

# **GEOCHEMISTRY OF SELECTED AQUIFERS IN TERTIARY ROCKS OF THE UPPER COLORADO RIVER BASIN IN WYOMING, COLORADO, AND UTAH**

***By* David L. Naftz**

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**BRUCE BABBITT, Secretary**

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

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For additional information  
write to:

District Chief  
U.S. Geological Survey, WRD  
2617 E. Lincolnway, Suite B  
Cheyenne, Wyoming 82001-5662

Copies of this report can be  
purchased from:

U.S. Geological Survey  
Branch of Information Services  
Box 25286, Denver Federal Center  
Denver, Colorado 80225

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## CONVERSION FACTORS AND ABBREVIATIONS

Multiply	By	To obtain
foot (ft)	0.3048	meter
gallon (gal)	3.785	liter
inch (in.)	0.2540	millimeter
mile (mi)	1.609	kilometer
pound (lb)	0.4536	kilogram

Degree Fahrenheit (°F) may be converted to degree Celsius (°C) by using the following equation:

$$^{\circ}\text{C} = 5/9 (^{\circ}\text{F}-32)$$

$$^{\circ}\text{F} = 9/5 (^{\circ}\text{C})+32$$

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

Abbreviations water-quality units used in this report:

mg/L = milligrams per liter  
meq = milliequivalent  
mmoles/L = millimoles per liter

# Geochemistry of Selected Aquifers in Tertiary Rocks of the Upper Colorado River Basin in Wyoming, Colorado, and Utah

By David L. Naftz

## ABSTRACT

The Bridger, Duchesne River, and Uinta Formations in the Green River Basin and Uinta Basin of Wyoming and Utah, and the Green River and Wasatch Formations in the Green River, Great Divide, Washakie, and Sand Wash Basins of Wyoming and Colorado, contain four important aquifers within the Tertiary rocks of the Upper Colorado River Basin. These four aquifers are the Bridger and Duchesne River-Uinta aquifers of the Green River Basin and Uinta Basin aquifer systems, the Laney aquifer (and associated Wilkins Peak confining unit) of the Green River Basin and Great Divide-Washakie-Sand Wash Basins aquifer system, and the Wasatch zone of the Wasatch-Fort Union aquifer of the Green River Basin and Great Divide-Washakie-Sand Wash Basins aquifer system. Water-quality data from these selected aquifers were compiled and mineralogical data were collected from the rocks that compose the aquifers; together, these data were used to show and further define areas of recharge, discharge, and interaquifer leakage, previously defined by potentiometric surfaces and projected flow paths. Water-quality data were compiled from existing water-quality information that included the National Water Data Storage and Retrieval System (WATSTORE) files of the U.S. Geological Survey, files of Petroleum Data Services in Norman, Oklahoma, and published reports. Mineralogical composition of the formations containing each aquifer was determined from previously published reports.

Trends associated with the chemical constituents for each of the basin aquifers sometimes are obscured because of local variations in the aquifer system and areas of interaquifer leakage. Evolution

of the chemical character of water within each of these aquifers along projected flow paths is characterized by increasing concentrations of dissolved solids and decreasing concentrations of exchangeable divalent cations relative to sodium concentrations. In each of the aquifers, cumulative-frequency plots identify water with small concentrations of sodium and fluoride characteristic of recharge areas. Comparison of molar ratios of calcium to chloride in the water from each aquifer to the molar ratio of calcium to chloride for local precipitation indicates that ratio values in water from each aquifer exceeding the corresponding ratio in precipitation generally are confined to aquifer recharge areas.

Changes in the concentrations of certain major and minor chemical constituents in the Bridger and Duchesne River-Uinta aquifers and the Wasatch zone of the Wasatch-Fort Union aquifer are caused by the processes of sodium-magnesium and sodium-calcium exchange on clay minerals, evapotranspiration and subsequent mineral precipitation, and the leaching of shales. In addition, changes of concentration are caused by interaquifer leakage and moving ground water reaching equilibrium with local calcite, dolomite, fluorite, and carbon dioxide. In water from the Laney aquifer and the Wilkins Peak confining unit, the previously noted reactions for the Bridger and Duchesne River-Uinta aquifers and the Wasatch zone of the Wasatch-Fort Union aquifer, coupled with dissolution of saline minerals from evaporative lake deposits, can be used to explain the variations in water quality. Because of the scarcity of water-quality and solid-phase data, the proposed chemical reactions cannot be substantiated with detailed geochemical speciation, mass-balance, or reaction-path calculations. Detailed

geochemical sampling on a local scale would be needed to develop a reliable and quantitative geochemical model for the aquifers in the study area.

## INTRODUCTION

The U.S. Geological Survey began a comprehensive study of ground water in the Upper Colorado River Basin (fig. 1) in 1981. The objective of the study, which is part of the Survey's Regional Aquifer System Analysis (RASA) program, is to quantitatively assess the occurrence, movement, and availability of ground water in the basin.

The Upper Colorado River Basin is characterized by both variable physiography and variable climate. The basin includes parts of four physiographic provinces: the Middle Rocky Mountains, the Wyoming Basin, the Southern Rocky Mountains, and the Colorado Plateaus (fig. 2). The basin is bounded by the Middle Rocky Mountains on the north and west, by the Southern Rocky Mountains on the east and by the Wasatch Plateau and other high plateaus on the south and west. Land-surface altitudes range from 3,100 to 8,000 ft in the intermontane basins to 14,000 ft in the mountains of Colorado. Arid to semiarid climates prevail over most of the basin; however, the higher plateaus and mountains have subhumid to alpine climatic zones.

Sedimentary basins of the Upper Colorado River Basin are the Green River Basin, the Uinta Basin, the Great Divide Basin (internally drained), the Washakie Basin, the Sand Wash Basin, and the Piceance Basin (not discussed in this report). Although the aquifer systems in the Tertiary rocks of these basins are for the most part hydraulically isolated within individual basins, several individual aquifers have been identified in more than one basin. Specifically, some ground water does move between the Great Divide, Washakie, and Sand Wash Basins forming one interbasin aquifer system referred to as the Great Divide-Washakie-Sand Wash Basins aquifer system.

One of the study approaches used in the Upper Colorado River Basin RASA was to analyze water-quality data from selected aquifers together with mineralogical data from their host rocks to identify directions of ground-water movement. The selected aquifers, which are in rocks of Tertiary age, include the Bridger and Duchesne River-Uinta aquifers in the

Green River Basin and Uinta Basin aquifer systems; the Laney aquifer (and associated Wilkins Peak confining unit) in the Green River Basin and Great Divide-Washakie-Sand Wash Basins aquifer systems; and the Wasatch zone of the Wasatch-Fort Union aquifer in the Green River Basin and Great Divide-Washakie-Sand Wash Basins aquifer systems (fig. 1). These aquifers were selected because adequate water-quality information was available for interpretation and they had not been studied previously. These aquifers principally are found in the northern half of the Upper Colorado River Basin of Wyoming, Colorado, and Utah. Due to inadequate water-quality data and (or) limited areal extent, other Tertiary formations were not studied. Changes in water quality along projected flow paths in the Piceance Basin north of the Colorado River are summarized by Robson and Saulnier (1981).

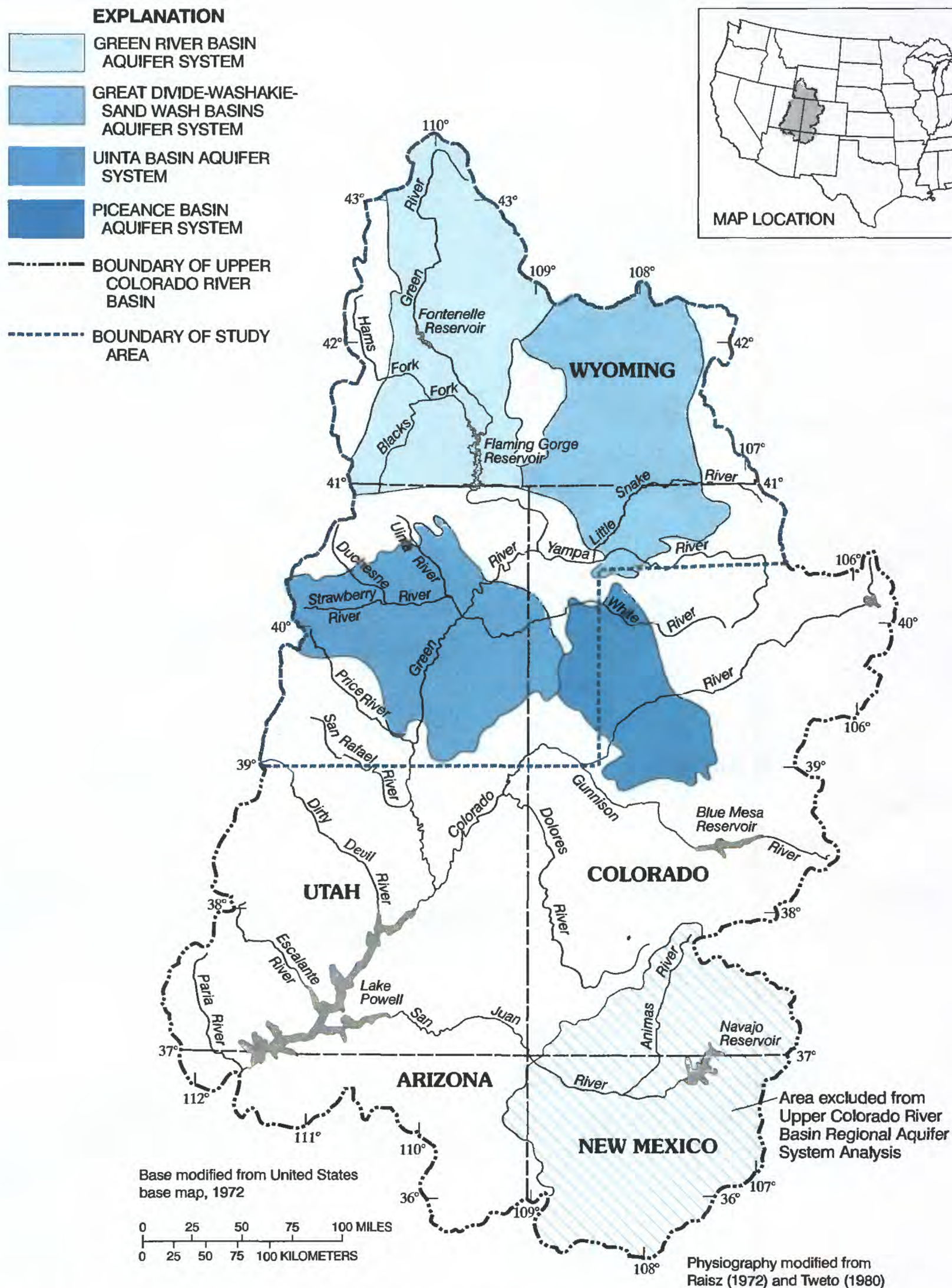
## Purpose and Scope

This report presents an analysis of available chemical data from selected aquifers in the Upper Colorado River Basin to substantiate areas of recharge to and discharge from each aquifer. In addition, the report characterizes the possible geochemical controls causing the observed changes in concentration for selected major and minor element constituents in each aquifer.

## Data Sources

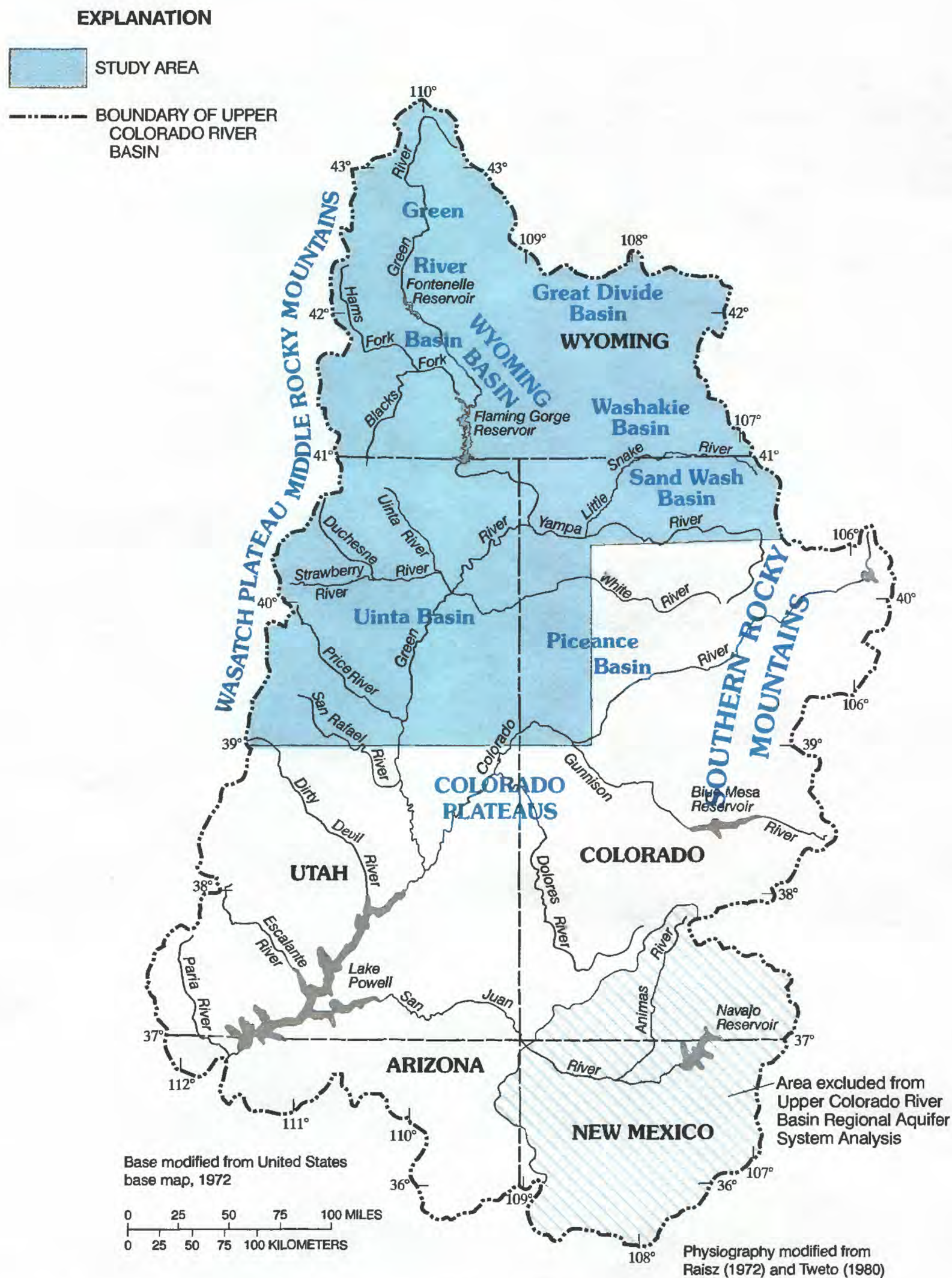
The water-quality data used to study the geochemistry of water from aquifers in rocks of Tertiary age are from the National Water Data Storage and Retrieval System (WATSTORE) files (U.S. Geological Survey, 1974) of the U.S. Geological Survey, the files of Petroleum Data Services in Norman, Oklahoma, and from published reports. Data in the WATSTORE file generally are from samples collected from wells developed for water supplies. Water-quality analyses from Petroleum Data Services generally are for samples collected by petroleum companies during drill-stem tests of oil wells. Only a limited amount of Petroleum Data Services data were used in this report because sampling interval information was not available or because contamination by drilling fluids was suspected.





**Figure 1.** Location of the study area and areal extent of basin aquifer systems in Tertiary sedimentary rocks of the Upper Colorado River Basin.





**Figure 2.** Drainage and physiographic subdivisions of the Upper Colorado River Basin.



The data often represent extremes of water quality in the aquifers within rocks of Tertiary age. For example, many of the data from Petroleum Data Services represent samples collected from deep wells penetrating potential oil reservoirs where the occurrence of water with large dissolved-solids concentrations is likely. Despite this known bias, data from all sources were combined for interpretation.

## Study Approach and Data-Analysis Methods

Corresponding water-quality data were compared to the potentiometric-surface map for each aquifer to substantiate and delineate the recharge and discharge areas, as well as the projected flow paths, in the aquifer. Concentration changes in selected chemical constituents in the water along the projected flow paths were used to identify possible chemical reactions causing the observed changes.

Systematic steps used to describe the geochemistry of ground water in each of the aquifers and its relation to recharge and discharge areas were as follows:

1. The mineral phases present in the formations were compiled from existing publications.
2. Maps showing the distribution in the dissolved-solids concentrations, water types, and log-molar ratios of calcium plus magnesium to squared-sodium concentrations were constructed; these maps were compared to potentiometric-surface maps.
3. Plots were made of the cumulative-frequency distribution of sodium and fluoride concentrations for the individual aquifers.
4. Maps showing the areal distribution of sodium and fluoride concentrations in each of the aquifers were constructed for the subgroups determined by the cumulative-frequency plots; these maps were compared to known recharge and discharge areas.
5. Maps showing the areal distribution of the ratios of calcium-to-chloride concentrations were constructed for each of the aquifers; these maps were compared to the potentiometric-surface map for each of the aquifers.

Calculations of log-molar ratios of calcium plus magnesium to squared-sodium concentrations have been used by Henderson (1984, p. 13–14) to evaluate direction of ground-water movement in two sandstone aquifer systems in the Northern Great Plains. Henderson found that the log-molar ratios of calcium plus magnesium to squared sodium in ground-water samples generally decreased along projected flow paths. This characteristic decrease is due to the exchange of calcium and magnesium ions in the water for sodium ions in clays.

Plots of the cumulative-frequency distribution for sodium and fluoride were used to identify subgroups within the water-quality data from each of the aquifers described in this study. Areal distribution of a group of a particular chemical constituent can help define ongoing geochemical processes along a flow path; these processes might be affecting the concentration of a particular constituent within an aquifer. For example, the cumulative-frequency plot of dissolved sodium from an aquifer might exhibit two distinct groups. One group, with smaller sodium concentrations, might indicate limited water-to-rock contact time from recharge areas; whereas the other group, with larger sodium concentrations, might indicate down-gradient areas of the aquifer where the water has had more water-to-rock contact time. This longer residence time may allow increased sodium concentration because of ion-exchange reactions on the clays. Applications of cumulative-frequency plots to the earth sciences and geochemistry are summarized by Sinclair (1976). Klusman and others (1980) used cumulative-frequency plots to differentiate soil samples from the Green River and Uinta Formations in Utah and Colorado.

In this study, cumulative-frequency plots were constructed by plotting the cumulative relative frequency (in percent) of the target population on probability paper. The cumulative-percentage scale on probability paper is graduated so that data from a single, normally distributed target population plot as a straight line. A mixture of data from two normal target populations plot as linear segments separated by a curved segment containing an inflection point. The location of the inflection point on the probability paper provides an estimate of the relative proportions of the two target subgroups. After the inflection point has been identified, the threshold value separating the two target subgroups can be defined by a procedure



described by Sinclair (1976). Areal distribution of the subgroups determined by the cumulative-frequency plots were compared to the projected flow paths in the aquifers for delineation of recharge and discharge areas.

Ratio values of calcium-to-chloride concentrations were used to identify possible reactions that occurred in ground water and to delineate recharge and discharge areas. The basic assumption was made that chloride is conservative. However, chloride concentration can increase downgradient because of possible leakage from shales or dissolution of saline-mineral phases. Comparison of ratio values of calcium-to-chloride concentrations in ground water to the corresponding mean ratio in precipitation helps to identify possible chemical reactions along projected flow paths. For example, if carbonate dissolution is active in recharge areas as a source of calcium in addition to evaporative concentration of calcium, the calcium-to-chloride ratio in the ground water from this area would exceed the mean calcium-to-chloride ratio value in precipitation from the area. This technique has been used by Kimball (1981, p. 10–13) to identify possible chemical reactions and projected flow paths occurring in ground water from the southeastern part of the Uinta Basin aquifer system.

## **STRATIGRAPHY OF FORMATIONS CONTAINING AQUIFERS AND CONFINING UNITS**

### **Duchesne River and Uinta Formations**

The Duchesne River-Uinta aquifer is contained within both the Duchesne River and Uinta Formations (fig. 3). The Duchesne River Formation, late Eocene to early Oligocene in age, is present in the northern part of the Uinta Basin. The Duchesne River Formation consists primarily of shale, siltstone, sandstone, and conglomerate (Hood, 1976, p. 8). Sandstone is most abundant in the lower part of the Duchesne River Formation; conglomerate is most abundant in the upper part. Local fractures in the formation contain secondary deposits of gypsum. Maximum thickness is about 3,000 ft in the center of the basin.

The Uinta Formation, middle to late Eocene in age, is present in the southern part of the Uinta Basin. The Uinta Formation consists primarily of thin-bedded

shale, siltstone, and fine-grained sandstone, with interbedded claystone and limestone (Hood, 1976, p. 8). The Uinta Formation grades from fluvial to lacustrine deposits toward the center of the Uinta Basin where the maximum thickness is as much as 5,000 ft.

### **Bridger Formation**

The Bridger Formation contains the Bridger aquifer in the central part of the Green River Basin aquifer system. The Bridger Formation is late Eocene in age and primarily consists of mudstone interbedded with crossbedded, tuffaceous mudstone (Bradley, 1964, p. 49). Volcanic-ash beds and limestone and marlstone layers also are found in the Bridger Formation. Carbonaceous sandstone, shale, and clay layers also are present in the Bridger Formation at some localities. In the southern and northeastern parts of the Green River Basin, the Bridger Formation locally is conglomeratic (Bradley, 1964, p. 53). Thickness of the Bridger Formation ranges from about 480 ft in the central part of the Green River Basin to 2,285 ft in the southern part of the basin.

### **Laney and Wilkins Peak Members of the Green River Formation**

The Laney Member of the Green River Formation is middle Eocene in age and is the uppermost unit in the Green River Formation in Wyoming. The Laney Member, found in the Green River Basin and Great Divide, Washakie, and Sand Wash Basins, primarily is a lacustrine deposit (Bradley and Eugster, 1969, p. 6–7). Within the Green River Basin, the Laney Member ranges in thickness from less than 200 ft in the vicinity of outcrop areas to more than 1,100 ft in the southern part of the aquifer system. Lithologies include varying amounts of interbedded oil shale, marlstone, fine-grained sandstone, siltstone, and minor beds of limestone and altered tuff. Near the center of the Green River Basin, the lower part of the Laney Member predominantly is low-grade oil shale (Bradley, 1964, p. 44). The organic content of the Laney Member decreases to the northwest. The lacustrine silt and sandstone of the Laney Member is replaced by fluvial sandstones and mudstones of the Bridger Formation to the north (Culbertson and others, 1980, p. 10). The



System	Series	Uinta Basin aquifer system		Great Divide-Washakie-Sand Wash Basins aquifer system		Green River Basin aquifer system	
		Stratigraphic units	Geohydrologic units	Stratigraphic units	Geohydrologic units	Stratigraphic units	Geohydrologic units
Tertiary	Pliocene						
	Miocene	Browns Park Formation	Locally important aquifers	Browns Park Formation	Locally important aquifers	Browns Park (?) Formation	Locally important aquifers
	Oligocene	Bishop Conglomerate		Bishop Conglomerate		Bishop Conglomerate	
		Duchesne River Formation	Duchesne River-Uinta aquifer	Washakie Formation	Washakie aquifer		
Eocene		Uinta Formation Parachute Creek Member Garden Gulch Member Douglas Creek Member Renegade Tongue Main body Wasatch Formation Green River Formation	Parachute Creek confining unit Douglas Creek-Renegade aquifer Wasatch-Green River confining unit	Laney Member Cathedral Bluffs Tongue Wilkins Peak Member New Fork Tongue Tipton Tongue Niland Tongue Luman Member Main body Fort Union Formation Battle Spring Formation Wasatch Formation Green River Formation	Green River confining unit Wasatch zone Wasatch-Fort Union aquifer Fort Union zone	Bridger Formation Laney Member Cathedral Bluffs Tongue Wilkins Peak Member New Fork Tongue Tipton Shale Member La Barge Member Luman Member Main body Fort Union Formation	Bridger aquifer Laney aquifer Wilkins Peak confining unit New Fork aquifer Tipton confining unit Wasatch zone Wasatch-Fort Union aquifer Fort Union zone
	Paleocene	North Horn Formation (part) Flagstaff Member	North Horn-Mesaverde aquifer (part)				

**Figure 3.** Generalized stratigraphic relation of aquifers and confining units in aquifer systems in Tertiary rocks [modified from Taylor and others (1986), and Love, Christiansen, and Ver Ploeg (1987)].



Laney Member of the Green River Formation contains the Laney aquifer only in the Green River Basin aquifer system (fig. 3). Even so, the Laney has small values of hydraulic conductivity in the southern part of the basin (Martin, 1996).

The Laney Member ranges in thickness from less than 400 ft to nearly 1,900 ft and is characterized by muddy marlstone and brown shales (Bradley, 1964, p. 44) within the Great Divide, Washakie, and Sand Wash Basins. The amount of organic matter and low-grade oil shales found in the Laney Member within the Great Divide, Washakie, and Sand Wash Basins increases to the northwest.

The Wilkins Peak Member of the Green River Formation underlies the Laney Member in the Green River and Great Divide, Washakie, and Sand Wash Basins, and it is considered a confining unit in both basins areas (fig. 3). Lithologies of the Wilkins Peak Member consist of lacustrine and evaporite beds of oil shale, marlstone, limestone, trona, and halite, with intertongues of sandstone, siltstone, and mudstone (Culbertson and others, 1980, p. 7). Thick beds of trona are found in the Wilkins Peak Member within the central part of the Green River Basin. The Wilkins Peak Member thins northward to extinction by onlap with the New Fork Tongue of the Wasatch Formation in the Green River Basin (fig. 3).

### **Fort Union and Wasatch Formations and Equivalent Units**

The geologic framework of the Paleocene and lower Eocene rocks is described collectively because the formations are lithologically similar. In general, the rocks consist of fluvial sediments, and their hydraulic properties depend on the number, thickness, and continuity of sandstone layers and lenses. The most areally extensive formations within the Paleocene and lower Eocene sequence of rock are the Fort Union and Wasatch Formations located in the Uinta, Green River, Great Divide, Washakie, and Sand Wash Basins. The rocks crop out over large parts of their areal extent.

Lithologically similar rocks make up the Fort Union Formation of Paleocene age and the main body of the Wasatch Formation of Paleocene and Eocene age. The Fort Union is characterized by interstratified sandstone, mudstone, shale, and coal beds; the Wasatch is characterized by fluvial, mostly piedmont, deposits.

The fluvial deposits are coarse grained near the mountains from which the sediments were derived and become more fine grained with increasing distance from the mountains.

The sequence of Paleocene and lower Eocene rocks is overlain by the Green River Formation. The contact generally coincides with a change in lithology from predominately fluvial sandstone and interbedded fine-grained material to predominately fine-grained lakebeds. As a result of changes in the size of the Eocene lakes, there is substantial intertonguing of the Wasatch and Green River Formations.

The Fort Union Formation accumulated to great thickness within the basins of southwestern Wyoming. Thickness exceeding 3,000 ft is common, with the greatest thickness being in the Great Divide and northern Green River Basins. Sandstone is the predominate rock type within the depositional trough of the northern Green River Basin. Within the Great Divide, Washakie, and Sand Wash Basins, the predominant sequence of rocks is interbedded sandstone of variable thickness with siltstone, shale, lignite, and coal. A westward thinning wedge of sandstone and conglomerate is located near the base of the Fort Union Formation. The Fort Union Formation constitutes the Fort Union zone of the Wasatch-Fort Union aquifer in the Green River Basin and the Great Divide-Washakie-Sand Wash Basins aquifer systems (fig. 3).

The Wasatch Formation in the Green River, Great Divide, Washakie, and Sand Wash Basins is a thick sequence of sandy shale and siltstone with varying amounts of channel sandstone, depending upon its proximity to a source area of material. Throughout the northern part of the Great Divide, Washakie, and Sand Wash Basins, a fluvial sheet of arkosic sandstone, called the Battle Spring Formation, dominates. This formation interfingers to the south and east with more typical red beds of Wasatch Formation as well as various members of the Green River Formation. The Wasatch Formation in the southern part of the Great Divide, Washakie, and Sand Wash Basins consists of a mixture of shale and sandstone. The Wasatch Formation and its equivalent (the Battle Spring Formation) constitute the Wasatch zone of the Wasatch-Fort Union aquifer in the Green River Basin and Great Divide-Washakie-Sand Wash Basins aquifer systems (fig. 3).

In the Green River Basin, the amount of sandstone varies both areally and vertically. Along the west side, Bradley (1964, p. 27) distinguished the New Fork



Tongue of the Wasatch Formation, consisting of mudstone and coarse-grained sandstone, and separated from the main body of the Wasatch Formation by the Tipton Shale Member of the Green River Formation. Along the southern part of the Green River Basin, the Wasatch Formation contains thick units of coarse conglomerate.

## **GEOCHEMISTRY OF SELECTED AQUIFERS**

In order to adequately describe the geochemical aspects of selected aquifers, it is necessary to discuss ground-water movement within the aquifers and the mineralogy of these solid-phase materials that compose the aquifers. The ground-water movement indicates ground-water flow paths. The mineralogy suggests potential dissolution products. The analyses of water at various points along the flow paths together with knowledge of the materials with which the ground water has been in contact, provide the opportunity to describe and understand the aquifer geochemistry.

### **Bridger and Duchesne River-Uinta Aquifers**

Because of the close proximity of the Bridger and Duchesne River-Uinta aquifers and their similar lithologies, these aquifers are discussed together; however, this does not imply that these aquifers are connected by a regional flow system. In fact, the Bridger aquifer is located in the Green River Basin primarily in Wyoming, whereas the Duchesne River-Uinta aquifer is located in the Uinta Basin primarily in Utah.

### **Ground-Water Movement**

The hydraulic conductivity of the Bridger aquifer in the Green River Basin aquifer system is small in unfractured areas but is large where the aquifer is fractured. Hydraulic-conductivity estimates from flow-model analysis of the Bridger aquifer range from 0.09 to 0.9 ft/d in the horizontal direction; the hydraulic conductivity is 0.000009 ft/d in the vertical direction (Martin, 1996). Saturated thickness of the Bridger aquifer varies from 0 ft along the northern, eastern, and western margins of the Green River Basin aquifer system to 1,000 ft along the southern margins (Martin, 1996).

In the Uinta Basin, the Duchesne River and Uinta Formations are classified as one geohydrologic unit because of their similar lithologies and hydrologic properties. This unit is called the Duchesne River-Uinta aquifer (fig. 3). Price and Miller (1975) and Hood (1976, p. 34–35) studied the hydrology of the Uinta and Duchesne River Formations in the Uinta Basin. Water-level measurements in areas where both the Uinta and overlying Duchesne River Formations occur indicate no difference between hydraulic head in the two formations (Hood, 1976, p. 34). Evidence for large vertical-head gradients in the aquifer was not found, but that observation could be the result of a scarcity of data.

Hydraulic conductivity of the Duchesne River-Uinta aquifer is related to lithology and degree of fracturing. According to Hood (1976, p. 31), the distribution of hydraulic conductivity, as indicated by core tests, is similar to the distribution of sandstone porosity. The hydraulic conductivity of cores generally is less than 1.5 ft/d.

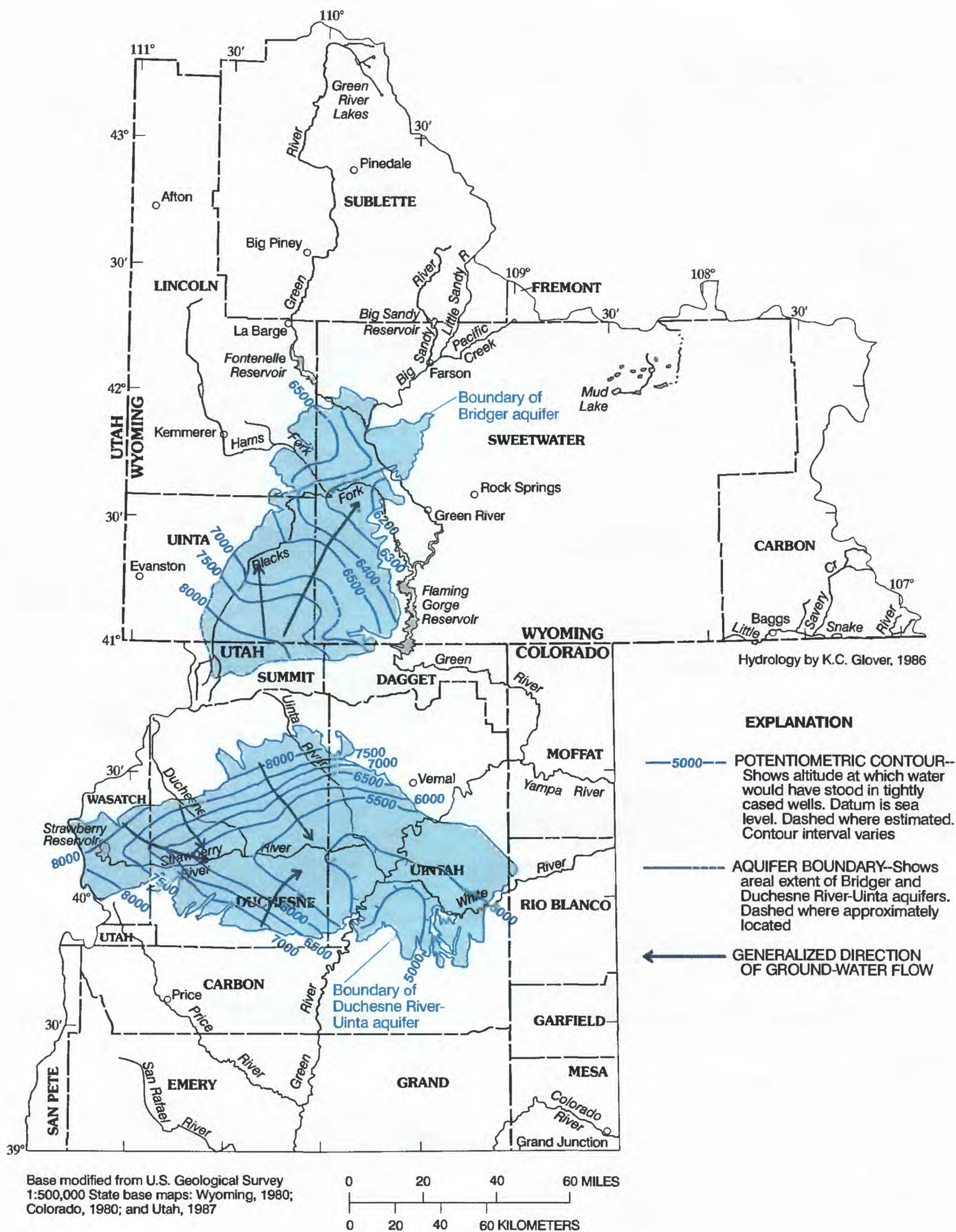
The potentiometric-surface map for the Bridger and Duchesne River-Uinta aquifers is shown in figure 4. The inference from the potentiometric-surface map is that recharge occurs in upland areas adjacent to the Uinta Mountains, where the amount of precipitation is large, and discharge occurs to the Green, Blacks Fork, and Duchesne Rivers.

### **Mineralogy**

Stratigraphic descriptions and mineralogical studies of the Bridger, Duchesne River, and Uinta Formations in the Green River and Uinta Basins were used to determine the mineral phases present within the Bridger and Duchesne River-Uinta aquifers. Due to the similar lithologies of the Washakie (Great Divide, Washakie, and Sand Wash Basins) and Bridger Formations (Green River Basin), mineralogical descriptions of the Washakie Formation were included when the mineralogical description of the Bridger Formation was compiled. The possible mineral phases that could be found in the Bridger, Duchesne River, and Uinta Formations are listed in table 1.

According to Bradley (1964, p. 49), volcanic ash beds make up as much as 15 to 20 percent of the Bridger Formation, with almost all sediments in the Bridger Formation having a volcanic source. No reference is made in the literature to volcanic deposits





**Figure 4.** Potentiometric contours and inferred flow paths for the Bridger and Duchesne River-Uinta aquifers, Green River Basin and Uinta Basin aquifer systems.



**Table 1.** Minerals present in the Bridger, Duchesne River, Uinta, and Washakie Formations, Green River Basin, Uinta Basin, and Great Divide, Washakie, and Sand Wash Basins, Wyoming, Utah, and Colorado

[From Bradley, 1964; Love, 1964; Roehler, 1970, 1973; Hood, 1976; and Dribus and Nanna, 1982]

Mineral name	Idealized chemical formula
Quartz	SiO <sub>2</sub>
Calcite	CaCO <sub>3</sub>
Plagioclase	Ca <sub>0.2</sub> Na <sub>0.8</sub> Al <sub>1.2</sub> Si <sub>2.8</sub> O <sub>8</sub>
Zircon	ZrSiO <sub>4</sub>
Biotite	K(Mg,Fe) <sub>3</sub> (AlSi <sub>3</sub> O <sub>10</sub> )(OH) <sub>2</sub>
Sphene	CaTiO(SiO <sub>4</sub> )
Hornblende	(Ca,Na) <sub>2-3</sub> (Mg,Fe,Al) <sub>5</sub> Si <sub>6</sub> (Si,Al) <sub>2</sub> O <sub>22</sub> (OH) <sub>2</sub>
Augite	(Ca,Na)(Mg,Fe,Al)(Si,Al) <sub>2</sub> O <sub>6</sub>
Sanidine	KAlSi <sub>3</sub> O <sub>8</sub>
Garnet group	-----
Apatite	Ca <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> (F,Cl,OH)
Illite	K <sub>0.6</sub> Mg <sub>0.25</sub> Al <sub>2.3</sub> Si <sub>3.5</sub> O <sub>10</sub> (OH) <sub>2</sub>
Kaolinite	Al <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub>
Montmorillonite	-----

in the Uinta or Duchesne River Formations in the Uinta Basin. The andesitic, dacitic, and rhyolitic tuffs found in the Bridger and Washakie Formations in the Green River Basin and Great Divide-Washakie-Sand Wash Basins contain plagioclase, hornblende, silicic glass, chloritized biotite, organic matter, augite, quartz, and sanidine, and small amounts of zircon, garnet, sphene, and apatite (Bradley, 1964, p. 49–54; Love, 1964, p. 6–7; Roehler, 1970, p. 181–187; Roehler, 1973, p. 21–22).

Dribus and Nanna (1982, p. 86), described the lithology of the Washakie Formation as interbedded volcanic claystone, arkosic volcanic arenite, tuff, and tuffaceous sandstones. Minerals associated with these lithologies include calcite, quartz, plagioclase, sanidine, and a siliceous matrix. The matrix comprises zeolites, clay, and silica derived from the devitrification of volcanic material (Dribus and Nanna, 1982, p. 86). Clay minerals described by Roehler (1973, p. 22), include illite, kaolinite, and montmorillonite in rocks throughout the Washakie Formation.

## Water Chemistry and Changes Along Flow Paths

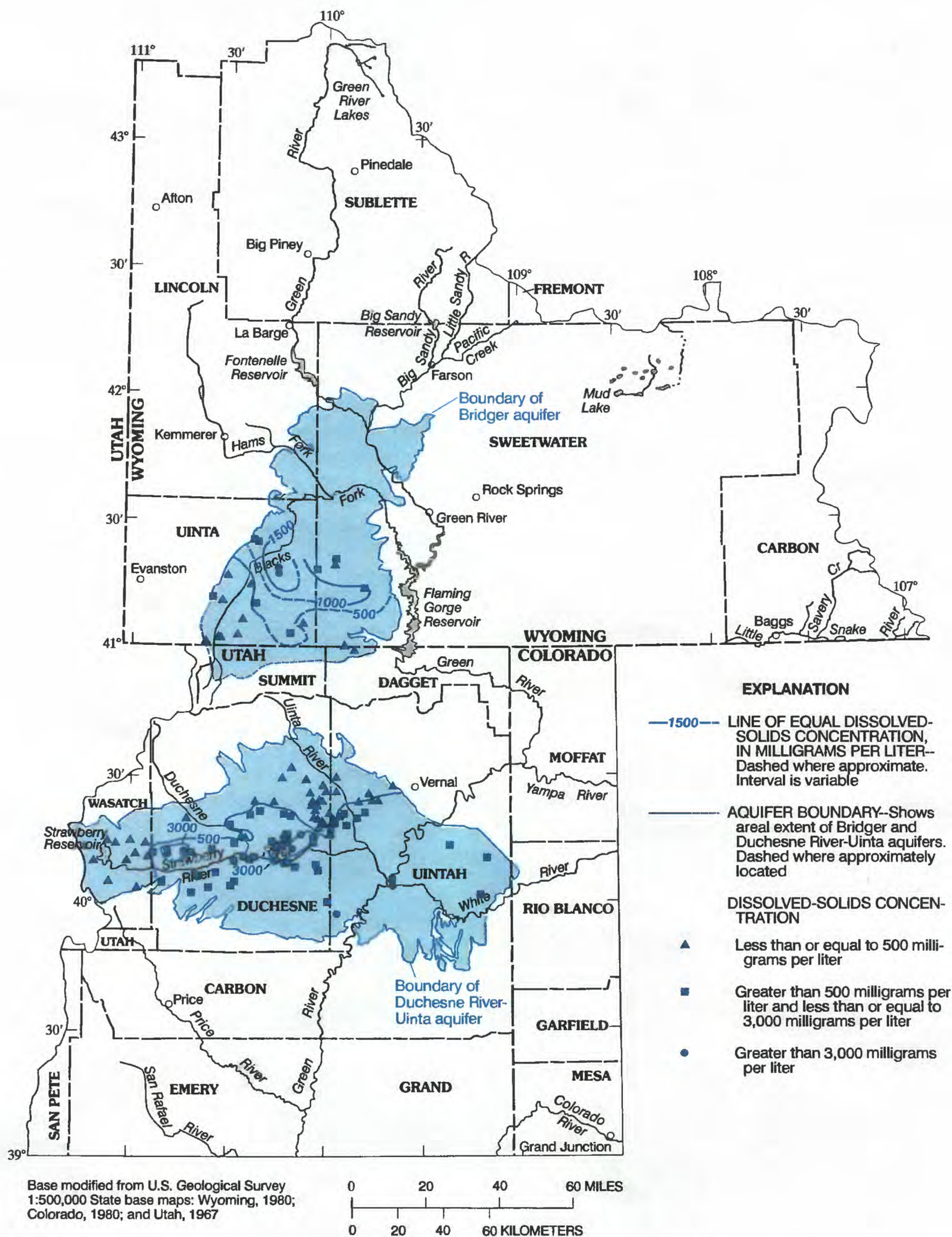
Maps showing the chemical constituents in water from the Bridger and Duchesne River-Uinta aquifers indicate systematic variations in the concentrations of major elements. The dissolved-solids distribution in the Bridger aquifer (fig. 5) indicates gradual increases in dissolved-solids concentrations from the southern margin of the Green River Basin aquifer system in a northeastern direction. This observed dissolved-solids increase in the Bridger aquifer is in general agreement with the flow paths projected from the potentiometric-surface map of the Bridger aquifer (fig. 4). Lack of water-quality and head data for the Bridger aquifer in the central parts of the Green River Basin aquifer system prevents further discussions of dissolved-solids changes along projected flow paths.

The dissolved-solids distribution in the Duchesne River-Uinta aquifer (fig. 5) indicates that the water with small dissolved-solids concentrations is limited to the recharge areas in the northern and western parts of the Uinta Basin aquifer system. Increases in dissolved-solids concentrations generally follow the flow paths inferred from the potentiometric surface map for the Duchesne River-Uinta aquifer (fig. 4). Most water with a dissolved-solids concentration larger than 3,000 mg/L is found in the central parts of the Duchesne River-Uinta aquifer adjacent to the Duchesne River (fig. 5). The absence of water with small dissolved-solids concentrations adjacent to the extreme southeastern limit of the aquifer suggests limited recharge in this region.

Areal variations of major chemical constituents for selected wells in the Bridger and Duchesne River-Uinta aquifers are shown in figure 6 in the form of Stiff diagrams (Stiff, 1951). These diagrams portray cationic and anionic concentrations of ground water on three horizontal axes extending on either side of a vertical zero axis.

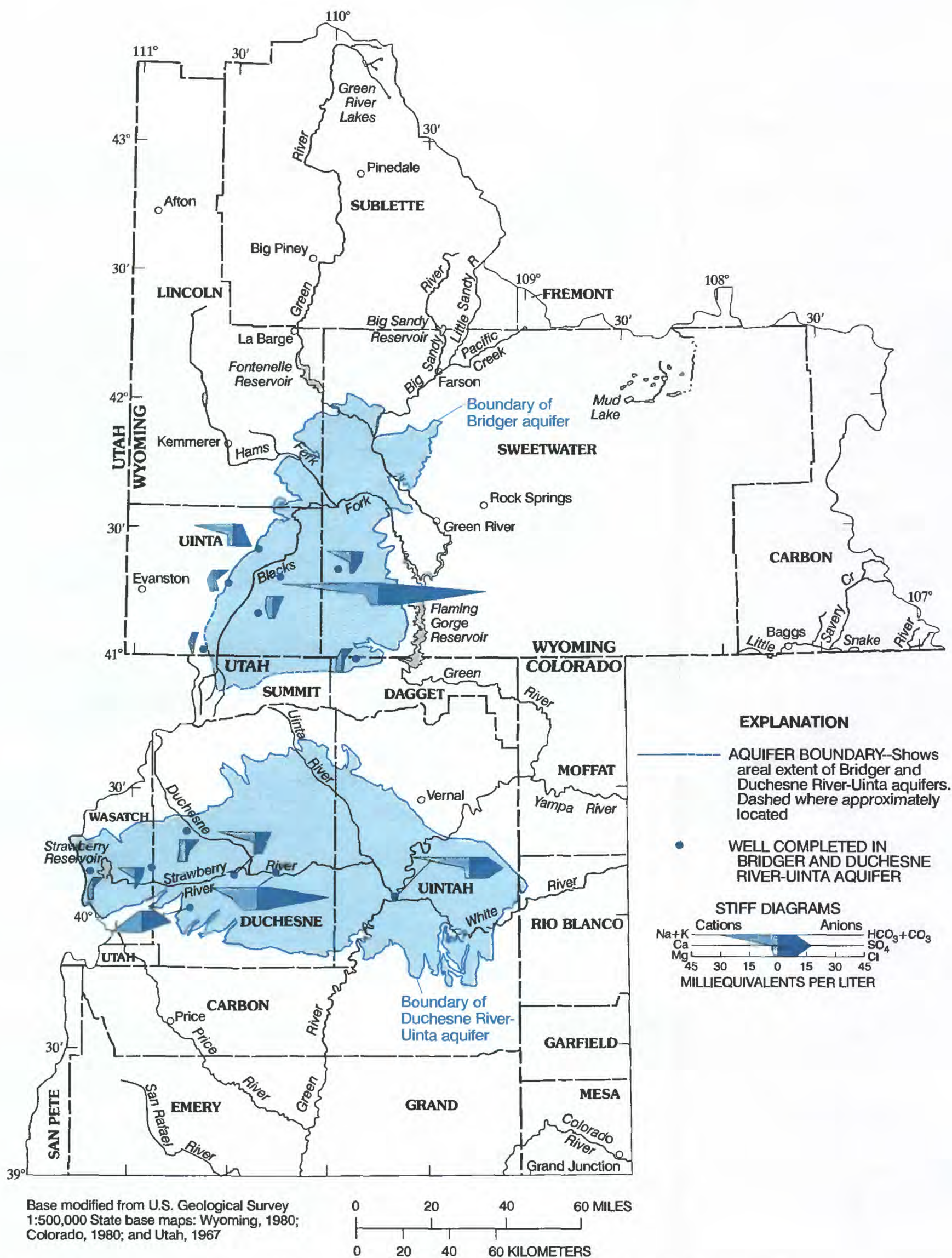
Water from probable recharge areas of the Bridger aquifer in the southern Green River Basin aquifer system generally is a calcium bicarbonate and magnesium bicarbonate type (fig. 6). The Stiff diagrams show increases in concentrations of sodium plus potassium, bicarbonate plus carbonate, sulfate, and chloride in the water along probable flow paths in the Bridger aquifer. Calcium and magnesium show small





**Figure 5.** Dissolved-solids concentrations for water from the Bridger and Duchesne River-Uinta aquifers, Green River Basin and Uinta Basin aquifer systems.





**Figure 6.** Stiff diagrams for major chemical constituent concentrations in water from the Bridger and Duchesne River-Uinta aquifers, Green River Basin and Uinta Basin aquifer systems.



increases in concentration relative to the waters recharging the aquifer, and several water samples show decreases in concentration of calcium and(or) magnesium compared to recharge waters.

Water in the recharge areas along the western outcrop of the Duchesne River-Uinta aquifer is predominantly a magnesium-bicarbonate and calcium-bicarbonate type (fig. 6). Stiff diagrams for water in the Duchesne River-Uinta aquifer show increases in concentrations of sodium plus potassium, carbonate plus bicarbonate, sulfate, and chloride along probable ground-water flow paths. In general, samples of down-gradient water in the Duchesne River-Uinta aquifer show decreases in calcium and magnesium relative to typical recharge water.

Relative increases in sodium concentrations coupled with relative decreases in calcium and magnesium concentrations can be interpreted as cation-exchange reactions, as shown in table 2 (reactions 5 and 6), with any clays present within the Bridger and Duchesne River-Uinta aquifers. The progression from positive to negative  $\log ([\text{Ca}] + [\text{Mg}]/[\text{Na}]^2)$  values was used by Henderson (1984) to identify areas of recharge and direction of flow in two ground-water systems in Montana and Wyoming. Based on the previously described mineralogy of the Bridger and Duchesne River-Uinta aquifers, possible sites for ion exchange include the clay minerals montmorillonite, illite, and kaolinite (table 1). Cation-exchange capacities for these minerals are: (1) kaolinite (3–15 meq/100 g);

(2) illite (10–40 meq/100 g); and (3) montmorillonite (80–150 meq/100 g) according to data compiled by Rose and others (1979, p. 197).

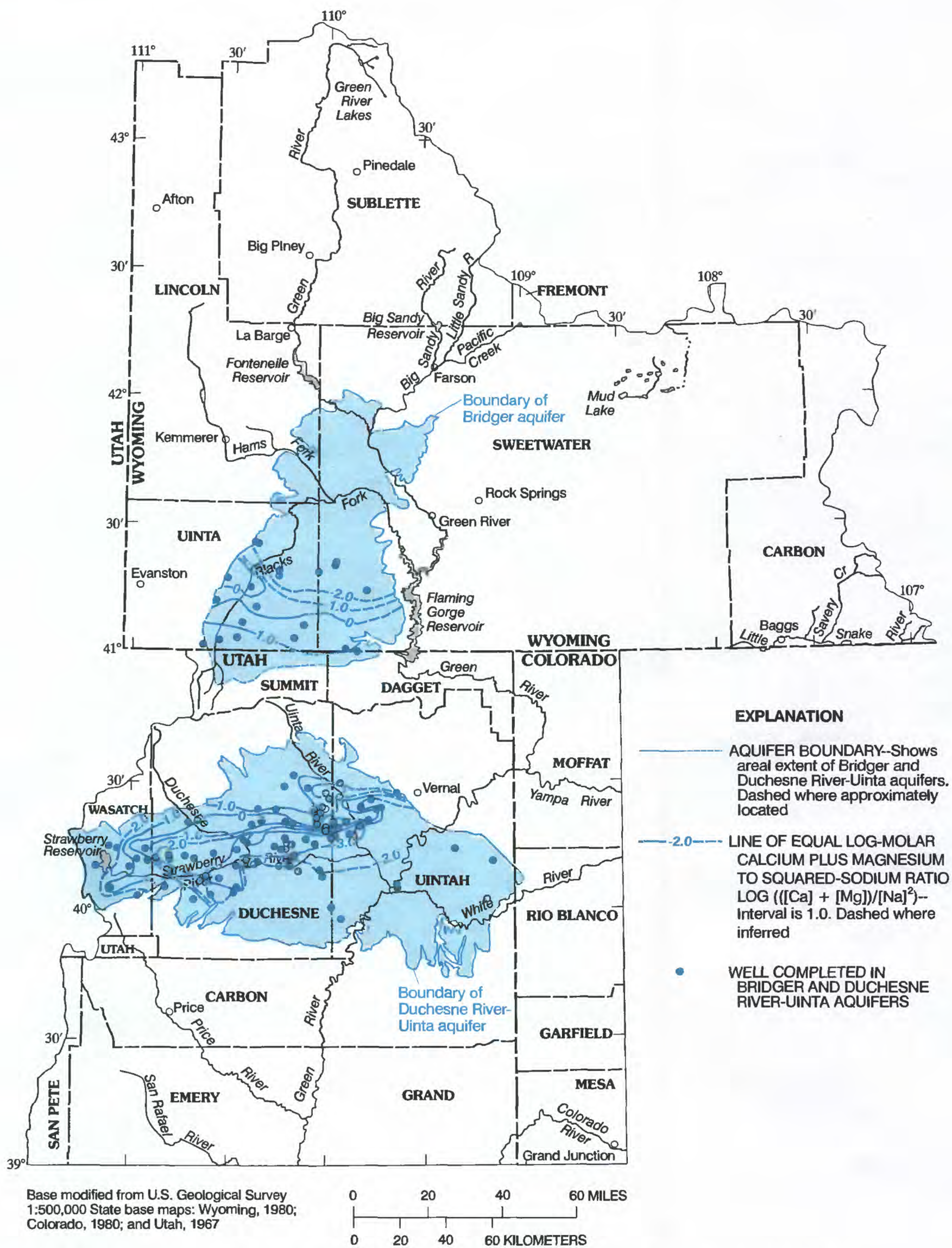
Water from the Bridger aquifer indicates positive  $\log ([\text{Ca}] + [\text{Mg}]/[\text{Na}]^2)$  values along the southern parts of the Green River Basin aquifer system, adjacent to the Uinta mountains, identifying this area as a recharge area (fig. 7). The progression of  $\log ([\text{Ca}] + [\text{Mg}]/[\text{Na}]^2)$  values from positive to negative generally follows flow paths inferred from the potentiometric-surface map (fig. 4) of the Bridger aquifer in the southern Green River Basin aquifer system. The localized area of positive  $\log ([\text{Ca}] + [\text{Mg}]/[\text{Na}]^2)$  values southeast of Evanston, Wyoming, and adjacent to Blacks Fork, indicate possible localized recharge from Blacks Fork. Based on the streamflow-gaging data in the Green River Basin (Martin, 1996), Blacks Fork, east of Evanston, is a losing stream. However, the ground-water flow model of the Green River Basin aquifer system indicated that Blacks Fork modeled together with Smiths Fork appears to be a gaining stream (Martin, 1996).

Water from the Duchesne River-Uinta aquifer in the Uinta Basin aquifer system indicates positive  $\log ([\text{Ca}] + [\text{Mg}]/[\text{Na}]^2)$  values along the western parts of the Uinta Basin aquifer system (fig. 7), where the potentiometric-surface map (fig. 4) indicates recharge. Approximately 10 miles east of Strawberry Reservoir the  $\log ([\text{Ca}] + [\text{Mg}]/[\text{Na}]^2)$  values become negative.

**Table 2.** Chemical reactions for mineral dissolution and weathering

Chemical reactions	Reaction number
$\text{CaSO}_{4(c)} = \text{Ca}^{2+} + \text{SO}_4^{2-}$ (anhydrite)	(1)
$\text{CaCO}_{3(c)} + \text{CO}_2 + \text{H}_2\text{O} = \text{Ca}^{2+} + 2\text{HCO}_3^-$ (calcite)	(2)
$\text{CaMg}(\text{CO}_3)_2(c) + \text{CO}_2 + \text{H}_2\text{O} = \text{CaCO}_3 + \text{Mg}^{2+} + 2\text{HCO}_3^-$ (dolomite) (calcite)	(3)
$2\text{Ca}_{0.2}\text{Na}_{0.8}\text{Al}_{1.2}\text{Si}_{2.8}\text{O}_8 + 2.4\text{CO}_2 + 10\text{H}_2\text{O} =$ (plagioclase) $1.2\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 1.6\text{Na}^+ + 0.4\text{Ca}^{2+} + 3.2\text{H}_4\text{SiO}_4 + 2.4\text{HCO}_3^-$ (kaolinite)	(4)
$\text{Ca}^{2+} + \text{Na}_2\text{EX} = 2\text{Na}^+ + \text{CaEX}$	(5)
$\text{Mg}^{2+} + \text{Na}_2\text{EX} = 2\text{Na}^+ + \text{MgEX}$	(6)





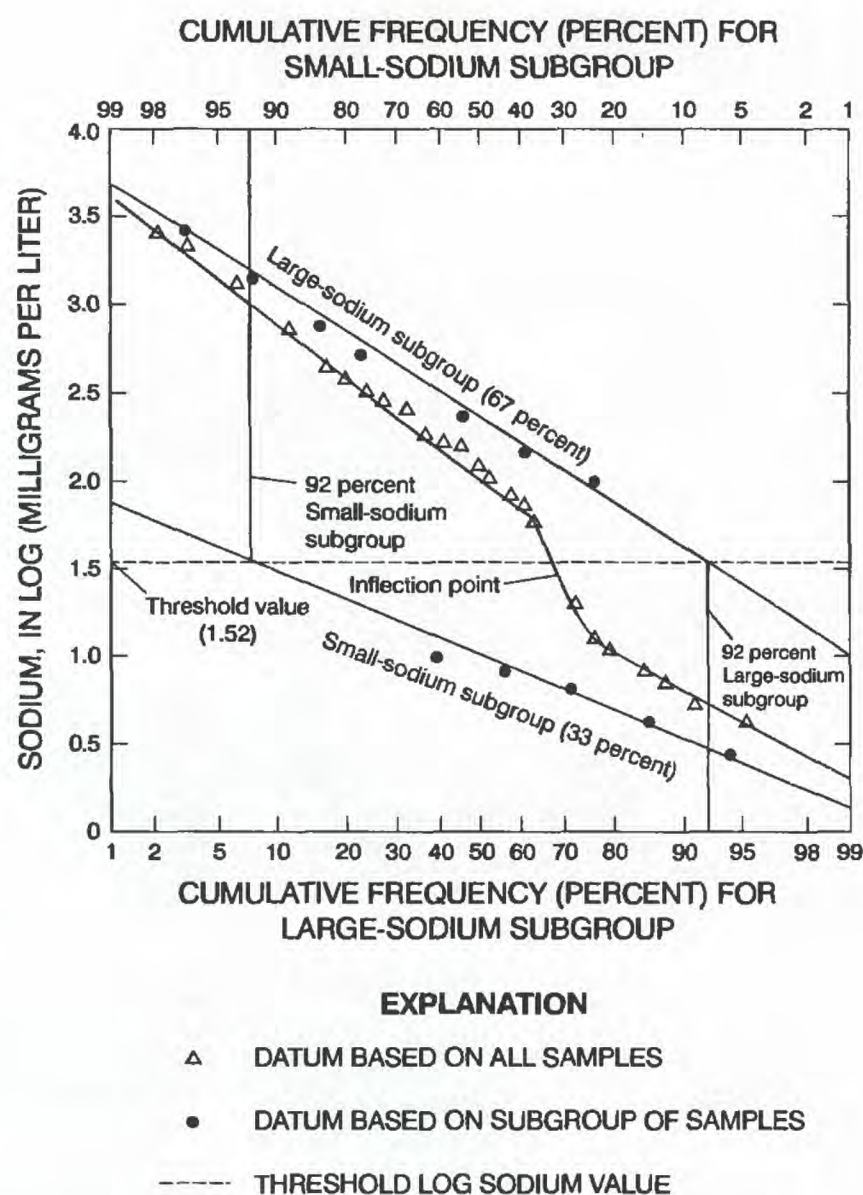
**Figure 7.** Log-molar ratios of calcium plus magnesium to squared-sodium concentrations in water from the Bridger and Duchesne River-Uinta aquifers, Green River Basin and Uinta Basin aquifer systems.



The absence of positive  $\log (([Ca]+[Mg])/[Na]^2)$  in the central part of the Uinta Basin aquifer system is in agreement with the potentiometric-surface map (fig. 4) that identifies the central part of the Uinta Basin aquifer system as a discharge area for the Duchesne River-Uinta aquifer. The values of  $\log (([Ca]+[Mg])/[Na]^2)$  adjacent to the Uinta River deviate from the basin trend. This deviation could be indicative of additional processes affecting the exchangeable cation concentrations other than cation exchange. Site-specific information is needed before further conclusions on the area adjacent to the Uinta River can be made.

The cumulative-frequency plot for sodium concentrations in the Bridger and Duchesne River-Uinta aquifers (fig. 8) shows the presence of two sodium subgroups with a mixing ratio of 67 and 33 percent of the total data set. Selection of a threshold value of 33 mg/L (1.52 log mg/L) describes about 92 percent of each sodium subgroup of samples. Although sodium could come from a variety of sources, probable sources within the Bridger and Duchesne River-Uinta aquifers include cation-exchange reactions (table 2; reactions 5 and 6) and dissolution of plagioclase feldspar (table 2; reaction 4). The distribution of ground-water samples from the two subgroups of sodium concentrations, defined by the threshold value of 33 mg/L, is shown in figure 9. Most ground-water samples with sodium concentrations less than or equal to the threshold value of 33 mg/L generally are found in recharge areas delineated by the potentiometric-surface map (fig. 4). Small sodium concentrations in water sampled from the recharge areas of the Bridger and Duchesne River-Uinta aquifers probably are the result of limited water-to-rock contact in recharge areas that would minimize sodic-feldspar dissolution. Furthermore, the positive  $\log (([Ca]+[Mg])/[Na]^2)$  values in recharge areas of the Bridger and Duchesne River-Uinta aquifers (fig. 7) indicate limited sodium increase from cation-exchange reactions.

The cumulative-frequency plot of fluoride concentrations for water from the Bridger and Duchesne River-Uinta aquifers (fig. 10) indicates an inflection point identifying two fluoride subgroups in the proportions of 59 percent and 41 percent of the total data. Selection of a threshold value of 0.9 mg/L (-0.06 log mg/L) describes about 82 percent of each subgroup. Wells with water above this threshold value generally are located in downgradient areas (fig. 11), as

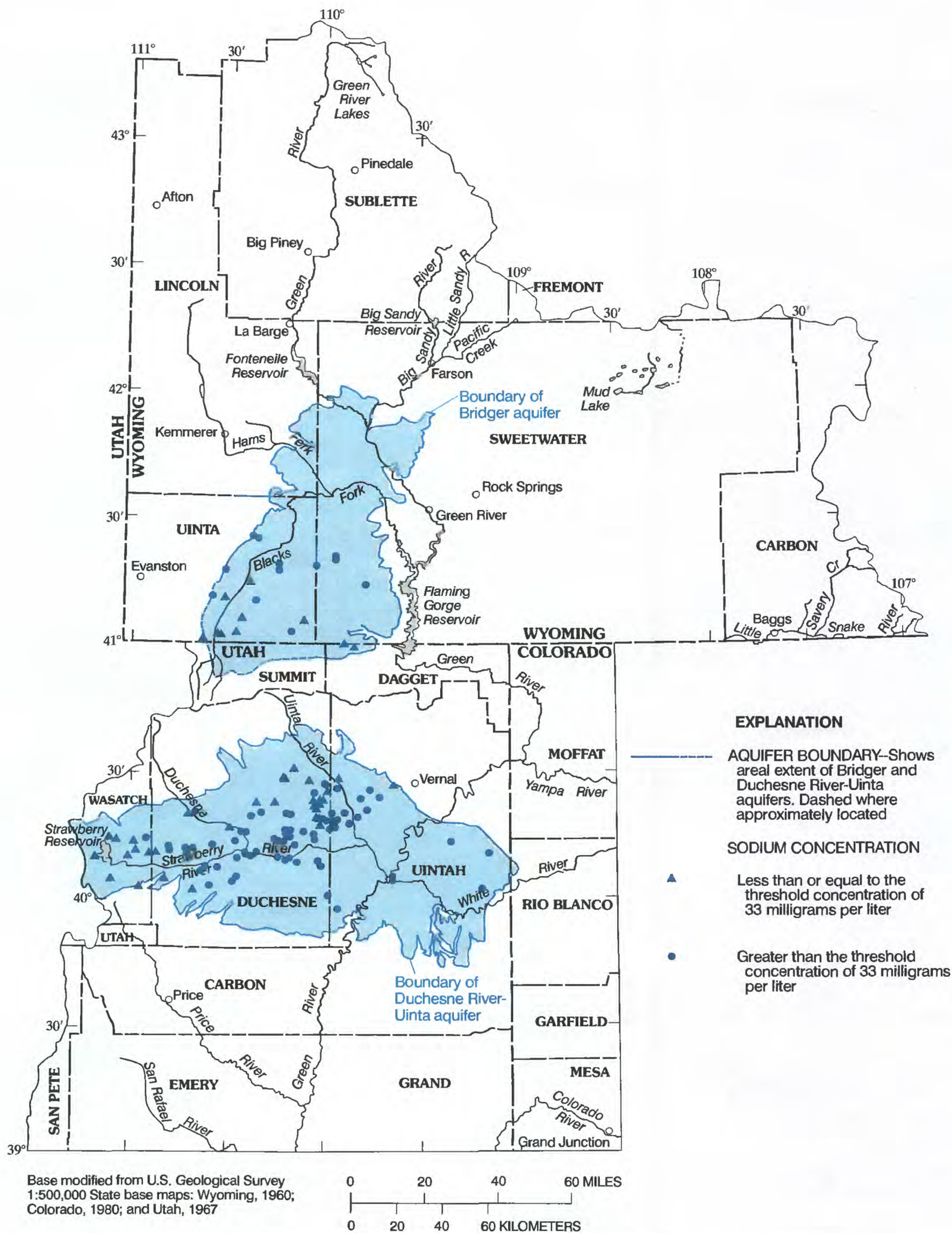


**Figure 8.** Cumulative-frequency plot of log sodium concentrations in water from the Bridger and Duchesne River-Uinta aquifers, Green River Basin and Uinta Basin aquifer systems.

defined by the potentiometric-surface map (fig. 4). Sources of fluoride in water include apatite, fluorite, rocks rich in alkali metals, and amphiboles where fluoride replaces part of the hydroxide (Hem, 1985, p. 121).

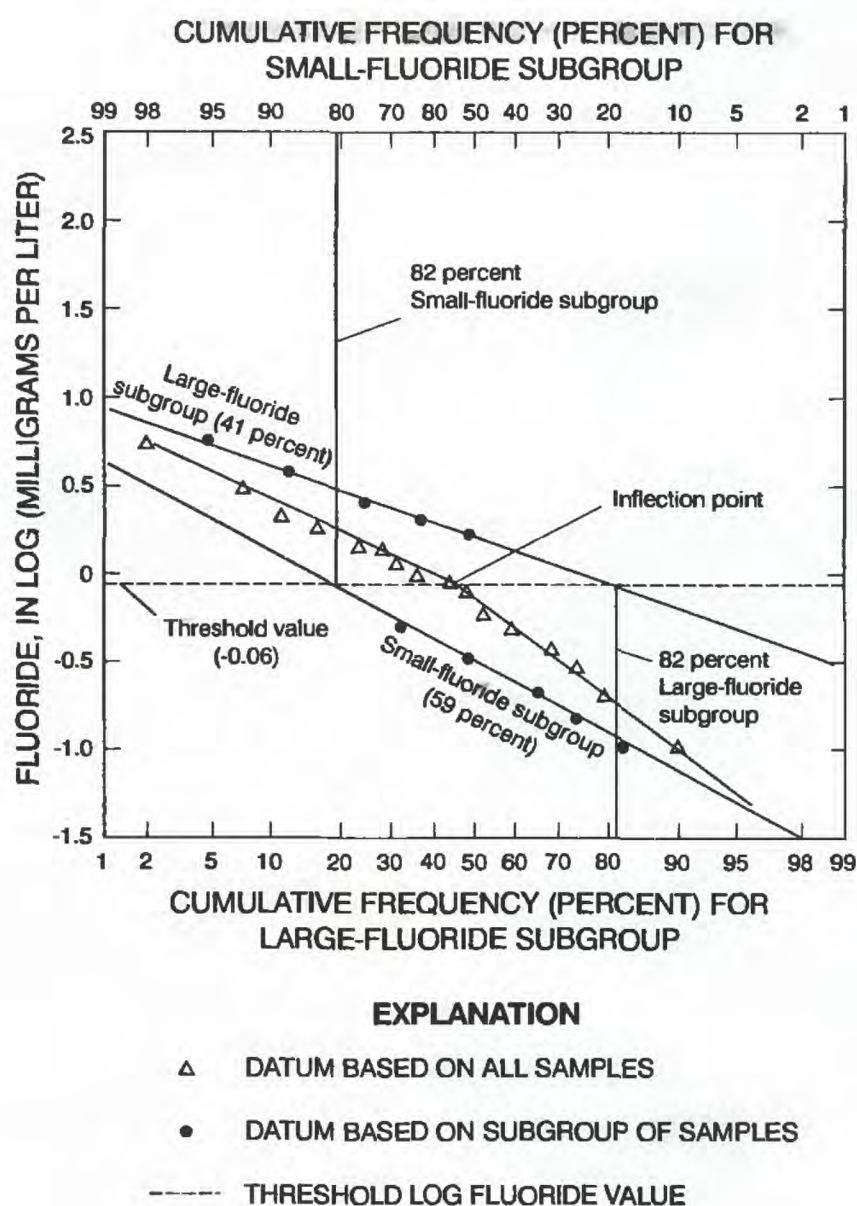
The mechanism for the increase of fluoride in downgradient areas in the Bridger and Duchesne River-Uinta aquifer is not known definitively. The presence of apatite (table 1) and possibly fluorite (not reported in the literature) in the Bridger and Duchesne River-Uinta aquifers could influence the fluoride concentration in the ground water. The median calcium concentration (15 mg/L for 49 samples) in ground water containing fluoride concentrations greater than or equal to 0.9 mg/L is lower than the corresponding median calcium concentration (50 mg/L for 53 samples) of ground water containing fluoride concentrations less than 0.9 mg/L. With lower calcium activities





**Figure 9.** Sodium concentrations in water from the Bridger and Duchesne River-Uinta aquifers, Green River Basin and Uinta Basin aquifer systems.





**Figure 10.** Cumulative-frequency plot of log fluoride concentrations in water from the Bridger and Duchesne River-Uinta aquifers, Green River Basin and Uinta Basin aquifer systems.

in downgradient water, the solubility of fluorite and apatite could allow the concentration of fluoride to increase.

Based on the mineralogical descriptions of the Bridger and Duchesne River-Uinta aquifers, distinct mineralogical forms of chloride are not present. Assuming the majority of dissolved chloride is derived from precipitation recharging the aquifers, ratio values of other solutes to chloride can be calculated and compared with ratios derived from evaporation only to help identify possible chemical reactions along inferred ground-water flow paths.

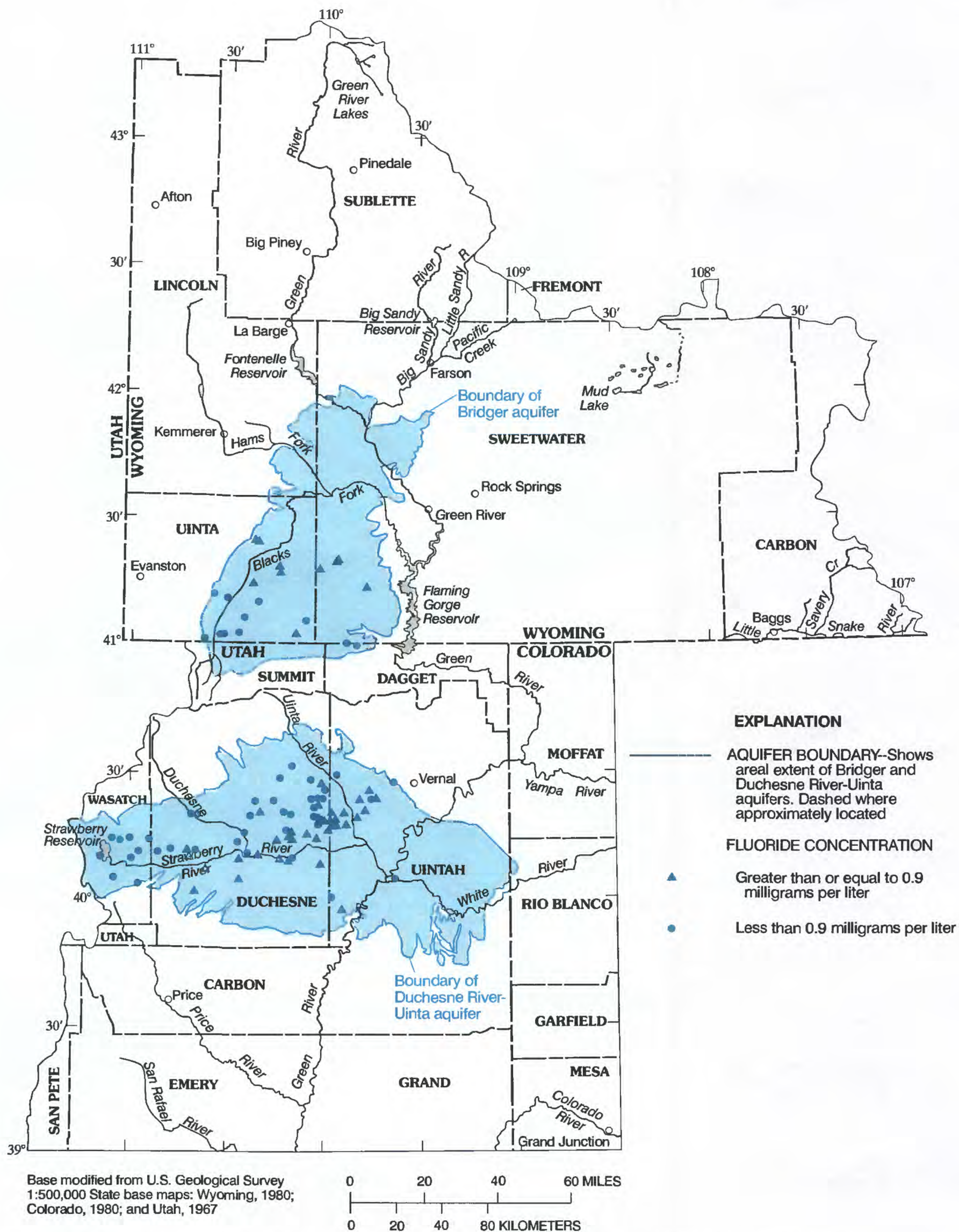
Comparisons of elemental ratios in precipitation with corresponding elemental ratios in ground water were used to provide information on areas of recharge, discharge, and possible chemical reactions that might

be occurring in the Bridger and Duchesne River-Uinta aquifers. Calcium and chloride concentrations from precipitation in the Uinta Basin aquifer system were estimated from data published by Kimball (1981, p. 10). Based on chemical analyses of the precipitation, the mean calcium concentration was 0.057 mmol/L and the mean chloride concentration was 0.022 mmol/L. Based on the mean concentrations of calcium and chloride, the mean mole ratio of calcium to chloride is 2.59. The concentration ratio calculated from precipitation for calcium to chloride was then compared to the calcium-to-chloride concentration ratios calculated from ground-water samples in the Bridger and Duchesne River-Uinta aquifers.

Calcium-to-chloride ratios exceeding the precipitation ratio (fig. 12) are generally confined to recharge areas indicated by the potentiometric-surface map of the Bridger and Duchesne River-Uinta aquifers (fig. 4). As shown in figure 12, calcium-to-chloride ratio values exceeding the corresponding precipitation ratio generally are located along the southern margin of the Green River Basin aquifer system and along the western and northern margins of the Uinta Basin aquifer system, as well as adjacent to the Strawberry River in the central part of the Uinta Basin aquifer system. Increases of calcium-to-chloride ratios relative to the corresponding ratio in precipitation are indicative of additional sources of calcium in addition to evaporative concentrations. One possible calcium source in the Bridger and Duchesne River-Uinta aquifers is carbonate dissolution by carbon-dioxide-charged water (table 2; reaction 2) in the recharge areas along the basin margins. The large calcium-to-chloride ratios found adjacent to the Strawberry River in the downgradient parts of the Duchesne River-Uinta aquifer (fig. 12) probably represent local recharge by streams. An additional source of calcium could be anhydrite dissolution (table 2; reaction 1) in recharge areas.

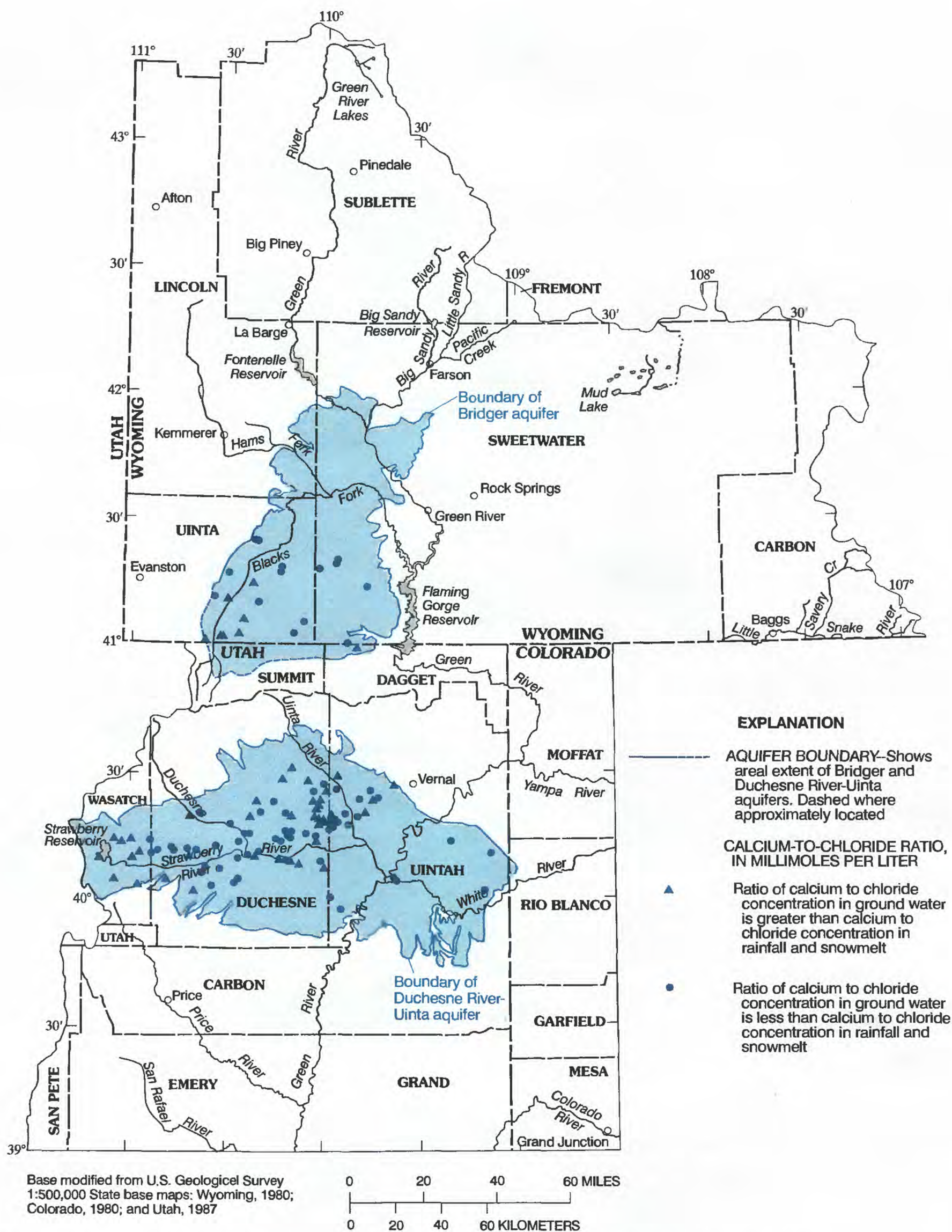
Ground water with calcium-to-chloride ratios less than the mean calcium-to-chloride ratio found in precipitation generally is found in downgradient water of the Bridger and Duchesne River-Uinta aquifers in both the Green River and Uinta Basin aquifer systems (fig. 12). Calcium-to-chloride ratio values that are smaller than the mean calcium-to-chloride ratio value in precipitation possibly are the result of chloride leakage from shales in the formation, water mixing with large-chloride concentrations, ion-exchange reactions, or calcite precipitation coupled with dolomite dissolution.





**Figure 11.** Fluoride concentrations in water from the Bridger and Duchesne River-Uinta aquifers, Green River Basin and Uinta Basin aquifer systems.





**Figure 12.** Calcium-to-chloride concentration ratios in water from the Bridger and Duchesne River-Uinta aquifers, Green River Basin and Uinta Basin aquifer systems.



## Laney Aquifer

Descriptions of the geochemistry of ground water in the Green River Formation were limited to the Green River Basin and Great Divide-Washakie-Sand Wash Basins aquifer systems in Wyoming. Previous studies concerning the quality of water from the Green River Formation in the Piceance Basin and Uinta Basin aquifer systems include those reported by Kimball (1981), Robson and Saulnier (1981), and Holmes and Kimball (1983). Because of the limited amount of water-quality data from water in the Green River Basin aquifer system in Wyoming, the following discussion is limited to the Laney aquifer and Wilkins Peak confining unit.

### Ground-Water Movement

Previous studies concerning the hydrology of the Green River Formation in the Green River Basin and Great Divide-Washakie-Sand Wash Basins aquifer systems include work by Welder and McGreevy (1966), Welder (1968), Collentine and others (1981), and Ahern and others (1981). Martin (1996) prepared a model of ground-water flow in aquifers in Tertiary rocks in the Green River Basin aquifer system. This is the first attempt at simulating ground-water flow on a basin scale.

With the exception of the Laney aquifer in parts of the Green River Basin aquifer system, the strata of the Green River Formation in Wyoming principally act as a confining unit (fig. 3). The hydraulic conductivity of the Laney aquifer is largest in areas adjacent to the Big Sandy River (Martin, 1996). Hydraulic-conductivity estimates from flow-model analysis for the Laney aquifer range from 0.04 to 17.3 ft/d in the horizontal direction and 0.00001 to 17.3 ft/d in the vertical direction (Martin, 1996). Small estimates of hydraulic conductivity, approaching those typical of confining units, are located in areas where the Laney aquifer is buried by the Bridger Formation (Martin, 1996).

Because of the lack of data, a potentiometric-surface map cannot be drawn for the Laney aquifer in either the southern part of the Green River Basin or the Great Divide-Washakie-Sand Wash Basins aquifer systems (fig. 13). Based on the water-level data currently available for the Laney aquifer, probable recharge areas occur around the Big Sandy River

irrigation project in the eastern part of the Green River Basin aquifer system (K.C. Glover, U.S. Geological Survey, written commun., 1986). Upward leakage of ground water from the underlying Wasatch zone of the Wasatch-Fort Union aquifer through fractures into the Laney aquifer is a probable source of recharge in the central part of the Green River Basin aquifer system. Discharge from the Laney aquifer occurs along the Big Sandy and Green Rivers.

### Mineralogy

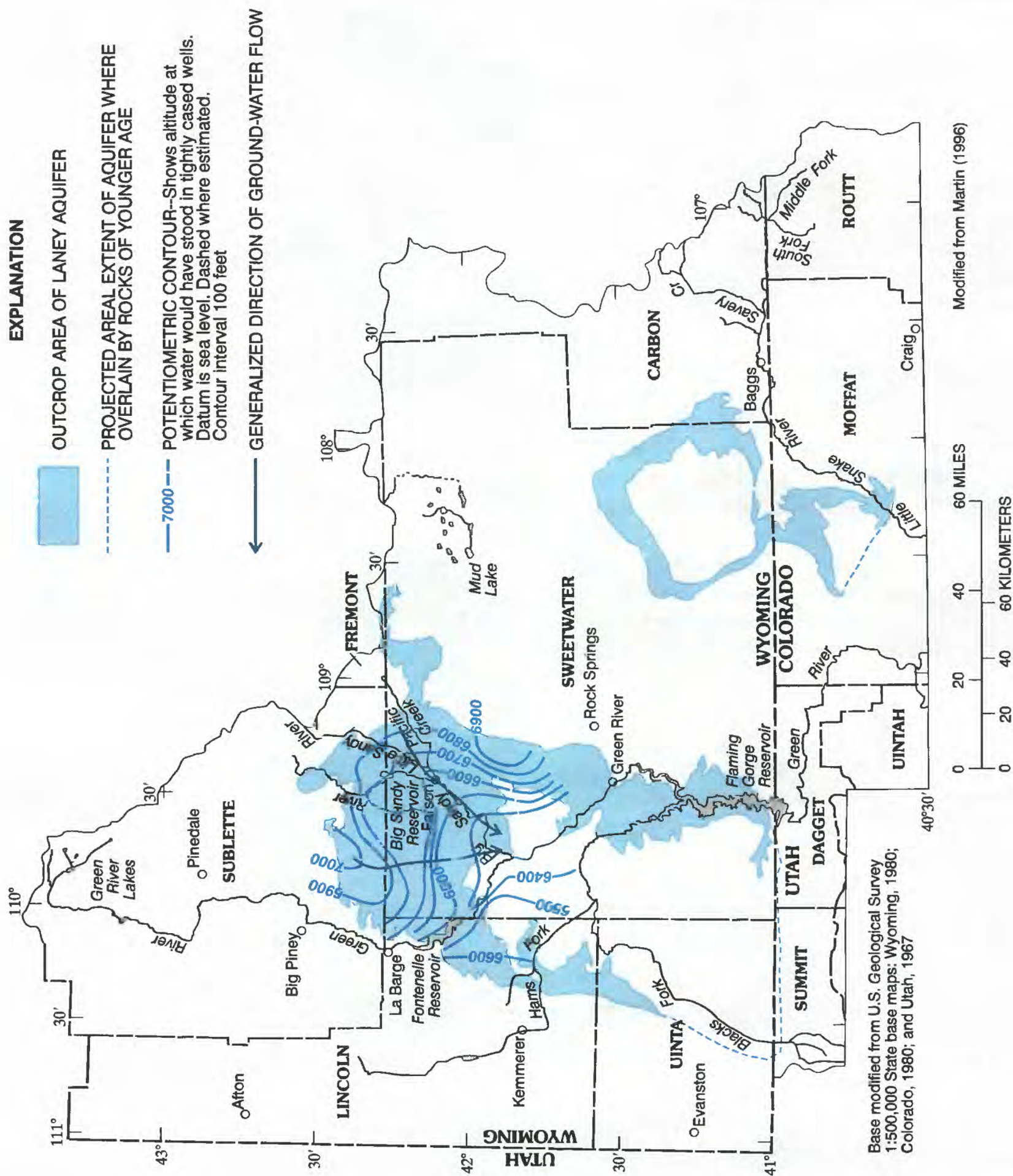
Stratigraphic descriptions and mineralogical studies of the Laney Member of the Green River Formation in the Green River Basin and Great Divide Basin and Washakie Basin were used to determine the minerals present in the aquifer systems. Minerals commonly found in the Laney Member are listed in table 3.

**Table 3.** Minerals present in the Laney Member, Green River Basin, Great Divide Basin, and Washakie Basin

[From Bradley, 1964; Love, 1964; Bradley and Eugster, 1969; Roehler, 1965, 1970; Culbertson and others, 1980; Dribus and Nanna, 1982]

Mineral name	Idealized chemical formula
Quartz	SiO <sub>2</sub>
Plagioclase	Ca <sub>0.2</sub> Na <sub>0.8</sub> Al <sub>1.2</sub> Si <sub>2.8</sub> O <sub>8</sub>
Calcite	CaCO <sub>3</sub>
Zircon	ZrSiO <sub>4</sub>
Biotite	K(Mg,Fe) <sub>3</sub> (AlSi <sub>3</sub> O <sub>10</sub> )(OH) <sub>2</sub>
Hornblende	(Ca,Na) <sub>2-3</sub> (Mg,Fe,Al) <sub>5</sub> Si <sub>6</sub> (Si,Al) <sub>2</sub> O <sub>22</sub> (OH) <sub>2</sub>
Chert	SiO <sub>2</sub>
Analcite	NaAl(SiO <sub>3</sub> ) <sub>2</sub> • H <sub>2</sub> O
Anhydrite	CaSO <sub>4</sub>
Augite	(Ca,Na)(Mg,Fe,Al)(Si,Al) <sub>2</sub> O <sub>6</sub>
Dolomite	CaMg(CO <sub>3</sub> ) <sub>2</sub>
Nahcolite	NaHCO <sub>3</sub>
Shortite	Na <sub>2</sub> CO <sub>3</sub> • 2CaCO <sub>3</sub>
Northrupite	Na <sub>2</sub> CO <sub>3</sub> • MgCO <sub>3</sub> • NaCl
Garnet group	-----
Epidote	Ca <sub>2</sub> (Al,Fe)Al <sub>2</sub> O(SiO <sub>4</sub> )(Si <sub>2</sub> O <sub>7</sub> )(OH)
Aragonite	CaCO <sub>3</sub>





**Figure 13.** Potentiometric contours and inferred flow paths in the Laney aquifer, Green River Basin aquifer system.



Love (1964, p. 14–15) noted chert nodules, anal-citized tuffs, and thick beds of anhydrite in stratigraphic descriptions of the Laney Member in the Green River Basin. In a stratigraphic description of the Laney Member by Roehler (1965, p. 147), thin beds of organic limestones are noted in the shallow lacustrine depositional environments along the western part of the Rock Springs Uplift. Bradley and Eugster (1969, p. 7) noted saline minerals in the bottom 20 ft of the Laney Member above the top of the Wilkins Peak Member. Shortite is reported to occur in the highest stratigraphic units of the saline facies of the Wilkins Peak Member; however, nahcolite possibly also occurs in the upper stratigraphic units of the saline facies. Culbertson and others (1980, p. 10) noted that shortite, northrupite, and nahcolite are saline minerals commonly associated with oil shales in the Green River Formation. On a local scale, channel sandstones derived from volcanic ash are found in the lower parts of the Laney Member in the vicinity of Green River, Wyoming. According to Bradley (1964, p. 47), minerals in these sandstone lenses include biotite, quartz, and hornblende.

Mineralogies of the Laney Member in the Green River Basin, Great Divide Basin, and Washakie Basin were described by Roehler (1970, p. 181–187) and Culbertson and others (1980, p. 10). Roehler (1970, p. 181–187) evaluated the nonopaque heavy minerals from Eocene rocks in the western part of the Great Divide Basin and Washakie Basin; nonopaque heavy minerals found in the Laney Member in this area include garnet, epidote, zircon, biotite, augite, and hornblende. Quartz, dolomite, feldspar, and aragonite are found in the Laney Member in the Green River Basin, according to Culbertson and others (1980, p. 10).

Minerals in the Wilkins Peak Member (Wilkins Peak confining unit) were described by Bradley and Eugster (1969, p. 7–12) and Culbertson and others (1980, p. 7). Minerals found in the Wilkins Peak Member of the Green River Formation included trona, halite, shortite, northrupite, nahcolite, dolomite, quartz, feldspar, and minor amounts of illite and pyrite.

### Water Chemistry and Changes Along Flow Paths

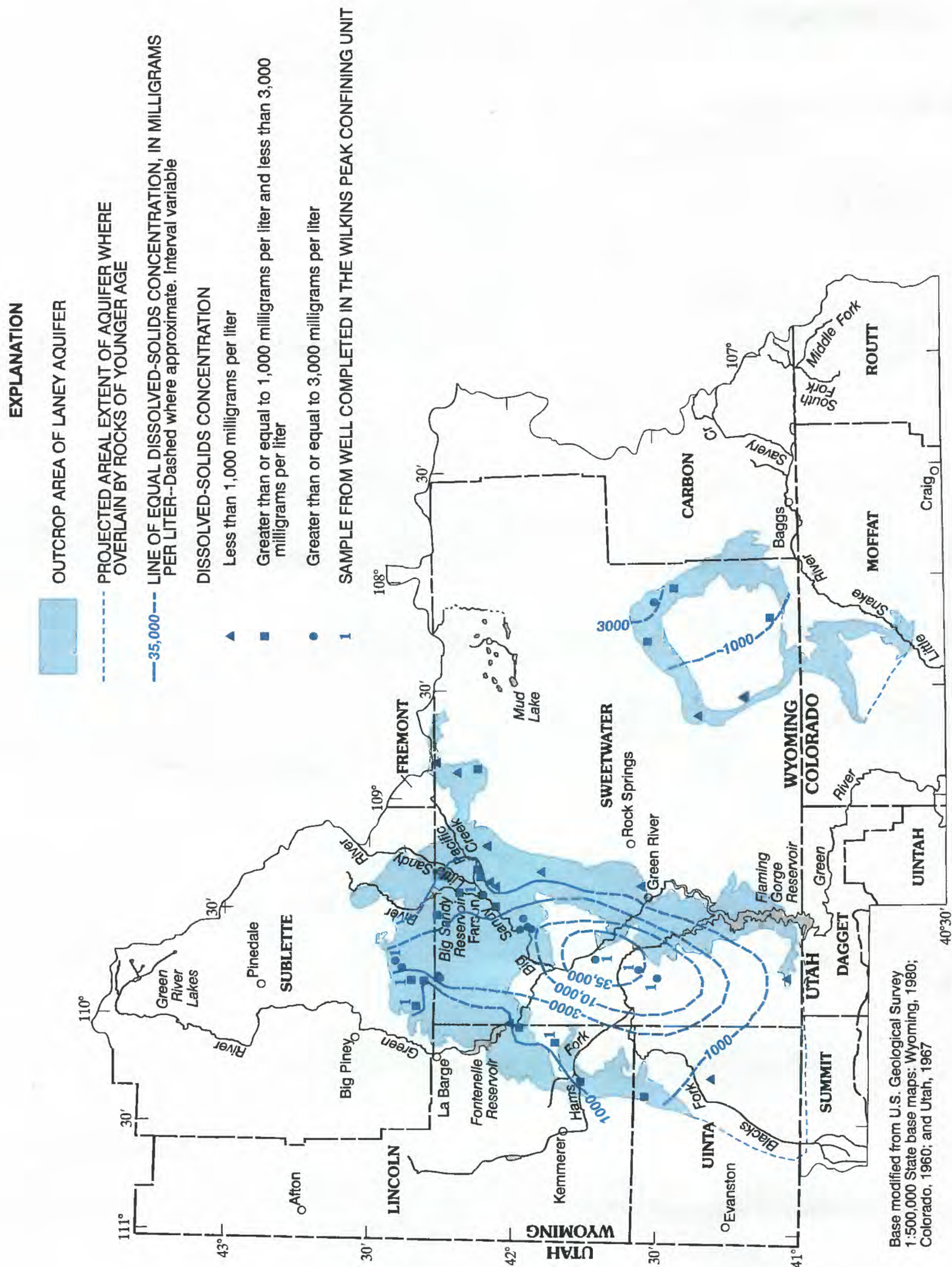
Maps showing the chemical constituents in the water from the Laney aquifer and the Wilkins Peak confining unit in the Green River Basin and Great Divide-Washakie-Sand Wash Basins aquifer systems indicate

systematic variations in the concentrations of major chemical constituents. The dissolved-solids distribution in the Green River Basin aquifer system (fig. 14) indicates gradual increases in dissolved-solids concentrations from the basin margins inward; this type of increase would be expected if mineral dissolution or leakage of highly mineralized water from shales or adjacent aquifers were occurring along flow paths. Limited water-quality data from the Laney Member in the Washakie Basin part of the Great Divide-Washakie-Sand Wash Basins aquifer system indicate a gradual increase in dissolved-solids concentration to the northeast (fig. 14). Insufficient head data in this area prevent the construction of a potentiometric-surface map or projection of generalized flow paths.

Separation of dissolved-solids data into major chemical constituents indicates the proportion of major cations and anions to the dissolved-solids concentrations in the Laney aquifer. Areal variations of major chemical constituents in selected wells in the Laney aquifer are shown in Stiff diagrams in figure 15 (Stiff, 1951). For the selected waters described by the Stiff diagrams, ground-water samples from the Laney aquifer along the basin margins generally are sodium-bicarbonate and sodium-sulfate water. Although not shown by the Stiff diagrams, water from the Wilkins Peak confining unit in the south-central part of the Green River Basin aquifer system, with dissolved-solids concentration above 25,000 mg/L, usually is dominated by sodium and carbonate plus bicarbonate ions.

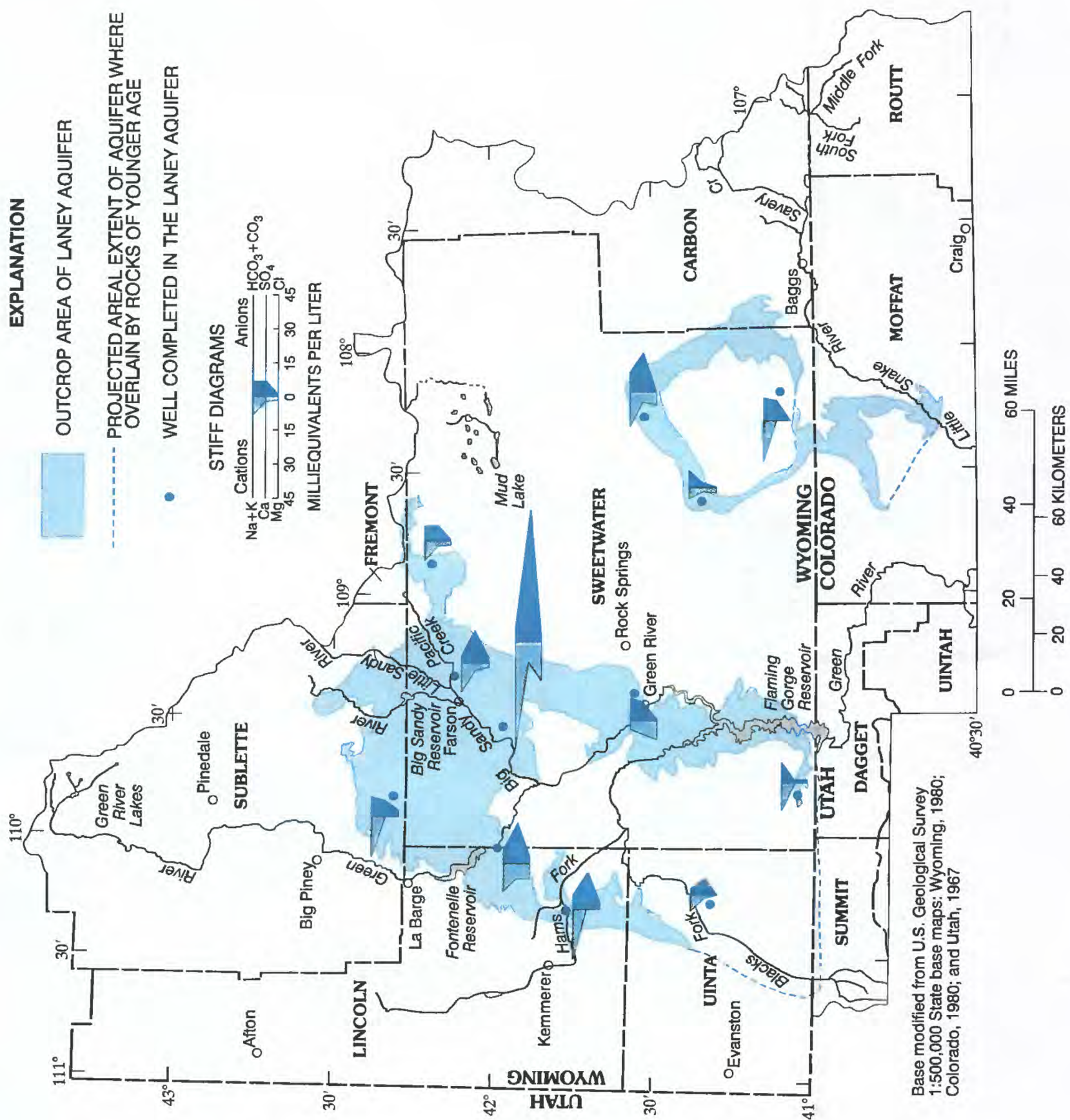
Relative increases in sodium concentrations coupled with relative decreases in calcium and magnesium concentrations can be interpreted as cation-exchange reactions (table 2; reactions 5 and 6) with clays in the Laney aquifer. Large sodium concentrations relative to calcium and magnesium concentrations also could be the result of dissolution reactions of sodic salts that are abundant in the Wilkins Peak confining unit and were reported in the lower parts of the Laney aquifer by Bradley and Eugster (1969, p. 7). Distribution of log-molar ratio values for the exchangeable divalent-to-monovalent cations,  $\log ([Ca] + [Mg])/[Na]^2$ , in water from the Laney aquifer and Wilkins Peak confining unit, is shown in figure 16. As shown in figure 16, ground water from the area of bedded trona and halite deposits in the Green River Basin, as outlined by Bradley and Eugster (1969, p. 6), exhibit the most neg-





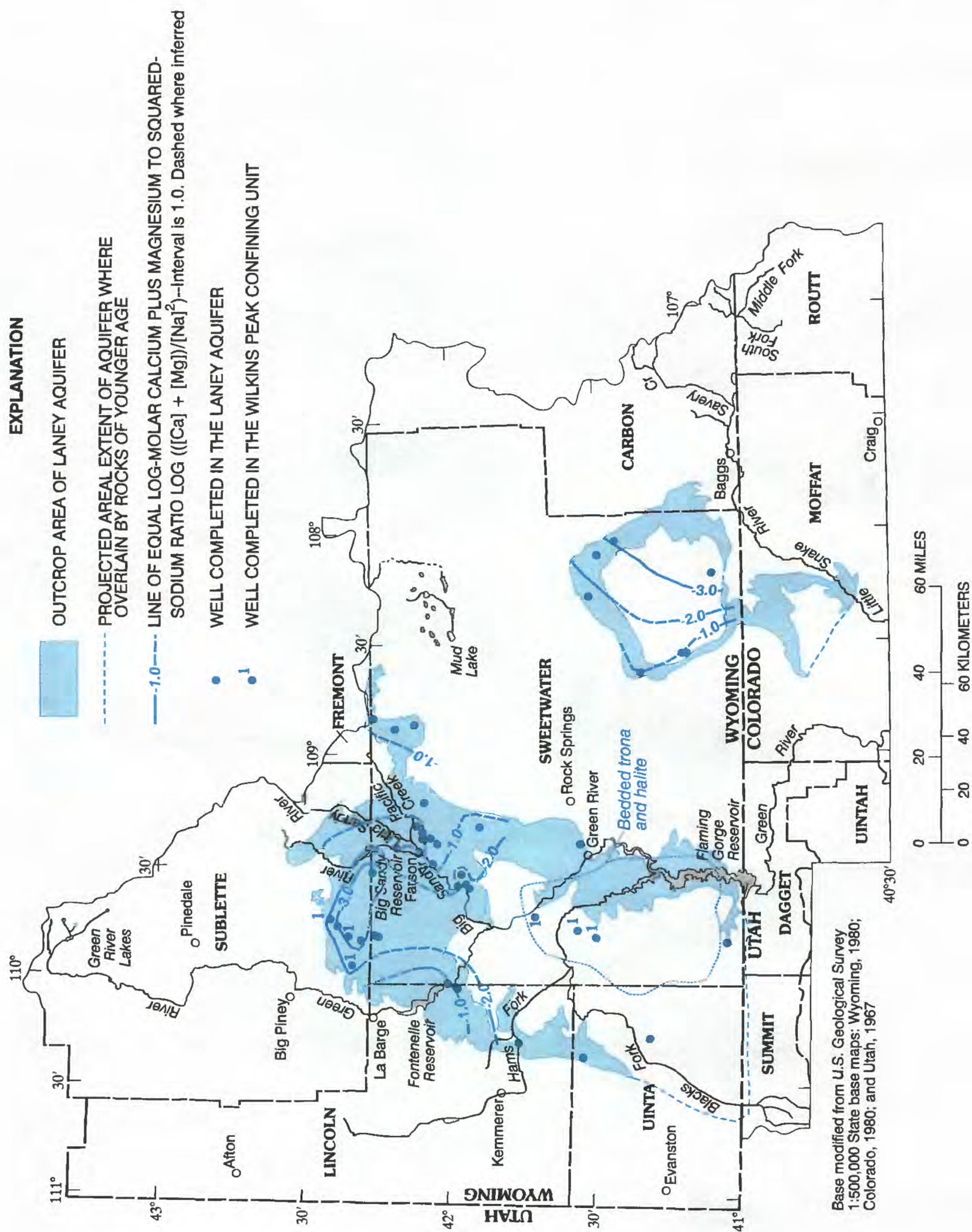
**Figure 14.** Dissolved-solids concentrations in water from the Laney aquifer and Wilkins Peak confining unit, Green River Basin and Great Divide-Washakie-Sand Wash Basins aquifer systems.





**Figure 15.** Stiff diagrams for major chemical constituent concentrations in water from the Laney aquifer, Green River Basin and Great Divide-Washakie-Sand Wash Basins aquifer systems.





**Figure 16.** Log-molar ratios of calcium plus magnesium to squared-sodium concentrations in water from the Laney aquifer and Wilkins Peak confining unit, Green River Basin and Great Divide-Washakie-Sand Wash Basins aquifer systems.



ative divalent-to-monovalent cation ratios, suggesting trona dissolution as the major sodium source. Less negative values of  $\log ([\text{Ca} + \text{Mg}] / [\text{Na}]^2)$  are found in the vicinity of Farson, Wyoming. This area is a probable recharge source to the Laney aquifer because of return flow from irrigation. Irrigation-return flow to the Laney aquifer probably is sufficiently high in sodium because of evaporation rather than cation-exchange reactions, making comparisons with calcium and magnesium concentrations of limited value. A decrease in  $\log ([\text{Ca} + \text{Mg}] / [\text{Na}]^2)$  values is found toward the center of the basin, probably indicative of downgradient water. The decrease is in general agreement with the potentiometric-surface map of the Laney aquifer in the Green River Basin aquifer system (fig. 13).

The clustering of  $\log ([\text{Ca} + \text{Mg}] / [\text{Na}]^2)$  values less than -3.0 immediately south of the Laney Member-Wasatch Formation contact of the Laney Member of the Green River Formation and the Wasatch Formation in the north-central part of the Green River Basin aquifer system (fig. 16) indicates possible upward leakage of water from the underlying Wasatch zone of the Wasatch-Fort Union aquifer into the overlying Laney aquifer. Water in the Wasatch zone in the vicinity of the Laney-Wasatch contact could have negative  $\log ([\text{Ca} + \text{Mg}] / [\text{Na}]^2)$  values from cation-exchange reactions. In addition, dissolution of sodium-bearing minerals in the Wilkins Peak confining unit probably would contribute high concentrations of sodium relative to calcium and magnesium during upward leakage to the Laney aquifer along fractures. Because of the lack of recharge to the Laney aquifer from surface sources in this area, water from the Wasatch zone, with negative  $\log ([\text{Ca} + \text{Mg}] / [\text{Na}]^2)$ , apparently is acting as a recharge source to the Laney aquifer in the north-central part of the Green River Basin aquifer system.

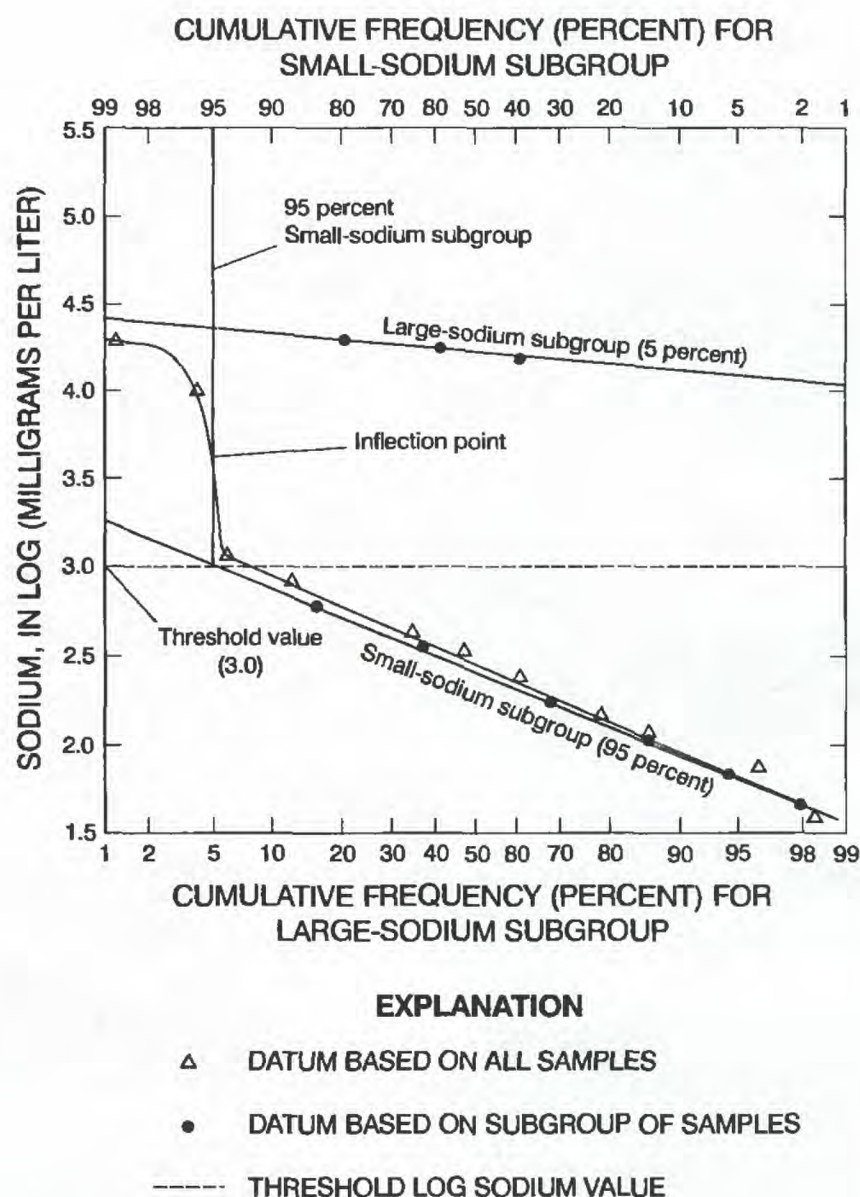
Although the Laney Member in the Great Divide-Washakie-Sand Wash Basins is considered part of the Green River confining unit (fig. 3), the  $\log ([\text{Ca} + \text{Mg}] / [\text{Na}]^2)$  from water in the Laney aquifer in the Great Divide-Washakie-Sand Wash Basins aquifer system indicates a decrease to the east (fig. 16). Assuming cation-exchange reactions are operative, changes in the  $\log ([\text{Ca} + \text{Mg}] / [\text{Na}]^2)$  could indicate recharge in the southwestern parts of the Washakie Basin aquifer system and possible basin flow to the east. Because a potentiometric-surface map cannot be

constructed for the Laney aquifer in the Washakie Basin, the possible flow path indicated from the changes in the  $\log ([\text{Ca} + \text{Mg}] / [\text{Na}]^2)$  cannot be verified. The general topographic expression of the Washakie Basin suggests a general flow pattern from the outcrop areas on the margins of the basin toward the basin center.

The cumulative-frequency plot of sodium concentrations in water from the Laney aquifer and Wilkins Peak confining unit in the Green River Basin and Washakie Basin part of the Great Divide-Washakie-Sand Wash Basins aquifer systems (fig. 17) indicates two sodium subgroups in the proportion of 95 percent and 5 percent of the data set. Selection of a threshold value of 1,000 mg/L (3.0 log mg/L) identifies 95 percent of the small-sodium subgroup and virtually all the large-sodium subgroup. Based on the mineralogical descriptions of the Laney aquifer and Wilkins Peak confining unit, possible sources of sodium include dissolution of plagioclase feldspar and cation-exchange reactions (table 2; reactions 4, 5, and 6). Unlike the Bridger and Duchesne River-Uinta aquifers, the presence of deposits in the Wilkins Peak confining unit in the south-central part of the Green River Basin aquifer system provides an important source of sodium in the form of sodic salts, such as shortite ( $\text{Na}_2\text{CO}_3 \cdot 2\text{CaCO}_3$ ), trona ( $\text{NaHCO}_3 \cdot \text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ ), and nahcolite ( $\text{NaHCO}_3$ ).

Areal distribution of samples from the two sodium subgroups (fig. 18) indicates that most ground water with sodium concentrations above the threshold value of 1,000 mg/L occurs in the downgradient discharge area of the Laney aquifer in the south-central part of the Green River Basin aquifer system. Areal distribution of sodium concentrations above the threshold value suggests dissolution of sodium bicarbonate salts, present in both the Wilkins Peak confining unit and the Laney aquifer in the south-central part of the Green River Basin aquifer system. The smallest sodium concentrations (less than 100 mg/L) in the Laney aquifer are found in close proximity to Farson, Wyoming. Small sodium concentrations in this area probably are indicative of irrigation water recharging the Laney aquifer. As mentioned previously, sodium concentrations in this part of the Laney aquifer probably are derived from evaporative concentration rather than cation-exchange reactions.





**Figure 17.** Cumulative-frequency plot of log sodium concentrations in water from the Laney aquifer and Wilkins Peak confining unit, Green River Basin and Great Divide-Washakie-Sand Wash Basins aquifer systems.

The cumulative-frequency plot of fluoride concentrations for water from the Laney aquifer and Wilkins Peak confining unit (fig. 19) indicates an inflection point identifying two fluoride subgroups in the proportions of 30 and 70 percent of the data set. Based on the frequency distribution of fluoride concentrations, sufficient overlap occurs between the two subgroups to warrant the use of two threshold values. A threshold value of 0.6 mg/L (-0.2 log mg/L) identifies 90 percent of the large-fluoride subgroup, while it also includes 48 percent of the small-fluoride subgroup. Using a threshold value less than 2.3 mg/L (0.36 log mg/L) identifies 90 percent of the small-fluoride subgroup, while including approximately 64 percent of the large-fluoride subgroup. This large amount of overlap between the two fluoride subgroups

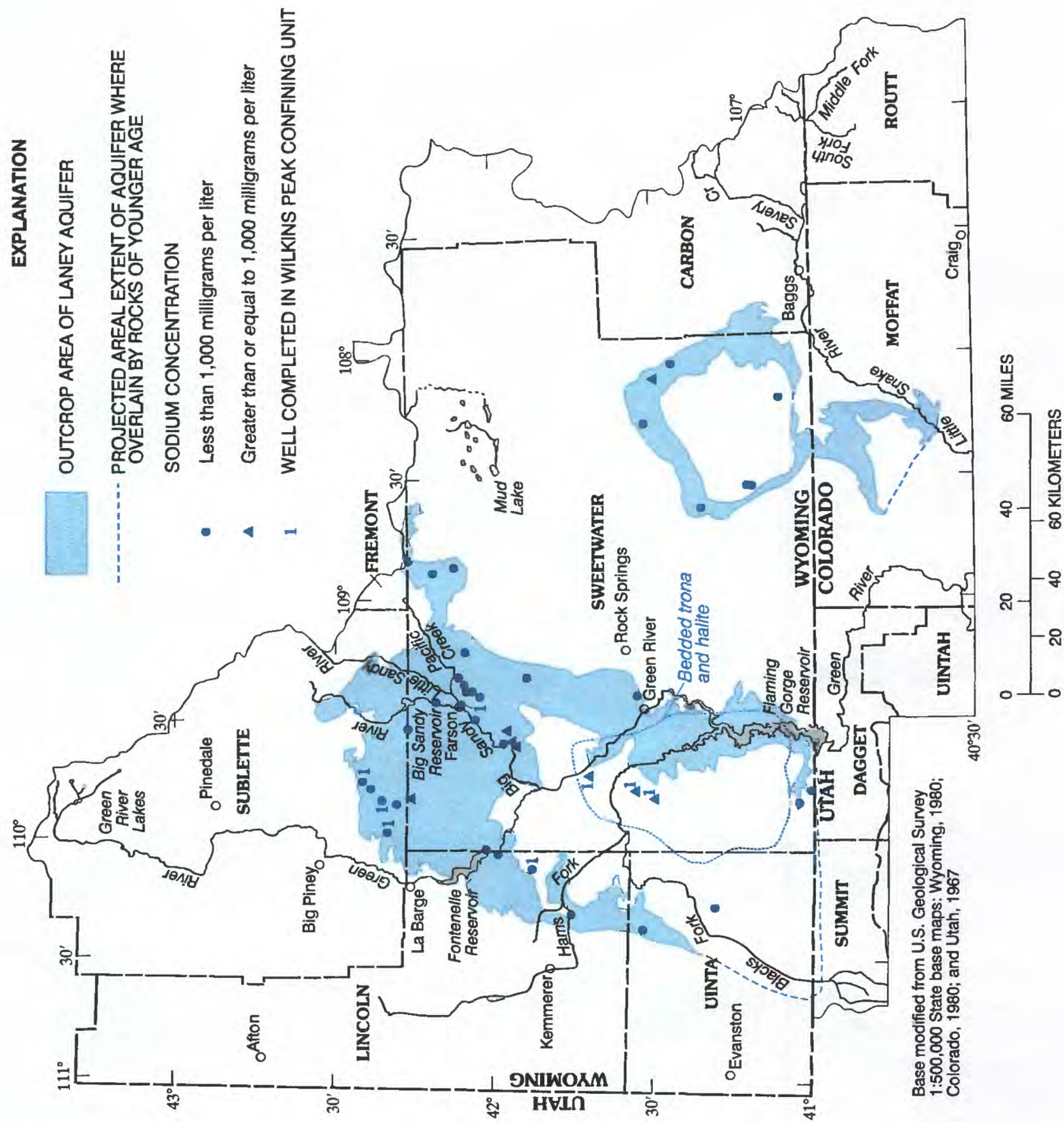
is indicative of multiple geochemical processes affecting fluoride concentrations.

Because of the large overlap between fluoride subgroups, three class intervals were used to plot the areal distribution of the fluoride concentrations in the Laney aquifer and Wilkins Peak confining unit (fig. 20). The class intervals include: (1) Fluoride concentrations larger than 2.3 mg/L (0.36 log mg/L), including 66 percent of the large-fluoride subgroup; (2) fluoride concentrations less than or equal to 2.3 mg/L (0.36 log mg/L) and more than or equal to 0.6 mg/L (-0.2 log mg/L), including the overlapping parts of both subgroups; and (3) fluoride concentrations less than 0.6 mg/L (-0.2 log mg/L), including 47 percent of the small-fluoride subgroup. Fluoride concentrations larger than 2.3 mg/L usually occur in down-gradient water; a majority of the fluoride concentrations smaller than 0.6 mg/L occur in probable recharge areas such as south and east of Farson, Wyoming, along the Green River, and in the western part of the Washakie Basin (fig. 20).

Unlike the calcium concentration in water from the Bridger and Duchesne River-Uinta aquifers, the calcium concentrations in water from the Laney aquifer and Wilkins Peak confining unit do not seem to correlate with fluoride concentrations. Median calcium concentration increases from a value of 54 mg/L in water with a fluoride concentration less than 0.6 mg/L, to a median calcium concentration of 56 mg/L in water with a fluoride concentration greater than 2.3 mg/L. Lack of a trend in calcium concentrations suggests that a mechanism other than calcium concentration is controlling fluoride concentrations. Although apatite was not indicated in the mineralogical descriptions of the Laney Member, if apatite  $[\text{Ca}_5(\text{PO}_4)_3(\text{F}, \text{Cl}, \text{OH})]$  is a source of fluoride in the water from the Green River Formation, phosphate concentrations in the water could exhibit a significant control on fluoride concentrations.

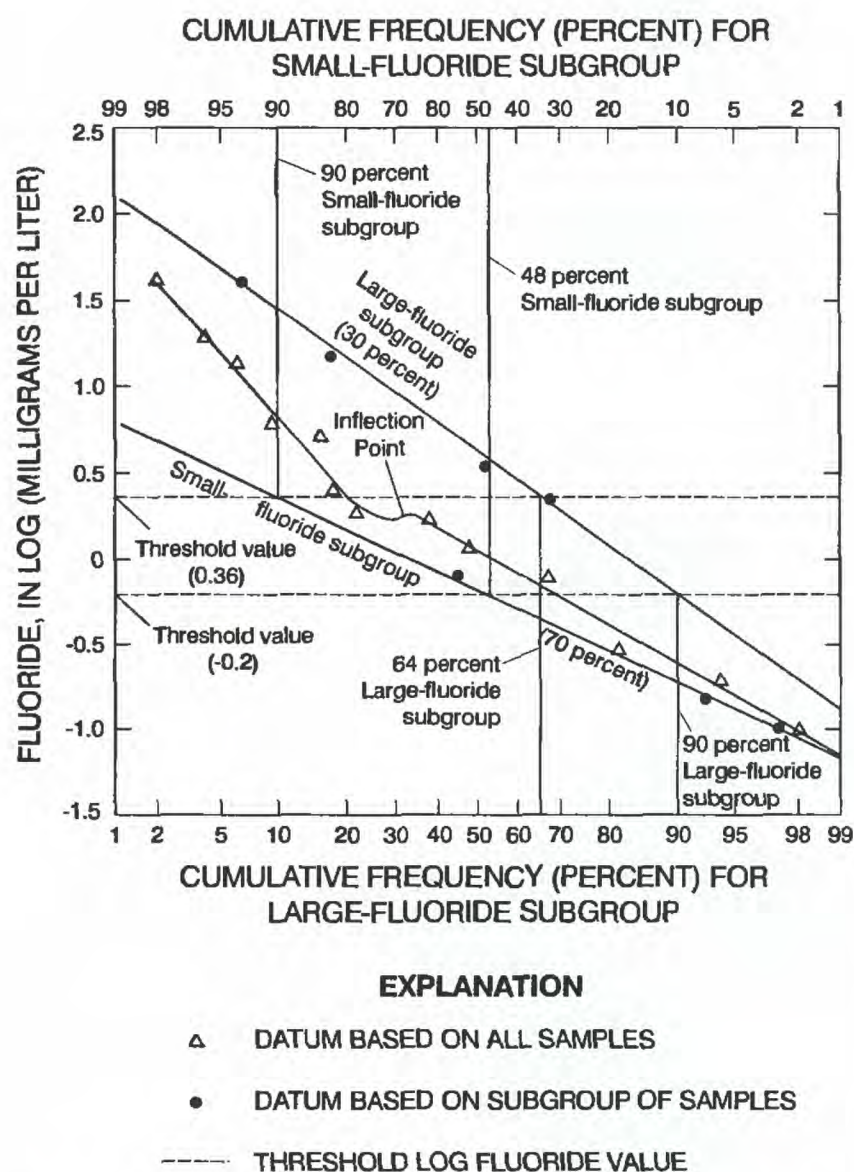
Chloride probably is conservative in the areas of the Laney aquifer, where interaquifer leakage is small and saline minerals do not exist. Chloride probably is not conservative in water from the Wilkins Peak confining unit, where saline minerals are common (for example, in the central part of the Green River Basin aquifer system). Considering these areas of non-conservative chloride behavior, calcium-to-chloride ratios in water from the Laney aquifer and Wilkins Peak confining unit can be compared to the calcium-to-





**Figure 18.** Sodium concentrations in water from the Laney aquifer and Wilkins Peak confining unit, Green River Basin and Great Divide-Washakie-Sand Wash Basins aquifer systems.





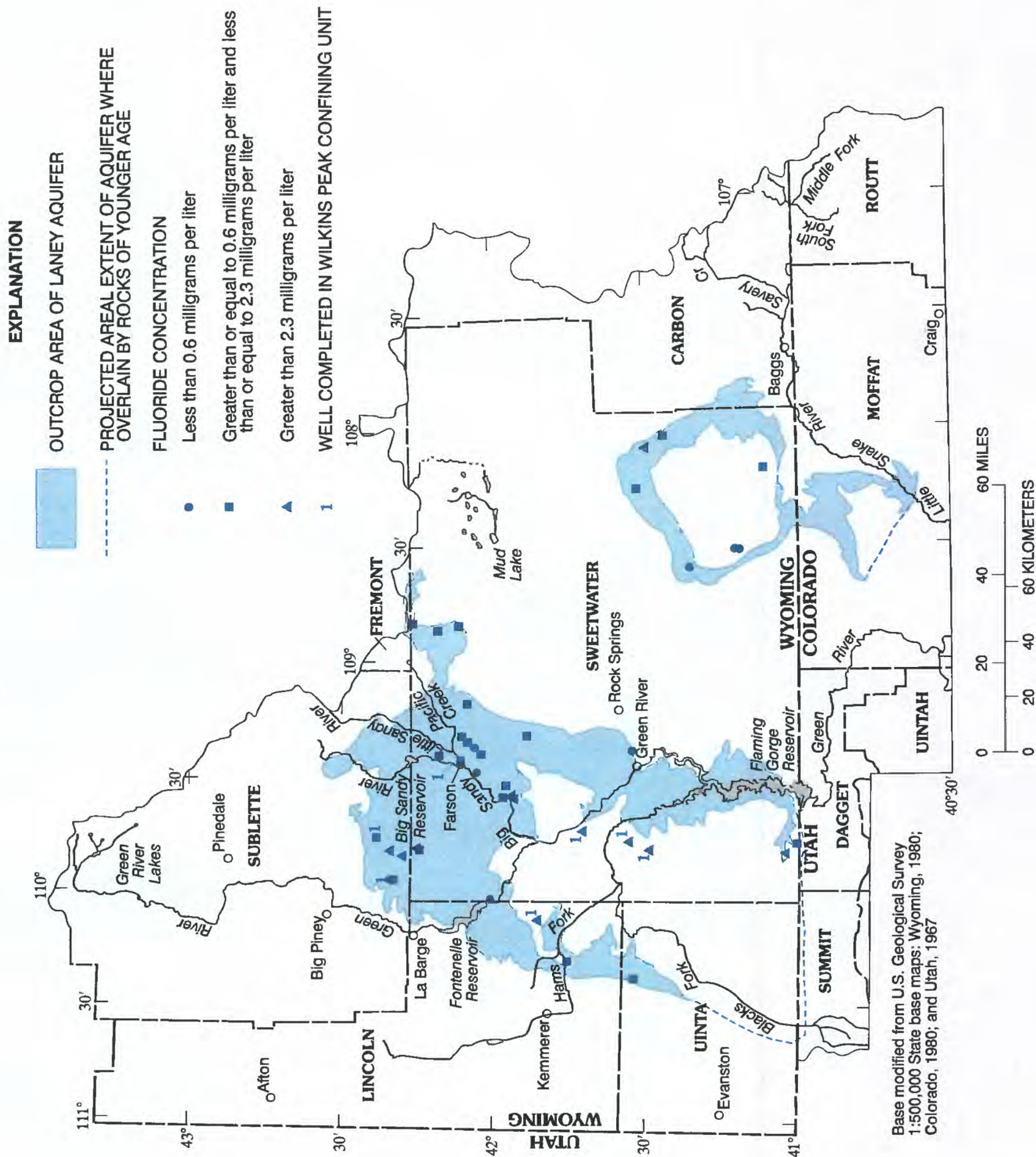
**Figure 19.** Cumulative-frequency plot of log fluoride concentrations in water from the Laney aquifer and Wilkins Peak confining unit, Green River Basin and Great Divide-Washakie-Sand Wash Basins aquifer systems.

chloride ratios in precipitation. These comparisons can be used as an indicator of possible chemical reactions that might be occurring in recharge areas and as an identifier of probable areas of interaquifer leakage and saline-mineral phases.

Calcium and chloride concentrations from precipitation in the Green River Basin aquifer system were estimated from unpublished data collected by the National Atmospheric Deposition Program station at Half Moon Lake, located approximately 10 mi northeast of Pinedale, Wyoming. Based on chemical analyses of the precipitation collected at the site from June 1982 through May 1983, the mean calcium concentration was 0.013 mmoles/L and the mean chloride concentration was 0.009 mmoles/L. Based on the mean concentrations of calcium and chloride, the mean mole ratio of calcium to chloride is 1.44.

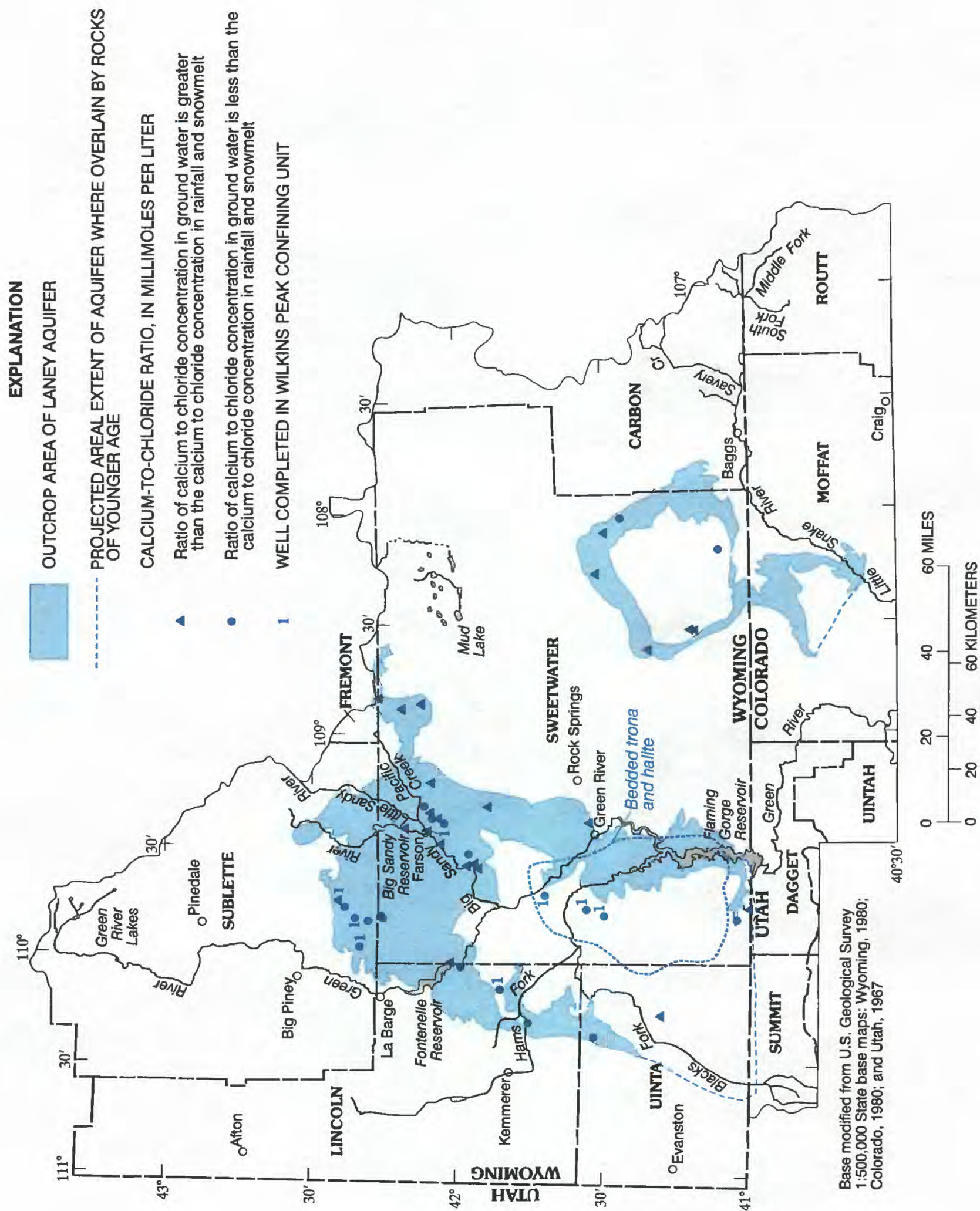
Ground water corresponding to an ionic ratio (mmoles calcium to mmoles chloride) different than the ionic ratio for calcium to chloride found in precipitation indicates possible chemical reactions are occurring in areas of the aquifer where chloride is assumed to be conservative. As shown in figure 21, most calcium-to-chloride ratios exceeding the precipitation-ratio value are found adjacent to major drainages in the Green River Basin aquifer system, and along outcrop areas of the Laney Member in the Green River Basin and the Washakie Basin part of the Great Divide-Washakie-Sand Wash Basins aquifer systems. These are also the probable areas in the Green River Formation where chloride is conservative. Increases of calcium-to-chloride ratios relative to the corresponding ratios in precipitation indicate additional sources of calcium plus additional calcium due to evaporative concentration. One possible calcium source in the Laney aquifer is carbonate dissolution by carbon-dioxide-charged water in recharge areas (table 2; reaction 2). The presence of anhydrite in the Laney aquifer (table 3) also could be a calcium source, according to reaction 1 (table 2). The proximity of elevated calcium-to-chloride ratios in the area around Farson, Wyoming, may indicate recharge to the Laney aquifer from irrigation in the area. Other areas of elevated calcium-to-chloride ratios adjacent to the Green River and Blacks Fork may indicate localized recharge to the Laney aquifer. Ground water with calcium-to-chloride ratios less than the corresponding ratio found in precipitation generally is located along the northern and south-central parts of the Laney aquifer and Wilkins Peak confining unit in the Green River Basin aquifer system. Small calcium-to-chloride ratios in the water along the northern part of the Laney aquifer in the Green River Basin aquifer system probably are the result of upward leakage of ground water from the underlying Wasatch zone of the Wasatch-Fort Union aquifer. Decreased calcium-to-chloride ratio values in water from the Wasatch zone could be the result of dedolomitization and cation-exchange reactions (table 2; reactions 3, 5, and 6), as well as from leakage of chloride from shales. The small calcium-to-chloride ratios found in the south-central part of the Green River Basin aquifer system possibly are the result of the nonconservative nature of chloride in this area, as a result of the presence of saline minerals associated with oil shales and evaporative lake deposits in the Laney aquifer and Wilkins Peak confining unit.





**Figure 20.** Fluoride concentrations in water from the Laney aquifer and Wilkins Peak confining unit, Green River Basin and Great Divide-Washakie-Sand Wash Basins aquifer systems.





**Figure 21.** Calcium-to-chloride concentration ratios in water from the Laney aquifer and Wilkins Peak confining unit, Green River Basin and Great Divide-Washakie-Sand Wash Basins aquifer systems.



## Wasatch Zone of the Wasatch-Fort Union Aquifer

### Ground-Water Movement

The surface- and ground-water resources of the Green River Basin and Great Divide-Washakie-Sand Wash Basins aquifer systems have been previously studied by Welder (1968), Welder and McGreevy (1966), Ahern and others (1981), and Collentine and others (1981). Martin (1996) developed a ground-water-flow model for the hydrologic system in Tertiary rocks in the Green River Basin aquifer system of Wyoming.

The Wasatch Formation and the Battle Spring Formation compose the Wasatch zone of the Wasatch-Fort Union aquifer in the Green River Basin and Great Divide-Washakie-Sand Wash Basins aquifer systems (fig. 3). The hydraulic conductivity of the Wasatch zone is largest in shallow parts of the northern Green River Basin aquifer system (6.5 ft/d) and along basin margins (0.3 ft/d). Average hydraulic conductivity from specific capacity and pumping tests conducted in the Wasatch zone in the Great Divide-Washakie-Sand Wash Basins aquifer system is 1.2 ft/d (K.C. Glover, U.S. Geological Survey, written commun., 1986).

As indicated by the potentiometric-surface map for the Wasatch zone (fig. 22), flow systems on a local scale dominate in the upper part of the Green River Basin aquifer system; basin flow dominates elsewhere in the Green River and Great Divide-Washakie-Sand Wash Basins. In general, recharge occurs in upland areas and outcrop areas adjacent to mountain ranges, and discharge occurs along major streams and rivers of the study area. Springs in the northern part of the Great Divide-Washakie-Sand Wash Basins aquifer system serve as major discharge points; to a lesser degree, springs associated with faulting near the Little Snake River in the southern part of the basin act as discharge points.

### Mineralogy

Stratigraphic descriptions and mineralogical studies of the Wasatch and Battle Spring Formations in the Green River Basin, Great Divide Basin, Washakie Basin, and Sand Wash Basin were used to determine the minerals present in the Wasatch zone of the Wasatch-Fort Union aquifer (table 4).

**Table 4.** Minerals present in the Wasatch Formation, Green River Basin, Great Divide Basin, Washakie Basin, and Sand Wash Basin

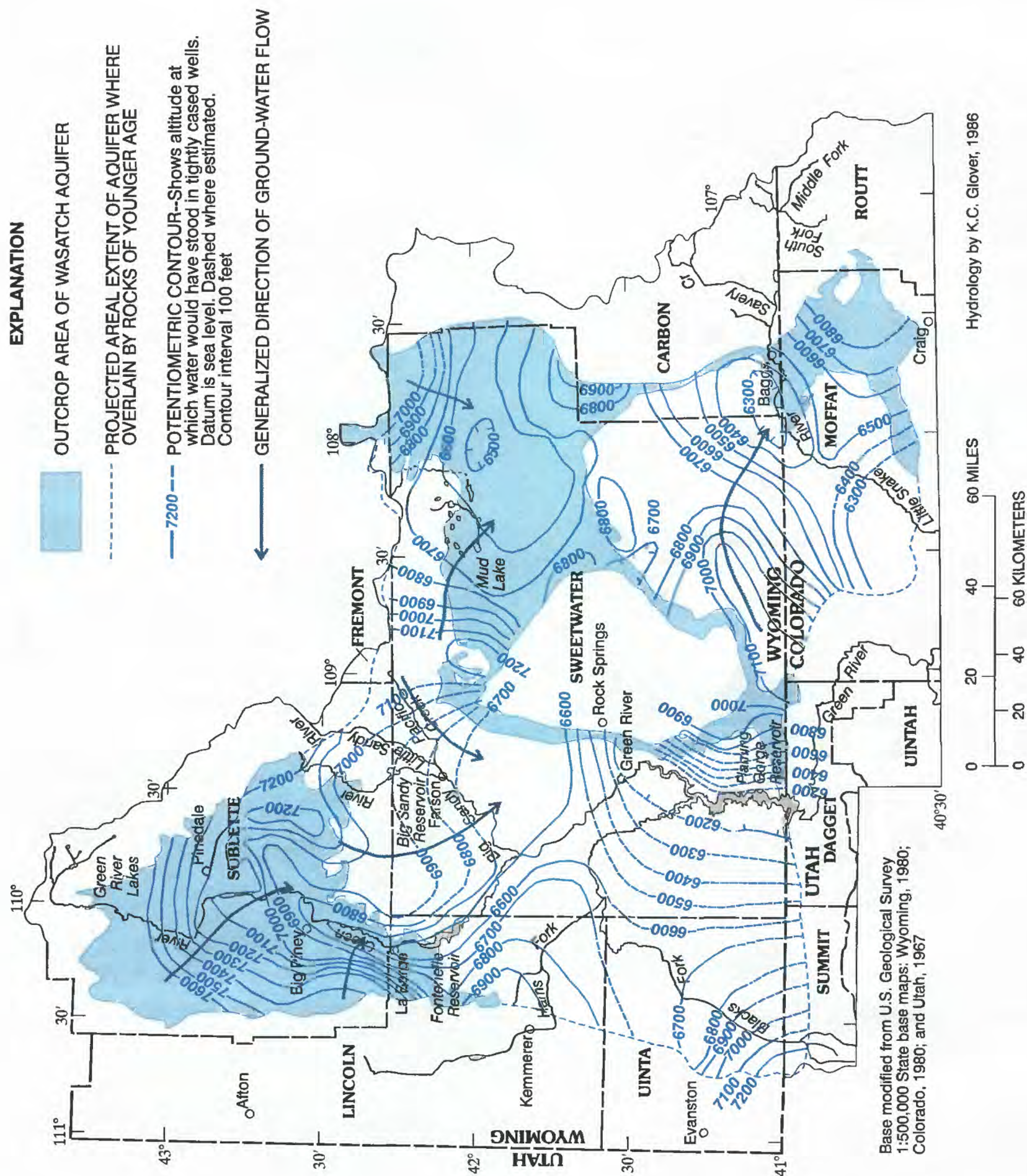
[From Masursky, 1962; Bradley, 1964; Dribus and Nanna, 1982; and Gebhardt and others, 1982]

Mineral name	Idealized chemical formula
Quartz	SiO <sub>2</sub>
Calcite	CaCO <sub>3</sub>
Plagioclase	Ca <sub>0.2</sub> Na <sub>0.8</sub> Al <sub>1.2</sub> Si <sub>2.8</sub> O <sub>8</sub>
Zircon	ZrSiO <sub>4</sub>
Muscovite	KAl <sub>2</sub> (AlSi <sub>3</sub> O <sub>10</sub> )(OH) <sub>2</sub>
Biotite	K(Mg,Fe) <sub>3</sub> (AlSi <sub>3</sub> O <sub>10</sub> )(OH) <sub>2</sub>
Epidote	Ca <sub>2</sub> (Al,Fe)Al <sub>2</sub> O(SiO <sub>4</sub> )(Si <sub>2</sub> O <sub>7</sub> )(OH)
Sphene	CaTiO(SiO <sub>4</sub> )
Hornblende	(Ca,Na) <sub>2-3</sub> (Mg,Fe,Al) <sub>5</sub> Si <sub>6</sub> (Si,Al) <sub>2</sub> O <sub>22</sub> (OH) <sub>2</sub>
Chlorite	(Mg,Fe) <sub>3</sub> (Si,Al) <sub>4</sub> O <sub>10</sub> (OH) <sub>2</sub> (Mg,Fe) <sub>3</sub> (OH) <sub>6</sub>
Tourmaline group	-----
Illite	K <sub>0.6</sub> Mg <sub>0.25</sub> Al <sub>2.3</sub> Si <sub>3.5</sub> O <sub>10</sub> (OH) <sub>2</sub>
Kaolinite	Al <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub>
Montmorillonite	-----
Garnet group	-----
Rutile	TiO <sub>2</sub>

Bradley (1964, p. 22) described the Wasatch Formation on the northern flank of the Uinta Mountains as thick units of coarse conglomerates composed of limestone boulders, quartzite, and hornblende schist. The Battle Spring Formation that intertongues with the main body of the Wasatch Formation in the Great Divide Basin is described by Bradley (1964, p. 48) as arkosic sandstone containing claystone and quartz fragments. He also noted that the weathered sands of the Battle Spring Formation are calcareous and contain concretions with limonitic centers, suggesting the presence of calcite and ferric oxyhydroxides.

Masursky (1962, p. 34–36) studied the mineralogy and petrography of the Battle Spring and Wasatch Formations in the northeastern part of the Great Divide-Washakie-Sand Wash Basins aquifer system. Feldspar is the most abundant mineral among particles greater than 4 mm; quartz is the most abundant mineral in all other size fractions. The most common cementing material is calcite, ranging up to 78 percent in one





**Figure 22.** Potentiometric contours and inferred flow paths for the Wasatch zone of the Wasatch-Fort Union aquifer, Green River Basin and Great Divide-Washakie-Sand Wash Basins aquifer systems.



sample. Other cements found by Masursky (1962, p. 35) include organic material, silica, and pyrite. Heavy mineral separations indicate the presence of trace amounts of chlorite, hypersthene, zircon, muscovite, biotite, tourmaline, pyrophyllite, garnet, pyrite, epidote, hornblende, and magnetite (in order of decreasing abundance). Most samples collected by Masursky (1962, p. 35) contained only a trace of clay, although clay is abundant in four of the samples. X-ray diffraction analysis of the clays indicate the presence of montmorillonite, illite, and kaolinite.

Roehler (1970, p. 181–187) evaluated the non-opaque heavy minerals from rocks of Eocene age in the western part of the Great Divide-Washakie-Sand Wash Basins aquifer system. Nonopaque heavy minerals found in the main body of the Wasatch Formation included (in weight percent of nonopaque, heavy minerals), hornblende (1 to 2 percent); epidote (1 to 2 percent); garnet (68 to 90 percent); zircon (2 to 11 percent); rutile (1 to 4 percent); tourmaline (1 to 3 percent); biotite (1 to 13 percent); and chlorite (1 to 2 percent).

Dribus and Nanna (1982, p. 14–16) have studied the petrography of the Wasatch Formation and its associated members in south-central Wyoming. Various degrees of alteration were noted for the feldspars and biotite grains. Secondary calcite formation also was noted in some samples.

### Water Chemistry and Changes Along Flow Paths

Dissolved-solids concentrations for water in the Wasatch zone of the Wasatch-Fort Union aquifer are shown in figure 23. The dissolved-solids distribution (fig. 23) indicates gradual increases in concentrations of dissolved solids from the basin margins inward, as would be expected if mineral dissolution or leakage of highly mineralized water from shales or adjacent aquifers were occurring along the generalized flow paths in the basin aquifer systems.

Areal variations of major chemical constituents for water from wells in the Wasatch zone are shown in Stiff diagrams (Stiff, 1951) in figure 24. For the selected samples described by the Stiff diagrams, decreases in calcium and magnesium are shown along the generalized flow paths in the basins. Carbonate-bicarbonate and sodium plus potassium concentrations generally increase along projected flow paths. Water in the central part of Green River Basin and the Great

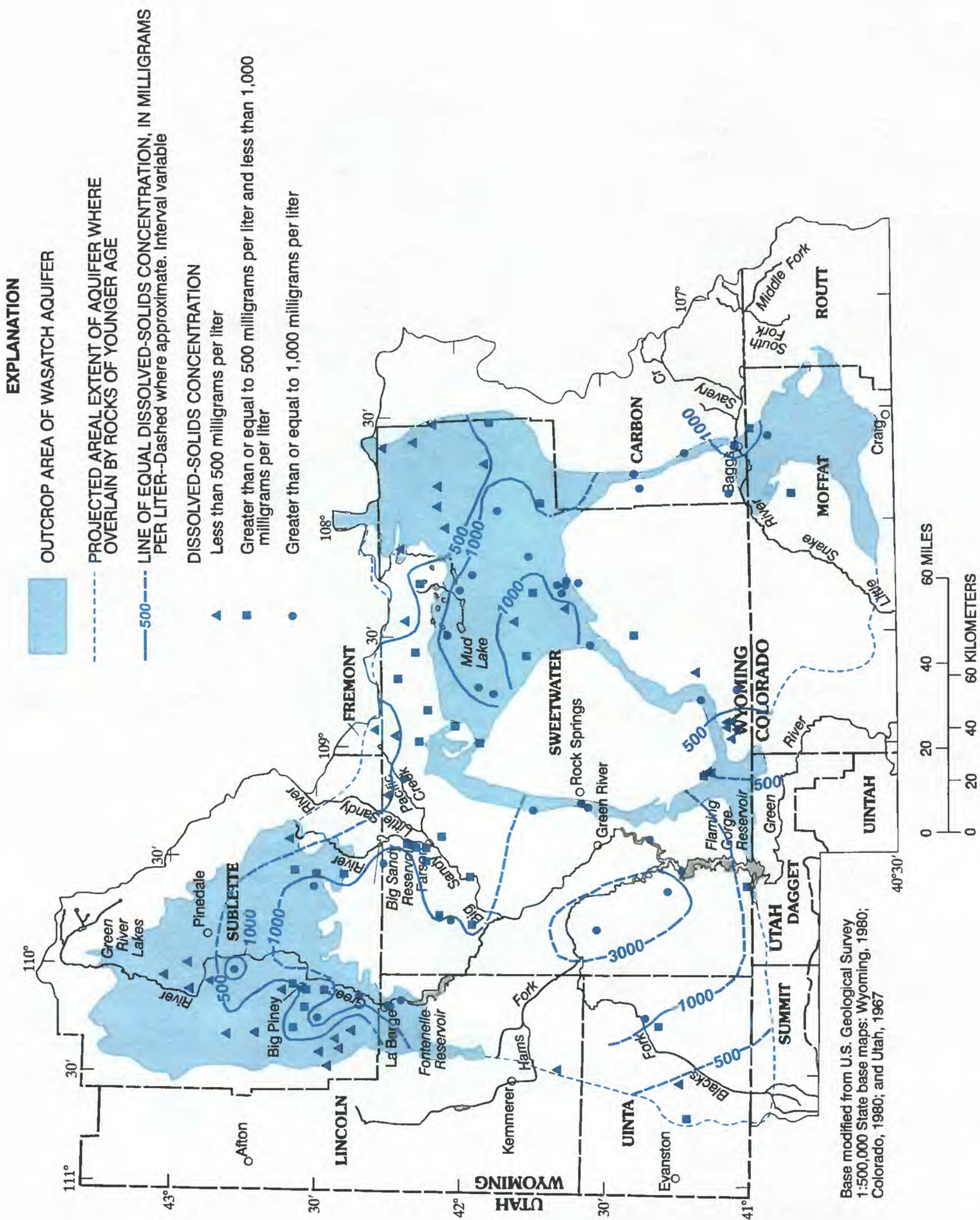
Divide-Washakie-Sand Wash Basins aquifer systems, with a dissolved-solids concentration greater than 1,500 mg/L, usually is dominated by sodium and chloride ions. Sulfate concentrations generally increase along projected flow paths.

Increases in sodium concentrations coupled with decreases in calcium and magnesium concentrations can be interpreted as cation-exchange reactions (table 2; reactions 5 and 6). Distribution of log-molar ratio values for the exchangeable divalent-to-monovalent cations ( $\log ([Ca] + [Mg]) / [Na]^2$ ) is shown in figure 25. Positive values of  $\log ([Ca] + [Mg]) / [Na]^2$  are characteristic of recharge areas in the northern parts of the Green River Basin and Great Divide-Washakie-Sand Wash Basins aquifer systems; negative values of  $\log ([Ca] + [Mg]) / [Na]^2$  are indicative of down-gradient water toward the center of the aquifer systems. Positive  $\log ([Ca] + [Mg]) / [Na]^2$  values found in the southern parts of the Green River Basin and Great Divide-Washakie-Sand Wash Basins aquifer systems (fig. 25) probably are indicative of recharge to the Wasatch zone. Based on the previously described mineralogy within the Wasatch zone, possible sites for ion exchange include the clay minerals montmorillonite, illite, and kaolinite.

The cumulative-frequency plot for sodium and the corresponding inflection point (fig. 26) indicates a mixing of two sodium subgroups in the proportions of 48 percent and 52 percent of the target population. Selection of a threshold value of 230 mg/L (2.36 log mg/L) describes about 88 percent of each subgroup. Based on the mineralogy within the Wasatch zone (table 4), possible sources of sodium in the Wasatch zone include cation-exchange reactions (table 2; reactions 5 and 6), mineral dissolution of plagioclase feldspar (table 2; reaction 4), as well as other silicate phases.

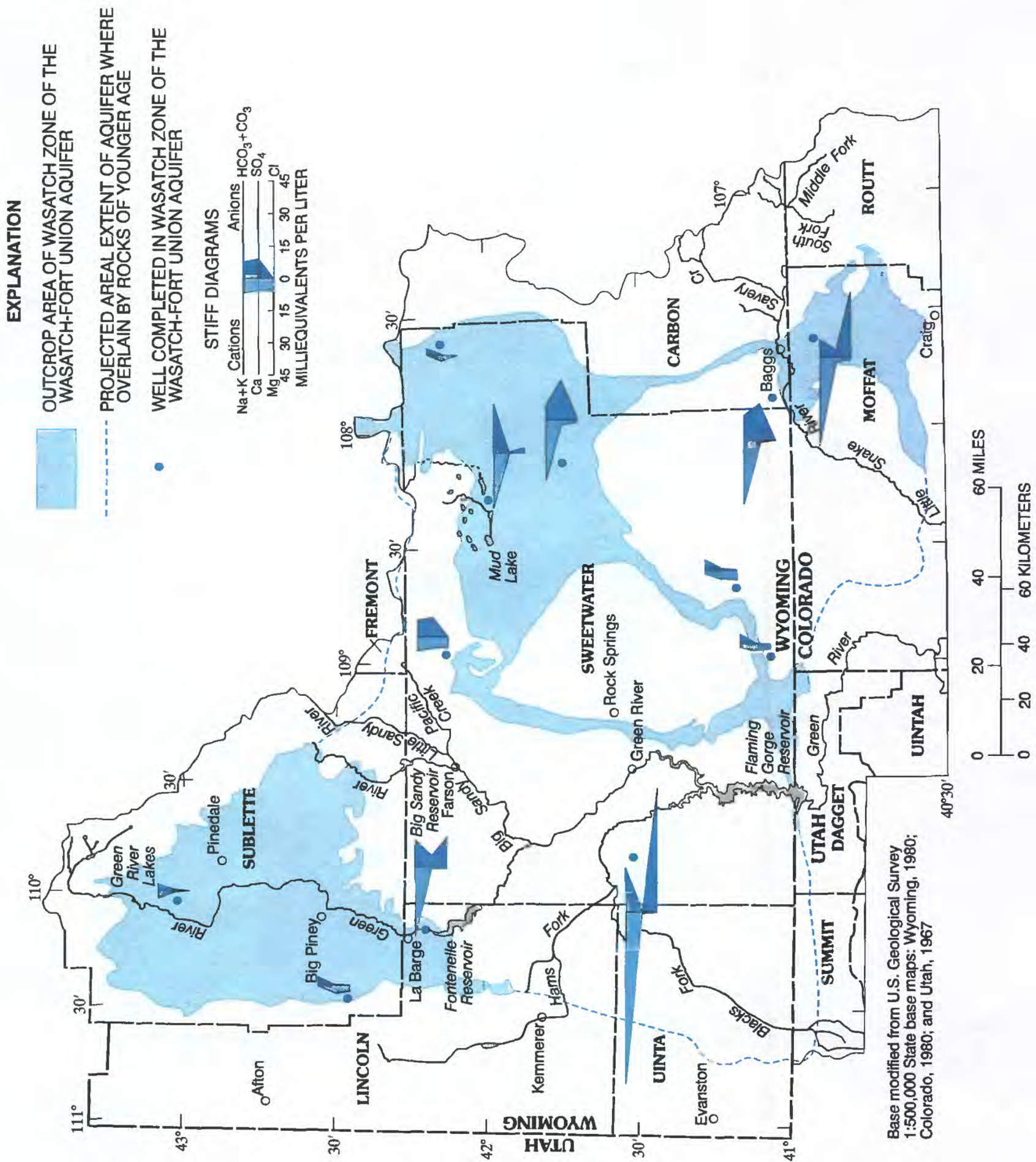
Distribution of ground-water samples from the two sodium subgroups, defined by the threshold value of 230 mg/L is shown in figure 27. Most ground water with sodium concentrations less than or equal to the threshold value of 230 mg/L evidently are found in recharge areas delineated by the potentiometric-surface map (fig. 22). Similar to the Bridger and Duchesne River-Uinta aquifers in Wyoming and Utah, small sodium concentrations in the recharge areas of the Wasatch zone probably are the result of limited water-to-rock contact that would minimize plagioclase-feldspar dissolution and cation exchange. Positive log





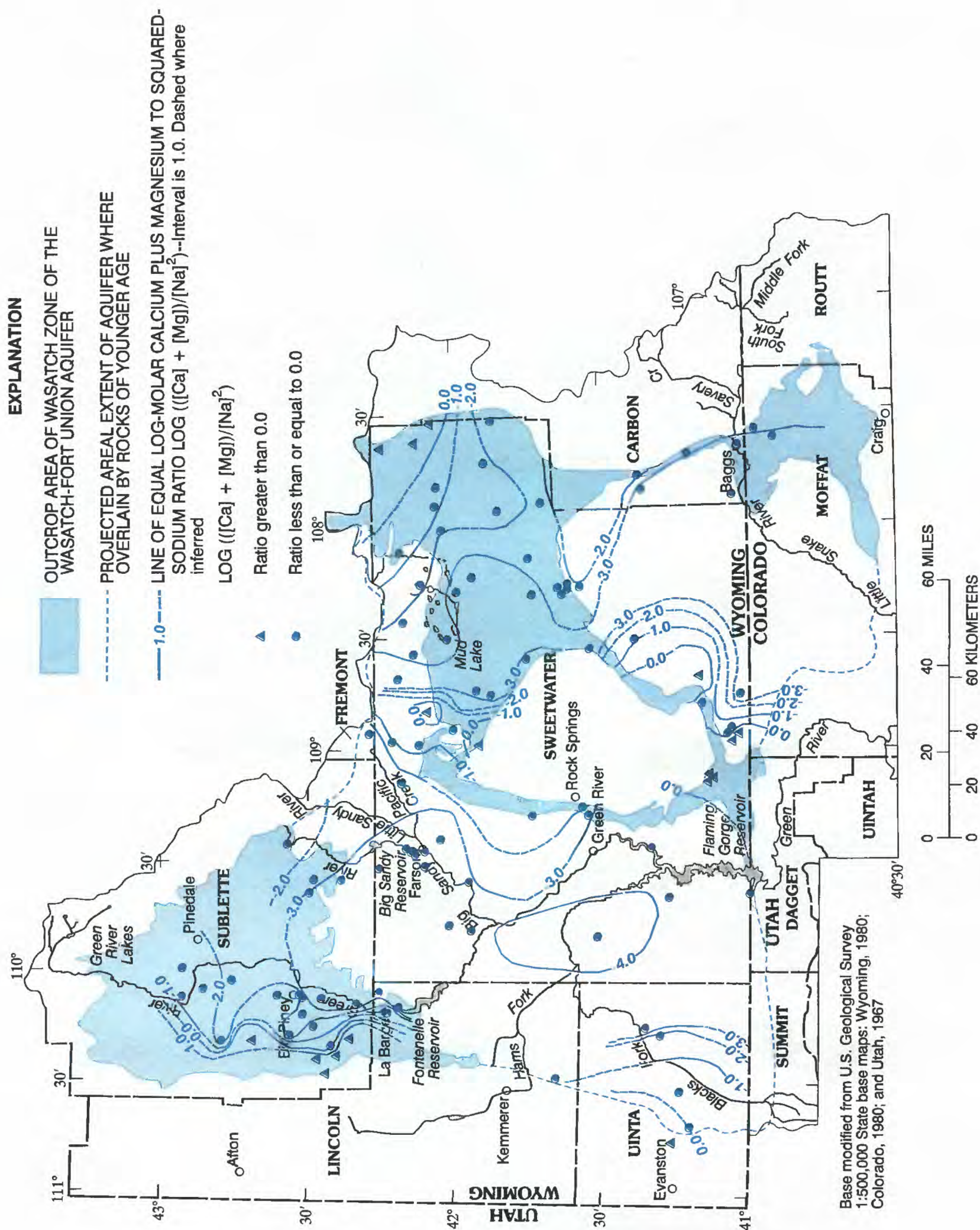
**Figure 23.** Dissolved-solids concentrations for water from the Wasatch zone of the Wasatch-Fort Union aquifer, Green River Basin and Great Divide-Washakie-Sand Wash Basins aquifer systems.





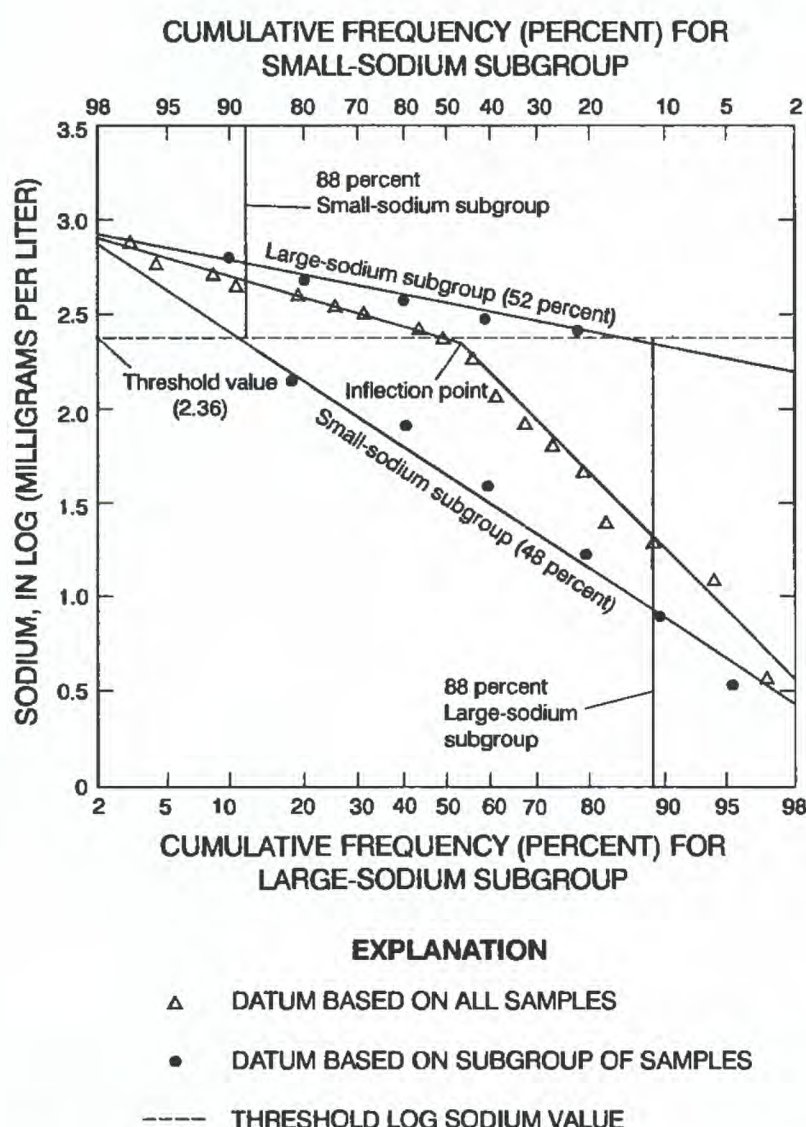
**Figure 24.** Stiff diagrams for major chemical constituent concentrations in water from the Wasatch zone of the Wasatch-Fort Union aquifer, Green River Basin and Great Divide-Washakie-Sand Wash Basins aquifer systems.





**Figure 25.** Log-molar ratios of calcium plus magnesium to squared-sodium concentrations in water from the Wasatch zone of the Wasatch-Fort Union aquifer, Green River Basin and Great Divide-Washakie-Sand Wash Basins aquifer systems.





**Figure 26.** Cumulative-frequency plot of log sodium concentrations in water from the Wasatch zone of the Wasatch-Fort Union aquifer, Green River Basin and Great Divide-Washakie-Sand Wash Basins aquifer systems.

$\frac{([Ca] + [Mg])}{[Na]^2}$  values in recharge areas of the Wasatch zone (fig. 25) indicate limited sodium increase from cation-exchange reactions. Water with sodium concentrations above the 230 mg/L threshold value generally are indicative of downgradient areas because of increases of sodium from ion-exchange reactions (table 2; reactions 5 and 6), plagioclase-feldspar dissolution (table 2; reaction 4), and possible upward leakage from underlying aquifers containing water with large sodium concentrations.

The cumulative-frequency plot of fluoride concentrations for the Wasatch zone (fig. 28) indicates an inflection point identifying two fluoride subgroups in the proportions of 20 percent and 80 percent of the data set. Selection of a threshold value of 4.0 mg/L (0.6 log mg/L) identifies about 97 percent of the small-sodium subgroup and 96 percent of the large-sodium subgroup. Similar to the distribution of the large-fluoride subgroups in water from the Bridger,

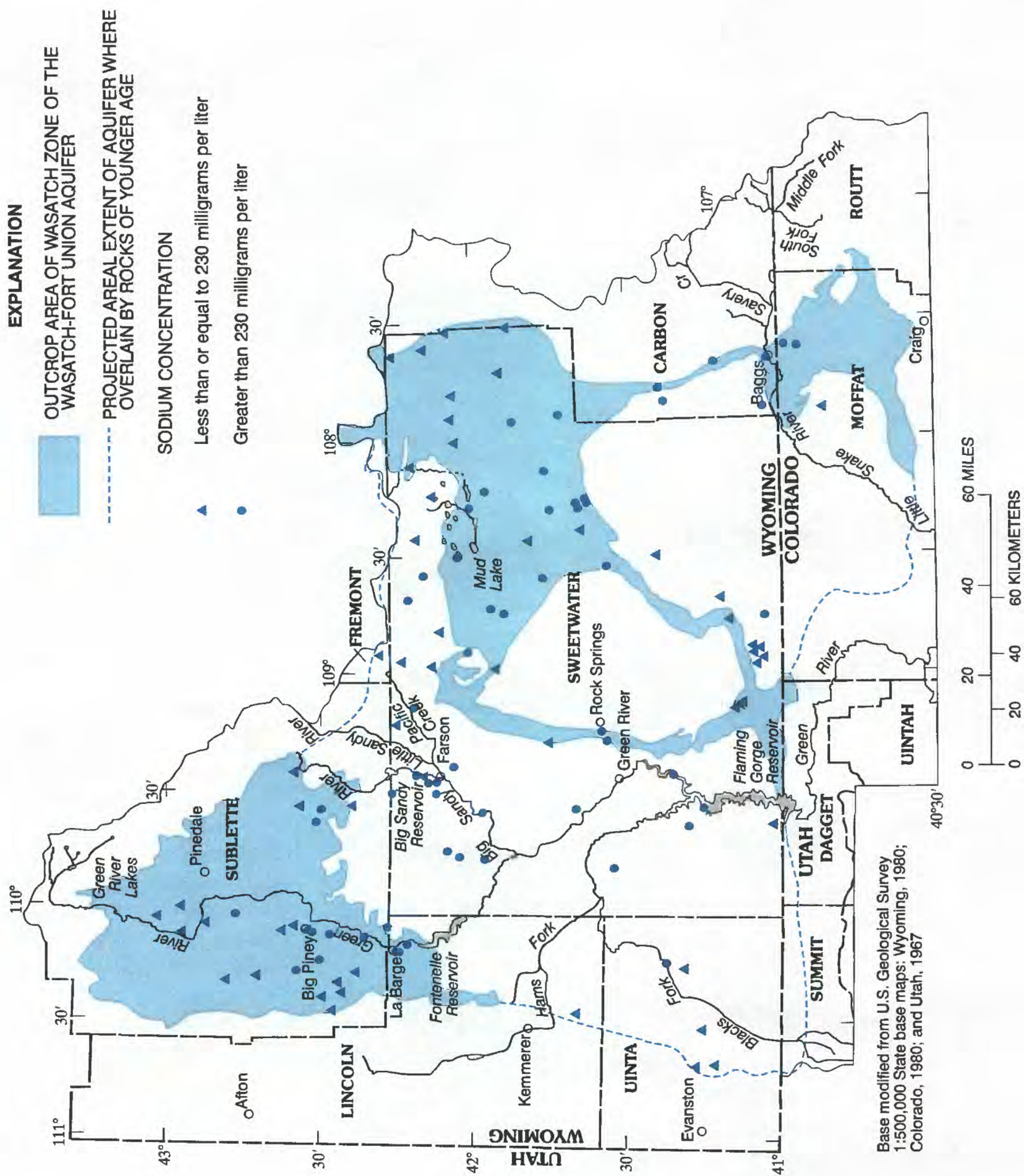
Duchesne River-Uinta, and Laney aquifers, fluoride concentrations larger than the threshold value in water from the Wasatch zone (fig. 29) are located in downgradient areas delineated by the potentiometric-surface map (fig. 22).

As discussed previously, sources of fluoride in water include apatite, fluorite, rocks rich in alkali metals, and amphiboles, in which fluoride replaces part of the hydroxide (Hem, 1985, p. 121). The mechanism for increases in fluoride in downgradient water in the Wasatch zone is not definitive; however, the relation between calcium and fluoride concentrations as defined by the threshold value for fluoride in the Wasatch zone is similar to the relation between calcium and fluoride in the Bridger and Duchesne River-Uinta aquifers. The median calcium concentration (1 mg/L for 19 samples) in ground water with a fluoride concentration greater than the threshold value of 4.0 mg/L is much less than the median calcium concentration (32 mg/L for 37 samples) in ground water with a fluoride concentration below the threshold value of 4.0 mg/L. Assuming that fluorite and apatite are present in the Wasatch zone, decreased calcium activities in downgradient water could increase the solubility of fluorite and apatite, which, in turn, could allow the concentration of fluoride to increase in the ground water.

The molar ratio of calcium-to-chloride concentrations for ground water from the Wasatch zone is shown in figure 30. The previously calculated mean calcium-to-chloride ratio (mmoles to mmoles) for precipitation in the Green River Basin of Wyoming is 1.44. Ground water corresponding to an ionic ratio (millimoles calcium to millimoles chloride) different than the ionic ratio for calcium-to-chloride concentrations found in precipitation indicates possible chemical reactions in areas of the aquifer where chloride is assumed to be conservative. Based on the mineralogy of the Wasatch Formation, chloride probably is conservative, except where chloride could be derived from leaching of shale units in the aquifer zone.

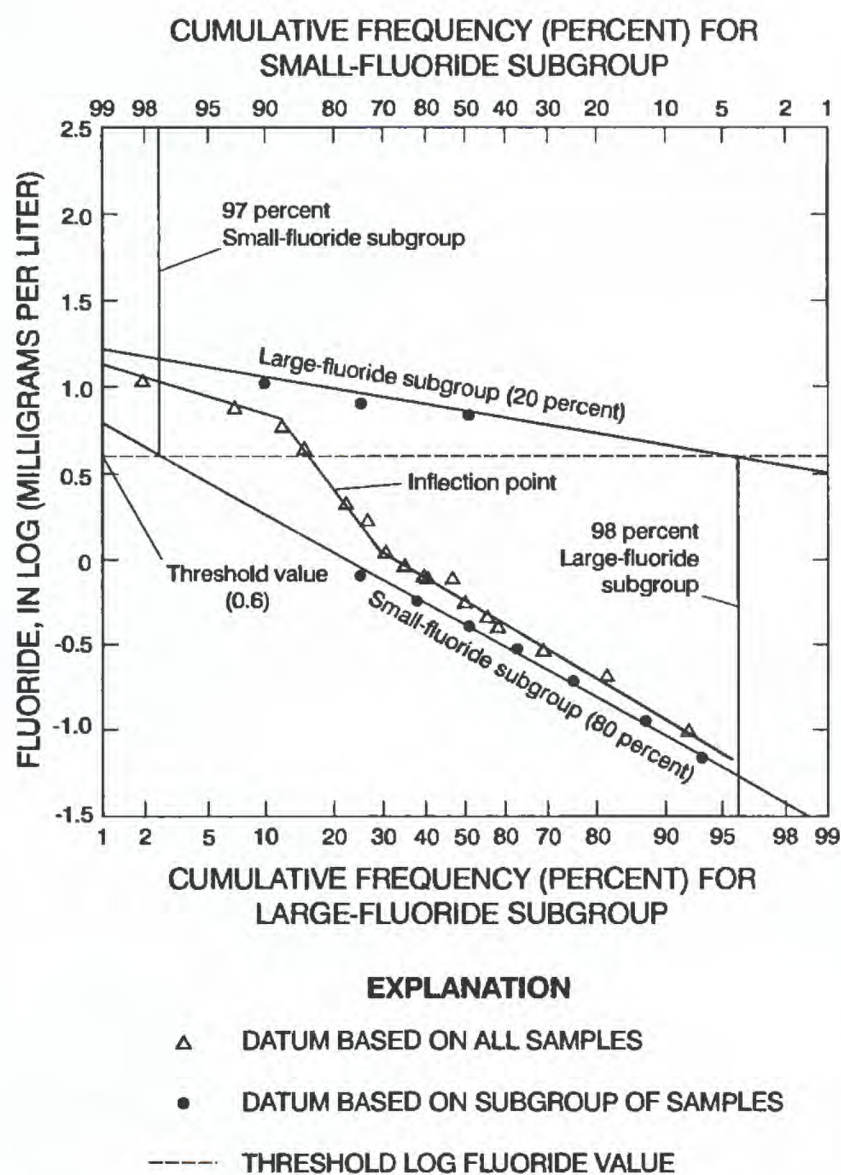
Most calcium-to-chloride ratios that exceed the calcium-to-chloride ratio in precipitation are found in previously defined recharge areas, including the northwestern part of the Green River Basin aquifer system and the northeastern and northwestern parts of the Great Divide-Washakie-Sand Wash Basins aquifer system (fig. 30). Similar to recharge water from the Bridger and Duchesne River-Uinta aquifers, the prob-





**Figure 27.** Sodium concentrations in water from the Wasatch zone of the Wasatch-Fort Union aquifer, Green River Basin and Great Divide-Washakie-Sand Wash Basins aquifer systems.





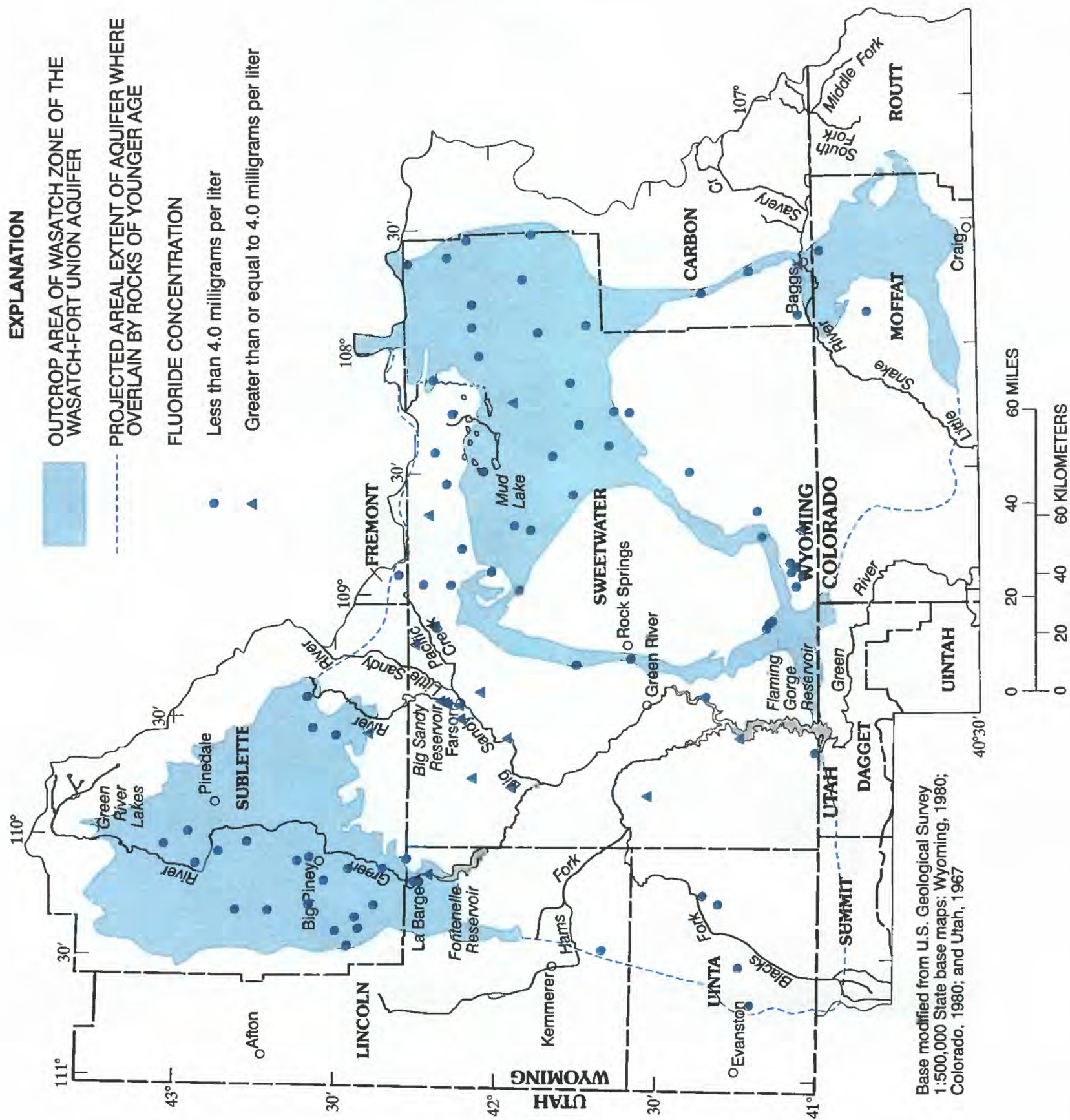
**Figure 28.** Cumulative-frequency plot of log fluoride concentrations in water from the Wasatch zone of the Wasatch-Fort Union aquifer, Green River Basin and Great Divide-Washakie-Sand Wash Basins aquifer systems.

able source of increased calcium concentrations in recharge areas of the Wasatch zone is carbonate dissolution by carbon-dioxide-charged water (table 2; reaction 2).

Ground water with calcium-to-chloride ratios below the calcium-to-chloride ratio in precipitation usually is found in the downgradient areas of the Wasatch zone of the Wasatch-Fort Union aquifer. As found in the Bridger and Duchesne River-Uinta aquifers, probable mechanisms for calcium depletion relative to chloride concentrations in water from the Wasatch zone include cation-exchange and incongruent dedolomitization processes (table 2; reactions 3 and 5).

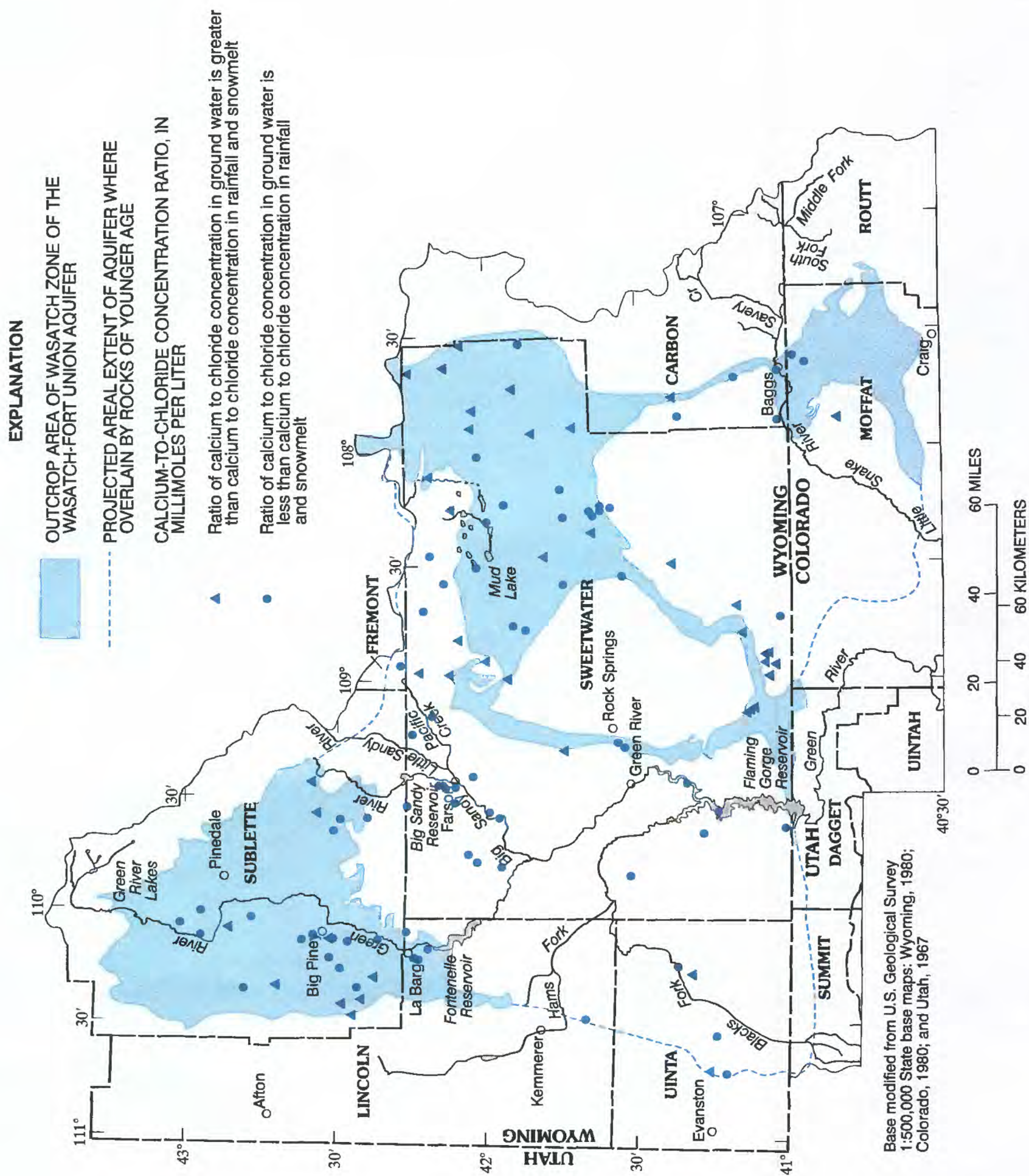
Small calcium-to-chloride ratios in water from the Wasatch zone also could be the result of movement of water with large chloride concentrations from lower zones or aquifers. Chloride concentrations in water from the Fort Union zone of the Wasatch-Fort Union aquifer below the Wasatch zone (fig. 3) in the vicinity of La Barge, Wyoming, range from 200 mg/L to 4,120 mg/L for five wells. According to K.C. Glover (U.S. Geological Survey, written commun., 1986), areas of significant vertical leakage exist in the Fort Union zone directly west of La Barge, Wyoming.





**Figure 29.** Fluoride concentrations in water from the Wasatch zone of the Wasatch-Fort Union aquifer, Green River Basin and Great Divide-Washakie-Sand Wash Basins aquifer systems.





**Figure 30.** Calcium-to-chloride concentration ratios in water from the Wasatch zone of the Wasatch-Fort Union aquifer, Green River Basin and Great Divide-Washakie-Sand Wash Basins aquifer systems.



## SUMMARY

Basin variations in concentrations of selected major and minor chemical constituents in the Bridger, Duchesne River-Uinta, and Laney aquifers, and the Wasatch zone of the Wasatch-Fort Union aquifer can be used to identify areas of recharge, discharge, and interaquifer leakage. Recharge areas in the selected aquifers or aquifer zones in Tertiary rocks generally are characterized by small dissolved-solids concentrations, positive  $\log (([\text{Ca}]+[\text{Mg}])/[\text{Na}]^2)$  values, and small concentrations of sodium and fluoride. Discharge areas in the aquifers or aquifer zones in Tertiary rocks generally are characterized by large dissolved-solids concentrations, negative  $\log (([\text{Ca}]+[\text{Mg}])/[\text{Na}]^2)$  values, and large concentrations of sodium and fluoride. Values of calcium-to-chloride ratios that exceed the calcium-to-chloride ratio in local precipitation generally are characteristic of recharge areas. Conversely, ratio values of calcium to chloride that are less than the calcium-to-chloride ratio in local precipitation generally are characteristic of discharge areas.

Variations in water quality between recharge and discharge areas for the aquifers or aquifer zones in Tertiary rocks can be accounted for on a qualitative scale by the use of data that include mineralogical descriptions of the aquifers or zones, basin trends in water quality, and comparisons of ionic ratios in ground water with corresponding precipitation ratios in each aquifer along projected flow paths. On the basis of information available, the probable chemical reactions occurring in the aquifers or aquifer zones in Tertiary rocks are summarized. Changes in concentrations of calcium, magnesium, sodium, chloride, and fluoride in the Bridger and Duchesne River-Uinta aquifers and the Wasatch zone of the Wasatch-Fort Union aquifer can be accounted for by sodium-magnesium and sodium-calcium exchange on clay minerals; evapotranspiration and subsequent mineral precipitation; interaquifer leakage; leaching of shales; and coming to equilibrium with local calcite, dolomite, fluorite, and carbon dioxide. In water from the Laney aquifer and Wilkins Peak confining unit, the previously noted reactions for the Bridger and Duchesne River-Uinta aquifers and Wasatch zone, coupled with dissolution of saline minerals from evaporative lake deposits, can be used to explain the observed variations in water quality. Because of the type of the water-quality data used, the proposed chemical reactions cannot be sub-

stantiated with detailed geochemical speciation, mass-balance, or reaction-path calculations. Detailed geochemical sampling on a local scale is needed before a reliable and quantitative geochemical model can be made for the aquifers in the study area.

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