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Isotopic and Geologic Studies to Identify the Sources of Sulfate in Groundwater Containing High Barium Concentrations

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ISOTOPIC AND GEOLOGIC STUDIES
TO IDENTIFY THE SOURCES OF SULFATE
IN GROUNDWATER CONTAINING HIGH BARIUM CONCENTRATIONS

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ABSTRACT

Dissolved barium in excess of the U.S. Environmental Protection Agency drinking water standard occurs in groundwater of a region of the Cambrian-Ordovician aquifer system in northeastern Illinois that is anomalously depleted in dissolved sulfate. The concentration of dissolved sulfate is an important control on the dissolved barium concentration because of the low solubility of the mineral barite (barium sulfate). The depletion of dissolved sulfate is believed to be due to bacterially mediated sulfate reduction occurring in zones of anaerobic conditions. Characteristics of the groundwater that support this interpretation are the presence of dissolved hydrogen sulfide, increased alkalinity, and ^{34}S enrichment in the dissolved sulfate.

Isotopic analyses determined that oxidation of sulfide minerals is the primary source for dissolved sulfate in groundwater in the unconfined region of the flow system and that dissolution of evaporite minerals is the primary source for dissolved sulfate present in mineralized groundwater in the confined region of the flow system. The source of the evaporite minerals is problematic. Evaporites are not known to be present in the flow system and isotopic analyses provided evidence that the dissolved sulfate was derived from evaporites of a different age than could occur in the Cambrian and Ordovician strata of the aquifer system.

The depletion of ^{18}O in groundwater in confined regions of the flow system is interpreted as evidence of the importance of glacial processes to recharge of the groundwater. Dissolved sulfate from marine evaporites of a younger geologic age may have been recharged to the flow system as a result of glacial processes. Further research is necessary to establish the relation between glacial events and the chemical composition of groundwater in confined regions of the Cambrian-Ordovician aquifer system.

KEY WORDS

aquifer properties/barite/barium/chemical properties/evaporite minerals/
glacial events/groundwater/microbial reactions/sedimentary rocks/stable
isotopes/sulfate

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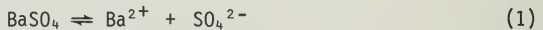
Isotopic analyses of groundwater samples in this research were performed by Tim Grundl as part of his Master's program at Northern Illinois University. The authors wish to thank the analytical laboratories of the Illinois State Water Survey and the Illinois Environmental Protection Agency for performing chemical analyses of groundwater samples for this research. The efforts of Michael Barcellona, Kenni James, and James Whitney of the Illinois State Water Survey, and Dorothy Bennett of the Illinois Environmental Protection Agency are especially appreciated.

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INTRODUCTION

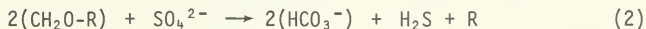
Chemical analyses of groundwater samples performed by the Illinois Environmental Protection Agency determined that the dissolved barium concentration in a large number of wells in Illinois exceeds the drinking water standard of 1.0 mg/L (U.S. EPA, 1973). The majority of wells exceeding the standard are located in northeastern Illinois. Research at the Illinois State Geological Survey (Gilkeson et al., 1978) established (1) that the affected wells in northern Illinois are all finished in bedrock of the Cambrian and Ordovician Systems, and (2) that the concentration of sulfate dissolved in groundwater is an important control on the concentration of dissolved barium.

For a significant number of groundwater samples, the ion-activity product of barium (Ba^{2+}) and sulfate (SO_4^{2-}) was in equilibrium with the mineral phase barite ($BaSO_4$) according to the following reaction:



This reaction requires an inverse relation between the activities of Ba^{2+} and SO_4^{2-} ions. High barium concentrations may occur only in groundwater that has a low concentration of dissolved sulfate. In a large region of northeastern Illinois, high barium concentrations occur in groundwater that is anomalously depleted in dissolved sulfate.

The depleted groundwater also commonly contains dissolved hydrogen sulfide. The reaction of sulfate ion (SO_4^{2-}) with organic matter ($\text{CH}_2\text{O-R}$), where R is an undefined radical, to form bicarbonate ion (HCO_3^-) and hydrogen sulfide (H_2S) can be written as follows:



Although thermodynamic calculations predict that the inorganic reduction of sulfate to sulfide is possible at the temperatures and pressures that exist in the aquifer system, it is well known from laboratory experiments that the inorganic reaction will not occur in the aquifer system. The inorganic reaction has been accomplished in the laboratory only at temperatures greater than 250°C (Goldhaber and Kaplan, 1974). Given the conditions in the aquifer system, however, the reduction of sulfate has been known to occur only through bacterial mediation of the reaction. Sulfate-reducing bacteria require an anaerobic environment and a source of organic carbon (Stumm and Morgan, 1970). The chemical composition of groundwater from rocks of the Cambrian and Ordovician Systems of northern Illinois was studied to determine if the depletion of dissolved sulfate could be the result of bacterial reduction. Stable isotopes of sulfur were analyzed because the bacterial reduction of sulfate results in a large fractionation of sulfur isotopes between sulfate and sulfide (Claypool et al., 1980).

The oxidation-reduction potential (Eh), the titration alkalinity, and the concentration of dissolved organic carbon in the groundwater were also studied. An attempt was made to culture anaerobic bacteria in groundwater from selected well sites, and stable isotopes of hydrogen and oxygen in the water molecule were analyzed to provide information on rock-water interactions and the history of groundwater in the flow system.

HYDROGEOLOGIC SETTING

The location of the study area in northeastern Illinois is shown in figure 1. A generalized column of rock-stratigraphic units and aquifers in northeastern Illinois is shown in figure 2. The terminology defining

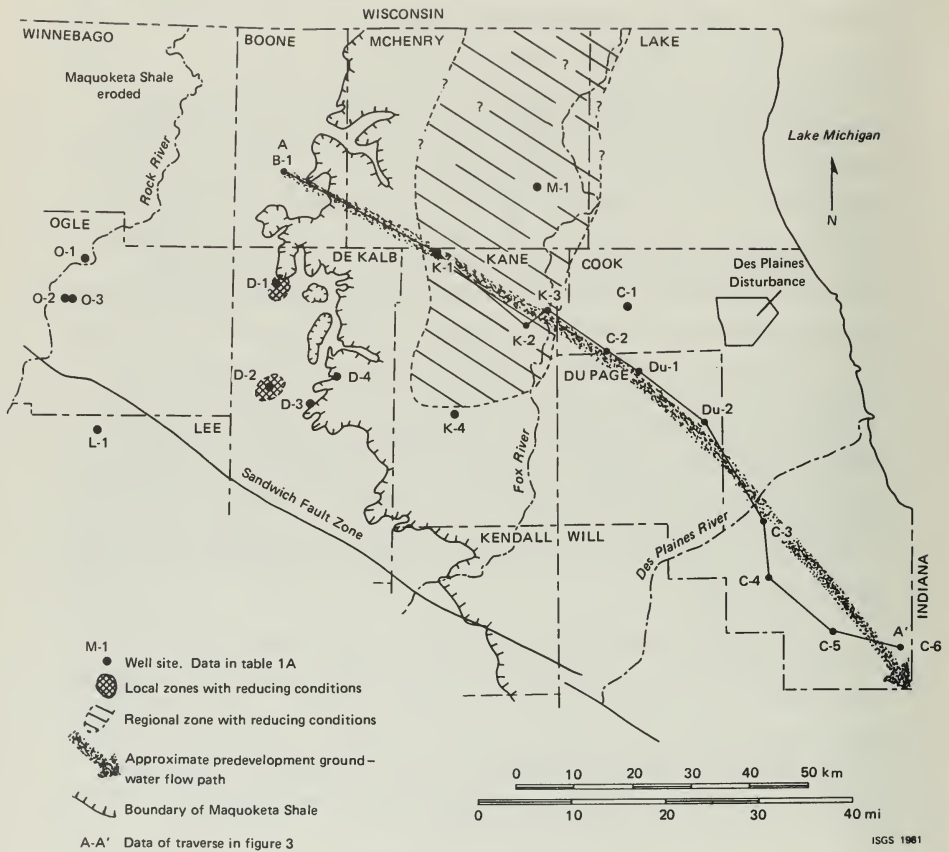


FIGURE 1. Map of the study area showing distribution of the Maquoketa Shale Group, approximate direction of groundwater flow in the Cambrian-Ordovician aquifer system before large groundwater withdrawals, zones of strong reducing potential, and well sites discussed in the text.

SYSTEM	SERIES	GROUP OR FORMATION	AQUIFER *	LOG	THICKNESS (m)	DESCRIPTION
QUATERNARY	PLEISTOCENE		Sands and Gravels		0-100	Unconsolidated glacial deposits pebbly clay (till), silt, sand and gravel Alluvial silts and sands along streams
SILURIAN	NIAGARAN	Racine	Silurian		0-120	Dolomite, very pure to argillaceous, silty, cherty, reefs in upper part
		Sugar Run				Dolomite, slightly argillaceous and silty
		Joliet				Dolomite, very pure to shaly and shale, dolomitic, white, light gray, green, pink, maroon
	ALEXANDRIAN	Kankakee	0-55		Dolomite, pure top 1' 2', thin green shale partings, base glauconitic	
		Elwood			Dolomite, slightly argillaceous, abundant layered white chert	
		Wilhelmi			Dolomite, gray, argillaceous and becomes dolomitic shale at base	
ORDOVICIAN	CINCINNATIAN	Maquoketa	0-75	Shale, red to maroon, oolites		
				Shale, silty, dolomitic, greenish gray, weak (Upper unit)		
	CHAMPLAINIAN	Galena	Galena Platteville	0-115	Dolomite, and/or limestone, cherty (Lower part)	
		Platteville			Dolomite, shale partings, speckled	
		Glenwood	Glenwood St. Peter		Dolomite and/or limestone, cherty, sandy at base	
		St. Peter			Sandstone, fine and coarse grained, little dolomite, shale at top	
	CANADIAN	Shakopee	Prairie du Chien	0-185	Sandstone, fine to medium grained; locally cherty red shale at base	
		New Richmond			Dolomite, sandy, cherty (oolitic); sandstone	
		Oneota Gunter			Sandstone interbedded with dolomite Dolomite, white to pink, coarse grained cherty (oolitic) Sandstone, medium grained, slightly dolomitic	
	CAMBRIAN	CROIXAN	Eminence	Eminence Potosi		0-75
Potosi			Dolomite, fine-grained, gray to brown, drusy quartz			
Franconia			Franconia	10-40		Dolomite, sandstone and shale, glauconitic, green to red, micaceous
Ironton			Ironton Galesville	35-65		Sandstone, fine to coarse grained, well sorted, upper part dolomitic
Galesville						
		Eau Claire	110-145	Shale and siltstone, dolomitic, glauconitic; sandstone, dolomitic, glauconitic		
		Elmhurst Member	Elmhurst Mt Simon	365-860	Sandstone, coarse grained, white, red in lower half, lenses of shale and siltstone, red, micaceous	
	Mt Simon					
PRE-CAMBRIAN	* Terminology of aquifer systems defined by Hughes, Kraatz, and Landon, 1969.					Granitic rocks

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FIGURE 2. Generalized column of rock stratigraphic units and aquifers in northeastern Illinois. (Prepared by M. L. Sargent, Illinois State Geological Survey, 1981.)

aquifer systems is from Hughes, Kraatz, and Landon (1969). The sequence from the Galena-Platteville Dolomite through the Ironton-Galesville Sandstone functions hydraulically as one aquifer (Walton, 1965) and is referred to as the Cambrian-Ordovician aquifer system. Depending upon local conditions and groundwater needs, wells penetrate the aquifer system to different depths. The main water-yielding units are the Glenwood-St. Peter Sandstone and the Ironton-Galesville Sandstone.

Shales in the Maquoketa Shale Group and the Eau Claire Formation are important confining units. The shales in the Eau Claire Formation separate the Cambrian-Ordovician aquifer system from deeper water-bearing units. The Elmhurst Sandstone Member at the base of the Eau Claire Formation and the Mt. Simon Sandstone are connected hydraulically and form the Mt. Simon aquifer system. No wells receive groundwater exclusively from the deeper aquifer system; wells usually penetrate only a few hundred feet into this aquifer because the water quality decreases with depth.

In north-central Illinois, where the Maquoketa Shale Group is eroded, recharge of the Cambrian-Ordovician aquifer system is produced from vertical leakage of meteoric water through glacial drift. The regional distribution of the Maquoketa Shale Group is shown in figure 1. In northeastern Illinois, where the Maquoketa strata overlies and confines the aquifer, much recharge is produced by vertical leakage through the shale from rocks of Silurian age or the glacial drift (Walton, 1965).

The exact configuration of the potentiometric surface of the Cambrian-Ordovician aquifer system before extensive groundwater withdrawal is unknown. Interpretation of early data indicates that under natural conditions the surface was relatively featureless and sloped gently to the southeast (Suter et al., 1959). Significant areas of recharge were in Boone and De Kalb Counties. Because of their topographic relief, major drainageways such as the Fox, Des Plaines, and Illinois Rivers must have had a significant effect on hydraulic gradients of the natural potentiometric surface.

As a result of large withdrawals of groundwater, broad, deep cones of depression have formed in Cook, Du Page, and Will Counties. The steepened hydraulic gradients have increased the transmittal of groundwater

toward the centers of heavy withdrawal (Sasman et al., 1977). Groundwater flow is from all directions toward these pumping centers.

In the Chicago region, the potentiometric surface of the aquifer has changed more than 210 meters (700 ft) in some localities (Sasman et al., 1977). Significant dewatering of the Galena-Platteville Dolomite has occurred in Will, Cook, Du Page, and eastern Kane Counties.

HYDROGEOCHEMISTRY

The location of the study area is shown in figure 1. Data on the chemistry of groundwater at well sites shown on figure 1 is presented in table 1A. Data on well construction is presented in table 1B. In the region where the Maquoketa Shale Group is eroded and significant recharge occurs from infiltration of meteoric waters, the major ions in groundwater are calcium, magnesium, and bicarbonate. Eastward and southeastward from this region the groundwater becomes more mineralized along the probable direction of predevelopment flow.

An estimated predevelopment flow line is shown by the shaded arrow in figure 1. The flow line is based on an interpretation of the predevelopment potentiometric surface (Suter et al., 1959) and does not consider the effects that anisotropy or heterogeneity in the rock strata may have on the direction of groundwater flow. The flow line is intended only as an approximation of groundwater flow in the aquifer system to provide a framework for the study of regional variation in the composition of groundwater. The locations of well sites along the flow line are shown on traverse A-A' in figure 1. Data on the chemical composition of the groundwater along the traverse A-A' are presented in table 2 and figure 3. The distribution of dissolved sulfate in groundwater of the Cambrian-Ordovician aquifer system for a region of northeastern Illinois is shown in figure 4. Over a large area of northeastern Illinois, the dissolved sulfate concentration in the aquifer system is less than 10 mg/L. East and southeastward of this region, the dissolved sulfate concentration increases rapidly and is present at concentrations of greater than 800 mg/L in southeastern Cook County. Sodium and chloride are other chemical constituents that are present in significant concentrations as the groundwater becomes more mineralized.

TABLE 1A.

Oxygen Isotopic Composition of the Water Molecule, Oxygen and Sulfur Isotopic Composition of the Sulfate Molecule, and Other Selected Dissolved Constituents in Groundwater from Wells Finished in Cambrian and Ordovician Bedrock in Northeastern Illinois. The Location of Well Sites is Shown in Figure 1. Information on Well Location and Construction is in Table 1B.

County- Well no.	pH	Eh (millivolts)	Dissolved constituents (mg/L)					Isotopic composition of water and dissolved sulfate (per mille)					
			Ba ²⁺	SO ₄ ²⁻	Cl ⁻	H ₂ S	Alkalinity as CaCO ₃	Hardness as CaCO ₃	Filterable residue	Total organic carbon	Water δ ¹⁸ O	Sulfate δ ³⁴ S	Sulfate δ ¹⁸ O
<u>Oxidized groundwater - unconfined</u>													
Boone-1	7.4	+310	0.3	27	8.7	0	308	347	350		-7.24	+2.40	+0.31
Lee-1	7.05	+405	0.1	73.4	27	0	308	410	487	21.0	-7.37	+5.78	+3.07
Ogle-1	7.35	+340	0.1	22	3.1	0	275	290	305		-7.39	+4.22	∞
Ogle-2	7.3	+370	0.03	8.4	9	0	336	350	356		-7.74	+4.99	+2.86
Ogle-3	7.45	+390	0.1	13.8	15	0	280	376	436		-7.65	+10.34	+8.97
<u>Slightly reduced to reduced groundwater - confined by fine-grained glacial drift</u>													
De Kalb-1	7.1	+15	0.21	28	6.4		377	390	418		-7.79		
							(<0.1 mg/L) present						
De Kalb-2	7.3	-35	1.0	4.9	1.5		240	158	250	2.32	-6.82		
							(<0.1 mg/L) present						
<u>Oxidized groundwater - unconfined - downgradient of reducing zone</u>													
De Kalb-3	7.3	+135	0.4	5	1.4	0	262	228	269		-7.36	+17.66	+14.62
De Kalb-4	7.1	+175	0.3	9.3	1.6	0	330	283	350	1.25	-7.19	+21.67	+15.70

TABLE 1A (continued)

County well no.	pH	Eh (millivolts)	Dissolved constituents (mg/L)						Filterable residue	Total organic carbon	Isotopic composition of water and dissolved sulfate (per mille)			
			Ba ²⁺	SO ₄ ²⁻	Cl ⁻	H ₂ S	Alkalinity as CaCO ₃	Hardness as CaCO ₃			Water δ ¹⁸ O	Sulfate δ ³⁴ S	Sulfate δ ¹⁸ O	
<u>Strongly reduced groundwater - confined by Maquoketa Shale Group</u>														
Kane-1			2.0	0.8	8.0	present		300	268	309				
Kane-2	7.4	-100	18.2	2.3	5.6	3.7		312	249	330	0.7	-8.05	+40.30	+2.50
Kane-3	7.4	-90	16.8	3.3	4.6	1.4		310	252	303	0.8	-7.82	+34.11	+4.77
McHenry-1	7.5	-45	13.8	1.9	2.1	0.55		326	226	260		-7.86		
<u>Slightly reduced to oxidized groundwater in transition zone - downgradient of strong reducing zone - confined by Maquoketa Shale Group</u>														
Kane-4	7.25	+10	0.7	9.5	4.0	0.25		288	256	298		-8.31	+31.40	+17.50
Cook-1	6.9	+185	1.5	10	3.2	0		273	230	295	0.50	-7.89		
Cook-2	6.9	+135	3.7	7.4	7	0 ^a		298	242	327	<0.1	-8.06	+29.05	+14.80
<u>Oxidized groundwater - downgradient of strong reducing zone - confined by Maquoketa Shale Group</u>														
Du Page-1			0.1	68	11	0		300	271	436				
Du Page-2	7.3	+235	0.05	64	34	0		294	306	457	<0.1		+23.40	+15.10
Cook-3			0.02	143	68	0		283	290	610				
Cook-4	7.2	+195	0.02	282	260	0		240	464	1085	<0.1	-9.25		
Cook-5	7.0	+215	0.01	498	150	0		246	560	1240	<0.1			
Cook-6	7.1	+145	0.02	832	337	0		216	840	2049		-9.67	+19.56	+15.91

a. Trace amounts of HS⁻ are intermittently present at this well site.

TABLE 1B
The Location, Depth, and Stratigraphic Section in the Open Well Bore for Well Sites Listed in Table 1A.

County- Well no.	Location			Well depth	
	Section	Township	Range	meters	feet
Boone-1	24	44N	3E	265	868
Cook-1	8	41N	10E	428	1405
Cook-2	36	41N	9E	437	1434
Cook-3	2	37N	12E	490	1608
Cook-4	2	36N	12E	513	1683
Cook-5	36	36N	13E	522	1713
Cook-6	7	35N	15E	557	1827
De Kalb-1	26	42N	3E	194	636
De Kalb-2	23	40N	3E	382	1254
De Kalb-3	33	40N	4E	366	1200
De Kalb-4	13	40N	4E	400	1312
Du Page-1	9	40N	10E	433	1420
Du Page-2	10	39N	11E	417	1370
Kane-1	3	42N	6E	293	962
Kane-2	16	41N	8E	396	1300
Kane-3	11	41N	8E	399	1310
Kane-4	32	40N	7E	425	1393
Lee-1	27	22N	11E	158	520
McHenry-1	33	44N	8E	427	1400
Ogle-1	32	25N	11E	218	715
Ogle-2	24	24N	10E	33	110
Ogle-3	24	24N	10E	102	335

a. Wells designated as Cambrian-Ordovician aquifer system are open in the interval from the Galena-Platteville Dolomite through the Ironton-Galesville Sandstone.

TABLE 2

Variation of Selected Constituents in Groundwater Including Stable Isotopes of Water and Sulfate Ion Along a Flow Path of the Cambrian-Ordovician Aquifer System in Northeastern Illinois. The Line of Flow Path is Shown in Figure 1. The Variation of Constituents Along the Flow Path is Graphically Presented in Figure 3.

Well no.	Isotopic composition (per mille)		Eh millivolts	Ba ²⁺ mg/L	SO ₄ ²⁻ mg/L	H ₂ S mg/L	Alkalinity ^d	
	Water	Sulfate ion					Hardness	
	$\delta^{18}O(H_2O)$	$\delta^{18}O(SO_4^{2-})$						
		$\delta^{34}S(SO_4^{2-})$						
<u>Oxidized ground water - unconfined</u>								
B-1	-7.24	+0.31	+310	0.3	27	0		0.89
<u>Reduced ground water - confined by Maquoketa Shale Group</u>								
K-1				2.0	0.8	present		1.12
K-2	-7.61b	+2.50	-100	18.2	2.3	3.7		1.25
K-3	-7.72b	+4.77	-90	16.8	3.3	1.4		1.23
<u>Ground water in transition zone - downgradient of strong reducing zone - confined by Maquoketa Shale Group</u>								
C-2	-8.06	+14.80	+135	3.7	7.4	0 ^c		1.23
<u>Oxidized ground water - downgradient of strong reducing zone - confined by Maquoketa Shale Group</u>								
Du-1				0.1	68	0		1.10
Du-2		+15.10	+235	0.05	64	0		0.96
C-3				0.02	143	0		0.97
C-4	-9.25		+195	0.02	282	0		0.51
C-5			+215	0.01	498	0		0.44
C-6	-9.67	+15.91	+145	0.02	832	0		0.26

a. Ratio calculated from alkalinity and hardness expressed as CaCO₃.

b. Median value from analysis of five samples.

c. Hydrogen sulfide present intermittently.

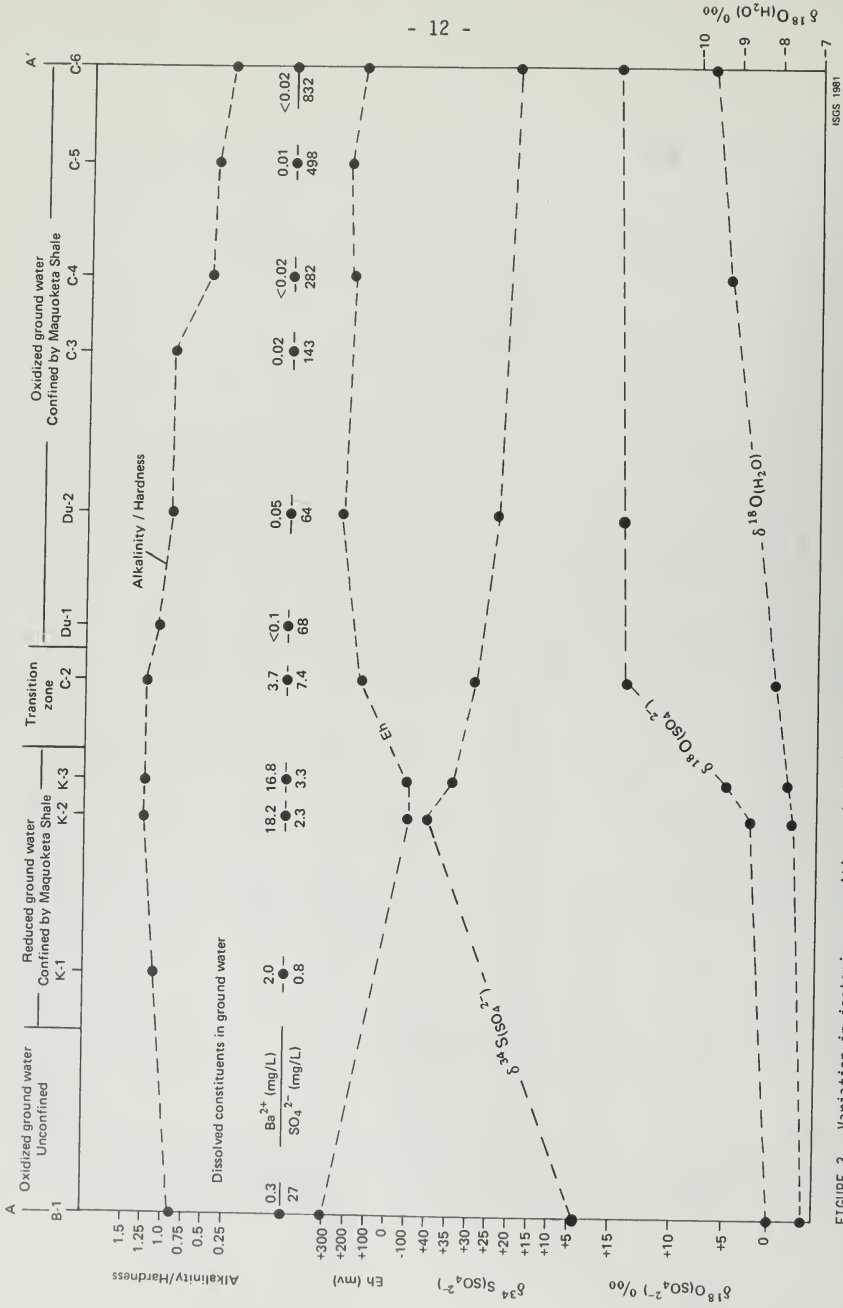


FIGURE 3. Variation in isotopic composition and chemistry that occurs along a groundwater flow path in the Cambrian-Ordovician aquifer system of northeastern Illinois. The location of the traverse is shown in figure 1. Analytical data along the traverse is listed in table 2.

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FIGURE 4. Distribution of dissolved sulfate in groundwater of the Cambrian-Ordovician aquifer system for a region of northeastern Illinois. (From Gilkeson and Cartwright, in press.)

The distribution of dissolved barium in groundwater of the Cambrian-Ordovician aquifer system for a region of northeastern Illinois is shown in figure 5, and the variation in dissolved barium that occurs along flow line A-A' is shown in figure 3. Groundwater from the Cambrian-Ordovician aquifer system exceeds the drinking water standard of 1.0 mg/L for barium over a large part of McHenry and Kane Counties, the western part of Lake County, the northwestern part of Du Page County, and the northeastern part of De Kalb County. At some well sites the dissolved barium concentration exceeds 15 mg/L. Groundwater with barium concentrations greater than 1.0 mg/L generally have dissolved sulfate concentrations less than 10 mg/L.

A common observation in confined groundwater flow systems is a general decrease in the oxidation-reduction (redox) potential of groundwater in the direction of flow. The decline in redox potential is believed to be caused by a sequence of oxidation-reduction reactions that reduces oxidized species initially present in the groundwater. These reactions are discussed by Stumm and Morgan (1970); Champ, Gulens, and Jackson (1979); and Cherry et al. (1979).

To characterize the variation in redox potential of groundwater in the Cambrian-Ordovician aquifer system, potentials were measured using a platinum electrode coupled to a calomel reference electrode mounted in an airtight chamber. The measurement technique is discussed by Back and Barnes (1965). In the present study, potentials were monitored using two platinum electrodes to guard against electrode "poisoning." Redox potentials of groundwater presented in table 1A are expressed as Eh in millivolts in terms of the normal hydrogen electrode. The platinum electrode values are used only in a qualitative sense to evaluate trends that are present within the flow system; the values are not to be interpreted within the framework of equilibrium thermodynamics.

In the western part of the study area, Eh values are relatively high where oxidized meteoric water recharges the Cambrian-Ordovician aquifer system through a thin cover of glacial drift. Examples are Lee-1, Ogle-2, Ogle-3, and Boone-1. As groundwater moves southeastward and becomes confined by fine-grained glacial drift and the Maquoketa Shale Group, there is a decrease in the redox potential. The change in redox potential that



FIGURE 5. Distribution of dissolved barium in groundwater of the Cambrian-Ordovician aquifer system for a region of northeastern Illinois. (From Gilkeson and Cartwright, in press.)

occurs along flow path A-A' (fig. 1) is shown on the traverse A-A' in figure 3. The redox decreases with the direction of groundwater flow to a zone of strong reducing potential in Kane County. The cross-hatched pattern in figure 1 delimits the region known to be a strong reducing zone. Eh values as low as -100 millivolts have been measured for groundwater within this zone. From central Kane County the zone extends northward along the Fox River Valley into McHenry County. The extent of this region in McHenry County cannot be accurately determined from the available information.

Anaerobic conditions also exist in localized areas where the Maquoketa is eroded and the flow system is confined by fine-grained glacial drift. Examples are well sites De Kalb-1 and De Kalb-2 (fig. 1 and table 1A). The regional extent of anaerobic conditions at these well sites is not well known.

One indication that bacterially mediated sulfate reduction may be occurring in the anaerobic zones is the presence of hydrogen sulfide in the groundwater. The reduction of sulfate (SO_4^{2-}) results in the generation of hydrogen sulfide (H_2S) and bicarbonate (HCO_3^-) as demonstrated in equation 2. In the range of pH present in the groundwater of the aquifer system, a significant amount of the hydrogen sulfide (H_2S) dissociates to form bisulfide (HS^-). The major source of titration alkalinity in the aquifer system is bicarbonate (HCO_3^-) from the dissolution of carbonate minerals. Bacterially mediated sulfate reduction would be expected to increase the titration alkalinity in groundwater through addition of HCO_3^- and HS^- . Thus the ratio of titration alkalinity to hardness would increase and act as an indicator of the process. The ratio of titration alkalinity to hardness (as equivalents of calcium carbonate) is shown for groundwater samples along traverse A-A' in figure 3. The titration alkalinity is enhanced relative to hardness in groundwater samples from the reducing zone and the transition zone downgradient of the reducing zone. As groundwater becomes more mineralized along the flow path there is a decline in the ratio of titration alkalinity to hardness (well site C-4 to C-6, fig. 3). The decline is possibly due to precipitation of carbonate minerals in this region of the flow system. Carbonate mineral equilibrium reactions in the flow system have not been investigated but are expected to be studied in the future.

Analyses of total organic carbon in groundwater samples from well sites in the study area are shown in table 1A. Organic carbon is generally present in samples from well sites located in the unconfined region of the aquifer system in north-central Illinois. Concentrations as great as 21.0 mg/L have been measured at well site Lee-1. The concentration of total organic carbon decreases along flow paths, and the measured concentrations from well sites located in the strong reducing zone were 0.7 mg/L at well site Kane-2 and 0.8 mg/L at well site Kane-3. Well sites located in a region of oxidized groundwater downgradient from the strong reducing zone contained total organic carbon in concentrations less than the limit of detection (<0.1 mg/L).

Experimental research conducted by Zobell and Grant (1942) determined that anaerobic microbial requirements of organic carbon are less than 0.1 mg/L. Analyses performed in the present research indicate that groundwater in the reducing zone has a sufficient concentration of organic carbon to support microbial activity. Attempts to culture sulfate-reducing bacteria in groundwater from wells within the strong reducing zone have been unsuccessful to date. However, methanogens were cultured in groundwater collected from well site Kane-2 (Risatti, 1981, Illinois State Geological Survey, personal communication). Groundwater from many of the wells in the strong reducing zone contain slight amounts of methane. Isotopic analyses of carbon in the methane determined that the methane was generated by microbially mediated reactions under anaerobic conditions (Coleman, 1981, Illinois State Geological Survey, personal communication).

STABLE ISOTOPE GEOCHEMISTRY

During this study, isotope ratios were determined for the water and the sulfate molecules: The ratio of oxygen -18 to oxygen -16 [$\delta^{18}\text{O}_{(\text{H}_2\text{O})}$] and the ratio of hydrogen -2 (deuterium) to hydrogen -1 [$\delta\text{D}_{(\text{H}_2\text{O})}$] were calculated for the water molecule. The ratio of sulfur -34 to sulfur -32 [$\delta^{34}\text{S}_{(\text{SO}_4^{2-})}$] and the ratio of oxygen -18 to oxygen -16 [$\delta^{18}\text{O}_{(\text{SO}_4^{2-})}$] were calculated for the sulfate molecule. The isotope ratios are expressed in delta units (δ) as per mille (parts per thousand, ‰) differences related to a standard. In this research, the δD and $\delta^{18}\text{O}$ are expressed as per mille differences

compared to the VSMOW standard of ocean water (Gonfiantini, 1978), and the $\delta^{34}\text{S}$ analyses referenced to Canyon Diablo meteoritic troilite (Rees, 1978). The equation for calculating the isotope ratio is

$$\delta\% = [(R_{\text{samp}} - R_{\text{std}}) / R_{\text{std}}] \times 1000 \quad (3)$$

where R_{samp} and R_{std} are the isotope ratios D/H , $^{18}\text{O}/^{16}\text{O}$, $^{34}\text{S}/^{32}\text{S}$ of the sample and the standard respectively.

Information on the sampling procedure and sample preservation is presented in a paper by Perry, Grundl, and Gilkeson (in press). A detailed discussion of analytical procedures is presented in a Master's thesis by Grundl (1980).

ISOTOPIC VARIATION IN THE WATER MOLECULE

Evaporation, condensation, and precipitation processes have a very important effect on the isotope ratio of meteoric water (Dansgaard, 1964). Also, because both condensation and isotope fractionation are strongly affected by temperature, the isotopic composition of precipitation is temperature dependent.

Water vapor from evaporation of the ocean is depleted in ^{18}O by approximately 12% to 15% and in D by 80% to 120% relative to ocean water. When the water vapor condenses, the rain or snow that forms is enriched in the heavy isotopes relative to the remaining water vapor. As the water vapor is circulated in northward-flowing continental atmospheric systems, the recurrence of evaporation-condensation events results in a latitudinal trend in the stable isotope composition of the water molecule. The δD and $\delta^{18}\text{O}$ composition of precipitation correlates on a global basis according to the equation

$$\delta\text{D}\% = -8 \delta^{18}\text{O} + 10 \quad (4)$$

that is known as the meteoric water line (Friedman, 1953; Craig, 1961; Dansgaard, 1964). For further information on processes that isotopically fractionate meteoric water, the reader is referred to a paper by Dansgaard (1964).

The isotopic composition of meteoric water is preserved after the water infiltrates the soil and enters a groundwater flow system. At the

high temperatures (50°C to 100°C) present in deep groundwater flow systems, the isotopic composition of water may be altered through chemical reaction with the aquifer rock.

δD and $\delta^{18}O$ values for brines in the Illinois, Michigan, and Alberta basins were determined during research by Clayton et al. (1966). Groundwater samples in each basin were found to have a large range of $^{18}O/^{16}O$ ratios. However, for each basin, the least saline groundwaters approached the meteoric water line; the more saline groundwaters departed from the meteoric water line in the direction of ^{18}O enrichment. The high temperatures in the brines (temperatures as high as 60°C in the Illinois Basin) were believed to be the major control on the ^{18}O enrichment through exchange with the aquifer strata.

Table 3 presents analyses for $\delta D_{(H_2O)}$ and $\delta^{18}O_{(H_2O)}$ for groundwater samples collected from eight well sites in Illinois for this research. Water temperatures at the well head ranged from 12.0°C to 22.8°C. Total dissolved minerals as filterable residue ranged from 269 mg/L to 2520 mg/L. The range in temperature and total dissolved minerals between the eight well sites encompasses the variation that occurs in the Cambrian-Ordovician aquifer system in Illinois where it is used as a source of potable water. The close relationship of the isotope data from the well sites to the meteoric water line is shown in figure 6. Because of the distribution of the data on the meteoric water line, Perry, Grundl, and Gilkeson (in press) concluded that exchange between the water molecule and the aquifer rock strata has been insignificant and that groundwater in the potable region of the aquifer system has retained a meteoric isotopic composition. The variation in $\delta D_{(H_2O)}$ and $\delta^{18}O_{(H_2O)}$ that occurs in the flow system is concluded to be caused by the variation in climatic conditions occurring when the water was recharged to the flow system. Contemporary meteoric water in northern Illinois has an average $\delta^{18}O_{(H_2O)}$ of about -7‰ (Graf, Friedman, and Meents, 1965). Groundwater samples collected for this study that were found to be greatly depleted in ^{18}O compared to the contemporary value, were recharged to the flow system during a much colder climate. The most depleted samples are from the southwestern portion of the aquifer system (Peoria, Fulton, McDonough, and Hancock Counties). $\delta^{18}O$ values of -11‰ to -12‰ are common in this region.

TABLE 3

Hydrogen and Oxygen Isotopic Composition, Temperature and Filterable Residue of Groundwater Samples from Selected Well Sites in Illinois.^a

County (Well no.)	Location		Range	Aquifer	Well depth		Filterable residue (mg/L)	Isotopic composition of water (per mille)	
	Section	Township			(m)	(ft)		T°C	$\delta^{18}O$
Cook-6 (C-6, Fig. 1)	7	35N	15E	Cambrian-Ordovician aquifer system	557	1827	1940	-62.54	-9.67
Dekalb-3 (De-3, Fig. 1)	33	40N	4E	St. Peter Sandstone-Ironton- Galesville Sandstone	366	1200	269	-52.10	-7.36
Kane-4 (K-4, Fig. 1)	32	40N	7E	Cambrian-Ordovician aquifer system	425	1393	299	-57.84	-8.31
Kane-2 (K-2, Fig. 1)	16	41N	8E	Cambrian-Ordovician aquifer system	399	1310	342	-48.09	-8.05
Peoria-1	25	7N	6E	Galena-Platteville Dolomite- St. Peter Sandstone	475	1560	1620	-89.32	-11.97
Peoria-2	24	11N	6E	Galena-Platteville Dolomite- St. Peter Sandstone	512	1680	1678	-88.20	-12.04
Peoria-3	13	11N	7E	Silurian Dolomite, Galena- Platteville Dolomite- St. Peter Sandstone	515	1691	2520	-55.98	-8.43
Stephenson-1	19	25N	7E	Silurian Dolomite, Maquoketa Group (shale and dolomite)	76	250	420	-49.69	-7.74

a. Isotopic data from Perry, Grundl, and Gilkeson (in press).
 b. Median value from two analyses.

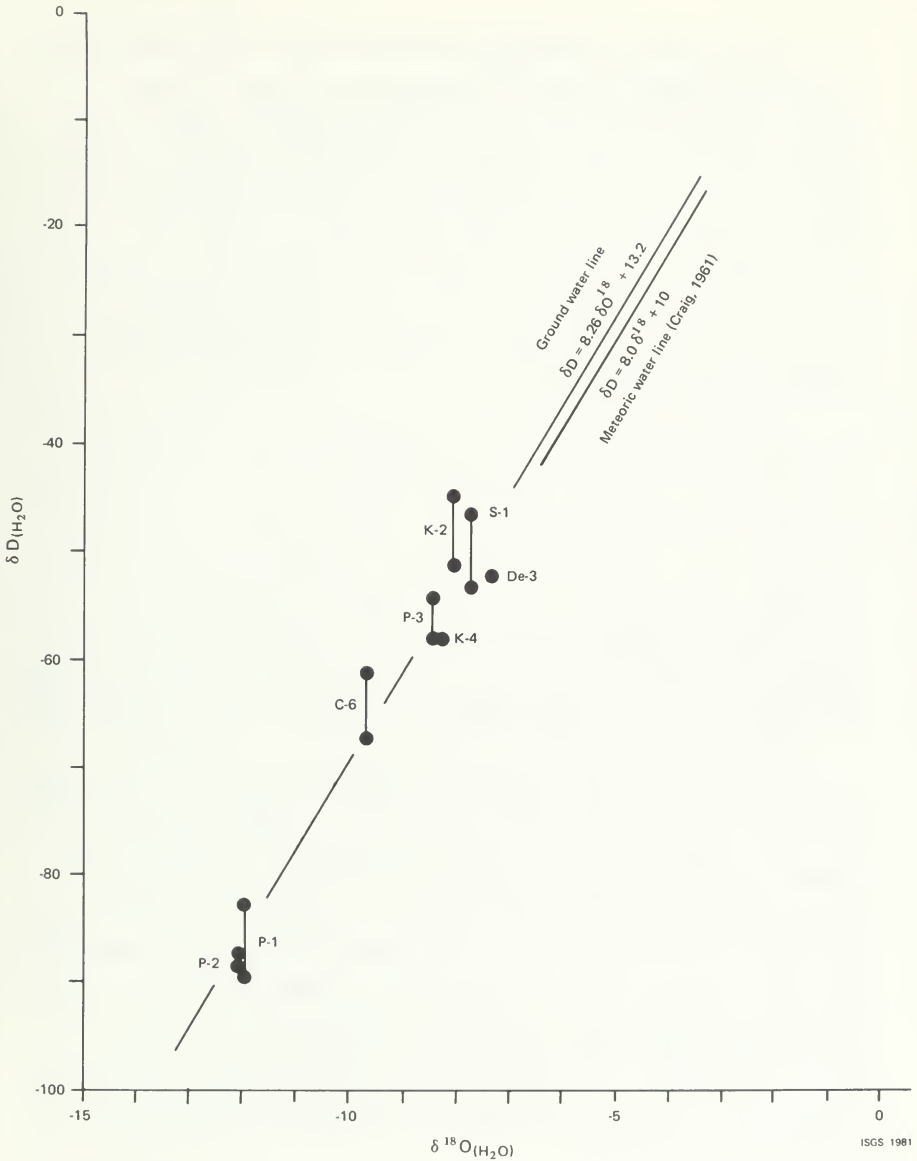


FIGURE 6. Covariation of ^{18}O and D in groundwater from selected well sites in northern Illinois. The close relationship of the data to the meteoric water line is shown. Data on individual well sites are presented in table 3. (Modified from Perry, Grundl, and Gilkeson, in press.)

The variation in $\delta^{18}\text{O}_{(\text{H}_2\text{O})}$ that occurs along a flow line (A-A') of the pre-development flow system in northeastern Illinois is shown in figure 3. The values range from -7.24‰ where the aquifer system is unconfined in north-central Illinois (well site Boone-1) to -9.67‰ in south-eastern Cook County (well site Cook-6). The isotopic data indicate that groundwater in the unconfined region of the aquifer system in north-central Illinois has an oxygen isotopic composition nearly identical to contemporary meteoric water. In the confined region of the aquifer system, the depletion of ^{18}O is compatible with an increased residence time of groundwater. Groundwater that is significantly depleted in ^{18}O requires a source of recharge related to glaciation.

Problems with determining the source of the isotopically depleted groundwater in the flow system and establishing a temporal framework for the groundwater on the basis of its ^{18}O isotopic composition are summarized in a discussion by Perry, Grundl, and Gilkeson (in press). During the Pleistocene Epoch the sources of recharge to the aquifer system were meteoric water and glacial melt water. The relative contribution of each source is not known and probably varied over time as a function of the glacial ice regimen. The isotopic composition of meteoric water in atmospheric circulation systems over the Midwest during the Pleistocene is not well understood. The actual isotopic composition of the glacial ice is also unknown.

It is also difficult to determine a temporal framework for the groundwater based on its oxygen isotopic composition. A common conclusion from a variety of studies (ice cores, ocean bottom sediments, and faunal assemblages) is that the Wisconsinan Stage of the Pleistocene Epoch ended very rapidly within a 3,000-year interval at about 13,000 years before the present. The present Midwest climate regime may have become established 10,000 years ago. In north-central Illinois, where the aquifer system is unconfined, the residence time of groundwater with contemporary isotopic composition may range from contemporary to several thousand years, possibly as great as 10,000 years. Groundwater in the confined region of the aquifer system that is significantly depleted in ^{18}O may have a residence time greater than 13,000 years.

ISOTOPIC VARIATION OF THE DISSOLVED SULFATE MOLECULE

In natural systems, sulfur is cycled between sulfate and sulfide reservoirs (Holser and Kaplan, 1966). Given the conditions of temperature and pressure in the Cambrian-Ordovician aquifer system in northeastern Illinois, the reduction of sulfate to sulfide requires anaerobic biologic mediation. During reduction (equation 2), the light sulfur isotope (^{32}S) is preferentially reduced to sulfide. The result is that the remaining dissolved sulfate reservoir becomes enriched in the heavier isotope ^{34}S . Claypool et al. (1980) concluded from a review of research on bacterial reduction of sulfate that a fractionation between the sulfate and the sulfide phase of approximately 40‰ is common in natural systems. Large fractionation effects of sulfur isotopes are known only to occur during the bacterial reduction of sulfate to sulfide. Significant fractionation of sulfur isotopes does not occur during the nonbiological reduction of sulfate to sulfide (Goldhaber and Kaplan, 1974) or during the dissolution or precipitation of sulfur-bearing minerals (Claypool et al., 1980).

Table 1A presents analyses for $\delta^{34}\text{S}(\text{SO}_4^{2-})$ in groundwater samples from the Cambrian-Ordovician aquifer system in northeastern Illinois. For well sites in the study area, the $\delta^{34}\text{S}(\text{SO}_4^{2-})$ of oxidized groundwater in the unconfined region of the aquifer system ranges from +2.40‰ to +10.34‰. Analyses of samples from seven well sites in the oxidized, unconfined region of the aquifer system in north-central Illinois were used to determine a median $\delta^{34}\text{S}(\text{SO}_4^{2-})$ of 5.07‰ with a range of 2.36‰ to 10.34‰ (data from this research and Perry, Grundl, and Gilkeson [in press]). The sulfate in oxidized groundwater in the unconfined flow system is isotopically light; and Perry, Grundl, and Gilkeson (in press) concluded that an important source of the sulfate was the oxidation of sulfide minerals dissolved during the recharge of meteoric water.

An additional minor source of sulfate is from precipitation recharged to the aquifer system. The concentration and isotopic composition of sulfate in rainfall over a region of the study area (southern Du Page County) were investigated by Holt, Engelkeimer, and Venters (1972). The average

$\delta^{34}\text{S}_{(\text{SO}_4^{2-})}$ of dissolved sulfate in rainfall was +5‰; the concentration of dissolved sulfate ranged from 1 to 10 mg/L. The results are similar to the observation of Rightmire et al. (1974) that dissolved sulfate concentrations in rainfall over continental areas usually range from 1 to 10 mg/L, with an average of 3 mg/L. The available data indicate that the dissolved sulfate derived from precipitation has a $\delta^{34}\text{S}_{(\text{SO}_4^{2-})}$ that is nearly identical to that of dissolved sulfate derived from dissolution and oxidation of sulfide minerals.

The variation in $\delta^{34}\text{S}_{(\text{SO}_4^{2-})}$ that occurs along the flow line A-A' in the predevelopment flow system in northeastern Illinois is shown in figure 3. A large fractionation of $\delta^{34}\text{S}_{(\text{SO}_4^{2-})}$ is apparent between oxidized groundwater in the unconfined region of the flow system and groundwater samples from well sites located in the strong reducing zone where the aquifer system is confined by Maquoketa Shale. The dissolved sulfate in the reducing zone is enriched in ^{34}S relative to the average composition of dissolved sulfate in the upgradient, unconfined region of the aquifer system with $\delta^{34}\text{S}_{(\text{SO}_4^{2-})}$ values of +40.30‰ at well site Kane-2 and +34.11‰ at well site Kane-3. The significance of the enrichment with regard to bacterially mediated sulfate reduction is discussed later in this paper.

In groundwater that is downgradient of the reduced zone, there is a decrease in the $\delta^{34}\text{S}_{(\text{SO}_4^{2-})}$ corresponding to a marked increase in both the dissolved sulfate concentration and the oxidation-reduction potential. However, the $\delta^{34}\text{S}_{(\text{SO}_4^{2-})}$ of dissolved sulfate in this region of the aquifer system is too enriched in ^{34}S (+23.40‰ at Du Page-2 and +19.56‰ at Cook-6) to have been derived from oxidation of sulfide minerals. Perry, Grundl, and Gilkeson (in press) concluded that a major portion of the dissolved sulfate in groundwater of this region was derived from dissolution of evaporite minerals, but recognized that the source of the evaporites was problematic. The sulfur isotopic composition of marine sulfates has varied systematically throughout geologic time as a function of the distribution of sulfur in the sulfate and sulfide reservoirs (Holser and Kaplan, 1966. Figure 7 presents $\delta^{34}\text{S}_{(\text{SO}_4^{2-})}$ values from worldwide analyses of evaporite sulfates of different geological ages. Average $\delta^{34}\text{S}_{(\text{SO}_4^{2-})}$ values for marine evaporites of North America are approximately +30‰ in the Cambrian and Ordovician Systems

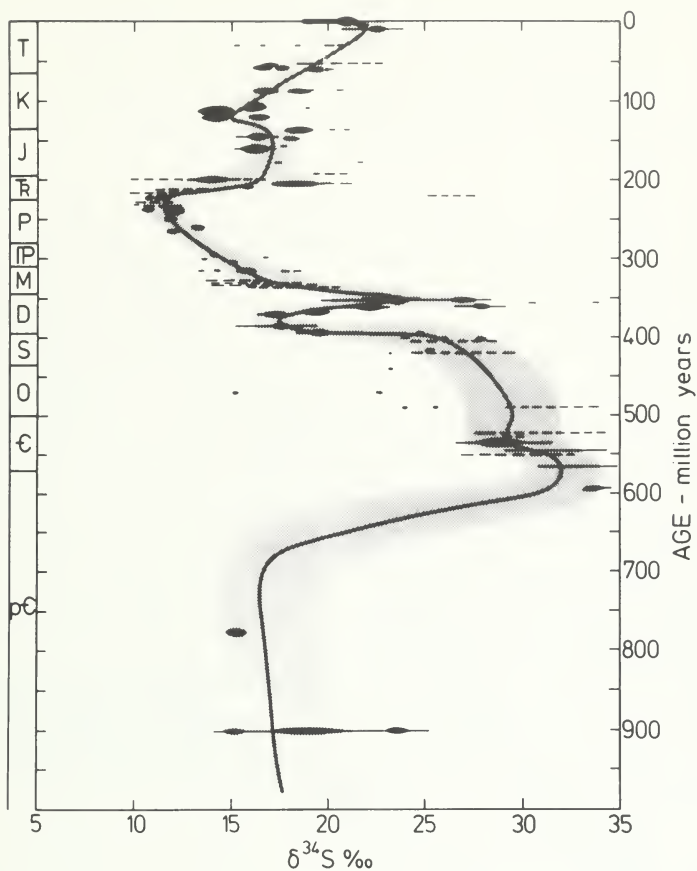


FIGURE 7. Summary of sulfur isotope-age curve for sulfate. Solid areas or lines qualitatively indicate the number of analyses, plotted at their most probable age. Horizontal dashed lines signify the range of relatively few analyses (Claypool et al., 1980).

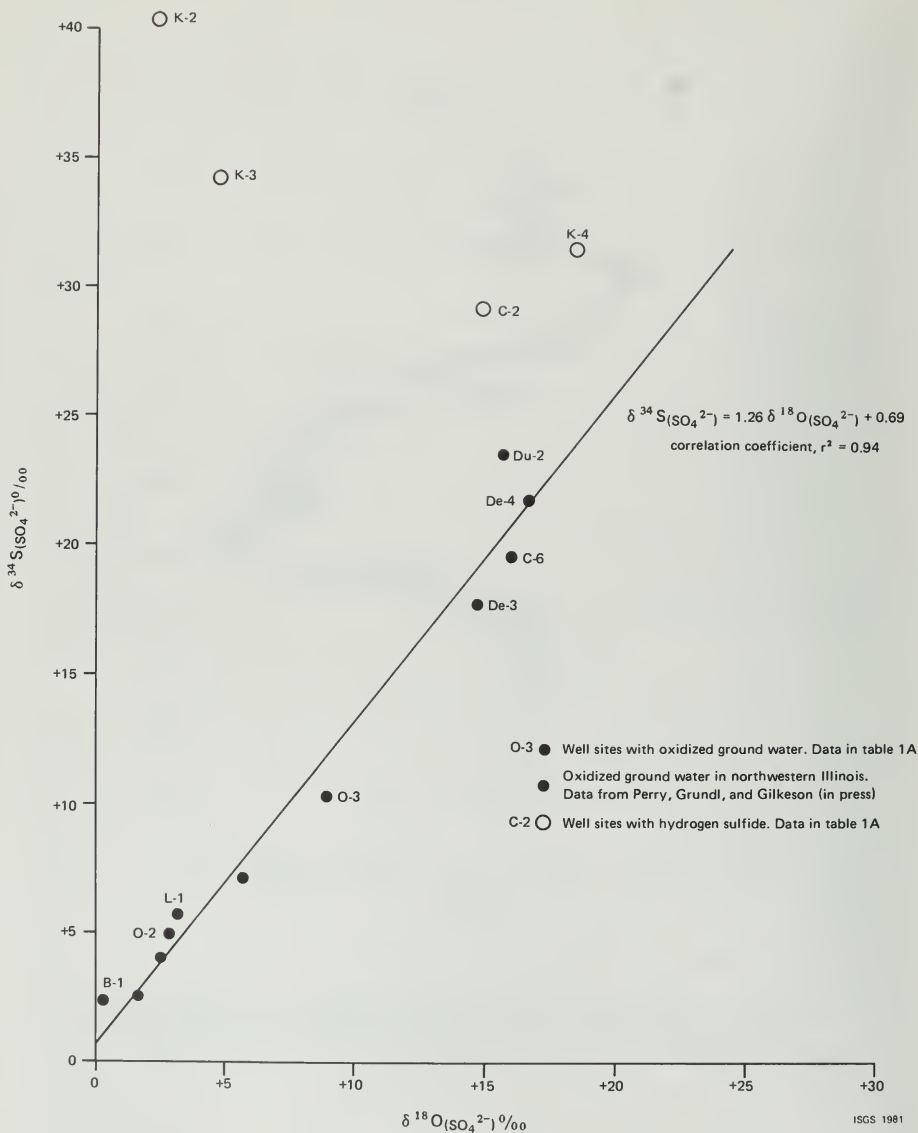


FIGURE 8. Covariation of $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ in dissolved sulfate in groundwater of the Cambrian-Ordovician aquifer system in northern Illinois. The linear relationship is for sulfide-free groundwater samples. The four sulfide-bearing groundwater samples that are displaced from the line are interpreted to be enriched in ^{34}S due to bacterial sulfate reduction.

(Claypool et al., 1980). The $\delta^{34}\text{S}(\text{SO}_4^{2-})$ of sulfide-free groundwater samples in the flow system are not sufficiently enriched in ^{34}S to indicate that sulfur is obtained from marine evaporites of Cambrian or Ordovician age. An additional problem is that marine evaporites are not known to be present in the Cambrian and Ordovician strata in northern Illinois. Another source of this dissolved sulfate is proposed in the discussion section of this paper.

The covariation of $\delta^{34}\text{S}(\text{SO}_4^{2-})$ and $\delta^{18}\text{O}(\text{SO}_4^{2-})$ in groundwater samples of the aquifer system is shown in figure 8. The relationship between $\delta^{34}\text{S}(\text{SO}_4^{2-})$ and $\delta^{18}\text{O}(\text{SO}_4^{2-})$ for the sulfide-free groundwater samples is described by the relation

$$\delta^{34}\text{S}(\text{SO}_4^{2-}) = 1.26 \delta^{18}\text{O}(\text{SO}_4^{2-}) + 0.69 \quad (5)$$

with a correlation coefficient, r^2 , of 0.94. The relationship includes sulfate derived from oxidation of sulfide minerals and sulfate derived from dissolution of sulfate minerals. Although the mechanism responsible for the observed relationship between the sulfide-free groundwater samples is not well understood at the present time, Perry, Grundl, and Gilkeson (in press) have concluded tentatively that it is due to mixing between groundwaters of two end member compositions. This mixing may be due to physical properties of the aquifer matrix that affect the miscible displacement of groundwater by an invading groundwater of a different chemical composition.

The greatest enrichment in ^{34}S is in groundwater samples from well sites located in the strong reducing zone (Kane-2 and Kane-3, table 1A) and in the transition zone (Cook-2 and Kane-4, table 1A) that is downgradient of the strong reducing zone. Determination of the fractionation of $\delta^{34}\text{S}(\text{SO}_4^{2-})$ that has occurred as a result of bacterial reduction of sulfate in the strong reducing zone requires determination of the $\delta^{34}\text{S}(\text{SO}_4^{2-})$ of the initial sulfate. Information on the isotopic composition of dissolved sulfate before significant reduction has occurred is provided by study of the covariation of $\delta^{34}\text{S}(\text{SO}_4^{2-})$ and $\delta^{18}\text{O}(\text{SO}_4^{2-})$. From experiments on bacterial reduction of sulfate, Mizutani and Rafter (1969) concluded that, at any stage of reduction, the ratio of ^{18}O enrichment to ^{34}S enrichment in the residual sulfate is approximately 1:4. This relationship is not

apparent in the analyses performed in the present research. The $\delta^{18}\text{O}(\text{SO}_4^{2-})$ for groundwater samples from well sites in the strong reducing zone (+2.50% at Kane-2 and +4.77% at Kane-3) are not significantly different from the median value of +3.75% obtained from analyses of sulfide-free groundwater samples from seven well sites in the oxidized, unconfined region of the aquifer system in north-central Illinois. However, the $\delta^{18}\text{O}(\text{SO}_4^{2-})$ values for the samples from the strong reducing zone differ significantly from those for samples from well sites downgradient of the strong reducing zone (+17.50% at Kane-4, +14.80% at Cook-2, and +15.91% at Cook-6). This data leads to the interpretation that the significant source of the dissolved sulfate in waters at well sites in the strong reducing zone is dissolved sulfate transported into the reducing zone from the upgradient, unconfined region of the aquifer system. The enrichment in ^{34}S is +40.23% for well site Kane-2 and +29.04% for well site Kane-3, compared to the median $\delta^{34}\text{S}(\text{SO}_4^{2-})$ value of +5.07% for seven sulfide-free groundwater samples from well sites in the oxidized, unconfined region of the aquifer system. Fractionation of this magnitude may occur through bacterial reduction of sulfate (Claypool et al., 1980).

The observation that no significant fractionation of $\delta^{18}\text{O}(\text{SO}_4^{2-})$ has occurred in the strong reducing zone is problematic and warrants further study. Fractionation may be concentration-dependent, and the insignificant isotopic fractionation of oxygen may be the result of the low concentrations of dissolved sulfate in the strong reducing zone.

DISCUSSION

The isotopic composition of the water molecule in groundwater of the unconfined region of the Cambrian-Ordovician aquifer system is evidence of the importance of glacial processes to the recharge of groundwater to the flow system. The role of glacial processes as a source of dissolved sulfate must also be considered. The mechanics of recharge related to glacial processes are not clearly understood; the mechanism proposed in this paper is that subglacial recharge of basal meltwater occurred during the recent glacial stages in Illinois (approximately 13,000 years before the present)

when glaciers occupied Lake Michigan with ice boundaries in the northeastern corner of the state. As a result of the geothermal gradient as well as the heat generated by friction, meltwater was present at the base of the continental glaciers (Weertman, 1972; Clayton and Moran, 1974; Freeze and Cherry, 1979). It is postulated that pressure from the glacial ice overburden caused basal meltwater containing sulfate and other salts to recharge into the Cambrian-Ordovician aquifer system through the floor of Lake Michigan. The subglacial recharge reversed regional hydraulic gradients and the meltwater flowed westward across the region to zones of discharge in the unconfined region of the aquifer system. Thus, the dissolved sulfate was derived from the glacial erosion of evaporites, and in addition, from recharge through evaporite sequences in the rock strata.

Extensive evaporite sequences are present east of Illinois in strata of the middle Devonian and the middle and upper Silurian rocks that underlie and flank Lake Michigan (Shaver et al., 1971). At present, the isotopic composition of sulfate in these strata is unknown. However, analyses in other areas of the world (fig. 7) have established a $\delta^{34}\text{S}_{(\text{SO}_4^{2-})}$ range of approximately +22‰ to +27‰ for rocks of middle and upper Silurian age. Analyses of strata of middle Devonian age have determined a $\delta^{34}\text{S}_{(\text{SO}_4^{2-})}$ range of approximately +17‰ to +19‰ (Claypool et al., 1980). Although sulfur isotopic analyses of evaporites in the Lake Michigan Basin are needed to confirm the postulated mechanism, the available data strongly indicate that the isotopic composition of sulfates in strata of the Lake Michigan Basin will be similar to the isotopic composition of sulfate derived from dissolution of sulfate minerals.

The hypothesis explains several characteristics of groundwater in the unconfined region that is downgradient of the strong reducing zone (table 1A). These include the isotopic composition of dissolved sulfate, the depletion of ^{18}O in the water molecule, the high oxidation-reduction potential of the groundwater, and the low concentrations of dissolved organic carbon.

The presence of oxidized groundwater in the confined region of the flow system, downgradient of the strong reducing zone, is anomalous. The

general evolutionary trend of groundwater in confined flow systems is toward a decrease in the redox potential along the direction of flow to an anaerobic state; groundwater further along the flow path remains anoxic. However, if the oxidized groundwater was recharged by a glacial process through the floor of Lake Michigan, then the groundwater did not pass through the strong reducing zone. The strong reducing zone is thought to have been present in interglacial flow systems. Recharge of groundwater with a distinct chemical composition due to glacial processes may have had a significant effect on chemical reactions in this zone. The rapid subglacial recharge of groundwater could have temporarily restricted the activity of anaerobic bacteria.

During passage through geologic materials, the miscible displacement of fluids with differing chemical compositions can be affected by the physical characteristics of the matrix. The sandstone matrix of the aquifer system can be partitioned into conducting pores, nonconducting-exchanging pores, and nonconducting-nonexchanging pores. The characteristics of pores in Ottawa sand (a commercial product mined from one of the sandstones of the Cambrian-Ordovician aquifer system) were determined during miscible displacement experiments conducted by Weeks, Stewart, and Weeks (1976). Only about 2 percent of the pores were nonexchanging (totally isolated). Forty percent of the pores were nonconducting but open to exchange through diffusion. The diffusion processes were thought to be relatively rapid because exchange was essentially complete after displacement of about two-pore-volumes.

In a broad region of the Cambrian-Ordovician aquifer system of northeastern Illinois, the postulated subglacial recharge would have resulted in the miscible displacement of groundwater with a high dissolved-barium concentration by groundwater with a high dissolved-sulfate concentration. The sulfate-bearing groundwater passing through conductive pore space in the aquifer matrix would interact through diffusion with groundwater containing dissolved barium in nonconductive, exchanging pores. A widespread condition of supersaturation with respect to the solubility product of barium sulfate would develop, and precipitation of finely disseminated barite could

occur. The isotopic composition of sulfate in the barite would be nearly identical to that of the dissolved sulfate, approximately +16‰ for $\delta^{18}\text{O}(\text{SO}_4^{2-})$ and +20‰ for $\delta^{34}\text{S}(\text{SO}_4^{2-})$. Chemical analyses have determined that barium occurs widely in the aquifer strata (Gilkeson et al., 1978). The presence of secondary barite has not yet been confirmed; however, sampling groundwater from a broad region of the aquifer system established that the activities of barium and sulfate are in chemical equilibrium with the mineral phase barite—evidence that the mineral is present in the strata (Gilkeson et al., 1978).

The isotopic composition of dissolved sulfate in groundwater samples from well sites De Kalb-3 and De Kalb-4 (table 1A and fig. 1) is evidence that glacially recharged groundwater was present to the limit of the aquifer's confinement by the Maquoketa Shale Group. For this region of the aquifer system, the isotopic composition of the low dissolved-sulfate concentration (<10 mg/L) is anomalous. The $\delta^{18}\text{O}(\text{H}_2\text{O})$ of groundwater at these well sites is contemporary with present-day meteoric water. The primary source of dissolved sulfate in these groundwater samples is interpreted to be dissolution of secondary barite precipitated in response to glacial recharge.

Dissolution of secondary barite may also be an important source of dissolved sulfate in groundwater samples from well sites Kane-4 and Cook-2 that are located in the transition zone downgradient of the strong reducing zone. The $\delta^{34}\text{S}(\text{SO}_4^{2-})$ composition of the groundwater at Kane-4 and Cook-2 indicates that an additional source of dissolved sulfate is ^{34}S -enriched sulfate transported in groundwater from the strong reducing zone. Significantly, the $\delta^{18}\text{O}(\text{SO}_4^{2-})$ composition of groundwater samples from well sites in the strong reducing zone (+2.50‰ at Kane-2 and +4.77‰ at Kane-3) indicates that secondary barite precipitated by glacial recharge is not present at this time. It is postulated that bacterial sulfate reduction has consumed this source of sulfate; therefore, a source of barium other than secondary barite is required to explain the high dissolved-barium concentrations in groundwater at these well sites. Depletion of barite would allow dissolution of barium from other sources in the strata.

A factor complicating the interpretation of analytical data is that well sites Kane-2 and Kane-3 in the strong reducing zone are constructed to receive groundwater from the entire Cambrian-Ordovician aquifer system. Groundwater produced from these wells is a blend from all the rock strata. Moreover, these wells were developed with explosives to increase production of groundwater from the Ironton-Galesville Sandstone. Comparison of chemical analyses of groundwater from well sites Kane-2 and Kane-3 to other wells in close proximity that were not developed with explosives indicates that there is a significant vertical variation in the chemical composition of the groundwater in the aquifer system; groundwater produced from the Ironton-Galesville Sandstone has a lower dissolved-sulfate concentration and a significantly higher dissolved-barium concentration than groundwater produced from other strata in the aquifer system.

At well sites Kane-2 and Kane-3, the composition of groundwater indicates that both sulfate reduction and methane formation are occurring in microenvironments in the rock strata. It is significant that methane is found in groundwater at these well sites. According to observations made in several studies of marine sediments, methane does not occur until sulfate reduction is complete (Goldhaber and Kaplan, 1974). The presence of methane is evidence that sulfate reduction has gone to completion in some microenvironments of the aquifer system.

After sulfate reduction has depleted barite (BaSO_4) in the rock strata, another source of barium would possibly be dissolution of witherite (BaCO_3). Laboratory experiments have determined the solubility products of these mineral phases to be 10^{-10} for barite and $10^{-8.8}$ for witherite (Sillén, 1964). Witherite has a greater solubility than barite; however, in microenvironments where sulfate reduction is occurring, witherite may be less soluble than barite because of the increased concentration of the bicarbonate ion due to sulfate reduction. In fact, sulfate reduction may result in precipitation of secondary witherite. With the completion of sulfate reduction, the concentration of the bicarbonate ion would decrease, resulting in dissolution of secondary witherite.

In an earlier section of this paper it was reported that confined groundwater in the Cambrian-Ordovician aquifer system in the west-central

part of Illinois is depleted in ^{18}O . Over a several-county region the $\delta^{18}\text{O}_{(\text{H}_2\text{O})}$ ranges from approximately -11‰ to -12‰. The isotopic composition requires that recharge of the groundwater was related to glacial process. The groundwater in this region is highly mineralized; dissolved sulfate concentrations range from 500 mg/L to as great as 1500 mg/L. Analyses of groundwater at six well sites in this region yielded a median $\delta^{34}\text{S}_{(\text{SO}_4^{2-})}$ value of +17.37‰ with a range from +16.13‰ to +19.23‰. The source of the dissolved sulfate is interpreted to be dissolution of evaporite minerals. However, similarly to the situation described for northeastern Illinois, evaporite minerals are not known to occur in the aquifer strata, and the isotopic composition of the dissolved sulfate is anomalous compared to values determined for evaporites of Cambrian and Ordovician age.

It is proposed that glacial processes have had a large effect on the chemical composition of groundwater in this region of the aquifer system. Because of the limited information available at the present time, it is only possible to speculate on the glacial processes involved. During the Woodfordian Substage of the Wisconsinan glaciation, two glacial events are recognized that may have been important to recharge of groundwater into the flow system. First, the Woodfordian glacier moved into Illinois out of Lake Michigan approximately 23,000 years before the present (Kempton and Gross, 1971), and at the maximum advance the ice front occupied the ancient drainageway of the Mississippi River along the east side of Stark, Peoria, and Tazewell Counties (Willman and Frye, 1970). The ancient valley (now occupied in part by the Illinois River) may have been a significant zone of discharge for groundwater in the Cambrian-Ordovician aquifer system. Overburden pressures of the glacial ice sheet would have reversed regional hydraulic gradients and recharged basal meltwater into the flow system. Subglacial recharge could have occurred during the approximate 2,000-year interval that glacial ice was present in this setting.

The second glacial event occurred later with the advance into north-central Iowa of the late Woodfordian-age Des Moines Lobe of the Wisconsinan Laurentide ice sheet about 14,000 years before the present (Kemmis, Hallberg, and Lutenegger, 1981). The maximum advance of the glacial ice was to the vicinity of Des Moines, Iowa. For approximately 1,000 years, the ice

sheet was situated over the principal recharge area for strata of the Cambrian and Ordovician systems in Iowa (Horick and Steinhilber, 1978). The glacier overlaid bedrock that contains marine evaporite minerals of middle Devonian and Jurassic age. The $\delta^{34}\text{S}$ composition of evaporites of middle Devonian and Jurassic age (fig. 7) are similar to the isotopic composition of dissolved sulfate in groundwater of the aquifer system in west-central Illinois.

Further study of the Cambrian-Ordovician aquifer system in western Illinois and its relation to the flow system in Iowa is necessary to determine the role of glacial processes with respect to the composition of the groundwater. The multiple glaciations of the Pleistocene are thought to have had large effects. Gilkeson and Cowart (in press) speculate that glacial processes are important to the distribution of isotopes of the uranium-238 decay series in the aquifer system. In the present paper, speculation is restricted to the effects of the most recent glaciation (late Wisconsinan). Radiocarbon dating of groundwater may establish the importance of Wisconsinan glacial events to the chemical composition of groundwater in the flow system.

SUMMARY

High dissolved-barium concentrations in the Cambrian-Ordovician aquifer system of northeastern Illinois occur in groundwater that is anomalously depleted in dissolved sulfate. The dissolved-sulfate concentration is an important control on the dissolved-barium concentration due to the low solubility of the mineral phase barite (barium sulfate). The isotopic and chemical composition of the groundwater indicate that the depletion of dissolved sulfate was due to bacterially mediated reactions. Field measurements of the oxidation-reduction potential and analyses of total organic carbon determined that conditions for anaerobic bacterial metabolism exist in zones of the aquifer system that are depleted in dissolved sulfate. Other characteristics of groundwater in these zones that indicate bacterial sulfate reduction are the presence of dissolved hydrogen sulfide, increased alkalinity, and enrichment in ^{34}S in the residual dissolved sulfate.

Isotopic analyses determined two principal sources of dissolved sulfate for the Cambrian-Ordovician aquifer system in northeastern Illinois. The most significant source of dissolved sulfate in the unconfined region of the flow system is the oxidation of sulfide minerals, and the primary source of dissolved sulfate in the mineralized groundwater in the confined region of the flow system is from dissolution of marine evaporite minerals. Evaporite minerals are also the primary source for dissolved sulfate in mineralized groundwater in the aquifer system in west-central Illinois. The source of the marine evaporite minerals is problematic. Evaporites are not known to occur in the Cambrian and Ordovician strata of the flow system. Also the isotopic analyses determined the dissolved sulfate to have been derived from evaporites that are not of Cambrian or Ordovician age.

The depletion of ^{18}O in groundwater in the confined region of the aquifer system is evidence of the importance of glacial processes to recharge. Recharge related to glacial processes is proposed as an explanation of the anomalous isotopic composition of dissolved sulfate. Late Woodfordian ice sheets occupied Lake Michigan with ice margins in the northeastern corner of Illinois. It is proposed that the ice sheet reversed regional hydraulic gradients, and significant recharge to the Cambrian-Ordovician aquifer system occurred by subglacial flow of meltwater through the floor of Lake Michigan. A source of dissolved sulfate is marine evaporites of Silurian and Devonian age that underlie Lake Michigan.

At the maximum advance of the Woodfordian, glacial ice was present over the ancient Mississippi River Valley in central Illinois. In this setting, subglacial recharge of basal meltwater may have occurred to the Cambrian-Ordovician aquifer system in west-central Illinois. However, the most recent glacial event that may be related to recharge of groundwater to the flow system in west-central Illinois was the advance of the Des Moines Lobe over the principal region of recharge into the Cambrian and Ordovician strata in northern Iowa. The confined flow system in west-central Illinois may be an extension of the flow system in Iowa. Possible sources of dissolved sulfate are evaporites of Jurassic age present in northern Iowa or evaporites of middle Devonian age present in central Iowa. Further research is necessary to establish the relation of glacial processes to the composition of groundwater in the flow system.

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