

Brine Chemistry in the Illinois and Appalachian Basins of Kentucky— Implications for Geologic Carbon Sequestration*

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Search and Discovery Article #80075 (2009)

Posted December 31, 2009

*Adapted from oral presentation at 2009 AAPG Eastern Section Meeting, Evansville, Indiana, September 20-22, 2009

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Abstract

Theoretical studies show the potential to dissolve up to 30% of injected CO₂ in formation water over a period of tens of years in sequestration projects. The dissolution is important because it removes CO₂ as a separate buoyant phase that would migrate upward. The extent of dissolution is partly influenced by formation-water salinity, and the relationship provided the motivation for examining brine chemistry data (480 samples) collected mostly from oil wells in the Appalachian and Illinois basins of Kentucky. Specifically, we analyzed salinity distribution with depth and stratigraphy and the influence of salinity on CO₂ solubility. The brine samples are from carbonate, clastic, and igneous-metamorphic rocks, ranging in age from Precambrian to Pennsylvanian, and span elevations of 1550 to -7765 ft (sea level reference). Two distinct salinity trends are observed in each basin, with Cambrian-Ordovician samples showing salinities significantly less than those predicted by trends in Silurian and younger reservoirs. Solubility calculations confirm that lower salinities along with higher pressures at depth result in more potential for solubility trapping in the Cambrian-Ordovician reservoirs. In addition, the contrast in salinity trends between younger and older reservoirs suggests the presence of an areally extensive seal in the Upper Ordovician that separates fluid populations. The sealing interval, which likely corresponds to the Maquoketa Shale and its equivalents, is significant because the seals overlie Knox Group carbonate reservoirs, which are a main sequestration target in Kentucky.

References

Kharaka, Y.K., D.R. Cole, J.J. Thordsen, E. Kakouros, and H.S. Nance, 2006, Gas–water–rock interactions in sedimentary basins: CO₂ sequestration in the Frio Formation, Texas, USA: *Journal of Geochemical Exploration*, v. 89. p. 183–186.

Duan, Zhenhao and Rui Sun, 2003, An improved model calculating CO₂ solubility in pure water and aqueous NaCl solutions from 273 to 533 K and from 0 to 2000 bar: *Chemical Geology*, v. 193, p. 253-271.

Duan, Zhenhao, Rui Sun, and C. Zhu, 2006, An improved model for the calculation of CO₂ solubility in aqueous solutions containing Na⁺, K⁺, Ca²⁺, Mg²⁺, Cl⁻, and SO₄²⁻: *Marine Chemistry*, v. 98 (2-4), p. 131-139.

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Motivation for Study

- Estimated worldwide capacity of 1,000 gigatonnes, deep saline aquifers are volumetrically most significant target for geologic sequestration (Holloway, 2001)
- **Trapping mechanisms: physical, residual, solubility, and mineral**
- 10's to 100's of years monitoring period
- **Solubility trapping will be one of the fastest reactions to occur**
(Kharaka et al., 2006)



Project Goals

Use archived formation water chemistry data to:

1. Analyze stratigraphic and depth distribution of aqueous dissolved constituents in Illinois and Appalachian basins
2. Use distribution to make inferences about hydrogeologic compartments and seals
3. Use chemistry data along w/ temperature and pressure data to estimate CO_2 solubility w/ EOS for brine- CO_2 solutions



Kentucky Geological Survey
 UNITED STATES DEPARTMENT OF THE INTERIOR
 GEOLOGICAL SURVEY
 WATER ANALYSIS

Location Newman, Kentucky (23-Q-27) (2,060 PSI-950 PSI) County Darless
 Source Well No. 1 Depth (ft) 1,832-31 Diam (in.)
 Cased to (ft) _____ Date drilled 1969 Point of col. _____
 Treatment _____ Owner J. W. Haley, and Elm Holder _____
 WBf ANYSAS _____ Wt. _____ field _____ Use _____
 Temp (°C) _____ Appear when col. _____
 Collected November 5, 1969 By H. B.
 Remarks Red Quadrangle, Field; Blrk City, AF zone. Gage: 75 BOPD, 50 BFD.

	mg/l	me/l		mg/l	me/l
Silica (SiO ₂)	72	---	Bicarbonate (HCO ₃)	325	5.33
Aluminum (Al)		---	Carbonate (CO ₃)		.00
Iron (Fe)	.00	---			
Manganese (Mn)	.26	---	Sulfate (SO ₄)	1,270	26.44
			Chloride (Cl)	51,000	1,040.71
			Fluoride (F)	5.3	.10
			Bromide (Br)	114	1.43
Calcium (Ca)	2,840	141.72	Iodide (I)	15	.12
Magnesium (Mg)	1,480	121.74	Nitrate (NO ₃)		
Sodium (Na)	27,000	1174.50			
Potassium (K)	173	4.42			
Total	1442.38	Total		1472.31	
	mg/l		Specific conductance (micromhos at 25° C)	105,000	
Dissolved solids:			pH	7.4	
Calculated	84,000		Color		
Residue on evaporation at 180°C	93,200		Density at 20.0°C.	1.062	
Hardness as CaCO ₃	113,000				
	12,900				

Lab. No. Col 53840 Field No. _____ Project KENTUCKY MID - GW DRINKS

Archived Formation Water Chemistry Data

- Administrative
- Anions
- Cations
- Water properties



Data Distribution to Date

Eastern Ky. 30 Counties 286 Analyses

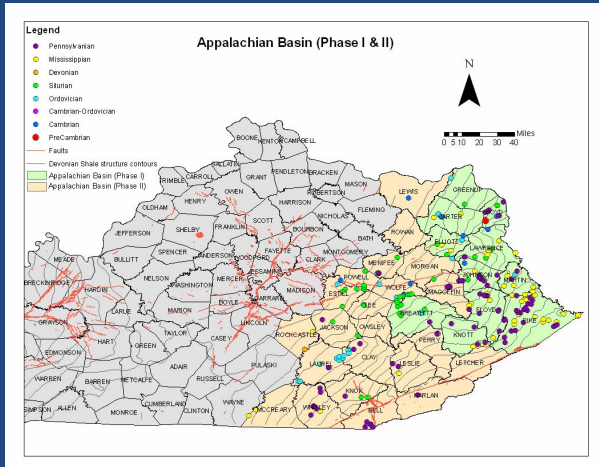
Bell	Lee
Boyd	Leslie
Breathitt	Lewis
Carter	McCreary
Clay	Magoffin
Elliott	Martin
Estill	Menifee
Floyd	Morgan
Harlan	Perry
Jackson	Pike
Knox	Powell
Knott	Rockcastle
Laurel	Whitley
Lawrence	Wolfe

Western Ky. 31 Counties 549 Analyses

Ballard	Henderson
Breckenridge	Hickman
Bullitt	Hopkins
Butler	Jefferson
Caldwell	Livingston
Carlisle	Lyon
Christian	McCracken
Crittenden	McClellan
Daviess	Marshall
Fulton	Meade
Graves	Muhlenberg
Grayson	Ohio
Hancock	Todd
Hardin	Trigg
	Union
	Webster



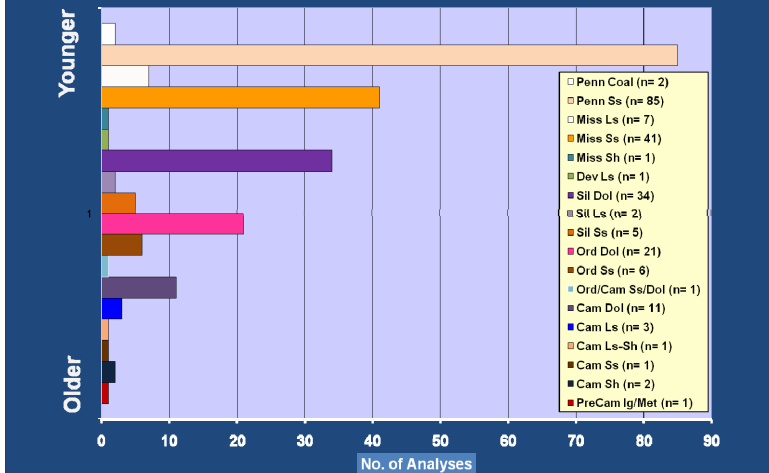
Sample Locations—Eastern Ky.



Presenter's Notes:

1. Map showing counties in eastern Kentucky for which water chemistry data have been compiled. First phase of work is shown in green and the second in tan.
2. Similar work has been conducted in western Kentucky, but data have not been vetted. Therefore, most examples will come from eastern Kentucky and the Appalachian basin.

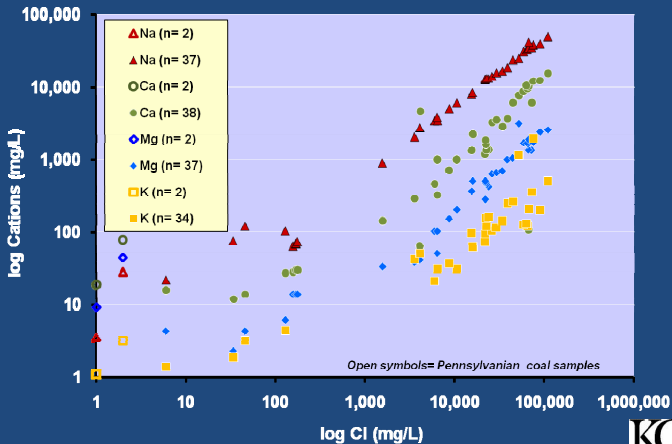
Stratigraphic Distribution of Data- Eastern Ky.



Presenter's Notes:

1. For this study, stratigraphic units were divided into broad age-rock unit categories, such as Pennsylvanian sandstone, Silurian dolostone, and Ordovician dolostone. In doing so we tried to develop hydrostratigraphic units that would allow us to recognize important seals and compartments and in which similar water-rock-CO₂ interactions might occur.
2. Most data are from the Upper Paleozoic (upper part of plot), specifically Pennsylvanian and Mississippian sandstone and carbonate reservoirs. Fewer data from the Ordovician and Cambrian.
3. In eastern Kentucky--no data from the Devonian Ohio Shale.

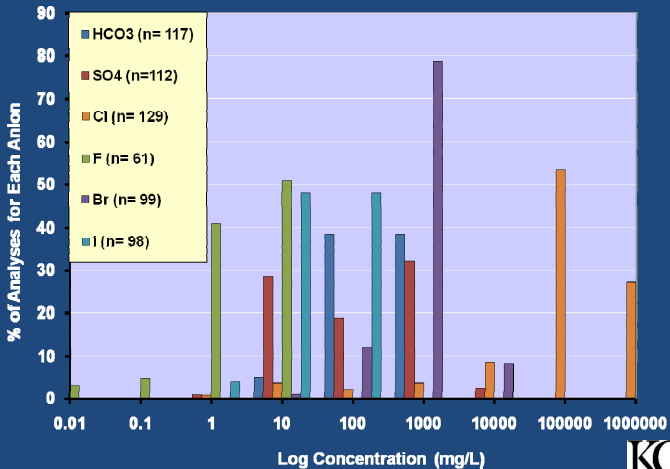
Pennsylvanian Ss and Coal Formation Water (Appalachian)



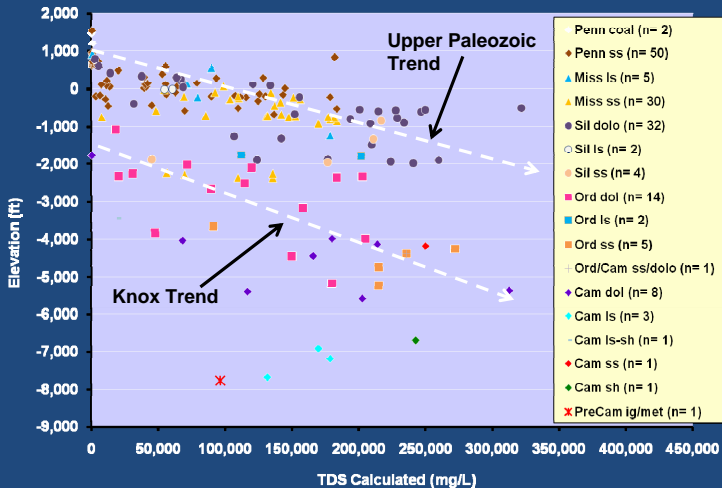
Presenter's Notes:

1. Representative plot of log Cl versus the log values for the major cations Na, Ca, Mg, and K. Plot demonstrates that Na is the dominant cation in the Pennsylvanian sandstone and coal samples, and a similar pattern holds for other rock-age units in both basins.
2. Note that Cl versus the cations tends to vary linearly for concentrations above about 1,000 mg/L, suggesting that composition is influenced by fairly simple dilution-evaporation processes. Below 1,000 mg/L, however, the patterns are more complex, likely reflecting water-rock interaction.

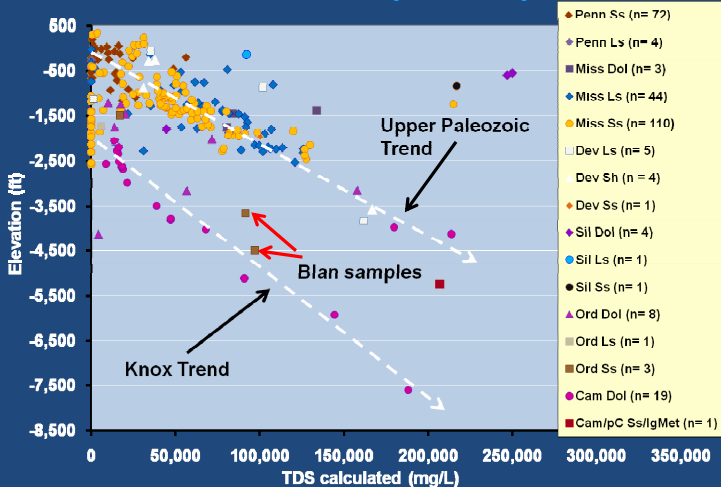
Anion Composition (Appalachian)



TDS vs Z (Appalachian)



TDS vs Z (Illinois)



CO₂ Solubility

- CO₂ Solubility estimated using equation of state (EOS) from Duan and Sun (2003) and Duan et al. (2006)
- **Aqueous solutions containing Na⁺, K⁺, Ca²⁺, Mg²⁺, Cl⁻, and SO₄²⁻**
- Predicts CO₂ solubility over wide range of temperature (273-533 K), pressure (0-2,000 bars), and ionic strength (0-4.5 molality) at two-phase coexistence (vapor-liquid, liquid-liquid)



CO₂ Solubility Results

- Eastern Ky. (Appalachian): CO₂ solubility estimates for Pennsylvanian-Silurian strata equal 0.099-0.369 mol/kg H₂O
- Eastern Ky. (Appalachian): CO₂ solubility estimates for Cambro-Ordovician strata equal 0.024-0.859 mol/kg H₂O
- Western Ky. (Illinois): CO₂ solubility estimates for Pennsylvanian-Silurian strata equal 0.187-0.536 mol/kg H₂O
- Western Ky. (Illinois): CO₂ solubility estimates for Cambro-Ordovician strata equal 0.082-0.824 mol/kg H₂O



Summary

- Difference in solute distribution w/ depth between Cambro-Ordovician and younger Paleozoic rocks in eastern and western Ky. suggests broadly distributed seal in upper Ordovician
- **Upper Ordovician seal is important b/c of numerous penetrations in the Devonian shale**
- Lower expected salinities for Cambro-Ordovician strata—most of which are below 2500'—suggests greater potential for solubility trapping of CO₂



Acknowledgements

- **Funding from the Kentucky Department of Energy Development and Independence (Energy and Environment Cabinet)**
- **Kentucky Consortium for Carbon Storage—new brine data from the KGS #1 Blan well**