

consistent with the hypothesis that regional recharge to this part of the aquifer system could be limited by the inability of the aquifer system to carry ground water away from the area. This area is largely coincident with the area of weak regional discharge (fig. 28).

Simulated discharge vectors indicate high magnitudes of horizontal regional flow in the carbonate-rock aquifer in the areas around the regional potentiometric highs (fig. 31B). High magnitudes of horizontal regional flow are also associated with the downstream end of the Wabash and White Rivers, the margin of the Illinois (structural) Basin, the Ohio River, an area west of the Scioto River, and the area east of the Sandusky River. Discharge vectors along part of the Lake Erie shore indicate that the magnitude of horizontal regional flow in the carbonate-rock aquifer in this area is fairly small. Ground-water flow may be predominantly vertical in this area because it is an area of regional ground-water discharge. Simulated discharge vectors were computed for the upper weathered zone water-bearing unit, but the relative magnitudes of flow in this poorly permeable unit are so small that the vectors do not show up at the scale of figure 31B.

It should be noted that the discharge vectors show only relative magnitudes of horizontal regional ground-water flow and do not indicate flow velocities. Additional information on the effective porosity of the aquifers would be necessary to compute flow velocities. Appropriate effective-porosity data for fractured carbonate rock are difficult to obtain and were not available for this investigation. Ground-water ages presented in the following section, however, provide insight into ground-water residence times.

The calibrated final model was not used to simulate potential effects of future pumpage on regional ground-water flow in the aquifer system. Data on future pumpage needs at the regional scale are not available, and any simulations of future pumpage at this time would be contrived. It is noteworthy, however, that only a small percentage of current pumpage is associated with the regional flow systems explicitly simulated with this model. Therefore, more water associated with such regional flow systems almost certainly could be used. The quality of the ground water associated with some parts of the aquifer system, however, may limit its use.

GEOCHEMISTRY

Geochemical data were collected from the Midwestern Basins and Arches aquifer system to investigate the relations among ground-water chemistry, aquifer mineralogy, and present and past patterns of regional flow. The data include a synthesis of basic data from more than 1,300 ground-water analyses of water samples from the aquifer system, as well as detailed chemical and isotopic analyses of ground water and aquifer material along general directions of regional flow. The analyses represent two hydrologic units (table 1) within the

Midwestern Basins and Arches aquifer system — aquifers within glacial deposits and the carbonate-rock aquifer — and were obtained from records in the U.S. Geological Survey's National Water Information System (NWIS) data base; files of the Indiana Department of Natural Resources, the Ohio Department of Natural Resources, and the Ohio Environmental Protection Agency; various published reports; and samples collected as part of this investigation. The data were compiled and analyzed to investigate the ground-water chemistry of the aquifer system on a regional scale. Ground-water chemistry of subregional areas of the Midwestern Basins and Arches aquifer system is described in the following reports: in Ohio, by Ohio Department of Natural Resources, Division of Water (1970), Norris and Fidler (1973), Norris (1974), Deering and others (1983), Breen and Dumouchelle (1991); and in Indiana, by Geosciences Research Associates, Inc. and Purdue University, Water Resources Research Center (1980) and Indiana Department of Natural Resources (1988, 1990). Analyses of brines from rocks of Silurian and Devonian age are found in Stout and others (1932), Lamborn (1952), Walker (1959), Stith (1979), Keller (1983) and Wilson and Long (1993a, b).

Data compiled from the literature and the available data bases were selected on the basis of the following criteria: (1) major-ion concentrations (Ca, Mg, Na, Cl, SO_4 , and HCO_3) were determined, (2) the analyses balanced electrochemically within 10 percent and, (3) lithologies of the water-producing units were determined. In cases where multiple analyses were available for a well, the most recent analysis that met the above criteria was selected. The dissolved-solids data for most of the analyses that were used in this report were calculated by summing the concentrations of all major constituents according to the method described in Fishman and Friedman (1989). Dissolved-solids concentrations for waters in the Illinois and Michigan Basins were estimated from borehole geophysical data where available laboratory determinations were sparse (D.J. Schnoebelen, U.S. Geological Survey, written commun., 1993).

New data that were collected during this investigation include detailed chemical and isotopic analyses of ground water from the aquifer system along general directions of regional ground-water flow, as determined from the map of the potentiometric surface of the carbonate-rock aquifer (fig. 12), and isotopic analyses of aquifer material collected from cores of glacial deposits and carbonate rock. The locations of the ground-water and aquifer-material samples are shown in figure 32. At each sampling location along four transects across the aquifer system, ground-water samples were collected from the carbonate-rock aquifer, and, where possible, from a glacial aquifer. Sampling was restricted to existing domestic wells or test wells; wells with short open intervals in the deep parts of the aquifer were generally not available. At each sampling location, an attempt was made to sample the deepest available well in the carbonate-rock aquifer in

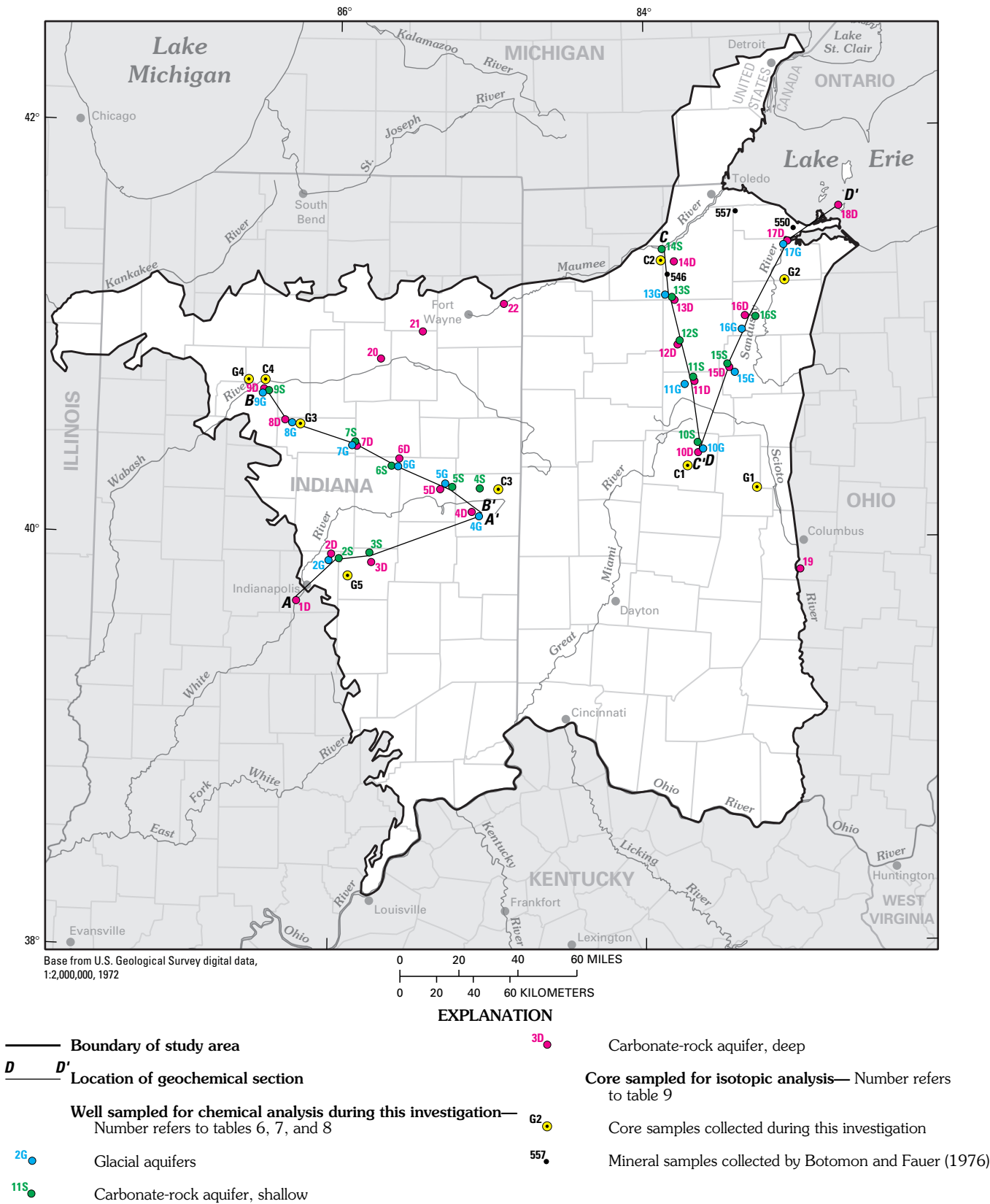


FIGURE 32.—Locations of wells sampled during this investigation, carbonate-rock and glacial cores sampled for isotopic analysis, and geochemical sections A-A', B-B', C-C', and D-D'.

order to intersect the dominant regional ground-water flow paths in the aquifer system. The deep bedrock wells are completed from 100 to nearly 450 ft into the carbonate-rock aquifer. To evaluate the effects of sampling the deep wells with long open intervals, RASA investigators also sampled a nearby well with a short open interval. These wells were shallow and completed in the top 5 to 50 ft of the carbonate-rock aquifer. Well depth and length of open interval for each well sampled are listed in table 6. Deep bedrock wells that are cased through the top part of the carbonate-rock aquifer are also noted in table 6. Where possible, a glacial well, a shallow bedrock well, and a deep bedrock well within several miles of each other were identified and grouped as a sample site.

Ground-water samples were collected during 1991-92 and analyzed for major and minor constituents according to the methods described in Fishman and Friedman (1989). Field determinations were made for pH, temperature, and alkalinity according to methods described in Wood (1976). Dissolved sulfide was determined in the field with a Hach DR-2000 spectrophotometer according to the procedure described in the instrument manual (Hach Chemical Company, 1989).

Samples were collected and analyzed for dissolved gas concentrations; stable isotope ratios of oxygen, hydrogen, carbon and sulfur; and the radioactive isotopes tritium (^3H) and carbon-14 (^{14}C) by use of standard methods. Samples of aquifer material were collected from cores in the core repositories of the Indiana Geological Survey and the Ohio Geological Survey. The samples were analyzed for carbon and sulfur isotopes by use of standard methods. By convention, stable isotope ratios are expressed in delta units (δ) as per mil (parts per thousand, or per mil) differences relative to the appropriate standard: Standard Mean Ocean Water (SMOW) for oxygen ($\delta^{18}\text{O}$) and hydrogen (δD), Pee Dee Formation belemnite for carbon ($\delta^{13}\text{C}$), and Canyon Diablo troilite for sulfur ($\delta^{34}\text{S}$). Tritium concentrations are expressed in tritium units (TU), and ^{14}C values are presented in percent modern carbon (pmc). The chemical and isotopic data are listed in tables 7-9.

SPATIAL DISTRIBUTION OF DISSOLVED-SOLIDS CONCENTRATIONS AND HYDROCHEMICAL FACIES

Knowledge of the spatial distribution of dissolved-solids concentrations and hydrochemical facies can help in distinguishing recharge and discharge areas, identifying areas of ground-water mixing, and estimating relative rates of ground-water flow. Water chemistry in the glacial and carbonate-rock aquifers was classified by calculating the dissolved-solids concentrations and the percentages of major cations and anions composing the total dissolved cations and anions, respectively. Maps were prepared showing the areal distribution of dissolved solids and hydrochemical facies indicated by the predominant cations and anions. These maps were

used to delimit zones of potable water in the carbonate-rock aquifer, to examine the relation between the glacial aquifers and the carbonate-rock aquifer, and to evaluate possible geochemical and hydrological processes that control the distribution of major dissolved solutes.

Generally, dissolved-solids concentrations in ground water increase along flow paths — from the surface to the saturated zone and through the aquifer — because of dissolution of minerals (Freeze and Cherry, 1979). Additional processes such as evaporation or evapotranspiration can increase concentrations of dissolved solutes. Some ground waters, notably brines, contain extremely high concentrations of dissolved solids because of combined effects of mineral dissolution and evaporation. Thus, dissolved-solids concentrations generally can be used as an indicator of the degree of chemical evolution of ground water in an aquifer system.

The predominant major ions in ground water can also be used as indicators of the important chemical and hydrologic processes in an aquifer system. Chebotarev (1955) characterized regional changes in the dominant anion species in ground water. The general evolutionary sequence that he observed for the dominant anions was HCO_3 to SO_4 to Cl , which correlated with increasing distance along the flow path and an increasing age of water. This anion sequence also corresponded to an increase in dissolved-solids concentration. Water containing predominantly bicarbonate is generally present in areas of active ground-water flushing, water containing predominantly sulfate is present where ground-water circulation is less active, and water containing predominantly chloride is generally present where ground-water flow is very sluggish and flushing of the aquifer is minimal. Back (1960) introduced the concept of hydrochemical facies based on the dominance of cations and anions. Using hydrochemical facies and dissolved-solids concentrations, he inferred the general sequence of reactions and hence the general directions of regional ground-water flow.

DISSOLVED-SOLIDS CONCENTRATIONS

Dissolved-solids concentrations of ground water from the Midwestern Basins and Arches aquifer system are shown in figures 33 and 34. Dissolved-solids concentrations in water from the glacial aquifers (fig. 33) range from less than 100 to greater than 2,600 mg/L; the median is 378 mg/L. In more than 80 percent of available water analyses for the glacial aquifers, dissolved-solids concentrations are less than 500 mg/L. Ground water with dissolved-solids concentrations less than 500 mg/L is found in the glacial aquifers across most of the study area, as is ground water with concentrations ranging from 500 to 1,000 mg/L. Concentrations greater than 1,000 mg/L, however, are restricted primarily to the northeastern part of the study area. Few analyses of water from the glacial aquifers are available for this area because many of the wells are completed in the underlying carbonate-rock aquifer rather

TABLE 6.—*Well construction information for wells sampled during investigation of the Midwestern Basins and Arches aquifer system, 1991–92*

[Map number is location in figure 32; ft, feet; --, not applicable; N.A., data not available; G, glacial aquifer; C-R, carbonate-rock aquifer; all depth data are in feet below land surface]

Well name	Map number	Well depth (ft)	Depth to bedrock (ft)	Depth to top of open interval (ft)	Depth to bottom of open interval (ft)	Length of open interval (ft)	Aquifer
Ross	10 G	102	--	N.A.	N.A.	N.A.	G
Birt	10 S	86	76	80	86	6	C-R
Ben Logan H.S.	10 D	340	97	160	340	^a 180	C-R
Searfoss	15 G	60	--	N.A.	N.A.	N.A.	G
Rife	15 S	39	34	34	39	5	C-R
Schoenberger	15 D	240	33	36	240	205	C-R
Beasley	16 G	81	--	61	81	20	G
Hill	16 S	80	52	63	80	17	C-R
Gillig	16 D	310	45	55	310	255	C-R
Lamalie	17 G	75	--	71	75	4	G
S-18	17 D	340	70	180	340	^b 160	C-R
Finnegan	18 D	185	2	26	185	159	C-R
Wilson	11 G	50	--	N.A.	N.A.	N.A.	G
Spencer	11 S	43	16	22	43	21	C-R
Stair	11 D	250	18	21	250	229	C-R
Francis	12 S	62	40	43	62	20	C-R
Augustine	12 D	320	6	9	320	311	C-R
Richard	13 G	81	--	N.A.	N.A.	N.A.	G
Kern	13 S	102	73	75	102	27	C-R
Auckerman	13 D	400	78	109	400	^c 291	C-R
Rice	14 S	35	32	32	35	3	C-R
City of Weston	14 D	500	65	410	500	^d 90	C-R
Hartman	19	144	114	114	144	30	C-R
Lacy	4 G	67	--	64	67	3	G
Hummel	4 S	121	88	90	121	31	C-R
Jones	4 D	201	119	122	201	79	C-R
Harrison	3 S	117	108	108	117	9	C-R
Martin	3 D	200	135	138	200	62	C-R
Lockhart	2 G	140	--	136	140	4	G
Mattingly	2 S	150	140	140	150	10	C-R
Merchant	2 D	310	170	170	310	140	C-R
Gates	1 D	320	88	88	320	^e 232	C-R
Bickford	5 G	45	--	41	45	4	G
Bartlett	5 S	106	74	74	106	32	C-R
Desoto Substation	5 D	265	88	91	265	174	C-R
Staggs	6 G	116	--	113	116	3	G
Ice	6 S	110	92	92	110	18	C-R
Underwood	6 D	302	161	162	302	140	C-R
Cohee	7 G	99	--	84	89	5	G
Ellis	7 S	102	49	55	102	47	C-R
Harmon	7 D	293	51	53	293	240	C-R
Fox	8 G	89	--	84	89	5	G
Skiles	8 D	202	63	64	202	138	C-R
Justice	9 G	62	--	59	62	3	G
Lee	9 S	113	65	67	113	46	C-R
Starbuck	9 D	182	76	79	182	103	C-R
Geradot	22	260	72	70	260	190	G, C-R
Stenzel	21	260	170	170	260	90	C-R
Rees	20	230	160	160	230	70	C-R

^aWell is cased through the top 83 ft of bedrock.

^bWell is cased through the top 110 ft of bedrock.

^cWell is cased through the top 31 ft of bedrock.

^dWell is cased through the top 345 ft of bedrock.

^eWell is open to the New Albany Shale (upper confining unit) from 88 to 204 ft below land surface.

TABLE 7.—*Chemical analyses of selected constituents in water from wells sampled during investigation of the Midwestern Basins and Arches aquifer system, 1991–92*[Map number is location in figure 32; $\mu\text{S}/\text{cm}$, microsiemens per centimeter at 25 degrees Celsius; mg/L, milligrams per liter; $\mu\text{g}/\text{L}$, micrograms per liter; --, data not collected]

Well name	Map number	Date of collection	Specific conductance ($\mu\text{S}/\text{cm}$)	pH (standard units)	Eh (millivolts)	Temperature (degrees Celsius)	Dissolved oxygen (mg/L)	Calcium (mg/L)	Magnesium (mg/L)	Sodium (mg/L)	Potassium (mg/L)
Ross	10 G	08-06-91	2,360	6.83	121	12.1	0.1	290	200	38	4.5
Birt	10 S	08-07-91	1,010	7.10	512	11.5	4.5	120	55	16	2.4
Ben Logan H.S.	10 D	07-28-92	707	7.35	397	13.8	.9	87	34	13	1.6
Searfoss	15 G	08-15-91	2,400	7.08	145	11.5	<.1	490	75	62	3.9
Rife	15 S	08-12-91	2,400	6.93	58	11.1	.1	490	69	46	4.6
Schoenberger	15 D	08-14-91	2,720	6.95	52	11.2	<.1	540	79	53	5.0
Beasley	16 G	08-19-91	772	7.32	70	10.5	.1	88	34	15	1.4
Hill	16 S	08-20-91	1,760	7.37	126	11.5	.1	200	75	71	4.0
Gillig	16 D	08-21-91	1,660	7.40	102	11.6	<.1	220	66	65	4.0
Lamalie	17 G	08-22-91	2,450	7.18	72	12.1	<.1	400	140	40	4.2
S-18	17 D	08-27-91	2,690	6.99	3	12.6	<.1	490	160	27	4.6
Finnegan	18 D	06-13-92	765	7.15	82	11.8	--	100	47	1.4	1.4
Wilson	11 G	08-03-92	1,470	7.38	35	11.3	<.1	190	72	47	3.5
Spencer	11 S	07-29-92	1,010	7.02	176	12.8	.1	140	50	16	2.4
Stair	11 D	08-04-92	1,070	7.21	153	11.4	.1	140	56	21	3.0
Francis	12 S	08-05-92	991	7.30	-36	12.1	--	120	48	19	3.6
Augustine	12 D	08-06-92	1,260	7.34	-79	11.3	<.1	140	62	41	3.8
Richard	13 G	07-30-92	2,080	7.85	67	11.5	.1	250	88	120	4.1
Kern	13 S	08-07-92	1,610	7.75	127	12.3	.1	170	57	120	3.2
Auckerman	13 D	08-13-92	1,690	7.20	-132	12.4	<.1	190	73	69	7.0
Rice	14 S	08-12-92	1,180	7.41	-88	12.8	.1	130	62	45	2.8
City of Weston	14 D	08-11-92	3,250	7.25	-96	12.9	<.1	540	180	74	3.7
Hartman	19	09-10-92	1,330	7.00	--	13.5	--	100	67	53	9.1
Lacy	4 G	09-06-91	670	7.42	72	7.4	<.1	86	36	11	1.2
Hummel	4 S	09-05-91	953	7.22	95	11.3	.1	110	58	22	2.0
Jones	4 D	09-03-91	695	7.19	126	11.3	<.1	98	35	8.8	1.8
Harrison	3 S	10-07-91	595	7.49	77	12.2	.2	76	26	14	1.3
Martin	3 D	09-04-91	570	7.40	56	13.5	<.1	77	26	16	1.0
Lockhart	2 G	09-09-91	1,140	7.23	104	12.4	<.1	110	35	87	3.4
Mattingly	2 S	09-11-91	1,060	7.32	70	12.1	.1	110	46	43	2.5
Merchant	2 D	09-10-91	908	7.30	--	13.2	--	100	43	31	2.3
Gates	1 D	10-08-91	1,210	7.41	-84	13.7	<.1	44	27	170	8.2
Bickford	5 G	09-03-92	958	7.17	97	13.0	<.1	110	44	32	1.9
Bartlett	5 S	09-01-92	765	7.26	143	12.0	.1	100	42	8.5	1.5
Desoto Substation	5 D	08-19-92	738	7.26	149	13.0	.2	96	37	10	1.5
Staggs	6 G	08-20-92	723	7.37	128	11.4	.1	100	32	10	1.3
Ice	6 S	09-02-92	713	7.31	132	12.6	<.1	88	35	12	3.2
Underwood	6 D	08-21-92	653	7.44	124	11.7	.1	79	32	19	2.1
Cohee	7 G	09-04-92	673	7.35	76	12.5	<.1	95	32	10	2.1
Ellis	7 S	08-24-92	746	7.34	123	12.0	<.1	96	34	13	2.2
Harmon	7 D	08-25-92	711	7.31	87	12.3	<.1	98	31	7.1	1.5
Fox	8 G	08-29-92	683	7.15	124	11.9	.1	75	29	18	1.4
Skiles	8 D	08-26-92	782	7.44	-1	13.3	<.1	92	34	17	0.90
Justice	9 G	08-27-92	736	7.20	113	12.4	.1	100	32	6.2	1.0
Lee	9 S	08-28-92	834	7.31	125	11.6	.1	100	39	13	2.9
Starbuck	9 D	05-29-92	655	7.22	-28	11.3	.1	75	35	11	3.4
Geradot	22	08-28-92	942	7.24	76	13.3	<.1	110	47	26	3.0
Stenzel	21	08-30-91	588	7.40	30	11.8	<.1	62	29	22	2.0
Rees	20	08-29-91	603	7.48	-68	12.1	<.1	59	22	45	5.1

TABLE 7.—*Chemical analyses of selected constituents in water from wells sampled during investigation of the Midwestern Basins and Arches aquifer system, 1991–92—Continued*[Map number is location in figure 32; $\mu\text{S}/\text{cm}$, microsiemens per centimeter at 25 degrees Celsius; mg/L, milligrams per liter; $\mu\text{g}/\text{L}$, micrograms per liter; --, data not collected]

Well name	Map number	Bicarbonate, as HCO_3 (mg/L)	Sulfate, as SO_4 (mg/L)	Sulfide (mg/L)	Chloride (mg/L)	Bromide (mg/L)	Silica (mg/L)	Dissolved solids, sum of constituents (mg/L)	Iron ($\mu\text{g}/\text{L}$)	Strontium ($\mu\text{g}/\text{L}$)	Dissolved organic carbon (mg/L)
Ross	10 G	533	1,200	<0.01	7.0	0.12	22	1,930	9,000	16,000	2.0
Birt	10 S	397	240	<.01	7.2	.04	11	665	4	13,000	1.0
Ben Logan H.S.	10 D	383	60	<.01	20	.04	10	427	3	8,900	.60
Searfoss	15 G	224	1,600	.02	23	.08	17	2,400	5,200	12,000	1.3
Rife	15 S	266	1,600	<.01	6.3	.08	17	2,430	3,100	12,000	1.2
Schoenberger	15 D	229	1,500	.01	17	.15	16	2,340	2,100	11,000	1.3
Beasley	16 G	346	120	.01	6.4	.05	13	454	520	4,400	1.1
Hill	16 S	168	850	<.01	16	.19	12	1,330	1,500	14,000	1.6
Gillig	16 D	179	860	<.01	15	.25	12	1,350	2,200	12,000	1.6
Lamalie	17 G	222	1,500	.02	37	.45	17	2,270	2,600	13,000	1.3
S-18	17 D	280	1,600	0.35	44	.36	12	2,490	780	12,000	1.6
Finnegan	18 D	528	19	1.1	2.2	.02	7.2	439	12	200	2.4
Wilson	11 G	285	610	.04	10	.09	15	1,110	2,700	17,000	1.0
Spencer	11 S	463	180	.02	28	.08	15	668	720	5,000	1.5
Stair	11 D	490	190	<.01	13	.07	20	702	3,100	13,000	1.1
Francis	12 S	454	170	.28	27	.12	16	656	770	27,000	1.3
Augustine	12 D	478	180	3.3	100	.16	16	784	14	4,700	1.3
Richard	13 G	89	1,100	.02	34	.32	11	1,670	1,700	14,000	1.1
Kern	13 S	144	750	<.01	35	.31	8.4	1,240	990	22,000	.80
Auckerman	13 D	283	530	23.3	110	.51	6.5	1,150	13	18,000	.90
Rice	14 S	227	440	2.3	12	.09	13	836	52	17,000	1.5
City of Weston	14 D	196	1,900	7.4	45	.38	9.0	2,860	350	10,000	1.0
Hartman	19	472	65	--	100	--	9.5	826	180	7,100	3.8
Lacy	4 G	432	33	.03	9.5	.06	19	416	2,800	3,200	1.1
Hummel	4 S	536	130	<.01	9.2	.09	20	630	2,200	11,000	1.7
Jones	4 D	466	6.5	<.01	4.4	.04	15	402	1,200	1,300	1.3
Harrison	3 S	390	0.10	.01	5.5	.10	16	334	1,400	620	1.7
Martin	3 D	397	<.10	.01	5.6	.04	20	344	1,000	530	1.6
Lockhart	2 G	427	49	<.01	150	.09	12	658	1,600	220	1.0
Mattingly	2 S	410	40	.02	140	.20	14	603	2,700	1,100	1.0
Merchant	2 D	395	28	<.01	85	.06	14	501	64	1,100	1.1
Gates	1 D	407	19	4.1	210	1.20	7.0	694	7	1,800	1.4
Bickford	5 G	439	83	.02	61	.04	15	566	2,200	430	.90
Bartlett	5 S	476	43	.02	6.0	.02	18	459	2,300	3,000	1.4
Desoto Substation	5 D	420	74	<.01	4.9	.02	15	453	1,600	5,200	1.2
Staggs	6 G	412	48	<.01	21	.03	20	439	1,900	1,500	1.2
Ice	6 S	439	42	.03	5.4	.03	17	426	1,100	4,800	1.2
Underwood	6 D	441	5.0	.03	8.6	.04	16	383	890	1,500	1.5
Cohee	7 G	401	40	.02	5.1	.02	17	403	2,000	1,600	1.1
Ellis	7 S	421	65	.01	12	.01	16	452	2,000	3,000	1.2
Harmon	7 D	376	65	<.01	14	.03	16	421	1,800	860	1.2
Fox	8 G	472	.40	<.01	5.3	.03	19	393	4,000	930	3.6
Skiles	8 D	371	43	.11	54	.06	17	445	2,100	510	1.7
Justice	9 G	377	71	<.01	26	.04	18	442	2,300	190	1.2
Lee	9 S	388	85	<.01	39	.07	15	489	1,700	1,500	.90
Starbuck	9 D	440	6.9	1.8	7.6	.05	10	368	8	1,100	1.0
Geradot	22	395	190	.01	35	.05	15	628	1,500	5,300	1.8
Stenzel	21	371	30	.03	1.9	.02	16	357	370	9,700	1.3
Rees	20	384	16	.13	2.9	.04	11	355	250	2,400	1.6

TABLE 8.—*Analyses of isotopes in water from wells sampled during investigation of the Midwestern Basins and Arches aquifer system, 1991–92*[Map number is location in figure 32; delta notation (δ) explained on p. C92; TU, tritium units; --, data not available]

Well name	Map number	$\delta^{18}\text{O}$ (per mil)	δD (per mil)	$\delta^{13}\text{C}$ (per mil)	$\delta^{34}\text{S}$, sulfate (per mil)	$\delta^{34}\text{S}$, sulfide (per mil)	Tritium (TU)	Carbon-14 (percent modern)
Ross	10 G	-8.35	-51.5	-14.9	-10.40	--	1.7	49.1
Birt	10 S	-8.60	-54.0	-14.2	-5.80	--	9.1	58.9
Ben Logan H.S.	10 D	-8.55	-54.5	-14.1	4.80	--	11.2	69.5
Searfoss	15 G	-8.10	-51.0	-16.6	4.00	--	3.4	37.9
Rife	15 S	-8.00	-50.0	-15.4	3.20	--	<.1	30.3
Schoenberger	15 D	-8.10	-50.0	-15.7	3.20	--	<.1	24.5
Beasley	16 G	-8.55	-56.5	-13.2	-9.60	--	<.1	54.6
Hill	16 S	-7.90	-48.5	-14.7	-7.60	--	<.1	6.2
Gillig	16 D	-7.85	-49.0	-13.7	-9.60	--	<.1	8.6
Lamalie	17 G	-8.40	-54.5	-10.8	23.30	--	<.1	3.9
S-18	17 D	-8.45	-54.5	-8.5	26.70	-42.40	<.1	4.7
Finnegan	18 D	-9.05	-59.0	-10.0	-3.20	-22.90	.5	47.7
Wilson	11 G	-7.95	-50.0	-15.4	-9.20	--	<.1	18.5
Spencer	11 S	-8.15	-51.0	-13.8	-9.80	--	10.9	58.1
Stair	11 D	-8.15	-50.5	-15.0	-7.70	--	6.2	55.7
Francis	12 S	-8.20	-51.5	-14.1	1.50	-53.20	11.6	45.0
Augustine	12 D	-8.05	-51.0	-15.3	-1.80	-51.50	10.6	62.0
Richard	13 G	-9.65	-65.5	-17.2	.30	--	.5	--
Kern	13 S	-9.90	-67.5	-13.3	6.60	--	<.1	1.3
Auckerman	13 D	-14.35	-99.5	-10.7	29.00	-27.80	<.1	0.2
Rice	14 S	-8.40	-55.0	-14.1	4.40	-33.00	<.1	8.8
City of Weston	14 D	-10.05	-67.5	-7.1	25.90	-42.50	<.1	1.4
Hartman	19	-8.45	-55.5	-1.2	20.50	--	.6	5.5
Lacy	4 G	-7.85	-47.5	-14.6	3.10	--	3.0	60.6
Hummel	4 S	-7.70	-46.5	-14.9	-7.90	--	<.1	56.1
Jones	4 D	-7.90	-49.0	-14.3	.40	--	<.1	56.9
Harrison	3 S	-7.15	-44.5	-12.7	--	--	<.1	43.4
Martin	3 D	-7.40	-46.0	-14.4	--	--	<.1	45.6
Lockhart	2 G	-7.50	-45.5	-14.1	2.40	--	16.9	100.0
Mattingly	2 S	-7.40	-46.0	-13.8	2.50	--	19.1	78.1
Merchant	2 D	-7.40	-45.0	-13.8	2.00	--	14.1	67.5
Gates	1 D	-6.95	-43.5	-11.0	--	2.2	<.1	1.2
Bickford	5 G	-7.70	-47.0	-14.9	-80	--	20.6	78.3
Bartlett	5 S	-7.60	-47.5	-14.4	-7.90	--	.3	61.8
Desoto Substation	5 D	-7.75	-47.5	-13.8	-10.00	--	.2	42.3
Staggs	6 G	-7.75	-46.5	-14.5	-2.10	--	7.8	66.8
Ice	6 S	-7.45	-46.5	-15.0	-2.20	--	.7	61.8
Underwood	6 D	-7.40	-44.5	-15.6	--	-43.40	<.1	35.7
Cohee	7 G	-7.65	-47.5	-14.7	-5.90	--	.4	58.0
Ellis	7 S	-7.65	-46.5	-15.1	-5.50	--	1.6	56.9
Harmon	7 D	-7.65	-46.5	-14.2	-3.90	--	10.9	68.0
Fox	8 G	-7.25	-45.0	-8.8	--	--	<.1	44.2
Skiles	8 D	-7.75	-47.0	-13.7	1.90	-37.80	20.0	51.3
Justice	9 G	-7.65	-48.5	-13.8	-.20	--	18.1	72.3
Lee	9 S	-7.75	-47.5	-14.2	3.00	--	15.0	65.3
Starbuck	9 D	-7.40	-45.5	-3.1	--	-12.20	<.1	28.1
Geradot	22	-7.75	-49.0	-16.2	-8.10	--	12.2	74.3
Stenzel	21	-7.60	-47.5	-14.9	9.40	--	<.1	35.1
Rees	20	-7.50	-46.5	-17.9	5.50	-27.60	<.1	20.8

TABLE 9.—Analyses of sulfur and carbon isotopes in carbonate rocks and glacial deposits from the Midwestern Basins and Arches Region

[Core locations shown in figure 32; delta notation (δ) explained on p. C92; --, data not available]

Core number	Geologic unit	Interval sampled (feet below land surface)	$\delta^{34}\text{S}$, sulfate (per mil)	$\delta^{34}\text{S}$, sulfide (per mil)	$\delta^{13}\text{C}$ (per mil)
^a 546	Detroit River Group-pyrite	--	--	-21.9	--
^a 550	Salina Group-anhydrite	--	24.9	--	--
^a 557	Lockport dolomite-pyrite	--	--	7.0	--
G1	Glacial deposits	3 – 25	-14.8	-13.1	--
G2	Glacial deposits	5 – 60	-9.8	-14.6	-.45
G3	Glacial deposits	18 – 70	-9.8	-12.8	-.05
G4	Glacial deposits	10 – 180	-9.9	-8.0	-.55
G5	Glacial deposits	12 – 130	-8.2	-14.0	.00
C1	Columbus Limestone	235	9.6	-24.9	1.45
	Salina Group	273 – 375	-1.0	-7.8	--
	Salina Group	425 – 575	8.2	-1.9	--
C2	Detroit River Group	35	26.4	-14.0	--
	Salina Group	100	6.5	-8.8	.10
	Salina Group	150	-.7	-7.1	-3.20
	Salina Group	301	28.3	-9.9	--
	Salina Group	350	9.2	-10.0	-.25
	Salina Group-bedded gypsum	320 – 465	28.7	--	--
	Lockport Dolomite	650	14.6	2.4	1.30
C3	Salamonie Dolomite	105	18.3	3.6	1.35
C4	Salina Group	20 – 173	-2.3	-6.8	--
	Salina Group-pyrite	173	--	-19.4	--

^aData from Botoman and Faure (1976).

than the less productive glacial deposits, which were derived from clay-rich lacustrine sediments.

Water from the carbonate-rock aquifer (fig. 34) ranges in dissolved-solids concentration from 170 to more than 350,000 mg/L. Where the carbonate-rock aquifer does not underlie the upper confining unit, dissolved-solids concentrations range from 170 to 3,830 mg/L; the median is 560 mg/L. Ground water with dissolved-solids concentrations less than 500 mg/L is present in many areas of the carbonate-rock aquifer where it is does not underlie the upper confining unit; however, it is found only locally in the northeastern part of the study area. Ground water with dissolved-solids concentrations between 500 and 1,000 mg/L is present primarily in the northeastern part of the area. Water with dissolved-solids concentrations greater than 1,000 mg/L in the carbonate-rock aquifer where the upper confining unit is not present is restricted to the northeastern part of the study area.

Dissolved-solids concentrations for the carbonate-rock aquifer where it underlies the upper confining unit also are shown in figure 34. Lines of equal dissolved-solids concentration are drawn for those areas in the basins where dis-

solved-solids concentrations are greater than 10,000 mg/L. The dissolved-solids concentration data for water in the structural basins are from wells completed in oil- and gas-producing zones within the carbonate rocks of Silurian and Devonian age. Dissolved-solids concentrations were computed either from chemical data of brines that were reported in the literature or calculated from borehole geophysical data (D.J. Schnoebelen, U.S. Geological Survey, written commun., 1993).

The distribution of dissolved-solids concentrations in the carbonate rocks differs greatly among the three structural basins (Appalachian, Michigan, and Illinois) in the Midwestern Basins and Arches Region:

Appalachian Basin—Dissolved-solids concentrations within the Appalachian Basin range from less than 10,000 to greater than 350,000 mg/L; all but two reported brine analyses list dissolved-solids concentrations greater than 200,000 mg/L. The few analyses that are available from the Appalachian Basin where the dissolved-solids concentrations are less than 100,000 mg/L indicate that the zone of transition from freshwater to saltwater is narrow. Chloride concentra-

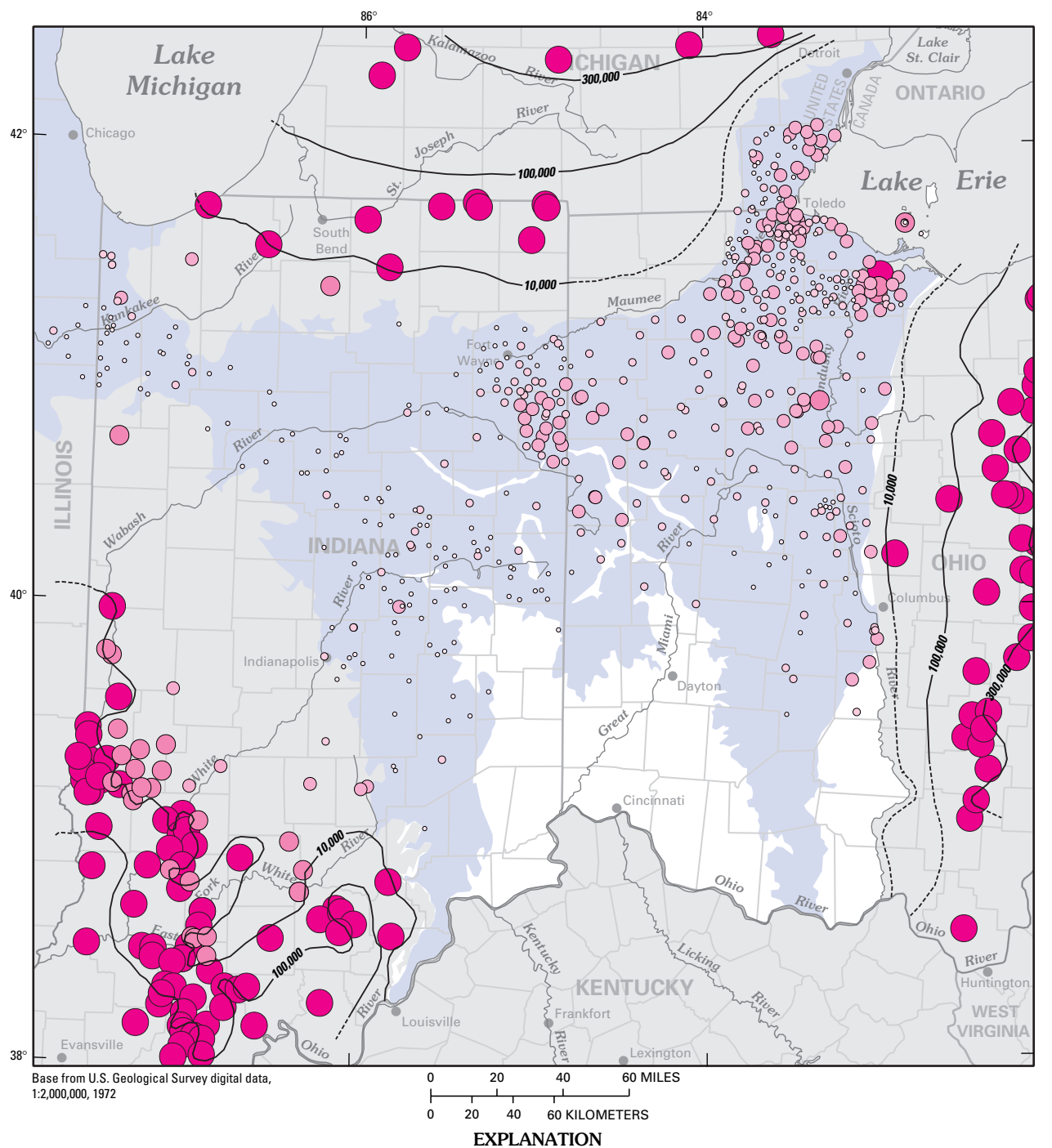


FIGURE 34.—Dissolved-solids distribution in ground water from the carbonate-rock aquifer in the Midwestern Basins and Arches aquifer system.

tions increase from less than 50 to greater than 9,300 mg/L within approximately 7 mi downbasin from where the carbonate-rock aquifer becomes confined above by the upper confining unit (Schmidt, 1979).

Michigan Basin—In the Michigan Basin, dissolved-solids concentrations of water from carbonate rocks of Devonian and Silurian age range from less than 10,000 to greater than 350,000 mg/L. The transition zone from freshwater to highly concentrated brine is comparatively wider than in the Appalachian Basin. Brines with dissolved-solids concentrations greater than 350,000 mg/L in the Michigan Basin are first noted more than 75 mi downbasin from the contact between the carbonate-rock aquifer and the upper confining unit, where it is exposed at the bedrock surface, whereas similarly concentrated brines in the Appalachian Basin are found less than 50 mi downbasin from where the carbonate rocks are confined.

Illinois Basin—Dissolved-solids concentrations of water from carbonate rocks of Devonian and Silurian age in the Illinois Basin range from less than 3,000 to greater than 100,000 mg/L. The contrast in the distribution of dissolved-solids concentrations between the Illinois Basin and the Appalachian and Michigan Basins is striking. The largest dissolved-solids concentrations in the Illinois Basin are approximately 150,000 mg/L, much lower than in the other two basins. Water with dissolved-solids concentrations less than 10,000 mg/L is found more than 70 mi downbasin from where the carbonate-rock aquifer dips beneath the upper confining unit.

Generally, the dissolved-solids concentration of water in structural basins increases with depth. In the Midwestern Basins and Arches aquifer system, dissolved-solids concentrations increase as the carbonate rocks dip toward the center of each structural basin (fig. 34). However, the relation between dissolved-solids concentration and depth is not consistent among the three basins. In the Appalachian and Michigan Basins, water with dissolved-solids concentrations of approximately 10,000 mg/L is first noted where the carbonate rocks are about 300 to 800 ft below land surface; in the Illinois Basin, water with dissolved-solids concentrations of approximately 10,000 mg/L is first noted where the carbonate rocks are more than 2,000 ft below land surface. The presence of dilute water at such depths in the Illinois Basin is unusual and has been investigated by various researchers (Clayton and others, 1966; Rupp and Pennington, 1987; Stueber and others, 1987; and Stueber and Walter, 1991). Several hypotheses have been advanced to explain the presence of the dilute formation water at the margins of the Illinois Basin and include (1) dilution of formation water by meteoric water of Pleistocene age, (2) precipitation of solid phases during mixing of formation water with meteoric water, and (3) increased infiltration through fracture systems within the carbonate rocks. The origin of dilute formation water in the carbonate rocks of Devonian and Silurian age is unclear, and further research is necessary to explain more fully the chemical and hydrologi-

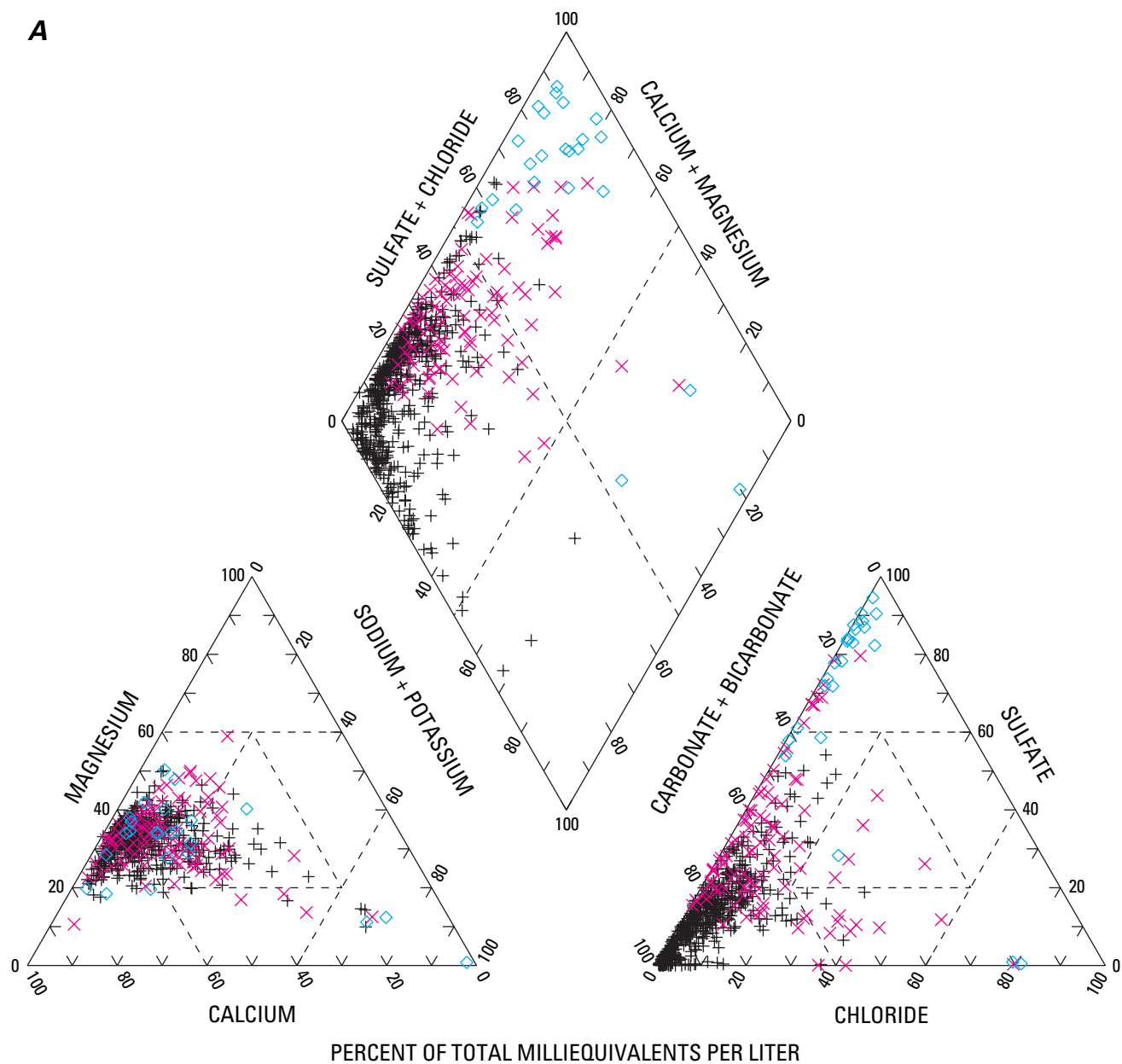
cal processes that have occurred in the Illinois Basin. Although water with dissolved-solids concentrations less than 10,000 mg/L is potentially potable (U.S. Environmental Protection Agency, 1984), the dilute formation water is produced as a by-product of oil and gas production and is not used as a source of drinking water.

The only regionally extensive areas of water with dissolved-solids concentrations greater than 10,000 mg/L in the Midwestern Basins and Arches aquifer system are beneath the upper confining unit in the structural basins. However, in a small area along Lake Erie near the mouth of the Sandusky River, ground water from the carbonate-rock aquifer contains dissolved-solids concentrations ranging from 10,000 to greater than 70,000 mg/L (Breen and Dumouchelle, 1991). Breen and Dumouchelle (1991) evaluated bromide and chloride data and concluded that the source of salinity in this area is halite dissolution. Although Janssens (1977) states that the extensive halite beds found in the Salina Group in eastern Ohio disappear more than 50 mi east of where the saline water is present, the data indicate that perhaps an isolated remnant of bedded halite may be present in the carbonate rocks in this area. All other available data indicate that water with dissolved-solids concentrations less than 10,000 mg/L is found throughout the total thickness of the carbonate-rock aquifer where it does not underlie the upper confining unit. Data are not available, however, in the northern part of the study area where the thickness of the carbonate-rock aquifer increases to more than 2,500 ft. Dilute ground water may not be present at depth in this area.

HYDROCHEMICAL FACIES

Identification of hydrochemical facies in the Midwestern Basins and Arches aquifer system was based on the distribution of water types in the glacial and carbonate-rock aquifers. Water types were defined by use of the trilinear plotting technique (Piper, 1944); the trilinear diagrams are shown in figures 35 and 36.

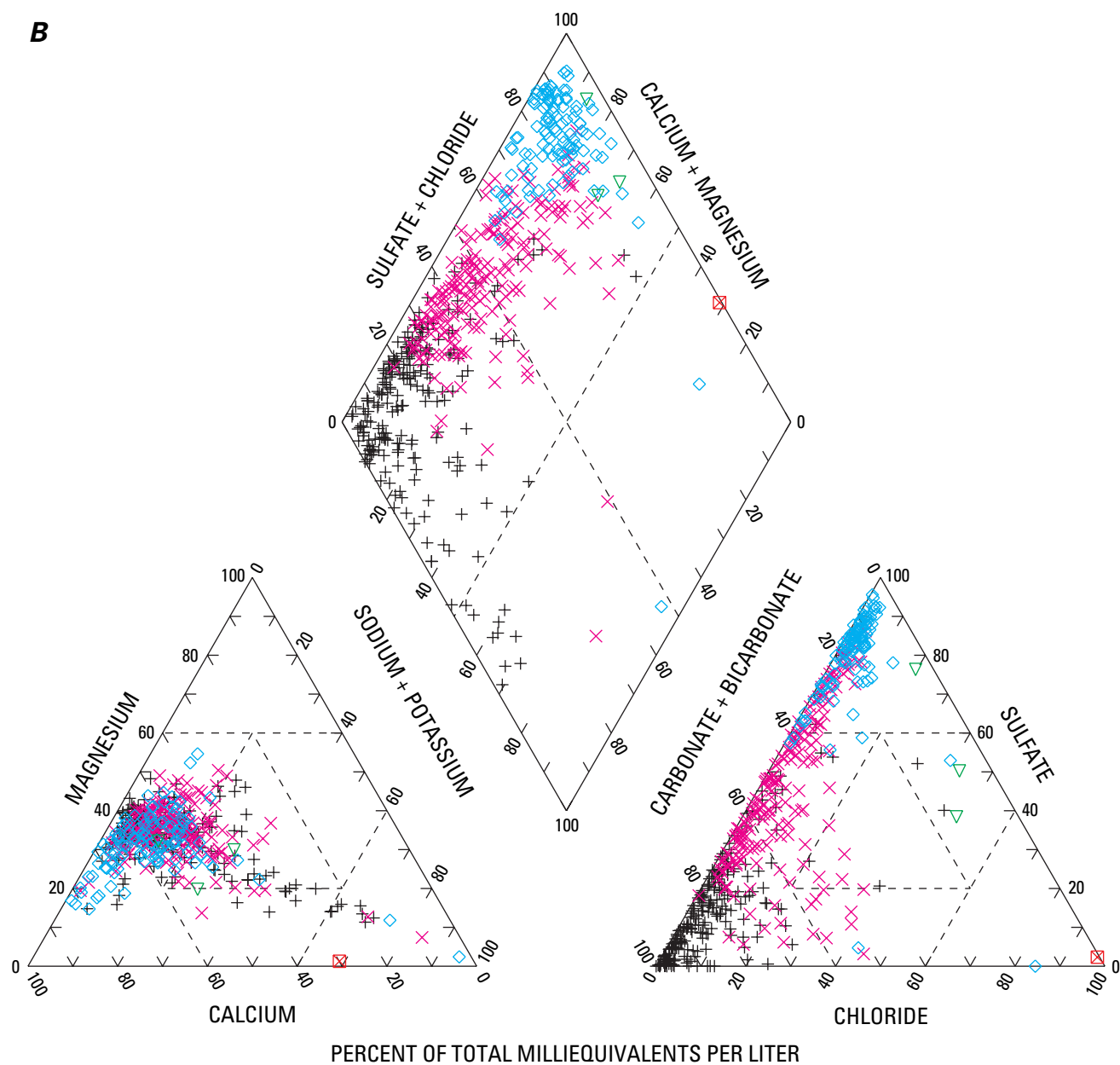
The seven water types that were identified in the Midwestern Basins and Arches aquifer system and their abundance are listed in table 10. The two most abundant water types in the glacial aquifers and in the carbonate-rock aquifer where it does not underlie the upper confining unit are Ca-Mg-HCO₃ and Ca-Mg-SO₄ types. Nearly 80 percent of all available ground-water analyses from the glacial and carbonate-rock aquifers would be classified as either of these two water types. The next most common ground-water types are Ca-Mg-Na-HCO₃ and Ca-Mg-Na-SO₄ and are distinguished from the more common Ca-Mg-HCO₃ and Ca-Mg-SO₄ waters by an increased percentage of dissolved sodium. The Cl-influenced ground-water type, present in small but notable quantities, is distinguished by chloride percentages that range from at least 20 percent to no more than 60 percent of the total anion milliequivalents. Na-Cl or Ca-Na-Cl type water

A**EXPLANATION**

Dissolved-solids concentration, in milligrams per liter

- + Less than or equal to 500
- × Greater than 500 and less than or equal to 1,000
- ◇ Greater than 1,000

FIGURE 35.—Trilinear diagram of water chemistry of the Midwestern Basins and Arches aquifer system, categorized by dissolved-solids concentration: (A) glacial aquifers.

B**EXPLANATION****Dissolved-solids concentration, in milligrams per liter**

- + Less than or equal to 500
- × Greater than 500 and less than or equal to 1,000
- ◇ Greater than 1,000 and less than or equal to 3,000
- ▽ Greater than 3,000 and less than or equal to 10,000
- ⊠ Greater than 10,000

FIGURE 35.—CONTINUED. Trilinear diagram of water chemistry of the Midwestern Basins and Arches aquifer system, categorized by dissolved-solids concentration: (B) carbonate-rock aquifer where it does not underlie the upper confining unit.

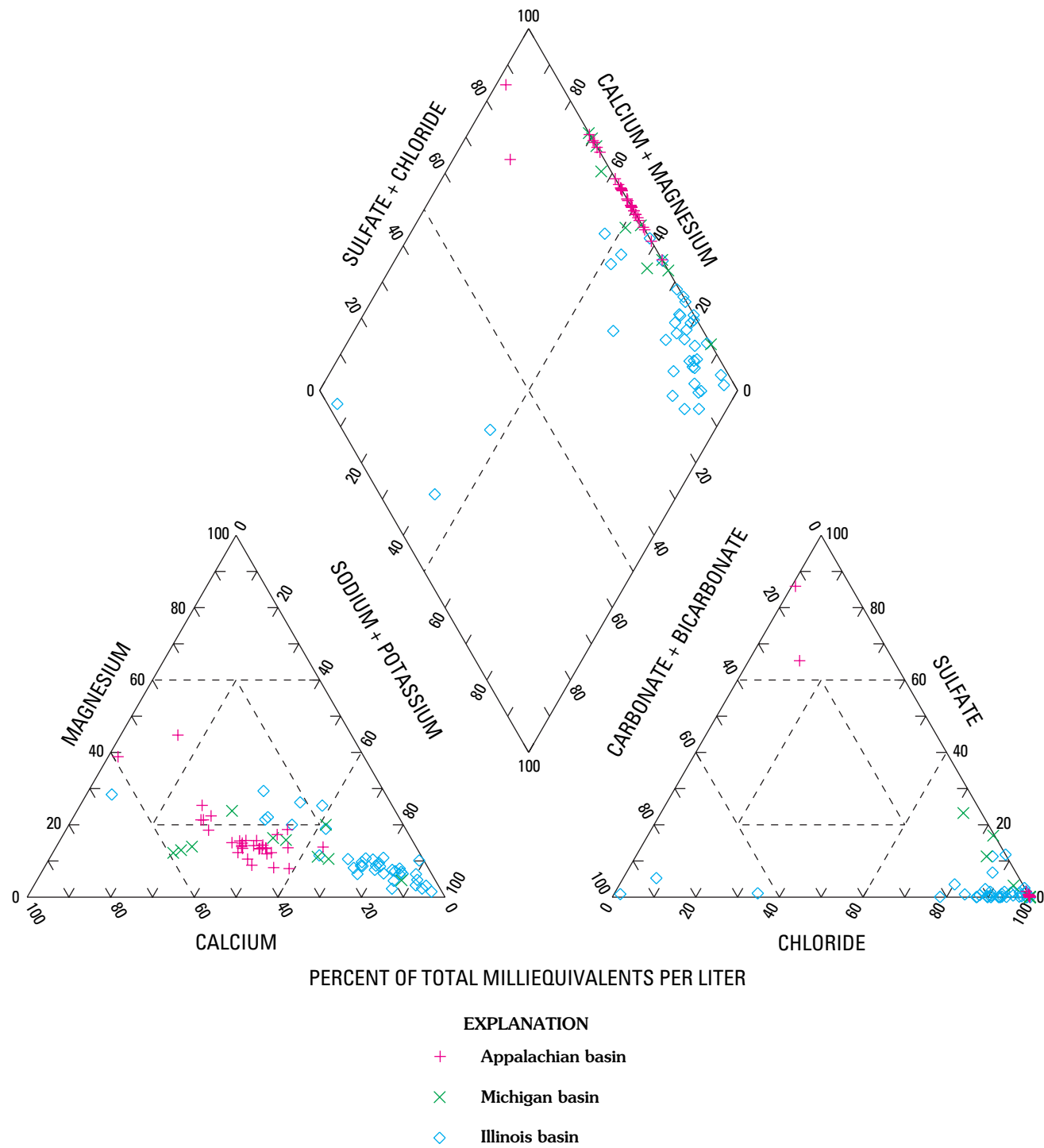


FIGURE 36.—Trilinear diagram of water chemistry in the carbonate-rock aquifer of the Midwestern Basins and Arches aquifer system where it underlies the upper confining unit, categorized by structural basin.

TABLE 10.—*Major water types, their specific cation and anion compositions, and their abundance in the glacial and carbonate-rock aquifers in the Midwestern Basins and Arches aquifer system*

[%; percent; --, data not available]

Water type	Cation types	Anion types	Number (percentage) of samples, by aquifer		
			Glacial aquifers ¹	Carbonate-rock aquifer	
				Does not underlie the upper confining unit ²	Underlies the upper confining unit ³
Ca-Mg-HCO ₃	Ca,Ca-Mg	HCO ₃	479 (75%)	215 (40%)	1 (1%)
Ca-Mg-SO ₄	Ca, Ca-Mg	HCO ₃ -SO ₄ SO ₄	69 (11%)	207 (38%)	2 (2%)
Ca-Mg-Na-HCO ₃	Ca-Mg-Na, Ca-Na	HCO ₃	55 (9%)	44 (8%)	2 (2%)
Ca-Mg-Na-SO ₄	Ca-Mg-Na, Ca-Na	HCO ₃ -SO ₄ , SO ₄	11 (2%)	41 (8%)	--
Na-HCO ₃	Na	HCO ₃	3 (<1%)	9 (2%)	--
Na-Cl or Ca-Na-Cl	Na, Ca-Na, Ca-Mg-Na	Cl	2 (<1%)	3 (<1%)	79 (93%)
Cl-influenced	All cation types	HCO ₃ -SO ₄ -Cl, HCO ₃ -Cl, SO ₄ -Cl	18 (3%)	20 (4%)	1 (1%)

¹Total number of samples from the glacial aquifers is 637.²Total number of samples from the carbonate-rock aquifer where it does not underlie the upper confining unit is 539.³Total number of samples from the carbonate-rock aquifer where it underlies the upper confining unit is 85.

predominates in the carbonate-rock aquifer where it underlies the upper confining unit; however, this water type is rare in other parts of the carbonate-rock aquifer and in the glacial aquifers. Na-HCO₃ water is uncommon in the aquifer system.

Hydrochemical facies (figs. 37 and 38) were identified for the glacial and carbonate-rock aquifers on the basis of the spatial distribution of water types in table 10. Large areas of the Midwestern Basins and Arches aquifer system are characterized by the presence of either the Ca-Mg-HCO₃ or the Ca-Mg-SO₄ type; these areas are called Ca-Mg-HCO₃ facies and Ca-Mg-SO₄ facies, respectively. The remaining areas of the aquifer system are not characterized by a single water type; rather, they are distinguished by the presence of either Ca-Mg-HCO₃ water or Ca-Mg-SO₄ water or both types, along with water types with increased percentages of sodium (Ca-Mg-Na-HCO₃, Ca-Mg-Na-SO₄, and Na-HCO₃ waters) and, in some places, sodium and chloride (Na-Cl and Cl-influenced waters). These areas where several different water types are present together are called multiple-water-type facies.

Hydrochemical facies of water from glacial aquifers are shown in figure 37. A Ca-Mg-HCO₃ facies in the glacial aquifer

extends throughout much of the Midwestern Basins and Arches Region. A facies of Ca-Mg-SO₄ water is present in the northeastern part of the aquifer system. Multiple-water-type facies are present in the glacial aquifers along the north and northwest boundaries between the underlying carbonate-rock aquifer and the upper confining unit. Another multiple-water-type facies is present in the south-central part of the study area where the glacial deposits are directly underlain by Ordovician-age shales and limestones (the upper weathered zone water-bearing unit).

Hydrochemical facies of water from the carbonate-rock aquifer are shown on figure 38. Ca-Mg-HCO₃ water is present in the carbonate-rock aquifer throughout much of the Midwestern Basins and Arches aquifer system except in the northeastern part, where it is highly localized. The predominant water type in the northeastern part of the study area is Ca-Mg-SO₄. Multiple-water-type facies are present in the carbonate-rock aquifer along the north boundary between the carbonate-rock aquifer and the upper confining unit. Another multiple water-type facies is present along a part of the west contact between the carbonate-rock aquifer and the upper confining unit.

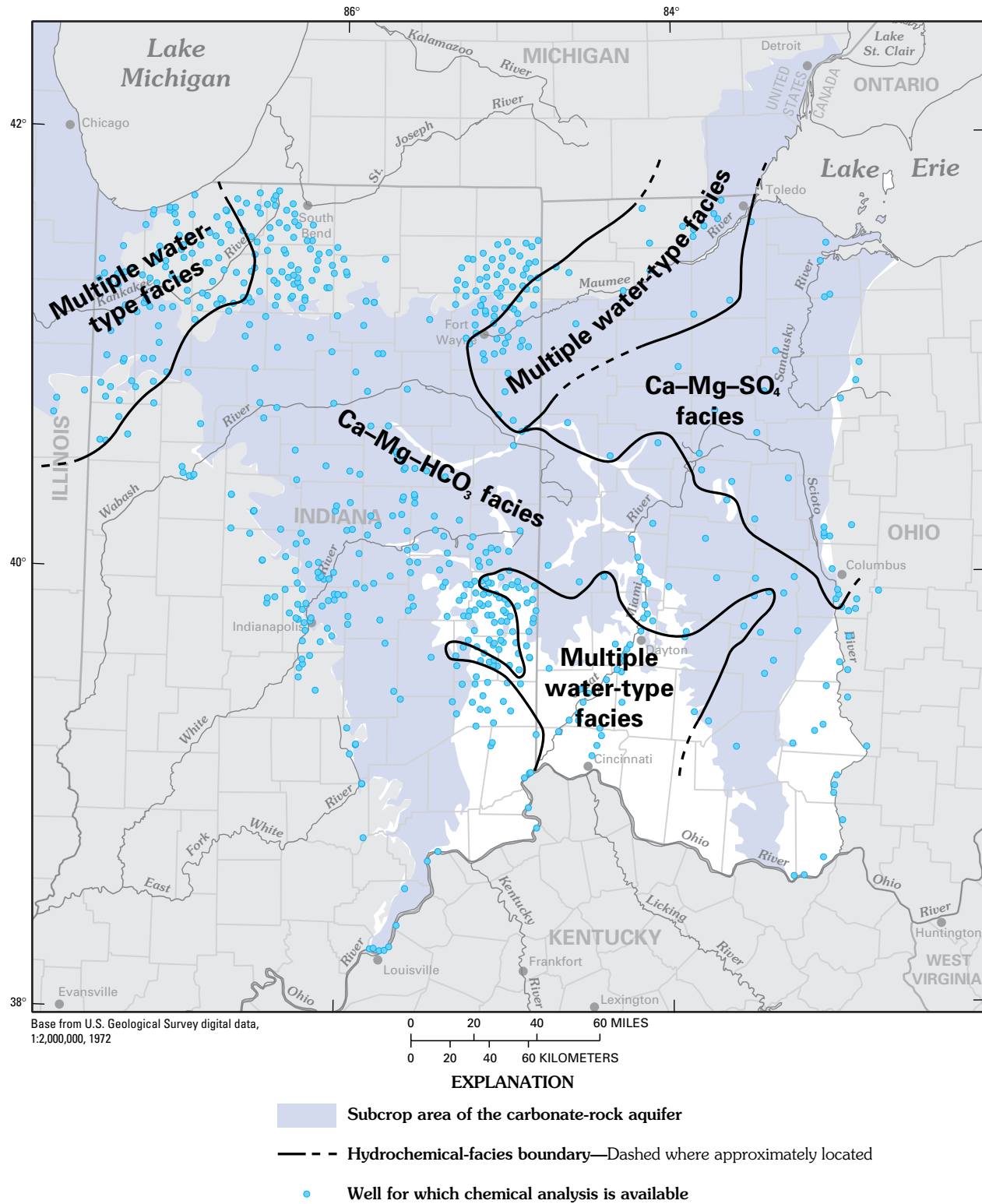


FIGURE 37.—Hydrochemical facies of ground water from the glacial aquifers in the Midwestern Basins and Arches aquifer system.

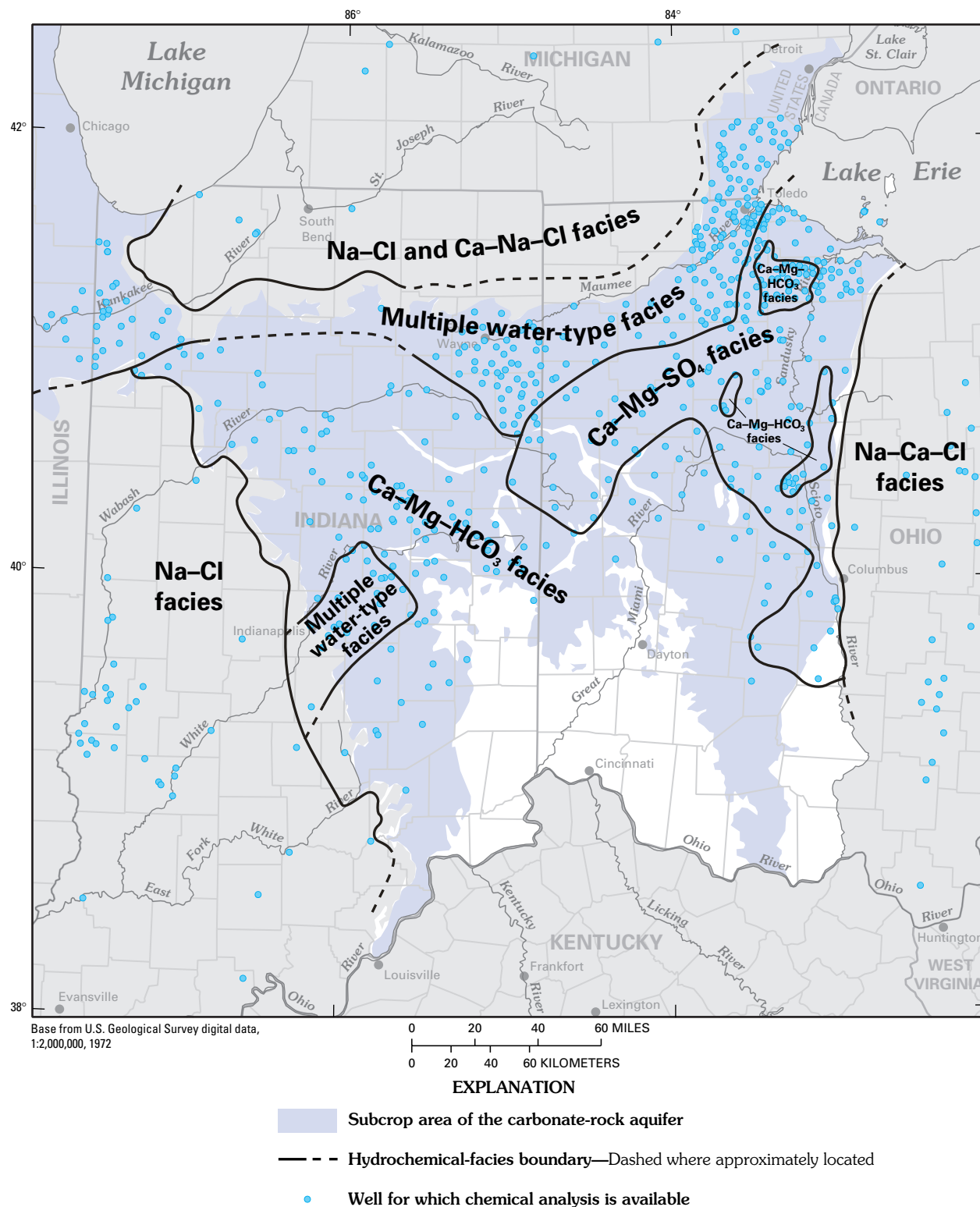


FIGURE 38.—Hydrochemical facies of ground water from the carbonate-rock aquifer in the Midwestern Basins and Arches aquifer system.

Water in the carbonate-rock aquifer in the Appalachian Basin is predominantly the Na-Ca-Cl type with nearly equal milliequivalent percentages of Na and Ca. In the Michigan Basin, water is either a Na-Cl or Ca-Na-Cl type, depending on the specific bedrock unit within the carbonate rocks from which the water is produced. The predominant water type in the Illinois Basin is Na-Cl; however, an area of Ca-Mg-Na-HCO₃ water is present in the basin as far as 15 miles downdip from where the carbonate-rock aquifer becomes confined.

RELATION BETWEEN DISSOLVED-SOLIDS CONCENTRATIONS AND HYDROCHEMICAL FACIES

Examination of figures 33, 34, 37, and 38 indicates a strong relation between the distribution of dissolved-solids concentrations and the distribution of hydrochemical facies in the glacial and carbonate-rock aquifers. The trilinear diagrams (figs. 35 and 36) of water from the glacial aquifers and the carbonate-rock aquifer, where it is does not underlie the upper confining unit, also show that water type changes as dissolved-solids concentrations change. The Ca-Mg-HCO₃ water found throughout the aquifer system is characterized by dissolved-solids concentrations that are generally less than 500 mg/L. Ca-Mg-SO₄ water has dissolved-solids concentrations that range from about 500 to more than 3,000 mg/L. As figure 35 shows, dissolved-solids concentrations increase as the percentage of sulfate in water increases. The dissolved-solids concentrations of ground water in the multiple-water-type facies are varied, as one would expect given the variability in water types in such facies.

Water type and dissolved-solids concentrations are also related in the carbonate-rock aquifer where it underlies the upper confining unit. Ground water from the carbonate-rock aquifer in each of the surrounding structural basins is categorized by basin on the trilinear diagram in figure 36. Based on the available analyses, waters from the Appalachian Basin have dissolved-solids concentrations that are generally greater than 200,000 mg/L and are Na-Ca-Cl type waters. Waters from the Michigan Basin range in dissolved-solids concentration from around 10,000 mg/L to more than 300,000 mg/L; water type changes from a Na-Cl to a Ca-Na-Cl as dissolved-solids concentrations increase. The dissolved-solids concentration in waters from the Illinois Basin is generally less than 100,000 mg/L, and the waters are primarily of the Na-Cl type.

Examination of figures 33, 34, 37, and 38 indicates that the spatial distribution of dissolved-solids concentrations and hydrochemical facies in the glacial and carbonate-rock aquifers is similar. The similarity likely reflects the hydraulic connection between the units. Ground water can flow through the glacial deposits and into the bedrock, then can discharge to streams and lakes back through the glacial deposits. Moreover, the source rock of the glacial deposits in the region is primarily the underlying bedrock (Strobel and Faure, 1987). Thus, the similarity in chemistry is also likely due to the pres-

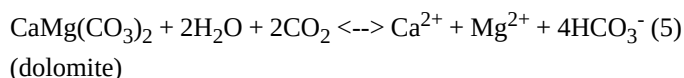
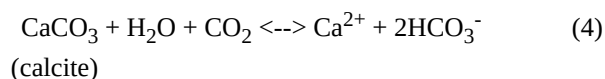
ence of the same reacting mineral phases in the glacial and carbonate-rock aquifers.

GEOCHEMICAL AND HYDROLOGICAL PROCESSES, BY WATER TYPE

The trends in major-ion chemistry in the Midwestern Basins and Arches aquifer system are controlled, in a large part, by interactions between ground water and minerals that compose the aquifers. Important geochemical reactions that can affect solute concentrations in ground-water systems include mineral dissolution and precipitation, oxidation and reduction, and ion exchange. Additional processes such as evaporation and mixing of water from various sources can also be important controls of solute concentrations. The extent to which these processes control ground-water chemistry is affected by the paths and rates of ground-water flow and the sequence of reactions in an aquifer system. The geochemical and hydrologic processes responsible for the various water types in the Midwestern Basins and Arches aquifer system are discussed in the following sections.

CALCIUM-MAGNESIUM-BICARBONATE WATER

Ca-Mg-HCO₃ water, the predominant type in the glacial and carbonate-rock aquifers, is generally produced by dissolution of the carbonate minerals calcite and dolomite. The reaction of calcite and dolomite with water and carbon dioxide can be written as follows:



Typically, CO₂ is derived from the oxidation of organic matter and root respiration in the soil zone and is dissolved by recharge water. Dolomite is more abundant than calcite in the aquifer system (Harrison, 1960; Steiger and Holowaychuk, 1971; Wilding and others, 1971; Casey, 1994); if dolomite dissolves according to equation 5, the molar proportions of [Ca+Mg] to [HCO₃] should be linear, with a slope of 0.5. A fairly strong relation exists between [Ca+Mg] and [HCO₃] for Ca-Mg-HCO₃ type water from the glacial and carbonate-rock aquifers (figs. 39 and 40); however, the Ca-Mg-SO₄ and Ca-Mg-Na-SO₄ water types do not follow the trend predicted by the dolomite dissolution model and are highly enriched in calcium and magnesium relative to bicarbonate ([Ca+Mg]/[HCO₃] > 0.5). The Ca-Mg-Na-HCO₃ waters plot slightly below the line and are depleted in calcium and magnesium relative to bicarbonate ([Ca+Mg]/[HCO₃] < 0.5). (The mechanism by which calcium and magnesium are depleted is ion

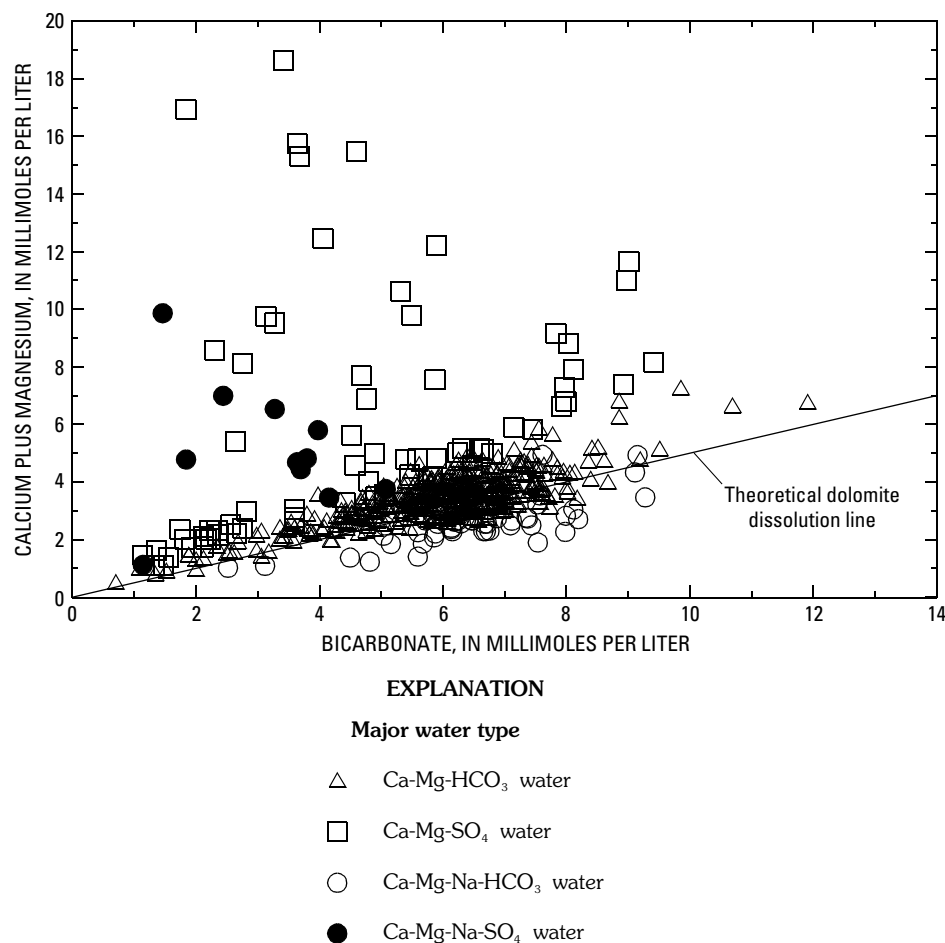


FIGURE 39.—Concentration of calcium plus magnesium as a function of bicarbonate concentration in ground water from the glacial aquifers in the Midwestern Basins and Arches aquifer system.

exchange of calcium and magnesium for sodium and is discussed in the section on “Sodium-Enriched Water.”)

The state of equilibrium between ground water and calcite, dolomite, and other minerals in the aquifer system can be evaluated by the computation of saturation indices (SI), expressed as

$$SI_{\text{mineral}} = \log(IAP/K_T), \quad (6)$$

where IAP is the ion-activity product of the mineral calculated from analytical data, and K_T is the thermodynamic equilibrium constant at the measured temperature of the water sample (Plummer and others, 1976). If the saturation index is negative, the water is undersaturated with respect to the particular mineral, and dissolution of the mineral is possible. If the saturation index is positive, the water is oversaturated with respect to the mineral, and precipitation of the mineral in the aquifer is possible. A saturation index of zero indicates that the mineral is in equilibrium with the water and that the tendency or rates of dissolution and precipitation should be equal. Thermodynamics can only indicate the potential for

such phase transfers. In reality, various kinetic factors may cause systems to behave differently than predicted (Nordstrom and Ball, 1989; Busby and others, 1991).

Saturation indices were calculated for calcite and dolomite (and other mineral phases discussed later in this report) by use of the computer model WATEQF (Plummer and others, 1976) and chemical data for the water collected as part of this investigation. The accuracy of the saturation index for predicting equilibrium of carbonate minerals depends largely on the accuracy of the field measurements of pH and alkalinity. Uncertainty in these and other analytical data produces an uncertainty estimate in the saturation index of ± 0.1 for calcite and ± 0.2 for dolomite (Nordstrom and Ball, 1989; Busby and others, 1991). Because the accuracy of the pH measurements could not be verified for much of the historical ground-water-chemistry data, saturation indices were not calculated for historical samples.

The saturation indices for calcite and dolomite generally do not correlate with dissolved-solids concentrations (fig. 41). Nearly all the Ca-Mg-HCO₃ water is in equilibrium or oversaturated with respect to calcite and dolomite, an indica-

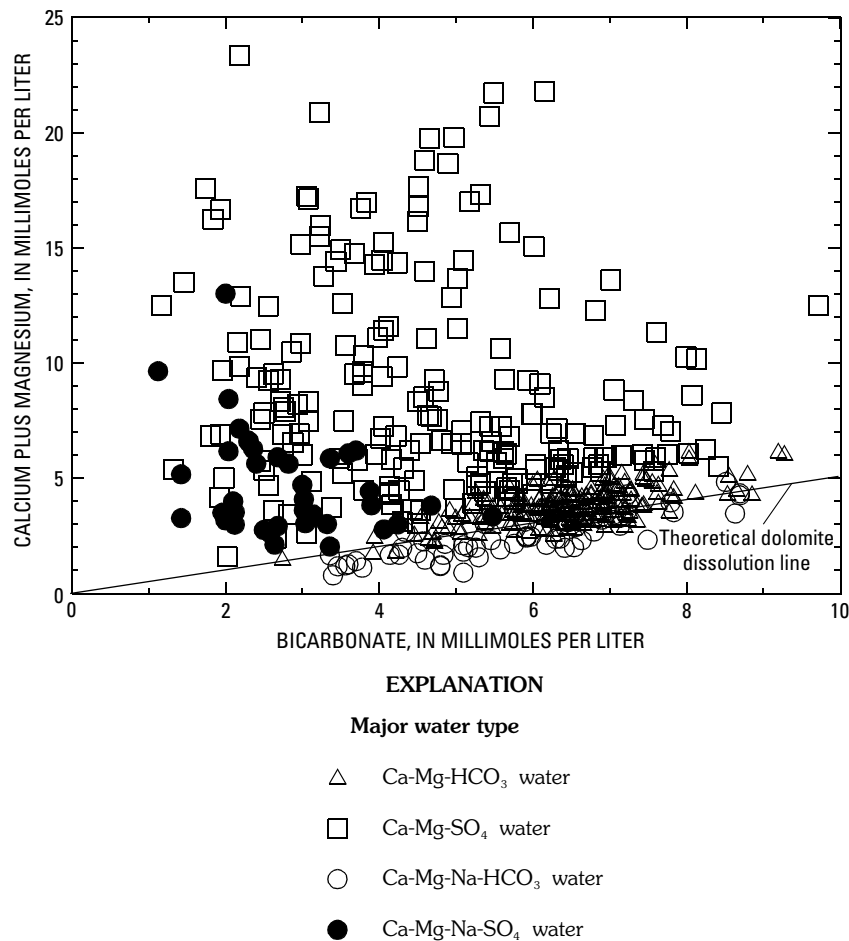


FIGURE 40.—Concentration of calcium plus magnesium as a function of bicarbonate concentration in ground water from the carbonate-rock aquifer in the Midwestern Basins and Arches aquifer system.

tion that carbonate mineral equilibria could be controlling concentrations of calcium, magnesium, and bicarbonate in Ca-Mg-HCO₃ water in the aquifer system. The tendency toward oversaturation with respect to calcite has been noted in other aquifers by Nordstrom and Ball (1989), who conclude that kinetic effects may inhibit calcite precipitation. Reactions that add calcium, magnesium, and bicarbonate or that consume carbon dioxide can promote oversaturation with calcite and dolomite. For example, dissolution of gypsum may add calcium at a rate that exceeds calcium removal by calcite precipitation, causing oversaturation with calcite. Several Ca-Mg-SO₄-type waters are saturated with calcite but are significantly undersaturated with respect to dolomite. Undersaturation with respect to dolomite is an important factor in dedolomitization, a process that can promote the formation of Ca-Mg-SO₄-type water. (Dedolomitization is discussed further in the next section.)

Ca-Mg-HCO₃ water is the predominant water type in the glacial and carbonate-rock aquifers because calcite and dolomite are abundant in these aquifers (Harrison, 1960; Steiger

and Holowaychuk, 1971; Wilding and others, 1971; Casey, 1994) and recharge takes place across most of the study area. A steady supply of CO₂ is available for carbonate dissolution in the glacial aquifers because ground-water recharge generally takes place through the organic-rich soils overlying these deposits. Dissolved CO₂ and other solutes are also recharged to the underlying bedrock because the glacial aquifers provide most of the recharge to the carbonate-rock aquifer at the regional scale.

CALCIUM-MAGNESIUM-SULFATE WATER

The predominant water type in the northeastern part of the Midwestern Basins and Arches aquifer system is Ca-Mg-SO₄. This water is characterized by high concentrations of dissolved solids, calcium, magnesium, and sulfate. The predominance of sulfate over bicarbonate and the lack of agreement of the Ca-Mg-SO₄ water with the simple dolomite dissolution model (figs. 39 and 40) indicates that other processes are controlling the chemistry of this water type. Two reactions can produce this type of water: (1) dedolomitization, which

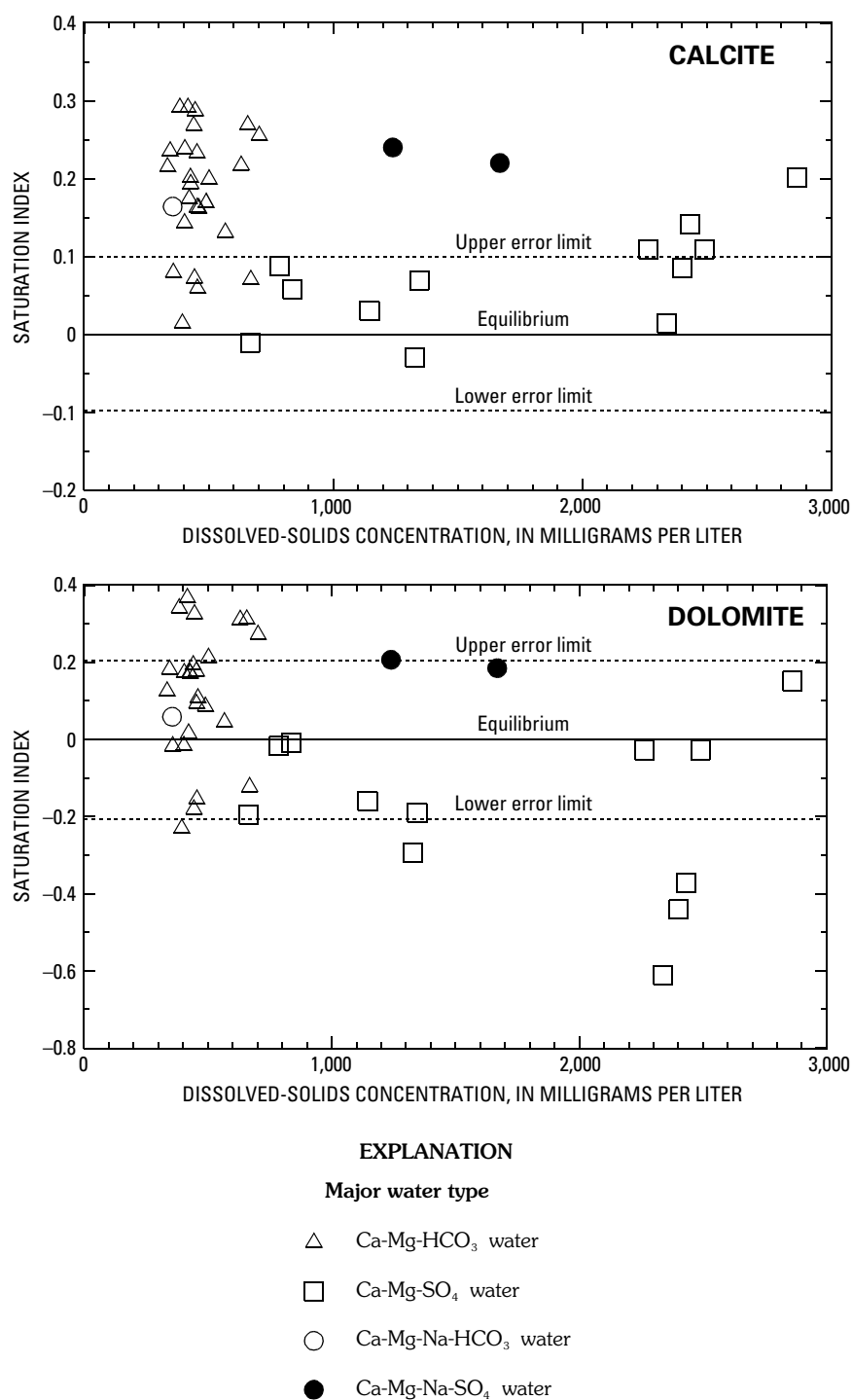
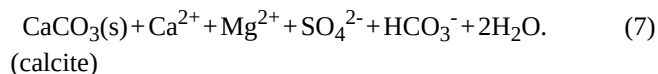
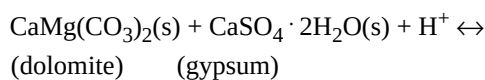


FIGURE 41.—Saturation indices of calcite and dolomite as a function of dissolved-solids concentration for water from wells in the Midwestern Basins and Arches aquifer system. (Error limits are due to analytical and thermodynamic data uncertainties. Points plotting within these lines are considered to be in equilibrium with the given mineral.)

involves dissolution reactions with carbonate minerals and gypsum, and (2) sulfuric acid neutralization, which involves dissolution of carbonate minerals with sulfuric acid generated by the oxidation of pyrite.

The results of investigations of other regional carbonate-rock aquifers show that dedolomitization may be a controlling process (Pearson and Rightmire, 1980; Back and others, 1983; Busby and others, 1991). Ground water that moves through the aquifer initially dissolves calcite, dolomite and gypsum (or anhydrite). Once calcite and dolomite reach saturation, gypsum is still undersaturated and continues to dissolve, adding calcium and sulfate to the water. Consequently, calcite becomes oversaturated and, as it precipitates, the bicarbonate concentration decreases. The decrease in bicarbonate concentration causes the water to be undersaturated with respect to dolomite and promotes dissolution of dolomite. Dissolution of dolomite causes increases in the concen-

tration of magnesium in the water. The overall reaction can be written as:



As the reaction proceeds, Ca:Mg ratios in the water decrease to 1.0, and sulfate concentrations increase. The ratio of $[\text{Ca}+\text{Mg}]/[\text{HCO}_3^-]$ is 1:1, in contrast to reaction 5, in which the ratio of $[\text{Ca}+\text{Mg}]/[\text{HCO}_3^-]$ is 1:2 or 0.5. On a plot of $[\text{Ca}+\text{Mg}]$ as a function of $[\text{SO}_4 + 0.5\text{HCO}_3^-]$, the dedolomitization reaction yields a straight line with a slope of 1. Plots of the water-chemistry data for the glacial aquifers (fig. 42) and the carbonate-rock aquifer (fig. 43) show very close agree-

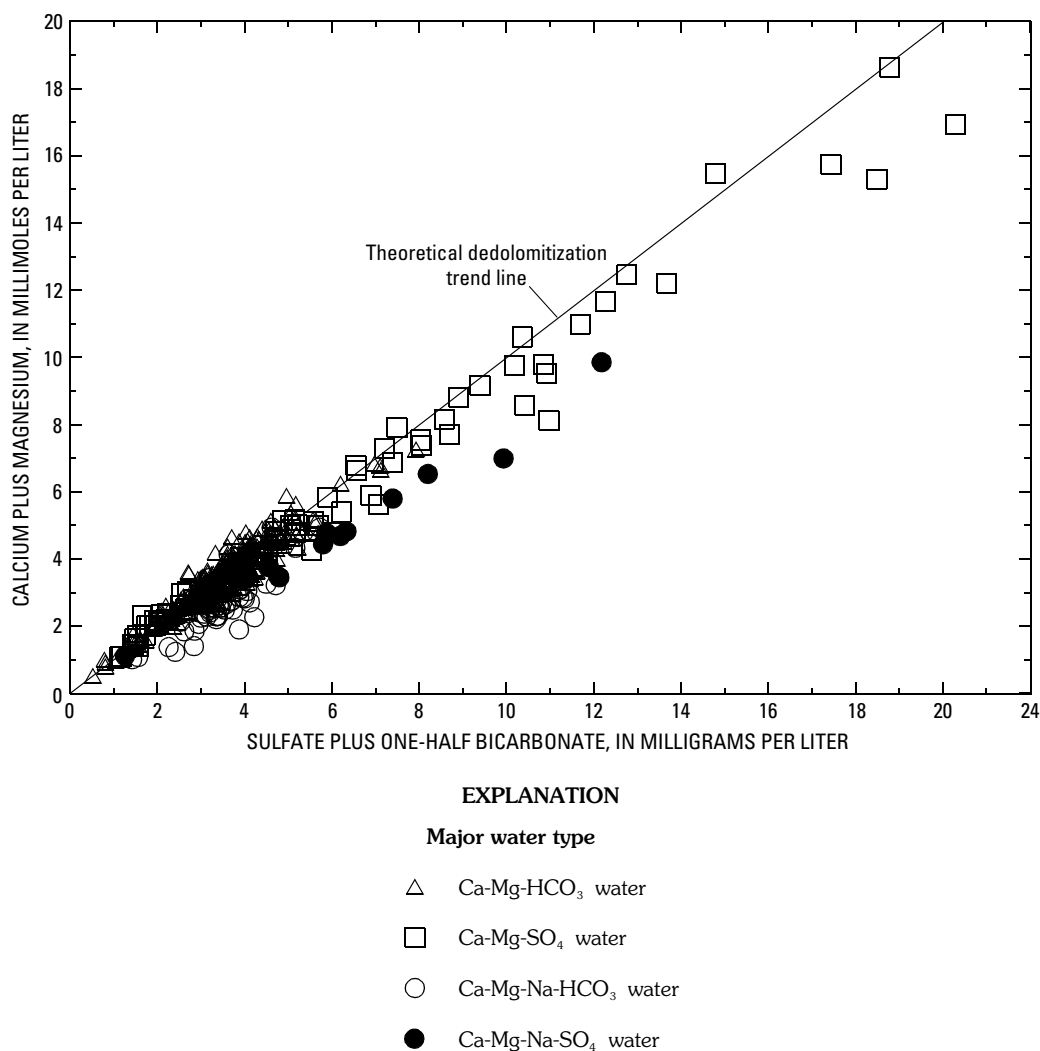


FIGURE 42.—Concentration of calcium plus magnesium as a function of concentration of sulfate plus one-half bicarbonate in ground water from the glacial aquifers in the Midwestern Basins and Arches aquifer system.

ment between the theoretical trend for the dedolomitization model and the trends for the Ca-Mg-HCO₃- and the Ca-Mg-SO₄-type waters. The Ca-Mg-Na-HCO₃- and Ca-Mg-Na-SO₄-type waters tend to plot below the 1:1 line.

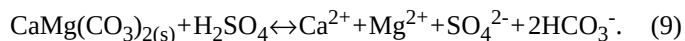
Gypsum saturation indices for ground water collected as part of this investigation (fig. 44) increase with increasing sulfate concentrations. A value of ± 0.2 is used as the estimate of uncertainty in the saturation index of gypsum. Saturation with respect to gypsum generally is indicated for a few samples in which sulfate concentrations are greater than about 1,500 mg/L. Gypsum would tend to dissolve in water that is undersaturated with respect to gypsum.

Dedolomitization is not the only process, however, that yields the relation between Ca, Mg, SO₄, and HCO₃ shown in figures 42 and 43. An alternative model involves dissolution

of dolomite by sulfuric acid (H₂SO₄) produced by the oxidation of pyrite (FeS₂):



(Nordstrom and others, 1979). The sulfuric acid reacts with dolomite:



The overall stoichiometry of the dissolved products in reaction 9 is identical to that of the dedolomitization reaction (7). Thus, either model could produce the trends shown in figures 42 and 43, and gypsum and (or) pyrite could be the sources of sulfate in the Ca-Mg-SO₄ water in the northeastern part of the aquifer system.

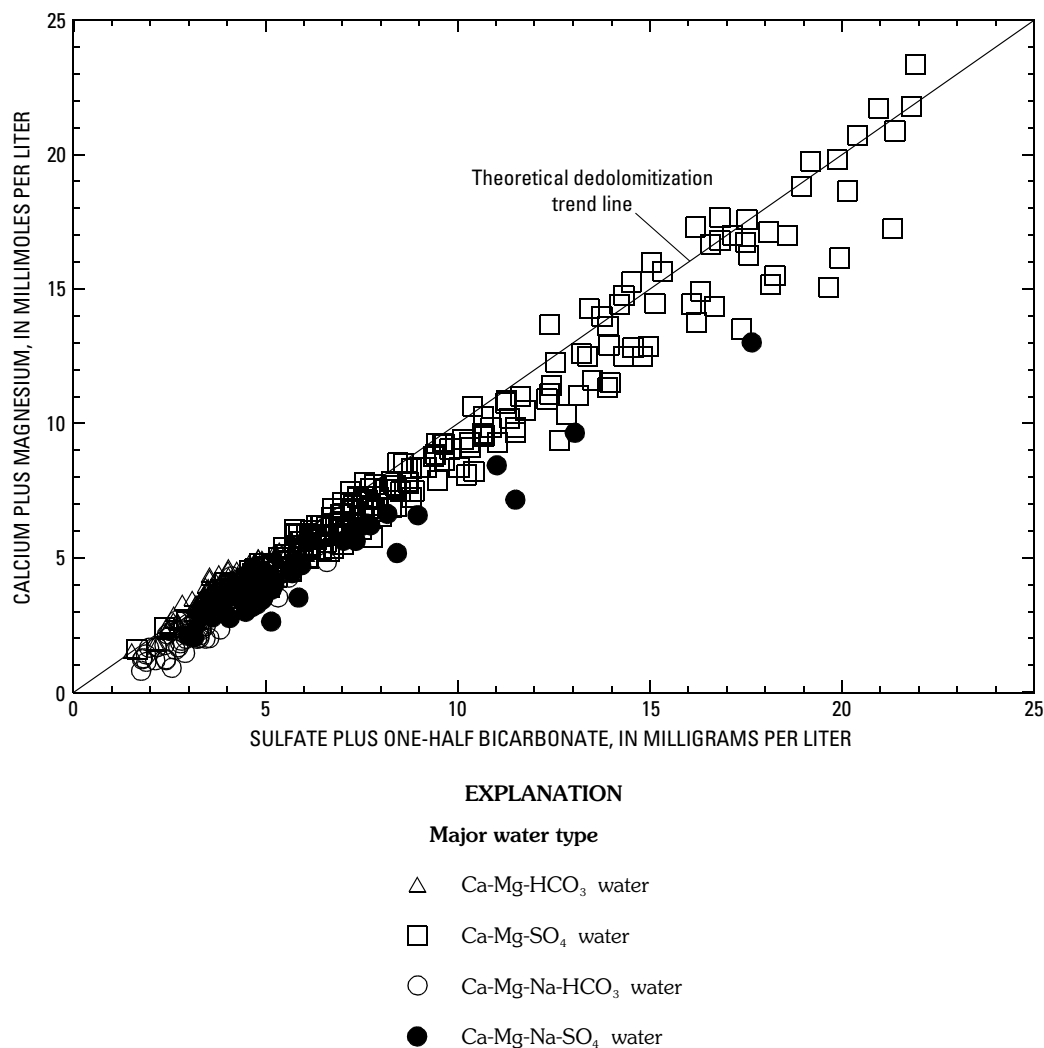


FIGURE 43.—Concentration of calcium plus magnesium as a function of concentration of sulfate plus one-half bicarbonate in ground water from the carbonate-rock aquifer in the Midwestern Basins and Arches aquifer system.

The mineralogy of the carbonate rocks indicates that gypsum and pyrite both are present in the northeastern part of the aquifer system. Gypsum beds as thick as 5.5 ft are present at or just below land surface in the rocks of the Salina Group in the Sandusky Bay area of northwestern Ohio (Carlson, 1991). Lesser quantities of gypsum are also found in carbonate rocks of Silurian and Devonian age throughout the northeastern part of the aquifer system. Pyrite is present in the Findlay Arch mineral district as defined by Carlson (1991) and is associated with a suite of ore minerals that includes celestite, fluorite, sphalerite, and galena. The Findlay Arch mineral district forms a northeasterly trending belt that extends from the Ohio and Indiana State line south of the Maumee River to the islands in Lake Erie. Structural controls on the mineralization in the Findlay Arch mineral district appear to be the Findlay Arch and the Bowling Green Fault zone (Carlson, 1991). Sul-

fide minerals are present throughout the carbonate rocks in the Findlay Arch mineral district, but they are generally concentrated at or just below surfaces of past erosion and in collapsed solution cavities (Botoman and Stieglitz, 1978). Abundant pyrite and marcasite are found in the Columbus Limestone in south-central Ohio and in the Devonian shales along the entire east boundary between the carbonate rocks and the younger shales (Carlson, 1991). Gypsum and sulfide minerals also may be present in the glacial deposits because the mineral composition of tills in the study area consists of fragments of the local bedrock (Strobel and Faure, 1987).

The isotopic composition of sulfur in mineral and dissolved phases can be useful in distinguishing sources of sulfate to ground water and determining whether dedolomitization, driven by gypsum dissolution, or sulfide-mineral oxidation is the predominant geochemical reaction in the

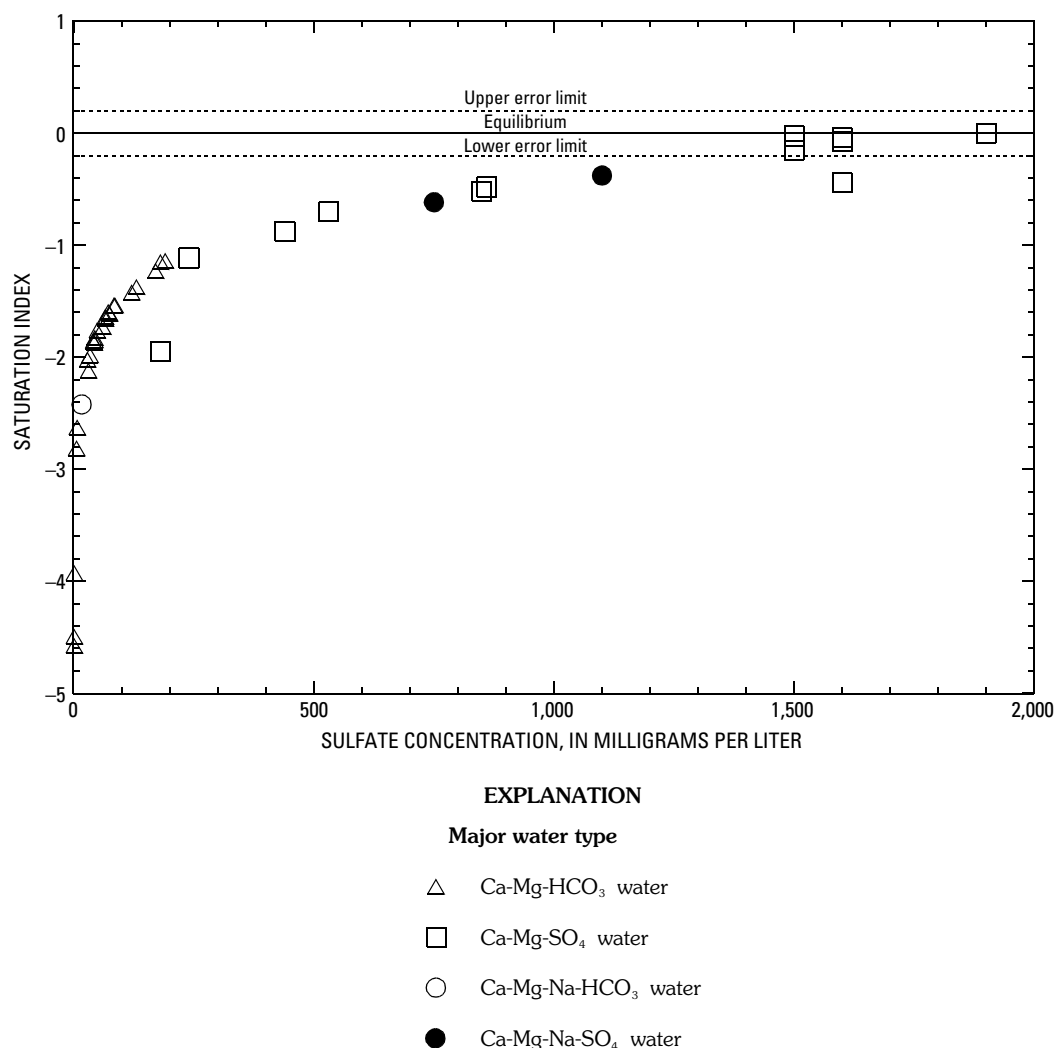


FIGURE 44.—Saturation indices of gypsum as a function of dissolved-sulfate concentration for water from wells in the Midwestern Basins and Arches aquifer system. (Error limits are due to analytical and thermodynamic data uncertainties. Points plotting within these lines are considered to be in equilibrium with gypsum.)

aquifer system (Pearson and Rightmire, 1980). The sulfur isotope data presented in tables 8 and 9 and discussed more fully in the section "Sulfur Isotopes" indicate that pyrite is the primary sulfate source for the glacial and carbonate-rock aquifers in most of the aquifer system; however, both pyrite and gypsum contribute sulfate to the Ca-Mg-SO₄-type ground water in the northeastern part of the aquifer system.

Deering and others (1988) noted that the chemistry of ground water in the carbonate-rock aquifer in northwestern Ohio is established chiefly by the mineralogy of the carbonate rocks. Other researchers (Norris and Fidler, 1973; Norris, 1974) have discussed the distribution of water types in western Ohio in the context of chemical evolution of bicarbonate-dominated water to sulfate-dominated water as ground water flows down the potentiometric gradient from the potentiometric high near the Bellefontaine Outlier to Lake Erie and to the Ohio River. The results of the ground-water flow model presented in the "Numerical Model" section, however, indicate that water in the aquifer system does not follow long, continuous paths from the highest potentiometric levels to Lake Erie or the Ohio River. Rather, ground-water recharge and discharge areas alternate across western Ohio. Thus, it is likely that the distribution of Ca-Mg-SO₄ water in the northeastern part of the aquifer system is primarily controlled by the mineralogy of the aquifer material.

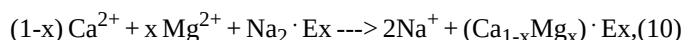
The relatively large area of Ca-Mg-HCO₃ water within the Ca-Mg-SO₄ facies in the carbonate-rock aquifer in northwestern Ohio corresponds to an area of thin or absent glacial deposits where the Lockport dolomite, a relatively pure dolomite (Janssens, 1977), crops out at the surface (fig. 5). The Ca-Mg-HCO₃ water also generally corresponds to areas of active ground-water recharge (fig. 28). Breen and Dumouchelle (1991) showed that, in northwestern Ohio, water in the carbonate-rock aquifer where the glacial deposits are thin or absent has tritium concentrations indicative of recharge since the 1950's. Thus, active ground-water flushing favors the formation of Ca-Mg-HCO₃ water in the carbonate-rock aquifer in the northeastern part of the study area where it is at or near the surface and recharge to the aquifer system occurs.

SODIUM-ENRICHED WATER

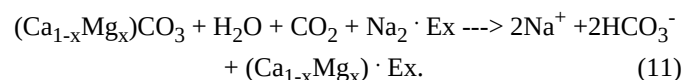
Multiple-water-type facies described in the preceding section (figs. 37 and 38), are characterized by the presence of one or more of the following ground-water types: Ca-Mg-Na-HCO₃, Ca-Mg-Na-SO₄, and Na-HCO₃. Many researchers have shown that an increase in sodium concentration in ground water without an associated increase in chloride can be caused by cation exchange of Ca²⁺ and Mg²⁺ ions for Na⁺ ions on clay minerals (Foster, 1950; Back, 1966; Freeze and Cherry, 1979; Thorstenson and others, 1979; Chapelle and Knobel, 1983). In an aquifer system with abundant carbonate

minerals, cation exchange may be accompanied by the dissolution of calcite and dolomite.

Na-HCO₃ water can be produced from Ca-Mg-HCO₃ waters by cation exchange on clay minerals according to the reaction:



where $0 \leq x \leq 1$. By combining reactions 4, 5, and 10, the overall stoichiometry of dissolution of calcite and dolomite and cation exchange may be represented as:



As Ca²⁺ and Mg²⁺ are removed from solution and are replaced with Na⁺ by cation exchange, the solution becomes undersaturated with respect to calcite and dolomite. The carbonate minerals dissolve, providing more Ca²⁺ and Mg²⁺ in solution to exchange with Na⁺ and causing HCO₃⁻ concentrations to increase. The Ca-Mg-Na-HCO₃ water in figures 39 and 40 plots below the line predicted by the dolomite-dissolution model; this pattern, which indicates that the water is enriched in bicarbonate and depleted in calcium and magnesium relative to the dolomite dissolution model, is consistent with cation-exchange reactions. Ca-Mg-Na-SO₄ water is associated with Ca-Mg-SO₄ water in the glacial and carbonate-rock aquifers and is likely formed by the mixing of Na-HCO₃ and Ca-Mg-SO₄ waters or incomplete cation exchange of the Ca-Mg-SO₄ waters. The Ca-Mg-Na-SO₄ water does not plot with the Ca-Mg-Na-HCO₃ water in figures 39 and 40 because of the additional calcium and magnesium from dedolomitization (7) or sulfuric acid neutralization (9).

Eberts and others (1990) and Lesney (1992) describe the presence of water ranging in composition from Ca-Mg-Na-HCO₃ to Na-HCO₃ in bedrock units underlying shales and siltstones of Mississippian age in northeastern Ohio. Their research attributes this chemistry to mixing of Na-HCO₃ water, produced by cation exchange in the shales and siltstones, with water in the underlying aquifers. A similar water composition of Ca-Mg-Na-HCO₃ to Na-HCO₃ is present in the carbonate-rock aquifer in the Midwestern Basins and Arches aquifer system where the carbonate-rock aquifer is overlain by Devonian shales (upper confining unit) along the margins of the Michigan Basin. This similarity indicates that Na- and HCO₃-enriched water produced by cation exchange in the shales is mixing with water in the underlying carbonate-rock aquifer. However, significant areas of Ca-Mg-Na-HCO₃ water, associated with some Na-HCO₃ water, are present in the carbonate-rock aquifer and the glacial aquifers where shales do not overlie the carbonate-rock aquifer south of the boundary between the aquifer and the upper confining unit. If Na-HCO₃ water from the upper confining unit is the source of Na-enriched water south of this boundary, then it

must have flowed in an updip direction out of the shales and into the adjacent carbonate-rock aquifer and associated glacial deposits.

Research on regional aquifers in the northern Midwest (Siegel and Mandle, 1984; Siegel, 1989, 1991) suggests a mechanism by which Na-HCO_3 water produced by cation exchange in the shales at the margin of the Michigan Basin may have moved into the carbonate-rock aquifer. On the basis of distributions of solutes and isotopes in water from the Cambrian-Ordovician aquifer in eastern Wisconsin, Siegel (1989, 1991) proposed that loading of glacial ice during Pleistocene glaciation may have reversed ground-water flow gradients and caused ground water from within the Michigan Basin to discharge at the west margin of the Michigan Basin in eastern Wisconsin. A numerical model that simulated ground-water flow during Late Wisconsinan glaciation in northern Illinois (Filley, 1985) showed that increased pore pressures may have caused water from within the Michigan Basin to discharge at the basin margins. Panno and Bourcier (1990) proposed that the formation of karst features in carbonate rocks adjacent to the Appalachian, Michigan, and Illinois Basins was caused by mixing of ground water and deep-basin saline water that was flushed from the basins during Pleistocene glaciation. A similar flow of ground water out of the Michigan Basin during the Pleistocene may have occurred at its southern margin, pushing through the Devonian shales and emplacing Na-HCO_3 water in the carbonate-rock aquifer and overlying glacial aquifers.

An alternative hypothesis for the presence of multiple-water-type facies along the northern boundary of the carbonate-rock aquifer and upper confining unit is cation exchange within the glacial and carbonate-rock aquifers. Some bedrock units within the Salina Group and carbonate rocks of Devonian age in northern Indiana and northwestern Ohio contain numerous thin shales (Janssens, 1977; Turner, 1977; Doheny and others, 1975). Cation exchange within these shale-rich carbonate rocks may result in the formation of Na-enriched water. Mazor and others (1993) suggest that significant differences in water composition in an area indicate that water may be stored in distinct pockets within an aquifer and that such pockets are caused by changes in lithology. Thus, the presence of multiple-water-type facies may be the result of a transitional bedrock lithology in the aquifer along the subcrop boundaries.

The Ca-Mg-Na-HCO_3 water found along the west subcrop boundary of the carbonate-rock aquifer is not associated with Na-HCO_3 water, nor is it as enriched in sodium as the Ca-Mg-Na-HCO_3 water along the north subcrop boundary of the carbonate-rock aquifer. The Ca-Mg-Na-HCO_3 water found in the carbonate-rock aquifer beyond the west boundary of the carbonate-rock aquifer and upper confining unit increases in chloride concentration in a downdip direction and most likely results from mixing of Ca-Mg-HCO_3 water with Na-Cl water from the Illinois Basin.

The multiple-water-type facies in the glacial aquifers in the south-central part of the study area is associated with the area where Ordovician shales and limestones (the upper weathered zone water-bearing unit) directly underlie the glacial deposits. Most of the water in this facies is the Ca-Mg-HCO_3 type; however, some ground water that is enriched in sodium or chloride or both is present in this area. Research on glacial buried-valley aquifers in the Great Miami River Valley (Dumouchelle and others, 1993) indicates two potential sources of sodium and chloride to the glacial aquifers. In the Great Miami River Valley, shallow ground water in highly permeable outwash valleys contains elevated concentrations of sodium and chloride that are related to human activities. Moreover, small amounts of moderately saline Na-Cl water discharges from the shale bedrock to the glacial aquifers in the Great Miami River Valley. Thus, sodium and chloride from both sources may be affecting the chemistry of water in the glacial aquifers in the south-central part of the aquifer system.

Water with elevated percentages of sodium and chloride is also present in the carbonate-rock aquifer where it is not overlain by the upper confining unit. Na-Cl or Cl-influenced ground water is uncommon in the carbonate-rock aquifer; most of the few areas of such water are within the multiple-water-type facies that borders the Michigan Basin. Possible sources of sodium and chloride to these ground waters include the dissolution of halite from the carbonate rocks, mixing with small amounts of formation brine from deeper bedrock units, or surface contamination by water affected by road-deicing salts or formation brine associated with petroleum exploration and production activities (Breen and Dumouchelle, 1991). The presence of Na-Cl water in the carbonate-rock aquifer along the margin of the Michigan Basin may also be related to the hydrodynamic displacement of brine by Pleistocene glaciation.

In summary, the exact geochemical and hydrologic processes responsible for the multiple-water-type facies are unknown, especially along the north boundary of the Midwestern Basins and Arches aquifer system. The distribution of water types in the multiple-water-type facies however, is clearly related to the change in lithology, from carbonate rocks to shales, at the boundaries of the carbonate-rock aquifer. The multiple-water-type facies along the margin of the Michigan Basin may also be related to changes in the ground-water flow regime during Pleistocene glaciation.

SODIUM-CHLORIDE AND CALCIUM-SODIUM-CHLORIDE WATER

Na-Cl type water with dissolved-solids concentrations less than 10,000 mg/L is present in the carbonate-rock aquifer beneath the upper confining unit at the margins of the structural basins. Its presence likely results from mixing of fresh water with brines from within the basins. Processes responsible for the chemistry of brines in the Illinois, Michi-

gan, and Appalachian Basins are complex (Stueber and others, 1987; Lowry and others, 1988; Walter and others, 1990; Stueber and Walter, 1991; Stueber and others, 1993; Wilson and Long, 1993a, b) and are beyond the scope of this report. Na-Cl, Na-Ca-Cl and Ca-Na-Cl type waters with dissolved-solids concentrations greater than 10,000 mg/L are present just beyond the boundary between the carbonate-rock aquifer and the upper confining unit in the Michigan and Appalachian Basins, an indication that the upper confining unit prevents water from recharging the carbonate-rock aquifer in these areas. The presence of water with dissolved-solids concentrations less than 10,000 mg/L in the Illinois Basin more than 70 mi downdip from the boundary of the carbonate-rock aquifer and the upper confining unit may be related to present or past patterns of flow in the carbonate-rock aquifer. Results of the regional ground-water flow model show that a small percentage of water may flow from the subcrop area down into the Illinois Basin. Such water could contribute to the current distribution of solutes. Other research on Illinois Basin brines (Clayton and others, 1966; Rupp and Pennington, 1987; Stueber and Walter, 1991) suggests that dilution of the brines may have occurred as a result of increased infiltration through fracture systems in the carbonate rocks or from meltwater that recharged the carbonate-rock aquifer during the Pleistocene. The origin of low dissolved-solids water deep in the Illinois Basin is uncertain, and more research would be needed for a full understanding of this part of the aquifer system.

INSIGHTS INTO REGIONAL FLOW PROVIDED BY GEOCHEMICAL DATA

Ground-water samples were collected from the glacial and carbonate-rock aquifers along four general directions of regional ground-water flow, as determined from the potentiometric surface map of the carbonate-rock aquifer (fig. 12). The locations of the sampling points are shown in figure 32. The data are listed in tables 7 and 8. Although the regional ground-water flow model indicates that ground water in the Midwestern Basins and Arches aquifer system does not follow long paths from the highest regional potentiometric levels to the lowest regional potentiometric levels, it is useful to evaluate the differences in ground-water chemistry along the general directions of regional ground-water flow.

MAJOR SOLUTES

Dissolved-solids and sulfate concentrations have been used as indicators of chemical evolution of ground water in various regional-scale carbonate-rock aquifers, such as the Floridan aquifer in Florida, the Edwards aquifer in Texas, and the Madison aquifer in parts of Montana, South Dakota and Wyoming (Plummer, 1977; Rye and others, 1981; and Busby and others, 1991). In these aquifers, concentrations of dis-

solved solids and sulfate generally increase along the principal directions of regional ground-water flow. Figures 45 and 46 show dissolved-solids and sulfate concentrations along geochemical sections A-A', B-B', C-C' and D-D' in the Midwestern Basins and Arches aquifer system. In general, no consistent systematic change in dissolved-solids and sulfate concentrations is evident along the geochemical sections. The deep bedrock wells along section C-C' are the only subset of the data indicating consistent increases in dissolved-solids and sulfate concentrations in the direction of regional flow. This general absence of systematic trends in chemistry along the general directions of regional ground-water flow indicates that the aquifer system is not characterized by long flow paths that are isolated from additions of recharge, as have been postulated for regional carbonate-rock aquifers in other parts of the United States.

Figures 45 and 46 also can be used to compare the chemistry of ground water from the glacial aquifers and the carbonate-rock aquifer. In general, dissolved-solids and sulfate concentrations in the glacial and carbonate-rock aquifers are similar. The only notable exception to this is sample 10G (fig. 32) from a glacial aquifer, which has considerably higher dissolved-solids and sulfate concentrations than samples 10S and 10D from the carbonate-rock aquifer.

In addition, figures 45 and 46 show the relation of chemistry between ground water from the shallow bedrock wells and ground water from the deep bedrock wells. In general, the dissolved-solids and sulfate concentrations in ground water from shallow bedrock wells were similar to those in ground water from deep bedrock wells. The exceptions are wells 4S and 4D and wells 14S and 14D. Of all the wells shown in figure 32, the wells that show the largest variations in ground-water chemistry with aquifer type or depth at a single sampling location (well groups 4, 10, and 14) are in the groups that have the greatest distance between the wells. Apparent variations with depth may be more related to spatial variability than to specific differences with depth.

ISOTOPES

Interpretation of isotopic data can often provide more insight into chemical and hydrologic processes than can be provided by interpretation of chemical data alone. The isotopic composition of ground water can be used to distinguish between competing reactions that contribute dissolved sulfur and carbon to water, to examine the possibility of different water masses mixing in an aquifer, and to estimate the relative or absolute ages of ground water in different parts of an aquifer system. Consequently, isotopic data can provide an independent confirmation of the interpretations made from the hydrologic and chemical data.

In this investigation, the stable isotopes $\delta^{34}\text{S}$ (for the sulfate and sulfide phases), $\delta^{18}\text{O}$, δD , $\delta^{13}\text{C}$ and the radioactive isotopes ^{14}C and tritium were measured in ground water

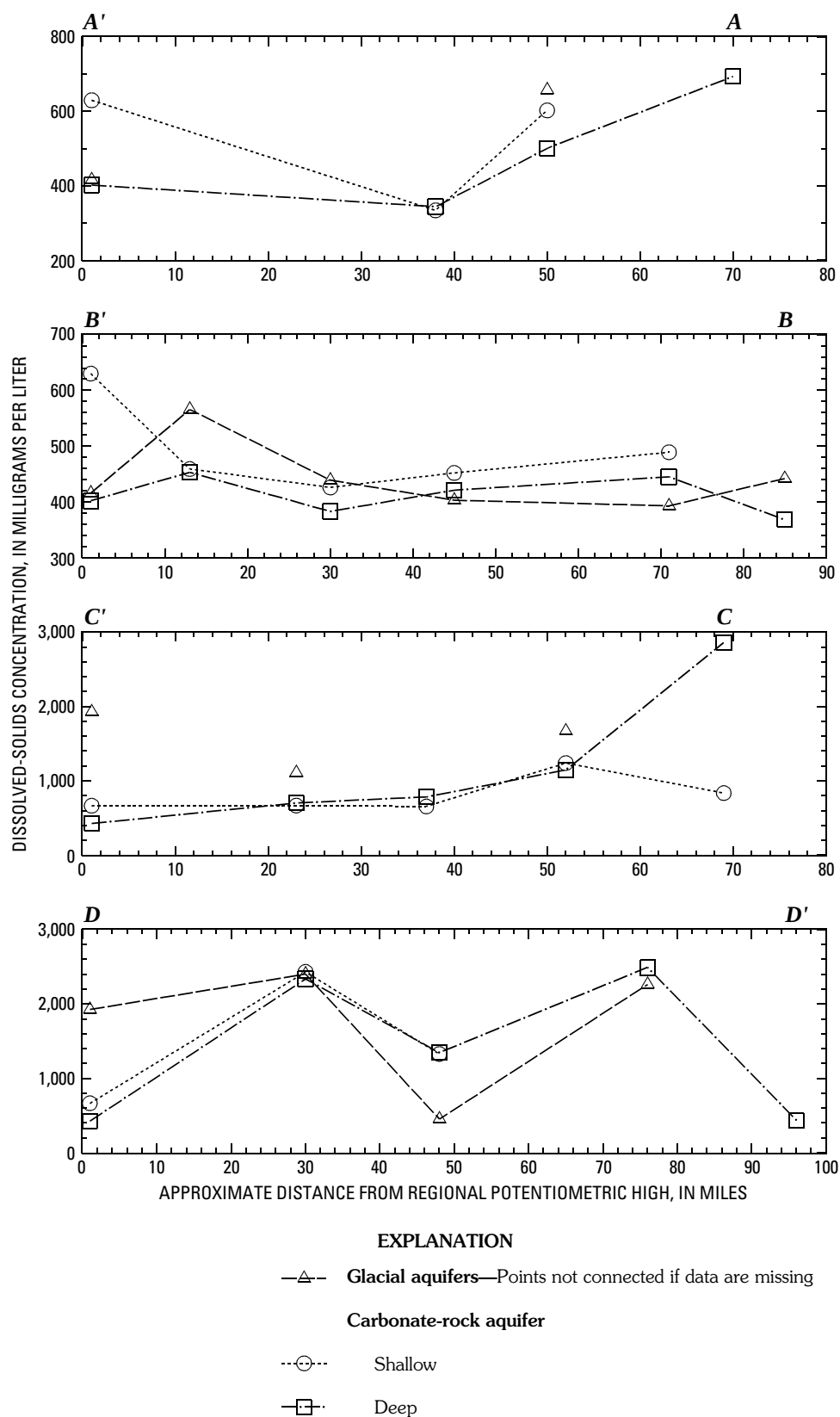


FIGURE 45.—Dissolved-solids concentration in water from wells in the Midwestern Basins and Arches aquifer system along geochemical sections A-A', B-B', C-C', and D-D' (locations of wells shown in fig. 32).

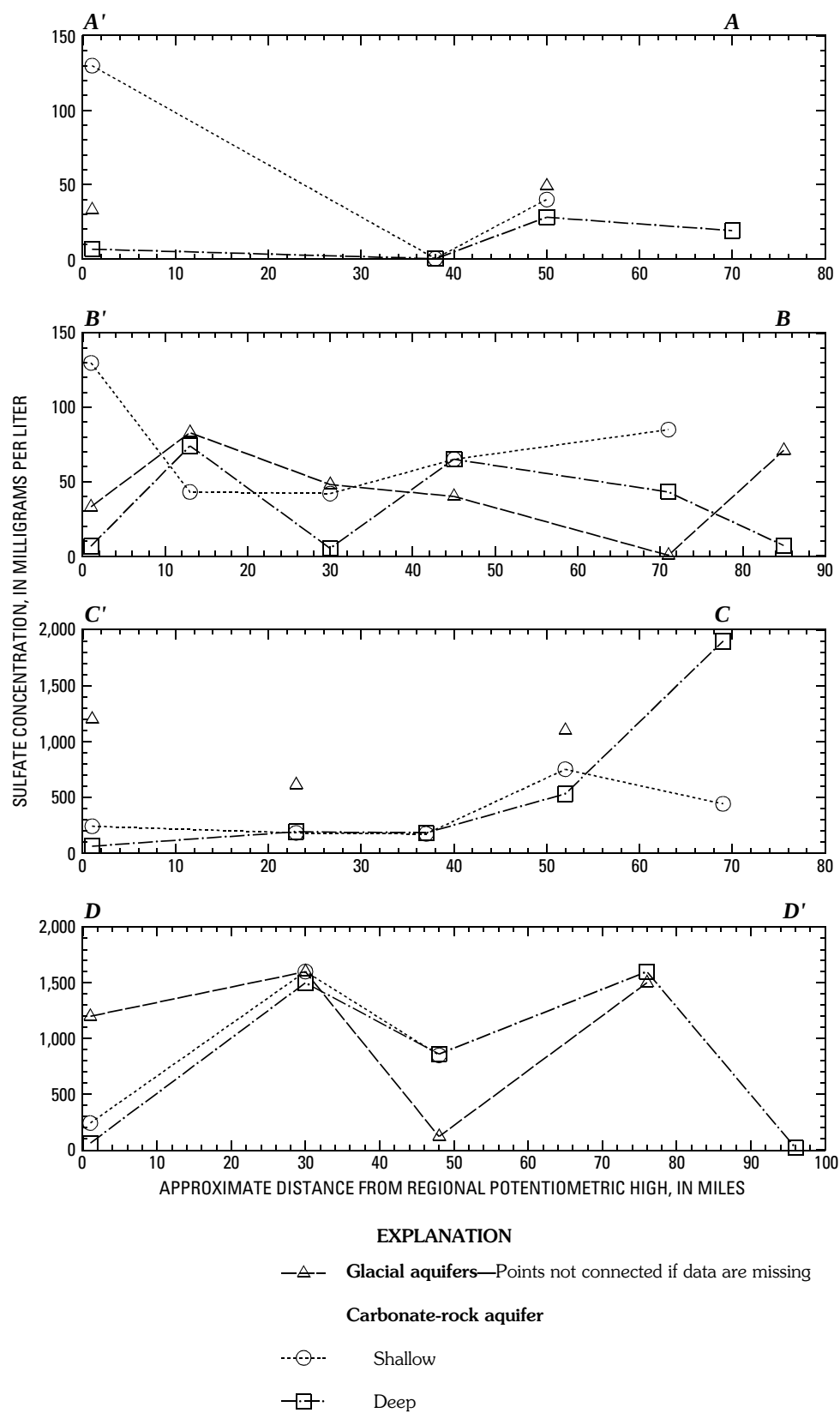


FIGURE 46.—Sulfate concentration in water from wells in the Midwestern Basins and Arches aquifer system along geochemical sections A-A', B-B', C-C', and D-D' (locations of wells shown in fig. 32).

along the four selected directions of regional ground-water flow. In addition, $\delta^{34}\text{S}$ (for the sulfate and sulfide phases) and $\delta^{13}\text{C}$ values for aquifer material, including glacial deposits and carbonate rocks, were determined at several locations within the study area. The isotopic data are summarized in tables 8 and 9 and are discussed in the sections that follow.

SULFUR ISOTOPES

Aquifer-material and ground-water samples were analyzed for sulfur isotopes to determine the origin of dissolved sulfate and sulfide and to assist in the identification of the geochemical processes that affect ground-water chemistry in the Midwestern Basins and Arches aquifer system. Because various geochemical processes such as sulfate reduction or dedolomitization can affect the ground-water ages calculated from the carbon isotope data, as well as the associated interpretations made about regional ground-water flow, it is important to be able to distinguish the sources of sulfur in the ground water.

The most abundant sulfur-containing minerals in the study area include pyrite and, in the northeastern part of the area, gypsum. Sedimentary sulfide minerals such as pyrite can exhibit a wide range in $\delta^{34}\text{S}$ values, from -70 to +70 per mil; however, $\delta^{34}\text{S}$ normally ranges from -30 to 10 per mil (Ohmoto and Rye, 1979). In gypsum derived from marine evaporites, $\delta^{34}\text{S}$ values reflect the isotopic composition of dissolved sulfate in the ocean at the time that the gypsum was deposited. Gypsum of Silurian and Devonian age has $\delta^{34}\text{S}$ values that range from about +16 to +30 per mil (Holser and Kaplan, 1966; Krouse, 1980).

Because such a wide range of $\delta^{34}\text{S}$ values is possible for sources of sulfur, samples of aquifer material, including glacial deposits and carbonate rocks, and samples of pyrite and gypsum from the carbonate rocks were analyzed for $\delta^{34}\text{S}$ of the sulfate and sulfide fractions to constrain the variability in sulfur isotope values of the aquifer material. The data are shown in table 9, along with sulfur isotope data on pyrite and anhydrite samples from Ohio first given in Botoman and Faure (1976).

The $\delta^{34}\text{S}_{(\text{sulfate})}$ values for gypsum and anhydrite samples, 28.7 per mil and 24.9 per mil, are in close agreement with those expected for marine sulfates of Silurian and Devonian age. The $\delta^{34}\text{S}_{(\text{sulfide})}$ values of the pyrite samples, -21.9 per mil, -19.4 per mil, and 7.0 per mil, fall within the expected range for sedimentary sulfides. Organic sulfur, which has $\delta^{34}\text{S}_{(\text{sulfide})}$ values similar to those of pyrite, was not specifically analyzed for, but it may be an additional source of reduced sulfur in the aquifer system.

The $\delta^{34}\text{S}_{(\text{sulfate})}$ values for the glacial deposits fall within a fairly narrow range, from -14.8 to -8.2 per mil, which is nearly identical to the range in $\delta^{34}\text{S}_{(\text{sulfide})}$ values for the same material, -14.0 to -8.0 per mil. These $\delta^{34}\text{S}_{(\text{sulfide})}$ values are within the same range as the $\delta^{34}\text{S}_{(\text{sulfide})}$ values deter-

mined for the pyrite samples collected in the area and indicate that pyrite is a likely source of solid-phase sulfide in the glacial deposits. A likely explanation for the similarity in the $\delta^{34}\text{S}_{(\text{sulfate})}$ and $\delta^{34}\text{S}_{(\text{sulfide})}$ values for the glacial deposits is that sulfide (pyrite) in the glacial deposits oxidized to sulfate and, in the presence of dissolved calcium from the dissolution of carbonate minerals, precipitated as gypsum. This process has been shown to occur in the tills of the Interior Plains Region in Canada (Hendry and others, 1986; Keller and Van Der Kamp, 1988). These researchers based their conclusions on the similarity in sulfur isotope values between reduced organic sulfur in unoxidized tills and the sulfate from gypsum crystals found in the oxidized tills. They suggest that a large-scale lowering of the water table during an extended dry climatic episode in western North America from 11,000 to 3,000 years before present produced geochemical changes in the till that resulted in the formation of the gypsum and the subsequent development of fractures in the oxidized till. Similar secondary gypsum has also been found in glacial deposits near the Great Lakes. Desaulniers and others (1981) note that secondary gypsum usually is found in fractures of clayey tills and glaciolacustrine clays in southwestern Ontario near Lake Erie. Authigenic gypsum crystals have been found in lacustrine clays within Wisconsinan glacial deposits in northeastern Ohio (Carlson, 1991). Possible gypsum crystallization has been noted by Strobel (1990) along fractures in clayey till in northwestern Ohio. Therefore, given the similarity in $\delta^{34}\text{S}_{(\text{sulfate})}$ and $\delta^{34}\text{S}_{(\text{sulfide})}$ values in the glacial deposits in the Midwestern Basins and Arches aquifer system, processes similar to those in the Interior Plains Region of Canada may have resulted in the formation of gypsum in the glacial deposits with an isotopically light sulfur signature.

The $\delta^{34}\text{S}_{(\text{sulfate})}$ values of the carbonate rocks are highly variable. The $\delta^{34}\text{S}_{(\text{sulfate})}$ values of core C3 and various intervals of core C2 range from 18.3 to 28.7 per mil and clearly reflect sulfate from marine evaporates of Silurian and Devonian age. However, $\delta^{34}\text{S}_{(\text{sulfate})}$ values of all other samples of the carbonate rocks range from -2.3 to 14.6 per mil and do not indicate a clearly defined sulfur source. The wide range in $\delta^{34}\text{S}_{(\text{sulfate})}$ values of the carbonate rocks may reflect post-depositional processes, such as cementation, recrystallization, dolomitization, and weathering, that affected the carbonate rocks in the study area (Casey, 1994). The range in $\delta^{34}\text{S}_{(\text{sulfide})}$ values of the carbonate rocks, from -24.9 to 3.6 per mil, is consistent with the $\delta^{34}\text{S}_{(\text{sulfide})}$ values of the pyrite samples from the study area.

Sulfur isotope ratios in ground water in the Midwestern Basins and Arches aquifer system (fig. 47) are highly varied; $\delta^{34}\text{S}_{(\text{sulfate})}$ values range from -10.4 to +44.1 per mil, and $\delta^{34}\text{S}_{(\text{sulfide})}$ values range from -53.2 to -12.2 per mil. Variability in sulfur isotope values of the aquifer material is a major control on the distribution of sulfur isotope values in ground water from the aquifer system. For example, in the western part of the study area where little or no gypsum is contained

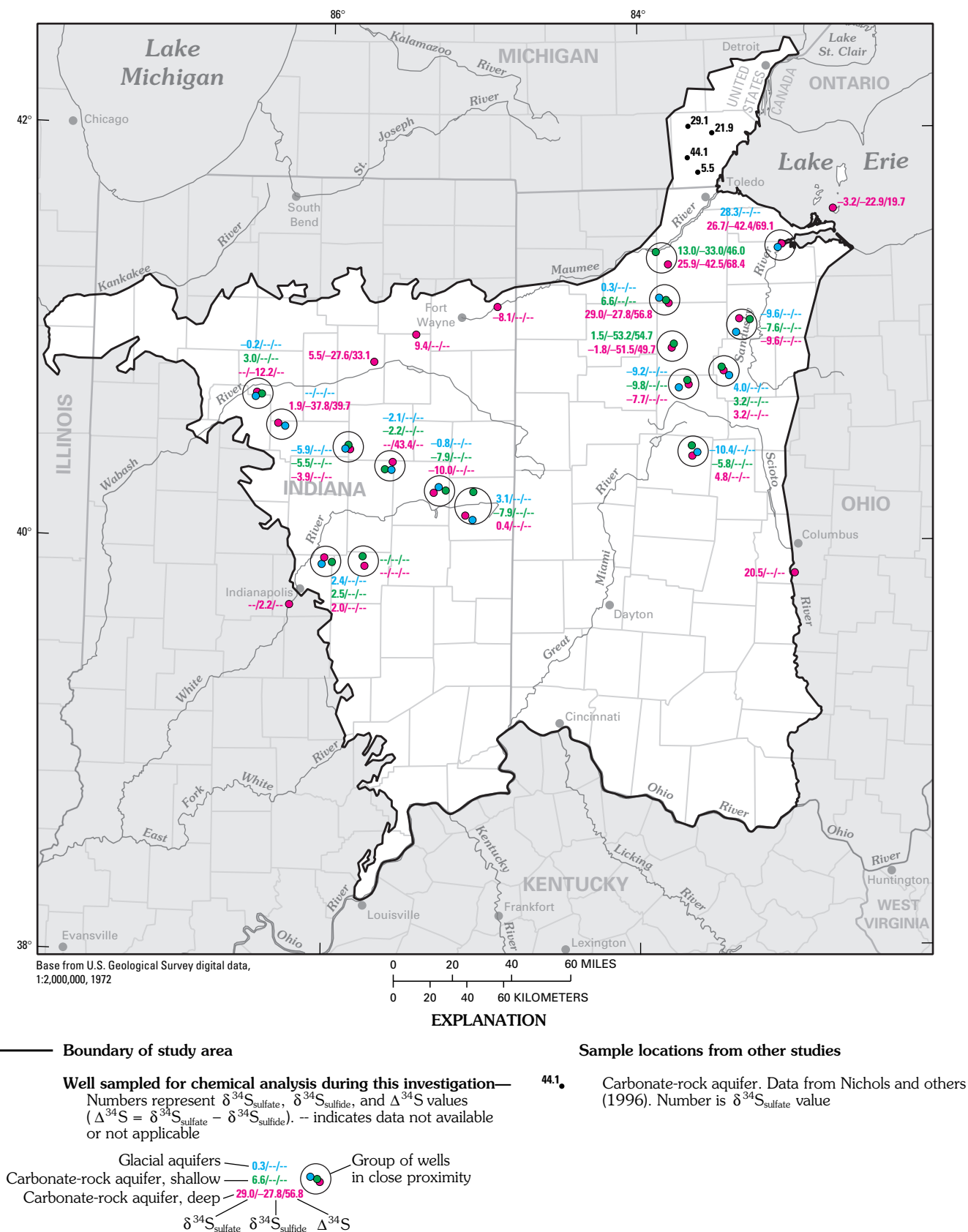
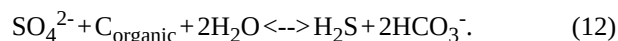


FIGURE 47.— $\delta^{34}\text{S}$ and $\Delta^{34}\text{S}$ values in water from wells in the Midwestern Basins and Arches aquifer system.

in the carbonate-rock aquifer, the highest $\delta^{34}\text{S}_{(\text{sulfate})}$ value in ground water is 9.4 per mil, an indication that the primary source of sulfate to ground water is from the oxidation of sulfide minerals or from the dissolution of gypsum formed by the oxidation of sulfide minerals. Ground water with $\delta^{34}\text{S}_{(\text{sulfate})}$ values consistent with the dissolution of marine gypsum or anhydrite of Silurian and Devonian age are found only in the northeastern part of the study area, coincident with the location of the only significant deposits of gypsum and anhydrite.

Sulfur isotope values in ground water reflect the $\delta^{34}\text{S}$ values of the sulfur source but are also dependent on chemical reactions that can cause isotopic fractionation. For example, sulfate reduction can affect the isotopic composition of dissolved sulfate in ground water. Sulfate reduction is mediated by bacteria, which reduce sulfate to sulfide and oxidize organic carbon to CO_2 under anaerobic conditions. The sulfate-reduction reaction can be written as



If the pH is greater than 7, HS^- will predominate over H_2S as the sulfide product (Garrels and Christ, 1990). Bacterial sulfate reduction preferentially incorporates ^{32}S into the sulfide product, causing the residual sulfate to be enriched in the heavier isotope, ^{34}S . Thus, as sulfate reduction progresses, $\delta^{34}\text{S}$ of sulfide will be less than that of sulfate, and $\delta^{34}\text{S}_{(\text{sulfate})}$ will increase relative to the original composition.

Bacterial sulfate reduction is the likely source of the dissolved sulfide in the Midwestern Basins and Arches aquifer system as indicated by the values of $\delta^{34}\text{S}_{(\text{sulfide})}$ in ground water from the aquifers, which range from -53.2 to -12.2 per mil (fig. 47). Sulfate reduction has probably produced the extensive areas of the carbonate-rock aquifer in northwestern Ohio that are characterized by dissolved sulfide concentrations exceeding 3.0 mg/L (Ohio Department of Natural Resources, 1970); sulfide concentrations as high as 70 mg/L were noted in this area. Dissolved sulfide is less abundant in other parts of the aquifer system.

The differences between the $\delta^{34}\text{S}_{(\text{sulfate})}$ values and the $\delta^{34}\text{S}_{(\text{sulfide})}$ values, Δ^{34} , are also shown in figure 47. The Δ^{34} values range from 19.7 to 69.1 per mil. The largest Δ^{34} values in the aquifer system, 69.1 and 68.4 per mil, were found for water from the deep bedrock wells near the Maumee River and Sandusky Bay. Equilibrium fractionation between sulfate and sulfide is estimated to be between 65 and 74 per mil (Pearson and Rightmire, 1980). Thus, the large Δ^{34} values in the northeastern part of the study area may indicate isotopic equilibrium between dissolved sulfate and sulfide. In addition, the large Δ^{34} values in ground water near the Maumee River and Sandusky Bay may indicate a long residence time in the aquifer; in the Floridan aquifer of central and southern Florida, for example, Δ^{34} values were reported to be directly related to ground-water residence time in the aquifer. In addi-

tion, the largest Δ^{34} values were found in the areas of the Floridan aquifer farthest from the recharge area (Rye and others, 1981).

The sulfur isotope data were also used to evaluate the processes responsible for the elevated concentrations of dissolved sulfate in much of the northeastern part of the study area. Ground waters with sulfate concentrations greater than 1,000 mg/L were found along geochemical sections C-C' and D-D'. These ground waters are saturated or nearly saturated with respect to gypsum, but their $\delta^{34}\text{S}_{(\text{sulfate})}$ values indicate several different sources of sulfate. The $\delta^{34}\text{S}_{(\text{sulfate})}$ values of 25.9, 26.7, and 28.3 per mil in ground water from wells 14D, 17D, and 17G (sulfate concentrations of 1,900, 1,600, and 1,500 mg/L, respectively) are consistent with the dissolution of Silurian-Devonian-age gypsum (or anhydrite). However, ground water with similar sulfate concentrations but $\delta^{34}\text{S}_{(\text{sulfate})}$ values that range from -10.4 to 4.0 per mil (wells 10G, 13G, 15G, 15S, and 15D) cannot be explained by the dissolution of Silurian-Devonian age gypsum (or anhydrite) but are consistent with pyrite as the sulfur source. The limit on the amount of sulfate that can be produced in ground water by pyrite oxidation (reaction 8) in a closed system is less than 25 mg/L owing to solubility constraints on dissolved-oxygen concentrations. Thus, closed-system pyrite oxidation could not generate the high sulfate concentrations that are found in the northeastern part of the aquifer system. Closed-system conditions are unlikely in much of the aquifer system, however, because the glacial aquifers are generally water-table aquifers, and the carbonate-rock aquifer is generally only semiconfined by the overlying glacial deposits. Thus, where pyrite is abundant in the glacial deposits, sulfate produced by the oxidation of pyrite (or other sources of reduced sulfur) in the glacial deposits may be continually added to the ground water as the water table rises and falls. Alternatively, high sulfate concentrations and isotopically light $\delta^{34}\text{S}_{(\text{sulfate})}$ values in ground water in the northeastern part of the aquifer system can be explained by the dissolution of gypsum composed of isotopically light sulfate, such has been noted in tills in Canada (Hendry and others, 1986; Keller and Van Der Kamp, 1988).

The sulfur isotope data include a wide range in sulfur isotope signatures of sulfur sources in the Midwestern Basins and Arches aquifer system. In addition, sulfur isotope values for ground water in the aquifer system are highly varied, and the geochemical and hydrological processes affecting sulfur isotope values are not completely understood. As a consequence, use of the sulfur isotope data to help constrain the possible mass balance reactions may not be particularly effective, and large uncertainties in the ^{14}C ages estimated for ground water in the aquifer system may result.

OXYGEN AND HYDROGEN ISOTOPES

Variation in the isotope ratios of $^{18}\text{O}/^{16}\text{O}$ and $^2\text{H}/^1\text{H}$ (deuterium/hydrogen) in meteoric water (water that originates in the Earth's atmosphere) results from a combination of physical and chemical processes that change the isotopic composition from that of seawater. By definition, the isotopic composition of seawater, Standard Mean Ocean Water (SMOW), is 0 per mil for both $\delta^{18}\text{O}$ and δD (Fritz and Fontes, 1980). Meteoric water is depleted in $\delta^{18}\text{O}$ and δD relative to seawater because of isotopic fractionation; the lighter isotopes, ^{16}O and ^1H , evaporate preferentially, whereas the heavier isotopes, ^{18}O and ^2H , are concentrated in seawater. The distribution of $\delta^{18}\text{O}$ and δD in modern precipitation is related to mean annual temperature and latitude (Dansgaard, 1964). Generally, a greater amount of fractionation takes place at colder temperatures than at warmer temperatures; hence, $\delta^{18}\text{O}$ and δD values decrease with a decrease in temperature, which corresponds to an increase in latitude or altitude. This covariance of $\delta^{18}\text{O}$ and δD is reflected by the composition of meteoric water throughout the world and defines an average meteoric water line (Craig, 1961) defined as

$$\delta\text{D} = 8\delta^{18}\text{O} + 10. \quad (13)$$

Ground water recharged under present-day climatic conditions should have an isotopic composition similar to that of present-day meteoric water. However, if ground water was recharged during a colder climate, its isotopic composition should be lighter than that of present-day precipitation but should still plot on the meteoric water line.

Values for the stable isotopes of oxygen and hydrogen in ground water samples that were collected as part of this investigation are listed in table 8; $\delta^{18}\text{O}$ values are shown spatially in figure 48. All the data plot on or slightly above the meteoric water line (fig. 49), an indication that the ground water in the Midwestern Basins and Arches aquifer system originated as atmospheric precipitation. Surface-water samples collected at U.S. Geological Survey Benchmark Stations in Indiana, Michigan and Ohio (Tyler Coplen, U.S. Geological Survey, written commun., 1992) were used to determine the isotopic composition of present-day recharge in the area. Most of the ground water in the aquifer system has an isotopic composition similar to surface water in the study area and therefore was most likely recharged under similar climatic conditions as the present. A few ground-water samples collected from the northeastern part of the study area are isotopically light relative to the rest of the ground-water samples and present-day recharge. These relatively light waters probably recharged the aquifer system during a climate colder than the present.

Ground water with isotopically light $\delta^{18}\text{O}$ values may represent either water that recharged aquifers beneath Wisconsinan-age ice sheets or meltwater from those ice sheets.

Estimates of the $\delta^{18}\text{O}$ value of Wisconsinan-age ice sheets range from -20 to -12 per mil (Yapp and Epstein, 1977; Desaulniers and others, 1981). Isotopically light ground water in areas around the Great Lakes has been previously found in east-central Michigan near Lake Michigan (Long and others, 1988) and southwestern Ontario near Lake Erie (Desaulniers and others, 1981; Clayton and others, 1966). The $\delta^{18}\text{O}$ values from these studies range from -18.5 to -7 per mil in Michigan and -17 to -9 per mil in southwestern Ontario.

The areas of isotopically light ground water in the Midwestern Basins and Arches aquifer system and in the areas discussed above are all associated with lowlands that were once occupied by late Wisconsinan glacial lakes (Wayne and Zumbege, 1965). The glacial deposits in these areas are typically lacustrine clays or clay-rich tills derived from the lacustrine sediments. The presence of clay-rich deposits in the areas once occupied by glacial lakes may inhibit ground-water recharge. In addition, glaciolacustrine clays in areas close to the Great Lakes are typically found near the base level of the various aquifer systems and are generally coincident with regional ground-water discharge areas. Vertical ground-water flow velocities through glaciolacustrine clays and clayey tills in southwestern Ontario (Desaulniers and others, 1981) were determined to be on the order of 40 to 80 ft in 10,000 years. Pore waters in these deposits exhibit a distinct regular shift in $\delta^{18}\text{O}$ values with depth from $\delta^{18}\text{O}$ values characteristic of present-day recharge at the water table to values between -14 to -17 per mil at depths of 60 to 100 ft. A similar decrease in $\delta^{18}\text{O}$ values with depth is seen in the Midwestern Basins and Arches aquifer system in well groups 13 and 14 and in the data presented by de Roche and Breen (1989). This decrease indicates that a lack of substantial recharge has likely preserved Pleistocene-age water in deeper parts of the aquifer system beneath the Maumee River Basin.

TRITIUM AND CARBON ISOTOPES

Tritium (^3H) and carbon-14 (^{14}C) are radioactive isotopes whose concentrations in ground water can be used as a guide to ground-water age. Estimated ground-water ages can help validate or refute interpretations made about ground-water flow based on other chemical and isotopic data or results of ground-water-flow modeling.

Because large quantities of tritium were introduced into the atmosphere during atmospheric testing of nuclear bombs from 1953 to the mid-1960's, tritium is a useful indicator of post-1953 recharge to ground water. Tritium concentrations in precipitation peaked at several thousand tritium units (TU; 1 TU is equal to 1 tritium atom in 10^{18} hydrogen atoms or 3.24 picocuries per liter, pCi/L) during 1963-64 (Michel, 1989). Since the signing of the nuclear test ban treaty in the late 1960's, tritium concentrations in present-day precipitation have been decreasing to the pre-bomb levels of 2 to 8 tri-

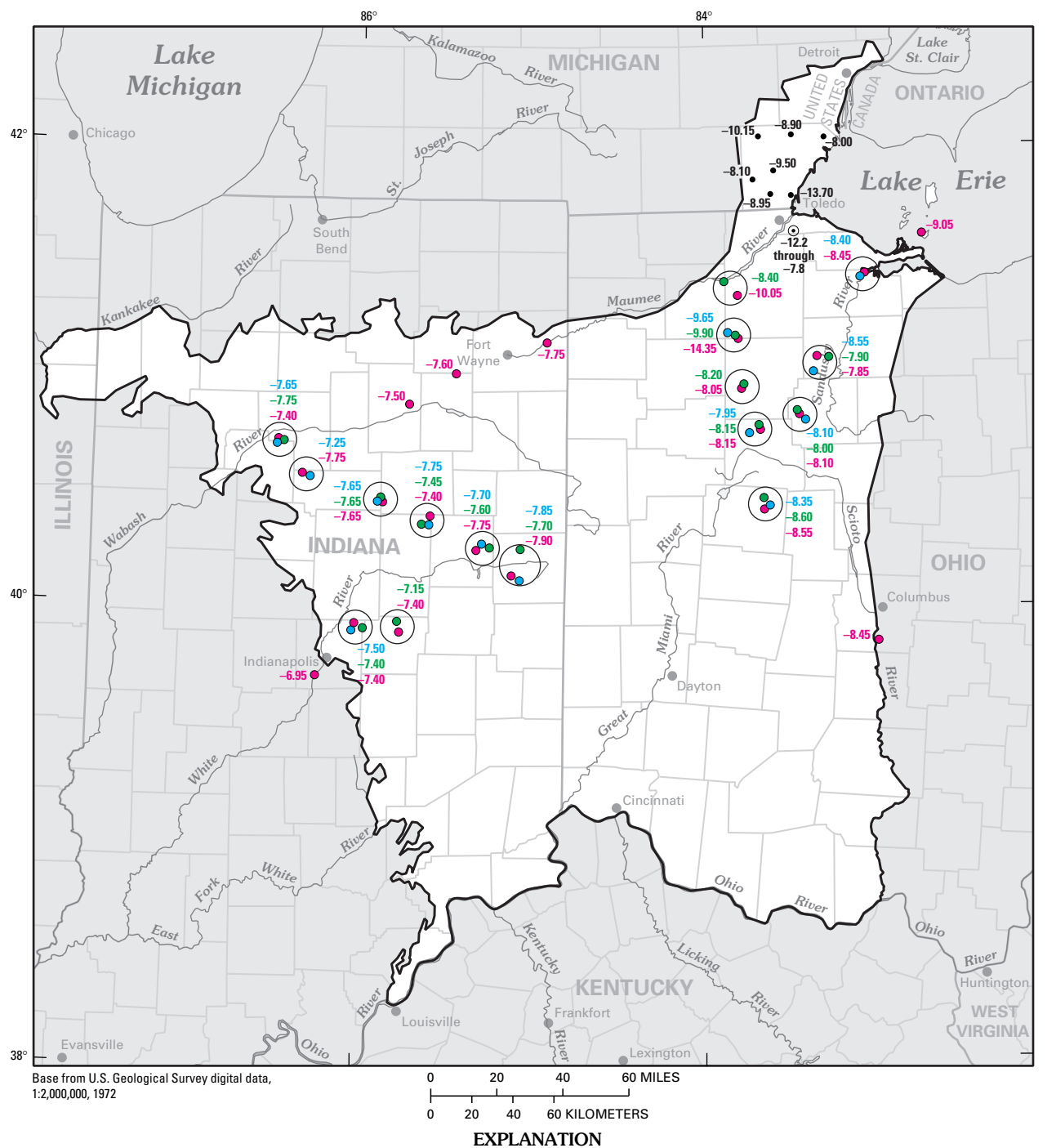


FIGURE 48.— $\delta^{18}\text{O}$ values in water from wells in the Midwestern Basins and Arches aquifer system.

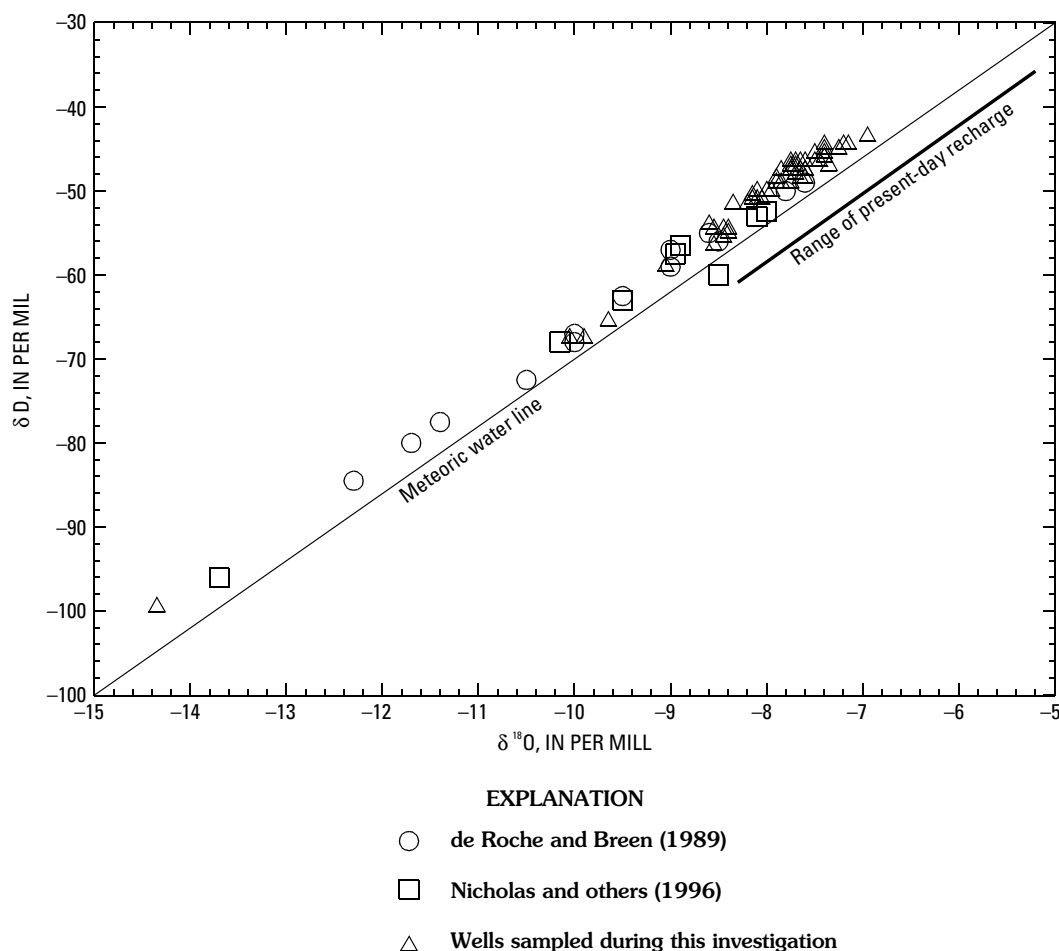


FIGURE 49.— $\delta^{18}\text{O}$ - δD relation for ground water in the Midwestern Basins and Arches aquifer system. (Other sources of data include de Roche and Breen [1989], and Nicholas and others [1996]).

tium units estimated by Thatcher (1962). Ground water derived exclusively from pre-bomb precipitation would have a maximum tritium concentration of 0.8 TU by the early 1990's if the maximum pre-bomb estimate of 8 TU in atmospheric precipitation is used (Plummer and others, 1993). For ground water with tritium concentrations greater than 0.8, some fraction of that water must have recharged the aquifer system since 1953.

Tritium concentrations for waters sampled as part of this investigation are listed in table 8 and shown spatially in figure 50. Ground water with tritium concentrations greater than 0.8 TU are found across most of the study area and indicate that post-1953 recharge has entered the aquifers in many parts of the Midwestern Basins and Arches aquifer system. Tritium concentrations vary somewhat predictably with depth; water from about half of the glacial and shallow bedrock wells has tritium concentrations greater than 0.8 TU, whereas only one-third of the deep bedrock wells produce tritiated water. Tritium concentrations are also spatially varied in the aquifer system. Ground water with tritium concentrations greater

than 0.8 TU is found in at least one well at nearly all sample locations; however, no ground-water samples from well groups 13, 14, 16, and 17 in the Maumee and Sandusky River Basins, including the wells completed in glacial aquifers, contain tritium. Breen and Dumouchelle (1991) determined that areas of the carbonate-rock aquifer in northwestern Ohio with tritium concentrations indicative of post-1953 recharge (fig. 50) are more likely to be found where the glacial deposits are absent or are less than 20 ft thick. A similar relation between tritium concentrations in ground water from the carbonate-rock aquifer and the thickness of the overlying glacial deposits is apparent in southeastern Michigan (Nicholas and others, 1996). This relation between tritium concentrations and thickness of glacial deposits is not apparent over the entire study area; the thickness of the overlying glacial deposits for wells producing water with tritium concentrations greater than 0.8 TU ranges from 6 to 160 ft. The thickness of the overlying glacial deposits for wells producing water with the highest tritium concentrations (greater than 15 TU) ranges from about 40 to 160 ft.

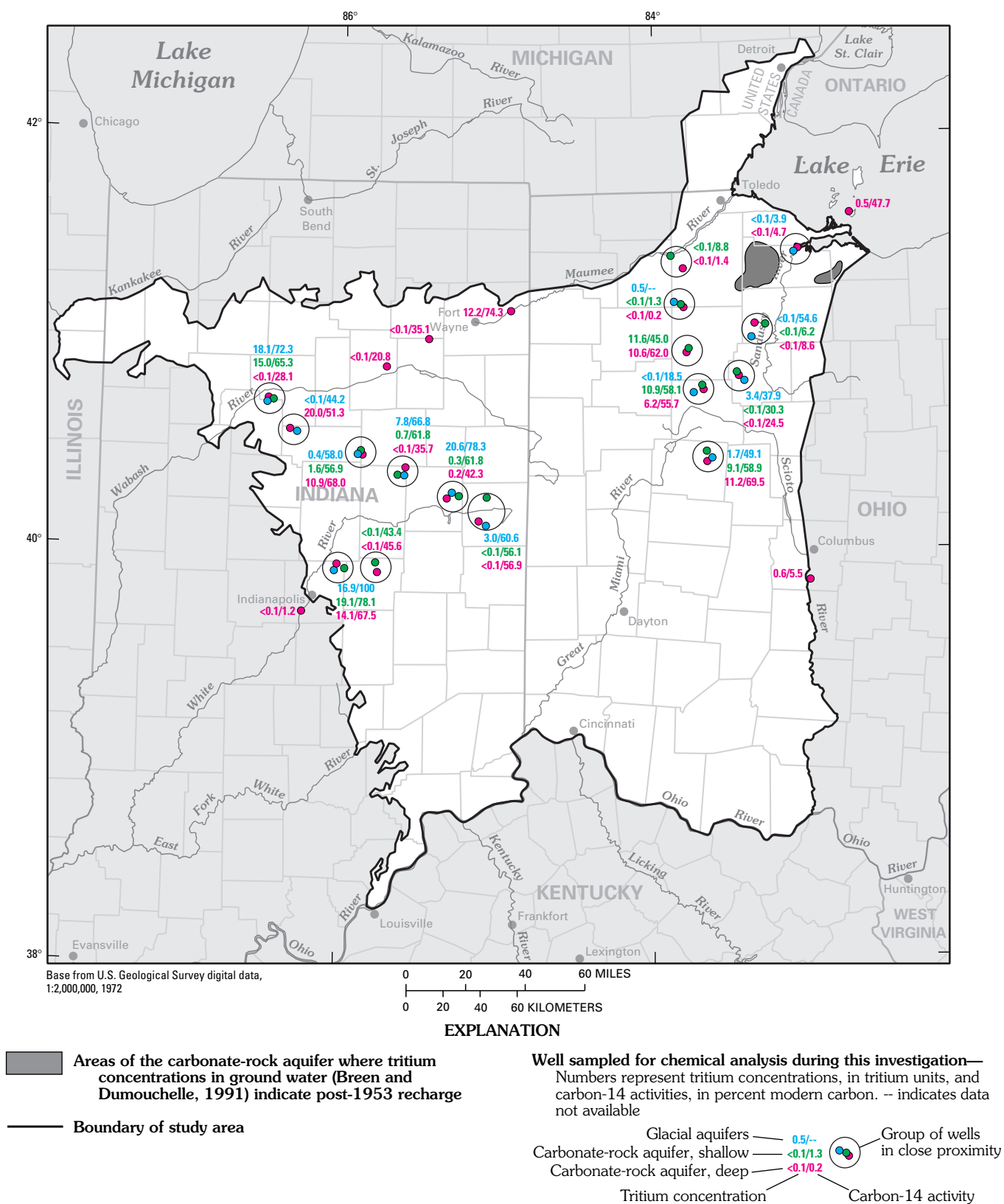


FIGURE 50.—Tritium concentrations and carbon-14 activities in water from wells in the Midwestern Basins and Arches aquifer system.

Tritium data can help in making qualitative estimates of ground-water ages on the order of tens of years. Alternatively, ^{14}C data can help date ground water that is thousands of years old. The maximum age that can be dated using ^{14}C is about 50,000 years given the isotope's half-life of 5,730 years (Freeze and Cherry, 1979). Ground-water samples were collected in the study area for ^{14}C analysis to help constrain ground-water ages and to help describe regional ground-water flow in the Midwestern Basins and Arches aquifer system. Values for $\delta^{13}\text{C}$ were also determined to provide information regarding the sources of dissolved inorganic carbon in the ground water and to help correct the measured ^{14}C values for the dilutional effects caused by various geochemical processes. The data are listed in table 8, plotted in figure 50 and discussed below.

The radioactive decay expression for ^{14}C can be expressed as

$$t = -8270 \ln(R), \quad (14)$$

where t equals the decay age of the carbon, in years, and R equals the measured ^{14}C activity of the sample expressed as a percentage of the ^{14}C activity of modern carbon (Mook, 1980). This equation indicates the time, in years, since the water was in contact with CO_2 in the soil zone; use of the equation requires the assumption that there have been no other inputs of dissolved inorganic carbon. However, dissolution of carbonate minerals or oxidation of organic matter can contribute nonradioactive carbon to ground water, diluting the amount of ^{14}C originally in the water and yielding an unadjusted age that is too old. To correct for nonradioactive carbon, an adjustment factor is added to the decay equation:

$$t = -8,270 \ln(R) + 8,270 \ln(Q). \quad (15)$$

For waters in which all the inorganic carbon is produced by the dissolution of carbonate minerals in the soil zone, the Q value is 1.0. The Q value will become some fraction of 1.0 if dissolution continues below the water table where exchange with soil-gas CO_2 cannot occur. Wigley (1975) has shown that in aquifers where CO_2 is not produced below the water table, the minimum Q value will not be less than 0.5. Where gypsum dissolution or the exchange of Ca^{2+} and Mg^{2+} for Na^+ drives the incongruent dissolution of dolomite under closed-system conditions (dedolomitization), or where CO_2 is produced by the oxidation of old organic matter during bacterially mediated sulfate reduction, Q values may be quite small because of the introduction of significant amounts of ^{14}C with zero activity. The Q values for ground water in the Madison Limestone in parts of Montana, South Dakota, and Wyoming, range from about 0.5, where minor dedolomitization has occurred, to less than 0.1, where ground waters have been affected by dedolomitization, cation exchange, and substantial sulfate reduction (Busby and others, 1991).

To produce accurate estimates of Q , one must use geochemical models that incorporate the effects of dedolomitization, sulfate-reduction, cation exchange, and isotopic exchange. This type of analysis, however, was beyond the scope of this investigation. As a first approximation, ^{14}C ages were estimated from Q values that were selected somewhat arbitrarily. The raw-age estimates ($Q=1.0$) were corrected by use of Q values of 0.5, 0.3, and in some cases, 0.2 (table 11). A Q value of 0.5 is expected for closed-system dissolution of carbonate minerals where no additional source of CO_2 is added and where no secondary mineral precipitates (Wigley, 1975). Thus, a Q value of 0.5 can overestimate the age of ground water that has undergone dedolomitization or sulfate reduction. A Q value of 0.3 was used in this investigation to account for geochemical reactions that produce additional sources of nonradioactive carbon to the ground water system. A Q value of 0.2 was used for ground waters with small ^{14}C activities and $\delta^{13}\text{C}$ values that are isotopically heavy. Much of the ground water in the aquifer system has $\delta^{13}\text{C}$ values of around -14 or -15 per mil; however, ground water from wells 1D, 13D, 14D, 17G, and 17D has $\delta^{13}\text{C}$ values that range from -11.0 to -7.1 per mil, an indication that a greater proportion of the dissolved inorganic carbon in these waters was derived from the dissolution of carbonate rocks with $\delta^{13}\text{C}$ values of about 0 per mil than in the waters with $\delta^{13}\text{C}$ values of around -14 or -15 per mil. Samples 8G, 9D, and 19 also have heavier $\delta^{13}\text{C}$ values (-8.8, -3.1, and -1.3 per mil) than do most other samples. These waters, however, have likely been affected by methanogenesis, a reaction in which organic matter is metabolized by methanogenic bacteria to produce CO_2 , methane (CH_4), and dissolved organic compounds. The concentration of dissolved methane in well 8G was 18.65 mg/L (Eurybiades Busenberg, U.S. Geological Survey, written commun., 1992). Ground water from wells 9D and 19 were not analyzed for dissolved methane, but these samples had elevated concentrations of dissolved organic carbon and (or) little or no dissolved sulfate, a composition consistent with methanogenesis. The age of these waters cannot be accurately determined without measuring the $\delta^{13}\text{C}$ value of the dissolved methane.

Also listed in table 11 are ages calculated by use of the method proposed by Pearson and White (1967), in which $\delta^{13}\text{C}$ values are used to correct for isotopic dilution due to congruent carbonate dissolution according to the equation

$$^{14}\text{C}(\text{adjusted}) = \quad (16)$$

$$^{14}\text{C}(\text{measured}) \times \left[\frac{\delta^{13}\text{C}_{\text{soil}} - \delta^{13}\text{C}_{\text{carbonate}}}{\delta^{13}\text{C}_{\text{water}} - \delta^{13}\text{C}_{\text{carbonate}}} \right],$$

TABLE 11.—*Summary of ^{14}C age estimates for ground water sampled during investigation of the Midwestern Basins and Arches aquifer system, 1991–92*

[Map number is location in figure 32. Q values are adjustment factors used to account for addition of nonradioactive carbon to the ground-water system. Negative ages indicate that local geochemistry does not reflect the assumed conditions used in assigning the Q value. Question mark indicates that age cannot be determined from available data. --, value not determined]

Well name	Map number	Age, Q = 1.0 (years)	Age, Q = 0.5 (years)	Age, Q = 0.3 (years)	Age, Pearson-White (years)	Pearson-White Q value	Q value(s) used for age estimate	Ground-water age (years)
Ross	10 G	5,900	200	-4,100	2,500	0.66	0.66	<50 – 2,500
Birt	10 S	<50	<50	<50	<50	--	--	<50
Ben Logan H.S.	10 D	<50	<50	<50	<50	--	--	<50
Searfoss	15 G	8,000	2,300	-1,900	5,500	.74	.74	<50 – 5,500
Rife	15 S	9,900	4,100	-100	6,700	.68	.68	6,700
Schoenberger	15 D	11,600	5,900	1,700	8,700	.70	.70	8,700
Beasley	16 G	5,000	-700	-5,000	600	.59	.59	600
Hill	16 S	23,000	17,300	13,000	19,500	.65	.3 – .65	13,000 – 19,500
Gillig	16 D	20,300	14,600	10,300	16,200	.61	.3 – .61	10,300 – 16,200
Lamalie	17 G	26,800	21,100	16,900	20,800	.48	.2 – .48	13,500 – 20,800
S-18	17 D	25,300	19,600	15,300	17,200	.38	.2 – .38	12,000 – 17,200
Finnegan	18 D	6,100	400	-3,900	-600	.44	.44	<50
Wilson	11 G	14,000	8,300	4,000	10,800	.68	.3 – .68	4,000 – 10,800
Spencer	11 S	<50	<50	<50	<50	.00	--	<50
Stair	11 D	<50	<50	<50	<50	.00	--	<50
Francis	12 S	<50	<50	<50	<50	--	--	<50
Augustine	12 D	<50	<50	<50	<50	--	--	<50
Richard	13 G	--	--	--	--	--	--	--
Kern	13 S	35,900	30,200	26,000	31,600	.59	.3 – .59	26,000 – 31,600
Auckerman	13 D	51,400	45,700	41,400	45,200	.48	.2 – .48	38,100 – 45,200
Rice	14 S	20,100	14,400	10,100	16,200	.63	.3 – .63	10,100 – 16,200
City of Weston	14 D	35,300	29,600	25,300	25,800	.32	.2 – .32	22,000 – 25,800
Hartman	19	24,000	18,300	14,000	-300	.05	--	?
Lacy	4 G	4,100	-1,600	-5,800	600	.65	.65	<50 – 600
Hummel	4 S	4,800	-1,000	-5,200	1,400	.66	.66	1,400
Jones	4 D	4,700	-1,100	-5,300	900	.64	.64	900
Harrison	3 S	6,900	1,200	-3,100	2,200	.56	.56	2,200
Martin	3 D	6,500	800	-3,500	2,800	.64	.64	2,800
Lockhart	2 G	<50	<50	<50	<50	--	--	<50
Mattingly	2 S	<50	<50	<50	<50	--	--	<50
Merchant	2 D	<50	<50	<50	<50	--	--	<50
Gates	1 D	36,600	30,800	26,600	30,700	.49	.2 – .49	23,300 – 30,700
Bickford	5 G	<50	<50	<50	<50	--	--	<50
Bartlett	5 S	4,000	-1,800	-6,000	300	.64	.64	300
Desoto Substation	5 D	7,100	1,400	-2,800	3,100	.61	.61	3,100
Staggs	6 G	<50	<50	<50	<50	--	--	<50
Ice	6 S	4,000	-1,800	-6,000	600	.67	.67	600
Underwood	6 D	8,500	2,800	-1,400	5,500	.69	.3 – .69	<50 – 5,500
Cohee	7 G	4,500	-1,200	-5,500	1,000	.65	.65	1,000
Ellis	7 S	4,700	-1,100	-5,300	1,400	.67	.67	<50 – 1,400
Harmon	7 D	<50	<50	<50	<50	--	--	<50
Fox	8 G	6,800	1,000	-3,200	-1,000	.39	--	?
Skiles	8 D	<50	<50	<50	<50	--	--	<50
Justice	9 G	<50	<50	<50	<50	--	--	<50
Lee	9 S	<50	<50	<50	<50	--	--	<50
Starbuck	9 D	10,500	4,800	500	-5,900	.14	--	?
Geradot	22	<50	<50	<50	<50	--	--	<50
Stenzel	21	8,700	2,900	-1,300	5,300	.66	.66	5,300
Rees	20	13,000	7,200	3,000	11,100	.80	.3 – .80	3,000 – 11,100

where ^{14}C (adjusted) is the ^{14}C activity adjusted for dissolution of carbonate rocks with known $\delta^{13}\text{C}$ values, ^{14}C (measured) is the measured activity in the water sample, $\delta^{13}\text{C}_{\text{soil}}$ is the isotopic composition of soil-gas CO_2 , $\delta^{13}\text{C}_{\text{carbonate}}$ is the isotopic composition of the carbonate minerals in the study area, and $\delta^{13}\text{C}_{\text{water}}$ is the isotopic composition of the dissolved inorganic carbon in the water sample. Values of $\delta^{13}\text{C}_{\text{soil}}$ in temperate climates vary from -25 to -18 per mil (Mook, 1980; Back and others, 1983); a value of -22.5 per mil was used in equation 16 for this investigation. Values of $\delta^{13}\text{C}_{\text{carbonate}}$ from samples of the carbonate-rock aquifer and the glacial aquifers are listed in table 9. The average $\delta^{13}\text{C}_{\text{carbonate}}$ value of the 10 samples, 0.0 per mil, was used in equation 16.

A summary of ages calculated from equations 15 and 16 is given in table 11. Ages were not calculated for the samples with tritium concentrations greater than 6 TU because such waters may contain a significant component of recent recharge with unknown amounts of bomb-derived ^{14}C . On the basis of the range of calculated ages and the chemical and isotopic data, each ground water sample was assigned an approximate age. In some ground water samples, tritium concentrations are between 0.8 and 3 TU and may represent a mixture of old water and recent recharge. Such waters were assigned an age ranging from less than 50 years to the age calculated by use of equation 16. Waters that are saturated with respect to calcite and dolomite and apparently unaffected by dedolomitization or sulfate reduction were assigned the age estimated from equation 16. The range of adjustment factors (Pearson-White Q value) for these waters is 0.56 to 0.67, which is in close agreement with the Q values calculated by Wigley (1975) for ground water that is undergoing congruent dissolution of calcite and dolomite in the soil zone and below the water table. Waters that have undergone dedolomitization or sulfate reduction were assigned a range of ages that bracket those calculated with a Q value of 0.3, or for waters with heavy $\delta^{13}\text{C}$ values, 0.2, and ages that were calculated by use of equation 16 (Pearson-White method).

The ground-water ages in the aquifer system are consistent with a conceptual model of regional ground-water flow in which the aquifer system alternately receives recharge and discharges across most of the study area except in the northeastern part, where the aquifer system does not receive a notable amount of recharge. Ground-water ages across most of the study area range from less than 50 years to several thousand years and generally do not follow any spatial trends. This pattern is consistent with a ground-water flow regime that is largely dominated by local flow systems that have short flow paths relative to the areal extent of the aquifer system. The oldest ground waters in the aquifer system range in age from at least 3,000 to possibly more than 40,000 years and are in the discharge areas in the northeastern part of the study area near the Maumee and Sandusky Rivers and Lake Erie. Relatively old waters were also found near the Wabash

River in northern Indiana and at the margin of the Illinois Basin where the upper confining unit overlies the carbonate-rock aquifer.

Ground water from wells 13S, 13D, and 14D ranges in age from about 22,000 to more than 45,000 years and has $\delta^{18}\text{O}$ and δD values expected for water recharged during the Pleistocene. The age ranges of ground water from wells 14S, 16S, 16D, 17G, and 17D are also Pleistocene; however, the $\delta^{18}\text{O}$ values are similar to those for present-day recharge. The retreat of Late-Wisconsinan glaciers in the Great Lakes area began about 13,300 years ago and was nearly complete by 10,000 years ago (Barry, 1983). Isotopic data presented by Yapp and Epstein (1977) indicate that the $\delta^{18}\text{O}$ and δD values of precipitation during the interval between 10,000 and 9,500 years before present were similar to those of present-day precipitation. Data on $\delta^{18}\text{O}$ values in mollusk shells from sediment cores in Lake Erie (Fritz and others, 1975) indicate a rapid increase in $\delta^{18}\text{O}$ values in water in Lake Erie after 13,000 years before present because of a rapid rise in average land temperatures. The lower ages presented in table 11 for ground water from wells 14S, 16S, 16D, 17G, and 17D range from 10,300 to 13,500 years. Because the isotopic composition of precipitation during this time period may have been similar to that of today, the $\delta^{18}\text{O}$ and δD data for these ground waters indicates that the lower age limits listed in table 11 for these waters may be the more reasonable. Thus, ground water from wells 13S, 13D, and 14D may represent water that recharged the aquifer system from beneath the glacial ice, whereas ground water from wells 14S, 16S, 16D, 17G, and 17D may represent precipitation that entered the aquifer system at the end of glaciation. Alternatively, Siegel (1991) observed a similar disparity between $\delta^{18}\text{O}$ values and estimated ^{14}C ages for Pleistocene-age ground water in the northern Midwest. He suggested that the calculated ground-water ages may be too great if $\delta^{13}\text{C}$ values of soil gas increased because of a reduction of the amount of organic matter that was present in the soil during the colder climate. As a result, the actual ages of ground water recharged during the Pleistocene may be less than those listed in table 11. Although considerable uncertainty is inherent in the absolute ages of ground water because of assumptions used in the calculations, the ages given in table 11 are helpful for evaluating the relative age of ground waters in the Midwestern Basins and Arches aquifer system.

VARIATION IN GROUND-WATER CHEMISTRY WITH DEPTH

The sampling methodology for this investigation, discussed earlier in this report, was designed to use existing wells to obtain as much information as possible on the variation in ground-water chemistry with depth in the Midwestern Basins and Arches aquifer system. Two types of deep bedrock wells were sampled: those that were open hole through the entire length of the well and those that were cased through

various lengths of the top section of the carbonate-rock aquifer (table 6). Data from these deep bedrock wells were compared to data from nearby shallow bedrock wells to assist in understanding the ground-water chemistry at depths as great as 450 ft below the top of the carbonate-rock aquifer.

A comparison of the chemical and isotopic data and the estimated ground water ages (tables 7, 8, and 11) between the shallow bedrock wells and the deep bedrock wells that are open hole through the entire length of the well shows that the chemistry and the ground-water ages between these wells are generally similar. The differences in ground-water ages in all these wells ranges from several hundred to less than 3,000 years. Of the pairs of shallow and deep bedrock wells that have ages greater than 50 years, ground water in the deep bedrock well is older than in the shallow bedrock well in well groups 3, 5, and 15; whereas ground water in the shallow bedrock well is older than in the deep bedrock well in well groups 4 and 16. The similarity between ground water from wells that are open only to the shallow part of the carbonate-rock aquifer and ground water from wells that are open to a much greater part of the carbonate-rock aquifer indicates that either (1) the chemistry and age of the ground water is similar throughout the sampled thickness of the carbonate-rock aquifer or (2) if ground water at depth has a distinctly different chemistry or older age, then the carbonate rocks are not transmissive enough at the greater depths to contribute significantly to the overall chemistry of the sampled water, and most ground water is produced from the upper part of the carbonate-rock aquifer.

Data from a shallow interval (less than 50 ft below the top of the aquifer) and an isolated deeper interval (as great as 450 ft below the top of the aquifer) within the carbonate-rock aquifer are available for well groups 10, 13, 14, and 17. A comparison of ground-water chemistry and ages between the shallow and deep bedrock wells at well groups 13 and 14 shows a systematic change in chemistry with depth and a distinctly different ground water in the deeper part of the carbonate-rock aquifer than in the shallow part. The chemical and isotopic data from these two well groups indicate that, in this area of the aquifer system, some recharge water enters the glacial aquifers and the shallow zones of the carbonate-rock aquifer but does not penetrate deeply into the aquifer system. In contrast, a comparison of ground-water chemistry and ages at well groups 10 and 17 shows little difference between the shallow and deeper parts of the aquifer system. At well group 10, tritium concentrations indicative of post-1953 recharge are found throughout the entire sampled thickness of the carbonate-rock aquifer. These wells are located at the highest potentiometric level in the aquifer system, where recharge rates to the deepest parts of the aquifer system should be relatively high. The chemical and isotopic data for ground water from wells 17G and 17D, located near the Sandusky River and Lake Erie, is quite similar. The age of the water in the overlying glacial aquifer is slightly older than

water from deeper within the carbonate-rock aquifer (13,500 years compared to 12,000 years, using the lower age limit as discussed in the previous section). This slight decrease in age with depth may reflect an upward flow of ground water as it discharges the aquifer system.

Chemical and isotopic data are also available for ground water that was sampled from specific intervals in three deep wells that penetrate the entire thickness of the carbonate-rock aquifer in northwestern Indiana (D.J. Schnoebelen, U.S. Geological Survey, written commun., 1993). Ground water was sampled from various 10-ft intervals of the carbonate-rock aquifer by use of an inflatable packer system. Hydrogeologic data for these three wells and a description of the packer technology are given in Arihood (1994). The chemical and isotopic data from all the sampled intervals in each well are very similar, an indication that there is no stratification of ground-water chemistry with depth in this part of the aquifer system; however, the samples do not represent water from the deepest part of the carbonate-rock aquifer because the rocks in the bottom 60 to 400 ft of the wells are not necessarily transmissive (Arihood, 1994).

SUMMARY AND CONCLUSIONS

Aquifers in Quaternary glacial deposits and underlying Silurian and Devonian carbonate rock in parts of Indiana, Ohio, Michigan, and Illinois compose an integrated regional-scale water-table aquifer system. This aquifer system generally lies between the Appalachian, the Illinois, and the Michigan (structural) Basins and is located along the axes of the Cincinnati, the Findlay, and the Kankakee Arches.

Glacial deposits within the study area are the result of multiple glacial advances and directly overlie the carbonate rocks along the axes of the structural arches in the central part of the study area. These glacial deposits mask the ancient bedrock topography and bury numerous valleys in the bedrock surface. The glacial deposits and the carbonate rocks are separated by a shale sequence along the margins of and within the surrounding structural basins.

The water table within the Midwestern Basins and Arches aquifer system generally is within the glacial deposits. Glacial aquifers typically consist of sands and gravels in outwash deposits or as discontinuous lenses within ground or end moraines. Because such lenses are not necessarily areally extensive, the glacial aquifers can supply large yields of ground water only locally.

An areally extensive aquifer is present in the carbonate rocks that underlie the glacial deposits. At the regional scale, the carbonate-rock aquifer is semiconfined by the finer grained glacial deposits where the aquifer directly underlies these deposits (subcrop area of the carbonate-rock aquifer) but is confined where the aquifer underlies the intervening shale sequence, called the upper confining unit, along the