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Groundwater geochemistry of the Yucatan Peninsula, Mexico: Constraints on stratigraphy and hydrogeology

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We report 87Sr/86Sr and ion concentrations of sulfate, chloride, and strontium in the groundwater of the northern and central Yucatan Peninsula, Mexico. Correlation between these data indicates that ejecta from the 65.5 m.y. old Chicxulub impact crater have an important effect on hydrogeology, geomorphology, and soil development of the region. Ejecta are present at relatively shallow subsurface depths in north-central Yucatan and at the surface along the Rio Hondo escarpment in southeast Quintana Roo, where they are referred to as the Albion Formation. Anhydrite/gypsum (and by inference celestite) are common in impact ejecta clasts and in beds and cements of overlying Paleocene and Lower Eocene rocks cored around the margin of the crater. The sulfate-rich minerals that are found in rocks immediately overlying the impact ejecta blanket, may either be partially mobilized from the ejecta layer itself or may have been deposited after the K/T impact event in an extensive pre-Oligocene shallow sea. These deposits form a distinctive sedimentary package that can be easily traced by the Eocene–Cretaceous 87Sr/86Sr signal. A distinct Sr isotopic signature and high SO4/Cl ratios are observed in groundwater of northwestern and north-central Yucatan that interacts with these rocks. Moreover, the distribution of the gypsum-rich stratigraphic unit provides a solution-enhanced subsurface drainage pathway for a broad region characterized by dissolution features (poljes) extending from Chetumal, Quintana Roo to Campeche, Campeche. The presence of gypsum quarries in the area is also consistent with a sulfate-rich stratigraphic “package” that includes ejecta.

The distinctive chemistry of groundwater that has been in contact with evaporite/ejecta can be used to trace flow directions and confirms a groundwater divide in the northern Peninsula. Information about groundwater flow directions and about deep subsurface zones of high permeability is useful for groundwater and liquid waste management in the area. Where it discharges at the coast, the unique chemistry of the groundwater that has interacted with the evaporite/ejecta strata may also have significant geomorphologic implications. While groundwater–seawater mixing at the coast has been shown to dissolve and erode limestone, PHREEQC modeling shows that mixing of water nearly saturated in CaSO4 with seawater has a less vigorous dissolution effect due to its high Ca content.

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Introduction

The objective of this study is to use groundwater geochemistry to increase knowledge of the (largely concealed) subsurface stratigraphy of the rocks of the Yucatan Peninsula, Mexico and of the groundwater flow paths within these karstic rocks. The research has practical significance because essentially all municipal, agricultural, and industrial water used on the Peninsula is pumped from the aquifer. Scientific value derives from increased knowledge of an important karst aquifer system and from increased knowledge of the nature and extent of the ejecta blanket produced by the terminal Cretaceous Chicxulub bolide impact.

Although soil cover in the area is thin or absent and bedrock exposure is nearly complete, the stratigraphy of the northern and east-central Yucatan Peninsula (here denoting the geographic area encompassed by the states of Yucatan and Quintana Roo) is poorly known. This is because weathering has caused extensive mineral dissolution and recrystallization, accompanied by loss of primary textural detail necessary for microfossil identification. In addition, exposure of Tertiary formations is highly selective because much of the region is a nearly flat plain, uninterrupted by stream valleys. Therefore many persistent rock units, which have dips of only a few degrees and are almost parallel to the land surface, do not crop out.
Much of what is known about regional stratigraphy of the Yucatan Peninsula comes from oil exploration (Lopez-Ramos, 1983; Ward, 1985). Rocks of the northern Peninsula, to depths of more than 500 m, are dominantly limestone and dolomite of Cretaceous and younger ages with significant evaporite lenses but rare siliciclastic units (Fig. 1). Drilling and seismic and magnetic exploration have revealed the outlines of the K/T Chicxulub impact crater in the northwestern part of the Peninsula (Rebolledo-Vieyra et al., 2000 and references therein; Gulick et al., 2008 and references therein), which has a probable age of 65.96 m.y. (Kuiper et al., 2008). A polymeric impact breccia that contains clasts of limestone, dolomite, and evaporite, as well as glass (now altered to clay) represents material that was ejected from that crater and widely dispersed. Rebolledo-Vieyra et al. (2000), Lefticariu et al. (2006), and others have used a limited number of drill cores to document and describe ejecta in several subsurface localities, all within the state of Yucatan. Others (Ocampo et al., 1996; Kenkmann and Schönian, 2006 and references therein) have described ejecta that crop out as the Albion Formation in Quintana Roo and Belize.

Although the relation of impact ejecta to evaporites (and hence evaporite dissolution) is highly plausible, it cannot be explicitly confirmed from available data except in drill cores from UNAM drill sites 5, 6, and 7 and from Yaxcopoil core (Rebolledo-Vieyra et al., 2000). Carbonate and evaporite are the predominant clast lithologies found in impact deposits from those localities. In UNAM 6 at Peto (Fig. 1) a Lower Eocene evaporite occurs immediately above what is interpreted as a collapse breccia formed during Paleocene subaerial exposure of impact ejecta (Lefticariu et al., 2006). Nevertheless, neither gypsum nor anhydrite is reported in outcrops of ejecta in southeast Quintana Roo (Pope et al. (2005), Schönian et al. (2005); Kenkmann and Schönian (2006)). Given the high solubility of gypsum and anhydrite, it is not surprising that these minerals would dissolve and not be found in surface outcrops. Whatever the precise relation between impact ejecta

![Fig. 1. Geology of the northern Yucatan Peninsula. (Base map redrafted from data of Servicio Geológico Mexicano, 2007.) Includes strontium isotope ratios of water from wells and cenotes reported in this study. Three digit numbers on the map represent the three digits past 0.70 in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios; read 827 as 0.70827. For detailed geology of the region within the box on this figure please refer to Kenkmann and Schönian (2006, Fig. 6); their map shows the Albion Island Formation (comprised of ejecta from the Chicxulub impact crater), which is too complex to delineate at the scale of Fig. 1.](image-url)
and evaporite, the large area of exposed Icaché Formation in eastern Campeche and southwestern Quintana Roo contains numerous gypsum quarries along and near Mexico Highway 186 (Fig. 1); and these coincide with occurrences of impact breccia reported in wells by Kenkmann and Schönian et al. (2006, Fig. 6).

The Yucatan Peninsula has particular advantages for the application of groundwater geochemistry to stratigraphic interpretation. These include: a lithology dominated by chemical sedimentary rocks of marine origin (limestone, dolomite, and evaporite), lack of aquitards, flat-lying beds that are continuous for long distances, and scarcity of terrigenous clastic rocks. A key characteristic of calcite, dolomite, gypsum, and celestite is that they contain significant quantities of strontium derived from strontium of the seawater in which they formed. This strontium has migrated long distances, and scarcity of terrigenous clastic rocks.

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The isotopic signatures of rocks of the Yucatan Peninsula may be imprinted on groundwater interacting with these rocks. A factor contributing to the quality of this isotopic signal in Yucatan groundwater is the scarcity of Cenozoic rocks with terrigenous materials. Indeed, the near-absence of residual soil in much of the northern Peninsula is one indication that illite and other rubidium-rich minerals are absent. Another is the low preservation of evaporite minerals in outcrops in northern Yucatan. The established relationships between groundwater geochemistry and known stratigraphy in the northern Peninsula can thus be extended to less well-studied areas in the central and southern Peninsula. Of particular interest are (1) a region in southern Quintana Roo, near the Belize border where Chicxulub impact ejecta crop out at the surface and (2) an adjacent and much more extensive area in south-central Campeche and Quintana Roo where recent mapping (Fig. 1) has confirmed the presence of a major submarine drainage system spatially related to extensive exposures of gypsum-bearing limestone of the Paleocene Icaché Formation. In this study we use groundwater ion geochemistry to show that the large numbers of well-preserved and related geomorphic features of these regions are closely linked to selective dissolution of gypsum. This gypsum may also occur within a sedimentary package that includes an impact ejecta layer reported by Schönian et al. (2005) and Kenkmann and Schönian (2006) to form a sedimentary blanket that overlies a Late Cretaceous karst surface in this area.

A saline intrusion composed of seawater, modified by exposure to carbonate and evaporite rocks of the aquifer system, underlies much of the northern Peninsula. This intrusion influences the chemistry of the overlying fresh water lens. Knowledge of the extent and circulation patterns within the seawater intrusion is important to groundwater management strategies (Back et al., 1979; Beddows et al., 2007; Marín et al., 2000; Perry et al., 1989, 2002; Stoessell et al., 1989). Studies of groundwater geochemistry, including the data and interpretations contained in this report, can help define the extent and compartment of the intrusion, indicate horizontal as well as vertical zones of high permeability, and refine our knowledge of groundwater flow patterns. It may also help evaluate processes of chemical weathering and the effect these processes have on regional landforms.

Sample collection and analysis

The interpretations and conclusions of this study are based primarily on ion and strontium isotope chemistry, including both data...
reported here for the first time and data that have previously been published as part of studies with a different emphasis; these data sources are indicated in the appropriate tables. Except for four rocks listed in Table 1, all samples in this report are of groundwater or surface water. A majority of the ion concentration measurements of these waters were made on samples collected and filtered...
in the field through 0.2 μm filters by Northern Illinois University (NIU) personnel. These samples were transported and stored in acid-washed high density polyethylene bottles or, in some cases, in Vacutainers as described by Perry et al. (2002). Analyses were made in the NIU geochemistry laboratory. Chloride and sulfate analyses were made by ion exchange chromatography using a Dionex anion suppressor and a conductivity cell. NIU strontium ion analyses were made with a Beckman V DC plasma spectrometer on samples acidified with nitric acid. Analytical techniques are described in more detail in Perry et al. (2002), and some of the analytical results are from that publication. The chemistry of an additional suite of samples analyzed at NIU was collected in 2004 and is reported here for the first time. Those samples are from a study in which hurricane precipitation was used as a groundwater tracer (Pedersen et al., 2005).

Additional data on ion chemistry of water from several deep cenotes (sinkholes) are taken from Stoessell (2006). Water samples from various depths from one of these cenotes, Xkocar, were analyzed by both Stoessell and by Pedersen (2007). The two data sets agree well, and Stoessell’s results are used here to facilitate consistent comparison with his measurements from other cenotes.

Sources of strontium isotope analyses are given in Table 1. Values have been normalized to isotope ratios reported for US National Institute of Standards and Technology (NIST) standard NBS 987, which is assigned an $^{87}$Sr/$^{86}$Sr ratio of 0.71025. Previously unpublished analyses of samples collected by Perry in 1997 were analyzed at the University of Texas, Austin, in the laboratory of Jay Banner, using techniques described by Banner and Kaufman (1994). Previously unpublished strontium isotope analyses of samples collected by Pedersen and Perry in 2004 were analyzed by Paytan in 2004 using an MAT Finnigan 261 mass spectrometer and analytical techniques described by Mearon et al. (2003).

**Results and discussion**

**Sources of ions in Yucatan groundwater**

All available strontium isotope data for water of the northern Yucatan Peninsula are listed in Table 1 and plotted in Fig. 1. In addition to our own data, the table includes strontium isotope analyses published by Hodell et al. (2004) and data published online by Stoessell (2006). A salient feature of strontium data plotted on the geologic map of the Peninsula (Fig. 1) is that a close correlation exists between the $^{87}$Sr/$^{86}$Sr ratio of fresh shallow groundwater (including the upper freshwater lens as sampled in lakes and cenotes) and the seawater isotope ratio appropriate for the geologic age in which the carbonate rocks of the local aquifer were deposited. This correlation provides a framework for interpreting deeper and/or less accessible parts of the aquifer system.

Three variables are particularly useful for identification of groundwater ion sources and flow directions: strontium concentration, strontium isotope composition, and chloride concentration. Sulfate ions are also important, and $\text{SO}_4/\text{Cl}$ ratios were discussed extensively by Perry et al. (2002). Chloride is generally a conservative ion; its presence in groundwater typically indicates seawater contribution to groundwater chemistry. In samples from the saline intrusion (in which seawater is an important contributor to strontium ion concentration) chloride ion can be used to
estimate the percentage of seawater strontium. The relationship between strontium ion concentration, chloride concentration, and strontium isotope ratios is illustrated graphically in Fig. 2 as plots of the reciprocal of molal strontium ion concentration (1/Sr) vs. 87Sr/86Sr ratio and between 1/Sr and the molal ratio of Sr/Cl.

As pointed out in the introduction, the shallow fresh groundwater lens tends to equilibrate with local exposures of carbonate rock, which, over much of the northern Peninsula, range in age from Oligocene–Miocene (87Sr/86Sr~0.7081) to Pliocene–Pleistocene (87Sr/86Sr~0.7090). Because carbonate in these rocks has a rather low concentration of strontium, the associated water composition plots on the right side of Fig. 2b and c.

The deep groundwater of the saline intrusion plots in the upper left quadrant of Fig. 2b. We note that this composition does not represent present-day seawater, suggesting interaction with aquifer rocks. An important constraint on the source of strontium of the saline intrusion is that, with one exception, the deep, saline water of wells and cenotes has a higher strontium ion concentration than seawater and an 87Sr/86Sr ratio that is similar to or very slightly higher than the ratio of the local rocks. The exception is Cenote Big Calica, 55 km south of Cancun and within 5 km of the eastern (Caribbean) coast, a zone in which extensive seawater penetration occurs (Smart et al., 2006; Beddows et al., 2007); the strontium in deep water from Big Calica appears to come entirely from seawater. Additional water samples with high 87Sr/86Sr and high strontium concentrations are from observation wells near the central north coast of Yucatan state (Fig. 2c).

Water samples from Cenote Azul, Lake Milagros, and Lake Baca-

lar in southern Quintana Roo and from Lakes Chichancanab and Esmeralda in southern Yucatan state (Fig. 1) have a Cretaceous–Eo-

cene 87Sr/86Sr ratio and plot in the lowermost left hand corner of Fig. 2a. These lakes presumably derive their strontium from disso-

lution of minerals either of Chicxulub impact breccia of northern Belize and southeastern Quintana Roo, mapped as the Albion For-

mation (Fig. 1 [cf. figure 6 of Kenkmann and Schönlin, 2006]) or from overlying early Tertiary evaporite. [Albion Formation 87Sr/86Sr is plotted for comparison in Fig. 2a at an arbitrary 1/Sr va-

tue of one.] Waters from along the Ticul Fault and western part of the Ring of Cenotes in Yucatan state also plot in the lower left quadrant of Fig. 2a. The 87Sr/86Sr ratio of these waters increases and their strontium concentration decreases from southeast to northwest, and they have distinctive Strontium/chloride ratios. The Sr/Cl ratios of these waters stem from known and postulated mixing with the saline intrusion (see below).

The saline intrusion of modified seawater underlying much of the north and northwest Yucatan Peninsula has an important effect on groundwater chemistry and groundwater circulation. The contribution of seawater strontium to a given groundwater sample can be estimated from the ratio of strontium to chloride as shown in Fig. 2d–f. Waters of Cenote Azul and of the companion lakes Chichancanab and Esmeralda, have values of 1000Sr/Cl that range from 10 to 100 (designated Group I in Fig. 2d). These waters have exceptionally low chloride concentrations for the Peninsula. In particular, the chloride concentration of water from all depths in Cen-

ote Azul is 1.2 mmoles/kg (Perry et al., 2002), indicating little or no mixing with modern seawater. It is significant that Cenote Azul, which also has the highest Sr/Cl ratio and the highest SO4/Cl ratio (Table 2), is the nearest of these surface water bodies to the Carib-

bean coast. Thus, in contrast to the northern Peninsular coastal zone and the northeastern Caribbean coast, there is no evidence for a sal-

ine intrusion along the southerwesternmost Caribbean coast from somewhere south of Tulum to the Belize border and probably much farther south (Fig. 1). One likely reason for this is that groundwater from southern Quintana Roo contains a high content of calcium and sulfate ions from gypsum dissolution; and, when mixed with sea-

water, the mixture is not capable of dissolving limestone to produce the exceptionally high cavern permeability and thus seawater infiltration inland, which is characteristic of the northeast coast.

A significant number of groundwater samples have 1000Sr/Cl ratios between 1 and 10 and are conveniently grouped together and labeled Group II. Most shallow groundwater samples from the interior of the Peninsula fall within this group. These samples from the interior are also characterized by relatively low strontium concentrations (high 1/Sr). For discussion, they are assigned to Group IIA (Fig. 2e), whereas deeper, saline water with higher stron-

tium content but a similar range of 1000Sr/Cl ratios comprises Group IIB (Fig. 2f).

Another distinctive group of samples that falls within Group IIB consists of shallow groundwater lying along the trace of the Ticul Fault and the western arm of the Ring of Cenotes (Fig. 1). These waters (Fig. 2d) become systematically more chloride-rich from southeast to northwest, and, as shown in Fig. 2a, they attain progressively higher 87Sr/86Sr ratios in the same direction. We attribute this trend to groundwater flow from southeast to northwest starting at a groundwater divide in the vicinity of Lake Chichancanab.

Waters that have 1000Sr/Cl ratios less than one are here as-

signed to Group III (Fig. 2e and f). Three of these, Chumkopo 2

Table 2

Sulfate–chloride relations in selected samples (data from Perry et al., 2002).

<table>
<thead>
<tr>
<th>Lat/Long</th>
<th>Location</th>
<th>SO4 (meq)</th>
<th>Cl (meq)</th>
<th>100 × SO4/Cl</th>
<th>Times Avg seawater</th>
</tr>
</thead>
<tbody>
<tr>
<td>20.40/89.53</td>
<td>Ticul Avg</td>
<td>3.67</td>
<td>6.87</td>
<td>53.4</td>
<td>5</td>
</tr>
<tr>
<td>20.11/89.93</td>
<td>Peto Avg</td>
<td>4.35</td>
<td>7.19</td>
<td>60.3</td>
<td>6</td>
</tr>
<tr>
<td>19.14/88.17</td>
<td>Lake Noblec</td>
<td>1.08</td>
<td>1.13</td>
<td>96.0</td>
<td>9</td>
</tr>
<tr>
<td>19.47/88.10</td>
<td>Lake Ocom</td>
<td>4.83</td>
<td>4.96</td>
<td>97.4</td>
<td>9</td>
</tr>
<tr>
<td>20.07/89.04</td>
<td>Tzucacab Avg</td>
<td>11.74</td>
<td>11.52</td>
<td>102.5</td>
<td>10</td>
</tr>
<tr>
<td>19.95/88.88</td>
<td>Sta.Rosa</td>
<td>3.65</td>
<td>2.6</td>
<td>140.4</td>
<td>14</td>
</tr>
<tr>
<td>19.95/88.04</td>
<td>Felipe Carrillo Puerto</td>
<td>10.06</td>
<td>6.9</td>
<td>145.8</td>
<td>14</td>
</tr>
<tr>
<td>19.58/88.59</td>
<td>Chunhuhub Pueblo</td>
<td>7.29</td>
<td>4.18</td>
<td>174.4</td>
<td>17</td>
</tr>
<tr>
<td>19.90/88.95</td>
<td>Catmis</td>
<td>19.68</td>
<td>10.82</td>
<td>181.9</td>
<td>18</td>
</tr>
<tr>
<td>19.90/88.94</td>
<td>Dziuche</td>
<td>7.79</td>
<td>2.27</td>
<td>343.5</td>
<td>33</td>
</tr>
<tr>
<td>19.24/88.55</td>
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<td>25.06</td>
<td>6.05</td>
<td>414.2</td>
<td>40</td>
</tr>
<tr>
<td>19.76/88.71</td>
<td>Esmeralda</td>
<td>28.95</td>
<td>4.02</td>
<td>720.3</td>
<td>70</td>
</tr>
<tr>
<td>19.88/88.77</td>
<td>Lake Chichancanab Avg</td>
<td>52.92</td>
<td>7.44</td>
<td>718.3</td>
<td>70</td>
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<tr>
<td>18.65/88.41</td>
<td>Bacalar Lagoon</td>
<td>22.21</td>
<td>2.93</td>
<td>757.2</td>
<td>74</td>
</tr>
<tr>
<td>19.49/88.50</td>
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<td>18.93</td>
<td>2.1</td>
<td>901.4</td>
<td>88</td>
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<tr>
<td>19.40/88.62</td>
<td>El Ramonal</td>
<td>13.24</td>
<td>1.21</td>
<td>1094.2</td>
<td>106</td>
</tr>
<tr>
<td>18.65/88.41</td>
<td>CenAzul Super</td>
<td>24.82</td>
<td>1.2</td>
<td>2061.9</td>
<td>200</td>
</tr>
<tr>
<td>18.65/88.41</td>
<td>CenAzul 20 m</td>
<td>24.61</td>
<td>1.21</td>
<td>2033.3</td>
<td>197</td>
</tr>
<tr>
<td>18.65/88.41</td>
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<td>25.73</td>
<td>1.22</td>
<td>2108.5</td>
<td>205</td>
</tr>
<tr>
<td>18.85/88.41</td>
<td>Cenote Azul Avg</td>
<td>25.05</td>
<td>1.21</td>
<td>2068.0</td>
<td>201</td>
</tr>
</tbody>
</table>
and 15 and Big Calica 8, are shallow samples from east coast cenotes. They differ from other shallow water samples only in their higher chloride content, which indicates greater seawater mixing. Among the deep, saline water samples, all Group III waters have relatively high chloride concentrations that, except in the case of Big Calica 29, are accompanied by strontium concentrations greater than seawater. [Seawater is also plotted with this group for reference.] Strontium-rich Group III waters are all from the saline intrusion except for Baldeoca, which is a spring of brackish water in the Celestun Estuary. A noteworthy compositional constraint is that any saline water with a concentration of strontium higher than seawater must have dissolved a significant amount of a strontium-rich mineral from the rocks of the aquifer. Known geologic relations strongly suggest that, in all cases where this has occurred, the strontium source is impact ejecta and/or immediately overlying evaporite with an indistinguishable (i.e. early Tertiary) $^{87} \text{Sr}/^{86} \text{Sr}$ ratio.

Neither shallow nor deep water of Cenote Big Calica fits the pattern displayed by other samples in Group III. The sample from the freshwater lens of Big Calica has strontium content typical of shallow non-saline groundwater, but it falls in Group III by virtue of its relatively high chloride content. Deep Big Calica water has both chloride and strontium concentrations similar to seawater. Thus, at the level detectable by our chemical data, Big Calica, which is only about 5 km from the Caribbean coast, appears to have a direct connection to the ocean but has no apparent connection with impact ejecta or other evaporite-bearing rock.

**Strontium from impact ejecta within the saline intrusion**

The most saline group of waters analyzed in this study (Fig. 2b and e, Group III) is from the pervasive saline intrusion and the zone of dispersion at the top of that intrusion. These deep samples have 1000Sr/Cl values between 0.1 and 1, and $^{87} \text{Sr}/^{86} \text{Sr}$ ratios that tend to be significantly “younger” (e.g. closer to present-day seawater composition) than the apparent age of shallow, fresh groundwater from the same cenote (Fig. 2b: Ucil, Xkolac, Chunmuko). Seawater itself has the approximate Sr and Cl ion chemistry of Group III. However, a number of water samples in this group have strontium concentrations that are several times that of seawater, and the maximum amount by which the strontium isotope ratio of these can be modified by direct seawater mixing is constrained by mass balance considerations. Gmitro (1986) first reported 0.38 mmoles/kg of strontium (four times the seawater concentration) for a water sample from 105 m in Cenote Ucil; and Perry et al. (2002) subsequently suggested that this strontium comes from ejecta or a deeply buried evaporite. Since then Stoessell (2006) and Pedersen (2007) have found high strontium concentrations in deep samples from Cenote Xkolac, and Stoessell (2006) has reported strontium concentrations in saline bottom water of several other deep cenotes (Fig. 2e, Table 1). Except for the 29 m sample from Cenote “Big Calica” all of these deep cenote waters have higher concentrations of strontium than that of seawater.

Given what is known of Yucatan stratigraphy the most reasonable mineral source of strontium for deep groundwater is celestite from either a pervasive K/T ejecta blanket or from an early Tertiary evaporite immediately overlying that blanket. Other minerals, specifically aragonite and gypsum, probably contribute strontium to Yucatan groundwater but, as discussed by Perry et al. (2002), only celestite ($\text{SrSO}_4$) has both the requisite strontium abundance and the sulfate content required to produce the strontium concentration and the correlation of strontium with sulfate observed in regional groundwater. Celestite has been found in rocks of the Yucatan Peninsula (Lefèbvre et al., 2006) but is rarely reported. Nevertheless, the presence of celestite as a source of strontium in Peninsular groundwater can be inferred from the occurrence of groundwater and surface water saturated or near-saturation with respect to this mineral and gypsum at UNAM 2, UNAM 5, Lake Chichancanab, and Cenote Azul (Perry et al., 2002). Gypsum, the most abundant mineral in many evaporites, is not commonly found in outcrops of the northern Peninsula; thus, it is not surprising that celestite, an accessory evaporite mineral with nondescript physical properties, would be overlooked.

Sufficient data are available to model whether the strontium ion excess observed in the deeper parts of the saline intrusion of Xkola, Ucil, and other cenotes can reasonably have been produced by dissolution in seawater of impact ejecta and/or Cretaceous–Eocene evaporite. Necessary constraints are provided by (1) the strontium ion concentrations of the relevant minerals and seawater (assumed to be conservative) and (2) the $^{87} \text{Sr}/^{86} \text{Sr}$ of both seawater and evaporite. For this calculation the saline intrusion is assumed to consist of seawater with a modern strontium isotope ratio (0.70920) mixed with some fresh water having a negligibly low concentration of strontium. Evaporite strontium is assumed to have an $^{87} \text{Sr}/^{86} \text{Sr}$ of 0.70787 as expected for marine sediments of the appropriate age. We calculate the expected $^{87} \text{Sr}/^{86} \text{Sr}$ of the resulting water and test our assumptions by comparing this value with the ratio observed in strontium-rich samples. According to our assumptions, the ratio of the chloride ion concentration of the groundwater sample to that of seawater, multiplied by the strontium concentration of seawater $(\text{Cl}_{\text{Gwtr}}/\text{Cl}_{\text{Sea}})$ is a measure of the fraction of seawater strontium in the sample. For seawater we use the ion concentrations given by Stoessell (2006) for seawater from Akumal, QR: $\text{Cl}_{\text{Sea}} = 0.079 \text{M}$ and $\text{Cl}_{\text{Sea}} = 576 \text{MmM}$. We define $m_{\text{Sea}}$ as the calculated “excess” strontium contributed to a groundwater sample by dissolving evaporite, expressed as millimoles of evaporite strontium per kg of sample water; $m_{\text{Sr}} = \text{millimoles/kg of strontium in the sample}$; $m_{\text{seawater}} = \text{millimoles/kg of strontium in seawater}$; and $(\text{Cl}_{\text{Gwtr}}/\text{Cl}_{\text{Sea}}) = \text{the ratio of the concentration of chloride in the sample to seawater chloride.}$ Then the concentration of seawater-derived strontium in any sample can be calculated as:

$$m_{\text{Gwtr}} = \frac{m_{\text{Sr}}}{(\text{Cl}_{\text{Gwtr}}/\text{Cl}_{\text{Sea}}) \cdot m_{\text{Sea}}} \quad (1)$$

and

$$m_{\text{feq}} = m_{\text{Gwtr}} - \left( \frac{\text{Cl}_{\text{Gwtr}}}{\text{Cl}_{\text{Sea}}} \cdot m_{\text{seawater}} \right) \quad (2)$$

Of the four stable isotopes of strontium only the abundance of $^{86} \text{Sr}$, the daughter of radioactive $^{87} \text{Rb}$, varies from one geologic environment to another, and its abundance is conveniently compared to $^{86} \text{Sr}$, which is of comparable abundance and has a mole fraction with respect to all strontium isotopes of 0.0986. Setting $^{86} \text{Sr} = 0.098600$ for both groundwater and seawater strontium, the mole fraction of $^{87} \text{Sr}$ in modern seawater, which has an $^{87} \text{Sr}/^{86} \text{Sr}_{\text{sea}} = 0.07092$, is:

$$^{87} \text{Sr}_{\text{Sea}} = 0.0792 \cdot 0.0986 = 0.039927.$$

Groundwater strontium $(\text{Sr}_{\text{Gwtr}})$ has two components of interest: $^{87} \text{Sr}_{\text{Gwtr}}$ and $^{86} \text{Sr}_{\text{Gwtr}}$, and their concentrations are related by the expression:

$$m_{\text{Sr}_{\text{Gwtr}}} \cdot \text{Sr}_{\text{Gwtr}} = m_{\text{Sr}_{\text{Gwtr}}} \cdot ^{86} \text{Sr} + m_{\text{Sr}_{\text{Gwtr}}} \cdot ^{87} \text{Sr}_{\text{Gwtr}} \quad (3)$$

Here we consider only the two strontium isotopes of interest, $^{87} \text{Sr}$ and $^{86} \text{Sr}$. If “excess” strontium in a sample of deep, saline water of the Yucatan aquifer comes from addition of strontium to a homogeneous Cretaceous–Eocene evaporite layer, the abundance of $^{86} \text{Sr}$ in that sample $(m_{\text{Sr}_{\text{Gwtr}}} \cdot ^{86} \text{Sr})$ is:

$$m_{\text{Sr}_{\text{Gwtr}}} \cdot ^{86} \text{Sr} = 0.098600 \cdot m_{\text{Sr}_{\text{Gwtr}}} \quad (4)$$

The $m_{\text{Sr}_{\text{Gwtr}}} \cdot ^{87} \text{Sr}_{\text{Gwtr}}$ contribution can be found by setting $(^{87} \text{Sr}/^{86} \text{Sr})_{\text{evaporite}} = 0.70787$.
and, from Eqs. (1) and (2):

\[
m_{\text{SrGwtr}} - \frac{87}{86}\text{Sr}_{\text{Gwtr}} = m_{\text{SrGwtr}} \cdot (\text{Sr}_{\text{Sam}}/\text{Sr}_{\text{Sea}}) \cdot m_{\text{SrSea}} + (0.069927 - 0.069796) \cdot (\text{Cl}_{\text{Gwtr}}/\text{Cl}_{\text{Sea}}) \cdot m_{\text{SrSea}}
\]

The calculated \(\frac{87}{86}\text{Sr}\) for a given groundwater is obtained from (4) and (5):

\[
(\frac{87}{86}\text{Sr})_{\text{Gwtr}} = m_{\text{SrGwtr}} \cdot \frac{(\frac{87}{86}\text{Sr})_{\text{Sam}}}{(\frac{86}{87}\text{Sr})_{\text{Gwtr}}} (\text{Sr}_{\text{Sea}}/m_{\text{SrGwtr}})
\]

For Akumal seawater, with \(\text{Cl}_{\text{Sea}} = 576 \text{ Mm/kg}\) and \(m_{\text{SrSea}} = 0.079\), this equation reduces to

\[
(\frac{87}{86}\text{Sr})_{\text{Gwtr}} = 0.70787 + 0.00133 \cdot (\text{Cl}_{\text{Gwtr}}/\text{Cl}_{\text{Sea}})
\]

This equation can be used to test whether Cretaceous–Eocene evaporite is a reasonable source of excess strontium in deep, saline Yucatan groundwater.

All waters in our sample suite (Table 1, Figs. 2b and e) having strontium concentrations higher than seawater and Sr/Cl ratios between one and four times that of seawater have calculated \(\frac{87}{86}\text{Sr}\) ratios that differ from the observed value by 0.0003 or less. The average of the difference between calculated and measured ratios for the seven samples having the greatest strontium excess is 0.00016. Two samples from greater than 300 m in the deep wells UNAM2 and UNAM5 have chloride concentrations greater than seawater. For these, \(\text{Cl}_{\text{Gwtr}}/\text{Cl}_{\text{Sea}}\) was taken to be 1. These high chloride values indicate that some chloride in water passing through Yucatan evaporite may be residual halite released from the rock as gypsum dissolves, but halite is less likely to remain in the rocks enclosing open-flow systems (cenotes and conduits) than in closed wells.

Agreement between modeled and measured isotope ratios is consistent with derivation of excess strontium from Cretaceous–Eocene evaporite. The association can be directly observed in UNAMS. Groundwater from there (Table 1) was sampled at the depth of the impact breccia layer. We consider that the mass balance calculation for strontium isotopes provides strong support for the presence of a strontium-rich layer containing evaporite minerals of late Cretaceous–early Tertiary age in contact with water of the saline intrusion over much or all of the northwest and north-central Yucatan Peninsula outside the Ring of Cenotes. This large area considerably extends the region of known Chicxulub impact ejecta confirmed by drilling (Rebolledo-Vieyra et al. (2000). Additional and independent confirmation comes from a breccia occurrence recently reported near Valladolid by (Urrutia et al., 2008). The area in which impact ejecta are indicated either by direct observation obtained by drilling or by strontium isotope measurement of deep, saline groundwater is indicated in Fig. 3. A different strontium isotope pattern is present along the east coast. First, impact ejecta occur at the surface in southeast Quintana Roo. These constitute the Albion Formation, described below. Second, water from Cenote “Big Calica”, in east-central Quintana Roo (Fig. 1) does not have a strontium excess compared to seawater, and its strontium isotope composition is essentially that of seawater (Fig. 2b). There are at least three possible reasons for this: (a) the deepest water in this cenote is still too shallow to be in contact

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**Fig. 3.** Relationship between ejecta/evaporite “package”, water table, structural, and geomorphic features: a first approximation. Two interpretations illustrated in this diagram are well established: (1) groundwater flow north and west through the Ticul Fault and western arm of the Ring of Cenotes and (2) presence of an ejecta layer and/or early Tertiary evaporite beneath the saline intrusion of the northwest and north-central Peninsula. Other interpretations require further testing. Whereas the Albion Formation crops out in southern Quintana Roo and in Belize its northern and western extent remains to be verified. Note that a change in coastal morphology occurs north of where the Albion Formation disappears; that change may be related to groundwater CaSO₄ content. Furthermore, clay content of the Albion Formation may act as an aquitard influencing drainage patterns in southern Quintana Roo (cf. Kenkmann and Schöner, 2006). Groundwater geochemistry suggests that the influence of a pervasive early Tertiary gypsum layer in southern Campeche and southeastern Quintana Roo on subsurface erosion and geomorphology depends on whether that layer is above or below the water table, which is closely controlled by sea level.
with an evaporite/breccia; (b) no strontium-rich layer was deposited there; or (c) a strontium-rich layer was once present but has completely dissolved as a result of rapid circulation between the coast and the Holbox Fracture Zone (Fig. 1) in a region of relatively high rainfall; thus current groundwater has no strontium-rich strata to interact with.

Geochemical expression of K-Early Tertiary layer in different geographic areas

The “Pockmarked Terrain”

A large region in the central northern part of the Peninsula that is characterized by an exceptionally high concentration of cenotes and other dolines, extends eastward from the Ring of Cenotes, and includes Cenotes Xkoolac and Ucil (Fig. 1). Perry et al. (1996, 2002) labeled this region the “Pockmarked Terrain”. They postulated that development of the unusual and extended karst in that area could have resulted, in part, from dissolution and collapse of a subsurface evaporite as well as from dissolution of carbonate rocks. That hypothesis is reinforced by the strontium isotope data presented here, which indicate the existence of a deep evaporite/ejecta layer beneath Cenotes Ucil and Xkoolac and by the discovery of evaporite in an observation well on the outskirts of Valladolid (Urrutia et al., 2008).

An additional factor associated with the Chicxulub impact that has possibly contributed to the extensive karstification of the region is a dense pattern of radial faults that has been documented offshore in the shallow pre-Tertiary basement near the pockmarked area (Gulick et al., 2008). These faults, which are perpendicular to the shoreline and project into the land, may have resulted in exceptional permeability development, opening this zone to extensive groundwater penetration. The enhanced permeability, of itself, may have been sufficient to produce subsurface dissolution of both carbonates and evaporites. However, in contrast to carbonate dissolution, solubility of gypsum, anhydrite, and celestite is not directly pH dependent and thus is perhaps more likely to take place within the saline intrusion, well below the water table, if deep groundwater circulation occurs. In that case, expansion accompanying hydration of anhydrite may have preceded and accelerated dissolution of gypsum associated with impact ejecta to produce the subsurface erosion that contributed to collapse features in the area.

Ticul fault and cenote ring

Based primarily on sulfate/chloride ratios, Perry et al. (2002) hypothesized that water of the region west of the groundwater divide at Lake Chichcanchanab flows northwest from the lake into and along the Ticul fault from whence it enters the western arm of the Ring of Cenotes. This groundwater eventually flows northward into the Celestun Estuary (Perry and Velazquez-Olman, 1996) (Fig. 1). Remarkably, although the flow path is 200 km long, the water level in Lake Chichcanchanab is only 3 m above mean sea level; equivalent to a gradient of 1.5 cm/km. Additional evidence for extensive groundwater movement along this flow path comes from chloride and strontium ion chemistry and from strontium isotope data introduced here. Samples for ion chemistry were taken from water of shallow municipal wells and from a piezometer forced into the silt bottom of Celestun Estuary (Table 2). The data show a progressive decrease in the ratio [SO4/Cl]groundwater/[SO4/Cl]seawater in water from the following towns along the Ticul fault (listed in order from southeast to northwest): Dziuche (ratio = 33), Catmis (18), Sta. Rosa (14), Tzcucab (10), and Ticul (5). (Localities are shown in Fig. 1.) These ratios may be compared to a ratio of 70 in water of the presumed source region, Lake Chichcanchanab. These observations are consistent with data recently published of these parameters in Celestun lagoon (Young et al., 2008).

Fig. 2a shows that, in going from southeast to northwest, a regular increase occurs in [87Sr/86Sr] of well waters that parallels the [SO4/Cl]groundwater/[SO4/Cl]seawater decrease. Thus, the [87Sr/86Sr] ratios become progressively “younger” in that direction, which is consistent with progressive incorporation of modern seawater. Groundwater strontium concentration also becomes progressively lower, and chloride becomes progressively higher as water moves along the flowpath as shown in Fig. 2d (Group IIB). These observations can be explained by upconing of water of an underlying saline intrusion accompanied by turbulent mixing of this saline water with channelized groundwater flowing through the fault system.

Cores show that Lake Chichcanchanab began to fill about 8200 14C years ago as worldwide sea level was rising and then proceeded to fill rapidly (Hodell et al., 1995; Brenner et al., 2003), suggesting that the lake has responded closely to changing sea level since the Pleistocene. It is likely that this close hydrodynamic contact with the ocean has been primarily by flow to the north through fault zones, as indicated by the groundwater chemistry, rather than by a shorter but more tenuous hydrologic connection with the Caribbean coast.

Seawater intrusion and fresh water–seawater mixing near the Caribbean coast

Back et al. (1979) showed that along the Caribbean coast in east-central Quintana Roo mixing of fresh groundwater with seawater produces a solution that aggressively dissolves limestone, forming bays (caletas) such as the one at Xel Ha. This erosive process has been confirmed by Stoessell et al. (1989), Smart et al. (2006) and by numerous other authors, and the process has a demonstrable effect on coastal erosion in northeast Quintana Roo.

Groundwater flowing to the southeastern coast of Quintana Roo near Chetumal is exposed to gypsum along its flow path (Perry et al., 2002). In consequence, it is qualitatively different from the groundwater arriving at the northeastern coast, and mixtures of this water with seawater may not be as erosive to limestone as the mixed coastal waters of east-central Quintana Roo. Specifically, calcium is enriched in these waters due to gypsum dissolution. Using the program PHREEQC (Parkhurst, 1995), Perry et al. (2002) confirmed that mixtures of seawater with water from Cenote Azul, located near the Caribbean coast in southeastern Quintana Roo (Fig. 1), would not dissolve limestone. Because it is now evident that high-calcium, high-sulfate water is common in a large part of the southeastern region, including northeastern Belize (Marfia et al., 2004), it may be worth future investigation to determine the effect of groundwater type and groundwater mixing on coastline erosion. A notable coastal transition occurs between Tulum and Chetumal.

Cenote Azul presents a curious anomaly. Its 64-m deep water column is homogeneous throughout and is characterized by an exceptionally high SO4/Cl equivalent ratio of 21 and an 87Sr/86Sr ratiotio of 0.70764. This chemistry indicates virtually no mixing with seawater. Perry et al. (2002) confirmed that mixtures of seawater with water from Cenote Azul, located near the Caribbean coast in southeastern Quintana Roo (Fig. 1), would not dissolve limestone. Because it is now evident that high-calcium, high-sulfate water is common in a large part of the southeastern region, including northeastern Belize (Marfia et al., 2004), it may be worth future investigation to determine the effect of groundwater type and groundwater mixing on coastline erosion. A notable coastal transition occurs between Tulum and Chetumal.

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water whose ion chemistry was not dominated by calcium sulfate dissolution.

Southeast Quintana Roo

The presence of Chicxulub impact ejecta at the Albion Island quarry in Belize was reported by Ocampo et al. (1996) and King et al. (2002). Pope et al. (2005) have subsequently discussed exposures of the Albion Formation in outcrops on the Ucum-La Union road, which follows the western (Mexican) escarpment of the Rio Hondo, and in a quarry in Quintana Roo (Fig. 1). Between these outcrops of ejecta in the southeast and the better-known rocks of northwestern Yucatan, there is a unique geomorphic region in which outcrops are both rare and strongly weathered. Groundwater geochemistry offers useful insight into the geology of this covered region.

Pope et al. (2005) reported the presence of shocked quartz in diamicite, spherule beds and other characteristic lithologies of the Albion Formation confirming that these are ejecta deposits. Schönian et al. (2005), Kenkmann and Schönian (2006), and Schönian (written communication, 2007) have examined the Albion Formation along the Ucum-La Union road and have mapped an area north and west of Chetumal (marked by a rectangle in Fig. 1), concluding (Schönian et al., 2005) that “a ground hugging, cohesive and highly erosive ejecta flow [overran], eroded and draped [over] a karstified [Late Cretaceous] land surface on the coastal drainage system.” Earlier, Perry et al. (2002) had recognized the distinctive topography and the high-sulfate content of groundwater in the region east and south of Lake Chichancanab, which they labeled the Evaporite Region. They postulated that: “If sulfate in the Evaporite Region comes predominantly from K/T impact breccia, lowered permeability of the aquifer there may result from the presence of a layer of suevite, altered to clay minerals.” Perry et al. (2002) based this hypothesis in part on the fact that waters of Lake Chichancanab and Cenote Azul, at the northwest and eastern margins respectively of the established part of the area in question, are saturated with respect to gypsum (as they are also with respect to celestite).

A newly available geologic map of the Yucatán Peninsula (Servicio Geológico Mexicano, 2007), on which Fig. 1 is based, both clarifies and complicates the stratigraphic and hydrogeologic relationships of the area. Complication arises because much of what has been recognized as impact ejecta by Pope et al. (2005) and Kenkmann and Schönian (2006) is mapped as Eocene (Lopez-Ramos, 1983). Nevertheless, the Albion Formation (Fig. 1) as Holocene alluvium can be seen by comparing the rectangle in the lower right of Fig. 1 with the map of ejecta shown in Fig. 6 of Kenkmann and Schönian (2006). This discrepancy comes about because the ejecta blanket material is poorly consolidated and can be distinguished conclusively from alluvium only by microscopic examination of the clasts and/or precise mineral age determination.

An ill-defined region of poorly exposed impact ejecta, partly covered by Tertiary limestone, extends east to the Caribbean coast from Lake Chichancanab on the north and continues south for an indeterminate distance into Belize. On the west, ejecta, where present, become covered along the highly irregular contact with the Paleocene Icaché Formation (Fig. 1).

Available data show that surface water and groundwater from the area have high SO_4/Cl ratios (Table 2). These ratios help evaluate the magnitude of the seawater contribution to the ion chemistry in this region as they did for groundwater along the Ticul Fault. Dilute waters from Lakes Ocom and Nohbec have [SO_4/Cl]_groundwater ratios nine times as great as the molal (or equivalent) ratio in seawater. The enrichment ratio for Cenote Azul is 200 times seawater; municipal groundwater sources of various towns and villages are 14–105 times enriched, and Lakes Chichancanab, Esmeralda, and Bacalar are about 70 times enriched. Furthermore, the ratio varies widely over distances of a few kilometers. For example, the ratio is 17 for groundwater of Chunuhub Pueblo and 88 for the Chunuhub Agricultural Station a few kilometers away, suggesting an inhomogeneous aquifer and/or low permeability. This variability contrasts sharply with the homogeneous character of the groundwater in the aquifer west and north of Lake Chichancanab. It may be useful for establishing the northeastern boundary of the ejecta blanketed region to note that groundwater from Felipe Carillo Puerto has an SO_4/Cl ratio that is 14 times the seawater ratio, whereas for Cenote Car Wash, which penetrates the saline intrusion and is our nearest source of data to the northeast (Fig. 1), the ratio within the fresh water lens is only 0.94 (Perry et al., 2002).

The geochemical distinctiveness of southeastern Quintana Roo is matched by an obvious and distinctive geomorphology with implications for hydrogeologic significance. This is most apparent in a transition zone that begins at or very near Lake Chichancanab. In southeastern Quintana Roo, east and south of Lake Chichancanab, there is a pattern of long sinuous lakes and discontinuous perennial streams. This suggests the presence of a near-surface aquitard that formerly supported a perched water table that has now been partially breached. In contrast, west and north of Lake Chichancanab, there is no surface drainage and only a thin soil cover. There, recharge water moves rapidly downward from the surface through permeable carbonate rocks to the groundwater table.

An evaluation of the ionic and isotopic composition of groundwater strontium gives added support for the presence of a widespread ejecta blanket in south and southeast Quintana Roo. Although the town of Peto lies only a few kilometers west of the blanketed region, it is well inside the main geomorphic area of the northwestern Peninsula, lacking aquitards, soil cover, and surface drainage. At Peto the impact ejecta, overlain by a thin layer of Lower Tertiary evaporite, is present, but it lies beneath Tertiary carbonate rock and is about 220 m below the water table (Lefciarciu et al., 2006). Shallow groundwater in municipal wells of Peto is not saturated with respect to either gypsum or celestite. Nevertheless, strontium concentration of this water is high (0.06 mmoles/kg, Perry et al., 2002) and the 87Sr/86Sr ratio is 0.70782, approximately at the upper limit of values from Albion Formation ejecta. As stated previously, Lake Chichancanab, which is only 25 km south of Peto, lies at the northwest edge of the proposed blanketed region. Its water is saturated with respect to both gypsum and celestite and has an 87Sr/86Sr ratio of 0.70776 (within the lower range of values for strontium from impact ejecta of the Albion Formation). Water of Lake Esmeralda, the southeastern extension of Lake Chichancanab, is near-saturation with gypsum and celestite and its 87Sr/86Sr ratio is 0.70776. Saturation of lake water with gypsum indicates that an evaporite formation is near the land surface.

The eastern shore of Lakes Chichancanab and Esmeralda is a scarp, about 20 m high, and the conclusion that best synthesizes available stratigraphic, geomorphic, and geochemical data is that the shore marks a fault, upthrust to the east, bringing ejecta and evaporite to the surface. Because the ejecta layer is overlain at Peto by early Tertiary evaporite, geochemical data leave open the possibility that patches of early Tertiary evaporite are present throughout southeastern Quintana Roo, much of which was originally mapped as Eocene (Lopez-Ramos, 1983). Nevertheless, the Albion Formation, known to have a high content of clay derived from altered glass (Ocampo et al., 1996; Kenkmann and Schönian, 2006) is the rock unit most likely to form the sparsely-exposed, weakly-consolidated sedimentary blanket mantling much of southeastern Quintana Roo.
In summary, there is evidence for a blanket of clay-rich ejecta east and south of Lake Chichancanab and no evidence for such a blanket a few kilometers west and north of the lake. The ejecta deposits and associated clays of the Albion Formation are the only rocks of the northern Peninsula known to be capable of acting as effective aquitards.

**Poljes of Campeche and southwestern Quintana Roo**

Poljes, also known as bajos, are karst solution features of various sizes that are abundant in eastern Campeche, southern Quintana Roo, and Belize (Fig. 1). They are closed basins with flat floors; their drainage is predominantly internal but may be augmented by seasonal perched surface streams that flow over dense clay layers and connect adjacent basins. Their floors can be as much as 100 m above the water table. These basins appear to have responded in complex ways to past climates, and some probably provided a rich agricultural resource for indigenous Maya during wet climate regimes (Beach et al., 2008).

Several characteristics of Yucatan poljes may help explain their origin. Recent mapping (Fig. 1) shows that they tend to be bounded by the gypsum-bearing Icaché Formation which elsewhere overlies Chixculub impact ejecta. The numerous gypsum quarries in this formation that are located along and near Mexican Highway 186 (Fig. 1) are one indication that this mineral is abundant in this area. Another significant observation is that where the interior subterranean drainage reaches the east coast, along the Rio Hondo escarpment it has very high SO₄ and Ca to Cl ratios. A recent reconnaissance by Perry et al. (2008) along the Mexican (western) side of the Rio Hondo shows that a large number of springs debouch into the Rio Hondo with water having a conductivity of about 1.8 mS (Perry et al., 2008), and observations by Marfiaa et al. (2004) confirm that groundwater in northern Belize has concentrations of Ca²⁺ and SO₄²⁻ in 1:1 proportion indicating probable dissolution of gypsum. Similarly, on the west coast of Campeche water analyses by the Mexican National Water Commission (CNA) give high-sulfate values and sulfate/chloride ratios (written communication from CNA, 2008). These chemical relations show that the chemistry of groundwater in the southeastern and southwestern Yucatan Peninsula is essentially the same as that of Lake Chichancanab, Cenote Azul, and Lake Bacalar. [Sr-isotope measurements are pending.]

We hypothesize that dissolving evaporite at the base of the Icaché Formation has formed a permeable layer that is acting as a preferential flow path eroding overlying limestone and forming or contributing to the formation of the many poljes of the region. [Larger poljes are named in Fig. 1. Smaller ones are identifiable as patches of Quaternary alluvium bounded by Eocene and Paleocene rocks.] By analogy with the stratigraphic section at Peto, the outcrops of ejecta along the Rio Hondo, and the relation of these to adjacent water bodies, it is reasonable that the gypsum-rich unit in Campeche and southwestern Quintana Roo is part of the ejecta blanket or, more likely, that it directly overlies the ejecta blanket. The fact that poljes tend to “bottom out” at the same stratigraphic level suggests that this level is marked by an aquitard, very likely the clay-rich portion of the ejecta blanket.

**Applicability**

Because there is no surface drainage over most of the area covered by this study, knowledge of groundwater hydrogeology is essential for water and liquid waste management. Specifically, practically all of the drinking water is from groundwater and not surface water sources. Groundwater studies of the geochemical parameters elucidated here can help determine the lateral extent of the saline intrusion, identify zones of low and high permeability, and trace groundwater movement in a complex karst system. Groundwater quality in the northern Yucatan Peninsula is being threatened by factory-style poultry and hog farms in the northwest and by exponential growth of tourism along the east coast in Quintana Roo. Breaching of a coastal aquitard threatens to reduce the thickness of the lens of fresh groundwater in northern Yucatan (Perry et al., 1989; Battllo, 2007). Exponentially increasing numbers of tourists who come to experience the impressive reefs along the Caribbean coast of Quintana Roo contribute pollution that threatens those same reefs. Chemical tracer studies can identify risk zones, and provide background information necessary to minimize or alleviate many of these problems.

In southern Yucatan state, geochemical modeling of additional data on strontium, chloride, and sulfate in groundwater north of the Ticul fault system will help to evaluate the contamination risk suggested in papers by Steinich et al. (1996), Steinich and Marín (1997), Marín et al. (2000). These researchers have suggested that a seasonal change in groundwater flow direction south of Merida may contaminate the municipal water supply of that city. In the same general area, groundwater geochemical tracers may help prevent locating large factory-style poultry and hog farms along groundwater flow paths that could contaminate both the Merida water supply and the Celestun Estuary.

Injection of municipal liquid waste into the saline intrusion has long been proposed for Merida (Marín et al., 2000) and has been tried on a limited basis. Although we do not address the question of whether this is a desirable approach to waste management, an extension of the present study may help determine whether/where permeable strata are present at suitable depths within the saline intrusion that have adequate permeability to accept fluid waste.

Dissolution of sulfate minerals may have made the ejecta layer a suitable stratum where it exists: near Valladolid, Tizimin, and other smaller cities. Ejecta almost certainly are not present beneath Merida, and this study provides no evidence for it beneath the rapidly developing east coast corridor south of Cancun (Fig. 1 and 3).

**Conclusions and implications**

Our results suggest that large areas of the Yucatan and Quintana Roo regions are underlain by an ejecta/evaporite complex that has provided a favorable pathway for groundwater movement and that the resulting layer of high permeability has produced subsurface erosion and distinctive surface morphological features. Important aquifer characteristics elucidated by this study, as well as the evidence for them, and their hydrogeologic consequences are presented in Table 3. Study of the isotopic composition of groundwater strontium from Hurricane Isadore indicates that several years-to-decades are required for groundwater to equilibrate chemically with diagenetically stabilized aquifer carbonate minerals of the northern Yucatan Peninsula, Mexico. This makes the ratio ⁸⁷Sr/⁸⁶Sr useful as a natural tracer for the general age of the groundwater and the degree to which groundwater has approached equilibrium with aquifer rocks, especially when used together with strontium, chloride, and sulfate ion concentrations. By using strontium isotopic and concentration data it is possible to distinguish stratigraphic relations in parts of the northern Yucatan Peninsula where these have hitherto been unknown or poorly defined (Fig. 3). Strontium chemistry outlines a region in Quintana Roo lying northwest of Lake Bacalar and possibly extending as far north and east as Lake Chichancanab. This area appears to be mantled by a blanket of poorly consolidated, clay-rich, celestite-bearing impact material of the Albion Formation. There is no
<table>
<thead>
<tr>
<th>Region</th>
<th>Important feature</th>
<th>Consequence</th>
<th>Relevant evidence</th>
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<tbody>
<tr>
<td><strong>I. Northern Yucatan Peninsula east of Ring of Cenotes</strong></td>
<td>A. Impact ejecta (and perhaps early Tertiary evaporite) within saline intrusion</td>
<td>(1) Partial dissolution produces a layer of high permeability within the saline intrusion - a layer possibly useful for liquid waste discharge (2) Subterranean erosion may be responsible for the cenote/doline-cidden geomorphology of north-central Yucatan state (&quot;Pockmarked Terrain&quot;)</td>
<td>Add strontium to groundwater of the saline intrusion, resulting in strontium concentrations greater than seawater. Calculated $^{87}\text{Sr}/^{86}\text{Sr}$ of added strontium is 0.7078</td>
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<td></td>
<td>B. Presence of saline intrusion beneath freshwater lens</td>
<td>Return flow influences ion chemistry in fresh water lens</td>
<td>Saline intrusion has been observed in water of a deep Santa Elena well and also throughout northern Yucatan state (1) Slight but regular increase in $^{87}\text{Sr}/^{86}\text{Sr}$ from east to west along flow path (resulting from progressive incorporation of seawater Sr with a ratio of 0.7092)</td>
</tr>
<tr>
<td></td>
<td><strong>II. Ticul Fault and Ring of Cenotes</strong></td>
<td>A. Presence of saline intrusion beneath freshwater lens</td>
<td>Return flow influences ion chemistry in fresh water lens</td>
</tr>
<tr>
<td></td>
<td>B. Ticul Fault and the western arm of Ring of Cenotes together from a major subsurface channel for groundwater flow</td>
<td>Results in a 200 km subsurface flow path that controls groundwater movement and water table in much of the central and northwestern Yucatan Peninsula</td>
<td>(1) Stratigraphy of mapped Albion Formation in SE Quintana Roo (2) Surface drainage pattern (3) Saturation of lake/cenote water in gypsum and celestite (4) Groundwater with $\text{Kt–Eocene}^{87}\text{Sr}/^{86}\text{Sr}$ ratio and high $\text{Sr/Cl}$ and $\text{SO}_4/\text{Cl}$</td>
</tr>
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<td></td>
<td><strong>III. Southeast Quintana Roo</strong></td>
<td>A. Terminal Cretaceous impact ejecta (Albion Formation containing both high clay content [partly or entirely devitrified glass] and Kt evaporite fragments) exposed near-surface</td>
<td>Clay acts as a &quot;blanket&quot; or near-surface aquitard preserving underlying pre-impact karst</td>
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<td>B. Possible outliers of early Tertiary evaporite</td>
<td>High and variable TDS in groundwater</td>
<td>Drill core from Peto has evaporite overlying impact breccia. (Observed $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is compatible with $\text{Kt–Eocene}$ evaporite.)</td>
</tr>
<tr>
<td></td>
<td>C. No saline intrusion</td>
<td>No mixing of fresh and saline water</td>
<td>(1) Low chloride content even in deep water from Cenote Azul (2) High ratios of $\text{SO}_4/\text{Cl}$ in Cenote Azul</td>
</tr>
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<td></td>
<td>D. Mixture of area groundwater with seawater is not aggressive to limestone</td>
<td>Proposed effect on coastal erosion: coast south of Tulum is different from coast north of Tulum. (Does not form caletas.)</td>
<td>Groundwater modeling (PHREEQC) shows that mixtures of Cenote Azul water (for example) with seawater would not dissolve limestone</td>
</tr>
<tr>
<td></td>
<td><strong>IV. Campeche-Southeast Quintana Roo-Southernmost Yucatan</strong></td>
<td>A. Gypsum-bearing Icaiche Fm</td>
<td>Gypsum dissolves to form widespread aquifer at base of the formation. This layer is capable of active erosion where it is uplifted above sea level. Widespread geomorphic feature. Variably important for agriculture</td>
</tr>
<tr>
<td></td>
<td>B. Poljes at base of gypsiferous Palocene Icaiche Fm</td>
<td>Flat, enclosed basins with residual soil and chert nodules</td>
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</table>
evidence that a seawater intrusion exists within this region, but studies of Hodell et al. (1995) and Brenner et al. (2003) indicate to us that Lake Chichancanab, on the northeastern boundary of this area, does respond directly to sea level fluctuation, probably through permeable fault zones entering into the Celestun Estuary on the northwest coast of Yucatan. A large area in northwest Yucatan appears to be underlain by a layer of K/T ejecta in which celestite is dissolving in water of a very extensive seawater intrusion. This area encompasses UNAM drill holes 2, 5, 6, and 7, and the Yaco-opol drill site (Rebolledo-Vieyra et al., 2000), extends to the northwest coast, and includes the Pockmarked Terrain, but it excludes the area inside the Ring of Cenotes. The eastern boundary of this region is not well defined, but it appears not to extend to the northern Caribbean coast and may be bounded by the Holbox Fracture Zone. A region exists on the east coast of Quintana Roo in which the saline intrusion does not interact with impact ejecta. Establishing the extent of this region, which is defined at present by data of Ronald (Stoessell, 2006) have been essential to this study. This is ACCEC Publication 56.

In addition to stratigraphic relations revealed by strontium data, $^{87}$Sr/$^{86}$Sr ratios confirm that groundwater with distinctive chemical composition moves in a northwesterly direction from the vicinity of Lake Chichancanab, through a permeable fault zone manifested at the surface by the Sierra de Tícul, into the western arm of the Ring of Cenotes, to finally debouch into the Celestun Estuary.

Our data also show that poljes, which are an important geomorphic feature in Campeche, southwest Quintana Roo and southernmost Yucatan state, appear to form by subterranean erosion induced by groundwater moving selectively through a sedimentary packet of dissolving evaporite minerals that are either part of the Chicxulub impact ejecta or an associated early Tertiary sedimentary layer. The capacity of this layer to erode limestone by dissolution and carrying off ions is greatest where it has been raised above the water table by the Tícul Fault. Facies changes within the ejecta blanket, particularly the relative content of evaporite material to altered silicate glass may also affect its hydrogeologic behavior.

Data presented here may be useful in determining the detailed character and extent of material ejected by the Chicxulub bolide impact. It may also help provide guidance for management of groundwater and liquid waste injection for a region of increasing population whose only supply of water is underground. Although this study is of a unique region, it demonstrates that groundwater and isotopic chemistry may be generally useful as tracers of groundwater movement and aquifer composition.

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Beddows, P.A., Smart, P.L., Whitaker, F.F., Smith, S.L., 2007. Decoupled fresh–saline groundwater circulation of a coastal carbonate aquifer: spatial patterns of geochemical evidence that a seawater intrusion exists within this region, but studies of Hodell et al. (1995) and Brenner et al. (2003) indicate to us that Lake Chichancanab, on the northeastern boundary of this area, does respond directly to sea level fluctuation, probably through permeable fault zones entering into the Celestun Estuary on the northwest coast of Yucatan. A large area in northwest Yucatan appears to be underlain by a layer of K/T ejecta in which celestite is dissolving in water of a very extensive seawater intrusion. This area encompasses UNAM drill holes 2, 5, 6, and 7, and the Yaco-opol drill site (Rebolledo-Vieyra et al., 2000), extends to the northwest coast, and includes the Pockmarked Terrain, but it excludes the area inside the Ring of Cenotes. The eastern boundary of this region is not well defined, but it appears not to extend to the northern Caribbean coast and may be bounded by the Holbox Fracture Zone. A region exists on the east coast of Quintana Roo in which the saline intrusion does not interact with impact ejecta. Establishing the extent of this region, which is defined at present by data of Ronald (Stoessell, 2006) have been essential to this study. This is ACCEC Publication 56.

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