



Pleistocene recharge to midcontinent basins: Effects on salinity structure and microbial gas generation

J. C. MCINTOSH,^{1,*} L. M. WALTER,¹ and A. M. MARTINI²

¹Department of Geological Sciences, University of Michigan, Ann Arbor, MI 48109-1063, USA

²Department of Geology, Amherst College, Amherst, MA 01002, USA

(Received July 3, 2001; accepted in revised form November 21, 2001)

Abstract—The hydrogeochemistry of saline–meteoric water interface zones in sedimentary basins is important in constraining the fluid migration history, chemical evolution of basinal brines, and physical stability of saline formation waters during episodes of freshwater recharge. This is especially germane for interior cratonic basins, such as the Michigan and Illinois basins. Although there are large differences in formation water salinity and hydrostratigraphy in these basins, both are relatively quiescent tectonically and have experienced repeated cycles of glaciation during the Pleistocene. Exploration for unconventional microbial gas deposits, which began in the upper Devonian-age Antrim Shale at the northern margin of the Michigan Basin, has recently extended into the age-equivalent New Albany Shale of the neighboring Illinois Basin, providing access to heretofore unavailable fluid samples. These reveal an extensive regional recharge system that has profoundly changed the salinity structure and induced significant biogeochemical modification of formation water elemental and isotope geochemistry.

New-formation water and gas samples were obtained from Devonian–Mississippian strata in the Illinois Basin. These included exploration wells in the New Albany Shale, an organic-rich black shale of upper Devonian age, and formation waters from over- and underlying regional aquifer systems (Siluro–Devonian and Mississippian age). The hydrostratigraphic relations of major aquifers and aquitards along the eastern margin of the Illinois Basin critically influenced fluid migration into the New Albany Shale. The New Albany Shale formation water chemistry indicates significant invasion of meteoric water, with δD values as low as -46.05‰ , into the shale. The carbon stable isotope system ($\delta^{13}C$ values as high as 29.4‰), coupled with $\delta^{18}O$, δD , and alkalinity of formation waters (alkalinity ≤ 24.08 meq/kg), identifies the presence of microbial gas associated with meteoric recharge. Regional geochemical patterns identify the underlying Siluro–Devonian carbonate aquifer system as the major conduit for freshwater recharge into the fractured New Albany Shale reservoirs. Recharge from overlying Mississippian carbonates is only significant in the southernmost portion of the basin margin where carbonates directly overlie the New Albany Shale.

Recharge of dilute waters ($Cl^- < 1000$ mM) into the Siluro–Devonian section has suppressed formation water salinity to depths as great as 1 km across the entire eastern Illinois Basin margin. Taken together with salinity and stable isotope patterns in age-equivalent Michigan Basin formation waters, they suggest a regional impact of recharge of $\delta^{18}O$ - and δD -depleted fluids related to Pleistocene glaciation. Devonian black shales at both basin margins have been affected by recharge and produced significant volumes of microbial methane. This recharge is also manifested in different salinity gradients in the two basins because of their large differences in original formation water salinity. Given the relatively quiet tectonic history and subdued current topography in the midcontinent region, it is likely that repeated cycles of glacial meltwater invasion across this region have induced a strong disequilibrium pattern in fluid salinity and produced a unique class of unconventional shale-hosted gas deposits. Copyright © 2002 Elsevier Science Ltd

1. INTRODUCTION

The midcontinent region of the United States is characterized by a number of intracratonic sedimentary basins (Fig. 1). Many of these basins contain fractured black shales, which could provide preferred recharge paths for meteoric waters related to Pleistocene deglaciation. Loading and unloading of thick glacial ice sheets may have enhanced natural fractures in basin sediment and increased hydraulic conductivity (Boulton and Caban, 1995; Walter et al., 1996). Importantly, Pleistocene glacial recharge to the Late Devonian Antrim Shale in the Michigan Basin has critically aided generation of microbial gas deposits along the shallow basin margins (Martini et al., 1996,

1998) (Fig. 2). Geochemical evidence for microbial methanogenesis includes the unusually high carbon isotope values ($+20$ to $+32\text{‰}$ PDB) for dissolved inorganic carbon (DIC) in Antrim Shale fluids and the covariance of δD values for methane and δD values for formation waters. In the Illinois Basin, the highly fractured New Albany Shale is reported to contain major accumulations of gas, analogous to the age-equivalent Antrim and Ohio shales (Appalachian Basin). This study investigates the role of Pleistocene glaciation on dilute water influx to the eastern margin of the Illinois Basin and subsequent microbial activity within the Late Devonian, organic-rich, New Albany Shale.

The infiltration of glacial meltwaters into the Illinois Basin is well documented and compelling; however, the majority of researchers focused on aquifers along the western margin of the basin (Bond, 1972; Siegel and Mandle, 1984; Siegel, 1989,

* Author to whom correspondence should be addressed (jmcintos@umich.edu).

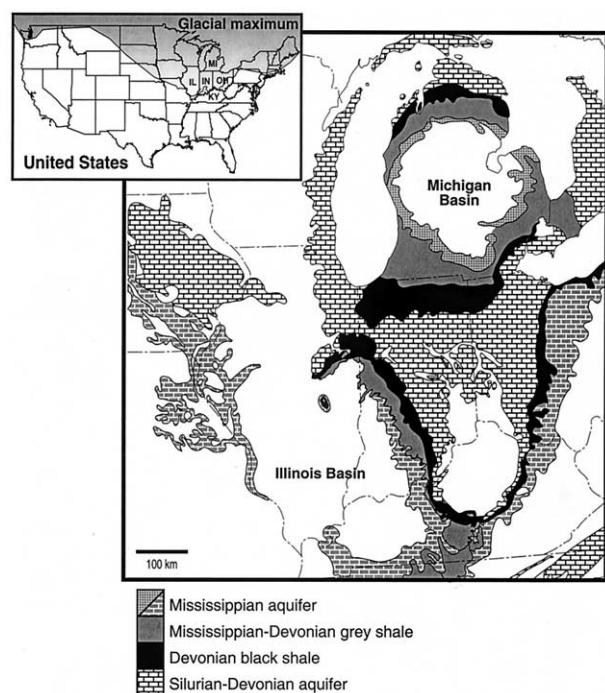


Fig. 1. Hydrogeologic framework of the Illinois and Michigan basins. Late Devonian organic-rich shale units are shown in black next to regional aquifer and aquitard systems. Southern extent of Pleistocene glaciation is shown in the inset of the United States.

1991; Stueber and Walter, 1994). Siegel (1989) identified regional invasion of Pleistocene waters into the Cambro-Ordovician aquifers in Wisconsin through southern Illinois. Other units, such as the Siluro-Devonian, Mississippiian, and Pennsylvanian aquifers have also been influenced by meteoric water invasion (Stueber and Walter, 1991; Stueber et al., 1993). However, the Devonian shales on the western margin are much less organic-rich and have a higher carbonate content, making them unlikely targets for gas exploration and drilling. Panno and Bourcier (1990) suggested that mixing of glacial meltwater with basinal brine along the southern margins of the Illinois and Michigan basins could be responsible for the formation of karst features. Water recharged from the basal melting of glaciers and associated overburden pressure could also flush brines from underlying aquifers, leading to saline discharges.

Although many workers have published data on Illinois Basin fluids (Meents et al., 1952; Clayton et al., 1966; Keller, 1983), few have analyzed carbon system parameters or stable isotopes that are essential to understanding the evolution of fluids and gases in basins (Clayton et al., 1966; Walter et al., 1990; Stueber and Walter, 1991, 1994; Stueber et al., 1993; Demir and Seyler, 1999). This study collected and analyzed fluid and gas samples from New Albany Shale wells along the eastern margin of the Illinois Basin where recent exploration enabled sampling over a relatively large geographic area. Importantly, prolific hydrocarbon exploration in stratigraphically adjacent Mississippiian and Devonian strata also permitted collection of fluids from these regional aquifer systems. Formation waters were fully characterized for elemental and stable isotopic compositions, with special focus on carbon system param-

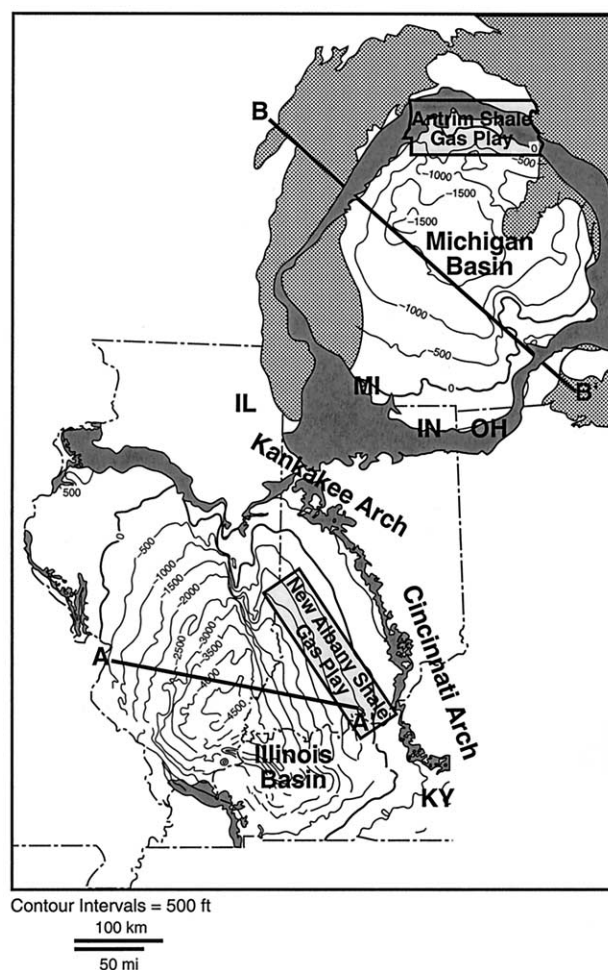


Fig. 2. Structure of the base of the Late Devonian black shales in the Illinois and Michigan basins overlain on the shale subcrop (shaded pattern). Microbial gas fields in the New Albany and Antrim shales are outlined. Note the cross-sectional lines pertaining to Figure 3.

eters and carbon isotope compositions of gas and dissolved inorganic carbon. The hydrogeochemistry of the New Albany Shale will be compared with the age-equivalent Antrim Shale in northern Michigan. Further comparisons will be made between fluid migration pathways in the Illinois Basin vs. those in the Michigan Basin and the overall regional impact of Pleistocene recharge in reorganizing formation water salinity structures.

2. HYDROGEOLOGIC FRAMEWORK

The Illinois Basin is an intracratonic sedimentary basin located in the midcontinent, United States (Fig. 1). The basin is underlain by Precambrian basement rocks, part of the eastern granite-rhyolitic province (Schmus et al., 1996). The structure of the basement rocks is reflected in the overlying Paleozoic strata, which dip gently basinward, 6 to 14 m/km (Zuppann et al., 1988). The basin is structurally confined by the Kankakee Arch to the north and the Cincinnati Arch to the east, separating it from the Michigan and Appalachian basins, respectively. The Ozark Dome, Mississippi River Arch, and Wisconsin Arch

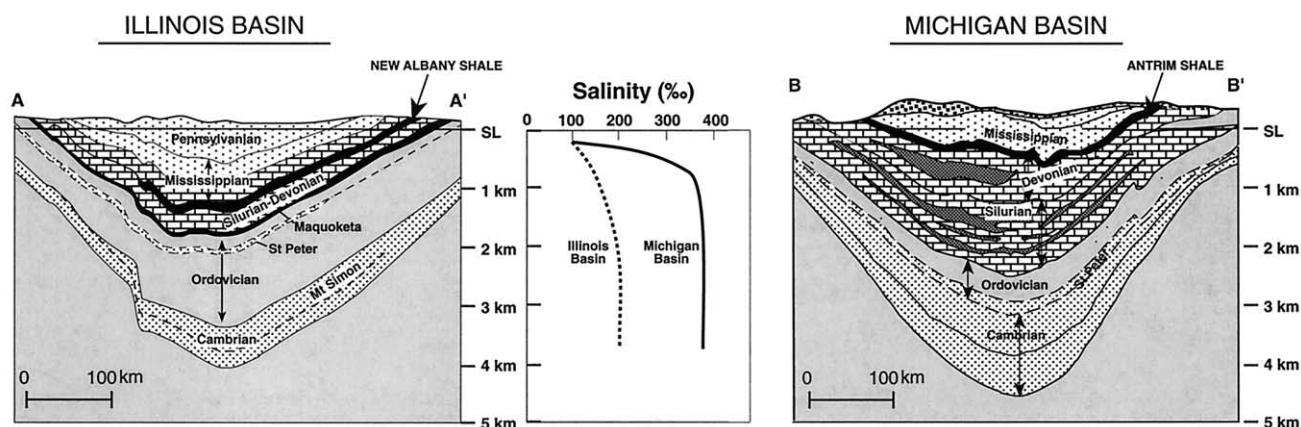


Fig. 3. Cross sections of Illinois and Michigan basins. Locations of cross-sectional lines are shown in previous figure. New Albany and Antrim Shales are highlighted in black; evaporite sequences are shown in dotted gray pattern within the Siluro-Devonian carbonates. The salinity profiles for Illinois and Michigan basinal fluids are also shown.

define the western margin of the basin. Major structural features of the basin include the Shawneetown–Rough Creek fault system along the southern margin and the La Salle Anticlinal Belt in the east-central part of the basin (Zuppann et al., 1988). The Michigan Basin, in comparison, is tectonically quiescent with few major fault systems. The basin is circular shaped, with the margin approximately outlined by Lake Michigan and Lake Huron.

The Paleozoic stratigraphy of the Illinois Basin, although similar to the Michigan Basin, has a few significant differences (Fig. 3). The New Albany Shale in the Illinois Basin is overlain by a thick sequence of Mississippian and Pennsylvanian strata (~0 to 1.4 km). In contrast, the bulk of the Pennsylvanian section in the Michigan Basin has been eroded, and the Antrim Shale is located at shallower depths than the New Albany Shale. The Antrim Shale is underlain by an extensive sequence of Silurian and Devonian carbonates and evaporites (~1 to 1.7 km), which significantly affect fluid chemistry and salinity structure. Evaporite sequences are absent in the Illinois Basin, which in part explains the large difference in overall fluid salinity relative to the Michigan Basin (Fig. 3). Both basins are overlain by Quaternary deposits of variable thicknesses and permeabilities largely related to Pleistocene glaciation.

The relation of major aquifers and aquitards along basin margins is an important control on fluid migration. Figure 4 compares the hydrostratigraphy of regional aquifers and aquitards in the Illinois and Michigan basins, highlighting the Late Devonian black shales. Along the eastern margin of the Illinois Basin, the New Albany Shale is a regional confining unit, underlain by the Silurian-Devonian aquifer system. The shale is overlain by the Borden Group, a confining unit, and the Mississippian carbonate aquifer system. The Antrim Shale is also capped by confining units, Mississippian shales, and underlain by Devonian carbonate aquifer systems.

The uppermost member of the New Albany Shale, the Clegg Creek, is the most organic-rich, with over 15 wt% total organic carbon (TOC) content (Hassenmueller and Leininger, 1987) (Fig. 4). The highest TOC in the Antrim Shale, on the other hand, is in the lower members (Lachine and Norwood). Along the eastern margin of the Illinois Basin, the New Albany Shale

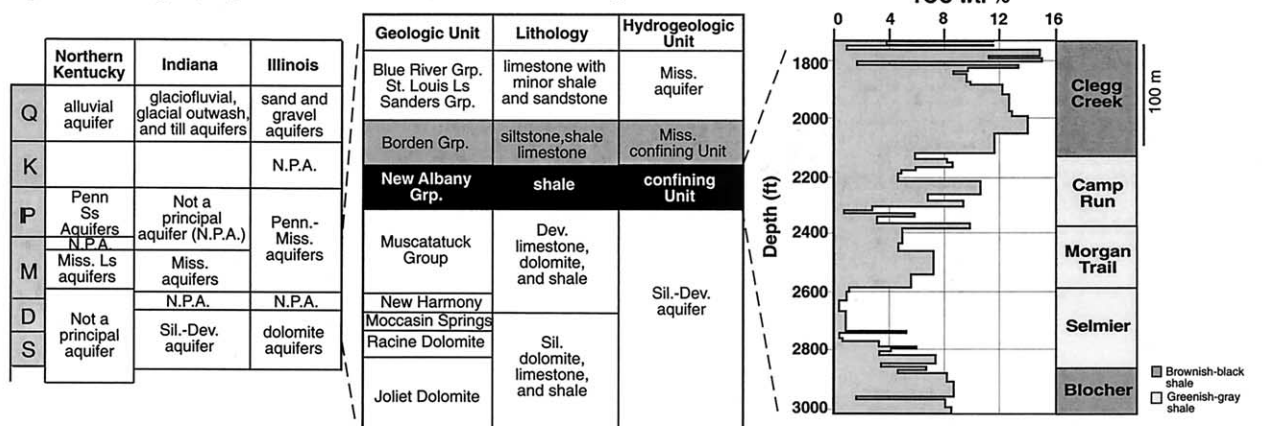
is brownish to black, fractured and thermally immature (vitrinite reflectance [R_o] values less than 0.6%) (Barrows and Cluff, 1984). To the west, the shale grades into greenish-gray, unfractured, organic-poor shales (Hassenmueller, 1993). The shale in the central Illinois Basin is within the oil and gas generation window ($R_o > 0.6\%$) (Cluff, 1979).

The regional pattern of strata in subcrop is shown in Figure 5a. The bedrock topography along the eastern margin of the Illinois Basin is relatively subdued, and surficial deposits are thin; significant recharge of dilute waters to the basin margin is more likely to have come from continental glaciation than current topographically driven flow. The New Albany Shale subcrop is inboard of the regionally expansive Silurian-Devonian carbonate aquifer subcrop and outboard of the impermeable Mississippian Borden Group. The thickness of the Borden Group, a deltaic deposit, varies with depth and location in the basin (Fig. 5b). In south-central Indiana, the Borden Group is relatively thick (~100 to 200 m), hydrologically isolating the New Albany Shale from overlying Mississippian carbonates (Fig. 5c). Along the southeastern margin of the basin (Kentucky), the Borden Group thins or is absent, and Mississippian carbonate aquifers directly overlie the New Albany Shale.

3. METHODS AND RESULTS

This study spanned two major collection efforts: one during exploration and development of the New Albany Shale (1997 to 1998) and a later concerted effort to collect formation waters from over- and underlying aquifers (1999). In addition, petrophysical data (well logs, TOC vs. depth, total gas content), and water and gas analyses were provided by industrial sources. Formation water and gas samples from the New Albany Shale were collected and analyzed for elemental and isotope geochemistry (65 wells sampled; sample locations are shown in Fig. 6a). The samples were collected directly from the well head and preserved immediately in the field against microbial degradation or degassing/oxidation artifacts. Temperature and pH were measured in the field. Water samples were filtered with a 0.45- μ m Micropore filter before being preserved for analyses. Alkalinity and anion aliquots were kept in high-density polypropylene bottles with no headspace, and cation samples were acidified to pH <2, with nitric acid. Aliquots for dissolved inorganic carbon and carbon isotope analyses were preserved with CuCl_2 and capped in glass serum vials. The oxygen and hydrogen stable isotope samples were sealed in glass scintillation vials. All

Hydrostratigraphy: Illinois Basin, eastern margin



Hydrostratigraphy: Michigan Basin

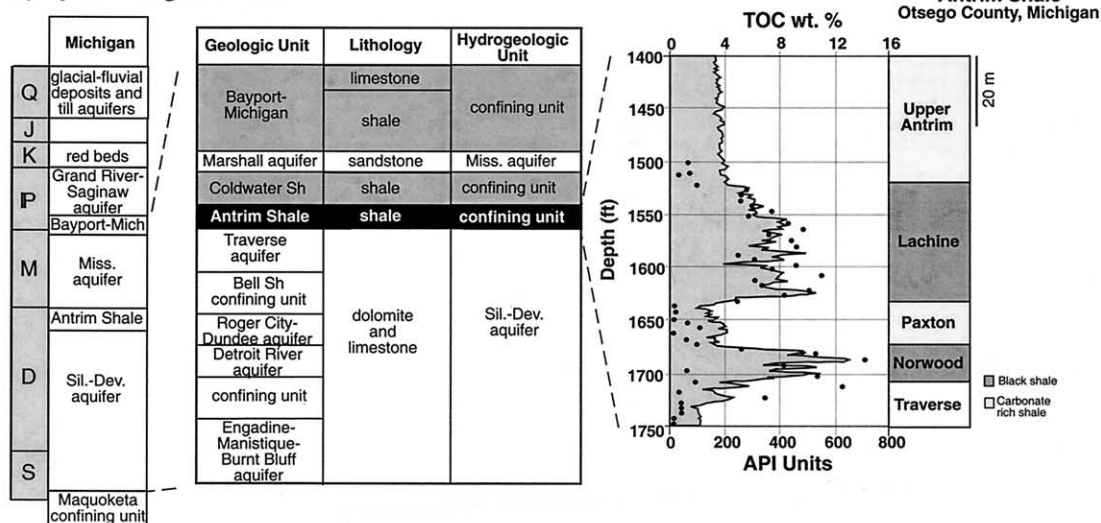


Fig. 4. Hydrostratigraphy of Illinois and Michigan Basins, showing major aquifers and aquitards; modified from Olcott (1992) and Lloyd and Lyke (1995). TOC content for New Albany and Antrim Shales shown at right. Antrim Shale TOC measurements are indicated by black dots overlain on the γ -ray log response (American Petroleum Institute units) (Decker et al., 1992).

samples were kept refrigerated until they could be analyzed. Gas samples were collected in previously flushed metal canisters.

Carbon system measurements and major ion analyses were obtained in the University of Michigan Experimental and Analytical Geochemistry Laboratory as soon after sampling as possible. Alkalinity was measured by electrometric end point titration with a Radiometer automated titration instrument (precision, $\pm 0.6\%$). Reverse alkalinity was obtained for a subset of samples with the same automated titration instrument. Cations were analyzed by inductively coupled plasma-atomic emission spectrometry with a Leeman Labs PlasmaSpec III system (precision, $\pm 2\%$). Anions were analyzed by ion chromatography (IC) with a Dionex 4000I series (precision, $\pm 1\%$). More detailed analytical methods are provided in Martini et al. (1998) and Walter et al. (1996). Density was measured in the laboratory, and dissolved organic carbon was determined for several samples with a Shimadzu TOC-5000 instrument.

A subset of water samples was analyzed for stable isotope chemistry (oxygen, hydrogen, and carbon) by Isotech Laboratories in Champaign-Urbana, Illinois, and the University of Michigan Stable Isotope Laboratory (precision, $\delta^{18}\text{O} = \pm 0.1\%$, $\delta\text{D} = \pm 2\%$, $\delta^{13}\text{C} = \pm 0.1\%$). Gas composition and stable isotope analyses (carbon and hydrogen on

methane and higher chain hydrocarbons) were also conducted by Isotech Laboratories (precision, $\delta^{13}\text{C} = \pm 0.1\%$, $\delta\text{D} = \pm 2\%$). The major ion and stable isotope chemistry of the New Albany Shale formation waters and associated gases are reported in Tables 1 to 3.

Major ion chemical data for Siluro-Devonian and Mississippian formation waters in the Illinois Basin were compiled from several published sources to constrain the hydrogeochemistry of the New Albany Shale and under- and overlying aquifer systems (Meents et al., 1952; McGrain, 1953; Walker, 1959; Keller, 1983; Stueber and Walter, 1991; Stueber et al., 1993). New sampling was necessary to augment this data set with carbon parameters and stable isotope analyses. New Siluro-Devonian formation water samples also helped to constrain regional aquifer system salinity structures, by adding data for wells in key areas, which were not sampled previously. Sample localities for new analyses and published data are shown in Figures 6b,c.

Sixty-four additional formation water samples were collected from Silurian, Devonian, and Mississippian strata in southern Illinois, Indiana, and northwestern Kentucky in July 1999. Wells were chosen in key areas, including those most likely to be influenced by meteoric recharge and in counties without previously published major ion or stable isotope data. Samples were obtained directly from oil well heads,

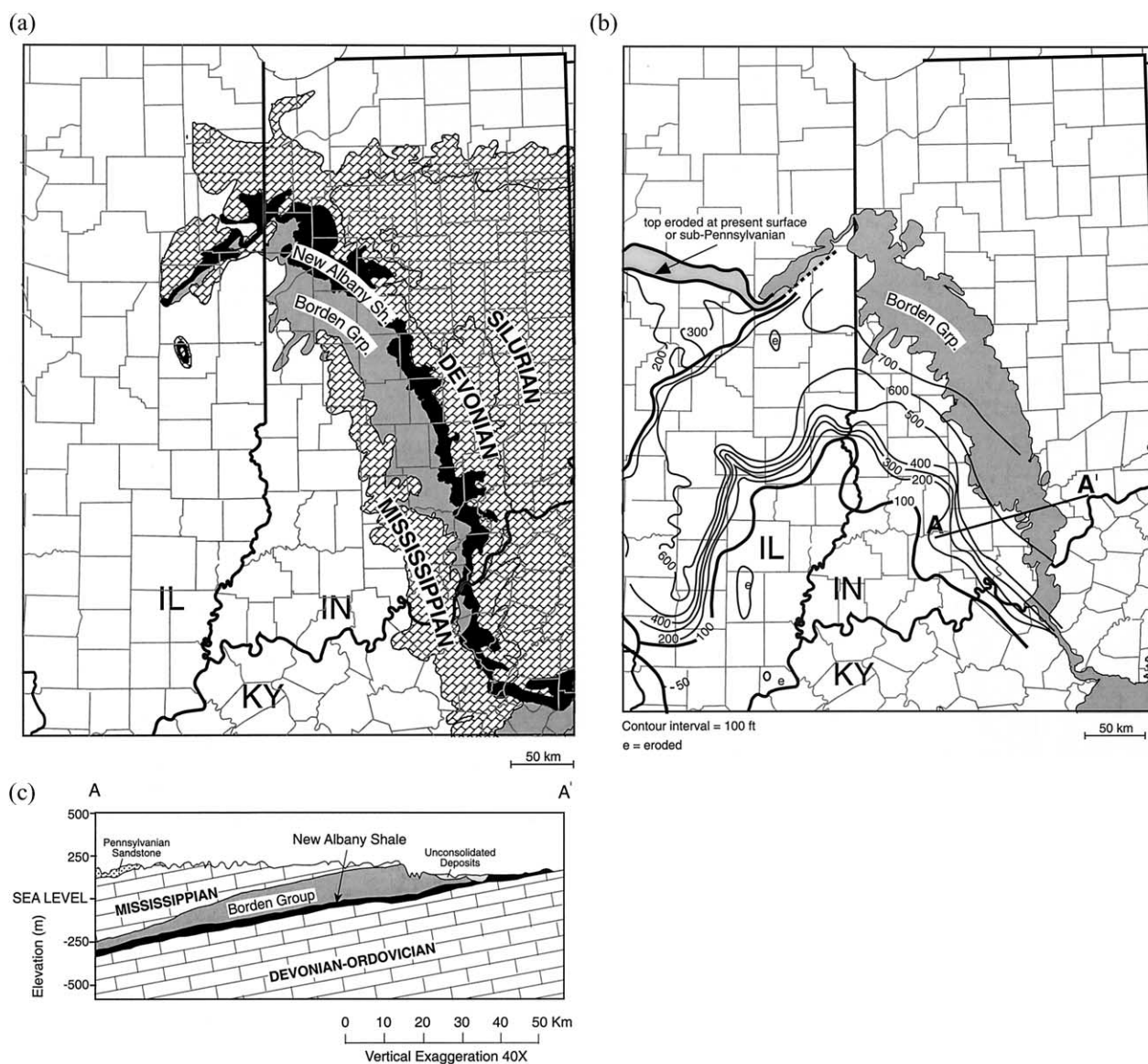


Fig. 5. (a) Regional subcrop map of aquifers and aquitards along the eastern margin of the Illinois Basin (modified from Lloyd and Lyke, 1995). (b) Isopach map showing thickness of the Borden Group, confining unit (modified from Rupp, 1991). (c) Cross section along eastern margin of the Illinois Basin highlighting major aquifers and aquitards adjacent to the New Albany Shale (modified from Rupp, 1989). Cross-sectional line shown in (b).

and water-flooded or commingled wells were avoided. The formation water samples were collected in plastic buckets and allowed to demulsify for several minutes. After separation, the brine was then siphoned through a spout at the bottom of the bucket. The conductivity and temperature were measured in the field. The air temperature during this field session was too high ($>105^{\circ}\text{F}$) to accurately measure the pH in the field. Waters were poured directly into presterilized Millipore Stericups (vacuum-driven disposal filtration systems) and filtered with a hand pump. The reservoir containers attached to the filters were then sealed, with no headspace, and kept refrigerated until the pH and alkalinity could be measured; aliquots were preserved for analysis later that day in an air-conditioned room. Alkalinity was determined by the Gran-Alkalinity titration method as described in Gieskes and Rogers (1973) (precision = $\pm 0.4\%$). Major ion and stable isotope chemistry was analyzed by means of the same methods as described for the New Albany Shale water samples. Silurian-Devonian and Mississippian-Pennsylvanian formation water analyses are reported in Tables 4 and 5.

Chloride was analyzed by titration with silver nitrate on an automated titration system; precision was $\pm 0.4\%$ (results identified as Cl_T in Table 5).

4. DISCUSSION

4.1. Formation Water Chemistry

4.1.1. Chloride Content

The New Albany Shale contains formation waters of variable salinity associated with mixed microbial and thermogenic gas. The formation water salinity pattern (Fig. 6a) along the eastern margin of the Illinois Basin shows that relatively dilute waters ($\text{Cl}^- < 300 \text{ mM}$) near the shale subcrop penetrate to significant depths in the basin. In southwestern Indiana, the chloride

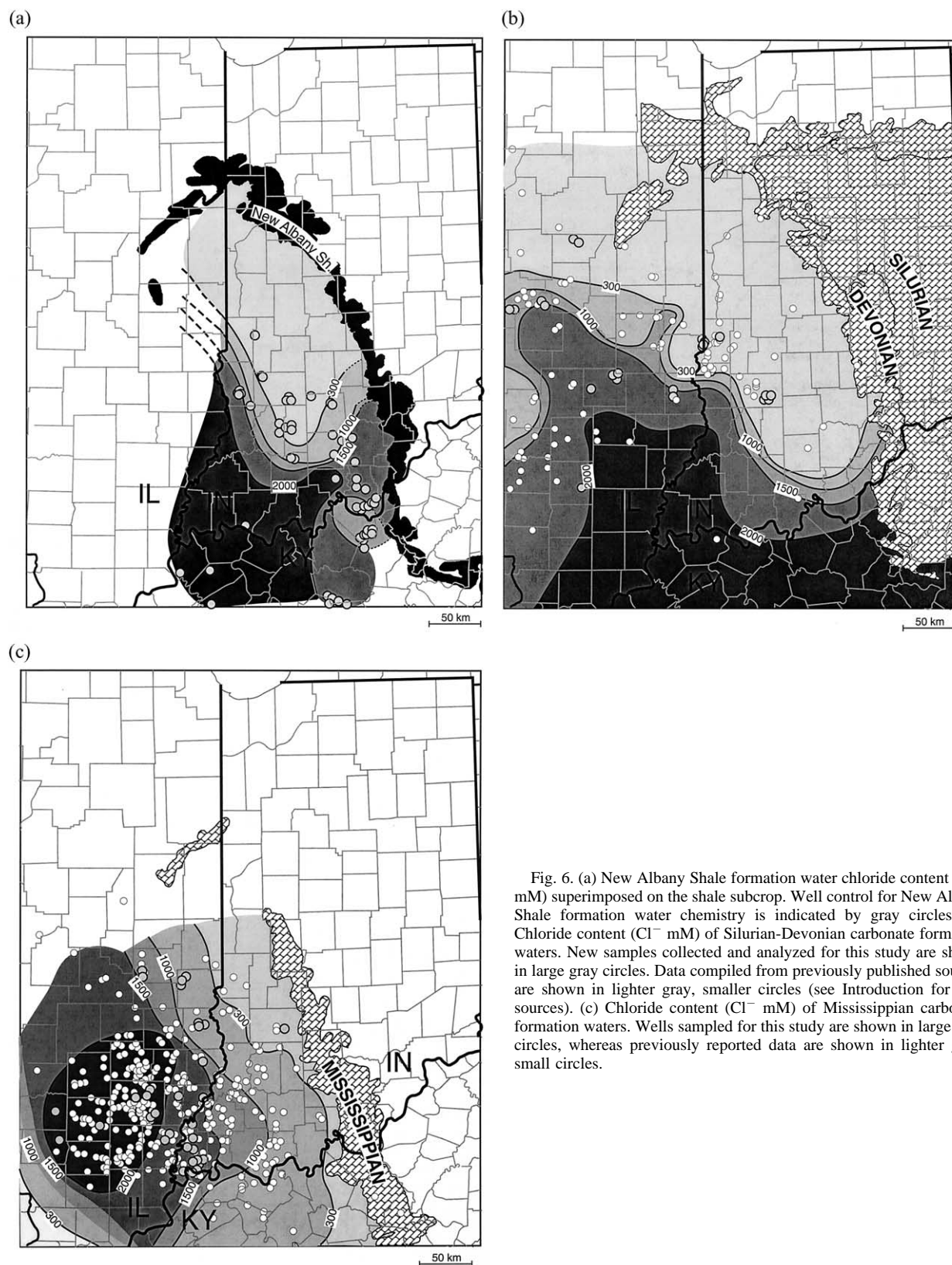


Fig. 6. (a) New Albany Shale formation water chloride content (Cl^- mM) superimposed on the shale subcrop. Well control for New Albany Shale formation water chemistry is indicated by gray circles. (b) Chloride content (Cl^- mM) of Silurian-Devonian carbonate formation waters. New samples collected and analyzed for this study are shown in large gray circles. Data compiled from previously published sources are shown in lighter gray, smaller circles (see Introduction for data sources). (c) Chloride content (Cl^- mM) of Mississippian carbonate formation waters. Wells sampled for this study are shown in large gray circles, whereas previously reported data are shown in lighter gray, small circles.

content increases rapidly from <300 to >2000 mM basinward. The major axis of freshwater incursion into the shale appears to have been from the northern margin of the basin, with a

north-to-south directional gradient in the chloride concentration. A second minor axis of dilute water recharge occurs along the southeastern margin of the basin, where a cluster of 1000 to

Table 1. Well location, carbon parameters, and stable isotope analyses for New Albany Shale fluids.

Sample	County	State	Latitude	Longitude	Depth (m)	Density (g/mL)	pH	Alk-T (meq/kg)	DIC (mmol/kg)	Acetate (mM)	DIC $\delta^{13}\text{C}$ (‰)	Water $\delta^{18}\text{O}$ (‰)	Water δD (‰)
1	Clay	IN	39.46200	-87.23047	549.8	1.003		6.85	6.24		10.3	-7.03	-42.00
2	Crawford	IN	38.29831	-86.39707	452.6		6.60	1.34		0.05			
3	Crawford	IN	38.29831	-86.39707	452.6	1.091	6.13	1.23		<0.04	-3.8	1.14	-10.81
4	Daviess	IN	38.74398	-86.97157	662.0	1.054		17.11				-3.20	-24.75
5	Daviess	IN	38.67757	-86.96241	650.7	1.027		16.38				-4.24	-29.12
6	Dubois	IN	38.47441	-86.85986	673.6	1.018		12.00				-5.20	-33.26
7	Dubois	IN	38.46238	-86.84980	664.5			10.89					
8	Greene	IN	38.93651	-86.87566	551.1	1.006		7.62					
9	Greene	IN	38.93509	-86.88889	549.2	1.006		8.11					
10	Greene	IN	38.94944	-86.87971	533.4	1.006		8.59					
11	Greene	IN	38.94109	-86.87969	520.0	1.005		7.97					
12	Greene	IN	38.93780	-86.87958	518.8	1.005		7.79					
13	Greene	IN	38.93498	-86.87036	550.2	1.005		1.70					
14	Greene	IN	38.93780	-86.87958	518.8	1.004	7.29	9.17		0.05	16.3	-7.54	-46.05
15	Greene	IN	38.94109	-86.87969	520.0	1.004	7.07	8.72		0.08			
16	Harrison	IN	38.06876	-86.14842	338.9		7.13	13.99		0.34			
17	Harrison	IN	38.06876	-86.14842	338.9	1.069	6.82	15.93		0.09	26.4	-1.16	-14.66
18	Harrison	IN	38.06056	-86.13829	292.0		6.16	12.49		<0.04			
19	Harrison	IN	38.06056	-86.13829	292.0	1.060	6.54	18.97		<0.04	28.3	-2.10	-18.93
20	Harrison	IN	38.08747	-86.05838	304.8	1.057	7.20	17.31		<0.03	27.4	-1.81	-15.37
21	Harrison	IN	38.10536	-86.02525	292.9	1.061	7.23	13.59		<0.03			
22	Harrison	IN	38.08407	-86.07005	295.4	1.058		15.40		0.09			
23	Harrison	IN	38.10351	-86.01513	281.0	1.071	7.21	11.58		<0.03	27.7	-0.63	-9.96
24	Harrison	IN	38.12583	-86.00644	307.8	1.070	7.70	6.00		0.15			
25	Harrison	IN	38.08038	-86.09282	295.0	1.066	7.09	15.79		<0.03	29.4	-1.56	-14.39
26	Harrison	IN	38.10376	-86.04498	286.8	1.071	7.23	12.88		<0.03			
27	Harrison	IN	38.08411	-86.09755	300.5	1.061	6.21	16.19		<0.03			
28	Martin	IN	38.71421	-86.90701	681.8	1.019							
29	Martin	IN	38.71609	-86.87865	601.7	1.010							
30	Martin	IN	38.71609	-86.87865	601.7	1.010	7.74	11.90				-6.24	-31.05
31	Martin	IN	38.72279	-86.88084	640.1	1.012	7.55	12.50		0.22			
32	Martin	IN	38.70803	-86.88638	640.1	1.009	7.53	13.90					
33	Martin	IN	38.70976	-86.87263	640.1	1.008	7.74	11.90				-6.44	-41.03
34	Sullivan	IN			670.6	1.063	6.88	18.06	20.86		22.1	-2.47	-17.09
35	Sullivan	IN	39.00645	-87.41886	670.6	1.066	6.72	13.17			24.1		
36	Sullivan	IN			670.6	1.074	6.71	17.51			24.2	-2.19	-12.86
37	Sullivan	IN			670.6	1.054	6.78	23.00			21.9	-2.99	-21.73
38	Warrick	IN	37.92975	-87.34320	838.2					1.93			
39	Washington	IN	38.62368	-86.22297	398.7		6.60	2.19		0.14			
40	Washington	IN	38.62368	-86.22297	398.7	1.068	6.65	2.36		<0.04	-0.6	-1.82	-19.66
41	Grayson	KY	37.35255	-86.46560	594.4	1.056	6.52						
42	Grayson	KY	37.34084	-86.43161	510.5	1.066	6.45					0.04	-13.74
43	Grayson	KY	37.31625	-86.39097	499.9	1.063	6.80					-0.56	-11.17
44	Grayson	KY	37.32544	-86.45603	530.4	1.076	6.85					1.38	-4.25
45	Hardin	KY	37.75833	-86.10830	372.5		7.05	18.35				-2.24	-13.90
46	Meade	KY	37.86477	-86.06604	292.9	1.056		7.63		1.40	19.7	-2.74	-19.34
47	Meade	KY	37.84616	-86.05710	283.5			4.41				-1.44	-16.61
48	Meade	KY	37.86175	-86.05107	267.9	1.053		15.94				-2.97	-20.71
49	Meade	KY	37.85884	-86.07498	292.6	1.055		10.07		1.20		-2.77	
50	Meade	KY	37.86810	-86.03513	295.6	1.050	6.29	14.30	15.84		23.1	-3.26	-21.77
51	Meade	KY	37.85748	-86.06663	281.9	1.053	6.42	22.50	23.07		26.5	-2.81	-18.72
52	Meade	KY	37.85627	-86.04269	258.8	1.039	6.40	11.60	10.46		22.9	-3.48	-19.49
53	Meade	KY	37.86071	-86.08160	327.4	1.057	6.21	19.50	17.58		25.9	-2.81	-16.48
54	Meade	KY	37.85198	-86.07146	283.5	1.057	6.39	13.30	12.80		26.1	-2.77	-18.95
55	Meade	KY	37.81941	-86.13655	358.1		6.86	18.09	21.49				
56	Meade	KY	37.82500	-86.14160	343.2		6.84	22.43	23.54				
57	Meade	KY	37.82500	-86.15833	392.9		6.32	22.12	26.45				
58	Meade	KY	37.83087	-86.14899	357.5		6.54	24.08	29.47		27.1	-2.56	-11.50
59	Meade	KY	37.84616	-86.09701	309.7		6.75	15.14	14.38				
60	Meade	KY	37.84167	-86.12500	325.2		6.45	21.58	22.70				
61	Meade	KY	37.84167	-86.09167	317.0			17.49					
62	Meade	KY	37.80833	-86.12500	340.2		6.59	15.45	20.21				
63	Meade	KY	37.80833	-86.14167	349.9		7.12	21.21	18.22		25.5	-3.21	-16.00
64	Meade	KY	37.84167	-86.12500	324.9		6.45	23.27	25.93				
65	Meade	KY	37.82674	-86.13264	340.5		6.43	21.58	25.69				

Table 2. Selected chemical analyses (mM) for New Albany Shale formation waters

Sample	Na	Ca	Mg	Sr	Cl	Br	SO ₄	Si	B	Li	Ba	Mn	Total Fe	K
1	50.46	0.65	1.15	0.03	48.97	0.10	0.03	0.24	1.46	0.00	0.01	0.02	0.00	0.40
2	1644.19	136.48	86.38	4.06	2234.13	4.01	6.31	0.18	0.29	5.07	0.03	0.02	0.06	15.70
3	1722.49	142.22	90.50	4.25	2259.52	4.09	6.56	0.17	0.28	4.98	0.03	0.02	0.10	15.29
4	1017.83	64.87	66.64	3.61	1285.87	2.39	4.60	0.49	0.77	4.73	0.05	0.00	0.07	14.83
5	495.87	25.20	30.48	2.37	607.98	1.39	0.39	0.62	0.94	2.28	0.06	0.02	0.05	11.99
6	336.67	16.99	17.44	1.29	397.55	0.94	0.07	0.47	0.76	0.92	0.12	0.03	0.65	8.41
7	635.06	37.30	32.62	1.14	723.84	1.30	8.78	0.17	0.58	2.31	0.01	0.02	0.31	3.32
8	63.07	4.77	4.10	0.17	73.91	0.16	0.27	0.19	0.26	0.19	0.01	0.00	0.00	1.07
9	69.60	4.99	4.20	0.17	79.27	0.18	0.02	0.20	0.30	0.22	0.01	0.01	0.02	0.60
10	70.03	5.11	4.36	0.17	79.75	0.18	0.04	0.19	0.27	0.20	0.01	0.00	0.01	0.44
11	67.86	4.79	4.24	0.17	78.05	0.15	0.10	0.17	0.27	0.16	0.01	0.00	0.00	0.31
12	70.90	4.79	4.11	0.16	78.82	0.16	0.03	0.19	0.27	0.17	0.02	0.00	0.00	0.40
13	66.55	1.38	3.57	0.12	74.30	0.15	0.01	0.03	0.24	0.14	0.00	0.00	0.00	0.73
14	70.90	5.51	4.32	0.17	80.11	0.16	0.02	0.19	0.30	0.18	0.02	0.00	0.00	0.81
15	70.47	5.34	4.36	0.17	81.52	0.16	0.01	0.20	0.29	0.18	0.01	0.00	0.00	0.80
16	1291.87	44.91	87.21	1.84	1672.78	2.77	0.27	0.23	0.20	9.13	0.11	0.01	0.49	8.54
17	1365.81	52.15	90.09	2.20	1655.85	2.77	0.16	0.21	0.21	9.09	0.14	0.01	0.51	8.72
18	1070.03	57.26	68.08	2.41	1430.18	2.37	1.16	0.20	0.20	6.67	0.07	0.01	0.36	8.82
19	1117.88	58.13	69.93	2.49	1427.36	2.37	0.87	0.22	0.20	6.60	0.03	0.02	1.48	8.34
20	1135.28	60.38	57.59	2.80	1365.30	2.65	0.07	0.20	0.20	7.98	0.31	0.01	0.33	12.33
21	1278.82	69.86	62.11	3.08	1514.81	2.67	0.03	0.22	0.19	8.07	0.19	0.01	0.22	11.74
22	1139.63	65.87	66.23	2.57	1418.90	2.60	1.75	0.22	0.17	5.94	0.04	0.01	0.43	10.33
23	1465.85	80.59	78.16	3.44	1729.20	3.12	0.53	0.22	0.19	8.82	0.13	0.01	0.35	12.66
24	1452.81	74.35	75.69	3.17	1692.52	3.14	<0.03	0.20	0.19	5.98	0.14	0.02	2.29	9.49
25	1331.01	73.60	77.33	3.13	1590.97	2.74	<0.03	0.20	0.19	6.73	0.30	0.01	0.49	9.39
26	1474.55	77.35	83.92	4.26	1785.61	2.93	<0.03	0.19	0.16	10.06	0.39	0.01	0.42	14.60
27	1335.36	69.11	76.92	3.25	1599.44	2.39	<0.03	0.21	0.19	6.97	0.29	0.01	0.45	10.51
28	352.33	19.36	18.84	1.24	433.09	0.89	1.48	0.57	0.72	1.46	0.05	0.06	1.51	9.77
29	188.78	7.51	9.38	0.52	217.29	0.51	0.01	0.20	0.58	0.56	0.03	0.01	0.04	2.61
30	200.09	9.42	10.02	0.61	234.47	0.49	0.03	0.16	0.53	0.54	0.04	0.01	0.00	1.87
31	239.23	11.17	10.49	0.68	261.04	0.56	0.05	0.13	0.55	0.56	0.04	0.03	0.41	1.98
32	167.46	8.61	7.65	0.43	192.69	0.46	0.11	0.19	0.52	0.44	0.04	0.02	0.17	1.52
33	163.11	7.80	7.30	0.45	185.53	0.39	0.30	0.16	0.51	0.41	0.03	0.01	0.00	1.64
34	1300.57	44.66	57.18	2.82	1564.65	2.66	2.54	0.40	1.04	0.81	0.03	0.05	3.99	0.47
35	1104.83	58.13	58.82	3.45	1288.91	2.42	7.60	0.44	1.49	1.89	0.26	0.02	1.05	0.78
36	1583.30	44.16	56.36	3.26	1852.84	2.81	0.58	0.41	0.60	3.24	0.17	0.08	5.01	1.29
37	1143.98	49.40	55.12	3.06	1302.10	2.33	7.80	0.16	0.81	0.21	0.01	0.05	2.56	0.36
38	2244.45	108.28	56.36	2.35	2730.61	4.03	14.78							39.39
39	1087.43	94.06	74.04	5.26	1509.17	3.60	0.50	0.15	0.28	2.82	0.18	0.02	0.42	7.21
40	1196.17	105.79	81.45	5.97	1689.70	3.57	0.28	0.18	0.30	2.95	0.21	0.01	0.13	8.64
41	1202.70	70.98	16.84	1.33	1408.50	2.72	0.00	0.13	0.12	6.60	0.08	0.01	0.36	3.86
42	1422.36	81.09	18.10	1.37	1693.81	2.81	1.08	0.12	0.15	7.74	0.07	0.04	0.04	3.12
43	1487.60	81.21	22.01	1.79	1707.51	2.96	2.02	0.11	0.13	9.58	0.03	0.01	0.10	5.12
44	1642.02	101.80	31.47	1.63	1926.87	3.13	0.41	0.05	0.20	7.66	0.16	0.10	0.94	5.65
45	835.15	70.11	45.25	1.62	1149.17	1.74	6.24	0.34	1.16	1.90	0.02	0.09	2.83	19.64
46	1065.68	72.36	63.76	2.51	1421.72	2.23	1.12	0.36	0.16	7.15	0.08	0.08	2.81	18.02
47	939.54	90.32	59.65	1.63	1289.14	2.09	0.53	0.28	0.20	5.29	0.06	0.20	7.65	29.90
48	1074.38	55.39	55.12	2.27	1334.27	2.09	0.14	0.28	0.16	6.90	0.09	0.04	1.00	12.13
49	1100.48	73.35	86.23	2.58	1390.89	2.18	0.23	0.23	0.13	6.83	0.09	0.05	1.86	11.84
50	959.11	80.09	52.04	2.44	1253.36	2.89	1.80	0.28	0.19	4.54	0.05	0.05	2.47	5.73
51	1083.08	55.44	55.53	2.70	1346.11	2.51	0.96	0.20	0.20	5.09	0.07	0.07	5.14	5.75
52	785.12	43.79	38.05	2.21	975.27	2.46	0.14	0.17	0.20	2.98	0.04	0.04	3.47	5.47
53	1148.33	55.39	69.93	2.67	1447.02	2.65	0.68	0.20	0.18	7.09	0.13	0.02	0.83	7.88
54	1130.93	57.39	65.41	2.78	1386.51	2.61	0.64	0.19	0.18	5.55	0.13	0.02	1.08	8.03
55	1083.08	49.15	63.76	3.25	1397.85	2.26	2.92	0.36	0.23	5.35	0.14	0.02	1.06	8.24
56	1113.53	51.90	55.12	3.02	1311.33	2.16	4.05	0.21	0.33	5.00	0.11	0.01	0.58	13.89
57	1087.43	46.66	66.64	3.15	1440.99		3.34	0.23	0.34	5.07	0.16	0.01	0.53	12.94
58	1135.28	43.16	74.04	3.09	1434.72	3.14	3.48	0.20	0.35	6.71	0.19	0.02	1.31	12.20
59	1013.48	58.13	72.81	2.31	1318.59	3.83	3.84	0.22	0.23	5.85	0.10	0.02	0.78	12.05
60	961.29	39.67	61.70	2.24	1253.88		3.86	0.20	0.50	6.08	0.13	0.02	1.09	17.93
61	1204.87	63.87	80.21	2.64	1422.15	1.91	3.63	0.32	0.55	8.73	0.21	0.02	0.79	19.82
62	1113.53	51.90	67.87	3.02	1445.37	2.28	3.96	0.20	0.22	5.76	0.17	0.01	0.42	7.31
63	848.19	41.17	44.84	2.29	1063.48	1.88	3.78	0.33	1.31	4.26	0.05	0.04	2.20	30.95
64	1104.83	45.16	76.92	2.84	1422.37	1.89	4.05	0.22	0.31	6.89	0.18	0.04	1.71	13.73
65	1143.98	49.15	70.34	3.29	1489.71	4.30	4.42	0.21	0.32	6.40	0.19	0.01	0.64	14.32

Table 3. Chemical composition and stable isotope analyses for New Albany Shale gas.

Sample	County	State	Methane (C ₁)			Carbon dioxide		Ethane (C ₂)		Propane (C ₃)	
			mol%	$\delta^{13}\text{C}$ (‰)	δD	mol%	$\delta^{13}\text{C}$ (‰)	mol%	$\delta^{13}\text{C}$ (‰)	mol%	$\delta^{13}\text{C}$ (‰)
3	Crawford	IN	60.90	−55.9		0.18		2.72	−48.6	0.66	−38.6
4	Daviess	IN	90.13			2.96	24.0	2.80		0.54	
5	Daviess	IN	89.64			3.69	14.5	1.25		0.18	
7	Dubois	IN	67.93			0.73		0.81		0.19	
14	Greene	IN	94.66	−54.2	−217	0.37	8.0	1.50	−39.7	0.05	
15	Greene	IN	82.45					1.48		0.31	
17	Harrison	IN	79.60	−54.6		3.30	18.3	0.91	−47.5	0.25	−36.9
19	Harrison	IN	70.90	−51.4		3.64	21.1	0.39	−46.2	0.12	−37.1
20	Harrison	IN	89.84	−53.3	−207	7.96		0.24			
21	Harrison	IN	91.45			6.50		0.42			
22	Harrison	IN	91.27			6.56		0.14			
23	Harrison	IN	92.43		−201	5.19		0.46		0.06	
24	Harrison	IN	93.91			2.93		0.87			
25	Harrison	IN	92.94		−207	5.36					
26	Harrison	IN	91.68			6.29		0.20			
27	Harrison	IN	91.33			5.54		0.09			
30	Martin	IN	94.30			1.34		0.29			
31	Martin	IN	54.96			1.32		0.16			
32	Martin	IN	65.95			0.98		0.20			
33	Martin	IN	90.69			1.14		0.98		0.15	
34	Sullivan	IN	91.22	−50.4	−188	3.91	15.9	3.40	−40.4	0.08	−21.9
35	Sullivan	IN	90.71	−49.5	−184	4.44	16.5	3.50	−41.5	0.09	−15.6
36	Sullivan	IN	92.17	−50.1	−186	2.93	15.6	3.50	−40.7	0.07	−18.0
37	Sullivan	IN	90.94	−49.8	−184	3.97	15.2	3.55	−41.3	0.11	−21.1
41	Grayson	KY	78.79	−52.7	−278	0.00		7.11	−46.6	2.85	−37.3
43	Grayson	KY	76.17	−52.5	−276	0.02		6.60	−46.1	2.93	−37.4
44	Grayson	KY	79.56	−52.7	−278	0.01		7.60	−46.8	2.93	−37.3
46	Meade	KY	83.60	−52.9		4.49	18.8	0.27	−44.5	0.07	−36.2
47	Meade	KY	84.40	−52.7		3.02	18.6	0.15	−44.4	<0.005	−36.0
48	Meade	KY	84.30	−53.8		3.99	18.7	0.12	−44.7	<0.005	−34.1
49	Meade	KY	84.30	−52.8		<0.005	19.7	4.90	−43.4	0.12	−34.0
50	Meade	KY	92.47	−55.4	−207	6.36	17.9	0.26	−44.8	0.04	
51	Meade	KY	90.76	−54.9	−207	0.01	18.6	0.16	−42.5	0.02	
53	Meade	KY	92.94	−52.9	−203	6.14	19.3	0.16	−42.3	0.02	
54	Meade	KY	92.41	−53.6	−204	6.65	18.8	0.13	−41.4	0.01	
55	Meade	KY	94.87			3.54		0.40		0.07	
56	Meade	KY	93.71			4.09		0.70		0.10	
57	Meade	KY	93.80			4.47		0.66		0.09	
58	Meade	KY	95.37	−51.8	−204	3.36	19.1	0.33	−43.8	0.06	
59	Meade	KY	92.66			6.13		0.44		0.07	
60	Meade	KY	93.07			3.87		1.32		0.28	
61	Meade	KY	93.55			4.40		0.68		0.13	
62	Meade	KY	94.39			3.91		0.42		0.08	
63	Meade	KY	95.57	−52.2	−200	2.30	18.6	0.25	−44.0	0.04	
64	Meade	KY	94.01			4.51		0.50		0.08	
65	Meade	KY	93.63			4.13		0.81		0.15	
66	Harrison	IN	91.50			6.06		0.29		0.05	
67	Harrison	IN	94.40			4.04		0.09			
68	Washington	IN	77.90	−65.4		0.11		1.37	−48.1	0.17	−32.9
69	Grayson	KY	80.76					7.82		3.07	
70	Grayson	KY	80.71					7.17		2.77	

1500 mM chloride waters is observed. The salinity pattern for the New Albany Shale waters is entirely unrelated to lateral position from the shale subcrop, suggesting that waters were not recharged laterally, relative to the basin margin.

The Siluro-Devonian formation waters show a similar salinity pattern to the New Albany Shale, with chloride concentration increasing north-to-south in the basin (Fig. 6b). Dilute waters ($\text{Cl}^- < 300$ mM) are observed to significant depths in the basin, indicating freshwater likely recharged the northern basin margin and migrated basinward. Evidence for freshwater recharge to the eastern margin of the Illinois Basin is consistent

with findings from studies along the western basin margin, which demonstrate that Pleistocene meltwaters have invaded the Siluro-Devonian aquifer system (Stueber and Walter, 1991). Siluro-Devonian formation waters in the central basin have high salinity concentrations typical of deep Na-Cl Illinois basinal brines (Meents et al., 1952).

The salinity pattern for the Mississippian aquifer system overlying the New Albany Shale is distinct from the Siluro-Devonian and New Albany Shale patterns (Fig. 6c). The chloride concentration increases systematically with distance from the carbonate subcrop. Salinity values increase from less than

Table 4. Well location, carbon parameters, and stable isotope analyses for Illinois Basin waters.

Sample	County	State	Formation	Latitude	Longitude	Depth (m)	T (°C)	Density (g/cc)	pH	AlkT (meq/kg)	DIC (mmol/kg)	DIC $\delta^{13}\text{C}$ (‰)	Water $\delta^{18}\text{O}$ (‰)	Water δD (‰)
<i>Mississippian-Pennsylvanian</i>														
1	Clark	IL	Carper	39.386	-88.004	289.6	18.3	1.045	7.03	10.51	10.01			
2	Clark	IL	St Louis	39.430	-87.987	104.8	16.8	1.023	6.96	16.50			-6.14	-40.6
3	Clark	IL	St Louis			103.6	16.5	1.027	6.84	15.82	15.92	12.20		
4	Coles	IL	Osage	39.425	-88.406	731.5	16.5	1.093	6.76	1.74	1.69	-11.12	-2.06	-26.5
5	Coles	IL	Osage	39.410	-88.406	731.5	16.6	1.091	6.66	1.28				
6	Crawford	IL	Cypress	39.049	-87.806	396.2	22.1	1.021	7.89	18.90	17.02		-5.84	-35.5
7	Crawford	IL	Cypress	39.049	-87.806	396.2	19.1	1.021	7.73	26.89				
8	Crawford	IL	Cypress	39.049	-87.806	396.2	22.5	1.021	8.03	19.17	18.42	-23.55		
9	Crawford	IL	Robinson	39.050	-87.788	274.3	23.1	1.025	7.25	23.53				
10	Edwards	IL	Waltersburg	38.431	-88.015	701.0	30.1	1.044	6.96	4.47			-3.65	-30.0
11	Jefferson	IL	St Genevieve	38.235	-88.750	940.9	26.0	1.100	6.38	0.77	1.03		-2.17	-30.2
12	Perry	IL	Cypress	38.148	-89.214	352.9	22.0	1.058	6.78	3.61	4.07			
13	Wabash	IL	Tar Springs	38.281	-87.906	384.0	19.3	1.071	7.30	3.45	3.08		-2.16	-21.6
14	Washington	IL	Benoist	38.309	-89.210	438.3	22.6	1.072	6.61	1.75	1.52	-3.73	-3.00	-24.5
15	Wayne	IL	Salem	38.307	-88.305	1188.7	20.1	1.107	7.09	2.61				
16	Wayne	IL	St Genevieve	38.422	-88.286	960.1		1.092	7.19	4.00				
17	Wayne	IL	St Genevieve	38.408	-88.305	1021.1	17.7	1.086	7.08	3.13		-15.56	-2.27	-24.1
18	Wayne	IL	St Genevieve	38.391	-88.396	1015.0		1.105	8.19	2.68				
19	Wayne	IL	St Louis/ Salem	38.321	-88.287	1219.2	18.5	1.108	7.03	2.43	1.47			
20	White	IL	Palestine	38.118	-88.051	640.1	25.3	1.045	7.51	11.19	9.91			
21	White	IL	Salem-St Louis	38.176	-88.035	1219.2	21.4	1.088	7.18	2.94	2.50	1.69	0.07	-17.8
22	Gibson	IN	Aux Vases	38.267	-87.927	835.2	24.2	1.078	7.02	3.13				
23	Greene	IN	Salem			224.0	19.0	1.011	6.81	10.94				
24	Lawrence	IL				429.2	18.3	1.027	7.13	6.51			-4.59	-31.4
25	Posey	IN	Cypress			766.6		1.074	7.36	9.00	7.85			
26	Posey	IN	Cypress			762.0	19.7	1.068	7.10	8.08	7.46			
27	Posey	IN	O'Hare			813.5	20.22	1.077	7.43	1.24	0.77		-0.62	-19.7
28	Posey	IN	Tar Springs			652.3	19.5	1.029	7.83	8.39				
29	Posey	IN	Waltersburg			609.6	22.0	1.052	7.02	6.56	6.38			
30	Posey	IN	Waltersburg			644.6	23.5	1.054	6.97	4.42	4.74			
31	Posey	IN	Waltersburg				23.8	1.052	6.94	5.98	6.54			
32	Henderson	KY	Aux Vases				18.0	1.062	7.78	8.38				
33	Henderson	KY	Cypress				21.5	1.053	6.89	9.84	10.08			
34	Henderson	KY	Waltersburg				21.7	1.025	7.39	7.93	6.97	-15.19	-4.37	-28.1
<i>Silurian-Devonian</i>														
35	Clark	IL		39.368	-87.545	609.6	23.8	1.008	7.19	11.68				
36	Clark	IL		39.368	-87.545	609.6	20.7	1.008	7.17	10.82				
37	Clark	IL		39.368	-87.545	609.6	26.2	1.008	7.11	12.10				
38	Clark	IL		39.368	-87.545	609.6	21.8	1.008	7.14	10.98		1.83	-6.58	-41.1
39	Crawford	IL		39.034	-87.881	838.2	22.8	1.129	6.88	1.86	1.11	1.01	-1.34	-24.9
40	Crawford	IL		39.049	-87.881	838.2	21.7	1.096	7.58	3.74				
41	Cumberland	IL	Geneva	39.179	-88.461	1143.0	27.5	1.079	6.60	7.16		-18.53	-2.89	-29.3
42	Effingham	IL	Geneva	39.167	-88.476	1143.0	35.1	1.080	7.16	5.66				
43	Effingham	IL	Geneva	39.155	-88.477	1143.0	21.5	1.080	7.07	6.14		-3.39	-2.95	-28.9
44	Effingham	IL	Geneva	39.069	-88.681	1143.0	19.1	1.080	6.72	6.31				
45	Jefferson	IL		38.235	-88.750	1505.4	19.2	1.148	6.77	0.80			1.79	-16.3
46	Greene	IN				446.5	22.0	1.010	7.29	14.54				
47	Greene	IN				446.5		1.010			15.06		-6.16	-42.2
48	Greene	IN				446.5	23.6	1.010	7.03	13.62				
49	Greene	IN				446.5	20.2	1.007	7.50	17.45	16.70	15.65	-6.64	-39.3
50	Sullivan	IN		39.166	-87.507	725.4	23.5	1.053	7.25	6.19				
51	Sullivan	IN		39.166	-87.507	725.4	22.6	1.074	7.46	4.83		1.32	-3.40	-34.6
52	Vigo	IN		39.442	-87.359	502.9	26.4	1.004	7.49	8.18				
53	Vigo	IN		39.442	-87.359	502.9	25.6	1.004	7.56	8.37				
54	Vigo	IN		39.442	-87.359	502.9	24.5	1.004	7.86	8.42	7.55			
55	Vigo	IN		39.442	-87.359	502.9	23.4	1.004	8.14	8.65				
56	Vigo	IN		39.442	-87.359	502.9	24.9	1.004	7.51	8.83				
57	Vigo	IN		39.442	-87.359	502.9	25.0	1.004	8.00	8.14	7.73			
58	Vigo	IN		39.442	-87.359	502.9	25.1	1.004	8.30	8.53				
59	Christian	IL		39.750	-89.188	571.5	22.7	1.077	6.94	1.14	1.05	6.38	-1.69	-21.7
60	Christian	IL		39.764	-89.207	571.5	21.0	1.090	7.37	1.97	1.70			
61	Sangamon	IL		39.722	-89.564	475.5	22.3	1.058	7.16	2.23				
62	Sangamon	IL		39.722	-89.564	486.5	18.2	1.060	7.73	1.96	1.44	-3.20	-2.43	-21.6
63	DeWitt	IL		40.261	-88.890	347.5	22.0	1.003	8.36	10.43				
64	DeWitt	IL		40.246	-88.871	347.5	20.6	1.003	8.22	9.74		-10.26	-8.62	-56.7

Table 5. Selected chemical analyses (mM) for Illinois Basin formation waters.

Sample	Na	Ca	Mg	Sr	Cl	Cl _T	Br	SO ₄	Si	B	Li	Ba	Mn	Total Fe	K
<i>Mississippian-Pennsylvanian</i>															
1	996.61	28.10	31.79	1.11	1176.54	1032.31	1.04	0.35	0.13	0.22	1.41	0.11	0.006	0.257	3.03
2	504.27	11.59	16.96	0.47	570.34	505.50	0.48	0.16	0.11	0.23	0.47	0.23	0.003	0.022	1.95
3	609.28	11.30	19.41	0.47	646.66	631.95	0.00	0.00	0.13	0.19	0.46	0.07	0.004	0.006	2.06
4	1728.84	128.02	66.24	3.92	2329.99	2056.66	3.02	5.06	0.27	0.65	4.45	0.01	0.013	0.061	12.74
5	1691.64	119.04	69.86	7.43	2304.19	2020.11	3.39	0.33	0.17	0.60	4.59	0.02	0.016	0.148	12.37
6	470.75	4.71	9.45	0.29	465.42	463.47	1.39	13.64	0.18	0.16	0.13	0.01	0.001	0.002	0.90
7	493.28	6.68	9.37	0.30	469.07	446.69	1.17	10.18	0.16	0.17	0.12	0.01	0.002	0.003	0.80
8	462.98	5.81	10.16	0.25	469.35	440.68	0.47	14.24	0.20	0.15	0.14	0.00	0.012	0.006	0.63
9	557.23	6.10	14.93	0.27	594.26	551.63	0.86	0.68	0.17	0.13	0.13	0.65	0.002	0.011	0.89
10	929.96	38.65	29.52	0.57	1160.08	1039.13	1.40	1.89	0.19	0.22	0.21	0.03	0.018	0.018	1.31
11	1818.61	131.70	124.12	6.26	2414.31	2202.27	3.46	3.59	0.15	0.36	1.00	0.01	0.020	0.365	4.63
12	1135.45	57.92	60.65	2.43	1342.73	1369.58	1.80	0.51	0.16	0.14	0.51	0.05	0.016	0.416	2.63
13	1343.81	103.69	51.24	3.04	1853.70	1598.04	2.83	3.05	0.19	0.22	0.37	0.01	0.029	0.020	1.88
14	1388.77	77.24	57.65	2.49	1765.42	1633.84	1.85	0.22	0.13	0.25	0.77	0.04	0.021	0.271	3.14
15	1940.46	190.06	115.78	2.07	2848.48	2362.97	4.05	15.14	0.20	1.58	2.52	0.00	0.010	0.021	14.71
16	1687.51	122.06	88.24	1.74	2251.92	2076.90	4.62	15.32	0.22	1.34	1.68	0.00	0.009	0.018	10.41
17	1606.01	101.22	78.56	1.60	2205.09	1804.80	8.32	21.75	0.20	0.42	0.71	0.00	0.009	0.001	4.88
18	1809.55	153.23	111.74	1.69	2145.46	2401.74	2.43	13.63	0.22	1.08	1.49	0.00	0.010	0.020	8.36
19	1919.98	180.66	104.31	1.82		2300.00	3.92	17.72	0.21	1.68	2.46	0.00	0.011	0.055	15.67
20	950.55	32.56	25.94	0.81	1119.78	994.74	1.65	10.25	0.33	0.25	0.18	0.01	0.011	0.007	0.64
21	1754.85	119.29	83.38	1.46	1853.04	1976.54	2.18	8.12	0.18	0.94	1.78	0.01	0.015	0.038	9.14
22	1382.72	110.01	93.10	1.80	1920.62	1739.59	3.50	13.21	0.19	0.53	0.92	0.00	0.013	0.027	3.79
23	150.23	25.83	24.93	0.32	171.50	165.42	0.36	29.41	0.22	0.32	0.35	0.00	0.004	0.006	1.18
24	518.50	27.04	16.85	0.34	549.81	500.29	0.83	41.42	0.19	0.17	0.12	0.00	0.017	0.025	0.95
25	1429.86	67.91	44.13	0.69	1803.09	1564.61	2.59	40.85	0.18	0.62	0.80	0.00	0.014	0.010	2.88
26	1372.03	59.88	39.27	0.63	1590.29	1480.70	1.81	38.61	0.18	0.50	0.69	0.00	0.007	0.013	2.43
27	1543.20	97.18	73.75	0.91	1896.41	1637.30	2.41	35.40	0.16	0.68	1.07	0.00	0.012	0.014	3.74
28	578.16	19.80	14.05	0.66	695.72	648.28	1.52	1.82	0.19	0.23	0.10	0.06	0.008	0.003	0.70
29	1228.74	34.42	32.81	0.44	1280.39	1323.76	1.38	55.75	0.20	0.40	0.32	0.00	0.022	0.010	1.32
30	1071.02	40.44	27.99	0.39	1169.67	1099.16	1.54	71.31	0.17	0.37	0.26	0.00	0.013	0.020	1.16
31	1049.61	29.86	27.43	0.37		1055.66	2.36	69.71	0.16	0.37	0.29	0.00	0.022	0.010	1.10
32	1171.21	72.14	70.29	0.78	1483.30	1323.90	2.23	31.24	0.15	0.50	1.19	0.00	0.008	0.016	1.81
33	1090.76	27.18	31.41	2.05		1216.36	0.00	21.88	0.14	0.28	0.52	0.01	0.010	0.010	1.80
34	559.79	12.52	10.59	0.30		530.73	2.33	5.64	0.14	0.28	0.23	0.00	0.006	0.005	0.99
<i>Silurian-Devonian</i>															
35	147.57	9.13	9.13	0.25	170.34	167.68	0.00	0.22	0.18	0.37	0.36	0.01	0.002	0.006	1.64
36	160.72	9.73	9.70	0.29	185.64	178.91	0.50	0.21	0.22	0.37	0.53	0.02	0.001	0.005	1.43
37	172.35	11.11	11.50	0.30	182.41	188.47	0.48	0.00	0.21	0.36	0.37	0.01	0.002	0.006	1.06
38	159.25	9.56	10.56	0.30	208.48	181.58	0.60	0.34	0.21	0.38	0.41	0.02	0.002	0.008	1.11
39	2479.73	239.78	153.08	4.30	3423.87	2923.20	4.46	4.68	0.16	2.18	3.24	0.01	0.018	0.033	30.38
40	1720.51	151.66	88.96	1.84	2063.15	2095.89	3.29	18.50	0.17	1.15	2.65	0.01	0.014	0.019	17.94
41	1495.22	92.18	60.13	1.25	1968.02	1774.96	1.32	5.91	0.10	0.27	1.60	0.10	0.007	0.035	8.25
42	1538.09	99.35	62.74	1.32	1958.90	1768.36	2.65	13.70	0.27	0.56	1.96	0.01	0.006	0.014	7.73
43	1645.63	101.76	63.86	1.44	2096.00	1790.48	3.48	3.74	0.24	0.53	2.01	0.04	0.011	0.017	7.70
44	1480.81	101.63	64.30	1.63	2140.45	1805.03	4.23	0.00	0.19	0.60	2.01	0.02	0.009	0.015	8.80
45	2573.31	255.36	104.86	5.54	3905.39	3338.76	12.09	5.73	0.13	1.49	2.65	0.01	0.029	1.008	29.70
46	186.79	14.81	9.76	1.24	219.84	215.68	0.84	0.13	0.21	0.48	0.41	0.11	0.002	0.006	1.53
47	186.84	15.38	15.78	1.16	224.20	204.22	0.95	0.28	0.23	0.48	0.40	0.16	0.001	0.003	1.86
48	184.31	14.22	14.76	1.50	272.43	235.48	0.79	0.46	0.21	0.47	0.42	0.09	0.002	0.004	1.86
49	145.53	9.98	12.51	0.64	174.48	161.74	0.55	0.29	0.22	0.47	0.50	0.05	0.001	0.004	1.79
50	896.99	89.17	68.31	2.16	1371.83	1153.73	3.15	15.83	0.21	0.85	1.79	0.00	0.008	0.016	9.10
51	1222.16	139.46	93.45	3.40	1909.23	1652.50	5.93	9.71	0.19	1.20	2.50	0.01	0.013	0.021	13.61
52	81.82	4.14	4.46	0.13	96.78	85.17	0.39	0.11	0.21	0.28	0.21	0.01	0.002	0.004	0.86
53	83.23	4.12	4.43	0.13	87.06	79.74	0.30	0.26	0.20	0.29	0.18	0.01	0.000	0.002	0.76
54	84.80	4.24	4.95	0.15	88.00	88.90	0.32	0.17	0.19	0.28	0.19	0.01	0.000	0.001	1.02
55	80.27	3.82	4.18	0.12	86.28	92.63	0.00	0.15	0.17	0.29	0.19	0.01	0.001	0.001	0.71
56	80.40	3.88	4.38	0.13	89.42	96.12	0.43	0.34	0.20	0.28	0.34	0.01	0.000	0.001	0.69
57	76.17	3.58	3.94	0.11	89.74	92.20	1.02	0.55	0.22	0.28	0.19	0.01	0.000	0.000	0.69
58	85.50	4.05	4.55	0.14	87.81	88.97	1.39	0.14	0.16	0.29	0.21	0.01	0.003	0.003	0.92
59	1272.02	96.53	78.82	2.26	1894.73	1727.05	2.81	0.50	0.16	0.33	1.52	0.13	0.012	0.030	8.53
60	1665.69	129.26	90.35	2.34	2259.56	2048.16	3.30	1.74	0.16	0.34	1.49	0.01	0.011	0.032	8.27
61	1128.19	89.69	61.32	2.32	1513.59	1357.21	2.28	0.56	0.15	0.28	1.14	0.04	0.008	0.017	7.06
62	1106.35	82.83	66.49	2.15	1405.97	1313.44	1.91	4.54	0.15	0.28	1.11	0.01	0.012	0.019	6.58
63	66.14	1.57	1.81	0.05	61.42	57.82	1.67	2.56	0.30	0.17	0.08	0.00	0.002	0.006	0.53
64	70.59	1.73	1.93	0.04		65.58	0.72	2.54	0.19	0.17	0.08	0.00	0.003	0.006	0.73

Illinois Basin Formation Waters

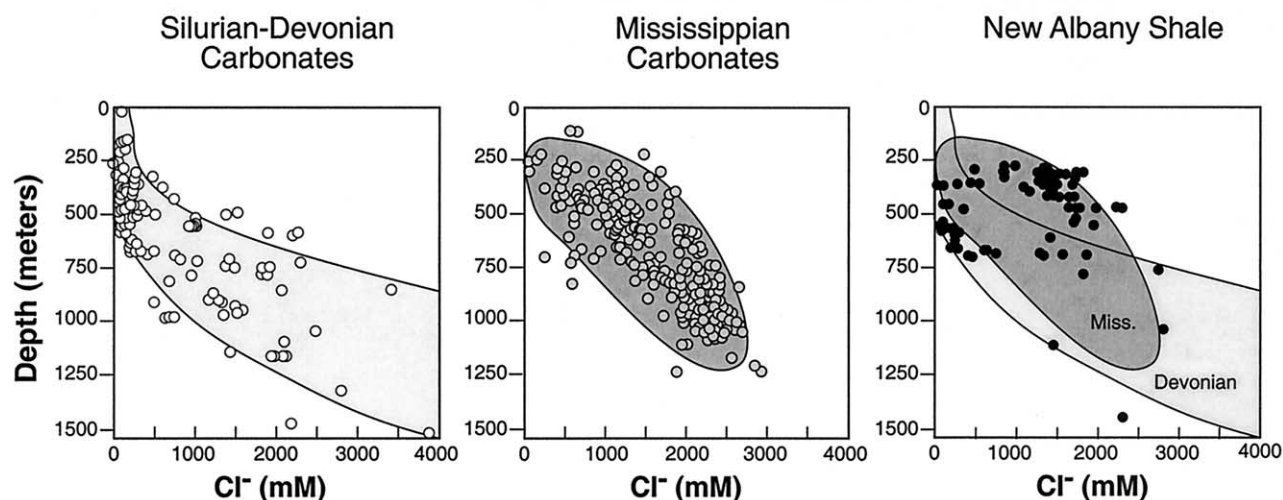


Fig. 7. Chloride vs. depth relations for Illinois Basin formation waters. Silurian-Devonian and Mississippian carbonate formation waters are shown separately and overlain with New Albany Shale fluids.

300 mM chloride near the subcrop to more than 2000 mM chloride in the central basin. Dilute waters are also found along the northern and western basin margins. Stueber et al. (1993) reported that Mississippian-Pennsylvanian brines in Illinois have been diluted extensively by meteoric water, most likely recharged during the pre-Pennsylvanian unconformity or by subaerial exposure of the carbonates. Unlike the Siluro-Devonian aquifers, the Mississippian carbonates contain relatively dilute waters along the southern margin, compatible with the regional arc of the carbonates along the southern limb of the basin. Karstification of Mississippian carbonates along the southern margin of the basin enhanced the permeability and porosity of the subcrop, allowing for greater recharge to the Mississippian aquifer system. The Mississippian clastic rocks (Chesterian Series) overlying the carbonates (Valmeyeran Series) have similar salinity stratification with depth and are included in the salinity pattern of the Mississippian aquifer system (Fig. 6c).

The chloride vs. depth profiles for the Siluro-Devonian formation waters show a distinct trend: dilute water, near potable at shallow depths, penetrates as deep as 1 km (Fig. 7). At depths greater than 1 km, the fluid salinity rapidly increases to values in excess of 3000 mM chloride. Formation waters in the Mississippian carbonates show a linear salinity–depth relation typical of basinal formation waters (Dickey, 1969), with no apparent suppression of salinity by freshwater like the Siluro-Devonian aquifer system. The New Albany Shale chloride content with depth values span the range observed for the Siluro-Devonian and Mississippian carbonates.

The New Albany Shale fluids can be divided into three groups on the basis of chloride content, hydrostratigraphic setting, and location along the eastern margin of the Illinois Basin (Fig. 8a): group 1, Silurian shelf; group 2, Mississippian recharge; and group 3, Basin brine. Group 1 contains relatively dilute waters to great depths (>600 m); the majority of samples fall within the Siluro-Devonian carbonate formation water salinity vs. depth profile (Fig. 8b). Group 2 contains intermediate

salinity fluids within the range of Mississippian carbonate formation waters. These samples are located in the karsted region along the southeastern margin of the basin, where the Borden Group is thin or absent. Group 3 has the greatest chloride concentration, resembling values for Illinois Basin Na-Cl brines, with little or no dilution from meteoric water. The three groups suggested for New Albany Shale fluids along the eastern margin of the Illinois Basin are consistent with distinct major ion and stable isotope chemistry, carbon system parameters, and gas chemistry, and are useful in determining timing and mechanism of gas generation and its relation to meteoric recharge.

4.1.2. Major Ion Chemistry

Siluro-Devonian and Mississippian formation waters from the eastern margin of the Illinois Basin have relatively uniform Ca/Mg ratios (~ 1.6) (Fig. 9a). The most saline New Albany Shale fluids, group 3 samples, have Ca/Mg ratios similar to the adjacent basinal brines. The more dilute New Albany Shale samples in group 1 are depleted in Ca^{2+} relative to Mg^{2+} , falling below the Mississippian and Siluro-Devonian formation water trend line. The most dilute, group 2, fall within the range of group 1 samples, whereas the more saline waters plot along the Siluro-Devonian and Mississippian trend line. Compared with the Antrim Shale in northern Michigan, the New Albany Shale fluids have similar Ca/Mg ratios. Both shales host formation waters, which are depleted in Ca/Mg relative to Michigan and Illinois basinal brines (Fig. 9b), regardless of the significant salinity and Na/Ca ratio differences between the two basins.

The Ca/Mg ratio in basinal brines is primarily controlled by water–rock reactions with carbonate minerals in the subsurface. Dissolution of calcite and dolomite contributes Ca^{2+} and Mg^{2+} ions to formation waters, as well as DIC. Subsequent precipitation of calcite removes Ca^{2+} and bicarbonate ions from the water, enriching the remaining solution in Mg^{2+} . There-

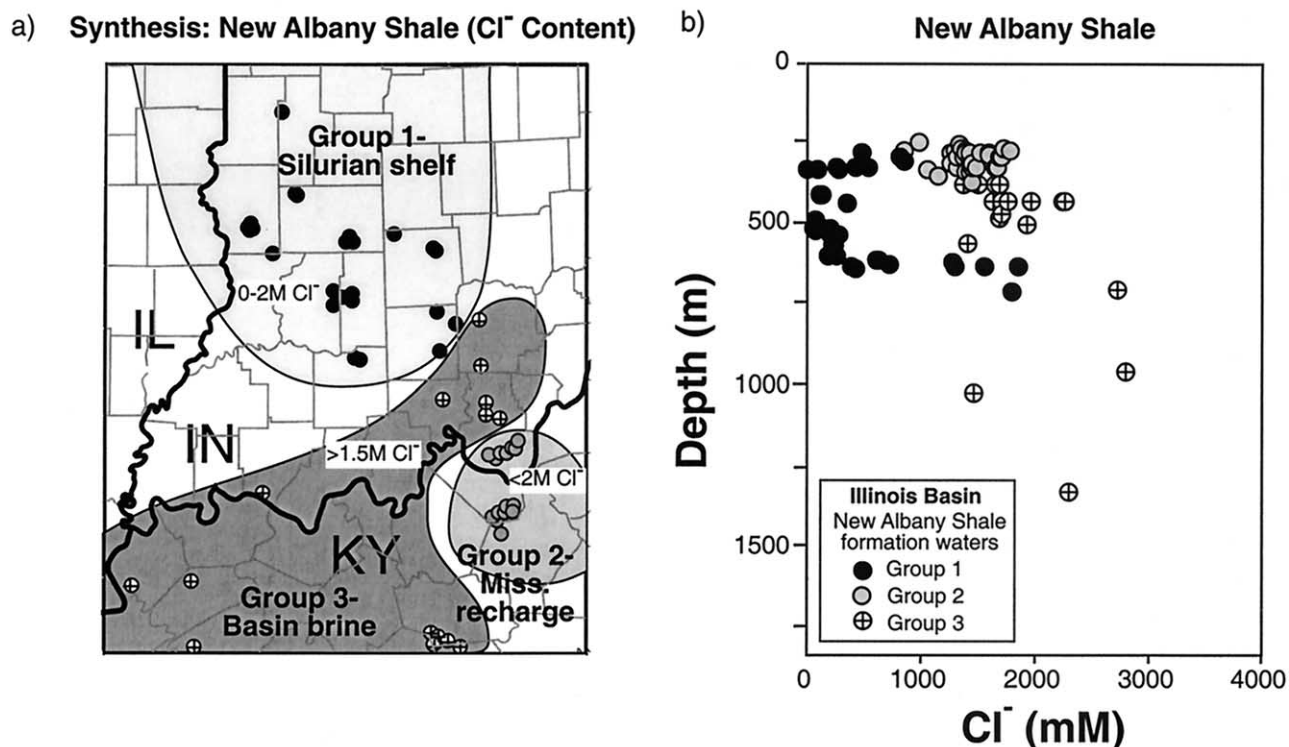


Fig. 8. (a) New Albany Shale samples divided into three distinct subgroups by well location, depth, hydrogeologic setting, and fluid chemistry. Group 1, Silurian shelf; group 2, Mississippian recharge; and group 3, Basin brine. The symbols and names for the three subgroups are used throughout this article. (b) Detailed view of New Albany Shale formation waters chloride vs. depth showing delineation of the three subgroups.

fore, Mg^{2+} maybe used as a conservative tracer of calcite precipitation. Both the New Albany Shale and Antrim Shale fluids show decreasing Ca/Mg ratios with increasing alkalinity, further indicating calcite precipitation (Figs. 9c,d).

The Ca/Mg ratios of shale formation waters may be an indicator of microbial methanogenic activity in the shale reservoirs: as alkalinity increases via methanogenesis, fluids become supersaturated with respect to calcite, leading to calcite precipitation. The geochemistry of calcite cements filling fractures in the Antrim Shale is described in Budai et al. (in press). As calcite precipitates in fractures, the Ca/Mg ratio of the remaining fluid decreases. The group 3 samples from the New Albany Shale have the highest Ca/Mg ratio and lowest alkalinity (Fig. 9c), consistent with their thermogenic gas history. Groups 1 and 2 have higher alkalinity values and lower Ca/Mg ratios, similar to the Antrim Shale samples in northern Michigan (Fig. 9d). These fluids most likely have been affected by methanogenesis. The Siluro-Devonian and Mississippian formation waters in the Illinois Basin have Ca/Mg ratios similar to the New Albany Shale fluids, much lower than the Silurian-Devonian waters in the Michigan Basin.

4.1.3. Sources of Water: Oxygen and Hydrogen Isotopes

Stable isotope chemistry of New Albany Shale waters provides evidence for recharge of Pleistocene meltwaters into the eastern margin of the Illinois Basin and generation of microbial gas. The oxygen and hydrogen isotope values of the shale

waters vary from meteoric water to basinal brine values (Fig. 10). Group 1 waters have the most negative $\delta^{18}\text{O}$ and δD values, with the majority of samples plotting along the meteoric water line (MWL) ($\delta\text{D} = 8\delta^{18}\text{O} + 10$) (Craig, 1961). These waters are also the most dilute, <300 mM chloride. Many of the group 1 samples fall within the range of local, present-day meteoric and surface water values ($\delta^{18}\text{O} \approx -4.5$ to -7.5‰) (Clayton et al., 1966; Drever, 1969; IAEA/WMO, 1998; Coplen and Kendall, 2000). Group 2 waters range from $\delta^{18}\text{O}$ and δD values, which span from the MWL to basinal brine values (Clayton et al., 1966). Group 3 waters plot to the right of the MWL, enriched in ^{18}O . The span of New Albany Shale $\delta^{18}\text{O}$ and δD values is typical of mixing diagenetically altered basinal brines ($\delta\text{D} = -5\text{‰}$, $\delta^{18}\text{O} = +2\text{‰}$) with meteoric water ($\delta\text{D} = -40\text{‰}$, $\delta^{18}\text{O} = -6.3\text{‰}$) (Hanor, 1987). The oxygen and hydrogen isotope trajectory of the shale waters follows the trend of Illinois Basin brines reported by Clayton et al. (1966). The Siluro-Devonian and Mississippian formation waters sampled also fall along the Illinois Basin brine trajectory. Siluro-Devonian oxygen and hydrogen isotope values likely represent mixing of meteoric waters with saline basinal fluids (Stueber and Walter, 1991). The range of $\delta^{18}\text{O}$ and δD values in Mississippian and New Albany Shale formation waters also likely reflects mixing of freshwater and brine.

The depth vs. $\delta\text{D}_{\text{H}_2\text{O}}$ relations of New Albany Shale fluids further suggest recharge of freshwater into the shale (Fig. 11a). Group 1 formation waters have the lowest δD values (<

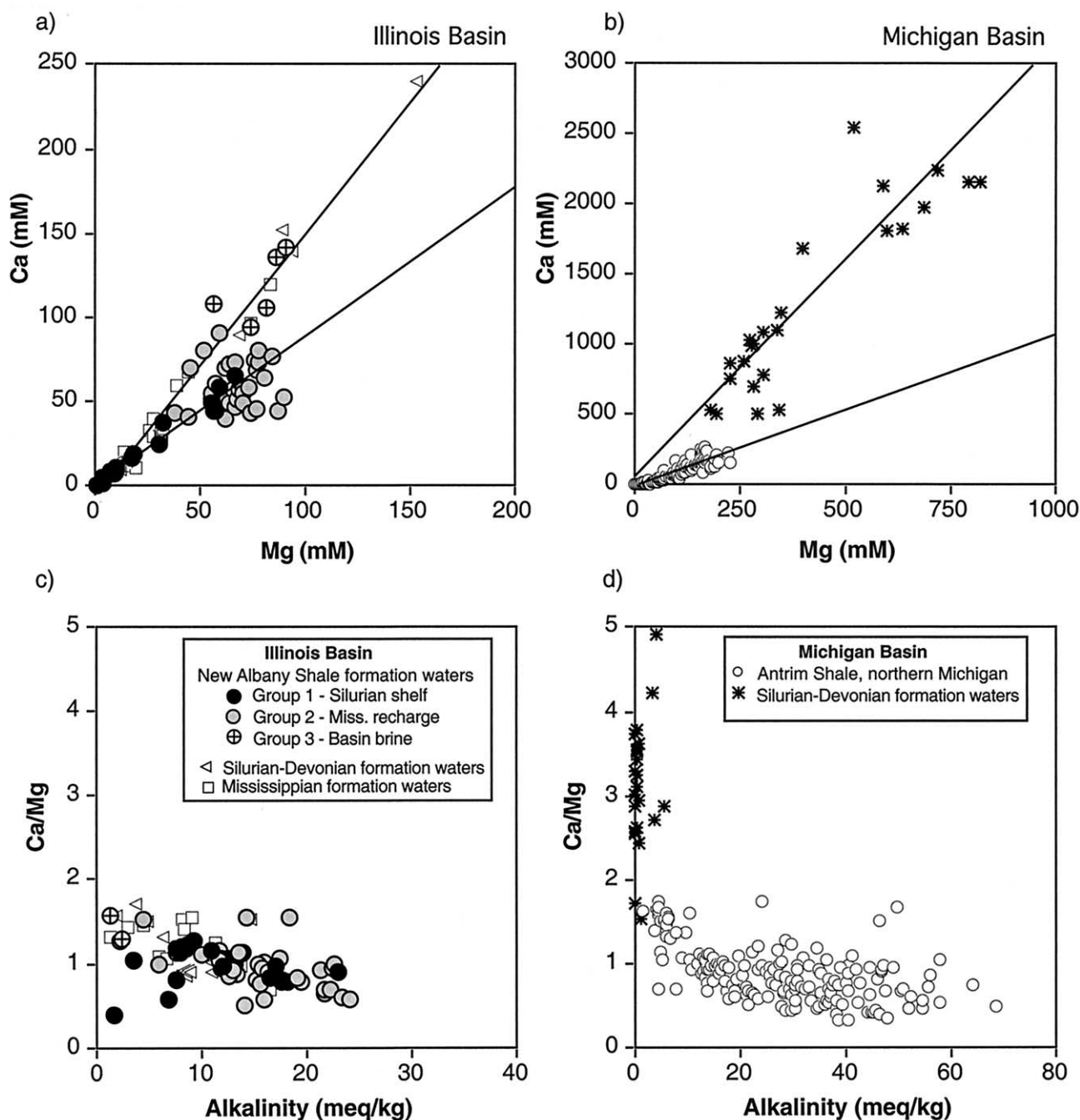


Fig. 9. Ca/Mg ratios for Late Devonian black shales compared with basinal brine. (a) New Albany Shale formation waters plotted relative to adjacent basinal brines. Regression lines shown for group 1 Silurian shelf New Albany Shale samples ($y = 0.886x + 1.003$, $r^2 = 0.974$), and Silurian-Devonian- to Mississippian-age formation waters ($y = 1.574x - 7.268$, $r^2 = 0.984$). (b) Ca/Mg ratios for Antrim Shale fluids in northern Michigan (Martini et al., 1998) compared with Silurian-Devonian Michigan Basin brines. Regression lines shown for northern Michigan Antrim Shale samples ($y = 1.086x - 10.763$, $r^2 = 0.829$) and Silurian-Devonian brines ($y = 3.122x + 57.293$, $r^2 = 0.747$). (c) Ca/Mg vs. Alkalinity for New Albany Shale fluids and adjacent formation waters. (d) Ca/Mg vs. alkalinity relations for Antrim Shale fluids and Siluro-Devonian formation waters in northern Michigan.

–25‰) and extend to >500 m depth. Group 2 and group 3 fluids have higher δD values, although the samples were from shallower depths in the basin. Clayton et al. (1966) reported δD values of ~ -80 ‰ and $\delta^{18}O$ values of -10 ‰ in shallow Illinois Basin water interpreted to be Pleistocene meltwater.

The reported $\delta^{18}O$ values for Pleistocene continental ice sheets range from -40 ‰ to -9 ‰ (Dansgaard and Tauber, 1969; Emiliani, 1971). The hydrogen isotope values for the group 1 fluids and volume of dilute water in the reservoir are more consistent with these glacial meltwater values than the group 2

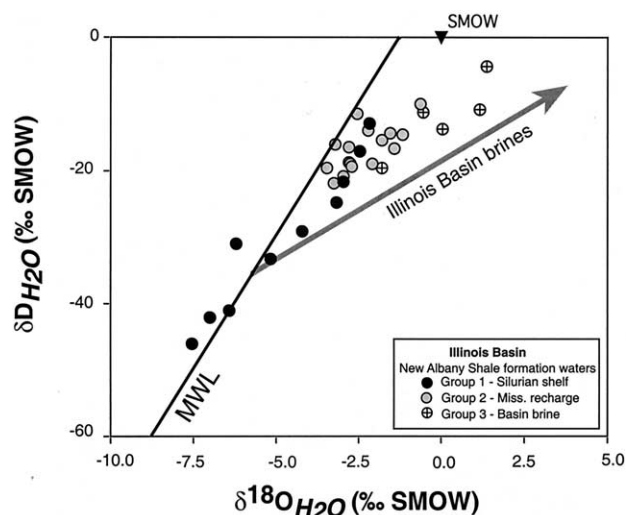


Fig. 10. δD vs. $\delta^{18}O$ relations for Illinois Basin fluids overlain on the Meteoric Water Line (MWL) (Craig, 1961). New Albany Shale formation waters are identified by subgroups (group 1, Silurian shelf; group 2, Mississippian recharge; group 3, Basin brine). The trend line for the Illinois Basin brines (Stueber and Walter, 1991) is shown in dark gray. The standard mean ocean water (SMOW) value is plotted for reference.

or group 3 waters. The Mississippian recharge waters ($\delta D = -10$ to -21‰) are more likely to have been recharged by relatively modern meteoric waters.

The bromide content of formation waters can also be used to determine mixing relations of basinal brines with freshwater

because bromide is a relatively conservative element. Basinal fluids typically have high bromide concentrations and δD values, whereas dilute waters have low bromide and δD values (Weaver et al., 1995). The New Albany Shale fluids have bromide and hydrogen isotope compositions spanning the range between basinal brine and freshwater values (Fig. 11b). There appears to be a mixing trend between group 1 dilute waters and group 3 fluids, with a freshwater end-member value of $\delta D = -43\text{‰}$ ($r^2 = 0.898$). A second dilute water end member may be extrapolated for the group 2 fluids mixing with basinal brine group 3 samples; however, the r^2 value is low (0.111). The bromide concentrations of Siluro-Devonian and Mississippian carbonate formation waters range from <1 mM to 12 mM, off the scale of Figure 11b. The Antrim Shale formation water chemistries also indicate mixing of freshwater with basinal brines (mixing trend shown in Fig. 11b, $r^2 = 0.767$). The Antrim Shale freshwater end-member δD value is isotopically depleted ($\delta D = -82\text{‰}$) relative to the New Albany Shale fluids.

Oxygen and hydrogen isotope values for the New Albany Shale, combined with major ion chemistry, indicate that Pleistocene meltwater and/or meteoric waters likely recharged the shale along the northern margin of the basin. The dilute, group 1 waters are most like the Pleistocene meltwaters, although the δD and $\delta^{18}O$ values of fluids are higher than reported glacial meltwater values. The chemistry of group 2 waters indicates that modern precipitation recharged the New Albany Shale along the southern margin of the basin, through the overlying Mississippian carbonates. Group 3 waters represent the basinal brine end member and have not been affected by freshwater incursion.

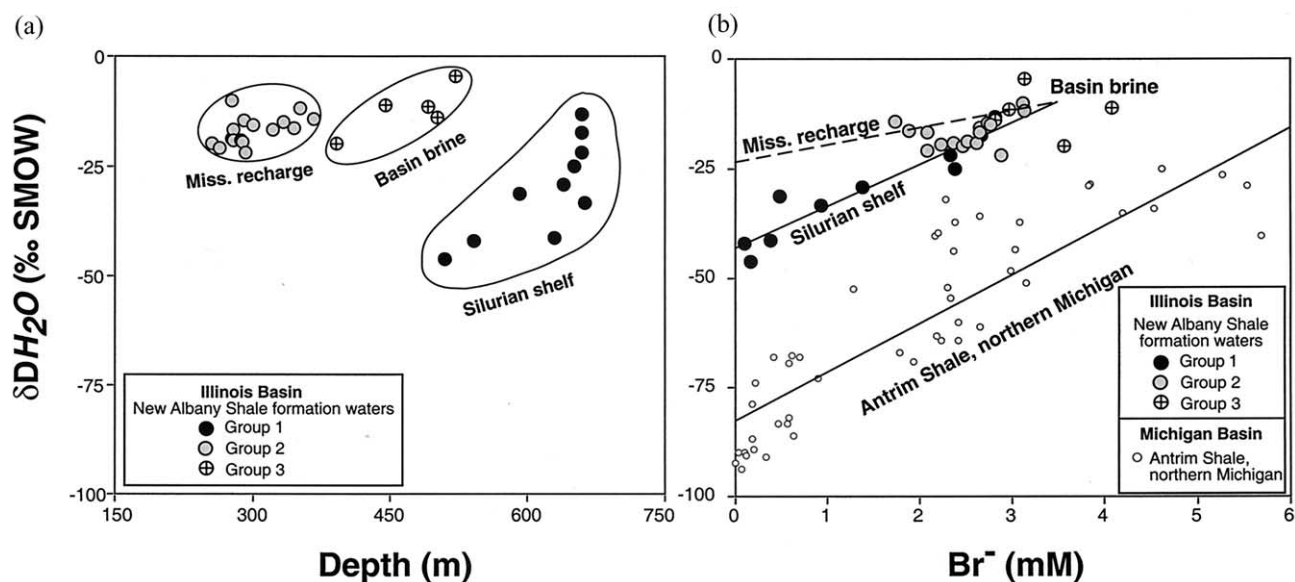


Fig. 11. a) δD values for New Albany Shale formation waters vs. depth. Three shale subgroups are outlined. (b) δD_{H_2O} vs. Br^- . Linear regression line shown in solid black for group 1 (Silurian shelf) New Albany Shale samples ($y = 9.578x - 42.977$, $r^2 = 0.898$). Dotted line represents possible trend line for group 2 (Mississippian recharge) samples. Antrim Shale samples from northern Michigan (Martini et al., 1998) are shown for comparison with the trend line ($y = 11.175x - 82.384$, $r^2 = 0.767$).

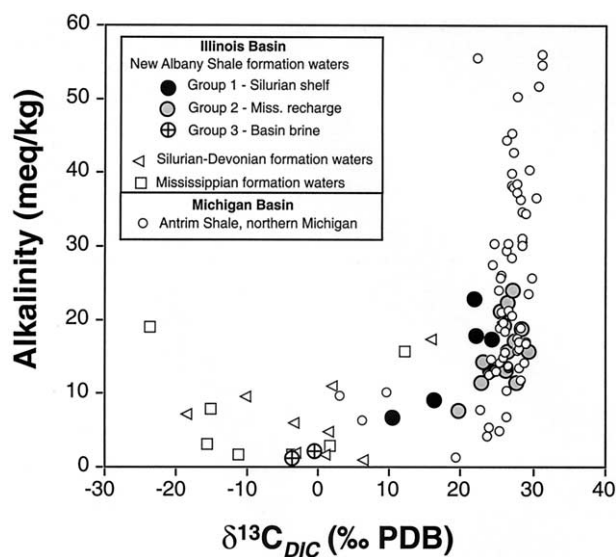


Fig. 12. Alkalinity vs. $\delta^{13}\text{C}$ values of DIC. New Albany Shale samples are shown by subgroup with the Antrim Shale samples, northern Michigan (small white circles) (Martini et al., 1998). Illinois Basin Silurian-Devonian and Mississippian formation waters are also shown.

4.2. Sources of Gas in the New Albany Shale

4.2.1. Evolution of Carbon: Alkalinity and C Isotopes

A full characterization of the carbon systematics and carbon isotope composition of formation waters can be useful in determining the dominant microbial process responsible for high alkalinity fluids. The Antrim Shale fluids, associated with bacterial gas production along the northern margin of the Michigan Basin, have relatively high $\delta^{13}\text{C}$ values for DIC coupled with high DIC concentrations (Martini et al., 1998) (Fig. 12). The DIC content of formation waters can be controlled by water-rock interactions with calcium carbonates, either through recharge from overlying glacial drift or from associated carbonate formations within the basin. Dissolved inorganic carbon can also be derived by microbial processes in the subsurface, such as methanogenesis or sulfate reduction. Both processes modify the carbon isotopic signature of the associated formation water.

Carbon isotope compositions of New Albany Shale fluids coupled with alkalinity or DIC content can be instructive in determining the carbon evolution of fluids and gas. Methane produced by microbial methanogenesis is typically depleted in ^{13}C ($\delta^{13}\text{C} = -110\text{‰}$ to -50‰) compared with thermogenic methane ($\delta^{13}\text{C} = -50\text{‰}$ to -20‰) (Whiticar, 1999). The low $\delta^{13}\text{C}$ values of bacterial methane result in an increase in the $\delta^{13}\text{C}$ value of DIC in associated waters. Fluids with high alkalinity (or DIC) and $\delta^{13}\text{C}$ values are indicative of methanogenesis (Martini et al., 1996). New Albany Shale formation waters show increasing $\delta^{13}\text{C}_{\text{DIC}}$ values with increasing alkalinity (Fig. 12). A mixing trend is apparent between a ground-water or basinal brine end member ($\delta^{13}\text{C} < 0\text{‰}$, alkalinity < 5 meq/kg) and high microbial gas fluids ($\delta^{13}\text{C} > 20\text{‰}$, alkalinity > 20 meq/kg). Group 1 and group 2 New Albany Shale waters show progressively increasing $\delta^{13}\text{C}$ values with increasing DIC. Group 3 waters have low alkalinity contents and low $\delta^{13}\text{C}$ values.

Sulfate reduction can also produce fluid with high alkalinity. However, as sulfate reduction progresses, the $\delta^{13}\text{C}$ values of associated fluids become increasingly more negative. The Silurian-Devonian and Mississippian formation waters show a likely pattern of sulfate reduction, with increasing alkalinity and decreasing $\delta^{13}\text{C}$ values (Fig. 12). A few fluids from over- and underlying units resemble the New Albany Shale alkalinity and $\delta^{13}\text{C}$ values; these waters are from the eastern margin of the Illinois Basin and are more likely associated with the shallow microbial gas play.

The potential for sulfate reduction in formation waters is important to consider because microbial methanogenesis does not become an important gas generating process until the sulfate has been depleted by sulfate reducing microbes (Whiticar, 1999). The relations between formation water alkalinity and dissolved sulfate concentrations are shown for New Albany Shale formation waters in Figure 13. Overall, the New Albany Shale fluids have low sulfate concentrations (most < 5 mM) relative to the adjacent Siluro-Devonian and Mississippian formation waters (Fig. 13a); there are not any notable differences among the three shale subgroups (Fig. 13b). The Antrim Shale formation waters contain even less sulfate ($\text{SO}_4^{2-} < 1$ mM) than the New Albany Shale fluids (Walter et al., 1996). The high sulfate in New Albany Shale waters may be explained by mixing of shale fluids with the relatively sulfate-rich Mississippian or Siluro-Devonian formation waters. The Mississippian carbonate formation waters have the greatest sulfate concentration, almost eight times that of the shale formation waters, consistent with other studies on Mississippian carbonate reservoir fluids in the Illinois Basin (Stueber et al., 1993). The Silurian-Devonian formation waters also contain high sulfate concentrations.

It is possible that some of the poor production of microbial methane from some New Albany Shale wells could be influenced by the presence of sulfate-reducing microbial populations outcompeting methanogens for organic substrates (Whiticar, 1999). This possibility makes it important to establish whether sulfate concentrations in shale formation waters can be maintained at low values by mineral solubility constraints. Stueber and Walter (1991) suggested that divalent cation concentrations (Ba^{2+} and Ca^{2+}) can be an important control on sulfate concentrations in Illinois Basin formation waters. In waters of high Ba^{2+} content, SO_4^{2-} contents will be maintained at relatively low values by barite precipitation. Concentrations of dissolved Ba^{2+} and SO_4^{2-} in New Albany Shale fluids are similar to Siluro-Devonian and Mississippian formation waters with low sulfate concentrations. Siluro-Devonian and Mississippian fluids with high SO_4^{2-} concentrations have very low Ba^{2+} as a result of limits imposed by barite solubility.

4.2.2. Produced Gas Composition

Unlike thermogenic processes, microbial methanogenesis produces CO_2 and CH_4 , with no higher chain hydrocarbons (ethane, propane). Also, the CO_2 and CH_4 produced by microbial methanogenesis are related isotopically to the hydrogen and carbon pools of the formation waters. Produced gas composition and isotope chemistry of the gas and associated formation waters can be useful in delineating the origin of hydro-

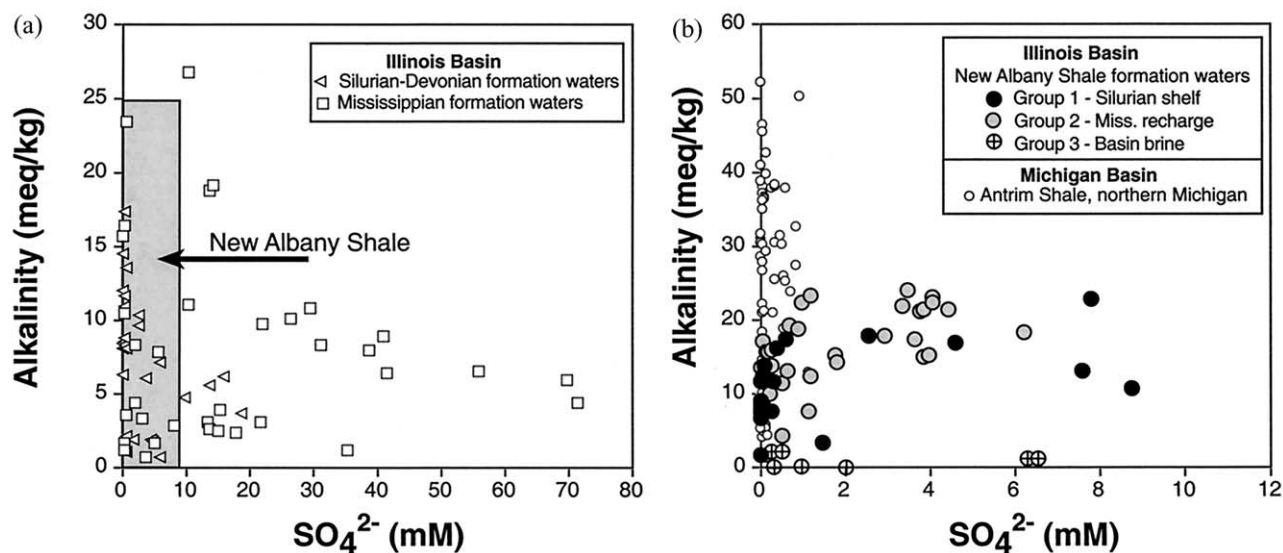
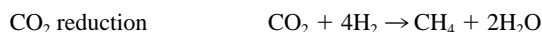


Fig. 13. (a) Alkalinity vs. SO_4^{2-} concentration comparing New Albany Shale fluids with adjacent formation waters (Silurian-Devonian and Mississippian). (b) Alkalinity vs. SO_4^{2-} for New Albany and Antrim shale formation waters. New Albany Shale samples are separated by group.

carbons in the New Albany Shale. Microbial methane is produced via two bacterial pathways:



The acetate fermentation process generates CO_2 , which is enriched in ^{13}C relative to the original organic precursor ($\delta^{13}\text{C} \sim -28$ to -30‰ , Antrim Shale organic carbon, northern Michigan) (Walter et al., 1996). The isotopic composition of CO_2 gas in turn controls the isotopic composition of DIC present dominantly as HCO_3^- in New Albany Shale formation waters (pH ~ 6 to 7). At isotopic equilibrium, the relationship between $\text{CO}_2(\text{g})$ and HCO_3^- isotope compositions is described by the equation:

$$1000\ln\alpha_{\text{HCO}_3\text{-CO}_2} = 9.552 \times 10^3/T - 24.09 \quad (02)$$

(IAEA, 1983). At typical groundwater temperatures of 15°C , the carbon isotope fractionation between CO_2 and HCO_3^- is approximately 8‰. Nearly all of the New Albany Shale samples fit the theoretical 8‰ fractionation line between DIC and CO_2 , similar to the Antrim Shale microbial samples (Fig. 14). The very positive $\delta^{13}\text{C}$ values of both the CO_2 and DIC from these wells require a microbial source during the generation of methane. Thermogenic CO_2 or DIC would have much more negative $\delta^{13}\text{C}$ values, closer to that of the kerogen undergoing maturation ($\sim -30\text{‰}$). Furthermore, the equilibrium relation between the $\delta^{13}\text{C}$ value of CO_2 gas and DIC in cogenetic fluids in a closed chemical system predicts an 8‰ fractionation between the two CO_2 species. Group 3 wells produced trace or no CO_2 , suggesting the absence of microbial activity.

The δD values of CH_4 and associated waters are indicative of gas origins and equilibrium relations between gases and associated fluids (Daniels et al., 1980; Balabane et al., 1987; Martini et al., 1996). The δD value of CH_4 from thermogenic gas

depends on the original isotopic signature of the precursor hydrogen in the organic matter. For the relatively immature thermogenic gases found in midcontinent basins, values between -200‰ and -280‰ are common (Walter et al., 1997; Martini et al., 1998). In contrast, for the microbial process of CO_2 reduction, the final δD value of the CH_4 produced is determined by the isotopic composition of the water in which it formed:

$$\delta\text{D}_{\text{CH}_4} = \delta\text{D}_{\text{H}_2\text{O}} + 160 (\pm 10\text{‰}) \quad (03)$$

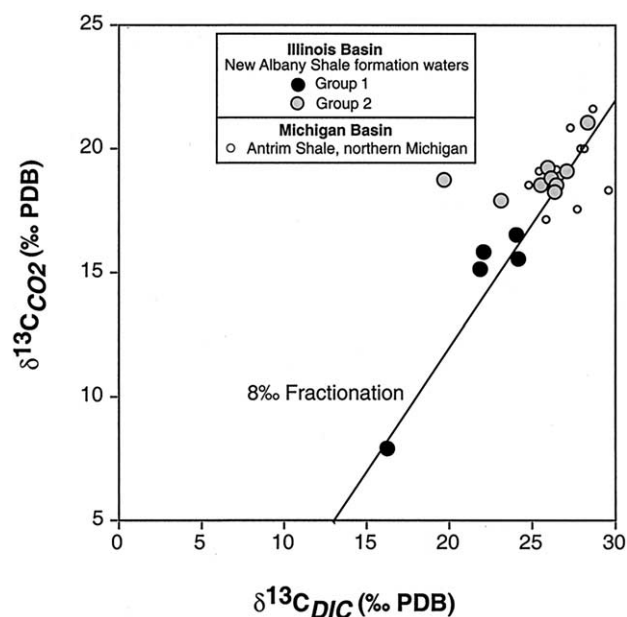


Fig. 14. $\delta^{13}\text{C}_{\text{CO}_2}$ vs. $\delta^{13}\text{C}_{\text{DIC}}$ values. New Albany and Antrim shale samples shown in relation to fractionation line for carbon isotopic equilibrium.

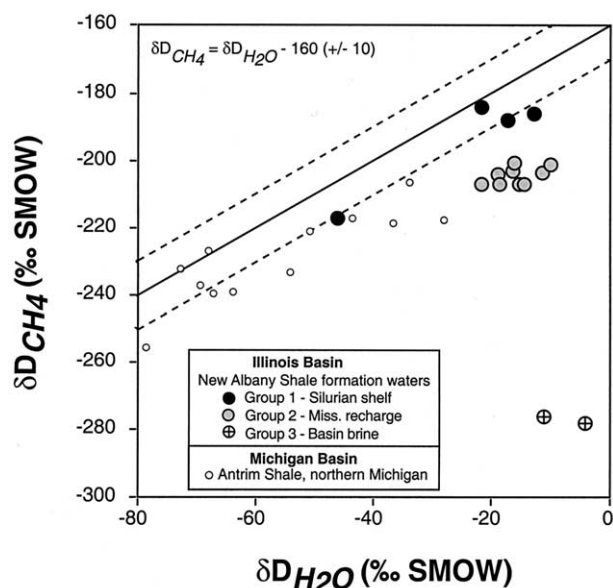


Fig. 15. Cross plot of δD values for methane vs. associated formation waters. Theoretical equilibrium line between microbial fractionation of methane and water shown in solid black line with $\pm 10\%$ error bars (Schoell, 1980). New Albany Shale samples shown by subgroup with Antrim Shale samples, northern Michigan, in small white circles (Martini et al., 1998).

(Schoell, 1980). The δD_{CH_4} values compared with the δD_{H_2O} values for coproduced waters from the New Albany Shale are shown in Figure 15. Group 1 samples fall very close to the theoretical line ($\delta D_{CH_4} = \delta D_{H_2O} + 160 \pm 10\%$), indicating they were affected by bacterial CO_2 reduction. Group 2 samples fall in a group offset somewhat from the theoretical line, but within the range seen for Antrim Shale samples from northern Michigan. These wells likely produced a component of thermogenic gas in addition to microbial gas. The group 3 samples are entirely unrelated to the theoretical CO_2 reduction line; they have isotopic values typical of thermogenic gases that have not been in equilibrium with associated waters.

The gas composition of New Albany Shale gases, in conjunction with stable isotope chemistry, further confirms the presence of methanogenic bacteria. Methanogenesis via acetate fermentation produces CO_2 and CH_4 , whereas thermogenic processes produce higher chain hydrocarbons like ethane and propane. The three New Albany Shale subgroups form discrete fields in a gas composition diagram (mol% CO_2 vs. log(methane/propane)) (Fig. 16). The group 2 samples contained the highest mol% CO_2 and greatest log wetness (CH_4/C_2H_6). The group 1 samples also contained high mol% CO_2 and gas wetness. The group 3 samples had the lowest mol% CO_2 and lowest log CH_4/C_2H_6 , consistent with a thermogenic origin. Walter et al. (in press) provide a more detailed description of the regional variations in the New Albany Shale produced and core gas geochemistry, and address the carbon isotope modification of gases by microbial oxidation.

5. IMPLICATIONS

Repeated Pleistocene glacial advances and retreats likely played a key role in recharge of dilute waters into the New

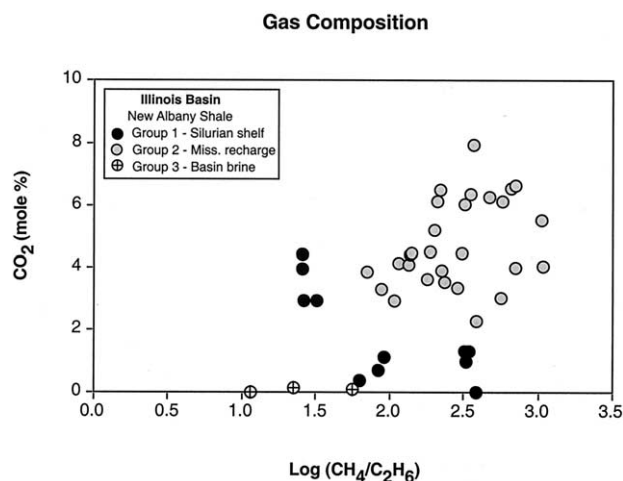


Fig. 16. New Albany Shale gas composition, CO_2 mol% vs. gas wetness [log(methane/propane)].

Albany Shale and underlying carbonates. Studies have shown that basal melting of continental ice sheets in the lower ablation zone could have provided adequate meltwater and hydrostatic head for recharge of dilute waters to basin margins (Siegel and Mandel, 1984; Boulton and Caban, 1995; Piotrowski, 1997). Glacially driven groundwater flow was likely to have been parallel to the Laurentide ice-sheet flow direction (Boulton et al., 1995), as illustrated in the north-to-south salinity gradients of the New Albany Shale and Siluro-Devonian carbonates. This groundwater flow likely extended far beyond the Laurentide ice sheet via high flux rates and potential gradients (Boulton and Caban, 1995). Glacial cycles can therefore significantly enhance fluid flow in deep aquifers and completely flush shallow flow systems, as evidenced by the work of Boulton et al. (1995) on the European Ice Sheet.

Continental ice sheets effectively reorganized groundwater flow systems from catchment-scale, topographically driven recharge to continental-scale glacially driven recharge (Boulton et al., 1995). The integration and enhancement of groundwater flow systems during Pleistocene glaciation evokes questions about the stability of basinal fluids and regional fluid migration pathways. Glaciation substantially changed the fluid migration pathway of formation waters within the Illinois Basin, from the tectonic-dominated south to north regime controlled by uplift of the Pascola Arch (Bethke, 1985, 1986; Bethke and Marshak, 1990; Bethke et al., 1991; Kesler et al., 1995; Keller et al., 2000), to the glacial-dominated recharge of freshwaters from the north. Reversal of basinal flow systems during Pleistocene glaciation was also recently documented for the Williston Basin. Grasby et al. (2000) suggested that Pleistocene-age waters infiltrated strata along the basin margin and penetrated deep into the basin, mixing with basinal brines.

The Silurian-Devonian carbonate aquifer system was the likely major avenue for dilute water recharge into the New Albany Shale along the eastern margin of the Illinois Basin. Recent studies that focused on the Siluro-Devonian aquifer system in the Kankakee arch region between the Illinois and Michigan basins also identified glacial meltwater in the carbonate aquifers (Eberts and George, 2000). The Silurian-De-

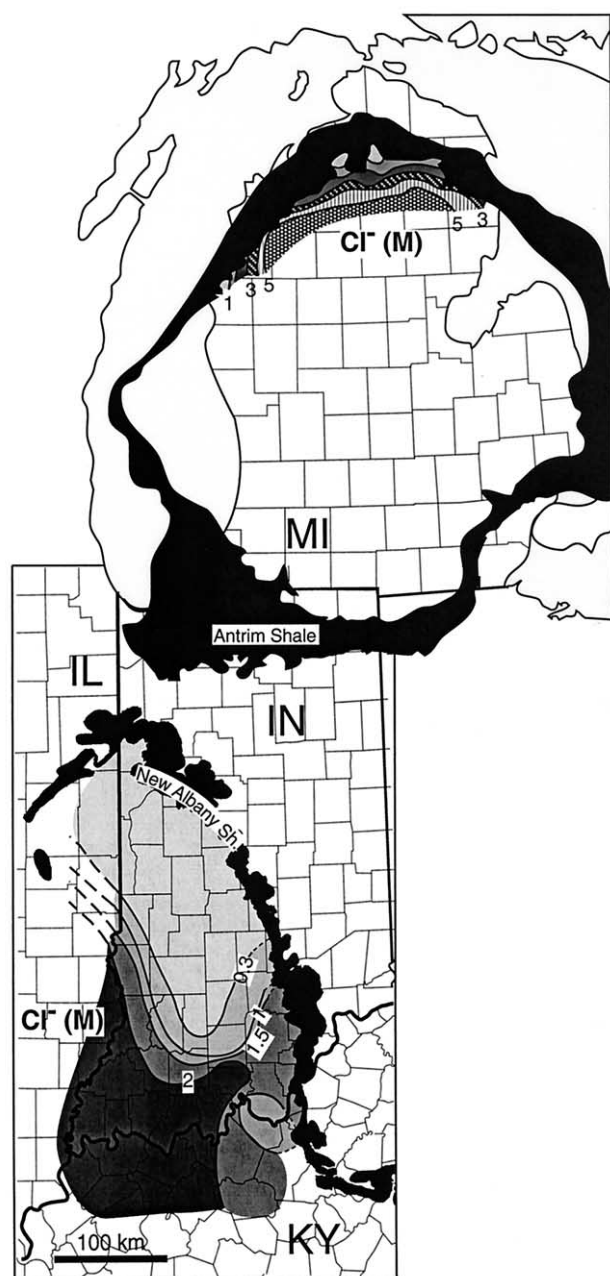


Fig. 17. Spatial variation of chloride content in Late Devonian black shale formation waters in the midcontinent region.

vonian carbonates are extensive in the midcontinent region and may have been major conduits for dilute water invasion into basin margins.

Late Devonian black shales along the margins of the Illinois and Michigan basins have been affected by recharge and produced significant volumes of microbial methane. This recharge also is manifested in different salinity gradients in the two basins because of their large differences in original formation water salinity (Fig. 17). The Antrim Shale formation waters contain higher salt concentrations along the Michigan Basin margin than the New Albany Shale along the Illinois Basin margin, even though the Antrim Shale is located at much

shallower depths than the New Albany Shale. The penetration of dilute waters into basin margins may be related to mechanisms of glacial melting beneath continental ice sheets and localized recharge. Given the relatively quiet tectonic history and subdued current topography in the midcontinent region, it is likely that repeated cycles of glacial meltwater invasion across this region has induced a strong disequilibrium pattern in fluid salinity and produced a unique class of unconventional shale hosted gas deposits.

Acknowledgments—Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research (PRF grant 35927-LMW). Additional support was provided by the Gas Research Institute under contract 5094. We thank K. L. Shelton, G. Garven, and D. I. Siegel for manuscript review. Members of the New Albany Shale GRI Consortium provided access to key water and gas samples as well as to timely production information. We also thank the Illinois Basin oil and gas operators, who gave generously of their time and expertise to facilitate our sampling of Siluro-Devonian and Mississippian formation waters. We thank the following people for their help in the field collection phase of the study: Tim Ku, John Hansen, Nate Diedrich, Andy Zimmerman, and Andy Logan. We acknowledge the talent of our graphic artist, Dale Austin. The laboratory analyses of gas and water samples were conducted in the EAGL Lab at the University of Michigan by laboratory managers John Hansen and Matt Handyside.

Associate editor: J. B. Fein

REFERENCES

- Balabane M., Galimov E., Herman M., and Letolle R. (1987) Hydrogen and carbon isotope fractionation during experimental production of bacterial methane. *Org. Geochem.* **11**, 115–119.
- Barrows M. H. and Cluff R. M. (1984) New Albany Shale Group (Devonian–Mississippian) source rocks and hydrocarbon generation in the Illinois Basin. In *Petroleum Geochemistry and Basin Evaluation* (eds. G. J. Demaison and R. J. Muris), pp. 111–138. Memoir 35. American Association of Petroleum Geologists.
- Bethke C. M. (1985) A numerical model of compaction-driven groundwater flow and heat transfer and its application to the paleohydrology of intracratonic sedimentary basins. *J. Geophys. Res.* **90**, 6817–6828.
- Bethke C. M. (1986) Hydrologic constraints on the genesis of the Upper Mississippi Valley mineral district from Illinois Basin brines. *Econ. Geol.* **81**, 233–248.
- Bethke C. M. and Marshak S. (1990) Brine migrations across North America—The plate tectonics of groundwater. *Ann. Rev. Earth Planet. Sci.* **18**, 287–315.
- Bethke C. M., Reed J. D., and Oltz D. F. (1991) Long-range petroleum migration in the Illinois Basin. *Am. Assoc. Petrol. Geol. Bull.* **75**, 925–944.
- Bond D. C. (1972) *Hydrodynamics in Deep Aquifers of the Illinois Basin*. Circular 470. Illinois State Geological Survey.
- Boulton G. S. and Caban P. (1995) Groundwater flow beneath ice sheets: Part II—On glacier tectonic structures and moraine formation. *Quat. Sci. Rev.* **14**, 563–587.
- Boulton G. S., Caban P. E., and Van Gijssel K. (1995) Groundwater flow beneath ice sheets: Part I—Large scale patterns. *Quat. Sci. Rev.* **14**, 545–562.
- Budai J. M., Martini A. M., Walter L. M., and Ku T. C. W. (in press) Fracture-fill calcite as a record of microbial methanogenesis and fluid migration: A case study from the Antrim Shale (Dev) Michigan Basin. *Geofluids*.
- Clayton R. N., Friedman I., Graf D. L., Mayeda T. K., Meents W. F., and Shimp N. F. (1966) The origin of saline formation waters: 1. Isotopic composition. *J. Geophys. Res.* **71**, 3869–3882.
- Cluff R. M. (1979) A preliminary assessment of the natural gas potential of the New Albany Shale group in Illinois. In *Proceedings of the Technical Sessions Kentucky Oil and Gas Association 43rd Annual*

- Meeting (ed. M. K. Luther), pp. 52–64. Kentucky Geological Survey.
- Coplen T. B. and Kendall C. (2000) Stable hydrogen and oxygen isotope ratios for selected sites of the U.S. Geological Survey's NASQAN and Benchmark Surface-Water Networks. Open File Report 00-160, pp. 128–131. U.S. Geological Survey.
- Craig H. (1961) Isotopic variations in meteoric waters. *Science* **133**, 1702–1703.
- Daniels L., Fulton G., Spencer R. W., and Orme-Johnson W. H. (1980) Origin of hydrogen in methane produced by *Methanobacterium thermoautotrophicum*. *J. Bacteriol.* **141**, 694–698.
- Dansgaard W. and Tauber H. (1969) Glacier oxygen-18 content and Pleistocene ocean temperatures. *Science* **166**, 499–502.
- Decker D., Coates J. M. P., and Wicks D. (1992) *Stratigraphy, gas occurrence, formation evaluation and fracture characterization of the Antrim Shale, Michigan Basin*. Gas Research Institute Topical Report 5091. Gas Res. Inst. Top.
- Demir I. and Seyler B. (1999) Chemical composition and geologic history of saline waters in Aux Vases and Cypress formations, Illinois Basin. *Aquat. Geochem.* **5**, 281–311.
- Dickey P. A. (1969) Increasing concentration of subsurface brines with depth. *Chem. Geol.* **4**, 361–370.
- Drever J. (1969) *The Geochemistry of Natural Waters: Surface and Groundwater Environments*. Prentice-Hall.
- Eberts S. M. and George L. L. (2000) *Regional Ground-Water Flow and Geochemistry in the Midwestern Basins and Arches Aquifer System in Parts of Indiana, Ohio, Michigan, and Illinois*. Professional Paper 1423-C C1–C103. U.S. Geological Survey.
- Emiliani E. (1971) The amplitude of Pleistocene climatic cycles at low latitudes and the isotopic composition of glacial ice. In *Late Cenozoic Glacial Ages* (ed. K. K. Turekian), pp. 183–187. Yale University Press.
- Gieskes J. M. and Rogers W. C. (1973) Alkalinity determination in interstitial waters of marine sediments. *J. Sediment. Petrol.* **43**, 272–277.
- Grasby S., Osadetz K., Betcher R., and Render F. (2000) Reversal of the regional-scale flow system of the Williston Basin in response to Pleistocene glaciation. *Geology* **28**, 7., 635–638.
- Hanor J. S. (1987) *Origin and Migration of Subsurface Sedimentary Brines*. Short Course 21. Society of Economic Paleontologists and Mineralogists.
- Hassenmueller N. R. (1993) New Albany Shale (Devonian and Mississippian) of the Illinois Basin. In *Petroleum Geology of the Devonian and Mississippian Black Shale of Eastern North America* (ed. R. C. Kefferle), pp. C1–C19. U.S. Geological Survey.
- Hassenmueller N. R. and Leininger R. K. (1987) *Oil Shale Prospects for the New Albany Shale in Indiana*. Special Report 40. Indiana Geological Survey.
- IAEA. (1983) *Isotope Techniques in the Hydrogeological Assessment of Potential Sites for the Disposal of High-Level Radioactive Wastes*. Technical Report Series 228. International Atomic Energy Agency.
- IAEA/WMO. (1998) Global network for isotopes in precipitation. The GNIP database. Release 3, October 1999. Available at: <http://isohis.iaea.org>.
- Keller S. J. (1983) *Analyses of Subsurface Brines of Indiana*. Geological Survey Occasional Paper 41. Indiana Department of Natural Resources.
- Keller T. J., Gregg J. M., and Shelton K. L. (2000) Fluid migration and associated diagenesis in the Greater Reelfoot rift region, Midcontinent, United States. *GSA Bull.* **112**, 1680–1693.
- Kesler S. E., Appold M. S., Martini A. M., Walter L. M., Huston T. J., and Kyle J. R. (1995) Na-Cl-Br systematics of mineralizing brines in Mississippi Valley-type deposits. *Geology* **23**, 641–644.
- Lloyd O. B. Jr. and Lyke W. L. (1995) *Ground Water Atlas of the United States: Segment 10—Illinois, Indiana, Kentucky, Ohio, Tennessee*. U.S. Geological Survey.
- Martini A. M., Budai J. M., Walter L. M., and Schoell M. (1996) Microbial generation of economic accumulations of methane within a shallow organic-rich shale. *Nature* **383**, 155–158.
- Martini A. M., Walter L. M., Budai J. M., Ku T. C. W., Kaiser C. J., and Schoell M. (1998) Genetic and temporal relations between formation waters and biogenic methane: Upper Devonian Antrim Shale, Michigan Basin, USA. *Geochim. Cosmochim. Acta* **62**, 10., 1699–1720.
- McGrain P. (1953) *Miscellaneous Analyses of Kentucky Brines*. Report of Investigations 7. Kentucky Geological Survey.
- Meents W. F., Bell A. H., Rees O. W., and Tilbury W. G. (1952) *Illinois Oil-Field Brines: Their Geologic Occurrence and Chemical Composition*. Illinois Petrol. 66. Illinois State Geological Survey.
- Olcott P. (1992) *Ground Water Atlas of the United States, Segment 9: Iowa, Michigan, Minnesota, Wisconsin*. Hydrologic Investigations Atlas 730-J. U.S. Geological Survey.
- Panno S. V. and Bourcier W. L. (1990) Glaciation and saline-fresh water mixing as a possible cause of cave formation in the eastern midcontinent region of the United States: A conceptual model. *Geology* **18**, 769–772.
- Piotrowski J. A. (1997) Subglacial hydrology in north-western Germany during the last glaciation: Groundwater flow, tunnel valleys and hydrological cycles. *Quat. Sci. Rev.* **16**, 169–185.
- Rupp J. A. (1989) *Cross Sections Showing Bedrock Geology of Indiana*. Special Report 48, plate 2. Indiana Geological Survey.
- Rupp J. A. (1991) *Structure and Isopach Maps of the Paleozoic Rocks of Indiana*. Special Report 48. Indiana Geological Survey.
- Schmus W., Bickford M., and Turek A. (1996) Proterozoic geology of the east-central midcontinent basement. In *Basement and Basins of Eastern North America* (eds. B. A. van der Pluijm and P. A. Catacosinos), pp. 7–32. Special Paper 308. Geological Society of America.
- Schoell M. (1980) The hydrogen and carbon isotopic composition of methane from natural gases of various origins. *Geochim. Cosmochim. Acta* **44**, 649–661.
- Siegel D. I. (1989) *Geochemistry of the Cambrian-Ordovician Aquifer System in the Northern Midwestern United States*. Professional Paper 1405-D. U.S. Geological Survey.
- Siegel D. I. (1991) Evidence for dilution of deep, confined ground water by vertical recharge of isotopically heavy Pleistocene water. *Geology* **19**, 433–436.
- Siegel D. I. and Mandle R. J. (1984) Isotopic evidence for glacial meltwater recharge to the Cambrian-Ordovician aquifer, north-central United States. *Quat. Res.* **22**, 328–335.
- Stueber A. M. and Walter L. M. (1991) Origin and chemical evolution of formation waters from Silurian-Devonian strata in the Illinois Basin, USA. *Geochim. Cosmochim. Acta* **55**, 309–325.
- Stueber A. M. and Walter L. M. (1994) Glacial recharge and paleohydrologic flow systems in the Illinois Basin: Evidence from chemistry of Ordovician carbonate (Galena) formation waters. *GSA Bull.* **106**, 1430–1439.
- Stueber A. M., Walter L. M., Huston T. J., and Pushkar P. (1993) Formation waters from Mississippian-Pennsylvanian reservoirs, Illinois Basin, USA: Chemical and isotopic constraints on evolution and migration. *Geochim. Cosmochim. Acta* **57**, 763–784.
- Walker F. H. (1959) *Natural Brines of Indiana and Adjoining Parts of Illinois and Kentucky*. Report of Progress 13. Indiana Geological Survey.
- Walter L. M., Stueber A. M., and Huston T. J. (1990) Br-Cl-Na systematics in Illinois Basin fluids: Constraints on fluid origin and evolution. *Geology* **18**, 315–318.
- Walter L. M., Budai J. M., Abriola L. M., Stearns C. H., Martini A. M., and Ku T. C. W. (1996) Hydrogeochemistry of the Antrim Shale northern Michigan Basin. *Gas Res. Inst.* 95/0251.
- Walter L. M., Budai J. M., Martini A. M., and Ku T. C. W. (1997) Hydrogeochemistry of the Antrim Shale in the Michigan Basin. *Gas Res. Inst.* 97/0127.
- Walter L. M., McIntosh J. C., Martini A. M., and Budai J. M. (in press) Hydrogeochemistry of the New Albany Shale, Illinois Basin. *Gas Res. Inst.* 5094.
- Weaver T. R., Frappe S. K., and Cherry J. A. (1995) Recent cross-formational fluid flow and mixing in the shallow Michigan Basin. *GSA Bull.* **107**, 697–707.
- Whiticar M. J. (1999) Carbon and hydrogen systematics of bacterial formation and oxidation of methane. *Chem. Geol.* **161**, 291–314.
- Zuppan C. W., Keith B. D., and Keller S. J. (1988) *Geology and Petroleum Production of the Illinois Basin, 2: Illinois and Indiana*. Kentucky Geological Society.