FLUID INCLUSION ANALYSIS OF FLUORITE IN POST-ALLEGHANIAN VEINS, VALLEY AND RIDGE PROVINCE, CENTRAL PENNSYLVANIA

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ABSTRACT

Fluorite-calcite-quartz mineralization was collected from post-Alleghanian veins in limestone of the Silurian-Devonian boundary near Allenport, PA. Microthermometric analysis focused on 2-phase (liquid + gas) fluid inclusions in fluorite, which are dominantly in primary fluid inclusion assemblages (FIAs). Temperatures of homogenization (T_h) (liquid + gas → liquid) were tightly constrained between 170.0 and 195.0°C. Final ice melting temperature (T_m) showed a narrow range of -20.1 and -21.3°C. Collecting T_m was complicated by the formation of hydrohalite under freezing conditions, requiring that samples needed to be melted completely between observations of each T_m. A secondary FIA confined to a damaged corner of a euhedral fluorite crystal exhibited a much wider T_h range (115.0˚C - 195.0˚C) than the inclusions in primary FIAs, but produced consistent T_m values at -21.0°C. The tight T_h range from primary FIAs fits into the broad T_h range reported by Howe (1988) of 160 ± 60°C for Mississippi Valley-type occurrences in central Pennsylvania and are roughly comparable to values reported by Evans and Battles (1999). T_h data from vein quartz in other local formations are radically different as well: Brallier Fm: 100 to 106.1°C (Curry, 2013), Mahantango Fm: >130 to 190°C (Scudder, 2014), Bald Eagle Fm: 228°C (Mutti *personal communication,* 2016).

INTRODUCTION

- Lab induced phase changes in fluid trapped in minerals provides information about the environment under which the fluid was trapped
- Fluid inclusion analysis has been used to reconstruct geologic events in the Valley and Ridge Province of the Appalachian Mountains (Ex: Howe, 1988; Evans and Battles, 1999)
- This study analyzes 2-phase (liquid + gas) inclusions in fluorite from NW striking post-Alleghanian veins in Silurian-Devonian limestone near Allenport, PA, in the eastern limb of the Broadtop Synclinorium (Evans, 2010) (Fig. 1)

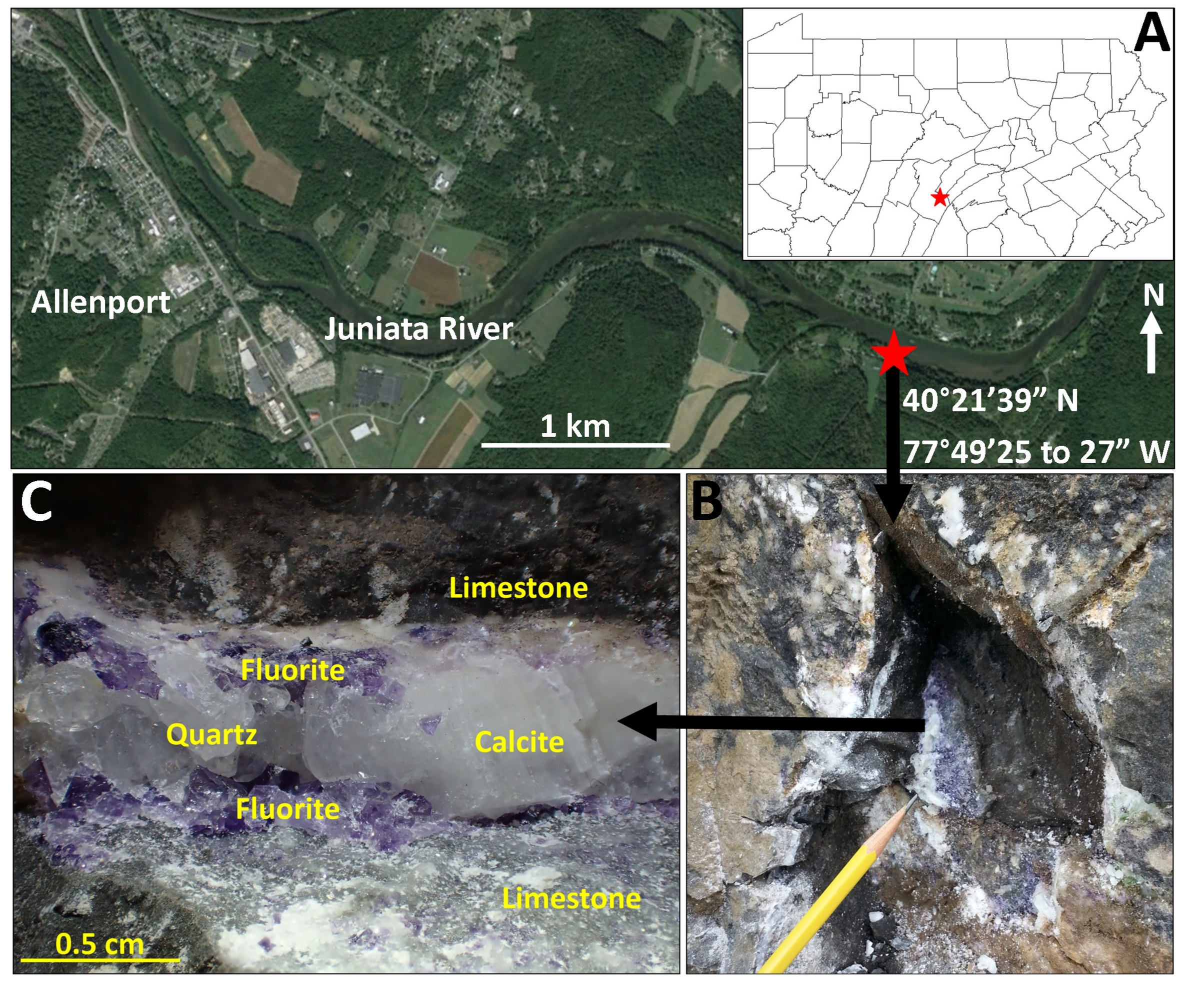

Figure 1: **A** Location map (base from Google Earth) showing sample site in Huntingdon County, PA. **B** Outcrop of vein mineralization in Tonoloway Fm limestone. **C** Hand sample of vein mineralization showing paragenesis: calcite, fluorite, calcite, quartz.

- For 2-phase aqueous inclusions in the same stratigraphic region of these samples, Evans and Battles (1999) reported 2 groups of data:
  - T_h of 60 to 158°C & salinity of 21.0 to 24.5 wt% NaCl equivalence
  - T_h of 155 to 250°C & salinity of 8.5 to 19.0 wt% NaCl equivalence
- Howe (1988) studied Mississippi-Valley type Pb-Zn occurrences in the Valley and Ridge Province, and found T_h of 160 ± 60°C for vein mineralization containing fluorite
- Curry (2013) examined hydrocarbon bearing fluid inclusions in vein quartz in the Brallier Fm and reported T_h of 100 to 106.1°C for 2-phase aqueous inclusions
- Scudder (2014) examined fluid inclusions in vein quartz in the Mahantango Fm and reported T_h of >130 to 190°C for 2-phase aqueous inclusions
- Mutti (*personal communication,* 2016) reported T_h with a mode of 228°C from 2-phase aqueous fluid inclusions in mineralization in the Bald Eagle Fm

METHODS

- Doubly polished thick sections (~100-150 µm) of vein mineralization (ex: Fig. 2 A) were prepared and mapped
- Microthermometric analysis performed using Olympus BX51 microscope with attached USGS-style gas flow fluid inclusion stage
- Only fluorite contains 2-phase (liquid + gas) inclusions, and these were the only inclusions analyzed due to time constraints
- Fluorite and quartz contain 1-phase gaseous inclusions (presumed CH_4-CO_2 mixtures), but calcite was not clear enough to resolve
- Samples were heated first to obtain **temperature of homogenization (T_h)** data (liquid + gas → liquid)
- Samples were later cooled to obtain **temperature of final ice melting (T_m)** data (solid + liquid + gas → liquid + gas)
  - Hydrohalite formed upon freezing (ex: Fig. 2 B) and metastable persistence past ice T_m complicated collection of T_m data
  - **Hydrohalite dissociation (T_d)** was not rigorously studied
- T_h and T_m data were collected for the same fluid inclusions wherever possible
- 3 fluorite grains were analyzed: sample F1 was from one vein and samples F2 and F3 were from an adjacent vein
  - All three fluorite grains were embedded in calcite with quartz grains present
- Samples F2 and F3 are fragile — some fluid inclusions burst before their T_h was reached. Those inclusions were not investigated.
- Primary FIAs (ex: Fig. 2B,C) and a secondary FIA (Fig. 2 D,E) were analyzed in F1, but only primary FIAs were analyzed in F2 & F3

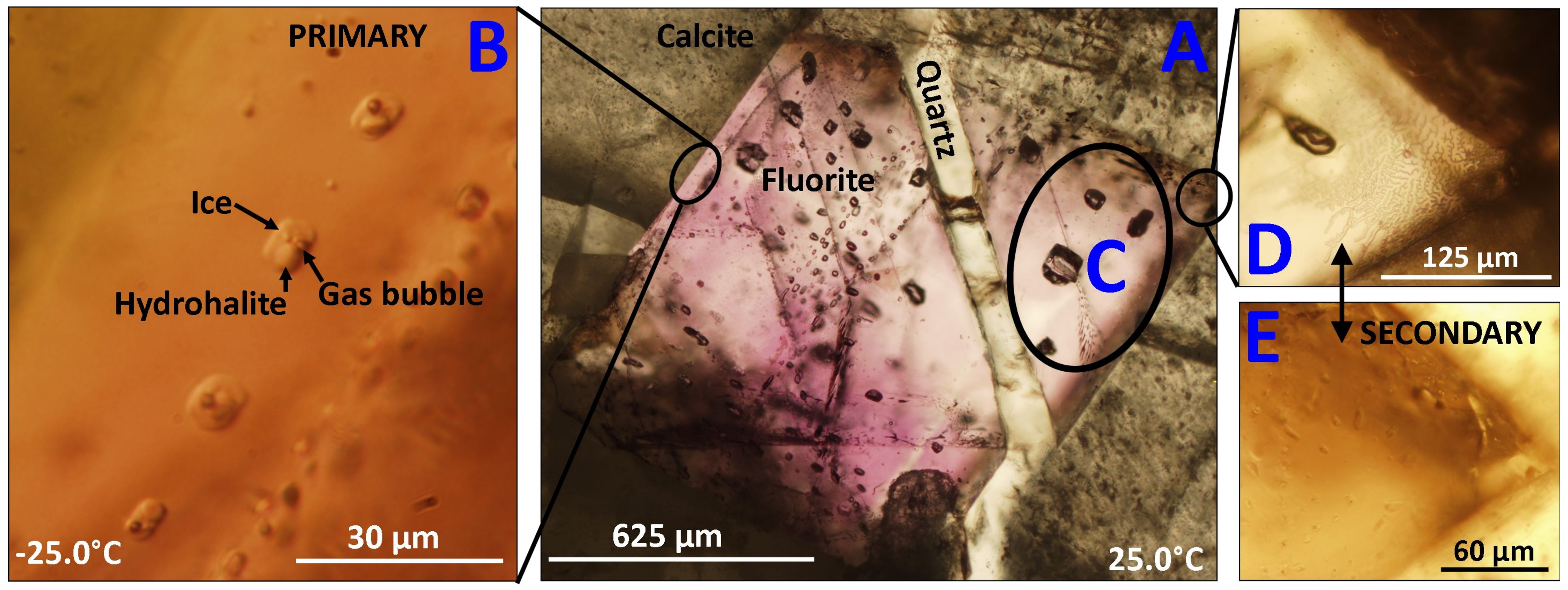

Figure 2: **A** Microscopic view of fluorite (sample F1) in thick section. **B** Close-up image of frozen primary fluid inclusions, which contain hydrohalite, ice, and gas bubbles. Primary FIA were found throughout the grain, but were heavily analyzed in circle **C**. **D** Close-up image of a damaged corner of the fluorite grain, which **E** hosts the secondary FIA. Pictures **D** and **E** show different levels of focus within the grain.

RESULTS

- Data is summarized in Figures 3 & 4
- 87 total T_h data points were collected
- T_h of all primary inclusions are within a fairly tight range: 170.0 to 195.0°C
- T_h of all secondary inclusions are within a much wider range: 115.0 to 195.0°C

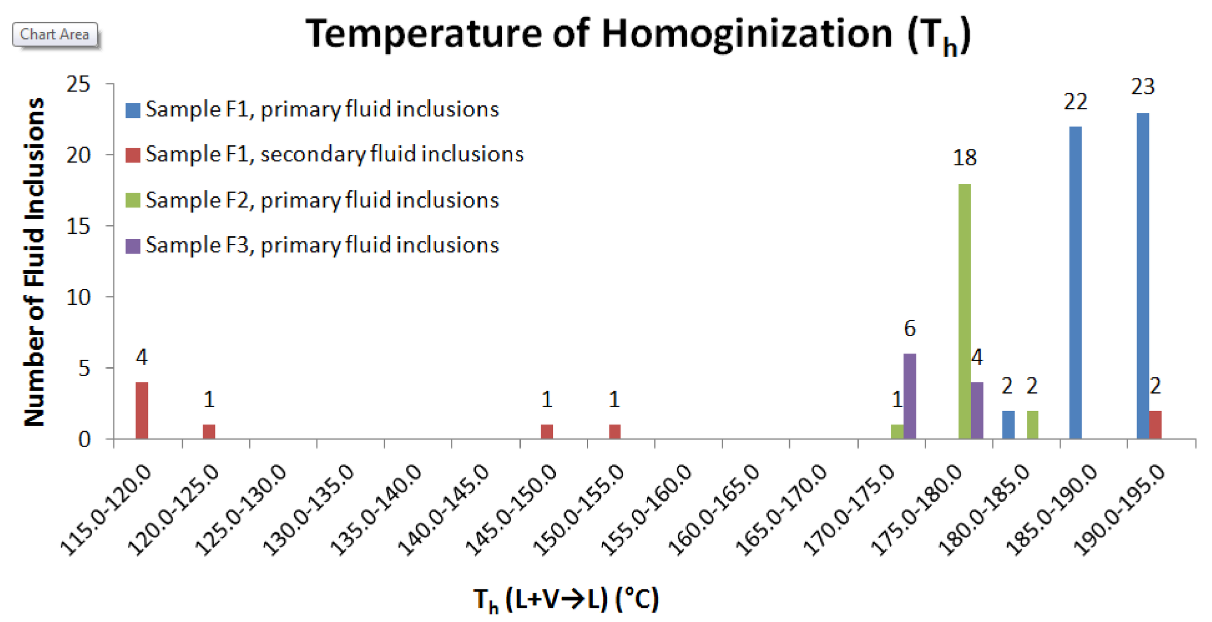

Figure 3 (Right) Bar graph showing the number of fluid inclusions demonstrating each homogenization temperature (within 5°C brackets).

- 72 total T_m data points were collected
- T_m of all inclusions within very tight range: –20.1 to –21.3°C
- Temperature of initial melting was indeterminate but 10s of degrees Celsius colder than T_m
- Hydrohalite:
  - T_d not thoroughly collected
  - Five T_d points recorded at -2.5°C
  - All dissociated by 0°C
- No inclusions had fluorescent liquid hydrocarbons

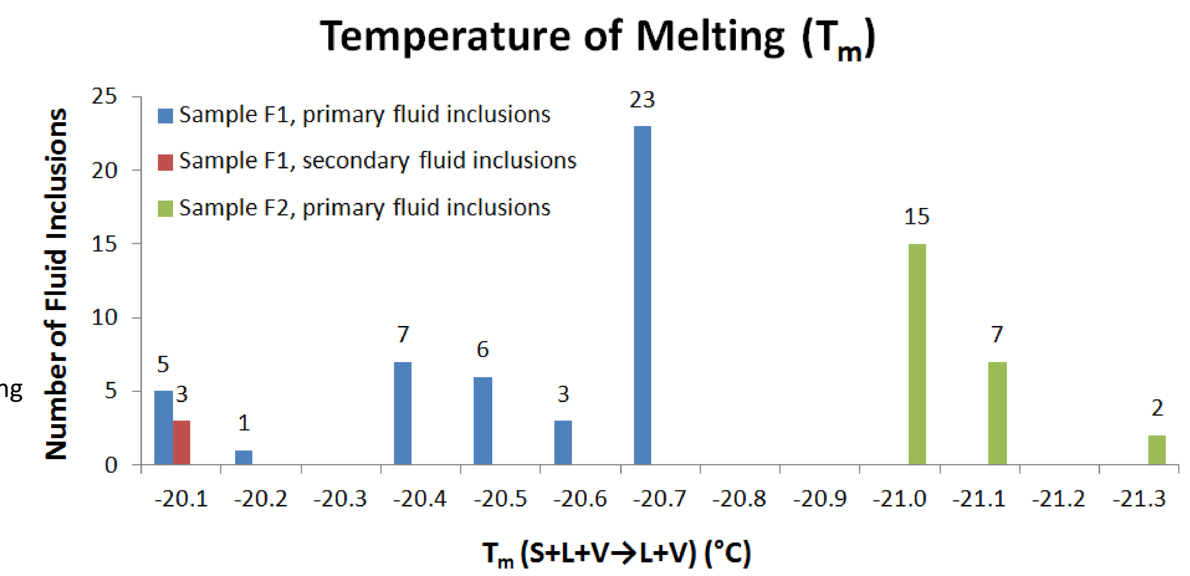

Figure 4 (Right) Bar graph showing the number of fluid inclusions demonstrating each melting temperature (within ±0.1°C).

DISCUSSION

T_m of Primary FIAs

- The salinity of the liquid in the inclusions can be determined in NaCl wt% equivalence by comparing observed T_m to the NaCl-H_2O vapor-saturated phase relations diagram (Bodnar, 2003)
- Within experimental error, T_m is indistinguishable from the eutectic temperature of the NaCl-H_2O binary system (-21.2°C), which corresponds to **23.2 NaCl wt% equiv**.
- Presence of hydrohalite on the liquidus demands salinities between **23.3 to 26.3 NaCl wt% equiv.,** indicating highly saturated brines (consistent with basinal brines)
- Temperature of initial melting << -21.2°C requires the presence of divalent ions
  - Ca^{+2} is abundant considering the presence of fluorite and calcite
  - There is no mineralogical indication of sulfate or sulfide in the system

T_h of Primary FIAs

- Consistent T_h throughout F1 indicate consistent temperature during fluorite growth
- T_h give a **minimum entrapment temperature of 170.0 to 195.0°C,** which corresponds to a **minimum depth of 8.5 to 9.75 km,** if one assumes a geothermal gradient of 20°C/km
- This depth indicates a **pressure correction of 280 to 325 MPa**, if one assumes a pressure gradient of 1 kb/3 km
- If we assume $P_f = P_L$ then 280 MPa indicates a **temperature of entrapment of 330°C** (Diamond, 2003)

Secondary FIA

- Avg. T_m of secondary fluid inclusions is –20.1°C, which fits in the range of the primary FIAs, and indicates that the entrapped fluid must still be highly saline basinal brine
- T_h ranges 80°C (115.0-195.0°C), suggesting there were pulses of fluid through the system much later during prolonged uplift

Relevance to Other Work

- The salinity of our primary inclusions is consistent with basinal fluids reported by Evans and Battles (1999)
- T_h reported by Evans and Battles (1999) for salinities similar to our samples are lower than our T_h, suggesting that our fluid was trapped in a deeper and hotter environment or during an episode of an elevated thermal pulse
- Our T_h fits within the T_h range given by Howe (1988), but the mineralization at Allenport distinctly lacks the sulfide mineralization of the Mississippi Valley-type occurrences studied by Howe
- The mineralization of our study is stratigraphically below Curry's (2013) and Scudder's (2014) samples. Our T_h are within the range of Scudder's data but completely different to Curry's data and lack the hydrocarbon inclusions dominant in Curry's samples.
- The T_h values reported for the mineralization in the stratigraphically lower Bald Eagle formation are hotter than our T_h values, as expected

Future Investigations

- Investigation of 1-phase gaseous inclusions by freezing studies and Raman spectroscopy
- More field work, especially structural data, to aid contextualization to the study to other data sets

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