

# Hydrothermal Fluid Origins in Mississippi Valley-Type Ore Districts: Combined Noble Gas (He, Ar, Kr) and Halogen (Cl, Br, I) Analysis of Fluid Inclusions from the Illinois-Kentucky Fluorspar District, Viburnum Trend, and Tri-State Districts, Midcontinent United States

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## Abstract

Samples were selected from three of the classic Mississippi Valley-type districts in the midcontinent area of North America. The Illinois-Kentucky fluorspar district belongs to the fluoritic subtype of Mississippi Valley-type districts, and the Ozark districts of the Viburnum Trend and Tri-State are representative of the Pb-rich and more typical Zn-rich subtypes of Mississippi Valley-type mineralization, respectively. Noble gas (Ar, Kr) and halogen (Cl, Br, I) data have been obtained simultaneously by noble gas mass spectrometry of inclusion fluids released by *in vacuo* crushing of irradiated fluorite, quartz, carbonate, and sphalerite samples. Additionally, He analyses have been obtained from nonirradiated fluorite from the Illinois-Kentucky fluorspar district.

Fluorite from the Illinois-Kentucky fluorspar district has a maximum  $^3\text{He}/^4\text{He}$  ratio of 0.35 Ra (where Ra = atmospheric  $^3\text{He}/^4\text{He}$  ratio of  $1.4 \times 10^{-6}$ ), higher than values typical of crustal fluids and confirming the presence of a minor mantle component, equal to less than 6 percent of the total He in the fluids of the Illinois-Kentucky fluorspar district.

The Br/Cl mol ratios of all the deposits are, with one exception, higher than the value of seawater ( $1.54 \times 10^{-3}$ ), ranging from  $1.69$  to  $3.70 \times 10^{-3}$ , and indicating acquisition of salinity by the evaporation of seawater beyond the point of halite saturation. Late quartz from the Tri-State district contains a very minor component of halite dissolution water and has a Br/Cl mol ratio of  $1.46 \times 10^{-3}$ . The I/Cl mol ratios are typical of oil field brines and are ubiquitously higher than what is attainable by the evaporation of seawater alone. I/Cl mol ratios are in the range of  $6$  to  $270 \times 10^{-6}$ , indicating that the fluids have interacted with I-rich organic matter present in sedimentary rocks.

In the Ozark districts,  $^{40}\text{Ar}/^{36}\text{Ar}$  ratios vary between 320 and 345 in the Tri-State and between 350 and 420 in the Viburnum Trend. In the Illinois-Kentucky fluorspar district  $^{40}\text{Ar}/^{36}\text{Ar}$  ratios reach values of 1,200. The corresponding concentrations of  $^{40}\text{Ar}_{\text{excess}}$  ( $^{40}\text{Ar}$  not attributable to radiogenic decay of  $^{40}\text{K}$  or an atmospheric source) are similarly elevated in the main-stage fluorite mineralization of the Illinois-Kentucky fluorspar district ( $6.8\text{--}18.2 \times 10^{-4} \text{ cm}^3\text{cm}^{-3}\text{H}_2\text{O}$ ) relative to the Viburnum Trend and Tri-State districts (mostly  $1.3\text{--}3.3 \times 10^{-4} \text{ cm}^3\text{cm}^{-3}\text{H}_2\text{O}$  and  $0.3\text{--}1.4 \times 10^{-4} \text{ cm}^3\text{cm}^{-3}\text{H}_2\text{O}$ , respectively).

Together the noble gas and halogen data indicate the existence of three brine provinces, (1) a regional Tri-State brine present throughout the Ozark region, (2) a Viburnum Trend brine, and (3) an Illinois-Kentucky brine. Furthermore, in the Viburnum Trend the halogen composition of main-stage dolomite is distinct from that of the main-stage sphalerite but identical to the regional hydrothermal dolomite seen in the Tri-State district. The data imply that mixing relationships in the Viburnum Trend are highly complex but are compatible with regional models in which the Tri-State brine, present throughout the Ozark region, was sourced in the Arkoma basin.