Chapter 3: Geochemical Characterization of Formation Waters in Kentucky and Implications for Geologic Carbon Storage

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Introduction

With an estimated worldwide capacity of at least 1,100 billion short tons, deep saline aquifers are volumetrically the most significant reservoir for storage of CO_2 in underground geologic reservoirs (Holloway, 2001). Once in the reservoir, CO_2 can be stored or trapped in a variety of modes, including physical trapping beneath a low-permeability seal (e.g., shale, salt), retention as an immobile phase in pore space (residual trapping), dissolution into the formation fluids (solubility trapping), and involvement in mineral-forming reactions (mineral trapping). The chemistry of waters in the storage reservoir — formation waters — will be one of the main influences on solubility and mineral trapping. Over shorter periods of tens to hundreds of years in which a geologic storage project would be monitored, solubility trapping will be especially important because dissolution of CO_2 into water will be one of the fastest reactions to occur in the reservoir (Kharaka and others, 2006). Though volumetrically not as significant as injection of CO_2 into saline reservoirs for storage, injection of CO_2 into oil reservoirs for enhanced oil recovery represents another storage possibility. The magnitude of CO_2 dissolution in the formation waters will affect the degree to which CO_2 is available for interaction with the oil.

The importance of formation-water chemistry in geologic carbon storage provided the motivation for this study, which used heretofore archived formation-water chemistry data that have been effectively out of the public domain for more than 20 years. Specifically, we analyzed the stratigraphic and depth distribution of dissolved constituents in formation waters from the Illinois Basin in western Kentucky and Appalachian Basin in eastern Kentucky to make inferences about hydrogeologic compartmentalization and sealing in Paleozoic strata. To estimate CO_2 solubility trapping potential, temperature, pressure, and chemistry data were used as inputs to calculate CO_2 solubility with an equation of state for aqueous solutions containing Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, and SO_4^{2-}.

Methods

Data constituting the foundation for this study came from 356 analyses of formation-water chemistry collected primarily from oil wells and a smaller number of waste-disposal and water wells (Table 3.1). The data came from 12 counties in western Kentucky and 11 counties in eastern Kentucky. Geologically, the analyses provide a record of formation-water chemistry from the Illinois and Appalachian Basins, respectively (Figs. 3.1–3.2). The data were part of archived paper records at the Kentucky Geological Survey, and individual analyses were recorded on USGS-format water data sheets. Chemistry data on the USGS sheets typically included cation and anion concentrations reported in mg/L; water property measurements such as pH, conductivity, density, and total dissolved solids (TDS); and administrative data such as well name and operator, Carter coordinate location, depth and stratigraphic interval sampled, and location at the surface where the sample was collected (Fig. 3.3). Many of the samples were collected in the late 1960's and early 1970's, but the motivation for their collection is unknown.

Stratigraphically, the water samples were collected from rocks that range in age from Precambrian to Pennsylvanian; most are Mississippian (61 percent) in the Illinois Basin and Mississippian and Pennsylvanian (69 percent) in the Appalachian Basin (Figs. 3.4–3.5). In both basins the fewest samples came from Ordovician and older rocks. Approximately 51 percent and 70 percent of samples from the Illinois and Appalachian Basins, respectively, were collected from clastic reservoirs such as the St. Peter, Cypress, Jackson, and Caseyville sandstones. With the exception of about 13 percent of New Albany Shale samples from the Illinois Basin, the remaining samples from both basins were collected from carbonate reservoirs such as the Knox, Laurel, McClosky, and Fort Payne (Table 3.1). The samples span a depth range of 579 to –7,605 ft in eastern Kentucky and 1,550 to –7,765 ft in western Kentucky (depths referenced to sea level). The deepest water sample in western Kentucky, collected from the DuPont WAD No. 1 well in Jefferson County, is from the Cambrian Mount Simon or basal sandstone.

Table 3.1. Summary of water analyses by depth and general stratigraphic unit. Depth ranges are referenced to sea level. The “Example Formations” column lists the most frequently encountered specific stratigraphic units within each broad “Age–Rock Type” category. “Carbonate” refers to a mixture of limestone and dolomite. Where combined, the first abbreviation is the dominant rock type.

Age–Rock Type	*No. of Analyses*	*Depth Range (ft)*	*Example Formations*
Illinois Basin			
Pennsylvanian sandstone	18	155 to –1,088	Caseyville, Tradewater
Mississippian sandstone	94	556 to –2,464	Cypress, Tar Springs
Mississippian carbonate	42	579 to –2,330	Paint Creek, Ste. Genevieve
Devonian shale	30	457 to –1,190	New Albany
Devonian carbonate	6	–62 to –3,831	Boyle, Clear Creek, Jeffersonville
Silurian carbonate	4	377 to –1,798	Laurel/Osgood, Lego
Ordovician sandstone	2	–1,498 to –3,165	Knox–Rose Run, St. Peter
Ordovician carbonate	7	–1,094 to –4,137	Knox–Beekmantown
Cambrian dolomite	18	–951 to –7,605	Knox–Copper Ridge
Cambrian-Precambrian sandstone, crystalline rocks	1	–5,256	Mount Simon, basal sandstone, igneous/metamorphic basement
Appalachian Basin			
Pennsylvanian coal	2	1,480 to 1,200	Elkhorn Nos. 2 and 3 coals
Pennsylvanian sandstone	50	1,550 to –572	Salt sand, Pottsville, Lee
Mississippian sandstone	35	62 to –2,362	Berea, Weir, Maxon, Injun
Mississippian limestone	5	920 to –1,229	Newman, Big Lime
Silurian sandstone	2	–1,327, –1,962	Big Six
Silurian dolomite	17	–393 to –1,981	Corniferous, Lockport
Ordovician sandstone	6	–4,264 to –6,623	Knox–Rose Run, St. Peter
Ordovician dolomite	4	–2,325 to –5,181	Knox–Beekmantown, Wells Creek
Cambrian dolomite	6	–2,680 to –5,573	Knox–Copper Ridge
Cambrian limestone	3	–6,913 to –7,671	Maryville
Cambrian sandstone	1	–4,174	basal sandstone
Cambrian shale	2	–3,938, –6,687	Rogersville, Conasauga
Precambrian crystalline rocks	1	–7,765	igneous-metamorphic basement

In eastern Kentucky, the deepest sample was collected from Precambrian metamorphic-igneous basement rock in the Inland Gas Inland No. 533 well in Boyd County (Table 3.1).

The counties for which water data were analyzed for this report reflect, in large part, an attempt to rank areas in Kentucky considered most prospective for geologic sequestration. For example, the eastern Kentucky counties lie on or near the Big Sandy River, which is an important corridor for present and future coal-fired plants. Similarly, in western Kentucky the analyzed counties include parts of the Green and Ohio River corridors. Data from the 23 counties discussed here represent a first phase of analysis, and future work will broaden the area of investigation. Indeed, a second phase of work has begun, and it will include analysis from counties coinciding with important river corridors along which existing and future coal-fired plants are or will be located.

In each basin, the chemistry data were analyzed to determine the main dissolved constituents by general age and rock-type categories (Table 3.1). The age–rock type categories provide a framework for analyzing temporal and stratigraphic variations in dissolved

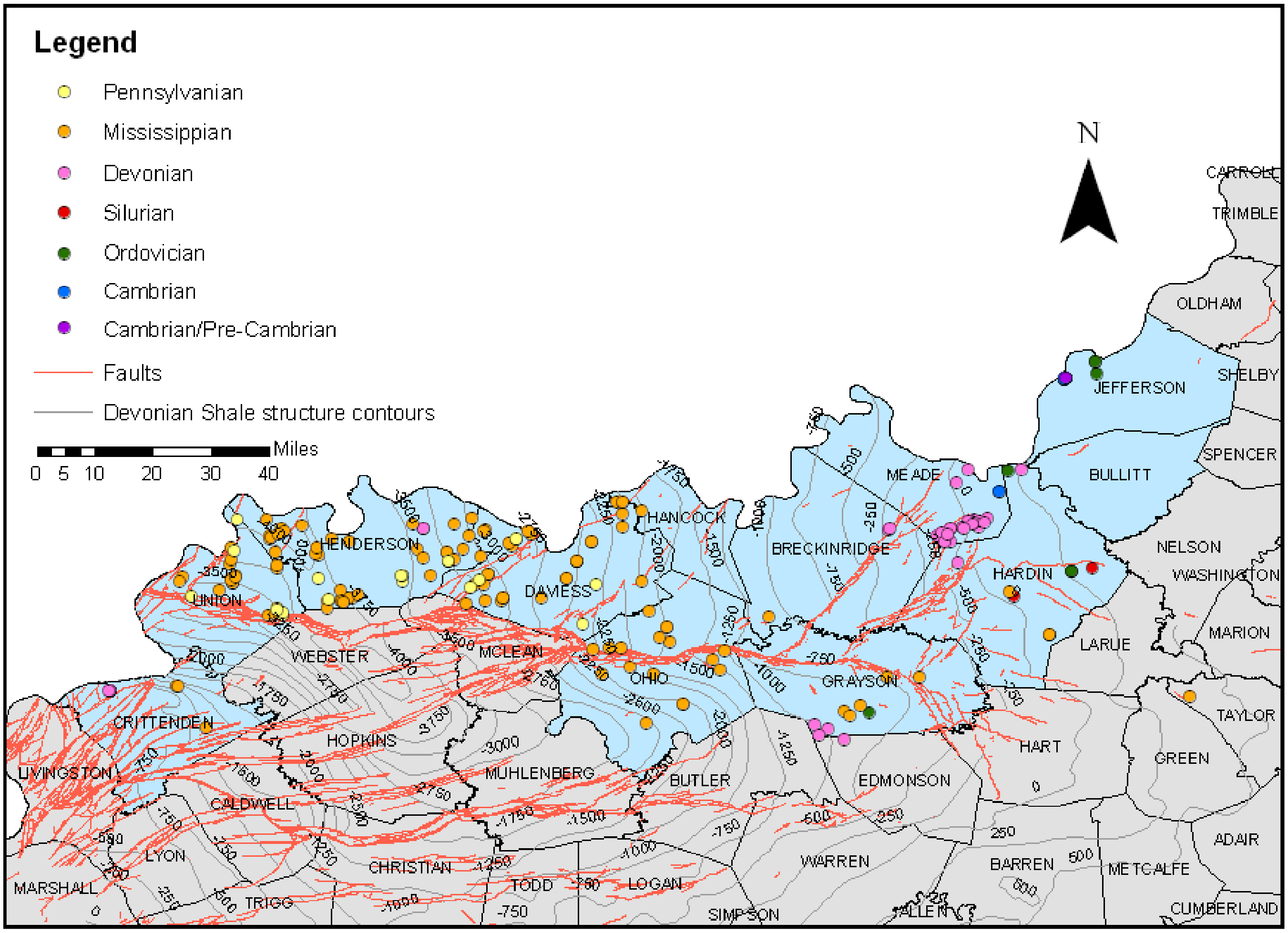


Figure 3.1. Locations and ages of rocks from which water samples were collected in western Kentucky.

constituents and the influence of general rock type on formation-water chemistry. The variation in dissolved constituents, especially Na^+ and Cl^-, also provides a basis for inferring the origin of the formation waters and processes (e.g., evaporation and mixing) that affected their composition.

The chemistry data also provide inputs for calculating the solubility of CO_2 in the formation waters. Solubility was estimated using an equation of state for aqueous solutions containing Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, and SO_4^{2-} from Duan and Sun (2003) and Duan and others (2006). The equation of state covers a wide range of temperature (273 to 533 K or 32 to 571°F), pressure (0 to 2,000 bars or 0 to 29,007 psi), and ionic strength (0 to 4.5 molality of salts) and predicts solubility at two-phase coexistence (vapor-liquid, liquid-liquid). Solubility of CO_2 is calculated by:

$$\ln m_{CO2} = \ln y_{CO2} Ø_{CO2} P - \mu_{CO2}/RT$$
$$-2\lambda_{CO2-Na}(m_{Na} + m_K + 2m_{Ca} + 2m_{Mg})$$
$$-\zeta_{CO2\text{-}Na\text{-}Cl} m_{Cl}(m_{Na} + m_K + m_{Mg} + m_{Ca})$$
$$+ 0.07 m_{SO4}$$

where T is absolute temperature in Kelvin, P is total pressure in bars, R is the universal gas constant (8.314 $JK^{-1}mol^{-1}$), m is the molality of components dissolved in water, y_{CO2} is the mole fraction of CO_2 in the vapor phase, $Ø_{CO2}$ is the fugacity coefficient of CO_2, μCO_2 is the standard chemical potential of CO_2 in liquid phase, $\lambda_{CO2}-Na^+$ is the interaction parameter between CO_2 and Na^+ and $\zeta_{CO2-Na+-Cl-}$ is the interaction parameter between CO_2 and Na^+ and Cl^-. Previously, a complex iterative process was needed to solve for the fugacity coefficient, $Ø_{CO2}$; however, Duan and others (2006) provided a noniterative equation to calculate $Ø_{CO2}$ as a function of temperature (T) and pressure (P):

$$Ø_{CO2} = c_1 + (c_2 + c_3T + c_4/T + c_5/(T-150))P$$
$$+ (c_6 + c_7T + c_8/T)P^2$$
$$(c_9 + c_{10}T + c_{11}/T)\ln P + (c_{12} + c_{13}T)/P$$
$$+ c_{14}/T + c_{15}T^2$$

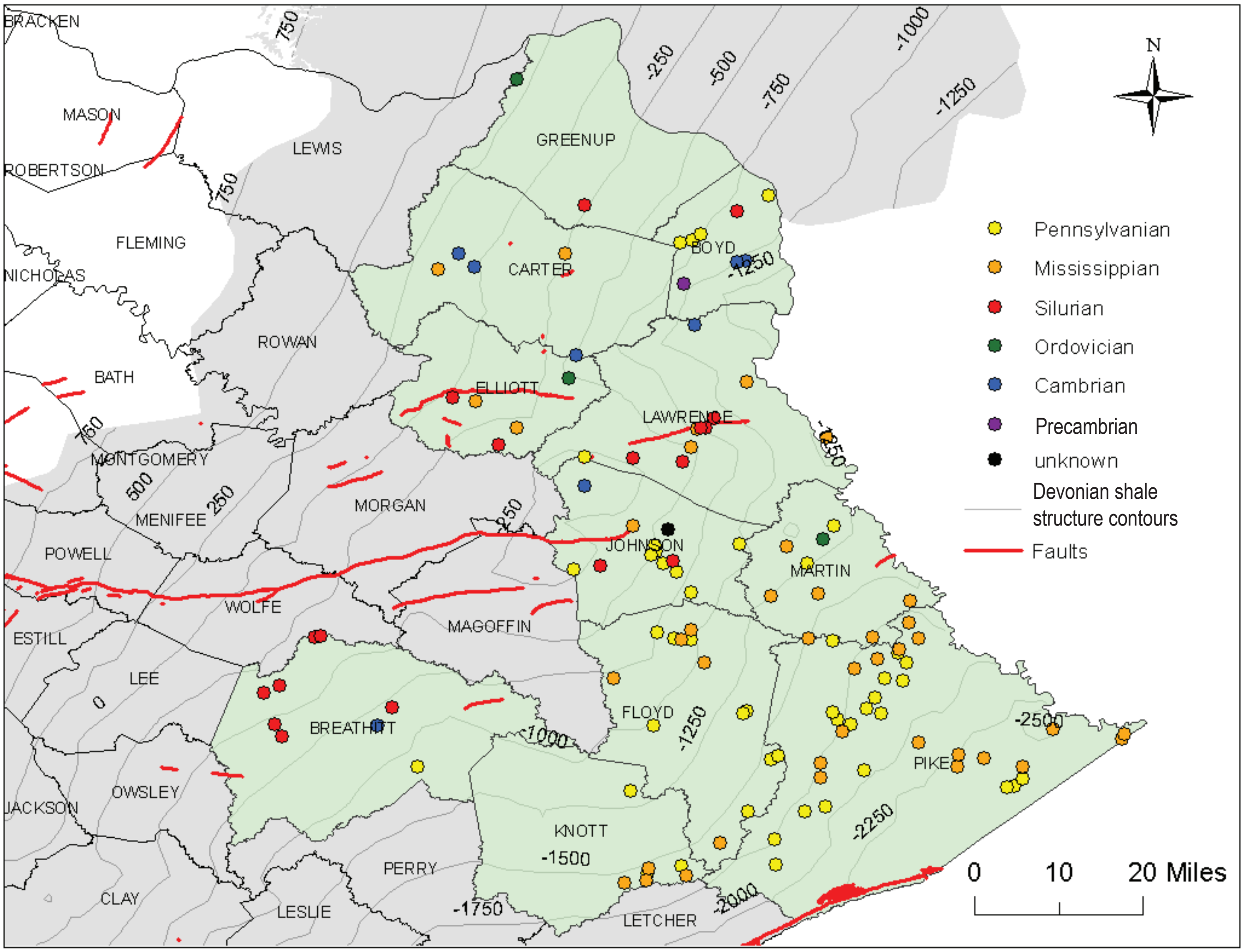


Figure 3.2. Locations and ages of rocks from which water samples were collected in eastern Kentucky.

where T is in Kelvin and P in bars. The parameters c_1, c_2, c_3, … c_{15} are provided in Duan and others (2006) for specific temperature and pressure ranges and were fitted to the values of $Ø_{CO2}$ as calculated from the equation of state from Duan and others (1992).

Reservoir temperature was estimated using the equation:

$$\text{Temperature } (^\circ\text{F}) = (0.0235 \text{ X sample depth}) + 54^\circ\text{F}$$

where 0.0235 is the geothermal gradient (°F/ft), sample depth (ft) is the approximate midpoint depth over the interval from which the sample was collected referenced to the ground surface, and 54°F is the average surface temperature in Kentucky. Reservoir pressure, assumed to be near or at hydrostatic pressure, was estimated with the equation:

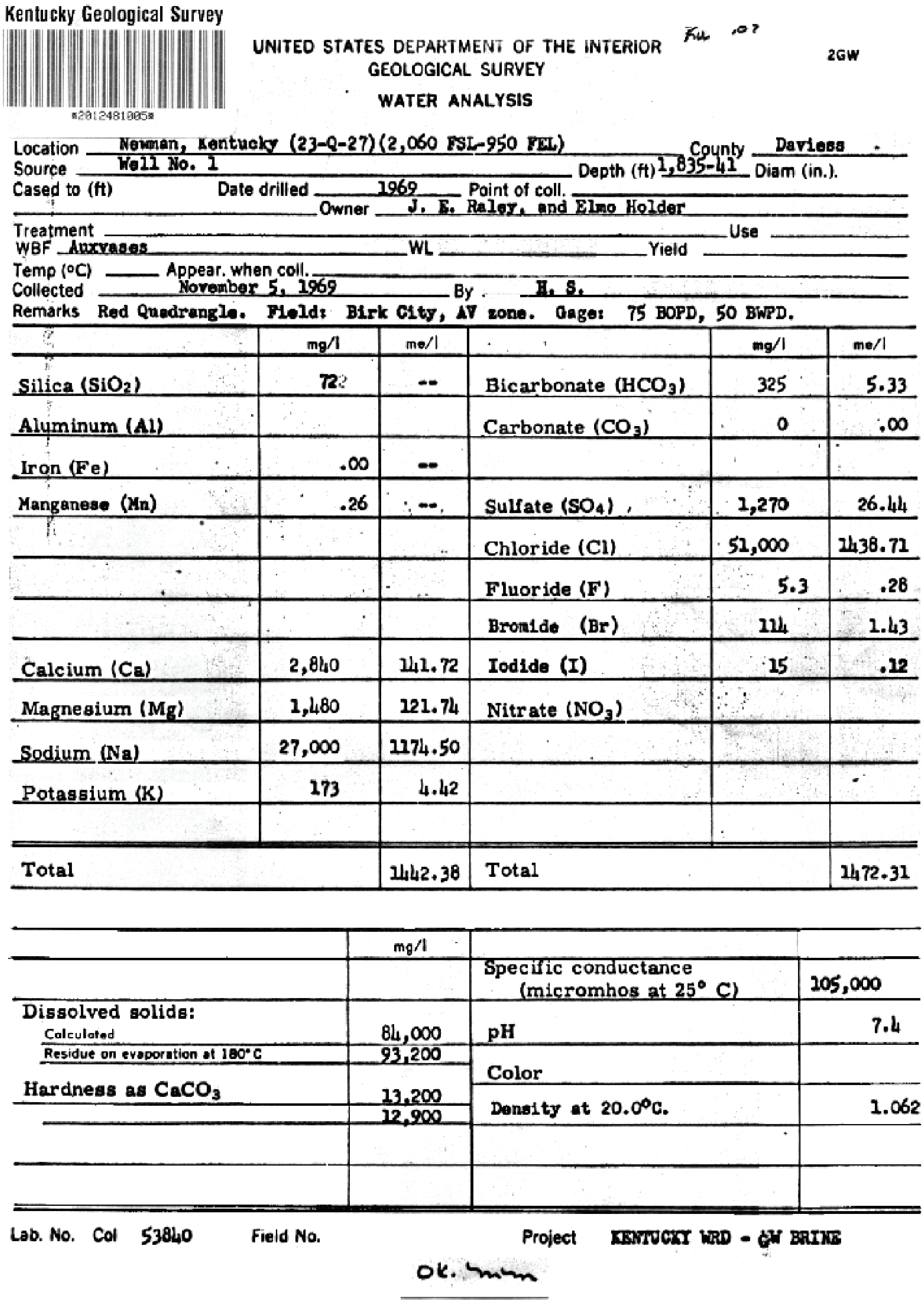
$$\text{Pressure (psi)} = 0.433 \text{ X sample depth}$$

where 0.433 is the average hydrostatic gradient (psi/ft) and sample depth (ft) is the approximate midpoint depth over the interval from which the sample was collected, referenced to sea level.

Results

Major Element Chemistry

Chloride (Cl^-) is the dominant anion in Appalachian and Illinois Basin samples, with concentrations on the order of 103 to 105 mg/L (Table 3.2). The large standard deviations with Cl^- and other anions and cations for a given age–rock type category results from averaging values for samples that were collected over a wide range of burial conditions. In the Illinois Basin, Cl^- is followed by SO_4^{2-} (102 to 103 mg/L), HCO_3^- (102 to 103 mg/L), Br^- (101 to 102 mg/L), and nearly equal amounts of F^- and I^- (100 to 101 mg/L), in order of decreasing concentration. The sequence, however,



Kentucky Geological Survey

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UNITED STATES DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY
WATER ANALYSIS

Location Newman, Kentucky (23-Q-27)(2,060 FSL-950 FEL) County Daviess
Source Well No. 1 Depth (ft) 1,835-41 Diam (in.).
Cased to (ft) Date drilled 1969 Point of coll.
Owner J. E. Raley, and Elmo Holder
Treatment Use
WBF Auxvases WL Yield
Temp (°C) Appear. when coll.
Collected November 5, 1969 By H. S.
Remarks Red Quadrangle. Field: Birk City, AV zone. Gage: 75 BOPD, 50 BWPD.

	mg/l	me/l		mg/l	me/l
Silica (SiO_2)	72	--	Bicarbonate (HCO_3)	325	5.33
Aluminum (Al)			Carbonate (CO_3)	0	.00
Iron (Fe)	.00	--			
Manganese (Mn)	.26	--	Sulfate (SO_4)	1,270	26.44
			Chloride (Cl)	51,000	1438.71
			Fluoride (F)	5.3	.28
			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: Calculated	84,000	pH	7.4
Residue on evaporation at 180°C	93,200		
		Color	
Hardness as $CaCO_3$	13,200	Density at 20.0°C.	1.062
	12,900		

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Figure 3.3. Example of USGS water data sheet that, along with other data sheets, was the principal source of data for this study.

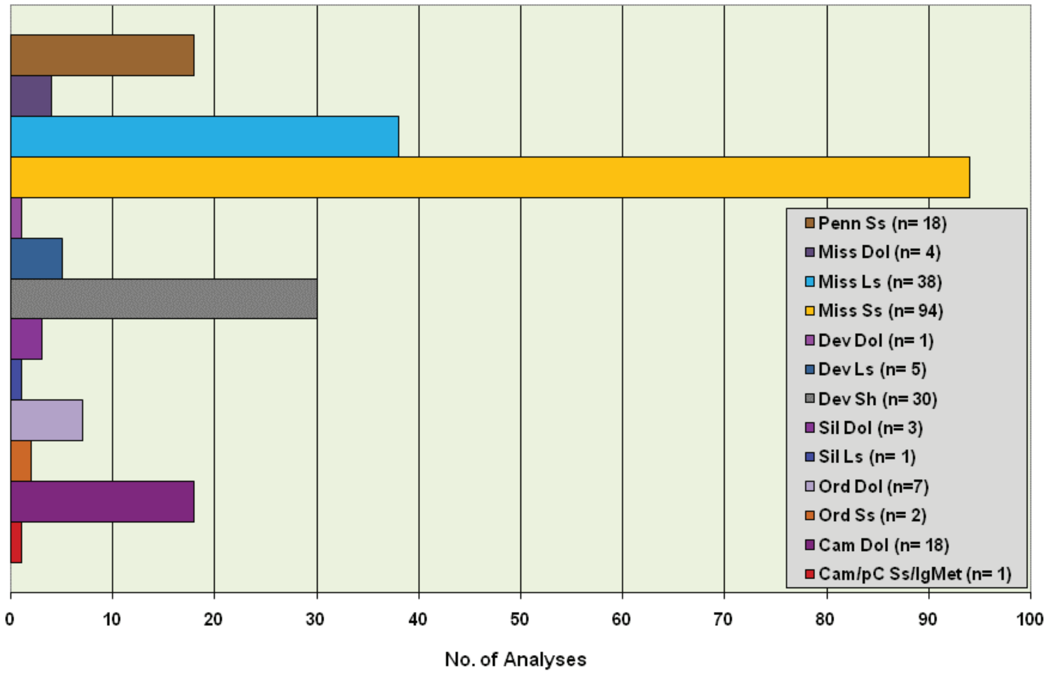

Figure 3.4. Stratigraphic distribution of formation-water data from western Kentucky (Illinois Basin).

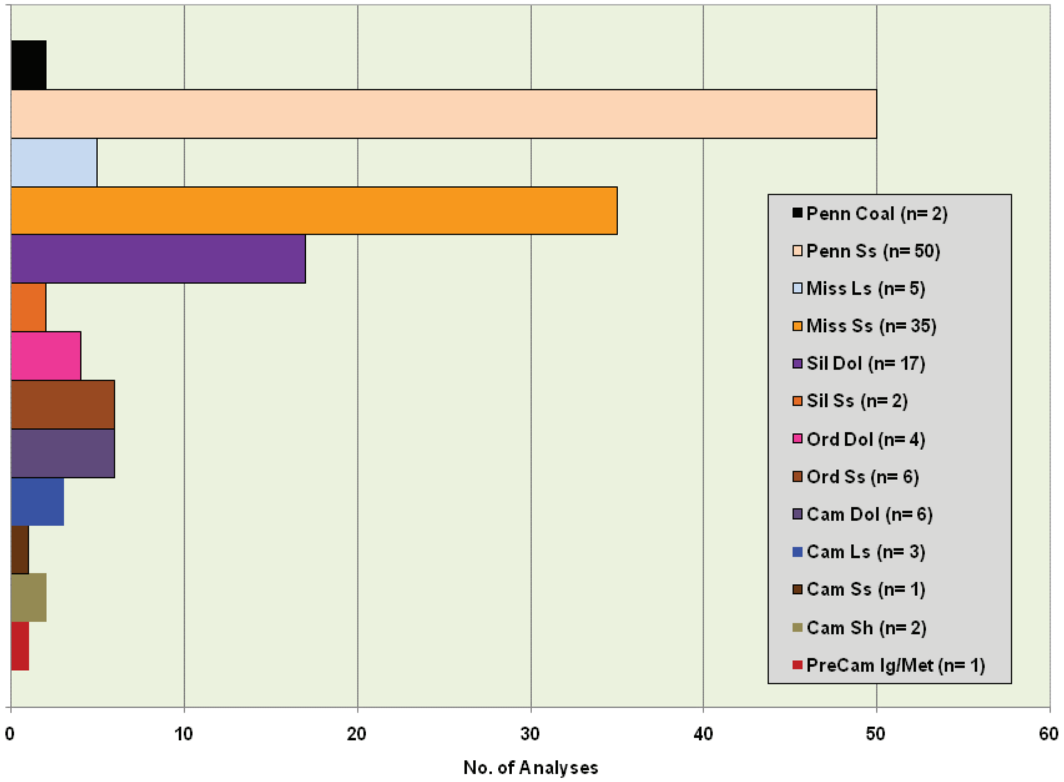

Figure 3.5. Stratigraphic distribution of formation-water data from eastern Kentucky (Appalachian Basin).

Table 3.2. Average (with one standard deviation) formation-water anion concentrations (mg/L). The number of measurements per average is in parentheses. Carbonate means a mixture of limestone and dolostone. Where combined, the first is the dominant rock type.

Age–Rock Type	*Cl^-*	*SO_4^{-2}*	*HCO_3^{-}*	*Br*	*F*	*I*
Illinois Basin						
Pennsylvanian sandstone	8,475 ± 5,492 (16)	1,614 ± 1,830 (16)	1,099 ± 1,249 (14)	21 ± 10 (10)	2.0 ± 2.4 (8)	1.2 1.5 (10)
Mississippian sandstone	27,735 ± 19,861 (72)	1,152 ± 1,465 (66)	349 ± 318 (64)	77 ± 59 (43)	1.5 ± 1.0 (39)	5.1 ± 3.7 (41)
Mississippian carbonate	40,618 ± 24,631 (36)	1,326 ± 1,007 (34)	229 ± 228 (32)	126 ± 78 (15)	2.9 ± 2.3 (18)	9.8 ± 5.1 (14)
Devonian shale	46,880 ± 16,498 (30)	219 ± 163 (30)	1,190 ± 671 (5)	204 ± 50 (23)	nd	nd
Devonian carbonate	27,605 ± 36,419 (6)	367 ± 233 (5)	340 ± 271 (5)	97 ± 36 (3)	1.6 (1)	1.6 ± 1.0 (3)
Silurian carbonate	25,580 ± 26,016 (4)	811 ± 748 (4)	307 ± 265 (4)	49 ± 62 (3)	1.6 ± 1.5 (3)	1.6 ± 2.6 (3)
Ordovician carbonate sandstone	9,026 ± 4,395 (11)	1,644 ± 751 (10)	274 ± 120 (8)	42 ± 19 (5)	1.8 ± 0.2 (4)	1.6 ± 1.8 (5)
Cambrian dolomite	26,130 ± 33,123 (16)	1,950 ± 1,022 (16)	263 ± 110 (16)	47 ± 26 (6)	1.8 ± 0.4 (13)	0.8 ± 0.7 (6)
Appalachian Basin						
Pennsylvanian sandstone	26.860 ± 28,280 (49)	10 ± 19 (39)	143 ± 150 (41)	202 ± 162 (30)	0.6 ± 0.5 (16)	7.3 ± 3.5 (30)
Mississippian carbonate sandstone	73,131 ± 40,648 (35)	50 ± 108 (29)	34 ± 48 (32)	313 ± 162 (30)	1.5 ± 1.5 (14)	11.1 ± 14 (30)
Silurian carbonate sandstone	116,555 ± 44,966 (19)	432 ± 488 (19)	96 ± 123 (19)	625 ± 572 (19)	4.6 ± 2.3 (11)	17.3 ± 9.9 (19)
Ordovician carbonate sandstone	125,639 ± 33,476 (8)	245 ± 192 (7)	140 ± 94 (7)	689 ± 403 (8)	5.5 ± 2.0 (6)	30.1 ± 9.9 (8)
Cambrian carbonate sandstone	112,064 ± 258 (11)	372 ± 353 (11)	83 ± 50 (11)	627 ± 375 (12)	7.6 ± 1.8 (7)	29.7 ± 16 (11)

does not apply to samples from the New Albany Shale, which have an average HCO_3^- value equal to 1,190 ±671 mg/L and exceed SO_4^{-2} by an order of magnitude. The average HCO_3^- value in the New Albany is the highest recorded in the study.

Samples from the Appalachian Basin, in contrast, have very different anion concentrations, both in terms of relative proportion and absolute value (Table 3.2). After Cl^-, the concentrations of anions, in decreasing order, are Br^- (102 mg/L), SO_4^{2-} (101 to 102 mg/L) or HCO_3^- (101 to 102 mg/L); and I^- concentrations (101 to 102 mg/L) are distinctly higher than F^- (100 to 101 mg/L). When comparing similar-age units and rock types between basins, SO_4^{2-} and HCO_3^- are higher in the Illinois Basin samples and Br^- and I^- are higher in Appalachian Basin samples.

Cations that belong to the alkaline metals (e.g., K+, Na+) and alkaline earth metals (e.g., Ca^{2+}, Mg^{2+}) primarily occur in solution as ionic-bonded compounds with Cl^- (Drever, 1988), and therefore it is appropriate to analyze cation concentrations and distribution as chloride compounds (Hanor, 1994; Worden, 1996). The analysis shows that Na^+ is the dominant cation and has a strong positive correlation with Cl^- (Table 3.3, Fig. 3.6). This observation accords with analyses of formation waters from sedimentary basins around the world (Hanor, 1994). Once in solution, Na^+ tends to be nonreactive with rock-forming minerals, and consequently

Table 3.3. Average (with one standard deviation) formation-water cation concentrations (mg/L). Number of measurements per average is in parentheses. Carbonate means a mixture of limestone and dolostone. Where combined, the first is the dominant rock type.

Age–Rock Type	*Na^+*	*Ca^{2+}*	*Mg^{2+}*	*K^+*
Illinois Basin				
Pennsylvanian sandstone	5,227 ± 2,798 (11)	346 ± 449 (14)	70 ± 71 (14)	26 ± 19 (10)
Mississippian sandstone	16,723 ± 10,583 (63)	1,419 ± 2,138 (64)	512 ± 508 (63)	157 ± 522 (43)
Mississippian carbonate	19,546 ± 13,214 (29)	2,817 ± 4,101 (30)	1,061 ± 729 (30)	112 ± 132 (16)
Devonian shale-carbonate	24,610 ± 8,418 (29)	2,642 ± 1,399 (30)	1,352 ± 541 (30)	478 ± 288 (25)
Silurian carbonate	8,547 ± 10,518 (3)	670 ± 897 (3)	576 ± 815 (3)	32 ± 44 (2)
Ordovician carbonate-sandstone	3,943 ± 2,566 (4)	812 ± 261 (7)	361 ± 110 (6)	133 ± 31 (3)
Cambrian dolomite-sandstone	12,291 ± 13,249 (16)	3,456 ± 5,161 (16)	886 ± 1,177 (16)	206 ± 124 (13)
Appalachian Basin				
Pennsylvanian sandstone	15,396 ± 14,883 (37)	3,529 ± 4,388 (38)	743 ± 852 (37)	197 ± 381 (34)
Mississippian carbonate-sandstone	33,643 ± 17,643 (28)	9,727 ± 5,621 (28)	2,090 ± 1,296 (28)	278 ± 201 (27)
Silurian carbonate-sandstone	45,233 ± 16,168 (17)	18,200 ± 9,423 (17)	4,682 ± 2,913 (17)	1,056 ± 1,022 (17)
Ordovician carbonate-sandstone	42,971 ± 8,143 (6)	29,341 ± 7,028 (5)	4,745 ± 2,140 (5)	2,975 ± 1,348 (6)
Cambrian dolomite-sandstone	40,871 ± 10,004 (7)	21,683 ± 12,808 (7)	3,200 ± 1,773 (7)	2,286 ± 1,244 (7)

its distribution can be used to infer processes such as dilution and evaporation that influence compositional evolution (Hanor, 1994). Most of the samples in this study show a well-defined linear distribution for Na^+ versus $Cl^–$ that intersects the average NaCl composition of seawater (Fig. 3.7). This distribution suggests that most samples in this study have a marine origin.

After Na^+, the concentration of cations, in decreasing order, is Ca^{2+}, Mg^{2+}, and K^+ (Fig. 3.6, Table 3.3); this relative distribution is similar to formation waters in other sedimentary basins (Hanor, 1994). Plots of Ca^{2+}, Mg^{2+}, and K^+ versus $Cl^–$ are similar to plots for Na^+ versus $Cl^–$, but often the slopes differ significantly. The difference implies that processes in addition to dilution and evaporation have affected water composition. For example, when compared to Na^+ versus $Cl^–$, plots for Mg^{2+} and K^+ versus $Cl^–$ for Cambrian-Ordovician Knox Group samples from the Appalachian Basin have significantly lower slopes (Fig. 3.8). The slope of Ca^{2+} versus $Cl^–$ for the same group of samples is slightly steeper compared to the slope of Na^{2+} versus $Cl^–$. Considered jointly, the shallower slope for Mg^{2+} and steeper slope for Ca^{2+} may reflect the process of dolomitization, in which Ca^{2+} is released into and Mg^{2+} taken out of the formation fluid according to the reaction:

$$2CaCO_3 + Mg^{2+} = CaMg(CO_3)_2 + Ca^{2+}.$$

Of the major cations typically measured, K^+ tends to have a distribution most dissimilar to that of Na^{2+}. The dissimilarity results, in large part, from the ease with which K^+, independent of $Cl^–$, is incorporated into clay minerals (Hem, 1992). A potential example of this is provided in the New Albany Shale, in which

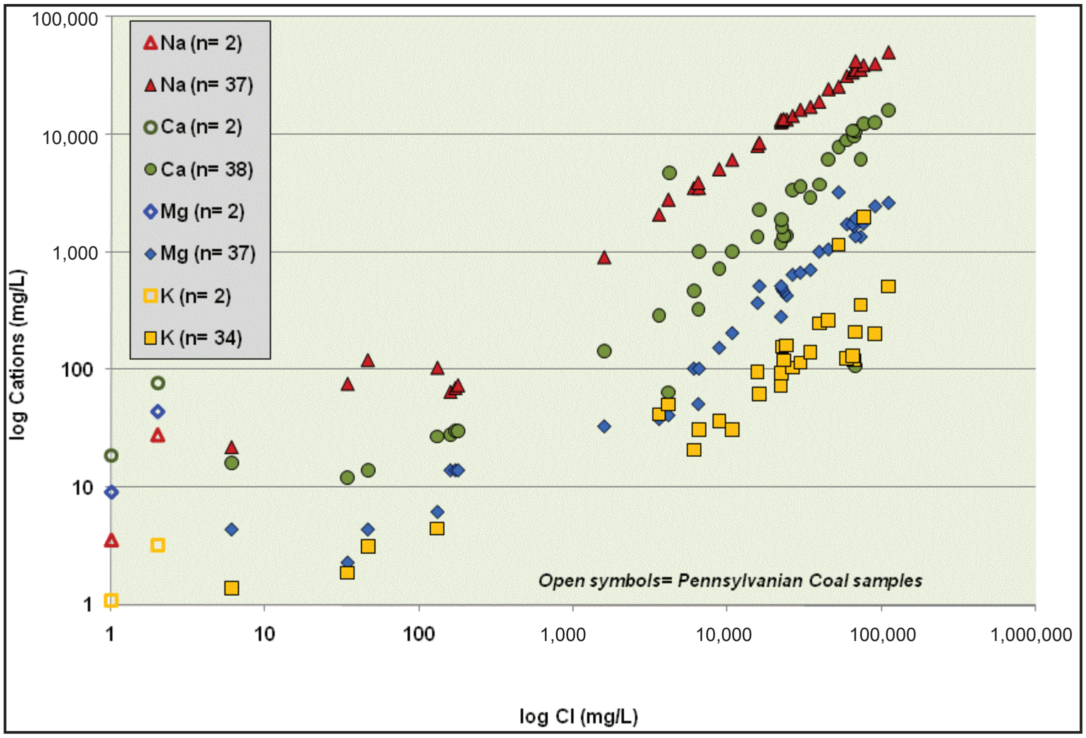

Figure 3.6. Na^+, Ca^{+2}, Mg^{+2}, and K^+ versus Cl for Pennsylvanian sandstone and coal reservoirs in eastern Kentucky (Appalachian Basin).

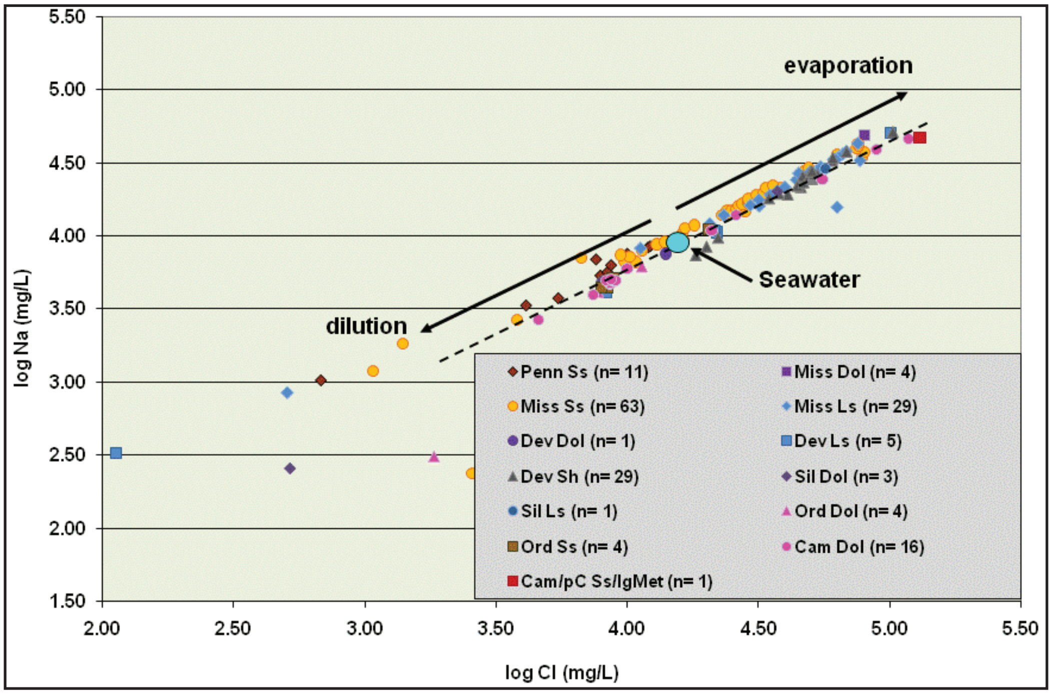

Figure 3.7. Log Na^+ versus log Cl by age–rock type in western Kentucky (Illinois Basin). Most data fall on or near a trend originating with a seawater composition subsequently altered by evaporation or dilution.

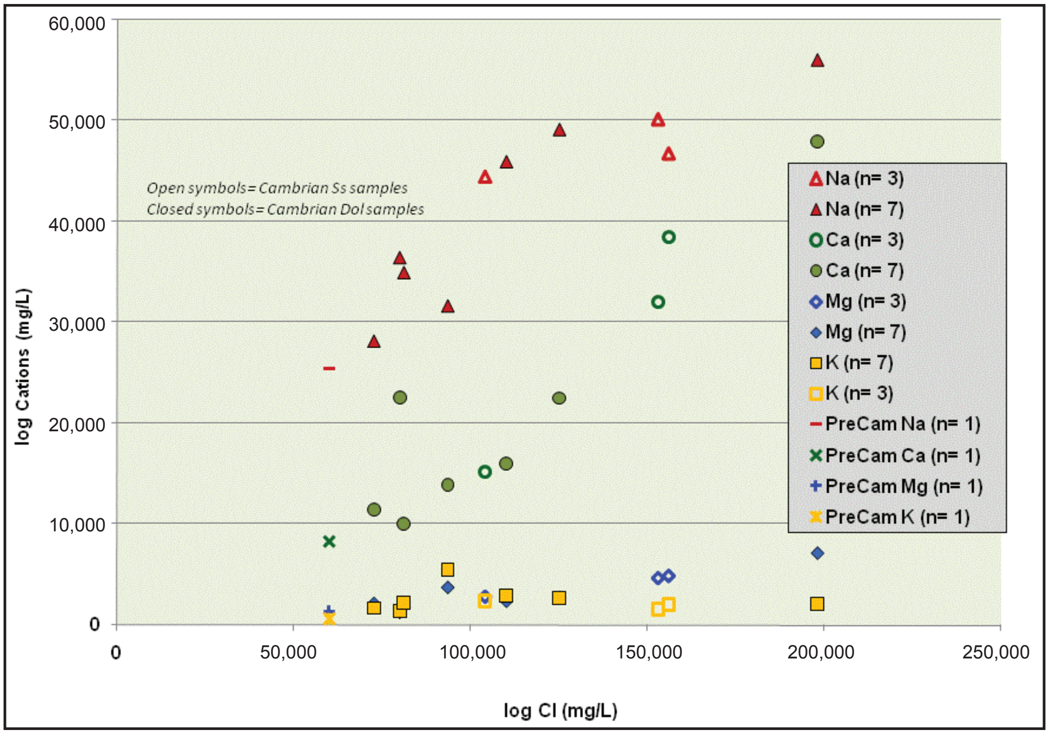

Figure 3.8. Na^+, Ca^{2+}, Mg^{2+}, and K^+ versus Cl^- for Ordovician-Cambrian sandstone and dolomite samples and a Precambrian igneous/metamorphic sample from eastern Kentucky (Appalachian Basin).

concentrations of K^+, Mg^{2+}, and Ca^{2+} vary significantly, whereas the concentration of Cl^- does not (Fig. 3.9).

Total Dissolved Solids

Total dissolved solids equals the total amount of solids (mg/L) remaining when a water sample is evaporated to dryness (Drever, 1988). This residual mass, called the residual TDS, represents the sum of all dissolved constituents. In addition to being measured through evaporation, TDS may also be calculated. The term "TDS" is equivalent to the term "salinity," and they are used interchangeably here.

When plotted versus depth, TDS values in the Appalachian Basin group into two populations (Fig. 3.10). A shallow population from 1,480 to –1,981 ft includes water samples from Pennsylvanian, Mississippian, and Silurian rocks. The shallow population is a fairly well-defined linear trend in which salinity increases approximately 230 mg/L per ft. Just below this shallow population is a small group of samples at approximately –2,200 ft that have salinities (approximately 25,000 to 150,000 mg/L) lower than what would be predicted by the trend of the shallow population. The group at –2,200 ft includes five samples from the Mississippian Berea Sandstone in Pike County and a sample from the Ordovician Wells Creek Dolomite in Greenup County. Geologic analysis shows that none of the wells are near faults, which would appear to preclude the possibility of meteoric water (i.e., rainwater) infiltration along a fault and into the reservoirs. Alternatively, the lower than expected salinities could result from field or analytical error but the occurrence of low salinity in five wells, all from the Berea Sandstone, suggests the possibility of an underlying geologic reason, at least for these samples.

A second population is defined by deeper TDS data distributed from –4,100 to –7,900 ft and includes samples from Ordovician, Cambrian, and Precambrian rocks (Fig. 3.10). Salinities for the deeper samples range from approximately 100,000 to 320,000 mg/L. The deeper data do not show a defined trend of salinity with depth, and indeed the deepest sample from the Precambrian is the most dilute in the deeper population. Over half of the deeper samples (53 percent) were collected from wells operated by Inland Gas Co. in Boyd County.

TDS values for samples from the Illinois Basin also define two populations, but the distribution of salinity versus depth differs from that for the Appalachian Basin (Fig. 3.11). Again, a shallow population is largely defined by data from 579 to –2,464 ft that includes Pennsylvanian, Mississippian, Devonian, and

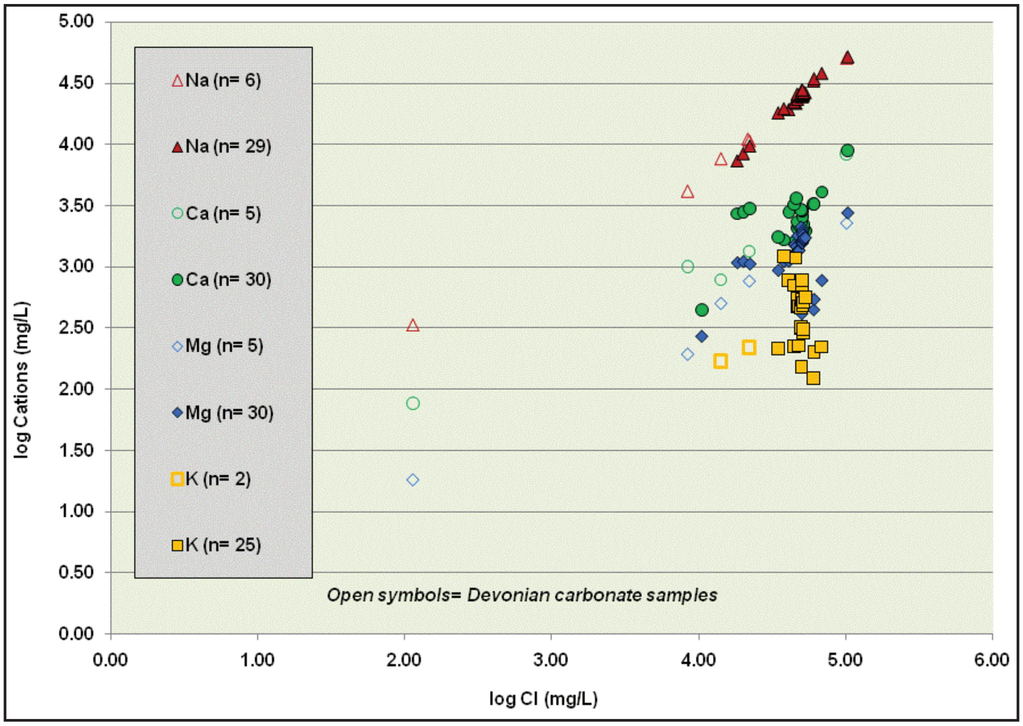

Figure 3.9. Na^+, Ca^{2+}, Mg^{2+}, and K^+ versus Cl^- for Devonian New Albany Shale samples from western Kentucky (Illinois Basin).

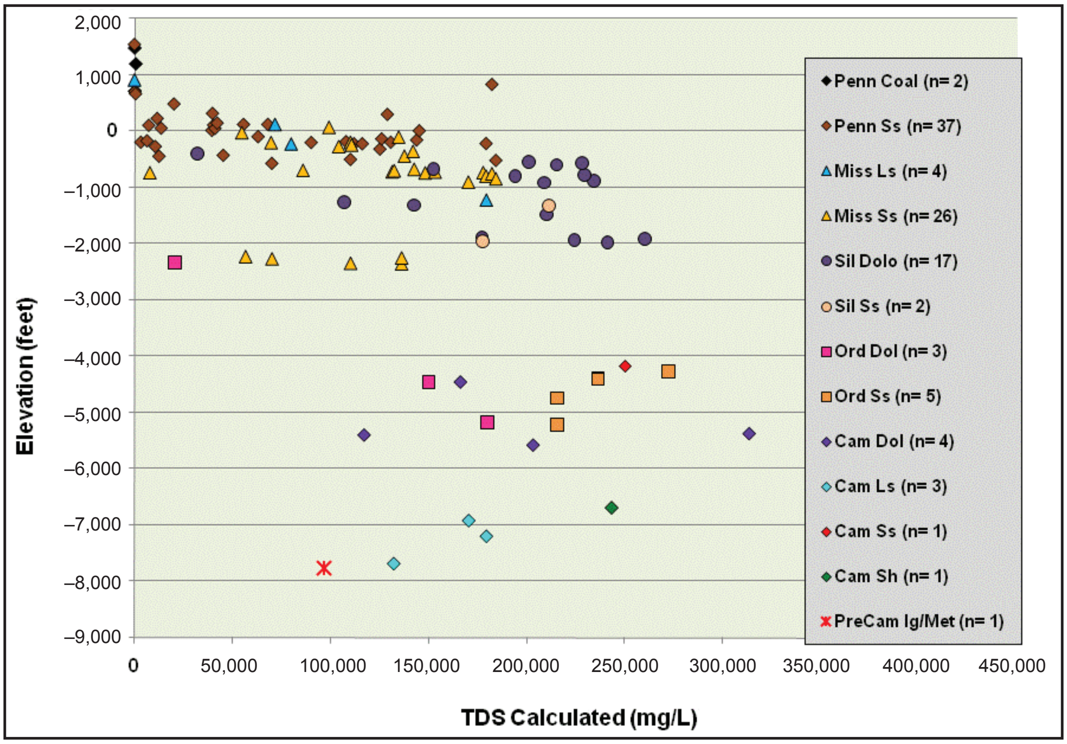

Figure 3.10. Salinity (TDS, mg/L) versus elevation (ft) by age–rock type for formation waters in eastern Kentucky (Appalachian Basin).

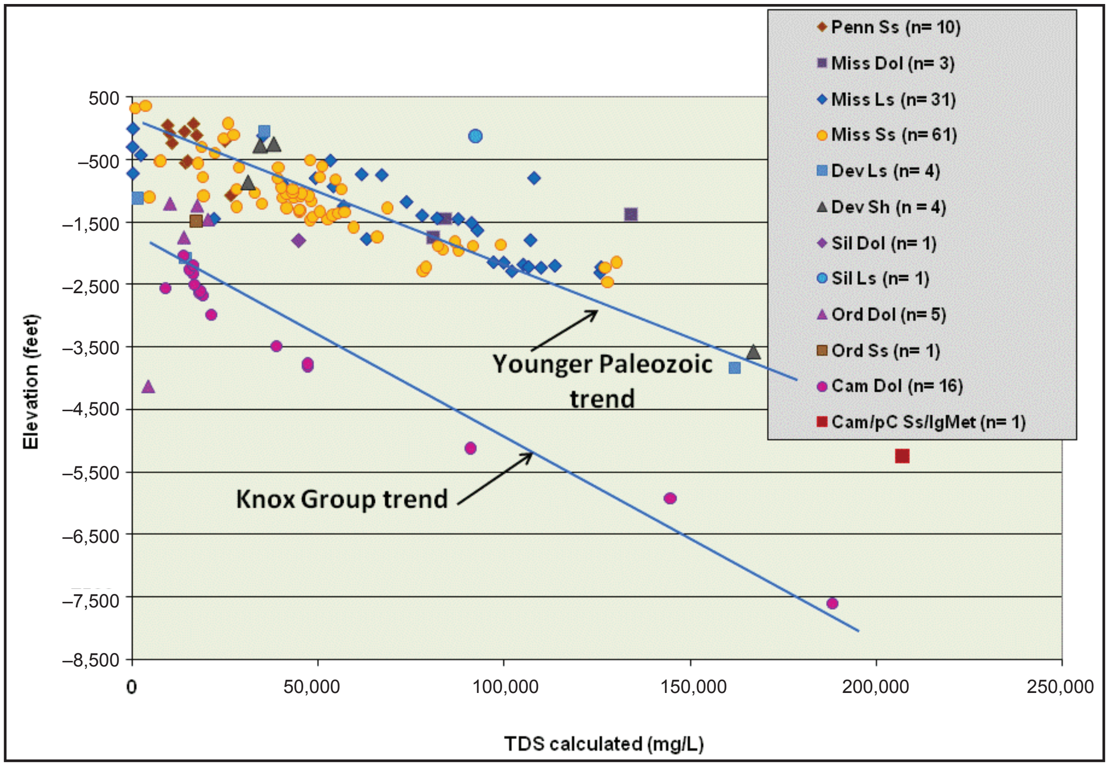

Figure 3.11. Salinity (TDS, mg/L) versus elevation (ft) by age–rock type for formation waters in western Kentucky (Illinois Basin).

Silurian samples. When projected deeper, the trend also includes Devonian samples at approximately –3,800 ft and a Precambrian sample at –5,256 ft. The trend through these samples defines an increase in salinity of approximately 80 mg/L per ft.

The second population of data is defined by samples from approximately –1,500 to –7,600 ft, most of which come from the Cambrian Knox Group (Fig. 3.11). The three deepest Knox samples (–5,125, –5,927, and –7,605 ft) were collected from the Shell M.D. Davis No. 1 well in Crittenden County, and most of the remaining Knox samples at –3,700 ft and shallower were collected from the DuPont WAD No. 1 and No. 2 wells in Jefferson County. Ordovician samples from the Wells Creek Dolomite and St. Peter Sandstone were also analyzed, and these samples plot near the intersection with the shallow data population. Consequently, it is difficult to determine if these samples should group with the shallow or Knox data. A best-fit line through the Knox samples defines an increase in salinity of approximately 60 mg/L per ft.

CO_2 Solubility

As illustrated in the equation of state from Duan and others (2006), the solubility of CO_2 in formation waters is a function of temperature and pressure, and the quantity and type of dissolved constituents and their interactions. Along with estimating the magnitude of dissolution, the relative strengths of these influences can be assessed by discriminating CO_2 solubility against these factors. One critical limitation is that the Duan and others (2006) equation of state is limited to samples having TDS values less than 200,000 mg/L. The limitation precluded us from calculating solubility in more-saline formation fluids that occurred in many of the age–rock type categories (Table 3.4). For example, 72 percent of Silurian and 56 percent of Ordovician samples from the Appalachian Basin had salinities too high to calculate CO_2 solubility. A further undesirable consequence of the salinity limitation is that it metamorphic-culled the high-salinity data, which, in turn, resulted in CO_2 solubility averages being higher for age–rock unit categories having many high-salinity samples. Other factors (e.g., pressure, temperature) being equal, however, the equation of state qualitatively predicts that more-saline samples will have lower CO_2 solubility compared to lower-salinity samples in the same age–rock type category.

In the Illinois Basin, CO_2 solubility plotted against TDS shows two sample population distributions, likely

Table 3.4. Average (with one standard deviation) CO_2 solubility in formation waters and the ranges of temperature and pressure over which solubilities were calculated. Where combined, the first is the dominant rock type. Number of analyzed samples is in parentheses after solubility averages with standard deviations.

Age–Rock Type	*Temperature (°C)*	*Pressure (bars)*	*Solubility Averages*
Illinois Basin			
Pennsylvanian sandstone	18–23	1–32	0.242 ± 0.229 (11)
Mississippian sandstone	15–51	1–73	0.536 ± 0.205 (66)
Mississippian limestone/ dolomite	16–49	1–68	0.520 ± 0.187 (6)
Devonian shale	25–67	8–106	0.392 ± 0.195 (5)
Devonian dolomite/ limestone	20–70	2–114	0.465 ± 0.387 (5)
Silurian dolomite/ limestone	20–43	1–53	0.239 ± 0.347 (4)
Ordovician sandstone	39, 65	44, 94	0.822 ± 0.024 (2)
Ordovician dolomite	36–73	32–123	0.806 ± 0.123 (5)
Cambrian dolomite	47–118	61–226	0.859 ± 0.090 (16)
Appalachian Basin			
Pennsylvanian sandstone/ coal	14–42	1–25	0.126 ± 0.141 (39)
Mississippian sandstone*	23–68	1–70	0.261± 0.172 (27)
Mississippian limestone	16–41	1–36	0.168 ± 0.137 (5)
Silurian dolomite/ sandstone*	31–48	12–58	0.369 ± 0.099 (7)
Ordovician dolomite/ sandstone*	58–109	69–197	0.646 ± 0.126 (4)
Cambrian limestone/ dolomite*	83–125	108–253	0.624 ± 0.082 (5)
Precambrian igneous/ metamorphic	126	230	0.824 (1)

*Samples with salinity greater than 200,000 mg/L and beyond the range of the Duan and others (2006) equation of state.

reflecting different solubility behavior (Fig. 3.14). For samples having TDS values greater than 50,000 mg/L, the data show a well-defined trend of decreasing CO_2 solubility with increasing TDS. The solubility of CO_2 decreases from approximately 0.75 to 0.55 mol/kg over the salinity range of 50,000 to 165,000 mg/L. The data in this region consist primarily of water samples from Mississippian limestone and sandstone reservoirs. When projected to lower-salinity and higher-CO_2 solubility values, the trend plots near Ordovician and Cambrian samples, many of which are from the Knox Group.

Other samples with TDS values less than 50,000 mg/L, in contrast, do not show a systematic variation in solubility with TDS, and the solubility values span a larger range from less than 0.1 to 0.75 mol/kg (Fig. 3.14). The lower-TDS values include samples primarily from Pennsylvanian and Mississippian sandstone reservoirs. The absence of a correlation in the lower-salinity regions suggests that other factors influence solubility. When CO_2 solubility is plotted against depth, which serves as a proxy for the effects of temperature and pressure, data from the lower-salinity Pennsylvanian and Mississippian reservoirs show a well-defined positive correlation (Fig. 3.15). Solubility increases with depth to approximately 2,000 ft, below which the data split into two populations. The lower population includes samples from Mississippian sand-

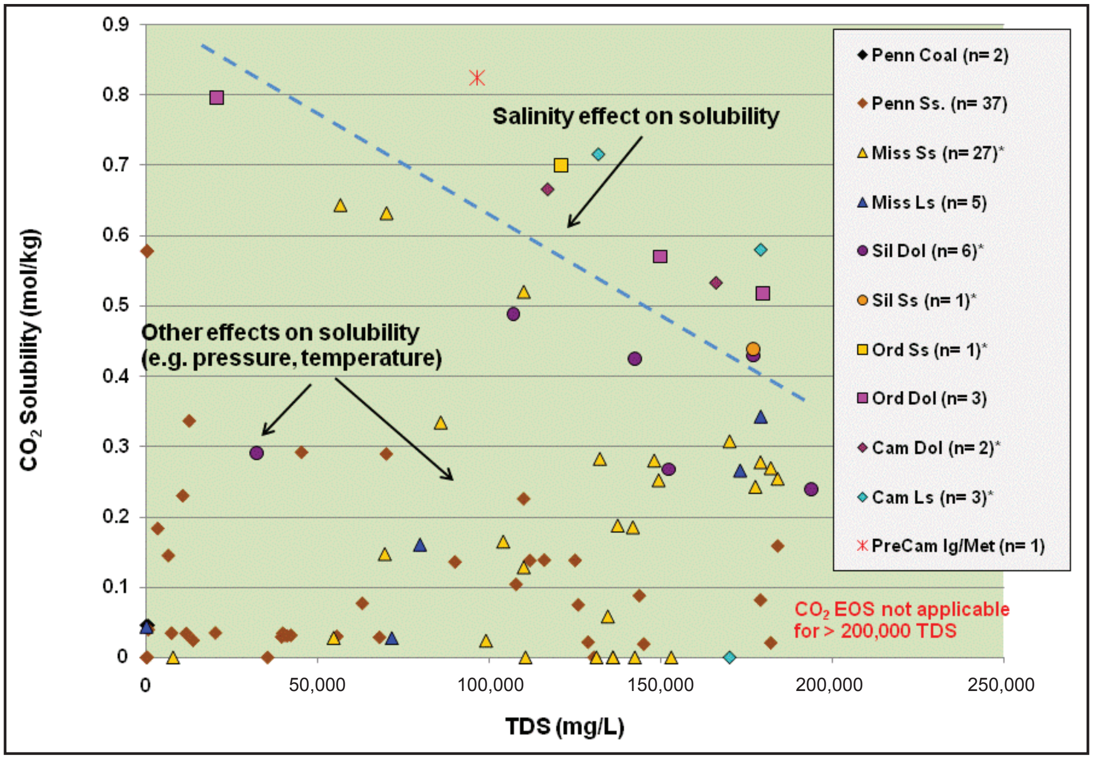

Figure 3.12. Salinity (TDS, mg/L) versus CO_2 solubility (mol/kg H_2O) by age–rock type category for samples in eastern Kentucky (Appalachian Basin).

stone and limestone reservoirs, and it shows a maximum for CO_2 solubility (approximately 0.7 mol/kg) at approximately 1,500 ft, below which solubility decreases. The second population consists of samples primarily from Cambrian dolomite (Knox Group) reservoirs and a smaller number from Ordovician sandstone (St. Peter) reservoirs. The second population shows increasing solubility to a depth of approximately 3,000 ft (solubility maximum of approximately 0.9 mol/kg), below which values decrease.

Similar to samples from the Illinois Basin, Appalachian Basin samples broadly define two regions of different CO_2 solubility behavior when plotted against salinity (Fig. 3.12). A group of higher-CO_2-solubility samples shows a moderately well-developed trend of increasing solubility (approximately 0.4 to 0.8 mol/kg) coincident with decreasing salinity (approximately 175,000 to 25,000 mg/L). This trend consists primarily of Precambrian, Cambrian, and Ordovician samples as well as some samples from Mississippian sandstone and Silurian dolostone reservoirs.

The majority of samples illustrated in Figure 3.12, however, show no systematic variation between CO_2 solubility and salinity. These samples, which come mostly from Pennsylvanian and Mississippian sandstone reservoirs, span a large range of salinity values (129 to 194,000 mg/L), and CO_2 solubility values are less than 0.32 mol/kg. Similar to the Illinois Basin samples, most of the Appalachian Basin Pennsylvanian and Mississippian samples come from relatively shallow depth (less than 2,500 ft), and when depth is plotted against CO_2 solubility, show a well-developed positive correlation (Fig. 3.13). In the same analysis, a second positive trend is defined by the Precambrian, Cambrian, and Ordovician samples.

Discussion

As stated in the "Introduction," the analysis of formation-water chemistry is an important part of assessing an area or basin for geologic carbon storage because it can provide information on potential cross-formation flow between aquifers and the presence of seals that subdivide basin strata into hydrogeologic compartments. When analyzed versus depth, salinity data in eastern and western Kentucky show evidence of a sealing interval.

Formation waters in Cambrian and Ordovician rocks are less saline than would be predicted by the shallow salinity gradients. With other factors such as pressure and temperature being constant, the solubility

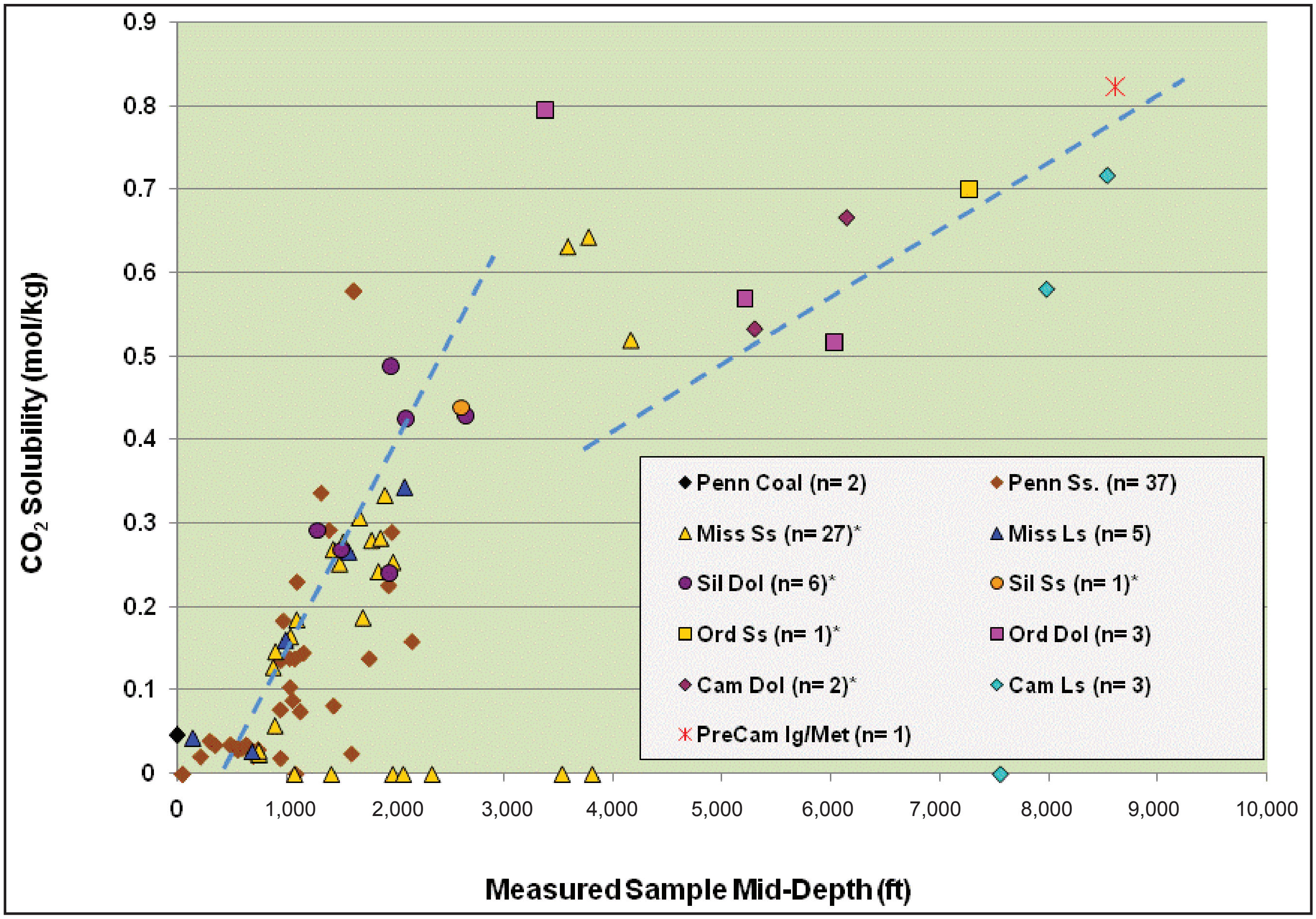

Figure 3.13. Measured depth (ft) versus CO_2 solubility (mol/kg H_2O) by age–rock type category for samples in eastern Kentucky (Appalachian Basin).

of CO_2 in water decreases with increasing salinity (Enick and Klara, 1990). This well-documented relationship thus suggests that more CO_2 could be dissolved into formation waters of Cambrian and Ordovician strata than would be predicted by the shallow salinity-solubility relations. The suggestion is supported by the CO_2 solubility calculations using the Duan and others (2006) equation of state, which show that the highest CO_2 solubilities in this study (approximately 0.65 to 0.86 mol/kg H_2O) are in samples from Ordovician and Cambrian rocks (Table 3.4, Figs. 3.12, 3.14).

The dissolution of CO_2 into formation water, or solubility trapping, is represented by the following reactions:

$$CO_2(g) + H_2O \leftrightarrow H_2CO_3$$
$$H_2CO_3 \leftrightarrow H^+ + HCO_3^-$$
$$HCO_3^- \leftrightarrow H^+ + CO_3^{-2}.$$

The main benefit of solubility trapping is that once CO_2 is dissolved, it no longer exists as a separate phase, be it gas or supercritical fluid, thereby removing the buoyancy forces that would cause it to migrate upward. Reservoir simulations suggest that, over tens of years, up to 30 percent of the injected CO_2 could dissolve in the formation water (Doughty and others, 2001). On a basin scale and over a longer period, modeling suggests that all injected CO_2 could dissolve into the formation water (McPherson and Cole, 2000). The carbonate species (e.g., HCO_3^-, CO_3^{-2}) that evolve from the dissociation of carbonic acid (H_2CO_3) in the above series of reactions also become available for incorporation into minerals such as calcite ($CaCO_3$) and magnesite ($MgCO_3$) through a process called mineral trapping. Mineral trapping is considered the most stable form of geologic storage, but it occurs over longer periods, on the order of thousands of years (Gunter and others, 1993).

Further enhancing the potential for storage in the Cambrian and Ordovician reservoirs is depth, which in

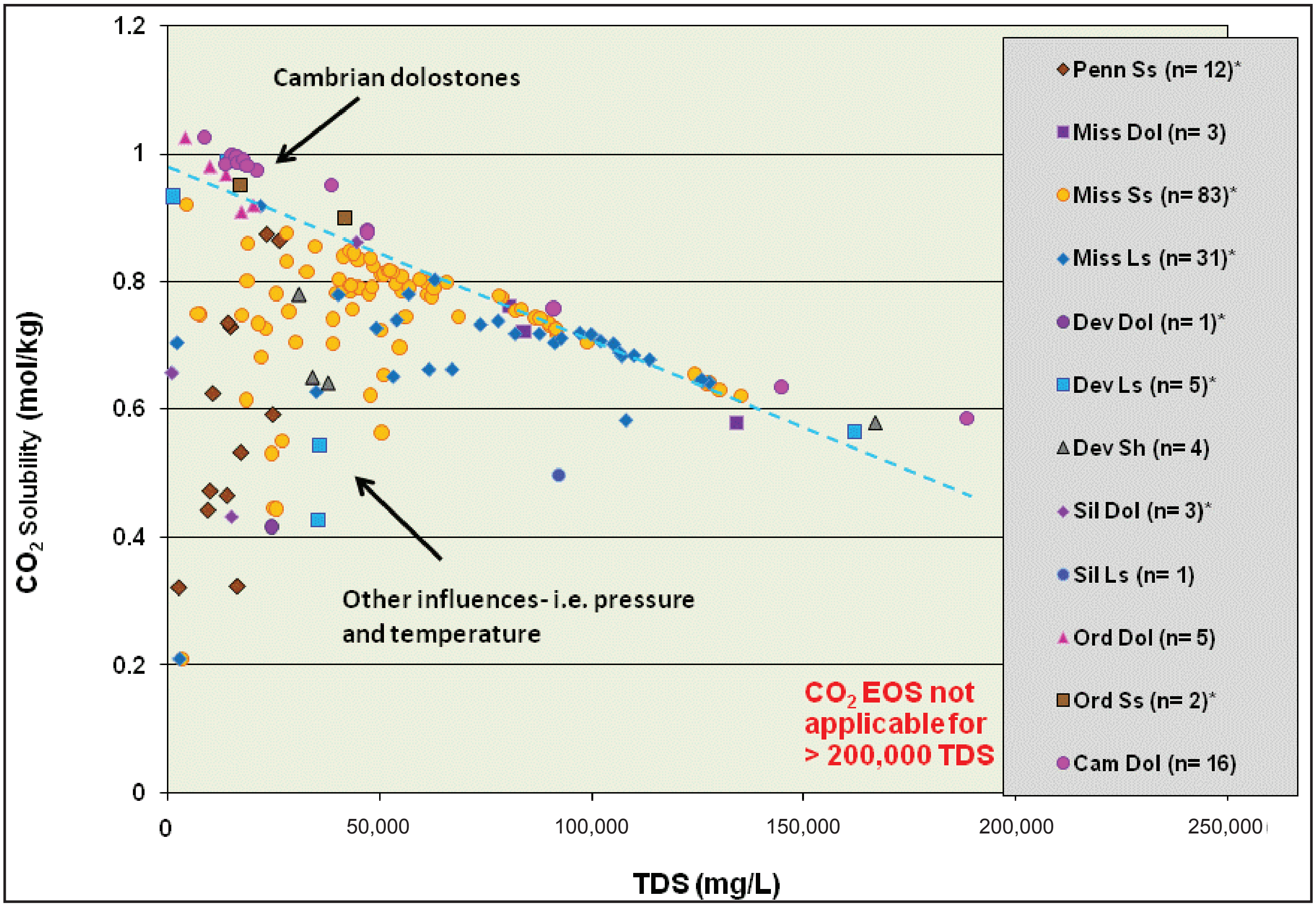

Figure 3.14. Salinity (TDS, mg/L) versus CO_2 solubility (mol/kg H_2O) by age–rock type category for samples in western Kentucky (Illinois Basin).

most cases is greater than the 2,500-ft threshold considered necessary to have supercritical CO_2 in the reservoir. In the Illinois Basin, samples from Cambrian and Ordovician reservoirs show increasing CO_2 solubility that reaches a maximum at about 3,000 ft and then decreases (Fig. 3.15). The subsequent decrease possibly reflects the interplay between temperature, pressure, and salinity in which increasing temperature results in a net decrease in CO_2 solubility. Cambrian and Ordovician samples in the Appalachian Basin, in contrast, show a continuous increase in solubility with depth (Fig. 3.13). The reason for the difference in solubility behavior with depth between basins is not clear and demonstrates the need to perform sensitivity studies to isolate the magnitude of influence of temperature, pressure, and salinity on CO_2 solubility.

Summary

This report is one of the first studies of formation-water chemistry in the context of geologic carbon storage in Kentucky. The water-chemistry data include samples from most Paleozoic reservoirs in the Illinois Basin of western Kentucky and the Appalachian Basin of eastern Kentucky. Important findings from this study are:

1. Formation waters in both basins consist primarily of Na^+ and Cl^-. The distribution of these and other species (e.g., Ca^{2+}, Mg^{2+}, K^+) suggests that the formation waters were derived from seawater and subsequently altered by evaporation, dilution, and water-rock interaction.
2. Salinity versus depth trends show the likely presence of an aerially extensive seal interval in Upper Ordovician rocks that separates Pennsylvanian, Mississippian, Devonian, and Silurian strata from Ordovician and Cambrian strata into broad hydrogeologic compartments. The interval would represent a primary seal for possible CO_2 storage res-

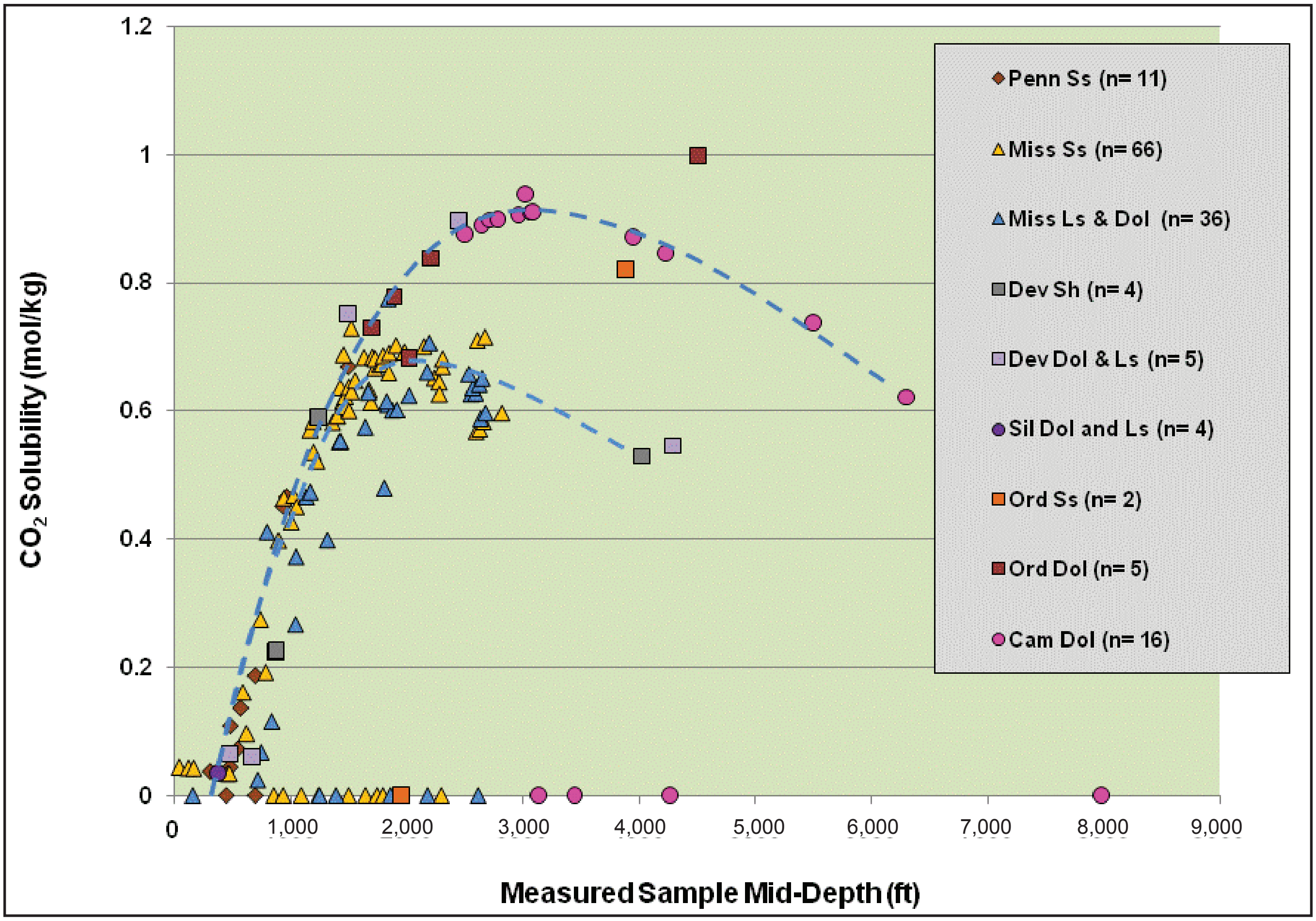

Figure 3.15. Measured depth (ft) versus CO$_2$ solubility (mol/kg H$_2$O) by age–rock type category for samples in western Kentucky (Illinois Basin).

ervoirs in the Cambrian-Ordovician Knox Group.

3. Though widely varying, measured salinity values (approximately 4,000 to 313,000 mg/L) in Cambrian and Ordovician reservoirs are often significantly less than what is predicted by salinity-versus-depth trends from shallower Pennsylvanian, Mississippian, Devonian, and Silurian samples. When analyzed with an equation of state for aqueous solutions containing Na$^+$, K$^+$, Ca^{2+}, Mg^{2+}, Cl$^-$, and SO$_4^{2-}$, the decreased salinity results in higher CO$_2$ solubilities (approximately 0.65 to 0.86 mol/kg H$_2$O) and hence more potential for solubility trapping in Cambrian and Ordovician reservoirs.

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