

# **Anomalous Thermal Indicators from the Authigenic Minerals in Upper Paleozoic Strata of the Michigan Basin\***

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Search and Discovery Article #10836 (2016)\*\*

Posted February 15, 2016

\*Adapted from oral presentation given at AAPG Eastern Section 44<sup>th</sup> Annual Meeting, Indianapolis, Indiana, September 20-22, 2015

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## **Abstract**

Indications of anomalous paleo-temperatures exist in strata of the Michigan Basin, USA. The thermal history of the basin was investigated through identification and analysis of authigenic components in two Upper Paleozoic strata, the Devonian Dundee Formation and Mississippian Marshall Sandstone. Formation conditions for diagenetic phases in both units were estimated through a variety of means and compared to conditions expected for a simple burial model. Authigenic clays identified in the Marshall via X-ray diffraction are expected to have formed at temperatures above what would have been produced by burial alone. Stable isotope and fluid inclusion analysis indicate the same for secondary carbonates in the Dundee. K-Ar age dating of Marshall authigenic illite provide ages of approximately 280 Ma. This age may reflect an illite formation period in the Permian or may be an integrated age representing multiple periods of illitization. Dolomite in the Dundee and illite in the Marshall are likely to have formed under hydrothermal conditions. The results of this study are part of a larger body of evidence that suggests episodic and extensive hydrothermal events have influenced the thermal history of the Michigan Basin. These events are due to the reactivation of faults in the Proterozoic rift that underlies the basin and maybe related to thermal convection within the igneous rift body or Appalachian tectonic events.

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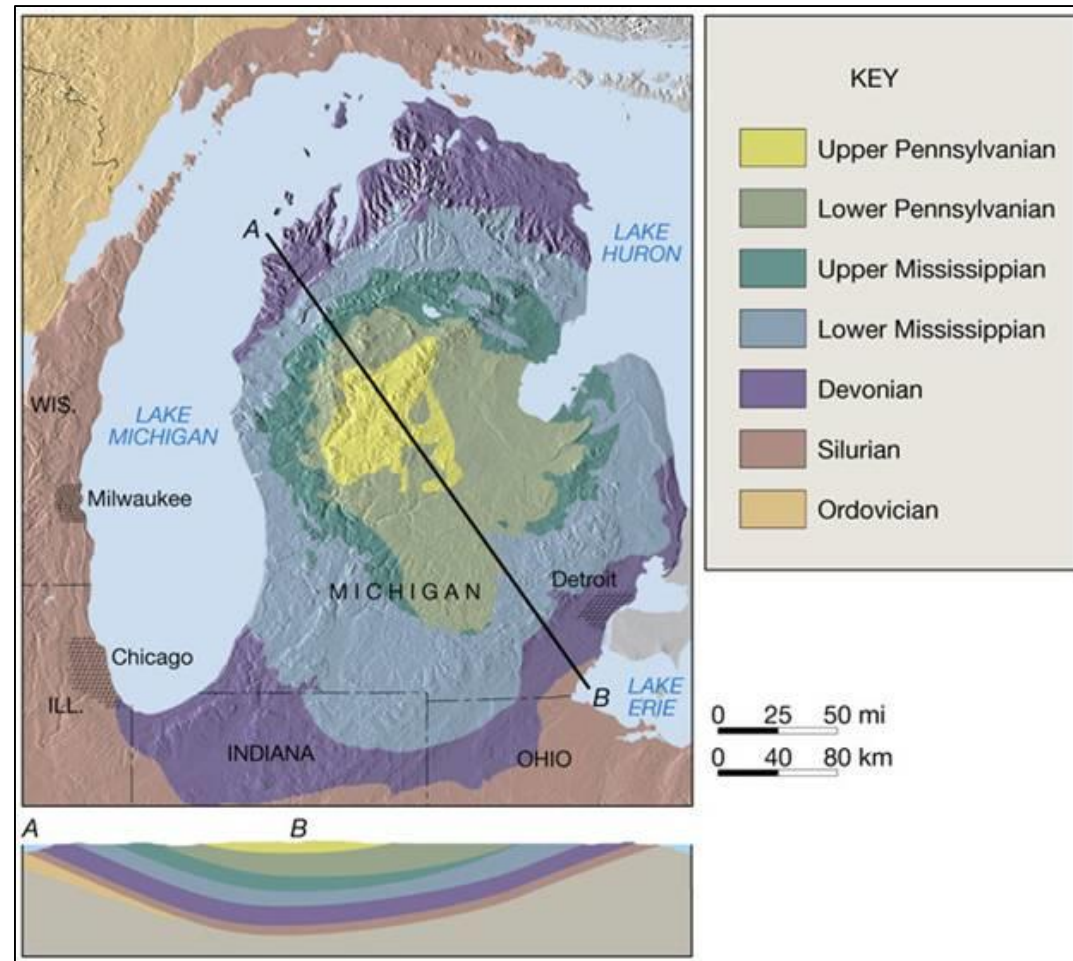


# Importance of Thermal History

- To understand the evolution of an intracratonic sedimentary basin you must understand its thermal history
- The thermal history is an important control on the occurrence oil and gas resources in said basin.
- Unconventional resource exploitation depends upon in situ thermal alteration

# Intro: Michigan Basin

- Circular intracratonic sedimentary basin.
- Up to 5km of sedimentary rock
- Most strata Paleozoic

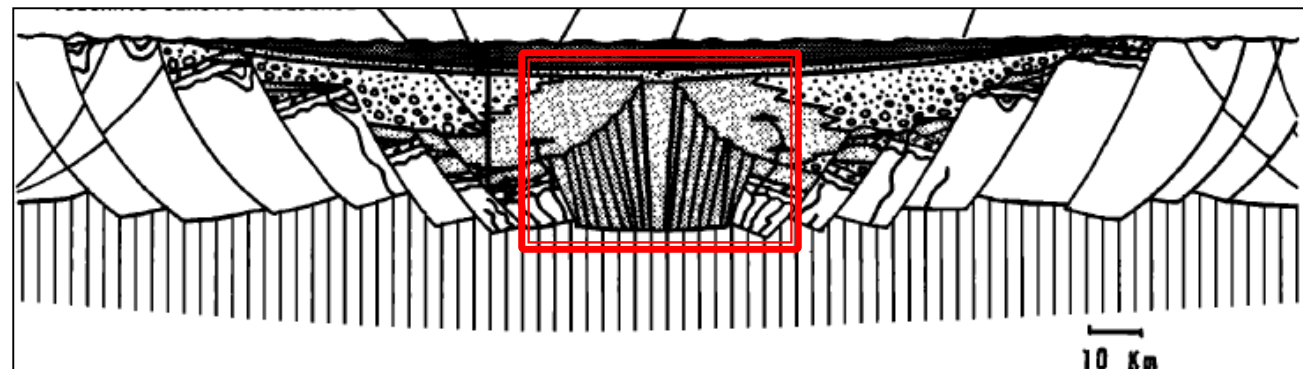
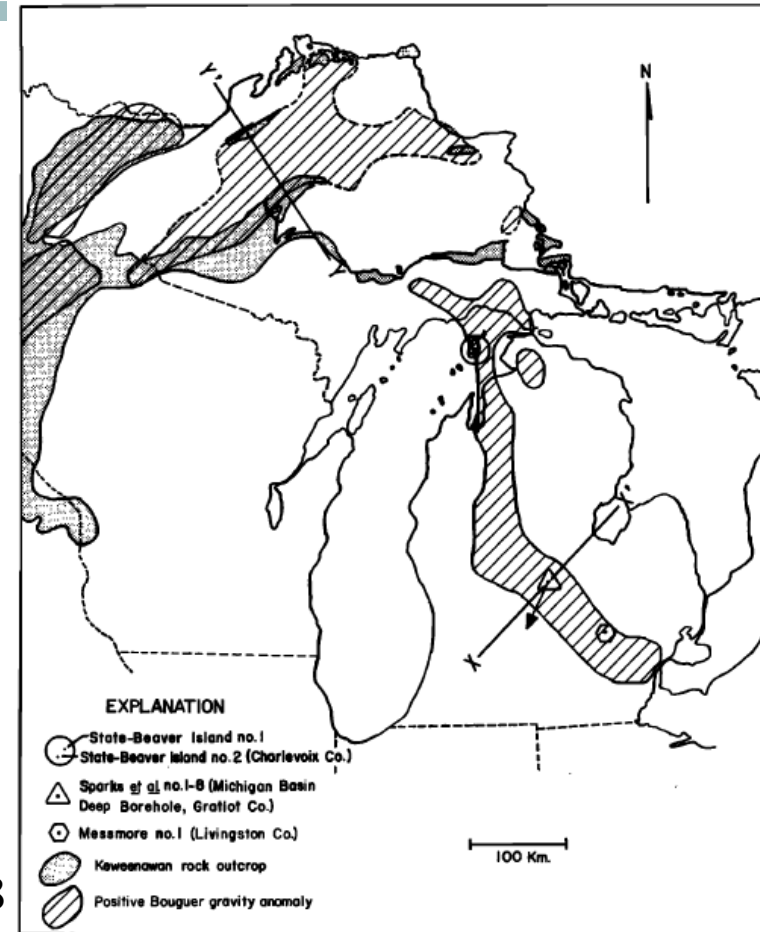




# Intro: Mid-Michigan Rift (MMR)

- Linear gravimetric and magnetic anomaly.
- Proterozoic Mid-Continent Rift System (Hinze et al., 1975).
- Related basement faults and fractures can extend into the overlying sedimentary strata (Prouty, 1988).

Fowler and Kuenzi, 1978



# Intro: Michigan Basin Thermal History

- Michigan basin diagenetic minerals & organic material indicate temperatures significantly higher than present-day burial temperatures.
- Current geothermal gradient is 19–22° C/km (Vugrinovich, 1988)
- Organic material
  - Only Ordovician should be mature. (Nunn et al., 1984).
    - Mature source rocks and coal shallower (East et al., 2012).
- Diagenetic mineralization
  - St. Peter illite (Girard & Barnes, 1995)
  - Hydrothermal dolomitization (Prouty, 1988; Coniglio et al., 1994; Luczaj et al., 2006; Haeri-Ardakani et al., 2013; and others)
- Basin brine
  - Thermal event (Ma et al., 2009)
  - Mantle signature (Castro et al., 2009)

PERIOD	GROUP	FORMATION		
CENOZOIC				
QUATERNARY		Glacial Drift	☼	
MESOZOIC				
JURASSIC	L	"Red Beds"		
PALEOZOIC				
PENNSYLVANIAN		Saginaw	☼	
MISSISSIPPIAN	Grand Rapids	Bayport		
		Michigan	☼	
		Marshall Sh		
		Coldwater Shale		
		Sunbury Shale		
DEVONIAN	L	Ellsworth Sh	☼	
		Belmont Sh	☼	
	Traverse	Antrim Shale	☼	
				☼
				☼
	M	Bellevue		
		Rogers City	☼	
		Reed City Anhy	☼	
	E	Reed City Dol.	☼	
		Lucas	☼	
Amherstburg		☼		
Sylvania		☼		
SILURIAN	L	Bois Blanc	☼	
		Garden Island	☼	
		B through Gunits	☼	
		A-2 Carbonate	☼	
		A-2 Evaporite	☼	
	E	A-1 Carbonate	☼	
		A-1 Evaporite	☼	
	Niagara			
		Clinton	☼	
		Catawba	☼	
ORDOVICIAN	L	Cabot Head Shale	☼	
		Maclure Dolomite	☼	
		Richmond	☼	
	M	Ulrich Shale	☼	
		Trenton	☼	
E	Black River	☼		
		Glenwood	☼	
CAMBRIAN	M	St Peter Sandstone	☼	
		Prairie du Chien	☼	
	L			☼
PRECAMBRIAN				

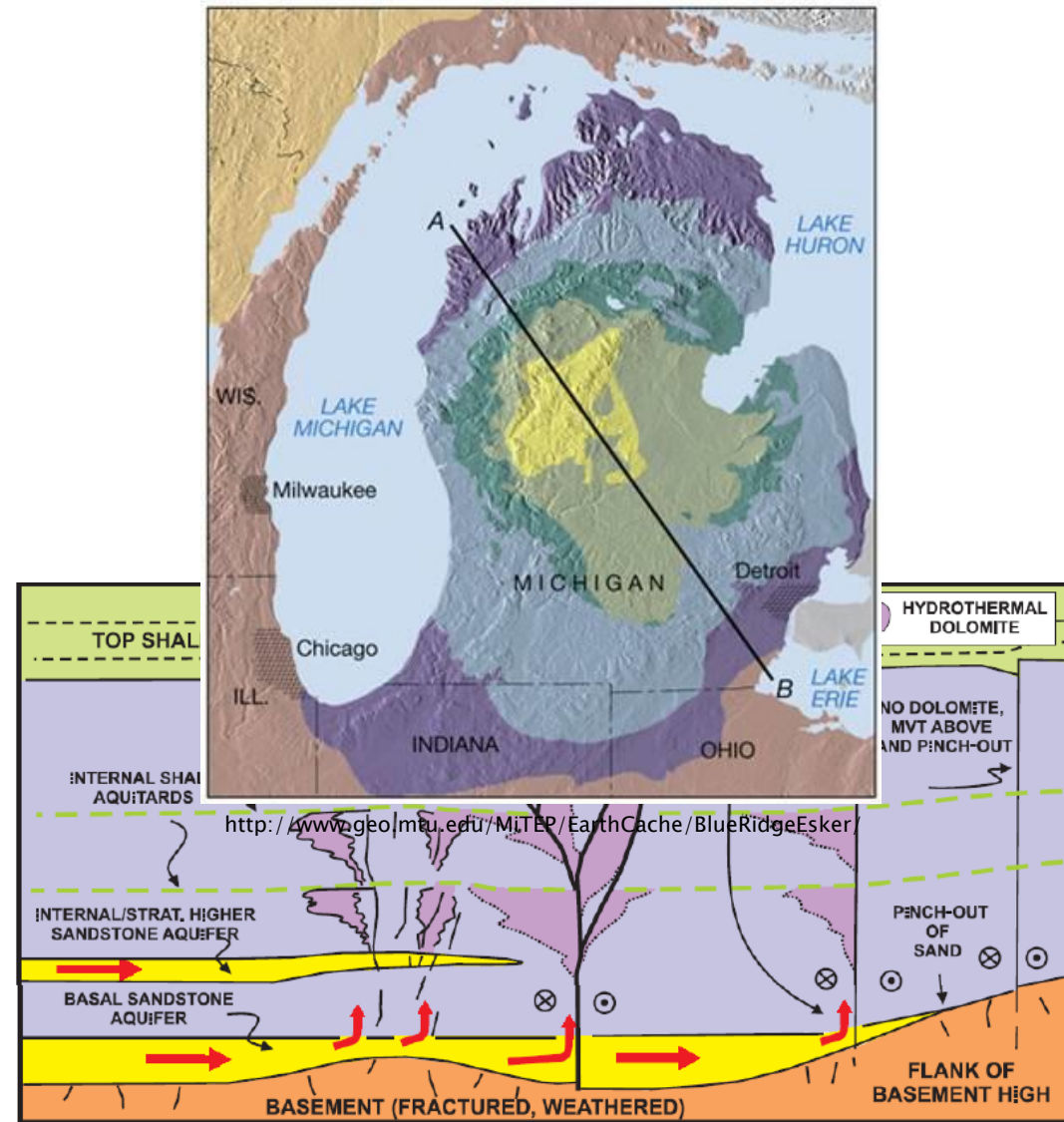
# Intro: Models for Elevated Paleo-temperatures

- **Burial**

- 0.3–3 km add. sed.
- Late Paleozoic–Early Mesozoic
- Would produce basin shaped alteration

- **Hydrothermal alteration**

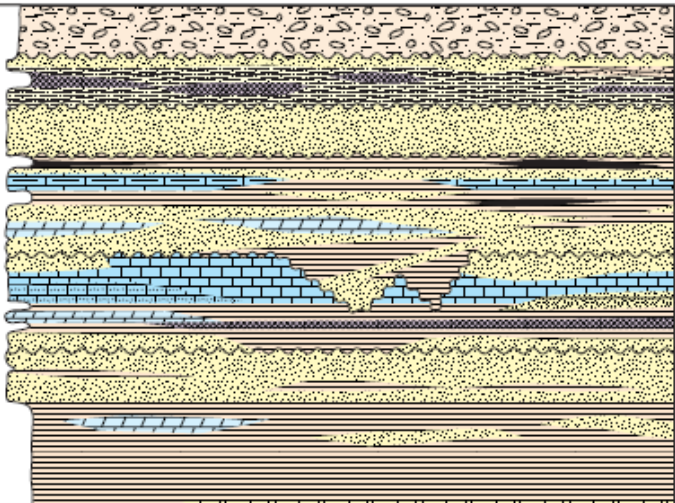
- Hot fluids migrating via basement rooted faults/fractures
- Shallow formations, deep brines
- Spatial relationship with structures
  - MMR
- Appalachian tectonic events



Davies & Smith, 2006

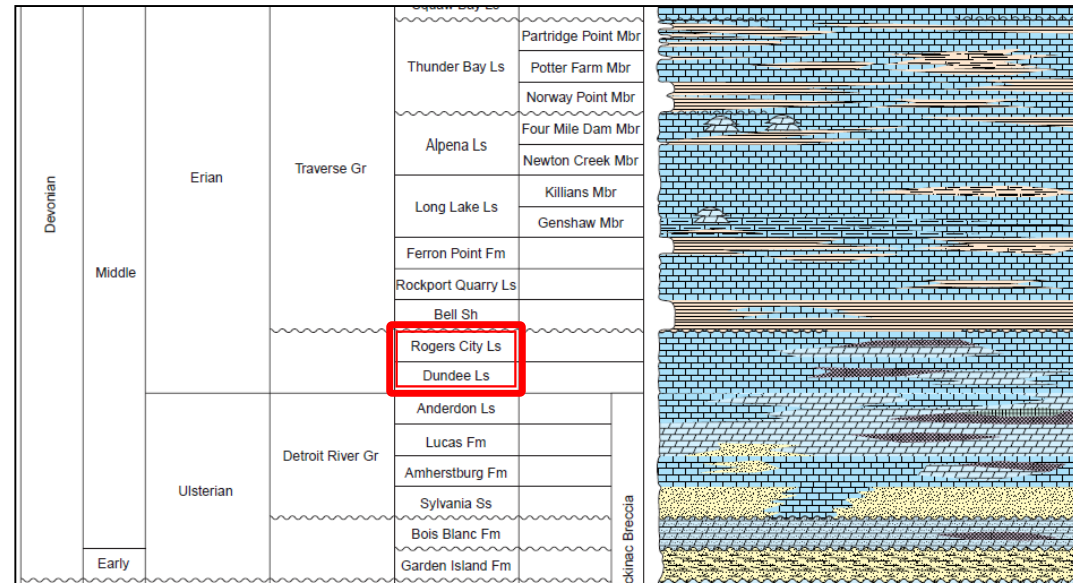
# Intro: Marshall Sandstone

- Early Mississippian (~345 Ma) shallow marine sandstone (Harrell et al., 1991).
- Authigenic components indicate elevated paleotemperatures
  - Zacharias et al., 1993
- Why focus on the Marshall?
  - Promising preliminary work
    - Illite cement in sandstone
      - Implications
    - Age data

ERA	PERIOD	EPOCH	NORTH AMERICAN STAGES	GROUP	FORMATION	MEMBER	Catacosinos et al., 2000
Cenozoic	Quaternary	Pleistocene	Wisconsinan		Glacial Drift		
Mesozoic	Jurassic	Middle	Oxfordian		Ionia Fm		
	Pennsylvanian	Late	Conemaugh		Grand River Fm		
		Early	Pottsville		Saginaw Fm		
					Parma Ss		
				Bayport Ls			
	Mississippian	Late	Meramecian		Michigan Fm		
					Marshall Ss		
		Early	Osagian		Coldwater Sh		
			Kinderhookian		Sunbury Sh		

# Intro: Dundee/Rogers City

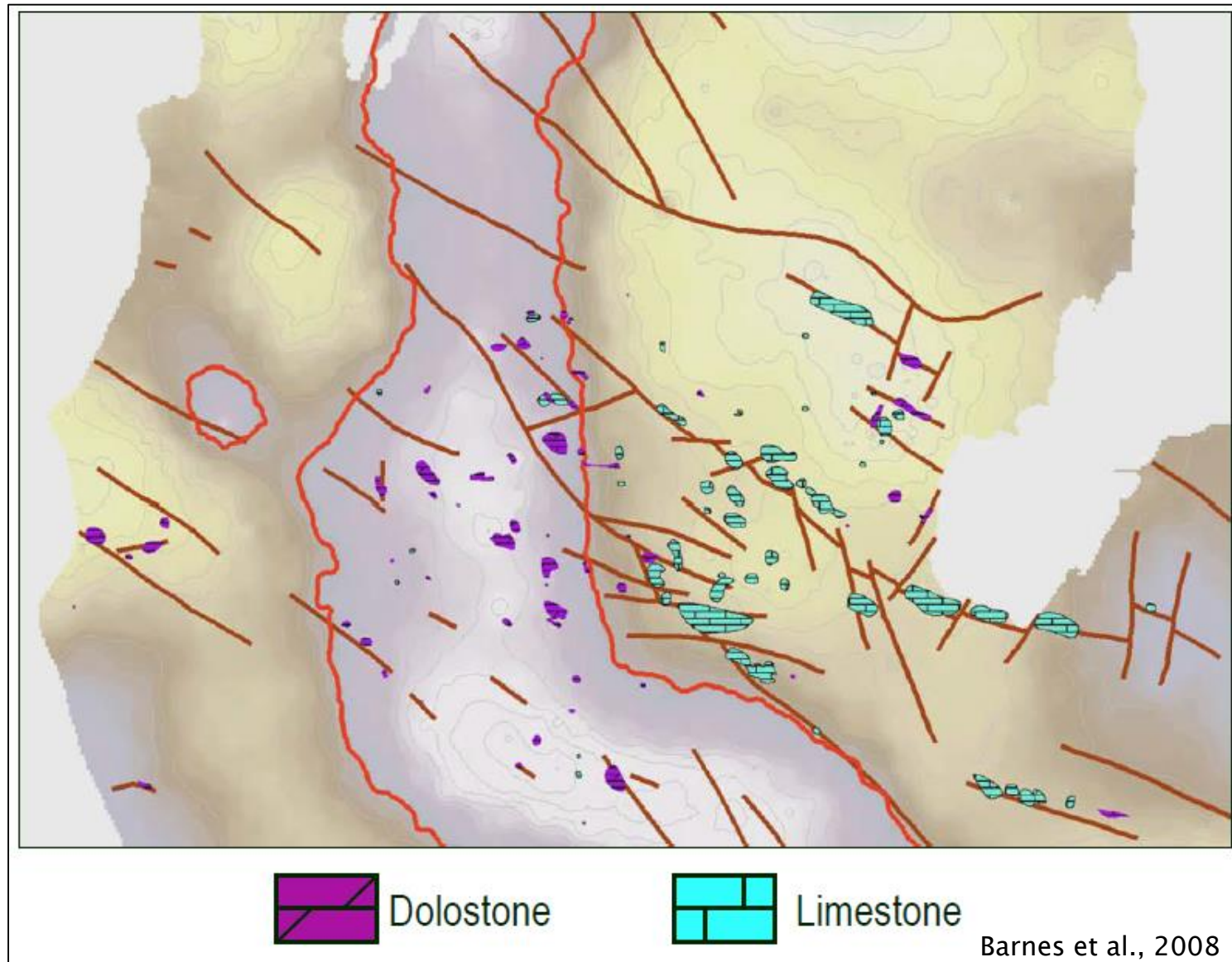
- Middle Devonian carbonate mudstone to grainstone
  - Coastal sabkha to shallow marine platform environment. (Catacosinos et al. 2001).
  - Is locally dolomitized in many parts of the Michigan basin
- Secondary saddle dolomite indicate elevated formation temp.
  - 120–150° C at 1.2km (Luczaj et al., 2006)
  - Isotopic analysis also supports high temp. (Smith Williams, 2003)
- Why focus on the Dundee?
  - Evidence for elevated temperatures
    - More complete analysis possible
  - Evidence of structural control of dolomitization (Barnes et al., 2008)



Catacosinos et al., 2000



# Intro: Dundee/Rogers City



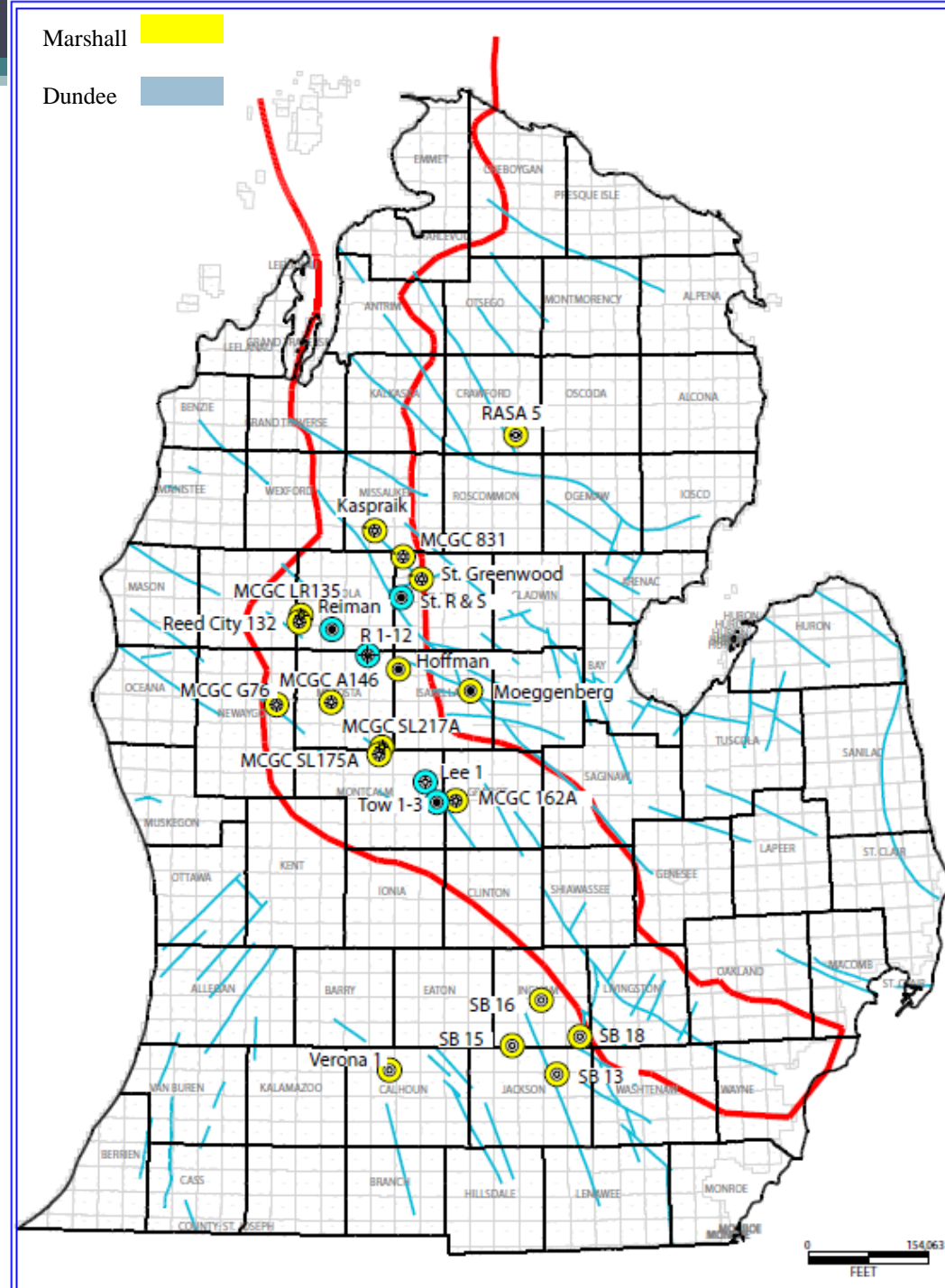
- Distribution of dolomite and limestone oil fields in the Michigan basin

# Research Questions

1. What authigenic minerals are found in the Marshall and Dundee Formations?  
Petrographic Microscopy, XRD
2. What were the conditions of formation for these minerals?  
Stable Isotopes, FIA, Literature
3. When did they form?  
K-Ar Age Dating
4. How do the conditions of formation compare with a simple burial model?
5. Are anomalous paleo-temperature indicators spatially related to the rift and known structures?  
Mapping

# Results: Marshall Sampling

- 18 Marshall Wells
  - 14–477m
  - 15 petrographic thin sections
  - 51 XRD samples
  - 3 K–Ar age dating samples



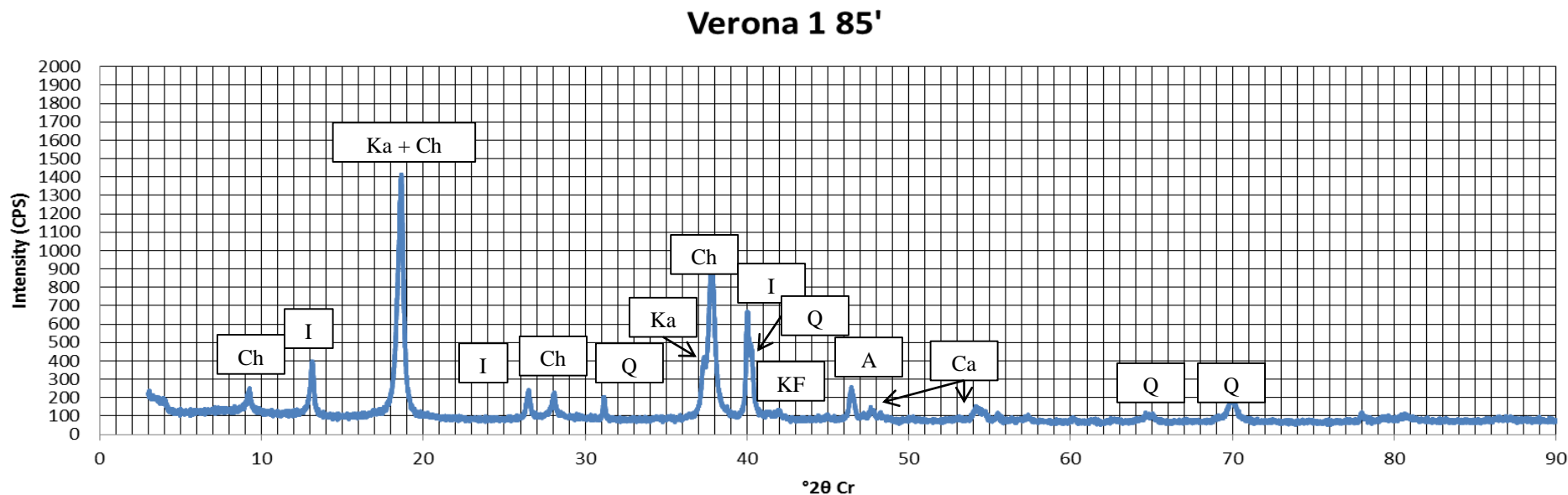


# Results: Marshall Petrography

- 15 “clean” sandstone thin sections were examined
- Identified Authigenic Minerals:
  - Quartz
    - Overgrowths
  - K-feldspar
    - Overgrowths
    - Dissolved and replaced by clays
  - Carbonates
    - Zoned Ankerite Rhombs
    - Poikilotopic Calcite Cement
  - Clay
    - Grain rimming, pore filling, K-feldspar replacing
    - “Micaceous” birefringence and crystallinity
  - Moderate burial (>2–4km) diagenetic mineral assemblage

# Results: Marshall XRD

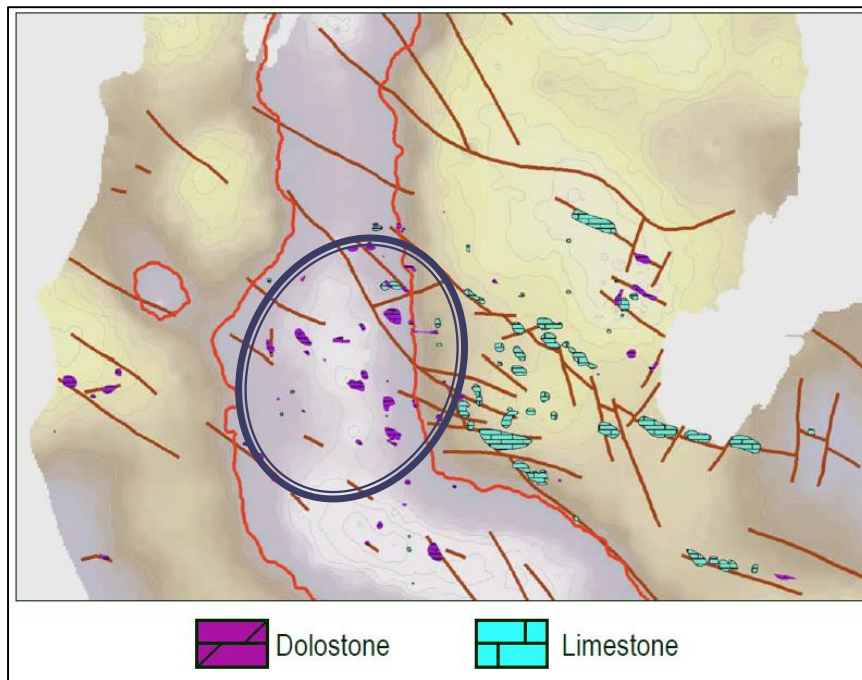
- Neoformed minerals identified for 51 Marshall sandstone samples via XRD
  - All detrital particles ( $>2\ \mu\text{m}$ ) removed
- Clays were identified as illite, kaolinite, and chlorite
  - “Micaceous” clays identified as illite
  - Kaolinite replaced K-feldspar, illite replaced kaolinite
    - Common sequence in sandstone (Meunier & Velde, 2004)



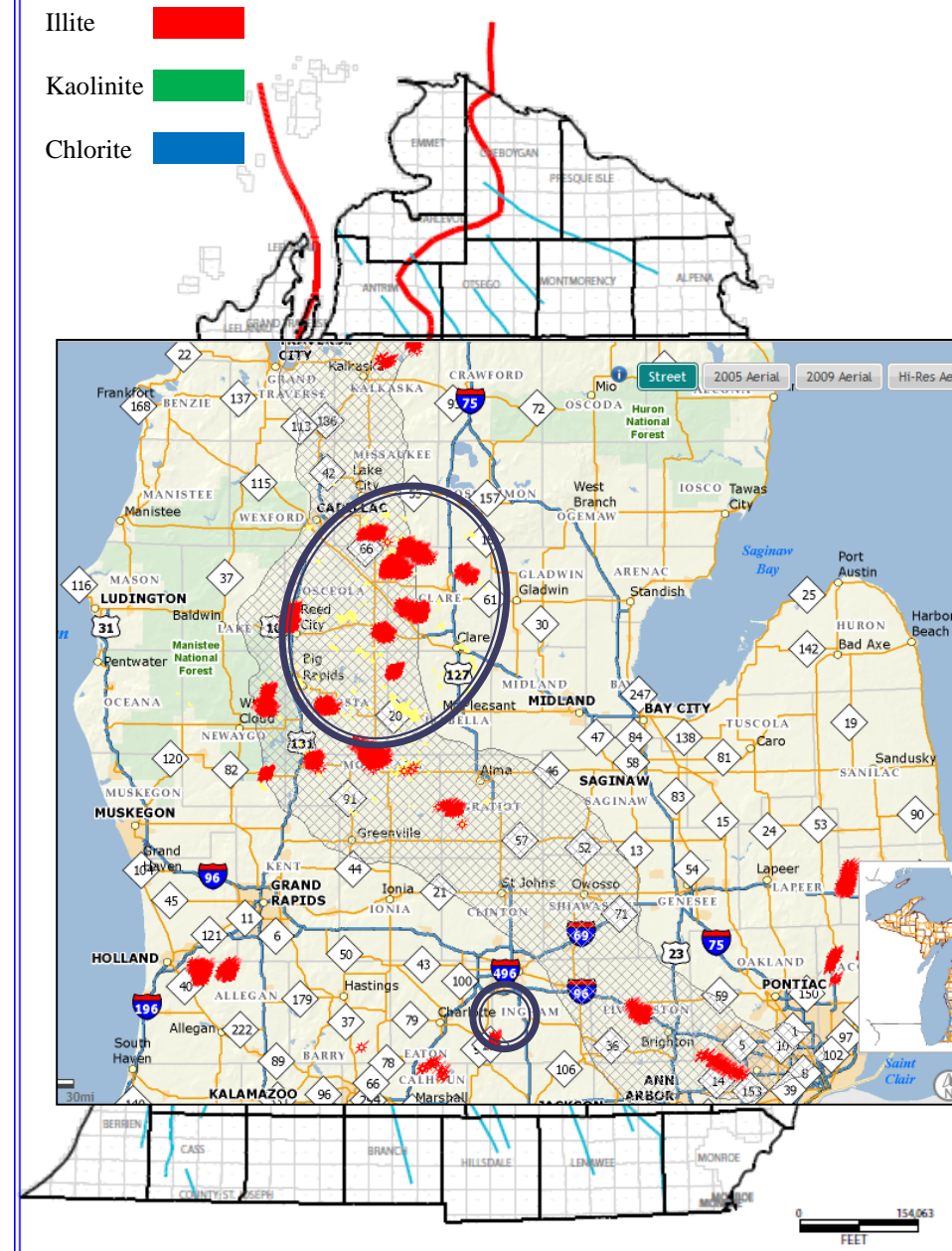
Depth (ft.)	Illite	Kaolinite	Chlorite
<b>MGSC 831</b>			
1432.5	X		
1434	X		
<b>State Greenwood</b>			
1462	x	X	
1466	X	x	
<b>MCGC NH 162-A</b>			
983.5	x	X	
1009.5	x	X	x
1012	x	X	x
1021.5	x	X	x
<b>Hoffman</b>			
1424	X	x	
1456	X		x
<b>Moeggenberg</b>			
1273		x	
1274	X	x	x
<b>MCGC SL-217-A</b>			
1252	X	x	
1253	X	X	X
<b>MCGC A-146</b>			
1380	X		
1400	x	X	
<b>Kaspraik</b>			
1520	X	x	?
1521	X	x	?
1523			
1524	X		x
1527	X	x	
1564	X	X	
<b>MCGC SL-175-A</b>			
1304	x	X	x
1353.5	x	X	X
<b>MCGC G-76</b>			
1139	x	X	
1161	x	X	X
1248	x	X	x
<b>MCGC LR-13-5</b>			
1250	X	X	
1279	x	X	

Depth (ft.)	Illite	Kaolinite	Chlorite
<b>REED CITY 132</b>			
1226	x	X	x
1232.3	X		
<b>RASA 5</b>			
520	x	x	X
531	x	x	X
<b>Verona 1</b>			
47	?	X	
65	x	X	X
80	x	X	X
85	x	X	X
97	x	X	X
123.5	x	X	X
<b>SB-18</b>			
389	x	X	
415	x	X	X
472	x	X	X
497	x	X	X
570	x	X	X
637	x	X	X
<b>SB-16</b>			
616.5	x	X	x
<b>SB-15</b>			
321	X	X	
327	X		
353	x	X	X
<b>SB-13</b>			
182	x	X	X
274	x	x	X

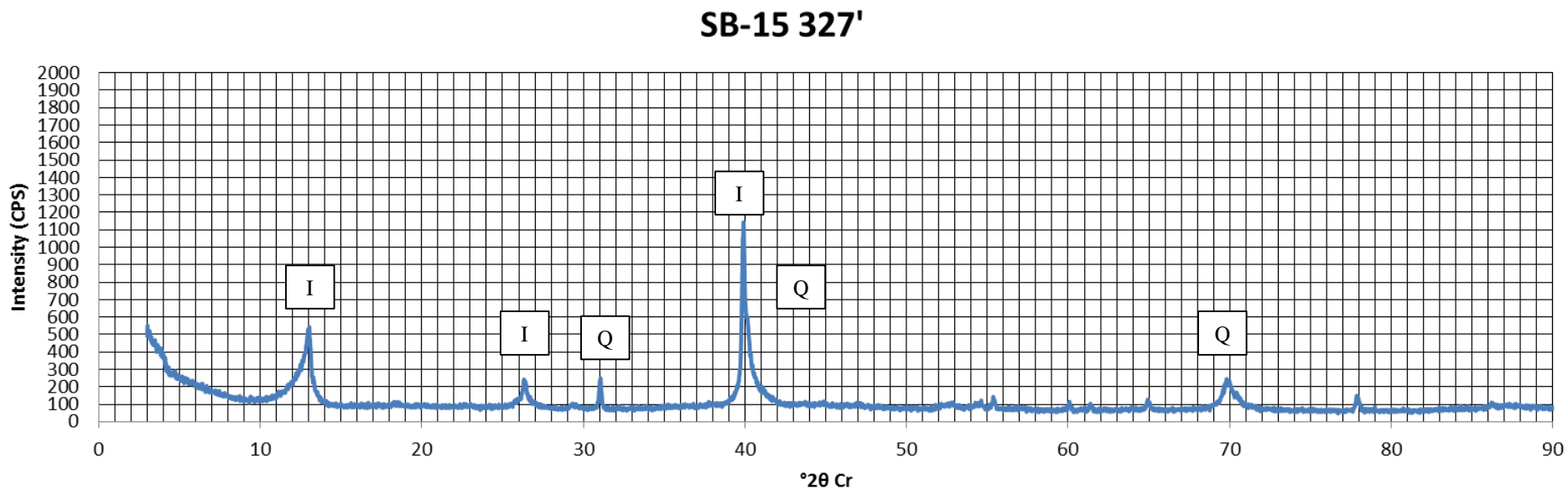
- X=major x=minor
- Illite– 18/18
- Kaolinite– 17/18
- Chlorite– 14/18



Barnes et al., 2008



# Results: Marshall XRD

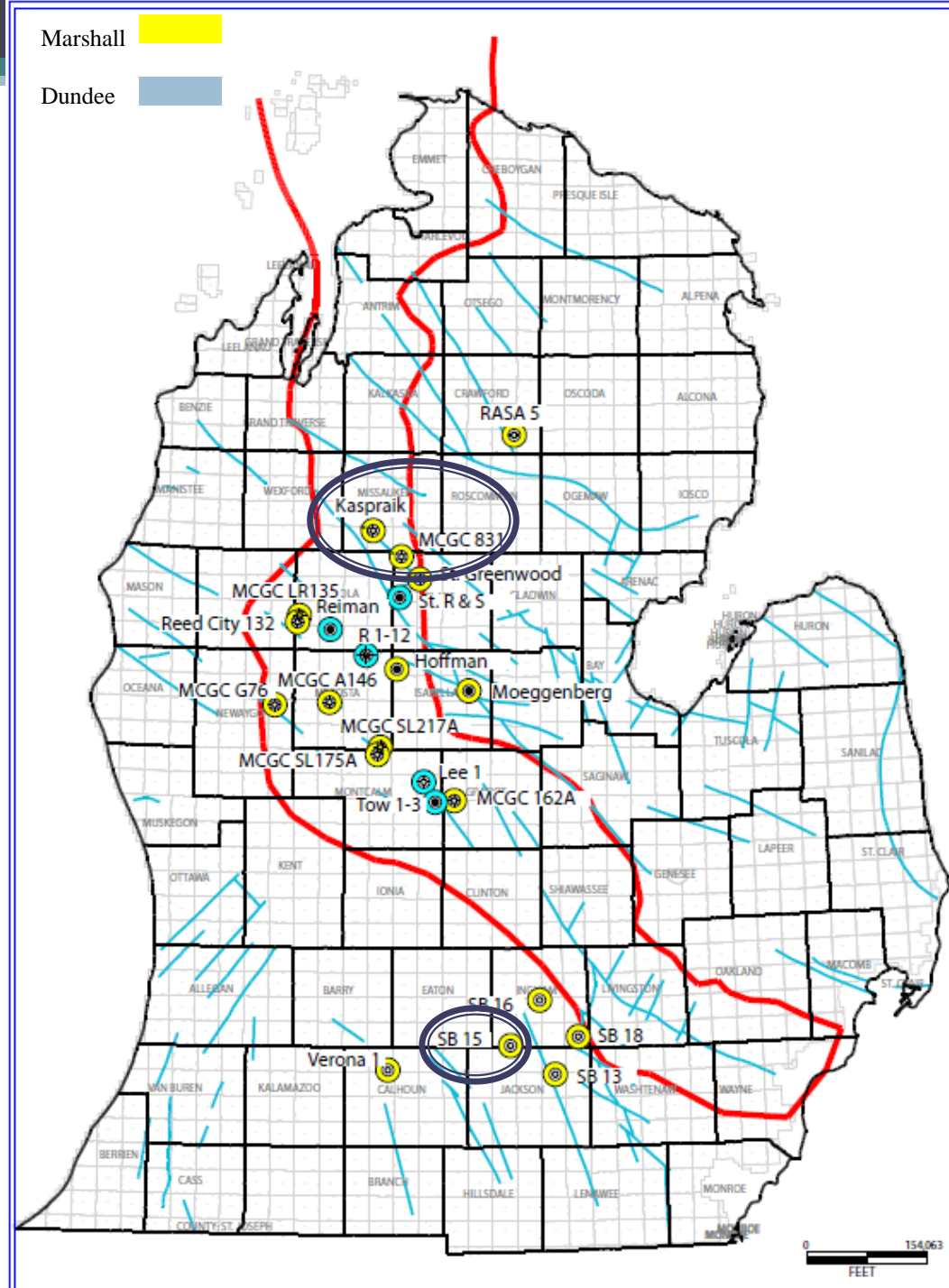


- Illite dominated XRD sample used for K–Ar age dating

# Results: K-Ar Age Dating

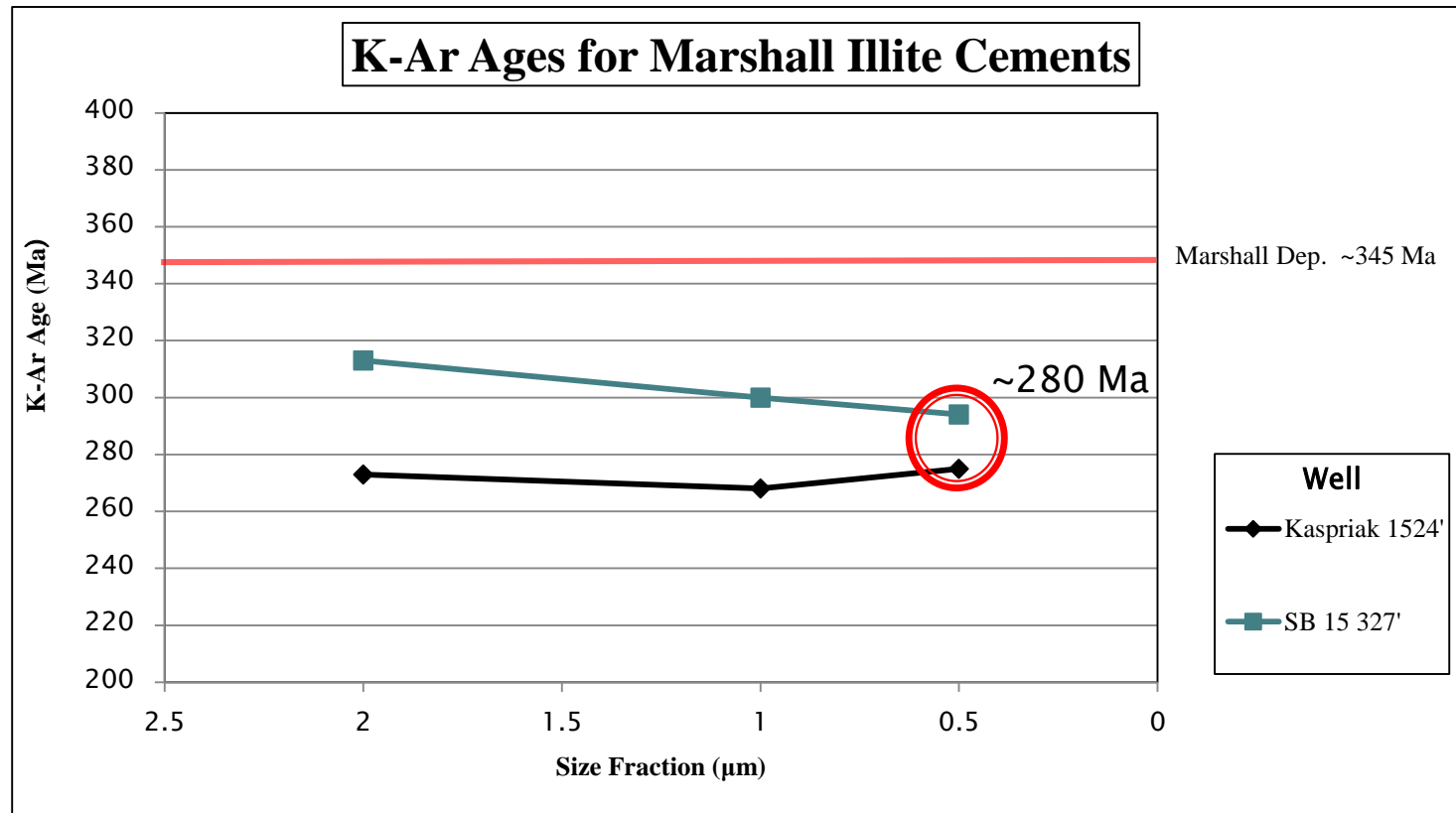
- 3 Samples

- Kaspraik 1524'
- MGSC 831 1432.5'
- SB 15 327'



# Results: K–Ar Age Dating

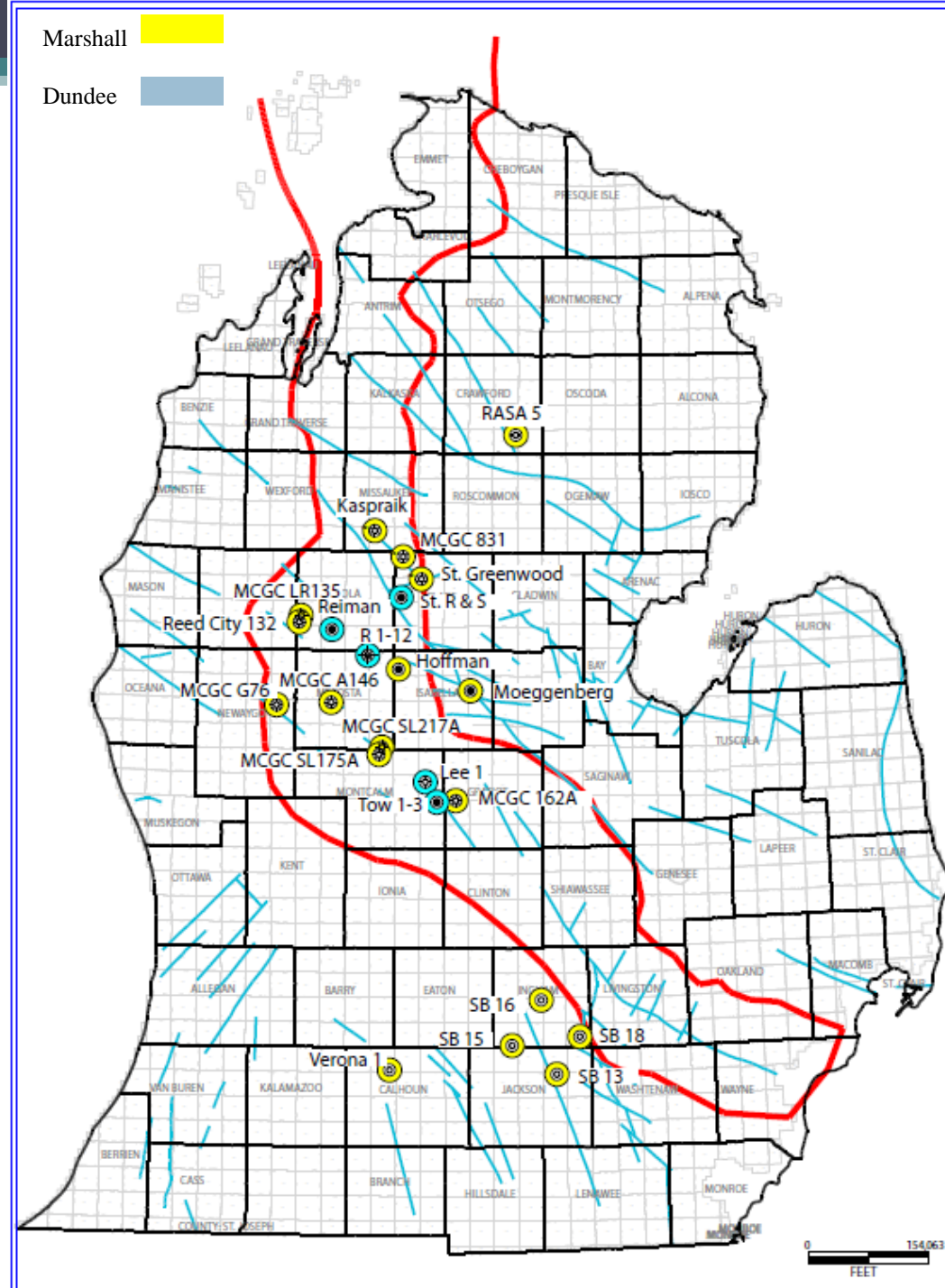
- Kaspraik  
275–268 Ma
- SB 15 313–  
294 Ma
- MGSC 831–  
No Results
- Authigenic
  - Integrated?





# Results: Dundee

- 5 Dundee Wells
  - 973–1203m
  - 11 thick sections
  - 203 fluid inclusion measurements
  - 37 stable isotope samples
    - Data for 33 stable isotope samples provided by Dr. David Barnes



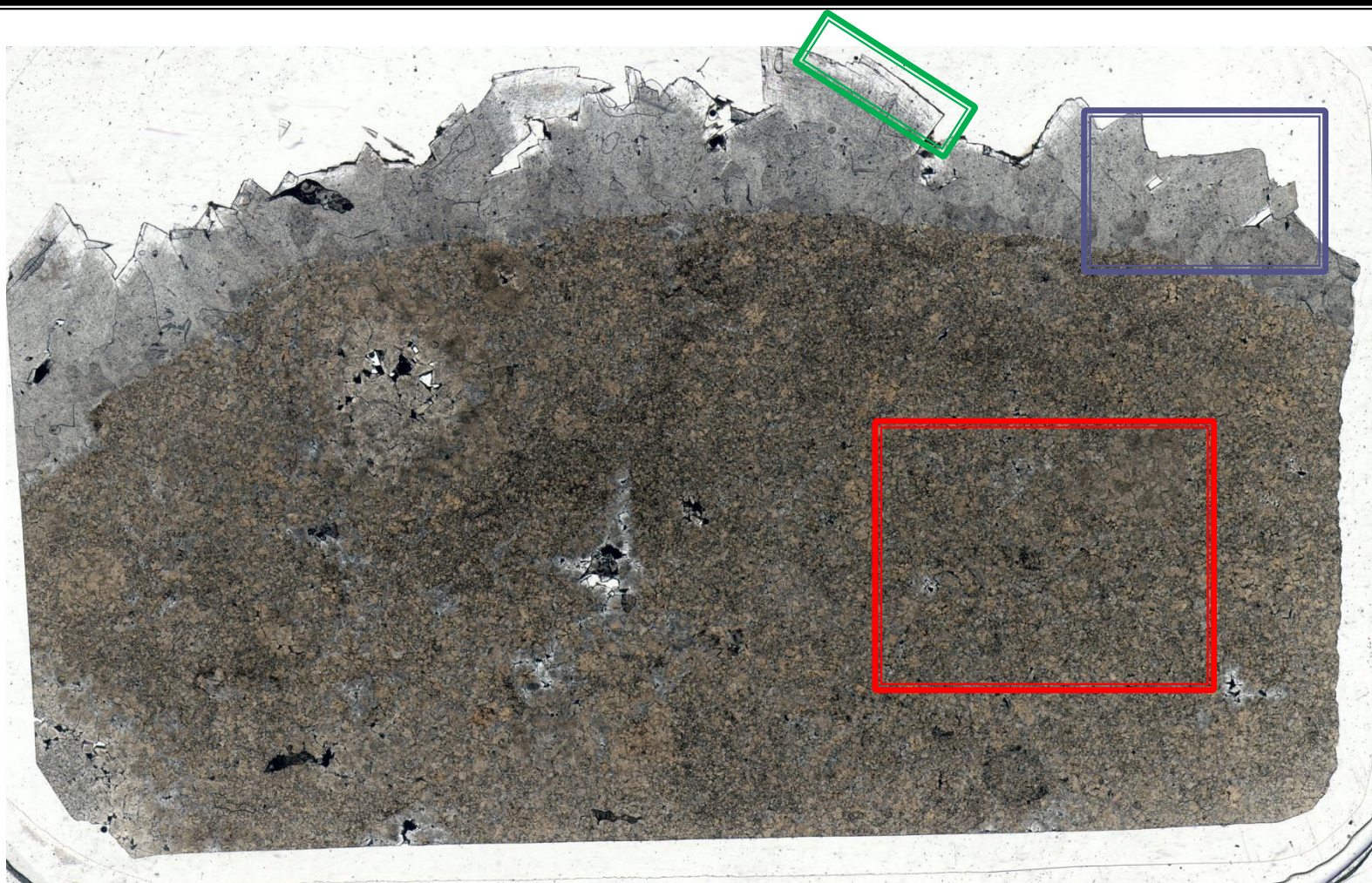


# Results: Dundee Petrography

- 11 thick sections
- Secondary components:
  - Dolomite
    - Mosaic
      - Replacive
    - Frac/vug
      - Neoformed, saddle
    - Overgrowth Dolomite
      - Neoformed, on other phases
  - Calcite
    - Fracture filling
  - Anhydrite
    - Fracture filling
  - Organic Material
    - Coats dolomite

# Results: Dundee Petrography

- Dolomite phases Lee 3466'



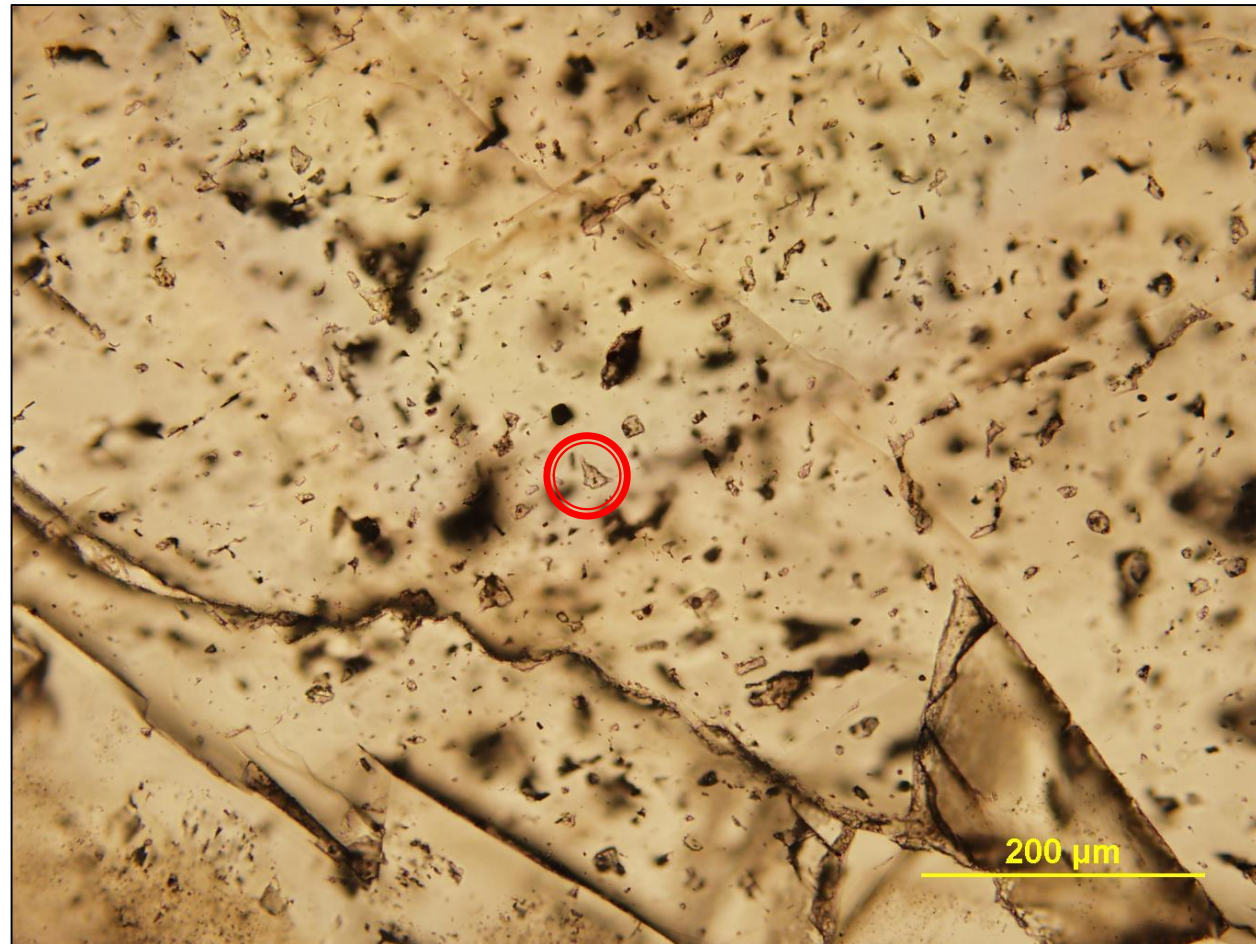
46 mm

- Mosaic
- Frac/Vug
- Overgrowth on saddle frac/vug



# Methods: Fluid Inclusion Analysis

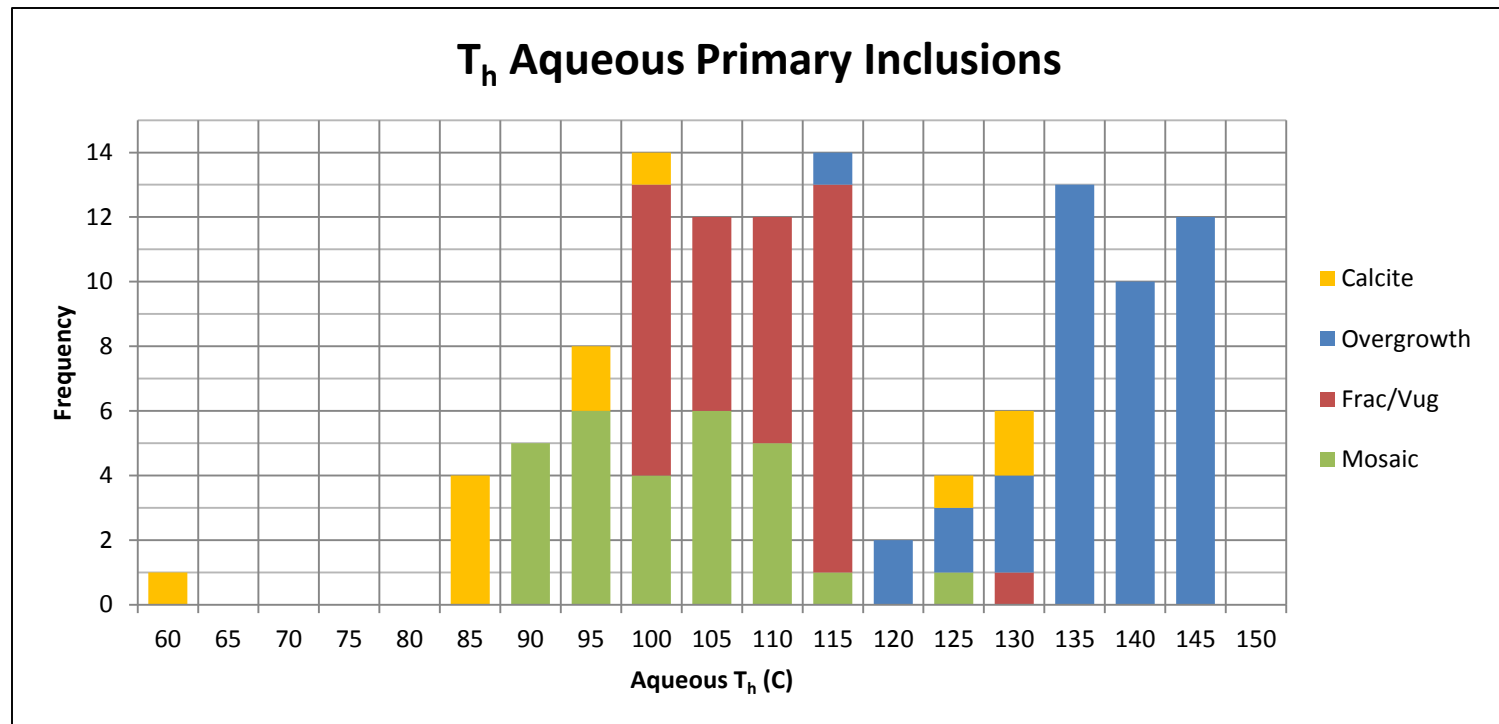
- Fluid inclusions
  - Small amount of fluid trapped in a crystal
    - Primary
    - Secondary
  - Record information about conditions during entrapment
    - $T_h$ 
      - Homogenization temp. of 2 phase inclusions
      - Minimum temp. or entrapment
    - $T_m$ 
      - Final melting temp.
      - Salinity of fluid
    - $T_e$ 
      - Eutectic temp.
      - Salt system of fluid



Tow 3191'

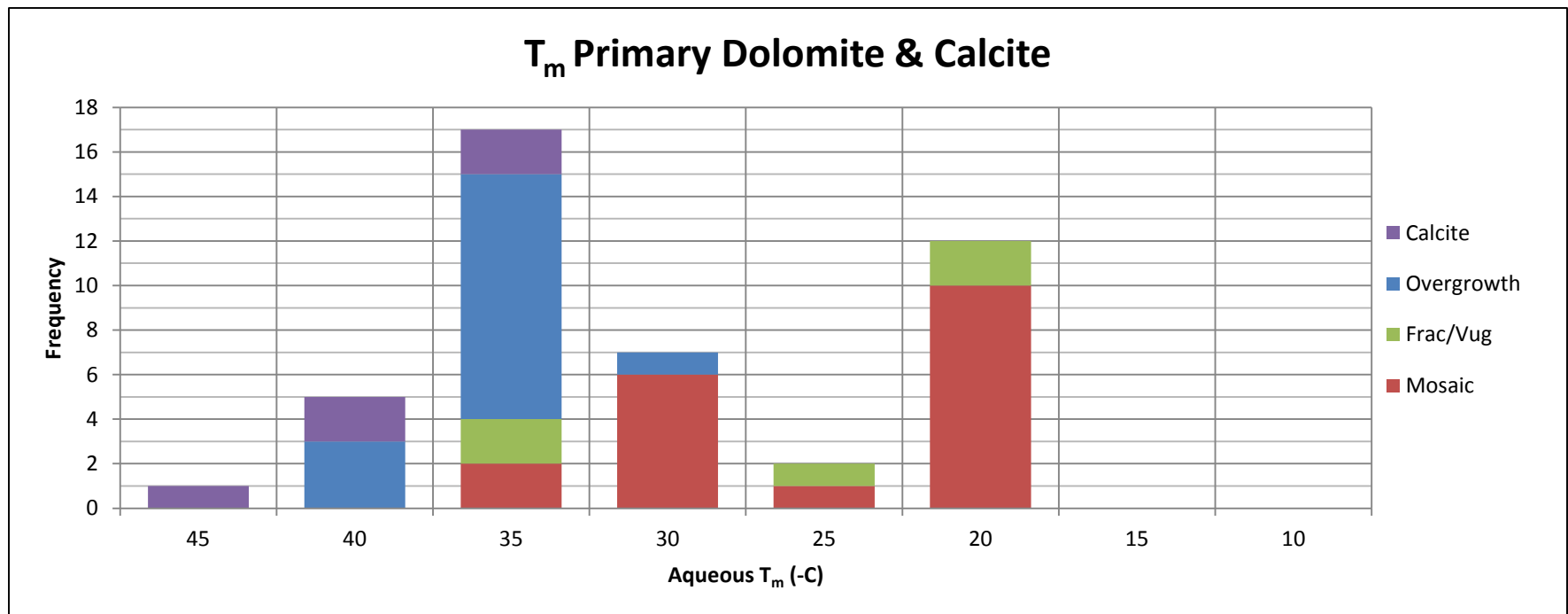
# Results: Fluid Inclusion Analysis

- Average  $T_h$  for Primary FI's varied by phase
  - Mosaic-95° C
  - Frac/Vug-106.5° C
  - Overgrowth-134° C
  - Calcite-96° C



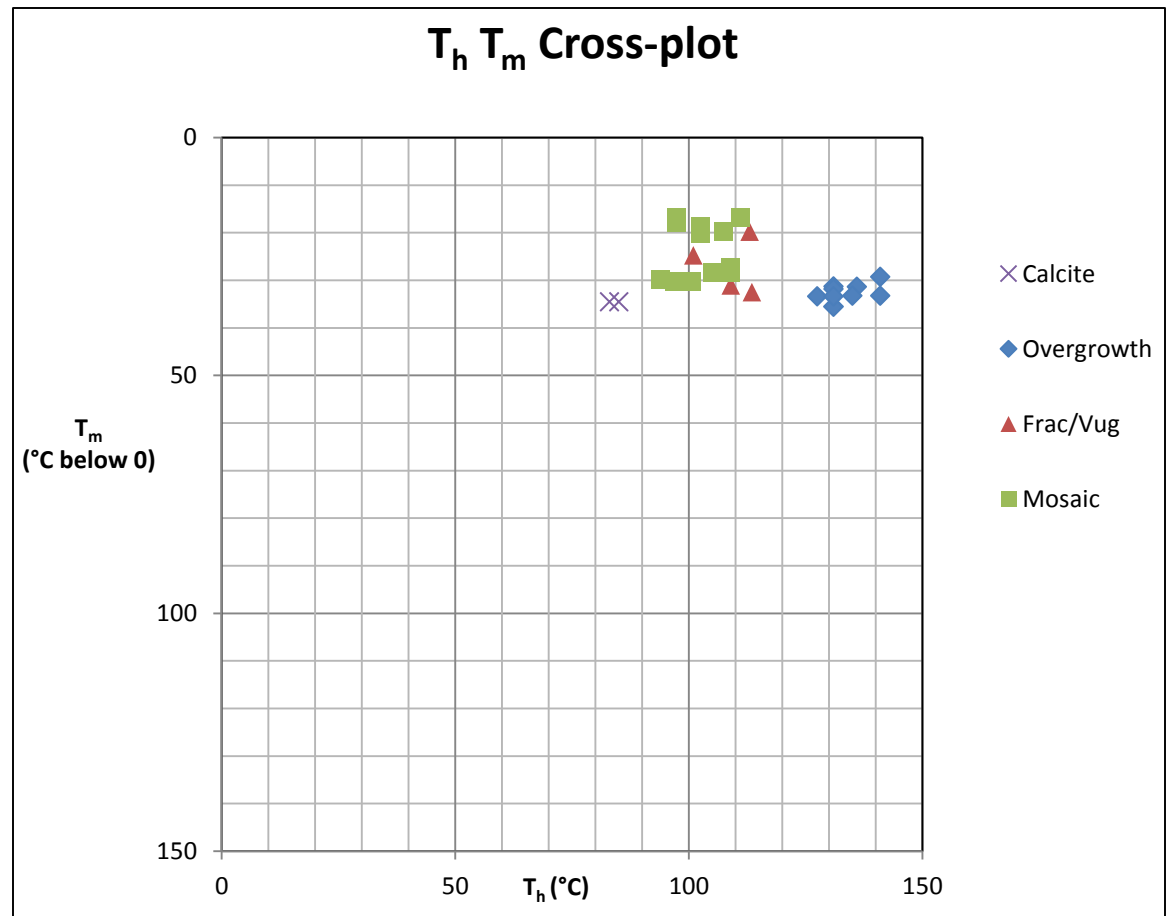
# Results: Fluid Inclusion Analysis

- Average  $T_m$  for primary FI's varied by phase
  - Mosaic–  $-22.5^\circ\text{C}$ , ~24% Na Cl equiv.
  - Frac/Vug–  $-25.6^\circ\text{C}$ , ~26% Na Cl equiv.
  - Overgrowth–  $-33.3^\circ\text{C}$  ~31% Na Cl equiv.
  - Calcite–  $-36.1^\circ\text{C}$ , ~33% Na Cl equiv.
- Na Cl equivalent salinities are ~7–10 x modern sea water



# Results: Fluid Inclusion Analysis

- Quality control
  - Phases cluster in cross-plot



# Results: Fluid Inclusion Analysis

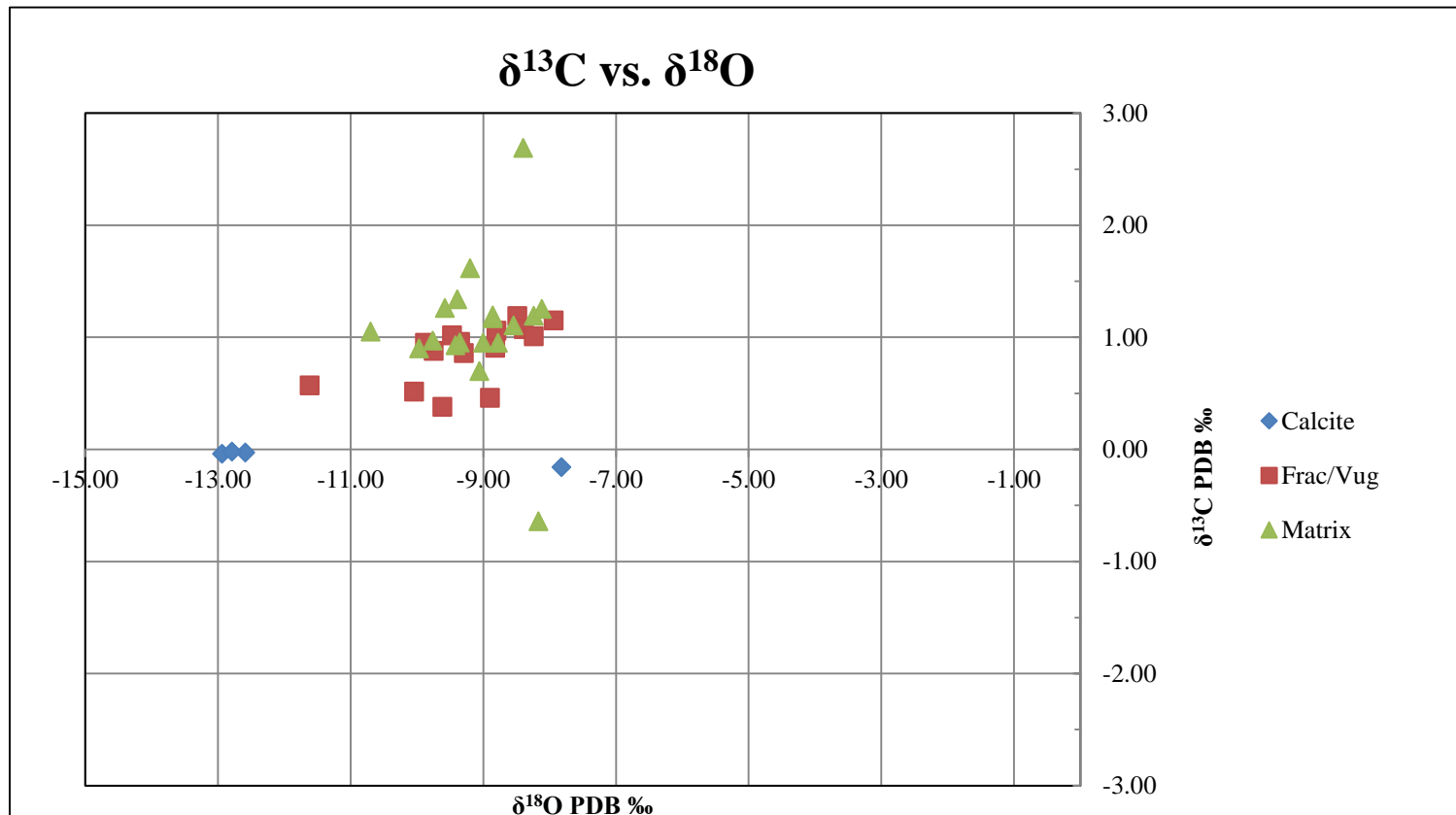
- 9  $T_e$  measurements recorded as ranges
  - -45 to -65° C
  - NaCl-CaCl<sub>2</sub>-MgCl<sub>2</sub>-H<sub>2</sub> salt system
    - Luczaj et al., 2006

Well	Depth	FIA	Phase	$T_e$ (-°C)
Lee	3466'	1	Overgrowth	65-55
Lee	3466'	1	Overgrowth	65-55
Lee	3466'	1	Overgrowth	65-55
Lee	3466'	1	Overgrowth	65-55
R1-12	3948'	1	Mosaic	65-50
R1-12	3948'	1	Mosaic	65-50
Tow	3191'	1	Mosaic	55-45
Tow	3191'	2	Frac/Vug	60-50
Tow	3191'	2	Frac/Vug	60-50

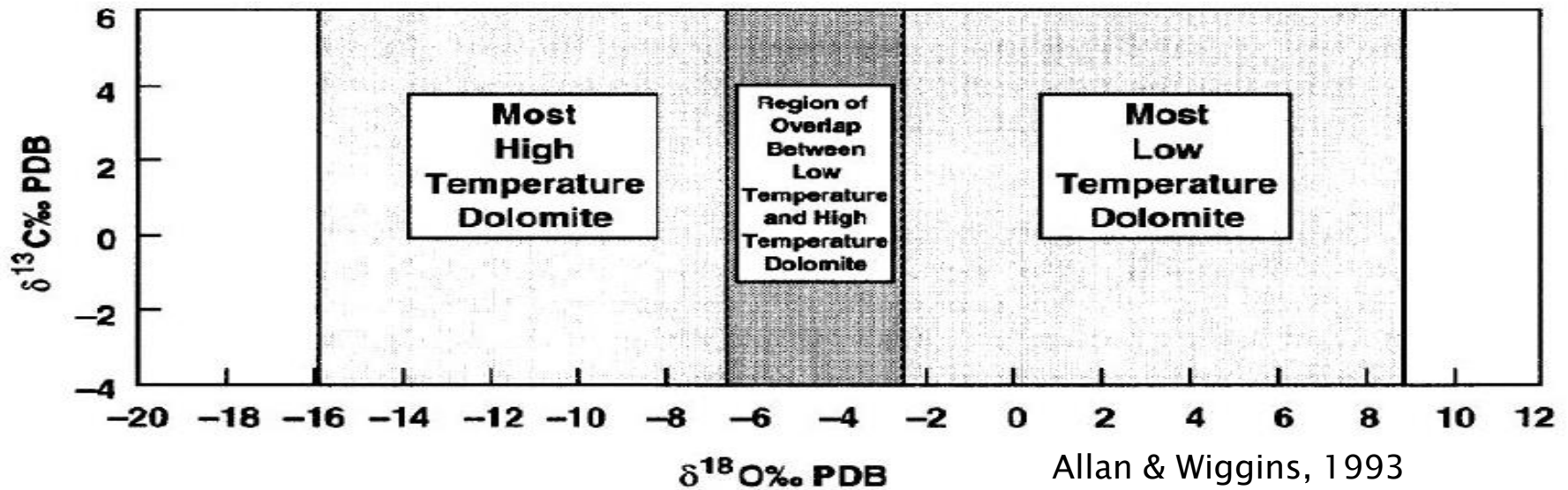
# Results: Stable Isotopes

- $^{18}\text{O}$  and  $^{13}\text{C}$  measurements for 37 Dundee samples
  - 18 mosaic, 15 frac/vug, and 4 calcite

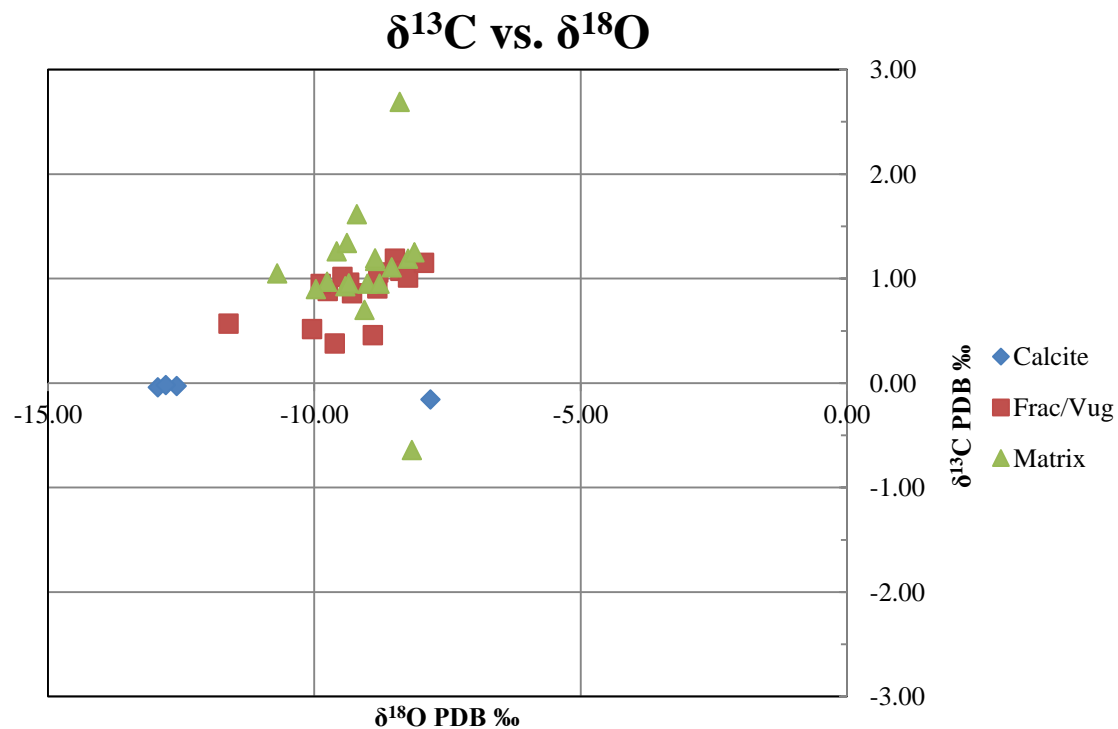
- Mosaic Avg. (PDB)
  - $-9.08 \delta^{18}\text{O}$
  - $+1.09 \delta^{13}\text{C}$
- Frac/vug Avg. (PDB)
  - $-9.24 \delta^{18}\text{O}$
  - $+0.87 \delta^{13}\text{C}$
- Calcite Avg. (PDB)
  - $-11.54 \delta^{18}\text{O}$
  - $-0.06 \delta^{13}\text{C}$





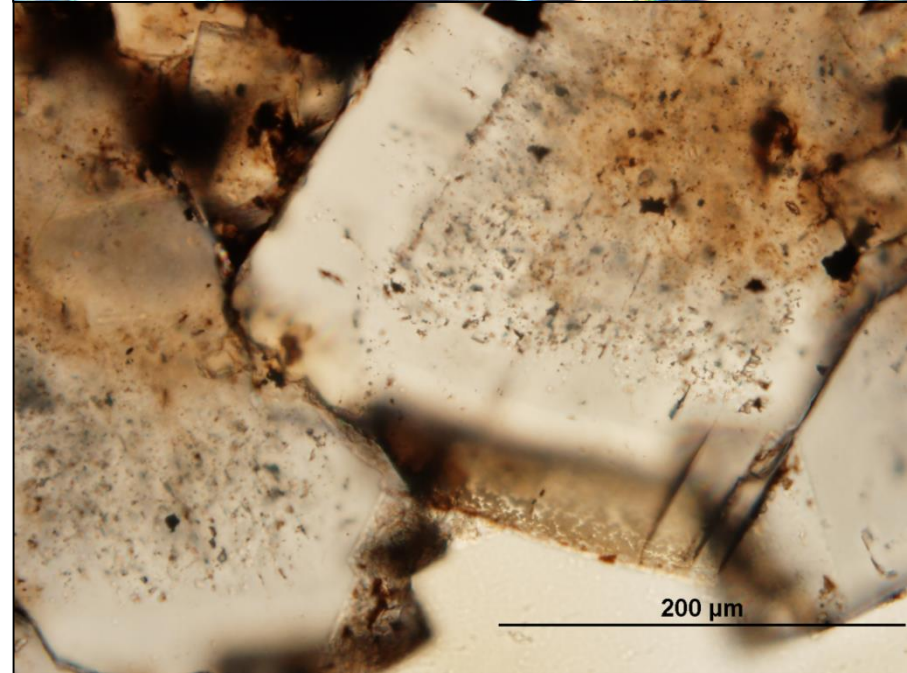
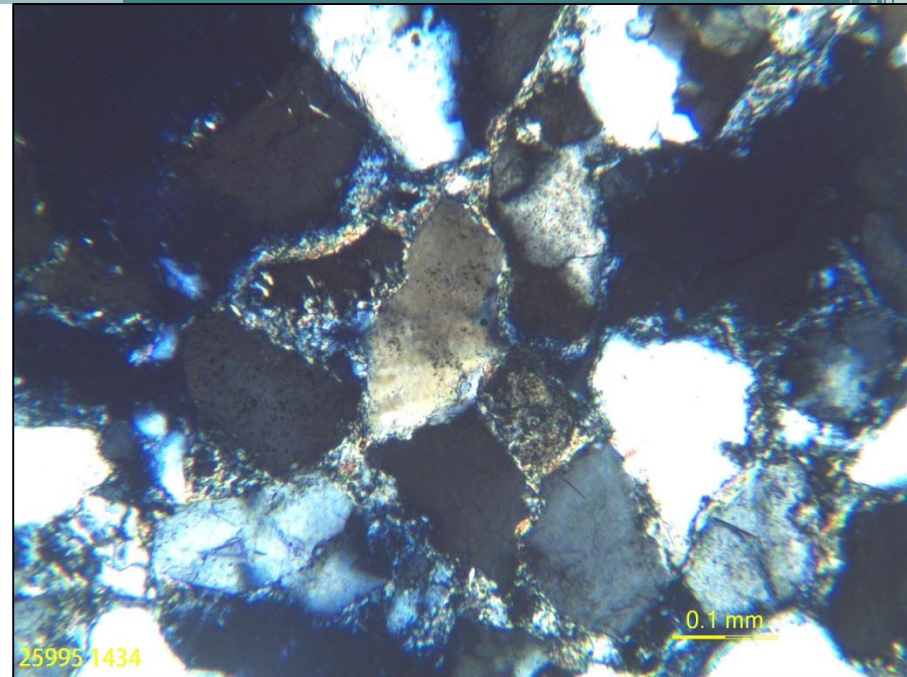


- Results are indicative of high temperature inorganic dolomitization



# 1. What authigenic minerals?

- Marshall
  - K-feldspar, quartz, ankerite, calcite, kaolinite, chlorite
    - Kaolinite replaced K-feldspar
  - Illite
    - Illite replaced kaolinite
- Dundee
  - Dolomite
    - Mosaic dolomite
    - Frac/vug dolomite
    - Overgrowth dolomite
  - Calcite
  - Anhydrite



## 2. Formation Cond.

- Marshall Sandstone

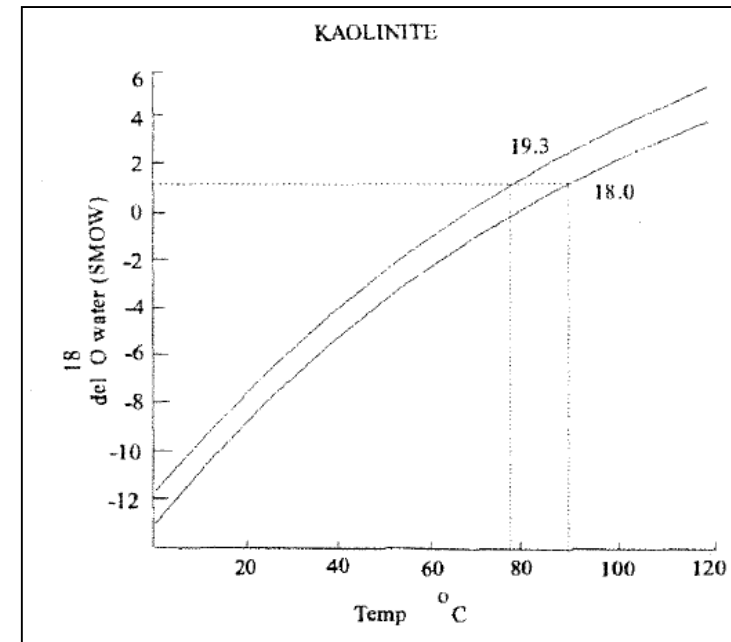
- Has experienced temperatures  $>80^{\circ}\text{C}$  during migration of deep basinal fluids through the formation

- Dundee Limestone

- Dolomitization occurred at temperatures of 90 to  $145^{\circ}\text{C}$  during the migration of deep basinal fluids through the formation

## 2. Formation Cond.

- Marshall Sandstone
  - Temperatures  $>80^{\circ}\text{C}$
  - Burial ( $>2\text{--}4\text{km}$ ) diagenetic assemblage
  - Zacharias et al., 1993
    - Chlorite:  $55\text{--}85^{\circ}\text{C}$
    - Ankerite:  $75\text{--}90^{\circ}\text{C}$
    - Kaolinite:  $80\text{--}90^{\circ}\text{C}$
  - Quartz overgrowths
    - Uncommon below  $80^{\circ}\text{C}$  (Wilkinson & Haszeldine, 2002)
  - Illite
    - Formation sandstone uncommon below  $100^{\circ}\text{C}$  (Wilkinson & Haszeldine, 2002)
    - Replaced kaolinite
      - Reaction related to temp. increase (Meunier & Velde, 2004)



Zacharias et al., 1993

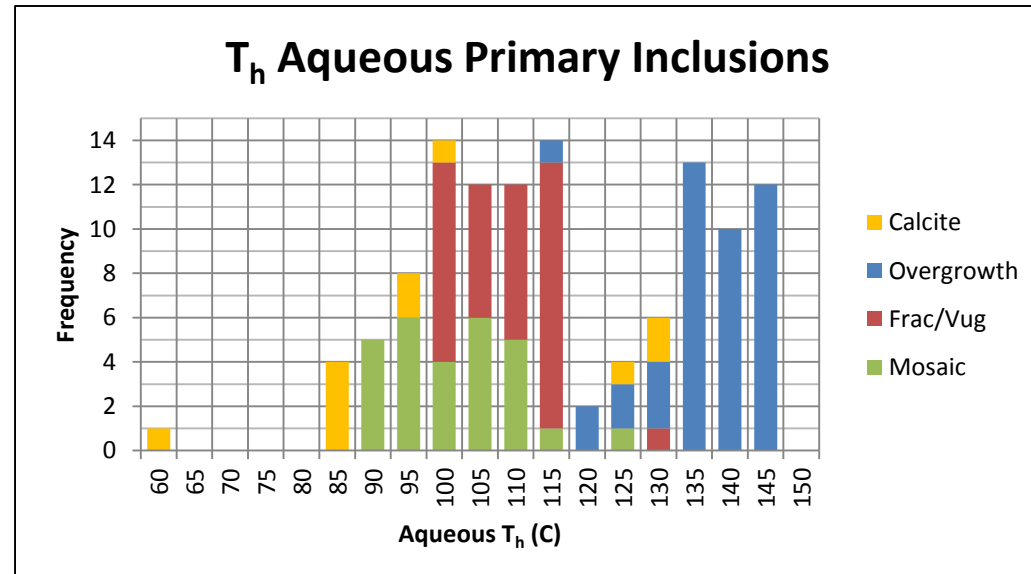
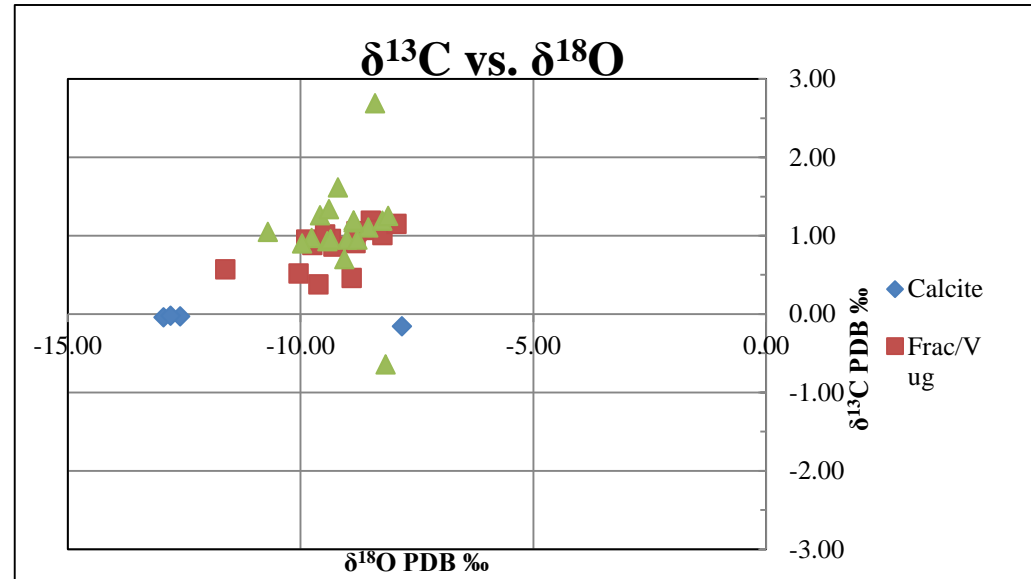
## 2. Formation Cond.

- Authigenic illite formation in sandstone
  - Requires high flow rates of  $K^+$  rich fluid (Wilkinson & Haszeldine 2002)
    - External  $K^+$  source needed (Meunier & Velde, 2004)
  - Formation generally attributed to hydrothermal fluid flow related to tectonic events (Lanson et al., 1996)

## 2. Formation Cond.

- Dundee Limestone

- Dolomitization occurred at temperatures of 90 to 145° C during the migration of deep basinal fluids through the formation
  - Authigenic components estimated formation temp.:
    - Mosaic: 90–110 ° C
    - Frac/vug: 100–115° C
    - Overgrowth: 130–145° C



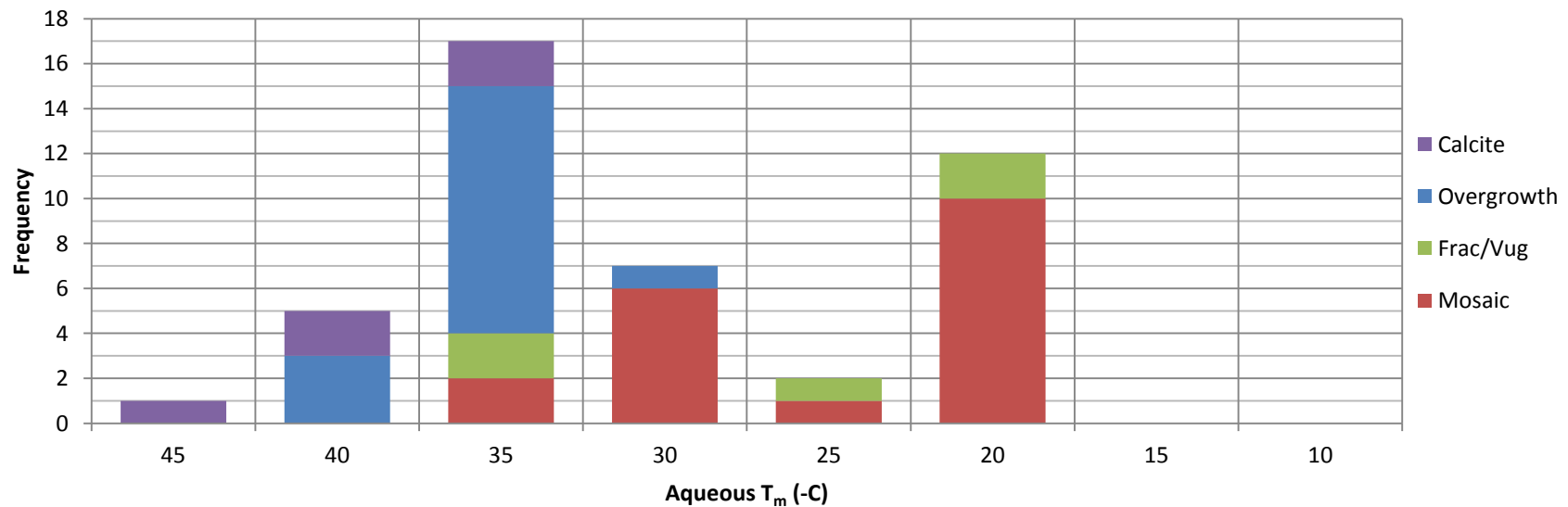


## 2. Formation Cond.

- Dolomitizing fluid
  - ~7–10 x salinity modern sea water
  - NaCl–CaCl<sub>2</sub>–MgCl<sub>2</sub>–H<sub>2</sub> salt system

Well	Depth	FIA	Phase	T <sub>e</sub> (-°C)
Lee	3466'	1	Overgrowth	65-55
Lee	3466'	1	Overgrowth	65-55
Lee	3466'	1	Overgrowth	65-55
Lee	3466'	1	Overgrowth	65-55
R1-12	3948'	1	Mosaic	65-50
R1-12	3948'	1	Mosaic	65-50
Tow	3191'	1	Mosaic	55-45
Tow	3191'	2	Frac/Vug	60-50
Tow	3191'	2	Frac/Vug	60-50

**T<sub>m</sub> Primary Dolomite & Calcite**



## 2. Formation Cond.

- Formation fluid isotopic composition
  - Dolomitizing fluid estimate
    - $-0.5$  to  $+2.00$   $\delta^{18}\text{O}$  SMOW

Phase	Avg $\delta^{18}\text{O}$ ‰ PDB	Avg $\delta^{18}\text{O}$ ‰ SMOW	Formation Temp °C	Est. Water $\delta^{18}\text{O}$ ‰ SMOW Low Temp	Est. Water High $\delta^{18}\text{O}$ ‰ SMOW High Temp
Calcite	Without 3195				
	-12.77	+19.03	80-100	+0.6	+1.8
	With 3195				
	-11.54	+21.90	80-100	+2.3	+4.6
Frac/Vug	-9.24	+21.39	100 to 115	+0.6	+2.3
Mosaic	-9.08	+21.56	90 to 110	-0.50	+2.00

- Marshall brine measurement
  - $+0.8$   $\delta^{18}\text{O}$  SMOW (Zacharias et al., 1993)

## 2. Formation Cond.

- Evidence for deep basinal brine migration
  - High salinity fluids
    - Marshall brine genetically related to Silurian brines (Ma et al., 2005)
    - Dundee fluids ~7–10 more saline than seawater
  - Fluids in both formations have interacted with basement
    - Marshall brine He (Ma et al., 2005)
    - Dundee brines mantle-like signature (Ma et al., 2009)
  - Illitization and dolomitization require chemical material from an outside source
    - External K<sup>+</sup> source needed for illitization (Meunier & Velde, 2004)
    - Outside source of Mg needed for dolomitization (Allan & Wiggins, 1993)

### 3. When did they form?

- Marshall (dep. age ~345 Ma)
  - ~280 Ma
    - Single period of illitization in the Permian?
    - Multiple illitization events?
- Dundee (dep. age ~390 Ma)
  - Cogenetic with Marshall?
  - Multiple episodes?

## 4. Comparison with Burial

	Marshall		Dundee	
	Shallowest	Deepest	Shallowest	Deepest
Depth (m)	14m	477m	973m	1203m
Current Temp (C)	15°	25°	35°	40°
0.5km Add. Burial Temp (C)	37°	47°	57°	62°
1km Add. Burial Temp (C)	47°	57°	68°	73°
2km Add. Burial Temp (C)	69°	79°	91°	95°
Illite/Dolomite Formation Temp.(C)	>80 °		130-145°	

- Features can not be explained by burial

- Temperature

- Require >2km burial

- Chemical mass

- Require external source

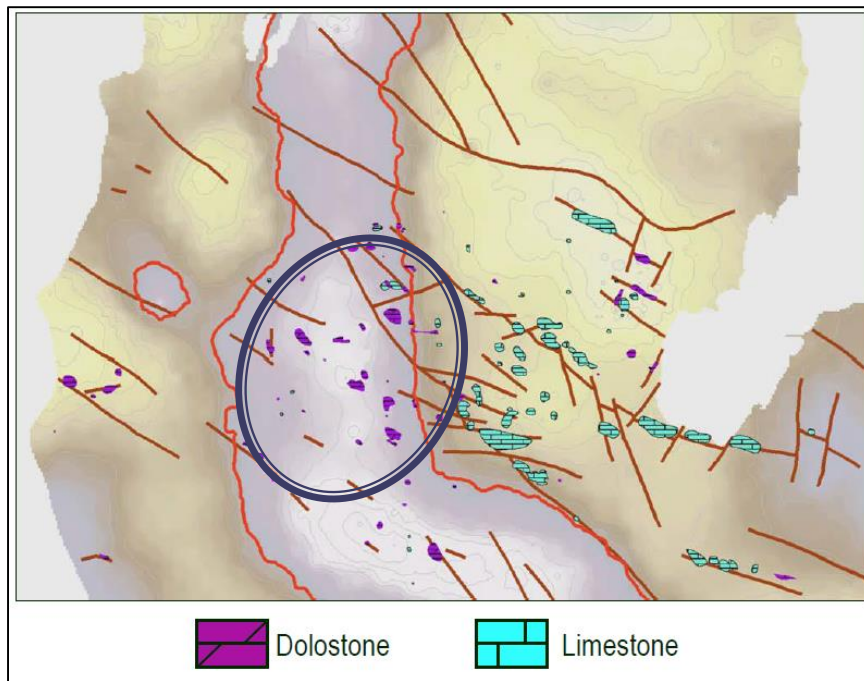
- Deep basin brine signature

Geothermal gradient of 22° C  
 Current assumes 15° C surface temp  
 Add. Burial assumes 25° C surface temp

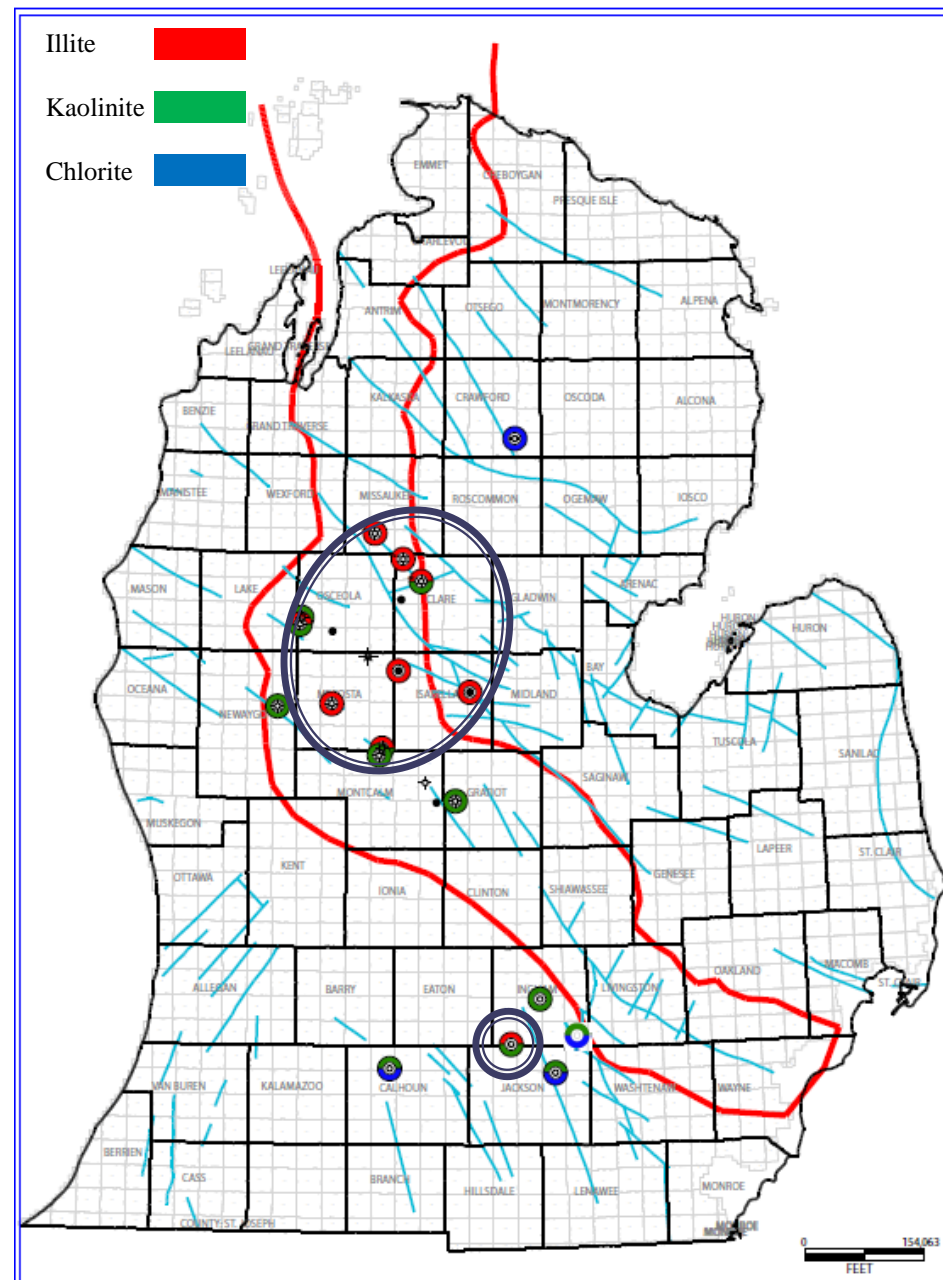
## 5. Distribution

- Are anomalous paleo-temperature indicators spatially related to the rift and known structures?
  - **Marshall**
    - Distribution of illite in the Marshall coincides w/ Dundee dolomitization and known structure
  - **Dundee**
    - Dolomitization common within the MMR gravity anomaly and near structure





Barnes et al., 2008

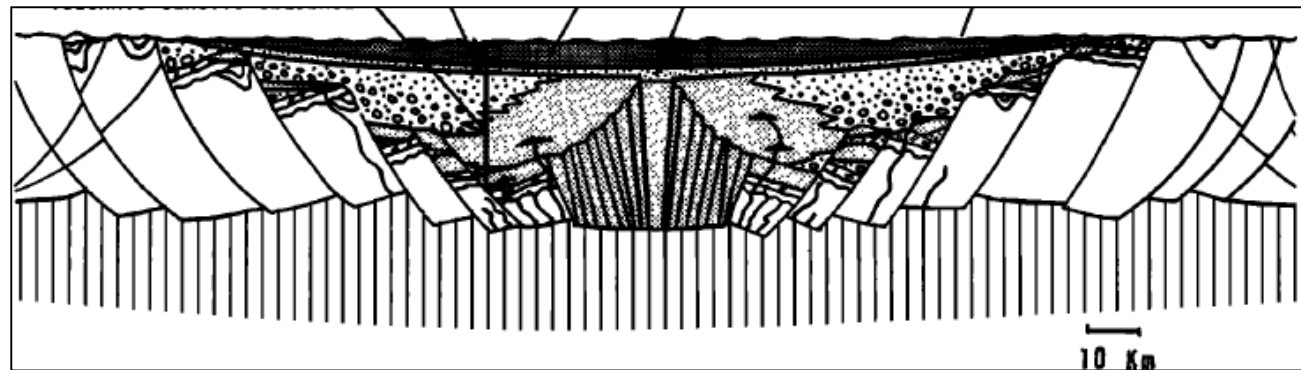
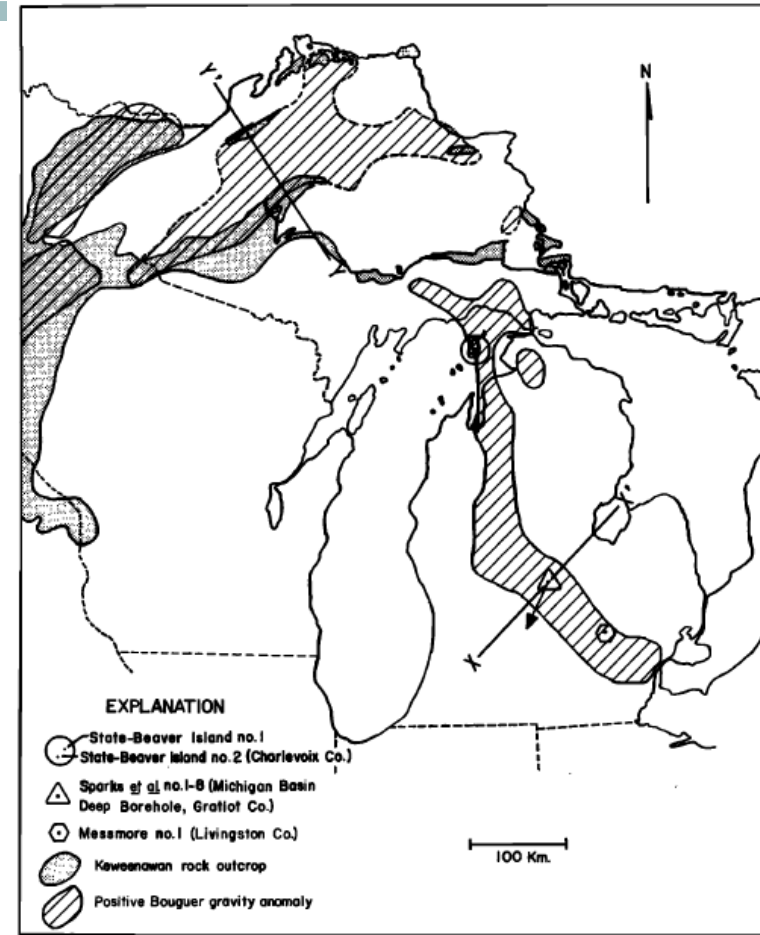


# Mechanism

- Hydrothermal Fluid Flow & Alteration
  - Burial alone would not provide the heat energy and chemical mass required
    - Need vehicle to be transported to the formation
  - Structural control is noted
    - Hydrothermal fluids would preferentially travel along faults, fractures, and along anticlines
    - MMR
      - Distribution of anomalous features (this study, Girard & Barnes 1995)
  - Shallow formations w/ deep basinal brines
    - Significant vertical flow component in the basin (Ma et al., 2005)
- Hydrothermal fluid flow results from tectonic events?

# Mechanism

- Appalachian Tectonic Events
  - Have affected the subsidence history of the basin (Howell & Van der Pluijm, 1999)
  - Hydrothermal illitization in the Appalachian basin and Mississippi Valley strata (Elliot & Aronson, 1987; Hay et al., 1988; Clauer et al., 2013)
  - Reactivation of MMR related basement rooted faults
    - Girard & Barnes, 1995; Castro et al., 2009; Ma et al., 2009
    - Mantle-like signature in basin brines (Castro et al., 2009)
  - Illite ages comparable
    - Marshall ~280 Ma
      - Alleghenian (320–260 Ma)
    - Ordovician St. Peter ~370–320 Ma (Girard & Barnes, 1995)
      - Integrated Acadian (420–360 Ma) & Alleghenian (320–260 Ma)

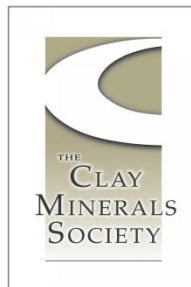
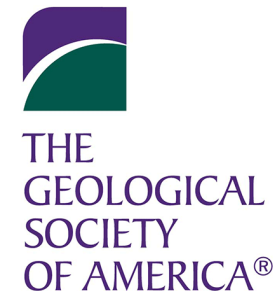
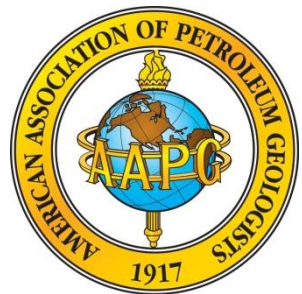


## Conclusions

- Evidence for anomalous paleo-temperatures is present in the Marshall Sandstone and Dundee Limestone
- This study and others indicate that hydrothermal fluid flow is the best explanation
  - Deep basinal fluids travelling along faults and fracture zones
- Distribution of anomalous features and basin brine chemistry suggest a connection with the MMR
  - Hydrothermal events maybe related to reactivation of MMR faults
- Illite K–Ar ages are comparable to Late Paleozoic Appalachian orogenies

# Acknowledgments

- Funding Sources
  - American Association of Petroleum Geologists
  - Michigan Basin Geological Society
  - Geological Society of America
  - Clay Mineral Society
  - W. David Kuenzi Research Fund
  - William and Linda Harrison Graduate Scholarship
  - Western Michigan University Graduate College



# Thank you

- Questions?



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