Paragenesis of Mineralized Fractures in Organic Rich Shales*

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Abstract

Mineralized fractures are common in organic-rich shales and are of interest because the mineralogy can influence shale brittleness and porosity/permeability. We have noted similarities in the paragenesis of mineralized fractures from several shale units of different ages and from different basins (Devonian Marcellus Shale [PA], Mississippian Barnett Shale [TX], Devonian/Mississippian Woodford Shale [OK], and Late Jurassic Haynesville Shale [TX]). The shales contain localized vertical/subvertical and some horizontal mineralized fractures that vary in width from thin (~ 0.04 mm), usually filled with calcite, to thick (> 0.2 mm), which have a complex mineralogy. Some fractures or veins are precompactional although most are interpreted to form late in the diagenetic sequence. The Barnett, Haynesville, and Marcellus contain complex fractures with calcite, dolomite, baroque dolomite, quartz, chalcedony, barite, celestine, pyrite, sphalerite, anhydrite, and albite. New work on the Woodford in southern Oklahoma indicates a similar mineralogy. Dissolution events also occur in the paragenetic sequences and some fractures are associated with brecciation. Fluid inclusion studies suggest interaction with multiple fluids, including hydrocarbons and hydrothermal fluids. Variation in cathodoluminescence and compositional variations within individual minerals indicate precipitation from evolving fluids. In some cases the minerals in the fracture extend into the surrounding shale, which could influence brittleness and the likelihood of reactivation. It is also clear that the nature of the fracture can be influenced by the composition of the host shale. The similar and anomalous mineral assemblages in the fractures from the different shales indicate alteration by similar fluids, internal and/or external, and suggest similar sources for the minerals. The results from different shales in different tectonic settings raise fundamental questions about whether the shales are open or closed systems.

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Paragenesis of mineralized fractures in organic rich shales

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Mineralized fractures are common in shales

Fundamental questions:

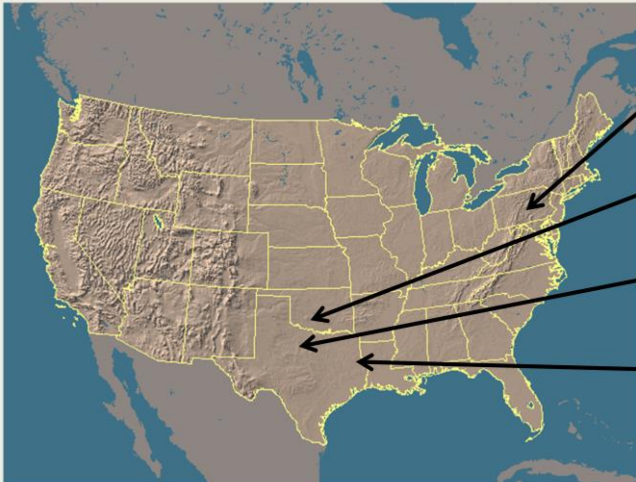
- What does the fracture mineralogy tell us about diagenesis and fluid flow?
- Are shales open or closed systems?
- How do mineralized fractures influence brittleness?
- Are healed fractures barriers to flow? Could they be conduits for flow? Do they affect production?
- Scale issues?

Presenter's notes: Shales can be significantly altered during diagenesis. Diagenetic studies on shale gas plays like the Marcellus are very important currently and in the future.
A better understanding of the paragenetic sequence of diagenetic events help predict both hydrocarbon prone and uneconomic regions, as diagenesis can have both positive and negative effects on reservoir quality.
Sphalerite found in vein from the Evanchick #1 Cherry valley Limestone.

Objectives

Test for similarities and differences between mineral paragenesis of fractures from shale units of different ages and from different basins

Test if shales open or closed systems



Devonian Marcellus Shale [PA] – core and outcrop

Devonian/Mississippian Woodford Shale [OK] – core and outcrop

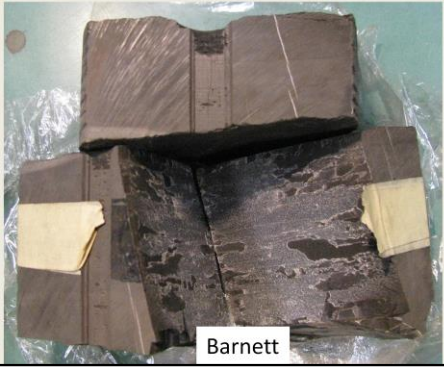
Mississippian Barnett Shale [TX] - core

Late Jurassic Haynesville Shale [TX] - core

Mineralized Fracture Types

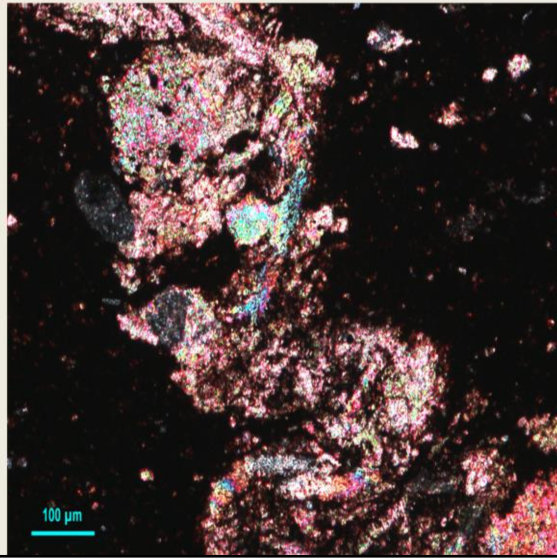
All shales contain localized vertical/subvertical and horizontal mineralized fractures

- Vary in width from thin (< 0.02 mm) to thick (> 0.2 mm)
- Commonly contain calcite and other minerals
- Faults zones and breccias have a complex mineralogy
- Natural hydraulic fractures

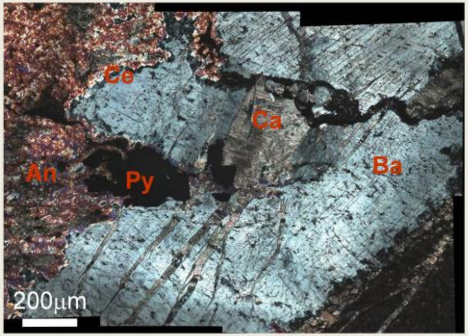


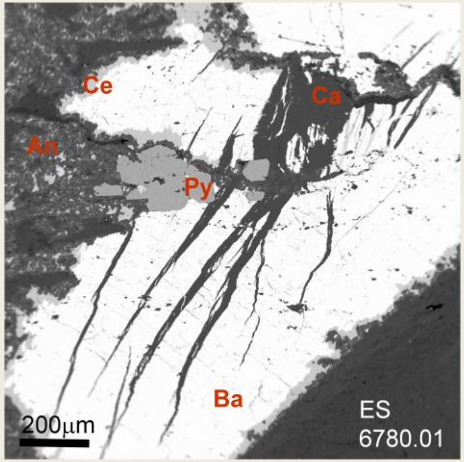
Precompactional fractures

Woodford



Late Mineralized fractures - Barnett





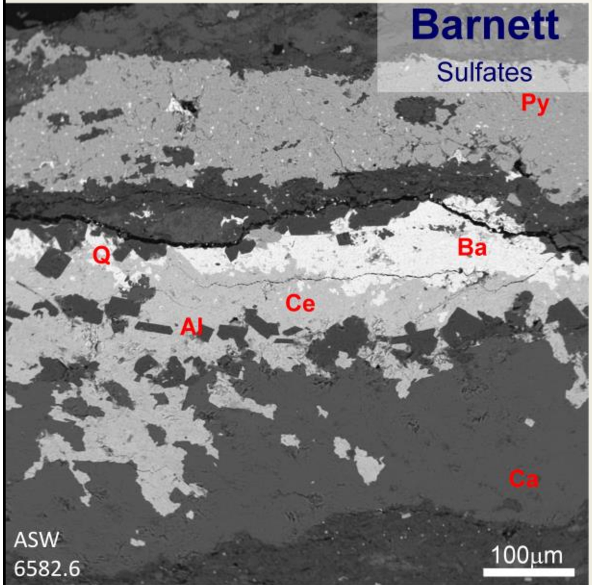
- Anhydrite, Celestine, barite, calcite, pyrite

- Refracturing and replacement, fluids migrated into mineralized fractures

Presenter's notes: SEM picture of a barite, celestine, anhydrite filled vein. Barite and celestine have been found in numerous veins throughout the Barnet and may add complexities during fracturing. Also note the complex mineralization history of this vein. The calcite has mineralized along fractures within the Barite.

Barnett

Sulfates



Complex paragenesis

- •Barite- Barium sulfate
- • Celestine- Strontium sulfate
- • Albite
- •Calcite
- •Pyrite
- •Quartz

Barite-Celestine solid solution – Change in fluid composition or changing temperature?

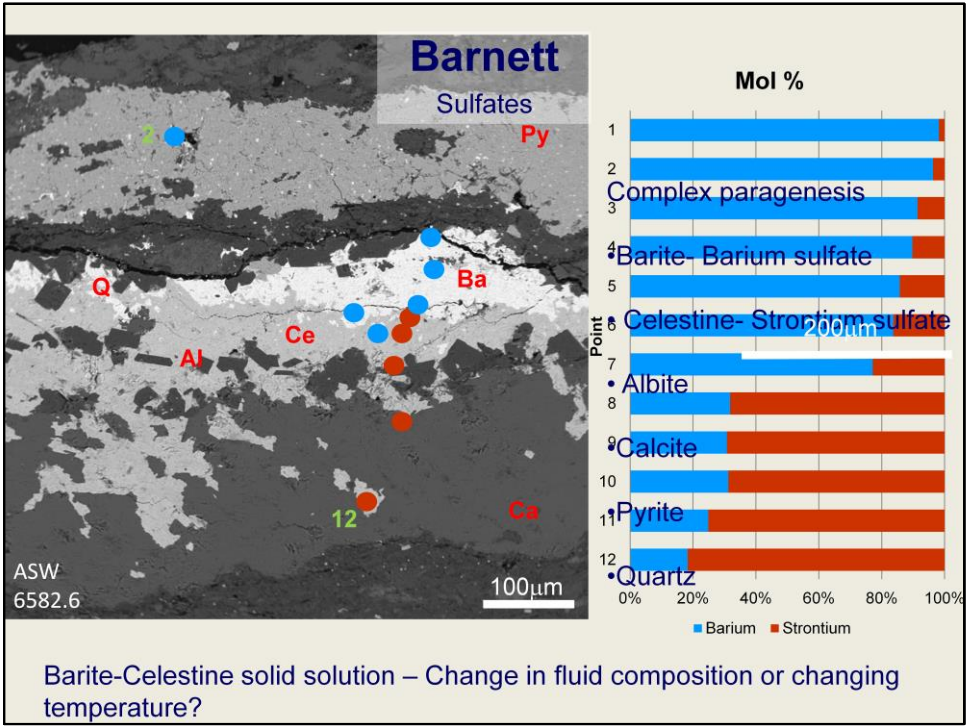
Presenter's notes: This is an SEM photo of one of our sulfate filled veins. Barite is a Barium rich sulfate. Celestine is a Strontium rich sulfate. Anhydrite is a Calcium rich sulfate. The white is Barite and the grey is Celestine.

Using the microprobe, we performed a transect across the vein to determine the Barium and Strontium geochemistry.

The graph on the right shows the relative amounts of Barium and Strontium from various points analyzed with Barium in Blue and Strontium in red.

There is a decrease in Barium with an increase in Strontium as we move across the vein.

This solid solution of Barite/ Celestine we view as evidence that these sulfates were from evolving fluids that had remobilized Barium and Strontium.



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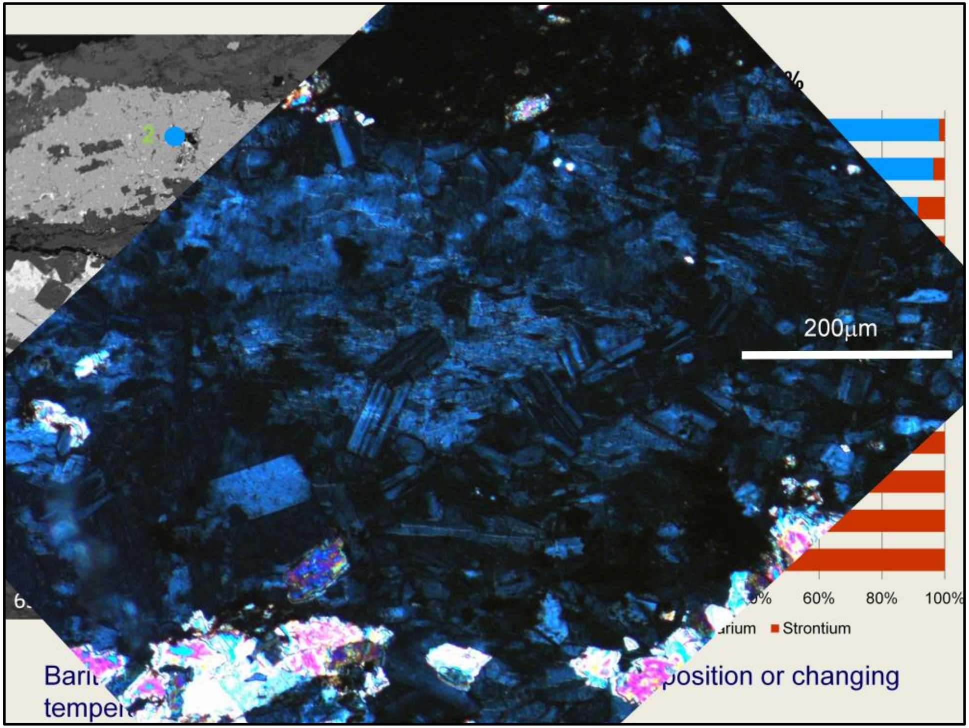

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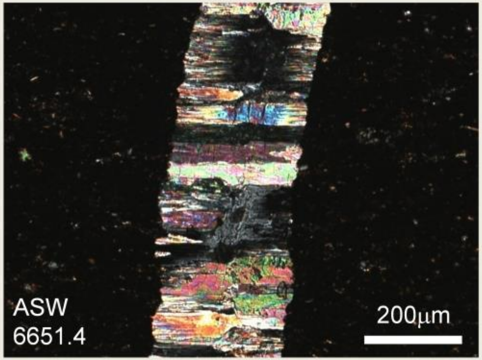
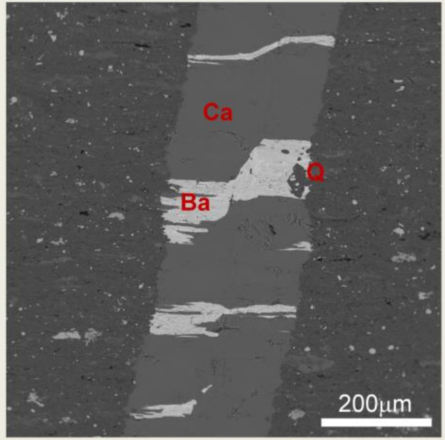
Barnett

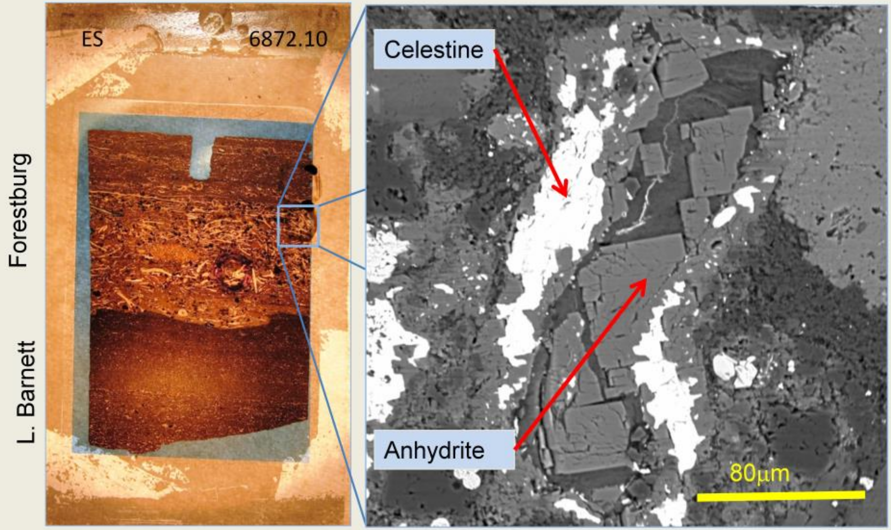
Vertical to Subvertical -Tectonic





- Near vertical fibrous calcite filled fracture partially replaced by barite
- Replacement of earlier formed minerals common

Celestine and Anhydrite

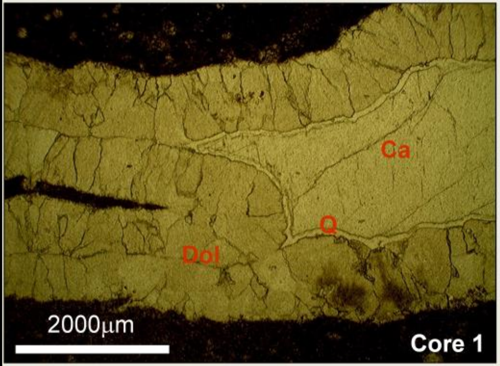


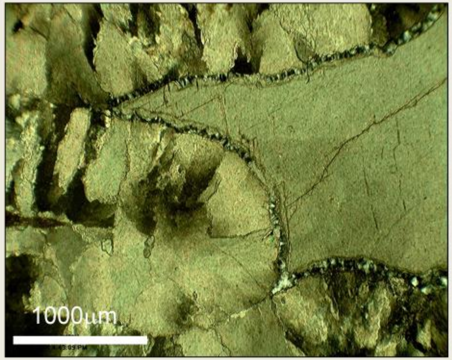
Base of Forestburg, anhydrite precipitated adjacent to celestine. ES 6872.10 in

Presenter's notes: At the base of the Forestburg, there is a shelly hash which lies unconformably on top of the Lower Barnett. Through SEM analysis, anhydrite was found adjacent to celestine, outside of a vein. Switching to cross polars, the blue and blue/purple mix make up the anhydrite while the cool grey blue is the celestine. While I am unsure of which mineral precipitated after which, I believe that the anhydrite may have precipitated after the celestine or at earliest co-precipitated.

Thin section of the interface between the Forestburg and Lower Barnett. Thick shell hash is seen in the Forestburg before an abrupt lithology change into what is traditionally known as the Lower Barnett Shale. Within the slide, there is a myriad of minerals, but specifically we see Anhydrite growing adjacent to Celestine.

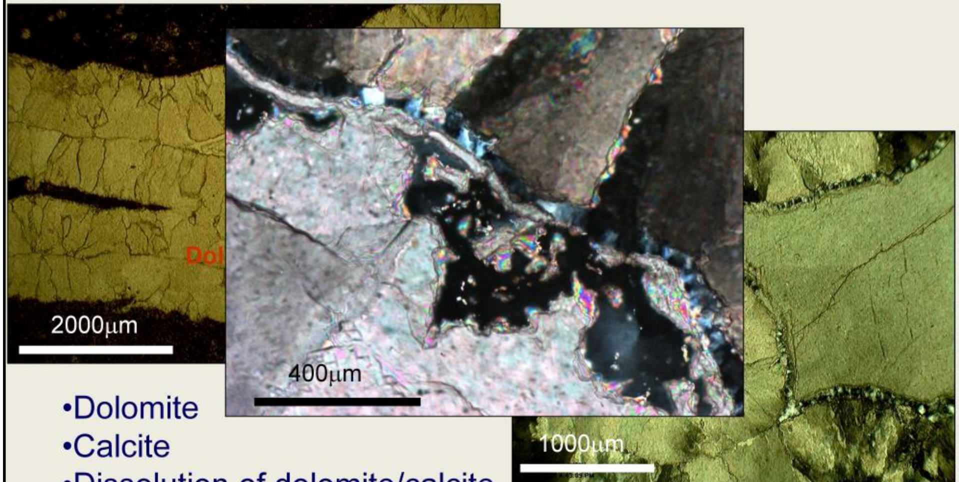
Dolomite, Calcite & Silica in Fractures - Barnett





- Dolomite
- Calcite
- Dissolution of dolomite/calcite
- Quartz
- Fluids are migrating into mineralized fractures

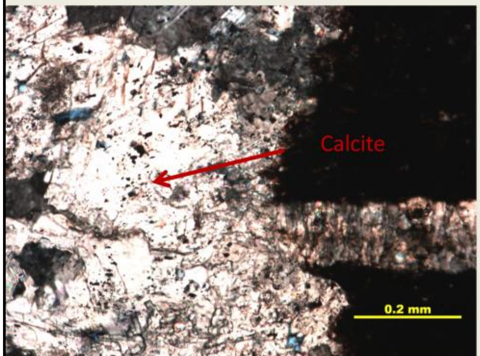
Dolomite, Calcite & Silica in Fractures - Barnett

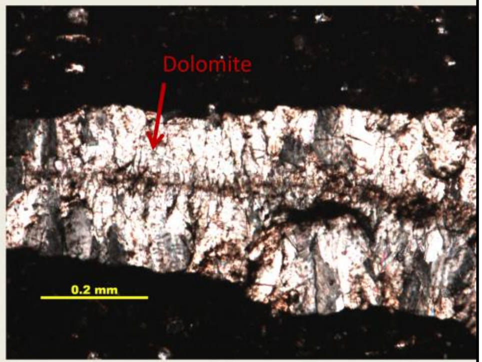


- Dolomite
- Calcite
- Dissolution of dolomite/calcite
- Quartz
- Fluids are migrating into mineralized fractures

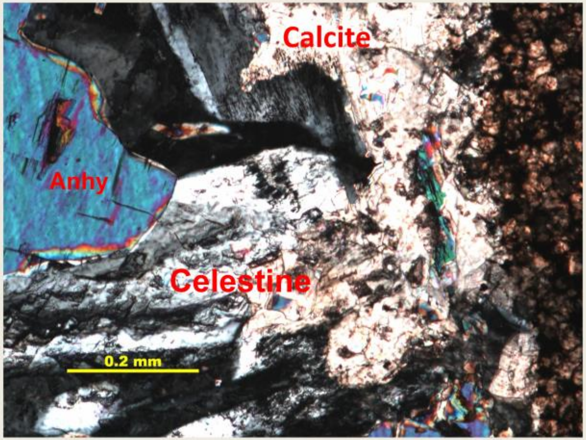
Haynesville

- Blocky calcite and dolomite





Haynesville - Complex Diagenesis – Breccias



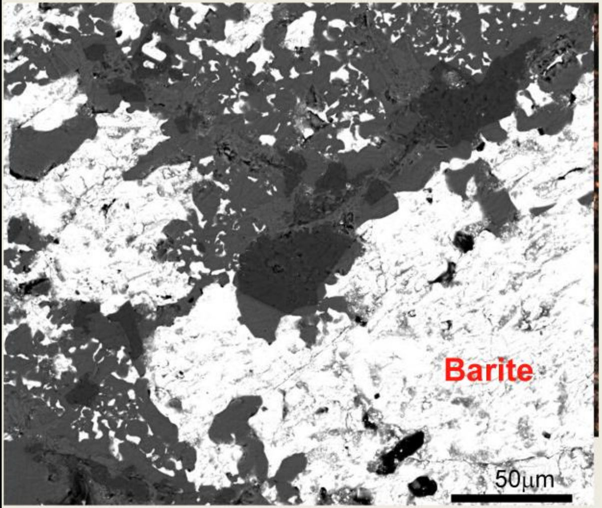
Barite

Anhydrite

Celestine

Calcite

Haynesville - Complex Diagenesis – Breccias



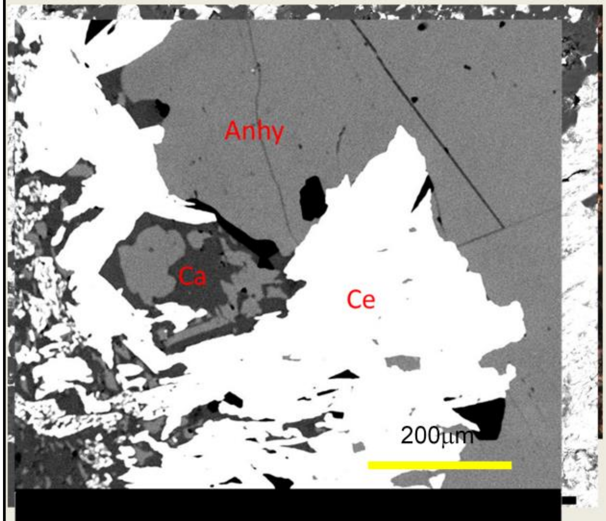
Barite

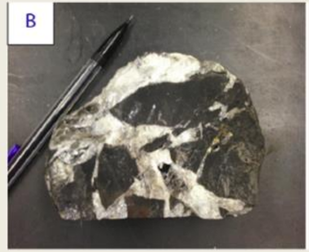
Anhydrite

Celestine

Calcite

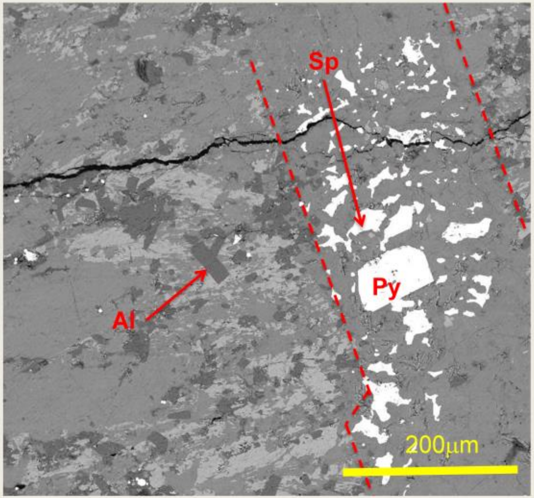
Haynesville - Complex Diagenesis – Breccias





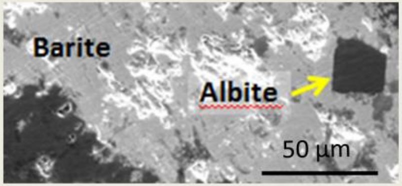
Barite
Anhydrite
Celestine
Calcite

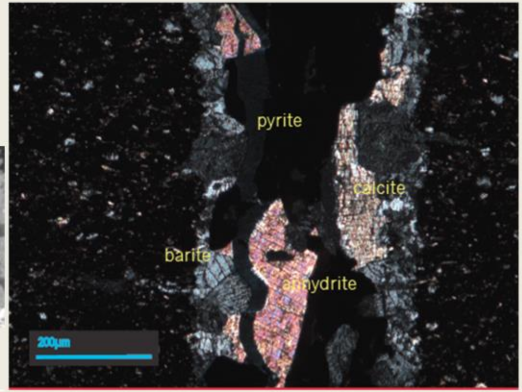
Mineralized fracture - Haynesville

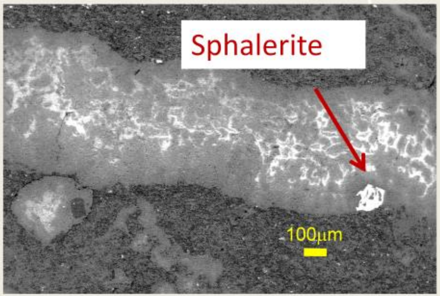


- Sphalerite
- Pyrite
- Albite

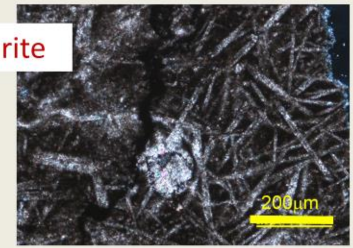
Marcellus





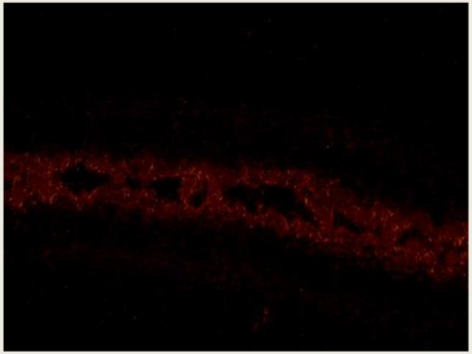


Barite



Marcellus

Cathodoluminescence

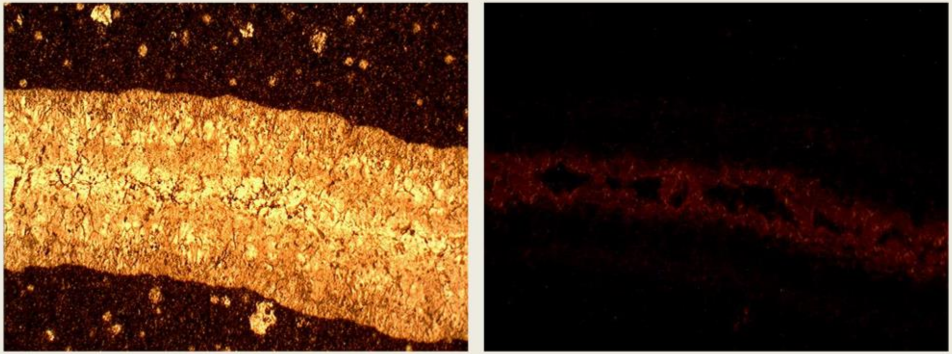


- Bitumen and hydrocarbon inclusion rich calcite is enriched in iron compared to the luminescent calcite

- Varying luminescence indicates evolving fluids

Marcellus

Cathodoluminescence



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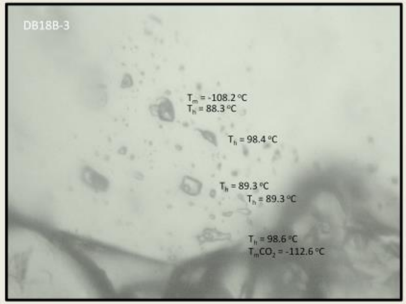
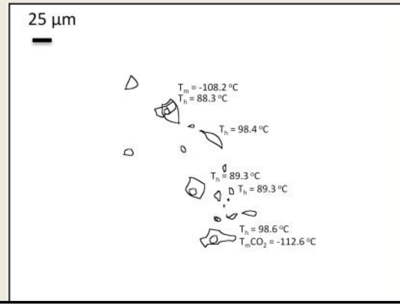
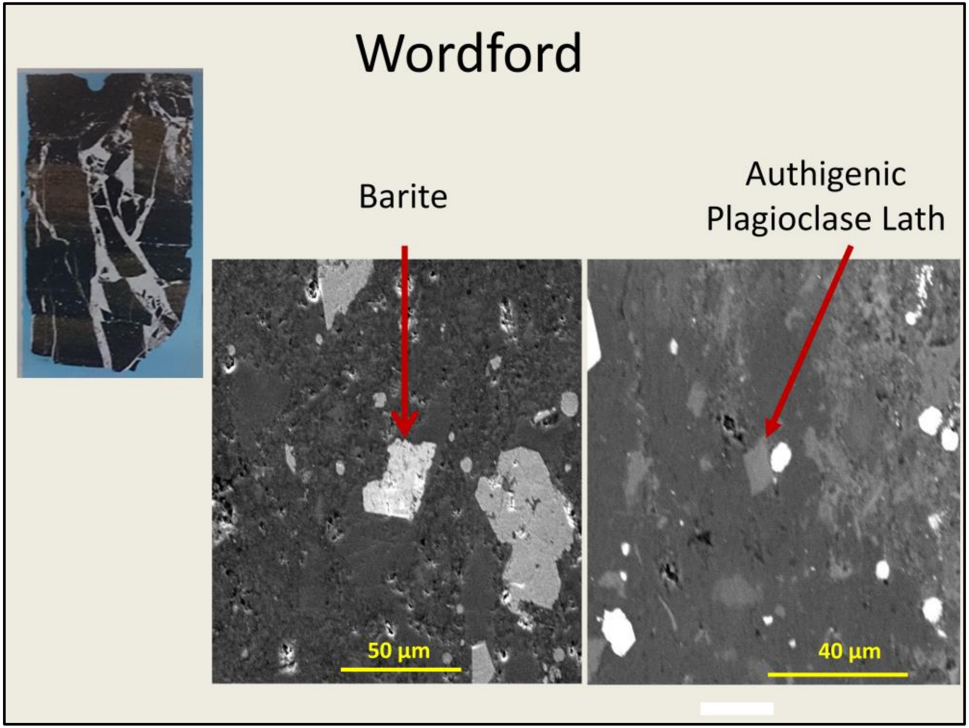
- Varying luminescence indicates evolving fluids

Marcellus mineralized fractures – Fluid inclusions

- At least two types of inclusions in calcite
  - $CH_4 + CO_2$
  - Single phase CH_4
- $CH_4 + CO_2$
  - T_{hH} between -88.3 to -98.6°C
  - T_{mCO2} between -109.7 and -112.6°C
- Relate to burial history
  - Moderate burial depths (~3.5 km)



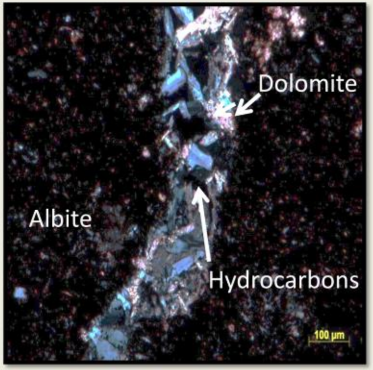


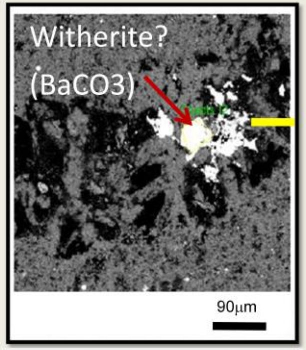


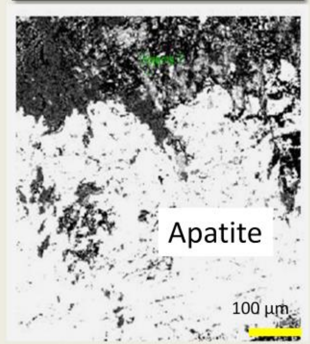
Presenter's notes:

- Here are two SEM pictures, the one on the left showing barite, and the one on the right showing an authigenic plagioclase lath
- From all of this it can be seen that this shale has been extensively altered, but the question remains as to when and how these diagenetic events occurred, which is where paleomagnetic techniques come into play.

Woodford





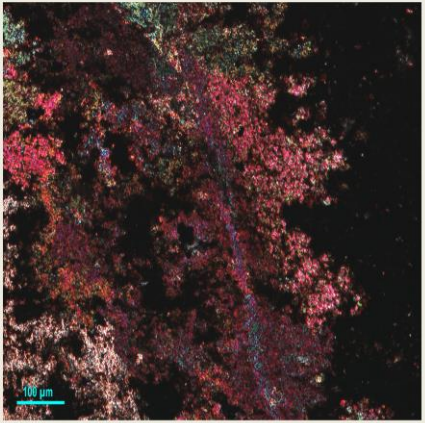


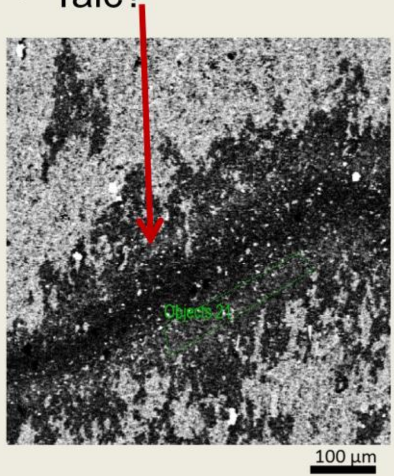
Presenter’s notes:

- W2
- Vertical fracture
- Authigenic albite vein being replaced by dolomite
- Hydrocarbon in the middle in between

Mineralized fracture extends into matrix

- Mg, Si, O peaks on EDAX
- Talc?



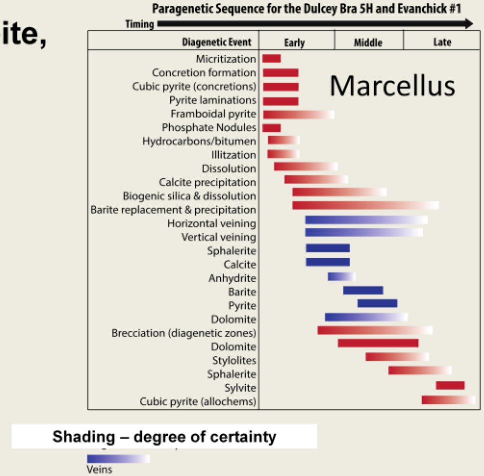


Woodford W2

Summary of paragenesis in mineralized fractures

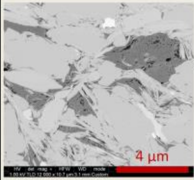
Mostly mid to late diagenesis

- **Calcite, dolomite, pyrite, albite, barite, anhydrite, and sphalerite are found in fractures in all four units**
- **Celestine – Haynesville and Barnett**
- **Woodford also contains witherite, albite in vein, talc?, and apatite**
- **Replacement of previously formed minerals in fractures is common – permeability pathways**

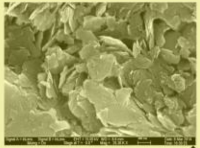


Origin of natural fractures – overpressuring?

Scale Issues



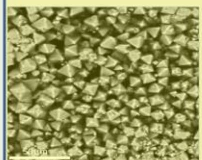
Nano pores in organic matter (Mark Curtis, OU MPG&E)



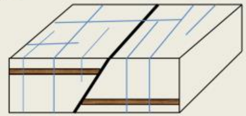
Pores in clays

Sedimentary structures

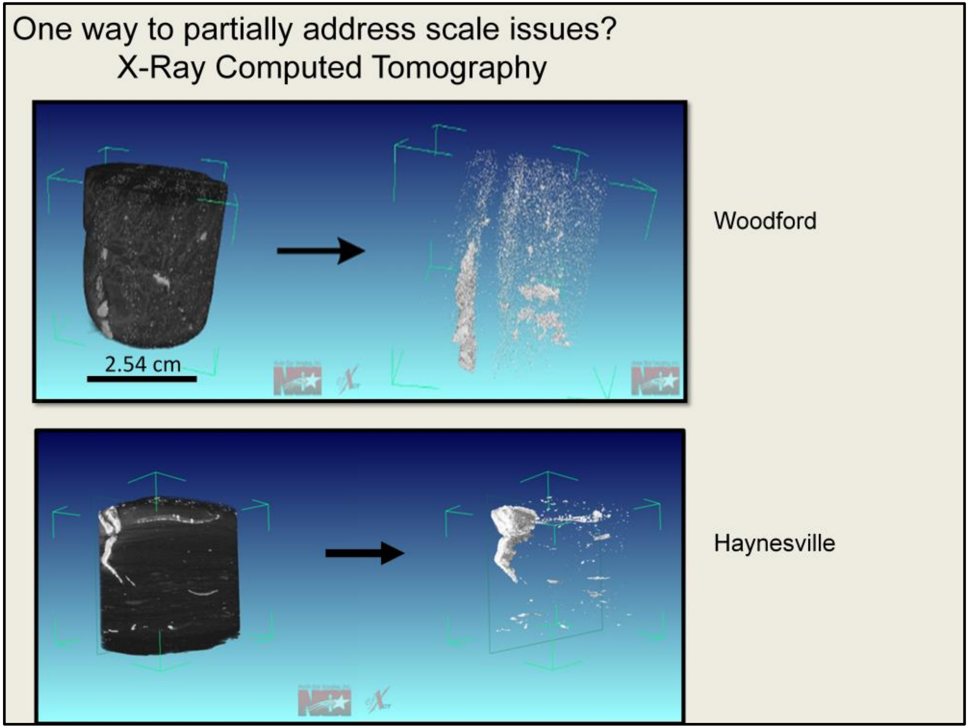
Pores in pyrite



Mineralized fractures



Large scale fractures and faults (can be missed if looking at cores)



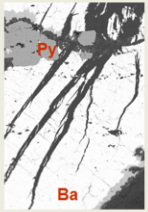
Presenter’s notes:

- W2
- X-ray computed tomography
- X-ray computed tomography (XRCT) scans were performed on representative 1-inch plugs from both shales. XRCT provides detailed 3-D imagery of the interior of rocks through a global X-ray scan that produces multiple grayscale images (e.g. Kectham, 2005). These images are stacked to render a 3-D image of a specimen.

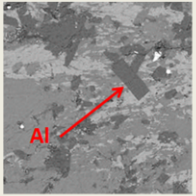
Discussion

Similar minerals in fractures from shales of different ages and from different basins

Most minerals in fractures in the Marcellus, Barnett, and Haynesviile can be explained by an internal source of fluids (Seawater, fluids released from smectite)



- **Barite –** Early, biologic?
  - Anaerobic oxidation of methane (e.g., Lash, 2015)
  - Redistributed early barite and celestine – barite is unstable in strongly reducing environments (Hanor, 2000); migrates into fractures

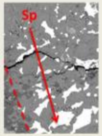


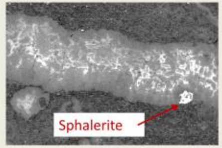
- **Albite** (authigenic) – models (Kastner, 1971)
  - Isochemical – components from the rock
    - Na from seawater or clay transformations
    - Si and Al from smectite
  - Migrating saline fluids – hydrothermal

Presenter's notes: Fluids can have multiple origins: tectonics (e.g. basinal saline brines), overpressuring caused by water expelled from compaction of sediments, and generation of hydrocarbons.

Discussion Cont.

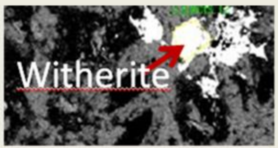
- **Sphalerite –** Internal or external source of fluids
  - Reports of early diagenetic sphalerite (Selleck, 2014)

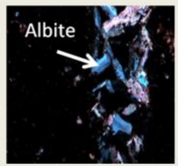


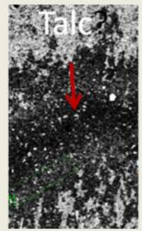


Woodford – Exception based on preliminary data

- **Witherite, Talc, and Apatite in fractures**
  - Suggest an external source, probably hydrothermal
  - Orogenic fluids related to Ouachita Orogeny
  - Complex open system







Conclusions

- Mineralized fractures are common - they can have a complex mineralogy
- Barnett, Marcellus, and Haynesville - largely closed system
- Woodford – Complex open system?
- Fluids are migrating into mineralized fractures and replacing previously formed minerals – permeability pathways
- Mineralized fractures can affect reservoir quality (e.g., brittleness)
- How connect different scales?