Role of Groundwater in the Formation of Fluorite Ore Deposits in the Illinois-Kentucky District, Central U.S.

Evidence from Fluid Inclusions and Numerical Reactive Transport Modeling

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Illinois-Kentucky district is one of several major “Mississippi Valley-type” (MVT) districts in central U.S.

- Products of regional groundwater flow system
- Pennsylvanian-Permian age
- 80 - 150° C
- 18 to 24 wt % TDS
- Carbonate-hosted
- Principal minerals
  - Ore: sphalerite, galena, barite, fluorite
  - Gangue: dolomite, calcite, quartz
Collision of Gondwanaland with North America during the Late Paleozoic

- mobilized groundwater across the North American mid-continent

http://jan.ucc.nau.edu/~rcb7/namP290.jpg
Most MVT deposits are dominated by sphalerite (ZnS) and galena (PbS)

Sphalerite ore
Central Tennessee district

Galena (marcasite) ore
Viburnum Trend, Southeast Missouri

Photo credit: Kevin Shelton
Illinois-Kentucky district is dominated by fluorite

- Fluorite:Zn = 47:1
- Fluorite:barite = 70:1
- Fluorite:Pb = 280:1

> 12 million tons of fluorite produced since 1812

What is different about the Illinois-Kentucky district compared to the more common Zn-Pb-dominant MVT occurrences?

Photo credit: John Rakovan
One difference between Illinois-Kentucky district and typical MVT deposits

- presence of coeval igneous rocks

Compiled from Grogan & Bradbury (1968) and Goldstein (1997)

Diatreme

Lamprophyre with calcite veining

Denny et al. (2015)
Seismic reflection profile across NW Illinois-Kentucky district

- Note loss of sedimentary layering definition in Hicks Dome (volcanic diatreme)

Other evidence of igneous involvement
- Elevated $^3\text{He}/^4\text{He}$
- Carbonatite REE signature in fluorite

Goldhaber et al. (1992)
Conceptual model and hypothesis for ore formation:

- The Illinois-Kentucky ores were precipitated from F-rich fluids
- The source of the F was from mafic to ultramafic magma underlying the district

*after Plumlee et al. (1995)*
How F-rich was the Illinois-Kentucky ore fluid?

Test hypothesis by measuring F concentration in fluid inclusions hosted by sphalerite

- SEM-EDS analysis of fluid inclusion decrepitates

Conceptual model of experimental methodology

Photomicrograph of fluid inclusions in fluorite
All fluid inclusion decrepitate mounds from Illinois-Kentucky sphalerite analyzed contained strong F signals.
Calculated F concentrations in IL-KY fluid inclusions

- $[\text{F}]:$ 680 to 4300 ppm

### Table: Solute Mound F Concentrations

<table>
<thead>
<tr>
<th>Solute Mound</th>
<th>F Concentration (ppm)</th>
<th>+ (ppm)</th>
<th>- (ppm)</th>
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<tbody>
<tr>
<td>IKNG1-3a</td>
<td>760</td>
<td>950</td>
<td>430</td>
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<tr>
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<td>2000</td>
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<tr>
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<td>1600</td>
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<tr>
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<tr>
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<td>1100</td>
<td>510</td>
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<tr>
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<td>610</td>
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</table>
F concentrations of 680 to 4300 ppm require low pH of 0 to 0.8

\[
\text{Ca}^{2+}_{(aq)} + 2\text{HF}_{(aq)} \rightleftharpoons \text{CaF}_2(s,fl) + 2\text{H}^+_{(aq)}
\]

- Typical pH values of MVT ore fluids: 4.0 to 5.5

Field evidence for highly acidic ore fluid
- Direct replacement of limestone by fluorite
- Mineralized breccias
- Thinning of limestone ore horizons
- Collapses exceeding 20 m
Low pH of ore fluid would have suppressed metal sulfide mineral precipitation

- May explain low sulfide mineral abundance in Illinois-Kentucky district
Test results using numerical reactive transport modeling

- How far can a 0 to 0.8 pH fluid travel through limestone before it is neutralized?
  - How much limestone will be dissolved?
  - What mineral assemblage will be produced?

- 500 x 500 x 500 m grid
- Fault with high pressure, HF-rich fluid source at base
- Multiple sedimentary layers containing brine
Fluid pressure

Note:
- Pressure gradient along and outward from fault
- Diffusion of pressure outward from fault
Fluid pressure and velocity

- 3000 y
pH

- Low pH confined to fault and immediate vicinity
Calcite

- Up to 7% calcite volume loss after 1,000 y
- Calcite loss limited to fault vicinity
Slumping caused by dissolution

- Hastie Quarry
Fluorite

- Model scenario effective at producing fluorite
- Up to 1.7% volume change after 1,000 y
Sphalerite

- Sphalerite precipitation suppressed
- $\sim 2.6 \times 10^{-6}$ % volume change after 1,000 y
Galena

- Galena precipitation also suppressed
- $5 \times 10^{-5}$ % volume change after 1,000 years
• Mineralizing groundwater in Illinois-Kentucky district was unusually rich in F (100’s to 1000’s of ppm)
• Such high F concentration in Ca-rich groundwater requires unusually low pH of 0 to 1
• Low pH would have suppressed precipitation of metal sulfide minerals
• Mineralizing groundwater was likely a mixture of magmatic HF-rich fluid with Ca-rich sedimentary brine
  • Genetic scenario fits well with observed mineral assemblage and limestone dissolution features observed in the field