Update on Geochemistry and Diagenetic Models

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Reservoir Characterization Group
at the New York State Museum

NETL

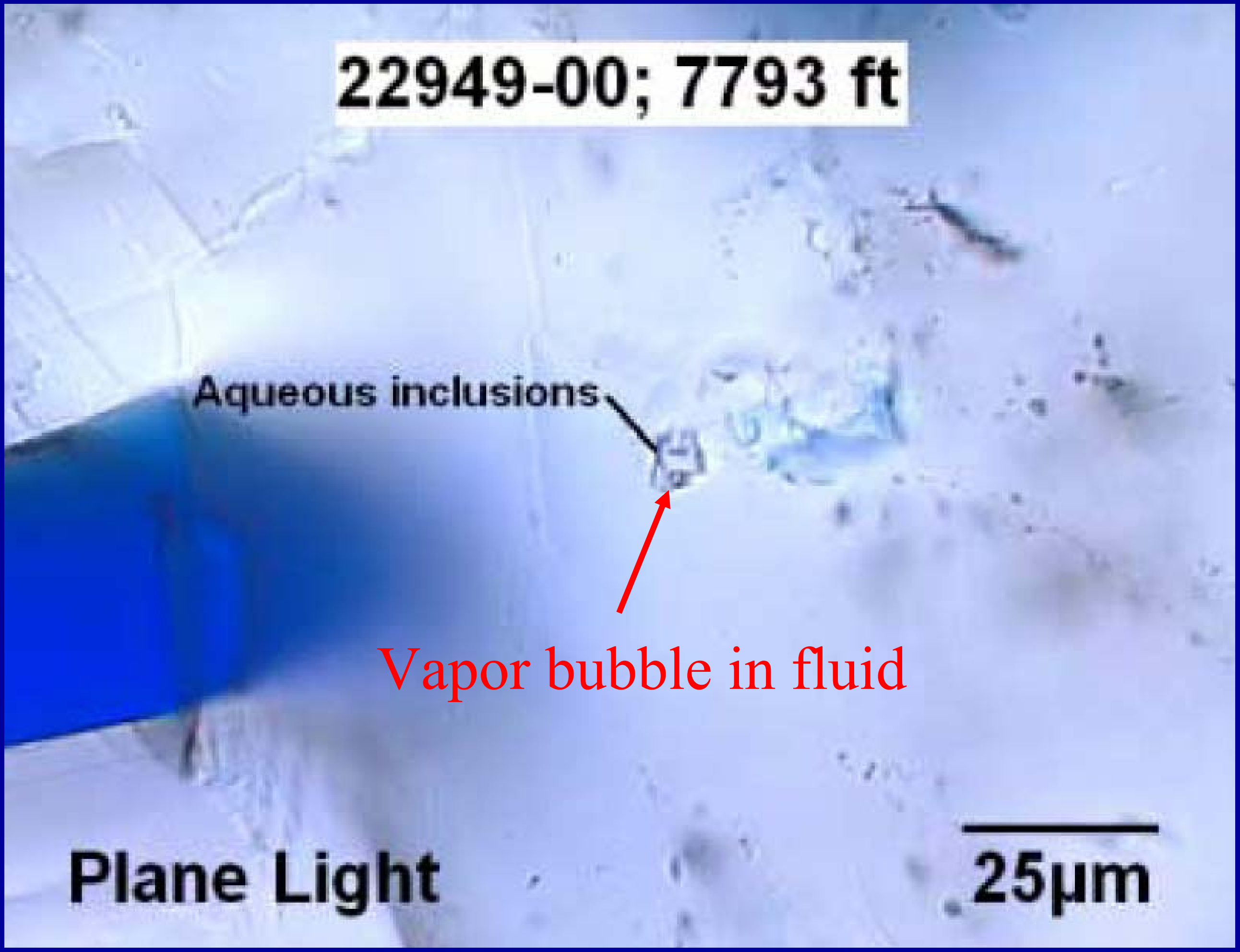
Biggest Well Onshore US in 2004:

- One of [Fortuna's] New York wells (Reed #1) produced at more than 40 million cubic feet per day, the best yield from any onshore well drilled in the U.S. last year

- Bloomberg, 2005

Outline

- Geochemical Analysis of TBR
  - Fluid inclusions
  - Stable isotopes
  - Trace elements
  - Strontium isotopes
- Are all dolomite types in TBR hydrothermal in origin?
- Carbon-13 isotope stratigraphy
  - How it works
  - Implications
- Possibility of age dating diagenetic feature in TBR

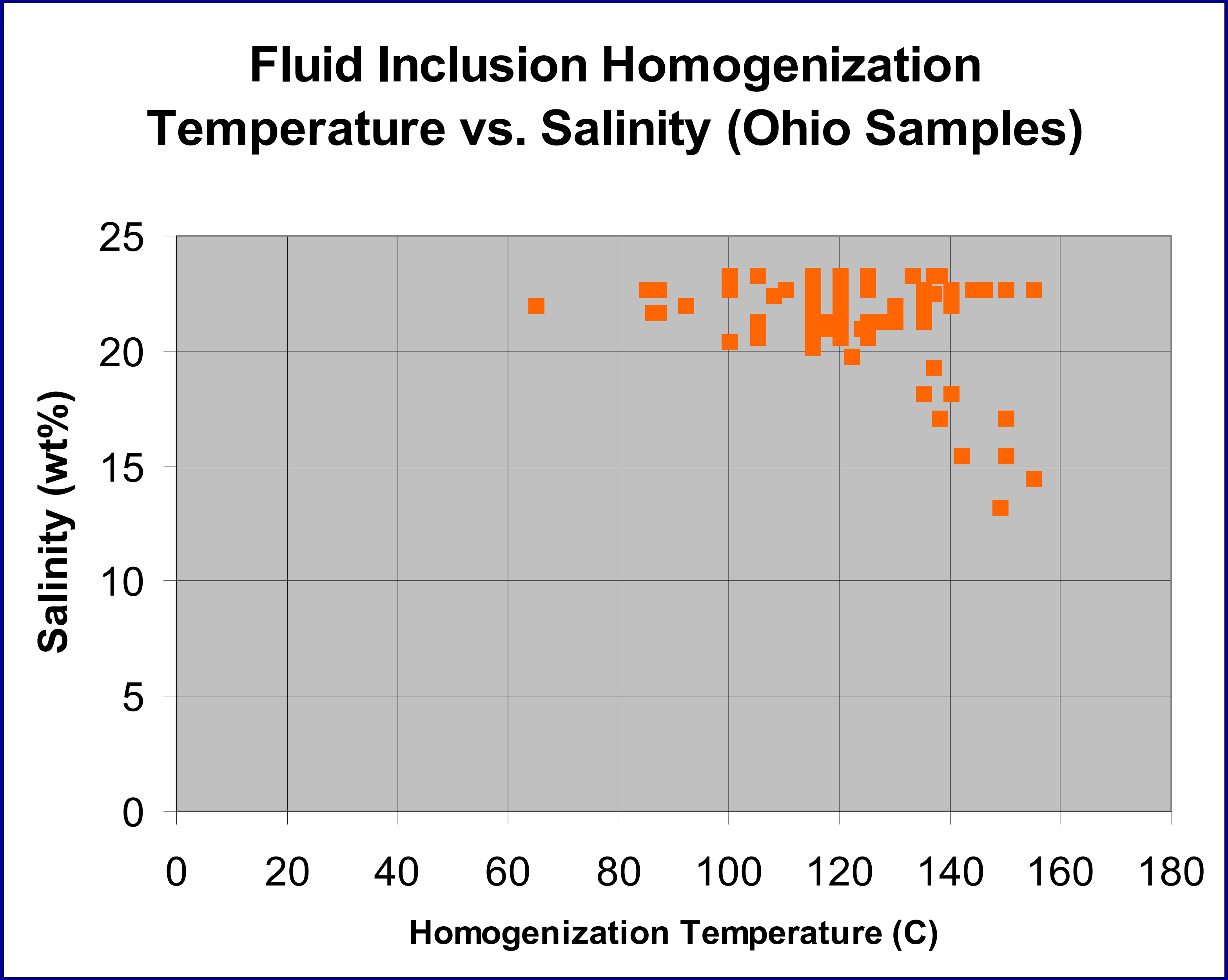


Homogenization temperature determined by heating sample until vapor bubble in two-phase inclusion disappears

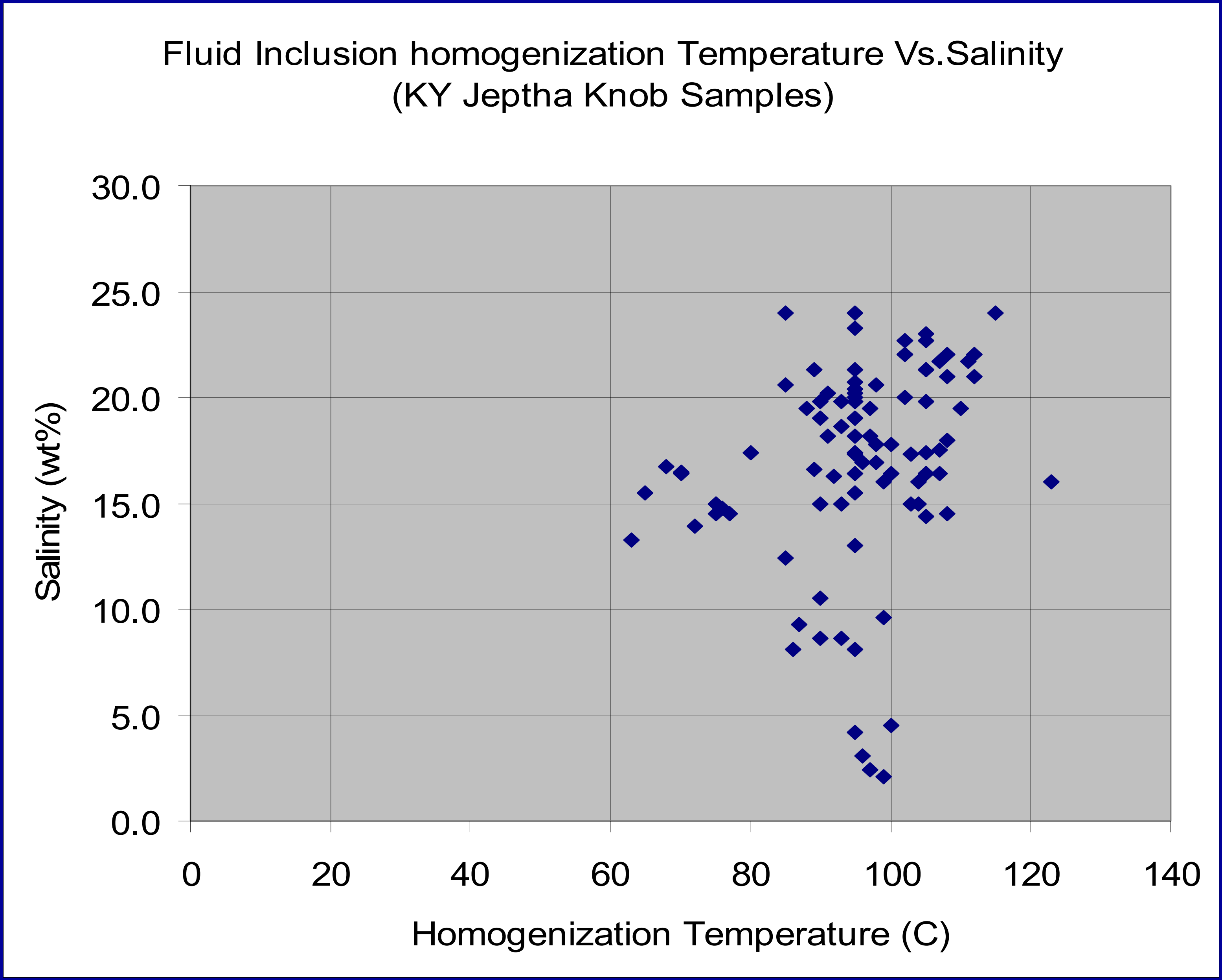
Salinity determined by cooling inclusion until it freezes, higher salinity fluids freeze at progressively lower temperatures

Table 11: Cisco #1-3267;1167 ft						
Population	**Fluor Color**	**Th hc (°C)**	**API hc (°)**	**Th aq (°C)**	**Tm aq (°C)**	**Sal (wt%)**
sec; outer zoned dol A	yellow-wht	110-120 (3)	N/A			
sec; outer zoned dol B	yellow-wht	105-120 (7)	N/A			
pr; dol transect pt1 C				149 (1)	-9.3	13.2
pr; dol transect pt2 C				142 (1)	-11.5	15.5
pr; dol transect pt3 C				138 (1)	-13.2	17.1
pr; outer zoned dol D				145-155 (3)	-11.0 to -12.0	15.0-16.0
pr; outer zoned dol E				150-160 (5)	-10.0 to -11.0	14.0-15.0
pr; outer zoned dol F				135-145 (3)	-14.0 to -15.0	17.8-18.6
pr; outer zoned dol G				145-155 (4)	-13.0 to -13.5	16.9-17.3
pr; outer zoned dol H				130-140 (4)	-14.0 to -15.0	17.8-18.6

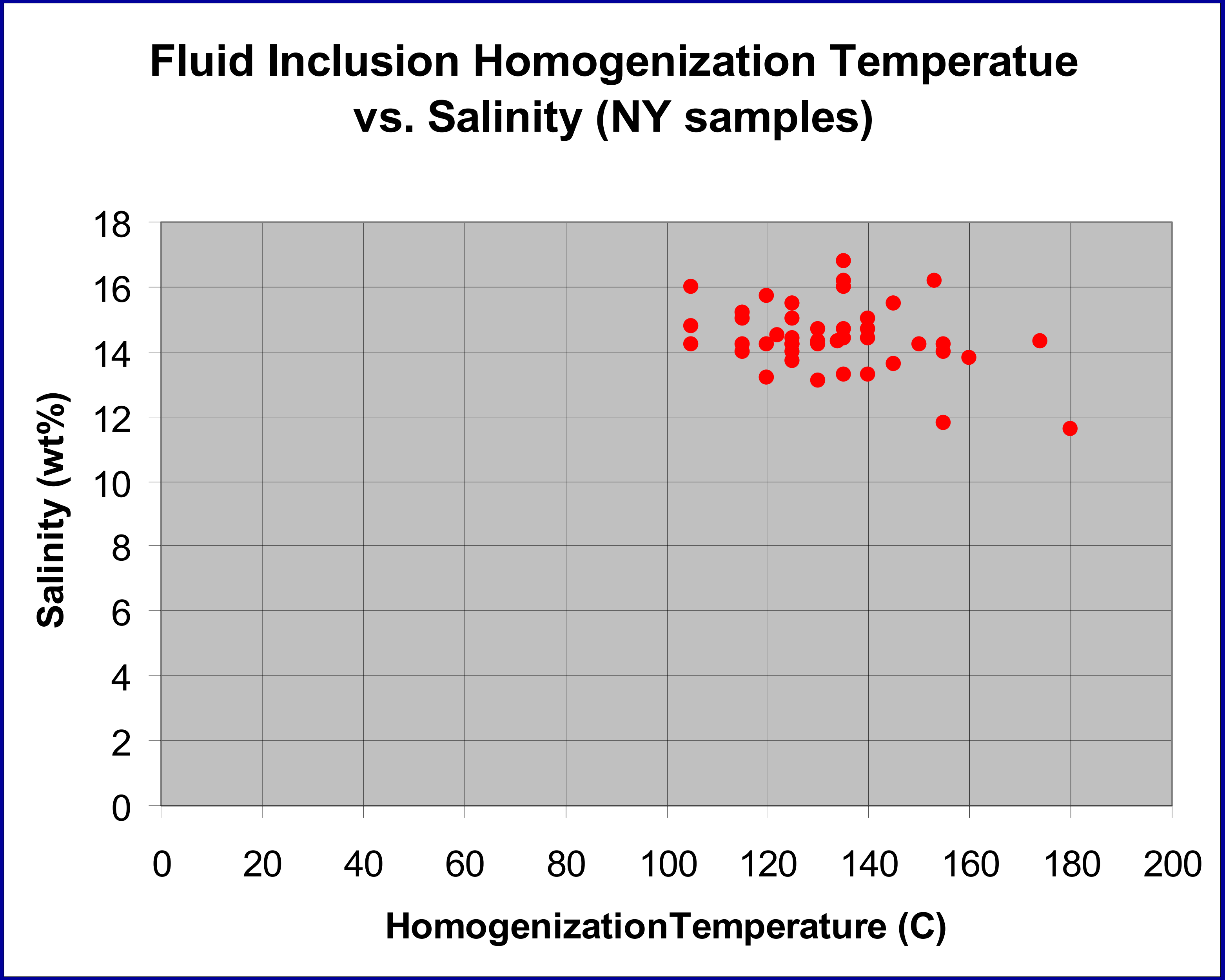
Fluid inclusion data from an Ohio sample: Tm aq (°C) = homogenization temperature or minimum temperature of fluid at time crystal formed (not corrected for pressure)



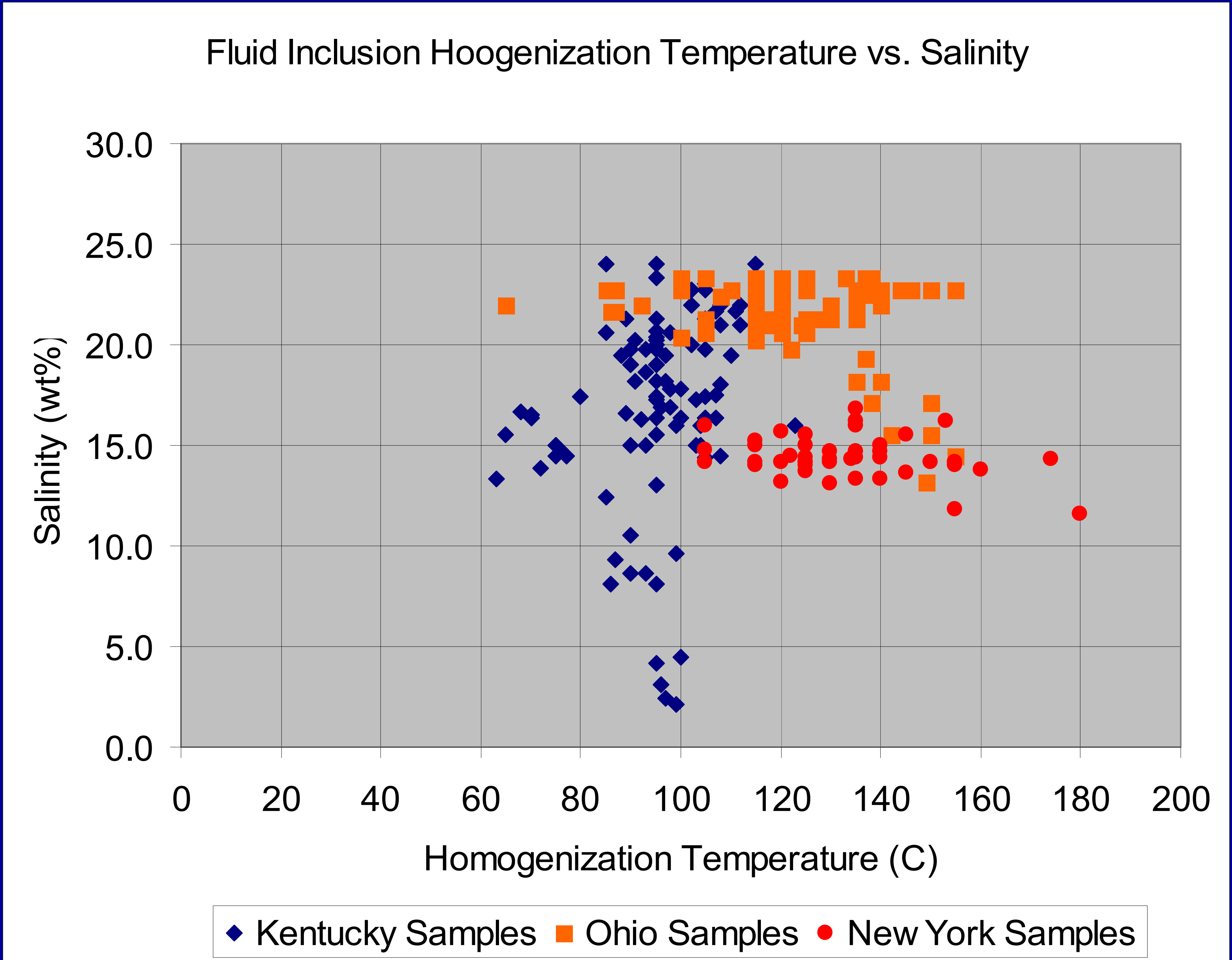
Most samples between 100-160ºC including cap and facies dolomite



Most samples 80-110 C, 15-24 wt%; Some very low salinity and T



Most samples 100-160º C (like Ohio), but salinity is significantly lower

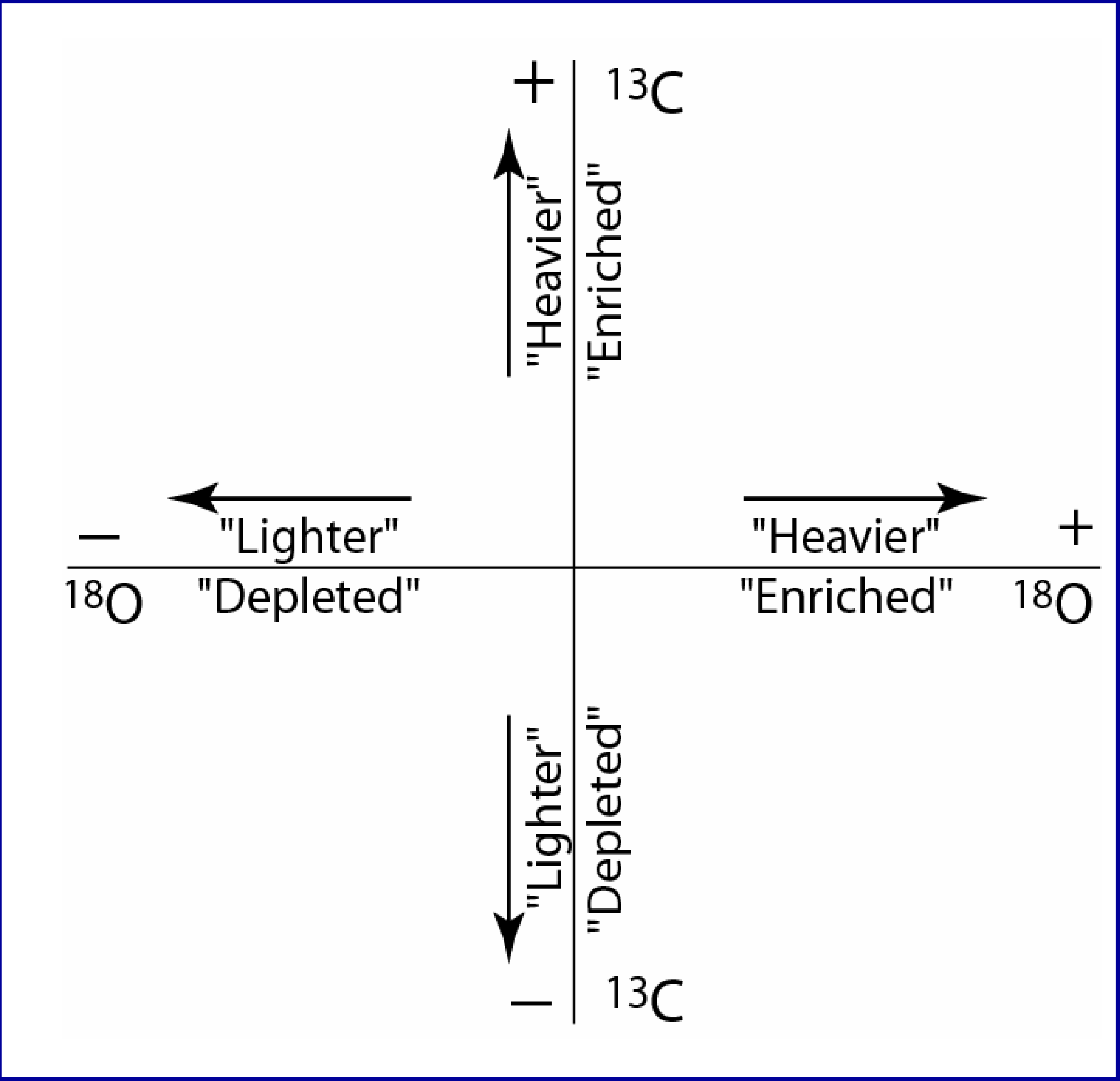


Fluid Inclusion Hoogenization Temperature vs. Salinity
Salinity (wt%)
30.0
25.0
20.0
15.0
10.0
5.0
0.0
0
20
40
60
80
100
120
140
160
180
200
Homogenization Temperature (C)
Kentucky Samples
Ohio Samples
New York Samples

Stable Isotopes

- Stable isotopes of Oxygen include
  - ^{16}O (99.763%)
  - ^{18}O (0.1995%)
  - ^{17}O (0.0375%) (not typically measured)
- Stable isotopes of Carbon include
  - ^{12}C (98.89%)
  - ^{13}C (1.11%)
- These are measured vs a standard (PDB)

$$\delta^{13}C = \frac{[(^{13}C/^{12}C)_{sample} - (^{13}C/^{12}C)_{standard}]}{(^{13}C/^{12}C)_{standard}} \times 1000$$

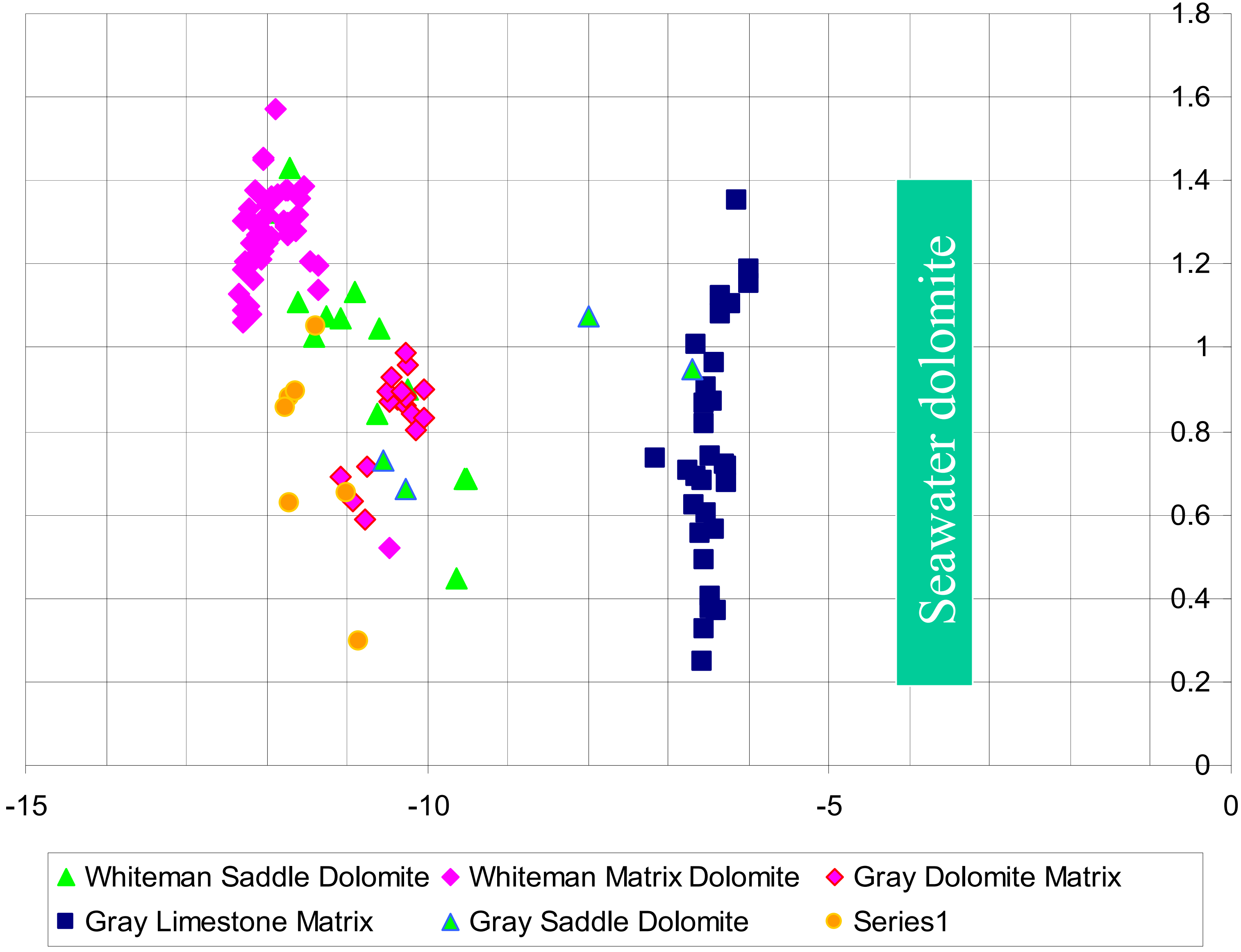


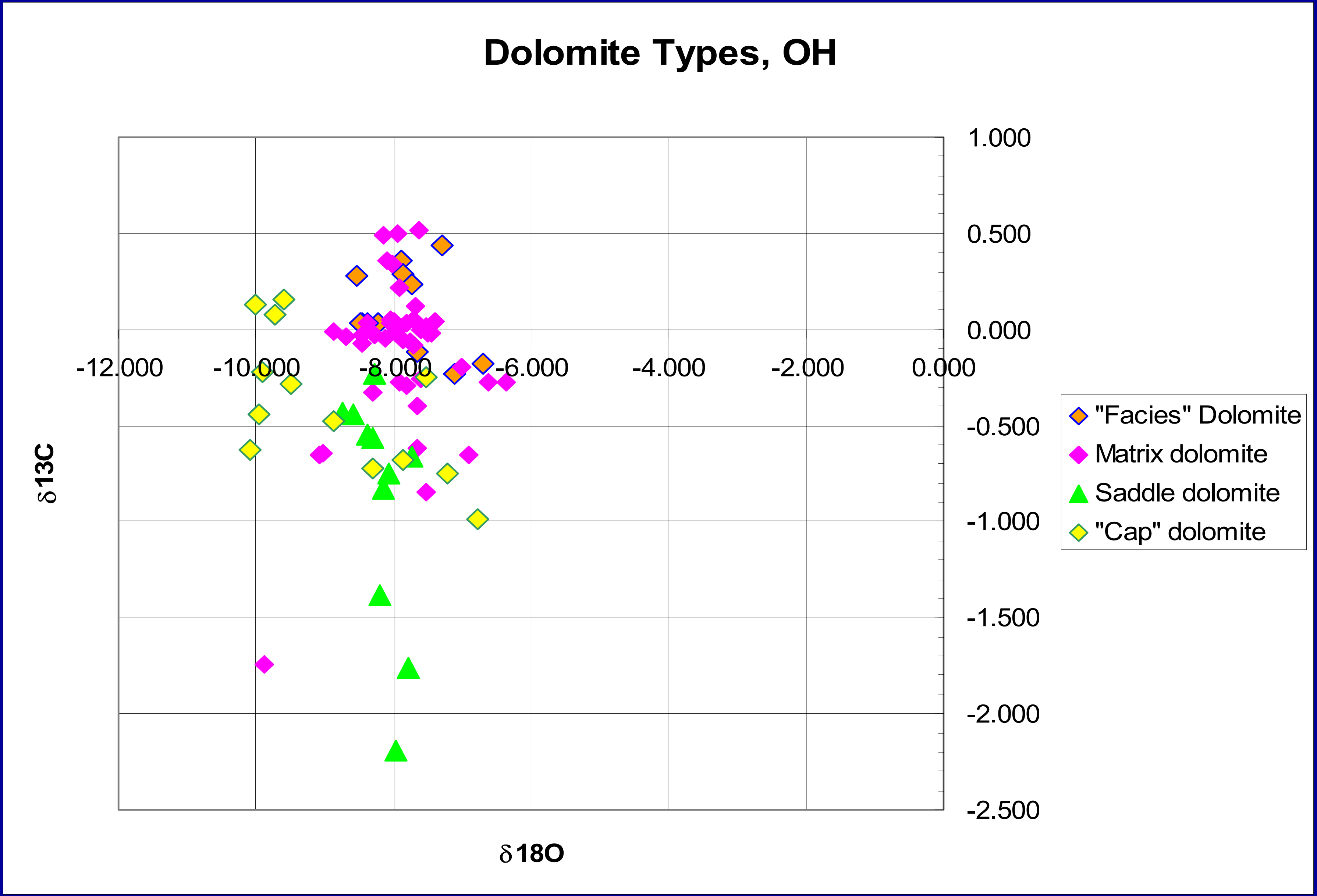
Terms used to describe trends in stable isotope values

Stable isotopes and dolomitization

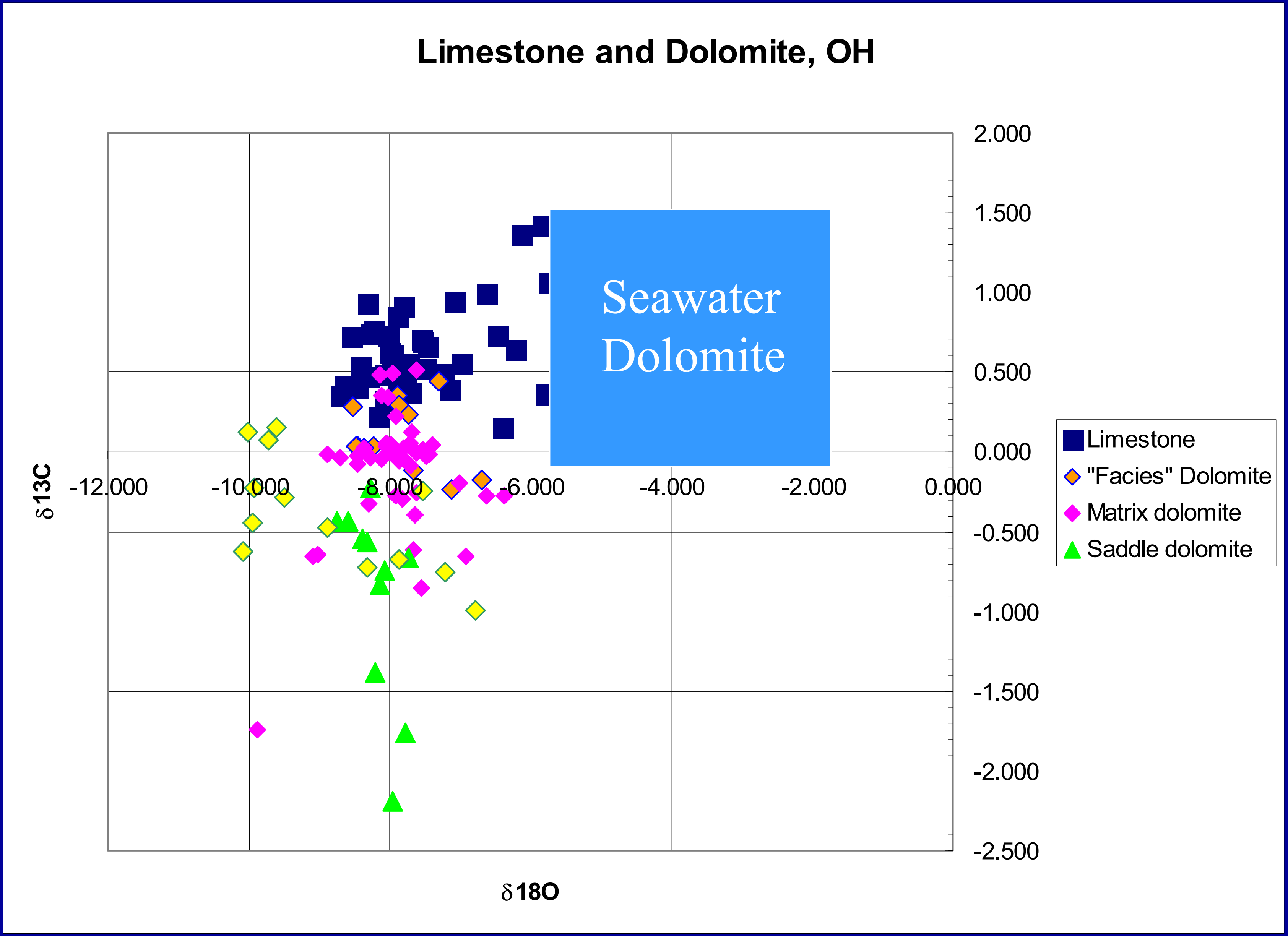
- We use oxygen isotopes to learn about the the dolomitizing fluid and environment
- Increasing temperature of the dolomitizing fluid causes d18O values to be progressively lighter or more negative
- Stable isotopes alone *cannot* be used to determine temperature of crystallization

NY Stable Isotopes

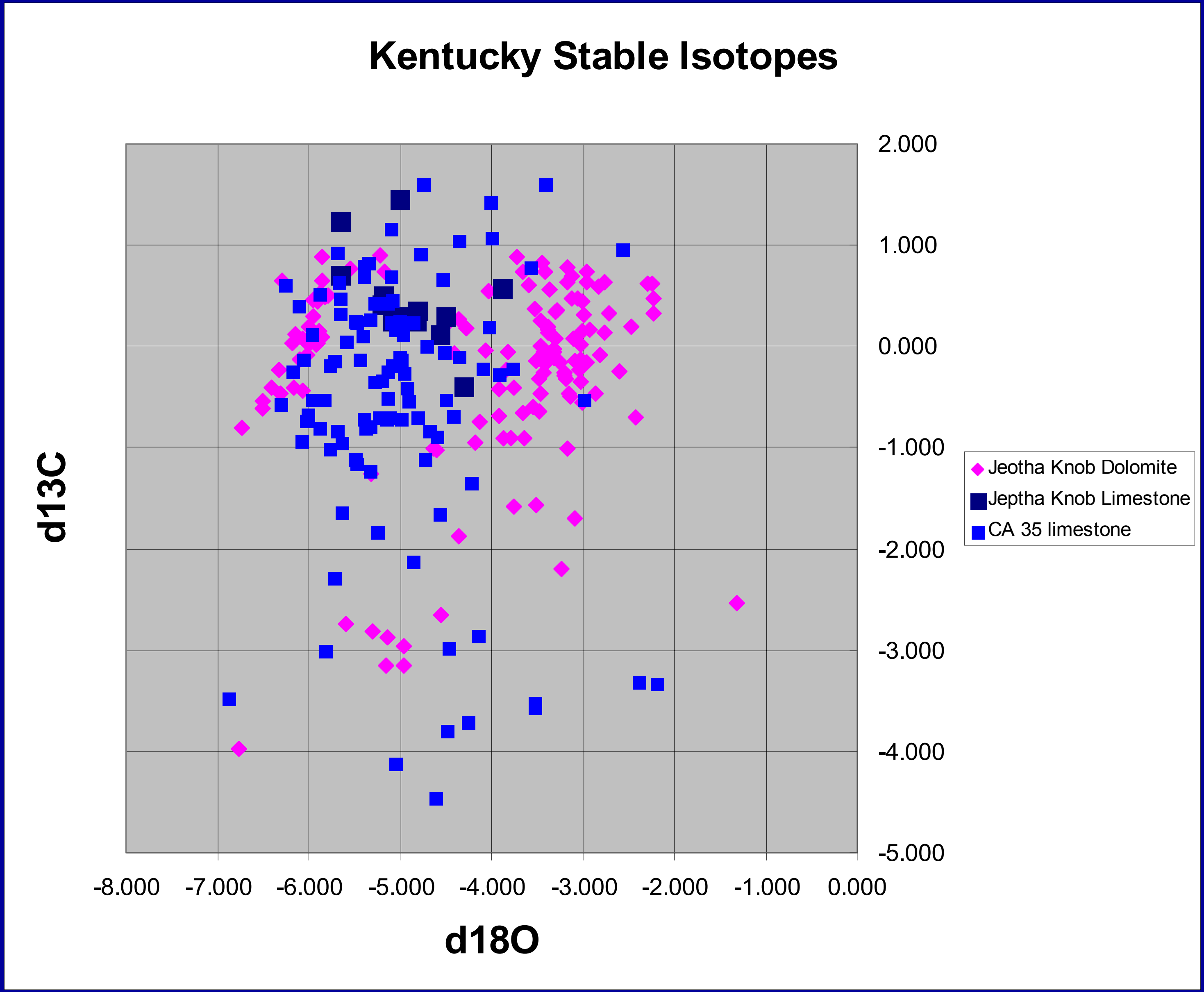




All dolomite types in Ohio have similar values suggesting same origin



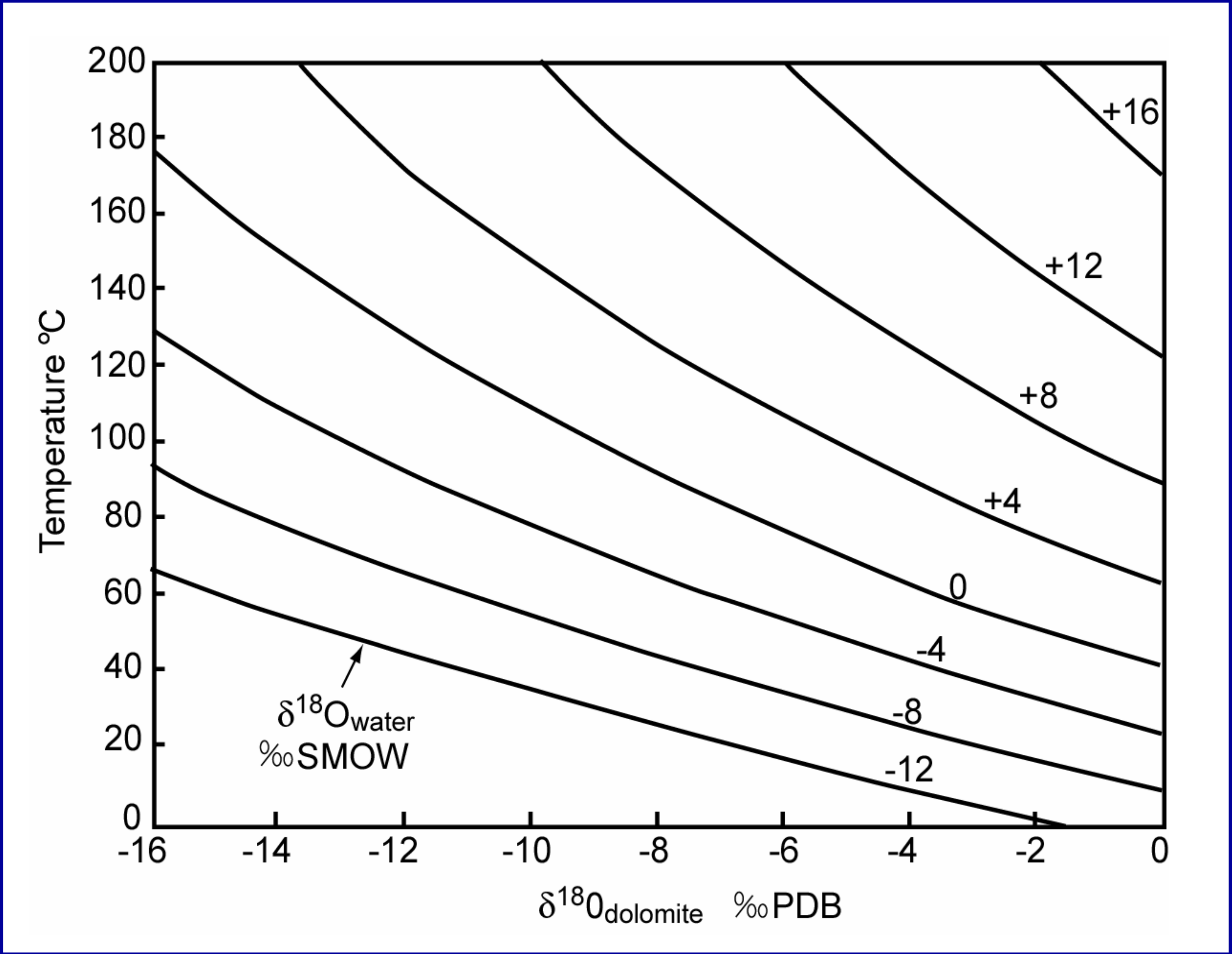
No dolomite plots where one would expect to see early dolomite



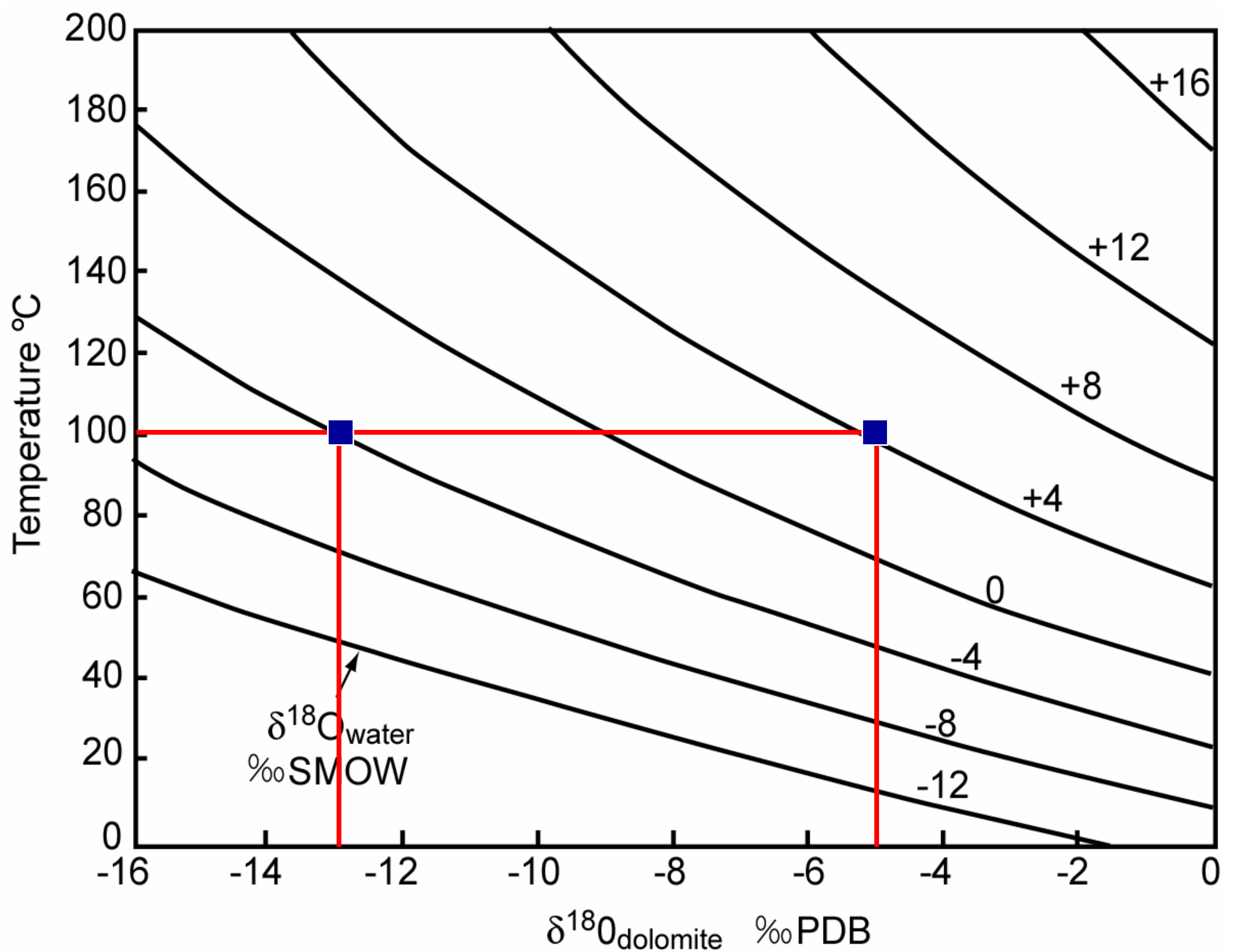
Kentucky dolomites are anomalous in that some dolomites are heavier than the limestones – they plot where "early" dolomite normally would

Problem: Varying Dolomite Values

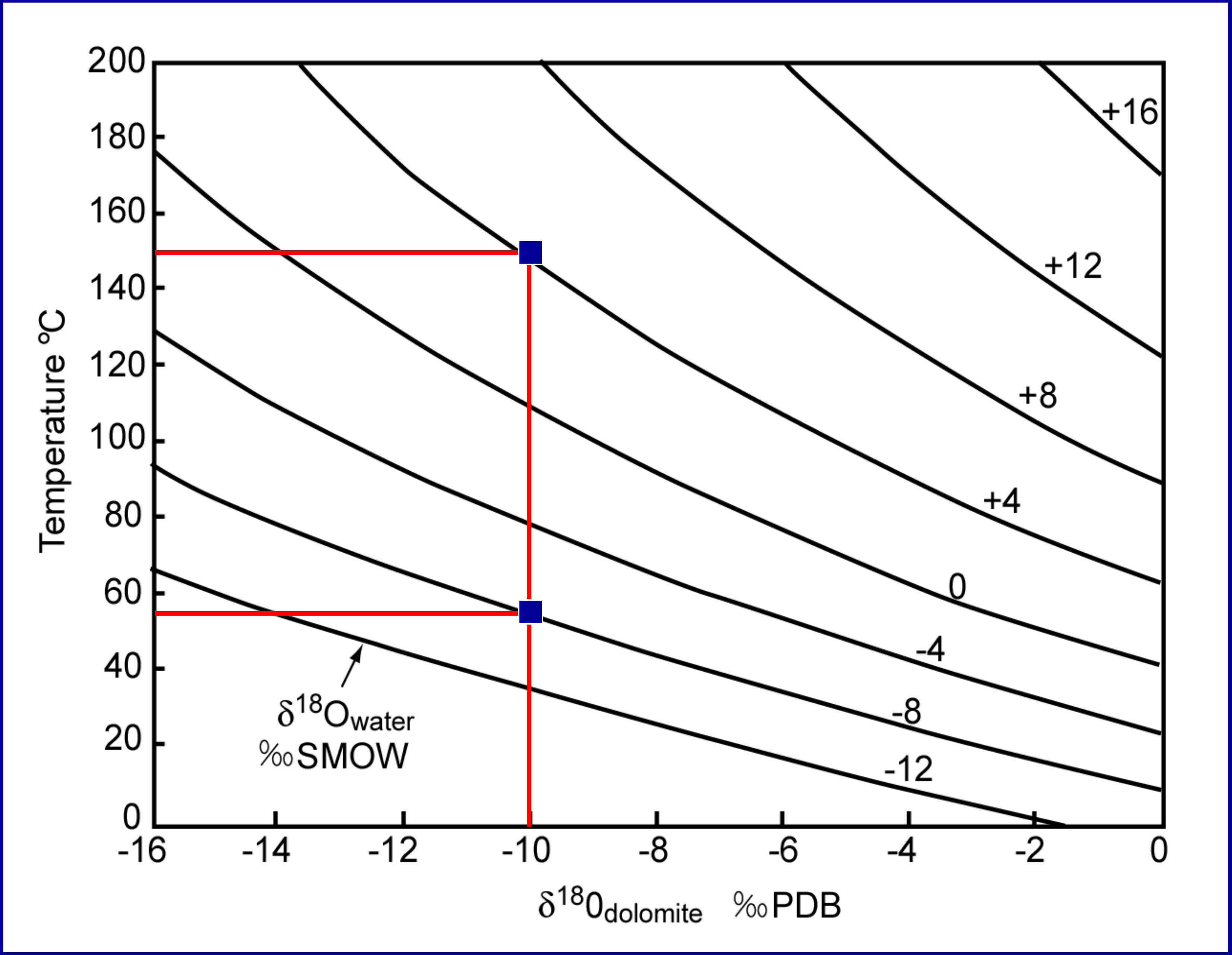
- These dolomites all occur around faults:
- NY $\delta^{18}O$ values range from -9 to -12 ‰
- OH values range from -7 to -9 ‰
- KY values range from –3 to – 6 ‰
- Could they all be hydrothermal? KY values look like classic early reflux dolomite
- Need to learn composition of fluid



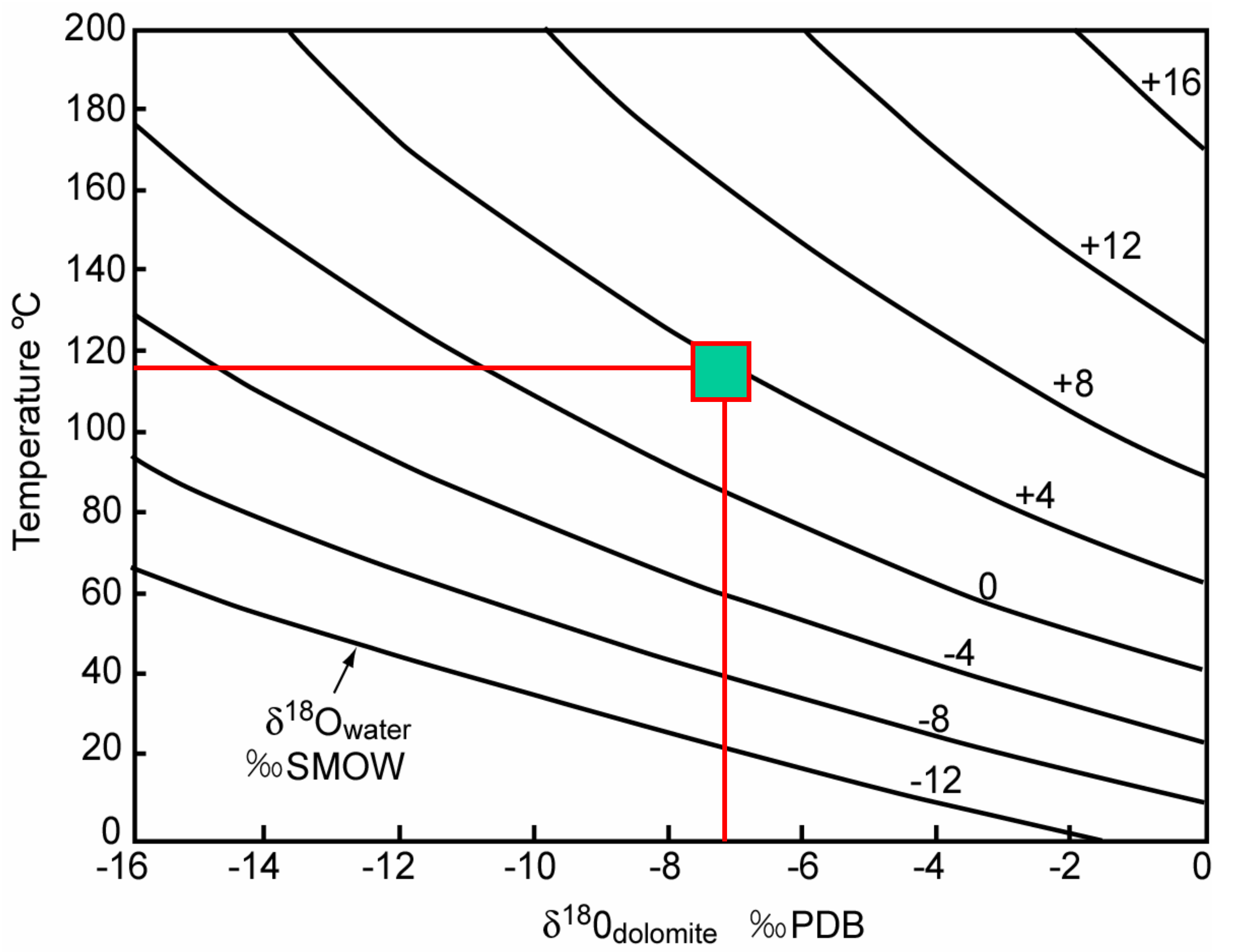
In order to interpret Stable isotopes, first must understand the composition of the fluid



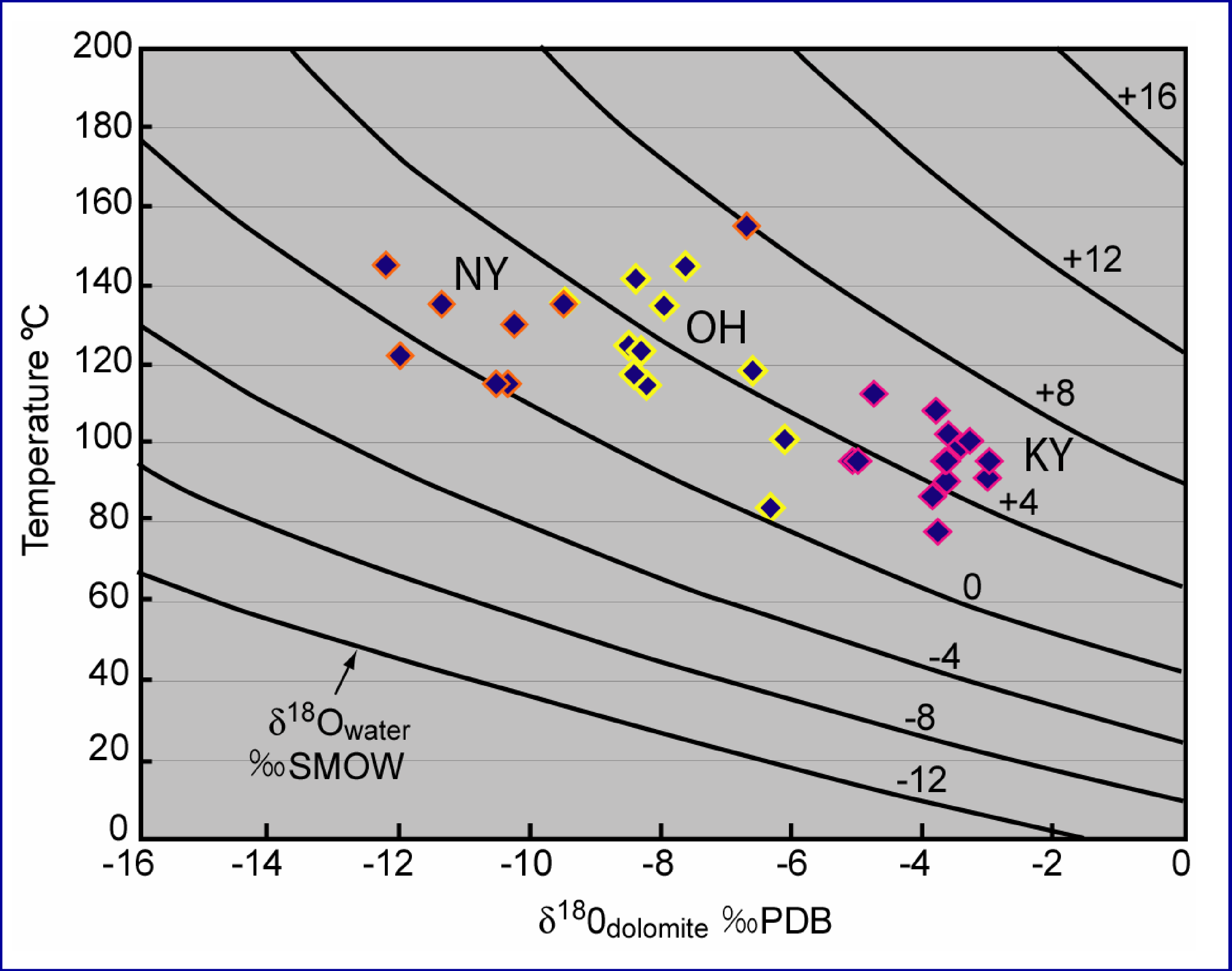
Same temperature (with two different fluid compositions) produces 2 very different stable isotope values



Different temperature (with two different fluid compositions) produces same stable isotope values

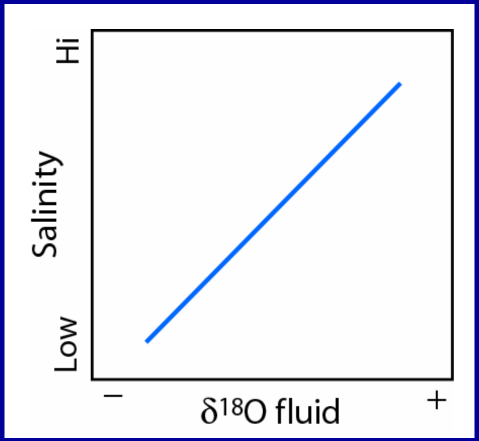


Can determine fluid composition by plotting fluid inclusions temps and stable isotope values for same samples



Fluid in NY was about +2 ‰, fluid in OH and KY was about +4‰

Salinity and $\delta^{18}O$



- Average for NY samples: 14.4 wt%
- Average for KY samples: 17.1 wt%
- Average for OH samples: 17.8 wt%
- The KY and OH samples formed from a more saline fluid that was also apparently heavier w.r.t. ^{18}O
- This makes sense: brines form due to evaporation – only ^{16}O evaporates so more saline brines should be enriched in ^{18}O
- NY brines either less evaporated or mixed with minor meteoric component in subsurface

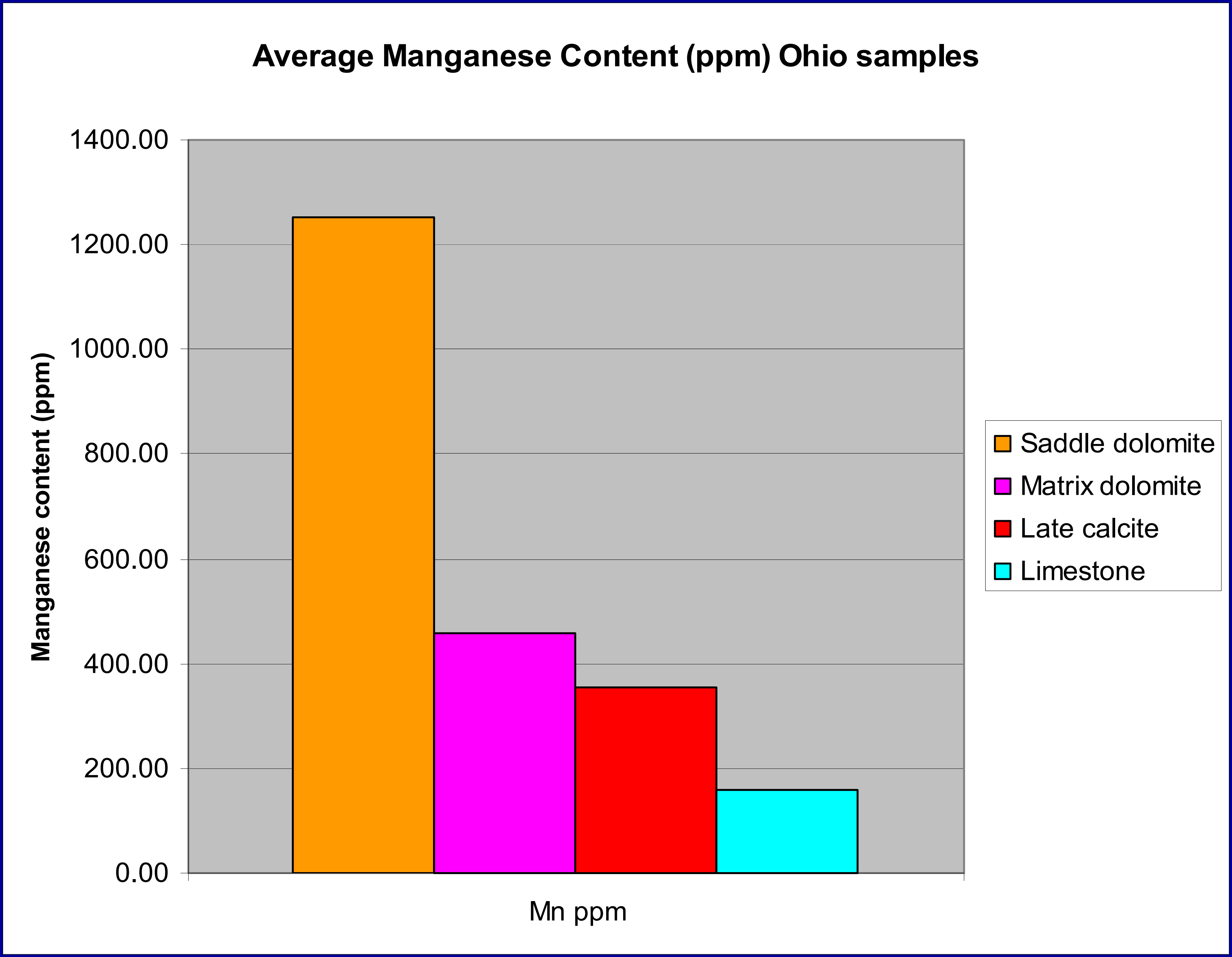
Trace Element Study

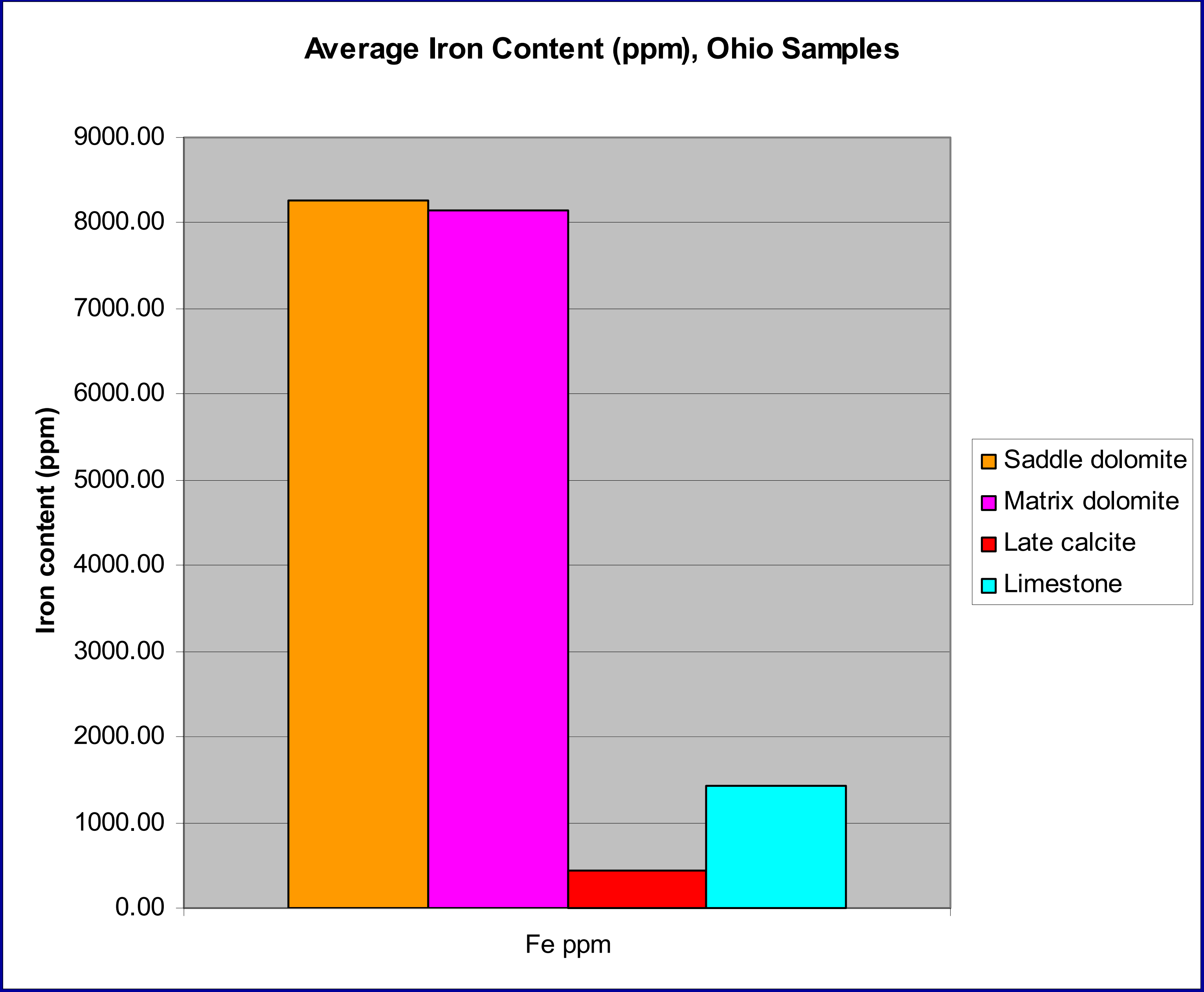
- Analysis of trace elements in dolomites is a good way to learn more about their origin
- Iron (Fe) and Manganese (Mn) are easily oxidized and therefore are virtually absent from seawater – Dolomites formed from seawater have very low Fe and Mn contents
- Fe and Mn are much more common in subsurface brines – Dolomites formed in subsurface therefore have much higher Fe and Mn contents

Trace Elements

Element	Seawater	Oil Field Brine
Ca	411 ppm	1,000-20,000
Fe	.002	.01-500
Mn	.0002	.1-100
Fe/Ca	10^{-6}	10^{-3}
Mn/Ca	10^{-7}	10^{-4} or 10^{-3}

From Allan and Wiggins, 1993


Average Manganese Content (ppm) Ohio samples
1400.00
1200.00
1000.00
800.00
600.00
400.00
200.00
0.00
Manganese content (ppm)
Mn ppm
Saddle dolomite
Matrix dolomite
Late calcite
Limestone

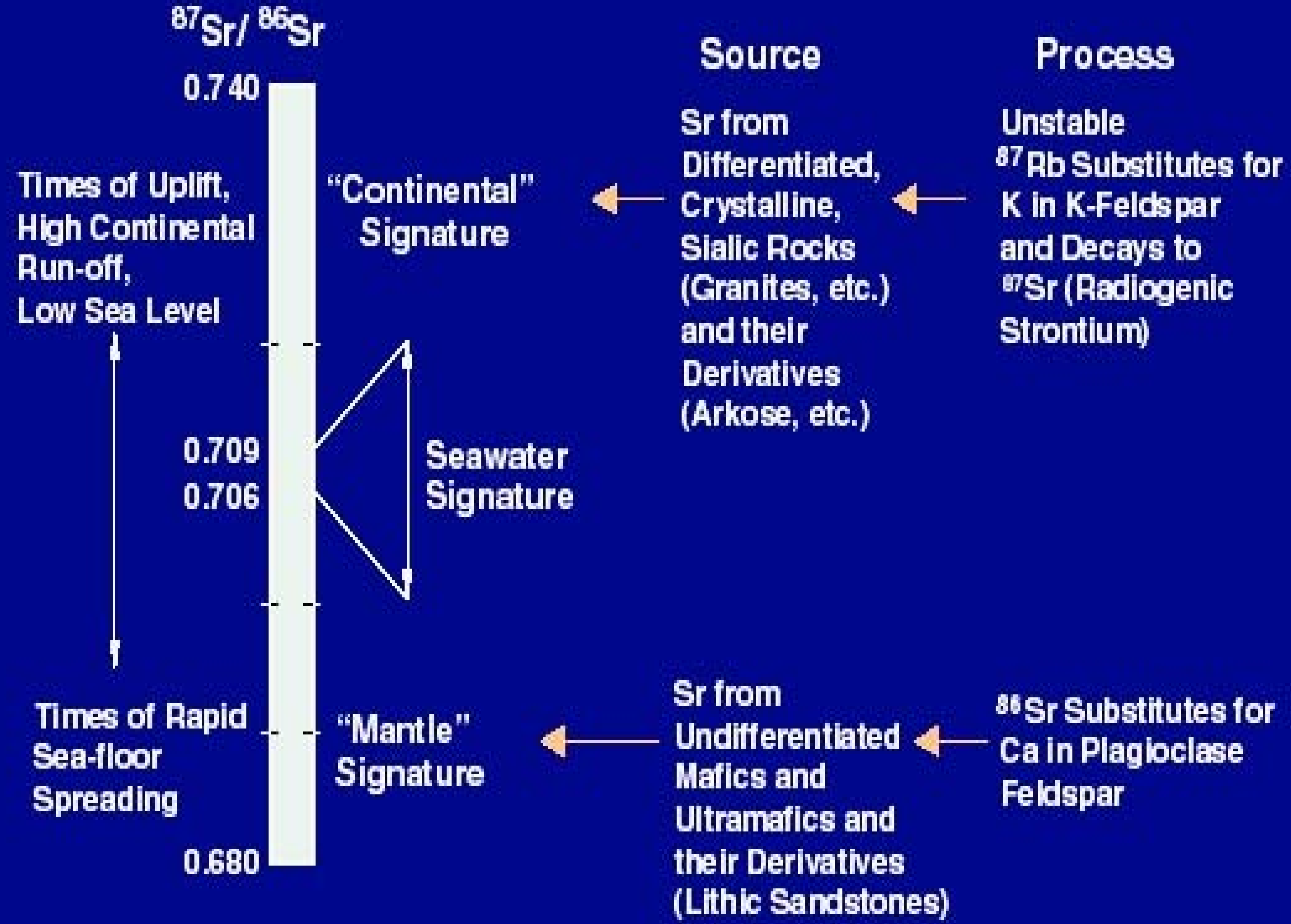


Average Iron Content (ppm), Ohio Samples
Iron content (ppm)
9000.00
8000.00
7000.00
6000.00
5000.00
4000.00
3000.00
2000.00
1000.00
0.00
Fe ppm
Saddle dolomite
Matrix dolomite
Late calcite
Limestone

Trace Elements

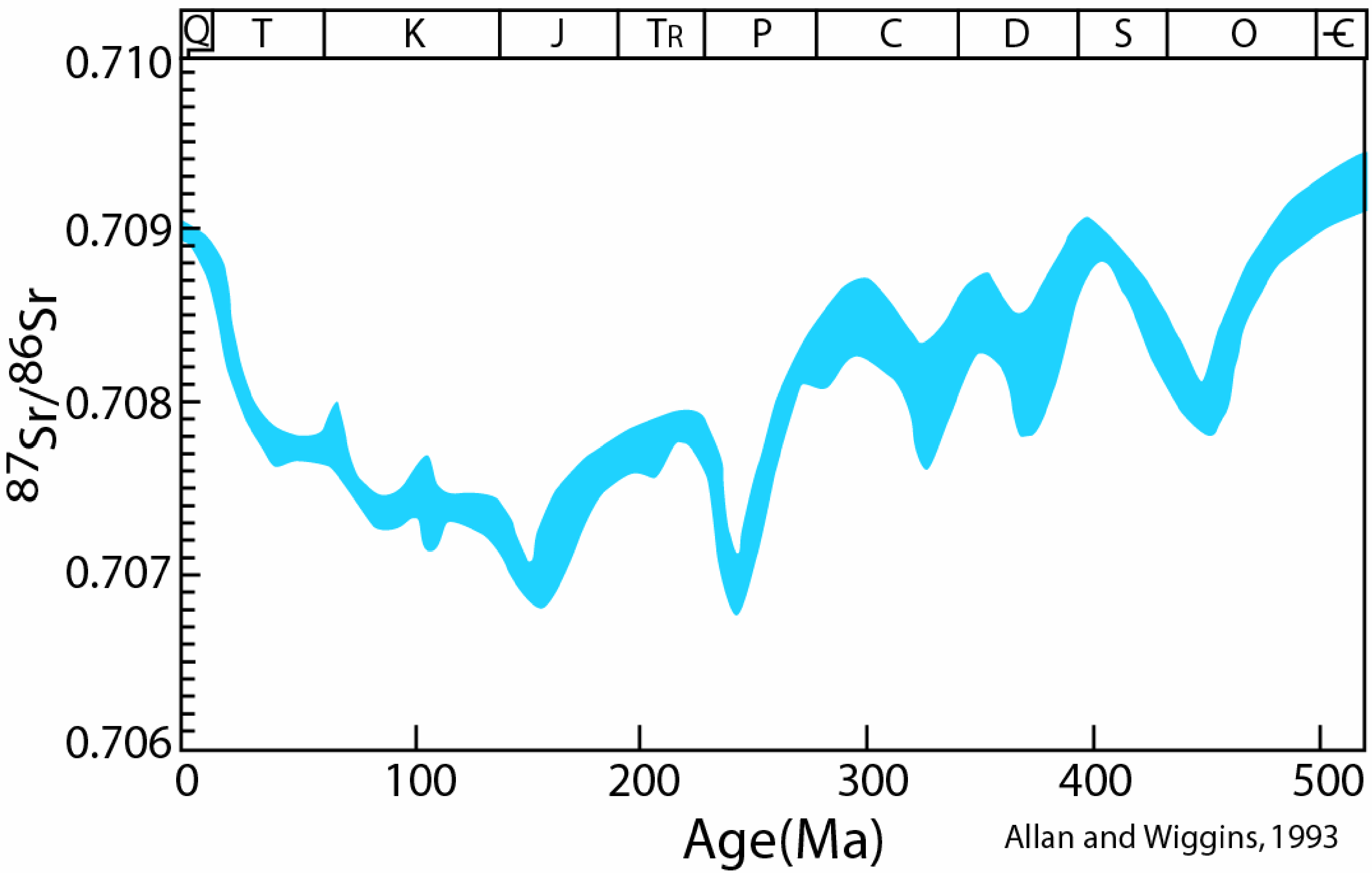
- NY dolomites have similar concentrations of Mn (~1800 ppm) and Fe (~9000 ppm)
- Fe and Mn concentrations support a burial origin for the dolomites
- Seawater dolomites should have little or no Fe or Mn

Sources of ^{87}Sr and ^{86}Sr and Paths Which Influence Sr Isotopic Composition of Paleo-Oceans

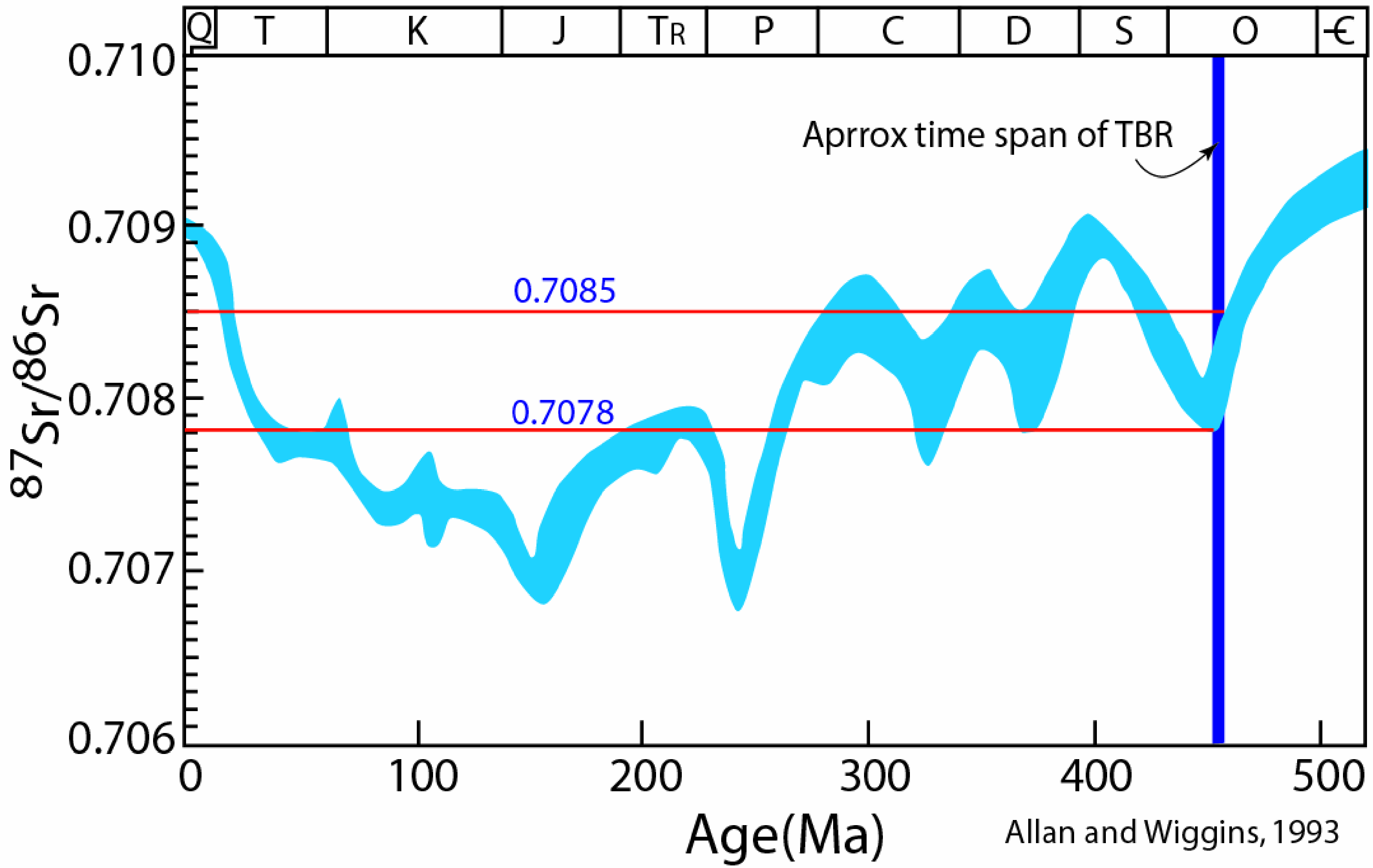


Allan and Wiggins (1993)

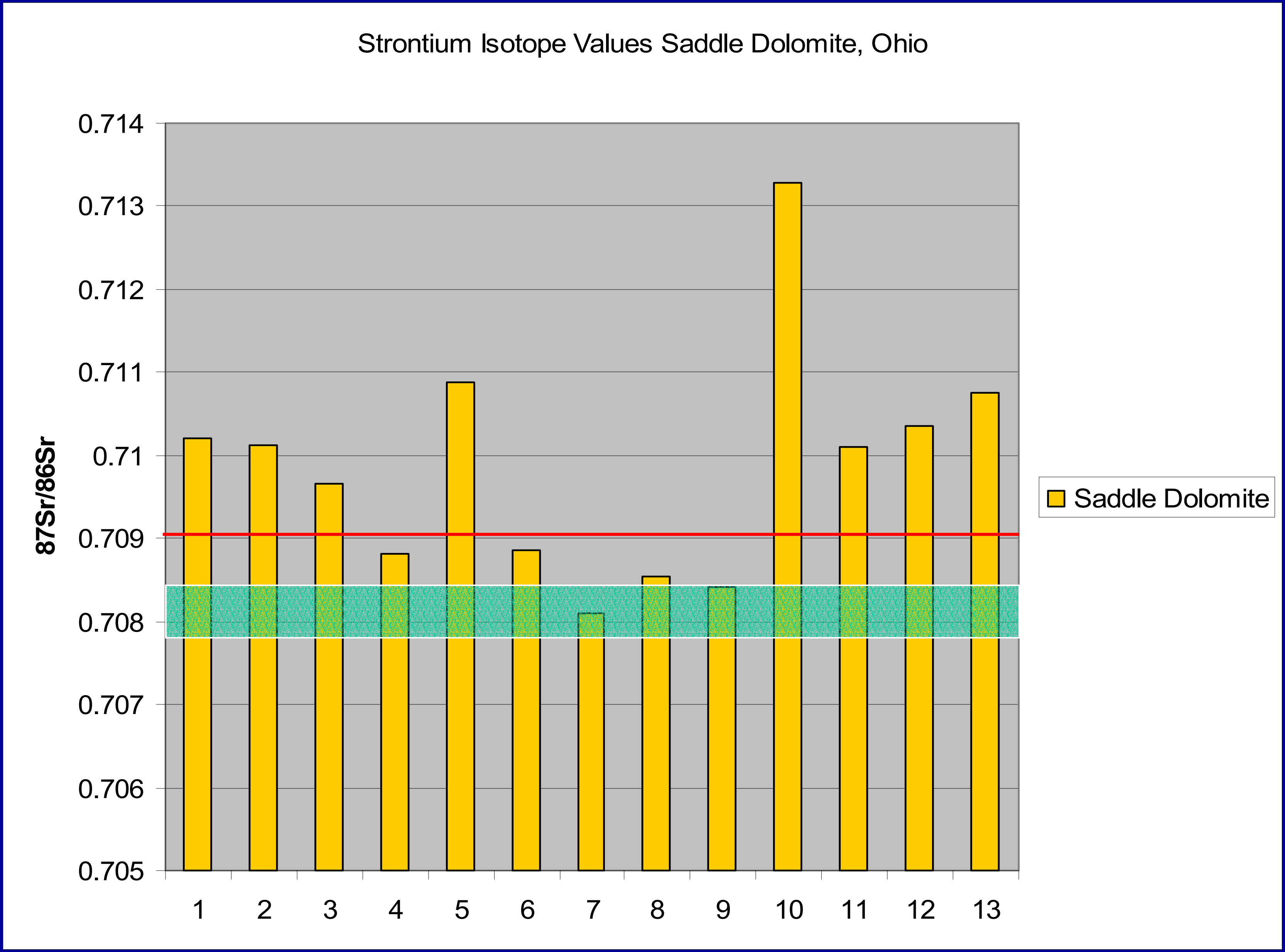
Strontium Isotope Composition of Seawater Through Time



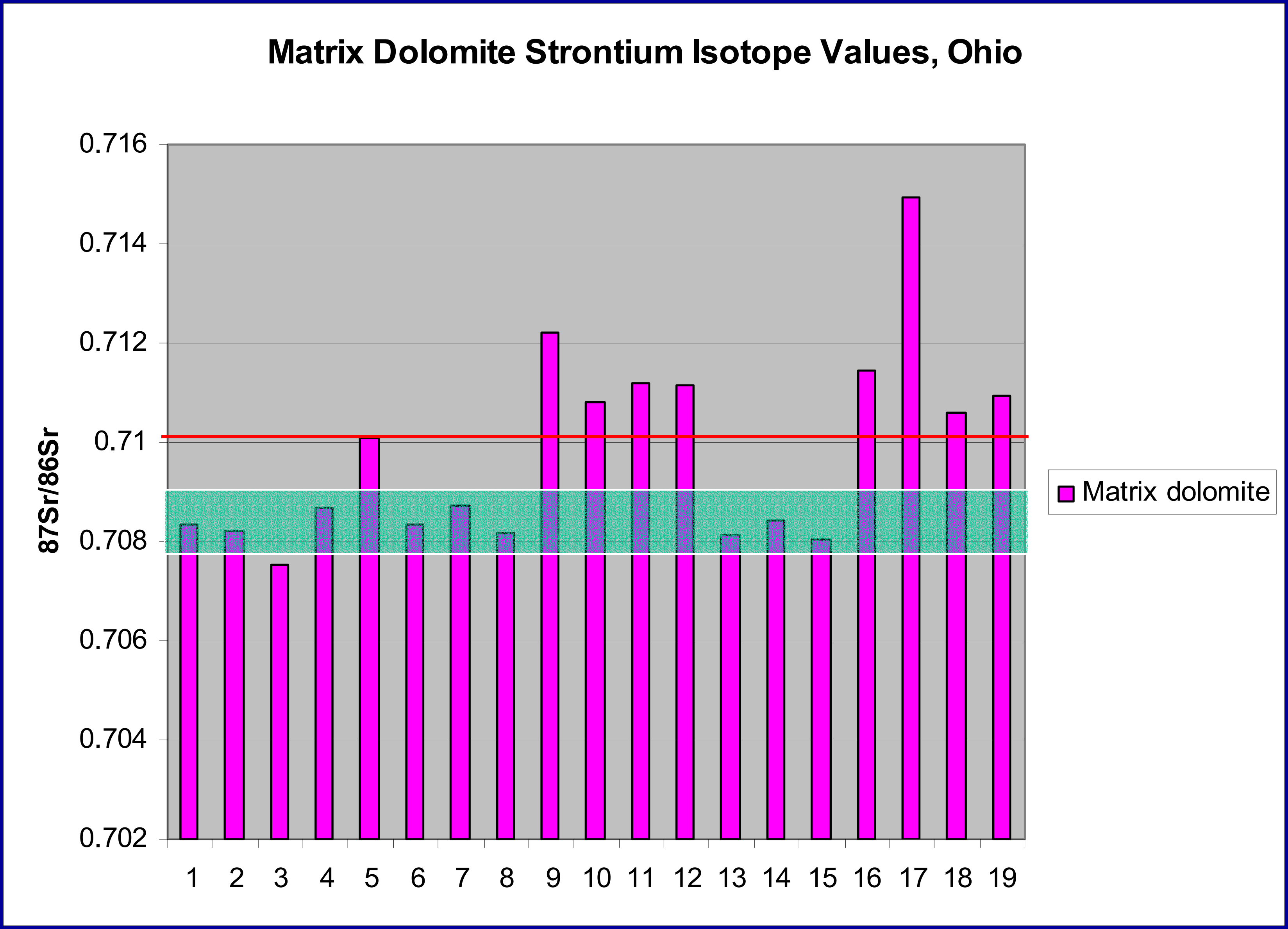
Strontium Isotope Composition of Seawater Through Time



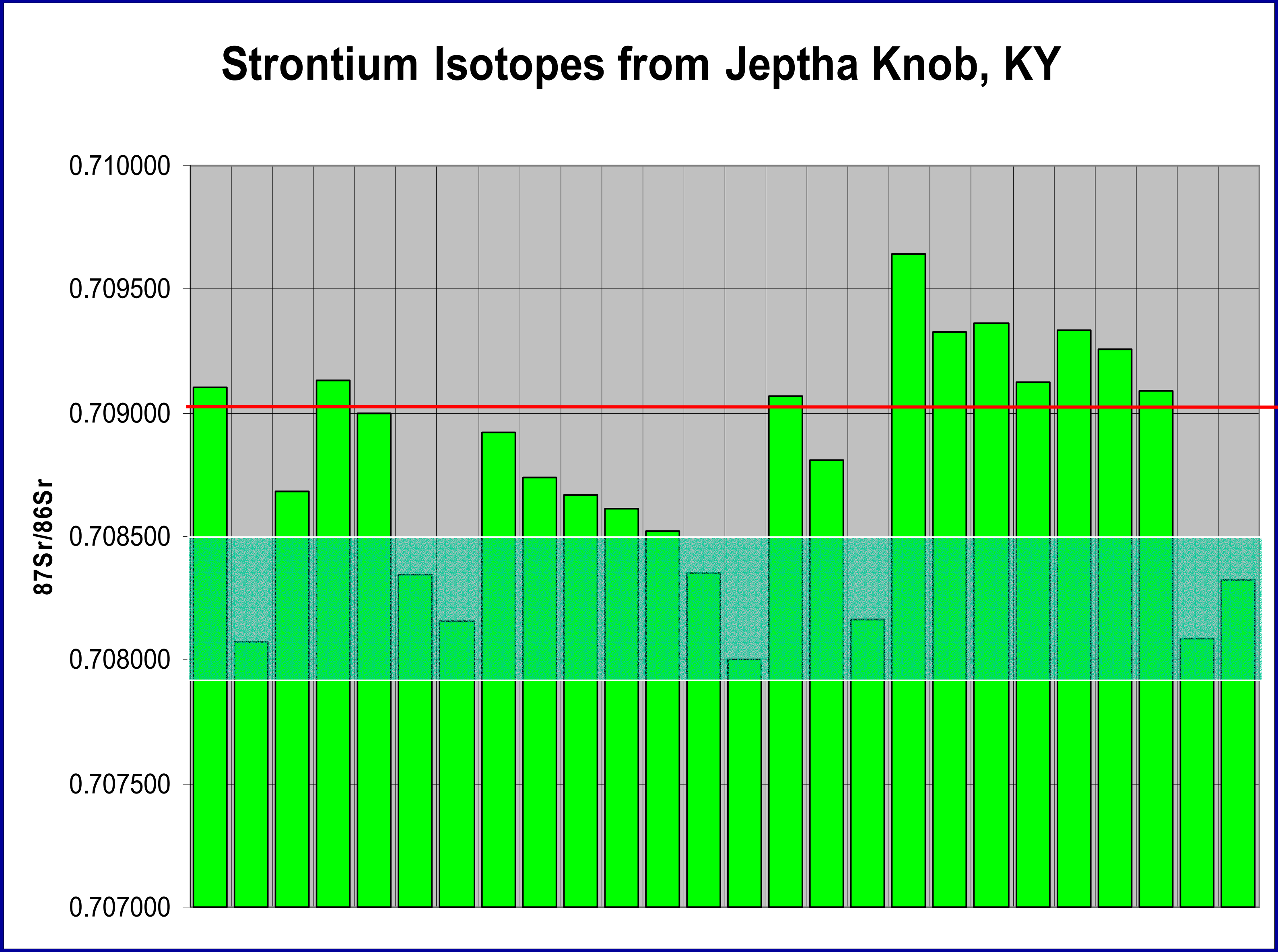
Allan and Wiggins, 1993



Almost all samples of saddle dolomite are radiogenic relative to Ordovician seawater (green shading) and most exceed max for Paleozoic



Some matrix dolomite is radiogenic, others have seawater values (inherited from precursor limestone?)



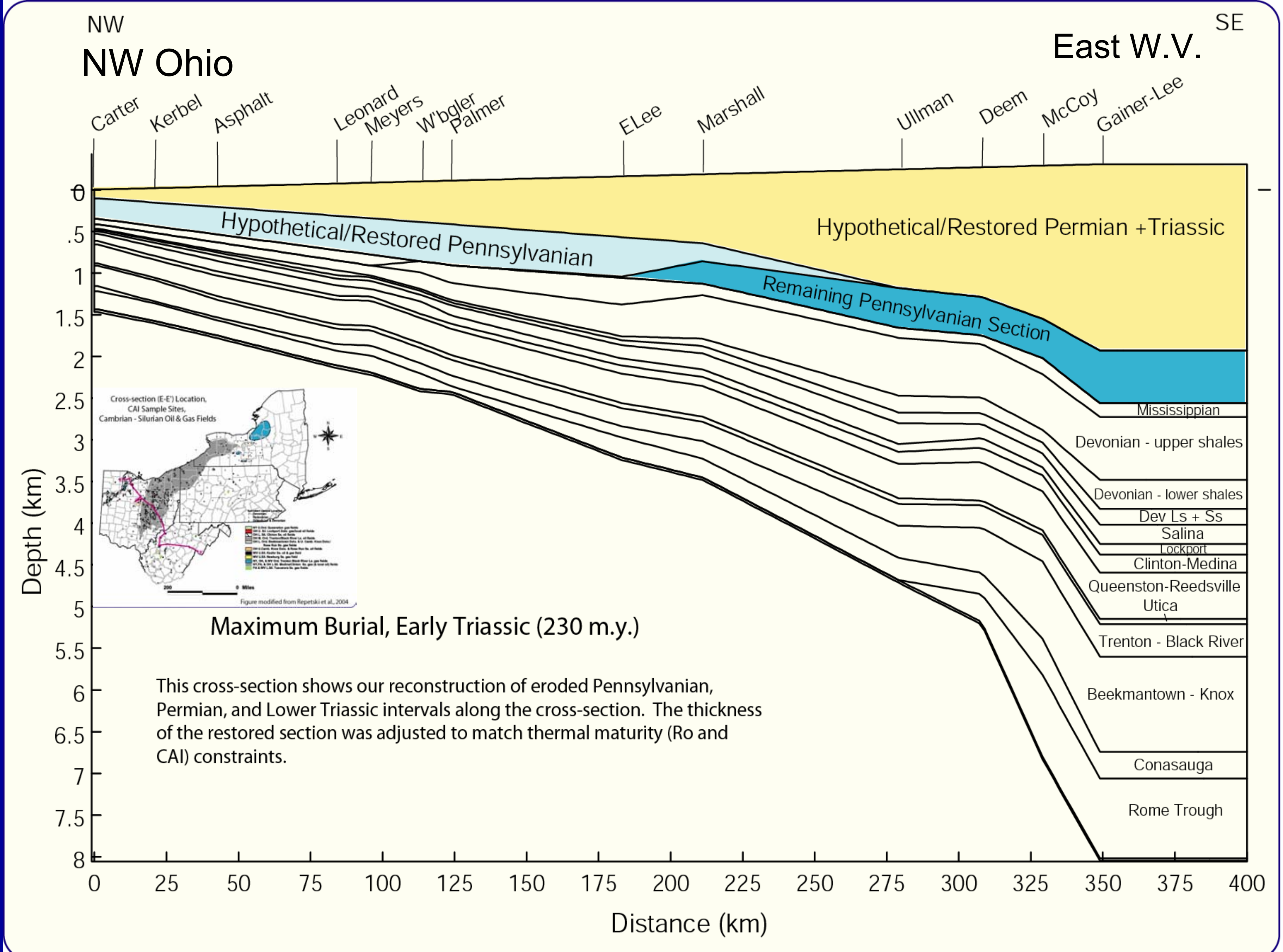
Similar distribution to matrix dolomite in OH, most are radiogenic

Summary

- Fluid inclusions, stable isotopes, strontium isotopes and trace elements all support a hot, subsurface origin for all the dolomite in the TBR
- The fluid that made the dolomite was hot, saline, +2 to +4 d18O, Fe- and Mn-rich and passed through basement rocks or immature siliciclastics prior to making the dolomite
- The link to faults strongly suggests a fault-related hydrothermal origin for the dolomites

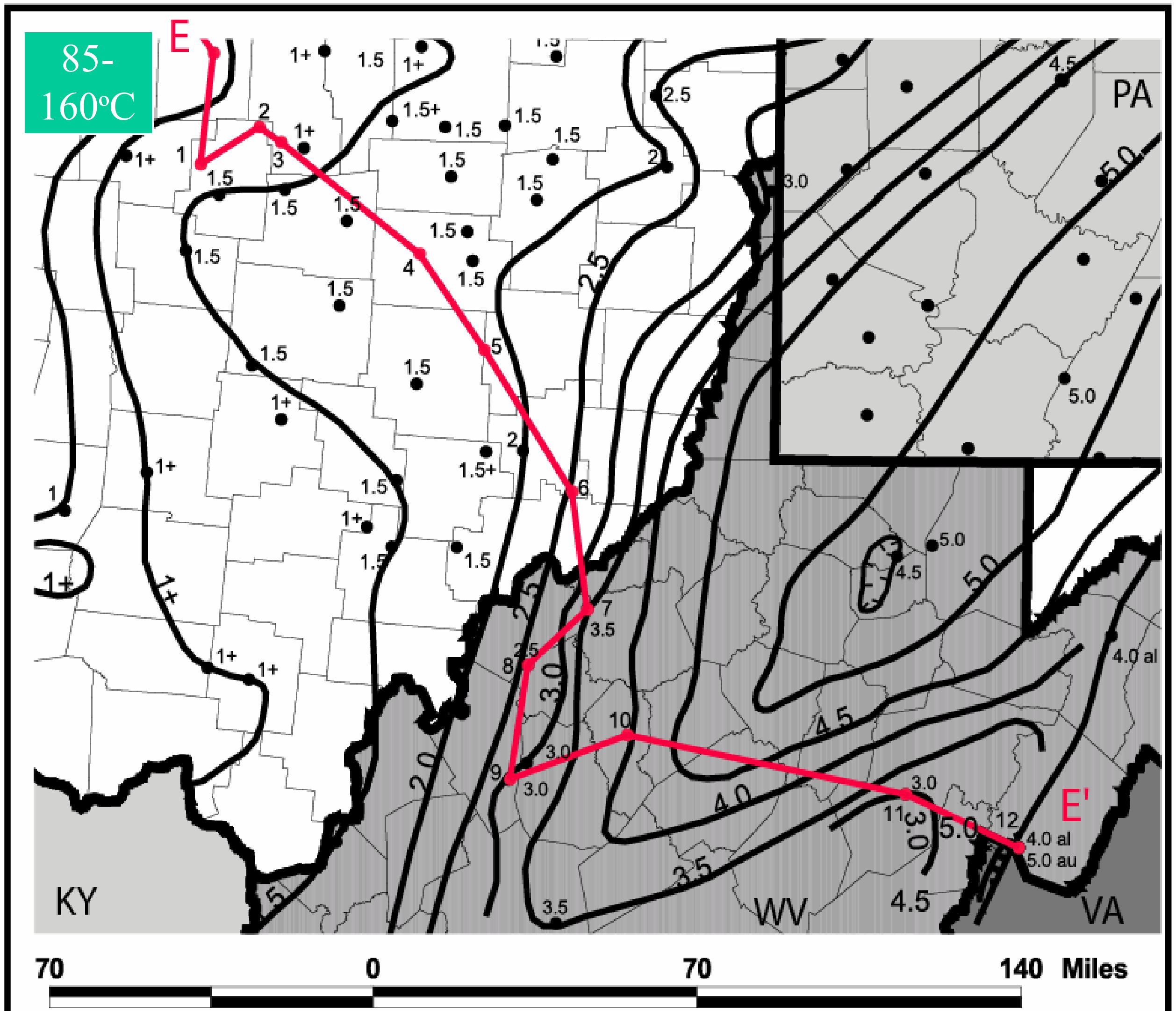
Are the TBR Dolomites Unequivocally Hydrothermal?

- A good way to demonstrate an unequivocally hydrothermal origin for dolomite is to show that the dolomites formed at a higher temperature than the ambient temperature ever was or was at the time of dolomitization
- This can be done using fluid inclusions and burial history plots



From Rowan et al., 2004

CAI Sample Sites in Ordovician Rocks



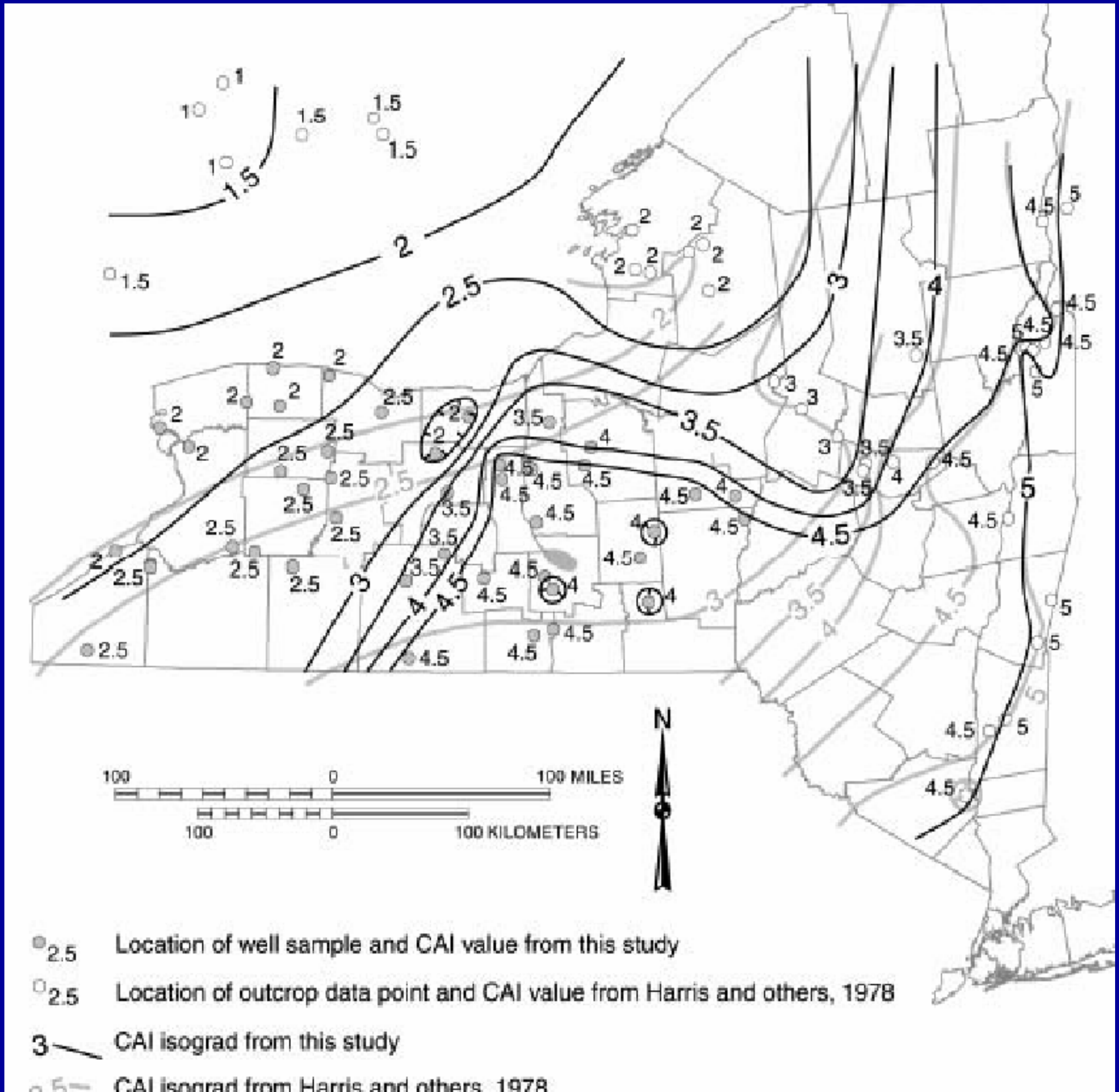
Repetski et al. (2002, in review, and in prep.)

CAI Values in NW Ohio are 1-1.5 which means maximum burial depth of 1800-2200 ft (600-750m), maximum burial temp. of about 40ºC

Primary dolomite fluid inclusion homogenization temps are 85-160ºC

Dolomite is *unequivocally* hydrothermal in origin

Rowan et al., 2004



Weary et al., 1995

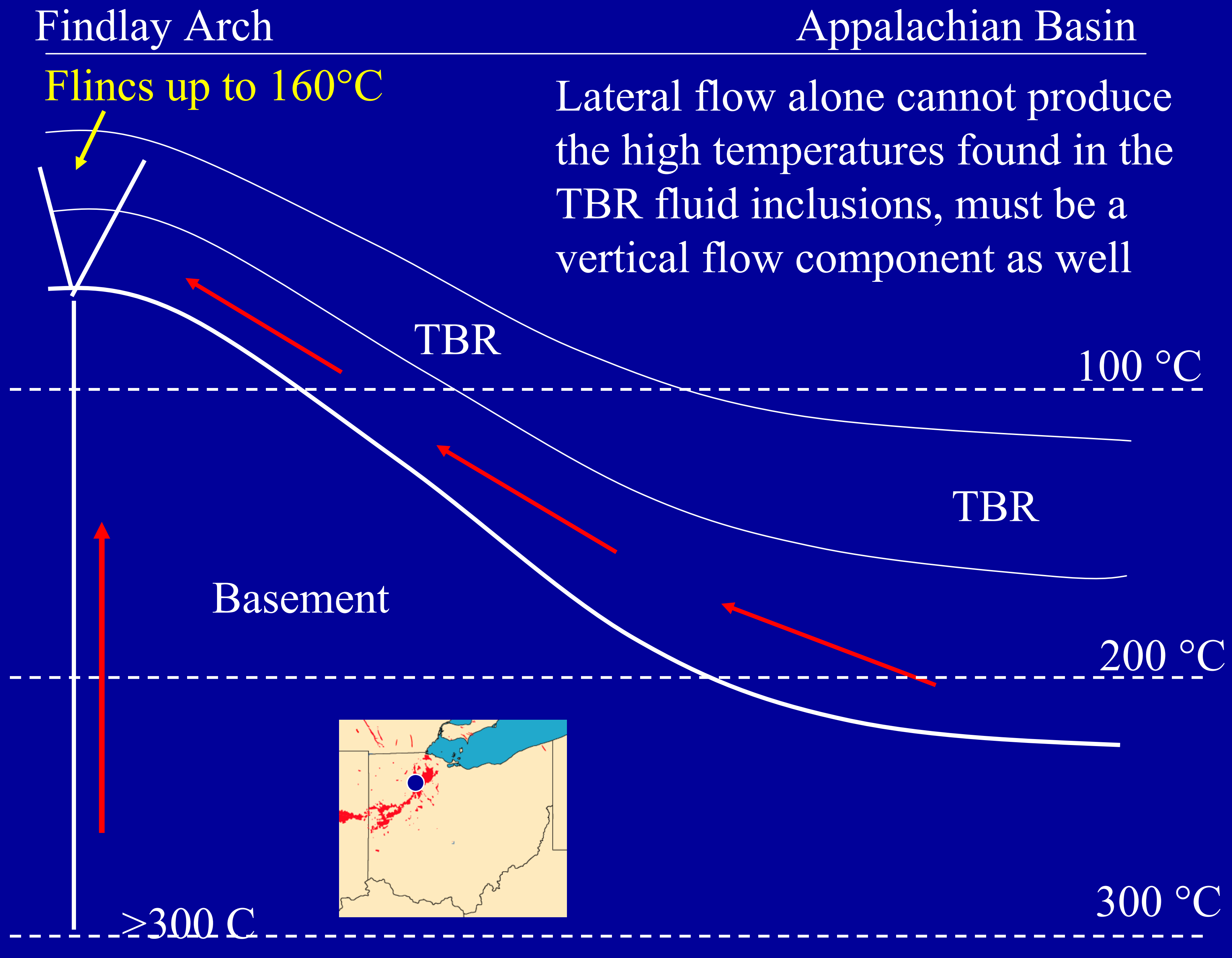
NY Fields are in area with very high CAI values that suggest burial to 15,000-25,000 feet and 150-300C

Homogenization temperatures for primary fluid inclusions are 110-170C

The origin of the NY dolomite is therefore equivocal (but almost certainly hydrothermal based on other attributes)

Location	Dolomite Fluid Inclusion Homogenization Temp. Range	Current Burial Depth (and temp.)	Estimated Maximum Burial Depth (based on CAI)	Estimated Maximum Burial Temp.	Unequivocally Hydrothermal? (Homogenization Temp > than maximum burial temp?)
Steuben Co., NY	Primary: 110-160°C Secondary: >200°C	7800 ft (63°C)	15,000-25,000 (Utica CAI 4.5)	150-300°C	**NO**
Chemung Co., NY	Primary: 120-160°C Secondary: >180°C	9530 ft (75°C)	15,000-25,000 (Utica CAI values 4.5)	150-300°C (CAI-4.5 Weary et al., 1995)	**NO**
Bowling Green Fault Zone, OH	Primary: 85-160°C Secondary: Oil bearing	1100-1500 ft (30°C)	1800-2200 ft (Utica CAI values 1-1.5)	40°C (CAI values 1-1.5)	**YES**
Albion Scipio (Allan and Wiggins, 1993)	Primary: 110-160°C	3500-4500 feet (45-55°C)	(Utica CAI values 1.5-2)	70-80°C	**YES**

CAI values from Weary et al., 1995; Rowan et al., 2004; Repetski et al., 2004



Findlay Arch
Appalachian Basin
Flincs up to 160°C
Lateral flow alone cannot produce the high temperatures found in the TBR fluid inclusions, must be a vertical flow component as well
TBR
100 °C
TBR
Basement
200 °C
300 °C
>300 C

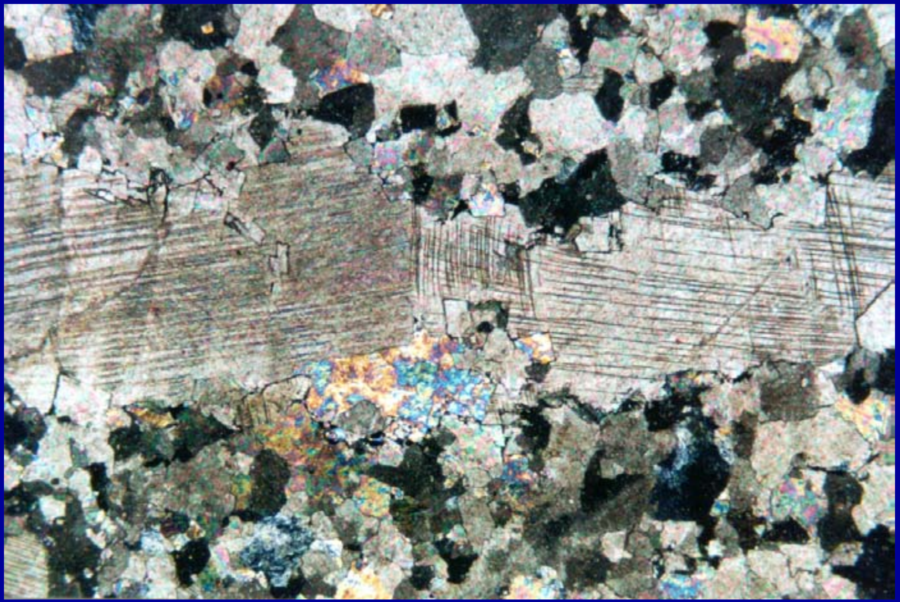
Implications of Fluid Inclusion data

- The high homogenization temperatures but low burial depths through time support an unequivocal hydrothermal origin for the KY, OH and MI dolomites
- The New York dolomites resemble the dolomites from Ohio and Michigan in every way and are also hydrothermal in origin even though they were subsequently buried to a higher temperature than is recorded in the fluid inclusions
- There is likely to have been a significant component of vertical fluid flow up faults

Hot Dolomitization Associated with Many Fault Types

- Negative Flower Structures formed over strike-slip faults– NY, ON, MI, elsewhere– Most fields occur in this setting – vuggy fractured matrix and saddle dolomite
- Normal faults – NE-SW trending faults mainly down to SE – such as Seebree Trough margin bounding fault, OH – matrix dolomitization, some saddle in matrix
- Positive Flower Structure – Jeptha Knob – this is controversial, but it appears that dolomitization and porosity occurs around positive flower structure in KY- matrix dolomitization, no obvious saddle

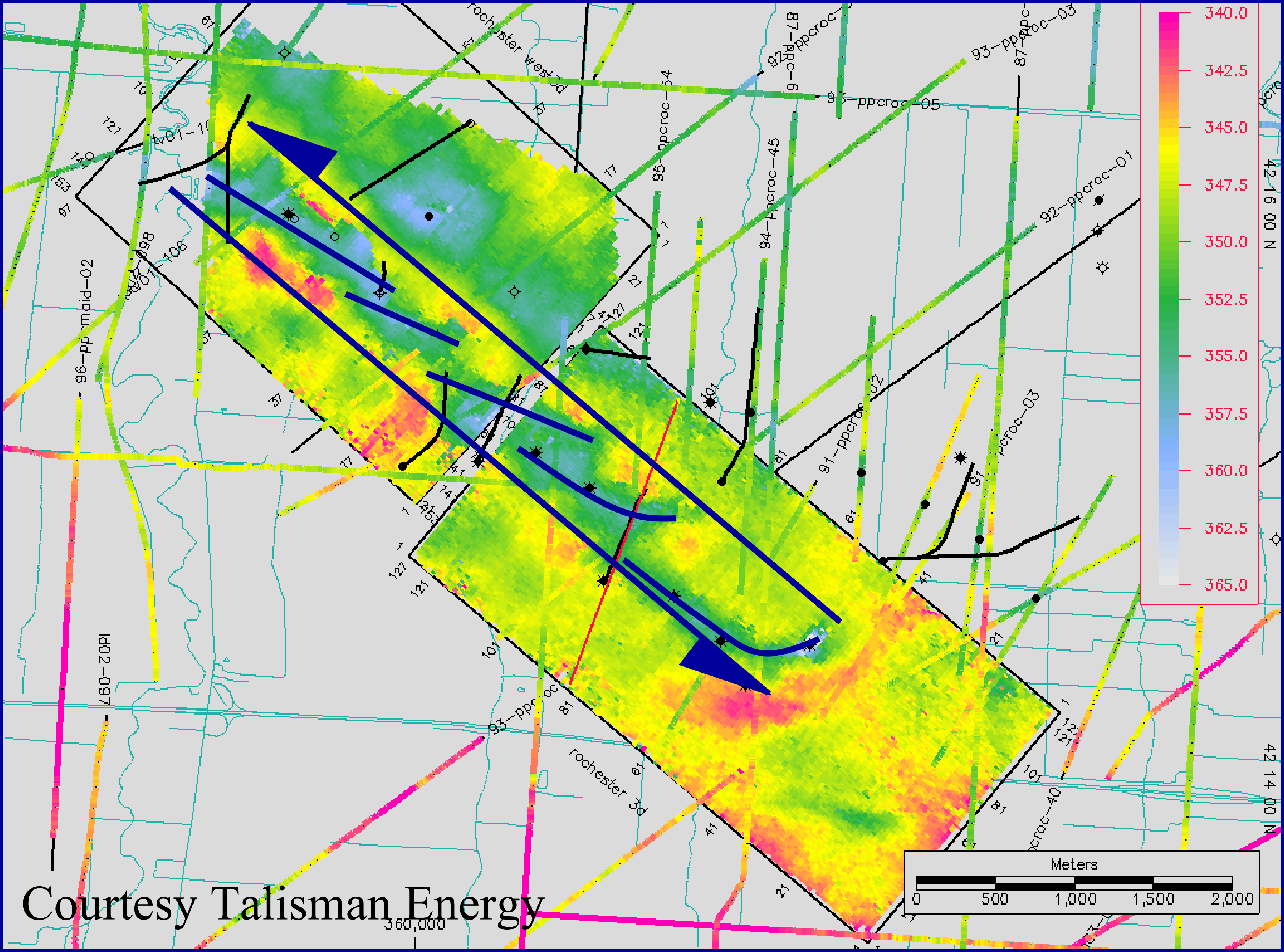
2.5 cm



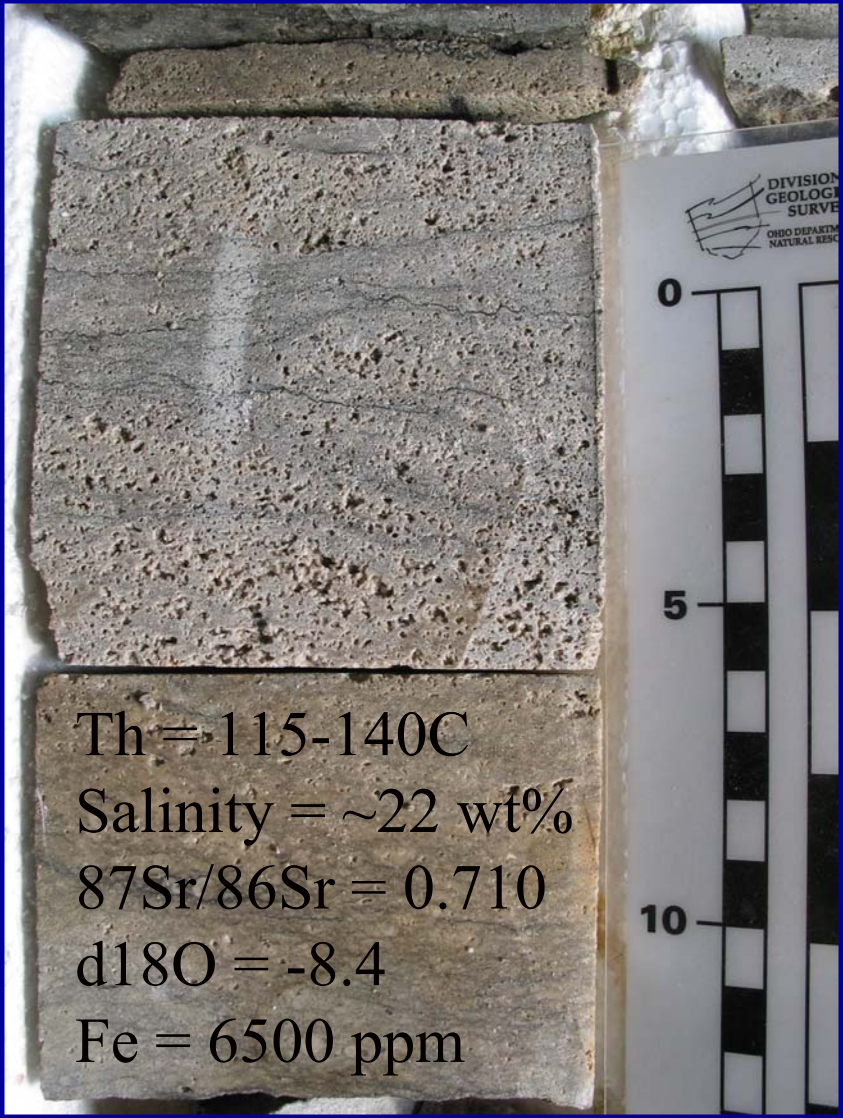
0.5mm

White saddle dolomite fills vugs and fractures and non-planar gray matrix dolomite replaces limestone

>95% of dolomite in BR of NY is gray matrix dolomite

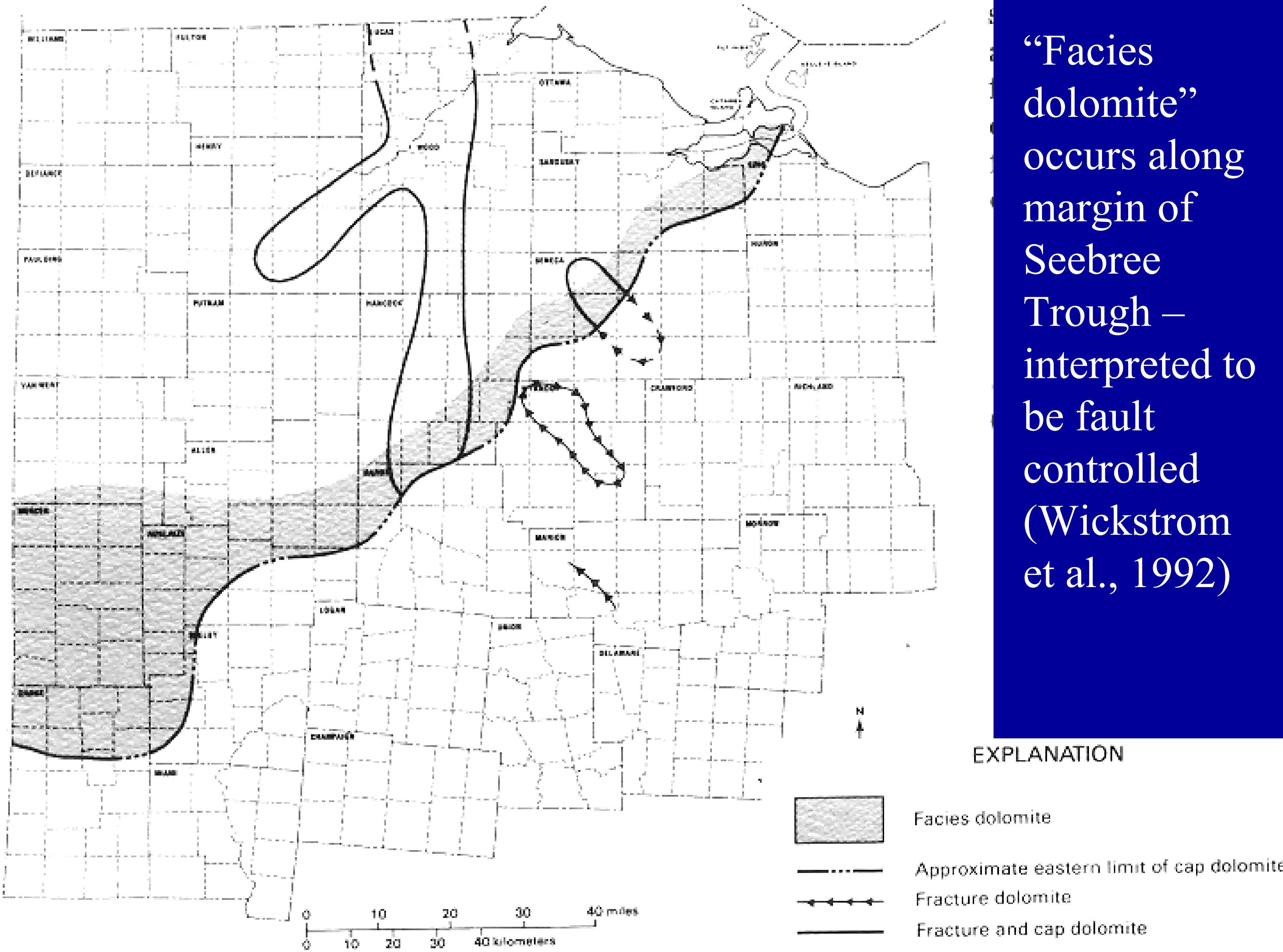


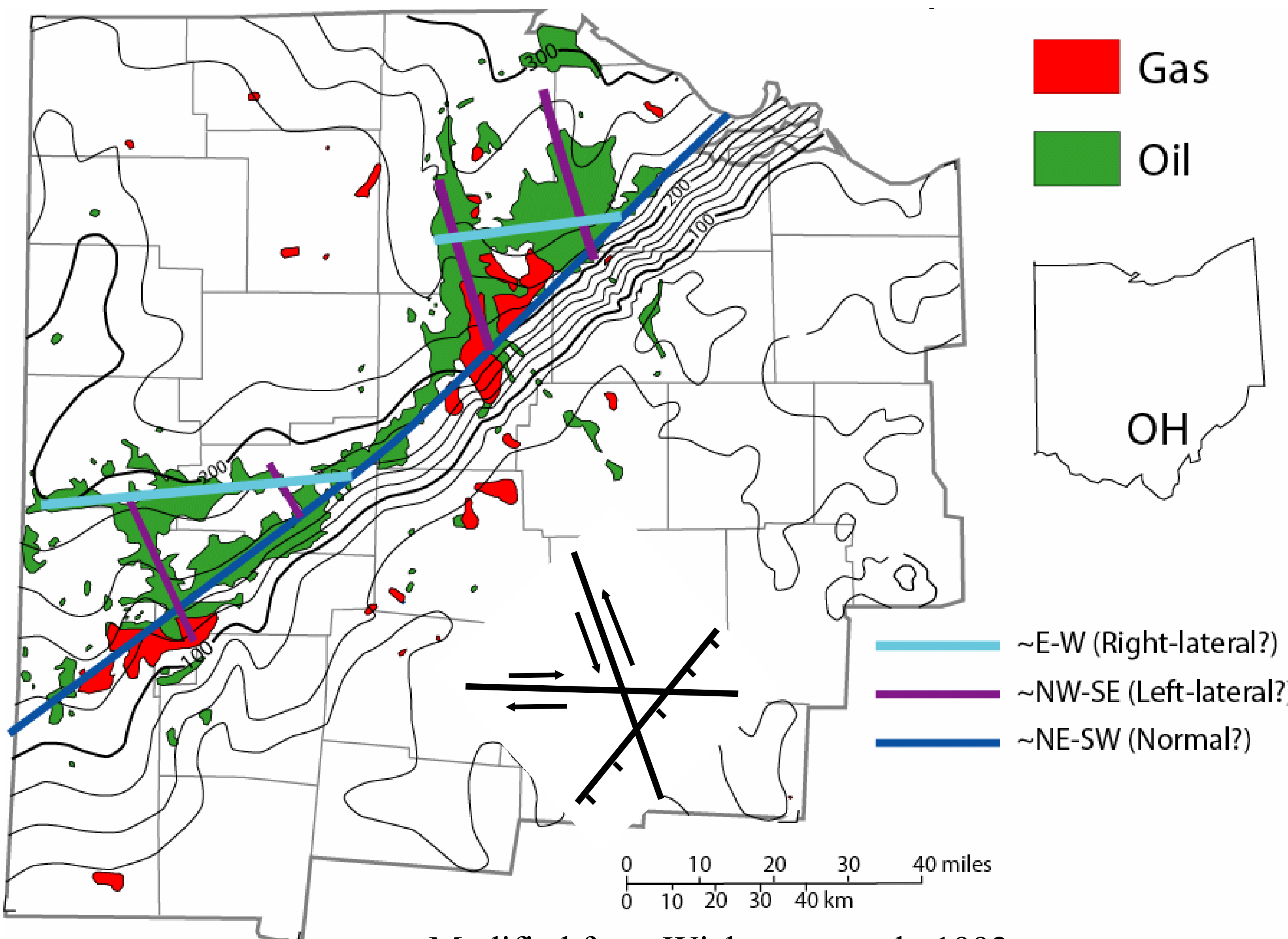
Rochester Field (ON) 3D surveys show en echelon Reidel Shears overlying left-lateral strike slip fault



"Facies" Dolomite –occurs along margin of Seebree Trough in OH and IN, matrix porosity, little obvious vug- or fracture-filling white saddle dolomite

“Facies dolomite” occurs along margin of Seebree Trough – interpreted to be fault controlled (Wickstrom et al., 1992)





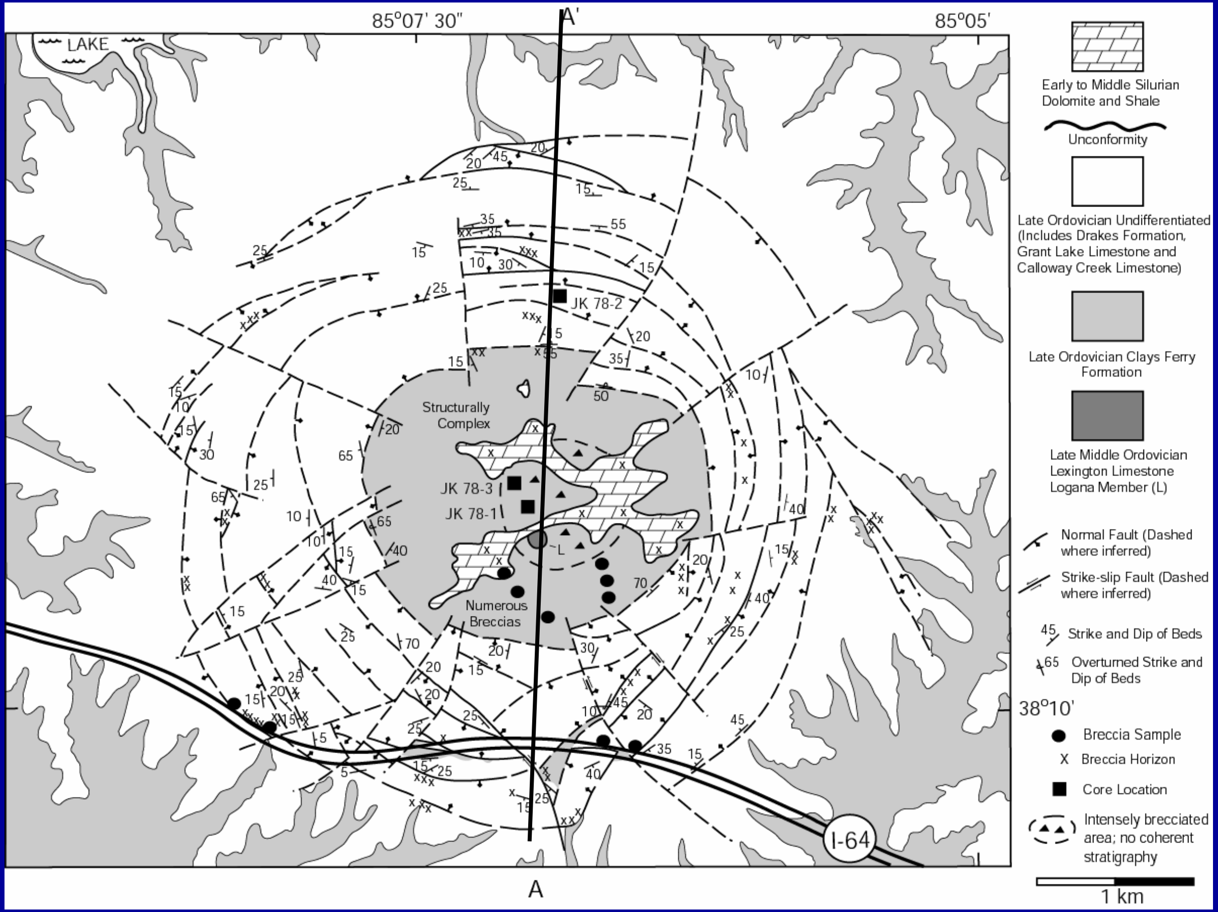
Modified from Wickstrom et al., 1992

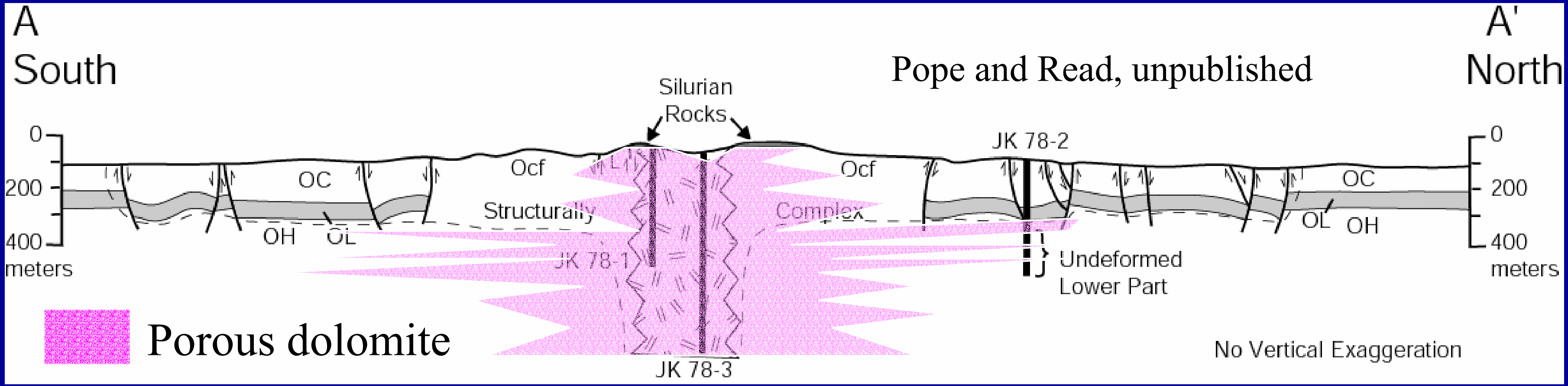
Dolomitization in Trenton occurs along margin with shale basin, around intraplatform wrench faults and at fault intersections

Jeptha Knob

The structure is pervasively dolomitized brecciated, fractured, faulted and very porous

Three cores drilled looking for minerals in KY survey collection



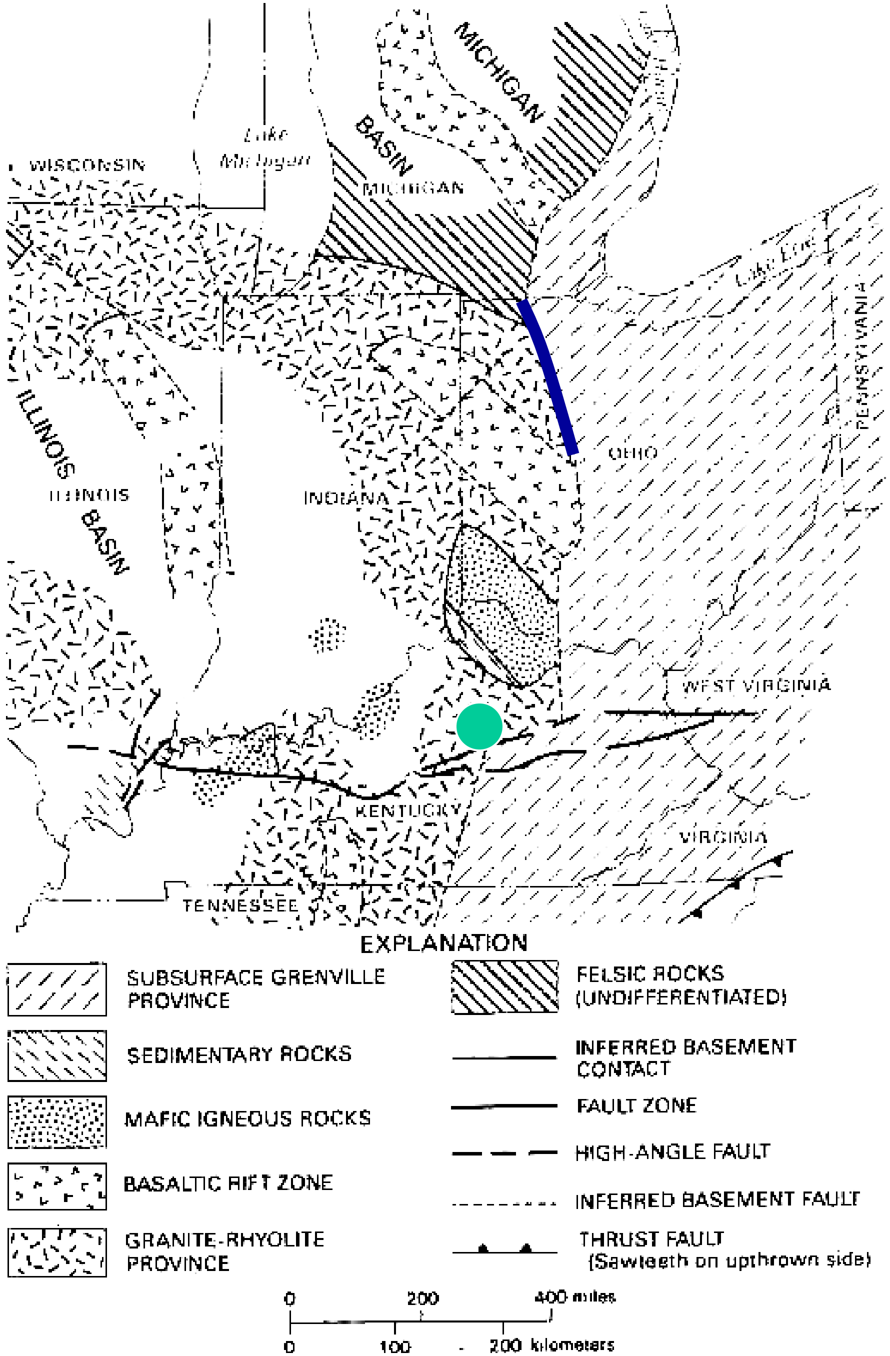


Jeptha Knob

Lexington (Trenton)

High Bridge (Black River)

Jeptha Knob is a positive feature historically interpreted to be an impact structure – it is interpreted by me to be a positive flower structure – The Trenton and Black River are pervasively dolomitized within the structure and are very porous and permeable – no saddle dolomite observed – (Fluid inclusions 80-110 C, 18 wt% salinity, radiogenic Sr, heavy $d^{18}O$)



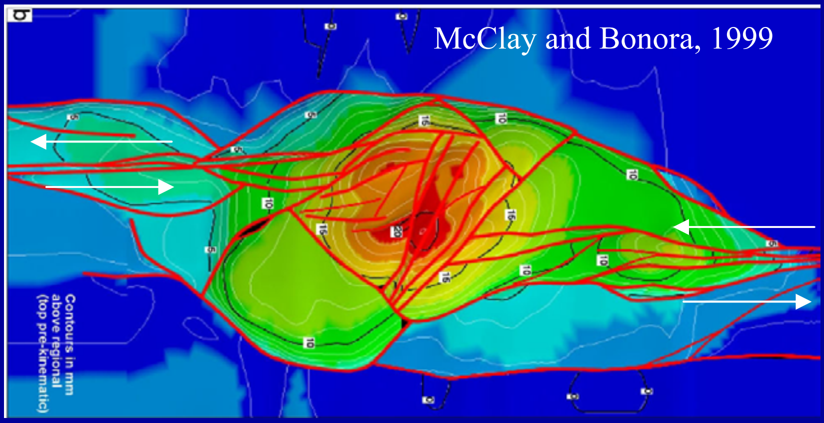
Wickstrom et al. 1992

Basement Map of Eastern US

Looks like major right lateral movement as occurred on 38th parallel lineament

Not sure, but it looks like Jeptha Knob occurs on or very near the lineament

If this is a compressional part of the fault zone, a positive flower structure could have formed



All Hydrothermal?

- The geochemistry suggests that all of the dolomite in the Trenton and Black River has at least a fault-related hydrothermal component
- This includes negative and positive flower structures associated with strike-slip faults and normal faults oriented NE-SW that are generally down to the SE

Matrix Dolomitization with no associated saddle Dolomite

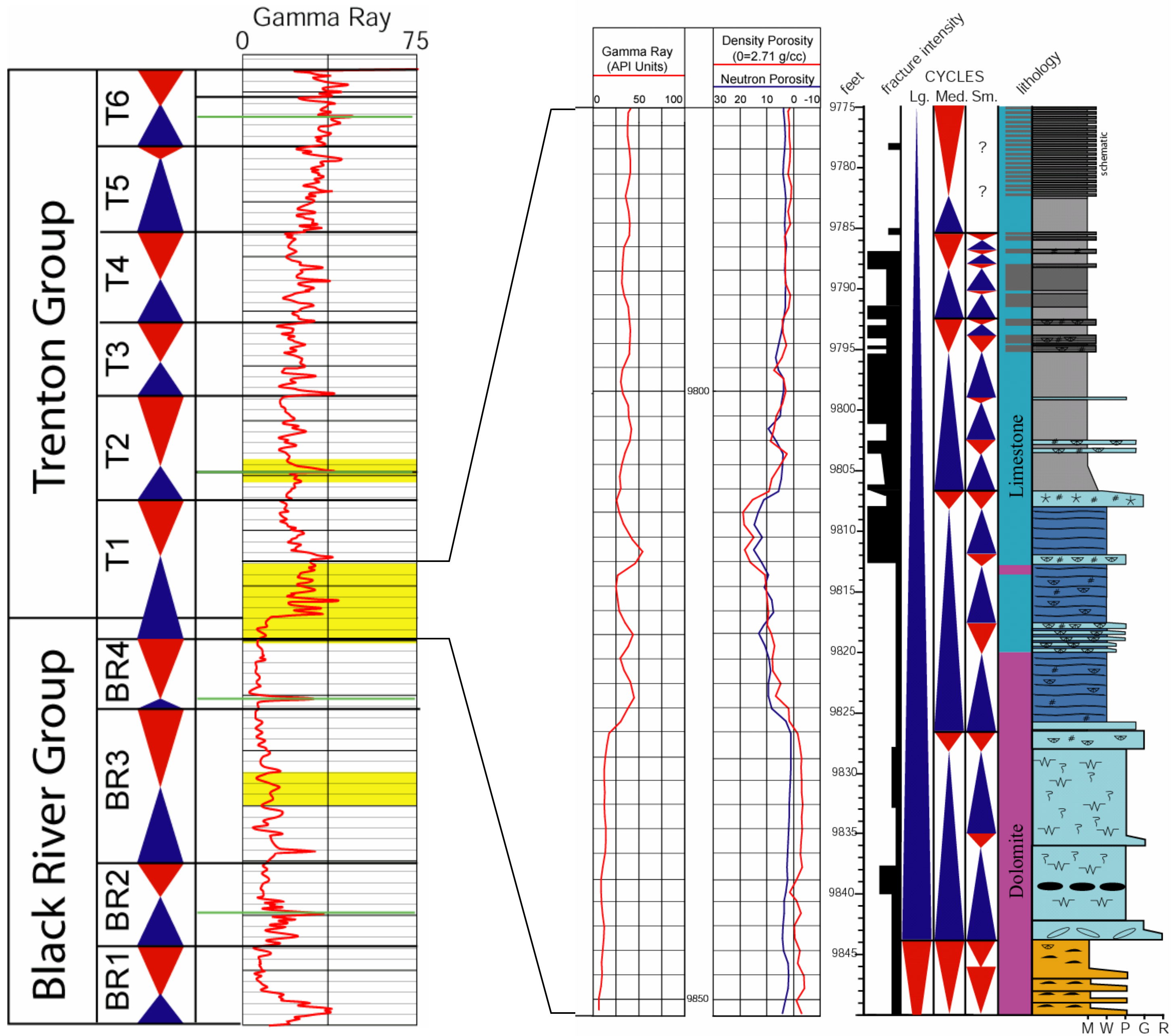
- “Cap” dolomite, “facies” dolomite and Jeptha Knob dolomite all have geochemical attributes of hydrothermal dolomite
  - High Fe and Mn
  - High Th and salinity fluid inclusions
  - Radiogenic 87Sr/86Sr
  - These rarely have saddle dolomite associated with them but they are still probably hydrothermal in origin

Chemostratigraphy

- Chemostratigraphy is done by using variations in some sort of geochemical attribute to find and correlate timelines between stratigraphic sections
- In this case, we are using Carbon-13 (^{13}C)
- The ^{13}C composition of seawater has varied over time and there are some time periods when there are significant variations over short time spans (as well as some where ^{13}C varied very little)
- Carbonates capture these variations in seawater and major shifts in isotope values can be correlated from well to well, providing a way to determine time lines

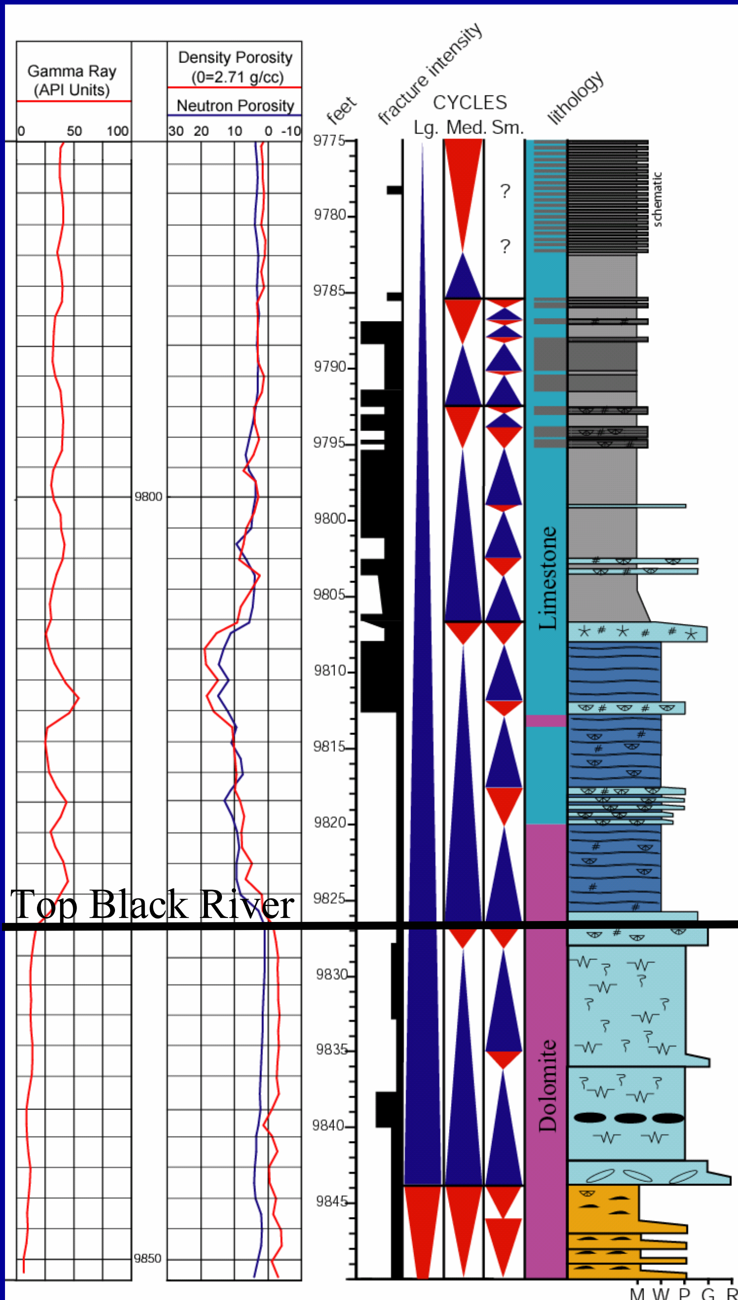
GICE

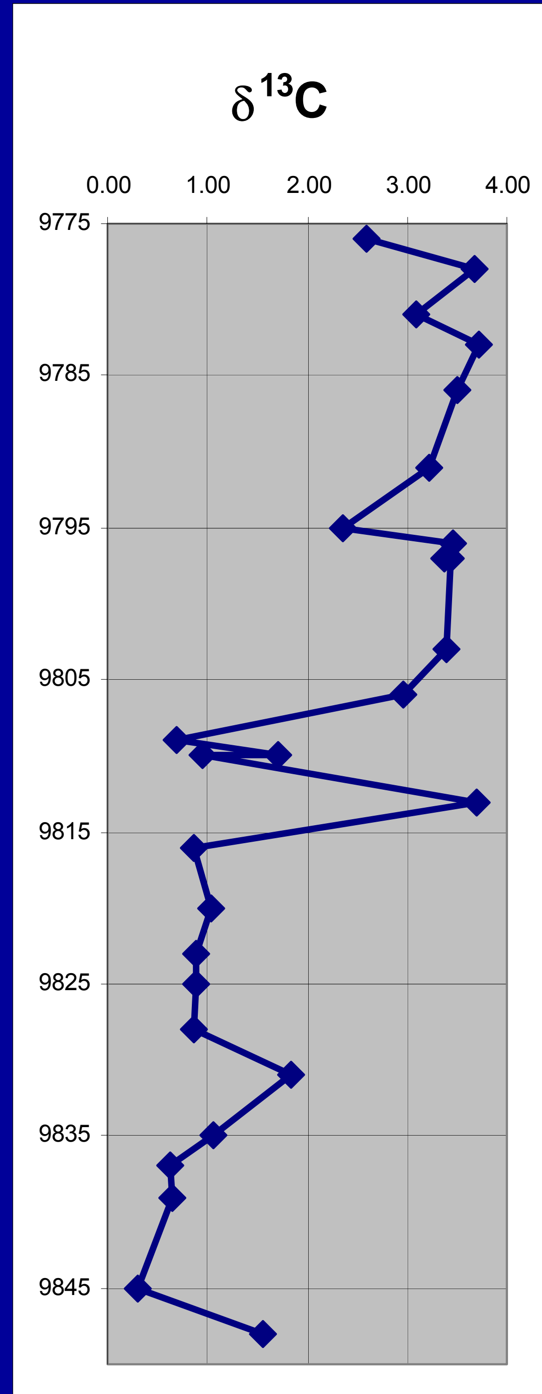
- The Guttenberg carbon isotope excursion (GICE) occurs near the Deicke and Millbrig bentonites has been correlated around the world (Barta, 2004)
- The occurrence of the GICE in the Matejka #1 core in NY was what got this project started



Gamma Ray
0
75
Trenton Group
T6
T5
T4
T3
T2
T1
Black River Group
BR4
BR3
BR2
BR1
Gamma Ray (API Units)
0 50 100
Density Porosity (0=2.71 g/cc)
Neutron Porosity
30 20 10 0 -10
9800
9850
feet
fracture intensity
CYCLES
Lg. Med. Sm.
lithology
9775
9780
9785
9790
9795
9800
9805
9810
9815
9820
9825
9830
9835
9840
9845
schematic
Limestone
Dolomite
M W P G R

Matejka # 1 Core



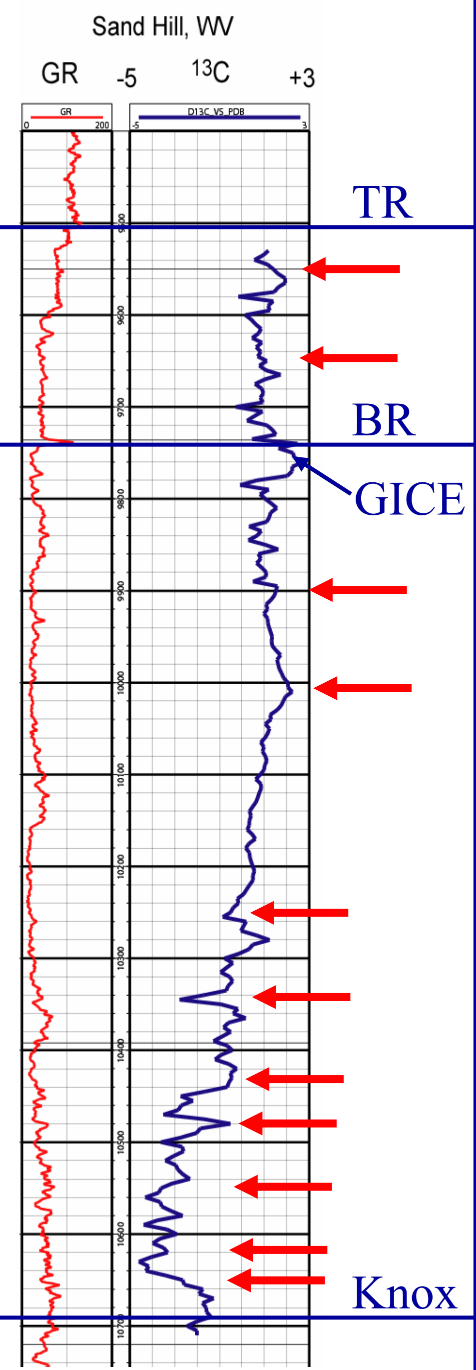


There is a significant shift in $\delta^{13}C$ just above the Trenton Black River boundary in New York which is called the Guttenberg Carbon Isotope Excursion (GICE) – this excursion has been correlated across US and to Europe (Barta et al., 2004)

Are there other shifts in TBR?

Chemostratigraphy Approach

- Sampled 6 key sections every 5-10 feet from Utica to Knox/Beekmantown
  - 3 from Ohio
  - 2 from Kentucky
  - 1 from WVA
- Plotted up curves with logs



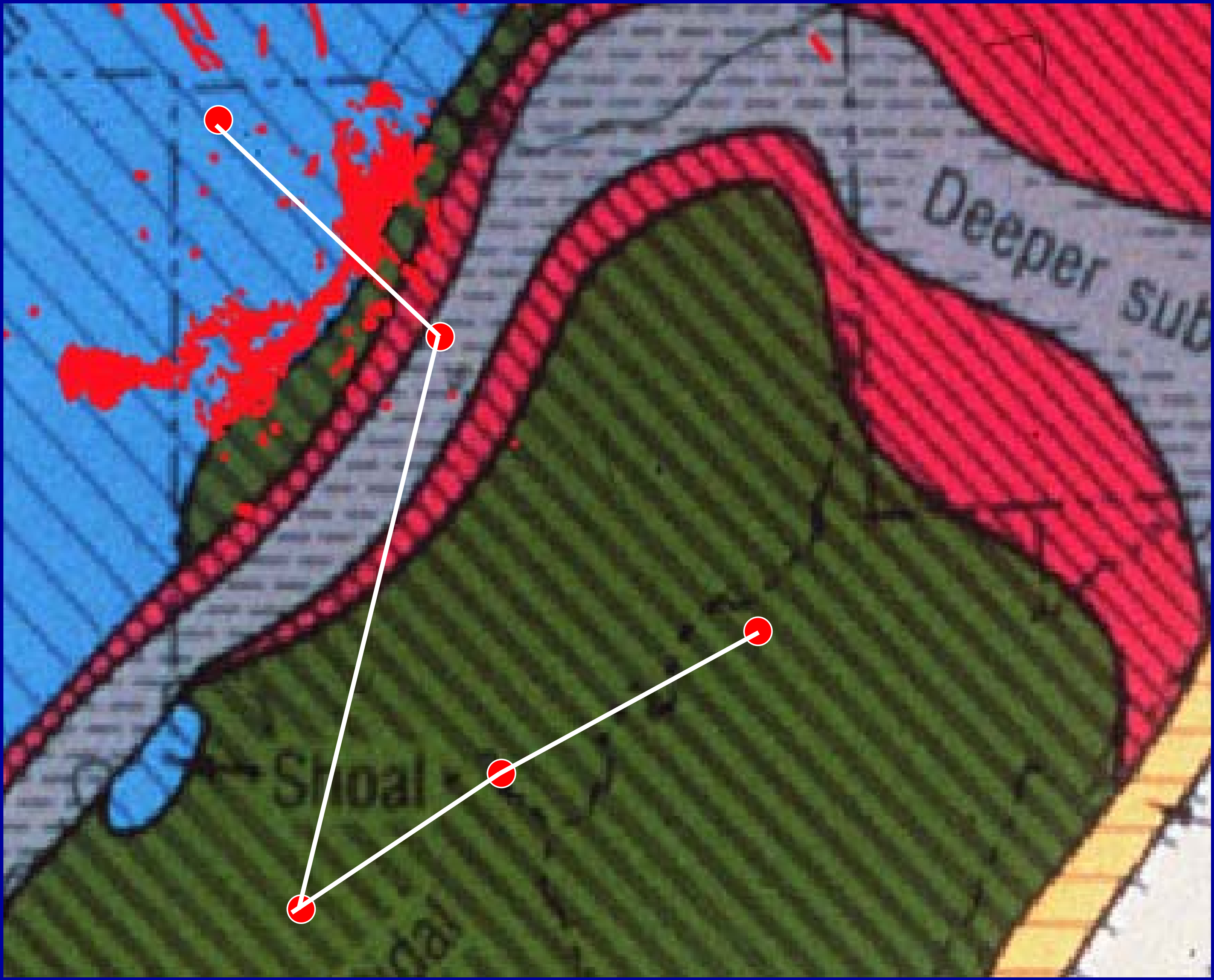
Chemostratigraphy

This shows the 13C plot and the Gamma Ray log for a deep well in West Virginia that has a continuous core

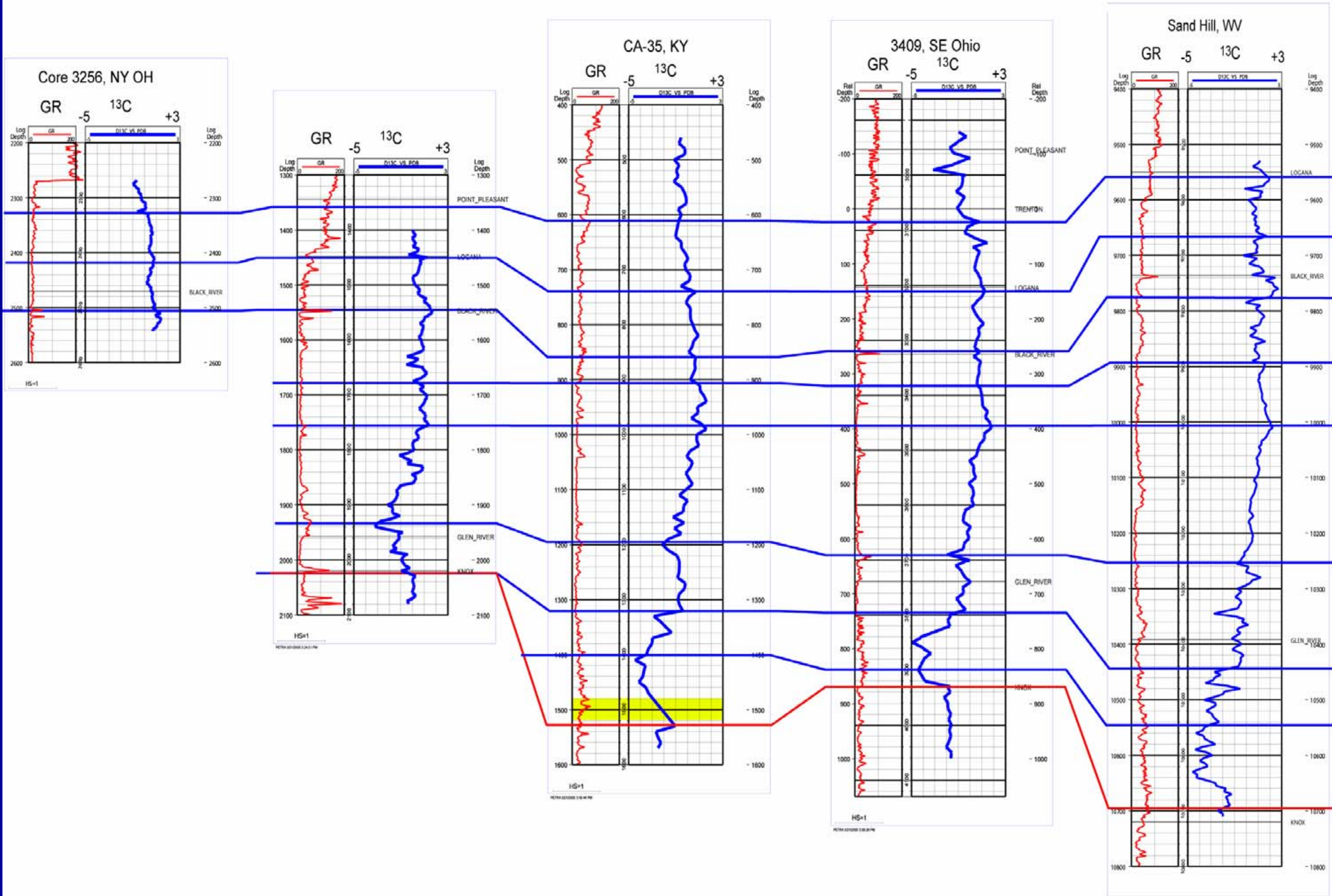
The GICE is obvious here and is a good marker

There are also many other excursions in this well that could make good markers

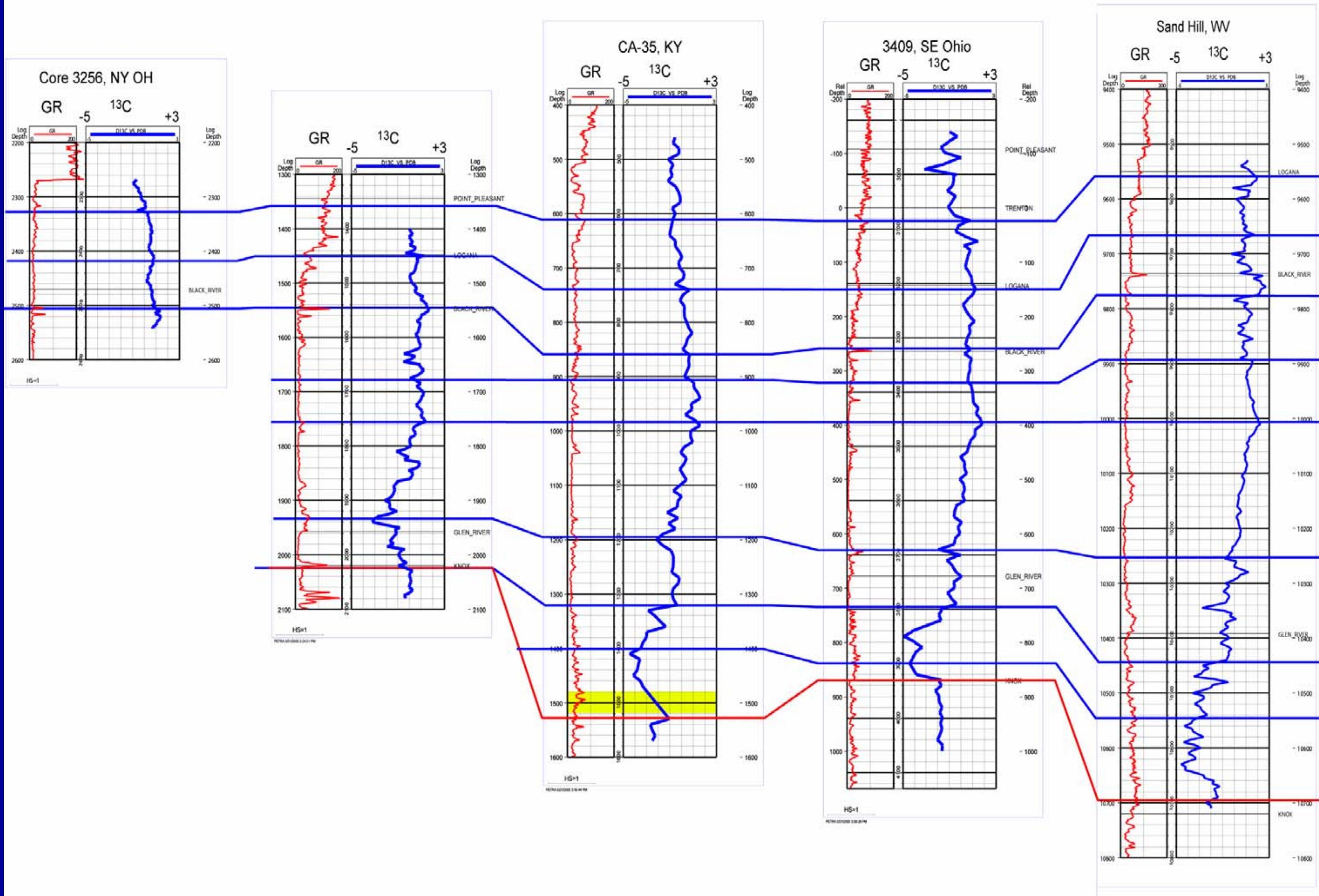
The next step is to see if the markers correlate from well to well



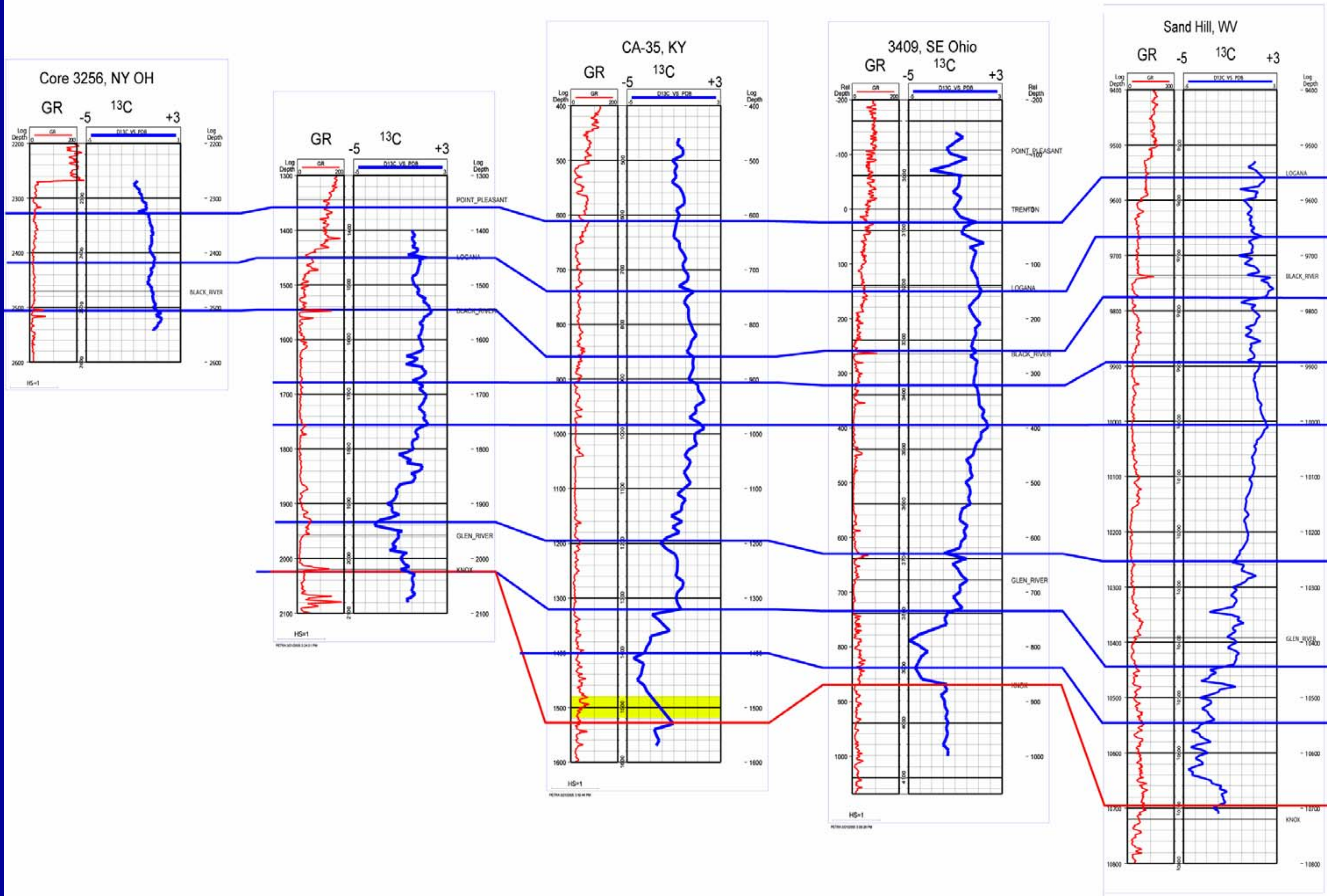
Approximate locations of cores studied for chemostratigraphy



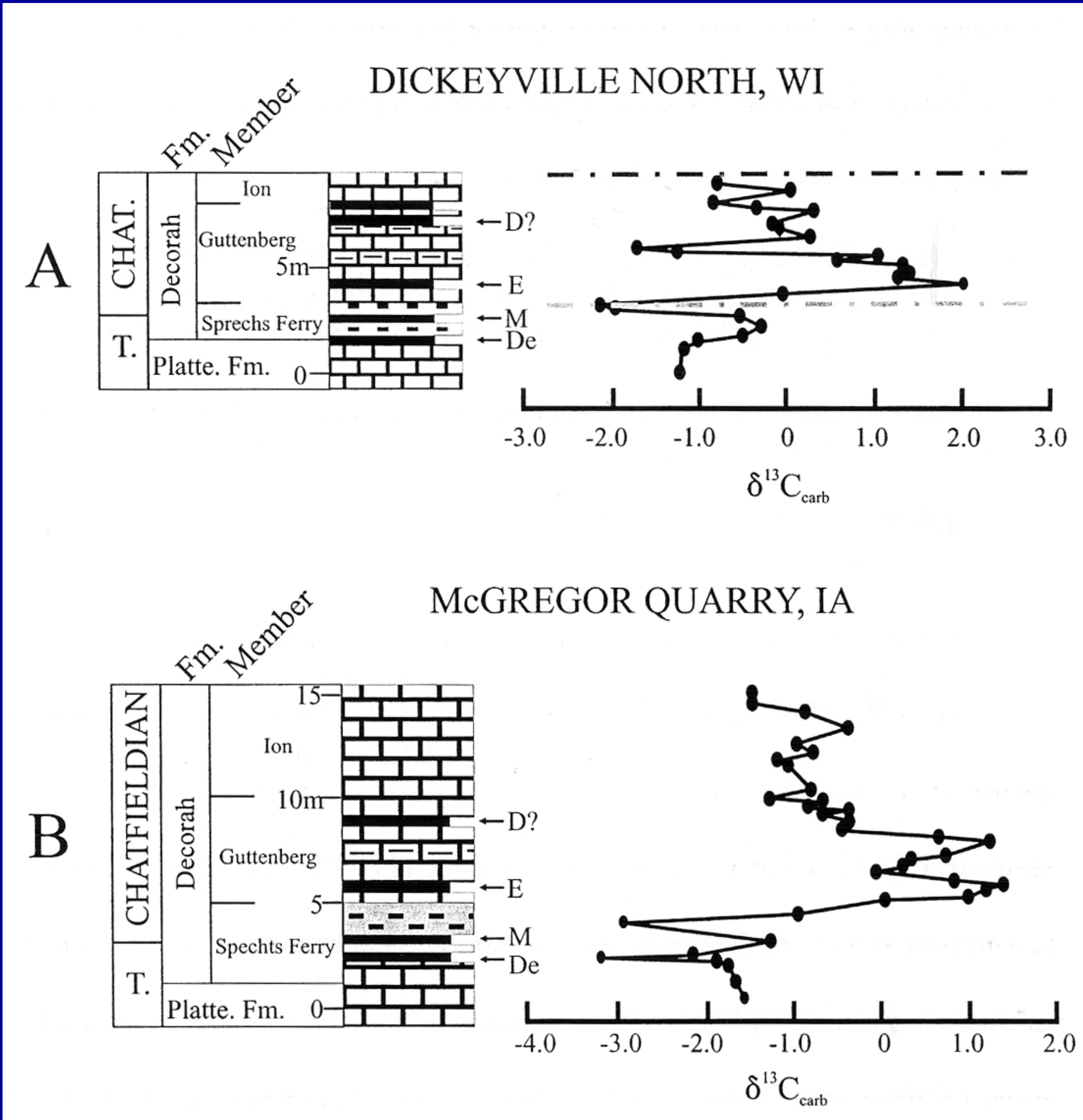
Core 3256, NY OH
GR
-5
13C
+3
CA-35, KY
3409, SE Ohio
Sand Hill, WV
POINT_PLEASANT
TRENTON
LOGANA
BLACK_RIVER
GLEN_RIVER
KNOX



Looks like there may have been major thinning in late BR time



Tighter sampling over key intervals may help resolve some uncertainty

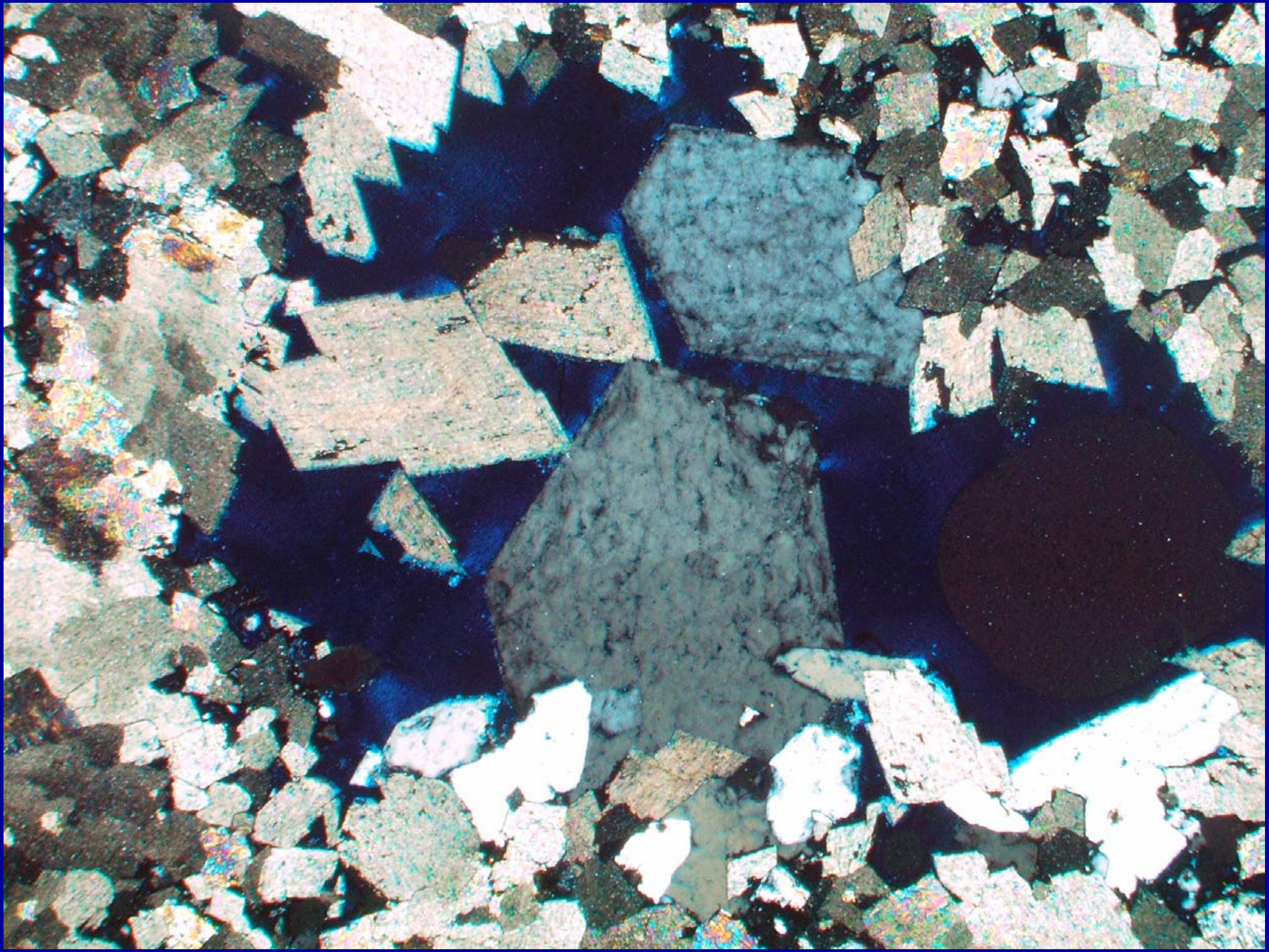


GICE occurs over a relatively thin interval in some sections – a 10 foot spacing interval might miss it

Other larger scale trends are obvious even at 10-foot sampling interval

Chemostratigraphy

- This is clearly a powerful tool because it gives time lines with which to correlate stratigraphy
- This in turn helps to identify periods of differential subsidence and tectonic activity and to work out what correlates with what
- We plan to do several key wells in PA and NY to see how they tie in
- It may also be very helpful in the Knox/Beekmantown where there are some significant excursions



Authigenic feldspar postdates dolomitization in two NY cores

Feldspar Age Dating

- Radiometric dates can be obtained from authigenic feldspar using $^{40}Ar/^{39}Ar$
- We are sending off some samples to be age dated at a fairly modest cost
- The date will provide a minimum age – that is if the feldspar is Devonian in age, the dolomitization would have to be Devonian or older, etc.