

## **Fluid Evolution in Cambrian-Ordovician Knox Group Reservoirs\***

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### **Abstract**

Archived formation water chemistry data (n~ 930) from Precambrian to Pennsylvanian rocks in the Appalachian and Illinois Basins of Kentucky were used to reconstruct basin hydrostatigraphy. The analysis shows that deeper Cambrian-Ordovician waters in the Knox Group were sometimes significantly less saline than what would be predicted by salinity trends in shallower Silurian and younger reservoirs. The contrast in salinity trends between younger and older reservoirs suggests the presence of an aurally extensive confining unit in Upper Ordovician strata that separates fluid populations possibly at the basin scale. Less saline waters in the Knox also suggest mixing with meteoric waters. The critical question, especially in deeper parts of the basins, is, are these relatively “young” meteoric waters that infiltrated along structural highs or “old” meteoric waters that penetrated exposure surfaces during or shortly after Knox deposition? The distinction is also important because the Knox is being evaluated as a possible carbon sequestration reservoir at depths of -2,500 ft (reference to sea level, SL) and deeper.

Recent measurements in two wells away from structural highs illustrate efforts to characterize the evolution of deeper Knox formation water chemistry. The KGS-Blan #1, located in Hancock County, Kentucky approximately 115 miles west of the Cincinnati arch crest, sampled waters from two Knox zones at -3,165 to -3,189 and -4,485 to -4,505 ft (SL) in the Beekmantown Dolomite and Gunter Sandstone, respectively. Salinities equaled 56,775 and 97,192 mg/L, respectively, and, were less than would be predicted for this depth relative to the shallower Paleozoic salinity trends. Farther south in the Planet Energy-West #1 in Hickman County, Tennessee, Knox waters sampled from the Chepultepec Dolomite at -1,569 to -2,299 ft (SL) contained 452 mg/L total dissolved solids. The low salinities are notable given the depth and location 60 miles west-southwest of the center of the Nashville Dome. In the absence of bedded salts, dilution and evaporation proportionately influence the concentration of chloride (Cl) and bromide (Br). Their respective

concentrations in the West well (Cl= 88 mg/L, Br= 0.3 mg/L) suggest that marine waters were diluted with meteoric water, whereas those for the Beekmantown (Cl= 41,300 mg/L; Br= 174 mg/L) and Gunter (Cl= 60,700 mg/L; Br= 293 mg/L) in the Blan well suggest evaporated marine waters. Notwithstanding the apparent different water evolution histories in the two wells, a meteoric influence in both is suggested by the delta18O and deltaD measurements. Values for the West (delta18O= -6.35 per mil, deltaD= -38.3 per mil) and Blan (delta18O= -5.1 to -5.5 per mil, deltaD= -40 to -41.5 per mil) wells are close to the meteoric water line. The next important step in our investigation is to address the “young.

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*Washington, D.C.*

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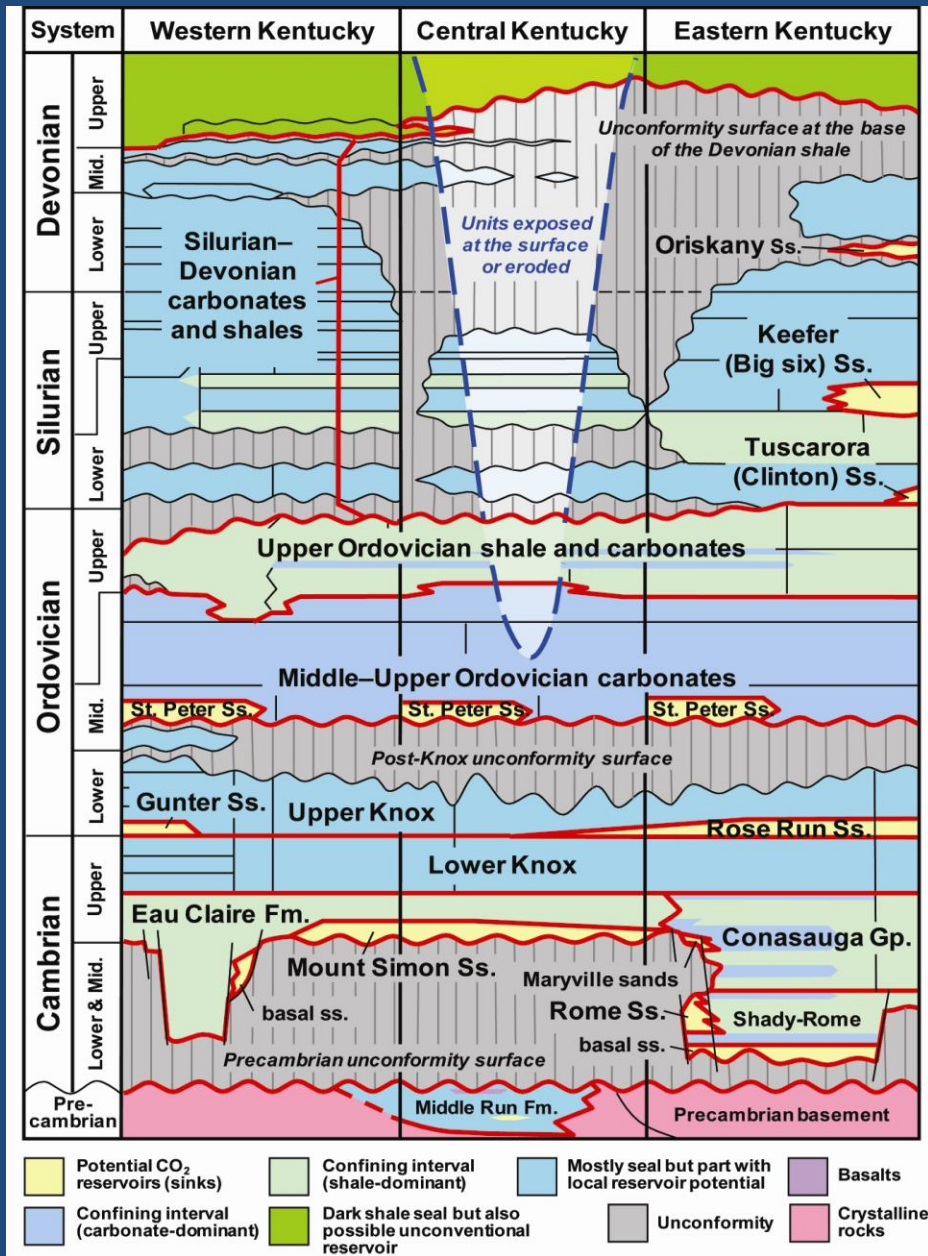


# Motivation for Research

- Formation water chemistry fundamental to understanding basin fluid flow and geochemical processes, and attendant distribution of resources
- Deeper saline aquifers volumetrically most significant target (>1,000 Gt) for geologic sequestration (IPCC, 2005)
- Ky.: 95% electricity from coal-fired plants
- Ky.: ~80 million tonnes of CO<sub>2</sub> in 2009 (EIA)



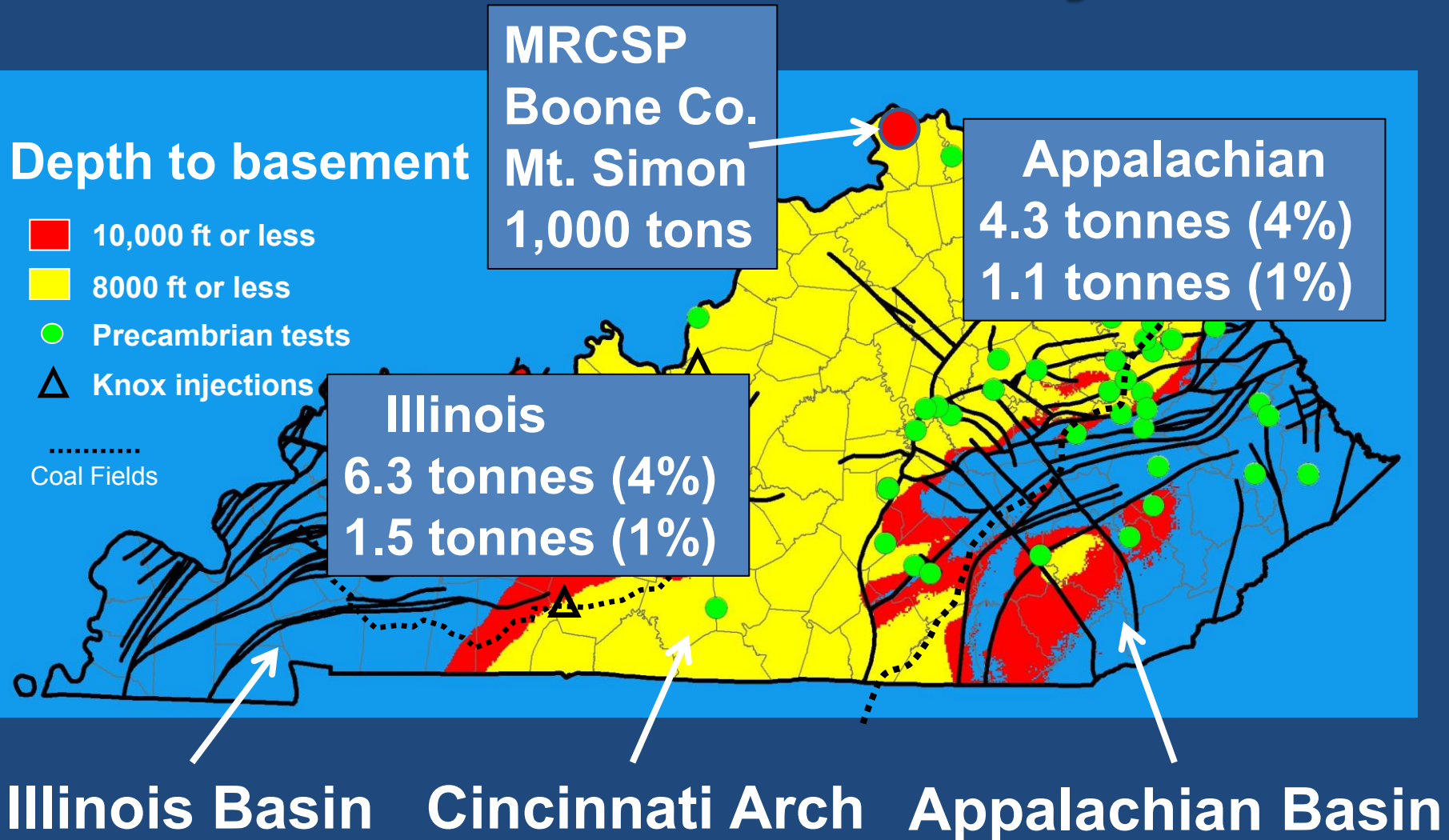
# Prospective Lower Paleozoic Saline Aquifers



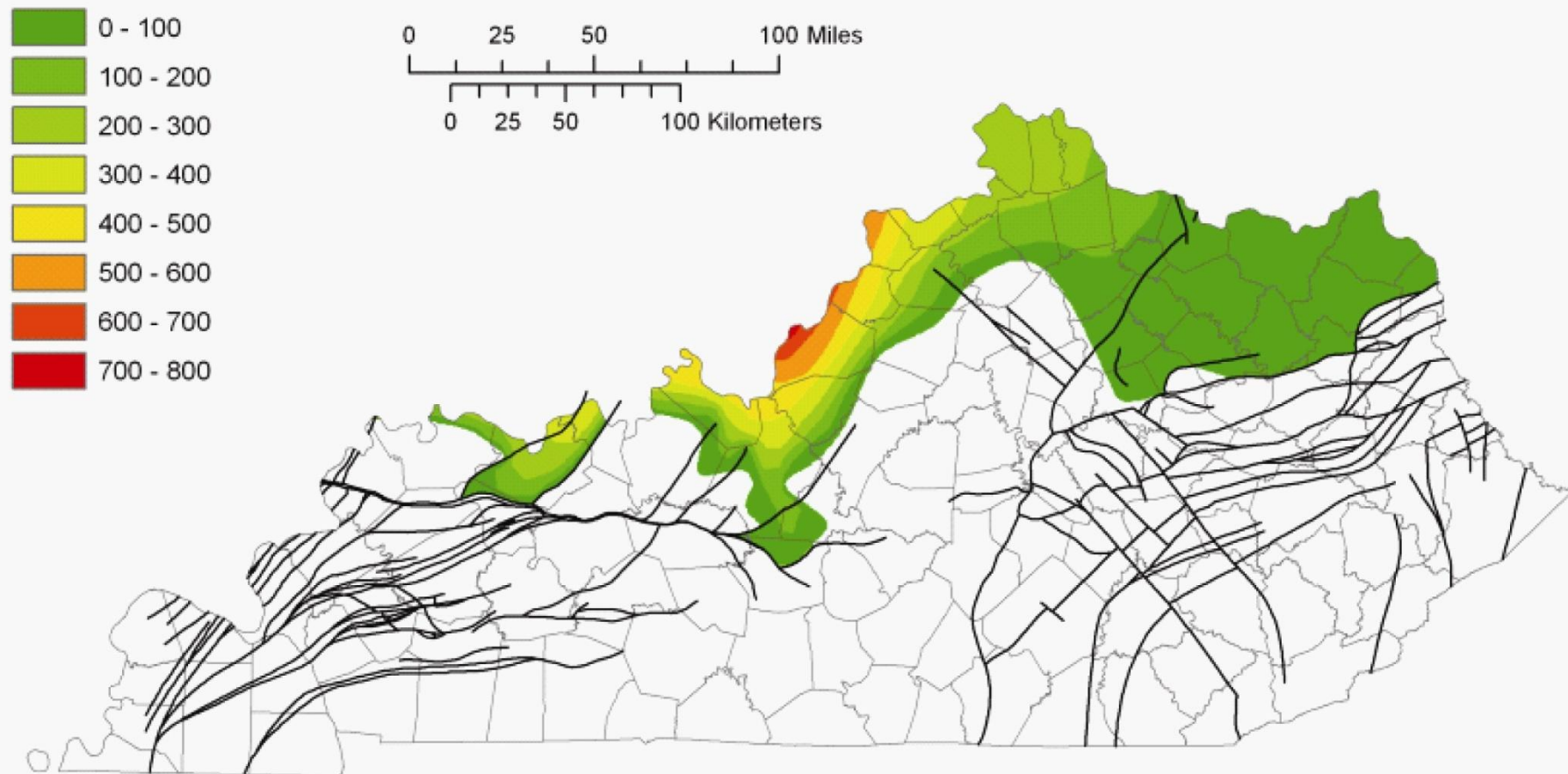
St. Peter Ss  
Beekmantown (Knox)  
Gunter/Rose Run Ss (Knox)  
Copper Ridge (Knox)  
Mount Simon Ss  
Rome Ss

*Courtesy of S. Greb, KGS*

# Basins in Kentucky

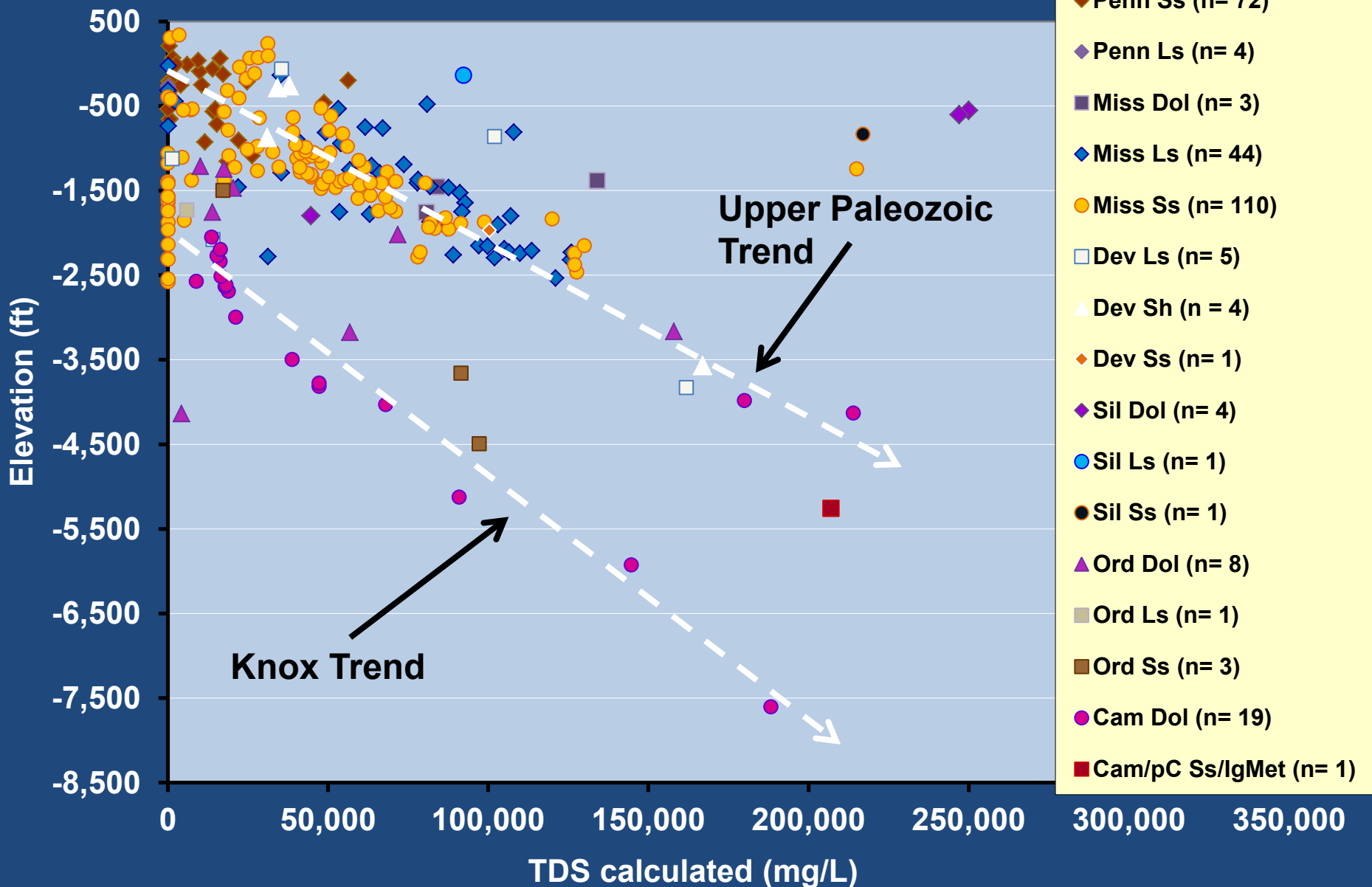


# Mount Simon Distribution



*From Solis and Greb (2010)*

# TDS vs Z (Illinois Basin)

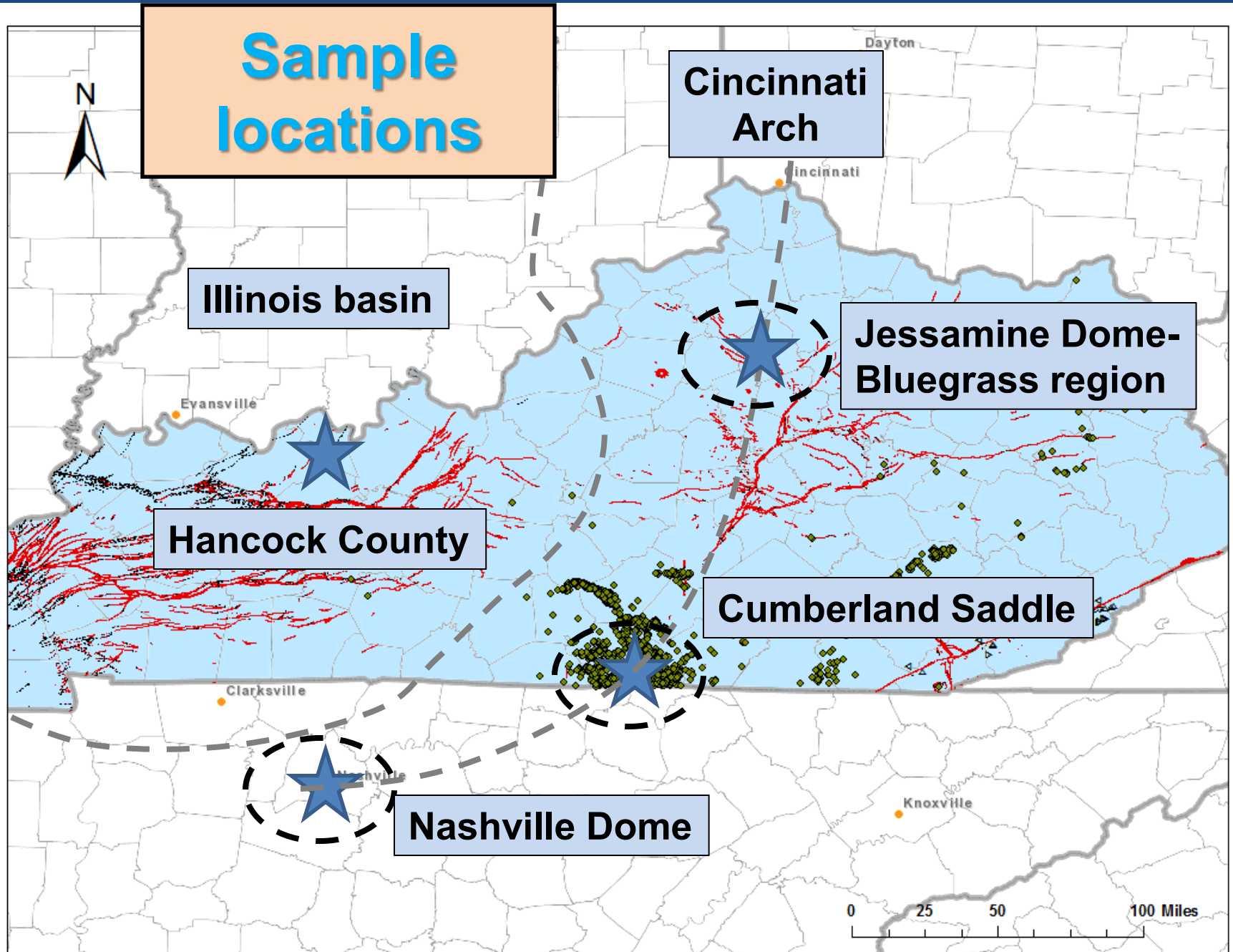


# Implications for Knox

- Difference in solute distribution w/ depth suggests broadly distributed upper Ordovician seal between Cambrian-Ordovician and younger Paleozoic rocks
- **Upper Ordovician seal important b/c of numerous penetrations in Devonian shale**
- Lower expected salinities for Cambro-Ordovician strata where  $> 2,500$  ft. suggests greater potential for solubility trapping of  $\text{CO}_2$
- **BUT, do less saline waters represent paleo-brackish waters or more recent mixing from meteoric infiltration along the Cincinnati arch?**



# Sample locations



# Knox Sample Locations

## Blan #1, Hancock Co., KY

- 2009 CO<sub>2</sub> test well: 300 tons CO<sub>2</sub> and 23,000 barrels brine injected into Knox
- NaCl-rich brines in Beekmantown (3,800-3,824 ft; 56,776 mg/L) and Gunter (5,120-5,140 ft; 97,192 mg/L)
- ✓ Bulk chemistry: Cl/Br
- ✓ Stable isotopes: d<sup>18</sup>O-H<sub>2</sub>O, dD-H<sub>2</sub>O

## KY Bluegrass (Galvin, 2006)

- NaCl and NaHCO<sub>3</sub> river (n= 1) and spring samples (n= 3)
- NaCl and NaHCO<sub>3</sub> GW well samples (n= 10) from Beekmantown (18-2,070 ft; 476-8189 mg/L)
- ✓ Bulk chemistry: Cl/Br
- ✓ Isotopes: d<sup>18</sup>O-H<sub>2</sub>O, dD-H<sub>2</sub>O, and <sup>36</sup>Cl



# Knox Sample Locations

## South-central KY

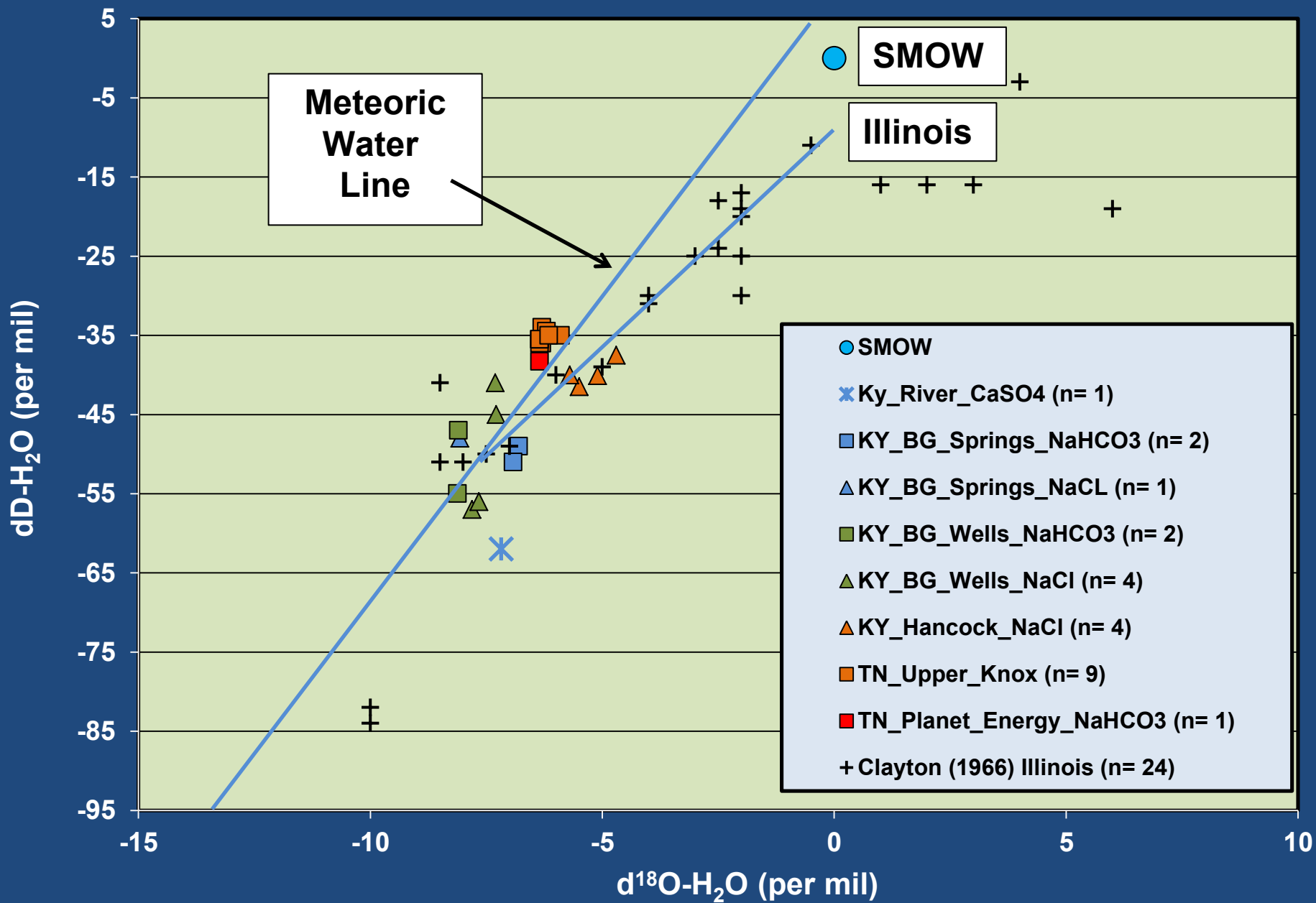
### Oil Province

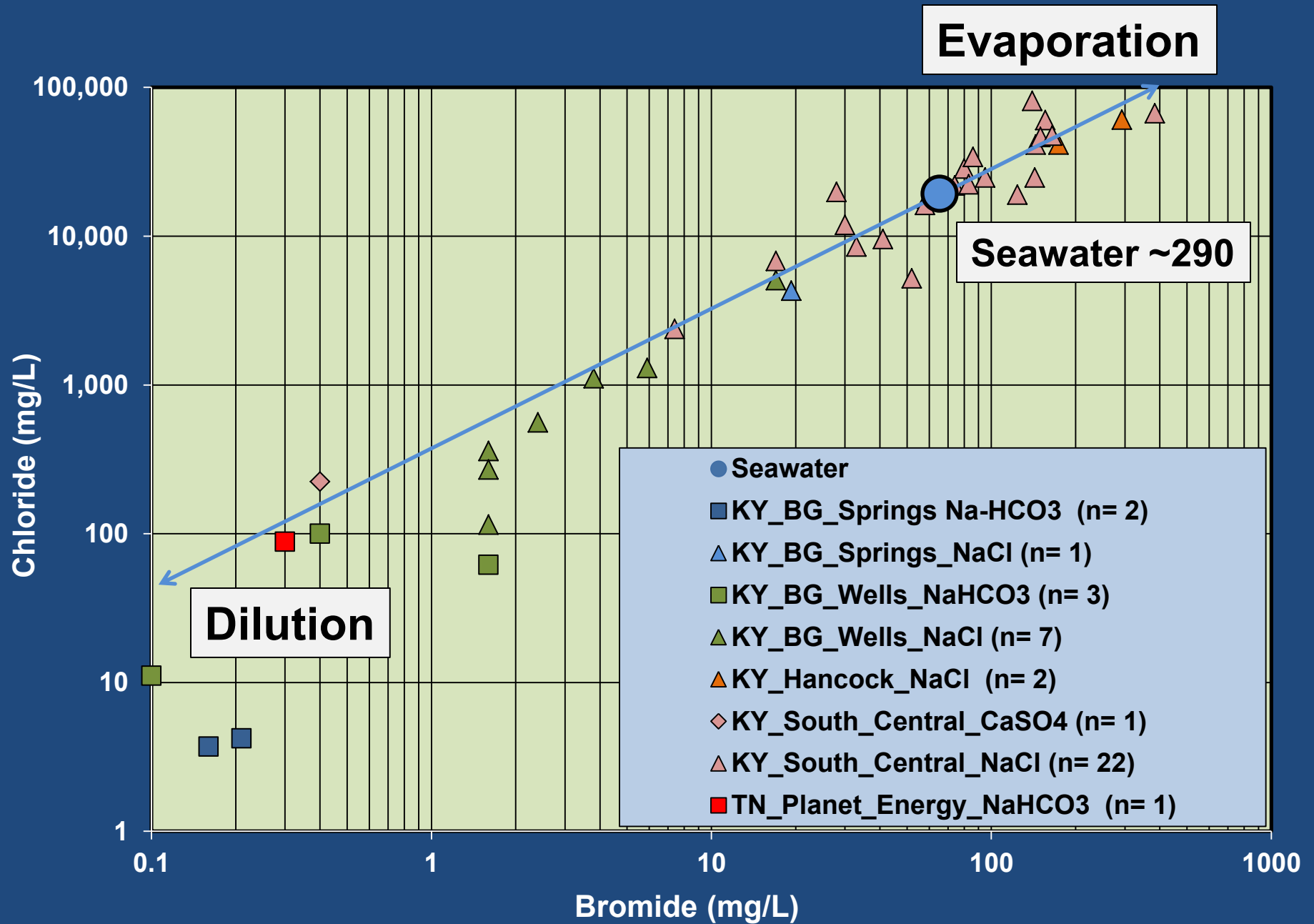
- Archived formation water chemistry data (n= 23)
- **Collected 1964-1971 from oil wells**
- Mostly NaCl-rich brines (12,400-108,000 mg/L) in Beekmantown (905-2,431 ft)
- ✓ *Bulk chemistry: Cl/Br*

## Nashville Dome, Tn.

- Earlier (1990) data (n= 8) collected mostly from water and oil exploration wells (USGS-Nashville)
- **CaHCO<sub>3</sub>-NaCl waters in upper Knox 100-2,518 ft (Chepultepec)**
- Planet Energy recent well (2,274-3,004 ft, 467 mg/L)
- ✓ *Bulk chemistry: Cl/Br*
- ✓ *Isotopes: d<sup>18</sup>O-H<sub>2</sub>O, dD-H<sub>2</sub>O, <sup>36</sup>Cl*



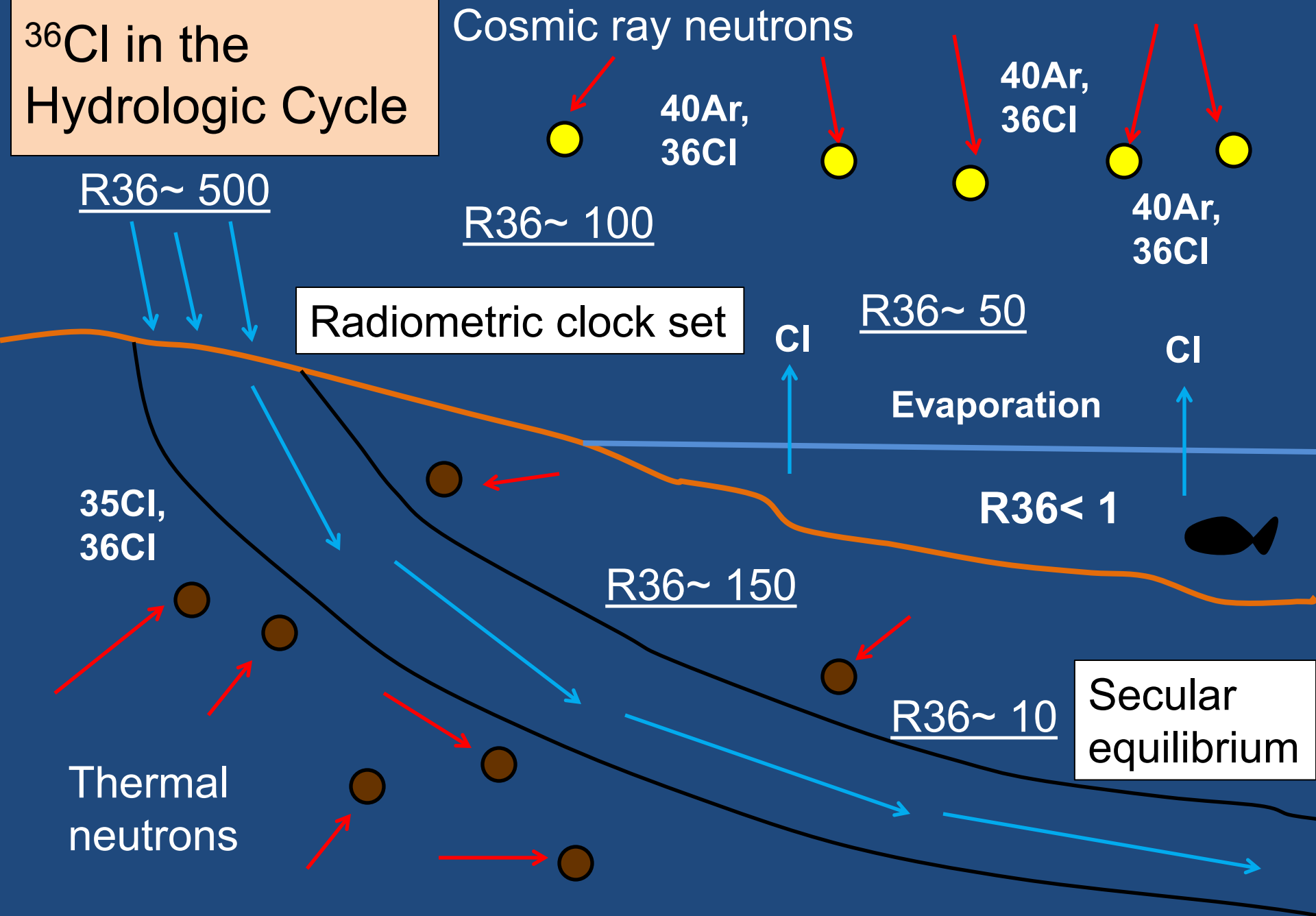




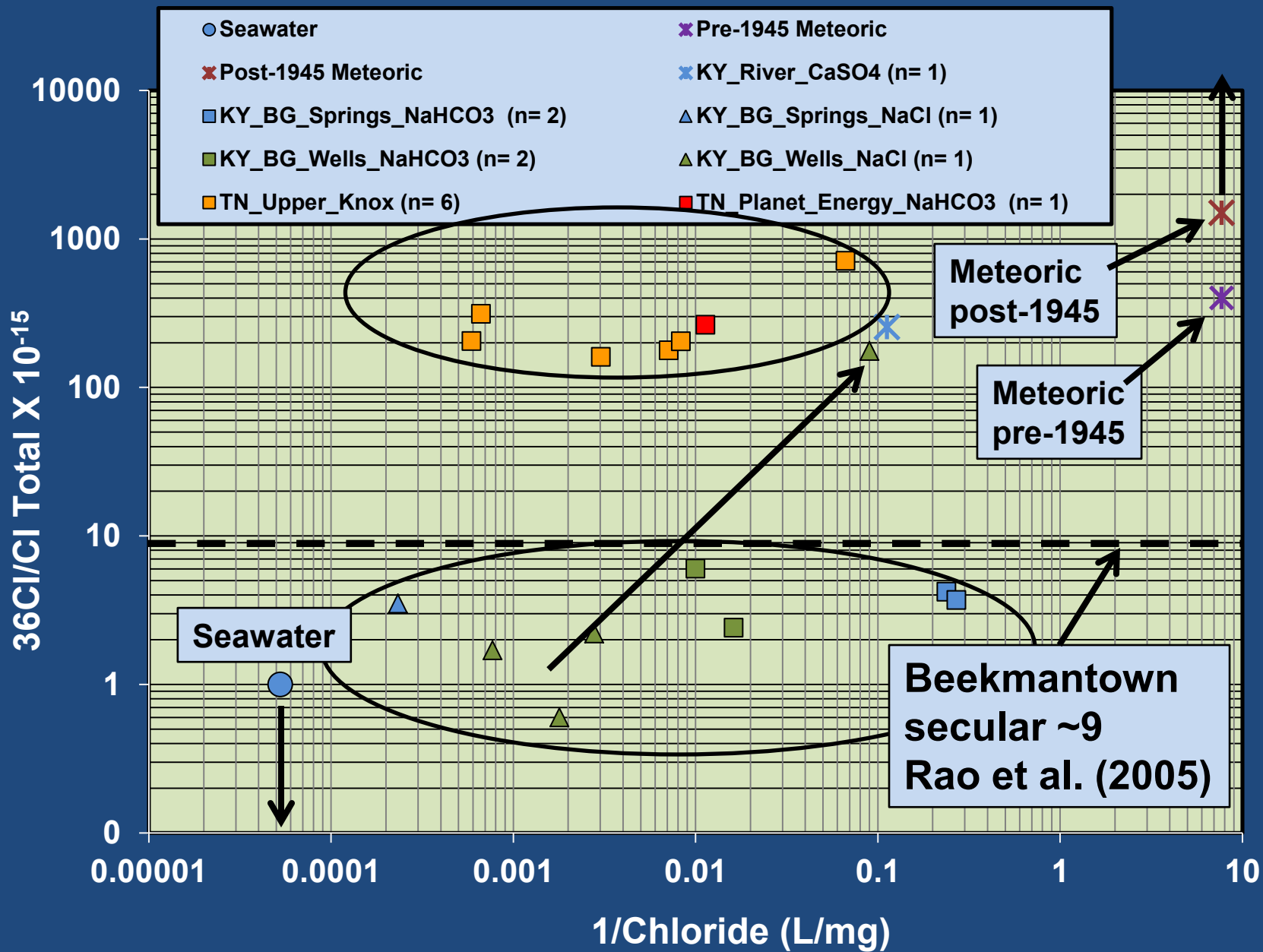
# 36-Chlorine Basic Chemistry

- Chlorine has 3 isotopes: 35 (75.77%), 36, and 37 (24.23%) of which 35 and 37 are stable
- $^{36}\text{Cl}$  produced in atmosphere by cosmic ray interactions w/  $^{40}\text{Ar}$
- $^{36}\text{Cl}$  decays to  $^{36}\text{Ar}$  w/  $t^{1/2} = 301,000$  yrs
- Viable for estimating ages of water 100 Ka to 1.5 Ma
- Resulting  $^{36}\text{Cl}/\text{Total Cl}$  ratios are small  $\sim 10^{-15}$  in atmosphere

# $^{36}\text{Cl}$ in the Hydrologic Cycle



*Simplified from Phillips (2010)*



# Summary

- Geochemical analysis of Knox formation waters at 3 widely separated locations along Cincinnati arch show distinct fluid evolution histories
- **South-central KY (Cumberland Saddle) associated with oil and Cl-Br values suggest seawater main compositional influence**
- $d^{18}\text{O}$  and  $d\text{D}$  of  $\text{H}_2\text{O}$  and Cl-Br analyses of Bluegrass KY (Jessamine Dome) and Nashville Dome (TN) samples indicate influence of meteoric water
- **BUT, meteoric  $\neq$  modern:  $^{36}\text{Cl}/\text{Cl}$  ratios analysis suggests likely modern waters for Nashville Dome but secular equilibrium for BG samples ( $> 1.5$  Ma) suggests “older” meteoric**
- Updip  $\text{CO}_2$  leakage a clear concern for TN area, but what about KY?



# Acknowledgements

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