GEOCHEMISTRY OF WATER IN AQUIFERS AND CONFINING UNITS OF THE NORTHERN GREAT PLAINS IN PARTS OF MONTANA, NORTH DAKOTA, SOUTH DAKOTA, AND WYOMING

REGIONAL AQUIFER-SYSTEM ANALYSIS

U.S. GEOLOGICAL SURVEY PROFESSIONAL PAPER 1402-F

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By JOHN F. BUSBY, BRIANT A. KIMBALL, JOE S. DOWNEY, *and*
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U.S. DEPARTMENT OF THE INTERIOR
MARCH 3, 1849

UNITED STATES GOVERNMENT PRINTING OFFICE, WASHINGTON: 1995

U.S. DEPARTMENT OF THE INTERIOR
BRUCE BABBIT, *Secretary*

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

Library of Congress Cataloging-in-Publication Data

Geochemistry of water in aquifers and confining units of the northern Great Plains in parts of Montana, North Dakota, South Dakota, and Wyoming / by John F. Busby . . . [et al.].
p. cm.—(Regional aquifer-system analysis —Northern Great Plains) (U.S. Geological Survey professional paper ; 1402–F)
Includes bibliographical references.
Supt. of Docs. no.: I19.16:P1402F
1. Water chemistry—Williston Basin. 2. Aquifers—Williston Basin. I. Busby, John F. II. Series. III. Series: U.S. Geological Survey professional paper ; 1402–F.
GB857.2.W55G46 1994
551.49'0978—d20 93–2838
CIP

For sale by USGS Map Distribution
Box 25286, Building 810
Denver Federal Center
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FOREWORD

THE REGIONAL AQUIFER-SYSTEM ANALYSIS PROGRAM

The Regional Aquifer-System Analysis (RASA) Program was started in 1978 following a congressional mandate to develop quantitative appraisals of the major ground-water systems of the United States. The RASA Program represents a systematic effort to study a number of the Nation's most important aquifer systems, which in aggregate underlie much of the country and which represent an important component of the Nation's total water supply. In general, the boundaries of these studies are identified by the hydrologic extent of each system and accordingly transcend the political subdivisions to which investigations have often arbitrarily been limited in the past. The broad objective for each study is to assemble geologic, hydrologic, and geochemical information, to analyze and develop an understanding of the system, and to develop predictive capabilities that will contribute to the effective management of the system. The use of computer simulation is an important element of the RASA studies, both to develop an understanding of the natural, undisturbed hydrologic system and the changes brought about in it by human activities, and to provide a means of predicting the regional effects of future pumping or other stresses.

The final interpretive results of the RASA Program are presented in a series of U.S. Geological Survey Professional Papers that describe the geology, hydrology, and geochemistry of each regional aquifer system. Each study within the RASA Program is assigned a single Professional Paper number, and where the volume of interpretive material warrants, separate topical chapters that consider the principal elements of the investigation may be published. The series of RASA interpretive reports begins with Professional Paper 1400 and thereafter will continue in numerical sequence as the interpretive products of subsequent studies become available.

Gordon P. Eaton

Gordon P. Eaton
Director

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[Plates are in pocket]

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METRIC CONVERSION FACTORS AND ABBREVIATIONS

Multiply	By	To obtain
inch (in.)	0.3048	meter
mile (mi)	1.609	kilometer
square mile (mi^2)	2.590	square kilometer
inch per year (in/yr)	25.40	millimeter per year
atmosphere (atm)	1.01325	pascals

Temperature in degree Celsius (°C) can be converted to temperature in degree Fahrenheit (°F) by using the following equation:

$$°F=9/5\ °C+32.$$

The following terms and abbreviations also are used in this report:

milligram per liter (mg/L)	mole (mol)
microgram per liter (µg/L	part per thousand (‰)
millimole per liter (mmol/L	part per million (ppm)

REGIONAL AQUIFER-SYSTEM ANALYSIS—NORTHERN GREAT PLAINS

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ABSTRACT

The Northern Great Plains Regional Aquifer System Analysis was an interdisciplinary project that began in 1981. The mission of the project was to derive an understanding of the ground-water resources of eastern Montana and Wyoming and all of North Dakota and South Dakota. The geochemical part of that project used data from the U.S. Geological Survey and other services to interpret the geochemical system of the northern Great Plains. These data were edited to contain a set of consistent variables. Water samples with an ionic balance that was more than 5 percent away from electroneutrality or that had a pH less than 6.5 or greater than 9.0 were deleted from the file. Trends in the concentration of dissolved solids and chloride were used to identify directions of flow. Recharge waters were defined as waters with dissolved-solids concentrations less than 1,000 mg/L, chloride concentrations less than 20 mg/L, and temperatures less than or equal to the mean temperature of 15°C.

Cambrian-Ordovician aquifer.—Concentrations of dissolved solids are less than 2,000 mg/L in the highlands and increase downgradient. The other major cations and anions, except sulfate, have the same trend as dissolved solids. Sulfate, as indicated by the increasing ratio of bicarbonate to sulfate, seems to be precipitating. Values of pH decrease with increasing dissolved solids from about 8.0 in the highlands to less than 7.0 downgradient. The conversion of a dioctahedral to a trioctahedral clay probably accounts for decreasing magnesium-to-calcium ratio as the water moves downgradient. The hydrochemical facies are an alkali-earth carbonate facies at the beginning of the flow path and change to an alkali-earth sulfate facies downgradient. Graphs showing the variabilities of sodium with chloride indicate dissolution of silicate phases at small concentrations; whereas, at concentrations near 10,000 mg/L, sodium and chloride are present in equimolar quantities. At concentrations near halite saturation, the chloride excess indicates that the contribution of calcium and magnesium chlorides becomes important. Concentrations of dissolved solids in the Williston basin, an area of limited flow, are greater than 300,000 mg/L and evolve into the sodium-chloride facies—a facies of typical evaporite dissolution.

Silurian-Devonian confining unit.—The concentration of dissolved solids, which is no more than 700 mg/L in the highlands, is greater than 10,000 mg/L throughout most of the area and exceeds 300,000 mg/L in the Williston basin. At the largest concentrations, there is an excess of chloride compared to sodium, which indicates precipitation of halite. The ratio of magnesium to calcium is typically about 0.4 but decreases to values near 0.07 in the Williston basin—a decrease that may result from the conversion of dioctahedral to trioctahedral clays. The calcium-magnesium-sulfate hydrochemical facies observed in the outcrop is replaced by the sodium-chloride facies elsewhere in the study area.

Madison aquifer.—The dissolved-solids concentrations in the Madison aquifer are substantially smaller than those in the Cambrian-Ordovician aquifer but have a similar regional distribution. Dissolved-solids concentrations less than 500 mg/L in the highlands increase in downgradient areas. Values of pH also have the same patterns as the Cambrian-Ordovician aquifer—larger in the highlands (7.5) and decreasing downgradient. The graphs of the variation of sodium with chloride show halite dissolution until chloride concentrations approach 150,000 mg/L; then values near halite saturation are approached. At larger concentrations, an excess of chloride is seen. The ratio of magnesium to calcium, about 0.1 in the highlands, decreases downgradient to values less than 0.01; this decrease may be caused by the conversion of dioctahedral to trioctahedral clay. The ratio of bicarbonate to sulfate is rather constant throughout most of the area but does decrease when larger concentrations of dissolved solids occur. This decrease may indicate continued dissolution of gypsum while the carbonate is held constant by an equilibrium control. Hydrochemical facies

follow a typical evolution from alkali-earth carbonates near the recharge area to a sodium-chloride facies far downgradient. The system, except in the Williston basin, is saturated with calcite and dolomite but below saturation with halite and gypsum. In the dilute part of the system, dedolomitization is accompanied by the dissolution of gypsum, organic matter, and the precipitation of pyrite; neither methaneogenesis nor cation exchange is a significant mechanism. As the evaporite facies at the periphery of the Williston basin is approached, the dissolved solids increase quickly, finally reaching values greater than 400,000 mg/L. In the Williston basin, pH values are about 6.5.

Pennsylvanian aquifer.—The smallest concentrations of dissolved solids occur in the highlands. These values increase downgradient to concentrations greater than 5,000 mg/L in the vicinity of the Bull Mountain basin, more than 100,000 mg/L in the Powder River basin of Wyoming and Montana, and more than 300,000 mg/L in the Williston basin. The pH values, which ranged from 6.5 to 9.0 pH units, are typically highest in the uplands and lowest in the Williston basin, Central Montana trough, and Powder River basin. The trend in sodium and chloride are the same as those of dissolved solids. At dissolved-solids concentrations less than about 10,000 mg/L there is excess sodium; from 10,000 to 300,000 mg/L, the mole ratio of sodium to chloride would be about 1:1, while at larger concentrations, there is a chloride excess. The continued dissolution of gypsum drives the downgradient decrease of the magnesium-to-calcium and bicarbonate-to-sulfate ratios. In the more dilute waters, the calcium-magnesium-bicarbonate and calcium-magnesium-sulfate facies are common, changing into a sodium-sulfate facies near the border of the Williston basin. The saturation indexes indicate that gypsum is below saturation everywhere except for an area north of the Pryor Mountains and in the Powder River, Bull Mountain, and Williston basins. Water is saturated with respect to calcite throughout the system. The principal mechanistic controls seem to be the dissolution of gypsum, dolomite, and evaporites.

Permian-Triassic-Jurassic confining unit.—The dissolved-solids concentration is less in this unit than in the others; 75 percent of the samples have a dissolved-solids concentration less than 7,000 mg/L. Dissolved-solids concentrations do exceed 10,000 mg/L in the Powder River basin. The values of pH range from 6.5 to 9.0; higher values typically occur in the uplands and decrease basinward. The other cations and anions usually have the same trends seen for dissolved solids. The ratio of magnesium to calcium ranges from 5.6 to 0.3. The decrease parallels the increase in dissolved solids. The hydrochemical facies indicate a trend from alkali-earth bicarbonate facies in the highlands to sodium-chloride-sodium-sulfate facies as the Williston basin is approached. Important mechanisms are dissolution of evaporites in the Williston basin area.

Lower Cretaceous aquifers.—The waters of the Inyan Kara aquifer in the uplands have dissolved-solids concentrations less than 500 mg/L. Calcium and magnesium decrease downgradient while the concentration of sulfate increases, but both show anomalous values near the Hartville uplift (more than 3,000 mg/L in Wyoming) and near the southern end of the Black Hills. Sulfate reduction is indicated by the downgradient increase in bicarbonate at the expense of sulfate. Chloride concentrations increase basinward. Ratios of deuterium to oxygen-18 plot on the meteoric-water line, which indicates that the increase is not caused by connate water. The waters of the Dakota aquifer are more concentrated but have the same pattern as the waters of the Inyan Kara aquifer. The basinal waters of the Dakota aquifer are more concentrated than those of the Inyan Kara aquifer; dissolved-solids concentrations are larger than 10,000 mg/L in the Bull Mountain basin and more than 150,000 mg/L in the Williston basin. Ions other than bicarbonate have the same trends as dissolved solids. Bicarbonate concentrations are larger than 3,000 mg/L in some places but generally are less than other ions. The basinal waters of the Dakota aquifer belong to a chloride facies. Mineral dissolution is judged inadequate to account for the concentrations of sodium and chloride in the Dakota aquifer, and, although upward leakage is favored by the hydraulics, it is eliminated as the principal source of chloride because concentrations of sodium and chloride in the Dakota aquifer are greater than those of the underlying Inyan Kara aquifer. The most probable source of salts is leakage from the overlying and underlying shales. Evidence is strong for leakage in the pinch-out area. Dissolved-solids concentrations increase abruptly; the change from bicarbonate anion–hydrochemical facies to the sulfate is typical of the Madison aquifer in this area, and the geothermal gradient changes from 0.7 to 0.11 °C per 100 ft to about 2 °C per 100 ft.

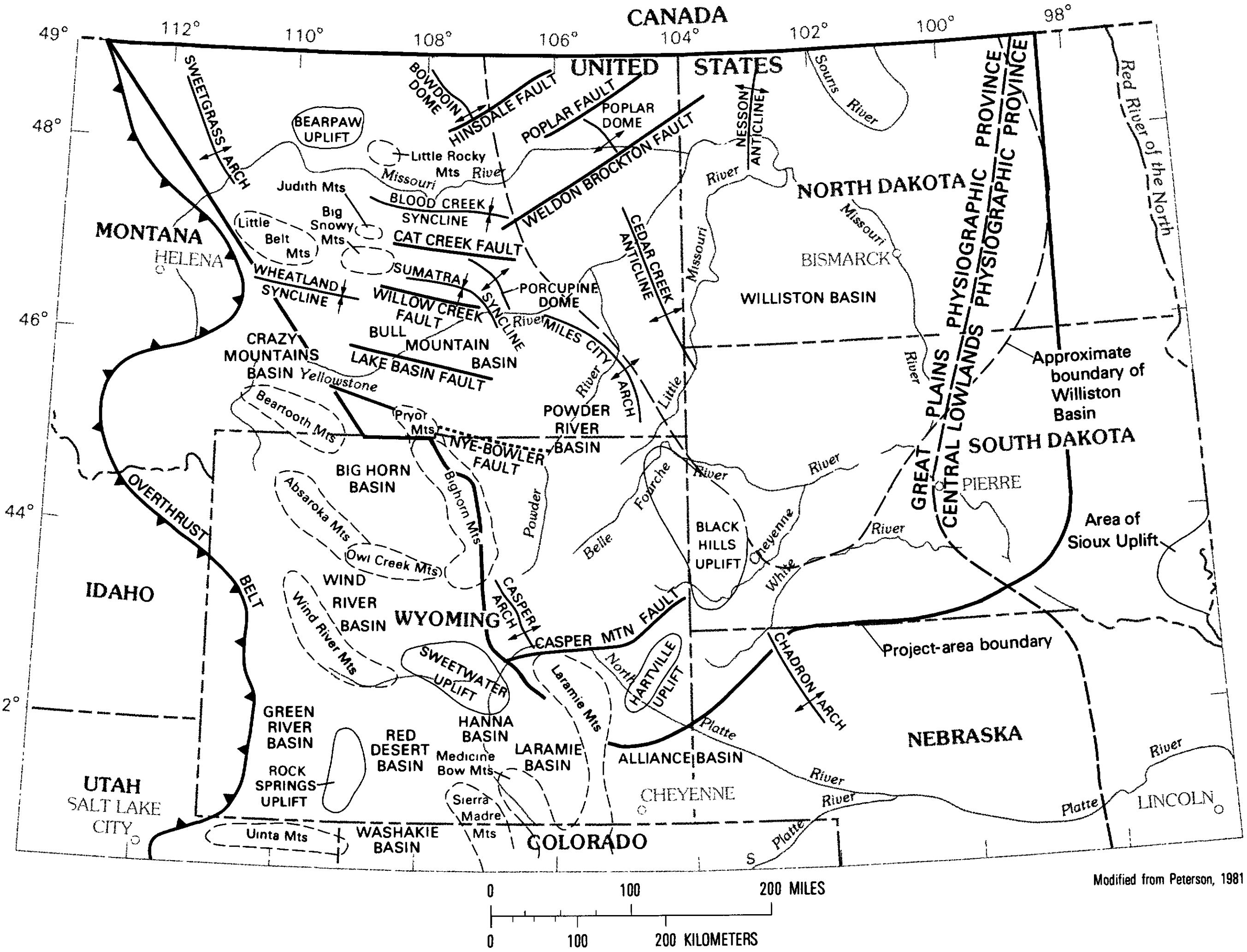
INTRODUCTION

The northern Great Plains physiographic province includes an area of more than 300,000 mi^2 in the north-central United States and adjoining parts of Canada. The area is bounded on the west by the Middle and Northern Rocky Mountains and on the east by the Central Lowland province. The physiographic province extends into Canada on the north; in general, however, this study was limited to the areas south of the United States-Canadian border (fig. 1). This study also included a part of the Central Lowland province in eastern North Dakota and South Dakota.

In general, the study area is characterized by broad, flat, gently rolling plains, underlain by sandstone and shale, that have been dissected by streams crossing the plains. At sites where streams have cut into the soft, underlying rocks, the relief may reach several hundreds of feet.

The broad, flat expanse of plains is interrupted by the Black Hills of South Dakota and by the Rocky Mountains. These highland areas are the sites of major recharge to the northern Great Plains aquifers (Downey, 1986).

Development of energy-related resources, power generation, industrial development, increasing irrigation, and increased water supply for domestic and municipal use in the area of the northern Great Plains are dependent on the availability of water resources. Streamflow historically has satisfied many of the water needs; however, surface water not only has been appropriated fully in much of the area but also is undependable because flows are extremely variable. Long-term, large-scale water needs will require development of productive bedrock aquifers, some of which have been little used in the past.



Modified from Peterson, 1981

FIGURE 1.—Location of study area and major geologic structures in and near the project area.

Without knowledge of the hydrologic characteristics of the ground-water system, of its chemical quality, and of its response to withdrawals, large, sustained yields of ground water cannot be produced efficiently, and sound management plans cannot be formulated.

Proper development, use, and conservation of ground-water resources can be achieved only through an understanding of the regional geologic framework (pls. 1 and 2; fig. 1) and its effect on the response of the hydrologic system to climate and water-supply development. Within the limits of time, personnel, and available data, the objectives of the Northern Great Plains Regional Aquifer-System Analysis (RASA) were as follows:

1. To define the regional geologic framework that controls ground-water flow;
2. To define the chemical characteristics of the water in the aquifers;
3. To define the ground-water flow patterns; and
4. To determine areas suitable for development with optimum well yields.

To accomplish these objectives, stratigraphy, mineralogy, hydrology, geophysics, sedimentary, and structural controls that govern permeability distribution and hydrologic properties of the aquifers were studied on a regional basis.

PURPOSE AND SCOPE

This report is one of several that resulted from the study and encompasses the geochemical aspects of the selected aquifers and confining units. Some interpretations in the report depend substantially on information obtained during a study of the Madison aquifer (Brown and others, 1984; Downey, 1984a).

The purpose of the geochemical study of the Northern Great Plains RASA was threefold:

1. To describe the regional trends of water chemistry of the aquifers and confining units;
2. To determine plausible mechanisms responsible for the present water chemistry;
3. To use geochemical data to identify areas of recharge and directions of flow.

The report is divided into sections that first detail the hydrogeologic setting of the northern Great Plains aquifers and confining units. These sections are followed by a description of the procedures used to construct, edit, and use the data base. The use of geochemical data to make hydrologic inferences is discussed next, and finally, the data are used to infer the geochemical processes that cause the observed trends. After compiling a geochemical data base, it was possible to follow through with the objectives of the study, as described above. Geochemical interpretations are given for waters from sedimentary rocks of Paleozoic through Early Cretaceous age.

GEOGRAPHIC SETTING

This study encompasses parts of the northern part of the Great Plains and Central Lowland physiographic provinces of the United States and includes northeastern Wyoming and eastern Montana, North Dakota, and South Dakota (fig. 1). Major physiographic features in the western part of the study area include the Bighorn Mountains, the Laramie Mountains, the Hartville uplift, the Big Snowy Mountains, and the Black Hills uplift. In the east, the study area is characterized by a nearly flat area that contains the broad, flat, lake plain formed by glacial Lake Agassiz in the northeastern part of North Dakota.

Glacial Lake Agassiz covered an area of about 200,000 mi^2 during the late Pleistocene, in the Canadian provinces of Ontario, Manitoba, and Saskatchewan and in Minnesota, North Dakota, and the northeastern part of South Dakota (Elson, 1967). However, during most phases of Lake Agassiz, the surface area probably did not exceed 80,000 mi^2.

The northern Great Plains regional aquifer study area is located in the interior of the North American Continent. The climate is classified as middle-latitude steppes and occupies a transitional zone between arid lands to the west and more humid climate to the east. In general, winters in the study area are cold and snowy with occasional blizzards. Summers have warm days and cool nights and isolated thunderstorms that occur in the late afternoons and evenings. The major weather systems that cross the area, however, bring a variety of weather in all seasons. Precipitation in the form of rain and snow occurs throughout the area; the least precipitation occurs in the interior of the area and the greatest in the mountainous highland areas in the west.

The major rivers draining the area include the Yellowstone, Missouri, North Platte, and Red River of the North and their tributaries. The Red River of the North forms the eastern boundary of the study area.

HYDROGEOLOGIC SETTING

The confined ground-water system of the northern Great Plains includes numerous permeable horizons; many of which are discontinuous, and all of which vary considerably in hydraulic properties from one location to another. During the study, five major subdivisions (pls. 1 and 2) of the regional aquifer system were made—Cambrian-Ordovician (AQ1), Madison (AQ2), Pennsylvanian (AQ3), Lower Cretaceous (AQ4), and Upper Cretaceous-Tertiary (AQ5) aquifers. The geochemistry of water in all but the Upper Cretaceous-Tertiary aquifer is considered in this report. Each of these aquifers is an aggregate of materials having widely varying permeabilities. Each has been identified as an aquifer primarily because vertical hydraulic-head differences within each unit tend to be much smaller than those between it and the adjacent unit. To some extent, the division is arbitrary and has been made to assist in analysis and discussion of the aquifer system as a whole.

These five major aquifers constitute one of the largest confined aquifer systems in the United States (Downey, 1986). The flow system extends more than 600 mi from mountainous recharge areas in Montana, Wyoming, and South Dakota to discharge areas in the eastern Dakotas and the Province of Manitoba, Canada. The total area involved is more than 300,000 mi^2. The geologic units that constitute each of the five major aquifers and the intervening confining units are summarized on plates 1 and 2 and briefly discussed below.

1. *Lower boundary.*—Consists of crystalline rocks of Precambrian age that underlie the study

area. On a regional basis, these rocks normally are not water bearing.

2. *Cambrian-Ordovician aquifer (AQ1).*—Consists of sandstones of Late Cambrian age and limestones of Middle and Late Ordovician age. This aquifer principally is composed of the Red River Formation but includes the Deadwood Formation of Cambrian and earliest Ordovician age, the Winnipeg Formation, and the over-lying Stony Mountain Formation of Ordovician age. The aquifer underlies about 217,000 mi^2 in western Montana, North Dakota, South Dakota, and northwestern Wyoming and extends into Canada, where it crops out along the Precambrian shield.
3. *Confining layer 1 (TK1).*—Consists of shale, shaly carbonates, evaporite, and halite beds of Silurian and Devonian age designated the Silurian-Devonian confining unit in this report. Although some evidence exists for solution of the halite beds along their margins, the halite beds are considered to be impermeable. The black, organic-rich shales of the Mississippian part of the Bakken and Englewood Formations are components of this confining layer.
4. *Madison aquifer (AQ2).*—Consists of siltstone, sandstone, limestone, and dolomite that are part of the Lodgepole and Mission Canyon Limestones of the Madison Group or the Madison Limestone and equivalent units. The limestone and dolomite of the Madison, in general, are fine textured and massive, and most of the permeability of the formation is secondary or fracture permeability. The Madison aquifer underlies about 210,000 mi^2 of the study area.
5. *Confining layer 2 (TK2).*—Consists of halite, evaporites, and limestone of the Upper Mississippian Charles Formation of the Madison Group or equivalent units of the Madison Limestone and the shale, limestone, and sandstone of the Kibbey, Otter, and Heath Formations of the Big Snowy Group. Geochemical data from this confining unit were available only from a small area of the northern Great Plains, and so they are not considered here.
6. *Pennsylvanian aquifer (AQ3).*—Consists of sandstones and limestones of the Minnelusa Formation, Tensleep Sandstone, and Amsden Formation (or Group where it is divided) and equivalents of Pennsylvanian age.
7. *Confining layer 3 (TK3).*—Consists of siltstone, shale, limestone, evaporite, and halite units of the Opeche Formation and Minnekahta Limestone of Permian age; Spearfish Formation of Permian and Triassic age; and the upper part of the Goose Egg and Chugwater Formations of Triassic age. The Gypsum Spring, Piper, Rierdon, Sundance, Swift, and Morrison Formations all of Jurassic age also are included in this confining unit that is designated the Permian-Triassic-Jurasic confining unit in this report. On the basis of information from model simulations (Downey, 1984a, 1986) and geochemical data, this confining layer seems to be the principal hydrologic barrier to the vertical leakage of water throughout most of the area between the underlying Paleozoic aquifers and the overlying Lower Cretaceous aquifers.
8. *Lower Cretaceous aquifers (AQ4).*—This unit consists of the sandstone and siltstone of the Lakota and Fuson Formations and the Fall River and Newcastle Sandstones of Early Cretaceous age. These formations or their equivalents underlie much of the northern Great Plains of the United States and extend into Canada. The Lower Cretaceous aquifers, also are known as the Dakota aquifer in North Dakota and as the Inyan Kara aquifer in South Dakota. Only the Dakota and Inyan Kara aquifers are considered in this report.
9. *Confining layer 4 (TK4).*—Consists of shale, siltstone, and limestone units above the Lower Cretaceous aquifers (AQ4) and includes the Mowry Shale of Early Cretaceous age and Belle Fourche Shale, Greenhorn Formation, Carlile Shale, Niobrara Formation, and Pierre Shale and their equivalents of Late Cretaceous age. The confining layer will not be discussed in this report because of insufficient geochemcal data.
10. *Upper Cretaceous-Tertiary aquifer (AQ5).*—Consists of Upper Cretaceous formations, such as the Fox Hills Sandstone and Hell Creek Formation and their equivalents, that overlie the Upper Cretaceous shale and siltstone of confining layer TK4. The Upper Cretaceous-Tertiary aquifer is also not discussed here because of insufficient geochemical data.

The present structure and paleogeography (fig. 1) of the northern Great Plains is directly related to the geologic history of the Cordilleran platform, which is a part of the stable interior of the North American Continent. During Paleozoic time, many structural features developed that affected the deposition of the various sedimentary units. Many of these structural features exist today and are important in determining the present hydrologic regimen for the aquifer systems that occur in the northern Great Plains.

Crystalline rocks of Precambrian age (fig. 1) form the basement in the northern Great Plains. Precambrian basement rocks are exposed in outcrops of the eastern and western parts of the project area and also occur at depths of more than 17,000 ft at the center of the Williston basin.

On a regional basis, little is known about the hydraulic properties of the Precambrian rocks. Available data indicate that these rocks contain only a small volume of water in joints and fractures, except along major fracture systems, where they may yield water to wells. This water is obtained from leakage from the overlying sedimentary sequence (Downey, 1984a, 1986). Therefore, the Precambrian rocks are not considered to be water yielding. Precambrian rocks in the study area represent the lower boundary of the regional aquifer system underlying the northern Great Plains.

During most of Paleozoic time, the study area was part of the Cordilleran platform. This broad, flat area was bordered on the west by the Cordilleran miogeosyncline, which trended approximately northward in Idaho and western Montana. Most of the detrital sediments in the synclinal trough came from the Antler orogenic belt that probably existed as an island arc system to the west that underwent intermittent tectonism during middle Paleozoic time. The Transcontinental arch, southeast of the study area, was low lying and sporadically contributed minor quantities of sediment that were spread thinly by currents across the platform. In general, the Cordilleran platform was a shallow-water marine depositional shelf that produced dominantly carbonate and evaporite sediments during most of Paleozoic time.

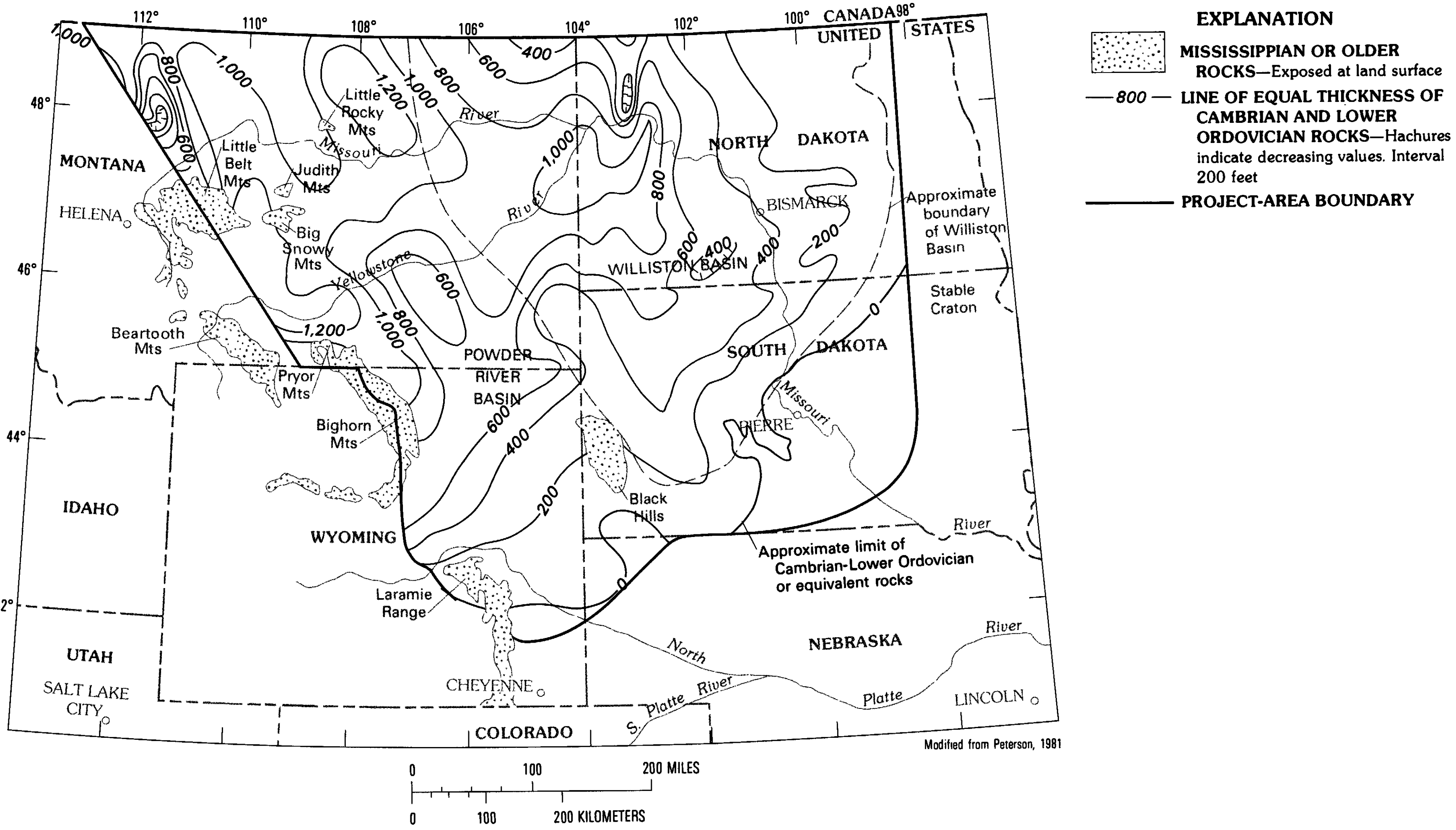
During the Pleistocene Epoch, the northern Great Plains aquifer system was subjected to changes of recharge-discharge relations caused by the four glaciations and three interglacial periods, as suggested by Downey (1986). At the time of maximum glacial advance, Wisconsin glaciation, the discharge area of the aquifer system was covered by a thick mass of ice that blocked discharge, forcing flow to the southeast. During interglacial periods, glacial ice was absent from the aquifer discharge areas, and the inferred flow direction returned to the northeast, similar to the present-day pattern. Except for local mountain glaciation, the highland areas in the western part of the northern Great Plains were not affected by continental glaciation and continued to be recharge areas for the bedrock aquifers.

The Black Hills uplift (fig. 1) was not a regionally significant tectonic element until Late Cretaceous time (Agnew and Tychsen, 1965) and had little effect on sedimentation during Paleozoic time. During the Mississippian age, the study area generally was covered by a shallow, warm sea probably less than a few feet deep (Sando, 1974). However, small areas did exist where deepwater sediments did accumulate. The warm sea was conducive to a high rate of biologic productivity and rapid accumulation and preservation of sediments. Shoals and reefs were a common aspect of the generally shallow-water conditions that prevailed in the study area. These shallow-water areas continually changed and shifted because of the effects of geologic forces in time and space. Many of these shallow areas or "knee-deep environments" had small reefs associated with them, in addition to many oolite and crinoid-bank shoals and lagoons. Lagoonal areas functioned as evaporating basins in which gypsum and halite precipitated and became incorporated into the lime-enriched bottom sediments. Gypsum commonly would precipitate in the lagoonal environments that frequently received influxes of seawater; whereas, evaporation seldom would proceed to the point of halite precipitation. Evidence of areas with more restricted circulation or faster evaporation rates is provided by the accumulations of bedded evaporite deposits that occur in the Williston basin and Central Montana trough.

CAMBRIAN-ORDOVICIAN AQUIFER

Rocks of Cambrian and Ordovician age (figs. 2 and 3) in the northern Great Plains consist of marine sandstone, shale, and limestone that represent the shoreward facies of a transgressive sea that occupied the area during Cambrian and Ordovician times. The principal water-yielding formations are the Deadwood and Emerson Formations of Cambrian and earliest Ordovician age and the Winnipeg, Red River, and Stony Mountain Formations of Ordovician age. These units are interconnected hydrologically and function as a single aquifer (Downey, 1984a, 1986).

Because of the great depth of the Cambrian-Ordovician aquifer, its use as a source of water is limited. Very little geochemical data concerning the aquifer are available on a regional scale. Most of the data that exist are from tests associated with the development of oil and gas wells.



Modified from Peterson, 1981

FIGURE 2.—Thickness and extent of the Cambrian and Lower Ordovician rocks in the northern Great Plains.

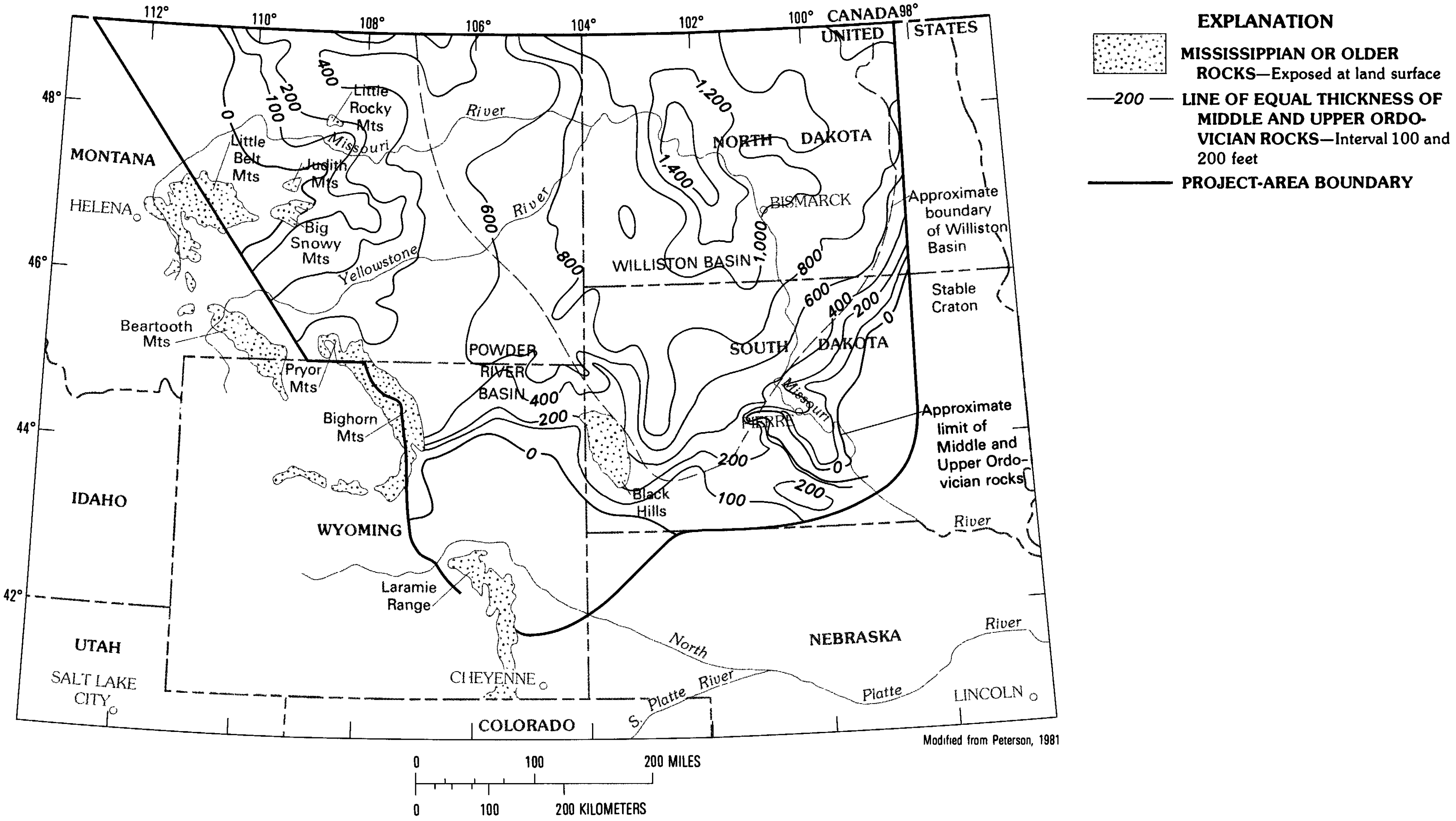


FIGURE 3.—Thickness and extent of the Middle and Upper Ordovician rocks in the northern Great Plains.

In the subsurface of South Dakota, the Deadwood Formation consists of about 640 ft of fine- to coarse-grained quartz sandstone interbedded with dolomitic limestone and shale (Steece, 1978). Where exposed in the Black Hills of South Dakota, the Deadwood Formation is of similar lithology; however, only about 450 ft of section is present. In the Black Hills, the Deadwood lies uncomformably on Precambrian schist and quartzite.

The Deadwood Formation is absent in extreme eastern North Dakota except for a small area in the eastern discharge area, where a thickness of about 100 ft of quartzose sandstone is present (Ballard, 1969). The Deadwood Formation is overlain by the Winnipeg Formation of Ordovician age. In areas where the Deadwood Formation is in hydrologic connection with the overlying Ordovician units, the formation was included as a part of the Cambrian-Ordovician aquifer in the hydrologic model of Downey (1984a).

Subsurface studies of the Ordovician rocks (fig. 3) in the Williston basin and adjoining areas include those by Porter and Fuller (1959, 1964), Fuller (1961), Patterson (1961), Carlson (1965), Carlson and Anderson (1965), Ballard (1969), Foster (1972), Armstrong (1980), and Peterson (1981). Ordovician rocks are major petroleum reservoirs in the Williston basin, and many exploratory wells penetrate these rocks. Ordovician rocks are not present in southeastern Wyoming, southwestern and southeastern South Dakota, and western Montana, because of nondeposition or because of removal by erosion during Devonian and Early Mississippian time. Thickness increases eastward and northward from zero in central Montana and northeastern Wyoming to more than 1,400 ft in the central part of the Williston basin.

The Winnipeg Formation is stratigraphically equivalent to the St. Peter Sandstone that occurs in the midwestern United States. In the western part of the study area, the formation consists of a clean, well-sorted, medium-grained sandstone with substantial porosity where it is not deeply buried (Peterson, 1978). Where the formation is deeply buried, the unit has little porosity and permeability because of silica cementation and compaction. In the eastern discharge area of North Dakota, the Winnipeg Formation consists of a sequence of shale, sandstone, and shaly limestone that ranges in thickness from 20 ft to about 140 ft (Armstrong, 1980). The sandstone units consist of very fine to fine rounded quartz grains with interbedded siltstone and shale.

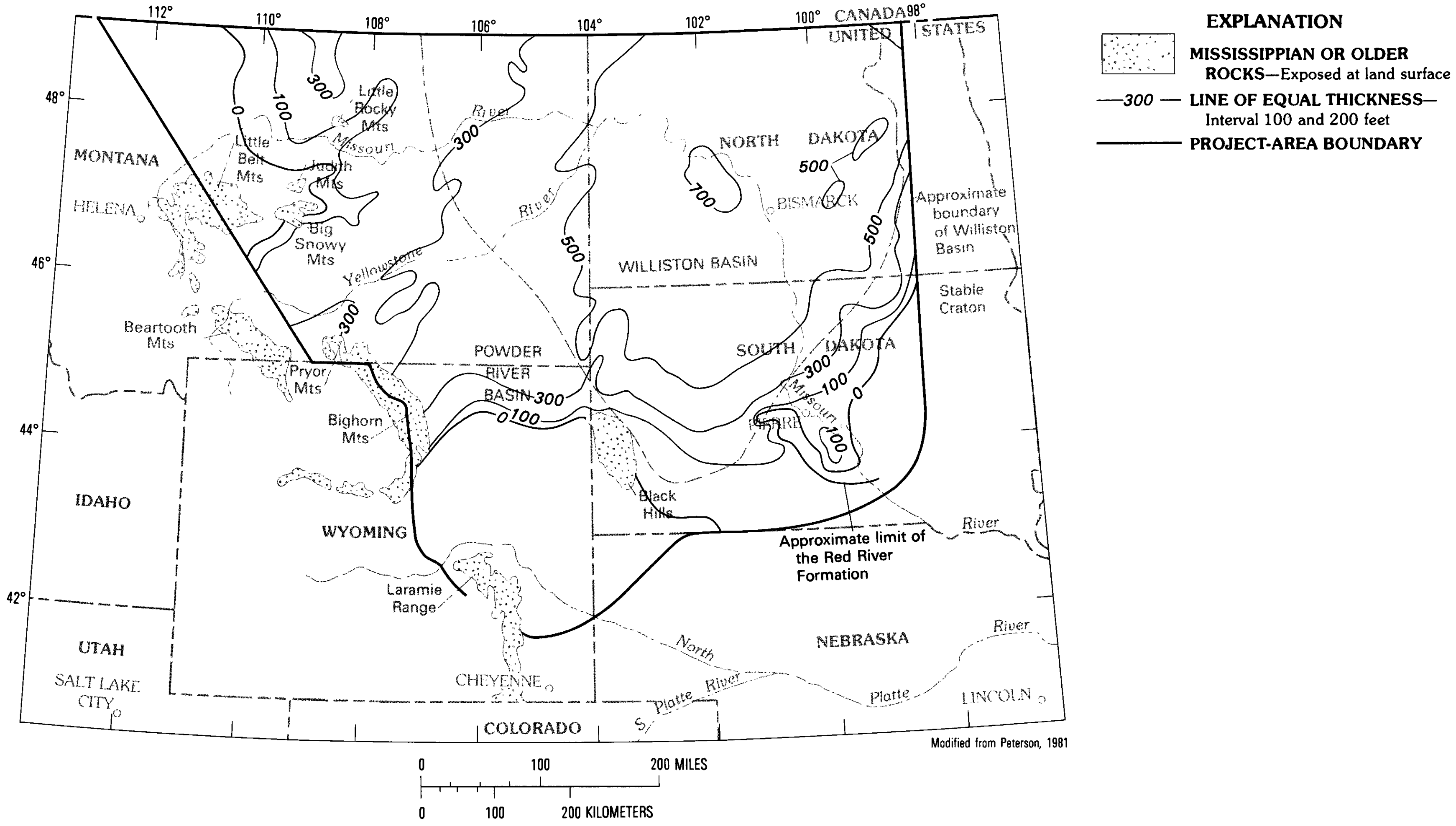
The Red River Formation (fig. 4), a carbonate sequence that overlies the beds of sandstone and shale of the Winnipeg Formation, extends outward toward the borders of the Williston basin. The Red River Formation is more than 700 ft thick in the central part of the Williston basin and is truncated by Devonian erosion around the borders of the basin and along a line extending between the central Black Hills and southern Bighorn Mountains (Peterson, 1981). According to Porter and Fuller (1964), the Red River in the center of the Williston basin consists of a lower unit of fragmented limestone and dolomite and an upper unit with three evaporite units of fragmented limestone and anhydrite.

The Stony Mountain Formation, which conformably overlies the Red River Formation, includes a lower shaly limestone and shale interval that, in general, is restricted to the interior of the Williston basin. This interval is truncated on the east and south, and grades into the upper part of the Bighorn Dolomite to the west (Peterson, 1981). The Stony Mountain Formation, the Upper Ordovician unit in the study area, is composed of carbonate, shaly carbonate, and anhydrite beds. This formation is gradational upward into the Interlake Formation (fig. 5); the upper part of the Interlake is of Silurian age according to Porter and Fuller (1964).

The Red River and Stony Mountain Formations were truncated by Devonian erosion around the periphery of the Williston basin. The Stony Mountain erosional edge is closer to the basin center than that of the underlying Red River Formation.

SILURIAN-DEVONIAN CONFINING UNITS

Rocks of Silurian and Devonian age (pl. 1; fig. 6) overlie the Red River and Stony Mountain Formations of Ordovician age in most of the study area. Silurian and Devonian rocks consist mainly of shaly carbonates, shale, and evaporites. Halite of Devonian age (fig. 7) occurs near the center of the Williston basin where the Silurian and Devonian section has a total thickness of more than 2,000 ft. The Devonian halites extend northward about 1,200 mi into Canada. The salt unit in the Prairie Formation, called informally the Prairie salt (fig. 7), is one of the principal halite units of Devonian age in the study area and contains many structural lows that occur along the margin of the halite and locally within the halite area. These structural lows have been attributed to collapse of the overlying formations caused by post-depositional solution of the halite (DeMille and others, 1964; Grossman, 1968). Because of the fine-grained lithology and the presence of evaporites in the Silurian and Devonian units, these formations are considered to be a confining



Modified from Peterson, 1981

FIGURE 4.—Thickness and extent of the Red River Formation of Late Ordovician age in the northern Great Plains.

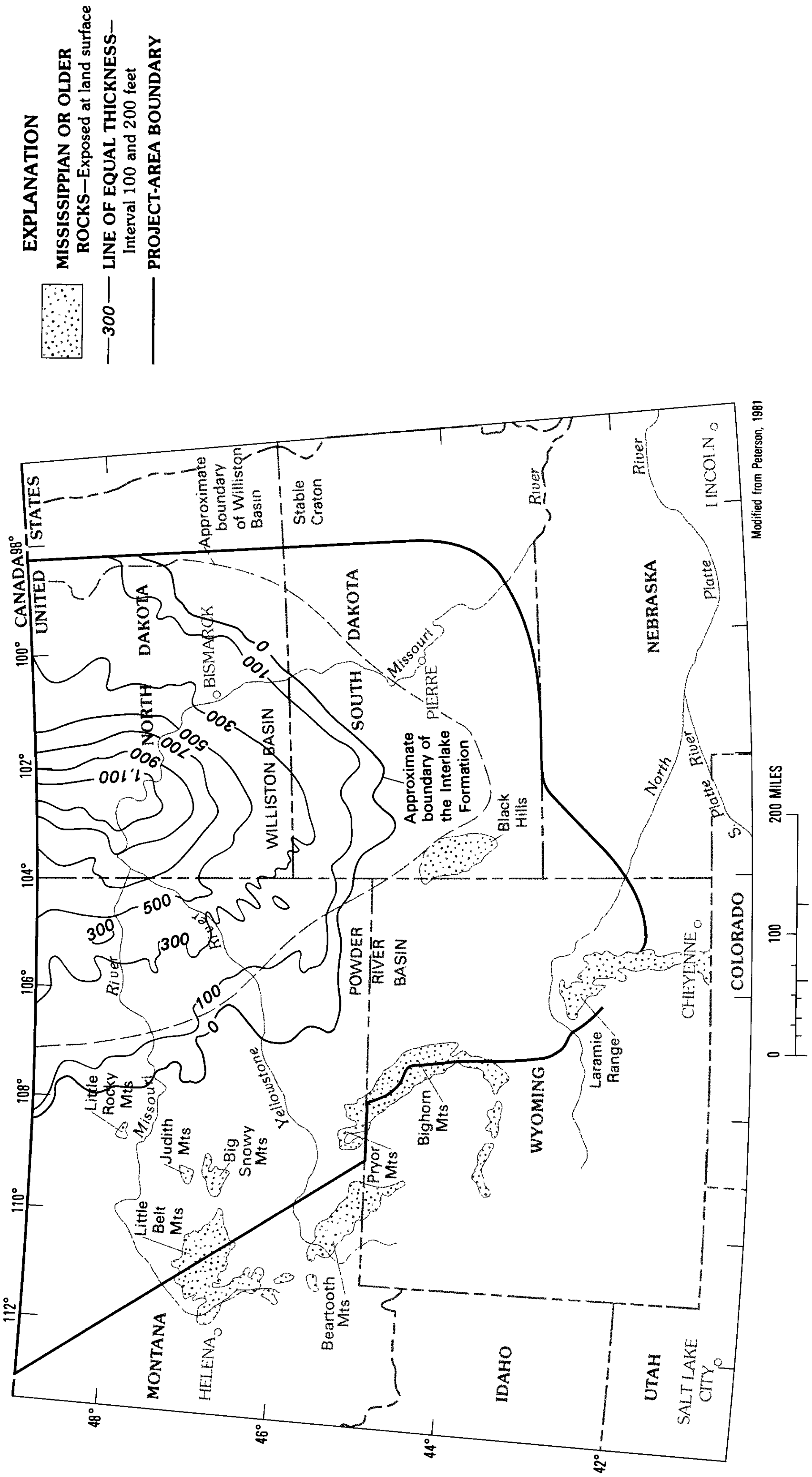


FIGURE 5.—Thickness and extent of the Interlake Formation of Late Ordovician and Silurian age in the northern Great Plains.

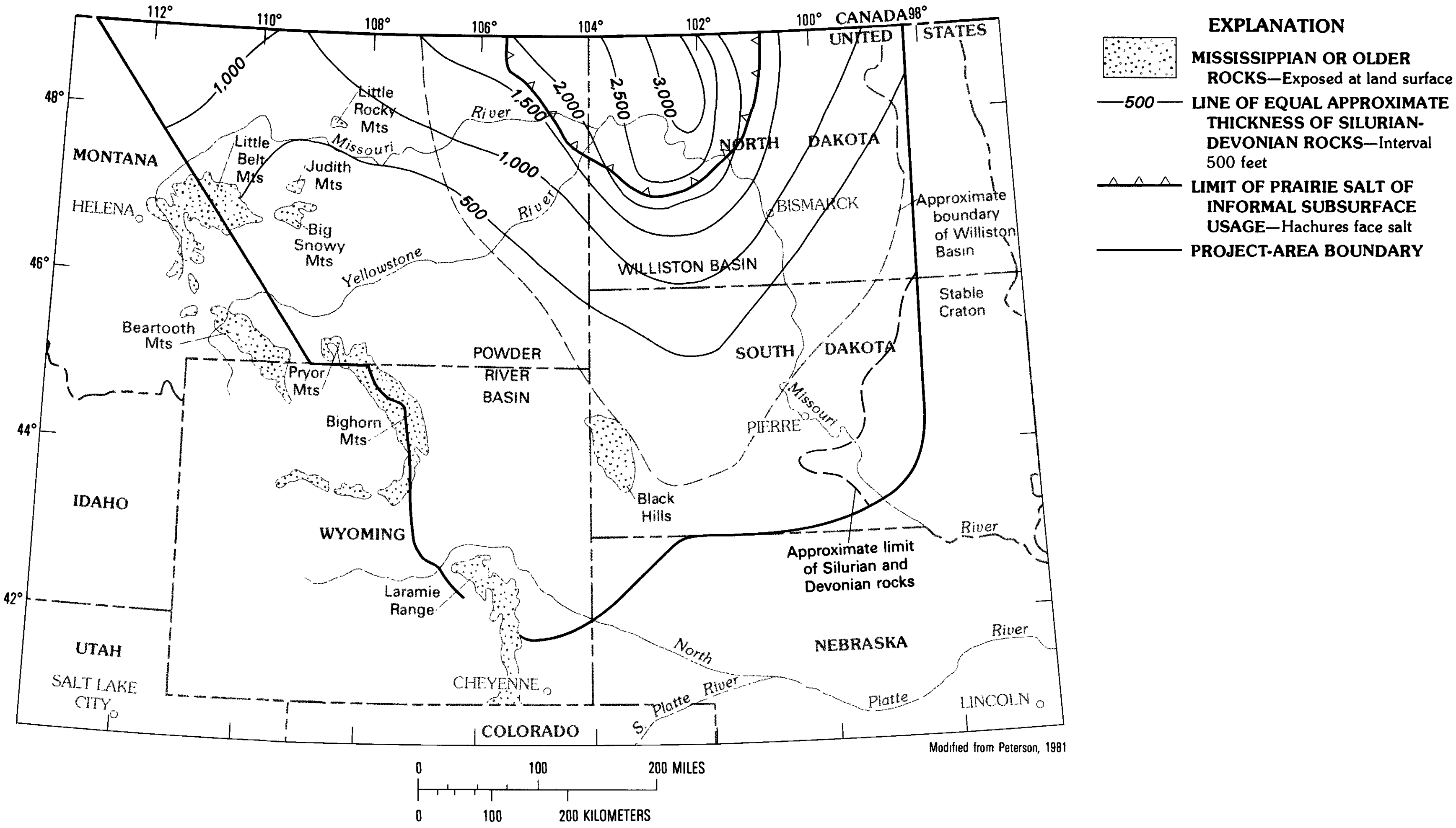


FIGURE 6.—Thickness and extent of Silurian and Devonian rocks in the northern Great Plains.

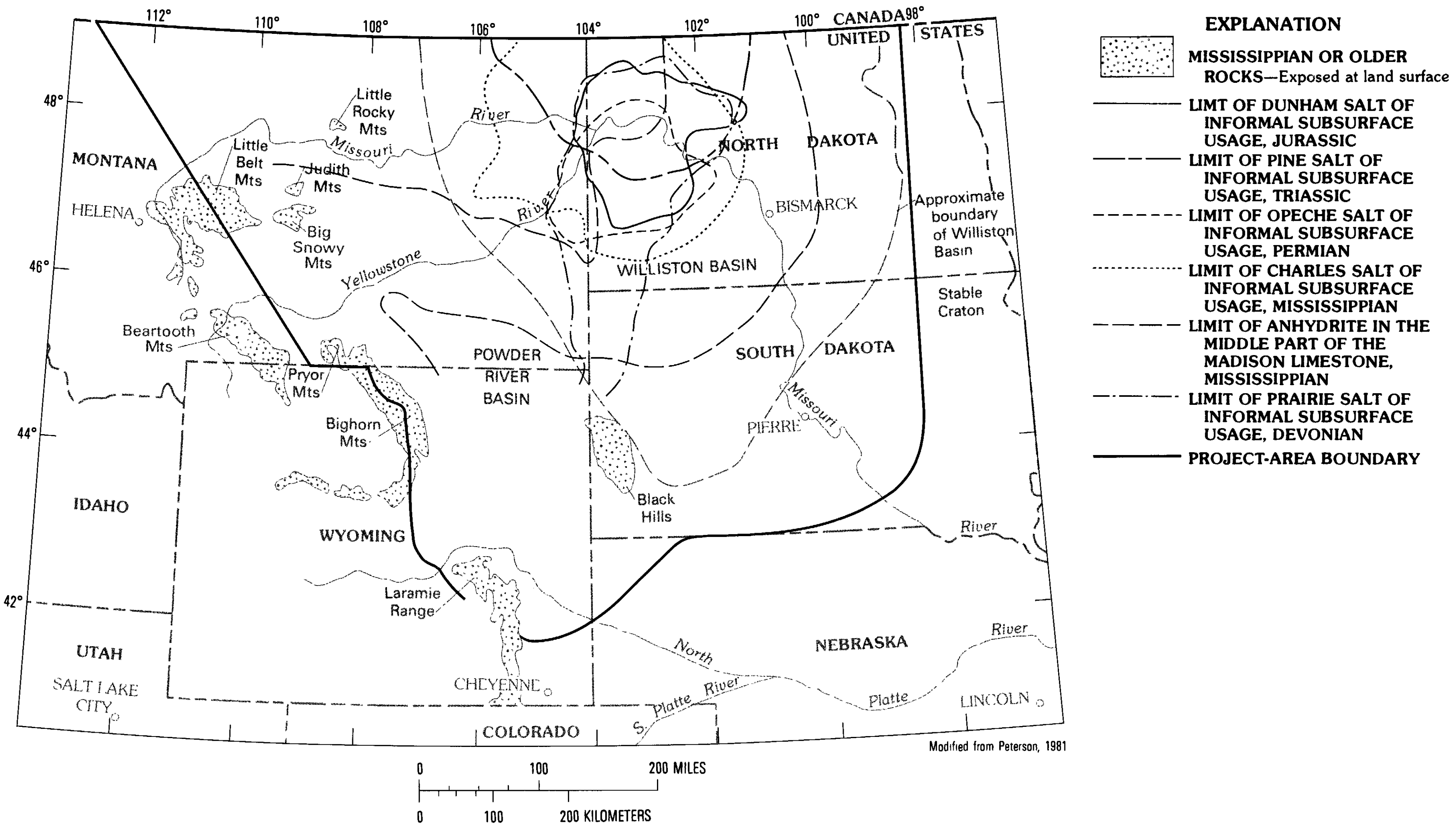


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FIGURE 7.—Extent of halite and evaporite units in the northern Great Plains.

unit for the underlying Cambrian-Ordovician aquifer (Downey, 1984a, 1986).

MADISON AQUIFER

Rocks of Mississippian age (fig. 1) overlie the Devonian formations in the study area. The lowermost Mississippian rock unit is the upper part of the Bakken Formation (fig. 8), which overlies the Devonian Three Forks Formation. The Bakken Formation consists of more than 100 ft of black, organic shale and siltstone and, where present, seems to be an excellent hydrologic confining bed. The Bakken Formation is considered to be a source bed for much of the petroleum that occurs in overlying formations. Overlying the Bakken Formation is a sequence of Mississippian rocks, mainly limestone and dolomite, that are termed the Madison Limestone or Madison Group where divided.

The Madison Limestone in the study area (fig. 9) consists of a sequence of marine carbonates and evaporites deposited mainly in a warm, shallow-water subtropical environment similar to that which exists today near the coast of southern Florida and the Yucatan, Mexico. Depositional environments grade laterally and vertically from shallow-marine carbonate and evaporite facies to deepwater facies. The Madison Group, from oldest to youngest, consists of the Lodgepole Limestone, Mission Canyon Limestone, and Charles Formation, or their stratigraphic equivalents, in other parts of the study area.

The Lodgepole Limestone is predominately a cyclic carbonate sequence consisting mainly of fossiliferous to micritic dolomite and limestone units that are argillaceous and thin bedded in most of the study area (Smith, 1972). The unit ranges from zero to more than 900 ft in thickness and averages about 300 ft in the study area. The Lodgepole overlies the Bakken Formation in the Williston basin.

The Mission Canyon Limestone consists of a coarsely crystalline limestone at its base, grading upward to finer crystalline limestone and evaporite minerals near the top (Brown and others, 1984). The formation contains one evaporite cycle and shares a second evaporite cycle with the lower part of the Charles Formation. Bedded evaporite units are absent in most of Wyoming and South Dakota, but evaporite deposits occur in southeastern Montana and northwestern North Dakota and gradually thicken in the vicinity of the Central Montana trough to a maximum thickness in the Williston basin. The Mission Canyon Limestone ranges from zero to more than 650 ft thick and averages about 300 ft in the study area.

The Charles Formation, the uppermost unit of the Madison Group, is a marine evaporite sequence consisting of anhydrite and halite (fig. 7) with inter-bedded dolomite, limestone, and argillaceous units. The Charles Formation ranges from zero to more than 300 ft thick and has an average thickness of about 250 ft in the study area. Pre-Jurassic erosion has removed most of the Charles Formation in the western and southern parts of the study area. Where present, the Charles Formation acts as a hydrologic confining unit for the underlying aquifers.

Development of karst (solution) features is common in the rocks of the Madison Limestone. Complex and interconnected solution features develop in limestones as part of the weathering process under tropical conditions when they are exposed at or near land surface (fig. 10). Sando (1974) described paleokarst features, which include enlarged joints, sink holes, caves, and solution breccias, that developed in the Madison Limestone in north-central Wyoming. He further indicated that most of the open spaces were filled by sand and residual products reworked by a transgressive sea during Late Mississippian time. Large extensive cave systems in outcrop areas of the Madison Limestone in the Bighorn Mountains and in the Black Hills are further evidence of the importance of the dissolution process in the development of secondary permeability in some of the units of the Madison Limestone.

Overlying the Charles Formation in parts of Montana, North Dakota, and South Dakota are rocks of Late Mississippian age that are part of the Big Snowy Group (fig. 11). The Big Snowy Group consists mainly of shale and sandstone units with minor limestone beds.

PENNSYLVANIAN AQUIFER

Rocks of Pennsylvanian age (pl. 1) overlie the Mississippian rocks in most of the study area and consist of marine sandstone, shales, siltstone, and carbonates. The Pennsylvanian rocks are known by many formational names; however, most are equivalent units.

Within the study area, the Tyler Formation of the Amsden Group generally is restricted to the Central Montana trough and the central Williston

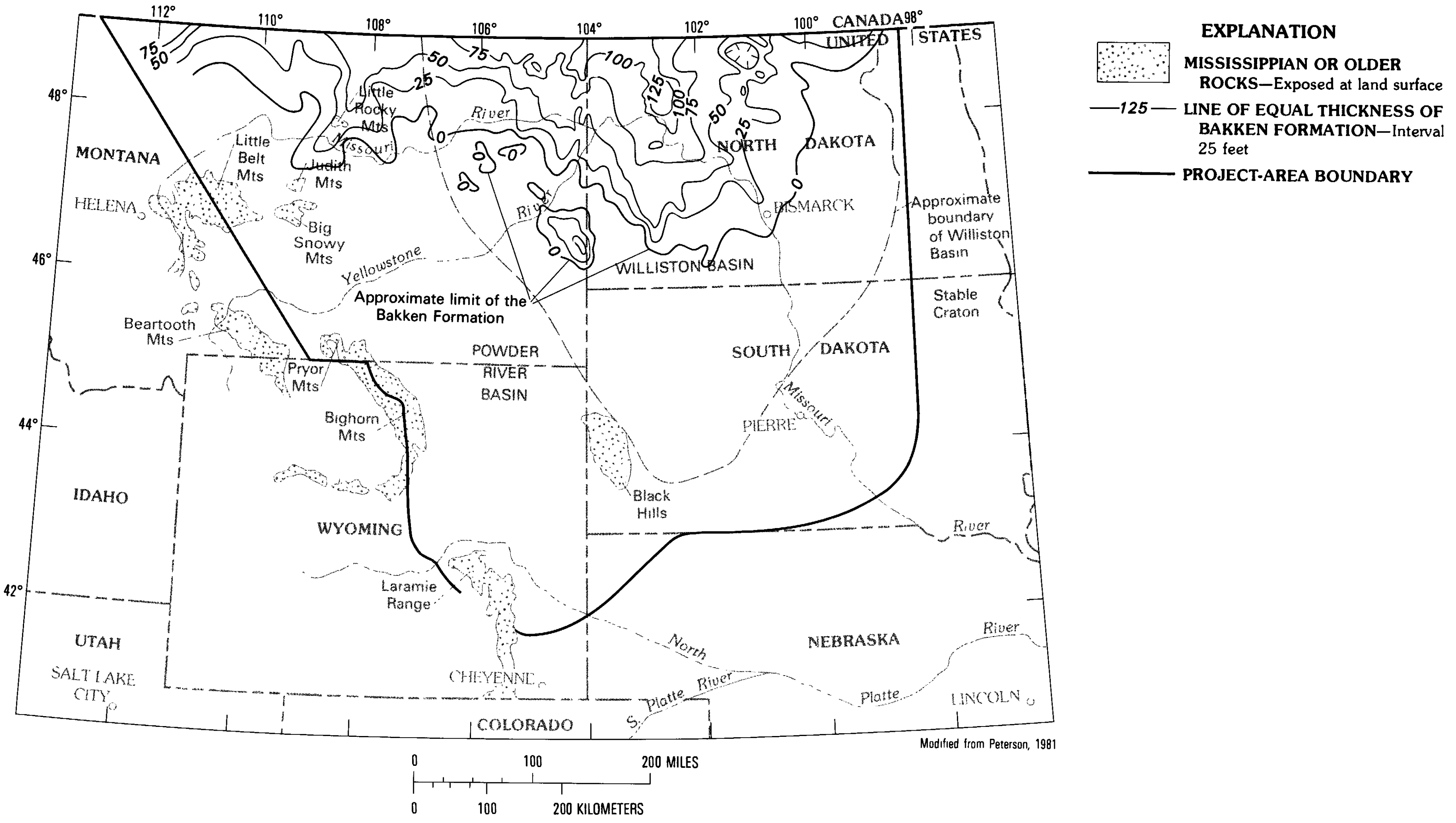

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FIGURE 8.—Thickness and extent of the Bakken Formation of Late Devonian and Early Mississippian age in the northern Great Plains.

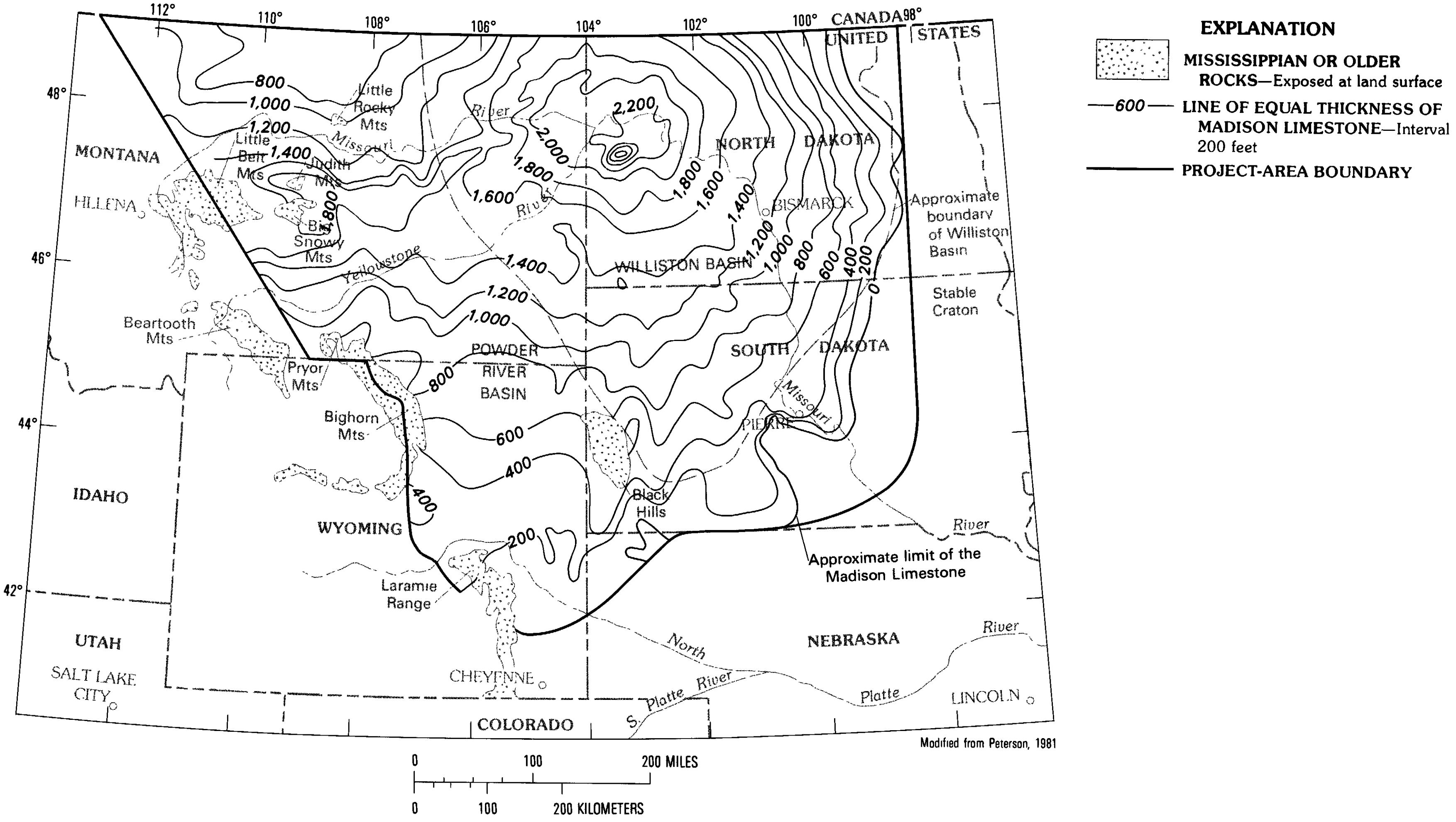


FIGURE 9.—Thickness and extent of the Madison Limestone of Mississippian age in the northern Great Plains.

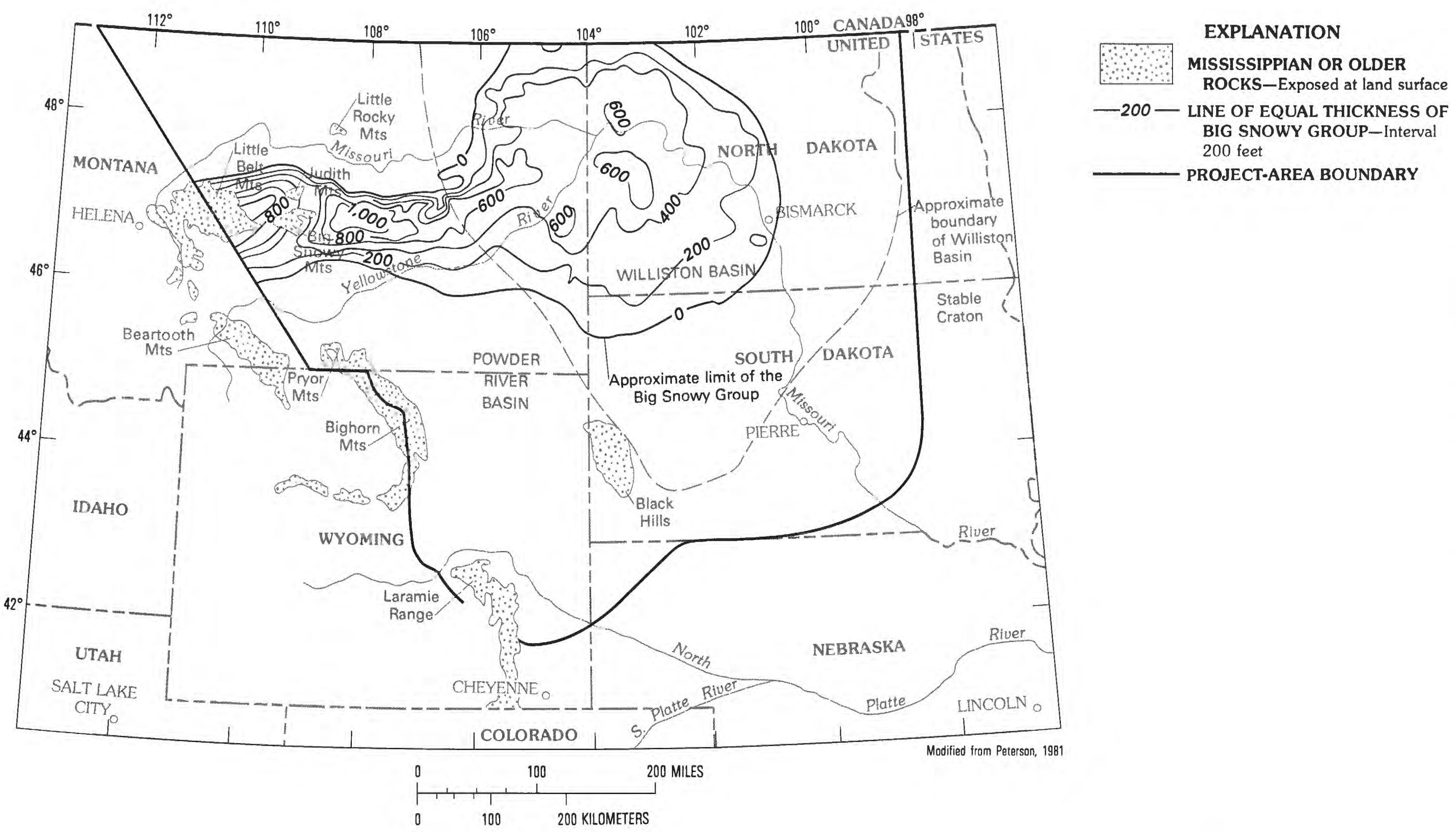


FIGURE 11.—Thickness and extent of the Big Snowy Group of Late Mississippian age in the northern Great Plains.

FIGURE 10.—Solution features in a marine limestone.

basin, but the formation seems to be equivalent to the lower part of the Amsden Formation in south-central Montana. The Tyler also seems to be equivalent to the lower part of the Minnelusa Formation in northwestern South Dakota and Wyoming and western North Dakota.

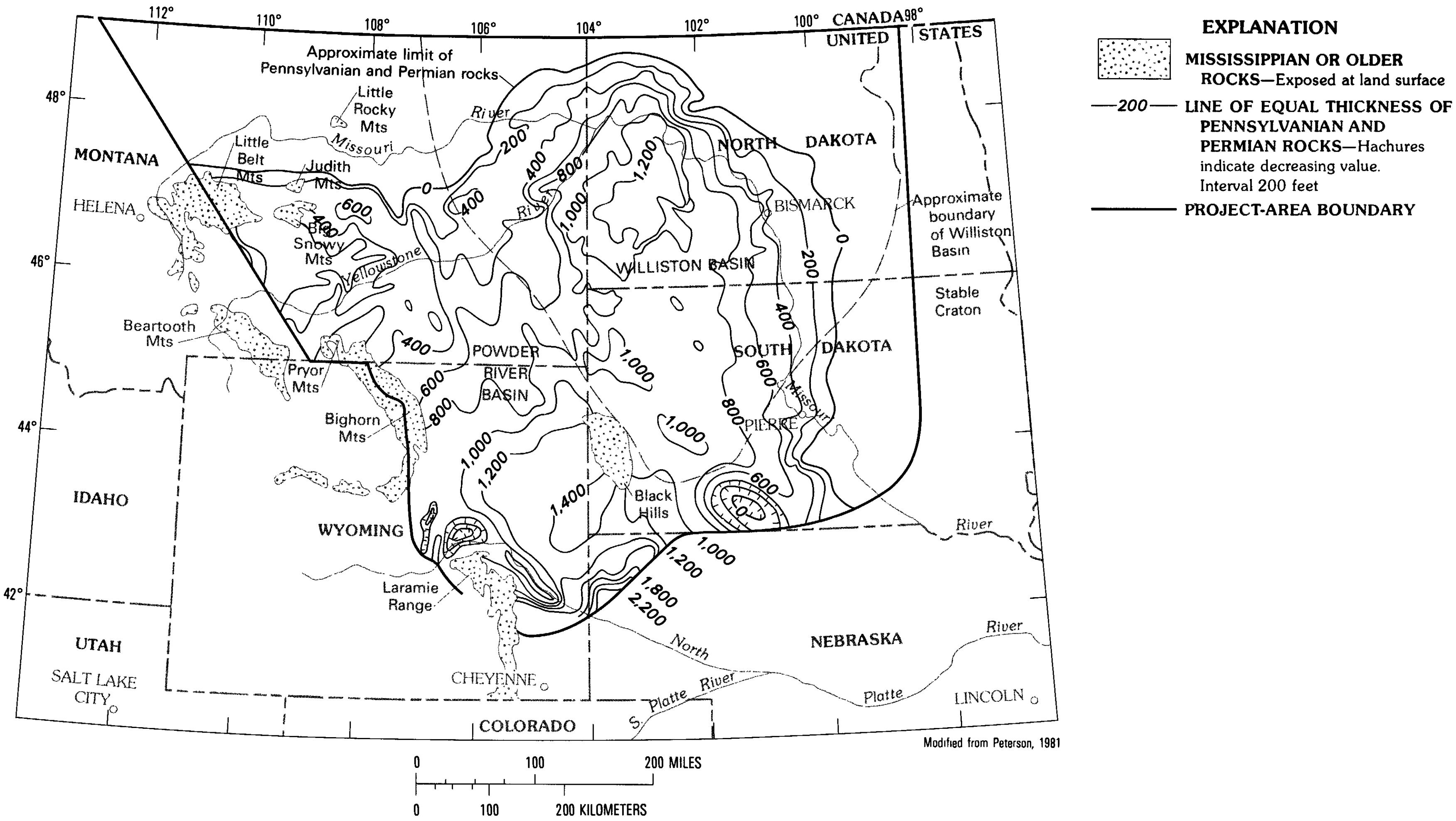
Middle Pennsylvanian rocks are represented by the Tensleep Sandstone in southern Montana and north-central Wyoming and by part of the Minnelusa Formation in the Williston basin, northeastern Wyoming, and western South Dakota. These rocks have been truncated by pre-Jurassic erosion progressively northward across central Montana, being completely removed approximately near the center of Montana (fig. 12).

Porous sandstone units of Pennsylvanian age are present in the Tensleep Sandstone in central to north-central Wyoming and south-central Montana and in the middle part of the Minnelusa Formation in western South Dakota along the east side of the Williston basin.

The uppermost part of the Minnelusa Formation in the Powder River and Williston basins and in the western part of South Dakota consists of sandstone, shale, and carbonate with interbedded anhydrite of Permian age. The sandstone facies extends northward into the southeastern part of the Williston basin. Sandstones in the upper Minnelusa are from the reworking of older Pennsylvanian sands, deposited from paleostructures to the west (Brown and others, 1984). Additional source areas for clastic sediments were the Sioux uplift and the Canadian Shield (north of the area shown in fig. 1). Locally, the Pennsylvanian rocks in the study area contain aquifers that are in hydraulic connection with the Madison aquifer, which provides a path for discharge of water from the Madison aquifer.

PERMIAN-TRIASSIC-JURASSIC CONFINING UNIT

Overlying the upper part of the Minnelusa Formation are the Permian Opeche Formation (pl. 1), the



Modified from Peterson, 1981

FIGURE 12.—Thickness and extent of the Pennsylvanian and Permian rocks in the northern Great Plains.

Minnekahta Limestone, and the lower part of the Spearfish Formation. The Opeche Formation is interbedded in the central part of the Williston basin with halite beds named the Opeche salt (fig. 7) (of informal usage). The Minnekahta Limestone overlies the Opeche Formation and halite units. Above the Minnekahta Limestone, the Pine salt (fig. 7) (of informal usage) of the Spearfish Formation contains more than 300 ft of bedded halite, which limits the vertical flow of water through this formation.

Rocks of Permian age in the study area are overlain by a sequence of red shale, siltstone, and evaporites that belong to the Goose Egg and Spearfish Formations of Triassic age (fig. 13). These formations are about 100-300 ft thick in the central Williston basin and thicken southwesterly to more than 900 ft in the Powder River basin.

Although shale and siltstone are the principal lithologies of the Triassic units in the study area, sandstone occurs to a limited extent in the eastern part of the Williston basin as elongate northeast-southwest trending sandy belts probably deposited by streams flowing off the adjacent Sioux uplift and Canadian Shield source areas located to the east. Triassic beds have been truncated by pre-Middle Jurassic erosion along the southern and eastern margins of the Alberta Shelf (Brown and others, 1984) and on the eastern side of the Williston basin.

Rocks of Jurassic age (fig. 14) overlie formations of Triassic age with a pronounced disconformity. These rocks, which consist of the Nesson, Piper, Rierdon, Swift, and Morrison Formations and their equivalents, are predominately carbonate, shale, and calcareous shale.

The Nesson Formation is divided into three informal members: A lower anhydrite member, which includes the Dunham salt (fig. 7) (of informal usage) that occurs in parts of the Williston basin; a middle shale member; and an upper carbonate member. The Piper Formation also is divided into three informal members: A lower shale and sandstone member deposited under nearshore conditions in central Montana; a middle limestone member; and an upper shale member. In north-central Montana, the Piper Formation thins substantially; it consists mainly of sandstone. The Rierdon Formation is composed mainly of shale, siltstone, and calcareous shale, and small amounts of sandstone occur along the eastern edge of the Williston basin.

The Swift Formation was deposited under marine conditions, and, in the western part of the study area, sandstones deposited as offshore bars compose most of the total thickness. In the eastern part of the study area, the formation consists mostly of silty shale. Upward coarsening occurs in about the upper one-third of the Swift Formation and usually is capped by thin sandstone or siltstone units. The formation is about 600 ft thick along the northern part of the Williston basin and thins to zero in western Montana and in eastern North and South Dakota. Generally, cementation of the Swift Formation is less than that of adjacent formations, possibly because of a lower primary porosity and less active diagenetic processes. The Swift Formation is less porous than the sandstones that occur in units of Early Cretaceous age, although in several localities sands occur that are more than 50 ft thick and have greater than 20-percent porosity.

The Morrison Formation was deposited as continental sand, silt, and clay on a plain that emerged after the regression of the sea that existed during the time of deposition of the Swift Formation. The Morrison is about 250 ft thick in south-central Montana and thins eastward to extinction in western North Dakota and South Dakota. A regional unconformity at the base of the Lower Cretaceous units locally truncates the Morrison and the upper part of the Swift Formation.

Total thickness of the Jurassic units in the study area ranges from less than 50 ft along the periphery of the Williston and Powder River basins to more than 1,200 ft. Rocks of Permian, Triassic, and Jurassic age, where present in the study area, are considered to be confining units for the flow of ground water from the underlying aquifers to overlying aquifers of Cretaceous age.

LOWER CRETACEOUS AQUIFERS

Rocks of Cretaceous age (pl. 2) consist of marine and nonmarine clastic sediments that range in thickness from zero in eastern North Dakota and South Dakota to more than 1,400 ft in west-central Montana (Anna, 1986). The Lakota and Fuson Formations of Early Cretaceous age are composed of fluvial sandstone, siltstone, and shale. The Lakota Formation consists mainly of sandstone and occasional conglomerate overlying an erosional surface cut into the underlying Morrison Formation of Jurassic age. Generally, the Lakota Formation is a channel and valley-fill deposit; although, in the subsurface, it is difficult to distinguish between the valley fill of the Lakota and the valley fill of the overlying Fuson Formation.

The Fuson Formation consists mainly of valley-fill and channel-margin deposits of silty shale with occasional sandstone units. Thickness of the Fuson Formation ranges from approximately 400 ft in central

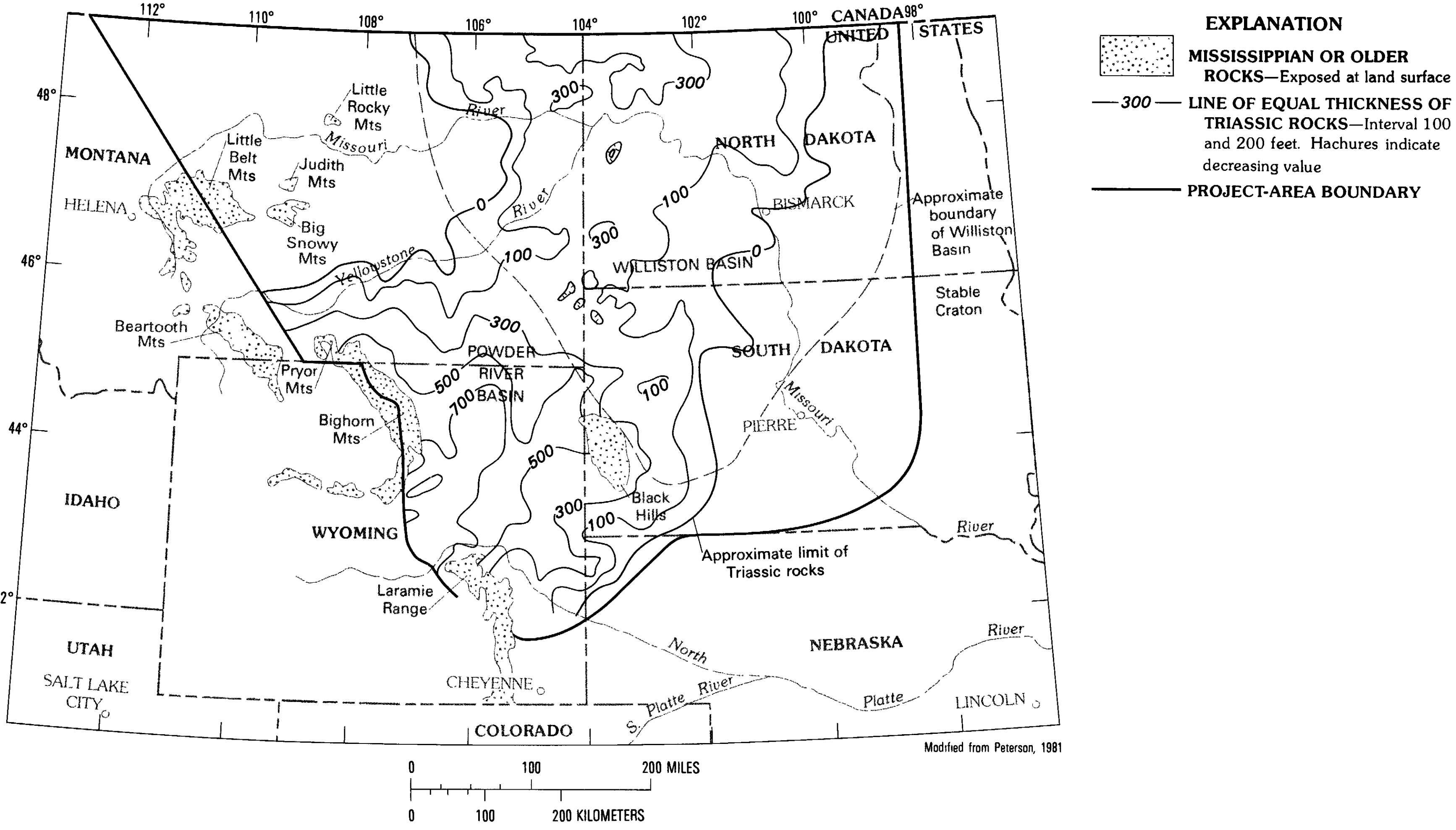


FIGURE 13.—Thickness and extent of Triassic rocks in the northern Great Plains.

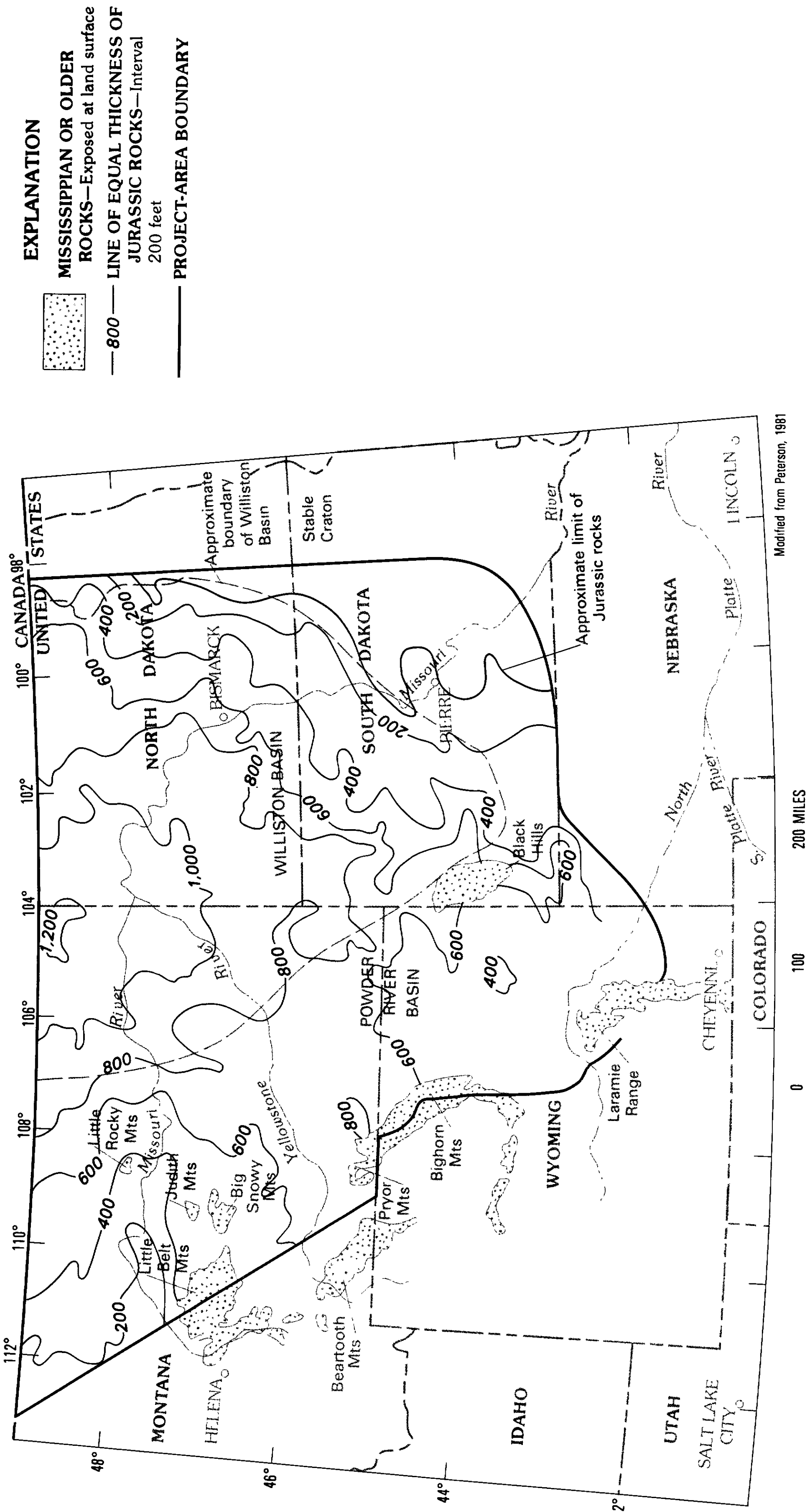


FIGURE 14.—Thickness and extent of Jurassic rocks in the northern Great Plains.

Montana to less than a few feet in eastern North Dakota and South Dakota and finally to zero in eastern South Dakota.

The Fall River Sandstone of Cretaceous age represents the initial advance of the Early Cretaceous sea, which deposited fine sand, silt, and clay under shallow-marine, tidal flat, coastal swamp, and deltaic conditions. Silt and shale deposits in central Montana and Wyoming indicate a deeper water environment in the study area.

In the Williston basin, analysis of cementation data indicates that these Lower Cretaceous formations have a greater quantity of silica cement than calcite cement. A trend surface analysis of cementation indicates northwest linear trends near the Cedar Creek anticline. The analysis also indicates that: (1) areas of less cement tend to overlie lineaments or fracture zones; and (2) areas of more cement overlie interlineament zones (Anna, 1986).

Porosity trends in these formations indicate areas of greater porosity are in the central and eastern parts of the study area, although porosity decreases eastward as overall thickness of the formations decreases. In the Powder River basin, all Cretaceous formations probably have less than 20-percent porosity.

The Lakota, Fuson, and Fall River Formations thin eastward and are truncated by pre-Newcastle erosion. Thicknesses of the three formations range from about 700 ft in central Montana to zero in eastern North Dakota and South Dakota.

The Skull Creek Shale of Early Cretaceous age consists of two marine facies—a lower, glauconitic siltstone, often termed basal silt, and an upper shale. The silt facies is regional but sand content increases into in central and south-central Montana. The upper shale facies was deposited under strong reducing conditions and consists mainly of black organic shale with associated pyrite. The formation ranges in thickness from zero in eastern South Dakota to more than 250 ft in parts of Montana, Wyoming, and western North Dakota and South Dakota.

Withdrawal of the sea at the end of Skull Creek time resulted in an unconformity at the base of the Newcastle Sandstone in eastern Wyoming and southeastern Montana. Later, the sea transgressed from west to east across the area, and development of extensive delta systems in eastern Montana and northeastern Wyoming occurred, and still later, in southeastern South Dakota. The deltas supplied sediment to shelf areas in east-central Montana and Wyoming.

Thickness of the Newcastle Sandstone is quite variable, ranging from zero in large areas of North Dakota, tens of feet in central Montana and Wyoming, to an abrupt increase of several hundred feet in southeastern North Dakota and eastern and south-central South Dakota. Porosity of the Newcastle Sandstone seems to be greater in areas where it is thicker. Calcite is a more prevalent cementing agent than silica in the Newcastle Sandstone (Anna, 1986).

As the sea encroached farther eastward during deposition of the Newcastle Sandstone, the Mowry Shale (pl. 2) was being deposited over the central and western part of the study area. The Mowry consists of dark, siliceous shale that contains fish scales and bone fragments. In the study area, a bentonitic clay, which is used as a regional time marker, marks the top of the Mowry Shale and also is used as the dividing unit between the Lower and Upper Cretaceous rocks. Thickness of the Mowry ranges from more than 700 ft in south-central Montana to zero in eastern North Dakota and eastern and southeastern South Dakota. All the Lower Cretaceous units, except the Mowry Shale, were grouped into the Lower Cretaceous aquifer by Downey (1984a). The Mowry Shale was incorporated into the overlying confining unit (pl. 2).

The sedimentary pattern of rocks of Late Cretaceous age in the northern Great Plains is associated with four main transgressions and regressions of shallow seas. The Belle Fourche Shale and Greenhorn Formation (pl. 2) were deposited as a continuation of the transgression of the sea which began during Early Cretaceous time. The Belle Fourche Shale consists of gray to black marine shale with numerous bentonite beds. The Greenhorn Formation consists of a thick sandstone sequence with interbedded shale and chalky shale. The overlying Carlile Shale consists of gray marine shale and interbeds of thin sandstone.

The Frontier Formation is the westward equivalent of the Belle Fourche Shale and Greenhorn Formation. Although the Frontier is restricted areally, the formation is 500–2,000 ft thick and consists of alternating beds of deltaic sandstone and shale.

The Niobrara Formation ranges in thickness from zero to about 160 ft; it consists of gray marine shale with lenticular chalky beds and is characterized by small, white calcareous lenses. Lithologic variations range from a dominant chalk facies in the east to mostly shale facies in the west.

The Pierre Shale directly overlies the Niobrara Formation in the study area. The Pierre consists of more than 3,000 ft of dark, montmorillonitic shale and interbedded sandstone that was deposited under marine conditions. Many of the sandstone units have been given formational status in western and central Montana and in the Powder River basin of Wyoming.

Although the Pierre Shale contains a number of sandstone units that are local aquifers, it is a confining unit to the underlying Lower Cretaceous aquifer in most of the area, as defined by Downey (1986).

The final regression of the Late Cretaceous sea deposited the Fox Hills Sandstone and the Hell Creek and Lance Formations, or their equivalents. These formations are areally extensive; the Fox Hills and Hell Creek crop out over sizeable areas in southern and central North Dakota.

The Fox Hills Sandstone and equivalent units consist of about 300 ft of deltaic and interdeltaic sandstone, siltstone, and shale. The Hell Creek Formation or Lance Formation ranges from about 350 to 1,500 ft thick and consists of fluvial sandstone, siltstone, and carbonaceous claystone, and thin lenticular coal beds in places. The Hell Creek Formation or Lance Formation is the meander-belt and delta-plain facies of the Fox Hills delta system. The Fox Hills and Hell Creek or Lance, where they exist, were considered a part of the Upper Cretaceous aquifer by Downey (1984b, 1986).

Peter (1984) divided the Lower Cretaceous aquifer of Downey (1984a) into two separate aquifers underlying most of the study area. The Inyan Kara Group or equivalents were considered part of the Inyan Kara aquifer and the Dakota Sandstone, Newcastle Sandstone, or Muddy Sandstone part of the Dakota aquifer (pl. 2). The two aquifers are separated in most areas by a confining unit consisting of the Skull Creek Shale or Taft Hill Member (pl. 2) of the Blackleaf Formation. The Skull Creek Shale, as well as all the geologic units below it, pinch out in central and eastern North Dakota and South Dakota where the two aquifers merge into a single hydrogeologic unit. Hydrologically, the basal Lower Cretaceous unit in eastern South Dakota, called the Dakota Sandstone, can be divided into an upper and lower part based on the hydrochemical facies, which are different in the lower Dakota aquifer than in the upper part in this area, as observed by many previous workers, such as Meinzer (1929). The Dakota Sandstone in extreme southeastern South Dakota also includes rocks of Late Cretaceous age.

The major tectonic units of the northern Great Plains, as shown in figure 1, not only affected the sedimentary characteristics by controlling the depositional environment but also directly affected hydrologic conditions. In general, the Cretaceous aquifers dip away from the uplifts toward the basin centers. The Cretaceous aquifers are exposed along the flanks of the Little Belt and Big Snowy Mountains and in the hills and ranges that encircle the Powder River basin (the Pryor Mountains, Bighorn Mountains, Laramie Range, Hartville uplift, and the Black Hills). The aquifers are more deeply buried in the basins, particularly the Williston, Powder River, and Bull Mountain basins. Within the basins, the aquifers are locally shallower in anticlines and arches. In eastern North and South Dakota, the Inyan Kara and Dakota aquifers are more shallow where tectonic activity has been minimal over the craton, but these aquifers are not exposed at land surface.

The Lower Cretaceous aquifers consist principally of lenticular sandstone bodies separated by silt and shale layers. In most of the northern Great Plains, the sediments were deposited unconformably over continental sandstones, siltstones, and shales of Jurassic age. In the eastern Great Plains, the Lower Cretaceous aquifers unconformably overlie aquifers of Paleozoic age. The thicker, identifiable sandstone bodies were deposited in fluviatile or near-marine environments. The approximate distribution of these sandstone bodies are shown in figures 15 and 16. The thickest sandstone bodies occur in a deltaic sequence in the Dakota Sandstone in southeastern South Dakota (fig. 16). The Dakota Sandstone or its equivalent intertongues with sandstone units in western South Dakota. The most extensive of these sandstone units is the Newcastle Sandstone, equivalent to the near-marine Muddy Sandstone of Wyoming and Montana. Thinner and less extensive sandstone beds also occur within the two major Lower Cretaceous shale units—the Skull Creek Shale in Montana and the Fuson Formation (or shale) in South Dakota.

The hydrology of the Cretaceous aquifers, in particular the Dakota aquifer, has been studied extensively within the last century because of the large quantities of water they have provided in eastern North Dakota and eastern South Dakota. Many investigations, such as those by Darton (1909), Swenson (1968), Schoon (1971), and Bredehoeft and others (1983), have described the movement of water in the aquifers and have hypothesized the sources of recharge. The sources of recharge have been of particular interest because the large volumes of water withdrawn from the Dakota aquifer and the high potentiometric surface in eastern South Dakota cannot be attributed to recharge from the Black Hills alone. Early interpretations were complicated further by an erroneous correlation of what is now known to be the Inyan Kara Group in the Black Hills with the Dakota Sandstone in eastern South Dakota. An understanding of the recharge to the Dakota and Inyan Kara aquifers has implications beyond being able to explain the source of water discharged by

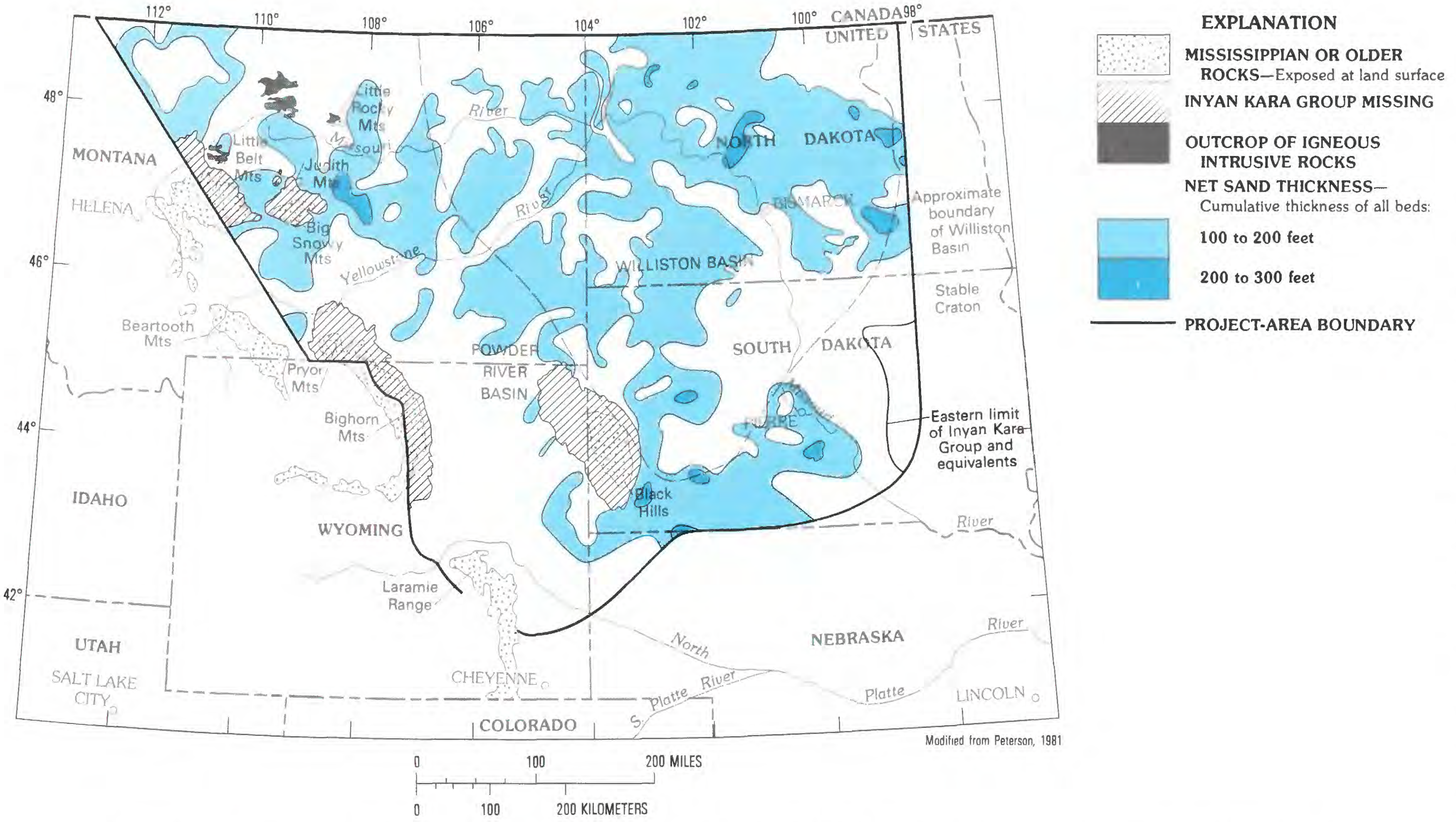
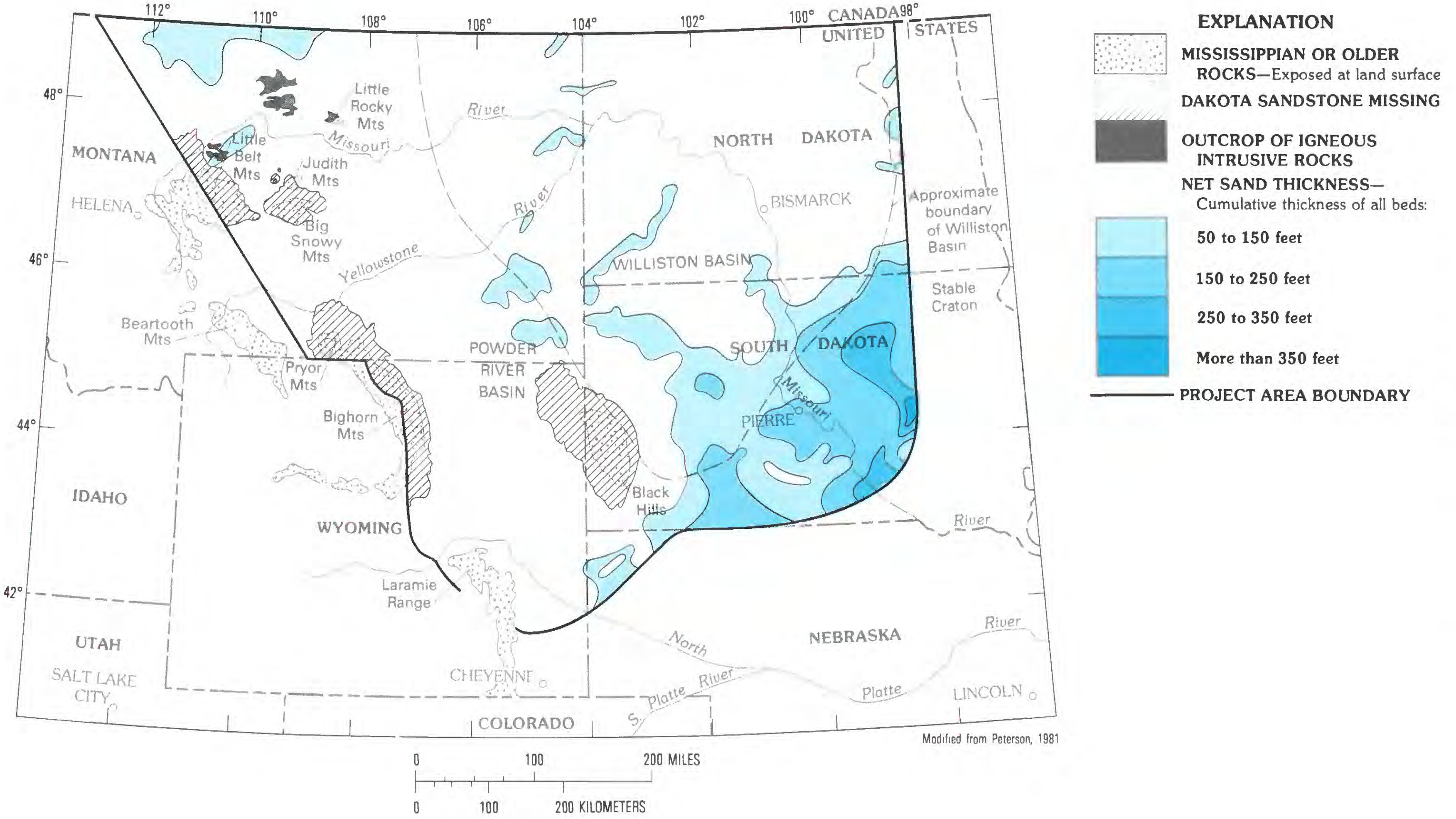


FIGURE 15.—Distribution of sandstone bodies more than 100 feet thick in the Inyan Kara Group and its equivalents in the northern Great Plains.



Modified from Peterson, 1981

FIGURE 16.—Distribution of sandstone bodies more than 50 feet thick in the Dakota Sandstone and its equivalents in the northern Great Plains.

flowing wells in eastern North Dakota and eastern South Dakota. Such diverse rock units as the Madison Limestone and the Pierre Shale have been proposed as sources of recharge, and understanding the flow of water through these units depends, in part, on an accurate interpretation of the flow of water in the Cretaceous aquifers.

In conjunction with this investigation of the regional aquifer systems of the northern Great Plains, Downey (1986) and Butler (1984) delineated the potentiometric surfaces of the various Lower Cretaceous aquifers and constructed numerical models of the existing ground-water flow system. Preliminary potentiometric maps for the Lower Cretaceous aquifers in Montana also have been prepared (G.W. Levings, U.S. Geological Survey, written commun., 1980). The maps provided information on the direction of ground-water flow that was used in the interpretation of the geochemistry of the aquifers.

SOURCES, CHARACTERISTICS, AND USE OF THE GEOCHEMICAL DATA

To accomplish the objectives of this study, it was necessary to compile a geochemical data base from many sources. Many local studies presented geochemical data from specific areas; however, prior to this study, there had been no attempt to compile the existing data into one large data base.

The geochemical data used in this study were compiled from the files of the U.S. Geological Survey and available commercial data files, such as Information Systems Program of the University of Oklahoma (Energy Resources Center), Chemical and Geological Laboratories in Casper, Wyoming, and Energy Laboratories, Inc., in Billings, Montana. The final compiled geochemical data base contains more than 16,000 entries in a machine-readable form.

CALCULATION OF MISSING VALUES

During compilation, when information for geologic units, fluid density, dissolved solids, or specific conductance was missing, an attempt was made to search the correct information from the Well History Control System files of the Petroleum Information Corp. If the search failed, the missing values were calculated where possible. The following are the calculation procedures that were used.

FLUID DENSITY

The calculation of fluid density was based on the assumption that the waters are a pure sodium chloride solution in which ion pairing is negligible. Three categories of waters require two different algorithms for the fluid-density calculations.

1. Density of water containing 7,000 mg/L or less dissolved solids was set to 1.0.
2. Density of water containing more than 7,000 mg/L dissolved solids, calculated as sodium chloride, was calculated by using data from Liley and Gambill (1973) by

$$\rho = 0.14 \log(DS) + 0.43 \qquad (1)$$

where ρ = solution density; and
DS = dissolved solids, in milligrams per liter.

DISSOLVED SOLIDS

The procedure outlined by Hem (1985) was used to calculate the sum of dissolved solids. For water in which concentrations were reported in parts per million, two procedures were followed:

1. If the concentration of dissolved solids was less than 7,000 ppm, the concentration of each component was considered to be equivalent to its concentration in milligrams per liter, and the dissolved-solids sum was calculated.
2. If the dissolved solids exceeded 7,000 ppm, the fluid density was used to convert the concentrations from parts per million to milligrams per liter. After conversion, the sum of constituents was calculated.

SPECIFIC CONDUCTANCE

Resistivity data were converted to specific conductance at 25°C by:

1. Adjusting the measured bottom-hole temperature to the equilibrium bottom-hole temperature (Wallace and others, 1979) by

$$T_E = T_L + (7.689 \times 10^{-14} D^3 - 3.888 \times 10^{-9} D^2 + 3.619 \times 10^{-5} D + 0.270245) D/100, \qquad (2)$$

where T_E = equilibrium bottom-hole temperature, in degrees Fahrenheit;
T_L = reported bottom-hole temperature, in degrees Fahrenheit; and
D = depth, in feet.

2. Adjusting the resistivity values to a temperature of 25 °C by the relation from Arps (1953):

$$R_{77} = R_T(T_E + 7.0)/82.0, \quad (3)$$

where R_{77} = resistivity at 77 °F (25 °C):
R_T = resistivity at the temperature of measurement; and
T_E = equilibrium bottom-hole temperature, in degrees Fahrenheit.

3. Calculating the specific conductance

$$SC = 10{,}000/R_{77}, \quad (4)$$

where SC = specific conductance, in microsiemens per centimeter; and
R_{77} = resistivity at 77 °F (25 °C).

DETERMINATION OF HYDROGEOLOGIC UNITS

The names for geologic units in several data compilations were local names, often used only in the oil industry. These informal names differ substantially from the geologic unit names contained in U.S. Geological Survey data files. In these instances, U.S. Geological Survey stratigraphic nomenclature was used to select replacement names equivalent to those of non-Survey samples.

EDITING OF THE DATA BASE

The data base was edited by inspection of the source of sample code and by application of the U.S. Geological Survey water-quality edit computer code. Source sample codes that indicated the possibility of contamination by drilling fluids were used to eliminate some samples. Only samples with pH values within the range of 6.5 to 9.5 were used because waters in the project area are known to generally be in that range. The lower limit of pH excluded waters from wells that have been affected by acid-fracture treatments. Samples with an electrical imbalance greater than 5 percent also were eliminated (Hem, 1985).

The edited data set was adequate for the preparation of maps and calculation of statistics. However, it generally was not adequate for use in geochemical models. Only data contained in the computer files of the U.S. Geological Survey were used in the calculation of saturation indexes (SI) by using the equilibrium model WATEQ2 (Ball and others, 1980). When the dissolved-solids concentration was greater than about 100,000 mg/L, the saturation indexes were calculated using a version of the geochemical model PHREEQE (Parkhurst and others, 1980) that included Pitzer equations (Harvie and Weare, 1980) to calculate activity coefficients.

HYDROLOGIC IMPLICATIONS OF GECHEMISTRY

The hydrologist commonly faces a lack of reliable hydraulic data for use in simulation of a ground-water flow system. Using geologic and geochemical information can help to partially overcome this problem. Examples are presented here of the applications of geochemistry to the solution of hydrologic problems.

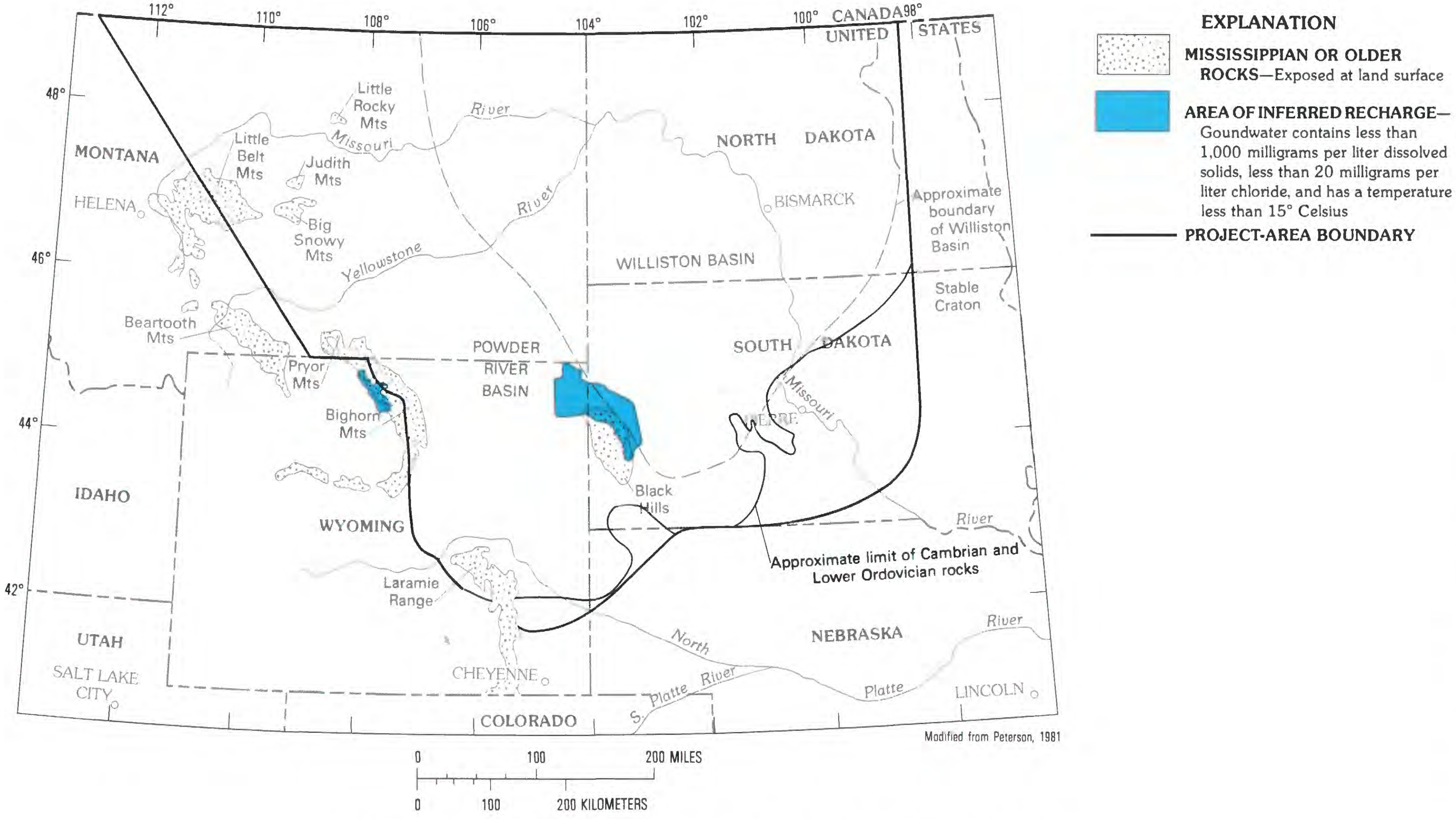
RECHARGE

Because waters within a recharge area have reacted with the soil and aquifer minerals for a relatively short time, it is assumed that these waters will be characterized by small concentrations of dissolved solids and particularly small chloride concentrations. The criteria used for identification of recharge water to the northern Great Plains regional aquifers, based on the above assumptions, were (1) a dissolved-solids concentration less than 1,000 mg/L; (2) a dissolved-chloride concentration less than 20 mg/L; and (3) a water temperature less than or equal to a mean air temperature of 15 °C.

A recharge map (fig. 17) was prepared by overlaying maps of dissolved-solids concentration, chloride, and water temperature for the Pennsylvanian aquifer and by outlining those areas where the recharge criteria were met. Similar maps prepared for the other major aquifers, but not included in this report, indicate that the areas of the Bighorn Mountains and the Black Hills contribute substantial quantities of recharge to the aquifers. Other uplifted areas seem to contribute relatively little water to the aquifers, a result consistent with conclusions reached by model simulation (Downey, 1984a, 1984b, 1986). Trends in dissolved solids and chloride also may indicate areas of leakage where large changes in concentrations occur away from recharge areas.

DIRECTION OF FLOW

Where hydraulic data were not available, maps of dissolved-solids and dissolved-chloride concentrations were used to infer ground-water flow paths. Concentrations of dissolved solids and chloride are expected to increase downgradient along flow paths. Relatively low concentrations of dissolved solids or chloride may indicate leakage between aquifers or flow along fault zones that have relatively large permeability, resulting in lower residence time of the water.



Modified from Peterson, 1981

FIGURE 17.—Areas of inferred recharge to the Pennsylvanian aquifer in the study area.

The flow paths used for analysis of the Paleozoic section (fig. 18) from the Cambrian-Ordovician through the Madison aquifers are, with the exception of flow path 5 in Wyoming, based on hydraulic data. Flow path 5 was deduced from the gradient in chloride concentrations in the Madison aquifer by the method described above for the Pennsylvanian aquifer. The geochemically and hydraulically derived flow paths are very similar. This similarity indicates a geochemical method of defining flow paths can benefit the hydrologic effort.

To describe the genesis of the water chemistry in the Lower Cretaceous aquifers, changes in ion concentrations and pH along flow paths were examined. The flow paths shown in figure 19 were selected in areas that had water analyses and adequate maps of the potentiometric surface. Flow paths are assumed to be at right angles to equipotential lines on a potentiometric surface map. Though it was assumed in drawing the flow paths that steady-state conditions exist, it is known that this is not true for all the flow paths. Withdrawals of water from the Dakota Sandstone in eastern South Dakota have been large enough during the past century to lower the potentiometric surface. This lowering has reversed the flow paths east of the James River, South Dakota (H.L. Case, III, U.S. Geological Survey, written commun., 1980). Conversely, comparison of two flow paths in the Dakota Sandstone in this area, which were drawn by using the recently mapped potentiometric surface with the surface drawn by Darton (1909), indicates that these paths have not changed in direction, though water levels been have lowered more than 100 ft in some areas.

CHEMICAL SIGNALS

Regional trends in solute concentrations, changes in hydrochemical facies, and variations in solute ratios are all chemical signals that indicate important geochemical processes. Chemical signals can be demonstrated by using maps of solute concentrations, ratios, and hydrochemical facies; solute-chloride plots; trilinear diagrams; equilibrium models; and graphs that indicate sulfate reduction.

MAPS OF CONSTITUENTS

The page-size maps used in this report originally were prepared at a scale of 1:2,500,000 from data averaged at the nodes of a grid. The averaging was necessitated by the clumped distribution of the data.

For many of the maps, it was difficult to locate contours precisely; however, the contours are a general indication of regional trends. Where data control is sparse, the contours are dashed. Consistent patterns in the data were almost always present, which enable interpretation of regional trends.

DISSOLVED SOLIDS AND pH

The map of dissolved solids is perhaps the best "quick-look" method available to the geochemist. Evaluating the regional trends in dissolved solids permits the preliminary location of areas of particular concern via the presence of anomalous highs or lows on the maps.

The dissolved-solids concentration is indicative of the nature of chemical processes that affect the water quality. Recharge water, which generally has a dissolved-solids concentration less than 1,000 mg/L, is relatively unaffected by salt dissolution. Throughout a large part of the northern Great Plains, concentrations of dissolved solids generally range from 3,000 to 10,000 mg/L. In this range, the water could be affected by the dissolution of gypsum and halite, but the dissolution of halite is minimal. To obtain concentrations of dissolved solids greater than 10,000 mg/L, a more extensive dissolution of halite is needed. The increase in dissolved solids can continue to concentrations as much as 320,000 mg/L before the water becomes saturated with respect to halite. At concentrations greater than 320,000 mg/L, calcium, magnesium, or potassium also will become important cations.

Of all water-quality characteristics reported, pH is probably the least reliable because of variation in procedures of sampling and analysis used by the various organizations contributing to the data base. Measurement of pH is best made at a sampling site by following careful procedures. The pH maps show onsite and laboratory values. The laboratory-measured values of pH especially are affected by the flux of carbon dioxide over time between the time of collection and analysis. Because of the error caused by this flux, the maps adequately represent trends in pH but not necessarily the true value of pH at a given point.

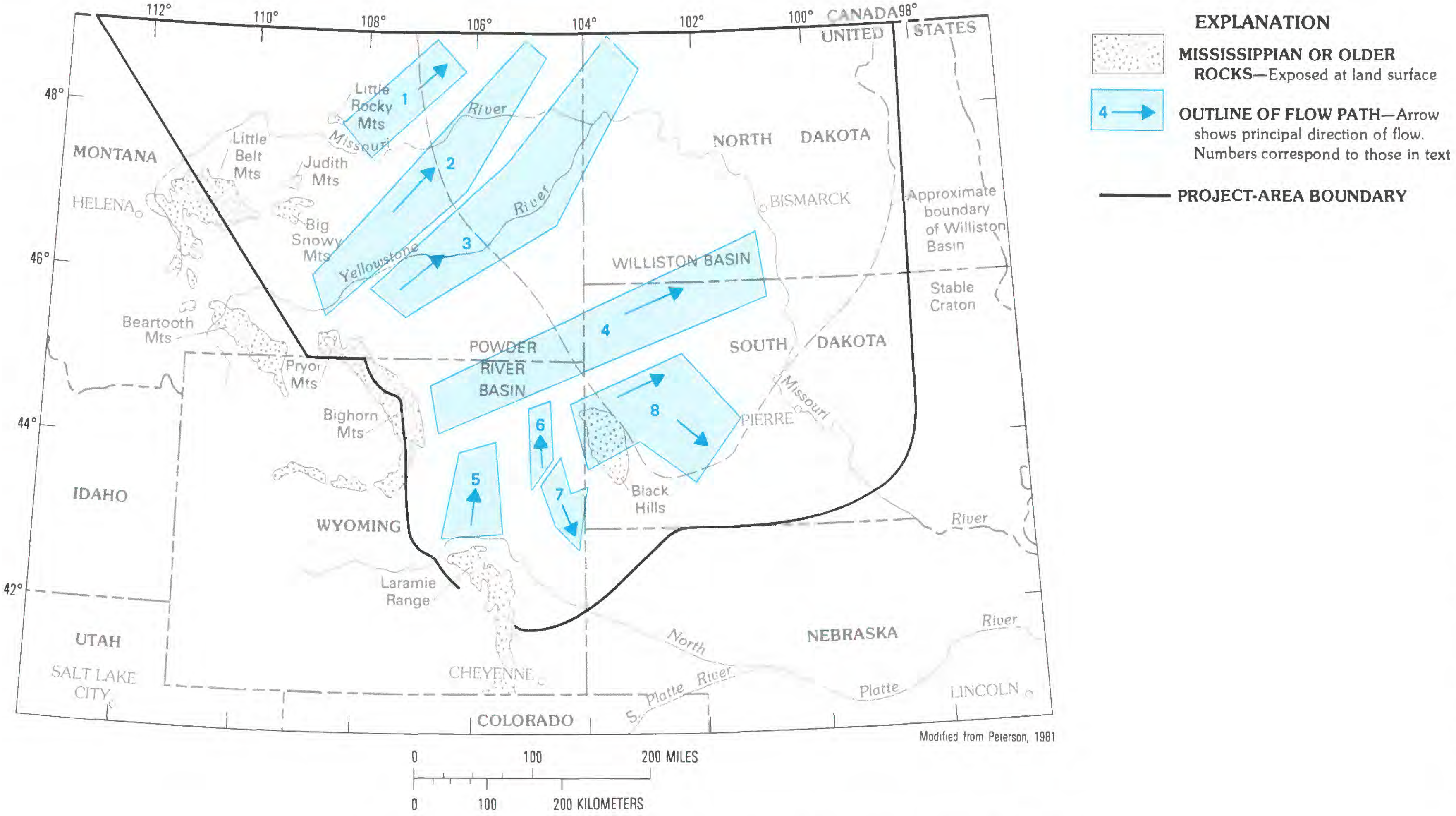
Some possible reasons for *decreasing* values of pH along a flow path are

1. The oxidation of pyrite,

$$2FeS_2 + 4H_2O + 7.5O_2 = Fe_2O_3 + 4SO_4^{-2} + 8H^+; \quad (5)$$

2. Organic oxidation,

$$2H_2O + 6Fe^{+2} + CH_2O = HCO^-_3 + 5H^+ + 6Fe^{+2}; \quad (6)$$



Modified from Peterson, 1981

FIGURE 18.—Flow paths used in analysis of geochemical data in the northern Great Plains.

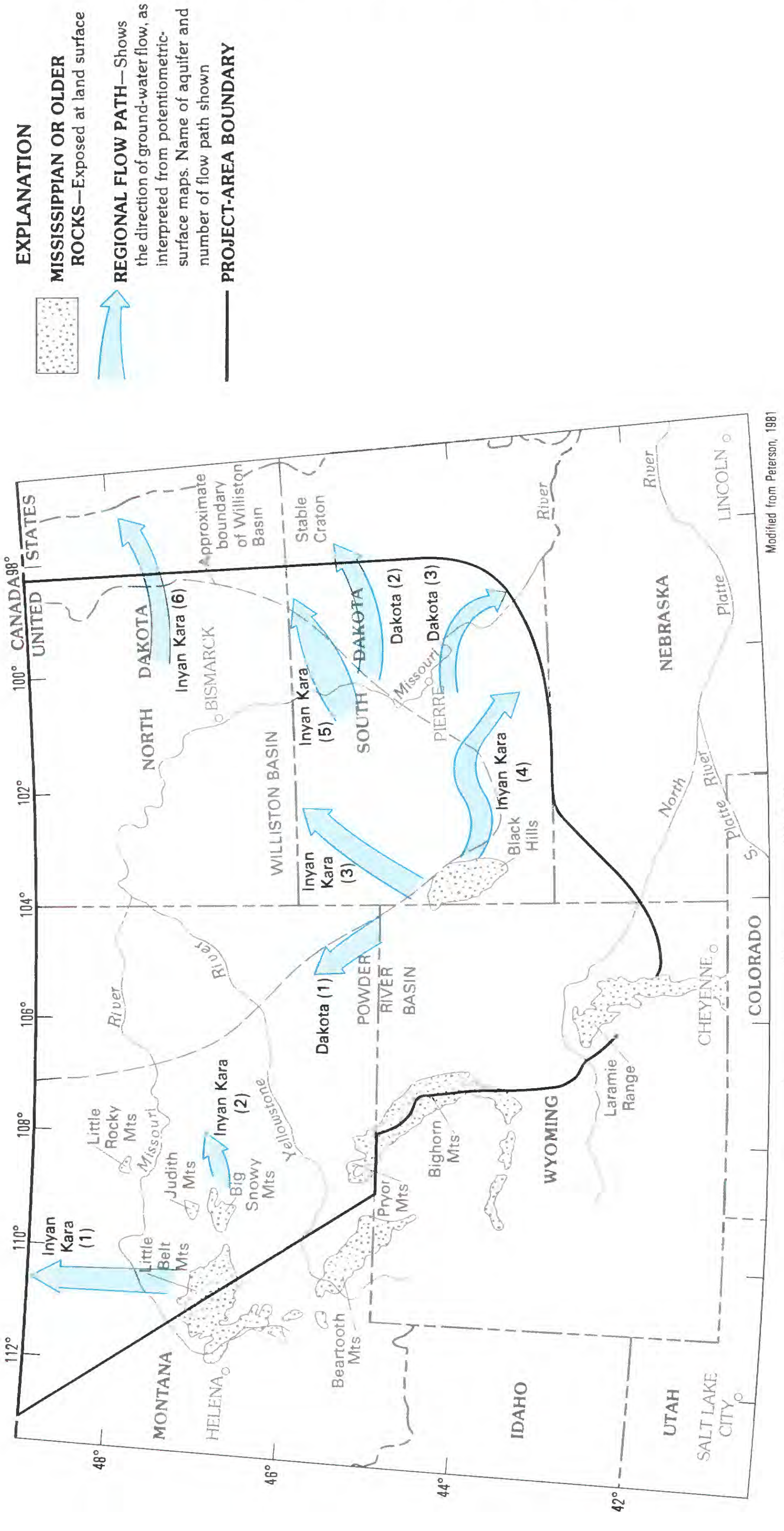


FIGURE 19.—Selected flow paths in the Lower Cretaceous aquifers in the northern Great Plains.

3. Mixing of waters that have different values of pH;
4. A change in lithofacies from one that contains a weak acid anion, such as carbonate, to one that contains a relatively large percentage of organic material; that is, low molecular-weight organic acids commonly associated with oil-field waters (Collins, 1975);
5. Precipitation of a phase incorporating the anion of a weak acid, such as a carbonate mineral, under closed-system conditions;
6. Methanogenesis,

$$4H^{+} + CH_2O + 4Fe^{+2} = 4Fe^{+3} + CH_4 + H_2O; \text{ and} \quad (7)$$

7. Cation exchange of hydrogen ion into solution from a clay mineral.

Values of pH also may increase downgradient. Among the possible reasons for a downgradient *increase* in values of pH are

1. A facies change from a virtually carbonate-free lithology to one that contains carbonate rocks or other weak-acid salts, for example, silicate minerals, that increase the pH if they undergo hydrolysis;
2. Mixing of waters with different values of pH;
3. Cation exchange of hydrogen ion onto a clay mineral; and
4. Contributions from organic material containing substantial nitrogenous bases.

CHLORIDE

Chloride generally is conservative in water (Carpenter, 1978; Eugster and Jones, 1979; Drever, 1982). Therefore, concentration maps of chloride may be used to interpret aquifer characteristics and boundary conditions and to identify interaquifer leakage. For example, small concentrations of chloride (less than 10 mg/L) normally indicate rapid movement of ground water in an aquifer; large concentrations may indicate that ground-water flow is sluggish. If there are evaporite minerals that contain chloride ions in the aquifer, the chloride concentration will increase substantially because of dissolution. If there are known sources of brine or large concentrations of chloride in underlying or overlying aquifers, the rapid increase of the chloride concentration could indicate leakage between the aquifers. In summary, maps of chloride concentration can be used to describe the ground-water flow system, particularly when used with geologic and hydrologic information.

MOLE RATIO OF MAGNESIUM TO CALCIUM

A map of the mole ratio of magnesium to calcium indicates relative changes in the dissolved concentrations of calcium and magnesium in the system. Magnesium is derived from the dissolution of the carbonate minerals—dolomite or magnesite—and silicate minerals, such as biotite and olivine. The most general mechanism by which magnesium is removed from ground water is by incorporation into the brucite layer of the 2:1 phyllosilicates, or the uptake of magnesium during dolomitization. Calcium commonly is acquired by the dissolution of carbonate minerals, such as calcite, dolomite, or aragonite; by the dissolution of evaporite minerals, such as gypsum and anhydrite; or by the dissolution of silicate minerals, such as anorthite. Calcium commonly is removed from ground water through the precipitation of calcite, gypsum, or anhydrite. Calcium and magnesium may be removed from solution through ion exchange for sodium.

Constancy in the ratio throughout a geographic area may indicate a chemical control by mineral equilibria; for example, equilibrium among the minerals calcite, dolomite, and gypsum or calcite, dolomite, and a clay mineral. The map also may be used to infer the plausibility of the dolomitization mechanism (Lippmann, 1973), which requires an aqueous mole ratio of magnesium to calcium of at least 6 to 11, depending on the salinity of the water (Bathurst, 1971):

$$2CaCO_{3_{(s)}} + Mg^{+2} = CaMg(CO_3)_{2_{(s)}} + Ca^{+2} \quad (8)$$

MOLE RATIO OF BICARBONATE TO SULFATE

A map of the ratio of bicarbonate to sulfate shows the relative changes in the concentrations of the bicarbonate and the sulfate ions. The means by which bicarbonate is added to solution are (1) the dissolution of carbonate minerals or hydrolysis of silicate minerals with carbon dioxide; (2) addition of carbon dioxide via decomposition of organic material (Foster, 1950); (3) sulfate reduction (Goldhaber and Kaplan, 1974; Thorstenson and others, 1979); and (4) methanogenesis (Collins, 1975). Bicarbonate ion may be removed from ground water by the precipitation of carbonate minerals, most commonly calcite.

Sources of sulfate include leakage from adjacent units, dissolution of sulfate minerals, such as gypsum or anhydrite, oxidation of a sulfide phase, such as pyrite, or oxidation of organic sulfur. Losses generally are attributed to sulfate reduction, which can be either bacterially mediated (Stumm and Morgan, 1981), or a nonbacterial chemical reaction driven by elevated temperatures at depth, or precipitation of gypsum or anhydrite.

MOLE RATIO OF SOLUTE TO CHLORIDE

As geochemical reactions occur, the mole ratio of reacting solutes to chloride changes in a characteristic manner. In the ground waters that are present in deep basins, the solutes often are derived from solution of saline minerals or from the mixing of marine water that has not been flushed from the system. In the northern Great Plains aquifers, the increase in chloride concentration, particularly the large increases of more than 100,000 mg/L, is because of the dissolution of halite and other marine salts that are present in some of the formations. Solutes that are part of the dissolving salts will maintain a constant solute-to-chloride ratio, while those solutes that participate in chemical reactions, either coming into solution or leaving solution, will have ratios that increase or decrease systematically.

HYDROCHEMICAL FACIES

Back (1966) advanced the concept of hydrochemical facies in terms of percentages of milliequivalents of cations and anions. Many genetic relations and evolutionary trends in water chemistry can be described by changes in hydrochemical facies. A new approach to identifying hydrochemical facies developed by Kimball (1992) has been used for this study. Hydrochemical facies are identified in terms of normative salts, rather than in terms of dominant, unassociated cations and anions. A normative salt composition represents a unique salt assemblage that would result if the given water were evaporated to dryness at 25 °C, 1 atm total pressure, and atmospheric carbon dioxide pressure—that is, at Earth-surface conditions. In calculating this normative salt assemblage, the cations and anions of the solution are quantitatively associated in the salt minerals. A computer code, SNORM, has been used to recast the chemical compositions of water samples into normative salt compositions (Bodine and Jones, 1986).

For describing hydrochemical facies, normative salts can be recast into 12 "simple-salts" (table 1). These 12 salts include the alkali-earth (calcium and magnesium) and alkali (sodium and potassium) salts of carbonate, sulfate, and chloride. To make reacting or equivalent concentrations the same for each salt, the sodium and potassium are doubled in salts of chloride, as with sodium chloride (Na_2Cl_2). Each simple salt then has a cation charge of 2. One can speak of a calcium carbonate water, a sodium carbonate water, or any combination of dominant simple salts, such as a calcium sulfate-sodium chloride water. Changes among the simple salts, which indicate changes in the hydrochemical facies, indicate processes that affect the water chemistry.

The facies labeled facies 1 on the maps and figures represent the facies of the most dilute water. The facies labeled facies 4 or facies 5 is the facies of the most concentrated water. The composition of these facies in terms of normative salts is far from constant, rather it will depend on the composition of the water associated with that facies as shown in tables of facies for individual hydrogeologic units.

TRILINEAR DIAGRAMS

Another means of determining changes in solute ratios and hydrochemical facies is with a trilinear diagram. Trilinear diagrams were used for analysis of the Lower Cretaceous aquifers. A computer code to prepare plots of trilinear diagrams, based on the diagrams of Hill (1940), was developed by Ruth Seidel and Joe S. Downey (Ruth Seidel, U.S. Geological Survey, written commun., 1980). Constant ion ratios are indicated in trilinear diagrams by changes that follow "tie lines" for two of the three axes. For example, if water with a given magnesium-to-calcium ratio obtains sodium through halite dissolution, the evolutionary path will follow a straight line from the initial ratio toward the sodium apex. Changes in hydrochemical facies can be seen by the clustering of data points on the trilinear diagram into distinct groups. However, sometimes the change between hydrochemical facies is gradual, and there is no distinct break between groups.

EQUILIBRIUM MODELS

Even though it is recognized that most natural waters are not in a state of chemical equilibrium, the calculation of equilibrium states furnishes the boundary conditions toward which the system is progressing.

TABLE 1.—*Possible simple salts calculated from normative salt assemblages*

Carbonates	Sulfates	Chlorides
Alkali-earth carbonates	Calcium sulfate ($CaSO_4$)	Calcium chloride ($CaCl_2$)
Calcium carbonate ($CaCO_3$	Magnesium sulfate ($MgSO_4$)	Magnesium chloride ($MgCl_2$)
Magnesium carbonate ($MgCO_3$)	Sodium sulfate (Na_2SO_4)	Sodium chloride (Na_2Cl_2)
	Potassium sulfate (K_2SO_4)	Potassium chloride (K_2Cl_2)
Alkali carbonates		
Sodium carbonate (Na_2CO_3)		
Potassium carbonate (K_2CO_3)		

Equilibrium calculations were made by using the computer code WATEQ2 (Ball and others, 1980). For equilibrium calculations in very concentrated solutions, such as the brines in the northern Great Plains aquifers and confining units, a version of the equilibrium model PHREEQE (Parkhurst and others, 1980) that uses the Pitzer equations to calculate activity coefficients was used (Harvie and Weare, 1980).

GEOCHEMISTRY OF WATER IN THE AQUIFERS AND CONFINING UNITS

Water in aquifers of the northern Great Plains have a varied range of chemical characteristics, from dilute recharge water to brine that is supersaturated with respect to halite. The following discussions point out the major geochemical characteristics of water in the aquifers and confining units and present the geochemical evidence of processes that affect the solutes in the water.

Discussions of changes along regional flow paths are presented only for the Cambrian-Ordovician, Madison, Pennsylvanian, and Lower Cretaceous aquifers. Geochemical maps for each of the aquifers and confining units are presented to show regional trends; they are not presented to provide site-specific information. The points that are shown on the maps represent individual well locations and average locations in areas that contain clusters of wells; however, individual wells are not differentiated from clusters.

CAMBRIAN-ORDOVICIAN AQUIFER

Samples of water from the Cambrian-Ordovician aquifer have been obtained from most of the area of the northern Great Plains. However, the majority of samples were obtained from wells located near the Cedar Creek anticline (fig. 1) and other areas where there has been oil exploration. The number of samples from wells in western Montana, Wyoming, and most of South Dakota is very limited, and map contours in those areas often are based on a small number of wells.

REGIONAL GEOCHEMICAL TRENDS

Regional distributions of dissolved-solids concentration, pH, chloride concentration, the ratios of magnesium to calcium and bicarbonate to sulfate, and hydrochemical facies are represented on maps of the northern Great Plains area. Only four regional flow paths (1, 2, 3, and 4; fig. 18) have a sufficient number of samples to permit the discussion of trends along the flow paths. Flow paths 5, 6, and 7 contain no data for the Cambrian-Ordovician aquifer, and flow path 8 had only three samples.

Summaries of regional and flow-path data from all the water samples from the Cambrian-Ordovician aquifer are presented in tables 2 and 3. In these tables and in those for subsequent aquifers and confining units, the minimum, 25th percentile, median or 50th percentile, 75th percentile, and maximum values of several constituents and ratios are presented. These statistics are used in the summary tables because geochemical data often are not normally distributed. In tables 2 and 3 and subsequent regional summary tables, the overall data for a hydrogeologic unit will include data that may not occur along the particular flow paths. Thus, a maximum concentration of a given element may not be one of the maximums for the individual flow paths. The same is also true for minimum values.

TABLE 2.—*Regional summary of chemical composition of water from the Cambrian-Ordovician aquifer*

[Concentration in milligrams per liter, except pH, which is in pH units, and mole ratios, which are dimensionless]

Constituent[1]	Number of samples[2]	Minimum	25th percentile	50th percentile	75th percentile	Maximum
Dissolved solids	289	115	8,380	31,400	76,800	397,000
pH	273	6.5	7.0	7.3	7.80	8.9
Calcium	287	7.6	450	1,000	2,800	56,000
Magnesium	285	.90	80	190	500	8,400
Sodium	287	.40	2,600	10,000	27,000	120,000
Potassium	31	.20	4.7	66	840	7,100
Chloride	287	.50	3,600	18,000	46,000	250,000
Sulfate	287	.40	920	1,400	1,900	7,900
Bicarbonate	286	17	195	293	404	3,650
Mole ratio of magnesium to calcium.	285	.04	.24	.30	.40	2.3
Mole ratio of bicarbonate to sulfate.	284	.01	.22	.34	.48	670

[1] A constituent can be the chemical elements dissolved in water, such as calcium; a property of water, such as pH; an indicator of overall water quality, such as dissolved solids; or a mole ratio of constituents.

[2] Used to calculate percentiles.

DISSOLVED SOLIDS AND pH

Water in the Cambrian-Ordovician aquifer, except in the recharge areas, generally has concentrations of dissolved solids in excess of 2,000 mg/L; concentrations are in excess of 300,000 mg/L near the depocenter of the Williston basin (figs. 2 and 20). The smallest concentrations are near uplift areas, principally the Black Hills and the Bighorn Mountains. Water quality indicates considerable variation as the dissolved-solids concentration increases.

The smallest concentrations of dissolved solids are near the Black Hills, where concentrations are less than 500 mg/L, and around the Bighorn Mountains (fig. 1), where concentrations are less than 2,000 mg/L. Another area of relatively small concentrations is along the Red River of the North, the eastern boundary of North Dakota, where concentrations generally range from 2,000 to 3,000 mg/L. Away from highland areas, dissolved-solids concentrations generally are from 5,000 to 10,000 mg/L. Around the periphery of the Williston basin, concentrations of dissolved solids change from less than 10,000 to more than 300,000 mg/L. Throughout a large area in eastern Montana and much of North Dakota, the aquifer contains brine and has dissolved-solids concentration of more than 100,000 mg/L. Dissolved-solids concentrations are largest in the Williston basin, along the Montana–North Dakota border, where concentrations are about 400,000 mg/L.

Geologic structure of the aquifer affects the dissolved-solids concentration in some areas. A structural effect, near the Bowdoin dome in Montana, is indicated by a decrease in concentration of dissolved solids along flow path 1 (fig. 20; see fig. 1 for structural features). A large change in dissolved-solids concentration occurs across a northeast-trending line in the center of flow path 4 at the Cedar Creek anticline (fig. 1). A large range of dissolved-solids concentrations occurs along this anticline, which indicates that there are local areas with evaporites. The existence of more dilute water near the Red River of the North in North Dakota and north and east of the Missouri River in South Dakota are evidence of leakage in these areas. The likelihood of contamination by oil-field drilling fluids is indicated by large concentrations in small, local areas of oil exploration.

TABLE 3.—*Chemical composition of water from the Cambrian-Ordovician aquifer from along selected flow paths*

[Concentrations in milligrams per liter, except pH, which is in pH units, and mole ratios, which are dimensionless]

Constituent[1]	Flow path (fig. 18)	Number of samples[2]	Minimum	25th percentile	50th percentile	75th percentile	Maximum
Dissolved solids	1	6	2,870	3,250	4,050	8,900	17,600
	2	6	72,200	76,900	91,900	219,000	282,000
	3	37	1,390	19,900	50,00	0 81,400	397,000
	4	9	459	2,720	4,150	35,000	220,000
pH (units)	1	6	6.6	6.7	6.8	6.9	7.1
	2	6	6.5	6.6	7.0	7.3	7.4
	3	35	6.6	6.9	7.2	7.7	8.7
	4	8	6.5	6.7	7.0	7.9	8.2
Calcium	1	6	450	450	500	540	620
	2	6	1,400	1,500	1,700	3,800	7,300
	3	37	190	800	1,500	3,600	56,000
	4	9	12	88	230	1,500	8,600
Magnesium	1	6	73	84	93	140	160
	2	6	300	320	420	820	850
	3	36	25	110	290	500	5,900
	4	9	2.0	22	40	200	1,600
Sodium	1	6	190	460	730	2,500	5,900
	2	6	26,000	27,000	34,000	78,000	110,000
	3	37	130	6,400	18,000	28,000	86,000
	4	9	5.1	610	1,300	12,000	75,000
Potassium	1	0	--	--	--	--	--
	2	1	1,000	1,000	1,000	1,000	1,000
	3	4	66	260	1,100	2,200	2,500
	4	1	2.5	2.5	2.5	2.5	2.5
Chloride	1	6	120	320	610	3,900	8,200
	2	6	41,000	45,000	53,350	130,000	170,000
	3	37	79	11,000	30,000	49,000	250,000
	4	9	3.00	520	1,500	20,000	130,000
Sulfate	1	6	1,300	1,500	1,700	2,600	2,700
	2	6	1,800	2,100	2,500	3,300	3,500
	3	37	26	840	1,100	1,300	6,200
	4	9	95	600	1,100	1,300	2,000
Bicarbonate	1	6	161	176	206	397	586
	2	6	156	163	217	334	399
	3	36	34	188	238	317	1,800
	4	9	68	236	365	534	1,130
Mole ratio of magnesium to calcium.	1	6	0.19	0.28	0.33	0.44	0.52
	2	6	.19	.20	.36	.60	.88
	3	36	.14	.22	.26	.32	.42
	4	9	.16	.18	.27	.43	.76
Mole ratio of bicarbonate to sulfate.	1	6	0.14	0.17	0.19	0.30	0.36
	2	6	.08	.10	.16	.19	.19
	3	36	.07	.26	.36	.42	.75
	4	9	.08	.33	.51	1.3	19

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[1] A constituent can be the chemical elements dissolved in water, such as calcium; a property of water, such as pH; an indicator of overall water quality, such as dissolved solids; or a mole ratio of constituents.

[2] Used to calculate percentiles

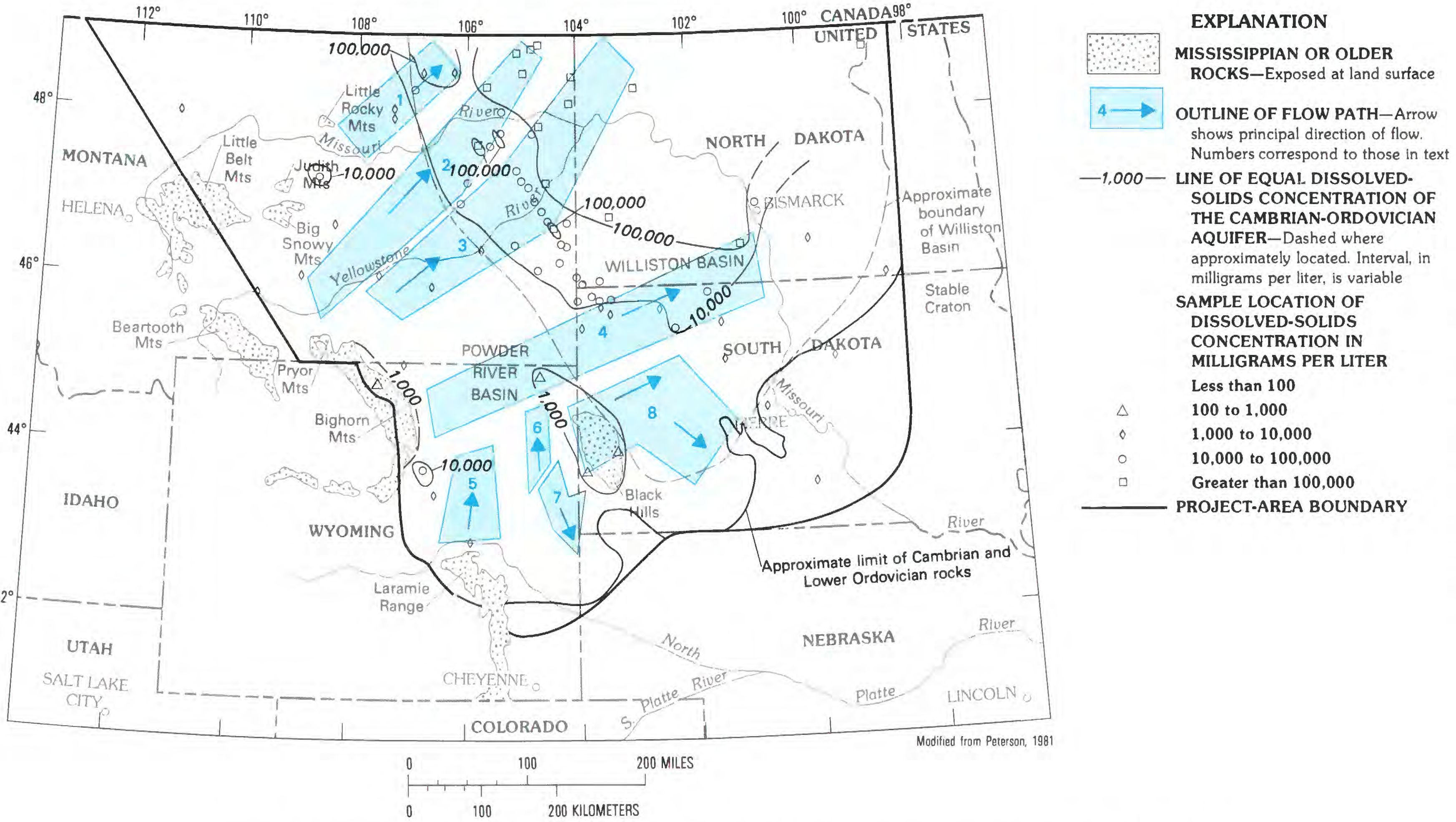


FIGURE 20.—Concentration of dissolved solids in water from the Cambrian-Ordovician aquifer in the northern Great Plains.

Measured pH exceeded 8.0 at some locations in the Cambrian-Ordovician aquifer (fig. 21), but values less than 6.5 occur in the Williston basin. The pH of the system has a general pattern of relatively alkaline values in the recharge areas, then decreases as the water flows downgradient. This general trend from higher values of pH in uplifted areas to lower values in basins indicates that pH decreases with increasing dissolved solids.

HYDROCHEMICAL FACIES

There are four main hydrochemical facies, expressed by simple-salt assemblages, in water from the Cambrian-Ordovician aquifer. Following is a listing of the simple salt composition of each facies, the mole percent of the simple salts, and the millimoles per liter of each simple salt in the facies. Only those simple salts that represent more than 5 mole percent of the dissolved solutes in solution are shown in this list. The increase of solutes is indicated by the millimoles per liter of solution for each of the simple salts.

Facies number	Simple-salt component	Mole percent	Millimoles per liter of solution
1	$MgCO_3$	41.4	0.34
	$CaCO_3$	40.8	.34
	Na_2CO_3	7.9	.07
2	$CaSO_4$	48.2	14.6
	Na_2Cl_2	28.9	8.7
	$MgCO_3$	14.8	4.5
	$MgSO_4$	7.0	2.1
3	Na_2Cl_2	79.6	221
	Na_2SO_4	11.5	32.0
	$CaSO_4$	6.7	18.6
4	Na_2Cl_2	72.5	927
	$CaCl_2$	13.2	169
	$MgCl_2$	12.8	164

Facies 1, which occurs in highland areas near the Black Hills and the Bighorn Mountains, is relatively dilute (fig. 22). This water has a dissolved-solids concentration of less than 200 mg/L and represents water that primarily has dissolved carbonate minerals in the recharge areas.

Away from the highland areas, principally at the western end of flow paths 2, 3, and 4, water changes chemical composition to a more calcium sulfate character—facies 2. This change to facies 2 involves the addition of almost 15 mmol/L of calcium sulfate, which indicates the dissolution of gypsum. Sodium chloride also becomes a substantial component.

Around the edges of the Williston basin there is another change in the chemical composition—facies 3. This facies consists principally of a sodium chloride water, but sodium sulfate and calcium sulfate are also components. The change to facies 3 involves the addition of about 220 mmol/L of sodium chloride but also an increase of sodium sulfate and calcium sulfate. If the sulfate is added from continued gypsum dissolution, this indicates that calcium is removed from solution, either by cation exchange for sodium or through precipitation of calcite. The chemical composition of facies 3 also could result from mixing of fresher water from the west with Williston basin brines.

Facies 4, which is principally in the Williston basin, has an additional 700 mmol/L of sodium chloride and also more than 300 mmol/L of calcium chloride and magnesium chloride salts. These components most likely result from dissolving evaporites in the basin.

SODIUM AND CHLORIDE

Most of the increase in dissolved-solids concentration in the Cambrian-Ordovician aquifer comes from increases in concentrations of sodium and chloride. The regional pattern of both solutes is similar and is represented by the map of chloride concentration (fig. 23). Chloride concentrations are relatively small in recharge areas, less than 100 mg/L. At a chloride concentration of less than 5,000 mg/L, the sodium concentration plots above the line of equal milliequivalents, which indicates dissolution of a mineral other than halite (fig. 24). Downgradient, there is a very large increase in concentrations toward the Williston basin where the sodium concentration is in excess of 50,000 mg/L and the chloride concentration exceeds 200,000 mg/L. When the chloride concentration exceeds 5,000 mg/L, sodium and chloride are present in essentially equal concentrations, which indicates a common source. However, even though sodium and chloride occur in approximately equal concentrations, this does not indicate their source–whether halite is present in the aquifer or was dissolved in water that leaked from an adjacent formation. Calcium, magnesium, and potassium also increase proportionally with chloride at chloride concentrations greater than 5,000 mg/L. But none of these constituents shows the one-to-one increase shown by sodium.

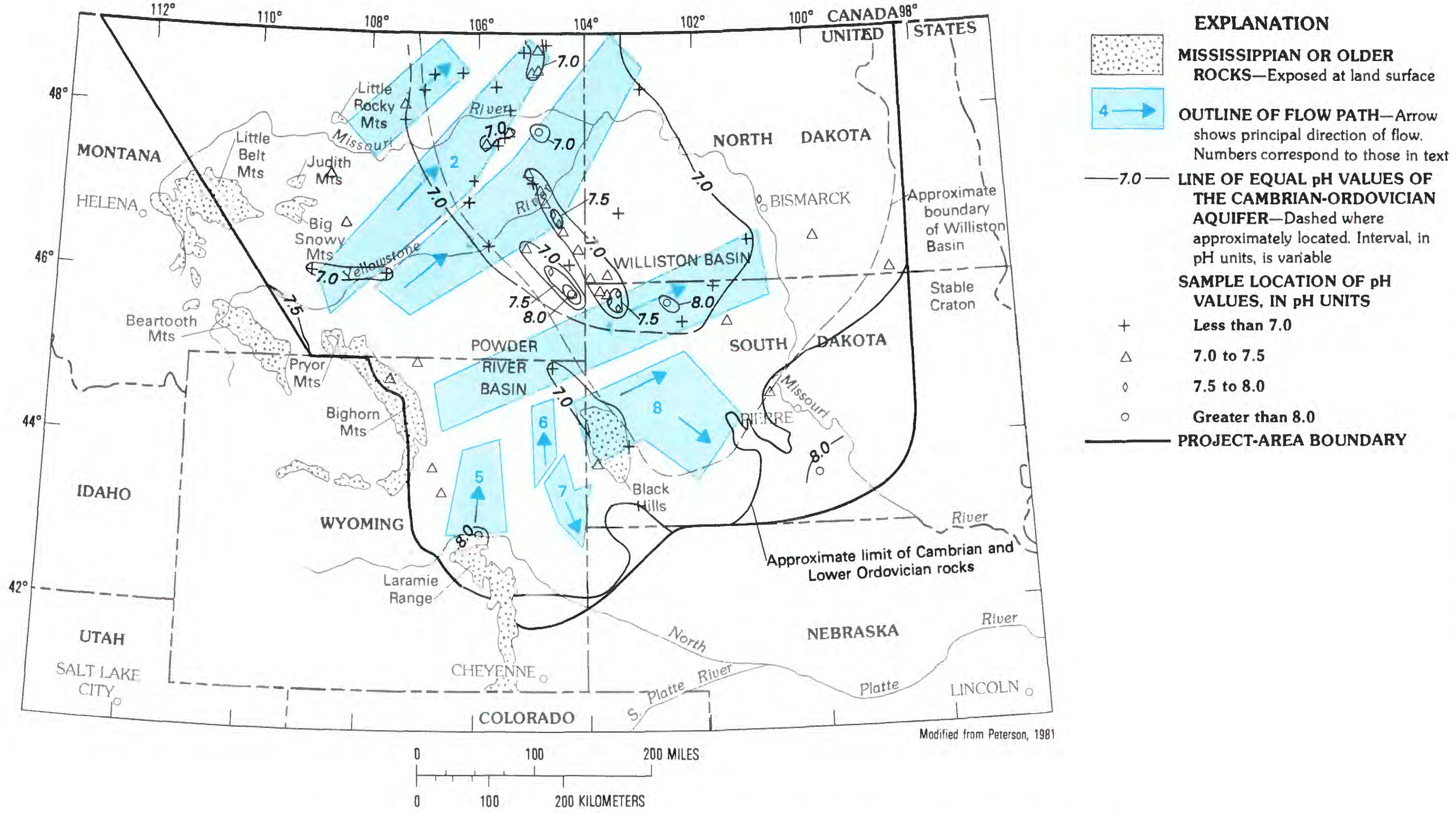


FIGURE 21.—Values of pH in water from the Cambrian-Ordovician aquifer in the northern Great Plains.

FIGURE 22.—Hydrochemical facies of water from the Cambrian-Ordovician aquifer in the northern Great Plains.

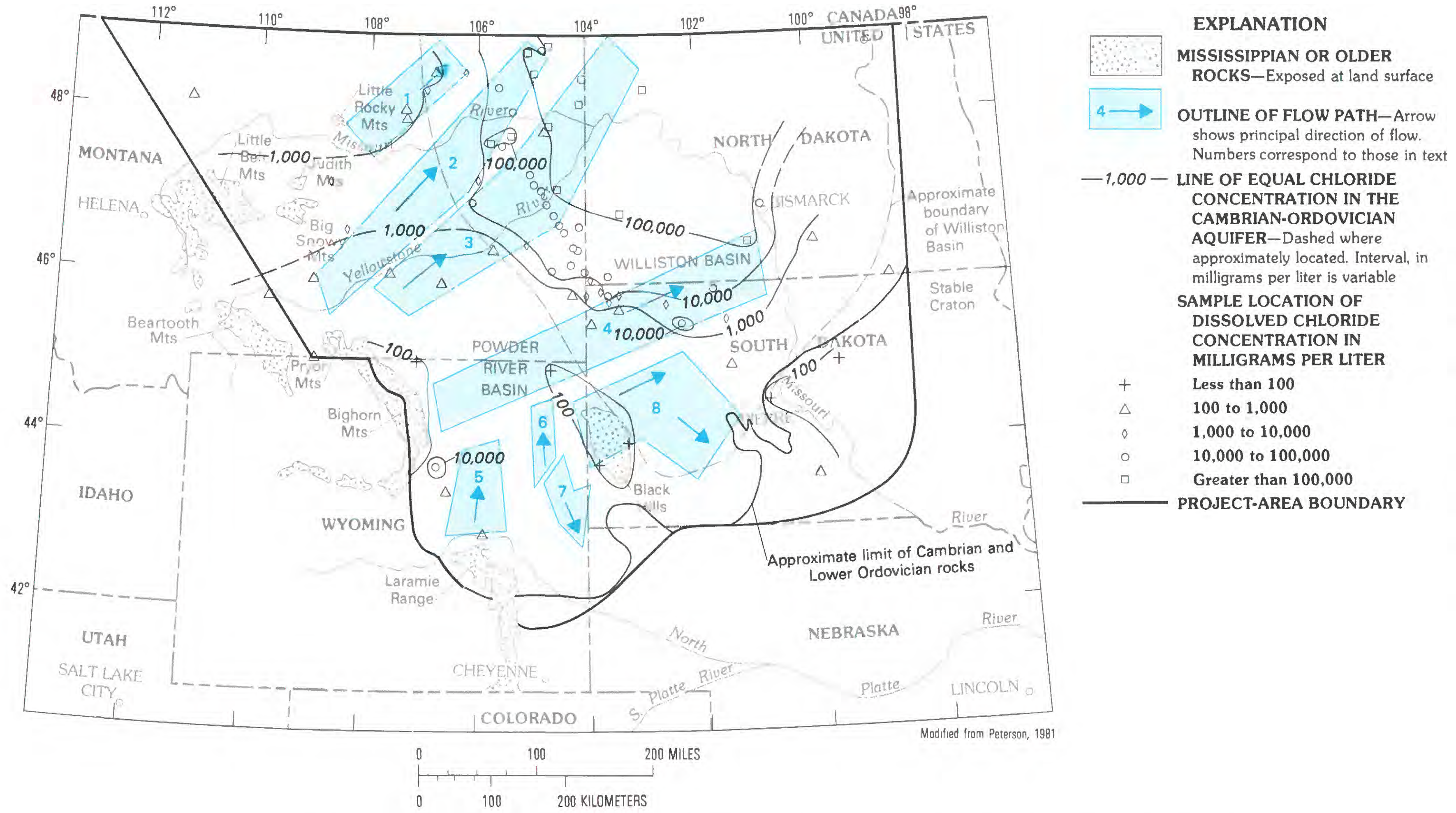


FIGURE 23.—Concentration of chloride in water from the Cambrian-Ordovician aquifer in the northern Great Plains.

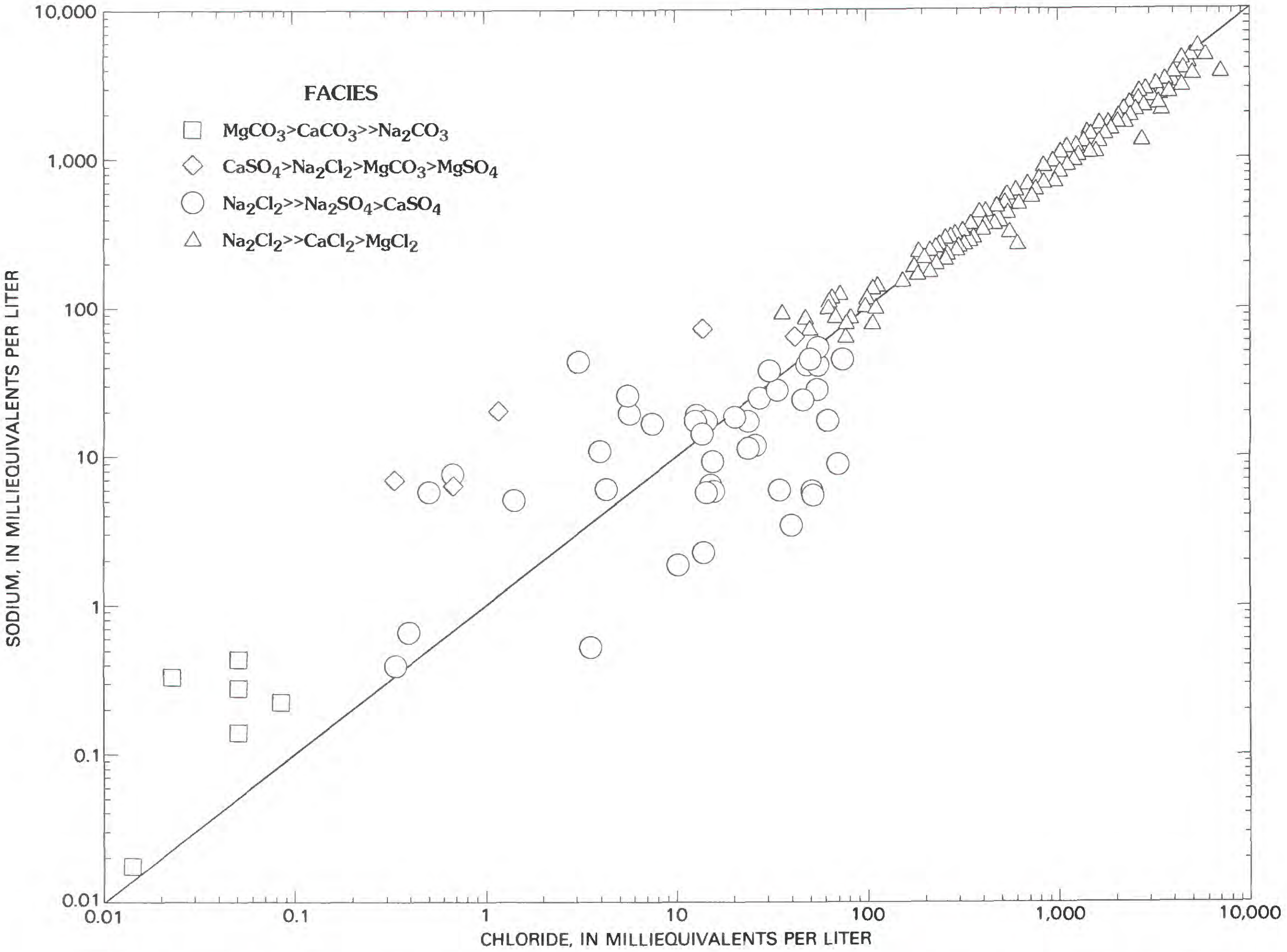


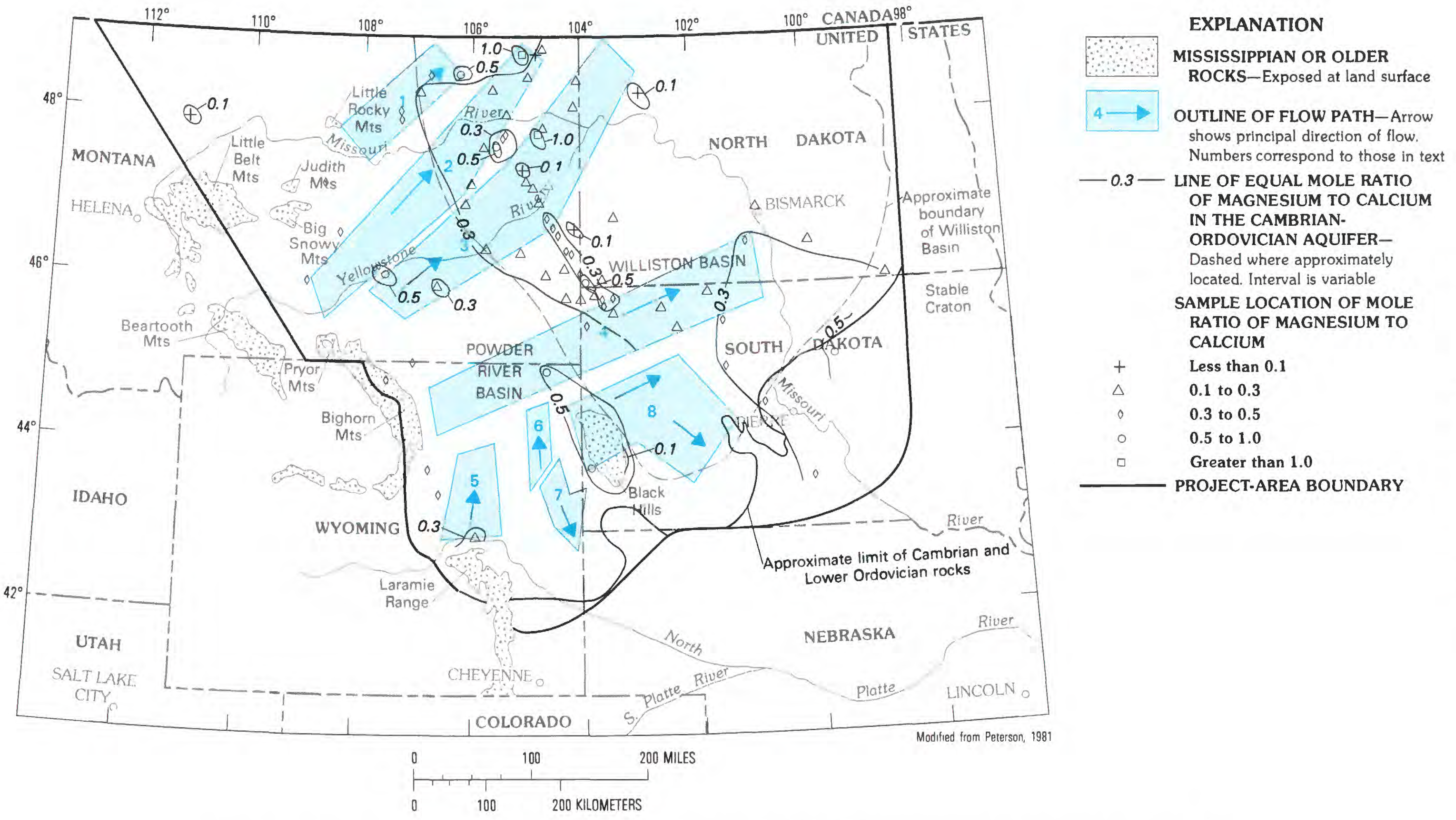
FIGURE 24.—Variation of sodium with chloride in water from the Cambrian-Ordovician aquifer in the northern Great Plains.

MOLE RATIO OF MAGNESIUM TO CALCIUM

The areal distribution of the mole ratio of magnesium to calcium (fig. 25) shows a downgradient decrease from values greater than 1.0 to a consistent value of about 0.2. In recharge areas, two extremes of this mole ratio are evident. In the northwestern part of the Big Horn Mountains, the upgradient mole ratio is less than 0.1. However, in most other uplifted areas, the mole ratio is greater than 1.0. The difference between the small and large mole ratios most likely has to do with the quantity of dolomite in rocks of the recharge area. If the rocks lack dolomite, then calcium concentrations dominate in recharge waters. In the Williston basin, at the end of the flow paths in eastern Montana, calcium possibly is removed by mineral precipitation and the magnesium-to-calcium mole ratio increases again. Generally, the mole ratio is inversely related to the concentration of dissolved solids. In samples with dissolved solids greater than about 1,000 mg/L, the ratio ranges from 0.1 to 0.8 and has no consistent trend.

MOLE RATIO OF BICARBONATE TO SULFATE

Throughout most of the of the northern Great Plains, the mole ratio of bicarbonate to sulfate is less than 1.0 (fig. 26). But values as large as 600 occur in recharge areas where water dissolves carbonate minerals. As the concentration of sulfate increases in the water, bicarbonate remains nearly constant, which causes the ratio to decrease. The mole ratio of bicarbonate to sulfate is extremely large in the Black Hills (about 75) as contrasted to waters in the Bighorn Mountains where the values are less than 10. Values in excess of 1.0 occur within the Williston basin because of decreasing sulfate concentrations; values greater than zero may result from precipitation of



Modified from Peterson, 1981

FIGURE 25.—Mole ratio of magnesium to calcium in water from the Cambrian-Ordovician aquifer in the northern Great Plains.

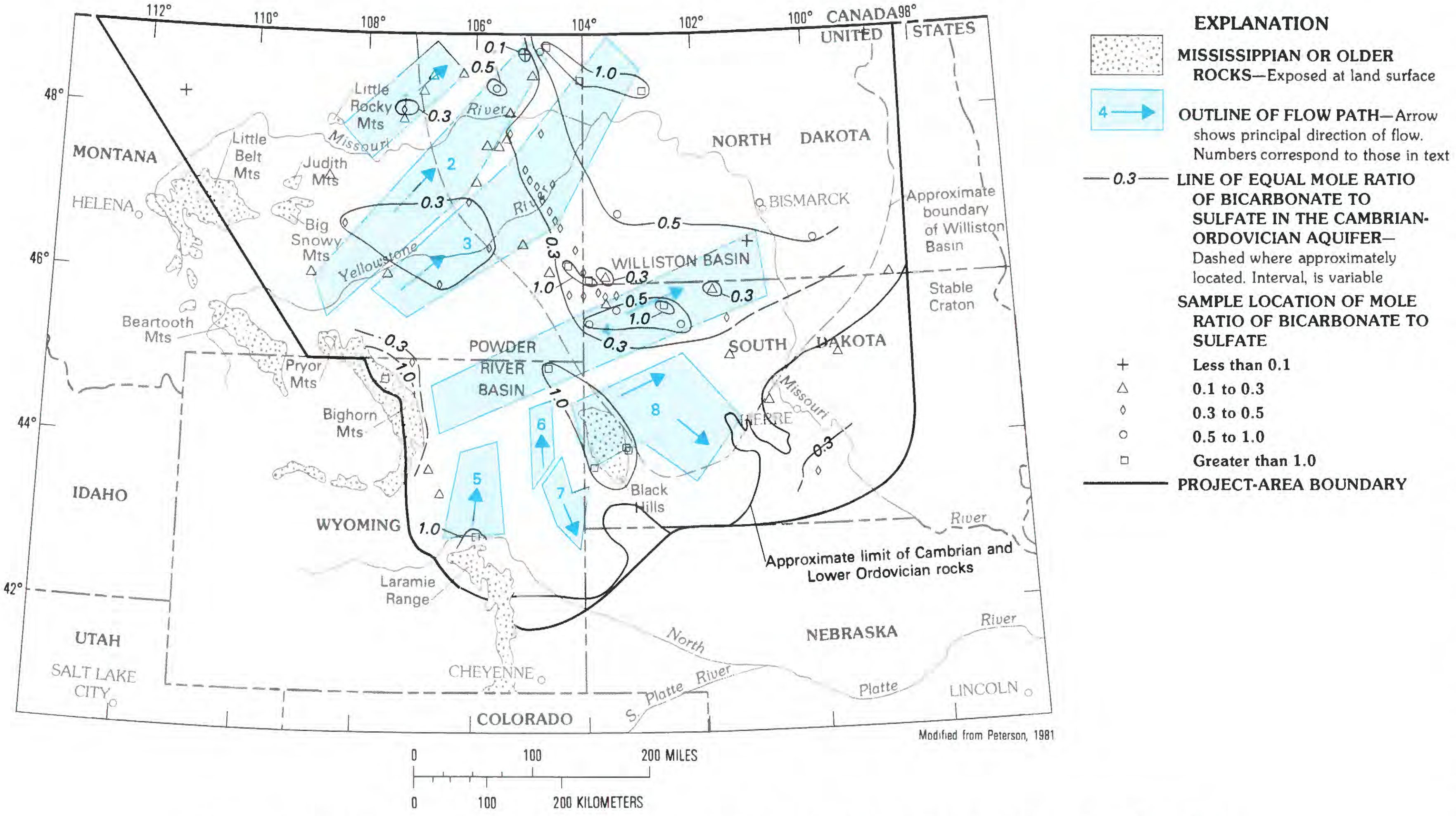


FIGURE 26.—Mole ratio of bicarbonate to sulfate in water from the Cambrian-Ordovician aquifer in the northern Great Plains.

gypsum. Because there is not a corresponding increase in bicarbonate, it is not likely that the decrease in sulfate concentrations is caused by sulfate reduction.

SUMMARY OF MOST PLAUSIBLE MECHANISMS

A summary of the set of most plausible mechanisms that cause the water chemistry observed in the Cambrian-Ordovician aquifer is listed in table 4. In the table, the mechanisms are presented in the order of occurrence along the flow path. Most all the mechanisms or reactions actually do occur simultaneously, but at certain locations along the flow path, some reactions dominate over others. In almost every instance, the major cause of change in water chemistry is the dissolution of evaporites. These evaporites include gypsum and halite. There may be some calcium chloride and magnesium chloride salts associated with the halite. When excess calcium occurs in solution, gypsum may be precipitated. Halite also may precipitate from water in the Cambrian-Ordovician aquifer (fig. 24).

SILURIAN-DEVONIAN CONFINING UNIT

The Silurian-Devonian confining unit contains water with very large dissolved-solids concentrations that exceed 400,000 mg/L in the Williston basin. The large dissolved-solids concentration could affect concentrations in the underlying and overlying aquifers. Water in this unit moves slowly compared to water in the underlying Cambrian-Ordovician aquifer and the overlying Madison aquifer. The slow rate of water movement makes a discussion of water-quality characteristics, in terms of flow paths, less useful than for the aquifer units. It may be more meaningful to discuss trends in chemical characteristics with respect to the variation in dissolved-solids concentration. Nevertheless, outlines of the flow paths in the underlying and overlying aquifers are shown on the maps to help make comparisons with other units. The trends of dissolved-solids concentration, pH, and major solutes and solute mole ratios are summarized in table 5.

REGIONAL GEOCHEMICAL TRENDS

The areal distribution of water samples from the Silurian-Devonian confining unit is much more limited than for other units. Almost all the samples are from wells in Montana and North Dakota. Within Montana, most of the samples are from oil fields located near two structural features, the Cedar Creek anticline and the Poplar dome (fig. 1). This areal distribution limits the ability to discuss regional trends in much detail.

TABLE 4—*Summary of plausible mechanisms controlling chemical composition of water from the Cambrian-Ordovician aquifer*

Mechanism	Evidence
Dissolution of calcite and dolomite.	Initial increase of calcium and magnesium concentrations near the beginning of flow paths 1, 2, 3, and 4. Dominance of bicarbonate in the uplifted areas.
Dissolution of gypsum.	Increase in calcium and sulfate concentrations away from recharge areas. Decrease in bicarbonate to sulfate mole ratio.
Precipitation of calcite.	Decrease in mole ratio of bicarbonate to sulfate. Change from facies 2 to 3 (fig. 21).
Dissolution of halite or mixing.	Increase in dissolved solids, sodium, and chloride; change from facies 2 to facies 3 and 4; decrease in mole ratio of magnesium to calcium; large increase in moles of sodium chloride.
Precipitation of gypsum.	Increase of bicarbonate-to-sulfate mole ratio and concurrent increase in magnesium to calcium mole ratio.

TABLE 5.—*Regional summary of chemical composition of water from the Silurian-Devonian confining unit*

[Concentrations in milligrams per liter, except pH, which is in pH units, and mole ratios, which are dimensionless]

Constituent[1]	Number of samples[2]	Minimum	25th percentile	50th percentile	75th percentile	Maximum
Dissolved solids	199	646	20,900	43,800	155,000	441,000
pH	198	6.5	6.7	7.1	7.5	8.5
Calcium	199	120	650	1,000	2,600	70,000
Magnesium	198	24	130	190	460	7,100
Sodium	197	110	7,100	15,000	57,000	170,000
Potassium	20	190	420	840	2,800	6,400
Chloride	199	12	10,000	24,000	92,000	270,000
Sulfate	199	150	1,600	2,100	3,000	17,000
Bicarbonate	197	29	248	358	496	5,430
Mole ratio of magnesium to calcium.	198	.07	.23	.29	.41	5.2
Mole ratio of bicarbonate to sulfate.	197	.01	.19	.28	.39	17

[1] A constituent can be the chemical elements dissolved in water, such as calcium; a property of water, such as pH; an indicator of overall water quality, such as dissolved solids; or a mole ratio of constituents.

[2] Used to calculate percentiles.

DISSOLVED SOLIDS AND PH

Although the concentration of dissolved solids in the Silurian-Devonian confining unit is mostly in excess of 10,000 mg/L (fig. 27), concentrations less than 1,000 mg/L are measured in the southeastern part of Montana, near recharge areas. Larger concentrations are present in water around the Williston basin in western Montana. In the basin itself, in North Dakota, concentrations greater than 400,000 mg/L are present. Slightly saline water near recharge areas acquires larger concentrations of solutes by dissolution of halite and other evaporite minerals that cause large changes in water-quality characteristics. The source of the salts is most likely the Devonian Prairie Formation.

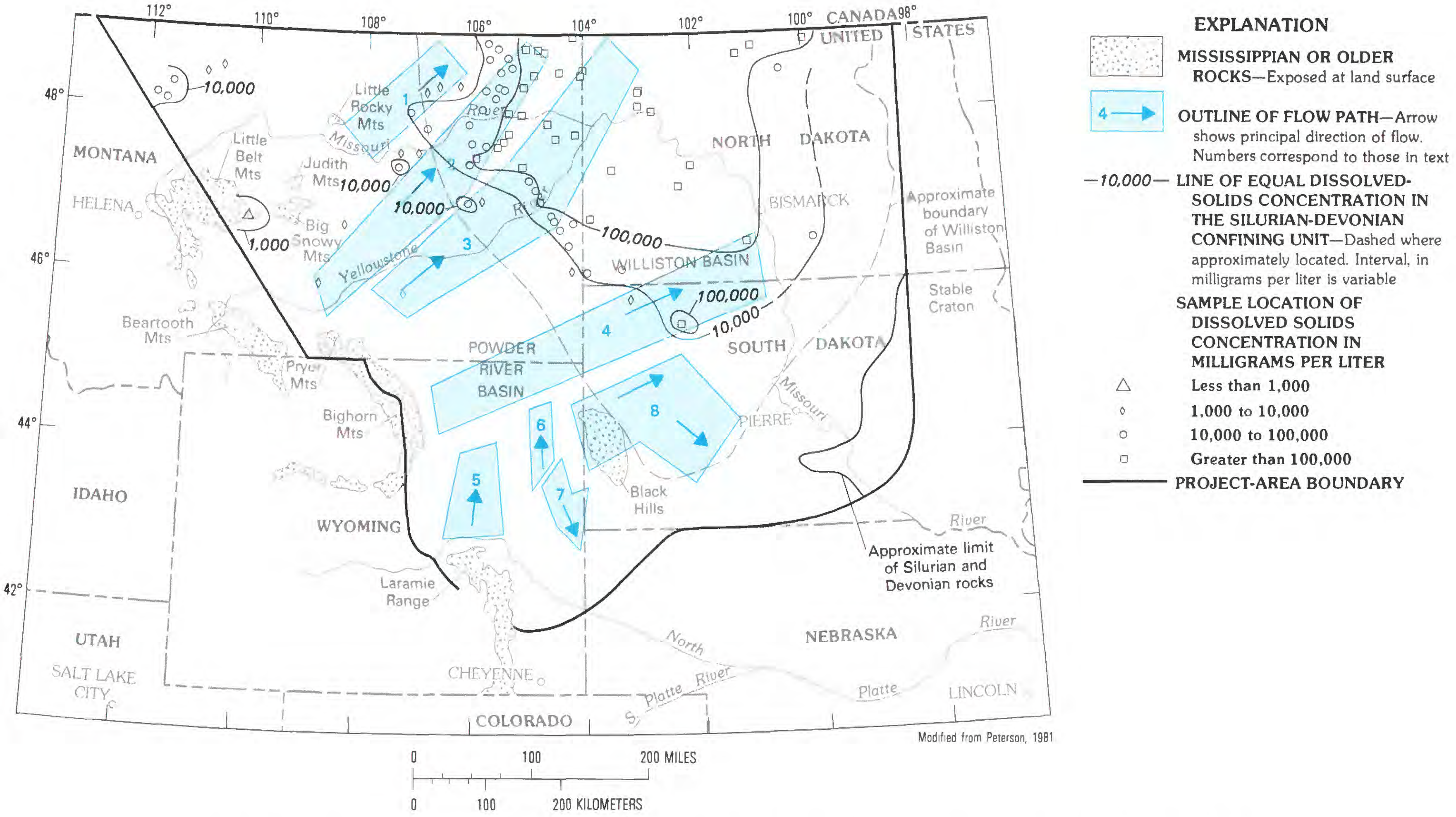
Values of pH are less than 7.0 near uplifted areas and increase toward the east to about 7.5 near the Montana-North Dakota border.

HYDROCHEMICAL FACIES

Within the large range of dissolved-solids concentration of samples from the Silurian-Devonian confining unit, four hydrochemical facies can be represented by simple-salt assemblages as follows:

Facies number	Simple-salt components	Mole percent	Millimoles per liter of solution
1	Na_2Cl_2	42.9	42.2
	Na_2SO_4	23.7	23.3
	$CaSO_4$	20.1	19.8
	$MgCO_3$	6.7	6.6
2	Na_2Cl_2	87.4	504
	$CaSO_4$	7.3	42.1
3	Na_2Cl_2	93.0	3,270
4	Na_2Cl_2	70.8	4,770
	$CaCl_2$	25.2	1,700

In each facies shown, sodium chloride is the principal simple salt. The areal location of each hydrochemical facies is not always distinct, particularly because so many of the water samples from the Silurian-Devonian confining unit are from wells around structural features, and the chemical



Modified from Peterson, 1981

FIGURE 27.—Concentration of dissolved solids in water from the Silurian-Devonian confining unit in the northern Great Plains.

character depends almost entirely on the extent of salt dissolution (fig. 28).

Facies 1, which ranges in dissolved-solids concentration from 646 to 10,500 mg/L, is nearly an equal mixture of chloride and sulfate components. The mixed-salt assemblage, which represents six cations and anions, is typical of a water derived from interaction with shales that contain many minerals as sources for solutes. There is an excess of sodium over chloride; the sodium-to-chloride ratio is about 1.9, which indicates that halite is not the only source of sodium. Facies 1 occurs mostly west of the Cedar Creek anticline in Montana (fig. 28; see fig. 1 for structure).

The sodium chloride character of the water becomes more dominant at larger dissolved-solids concentrations. Facies 2, which has a small calcium sulfate component, is transitional between facies 1 and facies 3, which is primarily a sodium chloride water. Facies 2, a sodium chloride facies with the small calcium sulfate component, has a dissolved solids concentration that ranges from about 20,000 to 100,000 mg/L. Facies 3 ranges from about 100,000 to more than 400,000 mg/L in dissolved-solids concentration. Samples of facies 2 are from the Cedar Creek anticline and the Poplar dome areas. Samples of facies 3 are from north of the Poplar dome in Montana.

Facies 4, which typically occurs in water with dissolved-solids concentrations greater than 300,000 mg/L, is quite different in chemical character. The greatest change is the increase in the calcium chloride component of the brine. This increase in the calcium chloride component is accompanied by an absolute decrease in the concentration of sodium, caused by halite precipitation. The samples are from the Williston basin in North Dakota.

The extent of water movement in the Silurian-Devonian confining unit is small compared to that in adjacent aquifers, but its effect on the geochemistry of water in other hydrogeologic units is pronounced. It is probable that the brines that occur in the Cambrian-Ordovician and Madison aquifers are derived from dissolution of the salts in the Silurian and Devonian rocks. The hydrochemical facies in this unit do not evolve one from another along horizontal flow paths as they do in the aquifers, but instead the facies represent the sum of chemical reactions that occur in water as it moves vertically through the confining unit (Downey, 1986).

Near highland areas (fig. 28; see fig. 1 for structure), there generally is the least mineral dissolution, but even this is much more mineral dissolution than in the adjacent aquifers in the same areas. In facies 2, 3, and 4, which are closer to the Williston basin, there is a large quantity of salt dissolution. The concentration of sodium chloride increases more than an order of magnitude between facies 1 and 2. Between facies 2 and 3 the increase is about 2,700 mmol/L, and between facies 3 and 4 the increase is about 1,500 mmol/L. A slightly larger increase in calcium chloride of about 1,700 mmol/L occurs between facies 3 and 4. These changes represent dissolution of large quantities of salt.

SODIUM AND CHLORIDE

Sodium and chloride account for most of the increase in dissolved-solids concentrations, and the regional distribution of chloride concentrations, which also represents sodium concentrations, is similar to that of dissolved solids (fig. 29). In water with a dissolved-solids concentration of about 325,000 mg/L, calcium and magnesium also are important components of the brine. Concentrations of sodium decrease, which indicates that the precipitation of halite removes sodium from the water (fig. 30). Because the sodium-to-chloride mole ratio of the brine is less than 1, halite precipitation causes the sodium concentration to decrease relative to chloride (Drever, 1982). Another indication of halite precipitation is the increasing mole ratio of the alkali-earth metals to chloride.

MOLE RATIO OF MAGNESIUM TO CALCIUM

The mole ratio of magnesium to calcium generally ranges from 0.2 to 0.4 with little variation. The small variation indicates that the two components may be acquired from a common source or may be controlled by carbonate equilibria. A few values greater than 0.5 occur in waters with dissolved-solids concentrations less than 10,000 mg/L. The smallest values occur in the brines of the Williston basin. Concentrations of magnesium and calcium increase with the increase in dissolved-solids concentration, but the increase of calcium is greater, which causes a decrease in the mole ratio of magnesium to calcium. It is unclear whether the decrease is caused by the uptake of magnesium in the transformation of dioctahedral to trioctahedral clays, by reaction with calcite to form dolomite, or simply by the regional variability of the calcium-to-magnesium mole ratio in the dissolving evaporite.

The regional trend of this mole ratio is shown in figure 31. The contours are not well defined, but the distribution shows larger mole ratios near the

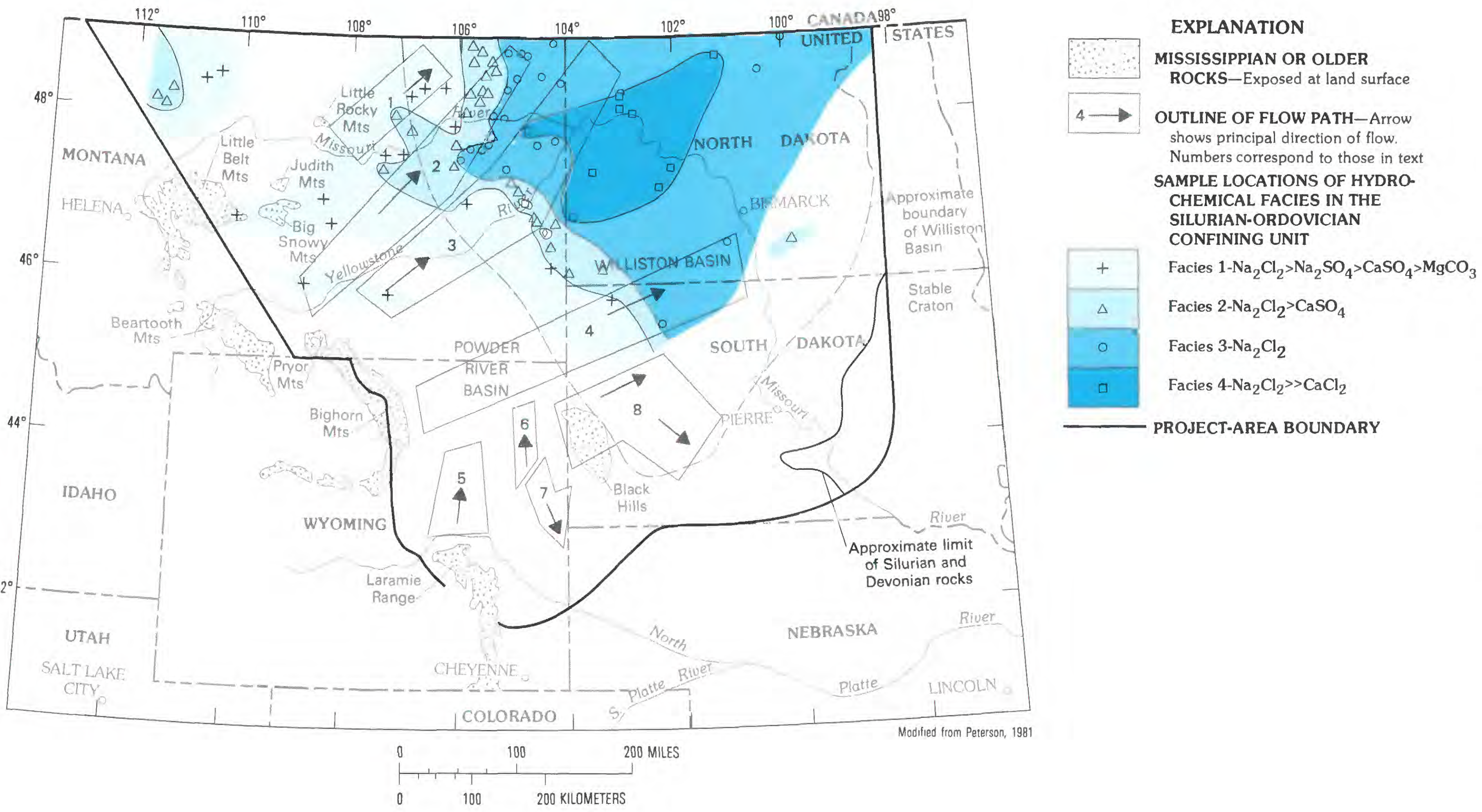


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FIGURE 28.—Hydrochemical facies in water from the Silurian-Devonian confining unit in the northern Great Plains.

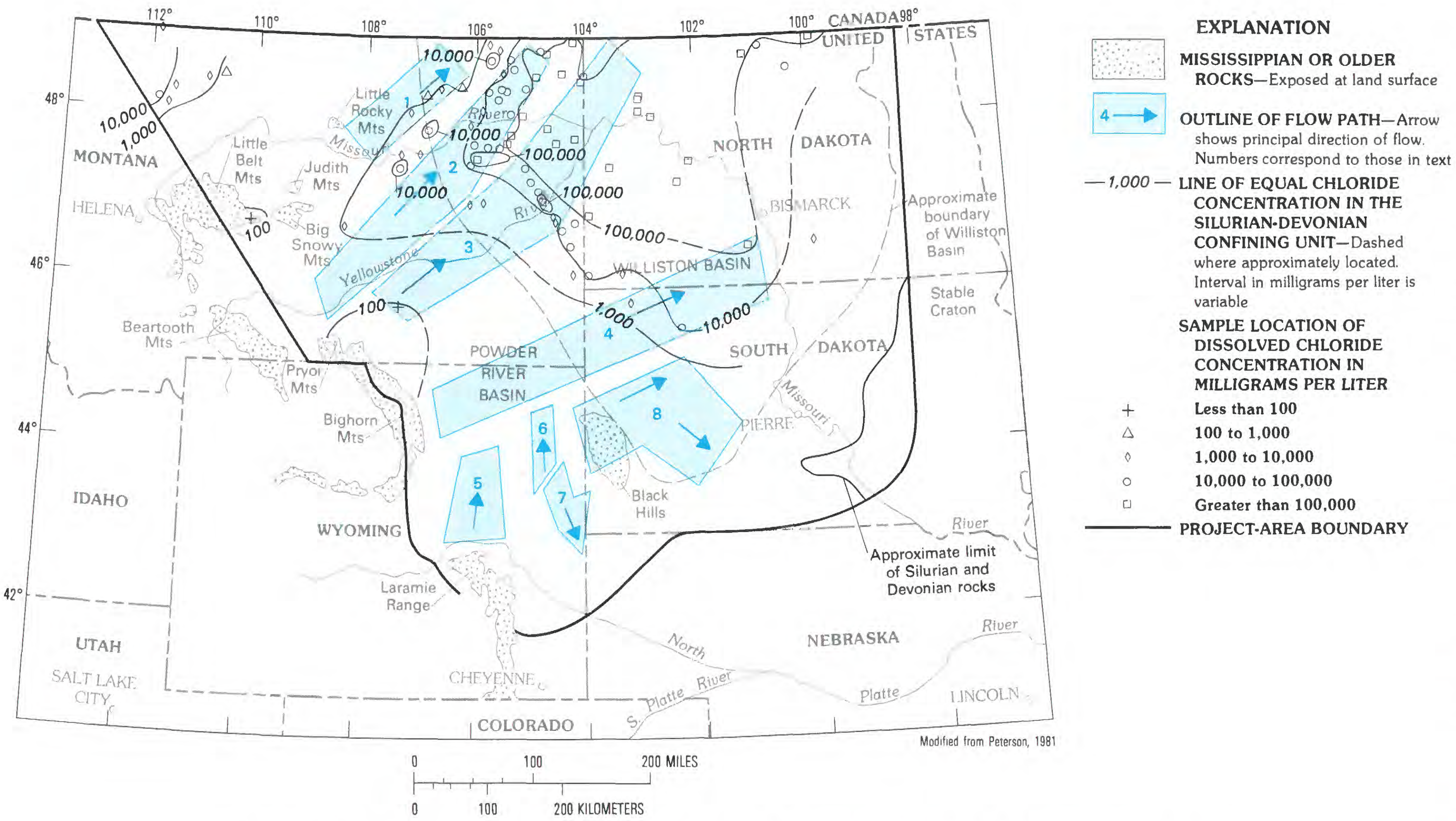

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FIGURE 29.—Concentration of chloride in water from the Silurian-Devonian confining unit in the northern Great Plains.

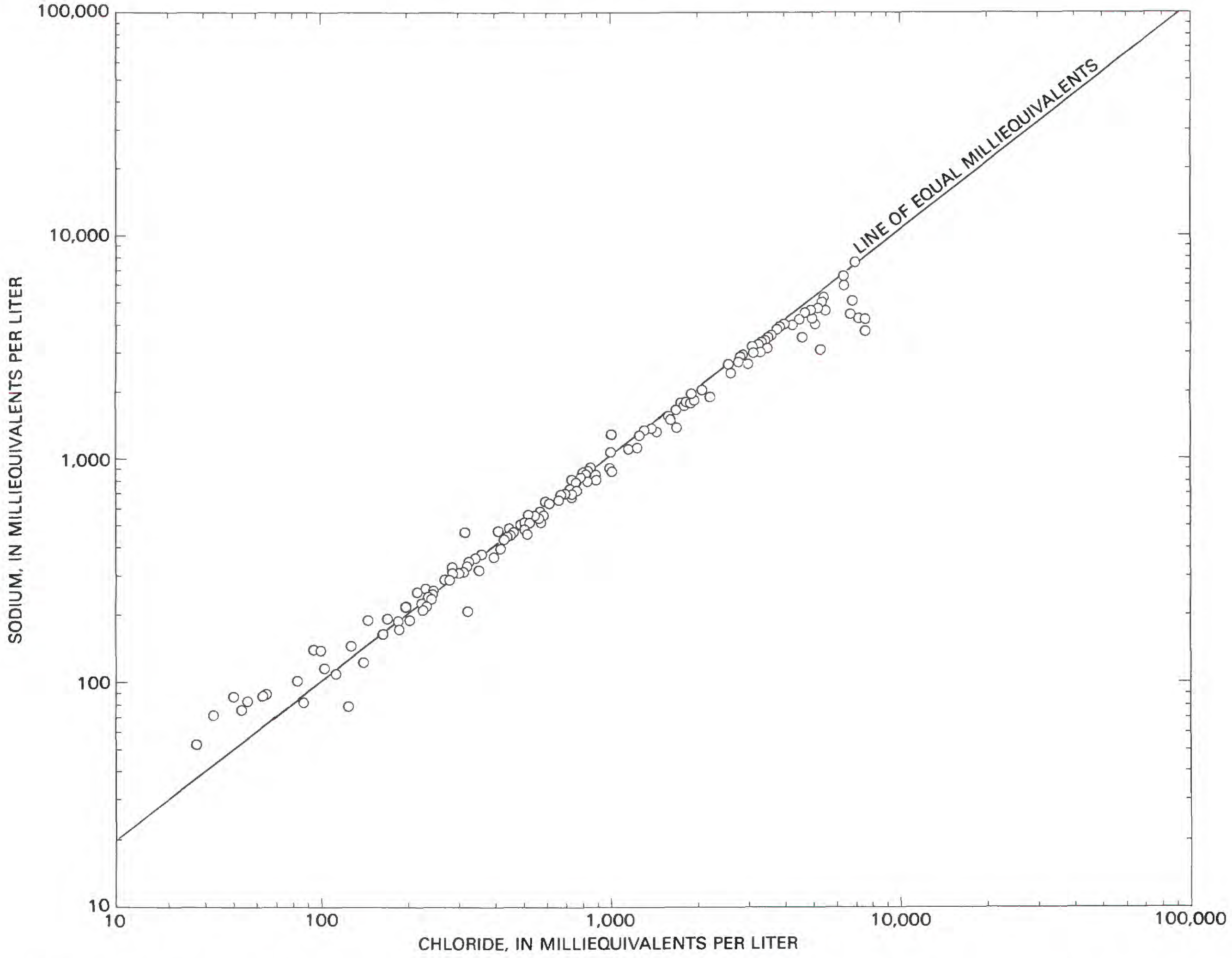


FIGURE 30.—Variation of sodium with chloride in water from the Silurian-Devonian confining unit in the northern Great Plains.

uplifted areas and then considerable variation in samples near the Cedar Creek anticline and the Poplar dome. The mole ratio of magnesium to calcium shows a general decrease from about 0.5 to 0.3 toward the Williston basin and then an increase on the other side of the Williston basin toward the eastern border of North Dakota. The mole ratio of magnesium to calcium shows a substantial decrease toward the center of the Williston basin from values of about 0.3 along the periphery of the basin to about 0.07 near the center of the basin.

MOLE RATIO OF BICARBONATTE TO SULFATE

The regional distribution shows a trend in the mole ratio of bicarbonate to sulfate opposite to that of the mole ratio of magnesium to calcium (fig. 32). There are very few samples from recharge areas, but the trend near the Big Snowy Mountains indicates a decrease from mole ratios greater than 1 to less than 0.4 downgradient. Throughout a large part of the area, this mole ratio varies little. The ratio ranges from 0.1 in the more dilute samples to more than 10 in the brines of concentrations greater than 300,000 mg/L dissolved solids. This indicates the loss of sulfate, while bicarbonate concentrations generally remain within the range of 100–1,000 mg/L.

SUMMARY OF MOST PLAUSIBLE MECHANISMS

Dissolution of evaporite salts has been suggested as a cause of the large change in chemical character of the water in the Silurian-Devonian confining unit. As dissolution of evaporites causes the concentration of dissolved solids to increase, calcium becomes a

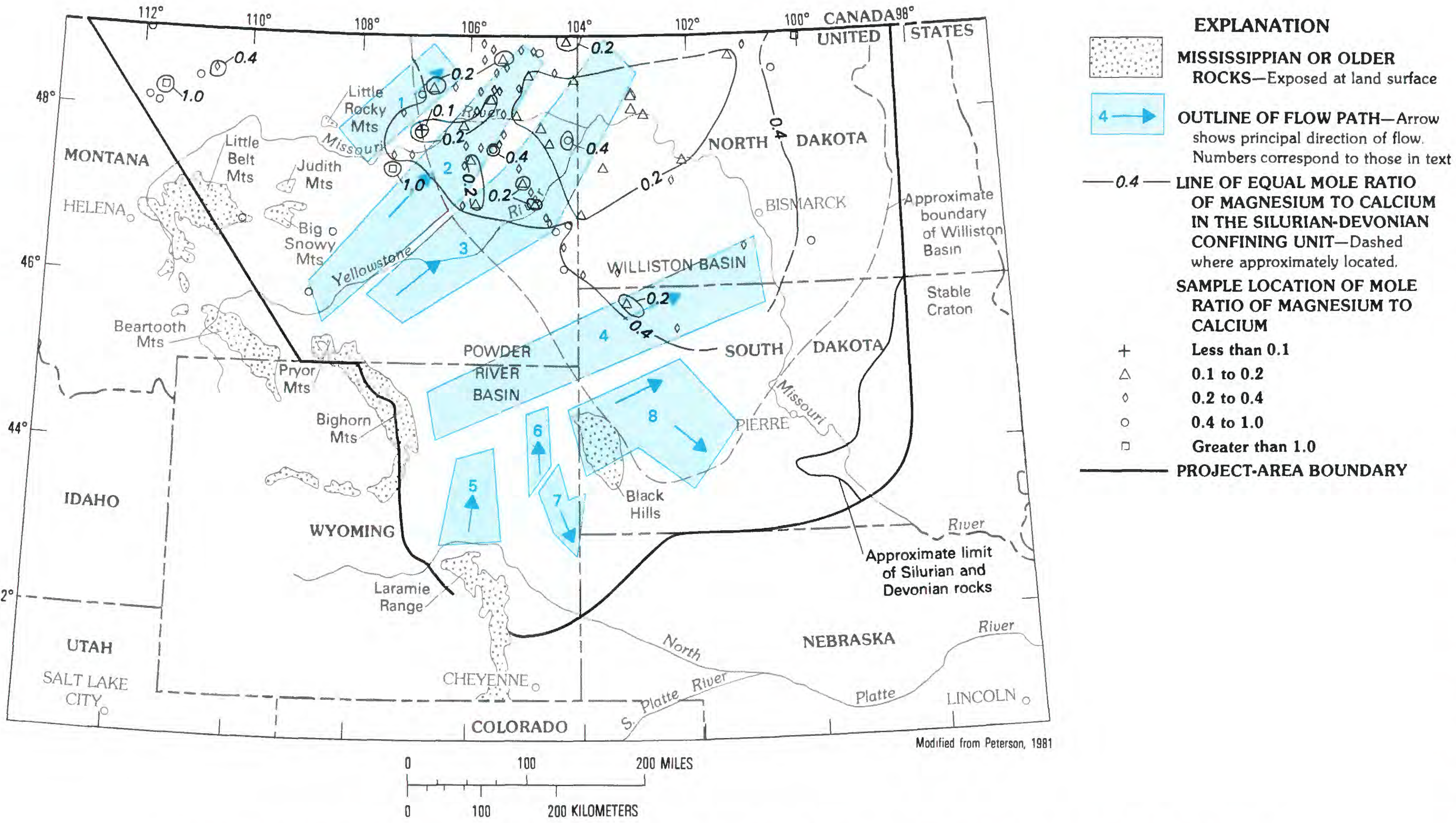


FIGURE 31.—Mole ratio of magnesium to calcium in water from the Silurian-Devonian confining unit in the northern Great Plains.

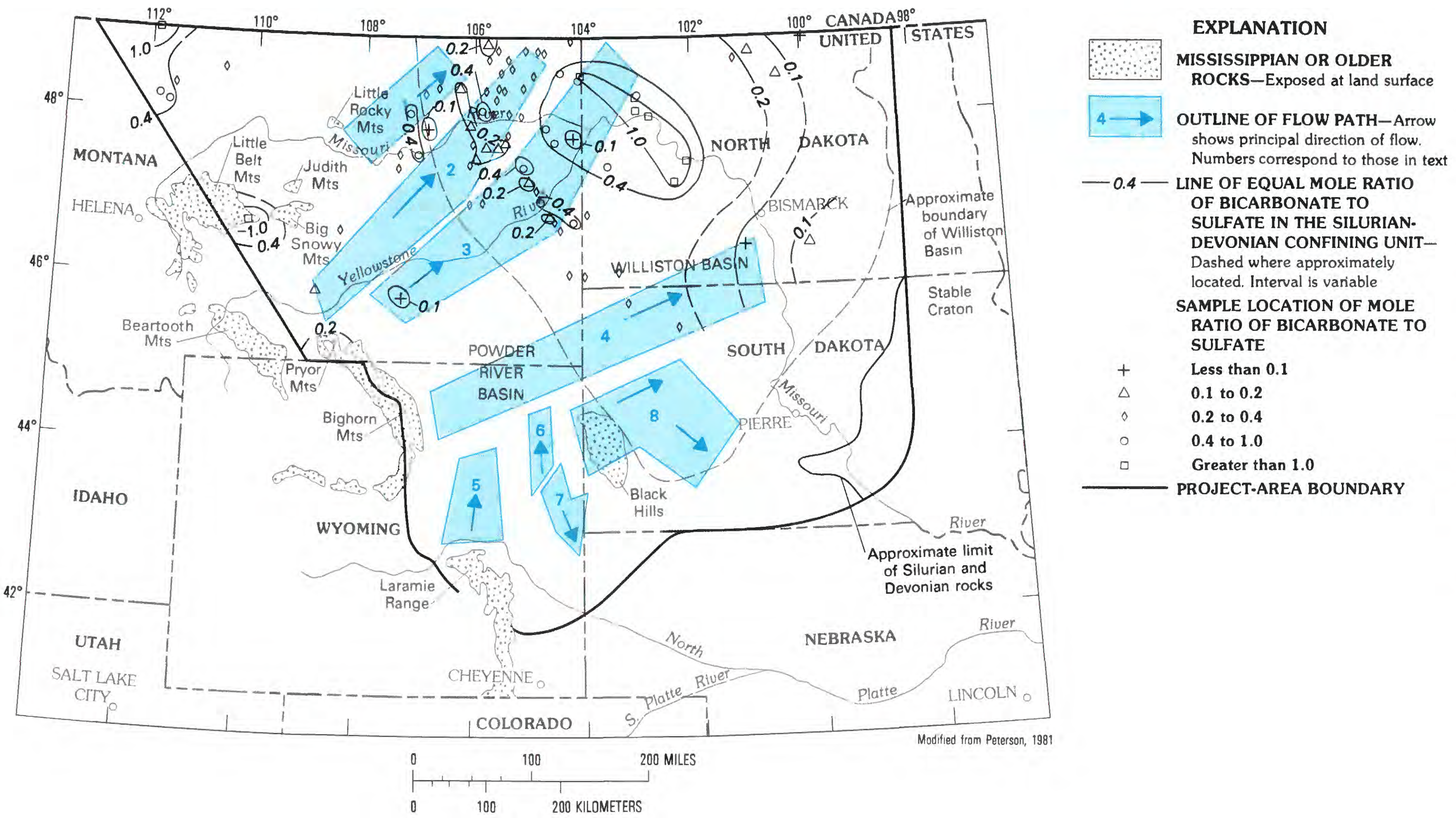


FIGURE 32.—Mole ratio of bicarbonate to sulfate in water from the Silurian-Devonian confining unit in the northern Great Plains.

substantial component of the brine. Although other chemical reactions affect the chemical character of the water, for the most part, these reactions are overshadowed by the changes because of salt dissolution.

The dissolution of halite is indicated by the sodium-to-chloride plot (fig. 30). Throughout the range of chloride concentration, sodium concentration indicates three different trends. In water from the sodium chloride + sodium sulfate + calcium sulfate facies (facies 1), the sodium-to-chloride mole ratio is much greater than 1. As evaporites are dissolved, the sodium-to-chloride component becomes dominant, and the majority of the sodium concentration is balanced by chloride—that is, the mole ratio becomes essentially 1. This trend continues as more halite is dissolved, and the dissolved-solids concentration becomes larger in the sodium chloride + calcium sulfate facies (facies 2). However, water from the sodium chloride facies (facies 3) has a slightly smaller sodium-to-chloride mole ratio. This smaller mole ratio results from the alkali-earth chloride components of the dissolving salt. When the water becomes saturated with respect to halite, the sodium-to-chloride ratio decreases from the line of equal milliequivalents. Sodium is removed from the solution, preferentially to chloride, because, as precipitation begins, the mole ratio of sodium to chloride is less than 1. When sodium is removed, the calcium chloride component of the water becomes substantial, which produces the sodium chloride + calcium chloride facies (facies 4).

The milliequivalent ratio of calcium to chloride follows a different trend from that of sodium to chloride (fig. 33*A*). The trend in this plot has four parts. From the most dilute samples to a chloride concentration of about 10,000 mg/L, the calcium-to-chloride milliequivalent ratio constantly decreases, which indicates that calcium is continually removed from solution by carbonate mineral precipitation. Calcium concentrations remain less than about 1,000 mg/L for this range. When the evaporite salts dissolve in samples from facies 4, the calcium-to-chloride milliequivalent ratio remains constant at about 1 to 2, the milliequivalent ratio of calcium chloride salt (fig. 33*A*). A rapid change in the milliequivalent ratio is apparent in water with chloride concentrations greater than 100,000 mg/L in facies 4. When chloride is removed from solution by halite precipitation, there is a large increase in the calcium-to-chloride ratio. This same pattern occurs with the magnesium-to-chloride milliequivalent ratios.

The bicarbonate-to-chloride milliequivalent ratio decreases throughout the entire concentration range, except for a few samples in the sodium chloride + calcium chloride facies (4) that have a larger milliequivalent ratio. In fact, the concentration of bicarbonate remains from 60 to 800 mg/L for the entire range of chloride concentration (fig. 33*B*). This pattern of variation differs from the pattern of variation of sulfate with chloride (fig. 33*C*). Initially, sulfate increases in samples with chloride concentrations that range from 10 to 400 mg/L; this increase results from the dissolution of gypsum or anhydrite. Then, in water from facies 2 and facies 3, the sulfate concentration remains within a definite range, similar to bicarbonate. This stability indicates an equilibrium control on sulfate that most likely involves gypsum or anhydrite precipitation. Because of this equilibrium control, the sulfate-to-chloride milliequivalent ratio decreases as sulfate is removed from solution. The relative increase in the bicarbonate-to-chloride milliequivalent ratio and the decrease in the sulfate-to-chloride milliequivalent ratio of water from facies 4 also could be affected by sulfate reduction that occurs at the same time as halite precipitation. However, for the most part, there does not seem to be an inverse relation between bicarbonate and sulfate.

A summary of the most plausible mechanisms that could cause the chemical trends in the Silurian-Devonian confining unit is presented in table 6. Dissolution of evaporite salts accounts for the greatest mass transfer, but other dissolution and precipitation reactions also are evident. The chemical reactions that are observed in the Silurian-Devonian confining unit are a good example of the effects of various chemical equilibria in deep basin brines.

MADISON AQUIFER

Water samples from the Madison aquifer are principally from the Madison, Lodgepole, and Mission Canyon Limestones of the Madison Group. Many samples have been obtained along geologic features where there has been oil exploration, but the overall areal representation of water samples from the Madison aquifer is good, in fact, better than for other hydrogeologic units because the good quality of the water in the Madison aquifer relative to the other formations has resulted in extensive development.

REGIONAL GEOCHEMICAL TRENDS

Water in the Madison aquifer undergoes large changes in chemical character throughout the northern Great Plains region. Changes in the vicinity of the Williston basin mostly are brought about by dissolution of evaporites. Other water-rock interactions

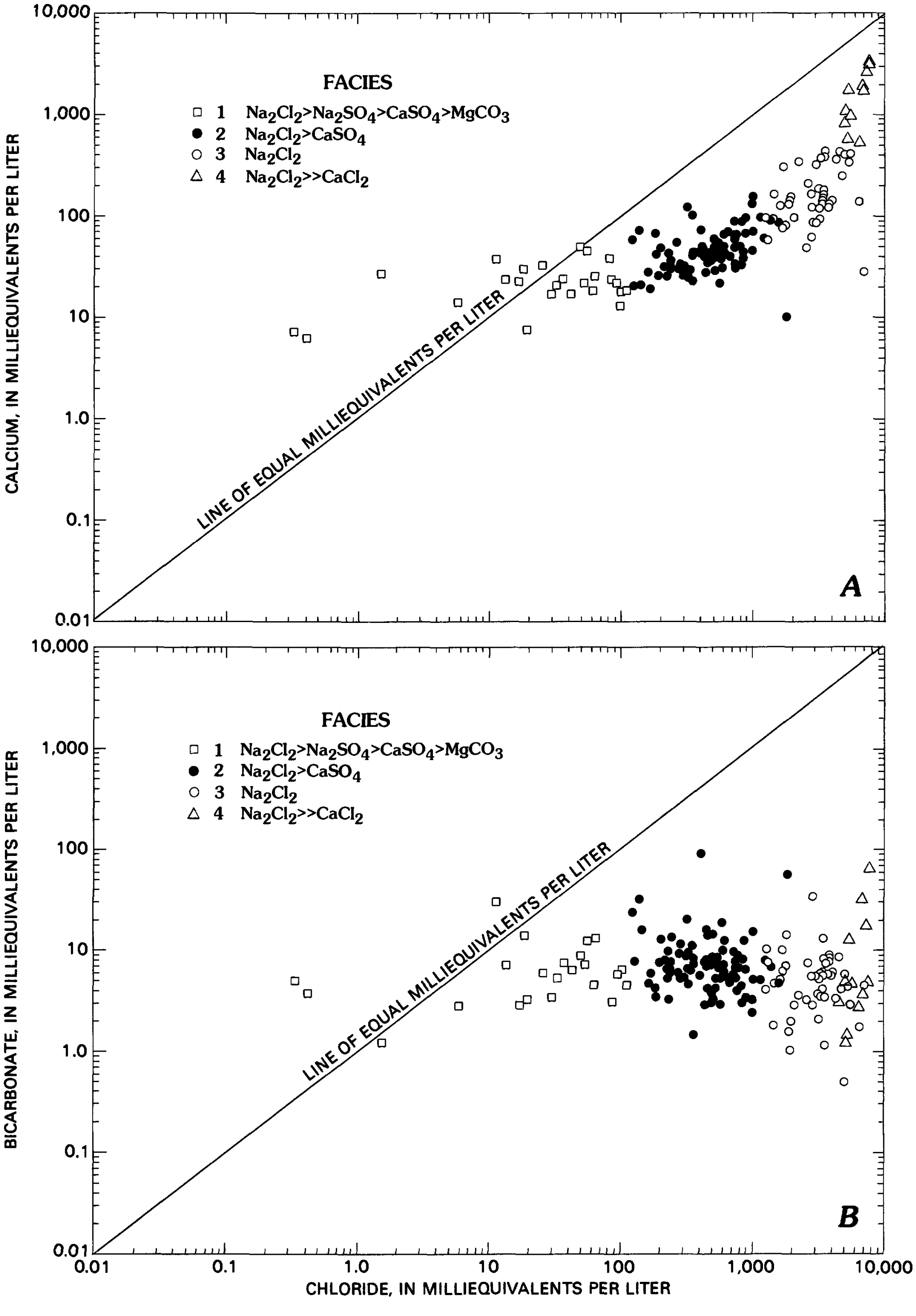
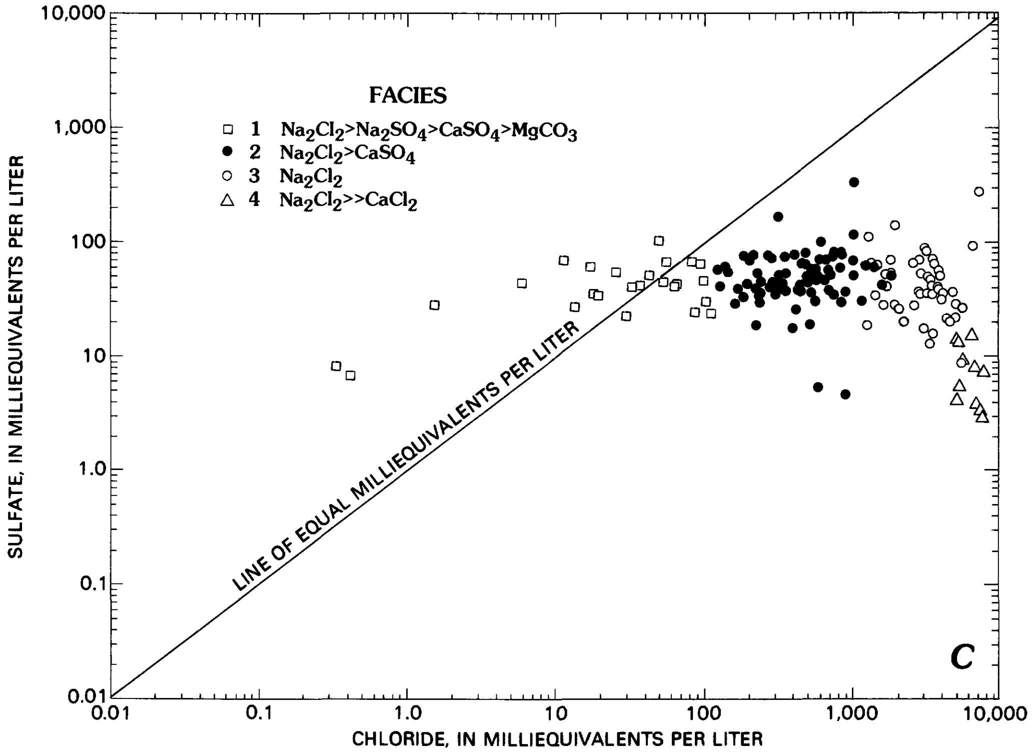


Figure 33 (above and facing page).—Variation of (*A*) calcium, (*B*) bicarbonate, and (*C*) sulfate with chloride in the Silurian-Devonian confining unit.



are indicated by the regional geochemical trends away from the Williston basin.

DISSOLVED SOLIDS AND pH

Regional trends in dissolved-solids concentration of water from the Madison aquifer (fig. 34; table 7) mostly indicate carbonate equilibrium reactions near highland areas and the dissolution of halite, leakage, or diffusion of deep basin brines from adjacent units. The concentration of dissolved solids increases by a factor of almost 10,000 between highland areas and the Williston basin. Near highland recharge areas, the concentration of dissolved solids is relatively small—less than 500 mg/L near the Black Hills and the Beartooth and Big Snowy Mountains. Slightly larger recharge concentrations of about 1,000 mg/L are present near the Laramie Range and the Bighorn Mountains in Wyoming. Away from each of these recharge areas, the concentration of dissolved solids increases; concentrations of as much as 10,000 mg/L occur near the Central Montana trough and as much as 5,000 mg/L occur away from the Black Hills. In central South Dakota, dissolved-solids concentrations

TABLE 6.—*Summary of plausible mechanisms controlling chemical composition of water from the Silurian-Devonian confining unit*

Mechanism	Evidence
Dissolution of gypsum and halite.	Large increase in dissolved solids, mole ratio of sodium to to chloride remains about 1. Decrease in ratio of bicarbonate to sulfate at concentrations of less than 1,000 mg/L dissolved solids.
Precipitation of gypsum.	At larger concentrations, the bicarbonate-to-sulfate ratio increases and is relatively large. Concentration of sulfate decreases.
Precipitation of halite	At dissolved-solids concentrations greater than 330,000 mg/L, sodium concentrations decrease as alkali-earth concentration increases.

less than 2,500 mg/L are present, which indicates that there may be a source of recharge in that area. Near the Williston basin, the dissolved-solids concentration exceeds 100,000 mg/L; the largest concentration is greater than 400,000 mg/L.

Large variations in dissolved-solids concentration can occur in a short distance. Along the Cedar Creek anticline in eastern Montana, dissolved-solids concentrations range from less than 10,000 to about 100,000 mg/L, possibly indicating areas where salt is being extensively dissolved. Variations also occur among the three principal geologic units at given locations but, generally, all three units show the same regional trend.

Changes along regional flow paths (fig. 34; table 8) indicate more detailed variations. In general, each flow path contains some samples that have concentrations of dissolved solids typical of recharge water or that are only slightly more concentrated. Flow paths 2 and 4 indicate increases from less than 200 to a range from 10,000 to 20,000 mg/L. Only flow path 3, which extends into the Williston basin, indicates the large increase of dissolved-solids concentration to greater than 100,000 mg/L. The large increase in dissolved-solids concentration may represent a lithologic change within the aquifer.

Values of pH indicate a consistent regional trend (fig. 35). Near recharge areas, pH is greater than 7.5. There is a large area of transition between recharge areas and the basins where pH consistently ranges from 7.0 to 7.5; this consistency may represent an equilibrium between the carbonate minerals, gypsum, and clay minerals in the formation. In the Williston basin, pH decreases even lower, approaching values near 6.5. The decrease of pH as solute concentrations increase may result from exchange of cations for hydrogen ions in clay minerals. However, the abundant carbonate minerals in the Madison aquifer would lessen this effect, only enabling a partial decrease in the pH.

Along individual flow paths, only rarely does pH change systematically (table 8). All the flow paths have a median pH that ranges from 7.0 to 7.6. Flow paths 2 through 6 include samples of recharge water with pH values greater than 7.5. According to Drever (1982), a pH greater than 7.5 is common in a water that is affected by weathering carbonate minerals.

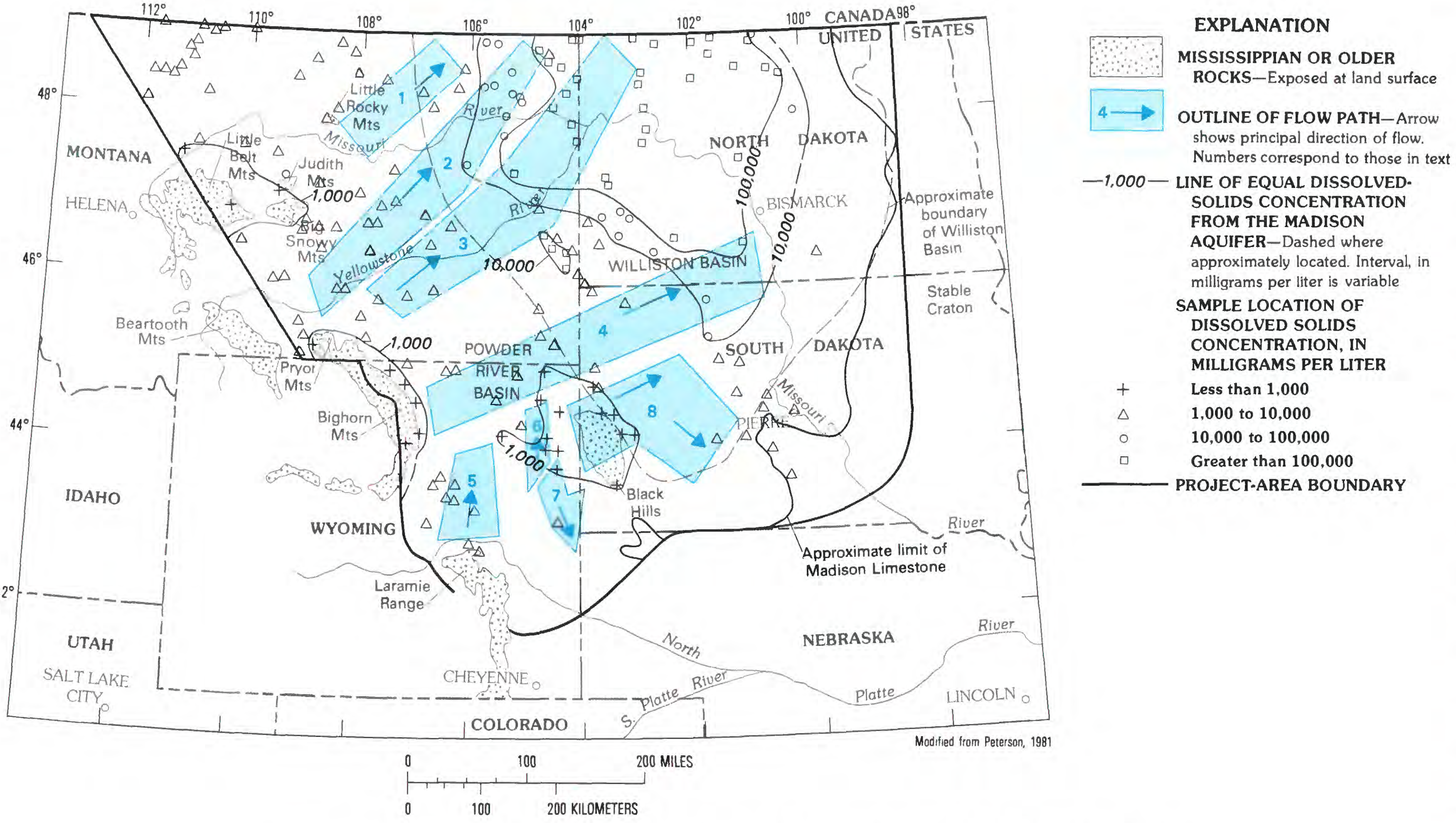
TABLE 7.—*Regional summary of chemical composition of water from the Madison aquifer*

[Concentrations in milligrams per liter, except pH, which is in pH units, and mole ratios, which are dimensionless]

Constituent[1]	Number of samples[2]	Minimum	25th percentile	50th percentile	75th percentile	Maximum
Dissolved solids	508	65.0	862	2,960	9,120	403,000
pH	400	6.5	7.0	7.3	7.7	9.0
Calcium	515	2.0	93	340	710	41,000
Magnesium	514	1.0	31	67	150	8,100
Sodium	497	.40	29	490	2,400	150,000
Potassium	218	.50	1.6	4.4	34	4,200
Chloride	508	.10	16	480	3,000	240,000
Sulfate	513	2.1	200	1,100	1,900	9,100
Bicarbonate	510	24	193	267	366	4,870
Mole ratio of magnesium to calcium.	514	<.01	.27	.40	.59	11
Mole ratio of bicarbonate to sulfate.	508	.02	.21	.41	2.1	1,400

[1] A constituent can be the chemical elements dissolved in water, such as calcium; a property of water, such as pH; an indicator of overall water quality, such as dissolved solids; or a mole ratio of constituents.

[2] Used to calculate percentiles.



Modified from Peterson, 1981

FIGURE 34.—Concentration of dissolved solids in water from the Madison aquifer in the northern Great Plains.

TABLE 8.—*Chemical composition of water from the Madison aquifer from along selected flow paths*

[Concentrations in milligrams per liter, except pH, which is in pH units, and mole ratios, which are dimensionless]

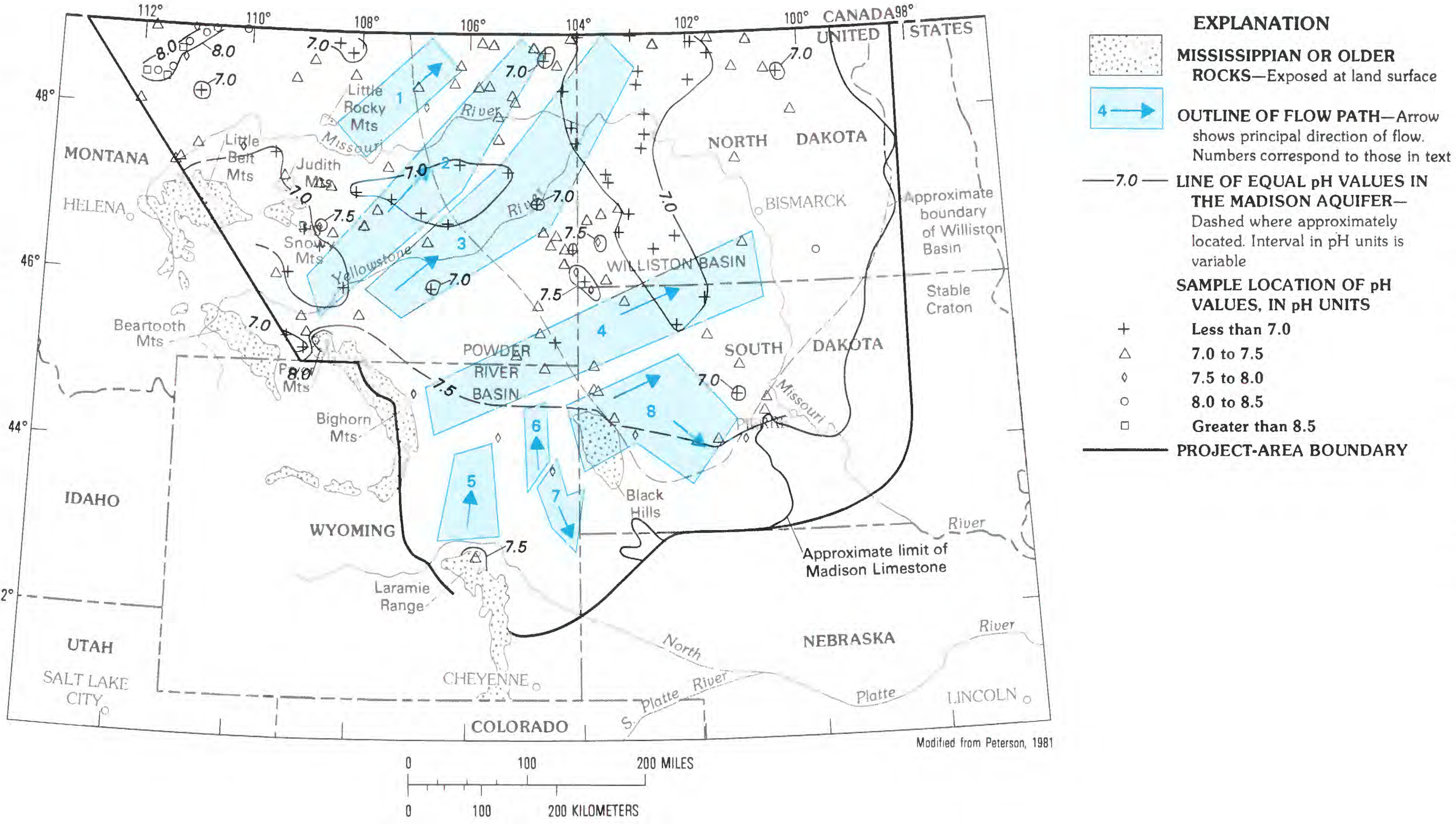
Constituent[1]	Flow path (fig. 18)	Number of samples[2]	Minimum	25th percentile	50th percentile	75th percentile	Maximum
Dissolved solids.	1	2	3,000	3,000	3,490	3,990	3,990
	2	30	2,490	5,660	34,900	67,500	163,000
	3	13	1,320	1,450	1,580	77,100	339,000
	4	15	513	1,010	2,630	5,430	234,000
	5	11	1,320	2,260	2,920	3,730	7,100
	6	14	278	426	468	665	834
	7	3	565	565	6,930	6,950	6,950
	8	3	222	222	1,100	1,120	1,120
pH	1	2	7.0	7.0	7.5	7.1	7.1
	2	26	6.5	6.8	7.0	7.5	8.0
	3	12	6.5	6.6	6.7	6.9	7.3
	4	14	6.8	6.9	7.1	7.5	7.9
	5	4	7.1	7.1	7.3	7.7	7.8
	6	7	6.8	7.0	7.6	7.7	7.8
	7	2	7.0	7.0	7.5	7.9	7.9
	8	3	7.1	7.1	7.4	7.6	7.6
Calcium	1	2	32	32	260	480	480
	2	30	220	440	1,100	1,800	6,200
	3	13	210	220	320	2,800	14,000
	4	18	98	180	280	880	6,800
	5	11	2.0	260	290	320	460
	6	14	56	72	93	120	180
	7	3	110	110	300	340	340
	8	3	46	46	230	270	270
Magnesium	1	2	16	16	78	140	140
	2	30	34	78	140	340	1,300
	3	13	28	31	57	340	1,300
	4	18	16	42	57	130	1,900
	5	11	13	36	44	56	67
	6	14	27	28	34	40	46
	7	3	35	35	60	61	61
	8	3	13	13	25	59	59
Sodium	1	2	630	630	800	960	960
	2	29	87	1,700	13,000	25,000	60,000
	3	13	48	94	170	26,000	120,000
	4	16	8.2	39	450	2,700	82,000
	5	11	100	380	560	750	2,400
	6	13	.90	2.9	9.0	19	20
	7	3	33	33	2,100	2,200	2,200
	8	3	2.4	2.4	18	23	23
Potassium	1	0	-	-	-	-	-
	2	5	38	67	99	140	150
	3	8	22	27	58	99	1,800
	4	6	3.4	6.8	8.1	18	35
	5	9	9	21	41	78	180
	6	11	.80	1.5	1.9	2.4	4.2
	7	1	6.1	6.1	6.1	6.1	6.1
	8	3	1.8	1.8	4.5	4.5	4.5

TABLE 8.—*Chemical composition of water from the Madison aquifer from along selected flow paths*—Continued

Constituent[1]	Flow path (fig. 18)	Number of samples[2]	Minimum	25th percentile	50th percentile	75th percentile	Maximum
Chloride	1	2	130	130	440	750	750
	2	30	40	1,700	19,000	38,000	97,000
	3	13	21	65	100	44,000	210,000
	4	18	7.0	55	64	980	140,000
	5	11	430	470	700	1,200	3,100
	6	14	1.2	1.5	1.7	4.1	11
	7	3	120	120	2,900	2,900	2,900
	8	3	1.5	1.5	21	27	27
Sulfate	1	2	1,700	1,700	1,800	1,900	1,900
	2	30	1,100	1,500	2,000	2,800	9,000
	3	13	620	740	810	1,100	2,800
	4	18	230	510	1,700	2,400	9,000
	5	11	310	850	910	970	1,200
	6	14	33	110	170	290	460
	7	3	120	120	1,300	1,400	1,400
	8	3	14	14	660	670	670
Bicarbonate	1	2	157	157	262	367	367
	2	29	82	305	374	436	772
	3	13	72	131	149	299	512
	4	18	110	204	253	380	945
	5	11	104	110	133	230	1,270
	6	14	177	196	267	274	275
	7	3	234	234	383	465	465
	8	3	92	92	158	242	242
Mole ratio of magnesium to calcium.	1	2	.48	.48	.65	.82	.82
	2	30	.12	.24	.30	.38	1.2
	3	13	.16	.21	.23	.27	.33
	4	18	.18	.26	.35	.42	.64
	5	11	.13	.22	.30	.35	.82
	6	14	.37	.44	.60	.74	.82
	7	3	.29	.29	.33	.54	.54
	8	3	.08	.08	.42	.90	.90
Mole ratio of bicarbonate to sulfate.	1	2	.13	.13	.24	.34	.34
	2	29	.11	.15	.29	.38	.49
	3	13	.18	.24	.29	.36	.47
	4	18	.11	.16	.27	.66	1.4
	5	11	.17	.17	.23	1.2	6.5
	6	14	.61	1.2	2.5	3.4	13
	7	3	.45	.45	.58	3.2	3.2
	8	3	.22	.22	.38	27	27

[1] A constituent can be the chemical elements dissolved in water, such as calcium; a property of water, such as pH; an indicator of overall water quality, such as dissolved solids; or a mole ratio of constituents.

[2] Used to calculate percentiles.



EXPLANATION

MISSISSIPPIAN OR OLDER ROCKS—Exposed at land surface

4 → OUTLINE OF FLOW PATH—Arrow shows principal direction of flow. Numbers correspond to those in text

—7.0— LINE OF EQUAL pH VALUES IN THE MADISON AQUIFER—Dashed where approximately located. Interval in pH units is variable

SAMPLE LOCATION OF pH VALUES, IN pH UNITS

+ Less than 7.0

△ 7.0 to 7.5

◊ 7.5 to 8.0

○ 8.0 to 8.5

□ Greater than 8.5

— PROJECT-AREA BOUNDARY

FIGURE 35.—Values of pH in water from the Madison aquifer in the northern Great Plains.

HYDROCHEMICAL FACIES

Five major hydrochemical facies can be identified in the Madison aquifer. The simple-salt compositions of each are given here.

Facies number	Simple-salt component	Mole percent	Millimoles per liter of solution
1	$CaCO_3$	42.2	2.25
	$MgCO_3$	40.7	2.16
	$CaSO_4$	14.0	.74
2	$CaSO_4$	65.0	16.2
	$MgCO_3$	11.8	2.93
	$MgSO_4$	11.1	2.75
	Na_2Cl_2	6.1	1.51
3	Na_2Cl_2	35.2	24.7
	$CaSO_4$	30.8	21.6
	Na_2SO_4	23.9	16.8
	$MgCO_3$	7.3	5.1
4	Na_2Cl_2	74.8	233
	$CaSO_4$	16.0	49.8
	Na_2SO_4	5.8	18.0
5	Na_2Cl_2	85.9	5,020
	$CaCl_2$	10.4	579

These facies each occur in water that has progressively larger concentrations of dissolved solids. The range of salt composition is from alkali-earth carbonates in facies 1 to sodium chloride and calcium chloride in facies 5. The progression of facies, which is observed along several flow paths, is discussed in detail below. The regional distribution of these facies is shown in figure 36. The regional trend of hydrochemical facies in the Madison aquifer is affected by the incongruent dissolution of dolomite driven by dissolution of gypsum, and, near the Cedar Creek anticline and Williston basin, by the dissolution of evaporite minerals.

Freeze and Cherry (1979) and Hanshaw and Back (1979) have described idealized changes of hydrochemical facies along a flow path. When a flow path begins near a recharge area in uplifted areas and continues toward deep basins, a progressive change generally occurs. Facies sequentially change from bicarbonate, to mixed sulfate + bicarbonate, then sulfate, then sulfate + chloride, and finally to chloride. The general trend of hydrochemical facies in the Madison aquifer is similar to the one presented by Freeze and Cherry. However, the change from one facies to another is rapid, often punctuated by changes in chemical character over small distances along a flow path. The increase in the concentrations of solutes is large because of the dissolution of existing evaporite minerals or upward leakage from the Cambrian-Ordovician aquifer through the Silurian-Devonian confining unit.

Each of the highland areas is surrounded by water of facies 1, which is basically a calcium carbonate and magnesium carbonate facies. The calcium sulfate component is small in facies 1 but increases considerably in water from facies 2. Facies 2 occurs away from recharge or highland areas. The next change in facies, from facies 2 to 3, mostly involves an increase in sodium chloride; however, the calcium sulfate and sodium sulfate components are important also. The quantity of sodium chloride in facies 3 represents almost 25 mmol/L. This quantity could come from dissolution of disseminated halite in the Madison aquifer. Because this facies occurs over a large area and does not occur only around the margin of the Williston basin, facies 3 probably is a result of dissolution and not of mixing with brine in the Williston basin.

Sodium chloride dominates facies 4, which mostly occurs around the edge of the Williston basin. This facies also occurs in the northwestern corner of the study area, but in that locality, it also has a sodium carbonate component, which indicates the possibility of sulfate reduction.

Just as in the two underlying hydrogeologic units, within Williston basin there is a sodium chloride and calcium chloride facies (5). In the Madison aquifer, this facies is associated with waters containing about 5,000 mmol/L of halite. The continuous sequence of brine facies from the Cambrian-Ordovician aquifer through the Madison aquifer in the Williston basin may indicate that leakage through the Silurian-Devonian confining unit affects the geochemical character of water in all three hydrogeologic units.

CONTROLS ON THE CHEMICAL CHARACTER OF THE WATER

Many chemical reactions are implicit in the discussion of solute-chloride trends. These reactions can be made explicit through mass-balance calculations that define mass transfer of mineral phases in the various reactions. Unique reactions cannot be determined because of the lack of mineralogic and isotopic data, but general reactions can be evaluated by using thermodynamic calculations.

The concentrations of each of the major solutes except bicarbonate increases with increasing dissolved-solids concentration. The large increases from less than 1,000 mg/L to greater than 100,000 mg/L could only be accomplished by the dissolution of evaporites within the Madison aquifer or by leakage of brines into the aquifer. Brines that

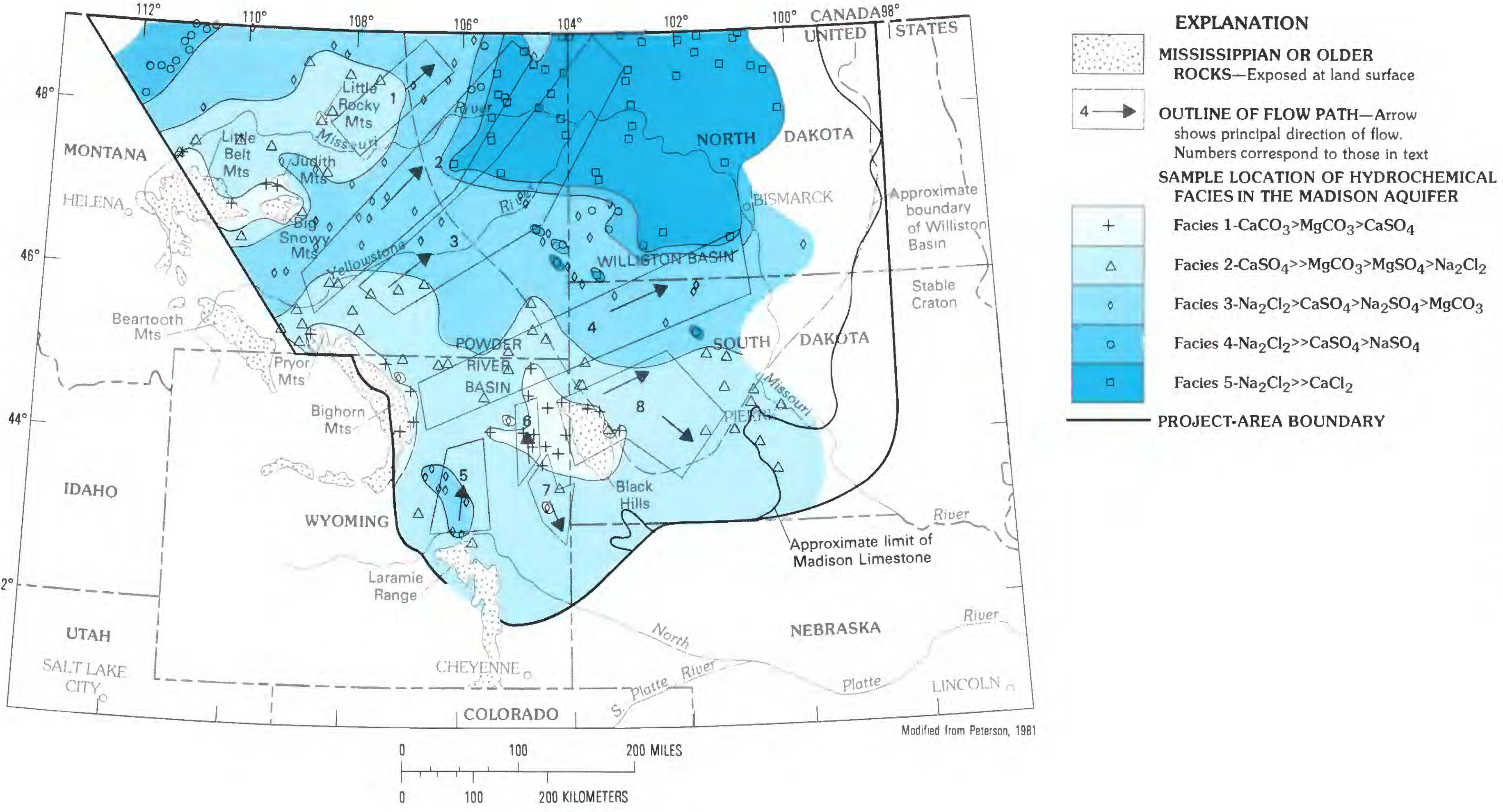


FIGURE 36.—Hydrochemical facies in water from the Madison aquifer in the northern Great Plains.

originate as pore fluids in salt beds may have migrated into the Madison aquifer. Such concentrated brines may have remained in place because of their high density. This mechanism of brine origin and emplacement has been suggested by Carpenter (1978) for brines in Mississippi.

The change from fresh recharge water to supersaturated brine could result from either salt dissolution or mixing of fresh waters with relict brines. Either process would cause the same trends in the solute-chloride plots.

MASS-BALANCE CALCULATION

The evolutionary pathways between hydrochemical facies were studied by using mass-balance calculations (Parkhurst and others, 1982). The sample with the median dissolved-solids concentration within each facies was used to represent the chemistry of that facies. The mass balances were calculated between these median analyses. The unknown chemical compositions of minerals in this complex system necessitate the use of pure end-member minerals in the calculations. Many of these chemical reactions were modeled in more detail by Busby and others (1991).

Facies 1.—The composition of recharge water was modeled as the reaction of carbonate minerals with carbon dioxide enriched water near the outcrop. Achieving mass balance required the addition of 1.700 mmol/L of carbon dioxide gas, 0.049 mmol/L of calcite, 1.152 mmol/L of dolomite, and minor quantities of gypsum and halite.

Facies 2.—The chemical reactions considered in the evolution from facies 1 to facies 2 include dissolution of dolomite, gypsum, and halite, and precipitation of calcite. Ion exchange also was considered but was determined to be minor compared to the dissolution reactions. The change from facies 1 to facies 2 can be described by dissolution of dolomite (1.563 mmol/L), gypsum (9.666 mmol/L), and halite (1.532 mmol/L), and the accompanying precipitation of calcite (4.637 mmol/L).

These reactants and products are consistent with solute-chloride changes. The calcium-to-chloride mole ratio, initially about 33, decreases to about 5. The change in magnesium-to-chloride mole ratio is similar. The halite input of 1.532 mmol/L can be attributed to disseminated halite in the Madison Limestone. Only the dissolution of gypsum is substantial at this stage of geochemical development.

Facies 3.—Dissolution reactions of gypsum and halite dominate the change to a sodium chloride + calcium sulfate facies. Gypsum continues to dissolve (8.850 mmol/L), but the evolution is dominated by the dissolution of halite (22.25 mmol/L). These main reactions are more evident in the change of chemical character of the water than the dedolomitization reaction, which is driven by gypsum dissolution.

Facies 4.—The chemical mass transfer that occurs to bring about the change to the sodium chloride facies is dominated by the dissolution of halite. Nearly 200 mmol/L of halite are dissolved into the water to obtain the measured concentrations of sodium and chloride. Dedolomitization seems to be of minor geochemical significance but might account for part of the change in the magnesium-to-calcium mole ratio. The change also requires dissolution of gypsum (15.9 mmol/L). Ion exchange of calcium or magnesium for sodium should be limited because of the large sodium concentrations in the ground water. A subset of this facies has a large bicarbonate component, which indicates sulfate reduction.

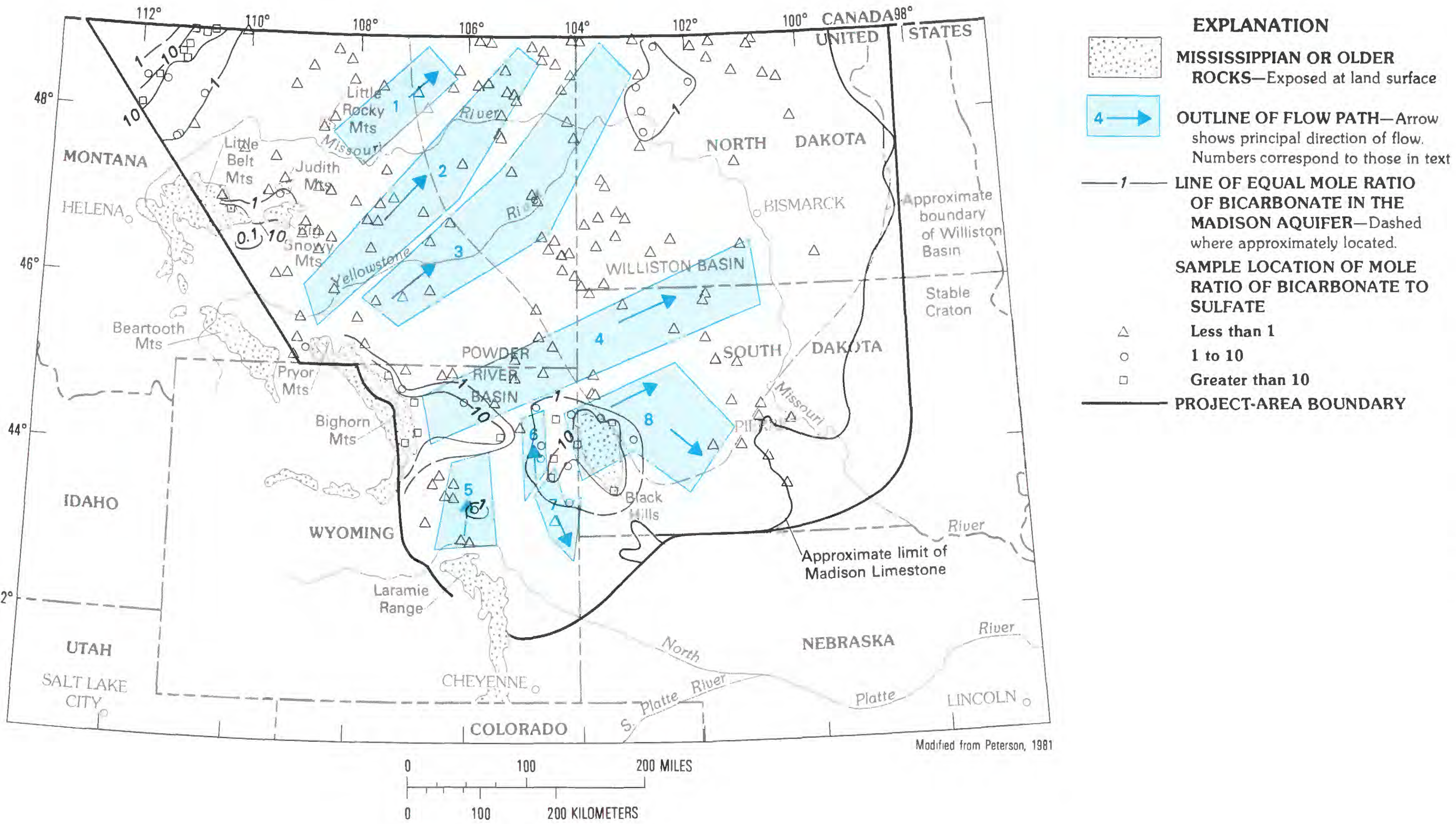
The bicarbonate-to-sulfate mole ratio of water in facies 4 ranges from 0.03 to 760. The facies occurs mostly on the edge of the Williston basin and north of the Sweetgrass arch (figs. 1, 36). The bicarbonate-to-sulfate ratios in these two areas differ (fig. 37). Around the Williston basin, the mole ratio generally ranges from 0.1 to 1, similar to values of the mole ratio throughout most of the study area. In northwestern Montana, near the Bearpaw uplift (fig. 1), the mole ratio is much larger, generally from 1 to 10. This larger ratio could be because of sulfate reduction, which causes a decrease of sulfate concentration and a concurrent increase in bicarbonate concentration.

Facies 5.—The quantity of chloride salts that are dissolved to produce the sodium chloride + calcium chloride facies is even greater than that which results in facies 4. About 4,200 mmol/L of sodium chloride are added to the ground water. However, a combined input of about 460 mmol/L calcium and magnesium chloride salts occurs. Too few analyses of potassium exist to adequately evaluate the input of potassium chloride salts, but they also are dissolved.

The large increase in calcium causes a loss of sulfate by gypsum precipitation (24 mmol/L). This loss of sulfate is supported by a small increase in the magnesium-to-calcium mole ratio that may result from the loss of some calcium to gypsum precipitation.

SATURATION INDEXES

Saturation indexes enable determination of thermodynamic constraints on proposed chemical reactions. Although the calculations are based on pure end-member minerals and likely do not indicate



Modified from Peterson, 1981

FIGURE 37.—Mole ratio of bicarbonate to sulfate in water from the Madison aquifer in the northern Great Plains.

mineralogic compositional variability within the Madison Limestone, they generally help to evaluate the proposed reactions. The saturation indexes for waters with dissolved-solids concentration greater than 100,000 mg/L were calculated by using a form of the Pitzer equation for activity coefficients.

The high quality data required for calculation of saturation indexes were not available for North Dakota. However, ground water in North Dakota is mostly of facies 5. Some generalization about this water can be made from the calculations. The regional trends of saturation indexes are shown for calcite (fig. 38), dolomite (fig. 39), and gypsum (fig. 40). The saturation indexes indicate undersaturation for these mineral phases in the recharge areas and oversaturation downgradient.

Although some recharge waters (those with the smallest dissolved-solids concentrations) are undersaturated with respect to calcite and dolomite, most samples are near saturation or are supersaturated. This level of saturation is maintained in all the brines that indicate large supersaturation.

Saturation with respect to gypsum increases away from highland areas (fig. 40). Recharge water is well below saturation with an index of about –2.0. Away from recharge areas, the Madison Limestone apparently contains more gypsum (or anhydrite). As the gypsum dissolves and sulfate concentrations increase, equilibrium is obtained. A typical saturation index of gypsum for water in facies 3 is −0.2, only slightly less than saturation. In facies 4, this index increases to 0.03, which is almost at equilibrium. The brine in facies 5 is supersaturated with respect to gypsum, having saturation indexes of about 0.2. All these calculations agree with the proposed reactions that produce the hydrochemical facies in the Madison aquifer.

Halite-saturation indexes encompass nine orders of magnitude. Halite saturation is obtained only in water in the Williston basin. As noted in the discussion of sodium-to-chloride mole ratios (fig. 41), there may be some halite precipitation from the ground water.

SODIUM AND CHLORIDE

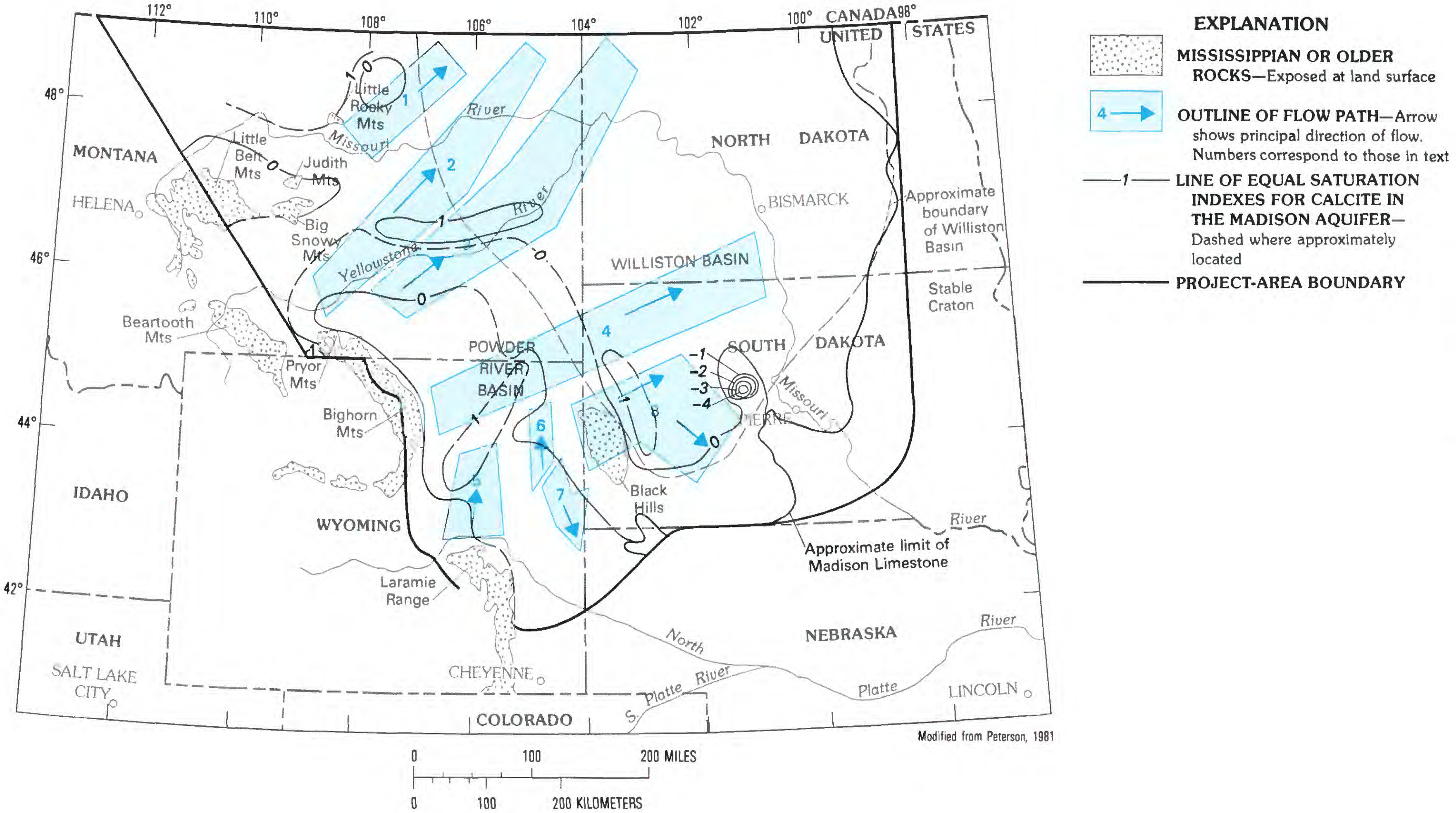
The concentrations of sodium and chloride, represented by the regional trend of chloride concentration (fig. 42), have the same trend as dissolved-solids concentration. The two elements vary in a similar manner, but concentrations of sodium exceed concentrations of chloride in recharge water (fig. 41). The dissolution of evaporite salts causes a change toward equal concentrations in terms of milliequivalents. Concentrations in the Williston basin generally show saturation with respect to halite. Those with the largest concentration of dissolved solids plot below the line of equal concentration (fig. 41), probably because of halite precipitation.

MOLE RATIO OF MAGNESIUM TO CALCIUM

The largest mole ratios of magnesium to calcium, generally greater than 0.5, are near the recharge areas in water that has a dissolved-solids concentration less than about 700 mg/L (fig. 43). Between recharge areas and the basins, the mole ratio generally ranges from 0.3 to 0.1. The decrease in the mole ratio may be caused by the dissolution of gypsum or anhydrite which adds calcium and not magnesium to the water or by the incorporation of magnesium into clay minerals. In the basins where dissolved-solids concentrations are greater than 10,000 mg/L, the mole ratio of about 0.25 is fairly constant. Samples with dissolved-solids concentrations greater than 100,000 mg/L generally have mole ratios less than 0.3. The smaller ratios could result from processes of dolomitization, incorporation of magnesium into clay minerals, or dissolution of calcium chloride salts. As gypsum precipitates, calcium and sulfate concentrations decrease.

Concentrations of calcium and magnesium in the various facies seem to have a common geochemical control; most likely this control is by carbonate equilibria. Three important trends are present in these solute chloride plots (figs. 44*A* and 44*B*). First, the milliequivalent ratios of calcium and magnesium to chloride decrease consistently from samples with the smallest concentrations up to samples with 5,300 mg/L chloride. Both solutes begin with solute-chloride milliequivalent ratios greater than 1, and the ratios decrease to much less than 1 during the geochemical evolution. Second, at larger chloride concentrations, calcium and magnesium concentrations increase proportionally at a 2:1 solute-chloride milliequivalent ratio, which indicates the input of alkali-earth chlorides; therefore, the bicarbonate concentration is no longer large enough to affect concentrations of the alkali-earth metals by calcite precipitation because alkali-earth chloride salts are being dissolved and are contributing an excess of calcium and magnesium to the ground water.

Third, a final trend in figures 44*A* and 44*B* is the increase in calcium and magnesium concentrations that is nearly independent of the chloride concentration—a trend consistent with halite precipitation. At this point, chloride is no longer maintained in solution, and the relative increase of



Modified from Peterson, 1981

FIGURE 38.—Saturation indexes with respect to calcite for water from the Madison aquifer in the northern Great Plains.

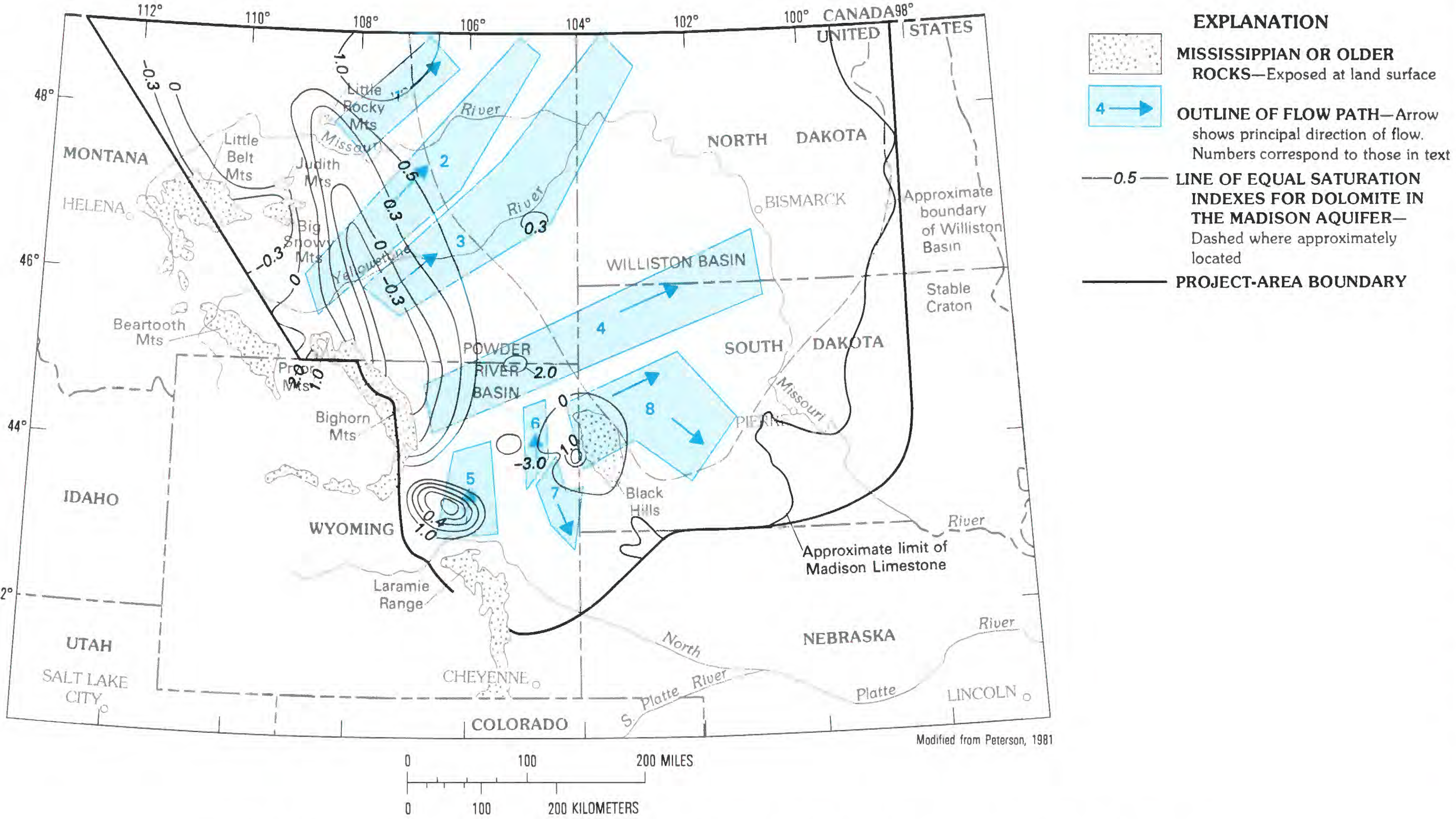


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FIGURE 39.—Saturation indexes with respect to dolomite for water from the Madison aquifer in the northern Great Plains.

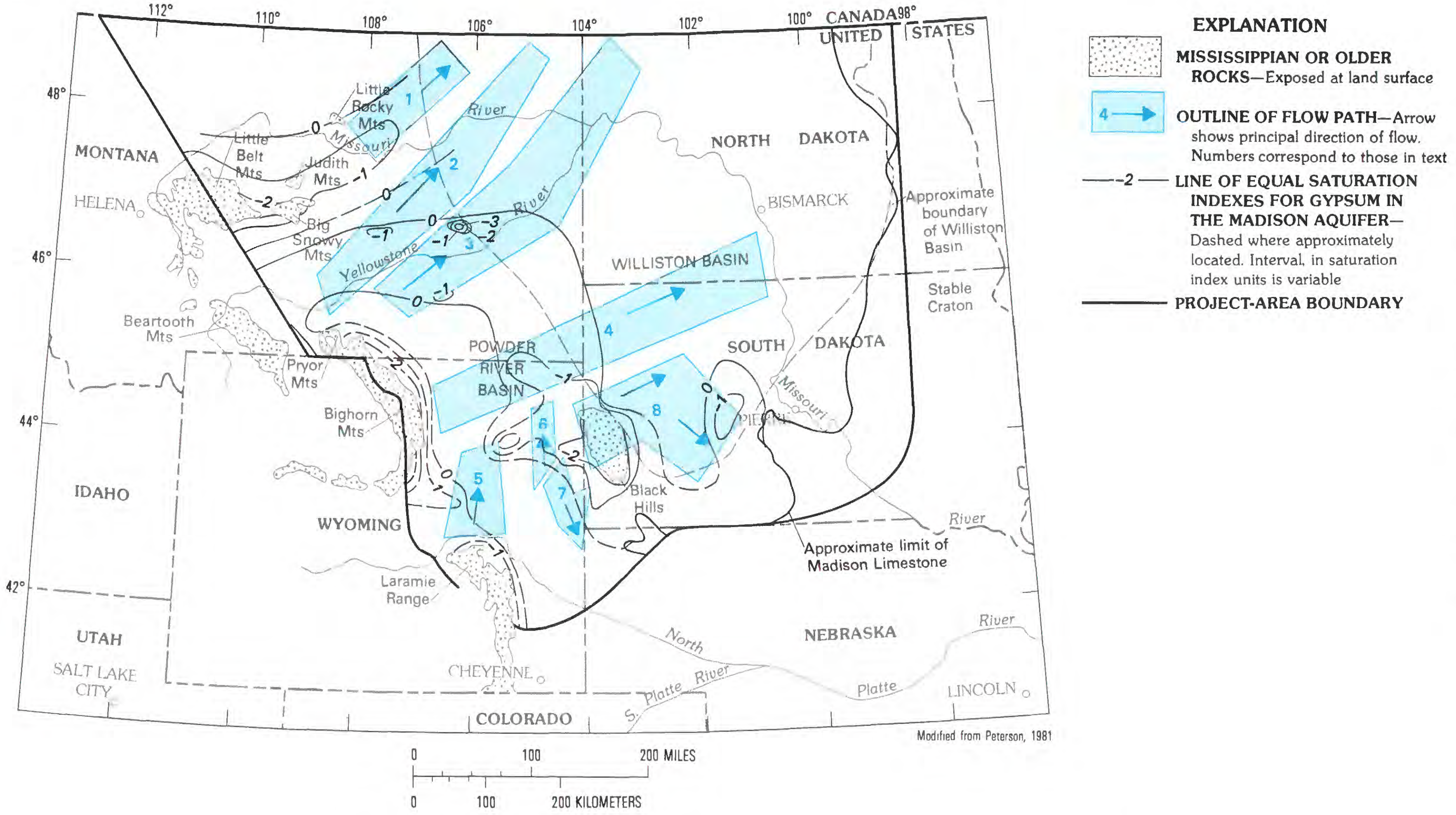

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FIGURE 40.—Saturation indexes with respect to gypsum for water from the Madison aquifer in the northern Great Plains.

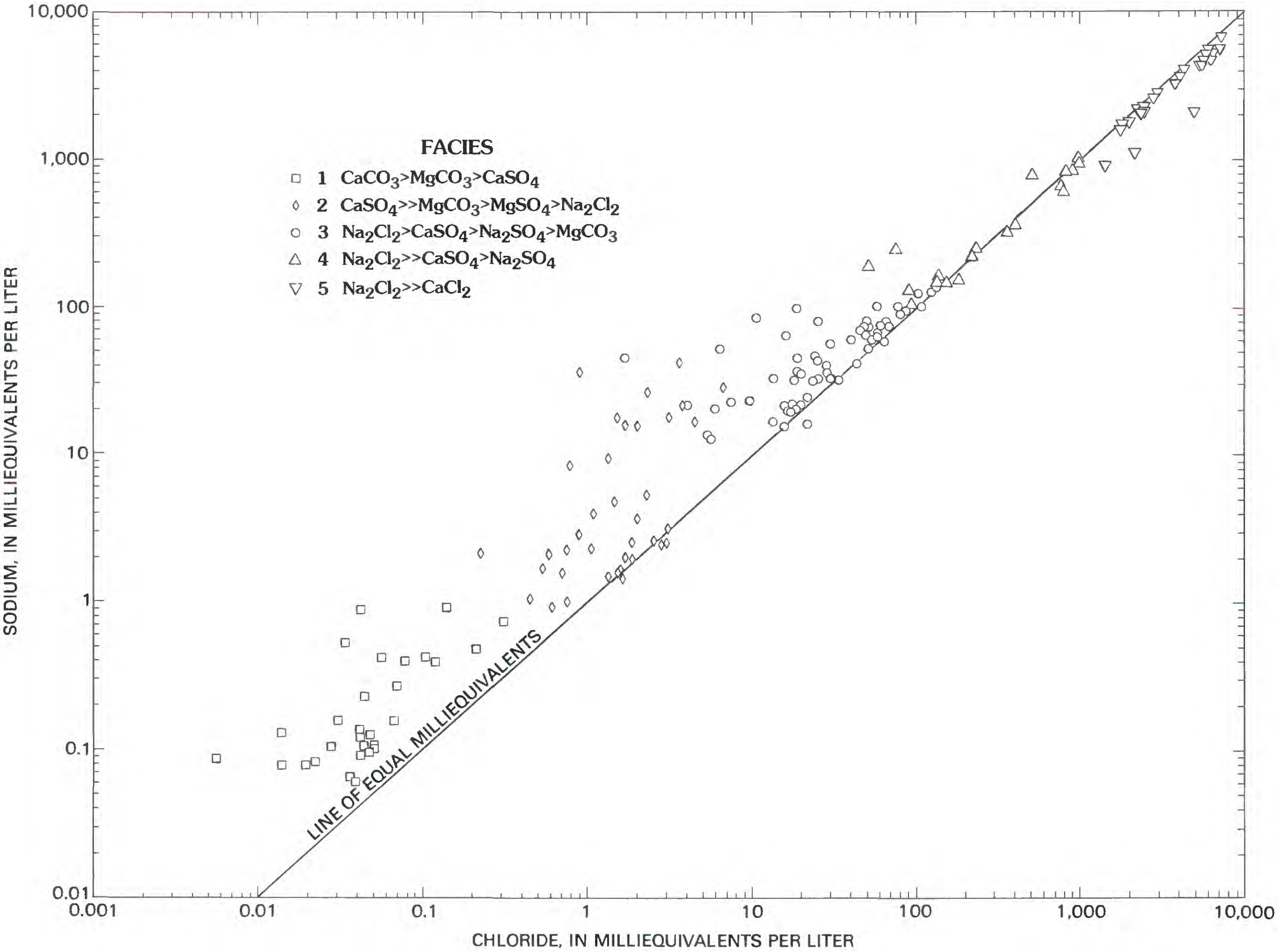


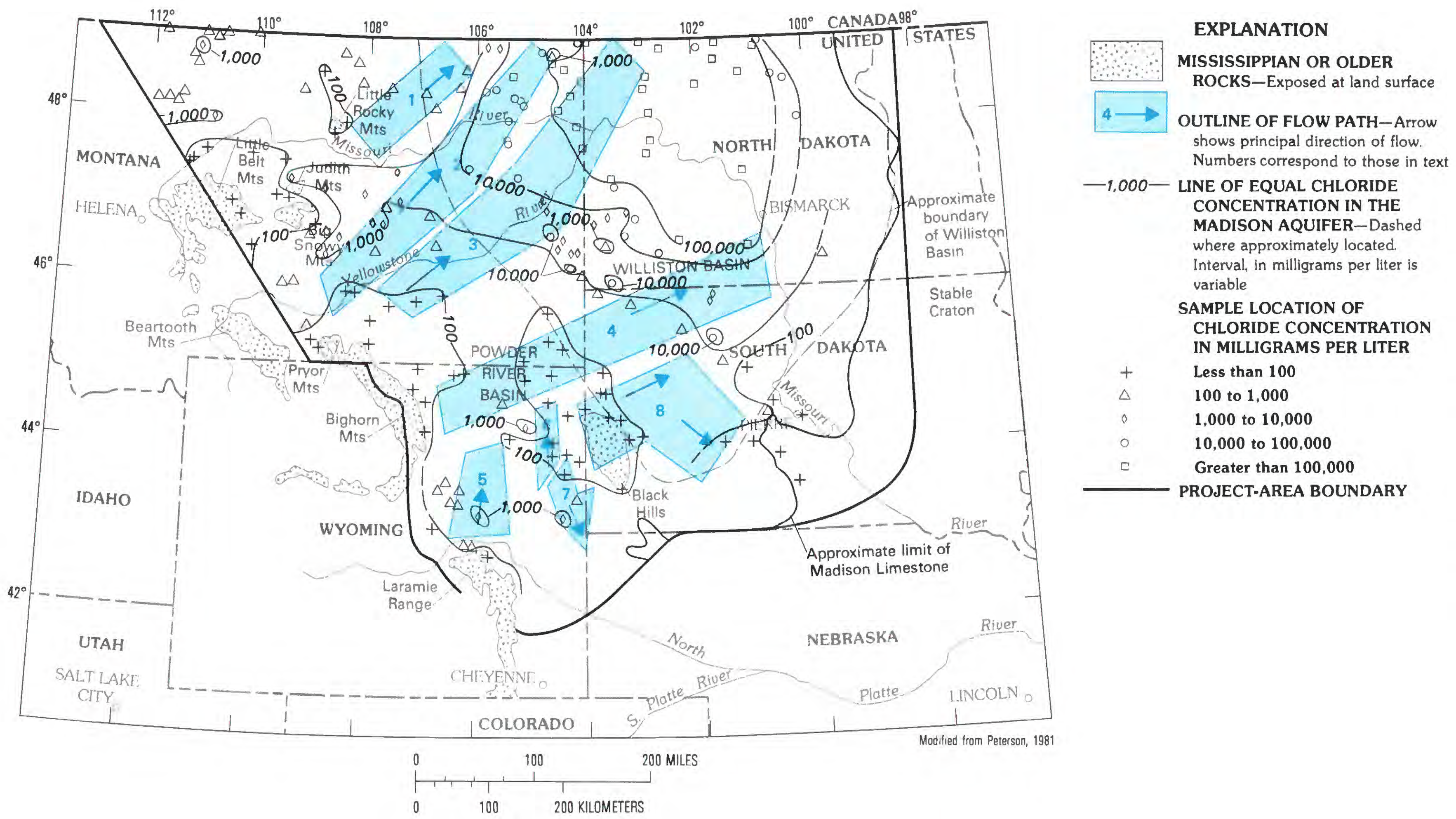
FIGURE 41.—Variation of sodium with chloride in water from the Madison aquifer in the northern Great Plains.

calcium gives a calcium chloride character to the brine.

The large variation in calcium concentrations is indicated by the data in tables 7 and 8. The concentration ranges from 2.0 to 41,000 mg/L. Each flow path indicates minimum concentrations typical of recharge water, which ranges from 2.0 to about 200 mg/L. Each flow path contains samples with larger concentrations, but the trends are not always progressively from smallest to largest concentration along the flow path. There are instances where the concentration increases and then remains fairly constant downgradient from that point. Flow path 3 contains the largest concentrations of calcium among the flow paths, as much as 14,000 mg/L.

The geochemistry of the Madison aquifer has been discussed by Busby and others (1983), who used samples from 77 carefully selected and properly sampled wells to study chemical reactions in the aquifer. Their work did not include the samples from North Dakota that are included in this study. The major conclusions of that work were as follows: (1) The most pervasive control on the ground-water chemistry is the incongruent dissolution of dolomite; (2) sulfate reduction is a significant process throughout most of the area; and (3) cation exchange seems to be a significant process only in the Central Montana trough.

A later study was based on 44 wells and used chemical modeling with stable isotope ratios for mass-balance calculations (Busby and others, 1991). The geochemistry was modeled as a closed system by adjusting model parameters until the mass transfer of carbon dioxide approached zero. The chemical mechanisms included in the modeling were dedolomitization, sulfate reduction, exchange of sodium in solution for calcium and magnesium on the clays (magnesium



Modified from Peterson, 1981

FIGURE 42.—Concentration of chloride in water from the Madison aquifer in the northern Great Plains.

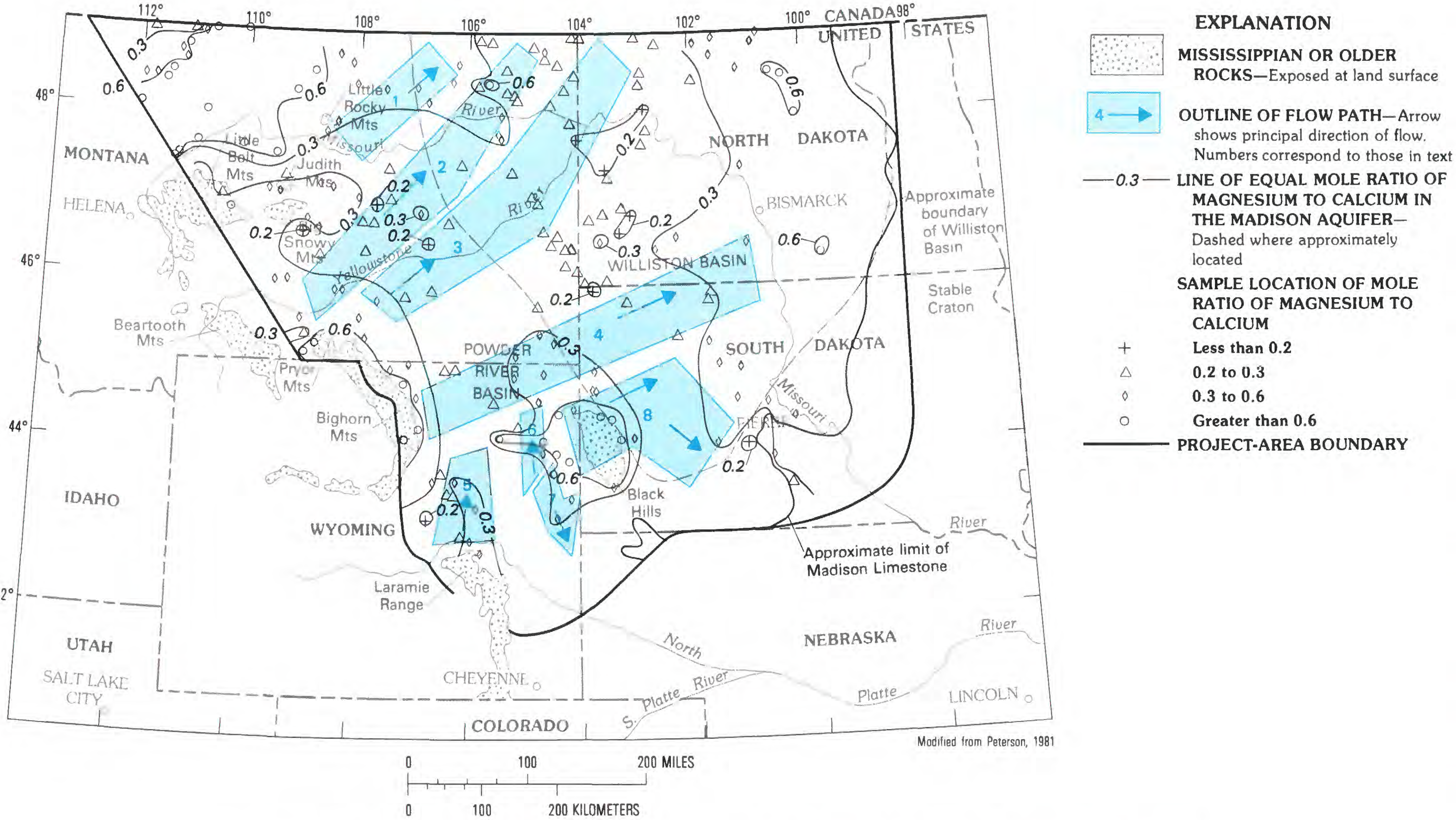


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FIGURE 43.—Mole ratio of magnesium to calcium in water from the Madison aquifer in the northern Great Plains.

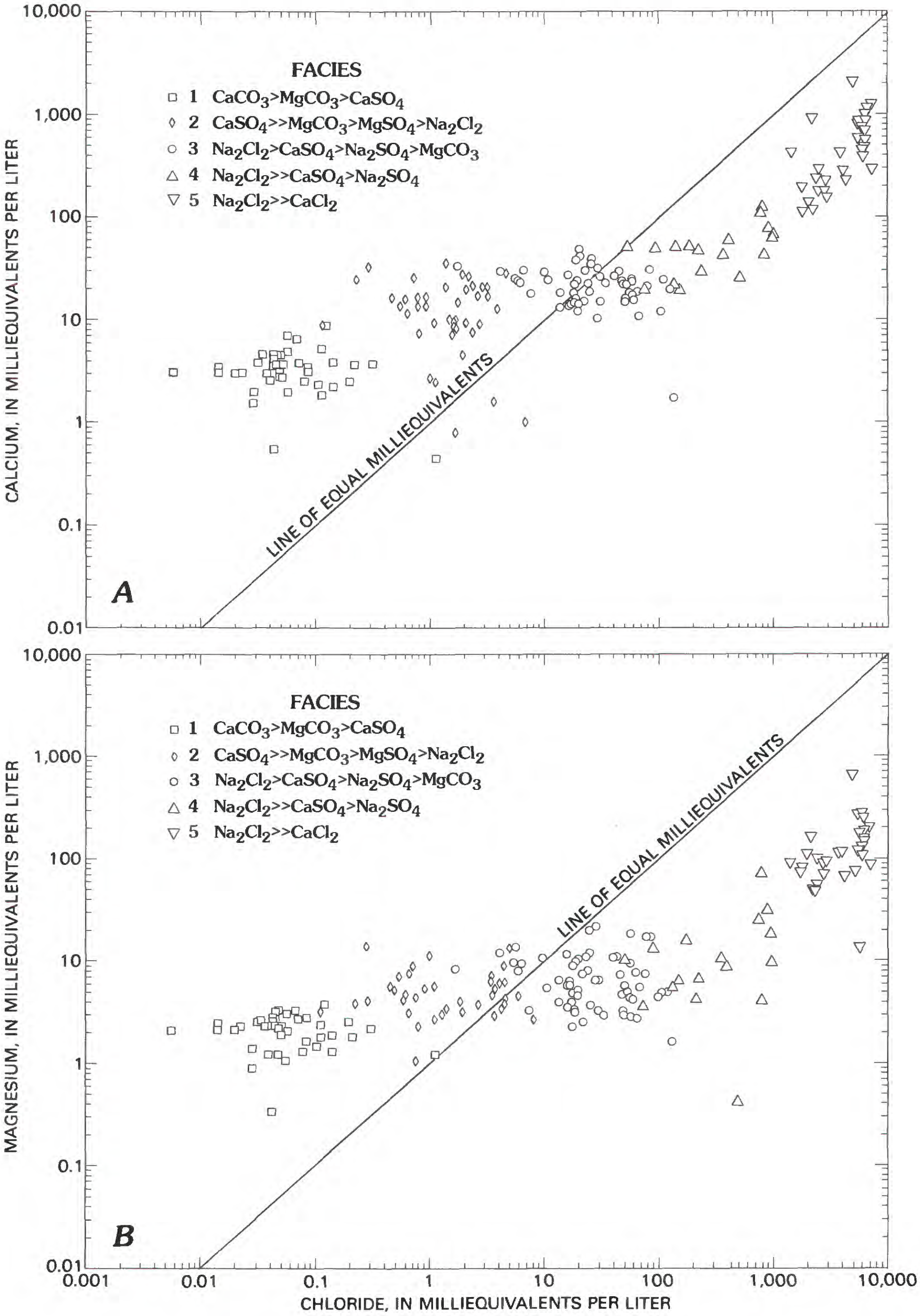


FIGURE 44.—Variation of (*A*) calcium and (*B*) magnesium with chloride in water from the Madison aquifer in the northern Great Plains.

ranged from 0 to 100 percent), methanogenesis, and addition of hydrogen sulfide from an external source. Values of δS^{34} of the solid gypsum were varied between 7.90 and 21.90 $^{o}/_{oo}$ along the various flow paths to force the closed-system condition (that is, no mass transfer of carbon dioxide gas) and to calculate the extent of sulfate reduction.

Dedolomitization was determined to be the predominant mechanism along all flow paths in the Madison aquifer near recharge areas, particularly near the Black Hills. Sulfate reduction was important along flow paths 2, 4, and 8 but not significant along flow paths 5, 6, and 7. Associated with the sulfate reduction were dissolution of minor quantities of organic matter, dissolution of ferric hydroxide, and precipitation of pyrite. Halite dissolution and ion exchange were determined to be important only along flow paths 2 and 3.

MOLE RATIO OF BICARBONATE TO SULFATE

A pattern similar to that of the magnesium-to-calcium mole ratio is observed for the bicarbonate-to-sulfate mole ratio (fig. 37). Soluble sulfate and chloride minerals have been removed in the uplifted areas over time, which leaves very little sulfate or chloride available to the recharge water; this loss of sulfate minerals over time results in a large bicarbonate-to-sulfate mole ratio in water from the recharge areas. The bicarbonate concentration apparently is controlled by carbonate equilibria and remains almost constant as dissolved-solids concentrations increase. As sulfate concentrations increase, the mole ratio decreases. This trend is reversed in the brines in North Dakota, where sulfate is lost from the water, causing an increase in the mole ratio.

Flow path 4 indicates a bicarbonate-to-sulfate mole ratio that generally is greater than 10 at the beginning of the flow path, followed by a decrease to a range of 0.12–0.5. The decrease in the bicarbonate-to-sulfate ratio indicates sulfate increases along the flow path, while bicarbonate typically remains constant. Near the Black Hills in flow paths 6 and 7, the mole ratios of bicarbonate to sulfate generally are larger than in the other flow paths; median values are 2.51 in flow path 6 and 0.58 in flow path 7.

The divergent trends of calcium and sulfate are shown in figures 44*A* and 45, respectively. This pattern is similar to solute patterns described by Eugster and Jones (1979, fig. 3) for the precipitation of a binary salt. At the chemical divide where precipitation begins, the calcium equivalents are greater than sulfate equivalents, and this results in the divergence in concentrations.

SUMMARY OF MOST PLAUSIBLE MECHANISMS

A summary of plausible mechanisms that could cause the observed water chemistry in the Madison aquifer is listed in table 9. Initially, the most common mechanisms for flow paths 2, 3, 4, 7, and 8 are dissolution of carbonate minerals from dedolomitization driven by gypsum dissolution, and then the dissolution of evaporite minerals away from highlands areas. These reactions cause increases of sodium, chloride, calcium, magnesium, and sulfate concentrations. Other mechanisms also are evident that affect the chemical character of the ground water. Precipitation of gypsum or anhydrite is important along flow paths 3, 4, and in the Williston basin. Chemical evidence of halite precipitation occurs in ground water that has a dissolved-solids concentration greater than 300,000 mg/L. Saturation with and subsequent precipitation of calcite begins early along every flow path.

PENNSYLVANIAN AQUIFER

Most of the water samples from the Pennsylvanian aquifer were from wells in western Montana and northeastern Wyoming that were completed in the Minnelusa and Tensleep Formations; a few samples were from North Dakota and South Dakota. Samples also were obtained from the Tyler Formation of the Amsden Group and the Amsden Formation where it is undivided.

REGIONAL GEOCHEMICAL TRENDS

Regional trends in water quality are discussed for the entire area by using maps to show distributions; then the trends for individual flow paths are used to indicate details of the trends. Summary statistics for the Pennsylvanian aquifer and the individual flow paths are listed in tables 10 and 11.

DISSOLVED SOLIDS AND pH

Dissolved-solids concentrations have a general pattern; small concentrations are near uplifted areas where rocks older than Pennsylvanian age are exposed, increasing concentrations are away from the uplifted areas, and the largest concentrations are in the basins (fig. 46; see fig. 1 for structure). The smallest concentrations (less than 100 mg/L) occur in the recharge areas of Montana. Concentrations increase downgradient, to the east, to more than 5,000 mg/L. In South Dakota, ground-water flow generally is eastward. Concentrations near the Black Hills are less than 1,000 mg/L and increase to the east, but not to the levels that occur in eastern Montana. Concentrations of dissolved solids greater than 300,000 mg/L are present in much of the Williston basin in North Dakota and Montana. Although there are few data to indicate the nature of the transition from smaller concentrations in Montana and Wyoming to the larger concentrations, most of the change is from increases in sodium, calcium, and chloride concentrations.

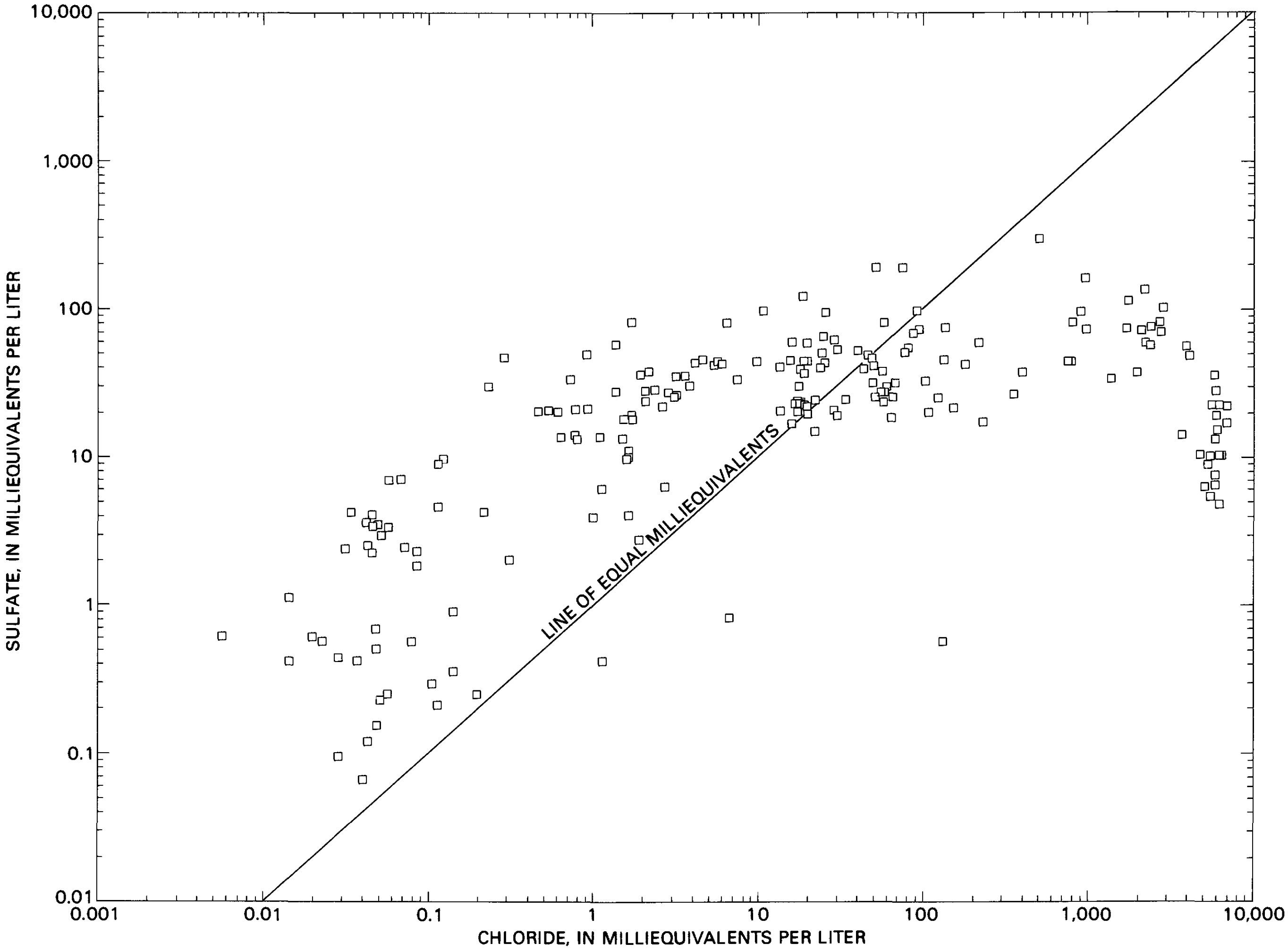


FIGURE 45.—Variation of sulfate with chloride in water from the Madison aquifer in the northern Great Plains.

Unlike the concentrations of dissolved solids in water from the underlying hydrogeologic units, concentrations in the Pennsylvanian aquifer in the Powder River basin exceed 100,000 mg/L. Because none of the underlying units has water with similar dissolved-solids concentrations, this increase in dissolved solids indicates that the source of dissolved solids is within the Pennsylvanian aquifer and not from upward leakage of water into the Pennsylvanian aquifer.

With respect to other aquifers, values of pH have a large range, from 6.5 to 9.0. The majority of values range from 7.2 to 7.9. Contours of pH have been chosen to show the location of extreme values (fig. 47). In general, these extreme values are located in either uplifted areas or in basins, and, thus, they have a significance in the regional trend. Near uplifted areas, values of pH generally are greater than 7.8, and at some locations greater than 8.2. Away from recharge areas, the values of pH decrease, generally to the range of 7.8–7.1; most samples from the Pennsylvanian aquifer have pH values in this range. The smallest values of pH occur in the downgradient areas, in or near the Powder River and Williston basins, and in the Central Montana trough. There are scattered values of pH greater than 8.2 and less than 6.8, but overall, the regional pattern seems consistent.

HYDROCHEMICAL FACIES

The hydrochemical facies of water in the Pennsylvanian aquifer do not indicate the same large range of dissolved-solids concentrations that facies in the other aquifers do. Five different hydrochemical facies in the Pennsylvanian aquifer are described here:

TABLE 9.—*Summary of plausible mechanisms controlling chemical composition of water from the Madison aquifer*

Mechanism	Evidence
Dissolution of calcite and dolomite.	Relatively small concentration of dissolved solids and dominance of calcium, magnesium, and bicarbonate in solution. Relatively small saturation indexes near uplifted areas. Results of mass-transfer modeling.
Dissolution of gypsum with carbonate equilibria (dedolomitization).	Increase of dissolved-solids concentrations to about 2,500 mg/L, mostly as increases in calcium and sulfate concentrations. Bicarbonate concentrations are relatively constant. Results of mass-transfer modeling.
Dissolution of gypsum.	Increase in calcium and sulfate concentrations and undersaturation of gypsum. Change from bicarbonate to sulfate facies. Result of mass-transfer modeling.
Cation exchange	Change from calcium sulfate to sodium sulfate simple salts. Results of mass-transfer modeling.
Dissolution of halite.	Increase in dissolved solids, sodium, and chloride to concentrations near halite saturation. Change from sulfate to chloride facies. Results of mass-transfer modeling.
Sulfate reduction	Increase in bicarbonate with decrease in pH. Bicarbonate-to-sulfate mole ratio increases in several samples. Results of mass-tranfer modeling.
Precipitation of gypsum.	Decrease of sulfate concentration and increase of bicarbonate-to-sulfate mole ratio as the dissolved-solids concentration increases from dissolution of halite. Results of mass-transfer modeling.

Facies number	Simple-salt components	Mole percent	Millimoles per liter of solution
1	$CaCO_3$	39.1	2.2
	$MgCO_3$	31.7	1.8
	$CaSO_4$	26.4	1.5
2	$CaSO_4$	66.5	25.4
	$MgSO_4$	14.1	5.4
	Na_2SO_4	7.7	2.9
	$MgCO_3$	6.4	2.4
3	Na_2SO_4	40.1	21.9
	$CaSO_4$	27.9	15.3
	Na_2Cl_2	23.1	12.6
	$MgCO_3$	5.9	3.2
4	Na_2SO_4	64.6	143.0
	Na_2Cl_2	25.5	56.5
5	Na_2Cl_2	88.0	1,185.4
	$CaSO_4$	5.3	11.7

The distribution of each hydrochemical facies is shown in figure 48. Facies 1 and 2 are dominant hydrochemical facies in highland areas and typically have dissolved-solids concentrations less than 2,500 mg/L.

As water flows away from the Black Hills and other recharge areas, the dissolution of gypsum or anhydrite produces a dominantly calcium sulfate facies (facies 2). Generally, the average increase in the concentrations of calcium and sulfate is equivalent to dissolving almost 24 mmol/L of gypsum, while the increase in the sodium chloride component is less than 1 mmol/L of dissolved halite. The concentrations of every major solute except bicarbonate are larger than in facies 1. The median dissolved-solids concentration of samples in facies 2 is 2,640 mg/L, while facies 1 has a median concentration of 317 mg/L.

As water flows farther downgradient, the chemical character changes again. The dominant calcium sulfate composition of facies 2 changes to a sodium sulfate + calcium sulfate composition that has about a 12 mmol/L increase in the sodium chloride component (facies 3). This increase indicates the beginning of substantial dissolution of halite. The concentrations of calcium and magnesium decrease, perhaps

TABLE 10.—*Regional summary of chemical composition of water from the Pennsylvanian aquifer*

[Concentrations in milligrams per liter, except pH, which is in pH units, and mole ratios, which are dimensionless]

Constituent[1]	Number of samples[2]	Minimum	25th percentile	50th percentile	75th percentile	Maximum
Dissolved solids	1,187	120	2,640	4,160	16,800	381,000
pH	1,123	6.5	7.2	7.5	7.9	9.0
Calcium	1,206	3.0	270	450	640	28,000
Magnesium	1,206	1.0	52	100	160	8,700
Sodium	1,191	.04	5.9	35	234	6,317
Potassium	440	.50	12	63	230	14,000
Chloride	1,204	.20	52	480	3,700	230,000
Sulfate	1,209	1.6	1,300	2,000	3,700	16,000
Bicarbonate	1,199	26	244	395	675	9,270
Mole ratio of magnesium to calcium.	1,196	.90	130	800	5,400	140,000
Mole ratio of bicarbonate to sulfate.	1,199	.01	.19	.29	.57	277

[1] A constituent can be the chemical elements dissolved in water, such as calcium; a property of water, such as pH; an indicator of overall water quality, such as dissolved solids; or a mole ratio of constituents.

[2] Used to calculate percentiles.

through exchange of calcium for sodium on clays, or the precipitation of carbonate minerals. The change in dissolved-solids concentration of the water is not great, only from a median of 2,640 to 3,570 mg/L.

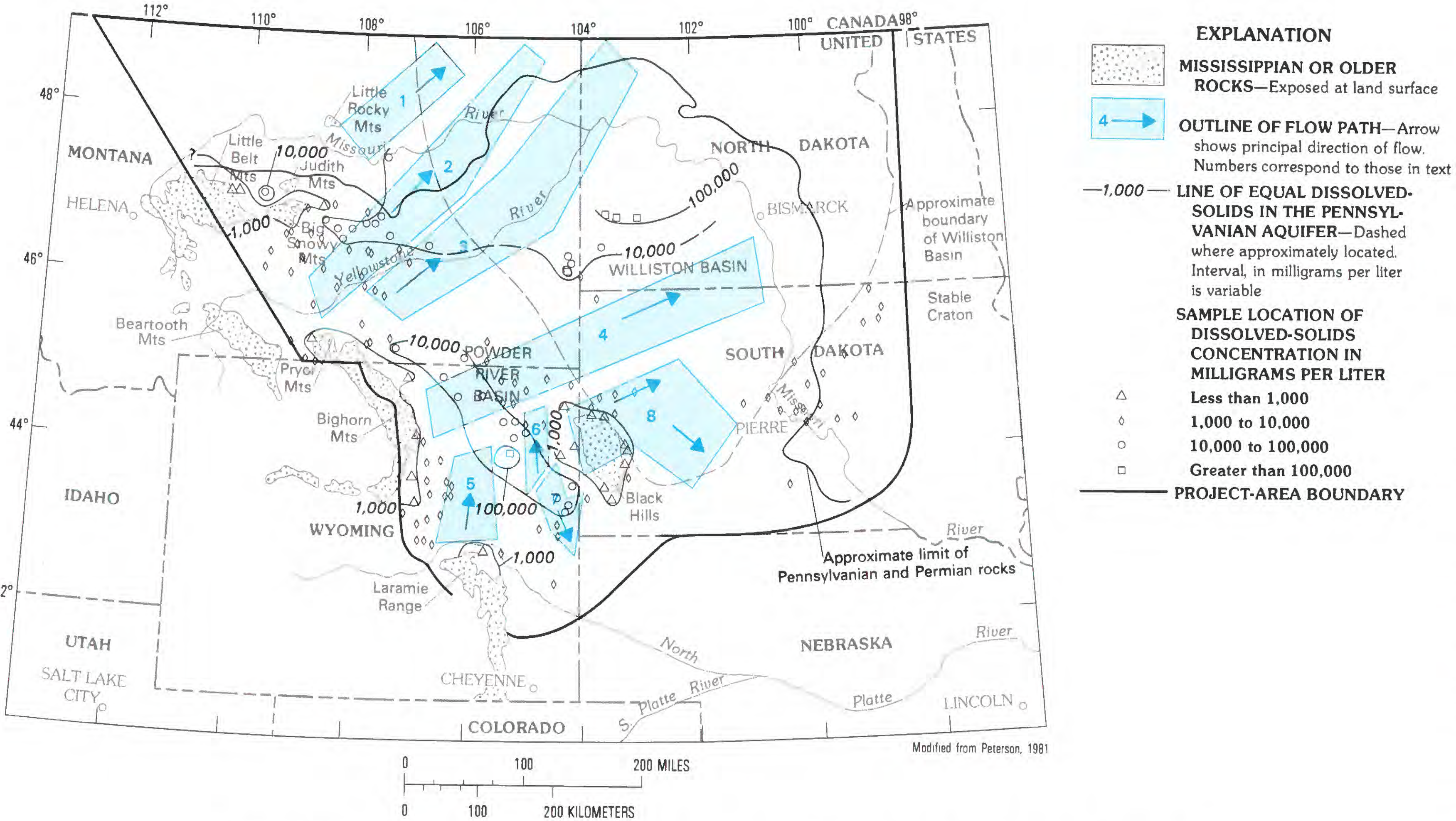
Facies 4 is distinguished from facies 3 by the complete replacement of calcium by sodium and a nearly fourfold increase in sulfate concentration—about 100 mmol/L. The percentage of the sodium chloride component remains nearly constant, but there is an increase of about 44 mmol/L. The median dissolved-solids concentration of this facies is 15,000 mg/L, about a fivefold increase from the previous facies.

Facies 5 has water with the largest dissolved-solids concentration in the Powder River basin and throughout the Williston basin. This facies has a sodium chloride composition. The dissolved-solids concentration of this facies ranges from 18,500 to 381,000 mg/L and has a median concentration of about 79,000 mg/L; the concentration depends on the extent of halite dissolution. The brine in the Powder River basin most likely is derived from the dissolution of salts within the Pennsylvanian rocks. There is no brine facies in the Powder River basin in the underlying units.

Saturation indexes with respect to calcite, dolomite, and gypsum are illustrated in figures 49 through 51. Water in most of the aquifer is supersaturated with calcite. Values decrease slightly in the recharge areas and increase downgradient. Dolomite is undersaturated in parts of the two major recharge areas but rapidly reaches saturation. Most samples are undersaturated with respect to gypsum. Waters in an area northwest of the Bighorn and Pryor Mountains do trend toward saturation with gypsum.

SODIUM AND CHLORIDE

The concentrations of chloride, apparently affected by salt dissolution, are substantially larger in basinal areas than near the uplifted areas (fig. 52; see fig. 1 for structural features). Concentrations of sodium and chloride have the same general pattern (fig. 53) and generally are equal at concentrations greater than 10,000 mg/L. Concentrations of both constituents are smallest in the recharge areas (10–20 mg/L) and are much larger downgradient toward the center of the basins. At dissolved-solids concentrations less than 10,000 mg/L, sodium concentrations mostly are greater than chloride concentrations. However, sodium concentrations have a large range, which



Modified from Peterson, 1981

FIGURE 46.—Concentration of dissolved solids in water from the Pennsylvanian aquifer in the northern Great Plains.

TABLE 11.—*Chemical composition of water from the Pennyslvanian aquifer from along selected flow paths*

[Concentrations in milligrams per liter, except pH, which is in pH units, and mole ratios, which are dimensionless]

Constituent[1]	Flow path (fig. 18)	Number of samples[2]	Minimum	25th per-centile	50th per-centile	75th per-centile	Maximum
Dissolved solids.	2	79	1,150	5,220	14,900	18,200	31,532
	4	149	449	2,560	4,130	12,900	61,900
	5	34	1,970	2,310	2,810	3,400	14,200
	6	51	914	3,390	5,080	14,700	106,000
	7	16	2,000	2,730	5,490	28,100	102,000
	8	1	253	253	253	253	253
pH	2	77	6.7	7.1	7.4	7.6	8.5
	4	148	6.5	7.3	7.6	7.9	8.5
	5	32	6.6	7.1	7.4	8.0	8.8
	6	48	6.7	7.0	7.5	7.8	8.2
	7	13	6.6	6.9	7.3	8.0	8.2
	8	1	7.3	7.3	7.3	7.3	7.3
Calcium	2	79	25	200	260	310	810
	4	152	65	400	490	620	1,900
	5	34	8.1	240	280	310	530
	6	51	130	500	580	710	1,110
	7	16	320	410	590	740	1,700
	8	1	60	60	60	60	60
Magnesium	2	79	8.0	33	46	61	380
	4	152	10	86	120	160	760
	5	34	2.0	27	36	47	160
	6	51	47	93	140	210	420
	7	16	56	120	160	260	820
	8	1	22	22	22	22	22
Sodium	2	79	82	1,500	4,800	6,000	11,000
	4	149	2.0	130	650	4,000	23,000
	5	34	160	390	540	840	4,100
	6	50	18	290	1,100	4,500	39,000
	7	15	30	420	1,500	9,100	26,000
	8	1	2.0	2.0	2.0	2.0	2.0
Potassium	2	8	10	14	35	5	65
	4	67	1.1	48	75	110	740
	5	24	28	69	120	140	200
	6	15	3.0	37	55	94	1,200
	7	7	36	100	180	450	510
	8	0	--	--	--	--	--
Chloride	2	79	35	330	1,900	3,300	8,900
	4	150	1.0	66	510	4,500	34,000
	5	34	160	300	460	730	1,800
	6	51	8.0	71	380	3,400	61,000
	7	16	27	810	1,100	12,000	43,000
	8	1	.20	.20	.20	.20	.20
Sulfate	2	79	510	2,200	6,300	7,900	12,000
	4	152	8.0	1,400	1,800	3,200	8,600
	5	34	700	1,000	1,200	1,400	9,000
	6	51	520	2,200	2,800	4,300	7,800
	7	16	520	1,100	2,100	4,900	11,000
	8	1	16	16	16	16	16

TABLE 11.—*Chemical composition of water from the Pennsylvanian aquifer from along selected flow paths*—Continued

Constituent[1]	Flow path (fig. 18)	Number of samples[2]	Minimum	25th percentile	50th percentile	75th percentile	Maximum
Bicarbonate	2	78	50	393	803	1,070	3,290
	4	152	51	220	305	490	1,130
	5	34	100	182	244	316	614
	6	51	98	220	293	469	891
	7	16	120	300	385	1,240	1,950
	8	1	279	279	279	279	279
Mole ratio of magnesium to calcium.	2	79	.10	.25	.33	.44	1.1
	4	152	.03	.32	.40	.51	1.1
	5	34	.01	.16	.22	.29	3.9
	6	51	.15	.32	.40	.51	.79
	7	16	.27	.34	.56	.61	.82
	8	1	.60	.60	.60	.60	.60
Mole ratio of bicarbonate to sulfate.	2	78	.04	.17	.23	.32	1.7
	4	152	.05	.20	.25	.34	54
	5	34	.08	.25	.31	.35	.79
	6	51	.06	.13	.15	.20	.80
	7	16	.06	.15	.39	.74	1.2
	8	1	27	27	27	27	27

[1] A constituent can be the chemical elements dissolved in water, such as calcium; a property of water, such as pH; an indicator of overall water quality, such as dissolved solids; or a mole ratio of constituents.

[2] Used to calculate percentiles.

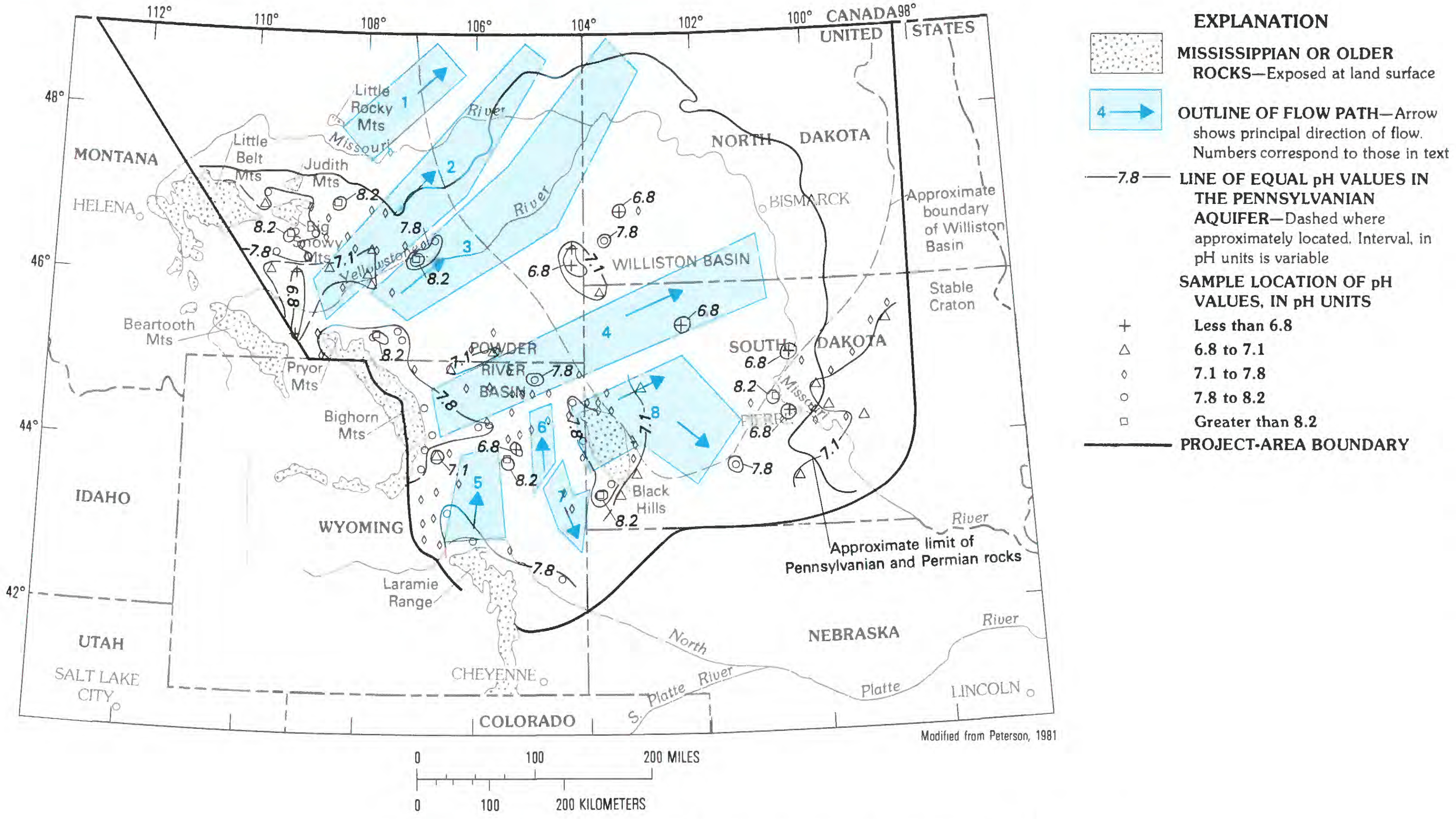
indicates that sodium is initially from sources other than halite. The concentration gradients of sodium and chloride increase toward the Williston and Powder River basins.

MOLE RATIO OF MAGNESIUM TO CALCIUM

The mole ratio of magnesium to calcium decreases downgradient from uplifted areas, from a value greater than 1.0 to a value of about 0.1 (fig. 54). Magnesium and calcium decrease with respect to chloride as the dissolved-solids concentrations increase. However, at the largest dissolved-solids concentrations, the mole ratio remains fairly constant. The mole ratio of magnesium to calcium is greater than 1.0 near the Black Hills and the Bighorn, Beartooth, and Big Snowy Mountains; it decreases downgradient to less than 0.3 and then increases to values more than 0.5. Larger magnesium-to-calcium mole ratios may indicate dedolomitization. Another reason for the increase back to values greater than 0.5 could be the loss of calcium, perhaps through the precipitation of gypsum from water with large concentrations of sulfate. The largest mole ratios are in the area southwest of the Big Snowy Mountains where the mole ratio is greater than 8.0.

MOLE RATIO OF BICARBONATE TO SULFATE

The mole ratio of bicarbonate to sulfate in water of the Pennsylvanian aquifer indicates a greater amount of variation than the mole ratio of magnesium to calcium. Throughout most of the area, the mole ratio only ranges from 0.1 to 0.5. The largest ratios (fig. 55) are in recharge areas and range from about 1.6 to 20. Values of the bicarbonate-to-sulfate mole ratio decrease a very short distance away from uplifted areas. In some areas, the contour at a value of 0.5 could not be located because of the steep gradient from values greater than 1.0 to those less than 0.5. The change indicates the constant concentration of bicarbonate and the rapidly increasing concentration of sulfate. Water in the Williston and Powder River basins have opposite patterns. In the Powder



Modified from Peterson, 1981

FIGURE 47.—Values of pH in water from the Pennsylvanian aquifer in the northern Great Plains.

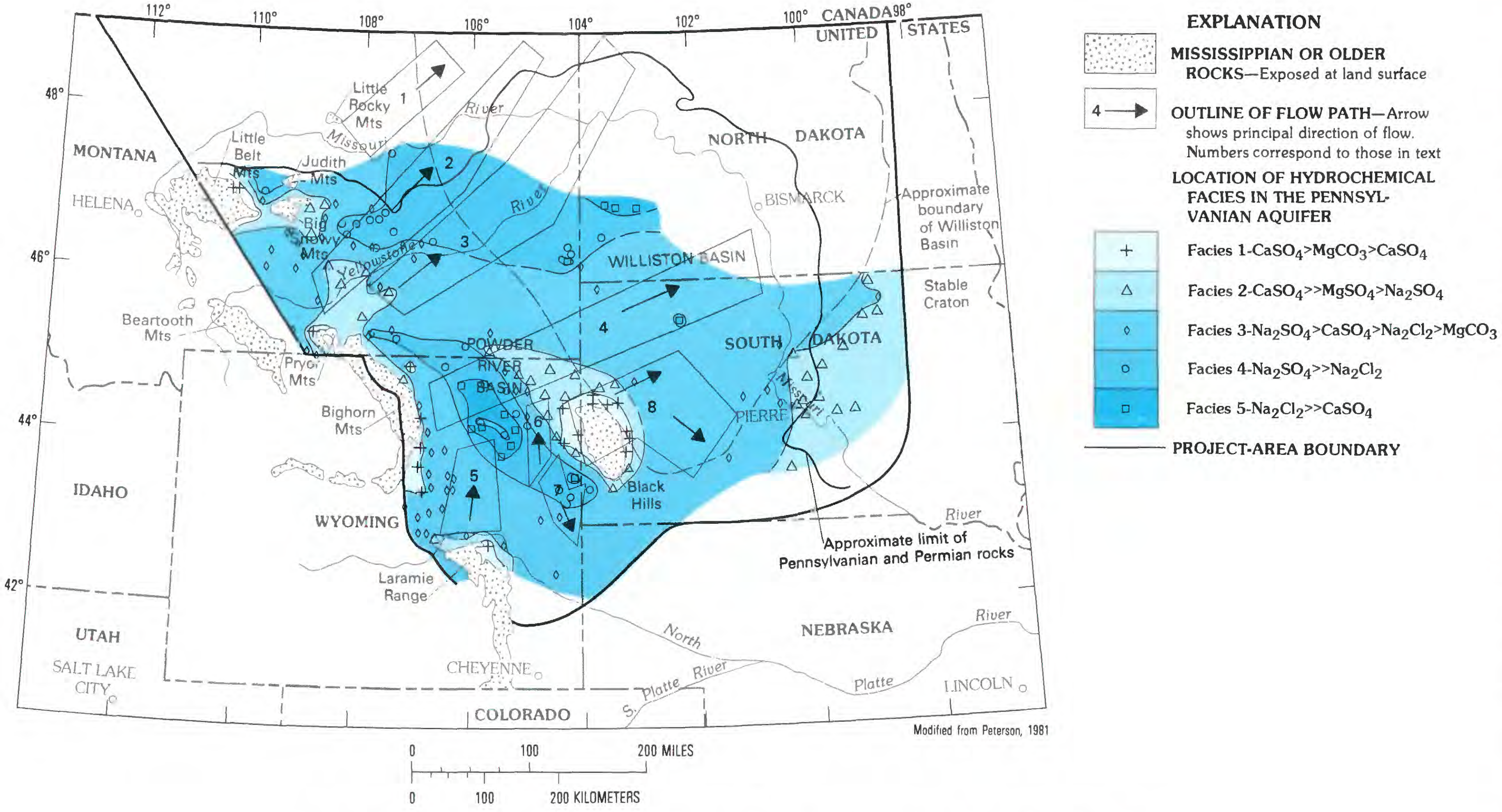


FIGURE 48.—Hydrochemical facies in water from the Pennsylvanian aquifer in the northern Great Plains.

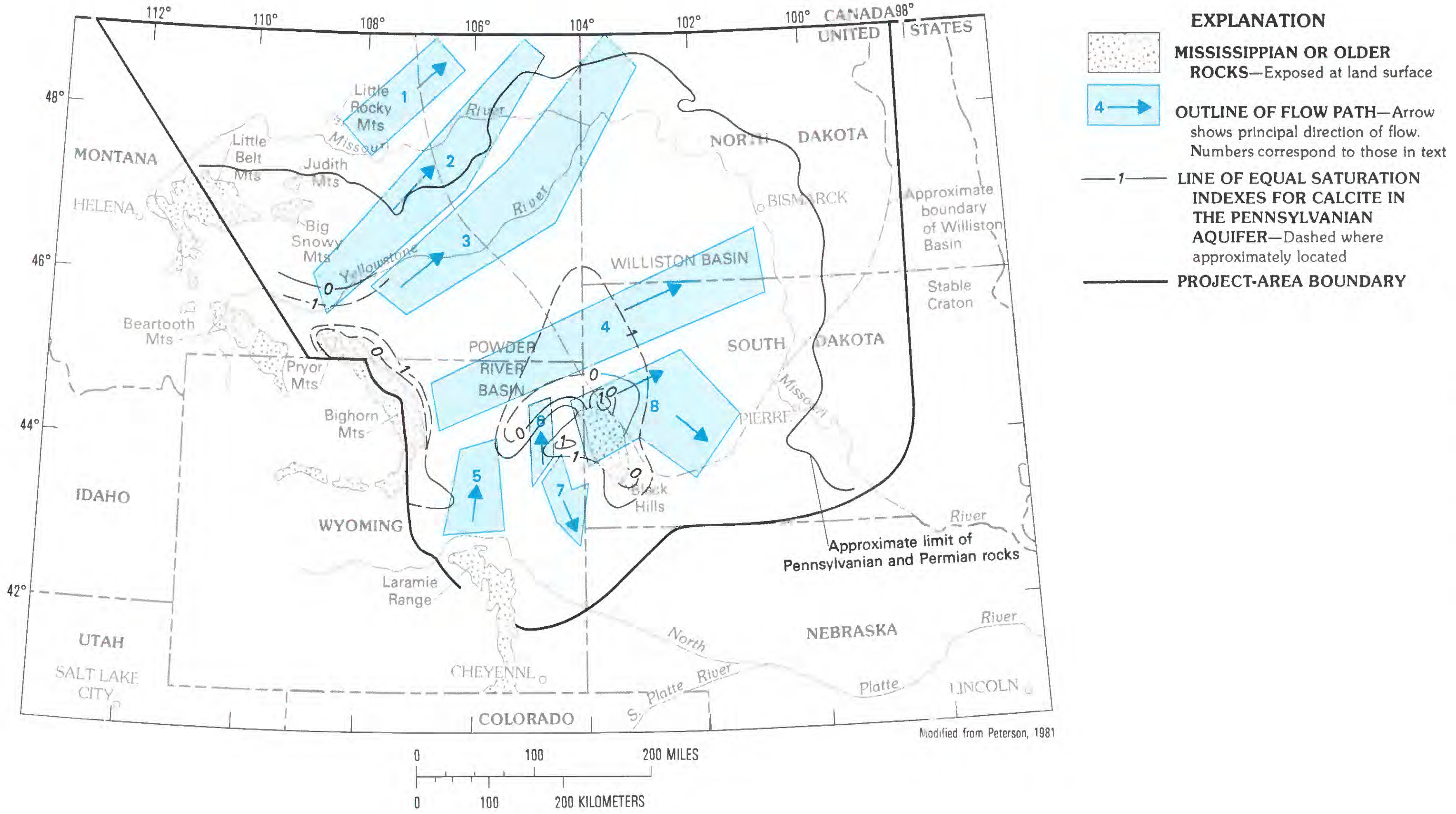


FIGURE 49.—Saturation indexes with respect to calcite for water from the Pennsylvanian aquifer in the northern Great Plains.

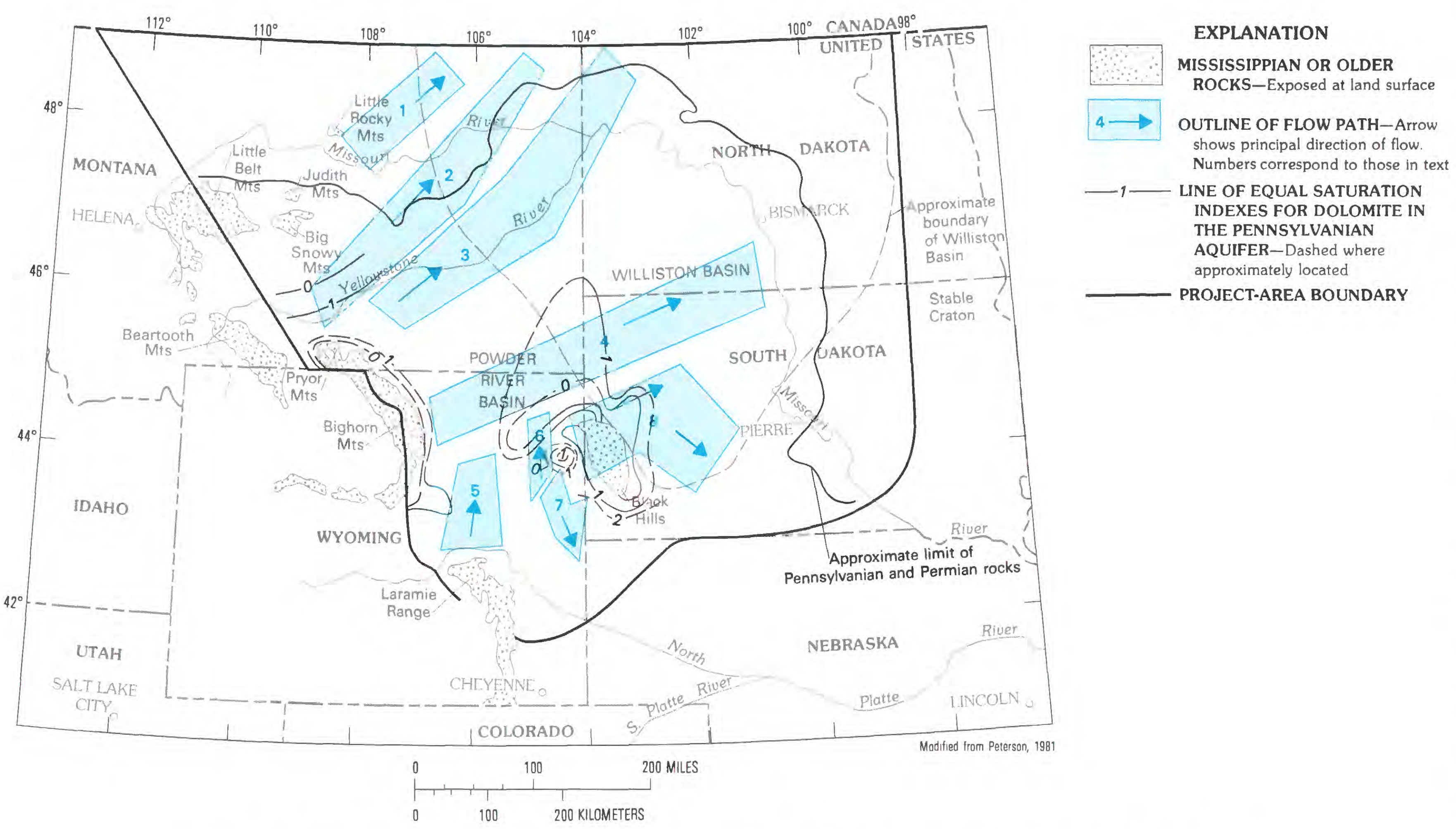


FIGURE 50.—Saturation indexes with respect to dolomite for water from the Pennsylvanian aquifer in the northern Great Plains.

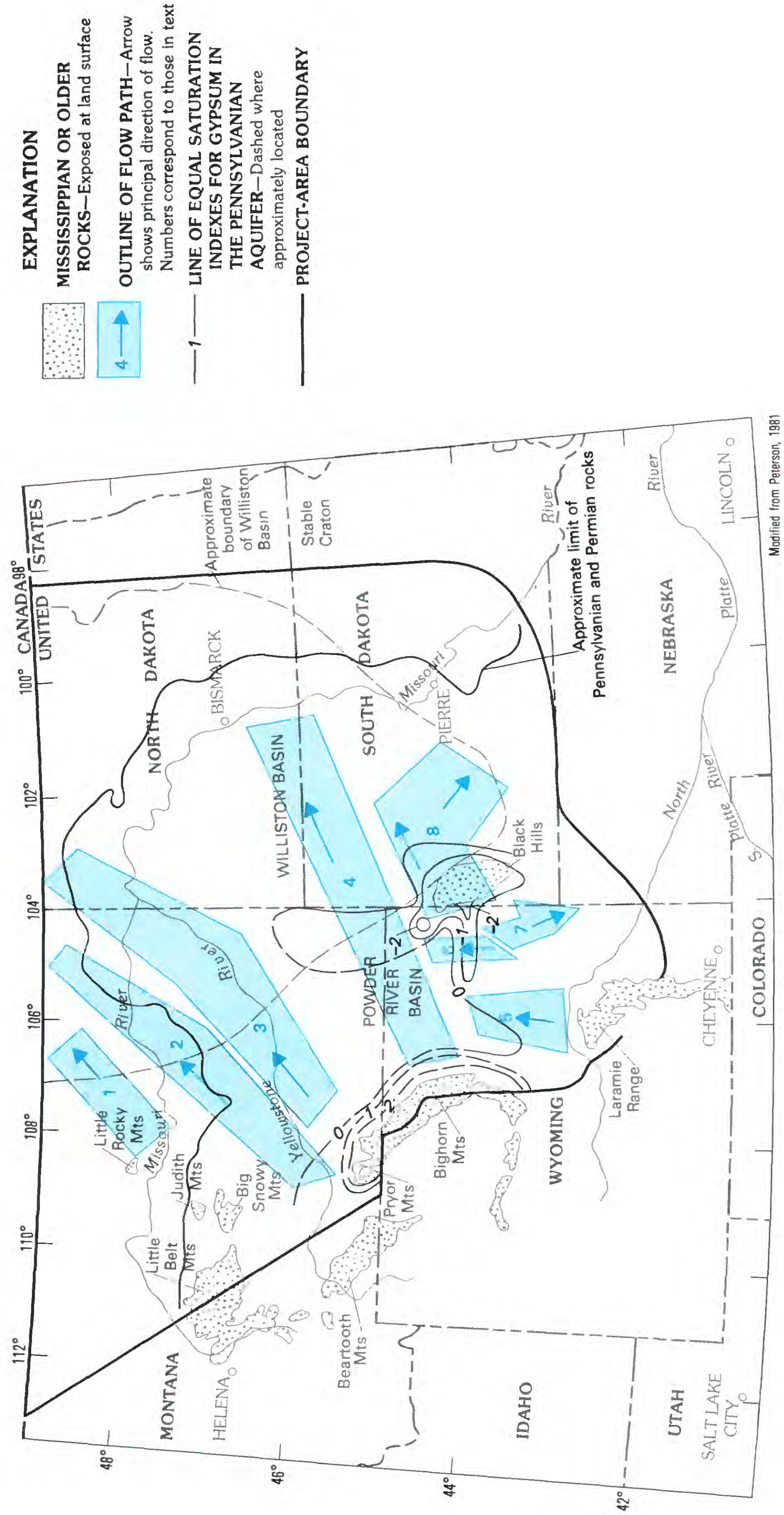


FIGURE 51.—Saturation indexes with respect to gypsum for water from the Pennsylvanian aquifer in the northern Great Plains.

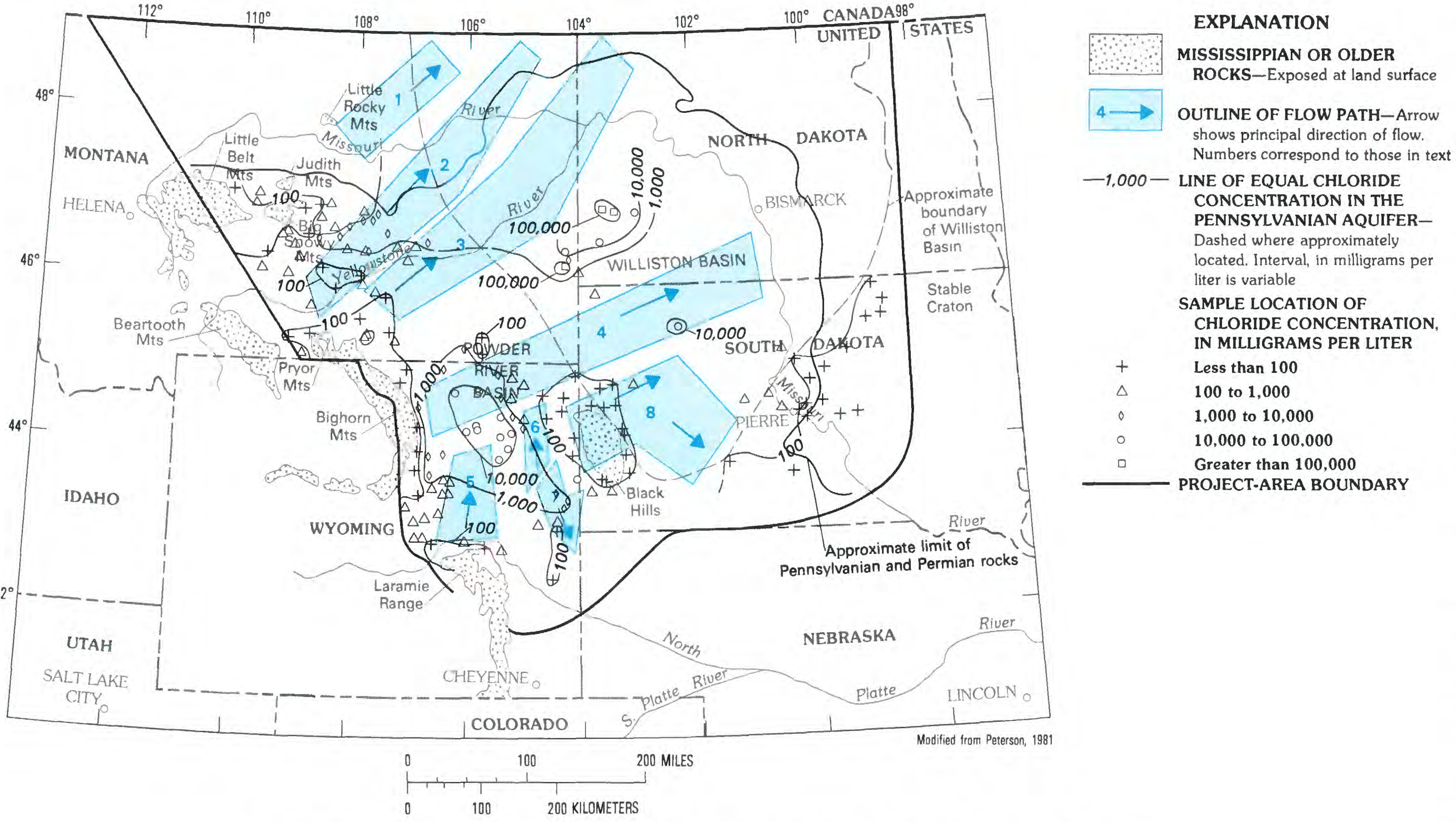


FIGURE 52.—Concentration of chloride in water from the Pennsylvanian aquifer in the northern Great Plains.

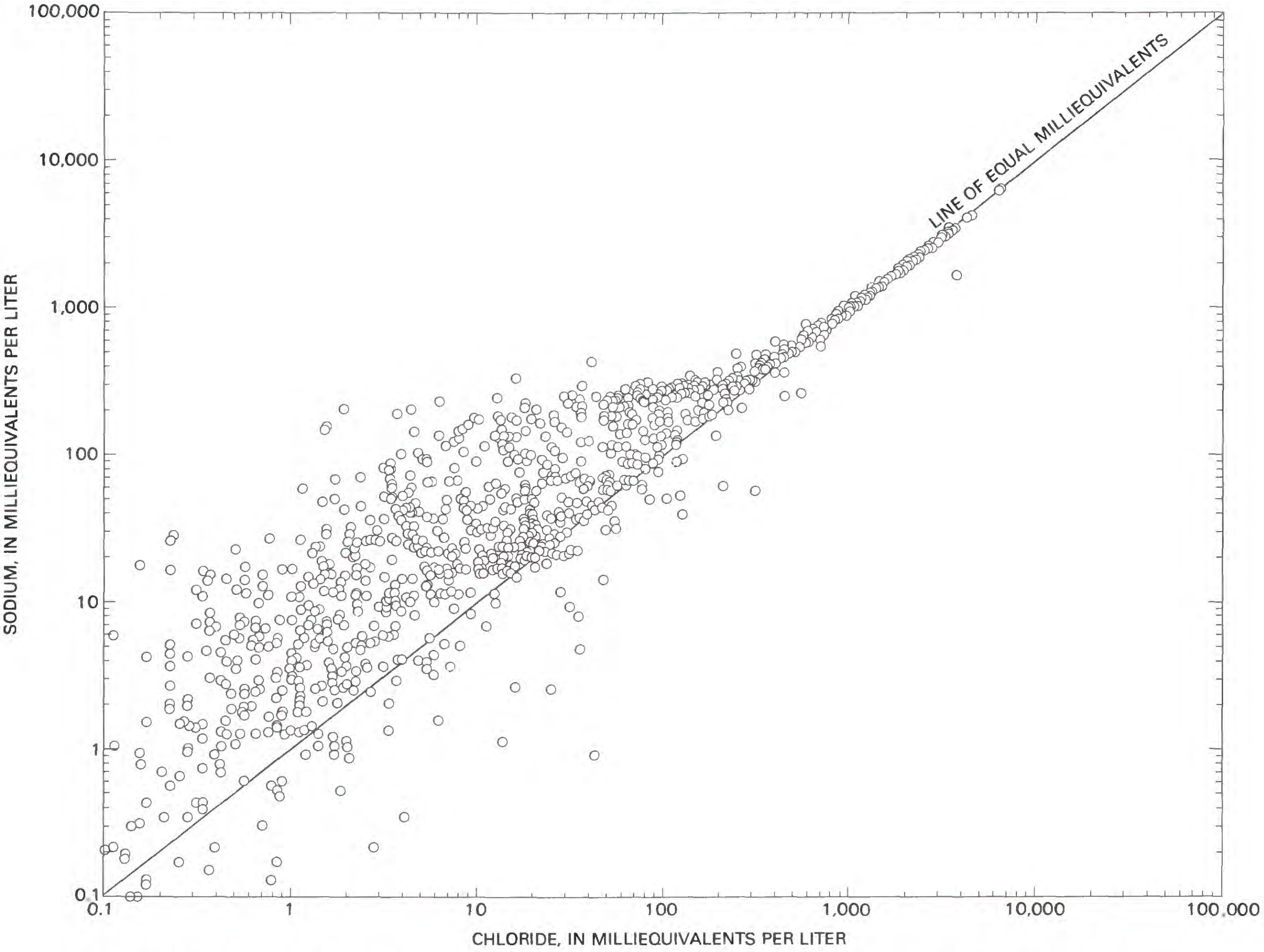


FIGURE 53.—Variation of sodium with chloride in water from the Pennsylvanian aquifer in the northern Great Plains.

River basin, values of the mole ratio increase from less than 0.3 to about 1.0. This same trend is present along flow path 2. In the Williston basin, values of the mole ratio are less than 0.1.

SUMMARY OF MOST PLAUSIBLE MECHANISMS

The largest changes in chemical composition result from the dissolution of gypsum or anhydrite and halite. These changes in chemical composition also could occur through upward leakage of brine into the aquifer. However, brine occurs in the Pennsylvanian aquifer in the Powder River basin in areas where there is no similar brine in underlying or overlying hydrogeologic units, which indicates that the source of the salts is the Pennsylvanian aquifer. The precipitation of carbonate minerals causes the concentrations of calcium and magnesium to decrease as the dissolved-solids concentration increases. A summary of plausible mechanisms that affect the water chemistry in the Pennsylvanian aquifer is listed in table 12.

PERMIAN-TRIASSIC-JURASSIC CONFINING UNIT

The geologic units that compose the Permian-Triassic-Jurassic confining unit (TK3) are shown on plates 1 and 2. Samples of ground water from this hydrogeologic unit are mostly from the Sawtooth, Swift, Sundance, and Morrison Formations, but there are also samples from the Minnekahta Limestone and the Spearfish, Piper, and Gypsum Springs Formations. The majority of water samples from this confining unit are from near the Bearpaw uplift in north-central Montana (fig. 1). Water samples also

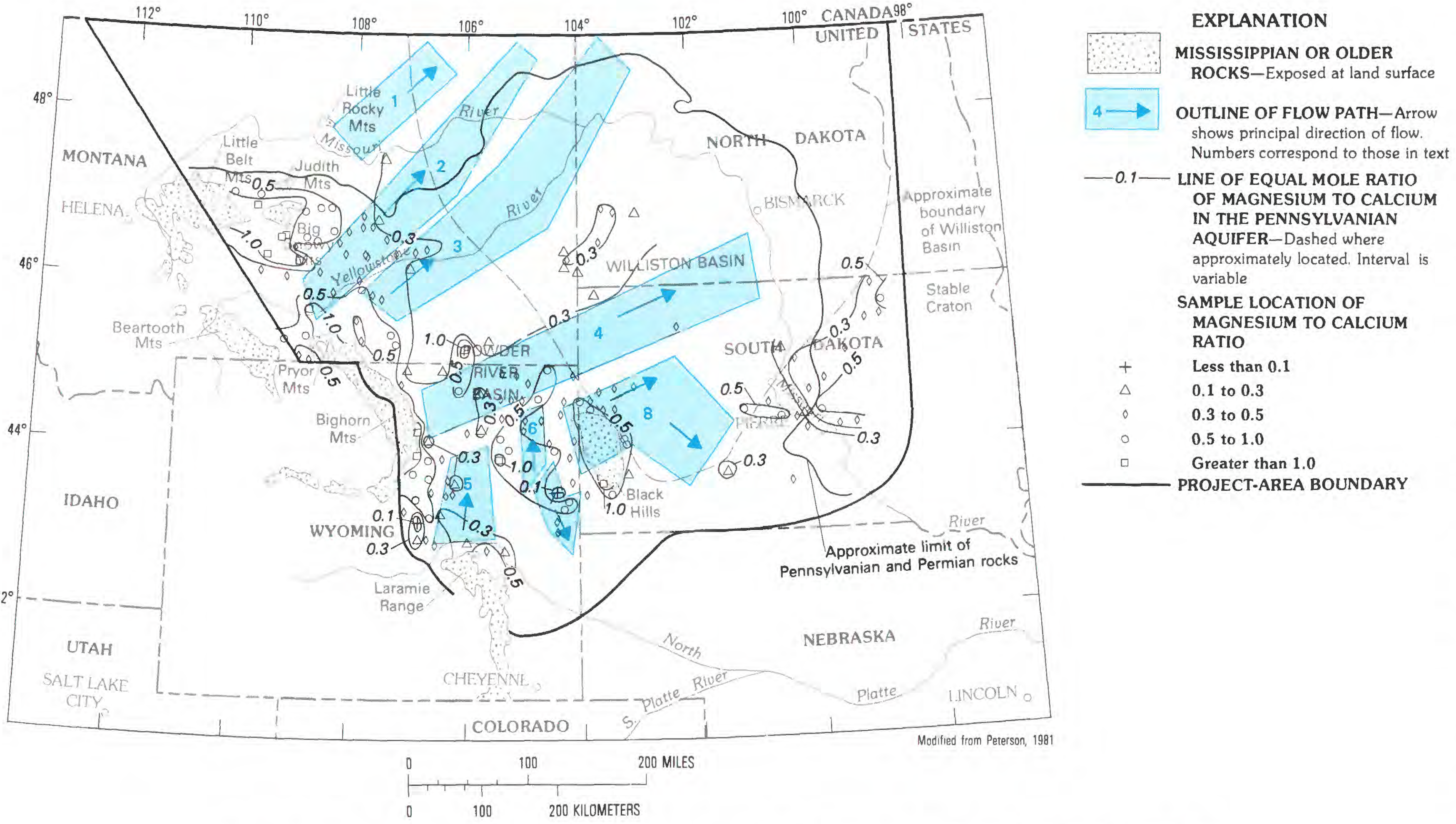


FIGURE 54.—Mole ratio of magnesium to calcium in water from the Pennsylvanian aquifer in the northern Great Plains.

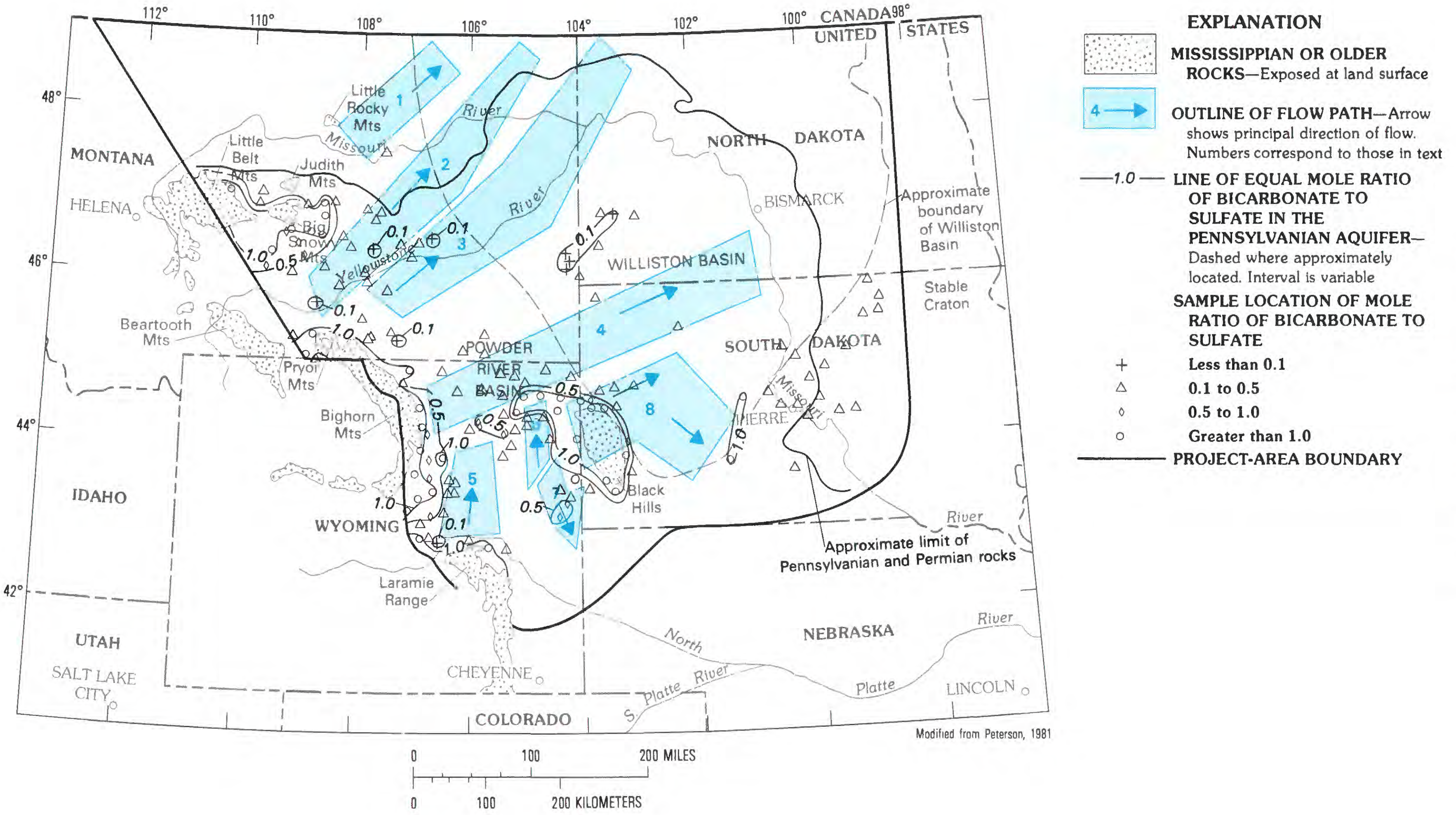


FIGURE 55.—Mole ratio of bicarbonate to sulfate in water from the Pennsylvanian aquifer in the northern Great Plains.

TABLE 12.—*Summary of plausible mechanisms controlling chemical composition of water from the Pennsylvanian aquifer*

Mechanism	Evidence
Dissolution of calcite and dolomite.	Water near highland areas contains mostly calcium, magnesium, and bicarbonate from the dissolution of carbonate minerals, indicated by the composition of water in uplifted areas. Relatively small concentrations of dissolved solids. Relatively small saturation indexes near uplifted areas (fig. 49).
Dissolution of gypsum.	Increase in calcium and sulfate concentrations and undersaturation of gypsum. Change from facies 1 to 2.
Dissolution of halite.	Increase in dissolved solids, sodium, and chloride to concentrations near halite saturation in the area of Williston basin. Evolution from facies 3 to 4 and 5.

were obtained from eastern Montana, the Laramie Range, the Powder River basin, the Black Hills area, and a few scattered samples from the Williston basin.

Because the residence time of the water is much greater in the Permian-Triassic-Jurassic confining unit than in the aquifers and because the concept of flow paths is less meaningful for a confining unit, a

TABLE 13.—*Regional summary of chemical composition of water from the Permian-Triassic-Jurassic confining unit*

[Concentrations in milligrams per liter, except pH, which is in pH units, and mole ratios, which are dimensionless]

Constituents[1]	Number of samples[2]	Minimum	25th percentile	50th percentile	75th percentile	Maximum
Dissolved solids	273	308	2,180	3,670	6,780	239,000
pH	249	6.5	7.4	7.9	8.3	9.0
Calcium	263	2.3	30	78	270	6,200
Magnesium	257	.7	12	28	78	1,400
Sodium	268	1.0	520	1,400	2,400	91,000
Potassium	76	1.6	5.7	12	25	200
Chloride	273	1.0	84	440	1,110	140,000
Sulfate	261	5.0	150	1,000	2,000	13,000
Bicarbonate	273	83	349	780	2,060	8,340
Mole ratio of magnesium to calcium.	257	.03	.36	.53	.84	5.6
Mole ratio of bicarbonate to sulfate.	261	.04	.29	1.2	8.9	1,100

[1] A constituent can be the chemical elements dissolved in water, such as calcium; a property of water, such as pH; an indicator of overall water quality, such as dissolved solids; or a mole ratio of constituents.

[2] Used to calculate percentiles.

summary of the chemical composition of samples from this hydrogeologic unit is listed in table 13.

REGIONAL GEOCHEMICAL TRENDS

The spatial distribution of ground-water samples limits the ability for a detailed discussion of regional geochemical trends. However, there are a sufficient number of samples to discuss some of the geochemical variations.

DISSOLVED SOLIDS AND pH

The range of dissolved-solids concentrations in water from the Permian-Triassic-Jurassic confining unit is much smaller than in the underlying confining units. Only two samples have been obtained with a dissolved-solids concentration in excess of 100,000 mg/L. The smaller dissolved-solids concentrations in this unit indicate that there is less dissolution of saline minerals or that the effect of upward leakage of brines is small.

The majority of samples have a dissolved-solids concentration that ranges from 1,000 to 10,000 mg/L, and the median, or 50th percentile, concentration is 3,670 mg/L. Samples with a dissolved-solids concentration less than 1,000 mg/L are from two uplifted areas, (1) the Big Snowy–Little Belt Mountains and (2) the Black Hills (fig. 56; see fig. 1 for structural features). Larger concentrations occur away from these uplifted areas. Concentrations greater than 10,000 mg/L are present in the Powder River basin and in a few other isolated areas. This slightly saline water could result from the dissolution of gypsum or anhydrite. Concentrations of dissolved solids remain less than 10,000 mg/L east of recharge areas in Montana.

No regional trend in pH exists among samples in the Permian-Triassic-Jurassic confining unit, and thus, a map of values of pH is not included. Values of pH range from 6.5 to 9.0 throughout the entire area. Near the Bearpaw uplift in Montana, values of pH are generally higher than those measured in other parts of the confining unit. Values of about 8.0 to 8.5 are common there and in other recharge areas. Values of pH are near neutrality near the Williston basin.

Some small areas of alkaline pH water (greater than 8.5) exist that could result from sulfate reduction, but the bicarbonate-to-sulfate mole ratio of the water is not large in these samples. The lowest, most acidic, values of pH are in water with the largest dissolved-solids concentrations, greater than 30,000 mg/L. At dissolved-solids concentrations smaller than this, there is no trend in values of pH.

HYDROCHEMICAL FACIES

The Permian-Triassic-Jurassic confining unit can be subdivided into five different hydrochemical facies (fig. 57), as characterized by the simple-salt components here:

Facies number	Simple-salt components	Mole percent	Millimoles per liter of solution
1	$CaSO_4$	47.5	7.8
	$MgCO_3$	28.4	4.7
	Na_2SO_4	19.6	3.2
2	$CaSO_4$	45.5	16.8
	Na_2SO_4	24.9	9.2
	$MgSO_4$	11.2	4.1
	$MgCO_3$	10.1	3.7
	Na_2Cl_2	6.8	2.5
3	Na_2SO_4	40.9	22.5
	Na_2CO_3	27.5	15.1
	Na_2Cl_2	25.8	14.2
4	Na_2CO_3	66.8	44.7
	Na_2Cl_2	28.5	19.1
5	Na_2Cl_2	47.7	79.0
	Na_2SO_4	42.2	28.2

These hydrochemical facies generally have a more mixed chemical composition than facies in aquifers. This composition can be expected when a hydrogeologic unit basically is fine grained and the ground water has a longer residence time than in an aquifer. Even though these hydrochemical facies are complex, they do indicate processes in the geochemical evolution of the ground-water chemistry in this hydrogeologic unit. However, this evolution does not indicate horizontal flow for this confining unit. The conceptual model of flow from Downey (1986) for this confining unit is that vertical flow is greater than horizontal flow and that this unit is an effective hydrologic barrier to most of the vertical flow.

Recharge water near the Big Snowy Mountains and the Black Hills has a similar chemical composition and has a dissolved-solids concentration less than 1,700 mg/L. This mixed composition in facies 1 is probably the result of weathering carbonate and sulfate minerals and subsequent loss of calcium through carbonate precipitation or cation exchange. Water in facies 1 is almost saturated with respect to calcite but undersaturated with respect to gypsum. Thus, as gypsum dissolves, there could be a loss of calcium through precipitation of calcite.

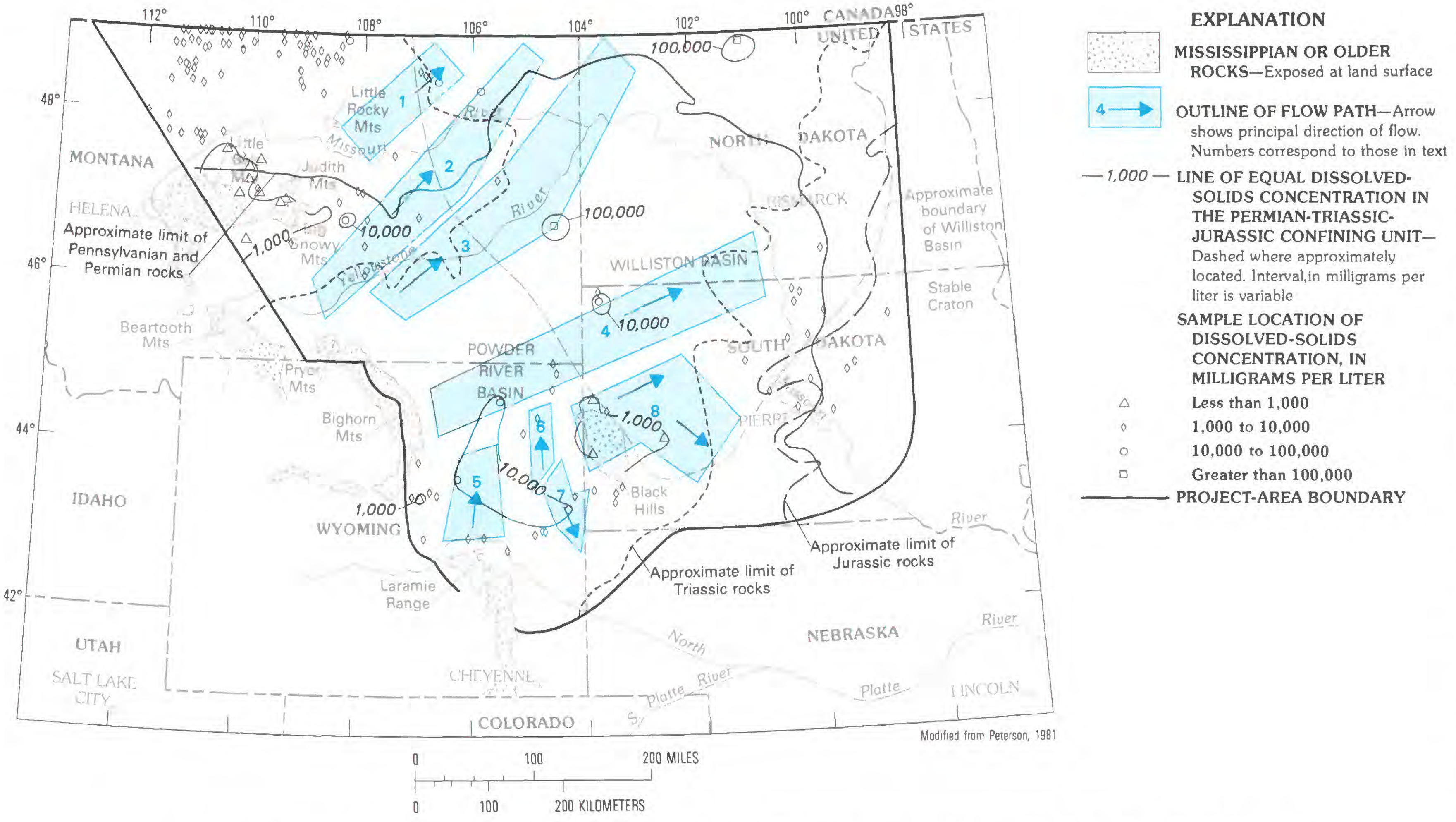


FIGURE 56.—Concentration of dissolved solids in water from the Permian-Triassic-Jurassic confining unit in the northern Great Plains.

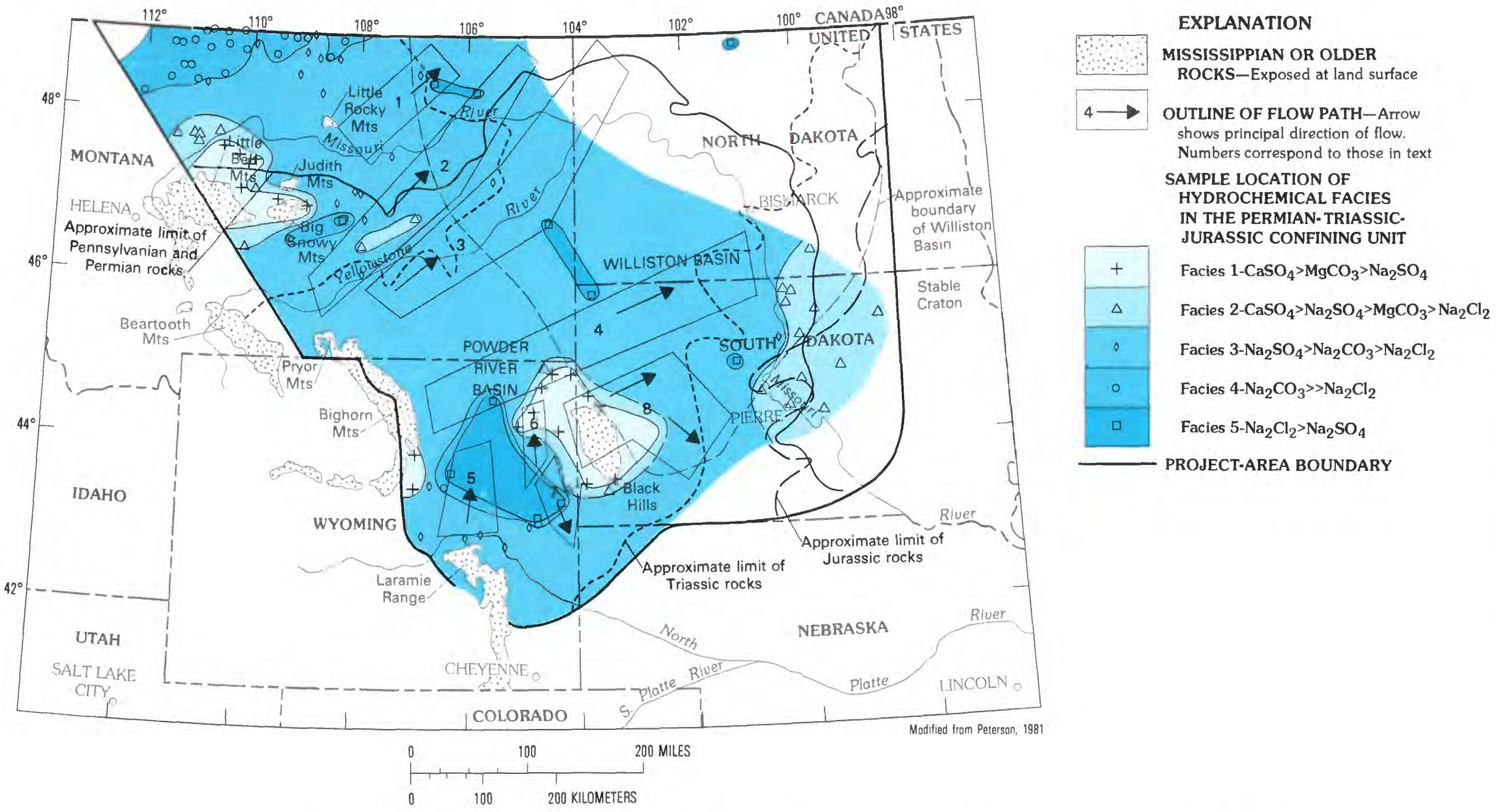


FIGURE 57.—Hydrochemical facies in water from the Permian-Triassic-Jurassic confining unit in the northern Great Plains.

Away from highland areas, a general increase in dissolved-solids concentration occurs, but the chemical composition of the water in facies 2 does not change very much, though the concentration of each of the major solutes except bicarbonate increases enough to consider this water a different hydrochemical facies. The dissolved-solids concentration ranges from 1,150 to 8,830 mg/L, but the majority of samples have concentrations less than 3,720 mg/L. Facies 2 occurs near the same uplifted areas as facies 1.

Facies 3 is characterized by small calcium and magnesium concentrations and increased chloride concentrations. The dissolved-solids concentration in facies 3 ranges from about 1,000 to 16,000 mg/L. Facies 3 generally occurs farther away from highland areas than facies 1 and 2.

Facies 4, generally with dissolved-solids concentration greater than 5,000 mg/L, essentially has a sodium carbonate + sodium chloride composition. Within this facies, samples with larger concentrations of dissolved solids, generally greater than 8,000 mg/L, have larger bicarbonate concentrations and smaller sulfate concentrations. This subset of facies 4 most likely is produced by sulfate reduction. Most of these samples that have larger bicarbonate concentrations are facies near the Canadian border in north-central Montana.

A sodium chloride + sodium sulfate water, facies 5, is defined by samples from eastern Montana and the Powder River basin and by a few samples from the Williston basin. Concentrations of dissolved solids in these samples are generally less than 12,000 mg/L, but in the Williston basin, one sample had a concentration of 239,000 mg/L. The chemical character of this facies could be a result of upward leakage from the Pennsylvanian aquifer, dissolution of halite within the confining unit, or both. The large dissolved-solids concentration in water from the Pennsylvanian aquifer in the Powder River basin could affect the dissolved-solids concentration in an adjacent unit without there being a large volume of vertical flow between them.

SODIUM AND CHLORIDE

The general increase in the concentration of dissolved solids is from the increasing concentration of chloride, sodium, and sulfate. The distribution of chloride concentrations is similar to that of dissolved-solids concentrations (fig. 58). The concentration of sodium is greater than the concentration of chloride in water with a dissolved-solids concentration less than about 15,000 mg/L (fig. 59). Sodium concentrations are much larger than chloride concentrations in these samples. Sodium concentrations are almost equal to those of sulfate. However, sulfate concentrations decrease in some areas. The larger sodium concentration could result from ion exchange or from the dissolution of sodium sulfate salts (Grossman, 1968). The largest increases of sodium and chloride are in basin centers.

MOLE RATIO OF MAGNESIUM TO CALCIUM

The mole ratio of magnesium to calcium (fig. 60) ranges from 0.03 to 5.6. In general, the mole ratio indicates a trend of largest values in recharge water and smaller values in basins. Overall, concentrations of calcium and magnesium tend to vary together, so there is not a large change in the magnesium-to-calcium mole ratio. The mole ratio generally decreases in water with larger dissolved-solids concentration. The map of magnesium to calcium mole ratio is not well defined. The regional trends are not as clear as those in dissolved-solids and chloride concentrations, but the map is presented to show the general pattern.

MOLE RATIO OF BICARBONATE TO SULFATE

The mole ratio of bicarbonate to sulfate (fig. 61) is variable throughout the northern Great Plains. In north-central Montana, large variations occur within small areas. In that area, near the Canadian border, the values of the mole ratios seem to occur in three zones in which the values decrease from west to east. The westernmost zone contains water that has values of the mole ratio of bicarbonate to sulfate greater than 100. Immediately to the east of this zone is a second zone in which the values of the mole ratio range from 10 to 100. A third zone contains water with values of the mole ratio less than 10.

The values of the mole ratio have differing extremes in uplifted areas. The values tend to be large at the north end of the Laramie Range and south of the Big Snowy Mountains. The values adjacent to outcrops are less than 1.0. Away from outcrops, the small bicarbonate-to-sulfate mole ratios in uplifted areas probably indicate the availability of sulfate minerals in these units that can be dissolved in recharge water. Large mole ratios away from uplifted areas probably indicate sulfate reduction.

SUMMARY OF MOST PLAUSIBLE MECHANISMS

Plausible mechanisms for observed changes in water quality in the Permian-Triassic-Jurassic confining unit

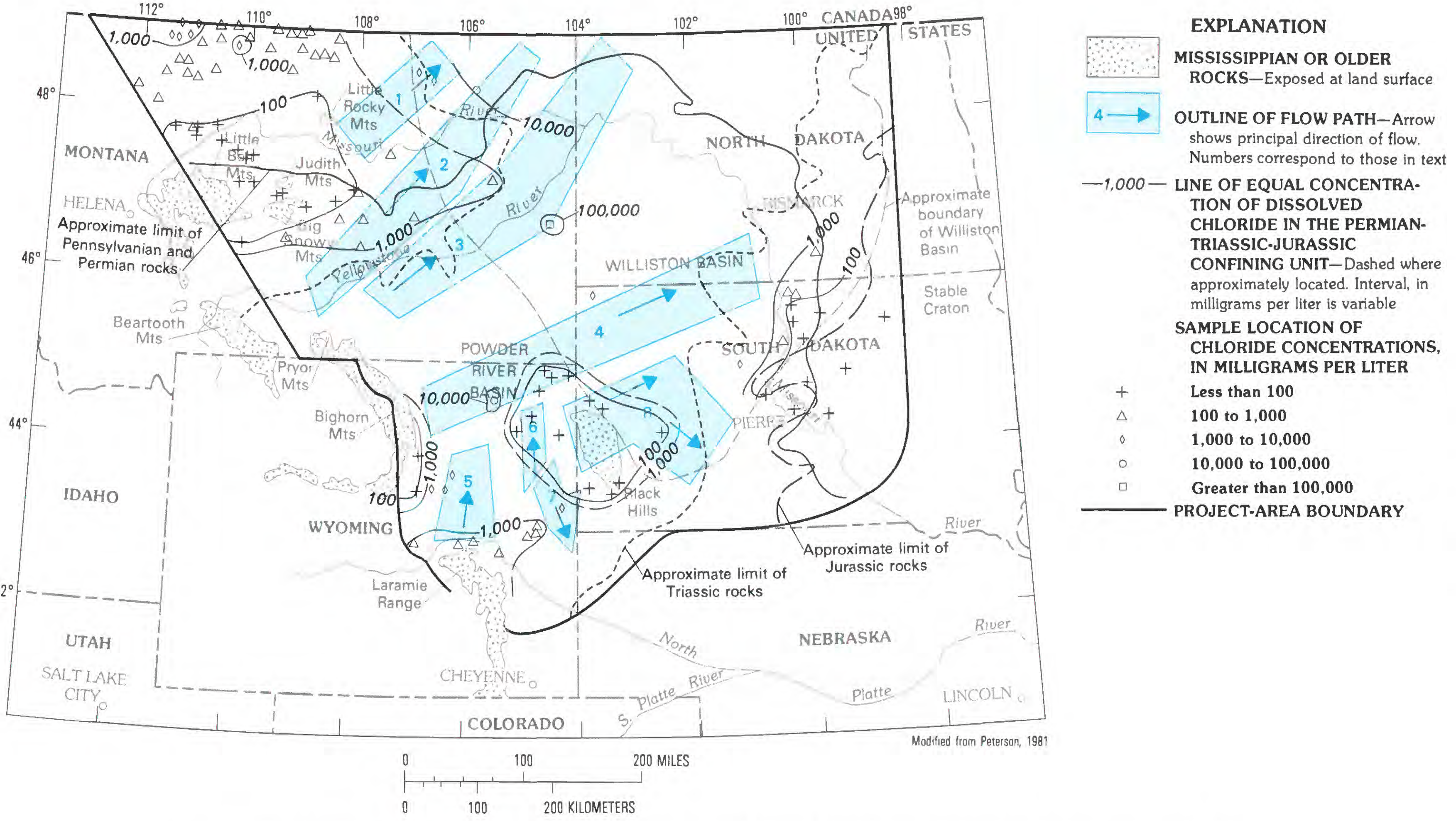


FIGURE 58.—Concentration of chloride in water from the Permian-Triassic-Jurassic confining unit in the northern Great Plains.

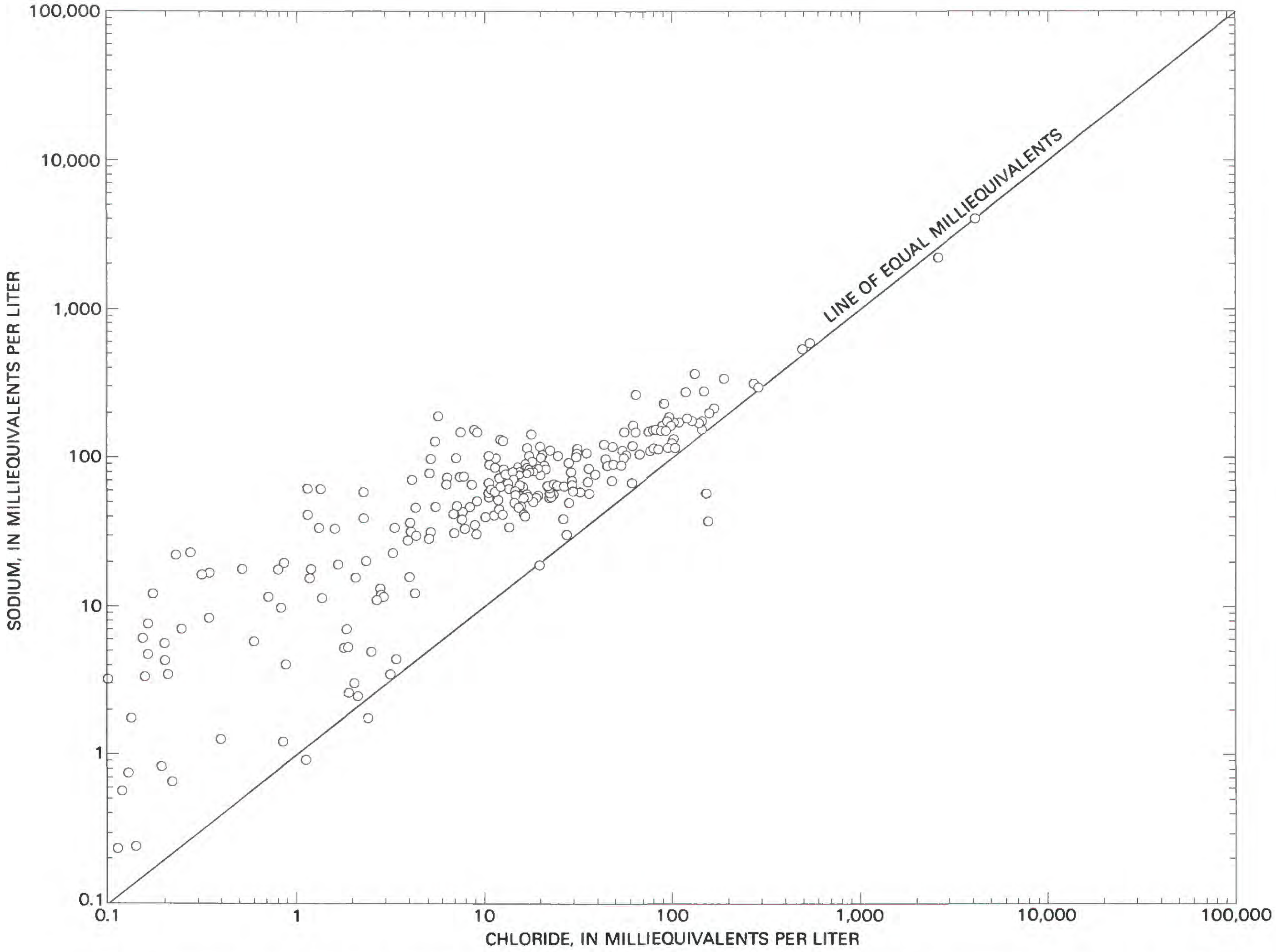


FIGURE 59.—Variation of sodium with chloride in water from the Permian-Triassic-Jurassic confining unit in the northern Great Plains.

include dissolution of carbonate minerals and gypsum, cation exchange, precipitation of carbonate minerals, sulfate reduction, and dissolution of halite or leakage (table 14). The initial chemical composition of the water in recharge areas results from weathering near the outcrop. Large calcium and sulfate concentrations away from recharge areas probably are caused by the dissolution of gypsum. There may be some cation exchange of calcium for sodium, but the change to a dominantly sodium water primarily is because of carbonate precipitation. Water in north-central Montana, which has a sodium sulfate + sodium chloride character, seems to undergo sulfate reduction, which produces a sodium bicarbonate + sodium chloride character. In the Williston basin and the Powder River basin, the chemical composition changes to a sodium chloride water.

LOWER CRETACEOUS AQUIFERS

The Lower Cretaceous aquifers (Downey, 1986) underlie nearly all the northern Great Plains and are sources of ground water throughout most of the area (fig. 19). The hydrogeologic setting of these aquifers varies greatly. Within 160 mi of the outcrop, the aquifers may be buried several thousand feet beneath younger rocks. In eastern North Dakota and eastern South Dakota, they are underlain by low-permeability shales. These aquifers may be described conveniently by dividing them into similar hydrogeologic areas (fig. 62); these areas are the uplands, the basins, and the pinch-out area in eastern North Dakota and eastern South Dakota.

In general, the water is less saline near the uplands. The water that has the largest saline

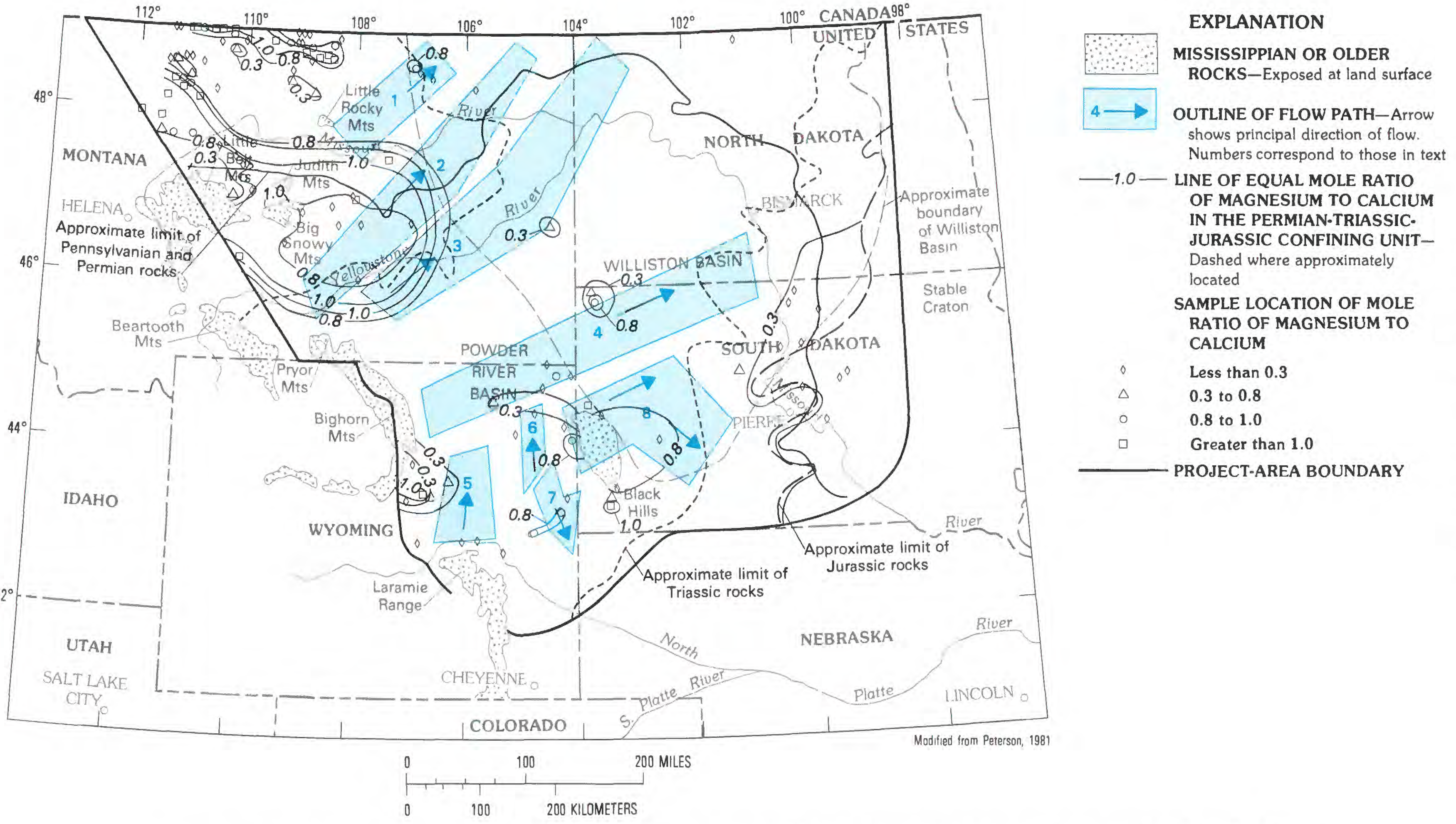
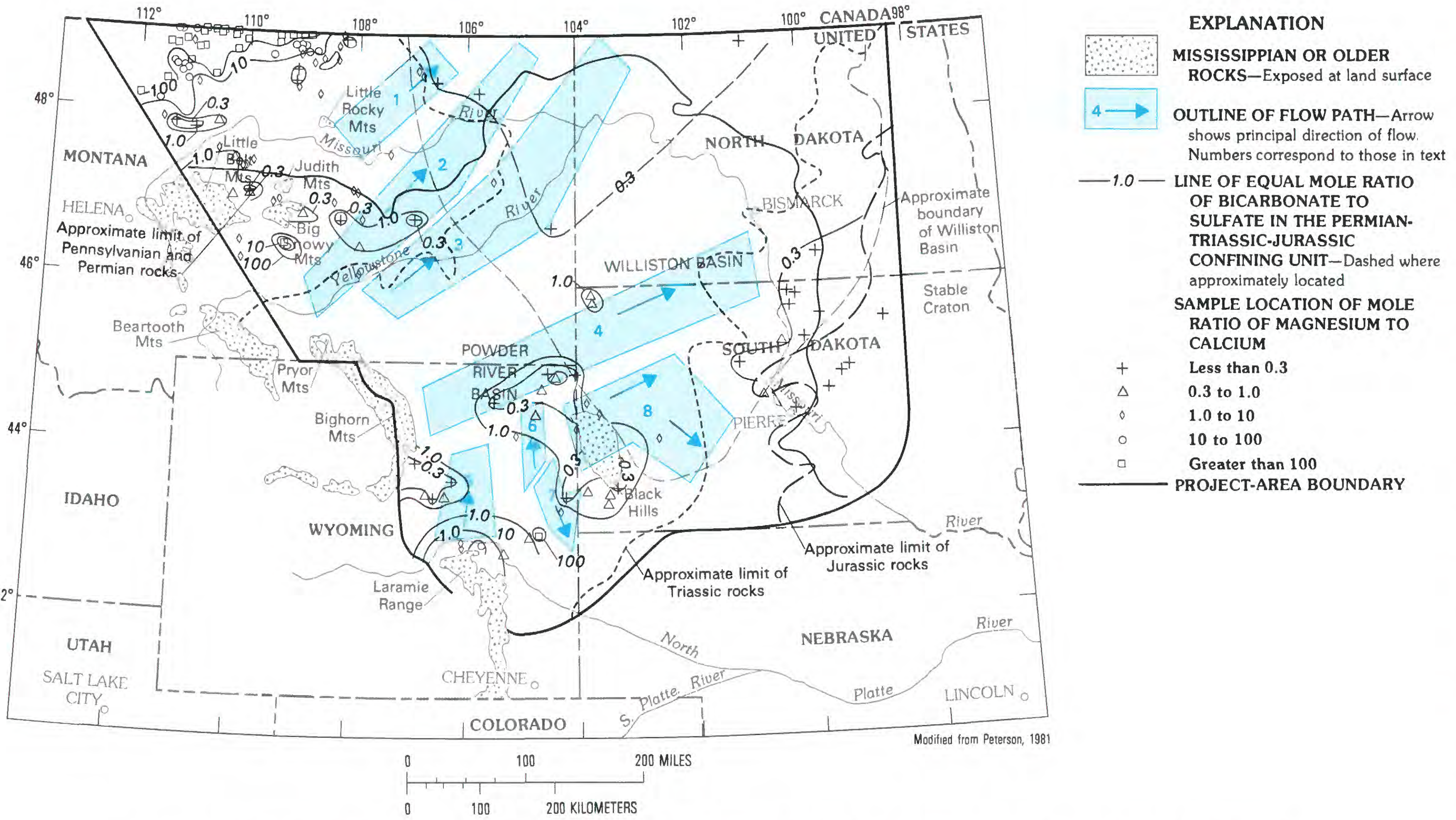


FIGURE 60.—Mole ratio of magnesium to calcium in water from the Permian-Triassic-Jurassic confining unit in the northern Great Plains.



Modified from Peterson, 1981

FIGURE 61.—Mole ratio of bicarbonate to sulfate in water from the Permian-Triassic-Jurassic confining unit in the northern Great Plains.

TABLE 14.—*Summary of plausible mechanisms controlling chemical composition of water from the Permian-Triassic-Jurassic confining unit*

Mechanism	Evidence
Dissolution of calcite or gypsum.	Concentration of calcium, bicarbonate, and sulfate in highland areas.
Cation exchange or calcite precipitation.	Decrease in relative concentrations of calcium and magnesium and the concurrent increase in sodium concentration. Change in facies from 2 to 3.
Sulfate reduction.	Large mole ratio of bicarbonate to sulfate. Change in facies from 3 to 4; no sulfate simple-salt component.
Dissolution of halite or leakage.	Increase in sodium and chloride concentrations. Change from facies 3 and 4 to facies 5, dominated by sodium chloride simple salt.

concentration occurs in the basins, mainly because the residence time of water in the aquifers in the basins is longer than in the uplands because of decreased permeability in the aquifer materials and because of smaller hydraulic gradient. In eastern North Dakota and eastern South Dakota, rocks older than the Dakota Sandstone pinch out in the subsurface confining units, are thinner, or do not exist in this area. Potentiometric surfaces of the underlying aquifers are higher than those of the Lower Cretaceous aquifers. As a result, water from underlying Paleozoic aquifers leaks upward in the pinch-out area. The water chemistry varies within the pinch-out area because of differences in chemical composition between the water upgradient in the Lower Cretaceous aquifers and underlying aquifers and the proportions of the waters mixed.

The chemical characteristics of water from the Lower Cretaceous aquifers of the northern Great Plains are affected principally by the chemistry of recharge water, water-rock interactions, and sulfate reduction of the water in the aquifers. Recharge occurs as either infiltration of precipitation and streamflow on the outcrop, which may be covered by soil, or as leakage from other aquifers. Depending on the chemistry of the leaking and receiving waters and the proportions of mixing between the two waters, leakage may increase the concentrations of some ions while decreasing others. Therefore, changes in water chemistry along a flow path that cannot be explained by the aquifer mineralogy may indicate leakage from another aquifer. This hypothesis is supported by the hydraulic-head difference between the aquifers and the water chemistry of both aquifers.

REGIONAL GEOCHEMICAL TRENDS

The presentation of regional geochemical trends will differ in format from that used for the underlying hydrogeologic units. Each of the hydrogeologic uplands, basins, and pinch-out areas will be discussed separately by using changes in ion concentrations and pH along hypothetical flow paths to demonstrate the geochemical evolution. The flow paths were drawn orthogonal to equipotential lines on maps of the potentiometric surfaces.

UPLAND AREAS

The areal distributions of dissolved solids, the major solutes, and the hydrochemical facies in the two aquifers that contain rocks of Early Cretaceous age, the Inyan Kara and Dakota aquifers, are discussed with respect to each of the three hydrogeologic areas. The upland areas are the hills and ranges where the aquifers have been uplifted and are exposed at land surface or are relatively shallow. As a result, the aquifers receive water from infiltration of precipitation and streamflow. The upland areas are the Little Belt, Big Snowy, Pryor, and Bighorn Mountains, the

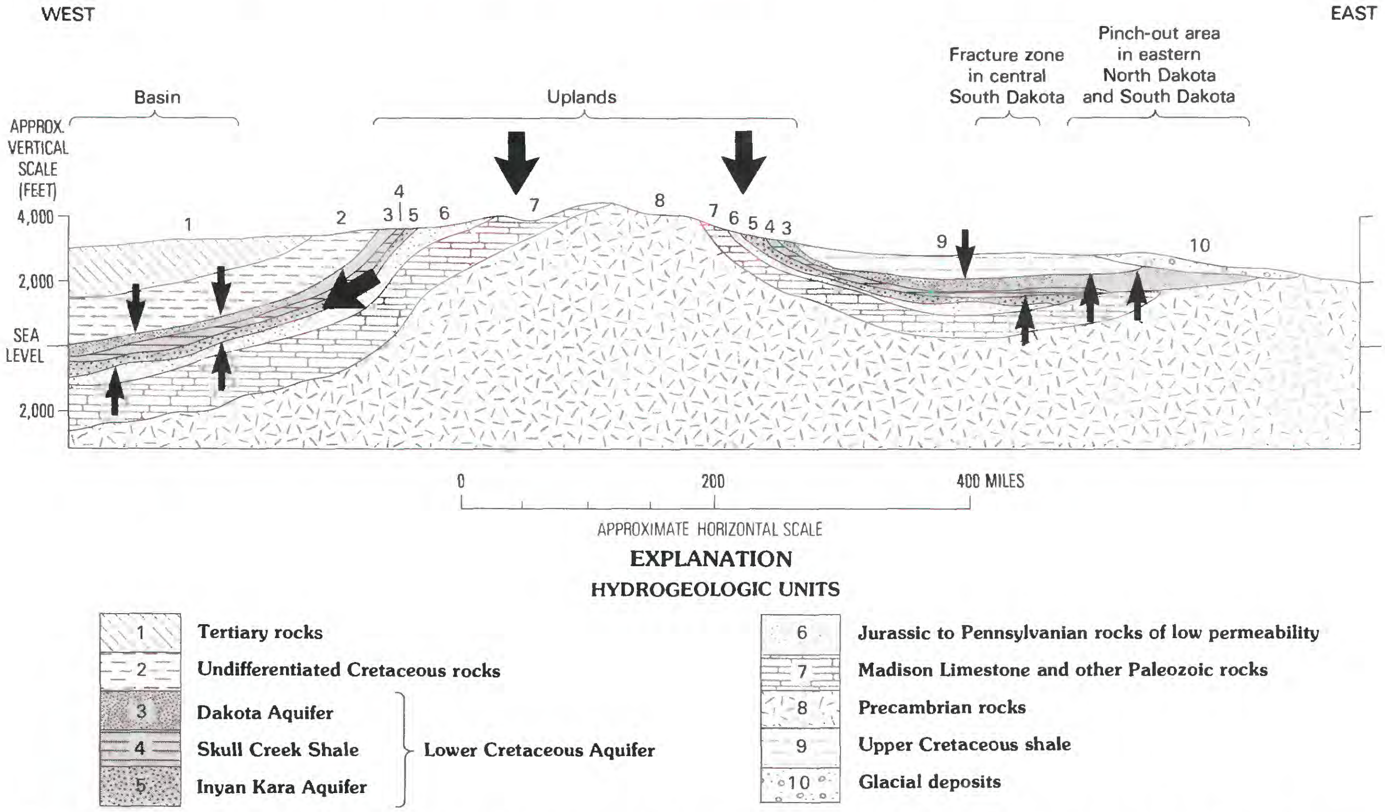


FIGURE 62.—Hydrogeologic areas important to the flow system of the Lower Cretaceous aquifers in the northern Great Plains. Arrows indicate direction of flow.

Laramie Range, and the Hartville and Black Hills uplifts (fig. 1). Characteristics of recharge water and the changes that occur as water moves downgradient toward the basins are discussed here for the two Lower Cretaceous aquifers.

INYAN KARA AQUIFER

The effect of recharge in the upland areas is shown on the ion-concentration maps of the Inyan Kara aquifer. Near outcrop areas, the concentration of dissolved solids in water from the Inyan Kara aquifer is less than 500 mg/L (fig. 63); sodium plus potassium is less than 500 mg/L (fig. 64); bicarbonate plus carbonate is less than 300 mg/L (fig. 65); and chloride is less than 250 mg/L (fig. 66). In general, calcium and magnesium concentrations are slightly larger in these outcrop areas than downgradient (figs. 67 and 68). The calcium concentration within 30 mi of the outcrops generally is 50–100 mg/L and, excluding the basins, less than 30 mg/L farther downgradient. In the same area, within 12 mi of the outcrop, the magnesium concentration is generally 15–40 mg/L and, excluding the basins, less than 10 mg/L farther downgradient. Sulfate concentration generally exceeds 500 mg/L in a zone about 30 mi wide adjacent to the outcrop areas bounding the southern Powder River basin (fig. 69). Sulfate concentrations exceed 3,000 mg/L in an area about 25 mi northwest of the Hartville uplift. In general, concentration of sulfate is less than 500 mg/L near the outcrop in the Black Hills and Bighorn Mountains. Small areas where sulfate concentration exceeds 500 mg/L also occur near the outcrop in central Montana.

Because of the small concentrations of chloride in most upland areas, the anion hydrochemical facies tend to be bicarbonate, sulfate, or a mixture of the two in most upland areas (fig. 70). Northeast of the Bighorn and Pryor Mountains, the facies is a mixture of bicarbonate and chloride, based on two data points, one 12 mi, the other 31 mi from the outcrop (see fig. 1 for structural features).

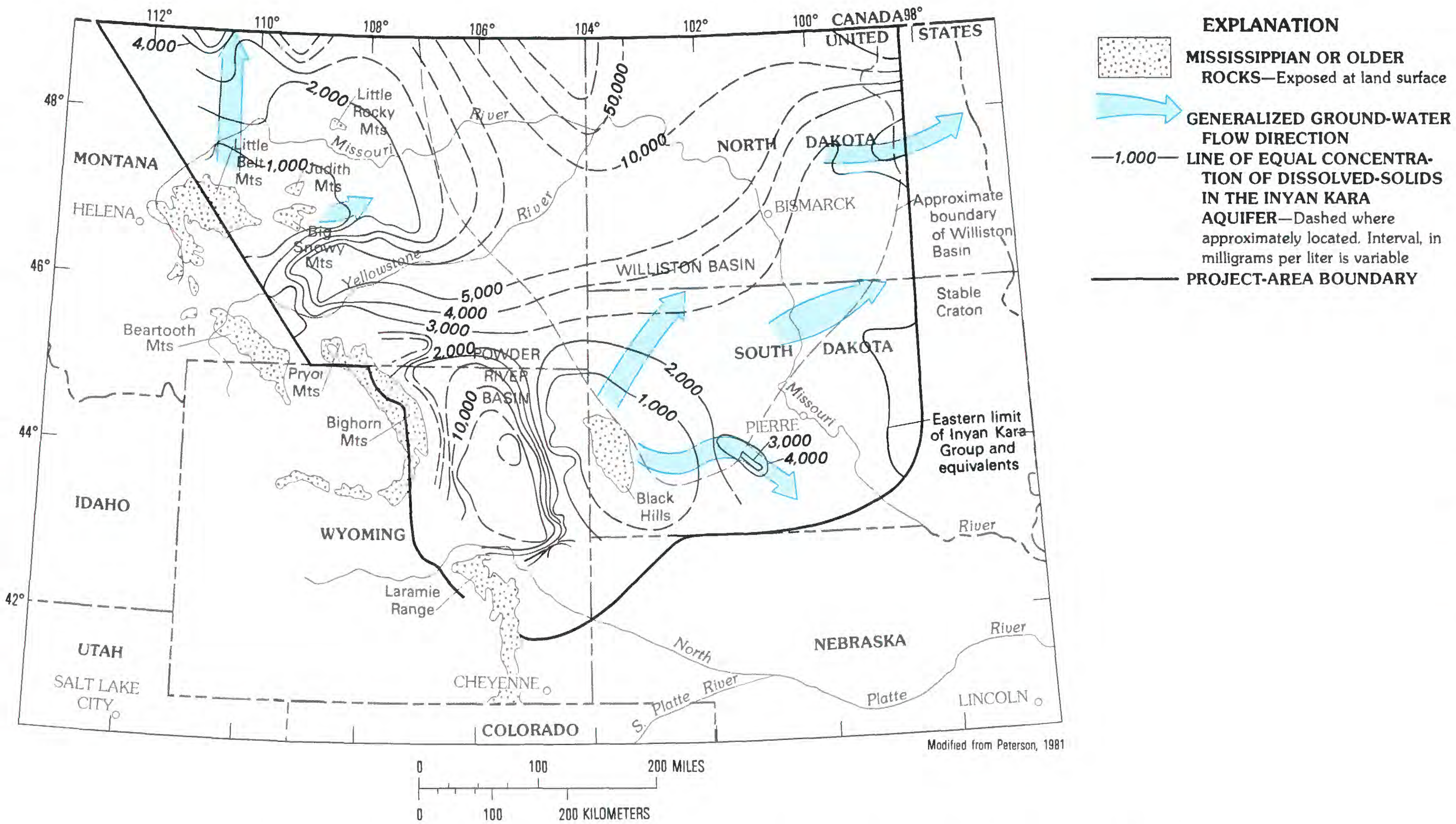


FIGURE 63.—Concentration of dissolved solids in water from the Inyan Kara aquifer in the northern Great Plains.

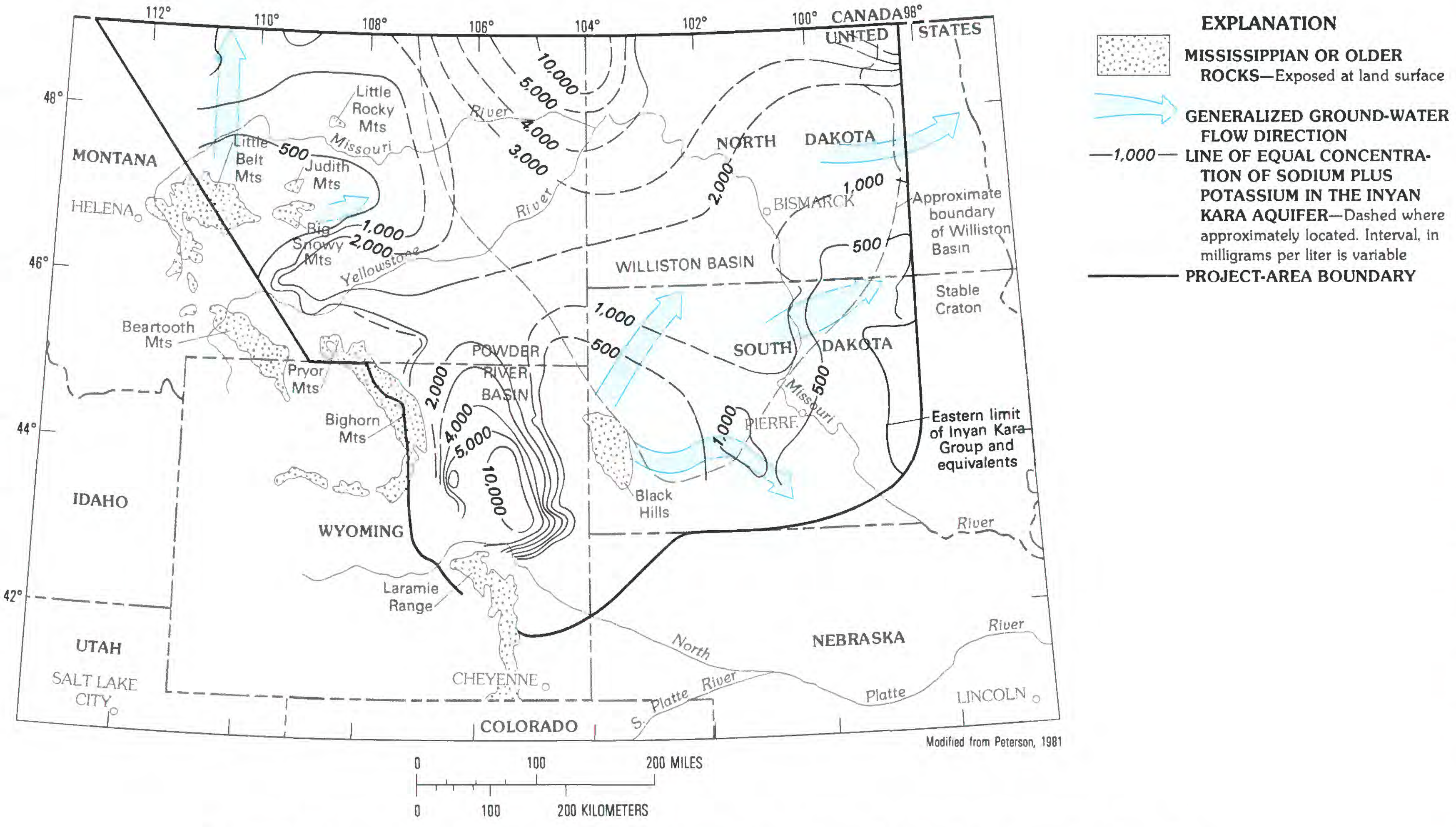


FIGURE 64.—Concentration of sodium plus potassium in water from the Inyan Kara aquifer in the northern Great Plains.

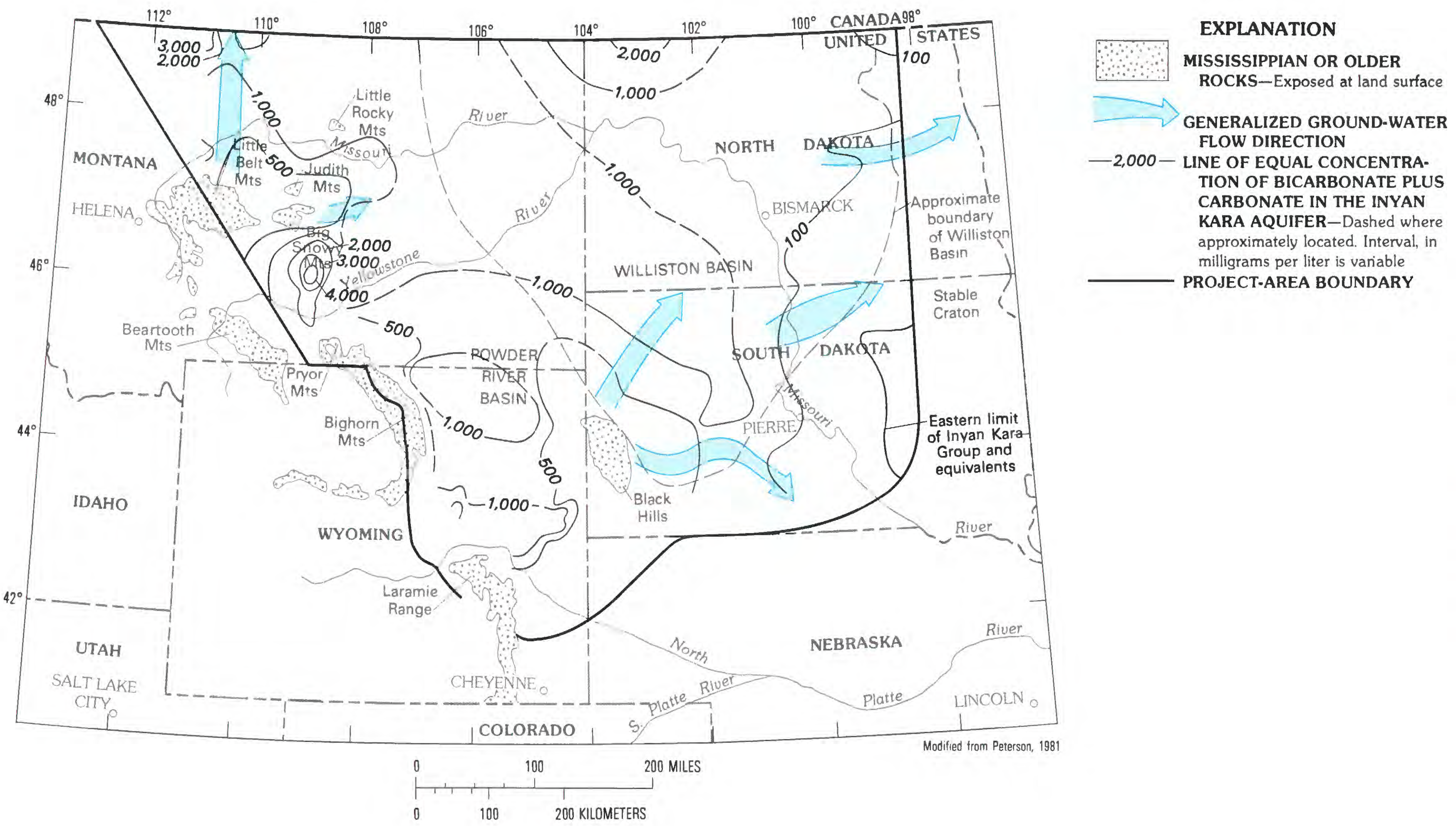


FIGURE 65.—Concentration of bicarbonate plus carbonate in water from the Inyan Kara aquifer in the northern Great Plains.

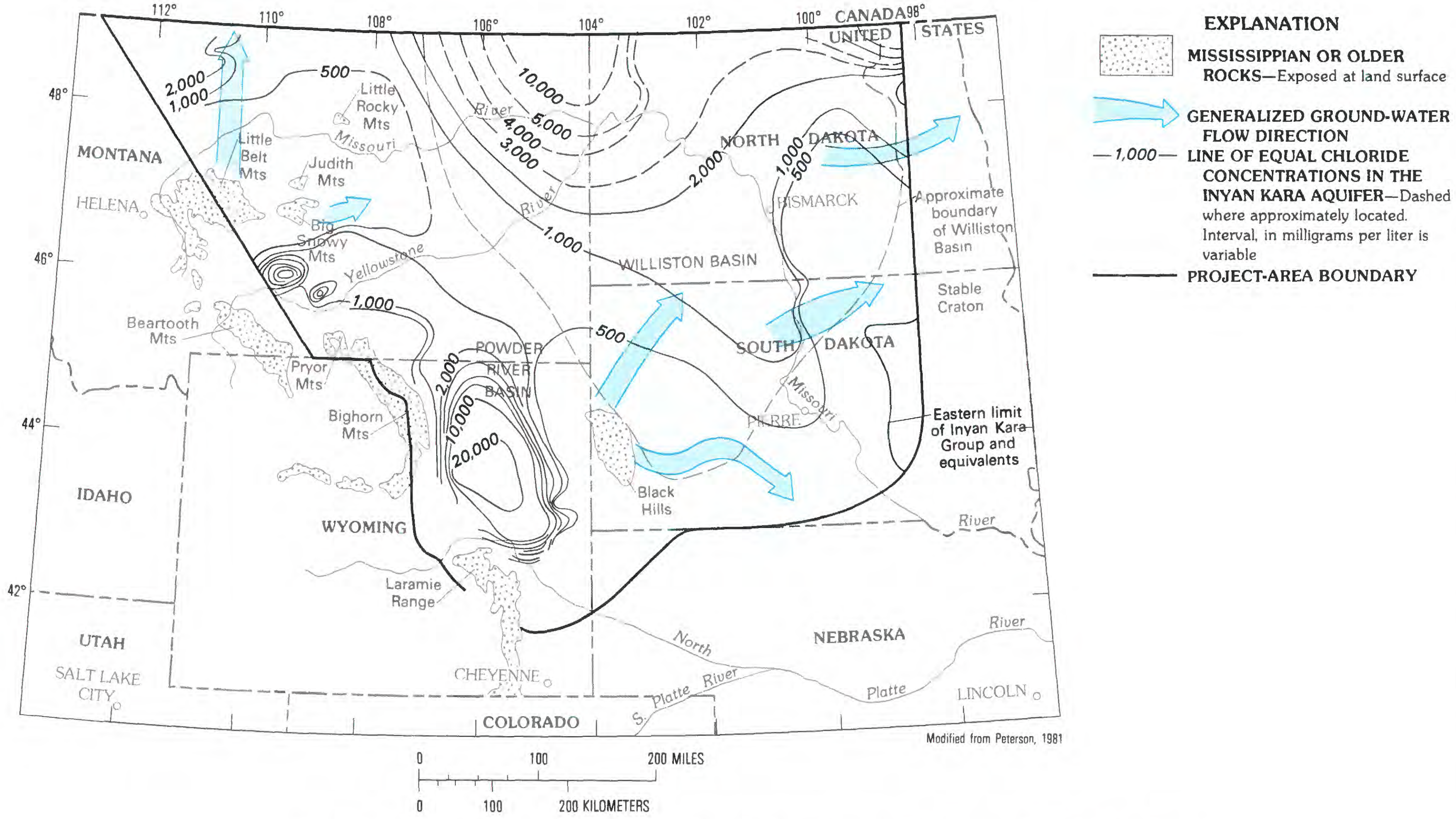


FIGURE 66.—Concentration of chloride in water from the Inyan Kara aquifer in the northern Great Plains.

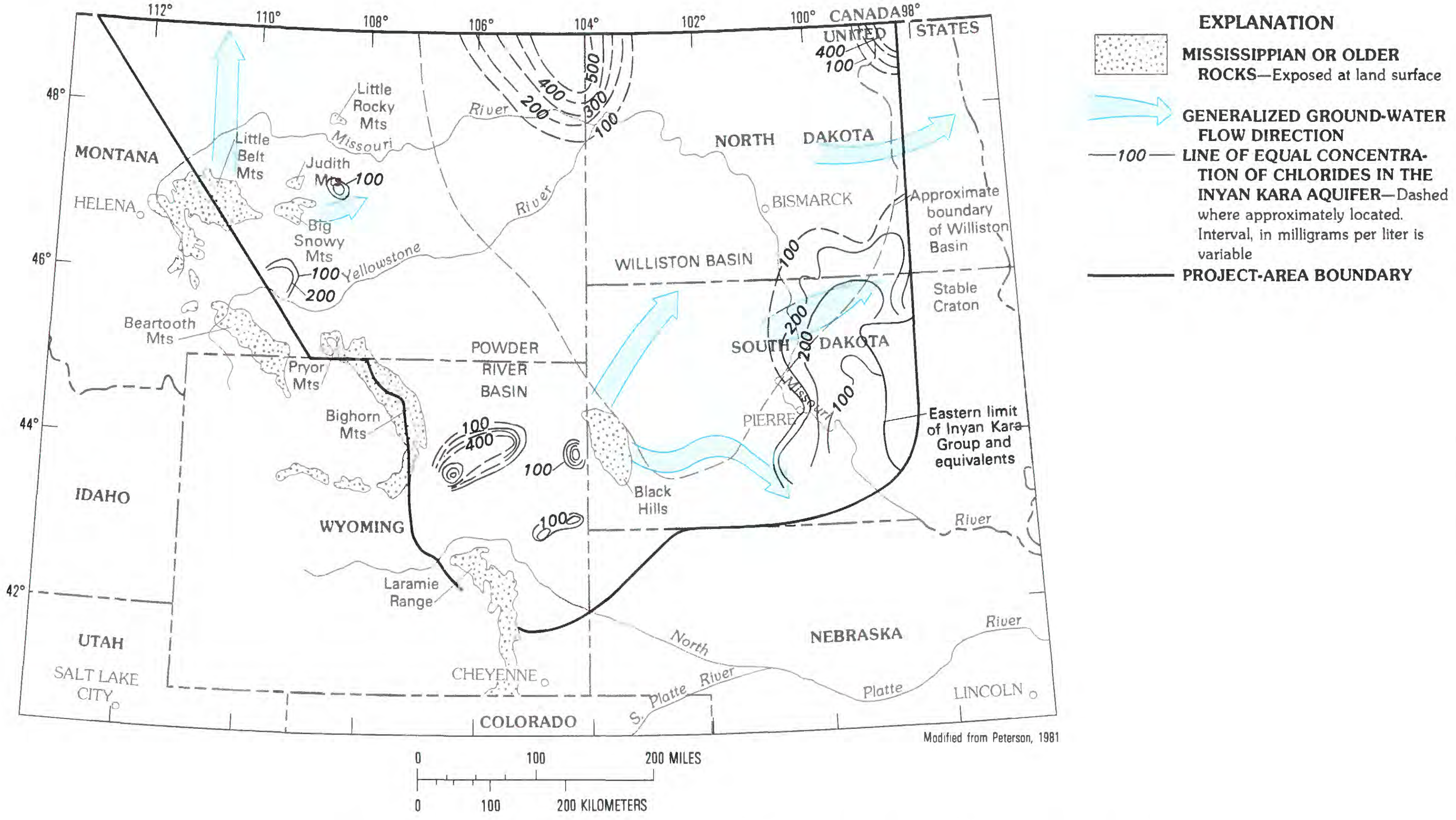


FIGURE 67.—Concentration of calcium in water from the Inyan Kara aquifer in the northern Great Plains.

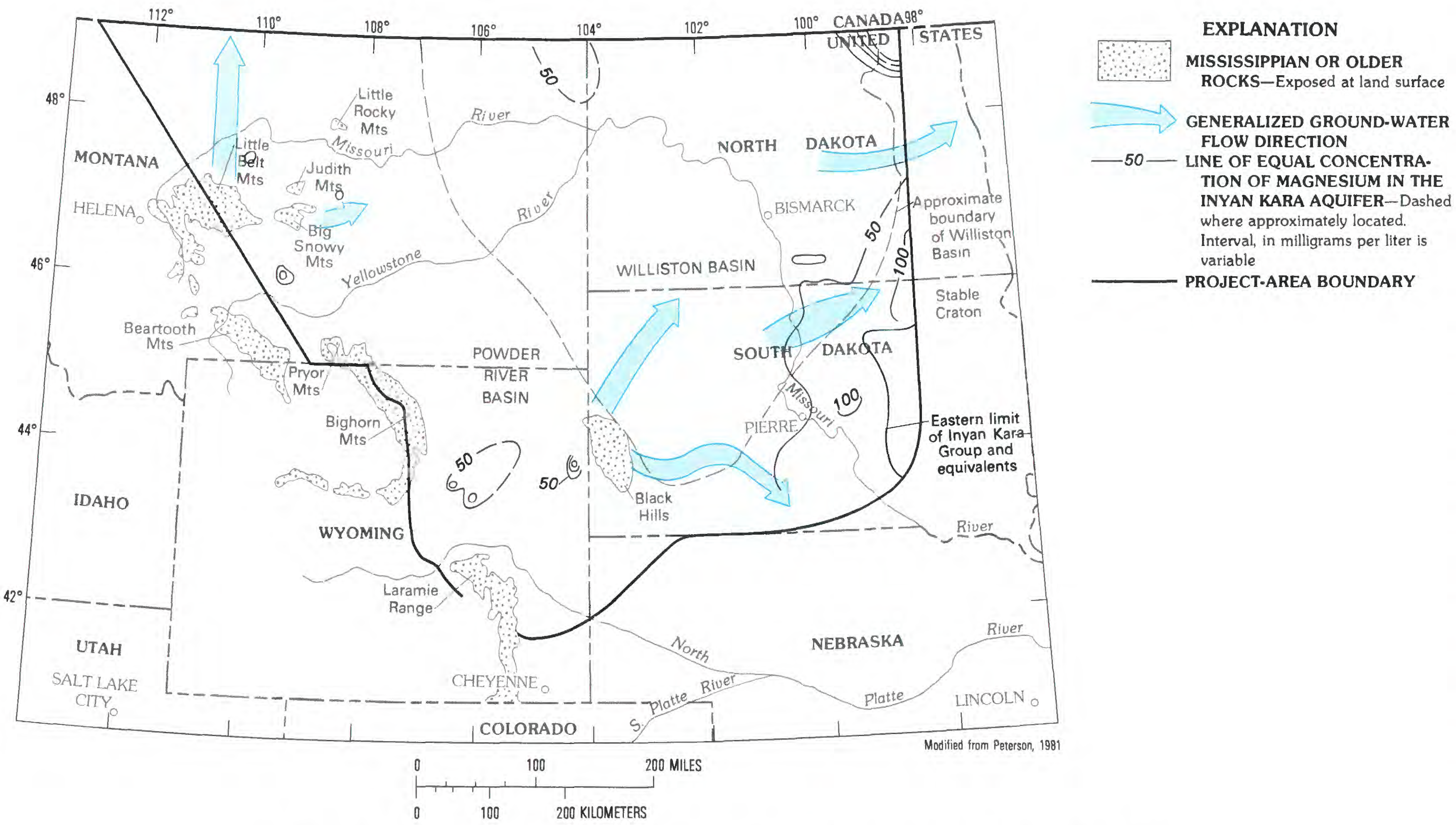


FIGURE 68.—Concentration of magnesium in water from the Inyan Kara aquifer in the northern Great Plains.

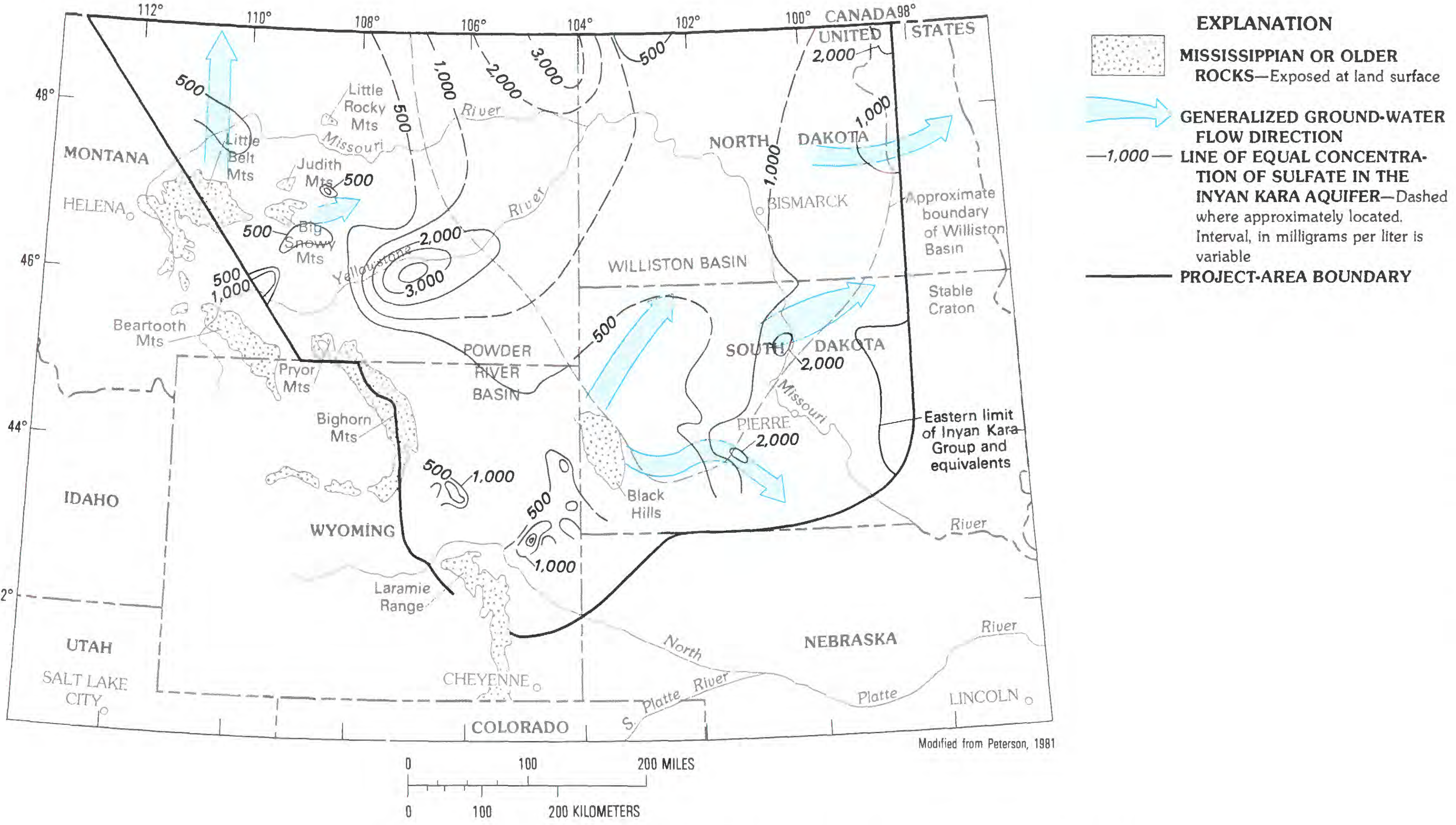


FIGURE 69.—Concentration of sulfate in water from the Inyan Kara aquifer in the northern Great Plains.

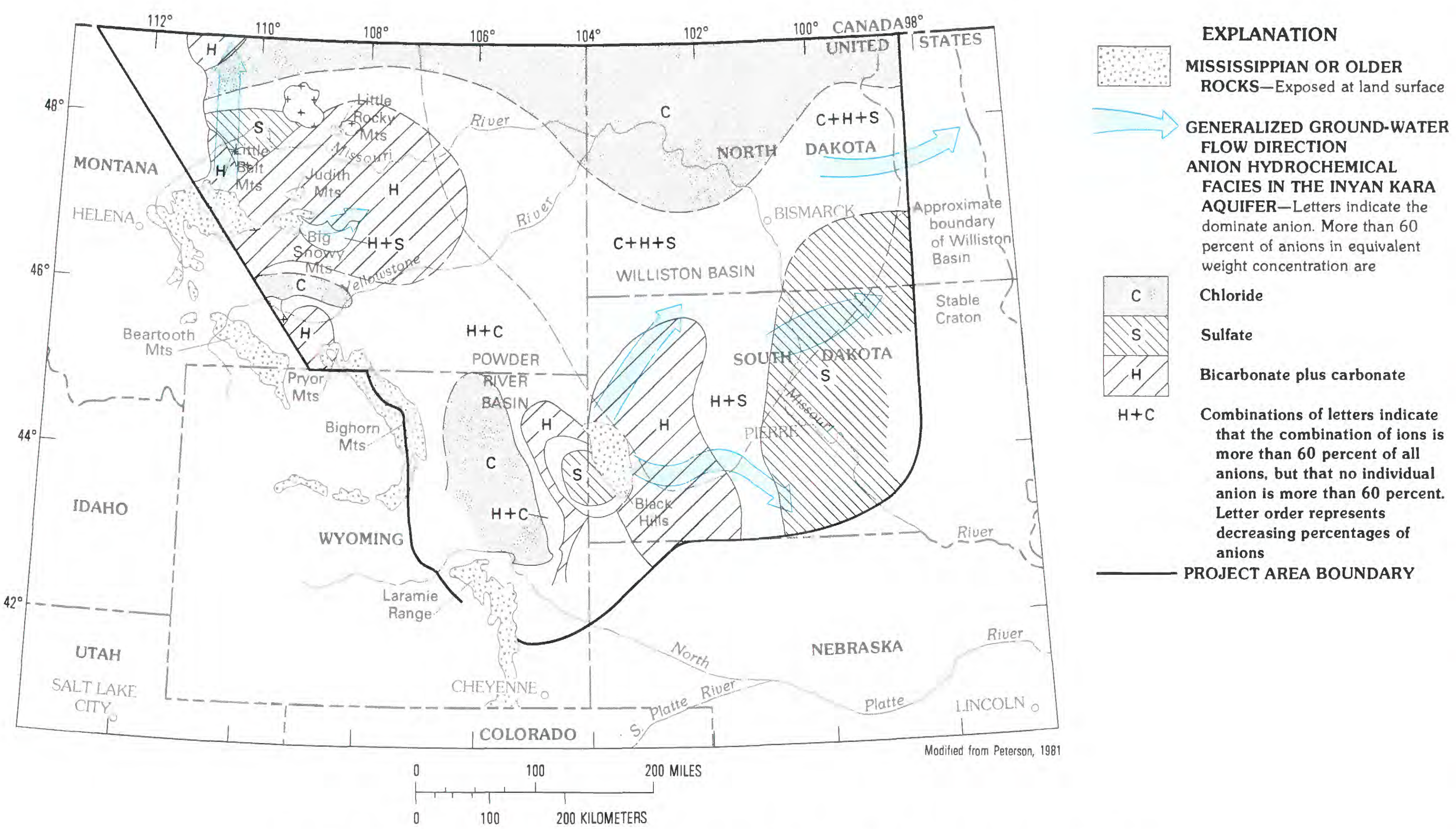


FIGURE 70.—Anion hydrochemical facies in water from the Inyan Kara aquifer in the northern Great Plains.

Dakota Aquifer

The concentrations of the principal ions in water from the Dakota aquifer are similar to those in the Inyan Kara in the upland areas where the Dakota also is recharged by infiltration of precipitation and streamflow. Concentration of dissolved solids in these areas of the Dakota aquifer is less than 3,000 mg/L (fig. 71); sodium is less than 1,000 mg/L (fig. 72); bicarbonate is less than 500 mg/L (fig. 73); and chloride is less than 250 mg/L (fig. 74). The sulfate concentration is less in water from the Dakota than the Inyan Kara aquifer (fig. 75). Within the upland areas, the largest concentrations of calcium (greater than 50 mg/L) and magnesium (greater than 15 mg/L) occur in a 12-mile-wide zone around the outcrop in the Hartville and Black Hills uplifts and in the Laramie Range (figs. 76 and 77). The hydrochemical facies is bicarbonate in the upland areas, except in the northern Black Hills uplift, or along the Montana–Wyoming State line, where the facies is a mixture of bicarbonate and sulfate (fig. 78; see fig. 1 for structural features).

Evolution Of Water Chemistry

In the recharge areas, near the outcrops of the Inyan Kara and the Dakota aquifers, the water chemistry is controlled by reaction of the water with soil and aquifer materials. Sulfate reduction becomes important as the water flows downgradient in the aquifer.

To illustrate the changes in the hydrochemistry as the water moves downgradient, analyses from flow path 2 in the Inyan Kara aquifer in central Montana and from flow path 1 in the Dakota aquifer in southeastern Montana, were investigated (see fig. 19 for flow-path locations).

Analyses from the Dakota aquifer flow path 1 are listed in table 15 and from Inyan Kara aquifer flow path 2 in table 16. Water-rock interactions and sulfate reduction change the chemistry of the water as it moves downgradient from the outcrop area toward the basins (figs. 79–82). As the water moves downgradient, calcium and magnesium carbonate cements are precipitated; the cements were identified in the Inyan Kara Group by Gott and others (1974). As calcium and magnesium carbonates are precipitated, concentrations of calcium and magnesium decrease from more than 60 percent of the cation population to less than 10 percent (figs. 79 and 80). Sulfide minerals may be oxidized locally, adding sulfate ions to the water. In the southern Black Hills, sulfate concentrations are in excess of 500 mg/L, possibly because of localized leakage from deeper aquifers (Gott and others, 1974).

Feldspar, which also occurs in the Inyan Kara Group (Gott and others, 1974), probably is weathering to clays, releasing calcium, sodium, potassium, and silica to solution, and producing a net increase in the concentration of sodium and pH (figs. 79 and 81). Cation exchange may be removing calcium and magnesium and adding sodium and potassium. The observed downgradient decrease in the concentration of dissolved sulfate with a concommitant increase in the concentration of dissolved bicarbonate is consistent with the bacterially mediated reduction of sulfate (Foster, 1950) (figs. 80–82).

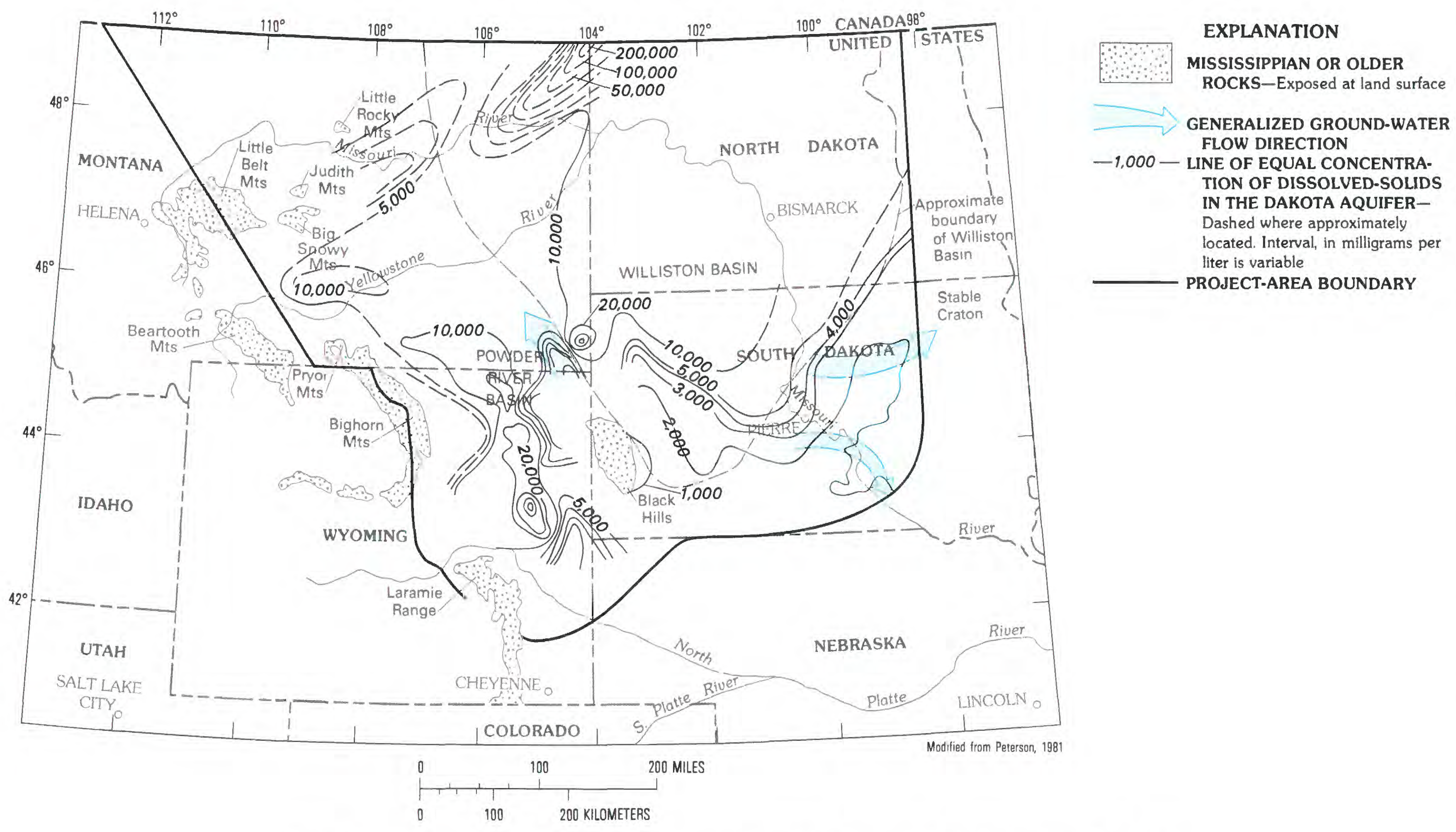
Chloride concentrations increase as the water moves downgradient toward basin centers (fig. 74), possibly because either leakage from other, more saline units is beginning to be substantial or because interstitial chloride in connate water is being released (Hem, 1970). The presence of connate water is not indicated by the stable isotope data. For example, a well in the Dakota aquifer, 100 mi east of the Black Hills, has a moderate concentration of chloride (920 mg/L) but a δO^{18} of –18.00 $^{\circ}/_{oo}$ (V–SMOW) and δD of –86.00 $^{\circ}/_{oo}$ (V–SMOW), values that are on the meteoric water line (Faure, 1977).

BASINS

The Bull Mountain, Powder River, and Williston basins are the three major basins in the northern Great Plains study area (fig. 1). Water from upland areas moves toward the basin through the Lower Cretaceous aquifers. Vertical leakage from underlying aquifers may add substantial volumes of water to the Inyan Kara and Dakota aquifers in the basins.

Inyan Kara Aquifer

The principal ion concentrations are always larger in the basins than in the uplands (figs. 63–69) and, for some ions, several orders of magnitude larger. Dissolved-solids concentrations, for example, exceed 10,000 mg/L in the Powder River and Williston basins. Sodium is the most abundant cation, exceeding 10,000 mg/L in the Powder River and Williston basins. Calcium exceeds 400 mg/L in the Bull Mountain and Williston basins and 1,000 mg/L in the Powder River basin. Bicarbonate concentrations exceed 4,000 mg/L in the Bull Mountain basin and 2,000 mg/L in the Powder River and Williston basins. Sulfate concentrations exceed 1,000 mg/L in the eastern part of Bull Mountain basin and the Williston basin. In the Powder River basin, sulfate concentrations are



Modified from Peterson, 1981

FIGURE 71.—Concentration of dissolved solids in water from the Dakota aquifer in the northern Great Plains.

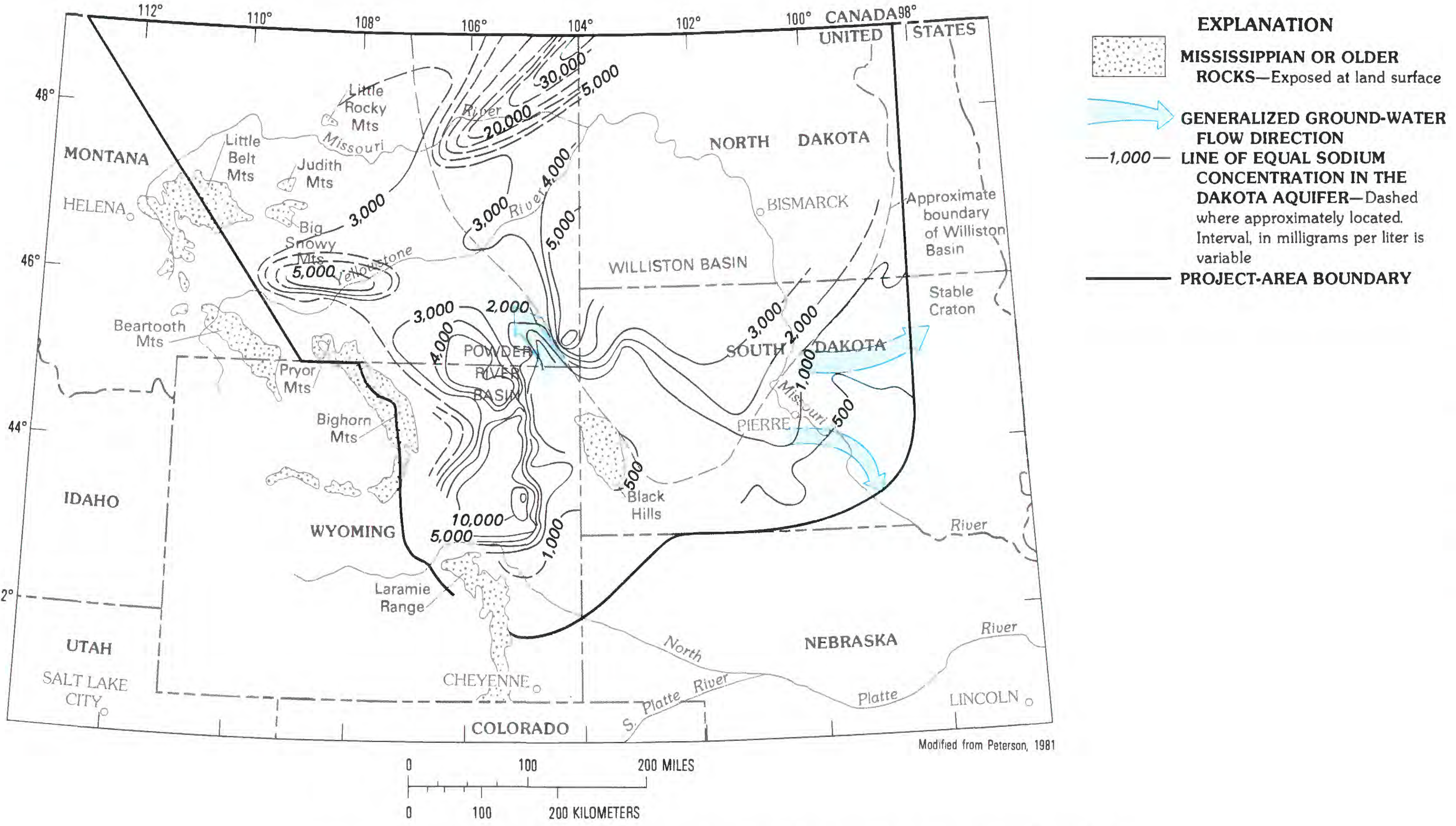


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FIGURE 72.—Concentration of sodium in water from the Dakota aquifer in the northern Great Plains.

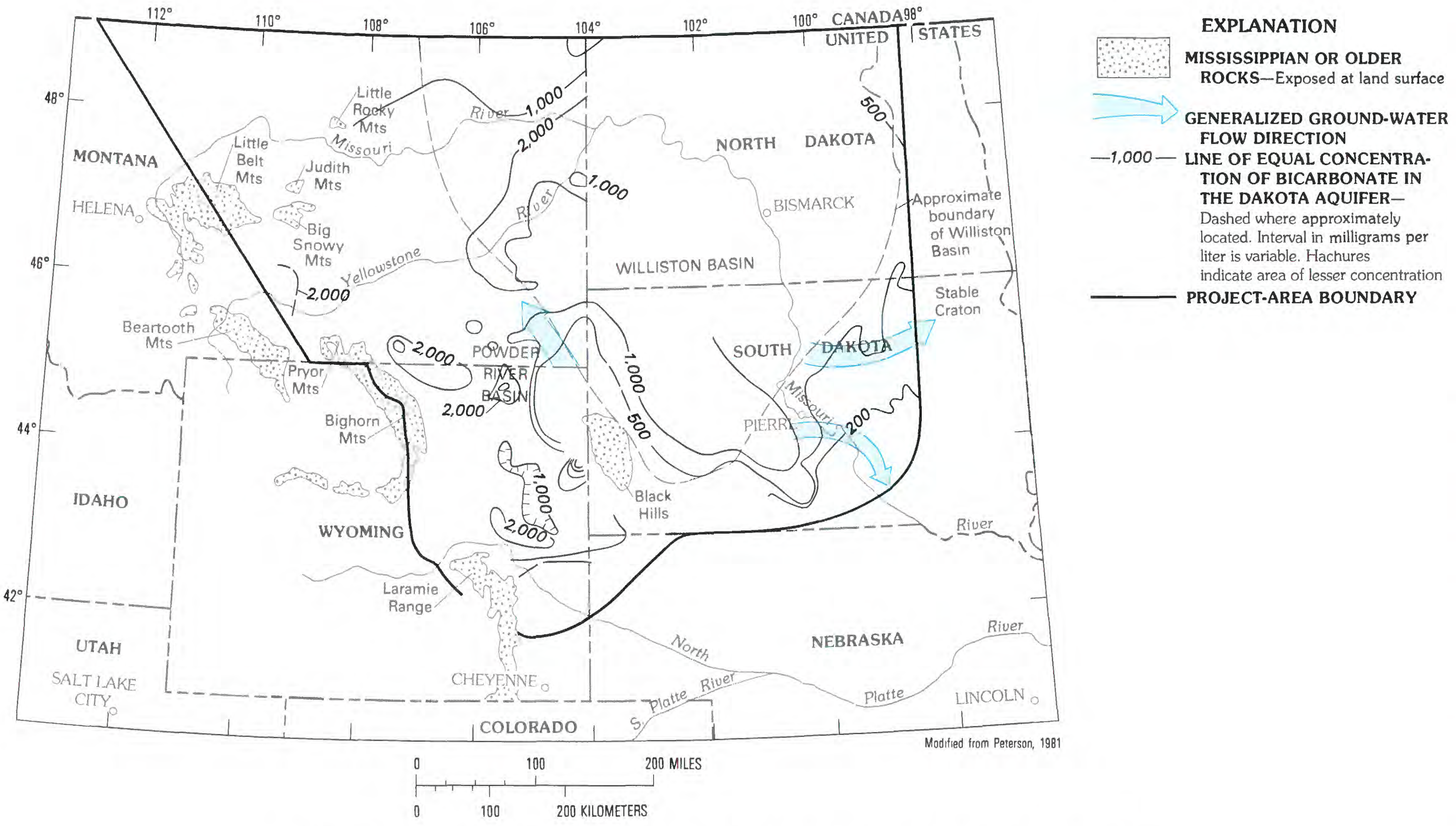

FIGURE 73.—Concentration of bicarbonate in water from the Dakota aquifer in the northern Great Plains.

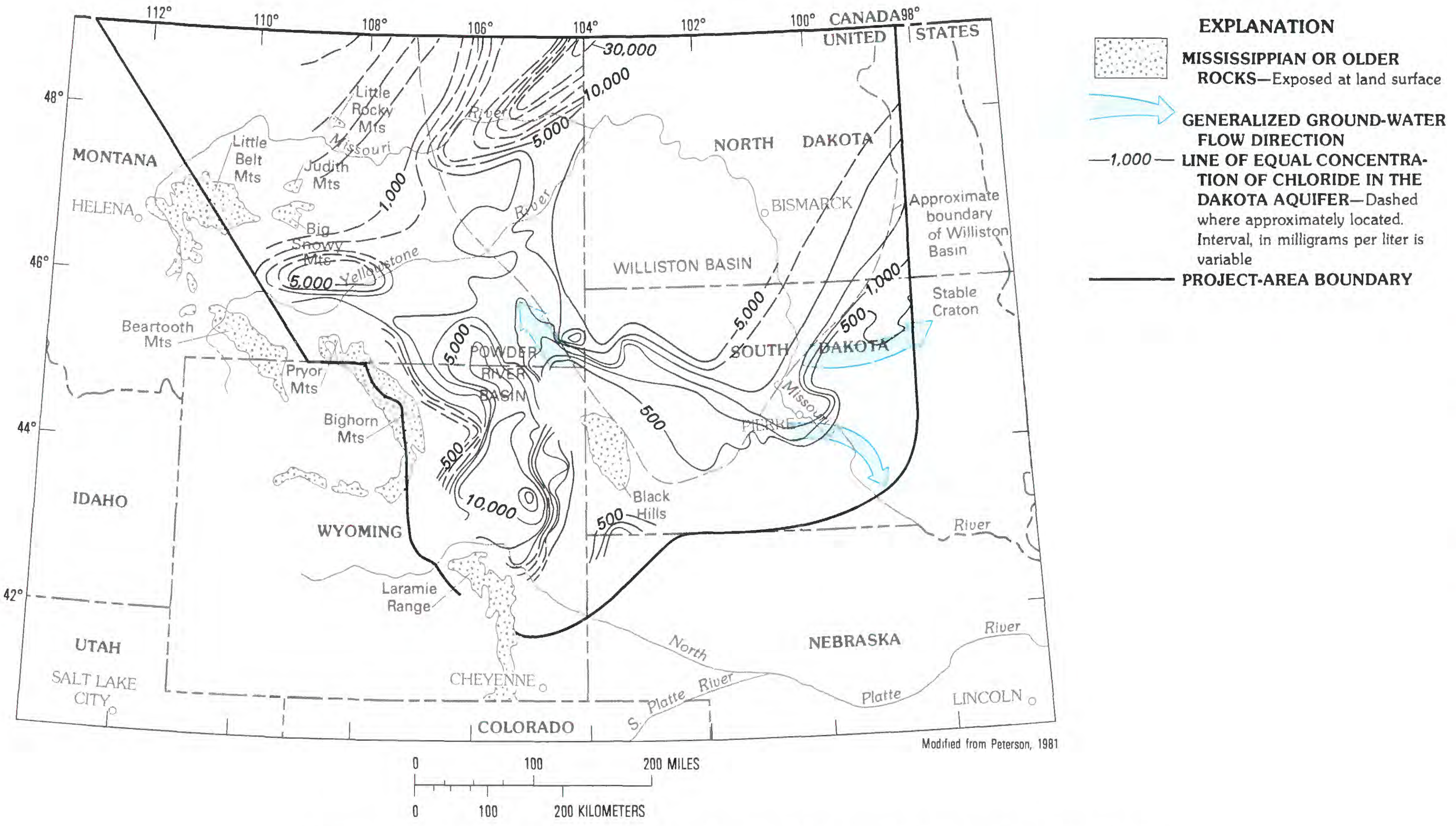

FIGURE 74.—Concentration of chloride in water from the Dakota aquifer in the northern Great Plains.

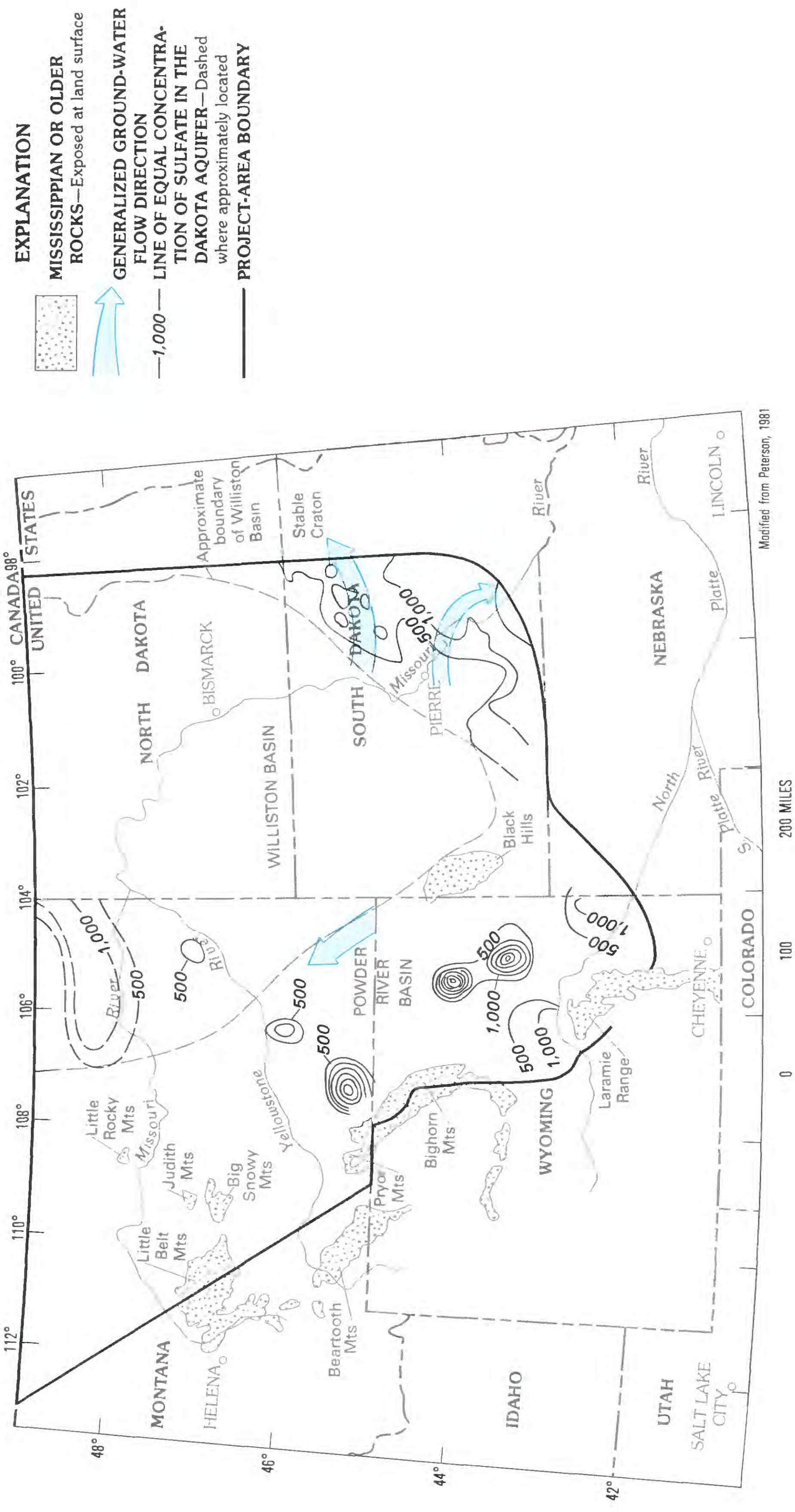

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FIGURE 75.—Concentration of sulfate in water from the Dakota aquifer in the northern Great Plains.

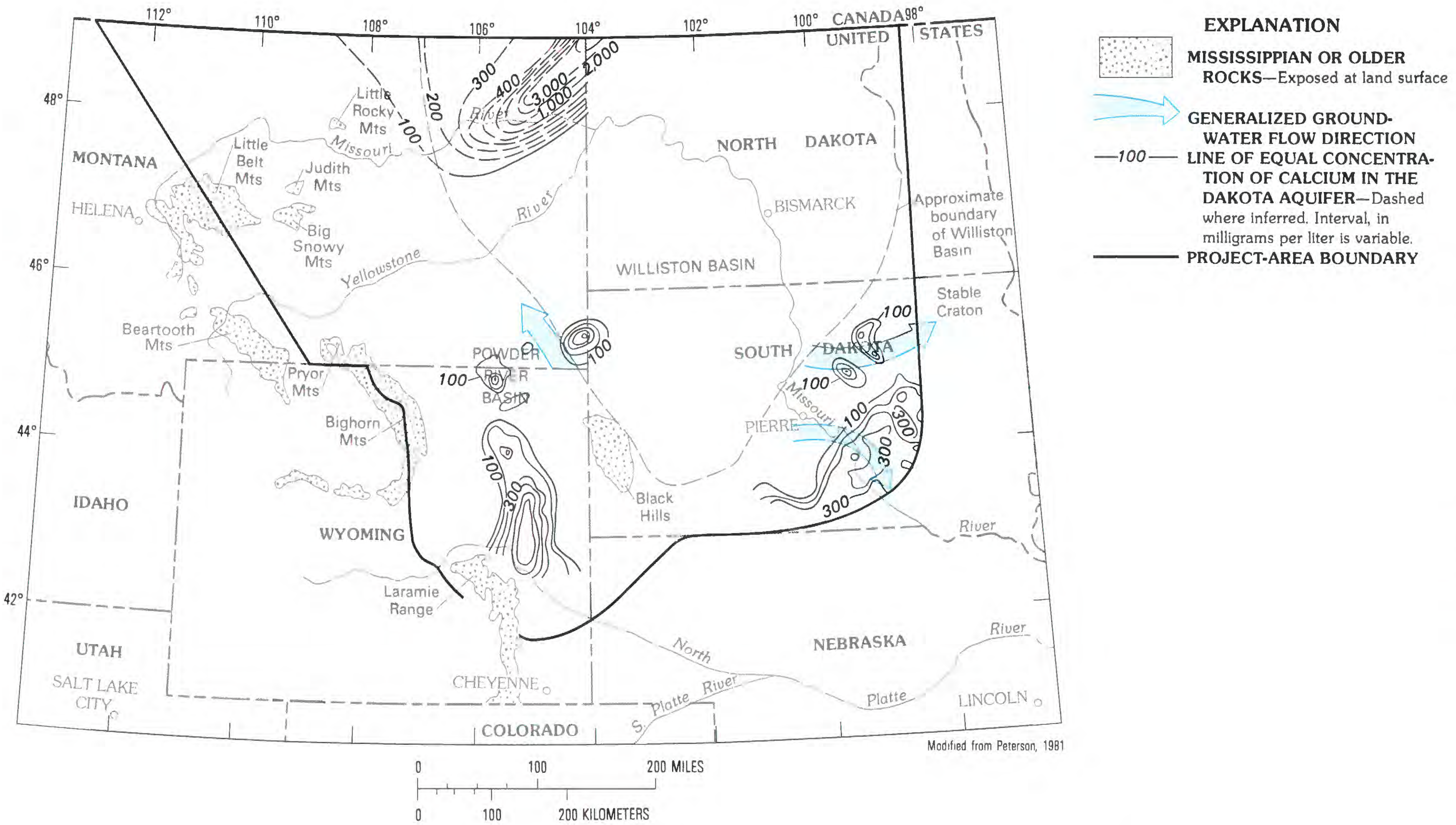

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FIGURE 76.—Concentration of calcium in water from the Dakota aquifer in the northern Great Plains.

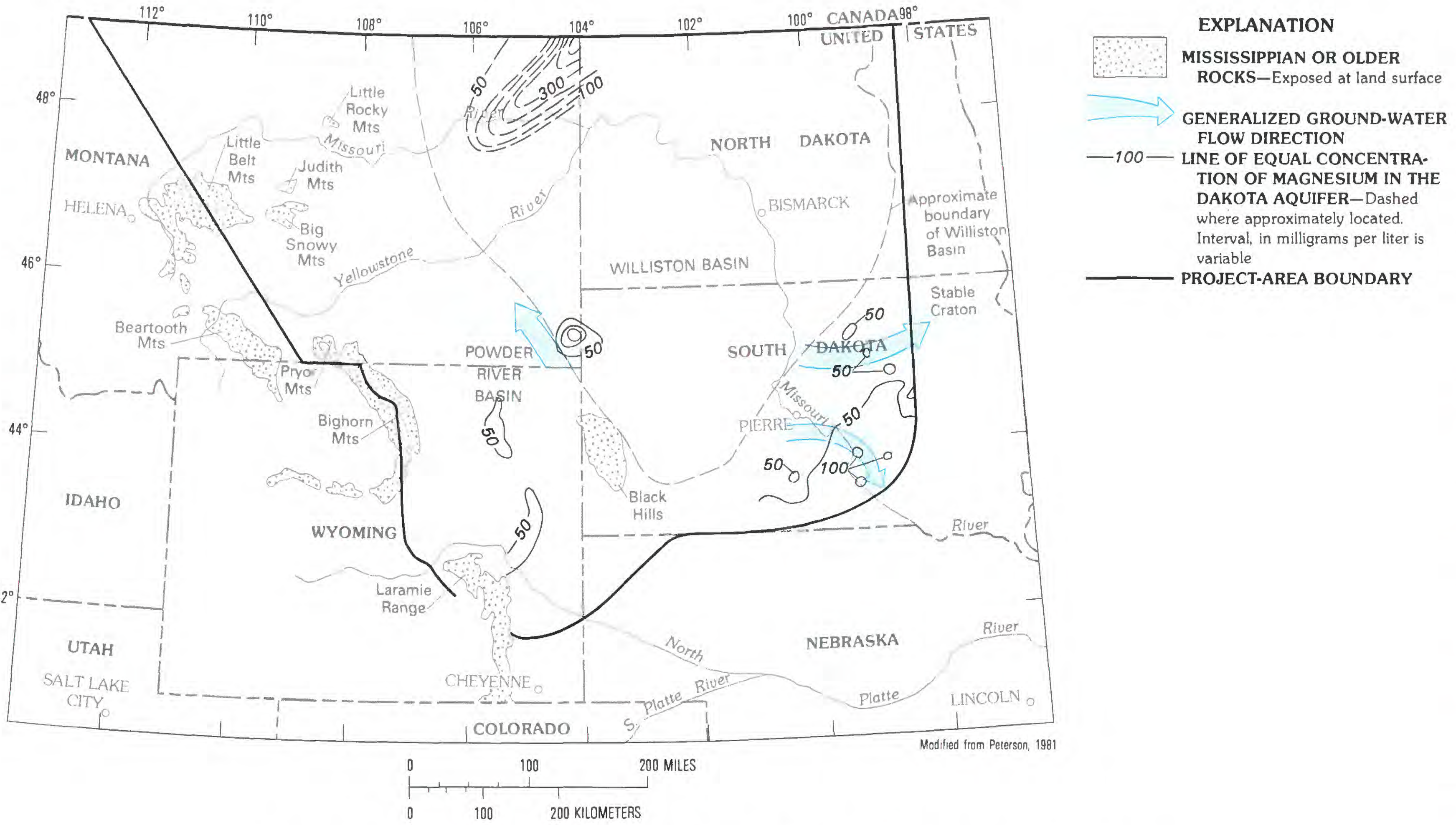

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FIGURE 77.—Concentration of magnesium in water from the Dakota aquifer in the northern Great Plains.

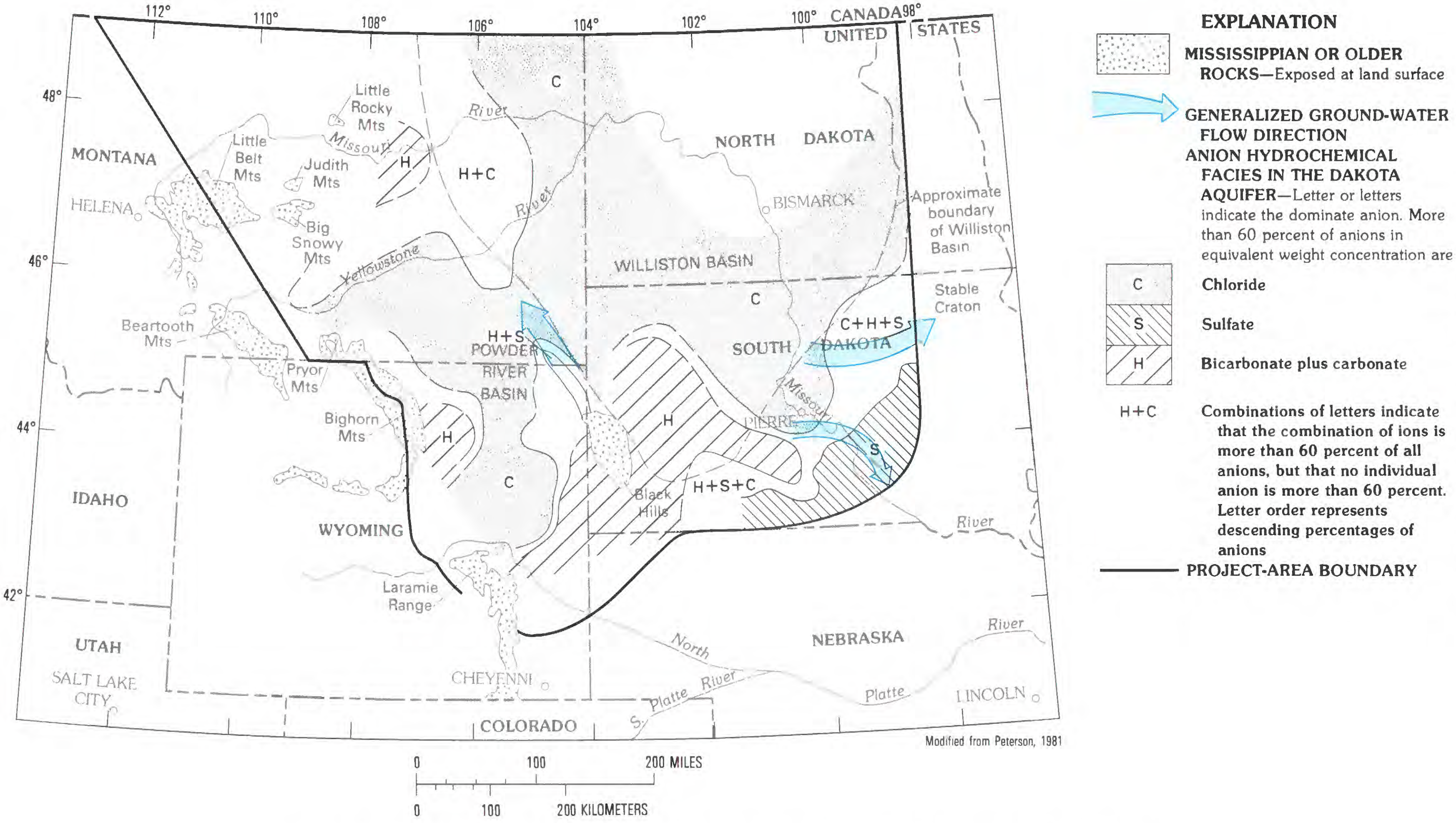

FIGURE 78.—Anion hydrochemical facies in water from the Dakota aquifer in the northern Great Plains.

TABLE 15.—*Chemical composition of water from flow path 1 of the Dakota aquifer in southeastern Montana*

[Location of flow path shown in figure 19. Listed in approximate downgradient order: a, Newcastle Sandstone; b, Muddy Sandstone; °C, °Celsius; pH, pH units, µS/cm, microsiemens per centimeter at 25 °Celsius; mg/L, milligrams per liter µg/L, micrograms per liter]

Station identification number	Sample number	Geologic formation	Temperature (°C)	pH	Specific conductance (µS/cm)	Dissolved solids, calculated (mg/L)	Dissolved iron µg/L)	Sodium	Potassium	Calcium	Magnesium	Chloride	Sulfate	Bicarbonate
								(mg/L)						
450256104274101	1	a	17	--	1,280	854	2,100	210	13	47	19	7.0	430	260
451300104324401	2	b	--	8.2	--	2,820	--	1,100	0	14	4.0	1,400	38	544
451535104501701	3	b	--	8.2	--	4,490	--	1,700	0	34	15	2,420	0	650
451446104573301	4	b	--	7.6	--	5,200	--	2,000	0	32	7.0	2,600	35	1,080
452821104391501	5	b	--	8.2	7,290	4,140	--	1,600	9	16	8.0	2,100	0	820
453255104570501	6	b	--	7.5	--	5,190	--	2,000	0	27	10	2,600	120	890
453153105110601	7	b	--	8.2	--	6,020	--	2,400	10	20	12	2,900	14	1,354
453153105110601	8	b	--	7.9	10,000	6,390	--	2,500	9	12	10	3,100	49	1,440

less than 500 mg/L. Chloride is the predominant anion in all three basins; concentrations exceed 10,000 mg/L. The anion hydrochemical facies in the three basins generally has a chloride or a mixed chloride and bicarbonate composition.

DAKOTA AQUIFER

The concentrations of the principal ions in water in the Dakota aquifer are generally larger in the basins than anywhere else (figs. 71–78). Dissolved-solids concentrations exceed 10,000 mg/L in the Bull Mountain and Powder River basins and exceed 150,000 mg/L in the Williston basin. Sodium concentrations exceed 5,000 mg/L in the Bull Mountain basin, 20,000 mg/L in the Powder River basin, and 70,000 mg/L in the northern part of the Williston basin. On the Montana–South Dakota border, sodium concentrations exceed 10,000 mg/L. Calcium concentrations are largest in the southern part of the Powder River basin, where they exceed 1,000 mg/L, and the Williston basin, where they exceed 4,000 mg/L. Near the Montana–South Dakota border, calcium concentrations exceed 500 mg/L. Magnesium concentrations are largest in the northern part of the Williston basin, exceeding 600 mg/L, and near the Montana–South Dakota border, exceeding 30 mg/L. The distribution of bicarbonate is dissimiliar from that of the other ions in the basins; though the concentrations exceed 3,000 mg/L in some of these basins, they are less than 1,000 mg/L in the south-central Powder River basin. In the same area, sulfate concentrations exceed 5,000 mg/L. Sulfate concentrations exceed 1,000 mg/L in the northern part of the Williston basin. Chloride concentrations exceed 5,000 mg/L in the Bull Mountain basin, exceed 100,000 mg/L in the Williston basin, and exceed 10,000 mg/L in the southern part of the Powder River basin. Water in each of these areas is dominated by large chloride concentrations, which produce a chloride hydrochemical facies (fig. 79).

EVOLUTION OF WATER CHEMISTRY

As the water moves into the basins from the uplands, the increase in the concentrations of most ions can be explained, in part, by mineral dissolution and residence time. Although minor quantities of chloride-bearing minerals have been reported in the basins of the Lower Cretaceous aquifers, the most likely source of this ion is leakage from the underlying brine-bearing units. A second likely source of chloride ion is the marine shales that occur above and below the Lower Cretaceous aquifers. Miller and Strausz (1980) report the hydraulic head of the Madison aquifer in the Powder River basin as greater than 3,730 ft above sea level, and H.L. Case, III (U.S. Geological Survey, written commun., 1984), reports the hydraulic head of the Inyan Kara aquifer in the same area ranges from 1,220 to 3,730 ft above sea level. Therefore, the potential for upward leakage from the underlying aquifers, through the chloride-rich confining units into the Inyan Kara aquifer, exists.

The presence of larger concentrations of sodium and chloride in the Dakota aquifer than in the underlying Inyan Kara aquifer is difficult to explain. Neither aquifer contains substantial quantitites of bedded halite to explain this observation (Anna, 1986). Leakage from the underlying Madison aquifer through the confining unit into the Inyan Kara aquifer, and finally into the Dakota aquifer, is indicated

TABLE 16.—*Chemical composition of water from flow path 2 of the Inyan Kara aquifer in central Montana*

[Location of flow path shown in figure 19. Listed in approximate downgradient order: a, Kootenai Formation; b, First Cat Creek sandstone of the Kootenai Formation; c, Second Cat Creek sandstone of the Kootenai Formation; d, Third Cat Creek sandstone of the Kootenai Formation; e, Lakota Formation; °C, °Celsius; pH, pH units, µS/cm, microsiemens per centimeter at 25 °Celsius; mg/L, milligrams per liter; µg/L, micrograms per liter]

Station identification number	Sample number	Geologic formation	Temperature (°C)	pH	Specific conductance (µS/cm)	Dissolved solids, calculated (mg/L)	Dissolved iron (µg/L)	Sodium	Potassium	Calcium	Magnesium	Chloride	Sulfate	Bicarbonate
								(mg/L)						
470555109275501	1	a	9.4	7.8	590	368	900	62	3	51	19	1.4	89	290
470500109272001	2	a	8.7	7.7	500	294	520	41	3	44	15	1.6	62	260
470419109271801	3	a	9.0	7.7	580	326	690	110	2	17	6.2	.9	33	320
465910109250801	4	a	8.2	6.9	270	128	10	2.7	2	39	8.4	2.3	9.2	130
470219109251001	5	a	8.9	7.1	600	372	2,800	6.2	3	78	35	2.2	120	260
470141109244201	6	a	9.5	8.0	430	196	10	5.0	1	45	25	2.3	10	220
465903109233301	7	a	10	--	270	132	0	0	0	30	15	5.0	23	120
470409109205901	8	a	7.0	--	690	374	100	0	0	48	63	8.0	48	420
471137109172201	9	d	--	6.5	540	355	--	22	4	60	19	1.0	210	80
470301108424101	10	d	22	7.4	610	402	200	56	5	48	20	5.3	140	260
470952108423201	11	c	21	7.8	1,200	732	210	250	3	18	7.3	2.2	240	430
470712108404201	12	d	17	7.7	650	391	1,600	130	2	9.6	4.6	1.7	120	250
470828108385001	13	d	14	7.8	725	408	1,400	120	3	17	8.6	1.7	130	260
471141108383501	14	d	13	8.3	900	516	50	180	3	9.6	4.5	1.5	170	300
470020108362801	15	d	14	8.1	1,450	898	10	330	2	5.1	2.0	33	300	460
470141108363001	16	d	18	7.1	1,580	1,120	830	98	11	160	75	27	550	410
470808108351001	17	d	14	8.2	610	348	240	130	1	3.0	1.2	2.6	73	280
470828108353801	18	d	21	--	710	413	440	150	2	3.2	1.9	3.6	120	270
465403108341801	19	d	27	7.5	960	644	10	190	5	28	12	1.7	230	360
465734108323001	20	d	14	7.3	950	615	--	160	8	40	16	4.2	220	340
471049108300001	21	d	12	8.5	1,270	704	40	260	1	3.6	1.1	21	270	300
470145108291501	22	d	14	7.3	1,240	797	30	140	11	80	34	4.6	350	360
465437108291101	23	d	--	8.3	--	513	--	180	0	16	5.0	48	180	171
465428108283601	24	e	--	8.0	3,640	2,900	--	850	9	110	43	120	1,300	960
471013108274301	25	d	--	7.6	9,920	6,480	--	2,000	0	660	180	2,000	3,500	300
471315109265201	26	d	15	7.8	1,050	618	270	230	1	2.7	0.9	1.5	210	350
470012108235901	27	d	16	8.0	1,250	721	20	270	3	6.0	2.0	19	210	430
470309108213801	28	d	16	7.6	1,110	690	820	250	3	8.9	3.1	9.0	200	440
470008108192801	29	d	24	8.1	1,700	1,120	390	390	3	6.9	2.0	16	500	410
465213108090401	30	a	--	8.0	3,140	2,140	--	920	0	6.0	0	110	0	2,250
470529108072101	31	c	--	8.7	--	1,054	--	420	0	2.0	2.0	25	290	641
470532108063901	32	d	--	8.5	--	1,180	--	510	0	0	0	160	76	890
470409108030601	33	d	16	8.2	1,500	926	170	350	1	2.1	0.4	16	330	460
470458108024601	34	a	--	--	--	1,160	--	470	0	0	0	28	240	860
470432108020001	35	a	--	--	--	785	--	310	0	0	0	38	230	420
470432108020001	36	a	--	8.4	--	1,100	--	420	0	0	0	38	260	580
470410108004001	37	d	--	7.6	--	1,990	--	790	0	45	7.0	200	1.0	1,920
470425108004001	38	b	--	--	--	1,110	--	480	0	0	0	150	0	980
470411108002801	39	a	--	--	--	1,350	--	570	0	0	0	140	22	1,260
470411108001501	40	b	--	--	--	1,690	--	710	0	0	0	330	0	1,320
470402108000901	41	b	--	--	--	1,860	--	770	0	0	0	620	0	960
470358107593701	42	b	--	--	--	1,590	--	660	0	0	0	460	0	950
470354107593701	43	b	--	--	--	1,500	--	620	0	0	0	430	0	920
470354107593701	44	b	--	--	--	2,100	--	860	0	0	0	800	0	900
470358107592301	45	b	--	--	--	1,370	--	580	0	0	0	340	0	920
470411107591801	46	b	--	--	--	1,490	--	620	0	0	0	400	0	950
470136107571501	47	a	--	--	--	512	--	220	0	0	0	30	85	420
470309107553201	48	a	--	--	--	1,400	--	620	0	0	0	50	41	1,400
465912107545701	49	d	--	8.0	1,530	974	350	360	2.0	3.9	.9	16	340	510
470259107545501	50	a	--	--	--	1,160	--	500	0	0	0	100	0	1,140

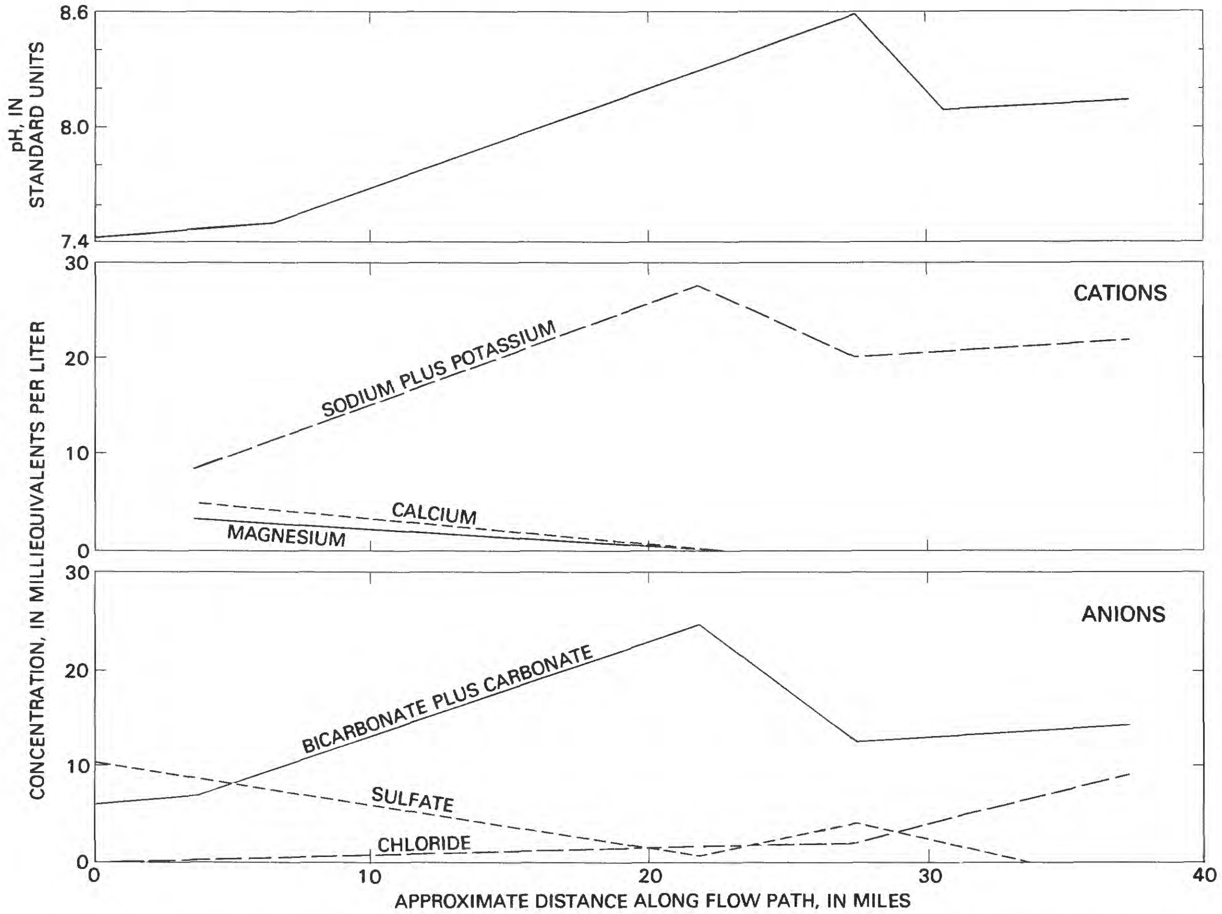

FIGURE 79.—Changes in concentrations of the principal ions along flow path 2 of the Inyan Kara aquifer in central Montana.

by the potentiometric surfaces of the Madison aquifer (Miller and Strausz, 1980) and of the Inyan Kara aquifer (H.L. Case, III, U.S. Geological Survey, written commun., 1984). However, if leakage were the source of chloride, the larger concentrations of sodium and chloride would occur in the Inyan Kara aquifer—the aquifer nearest the source of chloride. A third possible source of chloride in the Dakota aquifer is diffusion/advection from the overlying Mowry Shale and the underlying Skull Creek Shales.

PINCH-OUT AREA IN EASTERN NORTH DAKOTA AND EASTERN SOUTH DAKOTA

Aquifers older than the Dakota aquifer pinch out in eastern North Dakota and eastern South Dakota (figs. 19 and 62). As a result, the hydrogeologic system in this area is different from the system in the uplands and basins in the western part of the study area. Confining units are thinner or do not exist. Potentiomeric surfaces of the underlying aquifers are higher than those of the Inyan Kara and Dakota aquifers, which forces upward leakage, as described by Swenson (1968), Schoon (1971), and Koch (1980).

INYAN KARA AQUIFER

The distributions of the principal dissolved ions in the pinch-out area differ from those of the uplands and basins and provide evidence for leakage. The dissolved-solids concentration is less than 3,000 mg/L in eastern South Dakota and southeastern North Dakota. In northeastern North Dakota, dissolved-solids concentrations range from 3,000 to more than 20,000 mg/L; concentrations generally increase northward. Sodium concentrations have a similar

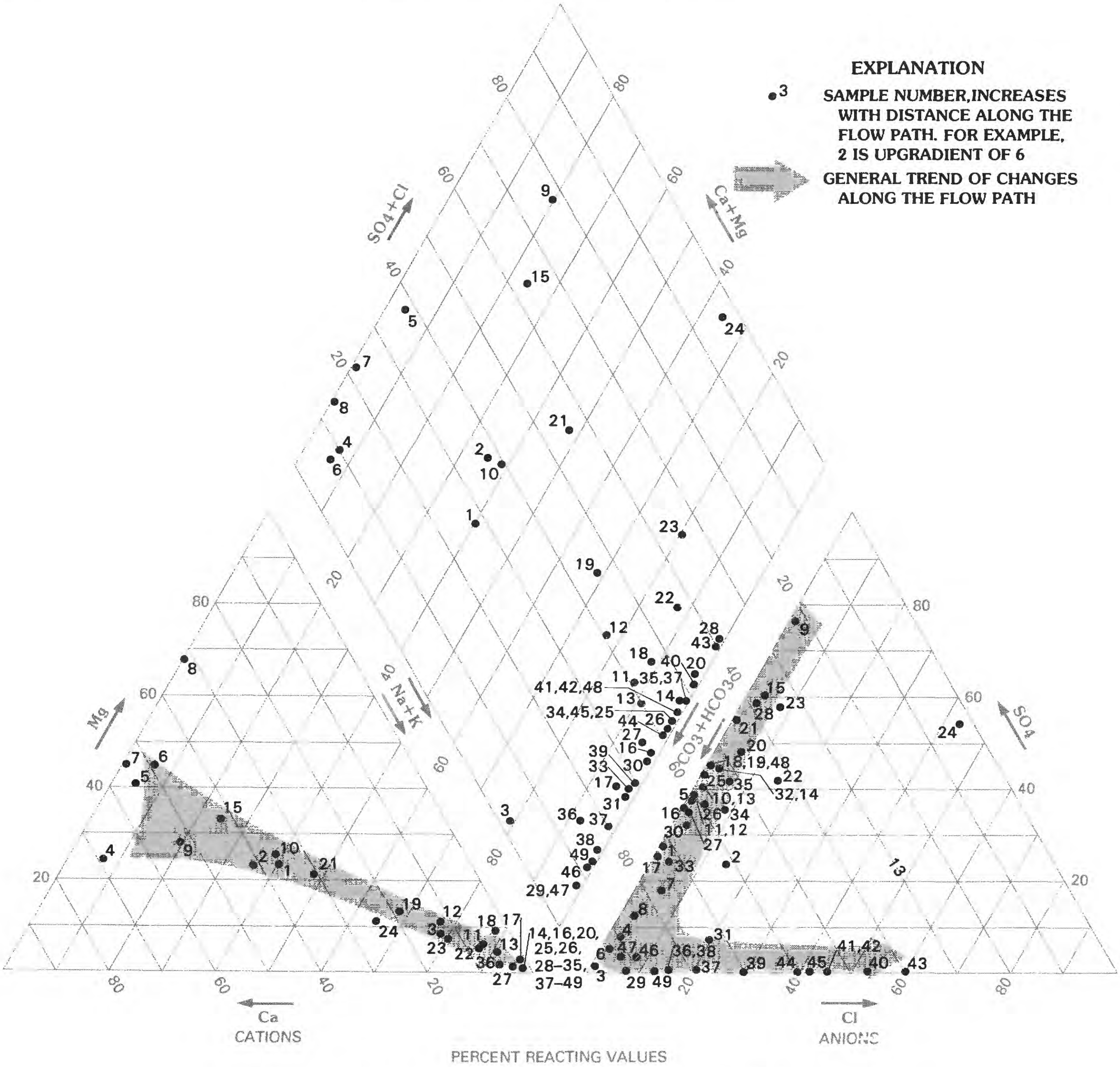

FIGURE 80.—Trilinear diagram for flow path 2 of the Inyan Kara aquifer in central Montana.

distribution; concentrations are less than 200 mg/L in eastern South Dakota and range from 1,000 mg/L to more than 6,000 mg/L in eastern North Dakota. Calcium concentrations range from 100 to 400 mg/L in eastern North Dakota and eastern South Dakota. Magnesium concentrations are as large as they are in the basins, ranging from 50 to 100 mg/L in most of the pinch-out area, and exceeding 300 mg/L in northeastern North Dakota. Bicarbonate concentrations are less than 300 mg/L in most of the pinch-out area. Concentrations of sulfate range from 1,000 to 1,300 mg/L in most of the area. Chloride concentrations are less than 100 mg/L in eastern South Dakota. In eastern North Dakota, chloride concentrations range from 100 to

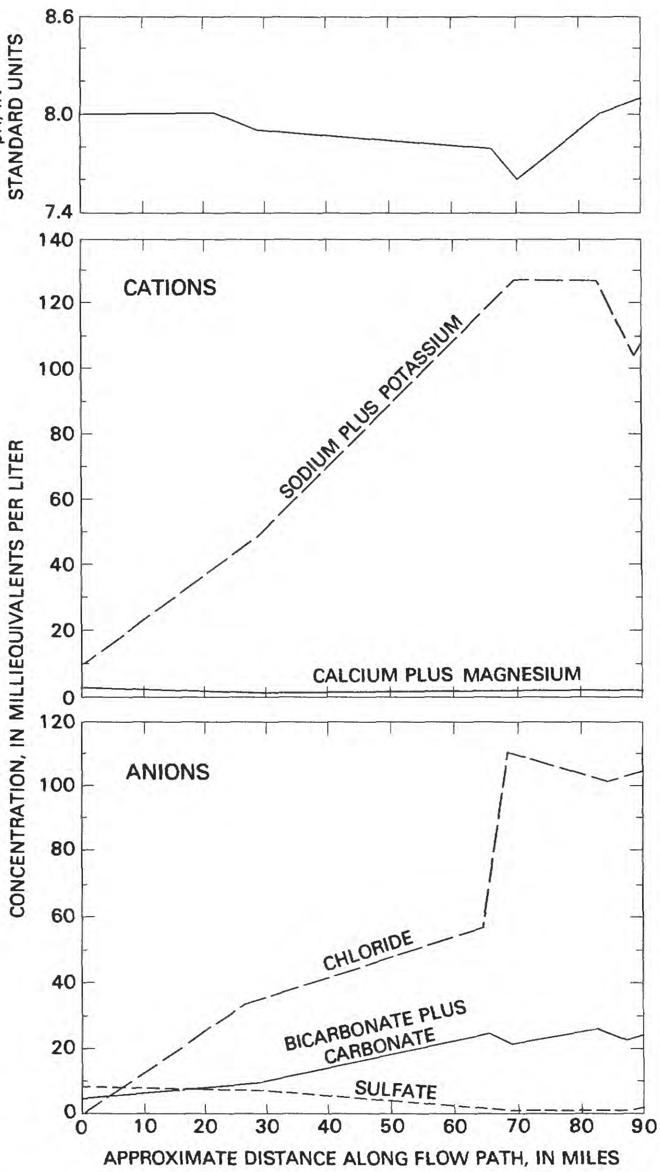

FIGURE 81.—Changes in concentrations of the principal ions along flow path 1 of the Dakota aquifer in southeastern Montana.

1,000 mg/L, except in the northeastern part of the State, where they exceed 10,000 mg/L. Sulfate is the dominant anion in eastern South Dakota, and a combination of all three major anions—sulfate, chloride, and bicarbonate—is present in eastern North Dakota. Chloride is the dominant anion in northeastern North Dakota (fig. 78).

Concentrations of dissolved solids, sodium, chloride, and sulfate in water from the Inyan Kara aquifer are unexpectedly large in south-central South Dakota in an area about 150 mi long and 100 mi wide (figs. 63–64, 66–69). This elliptical anomaly is parallel to flow path 4 in the Inyan Kara aquifer (fig. 19).

DAKOTA AQUIFER

The distributions of the principal ions in the water in the Dakota aquifer also provide information that indicates interaquifer leakage, as Swenson (1968) and Schoon (1971) have noted. Dissolved-solids concentrations range from less than 200 mg/L to about 2,000 mg/L, and are smallest in southeastern South Dakota, where they range from about 100 to 400 mg/L. Concentrations of calcium are substantially larger in South Dakota, where they range from about 100 to 400 mg/L. In small areas in northeastern South Dakota and eastern North Dakota, the concentrations of calcium exceed 100 mg/L (fig. 76). The distribution of magnesium is similar to that of calcium, which exceeds 50 mg/L in southeastern South Dakota. Concentrations of bicarbonate plus carbonate range from less than 100 to 500 mg/L. The smallest concentration is in southeastern South Dakota, in approximately the same area as the larger concentrations of calcium and magnesium. Concentrations of sulfate range from about 500 to 1,300 mg/L. The largest sulfate concentrations are in southeastern South Dakota and in southeastern North Dakota. Chloride concentrations are less than 200 mg/L in southeastern South Dakota. In northeastern South Dakota and southeastern North Dakota, chloride concentrations range from 200 to 2,000 mg/L. A dominantly sulfate hydrochemical facies is present in southeastern South Dakota, and a mixture of all three major anions—sulfate, chloride, and bicarbonate—dominates in northeastern South Dakota and southeastern North Dakota (fig. 78).

EVOLUTION OF WATER CHEMISTRY

In order to identify changes in ion concentrations in the water as it moves into the pinch-out areas, three flow paths in the Inyan Kara aquifer and two in the Dakota aquifer were investigated, and the chemical changes in the water along the flow paths were graphed. The flow paths are in four distinctive parts of the pinch-out area where vertical leakage is evident: eastern North Dakota, northeastern South Dakota, southeastern South Dakota, and the anomalous area in central South Dakota.

Leakage from the underlying Paleozoic aquifers in eastern North Dakota increases the chloride concentrations in the Inyan Kara aquifer to a lesser extent

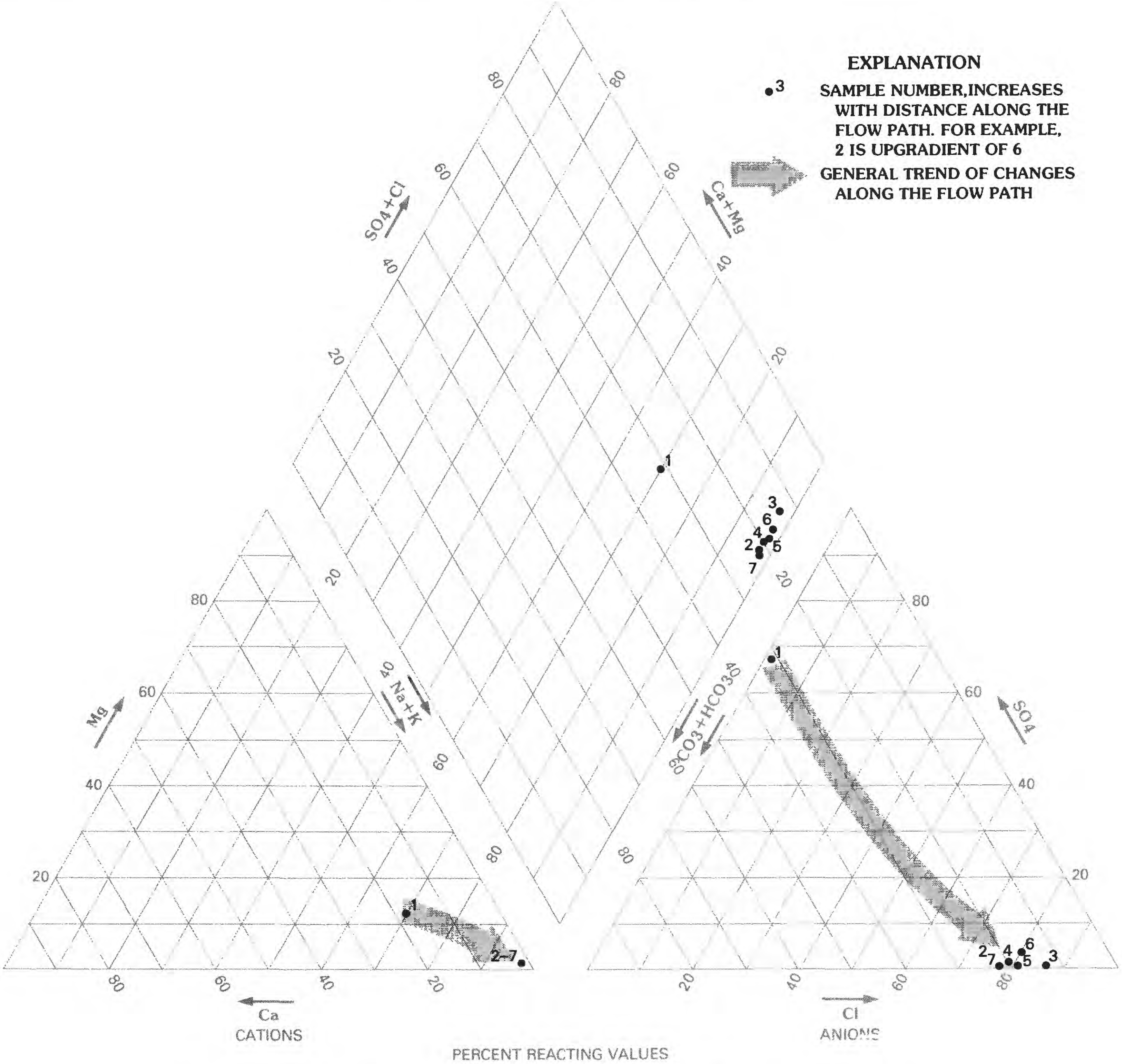

FIGURE 82.—Trilinear diagram for flow path 1 of the Dakota aquifer in southeastern Montana.

than in the basins. Chloride concentration in water from the Inyan Kara aquifer (fig. 66), exceeds 1,000 mg/L in eastern North Dakota. Analyses of the chemical composition of water from flow path 6 in the Inyan Kara aquifer in this area are listed in table 17.

Water in the underlying Paleozoic aquifers in North Dakota is more saline than that in the Inyan Kara aquifer. As a result, sodium, calcium, magnesium, and chloride concentrations increase downgradient as upward leakage from the Paleozoic aquifer system increases (table 17). Comparison of the ion-concentration maps for the Inyan Kara aquifer and the Madison aquifer indicates a similarity in concentrations of chloride and sodium in southeastern North Dakota.

TABLE 17.—*Chemical composition of water from flow path 6 of the Inyan Kara aquifer in eastern North Dakota*

[Location of flow path shown in figures 19. Listed in approximate downgradient order. All samples from the equivalents of the Inyan Kara Group; °C, °Celsius; pH , pH units, µS/cm, microsiemens per centimeter at 25 °Celsius; mg/L, milligrams per liter; µg/L, micrograms per liter]

Station identification number	Sample number	Temperature (°C)	pH	Specific conductance (µS/cm)	Dissolved solids, calculated (mg/L)	Dissolved iron (µg/L)	Sodium	Potassium	Calcium	Magnesium	Chloride	Sulfate	Bicarbonate
										(mg/L)			
473832099320201	1	21	8.3	4,210	4,920	60	980	3	5.2	1.2	320	1,300	4,704
472730099295802	2	--	8.2	4,590	6,050	1,200	1,100	4	6.8	3.2	440	1,200	6,707
472724099270501	3	9.4	8.7	4,320	6,050	520	1,000	3	4.0	1.9	350	1,200	7,100
472400099012001	4	12	8.1	4,490	5,390	–	1,000	40	8.0	6.1	430	1,200	5,500
472025098594401	5	10	8.1	4,420	4,980	–	1,000	16	4.0	4.9	300	1,200	5,000
472633097315501	6	--	7.7	4,690	4,210	100	970	24	60	21	930	730	3,000
473418097304401	7	6.0	7.3	6,640	5,370	3,400	1,000	46	370	120	1,400	1,500	1,900
472951097255702	8	9.0	7.8	5,480	4,780	–	800	39	310	110	940	1,500	2,200
472430097220701	9	7.0	7.3	4,520	4,130	–	820	34	140	44	660	1,200	2,500
472430097125301	10	7.0	7.6	5,370	4,860	–	1,100	38	110	30	800	1,400	2,800
474858097134601	11	8.0	7.7	7,190	6,060	–	1,100	33	330	130	1,600	1,200	3,400
474424097130201	12	10	7.1	–	5,400	–	1,000	28	300	92	1,300	1,300	2,800
474905097115001	13	9.0	7.8	7,070	6,130	–	1,200	30	330	100	1,500	1,400	3,200
474537097114001	14	10	8.0	6,210	5,230	–	1,100	39	230	77	1,200	1,400	2,400
474530097101702	15	9.0	7.9	6,740	5,330	–	1,200	35	230	83	1,400	1,400	2,000
474208097071301	16	14	7.4	4,940	5,180	–	780	12	300	130	480	2,000	3,000
474109097034901	17	--	7.6	5,770	6,240	–	900	0	250	86	1,200	1,000	2,800

Because of leakage along flow path 6 in the Inyan Kara aquifer, the anion hydrochemical facies changes from a sulfate-dominated mixed facies to a more saline chloride-dominated mixed facies near the Minnesota–North Dakota border (figs. 83 and 84). Because neither the Madison nor Pennsylvanian aquifers are present in this area and chloride concentrations in the Cambrian-Ordovician aquifer range from 10,000 to 75,000 mg/L, the more saline chloride facies in the Inyan Kara aquifer may be caused by direct leakage from the Cambrian-Ordovician aquifer.

Although downgradient changes in the water chemistry in the Inyan Kara and Dakota aquifers in northeastern South Dakota indicate upward leakage effects, the resultant water in each aquifer differs. Analyses of water from flow path 5 in the Inyan Kara aquifer and flow path 2 in the Dakota aquifer in northeastern South Dakota are listed in tables 18 and 19. In the Inyan Kara and Dakota aquifers, concentration changes are indicative of mixing with a water that contains small concentrations of sodium and chloride and larger concentrations of calcium, magnesium, and sulfate. Sodium and chloride concentrations decrease downgradient (figs. 85–88), while calcium and magnesium increase, then decrease. The concentrations of bicarbonate and carbonate decrease to a relatively constant value. In the Inyan Kara aquifer, sulfate concentrations decrease from an isolated area of large sulfate concentration (too small an area to be shown in fig. 69) to relatively constant values. Upgradient of flow path 5 in the Inyan Kara aquifer, the concentrations of sulfate are smaller. In the Dakota aquifer, sulfate concentrations increase downgradient.

Even though the trends in both aquifers are similar, the downgradient changes in the Dakota aquifer are smaller than those in the Inyan Kara. For example, chloride concentrations decrease from about 1,100 mg/L to less than 100 mg/L in the Inyan Kara aquifer. In the Dakota aquifer, chloride concentrations decrease from about 1,000 mg/L to less than 500 mg/L but are greater than 200 mg/L along most of flow path 2 in the Dakota aquifer.

The thinning of the confining units and the relative positions of the potentiometric surfaces in the pinch-out area are conducive to upward leakage. The potentiometric surface of the Madison aquifer along flow path 2 is about 660 ft higher than that of the Inyan Kara aquifer, which is about 160 ft higher than that of the Dakota aquifer (fig. 89).

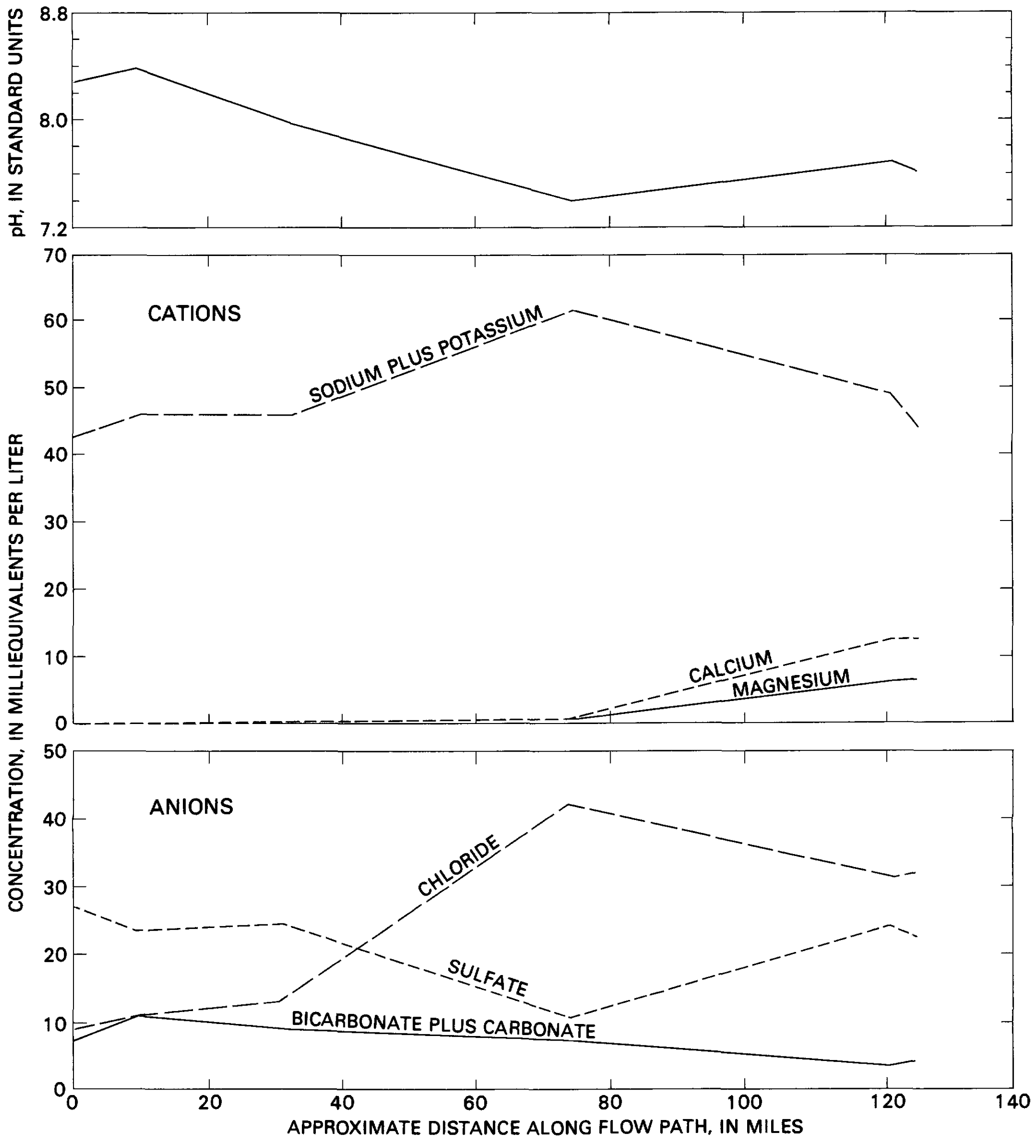

FIGURE 83.—Changes in concentrations of the principal ions along flow path 6 in the Inyan Kara aquifer in eastern North Dakota. See figure 19 for location of flow path (p. 32).

In southeastern South Dakota, the changes in the water chemistry in the Dakota aquifer are similar to the changes in the Inyan Kara aquifer in northeastern South Dakota. These changes in the water chemistry in the Dakota aquifer as it flows into southeastern South Dakota are illustrated by flow path 3 in the Dakota aquifer (figs. 90 and 91).

Concentrations of calcium, magnesium, and sulfate increase along flow path 3 in the Dakota aquifer and are dominated by calcium and sulfate along the flow path (figs. 90 and 91; table 20). The concentrations of calcium and magnesium are larger in southeastern South Dakota than in northeastern South Dakota (figs. 67, 68, 76, and 77). The abrupt change in chemical character of the water at a distance of about 15 mi along the flow path indicates the input of water with a different chemical composition into the aquifer. Sulfate often accounts for more than 60 percent of all the anions in water in the Dakota and the Madison aquifers in southeastern South Dakota,

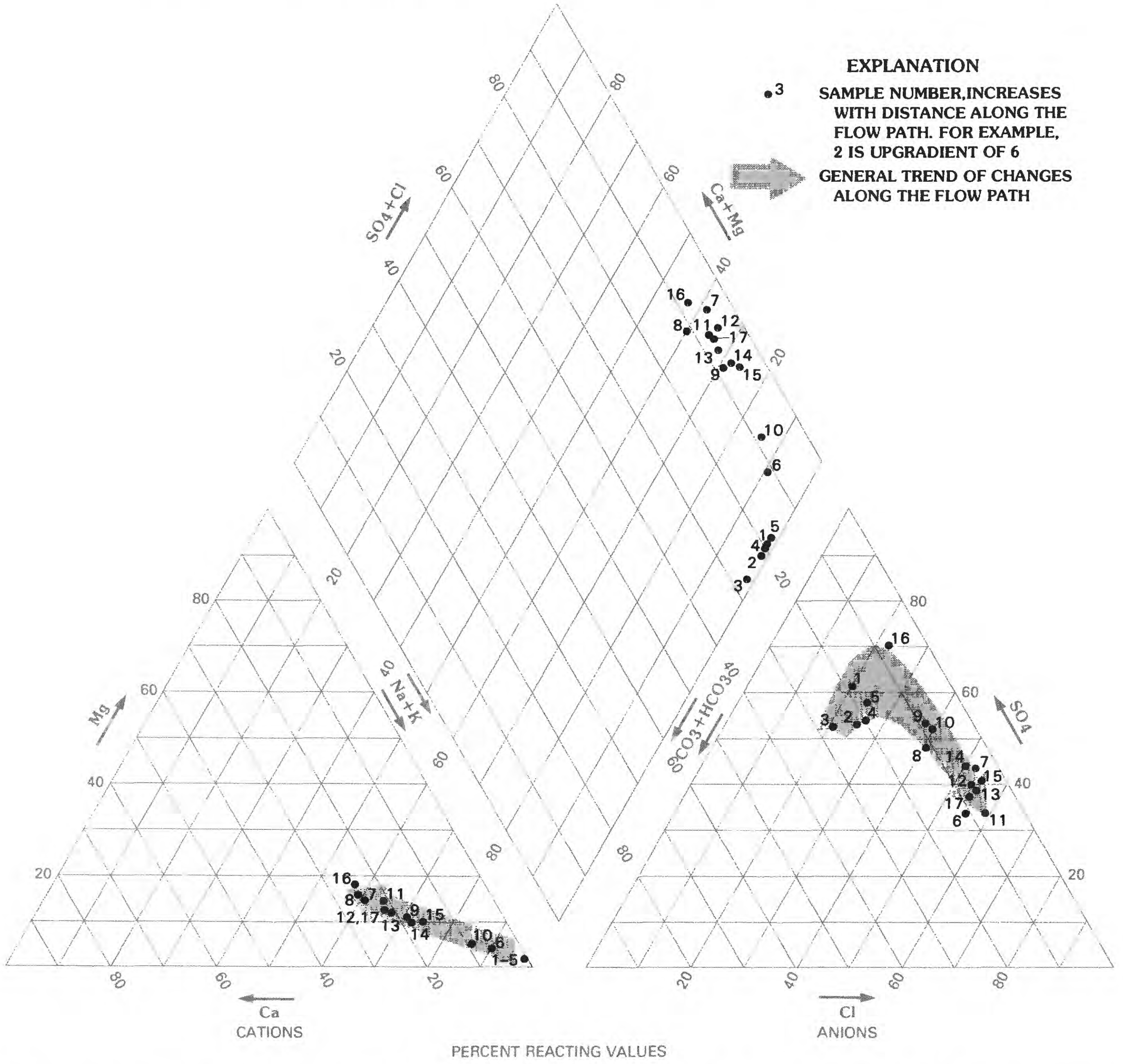

FIGURE 84.—Trilinear diagram for flow path 6 in the Inyan Kara aquifer in eastern North Dakota. See figure 19 for direction of flow path (p. 32).

which indicates the Madison could be the source of leakage.

As in northeastern South Dakota, the potential for upward leakage in southeastern South Dakota from underlying aquifers exists because the confining units are thinner and the potentiometric surface of the Dakota is lower than those in the deeper aquifers (fig. 92). Along flow path 3, the Skull Creek Shale and Inyan Kara aquifer pinch out over the Precambrian craton (fig. 92). The potentiometric surface of the Inyan Kara aquifer is approximately 200 ft above the potentiometric surface in the Dakota aquifer in

TABLE 18.—*Chemical composition of water from flow path 5 of the Inyan Kara aquifer in northeastern South Dakota*

[Location of flow path shown in figure 19. Listed in approximate downgradient order: a, Fall River Sandstone; b, Lakota Formation; c, Inyan Kara Group; °C, °Celsius; pH, pH units; µS/cm, microsiemens per centimeter at 25 °Celsius; mg/L, milligrams per liter; µg/L, micrograms per liter]

Station identification number	Sample number	Geologic formation	Temperature (°C)	pH	Specific conductance (µS/cm)	Dissolved solids, calculated (mg/L)	Dissolved iron (µg/L)	Sodium	Potassium	Calcium	Magnesium	Chloride	Sulfate	Bicarbonate
								(mg/L)						
451339100285301	1	a	33	7.4	7,660	6,900	1,100	1,500	48	300	74	1,100	2,300	3,200
452653100033501	2	a	26	7.8	2,250	2,900	1,200	190	24	310	89	110	1,300	1,800
452140099494501	3	a	23	--	2,690	2,950	30	330	22	230	58	80	1,300	1,900
453706100155001	4	c	--	--	3,800	1,130	220	620	10	150	36	320	1,200	2,300
454353100043101	5	c	--	--	2,600	3,200	20	230	21	280	73	120	1,200	2,600
454353100043101	6	c	--	7.7	--	2,860	3,200	270	23	280	76	120	1,300	1,600
454610099372702	7	a	27	6.7	2,510	2,850	2,800	140	25	340	100	63	1,300	1,800
453150099334301	8	a	24	7.6	3,040	3,455	2,700	590	15	130	32	110	1,300	2,600
454347098554201	9	a	26	7.8	2,340	2,820	1,700	140	25	340	85	48	1,300	1,800
454426098372402	10	a	20	7.4	2,610	2,860	--	320	28	210	63	55	1,300	1,800
454344098371901	11	a	20	8.3	2,740	2,780	1,500	420	29	140	43	61	1,200	1,803
455032098182701	12	a	16	8.1	3,280	3,270	230	740	9	23	4.2	110	1,300	2,200
455247098155601	13	a	18	8.0	3,280	3,260	160	710	12	31	5.9	120	1,300	2,200
455716098124701	14	c	20	8.1	3,150	3,160	430	670	12	37	12	100	1,300	2,100

TABLE 19.—*Chemical composition of water from flow path 2 of the Dakota aquifer in northeastern South Dakota*

[Location of flow path shown in figure 19. Listed in approximate downgradient order. All samples from the Dakota Sandstone; °C, °Celsius; pH, pH units, µS/cm, microsiemens per centimeter at 25 °Celsius; mg;L, milligrams per liter µg/L, micrograms per liter]

Station identification number	Sample number	Temperature (°C)	pH	Specific conductance (µS/cm)	Dissolved solids, calculated (mg/L)	Dissolved iron (µg/L)	Sodium	Potassium	Calcium	Magnesium	Chloride	Sulfate	Bicarbonate
							(mg/L)						
450055100073601	1	16	8.2	4,020	5,050	--	880	10	8.2	3.3	1,000	5.3	6,400
450247099571301	2	31	7.9	--	4,280	--	--	--	11	3.8	470	400	6,900
450247099571301	3	--	7.9	--	4,530	--	--	--	9.5	6.4	480	400	7,400
450247099571301	4	26	7.8	--	4,330	--	--	--	8.6	5.7	490	380	7,000
450247099571301	5	24	8.5	--	4,180	--	--	--	10	3.9	500	370	6,700
450023099571201	6	--	8.1	--	5,100	--	740	8	8.5	4.6	480	380	7,100
450050099565001	7	22	8.2	--	9 510	--	--	--	8.5	4.1	520	340	7,200
450232099172601	8	--	--	2,800	3,640	640	540	13	36	17	170	750	4,300
445852099074301	9	--	--	2,900	3,980	400	580	25	24	12	280	600	5,000
445953099024701	10	--	--	3,600	3,920	--	840	6	8.0	5.0	140	1,300	3,300
450121099001501	11	23	7.6	2,310	2,670	1,800	130	31	340	88	47	1,300	1,500
450159098544001	12	14	7.7	2,030	4,580	6,100	720	11	19	5.7	410	560	5,800
450159098544001	13	20	8.2	3,190	4,380	290	710	12	18	6.7	410	520	5,500
450840098444501	14	15	6.9	2,660	2,680	400	500	17	68	19	270	770	2,100
450840098444501	15	15	8.1	2,700	2,820	280	480	22	69	20	260	740	2,500
451436098335201	16	17	7.5	3,170	3,080	--	680	8	12	24	460	620	2,600
451436098335203	17	--	7.3	--	2,430	--	--	--	14	3.0	480	610	2,700
451531098401701	18	--	--	3,600	3,720	--	850	4	28	7.3	600	800	2,900
451114098262601	19	13	8.0	--	4,100	--	710	10	20	4.9	360	730	4,600
451114098262602	20	14	8.0	--	3,970	--	670	11	27	5.7	320	720	4,500

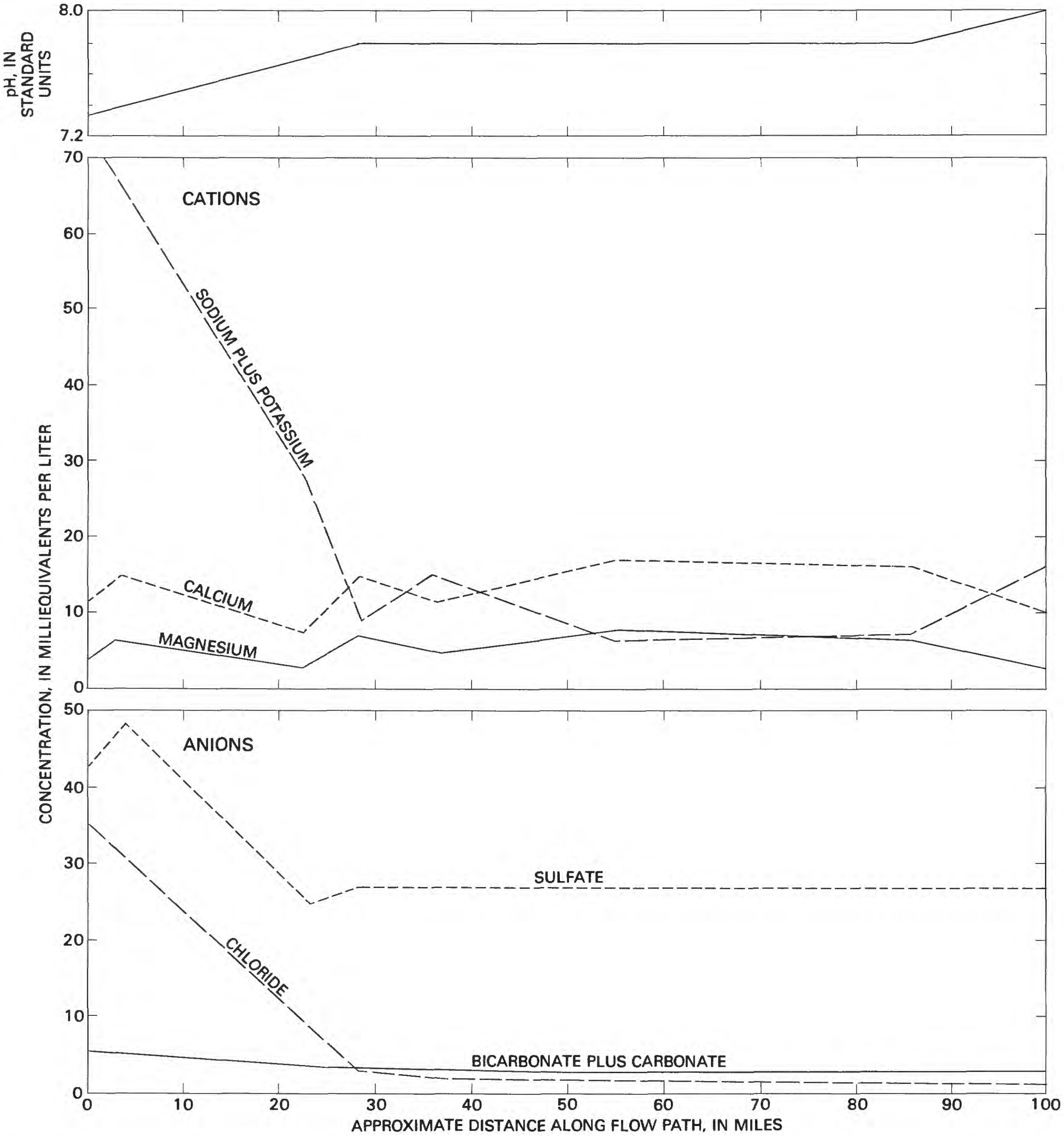

FIGURE 85.—Changes in concentrations of the principal ions along flow path 5 in the Inyan Kara aquifer in northeastern South Dakota. See figure 19 for location of flow path (p. 32).

southeastern South Dakota where the Inyan Kara aquifer is present. Information on the potentiometric surface of the Madison is poor, but the surface presumably is higher than that of the Inyan Kara aquifer.

The differences in water chemistry in the Lower Cretaceous aquifers in eastern North Dakota and eastern South Dakota may be partly explained by differences in the water prior to mixing, the chemistry of the water leaking upward, and the relative

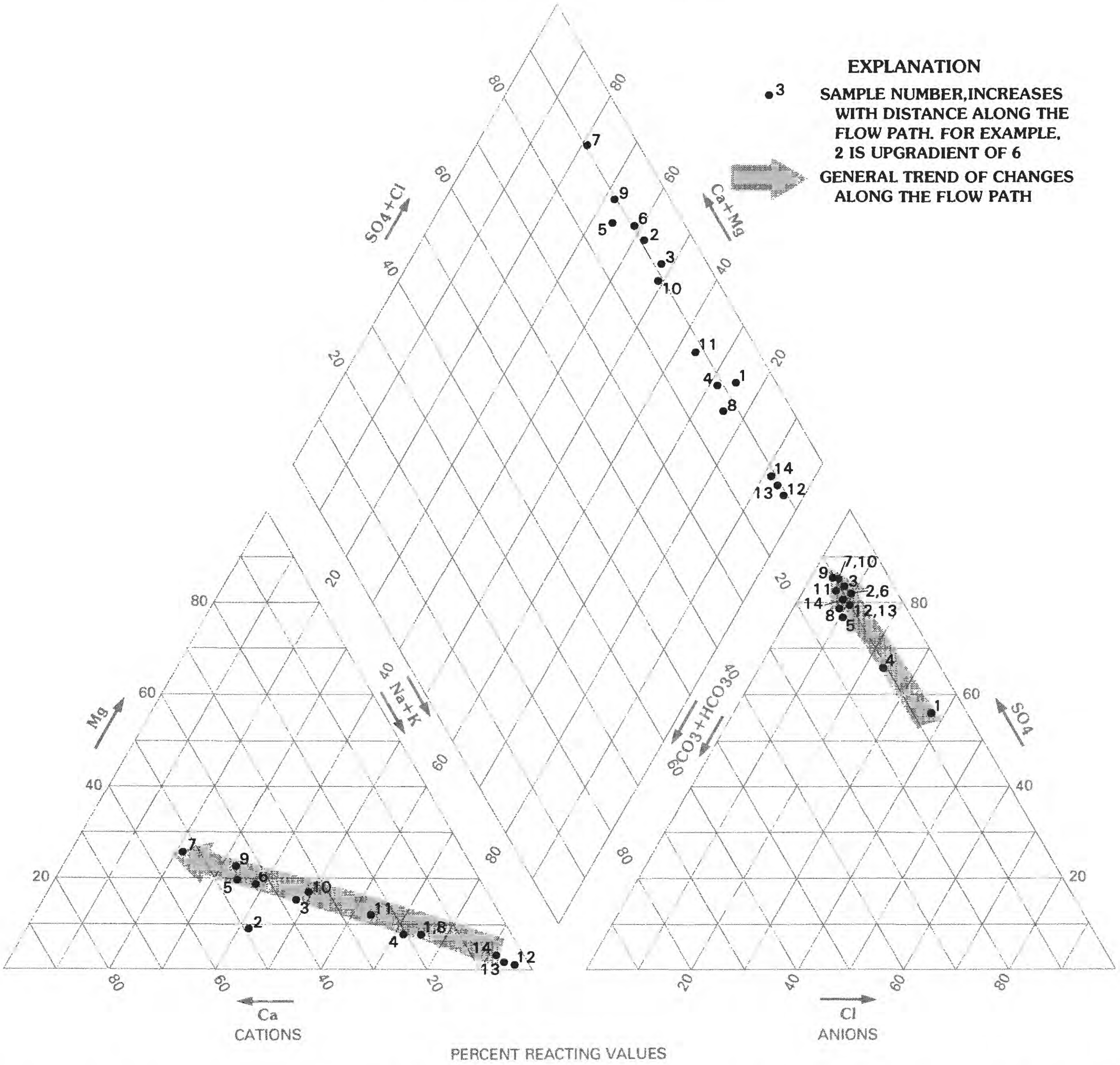

FIGURE 86.—Trilinear diagram for flow path 5 in the Inyan Kara aquifer in northeastern South Dakota. See figure 19 for location of flow path (p. 32).

proportions of the mixed water. The resultant mixed water in southeastern South Dakota may be predominantly from the deep underlying carbonate-evaporite Paleozoic aquifer system. Therefore, its chemistry is indicative of the long residence time of the water in a calcite-dolomite-gypsum system in the Inyan Kara aquifer in eastern South Dakota.

An area of larger anomalous sodium, sulfate, and chloride concentrations in water of the Inyan Kara aquifer exists in west-central South Dakota. This anomaly may be the result of upward leakage along fractures. Analyses from flow path 4 (figs. 93 and 94) in the Inyan Kara aquifer, which passes through this anomalous area, are shown in table 21.

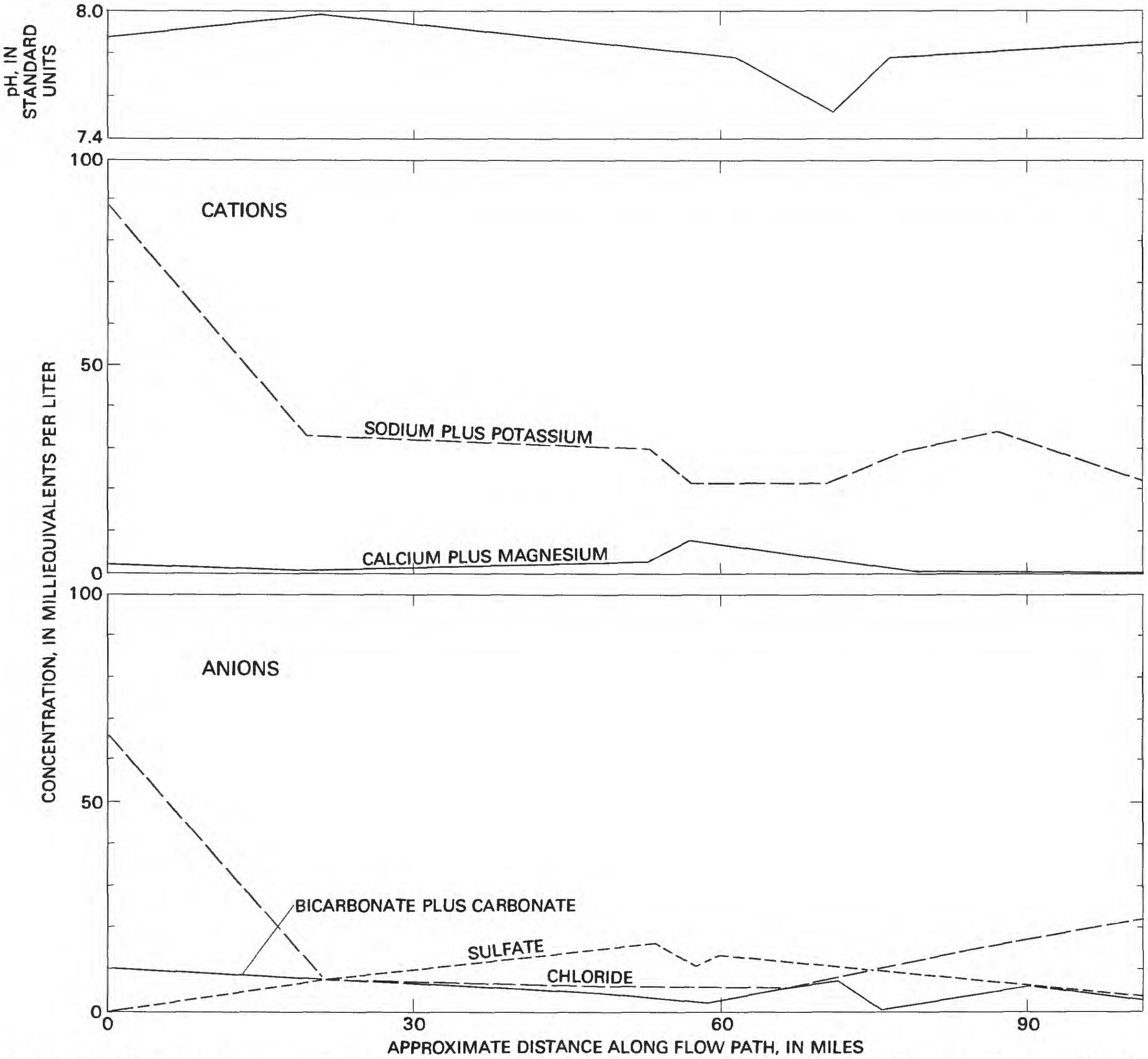

FIGURE 87.—Changes in concentrations of the principal ions along flow path 2 of the Dakota aquifer in northeastern South Dakota. See figure 19 for location of flow path (p. 32).

Concentrations of the principal ions along flow path 4 are shown in figure 93. In figure 94, the relative proportions of ions in water samples from the underlying Minnelusa and Sundance Formations of the Permian-Triassic-Jurassic confining unit (TK3) and the Madison Limestone in central South Dakota are compared to the water samples along flow path 4.

Along the beginning of the flow path (sample numbers 1 to 14, table 21), the trend is the same as along other flow paths that begin in an upland, recharge area: Concentrations of dissolved solids, sodium, and bicarbonate plus carbonate increase, and the concentrations of calcium and magnesium decrease; however, sulfate concentrations decrease then increase gradually, unlike the trends along the other two flow paths.

About 90 mi along the flow path, in the anomalous zone, the concentrations of sodium, sulfate, and chloride increase over a short distance (fig. 93). Concentrations of calcium and magnesium slightly increase, and the concentration of bicarbonate slightly decreases. The changes in ion concentrations

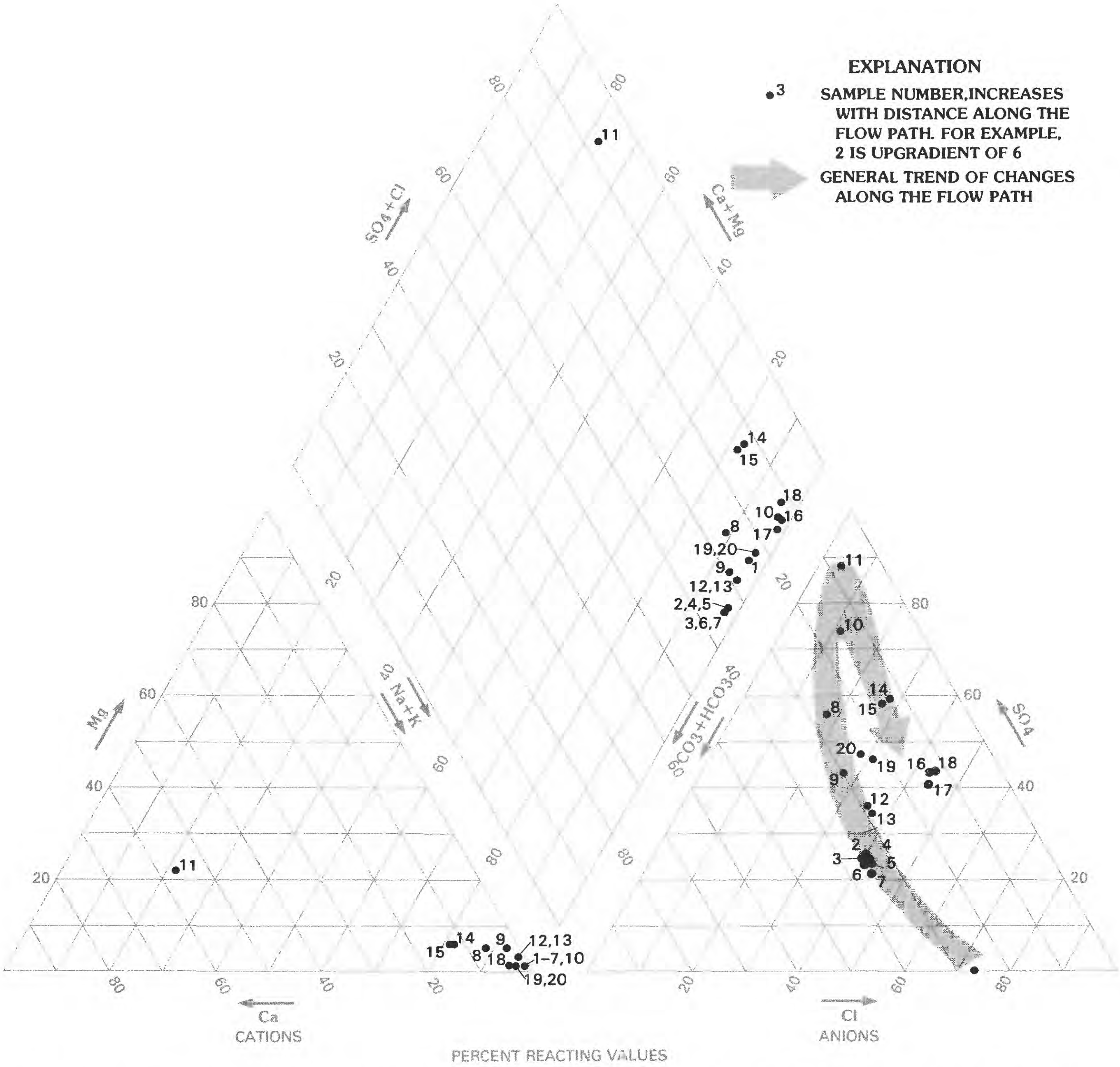

FIGURE 88.—Trilinear diagram for flow path 2 in the Dakota aquifer in northeastern South Dakota. See figure 19 for location of flow path (p. 32)

result in a change in anion hydrochemical facies from bicarbonate to sulfate, the same facies as water in the Madison Limestone and Minnelusa Formation in this area (fig. 94). Sodium remains the dominant cation perhaps because of ion exchange in the intervening shale.

In this area of anomalous concentrations, the geothermal gradient is 2.0 °C per 100 ft, as compared to 0.7–1.1 °C per 100 ft for eastern South Dakota (Adolphson and LeRoux, 1968). This difference in geothermal gradient also indicates leakage from the underlying aquifers into the Lower

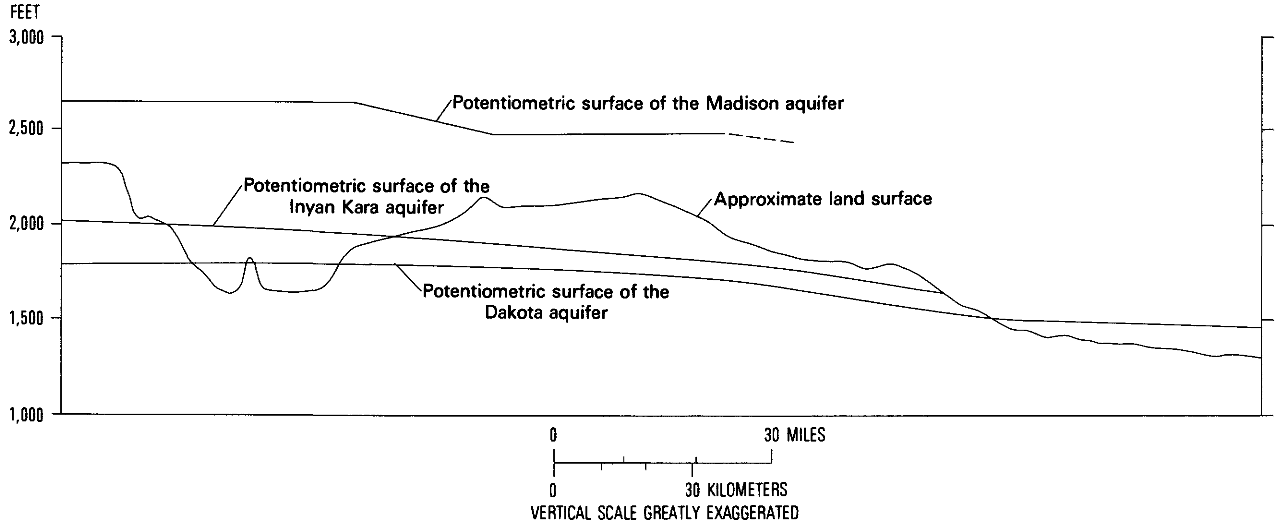

FIGURE 89.—Diagrammatic section showing potentiometric surfaces along flow path 2 in the Dakota aquifer in northeastern South Dakota (Water levels from H.L. Case III, U.S. Geological Survey, written commun., 1981; Miller and Strausz, 1980). See figure 19 for location of flow path (p. 32).

Cretaceous aquifers in this area. Adolphson and LeRoux (1968) suggested that a "hot-water belt" in south-central South Dakota is produced by leakage where the Paleozoic aquifers pinch out. However, the elliptical anomaly is northwest of this "hot-water belt."

The extent of leakage between aquifers is directly proportional to the vertical hydraulic conductivity of the intervening confining units and the gradient between the aquifers, and inversely proportional to the thickness of the intervening confining units. The confining units that separate the Paleozoic aquifers and the Inyan Kara aquifer are less than 300 ft thick in this area (fig. 95). The potentiometric surface of the Madison aquifer is higher than that of the Inyan Kara aquifer in the chemically anomalous area.

Hydrochemical, potentiometric, and geothermal anomalies that occur in the two Lower Cretaceous aquifers correlate with surface lineaments and suggest increased upward leakage through confining units in this area (Kolm and Peter, 1984). The area with larger sulfate concentrations, in central South Dakota (fig. 96), seems to be bounded by lineaments mapped by Cooley (1982) and by Kolm and Peter (1984). If the lineaments represent fractures in the confining units, the larger sulfate concentration could be caused by upward leakage through these fractures.

SUMMARY AND CONCLUSIONS

The Regional Aquifer System Analysis (RASA) program of the U.S. Geological Survey is a set of interdisciplinary studies designed to evaluate the Nation's ground-water resource. The Northern Great Plains RASA, a part of the larger National program, had the responsibility of evaluating the aquifers (Paleozoic and Mesozoic) underlying about 300,000 mi^2 of the northern Great Plains and Central Lowlands physiographic provinces.

The geochemical part of this study was designed to define areas of leakage, recharge, and directions of flow; to describe the regional trends in water chemistry of the aquifers and confining units; and to determine plausible mechanisms responsible for the observed chemistry. Major results from the study are given below:

1. Leakage from the underlying Madison aquifer into the overlying Lower Cretaceous Dakota aquifer has been identified as a plausible contributor to the water chemistry of the Lower Cretaceous aquifers. In addition to leakage, diffusion of sodium and chloride water from the shales overlying the Dakota aquifer has been postulated as a probable source of large chloride concentrations in the Dakota aquifer.

2. Recharge areas are defined as those areas with dissolved-solids concentrations less than 1,000 mg/L,

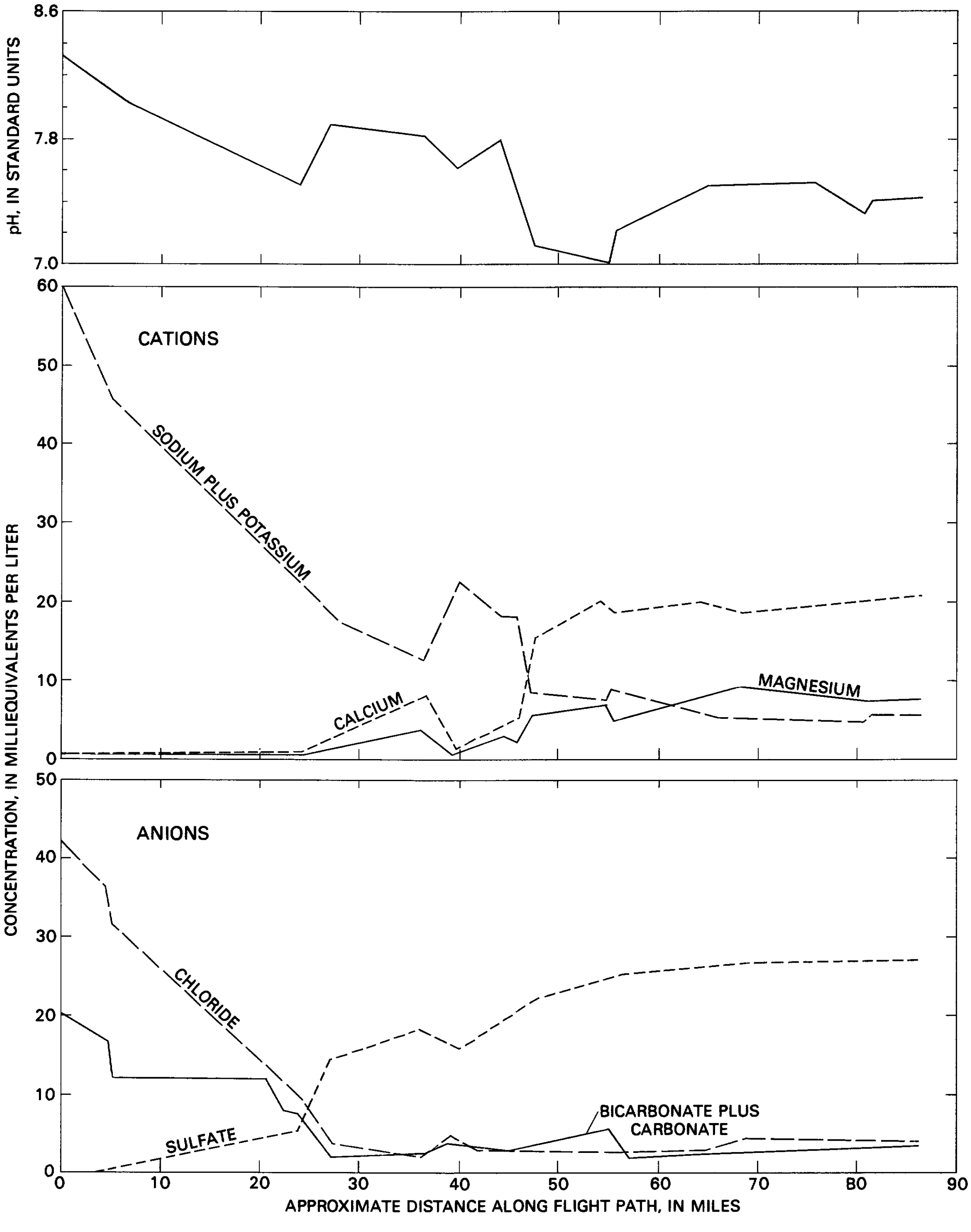

FIGURE 90.—Changes in concentrations of the principal ions along flow path 3 in the Dakota aquifer in southeastern South Dakota. See figure 19 for location of flow path (p 32).

chloride concentrations less than 20 mg/L, and a temperature of no more than 15 °C. The recharge areas typically are the highlands, principally near the Bighorn Mountains and the Black Hills.

3. Similar flow paths are defined using either hydraulic information, such as vector flux plots, or the gradient in dissolved-solids concentration (Downey, 1986).

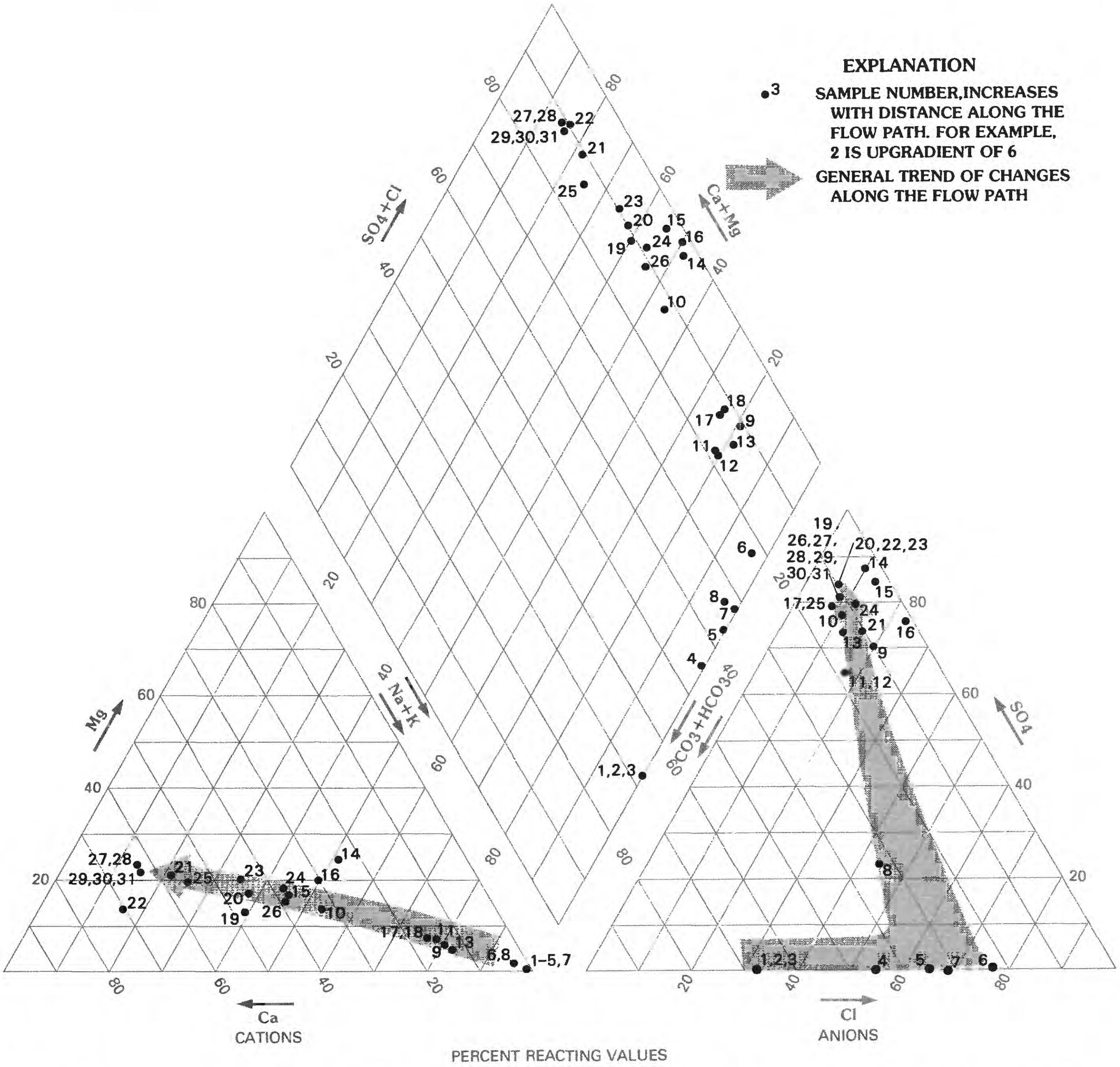

Figure 91.–Trilinear diagram for flow path 3 in the Dakota aquifer in southeastern South Dakota. See figure 19 for location of flow path (p. 32).

4. The basins, Bull Mountain, Powder River, and Williston, and the Central Montana trough are areas where the water chemistry is affected by the chemistry of an evaporitic basin, and although a significant part of the regional picture of the ground-water chemistry, they are not really part of any chemical-evolutionary path.

5. Within the basins, the dominant chemical control is the dissolution of evaporite minerals. At larger dissolved-solids concentrations (values near halite saturation; about 300,000 mg/L), there is a contribution by the alkali-earth chlorides to the water chemistry. This alkali-earth chloride contribution is indicated by the excess chlorides in the plot of

TABLE 20.—*Chemical composition of water from flow path 3 of the Dakota aquifer in southeastern South Dakota*

[Location of flow path shown in figure 19. Listed in approximate downgradient order: All samples from the Dakota Sandstone; °C, °Celsius; pH, pH units; µS/cm, microsiemens per centimeter at 25 °Celsius; mg/L, milligrams per liter; µg/L, micrograms per liter]

Station identification number	Sample number	Temperature (°C)	pH	Specific conductance (µS/cm)	Dissolved solids, calculated (mg/L)	Dissolved iron (µg/L)	Sodium	Potassium	calcium	Magnesium	Chloride	Sulfate	Bicarbonate
							(mg/L)						
440928100480501	1	38	7.8	5,440	3,190	160	1,300	7	9.5	0.4	1,100	0.0	1,570
440730100532501	2	46	8.2	3,480	2,250	170	850	6	4.4	.7	440	1.5	1,580
440730100532501	3	46	8.3	3,400	2,070	60	840	6	5.1	1.2	440	2.2	1,570
440730100532501	4	47	8.0	3,520	2,060	20	840	6	4.1	.9	430	6.8	1,580
440903100264601	5	16	8.4	--	2,610	--	1,000	7	9.2	6.1	1,100	.2	988
441037100250401	6	19	8.1	4,840	2,690	1,800	1,000	28	28	11	1,300	5.0	700
441513100054001	7	18	8.0	4,030	2,250	--	870	15	13	4.3	970	.8	760
440824100050401	8	31	7.5	2,410	1,410	--	510	10	15	6.2	370	270	470
440746100003601	9	24	7.9	2,170	1,380	10	390	14	58	14	140	700	130
440635099483401	10	25	7.8	2,260	1,590	1,800	300	10	160	40	88	900	180
440913099493401	11	23	7.6	2,230	1,450	4,600	400	14	68	16	140	700	230
440913099493401	12	21	8.0	2,200	1,440	340	390	15	66	18	140	700	230
441215099310501	13	14	--	2,180	1,560	--	150	17	260	80	90	1,100	20
441215009310501	14	18	--	--	2,090	--	190	17	360	69	150	1,300	0
441215099310501	15	20	8.3	1,930	1,400	50	260	8	140	55	170	760	10
440628099325501	16	--	--	2,800	1,870	--	450	20	88	24	80	1,100	220
440628099325501	17	22	8.2	2,570	1,740	50	470	15	79	18	84	980	200
441032099253701	18	24	7.3	2,420	1,970	1,400	250	15	280	48	87	1,200	180
441032099253701	19	24	7.8	2,380	1,860	1,800	240	18	260	62	85	1,100	200
440514099282501	20	24	7.0	2,690	2,140	10	150	19	390	88	190	1,200	200
440539099245901	21	22	7.2	2,460	8,200	6,100	110	16	450	54	90	1,300	170
440346099265401	22	21	7.3	2,540	2,100	4,700	250	20	290	78	81	1,300	180
435612099184101	23	13	8.1	4,110	3,120	490	480	34	380	110	190	1,800	250
435530099225601	24	--	7.6	2,460	1,880	1,100	150	23	330	73	110	1,100	200
435439099114201	25	21	7.3	2,560	1,890	2,100	285	22	230	55	92	1,200	180
434542099114601	26	20	7.0	2,480	2,100	2,110	88	20	410	94	110	1,300	170
434542099114601	27	20	7.9	2,550	2,110	2,100	100	21	410	89	110	1,300	160
434650099105001	28	20	7.0	2,470	2,090	2,500	83	19	410	94	99	1,300	170
434650099105001	29	20	7.9	2,470	2,100	2,600	90	20	410	97	96	1,300	170
434650099105004	30	20	7.0	2,470	2,110	2,400	86	19	420	92	110	1,300	160

sodium to chloride. The lowest pH values in water in the system (values at the arbitrarily imposed lower limit of 6.5 pH units) are detected in areas where waters have elevated dissolved-solids concentrations, such as in the Williston basin.

6. Outside of the basinal areas, the waters evolve along a typical chemical pathway while moving from recharge toward discharge areas. Waters in the highlands are dilute—generally less than 1,000 mg/L—and increase in concentration down the topographic gradient. The typical facies in the upland areas are the alkali-earth bicarbonate or sulfate facies, depending on the relative abundance of sulfate and carbonate minerals in the rocks. Sulfate, chloride, and sodium usually increase away from the recharge areas. Typically, pH has its largest value in the highlands and decreases downgradient to values that represent a slightly acid water.

7. In many instances, the mole ratio of bicarbonate to sulfate in water increases away from the recharge areas. Because the bicarbonate concentrations are relatively constant in water from the

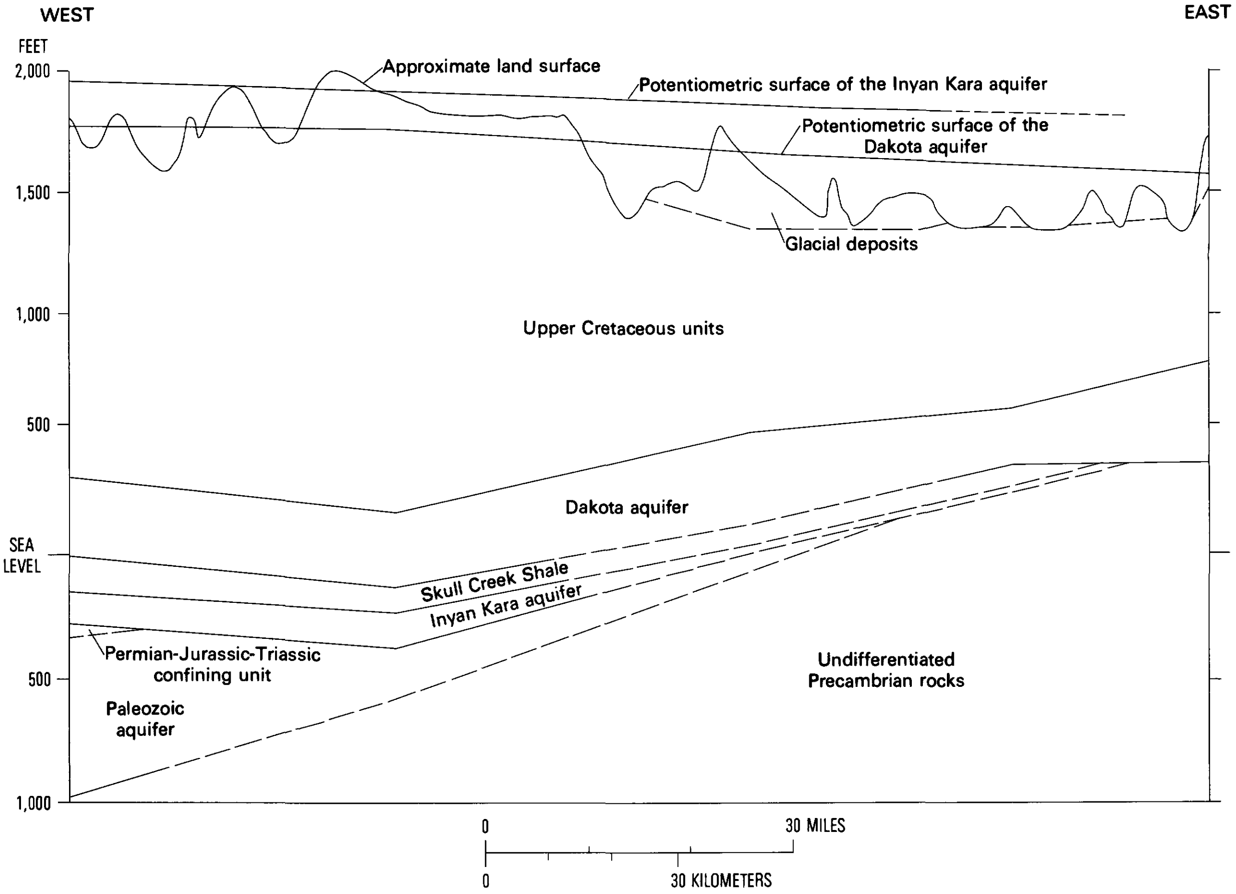

FIGURE 92.—Diagrammatic section showing potentiometric surfaces along flow path 3 in the Dakota aquifer in southeastern South Dakota. See figure 19 for location of flow path (p. 32).

Cambrian-Ordovician aquifer, the increase is attributed to a decrease in sulfate by precipitation.

8. The variation of sodium with chloride typically indicates excess sodium in the more dilute waters. The likely source of the excess sodium is silicate dissolution. At concentrations near 10,000 mg/L, the sodium and chloride are typically proportional to each other, which indicates the dissolution of an evaporite source. At larger concentrations, a contribution of dissolved alkali-earth chlorides becomes apparent.

9. The trends seen in the Cambrian-Ordovician aquifer are seen in the Madison aquifer. The Madison aquifer has been the subject of a more intensive study by Busby and others (1991). The mechanisms reported in that work and supplemented by this effort are dedolomitization coupled to the dissolution of gypsum; sulfate reduction with dissolution of minor quantities of organic material and ferric hydroxide; and the precipitation of pyrite. The dioctahedral to trioctahedral clay conversion also may be important in the control of magnesium in the Madison aquifer.

10. In each aquifer, the saturation indexes indicate the waters to be at or near equilibrium with calcite and undersaturated with gypsum (anhydrite) and dolomite.

11. Water chemistry of the confining units is more variable than that of the aquifers and lacks regional evolutionary trends. Dissolved-solids concentrations in the confining units are typically greater than those of the aquifers, presumably because of the increased reactivity of the finer grained sediments. The typical decreases in the mole ratio of magnesium to calcium along each flow path may indicate the conversion of dioctahedral to trioctahedral clays.

12. The patterns observed on the maps, graphs, and diagram for the water from the Pennsylvanian aquifer are consistent with the dissolution of evaporites and the dissolution of gypsum and dolomite.

TABLE 21.—Chemical composition of water from flow path 4 of the Inyan Kara aquifer in west-central South Dakota

[Location of flow path shown in figure 19. Listed in approximate downgradient order; a, Fall River Sandstone, b, Lakota Formation; c, Inyan Kara Group; °C, °Celsius; pH, pH units, µS/cm, microsiemens per centimeter at 25 °Celsius; mg/L, milligrams per liter; µg/L, micrograms per liter]

Station identification number	Sample number	Geologic formation	Temperature (°C)	pH	Specific conductance (µS/cm)	Dissolved solids, calculated (mg/L)	Dissolved iron (µg/L)	Sodium	Potassium	Calcium	Magnesium	Chloride	Sulfate	Bicarbonate
								(mg/L)						
440753103110801	1	c	--	8.0	–	535	–	41	0.0	97	31	3.0	250	230
440330103080001	2	b	26	7.2	720	498	0	32	7	75	29	7.8	210	280
440508102500201	3	c	--	7.7	–	449	–	150	0	10	2.0	4.0	160	250
434510102263101	4	b	40	7.3	630	432	2,400	82	9	45	10	2.6	160	250
435944102145801	5	a	39	8.6	1,060	710	40	270	3	2.0	.3	8.1	240	381
434755102145201	6	c	40	7.8	860	610	820	190	7	15	2.0	5.6	240	310
435936102143001	7	c	--	8.3	–	640	–	250	0	2.0	0	8.0	210	350
435950102142001	8	a	--	8.7	1,140	668	80	260	3	2.4	.3	9.0	200	393
435921102140601	9	c	--	7.7	–	660	–	250	.3	2.0	1.0	10	200	360
435256102400001	10	c	--	8.4	–	1,650	–	580	0	16	2.4	16	220	450
435908102073301	11	c	--	8.7	–	1,470	–	260	0	2.4	0	13	910	570
435237101574301	12	c	--	8.4	–	1,310	–	520	0	4.1	.8	27	280	964
435237101574201	13	a	17	8.4	2,090	1,280	1,500	530	8	3.4	.6	32	290	855
435237101574201	14	a	22	8.0	2,110	1,380	600	530	6	3.8	1.3	28	290	980
440202101394001	15	c	56	7.5	3,390	2,200	40	800	10	9.7	1.9	140	790	980
435805101350001	16	c	--	7.6	–	4,400	–	1,500	0	20	5.2	230	2,300	700
435515101284701	17	c	--	8.8	–	2,480	–	920	0	9.7	2.1	140	1,000	822
435516101284801	18	a	19	8.3	3,700	2,540	3,400	890	9	9.8	1.9	150	1,000	970
435516101284801	19	a	20	8.1	3,800	2,430	3,400	870	7	9.8	1.9	140	920	970
435655101314501	20	c	48	8.0	3,120	2,050	–	760	5	8.7	1.1	90	700	990
435655101314501	21	c	49	8.3	3,200	2,060	–	780	7	10	1.3	100	700	945
435655101314501	22	c	48	7.7	3,230	2,190	180	780	7	8.2	1.1	100	810	990
435957101214001	23	a	43	7.0	–	4,580	2,600	1,500	13	31	4.2	290	2,300	900
441033101073301	24	a	51	7.5	6,150	2,570	1,100	900	10	18	3.0	210	1,100	670
440325101141301	25	c	57	7.2	6,100	4,290	2,600	1,400	13	38	7.3	320	2,200	630
435320101125401	26	c	27	7.4	5,500	2,690	7,000	780	11	27	3.9	73	1,300	1,010
435528101120301	27	a	51	7.3	6,800	4,540	250	1,500	12	34	5.0	370	2,300	650
441030101112201	28	a	46	8.1	5,330	2,420	150	800	8	9.1	2.8	130	1,200	560
440312101081101	29	a	56	7.9	3,300	2,580	100	800	7	11	3.5	140	1,300	640
440312101081101	30	a	56	7.9	3,300	2,520	100	850	7	9.6	1.7	140	1,200	640
435011101053901	31	c	--	7.4	–	4,230	–	1,500	0	12	17	350	2,000	710
434036100545201	32	c	--	7.9	–	2,930	–	1,000	0	18	3.2	180	1,300	880
434025100552001	33	c	32	7.9	4,320	2,940	–	1,000	10	18	3.2	180	1,300	880
433652100501801	34	c	--	8.2	–	1,690	–	640	0	8.0	2.4	38	780	460

13. The patterns observed on the maps, graphs, and diagrams for waters from the Permian-Triassic-Jurassic confining unit are consistent with the dissolution of carbonates and evaporites, cation exchange, and sulfate reduction.

14. Although the concentrations of dissolved solids in the waters of the Dakota aquifer are substantially larger than those of the Inyan Kara aquifer, the Lower Cretaceous aquifers show the same chemical trends. In the uplands, the waters are part of the bicarbonate or sulfate facies and have small concentrations of dissolved solids. As the waters flow along the flow path from the highlands toward discharge areas, the concentrations of calcium and magnesium

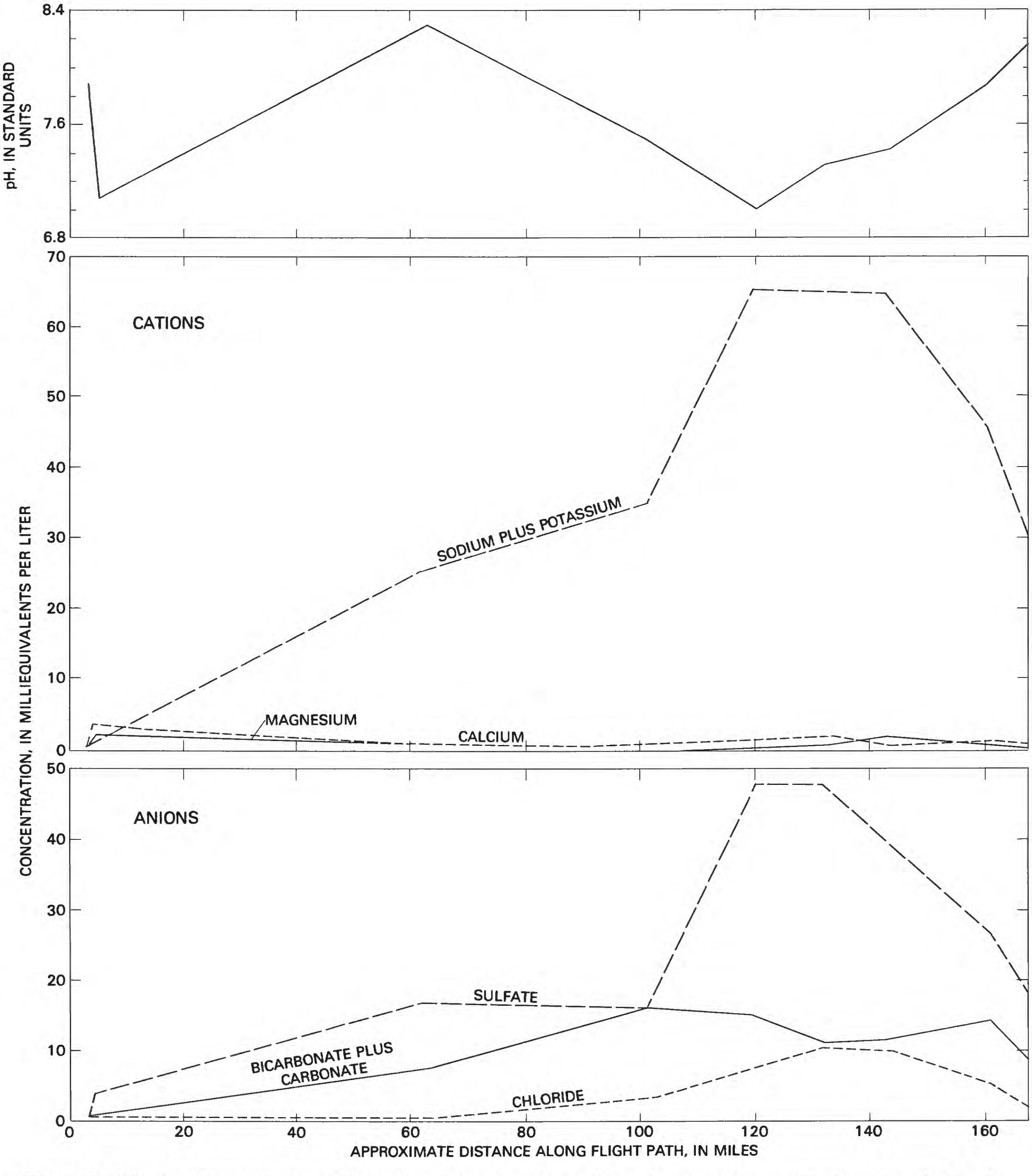

FIGURE 93.—Changes in concentrations of the principal ions along flow path 4 in the Inyan Kara aquifer in west-central South Dakota. See figure 19 for location of flow path (p. 32).

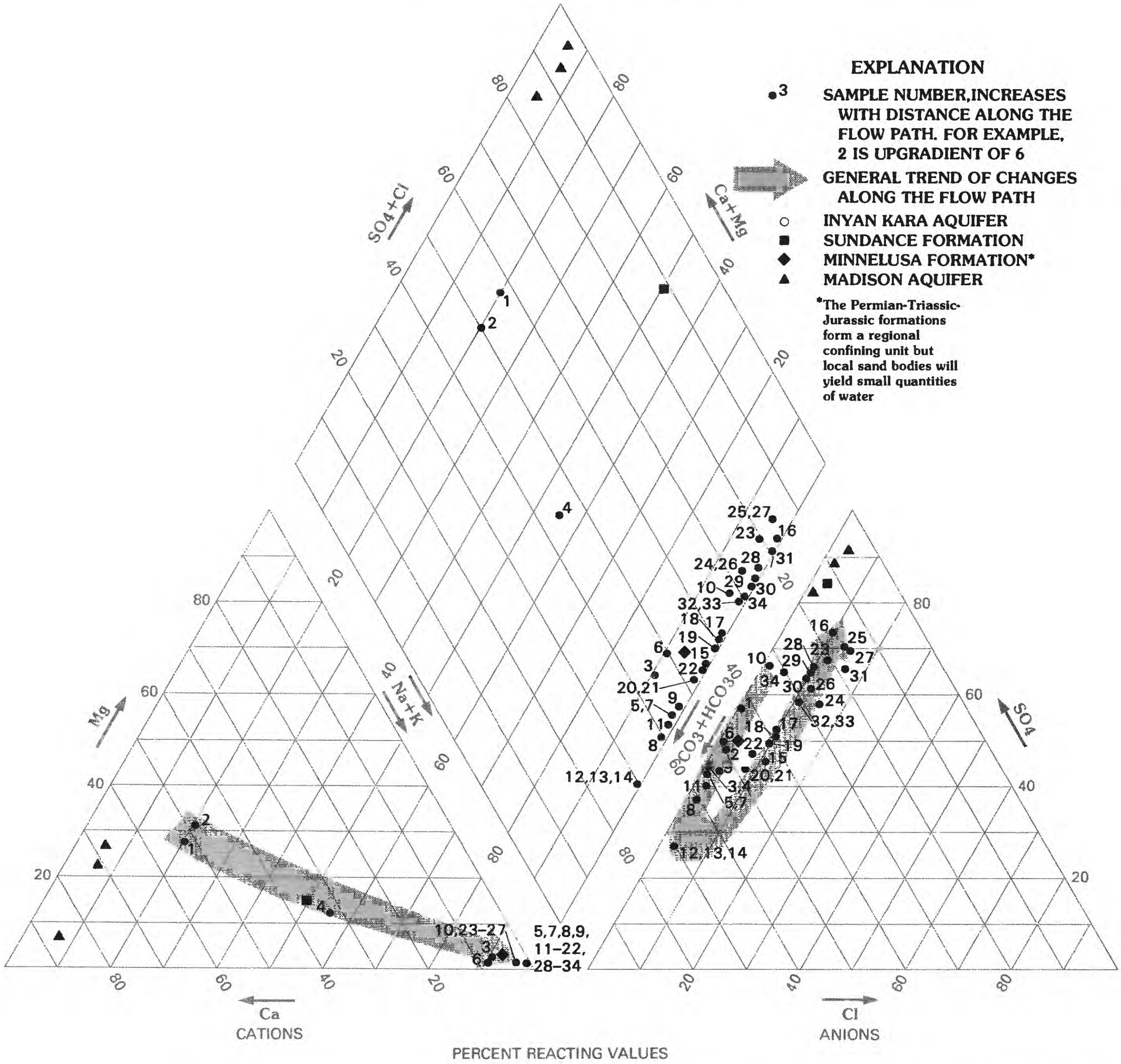

FIGURE 94.—Trilinear diagram for flow path 4 in the Inyan Kara aquifer in west-central South Dakota. See figure 19 for location of flow path (p. 32).

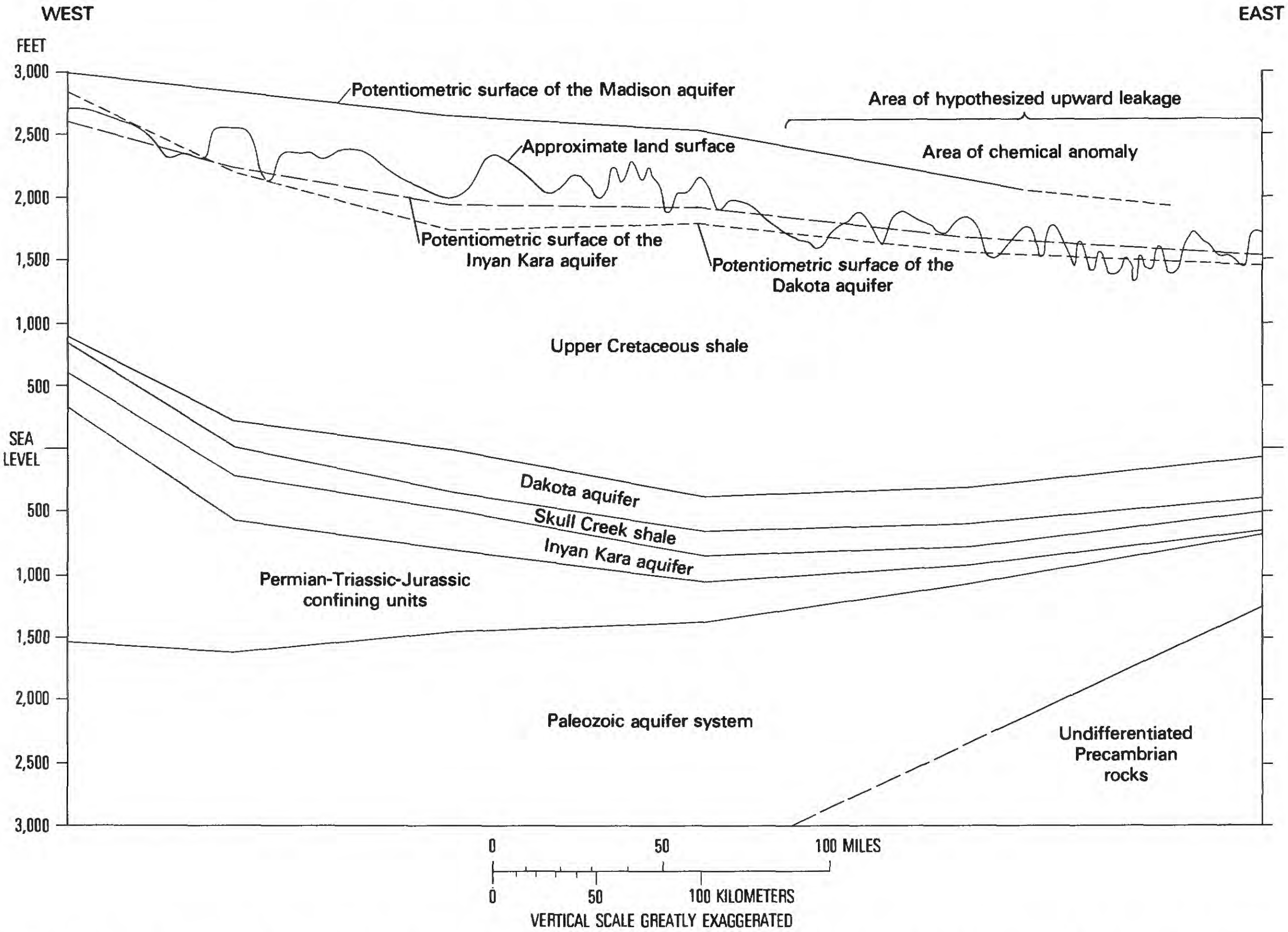

FIGURE 95.—Generalized cross section showing the potentiometric surfaces along flow path 4 in the Inyan Kara aquifer in west-central South Dakota. See figure 19 for location of flow path (p. 32).

decrease from more than 60 percent of the cations to less than 10 percent, while sulfate increases. Unusually large concentrations of sulfate in the southern Black Hills and near the Red River of the North may be because of leakage from the underlying Madison Formation into the overlying Dakota Formation.

15. The concentrations in the Dakota aquifer near the Williston basin are too large to be explained by aquifer mineralogy or water-rock interaction. Upward leakage from the Inyan Kara aquifer to the Dakota aquifer is a possibility, but the underlying Inyan Kara aquifer is more dilute than the Dakota aquifer.

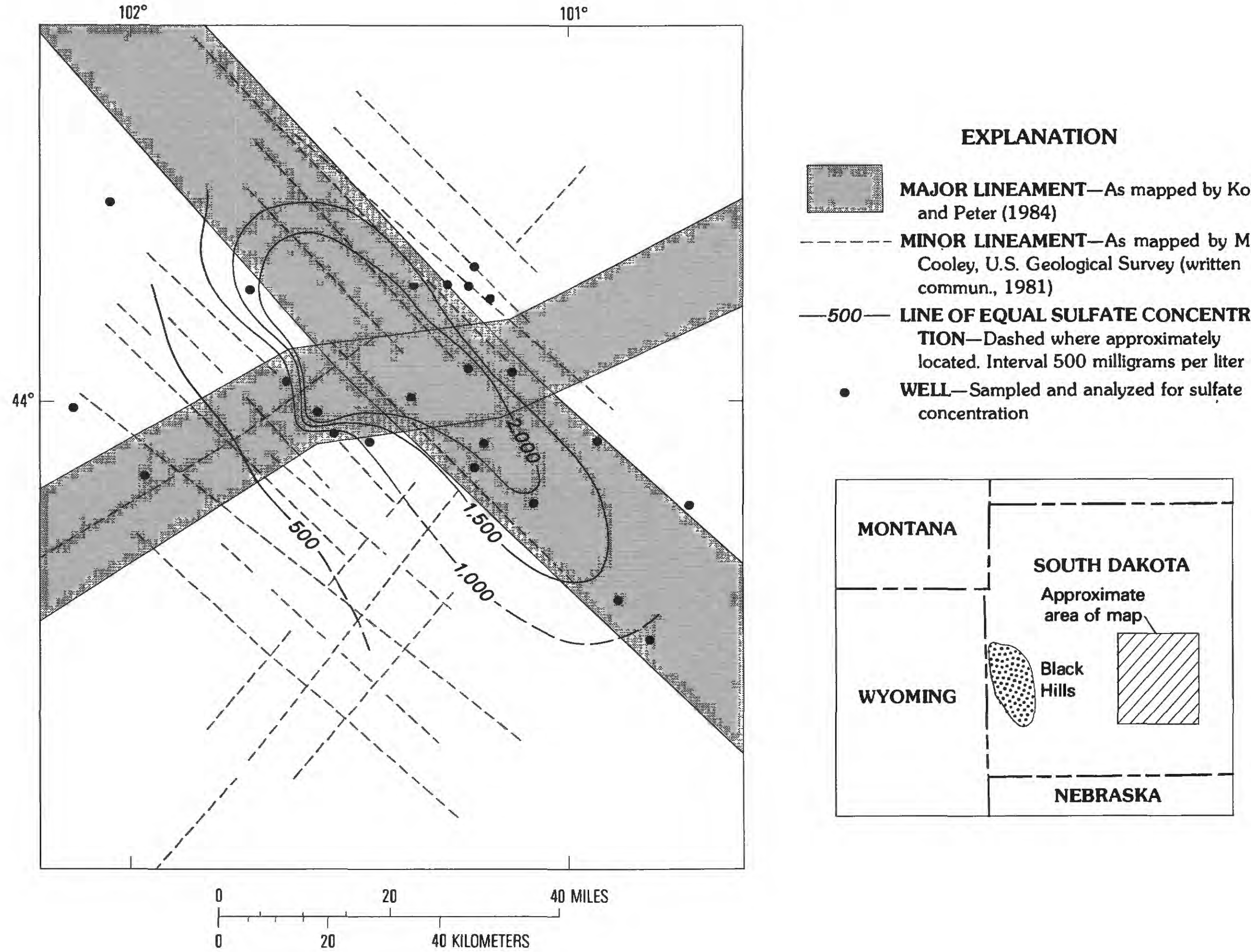

FIGURE 96.—Concentration of sulfate in water from the Inyan Kara aquifer in areas where surface lineaments are mapped, west-central South Dakota.

The most likely explanation is diffusion of chloride into the aquifer from the overlying shales.

16. The presence of connate waters in the Dakota aquifer is disproved by concentrations of deuterium and oxygen-18, which are on the meteoric water line.

17. The hypotheses relating the flow system and the geochemistry in the Lower Cretaceous aquifers require further testing. In particular, a chemical model of the mixing of water from the deeper, carbonate-evaporte aquifers with water from the sandstone aquifers has not been tested for agreement with the flow models. In addition, more information on the hydraulics and geochemistry of the marine shales is needed to substantiate the hypothesis of leakage from the shales to the Dakota aquifer. Isotopic data on fluids and solid phases also would help clarify the hypotheses.

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Published in the Central Region, Denver, Colorado
Edited by Thomas Kohnen
Cartography by Wayne Hawkins
Photocomposition by Marie F. Melone and Debra Sokol

*U.S. GOVERNMENT PRINTING OFFICE: 1995-673-046/86074