Possible Causes for Significant Variations in Chemical and Mineralogical Compositions Among the Major Ore Districts in the Mississippi Valley: Tri-State Zinc District, Southeast Missouri Lead District, and Southern Illinois-Kentucky Fluorite District

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ABSTRACT

Ore deposits of the major ore districts in the Mississippi Valley proper—the Tri-State Zinc, Southeast Missouri Lead, and Southern Illinois-Kentucky Fluorite Districts—share similar geological characteristics and contain most of the same minerals, but there are very significant differences in the abundances of certain minerals and elements. The Tri-State and Southeast Missouri Districts both contain galena and sphalerite as their main economic minerals, but Tri-State is dominated by zinc, whereas Southeast Missouri is dominated by lead. The ore fluids in the Tri-State District appear to have been generated within and traversed through mainly zinc-containing sedimentary rocks. The ore fluids in the Southeast Missouri District were generated within and traversed through zinc-bearing sedimentary rocks, but they also interacted with lead-bearing feldspar in Precambrian igneous basement rocks and feldspar in the overlying sedimentary Lomatite Sandstone. Tri-State contains very abundant silica, especially as jasperoid, in contrast to the Southeast Missouri ores, which contain only minor jasperoid. The much greater silica content of the Tri-State ore fluids may be due to leaching of silica during their traverse through the very cherty Mississippian limestones. Other differences among the three districts include copper, cobalt, nickel, germanium, gallium, silver, and fluorine. The variations among the three major Mississippi Valley-type districts in the Mississippi Valley are concluded to have resulted from (1) metals present at the sites of ore fluid generation, (2) metals present in rocks and ore deposits traversed by the ore fluids en route to the sites of deposition, and (3) intermixing of the ore fluids with other fluids during transport.

INTRODUCTION

The term Mississippi Valley-type (MVT) has gained wide acceptance, and ore deposits worldwide are distinguished and classified as MVT based on the characteristics that compare favorably with those of the ore deposits in the Mississippi Valley. The three major ore districts in the Mississippi Valley proper are the Tri-State Zinc District, Southeast Missouri Lead District, and Southern Illinois-Kentucky Fluorite District (Figure 1). These districts do have many characteristics that are very similar and form the basis for the MVT classification. However, those three major ore districts are also characterized by some marked differences in mineralogy and chemistry. The purpose of this paper is to draw attention to those differences and speculate on some possible reasons for those differences.

CHARACTERISTICS OF THE THREE MAJOR MVT DISTRICTS

The three major districts in the Mississippi Valley proper have many similarities that have allowed them to be grouped together into an MVT. The orebodies occur as horizontal runs or locally as sheets. Karst solution collapse structures can form important structural controls for the locations of many orebodies. Sedimentary structures in dolomitized limestones are important in the localization of many orebodies.

The ore deposits are composed of a small number of ore and gangue minerals. Those minerals have simple compositions. The common minerals are sphalerite (ZnS), galena (PbS), fluorite (CaF₂), chalcopyrite (CuFeS₂), pyrite (FeS₂), marcasite (FeS₂), calcite (CaCO₃), dolomite [CaMg(CO₃)₂], barite (BaSO₄) and quartz (SiO₂). The ore and gangue minerals replace limestone host rocks and are deposited as open-space fillings in vugs.

The temperature of deposition and salinity of ore fluids have been determined for the deposition of the ore and gangue minerals from study of the fluid inclusions contained. The ore and gangue minerals were deposited at low temperatures, typically from about 150 to 50°C, and the depositing fluids were very saline, typically from 20 to 30% sodium chloride (NaCl) equivalent.

SIGNIFICANT DIFFERENCES AMONG THE THREE MAJOR MVT DISTRICTS

Although the three major ore districts in the Mississippi Valley proper share many common geological features, they also have major differences in mineralogy and chemistry. The Tri-State and Southeast Missouri Districts differ greatly in the ratios of sphalerite to galena. Whereas Tri-State is dominated by sphalerite, the Southeast Missouri...
Lead District is dominated by galena. Similarly, whereas the Southern Illinois-Kentucky Fluorite District is dominated by fluorite, the Tri-State and Southeast Missouri Districts are totally lacking in fluorite. These and other mineralogical and chemical differences among the three major districts in the Mississippi Valley proper are discussed in the following sections.

**LEAD:ZINC RATIOS IN THE ORES**

The Tri-State District is dominated by sphalerite. The ratio of zinc to lead during mining from 1850 through 1964 was 4.117:1 (Brockie et al. 1968). Most MVT deposits worldwide are characterized by sphalerite dominant over galena. The MVT ore districts with sphalerite dominant include Tri-State, Northern Arkansas, Wisconsin-Illinois, East Tennessee, Central Tennessee, Pine Point, Northwest Territories, Polaris, Arctic, Alpine-type, Europe, Irish-type, Ireland, Upper Silesia, Poland, and others. Disregarding the fluorite, the zinc:lead ratio for the Southern Illinois-Kentucky Fluorite District is about 10:1 (Eric Livingston, former Chief Geologist, Ozark-Mahoning Company, Southern Illinois-Kentucky Fluorite District, e-mail communication, 2011).

The Southeast Missouri District differs greatly from the sphalerite-dominant districts in that galena dominates sphalerite by a ratio of more than 5:1. Galena-dominant MVT districts are rare. One example is the Leisvall District in Sweden (and similar nearby deposits), where galena was deposited in sandstones. Much of the Leisvall galena ore was deposited in disseminations or in spots about 1 in. (2.5 cm) in diameter, perhaps because of the former presence of some precipitant such as petroleum. The Leisvall ore has a striking similarity in appearance to the Lamotte Sandstone-hosted galena ore at the Indian Creek Mine in the Southeast Missouri Lead District.

This raises the question of why most MVT districts are dominated by sphalerite but only rare MVT districts are dominated by galena. The reason could well be that for the sphalerite-dominated districts, the ore fluids originated within and traveled through a column of Paleozoic sedimentary rocks that contained significant amounts of zinc and much smaller amounts of lead and other metals. For these zinc-rich districts, ore fluid had no significant involvement with potentially lead-bearing Precambrian basement rocks. In contrast, for the galena-dominated districts, the ore fluids traveled through Paleozoic carbonate rocks and reacted with Precambrian basement and Cambrian Lamotte Sandstone (partly derived from the basement). For Precambrian rocks in southeast Missouri, Aleinikoff et al. (1993) showed that the feldspar could contain as much as 12 to 13 ppm of lead in the feldspar. Feldspar in the overlaying Lamotte Sandstone, through which the ore fluids migrated, was found to contain 1 to 8 ppm of lead (Aleinikoff et
al. 1993). Kisvarsanyi (1977) and Viets et al. (1992) arrived at similar conclusions that much of the lead in the Southeast Missouri District was derived from the Precambrian.

The lead in the lead-rich Leisvall deposits of Sweden was formerly thought to have been derived from the overlying metal-rich Alum Shale, but recent studies have concluded that the lead comes from the underlying Precambrian rocks (David Rickard, Cardiff University, Wales, e-mail communication, 2011). A well-developed leach zone has been discovered in the top of the Precambrian basement rocks, and the uranium:thorium ratios (U:Th) of base-

ABUNDANCE OF HYDROTHERMAL SILIFICATION (JASPEROID)

The abundance of hydrothermal silification (jasperoid) varies markedly among the three major MVT districts. The Tri-State ores exhibit very abundant hydrothermal silification of the lime-

GERMANIUM AND GALLIUM CONTENTS OF SPHALERITE

Tri-State sphalerite contains small but elevated amounts of germanium (Ge) and gallium (Ga). Eagle-Picher Industries built a germanium plant at Miami, Oklahoma, to recover germanium from Tri-State zinc smelter residues, and for many years, it was the main domestic source of germanium. Hagni (1983a) determined, based on a large number (187) of analyses, that the average content of Tri-State sphalerite is 134 ppm of germanium, that reddish brown sphalerite averages slightly higher germanium contents (164 ppm), and that red sphalerites contain the highest germanium contents (298 ppm). Along this line, Rick Dingess, former Chief Geologist, ASARCO West Fork mine, Missouri (e-mail communication, 2011), who analyzed many Tri-State sphalerite specimens for germanium exploitation purposes, found an average content of 140 ppm. The gallium contents were even higher: 255 ppm for the average Tri-State sphalerite (187 analyses), 200 ppm for reddish brown sphalerite, and 400 ppm for red sphalerite (Hagni 1983).

Subsequent analyses of MVT sphalerites by Viets et al. (1992) found similar, but somewhat lower, germanium and gallium contents for the Tri-State and Southeast Missouri District sphalerites. They also analyzed sphalerite from the Northern Arkansas and Central Missouri Districts and found even lower germanium and gallium contents.

The origin of germanium and gallium in MVT sphalerite crystals is an interesting problem. Some geologists have concluded that the germanium and gal-

uranium contents of Tri-State sphalerite were also compared with smaller numbers of analyses for the Southeast Missouri and Southern Illinois-Kentucky Dis-

The average germanium and gallium contents of Tri-State sphalerite were also compared with smaller numbers of analyses for the Southeast Missouri and Southern Illinois-Kentucky Dis-

uranium:thorium ratios (U:Th) of base-

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Figure 2 Tri-State ores. (a, b) Limestone (light and medium gray) and chert (white) breccia cemented by jasperoid (dark gray). Hammer gives the scale. (c, d) Chert (white) breccia cemented by jasperoid (dark gray) that contains disseminated sphalerite. Specimens are about 11.8 in. (30 cm) long. (e) Transmitted light photomicrograph of chert under crossed nicols showing equant quartz grains. (f) Transmitted light photomicrograph of jasperoid under crossed nicols showing elongate quartz grains.
petroleum (Dan Stewart, former Chief Geologist, American Zinc, Tri-State District, personal communication, 1986). Petroleum dripped down on the walls of the M-bed (main mining horizon) ore runs. That the petroleum was present at the time of ore deposition is indicated by the presence of petroleum (Figure 3a) in some of the fluid inclusions in the Tri-State sphalerite (Wei 1975). Analyses of petroleum (crude oils, asphalts, and oils extracted from rocks) in Kansas and Oklahoma lend support to the source of gallium being from petroleum but not germanium (Erickson et al. 1954). Seventy-two percent of the 71 analyses detected gallium in concentration ranges of 0.0 to 0.000×, but only one of the analyses detected germanium (concentration range of 0.0×). It is interesting that 117 analyses of Kansas coals detected 6 to 116 ppm of germanium, and germanium was detected in all 117 of the analyses (Schleicher and Hambleton 1954; Schleicher 1959).

COPPER CONTENTS OF THE THREE MVT DISTRICTS

Most of the mines in the Southeast Missouri District recover copper (Cu) as a separate concentrate at the mill. In contrast, the other two districts contain insufficient copper to make a copper concentrate. The principal mineral that contains the copper is chalcopyrite. It commonly occurs as massive colloform grains that are deposited after disseminated sphalerite but before the deposition of galena. Locally, chalcopyrite and sphalerite show rhythmic colloform deposition in which bands of chalcopyrite and sphalerite alternate during deposition. Chalcopyrite also may occur as disseminated grains in massive replacement ores and as late crystals deposited in vugs.

Some of the ores in the Viburnum Trend are very copper-rich massive copper sulfide bodies, locally called bornite pods. They contain copper (and cobalt and nickel) sulfides and totally lack lead and zinc sulfides. These ores are characterized by textures that include (1) bornite spheroids, (2) bornite-chalcopyrite exsolution, (3) rhythmic bornite and chalcopyrite colloform deposition, and (4) layered chalcopyrite-borneite deposition (Hagni 1988, 1997, 2001, 2011, 2014). Eight bornite pods have been discovered in the Viburnum Trend. By contrast, bornite pods are absent from the Tri-State District and most other MVT districts.

This raises the question of why the Viburnum Trend ores contain enough copper to produce a copper concentrate, whereas the ores in the other two MVT districts and most MVT districts contain insufficient copper to recover. The reason may well relate to the interaction of Southeast Missouri District ore fluids with copper-iron ore deposits in the underlying Precambrian rocks. The ore fluids not only traveled and interacted with Paleozoic and Precambrian rocks, but also reacted with copper-bearing ore deposits in the basement, such as the Boss-Bixby copper-iron (Central and West Dome) deposits. That is, copper was leached from the Boss-Bixby copper-bearing deposits and redeposited by the ore fluids in the overlying Cambrian Bonnetteer Formation ores. Support for this interpretation comes from several sources. The Boss-Bixby deposit contains more copper than do other iron deposits in the Missouri Precambrian. The Boss-Bixby deposits are primarily magnetite, hematite, and some ilmenite, but copper is also present as chalcopyrite and bornite in the Boss-Bixby Central Dome deposit (Hagni and Brandom 1989; Figure 4a,b) and in the East Dome (Seeger 2003). Furthermore, the amounts of copper in the Viburnum mines increase toward the Boss-Bixby copper-iron deposit. In addition, studies of mineral asymmetry in the Viburnum Trend have shown a major component of ore fluid flow from the Magmont-Buick area (near the Boss-Bixby deposit; see Hagni 1983b). Finally, sulfur isotopes indicate interaction of the Viburnum Trend ore fluids with the Boss-Bixby deposit (Shelton et al. 1995).

COBALT AND NICKEL CONTENTS OF THE THREE MVT DISTRICTS

The Southeast Missouri District contains much more cobalt (Co) and nickel (Ni) than do the other two MVT districts. In the Tri-State and Southern Illinois-Kentucky Districts, cobalt and nickel occur only as trace elements in pyrite and marcasite. In the Southeast Missouri District, in addition to cobalt and nickel occurring as minor trace elements in pyrite and marcasite, they are sufficiently abundant to occur as a separate mineral phase, siegenite. Siegenite occurs throughout most of the orebodies mainly as coatings on chalcopyrite (Figure 3c), but also locally as coatings on sphalerite (Figure 3d). Nickel also occurs locally as late vug-lining millerite crystals deposited on octahedral galena, and that millerite commonly is partly to completely altered to polydymite (Figure 3e). The excess nickel from the alteration of millerite to polydymite is deposited as vaesite on the altered millerite-polydymite crystals. Less commonly, pyrite and marcasite contain growth zones of bravoite and vaesite (Figure 3f).

Periodically, a cobalt concentrate is produced at some of the mills in the Viburnum Trend. For ores that are low in copper and sufficiently high in cobalt content, the copper circuit in the mill may be used periodically to recover a cobalt concentrate rather than a copper concentrate. The cobalt and nickel contents of the Tri-State and Southern Illinois-Kentucky Districts are not sufficiently high to make mill concentrates of these metals.

This leads to why the ores of the Southeast Missouri District are much higher in cobalt and nickel than those of the Tri-State and Southern Illinois-Kentucky Districts. The reason probably is similar to the reason the copper content of ores in the Southeast Missouri District is higher. That is, the cobalt and nickel were derived principally by leaching of Precambrian cobalt- and nickel-bearing ore deposits, such as Boss-Bixby (Central and West Domes). Support for this interpretation comes from several sources. Cobalt and nickel are present in the Boss-Bixby ores as strongly zoned cobalt- and nickel-bearing pyrite. In addition, the cobalt and nickel contents of the Viburnum Trend ores increase as the Boss-Bixby deposits are approached (Jessey 1981; Hagni 1983a). The nickel:cobalt ratio decreases systematically away from the Boss-Bixby deposits (Jessey 1981; Hagni 1983a).
Figure 3  Reflected light photomicrographs of southeast Missouri ores (a, c, d, e, f) and Leisvall, Sweden, ore (b). (a) Fluid inclusions in sphalerite (yellow), some of which contain petroleum (black). (b) Mine face showing galena (black) in sandstone. Scale given by the Brunton compass (center low). (c) Siegenite (Sg, light yellow) deposited on chalcopyrite (Cp, dark yellow). (d) Siegenite (Sg, light yellow) deposited on sphalerite (Sl, light gray). (e) Millerite crystal (Mi, light yellow) partly replaced by polydymite (Pd, light violet) and coated by vaesite (Vs, dark gray) enclosed within galena (Gn, light gray). (f) Pyrite crystals (yellow) with zones of vaesite (medium gray) and bravoite (light brown) all enclosed in galena (Gn, light gray).
Figure 4 Boss-Bixby, Missouri, ores and Ol Doinyo Lengai, Tanzania. (a) Reflected light photomicrograph showing magnetite (Mt, light brown) and hematite (Hm, white) containing small exsolution ilmenite lamellae. (b) Reflected light photomicrograph showing chalcopyrite (Cp, yellow) and bornite (Bo, purple) with magnetite (Mt, light gray). (c) Ol Doinyo Lengai volcano. (d) Summit crater at Ol Doinyo Lengai. (e) Eruption of natrocarbonatite at Ol Doinyo Lengai. (f) Cathodoluminescence micrograph showing gregoryite (brown), nyerereite (orange), apatite (dark purple), and fluorite (light purple). Photographs in panels d and e courtesy of Abigale Church, and the specimen in panel f courtesy of Joerg Keller.
SILVER IN SPHALERITE IN THE THREE MVT DISTRICTS

The silver (Ag) contents of sphalerite in the MVT districts typically are very low. For Tri-State District ores, for example, the silver content averaged 5.1 ppm for 187 analyses (Hagni 1983a). Similarly, for the Southern Illinois-Kentucky District, the silver content in 43 analyses of sphalerite averaged 2 ppm (Hagni 1983a). In contrast, 28 analyses of sphalerite from the Southeast Missouri District averaged 434 ppm of silver.

The question then is why the Southeast Missouri District sphalerite contains elevated silver contents. One possible explanation may be that the ore fluids interacted with silver-bearing ore deposits in the Precambrian rocks. That is, the silver concentrations in Southeast Missouri District sphalerite may be due to leaching of silver from silver-bearing ore deposits in the Precambrian basement, similar to those deposits in the Silver Mine District of southeast Missouri (Hagni 1984a,b).

FLUORITE IN THE SOUTHERN ILLINOIS-KENTUCKY DISTRICT

Fluorite is greatly predominant over sphalerite and galena in the Southern Illinois-Kentucky District. The question that is immediately posed is whether MVT ore fluids from the Illinois Basin or elsewhere carrying zinc and lead interact with alkaline igneous-carbonatite complex-related fluorite at Hicks Dome.

Fluorite is very closely associated with alkaline igneous-carbonatite complexes worldwide. For example, at the present-day active volcano Ol Doinyo Lengai in Tanzania, carbonatite magma actively extrudes at the summit and at times violently explodes, draping the sides of the volcano (Figure 4c,d,e). Petrographic and cathodoluminescence microscopic examinations of those lavas have shown that they contain up to 5% fluorite (2.5% fluorine; Koberski and Keller 1995; Figure 4f). Similarly, large fluor spar deposits may be formed in connection with alkaline igneous-carbonatite complexes. At the Okorusu alkaline igneous-carbonatite complex in Namibia, fluor spar mines produced 110,000 tons of fluor spar concentrates in 2010. This production level is three times that of the production from the Southern Illinois-Kentucky District before mining ceased. Mines at a similar alkaline igneous-carbonatite complex at Amba Dongar in western India have been producing smaller amounts of fluor spar concentrates. Fluorspar mines at yet another alkaline igneous-carbonatite complex at Mato Preto in southern Brazil produced about 100,000 tons of fluor spar concentrate annually until it was closed in 1999. Several fluor spar mines at alkaline igneous-carbonatite complexes in Russia were productive before their closures. Finally, the Kenya Fluorspar Company mine at Kimwaver in western Kenya has been producing about 100,000 tons of fluor spar concentrate annually. Although that deposit has not been recognized as of alkaline igneous-carbonatite complex origin, those fluorite deposits have the mineralogical and chemical characteristics that lead this writer to conclude they are also related to an alkaline igneous-carbonatite complex.

The question then is what characteristics serve to distinguish alkaline igneous-carbonatite complex-related fluorite ores. Those ores typically replace carbonatites, limestones, and marbles. During the replacement, calcium from the host rock goes into solution and combines with fluorine to form fluorite (CaF$_2$). Carbonatite complex-related fluor spar ores typically contain abundant apatite. The presence of apatite in fluor spar ores is noteworthy because apatite is a deleterious constituent when the fluor spar ores are utilized for steel making. Carbonatite-related fluor spar ores also commonly contain locally elevated concentrations of rare earth elements (REE).

A massive fluorite deposit has been drilled at depth within the Hicks Dome structure in the Southern Illinois-Kentucky District (Brett Denny, Illinois State Geological Survey, personal communication, 2014). The results of the drilling have been largely confidential; however, limited literature indicates that the fluorite replaces brecciated limestone, contains abundant apatite, and contains elevated REE. These mineralogical characteristics are those of an alkaline igneous-carbonatite complex-related fluorite deposit. Several small outcrops of a carbonate breccia called the Grant Breccia that occur at Hicks Dome have been interpreted to be carbonatite (Reynolds et al. 1997). Further strengthening the carbonatite interpretation is the recent identification of the REE mineral synchysite in breccia in an outcrop at Sparks Hill (Denny et al. 2015, this volume). Synchysite is a common REE mineral in carbonatites, and it was identified as the mineral that carries REE values in the Okorusu, Namibia, carbonatite (Kogut et al. 1997). Thus, it may be readily concluded that regardless of whether the Hicks Dome fluorite ores replaced carbonatite or replaced brecciated carbonate rocks, the ores are clearly derived from an alkaline igneous-carbonatite complex. Furthermore, the origin of the abundant, previously mined shallow MVT fluorite ores in southern Illinois and Kentucky must be related to the deep Hicks Dome fluorite ores. One of two genetic relationships is possible: there was either (1) dissolution of older alkaline igneous-carbonatite-related Hicks Dome fluorite mineralization, followed by deposition of fluorite in the MVT deposits, or (2) mixing of two fluids, one alkaline igneous-carbonatite derived and the other MVT basin derived.

With respect to a mixing model, it is important to know the ages of Hicks Dome carbonatite and the previously mined MVT fluor spar ores. Denny et al. (2008) recently summarized age dating of the Southern Illinois-Kentucky District fluor spar ores by indicating dates from early Permian through late Jurassic. Dating of the igneous activity in the district has been consistent at about 270 Ma (million years ago), or early Permian (Denny et al. 2008). Reynolds et al. (1997) have argued that the best age determination for the Southern Illinois-Kentucky fluorite mineralization is Permian. They dated the Grant Breccia as Permian, and they concluded that carbonatite-related fluids mixed with Illinois Basin-derived MVT fluids during Permian time.
However, it seems to the author that if fluorite-bearing carbonate-related fluids were mixed with basin-derived lead-zinc-bearing MVT fluids, the previously mined MVT ores should have contained abundant apatite and some REE minerals. Those ores contained no apatite, nor did they contain independent REE minerals (Eric Livingston, e-mail communication, 2011). Thus, it seems more likely that the carbonate-related fluorspar ores had been emplaced in Hicks Dome before the introduction of the MVT fluids, and that fluorite was readily dissolved by the MVT fluids but that apatite and REE minerals were insoluble. Thus, it is concluded here that the Southern Illinois District contains abundant fluorite, whereas Tri-State and Southeast Missouri contain no fluorite because the basin-derived MVT fluids that mineralized the Southern Illinois-Kentucky District encountered carbonate-related fluorite in Hicks Dome and remobilized it to be deposited with the lead and zinc deposits in that district.

CONCLUSIONS

Although the three major ore districts in the Mississippi Valley proper have provided the basis for the classification of the MVT ore deposit class, there are very significant differences in the mineralogy among the ores in those three districts. It is concluded that the varied mineralogy of MVT deposits in the Mississippi Valley proper resulted from a variety of influences. For the Tri-State Zinc District, and for most zinc-dominant MVT deposits elsewhere in the world, most of the constituents originated both at the site of formation of the ore fluids and were also leached from sedimentary rocks during transport to their sites of deposition.

Fluid–rock interaction was responsible for the presence of other constituents in the ore districts. For the silica (jasperoid) in the Tri-State District, it was obtained by fluid–rock interaction (partial chert dissolution) during travel to the depositional sites. Lead in the Southeast Missouri District (and in the Leisvall District in Sweden) was also obtained by fluid–rock interaction (mostly leaching of lead from Precambrian lead-bearing feldspar) as the fluids traveled to the depositional sites.

Other constituents present in the ore districts resulted from fluid–ore deposit interaction. Much of the copper, cobalt, and nickel present in the Southeast Missouri District ores was derived by ore fluid leaching of metals present in the cobalt- and nickel-bearing Boss-Bixby copper-iron ore deposits in the Precambrian basement near the Viburnum Trend. The highly elevated amounts of trace element silver present in sphalerite in the Southeast Missouri District may well have originated by leaching of silver from silver-rich ore deposits in the Precambrian basement, such as those deposits in the Silver Mine District of Southeast Missouri.

Finally, some constituents in the MVT deposits may have resulted from mixing of the basinal brine ore fluids with other fluids during their travel to the sites of ore deposition. Germanium and especially gallium may have been derived from ore fluid mixing with petroleum. However, another possible source for germanium might well have been coal deposits, which typically contain elevated amounts of germanium. Similarly, the basinal brine fluids that deposited the ores in the Southern Illinois-Kentucky District may have mixed with fluorite-depositing fluids of alkaline igneous-carbonatite complex origin. Another possibility, however, is that the basinal brine leached fluorite from previously deposited Hicks Dome alkaline igneous-carbonatite complex-related fluorite ores.

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