# EFFECTS OF SEDIMENT DEPOSITIONAL ENVIRONMENT AND GROUND-WATER FLOW ON THE QUALITY AND GEOCHEMISTRY OF WATER IN AQUIFERS IN SEDIMENTS OF CRETACEOUS AGE IN THE COASTAL PLAIN OF SOUTH CAROLINA

U.S. GEOLOGICAL SURVEY
Open-File Report 91-202

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MARCH 3, 1849

# CONVERSION FACTORS AND ABBREVIATIONS

Inch-pound units of measurement in this report may be converted to metric (International System) units using the following conversion factors:

| Multiply inch-pounds units | By | To obtain metric units |
|---|---|---|
| foot (ft) | 0.3048 | meter (m) |
| foot squared per day ($ft^2/d$) | 0.0929 | meter squared per day ($m^2/d$) |
| square mile ($mi^2$) | 2.590 | square kilometer ($km^2$) |

Temperature in degrees Celsius (°C) can be converted to degrees Fahrenheit (°F) and follows:

$$^{0}F = 1.8\ ^{0}C + 32$$

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".

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## ABSTRACT

The quality and geochemistry of ground water is significantly affected by the depositional environment of aquifer sediments. Cretaceous sediments in the Coastal Plain of South Carolina have been deposited in fluvial, delta-plain, marginal-marine, and marine environments. Depositional environments of sediments within a single aquifer may grade from nonmarine, fluvial or upper delta-plain near the updip limit of the aquifer to transitional, lower delta-plain and to marine toward the coast.

In nonmarine sediments, the major source of inorganic carbon in the water is the decomposition of organic material. The major aqueous geochemical processes are the dissolution and alteration of silicate minerals. Silica comprises a major part of the dissolved constituents in water from these sediments.

In transitional and marine sediments the major aqueous geochemical processes are (1) the dissolution of calcium carbonate by hydrolysis and by carbonic acid derived from the decomposition of organic material and (2) the exchange of calcium in solution for sodium on the marine-clay minerals. The clay minerals may also serve as buffers by neutralizing the hydroxyl ion produced by the hydrolysis. The effects of incompletely flushed dilute saltwater on water quality increase toward the coast and toward the northeast.

## INTRODUCTION

The Atlantic and Gulf Coastal Plains of the United States are underlain by a system of aquifers and confining units that are similar in many geohydrologic and geochemical respects. The aquifers predominantly consist of unconsolidated sand or consolidated limestone of high permeability. confining units separating the aquifers predominantly consist of unconsolidated silt and clay or consolidated limestone of low permeability. These aquifers and confining units have a complex composition with local variations. General descriptions of the characteristics of one aquifer or confining unit may provide an understanding of others in the system.

In 1978 the U.S. Geological Survey (USGS) began a series of investigations known as the Regional Aquifer-System Analysis (RASA) Program to evaluate such large systems of aquifers throughout the United States. The objective of these studies is to define the regional geohydrology and to establish a framework of background geologic, hydrologic, and geochemical information that can be used for regional assessment of ground-water resources and in support of more detailed local studies (Sun, 1986, p. 6). Descriptions of the aquifer systems are developed at regional scales and many are supplemented by more detailed, subregional and localized descriptions.

One such investigation is the Southeastern Coastal Plain RASA in which the regional system of clastic aquifers in the Atlantic and Gulf Coastal Plains of the States of South Carolina, Georgia, Alabama, and Mississippi were studied. Subregional investigations in each state have been included as part of that investigation. Geohydrologic and geochemical descriptions have been developed as a part of the subregional investigation in South Carolina.

Aquifers in South Carolina generally dip less than those in many other parts of the Coastal Plain. Because of this, many wells have been drilled and information is available throughout the areal extent of the aquifers in South Carolina. Thus, the lithology and depositional environments of the sediments, the ground-water flow, the quality and geochemistry of the water, and the relations of depositional environments and ground-water flow to the quality and geochemistry of the water can be described over most of the areal extent of aquifers in the Coastal Plain of South Carolina.

## Purpose and Scope

The purposes of this report are (1) to describe the areal distribution of the dominant water-quality constituents, (2) to identify the major geochemical processes that affect the quality of water, and (3) to discuss the relations of sediment-depositional environments and ground-water flow to the quality and geochemistry of water in aquifers in sediments of Cretaceous age in the Coastal Plain of South Carolina.

Data used in this report are for water samples collected and analyzed between the early 1900's and 1983 using a variety of methods for collecting, preserving, and analyzing the samples. The major geochemical processes and their relation to sediment depositional environment in each of the Cretaceous aquifers is discussed.

## Study Area

The study area is located in the Coastal Plain of South Carolina (fig. 1). It is part of the Atlantic Coastal Plain physiographic province, which extends along the eastern coast of the United States. The Coastal Plain of South Carolina covers approximately 20,000 $mi^2$ or the southeastern two thirds of the State between the inner margin of Coastal Plain sediments (Fall Line) and the Atlantic Ocean (fig. 1).

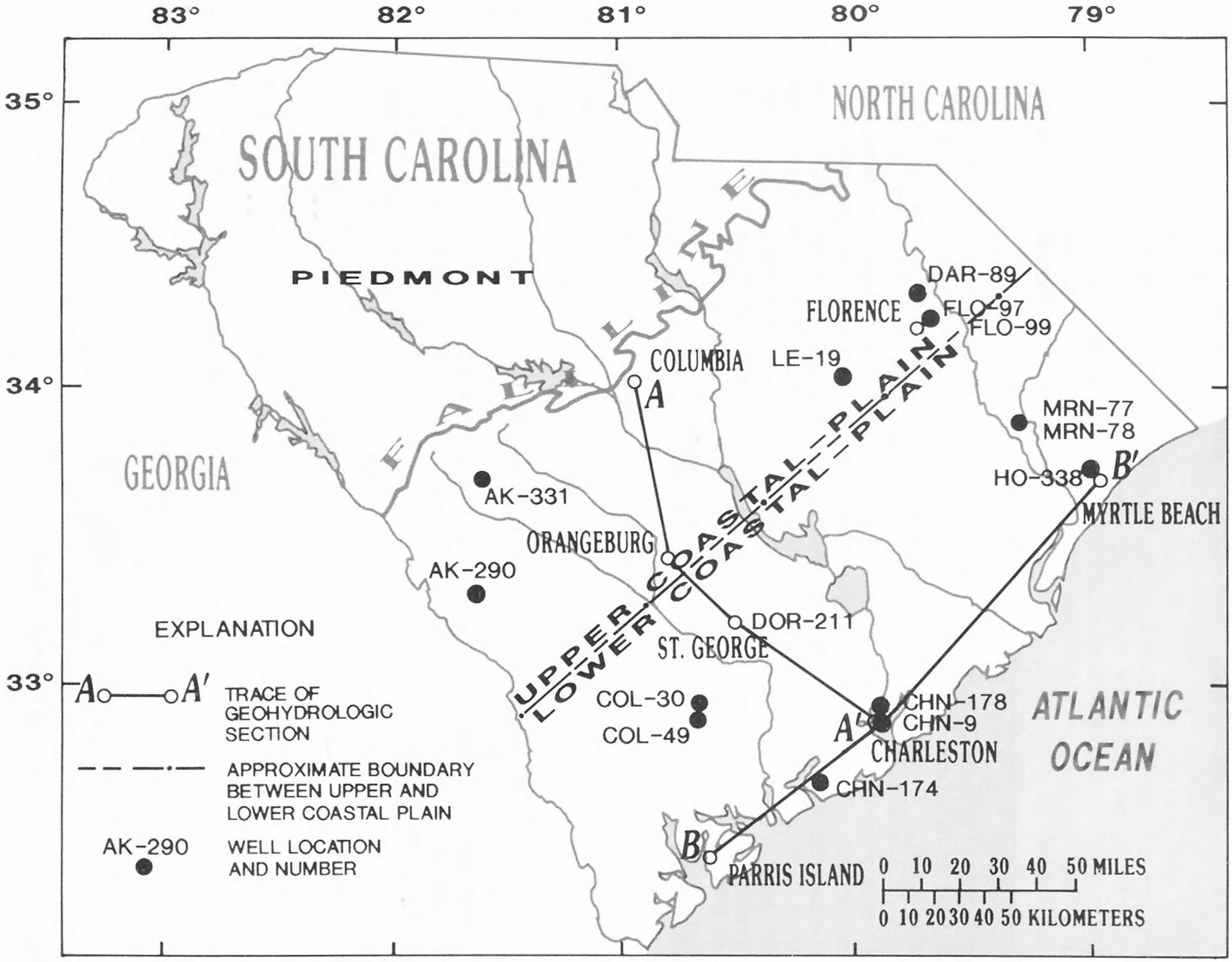

Figure 1.--Location of the Coastal Plain, geohydrologic sections, and other features in the Coastal Plain.

## Data Evaluation

Water-quality data used for this report are from the files of the USGS. They are primarily from analyses of water samples by USGS laboratories, but also include some analyses by State-agency laboratories and by private laboratories. Samples were collected between the early 1900's and 1983. A variety of methods was used for collecting, preserving, and analyzing samples. The accuracy of the data was evaluated by comparing the charge balance of the ions (within 10 percent), by comparing the residue on evaporation at 180 °C with the sum of dissolved constituents (within 10 percent), and by comparing the data from one sample with data from other samples in the area and with regional trends in the data. Data from representative analyses of samples from each aquifer are included in table 1.

Well-construction data and the altitude of land surface were used to determine the altitude of the screened intervals from which water samples were collected. These altitudes were compared with geohydrologic sections and maps of the altitudes of the tops of the aquifers and confining units (Aucott and others, 1987) tc determine the aquifer from which the samples were collected. This comparison was also used to determine which samples were composited from more than one aquifer and which samples were from sands contained within confining units. Samples from composites of more than one aquifer were not used because of problems resulting from mixing water from more than one aquifer; samples from sands in confining units were not used because they may be saltier due to less complete flushing or otherwise chemically do not represent water from the aquifer.

## SEDIMENT DEPOSITIONAL ENVIRONMENTS

The primary source of sediments of Cretaceous age comprising aquifers in the Coastal Plain of South Carolina was continental. Sediments from source areas were transported toward the sea by the river systems and were deposited in different environments between the source and the sea. These depositional environments graded from fluvial to delta-plain, to marginal-marine, and to marine. Sediments in an aquifer were deposited in environments grading from one depositional environment to another, representing different parts of the system deposited at approximately the same time. Sediments deposited in all environments are not present in each aquifer beneath the Coastal Plain of South Carolina. However, the gradation in environments probably continues seaward of the present coast. The lateral limits of each depositional environment cannot be accurately defined in detail because of the limited amount of data and because of the gradational characteristics of the depositional environments. Generalized delineations of depositional environments for the aquifers are based on Gohn and others (1977), Gohn and others (1978), Colquhoun and others (1983), Owens and Gohn (1985), and an evaluation of geophysical and lithologic logs for wells throughout the Coastal Plain.

Table 1.--Selected water-quality data for aquifers in sediments of Cretaceous age

[mg/L, milligrams per liter; dash, no determination; $SiO_2$; silica; <, less than]

| Well number | Depth to top of sample interval (feet) | Depth to bottom of sample interval (feet) | Solids, sum of constituents, dissolved (mg/L) | pH (standard units) | Carbon dioxide, dissolved (mg/L) | Bicarbonate, total (mg/L) | Carbonate, total (mg/L) |
|---|---|---|---|---|---|---|---|
| Black Creek aquifer | | | | | | | |
| AK- 290 | 392 | 465 | 16 | 5.8 | 10 | 4 | 0 |
| COL- 30 | -- | -- | 500 | 8.2 | 5.5 | 550 | 0 |
| CHN- 9[a] | -- | 1,260 | 2,655 | -- | -- | 1,115 | 41 |
| FLO- 99 | -- | -- | 77 | 6.0 | 38 | 24 | 0 |
| HO- 338 | 395 | 880 | 730 | 8.0 | 10 | 650 | -- |
| MRN- 77 | 325 | 355 | 340 | 8.72 | .9 | 290 | 22 |
| MRN- 78 | 517 | 537 | 760 | 8.57 | 2.1 | 490 | 12 |
| Middendorf aquifer | | | | | | | |
| AK- 331 | 280 | 300 | 14 | 5.1 | 25 | 2 | -- |
| CHN- 174 | 2,040 | 2,260 | 1,300 | 8.3 | 9.9 | 1,240 | 0 |
| CHN- 178 | -- | -- | 1,100 | 8.3 | 7.7 | 970 | 0 |
| COL- 49 | 1,600 | 1,660 | 230 | 9.0 | .3 | 220 | -- |
| FLO- 97 | 311 | 424 | 54 | 6.2 | 20 | 20 | 0 |
| LE- 19 | 386 | 536 | 50 | 6.7 | 7.0 | 22 | 0 |
| MRN- 78 | 748 | 768 | 470 | 8.1 | 4.8 | 380 | 0 |
| Cape Fear aquifer | | | | | | | |
| CHN- 174 | 2,510 | 2,520 | 2,800 | 8.1 | 11 | 880 | 0 |
| DAR- 89[a] | 530 | 624 | 193 | 7.2 | 12 | 70 | 0 |
| MRN- 78 | 1,010 | 1,030 | 1,500 | 7.52 | 43 | 890 | 0 |
| MRN- 78 | 811 | 831 | 1,500 | 7.6 | 33 | 820 | 0 |
| HO- 218 | 890 | 910 | 1,880 | 8.7 | -- | 876 | 54 |
| HO- 218 | 1,045 | 1,055 | 3,300 | 7.6 | -- | 1,240 | 0 |

[a] Water-quality analysis by a private laboratory.

Table 1.--Selected water-quality data for aquifers in sediments of Cretaceous age--Continued

[mg/L, milligrams per liter; dash, no determination; $SiO_2$; silica; <, less than]

| Well number | Chloride, dissolved (mg/L) | Sulfate, dissolved (mg/L) | Calcium, dissolved (mg/L) | Magnesium, dissolved (mg/L) | Sodium, dissolved (mg/L) | Potassium, dissolved (mg/L) | Silica, dissolved (mg/L as $SiO_2$) |
|---|---|---|---|---|---|---|---|
| **Black Creek aquifer** | | | | | | | |
| AK- 290 | 1.5 | 0.8 | 0.8 | 0.5 | 1.3 | 0.01 | 8.2 |
| COL- 30 | 4.0 | .9 | 2.7 | 1.1 | 200 | 4.7 | 17 |
| CHN- 9 | 944 | 0 | 14 | 8.3 | 1,014 | 41 | -- |
| FLO- 99 | 4.0 | 9.7 | 5.4 | 2.4 | 5.8[b] | -- | 37 |
| HO- 338 | 22 | 3.4 | 3.0 | 1.0 | 360 | 4.3 | 15 |
| MRN- 77 | 5.3 | 6.2 | 1.4 | .24 | 120 | 4.1 | 14 |
| MRN- 78 | 36 | <.2 | 2.3 | .46 | 190 | 3.7 | 17 |
| **Middendorf aquifer** | | | | | | | |
| AK- 331 | 2.0 | .9 | .8 | .2 | 1.3 | .2 | 5.5 |
| CHN- 174 | 88 | <1.0 | 3.0 | .07 | 540 | .06 | 16 |
| CHN- 178 | 130 | 4.9 | 2.0 | .7 | 460 | 3.2 | 18 |
| COL- 49 | 6.3 | 1.3 | .4 | .16 | 96 | .92 | 17 |
| FLO- 97 | 2.5 | 11 | 1.8 | 1.3 | 10[b] | -- | 17 |
| LE- 19 | 2.0 | 8.6 | 5.6 | 1.1 | 1.7 | 6.1 | 14 |
| MRN- 78 | 56 | 13 | 1.7 | .36 | 180 | 2.2 | 24 |
| **Cape Fear aquifer** | | | | | | | |
| CHN- 174 | 1,300 | 5.5 | 5.4 | 2.4 | 1,100 | 5.9 | 12 |
| DAR- 89[a] | 33 | 21 | 8 | 4 | 40[b] | -- | 15 |
| MRN- 78 | 370 | 120 | 9.9 | 2.6 | 480 | 6.6 | 32 |
| MRN- 78 | 360 | 120 | 12 | 3.4 | 580 | 6.1 | 34 |
| HO- 218 | 590 | 12 | 6.7 | 1.3 | 750 | 7.6 | 16 |
| HO- 218 | 1,330 | 4.0 | 13 | 4.2 | 1,290 | 9.3 | 15 |

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[b] Sodium plus potassium as sodium

Depositional environments of sediments influence the degree of diagenesis, the mineral content, and the grain size of the sediments. Composition of sediment deposited in different environments depends on the nature of the available sediment, the energy of the water transporting the sediment, and the relative freshwater-saltwater flows. Generally, sediments are coarser grained and less diagenetically altered closer to the source.

Sediments deposited in each environment generally may be identified by various characteristics. These characteristics include lithology, sequences of lithologies, and mineral content.

Fluvial environments of meandering and braided rivers result in two characteristically different types of sediment sequences (Selley, 1978, p. 39). Meandering rivers generally have less energy and carry less sediment than braided rivers. Sediments deposited in fluvial environments of meandering rivers consist of series of generally fining-upward sequences resulting from the lateral migration of the river channels (Selley, 1978, p. 40). At the bottom of each sequence are gravel and coarse-grained sand that were deposited in the high-energy environment of stream channels. These sediments grade upward into fine-grained sand, silt, and clay that were deposited in progressively shallower, lower energy water. The silt and clay layers are considerably thicker than the gravel and sand layers. These sediments are characteristically nonmarine; consist of quartz, clay minerals, and feldspar; are noncalcareous; have low solubilities; and react slowly with water.

Sediments deposited in braided rivers generally consist of thick layers of coarse-grained sand and thin layers of silt and clay. This results from the high energy and high sediment load of the river. These sediments are nonmarine and generally consist of minerals similar to those of sediments deposited in a meandering fluvial environment.

Sediments deposited in delta-plain environments consist of widely ranging grain size. Composition of sediments deposited in the delta plain represent a transition from that of the nonmarine, fluvial environments to that of the marginal-marine and marine environments (Selley, 1978, p. 3). Sediments deposited in the delta-plain environments contain sand, silt, and clay similar to that deposited in fluvial environments, but these sediments may be diagenetically altered and may contain some marine-clay minerals, shell material, and calcite cement, particularly toward the seaward limit of the delta plain. Deltaic deposits exhibit a coarsening upward sequence resulting from the prograding or seaward building of the delta (Selley, 1978, p. 125).

Sediments deposited in marginal-marine and marine environments are variable in composition. They are generally rich in organic material, are heterogeneous, and include fine- to medium-grained quartz sand; sodium-rich, marine silt and clay minerals; and abundant shell material. Calcite cementation is also common in these deposits. Although shell and calcite cementation are common, no thick limestone sequences are present in the Cretaceous sediments in the Coastal Plain of South Carolina. Numerous types of marginal-marine and marine environments exist, but for the purpose of this report it is not necessary to distinguish between these environments. In contrast to nonmarine deposits, marginal-marine and marine deposits tend to be more soluble and to react rapidly with water.

The discussion of the relations of depositional environments to the quality and geochemistry of water in the aquifers distinguishes only between nonmarine, transitional, and marine environments because these are the groupings of depositional environments that have the major effects on the quality and geochemistry of the water. Nonmarine environments include fluvial and upper delta-plain environments. Transitional environments are those deltaic environments where sediments grade from nonmarine to marine. The quality and geochemistry of water in transitional sediments are generally dominated by the marine sediments. Marine environments include both the marginal-marine and marine environments. In parts of the discussion, transitional environments are grouped with the marine environments. The following section on the geohydrology of the aquifers describes the general extent of the depositional environments of sediments of each aquifer and shows the gradational characteristics of the environments.

## GEOHYDROLOGY

The Coastal Plain aquifers of South Carolina consist of sediments of Late Cretaceous age and younger that overlie a pre-Cretaceous basement of crystalline and consolidated sedimentary rocks of Triassic age and older. These sediments thicken from the Fall Line toward the coast (fig. 2). Along the coast, sediments are thickest in the south (fig. 3) with approximately 1,300 ft (feet) of sediment at the South Carolina-North Carolina State line and more than 3,400 ft of sediment at the South Carolina-Georgia State line.

The difference in thickness of the sediments along the coast is a result of two structural features in the basement: the Cape Fear Arch and the Southeast Georgia Embayment (Maher, 1971). The Cape Fear Arch is a northwest-southeast oriented uplift in the basement located in North Carolina approximately parallel to the State line. The Southeast Georgia Embayment is a sedimentary basin in southeastern Georgia characterized by a seaward dipping downwarp in basement rocks.

The regional Coastal Plain aquifers of South Carolina, from deepest to shallowest, are the Cape Fear aquifer, the Middendorf aquifer, the Black Creek aquifer, the combined Floridan aquifer system and sand aquifer of Tertiary age, and the surficial aquifer (figs. 2 and 3). The generalized outcrop areas of these aquifers are indicated in figure 4. Although aquifer outcrop areas may be relatively wide, the interbedded sand and clay layers may create confined conditions at shallow depths.

The geologic units primarily associated with each aquifer are shown in table 2. The Cape Fear, Middendorf, and Black Creek aquifers in Cretaceous sediments are the three aquifers discussed in this report. Aucott and others (1987) provide the geohydrologic framework upon which this report is based.

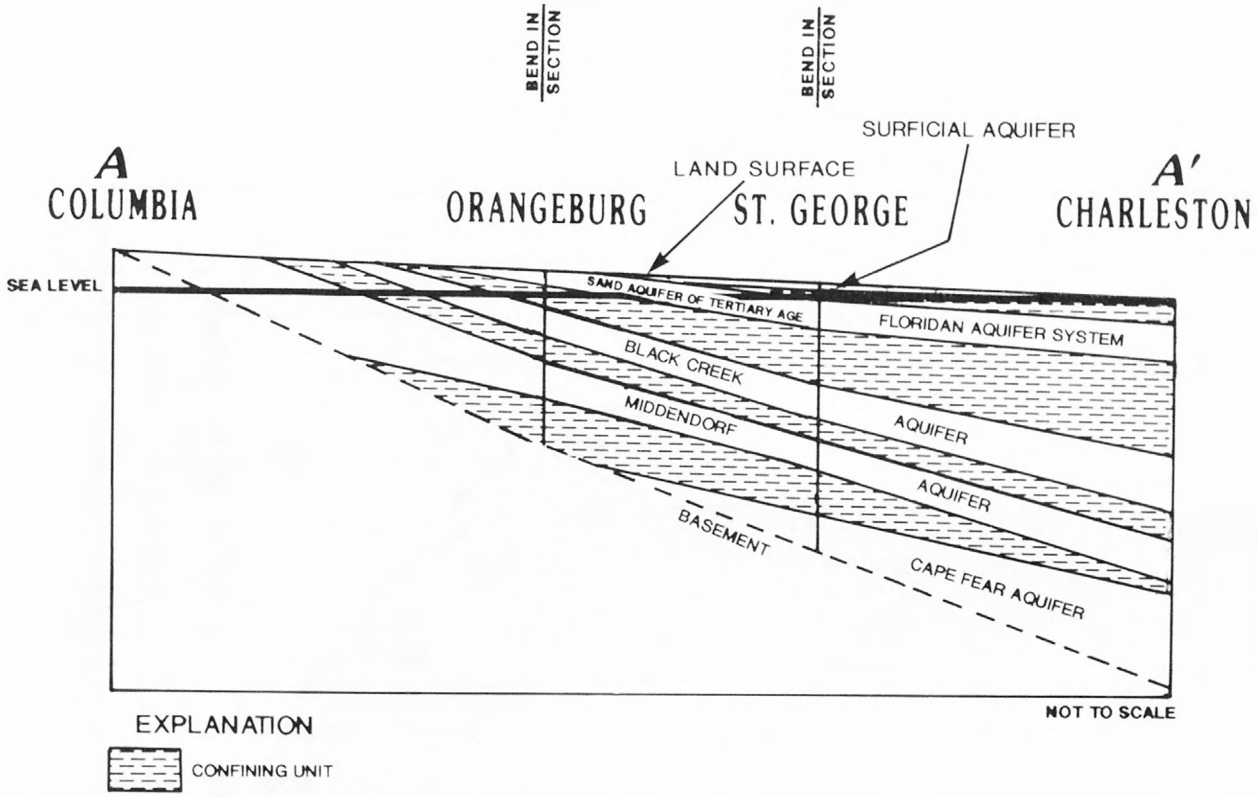


Figure 2.--Generalized geohydrologic section A-A' (modified from Aucott and Speiran, 1985a).

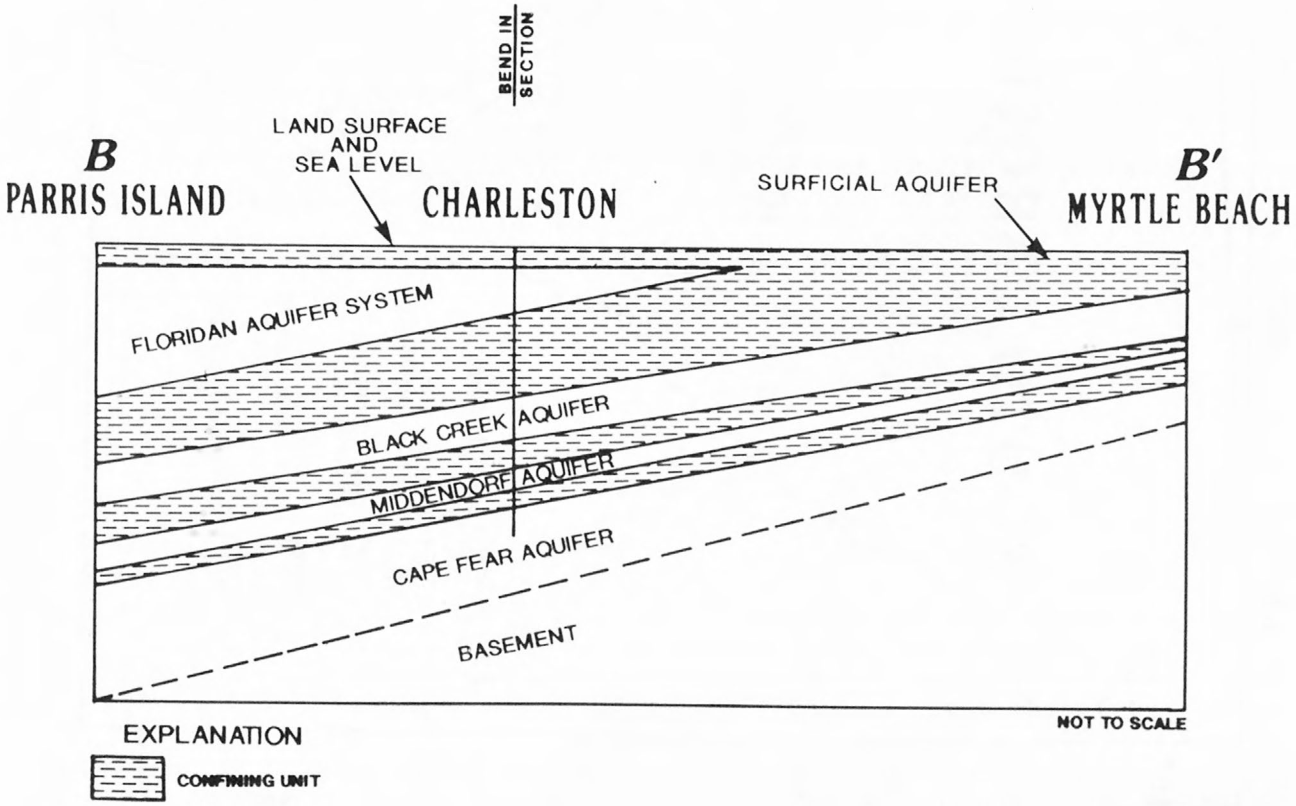
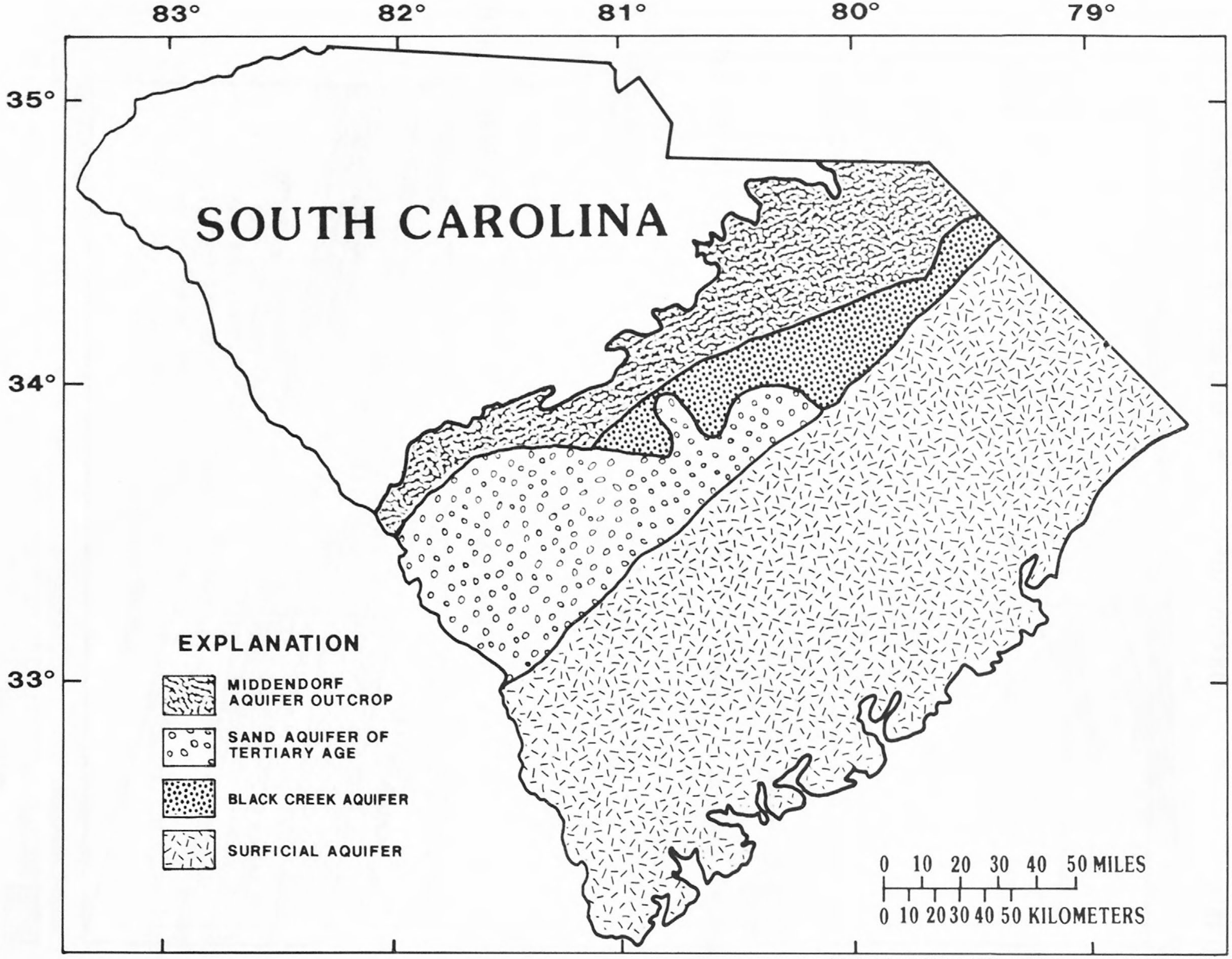


Figure 3.--Generalized geohydrologic section B-B' (modified from Aucott and Speiran, 1985a).



Adapted from Cooke, 1936, and Colquhoun and others, 1984.

Figure 4.--Generalized outcrop areas of Coastal Plain aquifers (modified from Aucott and Speiran, 1985c).

Table 2.--Geohydrologic correlations (modified from Aucott and others, 1987)

| Aquifer unit | Age of sediments | Principal geologic formations[a] |
|---|---|---|
| Surficial | Pleistocene | Coastal terrace deposits |
| Floridan aquifer system[b] (downdip) | Eocene | Ocala Limestone<br>Santee Limestone |
| Sand aquifer of Tertiary age (updip) | Eocene | Barnwell Formation<br>McBean Formation<br>Congaree Formation |
| | Paleocene | Black Mingo Formation (upper part) |
| Black Creek | Late Cretaceous | Black Creek Formation |
| Middendorf | Late Cretaceous | Middendorf Formation |
| Cape Fear | Late Cretaceous | Cape Fear Formation |

[a] These are geologic formations that are generally associated with a given aquifer. However, a given aquifer may not consist of the same formations in all areas, and locally an aquifer may consist of parts of additional formations not listed.

[b] Carbonate equivalent of the sand aquifer of Tertiary age.

The Coastal Plain of South Carolina can be divided into an upper and a lower part (fig. 1) on the basis of the geohydrology of the aquifers. The division as depicted is highly generalized. The upper Coastal Plain is the area near the Fall Line where the aquifers are recharged in interstream areas and ground water flows along short flow paths and discharges to nearby streams. Water not discharged to the streams flows from the upper to the lower Coastal Plain. The lower Coastal Plain is a region of areal discharge by diffuse upward leakage from aquifers in Cretaceous sediments to overlying aquifers. The permeability of the pre-Cretaceous rocks is significantly less than that of the Cretaceous sediments, and there is generally little interaction between water in the pre-Cretaceous rocks and overlying Coastal Plain aquifers.

## Cape Fear Aquifer

The Cape Fear aquifer, as defined in this report, generally consists of sediments of the Cape Fear Formation and underlying undifferentiated Cretaceous sediments (Aucott and others, 1987). It is the lowermost aquifer in the Coastal Plain of South Carolina. Less is known about the Cape Fear aquifer than other aquifers in Cretaceous sediments because of its depth, poor water quality, and low permeability.

In the literature, the Cape Fear aquifer has been referred to as the Tuscaloosa aquifer (Park, 1980) and aquifer A4 (Renken, 1984; Aucott and Speiran, 1985b; 1985c), and includes sediments formerly termed Middendorf aquifer by other authors (Zack, 1977; 1980; Colquhoun and others, 1983). The Cape Fear aquifer probably does not crop out in South Carolina (fig. 4) and its updip limit is not well defined (fig. 5). It is present throughout the lower Coastal Plain and the northeastern part of the upper Coastal Plain.

The Cape Fear aquifer consists of a series of thin, feldspathic sand and gravel layers separated by thick layers of silt and clay. The layers generally are present in fining-upward sequences, less than 15-ft thick, with gravel at the bottom grading into coarse-grained sand, fine-grained sand, silt, and clay (Gohn and others, 1978; G.S. Gohn, U.S. Geological Survey, oral commun., 1982). Fossils are sparse. These sequences are indicative of deposition in meandering fluvial environments. The coarse-grained sediments are predominantly red-, green-, and brown-mottled, noncalcareous quartz sands. The fine-grained sediments are typically red, reddish brown, or red and gray-green mottled clays. The clays are noncalcareous and micaceous with abundant kaolinite. Because these sediments primarily consist of silicate minerals of low solubility, geochemical reactions with water occur at slow rates. Sediments of the Cape Fear aquifer were deposited in nonmarine, fluvial to upper-delta-plain environments (Owens and Gohn, 1985, fig. 2-15B).

The areal extent and depositional environments of the aquifer and representative geophysical logs from it are shown in figure 5. Resistivity and spontaneous potential logs show small deflections from the center line that only extend for short depth intervals indicative of the thin sand and gravel layers. Close to the coast, deflection of the spontaneous potential (to the left) is greater than the deflection of the resistivity (to the right), indicative of the presence of saline water in the aquifer. Depositional environments may become marine seaward of the present coast.

Recharge to the Cape Fear aquifer occurs in two areas (Aucott and Speiran, 1985a; 1985c). In the interstream areas in the western part of the upper Coastal Plain of Georgia, the aquifer is recharged by precipitation on the outcrop and by leakage from overlying aquifers. In interstream areas in the northeastern part of the upper Coastal Plain of South Carolina, the aquifer is recharged by leakage from the overlying Middendorf aquifer. Water flows from the recharge area in Georgia across the lower Coastal Plain of South Carolina and into southeastern North Carolina, approximately parallel to the coast (fig. 6). In the upper Coastal Plain of South

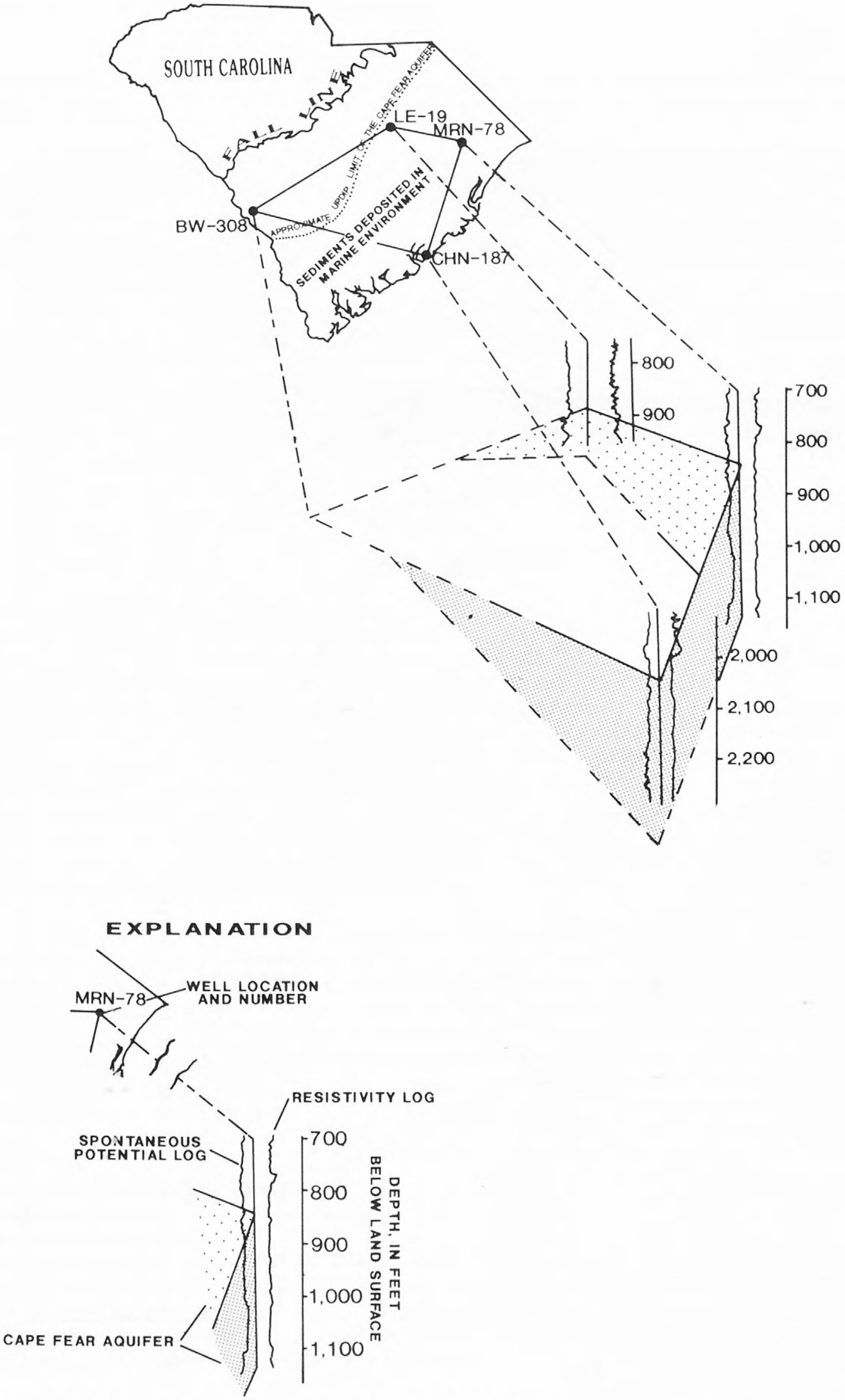


Figure 5.--Generalized depositional environments and representative geophysical logs of the Cape Fear aquifer.

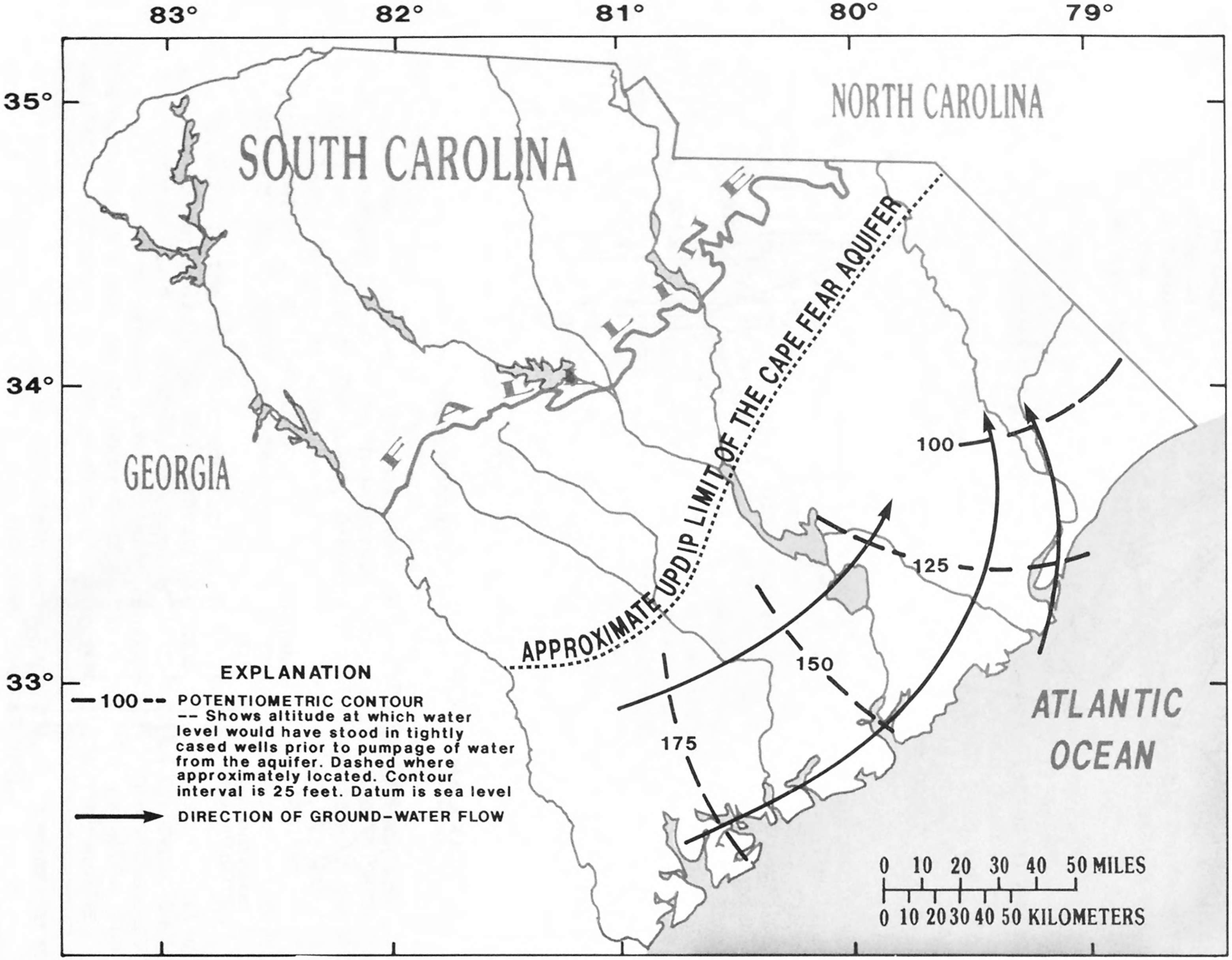


Figure 6.--Potentiometric surface and flow paths of water in the Cape Fear aquifer prior to development (modified from Aucott and Speiran, 1985c).

Carolina, sparse data indicate water flows from the interstream recharge areas toward streams in patterns similar to those of the Middendorf aquifer.

Discharge from the Cape Fear aquifer is by diffuse leakage to the overlying Middendorf aquifer near streams in the upper Coastal Plain of South Carolina and throughout the lower Coastal Plain of South Carolina and southeastern North Carolina. It probably is greatest in northeastern South Carolina and southeastern North Carolina (Aucott and Speiran, 1985a; 1985c).

The hydraulic characteristics of the Cape Fear aquifer are difficult to determine because of limited data. It is doubtful that the transmissivity of the aquifer is very high anywhere in South Carolina. On the basis of ground-water flow modeling, transmissivity of the Cape Fear aquifer ranges from about 1,100 to 3,600 $ft^2/d$ (feet squared per day) (Aucott, 1988, p. 38). The area of greatest transmissivity is in the southwestern part of the lower Coastal Plain.

## Middendorf Aquifer

The Middendorf aquifer, as defined in this report, generally consists of sediments of the Middendorf Formation and their stratigraphic equivalents but locally may include sediments of the overlying Black Creek Formation or the underlying Cape Fear Formation (Aucott and others, 1987). It is the middle of the three regional aquifers in Cretaceous sediments. This aquifer has been described as part the Tuscaloosa aquifer (Siple, 1967; Park, 1980) and has been called aquifer A3a3 (Renken, 1984; Aucott and Speiran, 1985b; 1985c). This aquifer generally corresponds with the lower sand of the overlying Black Creek aquifer of Zack (1977). It crops out along the Fall Line (fig. 4) and is present throughout the Coastal Plain of South Carolina. The Middendorf aquifer consists of sediments deposited in nonmarine, transitional, and marine environments (fig. 7).

In the upper Coastal Plain, sediments of the Middendorf aquifer are primarily light-gray, white, or buff, quartz sand and may interfinger with lenses of white, pink, or purple kaolinitic clay (Cooke, 1936; Siple, 1967; Colquhoun and others, 1983). The sediments generally were deposited in fluvial to upper-delta-plain environments (Colquhoun and others, 1983, p. 5; Owens and Gohn, 1985, fig. 2-15A) and consist of sparse to abundant amounts of feldspar, mica, staurolite, garnet, pyrite, monazite, and unidentified heavy minerals (Prowell and others, 1985, p. 8). Carbonate materials are absent from this part of the aquifer (D.S. Prowell, U.S. Geological Survey, oral commun., 1986). Sand layers in this part of the aquifer are thick and interbedded with thin clay layers. Sediments generally may be coarse-grained throughout most of the thickness of the aquifer but may have a coarsening-upward sequence farther downgradient. The thick layer of coarse-grained sediment is characteristic of deposition by a braided stream in fluvial environment. Coarsening upward is characteristic of deposition in a prograding delta-plain environment (Selley, 1978, p. 125). The minerals in this part of the Middendorf aquifer generally have low solubilities and react slowly with water.

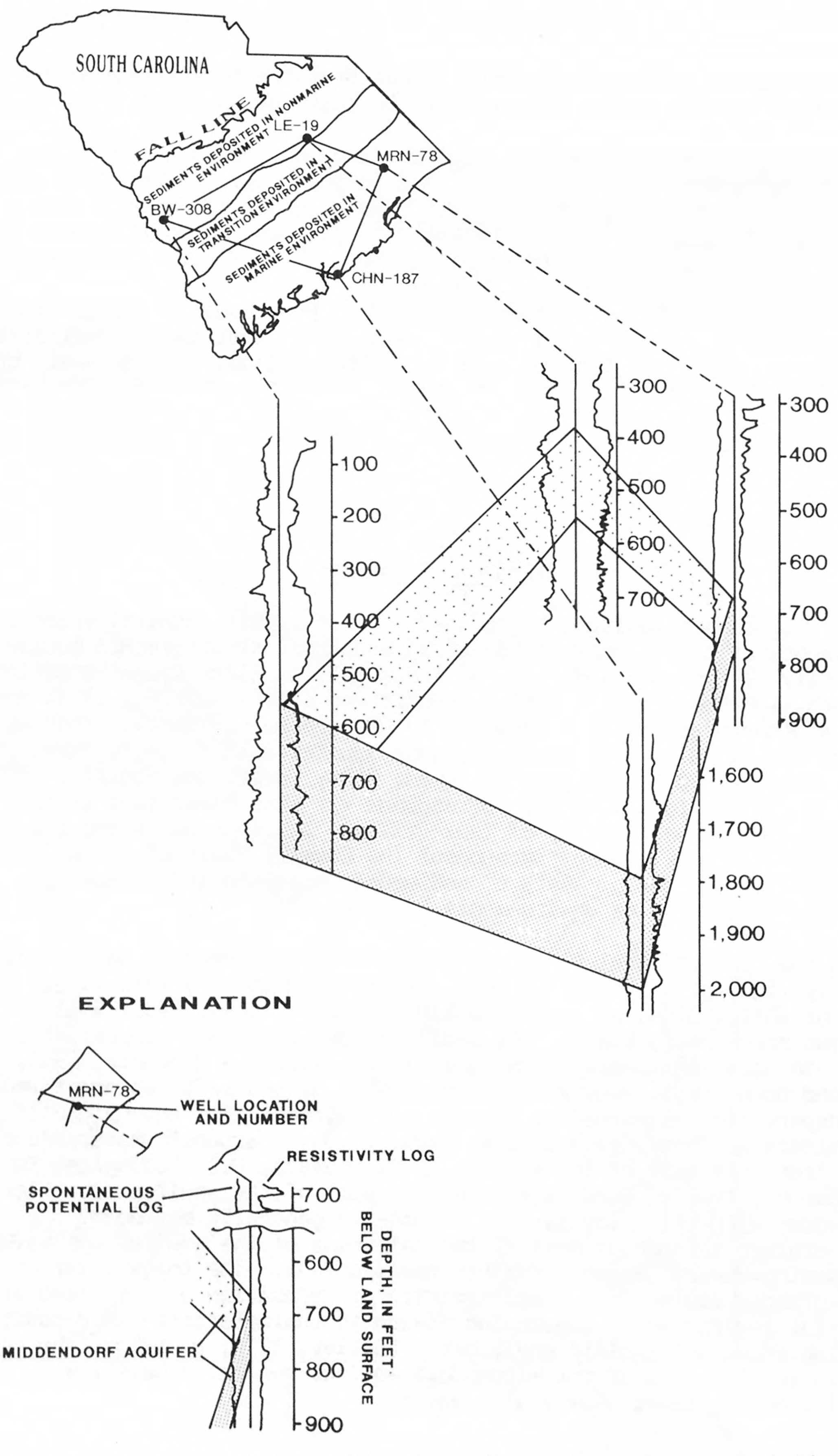


Figure 7.--Generalized despositional environments and representative geophysical logs of the Middendorf aquifer.

In the lower Coastal Plain the Middendorf aquifer consists of a sequence of fossiliferous, heterogeneous sediments which include gray, calcareous, silty clay and muddy, calcareous, fine- to coarse-grained sand (Gohn and others, 1978). The sand fraction is primarily quartz and feldspar with small amounts of plagioclase; the clay fraction consists of kaolinite, illite, and smectite; and the predominant heavy minerals are tourmaline, staurolite, and zircon (Gohn and others, 1977, p. 66). Lignite, glauconite, phosphate, and mica are common in the sediments. Sand layers are thinner, and clay layers are thicker in the lower Coastal Plain than in the upper Coastal Plain. Similarly, the aquifer is thinner in the lower than in the upper Coastal Plain (fig. 7). Shell material is locally abundant (G.S. Gohn, U.S. Geological Survey, oral commun., 1986). These sediments were deposited in environments grading from lower delta plain to marginal-marine and marine (Gohn and others, 1977, p. 69; Colquhoun and others, 1983, p. 11-27; Owens and Gohn, 1985, fig. 2-15A). Several of the minerals in the marine sediments are more soluble and react more rapidly with water than minerals in nonmarine sediments.

The Middendorf aquifer is recharged in interstream areas of the upper Coastal Plain by precipitation on its outcrop and by leakage from overlying aquifers (Aucott and Speiran, 1985a, p. 740). Water flows along short flow paths from the interstream recharge areas to streams in the upper Coastal Plain and along longer flow paths from the upper to the lower Coastal Plain (fig. 8). Flow in the lower Coastal Plain prior to pumpage was generally toward the east or northeast, nearly parallel to the coast. One of the major reasons for the direction of flow and head distribution in the Middendorf aquifer is that the permeability of the confining unit in Paleocene sediments overlying aquifers in Cretaceous sediments is less in the southwest than in the northeast. Because of this difference in permeability, the confining unit is more effective in inhibiting leakage between the aquifers in Cretaceous sediments and overlying aquifers in the southwestern than in the northeastern part of the lower Coastal Plain. Thus, prior to pumpage of water from the aquifers, upward discharge from the aquifers in Cretaceous sediments in the northeast decreased hydraulic head resulting in flow in that direction.

The Middendorf aquifer discharges to streams in the upper Coastal Plain, to the overlying Black Creek aquifer by diffuse leakage in the lower Coastal Plain, and to wells throughout the area. The greatest effects of pumpage on the potentiometric surface and flow patterns have occurred in the vicinity of the cities of Florence and Myrtle Beach (Aucott and Speiran, 1985b). Flow prior to pumpage has had a much greater effect on the distribution of water-quality constituents than present flow, because of the slow rate of water movement and the relatively recent development of these pumpage centers.

In the upper Coastal Plain the permeability of the sediments in the Middendorf aquifer is fairly uniform where sediments were deposited in nonmarine environments (Aucott and others, 1987). In the lower Coastal Plain the permeability of the sediments decreases toward the coast as the percentage of clayey material increases. This occurs where sediments were deposited in environments grading from lower delta plain to marine. The transmissivity of the Middendorf aquifer ranges from 300 to 30,000 $ft^2/d$ on

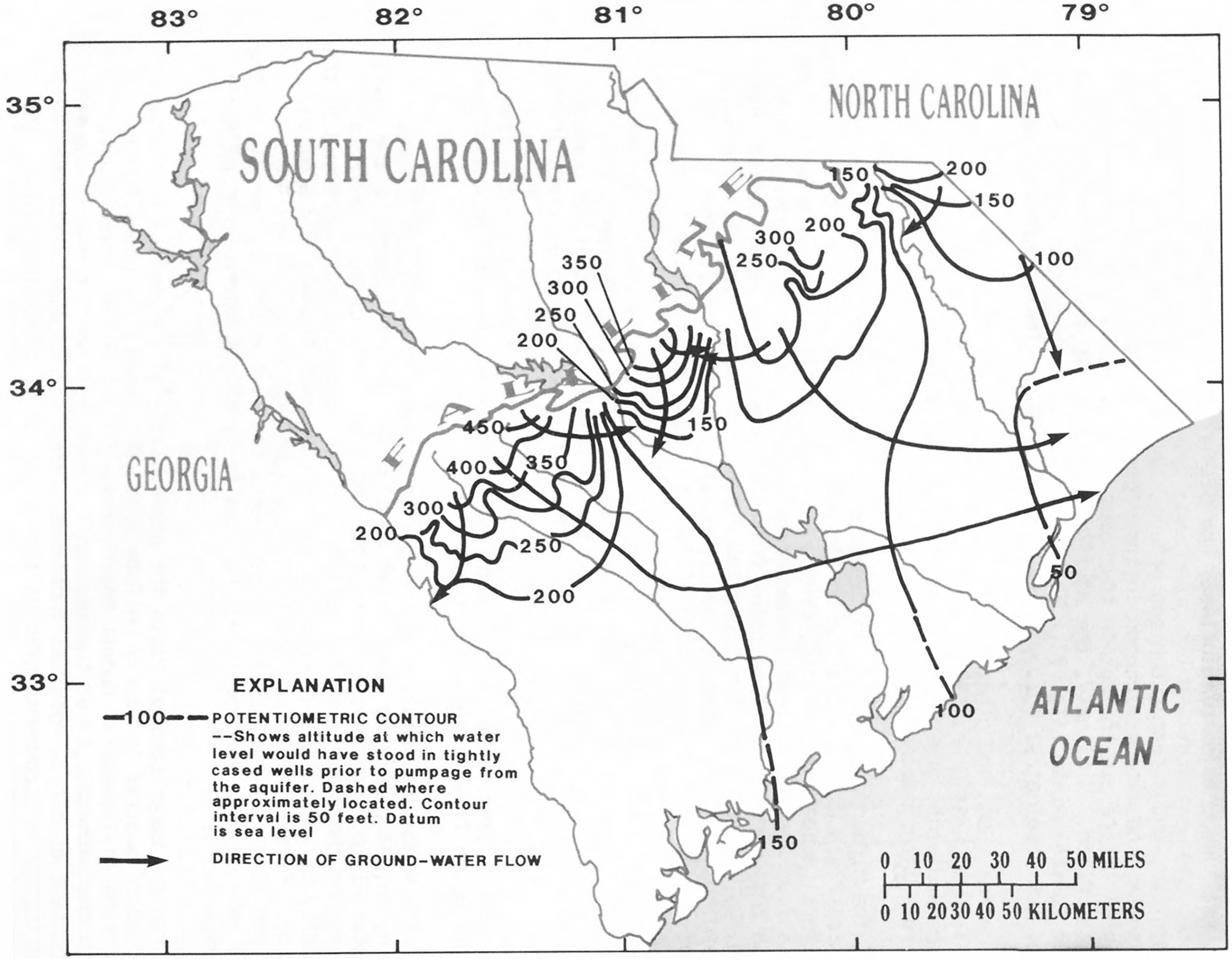


Figure 8.--Potentiometric surface and flow paths of water in the Middendorf aquifer prior to development (modified from Aucott and Speiran, 1985c).

the basis of ground-water flow modeling (Aucott, 1988, p. 38). In the upper Coastal Plain the transmissivity of the aquifer increases from the Fall Line toward the coast because of the thickening of the aquifer. It reaches a maximum in a band in the lower part of the upper Coastal Plain. The transmissivity of the aquifer decreases in the lower Coastal Plain because permeability of the sediments decreases. In the band of maximum transmissivity, the permeability and transmissivity are greater in the southwest than in the northeast because the sediments in the southwest are generally of similar thickness but consist of less clay and more coarse-grained sand. Although the transmissivity is less in the lower Coastal Plain part of the Middendorf aquifer, it is still greater than that of adjacent aquifers.

## Black Creek Aquifer

The Black Creek aquifer generally consists of sediments of the Black Creek Formation and its stratigraphic equivalents but locally may include sediments of the various overlying formations or the underlying Middendorf Formation (Aucott and others, 1987). It is the uppermost regional aquifer in Cretaceous sediments. This aquifer has also been called aquifer A3a2 (Renken, 1984; Aucott and Speiran, 1985b; 1985c) and the upper part of the former Tuscaloosa aquifer (Siple, 1967) in the western part of the upper Coastal Plain. It generally is equivalent to the upper, principal, and middle sands of the Black Creek aquifer of Zack (1977). This aquifer crops out in the northeastern part of the upper Coastal Plain downdip from the outcrop of the Middendorf aquifer (fig. 4). The updip limit of the Black Creek aquifer is closer to the Fall Line in the southwest where it subcrops than in the northeast where it crops out (fig. 9). Sediments of the Black Creek aquifer were deposited in nonmarine, delta-plain environments in the southwest that grade through transitional to marine environments along the coast (fig. 9).

The lithology of the Black Creek Formation has been described primarily in eastern and southern South Carolina by Cooke (1936), Siple (1946; 1959), Gohn and others (1977), Zack (1977), and Gohn and others (1978). Sediments comprising this part of the formation are primarily thin laminated layers of dark gray to black, calcareous, fossiliferous clay and gray, glauconitic, micaceous, fine- to medium-grained, quartz sand. Organic matter is generally abundant in the sediments, and parts of the sand layers are cemented with calcium carbonate. The predominant heavy minerals include chloritoid, staurolite, garnet, and tourmaline (Gohn and others, 1977, fig. 5). The clay content of the aquifer increases to the south. Shark teeth are abundant in the sediments (Zack, 1980). Sediments in these parts of the Black Creek Formation were deposited in environments grading from marginal-marine to marine (Gohn and others, 1977, p. 70; Colquhoun and others, 1983; Owens and Gohn, 1985, fig. 2-19). In the southwestern part of the upper Coastal Plain, sediments of the Black Creek aquifer were deposited in nonmarine and transitional, delta-plain environments (Colquhoun and others, 1983; Owens and Gohn, 1985, fig. 2-19) and contain less clay; little, if any, calcite; and more coarse-grained sand than sediments in this aquifer to the east and south.

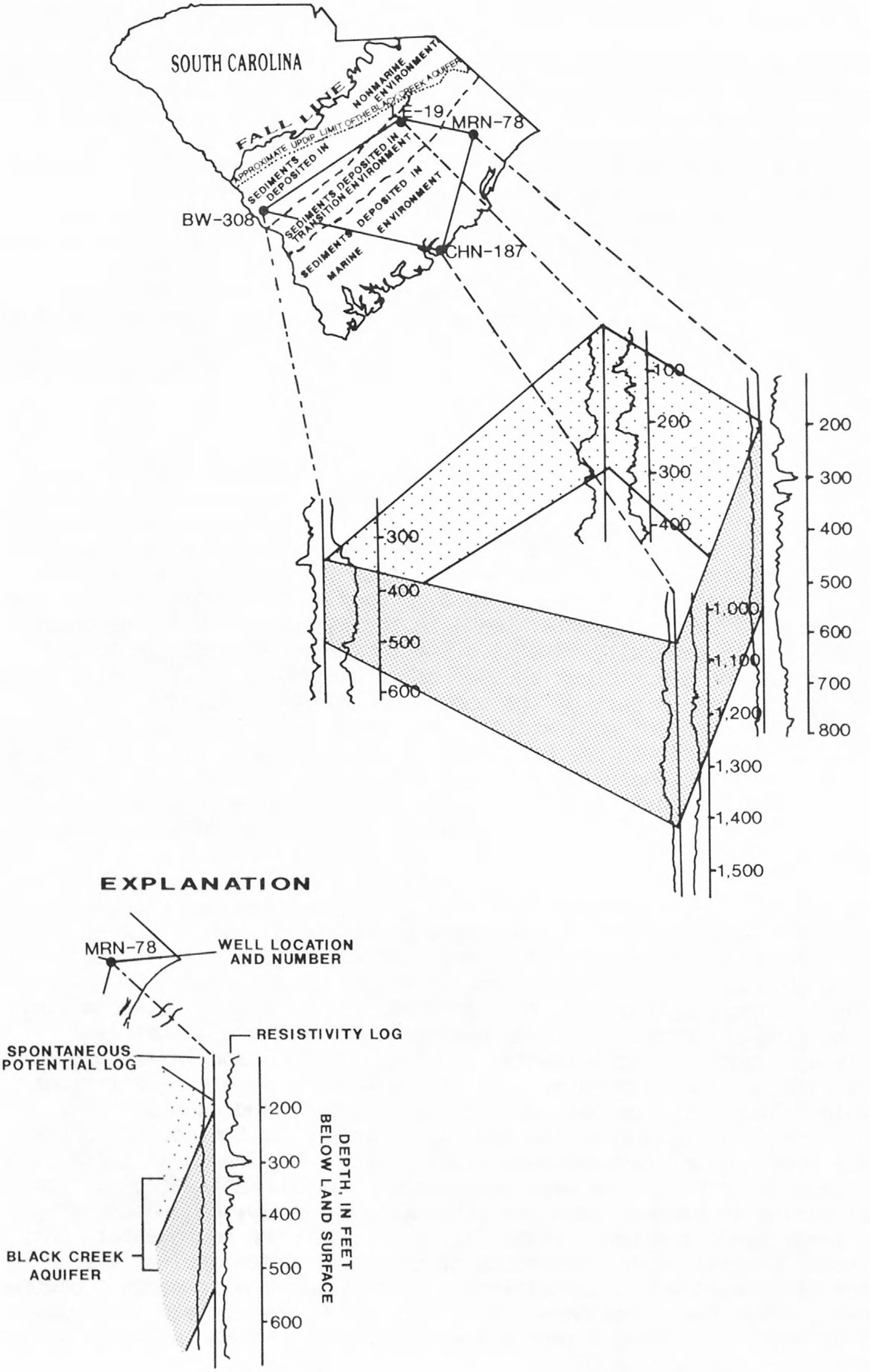


Figure 9.--Generalized depositional environments and representative geophysical logs of the Black Creek aquifer.

The Black Creek aquifer is recharged in interstream areas of the upper Coastal Plain by precipitation on its outcrop and by leakage from overlying aquifers (Aucott and Speiran, 1985a, p. 740). Water flows along short flow paths from the interstream recharge areas to streams in the upper Coastal Plain and along longer flow paths from the upper to the lower Coastal Plain (fig. 10). Flow in the lower Coastal Plain prior to pumpage was generally to the east or northeast in a pattern similar to that of the Middendorf aquifer. Discharge is to streams in the upper Coastal Plain, to overlying aquifers by diffuse upward leakage in the lower Coastal Plain, and to wells throughout the area. The major effects of pumpage on the potentiometric surface and on flow patterns are greatest in the vicinity of the city of Myrtle Beach (Aucott and Speiran, 1985b). Flow prior to pumpage has had a much greater effect on the distributions of water-quality constituents than present flow, because of the slow rate of water movement and the relatively recent development of pumpage centers.

The permeability of the Black Creek aquifer is relatively uniform in the northeastern part of the Coastal Plain. As a result, the transmissivity increases to a maximum as the aquifer thickness increases toward the coast, then tends to remain fairly constant as the aquifer thickness and permeability remain relatively uniform. The permeability of the aquifer in the southwestern part of upper Coastal Plain is greater than that of the northeastern part because it consists of more coarse-grained sand and less clay in the southwest. The permeability and transmissivity of the aquifer are much less toward the southern coast due to the presence of more fine-grained sediments than elsewhere in the aquifer.

## MAJOR GEOCHEMICAL PROCESSES

Numerous geochemical processes have major effects on the quality of water in aquifers in Cretaceous sediments in the Coastal Plain of South Carolina. Different processes dominate the quality of water in the parts of the aquifers deposited in different sedimentary environments.

The major geochemical processes and their interrelations are discussed in this section to provide an overview of geochemical processes occurring in the aquifers. The processes that occur in each aquifer, the effects of the processes on the quality of the water in each aquifer, and the relations of the processes to the depositional environment of the sediments in each aquifer will be subsequently discussed.

Among the significant geochemical processes are those that affect the concentrations of inorganic carbon in the ground water. Inorganic carbon exists in ground water as carbon dioxide ($CO_2$), carbonic acid ($H_2CO_3$), bicarbonate ion ($HCO_3^-$), and carbonate ion ($CO_3^{-2}$). The most likely sources of inorganic carbon in water from aquifers in Cretaceous sediments are (1) atmospheric carbon dioxide, (2) carbon dioxide from the aerobic and anaerobic decomposition of organic matter in the unsaturated and saturated sediments (including formation of soil gas), and (3) bicarbonate and carbonate from the dissociation of carbonic acid and from the dissolution of calcium carbonate in the aquifer sediments. The calcium carbonate may consist of shell material or calcite cement.

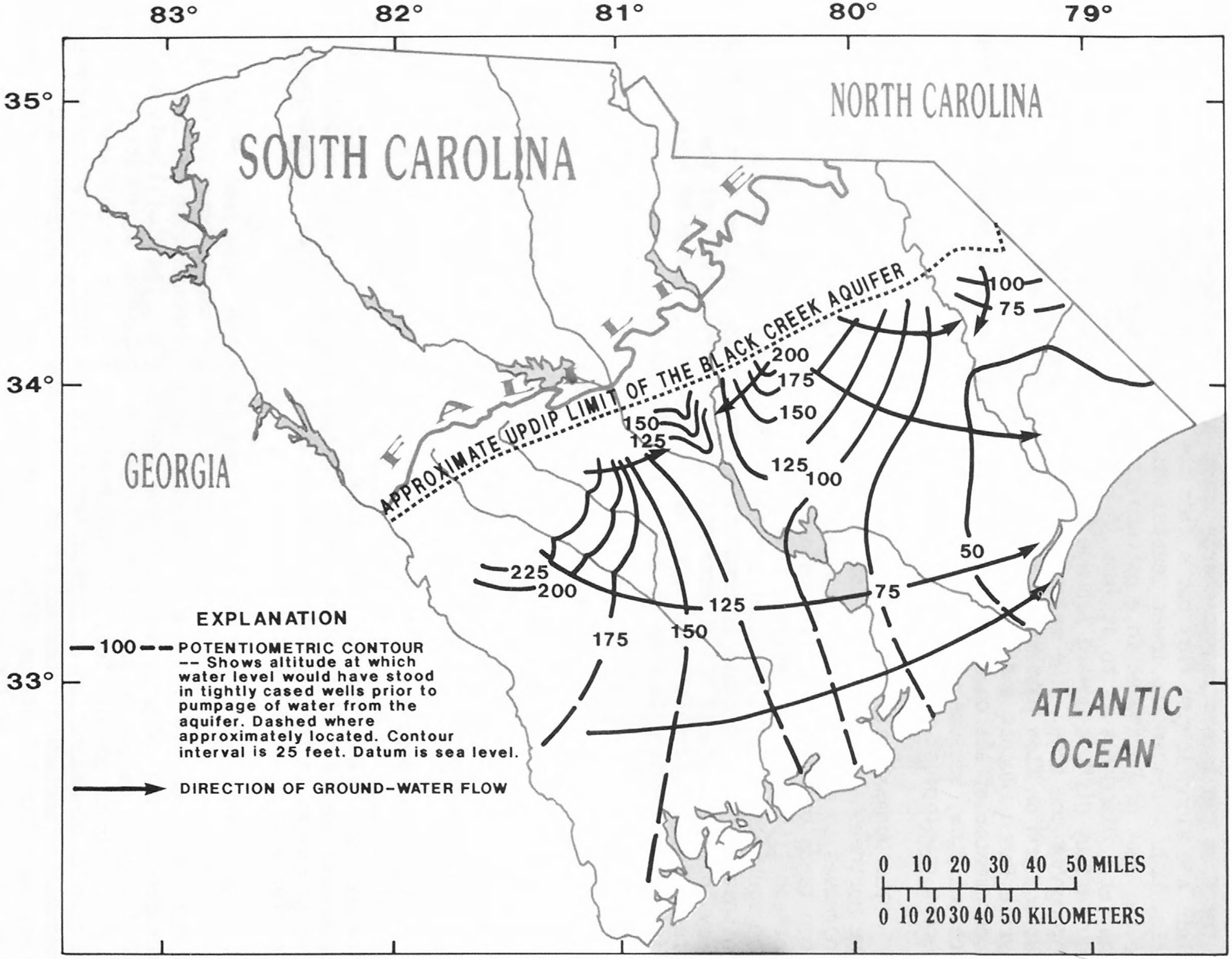


Figure 10.--Potentiometric surface and flow paths of water in the Black Creek aquifer prior to development (modified from Aucott and Speiran, 1985c).

The atmosphere is a potential source of carbon dioxide only where the aquifers are unconfined. These areas are limited because the interlayering of sand and clay causes aquifers to become confined, even in outcrop. The decomposition of organic carbon is a potential source of carbon dioxide wherever organic matter is present in the sediments. Such decomposition may be caused by abiotic (Foster, 1950, p.40) or biotic (Cedarstrom, 1946, p.234) processes. Carbon dioxide from these sources hydrolyzes to form carbonic acid by

$$CO_2 + H_2O \rightarrow H_2CO_3 \ , \qquad (1)$$

which first ionizes ($K_1 = 10^{-6.4}$ (Krauskopf, 1979, p. 554)) by

$$H_2CO_3 \rightarrow H^+ + HCO_3^- \ , \qquad (2)$$

and undergoes a second ionization ($K_2 = 10^{-10.3}$ (Krauskopf, 1979, p. 554)) by

$$HCO_3^- \rightarrow H^+ + CO_3^{-2}. \qquad (3)$$

Carbon dioxide may be the dominant form of inorganic carbon in water in some upgradient, nonmarine parts of the aquifers. Bicarbonate is the dominant form of inorganic carbon in the water in transitional and marine parts of aquifers in Cretaceous sediments as a result of calcium-carbonate dissolution. Carbonate also is present in significant concentrations where the pH of the water is greater than 8.3. Alkalinity is used in this report to reflect the combined effects of bicarbonate and carbonate in the water because of the widespread areal extent of waters in which pH is greater than 8.3 in aquifers in Cretaceous sediments.

Carbonic acid is important to the geochemistry of aquifers in Cretaceous sediments because of its potential role in geochemical processes including the dissolution of silicate and carbonate minerals. These processes consume hydrogen ions, shifting the carbonic acid equilibria toward the more ionized forms (eqs. 2 and 3), resulting in greater concentrations of bicarbonate and carbonate ions and a greater pH.

Various silicate minerals are present in Cretaceous sediments and may affect the quality of the water. One of the silicate reactions that may occur in upgradient areas is the dissolution of quartz by

$$\underset{\text{<quartz>}}{SiO_2} + 2H_2O \rightleftarrows H_4SiO_4. \qquad (4)$$

This reaction continues until silica ($SiO_2$) concentrations reach the quartz solubility of 6 mg/L (milligrams per liter) (Krauskopf, 1979, p. 132).

Among other silicate minerals that react with carbonic acid are sodium-calcium and potassium feldspar (K-feldspar). The reaction of K-feldspar with carbonic acid forms kaolinite (Garrels and Christ, 1965, p. 360) by

$$\underset{\text{K-feldspar}}{2KAlSi_3O_8} + 2H_2CO_3 + 9H_2O \rightarrow \underset{\text{kaolinite}}{H_4Al_2Si_2O_9} + 2K^+ + 2HCO_3^- + 4H_4SiO_4. \quad (5)$$

Both feldspar and kaolinite are abundant in the Cretaceous sediments of South Carolina (Gohn and others, 1977, fig. 4; Colquhoun and others, 1983). In this and other silicate reactions, carbonic acid is the only source of inorganic carbon. However, other acids such as organic acids may provide the needed hydrogen ion.

Calcium carbonate ($CaCO_3$) is abundant in Cretaceous sediments of many parts of the aquifers as shell material or calcite cement. Carbonates dissolve by reacting with carbonic acid and by hydrolysis (Krauskopf, 1979, p. 45). In the presence of sufficient carbonic acid, calcium carbonate dissolves by

$$CaCO_3 + H_2CO_3 \rightarrow Ca^{+2} + 2HCO_3^-. \quad (6)$$

Where insufficient carbonic acid is present, calcium carbonate dissolves by hydrolysis by the reaction:

$$CaCO_3 + H_2O \rightarrow Ca^{+2} + HCO_3^- + OH^-. \quad (7)$$

The carbonic-acid and hydrolysis reactions affect the concentrations of inorganic carbon and bicarbonate differently. In the carbonic acid reaction, two moles of bicarbonate form for every mole of calcium carbonate dissolved, and carbonic acid and calcium carbonate contribute equally to the concentrations of inorganic carbon. In the hydrolysis reaction, one mole of bicarbonate forms for every mole of calcium carbonate dissolved, and calcium carbonate alone contributes to the concentrations of inorganic carbon.

If the hydrolysis of calcium carbonate occurs because of limits on carbonic acid concentrations in microenvironments, the hydroxyl ion ($OH^-$) may be transported and neutralized by carbonic acid in other parts of the aquifer by

$$H_2CO_3 + Ca^{+2} + HCO_3^- + OH^- \rightarrow Ca^{+2} + 2HCO_3^- + H_2O. \quad (8)$$

The resulting net reaction is the same for the hydrolysis of calcium carbonate followed by the neutralization of the hydroxyl ion with carbonic acid (eqs. 7 and 8) as for the direct dissolution of calcium carbonate by carbonic acid (eq. 6).

Carbon-isotope data can aid in the determination of which sources of carbon contribute to the concentrations of inorganic carbon in ground water. These data compare the relative difference (in parts per mil ($^0/_{00}$)) between the ratio of carbon 13 ($^{13}C$) to carbon 12 ($^{12}C$) of a sample to that of a standard. This comparison is called $\delta^{13}C$. To determine possible sources of carbon, the $\delta^{13}C$ of a water sample is compared to that of possible sources. The $\delta^{13}C$ of inorganic carbon in the water depends on the $\delta^{13}C$ of the sources of the inorganic carbon and the ratios in which these sources contribute to the inorganic carbon. The $\delta^{13}C$ of inorganic carbon having only one source is equal to that of the source. The $\delta^{13}C$ of inorganic carbon from more than one source is equal to a weighted average of the $\delta^{13}C$ of each source ($\delta^{13}C_i$) based on the molar concentration of the sources ($m^{C_i}$):

$$\delta^{13}C = \sum_{o}^{i} \frac{(m^{C}i)\,(\delta^{13}C_i)}{\sum_{o}^{i} (mC_i)} \; .$$

Fractionation (the nonproportional addition or removal of $^{13}C$ and $^{12}C$) may also affect $\delta^{13}C$ (Drever, 1982, p. 336). Precipitation of calcite from solution may cause fractionation. Fractionation may also occur when methanogenic bacteria produce methane having light carbon and carbon dioxide having heavy carbon (Chapelle and Knobel, 1985) or by other decomposition processes in which $^{13}C$ and $^{12}C$ do not decompose in the same proportion. Also, preferential decomposition of organic compounds having a heavier carbon content than that of the average carbon may occur (F.H. Chapelle, U.S. Geological Survey, oral commun., 1987).

Reported values of $\delta^{13}C$ from different sources of inorganic carbon differ but fall within ranges. Pearson and Friedman (1970) report average $\delta^{13}C$ values for calcite of $0^0/_{00}$ Pee Dee Belemnite (PDB) standard, for atmospheric carbon dioxide of $-7^0/_{00}$ PDB, and for carbon dioxide from the decomposition of organic matter (whether it is soil gas in unsaturated sediments or products of the decomposition of lignite in saturated sediments) of $-25^0/_{00}$ PDB. In the following discussions, all $\delta^{13}C$ will be in comparison to the PDB standard.

The $\delta^{13}C$ of samples of calcite and lignite (organic carbon) from sediment cores from wells MRN-78 and DOR-211 in the Coastal Plain of South Carolina have a range of values (R.W. Lee, U.S. Geological Survey, written commun., 1985). The $\delta^{13}C$ of four samples of calcite were -5.9, -3.8, -1.2 and +1.2$^0/_{00}$ with an average of -2.4$^0/_{00}$. The $\delta^{13}C$ of four samples of organic carbon (lignite) were -25.2, -22.7, -20.8, and -13.7$^0/_{00}$. The sediment core containing the organic carbon with the -13.7$^0/_{00}$ value also contained calcite; accordingly, the organic carbon probably contained calcite and the $\delta^{13}C$ for that sample does not represent that of organic carbon. The average $\delta^{13}C$ for organic carbon excluding the anomalous sample is $-22.9\,^{0}/_{oo}$. The $\delta^{13}C$ values reported by Pearson and Friedman (1970) will be used in the following discussions because of the general uniformity of values for atmospheric carbon dioxide around the globe and the good agreement of their values with the values for calcite and organic carbon from the cores from wells MRN-78 and DOR-211.

Several exchange reactions between ions in solution and the marine-clay minerals also may be important geochemical processes. Calcium from the dissolution of calcium carbonate exchanges for sodium on the exchange sites of the sodium-rich clay minerals by

$$Ca^{+2} + Na_2(clay) \rightarrow 2Na^{+} + Ca(clay)\ . \tag{9}$$

The degree to which the exchange process proceeds depends primarily on the concentrations of the exchangeable ions in solution and on the clay and on the selectivity coefficients of the clays. The net reaction for calcium carbonate dissolution by carbonic acid followed by exchange of calcium for sodium is

$$CaCO_3 + H_2CO_3 + Na_2(clay) \rightarrow 2Na^{+} + 2HCO_3^{-} + Ca(clay)\ . \tag{10}$$

The net reaction for the hydrolysis of calcium carbonate followed by the exchange of calcium for sodium is

$$CaCO_3 + H_2O + Na_2(clay) \rightarrow 2Na^{+} + HCO_3^{-} + OH^{-} + Ca(clay)\ . \tag{11}$$

The molar ratio of sodium to bicarbonate for the carbonic acid reaction is 1:1 and for the hydrolysis reaction (equation 11) is 2:1.

If hydrolysis of calcium carbonate occurs, the hydroxyl ion may be involved in subsequent reactions thereby reducing the increase in the pH of the water from that expected. Such reactions may be between the hydroxyl ion and the marine-clay minerals. Clays have been identified as important buffers in seawater (Krauskopf, 1979, p. 534). One of the possible reactions with clays involves the inner layer metals, particularly ferric iron, in the smectite clay group (B.F. Jones, U.S. Geological Survey, oral commun., 1985). Hydroxyl ion may react with the ferric ion from the inner layer by the reaction:

$$Fe^{+3} + 3OH^{-} \rightarrow Fe(OH)_3 \tag{12}$$

forming slightly soluble ferric hydroxide. The charge balance of the clay and of the solution would be maintained by the replacement of the ferric ion on the clay with calcium from the hydrolysis of the carbonate by

$$3Ca^{+2} + 2Fe(clay) \rightarrow 2Fe^{+3} + Ca_3(clay)_2\ . \tag{13}$$

The combined reaction between the clay, dissolved calcium, and hydroxyl ion is

$$3Ca^{+2} + 6OH^{-} + 2Fe(clay) \rightarrow 2Fe(OH)_3 + Ca_3(clay)_2\ . \tag{14}$$

The equation incorporating this reaction with the hydrolysis reaction (eg. 7) is

$$6CaCO_3 + 6H_2O + 2Fe(clay) \rightarrow 2Fe(OH)_3 + 3Ca^{+2} + 6HCO_3^- + Ca_3(clay)_2 \quad . \qquad (15)$$

Half of the calcium formed by the hydrolysis of calcium carbonate would exchange for ferric ion and the other half would remain available for exchange of calcium for sodium (eq. 9). Combining equations 9 and 15, the net reaction for hydrolysis of calcium carbonate and the clay reactions is

$$6CaCO_3 + 6H_2O + 2Fe(clay) + 3Na_2(clay)$$

$$\rightarrow 2Fe(OH)_3 + 6Na^+ + 6HCO_3^- + Ca_3(clay)_2 + 3Ca(clay) \quad . \qquad (16)$$

This reaction results in a 1:1 molar ratio of sodium to bicarbonate and is the same as the ratio calculated for analyses of water from the aquifers. Thus, the clay minerals may act as an exchange medium of calcium for sodium and as a buffer, both of which would allow the dissolution of more calcium carbonate than would otherwise dissolve. Although support for these reactions is not provided by experimental data, the reactions are presented along with available supporting evidence.

Downgradient increases in concentrations of chloride in water from the aquifers in Cretaceous sediments indicate the presence of dilute saltwater, probably resulting from intrusion or incomplete flushing of seawater. Seawater could intrude into an aquifer then subsequently, partly or completely, flush from the aquifer during the alternating transgression and regression of the sea. The source of the saltwater is seaward of the present coast.

The low permeability of the aquifers in Crectaceous sediments in South Carolina probably causes a broad transition zone of dilute saltwater similar to that identified in the northern Atlantic Coastal Plain by Meisler and others (1984). The actual freshwater-saltwater interface in aquifers in Cretaceous sediments of South Carolina is seaward of the coast and only dilute saltwater of the transition zone is present onshore. Although Meisler and others (1984, p. 1) only consider chloride concentrations as low as 1,000 mg/L, concentrations possibly as low as 5 mg/L may indicate the presence of dilute saltwater in South Carolina.

Dilute saltwater in an aquifer may affect the quality and geochemistry of the water in several ways. One way is by contributing to concentrations of the various constituents originally present in the seawater. This in addition to the freshwater contribution of constituents, may inhibit certain geochemical reactions, may promote additional reactions, and may have no effect on other reactions. In addition to contributing constituents in the seawater, other reactions between the saltwater and sediments may be a major contributor to constituent concentrations. Many of these reactions may be the same in the saltwater as in the freshwater such as the dissolution of calcium carbonate, decomposition of organic matter, and the exchange reactions. Concentrations of constitutents resulting from many of these reactions may be much greater in the saltwater than in the freshwater, because the saltwater probably has been in the aquifer much longer than the freshwater as it may have repeatedly intruded into the aquifer during transgressions of the sea then partially but not totally flushed from the aquifer in a seaward direction during subsequent regressions.

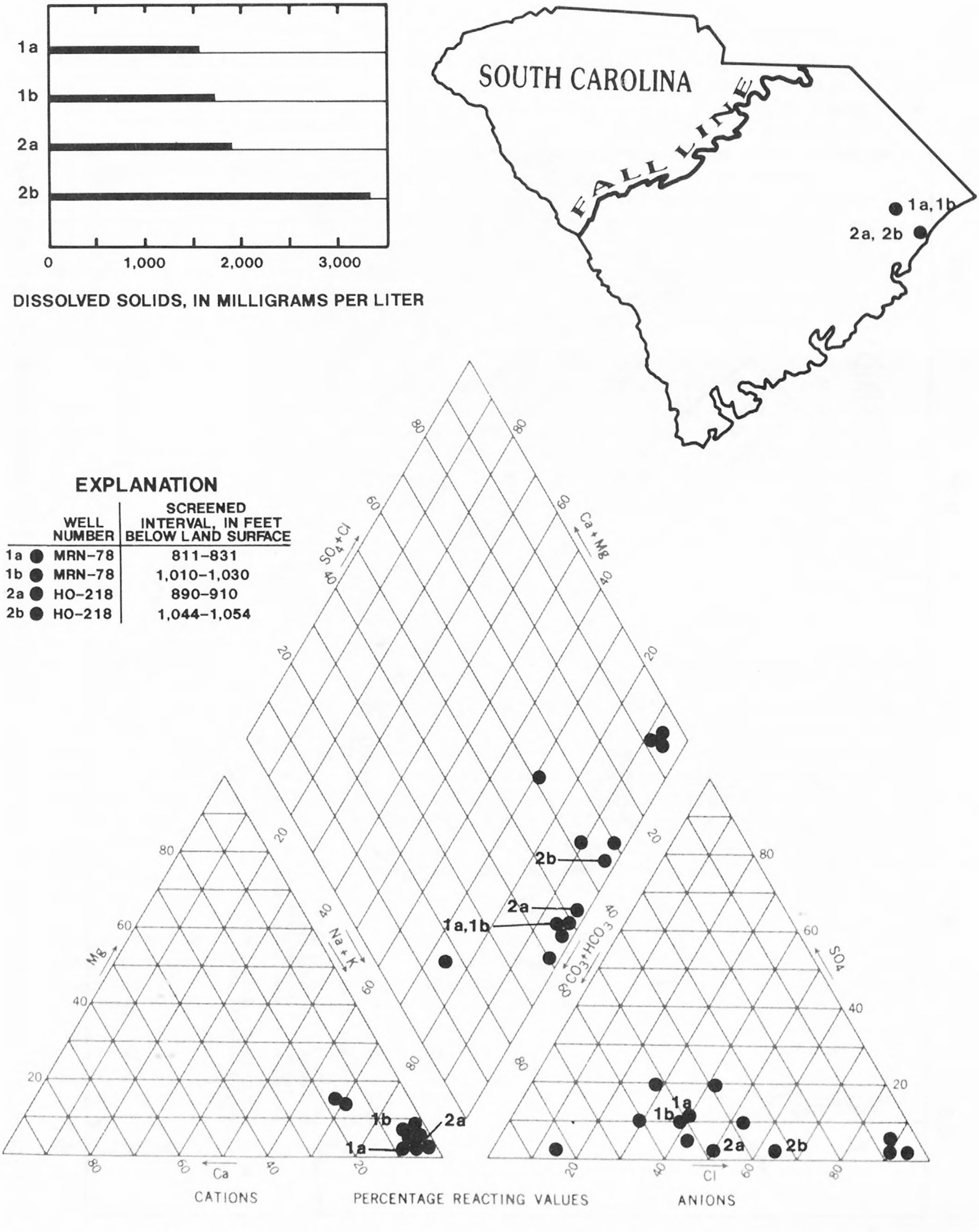
## EFFECTS OF DEPOSITIONAL ENVIRONMENT AND GROUND-WATER FLOW ON THE QUALITY AND GEOCHEMISTRY OF WATER

Depositional environments of sediments comprising an aquifer influence the geochemical characteristics of the water in the aquifer by affecting the degree of diagenesis, the mineral content, and the grain size of the sediments. The degree of diagenesis and the mineral content of the sediments determine the ions available and the rate at which dissolution, exchange, or other geochemical processes occur. The grain size of the sediments affects the amount of surface area available for geochemical reactions and the permeability of the sediments. The surface area is important because many geochemical processes occur at grain surfaces. The permeability of the sediments, in combination with the hydraulic gradient affects the duration of the water-mineral contact, the direction of flow, and the length of time required for freshwater to flush saltwater from the sediments. In summary, the amount of surface area available for water-mineral contact, combined with permeability and hydraulic gradient, largely control the degree to which various geochemical processes occur.

### Cape Fear Aquifer

Water quality differs vertically within the Cape Fear aquifer more than within other aquifers in Cretaceous sediments in the Coastal Plain of South Carolina due to the proximity of the freshwater-saltwater interface, to the incomplete flushing of dilute saltwater, and to the horizontal and vertical discontinuity of the permeable sediments. The discontinuity results from the meandering fluvial environment in which the sediments were deposited. This environment results in a less effective hydraulic connection between different gravel and sand beds within the Cape Fear aquifer than between the sand beds within other aquifers. Vertical differences in water quality are greatest near the freshwater-saltwater interface in the lower Coastal Plain where concentrations of dissolved solids are the greatest and increase with depth. The magnitude of these differences is indicated by data from wells MRN-78 and HO-218 (fig. 11). Vertical differences in water quality are greater in well HO-218, which is closer to the coast. Areal differences in concentrations of selected constituents are discussed only for water in the shallow part of the Cape Fear aquifer because of the limited data from deep in the aquifer and to allow comparisons of quality from similar parts of the aquifer.

Concentrations of several dissolved constituents in the Cape Fear aquifer increase from the upper Coastal Plain toward the coast and toward the northeast as indicated by the distribution in concentrations of dissolved solids (fig. 12). Concentrations of dissolved solids range from less than 250 to more than 6,000 mg/L. Concentrations of dissolved sodium and of dissolved chloride have similar distributions. Concentrations of



| | WELL NUMBER | SCREENED INTERVAL, IN FEET BELOW LAND SURFACE |
|---|---|---|
| 1a ● | MRN-78 | 811-831 |
| 1b ● | MRN-78 | 1,010-1,030 |
| 2a ● | HO-218 | 890-910 |
| 2b ● | HO-218 | 1,044-1,054 |

Figure 11--Concentrations of dissolved solids and relative concentrations of major ions in water from upper sands of the Cape Fear aquifer prior to 1983.

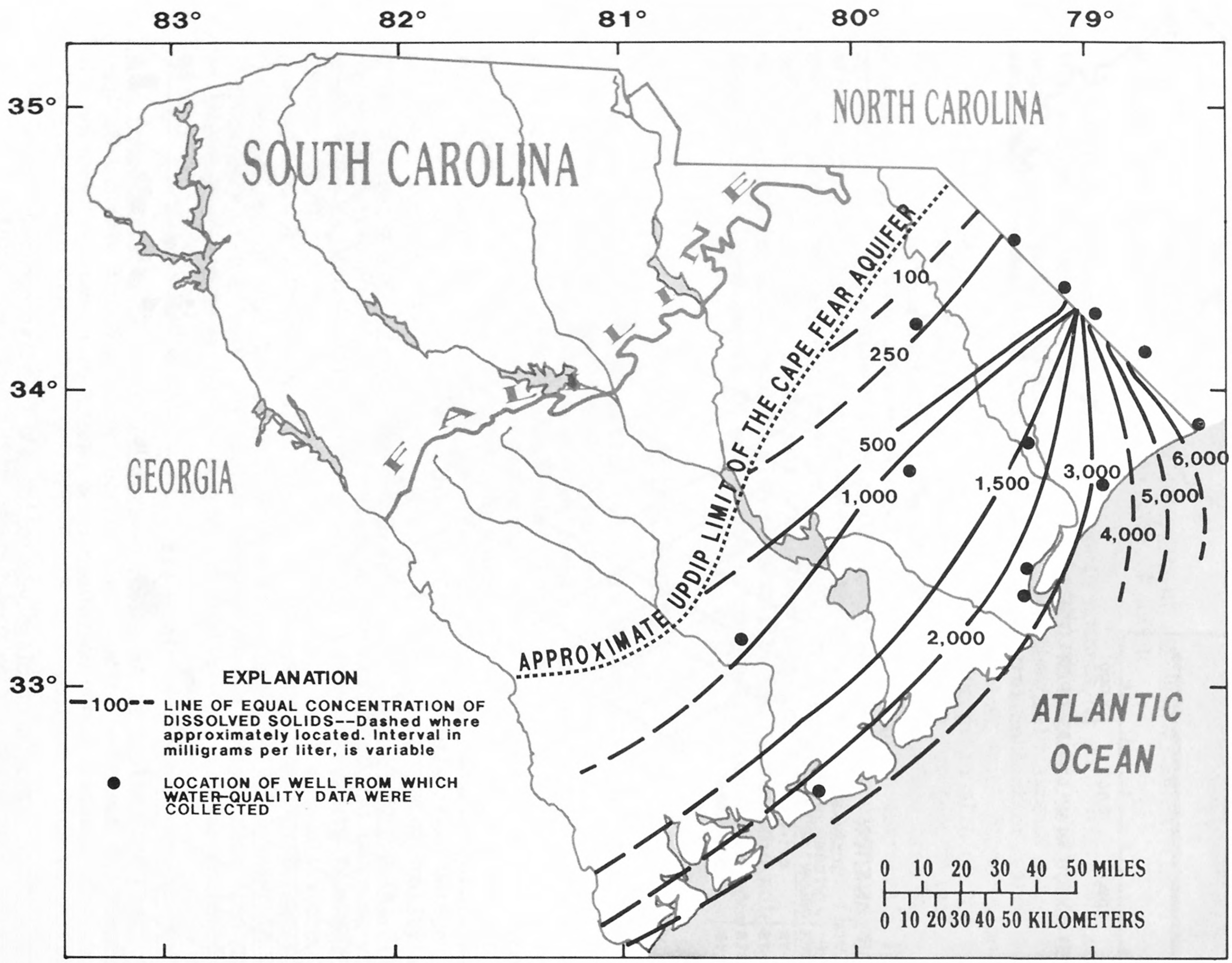


Figure 12.--Concentrations of dissolved solids in water from upper sands of the Cape Fear aquifer prior to 1983.

dissolved sodium increase from less than 50 to more than 2,000 mg/L (fig. 13) and concentrations of dissolved chloride range from 33 to more than 3,000 mg/L (fig. 14). Concentrations of alkalinity increase toward the coast, but not toward the northeast, ranging from about 60 to more than 1,000 mg/L as $CaCO_3$ (fig. 15). Concentrations of dissolved calcium and dissolved silica are distributed in patterns similar to each other (figs. 16 and 17) but different from those of dissolved sodium, dissolved chloride, and alkalinity. In the northeast, concentrations of dissolved calcium and silica increase from near the updip limit of the aquifer to an area near the boundary between the upper and lower Coastal Plains, then decrease toward the coast. Dissolved calcium concentrations range from less than 5 to more than 60 mg/L and dissolved silica concentrations range from less than 15 to about 35 mg/L.

The quality of water in the Cape Fear aquifer results more from the combined effects of ground-water flow patterns on the flushing of saltwater than does the quality of other aquifers in Cretaceous sediments. The effects of incompletely flushed dilute saltwater probably dominate the water quality of most, if not all, of the Cape Fear aquifer. This saltwater intruded into the aquifer during a series of transgressions of the sea that have occurred since the nonmarine sediments were deposited. Insufficient time has passed since intrusion to allow freshwater to completely flush the saltwater from the aquifer because of the low permeability of the sediments. The incomplete flushing causes relatively high concentrations of dissolved solids, dissolved sodium, and dissolved chloride (figs. 12-14).

The time required for the flushing of saltwater is long because of the direction and the length of ground-water flow paths. Water in the Cape Fear aquifer largely originates in Georgia and flows nearly parallel to the coast (fig. 6). A comparison of concentrations of dissolved solids, sodium, and chloride (figs. 12-14) with flow paths (fig. 6) shows that lines of equal concentration are almost parallel to flow paths. This includes northeastern South Carolina where high concentrations of these constituents extend farther inland than they do along the southern coast. The relation between alkalinity (fig. 15), and flow (fig. 6) is not as good as the relations with dissolved sodium and dissolved chloride, but patterns are still fairly similar.

An evaluation of geochemical processes and sources of most constituents not derived from the dilution of incompletely flushed saltwater would be highly speculative because of the similar orientation of the concentration contours and flow paths. This orientation results in almost no change in concentrations along many flow paths. However, slight differences in the orientation of actual concentration contours or flow paths from those depicted would produce either increasing or decreasing concentrations of constituents along flow paths. Such differences possibly exist but cannot be verified because the limited data do not allow a more detailed description of the system.

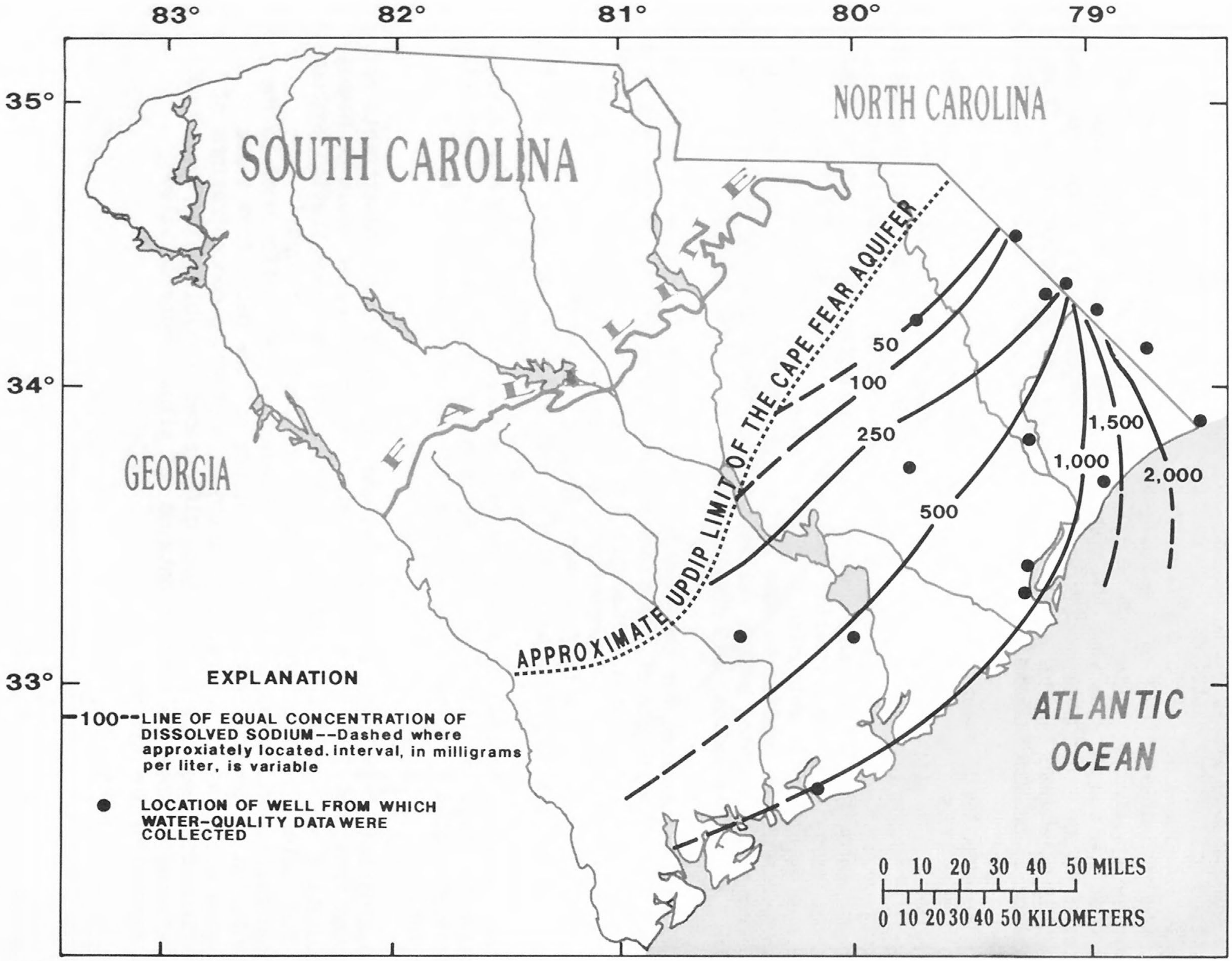


Figure 13.--Concentrations of dissolved sodium in water from upper sands of the Cape Fear aquifer prior to 1983.

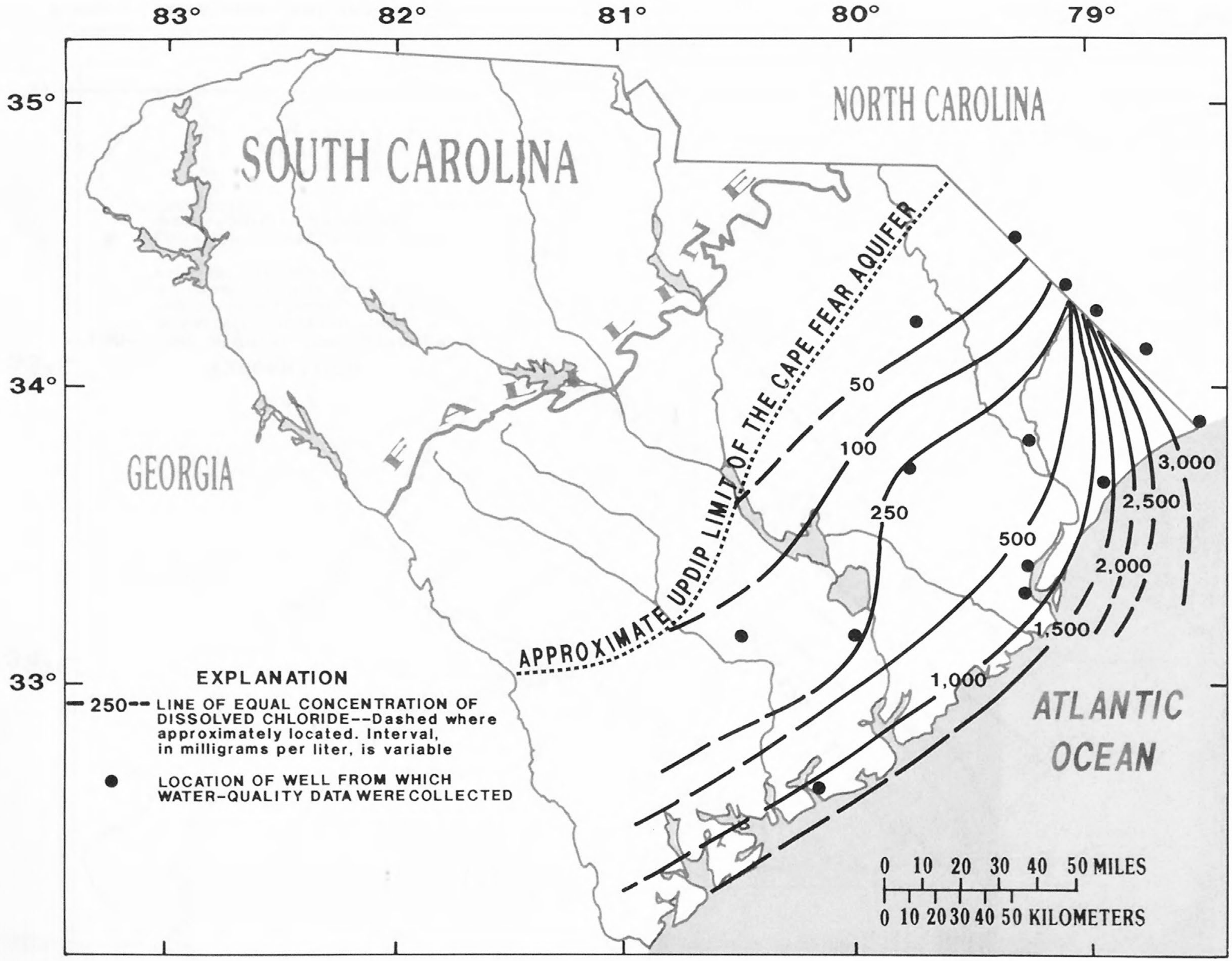


Figure 14.--Concentrations of dissolved chloride in water from upper sands of the Cape Fear aquifer prior to 1983.

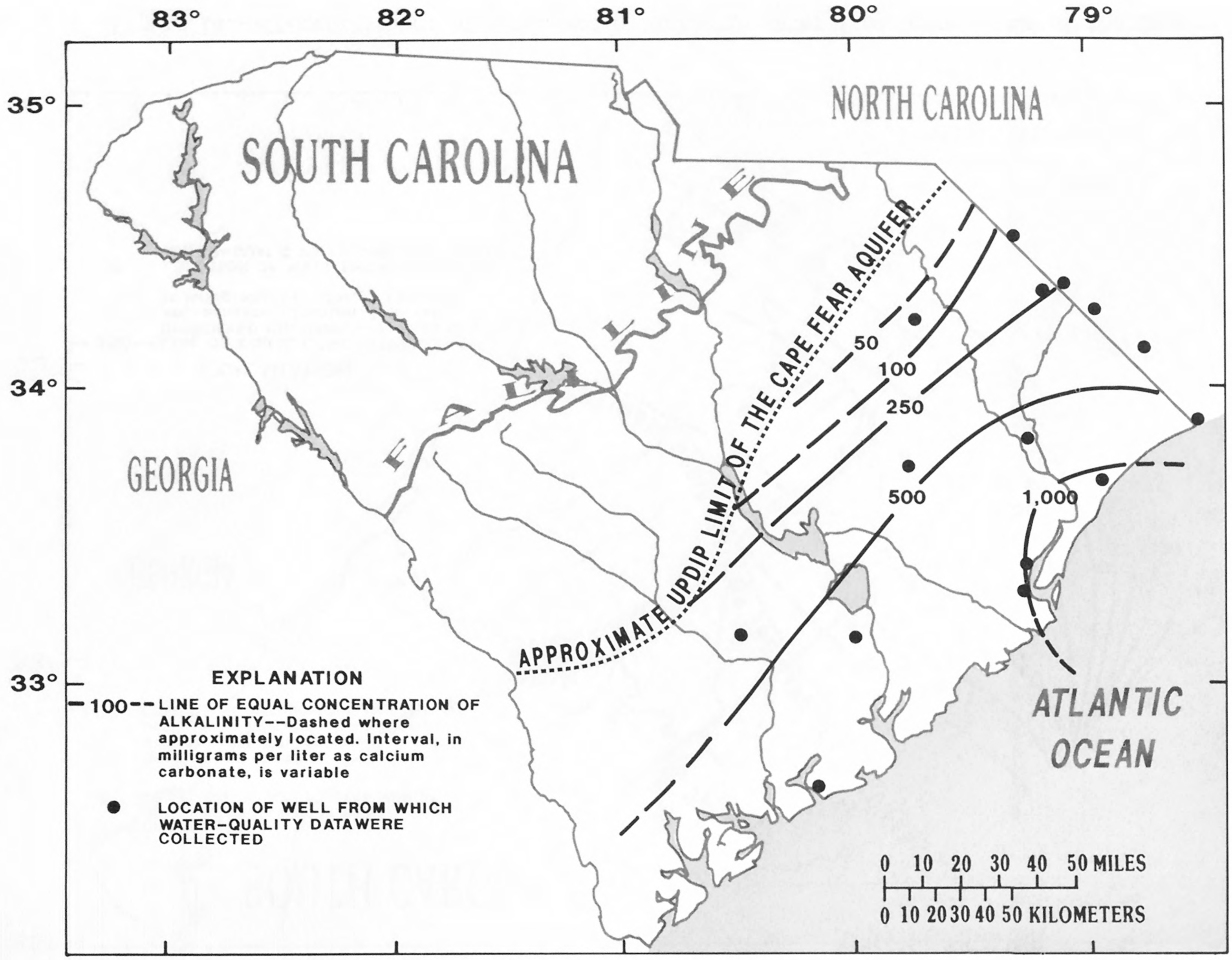


Figure 15.--Concentrations of alkalinity as calcium carbonate in water from upper sands of the Cape Fear aquifer prior to 1983.

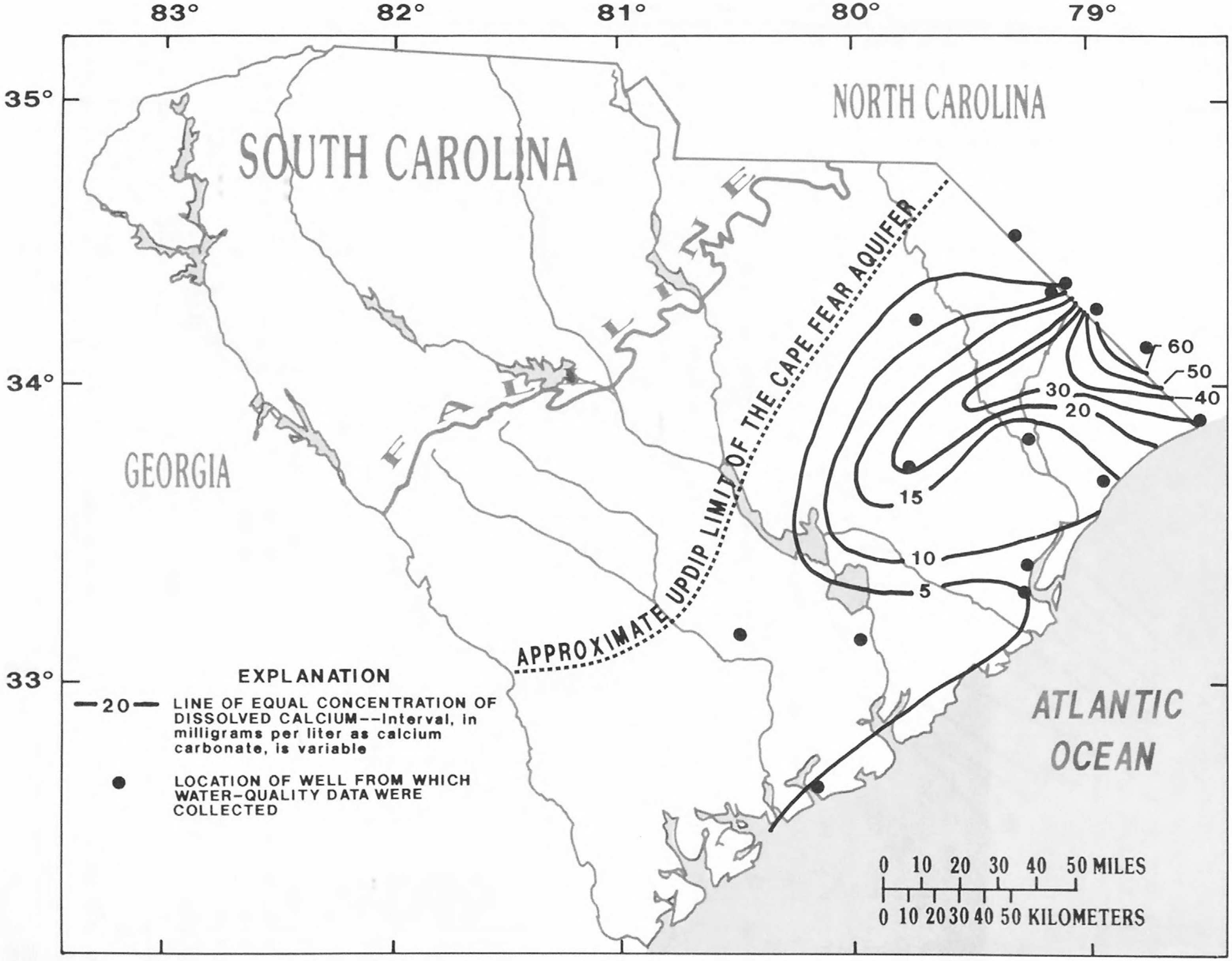


Figure 16.--Concentrations of dissolved calcium in water from upper sands of the Cape Fear aquifer prior to 1983.

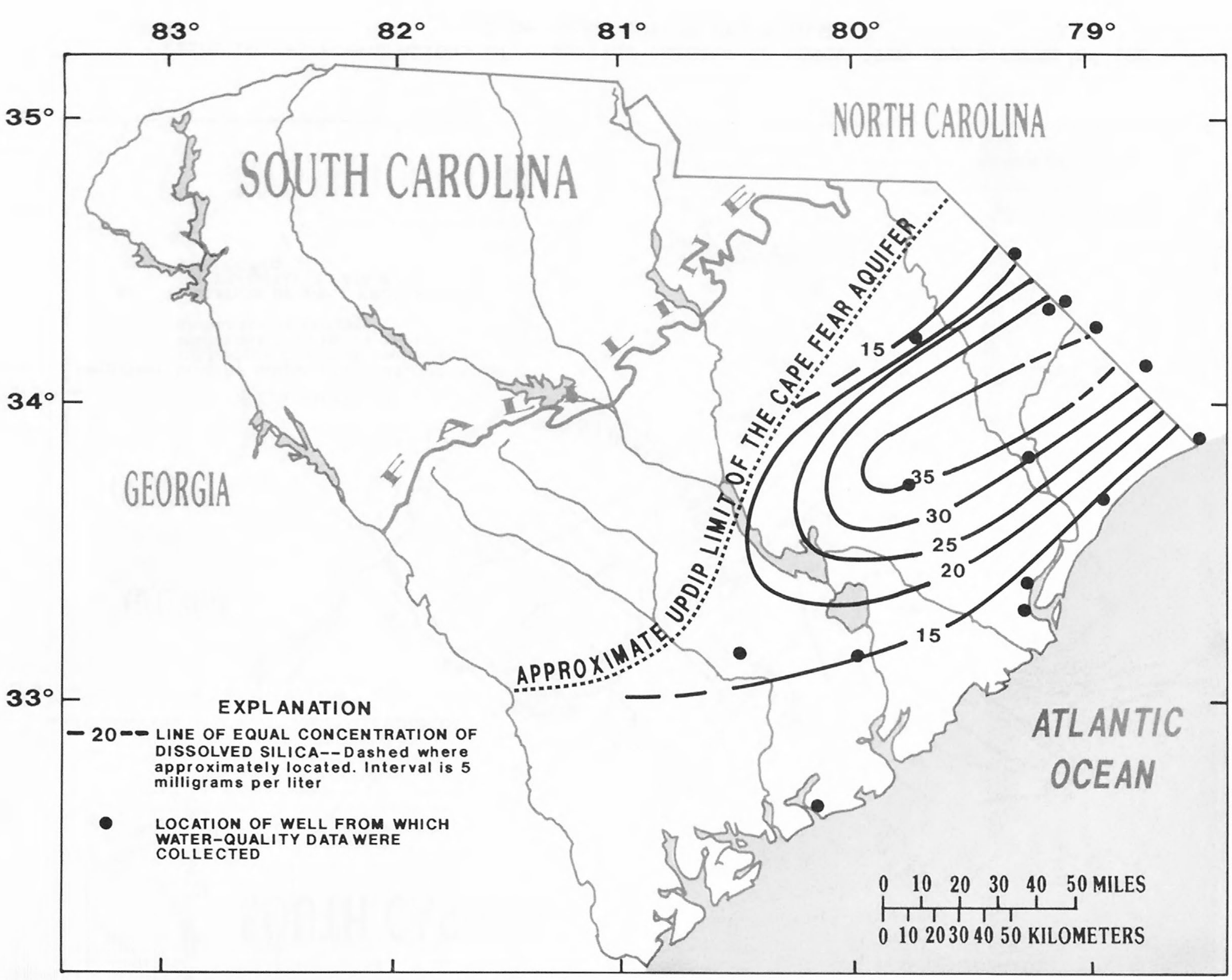


Figure 17.--Concentrations of dissolved silica in water from upper sands of the Cape Fear aquifer prior to 1983.

Although the source of bicarbonate and other ions in water from the Cape Fear aquifer cannot be determined with much confidence, several possibilities exist. Because of high concentrations of alkalinity in the water and of the lack of carbonates in the sediments, one of the most likely possibilities is that concentrations of constituents result from geochemical processes that occurred in the saltwater before it intruded into this part of the aquifer. If sediments in the part of the aquifer from which this water intruded contain calcareous material, reactions similar to those in the overlying Middendorf aquifer may occur. These reactions include the dissolution of carbonates (eqs. 6 and 7) and exchange of calcium for sodium (eq. 9). However, the possibility of these reactions in the Cape Fear aquifer cannot be evaluated at this time because prior flow patterns within the aquifer were probably much different than those of today.

The increase in concentrations of dissolved chloride, which indicates the direction of flushing of saltwater, occurs toward the coast and toward the northeast (fig. 14). The increase toward the coast probably occurs as a result of previous flow paths. The confining unit in Paleocene sediments that overlies the aquifers in Cretaceous sediments and controls flow within these aquifers probably is less permeable beneath the modern ocean because it was deposited in a deeper marine environment there. Thus, when seas were lower, flow in the Cape Fear aquifer may have been more perpendicular to the coast, causing a seaward flushing of saltwater. The increase in chloride concentration toward the northeast, which continues into southeastern North Carolina (Peek and Register, 1975), probably occurs because the area is near the end of the present ground-water-flow path for the Cape Fear aquifer (fig. 6).

## Middendorf Aquifer

Concentrations of most dissolved constituents are low, and are dominated by concentrations of dissolved silica in water from nonmarine sediments of the Middendorf aquifer. This is because the minerals in this part of the aquifer react slowly with the water and have low solubilities. Concentrations of several constituents in the water increase significantly downgradient toward the lower Coastal Plain where sediments of the Middendorf aquifer were deposited in marginal-marine to marine environments. This is because minerals in the marine sediments are more soluble and react more rapidly with the water than minerals in the nonmarine sediments.

These trends are indicated by the distribution in concentrations of dissolved solids which are less than 50 mg/L in much of the area of nonmarine sediments but increase in the area of marine sediments to more than 1,000 mg/L along the coast and more than 2,500 mg/L in the northeastern corner of the State (fig. 18). Patterns similar to those in dissolved solids are present in concentrations of dissolved sodium (fig. 19) and alkalinity (fig. 20). Although concentrations of dissolved chloride show a similar distribution (fig. 21), this distribution results more from the effects of depositional environment on the ground-water flow system and on

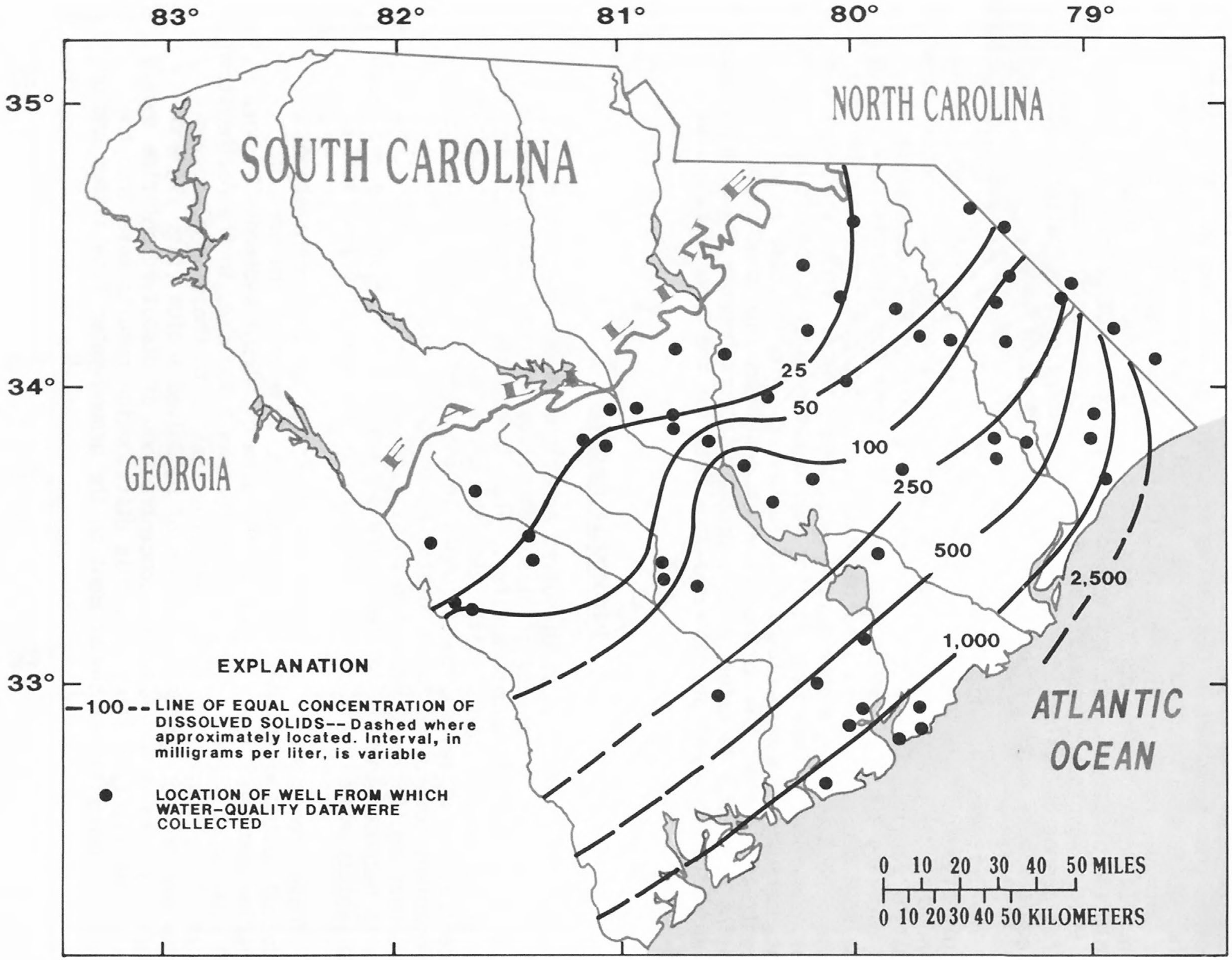


Figure 18.--Concentrations of dissolved solids in water from the Middendorf aquifer prior to 1983.

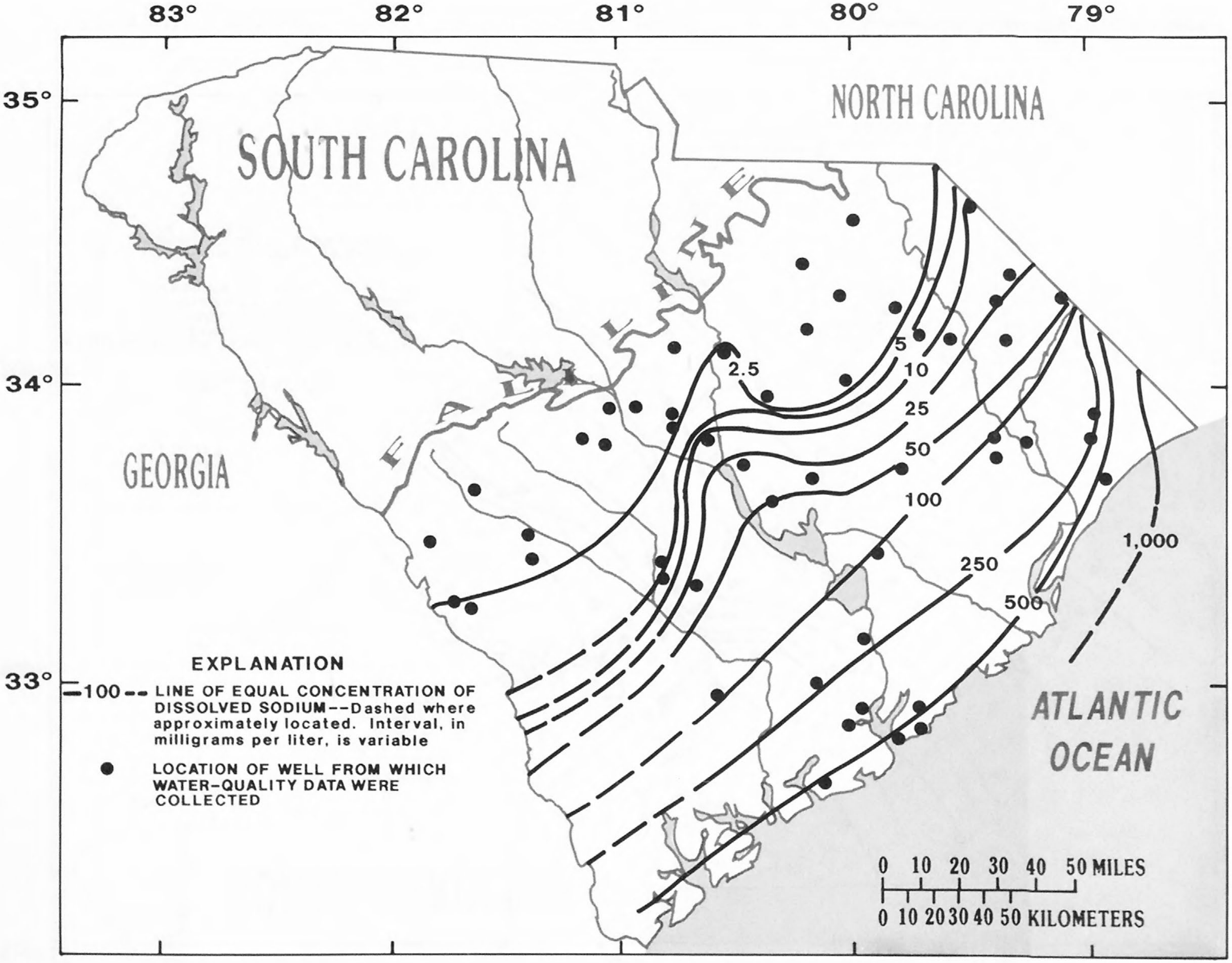


Figure 19.--Concentrations of dissolved sodium in water from the Middendorf aquifer prior to 1983.

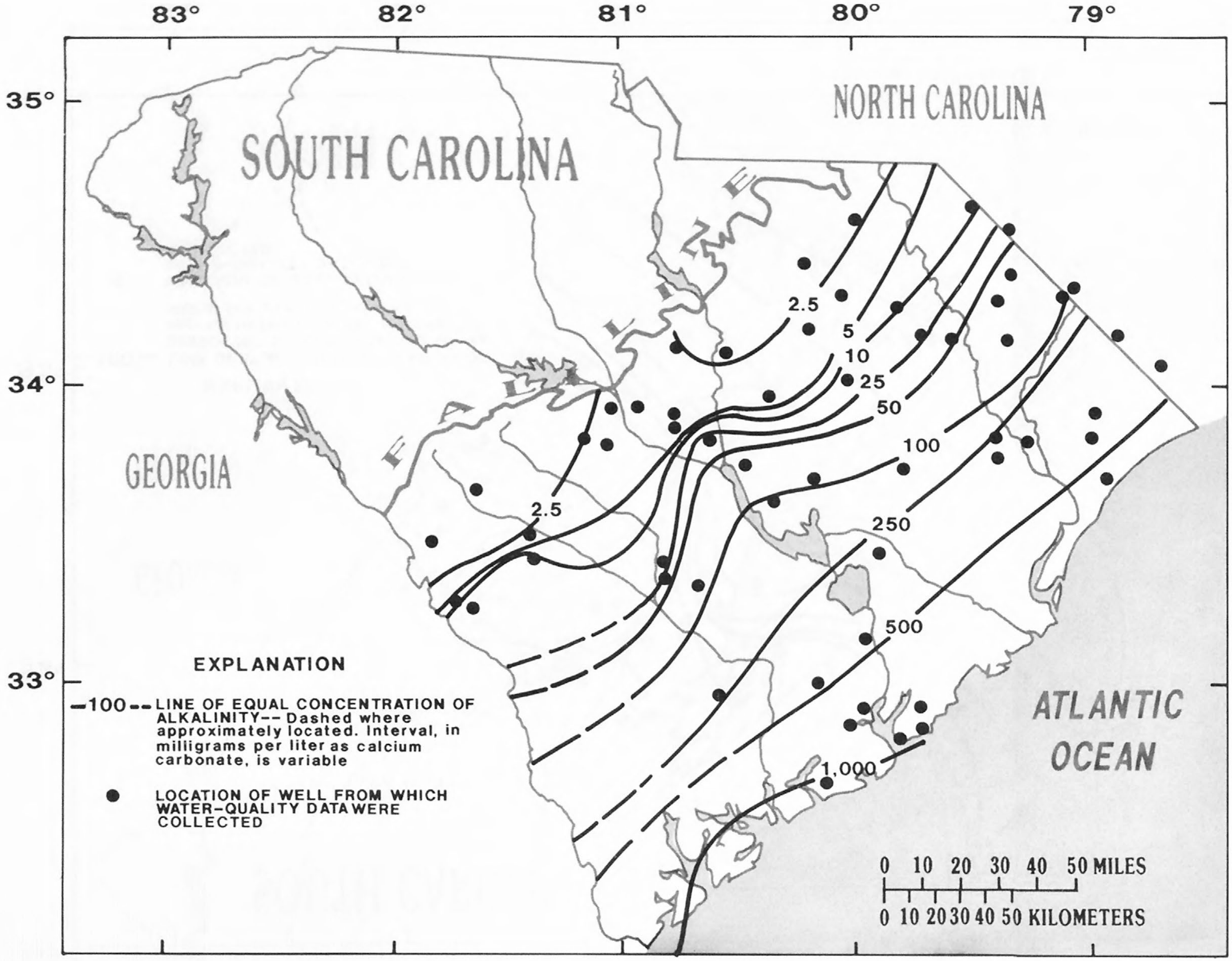


Figure 20.--Concentrations of alkalinity as calcium carbonate in water from the Middendorf aquifer prior to 1983.

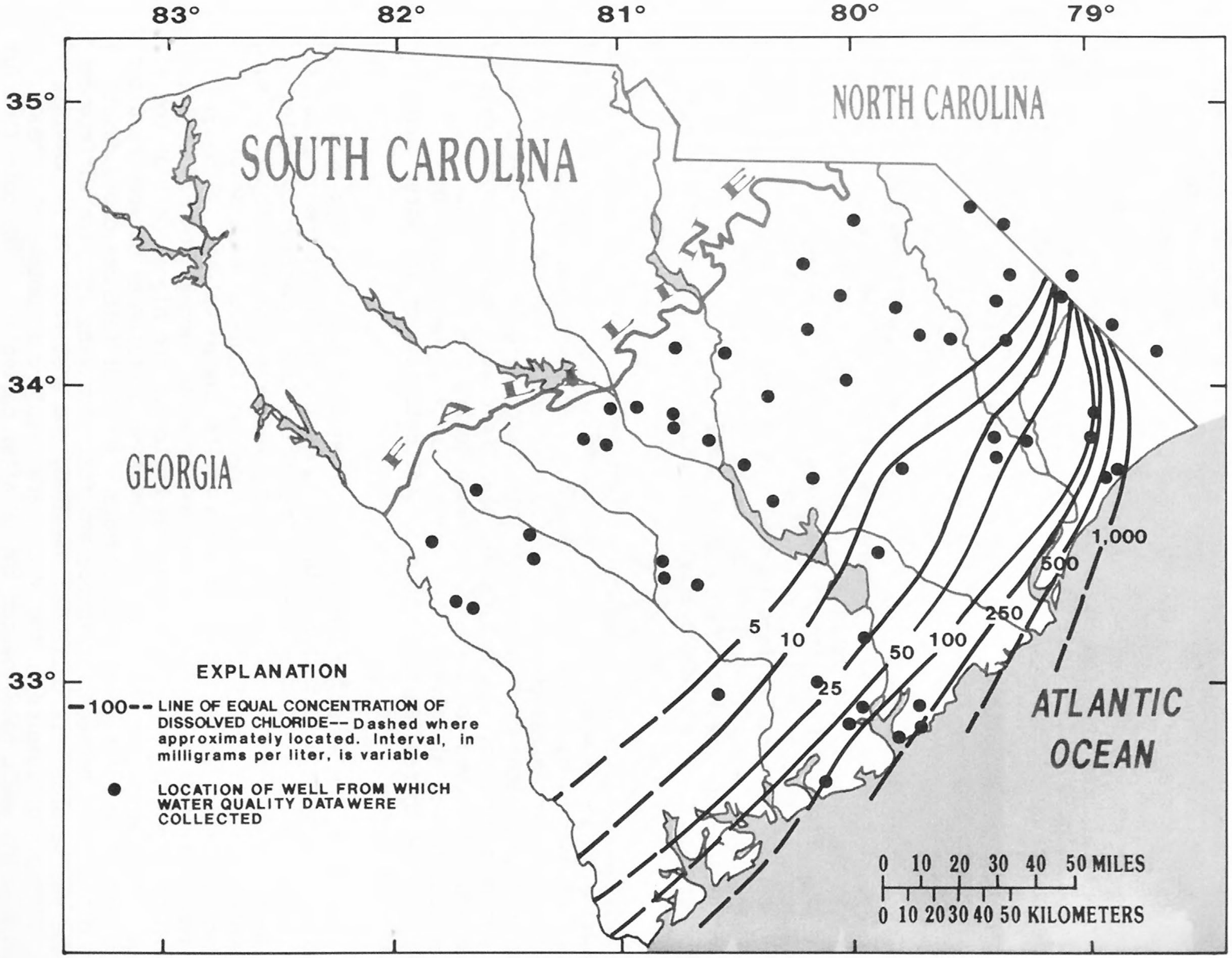


Figure 21.--Concentrations of dissolved chloride in water from the Middendorf aquifer prior to 1983.

the mixing of freshwater with incompletely flushed, dilute saltwater than from the effects of depositional environment on the geochemistry. Concentrations of sodium and alkalinity generally remain less than 5 mg/L in the nonmarine sediments but increase to greater than 1,000 mg/L in marine sediments. Concentrations of chloride are less than 5 mg/L in upgradient areas but increase to greater than 100 mg/L along the southern coast with concentrations greater than 1,000 mg/L along the northern coast.

Concentrations of dissolved calcium in water from the Middendorf aquifer differ less than concentrations of dissolved sodium, alkalinity, and dissolved chloride. Calcium concentrations increase from less than 1.0 mg/L in the nonmarine sediments to a little more than 5 mg/L in the transition from nonmarine to marine sediments, then generally decrease to less than 2.5 mg/L in the marine sediments (fig. 22). Along the coast concentrations of calcium again increase to greater than 2.5 mg/L and more than 25 mg/L in the northeast.

Concentrations of dissolved silica in the southwest increase downgradient from less than 5 to more than 15 mg/L in the nonmarine sediments but show little variability in most of the marine sediments (fig. 23). From the Fall line to the coast in the northeastern part of the State, concentrations of dissolved silica increase from less than 10 mg/L in the nonmarine sediments to more than 40 mg/L in the transitional sediments then decrease to about 15 mg/L in the marine sediments. The high silica concentrations are present in an area of similarly high concentrations in the underlying Cape Fear and overlying Black Creek aquifers.

Dissolved silica has a dominant effect on the quality of water from the nonmarine sediments where the ratio of the molar concentrations of dissolved anions divided by dissolved silica is about 1 or less (fig. 24) because molar silica concentrations are equal to or greater than the sum of the molar concentrations of the anions. This ratio increase downgradient into the marine sediments, approaching 50, near the coast, because concentrations of several dissolved constituents increase toward the coast, but concentrations of dissolved silica change little or decrease. This indicates the increasing role other constituents have on the water quality toward the coast.

The pH of the water in the Middendorf aquifer may be as low as 4.0 but generally ranges from 4.5 to 6.5 in the nonmarine sediments then increases over a short distance in the area of transition from nonmarine to marine sediments to values from 8.1 to 9.2 in the marine sediments (fig. 25). No pH contours less than 6.5 have been included on figure 25 because of variability and uncertainty in the data at the low pH values. Although the reported pH of water from the marine sediments ranges from 8.1 to 9.2, the pH of water in much of the area may be toward the higher part of the range. Many wells with multiple analyses have differences between reported pH values of up to one half unit or more. These differences could result from differences between laboratory and field analyses and from differences in the way samples were collected, handled, and analyzed. It is possible that exposure of samples to the atmosphere resulted in uptake of carbon dioxide which would have lowered the pH after collection. The potential for this has been pointed out by Garrels and Christ (1965, p. 83).

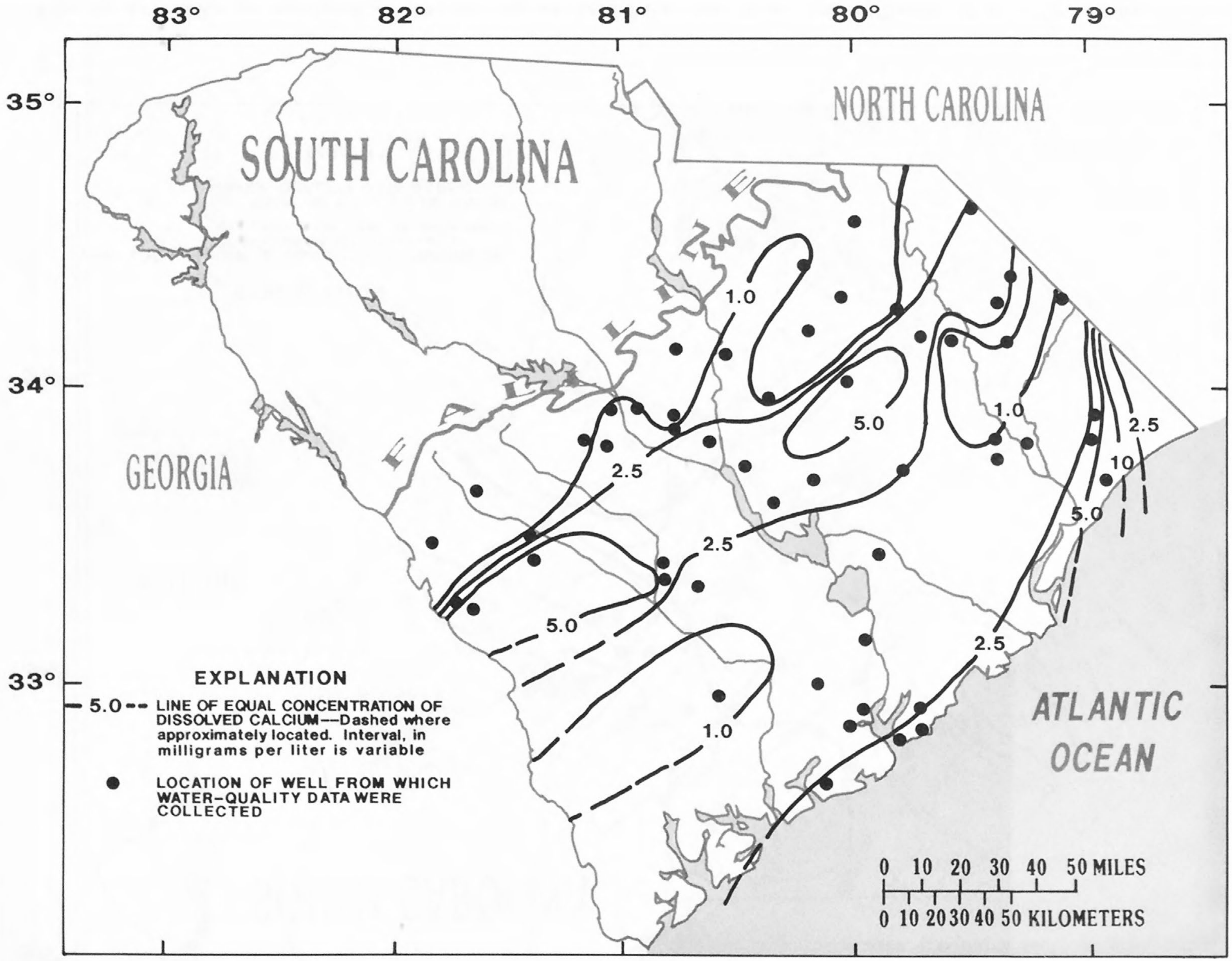


Figure 22.--Concentrations of dissolved calcium in water from the Middendorf aquifer prior to 1983.

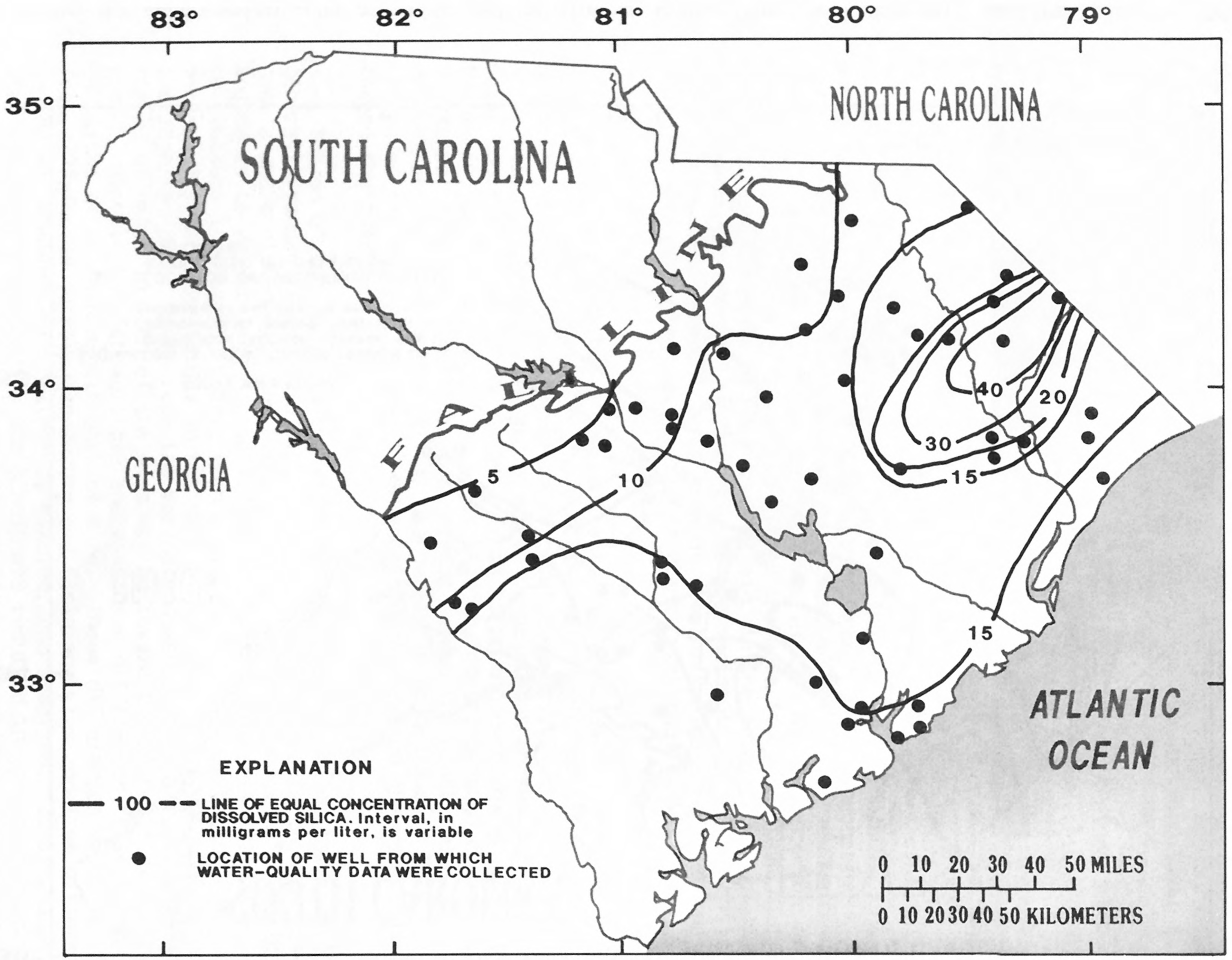


Figure 23.--Concentrations of dissolved silica in water from the Middendorf aquifer prior to 1983.

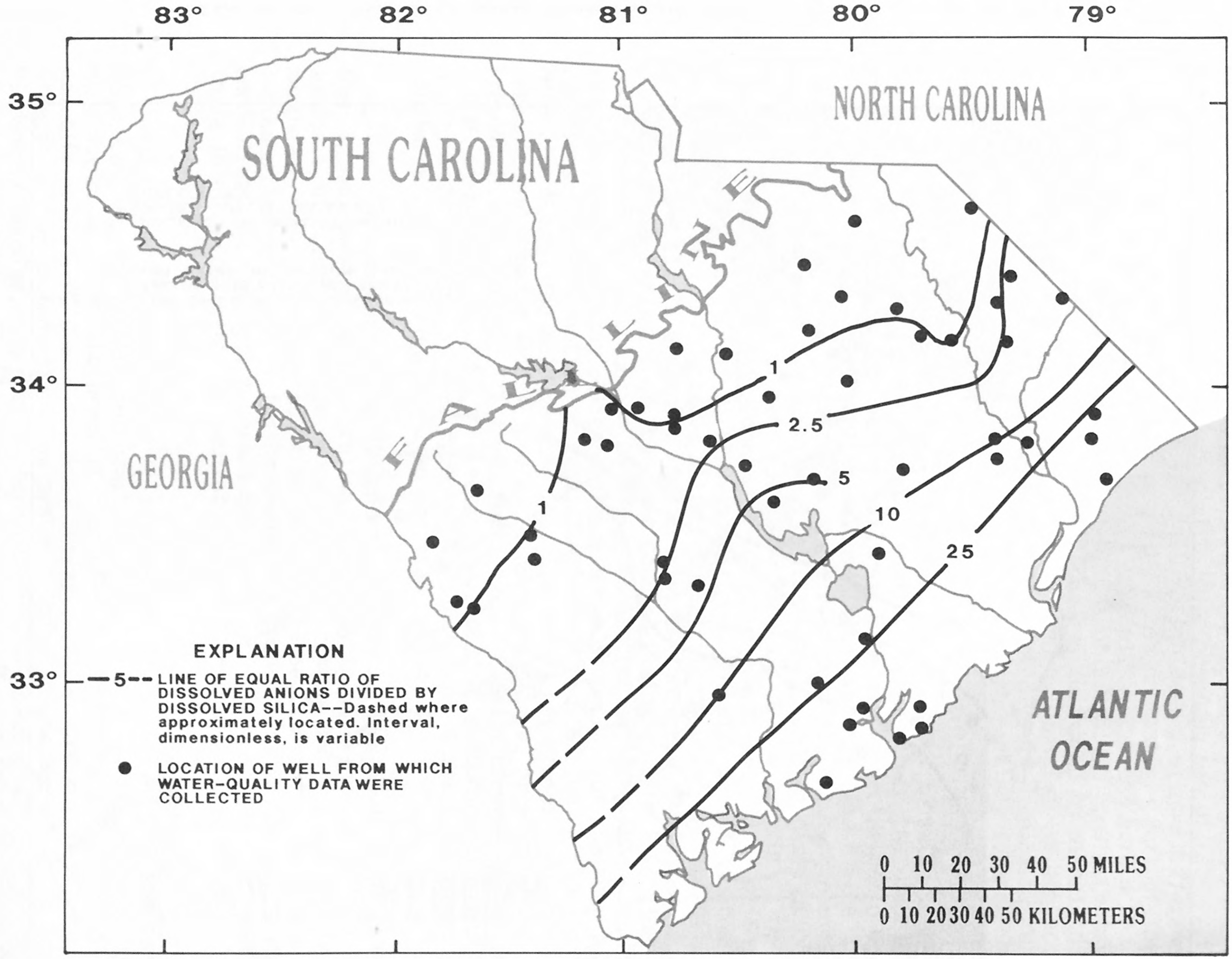


Figure 24.--Ratio of molar concentrations of dissolved anions divided by dissolved silica in water from the Middendorf aquifer prior to 1983.

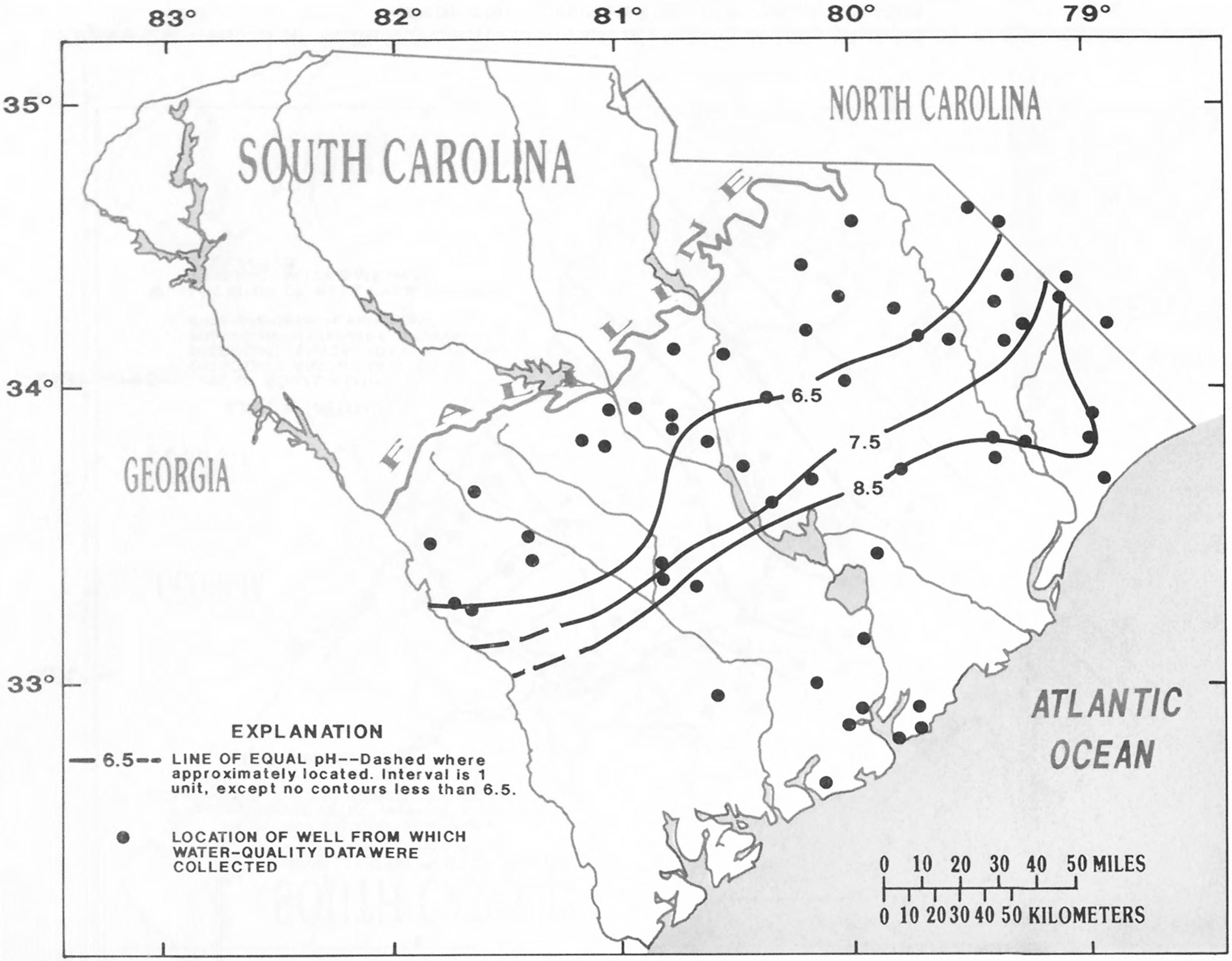


Figure 25.--The pH of water from the Middendorf aquifer prior to 1983.

The quality of water in the nonmarine sediments of the Middendorf aquifer probably reflects the quality of the recharge water, effects of the flow system, and the areal distribution in the mineral content of the sediments. The combination results in a high degree of variability in the dominant ions (fig. 26). In water with low concentrations of all constituents, such as that in the nonmarine sediments, slight differences in mineral content may readily change the water chemistry. Part of the differences may result from the effects of small analytical errors on interpretations involving low concentrations of dissolved constituents. In the marine sediments, the water quality becomes dominated by dissolved sodium and bicarbonate in middip areas and then by dissolved sodium and dissolved bicarbonate with increasing effects of dissolved chloride farther seaward where water quality is more affected by incompletely flushed saltwater.

One of the dominant groups of geochemical processes in water in nonmarine sediments of the Middendorf aquifer appears to be the dissolution and chemical alteration of various silicate minerals where the ratio of the molar concentrations of dissolved anions divided by dissolved silica approaches 1 (fig. 24). Several silicate reactions may occur. In extreme upgradient areas, the dissolution of quartz (eq. 4) and the dissolution or geochemical alteration of other silicate minerals probably occur. The dissolution of quartz only continues until the quartz solubility of 6 mg/L of $SiO_2$ (Krauskopf, 1979, p. 132) is attained, but dissolution of other silicate minerals may increase silica concentrations until the solubility of these minerals is attained. Quartz dissolution would be limited to an area in the western part of the upper Coastal Plain near the Fall Line on the basis of the distribution of silica concentrations (fig. 23). Although reactions with numerous silicate minerals may occur, one of the most likely reactions is the formation of kaolinite from K-feldspar (eq. 5) in the low pH environment. The acid causing this low pH may be a combination of carbonic and organic acids produced by decomposition of organic matter present in the aquifer. If the acid is carbonic acid, bicarbonate is formed and pH increases resulting in greater ionization of carbonic acid (eqs. 2 and 3) and formation of more carbonic acid (eq. 1). Quartz, feldspar, and kaolinite are all abundant in the nonmarine sediments.

The clay content of the Middendorf aquifer is greater in northeastern than in southwestern South Carolina. This may in part account for the increase in dissolved silica concentrations to more than 40 mg/L in the northeast. Increased contact time between the sediments and water and increased surface area of the sediments may account for the higher silica concentrations; however, minerals and geochemical processes different from those in other parts of the aquifer could also account for the high silica concentrations.

The coastward decrease in silica concentrations in water of the Middendorf aquifer in the northeast from greater than 40 to less than 15 mg/L may result from the precipitation of silicate minerals such as sodium smectite (R.W. Lee, U.S. Geological Survey, written commun., 1986) or effects of the ground-water-flow system. Prior to pumpage of water from the Middendorf aquifer, the northeastern part of the lower Coastal Plain was an area to which water flowed from areas in the southwest (fig. 8) where dissolved silica concentrations were low (fig. 23). The area in the

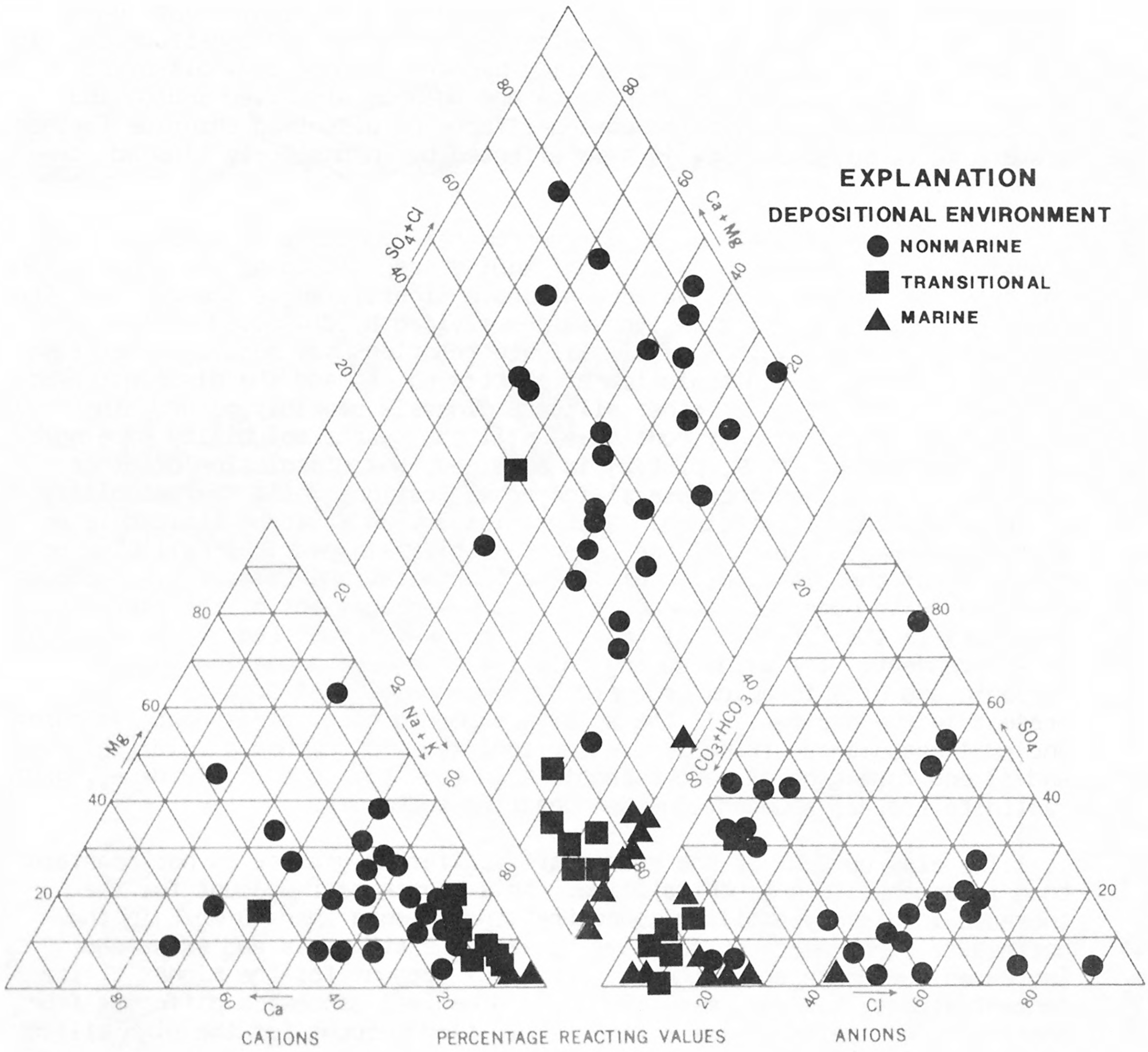


Figure 26.--Relative concentrations of major ions in water from the Middendorf aquifer prior to 1983.

northeast was also an area of discharge from the Middendorf aquifer to the overlying Black Creek aquifer (Aucott and Speiran, 1985a, p. 742). Thus, discharge of water having high silica concentrations and mixing of water having high silica concentrations with water having low silica concentrations may contribute to the decrease in dissolved silica.

Inorganic carbon in the form of carbonate and bicarbonate ions is a major dissolved constituent in much of the Middendorf aquifer. Potential sources of dissolved inorganic carbon in water from nonmarine sediments of the Middendorf aquifer are atmospheric carbon dioxide and carbon dioxide from the decomposition of organic carbon in surface soils and underlying aquifer sediments. Carbon dioxide from these sources hydrolyzes to form carbonic acid (eq. 1) which ionizes (eq. 2 and 3) and reacts with minerals as K-feldspar and other silicate minerals. Carbon dioxide from the decomposition of organic material is probably the major source of inorganic carbon in the nonmarine sediments. Organic material is present in the sediments, and the aquifer is confined throughout most of its areal extent (even in outcrop) so that atmospheric carbon dioxide ($\delta^{13}C = -7\,^{0}/_{00}$), is excluded. Carbon-isotope analyses indicate that $\delta^{13}C$ for the nonmarine sediments ranges from $-26\,^{0}/_{00}$ to $-21\,^{0}/_{00}$ (fig. 27) and that the major source of carbon dioxide probably is decomposition of organic matter ($\delta^{13}C = -25\,^{0}/_{00}$).

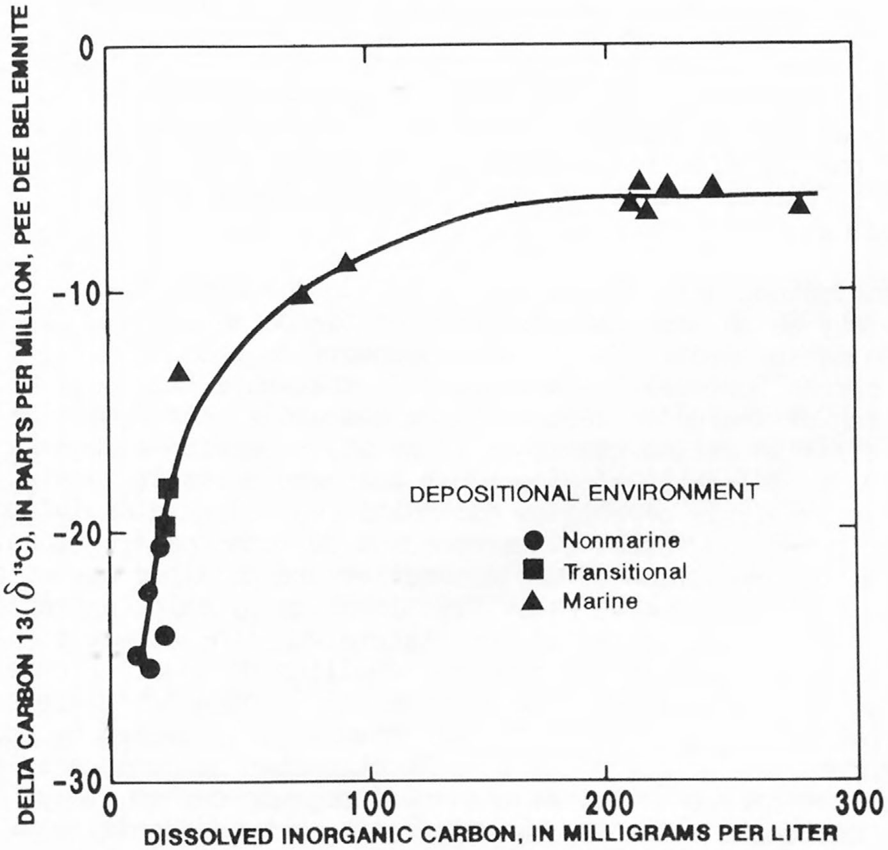


Figure 27.--Relation of concentrations of dissolved inorganic carbon to $\delta^{13}C$ in water from the Middendorf aquifer.

The dissolved constituents that predominate in water in marine sediments of the Middendorf aquifer are dissolved sodium and alkalinity (fig. 26), both of which significantly increase toward the coast (figs. 19 and 20). Alkalinity in the transitional and marine sediments results from the dissolution of calcium carbonate (calcite and shell). Concentrations of dissolved calcium increase slightly in the transitional sediments as a result of the calcium carbonate dissolution but decrease (fig. 22) as sediments become more marine and as concentrations of sodium increase from the exchange of calcium in solution for sodium on the sodium-rich clay minerals (eq. 9). Part of the increase in sodium concentrations along the coast results from the sodium chloride from the mixing of freshwater with incompletely flushed dilute saltwater.

Dissolution of calcium carbonate may occur by the action of carbonic acid on the carbonates (eq. 6), by hydrolysis of the carbonates (eq. 7), or by both reactions. Although dissolution with carbonic acid is the mechanism normally thought to cause the dissolution of calcium carbonate, Garrels and Christ (1965, p. 88) state that the effects of hydrolysis and of carbon dioxide in the soil atmosphere on calcium-carbonate dissolution have been underrated. This may also apply to carbon-dioxide production from decomposition of organic matter in deep sediments as discussed by Foster (1950). In marine sediments of the Middendorf aquifer, where the partial pressure of carbon dioxide ($pCO_2$) is low and the pH of the water is high (fig. 25), hydrolysis of calcium carbonate may be significant. The $pCO_2$ and pH of water in the marine sediments generally fall within the limits given by Plummer and others (1978, fig. 12) for dominance of hydrolysis of calcite over other calcite dissolution reactions. Zack (1980) also concluded that because of the low $pCO_2$ and high pH of the water, hydrolysis was one of the mechanisms of calcite dissolution in the Black Creek aquifer of northeastern South Carolina.

Carbon-isotope data also support, but do not prove the possibility that hydrolysis may be an important contributor to concentrations of alkalinity in water in marine sediments of the Middendorf aquifer. The $\delta^{13}C$ of inorganic carbon (primarily alkalinity) in the water increases with the concentration of inorganic carbon from about $-26^{0}/_{00}$ in nonmarine sediments to about $-6^{0}/_{00}$ in marine sediments (fig. 27). Calcium carbonate dissolution by nonfractionated carbonic acid would result in a $\delta^{13}C$ of about $-12.5^{0}/_{00}$. Hydrolysis of calcium carbonate (eg. 7) or dissolution by carbonic acid (eq. 6) formed by carbon dioxide from the fractionated or preferential decomposition of organic matter are possible causes of the increase in $\delta^{13}C$ to about $-6^{0}/_{00}$. Fractionation by calcite precipitation is not likely because the system is undersaturated with respect to calcite based on the use of the WATEQF chemical equilibrium model (Plummer and others, 1978) by Zack (1980). To achieve a $\delta^{13}C$ of $-6^{0}/_{00}$, approximately equal amounts of inorganic carbon would have to be provided by the dissolution of calcium carbonate by unfractionated carbonic acid and by hydrolysis. To produce equal amounts of inorganic carbon, twice the amount of calcium carbonate dissolves by hydrolysis as by carbonic acid. To continue this discussion on the possibility of hydrolysis, the exchange of calcium for sodium also must be evaluated.

Dissolved calcium resulting from the dissolution of calcium carbonate exchanges for sodium on the sodium-rich clay minerals in the aquifer (eq. 9) and causes the low concentrations of calcium throughout much of the Middendorf aquifer (fig. 22). The band of somewhat higher concentrations of calcium in the transition sediments probably results from the dissolution of calcium carbonate with limited exchange of calcium for sodium. Exchange may be limited where small amounts of the marine-clay minerals are present or where those present may be saturated with calcium. Along the coast and in the northeast, concentrations of calcium probably are greater because of the effects of dilute saltwater on the exchange reaction.

The exchange of calcium for sodium keeps the product of the activities of calcium and bicarbonate less than the solubility product of calcite by decreasing calcium concentrations. This allows continued dissolution of carbonates with the resulting high concentrations of sodium and alkalinity.

The molar ratio of sodium to alkalinity in the Middendorf aquifer is approximately 2:1 (fig. 28) (sodium to bicarbonate ratio of 1:1). This is the ratio obtained if carbonates dissolve by carbonic acid (eq. 6) or by hydrolysis-carbonic acid reactions (eq. 8). However, when calcium carbonate dissolves by hydrolysis in the absence of sufficient carbonic acid to subsequently neutralize the hydroxyl ion, and when calcium-sodium exchange occurs, the sodium to alkalinity ratio is 1:1 (sodium to bicarbonate ratio of 2:1) with the excess sodium ion balanced by the hydroxyl ion (eq. 11). However, at the existing pH, insufficient hydroxyl ion is present to provide this balance. Zack (1980) also reported a 1:1 sodium to bicarbonate ratio for the Black Creek aquifer. Based on the carbon-isotope data and the sodium to bicarbonate ratio, either carbonates are dissolving by carbonic acid derived from the fractionated or preferential decomposition of organic matter, hydrolysis is taking place with hydroxyl ion involved in subsequent reactions, or both are occurring.

Hydroxyl ion derived from the hydrolysis of calcium carbonate may be buffered by a mechanism other than the carbonate system because the pH remains less than would be expected (Garrels and Christ, 1965, p. 79) and appears to have a maximum of 9.2. Buffering cannot be provided by carbonic acid derived from the decomposition of organic matter through a mechanism other than fractionation or preferential decomposition reactions because such reactions yield the same net $\delta^{13}C$ ($-12.5^{0}/_{00}$) as the dissolution of carbonates by carbonic acid. Buffering to reduce concentrations of hydroxyl ion must come from another source and may result from the buffering capacity of the clay minerals. The importance of buffering by clay minerals in seawater is discussed by Krauskopf (1979, p. 534), indicating a possibility of similar effects in aquifers.

At the pH of water in the Coastal Plain aquifers of South Carolina, buffering is likely to be from the clays comprising the smectite group (B.F. Jones, U.S. Geological Survey, oral commun., 1985). Buffering could result from the formation of slightly soluble ferric hydroxide (eq. 12) with ferric ion provided by the inner layer of the clay minerals. Calcium resulting from the hydrolysis of calcium carbonate could exchange for the ferric ion (eq. 13) to maintain the charge neutrality of the clay minerals and of the solution. The net reaction for replacement of ferric ion on the clay

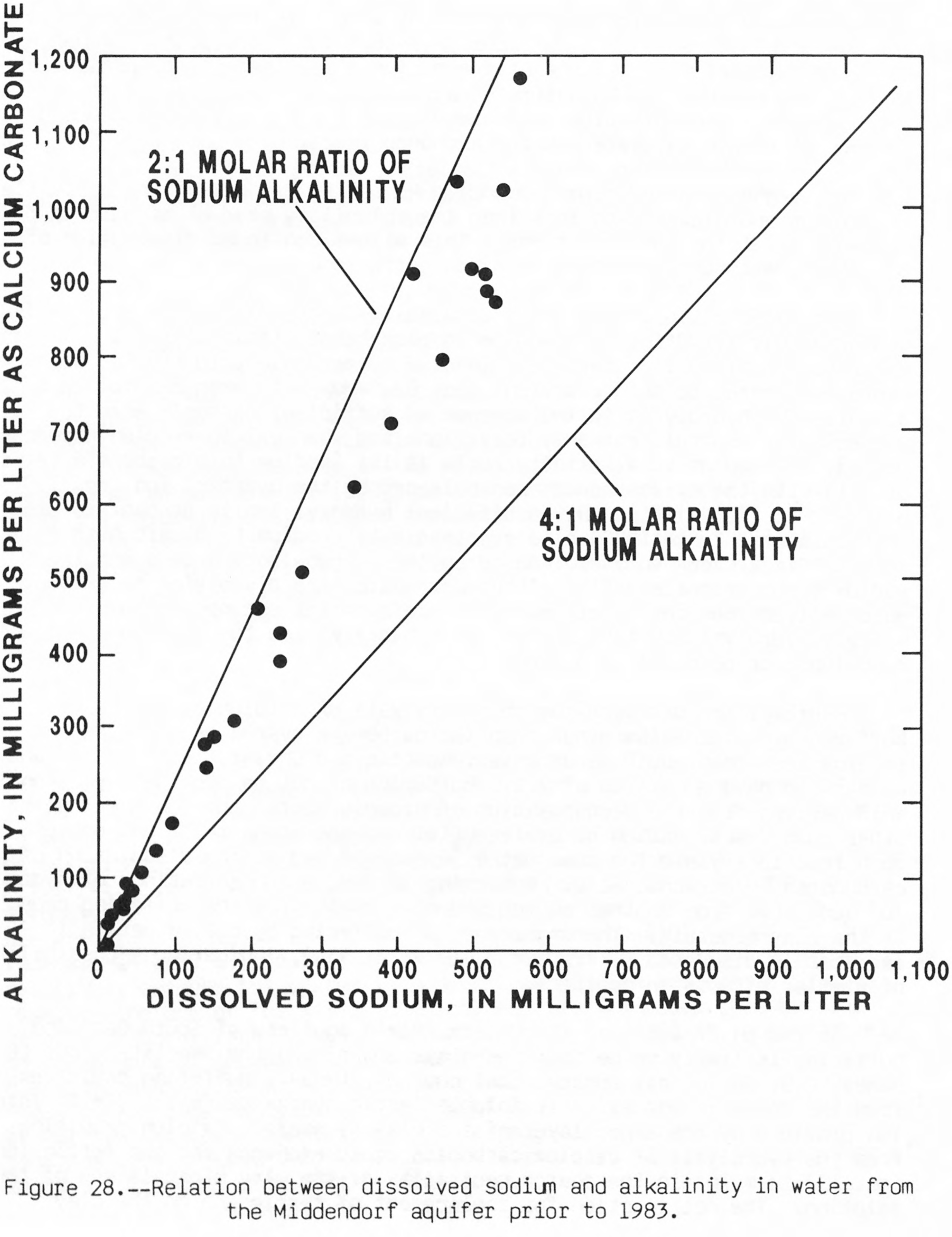


Figure 28.--Relation between dissolved sodium and alkalinity in water from the Middendorf aquifer prior to 1983.

minerals by calcium in solution and for the formation of ferric hydroxide is given by equation 14. Equation 15 incorporates these processes with the hydroloysis of calcium carbonate. By including calcium-sodium exchange (eq. 9) the net reaction (eq. 16) provides the sodium to bicarbonate ratio of 1:1 observed in water of the Middendorf aquifer. In this way the clay minerals may provide a medium for calcium-sodium exchange and a buffering mechanism for the hydroxyl ion formed by the dissolution of calcium carbonate.

Although the above discussion is designed to support the possibility of hydrolysis in the Middendorf and other aquifers, it is recognized that other processes, in particular the fractionated or preferential decomposition of organic matter, may produce the same observed conditions. An attempt has been made to discuss both strengths and weaknesses of the argument for hydrolysis. Hydrolysis of calcium carbonate is likely to occur in the Middendorf aquifer if organic matter present decomposes slowly enough that insufficient carbonic acid is produced to cause the amount of calcium carbonate dissolution occurring in the aquifer. It may be that carbonic acid from unfractionated decomposition, carbonic acid from fractionated and preferential decomposition, and hydrolysis are all major contributors to the dissolution of calcium carbonate. Each process may be the dominant reaction in different parts of the aquifer depending on local conditions which, in part, may result from the depositional environment.

Along the coast and in the northeastern part of the lower Coastal Plain near the North Carolina State line, the quality of water in the Middendorf aquifer is also affected by the incomplete flushing of dilute saltwater from the aquifer. This is indicated by higher concentrations of dissolved sodium (fig. 19) and of dissolved chloride (fig. 21). Concentrations of chloride in the aquifer are greatest in northeastern part of the lower Coastal Plain. This part of the aquifer is toward the end of the ground-water flow path (fig. 8) and is less completely flushed of saltwater than other parts of the aquifer.

The northeastern part of the aquifer in the lower Coastal Plain is the only major onshore part of the Middendorf aquifer with concentrations of dissolved chloride greater than 250 mg/L. Along the southern part of the coast, the Middendorf aquifer is the only aquifer in Cretaceous sediments with concentrations of chloride in the water less than 250 mg/L. The Middendorf aquifer has less silt and clay and more sand than the underlying Cape fear aquifer or the overlying Black Creek aquifer along the southern coast. This coarser texture probably results from differences in depositional environment. The Middendorf aquifer along the southern coast is more permeable and therefore more completely flushed than the other aquifers in Cretaceous sediments.

Although concentrations of dissolved chloride and other dissolved constituents increase in the northeast toward the end of the recent ground-water-flow paths, concentrations also increase toward the coast with equal-concentration contours almost parallel to the coast. This pattern in concentrations may result form previous flow paths created when sea level was low. When sea level was low, flow may have been more perpendicular to the coast to cause a seaward flushing of saltwater in the Middendorf aquifer as in the Cape Fear aquifer because the overlying confining unit in Paleocene sediments provides one of the primary controls on flow in all aquifers in Cretaceous sediments. Thus, during lower sea levels, flow may have been nearly perpendicular to the current coast.

The dominant geochemical processes resulting from sediment depositional environment affect relative concentrations of major ions in water of the Middendorf aquifer (fig. 26). In the nonmarine sediments where the dissolution of silicate minerals significantly affects water quality, no cations or anions consistently dominate the water quality. Slightly different minerals and geochemical processes may affect relative concentrations of constituents throughout the nonmarine sediments because of the low concentrations of dissolved solids.

Water in the marine sediments is primarily a sodium bicarbonate water, reflecting the dissolution of calcium carbonate and the calcium-sodium exchange. The relative concentrations of chloride increase toward the coast and are greater in the northeastern than in the southwestern part of the lower Coastal Plain because of less complete flushing of saltwater from the aquifer in the northeast toward the end of the ground-water flow path.

## Black Creek Aquifer

The quality and geochemistry of water of the Black Creek aquifer are similar to those of water from those parts of the Middendorf aquifer in which sediments were deposited in similar environments. Concentrations of most dissolved constituents are low and dissolved silica comprises a major part of the dissolved solids in water from a limited part of the Black Creek aquifer. This occurs because the sediments react slowly with water and have a low solubility in this area and because the nonmarine sediments present in this area are located over a more limited areal extent in the Black Creek aquifer than in the Middendorf aquifer. Concentrations of several constituents in the water increase significantly downgradient toward the coast where sediments were deposited in marine environments. Minerals in the marine sediments are more soluble and react more rapidly with water than minerals in the nonmarine sediments.

These trends are indicated by the distribution in concentrations of dissolved solids in water of the Black Creek aquifer which are less than 25 mg/L in a narrow band in the nonmarine sediments but increase to more than 2,500 mg/L in marine sediments along the southern coast (fig. 29). Patterns similar to those in distributions of dissolved solids are present in distributions in concentrations of dissolved sodium and alkalinity (fig. 30 and 31). Although concentrations of dissolved chloride show a similar distribution (fig. 32), this distribution results more from the effects of depositional environment on the ground-water flow system and on the mixing of freshwater with incompletely flushed dilute saltwater than from the effects of depositional environment on the geochemistry. Concentrations of dissolved sodium and alkalinity are less than 2.5 mg/L in part of the nonmarine sediments but increase to more than 1,000 mg/L in the marine

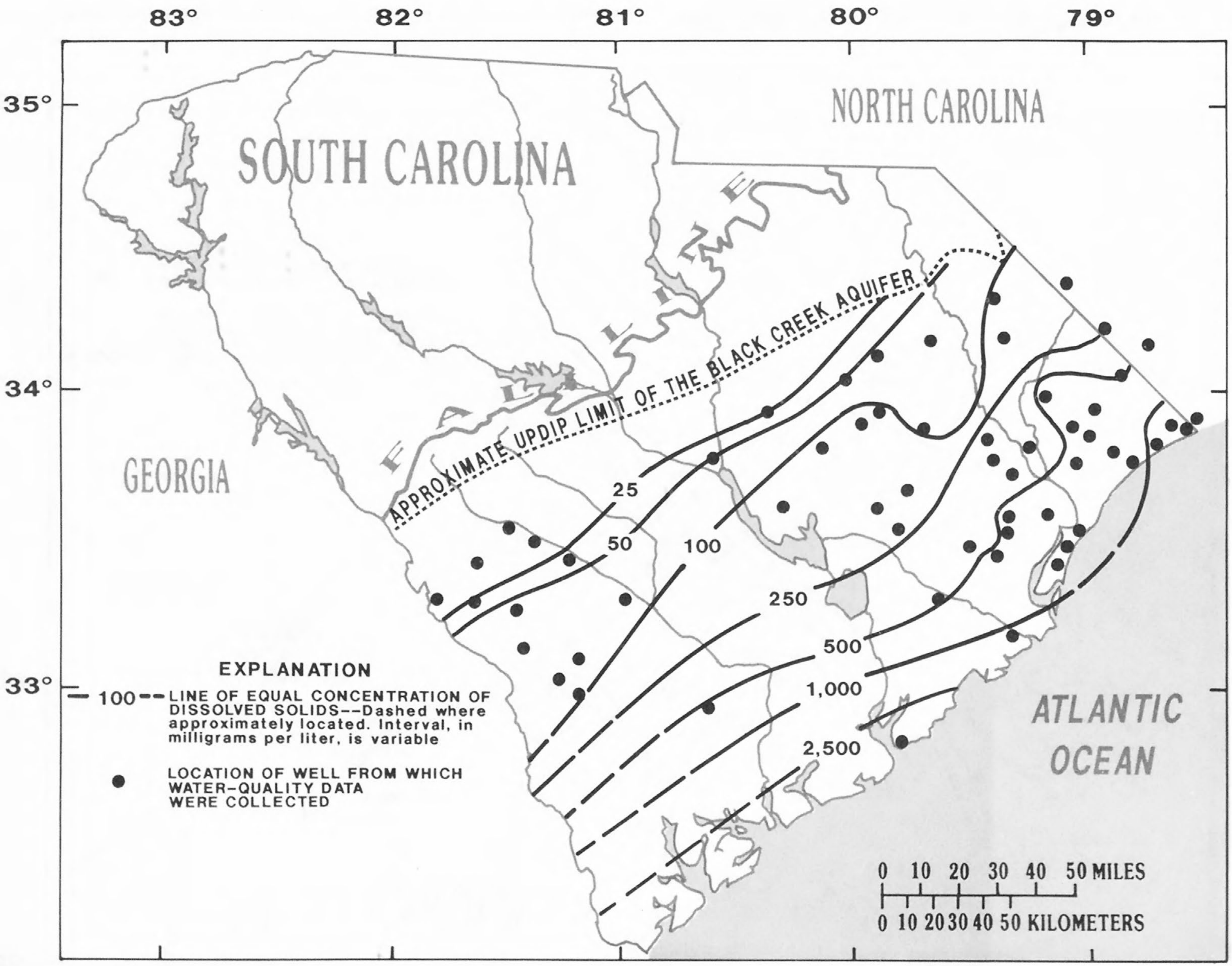


Figure 29.--Concentrations of dissolved solids in water from the Black Creek aquifer prior to 1983.

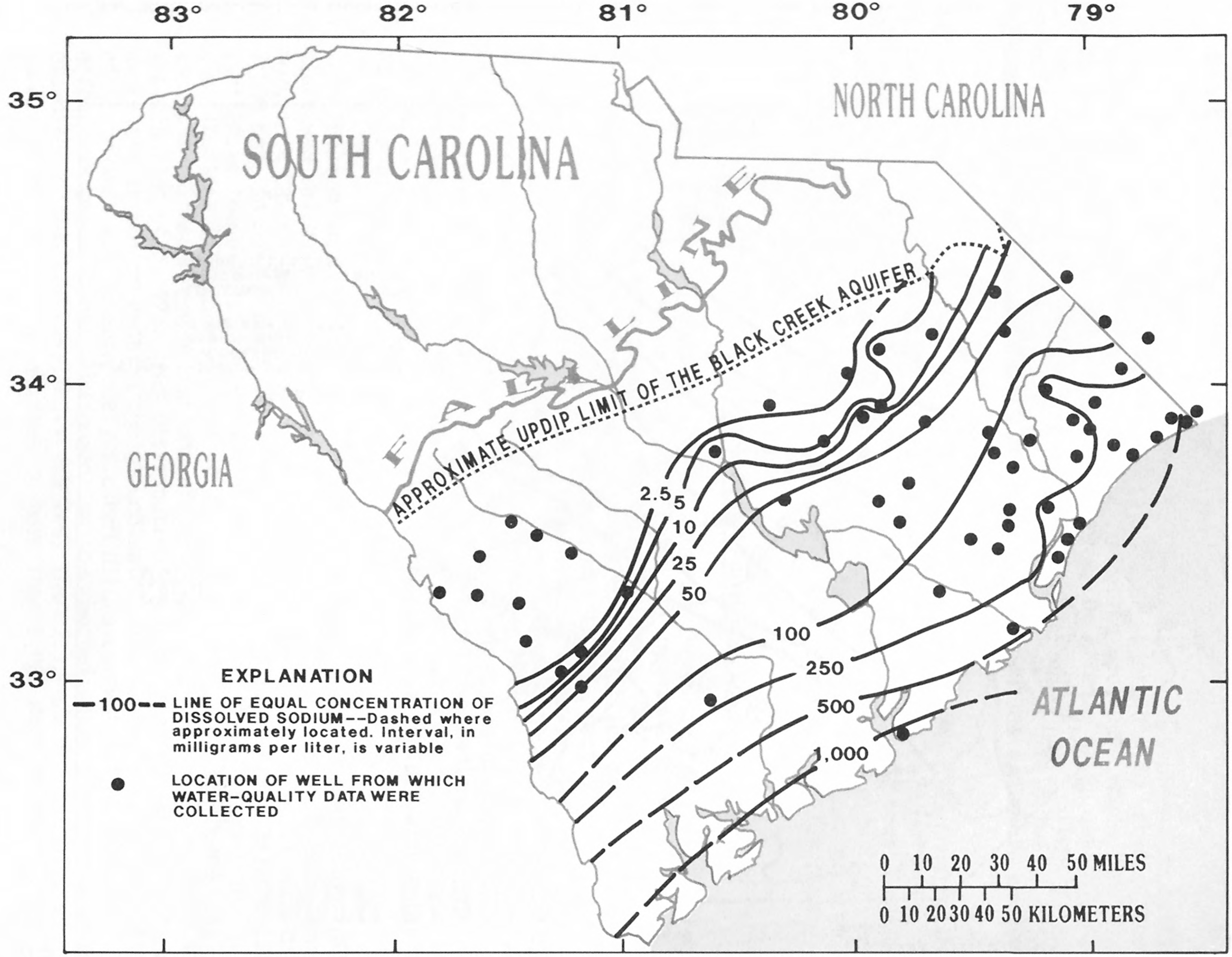


Figure 30.--Concentrations of dissolved sodium in water form the Black Creek aquifer prior to 1983.

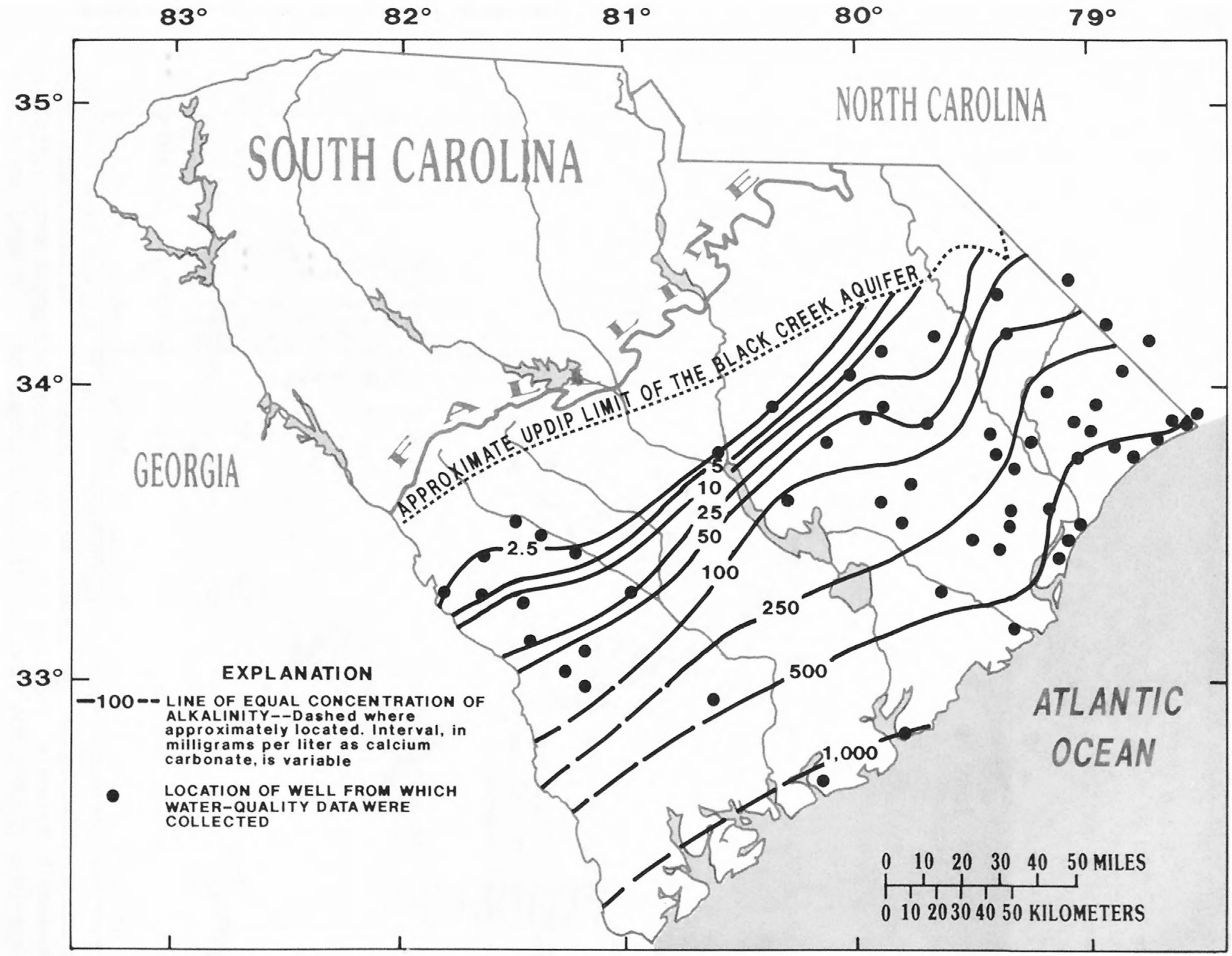


Figure 31.--Concentrations of alkalinity as calcium carbonate in water from the Black Creek aquifer prior to 1983.

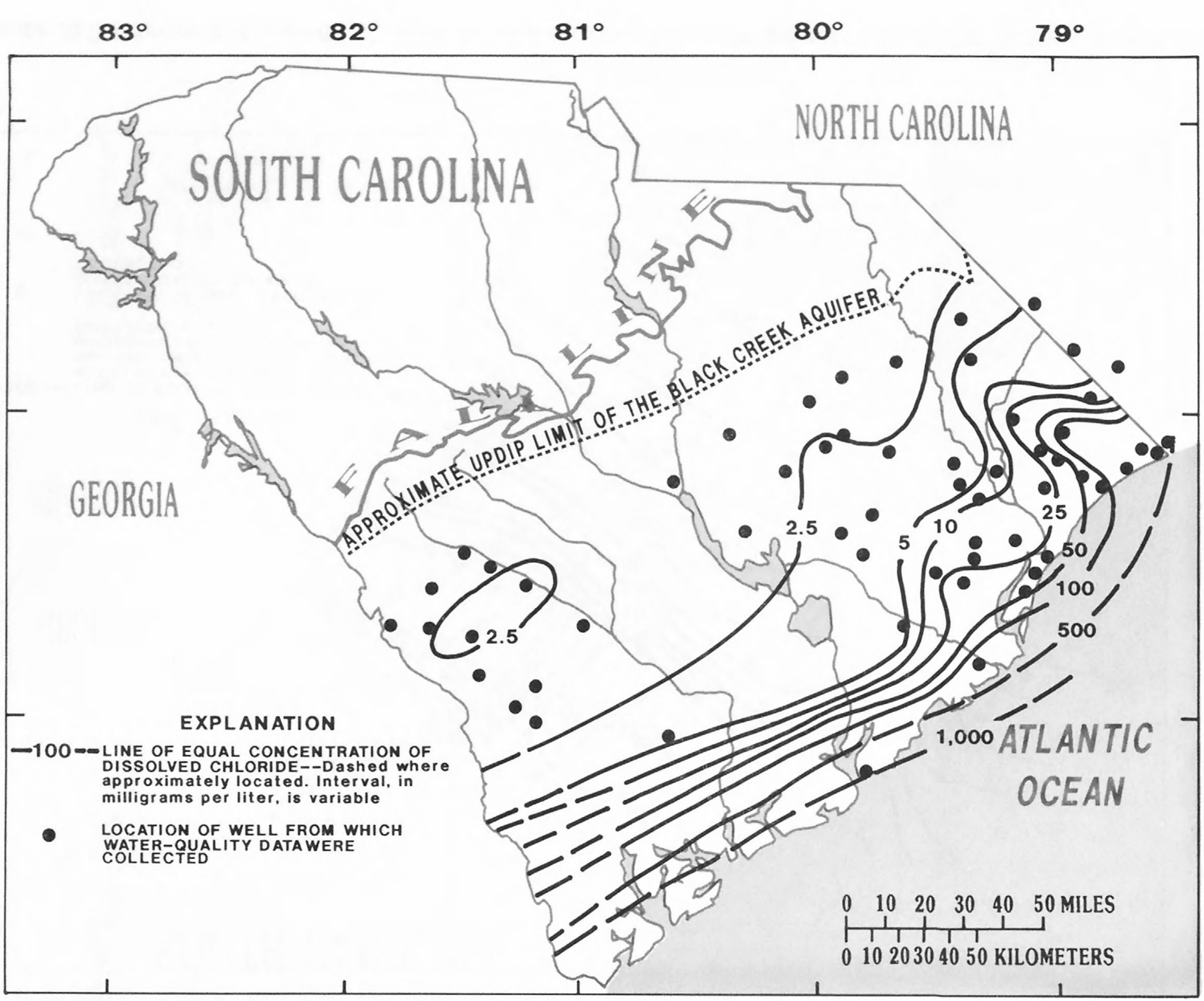


Figure 32.--Concentrations of dissolved chloride in water from the Black Creek aquifer prior to 1983.

sediments along the southern coast. Concentrations of dissolved chloride are less than 5 mg/L in about two thirds of the Black Creek aquifer, but increase to more than 900 mg/L along the southern coast.

Ranges in concentrations of dissolved calcium in water from the Black Creek aquifer are much less than those of dissolved sodium, alkalinity, and dissolved chloride. Concentrations of dissolved calcium are less than 2.5 mg/L in nonmarine sediments (fig. 33) but increase to 5 to 10 mg/L (locally, greater than 15 mg/L in the southwest) in a band that coincides with the transition from nonmarine to marine sediments. Concentrations decrease downgradient to less than 2.5 mg/L, then increase to between 5 and 10 mg/L along the coast.

Concentrations of dissolved silica in water of the Black Creek aquifer increase from less than 10 mg/L near its updip limit to more than 15 mg/L along the southern coast (fig. 34). In the northeast, concentrations increase downgradient to between 35 and 40 mg/L then decrease farther downgradient to less than 15 mg/L. This area of high dissolved silica coincides with similar areas of high dissolved silica in the underlying Middendorf and Cape Fear aquifers.

Dissolved silica has a dominant effect on the quality of water in the nonmarine sediments of the Black Creek aquifer. This area is approximately indicated by the band in the upper Coastal Plain in which the concentrations of dissolved solids are less than about 50 mg/L (fig. 29) and the ratio of the molar concentration of dissolved anions divided by dissolved silica approaches 1 or less (fig. 35). This band is wider in the southwestern than the northeastern part of the upper Coastal Plain. This ratio increases to more than 100 downgradient where concentrations of dissolved silica change little or decrease and concentrations of dissolved anions increase.

The pH of water from the nonmarine sediments of the Black Creek aquifer is less than 6.5 (less than 4.5 in some parts of the aquifer in the southwest) (fig. 36). In the marine sediments the pH increases to more than 7.5 and more than 8.5 throughout much of the aquifer.

Ions that dominate the quality of water in the nonmarine sediments of the Black Creek aquifer reflect the quality of recharge water, effects of the ground-water flow system, and effects of geochemical processes. Ions that dominate the quality of water in the nonmarine sediments are variable with no anions or cations consistently dominating the water chemistry (fig. 37). Part of the variability may result from the effects of small analytical errors on interpretations involving low concentrations of dissolved constituents. In the marine sediments, the water becomes dominated by dissolved sodium, dissolved bicarbonate, and greater amounts of dissolved chloride where the water quality is affected more by the incompletely flushed saltwater.

As in the Middendorf aquifer, dissolution of the various silicate minerals have a major effect on water quality in nonmarine sediments of the Black Creek aquifer. The hydrolysis of quartz (eq. 4) probably occurs over a limited area along the updip limit of the aquifer. Although dissolved silica was less than the quartz solubility in only one sample, analyses were

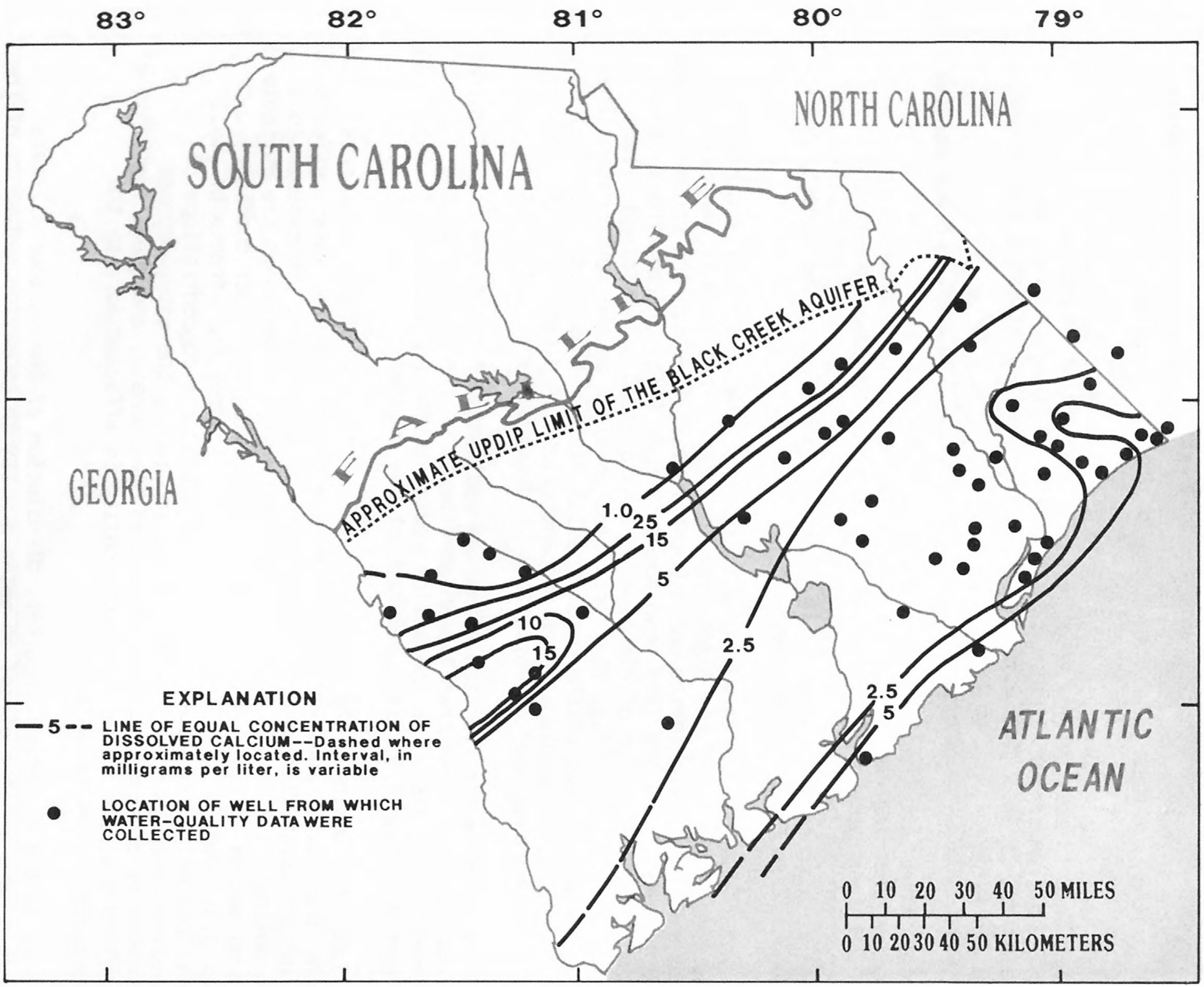


Figure 33.--Concentrations of dissolved calcium in water from the Black Creek aquifer prior to 1983.

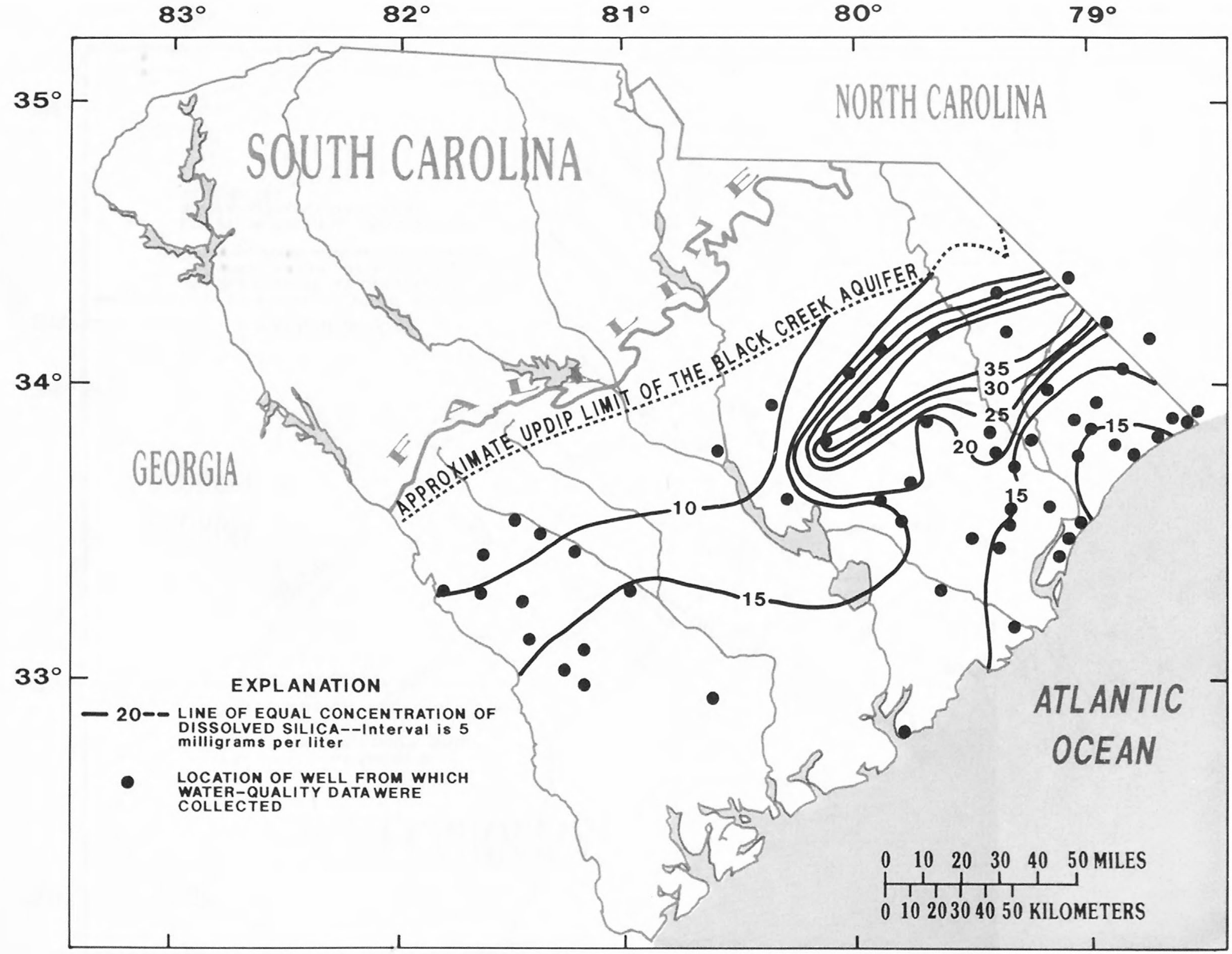


Figure 34.--Concentrations of dissolved silica in water from the Black Creek aquifer prior to 1983.

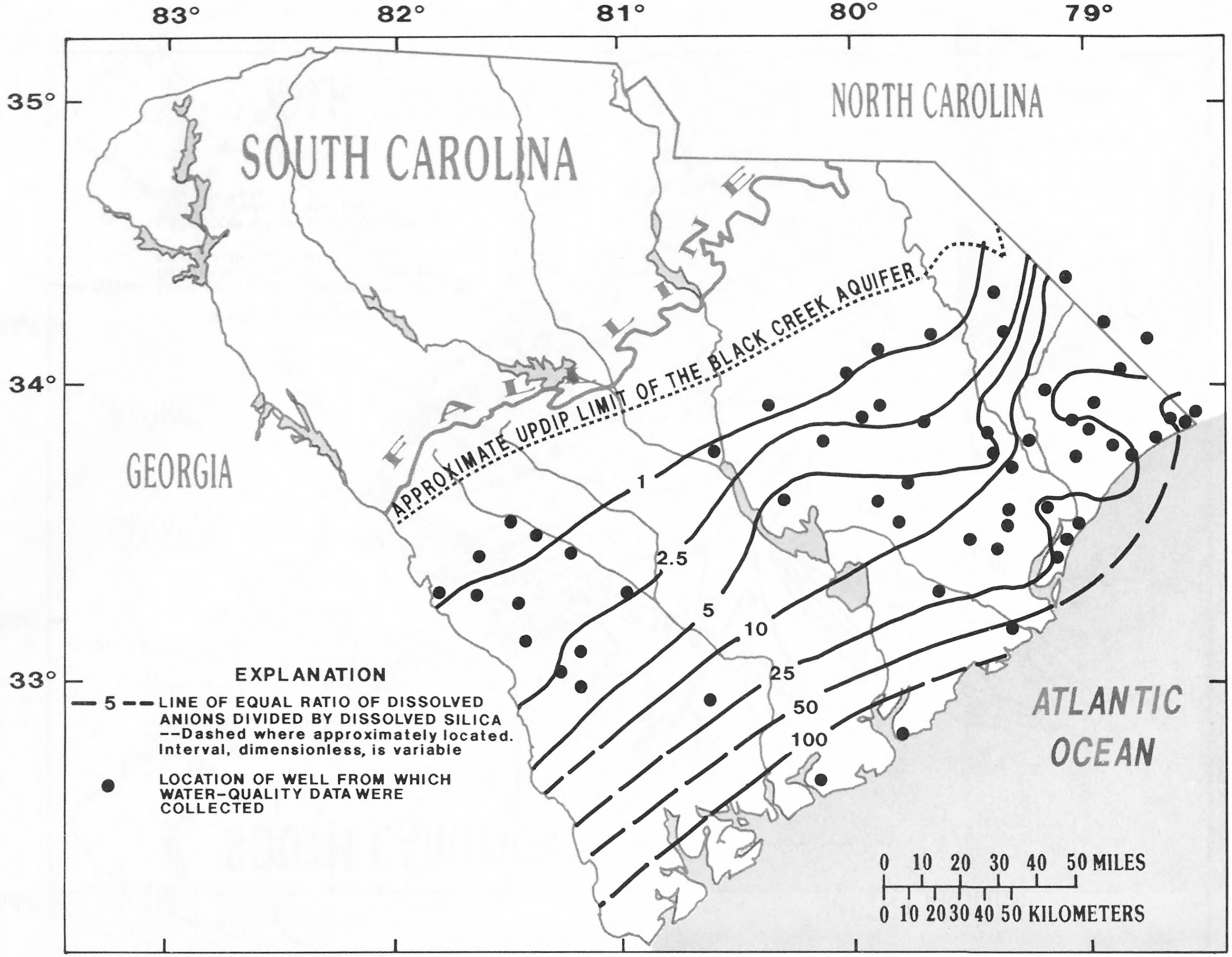


Figure 35.--Ratio of molar concentration of dissolved anions divided by dissolved silica in water from the Black Creek aquifer prior to 1983.

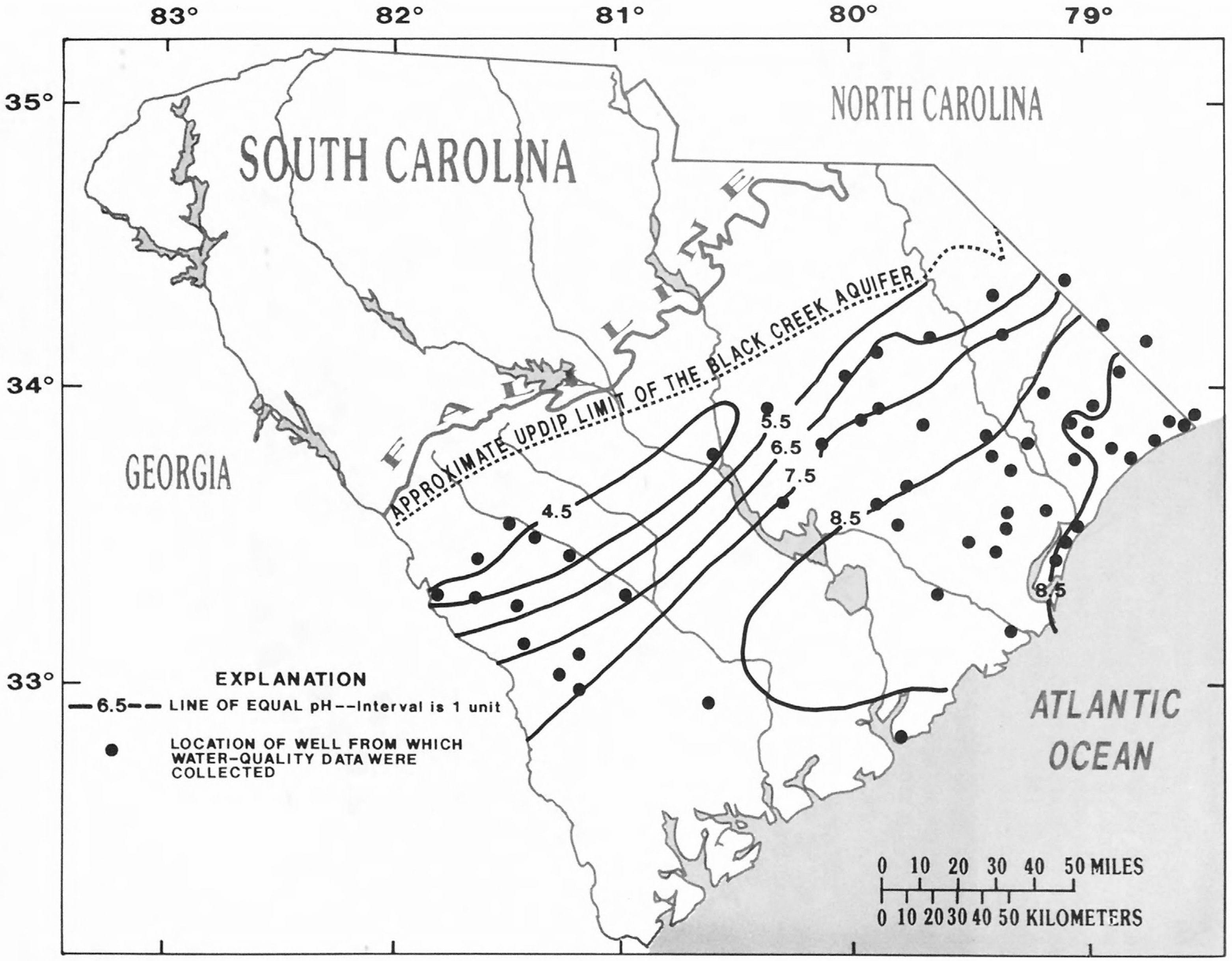


Figure 36.--The pH of water from the Black Creek aquifer prior to 1983.

Figure 37.--Relative concentrations of major ions in water from the Black Creek aquifer prior to 1983.

not available from samples from extreme upgradient parts of the aquifer. The reaction of K-feldspar with carbonic acid to form kaolinite (eq. 5) is one example of the other silicate reactions that may occur.

The downgradient decrease in dissolved silica in the northeast may result from a combination of precipitation of silicate minerals (R.W. Lee, U.S. Geological Survey, written commun., 1986), of discharge of high-silica water to streams and shallow aquifers, of lateral inflow of water from the southwestern part of the Black Creek aquifer (fig. 10) where dissolved silica concentrations are low (fig. 34), and of vertical leakage of low-silica water from the underlying Middendorf aquifer. Prior to pumpage of water from the Black Creek aquifer, the northeast was an area of discharge by upward leakage from the Middendorf aquifer to the Black Creek aquifer and from the Black Creek aquifer to shallower aquifers. Thus, discharge of water having high silica concentrations and mixing of water having high silica concentrations with water having low silica concentrations may contribute to the decrease in dissolved silica.

In the marine part of the Black Creek aquifer, the same major geochemical processes appear to dominate the geochemistry as in the marine part of the Middendorf aquifer. The downgradient dominance and increases in concentrations of dissolved sodium and alkalinity result from the dissolution of calcium carbonate (eqs. 6 and 7) and the exchange of calcium in solution for sodium on the sodium-rich clay minerals (eq. 9). This produces approximately a 1:2 sodium to alkalinity ratio (fig. 38) except in water having higher concentrations of chloride.

Although $\delta^{13}C$ data are limited (fig. 39), data indicate that the geochemical processes that contribute to the concentrations of inorganic carbon in the Black Creek aquifer may be similar to those present in the Middendorf aquifer. The $\delta^{13}C$ starts at -21.5 $^0/_{00}$ in nonmarine sediments and increases to -16.8$^0/_{00}$ in the transition from nonmarine to marine sediments. This reflects the change in the source of dissolved inorganic carbon from carbonic acid derived from the decomposition of organic materials in the nonmarine sediments to carbonic acid and the dissolution of calcium carbonate in the increasingly marine sediments (eqs. 6 and 7). The decomposition of organic matter in the nonmarine sediments is probably the primary source of most of the carbonic acid in the nonmarine part of the Black Creek aquifer, including outcrop, because the aquifer is confined throughout most of its areal extent and because of the interbedding of sand and clay layers.

Carbon-13 data from wells farther down the flow path in the marine sediments in the northeast indicate that dissolution of calcium carbonate by carbonic acid (eq. 6) and by hydrolysis (eq. 7) probably contribute to concentrations of inorganic carbon in the water. The $\delta^{13}C$ in water from the marine sediments of the Black Creek aquifer approaches -5$^0/_{00}$ similar to that of the Middendorf aquifer ($\delta^{13}C$ of about -6$^0/_{00}$). In the northeast a combination of hydrolysis of calcium carbonate and dissolution of calcium carbonate by carbonic acid may occur on the basis of the $\delta^{13}C$, of the low $pCO_2$, and of the high pH (fig. 36). The pH of water from the Black Creek aquifer is slightly lower than that from the Middendorf aquifer and decreases to the northeast. This probably results from greater $CO_2$ production, which may result from the greater organic carbon content of the Black Creek aquifer.

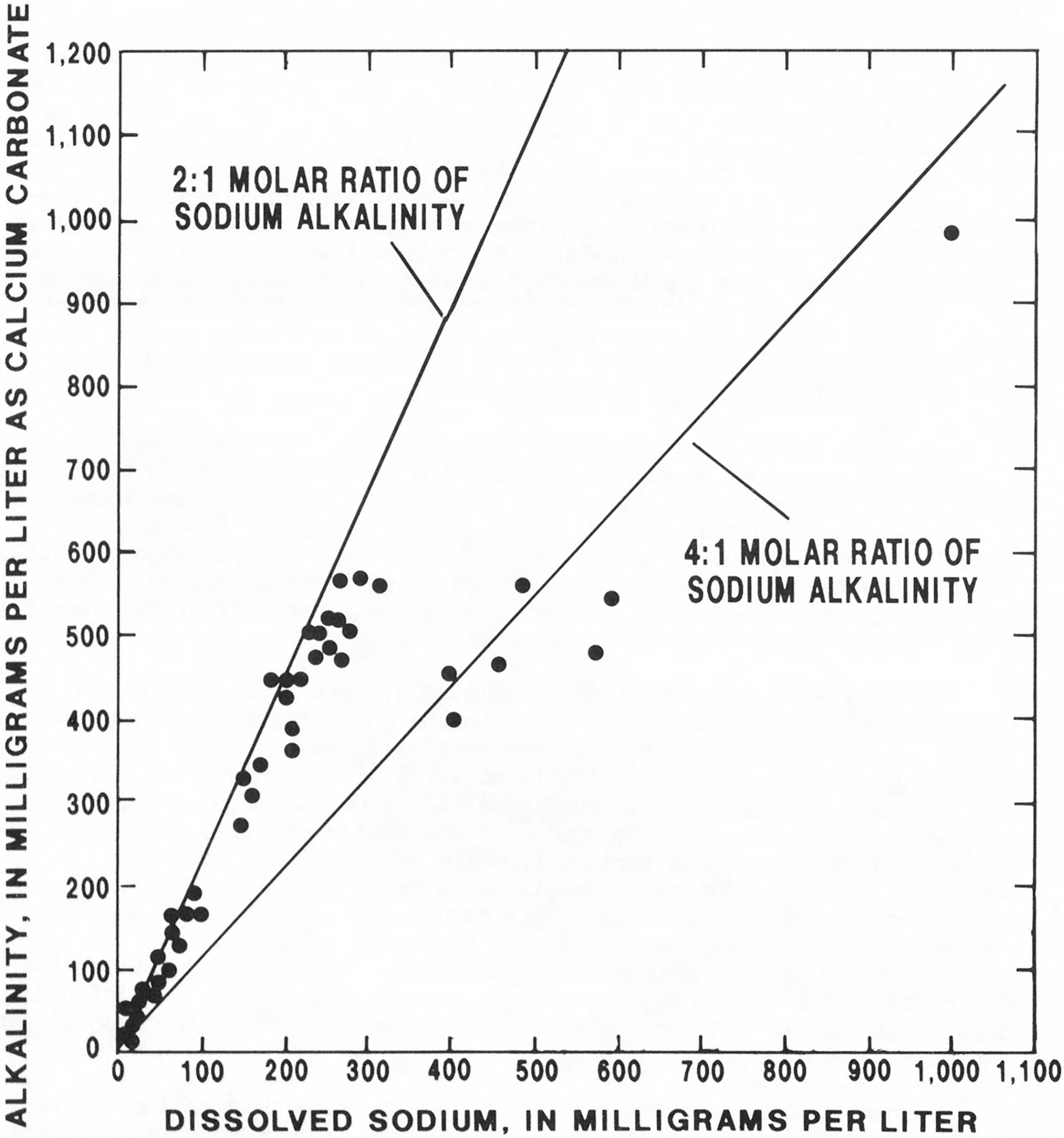


Figure 38.--Relation between dissolved sodium and alkalinity in water from the Black Creek aquifer prior to 1983.

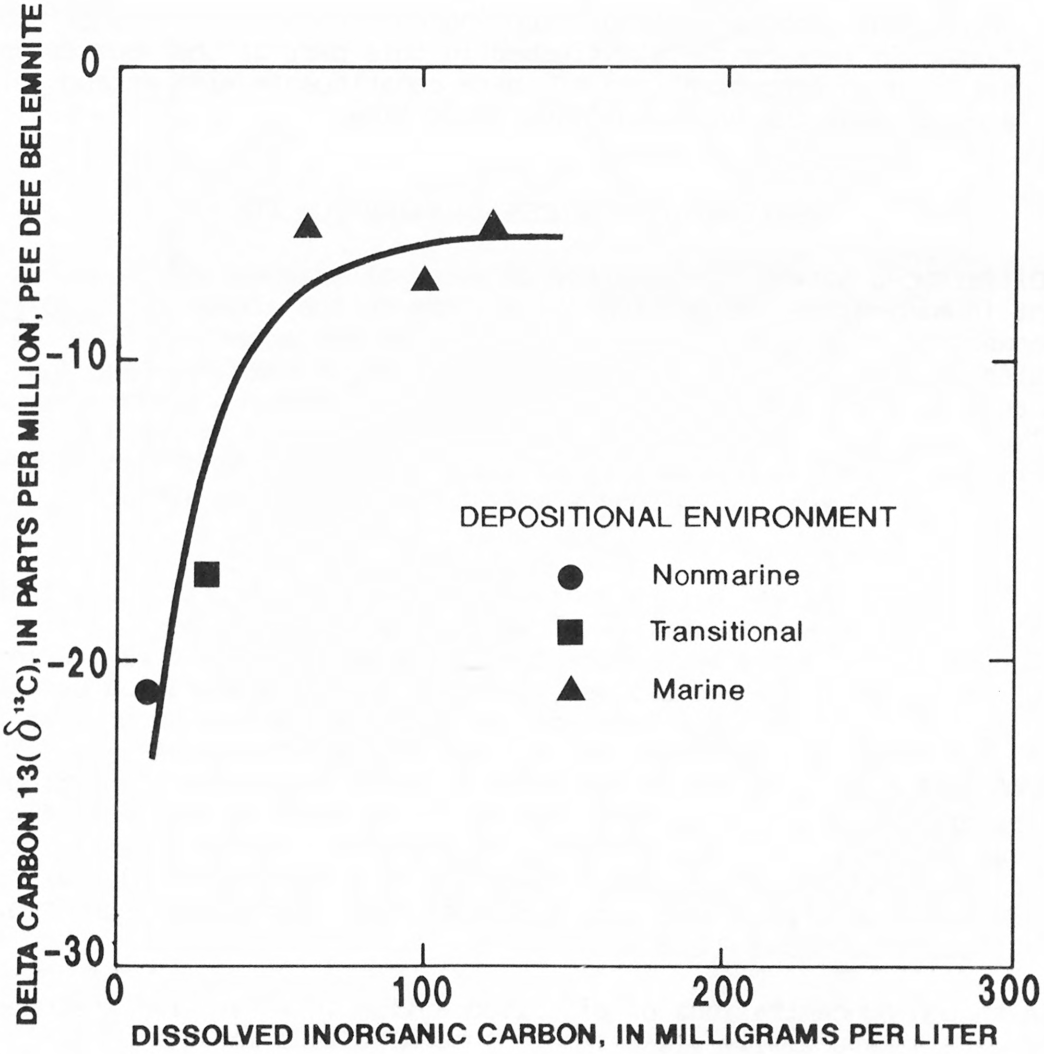


Figure 39.--Relation of dissolved inorganic carbon to $\delta^{13}$C in water from the Black Creek aquifer.

Along the southern coast, concentrations of dissolved solids (fig. 29), dissolved sodium (fig. 30), alkalinity (fig. 31), and dissolved chloride (fig. 32) are greater than in any other part of the Black Creek aquifer because of the low permeability and low potentiometric gradient of the aquifer. This causes the ground-water flow to be relatively sluggish so that more calcium carbonate dissolution and calcium-sodium exchange occur and saltwater is less completely flushed in this part of the aquifer than in other parts. High concentrations of these constituents also extend inland from the coast near the North Carolina State line.

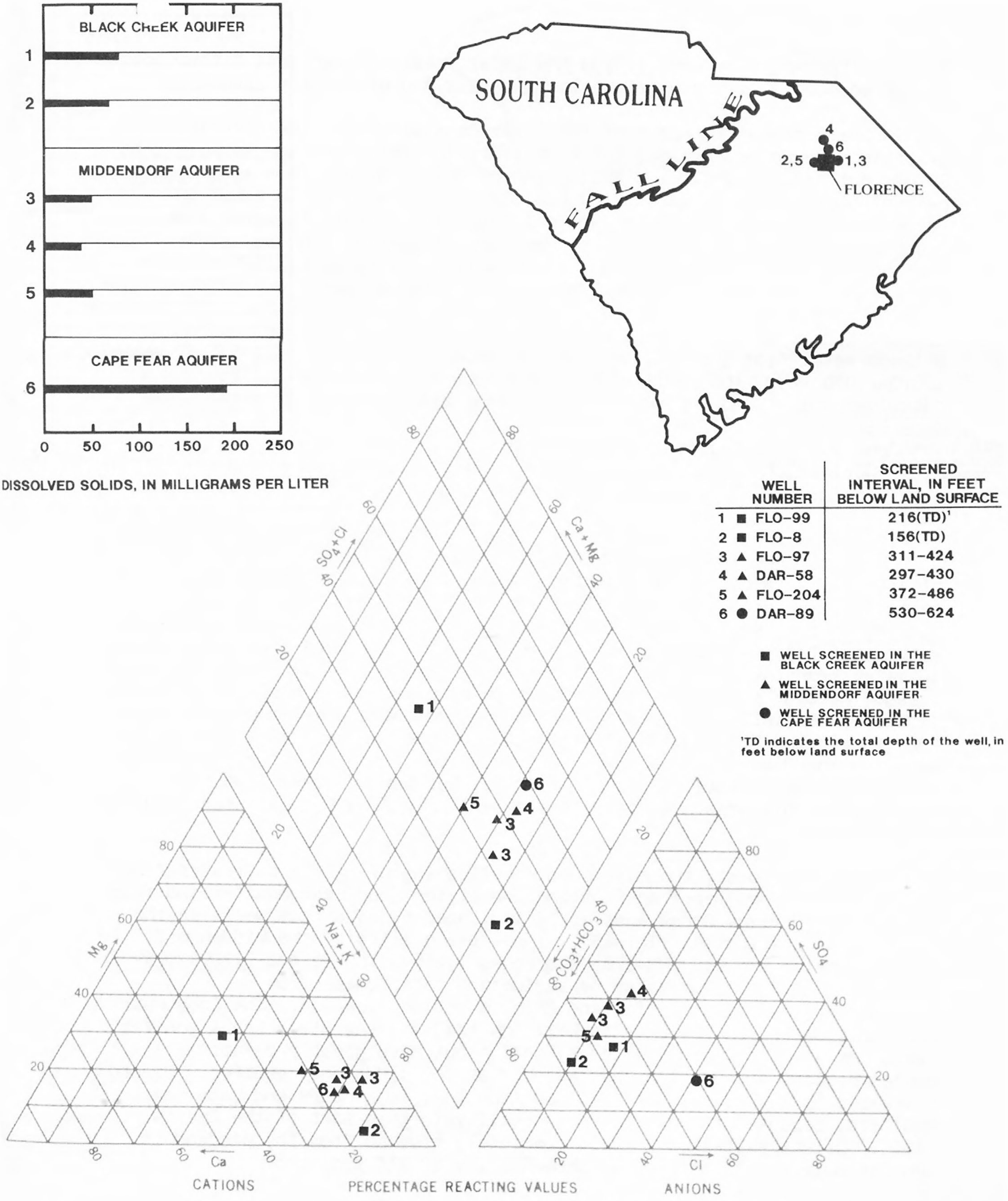
## VERTICAL DIFFERENCES IN WATER QUALITY

Differences between the quality of water of adjacent aquifers are present in many areas, reflecting differences in the effects of depositional environment on the geochemical processes and on the extent of flushing of saltwater in each aquifer. The quality of water in the Cape Fear and Middendorf aquifers can be differentiated by the greater concentrations of dissolved solids of the Cape Fear aquifer in most areas in which both aquifers are present. The quality of water in the Middendorf and Black Creek aquifers is similar in some areas and substantially different in other areas.

In the northeastern part of the upper Coastal Plain, in the vicinity of the city of Florence, the quality of water from the three aquifers in Cretaceous sediments can be differentiated primarily by differences in concentrations of dissolved solids (fig. 40). The concentration of dissolved solids in the Cape Fear aquifer (well DAR-89) is about four times that of the Middendorf aquifer (wells FLO-204, FLO-97, and DAR-58). The differences between quality of the water from the Black Creek and Middendorf aquifers are not as great as those between water from the Middendorf and Cape Fear aquifers. The concentration of dissolved solids in water from the Black Creek aquifer averages about twice (35 mg/L greater than) that from the Middendorf aquifer at the same locations (well pair FLO-99 and FLO-97 and well pair FLO-8 and FLO-204).

Although concentrations of dissolved solids in water from the Cape Fear aquifer are substantially greater than concentrations in water from the Middendorf aquifer, ions that dominate the water quality differ only slightly, with relative chloride concentrations greater in water from the Cape Fear aquifer (fig. 40). This probably occurs because of the effects of dilute concentrations of saltwater remaining in the Cape Fear aquifer.

Water from the the Black Creek aquifer may be differentiated from that of the Middendorf aquifer in some local areas by the relative concentrations of cations, but this difference does not appear to be consistent throughout the area. Relative concentrations of calcium and magnesium may be greater in water from the Black Creek aquifer in some cases as a result of the dissolution of calcium carbonate (well pair FLO-99 and FLO-97, fig. 40). However, at other locations, relative concentrations of calcium and magnesium may not be as great as in water from other parts of the Black Creek aquifer because of less dissolution of calcium carbonate or of a greater amount of calcium-sodium exchange (well pair FLO-8 and FLO-204).



| WELL NUMBER | SCREENED INTERVAL, IN FEET BELOW LAND SURFACE |
|---|---|
| 1 ■ FLO-99 | 216(TD)[1] |
| 2 ■ FLO-8 | 156(TD) |
| 3 ▲ FLO-97 | 311-424 |
| 4 ▲ DAR-58 | 297-430 |
| 5 ▲ FLO-204 | 372-486 |
| 6 ● DAR-89 | 530-624 |

■ WELL SCREENED IN THE BLACK CREEK AQUIFER

▲ WELL SCREENED IN THE MIDDENDORF AQUIFER

● WELL SCREENED IN THE CAPE FEAR AQUIFER

[1] TD indicates the total depth of the well, in feet below land surface

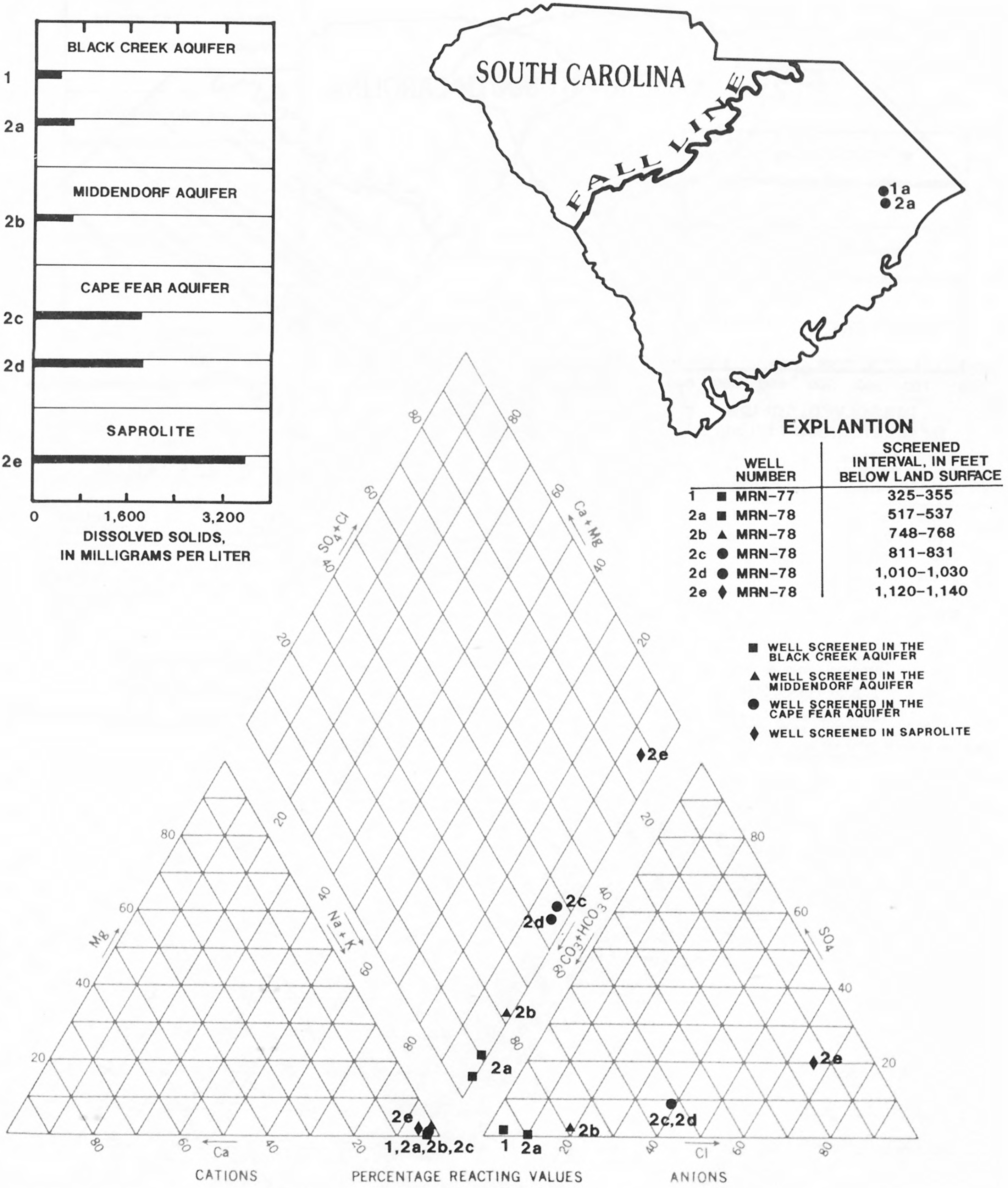
Figure 40.--Concentrations of dissolved solids and relative concentrations of major ions in water from aquifers in sediments of Cretaceous age in the northeastern upper Coastal Plain prior to 1983.

These differences may result from the local areal and vertical differences in the abundance of sodium-rich clay minerals and of calcium carbonate.

In the northeastern part of the lower Coastal Plain, the distribution of cations in water from all three aquifers in Cretaceous age is more than 95 percent sodium, and the distribution of anions grades from more than 90 percent bicarbonate in water from the Black Creek aquifer to about 50 percent bicarbonate and 50 percent chloride plus sulfate in water from the Cape Fear aquifer, as indicated by analyses of samples from wells MRN-77 and MRN-78 (fig. 41). Concentrations of dissolved solids generally increase with depth. Samples the 1,120- to 1,140-ft interval are from the saprolite underlying the Cape Fear aquifer. Differences are small in the concentrations of dissolved solids and percentages of dominant anions between water from the two zones of the Cape Fear aquifer (811-831 ft and 1,010-1,030 ft). These differences are much less than the differences in dissolved solids and in the dominant anions between water from the upper Cape Fear aquifer (811-831 ft) and the adjacent Middendorf aquifer (748-768 ft) from which saltwater is more completely flushed. Water from the Middendorf aquifer, in turn, is less completely flushed than water from the overlying Black Creek aquifer (325-355 ft and 517-537 ft).

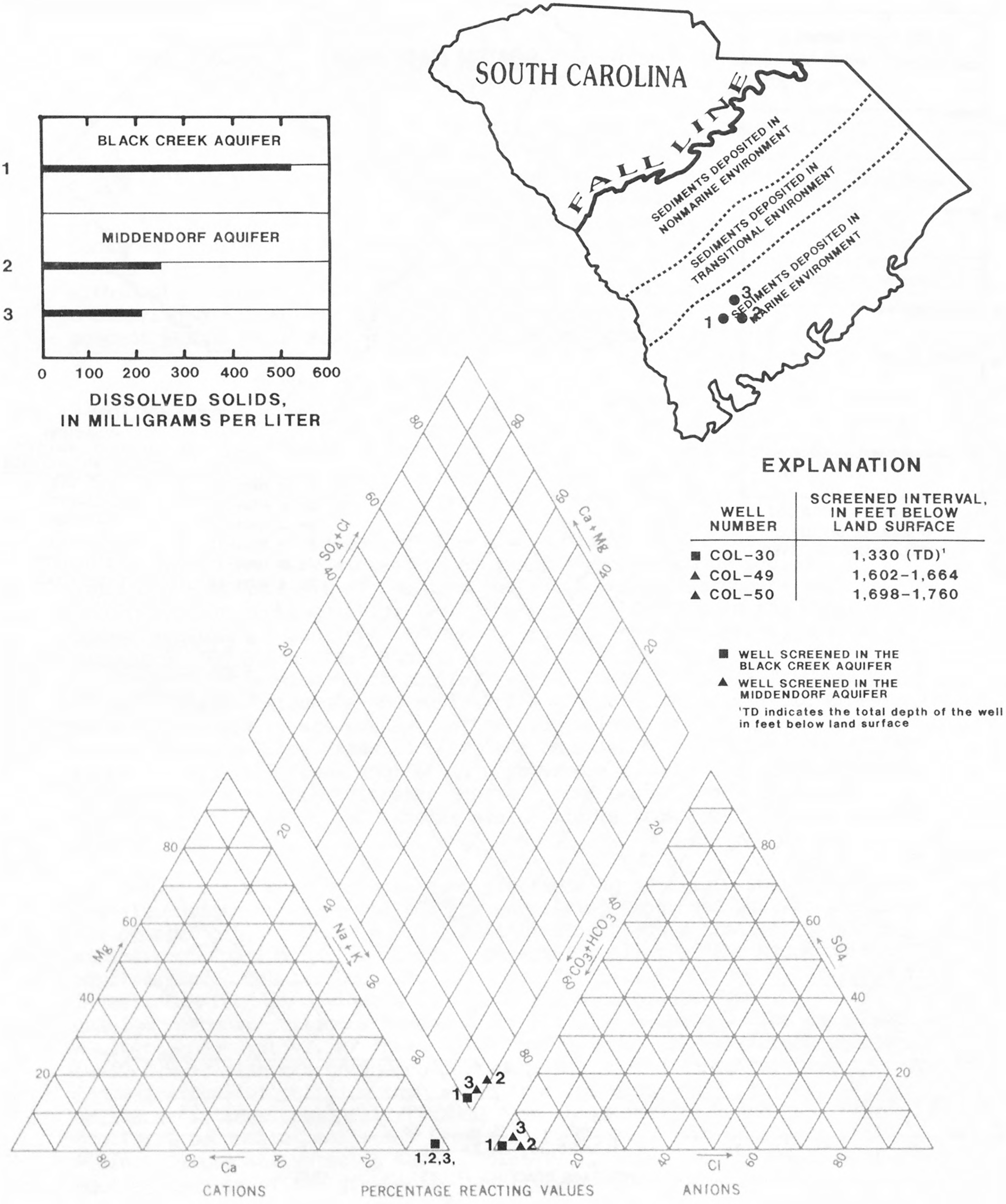
In the southwestern part of the lower Coastal Plain, the water quality of the Black Creek and Middendorf aquifers is dominated by sodium and bicarbonate as a result of the dissolution of calcium carbonate and calcium-sodium exchange (fig. 42). The major difference in the water quality of the two aquifers is that concentrations of dissolved solids in water from the Black Creek aquifer (well COL-30) are more than twice those in water from the Middendorf aquifer (wells COL-49 COL-50). This may occur because calcium carbonate and sodium-rich minerals characteristic of marine sediments initially are present farther upgradient and are generally more abundant in the Black Creek aquifer, and because the residence time of the water in the Black Creek aquifer is greater due to the lower permeability. It appears that dilute saltwater generally has been flushed from both aquifers in this area. No samples are available from the Cape Fear aquifer in this area.

Along the coast, the more complete flushing of dilute saltwater from the Middendorf aquifer than from the underlying Cape Fear aquifer and from the overlying Black Creek aquifer is indicated by data from wells in the vicinity of Charleston (fig. 43). The water quality of the Middendorf aquifer (wells CHN-14, CHN-178, and zones 2,155-2,160 ft and 2,209-2,259 ft in well CHN-174) is dominated by sodium and bicarbonate from calcium carbonate dissolution and calcium-sodium exchange. The Cape Fear aquifer (zone 2,513-2,522 ft in well CHN-174) and the Black Creek aquifer (well CHN-9) also are dominated by sodium but have greater relative concentrations of chloride than water from the Middendorf aquifer. Dilute saltwater is less completely flushed from the Black Creek and Cape Fear aquifers, because of their low permeability in this part of the Coastal Plain. Dilute saltwater is more completely flushed from the Middendorf aquifer because of the greater permeability of its sediments.



| WELL NUMBER | | SCREENED INTERVAL, IN FEET BELOW LAND SURFACE |
|---|---|---|
| 1 | ■ MRN-77 | 325–355 |
| 2a | ■ MRN-78 | 517–537 |
| 2b | ▲ MRN-78 | 748–768 |
| 2c | ● MRN-78 | 811–831 |
| 2d | ● MRN-78 | 1,010–1,030 |
| 2e | ◆ MRN-78 | 1,120–1,140 |

Figure 41.--Concentrations of dissolved solids and relative concentrations of major ions in water from aquifers in sediments of Cretaceous age at wells MRN-77 and MRN-78.



## EXPLANATION

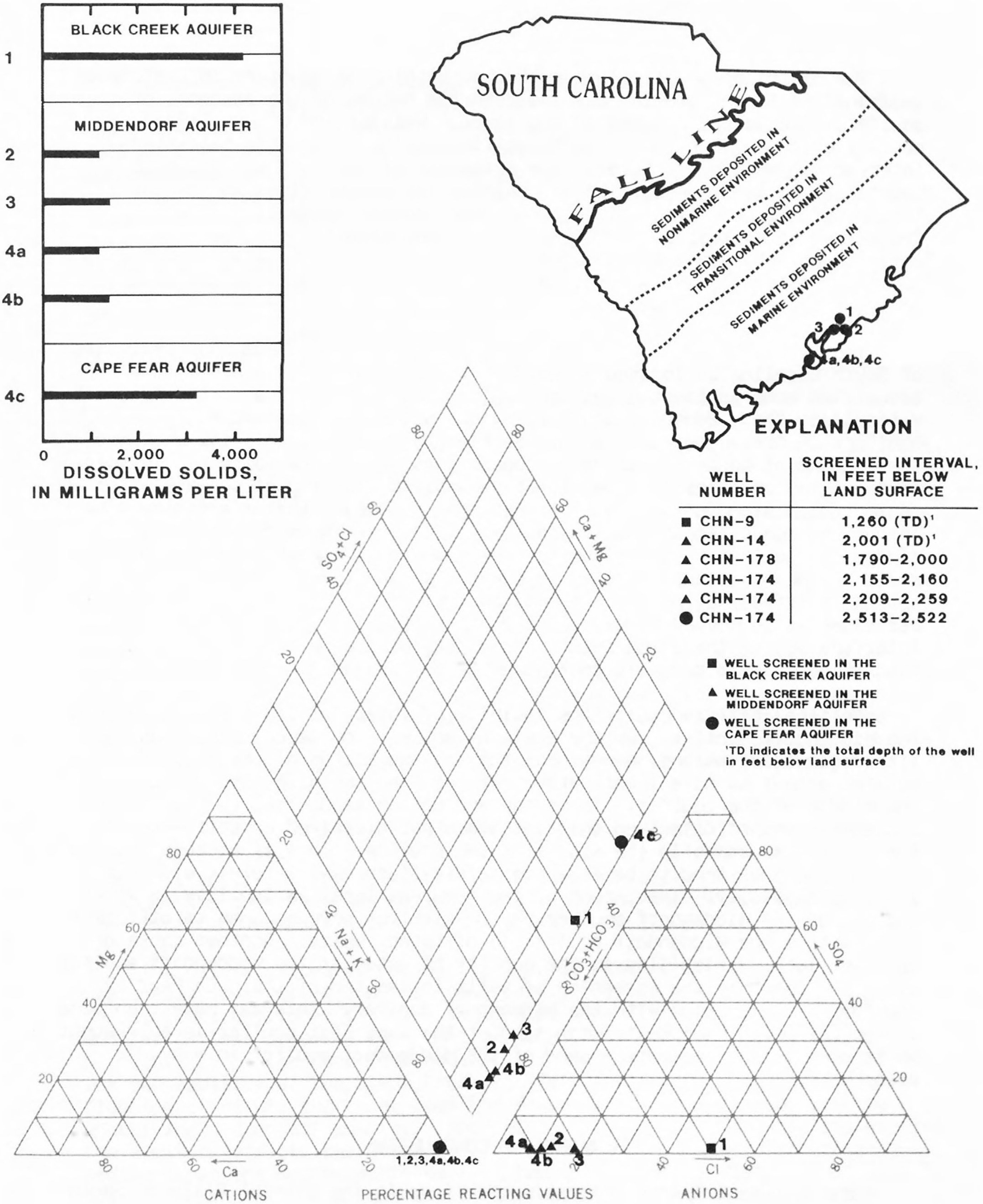
| WELL NUMBER | SCREENED INTERVAL, IN FEET BELOW LAND SURFACE |
|---|---|
| ■ COL-30 | 1,330 (TD)[1] |
| ▲ COL-49 | 1,602–1,664 |
| ▲ COL-50 | 1,698–1,760 |

■ WELL SCREENED IN THE BLACK CREEK AQUIFER

▲ WELL SCREENED IN THE MIDDENDORF AQUIFER

[1] TD indicates the total depth of the well in feet below land surface

Figure 42.-- Concentrations of dissolved solids and relative concentrations of major ions in water from aquifer in sediments of Cretaceous age at wells COL-30, COL-49, and COL-50 prior to 1983.



**EXPLANATION**

| WELL NUMBER | SCREENED INTERVAL, IN FEET BELOW LAND SURFACE |
|---|---|
| ■ CHN-9 | 1,260 (TD)[1] |
| ▲ CHN-14 | 2,001 (TD)[1] |
| ▲ CHN-178 | 1,790-2,000 |
| ▲ CHN-174 | 2,155-2,160 |
| ▲ CHN-174 | 2,209-2,259 |
| ● CHN-174 | 2,513-2,522 |

■ WELL SCREENED IN THE BLACK CREEK AQUIFER

▲ WELL SCREENED IN THE MIDDENDORF AQUIFER

● WELL SCREENED IN THE CAPE FEAR AQUIFER

[1] TD indicates the total depth of the well in feet below land surface

Figure 43.--Concentrations of dissolved solids and relative concentrations of major ions in water from aquifers in sediments of Cretaceous age in the vicinity of Charleston, S.C. prior to 1983.

The distribution of dilute saltwater within the aquifers in Cretaceous sediments of South Carolina may indicate the nature of the response of these aquifers to eustatic changes in sea level. Meisler and others (1984) present evidence that the current position of the freshwater-saltwater interface in aquifers in Cretaceous sediments of the northern Atlantic Coastal Plain is a nonequilibrium position for recent rises in sea level. This interface is characterized by a broad zone of transition from freshwater to saltwater. This transition zone results from the slow response of water in the low-permeability sediments to sea-level changes and probably reflects sea-level changes over much longer than 900,000 years (Meisler and others, 1984, p. 16).

The freshwater-saltwater interface in aquifers in Cretaceous sediments of South Carolina is located seaward of the present coast and only the transition zone is located onshore. Along the southern coast, the freshest water is in the Middendorf aquifer, which is the most permeable of the three aquifers in Cretaceous sediments. Saltier water lies both below and above the Middendorf aquifer. It would appear that the dilute saltwater in these parts of the aquifers is a result of incomplete flushing of seawater from an ancient high stand of sea level rather than a nonequilibrium position from intrusion from a recent rise in sea level, because the more permeable Middendorf aquifer contains the freshest water. The most permeable aquifer would be the fastest to respond to changes in sea level. However, the actual interface may be in a nonequilibrium position for the recent rise in sea level as indicated by Meisler and others (1984). Thus, although the interface may be intruding into the aquifer, dilute saltwater in the transition zone is probably continuing to be flushed from the aquifer.

Vertical differences in the salinity of waters also are present within the Middendorf aquifer. On the basis of analysis of geophysical logs and lithologic descriptions, sands near the top and bottom of the Middendorf aquifer appear to have lower permeabilities than the more massive sands in the middle of the aquifer. These top and bottom sands tend to have higher concentrations of dissolved chloride and other dissolved constituents near the coast than sands in the middle of the aquifer. This is because the top and bottom sands tend to be less completely flushed as a result of their lower permeability. Thus, much of the apparent local variability in water quality of the Middendorf aquifer may result from screens open to different sands within the Middendorf aquifer in different wells. Another cause of apparent local variability in the quality of water of the Middendorf aquifer along the coast is the screening of wells in the top of the Cape Fear aquifer in conjunction with the Middendorf aquifer. This may have been done in several wells because the top sand of the Cape Fear aquifer is only about 50 ft deeper than the bottom sand of the Middendorf aquifer in many areas.

## SUMMARY AND CONCLUSIONS

Cretaceous sediments comprising aquifers in the Coastal Plain of South Carolina were deposited in different environments. The depositional environments of each aquifer have a significant effect on the quality and geochemistry of water in the aquifers.

Sediments deposited in nonmarine (fluvial and upper delta plain) environments such as parts of the Middendorf and Black Creek aquifers in the upper Coastal Plain contain little, if any, calcium carbonate and sodium-rich clay minerals. Because of the slow dissolution and low solubility of the minerals in nonmarine sediments, concentrations of dissolved solids are less than in those parts of the aquifers consisting of transitional and marine sediments deposited in environments grading from lower delta plain to marine. The dissolution of silicate minerals has a significant effect on the geochemistry of these aquifers where the ratio of molar concentrations of dissolved anions divided by dissolved silica approaches 1.0. Carbon-13 data indicate that the major source of inorganic carbon in aquifers deposited in nonmarine environments is carbon dioxide from the decomposition of organic matter in the sediments.

Aquifers consisting of transitional and marine sediments deposited in environments grading from lower delta plain to marine contain various amounts of calcium carbonate and sodium-rich clay minerals. These aquifers include the lower Coastal Plain part of the Middendorf aquifer and much of the Black Creek aquifer. The geochemistry of these aquifers is dominated by the dissolution of calcium carbonate and the exchange of calcium for sodium on the sodium-rich clay minerals. Carbon-13 data indicate that the dissolution of calcium carbonate may occur by a combination of hydrolysis and of the action of carbonic acid derived from the unfractionated, fractionated, and preferential decomposition of organic matter. Although the hydrolysis reaction produces one hydroxyl ion for each bicarbonate ion produced, the pH of the water is less than might be expected for the hydrolysis reaction. This may occur because the clay minerals may act as a buffer, possibly by providing ferrous ion from the inner layer of the smectite clay minerals to form slightly soluble ferrous hydroxide. The ferrous ion would be replaced on the clays by calcium ions derived from the dissolution of calcium carbonate, thus maintaining charge balance in solution and on the clays.

The freshwater-saltwater interface in the aquifers in Cretaceous sediments is seaward of the present coast and only dilute saltwater of the zone of transition from saltwater to freshwater is present onshore. Although the interface may be intruding landward, the dilute saltwater of the transition zone is being flushed seaward.

The dilute saltwater has not been fully flushed from aquifers in Cretaceous sediments along the coast partly because of the effects of depositional environment of the sediments. The flushing of the Cape Fear aquifer is less complete than that of other aquifers because of the low permeability of the Cape Fear aquifer. In the southern coastal area, the low permeability of the Black Creek aquifer results in less complete flushing of dilute saltwater from the Black Creek aquifer than from the underlying Middendorf aquifer. Incomplete flushing of dilute saltwater from the aquifers affects the water quality of all three aquifers in Cretaceous sediments in the northeastern part of the lower Coastal Plain. This area is toward the end of the ground-water flow paths in all of these aquifers.

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