GEOCHEMISTRY OF THE FLORIDAN AQUIFER SYSTEM IN FLORIDA AND IN PARTS OF GEORGIA, SOUTH CAROLINA, AND ALABAMA

REGIONAL AQUIFER-SYSTEM ANALYSIS

Geochemistry of the Floridan Aquifer System in Florida and in Parts of Georgia, South Carolina, and Alabama

By CRAIG L. SPRINKLE

REGIONAL AQUIFER-SYSTEM ANALYSIS—FLORIDAN AQUIFER SYSTEM

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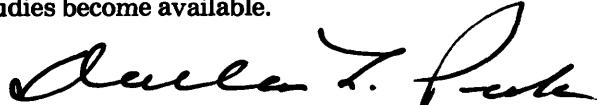
FOREWORD

THE REGIONAL AQUIFER-SYSTEM ANALYSIS PROGRAM

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

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

Dallas L. Peck
Director

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[Plates are in pocket]

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METRIC CONVERSION FACTORS

For readers who wish to convert measurements from the inch-pound system of units to the metric system of units, the conversion factors are listed below:

Multiply inch-pound units	By	To obtain metric units
inch (in)	2.540	centimeter (cm)
foot (ft)	0.3048	meter (m)
square foot per day (ft^2/d)	0.929	square meter per day (m^2/d)
cubic foot per second (ft^3/s)	0.02832	cubic meter per second (m^3/s)
mile (mi)	1.6093	kilometer (km)
square mile (mi^2)	2.590	square kilometer (km^2)
gallon per minute (gal/min)	0.06308	liter per second (L/s)
degree Fahrenheit (°F)	-32 (9/5)	degree Celsius (°C)

ALTITUDE DATUM

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

GEOCHEMISTRY OF THE FLORIDAN AQUIFER SYSTEM IN FLORIDA AND IN PARTS OF GEORGIA, SOUTH CAROLINA, AND ALABAMA

By Craig L. Sprinkle

ABSTRACT

The chemical quality of the ground water in the Floridan aquifer system is determined primarily by mineral-water interaction. However, some changes in water quality have been imposed by development, particularly near coastal pumping centers. A total of 601 chemical analyses, all from different wells, most completed in the upper part of the aquifer system, were used to describe the variations in water chemistry and to study the processes responsible for observed changes.

The Floridan aquifer system is a vertically continuous sequence of Tertiary carbonate rocks that are of generally high permeability and are hydraulically connected in varying degrees. The rocks are principally limestone and dolomite, but they grade into limy sands and clays near the aquifer system's updip limits. Major minerals in the aquifer system are calcite, dolomite, and, locally, gypsum or quartz; minor minerals include apatite, glauconite, and clay minerals such as kaolinite and montmorillonite. Trace amounts of metallic oxides or sulfides are present in some areas.

The aquifer system consists of the Upper and Lower Floridan aquifers, separated in most places by a less permeable confining unit that has highly variable hydraulic properties. Only the Upper Floridan aquifer is present throughout the study area. Freshwater enters the aquifer system in outcrop areas located primarily in central Georgia and north-central Florida. Discharge occurs chiefly to streams and springs and, to a lesser extent, directly into the sea. Most of the flow into and out of the system takes place where it is unconfined or where the upper confining unit is thin. Secondary permeability developed by dissolution of aquifer material is most prominent in these areas of dynamic flow.

Dissolved-solids concentrations in water from the Upper Floridan aquifer generally range from less than 25 milligrams per liter near outcrops to more than 25,000 milligrams per liter along the coasts. The dominant cations in the ground water are Ca^{2+}, Mg^{2+}, and Na^+; the dominant anions are HCO_3^-, Cl^-, and SO_4^{2-}. The concentration of Ca^{2+} is controlled primarily by calcite saturation. Concentrations of Mg^{2+}, Na^+, and Cl^- are highest where mixing of freshwater and saltwater occurs. Concentrations of HCO_3^- reflect the control of calcite solubility. The concentration of SO_4^{2-} is highest where gypsiferous rock units are present in the aquifer system.

The major geochemical processes that occur in the Upper Floridan aquifer, based on water-quality maps and computations using a geochemical model, are (1) dissolution of aquifer minerals toward equilibrium, (2) mixing of ground water with recharge, leakage, or seawater, (3) sulfate reduction, and (4) cation exchange between water and aquifer minerals.

Similar processes apparently control minor dissolved constituents, although quantification is difficult with the available data. Statistical tests of available nutrient data indicate that concentrations of N (nitrogen) species in unconfined recharge areas may be increasing over time; more detailed studies of all N species are needed to test this hypothesis, however. Data on trace metals, radionuclides, and man-made organic contaminants are limited. Available data indicate that most freshwater within the Upper Floridan is potable, but detection of pesticides in a few samples indicates that the system is susceptible to contamination from the land surface in some areas, particularly where its upper confining unit is thin or absent.

Geochemical models were used to examine changes in major chemical elements along selected ground-water paths within the Upper Floridan aquifer. Water in the Upper Floridan aquifer can be categorized into four hydrochemical facies, whose exact distribution is determined by confined or unconfined conditions of the aquifer and by chloride concentrations. The reaction models are considered plausible based on available chemical, isotopic, and hydrologic information, and they clearly reveal the dominant effects of aquifer confinement on ground-water chemistry. In unconfined areas, large volumes of dilute water recharge the system and dissolve minerals contained in the aquifer, thus enhancing the aquifer's permeability. In coastal areas, geochemical-model results indicate that the mixing of freshwater and seawater leads to carbonate dissolution or precipitation, depending in part on the ratio of freshwater to seawater. The geochemical models also indicate that significant sulfate reduction may occur in confined areas; this suggests that there is some flux of carbon into the aquifer system, a factor that must be considered when using ^{14}C measurements to determine ground-water-flow velocities.

INTRODUCTION

The Floridan aquifer system in the Southeastern United States is one of the most productive aquifer systems in the world. It is an areally extensive (fig. 1) sequence of carbonate rocks previously described as the
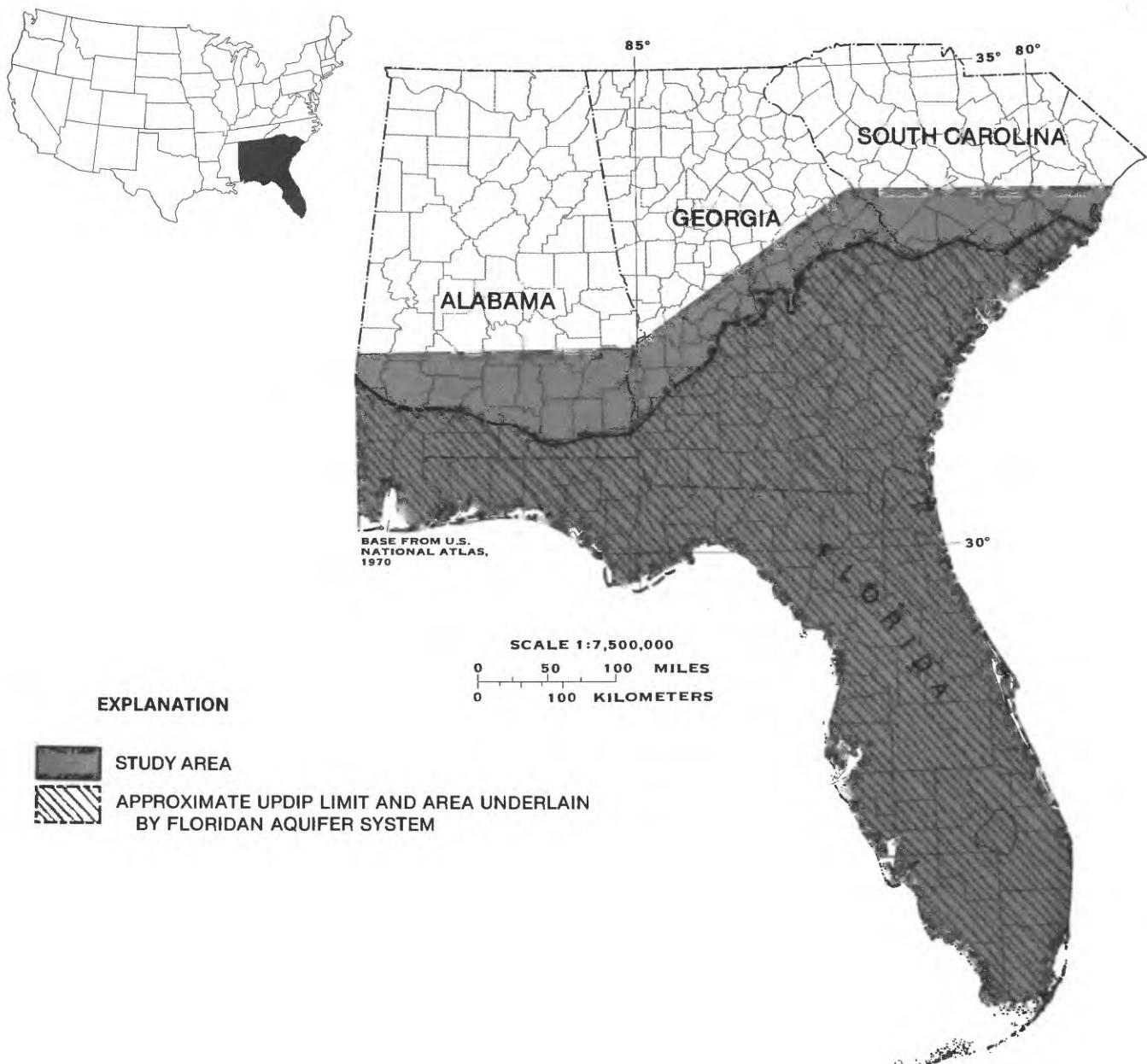
FIGURE 1.—Areal extent of the Floridan aquifer system.

Floridan aquifer in Florida (Parker and others, 1955) and the principal artesian aquifer in Florida, Georgia, Alabama, and South Carolina (Stringfield, 1966). More than 3 billion gallons of water are pumped from the aquifer system daily, making it the principal source of water for municipal, industrial, and agricultural use in southern Georgia and most of Florida. In large areas of Georgia and Florida, tremendous untapped reserves of freshwater are stored in the Floridan aquifer system. However, near some urban centers intensive development has led to declining water levels and localized degradation of water quality.

The chemical quality of ground water in the Floridan aquifer system is an important aspect to be considered in managing the aquifer. Specific information required for management includes a description of (1) the natural chemical character of both the aquifer and its water, (2) the processes that control the natural ground-water chemistry, (3) changes that have been imposed on water quality by development, and (4) actual or potential degradation of water quality which might limit future use.

In 1978, the U.S. Geological Survey began a study (Johnston, 1978) to describe the hydrogeologic frame-

work, geochemistry, and regional ground-water flow of the Floridan aquifer system. The Floridan study is one of several such studies in the Geological Survey's Regional Aquifer-System Analysis (RASA) program, which is a systematic effort to investigate aquifer systems that supply a major part of the Nation's water supply. The results of the Floridan RASA study are reported in U.S. Geological Survey Professional Paper 1403, which consists of the following chapters: A, summary (Johnston and Bush, 1988); B, hydrogeologic framework (Miller, 1986); C, hydraulics and regional flow (Bush and Johnston, 1988); D through H, subregional descriptions, including simulation of local water-supply problems; and I, geochemistry (this report).

PURPOSE AND SCOPE

The purposes of this report are to (1) summarize the available information on the mineralogy of the rocks and the quality of the water in the Floridan aquifer system and (2) describe the principal processes that have produced the present water chemistry.

One constraint of the RASA program was to use available data to the extent possible, in order to minimize costs and shorten time of study. Therefore, this report contains the published and unpublished results of many previous investigations. New chemical and isotopic data were collected in some areas, but a comprehensive program of water and rock sampling for chemical or isotopic analysis was not within the scope of the project. This report contains descriptions of climate, geological framework, hydrology, mineralogy, and chemistry of the Floridan aquifer system. The report concludes with a discussion of conceptual geochemical models and results of mass-transfer modeling of major chemical constituents in the Upper Floridan aquifer.

PREVIOUS REPORTS

A comprehensive bibliography of studies of the Floridan aquifer system published prior to 1965 is given in Stringfield (1966). A brief list of papers that discuss aspects of Floridan aquifer system geochemistry includes Back (1963), Hsu (1963), Hanshaw and others (1966), Kaufman and others (1969), Back and Hanshaw (1970), Hanshaw and others (1971), Rightmire and others (1974), Osmond and others (1974), Plummer (1975), Briel (1976), Kaufmann and Bliss (1977), Plummer (1977), Dalton and Upchurch (1978), Randazzo and Hickey (1978), Hanshaw and Back (1979), Rye and others (1981), Steinkampf (1982), and Plummer and others (1983). The other chapters of Professional Paper 1403 and interim reports by Ryder (1982), Tibbals (1981), and Krause (1982) should be consulted for more detailed

descriptions of the geology and hydrology of the Floridan aquifer system.

HYDROGEOLOGIC SETTING

CLIMATE AND RECHARGE

The study area (fig. 1) has a climatic range from temperate in the north to subtropical in the south and along the Gulf Coast. Mean annual temperatures range from about 18.6 °C in east-central Georgia to about 25.4 °C in the Florida Keys. These moderate air temperatures are partially reflected in ground-water temperatures measured in the Upper Floridan aquifer (fig. 2).

Precipitation is the primary source of recharge to the Floridan aquifer system. Annual precipitation (mostly rainfall) ranges from 40 inches (in) in Key West, Fla., to more than 65 inches in the Florida Panhandle and in southern Alabama. Most of the rainfall in Florida and the coastal areas of Alabama, Georgia, and South Carolina occurs as thunderstorms during the summer months. A significant part of the average annual rainfall in coastal areas may also be produced by tropical storms and hurricanes. In central Georgia, annual rainfall is more evenly divided between summer thunderstorms and cyclonic (frontal) storm systems that occur during winter and spring.

Stable isotope chemistry of the water that recharges the aquifer system is affected by the seasonal distribution of rainfall. As discussed by Gat (1980, p. 30), rainfall during the winter months is lighter in isotopes of ^{18}O and ^{2}H than during the summer months. Because evapo-
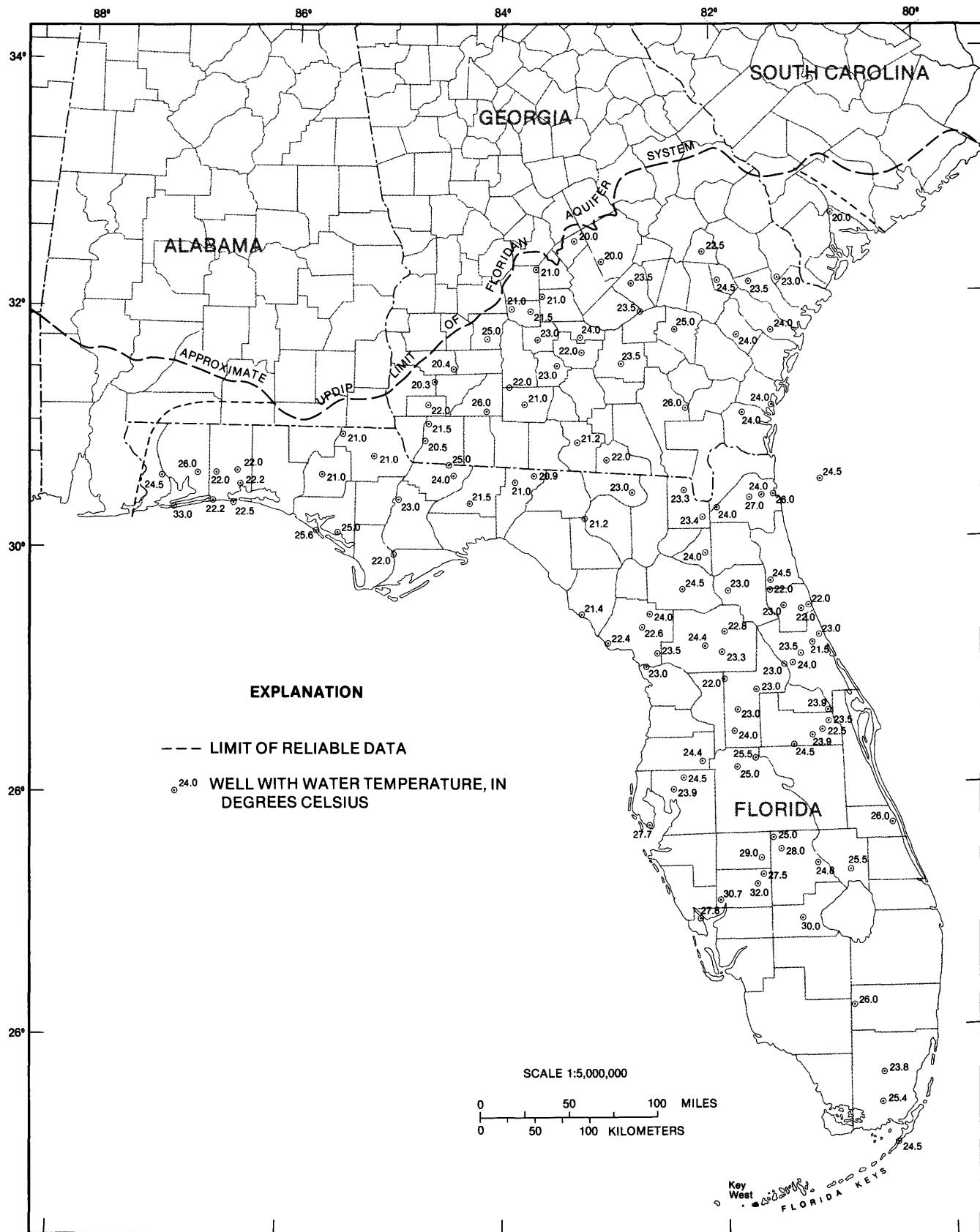
FIGURE 2.—Temperatures measured in water samples from selected wells in the Upper Floridan aquifer.

transpiration is less during winter than during summer, more winter rainfall recharges the aquifer system.

Isotopic data from wells in the Floridan aquifer system (fig. 3A) are plotted in figure 3B. The meteoric water line (Craig, 1961) in figure 3B is a relation developed from the isotopic composition of freshwater worldwide. As shown in figure 3B, the rainwater recharging the aquifer system in central Georgia is isotopically lighter (values of $\delta^{18}O$ and δ^2H are more negative) than recharge in central Florida. The Georgia data generally lie near and to the left of the meteoric line; the Florida data lie to the right and away from the line. This pattern probably results from subtle differences in the rate of the evaporation and condensation cycles of the rainfall recharging the aquifer system in the two States.

A few isotopic data plotted in figure 3B lie off the meteoric line, toward the point that represents standard mean ocean water (SMOW). The data points of shallow-deep pairs show a similar trend toward the SMOW reference point. These data suggest that mixing of seawater with freshwater has occurred in the aquifer system. In some areas, there is seawater deep within the aquifer system which may be tapped directly by wells (for example, wells 1, 2, and 3, fig. 3A). In other areas, remnant seawater at depth has been diluted by the freshwater flow system (for example, wells 4 and 6, fig. 3A).

The chemical quality of ground water in the Upper Floridan aquifer is derived initially from the chemical quality of recharge. The quality of ground water at any point in the Upper Floridan aquifer has evolved from a sequence of chemical reactions between the recharge water and aquifer materials. Later sections of this paper discuss reaction models that simulate the chemical evolution of ground water in the Upper Floridan. The chemistry of infiltration recharge is affected by processes, such as evaporation and dissolution of natural and manmade salts in soils, that tend to increase the concentrations of major ions in ground water above those of rainwater. Yet, for modeling purposes, estimates of the quality of recharge in areas where the aquifer is unconfined can be made from the chemistry of precipitation.

Available data on the chemistry of precipitation over the study area are sparse (fig. 4). A few studies have been made (for example, Junge and Werby, 1958; Lodge and others, 1968; Hendry and Brezonik, 1980; Irwin and Kirkland, 1980; National Atmospheric Deposition Program, 1980a–e, 1981a–c; Tanaka and others, 1980), but complete regional coverage is not available. The available data are summarized in table 1. As discussed by Gambell and Fisher (1966), sea salt is the most significant source of chloride in rainfall in coastal areas; they also noted a sharp decrease in chloride concentrations in rainfall collected farther inland. It is possible, therefore, that the data reported in table 1 for coastal cities are not representative of precipitation chemistry farther inland, where most of the recharge to the Upper Floridan occurs.

GEOLOGIC FRAMEWORK

The Floridan aquifer system as defined by Miller (1986, p. 44) is a vertically continuous sequence of carbonate rocks of generally high permeability that are mostly of Tertiary age; the rocks are hydraulically connected in varying degrees, and their permeability is generally an order to several orders of magnitude greater than that of the rocks bounding the system above and below. The system consists of rock units varying in age from Late Cretaceous to early Miocene and is composed of stratigraphic units previously included in the principal artesian aquifer described by Stringfield (1966) and in the Floridan aquifer in Florida described by Parker and others (1955). Figure 5 gives the general correlation of stratigraphic units and aquifer terminologies. The base of the system is shown in figure 6, simplified from a map by Miller (1986, pl. 33). As explained by Miller (1986), correlation of the geologic units that form the base of the system is imprecise at this time and, consequently, similar rocks may have different formation names in different States. Because the base of the aquifer system is a hydrologic boundary, corresponding to a substantial change in permeability, the age and lithology of the rock in which the base is mapped may vary considerably. In much of the region, the base of the system is in low-permeability, clastic rocks (locally calcareous) which separate the limestones of the Floridan aquifer system from deeper clastic aquifers. In peninsular Florida and southeastern Georgia, rocks containing bedded anhydrite form the base of the Floridan aquifer system.

The top of the aquifer system, shown in figure 7, is placed at the top of highly permeable carbonate rocks that are hydraulically connected (Miller, 1986, p. 46). This means the top of the system may lie within a stratigraphic unit rather than at its top. The approximate landward extent of the aquifer system is shown in figure 1. The line marking the approximate updip limit of the system has been placed where the system is less than 100 feet (ft) thick and where the clastic rocks interbedded with the limestone make up more than 50 percent of the section (Miller, 1986, p. 48). In central and southwestern Georgia, some clastic units that are stratigraphically equivalent to limestone units in the Floridan aquifer system are considered part of the Southeastern Coastal Plain sand aquifer system (Renken, 1984). In southern Georgia, the sand aquifer system transmits water generally in a southeasterly direction. Discharge from

EXPLANATION

○⁴ WELL NUMBER AND LOCATION IN FLORIDAN
     AQUIFER SYSTEM—Number corresponds to
     data plotted in figure 3B

A
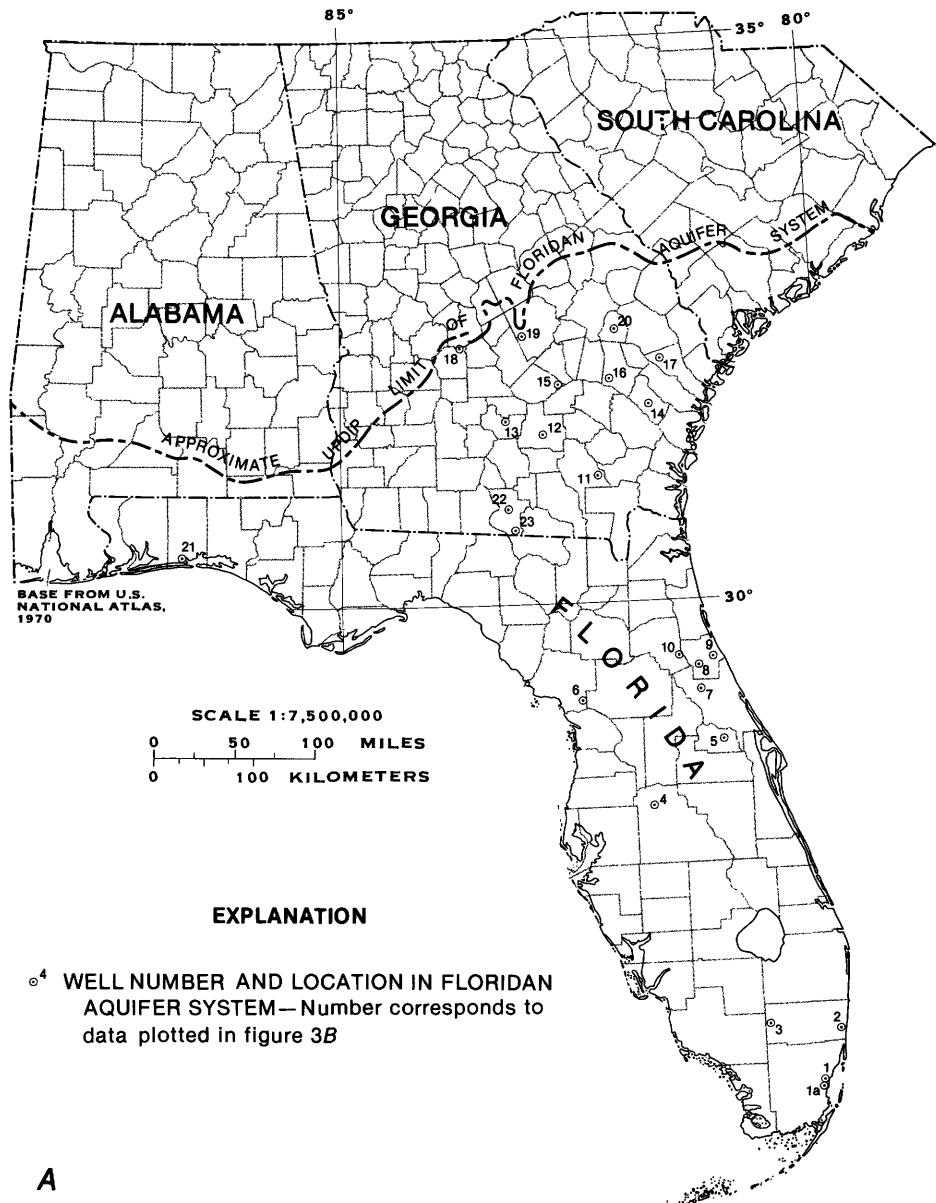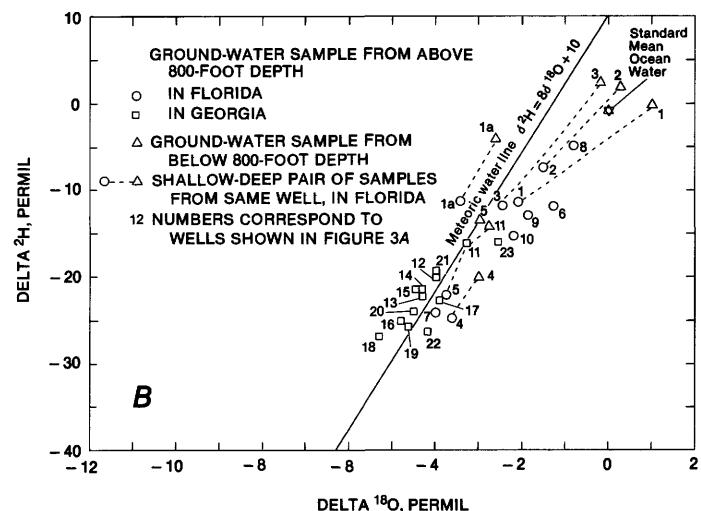
FIGURE 3—A, Location of wells in the Floridan aquifer system
sampled for hydrogen and oxygen stable isotopes; B, Delta²H and
delta¹⁸O of ground water from the Floridan aquifer system.
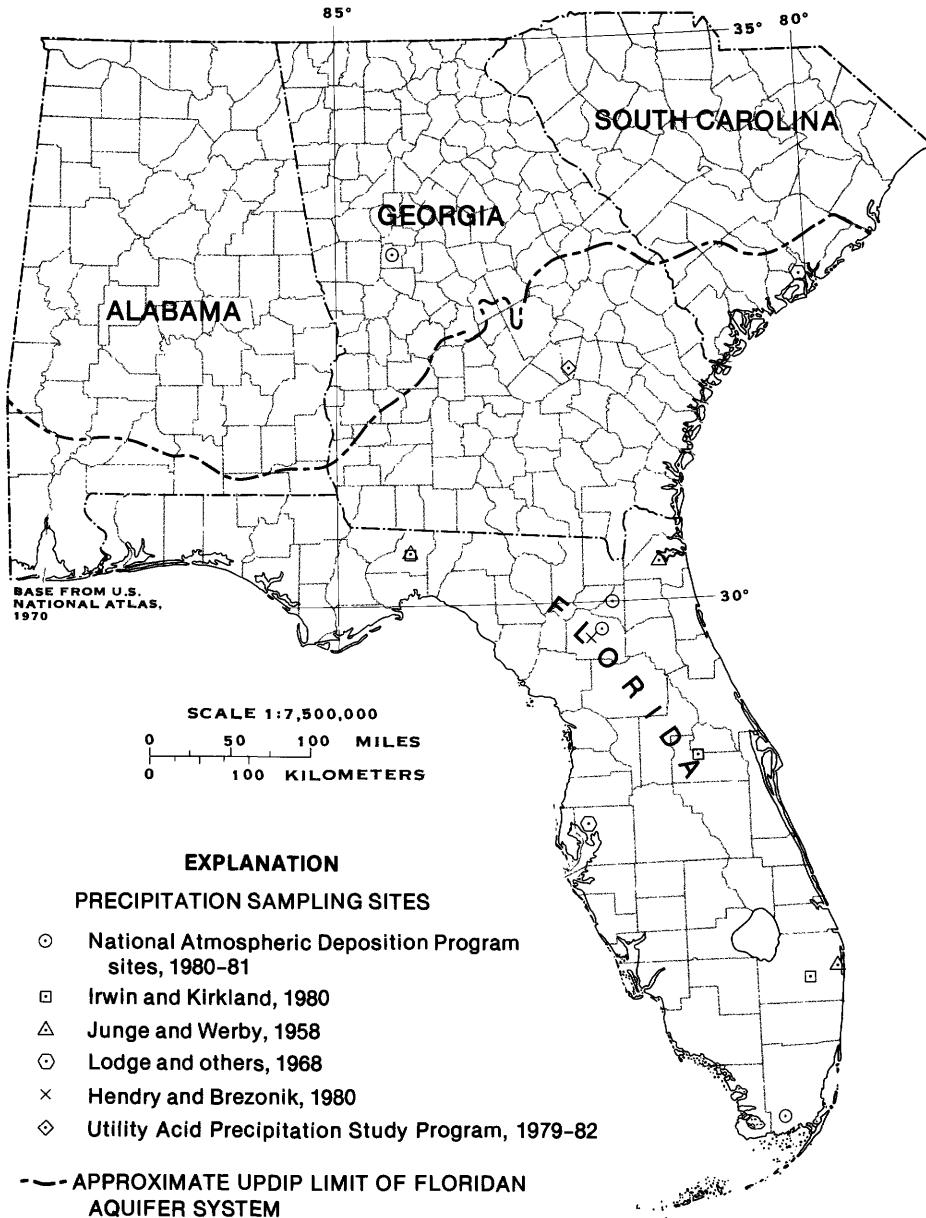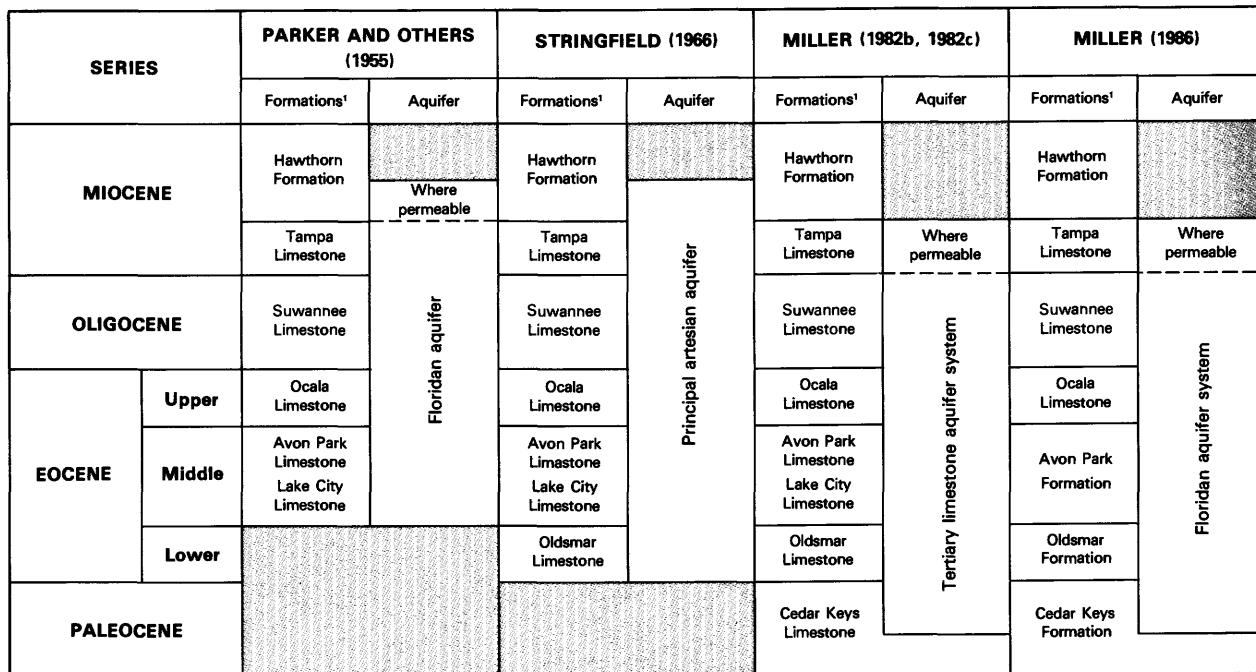
FIGURE 4.—Selected sampling sites for water quality of precipitation in Florida, Georgia, and
South Carolina.

underlying clastics into the Floridan aquifer system is occurring; some of the chemical effects of this discharge are discussed in later sections of this report. However, the total quantity and areal distribution of water transferred between the Floridan aquifer system and the Southeastern Coastal Plain sand aquifer system are not well understood. The Floridan aquifer system grades westward by facies change into clastic rocks but is interrupted in Alabama by the Mobile Graben and Gilbertown-Pickens-Pollard fault zones (fig. 8). On the downthrown sides of these faults, low-permeability clastics form a hydraulic barrier between the limestones of the Floridan on the east and stratigraphically equivalent

limestones lying north and west. In southeastern South Carolina, the younger limestone units of the system change facies into low-permeability clastics. Thus, in South Carolina, contours shown in figure 7 indicate the top of older limestone units, until they also become predominantly clastic toward the northeast (Miller, 1986).

The rocks making up the Floridan aquifer system vary in thickness from less than 100 ft in outcrop areas in Alabama, Georgia, and South Carolina to about 3,500 ft downdip in southwestern Florida. The system is composed primarily of limestones and dolomites throughout most of Florida and southeastern Georgia. Formations

SERIES		PARKER AND OTHERS (1955)		STRINGFIELD (1966)		MILLER (1982b, 1982c)		MILLER (1986)	
		Formations[1]	Aquifer	Formations[1]	Aquifer	Formations[1]	Aquifer	Formations[1]	Aquifer
MIOCENE		Hawthorn Formation	Where permeable	Hawthorn Formation		Hawthorn Formation		Hawthorn Formation	
		Tampa Limestone		Tampa Limestone		Tampa Limestone	Where permeable	Tampa Limestone	Where permeable
OLIGOCENE		Suwannee Limestone	Floridan aquifer	Suwannee Limestone	Principal artesian aquifer	Suwannee Limestone	Tertiary limestone aquifer system	Suwannee Limestone	Floridan aquifer system
EOCENE	Upper	Ocala Limestone		Ocala Limestone		Ocala Limestone		Ocala Limestone	
	Middle	Avon Park Limestone Lake City Limestone		Avon Park Limestone Lake City Limestone		Avon Park Limestone Lake City Limestone		Avon Park Formation	
	Lower			Oldsmar Limestone		Oldsmar Limestone		Oldsmar Formation	
PALEOCENE						Cedar Keys Limestone		Cedar Keys Formation	

[1] Names apply only to peninsular Florida and
   southeast Georgia except for Ocala
   Limestone and Hawthorn Formation.

FIGURE 5.—Generalized correlation chart and aquifer terminology of the Floridan aquifer system. (Modified from Johnston and Bush, 1988.)

TABLE 1.—*Average concentration of major ions and nutrients in wet precipitation in Florida, Georgia, and South Carolina*

[Concentrations in milligrams per liter. Dashes indicate constituent not analyzed]

Location of precipitation collector[1]	Major ion						Nutrient			
	Ca	Mg	Na	K	Cl	SO_4	NO_3	NH_4^+	Organic C	PO_4
Tampa, Fla.[2]	1.61	0.20	1.01	0.15	1.54	3.34	0.34	----	----	----
Charleston, S.C.[2]	0.44	0.82	1.06	0.22	1.43	2.75	0.71	----	----	----
Gainesville, Fla.[3]	0.41	0.12	0.44	0.20	0.98	2.05	0.84	0.13	5.20	----
Tallahassee, Fla.[4,5]	0.43	----	0.53	0.13	0.66	0.48	0.17	0.18	0.8	----
Loxahatchee, Fla.[4]	3.4	0.6	2.3	0.4	3.9	3.2	1.4	0.41	2.2	----
Maitland, Fla.[4]	1.1	0.3	1.0	0.5	1.6	2.6	1.3	1.0	4.0	----
Jacksonville, Fla.[5]	0.89	----	0.96	0.11	1.02	1.48	----	----	----	----
West Palm Beach, Fla.[5]	0.56	----	1.62	0.10	2.44	0.99	----	----	----	----
Bradford Forest, Fla.[6]	0.32	0.10	1.14	0.12	2.00	2.27	1.05	0.15	----	0.02
Austin-Cary Forest, Fla.[6]	0.76	0.11	1.29	0.34	1.23	2.52	2.70	0.13	----	0.01
Everglades National Park, Fla.[6]	0.23	0.11	0.73	0.11	1.23	1.37	0.74	0.17	----	0.07
Griffin, Ga.[6]	0.19	0.06	1.01	0.11	0.54	3.03	1.16	0.37	----	0.23
Uvalda, Ga.[7]	0.12	0.04	0.26	0.04	0.53	1.50	0.97	0.18	----	0.01

[1] Location map given in figure 4.
[2] Lodge and others, 1968. Nitrogen reported by authors as inorganic nitrogen (unspeciated).
[3] Hendry and Brezonik, 1980.
[4] Irwin and Kirkland, 1980. Average of bulk precipitation.

[5] Junge and Werby, 1958.
[6] National Atmospheric Deposition Program 1980–81. Average of weekly wet samples.
[7] Utility Acid Precipitation Study Program 1981–82. Average of 98 precipitation events.
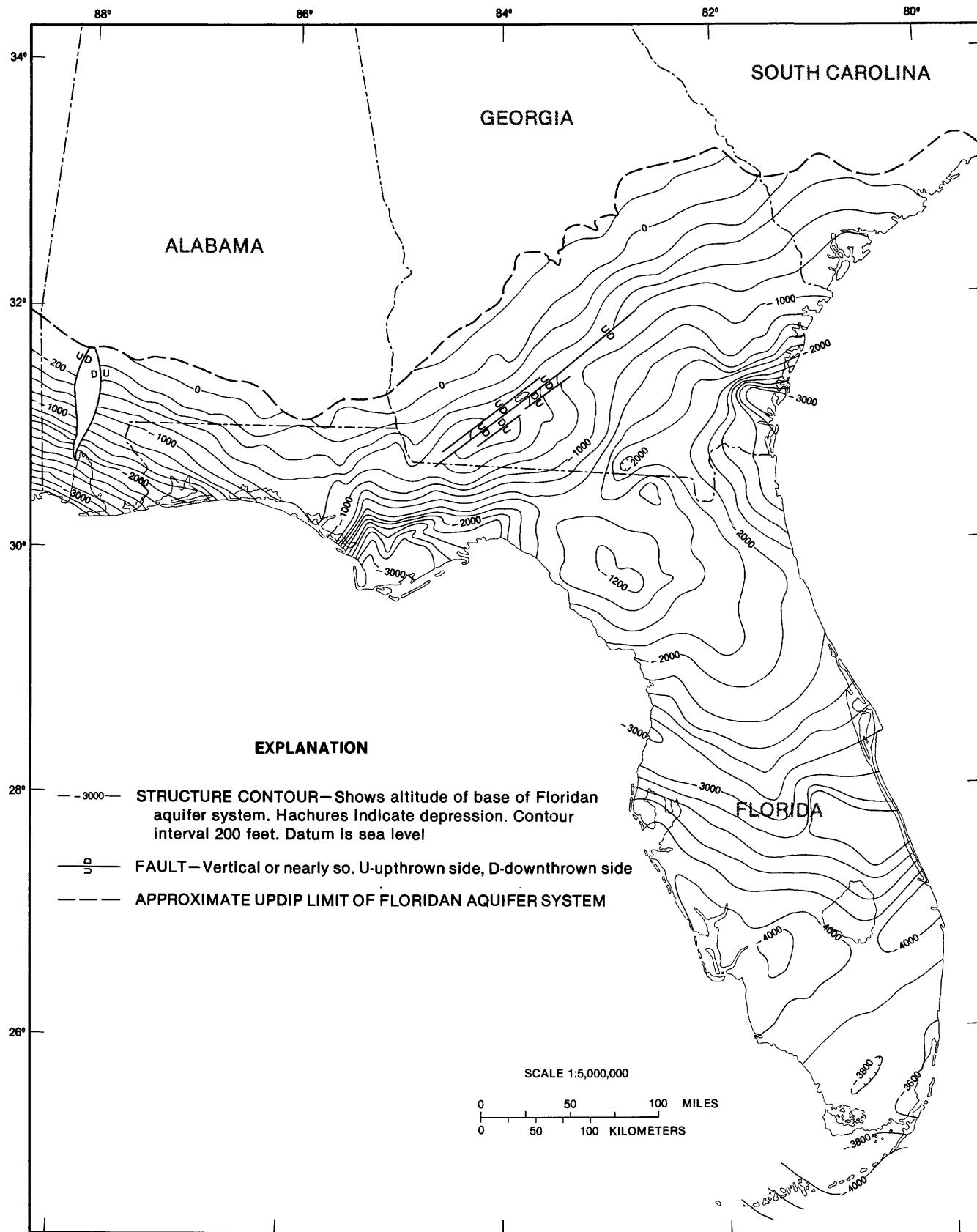
FIGURE 6.—Configuration of the base of the Floridan aquifer system. (Modified from Miller, 1986.)
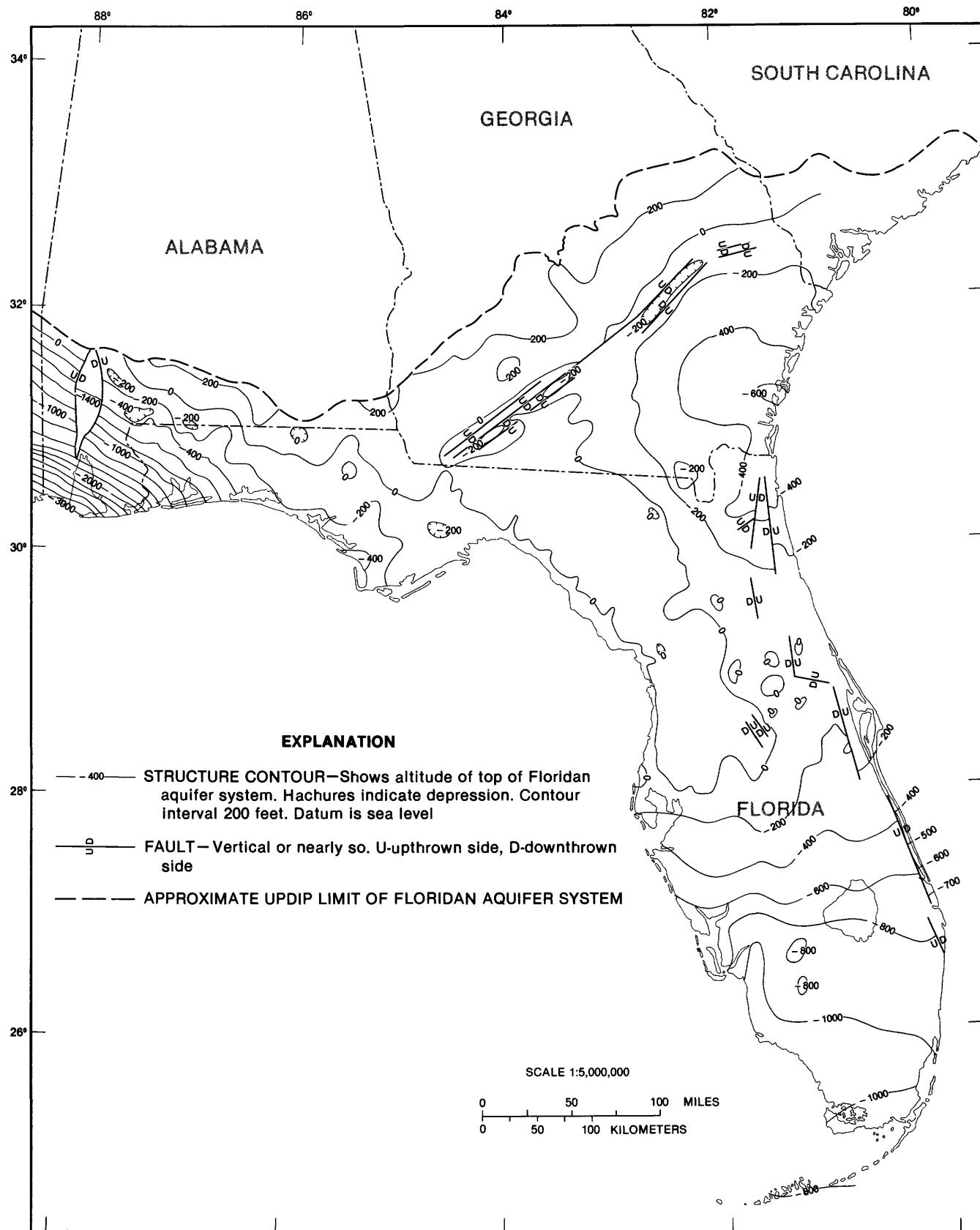
FIGURE 7.—Configuration of the top of the Floridan aquifer system. (Modified from Miller, 1986.)
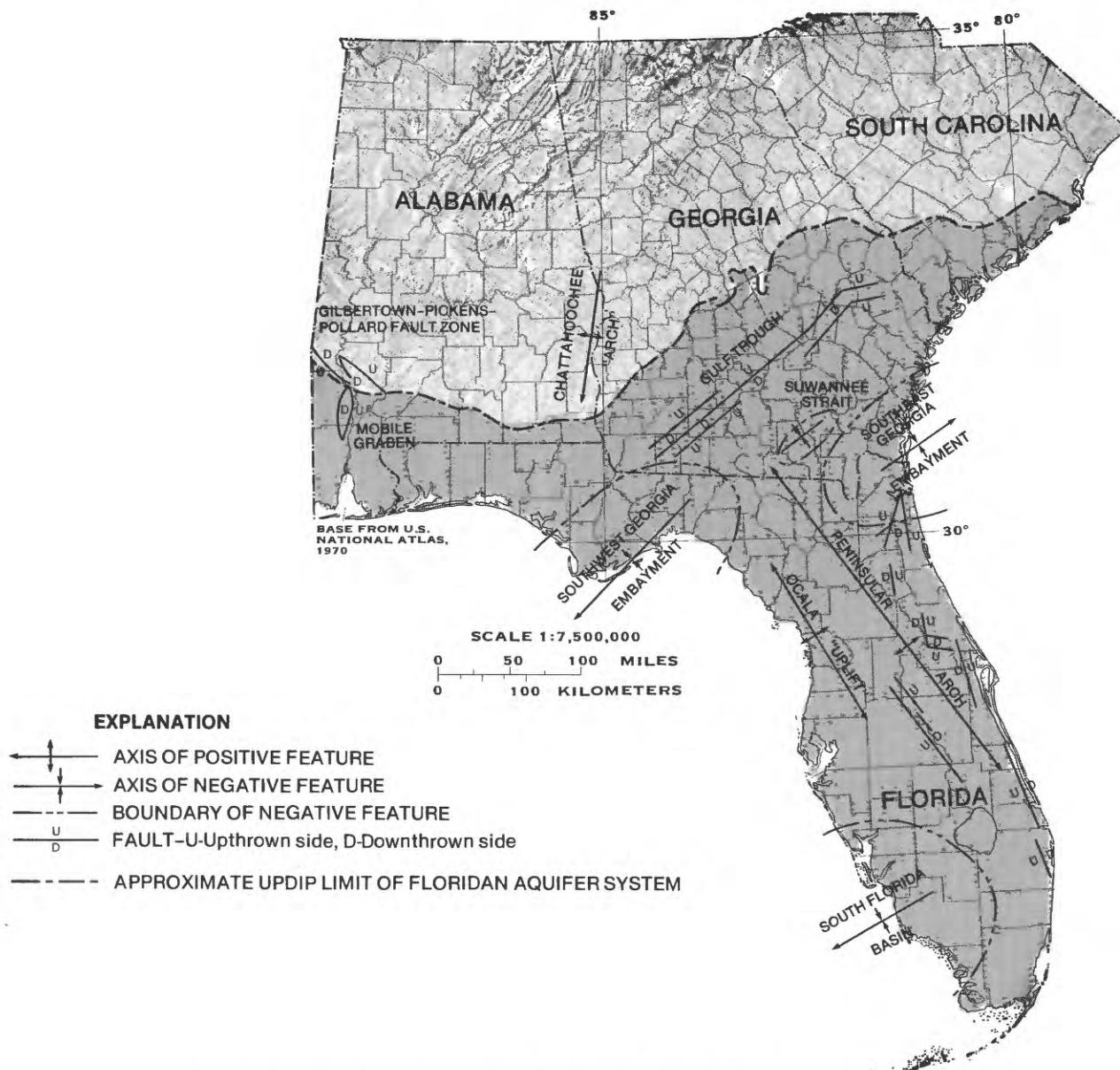
FIGURE 8.—Geologic structures affecting the Floridan aquifer system. (From Miller, 1986.)

within the aquifer system change facies, however, into more arenaceous clastics in western Florida and southeastern Alabama. In the southwestern and northeastern parts of the Coastal Plain of Georgia and in adjacent South Carolina, the limestones grade into limy sand and clay, both laterally and vertically. Between periods of deposition, limestone units of the Floridan aquifer system were locally exposed to subaerial weathering. Where weathering was extensive, sinkholes and other karst features developed. In many areas these paleosinkholes were filled with younger clay and sand, when the

seas again drowned the landscape (Stringfield, 1966, p. 200–202).

Miller (1986) has described the geology of the Floridan aquifer system in detail; therefore, the following discussion is much abbreviated. The youngest rocks making up the aquifer system crop out along an area extending through Alabama, Georgia, and South Carolina that approximately parallels the Fall Line. Outcrops in central peninsular Florida are related to major geologic structures—the Peninsular arch and the Ocala uplift (fig. 8). Where present in Alabama, Georgia, and South

Carolina, the rocks making up the aquifer system dip gently toward the sea. In Florida, the formations generally dip away from the positive structural features shown in figure 8 and dip toward the negative features. Development of the structures affecting the aquifer system began in the Early Cretaceous and extended through the late Tertiary.

The rocks of the aquifer system in peninsular Florida were deposited in shallow marine environments typified by the modern-day Bahama Banks. The nearshore intertidal deposits of coquina and coarse-grained limestones may grade laterally into lagoonal and subtidal micrites, locally containing peat and evaporites. In some units, bedded evaporites (primarily anhydrite or gypsum) that may have formed in sabka or tidal flat environments are present. The deep-water limestones are characteristically fine grained and fossil bearing, with only trace amounts of noncarbonate minerals.

Throughout most of the Paleocene and Eocene, deep-sea environments separated the northern Florida peninsula from panhandle Florida, Alabama, and Georgia. Into this trough were carried continental sediments from the north and northwest. Thus, the shallow marine carbonates of the Cedar Keys, Oldsmar, and Avon Park Formations grade progressively northward into limy muds, silts, and sands. During the late Eocene, a major transgression occurred and the Ocala Limestone was deposited over nearly all the region shown in figure 1. The Ocala is commonly a soft, chalky coquina containing minor chert and dolomite locally. This formation has high permeability throughout most of the study area; in fact, most of the water that discharges from the aquifer system comes from springs in the Ocala Limestone (Bush, 1982; Bush and Johnston, 1988). After the late Eocene, continentally derived sand, silt, and clay again were deposited with carbonates in Alabama, Georgia, and northern Florida. In peninsular Florida, the Suwannee Limestone was deposited in a shallow marine environment during the late Oligocene. Where present, the Suwannee Limestone is also a highly productive water-bearing formation.

During the early Miocene, parts of the region underwent cycles of emergence and submergence beneath the sea. The Tampa Limestone was deposited during this period, and in west-central Florida it contains both marine and freshwater limestones. In areas where the sea did not retreat, the Tampa Limestone merges without definite boundary into the overlying Hawthorn Formation; in emergent areas, an unconformity is present between these units. The Hawthorn Formation is a thick sequence of interbedded clay, sand, limestone, sandy phosphatic limestone, and marl. The Hawthorn is present over more than 50 percent of the area underlain by the Floridan aquifer system and is the major upper confining unit for the system.

MINERALOGY

The matrix of the Floridan aquifer system is composed primarily of calcite and dolomite, with minor gypsum, apatite, glauconite, quartz (or chert), clay minerals (kaolinite and montmorillonite?), and trace amounts of metallic oxides and sulfides. Locally, measurable amounts of peat are present as thin (1–5 millimeters; mm) layers in the limestone.

MAJOR MINERALS

Calcite, the most abundant mineral in the Floridan aquifer system, ranges in composition from stoichiometric calcite ($CaCO_3$) to magnesian calcite ($Ca_{0.96}Mg_{0.04}CO_3$) (Hanshaw and others, 1971, table 1). The magnesium content of calcite from aquifer cores in Waycross, Ga., and Polk City, Fla., ranged from 0 to 2.7 mole percent Mg, with three of four samples less than 1 percent. Although cores of the entire Floridan aquifer system have not been systematically analyzed, "magnesian calcites probably account for less than 0.1 percent of the [Floridan] limestones by weight" (Plummer, 1977, p. 802), owing to the instability of magnesian calcites relative to stoichiometric calcite in fresh or slightly saline water. Other elements present at trace levels in calcite are sodium, strontium, iron, and manganese. Data on iron and manganese content of calcite from the aquifer system are scarce; sodium and strontium may be present in calcite in concentrations as high as 440 and 600 parts per million (ppm) (Metrin, 1979), respectively, depending on the aqueous environment during formation of the mineral. The sodium and strontium contents of calcite analyzed by Metrin (1979) averaged less than 200 ppm and less than 500 ppm, respectively; these values were interpreted by Randazzo and others (1983) to indicate a brackish ground-water environment of diagenesis of middle and upper Eocene rocks (Upper Floridan aquifer) in west-central Florida.

The amount of dolomite in the aquifer system varies both laterally and vertically within and between formations. In a core obtained from a deep test well near Polk City, Polk County, Fla. (pl. 1), dolomite accounted for about 8 percent of the rocks of the Upper Floridan aquifer, about 95 percent of the rocks of the underlying confining unit, and about 9 percent of the rocks penetrated in the Lower Floridan aquifer (A.S. Navoy, U.S. Geological Survey, written commun., 1982). Near Waycross, Ga. (pl. 1), where the base of the Upper Floridan aquifer is also the base of the aquifer system, cores and cuttings from a deep test well were about 30 percent

dolomite (Matthews and Krause, 1984, pl. 1). In south-central Georgia and eastern Alabama, the aquifer system is composed entirely of the Ocala Limestone, and dolomite is absent from the system. Within the aquifer system, dolomite ranges in composition from stoichiometric dolomite ($CaMg(CO_3)_2$) to low-magnesium dolomite ($Ca_{1.12} Mg_{0.88}(CO_3)_2$) (Randazzo and Hickey, 1978, p. 1178). This variability in composition of dolomite undoubtedly affects its solubility in ground water. Recent petrographic studies by Cook (1984) indicate that the nonstoichiometric centers of dolomite crystals in the Floridan aquifer system have dissolved while the more stoichiometric rims have remained. Unfortunately, little is known about the location and volumetric occurrence of nonstoichiometric dolomite in the aquifer system. Furthermore, quantitative data on the solubility of nonstoichiometric dolomite are lacking. These factors prevent making more than general estimates of the saturation state of dolomite in the Floridan aquifer system.

The origin of dolomite within the aquifer system is a subject of continuing study (Hsu, 1963; Hanshaw and others, 1971; Randazzo and others, 1977; Randazzo and others, 1983). The magnesium content of dolomite is often cited as an indicator of the diagenetic environment during formation of the mineral (for example, Land, 1973; Veizer and Demovic, 1974; Folk and Land, 1975). Other elements that are present in dolomite in trace amounts are also used to indicate environments of diagenesis, especially strontium and sodium. Owing to its large ionic size, the strontium ion primarily replaces the calcium ion in the $CaCO_3$ "layer" of dolomite (Behrens and Land, 1972). Strontium has been determined in concentrations as high as 288 ppm in Eocene dolomite of west-central Florida (Sarver, 1978). Sodium ions are smaller than calcium ions but much larger than magnesium ions; thus, sodium should substitute primarily for calcium in the $CaCO_3$ "layer" of dolomite, although Land and Hoops (1973) suggested that sodium could substitute equally for either calcium or magnesium in dolomite. Sodium has been determined in concentrations as high as 1,200 ppm in Eocene dolomite of west-central Florida (Metrin, 1979). The high concentrations of sodium in dolomite of the Floridan aquifer system appear to indicate that the dolomite formed in moderately saline solutions (Randazzo and others, 1983). The magnesium, sodium, and strontium contents of dolomites in the aquifer system have been used in conjunction with rock textures as evidence for multiple diagenetic episodes in the development of the Upper Floridan aquifer in west-central Florida (Randazzo and others, 1977; Randazzo and Hickey, 1978; Randazzo and others, 1983).

The stable isotopes ^{13}C and ^{18}O in calcite and dolomite are also used as indicators of the diagenetic history of the rocks. The ^{13}C content provides evidence about the

sources of CO_2 available for dissolution and reprecipitation of the carbonate phases. The ^{18}O content of the carbonates is related to the aqueous environment of diagenesis, especially the temperature of the aquifer system during the last diagenetic episode. Available stable isotope data for dolomite and calcite from the aquifer system are presented in table 2. Many stable isotope data from carbonates have been reported as concentration relative to the Pee Dee belemnite (PDB), but the oxygen data in table 2 are reported relative to Vienna SMOW. The relation between these two standards is

$$\delta^{18}O_{PDB} = (0.97006\ \delta^{18}O_{SMOW}) - 29.94.$$

Except for two isotopically heavy samples, calcite ranges in $\delta^{13}C$ from about -0.5 to $+0.5$ o/oo (permil). The calcite samples from the deep zones (about 1,000 ft) of the Waycross and Green Swamp test wells may reflect the original seawater environment of formation, since the calcites have $\delta^{13}C$ values similar to surface seawater (Kroopnick and others, 1972). Methane has been detected in water samples from the 1,900- to 1,970-ft zone in the Waycross well (table 4), so it is also possible that the heavy $\delta^{13}C$ calcites in that well may result from in situ formation of calcite with isotopically heavy CO_2 produced by anaerobic bacteria. The lighter $\delta^{13}C$ calcites listed in table 2 were probably formed from isotopically light ground water.

The $\delta^{18}O$ content of calcites began to be used to determine paleotemperatures after Urey presented his classic paper in 1946 (Urey, 1947; Hoefs, 1980, p. 147–152). Attempts to use the $\delta^{18}O$ content of calcite samples from the Floridan aquifer system to estimate the paleotemperatures of ground water is hindered by several problems, the most intractable being the timing and pattern of diagenesis and the amounts of calcite precipitated in each diagenetic episode. For example, using oxygen isotopic fractionation factors given in Friedman and O'Neil (1977, fig. 13), the lowest and highest $\delta^{18}O$ values for calcite in table 2, and two values for $\delta^{18}O$ in ground water (fig. 3B), the following ranges in ground-water temperature (T) are obtained:

$\delta^{18}O$ calcite	$\delta^{18}O$ ground water	Δcalcite-ground water	T equilibrium
+26.7 o/oo	−2.5 o/oo (well 3)	29.2 o/oo	20 °C
+29.0 o/oo	−3.6 o/oo (well 4)	32.6 o/oo	12 °C

If the ground-water temperature is assumed to be 20 °C, the calcite data could be used to estimate the $\delta^{18}O$ value of ground water:

$\delta^{18}O$ calcite	T equilibrium	Δcalcite-ground water	$\delta^{18}O$ ground water
+26.7 o/oo	20 °C	29.5 o/oo	−2.8 o/oo
+29.0 o/oo	20 °C	29.5 o/oo	−0.5 o/oo

TABLE 2.—*Carbon and oxygen isotopic data for carbonate minerals from the Floridan aquifer system*

[Values of $\delta^{13}C$ and $\delta^{18}O$ in permil (o/oo) relative to Pee Dee belemnite and Standard Mean Ocean Water, respectively. Dashes indicate isotope not measured]

Sample number	Sample location	Dolomite		Calcite	
		$\delta^{13}C$	$\delta^{18}O$	$\delta^{13}C$	$\delta^{18}O$
1	Well 274[1] (near Brooksville, Fla.)	−7.5	+31.3	−0.4	+27.3
2	Well 519[1] (at Frostproof, Fla.)	−2.8	+32.7	+0.6	+28.9
3	Well 4750[1] (near Palmdale, Fla.)	−3.1	+32.2	−0.4	+26.7
4	Well 275[1] (at Groveland, Fla.)	----	----	+0.5	+27.3
5	Core from 14-meter depth near Inglis, Fla.[1]	+1.0	+33.4	----	----
6	Outcrop near Inglis, Fla.[1]	+0.7	+33.4	----	----
7	Outcrop at Inglis Canal Bridge[1]	+0.1	+33.2	----	----
8	Core, 763–773 feet, TW–1,[2] near Waycross, Ga.[3]	----	----	−0.7	+28.1
9	Core, 905–915 feet, TW–1, near Waycross, Ga.	−1.8	+32.7	----	----
10	Core, 1,056–1,066 feet (vein), TW–1, near Waycross, Ga.	−0.4	+32.3	----	----
11	Core, 1,056–1,066 feet (matrix), TW–1, near Waycross, Ga.	+2.5	+33.6	----	----
12	Core, 1,232–1,248 feet, TW–1, near Waycross, Ga.	----	----	+2.1	+29.0
13	Core, 1,375–1,385 feet, TW–1, near Waycross, Ga.	+1.8	+32.9	----	----
14	Core, 381–396 feet, Green Swamp TW, near Polk City, Fla.	−3.0	+31.9	----	----
15	Core, 544–561 feet, Green Swamp TW, near Polk City, Fla.	+1.2	+33.9	----	----
16	Core, 757–769 feet, Green Swamp TW, near Polk City, Fla.	+2.6	+33.2	----	----
17	Core, 955–978 feet, Green Swamp TW, near Polk City, Fla.	+3.0	+33.4	+0.5	+28.5
18	Core, 1,570–1,578 feet, Green Swamp TW, near Polk City, Fla.	+2.0	+31.8	----	----
19	Core, 1,959–1,968 feet, Green Swamp TW, near Polk City, Fla.	----	----	+2.0	+27.0
20	Core, 226 feet, test well MS, near Chiefland, Levy County, Fla.	+2.2	+34.4	----	----
21	Core, 277 feet, test well MS, near Chiefland, Levy County, Fla.	+0.6	+34.6	----	----
22	Core, 203 feet, test well 124, near Inglis, Levy County, Fla.	+2.6	+33.6	----	----
23	Core, 216 feet, test well TR21–2, near Lecanto, Citrus County, Fla.	+2.8	+33.7	----	----
24	Core, 175 feet, test well near Homosassa Springs, Citrus County, Fla.	+1.9	+33.1	[4]+0.3	[4]+33.1
25	Core, 250 feet, test well near Homosassa Springs, Citrus County, Fla.	+2.2	+34.7	----	----
26	Core, 452 feet, test well TR19–3, near Tooke Lake, Hernando County, Fla.	+2.0	+33.5	----	----
27	Core, 261 feet, test well TR17–1, near Hudson, Pasco County, Fla.	−2.6	+32.4	----	----
28	Core, 341 feet, test well TR6–3, near Bee Ridge, Sarasota County, Fla.	−3.2	+34.2	----	----
29	Core, 245 feet, test well TR4–2, near South Venice, Sarasota County, Fla.	−2.7	+33.6	----	----
30	Core, 364 feet, test well 101, near Bay Lake, Lake County, Fla.	+0.6	+34.0	----	----
31	Core, 642 feet, test well TR11–2, near Mango, Hillsborough County, Fla.	−1.8	+32.2	−2.4	[4]+32.5

[1] Data from Hanshaw and Back (1972, table 2).

[2] TW, test well.

[3] Precision of $\delta^{13}C$ and $\delta^{18}O$ data is ±0.2 permil. Pieces of core were selected to be monomineralic and ground to fine powder (−250 mesh). Secondary cements, if present, could affect the isotopic values reported.

[4] Values of $\delta^{13}C$ and $\delta^{18}O$ for calcite are questionable. Core samples were approximately 98 percent dolomite. Calcite could not be quantitatively extracted prior to isotopic analysis.

The heavier $\delta^{18}O$ estimated from ground water is about 2 o/oo more enriched than the heaviest modern-day ground-water samples from Georgia (fig. 3B). These estimates appear to indicate that recharge was derived from somewhat colder precipitation than occurs today.

Determining the stable isotope content of dolomite is a more complex problem because (1) the fractionation factors between water and dolomite are not known for temperatures below about 100 °C and (2) the influence of the isotopic content of the carbonate precursor is difficult to establish (Land, 1980, p. 88–93). The stable isotope data from dolomites presented in table 2 show a narrow range of values of $\delta^{18}O$ and a somewhat wider range of $\delta^{13}C$ values. Hanshaw and Back (1972, p. 147) concluded that dolomite with $\delta^{13}C$ values less than −1 o/oo had

formed in a ground-water environment that contained isotopically light bicarbonate ions, whereas dolomite with $\delta^{13}C$ values in the range of −1 to +3 o/oo apparently formed in a more marine environment. The isotopic data from the Waycross and Green Swamp test wells show a general increase in the $\delta^{13}C$ of carbonates with increasing depth. This is probably related to the development of the freshwater flow system within the aquifer system. At both the Waycross and Green Swamp test wells, the major permeability and greatest volume of freshwater flow occur in the upper few hundred feet of the limestone section. As depth increases, ground-water flow is more sluggish owing to a marked decrease in permeability. The deeper dolomite (and calcite) examined from both wells appear to have formed in a system "closed" to

CO_2-rich meteoric water (which is isotopically light in $\delta^{13}C$). Thus, the $\delta^{13}C$ content of the deep dolomite from the two test wells may have been inherited from preexisting carbonates. Assuming the dolomite inherited the isotopic content of a precursor carbonate phase (calcite?), the fractionation of $\delta^{18}O$ between the dolomite and the "coexisting" calcite (samples 12, 13, and 17, table 2) is in the appropriate range (+4 to +5 o/oo) for low-temperature diagenesis (Land, 1980, p. 90–92).

MINOR MINERALS

Gypsum is an important minor mineral in the Floridan aquifer system. Miller (1986) used the presence or absence of intergranular gypsum as an indicator to define confining units of the system. Cook (1984) and Thayer and Miller (1984) have used gypsum morphology and its association with sedimentary structures in dolomitic facies of the Avon Park Formation to determine depositional environments and diagenetic history of the rocks. Within the modern-day freshwater flow system, the continuous dissolution of gypsum leads to incongruent dissolution of dolomite and calcite precipitation (Plummer, 1977). Plummer and others (1983) used the sulfate produced from gypsum dissolution as a progress variable to study changes in Ca^{2+}, Mg^{2+}, $\delta^{13}C$, and pH along a ground-water flow path in the Upper Floridan aquifer. Isotopic ratios of $\delta^{34}S$ in dissolved sulfate (SO_4^{2-}) and from sulfate in gypsum have been used to describe some of the redox reactions of the aquifer system (Pearson and Rightmire, 1980; Rye and others, 1981; Plummer and others, 1983). The data on sulfur isotopes in gypsum from the aquifer system show that the sulfate was of marine origin (table 3), and not derived from oxidation of sulfides. Some of the gypsum samples listed in table 3 are heavier in $\delta^{34}S$ than modern marine water, indicating the gypsum may have formed in a reducing environment (Nielsen, 1979, p. 291–294). Data on the trace element composition of gypsum from the aquifer system are scarce; this lack of data may not be a serious obstacle in interpreting the geochemistry of the system, however, because the mineral tends to vary little in composition (Stewart, 1963, table 22; Deer and others, 1966, p. 466).

The minor mineral apatite (predominantly carbonate fluorapatite) is a potential source of calcium, fluoride, bicarbonate, phosphate, trace metals, and radionuclides in ground water of the Floridan aquifer system. Apatite is present in trace amounts throughout the system, varying in abundance areally and by formation. Over the entire region, apatite is most abundant in the Tampa Limestone in southwestern Florida. Less common occurrences of phosphatic minerals are in the upper Eocene and Oligocene limestones in southern Georgia and in northern and central Florida. In a few areas, the Hawthorn Formation, which makes up the major part of the upper confining unit of the aquifer system, and overlying Pliocene sediments are rich in phosphatic minerals containing uranium and other trace metals (Altschulter and others, 1958; Riggs, 1979). In recharge areas, ground-water leakage through the Hawthorn could increase Ca^{2+}, PO_4^{3-}, F^-, trace metal, and radionuclide concentrations in the Upper Floridan aquifer.

The two principal mineral varieties of silica in the aquifer system are chert (chalcedony) and quartz (detrital sand grains); opaline varieties of silica (tests from marine organisms) are rare in the limestones (Miller, 1986). Throughout most of peninsular Florida, the aquifer system contains very little detrital quartz or chalcedony (probably less than 1 percent everywhere). In panhandle Florida, southern Alabama, and Georgia, the aquifer system contains appreciable quantities of detrital quartz as the limestones grade laterally into limy sands and silts. In these areas aluminosilicate minerals, mostly clay minerals, are also relatively abundant.

Very little information on the identity of aluminosilicate (clay) minerals in the Floridan is available. Numerous workers mention "glauconite," "clay," or "clayey residues" in descriptions of cores and drilling chips, but few X-ray or other analytical data on these minerals are available. A few X-ray diffractograms were made during this study of cores of the Avon Park Formation in west-central Florida; these diffractograms indicated weak 7.1 angstrom (A) peaks (kaolinite) and trace 15 A peaks (montmorillonite?). The diffractograms also indicated that small amounts of potassium feldspar are present in zones of the Avon Park Formation. Where present, glauconite may be weathering to yield trace amounts of silica, aluminum, iron, and potassium to ground water. Riggs (1979, p. 216–218) discusses aluminosilicate weathering of Miocene rocks in central Florida; similar weathering processes (and minerals?) probably occur in the older rocks of the Floridan where the system is unconfined. According to Riggs (1979, p. 217), both phosphatic and siliceous mineral phases increase in aluminum content as weathering proceeds. He states:

In central Florida, the unaltered calcium phosphate occurs as a carbonate fluorapatite which grades upward to calcium-aluminum phosphate, occurring as crandallite and millisite. These change upward to the pure aluminum phosphate, wavellite.... The clay minerals have a similar gradational sequence. The clay minerals at the base consist of a montmorillonite-attapulgite assemblage which grades upward to a montmorillonite assemblage overlain by a montmorillonite-kaolinite assemblage and finally to a kaolinite assemblage.

This weathering sequence may affect silicates in the Floridan but not phosphatic minerals because of the abundance of carbonate minerals in the aquifer. Nathan and Sass (1981) have described the stability of carbonate fluorapatite in the presence of carbonate minerals; within

TABLE 3.—*Sulfur isotopic content of gypsum (anhydrite) from the Floridan aquifer system*

[In permil relative to troilite from Canyon Diablo meteorite]

Location	$\delta^{34}S$	Reference
Five gypsum samples from central Florida	+19 to +22	Pearson and Rightmire (1980, p. 246)
Core, test well, Waycross, Ga., 1,375–1,385 feet	+21.4	
Core, test well, Waycross, Ga., 1,723–1,733 feet	+22.2	
Core, test well, Green Swamp, Fla., 1,021–1,036 feet	+22.6	
Core, test well, Green Swamp, Fla., 1,894–1,903 feet	+23.2	
Sulfate from modern ocean water	+20	Hoefs (1980, p. 117)

the aquifer system, ground-water pH normally is in the range 7.0 to 8.5, which is an exceptionally stable environment for carbonate-fluorapatite. The possibility that weathering reactions similar to those described above might control the aluminum and silica concentrations in the Upper Floridan aquifer is discussed in greater detail later in this paper. Regardless of the actual minerals involved, weathering and diagenesis of aluminosilicates within the aquifer system are slow processes and, except possibly for potassium and silica, are relatively insignificant controls on the major element chemistry of ground water in the aquifer system.

The clay minerals in the aquifer system may have a significant role in controlling sodium and calcium concentrations, however, where cation exchange occurs. The importance of Ca^{2+} for $2Na^+$ exchange to produce sodium bicarbonate solutions in regional aquifers has been described by Renick (1924a), Foster (1950), Thorstenson and others (1979), Chapelle and Knobel (1983), and Lee (1985). The occurrence of sodium bicarbonate water within the Floridan aquifer system is limited to a small area of western panhandle Florida (pl. 9; also Barraclough and Marsh, 1962). The effects of cation exchange on the water chemistry of the aquifer system are discussed in following sections.
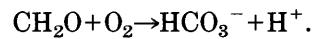
Trace amounts of sulfide minerals (primarily pyrite or marcasite) are present at depth throughout the system. These sulfide minerals generally form as a result of bacterially mediated sulfate reduction which generates hydrogen sulfide (H_2S), the source of rebarbative odors in many untreated water supplies. Hydrogen sulfide is a weak acid, so that the predominant species containing reduced sulfur in solution depends on pH. The activities of H_2S and HS^- are related by an acid dissociation constant $pK_{25\ °C}=6.96$. This means that at 25 °C and pH of 6.96, the activities of H_2S and HS^- in solution are

equal. In the normal range of pH conditions in the Upper Floridan aquifer (about pH 7.0 to 8.5), the dominant reduced-sulfur species is bisulfide. Sulfide (S^{2-} usually is present in the Upper Floridan only in minute amounts: for example, at pH of 7 and HS^- ($=H_2S$) concentration of 1 milligram per liter (mg/L), S^{2-} concentration is approximately 10^{-7} mg/L. This is sufficient, however, to precipitate many trace metal sulfides owing to the extremely low solubility of these minerals. Once formed, sulfide minerals are practically insoluble in pure water. However, when oxygen is available to reoxidize the sulfide to sulfate, the mineral can be dissolved. The uniformly low concentrations of trace metals in natural ground water from the Floridan aquifer system is in part related to lack of primary (and soluble) sources of trace metals. The almost ubiquitous formation of H_2S and precipitation of metallic sulfides maintain low trace metal concentrations throughout most of the aquifer system.
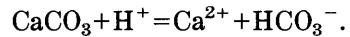
A geochemically important but relatively rare component of the Floridan aquifer system is carbonaceous residue, or peat. This organic material is not abundant in any horizon or rock unit, but occasionally occurs as lamellae or thin layers in the more deeply buried rocks. Some of this organic material is utilized by anaerobic microbes to reduce SO_4^{2-} to S^{2-} via the reaction

$$SO_4^{2-}+2CH_2O \rightarrow HS^-+2HCO_3^-+H^+,$$

where CH_2O is a generalized organic molecule containing the approximate ratio C:H:O of typical carbohydrates in sediments. The peat can also be readily oxidized by aerobic microbes, which convert organic carbon to HCO_3^- via the reaction

$$CH_2O+O_2 \rightarrow HCO_3^-+H^+.$$

Note that both of the above reactions produce acidity (H^+) and bicarbonate ion. The acidity may then be consumed by reaction with calcite:

$$CaCO_3+H^+=Ca^{2+}+HCO_3^-.$$

If the acidity reaction exists, then a net $3HCO_3^-$ will be produced for each mole of SO_4^{2-} reduced, or $2HCO_3^-$ for each mole of CH_2O oxidized by O_2. The HCO_3^- produced may be isotopically light in carbon ($\delta^{13}C$ about -25 o/oo) and, depending on quantities of peat oxidized, can measurably affect the ^{13}C content of ground water in the Upper Floridan aquifer. Even where the aquifer system is too anaerobic or too sulfate deficient to sustain sulfate-reducing bacteria, the peat may still be oxidized by heterotrophic bacteria. In the anaerobic environment, the primary byproducts of heterotrophic oxidation are molecular hydrogen and acetate, both of which are consumed by methanogenic bacteria to produce meth-

ane. Measurements of dissolved gases in water samples indicate that methane is present in the aquifer system in Georgia and Florida (table 4; Ehrlich and others, 1979). The methane produced in the anaerobic parts of the aquifer system is not confined there and could migrate upward into more oxidizing environments. In an oxidizing zone, the methane is converted by bacteria to CO_2, which could have a very low ^{13}C content ($\delta^{13}C$ ranging from -65 to -85 o/oo (Hoefs, 1980, fig. 47)).

The significance of reduced carbon sources and their isotopic contents in developing geochemical reaction models of the Upper Floridan aquifer in southwestern Florida is discussed in detail by Plummer and others (1983). Their calculations using $\delta^{13}C$ and $\delta^{34}S$ showed that where the aquifer system is confined (such as in southwestern Florida), input of reduced carbon was affecting the carbon isotope chemistry. As a result of the work by Plummer and others (1983), the methodology is available for quantitative interpretation of redox reactions involving carbon in regional aquifer systems. However, application of their methods to other parts of the Floridan aquifer system must await availability of data on environmental isotopes, dissolved gases, and aquifer mineralogy.

HYDROLOGY

The Floridan aquifer system generally consists of an Upper and Lower Floridan aquifer separated by a less permeable confining unit of highly variable properties (Miller, 1986). The upper and lower aquifers were defined on the basis of permeability; thus, aquifer boundaries in many places do not coincide with boundaries for either time-stratigraphic or rock-stratigraphic units. The Upper Floridan aquifer is present throughout the region and contains units ranging in age from middle Eocene to early Miocene (Miller, 1982a, 1982c, 1986). Several formations are included in the Upper Floridan aquifer, primarily the Tampa, Suwannee, and Ocala Limestones and the Avon Park Formation. The Lower Floridan aquifer is not present in parts of northwestern Florida and in Georgia inland from the coast (fig. 9; Miller, 1986). In these areas, there is little permeability contrast within the aquifer system. Where present, the Lower Floridan aquifer may consist of Paleocene to middle Eocene formations, but consists primarily of the Oldsmar and Cedar Keys Formations.

The major features of the regional flow system of the Floridan can be seen on potentiometric surface maps. An estimated potentiometric surface map of the Upper Floridan aquifer prior to development was made by Johnston and others (1980); a modified version of the map is shown in figure 10. The potentiometric surface shown in figure 10 represents an average, undeveloped condi-

tion of the Upper Floridan made from the best information and estimates available (Johnston and others, 1980). Several important hydraulic features of the flow system are evident. Depressions in the potentiometric surface indicate areas of natural discharge that occur along stream channels or near springs; simulation of the aquifer system indicates that almost 90 percent of natural discharge is to rivers and springs (Bush and Johnston, 1988). Along the coast of Florida, low heads generally indicate nearshore springs or seepage from submarine outcrops; simulation of predevelopment conditions indicates that less than 5 percent of the total discharge is directly into the sea. The high heads along the Georgia coast result from thick confinement by the Hawthorn Formation, and freshwater flow extends as far as 50 miles (mi) offshore (Johnston and others, 1982) in that area. The potentiometric high areas shown in figure 10 are areas of potential recharge to the aquifer system. The amounts of actual recharge can vary widely, however, owing to varying thicknesses of aquifer confinement and magnitude of local downward hydraulic gradients (Bush, 1982).

The Floridan aquifer system is remarkably productive. The exceptionally high permeability of some units within the aquifer system are the result of solutional enhancement of high primary permeabilities of the coquinas and fossiliferous limestones. As a result of the wide variation in hydrogeologic conditions in the Upper Floridan aquifer, transmissivity varies by more than three orders of magnitude (Bush and Johnston, 1988, pl. 2). Transmissivities of more than 1,000,000 square feet per day (ft^2/d) occur in the karst areas of west-central and northwestern Florida. The variability of depositional environments when the limestones were formed has also produced low-permeability units that are areally extensive—for example, in the Gadsden County area of northern Florida. In this area, transmissivities are less than 1,000 ft^2/d and vertical head gradients as large as 40 ft are maintained by low-permeability limestones in the Upper Floridan (Rosenau and Milner, 1981). Extending in a northeasterly direction from Gadsden County toward Candler County, Ga., is a series of grabens which markedly affect the transmissivity of the aquifer system. These geologic structures, collectively referred to as the Gulf Trough (fig. 8; Herrick and Vorhis, 1963; Gelbaum, 1978), have the principal effects of locally reducing the thickness of the limestone section, placing low-permeability clastics adjacent to highly permeable limestones, and creating steep hydraulic gradients in the vicinity of the grabens (fig. 10; Pascale and Wagner, 1981; Krause and Randolph, 1989). The Gulf Trough feature has created a damming effect on the southeasterly flow of ground water in the Floridan aquifer system,

TABLE 4.—Dissolved gases and bacterial organisms measured in water samples from wells in the Floridan aquifer system

[Do., ditto]

Well location	Well depth (feet)	Sample depth (feet)	Water temperature (degrees Celsius)	Dissolved gases (pressure in atmospheres at indicated temperature)[1]							MPN[2] (organisms per 100 milliliters)			
				N_2	O_2	Ar	CH_4	CO_2	He[3]	H_2	Total anaerobes	Total aerobes	Denitrifiers	Sulfate reducers
Waycross, Ga.	1,970	600–1,900	26.0	1.26	<0.001	0.017	0.002	0.0046	N.D.[3]	N.D.	—[4]	—	—	—
Do.	1,970	1,900–1,970	22.5	.99	<.001	.015	.001	.0024	0.008	0.26	10^3	10^4	10^3	10^2
Do.	1,970	1,100–1,900	—	—	—	—	—	—	—	—	10^4	10^4	10^4	10^2
Do.	1,970	900–1,100	—	—	—	—	—	—	—	—	10^7	10^3	10^5	10
Everglades test well (Broward County, Fla.)	2,810	811–816	24.3	1.23	.0007	.016	.0017	.0017	—	—	—	—	—	—
Do.	2,810	970–1,030	24.3	1.22	.0032	.015	.0014	.0010	—	—	10	10^3	10^4	1
Do.	2,810	2,500	24.7	[5]2.09	.076	.007	N.D.	.0022	—	—	10	10^5	10^4	10^2
Do.	2,810	895–1,124	26.2	1.22	.004	.018	.0014	.0017	—	—	10	10^7	10^3	10^2
Do.	2,810	895–1,249	26.2	1.20	.002	.015	.0012	.0017	—	—	10^2	10^6	10^4	10^2
Do.	2,810	1,428–1,618	25.8	1.16	.029	.013	.0008	.0009	—	—	—	—	—	—
Do.	2,810	2,457–2,810	24.7	.98	.002	.015	N.D.	.0027	—	—	—	—	—	—
South Miami, Fla.	2,960	1,005–1,037	23.0	1.02	.0026	.013	.0027	.0022	—	—	—	—	—	—
Do.	2,960	2,689–2,960	19.0	.96	.0033	.013	Trace	.0015	—	—	—	—	—	—
Plugged oil test well west of Jacksonville, Fla.	2,200	1,130–1,665	20.8	1.03	.0013	.0137	.038	.0095	—	—	—	—	—	—
Do.	2,200	1,665–1,935	20.5	.81	<.0003	.0108	.039	.0084	—	—	—	—	—	—
Do.	2,200	1,935–2,200	20.5	.88	.0008	.0147	.032	.0092	—	—	—	—	—	—
Grand Ridge city well, Jackson County, Fla.	200	[6,7]–200	23.0	1.11	.14	.014	N.D.	.0017	—	—	—	—	—	—
Altha city well, Calhoun County, Fla.	282	?–282	23.0	1.10	.026	.014	N.D.	.0019	—	—	—	—	—	—
Well near Otter Creek, Levy County, Fla.	679	?–679	22.6	1.16	<.0003	.014	.0007	.013	—	—	—	—	—	—
Well near Dalkeith, Gulf County, Fla.	505	?–505	27.0	1.31	.0005	.017	.0017	.0093	—	—	—	—	—	—
Well near Dakfield, Worth County, Ga.	120	?–120	20.6	1.17	.12	.013	N.D.	.0026	—	—	—	—	—	—
Well near Leesburg, Lee County, Fla.	190	?–190	20.1	1.00	.11	.012	<.0002	.0019	—	—	—	—	—	—
Well near Leary, Calhoun County, Fla.	142	?–142	20.4	1.06	.044	.013	N.D.	.0027	—	—	—	—	—	—
Well, eastern Early County, Ga.	125	?–125	20.3	1.19	<.002	.013	N.D.	.0051	—	—	—	—	—	—
Well, east of Newton, Ga.	225	?–225	20.3	1.04	.16	.012	N.D.	.0021	—	—	—	—	—	—
Well near Jakin, Early County, Ga.	125	?–125	21.1	1.09	.19	.013	N.D.	.0029	—	—	—	—	—	—
Well near Brinson, Decatur County, Ga.	185	?–185	20.5	1.13	.088	.013	<.0002	.0024	—	—	—	—	—	—
Well in southwest Seminole County, Ga.	150	?–150	20.8	1.22	.15	.014	N.D.	.0045	—	—	—	—	—	—
Camp Henderson, northern Santa Rosa County, Fla.[7]	815	702–815	22.0	—	—	—	.003	.0008	—	—	—	—	3	—
Shallow monitor at American Cyanamid Company, Santa Rosa County, Fla. (sampled 6/12/79)[7]	1,108	1,096–1,108	26.0	1.32	<.0008	.017	.098	.0015	—	—	460	—	—	—
Shallow monitor at Monsanto Company, Escambia County, Fla. (gases sampled 3/8/79; bacteria sampled 8/17/76)[7]	1,140	972–1,140	29.0	1.13	.0003	.014	.143	.0017	—	—	—	—	N.D.	—

[1] No corrections have been made for salting-out effects.
[2] MPN, most probable number.
[3] N.D., gas not detected.
[4] —, gas or bacterial organism not measured.
[5] Sample collected from an N_2-flushed thief sampler.
[6] ?, well-casing depth not known.
[7] Data from Hull and Martin, 1982, tables 24, 26, 28, 29, 30.
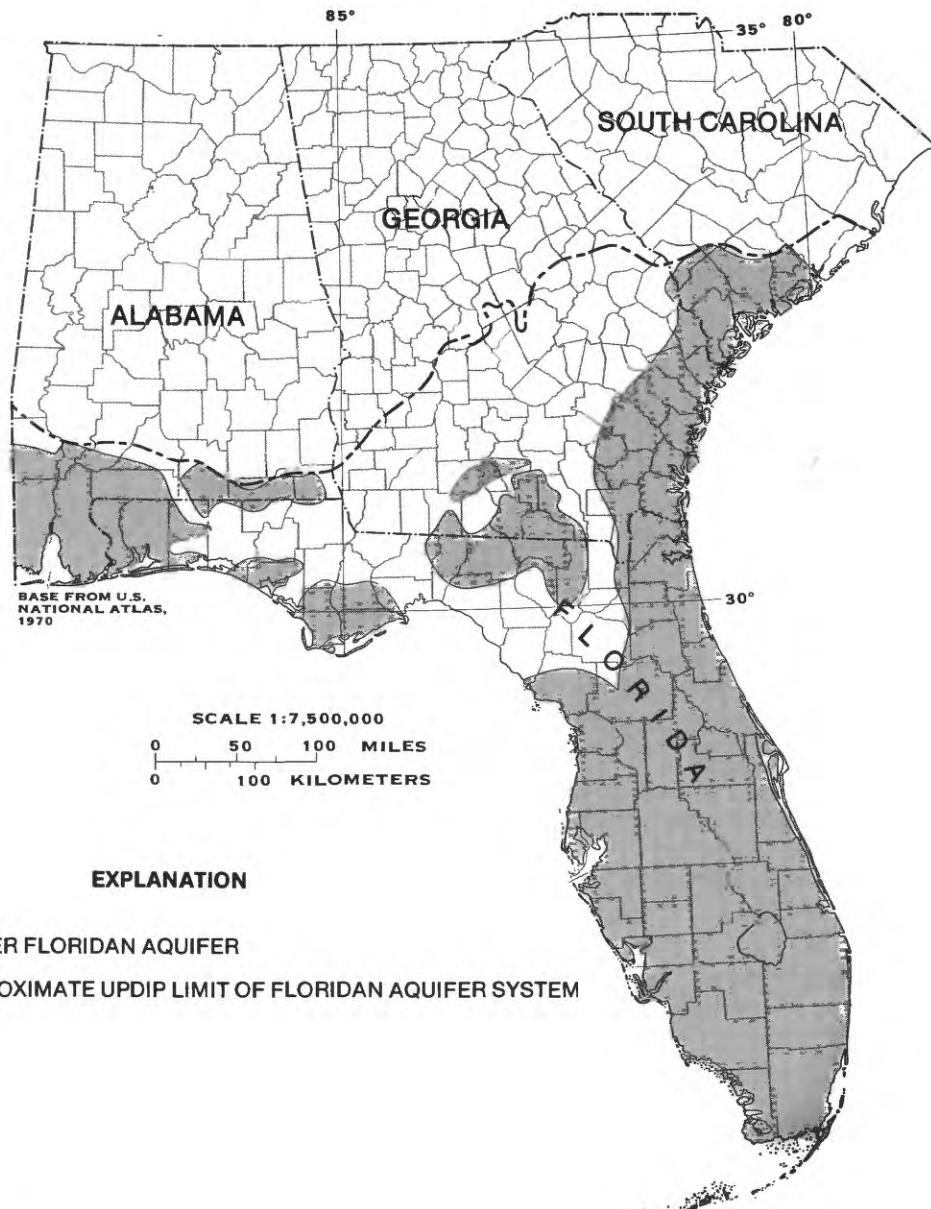
FIGURE 9.—Approximate areal extent of the Lower Floridan aquifer. (After Miller, 1986.)

thereby reducing the flow rates from outcrop areas toward the Georgia coast (Bush and Johnston, 1988).

Ground-water flow conditions in the Floridan aquifer system are directly related to the thickness and integrity of the overlying confining unit(s). Where the confining unit is thick (fig. 11), recharge and discharge rates are substantially less than in areas where the confining unit is thin or absent. Confinement retards development of secondary permeability by reducing the rates of circulation of freshwater which is undersaturated with calcite or dolomite. In some areas, high heads sustained by confinement prevent recharge from surficial sand aquifers. However, high heads sustained by confinement in coastal areas reduce encroachment of seawater, making the aquifer system a potentially more usable resource. In contrast, where the aquifer system is unconfined, recharge is rapid and plentiful, ground-water circulation and discharge rates are high, and secondary permeability can develop quickly.

Some effects of confinement on the chemistry of water in the Floridan aquifer system have been discussed by Back and Hanshaw (1970), Plummer (1977), and Plummer and others (1983). A major effect is that where the overlying confining unit is thick, the carbonate chemistry of the ground water evolves in isolation from atmospheric or soil-zone CO_2 gas (closed-system evolu-
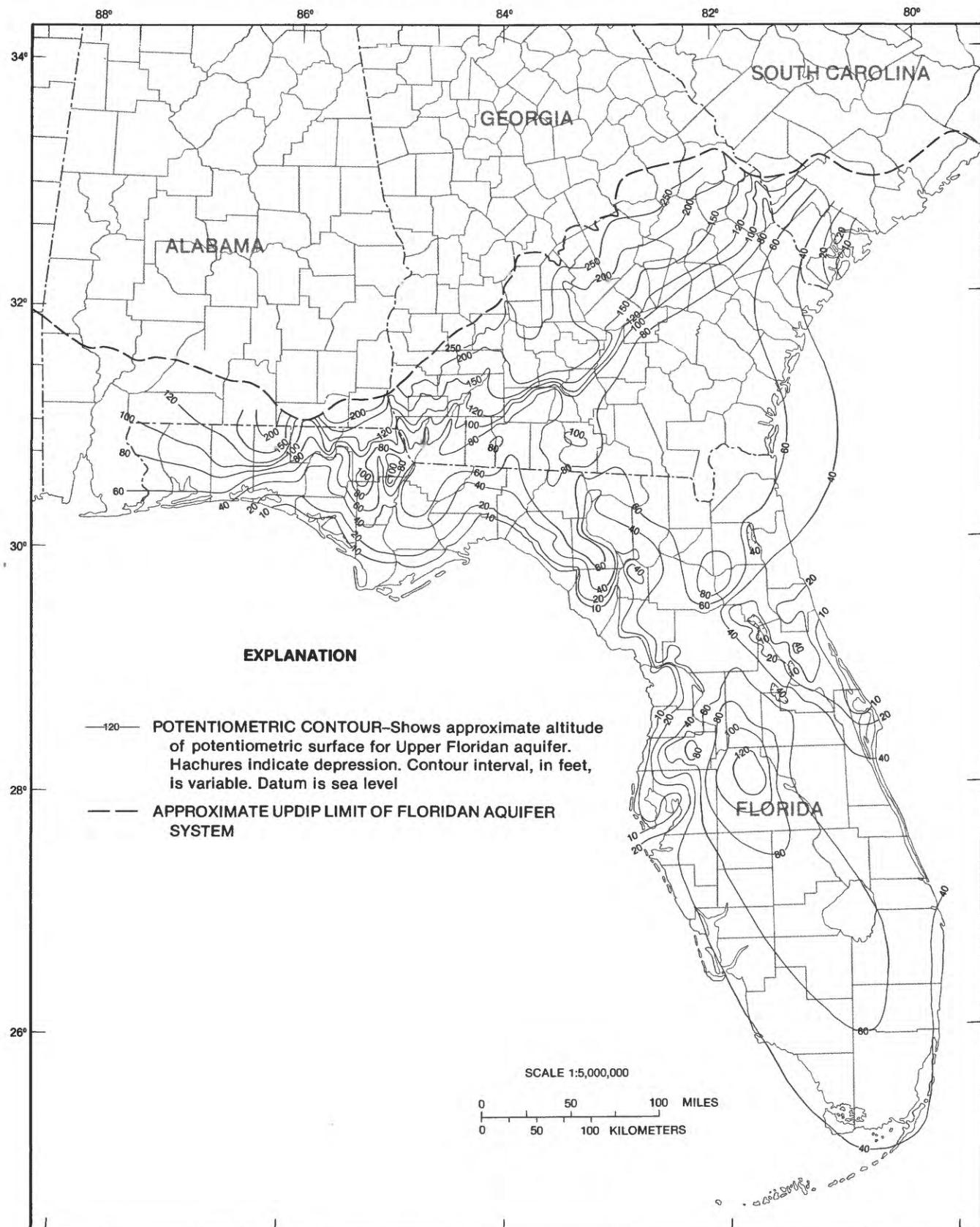
FIGURE 10.—Estimated potentiometric surface of the Upper Floridan aquifer prior to development. (From Johnston and others, 1980.)
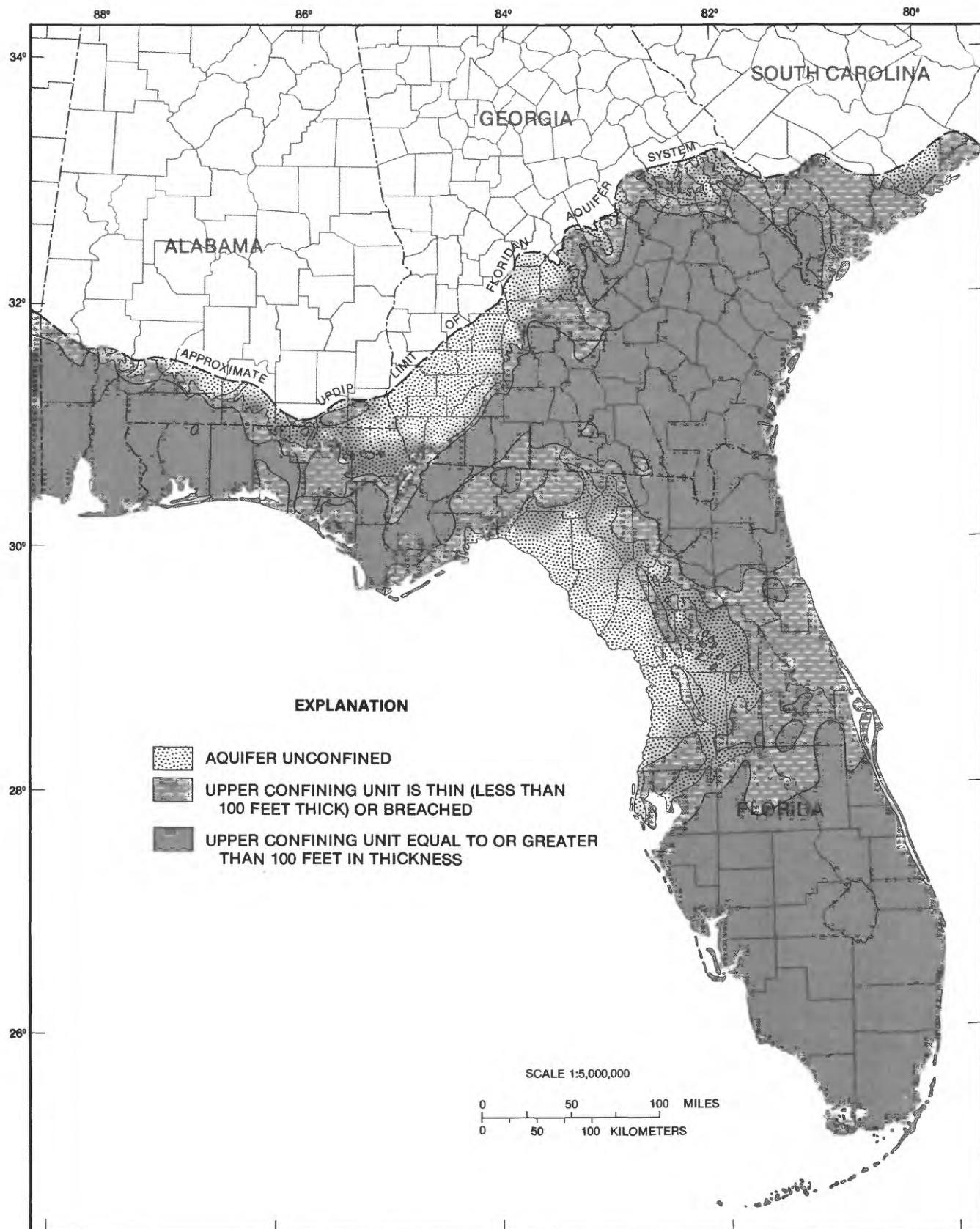
FIGURE 11.—Confined and unconfined areas of the Floridan aquifer system. (From Miller, 1986, pl. 25.)

tion). As discussed in a number of hydrology texts (for example, Freeze and Cherry, 1979, p. 109–111), dissolution of limestone (and development of secondary permeability) is enhanced in ground-water systems open to a large (infinite) source of CO_2 gas. A secondary effect of confinement is reduction in the rate of flushing of salty water from the system. Confinement may also allow changes in oxidation-reduction potential to develop owing to isolation of the ground water from atmospheric oxygen. Confinement can also protect the ground-water resource by reducing the amount of surface contaminants that reach the system.

The hydraulic effects of confinement on the system are clearly seen when areas of confinement (fig. 11) are compared with principal areas of recharge and discharge. A map of recharge and discharge areas of the Upper Floridan was developed (Bush and Johnston, 1988, pl. 11) from simulation of the steady-state predevelopment flow system; the map is reproduced in figure 12. Thick confinement in southeastern Georgia and in southern Florida extend the discharge zone (area of diffuse upward leakage, fig. 12) over thousands of square miles; in contrast, discharge zones in unconfined areas along the Gulf Coast of Florida are narrow, extending over a few hundreds of square miles. More dramatic effects of confinement are seen when ground-water fluxes are compared between confined and unconfined areas. Bush and Johnston (1988, fig. 22) subdivided the aquifer system into major ground-water areas bounded by flow lines, so that within each area, ground-water discharge equals recharge in the steady-state condition. The total simulated discharge from the Floridan aquifer system prior to development was approximately 21,700 cubic feet per second (ft^3/s) (fig. 13). Simulation showed that approximately 90 percent of this discharge occurred as springflow or discharge to streams in areas where the upper confining unit is thin or absent. By comparing figures 11 and 13, the effects of confinement on ground-water flow activity in different ground-water areas may be seen. For example, areas II, III, and IV are mostly unconfined, occupy about one-fifth of the land area where the Floridan aquifer system is present, and together account for about 63 percent of the total predevelopment discharge. Areas V and VII are mostly confined and occupy about half of the area underlain by the Floridan, yet they contribute only about 13 percent of the total predevelopment discharge from the system. Pumpage from the Floridan aquifer system of about 3 billion gallons per day (gal/d) (early 1980's) represents about 17 percent of total discharge (Bush and Johnston, 1988). This pumpage has resulted in water-level declines of more than 10 ft in three large areas—western panhandle Florida, west-central Florida, and along the Atlantic Coast from Jacksonville to north of Savannah (Bush and

Johnston, 1988, pl. 6). Nonetheless, ground-water development has not greatly altered the fact that most of the discharge from the Upper Floridan aquifer is to springs and streams.

This brief characterization of the flow system is sufficient for the following discussion of aquifer geochemistry; for more detailed descriptions of both the aquifer system and models developed to simulate its ground-water flow, the reader is referred to Bush (1982), Krause (1982), Ryder (1982), Tibbals (1981), and chapters C, D, E, F, and H of Professional Paper 1403 (Bush and Johnston, 1988; Krause and Randolph, 1989; Tibbals, in press; Ryder, 1986; Maslia and Hayes, 1988).

DESCRIPTION OF GROUND-WATER CHEMISTRY

METHODOLOGY

The majority of the data used in this investigation are from previous analyses of water samples from wells and springs in the Floridan aquifer system. These data were obtained during the period 1950 to 1982 as part of areal hydrologic studies by the U.S. Geological Survey in cooperation with Federal, State, and local governmental agencies and are currently available in computer files maintained by the Geological Survey (U.S. Geological Survey, 1974, 1975). Chemical data from springs were used primarily to obtain a better understanding of the hydrogeochemistry of the Upper Floridan where it is unconfined. Chemical data from springs were also used to supplement the well data to obtain a better regional description of selected constituents. Wells with chemical data were selected on the basis of (1) depth of well penetration into the Upper or Lower Floridan aquifer, (2) areal coverage of the entire Floridan aquifer system, and (3) relatively complete chemical data in computer storage. After a preliminary review of about 52,000 water analyses from more than 7,000 wells and about 250 springs in Alabama, Florida, Georgia, and South Carolina, a subset of 601 analyses (representing 601 wells) was chosen to characterize the major ion chemistry of the Upper Floridan aquifer. Of these 601 wells, 404 are open to more than half the total thickness of the Upper Floridan at the well and none penetrate below the base of the aquifer. Very few chemical data from wells in the Lower Floridan aquifer were available for this study. Owing to the scarcity of chemical and hydrologic data from the Lower Floridan, this report emphasizes geochemical properties and processes in the Upper Floridan aquifer. Discussion of the hydrogeochemistry of the Lower Floridan aquifer is limited to maps showing distribution of chloride and concentrations of dissolved solids.
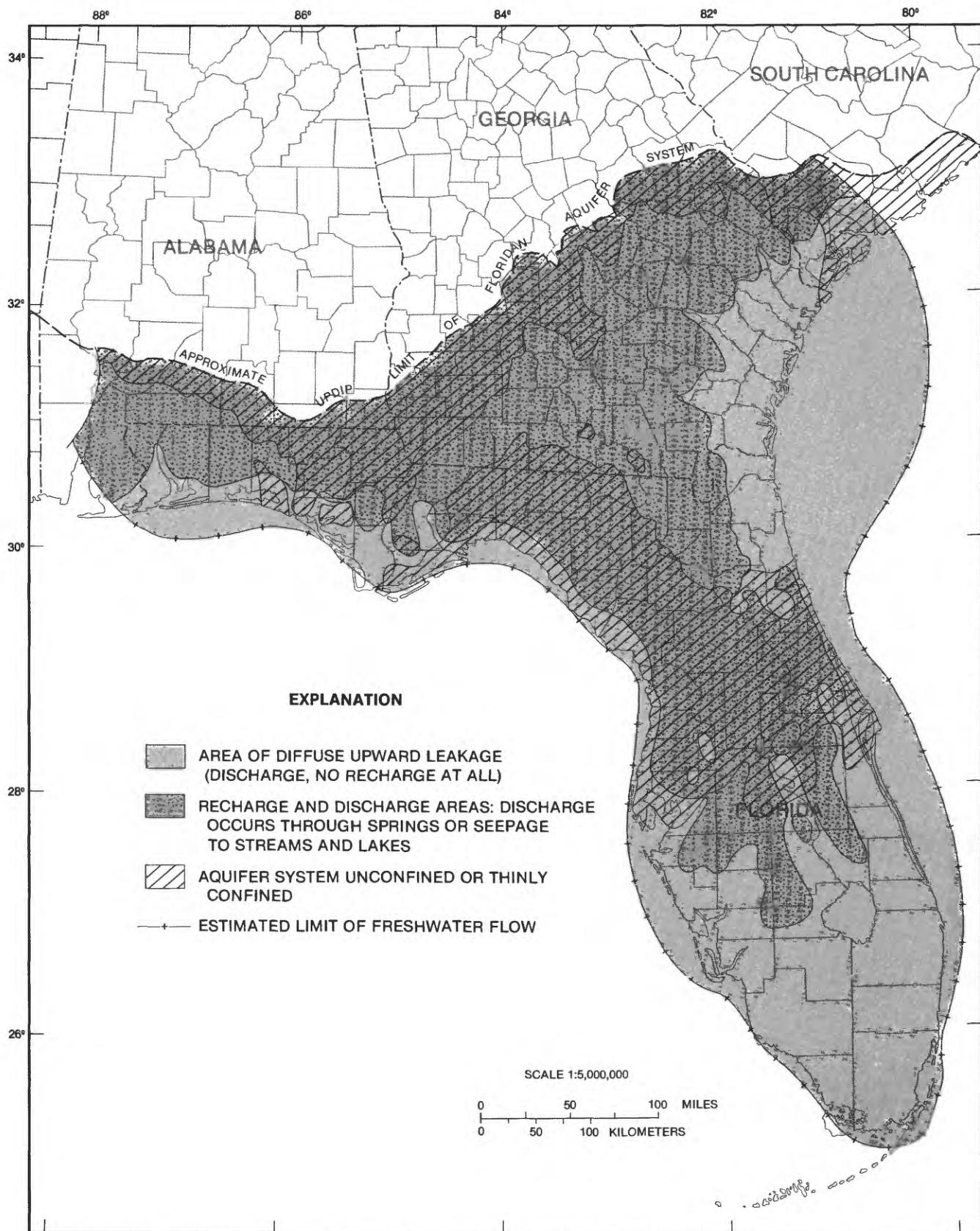
FIGURE 12.—Areas of discharge from and recharge to the Upper Floridan aquifer. (From Bush and Johnston, 1988.)
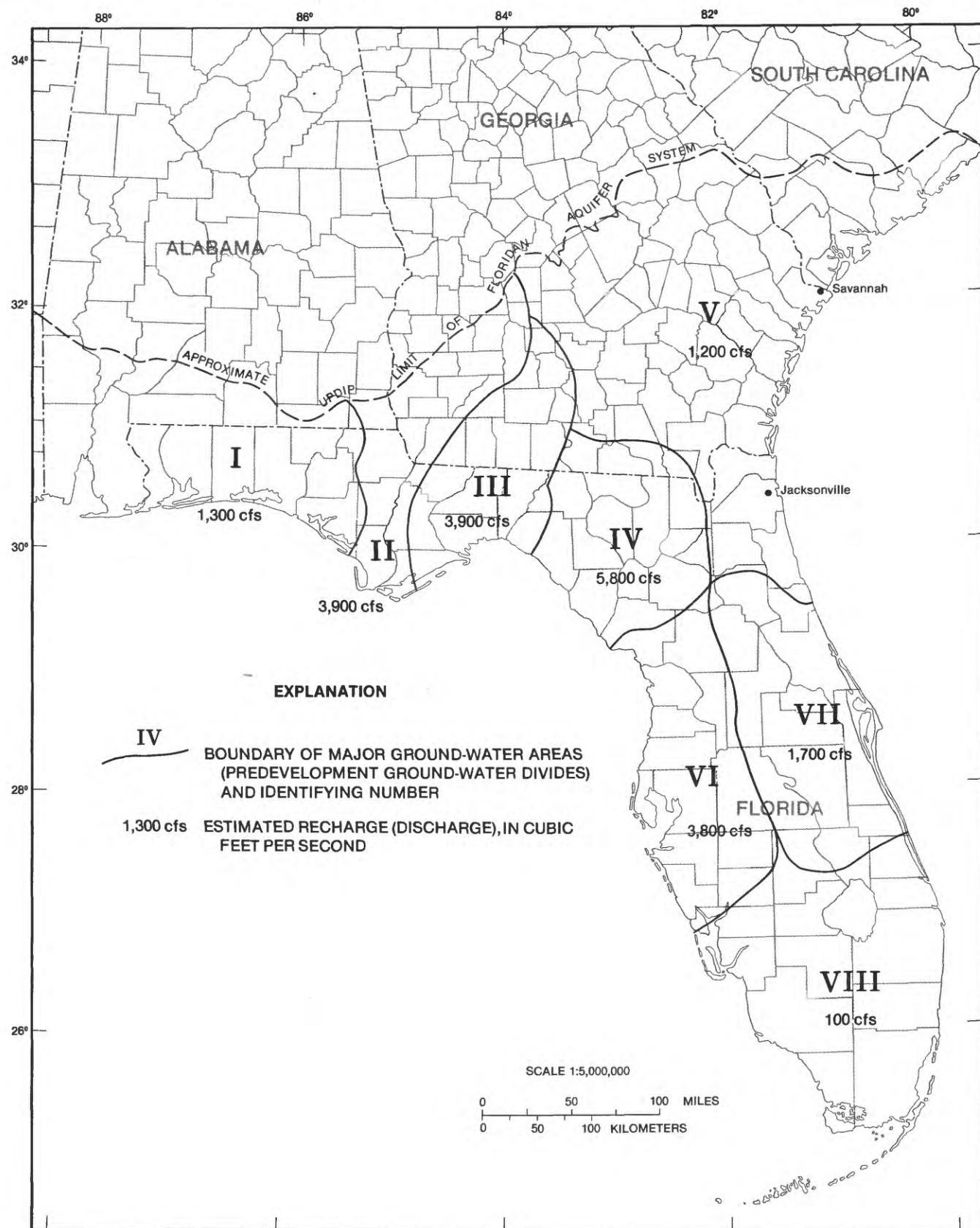
FIGURE 13.—Estimated predevelopment discharge from major ground-water areas of the Upper Floridan aquifer. (From Bush and Johnston, 1988.)

Methods for collecting and analyzing water samples have changed considerably during the period 1950 to 1982; therefore, comparing old and new chemical analyses of water samples requires some caution. Early techniques for collecting and analyzing common chemical constituents and trace metals emphasized collection of clear samples and acidification of trace metal samples with acetic acid (Rainwater and Thatcher, 1960). After about 1970, samples were routinely passed through a 0.45-micrometer (μm) filter and acidified in the field with nitric acid to pH 2.0 in order to preserve cations in solution (Brown and others, 1970; Skougstad and others, 1979). Nutrient samples, when collected, were filtered and preserved by chilling to 4 °C for "dissolved" species; unfiltered water samples were chilled to 4 °C for "total" nutrient species. Field measurements of temperature and specific conductance were routinely made throughout the 32-year (yr) period; field measurements of pH and alkalinity were routinely performed by the Geological Survey in Florida and Georgia after about 1970. Because of the need for accurate pH and alkalinity determinations for making mineral saturation calculations (Back, 1963; Barnes, 1964), only analyses of water samples collected after 1970 were used for mineral equilibria calculations during this study. The stable isotope data presented in this paper were obtained by the techniques of Epstein and Mayeda (1953), Bigeleisen and others (1952), McKinney and others (1950), and Gleason and others (1969). The ^{14}C data reported were obtained by methods described by Thatcher and others (1977, p. 17–22). Trace organic chemicals were analyzed by methods described by Goerlitz and Brown (1972) and Wershaw and others (1987).

Most of the analyses used in this study were originally reported in units of milligrams per liter (mg/L) or micrograms per liter (μg/L). For ease of comparison with other studies and with regulatory criteria, the majority of figures and tables in this report present chemical data in these units. For geochemical calculations, however, the molal unit (moles of a substance per kilogram of water) is more appropriate. The conversion from milligrams per liter to millimolal (mmolal) is made by applying the following equation:

$$\text{Substance A (mmolal)} = \frac{\text{concentration of A (mg/L)}}{\substack{\text{formula wt. of A (mg/mmol)} \times \text{solution density} \\ \text{(kg}_S\text{/L)} \times [1 - (\text{dissolved solids (ppm)} \times 10^{-6})] \\ \text{(kgH}_2\text{O/kg}_S\text{)}}}$$

Note that dissolved solids measured in milligrams per liter is approximately equal to dissolved solids expressed as parts per million in dilute solutions (solutions with density approximately 1.000 and containing dissolved solids less than 5,000 mg/L).

Chemical analyses by themselves reveal little about processes that change the chemical character of ground water as it moves through the Floridan aquifer system. One of the principal methods of interpreting natural ground-water geochemistry is to assume that all dissolved species are at equilibrium. This assumption permits the use of thermodynamic models of aqueous solutions to calculate the distribution of dissolved species, a technique adopted for this study. A wide variety of computer-based models is available to calculate distributions and activities of dissolved species (Nordstrom and others, 1979). Once the species activities are calculated, the saturation state of the solution (that is, ground water) with respect to minerals and gases can be tested. Additional computations can also be made that quantitatively predict the evolution of an initial solution into a final solution by mixing and reaction with other solutions, gases, or solids (Helgeson and others, 1970; Plummer and Back, 1980; Plummer and others, 1983).

The aqueous model used during this study is contained in a computer program called WATEQF (Plummer and others, 1978). Except as noted in the following text and in tables 9, 10, and 11, the same values of equilibrium constants, ion-pairing constants, reaction enthalpies, and temperature-dependent analytical expressions for equilibrium constants of the aqueous species listed in WATEQF (Plummer and others, 1978, table 1 and attachment A) were also used in this study. Activity coefficients were calculated for samples containing less than 1,000 mg/L dissolved solids by using the Debye-Huckel equation (Truesdell and Jones, 1974, p. 240–241); otherwise, the Davies equation (Plummer and others, 1978, p. 5) was used. WATEQF calculates both activities of aqueous species and departure from equilibrium (saturation index, or S.I.) for many solid phases (minerals) and gases that might be in contact with the aqueous phase. The S.I. is expressed as

$$\text{S.I.} = \log (\text{IAP/K}_T)$$

where

IAP = ion activity product of the components of the solid or gaseous phase, and

K_T = solid or gaseous phase solubility equilibrium product at the specified temperature.
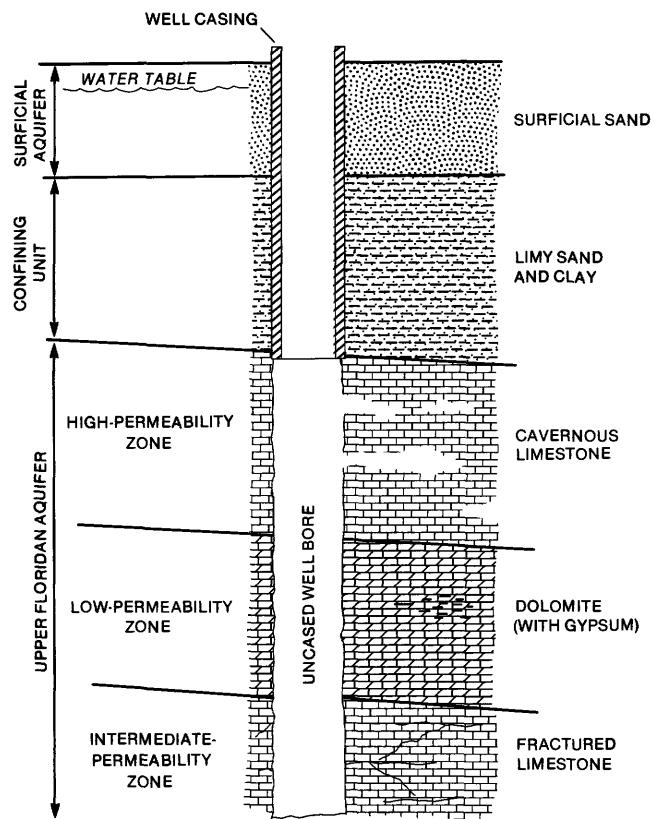
When S.I. is equal to 0, the solid or gaseous phase is in equilibrium with the aqueous phase. When S.I. is less than 0, the solid or gaseous phase is undersaturated, that is, the phase has thermodynamic potential to dissolve. When S.I. is greater than 0, the solid or gaseous phase is supersaturated, and the phase has the potential to exsolve by precipitation or volatilization. If present in the aquifer system, minerals probably are dissolving when negative saturation indices are calculated,

although the dissolution rates may be exceedingly slow. However, a potential to precipitate when S.I. is greater than 0 does not by itself cause minerals to form in the aquifer; there are other factors such as mineral surface topography, surface poisoning, and nucleation energy that may inhibit the formation and growth of a mineral (Drever, 1982, p. 116–124).

Description of the regional geochemistry required interpretation of both chemical and hydrologic data, because of ground-water mixing that affects water samples collected from wells or springs. Springflow is related to hydraulic heads within each permeable zone that contributes springflow and to amounts of recharge that occur throughout the spring's catchment area. Thus, a seasonal and year-to-year variation in the "mix" at the spring outlet is possible. This variation has not been directly observed during this study, but records of water analyses from, for example, Rainbow and Silver Springs in Marion County, Fla. (Rosenau and others, 1977, p. 269–281), show both seasonal and long-term variation, especially in sulfate and hardness. Osmond and others (1974) used uranium isotopes to separate the various shallow- and deep-flow contributions to Rainbow and Silver Springs; their methods, however, were not adopted for this study.

Samples from wells are also affected by mixing of ground water among permeable zones, because practically all the wells drilled into the Floridan aquifer system are open-bore wells (shown schematically in fig. 14). An open-bore well effectively "short circuits" the natural variations in vertical permeability, so that very small changes in head with depth are sufficient to cause flow within the bore. The important features of typical wells in the Upper Floridan aquifer are as follows: (1) the well casing generally extends only to the first rock layer encountered; (2) the well bore is open to both high- and low-permeability zones below the bottom of the casing; (3) under nonpumping conditions, water may migrate freely within the bore among zones of different hydraulic heads; and (4) under pumping conditions, the greatest amount of water is produced from zones that have the greatest horizontal permeability, regardless of static heads. These features produce a variety of possible "mixing scenarios" (table 5) for the water produced from a well. When a well in the Floridan aquifer system encounters saline water at depth, water-density effects will also affect the "mix" in pumped samples (Kohout and Hoy, 1963).

Mixing that occurs within the well bore (or spring) affects interpretation of the aquifer geochemistry by (1) modifying solution temperatures, (2) changing environmental isotope ratios, (3) changing the water's ionic strength, (4) changing net partial pressures of dissolved gases, and (5) altering solution pH and Eh. The latter

Diagrammatic, not drawn to scale.

FIGURE 14.—Typical well constructed in the Upper Floridan aquifer.

three effects are potentially significant in affecting solubilities of minerals, especially of calcite and dolomite. Many papers have been written discussing the effects of mixing on carbonate equilibria (Bogli, 1964; Ernst, 1964; Thrailkill, 1968; Runnells, 1969; Hanshaw and others, 1971; Badiozamani, 1974; Plummer, 1975; Wigley and Plummer, 1976; Hanor, 1978; Back and others, 1979). The essence of these papers is that when two waters of different CO_2 partial pressure (P_{CO_2}) or ionic strength are mixed, the molalities and activities of ions and species in the final mixture are not linearly related to the end-member values.

Wigley and Plummer (1976) discussed five factors affecting the nonlinear behavior of ion activities in mixtures, of which three are the most important in affecting the carbonate equilibria within the Upper Floridan: (1) the algebraic effect, (2) the ΔP_{CO_2} effect, and (3) the ionic strength effect. The algebraic effect describes the tendency of two dissimilar but carbonate-mineral-saturated solutions to produce oversaturated mixtures. In contrast, the ΔP_{CO_2} effect describes the tendency of undersaturated mixtures to form from solutions with different initial P_{CO_2}; if one end member contains much higher

TABLE 5.—*Examples of mixing ground water within open-bore wells in the Floridan aquifer system*

	a. Casing to top of Floridan aquifer system; heads decrease with depth	b. Casing to rock in overlying confining unit; heads decrease with depth	c. Casing to top of Floridan aquifer system; heads increase with depth	d. Casing to rock in overlying confining unit; heads increase with depth
Type I: Well idle for long time; pumping (or flowing) for short time prior to sampling	Water sample is from Floridan; water from shallowest permeable zone invades deeper zones; water sample is a mixture, may be chemically similar to water from shallowest highly permeable zone	Water sample is from confining unit and Floridan; water from confining unit invades deeper zones; water sample is mixture from Floridan and confining unit in unknown proportions	Water sample is from Floridan; water from deepest permeable zone invades shallower zones; water sample is a mixture, may be chemically similar to water in deepest highly permeable zone	Water sample is from confining unit and Floridan; water from deepest permeable zone invades shallower zones (including confining unit); water sample is a mixture, may be chemically similar to water in deepest permeable zone
Type II: Well pumped for sampling soon after drilling completed	Water sample is from Floridan; water from shallowest permeable zone beginning to invade deeper zones; water sample is a mixture from all permeable zones, dominated by most permeable zone	Water sample is from confining unit and Floridan; water from confining unit beginning to invade deeper zones; water sample is a mixture from all permeable zones, dominated by most permeable zone	Water sample is from Floridan; water from deepest permeable zone beginning to invade shallower zones; water sample is a mixture from all permeable zones, dominated by most permeable zone	Water sample is from confining unit and Floridan; water from deepest permeable zone beginning to invade shallower zones (including confining unit); water sample is a mixture from all permeable zones, dominated by most permeable zone
Type III: Well pumped (or flowing) "continuously" prior to sampling	Water sample is from Floridan; each permeable zone yields water to mix in bore depending on permeability; water sample is a mixture dominated by most permeable zone	Water sample is from confining unit and Floridan; each permeable zone yields water to mix in bore depending on permeability; water sample is a mixture dominated by most permeable zone	Water sample is from Floridan; each permeable zone yields water to mix in bore depending on permeability; water sample is a mixture dominated by most permeable zone	Water sample is from confining unit and Floridan; each permeable zone yields water to mix in bore depending on permeability; water sample is a mixture dominated by most permeable zone

P_{CO_2}, the ΔP_{CO_2} effect can overwhelm the algebraic effect. The third effect also describes a tendency for mixtures to become undersaturated, since the activities of ions in the mixture are nonlinearly related to the ionic strength of the mixture, even though the ionic strength of the mixture is related to the two end-member compositions.

Some effects of mixing water from different aquifer layers on the chemistry of samples from open-bore wells can be illustrated using theoretical mixtures of water samples collected from two deep wells in the Upper Floridan aquifer near Waycross, Ga. (Matthews and Krause, 1984). During this study, a pumping test was conducted on well TW–1 which penetrates the entire Floridan from 625 to 1,856 ft. Chemical analyses (table 6) indicate strong similarities between samples from TW–1 collected after pumping at 2,000 gallons per minute (gal/min) for nearly 48 hours and samples obtained from the same well during packer testing of permeable zones. One anomaly in the analytical results is the carbon-14 value for the pumping test sample. This sample also contained measurable tritium (3 tritium units), indicating some atmospheric contamination of the water sample.

Packer tests of selected intervals in TW–1 indicated that heads increased only a few tenths of a foot with depth (Matthews and Krause, 1984, p. 10). Matthews and Krause (1984, p. 11) also reported data from flow-meter surveys of TW–1 while pumping at a rate of about 1,900 gal/min. They calculated the following yields from different permeable zones:

Interval, feet below land surface	Yield, gallons per minute	Percentage of total flow
635–750	1,100	58
750–900	500	26
940–970	60	3
1,070–1,090	240	13
		100

Even though well TW–1 was not sampled until several months after completion, mixing of water between different zones was apparently minimized by lack of large head differences within the open interval and the comparatively low permeability of the rocks below 1,101 ft. Thus, the flow and chemical data are mutually consistent; they indicate that the water pumped from TW–1, which is 1,856 ft deep, comes almost entirely from the interval of about 635 to 1,101 ft.

TABLE 6.—*Chemical analyses of water from wells in the Upper Floridan aquifer near Waycross, Ga.*

[Molalities, saturation indices, ionic strengths, and log P_{CO2} computed by WATEQF (Plummer and others, 1978). Dashes indicate constituent not analyzed. g/mL, grams per milliliter; PDB, Pee Dee belemnite; SMOW, Standard Mean Ocean Water; CDM, Canyon Diablo meteorite]

	Well and sample depth (feet below land surface)			
	TW-2 1,901 to 1,966	TW-1 packer set at 1,101; sample from 1,101 to 1,856	TW-1 packer set at 1,101; sample from 635 to 1,101	TW-1 pump test; well open from 635 to 1,856
Date of sample	05-08-81	06-08-81	06-09-81	06-17-81
Water temperature, °C	22.5	23.8	23.1	24.0
Field pH	8.09	7.16	8.10	7.74
Density, g/mL at 20 °C	1.023	1.004	0.999	0.999
Ionic strength	5.41×10^{-1}	9.75×10^{-2}	6.60×10^{-3}	6.64×10^{-3}
$-\text{Log } P_{CO2}$	3.401	1.957	2.786	2.405
^{14}C activity, percent modern	----	0	4.3±0.6	16.5±1.5
Concentration, in millimoles per kilogram water				
Calcium (Ca)	21.11	14.49	1.074	1.099
Magnesium (Mg)	28.58	15.24	0.741	0.741
Sodium (Na)	398.7	20.47	0.697	0.653
Potassium (K)	6.182	0.486	0.061	0.049
Aluminum (Al)	0.004	0.002	0.001	0
Iron (Fe)	0.032	0.017	0.036	<0.001
Manganese (Mn)	0.006	0.001	0.002	0
Strontium (Sr)	0.207	0.106	0.003	0.003
Silica (SiO$_2$)	0.268	0.350	0.500	0.783
Field alkalinity, as CaCO$_3$	1.650	3.501	3.682	3.722
Chloride (Cl)	397.7	19.20	0.424	0.395
Sulfate (SO$_4$)	52.42	28.66	0.417	0.469
Fluoride (F)	0.302	0.416	0.032	0.026
Bromide (Br)	0.832	0.058	0.004	0.004
Sulfide (S)	0.025	0.033	0.026	----
Nitrite (NO$_2$) + nitrate (NO$_3$), as N	<0.001	<0.001	<0.001	----
Ammonia (NH$_4$) + organic nitrogen, as N	0.207	0.044	0.009	----
Orthophosphorus, as P	<0.001	<0.001	<0.001	----
Total phosphorus, as P	<0.001	<0.001	<0.001	----
Stable isotope ratios, in parts per thousand				
^{13}C/^{12}C$_{PDB}$	-4.7	-3.0	-12.1	-12.4
^{18}O/^{16}O$_{SMOW}$	-2.8	-3.3	-3.2	-3.1
^{2}H/^{1}H$_{SMOW}$	-14.5	-17.0	-15.5	-17.0
^{34}S/^{32}S$_{CDM}$	----	22.1	22.3	23.5
Saturation indices				
Calcite	0.72	0.25	0.58	0.26
Dolomite	1.73	0.68	1.11	0.47
Gypsum	-0.01	0.00	-2.14	-2.08

The samples from well TW-1 are typical of those collected from type II-c wells (table 5). Suppose, however, that the Waycross wells were resampled after 20 yr (type I-c well), or that the hydrologic conditions at the wells were different and that significant flow occurred between zones prior to the initial sampling. The chemistry of "samples" collected under various mixing conditions may be simulated using the chemical data in table 6 and the program PHREEQE (Parkhurst and others, 1980). Prior to mixing, PHREEQE was used to balance the net electrical charge of the chemical analyses given in table 6 by addition of K$^+$ or Cl$^-$, so that upon mixing the solution pH could be calculated by change in charge balance. Each analysis was also brought to calcite equilibrium by adding CO$_2$, which may have degassed from the water samples prior to field measurement of alkalinity and pH. The following changes were made to the analytical data shown in table 6:

Water sampling zone	Millimoles added			New solution		
	K$^+$	Cl$^-$	CO$_2$	pH	$-\log P_{CO2}$	Ionic strength
635-1,101	0.536	0	0.266	7.50	2.171	6.9×10^{-3}
1,101-1,856	0	0.166	0.324	6.90	1.694	9.76×10^{-2}
1,901-1,966	0.904	0	0.241	7.22	2.381	5.42×10^{-1}

The large change in pH caused by bringing the samples to calcite equilibrium appears to indicate errors in the alkalinity and pH determinations made during sampling. The collection of samples from deep wells is probably best accomplished by a closed-system apparatus (Wood, 1976), but during testing of the Waycross wells these conditions were not always satisfied.

Assuming the Waycross wells were shut in for 20 yr prior to resampling, the slight head differences measured in the wells could produce "samples" having varying chemistries, as shown in figure 15*A*. If head relationships were different and heads decreased with depth, there would be no significant change in water chemistry from that measured in 1981 because the greatest permeability occurs in the upper part of the wells (635–1,101 ft). However, if the zone from 1,901 to 1,966 ft had higher hydraulic conductivity or much higher heads (or both), saline water could invade the shallower permeable zones. "Samples" from the Waycross wells might then be similar to the mixtures shown in figure 15*B*. Other situations could be simulated by varying the estimated amounts of water entering the well bore from different zones. These examples illustrate the potential effects of mixing in open-bore wells on chemistry of samples. Large differences in analytical results between samples taken years apart might be related to mixing rather than to changes in the regional or local flow system. The examples also illustrate the complexities of interpreting new "first-time" samples from old open-bore wells. For additional discussion of the effects of well construction and pumpage on water samples, the reader is referred to Claassen (1982).

The uncertainties introduced by mixing in open-bore wells can be decreased by sampling only those wells that have been pumped or have flowed almost continuously since being drilled (type III, table 5). These wells would yield water from the same highly permeable zone year after year. Collecting water samples from a network of "continuously" flowing municipal or irrigation wells will provide a regional view of the geochemistry of the aquifer system. This method was used in peninsular Florida by Back and Hanshaw (1970). However, in exchange for obtaining unmixed samples from highly productive zones, some deficiencies in this sampling scheme must be accepted, including the following: (1) municipal and irrigation wells tend to produce only good-quality water; thus poor-quality, saline, or briny zones that occur in the system may not be detected; (2) regionally, zones of high permeability are not always continuous, and the production zones tapped by widely separated wells may yield water that traveled by different flow paths at different rates; and (3) regionally, high-permeability zones most commonly occur in the Ocala Limestone, which is almost entirely calcite.

Deeper water-bearing zones (older rock units) may contain more dolomite, gypsum, apatite, peat, or other solid phases which can markedly influence the regional ground-water chemistry.

Whether or not mixing has affected ground-water samples, calculations of calcite and dolomite saturation indices are dependent on accurate measurements of pH and dissolved inorganic carbon species (alkalinity) (Back, 1963; Langmuir, 1971; Pearson and others, 1978). The "adjustments" of analyses discussed above indicate that the greatest change in calcite (or dolomite) saturation is made when CO_2 concentrations are changed. For example, the original water analysis from the 635–1,101-ft zone of the Waycross well had an S.I.$_{calcite}$ of +0.58 at a field pH of 8.10 (table 6). "Addition" of 0.266 mmol of CO_2 (per kilogram of H_2O) brought the analysis to equilibrium with calcite at a pH of 7.50. One might question whether this amount of degassing would be observable in the field: using the ideal-gas law, the loss of 0.266 mmol of CO_2 per kilogram of H_2O from a 50-mL sample (used to measure pH) represents 0.325 mL of pure CO_2 gas (at 25 °C and 1 atmosphere). Thus, even though nonstoichiometric phases may be reacting, most of the supersaturation of carbonate minerals calculated from historic water analyses from the Floridan aquifer system is probably the result of CO_2 outgassing and change from in situ alkalinity and pH.

MAJOR CONSTITUENTS

CALCIUM

Calcium is a principal component of the major minerals in the Floridan aquifer system and therefore is a major dissolved constituent in ground water in most of the region. Concentrations of calcium ion (Ca^{2+}) in water from the Upper Floridan aquifer vary from less than 5 mg/L in western panhandle Florida to more than 570 mg/L in deep, gypsiferous zones in southwestern Florida (pl. 1). The concentration of Ca^{2+} is controlled throughout most of the aquifer system by mineral saturation and (or) cation exchange. The important reactions are

1a. $CaCO_3(calcite) = Ca^{2+} + CO_3^{2-}$,
   log $K_{25\ °C} = -8.48$ (Plummer and Busenberg, 1982),

1b. $Ca_{0.97}Mg_{0.03}CO_3(Mg\text{-}calcite) = 0.97Ca^{2+} + 0.03Mg^{2+} + CO_3^{2-}$, log $K_{25\ °C} = -8.60$ (Plummer and MacKenzie, 1974, table 3),

2. $CaMg(CO_3)_2(dolomite) = Ca^{2+} + Mg^{2+} + 2CO_3^{2-}$, log $K_{25\ °C} = -17.09$ (Robie and others, 1978),

3. $CaSO_4 \cdot 2H_2O(gypsum) = Ca^{2+} + SO_4^{2-} + 2H_2O$, log $K_{25\ °C} = -4.602$ (L.N. Plummer, U.S. Geological Survey, oral commun., 1982), and
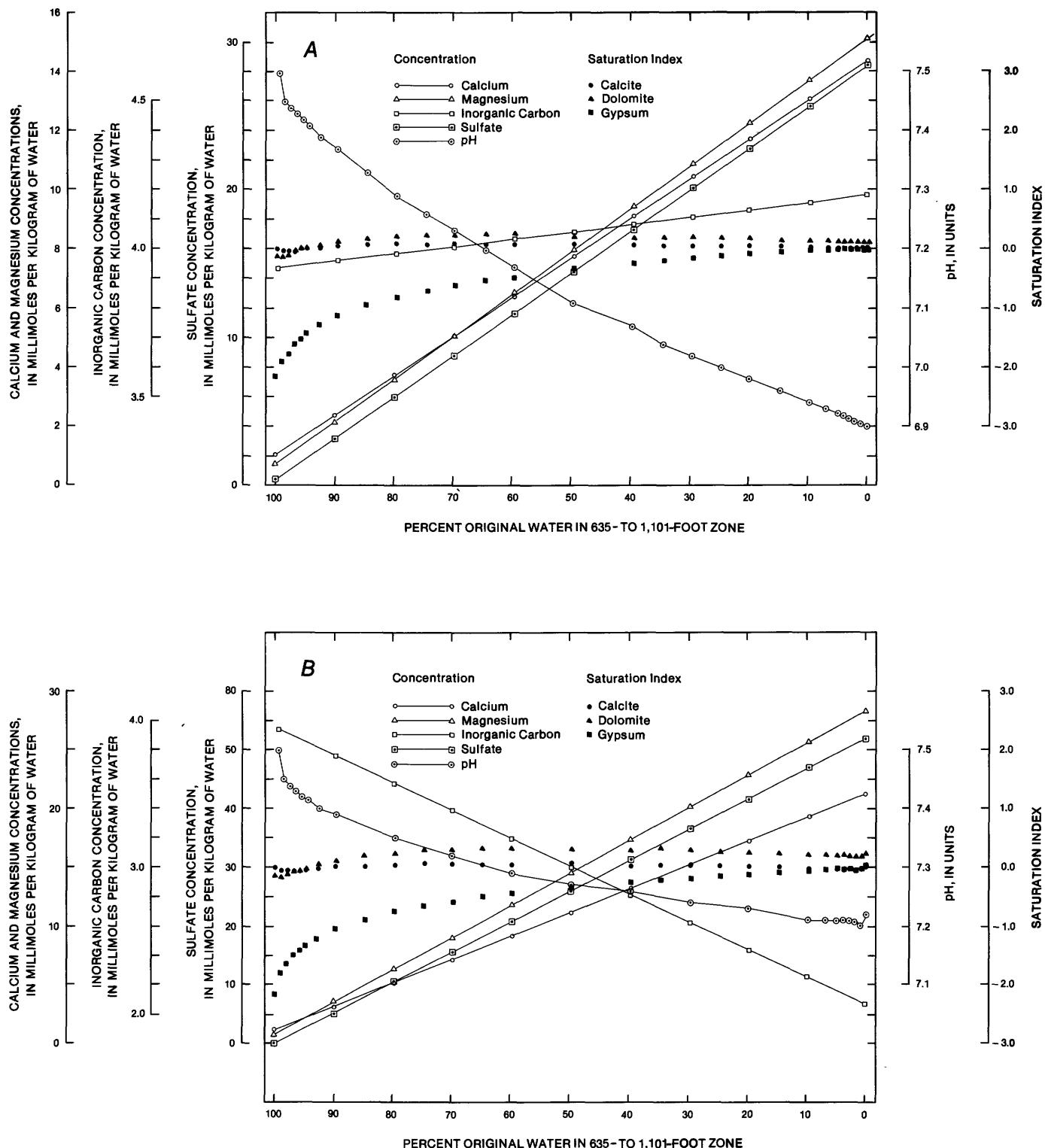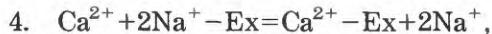
FIGURE 15. — Results of theoretically mixing waters from two zones within a deep well in the Upper Floridan aquifer near Waycross, Ga., 20 years after well completion: A, water from 1,100- to 1,856-foot zone invades 635- to 1,101-foot zone; B, water from 1,901- to 1,966-foot zone invades 635- to 1,100-foot zone.

4. $Ca^{2+} + 2Na^+ - Ex = Ca^{2+} - Ex + 2Na^+,$

where K is the solubility constant at equilibrium at 25 °C and Ex is the cation-exchange site on a solid phase.

The solubility equilibrium constant of 3 mol percent Mg-calcite (-8.60 shown in reaction 1b) is very close to pure calcite (-8.48 shown in reaction 1a), but, being slightly lower, it indicates that 3 mol percent Mg-calcite is actually more stable than pure calcite at 25 °C and 1 atmosphere pressure. Data for calculating the equilibrium solubility of Mg-calcite is being revised (L.N. Plummer, U.S. Geological Survey, oral commun., 1983), so that equilibrium constants for Mg-calcite can be more accurately compared with the equilibrium constant values of calcite derived by Plummer and Busenberg (1982). For the purposes of this discussion, either phase may be considered important in affecting the Ca^{2+} concentrations of ground water in the Upper Floridan aquifer.

Calcite is important in controlling concentrations of Ca^{2+} and CO_3^{2-} in ground water because the mineral readily dissolves or precipitates in response to changes in concentration of the two ions. A map of calcite S.I. computed by WATEQF (fig. 16) was prepared using water analyses from selected wells in the Upper Floridan aquifer. The analyses included field measurements of temperature, pH, and alkalinity in addition to concentrations of major species, and the selected wells were located along major flow paths or major ground-water divides (see fig. 13). Given an estimated range of error in field pH of ± 0.1 unit, an estimated range of error in field alkalinity of ± 10 percent, and the potential for CO_2 outgassing, a calculated S.I. in the range of -0.2 to $+0.2$ is considered indicative of saturation with calcite.

From figure 16, it appears that the S.I. of calcite for ground water in most of the Upper Floridan aquifer varies no more than 0.2 log unit from 0.0, indicating saturation with calcite. Ground water is undersaturated with calcite in outcrop areas of southwestern Georgia, southeastern Alabama, and north-central Florida. In these areas, the aquifer system is exposed or is covered with only a veneer of residuum or surficial sand, thus allowing frequent direct recharge of mildly acidic rainfall. The small area of undersaturation in east-central Florida is a local recharge area where the Upper Floridan aquifer is confined by thick sand and clay deposits. The confining unit is locally breached, however, by sand-filled sinkholes (Wyrick, 1960, p. 27), and, apparently, reaction between rainwater and calcareous sediments in the sinkholes is sufficiently slow relative to downward movement of recharge water that ground water in the Upper Floridan aquifer is undersaturated with calcite. The large area of apparent undersaturation in east-central Georgia may be related to local cation exchange of sodium for calcium, which reduces calcium

concentrations (see pl. 1) and brings ground water below saturation with calcite. An alternative hypothesis is that underlying Cretaceous and Tertiary sand aquifers are discharging dilute sodium-bicarbonate water into the Upper Floridan aquifer. Other chemical effects that might be explained by this leakage hypothesis are discussed on the following pages.

Large deviations from calcite saturation occur in coastal areas of Florida and Georgia, where saline water (seawater?) is present in the Upper Floridan aquifer. As wells are pumped for sampling, freshwater and saline water mix within the well bore, producing a mixed water at the wellhead that is not in equilibrium with calcite. Theoretical studies by Plummer (1975) showed that mixing of calcium-carbonate ground water and at least 10 percent seawater would produce a mixture oversaturated with calcite. The ground water in coastal areas of Georgia and Florida also contains appreciable amounts of dissolved gypsum, which influences the S.I. calculation through the common Ca^{2+} ion. Other wells, especially in southwestern Florida, tap several permeable zones that contain either calcium-sulfate or calcium-bicarbonate water (pl. 9); pumping these wells produces a water mixture that often is oversaturated with calcite.

The amount of calcite and dolomite dissolved in ground water is determined primarily by the amount of CO_2 in solution. Thus, Ca^{2+} (and Mg^{2+}) concentrations are markedly affected by CO_2-dissolved carbonate equilibria. Garrels and Christ (1965, p. 74–92) and Stumm and Morgan (1981, p. 171–185) describe the geochemical relations of dissolved carbonate species, pH, and carbonate minerals. The important features of solutions with carbonate species are that in the absence of strong buffers, increasing CO_2 partial pressure (by organic decay, for example) lowers solution pH and decreases the CO_3^{2-} concentration, allowing more carbonate minerals to dissolve. Decreasing CO_2 partial pressure (for example, by decreasing ground-water pressure during pumping) tends to raise solution pH, increase CO_3^{2-} concentrations, and possibly precipitate carbonate minerals. Mixing of different ground-water solutions in open-bore wells or along the saltwater-freshwater interface can also affect the carbonate equilibria and saturation level of carbonate minerals in the Upper Floridan aquifer, as discussed previously.

Concentrations of Ca^{2+} of less than 1 millimole per liter (mmolar), approximately 40 mg/L, occur in small areas of central Florida (pl. 1). In these areas the Upper Floridan aquifer is unconfined (fig. 11) and ground water is undersaturated with calcite and dolomite (figs. 16, 18). Simulation of the predevelopment flow system in east-central Florida (Tibbals, in press) indicates that substantial recharge to the system occurs in these areas. This recharged water passes through sandy soils or enters the
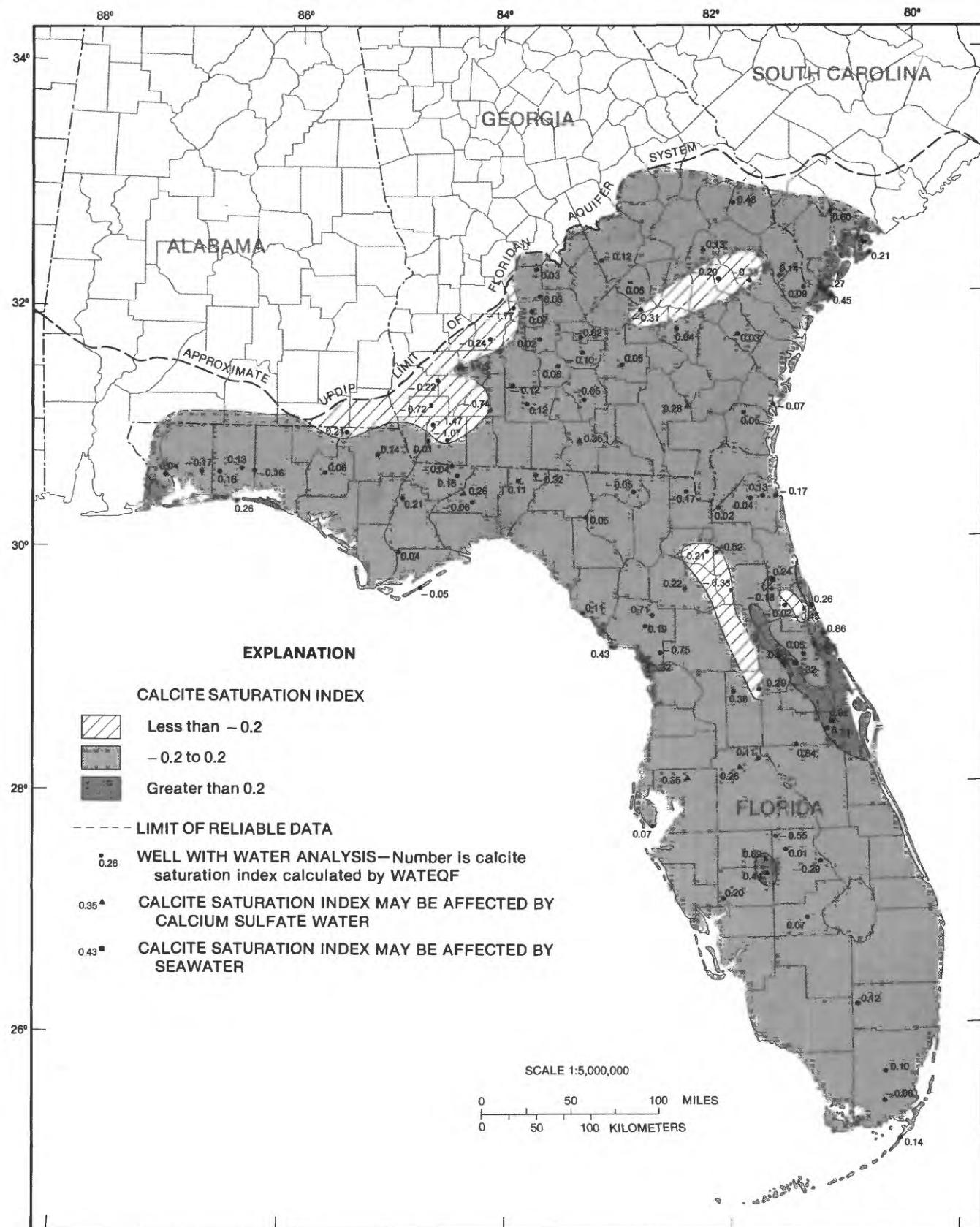
FIGURE 16.—Calcite saturation index computed from analyses of water samples from selected wells in the Upper Floridan aquifer.

aquifer system directly through sinkholes or drainage wells. Water downgradient contains higher Ca^{2+} concentrations, as calcite and dolomite have dissolved to reach equilibrium. In the St. Johns River valley, high Ca^{2+} concentrations occur because of remnant saline water (seawater?) in the Upper Floridan aquifer. The presence of saline water so far from the coast is discussed in more detail in the section on chloride concentrations in the Upper Floridan. Low concentrations of Ca^{2+} and HCO_3^- (less than 40 and 122 mg/L, respectively) and carbonate mineral undersaturation occur in the outcrop area near Lee County in southwestern Georgia and near Houston County in southern Alabama. These sites lie within ground-water area II (fig. 13), which has nearly the highest predevelopment discharge rates per square mile of any part of the Upper Floridan aquifer. In these areas, the amount of dilute recharge dominates the chemistry of water in the aquifer. In outcrop areas northeast and west of area II, however, Ca^{2+} and HCO_3^- concentrations are higher, perhaps because chemistry of recharge and amounts of recharge are quite different from the rest of area II. Two additional areas of low Ca^{2+} (less than 40 mg/L) are mapped in southwestern and east-central Georgia. In these areas, the Upper Floridan is thickly confined, amounts of recharge are small, and ground-water circulation is slower than in upgradient areas. It may be that the Ca^{2+} concentrations result from small amounts of local recharge that is chemically very different from recharge in the upgradient areas.

A narrow zone of low Ca^{2+} concentrations (less than 40 mg/L) extends from Gadsden County in Florida to Ben Hill County in Georgia and lies almost entirely within ground-water area III (fig. 13). This zone is adjacent to and upgradient from the Gulf Trough grabens (fig. 8). As mentioned previously, in southwestern Georgia the Upper Floridan is underlain by calcareous sands of early and middle Eocene age. These sands locally contain dilute $Na^+ - HCO_3^-$ or $Ca^{2+} - Na^+ - HCO_3^-$ type ground water (Lee, 1984). Hydraulic gradients in these sands indicate that ground water could leak into the Floridan aquifer system along the northwestern margin of the Gulf Trough. This leakage may explain the slight dilution of Ca^{2+} and HCO_3^- concentrations (pls. 1, 3), the change in Na/Cl molar ratios (fig. 21A), and the slight increase in Na^+ concentrations (pl. 4) that occurs locally in water from the Upper Floridan aquifer. Preliminary simulation of flow in the sand aquifers indicates that less than 50 ft^3/s is leaking into the Upper Floridan over this area (R.A. Barker, U.S. Geological Survey, oral commun., 1984). The earlier discussion of ground-water area III highlighted the large discharge from the Upper Floridan aquifer (3,900 ft^3/s). However, about three-fourths of the discharge from area III occurs from large springs and river seepage near the Gulf Coast. Where the zone of low

Ca^{2+} concentrations is mapped, ground-water flow is much more sluggish; steady-state simulation of the predevelopment flow system indicates that only about 500 ft^3/s are locally recharging the system (Bush, 1982). These initial flow computations indicate that it is reasonable to assume that leakage from the Eocene sand units is producing the chemical changes noted in water in the Upper Floridan aquifer. More chemical data from both the Eocene sands and the water-table aquifer are required in order to better estimate the contribution of each source to the total recharge of the Upper Floridan aquifer in the area of the Gulf Trough.

Ground water in the Upper Floridan aquifer is saturated with calcite, but not with dolomite (figs. 16, 18), throughout the Gulf Trough area. Ca^{2+} concentrations increase to 1 to 2 mmolar (40 to 80 mg/L) in the Gulf Trough area, but dissolved magnesium concentrations generally remain constant at about 0.5 to 1 mmolar (12 to 24 mg/L), as shown in plate 2. Dissolution of gypsum rather than dolomite is probably increasing Ca^{2+} concentrations in the Gulf Trough area, since sulfate concentrations are also locally higher in the vicinity of the grabens (pl. 7). Downgradient from the Gulf Trough, some recharge through the overlying confining beds occurs, adding dilute Ca^{2+}-HCO_3^- water to the Upper Floridan aquifer and thus maintaining Ca^{2+} concentrations at about 1 to 2 mmolar (40 to 80 mg/L) and calcite at saturation, while reducing the sulfate concentration. Dissolved magnesium concentrations in the area downgradient from the Gulf Trough are probably affected by both dilution with recharge water and dissolution of dolomite where the mineral is undersaturated. The result is that dissolved magnesium concentrations downgradient from the Gulf Trough are relatively unchanged.

The second large area of low Ca^{2+} concentrations is in southeastern Georgia, shown in plate 1 as a circular area centered near the intersection of Bulloch, Bryan, and Evans Counties. The confining unit overlying the Upper Floridan aquifer in this area is thick, the aquifer has low ground-water circulation rates, and predevelopment recharge averages less than 0.3 inch per square mile per year (in/mi²/yr) (Bush, 1982). Upward leakage of dilute water from underlying Eocene sand aquifers appears to be the cause of this extensive area of low Ca^{2+} concentrations. Upward leakage from the sand aquifers probably occurs only in Toombs, Chandler, and northern Bulloch Counties, based on the location of the Gulf Trough (fig. 8) and the updip limit of the Lower Floridan aquifer (fig. 9). At the time of this study hydraulic head and chemical data were not available from the Eocene sand aquifers in these three counties, so head relationships between the two aquifer systems and chemical composition of water from the sand aquifers were unknown. Preliminary simulation of ground-water flow

in the sand aquifers indicates that less than $\frac{1}{2}$ in of diffuse upward leakage is occurring in this area (Barker, 1986). Nevertheless, the changes in water chemistry within the Upper Floridan aquifer appear to be caused by this small amount of leakage. The upward leakage is probably dilute Na^+-HCO_3^- water from the underlying sand aquifers, since Ca^{2+} concentrations decrease while HCO_3^- concentrations (pl. 3) remain almost constant, Na^+ is locally in great excess over Cl^- (fig. 21A), dissolved silica increases (fig. 30), and ground water in the Upper Floridan aquifer becomes undersaturated with both calcite and dolomite (figs. 16, 18).

Unlike southwestern Georgia, the area of low Ca^{2+} concentrations in east-central Georgia extends downgradient well past the Gulf Trough; the low Ca^{2+} concentrations persist in the Upper Floridan almost to the Georgia-South Carolina coast. Hydraulic gradients are small in this area (fig. 10), suggesting that the Gulf Trough has less of a "damming" effect on ground-water flow. Certainly the geologic structure has much less influence on the local water chemistry of the Upper Floridan: SO_4^{2-} concentrations do not increase in the vicinity of the grabens (pl. 7); nor do Mg^{2+} concentrations increase (pl. 2), even though dolomite is locally undersaturated. Under predevelopment conditions, the low-Ca^{2+} concentration area contained both recharge and discharge areas of the Upper Floridan (fig. 12); therefore, recharge from overlying confining beds cannot be diluting Ca^{2+} concentrations in the discharge area. Upward leakage from the Lower Floridan aquifer is an unlikely source of low Ca^{2+} concentrations in the discharge area of the Upper Floridan aquifer, because water in the Lower Floridan generally contains higher concentrations of dissolved constituents than the Upper Floridan (see fig. 27). Also, simulation of the predevelopment flow system indicated that very small quantities of upward leakage from the Lower Floridan occur in this area (Krause, 1982). Apparently, low Ca^{2+} concentrations persist in the Upper Floridan almost to the coast because calcite is at saturation and gypsum and dolomite are locally scarce. As discussed in the following pages, a mixed-bicarbonate facies (pl. 9) occurs in the discharge part of this low-Ca^{2+} concentration area. The occurrence of this facies implies that sodium-rich water is recharging the Upper Floridan aquifer in sufficient quantities to alter the normal calcium (or calcium-magnesium) predominance in dilute ground water in the system. The chemistry of water in the Lower Floridan aquifer in this area is not known, but it may be similar to the water chemistry in Tertiary sand aquifers, since the Lower Floridan is stratigraphically equivalent to and hydraulically connected with these sands. Without further information from both the sand aquifers and the Lower

Floridan, description of the processes affecting the geochemistry of the Upper Floridan in this area must remain conjectural.

Cation-exchange is apparently responsible for the low Ca^{2+} concentrations in water from the Upper Floridan aquifer in panhandle Florida. In this area, there are abundant exchange materials (primarily clays) in the aquifer. Also, the system's upper confining unit is thick, so that the diluting effects of freshwater recharge are almost zero (Bush, 1982; Bush and Johnston, 1988). The map of Na^+/Cl^- molar ratios (fig. 21A) indicates a large overabundance of Na^+ in the area, yet this excess Na^+ is apparently not due to silicate weathering, as discussed in a later section. Although Ca^{2+} concentrations are low, calcite (and dolomite) are at saturation in this area (figs. 16, 18) because bicarbonate concentrations are locally very high (pl. 3). The causes of the high bicarbonate concentrations in this area are discussed in a later section.

In coastal areas, water in the Upper Floridan aquifer mixes with seawater as the system discharges into the ocean. Both theoretical studies (Runnells, 1969; Plummer, 1975; Wigley and Plummer, 1976) and field studies (Back and others, 1979) have shown that mixing of calcite-saturated ground water with calcite-saturated seawater may lead to ground water that is undersaturated with respect to calcite. The freshwater-seawater mixture may also be at or above saturation with respect to dolomite, depending on P_{CO_2}, pH, and magnesium content of the mixture. The effects of mixing typical calcite-saturated freshwater from the Upper Floridan (table 7) and seawater in various proportions were calculated using the program PHREEQE (Parkhurst and others, 1980). During mixing computations, the model added calcite to or removed calcite from the mixed solution in order to maintain calcite saturation. The results in table 8 and figure 17 show that the large increase in Ca^{2+} concentrations in coastal areas of the Upper Floridan aquifer are due primarily to the Ca^{2+} added by seawater, not to calcite dissolution. The theoretical results of table 8 indicate that mixing seawater with ground water like that from the Inglis well (pl. 1) should dissolve the greatest amounts of calcite. This is due to both the ΔP_{CO_2} and the ionic-strength effects mentioned previously. The high total CO_2 concentration in the Inglis water sample (table 7) does not commonly occur in ground water from the Upper Floridan aquifer, but has been exceeded in a few analyses reviewed during this study. The analysis from the well near Hull (pl. 1) is more typical of the total CO_2 concentration (table 7) in the Upper Floridan aquifer. The analysis from the Green Swamp well (pl. 1) is typical of total CO_2 (table 7) measured in water samples from recharge areas in Georgia and central Florida.

TABLE 7.—*Chemical analyses of water from wells in the Upper Floridan aquifer and seawater used in theoretical mixing calculations*

[In millimoles per kilogram of water, unless otherwise indicated]

Constituent	Hull[1] well	Green Swamp well	Inglis well	Sumatra well	Seawater[2]
Well depth, feet	1,411	856	155	200	----
Water temperature, °C	30.7	25.0	23.0	22.0	25.0
pH, units	7.39	7.98	7.30	7.52	8.22
Titration alkalinity, milliequivalents per liter	3.437	2.398	5.456	4.456	2.293
Ca^{2+}	2.747	0.851	2.496	0.973	10.527
Mg^{2+}	2.347	0.396	0.263	1.234	54.391
Na^+	4.006	0.210	0.309	0.566	479.323
K^+	0.118	0.023	0.010	0.072	10.446
Sr^{2+}	0.309	0.004	0.002	0.035	0.095
SiO_2	0.417	0.234	0.075	0.316	0.073
Cl^-	5.647	0.221	0.282	0.220	558.629
F^-	0.084	0.011	0.011	0.037	0.075
SO_4^{2-}	3.230	0.015	0.146	0.188	28.893
HCO_3^-	3.445	2.400	5.460	4.460	2.069
$^3CO_3^{2-}$	0.0191	0.0107	0.0049	0.0064	0.221
Total CO_2	3.670	2.423	6.002	4.722	
Log P_{CO_2}, atmospheres	−2.078	−2.826	−1.809	−2.120	[4]−3.399

[1] Well locations shown on plate 1.

[2] Seawater data from Nordstrom and others (1979, table 3).

[3] Calculated from total HCO_3^-, pH, and analytic expression for log K_T given in WATEQF (Plummer and others, 1978, reaction 69, p. 20).

[4] Calculated by WATEQF (Plummer and others, 1978).

FIGURE 17.—Theoretical changes in calcium concentration in mixtures of ground water from the Upper Floridan aquifer and seawater. Dark bars represent calcium added (or removed) to maintain calcite saturation in the mixture.

Back and Hanshaw (1970) emphasized that the observed differences in the hydrology and chemistry of the limestone aquifers in the Yucatan and Floridan peninsulas were directly related to the presence of a confining unit in Florida and the absence of a confining unit in the Yucatan. The principal hydraulic effects of confinement on the Floridan aquifer system are to (1) reduce the potential for direct recharge from precipitation, thus reducing the amount of dissolution of rock minerals such as calcite, and (2) increase the potential for deep circulation, thus resulting in substantial chemical changes in the ground water as it moves downgradient. Plummer (1977) and Plummer and others (1983) showed that water in the Upper Floridan aquifer chemically evolves in a predictable way as it moves downgradient from the central Florida potentiometric high. This chemical evolution is governed by only a few reactions: dolomite dissolution driven by irreversible gypsum dissolution, calcite precipitation, and sulfate reduction. Although these reactions occur at different rates and in different amounts depending on the flow path of water through the confined system, the ground water evolves into solutions chemically similar to the samples from the Hull and Sumatra wells (table 7). As the calculations of

table 8 show, theoretical mixtures of seawater with waters from the Hull and Sumatra wells will dissolve much less calcite than mixtures of seawater and water from the well near Inglis (unconfined system evolution). The methods used by Back and others (1979, table 2) to calculate the amounts of calcite dissolved in the mixing zone in Yucatan cannot be used with the data available from the Upper Floridan aquifer. Nevertheless, the chemical process occurring in the Yucatan does appear to be operating in the unconfined areas of the Upper Floridan aquifer in west-central Florida (ground-water areas III, IV, and VI, fig. 13), because the results of the theoretical mixing calculations for the water from the Inglis well and seawater are very similar to the results given in Back and others (1979, figs. 9, 10).

The highest concentrations of Ca^{2+} in water from the Upper Floridan aquifer occur where gypsum solubility is the geochemical control. Dissolution of gypsum (reaction 3) may add large amounts of Ca^{2+} to solution; if small amounts of bicarbonate are also present, the ground water could become oversaturated with calcite. If calcite then precipitates (reaction 1) to maintain equilibrium, Ca^{2+} and CO_3^{2-} are both removed, leading to undersat-

TABLE 8.—*Theoretical results of mixing four types of ground water from the Upper Floridan aquifer with seawater (SW), while maintaining equilibrium with calcite*

[Chemical data used to calculate these results are given in table 7. mmoles, millimoles. Dashes indicate calculation not performed]

Well name (locations shown on pl. 1)	Mixing with no reaction[1]		Mixing with calcite at equilibrium[2]					
	Ionic strength	Ca^{2+} added, in mmoles	Calcite dissolved, in mmoles	Total Ca^{2+} added, in mmoles	pH	Log P_{CO2}, in atmospheres	Saturation indices	
							Mg-calcite[3]	Dolomite
Hull (with CO_2)	0.0211	----	----	----	7.19	−1.87	0.120	0.050
Hull − 1% SW	0.0278	0.0778	0.0118	0.0896	7.20	−1.89	0.119	0.117
− 2% SW	0.0344	0.1557	0.0223	0.1779	7.21	−1.91	0.120	0.177
− 5% SW	0.0543	0.3892	0.0415	0.4307	7.24	−1.95	0.124	0.308
− 10% SW	0.0872	0.7783	0.0530	0.8313	7.27	−2.01	0.128	0.444
− 20% SW	0.1526	1.5566	0.0451	1.6017	7.30	−2.08	0.133	0.593
− 30% SW	0.2179	2.3349	0.0203	2.3552	7.31	−2.15	0.135	0.678
Green Swamp (with CO_2)	0.0039	----	----	----	7.71	−2.55	0.110	−0.269
Green Swamp − 1% SW	0.0109	0.0968	0.0112	0.1080	7.74	−2.59	0.116	0.048
− 2% SW	0.0178	0.1936	0.0159	0.2095	7.75	−2.62	0.121	0.204
− 5% SW	0.0383	0.4840	0.0186	0.5026	7.76	−2.65	0.128	0.424
− 10% SW	0.0723	0.9679	0.0119	0.9798	7.74	−2.66	0.132	0.571
− 20% SW	0.1398	1.9358	−0.0110	1.9248	7.69	−2.66	0.136	0.684
− 30% SW	0.2069	2.9037	−0.0367	2.8670	7.65	−2.66	0.137	0.735
Inglis (with CO_2)	0.0086	----	----	----	6.98	−1.49	0.089	−0.931
Inglis − 1% SW	0.0156	0.0803	0.0706	0.1510	7.01	−1.52	0.099	−0.477
− 2% SW	0.0225	0.1607	0.1208	0.2815	7.03	−1.55	0.106	−0.272
− 5% SW	0.0430	0.4017	0.2098	0.6115	7.07	−1.60	0.115	0.027
− 10% SW	0.0769	0.8034	0.2769	1.0803	7.11	−1.67	0.121	0.252
− 20% SW	0.1439	1.6068	0.3103	1.9171	7.15	−1.76	0.128	0.460
− 30% SW	0.2105	2.4102	0.2935	2.7037	7.18	−1.85	0.131	0.568
Sumatra (with CO_2)	0.0073	----	----	----	7.48	−2.08	0.120	0.138
Sumatra − 1% SW	0.0141	0.0956	0.0180	0.1135	7.49	−2.11	0.120	0.241
− 2% SW	0.0210	0.1911	0.0282	0.2194	7.50	−2.13	0.122	0.317
− 5% SW	0.0414	0.4778	0.0395	0.5173	7.51	−2.16	0.126	0.453
− 10% SW	0.0752	0.9557	0.0377	0.9934	7.50	−2.19	0.130	0.564
− 20% SW	0.1423	1.9113	0.0174	1.9287	7.47	−2.22	0.133	0.661
− 30% SW	0.2090	2.8670	−0.0071	2.8599	7.46	−2.26	0.134	0.707

[1] Mixing and reaction to calcite equilibrium were calculated using PHREEQE (Parkhurst and others, 1980).

[2] Each water was initially charge balanced (by adding Na^+ or Cl^-), then CO_2 was added (removed) to bring the solution to equilibrium with calcite. All subsequent mixing and reactions to calcite equilibrium were calculated as closed, isothermal systems, using the reported temperature of each ground-water sample.

[3] S.I. for $Ca_{0.97} Mg_{0.03} CO_3$ calculated using log $K_T = -8.60$ and ΔH (enthalpy) estimated at −2.60 kilocalories per mole.

uration and possibly to dissolution of dolomite (reaction 2). This dedolomitization process has previously been described in both the Floridan aquifer system and the Madison Limestone of the Northern Great Plains aquifer system (Back and others, 1983; Plummer and others, 1983). The quantitative effect of this reaction sequence on ground-water chemistry is directly dependent on the local abundance of gypsum; the map of sulfate concentrations (pl. 7) gives a general indication of areas where gypsum is present in more than trace quantities in the Upper Floridan aquifer. The ranges of sulfate concentration shown in plate 7 indicate that less than about 0.5 mmol of gypsum has dissolved per liter of water in areas where dolomite is at saturation. Sulfate reduction may have decreased the observed Ca^{2+} concentrations slightly in some areas, but, from the reaction stoichiometry, the low levels of sulfate imply that less than 0.5 mmol of dolomte per liter of water should have dissolved incongruently.

MAGNESIUM

Magnesium is a major component of dolomite and a minor component of calcites, and possibly of phosphatic minerals, in the Upper Floridan aquifer. Magnesium ion (Mg^{2+}) is therefore a major dissolved constituent in the freshwater parts of the aquifer system. Concentrations of Mg^{2+} in seawater are about 1,320 mg/L; thus, where brackish or saline water is present, Mg^{2+} concentrations may equal or exceed Ca^{2+} concentrations. Mg^{2+} concentrations in water from the Upper Floridan (pl. 2) range from less than 1 mg/L in outcrop areas to more than 1,000 mg/L in coastal areas where seawater is present in the aquifer. As shown in plate 2, magnesium concentrations

are less than about 1 mmol/L (24 mg/L) in most areas of the Upper Floridan.

Like Ca^{2+}, the concentration of Mg^{2+} is controlled by mixing of freshwater with seawater, carbonate mineral saturation, or ion exchange. The chemical reactions are

1. $CaMg(CO_3)_2 = Ca^{2+} + Mg^{2+} + 2CO_3^{2-}$

2. $Ca_{0.97}Mg_{0.03}CO_3 = 0.97Ca^{2+} + 0.03Mg^{2+} + CO_3^{2-}$

3. $Mg^{2+} + 2Na^+ - Ex = Mg^{2+} - Ex + 2Na^+$

The equilibrium solubility constants for reactions 1 and 2 were given in the preceding discussion of calcium geochemistry. Reaction 1 is the likely source of Mg^{2+}, and reaction 2 is the most likely sink for Mg^{2+} (Plummer, 1977, p. 809), in ground water in the Upper Floridan aquifer.

The dissolution of dolomite (reaction 1) is the most important reaction controlling Mg^{2+} concentrations in freshwater parts of the Upper Floridan aquifer. A map showing the S.I. of stoichiometric dolomite (log $K_t = -17.09$ at 25 °C) calculated from selected water analyses (fig. 18) indicates that water in large areas of the Upper Floridan is near saturation with the mineral. Significant undersaturation occurs in Georgia and central Florida, apparently because the mineral is absent or is present in only trace amounts in the permeable section. Significant oversaturation was calculated for water in downgradient areas and may be related to a combination of factors, including (1) errors in analytical data, especially pH and alkalinity measurements, (2) local mixing of chemically different ground waters due to open-bore wells, (3) local occurrence of more soluble, nonstoichiometric dolomites, or (4) inhibition of dolomite crystallization due to kinetic effects. Recent compilations of papers on dolomitization processes (Zenger and others, 1980; Zenger and Mazzullo, 1982) stress the occurrence of "metastable" forms of the mineral in recent sediments and evidence of recrystallization to more stable forms in older rocks. Cook (1984) reported that dolomite crystals in the Avon Park Formation were compositionally zoned, with calcium-rich crystal centers apparently leached selectively over the more stoichiometric rims. Ground water in contact with the rocks containing these crystals was very saline (dissolved solids ranging from 10 to 35 grams per liter (g/L)) and oversaturated with dolomite, yet no dolomite precipitation could be detected by petrographic or scanning-electron-microscopy methods. These results indicate that any or all of the four factors could lead to the apparent dolomite oversaturation in downgradient regions of the Upper Floridan aquifer.

In contrast to Ca^{2+}, there are large areas where Mg^{2+} concentrations in water from the Upper Floridan are less than 0.5 mmolar (<12 mg/L) (pl. 2). Areas of low Mg^{2+} concentration in Georgia and central Florida coincide with recharge areas of the system, where the aquifer is composed primarily of calcite and contains relatively dilute water. The low concentrations of Mg^{2+} in panhandle Florida are most likely the result of ion exchange within the aquifer system. The processes involved in sodium-for-magnesium exchange are generally the same as those involved in sodium-for-calcium exchange, although the sorption strength of most clays for Mg^{2+} may be less than for Ca^{2+}. The exchange of Na^+ for Mg^{2+} might proceed, since Ca^{2+} concentrations in the panhandle area are also very low (pl. 1). As shown in figure 18, significant dolomite undersaturation has been measured in some water samples from the panhandle area. These results indicate that dolomite precipitation is not the mechanism responsible for decreasing Mg^{2+} concentrations in that area. Formation of authigenic Mg^{2+}-bearing silicate minerals might account for some of the observed Mg^{2+} loss in panhandle Florida, but mineralogical data and data on aluminum and silica concentrations (discussed later in this paper) are insufficient to test this possibility.

Concentrations of Mg^{2+} in water from the Upper Floridan aquifer in Georgia and Florida generally increase in a downgradient direction. These increases occur even though dolomite is apparently saturated or supersaturated in much of the area. The dedolomitization process (Back and others, 1983) could increase Mg^{2+} concentrations and still maintain near-saturation of dolomite in the aquifer. During dedolomitization, approximately 0.40 mole of dolomite dissolves for each mole of gypsum, while approximately 0.83 mole of calcite precipitates. These reactions tend to lower pH while increasing P_{CO_2}. If ground water is oversaturated with respect to stoichiometric dolomite, however, only less stable dolomite phases should be dissolving. Uncertainties in the solubility and stoichiometry of dolomites within the Upper Floridan aquifer combined with imprecision in determining in situ pH and alkalinity (by making these measurements in "mixed" water samples from the aquifer) preclude an unequivocal definition of the source of Mg^{2+} in downgradient areas.

The highest concentrations of Mg^{2+} occur where saline water (seawater?) is present in the Upper Floridan aquifer. In coastal areas of Florida, in the valley of the St. Johns River, and in southern Florida where chloride concentrations are greater than 1,000 mg/L (pl. 6), the aquifer contains at least 5 percent seawater. If the freshwater-seawater mixing is conservative for Mg^{2+} ion, this amount of seawater would add about 67 mg/L of Mg^{2+}. Theoretical mixing of saline water and freshwater from the Upper Floridan generally produces solutions oversaturated with dolomite (table 8); however, it is uncertain whether dolomite actually precipitates, thus serving as a control on Mg^{2+} concentrations in the mixing
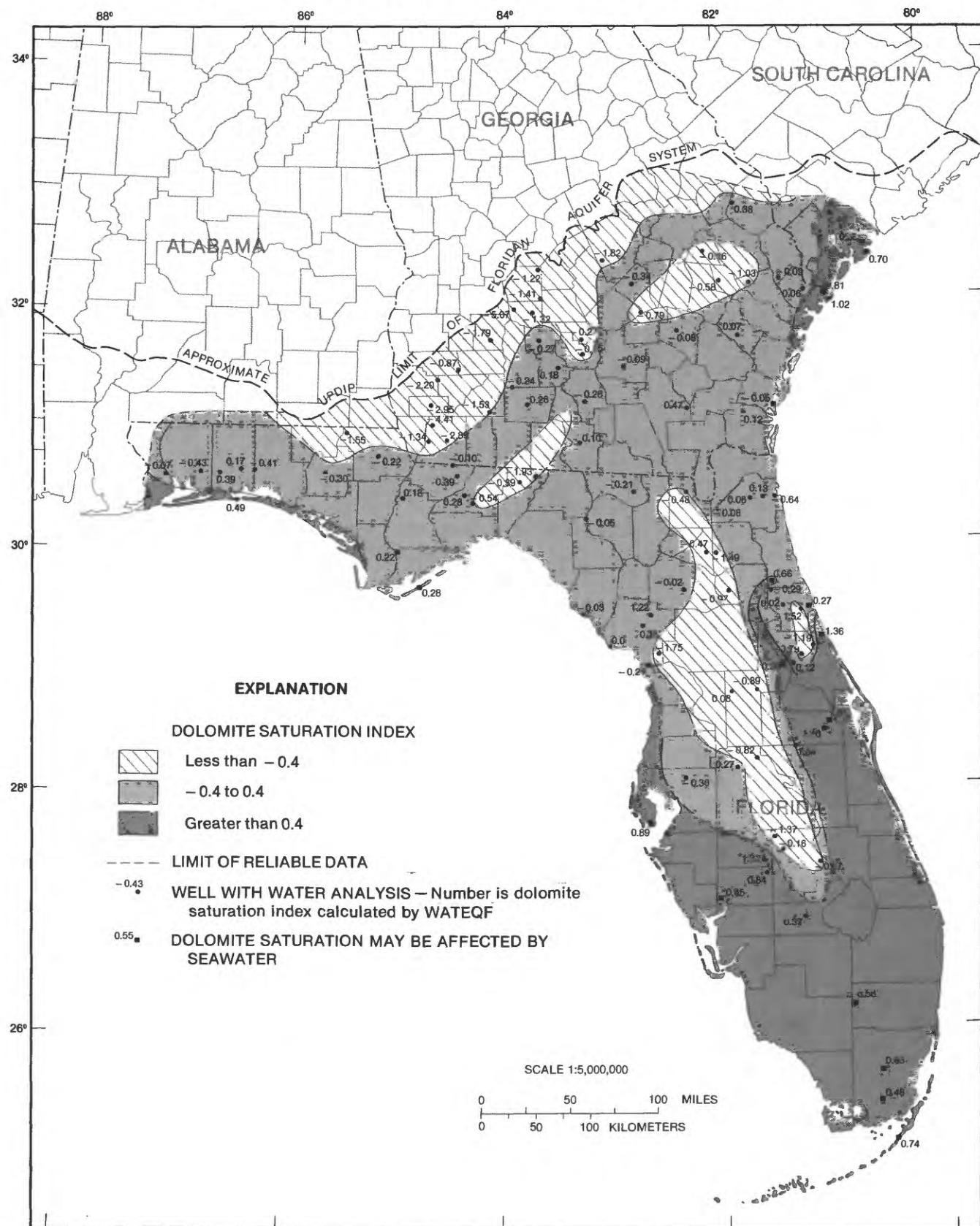
FIGURE 18.—Dolomite saturation index computed from analyses of water samples from selected wells in the Upper Floridan aquifer.

zone. Studies cited in the "Mineralogy" section of this paper indicate that dolomite in upper Eocene rocks of the Gulf Coast of Florida formed in a mixing zone where salinity was lower than the salinity of seawater. Whether or not dolomite is actively forming in coastal mixing zones of the Floridan aquifer system needs further study.

TOTAL HARDNESS

Total hardness is a water-quality property of limited geochemical significance, but it is important for certain water uses; high levels of total hardness may cause excessive scale in pipes and boilers. Figure 19 shows the total hardness of water from the Upper Floridan aquifer. "Hardness" is a term that has long described certain chemical properties of water, yet it is a term that is difficult to define exactly. For years, the hardness of water was defined by the reaction of water with soap ("hard" water tended to form an encrustation or curd). Because all multivalent cations (especially the commonly found alkaline-earth cations—calcium, magnesium, strontium, and barium) can contribute to the soap reaction, a practical definition of hardness is "the effect of alkaline-earth cations" (Hem, 1985, p. 158). Today, hardness can be measured by titrating a water sample with a reagent that reacts with multivalent metal cations (alkaline earths, plus iron, manganese, zinc, copper, lead, and others, if present). More routinely, however, total hardness (as $CaCO_3$) is calculated by multiplying by 50.05 the sum of milliequivalents per liter of the alkaline earths (Skougstad and others, 1979, p. 281). Because most metal cations are present in only trace amounts, the total hardness of ground water in the Upper Floridan aquifer is due primarily to calcium and magnesium ions.

The total hardness of water in the Upper Floridan aquifer varies from less than 50 to more than 5,000 mg/L as calcium carbonate ($CaCO_3$). Generally, where the aquifer system is composed only of limestone, the total hardness is equivalent to carbonate hardness and is less than 120 mg/L. Ground water with higher total hardness usually results from (1) dissolution of other aquifer minerals, primarily dolomite and gypsum, (2) mixing of freshwater with residual saline ground water, (3) encroachment and mixing of modern-day seawater, or (4) contamination. Natural softening of the ground water by cation exchange may be responsible for the low hardness in Escambia and Santa Rosa Counties, Fla. (fig. 19).

The noncarbonate hardness of water in the Upper Floridan aquifer ranges from less than 10 to more than 4,000 mg/L as $CaCO_3$ (fig. 20). Noncarbonate hardness is the difference between total hardness and alkalinity (Skougstad and others, 1979, p. 283). Noncarbonate hardness is due to alkaline-earth salts other than carbon-ates and bicarbonates; in the Upper Floridan aquifer, the noncarbonate hardness in freshwater areas results primarily from dissolution of gypsum. As discussed previously, deep wells in the Upper Floridan are likely to yield highly mineralized water. Because the gypsum content of the Floridan aquifer system generally increases with depth, total hardness (and noncarbonate hardness) of the ground water also increases with depth. In coastal areas, the salts in seawater may also contribute to noncarbonate hardness in the Upper Floridan aquifer.

The U.S. Geological Survey classifies water on the basis of total hardness (in milligrams per liter as $CaCO_3$) as follows (Hem, 1970, p. 225):

0–60	Soft
61–120	Moderately hard
121–180	Hard
More than 180	Very hard

Much of the water in the Floridan aquifer system that is very hard may be unsuitable for industrial uses without treatment. For domestic use, there is a higher level of tolerance, apparently through decreased consumer sensitivity after continual use (National Academy of Sciences/National Academy of Engineering, 1972, p. 68). Medical studies (Muss, 1962; Schroeder, 1966; Sauer, 1974; Marier and others, 1979) have found a significant correlation between increased levels of hardness in drinking water and a decreased risk of cardiovascular disease in humans.

BICARBONATE AND CARBONATE

The principal anion in most of the ground water in the Upper Floridan aquifer is bicarbonate (HCO_3^-). Plate 3 shows that HCO_3^- concentrations range from 2 to 4 mmol/L (122 to 244 mg/L) throughout most of the region. Sources of HCO_3^- in ground water are (1) dissolution of CO_2 gas in recharge water, principally within the soil zone, (2) dissolution of carbonate minerals, and (3) biochemical oxidation of organic materials. Many of the papers cited in previous sections discuss carbonate equilibria in natural waters; within the Upper Floridan aquifer the carbonate system is the strongest natural buffer, tending to maintain ground-water pH within the range 7.0 to 8.5. In this range the predominant carbonate species is HCO_3^-. At a pH of about 10.3, HCO_3^- and CO_3^{2-} are equal in concentration, and at a pH of about 6.3, H_2CO_3 (aqueous CO_2) and HCO_3^- are equal in concentration (Hem, 1970, fig. 19).

Many papers attempt to relate the total CO_2 dissolved in ground water to the CO_2 of the soil zone in recharge areas because of the effects CO_2 equilibria exert on both rock dissolution (for example, Thrailkill, 1968; Langmuir, 1971; Shuster and White, 1972; Long and Saleem, 1974; Drake and Wigley, 1975; Harmon and others, 1975;

EXPLANATION

TOTAL HARDNESS OF WATER, IN
    MILLIGRAMS PER LITER AS CaCO$_3$

0 to 60

61 to 120

121 to 180

Greater than 180

——— LIMIT OF RELIABLE DATA

— — — APPROXIMATE UPDIP LIMIT OF FLORIDAN AQUIFER SYSTEM

○   WELL–Penetrating less than half of upper
        permeable zone

•   WELL– Penetrating half or more of upper
        permeable zone

SCALE 1:5,000,000
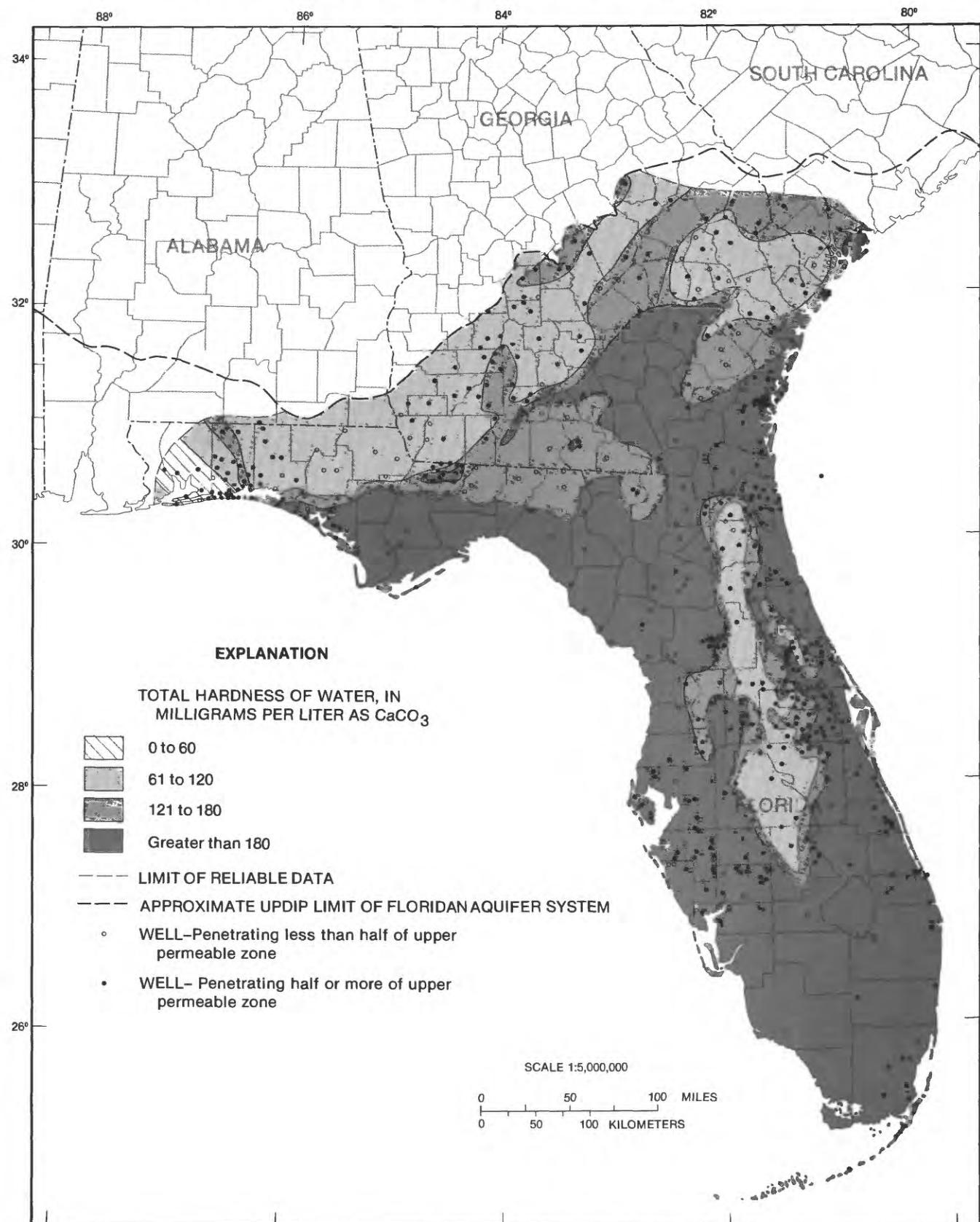
FIGURE 19.—Total hardness of water from the Upper Floridan aquifer.

EXPLANATION

NONCARBONATE HARDNESS, IN
MILLIGRAMS PER LITER AS CaCO3

0 to 60

61 to 120

121 to 180

Greater than 180

LIMIT OF RELIABLE DATA

APPROXIMATE UPDIP LIMIT OF FLORIDAN AQUIFER SYSTEM

SCALE 1:5,000,000

0   50   100   MILES

0   50   100   KILOMETERS
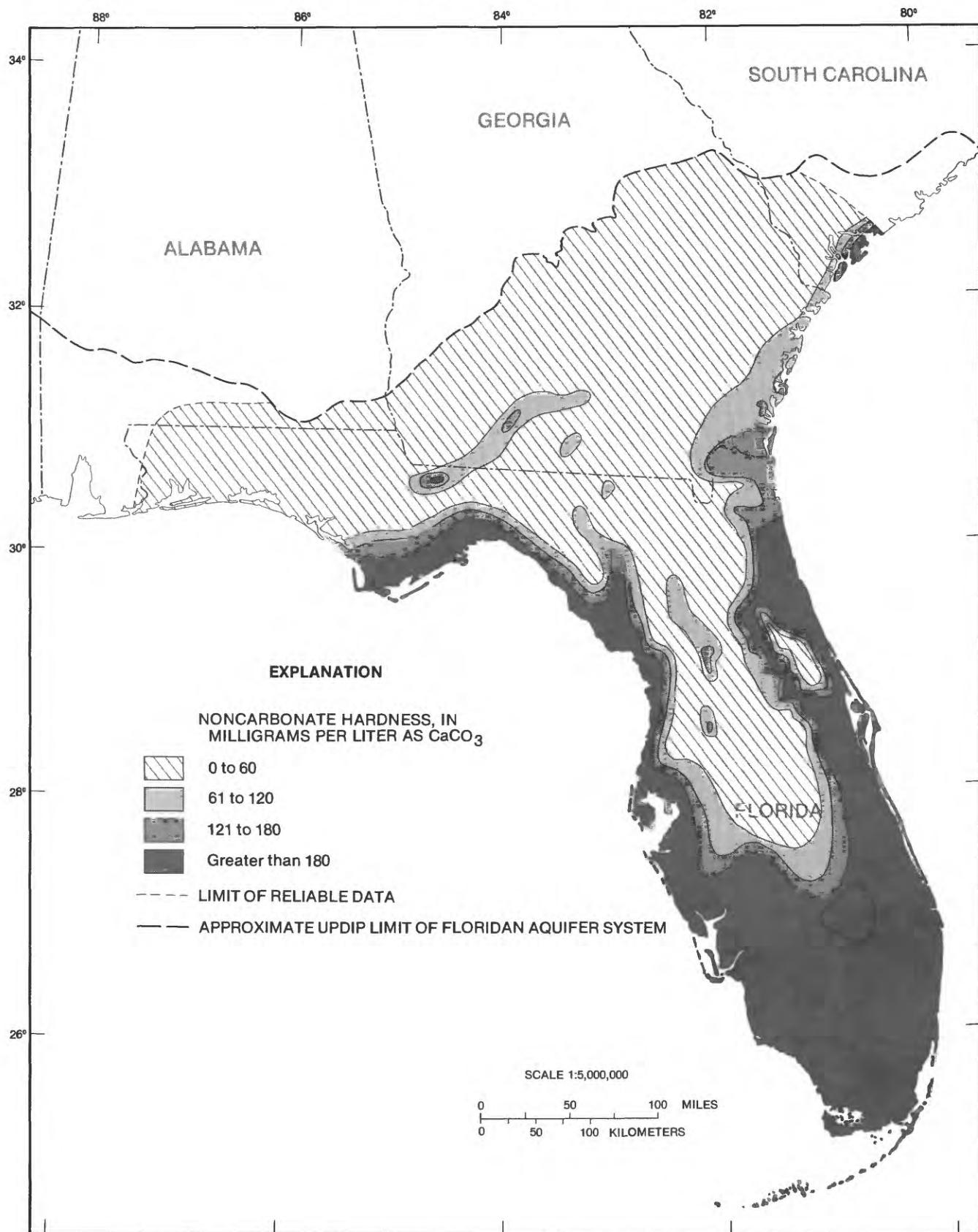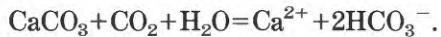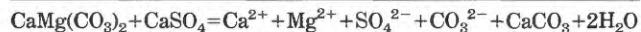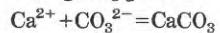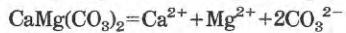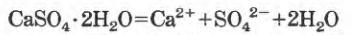
FIGURE 20.—Noncarbonate hardness of water from the Upper Floridan aquifer.

Trainer and Heath, 1976; Pitman, 1978) and the carbon isotope content of ground water (for example, Pearson and Hanshaw, 1970; Rightmire and Hanshaw, 1973; Deines and others, 1974; Fritz and others, 1978; Pearson and others, 1978; Rightmire, 1978). Drake and Wigley (1975) derived a general relation between soil P_{CO_2} and soil zone temperature which explained the P_{CO_2} in calcium-carbonate-saturated ground water that had evolved under essentially "closed system" conditions. Trainer and Heath (1976) developed a preliminary model of the bicarbonate concentrations in ground water from eastern North America using the timing of principal recharge (seasonal factor), soil and vegetation cover, soil zone P_{CO_2}, and soil zone temperature; their model generally accounted for observed latitudinal variations in dissolved carbonate species. Trainer and Heath cautioned, however, that data required for model computations were scanty and that, therefore, the parameter values assumed to make initial calculations needed to be field tested and refined both for better understanding of the processes involved and for making better quantitative evaluations. This prudent counsel is justified by nearly all the studies cited. Given the current understanding of the processes involved, quantitative evaluations of rock dissolution rates and carbon isotope contents in ground water may be made only after soil CO_2 pressures, soil temperatures, and soil water chemistry have been determined at a local scale.

The close relation between HCO_3^- concentrations and Ca^{2+} concentrations (pls. 1, 3) indicates that calcite solubility generally controls both Ca^{2+} and HCO_3^- concentrations in the Upper Floridan aquifer:

$$CaCO_3 + CO_2 + H_2O = Ca^{2+} + 2HCO_3^-.$$

The dedolomitization reactions mentioned in the previous section have some effect on the total carbonate species in solution. As can be seen by combining the reactions involved,

$$CaSO_4 \cdot 2H_2O = Ca^{2+} + SO_4^{2-} + 2H_2O$$
$$CaMg(CO_3)_2 = Ca^{2+} + Mg^{2+} + 2CO_3^{2-}$$
$$Ca^{2+} + CO_3^{2-} = CaCO_3$$

$$\overline{CaMg(CO_3)_2 + CaSO_4 = Ca^{2+} + Mg^{2+} + SO_4^{2-} + CO_3^{2-} + CaCO_3 + 2H_2O}$$

total dissolved inorganic carbon should increase 1 mol for each mole of gypsum dissolved. Because the abundance of gypsum in the Upper Floridan aquifer is relatively low over most of the region, the general effect of these reactions on HCO_3^- concentrations is small. In northeastern and west-central Florida, sulfate and magnesium concentrations are higher than expected from seawater dilution (based on Cl^- concentration), and the dedolomi-

tization reaction might be increasing the HCO_3^- concentration above 244 mg/L in these areas. Ground water in these two confined areas also contains measurable HS^- concentrations (fig. 26), indicating that oxidation of a reduced carbon species (peat?) is occurring. Although sulfate reduction produces CO_2, the process probably increases local concentrations of HCO_3^- by only small amounts: Plummer and others (1983, p. 679) used ^{13}C and [34]S data to calculate that only about 6 percent of the total inorganic carbon added to ground water between Polk City and Wauchula, Fla., came from oxidation of peat.

Along the Gulf Coast of Florida, high HCO_3^- concentrations are mapped far inland from areas high in Ca^{2+} and Mg^{2+}; high Ca^{2+} and Mg^{2+} concentrations occur nearer the coast, where seawater and freshwater mix in the aquifer. The anomalously high HCO_3^- concentrations might be related to increased dissolution of the aquifer in this unconfined recharge area (open-system dissolution) except that the chemical analyses from this area show excess anions, and the HCO_3^- concentrations are not balanced by the sum of the Ca^{2+} and Mg^{2+} concentrations (compare pls. 1, 2, 3). Much of this area is covered by hardwood and pine forests which generate organic litter high in soluble organic acids. These organic acids might be present in locally high concentrations in the water that recharges the Upper Floridan aquifer, and thus might have been titrated (along with inorganic carbon species) in the alkalinity determination. This hypothesis cannot be tested with the available data because dissolved organic carbon content was not determined in the original water samples. Some water samples from this area are colored, but quantitative estimates of the organic carbon content cannot be made because iron and manganese in solution also contribute to color. Whether or not the alkalinity titration measured only inorganic carbon species, the cation-anion imbalance is apparently due to unmeasured cations, possibly iron and ammonia. If these constituents are present in concentrations high enough to affect the charge balance, then significant biochemical activity is occurring in the aquifer. Biochemical activity could produce the excessive HCO_3^- "measured" by the alkalinity titration, but the exact nature and quantitative importance of the biochemical processes are unknown at this time. Seawater-freshwater mixing in the aquifer along the Gulf Coast is probably responsible for some dissolution of limestone and increase of HCO_3^- concentrations. Theoretical calculations (table 8) indicate that only about 0.3 mmol (<20 mg/L) of HCO_3^- would be added to ground water by calcite dissolution during mixing. A few wells in the Upper Floridan aquifer along the Gulf Coast yielded water samples with HCO_3^- concentrations greater than 350 mg/L, an almost 100-mg/L increase in HCO_3^- concentrations over samples from wells farther inland.

Apparently, freshwater-seawater mixing is responsible for only a fraction of the increase in HCO_3^- concentrations in water from wells in the Upper Floridan aquifer along the Gulf Coast of Florida. Most of the increased HCO_3^- in solution appears to be due to undefined biochemical processes occurring locally in the aquifer.

The area of high HCO_3^- concentrations in east-central Florida is partly related to the local recharge area in western Volusia County. Here, the confining unit overlying the Upper Floridan is thin and consists of calcareous sand, and recharge is sufficiently abundant to produce undersaturation with calcite and dolomite. On the eastern flank of the recharge area, calcite and dolomite apparently dissolve under a partly open system, producing moderately high HCO_3^- concentrations. The HCO_3^- concentrations are probably augmented by carbonate mineral dissolution occurring in the residual(?) seawater-freshwater mixing zone between the recharge area and the coast. Sulfate reduction also occurs locally, which adds some HCO_3^- to the ground water, but quantification is not currently possible because isotopic data are insufficient to calculate amounts of sulfide produced. Nearer the coast, Ca^{2+} and Mg^{2+} concentrations increase owing to greater amounts of seawater in the Upper Floridan aquifer, and both calcite and dolomite are supersaturated. The decline in HCO_3^- concentrations in the same area appears to be the result of calcite (and dolomite?) precipitation.

In western panhandle Florida, concentrations of HCO_3^- in water from the Upper Floridan aquifer are at the highest levels observed in this study. As discussed previously, Ca^{2+} concentrations in the area are very low, being controlled by cation exchange or calcite saturation. This is the only area where the Upper Floridan contains a sodium-bicarbonate hydrochemical facies (pl. 9). Upgradient concentrations of HCO_3^- are also anomalously high compared with other confined areas of the Upper Floridan. Measurable amounts of HS^- (fig. 26) indicate that the HCO_3^- concentration has been supplemented by microbial oxidation of organic material and sulfate reduction. However, upgradient sulfate concentrations are low—less than 20 mg/L (pl. 7)—indicating that sulfate reduction may not locally be an important source of CO_2 to the system. Nearer the coast, the seawater content of the ground water increases, based on evidence from chloride concentrations (pl. 6). In the western panhandle area, conservative mixing should produce sulfate concentrations of at least 140 mg/L where Cl^- concentrations are above 1,000 mg/L. Since observed sulfate concentrations are below 10 mg/L in the western panhandle, significant sulfate reduction must have occurred sometime in the past. As mentioned previously, ground-water flow within the Upper Floridan aquifer is sluggish in this area. It appears, therefore,

that the amount of CO_2 generated by sulfate reduction should currently be very small because sulfate concentrations are low and inflow of sulfate-rich water is not occurring under modern-day flow conditions. The high HCO_3^- concentrations measured in this area may be a chemical residue of previously higher levels of microbial activity in the Upper Floridan. Measurements of $\delta^{13}C$ and $\delta^{34}S$ in ground water from this area need to be made before the total effect of sulfate reduction on local HCO_3^- concentrations can be determined.

Although oxidation of organic materials is traditionally thought to be responsible for producing most of the bicarbonate in sodium-bicarbonate ground water (Renick, 1924b; Foster, 1950; Chapelle, 1983), this process appears to be of minor importance in western panhandle Florida, primarily because the Upper Floridan aquifer locally contains so little organic material. An exchange-driven carbonate-disequilibrium process previously described in sand aquifers (Foster, 1950; Back, 1966; Zack and Roberts, in press) may be the process generating the high HCO_3^- concentrations in the western panhandle area. As $2Na^+$ for Ca^+ exchange occurs, carbonate minerals become locally undersaturated, allowing a small amount of calcite (and dolomite, if present) to dissolve and reestablish saturation. As ground water moves downgradient, the exchange-dissolution reactions progressively add bicarbonate and remove Ca^{2+} from solution. The carbon isotopic content of HCO_3^- in water from the Upper Floridan aquifer can be used to test this progressive disequilibrium hypothesis; unfortunately, the only $\delta^{13}C$ measurement in this area is from a well tapping the uppermost part of the Lower Floridan aquifer in northern Santa Rosa County, Fla. (regional monitor #3 of Hull and Martin, 1982; see pl. 3 for location). A sample from this well contained -4.5 o/oo $\delta^{13}C$; other major constituents measured in samples from this well (Hull and Martin, 1982, table 25) were similar to those in samples from the Upper Floridan aquifer in the area. Because the monitor well is located so near the updip limit of the Lower Floridan (fig. 9), it may be assumed that the hydrochemistry of the Lower Floridan aquifer is approximately that of the Upper Floridan aquifer in this area. If this assumption is valid, the $\delta^{13}C$ content of the Lower Floridan sample indicates that isotopically heavy carbonate species were added to solution, since $\delta^{13}C$ in the monitor well sample is heavier than in samples from recharge areas of the aquifer system (table 17). Alternatively, isotopically heavy carbonate may have been added to solution during methane production. Data from table 2 indicate that calcite (and dolomite) from the Upper Floridan have $\delta^{13}C$ near 0.0; if these minerals dissolve in a closed system, the $\delta^{13}C$ of the HCO_3^- in ground water would increase. In the panhandle area, there have been few measurements of

methane in water in the Upper Floridan; nonetheless, methane has been detected in three wells in Escambia and Santa Rosa Counties (table 4). Unfortunately, the regional effect of methane production on $\delta^{13}C$ of HCO_3^- in water in the Upper Floridan aquifer cannot be determined until the concentrations and $\delta^{13}C$ of methane have been more extensively measured. Lacking adequate data on either biogenic CO_2 or CH_4 contributions to the $\delta^{13}C$ content of water in the Upper Floridan in this area, the progressive dissolution of aquifer minerals seems a plausible explanation of the observed $\delta^{13}C$ at the monitor well. Further testing of the hypothesis must await more data from this area.

The lowest HCO_3^- concentrations in water from the Upper Floridan aquifer are in southern Alabama and southwestern Georgia. The aquifer is unconfined in these areas (fig. 11), and recharge reaches the aquifer after passing through thin, sandy residuum. Apparently, only small amounts of calcite react with the recharge water in the soil zone because HCO_3^- concentrations are low and ground water is undersaturated with calcite throughout these areas (fig. 16). Simulation of the predevelopment flow system in these areas (Bush and Johnston, 1988) indicates that discharge to the many streams draining the area is rapid and ground-water circulation rates are high. The intensity of local ground-water recharge and discharge is probably the most significant factor affecting the low HCO_3^- concentrations in the outcrop areas. An additional factor is the apparent lack of calcite reaction in the soils of this area. Other parts of the Upper Floridan where the upper confining unit is thin or absent have similarly high circulation rates, yet HCO_3^- concentrations are generally greater than 2 mmol (244 mg/L).

Another area of low HCO_3^- concentration is mapped in Decatur and Mitchell Counties, Ga. The low HCO_3^- concentrations occur in a narrow region immediately upgradient from a low-Ca^{2+}-concentration area adjacent to the Gulf Trough, which was discussed previously. These low HCO_3^- concentrations occur in an unconfined area, but there is no apparent reason for them to occur upgradient from the area of low Ca^{2+} concentration. As discussed previously, the underlying Eocene sand aquifers probably contain dilute water, dominated primarily by Na-HCO_3^- or Ca^{2+}-Na^+-HCO_3^- ions. Conservative mixing of these types of water with the water dominated by Ca^{2+}-HCO_3^- that is present in the Upper Floridan should dilute Ca^{2+} and HCO_3^- equally. If the dilution occurs with a Na^+-HCO_3^- water, dissolved calcium should decrease even more than dissolved bicarbonate. At this time the best explanation seems to be that cumulative errors in determination of pH and alkalinity indicate an apparent decrease in HCO_3^- concentrations that is greater than the decrease in Ca^{2+} concentrations.

SODIUM AND POTASSIUM

The concentration of dissolved sodium (Na^+) and potassium (K^+) in water from the Upper Floridan aquifer ranges over several orders of magnitude. The lowest concentrations are near the concentrations in rainfall: about 1 mg/L of Na^+ and 0.2 mg/L of K^+ (table 1). In the coastal mixing zones and in inland areas where remnant seawater is present in the Upper Floridan, Na^+ concentrations exceed 500 mg/L, and K^+ concentrations exceed 20 mg/L. Over most of the region, Na^+ concentrations are less than 1 mmolar (<23 mg/L) (pl. 4) and K^+ concentrations are less than about 0.1 mmolar (<5 mg/L) (pl. 5).

Sodium and potassium are alkali metals which are highly soluble in water, and once dissolved, their ions tend to remain in solution. Both Na^+ and K^+ may exchange with other cations on clay minerals, but exchange reactions generally tend to increase the concentration of Na^+ and K^+ in dilute ground water. To determine areas where cation exchange might be occurring in the Upper Floridan, figure 21A was prepared showing molar excess Na^+ over Cl^- in ground water. Assuming either seawater or halite to be the source of Na^+, the "normal" molar ratios of Na^+ to Cl^- in ground water should occur in the range 0.86 to 1.0. Precipitation over the region generally shows excess Na^+ because of leaching of soil particulates in the atmosphere (Junge and Werby, 1958, p. 419–420); the average Na^+/Cl^- molar ratio in precipitation over the region (table 1) is 1.23. A large excess of Na^+ over Cl^- in areas where the system is known to contain trace amounts of clay minerals is interpreted as evidence of exchange of $2Na^+$ for Ca^{2+}. In unconfined areas of the system, excess Na^+ over Cl^- may be the result of sodium being leached from fertilizers applied to the soils. The very low Na^+/Cl^- ratios in central Georgia are calculated from water samples having very low concentrations of both sodium and chloride. Although the exchange of $2Na^+$ for Ca^{2+} is a reversible process, these low ratios in central Georgia more likely are due to (1) analytical error in determining sodium and chloride in the water samples or (2) unidentified chloride sources in the recharge areas that are not sodium rich.

In most of the region, Na^+ concentrations are low owing to the trace amounts of Na^+ in precipitation and in the principal minerals of the aquifer system. Using trace metal data from Metrin (1979), calculations indicate that for each mole (about 100 g) of calcite dissolved, about 14 mg of Na^+ would be added to solution; similarly, about 155 mg of Na^+ would be added for each mole (about 185 g) of dolomite dissolved. Concentrations of Ca^{2+} and Mg^{2+} indicate that only about 1–2 mmol of calcite and about 0.5 to 1 mmol of dolomite are dissolved in the freshwater of the Upper Floridan. Dissolution of carbon-

ate minerals can add only a few tenths of a milligram per liter of Na$^+$ to freshwater in the aquifer; the remainder apparently is derived from evaporated precipitation recharging the system and other mineral sources, including ion exchange. Higher concentrations of Na$^+$ present in some inland areas are generally the result of remnant seawater in the Upper Floridan aquifer, as indicated by high Cl$^-$ concentrations. For example, in Gadsden County, Fla., low-permeability zones in the Upper Floridan retain moderately saline water; water samples from the aquifer in this area contain high concentrations of all major ions in seawater (Pascale and Wagner, 1981). High concentrations of the major ions in seawater also occur in the Upper Floridan aquifer in the valley of the St. Johns River, where seawater may have entered the aquifer during the Pleistocene. In the western panhandle of Florida, high Cl$^-$ concentrations (pl. 6) indicate that remnant seawater is present in the Upper Floridan in extreme southwestern Santa Rosa County and in southern Escambia County. Sodium concentrations increase in a downgradient direction, beginning about 30 mi northeast of this area, in southwestern Okaloosa County (pl. 4). Where increases in Na$^+$ begin, Na$^+$/Cl$^-$ ratios are high (fig. 21A) and are accompanied by progressive downgradient decreases in Ca^{2+} concentrations (pl. 1). These concurrent changes in concentration in the downgradient direction are apparently due to ion exchange of 2Na$^+$ for Ca^{2+}. The large area of slightly higher Na$^+$ concentrations centered near Brunswick, Ga., is due to upward seepage of deeper saline water induced by many years of heavy pumpage. The hydraulic effects of the pumpage are discussed in detail by Krause and Randolph (in press); earlier studies of the chemical effects of pumpage in the Brunswick area emphasized local increases in chloride concentration (Wait, 1965; Gregg and Zimmerman, 1974). The pattern shown in plate 4 is not exactly duplicated in plate 6 because the maps were drawn with different ranges of concentration.

A map of K$^+$/Cl$^-$ molar ratios in the Upper Floridan aquifer (fig. 21B) shows characteristically low ratios (<0.06) in coastal areas and in south Florida where seawater is present in the aquifer; the lowest ratios are near 0.02 (the ratio in seawater) where both Cl$^-$ and K$^+$ concentrations are highest in the Upper Florida. Low K$^+$/Cl$^-$ ratios also occur in Volusia County, Fla., and in outcrop areas of northwestern Florida, southern Alabama, and north-central Georgia. The ratios in these areas are less than 0.14, the average ratio in precipitation over the region (table 1). The loss of K$^+$ relative to Cl$^-$ is probably due to uptake of K$^+$ by plants, as K$^+$ and Cl$^-$ concentrations in ground water are not much more than average values for precipitation in these areas. Higher K$^+$/Cl$^-$ ratios occur throughout most of central and panhandle Florida, and in southern Georgia; in these areas, evaporation increases both K$^+$ and Cl$^-$ concentrations in water recharging the system, but the K$^+$/Cl$^-$ ratios are nearer values for precipitation. The highest K$^+$/Cl$^-$ ratios occur in east-central Georgia and in western panhandle Florida. As previously discussed, ion exchange is probably responsible for the relative increase in K$^+$ concentrations in the panhandle area. In east-central Georgia, dilute water may be leaking into the Upper Floridan aquifer from underlying sand aquifers; this recharge could slightly increase K$^+$ concentrations and raise K$^+$/Cl$^-$ ratios in the Upper Floridan. The high K$^+$/Cl$^-$ ratios in southwestern Georgia occur in an area of extensive agriculture development and where the confining unit overlying the Upper Floridan is thin; surficial recharge enters the aquifer containing increased concentrations of K$^+$ due to leaching of fertilizers.

Potassium concentrations in most water from the Upper Floridan aquifer are low, because K$^+$ concentrations in precipitation are very low and K$^+$-bearing minerals in the aquifer are present only in trace amounts. Aluminosilicate minerals containing potassium (glauconite, potassium feldspar, and micas?) that are present in trace quantities can dissolve and add very small amounts of K$^+$ to ground water. Unlike Na$^+$, K$^+$ does not occur as a trace constituent in calcite or dolomite, owing to the much larger size of the K$^+$ ion. Except for western panhandle Florida, K$^+$ concentrations are therefore closely related to the amount of seawater (as indicated by chloride concentrations) in the Upper Floridan aquifer. In the western panhandle area, ion exchange (2K$^+$ for Ca^{2+} or Mg^{2+}) increases K$^+$ concentrations by about 5 mg/L. As discussed in a later section, silicate weathering is not considered a primary source of K$^+$ (or Na$^+$) in this part of the system, because dissolved-silica concentrations do not increase, and silica cements (or grain overgrowths) have not been reported in well cuttings or cores from the area.

CHLORIDE

The second important anion in water in the Floridan aquifer system is chloride (Cl$^-$). The principal source of Cl$^-$ is seawater; natural salts of Cl$^-$ (evaporite minerals) are not present in the system, and addition of Cl$^-$ salts to remove road ice is not common practice in the region. The data in table 1 indicate that recharge water should be very low in Cl$^-$ concentration, and Cl$^-$ concentrations in the Upper Floridan aquifer are nearly zero in recharge areas. In nearly all coastal areas, wells that fully penetrate the Upper Floridan yield water having Cl$^-$ concentrations that approach that of seawater, about 19,500 mg/L. Plate 6 depicts the general distribution of Cl$^-$ concentration in water produced from the Upper Floridan aquifer. The map shows higher Cl$^-$ concentrations in
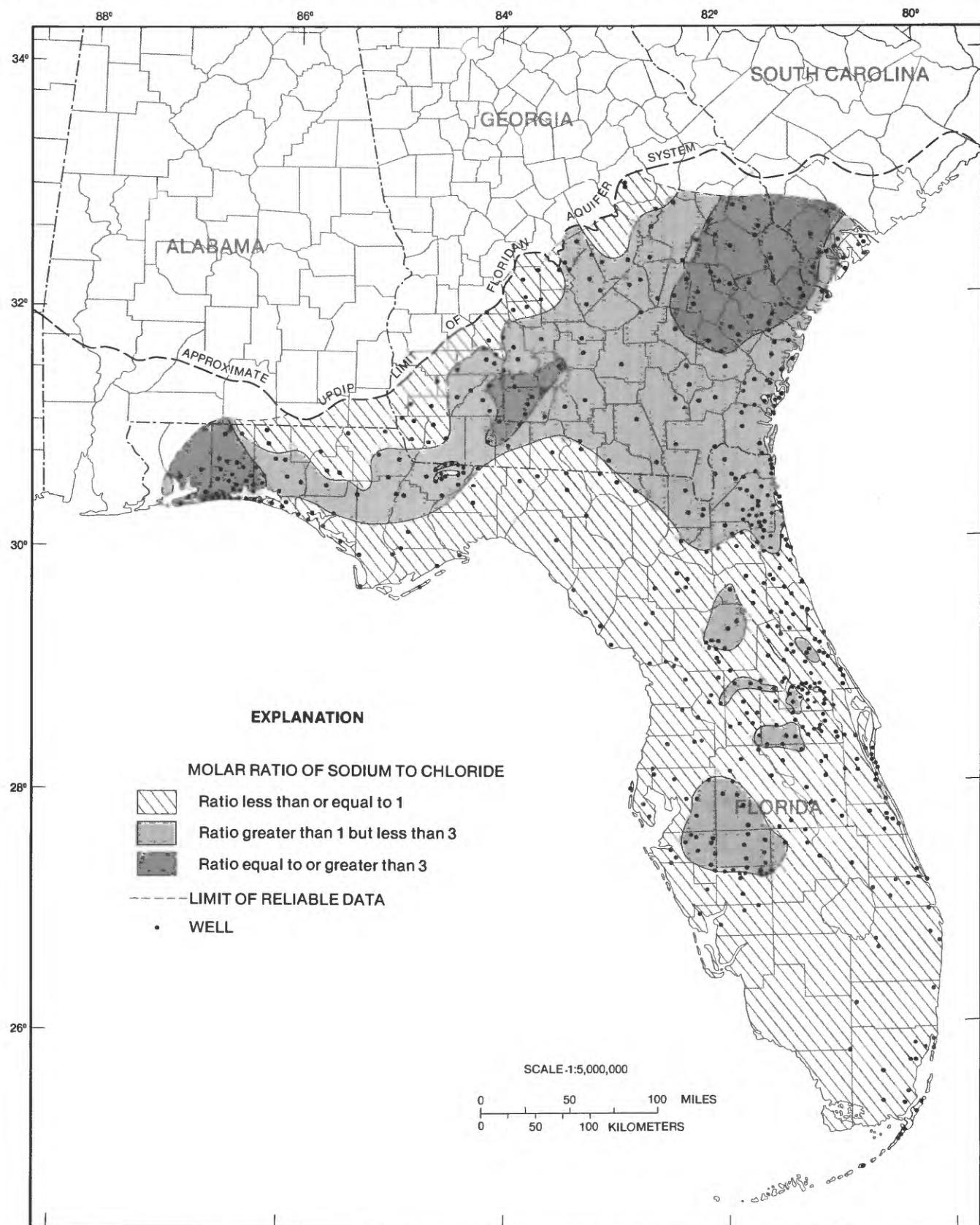
FIGURE 21A.—Sodium-to-chloride molar ratios in water samples from wells in the Upper Floridan aquifer.
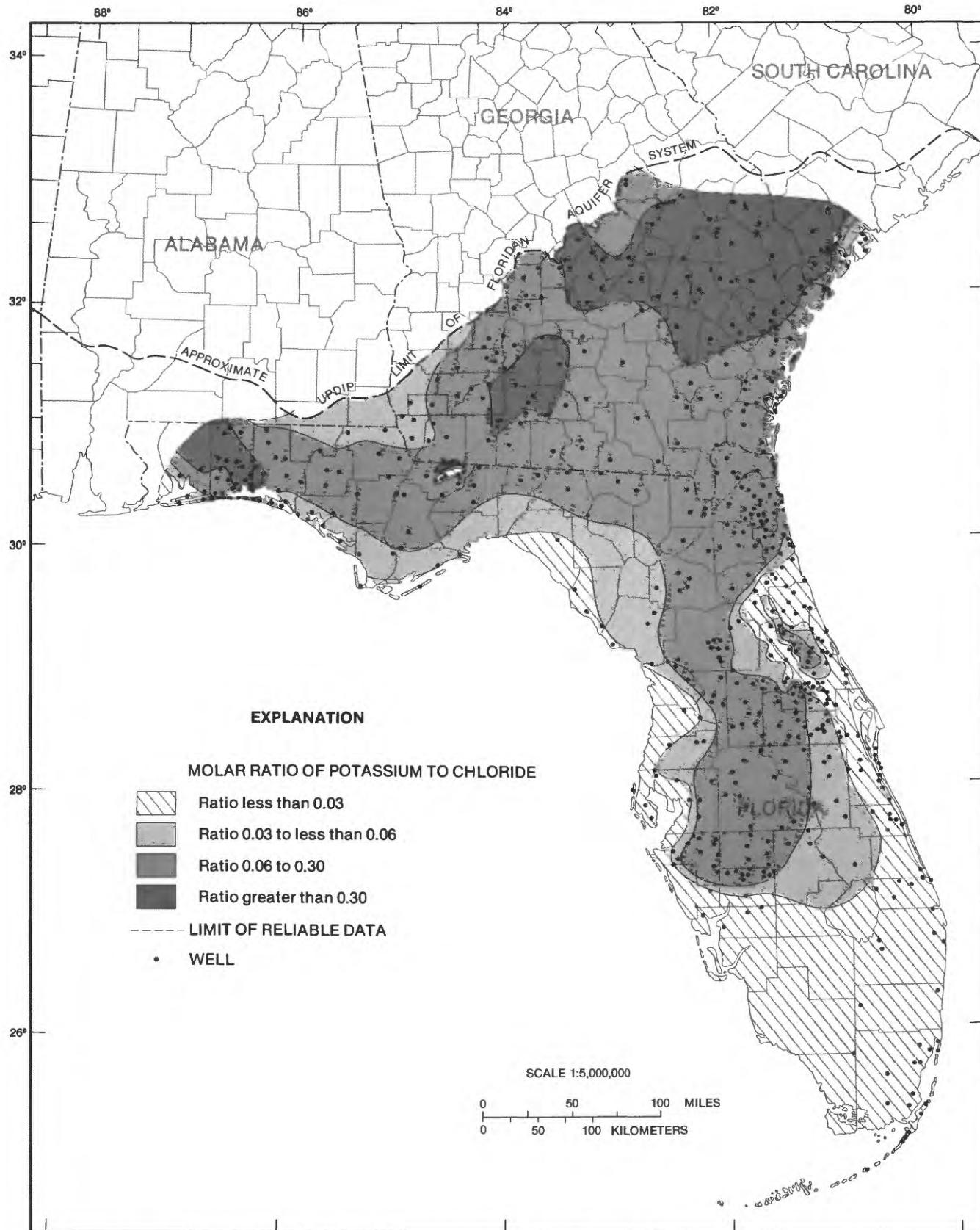
FIGURE 21B.—Potassium-to-chloride molar ratios in water samples from wells in the Upper Floridan aquifer.

inland areas than did earlier chloride maps of the Upper Floridan (Shampine, 1965a; Stringfield, 1966, fig. 3b), because this map was made using data from selected deep wells that penetrate at least half the thickness of the Upper Floridan. Deep wells tend to have higher Cl⁻ concentrations than shallow wells because the water in the Upper Floridan is chemically stratified. Figure 22 shows the Cl⁻ concentration in the upper 200 ft of the aquifer system. Throughout most of the region, the upper 200 ft of the system are either Ocala or Suwannee Limestone (see Miller, 1986, pl. 26). Both formations are highly permeable, generally contain water having Cl⁻ concentrations of less than 250 mg/L, and are capable of supplying very high yields to wells. Along the Gulf Coast and in south-central Florida, wells that penetrate only a few tens of feet into the Upper Floridan may produce water having Cl⁻ concentrations of less than 250 mg/L, but wells penetrating more than 100 ft will probably yield water of higher Cl⁻ content.

A map (fig. 23) of the base of freshwater flow in the Floridan aquifer system was compiled using Cl⁻ concentration data from deep wells and the estimated predevelopment potentiometric surface map (fig. 10) by Johnston and others (1980). The base of freshwater flow was defined as the midpoint of the saltwater-freshwater transition zone in coastal areas; where available, known Cl⁻ concentrations of 10,000 mg/L were used as the chemical definition of the midpoint. Where variations in Cl⁻ concentration with depth were not available, the location of the midpoint was calculated using the Hubbert interface relation (Hubbert, 1940, p. 864) and known (or estimated) predevelopment freshwater heads. The depth of the midpoint calculated from freshwater heads in inland areas is generally below the base of the Floridan aquifer system; in those areas, the geologic base of the aquifer system (Miller, 1986, pl. 33) is shown (fig. 23).

High chloride concentrations shown in plate 6 along the St. Johns River, along the eastern coast of Florida, and in southern Florida may be the result of incomplete flushing of Pleistocene seawater by the modern-day freshwater flow system (Stringfield, 1966, p. 209). Wyrick (1960) and Leve (1983) believed deeper, brackish water rises along fault zones in northeastern Florida because of higher freshwater heads in the Lower Floridan aquifer. Recent studies (Miller, 1986) suggest that faults mapped in the St. Johns River valley affect only the uppermost part of the Upper Floridan aquifer and do not penetrate deeply into the aquifer system. At this time, the known hydrologic effects of faults mapped in Duval, St. Johns, Putnam, and Volusia Counties are limited to ground-water chemical changes. The necessary measurements to determine whether the faults affect the hydraulic characteristics of the aquifer at depth have not been made (Tibbals, in press). In eastern

and southern Florida, both incomplete flushing of Pleistocene seawater and brackish-water intrusion along fault zones appear to contribute, in varying amounts, to the Cl⁻ content of water in the Upper Floridan aquifer.

In south Florida, ground water from the Upper Floridan aquifer discharges upward by diffuse leakage through thick confining beds. Simulations of the steady-state aquifer system indicate very sluggish ground-water circulation south of Lake Okeechobee, with upward leakage of freshwater less than 0.1 inch per year (in/yr) (Bush, 1982, p. 18–19). Kohout (1967) proposed a new conceptual flow system for the Floridan aquifer system in south Florida. His theory suggests that geothermal energy drives a cyclic flow system: as seawater flows inland at the base of the aquifer system, brackish water returns to the sea in the upper parts of the Floridan. This theory assumes that sufficient freshwater flows through the system in south Florida to mix with the seawater, lower its density, and maintain the required hydraulic gradients. The theory further assumes good hydraulic connection between the deep, highly permeable Boulder Zone in the Lower Floridan aquifer of southern Florida and the overlying parts of the Floridan aquifer system. Chemical data from deep test wells in Broward County, Fla., (Meyer, in press b) have established a landward ^{14}C gradient in the Boulder Zone. Using data from deep test wells at Fort Lauderdale and in western Broward County, Meyer (in press b) has shown that an inland hydraulic gradient of about 8.5×10^{-7} foot per foot (ft/ft) exists between the wells. The available data indicate that seawater flow is very sluggish through the highly permeable Boulder Zone. Meyer used estimates of hydraulic parameters of the Boulder Zone and head measurements to show that average particle velocities between the wells in western Broward County and Fort Lauderdale range between about 30 and 60 feet per year (ft/yr), which compares favorably with a velocity of about 55 ft/yr calculated from differences in ^{14}C activity in the seawater samples from each well. The flow path(s) and flow zone(s) that carry the brackish water back to the sea, completing Kohout's proposed cycle, were not identified during this study.

In the Savannah area of Georgia and South Carolina, the high chloride concentrations in water from the Upper Floridan aquifer are attributed to lateral saltwater encroachment (Counts and Donsky, 1963). Long-term withdrawals in this area have lowered the freshwater head, resulting in very slight migration of the freshwater-saltwater interface toward the center of pumpage. Similarly, long-term pumpage in coastal cities of southeastern Georgia and northeastern Florida has caused decline of the freshwater head in the Upper Floridan aquifer. In this area, however, the decline in head has induced upward migration of brackish water
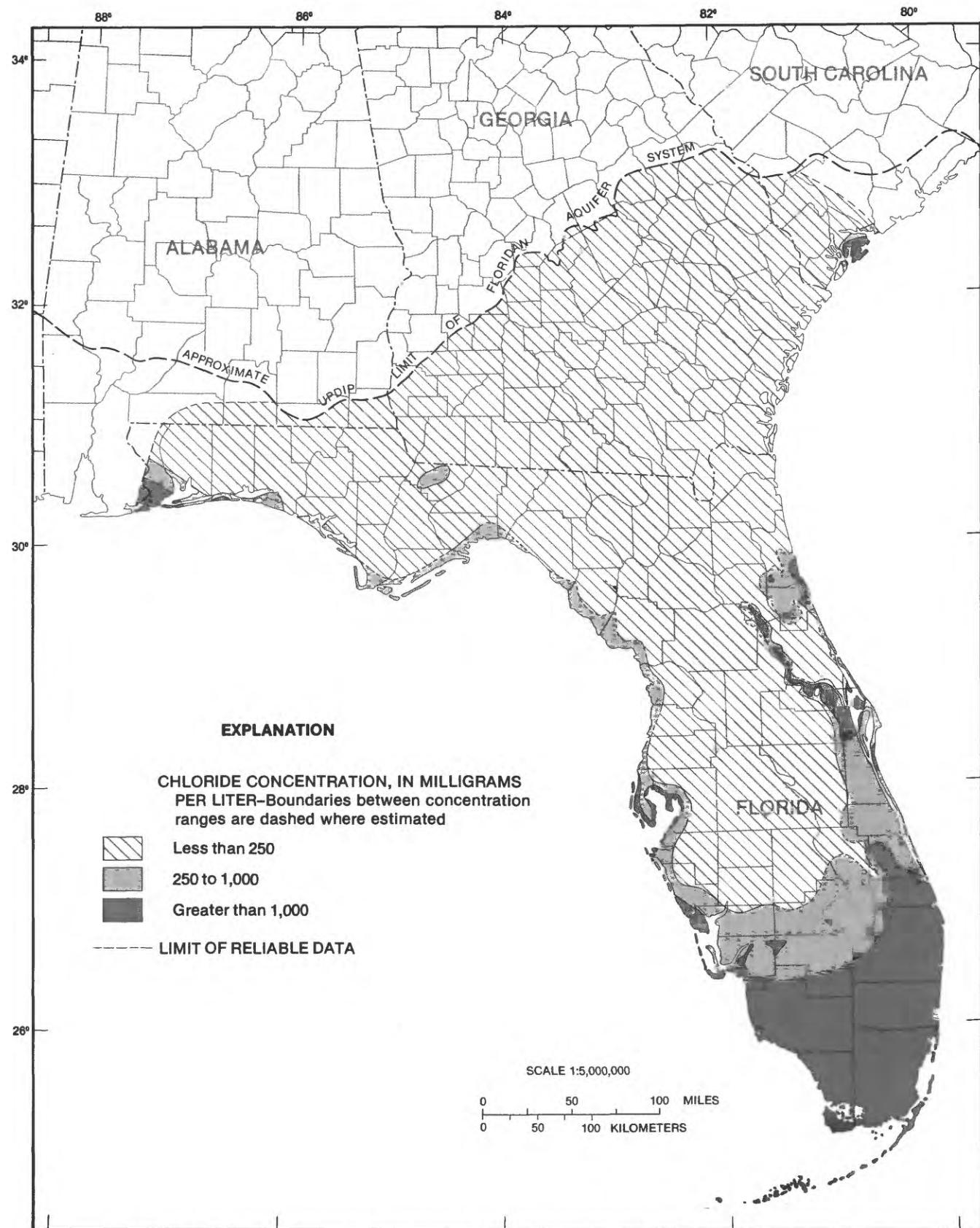
FIGURE 22.—Chloride concentrations in water from the upper 200 feet of the Floridan aquifer system.
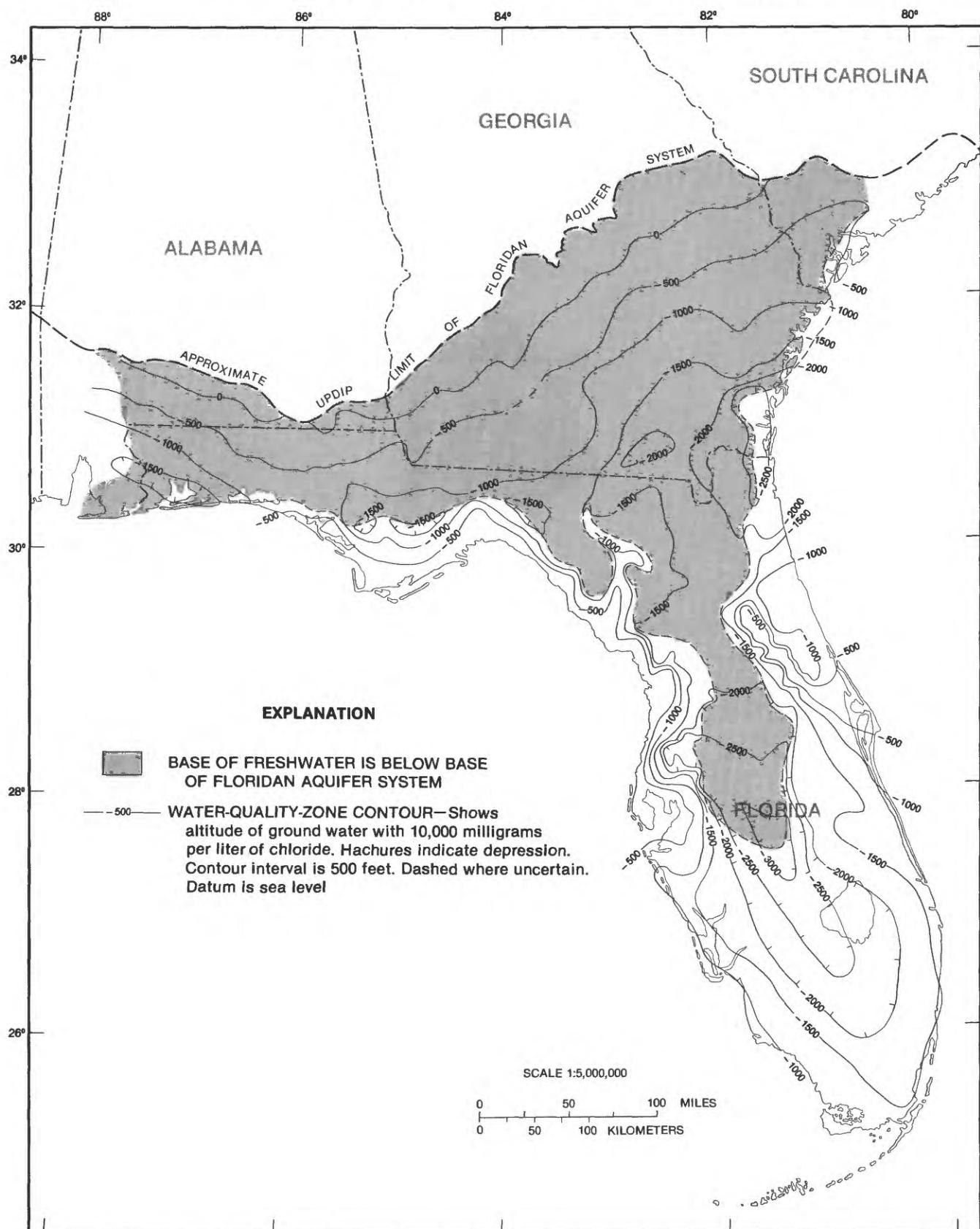
FIGURE 23.—Altitude of the estimated base of freshwater flow in the Floridan aquifer system.

(Stewart, 1960; Wait, 1965; Gregg and Zimmerman, 1974; Fairchild and Bentley, 1977; Leve, 1983). The possibility that lateral seawater encroachment could affect Cl^- concentrations along the coast of southeastern Georgia and northeastern Florida was discounted by Johnston and others (1982) because the freshwater-saltwater interface in the Upper Floridan aquifer is more than 50 mi offshore from Jacksonville, Fla.

The high chloride concentrations in Escambia and Santa Rosa Counties in the western panhandle of Florida probably result from incomplete flushing of residual seawater. Lateral ground-water movement toward the west and south is restricted in this area because there is a gradual facies change to low-permeability clastics, pinching out the aquifer system. Northwest of this area, faults associated with grabens in western Alabama (fig. 8) form a barrier to lateral ground-water flow. Under modern-day head conditions, fresh ground water may gradually displace the brackish ground water, which must leak slowly upward through thick confining beds. The high chloride concentrations in Gadsden County, northwest Florida, also appear to result from incomplete flushing of residual seawater (Pascale and Wagner, 1981). Although Johnston and others (1981) show a potentiometric high in this area, freshwater recharge to the aquifer is probably very low. As mentioned previously, the Upper Floridan aquifer in this area has low transmissivity (less than 1,000 ft^2/d), and vertical head differences as great as 40 ft are sustained with virtually no pumping. Plate 6 also shows high chloride concentrations along most of the Gulf Coast of Florida, where heads in the Upper Floridan aquifer are near sea level and the freshwater-saltwater interface occurs within the aquifer (Reichenbaugh, 1972; Mills and Ryder, 1977; Trapp, 1977; Sinclair, 1978; Hickey, 1979; Hickey and Barr, 1979). As stated previously, only very shallow wells in the Upper Floridan aquifer along the Gulf Coast should produce water of low chloride content.

A map of chloride concentrations in the Lower Floridan aquifer (fig. 24) was prepared using available chemical data and estimated predevelopment heads. Because available data are few and the deep wells are generally not fully penetrating, Cl^- concentrations in many areas must be estimated. The two principal assumptions used to map the available data were as follows: (1) data from fully penetrating wells were given more weight than shallower wells and (2) at boundaries of the Lower Floridan where it merges with the Upper Floridan, Cl^- concentrations in both the Lower and Upper Floridan aquifers were assumed to be equal. In areas for which there were no chemical data, predevelopment head differences between the Upper and Lower Floridan aquifers were assumed to be 1 to 5 ft (Bush, 1982, p. 19). Figure 24 shows freshwater (low Cl^-) in many areas

extending to the base of the aquifer system. In central Florida, chemical data are available to verify that freshwater is present in the Lower Floridan aquifer. Areas of low-Cl^- water shown in figure 24 might be explored as a potential supply if dissolved solids (pl. 8) are not too high and shallow supplies are insufficient. Areas of high Cl^- concentrations in figure 24 correspond to the presence of saltwater. Pumpage in coastal cities of southeastern Georgia and northeastern Florida has lowered the freshwater heads in the Upper Floridan aquifer (and also presumably lowered the heads in the Lower Floridan) so that saltwater is migrating upward. The areal extent of head declines in the Lower Floridan aquifer are not well known; thus the area affected by saltwater is restricted to the regions of greatest head decline in the Upper Floridan. In the valley of the St. Johns River, high Cl^- concentrations are mapped on the assumption that the Lower Floridan has been incompletely flushed of seawater that invaded the aquifer system during the Pleistocene.

SULFATE

The sulfate radical (SO_4^{2-}) is a principal component of gypsum and anhydrite, two highly soluble minerals which are likely to occur throughout the aquifer system. SO_4^{2-} concentrations in the Upper Floridan aquifer vary from nearly zero in recharge areas to as much as 4,000 mg/L where gypsum may occur as a few percent of the total rock volume. Plate 7 depicts the general distribution of SO_4^{2-} concentration in water produced from wells that yield from the entire Upper Floridan aquifer. This map has a different appearance from an earlier SO_4^{2-} concentration map of the Upper Floridan (Shampine, 1965c) because plate 7 was drawn using data from selected deep wells. Some analyses of sulfate-rich ground water known to be present in middle and upper Eocene rocks in the Floridan aquifer system were not used in the preparation of plate 7. The base of the Upper Floridan aquifer is established in places by the presence of intergranular gypsum (or anhydrite) (Miller, 1986), and plate 7 was constructed using chemical data from wells that do not penetrate the base of the Upper Floridan. Thus, a few high SO_4^{2-} concentrations previously reported in the Ocala Limestone and Avon Park Formation of southern Georgia and northern Florida (for example, Wait, 1960; Meyer, 1962; Sever, 1965, 1972; Krause, 1979) do not appear on this map. Over most of the region, SO_4^{2-} concentrations are less than 0.5 mmolar (about 50 mg/L). Available data on ^{34}S content of sulfate in the Upper Floridan aquifer (table 17) indicate that almost all the sulfate is derived from gypsum dissolution or seawater mixing; very little sulfate is derived from the oxidation of sulfide minerals (which have very low ^{34}S content). Since
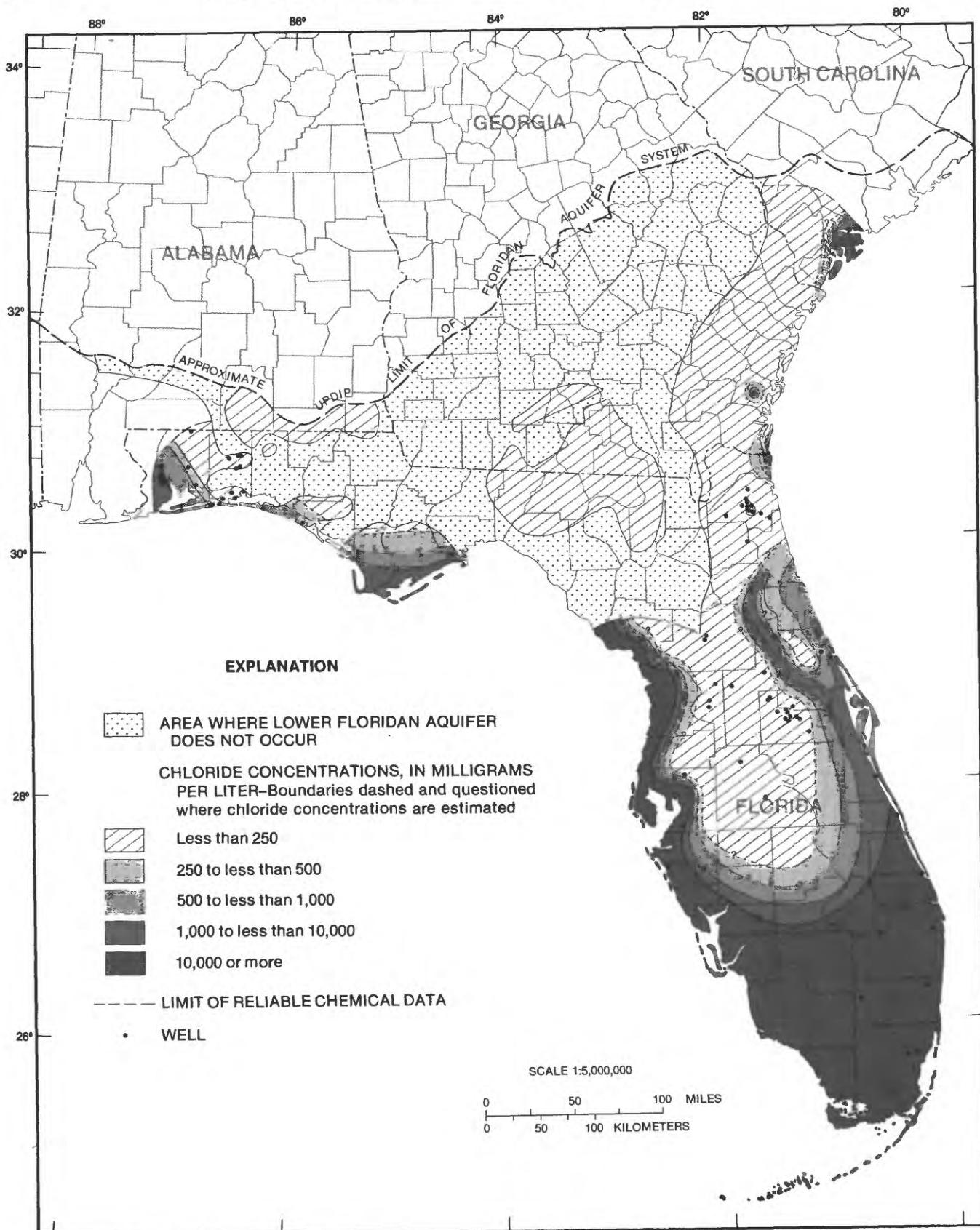
FIGURE 24.—Chloride concentrations in water from the Lower Floridan aquifer.
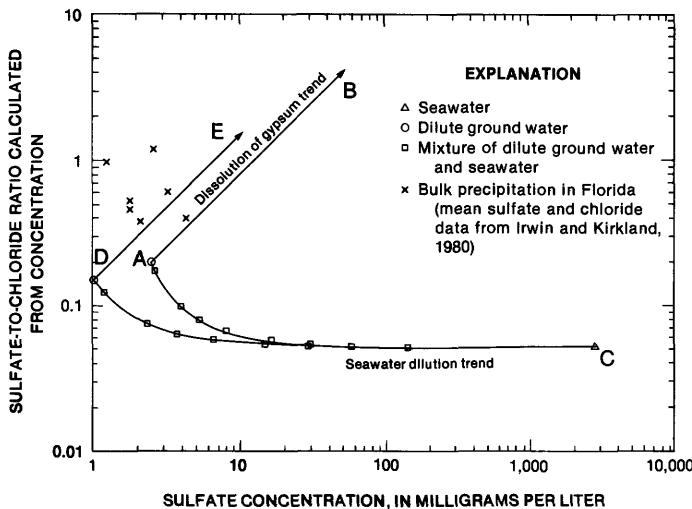
FIGURE 25.—Relation of sulfate-to-chloride ratios to sulfate concentrations in water from the Upper Floridan aquifer. (Modified from Rightmire and others, 1974.)

seawater contains about 2,750 mg/L of SO_4^{2-}, plate 7 shows high SO_4^{2-} concentrations along the west coast of Florida where predevelopment freshwater heads are low. Only very shallow wells along the Gulf Coast should produce water with low sulfate content from the Floridan aquifer system.

In south Florida and along the eastern coast of Georgia and Florida, high SO_4^{2-} concentrations are present as a result of both seawater and dissolution of gypsum (Counts and Donsky, 1963; Stringfield, 1966; Rightmire and others, 1974). Figure 25 (modified from Rightmire and others, 1974, fig. 2) shows two trends between SO_4^{2-} concentration and the SO_4^{2-}/Cl^- ratio that may be used to identify the source(s) of SO_4^{2-} in an individual ground-water sample. The trend lines shown in figure 25 were drawn using assumed SO_4^{2-} and Cl^- concentrations in dilute ground water (points A and D). If more mineralized ground water were the "starting point," the trend of gypsum dissolution would be shifted to the right but would retain the same slope, whereas the seawater dilution line would show more curvature (see Steinkampf, 1982, fig. 10). Analyses that plot near line A–B or D–E in the figure indicate that solution of gypsum (or anhydrite) is the primary source of SO_4^{2-}. Analyses plotting near the line A–C or D–C indicate a conservative mixing trend between dilute ground water and seawater. Analyses that plot in the region between the trend lines indicate that both solution of gypsum and mixing with seawater are sources of SO_4^{2-} in the water sample.

Precipitation samples plot on figure 25 considerably above the seawater dilution line, indicating that the ratios of SO_4^{2-}/Cl^- in precipitation samples from Florida (table 1) are higher than the ratio in seawater. If rainfall over central Florida were composed of distilled water and seawater spray, lines A–C and D–C would originate

at the precipitation values of SO_4^{2-} and Cl^-, extend parallel to the horizontal axis, and terminate at the seawater plot position. The "additional" SO_4^{2-} in precipitation may come from land-derived solid particulates containing sulfate, H_2S formed by decay of organic material, volcanic emissions of H_2S and SO_2, and SO_x emissions from industrial processes and combustion of fossil fuels. Junge and Werby (1958, p. 424) calculated that in 1956 as much as 33 percent of the excess SO_4^{2-} in rainfall worldwide was due to industrial emissions. All the reduced sulfur emissions are ultimately oxidized to SO_4^{2-}, creating acidic rainfall, the topic of many recent papers (Dailey and Winslow, 1980). Of course the acidity of rainfall should have no measurable effect on pH of ground water in the Upper Floridan aquifer because of the abundance of carbonates in the Floridan aquifer system. The sulfur isotopic content of these emissions varies according to the source(s); the SO_x emissions can only be estimated to be lighter than either volcanic emissions or the gypsum-derived sulfate in the Upper Floridan aquifer (Hoefs, 1980, p. 45–51, 88).

Isotopically light sulfate (from SO_x sources?) in rainfall may be responsible for the anomalously light $\delta^{34}S_{SO_4}$ values reported in ground water in Upper Floridan recharge areas (table 17; Rightmire and others, 1974, table 2). Testing of this hypothesis must await more data on the sulfur isotope content of both rainfall and ground water in the recharge areas. Such data might also be used to quantify the total SO_x-derived sulfate in recharge to the Upper Floridan.

The variation in sulfate concentration with depth in the Upper Floridan aquifer is another example of chemical stratification within the aquifer. For example, in central and northwestern Florida, SO_4^{2-} concentrations of more than 250 mg/L occur at depth in areas of high recharge. Although deep circulation is minimal in these areas, the shallow flow system is extensive and supports large springs: Silver Springs in Marion County, Fla., one of the largest such springs, has an average SO_4^{2-} concentration of about 40 mg/L and an average discharge of 825 ft^3/s. Osmond and others (1974, p. 1095) calculated that about 60 percent of the flow of Silver Springs originates in the "upper 100 feet of the . . . [Ocala Limestone] which is at or near the land surface." High SO_4^{2-} concentrations also occur in some shallow wells in the Upper Floridan in the Gulf Trough area of southwestern Georgia and in Gadsden County, Fla. The relation of SO_4^{2-}/Cl^- ratios and SO_4^{2-} concentrations indicates that remnant seawater containing small amounts of dissolved gypsum is the source of the high SO_4^{2-} concentrations in the Gadsden County area. In southwestern Georgia, the SO_4^{2-}/Cl^- and SO_4^{2-} concentration data indicate that gypsum is the source of high SO_4^{2-} concentrations. High SO_4^{2-} concentrations also occur in the vicinity of Val-

dosta and Brunswick, Ga., where large ground-water withdrawals have induced upward migration of highly mineralized water from deeper formations (Wait, 1965; Krause, 1979). Data from deep wells indicate that high SO_4^{2-} concentrations occur at depth in most of the study area except east-central and panhandle Florida. Thus, where the Upper Floridan aquifer is stressed by heavy pumpage, increases in SO_4^{2-} concentration may occur.

Bacterial reduction of sulfate probably occurs in all parts of the aquifer system; the importance of this process over the entire study area is difficult to determine owing to a lack of mineralogic and sulfur isotopic data. What is known is that bisulfide (HS^-) is present over most of the region, but in highly variable concentrations (fig. 26). This variability in measured concentrations depends on several factors (Rye and others, 1981, p. 1943), such as (1) availability of organic material for sulfate reduction, (2) degree of confinement of the aquifer and loss of H_2S by diffusion, (3) availability of trace metals for reaction with the sulfide, and (4) loss of H_2S during sample collection or by inadequate sample preservation. The amount of HS^- measured in water samples might be only a fraction of the total sulfate reduction occurring in the Upper Floridan aquifer. It is possible that the trace amounts of dissolved iron in the system are sufficient over time to form iron sulfides (pyrite?) and consume most of the sulfide formed in the biochemical reaction. Plummer and others (1983, table 4) tested this hypothesis by assuming that the source of dissolved iron was the trace amounts of iron in carbonates; their mass-balance models showed that large amounts of sulfate could be reduced by methane oxidation with concurrent precipitation of pyrite. However, calculations of sulfur isotope balance indicated that such models were not feasible; the methane oxidation-pyrite formation models predicted values of $\delta^{34}S_{SO_4}$ more than 20 o/oo heavier than was analyzed in water samples. The work of Plummer and others (1983) indicates that reduction of large amounts of sulfate and formation of large amounts of pyrite in the Upper Floridan are rather unlikely, especially since no enrichment of as much as 10 o/oo $\delta^{34}S_{SO_4}$ has been measured in water samples (table 17). The role of bacterial sulfate reduction in lowering SO_4^{2-} concentrations is probably limited to panhandle Florida, where gypsum is scarce and ground-water flow is sluggish. The low SO_4^{2-} concentrations mapped in southern Escambia and southwestern Santa Rosa Counties, Fla., occur in an area of high Cl^- concentrations, indicating that residual seawater is present in the aquifer system. Locally, the SO_4^{2-}/Cl^- ratio is lower than expected from dilution of seawater, and high concentrations of HCO_3^- indicate that bacterial reduction of sulfate may be an important factor in lowering SO_4^{2-} concentrations.

DISSOLVED SOLIDS AND HYDROCHEMICAL FACIES

In water from the Upper Floridan aquifer, dissolved-solids concentrations vary from less than 25 mg/L near outcrops to more than 25,000 mg/L along the coasts. Within the system, the dominant cations are Ca^{2+}, Mg^{2+}, Na^+, and K^+ and the dominant anions are HCO_3^-, Cl^-, and SO_4^{2-}. Locally, smaller amounts of dissolved iron, manganese, nitrate, phosphate, fluoride, strontium, sulfide, and silica also contribute to the dissolved-solids concentration. Generally, the dissolved-solids concentration of water from the Upper Floridan aquifer is less than 250 mg/L. In coastal areas, the Upper Floridan contains seawater, and fully penetrating wells may yield water with dissolved-solids concentrations approaching that of seawater, about 36,000 mg/L. Plate 8 shows the general distribution of dissolved-solids concentrations in water produced from wells that yield from the entire Upper Floridan aquifer. The map in plate 8 shows more mineralized water in inland areas than was shown in an earlier map by Shampine (1965b), because plate 8 was made using data from selected deep wells. In coastal and south-central Florida, very shallow wells in the Upper Floridan may produce water with concentrations of dissolved solids of less than 500 mg/L, but wells penetrating deeper than 100 ft will probably yield more mineralized water.

Generally, dissolved-solids concentrations in the Upper Floridan aquifer are maintained at less than 500 mg/L by saturation with calcite and dolomite, and by the limited presence of more soluble minerals such as gypsum; higher concentrations are generally due to the presence of seawater. High dissolved-solids concentrations along the coast of southeastern Georgia and northeastern Florida cannot entirely be attributed to seawater, however, because chloride concentrations in the Upper Floridan are not high. Extensive development of the Upper Floridan aquifer in this area has produced large head declines from predevelopment levels (Bush and Johnston, 1988, pl. 6). Declining heads apparently have induced water from the Lower Floridan aquifer to move upward or laterally, gradually increasing dissolved-solids concentrations over a large area. Recent studies of the effects of ground-water development in northeastern Florida (Fairchild and Bentley, 1977; Leve, 1983; Brown, 1984) indicate that water entering the Upper Floridan aquifer has increased the chloride concentrations in only a few wells as much as 50 mg/L, even though test wells indicate that water in the deepest parts of the Lower Floridan aquifer is a very saline, sodium-chloride type (Brown, 1980). Other data and studies cited in Brown (1984) indicate that highly mineralized, low-chloride water may have been present throughout most of the upper part of the Lower Floridan aquifer prior to devel-
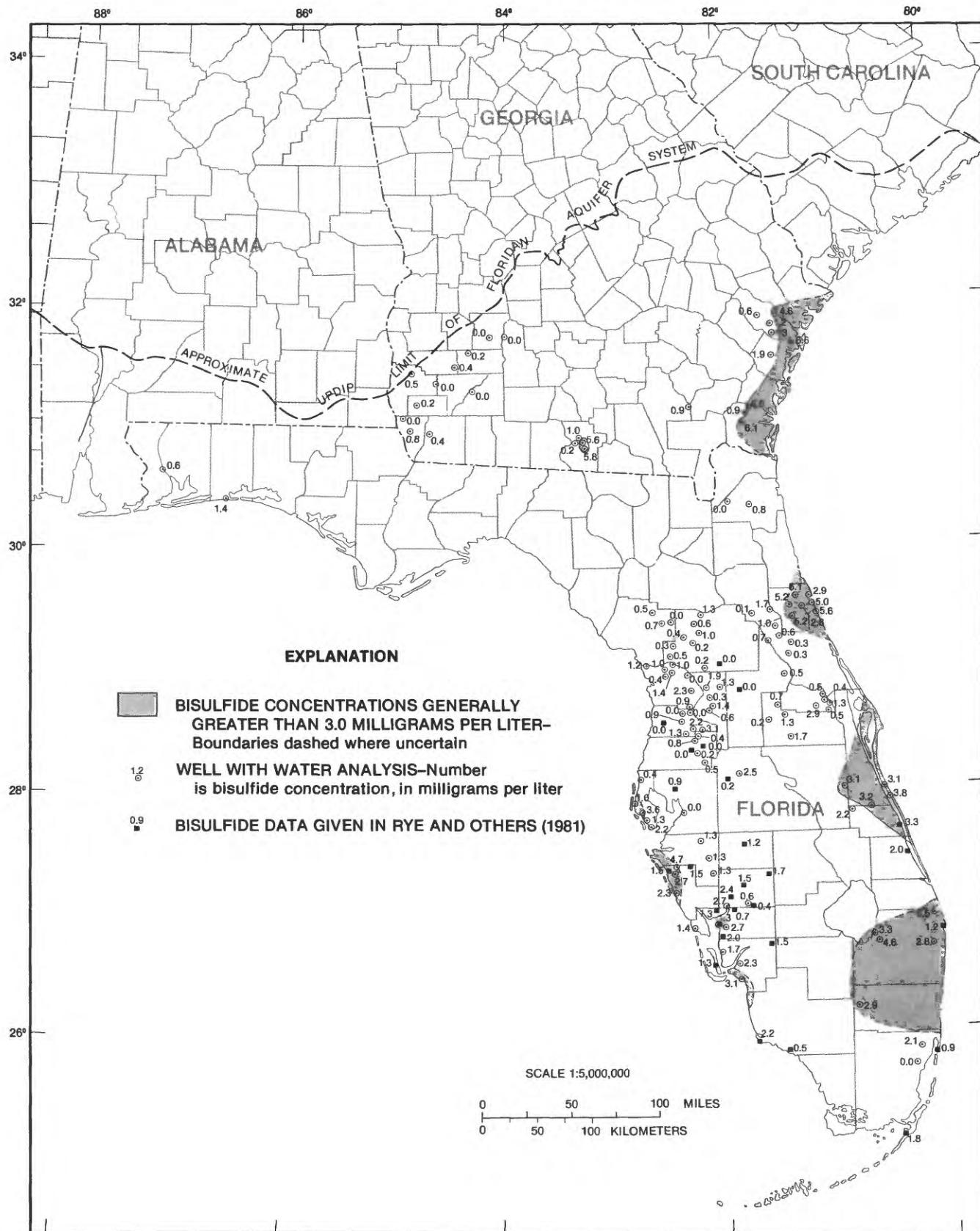
FIGURE 26.—Bisulfide concentrations in water samples from selected wells in the Upper Floridan aquifer.

opment. As heads declined, this low-chloride water began to move upward into the Upper Floridan aquifer. Recharge by highly mineralized, but initially low-chloride, water from the Lower Floridan appears to account for the increase in dissolved-solids concentrations in the Upper Floridan in this area.

Figure 27 shows the distribution of dissolved-solids concentrations in the Lower Floridan aquifer. This figure was prepared using both available chemical data and estimated heads in the system. There are few wells penetrating the Lower Floridan for which there are chemical data, and these wells do not generally penetrate the full thickness of the aquifer. Thus, figure 27 was made on the basis of the following assumptions: (1) data from fully penetrating wells should have more significance than data from shallower wells; (2) where the Lower Floridan merges with the Upper Floridan aquifer, dissolved-solids concentrations in the Lower Floridan are the same as concentrations in the Upper Floridan; and (3) chemical and hydraulic processes that control the chemistry of the Upper Floridan are also occurring in the Lower Floridan. As mentioned previously, heads in the Lower Floridan aquifer were assumed to be only 1 to 5 ft different from predevelopment heads in most areas of the Upper Floridan aquifer (Bush, 1982, p. 19). Where heads are high and fresh (low-chloride) water may be present to the base of the aquifer system (fig. 23), dissolved-solids concentrations should be controlled by the solubility of aquifer minerals. Because calcite and dolomite are at saturation in most of the Upper Floridan, these minerals were assumed to be at saturation throughout the Lower Floridan, and dissolution of gypsum (anhydrite) was assumed to have the greatest effect on dissolved-solids concentrations in low-chloride areas. Where estimated predevelopment heads are lower, both seawater and mineral dissolution will affect dissolved-solids concentrations. Although a hydrochemical facies map of the Lower Floridan could delineate areas where different geochemical processes are predominant, the data are insufficient to make such a map.

Areas where certain ions dominate the dissolved-solids content of ground water in the Upper Floridan aquifer are shown in plate 9. These dominant-ion patterns are called hydrochemical facies (Back, 1960, 1966). As stated by Back (1966, p. A1), "the facies reflect the response of chemical processes operating within the lithologic framework and also the pattern of flow of the [ground] water." Plate 9 was prepared by calculating and plotting the dominant cation(s) and anion(s) for all wells shown which had analyses of the major ions previously discussed. The area designated "Mixed" contains water with neither a single cation or anion constituting more than 50 percent of the total equivalence of cations or anions, nor any two

cations or anions constituting more than 75 percent of the total equivalence of cations or anions. The total cation or anion equivalence was calculated by dividing the concentration of each major cation or anion by its molecular weight, multiplying by its ionic charge, and adding the individual values (Hem, 1970, p. 82).

Study of the hydrochemical facies map suggests that there are four principal geochemical processes operating in the Upper Floridan aquifer:

1. Dissolution of aquifer minerals toward equilibrium as ground water moves from recharge to discharge areas,
2. Mixing of fresh ground water with seawater in coastal areas, or with residual saline water where retained by low-permeability rocks,
3. Mixing of ground water with recharge water, and
4. Cation exchange between water and aquifer minerals.

Each of these processes exhibits distinctive features on the hydrochemical facies map, as discussed below.

In most of Georgia and central Florida, mineral dissolution produces low to moderate increases in dissolved solids and diagnostic changes in dominant-ion chemistry. Ground water in the Upper Floridan aquifer in these areas is generally calcium-bicarbonate dominated, and dissolved-solids concentrations are generally less than 500 mg/L. Where dissolution of dolomite adds sufficient Mg^{2+} to the water, a calcium-magnesium-bicarbonate facies develops. Along the coast of Georgia and northern Florida, gypsum dissolution adds SO_4^{2-} and a calcium-magnesium-bicarbonate-sulfate facies develops. In southwestern Florida and in the Gulf Trough area of Georgia and Florida, gypsum is relatively abundant; sulfate is the predominant anion, and a calcium-magnesium-sulfate facies occurs.

Vertical mixing of freshwater and seawater occurs naturally in coastal areas along freshwater-saltwater transition zones. In these zones the water chemistry gradually changes from a calcium-magnesium-bicarbonate type with low dissolved solids near the top of the zone, to seawater at the bottom. Along the northwestern Gulf Coast of Florida the Upper Floridan aquifer is both highly permeable and unconfined; in this area the zone of transition is narrow (a relatively sharp interface occurs). Reichenbaugh (1972) presented data from Pasco County, Fla., indicating that the zone of transition is locally less than 200 ft thick. In contrast, along the east coast of central Florida the Upper Floridan aquifer is less permeable and is confined; no wells penetrate through the transition zone in this area, but available chloride data suggest that the zone is much thicker. Similar changes in hydrochemical facies occur along the coasts of central Florida and southeastern South Carolina because some seawater mixes with freshwater when a deep well is pumped. The small amounts of

EXPLANATION

AREA WHERE LOWER FLORIDAN AQUIFER
DOES NOT OCCUR

DISSOLVED-SOLIDS CONCENTRATIONS,
IN MILLIGRAMS PER LITER–Boundaries dashed
and questioned where dissolved-solids
concentrations are estimated

Less than 250

250 to less than 500

500 to less than 1,000

1,000 to less than 10,000

10,000 or more

LIMIT OF RELIABLE CHEMICAL DATA

WELL

SCALE 1:5,000,000

0   50   100   MILES

0   50   100   KILOMETERS

FIGURE 27.—Dissolved-solids concentrations in water from the Lower Floridan aquifer.

seawater, noted in samples from deep wells, are sufficient to change the water from calcium-magnesium-bicarbonate dominated to water with approximately equal proportions of all major constituents (designated "Mixed" in pl. 9). As the seawater content of the Upper Floridan aquifer increases, the dissolved-solids concentrations increase and there is a hydrochemical facies change to a sodium-chloride type of water. The effects of freshwater-saltwater mixing on samples from deep wells in coastal areas depend on the depth (position) of the transition zone, the depth of the well, and the pumping rate. Water from lightly pumped, shallow wells in most coastal areas should not be greatly affected by the seawater, and might be quite similar to freshwater from wells farther inland.

Mixing of ground water and residual saline water produces hydrochemical facies and dissolved-solids concentrations similar to those that result from mixing of ground water and modern-day seawater, except the facies occur in areas where a freshwater-saltwater transition zone in the Upper Floridan aquifer currently is not hydraulically possible. In south Florida, the aquifer system is extensively confined and residual saline water is present in the Upper Floridan. Tests in the Alligator Alley well in western Broward County (pl. 1) indicate that freshwater and saline water zones are intercalated (Meyer, in press b). Water samples from low-permeability zones in younger rocks contained Cl^- concentrations greater than those in samples from high-permeability zones in older (deeper) rock units. These results indicate that ground-water circulation in south Florida has been more effective in removing the residual saline water from the most permeable zones, not the shallowest zones, as one might expect. As mentioned previously, seawater probably entered the aquifer system along the St. Johns River valley during the Pleistocene (Stringfield, 1966) and has not been removed by the modern-day freshwater flow system. Mixing of this "residual seawater" with freshwater could produce the high dissolved-solids concentrations and sodium-chloride facies in this inland valley far from the sea.

An alternative explanation for the highly mineralized water in the Upper Floridan aquifer along the St. Johns River valley has been offered by Wyrick (1960) and Leve (1983). They suggest that deep saline water is rising into the Upper Floridan along fault zones in northeastern Florida, owing to higher heads occurring at depth. Invasion of the Upper Floridan aquifer by deeper, more mineralized water has been documented in Valdosta, Ga. (Krause, 1979), Brunswick, Ga. (Wait, 1965), and Nassau County, Fla. (Fairchild and Bentley, 1977). It is significant that each of these areas has high pumpage from the Upper Floridan. Only in the Brunswick area, however, has invasion of saline water caused higher dissolved

solids and a change to sodium-chloride facies in the Upper Floridan aquifer. The narrow band of calcium-magnesium-sulfate facies in northeastern Florida is apparently not related to mineral dissolution since the aquifer in this area is not gypsiferous. Upconing of mineralized water along fault zones may be the cause of this anomalous occurrence of sulfate dominance. Prior to development, the aquifer system was discharging to the St. Johns River, where the narrow band is mapped; the May 1980 potentiometric map (Johnston and others, 1981) indicates that the modern-day flow system is discharging to the river and to a pumping center on the south side of Jacksonville. These discharge patterns may have prevented the spread of the calcium-magnesium-sulfate facies eastward toward the coast.

Mixing recharge water with ground water causes variable chemical effects, depending on both the chemistry and the amount of recharge. Recharge from underlying sand aquifers in southwestern Georgia locally affects both Ca^{2+} and HCO_3^- concentrations, but the quantity of recharge is not enough to change the predominant ions mapped in that area. Recharge through overlying sediments in the area immediately southeast of the Gulf Trough is more substantial (Krause and Randolph, 1989). This recharge is probably Ca^{2+}-HCO_3^- type and is low in dissolved-solids concentration. The amount of recharge and the increase in ground-water circulation south of the trough affects dissolved-solids concentrations significantly. In the area of the trough, dissolved-solids concentrations are in the range of 250–500 mg/L, but through most of Leon County, Fla., and Thomas, Brooks, Cook, and Berrien Counties, Ga., concentrations are less than 250 mg/L. Also, the predominant ions change from calcium-magnesium-sulfate facies in the trough area to calcium-bicarbonate facies, typical of other recharge areas of the Upper Floridan. Recharge from underlying sand aquifers in east-central Georgia lowers Ca^{2+} concentrations and raises Na^+/Cl^- molar ratios but has no major effect on dissolved-solids concentrations or hydrochemical facies. Nearer the coast, in southeastern Georgia, a mixed-bicarbonate facies is mapped. In this area the Lower Floridan aquifer is probably discharging into the Upper Floridan, since this was a predevelopment discharge area for the Upper Floridan (fig. 12), and the cone of depression created by pumping near Savannah should further enhance upward discharge from the Lower Floridan. The chemistry of water in the Lower Floridan in the area is not known, but from the chemical changes noted in the Upper Floridan aquifer, estimates can be made. The water in the Lower Floridan must contain higher Na^+ concentrations than the water in the Upper Floridan, since mixing tends to increase Na^+ concentrations. Concentrations of Ca^{2+} in the Lower Floridan may be the same as or lower

than in the Upper Floridan; the effects of mixing on Ca^{2+} concentrations are not noticeable, and calcite is maintained at equilibrium. Simulation of the predevelopment flow system in this area indicates that small quantities of water flow from the Lower to the Upper Floridan aquifer (Krause, 1982); somewhat larger quantities may now be flowing because of development and pumpage from the Upper Floridan.

Ion exchange may be an alternative explanation for some of the patterns of hydrochemical facies discussed above. In east-central Georgia, the Upper Floridan aquifer is composed primarily of limestone, but even small quantities of clay minerals might be sufficient to exchange the required amounts of Na^+ for Ca^{2+}. As with other geochemical questions unanswered in this report, detailed mineralogical studies are needed to test this hypothesis. Only in the western Florida Panhandle does ion exchange seem the most probable mechanism for developing the hydrochemical facies mapped in the Upper Floridan aquifer. In that area, the normal downgradient change from calcium-magnesium-bicarbonate to mixed facies does not occur. Rather, a mixed-bicarbonate facies evolves, which farther downgradient becomes a sodium-bicarbonate facies. There is a net loss of Ca^{2+} in the downgradient direction, which could result from calcite precipitation, as HCO_3^- concentrations are very high and calcite is at saturation. The source of additional Na^+ is probably ion exchange because available chemical data indicate that mineral weathering is not a major source. Infiltration of Na^+-rich water is not possible since this is a discharge area for the Upper Floridan. Nor is upward leakage a plausible source, because, except in western Okaloosa County, Fla., the almost impermeable Bucatunna Formation separates the Upper and Lower Floridan aquifers. In addition, throughout most of Santa Rosa County, Fla., the Lower Floridan contains high Cl^- and dissolved-solids concentrations (figs. 24, 27), while concentrations of these constituents are low in the Upper Floridan, except in the vicinity of Pensacola Bay. Taken together, the chemical and hydrologic data indicate that ion exchange is the mechanism producing the sodium-bicarbonate facies that occur in the Upper Floridan aquifer in the western panhandle area.

MINOR CONSTITUENTS

FLUORIDE

The fluoride (F^-) concentration in water in the Upper Floridan aquifer varies from nearly zero near outcrop areas to more than 4 mg/L in western Florida (fig. 28). Over most of the region, the F^- concentration is less than 1.0 mg/L, well within the mandatory standard (based on the annual average of maximum daily air temperatures) of 1.4 to 1.8 mg/L for drinking water in the region (U.S. Environmental Protection Agency, 1975). In coastal areas, mixing of fresh ground water with seawater brings F^- concentrations to approximately 1.5 mg/L, depending on the depth of the well and the amount of seawater in the Upper Floridan aquifer.

Water recharging the aquifer system is the principal source of F^- in the freshwater parts of the system. In unconfined areas, F^- concentrations are very low, reflecting the low concentrations of F^- in rainfall: Irwin and Kirkland (1980) reported that F^- concentrations in rainfall at Maitland and Ocala, Fla., averaged 0.1 mg/L (range, 0.0 to 0.2 mg/L at Maitland and 0.0 to 0.3 mg/L at Ocala). Where the aquifer system is confined, recharge water contains F^- dissolved from carbonate fluorapatites, which are relatively abundant in the Miocene sediments of the system's upper confining unit. Once the F^- in recharge water enters the Upper Floridan aquifer, it appears to be chemically conservative. Fluorite (CaF_2) is consistently undersaturated in water samples from the Upper Floridan and should not be controlling F^- concentrations. Fluoride-bearing apatites may control F^- concentrations, but these minerals form very slowly and are generally highly oversaturated in water samples from wells in the Upper Floridan aquifer (table 9, fig. 29). Anion exchange of F^- for hydroxyl ions (OH^-) in apatite is well known (for example, Krauskopf, 1979, p. 74) and probably occurs to some degree in the Upper Floridan. The extent to which anion exchange removes F^- from ground water in the Upper Floridan aquifer cannot be determined at this time, owing to lack of data on the quantity and chemical composition of apatite in the aquifer.

It is difficult to prove with available data that equilibrium between ground water and a carbonate fluorapatite phase is (or is not) controlling F^- concentrations. The use of WATEQF to calculate the S.I. of various apatite species in water samples from the Upper Floridan aquifer is complicated by several factors: (1) phosphate concentrations were determined in Upper Floridan water samples that had passed through a relatively coarse filter (0.45 micrometer (μm)), thus allowing whole microorganisms or parts of microorganisms to be analyzed along with "dissolved" phosphate (see later section on "Nutrients"); (2) apatites in nature occur as a solid-solution series containing variable amounts of calcium, sodium, magnesium, strontium, phosphate, carbonate, sulfate, and hydroxide (McClellan and Lehr, 1969; Baturin and others, 1970; McArthur, 1978; Manheim and others, 1980; Gulbrandsen and others, 1984), and each species has a different solubility in ground water (Brown, 1960; Roberson, 1966; Wier and others, 1971; Chien and Black, 1976; Nathan and Sass, 1981); and (3) the composition of apatites in the Floridan aquifer system is not
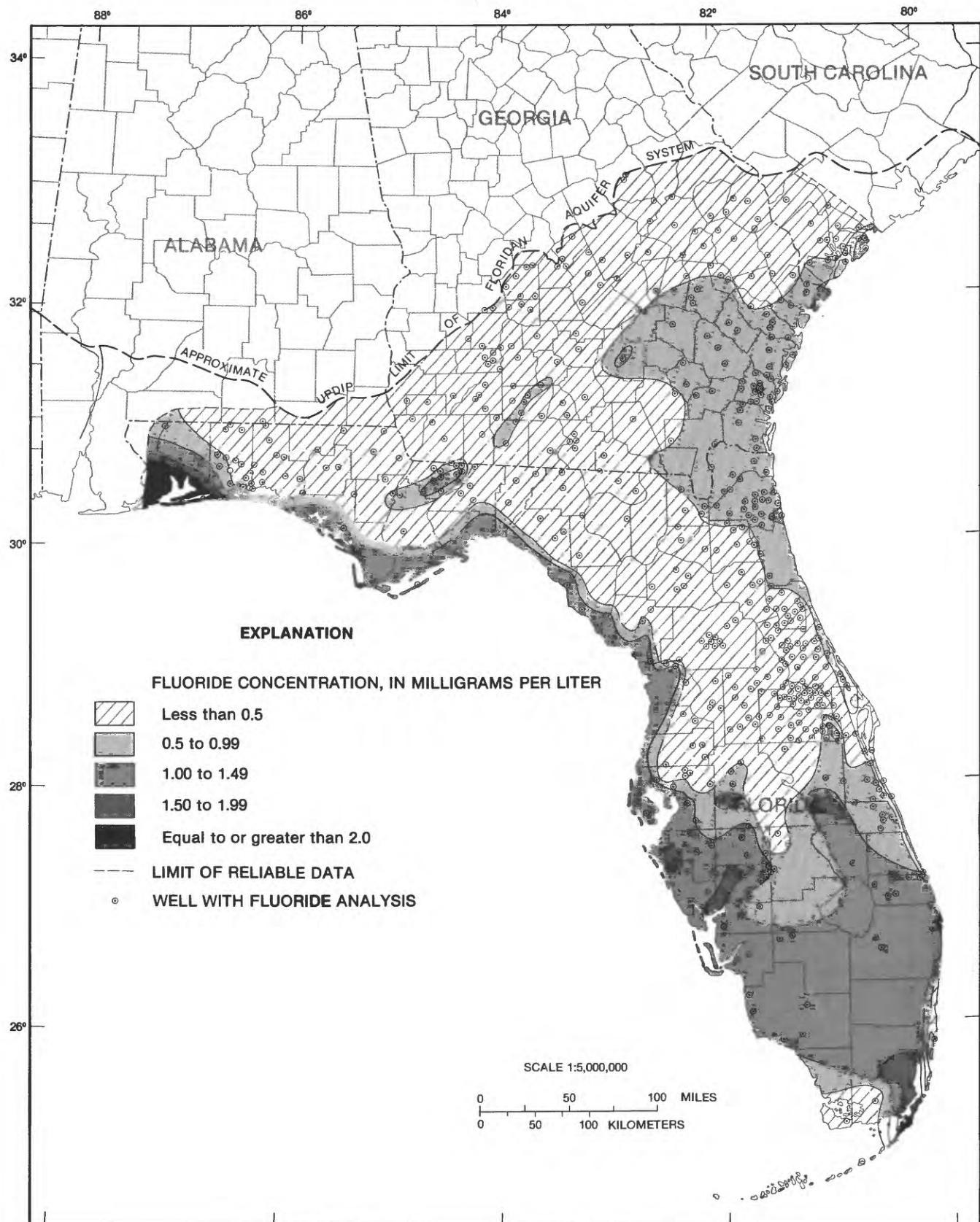
FIGURE 28.—Fluoride concentrations in water from the Upper Floridan aquifer.
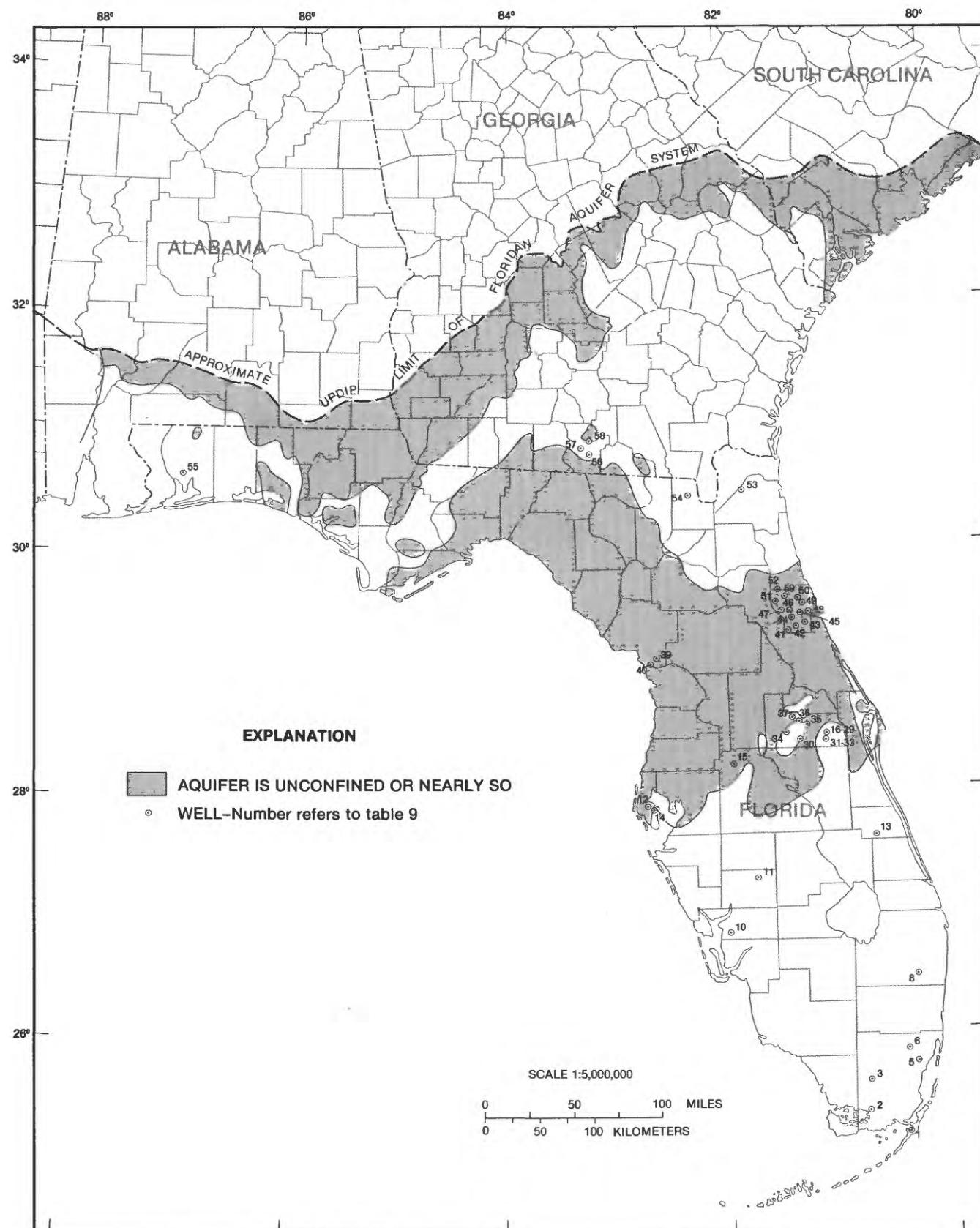
FIGURE 29.—Wells in the Upper Floridan aquifer with water analyses of phosphate and fluoride.

TABLE 9.—*Ion activities and saturation indices of apatites calculated by WATEQF using selected chemical analyses of water from wells in the Upper Floridan aquifer*

Well number[1]	Water temperature, in °C	−Log₁₀ ion activity							Saturation index				
		H⁺	Ca²⁺	Mg²⁺	Na⁺	PO₄³⁻	CO₃²⁻	F⁻	Fluor-apatite[2]	Hydroxy-apatite[2]	Carbonate fluorapatites[3]		
											Florida	North Carolina	Tennessee
1	27.5	7.90	2.99	2.56	1.27	11.13	4.99	4.25	9.3	0.1	6.6	15.2	13.0
	27.5	7.40	2.99	2.60	1.27	12.22	5.46	4.17	6.1	−3.6	10.8	9.6	7.0
2	29.0	7.70	2.87	2.56	1.22	11.64	5.25	4.44	8.2	−0.9	14.5	13.1	10.7
	25.4	8.15	3.10	2.57	1.29	11.48	5.44	4.86	7.0	−1.4	12.0	10.4	8.1
3	25.0	7.50	3.13	2.77	1.54	12.01	5.29	4.08	6.1	−3.8	10.8	9.6	7.1
	25.5	7.90	3.14	2.70	1.55	11.15	4.91	4.17	8.5	−0.8	15.2	13.8	11.7
	23.8	7.60	3.14	2.78	1.54	11.90	5.22	4.16	6.2	−3.5	11.1	9.9	7.4
5	22.0	7.90	3.02	2.70	1.51	12.14	5.04	4.17	6.1	−3.4	11.2	10.1	7.30
	23.0	8.30	3.06	2.64	2.53	11.02	4.67	4.18	9.2	0.2	16.9	15.5	13.3
6	24.5	8.50	3.41	2.51	1.49	10.51	4.29	3.92	9.4	0.3	17.1	15.7	13.5
8	15.0	7.50	2.61	2.84	0.39	12.07	5.79	4.33	8.0	−2.0	14.8	13.4	11.1
10	35.3	7.14	2.61	1.94	0.57	12.59	6.05	4.87	6.4	−2.6	10.6	9.3	6.6
11	30.5	7.40	2.91	3.00	3.10	10.70	5.59	4.01	11.3	1.5	19.3	17.2	16.4
12	25.0	7.50	2.61	3.50	2.68	11.47	5.10	4.57	9.8	0.5	17.4	15.7	13.7
	25.0	7.50	2.61	3.54	2.72	11.46	5.09	4.65	9.8	0.5	17.2	15.5	13.6
13	25.5	7.10	3.13	3.06	2.49	11.76	5.77	4.51	6.4	−3.4	10.5	8.8	6.9
14	25.0	7.60	2.81	3.16	2.42	12.29	5.00	5.36	5.6	−2.9	9.5	8.1	5.1
15	26.5	7.01	2.51	3.75	3.93	12.57	6.08	5.06	6.6	−2.7	10.4	8.5	6.7
	26.0	7.25	2.46	3.71	3.86	11.69	5.86	4.89	9.6	0.4	16.0	13.9	12.6
	26.0	7.05	2.53	3.68	3.85	12.51	6.06	5.06	6.6	−2.7	10.6	8.6	6.8
16	25.0	7.10	2.81	3.35	2.45	11.61	5.67	4.87	8.1	−1.3	13.6	11.7	9.9
17	25.0	6.70	2.77	3.37	2.45	12.13	6.03	4.75	6.9	−3.1	11.3	9.5	7.6
19	25.5	7.30	2.78	3.35	2.42	11.36	5.47	4.88	9.0	−0.2	15.3	13.5	11.7
20	25.5	6.60	2.75	3.32	2.46	12.36	6.12	4.88	6.1	−3.8	9.9	8.1	6.1
21	24.5	7.10	2.68	3.49	2.51	11.40	5.64	5.05	9.2	−0.1	15.5	13.5	11.9
22	25.0	7.10	2.69	3.32	2.25	11.95	5.63	5.06	7.5	−1.8	12.6	10.9	8.7
23	24.5	7.00	2.82	3.48	2.98	11.49	5.77	5.04	8.3	−1.2	13.5	11.5	9.9
24	24.0	6.90	2.82	3.42	2.93	11.60	5.91	5.04	7.9	−1.7	12.8	10.8	9.3
25	24.0	7.55	2.84	3.42	3.03	10.84	5.25	5.34	9.7	1.2	16.4	14.3	12.7
	24.0	6.90	2.82	3.40	3.01	11.68	5.92	4.86	7.8	−1.9	12.8	10.8	9.3
26	26.0	7.10	2.79	3.49	2.77	11.39	5.63	5.04	8.7	−0.5	14.5	12.5	10.9
27	25.0	6.80	2.60	2.62	1.43	13.03	6.91	4.99	4.8	−4.8	7.2	5.6	3.4
28	25.0	8.30	2.96	3.38	2.75	11.02	4.61	5.04	8.9	0.8	15.6	13.9	11.7
29	25.5	8.00	2.93	3.71	3.10	11.27	4.74	4.73	8.7	0.0	15.1	13.4	11.4
30	23.0	7.10	3.18	3.58	3.17	11.00	5.91	5.02	7.9	−1.5	12.4	10.2	9.1
	23.0	6.90	3.11	3.59	3.19	11.26	6.08	5.03	7.4	−2.2	11.6	9.4	8.2
31	26.0	7.10	2.67	3.33	2.25	11.59	5.63	4.89	8.9	−0.5	15.1	13.2	11.4
32	26.0	7.00	2.68	3.34	2.28	12.56	5.73	4.89	5.9	−3.6	9.9	8.4	5.9
33	26.5	7.10	2.67	3.30	2.22	11.65	5.65	4.89	8.7	−0.7	14.8	12.9	11.1
34	25.0	7.30	3.04	3.50	3.40	10.72	5.56	5.03	9.4	0.3	15.5	13.2	12.1
35	23.0	7.30	3.10	3.60	3.46	10.93	5.71	5.32	8.2	−0.7	13.0	10.7	9.5
36	24.0	6.80	3.07	3.82	3.45	11.29	6.13	5.32	7.3	−2.1	11.1	8.7	7.6
37	24.5	7.50	3.26	3.90	3.42	11.10	5.68	5.01	7.2	−1.7	11.3	9.1	7.8
39	25.0	7.30	2.80	3.85	3.36	10.61	5.38	5.33	10.7	1.9	17.8	15.5	14.3
	23.0	7.30	2.79	3.76	3.55	11.61	5.36	5.03	8.0	−1.2	13.4	11.5	9.7
40	27.0	7.15	2.96	3.23	2.45	11.79	5.50	5.05	6.7	−2.5	10.9	9.2	7.0
41	24.0	7.20	3.17	3.52	3.11	11.29	5.83	5.02	7.1	−2.1	11.1	9.0	7.6
42	20.0	6.50	2.75	3.71	3.01	12.54	6.07	5.03	5.3	−4.8	8.5	6.7	4.7
43	23.0	6.90	2.74	3.97	2.92	11.47	5.68	5.33	8.4	−0.9	13.8	11.7	10.0
44	23.0	7.13	2.82	2.93	1.85	11.48	5.68	5.09	8.1	−1.1	13.8	12.0	10.0
45	23.5	7.01	2.73	3.52	2.70	11.28	5.54	5.34	9.0	−0.2	15.0	13.0	11.3
46	22.0	6.88	2.70	2.78	1.93	12.53	5.99	4.80	5.9	−4.0	9.9	8.4	6.0

TABLE 9.—*Ion activities and saturation indices of apatites calculated by WATEQF using selected chemical analyses of water from wells in the Upper Floridan aquifer—Continued*

Well number[1]	Water temperature, in °C	$-\text{Log}_{10}$ ion activity							Saturation index		Carbonate fluorapatites[3]		
		H^+	Ca^{2+}	Mg^{2+}	Na^+	PO_4^{3-}	CO_3^{2-}	F^-	Fluor-apatite[2]	Hydroxy-apatite[2]	Florida	North Carolina	Tennessee
47	22.0	7.22	2.66	2.77	1.85	11.81	5.72	4.94	8.1	−1.3	14.0	12.2	10.2
48	24.0	6.58	2.83	3.38	2.93	11.89	6.01	5.34	6.6	−2.9	10.5	8.5	6.7
49	22.0	6.55	2.79	3.81	3.06	11.92	6.09	5.33	6.7	−2.9	10.6	8.5	6.9
50	22.5	6.90	2.75	3.60	2.61	11.32	5.71	5.04	9.0	−0.6	15.2	13.1	11.6
51	23.0	7.60	2.88	2.99	2.24	11.23	5.49	5.07	8.6	−0.2	14.6	12.7	10.9
52	22.0	7.22	2.70	2.68	2.29	11.80	5.93	4.71	8.1	−1.5	13.9	12.1	10.3
53	20.5	7.20	2.63	2.90	3.45	11.43	5.67	4.48	9.8	−0.1	17.0	15.0	13.7
	20.5	7.10	2.72	2.98	3.52	11.64	6.74	4.59	8.6	−1.3	13.9	11.6	10.9
	20.8	7.18	3.05	3.42	3.65	11.04	5.67	4.85	8.5	−1.0	14.0	11.8	10.7
54	22.3	7.40	3.15	3.34	3.36	11.92	5.48	4.55	5.7	−3.9	9.4	7.7	5.7
55	24.0	8.86	4.59	4.84	1.90	10.22	3.52	3.75	4.5	−4.4	7.9	6.8	4.2
	26.5	8.90	4.87	4.96	1.93	9.86	3.46	3.89	4.1	−4.5	6.7	5.5	3.1
56	25.0	8.00	3.02	4.00	3.81	10.59	5.29	5.32	9.6	1.5	15.8	13.4	12.3
	20.5	7.60	3.07	3.95	3.85	10.96	5.69	5.02	8.5	−0.5	13.7	11.4	10.4
	21.0	8.10	3.03	3.99	3.82	10.65	5.21	5.02	9.7	1.2	16.1	13.9	12.7
57	20.9	7.90	3.23	3.55	3.90	11.29	5.16	4.84	6.9	−2.0	11.3	9.5	7.7
	21.5	7.80	3.24	3.55	3.94	10.35	5.23	4.84	9.7	0.8	16.0	13.8	12.8
	21.5	7.60	3.25	3.55	3.93	10.71	5.44	4.71	8.7	−0.6	14.2	12.0	11.0
58	19.9	8.00	3.30	3.63	3.86	10.27	5.14	5.31	9.1	0.8	14.9	12.5	11.4
	22.0	7.92	3.30	3.60	3.87	10.56	5.16	4.84	8.8	0.0	14.4	12.3	11.1
	21.5	7.60	3.35	3.60	3.81	10.76	5.48	4.84	7.9	−1.3	12.7	10.5	9.4
59	22.5	7.40	2.72	2.89	2.11	12.14	5.51	4.92	6.9	−2.3	11.8	10.3	7.9

[1] Well locations are shown in figure 29.

[2] Fluorapatite ($Ca_5(PO_4)_3F$), log K_{FAP} = −66.79 at 25 °C; hydroxyapatite ($Ca_5(PO_4)_3(OH)$), log K_{HAP} = −59.35 at 25 °C; temperature dependence of the equilibrium constants was computed by WATEQF from the Van't Hoff equation, using ΔH_{FAP} = 19.695 and ΔH_{HAP} = 17.225 kilocalories per mole.

[3] Mineral formulas and equilibrium log K_{SP} at 25 °C of carbonate apatites in citrate-extracted phosphate rocks (Chien and Black, 1976, tables 1 and 4):

Florida—$Ca_{9.71}Na_{0.21}Mg_{0.08}(PO_4)_{5.19}(CO_3)_{0.81}F_{2.32}$, log K_{SP} = −117.8
North Carolina—$Ca_{9.54}Na_{0.33}Mg_{0.13}(PO_4)_{4.80}(CO_3)_{1.20}F_{2.48}$, log K_{SP} = −114.4
Tennessee—$Ca_{9.85}Na_{0.11}Mg_{0.04}(PO_4)_{5.56}(CO_3)_{0.44}F_{2.18}$, log K_{SP} = −118.7.
No correction of log K_{SP} was made for solution temperatures different from 25 °C, due to lack of enthalpy data for the minerals.

known, so the choice of solubility product constant to use in computing the S.I. is questionable. Furthermore, the possibility that an amorphous calcium phosphate compound is controlling F^- concentrations cannot be dismissed, even though a study by Gulbrandsen and others (1984) casts doubt on the long-term stability of these compounds, even in a freshwater environment. Therefore, the apparent oversaturation of ground water in the Upper Floridan aquifer with respect to fluoride-bearing apatites may not be real; some species of carbonate fluorapatite may be in equilibrium with the ground water. More data on both dissolved-phosphate concentrations in ground water and composition of apatite species in the aquifer are required to determine whether or not mineral equilibria actually control F^- concentrations in the Upper Floridan aquifer.

SILICA AND ALUMINUM

Concentrations of dissolved silica in water from the Upper Floridan aquifer vary from about 1 to about 80 mg/L (about 0.02 to about 1.33 mmol as SiO_2), values fairly typical of natural waters (Hem, 1970, p. 109). The general distribution of dissolved silica in the Upper Floridan is shown in figure 30. The data along flow paths shown in figure 30 are used in a later discussion of the chemical controls on dissolved aluminum in the Upper Floridan. The highest concentrations of dissolved silica generally occur in the Upper Floridan aquifer in Georgia and South Carolina, where chalcedony and aluminosilicate minerals may be locally more abundant. In these areas, recharge from underlying sand aquifers may increase dissolved-silica concentrations in the Upper Floridan, as silica concentrations in the sand aquifers locally range from about 20 to 50 mg/L (Lee, 1984, table 3). At 25 °C, concentrations of dissolved silica near 0.10 mmolar (6 mg/L) are in equilibrium with quartz, and concentrations of 0.50 mmolar (30 mg/L) are near equilibrium with chalcedony (fig. 31). In 905 analyses of water from the Upper Floridan aquifer, 95 percent of the measured silica concentrations were in the range 5.5 to

EXPLANATION

— — — — LIMIT OF RELIABLE DATA

A —— *A'* LINE OF WELLS ALONG FLOW PATH

⊙0.12 WELL–Number represents dissolved-silica concentration, In millimoles per kilogram of water

SCALE 1:5,000,000

| 0 | 50 | 100 | MILES |
| 0 | 50 | 100 | KILOMETERS |

FIGURE 30.—Concentrations of dissolved silica in water samples from selected wells in the Upper Floridan aquifer.

37 mg/L; the median concentration was 14 mg/L. The data plotted in figure 31 suggest that the lower limit of dissolved silica is quartz solubility and the upper limit of dissolved silica is the solubility of chalcedony. Concentrations of dissolved silica higher than 40 mg/L may be the result of local contamination, dissolution of local sources of highly soluble silicate phases(?), or water-sampling and analytical errors.

As mentioned in a previous section, the high Na^+ concentrations in the Upper Floridan aquifer in the Florida Panhandle do not appear to result from weathering of silicate minerals. As shown in figure 30, dissolved-silica concentrations in this area are near the median value for the entire aquifer; also, dissolved-silica concentrations do not increase in a downgradient direction. A water sample from a well in the Upper Floridan aquifer in eastern Escambia County, Fla., was analyzed for dissolved aluminum (fig. 32) and therefore could be used to calculate saturation indices of sodium-silicate minerals using WATEQF and the log K_{eq} data of table 10. The calculated results for the shallow monitor well (sampled on March 15, 1971) are shown below:

Mineral name	Formula	Saturation index
Analcime	$NaAlSi_2O_6 \cdot H_2O$	+0.99
Na-beidellite	$Na_{0.33}Al_{2.33}Si_{3.67}O_{10}(OH)_2$	+3.38
(Low) albite	$NaAlSi_3O_8$	+1.45
(Aberdeen) Montmorillonite	$(H,Na,K)_{0.42}Mg_{0.45}Fe^{3+}_{0.34}Al_{1.47}Si_{3.82}O_{10}(OH)_2$	+5.06
(Belle Fourche) Montmorillonite	$(H,Na,K)_{0.28}Mg_{0.29}Fe^{3+}_{0.23}Al_{1.58}Si_{8.93}O_{10}(OH)_2$	+5.47

These results suggest that the excess Na^+ is not due to dissolution of these phases, if they occur in the rocks of the area. If some unidentified sodium-silicate phase were dissolving, the silica added by dissolution must be precipitating almost simultaneously in some more stable phase(s), since dissolved-silica concentrations are not increasing. Assuming that the major control on silica concentrations in the Upper Floridan aquifer is the solubility of quartz or chalcedony, then the dissolution of sodium silicates should lead to formation of chalcedony cements or quartz grain overgrowths. Lithologic logs of test wells in Escambia and Santa Rosa Counties (Hull and Martin, 1982) do not mention the occurrence of chalcedony cements or overgrowths in the rocks of the Upper Floridan aquifer, although detailed microscopic studies were not made. Without detailed mineralogic and petrographic studies of the aquifer materials in the panhandle area, the presumption that silicate weathering does not cause the high Na^+ concentrations in the area cannot be proven correct; however, the available data and calculations cited above tend to support the presumption.
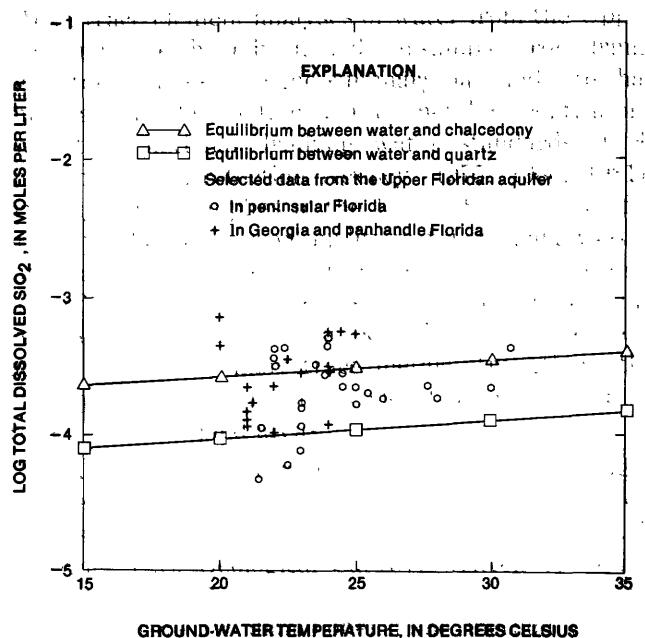
FIGURE 31.—Relation between dissolved silica and temperature in water samples from selected wells in the Upper Floridan aquifer.

The available data on dissolved-aluminum concentrations in the Upper Floridan aquifer are scarce and are not well distributed over the study area (fig. 32). Only 144 analyses of dissolved aluminum were made of water samples from 107 wells during the period 1970–82. The maximum reported concentration was 0.3 mg/L, but 95 percent of the measured concentrations were less than 0.1 mg/L (about 3.7 mmol per kilogram of water). The 44 analyses of dissolved aluminum shown in figure 32 were selected to give maximum areal coverage; where two (or more) proximate wells had analyses, the analysis from the deeper well was selected. Because "dissolved" aluminum concentrations were analyzed from water samples that had been treated at the well site by passing them through a 0.45-µm filter and acidifying to pH 2.0 with concentrated nitric acid, some uncertainties are introduced in interpretation of the aluminum data. Some particulate aluminum phases may pass through a 0.45-µm filter (Kennedy and others, 1974; Barnes, 1975). Dissolved-aluminum concentrations of about 0.1 to 1 mmol in water with pH between 7 and 8 are in equilibrium with crystalline $Al(OH)_3$ (gibbsite) (fig. 33; Reesman and others, 1969; Hemingway, 1982). The data plotted in figure 33 indicate that some water samples from the Upper Floridan aquifer contained almost an order of magnitude too much "dissolved" aluminum to be in equilibrium with gibbsite.

To test the possibility that other aluminum or aluminosilicate phases might be controlling dissolved-aluminum concentrations, the 44 selected analyses were processed
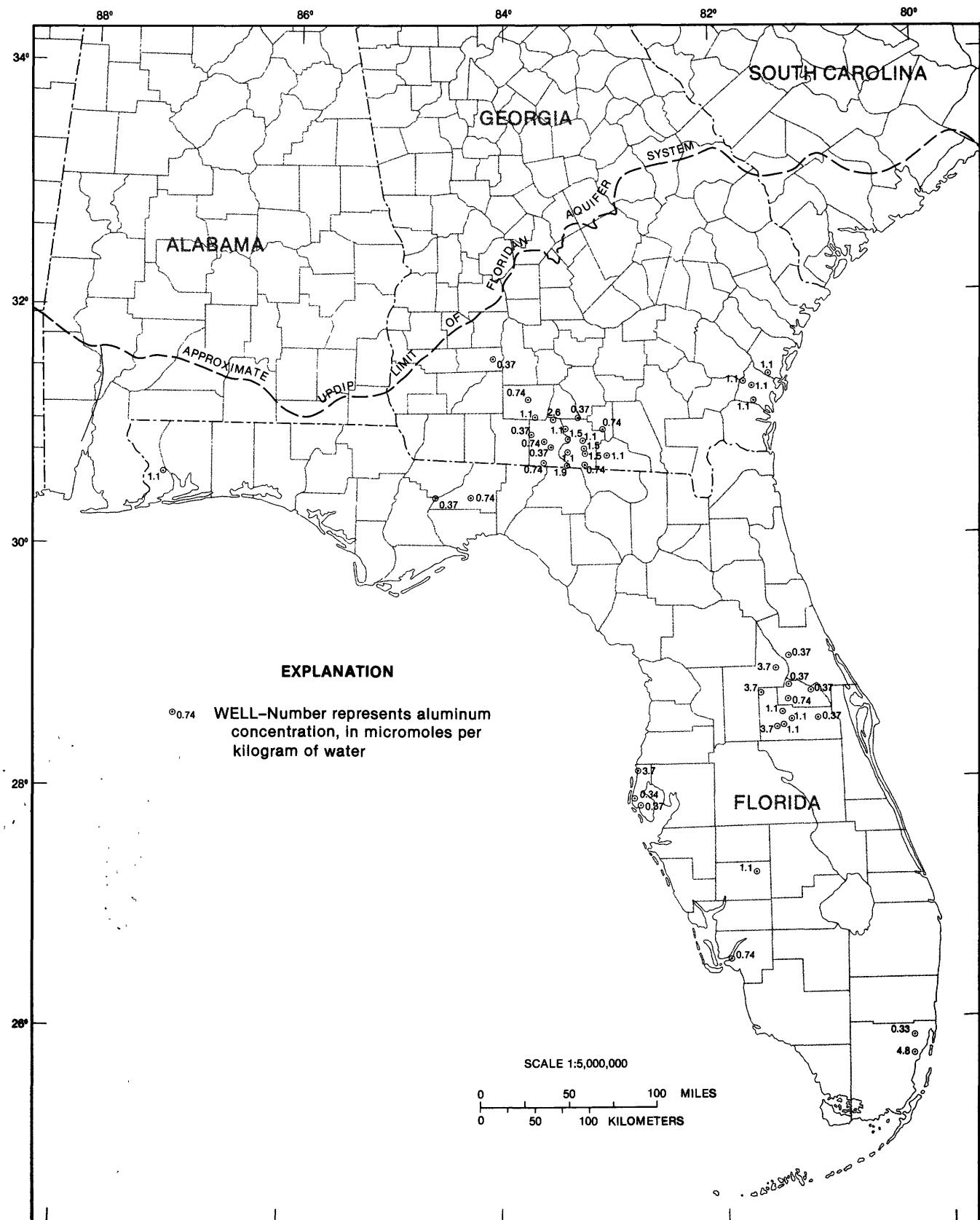
FIGURE 32.—Concentrations of aluminum in water samples from selected wells in the Upper Floridan aquifer.

TABLE 10.—*Summary of thermochemical data and saturation indices for selected mineral phases, calculated by WATEQF from 44 analyses of ground water from wells in the Upper Floridan aquifer*

[kcal/mol, kilocalories per mole]

Phase	Log K_{eq} (equilibrium constant) at 25 °C	$\Delta H°r$ (enthalpy), in kcal/mol	Saturation index			
			Mean	Maximum	Minimum	Standard deviation
Quartz	−3.973	5.35	0.464	0.943	−0.137	0.264
Chalcedony	−3.523	4.615	0.011	0.485	−0.400	0.262
Silica glass	−2.969	3.56	−0.548	−0.080	−1.149	0.260
Gibbsite	−33.91	17.25	1.193	2.357	−0.035	0.434
Al(OH)$_3$, amorphous	−31.61	12.99	−1.127	0.036	−2.284	0.426
Kaolinite	−40.29	52.81	5.789	7.684	3.011	0.980
Halloysite	−37.02	48.36	2.498	4.364	−0.205	0.967
(Low) Albite	−20.40	26.67	0.590	2.886	−1.550	1.059
Microcline	−22.16	31.63	1.262	3.081	−0.932	0.934
Na-beidellite	−49.33	62.34	6.486	9.036	3.383	1.275
Ca-montmorillonite	−49.08	60.46	6.169	8.724	2.920	1.287
Belle Fouche montmorillonite	−34.97	0.0	6.604	8.715	4.309	1.096
Aberdeen montmorillonite	−29.78	0.0	5.973	8.118	3.623	1.116
Wairakite	−26.62	26.14	−2.782	−0.355	−4.895	1.218
Laumontite	−30.96	39.61	1.618	4.126	−0.644	1.246
Analcime	−16.27	21.21	−0.032	0.994	−1.867	0.952
Muscovite	−56.03	72.81	7.644	10.643	4.669	1.310
Phillipsite	−19.86	0.0	−0.626	1.346	−2.915	1.025
Pyrophyllite	−46.68	59.72	5.145	7.754	2.102	1.301
Leonhardite	−75.47	90.83	16.839	21.924	12.123	2.520

by WATEQF using free energies and enthalpies given in table 11. The program calculated S.I. for mineral phases that might be present in trace quantities in the Upper Floridan aquifer (table 10). A temperature of 25 °C was

FIGURE 33.—Relation between dissolved aluminum and pH in water samples from selected wells in the Upper Floridan aquifer.

chosen for the log K_{eq} values since most of the ground water in the Upper Floridan aquifer is near this temperature (fig. 2). The summary statistics in table 10 indicate that amorphous Al(OH)$_3$ is the only aluminum-containing phase that is consistently undersaturated in the water samples analyzed. Adularia (a K$^+$-feldspar variety), albite, halloysite, and phillipsite (a Na$^+$, K$^+$-bearing zeolite) are often undersaturated, indicating that these phases could increase dissolved-aluminum concentrations if the minerals actually are present in the aquifer. The mean saturation index for gibbsite is near zero, which may indicate that gibbsite controls aluminum concentrations in some places. Drever (1982, fig. 5–4), however, shows that gibbsite is an equilibrium control on dissolved aluminum only when activities of dissolved silica (H$_4$SiO$_4$) are less than approximately $10^{-4.5}$ (less than 2 mg/L in dilute solutions). At higher dissolved-silica concentrations, the total activity of dissolved-aluminum species should be much less, owing to the formation of stable aluminosilicate phases. The data in table 10 show that only halloysite and albite are not highly oversaturated in some of the water samples analyzed. The amount of oversaturation may be due to the passage of particulate Al-bearing phases through the 0.45-μm filter, thus increasing the concentration of "dissolved" aluminum reported.

An alternative approach to evaluating dissolved SiO$_2$ and Al^{3+} in the Floridan aquifer system is the method of

TABLE 11.—Standard-state (25 °C, 1 atmosphere) Gibbs free energies (ΔG°) and enthalpies (ΔH°) of selected phases in the system Na₂O-K₂O-CaO-Al₂O₃-SiO₂-H₂O

[kcal/mol, kilocalories per mole; J mol⁻¹, joules per mole. Dashes indicate calculation not performed]

Phase or species	Mineral name	ΔG°, in kcal/mol	ΔH°, in kcal/mol	Source[1]
H_2O		-56.69	-68.32	R
OH^-		-37.60	-54.98	R
Na^+		-62.60	-57.43	R
K^+		-67.52	-60.27	R
Ca^{2+}		-132.30	-129.74	R
Al^{3+}		-116.97	-126.91	R
$Al(OH)^{2+}$		-166.8	-183.3	B[2]
$Al(OH)_2^+$		-216.57	----	B[2]
$Al(OH)_4^-$		-312.35	-356.13	B[2]
H_4SiO_4 (aqueous)		-312.62	-348.95	R
SiO_2	quartz	-204.66	-217.66	R
SiO_2	glass	-203.29	-215.87	R
SiO_2	chalcedony	-204.0	-216.9	P[2]
$Al(OH)_3$	gibbsite	-276.03	-309.07	R
$Al_2Si_2O_5(OH)_4$	kaolinite	-908.07	-984.73	R
$Al_2Si_2O_5(OH)_4$	halloysite	-903.61	-980.28	R
$Al_2Si_4O_{10}(OH)_2$	pyrophyllite	$-1,258.58$	$-1,347.94$	R
$NaAlSi_3O_8$	(low) albite	-887.12	-940.52	R
$NaAlSi_2O_6 \cdot H_2O$	analcime	-738.94	-791.07	R
$Na_{0.33}Al_{2.33}Si_{3.67}O_{10}(OH)_2$	Na-beidellite	$-1,282.98$	$-1,372.1$	G&M[3]
$KAlSi_3O_8$	microcline	-894.44	-948.30	R
$KAl_3Si_3O_{10}(OH)_2$	muscovite	$-1,338.59$	$-1,428.48$	R
$CaAl_2Si_4O_{12} \cdot 2H_2O$	wairakite	$-1,476.9$	$-1,580.74$	P[2]
$CaAl_2Si_4O_{12} \cdot 4H_2O$	laumontite	$-1,596.2$	$-1,730.85$	P[2]
$Ca_2Al_4Si_8O_{24} \cdot 7H_2O$	leonhardite	$-3,154.19$	$-3,404.99$	R
$Ca_{0.17}Al_{2.33}Si_{3.67}O_{10}(OH)_2$	Ca-montmorillonite	$-1,283.82$	$-1,372.7$	G[3]

[1] R, Robie and others (1978), except ΔG° water $= -237,181$ J mol⁻¹.

[2] ΔG°, ΔH° computed from data in this table and log K data in: B, Ball and others (1978); P, Plummer and others (1978).

[3] ΔG° computed from data in this table and "apparent" equilibrium log K for kaolinite-Ca-montmorillonite (log K = −12.5 (Garrels, 1967)) and kaolinite-Na-beidellite (log K = −7.0 (Garrels and MacKenzie, 1967)). ΔH° values calculated from ΔG° and estimates of entropy given in footnotes e and f in table 12 of Helgeson (1969).

Thompson (1955, in Drever, 1982, p. 97), who suggested that Al_2O_3 might be treated as a conservative component in the weathering of silicates. That is, silicate minerals are assumed to dissolve incongruently to new minerals while aluminum is retained among the solid phases. Using this assumption, stability diagrams of the systems K_2O-Al_2O_3-SiO_2-H_2O, Na_2O-Al_2O_3-SiO_2-H_2O, and CaO-Al_2O_3-SiO_2-H_2O at 25 °C were prepared (figs. 34A-34C) using the data listed in table 11. The data in table 11 are consistent with diagrams drawn by Drever (1982, figs. 5-5, 5-8) and the solubilities of quartz and amorphous silica used by WATEQF. Chemical data from wells along lines following several flow paths (fig. 30) were selected, the log activities of K^+, H^+, Na^+, Ca^{2+} and H_4SiO_4 were calculated by WATEQF, and selected ratios were plotted against the activity of H_4SiO_4 (fig. 34). While the wells along flow paths A-A', B-B', and C-C' are generally representative of freshwater parts of the aquifer, wells in downgradient segments of flow paths D-D' and E-E' are representative of saline parts of the aquifer system. Data from wells along flow path C-C' show the least change in Na^+/H^+ or K^+/H^+ activities, as this flow path is through an unconfined, highly permeable part of the aquifer system. The data from the freshwater areas tend to cluster around the logarithmic (log) value of the activity ratio of K^+/H^+ of about 3 and the log value of the activity ratio of Na^+/H^+ of about 4; the ratios from the more saline areas are about 1 log unit higher.

Figure 34 indicates no simple pattern of incongruent silicate weathering. The data from the freshwater flow paths A-A', B-B', and C-C' do not exhibit systematic changes; most of the data plot within the kaolinite stability field. The data plotted in figure 34C show no systematic changes in the $Ca^{2+}/(H^+)^2$ activity ratio. The lack of trend in the data plotted in figure 34C does not rule out the possibility of diagenesis of calcium-bearing silicates in the aquifer system. Silicate weathering is
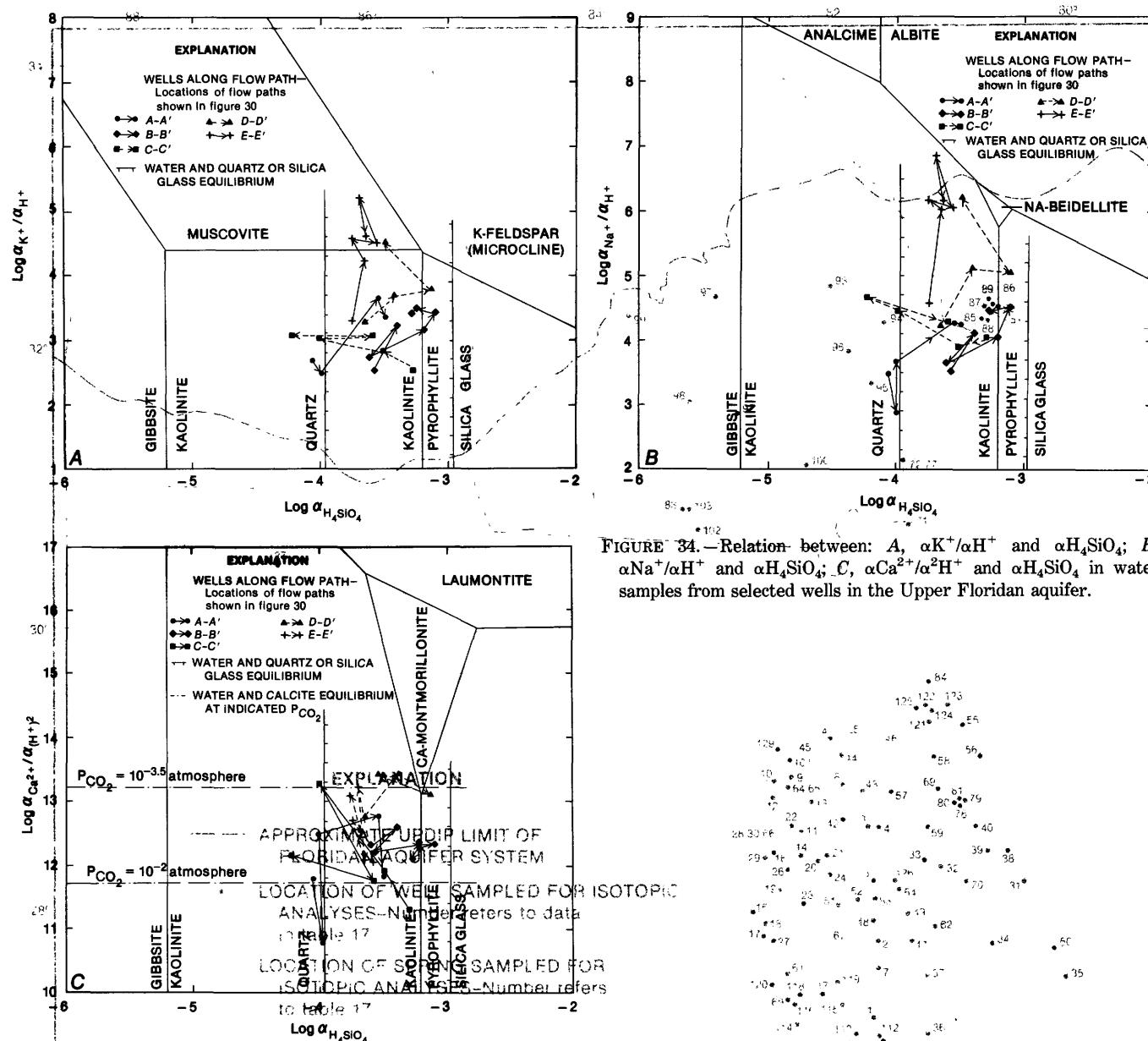
FIGURE 34.—Relation between: A, $\alpha K^+/\alpha H^+$ and αH_4SiO_4; B, $\alpha Na^+/\alpha H^+$ and αH_4SiO_4; C, $\alpha Ca^{2+}/\alpha^2 H^+$ and αH_4SiO_4 in water samples from selected wells in the Upper Floridan aquifer.

probably occurring, but concentrations of calcium and hydrogen ions are greatly influenced by changes in carbonate equilibria. Small changes in concentrations of these ions due to silicate dissolution are masked by the much larger effects of dedolomitization in most of the aquifer system. In contrast, the data from the more saline flow paths D-D' and E-E' show systematic changes—the upgradient data plot near the middle of the kaolinite field, and the downgradient data plot near phase boundaries in both figures 34A and 34B. In figure 34B the downgradient data from flow paths D-D' and E-E' plot approximately parallel to the kaolinite-Na-beidellite phase boundary, indicating that the boundary for smectites in the aquifer system may occur at slightly lower dissolved silica activities. The downgradient pro-

gression toward the smectite stability field (fig. 34B) is typical of the general pattern of feldspar weathering (Drever, 1982, p. 141–157 and 163–198, cites examples from the literature). However, the apparent progression toward the kaolinite-muscovite phase boundary (fig. 34A) is not necessarily real and may be related to the choice of minerals used to construct the two-dimensional stability diagram.

Given the uncertainties in composition, equilibrium solubility, and distribution of silicate minerals within the aquifer system, only the most general conclusions can be drawn from the available silica and aluminum data. Dissolved-silica concentrations appear to be controlled primarily by the solubility of chalcedony, although quartz may be the control in parts of the Floridan where

TABLE 12.—*Summary statistics for nitrogen (N) and phosphorus (P) concentrations in water from the Upper Floridan aquifer, calculated from selected water analyses and reported as elemental N or P*

Species		Number of samples	Concentration, in milligrams per liter					
			Maximum	75 percentile	Median	Mean	25 percentile	Minimum
Total - N	(F)[1]	26	4.7	0.80	0.52	1.07	0.31	0.08
Ammonia (NH_4)-N	(F)	44	2.1	0.52	0.29	0.40	0.15	0.01
Organic (Org)-N	(F)	35	4.6	0.37	0.20	0.45	0.05	0
Nitrite (NO_2)-N	(F)	112	0.06	<0.01	0	<0.01	0	0
Nitrate (NO_3)-N	(F)	328	3.16	0.09	0	0.14	0	0
NH_4 + Org (KJD)-N	(F)	36	4.7	1.03	0.55	0.83	0.33	0.08
NO_2+NO_3-N	(F)	56	3.0	0.05	0.05	0.19	0.01	0
Total - N	(UF)	273	8.67	1.61	1.45	1.48	1.18	0.06
NH_4-N	(UF)	293	2.1	1.25	1.0	0.86	0.41	0
Org-N	(UF)	275	1.2	0.35	0.2	0.24	0.07	0
NO_2-N	(UF)	331	0.55	<0.01	<0.01	0.01	<0.01	0
NO_3-N	(UF)	332	7.6	0.02	0	0.31	0	0
KJD-N	(UF)	270	2.54	1.5	1.34	1.11	0.84	0
NO_2+NO_3-N	(UF)	260	7.78	0.08	0.01	0.37	<0.01	0
Total - P	(F)	34	2	0.07	0.02	0.10	<0.01	0
Orthophosphate (PO_4)-P	(F)	83	2	0.05	0.02	0.05	<0.01	0
Total - P	(UF)	270	1.8	0.08	0.06	0.07	0.03	0
PO_4-P	(UF)	261	1.2	0.08	0.05	0.06	0.02	0

[1] F, filtered water sample; UF, unfiltered (whole) water sample.

ground-water flow is very sluggish. Aluminum concentrations are likely very low, possibly controlled by (1) the solubility of gibbsite or (2) the alteration of kaolinite to mixed-layer clays (smectites).

NUTRIENTS

The occurrence of the principal nutrients, nitrogen (N) and phosphorus (P) species, in the Upper Floridan aquifer was investigated by retrieval of all N and P data available for the 601 wells used to describe the major ion chemistry. A total of 648 analyses (from 591 wells) of various N and P species were compiled into a data set and statistically analyzed using procedures available in SAS (SAS Institute, 1979). Table 12 reports summary statistics for both total and dissolved nutrient-species concentrations. The 648 analyses contained some qualified values. Especially common were concentrations reported as less than a threshold value (detection limit). For "less than" qualified values, a concentration of one-half the threshold value was substituted before any statistical tests were performed. The data in table 12 show that except for dissolved nitrate, the preponderance of analyses of N and P species were made on whole water samples; thus, bacteria in the water were analyzed, along with any trace solids (minerals) containing N or P forms. These whole-water analyses are probably representative of "available" N, however, since microorganisms can easily reduce and assimilate organic N. The orthophosphate (PO_4) in organic material (or minerals) is readily assimilated in any case.

The data shown in table 12 indicate that low concentrations of P occur throughout the Upper Floridan aquifer; 75 percent of the samples contained less than 0.1 mg/L of P. At these low concentrations, P dissolved in ground water may be limiting to the growth of bacterial populations in the aquifer, if mineral sources of P are not available. Bacteria contain mole ratios of carbon(C):N:P of 47.3:7.3:1 (Fenchel and Blackburn, 1979, table III, p. 16). This means that to assimilate, for example, 0.05 mg/L of P completely, the bacterial population needs only 0.17 mg/L of N and 0.92 mg/L of C. In the Upper Floridan aquifer, the median concentration of NH_4 nitrogen in more than 290 samples was 1.0 mg/L (table 12) and the median concentration of dissolved organic carbon in 48 samples was 4.0 mg/L (table 18). Both are well above the amounts required for a bacterial population to assimilate 0.05 mg/L of P, the median concentration of P, even if other sources of N and C were not available. Bacterial assimilation of the median concentration of P calculated for filtered water samples (0.02 mg/L, table 12), that is, P in "true" solution, would require even less N or C in solution.

The sources of the various N and P species in the Upper Floridan aquifer are not well defined over the aquifer's areal extent. As described previously, the Upper Floridan aquifer contains trace amounts of phosphate minerals in many areas; the overlying Hawthorn Formation contains economic concentrations of phosphate minerals in southwestern and north-central Florida. Wherever recharge through the Hawthorn can

occur, dissolved-phosphate concentrations may increase in the Upper Floridan aquifer. In unconfined areas, both phosphate and nitrate dissolved from fertilizers or dissolved in other manmade discharges may also enter the Upper Floridan. Although some generalizations can be made concerning nutrient distributions within the aquifer system, the reader should use local data (whenever possible) to evaluate bacterial growth conditions in the Upper Floridan aquifer.

Because N species are present in moderate concentrations in the ground water and no mineral sources of N exist within the Floridan aquifer system, the occurrence of individual species and total concentration of N were examined to determine the likely sources (and sinks) of the element. Three hypotheses were tested by statistical analysis of the nutrient data set:

1. The aquifer system is in a state of natural dynamic equilibrium, where total N input (through precipitation) equals output (via ground-water discharge) from the system. Individual N species may not be distributed uniformly within the system, but total N concentrations are similar in recharge and discharge areas. No trend of increasing or decreasing N concentrations over time is observed in recharge or discharge areas.

2. Man's activities at land surface have affected the input levels of N through leaching of fertilizers and land application of wastes from industrial or municipal water-treatment plants. The aquifer system is not in dynamic equilibrium; some individual species and total N concentrations in unconfined recharge areas are significantly higher than in discharge areas. Nutrient analyses of ground water in unconfined recharge areas show a time trend of increasing total N concentrations; nutrient analyses from discharge areas do not show any time trends.

3. Man's activities have affected the input levels of N by leaching of fertilizers and spreading of wastes, and through direct recharge of the aquifer system with nitrogen-rich water via drainage or disposal wells (point sources). The system is not in dynamic equilibrium; some individual species and total N concentrations are significantly higher in both confined and unconfined recharge areas than in confined discharge areas. Nutrient analyses of ground water in recharge areas show a time trend of increasing total N concentrations; nutrient analyses from discharge areas do not show any time trends.

To perform statistical tests of these hypotheses, each nutrient analysis was designated by the location of the well sampled as a confined or unconfined area (fig. 11); each analysis was also designated by location of the well

sampled as an area of recharge or discharge through diffuse upward leakage (fig. 12). Statistical tests were performed on P species, as well as N species, as an independent test of the time-trend aspects of the three hypotheses.

Before testing the three hypotheses, the problem of missing values of total N (TOT-N) and total P (TOT-P) had to be overcome. Although 273 measurements of TOT-N were available in the original data set (table 12), these analyses were made of water samples from only 21 wells. Review of the data set revealed that nitrate N (NO_3-N) had been measured in filtered water samples (F) from the most wells—328 samples from 134 wells (table 12)—in the original data set. The most frequently measured nitrogen species—NO_3-N in unfiltered water samples—was measured in 332 samples from 46 wells (table 12). To obtain the greatest areal coverage of nutrient data for hypothesis testing, missing concentrations of total N and P species were estimated from dissolved concentrations for each water analysis according to the following regression equations:

$$PO_4\text{-}P = 0.99235 * PO_4\text{-}P(F), \quad r^2 = 0.830, \ n = 23, \qquad \text{(N1)}$$

$$NO_3\text{-}N = 1.01186 * NO_3\text{-}N(F), \quad r^2 = 1.000, \ n = 37, \qquad \text{(N2)}$$

$$NO_2 + NO_3\text{-}N = 0.98855 * (NO_2 + NO_3\text{-}N)(F), \qquad \text{(N3)}$$
$$r^2 = 0.999, \ n = 7,$$

$$KJD\text{-}N = 1.05631 * KJD\text{-}N(F), \quad r^2 = 0.897, \ n = 7, \qquad \text{(N4)}$$

$$NH_4\text{-}N = 1.01822 * NH_4\text{-}N(F), \quad r^2 = 0.996, \ n = 11, \qquad \text{(N5)}$$

where r^2 is the coefficient of determination (r is commonly called the correlation coefficient) and n is the degree of freedom, which is the number of water samples used in the regression minus the number of parameters in the regression equation, and KJD-N is organic nitrogen as determined by the Kjeldahl method. The symbols for the independent variables (N and P species) are the same as shown in table 12. The intercepts of the regression lines were not included in equations N1 through N5 because the intercepts were not significantly different from zero at the 95 percent confidence level. The r^2 statistic is a measure of how much variation occurs in the dependent variable between the values calculated by the regression equations and the observed values. When r^2 is equal to 1.000, the correlation between the regression equations and the observed values is perfect. For n less than 5, the model is probably an untrustworthy predictor of the dependent variable, regardless of the value of r^2.

After estimating concentrations of total species, models to estimate missing TOT-N and TOT-P concentrations from total species concentrations were developed by using single- and multiple-regression techniques. Estimates of TOT-N were made preferentially by two-variable equations, whenever values of both independent

TABLE 13.—Mean and standard deviation of nutrient concentrations in selected water samples from wells in different hydrologic settings in the Upper Floridan aquifer

[In milligrams per liter, unless otherwise indicated]

Nutrient species	Hydrologic setting			
	Unconfined recharge area	Unconfined discharge area	Confined recharge area	Confined discharge area
TOT-N	m=1.53, s=0.90, n=110[1]	m=1.27, s=0.25, n=43	m=1.48, s=0.78, n=9	m=1.36, s=0.68, n=330
NO$_3$-N	m=0.71, s=1.09, n=132	m=0.07, s=0.15, n=102	m=0.26, s=0.79, n=16	m=0.10, s=0.56, n=372
NO$_2$+NO$_3$-N	m=0.99, s=1.23, n=81	m=0.14, s=0.19, n=12	m=0.05, n=1	m=0.11, s=0.72, n=214
KJD-N	m=0.13, s=0.28, n=46	m=1.42, s=1.70, n=9	m=0.65, n=1	m=1.26, s=0.44, n=242
NH$_4$-N	m=0.05, s=0.07, n=52	m=0.28, s=0.22, n=10	m=0.64, n=1	m=0.97, s=0.40, n=262
TOT-P	m=0.03, s=0.04, n=71	m=0.21, s=0.60, n=14	m=0.03, s=0.04, n=6	m=0.07, s=0.12, n=256
PO$_4$-P	m=0.03, s=0.04, n=45	m=0.17, s=0.52, n=14	m=0.03, s=0.04, n=6	m=0.06, s=0.09, n=255

[1] m, population mean; s, population standard deviation; n, number of observations.

variables were available. For both TOT-N and TOT-P, the regression model with the largest r^2 value was used, whenever the independent variable(s) was (were) available. The regression models used to estimate missing values of TOT-N and TOT-P are shown below:

$$TOT\text{-}P = 1.14744 * DIS\text{-}P - 0.00891, \quad r^2 = 0.996, \quad n = 7 \quad (N6)$$

$$TOT\text{-}P = 1.21716 * PO_4\text{-}P, \quad r^2 = 0.972, \quad n = 267 \quad (N7)$$

$$TOT\text{-}N = 1.00221 * (NO_2 + NO_3\text{-}N) + 1.00442 * \quad (N8)$$
$$KJD\text{-}N - 0.01451, \quad r^2 = 0.999, \quad n = 219$$

$$TOT\text{-}N = 1.01636 * NO_3\text{-}N + 1.01557 * KJD\text{-}N \quad (N9)$$
$$- 0.01449, \quad r^2 = 0.999, \quad n = 264$$

$$TOT\text{-}N = 1.00124 * (NO_2 + NO_3\text{-}N) + 1.12585 \quad (N10)$$
$$* NH_4\text{-}N + 0.10098, \quad r^2 = 0.966, \quad n = 221$$

$$TOT\text{-}N = 1.00238 * NO_3\text{-}N + 1.12241 * NH_4\text{-}N \quad (N11)$$
$$+ 0.14350, \quad r^2 = 0.945, \quad n = 270$$

$$TOT\text{-}N = 0.73328 * (NO_2 + NO_3\text{-}N) + 1.14418, \quad (N12)$$
$$r^2 = 0.722, \quad n = 221$$

$$TOT\text{-}N = 0.69936 * NO_3\text{-}N + 1.22294, \quad r^2 = 0.660, \quad (N13)$$
$$n = 270,$$

where DIS-P is dissolved phosphorus.

Clearly, the regression equation for predicting TOT-N (eq. N8) should have a coefficient of determination of 1.000 and a zero intercept. The calculated coefficients and nonzero intercept in equation N8 are due to estimating concentrations of total species from concentrations of dissolved species. Regression equations for estimating concentrations of TOT-N from either KJD-N or NH$_4$-N alone had r^2 less than 0.005 and were not used.

Standard parametric methods (analysis of variance) were not used to test the three hypotheses, because the data for the seven nutrient species were highly skewed—the lowest concentrations had the highest number of observations. Instead, the Kruskal-Wallis nonparametric test (SAS, 1979, p. 331–334) with an approximate significance test (chi square) was employed. The

concentration data for the seven nutrient species were subdivided into four subgroups on the basis of hydrologic setting of the well; for example, nutrient concentrations measured in a water sample from a well in an unconfined recharge area of the Floridan aquifer system were added to the "unconfined recharge" subgroup. The mean, standard deviation, and number of samples of each nutrient species in each subgroup are given in table 13. The results of comparing concentrations of the nutrient species subgroup by subgroup, using the Kruskal-Wallis procedure, are given in table 14.

The results of statistical tests of the N-species data indicate that total concentrations of N are similar in recharge and discharge areas and in confined and unconfined areas, and between cross-combinations of the different hydrogeologic settings. Comparison of the total concentration of N in unconfined recharge areas with the total concentration of N in confined discharge areas also showed no significant differences (table 14, pt. IV). The individual N species did exhibit significant differences, however, which hint at biogeochemical processes occurring in the Upper Floridan aquifer. The results shown in table 14 indicate that nitrate reduction occurs practically everywhere in the aquifer system. Even unconfined areas show changes in N species from more oxidized to more reduced forms between recharge and discharge areas. The quantitative effects of ground-water flow and aquifer confinement on changes in N species concentrations cannot be learned from these statistical tests, because changes in N species concentrations along individual flow paths were not calculated. The results of statistical tests on data from the entire aquifer system suggest, however, that there is a quantitative decrease in oxidized N species and a quantitative increase in reduced N species from recharge areas to discharge areas. These biochemical transformations in the aquifer system should be more carefully studied and quantified, because both fermentative nitrate reduction and denitrification can affect the carbonate chemistry of the ground water, especially the isotopic composition of the dis-

TABLE 14.—*Effect of hydrologic setting on nutrient concentrations measured in selected water samples from wells in the Upper Floridan aquifer*

Part I:	Hydrologic setting of well			
Nutrient	Unconfined	Confined	Recharge	Discharge
TOT-N	N.S.[1]	N.S.	N.S.	N.S.
NO$_3$-N	+	−	+	−
NO$_2$+NO$_3$-N	+	−	+	−
KJD-N	−	+	−	+
NH$_4$-N	−	+	−	+

Part II:	Hydrologic setting of well			
	Recharge		Discharge	
Nutrient	Unconfined	Confined	Unconfined	Confined
TOT-N	N.S.	N.S.	N.S.	N.S.
NO$_3$-N	+	−	N.S.	N.S.
NO$_2$+NO$_3$-N	−−−[2]	−−−−	N.S.	N.S.
KJD-N	−−−−	−−−−	N.S.	N.S.
NH$_4$-N	−−−−	−−−−	−	+

Part III:	Hydrologic setting of well			
	Unconfined		Confined	
Nutrient	Recharge	Discharge	Recharge	Discharge
TOT-N	N.S.	N.S.	N.S.	N.S.
NO$_3$-N	+	−	N.S.	N.S.
NO$_2$+NO$_3$-N	+	−	−−−−	−−−−
KJD-N	−	+	−−−−	−−−−
NH$_4$-N	−	+	−−−−	−−−−

Part IV:	Hydrologic setting of well	
Nutrient	Unconfined recharge	Confined discharge
TOT-N	N.S.	N.S.
NO$_3$-N	+	−
NO$_2$+NO$_3$-N	+	−
KJD-N	−	+
NH$_4$-N	−	+

[1] N.S., not significant at the 99 percent confidence level; +, group higher than alternative hydrologic setting; −, lower than alternative hydrologic setting.
[2] Analysis of variance not made, because sample population was less than 5.

solved carbonate species. Recent work by Plummer and others (1983) has shown methods for quantifying the effects of biochemical reactions involving sulfate on the $\delta^{13}C$ and $\delta^{14}C$ content of the ground water in the Floridan aquifer system. Considering the widespread occurrence of nitrate reduction implied by these results, efforts should be made to gather the necessary chemical and isotopic data to quantify both the amount of nitrate reduction occurring in the Upper Floridan aquifer and the effect of nitrate reduction on the carbon isotopic composition of the ground water.

To test for time trends in the selected nutrient data, a nonparametric test was employed. Water-quality data that are skewed (serially correlated) and exhibit seasonality can be examined for time trends using a procedure called the seasonal Kendall test, developed by Hirsch and others (1982). As previously stated, the selected nutrient data were highly skewed. A test of seasonality using standard analysis of variance of monthly group means (other time groups were also tested) showed that at the 98-percent confidence level the nutrient analyses from the 591 selected wells had significantly different monthly means; that is, the data exhibited seasonality. A nonparametric test, the Wilcoxon two-sample test (SAS, 1979, p. 331), also indicated seasonality at the 95-percent confidence level. Having determined skewness and seasonality in the data set, tests for serial correlation were considered unnecessary before applying the seasonal Kendall test.

The seasonal Kendall test has been written into a SAS procedure by Crawford and others (1983). Although they warn that the test is "not robust against serial correlation," these authors (p. 50) suggest that for ground water, the use of fewer than 12 groups (monthly) "will help avoid serious problems due to serial correlation." Therefore, time-trend tests were performed using the seasonal Kendall test with the number of data groups ranging from 12 to 2. The results of testing for time trends with concentration data grouped variously from monthly to semiannually were not predictable. For a nutrient species in the same hydrologic setting, the probability that no trend existed might increase uniformly, decrease uniformly, increase to a peak and then decrease, or be erratic as the number of groups was reduced. The possibility that significant differences in concentrations of nutrient species might be observed on a monthly or bimonthly interval seems remote for the Floridan aquifer system, if the system is subjected to areally diffuse, low-concentration inputs (hypotheses 1 and 2). The seasonal Kendall test results are reported in table 15 for only quarterly and semiannual groups, because these results might be significant.

The results of testing the selected nutrient data for time trends were inconclusive. A positive time trend for P species was indicated only for the entire data set and for the confined discharge areas. Possibly the "significant" trends in P concentrations are an artifact of changes in ground-water sampling procedures during the period of record (1965–83). During the period 1973–80, nutrient samples were chilled to 4 °C but no chemical preservatives were added to the sample; from 1965 to 1973, and beginning again in late 1980, mercuric chloride was added to nutrient samples prior to chilling to 4 °C. These changes in preservation technique, accompanied by a gradually increasing number of samples collected from year to year, may account for the very slight positive trend in P concentrations. The very small negative slopes calculated for N species in different hydrologic settings probably also are the result of these changes in sampling technique. The positive slope calcu-

TABLE 15.—*Trend probabilities (Tp) and estimates of slope (S) calculated from nutrient concentrations in selected water samples from wells in different hydrologic settings in the Upper Floridan aquifer*

[Samples were collected during the period 1965–83]

	TOT-N	NO$_3$-N	NO$_2$+NO$_3$-N	KJD-N	NH$_4$-N	TOT-P	PO$_4$-P
Entire data set:							
<u>Quarterly</u>							
Tp[1]	0.437	0.000	0.000	0.027	0.920	0.009	0.001
S[2]			−0.008	−0.031		0.001	0.002
Semiannually							
Tp	0.862	0.010	0.000	0.641	0.482	0.013	0.004
S			−0.010			0.002	0.002
Unconfined recharge areas:							
<u>Quarterly</u>							
Tp	0.156	0.000	0.308	0.908	0.720	0.179	0.656
S		0.105					
Semiannually							
Tp	0.735	0.002	0.318	0.471	0.801	0.495	0.876
S		0.055					
Unconfined discharge areas:							
<u>Quarterly</u>							
Tp	0.282	0.414	0.341	0.308	0.221	1.000	1.000
S							
Semiannually							
Tp	0.336	0.269	0.368	0.221	0.452	0.656	0.458
S							
Confined recharge areas:							
<u>Quarterly</u>							
Tp	0.165	0.012	N.C.[3]	N.C.	N.C.	1.000	1.000
S		−0.009					
Semiannually							
Tp	0.112	0.023	N.C.	N.C.	N.C.	1.000	1.000
S		−0.015					
Confined discharge areas:							
<u>Quarterly</u>							
Tp	0.464	0.000	0.000	0.014	0.285	0.004	0.001
S			−0.002	−0.029		0.001	0.002
Semiannually							
Tp	0.961	0.002	0.001	0.132	0.170	0.030	0.017
S			−0.003			0.002	0.002

[1] Trend probabilities greater than 0.05 are not considered significant; that is, the null hypothesis that no trend exists is not rejected for Tp>0.05.

[2] Slope estimates are indicated in units of milligrams per liter per year only for significant trend probabilities. The actual values of S are not given when S was several orders of magnitude lower than the analytical detection limit.

[3] N.C. - Tp and S were not computed because sample population less than 5.

lated for nitrate concentrations measured in unconfined recharge areas is, however, too large to be an artifact of sampling technique. The observed trend of increasing nitrate concentrations in ground water in unconfined recharge areas of the Upper Floridan aquifer probably results from increased development (residential, agricultural, and commercial) in the region during the period 1965–83. It is uncertain why only nitrate shows a significant time trend in the unconfined recharge areas; perhaps the regression equations for estimating the other N species, especially TOT-N, are sufficiently inexact to mask any trends. A more likely explanation is that the N species measured are not the predominant N species produced by bacterial reduction of nitrate occurring in unconfined recharge areas. In the Upper Floridan aquifer, dissimilative nitrate reduction to N$_2$ (denitrification) may be a quantitatively important process, but its gaseous product is not measured routinely. Restating comments made previously, efforts should be made to study the processes and effects of nitrate reduction occurring in the Upper Floridan.

In summary, the results of the statistical tests of the selected nutrient data indicate that the aquifer system may be in dynamic equilibrium with respect to N: no

significant differences in total N were observed between unconfined or confined areas, or between recharge and discharge areas, or in cross-combinations of the different hydrologic settings. However, a significant time trend of increasing nitrate concentrations was determined in the unconfined recharge areas. The results of these tests, therefore, do not preclude the possibility of the dynamic nonequilibrium hypotheses 2 or 3 being true. It is also possible that the flow system is in dynamic equilibrium *and* that man's activities have affected N concentrations in the unconfined recharge areas. Denitrification and loss of N_2 gas may be quantitatively important in removing the N added as nitrate in the unconfined recharge areas, but further studies are needed to test this hypothesis. Although this study was inconclusive in describing the N chemistry and the effects of nonpoint pollution on the geochemistry of the aquifer system, the effects of point sources of pollution on N chemistry in the aquifer system have previously been documented. Some of these site-specific studies are cited in the later section on trace organic contaminants.

TRACE METALS AND ENVIRONMENTAL ISOTOPES

The criteria for selection of water-quality data to describe the common ions were modified to obtain the statistical analyses discussed in this section. In order to have a larger sample population, all trace metal analyses dated 1970 or later from wells and springs in the Upper Floridan aquifer were used for the trace metals interpretations, regardless of well depth or areal coverage. Only wells that might be associated with disposal of wastes were excluded; this was done to avoid potential point-source bias in the regional description of the "natural" variability in minor element concentrations. Table 16 gives statistical summaries of trace metal concentrations in the Upper Floridan aquifer; figure 35 shows the general location of the wells and springs that were sampled. Although figure 35 shows many sampling sites, most wells and springs were analyzed for only iron and manganese; the areal distribution of samples for most other trace metals is very limited. Filtration of water samples through 0.45-μm filters affects trace metals in the same manner as it does aluminum. As discussed by Hem (1985, p. 130–131), many particulate metal hydroxides that are small enough to pass through a filter of this size have adsorbed trace metals. When the filtered sample is acidified, the particulates and sorbed metals are dissolved, and analysis reports concentrations of the trace metals as though they were actually in solution in ground water. Interpretation of these "dissolved" element data by assuming mineral solubility control over trace metal concentrations may be unproductive or misleading.

Most trace element analyses of water from the Upper Floridan aquifer have been made on samples from drinking water supplies, and the summary data indicate that almost all samples contained trace metal concentrations lower than national drinking water standards (U.S. Environmental Protection Agency, 1975, 1980, 1981). Drinking water supplies in the Upper Floridan aquifer tend to produce only good-quality water, and analyses of water samples from these sources may not be representative of the entire aquifer system. Although sampling over the entire region has not been done, the absence of natural sources of many trace metals strengthens the presumption that very low concentrations should be present in unsampled areas.

Selenium (Se) concentrations greater than 0.005 mg/L in table 16 may be due to random errors in chemical analysis, especially Se analyses made prior to 1975 (R.J. Pickering, U.S. Geological Survey, written commun., 1981). Prior to 1975, the Geological Survey analyzed Se by the colorimetric diaminobenzidine method (Brown and others, 1970), which may have contained (undocumented) positive interferences. Analyses of Se made by the Geological Survey after 1975 have used the atomic absorption with hydride generation method (Skougstad and others, 1979); very few concentrations greater than 0.001 mg/L of Se have been reported since use of this method began. The Geological Survey has examined its historical data on Se concentrations in surface water, but no regional pattern exists either areally or temporally. At this time (1986), the Geological Survey considers that, for water samples analyzed by its laboratories before 1975, reported concentrations of dissolved and total Se greater than 0.005 mg/L are probably incorrect, and concentrations of dissolved Se greater than 0.001 mg/L are questionable.

The few high trace metal concentrations reported in table 16 may be related to very local conditions, possibly influenced by local contaminant sources or well construction. The low solubility of minerals composed of trace metal cations and sulfide, oxide, or hydroxide anions should limit dissolved trace metal concentrations to very low levels in most of the Upper Floridan aquifer. In areas where the Upper Floridan contains dissolved oxygen, many trace metals form insoluble oxides or hydroxides in the mildly alkaline ground water. Even trace elements that form soluble oxyanions tend to absorb strongly to particulate metal hydroxides and become "immobilized." In areas where reducing conditions are present, hydrogen sulfide is prevalent and will react with many trace metals to form insoluble metal sulfides. Thus, while contamination may locally produce abnormally high concentrations of dissolved trace metals, (bio)chemical reactions within the Upper Floridan aquifer cause many metals to precipitate from solution near the contaminant
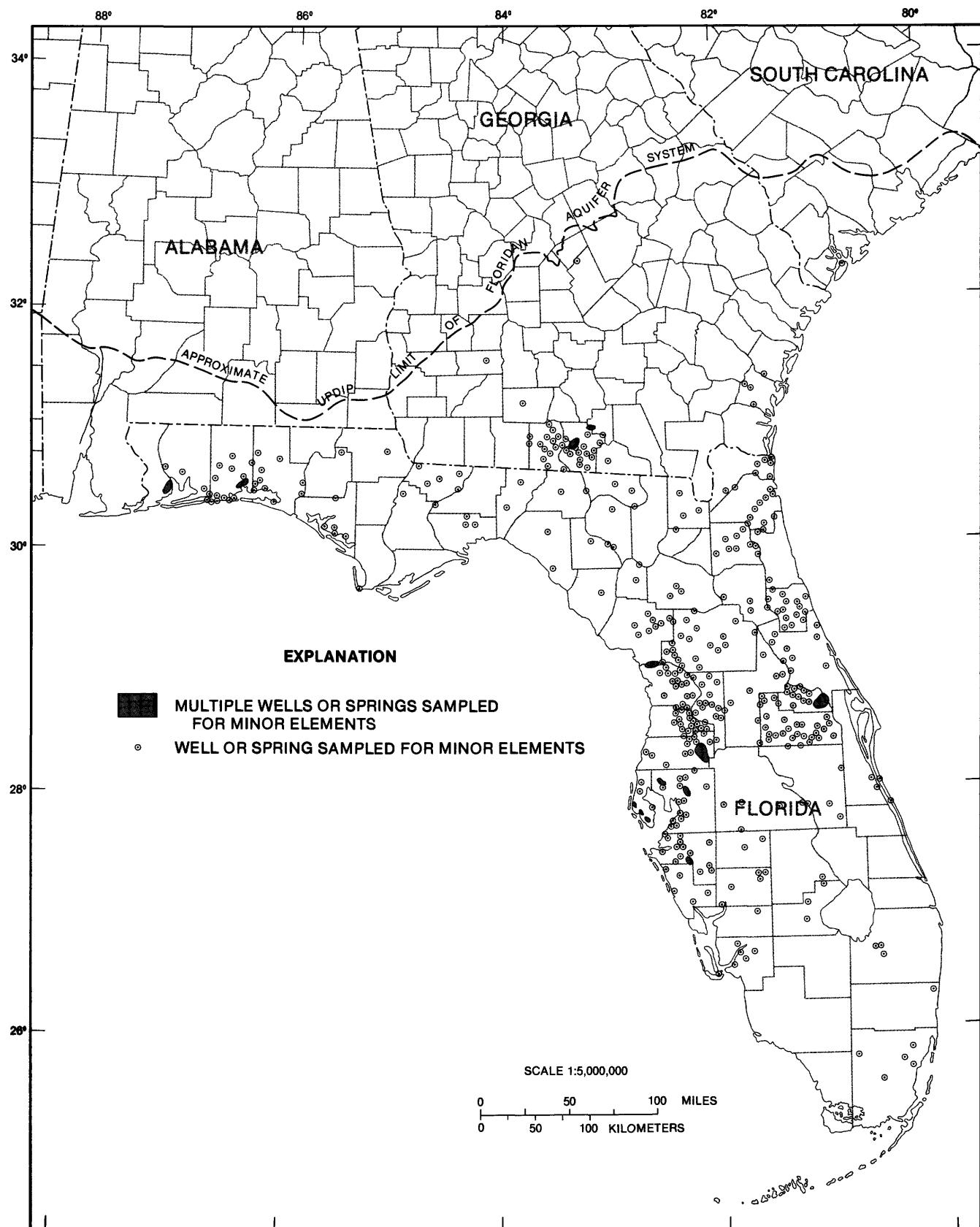
FIGURE 35.—Wells and springs in the Upper Floridan aquifer sampled for minor elements.

TABLE 16.—*Summary of selected minor element concentrations in water from the Upper Floridan aquifer*

[In milligram per liter. Dashes indicate calculation not performed]

Constituent	Number of samples	Maximum	95-percentile	75-percentile	Median	25-percentile	5-percentile	Minimum	Remarks
Arsenic, dissolved	198	0.035	0.015	0.004	0.001	0.001	0.000	0.000	[1]MCL 0.05
Arsenic, total recoverable	135	.044	.008	.002	.001	.001	.000	.000	
Barium, dissolved	19	.12	.12	.10	.10	.020	.000	.000	MCL 1.0
Barium, total recoverable	38	.30	.21	.10	.10	.10	.10	.10	
Boron, dissolved	98	4.2	.64	.12	.040	.020	.000	.000	
Boron, total recoverable	10	.46	.46	.11	.040	.027	.020	.020	
Cadmium, dissolved	169	.020	.005	.002	.000	.000	.000	.000	MCL 0.01
Cadmium, total recoverable	130	.008	.003	.002	.000	.000	.000	.000	
Chromium, dissolved	130	.020	.011	.003	.000	.000	.000	.000	MCL 0.05
Chromium hexavalent, dissolved	69	.010	.005	.000	.000	.000	.000	.000	
Chromium, total recoverable	118	.15	.041	.020	.020	.010	.010	.000	
Cobalt, dissolved	69	.040	.003	.000	.000	.000	.000	.000	
Cobalt, total recoverable	105	.010	.005	.002	.000	.000	.000	.000	
Copper, dissolved	196	.030	.010	.003	.002	.000	.000	.000	[2]WQC 1.0
Copper, total recoverable	113	.17	.043	.007	.003	.002	.000	.000	
Iron, dissolved	503	46	2.1	.15	.030	.010	.010	.000	
Iron, total recoverable	143	41	4.8	1.5	.44	.10	.020	.010	
Lead, dissolved	210	.12	.022	.006	.002	.000	.000	.000	MCL 0.05
Lead, total recoverable	116	.17	.036	.013	.005	.002	.000	.000	
Lithium, dissolved	29	.21	.20	.025	.010	.010	.002	.001	
Manganese, dissolved	204	5.7	.083	.017	.010	.010	.005	.000	
Manganese, total recoverable	133	.88	.063	.025	.010	.010	.010	.000	
Mercury, dissolved	145	.023	.0005	.0005	.0005	.0005	.000	.000	MCL 0.002
Mercury, total recoverable	148	.014	.0006	.0005	.0005	.0002	.0001	.0001	
Molybdenum, dissolved	24	.090	.083	.007	.001	.001	.001	.001	
Molybdenum, total recoverable	6	.007	.007	.006	.002	.001	.001	.001	
Nickel, dissolved	36	.029	.023	.002	.000	.000	.000	.000	WQC 0.0134
Selenium, dissolved	114	[3].013	.008	.004	.002	.001	.000	.000	MCL 0.01
Selenium, total recoverable	74	[3].006	.001	.001	.001	.001	.000	.000	
Silver, dissolved	1	.020	----	----	----	----	----	----	MCL 0.05
Silver, total recoverable	22	.002	.002	.000	.000	.000	.000	.000	
Strontium, dissolved	951	67	24	5.7	.47	.090	.001	.000	
Vanadium, dissolved	24	.67	.63	.055	.003	.000	.000	.000	
Zinc, dissolved	185	1.6	.087	.020	.010	.003	.000	.000	WQC 5.0
Zinc, total recoverable	113	.30	.15	.056	.020	.020	.003	.000	

[1] MCL, Maximum contaminant level for community water systems (U.S. Environmental Protection Agency, 1975).

[2] WQC, Water quality criteria (U.S. Environmental Protection Agency, 1980, 1981).

[3] Historical selenium concentrations greater than 0.005 mg/L are highly suspect; see text for discussion.

source. Only when the contaminant source might contain chemicals that form soluble complexes with the dissolved metals, or might contain chemicals that kill the naturally occurring sulfate-reducing bacteria in the system, should high concentrations of dissolved trace metals be present more than a few hundreds or thousands of feet from the source. Measurable concentrations of many trace metals can be expected to be present throughout the aquifer system, owing to the low (but nonzero) solubility of cation-hydroxide complexes (Baes and Mesmer, 1976; Stumm and Morgan, 1981, ch. 6). Fortunately, however, chemical conditions in the Floridan aquifer system are such that high concentrations of trace metals will not normally be present.

The occurrence of stable isotopes and radioactive elements in ground water in the Upper Floridan aquifer has not been regionally investigated. Stable carbon (^{13}C), sulfur (^{34}S), and radiocarbon (^{14}C) data from the Upper Floridan in peninsular Florida and coastal Georgia and South Carolina are available in published reports (Hanshaw, Back, and Rubin, 1965; Hanshaw, Back, Rubin, and Wait, 1965; Back and others, 1970; Pearson and Hanshaw, 1970; Plummer, 1977). Selected published data and new isotopic data collected during this study are

compiled in table 17; well locations for the data in table 17 are shown in figure 36. Methods for interpretation of ^{14}C data have undergone considerable revision since the mid-1960's; techniques for interpreting ^{14}C in hydrologic systems were recently reviewed by Mook (1980). Current methods for interpreting ^{14}C require analyses of stable isotopes, especially of ^{13}C and ^{34}S, in the dissolved, solid, and gas phases of the system. Recent papers (Back and others, 1983; Plummer and others, 1983) discuss some of the complexities and unresolved problems of interpreting ^{14}C data from carbonate aquifer systems. The techniques of the workers cited above were of limited applicability in this regional study because of the lack of data on stable isotopes in the important reacting phases. As more of the required data are collected, a better understanding of ground-water flow velocities and reaction rates in different parts of the Upper Floridan aquifer will be obtained.

Limited data on other radionuclide concentrations in the Floridan aquifer system are also available; for example, both tritium (Stringfield, 1966, p. 149–151; Pearson and Hanshaw, 1970, p. 282; Osmond and others, 1971, p. 45–54; Faulkner, 1973, p. 68–69) and uranium (U) concentrations (Osmond and others, 1968; Kaufman and others, 1969; Osmond and others, 1971, 1974; Briel, 1976; Cowart and others, 1978; Osmond, 1980) have been measured. The data reported indicate that very low or zero concentrations of tritium occur in the Floridan aquifer system, except where the system is unconfined or where sinkholes have breached thin confining units. The tritium concentrations listed below were selected from data reported by Osmond and others (1971, table 8) from wells and springs in Leon, Gadsden, and Wakulla Counties of northwestern Florida.

Sample number	Sample location	Aquifer	Casing/well depth, in feet	Tritium concentration, in tritium units
LG-01	Well #6, Tallahassee well field	Upper Floridan aquifer, semi-confined	170/413	6.1±0.5
LG-018	Well near Bradford Brook on Route 61S	Upper Floridan aquifer, semi-confined	140/220	73.8±10.8
WS-04	Wakulla Springs, sampled at 85-foot depth	Upper Floridan aquifer, unconfined	—	33.7±2.3
GG-01	Havana municipal well	Upper Floridan aquifer, confined	418/692	0±0.18

These data show typical effects of confinement on the tritium content in water samples taken from the Upper Floridan aquifer. Comparison of the tritium concentrations measured in wells LG–01 and LG–018 further illustrate the vertical stratification of water chemistry in the aquifer system. The papers cited report that dis-

solved U concentrations in the Upper Floridan aquifer are generally less than 10 parts per billion (ppb). The principal source of dissolved U in the Floridan aquifer system is phosphatic minerals (primarily apatites) that are present in the aquifer and overlying sediments. These minerals may contain as much as 75,000 ppb of U, which has been measured in apatite pellets in the Hawthorn Formation (Altschulter and others, 1958, table 19). Because the apatite content of rocks making up the Floridan aquifer system is very low, the principal source of dissolved U may be recharge through the upper confining unit, composed mostly of the Hawthorn Formation. In his summary paper, Osmond (1980) presents an overview of the principles and several examples of application of U isotopes to hydrologic studies, but he concludes (p. 261) that "confusion regarding the mechanism of fractionation, and uncertainty regarding the significance of regional variations, [have] tended to hold back progress in application [of uranium isotopes] to hydrologic problems."

A radioactive isotope of uranium, radium-226 (Ra-226), has been reported to be present in concentrations exceeding drinking water standards in a few wells and streams in southwestern Florida (U.S. Environmental Protection Agency, 1974; Irwin and Hutchinson, 1976; Kaufmann and Bliss, 1977; Sutcliffe and Miller, 1981). Irwin and Hutchinson (1976, table 1) reported results of sampling for Ra-226 in wells and streams in areas of both active phosphate mining and undisturbed phosphate deposits in central and northern Florida. They found that 5 of 30 samples from the Floridan aquifer system exceeded the recommended drinking water standard of 5 picocuries per liter (pCi/L) (U.S. Environmental Protection Agency, 1975). Sutcliffe and Miller (1981, table 1) presented data indicating that the highest Ra-226 concentrations were present in water from phosphate-rich sediments (primarily the Hawthorn and Tamiami Formations), but that deeper wells in the Upper Floridan aquifer (Ocala Limestone) contained as much as 6.3 pCi/L of Ra-226. These few results illustrate the potential mobility of U-236 and Ra-226 in ground water, and they further suggest that more analyses should be made of Ra-226 in water from the Upper Floridan aquifer in areas of known phosphate deposits.

TRACE ORGANIC CONTAMINANTS

Measurements by the Geological Survey of organic chemicals in the Floridan aquifer system date back to 1960, when total organic carbon was first analyzed. Early analytical techniques measured only gross quantities of organics such as oils and waxes (grease), phenols, and organic carbon in ground water (Rainwater and Thatcher, 1960; Goerlitz and Brown, 1972). As more powerful analytical tools developed, specific compounds
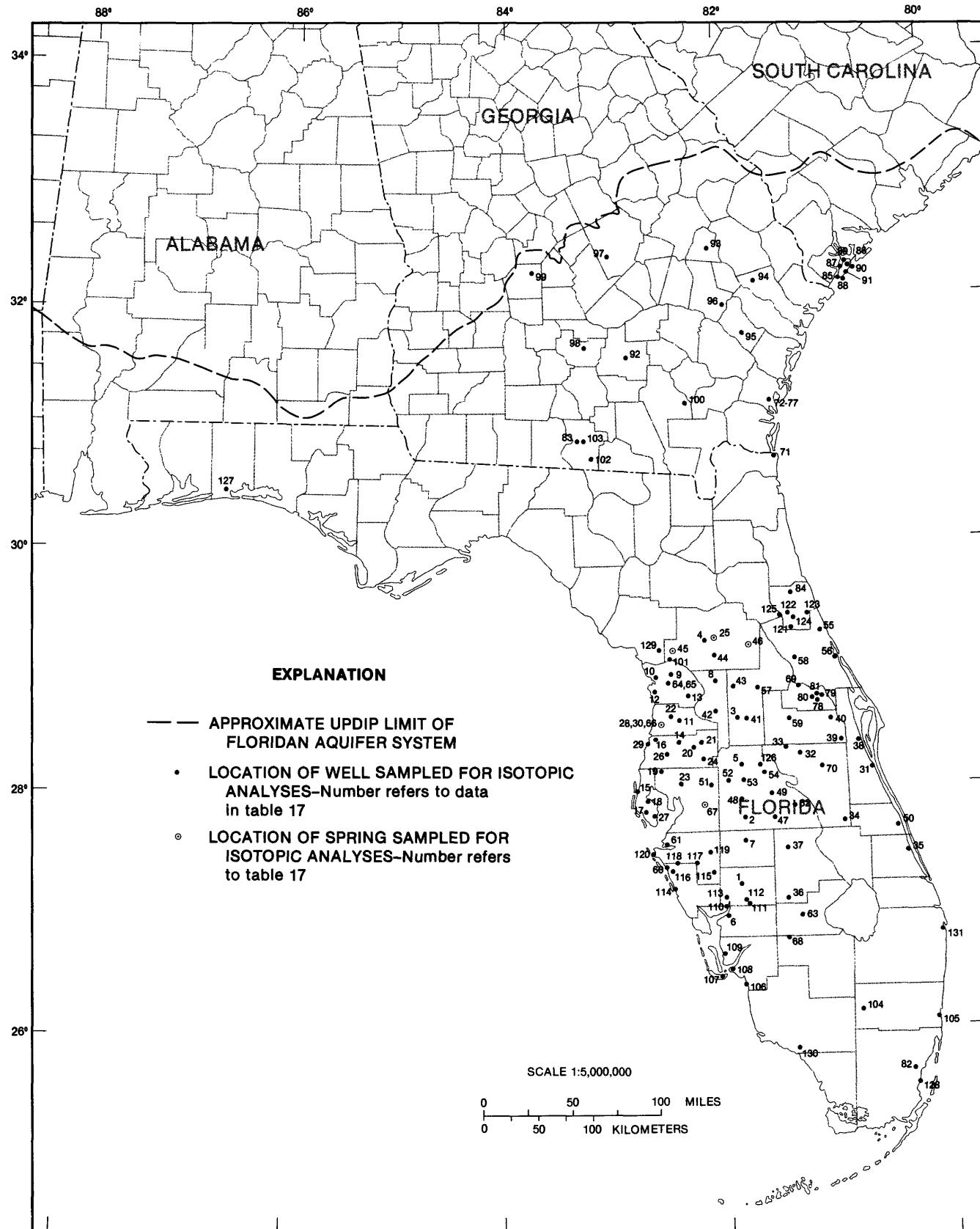
FIGURE 36.—Wells and springs in the Floridan aquifer system sampled for stable and radioactive isotopes.

TABLE 17.—*Stable and radioactive isotope content measured in water samples from wells and springs in the Upper Floridan aquifer*

[Dashes indicate no measurement]

Map number[1]	Well or spring name	Sample date	Stable isotope content, per thousand[2]				Radioactive isotope content[3]		Source[4]
			$\delta^{13}C$	$\delta^{18}O$	$\delta^{2}H$	$\delta^{34}S_{SO_4}$	[14]C, in percent modern	[3]H, in tritium units	
1	Arcadia	1/64	−8.3	−1.62	0.0	24.5	3.0	0.1 ± 1	A, D, N
2	Fort Meade	1/64	−10.8	----	----	----	17.3	0.2 ± 1	D
3	Groveland	1/64	−10.0	----	----	----	34.0	----	D
4	Ocala	1/64	−10.4	----	----	----	33.5	----	D
5	Polk City	1/64	−11.4	----	----	----	34.3	----	D
6	Cleveland	1/64	−6.0	−1.55	----	----	3.3	----	A, D
7	Wauchula	1/64	−8.5	−2.25	----	24.9	4.4	----	A, D, N
8	Wildwood	1/64	−11.3	----	----	10.5	43.6	----	D, N
9	Beverly Hills	2/65	−10.5	----	----	----	63.0	----	A
10	Crystal River	2/65	−10.5	----	----	----	44.4	----	A
11	Brooksville	2/65	−12.2	----	----	23.1	43.8	----	C, N
12	Homosassa	2/65	−10.9	----	----	----	42.4	----	A
13	Floral City	2/65	−14.9	----	----	12.5	68.3	----	A, N
14	Private well near Darby	2/65	−11.2	----	----	----	56.1	----	A
15	Clearwater	2/65	−13.6	----	----	----	40.0	----	B
16	Swartzell	2/65	−11.0	----	----	----	26.4	----	A
17	Kenneth City	2/65	−10.8	----	----	----	7.5	----	A
18	County well near High Point	2/65	−13.0	----	----	----	29.1	----	A
19	Private well near Citrus Park	2/65	−11.1	----	----	----	53.5	----	A
20	San Antonio	2/65	−10.3	----	----	9.8	45.5	----	A, N
21	Dade City	2/65	−11.9	----	----	17.7	39.4	----	A, N
22	Private well near Tooke Lake	2/65	−12.5	----	----	----	41.1	----	A
23	Temple Terrace	2/65	−11.4	----	----	----	41.8	----	A
24	Zephyrhills	2/65	−12.7	----	----	14.3	51.0	----	A, N
25	Silver Springs	2/65	−11.2	----	----	----	45.4	----	A
26	Cleveland Dairy near Drexel	2/65	−12.2	----	----	----	1.7	----	A
27	St. Petersburg	2/65	−10.5	----	----	----	26.2	----	A
28	Weeki Wachee Springs	2/65	−12.2	----	----	----	41.0	----	A
29	Hudson	2/65	−14.7	----	----	---	62.6	----	A
30	Well at Weeki Wachee Springs	2/65	−10.8	----	----	15.5	38.3	----	A, N
31	Eau Gallie	7/65	−9.9	----	----	----	4.3	----	A
32	St. Cloud	7/65	−9.8	----	----	----	9.2	----	A
33	Kissimmee	7/65	−9.3	−1.65	−0.4	----	8.4	----	A
34	Yeehaw Junction	7/65	−5.9	----	----	----	1.8	----	A
35	Fort Pierce	7/65	−2.4	−1.29	−0.2	27.4	2.1	11 ± 2	A
36	Graham Dairy near Venus	7/65	−9.4	----	----	----	4.3	----	A
37	Sebring	7/65	−10.4	----	----	----	20.5	----	A
38	Cocoa	7/65	−9.3	----	----	----	7.5	----	A
39	Orange County well field	7/65	−7.3	----	----	----	1.2	----	A
40	Flowing well near Christmas	7/65	−8.9	----	----	----	5.1	----	A
41	Clermont	7/65	−10.0	----	----	----	41.6	----	A
42	Webster	7/65	−11.3	----	----	----	54.4	----	A
43	Leesburg	7/65	−10.8	----	----	8.1	33.9	----	A, N
44	Belleview	7/65	−10.0	----	----	20.4	33.4	----	A, N
45	Rainbow Springs	7/65	−9.7	----	----	----	45.1	----	A
46	Juniper Springs	7/65	−9.1	----	----	----	32.5	----	A
47	Frostproof	7/65	−9.2	−1.22	0.2	----	6.7	0 ± 1	G
48	Bartow	7/65	−11.7	−2.80	----	----	43.5	----	A
49	Lake Wales	7/65	−9.4	----	----	----	20.8	----	A
50	Vero Beach	7/65	−3.6	2.12	−0.1	29.6	1.8	----	A, N
51	Plant City	7/65	−11.8	----	----	----	10.5	----	A
52	Lakeland City	7/65	−10.7	−0.50	----	----	24.9	----	A

Footnotes at end of table.

TABLE 17.—*Stable and radioactive isotope content measured in water samples from wells and springs in the Upper Floridan aquifer—Continued*

[Dashes indicate no measurement]

Map number[1]	Well or spring name	Sample date	Stable isotope content, per thousand[2]				Radioactive isotope content[3]		Source[4]
			$\delta^{13}C$	$\delta^{18}O$	$\delta^{2}H$	$\delta^{34}S_{SO_4}$	^{14}C, in percent modern	^{3}H, in tritium units	
53	Auburndale	7/65	−10.0	----	----	----	20.5	----	A
54	Haines City	7/65	−10.4	−1.20	----	----	31.8	----	A
55	Ormond Beach	7/65	−9.2	----	----	----	19.3	----	A
56	New Smyrna Beach	7/65	−10.3	----	----	----	24.5	----	A
57	Mount Dora	7/65	−10.5	----	----	----	44.9	----	A
58	Deland	7/65	−11.2	----	----	----	39.8	----	A
59	Orlando	7/65	−10.1	----	----	----	24.3	----	A
60	Sarasota	7/65	−9.1	----	----	22.8	1.2	----	A, N
61	Ellentown	7/65	−5.9	----	----	----	1.5	----	A
62	Indian Lake Estates	7/66	−10.4	----	----	----	5.8	----	A
63	Palmdale	7/66	−3.9	−1.60	----	----	0.6	0.6 ± 1	A
64	Lecanto #6 (city well)	7/66	−11.8	----	----	----	51.1	15 ± 2	G
65	Lecanto #5 (city well)	7/66	−11.5	----	0.0	----	50.0	36 ± 4	G
66	Weeki Wachee #11 (city well)	7/66	−13.7	----	−0.3	----	62.4	103 ± 16	G
67	Lithia Springs	7/66	−12.6	----	----	----	27.1	----	A
68	LaBelle	7/66	−9.8	----	----	----	1.6	----	A
69	Sanford	7/66	−10.5	----	----	----	23.9	----	A
70	Holopaw	7/66	−9.6	----	----	----	5.2	0.7 ± 1	G
71	Fort Clinch	3/67	−10.4	−0.05	----	----	----	----	A
72	Brunswick J35	2/63	----	----	−1.4 ± 0.1	----	3.5 ± 1.5	----	E
73	Brunswick D182	2/63	----	----	−1.5 ± 0.1	----	2.9 ± 1.5	----	E
74	Brunswick J11	2/63	----	----	−1.5 ± 0.1	----	2.0 ± 1.5	----	E
75	Jekyll Island J87	2/63	----	----	−1.1 ± 0.1	----	1.3 ± 1.5	----	E
76	Brunswick J12	2/63	----	----	−1.4 ± 0.1	----	2.0	----	E
77	Brunswick J77	2/63	----	----	−1.3 ± 0.1	----	3.0	----	E
78	Cockran Forest E. Well	3/82	−9.8	−3.7	----	----	31.2	----	H
79	Yarborough E. Well	3/82	−9.3	−3.8	−21.5	----	41.4	----	H
80	Cockran Forest W. Well	3/82	−10.0	−1.2	−9.0	----	4.2	----	H
81	Geneva test well	6/81	----	−3.7	−21.0	----	----	----	H
82	Kendall Lakes at 1,290 ft.	7/71	−2.0	----	----	----	5.6 ± 0.7	----	I
83	Pine Ridge near Valdosta	11/80	−13.7	−3.7	−20.0	----	----	----	L
84	ID# 293504081183601	2/82	−7.6	−2.0	----	----	<2.2	−12.5	K
85	Hilton Head Island BFT–314	4/65	−8.96	----	----	----	2.3	----	F
86	Hilton Head Island BFT–287	4/66	−12.85	----	----	----	40.0	----	F
87	Hilton Head Island BFT–317	4/66	−8.67	----	----	----	18.7	----	F
88	Hilton Head Island BFT–343	4/66	−5.06	----	----	----	1.4	----	F
89	Hilton Head Island BFT–315–190	4/65	−14.95	----	----	----	16.9	----	F
	Hilton Head Island BFT–315–483	4/65	----	----	----	----	4.0	----	F
90	Hilton Head Island BFT–407	4/66	−13.07	----	----	----	11.3	----	F
91	Hilton Head Island BFT–101–543	4/65	−6.71	----	----	----	3.5	----	F
	Hilton Head Island BFT–101–609	4/65	+0.54	----	----	----	2.1	----	F
	Hilton Head Island BFT–101–693	4/65	----	----	----	----	1.7	----	F
92	Douglas	8/81	−11.7	−4.0	−20.0	----	----	----	M
93	Metter	9/81	−9.6	−4.3	−23.0	----	----	----	M
94	Pembroke	9/81	−6.5	−3.9	−22.0	----	----	----	M
95	Ludowici	9/81	−7.2	−4.2	−21.0	----	----	----	M
96	Glennville	9/81	−9.6	−4.5	−24.0	----	----	----	M
97	Cadwell	8/81	−14.5	−4.4	−24.5	----	----	----	M
98	Ocilla	8/81	−8.9	−4.2	−21.5	----	----	----	M
99	Domestic well near Pinehurst	8/81	−10.0	−5.1	−25.5	----	----	----	M

Footnotes at end of table.

TABLE 17.—*Stable and radioactive isotope content measured in water samples from wells and springs in the Upper Floridan aquifer—*
Continued

[Dashes indicate no measurement]

Map number[1]	Well or spring name	Sample date	Stable isotope content, per thousand[2]				Radioactive isotope content[3]		Source[4]
			$\delta^{13}C$	$\delta^{18}O$	$\delta^{2}H$	$\delta^{34}S_{SO_4}$	[14]C, in percent modern	[3]H, in tritium units	
100	Waycross test well 650–900 ft.	6/81	−12.2	−3.3	−16.0	24.1	4.4	0.3	M
	650–1,100 ft.	6/81	−12.1	−3.2	−15.5	22.3	4.3	0.3	M
	1,100–1,900 ft.	6/81	−3.0	−3.3	−17.0	----	0.0	0.1	M
	1,902–1,970 ft.	5/81	−4.7	−2.8	−14.5	----	----	0.1	M
	650–1,900 ft.	6/81	−12.4	−3.1	−17.0	23.5	16.4	0.4	M
101	Dunnellon	9/81	−9.2	−1.6	−12.0	----	45.5	----	M
102	Travel Lodge near Lake Park	11/80	−14.4	−2.55	−15.5	----	----	----	L
103	Valdosta	11/80	−14.0	−4.25	−22.0	----	----	----	L
104	Everglades test well	10/81	−1.2	−2.5	−12.0	23.1	11.9	----	M
105	Ft. Lauderdale	10/81	−2.4	−1.7	−7.5	24.4	3.1	----	M
106	Bay Beach Golf Club	7/80	−3.7	----	----	----	----	----	J
107	Private well near Sanibel	7/80	−4.4	----	----	----	----	----	J
108	Private well near East Punta Rassa	7/80	−5.1	----	----	----	----	----	J
109	Pine Island Water Association	7/80	−4.6	----	----	21.0	----	----	J
110	ROMP well near Harbor Heights	7/80	−6.4	----	----	22.4	----	----	J
111	J.R. Aborgia	7/80	−8.6	----	----	21.7	----	----	J
112	Roper Groves	7/80	−7.1	----	----	----	----	----	J
113	Gen. Devel. Corp. near Hull	7/80	−4.9	----	----	22.2	----	----	J
114	Southbay Utilities near Laurel	7/80	−7.0	----	----	21.4	----	----	J
115	Edgeville	7/80	−8.4	----	----	----	----	----	J
116	B. Jones golf course in Sarasota	7/80	−8.4	----	----	----	----	----	J
117	Verna	7/80	−6.0	----	----	21.4	----	----	J
118	Private well near Beverly Terrace	7/80	−8.6	----	----	----	----	----	J
119	Near Myakka Head	7/80	−10.2	----	----	24.2	----	----	J
120	Manatee Fruit Co. near Cortez	7/80	−10.0	----	----	----	----	----	J
121	Firetower near Cody's Corner	2/82	−11.1	−2.1	−13.0	----	35.8	----	K
122	Harper well near St. John's Park	2/82	−10.1	−1.8	−11.0	----	<3.6	----	K
123	Karona	2/82	−7.3	−1.8	−13.0	----	19.1	----	K
124	Private well near Deanville	2/82	−8.8	−0.7	−4.5	----	3.2	----	K
125	Stock well—SE of Crescent Lakes	2/84	−9.0	−1.9	−11.5	----	<6.8	----	K
126	Polk City test well 836–856 ft.	12/79	−8.8	−2.8	−13.0	----	----	----	M
	1,815 ft.	11/80	----	−3.0	−20.0	----	----	----	M
127	Fort Walton cemetery	10/79	−4.5	−4.0	−19.5	----	1.3	----	M
128	Miami	10/81	−3.9	−2.3	−11.5	22.5	6.8	----	M
129	Private well near Lebanon	9/81	−9.2	----	----	----	45.5	----	M
130	Everglades	7/66	−7.7	----	----	21.4	1.2	----	A, N
131	Peanut Island	7/66	−6.8	----	----	25.7	0.3	25.7	A, N

[1] Numbers refer to well locations shown in figure 36.

[2] The δ values are defined by

$$\delta = \left[\frac{R_{sample}}{R_{standard}} - 1\right] \times 1,000.$$

For $\delta^{13}C$, $R = {}^{13}C/{}^{12}C$; for $\delta^{18}O$, $R = {}^{18}O/{}^{16}O$; for $\delta^{2}H$, $R = {}^{2}H/{}^{1}H$; and for $\delta^{34}S$, $R = {}^{34}S/{}^{32}S$. The standards are: ^{13}C - Pee Dee belemnite; ^{18}O and ^{2}H - Vienna Standard Mean Ocean Water; ^{34}S - troilite from the Canyon Diablo meteorite.

[3] Radioactive isotope activities are measured by counting the number of disintegrations per minute. ^{14}C activity is reported in percent modern, relative to the activity of oxalic acid from the National Bureau of Standards:

$$^{a}{}^{14}C = \frac{A_{sample}}{A_{ox-NBS}} \times 100.$$

Tritium (^{3}H) activity is reported in tritium units: 1 TU = 7.1 disintegrations per minute per gram water.

[4] Data sources:

A - Unpublished data from B. Hanshaw and W. Back, U.S. Geological Survey.   H - Unpublished data from G. Phelps, U.S. Geological Survey.

B - Rightmire and Hanshaw (1973).   I - Unpublished data from U.S. Geological Survey files, Florida District-WRD.

C - Back and Hanshaw (1970).   J - Unpublished data from W. Steinkampf, U.S. Geological Survey.

D - Hanshaw, Back, and Rubin (1965).   K - Unpublished data from A. Navoy, U.S. Geological Survey.

E - Hanshaw, Back, Rubin, and Wait (1965).   L - Unpublished data from M. Baedecker, U.S. Geological Survey.

F - Back and others (1970).   M - This study.

G - Pearson and Hanshaw (1970).   N - Rightmire and others (1974).

could be quantified, and more tests for possible organic contaminants in the Upper Floridan aquifer were made. The following table shows that some potential contaminants were first measured by the Geological Survey as recently as 1982.

Organic constituent measured in water samples from the Upper Floridan aquifer	Date of earliest available analysis in WATSTORE
Total organic carbon	January 1, 1960
Dissolved organic carbon	March 7, 1972
Methylene-blue active substances	January 21, 1971
Oil and grease	April 22, 1975
Phenols	May 19, 1970
Tannins and lignins	October 17, 1979
Organochlorine compounds	March 7, 1972
Organophosphorous insecticides	March 7, 1972
Chlorophenoxy-acid herbicides	March 7, 1972
Triazine herbicides	May 18, 1982
Carbamate insecticides	May 18, 1982

Given the public's increased awareness of, and concern about, ground-water contamination, testing for potential organic contaminants will probably occur with higher frequency in the future.

A statistical summary of organic chemicals measured in water samples from the Upper Floridan aquifer is presented in table 18. These data show that the majority of organic compounds were below the threshold of detection when analyzed. The data summarized in table 18 were compiled from analyses of water from wells not specifically used for artificial drainage, sewage injection, or industrial-waste disposal, in order to measure the variability and presence of organic chemicals derived from "nonpoint" sources. After wells whose names indicated an association with "point" contaminant sources were excluded, the remaining data set contained a few analyses with measurable quantities of organochlorine compounds, organophosphorous insecticides, and herbicides (table 18). This suggests that the Upper Floridan aquifer is probably susceptible to contamination by organic compounds derived from nonpoint sources.

The Upper Floridan probably is susceptible to nonpoint source contamination only in unconfined or thinly confined areas. Recently, a study was completed of the heavily irrigated agricultural area in the Dougherty Plain of southwestern Georgia, where the Floridan aquifer system is thinly confined. Hayes and others (1983) reported measurable amounts of pesticides in four wells in the Upper Floridan aquifer, but they concluded (p. 58) that "the areal extent, severity, and the long-term effects of pesticides upon the quality of water from the [Upper Floridan] cannot be determined from the available data." Wells (or springs) containing organic contaminants also are present in other parts of the aquifer system where the overlying confining unit is thin or absent (fig. 37). An interesting feature shown in figure 37 is that wells containing organic contaminants are present in Lowndes County, Ga., where the Upper Floridan aquifer is confined. In the Lowndes County area, the aquifer receives considerable recharge from surface streams by inflow through sinkholes (Krause, 1979, p. 11–12, 23–29). Direct recharge through sinkholes (or drainage wells) reduces the possibility of biochemical or photochemical degradation of organic compounds and reduces the amount of sorption of contaminants onto clay minerals and organic matter contained in confining units. In south Georgia, once organic contaminants enter the Upper Floridan aquifer, biochemical degradation may occur, but sorption is limited by the paucity of clay minerals and organic matter in the aquifer system. In south Florida, organic contaminants were detected in three wells (fig. 37). These wells were apparently affected by wastes from nearby sewage-injection wells, as there is no possibility that a surface, nonpoint source of contamination was responsible for the organic compounds measured in these wells. The entire southern third of Florida is an area of diffuse upward leakage from the Upper Floridan aquifer (fig. 12); therefore, there is no apparent potential for contaminants from nonpoint surface sources to enter the aquifer in this area.

Disposal of sewage and waste in wells in the Floridan aquifer system has been considered for many years (for example, McCallie, 1904). Injection of treated sewage and industrial wastes in wells completed in saline parts of the Lower Floridan aquifer has increased sharply since the 1970's. Disposal of excess storm runoff via drainage wells open to the Upper Floridan aquifer (containing freshwater) is extensive in the Orlando area. The hydrologic and geochemical effects of these practices tend to be local and depend on individual well construction, aquifer hydraulic characteristics, and ground-water flow in the immediate vicinity of the well, and on the chemistry and volume of injected waste or drainage water. Therefore, the effects of these practices are described in those chapters of this Professional Paper dealing with subregional areas rather than in this regional overview of ground-water chemistry. Chapter E discusses the effects of drainage wells in the Orlando area. Chapter G describes injection of treated sewage into wells in the Miami-Palm Beach coastal area. Other papers dealing with this topic are as follows:

- Drainage wells—Kimrey (1978), Kimrey and Fayard (1982), Schiner and German (1983);

- Deep-well injection of wastes—Goolsby (1972), Kaufman and others (1973), Wilson and others (1973), Kaufman and McKenzie (1975), Ehrlich and others (1979), Meyer (1980), Vecchioli (1981), Hickey (1982), and Merritt (1983).

TABLE 18.—*Summary of organic chemicals analyzed in selected water samples from the Upper Floridan aquifer*

[Units are micrograms per liter, unless otherwise indicated. mg/L, milligrams per liter. Dashes used when compound or measure was not detected at higher percentile]

Category/Constituent	Number of samples	Maximum	95 per-centile	75 per-centile	Median	25 per-centile	5 per-centile	Minimum	Detection level	Remarks
Cross measures										
Carbon, organic dissolved (mg/L)	48	40	17	8.8	4.0	1.0	ND[1]	ND	0.1	
Carbon, organic total (mg/L)	171	35	11	6.0	1.0	ND	----	ND	0.1	
Methylene blue active substance (mg/L)	20	0.10	0.10	0.10	ND	----	----	ND	0.01	
Oil and grease, total recoverable (mg/L)	12	7	5	1	ND	----	----	ND	1	
Phenols	23	19	19	6	1	ND	ND	ND	1	
Tannins and lignins (mg/L)	8	2.0	2	2.0	1.5	0.8	0.4	0.4	0.1	
Organochlorine compounds										
Aldrin, total	47	ND	----	----	ND	----	----	ND	0.01	[2]WQC .00074
Chlordane, total	47	ND	----	----	ND	----	----	ND	0.1	WQC .0046
DDD, total	47	ND	----	----	ND	----	----	ND	0.01	
DDE, total	47	ND	----	----	ND	----	----	ND	0.01	
DDT, total	47	ND	----	----	ND	----	----	ND	0.01	WQC .00024
Dieldrin, total	47	0.02	ND	----	ND	----	----	ND	0.01	
Endosulfan, total	24	ND	----	----	ND	----	----	ND	0.01	WQC .00071
Endrin, total	47	ND	----	----	ND	----	----	ND	0.01	[3]MCL 0.2; WQC 1
Heptachlor, total	47	ND	----	----	ND	----	----	ND	0.01	WQC .00278
Heptachlor epoxide, total	47	ND	----	----	ND	----	----	ND	0.01	
Lindane, total	47	ND	----	----	ND	----	----	ND	0.01	MCL 4.0
Methoxychlor, total	28	ND	----	----	ND	----	----	ND	0.01	MCL 100
Mirex, total	15	ND	----	----	ND	----	----	ND	0.01	
Perthane, total	23	0.1	0.1	0.1	ND	----	----	ND	0.1	
Polychlorinated biphenyls, total	47	ND	----	----	ND	----	----	ND	0.1	WQC .00079
Polychlorinated naphthalenes, total	36	ND	----	----	ND	----	----	ND	0.1	
Toxaphene, total	47	1.0	1.0	ND	ND	----	----	ND	0.01	
Organophosphorous insecticides										
Diazinon, total	9	0.02	0.02	ND	ND	----	----	ND	0.01	
Ethion, total	9	ND	----	----	ND	----	----	ND	0.01	
Malathion, total	9	ND	----	----	ND	----	----	ND	0.01	
Methyl parathion, total	9	ND	----	----	ND	----	----	ND	0.01	
Methyl trithion, total	9	ND	----	----	ND	----	----	ND	0.01	
Parathion, total	9	ND	----	----	ND	----	----	ND	0.01	
Trithion, total	9	ND	----	----	ND	----	----	ND	0.01	
Chlorophenoxy acid herbicides										
Silvex, total	38	0.36	0.02	ND	ND	----	----	ND	0.01	
2, 4-D, total	38	0.02	.01	ND	ND	----	----	ND	0.01	MCL 100
2, 4, 5-T, total	38	ND	----	----	ND	----	----	ND	0.01	MCL 10
Triazine herbicides										
Atrazine, total	10	ND	----	----	ND	----	----	ND	0.1	
Prometone, total	10	ND	----	----	ND	----	----	ND	0.1	
Prometryne, total	10	ND	----	----	ND	----	----	ND	0.1	
Propazine, total	10	ND	----	----	ND	----	----	ND	0.1	
Simazine, total	10	ND	----	----	ND	----	----	ND	0.1	
Simetryne, total	10	ND	----	----	ND	----	----	ND	0.1	
Carbamate insecticides										
Methomyl, total	10	ND	----	----	ND	----	----	ND	0.5	
Propham, total	10	ND	----	----	ND	----	----	ND	0.5	

[1] ND, Constituent below the threshold of detection.

[2] WQC, Water-quality criteria (U.S. Environmental Protection Agency, 1980, 1981).

[3] MCL, Maximum contaminant level for community water systems (U.S. Environmental Protection Agency, 1975).
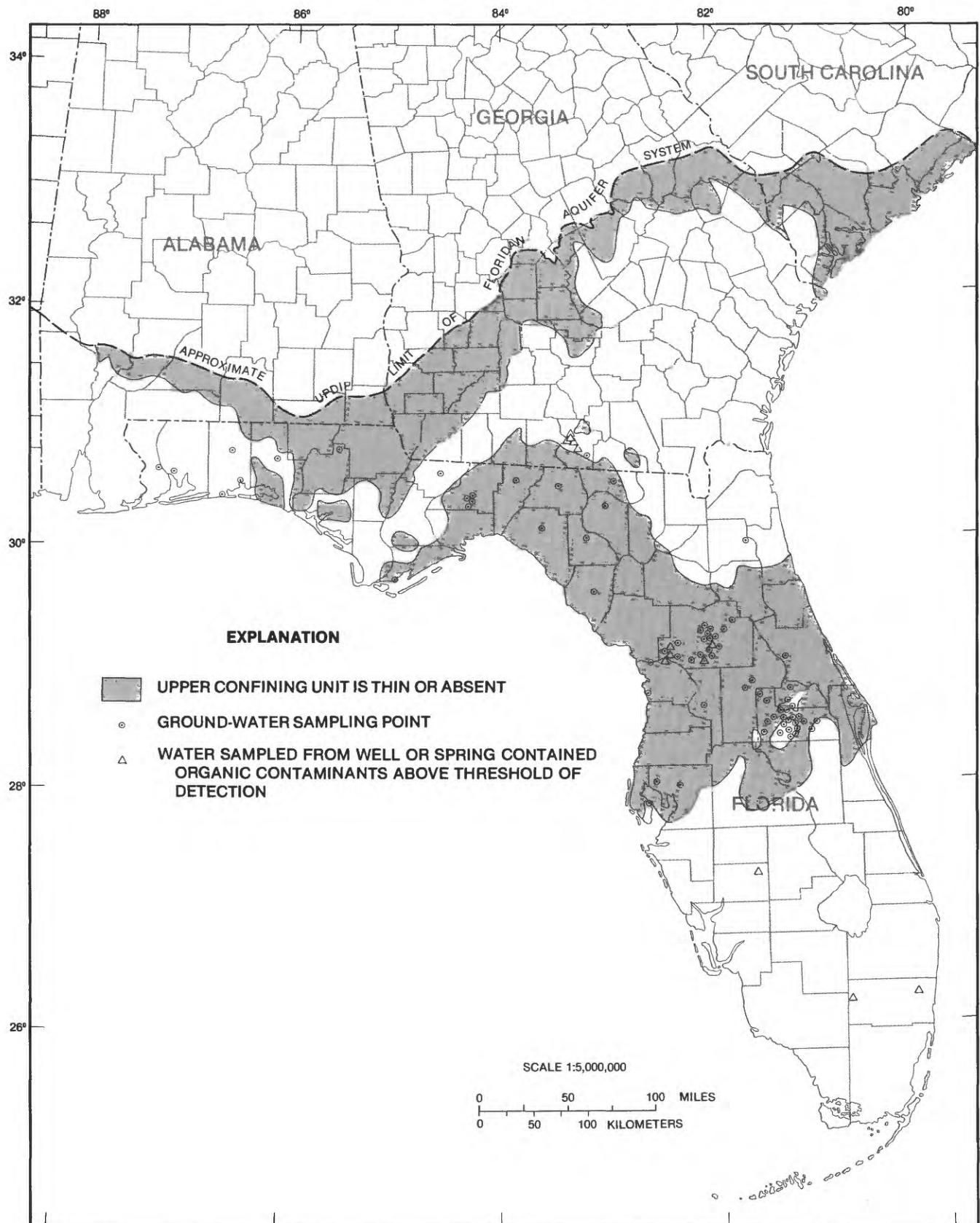
FIGURE 37.—Wells and springs in the Upper Floridan aquifer sampled for organic contaminants.

MAJOR GEOCHEMICAL PROCESSES

Since 1977, studies of regional aquifer systems have used reaction and mass-transfer simulations to determine geochemical processes and to evaluate the mass of major constituents transferred between phases in the flow systems (Plummer, 1977; Thorstenson and others, 1979; Plummer and Back, 1980; Back and others, 1983; Chapelle, 1983; Plummer and others, 1983; Lee, 1985; Henderson, 1985; Plummer, 1985). These studies developed and refined the techniques of earlier theoretical studies (for example, Garrels, 1967; Garrels and MacKenzie, 1967; Helgeson, 1969; Helgeson and others, 1970). One reason for employing these geochemical models is to determine fluxes of carbon so that measurements of ^{14}C in ground water can be "corrected" and flow velocities can be computed. Plummer (1977) and Plummer and others (1983) showed that the most definitive tests of plausible reactions in the Floridan aquifer system required (1) data on aquifer mineralogy, (2) analyses of ground-water samples for stable isotopes and dissolved gases, and (3) accurate thermodynamic data to use in the aqueous model. Mineralogic and isotopic data are not available for most of the Floridan aquifer system; therefore, the following discussion is limited to development of reaction models in selected areas of the Upper Floridan aquifer. The geochemical models developed for this study are valid within the constraints of available thermodynamic and chemical data, but determination of aquifer mineralogy and isotope content of ground water throughout the aquifer system is needed to make accurate reaction models that allow computation of flow velocities.

A simplifying assumption used to develop previous reaction and mass-transfer models was that the chemical data used in the models were collected along a "flow path" extending downgradient from a recharge area to a discharge area. A related assumption was that hydrodynamic dispersion was an unimportant process compared with the chemical reactions (see Wigley and others, 1978, app. A). The flow path assumption means the chemistry of the ground water would evolve in a closed, but not isolated, system. Geochemical reactions occur only as ground water flows downgradient and there is no mass flux across the flow line. However, there may be head or temperature changes, and the energy flux may not be zero. The flow path assumption may not be valid for some of the models discussed below. For example, along flow path $F–F'$ (fig. 38) the Upper Floridan aquifer is unconfined and water readily enters or leaves the aquifer system between wells; similar open-system conditions occur along parts of flow paths $G–G'$ and $H–H'$ and all of flow path $J–J'$.

The previous discussions indicate that the major hydrologic factors influencing ground-water chemistry in the Upper Floridan aquifer are the presence or absence of thick overlying confining layers and mixing where saline water or seawater is present in the aquifer. A conceptual framework for developing the reaction models was formed, based on the assumption that ground water in the Upper Floridan aquifer occurs in four general "hydrochemical environments" in which a few plausible reactions control the chemistry of major elements. These four hydrochemical environments are

A. Areas where the flow system is unconfined or thinly confined and Cl$^-$ concentrations are less than 500 mg/L,

B. Areas where the flow system is unconfined or thinly confined and Cl$^-$ concentrations are equal to or greater than 500 mg/L,

C. Areas where the flow system is confined and Cl$^-$ concentrations are less than 500 mg/L, and

D. Areas where the flow system is confined and Cl$^-$ concentrations are equal to or greater than 500 mg/L.

Figure 38 shows the general location of these four "hydrochemical environments" and the location of wells along flow paths used in reaction modeling. Reaction models are discussed for three of the four hydrochemical environments; simulations of mixing reactions occurring in areas belonging to hydrochemical environment B along the Gulf Coast of Florida were discussed previously. The plausible reactions controlling the chemistry of major elements in each hydrochemical environment are listed in table 19. The reactions listed in table 19 show stoichiometric calcite and dolomite phases only, because these phases have well-defined equilibrium constants. These phases may not be the reacting phases in all parts of the Upper Floridan aquifer. Although Plummer and MacKenzie (1974) showed that 2 percent Mg-calcite is more stable than stoichiometric calcite, Plummer (1977) showed that water from the Upper Floridan aquifer in central Florida is consistently oversaturated with this phase, implying that neither low-Mg nor stoichiometric calcite always precipitates at calculated saturation levels of 0. Stoichiometric carbonates are adequate for developing the plausible mass-transfer models, because the reactions satisfying the set of chemical equations describing the mass change between wells is nonunique. The models chosen to describe the geochemical evolution of ground water between wells in the Upper Floridan aquifer are plausible, but there are many other reaction models that could account for the chemical mass changes.

The models described below were developed using mass-balance (Parkhurst and others, 1982) and mass-transfer techniques (Plummer and others, 1983; Plummer, 1985). The mathematical expressions used and the methods for their solution are discussed in detail by the
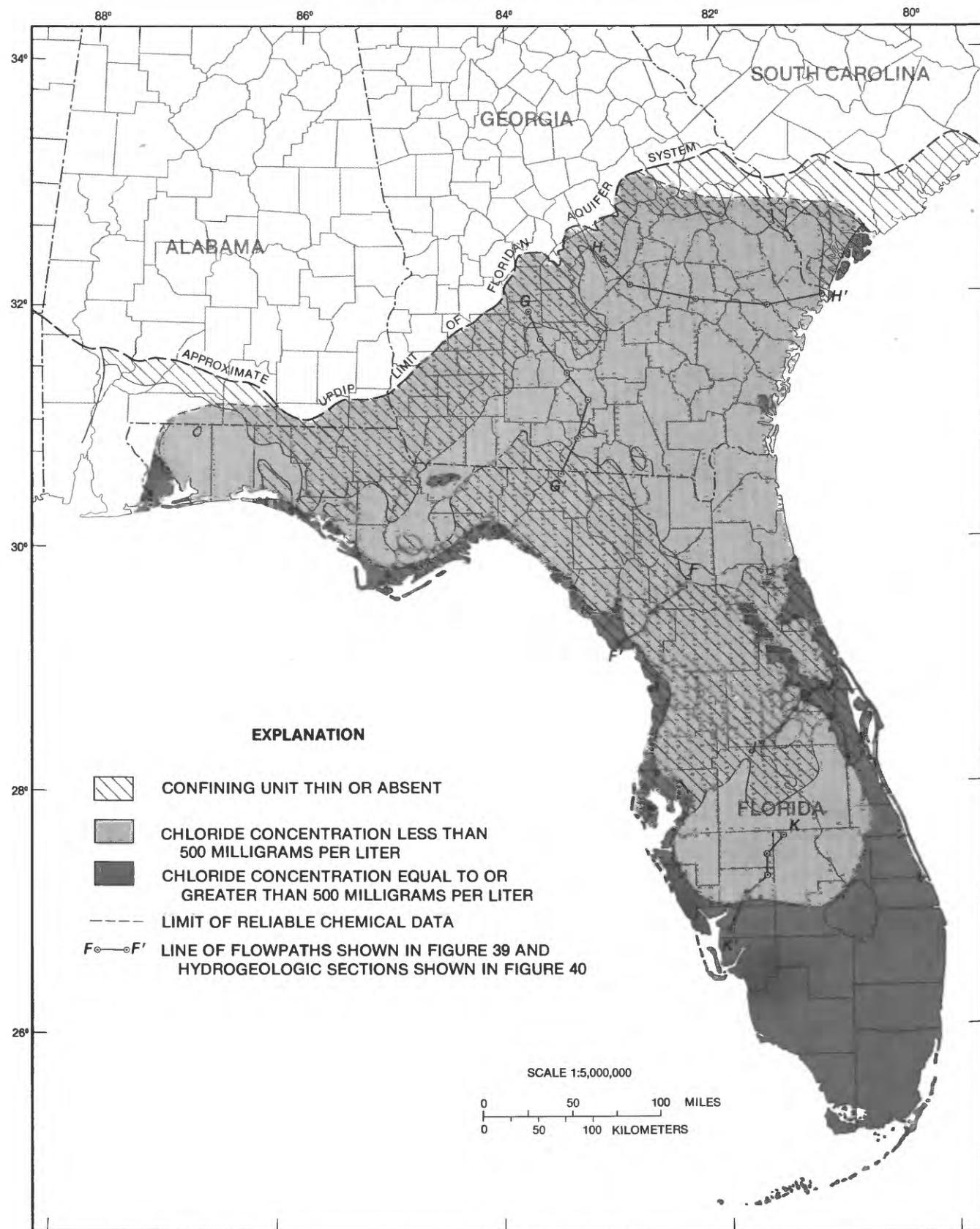
FIGURE 38.—Relation of chloride concentrations to confined-unconfined conditions of the Upper Floridan aquifer.

TABLE 19.—*Plausible reactions controlling the chemistry of major elements in ground water in four conceptual environments in the Upper Floridan aquifer*

Hydrochemical Environment A—Aquifer is unconfined or thinly confined and Cl^- concentrations are less than 500 milligrams per liter:

A1)   Ground water + Recharge = => Mixture
A2) $CaCO_3 + CO_2 + H_2O <= => Ca^{2+} + 2HCO_3^-$
A3) $CaMg(CO_3)_2 <= => Ca^{2+} + Mg^{2+} + 2CO_3^{2-}$
A4) $CaSO_4\ 2H_2O <= => Ca^{2+} + SO_4^{2-}$
A5) $Na_2(CLAY) + Ca^{2+} <= => 2Na^+ + Ca(CLAY)$ (ion-exchange)

Hydrochemical Environment B—Aquifer is unconfined or thinly confined and Cl^- concentrations are equal to or greater than 500 milligrams per liter:

B1) $CaCO_3 + CO_2 + H_2O <= => Ca^{2+} + 2HCO_3^-$
B2) $CaMg(CO_3)_2 <= => Ca^{2+} + Mg^{2+} + 2CO_3^{2-}$
B3) $CaSO_4\ 2H_2O <= => Ca^{2+} + SO_4^{2-}$
B4)   Seawater + Freshwater = => Mixture

Hydrochemical Environment C—Aquifer is confined and Cl^- concentrations are less than 500 milligrams per liter:

C1)   Ground water + Recharge = => Mixture
C2) $CaCO_3 + CO_2 + H_2O <= => Ca^{2+} + 2HCO_3^-$
C3) $CaMg(CO_3)_2 <= => Ca^{2+} + Mg^{2+} + 2CO_3^{2-}$
C4) $CaSO_4\ 2H_2O <= => Ca^{2+} + SO_4^{2-}$
C5) $Na_2(CLAY) + Ca^{2+} <= => 2Na^+ + Ca(CLAY)$ (ion-exchange)
C6) $SO_4^{2-} + 2CH_2O = => H_2S + 2HCO_3^-$ (organic-C oxidation via sulfate reduction)

Hydrochemical Environment D—Aquifer is confined and Cl^- concentrations are equal to or greater than 500 milligrams per liter:

D1) $CaCO_3 + CO_2 + H_2O <= => Ca^{2+} + 2HCO_3^-$
D2) $CaMg(CO_3)_2 <= => Ca^{2+} + Mg^{2+} + 2CO_3^{2-}$
D3) $CaSO_4\ 2H_2O <= => Ca^{2+} + SO_4^{2-}$
D4) $Na_2(CLAY) + Ca^{2+} <= => 2Na^+ + Ca(CLAY)$ (ion-exchange)
D5) $SO_4^{2-} + 2CH_2O = => H_2S + 2HCO_3^-$ (organic-C oxidation via sulfate reduction)
D6)   Seawater + Freshwater = => Mixture

cited references and are not repeated here. However, the principal assumptions of the models used during the study are summarized below.

1. The principal reactive components of the system are CO_2, calcite, dolomite, gypsum, reversible cation-exchange on an unspecified solid phase, and an unspecified carbohydrate (CH_2O) source for sulfate-reducing bacteria.
2. A mineral will be dissolved when it is in contact with ground water that is undersaturated with respect to that mineral.
3. Unconfined recharge or leakage across confining units occurs only in recharge areas of the Upper Floridan aquifer.
4. The chemistry of recharge, leakage, and seawater is approximated by the data given in table 20.

TABLE 20.—*Estimated compositions of solutions mixing with ground water in the Upper Floridan aquifer*

[Concentrations are in millimoles per kilogram of water, unless otherwise indicated]

	Unconfined recharge	Confining-unit leakage	Leakage from underlying or adjacent sand aquifer	Seawater[1]
pH, units	7.45	7.88	8.13	8.22
[2]$-\log P_{CO_2}$	2.50	2.89	3.09	3.42
Calcium (Ca)	0.7491	0.8218	0.3254	10.661
Magnesium (Mg)	0.0161	0.0161	0.0949	55.083
Sodium (Na)	0.0797	0.0797	1.1782	485.418
Potassium (K)	0.0076	0.0076	0.1155	10.579
Chloride (Cl)	0.0700	0.0700	0.0880	566.751
Inorganic carbon (C)	1.5313	1.6039	1.7599	2.138
Sulfate (SO_4)	0.0036	0.0036	0.0785	29.259

[1] Data from seawater test case of Nordstrom and others (1979).

[2] P_{CO_2} and total inorganic carbon were calculated with PHREEQE assuming a water temperature of 25 °C. See text for further discussion.

The chemistry of the freshwater in table 20 was estimated using PHREEQE (Parkhurst and others, 1980). The chemistry of unconfined recharge was estimated initially with a solution containing (except for sulfate) twice the average concentrations of major ions in wet precipitation (table 1). PHREEQE was used to equilibrate this solution with calcite to a S.I. of -0.5 at 25 °C under open-system conditions with P_{CO_2} at $10^{-2.5}$ atmosphere. The twofold increase in concentrations is justified by the ratio of rainfall (approximately 53 in/yr) to recharge in unconfined and internally drained (karstic) areas of the Upper Floridan aquifer. Bush and Johnston (1988) estimated recharge ranges from 15 to 20 in/yr in those areas. Further, twice the average Cl^- concentrations in precipitation is about equal to the Cl^- concentrations in water samples from unconfined areas. SO_4^{2-} concentrations in unconfined recharge were estimated to be about 0.0036 mmolal, based on the SO_4^{2-}/Cl^- molal ratio in seawater and the estimated Cl^- concentration of the recharge. Recent measurements of SO_4^{2-} in precipitation (table 1) are higher than SO_4^{2-} concentrations in the aquifer in unconfined areas, possibly because modern-day precipitation contains "excess" SO_4^{2-}, as previously discussed. The estimated SO_4^{2-} concentration in unconfined recharge approximates the SO_4^{2-} concentrations near the outcrop area of the aquifer system (see data for Wenona and Bronson, table 21). The water entering the Upper Floridan aquifer through the overlying confining unit is termed "confining-unit leakage"; its chemistry was simulated by equilibrating the surficial recharge described above with calcite at 25 °C in a system closed to CO_2. Again, PHREEQE was used tocalculate solution pH and masses of dissolved constituents. The third solution in table 20 is an estimated composition of water entering the Upper Floridan aqui-

fer from adjacent or underlying sand aquifers in southern Georgia. The chemistry of this leakage was estimated by averaging the concentrations of major ions in analyses of samples from wells 39, 40, 41, 42, 48, and 72 penetrating the sand aquifer, as reported by Lee (1984). PHREEQE was used to equilibrate this average ground water with calcite at 25 °C in a system closed to CO_2.
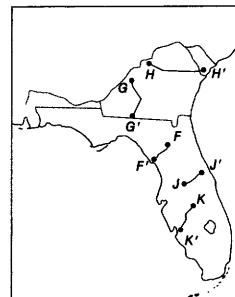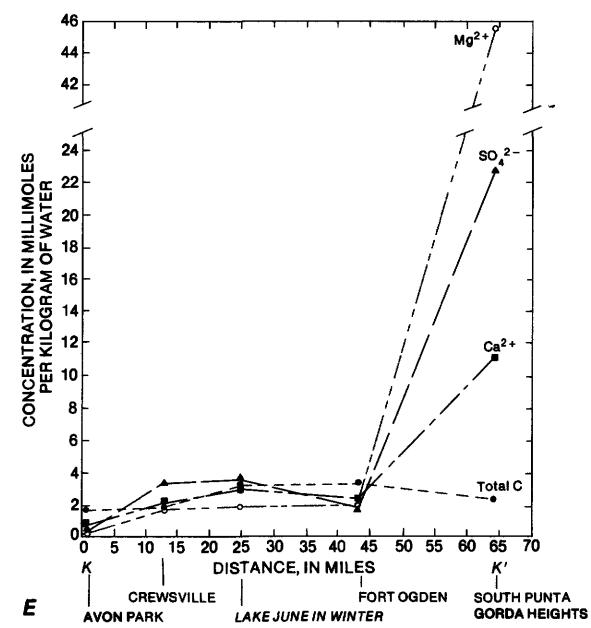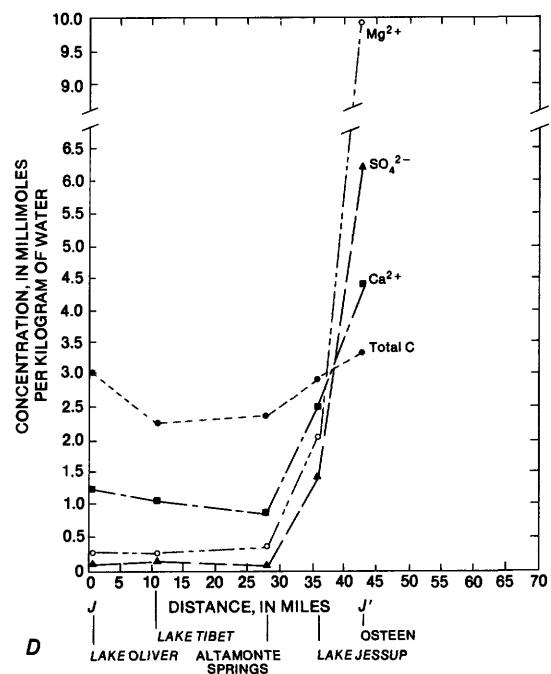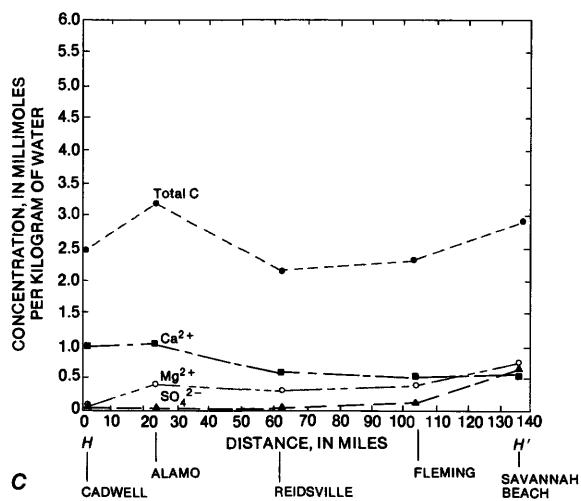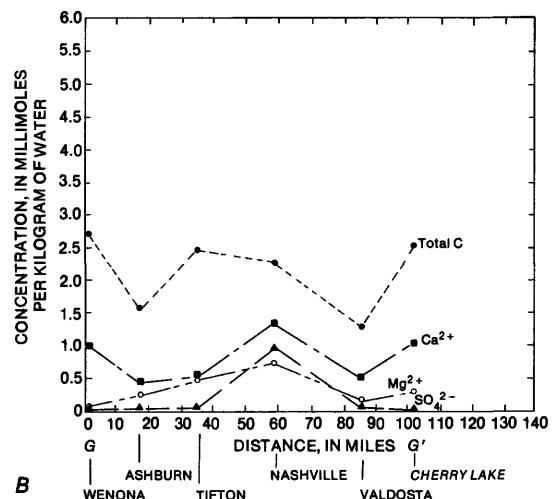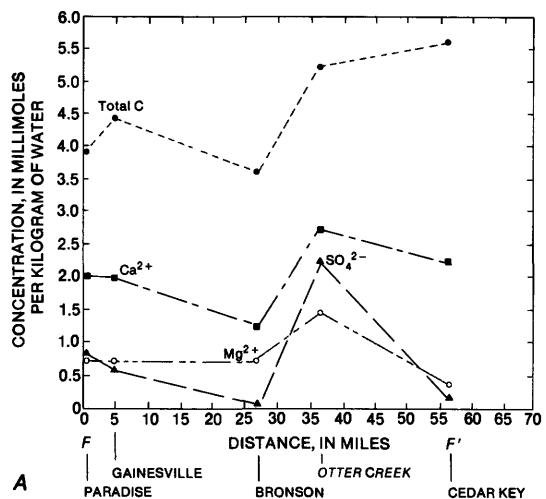
The five hydrogeologic sections shown in figure 38 were chosen to illustrate the principal features of the three hydrochemical environments and to test with chemical data some concepts of the flow system in the Upper Floridan aquifer. The changes in selected major elements along each section are shown in figure 39; the data used for model computations are given in table 21. Well locations and the general direction of ground-water flow along each section are shown in figure 40. Figure 40 shows that some wells do not fully penetrate the Upper Floridan aquifer; also, the Osteen well (fig. 40D) penetrates the Upper Floridan, but its exact depth is not reported. Chemical data from these wells may not be representative of the entire aquifer in the vicinity of the well. The lack of fully penetrating wells should not detract appreciably from interpretations of chemical changes and their relation to flow where chemical stratification is not significant, especially in areas where the aquifer is thin or flow is vigorous. In areas where chemical stratification is significant, such as coastal areas or areas where flow is stratified or sluggish, lateral changes in water chemistry may be less significant than vertical changes in the vicinity of a given well. Until the vertical differences in water chemistry of the Upper Floridan aquifer are determined in many more areas, understanding of the chemical effects of mixing waters from adjacent permeable layers will be incomplete and somewhat speculative. In addition, quantitative chemical models that test theories of inter- or intra-aquifer flow will be highly speculative.

The set of plausible reactions along flow path $F-F'$ (Paradise to Cedar Key) is shown in figure 41A. The reaction model reflects the largely unconfined nature of the Upper Floridan aquifer: significant recharge occurs between Gainesville and Bronson and between Otter Creek and Cedar Key (fig. 41A). The well near Otter Creek was sufficiently deep that recharge apparently has little effect on water chemistry. That is, the water sample may represent a mixture of dilute recharge and more mineralized water from depth, with a "net" reaction of mineral dissolution as shown. The data in table 21 indicate that the SO_4^{2-} concentration at Bronson is anomalously low compared with Na^+ and Cl^- concentrations; the reported SO_4^{2-} concentration may be in error. An alternative reaction model that assumed that sulfate reduction and unconfined recharge had reduced sulfate concentrations between Gainesville and Bronson was not

used, because, although the model added 0.037 mmol of CH_2O and removed 0.054 mmol of H_2S, it also required 0.302 mmol of gypsum to be removed (precipitated) in ground water highly undersaturated with respect to gypsum. The model from Bronson to Otter Creek assumed a SO_4^{2-} concentration at Bronson equal to 60 percent of the SO_4^{2-} at Gainesville plus 40 percent of the SO_4^{2-} in unconfined recharge, that is, 0.364 mmolal of SO_4^{2-}.

A set of plausible reactions along flow path $G-G'$ (Wenona to Cherry Lake) is shown in figure 41B. The confining unit overlying the Upper Floridan aquifer is thin or absent at the northern and southern ends of the flow path, but only between Valdosta and Cherry Lake does a "large" amount of dilute recharge account for the chemical mass changes. A small amount of leakage from the sand aquifer to the Floridan aquifer system is indicated between Wenona and Ashburn, although ion exchange can also explain the chemical differences between the two wells. The leakage model indicates that about one-third of the water sampled at Tifton is derived from the sand aquifer. This amount of inflow might be too large, and would be less if ground water in the sand aquifers contains more Na^+ than is assumed (table 20). An ion-exchange model between Ashburn and Tifton that accounts for the chemical changes (using Na^+ balance) calculated similar changes in carbonates, about 0.024 mmol of gypsum dissolved, and about 0.332 mmol of Na^+ exchanged for 0.166 mmol of Ca^{2+}. Between Tifton and Nashville, ground water flows across the Gulf Trough and increases in both Na^+ and Cl^- concentration. The net reaction shows a "trace" of seawater (less than 1 percent) at Nashville, but the actual amount of saline water added could be greater if more dilute recharge occurs downgradient from the Gulf Trough. No model between Nashville and Valdosta accounted for all the observed chemical changes. The reactions shown in figure 41B do not completely account for the change in SO_4^{2-} concentrations, which at Valdosta are very low. An alternative model that assumed all of the water at Valdosta was derived entirely from local unconfined recharge calculated 0.368 mmol of calcite and 0.134 mmol of CO_2 would be removed, and 0.057 mmol of gypsum and 0.111 mmol of dolomite would be added per kilogram of water between the wells. The alternative model is not entirely unreasonable, as the Upper Floridan aquifer in the Valdosta area receives large quantities of recharge through sinkholes (Krause, 1979). Measurement of tritium concentrations in the vicinity of Valdosta might test the validity of the alternative models.

The plausible reaction models for flow path $H-H'$ are shown in figure 41C. Near outcrop areas the models indicate that CO_2 gas, dolomite, and gypsum are added, while calcite dissolves to saturation, then precipitates to

maintain saturation. Between Alamo and Fleming, Ca^{2+} and Cl^- concentrations decrease, while Na^+ and SO_4^{2-} increase. Concentrations of inorganic C and Mg^{2+} first decrease, then increase. The pattern of Cl^- decrease is interpreted as leakage of dilute water from underlying sand aquifers. The leakage accounts for some of the measured chemical changes, but the quantities cited in figure 41C are dependent on the estimates of local water chemistry in the sand aquifer and may be quite small if water in the sand is more dilute. For example, if the leakage contains approximately 0.178 mmolal less of Na^+-HCO_3^-, mixing 39 percent of sand leakage with Alamo water produces Reidsville water with loss of 0.138 mmol of $CaCO_3$ and 0.178 mmol of CO_2 per kilogram of water. This mixture requires no precipitation of dolomite and loss of 0.003 mmol of gypsum per kilogram of water (within analytical error for SO_4^{2-}) to balance. Other models involving ion exchange or ion exchange plus sulfate reduction were not plausible because they could not adequately account for the changes in Mg^{2+} and inorganic C between the wells. Between Reidsville and Fleming a recharge model based on Na^+ balance is the most plausible, but it does not account for changes in Cl^- concentration. It is possible that the Cl^- concentration reported at Fleming is too low. The model also requires some CO_2 input, even though the aquifer system is confined in this area. The amount of leakage seems large, but flow in the Upper Floridan aquifer between Reidsville and Fleming is sluggish (fig. 13), so that a low rate of leakage from the sand aquifers over a long period of time might produce the observed chemical changes. More complete analyses of water chemistry and stable isotopes from both the sand aquifer and the Upper Floridan aquifer are needed to better define the hydrochemical reactions between Reidsville and Fleming. The ion-exchange model between Fleming and Savannah Beach requires that a trace amount of seawater (0.2 percent) be added to balance the increase in Cl^- concentration between the wells. The model also requires CO_2 input, although, as discussed later, there may be carbon input from sulfate reduction in this area.

Plausible reaction models along flow path J-J' from Lake Oliver to Osteen, Fla., are shown in figure 41D. The confining unit overlying the Upper Floridan aquifer is thin in the upgradient areas, and the model indicates that recharge occurs between Lake Oliver and Lake Tibet. As with flow paths G-G' and H-H', the recharge flux may be large, but the amount of this flux needed to account for the observed chemical differences need not be very large, when the total flux in the Upper Floridan in these areas is small (see fig. 13). Note that the model

does not account for the increase in Na^+ and Cl^- concentrations between the wells (table 21). This increase may be due to the greater depth of the Lake Tibet well. Chemical stratification of the Upper Floridan aquifer could produce a mixture at Lake Tibet that is composed of more mineralized water and dilute recharge added between the wells. Between Lake Tibet and Altamonte Springs, the aquifer system is more thickly confined, and the increase in inorganic C may result from sulfate reduction as well as CO_2 input. The apparent loss of SO_4^{2-} between these wells is attributed to dilution by recharge, although sulfate reduction may play a role. Similar reactions likely continue to occur toward Osteen because HS^- concentrations increase in that direction (fig. 26) and the $\delta^{13}C$ of the water near Lake Jessup is light (see wells 78–80, fig. 36 and table 17). Computation of the amounts of C input as CO_2 and as CH_2O could not be accomplished, because the necessary sulfur isotopic data were not available during this study. An interesting feature of the models between Altamonte Springs and Osteen is the "excess" Mg^{2+} and SO_4^{2-} that occurs when enough seawater is added to get a Cl^- balance. The models balance this "excess" by removing gypsum and dolomite, but whether these minerals actually have precipitated in this part of the flow system is not known. Better definition of the chemistry and isotopic content of the saline water in the valley of the St. Johns River would clarify the reactions accompanying the mixing, as well as provide important data needed to understand the source of the saline water.

Plausible reaction models for flow path K-K' are shown in figure 41E. Chemical reactions and mass-transfer models of this part of the Upper Floridan aquifer were discussed by Plummer and others (1983). The confining unit of the Upper Floridan is thick along this flow path; nonetheless, the general downgradient increase in inorganic C is modeled here using CO_2 as the carbon source. Plummer and others (1983) showed that a mix of CO_2 and reduced carbon may be entering the system in this area, but the data needed to separate the amounts of carbon from each source were not available during this study. The models indicate a rather large amount of dedolomitization compared with other parts of the flow system. Thye local abundance of gypsum in the aquifer clearly affects the importance of this process. The chemical differences along flow path K-K' between Lake June in Winter (LJIW) and South Punta Gorda Heights (SPGH) are difficult to interpret with the available data. Chemical stratification of the Upper Florida Aquifer may be indicated by the fact that concentrations of Ca^{2+}, Mg^{2+}, and SO_4^{2-} in water from the LJIW well are higher than in water from the downgradient Ft. Ogden well, which is about 300 ft shallower than the LJIW well. However, the Ft. Ogden well is nearer the coast, and

◀ FIGURE 39.—Variation in concentrations of dissolved calcium, magnesium, sulfate, and total inorganic carbon downgradient along flow paths: A, F-F'; B, G-G'; C, H-H'; D, J-J'; E, K-K'.

TABLE 21.—*Selected chemical analyses of ground water from the Upper Floridan aquifer used in reaction modeling*

[Concentrations are in millimoles per kilogram of water, unless otherwise indicated. μmolal, micromolal]
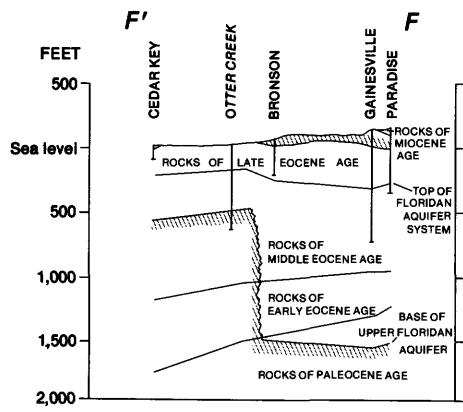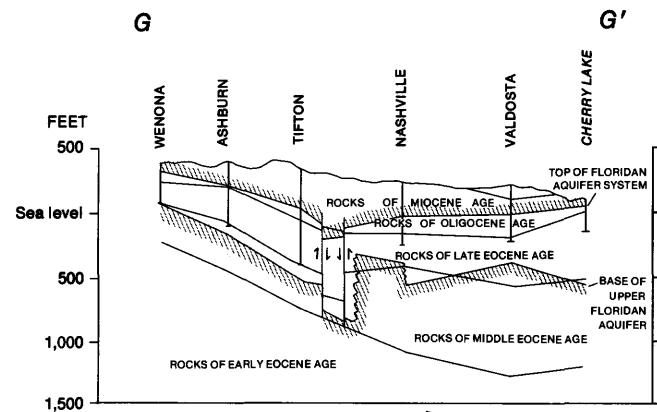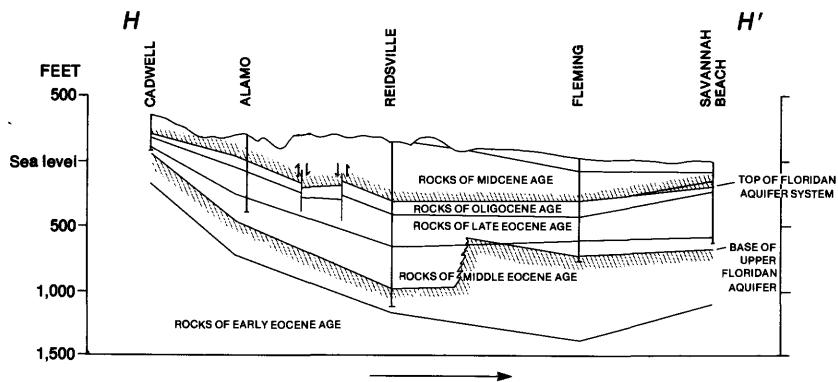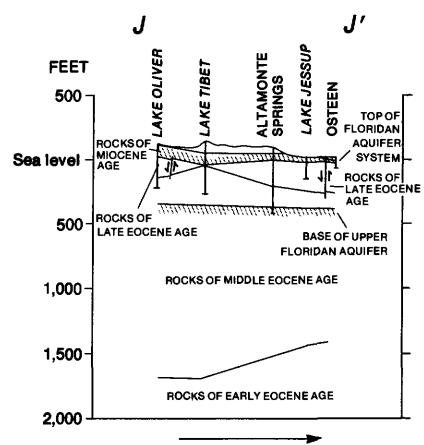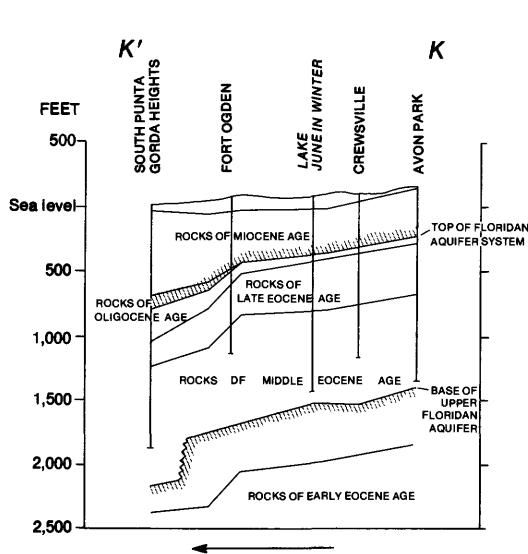
Name used in this report (well number in WATSTORE)	Sample date	Water temperature, °C	pH, units	Calcium	Magnesium	Sodium	Potassium	Chloride	Sulfate	Bicarbonate	Total inorganic carbon[1]	Fluoride	Silica	Remarks
								SECTION F–F'						
Paradise (29420908217301)	May 6, 1975	23.5	8.1	2.022	0.700	0.387	0.026	0.339	0.729	3.869	3.856	0.011	0.266	Fe=0.5 μmolal; Sr=4.1 μmolal
Gainesville (29384208219180l)	May 14, 1971	24.5	7.4	2.047	0.617	0.348	0.028	0.367	0.604	4.099	4.409	0.021	0.316	Sr=0.1 μmolal; NO₃=17.7 μmolal
Bronson (29264008238120l)	Oct. 18, 1978	24.0	8.15	1.223	0.658	0.239	0.008	0.248	0.005	3.607	3.593	0.005	0.105	Fe=32.2 μmolal; Sr=0.7 μmolal
Otter Creek (29210908242290l)	June 19, 1980	22.6	7.3	2.746	1.482	0.958	0.067	0.790	2.188	4.756	5.215	0.047	0.266	Fe=19.7 μmolal; Sr=28.6 μmolal; NH₄=6.7 μmolal; Mn=0.1 μmolal
Cedar Key (29111808301060l)	June 19, 1980	22.4	7.5	2.197	0.272	1.393	0.041	1.326	0.115	5.247	5.564	0.005	0.060	NH₄=17.2 μmolal; Mn=0.3 μmolal; Fe=16.3 μmolal; PO₄=0.3 μmolal; Sr=2.5 μmolal
								SECTION G–G'						
Wenona (31555808343530l)	Aug. 24, 1981	21.0	7.7	1.050	0.033	0.074	0.013	0.079	0.001	2.644	2.744	0.005	0.217	PO₄=0.3 μmolal; Sr=0.7 μmolal; NH₄=1.7 μmolal; Al=0.7 μmolal
Ashburn (31421808339240l)	Aug. 25, 1981	23.0	8.13	0.475	0.247	0.087	0.018	0.054	0.010	1.560	1.562	0.021	0.267	Sr=5.1 μmolal; Al=0.7 μmolal
Tifton (31291908329150l)	Jan. 23, 1974	23.0	8.0	0.524	0.535	0.479	0.043	0.113	0.034	2.459	2.483	0.005	0.266	Fe=1.8 μmolal; Al=1.1 μmolal; NO₃=1.5 μmolal; Mn=0.2 μmolal
Nashville (31123708313520l)	June 18, 1970	—[2]	7.6	1.301	0.743	0.436	0.031	0.566	0.992	2.170	2.264	0.005	0.551	Fe=0.5 μmolal; Sr=3.1 μmolal
Valdosta (30493008316500l)	Mar. 12, 1974	20.0	8.1	0.549	0.128	0.213	0.015	0.186	0.060	1.246	1.252	0.005	0.183	Fe=0.2 μmolal; Al=0.7 μmolal; Mn=0.2 μmolal
Cherry Lake (30354908325250l)	June 10, 1980	20.8	7.5	1.073	0.259	0.104	0.015	0.116	0.040	2.459	2.620	0.021	0.283	PO₄=0.6 μmolal; Sr=0.9 μmolal; NH₄=0.6 μmolal; NO₃=37.1 μmolal
								SECTION H–H'						
Cadwell (32201808302440l)	Aug. 31, 1981	20.0	7.6	0.999	0.025	0.074	0.038	0.073	0.007	2.281	2.398	0.005	0.433	Sr=1.4 μmolal; Al=0.4 μmolal
Alamo (32085708246430l)	Aug. 26, 1981	23.5	7.6	1.049	0.338	0.144	0.056	0.136	0.040	3.001	3.143	0.011	0.467	Sr=5.8 μmolal; Al=0.7 μmolal
Reidsville (31583708209370l)	Sept. 1, 1981	26.0	8.0	0.624	0.243	0.479	0.084	0.124	0.051	2.199	2.216	0.021	0.366	Sr=3.7 μmolal
Fleming (31521408123530l)	May 26, 1976	24.0	7.9	0.525	0.408	0.697	0.072	0.096	0.081	2.314	2.351	0.026	0.517	Fe=0.4 μmolal; Sr=5.4 μmolal; Al=0.7 μmolal
Savannah Beach (32012408051010l)	Aug. 6, 1985	23.2	7.99	0.625	0.741	2.091	0.097	1.215	0.698	2.905	2.927	0.037	0.633	Fe=0.1 μmolal; Sr=12.6 μmolal; B=7.4 μmolal; PO₄=0.8 μmolal; NH₄=44.4 μmolal

TABLE 21.—Selected chemical analyses of ground water from the Upper Floridan aquifer used in reaction modeling—Continued

[Concentrations are in millimoles per kilogram of water, unless otherwise indicated. μmolal, micromolal]
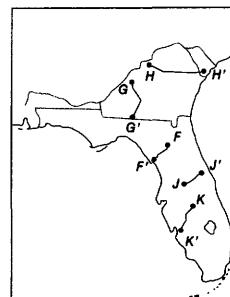
Name used in this report (well number in WATSTORE)	Sample date	Water temperature, °C	pH, units	Calcium	Magnesium	Sodium	Potassium	Chloride	Sulfate	Bicarbonate	Total inorganic carbon[1]	Fluoride	Silica	Remarks
						SECTION J-J'								
Lake Oliver (28220208138 4601)	Apr. 25, 1972	25.0	7.9	1.248	0.272	0.161	0.020	0.141	0.017	3.049	3.095	0.011	0.216	Sr=1.8 μmolal
Lake Tibet (28273208129 3001)	Sept. 5, 1977	23.0	7.5	1.073	0.255	0.218	0.046	0.276	0.135	2.131	2.264	0.005	0.145	Fe=0.5 μmolal; Sr=1.1 μmolal; Al=1.5 μmolal; Mn=0.2 μmolal
Altamonte Springs (28391008119 4901)	June 26, 1973	24.5	7.8	0.848	0.333	0.239	0.020	0.451	0.058	2.295	2.352	0.016	0.183	Sr=2.4 μmolal
Lake Jessup (28442908114 4501)	Apr. 25, 1973	22.0	7.8	2.500	2.019	21.79	0.410	23.45	1.460	2.890	2.943	0.016	0.163	Fe=0.4 μmolal; Sr=25.2 μmolal
Osteen (28472408108 5301)	June 21, 1974	23.5	7.2	4.379	10.725	104.7	1.693	118.8	6.055	2.893	3.156	0.016	0.184	Fe=0.2 μmolal; Sr=125.9 μumolal; NO₃=12.94 μmolal
						SECTION K-K'								
Avon Park (27352708131 0801)	Nov. 10, 1977	25.0	7.6	0.499	0.222	0.187	0.018	0.257	0.026	1.377	1.443	0.005	0.165	Sr=14.8 μmolal
Crewsville (27243808136 5701)	Apr. 22, 1971	29.0	8.2	2.097	1.646	0.387	0.041	0.254	3.104	2.033	1.992	0.047	0.233	
Lake June in Winter (27174808135 4801)	Aug. 1, 1972	27.5	7.7	2.997	2.058	2.177	0.077	2.823	3.438	2.953	3.026	0.053	0.350	Sr=217.0 μmolal
Fort Ogden (27044208149 4301)	Aug. 20, 1980	31.2	7.41	2.248	1.894	5.660	0.100	8.753	1.980	2.953	3.136	0.042	0.367	Fe=0.5 μmolal; Sr=491.3 μmolal; Br=17.5 μmolal; Mn=0.2 μmolal
South Punta Gorda Heights (26492308201 3701)	Oct. 16, 1980	35.3	7.14	11.102	45.754	387.08	9.310	456.4	23.16	2.221	2.335	0.043	0.168	Fe=13.9 μmolal; PO₄=0.6 μmolal; Sr=253.9 μmolal; Mn=0.6 μmolal

[1] Computed from measured pH and alkalinity with WATEQF.
[2] Value not reported.
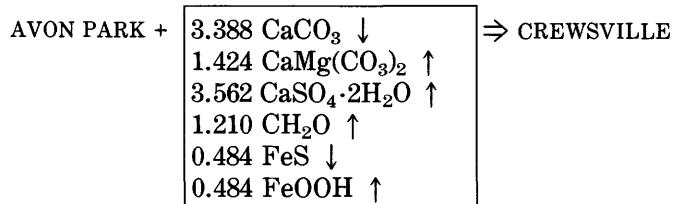
A


B

C

D

E

0   10   20   30 MILES
0 10 20 30 KILOMETERS
Vertical scale greatly exaggerated

EXPLANATION

CONFINING UNIT

← GENERAL DIRECTION OF
   GROUND-WATER FLOW

⊥ WELL

⫰ FAULT—Arrows indicate
   relative vertical movement

Na^+ and Cl^- concentrations increase about threefold over concentrations at the the LJIW well. The reaction model shown in figure 41E accounts for the decrease in Ca^{2+}, Mg^{2+}, and SO_4^{2-} concentrations but does not account for the increase in Na^+ and Cl^-. Reaction models using mixtures of seawater, confining-unit leakage, and water from LJIW calculated excesses of SO_4^{2-} and Mg^{2+} at Ft. Ogden. A similar problem occurs with the data between Ft. Ogden and SPGH, in that the modeled freshwater-seawater mixture accounts for changes in Ca^{2+}, Mg^{2+}, Cl^-, and inorganic C but calculates an excess of SO_4^{2-} (about 0.7 mmol) in the coastal well. Obviously, accuracy in an aqueous mixing model is dependent on accurate knowledge of end-member compositions. Since the composition of "seawater" in the Upper Floridan aquifer between the LJIW and SPGH wells is not known, the reaction models are only illustrative and are not quantitatively reliable.

As stated previously, the reaction models for flow paths $H-H'$, $J-J'$, and $K-K'$ do not include sulfate reduction to explain the chemical evolution of ground water. As indicated by the values given in figure 41, there is a nonzero carbon flux in downgradient areas, and, as previously discussed, sulfate reduction occurs to some degree throughout the Upper Floridan aquifer (fig. 26). Sulfate reduction could account for changes (increases) in inorganic carbon concentrations observed in samples from downgradient wells, but the process also leads to increases in the $\delta^{34}S$ of dissolved sulfate. For example, in flow path $K-K'$, between the Avon Park and Crewsville wells, a reaction model with sulfate reduction yields the following mass transfer:

AVON PARK +
| 3.388 $CaCO_3$ ↓ |
| 1.424 $CaMg(CO_3)_2$ ↑ |
| 3.562 $CaSO_4 \cdot 2H_2O$ ↑ |
| 1.210 CH_2O ↑ |
| 0.484 FeS ↓ |
| 0.484 FeOOH ↑ |
⇒ CREWSVILLE

where downward arrows indicate that the substance is removed from ground water and upward arrows, that the substance is added to ground water. The masses "transferred" per kilogram of water in this model can be used to calculate the $\delta^{34}S$ of the sulfate in water from the Upper Floridan aquifer at Crewsville. The sulfur isotope equation of Plummer (1985) can be rewritten as follows:

$$\delta^{34}S_{cr}=[(\delta^{34}S_{ap})(m_{ap})+(\delta^{34}S_{gyp})(m_{gyp})$$
$$+(\delta^{34}S_{fes})(m_{fes})]/m_{cr}$$

where

$\delta^{34}S_{cr}$ = estimated $\delta^{34}S$ of dissolved sulfate at Crewsville,

$\delta^{34}S_{ap}$ = $\delta^{34}S$ of dissolved sulfate at Avon Park (estimated to be +25 o/oo from well 7, table 17 and fig. 36),

m_{ap} = mass of dissolved S per kilogram of water at Avon Park (0.026 mmol, table 21),

$\delta^{34}S_{gyp}$ = $\delta^{34}S$ of gypsum between Avon Park and Crewsville (estimated to be +22 o/oo from table 3),

m_{gyp} = mass of gypsum added (+) or removed (−) per kilogram of water in reaction model (+3.562 mmol),

$\delta^{34}S_{fes}$ = $\delta^{34}S$ of iron sulfide (estimated to be −25 o/oo, see below),

m_{fes} = mass of iron sulfide added (+) or removed (−) per kilogram of water in reaction model (−0.484 mmol), and

m_{cr} = mass of dissolved S per kilogram of water at Crewsville (3.104 mmol, table 21).

The $\delta^{34}S$ of pyrite used in the above equation is estimated to be about −25 o/oo based on a sulfate-sulfide fractionation factor of about 50 o/oo in this area (Rye and others, 1981).

The $\delta^{34}S$ of the water at Crewsville is estimated to be about +29.4 o/oo using the above equation. This value is about 5 o/oo heavier than the $\delta^{34}S$ reported at Arcadia (well 1, table 17 and fig. 36), which is slightly downgradient from Crewsville. The computation indicates that a model that relies on sulfate reduction as the sole source of inorganic carbon is incorrect. This problem has been previously discussed by Plummer and others (1983). The isotopic data needed to compute reaction models involving multiple sources of carbon were not available for most parts of the flow system during this study. The models in figure 41 use CO_2 as the carbon source, even though the aquifer system is confined in most downgradient areas and, therefore, should be "closed" to CO_2. The work of Plummer and others (1983) and the models presented here indicate that carbon sources are available to react in confined areas of the Floridan aquifer system, and that the process of sulfate reduction cannot by itself explain the observed changes in inorganic carbon concentrations.

The plausible models indicate that the chemistry of major elements in the Upper Floridan aquifer is dominated by the dynamic nature of the flow system: in unconfined areas, large amounts of dilute recharge enter the aquifer system, dissolving the minerals of the aquifer matrix and enhancing permeability. In coastal areas, mixing of freshwater and seawater creates the potential

◄ FIGURE 40.—Geohydrologic sections—A, $F-F'$: Alachua County to Levy County, Fla.; B, $G-G'$: Crisp County, Ga., to Madison County, Fla.; C, $H-H'$: Laurens County to Chatham County, Ga.; D, $J-J'$: Orange County to Volusia County, Fla.; E, $K-K'$: Highlands County to Charlotte County, Fla.

A

UNCONFINED RECHARGE + [0.136 $CaCO_3$ ↓ / 0.684 $CaMg(CO_3)_2$ ↑ / 0.725 $CaSO_4 \cdot 2H_2O$ ↑ / 1.094 CO_2 ↑] ==> PARADISE

83 PERCENT PARADISE WATER + 17 PERCENT UNCONFINED RECHARGE + [0.209 $CaCO_3$ ↑ / 0.036 $CaMg(CO_3)_2$ ↑ / 0.674 CO_2 ↑] ==> GAINESVILLE

60 PERCENT GAINESVILLE WATER + 40 PERCENT UNCONFINED RECHARGE + [0.587 $CaCO_3$ ↓ / 0.281 $CaMg(CO_3)_2$ ↑ / 0.358 CO_2 ↑] ==> BRONSON

BRONSON WATER + [1.125 $CaCO_3$ ↓ / 0.824 $CaMg(CO_3)_2$ ↑ / 1.824 $CaSO_4 \cdot 2H_2O$ ↑ / 1.099 CO_2 ↑] ==> OTTER CREEK

5 PERCENT OTTER CREEK WATER + 95 PERCENT UNCONFINED RECHARGE + [1.165 $CaCO_3$ ↑ / 0.181 $CaMg(CO_3)_2$ ↑ / 2.318 CO_2 ↑] ==> CEDAR KEY

B

UNCONFINED RECHARGE + [0.285 $CaCO_3$ ↑ / 0.018 $CaMg(CO_3)_2$ ↑ / 0.892 CO_2 ↑] ==> WENONA

99 PERCENT WENONA WATER + 1 PERCENT SAND RECHARGE + [0.789 $CaCO_3$ ↓ / 0.213 $CaMg(CO_3)_2$ ↑ / 0.008 $CaSO_4 \cdot 2H_2O$ ↑ / 0.808 CO_2 ↓] ==> ASHBURN

64 PERCENT ASHBURN WATER + 36 PERCENT SAND RECHARGE + [0.239 $CaCO_3$ ↓ / 0.342 $CaMg(CO_3)_2$ ↑ / 0.404 CO_2 ↑] ==> TIFTON

68 PERCENT TIFTON WATER + 32 PERCENT CONFINED RECHARGE + trace SEAWATER + [0.668 $CaCO_3$ ↓ / 0.373 $CaMg(CO_3)_2$ ↑ / 0.943 $CaSO_4 \cdot 2H_2O$ ↑] ==> NASHVILLE

15 PERCENT NASHVILLE WATER + 85 PERCENT UNCONFINED RECHARGE + [0.190 $CaCO_3$ ↓ / 0.202 CO_2 ↓] ==> VALDOSTA

39 PERCENT VALDOSTA WATER + 61 PERCENT UNCONFINED RECHARGE + [0.190 $CaCO_3$ ↑ / 0.199 $CaMg(CO_3)_2$ ↑ / 0.014 $CaSO_4 \cdot 2H_2O$ ↑ / 0.610 CO_2 ↑] ==> CHERRY LAKE

C

UNCONFINED RECHARGE + [0.175 $CaCO_3$ ↑ / 0.009 $CaMg(CO_3)_2$ ↑ / 0.004 $CaSO_4 \cdot 2H_2O$ ↑ / 0.551 CO_2 ↑] ==> CADWELL

CADWELL WATER + [0.295 $CaCO_3$ ↓ / 0.313 $CaMg(CO_3)_2$ ↑ / 0.032 $CaSO_4 \cdot 2H_2O$ ↑ / 0.414 CO_2 ↑] ==> ALAMO

68 PERCENT ALAMO WATER + 32 PERCENT SAND RECHARGE + [0.173 $CaCO_3$ ↓ / 0.016 $CaMg(CO_3)_2$ ↓ / 0.273 CO_2 ↓] ==> REIDSVILLE

69 PERCENT REIDSVILLE WATER + 31 PERCENT SAND RECHARGE + [0.239 $CaCO_3$ ↓ / 0.211 $CaMg(CO_3)_2$ ↑ / 0.022 $CaSO_4 \cdot 2H_2O$ ↑ / 0.094 CO_2 ↑] ==> FLEMING

FLEMING WATER + trace SEAWATER + [0.487 $CaCO_3$ ↓ / 0.226 $CaMg(CO_3)_2$ ↑ / 0.560 $CaSO_4 \cdot 2H_2O$ ↑ / 0.219 ION-EXCHANGE / 0.612 CO_2 ↑] ==> SAVANNAH BEACH

D

UNCONFINED RECHARGE + [0.230 $CaCO_3$ ↑ / 0.255 $CaMg(CO_3)_2$ ↑ / 0.013 $CaSO_4 \cdot 2H_2O$ ↑ / 0.823 CO_2 ↑] ==> LAKE OLIVER

37 PERCENT LAKE OLIVER WATER + 63 PERCENT UNCONFINED RECHARGE + [0.131 $CaCO_3$ ↓ / 0.145 $CaMg(CO_3)_2$ ↑ / 0.127 $CaSO_4 \cdot 2H_2O$ ↑] ==> LAKE TIBET

42 PERCENT LAKE TIBET WATER + 58 PERCENT CONFINED RECHARGE + [0.296 $CaCO_3$ ↓ / 0.218 $CaMg(CO_3)_2$ ↑ / 0.334 CO_2 ↑] ==> ALTAMONTE SPRINGS

96 PERCENT ALTAMONTE SPRINGS WATER + 4 PERCENT SEAWATER + [1.575 $CaCO_3$ ↑ / 0.538 $CaMg(CO_3)_2$ ↓ / 0.216 $CaSO_4 \cdot 2H_2O$ ↑ / 0.100 CO_2 ↑] ==> LAKE JESSUP

82 PERCENT LAKE JESSUP WATER + 18 PERCENT SEAWATER + [1.339 $CaCO_3$ ↑ / 0.608 $CaMg(CO_3)_2$ ↓ / 0.284 $CaSO_4 \cdot 2H_2O$ ↓ / 0.231 CO_2 ↑] ==> OSTEEN

E

UNCONFINED RECHARGE + [0.478 $CaCO_3$ ↓ / 0.206 $CaMg(CO_3)_2$ ↑ / 0.022 $CaSO_4 \cdot 2H_2O$ ↑ / 0.022 CO_2 ↓] ==> AVON PARK

AVON PARK WATER + [2.904 $CaCO_3$ ↓ / 1.424 $CaMg(CO_3)_2$ ↑ / 3.078 $CaSO_4 \cdot 2H_2O$ ↑ / 0.605 CO_2 ↑] ==> CREWSVILLE

CREWSVILLE WATER + [0.154 $CaCO_3$ ↑ / 0.412 $CaMg(CO_3)_2$ ↑ / 0.334 $CaSO_4 \cdot 2H_2O$ ↑ / 0.058 CO_2 ↑] ==> LAKE JUNE IN WINTER

32 PERCENT LAKE JUNE IN WINTER WATER + 68 PERCENT CONFINED RECHARGE + [1.373 $CaCO_3$ ↓ / 1.225 $CaMg(CO_3)_2$ ↑ / 0.879 $CaSO_4 \cdot 2H_2O$ ↑] ==> FORT OGDEN

20 PERCENT FORT OGDEN WATER + 80 PERCENT SEAWATER + [0.913 $CaCO_3$ ↑ / 1.192 $CaMg(CO_3)_2$ ↑ / 3.297 CO_2 ↓] ==> SOUTH PUNTA GORDA HEIGHTS

FIGURE 41.—Plausible reaction models of chemical evolution of ground water in the Upper Floridan aquifer along flow paths: A, F-F'; B, G-G'; C, H-H'; D, J-J'; E, K-K'. Concentrations are in millimoles per kilogram of H_2O. ↑ indicates substance is added to ground water; ↓ indicates substance is removed from ground water.

for carbonate mineral dissolution or precipitation, depending on the ratio of freshwater to seawater in the mixture. In areas where flow is sluggish, remnant gypsum or seawater may increase concentrations of major chemical elements above 1,000 mg/L. The reaction models also indicate that fluxes of carbon occur throughout the flow system, even in areas where the Upper Floridan aquifer is thickly confined. These nonzero carbon fluxes complicate interpretation of ^{14}C data and computation of flow velocities from radiometric dating of water "age."

SUMMARY

The Floridan aquifer system occurs in parts of four southeastern States and is one of the most productive aquifer systems in the world. More than 3 billion gallons of water are pumped from the aquifer system daily, yet there are tremendous untapped reserves of freshwater. Near some urban centers, intensive development of the ground-water resource has led to declining water levels and localized water-quality degradation.

The region underlain by the Floridan aquifer system has a climatic range from temperate to subtropical; annual precipitation (mostly rainfall) generally ranges from 40 to 65 in. The chemistry of major ions in precipitation is dominated by salts in sea spray, except for Na^+ and SO_4^{2-}; sources of the additional Na^+ and SO_4^{2-} are speculative at this time.

The Floridan aquifer system is a vertically continuous sequence of Tertiary carbonate rocks of generally high permeability. Limestones and dolomites are the principal rock types in the aquifer system, although in southwestern and northeastern Georgia and in adjacent South Carolina, the limestones grade into limy sands and clays. The Floridan is composed primarily of calcite and dolomite. Minor minerals include gypsum, apatite, glauconite, quartz (or chert), clay minerals (kaolinite and montmorillonite), and trace amounts of metallic oxides and sulfides.

The aquifer system generally consists of an Upper and Lower Floridan aquifer separated by a less permeable confining unit having highly variable hydraulic properties. The Upper Floridan aquifer is present throughout the study area; the Lower Floridan aquifer is not present in most of northern Florida and Georgia. Recharge occurs primarily in outcrop areas of Alabama, Georgia, and north-central Florida. Most discharge is to rivers and springs; only about 5 percent of the predevelopment discharge was directly into the sea. The quantity of ground-water flow in the system is affected by the extent of confinement. Where the system is unconfined, recharge is rapid and plentiful, ground-water circulation and discharge rates are high, and secondary permeability is developed by mineral dissolution. Where confining

units are thick, the carbonate chemistry of the ground water evolves in a closed system and development of secondary permeability is slow. A secondary chemical effect of confinement is reduction in the rate of flushing of (residual) salty water from the aquifer system.

After review of about 52,000 chemical analyses of water from more than 7,000 wells, a subset of 601 analyses (representing 601 wells) was chosen to characterize the chemistry of major ions in the Upper Floridan. Because fewer than 100 wells penetrating the Lower Floridan aquifer were available during the study, the regional description of the Lower Floridan is limited to maps that show estimated Cl^- and dissolved-solids concentrations. Description of chemical patterns within the Upper Floridan aquifer required interpretation of chemical data from water samples collected at different depths, because of mixing that occurs within the open-bore wells commonly drilled in the aquifer. Mixing affects water chemistry by (1) modifying temperatures, (2) changing environmental isotope ratios, (3) changing ionic strength, (4) changing net partial pressures of dissolved gases, and (5) altering solution pH and Eh.

Regional hydrogeochemistry is depicted in maps that show the distribution and concentration of major cations and anions, selected minor elements, and nutrients. Calcium is the major cation in fresh ground water; concentrations generally range from 5 to 570 mg/L. The concentration of Ca^{2+} is controlled primarily by calcite saturation, although gypsum solubility may locally be the geochemical control. Gypsum dissolution can cause dedolomitization of the aquifer, but sulfate and magnesium concentrations and lack of significant sulfate reduction indicate that dedolomitization dissolves less than 0.5 mmol of dolomite per liter of water over much of the Floridan's area of occurrence. Concentrations of Mg^{2+} in the Upper Floridan aquifer generally range from 1 to 1,000 mg/L; the highest Mg^{2+} concentrations occur where the Upper Floridan contains seawater. Where the aquifer contains freshwater, Mg^{2+} concentrations generally increase in downgradient directions because of dedolomitization of the aquifer. Data are insufficient to prove that formation of dolomite limits Mg^{2+} concentrations in the Upper Floridan. The lowest concentrations of Na^+ and K^+ are nearly equal to the concentrations in rainfall—about 1 mg/L of Na^+ and 0.2 mg/L of K^+. In coastal areas, Na^+ concentrations exceed 500 mg/L and K^+ concentrations exceed 20 mg/L. Cation exchange is indicated in parts of Georgia and in the Florida Panhandle where Na^+/Cl^- and K^+/Cl^- ratios are high. Moderately high Na^+/Cl^- and K^+/Cl^- ratios in the Upper Floridan aquifer in southwestern Georgia may be due to inflow from the underlying or adjacent sand aquifers, but may also result from Na^+ and K^+ added to ground water by leaching of fertilizers on the land surface.

The principal anions in the ground water are HCO_3^-, Cl^-, and SO_4^{2-}. Carbonate buffering in the Upper Floridan aquifer maintains the pH of ground water within the range 7.0 to 8.5. Bicarbonate is the principal anion in freshwater areas, and concentrations of HCO_3^- range from 122 to 244 mg/L; this reflects the control that calcite solubility exerts over HCO_3^- concentrations. The high HCO_3^- concentrations in extreme western Florida apparently result from cation-exchange-driven carbonate disequilibrium. Concentrations of Cl^- are nearly zero in recharge areas; the highest Cl^- concentrations are found where seawater is present in the Upper Floridan aquifer. Regionally, shallow wells completed in the Upper Floridan yield water having Cl^- concentrations of less than 250 mg/L and may be an adequate source of supply for domestic or industrial purposes. The high Cl^- concentrations along the St. Johns River and the eastern coast of Florida and in southern Florida may be due to incomplete flushing of Pleistocene seawater. High Cl^- concentrations in parts of the aquifer near coastal cities in Georgia and Florida are related to pumpage. Concentrations of SO_4^{2-} range from about zero in recharge areas to more than 3,500 mg/L in deep gypsiferous units. Bisulfide (HS^-) occurs throughout the aquifer system in low concentrations (<1 mg/L) as a result of sulfate reduction, but the amount of HS^- measured in water samples may indicate only a fraction of the total sulfide actually formed.

The major geochemical processes that occur in the Upper Floridan aquifer are

1. Dissolution of aquifer minerals toward equilibrium;
2. Mixing of ground water with seawater, recharge, or leakage;
3. Sulfate reduction; and
4. Cation exchange between water and rock minerals.

In recharge areas, calcite dissolution produces ground water that is calcium-bicarbonate dominated, and dissolved-solids concentrations are generally less than 250 mg/L. Downgradient, dissolution of dolomite leads to a calcium-magnesium-bicarbonate hydrochemical facies. Where gypsum is abundant, sulfate becomes the predominant anion. In coastal areas, seawater increases the dissolved-solids concentrations and hydrochemical facies change to sodium chloride. Leakage from underlying or adjacent sand aquifers in south-central Georgia enters the Upper Floridan and lowers dissolved-solids concentrations but does not change the hydrochemical facies. In the western panhandle of Florida, cation exchange leads to development of a sodium-bicarbonate facies.

The same processes that control the occurrence and distribution of major constituents also control the occurrence of many minor constituents. Concentrations of F^- range from about zero near the outcrop to about 4 mg/L in western Florida; over most of the study area, the F^-

concentration is less than 1.0 mg/L, well within the maximum contaminant level for drinking water. The principal source of F^- in freshwater is recharge; once F^- enters the system, it appears to be chemically conservative. Concentrations of dissolved silica range from about 1 to about 80 mg/L; highest concentrations occur in Georgia and South Carolina. Silica concentrations appear to be controlled by the solubility of quartz or chalcedony. Low concentrations of P (phosphorus species) occur throughout the Upper Floridan aquifer; 75 percent of water samples from the aquifer contained less than 0.1 mg/L of total P. No mineral sources of N (nitrogen) species have been detected within the aquifer system, yet moderate concentrations have been detected in water samples. Statistical tests indicate that the aquifer system has a uniform total N concentration, although man's activities may be affecting concentrations of N species in unconfined recharge areas. Areal differences in N-species concentrations indicate that nitrate reduction may be important in controlling N concentrations. Denitrification may significantly reduce N concentrations in unconfined areas of the aquifer system, but further studies are needed to confirm this hypothesis.

Data on the occurrence of trace metals, stable isotopes and radioisotopes, and organic contaminants in the Floridan aquifer system are very limited. Almost all water samples that have been analyzed for trace metals are within drinking water standards, although most samples have been analyzed for only iron and manganese. High trace metal concentrations are uncommon in the Upper Floridan aquifer and are generally related to a nearby contaminant source or to faulty well construction. Selected data on stable isotopes of O, H, and C were compiled on a regional basis for the first time. Available ^{14}C data were also compiled, but use of the ^{14}C data to compute ground-water flow velocities is hindered by the lack of stable isotope data on reacting phases. Other natural radioisotopes are present in such low concentrations that their hydrologic significance is difficult to determine. A product of uranium decay, Ra-226, has been reported in concentrations that exceed drinking water standards (5 pCi/L) in wells in southwestern Florida, but the exact sources and processes that control Ra-226 concentrations have not been determined. Analyses of organic compounds determined by the Geological Survey date back to about 1960, but many manmade organic compounds were first analyzed as recently as 1982. The majority of organic compounds tested were below the threshold of detection; however, detection of manmade organic compounds in a few samples indicates that the flow system is susceptible to contamination in some areas.

Plausible reaction models of downgradient changes in chemical composition indicate that the geochemistry of

the Upper Floridan aquifer is dominated by the dynamic nature of the flow system. In unconfined areas, large volumes of dilute water recharge the system, dissolve minerals in the aquifer matrix, and enhance permeability. In coastal areas, mixing of freshwater with seawater creates the potential for calcite and dolomite dissolution or precipitation, depending on the ratio of freshwater to seawater in the mixture. In areas where flow is more sluggish, concentrations of major elements are increased by dissolution of gypsum or mixing with residual saline water. Ion exchange and sulfate reduction are plausible reaction models in parts of the system. Reaction models indicate that a nonzero carbon flux occurs in almost all parts of the system; this complicates the use of ^{14}C measurements to determine ground-water-flow velocities.

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