Selected Geochemical Characteristics of Ground Water from the Marshall Aquifer in the Central Lower Peninsula of Michigan

By P.B. GING, D.T. LONG, and R.W. LEE

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BRUCE BABBITT, Secretary

U.S. GEOLOGICAL SURVEY
Gordon P. Eaton, Director

For additional information write to:

District Chief
U.S. Geological Survey
Water Resources Division
6520 Mercantile Way, Suite 5
Lansing, MI 48911-5991

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CONVERSION FACTORS

Multiply	By	To obtain
foot (ft)	0.3048	meter
gallon (gal)	3.785	liter
mile (mi)	1.609	kilometer
pound (lb)	453.6	gram

Degrees Fahrenheit (°F) can be converted to degrees Celsius (°C) by using the following equation:

$$°C = (°F - 32) / 1.8$$

VERTICAL DATUM

Sea level: In this report, "sea level" refers to the National Geodetic Vertical Datum of 1929 (NGVD of 1929)--a geodetic datum derived from a general adjustment of the first-order level nets of both the United States and Canada, formerly called Sea Level Datum of 1929.

WATER-QUALITY INFORMATION

Abbreviated water-quality units used in this report: Chemical concentration in water is given in milligrams per liter (mg/L). Milligrams per liter is a unit expressing the concentration of chemical constituents in solution as weight (milligrams) of solute per unit volume (liter) of water. For concentrations less than 7,000 mg/L, the numerical value is the same as for concentrations in parts per million. Dissolved-solids concentration is reported as the sum of major anion and cation species from chemical analysis.

Isotopic composition of water is expressed as per mil (parts per thousand) differences in the measured isotopic ratios of the sample and SMOW (Standard Mean Ocean Water, the ^{18}O and ^{2}H isotopic standard). The unit $\delta^{18}O$ is the standard expression of the ratio of the ^{18}O ion with respect to the ^{16}O ion. The unit δD is the standard expression of the ratio of the ^{2}H ion (deuterium) with respect to the ^{1}H ion.

ABBREVIATIONS

RASA: Regional Aquifer Systems Analysis
WATSTORE: U.S. Geological Survey National WATer Data STOrage and REtrieval System

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Abstract

Chemistry and stable-isotope data for water from wells completed in the Marshall aquifer within the Michigan Basin were used to prepare maps that show areal variations of $\delta^{18}O$; distribution of dissolved solids, dissolved chloride, dissolved iron, and dissolved sulfate; and distribution of hydrochemical facies. Delta oxygen-18 values indicate the presence of modern meteoric water ($\delta^{18}O$ approximately -10 parts per mil) as well as isotopically light meteoric water ($\delta^{18}O$ less than -15 parts per mil). Isotopically light ground water is present in the Michigan Lowland. Dissolved-solids concentrations range from 273 to 412,000 milligrams per liter, and dissolved-chloride concentrations range from less than 10 to greater than 250,000 milligrams per liter. Dissolved-solids and dissolved-chloride concentrations increase toward the center of the study area. Dissolved-iron concentrations which range from less than 0.002 to 100 milligrams per liter, are low in the subcrop areas, and increase toward the center of the study area. Dissolved-sulfate concentrations range from 4.5 to 3,500 milligrams per liter and generally increase then decrease from the subcrop area toward the center of the study area. Most ground water in the Marshall aquifer is classified as either a calcium bicarbonate or a sodium chloride type.

INTRODUCTION

In 1978, the U.S. Geological Survey initiated the Regional Aquifer-System Analysis (RASA) Program (Weeks and Sun, 1987). The objective of the RASA program is to define the regional hydrogeology and establish a framework of background information—geologic, hydrologic, and geochemical—that are useful for regional assessment of ground-water resources and support of detailed local studies. In 1985, the U.S. Geological Survey began a study to describe the hydrogeologic framework, geochemistry, and regional ground-water flow of the glacial and bedrock aquifers in the Michigan Basin (Mandle, 1986).

This report describes the areal variations of selected geochemical characteristics of ground water from the Marshall aquifer of the Michigan Basin. The Michigan Basin RASA study area is a 22,000-square-mile area in the central part of the Lower Peninsula of Michigan that is bounded by the contact between the Coldwater Shale and the Marshall Sandstone (fig. 1).

Chemical analyses of water from wells completed in the Marshall aquifer were compiled and plotted to construct maps that illustrate selected geochemical characteristics of water in the study area. Chemical data used to construct the maps represent water samples from wells completed at various depths in the Marshall aquifer. Therefore, the maps only represent general areal distributions of dissolved constituents, stable isotopes, and hydrochemical facies.

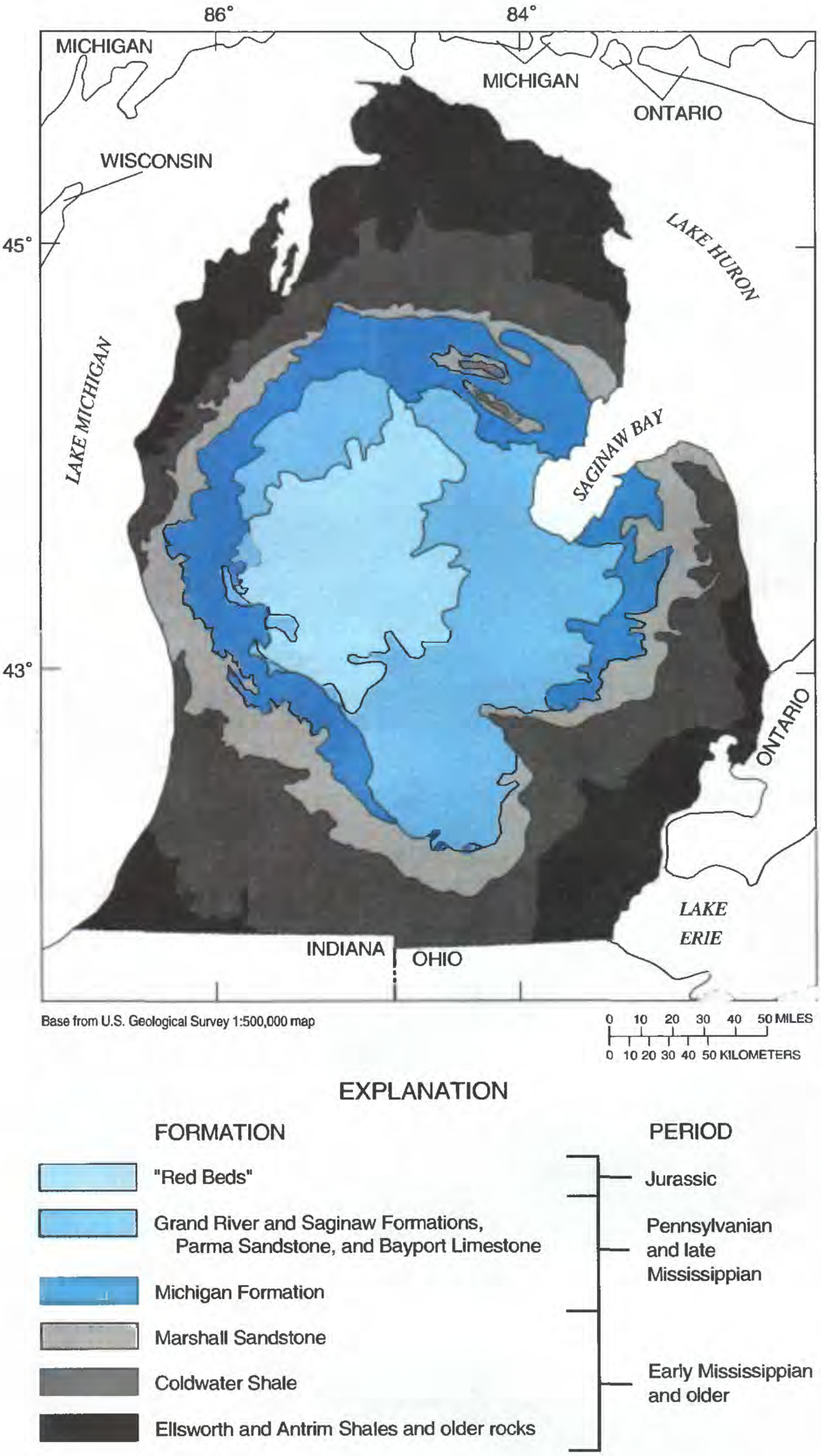


Figure 1. Bedrock geology of the Lower Peninsula of Michigan. (Modified from Westjohn and Weaver, 1996a.)

In addition to the chemical and isotopic data collected for the Michigan Basin RASA study (Dannemiller and Baltusis, 1990), chemical data were obtained from the U.S. Geological Survey's Water Data Storage and Retrieval data base, from Wood (1969), and from Clayton and others (1966).

The authors thank the Michigan Department of Public Health, especially Mark Breithart, for providing valuable data and general information. The Michigan Department of Natural Resources provided access to well logs and chemical data of Michigan Basin brines.

GEOHYDROLOGIC FRAMEWORK

The Michigan Basin is an ovate basin in which an extensive accumulation of sedimentary rocks is present in the Lower Peninsula of Michigan and parts of the Upper Peninsula, Illinois, Ohio, Indiana, Wisconsin, and Ontario, Canada. Sedimentary rocks of Precambrian through Jurassic age are more than 17,500 ft thick near the center of the basin (Lillienthal, 1978). Sedimentary rocks are mantled by glacial deposits of Pleistocene age.

Four aquifers are recognized in the Michigan Basin RASA study area: the Glaciofluvial, Saginaw, Parma-Bayport, and Marshall aquifers (fig. 2). Glaciofluvial aquifers dominantly consist of thick sequences of sand and gravel; however, in parts of the study area, they consist of sand and gravel beds within till or other fine-grained glacial deposits.

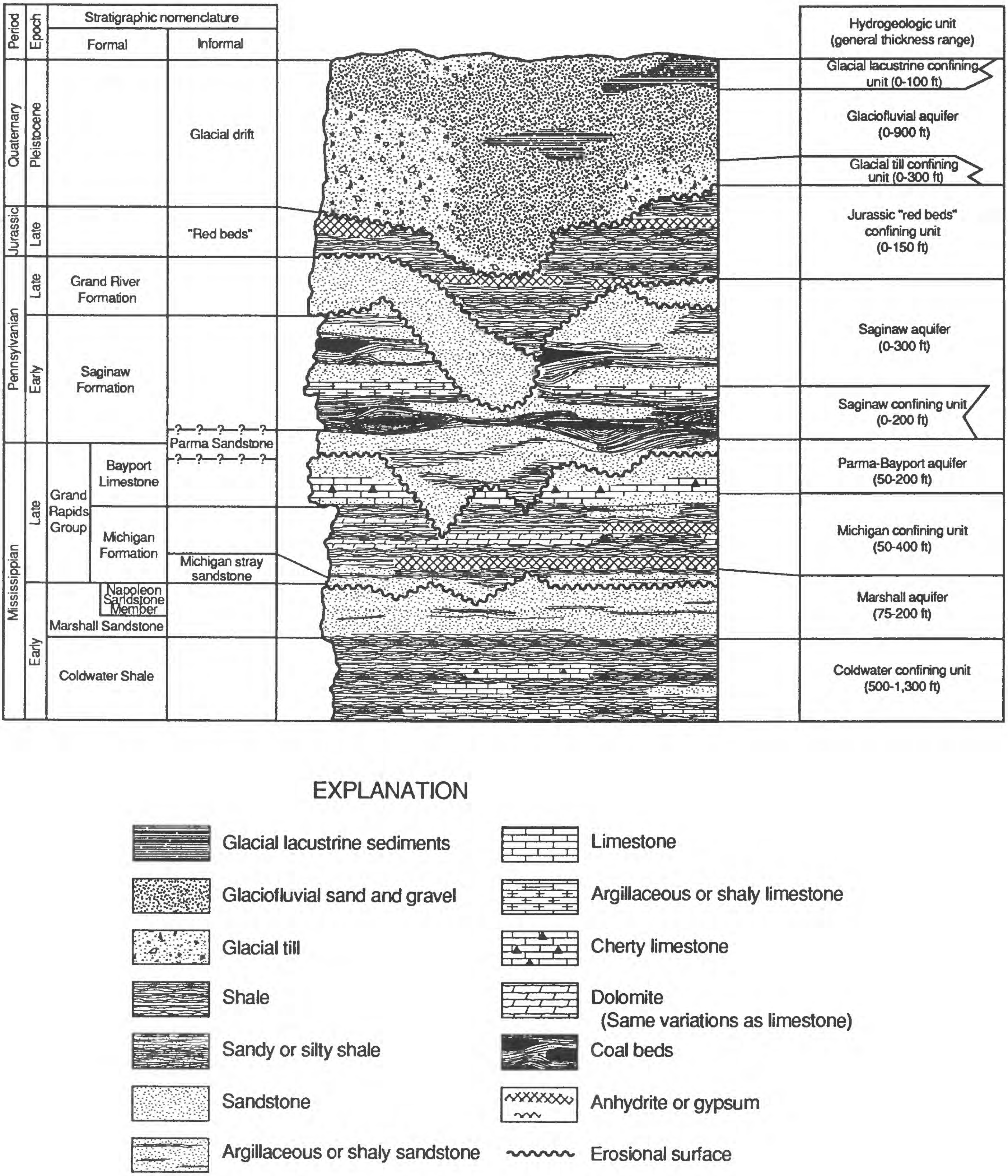


Figure 2. Relation between stratigraphic and hydrogeologic units in the Lower Peninsula of Michigan (from Westjohn and Weaver, 1996a).

In this report, the uppermost aquifer (Glaciofluvial) is referred to as a single unit even though it is composed of multiple sand and gravel layers. Red beds of Jurassic age overlie the Saginaw aquifer in the west-central part of the study area. These "red beds" are dominantly composed of red mud, poorly consolidated red shale, gypsum, and minor amounts of sandstone. More than 400 ft of freshwater-bearing glacial deposits overlie the Jurassic red beds. Consequently, wells are rarely completed in the red beds or the underlying bedrock aquifers, and water-quality data for the underlying units are scanty. Together with the fine-grained glacial deposits, "red beds" form subregional confining units (Westjohn and others, 1994).

Rocks of Pennsylvanian age have been subdivided into the Saginaw Formation (Early Pennsylvanian) and the Grand River Formation (Late Pennsylvanian) (Michigan Geological Survey, 1964). Sandstones and shales of these formations are intercalated and constitute the dominant lithology in some parts of the study area. Siltstone, limestone, and coal are minor contributors to the total thickness of the Pennsylvanian rock sequence. For characterization of the hydrogeological framework of the Michigan Basin aquifer system, the composite thickness of the Pennsylvanian sandstones is grouped to form the Saginaw aquifer (Westjohn and Weaver, 1996a). Sandstones, which are the most productive aquifer materials in the unit, generally are less than 100 ft thick except in the east-central part of the basin, where the composite thickness of sandstones ranges from 200 to 370 ft (Westjohn and Weaver, 1996a).

In most areas of the basin, shale underlies the Saginaw aquifer. This shale, which constitutes the Saginaw confining unit and separates the Saginaw aquifer from the Parma-Bayport aquifer, and ranges in thickness from 0 to 300 ft (Westjohn and Weaver, 1996a). The Parma-Bayport aquifer ranges from 100 to 150 ft in thickness and consists of the Parma Sandstone and Bayport Limestone (Westjohn and Weaver, 1996a). The Parma Sandstone contains sandstone, shale, siltstone, and thin lenses of limestone (Cohee, 1965). The Bayport Limestone is predominantly limestone, sandstone, and sandy limestone (Cohee, 1965).

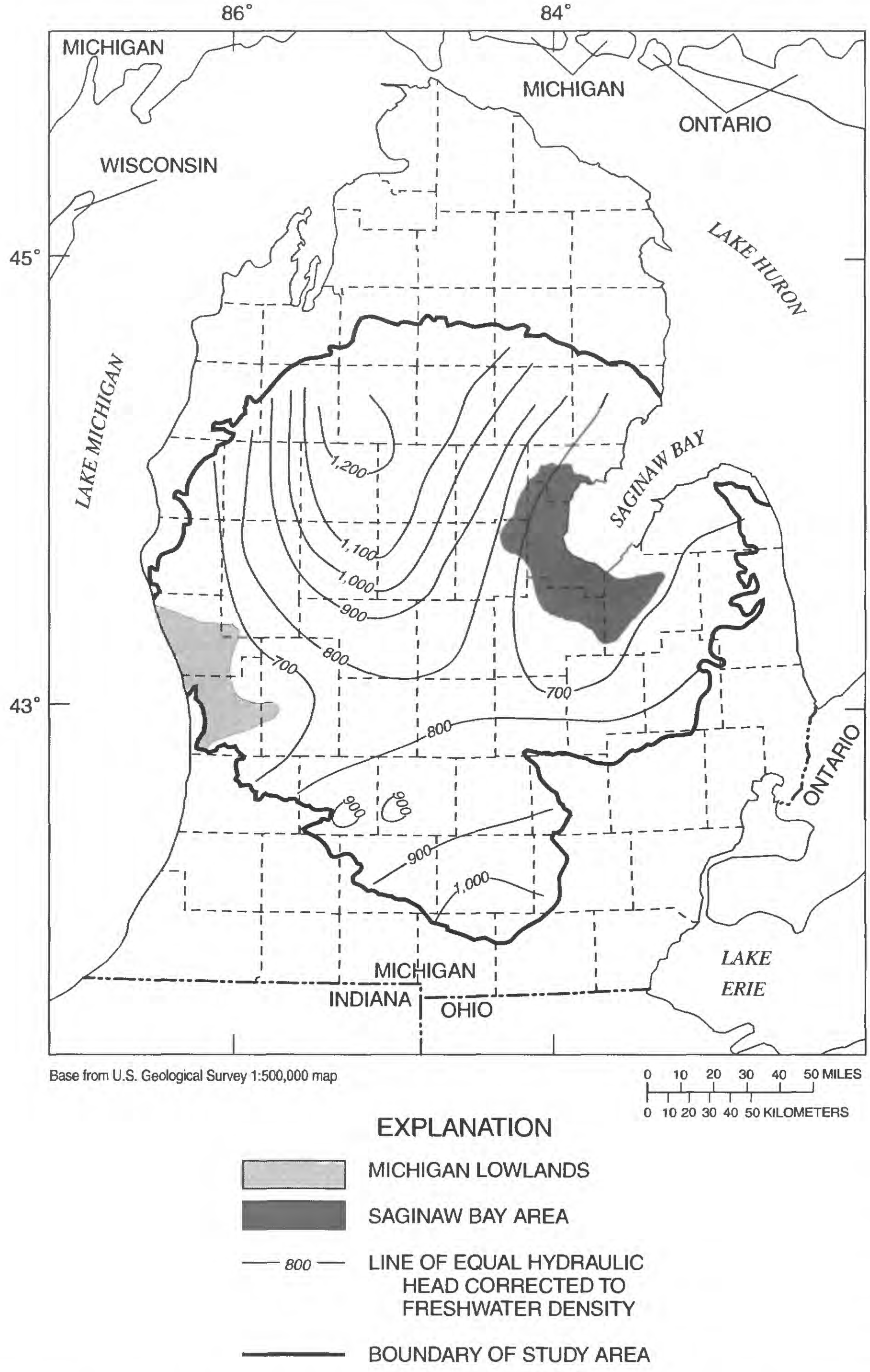
Underlying the Parma-Bayport aquifer is the Michigan confining unit, which is an intercalated sequence of thin bedded limestone, dolomite, shale, gypsum, anhydrite, and lenses of sandstone. The unit ranges in thickness from 50 ft near the fringes of the subcrop area to about 400 ft over the central part of the study area (Westjohn and Weaver, 1996a).

The Marshall aquifer is the lowermost aquifer in the RASA study area and includes the Marshall Sandstone (formal stratigraphic unit) and sandstones that form the lower part of the Michigan Formation (fig. 3). The basal unit of the Marshall Sandstone consists of 50 to 100 ft of a micaceous sandstone or micaceous siltstone with very low permeability that overlies the Coldwater Shale (Westjohn and Weaver, 1996b). Above this unit is a permeable fine to medium grained sandstone (generally 50 to 125 ft in thickness). This unit commonly is referred to as the lower Marshall, or Marshall Sandstone member (Westjohn and Weaver, 1996b). The lithologic relations of strata that overlie this unit are complex.

In most areas within the Marshall subcrop, there is a permeable sandstone, the upper Marshall (or Napoleon Sandstone member). Its thickness ranges from 50 to 125 ft and it is hydraulically similar to the lower Marshall. Observations made from geophysical logs show that where the lower Marshall is thin the upper Marshall is thick and conversely where the lower Marshall is thick, the upper Marshall is thin (Westjohn and Weaver, 1996b). Additional sandstones overlie the upper Marshall, but these are usually intercalated with lithologies typical of the Michigan Formation (Michigan Stray Sandstones) (fig. 2). These sandstones appear to be "shoestring" type sands, which are laterally discontinuous and rarely exceed 10 ft in thickness.

The Coldwater confining unit is primarily a shale with local occurrences of limestones, dolomites, and sandstones. Cohee and others (1951) state that thicknesses range from 500 ft in the east to more than 1,100 ft in the west.

Ground water in the Marshall aquifer has the potential to flow toward Saginaw Bay and the Michigan Lowland (fig. 3; Mandle and Westjohn, 1989). The Michigan Lowland is defined as the southwestern part of the Lower Peninsula where lacustrine deposits are the dominant surficial material.



Base from U.S. Geological Survey 1:500,000 map

Figure 3. Predevelopment equivalent freshwater heads in the Marshall aquifer, Lower Peninsula of Michigan (Barton and others, 1996, fig. 8) and location of Saginaw Bay and the Michigan Lowland.

SELECTED GEOCHEMICAL CHARACTERISTICS

The general distributions of selected dissolved-chemical constituents, stable isotope values, and hydrochemical facies are illustrated using maps prepared for the Marshall aquifer. The maps include areal variation of $\delta^{18}O$ and distributions of dissolved solids, chloride, iron, and sulfate, and hydrochemical facies.

Stable Isotopes of Oxygen and Hydrogen

The isotope composition of oxygen and hydrogen in water is reported in terms of the difference of the $^{18}O/^{16}O$ and $D/^{1}H$ ratios relative to a standard called Standard Mean Ocean Water (SMOW). The isotope ratios are reported as $\delta^{18}O$ and δD, where δ is expressed as a per mil deviation from that of the standard SMOW by use of the formula

$$\delta = \frac{[R_x - R_{std}]}{R_{std}} \times 1,000,$$

where R_x is the isotopic ratio in the sample and R_{std} is the isotopic ratio in the standard (Faure, 1986). As indicated in the formula, the ratio is multiplied by 1,000 because the differences between the standard and the sample commonly are small. Water with a negative δ value is enriched in the lighter isotope (^{16}O or H) compared to SMOW.

Water with a positive δ value is enriched in the heavier isotope (^{18}O or D) relative to SMOW. Different $\delta^{18}O$ compositions can be used to identify ground-water masses, to indicate mixing of water masses, and to determine indirectly the relative ages of water masses (Long and others, 1986).

The relation of δD and $\delta^{18}O$ for 120 ground-water samples collected from the Marshall aquifer is shown in figure 4. These data are compared to the global meteoric water line of Craig (1961) and a local meteoric water line (Simcoe line) developed for Simcoe, Ontario, Canada (Desauliniers and others, 1981). The Simcoe data were collected from precipitation about 120 mi east of the study area.

Two trends are evident in figure 4. Delta D and $\delta^{18}O$ data that plot parallel to and between the global meteoric and Simcoe lines range from -17.0 to -8.5 per mil and are interpreted to represent meteoric ground water in the Marshall aquifer. The $\delta^{18}O$ values that range from -12.00 to -8.5 per mil are consistent with isotope values of modern precipitation in the Lower Peninsula of Michigan (Sheppard and others, 1969; G.J. Larson, Michigan State University, written commun., 1992) and, therefore, are interpreted to represent modern meteoric (post glacial) ground water in the Marshall aquifer. Values of $\delta^{18}O$ less than -12.0 per mil, however, are lighter than is expected for modern recharge (Regalbuto, 1987). These anomalous data indicate that ground water recharged the system when the climate was cooler than it is now (such as during the most recent glaciation). Thus, ground water might be recharged by glacial meltwater depleted in the $\delta^{18}O$ isotope during periods of glacial-ice advances in Michigan (Long and others, 1988) as has been proposed for isotopically light water in other ground-water systems (Desauliniers and others, 1981; Siegel and Mandle, 1984).

Ground-water compositions that plot to the right of the global meteoric and Simcoe-water lines have $\delta^{18}O$ values as high as 0.75 per mil. These samples are mostly brine (>100,000 mg/L dissolved solids) from deep wells near the center of the study area. Brines from sedimentary basins typically plot to the right of the global meteoric water line (Kharaka and others, 1987). They do not usually plot near seawater or along a mixing trend between seawater and meteoric water.

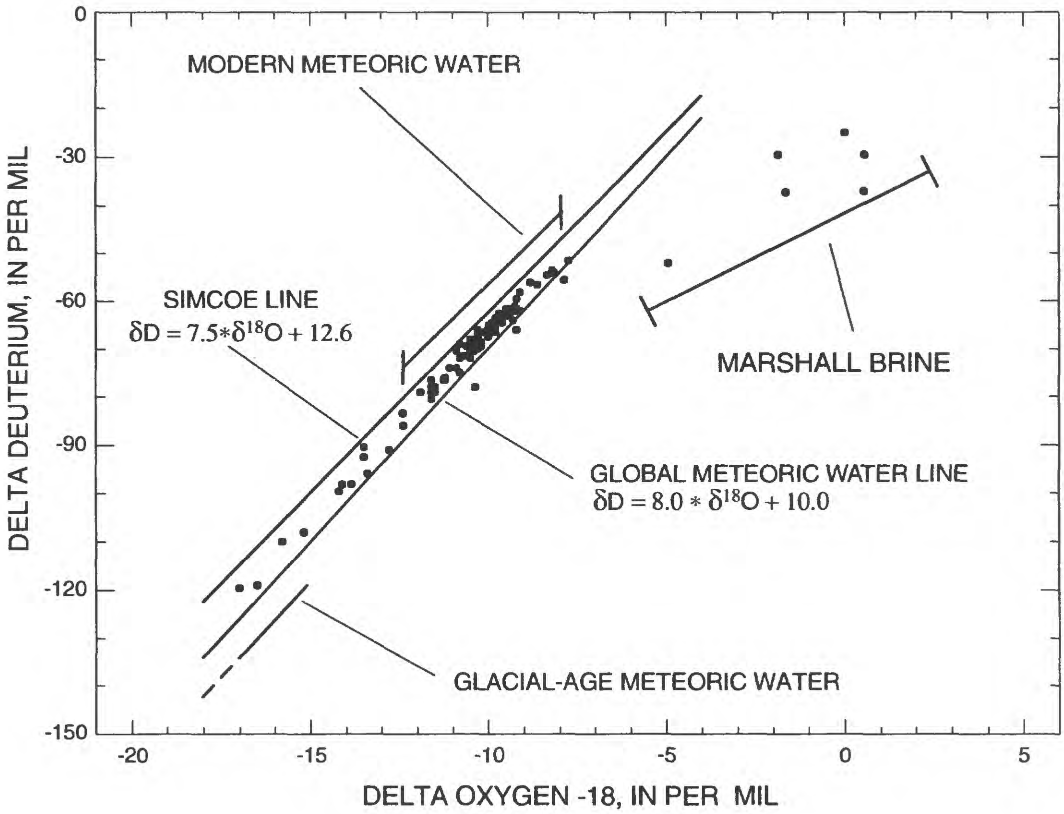
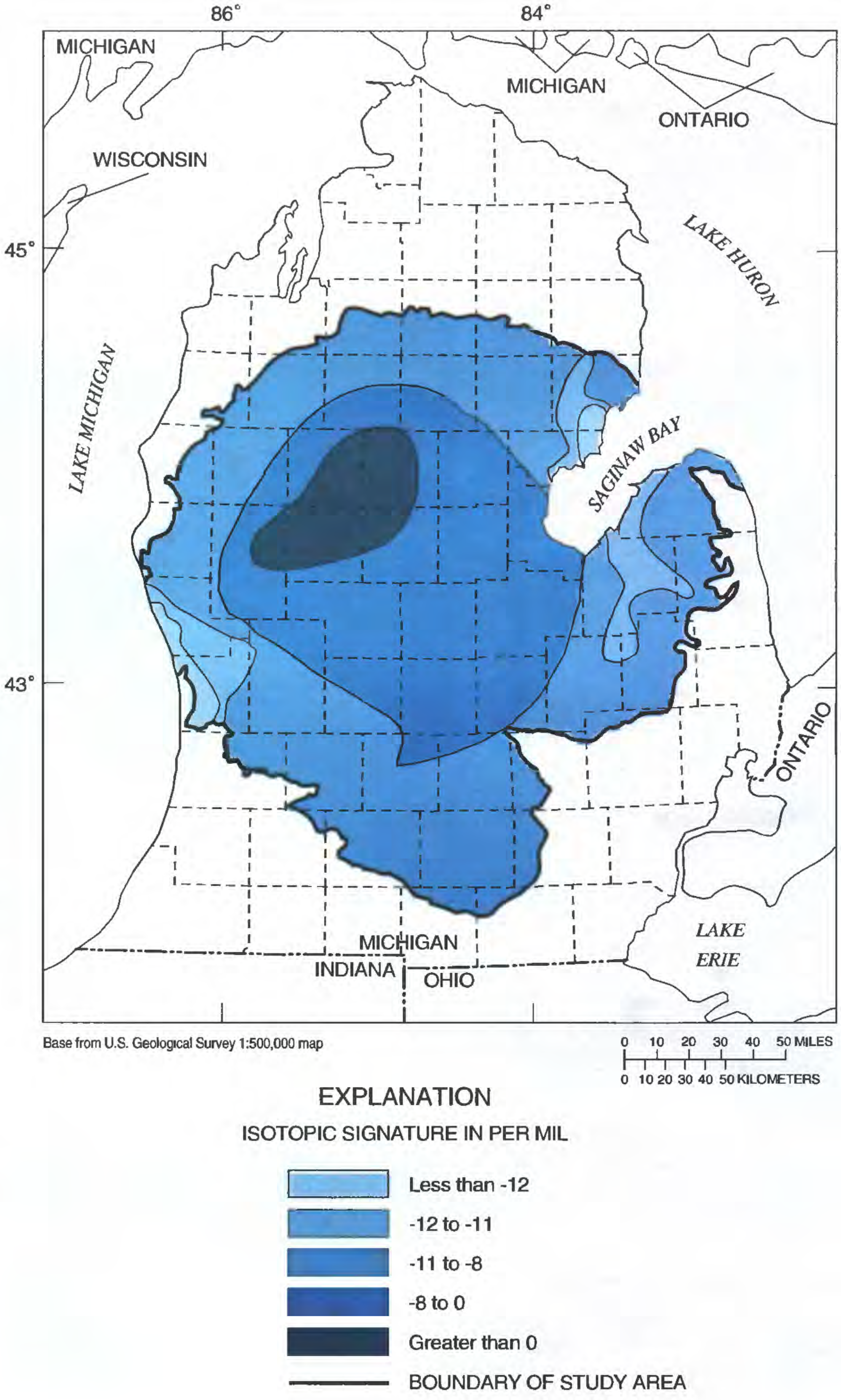


Figure 4. Relation between delta deuterium and delta oxygen-18 for ground water from the Marshall aquifer, Lower Peninsula of Michigan.

Wilson and Long (1993a) interpreted the range of the isotopic values of brine from formations of Devonian age in the Michigan Basin to be from the mixing of evaporated seawater and meteoric water. A similar interpretation of the isotopic signature of brines in other sedimentary basins has been made by other investigators (Knauth and Beeunas, 1986). The isotopic values of brine from the Marshall aquifer are similar to those in the Devonian Formations in the Michigan Basin. Therefore, the isotopic values of brine in the Marshall aquifer are most likely the result of the mixing of evaporated seawater and meteoric water.

The areal variation of $\delta^{18}O$ determined from 120 samples from the Marshall aquifer is shown in figure 5. Trends in δD generally are the same as those for $\delta^{18}O$ (fig. 4) and, therefore, are not included as a map in this report. The $\delta^{18}O$ values of water from the Marshall aquifer generally become isotopically heavier toward the central part of the basin. Values at the margins of the study area are about -10 per mil, in the center, they exceed 0.0 per mil. The $\delta^{18}O$ values around the margins of the study area coincide with those for modern meteoric water. The isotopically heavy values in the central part of the basin are those of a brine that has been generated from the evaporation of seawater. The heavy water may retain its isotopic signature because these deeper waters are relatively isolated from interaction with modern meteoric water.



Base from U.S. Geological Survey 1:500,000 map

Figure 5. Variation of delta oxygen-18 in ground water from the Marshall aquifer, Lower Peninsula of Michigan.

The lightest values (less than -11 per mil) are found in the Michigan Lowland and in the northeastern part of the study area adjacent to Saginaw Bay. In these areas, water recharged the aquifer when the climate was cooler. The distributions of data in figures 4 and 5 are consistent with a hydrodynamic model in which modern meteoric (postglacial) and glacial-age meteoric waters have mixed to cause a continuum of plotted values. An alternative hypothesis to explain the variation in $\delta^{18}O$ is change in the isotopic value of recharge water due to the gradual change in climate from a cooler period. The light isotopic ground water is retained in the aquifer because of slow flushing of the system by recent recharge water.

Dissolved Constituents

Dissolved Solids

Dissolved-solids concentrations of 243 groundwater samples from the Marshall aquifer were determined by summing major cations and anion species. The areal distribution of these concentrations, which range from 273 to 412,000 mg/L, is shown in figure 6. Water from the northeastern, southern, and southeastern subcrop areas has a dissolved-solids concentration that is generally less than 1,000 mg/L, and, locally, less than 500 mg/L. Water from deep wells in the central part of the aquifer has dissolved-solids concentrations that commonly exceed 100,000 mg/L, and locally exceed 300,000 mg/L.

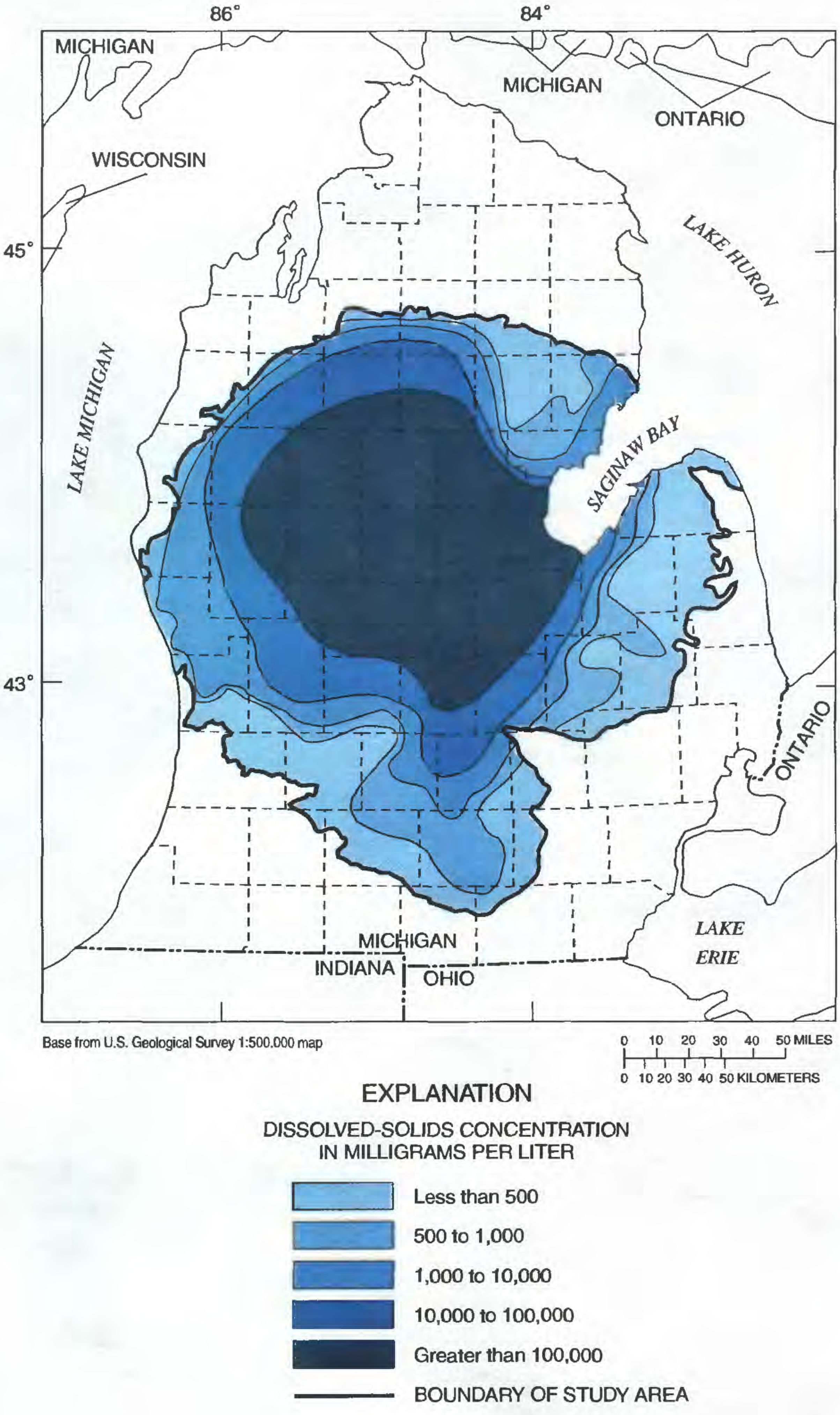


Figure 6. Distribution of dissolved solids in ground water from the Marshall aquifer, Lower Peninsula of Michigan.

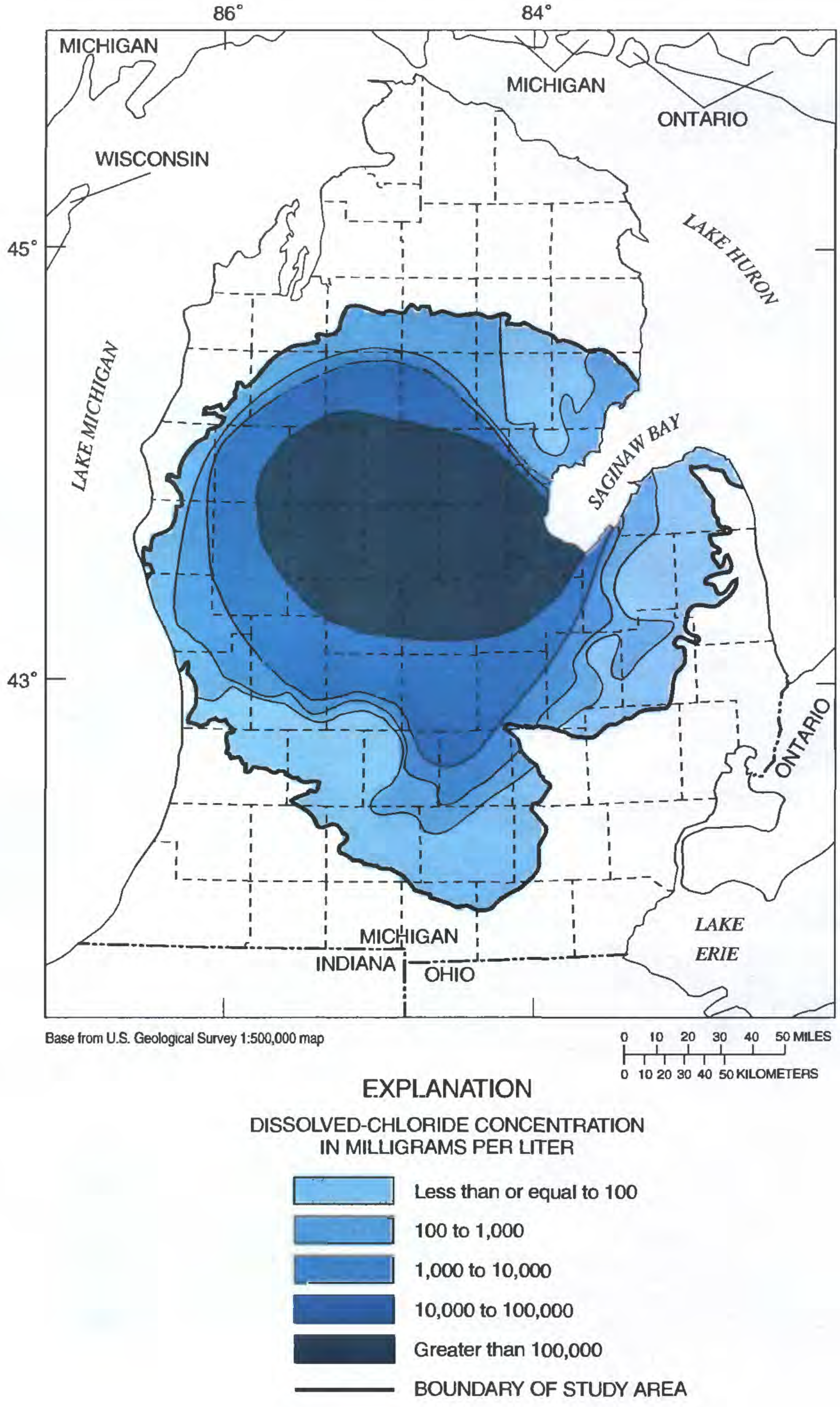
Dissolved-solids concentrations increase downdip from subcrop areas and form a pattern of concentric lines of equal value that approximate the shape of the study area. The source of high dissolved solids probably is brine that originated through the evaporation of seawater. The source of dissolved solids in freshwater is primarily recharge water modified by rock-water interaction involving carbonate and silicate rocks.

Dissolved Chloride

Dissolved-chloride concentrations in 243 ground-water samples from the Marshall aquifer range from less than 10 to greater than 250,000 mg/L. This distribution of dissolved chloride is shown in figure 7. Chloride concentrations generally are less than 100 mg/L in water from the northeastern, southern, and southeastern subcrop areas. Water from the central part of the aquifer generally has a concentration greater than 100,000 mg/L. The source of dissolved chloride downdip from the subcrop area is most likely brine that originated through the evaporation of seawater.

Dissolved Iron

Dissolved-iron concentrations represent the combined concentrations of Fe^{+2} and Fe^{+3}. Dissolved-iron concentrations in 150 ground-water samples from the Marshall aquifer range from less than 0.002 to 100 mg/L (fig. 8). The concentrations are lowest in subcrop areas and increase toward



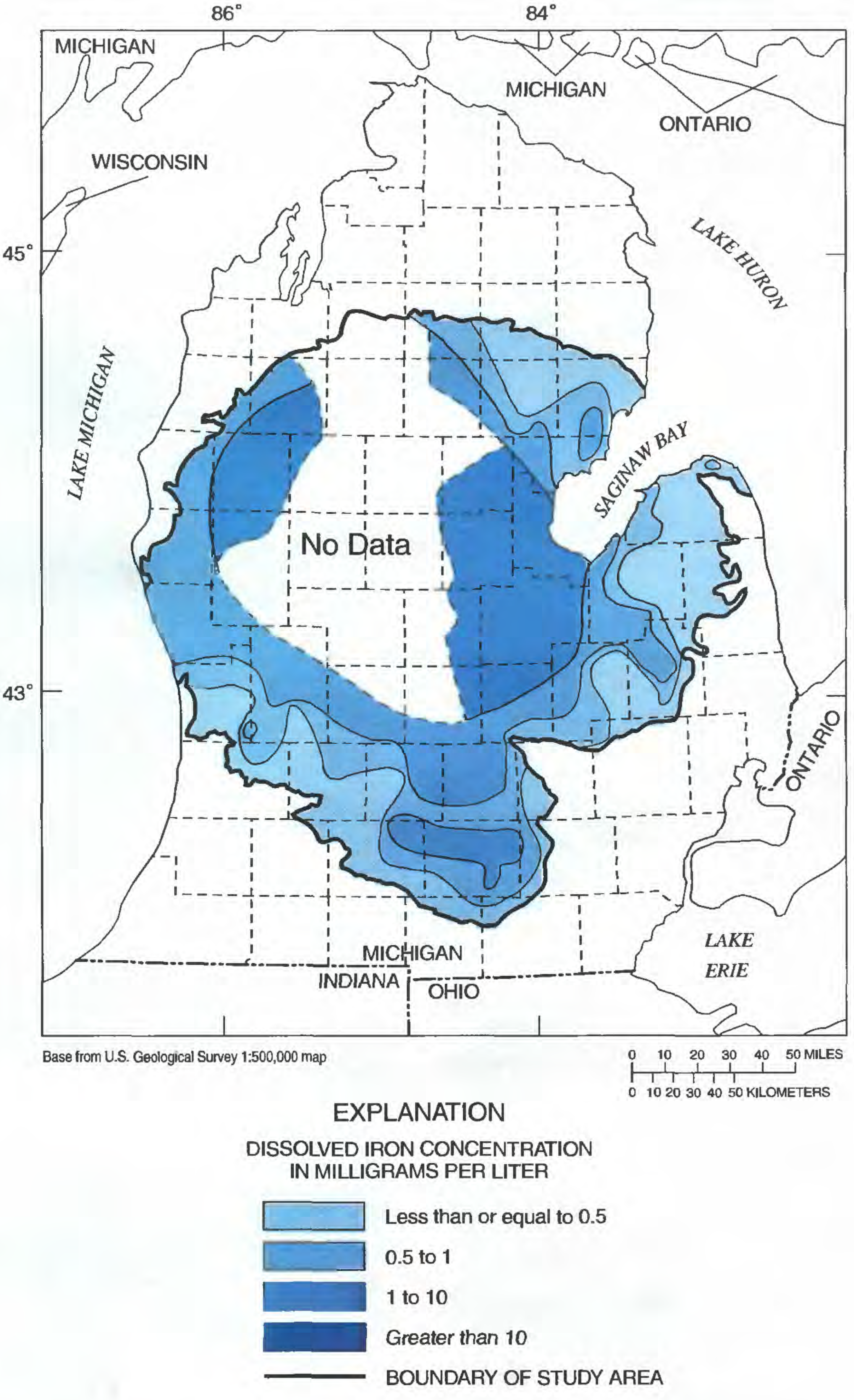
Base from U.S. Geological Survey 1:500,000 map

Figure 7. Distribution of dissolved chloride in ground water from the Marshall aquifer, Lower Peninsula of Michigan.

the center of the study area. The higher concentrations probably are related to increased iron solubility because of more anoxic conditions and higher dissolved-chloride concentrations (Long and Angino, 1977; Lee, 1985) in the center of the study area. Locally, high concentrations exist in ground water from southern and northeastern parts of the study area. These locally high concentrations probably are caused by changes in the oxidation-reduction state of the ground water as water enters the system during recharge and moves down the ground-water-flow path.

Dissolved Sulfate

Concentrations of dissolved sulfate in 243 ground-water samples from the Marshall aquifer range from 4.5 to 3,500 mg/L. From the southeastern through western parts of the study area, dissolved-sulfate concentrations increase and then decrease from the subcrop area to the center of the study area (fig. 9). Concentrations decrease from the center to the northeastern part of the study area. Dissolved sulfate in ground water in subcrop areas is initially derived from the recharge water which includes sulfate in precipitation. An additional source of sulfate may be the dissolution of gypsum and anhydrite which are believed to be unevenly distributed in the overlying glacial deposits (Wood, 1969) and the Michigan Formation (fig. 2). The increased sulfate concentrations downdip probably are caused by the continued dissolution of sulfate minerals in the aquifer. The decrease in



Base from U.S. Geological Survey 1:500,000 map

Figure 8. Distribution of dissolved iron in ground water from the Marshall aquifer, Lower Peninsula of Michigan.

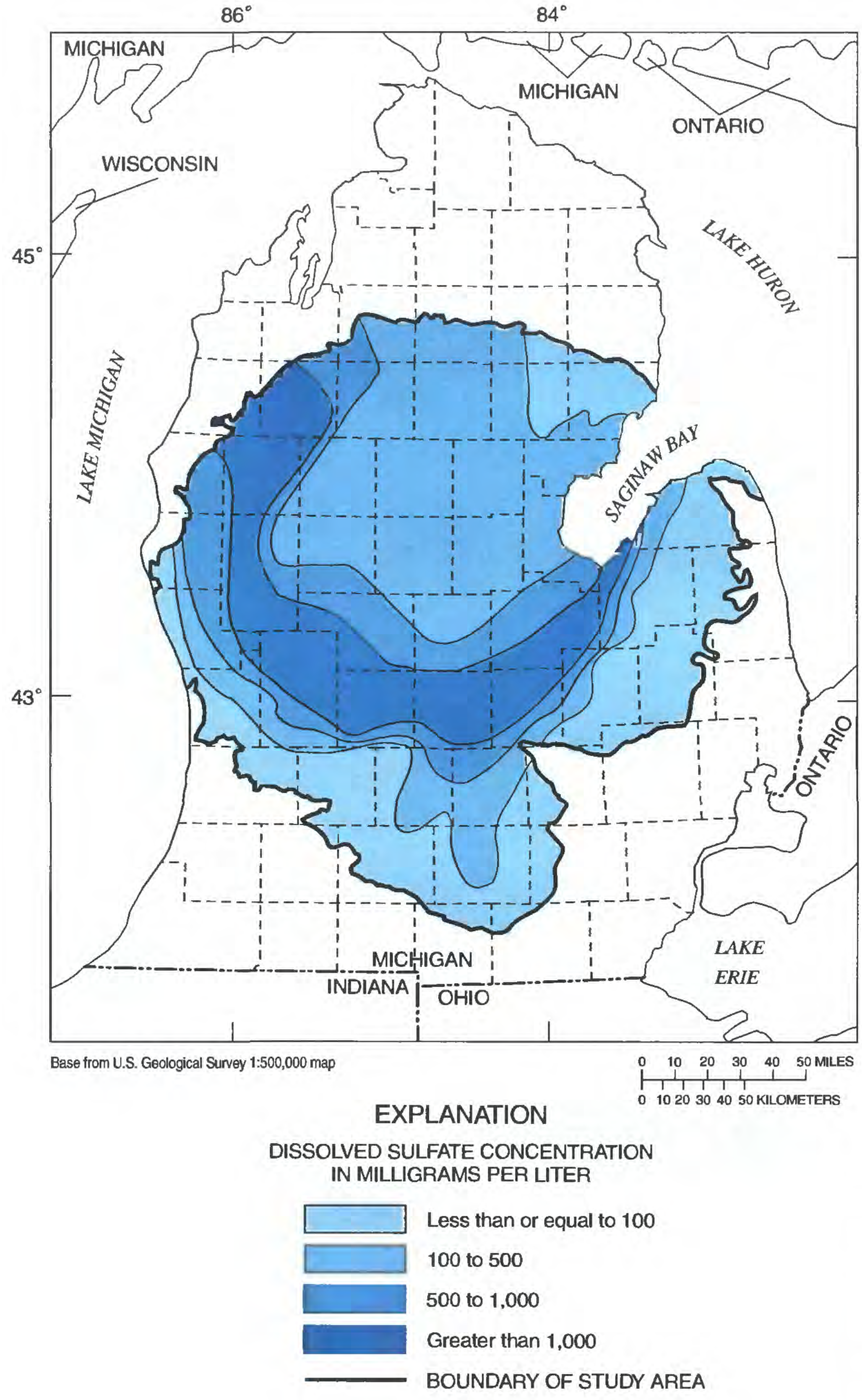


Figure 9. Distribution of dissolved sulfate in ground water from the Marshall aquifer, Lower Peninsula of Michigan.

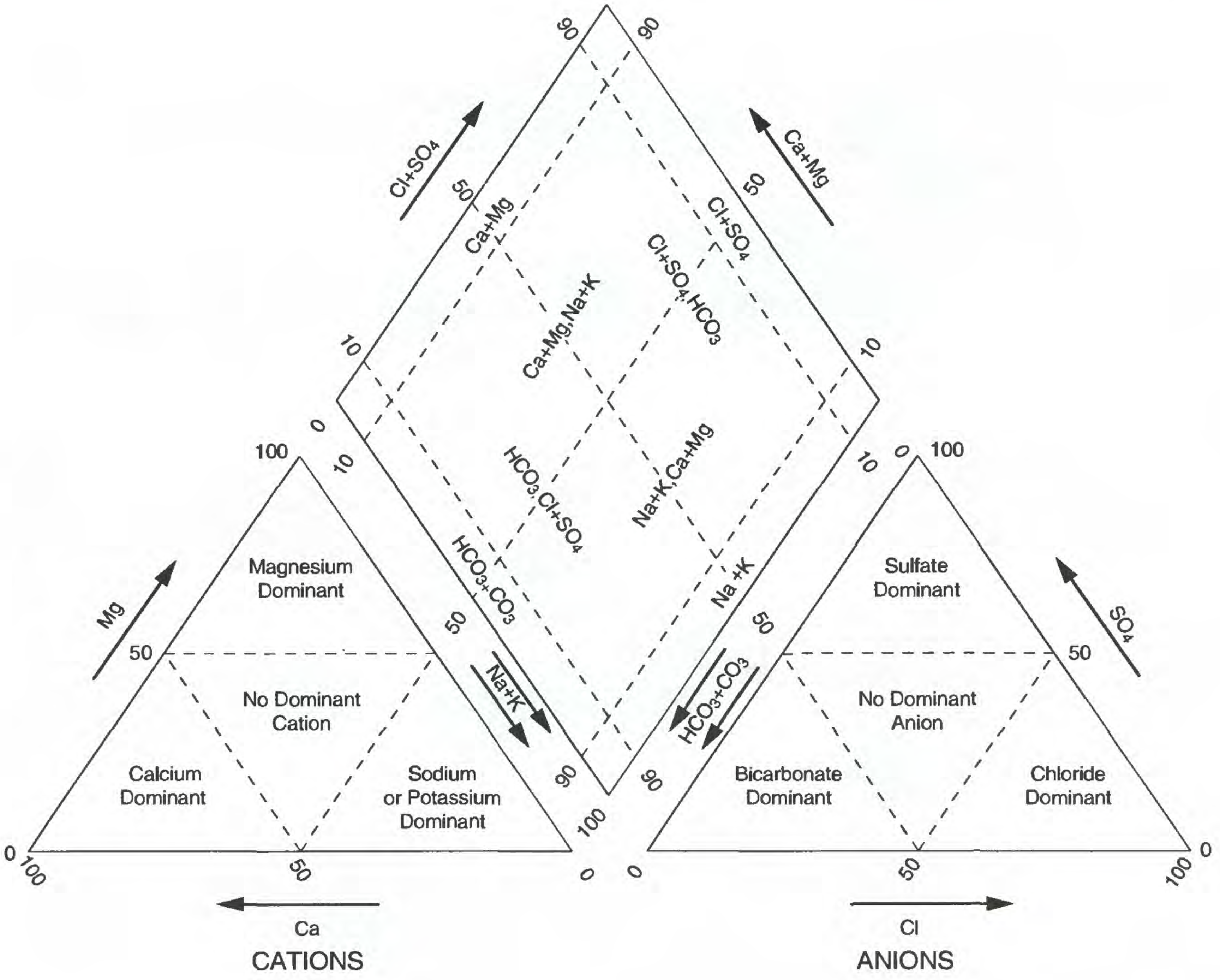
dissolved sulfate toward the center of the study area probably is due to the presence of formation brine in the system that has undergone sulfate reduction (Collins, 1975). Wilson and Long (1993a) have stated a similar conclusion about the similar spatial patterns of dissolved-sulfate concentrations in ground water from Devonian aquifers.

Hydrochemical Facies

Piper Diagrams

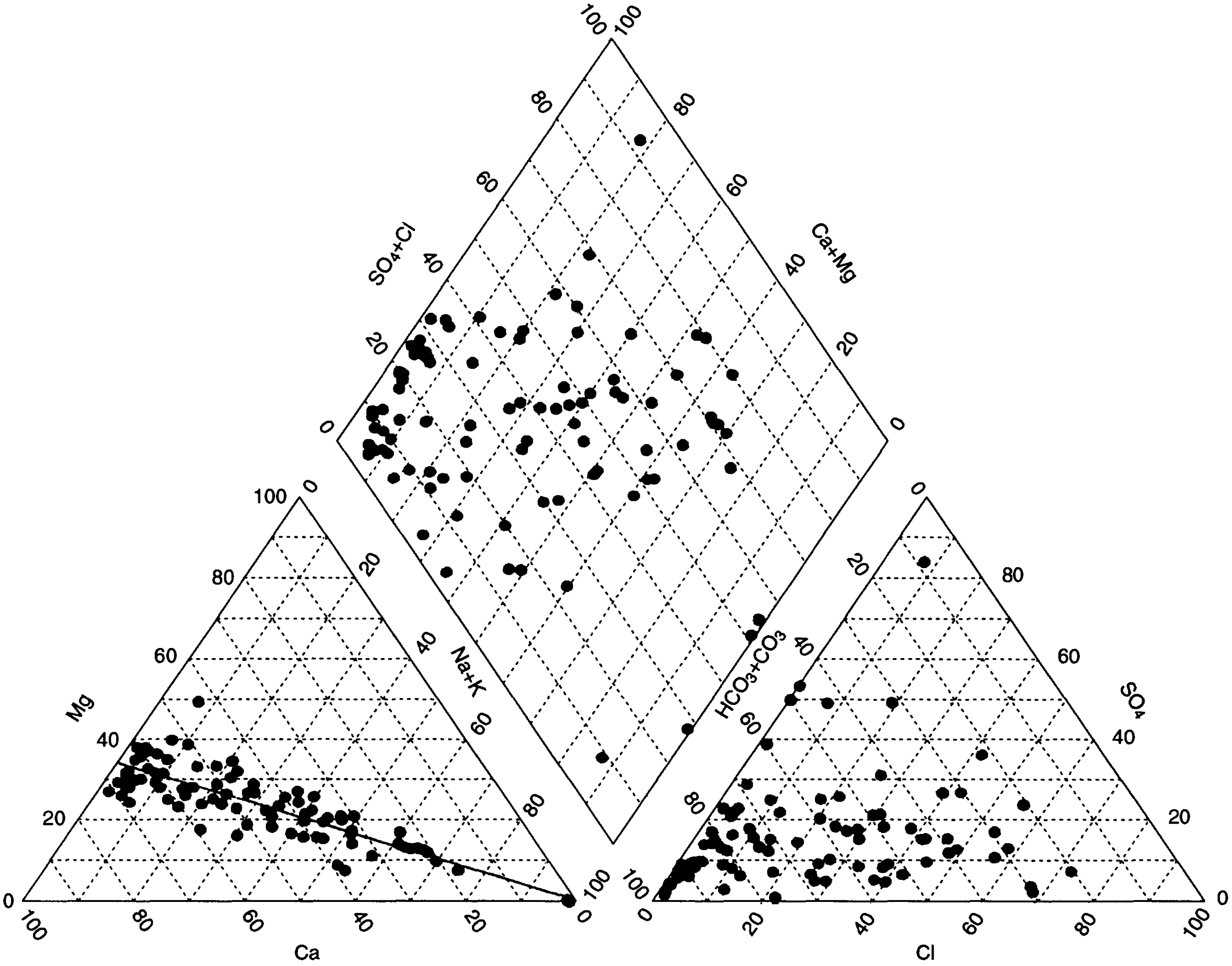
The concept of hydrochemical facies is a means of describing the chemical character of water (Back, 1961). Piper (1944) developed a diagram, commonly referred to as a "Piper plot," that enables the classification of water on the basis of six chemical components. The Piper plot allows easy visual chemical comparisons of the chemistry of water samples, identification of water with similar chemical characteristics, evaluation of mixing among waters having different characteristics, and possible determination of the chemical evolution of ground water. Chemical components used consist of three cation (calcium, magnesium, and sodium plus potassium) and three anion (chloride, sulfate, and carbonate plus bicarbonate) species or groups of species. These ions account for the electrical balance in most natural water (Hem, 1989). Values are plotted on a diagram by converting cation and anion concentrations to milliequivalents per liter and then calculating relative percentages of cation and anion species or groups of species. For diagrammatic purposes, cations and anions each sum to 100 percent. Values of each sample are plotted on respective cation and anion ternary diagrams and also on a central diamond-shaped diagram (fig. 10*A*).

Locations of the samples on ternary diagrams are the basis for identifying a hydrochemical facies of a ground-water sample (fig. 10*A*). A ground-water sample is classified in terms of its dominant cation and anion. For simplification of terminology, potassium is not mentioned in the cation facies in the rest of this report because of the minor importance for determining facies. Likewise, carbonate is not mentioned in the anion facies. The dominance criteria is based on percentage of milliequivalents of major cations (calcium, magnesium, and sodium) and major anions (chloride, sulfate, and bicarbonate). For example, if sodium and chloride ions were greater than 50 percent of total cations and anions, respectively, the water would be classified as dominated by sodium and chloride. For this report, a water sample in which no



A. Classification scheme for hydrochemical facies.

Figure 10. Modified Piper plot of the classification scheme for hydrochemical facies and Piper plots for ground water from the Marshall aquifer, Lower Peninsula of Michigan, at various ranges of dissolved-solids concentrations.



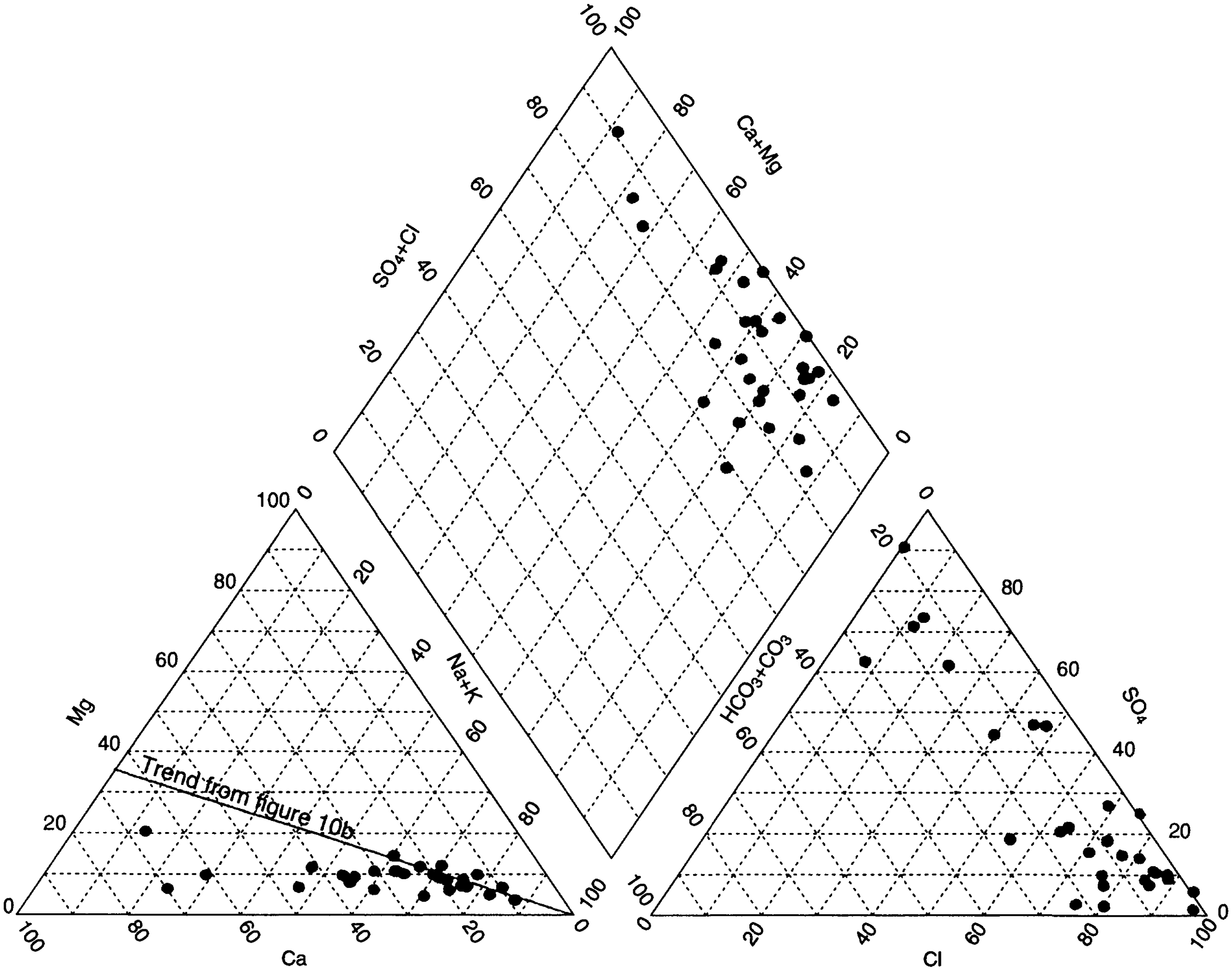
B. Dissolved-solids concentrations less than or equal to 1,000 milligrams per liter. Trend in the cation ternary diagram (lower right) is depicted by a line.

Figure 10.—*Continued.*

cation or anion exceeds 50 percent of the total cations or anions is classified as no dominant cation or no dominant anion.

A major limitation in making interpretations from Piper plots is that water samples with very different dissolved-solids concentrations, but with the same relative proportions of cation and anion species, will plot at the same position on the diagram. This limitation can be handled in many ways (Hem, 1989). In this study, this limitation is addressed by constructing three Piper plots for each aquifer (figs. 10*B* and 10*D*) in which the samples are grouped according to the concentration of dissolved solids. The ranges of dissolved-solids concentration selected for the plots are less than or equal to 1,000 mg/L (low), 1,001 to 10,000 mg/L (intermediate), and greater than 10,000 mg/L (high). The limits were rough estimates of populations based on frequency histograms. The data used to construct the Piper plot of ground water from the aquifer consist of water analyses with less than 10 percent charge imbalance.

At the low concentration range of dissolved-solids concentrations, most of the ground-water compositions plot as calcium-bicarbonate dominant. On the cation ternary diagrams, however, data plot along the same trend from the calcium-dominant area to the sodium dominant area (fig. 10*B*).



C. Dissolved-solids concentrations from 1,001 to 10,000 milligrams per liter. Data in the cation ternary (lower right) are compared to the cation trend line from figure 10*B*.

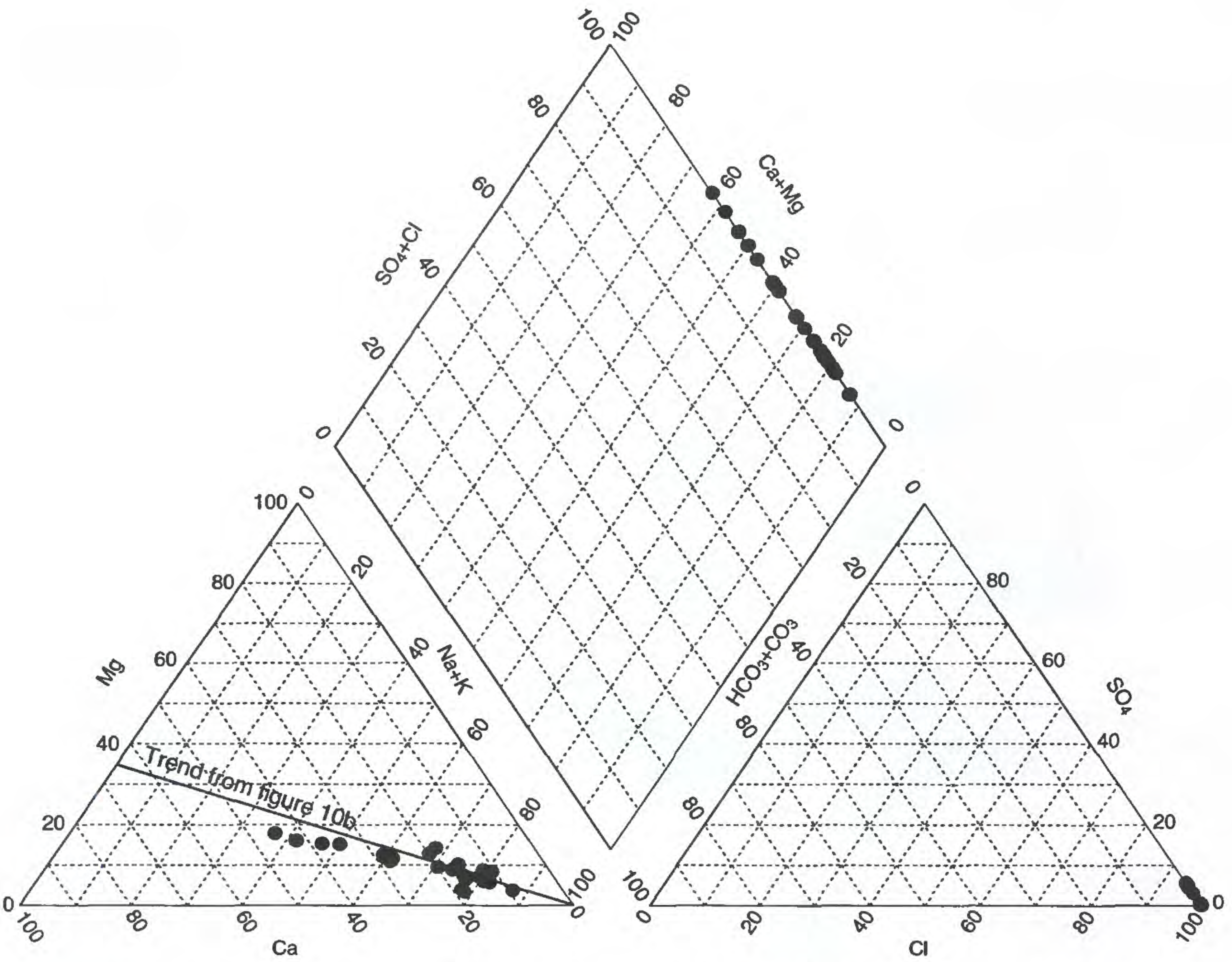
Figure 10.—*Continued.*

With increasing dissolved-solids concentrations, the loci of data along the trend in the cation ternary diagram shifts more towards the sodium corner (figs. 10*C* and 10*D*). In general, along the trend from the calcium field to the sodium field, dissolved solids in the samples increases. However, at high dissolved solids in the Marshall aquifer (fig. 10*D*), many of the samples with the most concentrated samples plot closer to the calcium area. The slope of the trend of the cation data in at intermediate and high dissolved-solids concentrations (figs. 10*C* and 10*D,* respectively) is different from the slope of the cation data at low concentrations (fig. 10*A*).

Within the anion ternary diagram, the data cluster changes from a loci in the bicarbonate field (fig. 10*B*), to a trend line between the sulfate corner and the chloride corner (fig. 10*C*), and to a loci at the chloride corner (fig. 10*D*).

Hydrochemical Facies

A hydrochemical facies map (fig. 11) for the Marshall aquifer was prepared to show the areal distribution of the facies as classified on the Piper plots (figs. 10*B* to 10*D*). A few samples had either no dominant cation or no dominant anion. These were primarily individual samples scattered throughout the study area and are not included in the figures.



D. Dissolved-solids concentrations greater than 10,000 milligrams per liter. Data in the cation ternary (lower right) are compared to the cation trend line from fig. 10*B*.

Figure 10.—*Continued.*

Three dominant hydrochemical facies are observed in ground water from the Marshall aquifer; calcium bicarbonate, sodium chloride, and a third type that has no dominant cation, but with chloride as the dominant anion (no dominant chloride) (fig. 11). In the southern and portions of the eastern parts of the study area, water from the Marshall aquifer is calcium bicarbonate dominant. Ground water in about two-thirds of the study area is sodium chloride dominant. In the center of the study area, ground water from deep wells in the Marshall is no dominant chloride facies that have high concentrations of calcium and sodium. Locally, in the southern part of the study area, calcium sulfate facies are present.

Sodium bicarbonate, sodium no dominant, no dominant bicarbonate, and no dominant facies are the transitions among the three major hydrochemical facies discussed above. The no dominant facies in the southern part of the study area includes ground-water samples that are calcium bicarbonate, sodium bicarbonate, sodium chloride, and calcium no dominant types. The no dominant facies in the northern part contains ground-water samples with facies similar to the no dominant samples in the south as well as no dominant bicarbonate, and sodium no dominant types. The variety of ground-water types comprising the areas of the no dominant facies is in part the result of combining data from water in wells completed at various depths.

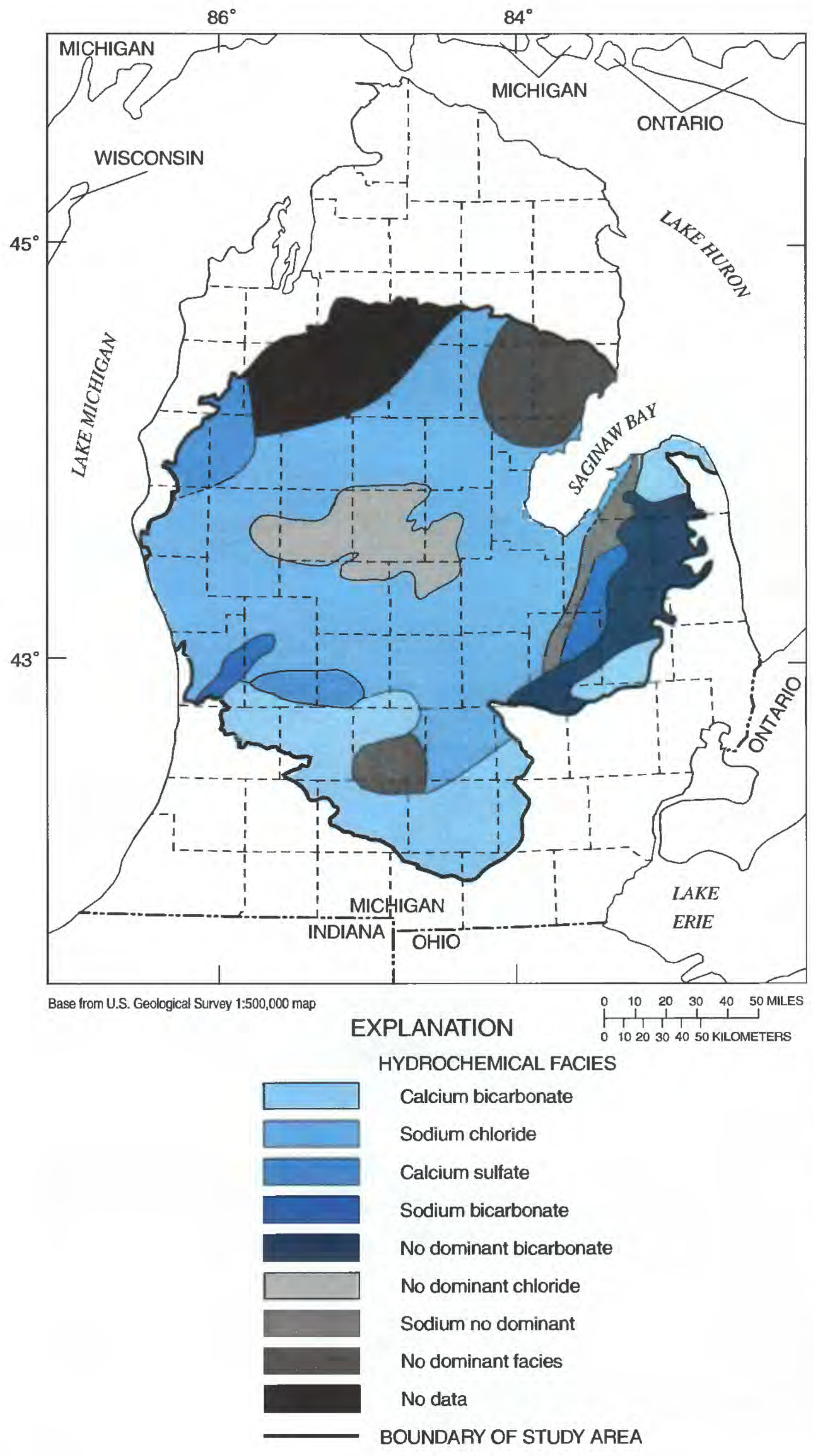


Figure 11. Distribution of hydrochemical facies for ground water from the Marshall aquifer, Lower Peninsula of Michigan.

The most regular change among hydrochemical facies in the Marshall aquifer is found in the eastern subcrop area. Toward the center of the study area, ground water changes from calcium bicarbonate to no dominant bicarbonate to sodium bicarbonate to sodium no dominant to sodium chloride and to no dominant chloride. Similar changes in facies are observed in other areas of the Marshall aquifer.

DISCUSSION

At low dissolved-solids concentrations (<1,000 mg/L), the ground water is mostly calcium bicarbonate dominant. Meteoric water commonly evolves from precipitation that is sodium or calcium sulfate dominant to ground water that is calcium bicarbonate dominant soon after infiltration (Berner and Berner, 1987). The calcium bicarbonate facies, predominant in subcrop areas of the aquifer, is consistent with water having dissolved carbonate minerals after recently recharging the aquifer. Calcium bicarbonate dominant water is a common type of meteoric ground water (Back, 1961; Berner and Berner, 1987) and is typical for ground water in the carbonate mineral rich glacial till of upper Midwestern United States (Freeze and Cherry, 1987).

At high dissolved-solids concentrations (>10,000 mg/L), ground water is commonly sodium chloride dominant, because of mixing with brine and/or dissolution of halite. The sodium chloride facies in the Marshall aquifer is typical for brines that formed by high degrees of evaporation of sea water (past halite precipitation) and that interact with calcite and dolomite (Collins, 1975; Wilson and Long, 1993b). At very high degrees of evaporation and water-rock interaction, water chemistry can change to a calcium chloride type. An area of calcium chloride dominant water was not found in the brines of the Marshall aquifer. However, the area of no dominant chloride hydrochemical facies in the center of the aquifer (fig. 11) is characterized by high proportions of sodium and calcium. These are the highly concentrated samples that plot towards the calcium area in figure 10*D*. Thus, the Marshall brine was evolving to a calcium chloride type.

Two major processes control dissolved-solids concentrations for water with concentrations between 1,000 to 10,000 mg/L (fig. 10*C*). One is the mixing of ground water with brine (and/or halite dissolution) and the other is dissolution of gypsum. Dissolution of gypsum alone can significantly increase the dissolved-solids concentration of water. For example, a geochemical simulation using PHRQPITZ (Plummer and others, 1988) shows that a solution with an initial dissolved-solids concentration of 202 mg/L will increase to greater than 2,000 mg/L on the dissolution of gypsum to saturation (in equilibrium with calcite). Dissolution of gypsum also will increase the relative amount of calcium in solution. This additional source for calcium could account for the slope of the cation trend in figures 10*C* and 10*D* to be lower than slopes for the cation trends at low dissolved-solids concentrations (fig. 10*B*).

Calcium sulfate minerals are distributed throughout the aquifer system (Wood, 1969). Calcium sulfate facies in the Marshall aquifer is caused by the dissolution of calcium-sulfate minerals and perhaps by the input of water that has dissolved gypsum or anhydrite in the overlying Michigan Formation (fig. 2).

SUMMARY

Maps based on chemical analyses of ground water from the Marshall aquifer, central Lower Peninsula of Michigan, were prepared to show areal variations of $\delta^{18}O$ and concentrations of dissolved solids, dissolved chloride, dissolved sulfate, dissolved iron and hydrochemical facies.

Interpretation of δD and $\delta^{18}O$ relations indicate that brine from the evaporation of sea water, modern meteoric and glacial-age meteoric water are present in the Marshall aquifer. Trends in the values of δD and $\delta^{18}O$ indicate mixing of modern meteoric with and glacial-age meteoric water and brine. The $\delta^{18}O$ values of the ground water become heavier toward the center of the study area. The lighest values are adjacent to Saginaw Bay.

Areal-distribution maps of dissolved solids and dissolved chloride in the Marshall aquifer show that the samples with high concentration are from deep wells in the center of the study area and that the most dilute samples are in the subcrop areas. The source for high-dissolved solids and dissolved-chloride concentrations is from brine. Sources for dissolved solids and chloride in freshwater generally are those components in the recharge water and water-rock interaction.

Dissolved-iron concentrations are low in the subcrop areas and increase toward the center of the basin. Locally high concentrations of dissolved iron in subcrop areas are the result of changes in the oxidation-reduction state of the system. In the southern, southeastern, and western parts of the study area, dissolved-sulfate concentrations increase and then decrease from the subcrop to the center of the study area. Sulfate is derived from recharge, which includes sulfate in precipitation as well as that from sulfate minerals. Concentrations of dissolved sulfate also have been affected by sulfate reduction.

Distributions of data on Piper plots show a trend from the calcium dominant area to the sodium dominant area. At low dissolved-solids concentration, the data are weighted to calcium dominant; at high dissolved-solids concentrations, they are weighted to sodium dominant. Water samples in the anion ternary diagram plot mainly between bicarbonate and chloride dominant at low dissolved-solids concentrations, between chloride and sulfate dominant at intermediate dissolved-solids concentrations, and as chloride dominant at high dissolved-solids concentrations.

Three dominant hydrochemical facies in ground water from the Marshall aquifer are calcium bicarbonate, sodium chloride, and no dominant chloride. Ground water in the southern part and other areas around the subcrop of the Marshall aquifer is dominated by a calcium bicarbonate facies. Ground water in about two-thirds of the interior of the basin area is dominated by the sodium chloride facies.

Sodium chloride dominant water is from brine originating from evaporation of seawater past halite precipitation.

Toward the center of the study area, hydrochemical facies of ground water change to the no dominant chloride facies that is typical for brines formed by evaporation of seawater well past halite precipitation and by interaction with calcite and dolomite. In the southern part of the study area, calcium-sulfate facies are present as a result of dissolution of calcium sulfate minerals and, perhaps, the input of water that has undergone water-rock interactions in the Michigan Formation overlying parts of the aquifer.

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