Chapter 7

Hydrogeology of the Yucatán Peninsula

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GENERAL GEOLOGY OF THE NORTHERN YUCATÁN PENINSULA

The northern Yucatán Peninsula, Mexico is a partially emergent carbonate platform with an extensive continental shelf. Mesozoic- and Cenozoic-era limestone, dolomite, and anhydrite overlie deeply buried Paleozoic-era crystalline and sedimentary rocks. The peninsular aquifer system has developed in nearly horizontal, highly-permeable rocks that are dominantly Tertiary period limestones and dolostones. These are thinly covered by Holocene and Pleistocene epoch carbonate rocks and sediments along the coast, as well as by a thin cover of soil inland. Rocks are both porous and permeable, and permeability exists on two scales: cavernous (fracture) and intergranular (porous medium).

Exceptionally permeable zones are developed along faults, perhaps generated by Eocene epoch Caribbean plate movements in the east and, in the northwest, by crustal relaxation and/or basin loading caused by the impact of a large meteorite or comet (Hildebrand et al. 1995). An additional prominent fault, the Ticul Fault Zone (Figure 7.1), whose origin is difficult to assign to a specific tectonic event, is present in the northwest portion of the peninsula. These faults are important as channels for groundwater movement.

Eugene Perry acknowledges financial support from NSF Grants EAR-9304840 and EAR-9902971, as well as from the Northern Illinois University (NIU) Graduate School. Velazquez-Oliman acknowledges a graduate fellowship from the Consejo Nacional de Ciencia y Tecnologia and from the Direccion General de Asuntos del Personal Academico (DGAPA). We thank Ing. Ismael Sanchez for providing us with a sample of rainwater from Tropical Storm Mitch and Willard Moore for permitting us to include his ^{226}Ra measurements.

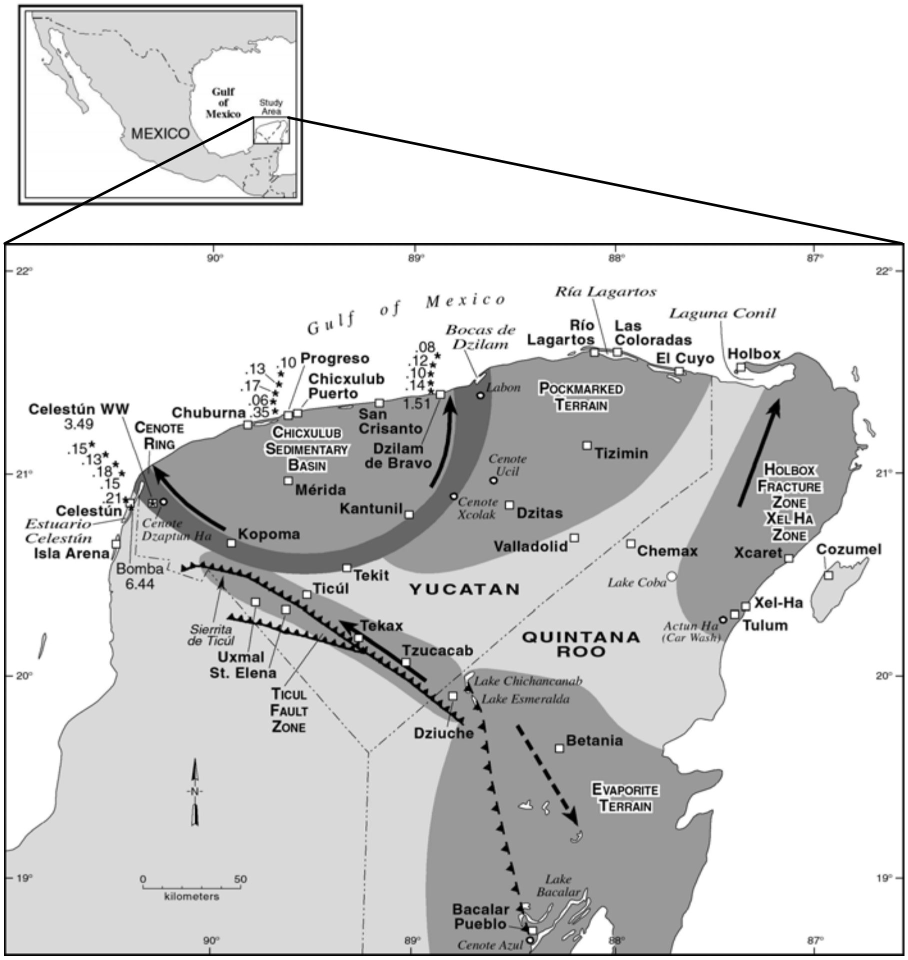

FIGURE 7.1 Map of the northern Yucatán Peninsula showing the major geostructural features and an outline of hydrogeochemical terrains discussed in the text. (Inset map of Mexico shows location of study area). Radium (^{226}Ra) isotope values in dpm/l are shown for three seaward traverses, starting from Celestun, Progreso, and Dzilam de Bravo, and extending 20 km seaward. ^{226}Ra is also plotted for "Bomba" (a coastal spring) and for the Celestun Water Works (WW). Faults are indicated by lines with serrated edges, dashed where uncertain. Groundwater flow directions are indicated by large arrows, dashed where uncertain.

Over almost the entire northern region, a thin freshwater lens is underlain by a marine saline intrusion. North of the Champoton River, in Campeche, there are no permanent streams of more than a few hundred meters length along the west and north coasts. On the east coast of the peninsula, significant streams are not present in Mexico, but do occur in Belize. An extensive aquitard has developed within the surface calcrete layer along the entire north coast from Isla Arena (Campeche) to Holbox

(Quintana Roo); but, with this exception, there are no extensive aquitards beneath the northern peninsula.

The distinctive geology and hydrogeology of the region have had a strong effect on its biota as well as on the culture of its early indigenous inhabitants. Weathering residue of the exceptionally pure carbonate rocks has produced remarkably little soil cover, and may have significantly limited available trace nutrients. Furthermore, even though rainfall is seasonably abundant over much of the peninsula, water is readily available only at specific sites because of the absence of surface streams. Access to water by humans during the pre-colonial period was thus limited to water that could be obtained from sinkholes in limestone [cenotes, after the Maya "dzonot"], from primitive hand-dug wells, or from precipitation collected in various storage devices like those sketched by Frederick Catherwood (Figure 7.2) and described at Uxmal by Stevens ([1843] 1962).

Except for agriculture, the region offers limited natural resources. Easily worked building stone was one factor facilitating monumental pre-Columbian architecture (ambitiously recycled as churches and monasteries after

FIGURE 7.2 Aguada, natural water-filled depression at Uxmal as sketched by Frederick Catherwood. Storage capacity of such natural features was developed and enhanced by Maya hydraulic engineering in the water-stared region south of the Sierrita de Ticul where depth to the water table exceeds 100 m, and cenotes are not present. (*Source:* From an illustration in Stephens [1843] 1962.)

the Spanish Conquest). Also useful was a distinctive and ubiquitous weathering product of the limestone of the Yucatán Platform—sascab (as follows), which can easily be processed to make building mortar.

Petroleum, which might be expected in the geologic environment of the peninsula, has not been reported. Metals are notably absent. Even flint, which commonly occurs in carbonate rocks, is lacking. It would have been important in a pre-Columbian economy, as evidenced by tiny and delicate imported blades of obsidian found at Maya archaeological sites. The major exportable mineral resource from the area in pre-colonial time was salt, the production of which was aided by the nature of coastal hydrogeologic processes then, as it is now.

SOILS

Distinctive characteristics of the soil and surficial carbonate layers of the Yucatán Peninsula strongly affect evapotranspiration, groundwater infiltration, and recharge. It is ironic that although rock exposure on Yucatán is almost complete in some areas, detailed stratigraphy is not well known, in large part because of the extensive alteration of surface rock. The result of this alteration is a nearly impermeable surface layer of calcrete up to about 3 meters (m) thick that covers much of the northern peninsula. Quiñones and Allende (1974) call this calcrete layer a “carapace” and attribute its formation to recrystallization of aragonite and high-magnesium calcite to form a more stable mineral, low-magnesium calcite. Beneath the carapace is a layer of low magnesium calcite, almost completely lacking in cement, known as “sascab.” Gerstenhauer (1987) notes that the development of these two layers is correlated and attributes sascab development to infiltration of water. Tulaczyk (1993) reports three occurrences of sascab in northern Quintana Roo in which no overlying carapace is present, but which contain “clasts” that could be residues of such a layer destroyed by weathering. These occurrences of what he refers to as diamictic sascab may tentatively support Gerstenhauer’s model in which sascab and calcrete developed together during the Mio-Pliocene epoch under weathering conditions different from those of today.

In many parts of northern Yucatán, the thickness of the soil cover over bedrock is a few centimeters (cm) at most. Rarely is this thickness more than a meter, except in karst depressions such as “aguadas.” The hydrogeologic significance of scarce soil cover is that meteoric precipitation can move quickly from the surface directly into the aquifer through fractures or sinks in the almost ubiquitous calcrete layer. This is a major reason for the absence of surface drainage on the peninsula. Whatever rainfall is not evaporated or absorbed in the sascab layer moves almost immediately into the aquifer.

Variants of three possible sources exist for the soil that is present in northern Yucatán: (1) residual insoluble material derived from dissolution of carbonate rock, (2) volcanic dust from Central American volcanoes, and (3) dust from more remote sources. Gmitro (1986), who examined the insoluble residue from acid dissolution of several Yucatán carbonate rocks, reported that values close to 0% were most common, and that values seldom exceeded 10 percent.

Pope et al. (1996) have correlated soil maps and geologic maps of the Yucatán Peninsula and report a clear relation between soil type and bedrock age, consistent with persistence of residual soil that is, in some cases, as old as the Eocene. Few analyses of Yucatán soils or argillaceous sediments are available. Schultz et al. (1971) examined three clay beds, used as pottery clays, that are 1–2 m thick and are interbedded with limestone of probable Eocene age. One occurrence is from near Ticul, and the other two occurrences are from the vicinity of Becal, which is about 50 kilometers (km) to the west. These clays, dominated by particles smaller than 0.25 microns (μ), consist predominantly of mixed layered kaolinite-montmorillonite, with quartz as the dominant mineral or dominant additional mineral in the sample fraction greater than 1μ in diameter. The authors presume the deposits to be residual material derived indirectly from airborne pyroclastic material. The insoluble residue left after standard acid leaching of samples of limestone that stratigraphically overlie the clay horizon at Ticul constitutes 0.5–5 percent of the rock mass and is composed of montmorillonite (Schultz et al. 1971).

The slow rate at which soil has accumulated over the Yucatán Peninsula raises the possibility that an appreciable soil component comes from wind-blown dust originating in Africa. The amount of mineral dust from West Africa that is precipitated each year in Miami, Florida, has been estimated to be 1.25 $\mathrm{gm \cdot m^{-2} yr^{-1}}$ (based on measurements during 1982–1983; see Prospero 1999). Dominant minerals in West African dust are illite and kaolinite, with lesser amounts of smectite, montmorillonite, and chlorite. Relative percentage of these minerals varies with latitude, with kaolinite dominating at low latitudes; because the West African dust plume extends over Yucatán, the Miami measurements may be relevant to the rate and source of dust deposition in Yucatán. Oxygen isotope analysis of the quartz fraction of soils, and of insoluble residues from carbonate rocks of the Yucatán Peninsula, could, perhaps, distinguish between these sources (Rex et al. 1969).

REGIONAL HYDROGEOLOGY

Porous, permeable karst carbonate of the Yucatán Peninsula contains a fresh groundwater lens underlain by a saline intrusion whose depth is defined approximately by the Ghyben-Herzberg relation

$$d_i = 40 \cdot d_x,$$

where d_x = elevation above mean sea level (msl) and d_i = depth of interface between fresh and saline water [density 1.025 grams per cubic centimeter ($gm \cdot cm^{-3}$)]. The nearly flat water table (gradient 2 centimeters per kilometer [cm/km]) is controlled by sea level and, to a lesser extent, by recharge from the annual precipitation of 500 to 1500 millimeters (mm) (Chavez-Guillen 1986, 1988). Ion content of the groundwater comes primarily from mixing with the seawater intrusion and from dissolution of minerals.

Water for human use is accessible where cenotes developed along geologic structures (Cenote Ring, Holbox Fracture Zone), near the coast where the water table is near the surface, and in north-central Yucatán where weathering has resulted in extensive karstification. The depth of the water table increases inland, from greater than 20 m in Ticul to deeper than 100 m in the Puuc region south of the Sierrita de Ticul.

The terminal Cretaceous Chicxulub Impact Crater, centered approximately on Chicxulub Puerto (lat. 21^{o}20' N, long. 89^{o}35' W), has influenced hydrogeology by producing a basin of subsidence that has partially escaped erosion and karstification (Hildebrand et al. 1995; McClain 1997; Perry et al. 1995; Pope et al. 1996). Geologic structures that influence groundwater movement (see Figure 7.1) include the Cenote Ring (or “Ring of Cenotes”), a permeable zone surrounding the Chicxulub Sedimentary Basin; the Ticul Fault Zone (delineated by the Sierrita de Ticul); and the Holbox Fracture Zone in northeastern Quintana Roo (Tulaczyk et al. 1993; Southworth 1985).

Other notable geomorphic/hydrogeologic features are (1) the north coast, characterized by a shallow ramp, nearly-continuous dune ridge, cienaga (saline swamp), and exposed rock (tsekel); (2) the fault-bounded east coast; (3) the north-central plain with strongly developed karst features (“Pockmarked Terrain”); (4) a region of poljes—large, flat enclosed basins whose geologic origin is uncertain—south of the Sierrita de Ticul; and (5) the zone of high-sulfate groundwater, located south and east of Lake Chichancanab in Quintana Roo. Aspects of regional hydrogeology are presented in papers by Back and Hanshaw (1970); Marin et al. (1990); Moore, Stoessell, and Easley (1992); Perry et al. (1989, 1995); Pope, Rejmankova, and Paris (2001); Reeve and Perry (1994); Stoessell et al. (1989); and Stoessell (1995).

EVAPORITES/BRECCIA AS A SOURCE OF GEOCHEMICAL TRACERS

Chemical tracers are proving useful in understanding groundwater movement and rock-water interaction in the Yucatán aquifer. These include, in particular, the major ions calcium (Ca^{2+}), magnesium (Mg^{2+}), sulfate (SO_4^{2-}), bicarbonate (HCO_3^-), and chloride (Cl^-), as well as the minor ion strontium (Sr^{2+}). Analyses have been presented by Perry et al. (1995); Stoessell et al. (1989); Moore, Stoessell, and Easley (1992); and Velazquez-Oliman (1995). The brief summary presented here is based on about 60 major element analyses and 65 additional SO_4^{2-}/Cl^- ratios of ours that have not yet been published. Several isotopes also provide useful hydrogeologic information. These include oxygen ($\delta^{18}O$)–hydrogen (δ^2H) composition of groundwater, surface water, and precipitation; $\delta^{34}S$ composition of sulfides and sulfate (SO_4^{2-}); $^{87}Sr/^{86}Sr$ ratios in rocks and water; and various isotopes of radium (e.g., ^{226}Ra).

Almost all fresh groundwater of the Yucatán platform is at (or near) saturation equilibrium with calcite and (depending on the value assumed for the solubility product constant, K_{sp}) with dolomite. This is expected in an aquifer system dominated by carbonate rocks.

As reported by Perry et al. (1995), ratios of SO_4^{2-}/Cl^- (or Cl^-/SO_4^{2-}) have helped determine mixing and flow patterns of Yucatán groundwater. The ratio $100 \cdot SO_4^{2-}/Cl^-$, expressed in chemical equivalents, is 10.3 for seawater; ratios close to this are observed in much of the northern part of the peninsula. This implies two things:

1. Over much of the peninsula, a major source of ions in the fresh groundwater lens comes from mixing with the underlying saline intrusion, which has been determined to be present as far inland as St. Elena (about 100 km; see Figure 7.1).
2. In most cases, SO_4^{2-} behaves as a conservative ion. Exceptions to the latter observation, to be discussed subsequently, are
    a. unusual cases in which oxidation–reduction (REDOX) reactions have converted SO_4^{2-} to H_2S and HS^-, and
    b. the case of Lake Chichancanab, a few kilometers from the southeast border of Yucatán (see Figure 7.1), which is in saturation equilibrium with gypsum; thus, the SO_4^{2-} concentration in this lake is governed by gypsum solubility.

The evaporite beds that produce high-sulfate water in Lake Chichancanab also affect the groundwater geochemistry of a considerable area in central Yucatán, with consequences for tracing groundwater movement; for rock diagenesis; and, in practical terms, for agricultural productivity. Two possible SO_4^{2-} sources are present in the area. Eocene gypsum-bearing evaporite has been reported in Quintana Roo (Lopez Ramos 1973), and gypsum and anhydrite are also abundant in impact breccia from the Chicxulub Crater (Rebolledo-Viera et al. 2000; Ward et al. 1995). Either of these could be the source of the 2,600 parts per million (ppm) SO_4^{2-} that has found in water of Lake Chichancanab and of high SO_4^{2-} values in groundwater of what is labeled the Evaporite Terrain in Figure 7.1. Gypsum is regularly precipitated around the lake bank, and celestite ($SrSO_4$) is in saturation equilibrium in the lake water. It is reasonable to postulate that the steep eastern bank of Lake Chichancanab is a fault—upthrust to the east—and that this fault exposes K/T breccia to dissolution by shallow groundwater. A reconnaissance study of groundwater south and east of Lake Chichancanab indicates an apparent lineament of water of high and variable SO_4^{2-}/Cl^- ratio extending from Lake Chichancanab to Cenote Azul on the southeast coast of Quintana Roo, near Bacalar Pueblo.

SO_4^{2-}/Cl^- ratios show that groundwater from the vicinity of Lake Chichancanab moves northwestward through the Ticul Fault Zone (see Figure 7.1), then northward through the western arm of the Cenote Ring into Estuario Celestun (Velazquez-Oliman 1995; Perry et al. 1995). It is also possible that one or more additional sources of shallow evaporite-bearing rock is present as a SO_4^{2-} source for groundwater south of Lake Chichancanab in the Evaporite Terrain.

The Cenote Ring is a major channel for groundwater movement in northern Yucatán. This is confirmed by SO_4^{2-}/Cl^- determinations of groundwater and by groundwater table elevations that were reported by Marin (1990) and Marin et al. (1990). Subsequent unpublished measurements by Perry and Zhang (based on first-order INEGI benchmarks) indicate that multiple groundwater divides exist in the system (cf Steinich et al. 1996), and that the highest groundwater elevation on the northern peninsula occurs approximately at Lake Chichancanab (4 m above msl), indicating the flow directions shown in Figure. 7.1.

COASTAL REGION

The hydrogeology and many of the physical and geochemical characteristics of the coastal area can best be understood with reference to two features. First, water arrives at this coast exclusively as groundwater, and much of this groundwater is channeled into specific zones in response to structural features such as faults or lineaments. This explains the presence of three of the important north coast freshwater discharge zones: Estuario Celestun, Bocas de Dzilam, and Laguna Conil. Second, a coastal aquitard has produced a sort of groundwater "sandwich" along the north coast.

Where fully developed, as at Celestun, the persistent sand dune that overlies this coastal aquitard has the following hydrologic components (from the uppermost downward; see Figure 7. 3):

A. a thin layer of freshwater produced by local precipitation;
B. a thin layer of saline water in direct contact with seawater;
C. the calcrete aquitard upon which the dune rests; the aquitard prevents vertical water movement.

Beneath it, the multilayer hydrogeologic "sandwich" is completed by

D. the coastal edge of an extensive freshwater lens that constitutes the major peninsular aquifer (with a dynamic hydrostatic head that remains higher than sea level);
E. the dispersion zone, a zone of variable thickness of active mixing between the freshwater lens (D) above and the saline intrusion (F) below; and
F. the saline intrusion that penetrates many kilometers inland. Here, as elsewhere, the freshwater lens floats on the saline intrusion, but mixing of these two layers may be particularly active beneath the confining aquitard because the whole system responds to tides (Reeve 1990).

Seawater flows inland within the unconfined upper part of the system, and through the coastal dune, in response to solar-induced evaporation in the cienaga (saline swamp) that occurs on the landward side of the dune ridge (Figure 7.3). The development of this coastal system is discussed below.

The distinctive and widespread north-coastal aquitard formed from the coastal portion of the ubiquitous surface calcrete layer of the peninsula in response to several factors (Perry et al. 1989). These include the low gradient of the land surface (measured in cm/km), the steady rise in sea level for the past 17,000 years (Fairbanks 1989; Coke, Perry, and Long 1991), direct control of the groundwater table by sea level, saturation of groundwater with respect to calcite, and tropical climate with high rate of evaporation of surface water. Perry et al. (1989) have incorporated these factors into the following model to explain observed characteristics of the aquitard.

As shown in Figure 7.4, the groundwater table near the north coast intersects the land surface along a broad band where water comes to the surface and evaporates. Land surface at Mérida (35 km inland) is only 8 m above msl—yielding an average land gradient of about 20 cm/km. (East of Progreso [see Figure 7.1], the slope of the land surface is somewhat steeper than 20 cm/km, whereas in the vicinity of Celestun to the west, the gradient is much less.) The slope of the land is so small that seasonal variation of the

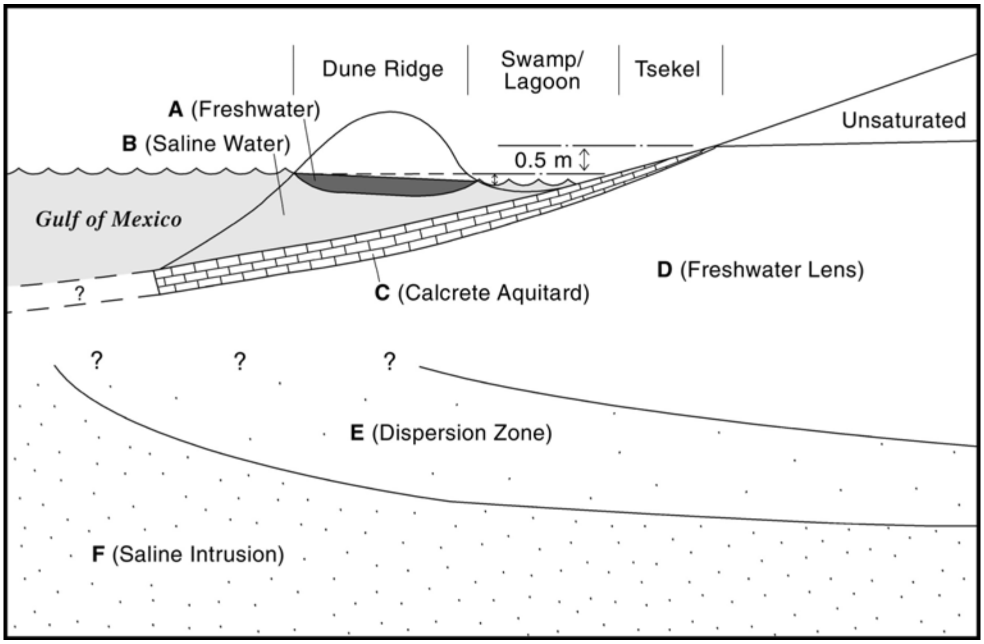

FIGURE 7.3. Schematic cross section of an aquifer system at the coast. A = a thin layer of freshwater produced by local precipitation; C = calcrete aquitard. The flow of salt water through the dune ridge results from the pumping effect of evaporation in the swamp/lagoon (cienega). Other units are lobeled as they appear in the text.

water table causes its intersection with the land surface to migrate on the order of 1 km or more during each yearly rainfall cycle (the “transition zone” of Figure 7.4). Because virtually all Yucatán groundwater is saturated with respect to calcite, evaporation of water along this transition zone results in the precipitation of calcite, which fills pore spaces and fractures in the nearly ubiquitous layer of surface calcrete. This has produced a wide swath of impermeable surface calcrete that is almost devoid of soil (the tsekel zone in Figure 7.3 and 7.4) along much of the north coast. Over time, slowly rising sea level has propagated the tzekel zone inland and upward to produce the confining layer or aquitard shown in Figure 7.3 and 7.4.

As postulated by Gerstenhauer (1987), and supported by observations of Tulaczyk et al. (1993), the calcrete layer that extends over Yucatán is perhaps millions of years old. Surface water can penetrate this calcrete layer only through fractures produced by subsurface weathering and collapse. At inland sites where the calcrete layer is well exposed, it is seen to be composed of individual blocks (with an average size of several meters) that are separated from each other by narrow, continuous cracks. Within the tsekel these cracks are filled by calcite, more or less as they form; this

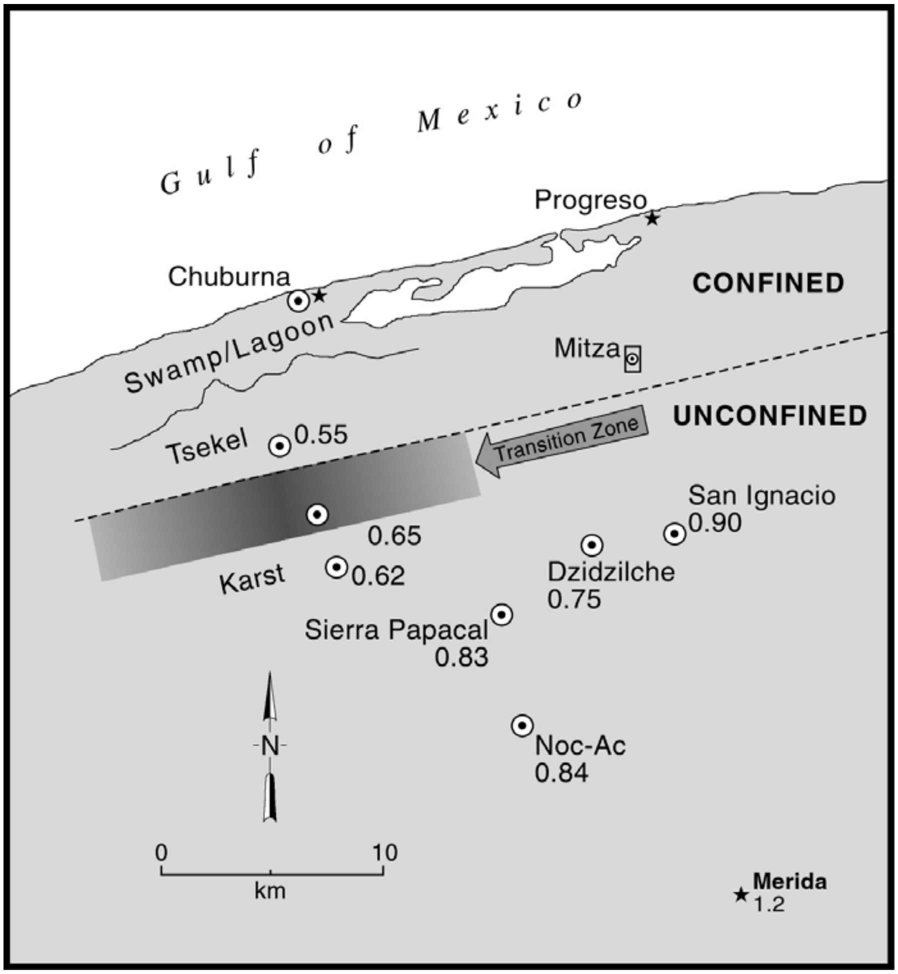

FIGURE 7.4. Detail of the coast showing water table elevations and coastal zones. Groundwater table comes to surface seasonally in the "transition zone". Numbers are depth to the groundwater table in meters (m). (*Source:* Perry et al. 1995.)

sealing process, which must be continuous, may be the most important factor in keeping the confining layer intact. Nevertheless, only spaces with widths measured in millimeters can be filled by cementation. Thus, cenotes and large fractures that have become incorporated in the tsekel are not sealed by cementation.

The aquitard formed by filling of voids in the calcrete layer is typically about 0.5-m thick (Sanborn 1991), and it extends into the Gulf of Mexico for an undetermined distance, creating, in effect, a dam that groundwater must flow under or over to reach the gulf. As a consequence, groundwater in the coastal region is under a positive head, which at Chuburna is about 40 cm (Perry et al. 1989).

As noted above, a beach of carbonate sand (consisting in part of high magnesium calcite and aragonite) has developed seaward of the tsekel and above the coastal aquitard. Saltwater from the Gulf of Mexico moves inland through this dune ridge and forms an evaporative lagoon (or coastal swamp) between the dune ridge and the tsekel (Figure 7.3). Under suitable circumstances, evaporation proceeds to the point at which halite and other evaporite minerals precipitate. This natural process has been enhanced by the construction of evaporating ponds (charcas) in Celestun, San Crisanto, El Cuyo, and other places, and is the basis for indigenous salt harvesting that has now been developed on a modern commercial scale at Las Coloradas. (The fact that seawater must move through the coastal dune to produce observed concentrations of halite is an aspect of the coastal system that may have escaped the notice of some people studying the coastal swamp and lagoons, and of those people harvesting salt.)

In cenotes that have, in effect, been moved into the tsekel or coastal swamp by rising sea level, groundwater flow is reversed, and these cenotes become springs of fresh or brackish water. Around some cenotes within the coastal swamp, salinity gradients persist over time and have produced circular bands of vegetation with distinct salinity tolerances. Roots of this vegetation trap organic matter and sediments to form small circular islands (petenes) (Febles and Batllori 1995). The aquitard persists for an undetermined distance into the Gulf of Mexico; drowned cenotes, in shallow coastal waters, form submarine springs that are well known to local fishermen (Figure 7.5).

ORIGIN OF THE COASTAL LAGOONS

Before modern coastal development, the north coast of the Yucatán Peninsula consisted of an almost continuous dune ridge, broken only in a few places by largely subterranean outflows of freshwater that created shallow, swampy, brackish-to-saline estuaries. Based on observations of the effects of Hurricane Gilbert, the dune ridge may have been frequently (but temporarily) breached by tropical storms.

Diego de Landa ([1566] 1998) mentioned Ría Lagartos, and Stevens ([1843] 1962) described Bocas de Dzilam. Estuario Celestun is another such system. Estuario Celestun and Bocas de Dzilam are located at the seaward extensions of the Cenote Ring and are fed by groundwater flowing through the fracture system associated with the Chicxulub Impact Crater (Perry et al. 1995; Pope, Rejmankova, and Paris 2001). The most open of these systems is Laguna Conil on the easternmost north coast; there, groundwater (and occasional overland flow) is channeled through the Holbox Fracture Zone (Tulaczyk et al. 1993) extending from Lake Coba to the coast. Groundwater movement to the coast is more diffuse at Ría Lagartos, but aligned wetlands appear south of El Cuyo on the map accompanying Lillo et al. (1999).

FIGURE 7.5. Xbulla, a drowned cenote about 0.5 km seaward from the coast and about 10 km east of Dzilam de Bravo, The vigorous outflow of freshwater from this cenote/spring into the Gulf of Mexico that is apparent in this photograph results from a hydrostatic head of about 0.5 m.

Development of the unusual coastal lagoons of the Yucatán Peninsula is based, in part, on the geochemistry of carbonate rocks and specifically on their behavior in coastal aquifers. Back et al. (1979) demonstrated that "caletas" of the Caribbean coast of the peninsula, such as Xel-Ha, formed (and continued to develop) by solution of solid carbonate rock along fractures intersecting the coast. The dissolution results from the decidedly nonlinear behavior of freshwater and saltwater when they are mixed. As pointed out by Badiozamani (1973), the mixing of two waters, both saturated with respect to calcium carbonate, can form an aggressively unsaturated water.

Back et al. (1979) to demonstrate that the unsaturated mixed water that forms where large freshwater discharges occur on the east coast is responsible for coastal erosion and caletas development along that coast. There, discharges occur through fractures in solid rock, and corrosion of cavern walls and collapse of roof blocks are evident.

In contrast, almost all sites of groundwater discharge along the gently sloping north coast are hidden by sand and silt. Nevertheless, conditions for chemical corrosion are present there as well. Much of the north-coast sand and silt is derived from the shells of marine organisms and is composed of high magnesium calcite and/or aragonite—minerals that are relatively soluble when compared to low magnesium calcite. Mixing of fresh and saline water can occur anywhere within the plumbing system, including within the sediment column. Although direct evidence is lacking, Perry and Velazquez-Oliman (1996) calculated that a wide range of mixtures of seawater with groundwater from Kopoma (which is typical of the water delivered by the Cenote Ring to Estuario Celestun) is capable of dissolving both calcite and aragonite. Surface water collected from the estuary in the dry month of May was found to be supersaturated with respect to both calcite and aragonite, as was a sample of groundwater taken from a piezometer driven through the mud and silt of the estuary. However, a mixture of roughly equal parts of these two waters produces a water still supersaturated with respect to calcite, but approximately at saturation with respect to the more soluble aragonite.

Perry and Velazquez-Oliman (1996) interpreted this result to mean that groundwater arriving at Estuario Celestun mixes with seawater and dissolves as much of the aragonitic and high magnesium calcite fraction of the carbonate silt and sand as it is capable of before discharging into the Gulf of Mexico. This implies that lagoons of the north coast are maintained by a balance between the supply of carbonate sand by the steady westward current, physical transport of particulate matter by freshwater discharge, and chemical dissolution of the least stable carbonate minerals in the sediment. A still untested corollary of this hypothesis is that sediments within the estuary are predicted to have a higher percentage of stable low magnesium calcite than the sediment load carried by the longshore current.

It is noteworthy that the piezometer used to collect the groundwater sample within the estuary was driven for about one meter into soft sediment. At that depth it encountered a layer of coarse, friable material. Water within the friable layer is partially confined by fine sediment and, in this case, rose in the piezometer tube to a level several centimeters above the water in the estuary. Such piezometers can be set in many parts of the estuary with similar results. It seems probable that the coastal aquitard has been eroded (or corroded) here (although the aquitard is present beneath Celestun, a town built on the coastal dune), and that corrosion of sediment grains may be widespread within the sediment column.

Although Ría Lagartos is not associated with the conspicuous structural features observed at Celestun and Bocas de Dzilam, it does have a large number of brackish water springs within the estuarine channel (Pope and Duller personal communication; Perry personal observation), including one that has several centimeters of head that has been encased in a large concrete drain pipe to supply water to fishermen. A moderate-sized salt extraction facility exists at Las Coloradas. Evaporation ponds have been placed along the sand dune, a placement that may have the undesired consequence of limiting entry of seawater [and, hence, sodium (Na^+) and chloride (Cl^-) ions that form halite, NaCl] to Ría Lagartos.

Geochemistry of groundwater of the northern part of the east coast, especially in the Xcaret-Tulum area, has been studied in detail by Stoessell et al. (1989) and Stoessell (1995), and in the Xel Ha Zone by Back et al. (1979) and Back et al. (1986). It is similar in many respects to the geochemistry of water on the north coast of the peninsula, in that calcite-saturated groundwater combines with seawater to produce a mixed water that causes coastal erosion. The principal difference between the development of the two coasts appears to result from structural and stratigraphic differences. The east coast contains Pleistocene dunes that are raised, lithified, and fault-bounded (Weidie 1985). That contrasts with the gently sloping north coast described above. Farther south along the east coast (near Bacalar), there are freshwater lakes and cenotes very close to the coast whose waters have low chloride (Cl^-) content, indicating little contact with seawater [e.g., 104 parts per million (ppm) Cl^- for Lake Bacalar and 44 ppm for nearby Cenote Azul, compared to > 19,000 ppm for seawater]. Lake Bacalar is long, narrow, and low-lying, and its lack of contact with the sea is in apparent contrast to Estuario Celestun (on the west) or Xel-Ha (on the east). The difference may result from the chemistry of groundwater reaching this lake. Lake Bacalar water contains 1070 ppm SO_4^{2-}, and adjacent Cenote Azul contains 1240 ppm SO_4^{2-}.

Cenote Azul is a deep, well-mixed lake with a bottom measured at 64 m, and it apparently reflects closely the composition of groundwater arriving at this coast. Our analysis of Cenote Azul water shows it to be nearly saturated with respect to gypsum and strongly supersaturated with respect to both calcite and aragonite. (The saturation index for aragonite in this water is 0.58.) In contrast with Celestun or Xel-Ha, mixing of this water with seawater does not produce an aggressive water—a 50/50 mixture is still supersaturated with respect to both minerals. This absence of an aggressive water may be the major factor distinguishing Lake Bacalar from other coastal water bodies on the northern peninsula.

OTHER STUDIES

Radium

Carbonate minerals incorporate an appreciable concentration of uranium (U) into their structure. Consequently, intermediate radioactive decay products such as radium (Ra) are released when the host carbonate dissolves. Moore (1996a, b) has shown that several radium isotopes, which can be detected at low concentration, can be used to estimate hitherto hidden fluxes of groundwater to the ocean.

Because groundwater is virtually the only form of discharge to the ocean from the northern Yucatán Peninsula, radium (^{226}Ra) isotopes were tested to quantify Yucatán groundwater discharge. Enhanced carbonate dissolution in the mixing zone was expected to produce a strong, easily measured signal. We made three traverses into the Gulf of Mexico, in directions approximately perpendicular to the coast, out to approximately 20 km (see Figure 7.1): one seaward from near Celestun, another from Progreso, and a third (collected by a former graduate student, J. Zhang) from Dzilam de Bravo (near Bocas de Dzilam). Preliminary results of ^{226}Ra measurements of these samples show that, at 20 km, ^{226}Ra values of 0.1 and 0.08 disintegrations per minute per liter (dpm/l) were comparable to values of 0.07 to 0.09 dpm/l for open water in the Gulf of Mexico (Moore personal communication). The most shoreward sample from the Dzilam de Bravo traverse has an exceptionally high value for a marine sample; the two reference samples taken on land are also exceptionally high. This is good news for future modeling of groundwater discharge, but perhaps not so good news for residents of the peninsula—the terrestrial background sample taken from the Celestun water works exceeds U.S. Environmental Protection Agency (EPA) guidelines for drinking water.

Hurricanes and groundwater

Measurement of oxygen (^{18}O) and hydrogen (^{2}H) isotopes in natural waters has become part of the standard set of geochemical tools used in hydrologic studies. Both isotopes are being used as natural tracers in order to refine our understanding of the water cycle on the Yucatán Peninsula. In particular, Lawrence and Gedzelman (1996) have observed that hurricanes and severe tropical storms deliver rain that is ^{18}O-depleted in comparison to normal tropical precipitation.

Because of the frequency with which hurricanes (and tropical storms that evolve into or degenerate from hurricanes) pass over the Yucatán Peninsula (Figure 7.6), we began in 1997 to collect background data from municipal wells, cenotes, lakes, the ocean, and rain to test whether severe tropical precipitation can serve as a tracer for the recharge of groundwater. Factors that make the peninsula a particularly good place to attempt groundwater tracer tests include storm frequency, lack of soil (and consequent rapid infiltration), lack of surface runoff, low hydraulic gradient, extensive saline intrusion, and high aquifer permeability. Evidence that the aquifer responds quickly to severe tropical storms comes from the report by Marin et al. (1990) that Hurricane Gilbert, which passed directly over northern Yucatán in 1988, was followed immediately by a general rise of approximately one meter in the water table.

Opal and Roxanne passed over the Yucatán Peninsula in 1995, as did Dolly in 1996. In 1998, Hurricane Mitch devastated much of Nicaragua, Guatemala, and parts of the Mexican state of Chiapas. Then, with diminished intensity, it passed over Yucatán as a tropical storm, depositing 4 cm of precipitation at Mérida. Even though most of the storm's energy had dissipated before it arrived in Yucatán, groundwater and surface water was collection immediately afterward. Because the isotope sampling program began in the middle of an unusually frequent series of storm events, sufficient background data for rigorous analysis are lacking. Nevertheless, accumulated qualitative evidence shown that the stable isotope composition of Yucatán groundwater does respond to tropical storm events; demonstrating that the isotope composition of water in the freshwater lens changes rapidly. From the latter observation, residence time of water in the freshwater lens is relatively short.

Stable isotope tracer studies of groundwater are possible because, as a result of isotope fractionation related to evaporation and precipitation, there

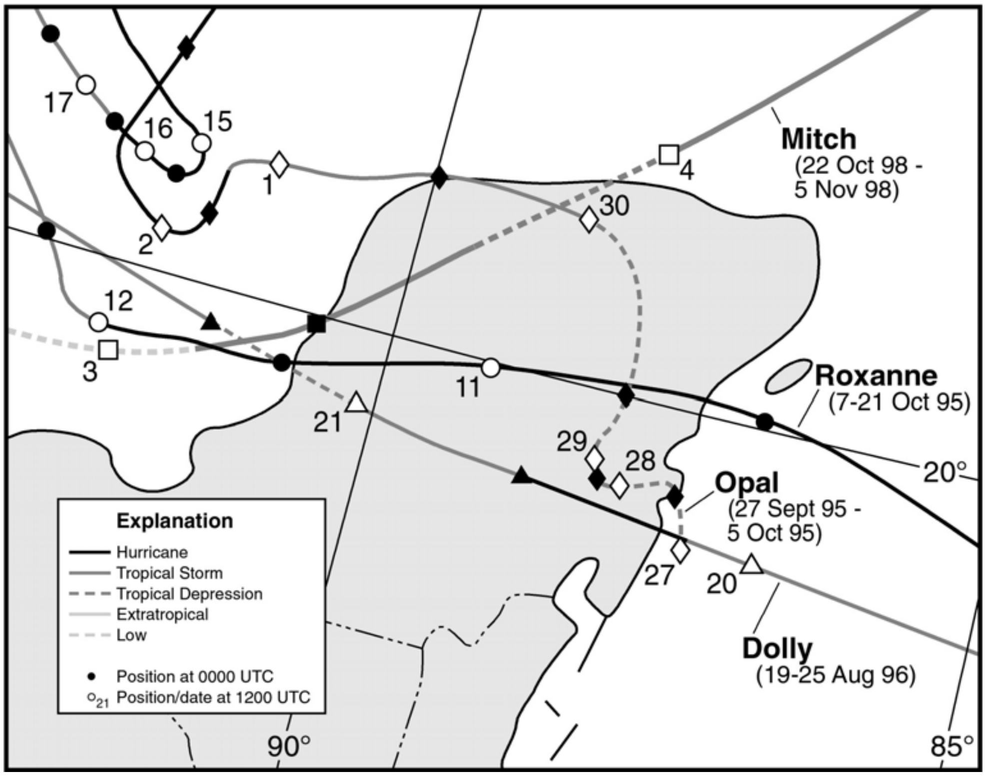

FIGURE 7.6. Tracks of recent hurricanes and tropical storms across the Yucatan Peninsula (from the National Atmospheric and Space Administration [NOAA]). Tropical storms/hurricanes are Dolly (Δ), Mitch (□), Opal (◊), Roxanne (○). Filled symbols: 0000 Universal Time (UTC); open symbols: 1200 UTC.

is a remarkably regular relation between ^{2}H and ^{18}O in worldwide precipitation as shown:

$$\delta^{2}H = 8\delta^{18}O + 10$$

In this equation, $\delta^{2}H$ and $\delta^{18}O$ are parts per thousand (‰) ratios of the heavy isotopes to the more abundant isotopes, ^{1}H and ^{16}O respectively, compared to the same ratio in Vienna Standard Mean Ocean Water (VSMOW).

The above relationship, commonly referred to as the “Meteoric Water Line” (MWL), is remarkably general; as a result, rainwater is accurately “tagged” as to its origin. The most common process that can move water away from the MWL is evaporation, which, on a hydrogen-oxygen isotope plot (with $\delta^{2}H$ as ordinate and $\delta^{18}O$ as abscissa), shifts water down and to the right of the line.

Figure 7.7 shows the MWL together with the $\delta^{2}H$-$\delta^{18}O$ isotope composition of Yucatán groundwater and rainwater. The figure includes an analysis of a sample of rain from Tropical Storm Mitch, which was collected for us in Mérida on 3 November 1998 by Ing. Ismael Sanchez. Its $\delta^{18}O$ value of –9.11‰ is well within the range of tropical storm values reported by Lawrence and Gedzelman (1996), and its $\delta^{2}H$ value is -60.5‰. The composition of this water falls close to the MWL. It is more depleted in ^{2}H and ^{18}O than any other sample we have analyzed from Yucatán. Most of the groundwater samples are from municipal wells that typically pump water from depths on the order of 20 m within the freshwater lens.

Water samples taken in 1997 from Betania and Dziuche, in the south-central part of the study area, are more depleted than other samples in this sample suite (Figure 7.8a and 7.8b). These samples are from an area directly in the path of Hurricane Roxanne in 1995. This is also a transitional region where some seasonal streams are found. It may be that hydraulic conductivity of the aquifer is less here and that these stations were still recovering from the hurricane.

Of 11 localities for which data are available for both 1997 and 1998, nine increased in $\delta^{2}H$ for an average increase of 5‰ from one year to the next. The average change in $\delta^{18}O$ was less, amounting to only +0.2‰. In no case did the 1998 waters (sampled after the passage of Mitch) move on a $\delta^{2}H$-$\delta^{18}O$ diagram in a direction indicating mixing with water from this tropical storm. In three of the localities sampled in both years, it was possible to sample shallow, completely covered cenotes within a few hundred meters of deeper municipal wells. In each of these localities, the isotopic composition of the shallow (cenote) water was significantly different from the corresponding well water. The general trend of the data suggests a system recovering from earlier (and locally more severe) tropical storms or hurricanes such as Opal, Roxanne, and Dolly.

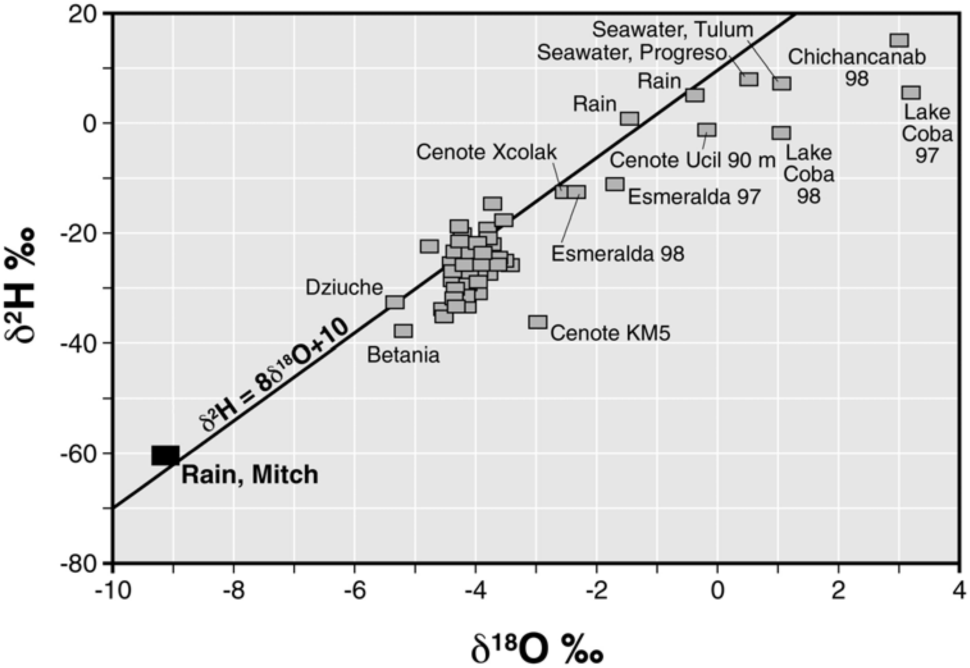

FIGURE 7.7. Hydrogen (ʒ^{2}H) and oxygen (ʒ^{18}O) isotope data from northern Yucatan plotted with reference to the "meteoric water line" (MWL).

Sulfur isotopes

Socki (1984) examined the sulfur isotope relationship in several Yucatán wells and cenotes. The most interesting of these is Cenote Xcolak (see Figure 7.1), which is 120 m deep. The interface between fresh and saline water is sharp at 50 m. Above that depth, water is thoroughly mixed, whereas below it is anoxic and contains increasing concentrations of hydrogen sulfide (H_2S) with depth. The cenote collects organic matter from a catchment area several times its size, and the organic matter reacts with sulfate-rich saline water below the interface according to the general reaction:

$$SO_4^{2-} + 2CH_2O = H_2S + 2HCO_3^-$$

At the bottom of Cenote Xcolak, the isotopic composition of SO_4^{2-} shifts from a seawater $\delta^{34}S$ value of 21‰, found in deep Yucatán wells, to $\delta^{34}S$ 42.6‰. Sulfide values (total reduced sulfur precipitated by silver nitrate, $AgNO_3$) were lowest at intermediate depths, reaching a minimum of $\delta^{34}S$ –33‰ at 80 m.

If oxidation-reduction reactions of this type were common in Yucatán groundwater, it would not be possible to use SO_4^{2-} or SO_4^{2-}/Cl^- as groundwater tracers. In fact, ratios of SO_4^{2-}/Cl^- significantly lower than the seawater ratio are relatively rare. Most variations from this ratio are toward

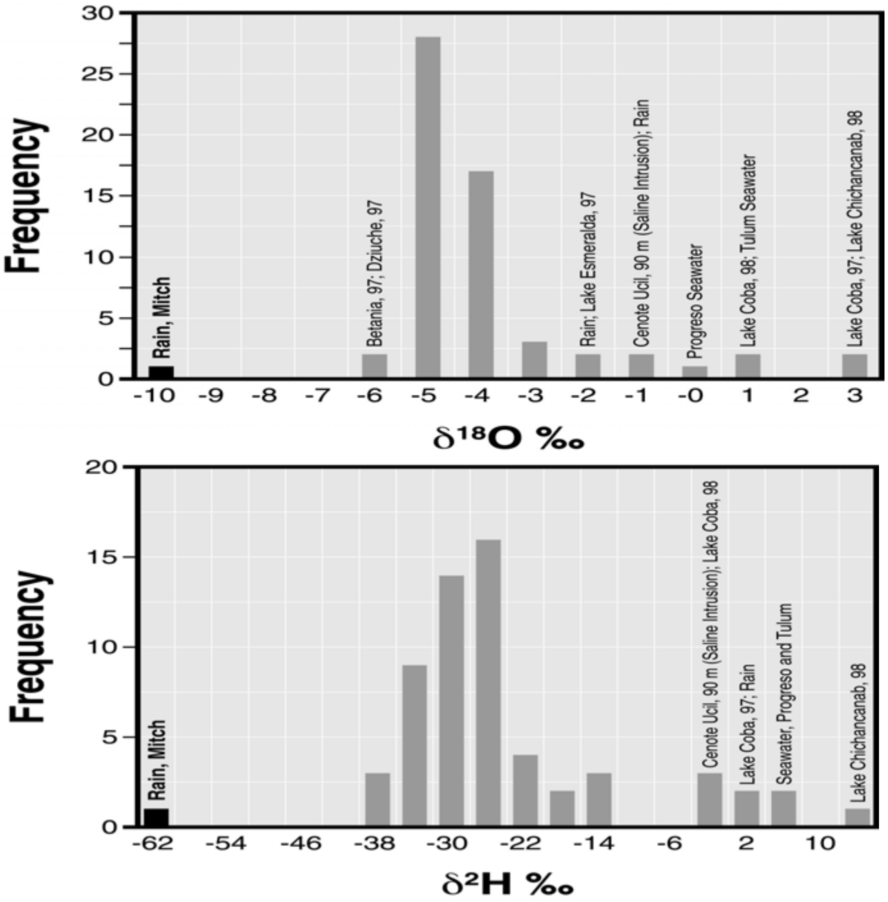

FIGURE 7.8a and 7.8b. Histograms of oxygen (δ^{18}O) and hydrogen ((δ^{2}H) isotopic composition of Yucatán waters.

higher values, indicating that such reactions are relatively uncommon except where the aquifer is exposed to organic matter.

CONCLUSION

The unique combination of tropical climate, a partially emergent carbonate platform, and geologic history (giving rise to such features as specific faulting patterns and the selective exposure of evaporites) combine to make Yucatán a valuable environment in which to study the hydrogeology of carbonate rocks. There is almost no surface runoff on the northern Yucatán Peninsula. Because of the relative homogeneity of the near-surface rocks of Yucatán, their near-horizontal bedding, and the absence of extensive aquitards (other than the coastal aquitard), faults have a major influence in collecting and channeling groundwater.

Most groundwater of the peninsular aquifer closely approaches chemical equilibrium with calcite. Surface water of Lake Chichancanab is saturated with respect to gypsum, but all analyzed groundwater from the freshwater lens is undersaturated with respect to this mineral. Nevertheless, some groundwater from the area around Lake Chichancanab does have a high SO_4^{2-} content, making sulfate a useful groundwater tracer. Other groundwater receives its dominant component of anions from the saline intrusion, as shown by chemical equivalent ratios of $100 \cdot SO_4^{2-}/Cl^-$, which are similar to the marine value of 10.3. The fact that values of this ratio approaching 10.3 are found over a large part of the peninsula confirms that the saline intrusion is truly extensive. Groundwater has had a major role in the sculpting of coastal features both by creating the coastal aquitard and also by providing freshwater that, when combined with seawater, forms an aggressive mixed water partly responsible for developing and maintaining coastal openings. This is true not only on the east coast, where it has long been recognized, but also on such north-coast openings as Celestun and Ría Lagartos.

Stable isotope determinations of oxygen (^{18}O) and hydrogen (^{2}H) show not only that severe precipitation from Tropical Storm Mitch was distinctly different from normal precipitation on the peninsula, but also that the Yucatán aquifer is a dynamic system. Each station that was sampled in both 1997 and 1998 showed a significant change in groundwater isotopic composition, with isotopically "heavier" values in 1998 than in 1997 suggesting that the aquifer was still recovering from being hit by storms such as Opal, Roxanne, and Dolly in 1995 and 1996. Other isotope tracers including radium and sulfur, discussed here, and strontium (not discussed) promise to enhance our understanding of aquifer behavior significantly.

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