KESLER S. E., and JONES H. D. (1990) Rb-Sr dating of sphalerites from Tennessee and the genesis of Mississippi Valley type ore deposits. *Nature* **346**, 354–357.
- OHLE E. L. (1980) Some considerations in determining the origin of ore deposits of the Mississippi Valley type, pt. II. *Econ. Geol.* **75**, 161–172.
- OLIVER J. (1986) Fluids expelled tectonically from orogenic belts; Their role in hydrocarbon migration and other geologic phenomena. *Geology* **14**, 99–102.
- RHODES D., LANTOS E. A., WEBB R. J., and OWENS D. C. (1984) Pine Point orebodies and their relationship to the stratigraphy, structure, dolomitization, and karstification of the middle Devonian barrier complex. *Econ. Geol.* **79**, 991–1055.
- RUIZ J., KELLY W. C., and KAISER C. J. (1985) Strontium isotopic evidence for the origin of barites and sulfides from the Mississippi Valley-type ore deposits in Southeast Missouri—A discussion. *Econ. Geol.* **80**, 773–778.
- SHANNON R. D. (1976) Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Cryst.* **A32**, 751–767.
- SHEPHERD T. J. and DARBYSHIRE D. P. F. (1981) Fluid inclusion Rb-Sr isochrons for dating mineral deposits. *Nature* **290**, 578–579.
- SHEPHERD T. J., DARBYSHIRE D. P. F., MOORE G. R., and GREENWOOD D. A. (1982) Rare earth element and isotopic geochemistry of the North Pennine ore deposits. *Bull. Bur. Mech. Gites Min.* **11**, 371–377.
- SKALL H. (1975) The paleoenvironment of the Pine Point lead-zinc district. *Econ. Geol.* **70**, 22–47.
- STACEY J. S. and KRAMERS J. D. (1975) Approximation of terrestrial lead isotope evolution by a two-stage model. *Earth Planet. Sci. Lett.* **26**, 207–221.
- STEIN H. J. and KISH S. A. (1985) The timing of ore formation in southeast Missouri: Rb-Sr glauconite dating at the Magmont Mine, Viburnum Trend. *Econ. Geol.* **80**, 739–753.
- STEIN H. J. and KISH S. A. (1991) The significance of Rb-Sr glauconite ages, Bonnetterre Formation, Missouri: Late Devonian-Early Mississippian brine migration in the Midcontinent. *J. Geol.* **99**, 1468–1481.
- STUBER A. M., PUSHKAR P., and HETHERINGTON E. A. (1984) A strontium isotopic study of Smackover brines and associated solids, southern Arkansas. *Geochim. Cosmochim. Acta* **48**, 1637–1649.
- SUK D., PEACOR D. R., and VAN DER VOO R. (1990) Replacement

of pyrite framboids by magnetite in limestone and implications for palaeomagnetism. *Nature* **345**, 611–613.

SVERJENSKY D. A. (1986) Genesis of Mississippi Valley-type lead-zinc deposits. *Ann. Rev. Earth Planet. Sci.* **14**, 177–199.

SWINDEN H. S., LANE T. E., and THORPE R. I. (1988) Lead-isotope compositions of galena in carbonate-hosted deposits of western Newfoundland: Evidence for diverse lead source. *Canadian J. Earth Sci.* **25**, 593–602.

TAYLOR M., KESLER S. E., CLOKE P. L., and KELLY W. C. (1983) Fluid inclusion evidence for fluid mixing, Mascot-Jefferson City zinc district, Tennessee. *Econ. Geol.* **78**, 1425–1439.

TULL J. F. and GROSZOC T. L. (1990) Nested Paleozoic “successor” basins in the southern Appalachian Blue Ridge. *Geology* **18**, 1046–1049.

UNRUG R. and UNRUG, S. (1990) Paleontological evidence of Paleozoic age for the Walden Creek Group, Ocoee Supergroup, Tennessee. *Geology* **18**, 1041–1045.

WHITE D. E. (1968) Environments of generation of some base-metal ore deposits. *Econ. Geol.* **63**, 301–335.

APPENDIX: SAMPLE IDENTIFICATION

Numbers and descriptions for samples used in this study are listed below. Samples were selected for analysis on the basis of purity of sphalerite (absence of solid inclusions) and abundance of apparently primary fluid inclusions. Samples from east Tennessee and Newfoundland contain large (+20 μm), solitary, primary (?) aqueous inclusions in enclaves of undeformed sphalerites, with smaller secondary inclusions along deformation planes. Fluid inclusions in Pine Point and Monte Cristo samples were smaller and of less obvious origin.

Immel Mine, East Tennessee District

I-17 banded yellow-brown sphalerite from lower R and S bed (-7 to -10 beds)

I-23 massive, coarse grained sphalerite and white, sparry dolomite in upper 70 beds primary dolomite
I-24 coarse grained sphalerite ore in “channel” into limestone (-1 to -4 beds)

Monte Cristo Mine, Arkansas

AR-4 medium, yellow-brown sphalerite crystals up to 2 cm in silicified dolomitic breccia

Newfoundland Zinc District, Newfoundland, Canada

DH-1 massive, red-brown sphalerite from C zone; early
DH-2 colloform, extremely fine crystalline sphalerite from main ore body (L Zone); early
DH-3 coarse crystalline brown to yellow sphalerite from main ore body (L Zone); early
DH-4 coarse crystalline, brown to yellow sphalerite from T zone at west end of L zone; possibly intermediate age between early and late sphalerite
DH-5 coarse crystalline, yellow-brown sphalerite from pillars of massive ore (L-zone); late
DH-6 very coarse crystalline yellow-black sphalerite from main ore body (L-zone); late

Pine Point District, Northwest Territories, Canada

O-28-2 O-28 ore body; 2.5 cm dark brown, banded sphalerite, crust overgrown by white sparry dolomite; white dolomite wall rock
PP-J44 J44 ore body; colloform aggregate of fine grained, acicular sphalerite, three distinct color bands, each about 3 mm thick
PP-N38 N-38 orebody; colloform aggregate of fine grained acicular sphalerite on skeletal galena