Timing of Mississippi Valley-type mineralization: Relation to Appalachian orogenic events

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ABSTRACT

Although Mississippi Valley-type deposits in Lower Ordovician carbonate rocks of the Appalachian orogen are commonly interpreted to have been precipitated by basinal brines, the timing of brine migration remains poorly known. Late Paleozoic K-Ar isotopic ages on authigenic K-feldspar, which is widespread in Appalachian carbonate rocks, as well as evidence of paleomagnetic overprints of similar age, have focused attention on the possibility that these Mississippi Valley-type deposits formed as a result of late Paleozoic deformation. Geologic and geochemical similarities among most of these deposits, from Georgia to Newfoundland, including unusually high sphalerite/galena ratios, isotopically heavy sulfur, and relatively nonradiogenic lead, suggest that they are coeval. Sphalerite "sand" that parallels host-rock layering in many of the deposits indicates that mineralization occurred before regional deformation. Although the late Paleozoic age of deformation in the southern Appalachians provides little constraint on the age of Mississippi Valley-type mineralization, deformation of these deposits in the Newfoundland Appalachians is early to middle Paleozoic in age. Thus, if Ordovicianhosted, Appalachian Mississippi Valley-type deposits are coeval, they must have formed by middle Paleozoic time and cannot be the product of a late Paleozoic fluid-expulsion event. This hypothesis has important implications for basin evolution, fluid events, and remagnetization in the Appalachians.

INTRODUCTION

The most widespread and economically important Mississippi Valley-type deposits in the Appalachians (Fig. 1) are found in Lower Ordovician shelf carbonates from Alabama to Newfoundland (Hoagland, 1976). These deposits formed from saline brines, making them the most visible products of dewatering of Appalachian sedimentary basins (Colton, 1970; Kesler et al., 1988, 1989). Unfortunately, a lack of suitable minerals with high or variable isotopic ratios has made it difficult to determine directly

the age of these deposits. Paleomagnetic and isotopic age measurements, which have been made on authigenic minerals in lower Paleozoic carbonate rocks in the southern and central Appalachians (Bachtadse et al., 1987; Elliott and Aronson, 1987; Hearn et al., 1987), have been used to support the hypothesis that the Mississippi Valley-type mineralization took place during late Paleozoic fluid expulsion from the evolving Appalachian-Ouachita orogen (Leach and Rowan, 1986; Oliver, 1986; Duane and de Wit, 1988; Clendenin and Duane, 1990; Bethke

and Marshak, 1990). As discussed below, the apparent synchroneity of these deposits, along with their deformational history in Newfoundland, limits the age of mineralization to middle Paleozoic time.

GEOLOGIC AND ISOTOPIC SIMILARITIES OF ORDOVICIAN-HOSTED MISSISSIPPI VALLEY-TYPE DEPOSITS

Ordovician-hosted Mississippi Valley-type deposits in the Appalachian orogen have nu-

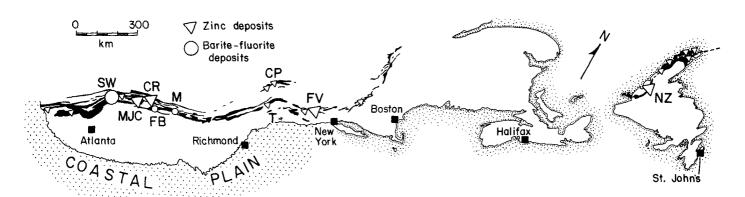


Figure 1. Distribution of Cambrian to Early Ordovician platform carbonates in Appalachian orogen (after Williams, 1978) showing Mississippi Valley-type deposits and prospects hosted by Knox Group (Tennessee), Beekmantown Group (Pennsylvania), and St. George Group (Newfoundland) (after Secrist, 1924; Currier, 1935; Edmunson, 1938; Maher, 1970; Smith, 1977; D. F. Sangster, 1989, written commun.). SW = Sweetwater, MJC = Mascot-Jefferson City, CR = Copper Ridge, FB = Fall Branch, M = Marion, T = Timberville, FV = Friedensville, CP = central Pennsylvania, NZ = Newfoundland zinc. Austinville-Ivanhoe district in Virginia, which is sometimes included in this group (Hearn et al., 1987; Swinden et al., 1988) is in Lower Cambrian Shady Dolomite.

merous geologic characteristics that distinguish them as a group. They are hosted by the same shelf carbonate sequence, known as the Knox Group in Alabama, Georgia, Tennessee, and southern Virginia, the Beekmantown Group in northern Virginia, Maryland, and Pennsylvania, and the Port-au-Port and St. George Groups in Newfoundland (Hoagland, 1976). Mineralization is closely associated with karst breccias that formed during Middle to Late Ordovician emergence of the carbonate platform (Harris, 1971; Howe, 1981; Lane, 1989). Sphalerite in the deposits is anomalously low in iron and enriched in cadmium (Hoagland, 1976). Galena and chalcopyrite are rare (Sangster, 1983), and

barite and fluorite are important only in distinct districts. The only common gangue mineral is sparry dolomite.

Most fluid-inclusion filling temperatures range from about 110 to 170 °C for the sphalerite deposits (Roedder, 1971; Zimmerman and Kesler, 1981; Howe, 1981; Taylor et al., 1983; Lane, 1989). Limited sulfur isotopic data (Table 1) suggest that most of these deposits contain unusually heavy sulfur. Analyses reported here for the eastern Tennessee and Newfoundland deposits, as well as those reported by Howe (1981) for some Nittany arch (central Pennsylvania) mineralization, are between +20% and +30% (Fig. 2), in contrast to values from other

Mississippi Valley-type deposits in North America, which are generally below +20%0. The results reported here for the Friedensville deposit, which are considerably lighter than those seen in the other deposits, might represent contamination of the mineralizing system by diagenetic sulfur, as also seen in some Nittany arch deposits (Howe, 1981). Although lead isotopic compositions of these deposits, including one new analysis of galena from the Immel mine (Table 2), form separate clusters for each district, all of the clusters are less radiogenic than most lead in other North American deposits (Fig. 3).

RELATION OF MISSISSIPPI VALLEY-TYPE MINERALIZATION TO REGIONAL DEFORMATION

The simplest interpretation of the geologic and geochemical similarities listed above is that the Ordovician-hosted, Appalachian Mississippi Valley-type deposits are coeval. Although both ore and host rocks are deformed (Hoagland, 1976), a predeformation age is indicated for mineralization by sphalerite "sands," where layers of dolomite with local detrital sphalerite fill openings in the ore-bearing breccias (Kendall, 1960; Hoagland, 1976, Fig. 10). Parallelism between layering in these sands and that in the enclosing rocks, especially at Copper Ridge (Fig. 1), where dips are relatively steep (Hill, 1969), requires that mineralization preceded deformation. Thus, the age of deformation provides a younger limit on the age of Appalachian Mississippi Valley-type mineralization.

Regional deformation in the Valley and Ridge province of the southern and central Appalachians, where Mississippi Valley-type mineralization is best known, is dominated by the Permian-Carboniferous Alleghanian orogeny (Fig. 4; Rodgers, 1967; Lash and Drake, 1984; Hatcher, 1987; Horton et al., 1989). In contrast, geologic relations in the Newfoundland Appalachians indicate that deformation was early to middle Paleozoic in age (Fig. 4; Williams, 1984; van der Pluijm and van Staal, 1988). In Newfoundland, Middle Ordovician obduction of the Humber Arm and Hare Bay ocean-floor allochthons onto lower Paleozoic continental-margin deposits (Williams, 1984) was followed by pre-Late Devonian folding and thrusting (Cawood and Williams, 1988), which deformed the shelf carbonates and associated Mississippi Valleytype ores (Lane, 1989). Late Paleozoic folding and thrusting is absent in these areas of Newfoundland (see also Rast, 1988), although minor late Paleozoic deformation is observed in narrow zones around strike-slip faults (Fig. 4B) such as near Deer Lake.

It follows from these observations that, if the geologically and geochemically similar Ordovician-hosted Mississippi Valley-type deposits are

TABLE 1. SULFUR ISOTOPE COMPOSITIONS, APPALACHIAN MISSISSIPPI VALLEY-TYPE DEPOSITS

Location, sample number	mineral	³⁴ \$ (⁰ /00)
Eastern Tennessee		
Mascot-Jefferson City district		
New Market West, NMW-51	Sphalerite	+31.0
Young, YNG-51	Sphalerite	+29.9
Copper Ridge district	•	
Flat Gap, ER-65-43	Sphalerite	+28.7
Flat Gap, ER-65-43	Galena	+24.89
Pennsylvania		
Friedensville district		
FV-1	Sphalerite	- 4.6
FV-1050A1	Sphalerite	- 6.1
Newfoundland		
Newfoundland Zinc deposit		
NFZ-1	Sphalerite	+21.0
NFZ-6	Sphalerite	+22.3

Note: Data for Copper Ridge district are from Rye (1974), and samples were described in Roedder (1971). Other analyses were performed by Geochron, Inc. on samples from our collections. Average isotope ratio for Ordovician-hosted Appalachian deposits (excluding values <+5 $^{\rm O}$ /oo and including data of Howe, 1981) is +23.9 $^{\rm O}$ /oo.

TABLE 2. LEAD ISOTOPE RATIOS, APPALACHIAN MISSISSIPPI VALLEY-TYPE DEPOSITS

Location	Mine	²⁰⁶ Pb/ ²⁰⁴ Pb	²⁰⁷ Pb/ ²⁰⁴ Pb	²⁰⁸ Pb/ ²⁰⁴ Pb
Eastern Tennessee				
Mascot-Jefferson City	Immel	19.414	15.729	39.507
Mascot-Jefferson City	Jefferson City	19.56	15.77	39.66
Copper Ridge	Flat Gap	19.17	15.76	39.46
Pennsylvania				
Friedensville		19.24	15.68	39.66
Bamford		18.74	15.75	38.70
German Valley (Califon)		18.68	15.68	38.39
Birmingham	Keystone (?)	18.61	15.71	38.80
Newfoundland (average)		17.970	15.487	38.608

Note: Analyses for eastern Tennessee and Pennsylvania are from Brown (1962), Heyl et al. (1966), and this study (Immel Mine analysis by D. Krstic and G. L. Cumming, University of Alberta). Newfoundland average is from data in Table 1 (Swinden et al., 1988).

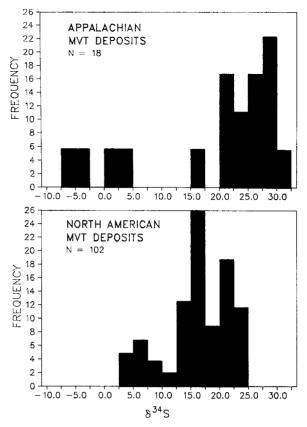


Figure 2. Frequency diagrams comparing sulfur isotopic ratios in sphalerite from Ordovician-hosted Mississippi Valley-type (MVT) deposits in Appalachian orogen with those in other North American MVT deposits. Data are from Table 1 (this paper), Rye (1974), Howe (1981), and compilation of Richardson et al. (1988). Some prospects in Nittany arch area and Friedensville district in eastern Pennsylvania contain distinctly lighter sulfur, which could be from diagenetic pyrite such as observed in Nittany arch area (Howe, 1981).

cant mineralization took place earlier in the evolution of the orogen. This hypothesis is supported by a recent Middle Devonian Rb-Sr isochron age (377 ±29 Ma) obtained for sphalerite separates from the Coy mine in eastern Tennessee (Nakai et al., 1990). Although the host for Sr in this sphalerite could be feldspar or phyllosilicate, the data record an important prelate Paleozoic fluid event in the western part of the southern Appalachians. In view of the suggested relation between mineralization and remagnetization (Oliver, 1986), we note that the Middle Ordovician-Middle Devonian time interval suggested here for Mississippi Valley-type mineralization corresponds to that determined by Hodych (1989) for paleomagnetic remagnetization of the Table Head Group platform carbonates in western Newfoundland. Thus, late Paleozoic fluid expulsion in the southern Appalachians apparently reset all previous paleomag-

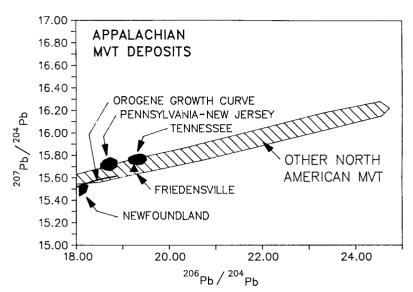


Figure 3. Ratios of uranium-derived Pb vs. ²⁰⁴Pb for Ordovician-hosted, Appalachian Mississippi Valley-type deposits (MVT) (see Table 2, this paper; Brown, 1962; Heyl et al., 1966; Swinden et al., 1988; Doe and Zartman, 1979).

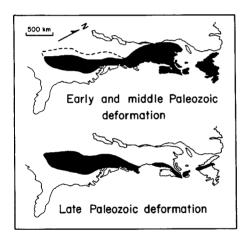


Figure 4. Regional distribution of Paleozoic deformation in Appalachian orogen (modified from Williams, 1984).

netic directions, primary as well as remagnetized, including those in the Mississippi Valley-type ore (Bachtadse et al., 1987).

CONCLUSIONS

Geologic and geochemical similarities among Ordovician-hosted, Appalachian Mississippi Valley-type deposits suggest that they formed by generally similar processes at approximately the same time. Thus, the observation that ores in Newfoundland were deformed before Late Devonian time limits the age of Mississippi Valley-type mineralization in the Appalachian orogen to Middle Ordovician to Middle Devonian. This conclusion is important for considerations

coeval throughout the Appalachians, they must have formed between Middle Ordovician and Middle Devonian time. Permissive evidence for an age in this range is provided by the isotopic data. For example, sulfur isotopic ratios of sphalerite in these deposits are most similar to Cambrian and Ordovician seawater sulfate (Claypool et al., 1980). With the exception of some values up to +25°/00 in Devonian time, younger seawater sulfate was lighter and could not have been a source of the sulfur in these deposits. Similarly, the relatively nonradiogenic character of lead in these deposits and its homogeneity favor derivation from young, well-mixed sediment.

Although none of these observations is conclusive, combined they argue strongly that formation of Ordovician-hosted, Appalachian Mississippi Valley-type mineralization was not confined to late Paleozoic time, and that signifi-

of (1) basin evolution, (2) fluid events, and (3) remagnetization in the southern and central Appalachians, where the early history is poorly preserved and the area is dominated by the late Paleozoic Alleghanian overprint. In particular, the temporal constraints imply the occurrence of more than one Paleozoic regional fluid flow event in eastern North America.

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