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ISOTOPIC STUDIES OF THE NATURAL SOURCES OF
RADIUM IN GROUNDWATER IN ILLINOIS

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ABSTRACT

Stable and radioactive isotopes in groundwater were studied in an investigation of the natural geologic sources of high concentrations of ^{226}Ra and ^{228}Ra in confined aquifers in the Cambrian and Ordovician bedrock of northern Illinois. The covariation of $\delta^{18}\text{O}$ and δD determined that the groundwater has a meteoric isotopic composition. Groundwater in unconfined aquifers has $\delta^{18}\text{O}$ values (-6.6 to -7.9 ‰) that are similar to contemporary meteoric water. However, a source of recharge related to glaciation is required for groundwater in confined aquifers of the Cambrian and Ordovician that is significantly depleted in ^{18}O ($\delta^{18}\text{O}$ values range to -12.7 ‰ and are less than -9 ‰ over large regions). The covariation of $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ in dissolved sulfates determined a mixing line between two sources; oxidation of sulfide minerals and dissolution of marine evaporites. Dissolved sulfates from evaporite sources are present in large concentrations in confined aquifers but are of a different isotopic composition than evaporites of Cambrian or Ordovician age. Glaciation may be important with regard to recharge of the sulfates. The $^{234}\text{U}/^{238}\text{U}$ activity ratio in groundwater from the Cambrian and Ordovician are unexpectedly high; values range from 2.1 to 40.7. The lowest ratios occur in primary recharge zones. In confined aquifers values are greater than 20 over large regions. Alpha recoil damage is a mechanism that contributes to the disequilibrium. However, the regional variation in activity ratios and in ^{234}U concentrations supports the concept that glacial recharge has contributed to the high ratios. Radiological and geochemical mechanisms that partition ^{238}U , ^{234}U and ^{230}Th on the sandstone matrix are important to the dissolved ^{226}Ra concentration.

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The authors are grateful to the staff members of the United States Geological Survey who provided the opportunity to collect groundwater samples from packer tests that they conducted at deep boreholes near Zion in Lake County, and near Galena in Jo Davies County. The packer testing was supervised by Harley Young of the Madison, Wisconsin office of U.S.G.S.

This research program greatly benefitted from earlier studies by other scientists. Henry Lucas of the Argonne National Laboratory provided historical analyses on radium-226 and radium-228 in groundwater. The high disequilibrium between uranium isotopes in groundwater in Illinois was first noted by J. K. Osmond of Florida State University.

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INTRODUCTION

This report presents findings from an isotopic study of mechanisms responsible for the natural occurrence of two isotopes of the radioactive element radium (radium-226 in the uranium-238 decay series and radium-228 in the thorium-232 decay series) in groundwater of Illinois at concentrations that exceed the limits imposed in the National Interim Primary Drinking Water Regulations (U.S. Environmental Protection Agency, 1975). The present report is part of a larger research program that is concerned with geochemical mechanisms that control the occurrence of radium and barium in groundwater. Radium and barium are both alkaline-earth cations with similar chemical properties.

The research program has generated several reports. Gilkeson et al. (1978) presented analyses of rock samples for barium and radioactive elements, and established that the dissolved sulfate concentration was an important control on the concentration of barium in groundwater. Perry, Grundl, and Gilkeson (1982) reported on the variation of stable isotopes of oxygen, hydrogen and sulfate in groundwater from the Cambrian and Ordovician bedrock and established the importance of glaciation to the recharge of groundwater in confined aquifers. Gilkeson, Perry, and Cartwright (1981) discussed evidence that the anomalous depletion of sulfate in groundwater with high barium concentrations was due to bacterially mediated chemical reactions. Gilkeson and Cowart (1982) described the extreme enrichment in uranium-234 in groundwater from the Cambrian and Ordovician bedrock. Gilkeson et al.

(1983) presented findings on radiological and geochemical mechanisms that control the concentrations of dissolved radioactive elements including radium, uranium, radon, and thorium.

This report presents maps that show the distribution of stable and radioactive isotopes in groundwater from the Cambrian and Ordovician bedrock in northern Illinois and discusses mechanisms that are responsible for the regional trends. Stable isotopes analyzed include oxygen and hydrogen in the water molecule and oxygen and sulfur in the dissolved sulfate molecule. Radioactive isotopes include radium-226, radium-228, uranium-238 and uranium-234. Field methods used in the collection and preservation of samples are described in Gilkeson et al. (1983). Analytical methods for stable isotopes are presented in Perry, Grundl and Gilkeson (1982) and Grundl (1980). Analytical methods for the radioactive isotopes are discussed in Gilkeson et al. (1983), and Osmond and Cowart (1976).

HYDROGEOLOGIC SETTING AND MAJOR IONS IN GROUNDWATER

The study area for this report is the part of northern Illinois where public and industrial groundwater supplies are produced from aquifers in the Cambrian and Ordovician bedrock (fig. 1). South of the study area water quality in the Cambrian and Ordovician is undesirable because of the high concentrations of dissolved minerals in the groundwater.

A generalized column of rock-stratigraphic units in northern Illinois is shown in figure 2. The Cambrian and Ordovician bedrock is composed of thick sections of sandstone and dolomite interbedded with shale. In downward order, the stratigraphic units are the Maquoketa Shale Group, Galena and Platteville Dolomite Groups, Glenwood-St. Peter Sandstone and Prairie du Chien Group of Ordovician age, the Eminence Formation, Potosi Dolomite, Franconia Formation, Ironton-Galesville Sandstone, Eau Claire Formation, and Mt. Simon Sandstone. Shale in the upper part of the Eau Claire Formation is a significant aquitard hydraulically separating the Ironton-Galesville Sandstone from the Elmhurst Sandstone Member (basal Eau Claire) and the Mt. Simon Sandstone.

On a regional scale the significant aquifers are the sandstones, including the St. Peter, the Ironton-Galesville, the Elmhurst Member in the basal Eau Claire Formation, and the Mt. Simon. The Ironton-Galesville Sandstone is the most productive aquifer over a major part of the study area. Production of groundwater from wells is often increased through the detonation of explosives in the Ironton-Galesville section of the open borehole.

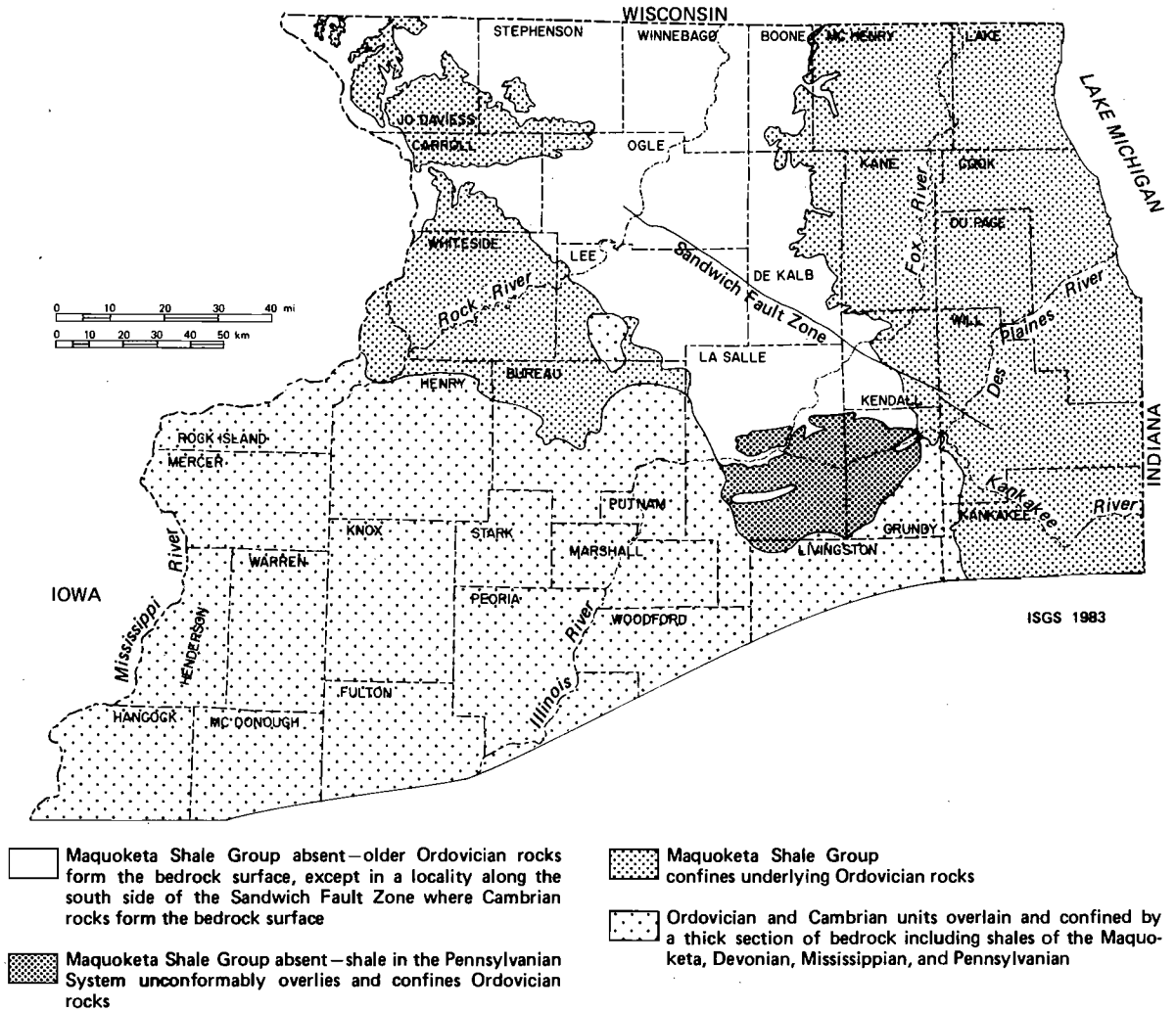


FIGURE 1. Geologic map of the area of northern Illinois where groundwater supplies are produced from the Cambrian and Ordovician bedrock. Sources of information are Willman et al. (1967) and Willman et al. (1975).

SYSTEM	SERIES	GROUP OR FORMATION	LOG	THICKNESS (m)	DESCRIPTION
Quaternary	Pleistocene			0-180	Unconsolidated glacial deposits - pebbly clay (fill), silt, and gravel; loess (windblown silt); and alluvial silt, sand, and gravels.
Tertiary and Cretaceous				0-30	Sand and silt.
Pennsylvanian				0-150	Mainly shale with thin sandstone, limestone and coal.
Mississippian	Valmeyeran	St. Louis Salem Warsaw Keokuk- Burlington		0-180	Limestone; cherty limestone; green, brown and black shale; silty dolomite.
	Kinderhookian				
Devonian				0-120	Shale, calcareous; limestone strata, thin.
Silurian	Niagaran			0-140	Dolomite, silty at base, locally cherty.
	Alexandrian	Kankakee Edgewood			
Ordovician	Cincinnatian	Maquoketa		0-75	Shale, gray or brown; locally dolomite and/or limestone, argillaceous.
	Champlainian	Galeña		0-140	Dolomite and/or limestone, cherty; Dolomite, shale partings, speckled; Dolomite and/or limestone, cherty, sandy at base.
		Platteville			
		Glenwood			
		St. Peter		0-200	Sandstone, fine- and coarse-grained; little dolomite; shale at top. Sandstone, fine- to medium-grained, locally cherty red shale at base.
Canadian	Prairie du Chien Group Shakopee New Richmond Oneota		30-400	Dolomite, sandy, cherty (oolitic), sandstone. Sandstone, interbedded with dolomite. Dolomite, white to pink, coarse-grained, cherty (oolitic), sandy at base.	
	Eminence and Potosi Franconia				
Cambrian	Crolxan	Ironton		20-80	Sandstone, fine- to medium-grained, well sorted, upper part dolomitic.
		Galeeville		75-140	Shale and siltstone; dolomite, glauconitic; sandstone, dolomitic, glauconitic.
		Eau Claire Proviso Lombard Elmhurst		150-790	Sandstone, coarse-grained, white, red in lower half, lenses of shale and siltstone, red, micaceous.
		Mt. Simon			

FIGURE 2. Generalized column of rock-stratigraphic units in northern Illinois.

The yield of groundwater from the dolomite bedrock units is variable, depending upon the number and areal interconnections of joints, fractures, and crevices. The contribution of groundwater from the shale bedrock to the open borehole is generally small.

Figure 1 shows that in most of the study area the Cambrian and Ordovician bedrock is overlain and confined by shale. In the southwestern part of the study area (the region west of the Illinois River in figure 1) the confining units include shale of the Maquoketa, Mississippian, and Pennsylvanian. In the southwestern region the Pennsylvanian forms the bedrock surface except where absent along the western margin. In the eastern and northwestern part of the study area the Mississippian and Pennsylvanian are absent and confinement is by the Maquoketa Shale Group. In these regions the Maquoketa or the Silurian Dolomite forms the bedrock surface. In a restricted region of La Salle and Grundy County (fig. 1) the Maquoketa and younger rocks are absent because of erosion and the Cambrian and Ordovician are confined by shales of the Pennsylvanian. Note that in a small locality of La Salle County and a small locality along the Illinois River in Grundy County, the Pennsylvanian is absent and the Galena and Platteville or the Glenwood-St. Peter forms the bedrock surface.

Figure 1 shows that the Maquoketa Shale Group is absent over much of the north-central and northwestern part of the study area, and that older rocks form the bedrock surface. In the northwestern region the Maquoketa Shale Group is present on some uplands and confines underlying rocks. In some localities where the Maquoketa is absent, fine-grained glacial drift and/or dense unfractured dolomite of the Galena and Platteville Groups serve as confining units.

The major ion chemical composition of groundwater in the Cambrian and Ordovician are discussed briefly in this report. Additional information is presented in Sasman et al. (1982) and Gilkeson et al. (1983). The regional variation in total dissolved solids is illustrated in figure 3. Over the northern part of the study area dissolved solids range from approximately 250 to 500 mg/L. The figure shows that concentrations increase to the east, south and southwest. Dissolved solids concentrations are greater than 1000 mg/L over eastern Cook County and southern Will, Grundy, and La Salle Counties. Concentrations greater than 1000 mg/L occur in an extensive region of the southern and western parts of the study area and exceed 3000 mg/L along the southwestern margin.

In this report the classification of Freeze and Cherry (1979) is used to categorize groundwater based on total dissolved solids. The categories are as follows: fresh water, 0-1000 mg/L; brackish water, 1000-10,000 mg/L; saline water, 10,000-100,000 mg/L; brine water, greater than 100,000 mg/L.

The majority of wells in the southwestern region are constructed to produce groundwater from the Galena-Platteville and/or St. Peter. Figure 3 shows that some wells are completed only in the Galena-Platteville. Water quality in these wells is very similar to water quality in nearby wells that are also open to the St. Peter. Crevices and fractures in the dolomite may be hydraulically open to the sandstone and when these wells are pumped, a major component of groundwater is probably produced from the St. Peter. A few wells located in the southwestern part of Knox County and the northwestern part of Fulton County

produce groundwater from the Ironton-Galesville that is not more mineralized than groundwater from shallower aquifers. In fact, the limited information indicates that the Ironton-Galesville may have better water quality than the Galena-Platteville or St. Peter.

An interesting feature on figure 3 is the zone of less mineralized groundwater that extends southward through Warren and Knox County. Dissolved solids concentrations are less than 1500 mg/L through the central part of Warren County. Concentrations increase rapidly to the south and west of the zone. The zone is also present in the regional variation of dissolved sulfates (fig. 4) and $\delta^{18}O$ in the water molecule (fig. 5). Speculation on the relation of the zone to glacial recharge is presented in the discussion section of this report.

The major ions in groundwater that has less than 500 mg/L dissolved solids are calcium, magnesium, and bicarbonate. Sulfate and chloride are generally present at low concentrations in the dilute groundwater. However, the concentrations of these ions become significant in confined regions where the total dissolved solids are greater than 500 mg/L. The regional variation in the concentration of dissolved sulfate is presented in figure 4. Sulfate concentrations increase rapidly across the eastern side of Cook County and exceed 800 mg/L in the southeastern corner of the county. The highest sulfate concentrations are present in the southwestern region of the study area. Concentrations are greater than 200 mg/L over most of the region and exceed 600 mg/L over a large area. Very low concentrations of dissolved sulfate are present in a region of northeastern Illinois where groundwater

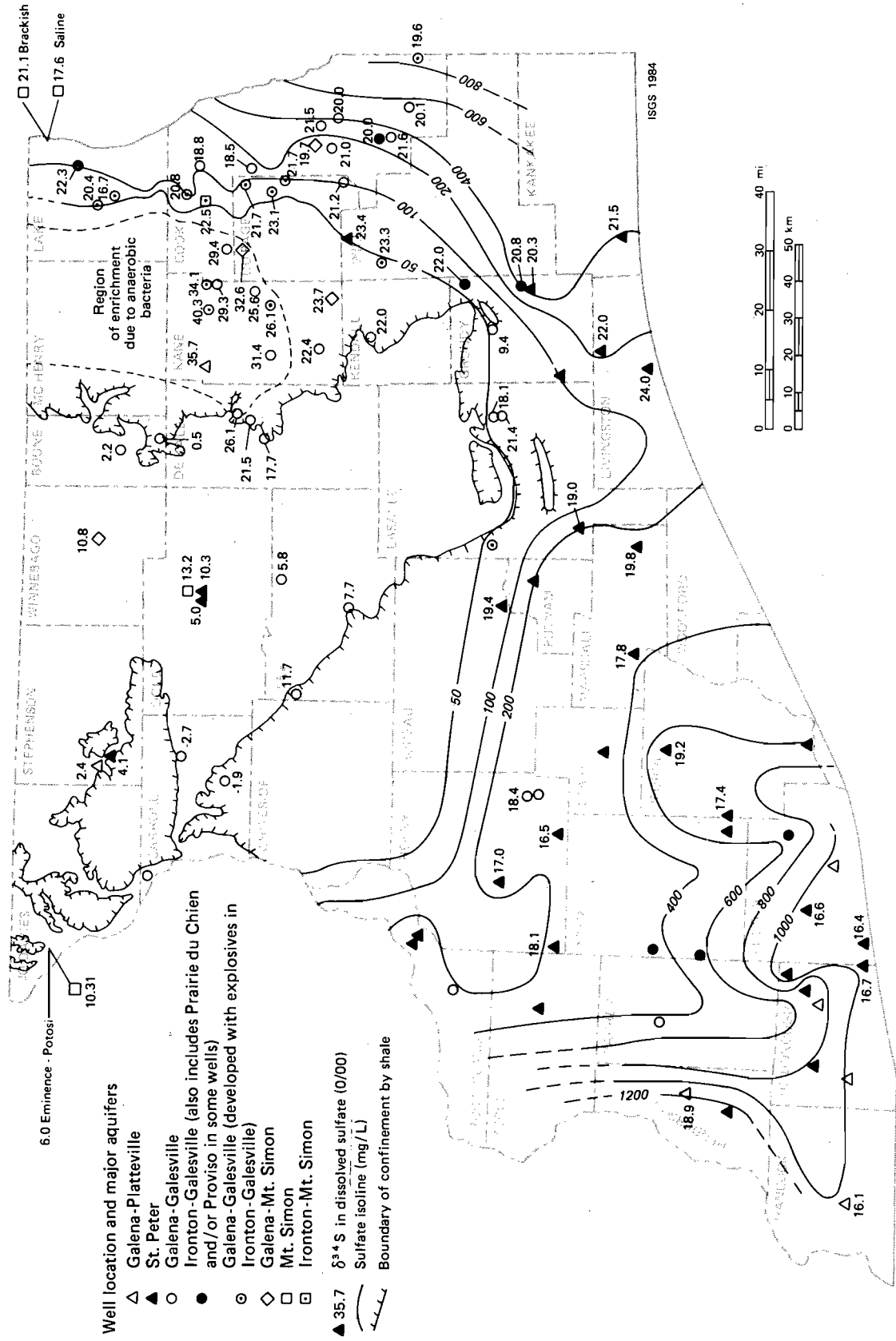


FIGURE 4. Distribution of dissolved sulfate in groundwater from wells in the Cambrian and Ordovician bedrock. Symbols depict major aquifers for discrete wells. Numerical values shown at wells are the $\delta^{34}\text{S}$ of dissolved sulfate.

from the Cambrian and Ordovician has high dissolved barium concentrations. Here the depletion of sulfates is caused by bacterially mediated reactions in an anaerobic environment (Gilkeson, Perry, and Cartwright, 1981). The region of sulfate depletion and bacterial enrichment of $\delta^{34}\text{S}$ in the residual sulfate is shown in figure 4.

Groundwater in the Cambrian and Ordovician with less than 500 mg/L dissolved solids generally has less than 25 mg/L chlorides. However, chloride concentrations are commonly greater than 100 mg/L in groundwater with dissolved solids greater than 1000 mg/L. Chloride concentrations are greater than 250 mg/L throughout most of the study area where dissolved solids are greater than 1500 mg/L. An interesting feature is the relatively higher concentration of chloride in the south-central region of the study area (southern La Salle and Grundy Counties, southwestern Will County, western Kankakee County, Livingston and Woodford Counties, and eastern Marshall, Putnam and Bureau Counties). Chloride concentrations are greater than 500 mg/L at wells in Livingston, southern La Salle, Woodford and eastern Marshall Counties. Sodium and chloride are major ions in groundwater from these wells.

STABLE ISOTOPES IN GROUNDWATER

During this study, isotope ratios were determined for the water and the sulfate molecules: The ratio of oxygen -18 to oxygen -16 $\{\delta^{18}O\}$ and the ratio of hydrogen -2 (deuterium) to hydrogen -1 $\{\delta D\}$ were calculated for the water molecule. The ratio of sulfur -34 to sulfur -32 $\{\delta^{34}S\}$ and the ratio of oxygen -18 to oxygen -16 $\{\delta^{18}O\}$ were calculated for the sulfate molecule. The isotope ratios are expressed in delta units (δ) as per mille (parts per thousand, $^0/_{00}$) differences related to a standard. In this research, the δD and $\delta^{18}O$ are expressed as per mille differences compared to the VSMOW standard of ocean water (Gonfiantini, 1978), and the $\delta^{34}S$ analyses referenced to Canyon Diablo meteoritic troilite (Rees, 1978).

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. As 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 $\delta^{18}O$ composition of precipitation correlates on a global basis according to the equation

$$\delta D^0/_{00} = 8\delta^{18}O + 10 \quad (1)$$

that is known as the meteoric water line (Friedman, 1953; Craig, 1961; Dansgaard, 1964).

The isotopic composition of meteoric water is preserved after the water infiltrates the soil and enters a groundwater flow system. However, 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. Research by Clayton et al. (1966) established that brines in the Illinois, Michigan, and Alberta basins were enriched in ^{18}O . The high temperatures in the deep flow systems were believed to be the major control on the ^{18}O enrichment through exchange with the aquifer strata.

In the present research, analyses for both δD and $\delta^{18}\text{O}$ were conducted on groundwater samples that were collected from eight wells in the study area. The range in temperature and total dissolved minerals for the eight samples encompasses the variation that occurs in fresh and brackish groundwater from the Cambrian and Ordovician in the study area. The covariation of δD and $\delta^{18}\text{O}$ in the groundwater samples exhibited a close relationship to the meteoric water line and Perry, Grundl and Gilkeson (1981) concluded that exchange between the water molecule and the aquifer rocks has been insignificant and that groundwater in the study area has retained a meteoric isotopic composition.

The regional variation of $\delta^{18}\text{O}$ in the water molecule for groundwater from aquifers in the Cambrian and Ordovician is from -6.6 to $-12.7^{\circ}/_{00}$ (fig. 5). In the north-central and northwestern region of the study area, the variation is from $-6.6^{\circ}/_{00}$ to $-7.9^{\circ}/_{00}$, a range that is comparable to contemporary meteoric water in northern Illinois (Graf, Friedman, and Meents, 1965). The heaviest isotopic values are

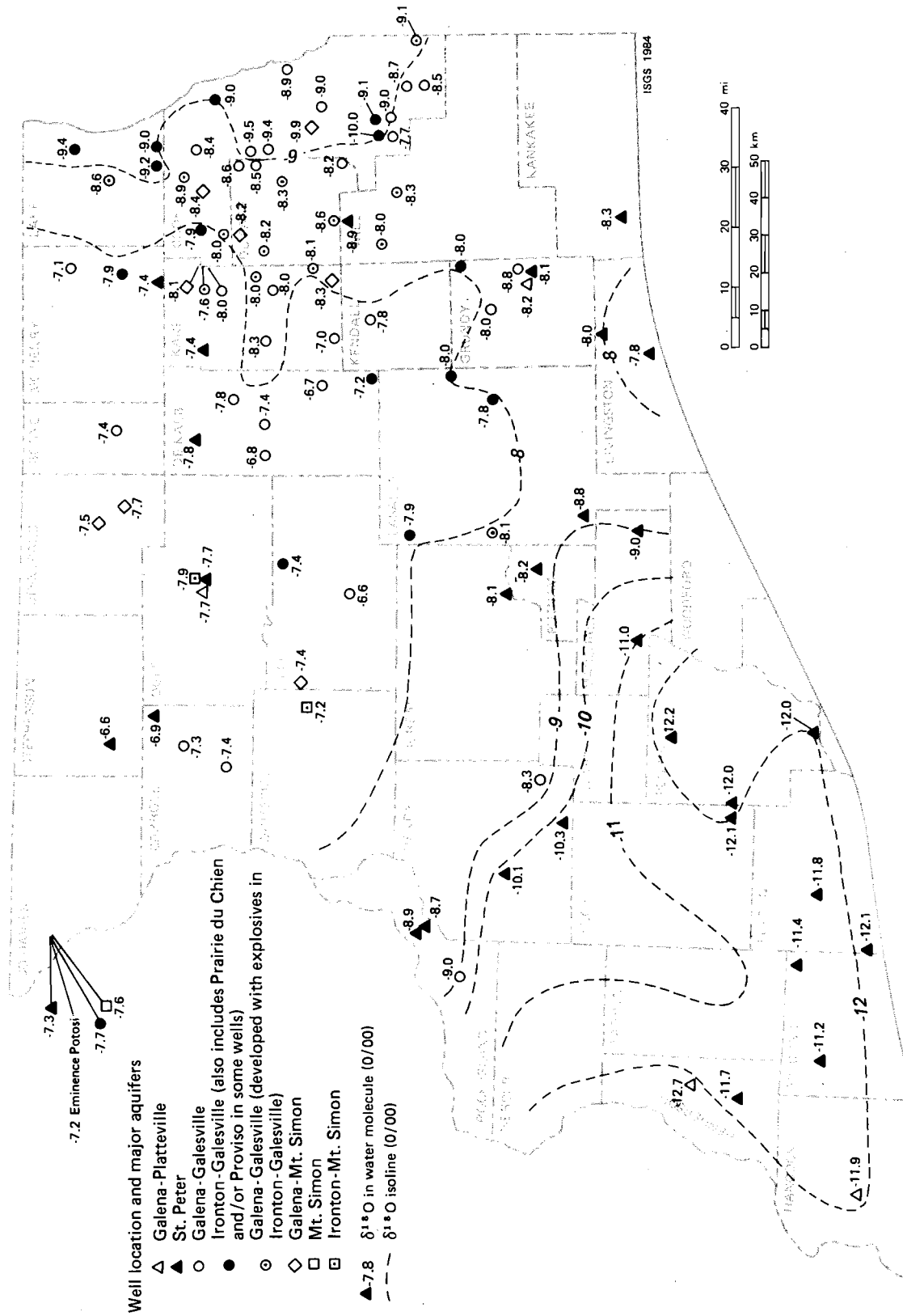


FIGURE 5. Distribution of $\delta^{18}\text{O}$ in groundwater from supply wells in the Cambrian and Ordovician bedrock. Symbols depict major aquifers for discrete wells.

present in groundwater in primary recharge zones to the Cambrian and Ordovician. Downgradient of the recharge zones the values for $\delta^{18}O$ become lighter.

Figure 5 illustrates that groundwater in confined regions of the study area are depleted in ^{18}O compared to the contemporary value. Perry, Grundl, and Gilkeson (1982) concluded that a source of recharge related to glaciation was required for groundwater in confined regions of the study area that is significantly depleted in ^{18}O . $\delta^{18}O$ values of -8 to $-10^0/00$ are present over a large region in the eastern part of the study area with values ranging from -9 to $-10^0/00$ in eastern Lake and Cook Counties. The most depleted values are present in the southwestern region of the study area. Values are less than $-9^0/00$ over most of the region and range to $-12.7^0/00$. The most negative values are along the western, southern and eastern margins of the region.

The isotope data suggests a zone with $\delta^{18}O$ values between -10 to $-11^0/00$ extends southward through Knox and Warren Counties. This zone is also shown by the variation in total dissolved solids (fig. 3) and dissolved sulfate (fig. 4). The significance of the zone to multiple glacial recharge events is considered in the discussion section of this report.

ISOTOPIIC VARIATION IN THE DISSOLVED SULFATE MOLECULE

Within the study area, there is a great variation in dissolved sulfate concentration in groundwater of the Cambrian and Ordovician with large concentrations present in confined regions (fig. 4). The

isotopic variation of $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ in dissolved sulfate was investigated to provide information on the geologic sources of the sulfate. In natural systems, sulfur is cycled between sulfate and sulfide reservoirs. These reservoirs have characteristic sulfur isotopic compositions (Holser and Kaplan, 1966).

In natural groundwater systems the reduction of sulfate to sulfide requires anaerobic biologic mediation. The anaerobic bacteria preferentially reduce the light sulfur isotope (^{32}S) to form sulfides. Although a large fractionation of sulfur isotopes occurs during reduction of sulfate to sulfides, there is not a significant fractionation during the precipitation or dissolution of sulfur-bearing minerals (Claypool et al., 1980). Therefore, dissolved sulfates that are derived from oxidation of sulfide minerals will have an isotopically light sulfur composition.

The isotopic composition of sulfur in 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). Dissolved sulfate derived from dissolution of marine evaporites such as gypsum or anhydrite will have an isotopic composition that reflects the geologic age of the source.

The covariation of sulfur and oxygen isotopes in dissolved sulfate for 82 groundwater samples collected from wells located throughout the study area is shown in figure 6. The relationship between $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ for 69 of the groundwater samples is described by the regression line,

$$\delta^{34}\text{S} = 1.26 \delta^{18}\text{O} + 0.46 \quad (2)$$

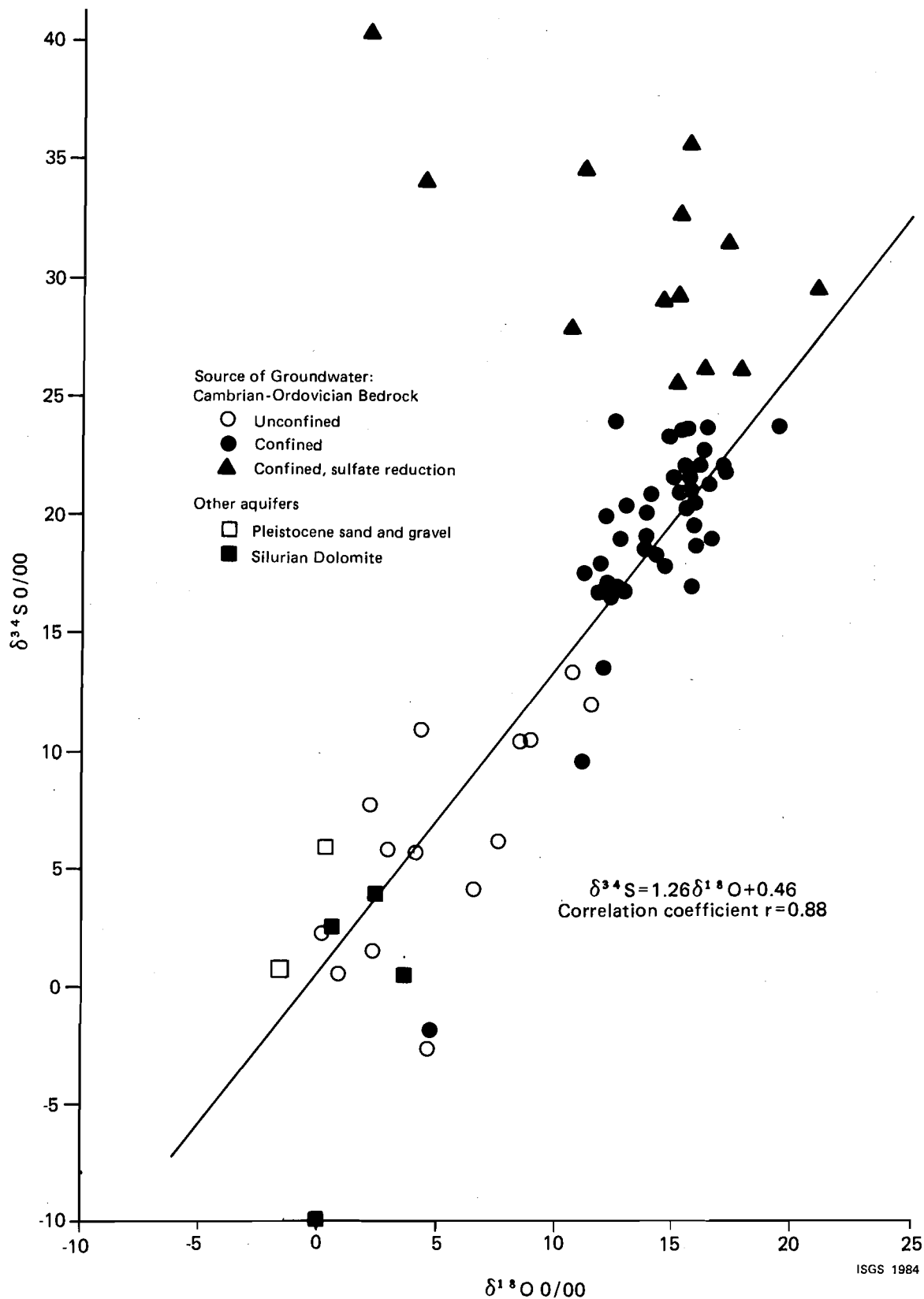


FIGURE 6. Covariation $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ in dissolved sulfate in groundwater from wells in northern Illinois. The majority of samples are from the Cambrian and Ordovician. A few samples are from the glacial drift and from the Silurian Dolomite.

with a correlation coefficient, r , of 0.88. The well-correlated data set confirms the tentative conclusion of Perry, Grundl, and Gilkeson (1982) that the isotope variation represents a mixing line between sulfates of two dominant compositions; isotopically light sulfates derived from oxidation of sulfide minerals and isotopically heavier sulfates derived from dissolution of marine evaporites. Groundwater samples in the Cambrian and Ordovician that display the lightest values are in primary recharge zones in the north-central and north-western parts of the study area (fig. 4). The values in these samples are similar to the values for groundwater samples from the glacial drift and from the Silurian Dolomite in northeastern Illinois. The covariation of sulfur and oxygen isotopes in two samples from sand and gravel deposits and in four samples from the Silurian Dolomite are shown in figure 6. The Silurian Dolomite in northern Illinois is believed to be a significant source for the light sulfate in groundwater. Disseminated sulfide minerals (primarily marcasite, lesser amounts of pyrite and sphalerite) occur in the Racine Formation of the Silurian (Donald Mikulic, personal communication). An additional source of light sulfur is the asphaltum that is common in vugs in reefs of the Racine (Bretz, 1939). Analyses in the present research and in Holt, Engelkeimer and Venters (1972), have determined that the $\delta^{34}\text{S}$ for six groundwater samples from wells finished in the Silurian Dolomite in northeastern Illinois ranges from -13.4 to +0.86⁰/₀₀. The light isotopic composition indicates that sulfides are the source of the dissolved sulfates.

Glacial ice advances out of Lake Michigan during the Illinoian and Wisconsinan eroded and incorporated dolomite of the Racine Formation into the glacial drift of northern Illinois (Bretz, 1939). Therefore, sulfides from the Silurian are a potential source for the isotopically light sulfate dissolved in groundwater of the glacial drift and in the Cambrian and Ordovician bedrock in zones of primary recharge in north-central and northwestern Illinois.

Downgradient of the primary recharge zones in northern Illinois, with an increase in flow path and residence time of groundwater in the bedrock, the $\delta^{34}\text{S}$ of dissolved sulfate changes to heavier values. Examples of this trend are shown by wells on an upland in central Ogle County and by samples collected at the USGS packer test near Galena in Jo Davies County (fig. 4). In the Ogle County setting values vary from $+5.0^0/_{00}$ for a well open to the Galena-Platteville, to $+10.3^0/_{00}$ for groundwater from the St. Peter, to $+13.2^0/_{00}$ for a sample from a well open in the interval from the Ironton-Galesville into the Mt. Simon. At the packer test in Jo Davies County values ranged from $+6.0^0/_{00}$ for a sample from the Eminence and Potosi Dolomite to $+10.3^0/_{00}$ for a sample from the Mt. Simon Sandstone. The observed trends are consistent with mixing between sulfates of two dominant compositions.

Groundwaters that exhibit a dominant composition of dissolved sulfate from dissolution of marine evaporites are present where the Cambrian and Ordovician aquifers are confined over large regions. As shown in figure 4 $\delta^{34}\text{S}$ values range from $+16.1$ to $+19.4^0/_{00}$ in the southwestern part of the study area in groundwater with dissolved

sulfate concentrations that vary from 100 to greater than 1200 mg/L. In the eastern part of the study area the variation is from +16.7 to +24⁰/₀₀ in groundwater with dissolved sulfate concentrations ranging from 50 to greater than 800 mg/L.

Perry, Grundl, and Gilkeson (1982) concluded that a major source of dissolved sulfate in groundwater from the confined aquifers is dissolution of evaporite minerals, but recognized that the source of the evaporites was problematic. Average $\delta^{34}\text{O}$ values for marine evaporites of North America are approximately +30⁰/₀₀ in the Cambrian and Ordovician Systems (Claypool et al., 1980). The $\delta^{34}\text{S}$ of 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.

Gilkeson, Perry and Cartwright (1981) advanced a glacial recharge mechanism to explain the anomalous isotopic composition of both the water molecule and the dissolved sulfate present in the confined Cambrian and Ordovician aquifers.

Figure 6 shows that a number of groundwater samples plot above the mixing line with $\delta^{34}\text{S}$ values ranging from +25.6 to +40.3⁰/₀₀. The ^{34}S enriched samples are from a region of northeastern Illinois where dissolved sulfate concentrations are anomalously low and the concentration of dissolved barium exceeds the drinking water standard. Gilkeson, Perry, and Cartwright (1981) interpret the depletion of dissolved sulfate is due to bacterially mediated reactions occurring

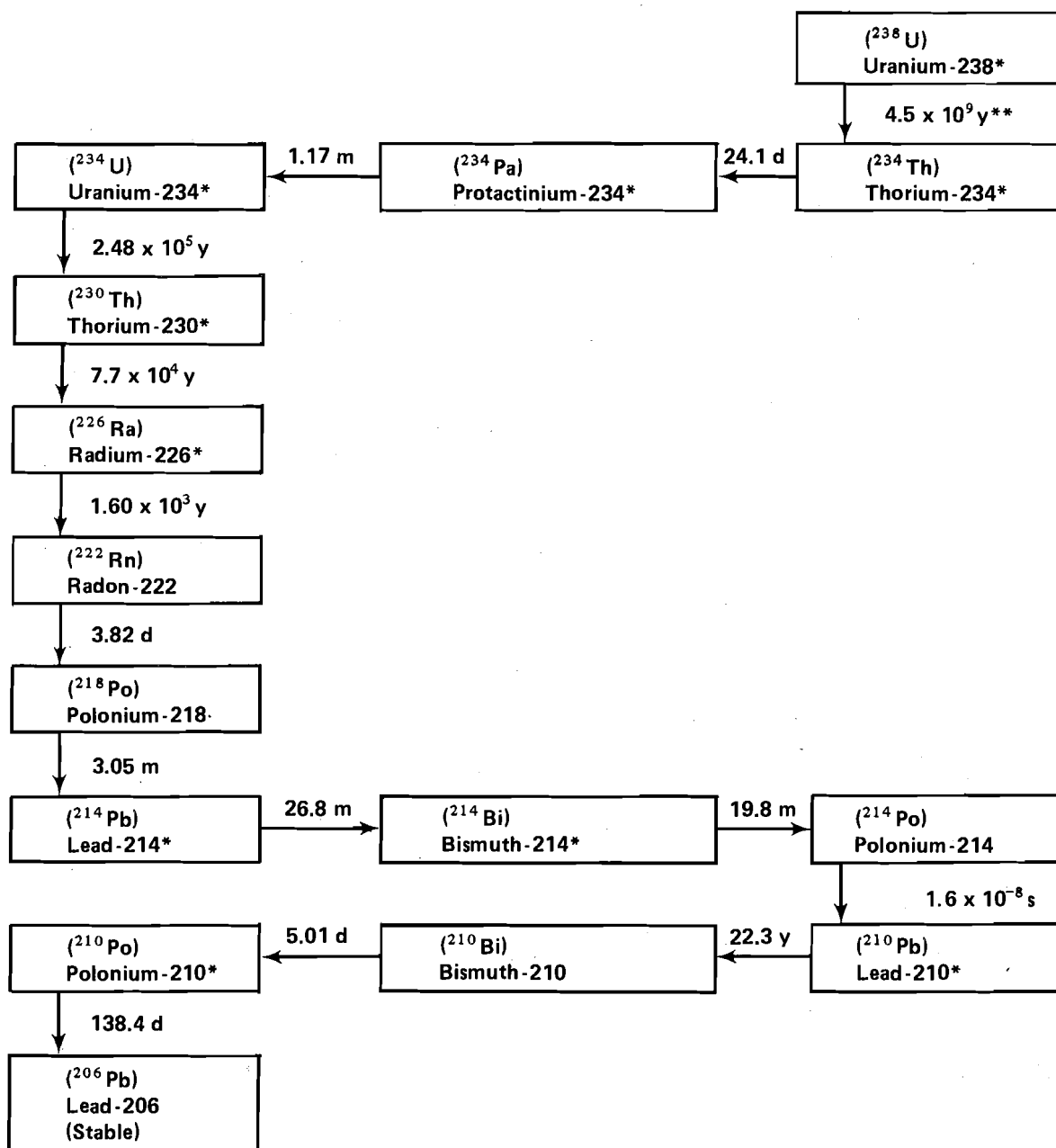
in anaerobic environments. Characteristics of the groundwater that support this interpretation are the presence of hydrogen sulfide, increased alkalinity, and enrichment of the heavy sulfur isotope (^{34}S) in the residual dissolved sulfate. Chemical and stable isotope analyses indicate that the region of microbial sulfate reduction (shown in fig. 4) includes east-central De Kalb County, central and northern Kane County, northwestern Du Page County, northwestern Cook County, western Lake County, and central and eastern McHenry County.

RADIOISOTOPES IN GROUNDWATER

The study of geochemical mechanisms that control the occurrence of radium-226 (^{226}Ra) and radium-228 (^{228}Ra) in groundwater requires knowledge of the distribution of other radioactive elements in the decay series. The naturally occurring long-lived radioactive elements uranium-238 (^{238}U) and thorium-232 (^{232}Th) are the parents of the radioactive decay series shown in figures 7 and 8. Geochemical and radiological mechanisms that control the occurrence of ^{226}Ra and ^{228}Ra in groundwater are presented in a report by Gilkeson et al (1983). The mechanisms are discussed briefly here.

^{228}Ra is the first daughter nuclide in the ^{232}Th decay series. Because of its short half-life (5.75 years), ^{228}Ra will not migrate significant distances in confined aquifers from its site of generation. Thorium ions have very slight solubilities in groundwater; therefore, the distribution of ^{232}Th in the bedrock is an important control on the occurrence of ^{228}Ra in groundwater.

The mechanisms that control the occurrence of ^{226}Ra in groundwater are more complex than for ^{228}Ra because of its longer half-life (1600 years), and because of the position of the nuclide in the ^{238}U decay series. The precursor nuclides to ^{226}Ra , in order of occurrence, are ^{238}U , ^{234}Th , ^{234}Pa , ^{234}U , and ^{230}Th . Significant disequilibrium between the nuclides may occur in groundwater flow systems because of differences in the chemical and radiological properties of the nuclides. An important source of ^{226}Ra in groundwater in confined aquifers in the Cambrian and Ordovician is the accumulation of nuclides of ^{238}U , ^{234}U ,



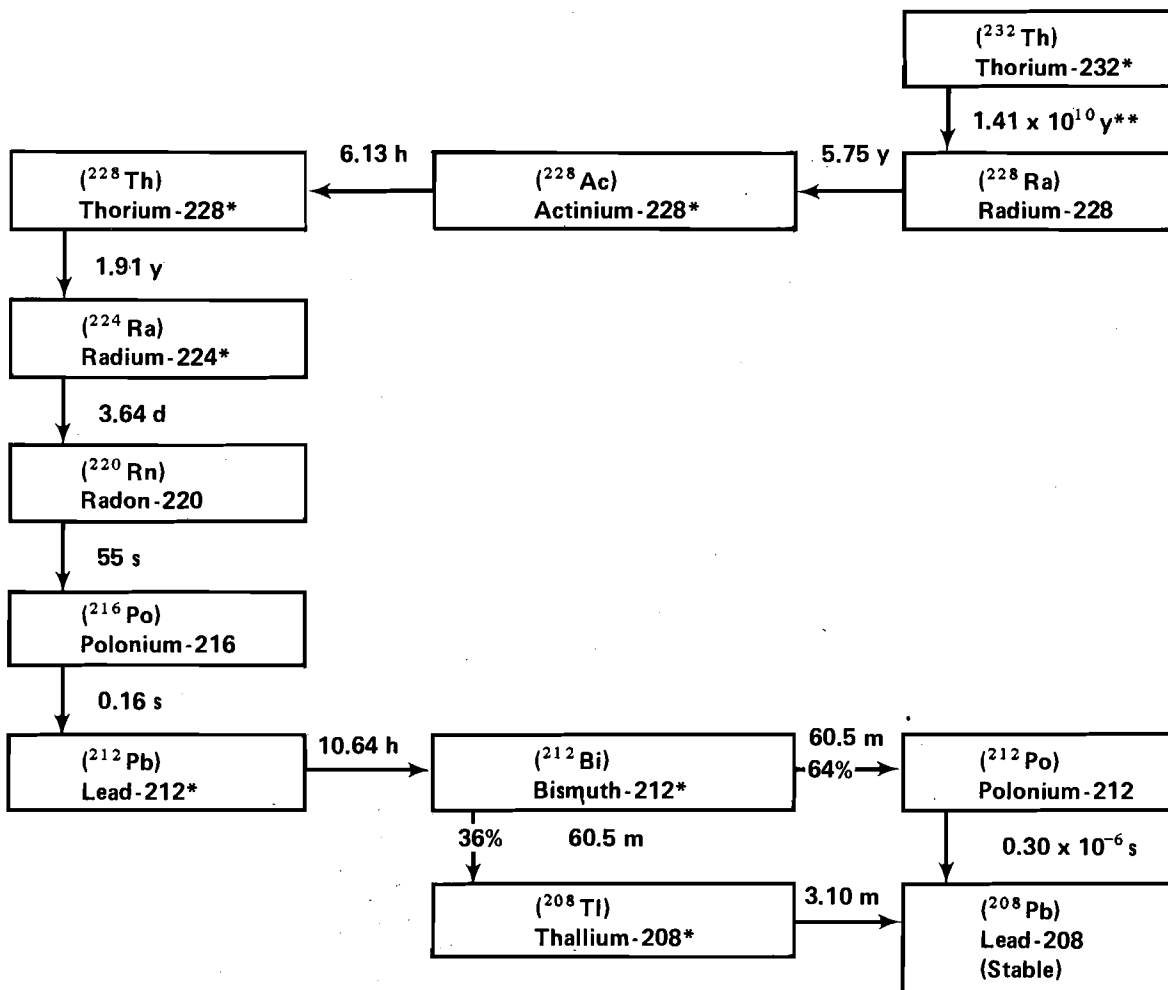
Note: Vertical direction represents alpha decay; horizontal direction represents beta decay.

* Also gamma emitters

** Times shown are half-lives: y = years; d = days; h = hours; m = minutes; s = seconds

ISGS 1983

FIGURE 7. The radioactive decay series of uranium-238.



Note: Vertical direction represents alpha decay; horizontal direction represents beta decay.

* Also gamma emitters

** Times shown are half-lives: y = years; d = days; h = hours; m = minutes; s = seconds

ISGS 1983

FIGURE 8. The radioactive decay series of thorium-232.

and ^{230}Th on the sandstone matrix due to radiological mechanisms (alpha recoil damage) and to the groundwater transport of uranyl ions. The desorption of ^{226}Ra from the sandstone matrix is directly related to the ionic strength of groundwater.

URANIUM ISOTOPES

Analyses for ^{234}U and ^{238}U were performed on fresh and brackish groundwater samples collected from 130 wells in Illinois that produce groundwater from the Cambrian and Ordovician bedrock. The mass concentration of dissolved uranium ranged from less than $0.002\ \mu\text{g/L}$ to $1.10\ \mu\text{g/L}$; the combined activity concentration of ^{234}U and ^{238}U in the samples ranged from less than $0.1\ \text{pCi/L}$ to $7.9\ \text{pCi/L}$. All samples with activity concentrations greater than $1.0\ \text{pCi/L}$ were greatly enriched in ^{234}U . The greatest dissolved uranium concentration measured in the study area was a mass concentration of $15.3\ \mu\text{g/L}$ and a combined activity concentration of $92.2\ \text{pCi/L}$ in a saline groundwater sample collected from the basal section of the Mt. Simon at the U.S.G.S. borehole in Lake County.

The oxidation-reduction potential is an important control on the dissolved uranium concentration. Gilkeson et al. (1983) determined that dissolved uranium concentrations were less than $0.08\ \mu\text{g/L}$ in all groundwater samples in the study area with Eh values of -50 millivolts or lower.

Figure 9 presents the distribution of the $^{234}\text{U}/^{238}\text{U}$ activity ratio for groundwater samples collected from the Cambrian and Ordovician. The ratios range from 2.0 for samples from wells in the southeastern

corner of De Kalb County and central Ogle County to 40.7 for a sample from a well in the southern part of La Salle County. The lowest ratios occur in primary recharge zones in regions where the Cambrian and Ordovician are unconfined. In this hydrogeologic setting the activity ratio increases with an increase in flow path and residence time of groundwater in the aquifers. The increase is illustrated by samples from wells located in central Ogle County and by samples from the U.S.G.S. packer test in Jo Davies County (fig. 9).

For three wells located in an area of primary recharge on an upland in Ogle County, the activity ratios are 2.1 for groundwater in the Galena-Platteville, 6.5 for groundwater in the St. Peter, and 11.2 for groundwater from a well open in the interval Ironton-Galesville to Mt. Simon. The activity ratios in the groundwater samples collected in the U.S.G.S. packer test in Jo Davies County were 15.6 in the St. Peter Sandstone, 21.6 in the Ironton-Galesville and 25.6 in the Mt. Simon. The higher ratios in the packer test samples reflect the location of the open borehole in lowland along the Galena River that is a zone of groundwater discharge. A component of groundwater in the discharge zone is from regions of northwestern Illinois where the Cambrian and Ordovician are confined by the Maquoketa.

The analyses presented in figure 9 illustrate the marked increase in $^{234}\text{U}/^{238}\text{U}$ activity ratios that occurs where the Cambrian and Ordovician are overlain and confined by shale bedrock. Also note that the activity ratios in the confined aquifers exhibit regional trends. In the southwestern region of the study area the activity ratios range from 5.4 to 14.8; over a large part of this region the ratios are less than 8.

A significant feature on figure 9 is the zone of high ratio groundwater that extends from the northeastern part of the study area southwestward through Du Page County into central Kane County, northeastern Kendall County and northwestern Will County. Groundwater within this zone has activity ratios greater than 20; in the northeastern part of the zone ratios range from 25 to 35. A second zone of high ratio groundwater is present in Grundy County, southern La Salle County, the northern margin of Livingston County, and eastern Marshall County. Activity ratios in this zone range from 20 to 40.7. The two zones are both located along a northeast to southwest trend and may be genetically related. The zones are separated by lower ratio groundwater (values from 6.1 to 15.2) present in southwestern Will County and northeastern Grundy County.

The widespread and extreme disequilibrium between ^{234}U and ^{238}U that occurs in groundwater from the Cambrian and Ordovician bedrock of the study area is unique. The high activity ratios have not been found in other flow systems. Other researchers have reported values for groundwater that range from 0.5 to 12.3. Only a few investigators have reported ratios greater than 5. Kronfeld (1974) reported ratios as high as 12.3 for groundwater in a confined sandstone aquifer in Texas. Activity ratios ranging from 5.5 to 10.5 were measured in confined aquifers in the Cambrian and Ordovician bedrock in the tri-state region of Missouri, Kansas and Oklahoma (Cowart, 1981). The aquifer units (sandstones and dolomites) have lithologies that are similar to the Cambrian and Ordovician aquifers in northern Illinois.

The disequilibrium present in groundwater in the tri-state region and in Texas is believed to be due to precipitation of ^{238}U as diffuse coatings on the sandstone matrix. ^{234}U is preferentially mobilized from these coatings because of its radiogenic origin.

Laboratory research has directly established that the recoil from alpha particle disintegration preferentially mobilizes daughter nuclides. Fleisher (1980) has established two mechanisms for enrichment: 1. Direct recoil of the ^{234}Th nucleus (from ^{238}U decay) into solution may occur. The short-lived ^{234}Th decays to ^{234}U thereby enriching the groundwater in ^{234}U while depleting the surface of the solid. 2. A large number of the recoiling nuclei pass through the groundwater to become embedded in adjacent grains of the aquifer matrix, leaving fission tracks open to the surface. Natural groundwaters have the potential to efficiently leach the embedded nuclei from the tracks.

The enrichment mechanisms described by Fleisher (1980) are believed to contribute to the disequilibrium present in groundwater in northern Illinois. However, the much higher activity ratios present in northern Illinois as compared to the values in the tri-state region and in Texas may be the result of additional factors. The significance of the high $^{234}\text{U}/^{238}\text{U}$ disequilibrium to the glacial recharge of groundwater to the Cambrian and Ordovician bedrock is considered in the discussion section of this paper.

RADIUM ISOTOPES

The National Interim Primary Drinking Water Regulations promulgated by the U.S. Environmental Protection Agency (1975) state that the combined ^{226}Ra and/or ^{228}Ra contaminant level shall not exceed 5 pCi/L.

Concentrations above this level occur over a large part of the study area in groundwater in the Cambrian and Ordovician bedrock. All analyses on radium isotopes presented in this report were performed at the Argonne National Laboratory. The data set includes analyses performed in the present research program and historical analyses from earlier research at the Argonne National Laboratory. The earlier research includes reports and papers by Stehney (1955), Lucas and Ilcewicz (1958), Krause (1959, 1960), Holtzman (1964), Bennett, Bell and Markwood (1976), and unpublished analyses from the files of Henry Lucas and Richard B. Holtzman.

Gilkeson et al. (1983) compared analyses from the present research to the historical data and determined that over a period of time ranging up to 23 years, the concentration of dissolved radium in discrete aquifer units of the Cambrian and Ordovician has not changed. Also, the concentration of ^{226}Ra and ^{228}Ra in groundwater produced from most public supply wells has not changed over time. An important finding of Gilkeson et al. (1983) was that the high dissolved concentrations of ^{226}Ra and ^{228}Ra are present in groundwater from sandstones - the productive aquifers in the Cambrian and Ordovician bedrock. Groundwater produced from dolomites has lower concentrations. Radium concentrations in groundwater from the Maquoketa Shale is very low (less than 1 pCi/L). The variation in radium concentrations over time observed in a limited number of wells was related to three mechanisms: 1. The variations were due to modifications in well construction that altered the quantity of groundwater produced from discrete aquifer units. These modifications include: changes to the well casing, well depth, and

development with explosives or acid to increase productivity from discrete rock units. 2. For wells that were open to several aquifer units, a change in the rate of pumping or the duration of pumping often resulted in changes in the quantity of groundwater produced from discrete aquifers and a corresponding change in radium concentrations. 3. In a few wells that were open to several aquifer units, the mixing of incompatible groundwaters from discrete aquifers resulted in the coprecipitation of radium with the formation of the mineral species barite. In these wells the variation in dissolved radium concentration was related to the precipitation-dissolution of barite in the well bore.

The data set includes analyses of both ^{226}Ra and ^{228}Ra for groundwater samples from 129 wells that produce from the Cambrian and Ordovician. The range in the combined concentrations is from 2.3 to 53.5 pCi/L. Only nine of the samples were in compliance with the maximum contaminant level of the drinking water standard. The regional variation in ^{226}Ra and ^{228}Ra in groundwater from the Cambrian and Ordovician is shown in figure 10. On this figure symbols are used to identify the aquifers that provide groundwater to wells. The figure also shows analyses for groundwater samples collected during the U.S.G.S. packer tests located at boreholes near Zion in Lake County and near Galena in Jo Daviess County.

The lowest combined concentrations for the two nuclides occur in groundwater samples from wells in the north-central and northwestern regions of the study area in zones of primary recharge where the Maquoketa Shale Group is absent. In this setting groundwater has had a short residence time in the Cambrian and Ordovician bedrock. It is

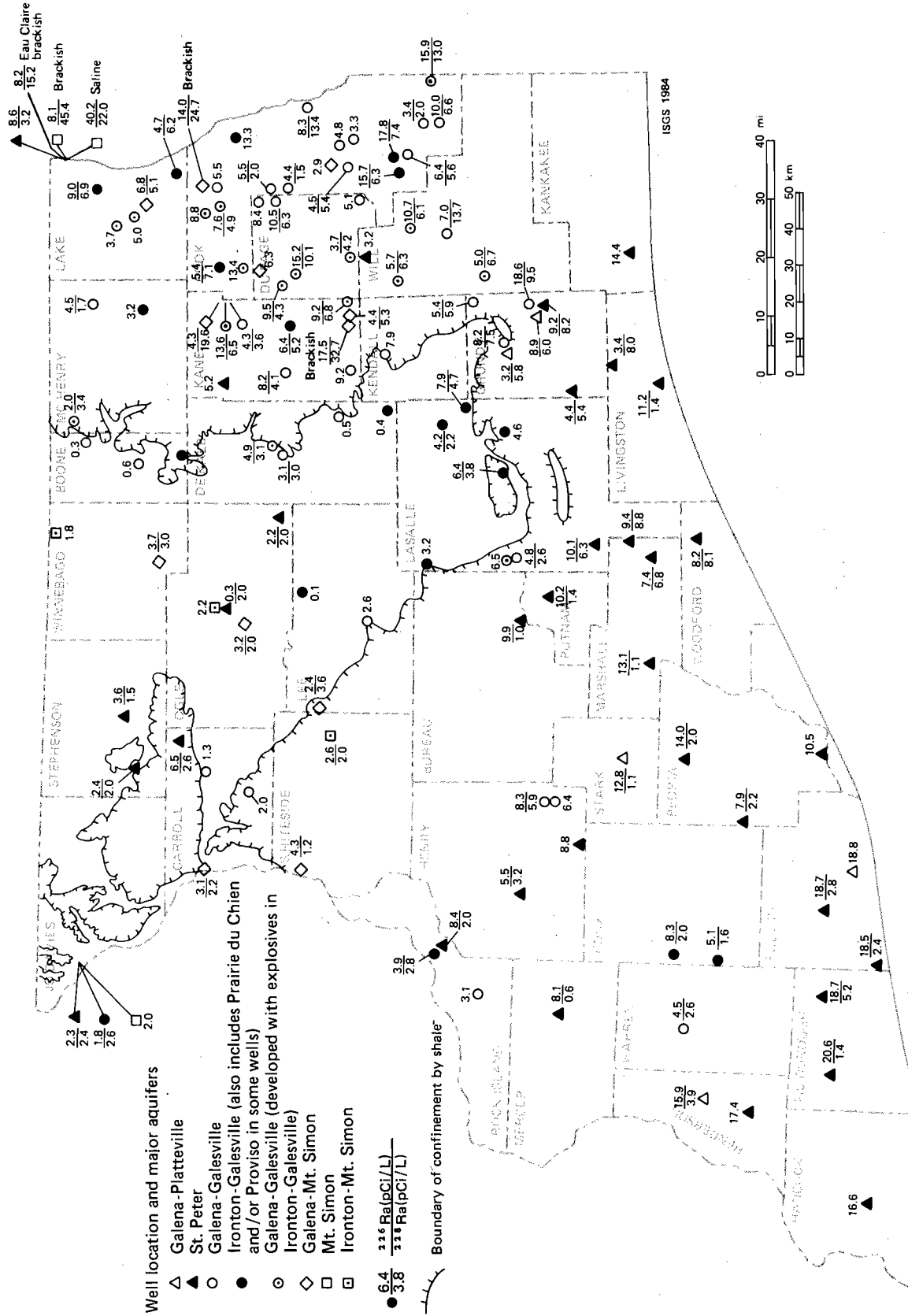


FIGURE 10. Distribution of ^{226}Ra and ^{228}Ra in groundwater from supply wells in the Cambrian and Ordovician bedrock. Single values shown at a few wells are ^{226}Ra . Symbols depict major aquifers for discrete wells. All analyses performed at the Argonne National Laboratory.

especially true that the lowest ^{226}Ra concentrations occur in this hydrogeologic setting. Downgradient of the primary recharge zones, there is a marked increase in the ^{226}Ra concentration. For the northwestern part of the study area the highest combined concentrations are present where the aquifers are confined by the Maquoketa with the increase largely due to greater concentrations for ^{226}Ra .

In the southwestern part of the study area the combined concentration for the two radium nuclides range from 6.7 to 24 pCi/L with concentrations greater than 10 pCi/L occurring over most of the region. The ^{228}Ra concentrations range from 0.6 to 5.9 pCi/L and are generally less than 3.0 pCi/L over a large part of the region. The concentrations of ^{226}Ra range from 3.1 to 20.6 pCi/L; the highest concentrations are present in brackish groundwater from the stratigraphic interval Galena-Platteville to St. Peter. An interesting feature in the southwestern region is the lower ^{226}Ra concentrations present in groundwater from wells that are open to the Ironton-Galesville Sandstone. The lower concentrations may be the result of the lower total dissolved solids concentrations in groundwater from these wells. A direct relation between ^{226}Ra concentrations and total dissolved solids was determined by Emrich and Lucas (1963) and Gilkeson et al. (1983). Another feature that may lower the ^{226}Ra concentration is that these deeper wells are open to produce groundwater from dolomites in the Prairie du Chien Group and in the Eminence and Potosi. Groundwater from the dolomites would have low values of ^{226}Ra . The quantity of groundwater produced from the dolomites to individual wells is not accurately known.

The combined concentration of the two radium nuclides in fresh or brackish groundwater samples from wells that produce from confined aquifers in the eastern part of the study area ranges from 5.4 to 53.5 pCi/L; for this region the range in ^{226}Ra is from approximately 2 to 19 pCi/L. The highest combined concentration for all samples collected in the study area was 62.2 pCi/L (40.2 pCi/L for ^{226}Ra , 22.0 pCi/L for ^{228}Ra) for a saline groundwater sample collected from the lower section of the Mt. Simon Sandstone at the U.S.G.S. open borehole in Lake County.

A striking feature in the eastern part of the study area is the presence of the highest ^{228}Ra concentrations in brackish groundwater produced from the Mt. Simon Sandstone. The measured concentrations are 24.7 pCi/L for public supply well no. 17 at Mt. Prospect in Cook County, 32.7 pCi/L for public supply well no. 9 at Aurora in Kane County and 45.4 pCi/L for a sample collected at the U.S.G.S. borehole in Lake County. The concentration of total dissolved solids for the three samples ranges from 1,050 to 6,000 mg/L. Remedial measures were taken at the municipal wells to stop production of brackish groundwater from the Mt. Simon. The source of the high ^{228}Ra concentrations in brackish groundwater from the Mt. Simon is not well understood at the present time. Unlike the concentration of ^{226}Ra , the concentration of dissolved ^{228}Ra is not directly related to the ionic strength of groundwater (Gilkeson, et al., 1983). The high dissolved ^{228}Ra concentrations in the Mt. Simon may be due to a greater abundance of thorium-bearing feldspar minerals in the matrix of the bedrock.

The comparison of analyses of potable groundwater from public supply wells in the eastern part of the study area to the construction of the wells led to the following findings in Gilkeson et al. (1983):

1. The high ^{226}Ra and ^{228}Ra concentrations are in groundwater produced from the sandstones, with the highest concentrations present in the Ironton-Galesville.
2. The highest combined concentrations were from public supply wells that were constructed to produce groundwater mainly from the Ironton-Galesville.

The presence of the high radium concentrations in the productive aquifer units presents difficulties to remedial measures to meet compliance with the drinking water standard. A measure that may lower the radium concentration for some wells is to construct the well with an open borehole to several rock units in addition to the St. Peter and Ironton Galesville, including the Prairie du Chien, Eminence, Potosi, Eau Claire and the upper section of the Mt. Simon.

This design may lower radium concentrations; however, at most wells the combined concentrations will still exceed the drinking water standard. It is important not to drill deep into the Mt. Simon where brackish groundwater has high concentrations of both nuclides.

Many communities in northern Illinois produce groundwater from several wells that are finished in different aquifers. Groundwater produced from aquifers other than the Cambrian and Ordovician bedrock has very low concentrations of radium. The blending of groundwater from these other aquifers (principally sand and gravel or Silurian Dolomite) with groundwater from the Cambrian and Ordovician bedrock may result in a finished groundwater that is in compliance with the drinking water regulations. Surface water supplies also have very low

concentrations of radium. Chicago and many other communities are supplied water from Lake Michigan. The City of Elgin in northeastern Illinois has recently completed construction of a facility to treat water from the Fox River. Several other communities in northern Illinois use rivers or reservoirs for water supplies.

The efficient removal of radium by two conventional water treatment processes (ion exchange softening and lime softening) was determined in a study by Bennett, Bell, and Markwood (1976). Several communities use these treatment processes.

DISCUSSION

The isotopic composition of the water molecule is evidence of the importance of glacial processes to the recharge of groundwater to confined aquifers in the Cambrian and Ordovician bedrock of northern Illinois. Similar studies with stable isotopes by Siegel and Mandle (in press) have established that glacial recharge to confined aquifers in the Cambrian and Ordovician has occurred over an extensive part of north-central United States.

The mechanisms of recharge related to glacial processes is not clearly understood. 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 to recharge into the Cambrian and Ordovician bedrock. It is important to consider that these glacial recharge events were repeated with the numerous advances of continental ice sheets into Illinois during the Pleistocene. The marked variation in the configuration of the different ice lobes and their direction of advance across the study area had large effects on the recharge events (fig 11).

The highest activity ratios (values from 25 to 40) occur in the eastern part of the study area where groundwater would have been recharged during the Wisconsinan. Wisconsinan glaciers did not advance over the southwestern region of the study area. The low activity ratios (values from 5 to 11) in groundwater of the Ordovician bedrock

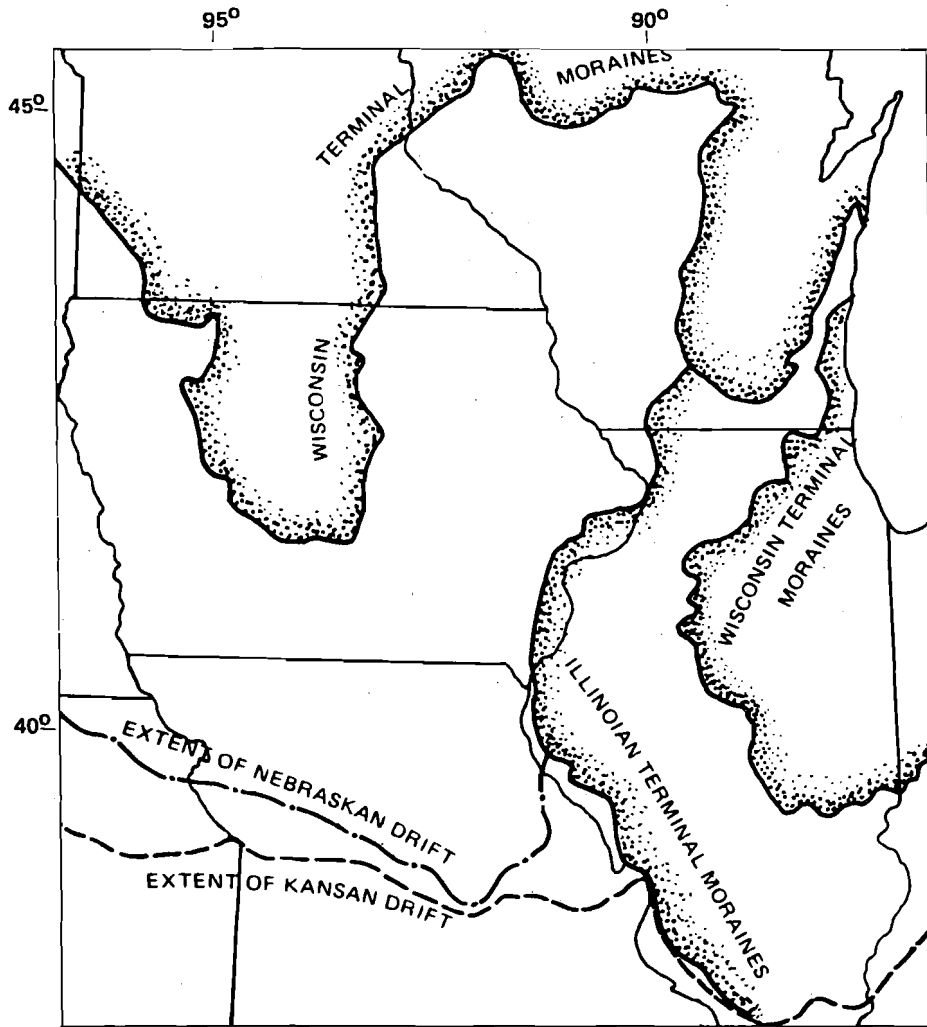


FIGURE 11. Extent of Pleistocene glaciations in a region of North-Central United States, including Illinois (from Siegel and Mandle, in press).

in the southwestern region may reflect recharge by an earlier glacial advance. The activity ratio diminishes over time as the excess ^{234}U disintegrates. It is possible that groundwater in the Cambrian and Ordovician bedrock in the southwestern region is quite old, and that recharge was due to glacial advances during the early Illinoian or older stages.

The northeastern part of the study area is where groundwater would have been recharged during the Wisconsinan by the most recent glacial advances. At this time glaciers occupied Lake Michigan with ice boundaries in the northeastern corner of the state. Mathematical modelling by Filley and Parizek (1983) supports the finding of Gilkeson, Perry and Cartwright (1981) that pressure from the glacial ice overburden caused basal meltwater to recharge into the Cambrian and Ordovician through the floor of Lake Michigan. The zone of high activity ratios in the northeastern part of the study area (fig. 9) may define a plume of groundwater recharged by the most recent glacial advances. The highest ^{234}U concentrations measured in potable groundwater in the study area (3-6.7 pCi/L) are within this zone in Lake and Cook County.

The recharge of groundwater enriched in ^{234}U to sandstone aquifers in the Cambrian and Ordovician would be important to the concentration of dissolved ^{226}Ra . However, extent of preferential dissolution of ^{234}U in glacial environments has not been established. Analyses on uranium isotopes in glacial materials are limited. A few analyses presented in Cherdyntsev (1971) determined that glacial tills were greatly depleted in ^{228}U as compared with ^{232}Th and also depleted

in ^{234}U as compared with ^{238}U . Additional analyses on glacial sediments and glacial meltwaters are necessary to confirm the extraction of uranium with preferential extraction of ^{234}U .

SUMMARY

Stable and radioactive isotopes in groundwater were studied in an investigation of the natural geologic sources of high concentrations of ^{226}Ra and ^{228}Ra in groundwater from the Cambrian and Ordovician bedrock in northern Illinois. The combined concentrations of the two nuclides ranged from 2.3 to 53.5 pCi/L; the majority of analyses exceed the maximum contaminant level of 5.0 pCi/L. The lowest concentrations are in primary recharge zones in north-central Illinois where the Cambrian and Ordovician aquifers are unconfined. The highest combined concentrations are in mineralized groundwater in regions where the Cambrian and Ordovician bedrock are overlain and confined by shale bedrock. The high dissolved radium concentrations are present in the productive aquifer rocks - the sandstones. The secondary accumulation of ^{238}U , ^{234}U and ^{230}Th as diffuse coatings on the sandstone matrix is an important source of ^{226}Ra . The desorption of ^{226}Ra from the matrix is directly related to the mineralization of the groundwater. The highest ^{228}Ra concentrations are present in brackish groundwater from the Mt. Simon Sandstone in northeastern Illinois. Feldspars present as accessory minerals in the sandstones are a potential source of the ^{228}Ra .

The stable isotope composition of the water molecule has established that glacial processes are important to the recharge of groundwater in confined aquifers. Groundwater in primary recharge zones in the north-central part of the study area has $\delta^{18}\text{O}$ values (-6.6 to -7.9‰) that are similar to contemporary meteoric water. However,

recharge during a much colder climate is indicated for groundwater in confined aquifers where $\delta^{18}\text{O}$ values range to -12.7‰ and are less than -9‰ over large regions.

The covariation of $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ in dissolved sulfate from Cambrian and Ordovician aquifers defines a mixing line between two dominant sources; oxidation of sulfide minerals and dissolution of marine evaporites. Sulfates derived from oxidation of sulfides are present in groundwater with low sulfate concentrations (generally less than 25 mg/L) in zones of primary recharge. Disseminated sulfides in the Silurian Dolomite are believed to be an important source of the sulfate. The sulfides were incorporated into glacial tills in northern Illinois. Sulfate with a dominant source from dissolution of marine evaporites are present in groundwater with high sulfate concentrations (100-1200 mg/L) in confined aquifers. The marine evaporite source of the sulfates is of a different geologic age than Cambrian or Ordovician. Glacial processes are believed to be responsible for recharge of the sulfates.

Groundwater from the Cambrian and Ordovician exhibits a unique enrichment in ^{234}U . The activity ratio of ^{234}U to ^{238}U ranges from 2.0 to 40.7. The lowest ratios are present in unconfined aquifers in primary recharge zones. Ratios greater than 20 occur over large areas where the Cambrian and Ordovician are confined. The regional distribution of activity ratios and ^{234}U concentrations support a glacial recharge mechanism. Low-activity ratios are present in groundwater in confined aquifers in the southwestern part of the study area where glacial recharge is older than the Wisconsinan. The highest activity

ratios and ^{234}U concentrations are present in groundwater in the northeastern part of the study area where glacial recharge is related to the most recent glacial stages in Illinois.

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