

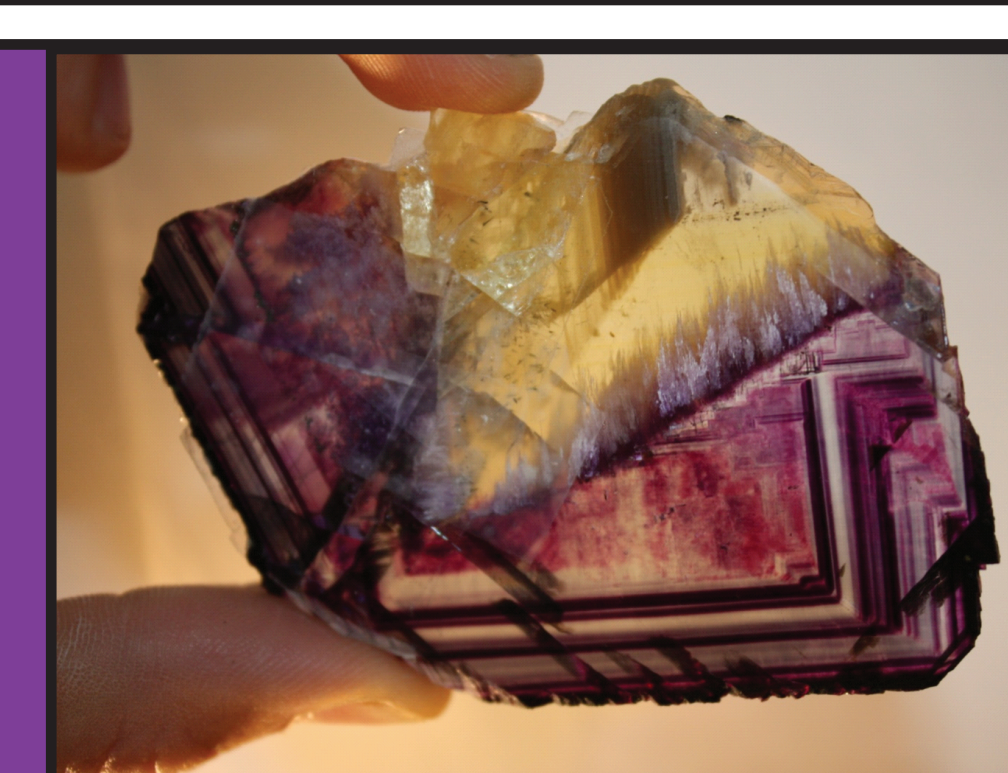


# The Mineral Chemistry of Purple and Yellow Fluorite: Insights from High Resolution FTIR Spectroscopy

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## Abstract

Banded fluorite samples from the Cave-In-Rock Fluorspar District, Illinois offer insights into the evolving hydrothermal fluids that hosted sulfide ore deposition. Earlier studies have shown that fluids responsible for the Cave-In-Rock deposits followed similar trends in crystallization temperature, salinity, and isotope systematics. However, these studies failed to identify chemical and/or environmental factors that correlate with the observed prominent color banding. We present detailed micro-FTIR analyses of hydrous species within a gemmy fluorite specimen from the Hill Mine. Our analyses represent the first high-resolution (100  $\mu$ ) IR analyses on fluorite. The specimen consists of a yellow core with a thick coating of alternating purple and colorless bands. We have identified a prominent broad peak at 3400  $\text{cm}^{-1}$  and four sharp peaks at 1400, 1550, 1650, & 1740  $\text{cm}^{-1}$ . We show that yellow fluorite has order of magnitude higher absorbance at 3400 and 1650 (common features associated with hydroxyl stretching and bending of molecular water, respectively) but no absorbance at 1400. Colorless and purple bands show appearance of the 1740 band, and no absorbance at 1400. The peak heights at 3400 & 1650 generally correlate with one another within bands, but do not show distinct differences across purple and colorless bands.

## The Cave-In-Rock Fluorspar District: Anatomy of an Ore Deposit

- The Cave-In-Rock Fluorspar District is a Mississippi Valley Type ore deposit located in southern Illinois. It has been the subject of intense study in order to characterize the nature of the fluids that generate MVT-Type deposits.
- MVT-Type deposits formed in Illinois during the Late Paleozoic (associated with the formation of Pangea) and the Tertiary (associated with the Alpine and Laramide Orogenies).
- Valuable concentrations of Pb and Zn sulfide ores are hosted within carbonate formations.
- Previous studies on fluid inclusions trapped in fluorite crystals document changes in the host hydrothermal fluid: stable isotope compositions, salinity, and homogenization temperatures show evidence for a 2-stage fluid evolution.

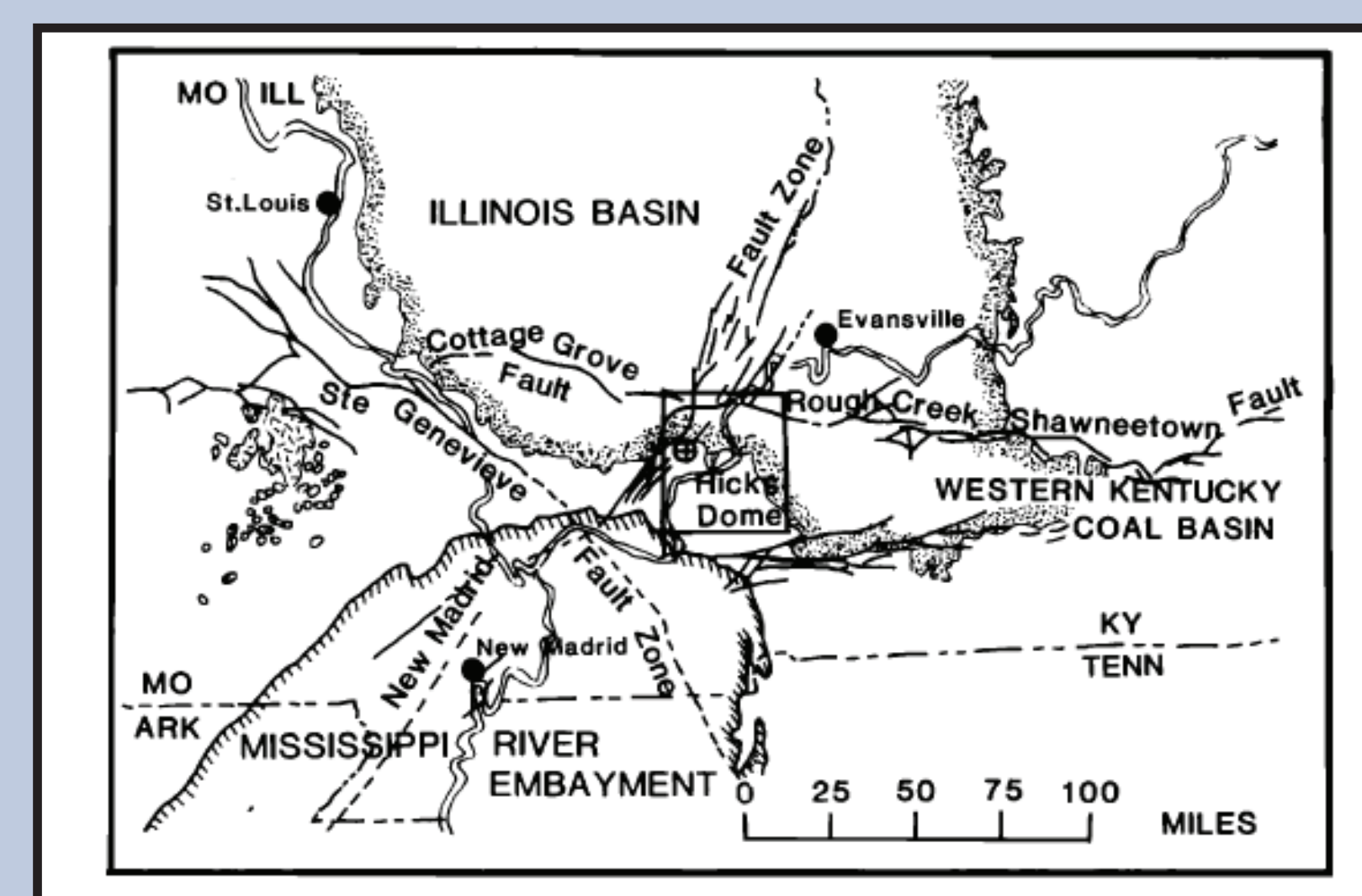


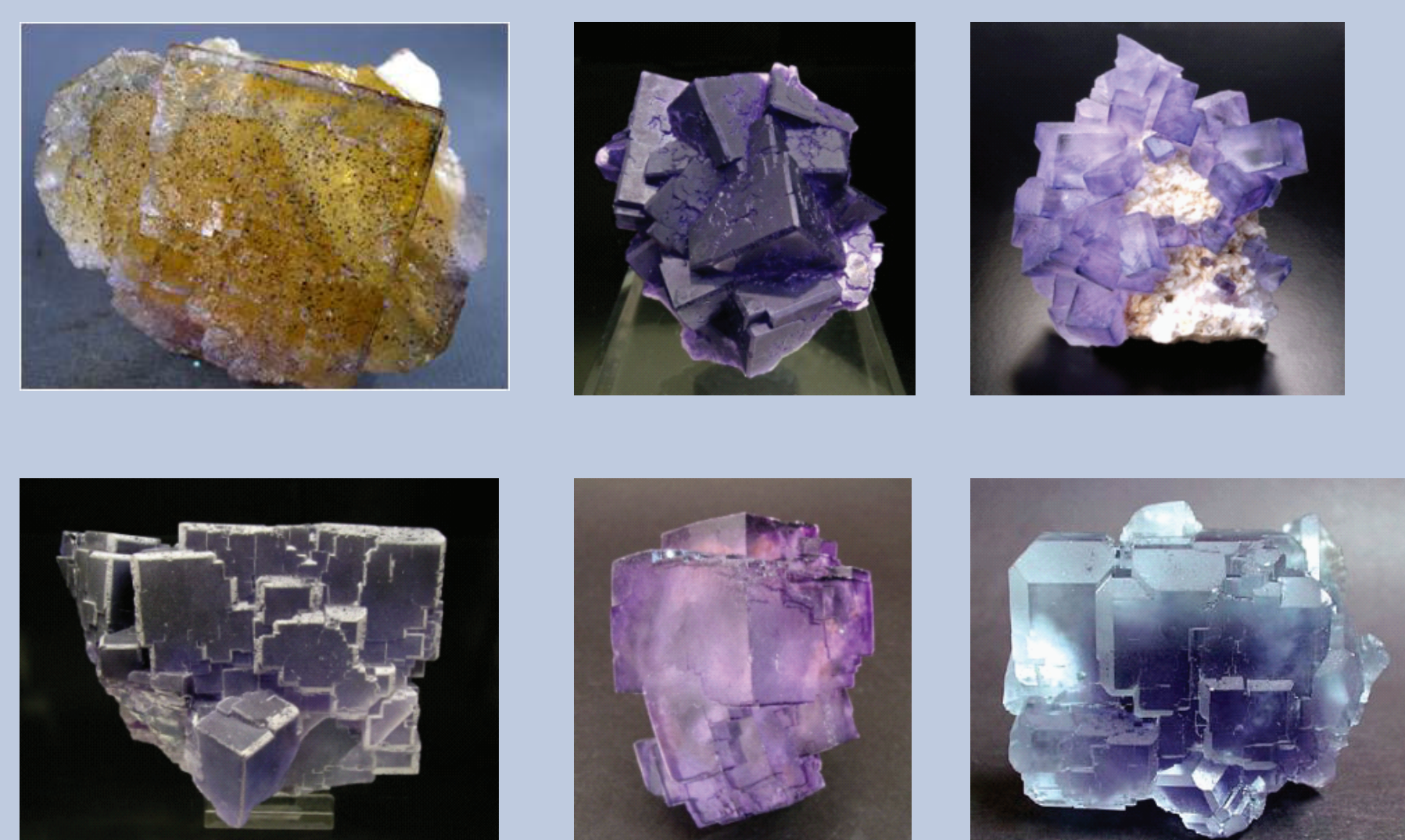
Figure from Spry & Fuhrmann, 1994

- We have chosen a well-studied, multi-colored, gemmy fluorite crystal from the Hill Mine of the Cave-In-Rock Fluorspar District for spectroscopic analysis.
- Uniform geochemical indicators are observed across the entire fluorite crystal, except within the dark purple rim labeled P7.
- The cause of brilliant color variations in fluorite is unknown. Here, we test whether color differences actually reflect meaningful changes in the host fluid environment during crystal growth.

### 2-Stage Fluid Evolution

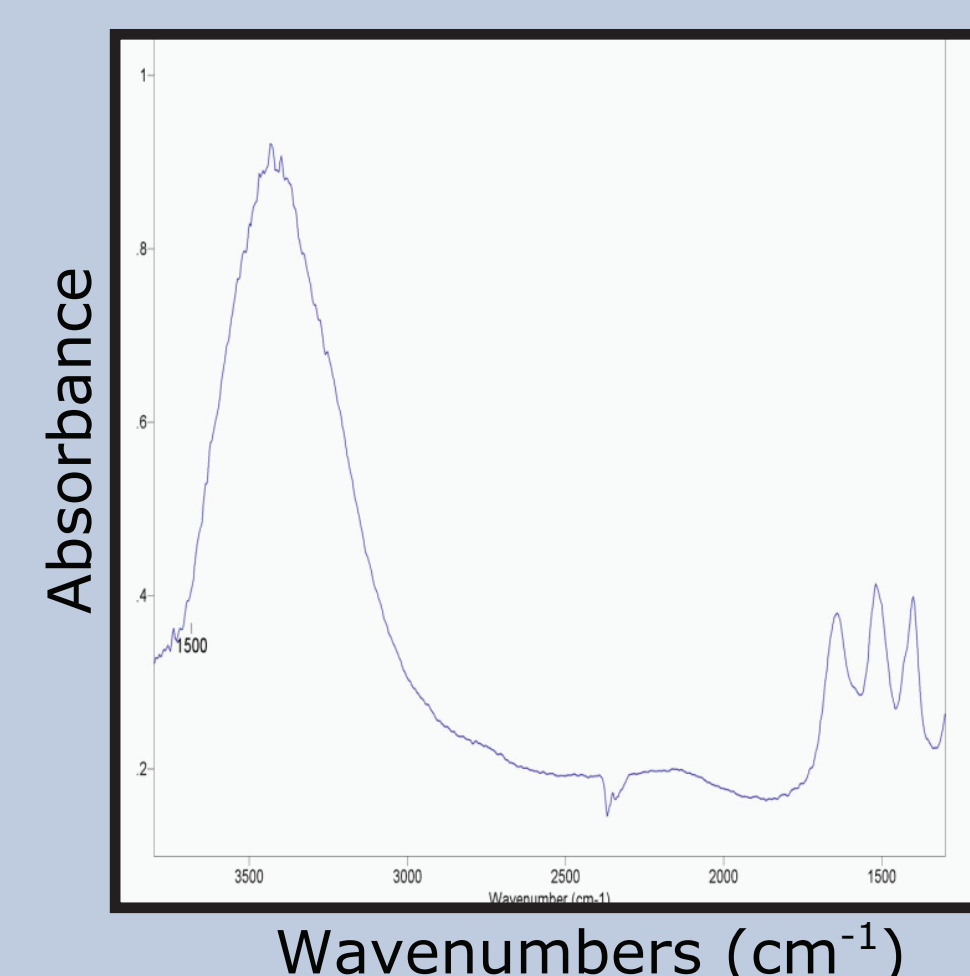
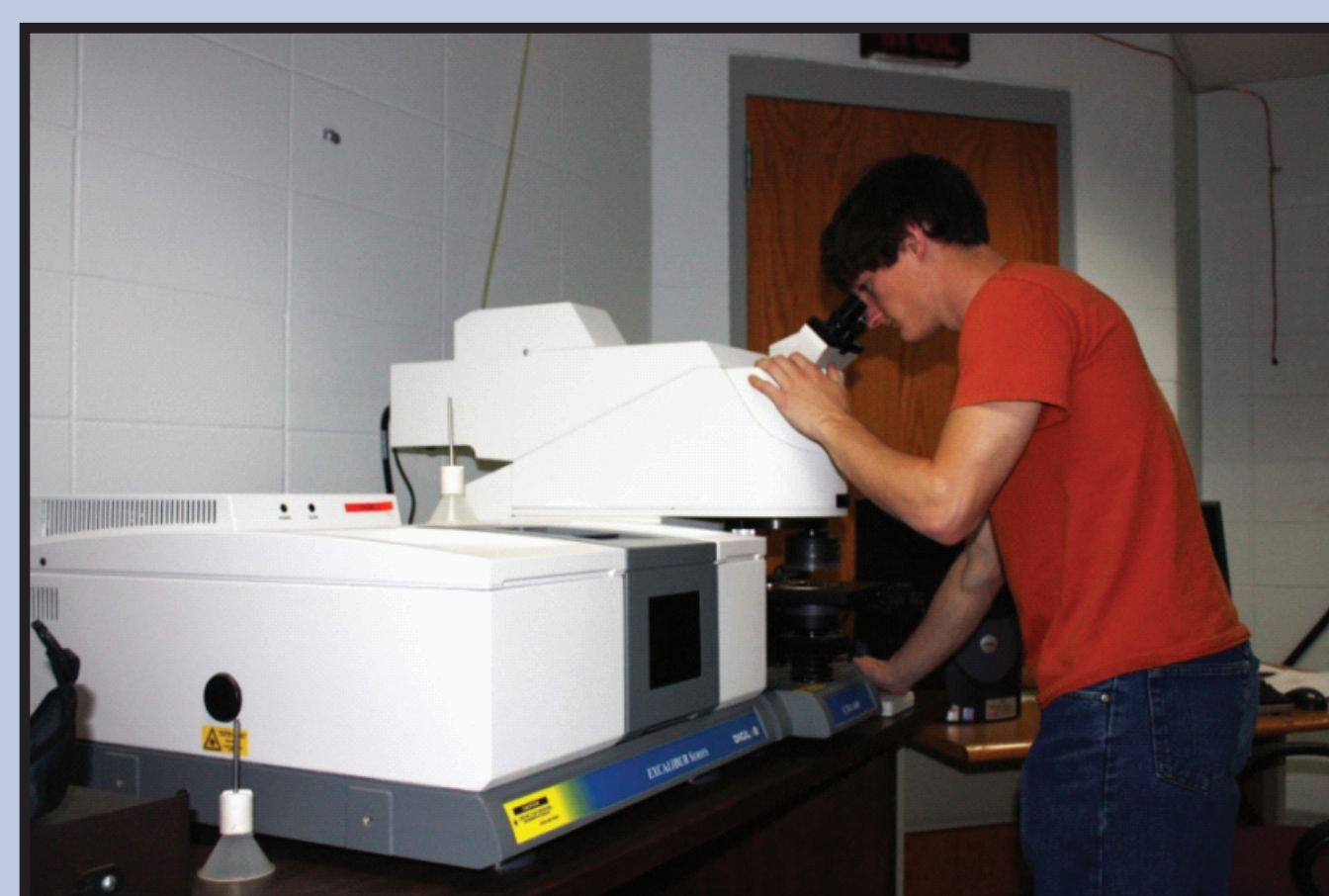
	Core	Rim (P7)
Mineralogy:	fl, sph, gl, qtz	cc + ba
Homog. Temp:	$\sim 145^\circ\text{C}$	$\sim 125^\circ\text{C}$
Salinity:	20% NaCl	<10% NaCl
H Isotopes:	$\delta\text{D} = -25\text{‰}$	$\delta\text{D} = -40\text{‰}$

## Nature of Fluorite



- Cubic mineral
- Gem quality
- Stunning growth bands
- Fluorescent
- $\text{CaF}_2$
- Any color!

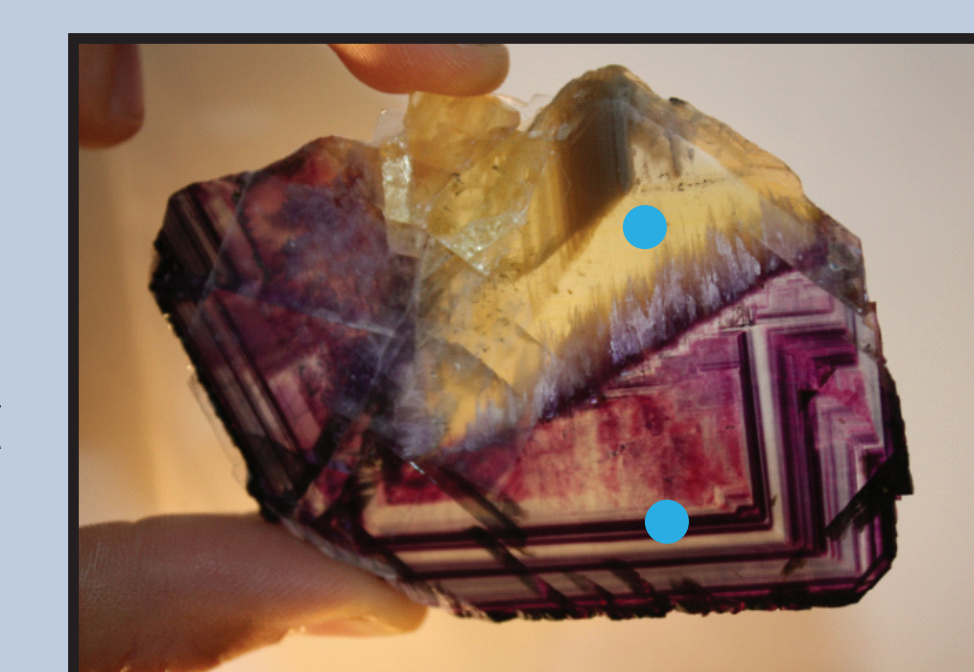
## Hydrous Impurities in Fluorite



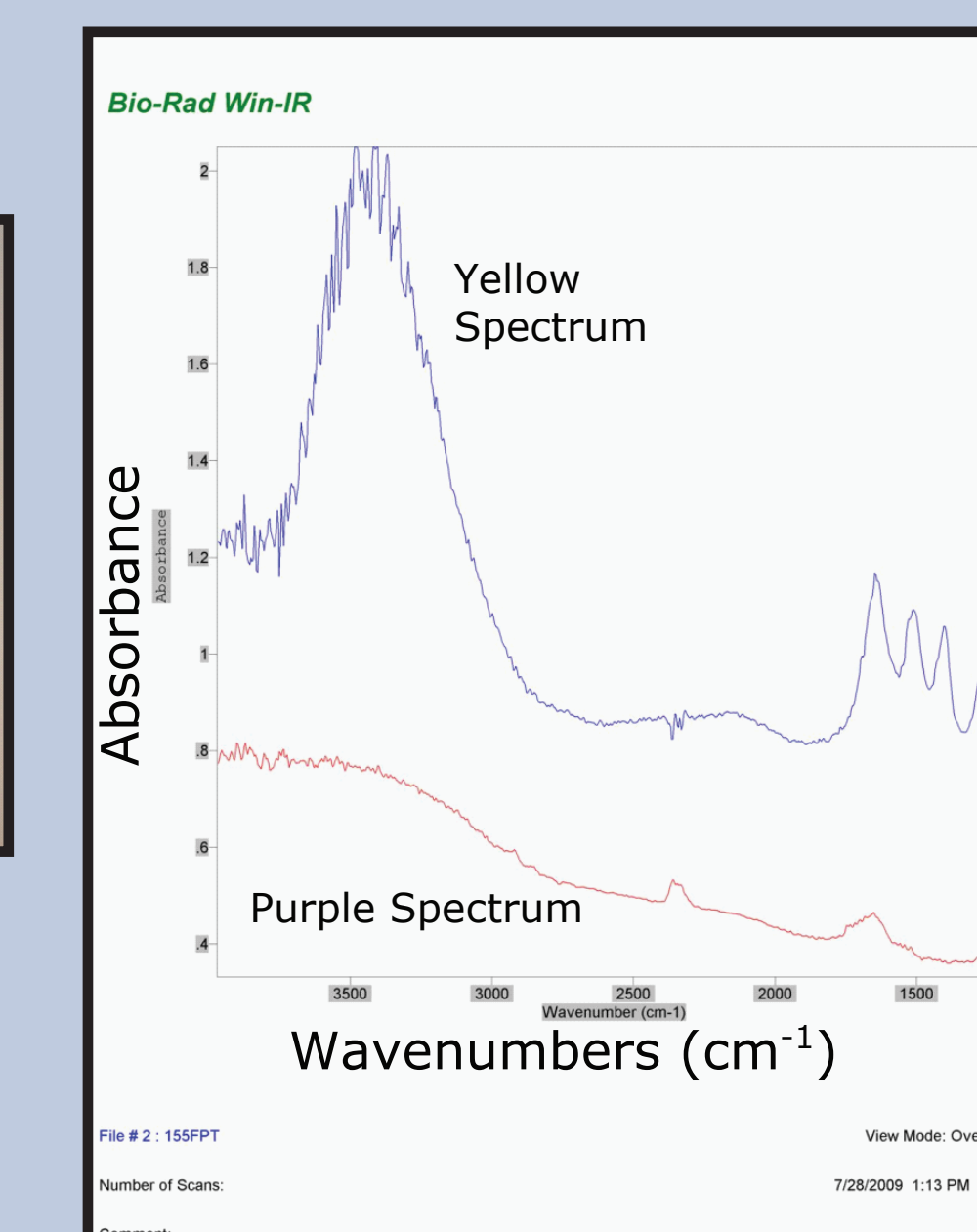
- This study focuses on the variations in the abundance of hydrous impurities in this fluorite crystal.
- MVT deposits were formed from water-dominated fluid systems.
- Infrared spectroscopy is ideal for measuring Hydrogen-bearing impurities.
- First high resolution spectroscopic analyses of fluorite.
- Absorption at 3400 wavenumbers is due to the fundamental O-H stretch of the hydroxyl species (an OH not charge balanced by H).
- Absorption at lower energies (1650 wavenumbers) is due to the bending of trapped molecular water.
- We have successfully tracked the growth of hydrothermal quartz crystals using these absorption bands.

## Color Differences

- Over 590 scans
- Two colors:  
Two unique spectroscopic signatures

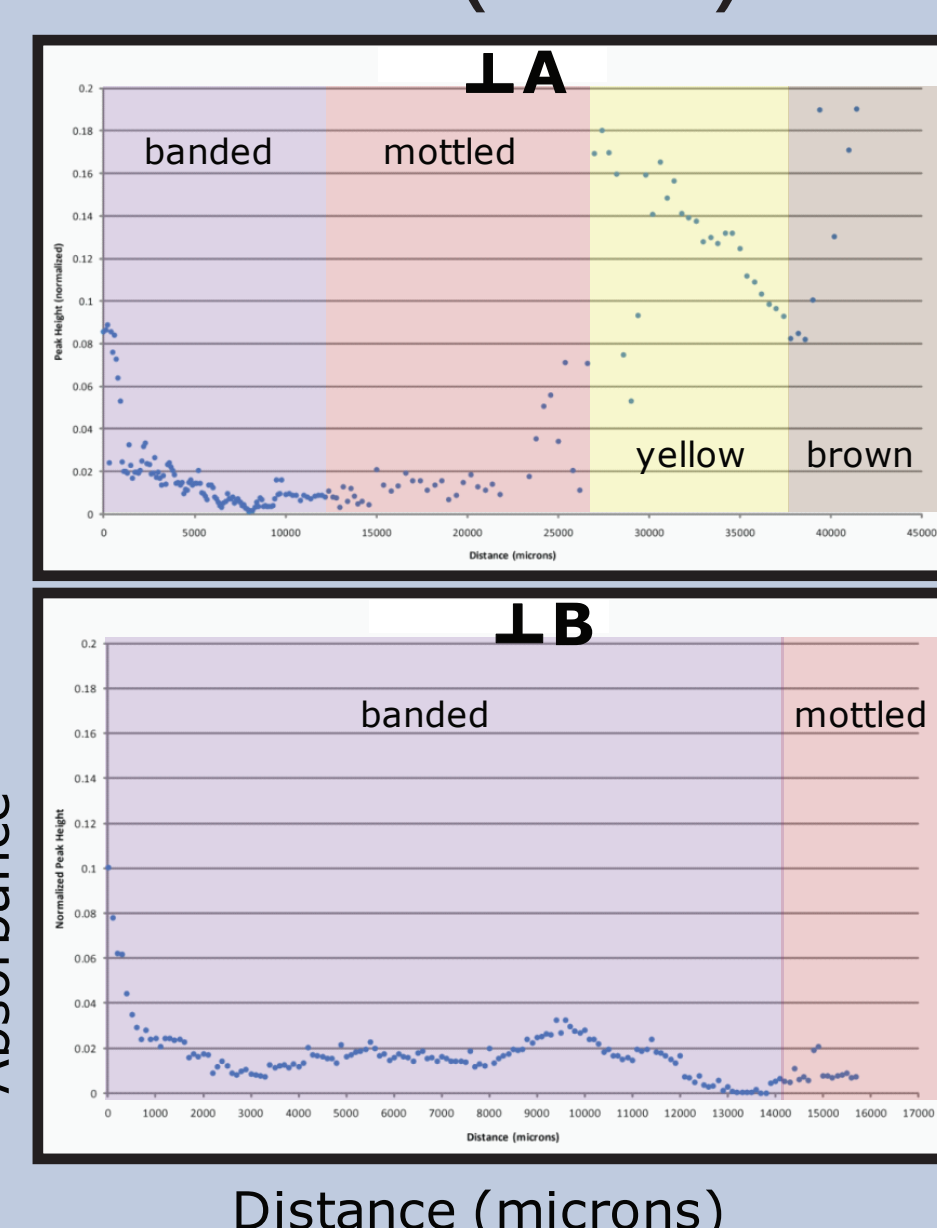


- All yellow regions show order-of-magnitude more absorbance due to the presence of hydroxyl species (3400) when compared to the purple and colorless bands.
- Both color regions show molecular water at 1650 wavenumbers.
- Yellow regions of the crystal show two previously unrecognized peaks at 1550 and 1400 wavenumbers.
- Purple and colorless regions exhibit a third unknown absorption band at 1740 wavenumbers (not present in the yellow regions).
- 3400 and 1650 peaks track together across all regions of the crystal.
- Color changes may reflect meaningful geochemical changes in the fluid environment in which the crystal is growing.

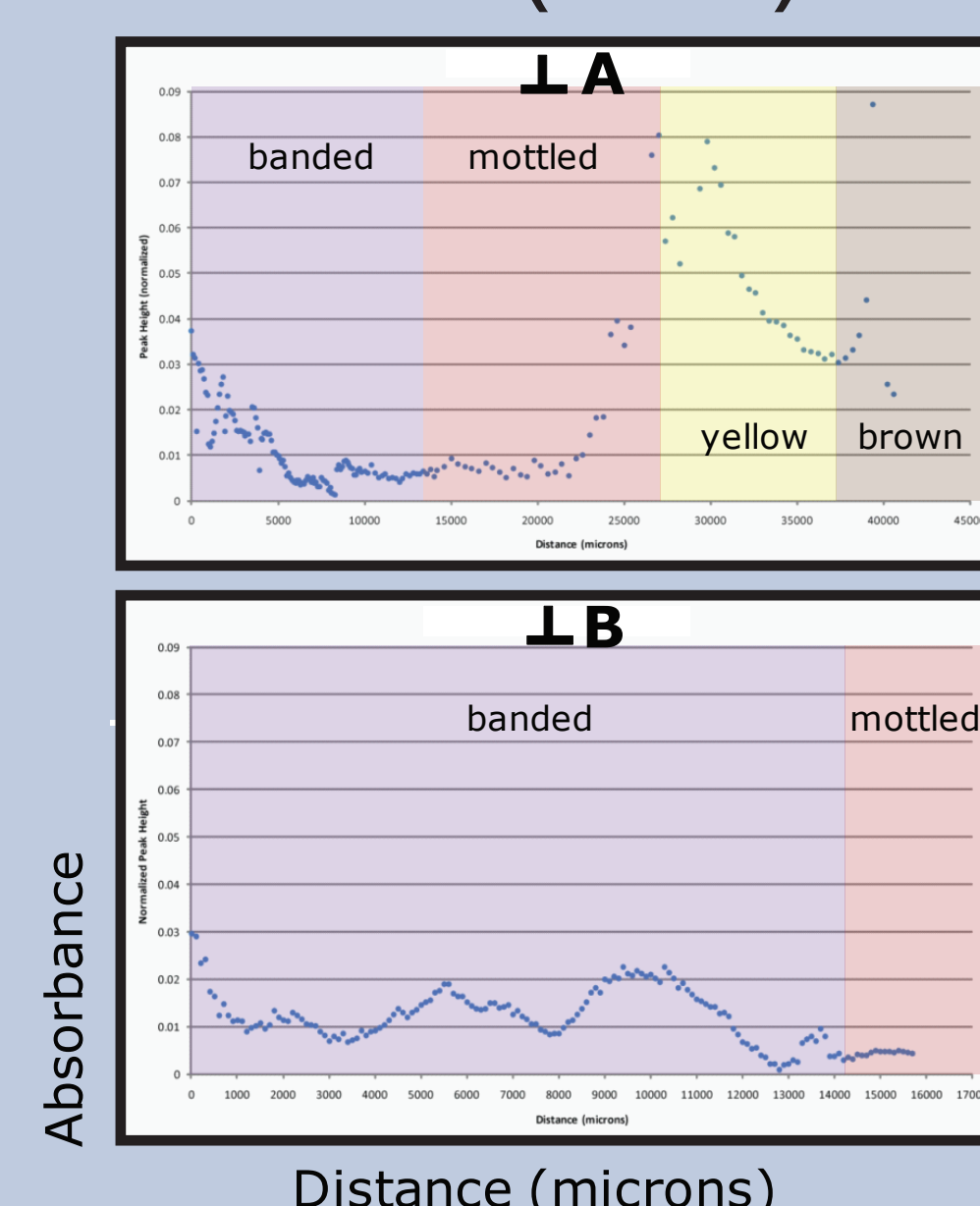


## Perpendicular Traverses

### 3400 ( $\text{cm}^{-1}$ )

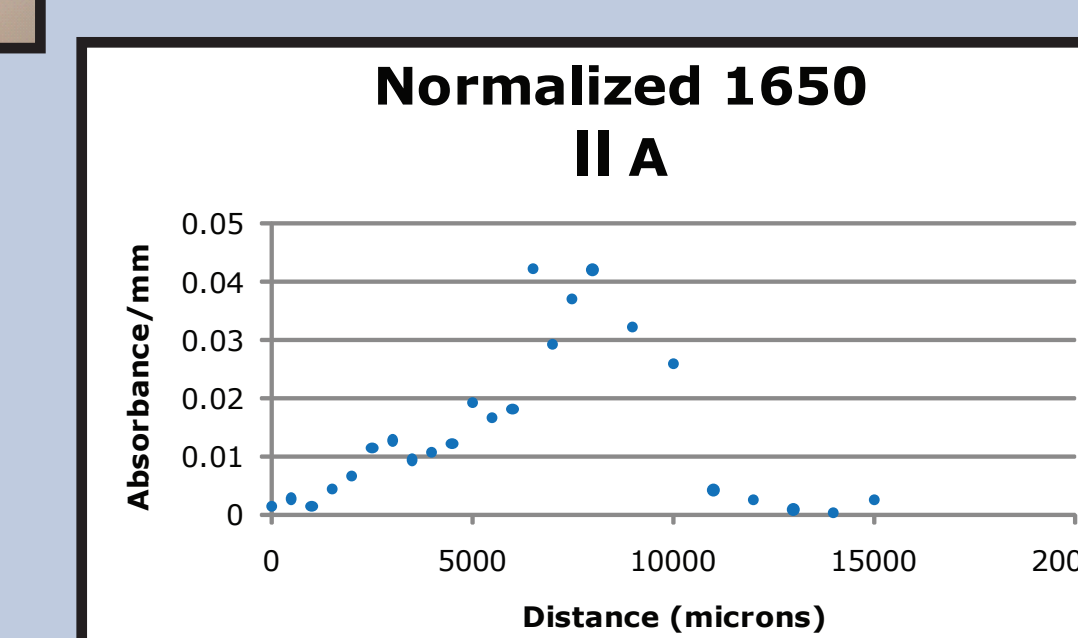
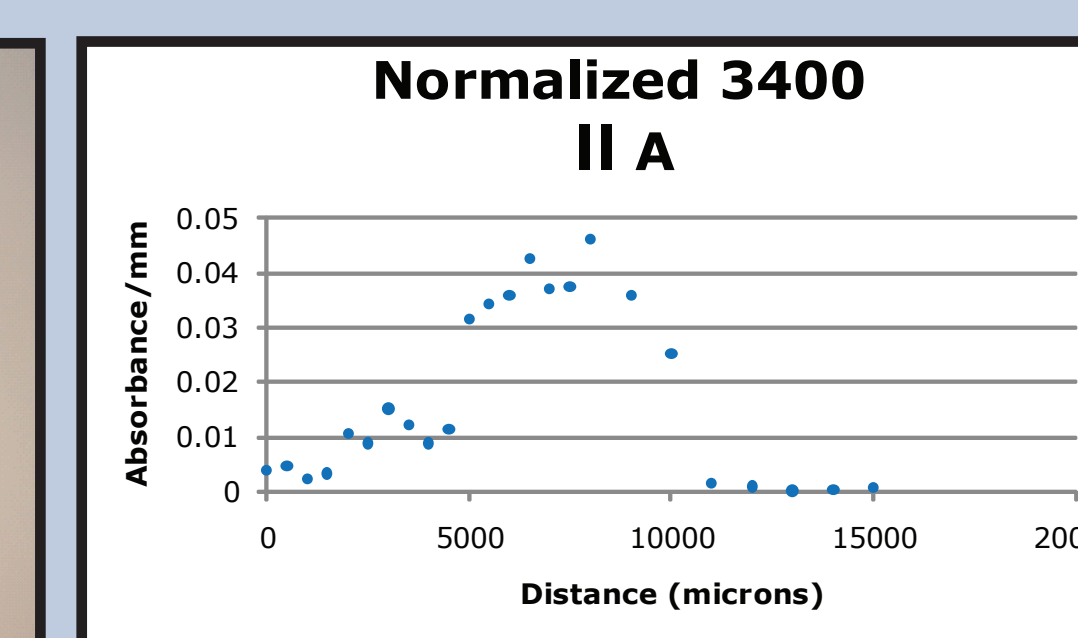
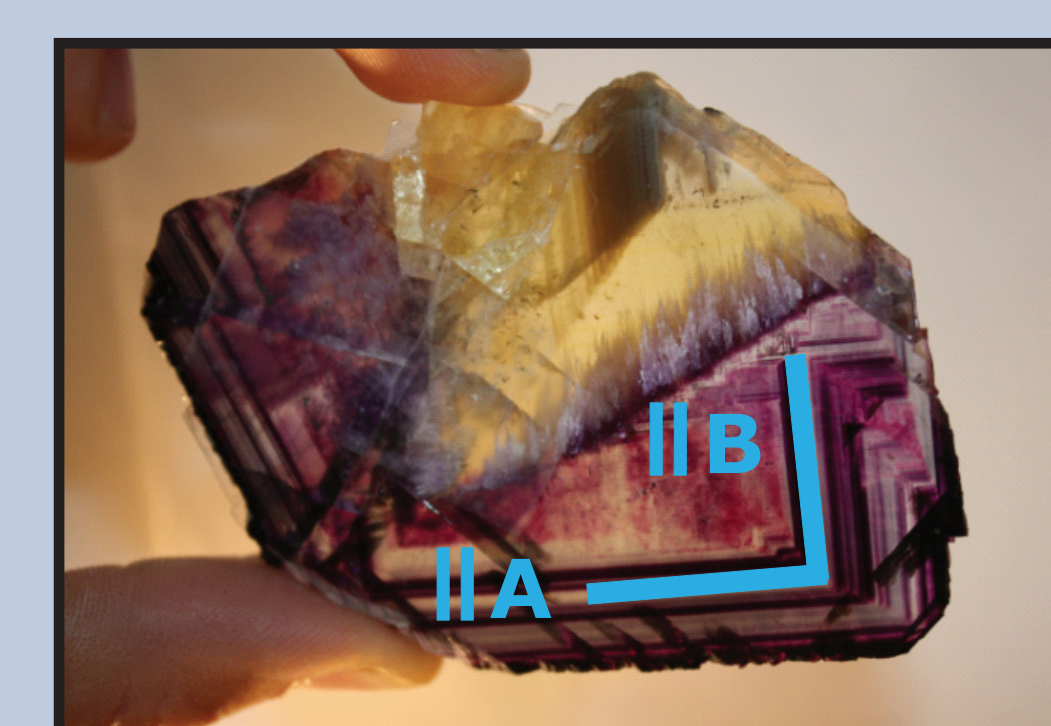


### 1650 ( $\text{cm}^{-1}$ )



- Order-of-magnitude higher impurity concentrations in yellow and brown regions of the crystal.
- Sharp increase in the concentration of hydrous impurities at the rim of the crystal (P7).
- No direct correlation between absorbance of hydrous species and purple vs colorless band.
- Hydrous impurities in fluorite do not reflect geochemical variations in host fluid composition during crystal growth.

## Parallel Traverses



- Cubic mineral, so all faces expose the same atomic arrangement to the host fluid during crystal growth.
- Uptake in impurity concentration is not constant for a particular face at a particular time during growth.
- We observe profound variations in the concentration of hydrous impurities along a visible isochron.
- Observed variations could be due to post-crystallization features such as fractures or due to variations in surfactants (such as organic clusters) on a growth face.
- Hydrous impurity concentrations do not correlate with intensity of color within purple bands.

## Acknowledgments

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Richardson, C. K., Rye, R. O., and Wasserman, M. D., 1988, The Chemical and Thermal Evolution of the Fluids in the Cave-in-Rock Fluorspar District, Illinois: Stable Isotope Systematics at the Deardorff Mine, *Economic Geology*, Vol. 83, pp. 765-783.

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## Observations and Conclusions

- The profound change in fluid chemistry seen in previous studies (at P7) is reflected in the IR.
- The abundance and character of hydrous impurities in yellow regions of the crystal are distinct from those in purple and colorless regions.
- The abundance of hydrous impurities in purple and colorless regions are highly variable within and across visible growth bands.
- X-OH concentrations correlate with molecular water (HOH) in all regions of the crystal.
- Variations in hydrous species within purple and colorless bands may reflect post-crystallization processes such as fracture formation.