

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

U.S. GEOLOGICAL SURVEY PROFESSIONAL PAPER 1403-I



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

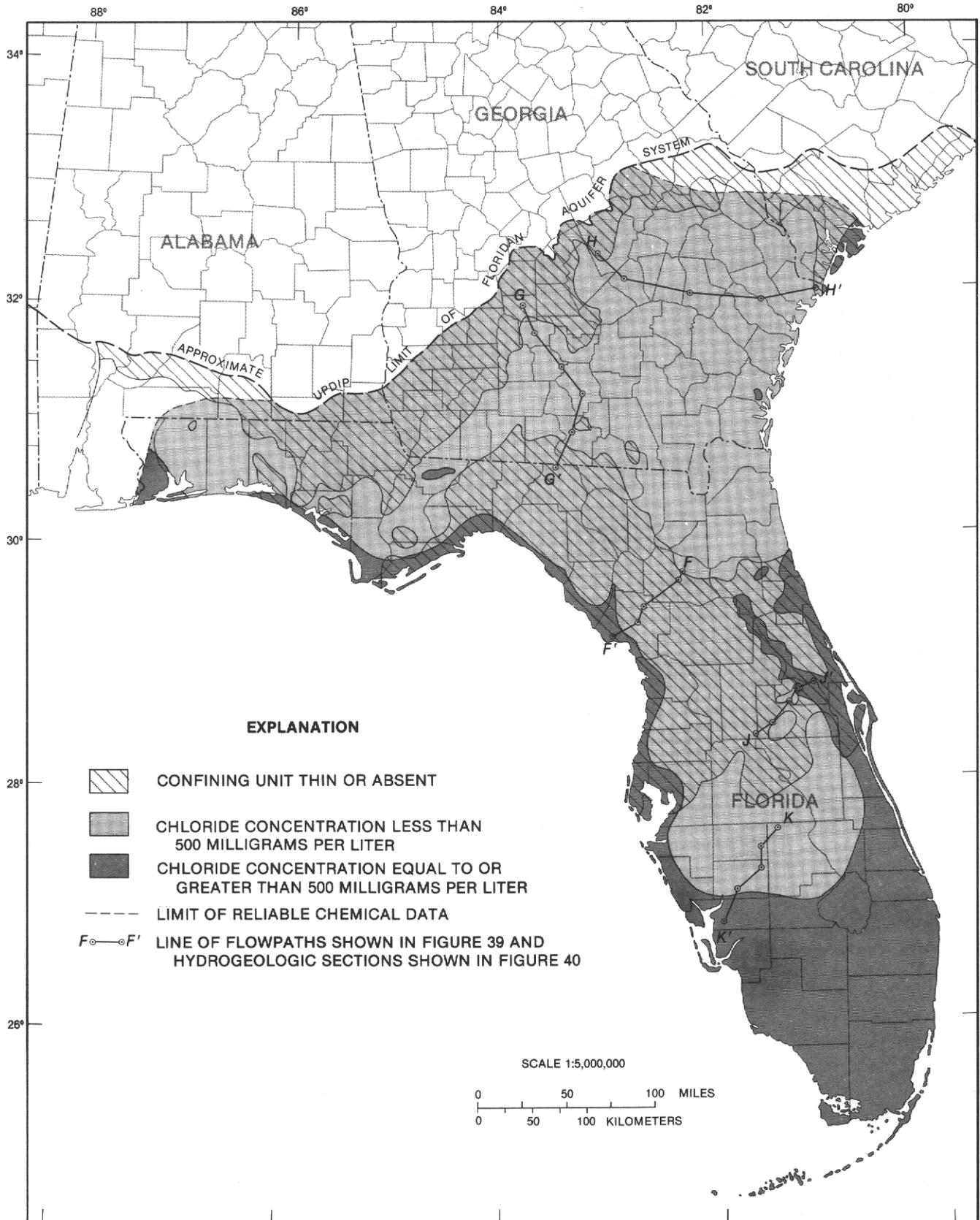


FIGURE 38.—Relation of chloride concentrations to confined-unconfined conditions of the Upper Floridan aquifer.

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 \Rightarrow Mixture
A2)	$\text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{Ca}^{2+} + 2\text{HCO}_3^-$
A3)	$\text{CaMg}(\text{CO}_3)_2 \rightleftharpoons \text{Ca}^{2+} + \text{Mg}^{2+} + 2\text{CO}_3^{2-}$
A4)	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O} \rightleftharpoons \text{Ca}^{2+} + \text{SO}_4^{2-}$
A5)	$\text{Na}_2(\text{CLAY}) + \text{Ca}^{2+} \rightleftharpoons 2\text{Na}^+ + \text{Ca}(\text{CLAY})$ (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)	$\text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{Ca}^{2+} + 2\text{HCO}_3^-$
B2)	$\text{CaMg}(\text{CO}_3)_2 \rightleftharpoons \text{Ca}^{2+} + \text{Mg}^{2+} + 2\text{CO}_3^{2-}$
B3)	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O} \rightleftharpoons \text{Ca}^{2+} + \text{SO}_4^{2-}$
B4)	Seawater + Freshwater \Rightarrow Mixture
Hydrochemical Environment C—Aquifer is confined and Cl^- concentrations are less than 500 milligrams per liter:	
C1)	Ground water + Recharge \Rightarrow Mixture
C2)	$\text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{Ca}^{2+} + 2\text{HCO}_3^-$
C3)	$\text{CaMg}(\text{CO}_3)_2 \rightleftharpoons \text{Ca}^{2+} + \text{Mg}^{2+} + 2\text{CO}_3^{2-}$
C4)	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O} \rightleftharpoons \text{Ca}^{2+} + \text{SO}_4^{2-}$
C5)	$\text{Na}_2(\text{CLAY}) + \text{Ca}^{2+} \rightleftharpoons 2\text{Na}^+ + \text{Ca}(\text{CLAY})$ (ion-exchange)
C6)	$\text{SO}_4^{2-} + 2\text{CH}_2\text{O} \rightleftharpoons \text{H}_2\text{S} + 2\text{HCO}_3^-$ (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)	$\text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{Ca}^{2+} + 2\text{HCO}_3^-$
D2)	$\text{CaMg}(\text{CO}_3)_2 \rightleftharpoons \text{Ca}^{2+} + \text{Mg}^{2+} + 2\text{CO}_3^{2-}$
D3)	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O} \rightleftharpoons \text{Ca}^{2+} + \text{SO}_4^{2-}$
D4)	$\text{Na}_2(\text{CLAY}) + \text{Ca}^{2+} \rightleftharpoons 2\text{Na}^+ + \text{Ca}(\text{CLAY})$ (ion-exchange)
D5)	$\text{SO}_4^{2-} + 2\text{CH}_2\text{O} \rightleftharpoons \text{H}_2\text{S} + 2\text{HCO}_3^-$ (organic-C oxidation via sulfate reduction)
D6)	Seawater + Freshwater \Rightarrow 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 $\text{SO}_4^{2-}/\text{Cl}^-$ 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 to calculate solution pH and masses of dissolved constituents. The third solution in table 20 is an estimated composition of water entering the Upper Floridan aquifer

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 CO₂.

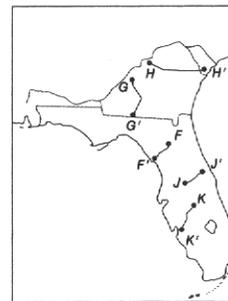
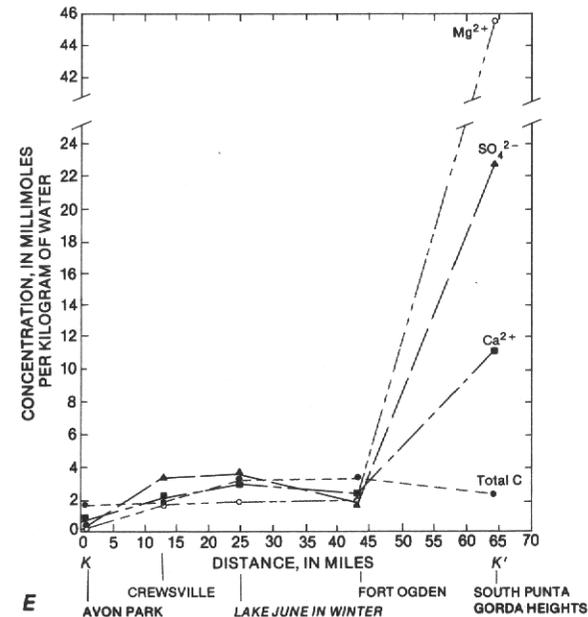
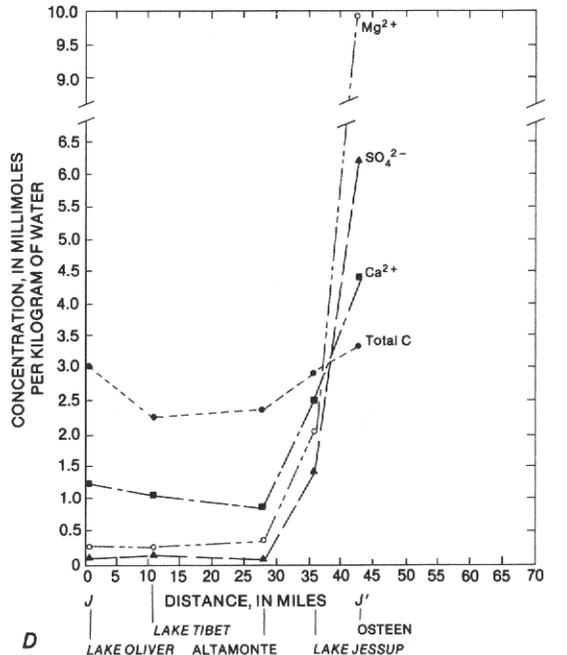
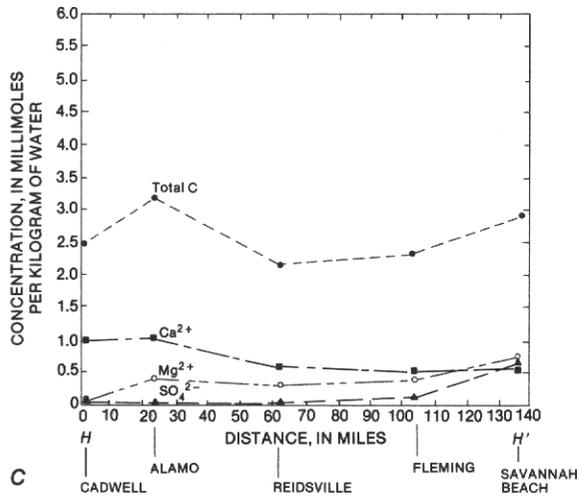
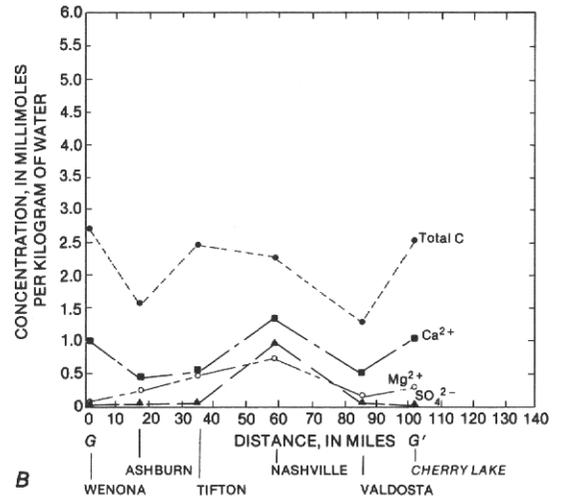
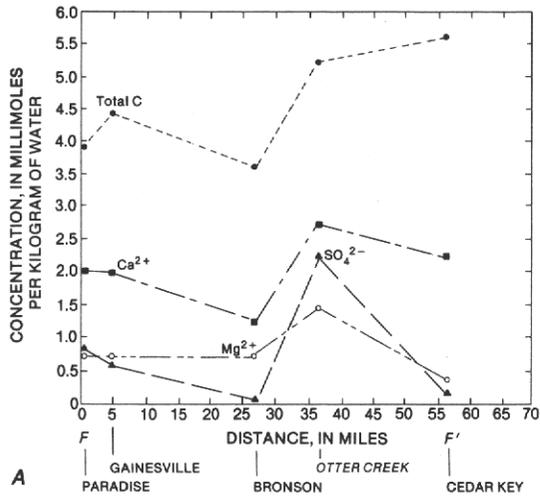
The five hydrogeologic sections shown in figure 38 were chosen to illustrate the principal features of the three hydrochemical environments and to test with chemical data some concepts of the flow system in the Upper Floridan aquifer. The changes in selected major elements along each section are shown 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 SO₄²⁻ concentration at Bronson is anomalously low compared with Na⁺ and Cl⁻ concentrations; the reported SO₄²⁻ 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 CH₂O and removed 0.054 mmol of H₂S, 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 SO₄²⁻ concentration at Bronson equal to 60 percent of the SO₄²⁻ at Gainesville plus 40 percent of the SO₄²⁻ in unconfined recharge, that is, 0.364 mmol of SO₄²⁻.

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 Ca²⁺. 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 SO₄²⁻ 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 CO₂ 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 CO₂ 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 $\text{Na}^+\text{-HCO}_3^-$, 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 $J\text{-}J'$ 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 $G\text{-}G'$ and $H\text{-}H'$, 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 $\delta^{13}\text{C}$ 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 $K\text{-}K'$ 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. The local abundance of gypsum in the aquifer clearly affects the importance of this process. The chemical differences along flow path $K\text{-}K'$ 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, $F\text{-}F'$; B, $G\text{-}G'$; C, $H\text{-}H'$; D, $J\text{-}J'$; E, $K\text{-}K'$.

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. μ molal, micromolal]

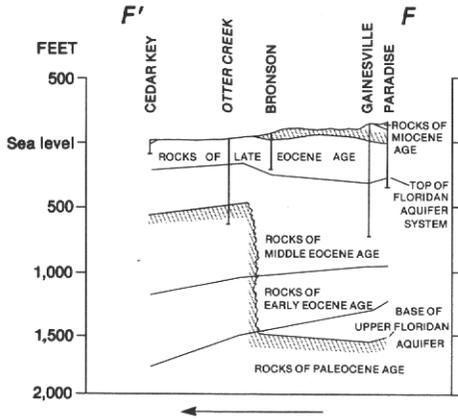
Name used in this report (well number in WATSTORE)	Sample date	Water temperature, °C	pH, units	Calcium	Magnesium	Sodium	Potassium	Chloride	Sulfate	Bicarbonate	Total inorganic carbon ¹	Fluoride	Silica	Remarks
SECTION F-F'														
Paradise (294209082173101)	May 6, 1975	23.5	8.1	2.022	0.700	0.387	0.026	0.339	0.729	3.869	3.856	0.011	0.266	Fe=0.5 μ molal; Sr=4.1 μ molal
Gainesville (293842082191801)	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 μ molal; NO ₃ =17.7 μ molal
Bronson (292640082381201)	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 μ molal; Sr=0.7 μ molal
Otter Creek (292109082422901)	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 μ molal; Sr=28.6 μ molal; NH ₄ =6.7 μ molal; Mn=0.1 μ molal
Cedar Key (291118083010601)	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	NH ₄ =17.2 μ molal; Mn=0.3 μ molal; Fe=16.3 μ molal; PO ₄ =0.3 μ molal; Sr=2.5 μ molal
SECTION G-G'														
Wenona (315558083435301)	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	PO ₄ =0.3 μ molal; Sr=0.7 μ molal; NH ₄ =1.7 μ molal; Al=0.7 μ molal
Ashburn (314218083392401)	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 μ molal; Al=0.7 μ molal
Tifton (312919083291501)	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 μ molal; Al=1.1 μ molal; NO ₃ =1.5 μ molal; Mn=0.2 μ molal
Nashville (311237083135201)	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 μ molal; Sr=3.1 μ molal
Valdosta (304930083165001)	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 μ molal; Al=0.7 μ molal; Mn=0.2 μ molal
Cherry Lake (303549083252501)	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	PO ₄ =0.6 μ molal; Sr=0.9 μ molal; NH ₄ =0.6 μ molal; NO ₃ =37.1 μ molal
SECTION H-H'														
Cadwell (322018083024402)	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 μ molal; Al=0.4 μ molal
Alamo (320857082464301)	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 μ molal; Al=0.7 μ molal
Reidsville (315837082093701)	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 μ molal
Fleming (315214081235301)	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 μ molal; Sr=5.4 μ molal; Al=0.7 μ molal
Savannah Beach (320124080510101)	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 μ molal; Sr=12.6 μ molal; B=7.4 μ molal; PO ₄ =0.8 μ molal; NH ₄ =44.4 μ molal

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

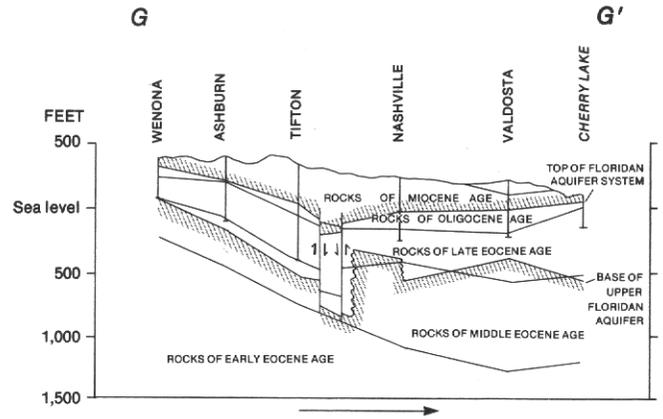
[Concentrations are in millimoles per kilogram of water, unless otherwise indicated. μmolal , micromolal]

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 (282202081384601)	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 (282732081293001)	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 (283910081194901)	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 (284429081144501)	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 (284724081085301)	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 μmolal ; NO ₃ =12.94 μmolal
SECTION K-K'														
Avon Park (273527081310801)	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 (272438081365701)	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 (271748081354801)	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 (270442081494301)	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 (264923082013701)	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 ; PO ₄ =0.6 μmolal ; Sr=253.9 μmolal ; Mn=0.6 μmolal

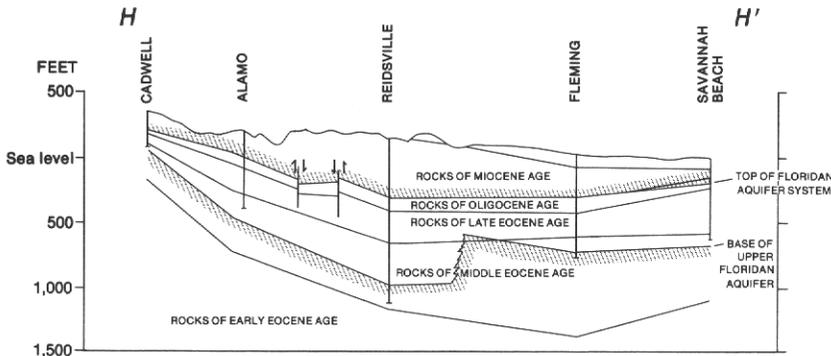
¹ Computed from measured pH and alkalinity with WATEQF.² Value not reported.



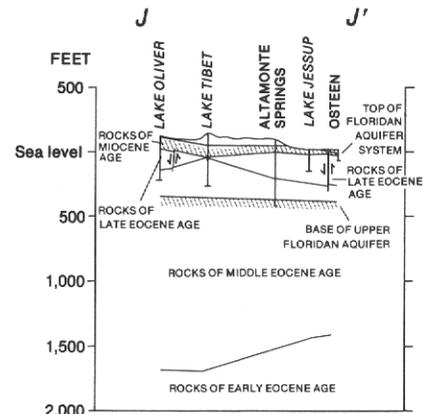
A



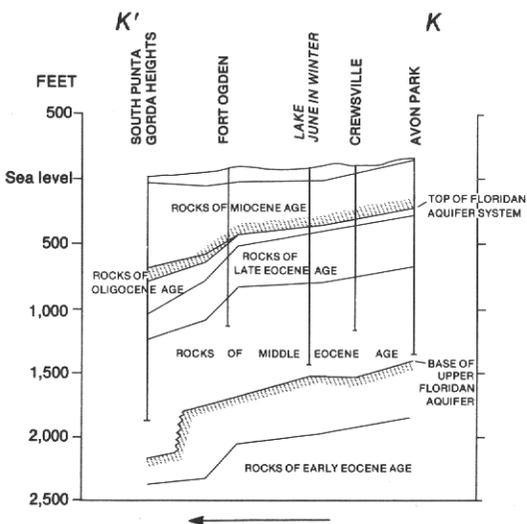
B



C



D

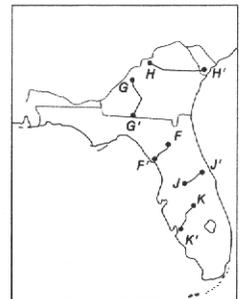


E

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

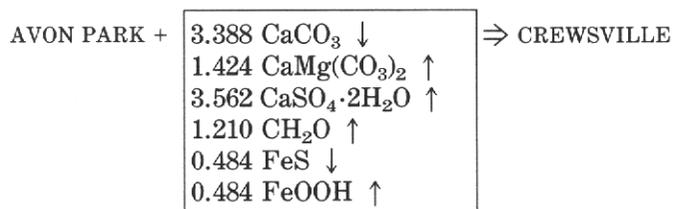
EXPLANATION

-  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 Ca²⁺, Mg²⁺, and SO₄²⁻ 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 SO₄²⁻ and Mg²⁺ 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 Ca²⁺, Mg²⁺, Cl⁻, and inorganic C but calculates an excess of SO₄²⁻ (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 δ³⁴S 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:



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 δ³⁴S of the sulfate in water from the Upper Floridan aquifer at Crewsville. The sulfur isotope equation of Plummer (1985) can be rewritten as follows:

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

where
 δ³⁴S_{cr} = estimated δ³⁴S of dissolved sulfate at Crewsville,
 δ³⁴S_{ap} = δ³⁴S of dissolved sulfate at Avon Park (estimated to be +25 ‰ 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),
 δ³⁴S_{gyp} = δ³⁴S of gypsum between Avon Park and Crewsville (estimated to be +22 ‰ from table 3),
 m_{gyp} = mass of gypsum added (+) or removed (-) per kilogram of water in reaction model (+3.562 mmol),
 δ³⁴S_{fes} = δ³⁴S of iron sulfide (estimated to be -25 ‰, 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 δ³⁴S of pyrite used in the above equation is estimated to be about -25 ‰ based on a sulfate-sulfide fractionation factor of about 50 ‰ in this area (Rye and others, 1981).

The δ³⁴S of the water at Crewsville is estimated to be about +29.4 ‰ using the above equation. This value is about 5 ‰ heavier than the δ³⁴S 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 CO₂ as the carbon source, even though the aquifer system is confined in most downgradient areas and, therefore, should be "closed" to CO₂. 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.

UNCONFINED RECHARGE	+	0.136 CaCO ₃ † 0.684 CaMg(CO ₃) ₂ † 0.725 CaSO ₄ ·2H ₂ O † 1.094 CO ₂ †	==>	PARADISE	UNCONFINED RECHARGE	+	0.285 CaCO ₃ † 0.018 CaMg(CO ₃) ₂ † 0.892 CO ₂ †	==>	WENONA
83 PERCENT PARADISE WATER + 17 PERCENT UNCONFINED RECHARGE	+	0.209 CaCO ₃ † 0.036 CaMg(CO ₃) ₂ † 0.674 CO ₂ †	==>	GAINESVILLE	99 PERCENT WENONA WATER + 1 PERCENT SAND RECHARGE	+	0.789 CaCO ₃ † 0.213 CaMg(CO ₃) ₂ † 0.008 CaSO ₄ ·2H ₂ O † 0.808 CO ₂ †	==>	ASHBURN
60 PERCENT GAINESVILLE WATER + 40 PERCENT UNCONFINED RECHARGE	+	0.587 CaCO ₃ † 0.281 CaMg(CO ₃) ₂ † 0.358 CO ₂ †	==>	BRONSON	64 PERCENT ASHBURN WATER + 36 PERCENT SAND RECHARGE	+	0.239 CaCO ₃ † 0.342 CaMg(CO ₃) ₂ † 0.404 CO ₂ †	==>	TIFTON
BRONSON WATER	+	1.125 CaCO ₃ † 0.824 CaMg(CO ₃) ₂ † 1.824 CaSO ₄ ·2H ₂ O † 1.099 CO ₂ †	==>	OTTER CREEK	68 PERCENT TIFTON WATER + 32 PERCENT CONFINED RECHARGE + trace SEAWATER	+	0.688 CaCO ₃ † 0.373 CaMg(CO ₃) ₂ † 0.943 CaSO ₄ ·2H ₂ O †	==>	NASHVILLE
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	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 † 0.189 CaMg(CO ₃) ₂ † 0.014 CaSO ₄ ·2H ₂ O † 0.610 CO ₂ †	==>	CHERRY LAKE

A

B

UNCONFINED RECHARGE	+	0.175 CaCO ₃ † 0.009 CaMg(CO ₃) ₂ † 0.004 CaSO ₄ ·2H ₂ O † 0.551 CO ₂ †	==>	CADWELL	UNCONFINED RECHARGE	+	0.230 CaCO ₃ † 0.255 CaMg(CO ₃) ₂ † 0.013 CaSO ₄ ·2H ₂ O † 0.823 CO ₂ †	==>	LAKE OLIVER
CADWELL WATER	+	0.295 CaCO ₃ † 0.313 CaMg(CO ₃) ₂ † 0.032 CaSO ₄ ·2H ₂ O † 0.414 CO ₂ †	==>	ALAMO	37 PERCENT LAKE OLIVER WATER + 63 PERCENT UNCONFINED RECHARGE	+	0.131 CaCO ₃ † 0.145 CaMg(CO ₃) ₂ † 0.127 CaSO ₄ ·2H ₂ O †	==>	LAKE TIBET
68 PERCENT ALAMO WATER + 32 PERCENT SAND RECHARGE	+	0.173 CaCO ₃ † 0.016 CaMg(CO ₃) ₂ † 0.273 CO ₂ †	==>	REIDSVILLE	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
69 PERCENT REIDSVILLE WATER + 31 PERCENT SAND RECHARGE	+	0.239 CaCO ₃ † 0.211 CaMg(CO ₃) ₂ † 0.022 CaSO ₄ ·2H ₂ O † 0.094 CO ₂ †	==>	FLEMING	96 PERCENT ALTAMONTE + SPRINGS WATER + 4 PERCENT SEAWATER	+	1.575 CaCO ₃ † 0.538 CaMg(CO ₃) ₂ † 0.216 CaSO ₄ ·2H ₂ O † 0.100 CO ₂ †	==>	LAKE JESSUP
FLEMING WATER + trace SEAWATER	+	0.487 CaCO ₃ † 0.226 CaMg(CO ₃) ₂ † 0.560 CaSO ₄ ·2H ₂ O † 0.219 ION-EXCHANGE 0.612 CO ₂ †	==>	SAVANNAH BEACH	82 PERCENT LAKE JESSUP WATER + 18 PERCENT SEAWATER	+	1.339 CaCO ₃ † 0.608 CaMg(CO ₃) ₂ † 0.284 CaSO ₄ ·2H ₂ O † 0.231 CO ₂ †	==>	OSTEEN

C

D

UNCONFINED RECHARGE	+	0.478 CaCO ₃ † 0.206 CaMg(CO ₃) ₂ † 0.022 CaSO ₄ ·2H ₂ O † 0.022 CO ₂ †	==>	AVON PARK
AVON PARK WATER	+	2.904 CaCO ₃ † 1.424 CaMg(CO ₃) ₂ † 3.078 CaSO ₄ ·2H ₂ O † 0.605 CO ₂ †	==>	CREWSVILLE
CREWSVILLE WATER	+	0.154 CaCO ₃ † 0.412 CaMg(CO ₃) ₂ † 0.334 CaSO ₄ ·2H ₂ O † 0.056 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 ·2H ₂ O †	==>	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

E

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 H₂O. † 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.