

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

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REGIONAL AQUIFER-SYSTEM ANALYSIS—FLORIDAN AQUIFER SYSTEM

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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 15A. 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 15B. 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.

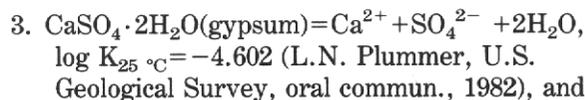
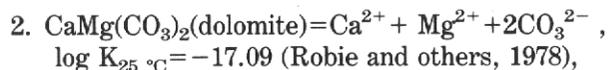
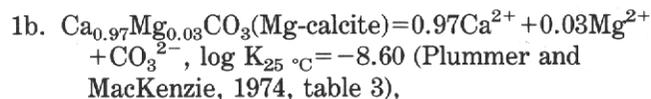
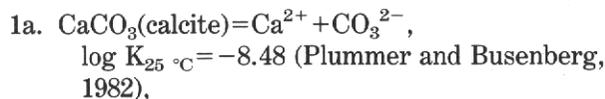
Deeper water-bearing zones (older rock units) may contain more dolomite, gypsum, apatite, peat, or other solid phases which can markedly influence the regional ground-water chemistry.

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 CO₂ 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 CO₂ (per kilogram of H₂O) 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 CO₂ per kilogram of H₂O from a 50-mL sample (used to measure pH) represents 0.325 mL of pure CO₂ 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 CO₂ outgassing and change from in situ alkalinity and pH.

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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 (Ca²⁺) 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 Ca²⁺ is controlled throughout most of the aquifer system by mineral saturation and (or) cation exchange. The important reactions are



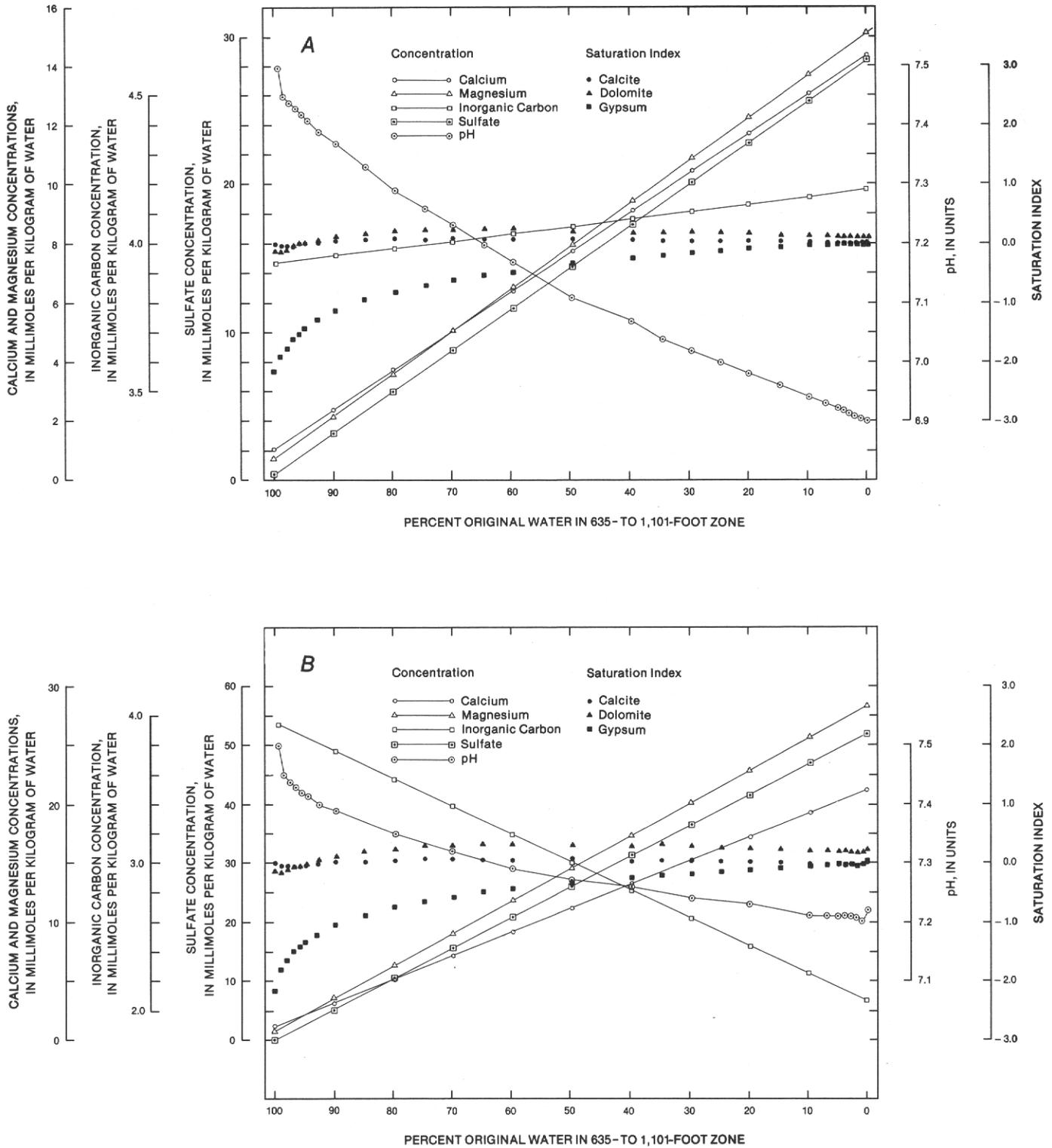
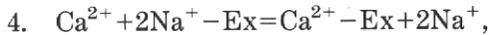


FIGURE 15. — Results of theoretically mixing waters from two zones within a deep well in the Upper Floridan aquifer near Waycross, Ga., 20 years after well completion: A, water from 1,100- to 1,856-foot zone invades 635- to 1,101-foot zone; B, water from 1,901- to 1,966-foot zone invades 635- to 1,100-foot zone.



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

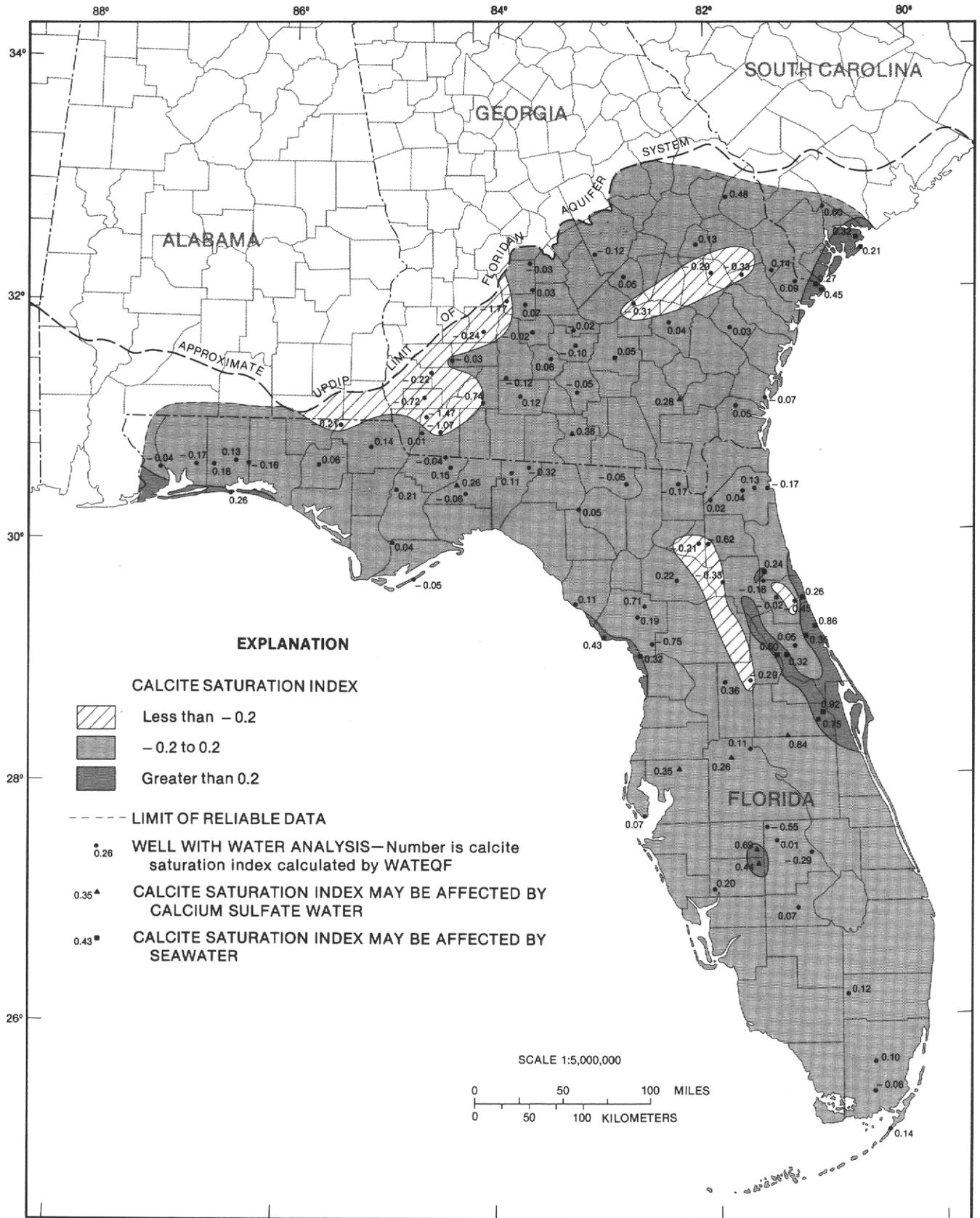


FIGURE 16.—Calcite saturation index computed from analyses of water samples from selected wells in the Upper Floridan aquifer.

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 $\text{Na}^+ - \text{HCO}_3^-$ or $\text{Ca}^{2+} - \text{Na}^+ - \text{HCO}_3^-$ 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 $\text{Ca}^{2+} - \text{HCO}_3^-$ 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 ($\text{in}/\text{mi}^2/\text{yr}$) (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 $\text{Na}^+\text{-HCO}_3^-$ 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
CO 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 _{CO₂} , 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 HCO₃⁻, 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).

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

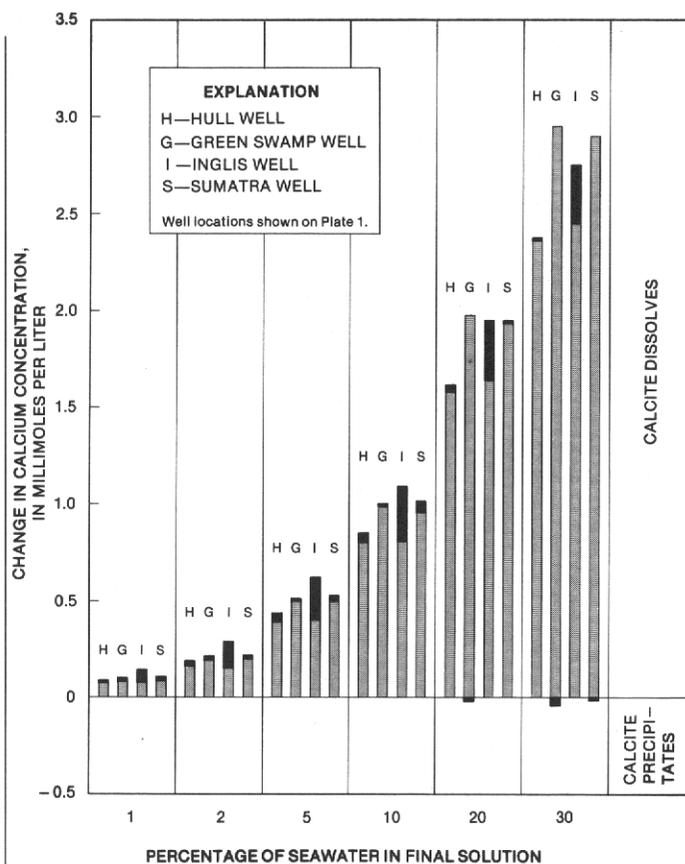


FIGURE 17.—Theoretical changes in calcium concentration in mixtures of ground water from the Upper Floridan aquifer and seawater. Dark bars represent calcium added (or removed) to maintain calcite saturation in the mixture.

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 Ca²⁺ 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 Ca²⁺ 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, Ca²⁺ and CO₃²⁻ 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 CO₂ 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}CO₃ 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 Ca²⁺ concentrations slightly in some areas, but, from the reaction stoichiometry, the low levels of sulfate imply that less than 0.5

mmol of dolomite 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 (Mg²⁺) is therefore a major dissolved constituent in the freshwater parts of the aquifer system. Concentrations of Mg²⁺ in seawater are about 1,320 mg/L; thus, where brackish or saline water is present, Mg²⁺ concentrations may equal or exceed Ca²⁺ concentrations. Mg²⁺ 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. $\text{CaMg}(\text{CO}_3)_2 = \text{Ca}^{2+} + \text{Mg}^{2+} + 2\text{CO}_3^{2-}$
2. $\text{Ca}_{0.97}\text{Mg}_{0.03}\text{CO}_3 = 0.97\text{Ca}^{2+} + 0.03\text{Mg}^{2+} + \text{CO}_3^{2-}$
3. $\text{Mg}^{2+} + 2\text{Na}^+ - \text{Ex} = \text{Mg}^{2+} - \text{Ex} + 2\text{Na}^+$

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

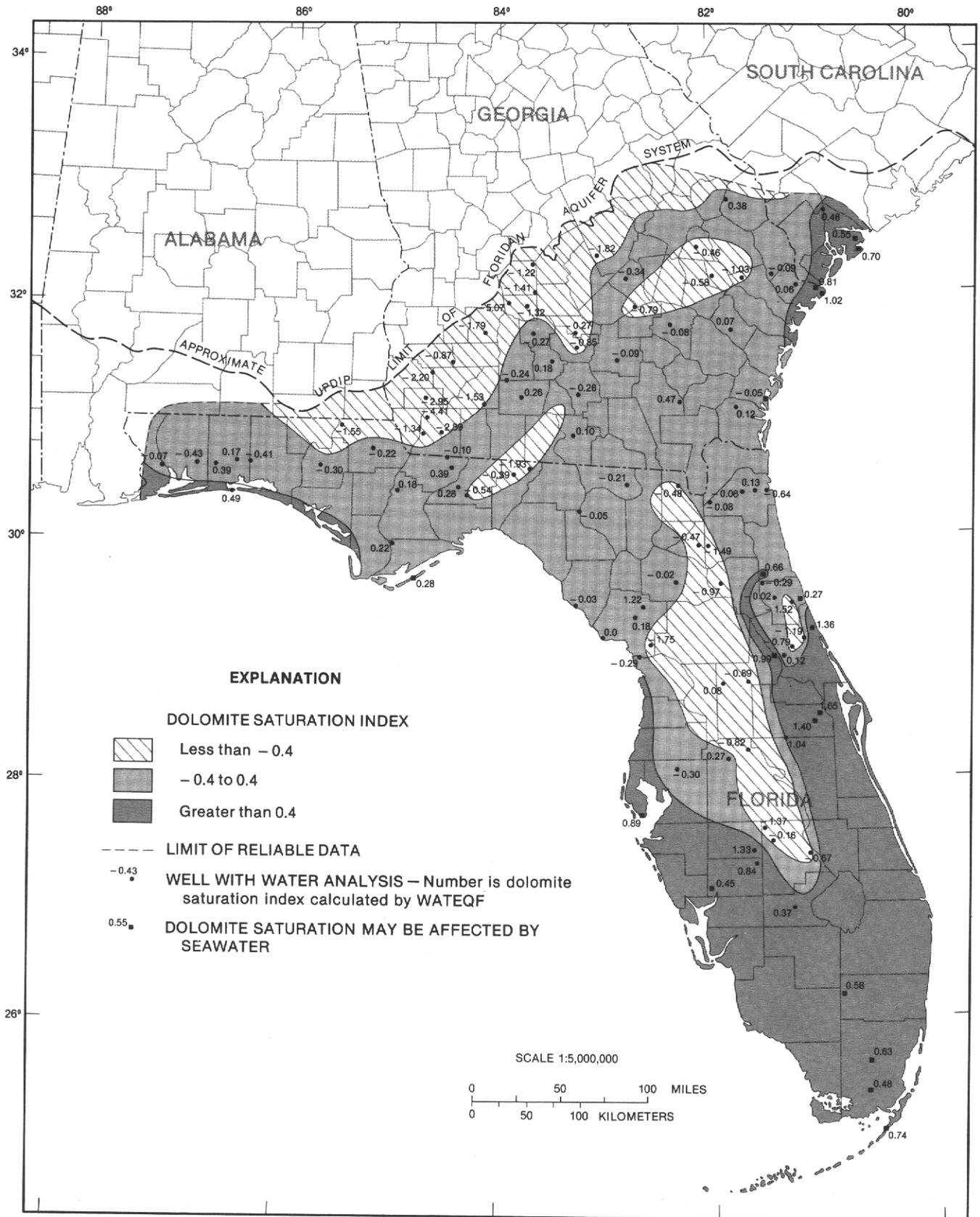


FIGURE 18.—Dolomite saturation index computed from analyses of water samples from selected wells in the Upper Floridan aquifer.

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;