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University of Nevada

Reno

✓ Chemical Hydrogeology of the Carbonate Peninsulas
of Florida and Yucatan

A dissertation submitted in partial fulfillment of the
requirements for the degree of Doctor of Philosophy

by

William Back

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ABSTRACT

Aquifers of the peninsulas of Florida and northern Yucatan are Tertiary marine carbonate formations showing great lithologic and faunal similarities. In addition, the tropical to subtropical climates of the two areas are similar, with annual rainfall of about 1000 to 1500 mm.

Despite similarities in these fundamental controls, contrasts in the hydrologic and geochemical systems are numerous and striking. For example, Florida has many rivers; in the Yucatan there are none. Maximum thickness of fresh ground water in Florida is about 700 meters; in the Yucatan it is less than 70 meters. In Florida the gradient of the potentiometric surface averages about 1 meter per kilometer; in the Yucatan it is exceedingly low, averaging about 0.02 meter per kilometer. In Florida the chemical character of water changes systematically downgradient owing to solution of minerals of the aquifer and corresponding increases in total dissolved solids, sulfate, calcium, and Mg-Ca ratio; in the Yucatan no systematic change exists, and dominant processes controlling the chemical character of the water are solution of minerals and simple mixing of the fresh water and the body of salt water that underlies the peninsula at shallow depth.

Hydrologic and chemical differences are caused in part by the lower altitude of the Yucatan plain. More importantly, however, these differences are due to the lack of an upper confining bed in the Yucatan that is hydrologically equivalent to the Hawthorn Formation of Florida. The Hawthorn cover prevents recharge and confines the artesian water except where it is punctured by

sinkholes, but sands and other unconsolidated sediments fill sinkholes and cavities and impede circulation. In the Yucatan the permeability of the entire section is so enormous that most rainfall, charged with CO_2 gas from the lush vegetation and the soil, immediately infiltrates to the water table and then moves laterally to discharge areas along the coasts.

Inasmuch as the equilibrium constant for dolomite of 2×10^{-17} is exactly the square of the calcite equilibrium constant ($10^{-8.35}$), the Mg/Ca must be unity for the three-phase equilibrium, calcite-dolomite-water. With time and length of travel path in the Floridan system, the Mg/Ca in water increases systematically downgradient and approaches unity; saturation with respect to the two carbonates also increases and reaches limits of 170 percent for calcite and 200 percent for dolomite ($\text{IAP}/K_{\text{eq}} \times 100 = \text{percent}$).

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Chemical Hydrogeology of the Carbonate Peninsulas of Florida and Yucatan

INTRODUCTION

The purpose of this paper is twofold: (1) to describe the geochemistry of water in carbonate terranes and (2) to identify and interpret the effects of various geologic controls on the ground-water flow pattern and on the resulting chemical character of water. The procedure used in this study is to describe the geology, hydrology, and geochemistry of a central portion of the Florida Peninsula, a classic limestone terrane, and make a comparative evaluation with that of the Yucatan Peninsula, a similar but somewhat diverse portion of the same geologic environment.

Owing to greater solubility of carbonate minerals compared to silicate minerals, limestone generally is more permeable than other jointed rocks, such as granite or sandstone. In order to understand controls on secondary permeability and porosity distribution, including recementation of limestone aquifers, it is necessary to identify and evaluate effects of solution and precipitation of carbonate minerals. It is well established that solution of carbonate minerals is influenced by pH, temperature, effect of other ions in solution, and carbon dioxide content. The question becomes, how can interrelations of these factors be studied to evaluate their relative effectiveness under natural conditions. One approach to the problem is to apply concepts of thermodynamics to ground-water systems. The hypothesis is that the law of mass action provides a thermodynamic model which can describe the geochemical system of a carbonate aquifer.

A chemical equilibrium method aids in understanding geologic processes, such as formation of fissures and caverns, precipitation of calcium carbonate in these openings, recrystallization of limestone, formation of dolomite, and deposition of calcareous cement in sandstone bodies. The fundamental questions considered in this study are (1) is water in equilibrium with carbonate minerals of the aquifer, and if not, is it undersaturated or supersaturated; (2) in what way is departure from equilibrium controlled by the ground-water flow pattern; and (3) what are the primary geologic controls on the flow pattern. Answers to these questions are useful in water management activities because they improve our ability to predict which, if any, chemical changes may occur as a result of imposing stresses, such as increased pumping or artificial recharge, on a hydrologic system.

This dissertation is a unification of ideas and concepts of selected topics that have been developed during the past several years. The data contained here are from my files, notes, and manuscripts, some of which have been published (Back and Hanshaw, 1965, 1967). At the beginning of the study (about 1962), the stratigraphy of Florida was rather well known and a potentiometric map was available. My primary activities concerning the topic of this dissertation have been to provide (1) a description and clarification of the geochemistry of water in the study area of the principal artesian system of Florida, (2) a hypothesis for the hydrogeology of the Yucatan Peninsula, (3) a description of the geochemistry of water in the Yucatan, and (4) a comparison of the chemical character of water of the two peninsulas and an explanation of their hydrologic controls.

PRINCIPLES OF CHEMICAL THERMODYNAMICS

Energy distribution within all systems, physical and chemical, is such that all processes strive toward equilibrium. The concept of chemical equilibrium is expressed by the law of mass action which states that the rate of a chemical reaction is proportional to the active mass of the reacting substances at a particular time. For example, in the general reaction where a moles of A react with b moles of B to form c moles of C and d moles of D, commonly written as



an important factor in determining the rate of reaction is not simply the quantity of reactant but rather the quantity per unit volume. At equilibrium, the rate of reaction to the right in equation (1) is just equalled by the rate to the left, in which case the equilibrium constant, K , is given by:

$$K = \frac{\alpha_C^c \alpha_D^d}{\alpha_A^a \alpha_B^b} \quad (2)$$

where α denotes thermodynamic concentration or activity and K is either K_{eq} for a mineral or K_{iap} calculated from a water analysis. In very dilute solutions, activity is essentially equal to chemical concentration, but as a solution becomes more concentrated, components of the solution cease behaving ideally; their effective concentration or activity does not change proportionally with the concentration. A correction for deviations from ideality is

necessitated by the fact that, as the concentration of a solution is increased, ions interact with one another and with water molecules to form complexes and hydrated units. For this reason, it becomes necessary to change from standard units of chemical concentration to those of activity in order that ion activity products, K_{iap} , may be compared with laboratory-determined equilibrium constants, K_{eq} , to ascertain which minerals are in equilibrium with, and therefore presumably controlling, the chemistry of the water. The K_{iap} , when compared with the equilibrium constant, determines departure from equilibrium of water with respect to calcite. If the ratio $K_{iap}:K_{calcite}$ is equal to 1 (100 percent), the water is saturated with respect to calcite; a ratio less than 1 (less than 100 percent) denotes undersaturation; and a ratio greater than 1 (greater than 100 percent) denotes supersaturation.

Most chemical analyses of waters are expressed in units of parts per million (ppm) or equivalents per million (epm). To convert these values to activity, it is necessary to change them to units of molality. A one molal solution is defined as one which contains a mole (formula weight in grams) of solute in 1000 grams of water. Molar concentrations are not used in thermodynamic studies (molar solutions are referred to a liter of water) owing to the temperature dependency of the volume and, hence, concentration of such solutions. To convert from ppm or epm to molality, the following relationships may be used:

$$\text{molality} = \frac{\text{ppm} \times 10^{-3}}{\text{formula weight in grams}} \quad (3)$$

and

$$\text{molality} = \frac{\text{epm} \times 10^{-3}}{\text{valence of the ion}} \quad (4)$$

In dilute solutions, molality is nearly equal to activity; for more concentrated solutions, a correction factor must be used. The correction factor which provides a connection between activity, a_i , and molality, m_i , of individual ionic species is given by

$$\gamma_i = \frac{a_i}{m_i} \quad \text{or} \quad a_i = \gamma_i m_i \quad (5)$$

where γ_i is the activity coefficient of component i . The activity coefficient for various ions may be calculated from standard water analyses by use of the empirical Debye-Hückel equation which states that

$$\log \gamma_i = \frac{-Az_i^2 \Gamma^{1/2}}{1 + a_i B \Gamma^{1/2}} \quad (6)$$

where A and B are temperature-dependent constants, z_i is the charge on the ion, a_i represents the effective diameter of the ion in solution, and Γ is the ionic strength of the solution. Values for A , B , and a_i may be obtained from texts on physical chemistry or solution chemistry. The ionic strength may be calculated from the expression

$$\Gamma = \frac{1}{2} \sum_i m_i z_i^2 \quad (7)$$

The Debye-Hückel equation gives reasonably reliable values for activity coefficients up to ionic strengths of 0.1; this corresponds to concentrations in typical natural waters of about 5000 to 8000 ppm.

In summary, to convert from standard chemical analyses to activities: (1) convert reported units to molality, m_i ; (2) calculate ionic strength, I ; (3) determine individual ion activity coefficients, γ_i ; and (4) multiply m_i by γ_i to obtain individual ion activities, a_i . The ion activity product, K_{iap} , is determined for every reaction for which thermochemical data are available and compared with the equilibrium constant, K_{eq} , to determine what control each solid mineralogic phase has on chemistry of the water.

Although it is not generally the function of chemical geohydrologists to determine equilibrium constants for minerals, they must be able to obtain desired information from laboratory work of physical chemists and geochemists. Because equilibrium constants for minerals are not given directly by the physical-chemical laboratories, but rather the free energy is reported, it is necessary to calculate K_{eq} from tables of free energies.

The Gibbs free energy function, ΔG , provides a true measure of the driving force of a chemical reaction. The Gibbs free energy of reaction, ΔG_R° , is the sum of the free energies of formation of products less the sum of free energies of formation of reactants; that is,

$$\Delta G_R^\circ = \sum \Delta G_F^\circ \text{ products} - \Delta G_F^\circ \text{ reactants} \quad (8)$$

When ΔG_R° is zero, there is no net chemical work obtainable; the system is in equilibrium. If ΔG_R° is negative, the process may proceed spontaneously; a positive value means that work (energy) must be put into the system for the reaction to proceed. The equilibrium constant can be calculated from Gibbs free energy of reaction according to the relation

$$\Delta G_R^\circ = -RT \ln K_{eq} \quad (9)$$

where R is the gas constant and T is temperature in degrees Kelvin.

Standard state for calculation of free energy values is commonly taken as the pure substance at 25°C and one atmosphere total pressure. Because natural waters are generally at some temperature other than 25°C, it is necessary to extrapolate free energy data from 25°C to the temperature of the water. This may be done by using the Gibbs-Helmholtz equation which states that at constant pressure

$$\Delta G = \Delta H + T \left(\frac{\delta(\Delta G)}{\delta T} \right)_P \quad (10)$$

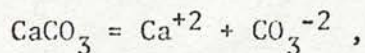
where ΔH is enthalpy or heat of reaction; i.e., enthalpy is the heat change which occurs during a chemical process at constant pressure. By differentiation and combination of the last two equations, we arrive at the van't Hoff equation:

$$\left(\frac{\delta \ln K_{eq}}{\delta T} \right)_P = \frac{\Delta H}{RT^2} \quad (11)$$

which may be used to calculate equilibrium constants at temperatures other than 25°C. This equation is a fair approximation if T does not vary more than a few degrees from 25°C; for greater variation, the assumption that ΔH is independent of temperature change is invalid.

The principal significance of the equilibrium constant in chemical geohydrology is that it provides a means of calculating departure from equilibrium between the aqueous phase and solid mineralogic phases. Departure is determined by comparison of the thermodynamic equilibrium constant, K_{eq} , with the ion activity product, K_{iap} , which is calculated from chemical analysis of water.

Measurements of departure from chemical equilibrium between ground water and the minerals which comprise an aquifer aid in delineating principal areas of recharge and in predicting areas subject to solution or deposition of minerals. Equilibrium studies also increase our knowledge of the minerals that control chemistry of water and of the changes that may occur with time or because of application of stress upon hydrologic systems. To determine whether water is in equilibrium with a particular mineral, we need to know only the equilibrium constant, $K_{mineral}$, obtained from physical-chemical laboratories; other variables necessary to calculate an equivalent constant, ion-activity product, K_{iap} , are obtained from the chemical analysis of water. For example, in solution of calcite, we have



and the law of mass action gives us

$$K_{\text{calcite}} = \frac{\alpha_{\text{Ca}^{+2}} \cdot \alpha_{\text{CO}_3^{-2}}}{\alpha_{\text{CaCO}_3}} \quad (12)$$

By definition, activity of pure water or of a solid phase is equal to 1.

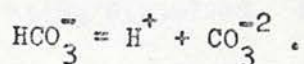
In a like manner, the ion-activity product is

$$K_{\text{iap}} = \alpha_{\text{Ca}^{+2}} \cdot \alpha_{\text{CO}_3^{-2}} \quad (13)$$

The activities used are calculated from the chemical analysis of the water; that is,

$$\alpha_{\text{Ca}^{+2}} = \gamma_{\text{Ca}^{+2}} \cdot M_{\text{Ca}^{+2}} \quad (14)$$

where M is molality. However, because the dominant carbonate species in solution in water is bicarbonate rather than carbonate ion, we use the reaction



The equilibrium constant for the equation is given by

$$K_{\text{HCO}_3^-} = \frac{\alpha_{\text{H}^+} \cdot \alpha_{\text{CO}_3^{-2}}}{\alpha_{\text{HCO}_3^-}} \quad (15)$$

From these equations, we obtain

$$\alpha_{\text{CO}_3^{-2}} = \frac{K_{\text{HCO}_3^-} \cdot \alpha_{\text{HCO}_3^-}}{\alpha_{\text{H}^+}} \quad (16)$$

where $K_{\text{HCO}_3^-}$ is a thermodynamic constant at a given temperature, activity of the bicarbonate is calculated from chemical analysis of the water, and activity of the hydrogen ion is the pH of the water. From the form of equation (13), it is seen that K_{iap} for calcite and aragonite is the same.

By making temperature corrections, the ion activity product for CaCO_3 can be calculated from activities of calcium and carbonate ions determined from equations (14) through (16) and compared with the equilibrium constant K_{calcite} . Equilibrium constants used in these calculations are given in Table 1.

Because all systems in nature tend toward equilibrium, we know that where water is undersaturated with respect to a mineral, this mineral is being dissolved. However, because of kinetic effects, we cannot categorically say that where the water is supersaturated with respect to a mineral, that mineral is necessarily being precipitated. Further work is needed on this topic.

Table 1.-- Equilibrium constants for calculation of calcium carbonate saturation

Temperature (°C)	$\log K_{\text{H}_2\text{CO}_3}$ ^{1/}	$\log K_{\text{HCO}_3}$ ^{2/}	$\log K_{\text{calcite}}$ ^{3/}
10	-6.464	-10.488	-8.153
15	-6.419	-10.429	-8.216
20	-6.382	-10.376	-8.277
21	-6.375	-10.367	-8.289
22	-6.368	-10.356	-8.302
23	-6.362	-10.347	-8.314
24	-6.357	-10.338	-8.321
25	-6.350	-10.329	-8.338
26	-6.345	-10.320	-8.350
27	-6.340	-10.312	-8.362
28	-6.335	-10.304	-8.374
29	-6.331	-10.296	-8.386
30	-6.326	-10.288	-8.398
35	-6.308	-10.251	-8.456

^{1/} Calculated from Harned and Davis (p. 2030, 1943)

^{2/} Calculated from Harned and Scholes (p. 1706, 1941).

^{3/} Calculated from Larson and Buswell (p. 1673, 1942).

PHYSICAL FEATURES OF THE TWO PENINSULAS

Hydrogeology

An application of these chemical principles is made by considering the hydrologic conditions of central Florida and the Yucatan Peninsula. As in every ground-water system, distribution of chemical constituents is controlled by the form of the flow net which is in turn dependent upon geologic, physiographic, and meteorologic controls.

The regional geologic setting of Florida and the Yucatan Peninsula (Figure 1) consists primarily of marine sediments of Tertiary age overlying Cretaceous deposits surrounding the Gulf of Mexico. The principal artesian aquifer, which is the source of nearly all artesian water of Florida and southeastern Georgia, consists chiefly of limestone ranging in age from Middle Eocene to Middle Miocene. The same sequence of formations is continuous around the Gulf of Mexico with Florida being at one end and the Yucatan Peninsula at the other. The principal artesian aquifer is one of the most extensive limestone aquifers in the United States. It is at or near the land surface in areas where Tertiary limestones crop out in a broad belt extending from western Florida through southeastern Alabama, Georgia, and southeastern Carolina, approximately paralleling the Fall Line. Rocks of Paleocene through Oligocene age, shown cropping out in Florida on the Ocala arch, are dominated by Ocala Limestone of Upper Eocene age, and the same sequence shown cropping out in the Yucatan is dominated by the Pisté Member of similar age. The Ocala Limestone is one of the most productive

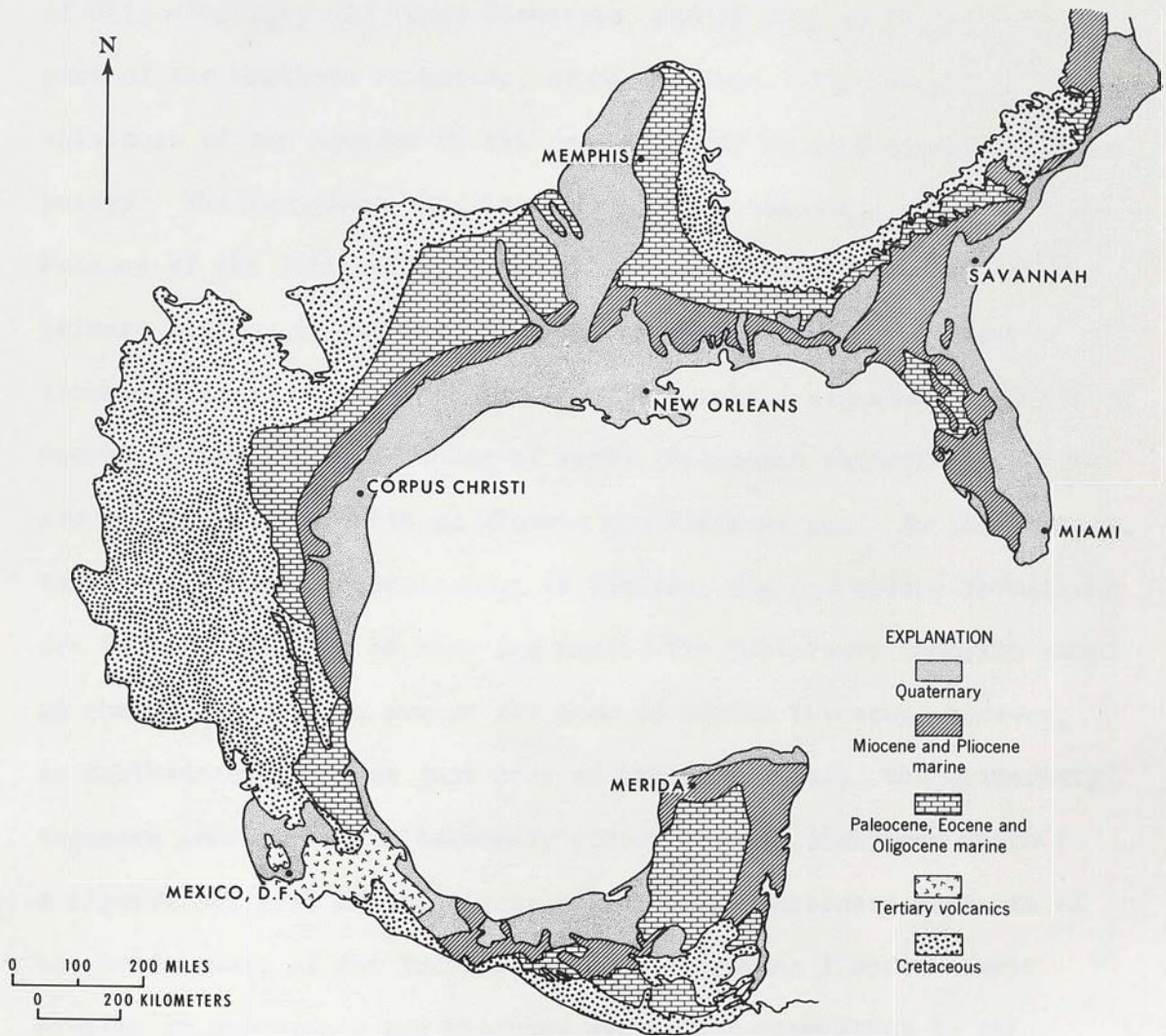


Figure 1.--Generalized map showing regional geology of the Florida and Yucatan Peninsulas.

formations of the principal aquifer. As shown in Table 2, the principal artesian aquifer in the area of study includes the following formations or equivalents from bottom to top: Lake City Limestone, Tallahassee Limestone, and Avon Park Limestone of Middle Eocene age; Ocala Limestone of Late Eocene age; Suwannee Limestone of Oligocene age; and Tampa Limestone, and in some places the lower part of the Hawthorn Formation, of Miocene age. The maximum thickness of the aquifer in the area of study is approximately 300 meters. The principal artesian aquifer does not exist in the Yucatan because of the lack of low permeability confining beds; however, the primary aquifer is composed of the same stratigraphic sequence of limestone as in Florida, and these relationships are shown on Table 3. Overlying this first grouping of rocks (Paleocene through Oligocene) are the marine sediments of Miocene and Pliocene age. In the Yucatan, these are primarily limestones; in Florida, the equivalent formations are composed chiefly of clay and marl. The Quaternary deposits shown on the map of Florida are in the form of marine terraces; however, in southeastern Florida (not part of the study area), the Quaternary sequence consists of an extremely porous coquina limestone which is a significant part of the Biscayne aquifer. Quaternary deposits of the north coast of the Yucatan are also a coquina limestone very similar in appearance and presumed hydrologic properties to the Biscayne aquifer. Stratigraphic relationships of the principal artesian aquifer in the Florida study area are shown on the fence diagrams (Figures 5 through 10) which provide a hydrogeologic base for geochemical interpretations.

TABLE 2.--General hydrogeologic description of central Florida^{1/}

Series	Stratigraphic unit	Thickness (meters)	Lithology	Water-bearing properties
Recent and Pleistocene	Primarily marine terraces	0-75	Sand, gravel, clay, shells, limestone, and marl.	Yields water to shallow wells
Pliocene	Alachua and Bone Valley Formations	0-35	Phosphatic sand and clay.	Yields small quantities of water to shallow wells.
Miocene	Hawthorn Formation	0-60	Sand, clay, and marl. Hawthorn consists chiefly of interbedded sand, clay, and limestone and sandy phosphatic limestone and marl.	Yields small to moderate quantities of artesian and nonartesian water. Major part of Hawthorn forms the confining layer for the underlying artesian water, but lower part forms the upper part of the principal artesian aquifer.
	Tampa Limestone	0-90	Limestone with sands, silts, and clay. Some parts of the limestone are silicified. The formation contains many solution cavities in recharge area.	Yields moderate amounts of water but generally less than underlying Eocene formations.
Oligocene	Suwannee Limestone			
Upper Eocene	Ocala Limestone	15-120	Consists chiefly of calcitic limestone.	Ocala Limestone is one of the most productive formations of the principal artesian aquifer.
Middle Eocene	Avon Park Limestone	150-240	Cream-colored to brown chalky limestone and dolomite. Contains gypsum and chert.	Avon Park and Tallahassee Limestones are principal source of water in areas where overlying limestone is thin or absent.
	Tallahassee Limestone			
	Lake City Limestone	35-300	Alternating beds of dark-brown dolomite and chalky limestone. Gypsum is present in central part of peninsula.	Oldest formation of the principal artesian aquifer and an important source of artesian water in some areas.

Principal artesian aquifer

Table 2.--General hydrogeologic description of central Florida - continued

Series	Stratigraphic unit	Thickness (meters)	Lithology	Water-bearing properties
Lower Eocene	Oldsmar Limestone	75-300	Limestone containing chert and gypsum in central part of peninsula.	Contains salt water.
Paleocene	Cedar Keys Limestone	50-685	Gray and cream-colored to white limestone containing gypsum and some anhydrite stringers and oolitic lenses.	Contains salt water.
Cretaceous and older				Contains salt water.

^{1/} Modified from Stringfield (1966).

TABLE 3.--General hydrogeologic description of the northern part of the Yucatan Peninsula^{1/}

Series	Stratigraphic unit	Maximum thickness (meters)	Lithology	Water-bearing properties
Recent and Pleistocene	Not named	100	Limestone consisting of cream-colored coquinas with a porous cryocrystalline calcareous matrix, which are locally strongly weathered; contains large quantities of pelecypod shells.	All formations of Tertiary age are permeable, and extremely permeable near the surface. Salt water exists in all formations at a depth of a few tens of meters below land surface.
Pliocene and Miocene	Carrillo Puerto Estero Franco Bacalar	200	Coquina limestones and yellowish hard massive limestone; with arenaceous interbeds.	
Oligocene	Not named	330	Limestone, white to cream, with white clay and siliceous layers.	
Upper Eocene and Upper Middle Eocene	Chichen-Itza Formation Chumbec Member	100	Limestone, white, massive, crystalline resembles saccharoidal marble; equivalent to Ocala Limestone of Florida	
Middle Eocene	Pist�e Member	Several 100	Limestone, yellow, massive, fine-grained, microcrystalline; large areas of outcrop equivalent to Avon Park and Tallahassee Limestones of Florida.	
Lower Eocene and Paleocene(?)	Xbacal Member	?	Similar to overlying limestone; equivalent to Oldsmar Limestone of Florida.	

TABLE 3.--General hydrogeologic description of the northern part of the Yucatan Peninsula - continued

Series	Stratigraphic unit	Maximum thickness (meters)	Lithology	Water-bearing properties
Eocene and Paleocene(?)	Icaiche Formation	?	Limestone, marl and shale, contains some chert.	
Eocene and Paleocene(?)	Undifferentiated	?	Marl and shale, with intercalations of limestone, contains some chert.	
Cretaceous and older	Undifferentiated	?	Marl and shale, with some limestone and dolomitic limestone.	

^{1/} Modified from Bonet and Butterlin (1965) and Murray and Weidie (1965).

Physiography of the Floridan Peninsula

The dominant physiographic feature of the study area of Florida is a central peninsula-shaped upland surrounded by an irregular belt of coastal lowlands and plains. The central upland is a portion of a regional feature that extends southeastward through the state from the Georgia state line and occupies roughly the middle of the northern third of the Florida Peninsula (Murray, chap. 8, 1961). It is an area of diverse topography: continuous swamps; hills; broad, flat areas; and numerous lakes. The entire region is underlain by calcareous beds whose solution has given rise to widespread sinkholes and depressions and a modified karst topography. Innumerable lakes dot the landscape and, combined with rolling topographic features, warm climate, and tropical vegetation, produce a most delightful landscape. Much of the lowlands between the central upland and the sea is dominated by coastal terraces comprised of sand and gravel deposits.

As shown on Figure 2, most of the land surface of central Florida is lower than 30 meters above sea level, and coastal areas and lower areas of the stream valleys are less than 15 meters. The elongated ridge trending in nearly a north-south direction contains most of the sinkholes and lakes which are the headwaters of many of the rivers of central Florida. Highest elevations, slightly more than 75 meters, occur in Pasco and Hernando Counties and in western and northwestern Polk County.

Gradients of the streams originating in the ill-defined north-south divide of low rolling hills are low and generally inadequate for carrying away runoff following periods of heavy rainfall.

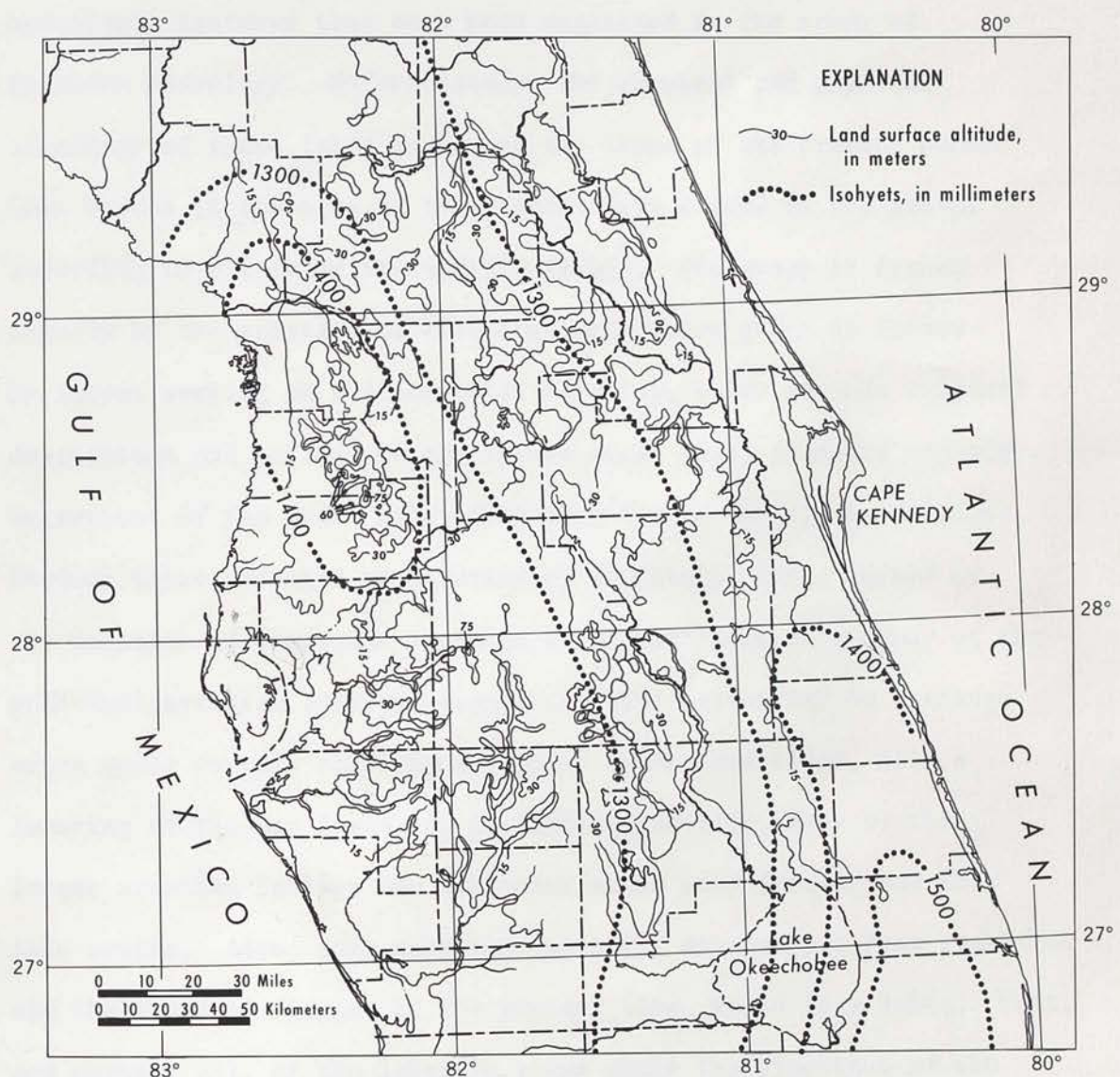


Figure 2.--Topographic map of central Florida showing distribution of rainfall.

Consequently, there are sizable areas of swamp and marshland near the headwaters of these streams. Largest of these areas is the Green Swamp in northern Polk and southern Lake and Sumpter Counties.

The lakes of Florida are significant physiographic and hydrologic features that have been neglected in the study of Floridan hydrology. Unfortunately, the chemical and physical limnology of these lakes is beyond the scope of the present paper. Lake basins in the area of this report were placed in two groups according to origin by Stringfield (1966). One group is formed chiefly by the solution of limestone; the other group is formed by forces working on the surficial material, which include original depressions and hollows on the former ocean floor that are exposed by retreat of the sea. Lakes that were formed chiefly by solution include those affected by jointing or faulting. Lakes formed by the solution of limestone are especially pertinent to a study of the principal artesian aquifer because the lake basins may be recharge areas under certain conditions. Under other conditions, with a lowering of the sea level, as in Pleistocene time, many of the larger artesian springs and sinkholes would stop flowing and form lake basins. Also, some submarine springs, discharging from sinkholes off the coast of Florida at the present time, would form lakes. Most, and perhaps all, of the lakes in areas where the limestone of the principal aquifer is at or near the surface are in basins formed chiefly by solution of the limestone and collapse of a section of cavern roof. Most of the lakes in a lake region in the central highlands of Florida occupy old, partially filled sinkholes and are hydrologically connected to the ground-water body.

Physiography of the Yucatan Peninsula

In the Yucatan, the area of study covers about the northern one-third of the peninsula and consists primarily of a rather level plain with a maximum elevation of about 40 meters above sea level. Southward the land rises gradually, with occasional weak folds and low cuesta-formed ridges in highly eroded Eocene limestone, forming a low hilly surface of about 130 meters elevation. The first significant hills are the Sierrita de Ticul, a ridge that rises to a maximum of 50 meters above the surrounding plain and marks a boundary between the flat Yucatecan Plain to the north and the hilly Campeche area to the south. Most of the Yucatan Peninsula is characterized by a karst surface. In the area studied, the physiography could be called microkarst owing to the low elevation and extremely rugged microrelief caused by the great number of steep-walled sinks and erosional remnants. No integrated drainage system has developed, and no rivers exist in this part of the peninsula. Extremely rugged relief and lack of rivers are caused by highly weathered and extremely porous limestone that is exposed everywhere at the surface.

The only bodies of fresh water seen in the Yucatan, even after heavy rains, are in steep-walled sinkholes called "cenotes" that intercept the water table and in clay-lined depressions called "aquadas."

Climate of Peninsular Florida

The area of study in Florida extends from a latitude of about 27° to slightly north of latitude 29°. Consequently, the climate of the area is tropical to subtropical. Primary climatic controls for the area are relatively low latitude, proximity to the Atlantic Ocean and Gulf of Mexico, and numerous inland lakes. As shown on Figure 2, mean annual rainfall ranges from about 1300 to 1500 millimeters (mm). Although rainfall is distributed rather evenly throughout the area, it is distributed most unevenly throughout the year, with more than half occurring in the four-month period June through September. The start and end of the summer rainy season are abrupt, with June rainfall tending to be nearly double that of May, and September about twice that of October. Although the beginning and end are always abrupt and rather dramatic, the actual periods of time can vary considerably with the beginning starting as early as the first part of May or being delayed as late as the end of June, with a corresponding range in period for the end of the rainy season. Most summer rainfall is derived from local showers or thunderstorms; many places average more than 80 thunderstorms per year, and some average more than 100. Showers are often heavy, usually last only an hour or two, and generally occur near the hottest part of the day. Daylong summer rains are usually associated with tropical disturbances and therefore are infrequent. Even in the wet season, duration of rainfall is generally less than 10 percent of the time. Because most summer rains are local in character, large differences in monthly and annual totals at nearby points are common, but precipitation is more uniform

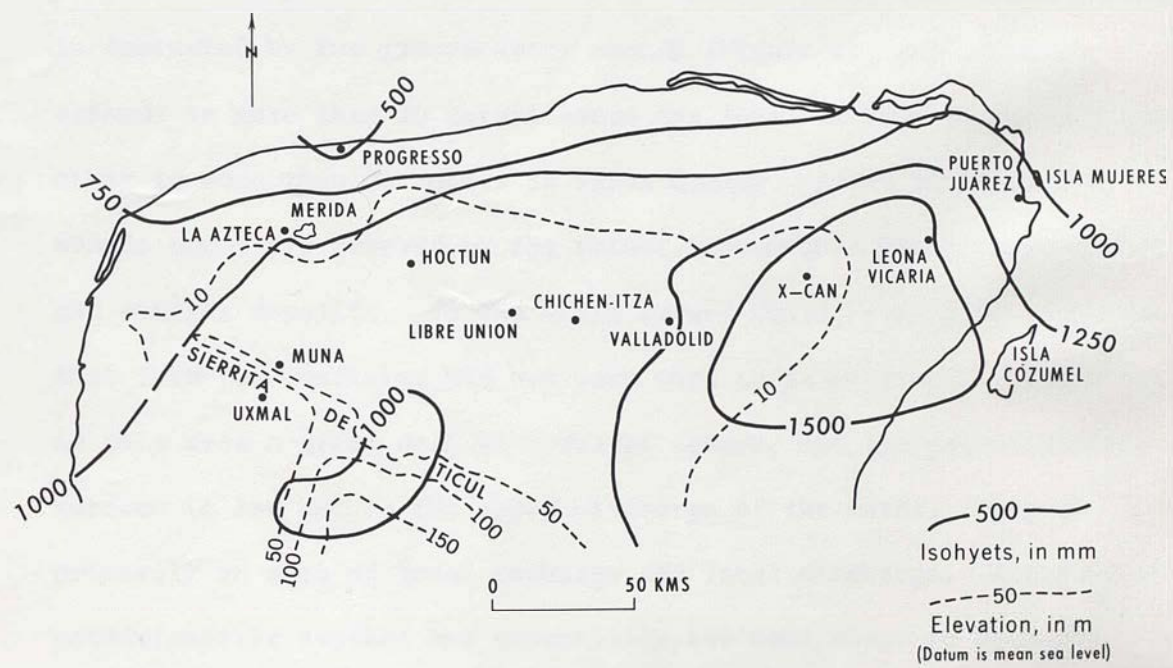


Figure 3.--Physiographic map of northern Yucatan Peninsula showing lines of equal rainfall and location of sampling points.

In summary, the lithology, stratigraphy, climate, and general physiography of the two peninsulas are quite similar; yet the hydrology in both the physical and chemical aspects is remarkably different. These contrasts and their controls are identified and discussed in the following sections of this paper.

Ground-water Flow Patterns

The flow pattern within the principal artesian aquifer of Florida is dominated by two ground-water mounds (Figure 4), one of which extends to more than 40 meters above sea level in Polk County and the other to more than 25 meters in Pasco County. Areas in which the mounds occur are covered by the rather impermeable Hawthorn Formation and younger deposits. To the north toward Ocala, overlying sediments that form the confining bed are very thin to nonexistent. Therefore, in this area a great deal of recharge occurs, but the potentiometric surface is low due to the rapid discharge of the water. This is primarily an area of local recharge and local discharge. Although the potentiometric surface has essentially the same shape to both the north and south, less recharge occurs in the southern portion of the elongated dome due to a thicker confining bed and lower transmissivity of the aquifer.

Figure 5 is a fence diagram that shows the generalized vertical component of the major ground-water flow of central Florida with arrows indicating the direction of movement. Water from a Polk County high moves outward in all directions and is discharged near the coast in eastern and western directions. Toward the north, water is discharged through the many springs that exist in the area of the

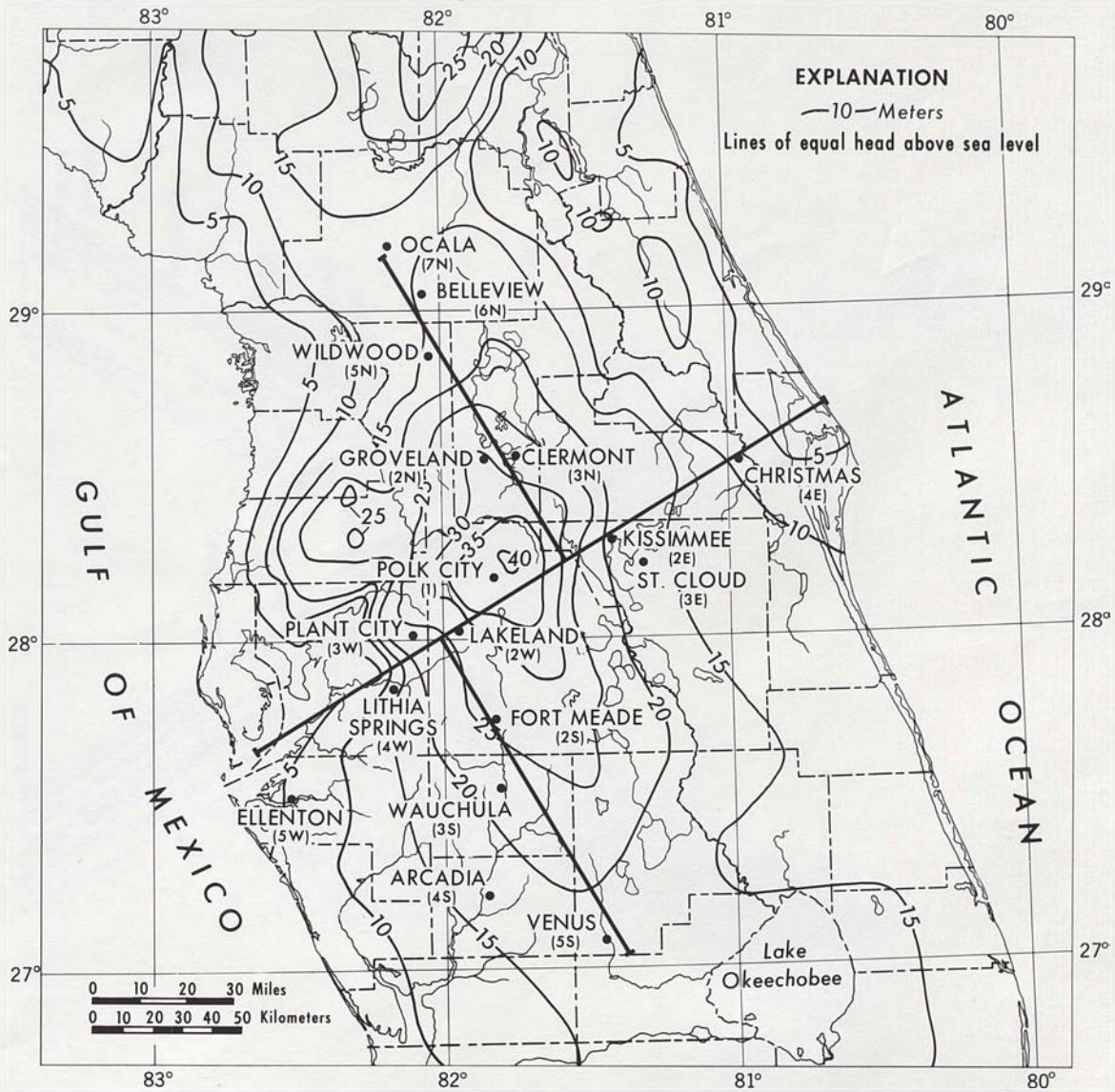


Figure 4.--Potentiometric map of central Florida showing location of sampling points and fence diagrams.

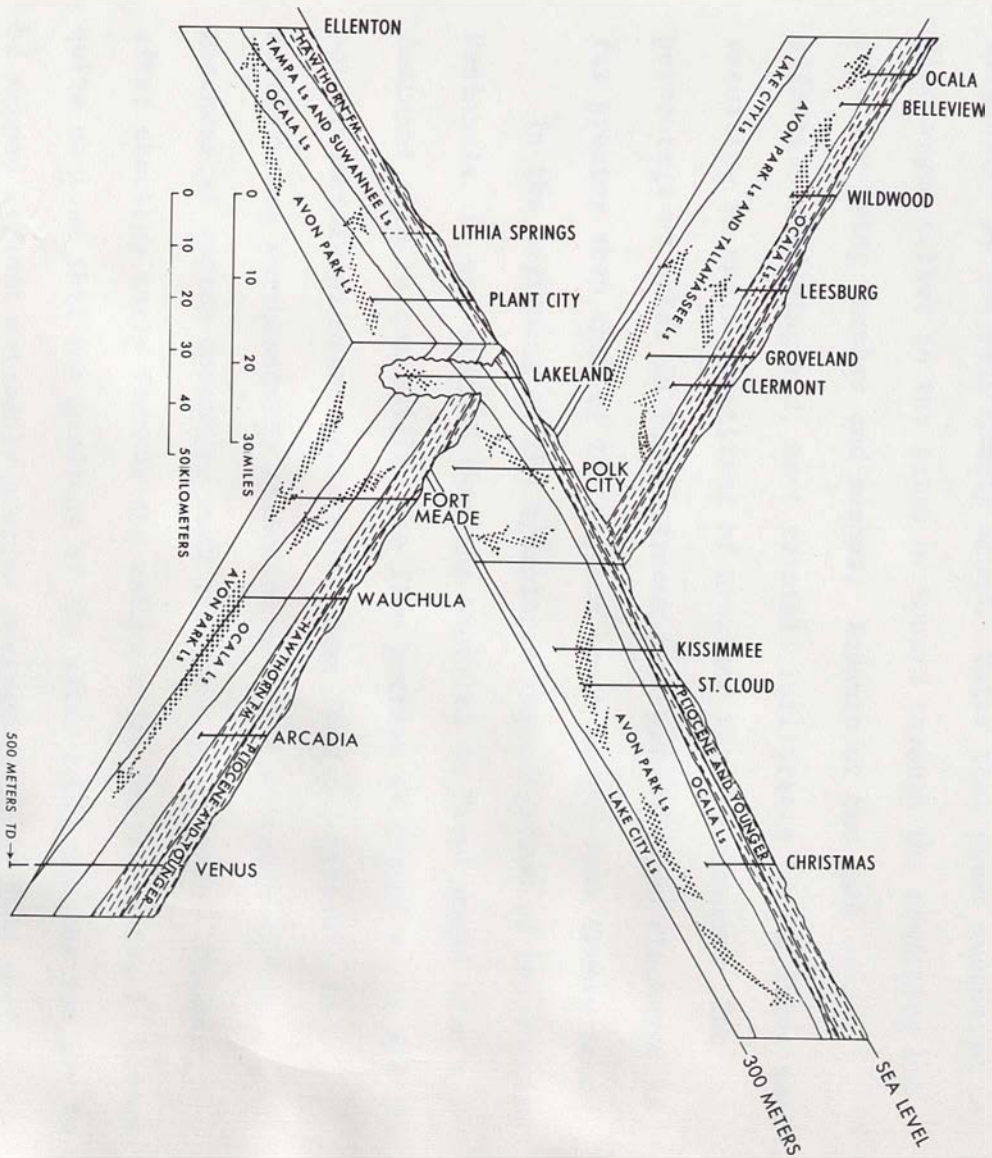


Figure 5.--Fence diagram with arrows showing major ground-water flow in central Florida.

ground-water saddle formed by the Polk County mound and the high area farther to the north. The area from the Polk County high to the saddle contains two rather distinct flow nets, one a shallow system of local recharge in which the flow is essentially short-circuited and locally discharged and the other a deeper circulating system which originates at the Polk County mound. Water that flows southward is discharged either to the ocean or upward through the confining bed into low-lying marshes and swamps. Because of the lack of an effective confining bed, most rainfall infiltrates to the water table, resulting in small quantities of overland flow to streams. The percentage of water in these streams from ground-water discharge is far greater than that of the streams south of the Polk County mound.

In the beginning of the hydrologic investigation of the Yucatan Peninsula, it was assumed that the Sierrita de Ticul would have a dominant role in controlling the flow pattern of ground water and the potentiometric gradient would slope away from the Sierrita in a northern and northeasterly direction and that we would discover a geochemical system operating much like that of Florida. However, after checking early records and making a few measurements, it became quite obvious that the gradient of the water table was far too low to be mapped without extremely precise determination of land surface elevation. However, even with additional measurements, we would still not have an adequate understanding of the hydrologic system nor of the geochemistry, because the downgradient flow pattern would not be a major control. Therefore it became obvious that (1) the usual physical measurement and description of a ground-water system

would be inadequate for the necessary understanding of this area and
(2) the hydrology must be worked out by use of geochemical concepts,
as discussed in the following sections of this paper.

GEOCHEMISTRY

Spatial Distribution of Chemical Constituents

Floridan Peninsula

Although it was obvious that ground water of central Florida is hydrologically connected into one major system, it was necessary to determine if that hydrologic system also was comprised of one geochemical system. Therefore, specific conductance was measured in the field at all wells selected for sampling for geochemical study. Conductance was plotted on a map, and the distribution indicated that the lowest conductance was in the areas with highest potentiometric surface and greatest recharge, with a corresponding increase down-gradient from these areas. It was concluded that the wells, although with a wide range in total depth, were sampling portions of the same hydrologically-connected geochemical system. Location of the geochemical sections are shown on the potentiometric map (Figure 4). The length of the line at the location of each geographic name on the fence diagrams indicates well depth. The well depths sampled during this study ranged from about 100 meters to 500 meters. A standard chemical analysis for samples from each of these wells is given in Table 4.

The total dissolved solids distribution is shown on the fence diagram in Figure 6 and clearly demonstrates the lower concentration of constituents in the area of the ground-water mound and in the area of recharge, with an increase in total dissolved solids down-gradient in all four direction. The highest total dissolved solids

Table 4.--Selected analyses of ground-water samples from central Florida and the Yucatan Peninsula

Index no.	Location	Date of collection	Temperature (°C)	Field pH	Milligrams per liter										Dissolved solids residue at 180°C (mg/l)	Specific conductance (micro-mhos at 25°C)
					SiO ₂	Ca	Mg	Na	K	HCO ₃	SO ₄	Cl	F	NO ₃		
<u>Florida</u>																
1	Polk City	3/15/62	23.8	8.00	0.2	34	5.6	3.2	0.5	124	2.4	4.5	0.1	0.1	138	216
2N	Groveland	3/13/62	23.7	7.80	11	42	4.1	3.6	.5	143	1.6	6.5	---	.1	148	255
3N	Clermont	3/20/62	24.7	7.89	11	25	5.7	5.3	.5	92	3.2	9.5	.1	3.8	112	192
4N	Leesburg	3/12/62	23.6	7.62	15	46	6.7	6.0	1.2	168	2.8	10	.3	.1	172	290
5N	Wildwood 2	3/9/62	23.8	7.59	10	51	2.6	4.7	.2	150	3.2	8.0	.2	3.8	158	290
6N	Belleview 1	3/9/62	22.9	7.59	11	58	8.6	5.0	.6	171	36	8.0	.2	4.1	248	380
7N	Ocala 3	3/8/62	24.9	7.50	11	100	15	7.9	1.0	197	153	12	.2	1.9	420	610
2W	Lakeland	3/16/62	26.3	7.62	18	54	14	6.9	1.0	253	3.6	8.5	.2	.2	238	395
3W	Plant City	5/11/62	26.3	7.62	24	66	11	12	.8	244	.0	12	.4	.1	238	430
4W	Lithia Spgs.	5/11/62	24.5	7.79	15	61	8.6	12	.8	128	66	18	.4	2.9	266	440
5W	Ellenton	5/10/62	26.2	7.58	22	140	68	19	2.7	178	458	25	1.7	.0	874	1200
2E	Kissimmee	5/7/62	24.9	8.10	12	33	2.3	3.9	.8	116	2.8	4.0	.6	.0	115	228
3E	St. Cloud	5/7/62	25.9	7.89	14	51	7.5	7.6	1.1	155	38	9.0	.7	.1	209	370
4E	Christmas	5/5/62	23.8	7.33	18	146	51	340	12	247	254	620	.4	.5	1770	2600
2S	Ft. Meade	3/14/62	26.6	7.75	16	58	17	6.1	.7	163	71	9.0	.4	.1	272	428
3S	Wauchula	5/10/62	25.4	7.69	18	66	29	8.3	2.0	168	155	10	.7	.0	392	600
4S	Arcadia	5/10/62	26.3	7.44	31	106	60	21	3.7	206	344	28	2.2	.0	726	1000
5S	Venus	3/23/63	30.8	7.83	----	80	44	138	4.5	108	202	275	----	----	780	1300
<u>Yucatan</u>																
Y-1	X-Can	5/2/66	24.1	7.22	5.1	94	28	16	.6	382	5.9	34	.2	14	4.8	685
Y-2	Chichen Itza	4/30/66	26.4	7.10	33	83	7.2	14	3.3	253	1.8	34	.3	7.4	338	511
Y-3	Hoctun	4/30/66	27.6	7.15	6.8	82	9.0	25	7.6	252	17	40	.1	38	371	595
Y-4	Leona Vicaria	5/2/66	24.6	6.98	3.9	100	23	51	1.6	402	14	76	.2	1.0	503	831
Y-5	Libre Union	4/30/66	28	6.95	11	120	29	65	3.1	409	18	136	.2	20	687	1060
Y-6	Valladolid	4/30/66	28	7.30	7.9	130	31	82	7.1	430	21	157	.2	29	755	1170
Y-7	Merida	5/4/66	26.8	7.00	8.3	111	34	133	3.5	394	38	229	.2	18	865	1350
Y-8	Muna	5/4/66	23	7.40	31	171	74	234	10	381	350	377	.6	21	1640	2270
Y-9	Puerto Juarez	5/2/66	24.9	7.12	3.6	111	34	222	8.3	328	58	414	.2	4.2	1170	1850
Y-10	Cocoterros	5/3/66	26.8	6.90	12	155	119	837	30	460	206	1500	.4	15	3500	5190
Y-11	Isla Mujeres	5/1/66	27.5	7.30	.4	145	166	1060	41	516	259	1920	1.2	11	4340	6390

shown on these sections is 1770 milligrams/liter (mg/l); however, additional data shows that water near the coasts and south of Lake Okeechobee has a far greater concentration and approaches the salinity of ocean waters. This body of salt water underlies the entire Florida Peninsula and ranges in depth from near sea level at parts of the shoreline to about 700 meters in central Florida. The interface between fresh water and salt water forms one of the boundaries of the fresh-water system. Mapping of other constituents shows a similar pattern with a downgradient increase in chloride, sulfate, calcium, and magnesium. The bicarbonate ion is rather unique in that the concentrations are essentially uniform and do not show the pronounced downgradient increase.

The general chemical character of the water reflects a combined effect of the chemical activity between water and limestone and the flow pattern within the aquifer. One effective method of comparing analyses is to calculate the percentage of each constituent, in milliequivalents per liter (meq/l), and plot on a standard trilinear diagram (Figure 7). Six variables, representing the major constituents, are thereby reduced to a single point whose position in the diamond-shaped field of the diagram indicates the chemical character of the water. The two triangles show relative concentrations of individual cations and individual anions.

Within the study area, most water is of the calcium bicarbonate type. This is indicated by the grouping of analyses at the left apex of the diamond-shaped portion of Figure 7. The Polk City well (1) is close to the highest part of the potentiometric surface, and from here

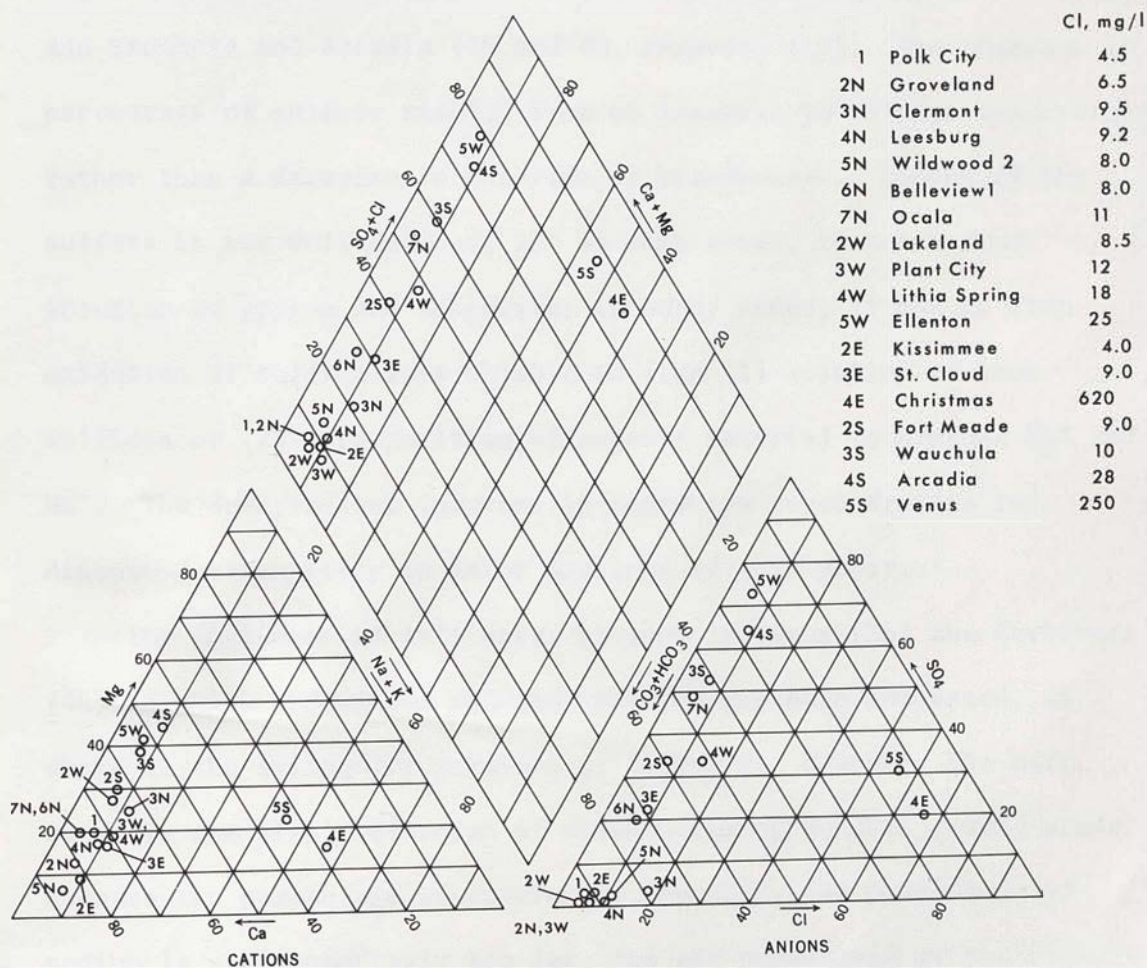


Figure 7.--Trilinear diagram of analyses of ground water from central Florida .

the water flows radially downgradient. The sampling points are numbered and arranged in a corresponding downgradient order.

Chloride concentration (in mg/l) is tabulated on Figure 7 to show the amount of increase downgradient.

The downgradient increase in the percentages of sulfate and magnesium is seen in analyses of wells from Ocala (7N), Ellenton (5W), and Wauchula and Arcadia (3S and 4S, respectively). The increase in percentage of sulfate results from an increase in sulfate concentration rather than a decrease in chloride or bicarbonate. Source of the sulfate is not well defined, but in some areas, it comes from solution of gypsum and anhydrite; in other areas, it may be from oxidation of sulfide ions which come from (1) solution of iron sulfides or (2) decomposition of organic material to produce H_2S and HS^- . The downgradient increase in magnesium concentration is discussed extensively in later sections of this paper.

The influence of salt water is seen in Venus (5S) and Christmas (4E) in which sodium and chloride percentages have increased, as shown in the triangular portions of Figure 7. However, the salt water is not simple dilution of ocean water by potable ground water because the percentage of calcium is too high, the percentage of sodium is correspondingly too low, and the percentage of bicarbonate is too high. This would indicate that additional calcium carbonate has gone into solution. This is what we would expect to observe, based on thermodynamic principles, because salt water can dissolve more limestone than can fresh water. This is caused by the effect that total dissolved solids has on the activity of each ion in solution. For example, let us assume a solution saturated with

respect to calcite; if we add NaCl, the ionic strength will increase, which causes a decrease in the activity coefficient. In order for the activity to remain at the value required for saturation, molality of the Ca^{+2} must increase through greater solution of limestone. Encroachment of salt water could therefore result in greater permeability of the limestone.

Departure of the water from equilibrium with respect to calcite is shown in Figure 8. Again, we have a similar distribution with water in the recharge areas being more undersaturated than that in areas downgradient. Equilibrium conditions are represented by the 100 percent line, plus or minus 10 percent for measurement error. Undersaturation by percentages is less than 100; supersaturation by percentages, more than 100. No doubt, the waters are dissolving calcite in areas designated as undersaturated, but due to kinetic effects, we cannot categorically say that calcite is being precipitated in areas of supersaturation. Because the chemical constituents of aragonite are exactly the same as for calcite, the distribution pattern showing departure of the water from equilibrium with respect to aragonite is directly comparable to that for calcite. All of the water sampled is undersaturated with respect to aragonite with the exception of the sample from Venus (5S). The water is, of course, more undersaturated with respect to aragonite in the areas in which it is undersaturated with respect to calcite and shows a down-gradient increase for aragonite the same as that for calcite.

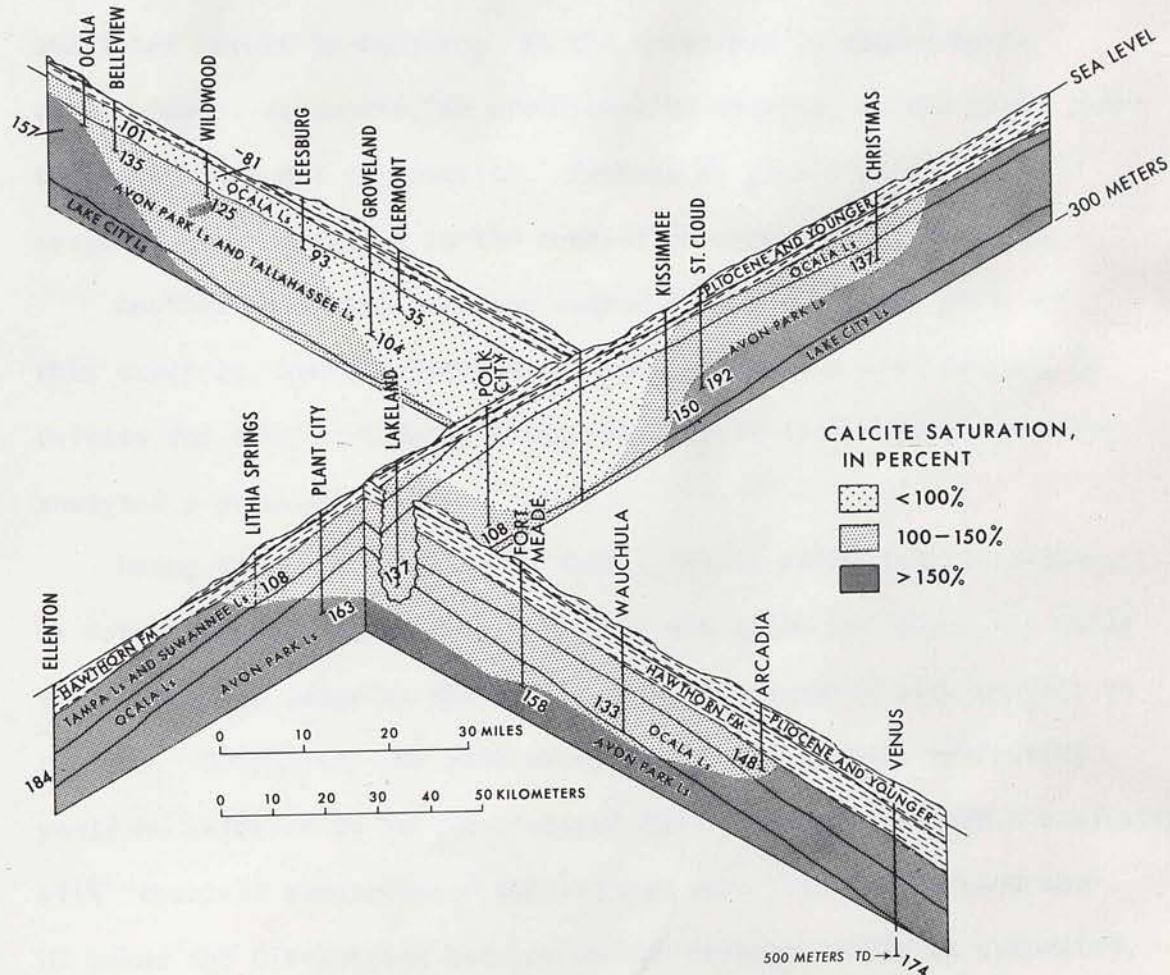


Figure 8.--Fence diagram showing equilibrium conditions between calcite and water of central Florida.

An important question raised by this study is, how can water maintain conditions of supersaturation with respect to calcite over long periods of time. It is suggested that the water may be in equilibrium with magnesium calcite, which has a lower solubility than calcite and will continue to dissolve until equilibrium with aragonite is obtained. Once equilibrium is obtained, aragonite may precipitate and later invert to calcite. In the ocean and in closed-basin environments, aragonite, in preference to calcite, is the usual phase to precipitate out of solution. Perhaps in ground water also, aragonite, not calcite, is the control on carbonate equilibrium.

Another important question raised during the early phase of this study is, how can water remain undersaturated with respect to calcite for long periods of time. Thrailkill (1968) has carefully analyzed a related problem.

Using the geochemical data from caves in which calcium carbonate is depositing, he assumes that because the caves are above the water table, seepage water in the vadose zone is saturated with respect to calcite. Ordinarily the zone above the saturated zone (phreatic) would be referred to as "unsaturated zone"; however, to avoid confusion with "chemical saturation," the archaic term "vadose" is used here. He makes the distinction between vadose seepage, which is saturated, and vadose flow, which is believed to be undersaturated. Accepting that this is true, he then addresses himself to the question of how solution of limestone can occur below the water table; that is, how can water become undersaturated after it reaches the main water body. He concludes that the major controls generating conditions of

undersaturation are (1) temperature effect, (2) mixing effect, and (3) flow rate. If more rainfall occurs during warm summer months, it is possible that the infiltrating water has a temperature slightly higher than that of the main water body. If the infiltrating water becomes saturated with respect to calcite and is cooled in an environment in which carbon dioxide gas is available, the water will become undersaturated because of the cool water's added capacity to dissolve CO_2 and thereby dissolve more calcite. However, it would be expected that as the water adjusted to its new environment, it would dissolve enough calcite to again come into equilibrium. During the present study, it has not been possible to collect any field data to determine whether the vadose seepage is truly saturated with respect to calcite or whether it also is undersaturated, as is ground water in the recharge areas.

In discussing the second control, Thrailkill shows that the effect of mixing two solutions, both saturated with respect to calcite but in equilibrium with vapor phases at different values of partial pressure of carbon dioxide, will result in undersaturation. Again, without reliable samples of water from the vadose zone, it is impossible to determine whether the P_{CO_2} is different from the P_{CO_2} in ground water, and if so, if this difference is maintained for long travel paths. We would expect that with availability of calcite, the new mixture with the resulting P_{CO_2} would attain equilibrium by additional solution of calcite. Thrailkill recognizes that the mixing effect will result in significant saturation only under optimum conditions and that it tends to be ineffective when the vadose seepage

or the ground water is supersaturated with respect to calcite or is at equilibrium with a high P_{CO_2} .

The third control, flow rate, is significant because during times of high flow in streams, water tends to be undersaturated with respect to calcite, and during low flow, is in equilibrium or supersaturated. If water during times of high flow enters the ground-water body, this would, of course, cause the ground water to be undersaturated. However, if the kinetics are as rapid as the laboratory experiments would indicate (Weyl, 1958), we would expect that the water would come into equilibrium in a shorter flow distance than indicated on Figure 8.

In summary, Thrailkill's excellent study has shown how calcite can be deposited above the water table and can be dissolved below the water table. However, we are still unable to answer the question as to how the ground water can remain undersaturated. The answer may be simply that the kinetics of the reaction are far slower than laboratory experiments would indicate.

The distribution pattern with departure from equilibrium with respect to dolomite is shown in Figure 9. The equilibrium constant used is 2×10^{-17} (Isu, 1963, and Barnes and Back, 1964). The same general pattern is shown with water in the recharge areas being undersaturated with respect to dolomite and progressively obtaining equilibrium and supersaturation downgradient. The lack of equilibrium with respect to dolomite in the recharge areas is no doubt controlled by the low magnesium content of ground water and perhaps by the kinetics of the reaction. As the water moves downgradient, calcium

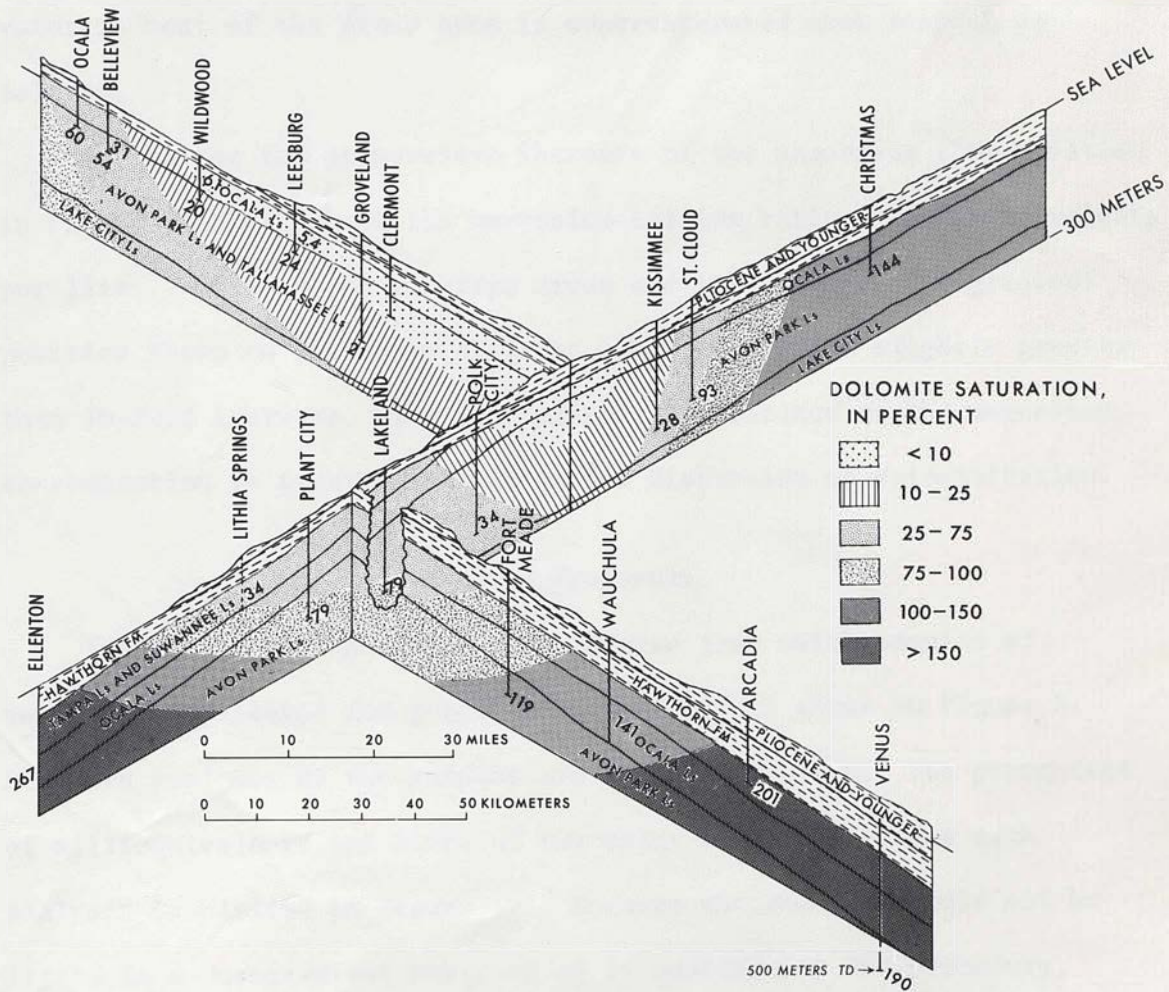


Figure 9.--Fence diagram showing equilibrium conditions between dolomite and water of central Florida.

concentration increases by an order of about 3, and magnesium concentration increases far more significantly, a factor of up to 30 times the concentration of magnesium in the recharge area. The increase in magnesium content is caused by the greater solubility of the magnesium-calcite compared to pure calcite. The concentration of calcium is maintained at a rather constant value because ground water in most of the study area is supersaturated with respect to calcite.

We can see the progressive increase of the magnesium concentration in Figure 10 which shows the magnesium-calcium ratio in milliequivalents per liter. Between the recharge areas and the farthest downgradient position shown on the fence diagrams, the ratio has a slightly greater than 10-fold increase. The geochemical significance of the magnesium concentration is treated further in the discussion of dolomitization.

Yucatan Peninsula

The location of points in the Yucatan from which samples of water were collected for geochemical analysis is shown in Figure 3. Standard analyses of the samples are shown in Table 4. The percentage of milliequivalents per liter of the major constituents for each analysis is plotted in Figure 11. Because the analyses could not be listed in a downgradient position as is customarily the procedure, they are shown in order of increasing chloride concentration.

Analyses 1 through 6 are of water samples with lowest total dissolved solids and are a calcium-bicarbonate type as expected for water from a limestone aquifer. The next two analyses of samples from Merida and Muna are an indistinct type with no cation or anion species

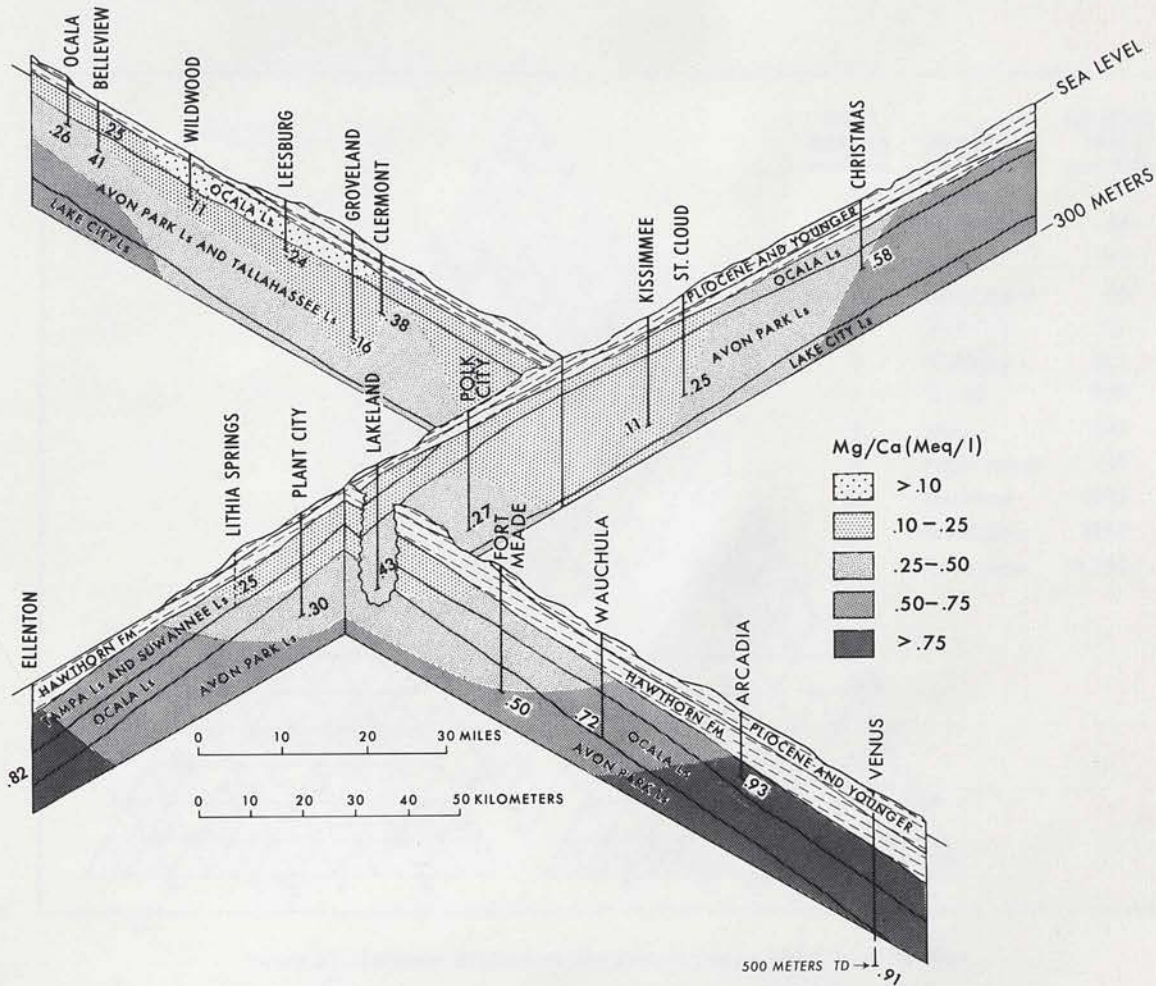


Figure 10.--Fence diagram showing distribution of Mg/Ca in ground water of central Florida.

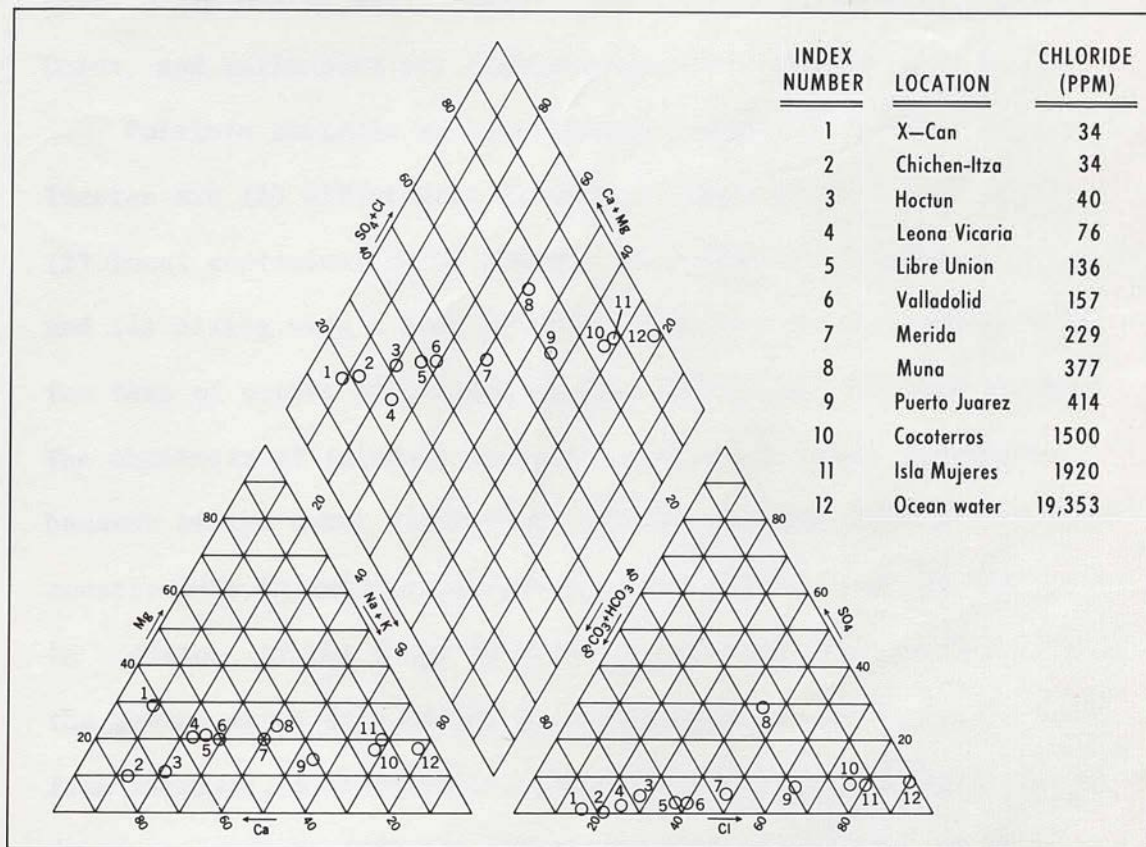


Figure 11.--Trilinear diagram of analyses of ground water from Yucatan.

exceeding 50 percent of the total constituents. The last three analyses are brackish ground water from near the coast and are sodium-chloride-type water. The analysis identified as "Cocoterros" is from the hotel of that name at the eastern edge of Progreso. The analysis identified as "Merida" is from La Azteca Ranch a few miles west of the city. The samples were collected at the end of the dry season, April 30 to May 3, 1966. Samples from X-Can, Leona Vicaria, Libre Union, and Valladolid are from cenotes; the rest are from wells.

Possible controls on the chemical character of water in the Yucatan are (1) differences in chemical composition of rainfall, (2) local contamination by sewage, (3) solution of carbonate minerals, and (4) mixing with a body of salt water that is believed to be a few tens of meters below land surface throughout the area of study. The chemistry of rainfall is believed to be of minor importance because of the great differences between the concentration of major constituents in rainfall and that of the ground water in the Yucatan. In addition, if the range in chloride and total dissolved solids of the ground water from different locations were due to cyclic salts from rainfall, a distribution pattern would form showing a systematic decrease landward from the prevailing wind direction. No such pattern can be detected.

Domestic and village sewage locally contaminate water in the aquifer as indicated by the moderately high concentration of nitrate. In addition, ground-water supplies contaminated by sewage commonly have a concentration of chloride higher than that of water from the potable portion of the aquifer. However, sewage cannot be

considered a dominant control on the observed chemical character of the water. If the wide range of chloride concentration and total dissolved solids were due to sewage contamination, a correlation would exist between chloride and nitrate concentration; none exists (Table 4). Therefore, the dominant processes controlling the chemical character are solution of carbonate minerals and mixing with subsurface salt water.

This is clearly shown in the diamond portion of Figure 11. The water with lowest chloride concentration, analysis number 1, is in a typical position on the figure for water from carbonate aquifers. The position of each succeeding analysis, as the chloride concentration increases, describes a straight line to the position of standard ocean water plotted as sample number 12. Analysis number 8, slightly off the line, is from an area near the Sierrita. It differs from the other analyses in having a high calcium and sulfate concentration, possibly indicative of the occurrence of gypsum or anhydrite in that area. Anhydrite beds have been discovered at a depth of 125 meters at X-Can and at depths ranging from 100 to 150 meters in most areas south of the Sierrita de Ticul. The straight line plot of all other analyses indicates that the water sampled has been in contact with no minerals other than the carbonate minerals of calcite, aragonite, and dolomite; that is, this is a mineralogically uniform aquifer.

The trend of the data in Figure 11 clearly indicates little change in the chemical character of the water due to any processes other than simple mixing with ocean water and solution of carbonate rock. The relative effects of these two processes are shown in

Table 5 for the sample of water from Isla Mujeres. This analysis has the highest total dissolved solids of any sample collected. Table 5 shows that this sample of ground water on Isla Mujeres has its origin as ocean water which has been diluted by rainwater infiltration by a factor of about 10. In other words, if we consider concentrating ground water by a factor necessary to increase the chloride content to be equal to that of sea water, in this case 10.08, we would obtain the resulting analysis as indicated. The difference indicates those changes that have occurred due to the solution of minerals. The primary changes are a great increase in bicarbonate and calcium concentration and a smaller increase in magnesium concentration, as would be expected from solution of calcite and dolomite. Agreement of sodium and potassium concentrations between the two analyses is excellent. Decrease of the sulfate ion may be the result of a sulfate-reducing bacteria whose metabolic processes generate carbon dioxide which forms bicarbonate ion. Strontium is a common constituent of carbonate rocks; therefore, solution of these rocks will increase the strontium content of ground water. The relatively high concentration of fluoride is significant and should be explored further. Typical ground water in Florida has a similar concentration of fluoride and presumably is from phosphate material in Tertiary limestones and Miocene sediments. Even though the analysis of water from Isla Mujeres used to calculate Table 5 is the most concentrated sample collected during this study, calculations comparing other analyses with ocean water give similar results.

Table 5.--Comparison of ocean water and ground water on Isla Mujeres

	Chemical analysis Isla Mujeres (mg/l)	Hypothetical ground water ^{1/} (mg/l)	Chemical analysis ocean ^{2/} (mg/l)	Comparability ^{3/} (percent)
Ca	145	1,462	413	354
Mg	166	1,673	1,294	129
Na	1,060	10,684	10,760	99.1
K	41	413	387	106
HCO ₃	516	5,201	142	370
SO ₄	259	2,610	2,712	96
Cl	1,920	19,353	19,353	100
Sr	3.3	33	8	410
F	1.2	12	1	1,200

^{1/} (hypothetical ground water) = (chemical analysis, Isla Mujeres) X (concentration factor, 10.08).

^{2/} Culkin, 1965, p. 122.

^{3/} (comparability) = (hypothetical ground water) X 100/ocean water.

The degree to which the water has obtained equilibrium with the three common carbonate minerals is shown in Table 6. An ion activity product is calculated from the chemical analysis of the water; this value is compared with the equilibrium constant for the particular mineral under consideration. A value of 100 percent on Table 6 represents equilibrium between the mineral and the water. Those analyses with values lower than 100 percent are undersaturated and capable of dissolving more mineral; analyses with values greater than 100 percent are supersaturated. Ground-water samples from Valladolid, Muna, and Isla Mujeres are supersaturated with respect to calcite, aragonite, and dolomite. Therefore, such minerals may be forming at those locations. For example, on Isla Mujeres beach rock is forming; the high value for saturation with dolomite (Table 6) suggests that this island would be a likely place to observe dolomitization processes.

Geochemical Interpretation and Comparison of Florida and the Yucatan

Some of the striking differences in the chemical character of the water between the two peninsulas have been described and are summarized in Figure 12 which shows the changes in the chemical constituents as the water becomes more concentrated. This illustration is a combination of Figures 7 and 11. As stated earlier, the hypothesis that was deduced from this graph is that one of the dominant controls on the chemistry of the water of the Yucatan is a mixing of potable water with underlying salt water. In order to test this hypothesis, the magnesium-calcium ratio was plotted against the chloride concentration, as shown in Figure 13. We see that for the Yucatan analyses, an

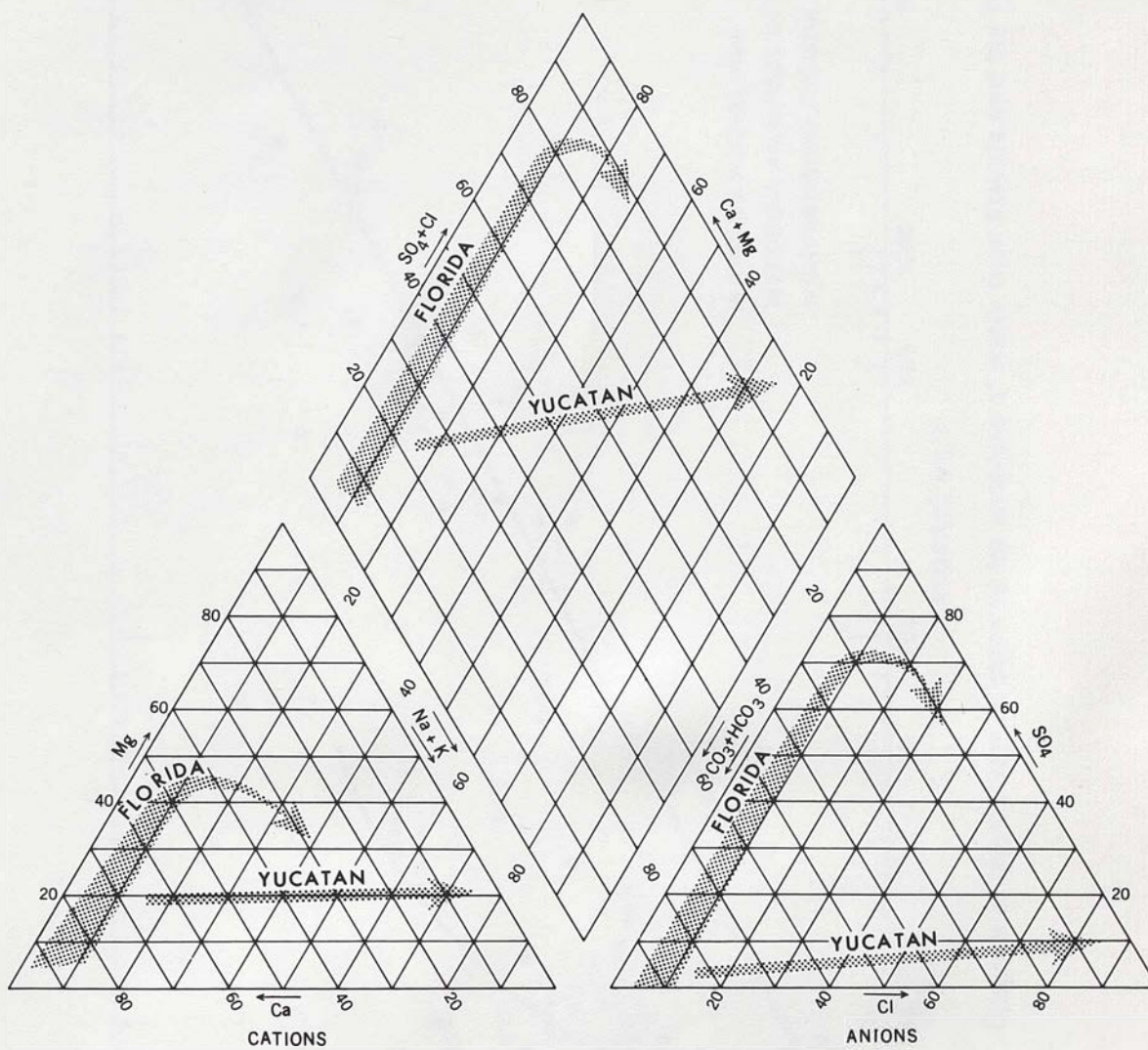


Figure 12.--Trilinear diagram showing the geochemical path of ground water for the two peninsulas.

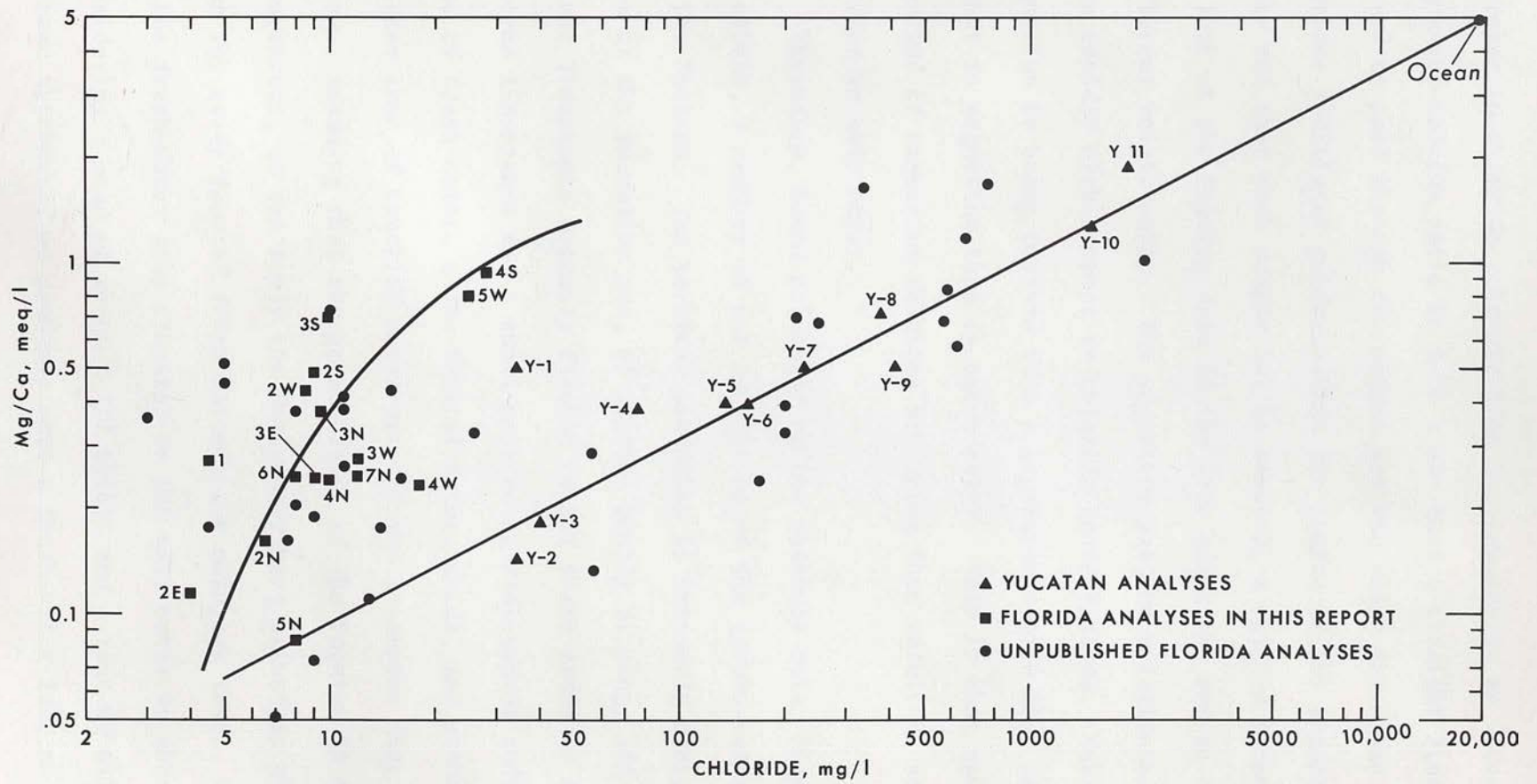


Figure 13.--Diagram of Mg/Ca versus chloride for analyses of water from Florida and the Yucatan.

increase in chloride concentration corresponds to an increase in magnesium-calcium ratio in such a way that a straight line can be fitted to pass through the points and the value for ocean water. This provides additional evidence that the source of the magnesium is ocean water and that each sample is, in essence, a diluted ocean water. When we look at the Florida data on the same graph, we see an entirely different relationship. The magnesium-calcium relationship increases more rapidly with respect to chloride concentration. This means that magnesium is being derived from a magnesium source that is relatively richer in magnesium than is ocean water. This is what would be expected if magnesium calcites are going into solution, as mentioned earlier in this paper.

Therefore, based primarily on the chemical data, Figure 14 is, in effect, a summary of our conception of the ground-water hydrology of the Yucatan. The vertical dimension is extremely exaggerated; dips of the formation are, of course, gently dipping, and we have Eocene limestones actually flanked on all three sides by Pliocene-Miocene limestones and a small portion of Pleistocene sediments. The lens of fresh water, a few tens of meters thick, and probably a much thicker zone of brackish water overlies the extensive body of salt water. Assuming that the permeability of the Yucatan is fairly homogeneous, we can apply the Ghyben-Herzberg principle which states that for every foot of fresh water above mean sea level, the thickness of the fresh-water lens floating on the salt water is about 40 feet. Considering a head of about 1 1/2 meters and a zone of diffusion of unknown thickness, we probably have a fresh-water lens of no more

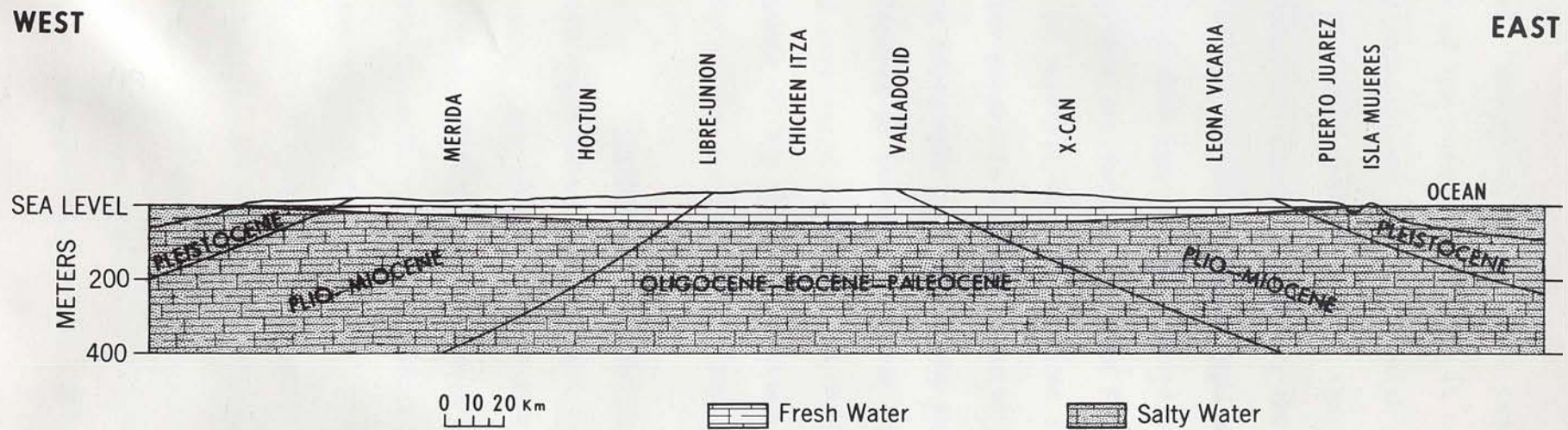


Figure 14.--Diagrammatic section of the Yucatan showing the relative distribution of the fresh and salty water.

than 70 meters. The water level in the cavernous limestone in the northern part of the Yucatan Peninsula is near sea level because the sinkholes and cavities are not filled with permeable, unconsolidated sands. Many sinkholes and cavities in the limestone of Florida are filled with permeable sands that filter the water and reduce permeability enough to give a higher head than in the Yucatan.

The Yucatan does not contain Miocene clay and marl, such as those that overlie the limestone in the Florida Peninsula and cause infiltration of rainfall to the saturated zone to be slow. The covering of low-permeable material permits the development of the gently rolling topography of Florida and provides the hydrologic base for the development of integrated stream systems. If the Hawthorn Formation and associated deposits were stripped from Florida, the resulting surface of the exposed limestone aquifer would be quite similar to the present surface of the Yucatan.

Carbonate Geochemistry

It appears significant that all the analyses on Figure 13 have a magnesium-calcium ratio of less than 1 with the exception of a few analyses with high chloride values that are near the shoreline in both Florida and the Yucatan. These data suggest that there may be a mineralogic control operating in Florida and the Yucatan that limits the magnesium-calcium ratio in ground water. A possible controlling mineral is dolomite, and perhaps dolomitization of limestone is occurring in the ground-water environment. Owing to many unanswered questions relating to the genesis of dolomite, and great interest in the processes of dolomitization, this idea is explored further.

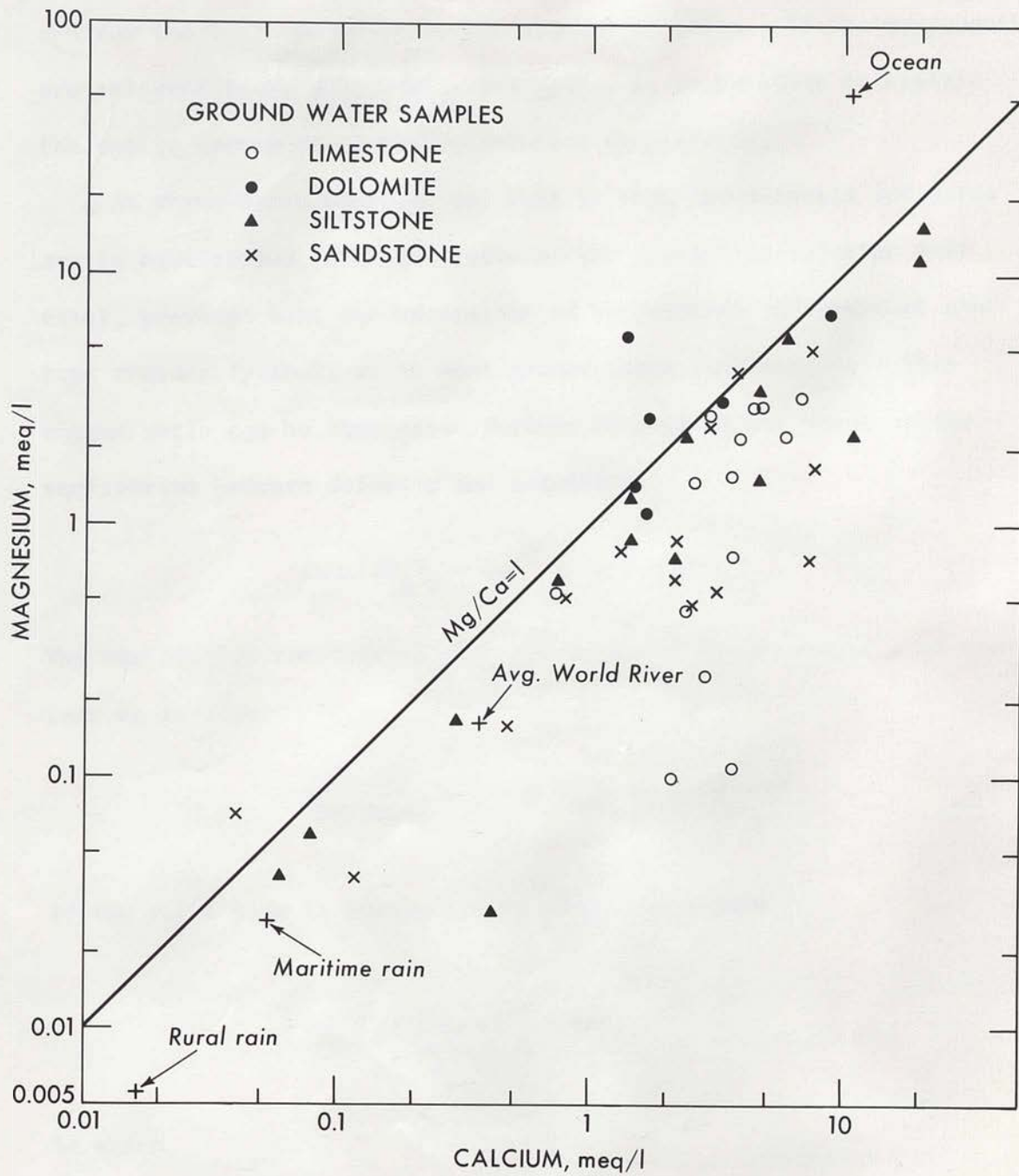
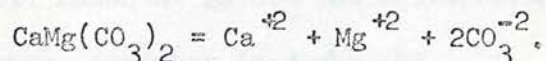


Figure 15.--Plot of Mg versus Ca for samples from various aquifers.

In order to test the hypothesis that calcite and dolomite are two of the major controls on the geochemistry of water in carbonate terrains, it is necessary for our phases to be calcite and dolomite and for the third phase to be the aqueous solution. If the components are selected to be H_2O , CaCO_3 , and MgCO_3 , it is possible to explain the entire system of carbonate solution equilibrium.

At three-phase equilibrium, that is when the minerals and water are in equilibrium, a unique ratio of the species in solution must exist, provided that the excursions of temperature and pressure are kept reasonably small as in most ground-water environments. This unique ratio can be considered further by writing the equation for equilibrium between dolomite and solution:



The equilibrium constant, K_{dolomite} , is equal to the activity of the ions as follows:

$$K_{\text{dolomite}} = \alpha_{\text{Ca}^{+2}} \cdot \alpha_{\text{Mg}^{+2}} \cdot (\alpha_{\text{CO}_3^{-2}})^2.$$

If the right side is multiplied by $\frac{\alpha_{\text{Ca}^{+2}}}{\alpha_{\text{Ca}^{+2}}}$, we obtain

$$\alpha_{\text{Mg}^{+2}} \cdot \frac{(\alpha_{\text{Ca}^{+2}})^2}{\alpha_{\text{Ca}^{+2}}} \cdot (\alpha_{\text{CO}_3^{-2}})^2$$

in which

$$(\alpha_{\text{Ca}^{+2}})^2 \cdot (\alpha_{\text{CO}_3^{-2}})^2 = (K_{\text{calcite}})^2.$$

We obtain

$$K_d = \frac{\alpha_{Mg}^{+2}}{\alpha_{Ca}^{+2}} \cdot K_c^2$$

or

$$\frac{\alpha_{Mg}^{+2}}{\alpha_{Ca}^{+2}} = \frac{K_d}{K_c^2} = \text{a constant,}$$

which means that for three-phase equilibrium, dolomite-calcite-solution, the $\frac{\alpha_{Mg}^{+2}}{\alpha_{Ca}^{+2}}$ is fixed at constant value.

This constant may vary slightly if we are not dealing with pure end members; that is, if the calcite contains a minor amount of magnesium ion or if the dolomite contains extra calcium or magnesium instead of a 50-50 stoichiometric amount. The equilibrium constant for calcite is well known at 25°C. The equilibrium constant for dolomite is, however, somewhat in doubt; $K_{dolomite}$ determined by several laboratories differs by as much as three orders of magnitude. More recent work has estimated the equilibrium constant for dolomite from the composition of various subsurface waters, and these are all in the range of 1.5 to 3.0×10^{-17} (Barnes and Back, 1964, and Hsu, 1963).

In Figure 16 are plotted the magnesium versus calcium concentrations of samples from Florida and the Yucatan, Again, as with data from Figure 15 from various types of aquifers, most of the points fall below the magnesium-calcium ratio of 1. The three points from Florida above the line have a magnesium-calcium ratio greater than 1; these wells all occur along the coast and produce a mixture of oceanic waters and the potable waters of the aquifer which

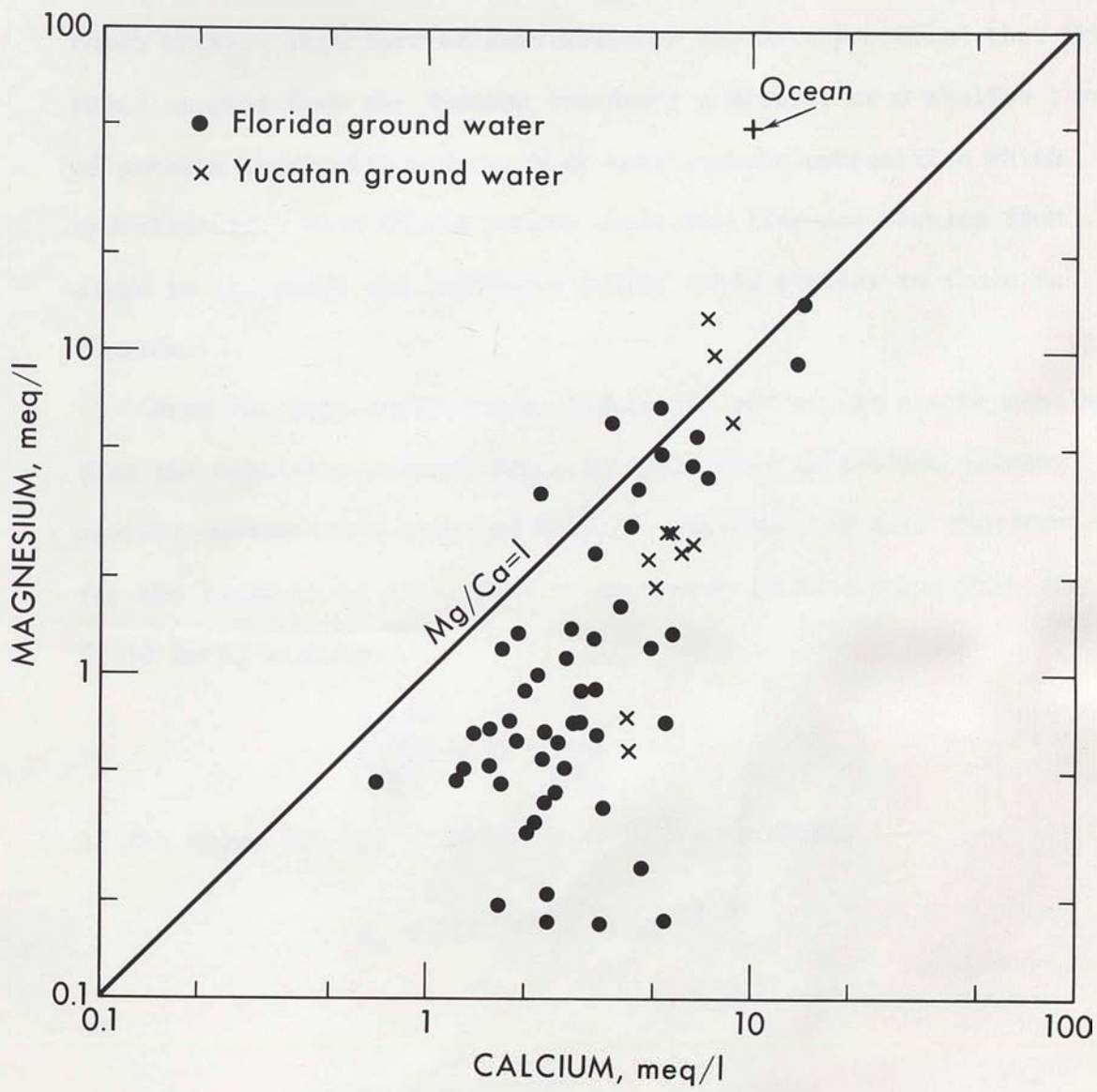


Figure 16.--Plot showing the limiting control of Mg/Ca of unity for Florida and Yucatan.

have a lower magnesium-calcium ratio. Apparently these waters are supersaturated with the phases under consideration. Of particular interest and corroborating the above statements about the Florida water are the analyses from the Yucatan. These fall within an almost straight line which passes through the magnesium-calcium point for ocean water. This further substantiates the interpretation that the water samples from the Yucatan represent a mixture of a shallow layer of potable water with a large body near oceanic composition which underlies it. Both of the points above the line are samples from close to the coast and represent saline wells similar to those in Florida.

From the data presented in Figures 15 and 16, it can be concluded that the magnesium-calcium ratio is apparently controlled in many aquifer systems at a value of unity. Therefore, if 1 is the constant for the equation of three-phase equilibrium as it appears from the field data, we have

$$\frac{\alpha_{Mg}^{+2}}{\alpha_{Ca}^{+2}} = 1; \quad \frac{K_d}{K_c^2} = 1.$$

If the value for K_c , at 25°C, is $10^{-8.35}$, we obtain

$$K_d = (10^{-8.35})^2 = 10^{-16.7}$$

or

$$K_d = 2 \times 10^{-17}$$

which lends further support to this being the correct value for the equilibrium constant for dolomite.

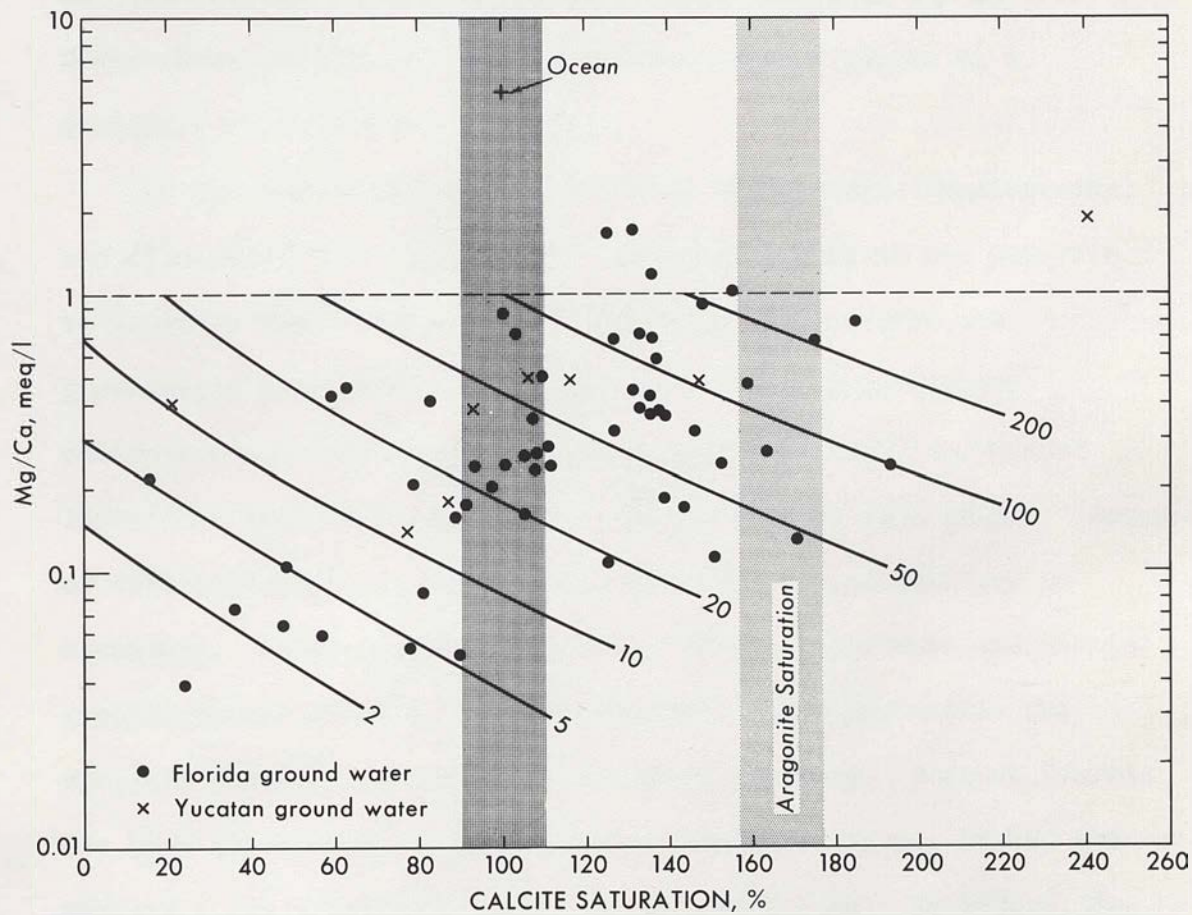


Figure 17.--Diagram showing relationship between the Mg/Ca and equilibrium conditions for aragonite, calcite (shaded areas), and dolomite (solid lines).

CONCLUSIONS

This study demonstrates that (1) the law of mass action provides an adequate model for interpreting the geochemical system and (2) that the equilibrium method provides a rational basis for identification of the reactions and processes that generate the resulting chemical character observed in nature. Even if the system is not in equilibrium, we are able to predict which reactions may be occurring. Under these conditions, the equilibrium concept serves as a reference point for interpretation.

In the hydrologic systems studied, the geology, physiography, and climatology are all dominant controls, and it is not possible to separate their effect on the resulting flow pattern and geochemical processes. As a result of similar depositional environments, major aquifers in both peninsulas are composed of limestones that were deposited in fairly shallow warm waters. Because of this lithology, it follows that much of the permeability is secondary. After deposition of the sediments, tectonic and physiographic forces exerted a major influence. Both peninsulas are emergent portions of a broader carbonate platform. Because Florida has been elevated to a greater height above sea level, it has the potential for a higher head in the saturated zone. Therefore, due to the lower altitude of the Yucatan Peninsula, it would be impossible to generate heads as high as those observed in Florida regardless of the permeability distribution or the amount of recharge water available. However, a major lithologic control on the head distribution of Florida is the Hawthorn Formation and associated sediments of low permeability.

Because these sediments decrease leakage rates, and thus decrease the volume of water reaching the limestone, the amount of solution is lessened, which in turn slows development of secondary permeability. In addition, the secondary porosity and permeability developed by solution in the upper part of the limestone aquifer are decreased by filling the channels and sinks with sand and clay of the clastic deposits. This filling process could have occurred during deposition of the Miocene sediments or during development of the subterranean karst surface. Also, if the clays had not been deposited in Florida, we would not have gently rolling topography with integrated stream drainages that have developed because of "rejected recharge," but rather we would have a rugged karst topography very similar to that of the Yucatan.

In addition, even though the climate of the two peninsulas is quite similar and considering the effect of differences in lithology and physiography, we cannot rule out the role of meteorologic phenomena. If the Yucatan did not have a warm humid climate, the ground-water flow pattern could be appreciably different. That is, if the Yucatan were in a cold climate, we would not have the lush vegetation that contributes high quantities of carbon dioxide gas to the infiltrating water. Without the high partial pressure of CO_2 , we would not have the solution that has occurred in the Yucatan, and the top portion of the aquifer would be far less permeable than it now is. However, the effect is counteracted to a certain extent by the lower solubility of CO_2 in warmer water which decreases the solvent power of the water.

This study has further demonstrated that in order to understand the controlling chemistry of an aquifer, we must know the hydrology. There is no such thing as a water analysis "typical" of carbonate aquifers; we must know in which part of the system the sample was obtained--recharge area, discharge area, or area of lateral movement. In addition, was the sample obtained near the boundary of a system? If so, what sort of a boundary--mineralogic, lithologic, or chemical? Is the sample mixed water from two sources, such as the interface in areas of salt-water encroachment? The geochemical processes cannot be studied outside their natural geologic and hydrologic environments. Equally important, this study has also demonstrated that in some areas, even hydrologically simple ones, it is not possible to analyze the hydrologic system by purely physical measurements; often the key to understanding lies in the results of geochemical processes. It was only through the geochemical investigation that the shallow boundary of the fresh-water system in the Yucatan was identified as being the salt-water interface.

This study further emphasizes the great need for an integrated study of all controls affecting the ground-water flow. This is particularly important at a time when so many conceptual models--analog, digital, and economic--are being developed to optimize utilization of our water resources. It is not adequate to investigate a small area and determine whether it is suitable for waste disposal, recharge of potable water, or development of water supplies. The areal investigation must be looked at within its total hydrologic system. Within every system some areas are more suitable for injection of

materials than for withdrawal of ground water. Controls of the various portions of the system must be clearly identified, and their relative role evaluated in relation to the potential use of that area.

A great deal of work remains to be done on the general topic of carbonate geochemistry and carbonate hydrology. In the Florida Peninsula alone, there are many unanswered questions: What is the effect of the physical and chemical limnology of the lakes on the shallow aquifer system and on the major artesian system? We know little about the mineralogy, permeability distribution, or chemistry of the water in the confining beds in Florida. Even the mineralogy of the aquifer is inadequately known. Such questions arise as: is there any aragonite; where is the dolomite; what percentage of the calcite is magnesium calcite; what is the chemistry of the water in the vadose zone; how do we compare the partial pressure of CO_2 in the vadose zone with that in the phreatic zone; what is the role and influence of the sulfur cycle in solution and deposition of carbonate minerals; and how do we resolve the question of kinetics of the reactions, that is, between apparently fast reactions obtained in the laboratory and the fact that the ground water remains undersaturated for long periods of time.

Additional understanding of certain topics of limestone hydrology can be obtained by application of isotopic geochemistry which is beyond the scope of this dissertation. Interpretation of radiocarbon, C-12, and C-13 analyses of both Florida and the Yucatan is being made in a corroborative study in which the preliminary results substantiate the concepts and conclusions presented here. It would probably be

fruitful to undertake a study of the tritium concentration of water in the Yucatan.

A full understanding of certain aspects of these questions is no doubt indeterminant. However, at the present time, it probably is not possible to identify which are not suitable for further investigation. The best we could do would be to list these problems in order of priority, and the order or priority is always quite subjective, with the background, talent, and interest of the investigator being a dominant influence. Nevertheless, a great challenge remains in unraveling the complexities of carbonate hydrology.

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