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

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ABSTRACT

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

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

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

1. Introduction

Mississippi Valley-type (MVT) Zn-Pb mineralization is widely distributed in the Paleozoic carbonate rocks of the North American mid-continent (Fig. 1). Most of this mineralization consists of no more than a few grams of Zn and Pb sulfide, but rare ore deposits may contain millions of tons of these metals. The great contrasts in scale of mineralization raise the question of whether fundamentally different genetic processes and sources of Pb and S were involved in the formation of trace and ore-scale mineralization, or whether trace and ore-scale mineralization are different expressions of essentially the same genetic processes and sources of Pb and sulfur. This assessment has so far been difficult to make because little information about the trace occurrences of MVT mineralization has been available to compare to the much more thoroughly studied MVT ore deposits.

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

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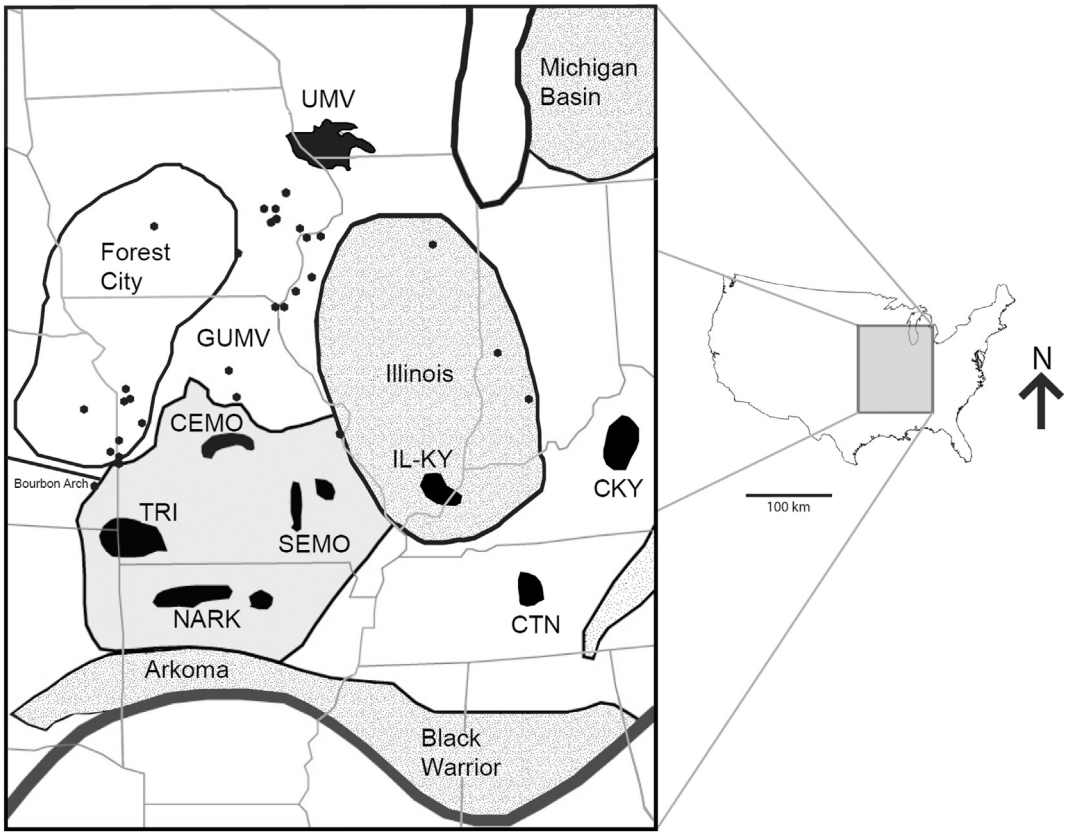

Fig. 1. Map of the U.S. midcontinent showing the locations of trace MVT occurrences analyzed in this study, which are represented by black circles. MVT ore districts are shown as black polygons. Sedimentary basins are represented by a stippled pattern, the Ouachita orogeny is shown in dark gray, and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

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

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

Cathodoluminescence has yielded insights into the origin of some trace MVT occurrences. Garvin (2003) found that some of the trace MVT occurrences fringing the Upper Mississippi Valley (UMV) ore district may be genetically related to the UMV ores in that they have in common a jasperoid phase showing a characteristic brown cathodoluminescence, whereas quartz from other trace MVT occurrences in the region shows blue cathodoluminescence and are thought to be diagenetic in origin.

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

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