### **Acknowledgments**

### **Introduction**



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# **Paleo-fluid evolution in Western Kentucky Fluorspar District**

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Petrographic observations were made with an Olympus BX-51 microscope with 4x, 10x, 40x, and 100x objectives and a biological-style X-Y stage, to allow for precise control over the sample at high magnifications. An Olympus UV lamp was used to determine if there were any hydrocarbon-bearing fluid inclusions in our samples. The microscope was equipped with an Olympus DP74 camera with the ability to take composite photos and show a live feed to allow for easier observation during microthermometry. Microthermometry was performed on a Linkam THMSG600 heating and cooling stage and a Linkam CI 94 liquid nitrogen pump controller with a temperature range of -196°C to 600 $\degree$ C and a resolution of 0.1 $\degree$ C. Due to the lack of water-cooling system, our observations were kept under 200°C to avoid damaging the objectives. The equipment was calibrated by measuring the final ice melting temperature (Tm) of fluid inclusions in three known standards, pure H<sub>2</sub>O, H<sub>2</sub>O-CO<sub>2</sub>, and KCl. The accuracy of the data is +/- 0.1<sup>o</sup>C.

### **Results & Discussion**

The Western Kentucky Fluorspar District (WKFD) is well-known for Mississippi Valley-type (MVT) mineral deposits and enigmatic alkaline igneous intrusions. However, the genetic relationship between the igneous activity and the mineralization is poorly understood. Fluid inclusion analysis provides a suitable method to explore a potential genetic linkage. Fluid inclusions are liquid or gas-filled voids within a crystal. They form when imperfections in the crystal structure are sealed off by crystal growth. The voids containing the fluids are categorized into three types: primary, pseudosecondary, and secondary. Fluid inclusions that form at the time of mineral precipitation are primary, fluid inclusions that are formed in a micro-vein within a mineral during deformation followed by renewed mineral growth are pseudosecondary, and fluid inclusions formed in micro-veins after mineral precipitation was complete are secondary (Goldstein and Reynolds, 1994). The fluid that is trapped in the inclusions can provide valuable information on the mineralizing fluids present at the time the inclusions became sealed. Through petrographic observations and microthermometry, information on the temperature, pressure, and composition of the mineralizing fluid, as well as its later thermal evolution, can be constrained (Goldstein and Reynolds, 1994). The original goal of this study was to establish or reject a genetic relationship between calcite cements present in igneous dikes and those calcite cements associated with MVT mineralization. However, after extensive petrographic analysis, no suitable primary fluid inclusions were found in the samples that could be used to test this hypothesis. Secondary fluid inclusions are abundant; thus, the revised goal of the project was to evaluate how the fluids trapped in these inclusions fit into the paleo-evolution history of the district.



- o FIA-F1: Secondary. Shows evidence of necking down. Two-phase aqueous liquid (L) + vapor (V) fluid inclusions (Fis) and fluorescent single-phase solid (S) FIs. No homogenization temperatures (Th) measured (chip lost).
- o FIA-F2: Secondary. Shows evidence of necking down. Two-phase aqueous L+V FIs, single-phase fluorescent S FIs, two-phase fluorescent S+L FIs. *Th of aqueous L+V FIs ranged between 98°C and 187°C* (Th above 200°C not measured due to instrument limitations).
- o FIA-F3: Secondary. Shows evidence of necking down. Two-phase aqueous L+V FIs, single-phase fluorescent S FIs, and single-phase L FIs. *Th of aqueous L+V FIs ranged from 43oC to 49oC.*
- o **FIA-C1:** Primary (?). Shows evidence of necking down. Two-phase aqueous L+V FIs and single-phase L FIs inclusions. No Th measured due to small size of FIs.
- o **FIA-C2:** Primary (?). Shows evidence of necking down. Two-phase aqueous L+V FIs, single-phase L FIs, twophase fluorescent S+L FIs (L is not fluorescent), and single-phase fluorescent S FIs. *Th of aqueous L+V FIs ranged from 32oC to 80oC.*

- o **FIA-C1:** Primary (?). Shows evidence of necking down. Two-phase aqueous L+V FIs, two-phase fluorescent L+V FIs, and single-phase fluorescent S FIs. *Th of L+V FIs range from 27oC to 95oC.*
- o FIA-C2: Primary (?). Shows evidence of necking down. Two-phase aqueous L+V FIs, two-phase fluorescent L+V FIs inclusions and fluorescent S FIs. *Th of L+V FIs range from 43oC to 118oC.*

- o **FIA-S1**: Secondary. Shows evidence of necking down. Two-phase aqueous L+V FIs and single-phase L FIs. *Th of aqueous L+V FIs range from 99oC to 115oC.*
- o FIA-S2: Secondary. Shows evidence of necking down. Two-phase aqueous L+V FIs and single-phase L FIs. *Th of aqueous L+V FIs range from 89oC to 128oC.*
- o **FIA-C1:** Primary (?). Shows evidence of necking down. Two-phase aqueous L+V FIs and single-phase L FIs. *Th of aqueous L+V FIs range from 82oC to 106oC.*







## Methods <del>Conclusions</del>

Fig. 1: Geologic map of the Western Kentucky Fluorspar District (WKFD). Note the NW-SE trending, Permian dikes colored red on the map (Lukoczki et al., 2021).

Our petrographic and microthermometric study of three samples BCH-5 3.17 (Fig. 2), S-35-560A (Fig. 5), and S-57 232.67A (Fig. 8) has produced information on ten individual fluid inclusion assemblages (FIA).

#### - **Sample BCH-5 3.17**

Cluff, R .M., and Byrnes, A.P., 1990, Lopatin analysis of maturation and Petroleum generation in the Illinois basin: American Association of Petroleum Geologists Memoir  $51, p. 425 - 454.$ 

#### - **Sample S-35-560A**

#### - **Sample S-57 232.67**

The WKFD is understood to have undergone several episodes of hydrothermal activity that resulted in multiple generations of mineralization (e.g., Richardson et al 1984). This study has made the following conclusions on how the fluids within secondary inclusions fit into the paleo-evolution history of the district.

- The presence of hydrocarbon FIs in calcite veins that cross-cut Permian dikes suggests the host calcite and the fluids trapped in secondary inclusion must also be of Permian age based on Permian oil migration from the New Albany Shale according to Cluff and Byrnes (1990).
- The wide range of Th values for hydrocarbon-rich FIs in the studied calcite may be a result of variable fluid density due to subtle chemical differences in the trapped fluid.
- The higher Th of yellow UV-fluorescent hydrocarbon-rich FIs in the calcite compared to those with blue fluorescent color with lower Th values correspond well to greater thermal maturity of higher temperature fluids.
- The Th values collected from the calcite and sphalerite overlap with those collected on primary fluid inclusions of sphalerite (Richardson et al., 1984; and Spry et al., 1994; Pelch et al., 2015), which may indicate that the fluids in the secondary inclusions were present in the system shortly after the precipitation of the sphalerite. The low Th of the secondary FIs in the studied fluorite sample likely record a near-surface meteoric fluid
- significantly cooler than the mineralizing fluids in the region.

is 2.7 x 4.5 cm.

Fig. 5: Scan of thin section slide S-35-560A. Size of the slide is 2.7 x 4.5 cm.

Goldstein, R.H., and Reynolds, T.J., 1994, Systematics of fluid inclusions in diagenetic minerals: Society of Economic Geologists and Paleontologists Short Course 31. Lukoczki et al., 2021, Phase I Earth MRI Activities in the Western Kentucky Fluorspar District, unpublished report.

Pelch, M.A., Appold, M.S., Emsbo P., Bodnar, R.J., 2015, Constraints from Fluid Inclusion Compositions on the Origin of Mississippi Valley-Type Mineralization in the Richardson, C.K., and Pinckney, D.M., 1984, The chemical and thermal evolution of the fluids in the Cave-in-Rock fluorspar district, Illinois: Mineralogy, paragenesis, and

Fig. 2: Scan of thin section slide BCH-5 3.17. Size of the slide Fig. 3: Image of FIA-F2 showing highly variable L:V ratios providing evidence of necking down after phase separation.

Illinois-Kentucky District: Economic Geology, v.110, p. 787–808. fluid inclusions: Economic Geology, v. 79, p.1833–1856. Economic Geology, v. 89, p. 288–306.





Fig. 6: Image of FIA-C1. The darker brown inclusions trapped hydrocarbon fluids that likely migrated during the Permian indicating a relatively early diagenetic origin of the host calcite within a Permian dike.



Fig. 8: Scan of thin section slide S-57 232.67. Size of the slide is 2.7 x 4.5 cm.

Spry, P.G., and Fuhrmann, G.D., 1994, Additional fluid inclusion data for the Illinois-Kentucky fluorspar district: Evidence for the lack of a regional thermal gradient:

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Fig. 4: Histogram of homogenization temperatures. The wide range of Th values in FIA-F2 may be a result of the necking down. Low Th values of FIA-F3 suggest the entrapment of cooler meteoric fluids.

Fig. 7: Histogram of homogenization temperatures. The wide range of Th values of could be a result of chemical variation in the hydrocarbon fluids. The inclusions with the highest Th values fluoresce yellow under UV light suggesting greater thermal maturity relative to the inclusions that fluoresce blue.



Fig. 9: Image of FIA-S2. The lateral association and tapering edges of the fluid inclusions are strong petrographic evidence for necking down.

Fig. 10: Histogram of homogenization temperatures. The Th values collected overlap with Th values from primary inclusions collected in sphalerite (Richardson et al., 1984; and Spry et al., 1994; Pelch et al., 2015) potentially indicating that secondary inclusions trapped fluids similar to the original mineralizing fluids.