Groundwater Sr, Cl, and SO_4 chemistry in the western and southern Yucatan Peninsula: insight into formation of Edzna Valley, Mexico

E.C. Perry
Department of Geological and Environmental Science, Northern Illinois University, DeKalb, IL 60115, USA

G. Velazquez-Oliman
Estudios Hidrogeologicos y, de Calidad Ambiental, Pto Morelos, Quintana Roo, Mexico

N. Wagner
Southern Illinois University, Carbondale, IL, USA

A. Paytan & J. Street
Institute of Marine Sciences, University of California Santa Cruz, Santa Cruz, CA 95064, USA

ABSTRACT: Strontium isotope chemistry, presented here, combined with previously obtained groundwater ion chemistry elucidates the stratigraphy of buried sedimentary rocks of the southern Yucatan Peninsula, Mexico. Whereas in groundwater of the northern Peninsula, ion chemistry is dominated by contact with a saline intrusion, the groundwater of southern Campeche and southern Quintana Roo has high SO_4/Cl and Sr/Cl indicating extensive contact with beds of dissolving gypsum (and celestite) in the subsurface. The newly-obtained strontium isotope data presented here strengthen a conclusion of previous research, namely that, in marked contrast with the north, there is no saline intrusion in the southern Peninsula. $^{87}Sr/^{86}Sr$ measurements confirm that much of the evaporite that is contributing ions to southern Peninsula groundwater has a Kt-Eocene seawater isotope signature. A key conclusion from combined study of Sr, Sr isotopes, Cl, and SO_4 is that a large geomorphic feature in western Campeche, the Valley of Edzna polje, was once occupied by a post-Eocene seawater incursion.

1 INTRODUCTION

Groundwater ion content of Sr, Cl, and SO_4 and $^{87}Sr/^{86}Sr$ has been effective in elucidating stratigraphy of the flat-lying rocks of the northern Yucatan Peninsula, Mexico (Perry et al. 2009). The technique is particularly useful in this area where rock exposure is limited. The relatively soluble subsurface rock units contribute ions to groundwater, and their age and composition can be inferred based on groundwater chemistry. Here we utilize this geochemical approach to study the stratigraphy of southern Quintana Roo and eastern Campeche (where groundwater enters the Caribbean Sea through Lake Bacalar and the Rio Hondo) and of western Campeche (where we report geochemical evidence of an Oligocene or later marine incursion into what is now the Valley of Edzna polje).

The Yucatan Peninsula is a sedimentary platform whose accessible rocks consist largely of karstified Cenozoic carbonates (Fig. 1). Aspects of the relevant geology and hydrogeology of the region are summarized in Perry et al. (2009). The stratigraphy of much of the Peninsula is poorly known, even in the north and west where most of the recent geologic research has been concentrated, where soil cover is thin or absent, and where bedrock exposure is nearly complete.

Rocks of the Peninsula to depths of more than 500 m are dominantly limestone and dolomite of Cretaceous and younger age with rare siliciclastic units except in the south. The precise relation of evaporite beds to Chicxulub impact breccia, which also contains gypsum and anhydrite, remains to be determined (Perry et al. 2009). An evaporite unit, interpreted as lower Eocene, is present at depths of 225-265 m in drill hole UNAM 6 at Peto, Yucatan (20.11°N, 88.93°W). This evaporite unit occurs immediately above what is interpreted as a collapse breccia formed during Paleocene subaerial exposure of impact ejecta (Lefticariu et al. 2006). Farther south, in Quintana Roo and Belize, ejecta from the Chicxulub meteorite impact crop out as the Albion Formation (Ocampo et al. 1996, Kenkmann & Schönian 2006, and references therein). Whatever the precise relation between impact ejecta and evaporite, the large area of exposed Paleocene Icaiché Formation in eastern Campeche and southwestern Quintana Roo contains one or more beds of gypsum exposed in numerous gypsum quarries and outcrops along and near Mexico Highway 186 (Fig. 1). These gypsum exposures coincide with occurrences of Chicxulub impact ejecta reported in wells by Kenkmann & Schönian et al. (2006, Fig. 6); and weathering of gypsum beds may contribute to the physiographic pattern of internal drainage and polje formation in Campeche and southern Quintana Roo.

The principal sources of inorganic ions in groundwater (and surface water) of the Yucatan Peninsula are seawater from a saline intrusion and the dissolution of minerals from aquifer rocks. Most Yucatan groundwater is in approximate equilibrium with calcite and dolomite of the aquifer (Perry et al. 2002). Cl and SO_4 typically behave conservatively except where redox processes are active within the aquifer. Thus, the ratio of SO_4/Cl in seawater (100xSO_4/Cl equivalent of about 10.3) indicates exchange between an upper lens of fresh groundwater and a deeper intrusion of modified seawater. Values significantly higher indicate dissolution of gypsum from evaporite. Low values, which are unusual, indicate sulfate reduction (Perry et al. 2002, 2009 & in press). Sr in groundwater has proven to be a reliable indicator of contact of the groundwater with an evaporite in this area (Perry et al. 2002). Apparently, celestite ($SrSO_4$) is a ubiquitous minor mineral in evaporites of the region. Thus, a Sr/Cl ratio higher than the seawater ratio is an additional indicator of the presence of evaporite in the aquifer, and this criterion is useful even for deep groundwater of the saline intrusion.

Strontium isotopes provide another useful tracer. Unless subsequently altered, $^{87}Sr/^{86}Sr$ values of minerals precipitated from seawater record the Sr isotopic composition of the water from which they crystallized. Therefore, the changes in seawater $^{87}Sr/^{86}Sr$ over time (McArthur et al. 2001) can be used to date marine chemical sedimentary rocks including evaporites and thus used as a stratigraphic tool.

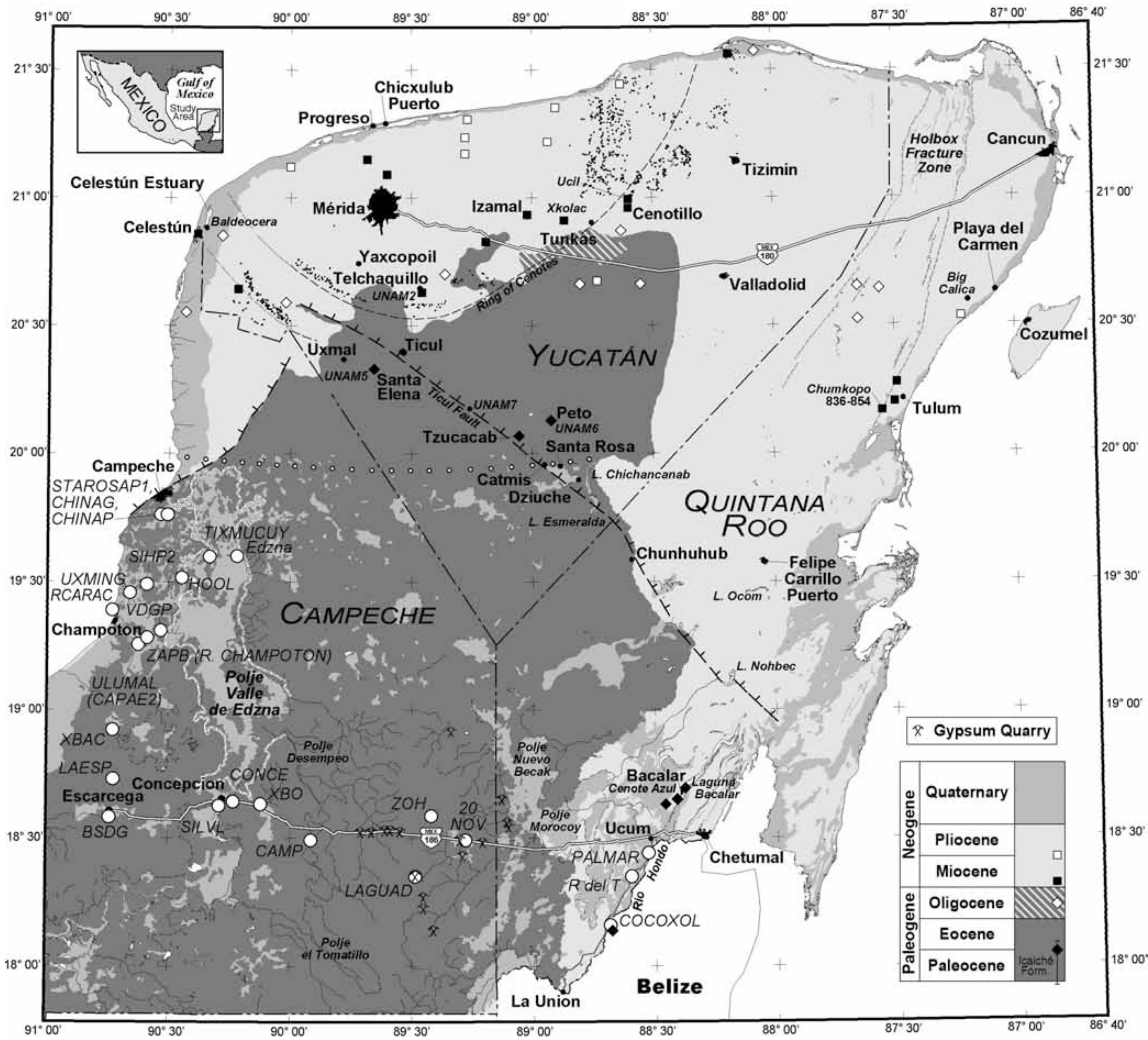


Figure 1. Geologic map of the Yucatan Peninsula (after Perry et al. 2009 & in press). Apparent $^{87}Sr/^{86}Sr$ "ages" of groundwater reported in that paper are as shown in the legend. Location of water samples of this study are shown as open circles.

2 DISCUSSION

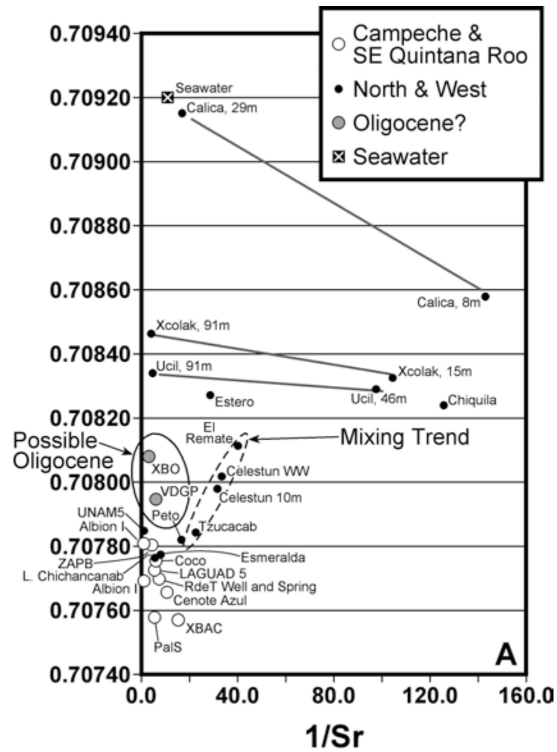
In a preliminary study of groundwater geochemistry in Campeche and southern Quintana Roo Perry et al. (in press) used plots of SO_4 vs Cl and 1000Sr/Cl vs 1/Sr to establish that, in contrast to the northern Peninsula (where an extensive saline intrusion exists) there is no evidence for a saline intrusion in most of the southern Peninsula. They determined that abundant SO_4 from an evaporitic source is present in groundwater throughout much of southern Campeche, making the groundwater there of questionable value for municipal water and for many agricultural uses. In contrast, water in shallow lakes and ponds, fed by precipitation and isolated from the groundwater by an extensive clay layer (possibly derived from Chicxulub impact ejecta) is free of SO_4 and other ions. Perry et al. (in press) did not include Sr isotope data in that study, and consequently some of the conclusions of the study are ambiguous.

Here we extend the previous study and incorporate nine $^{87}Sr/^{86}Sr$ measurements of groundwater from Campeche and southern Quintana Roo. These isotopic data are presented in Table 1 together with previously reported Cl, SO_4, and Sr ion data from Perry et al. (in press).

Table 1. Molal ratio (1000x(Sr/Cl), 1/Sr, $^{87}Sr/^{86}Sr$, and map labels of groundwater samples from Campeche and southern Quintana Roo.

Name	1000xSr/Cl Molal	$^{87}Sr/^{86}Sr$	1/Sr 1/meq	Label
Xbacab well	71.63	0.70757	15.15	XBAC
Palmar spring	84.42	0.70758	5.42	PalS
Rancho del Toro well	76.96	0.70770	7.12	RdeTW
Rancho del Toro spring	76.02	0.70770	7.24	RdeTS
La Guadalupe spring	9.24	0.70773	5.45	LAGUADS
Cocoyol well	88.70	0.70775	5.64	Coco
El Zapote river	15.64	0.70780	4.36	ZAPB
Villa de Guadalupe well	102.26	0.70795	5.95	VDGP
Xbonil well	180.86	0.70808	3.12	XBO
Sea (Approx)	0.20	0.70920	10.80	

The new data largely confirm the conclusions previously reported by Perry et al. In addition, the new isotope data provide further constraints and lead to one unique conclusion. Specifically, the strontium isotopic composition of groundwater from wells in two villages on the edge of the Edzna Valley polje in western Campeche is significantly different from the isotopic composition of groundwater from wells and springs known to be in contact with Paleocene evaporite in southeastern Campeche. Based on the strontium isotope data alone it would be possible to attribute this result to contamination by modern seawater, which would cause an isotope shift toward a higher $^{87}Sr/^{86}Sr$ ratio relative to a pure Paleocene signature. However, the ion concentration and ratios data are not consistent with this interpretation. Mixing with seawater would also introduce chloride, and the two water samples from Edzna Valley have among the highest Sr/Cl and SO_4/Cl ratios of any samples measured, not only in this study but also in previous sampling of water of the Peninsula. The power of this result can be seen from twin plots of $^{87}Sr/^{86}Sr$ vs 1/Sr (Fig. 2A) and of 1000xSr/Cl vs 1/Sr (Fig. 2B).



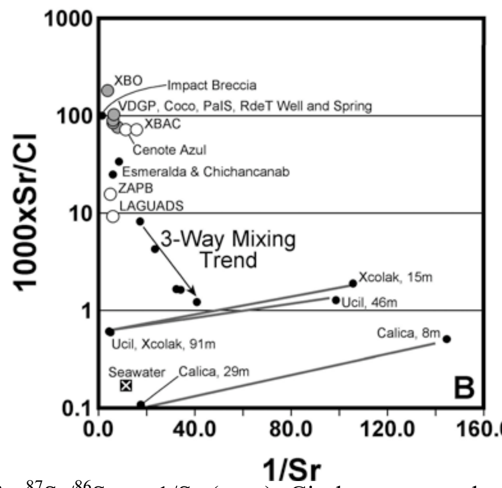


Figure 2A. $^{87}Sr/^{86}Sr$ vs 1/Sr (meq). Circles are samples of this study. Black square with cross is seawater. Black dots are from Perry et al. 2009. Filled circles (XBO and VDGP) have ratios higher than Cretaceous-Eocene ratios and are of possible Oligocene or younger age.

Figure 2B. 1000xSr/Cl (molal ratio) vs 1/Sr (meq). Symbols as in Figure 1A. Deep and shallow pairs from cenotes with water columns that extend into the saline interface are connected by tielines to show mixing trends; numbers are depths in meters. Note that XBO and VDGP have high Sr/Cl ratios corresponding to very low Cl concentration.

3 CONCLUSIONS

Figure 2B shows that when using the conservative Cl ion as a normalizing factor, samples XBO and VDGP are more enriched in strontium with respect to seawater than any other samples measured in the entire Yucatan Peninsula. On the other hand, Figure 2A shows that, whereas waters in contact with known evaporites of the Peninsula have relatively low $^{87}Sr/^{86}Sr$ ratios (averaging 0.70774) that cluster around values for Cretaceous-Eocene seawater, the ratios in the two samples from Edzna Valley have higher ratios (0.70795 and 0.70808), which are closer to the Sr isotope ratio in modern seawater (0.7092). In fact, the ratios in XBO and VDGP are characteristic of Oligocene seawater. This strongly suggests that the Valley of Edzna, which is about 100 km long and is nowhere more than 50 m above mean sea level, was invaded by the ocean during the Oligocene or later and that it existed as a basin in which seawater evaporated long enough to form an appreciable deposit of gypsum. This event likely happened during the Oligocene, when a rise in sea level is recorded (Miller et al. 2005). Note, however, that timing of this event is not well constrained by the strontium isotope ratio, which provides only a minimum age because it is likely that mixing occurred between seawater and groundwater draining the Paleocene evaporite to the east. If confirmed by further analyses, this study will help understand the Paleogene history of the region and, more specifically, our understanding of the formation of a major geomorphic feature, the Edzna Valley polje.

REFERENCES

Kenkmann, T. & Schönian, F. 2006. Ries and Chicxulub: impact craters on Earth provide insights for Martian ejecta blankets. *Meteorit. Planet. Sci.* 41(10): 1587–1603.

Lefticariu, M., Perry, E.C., Ward, W.C., Lefticariu, L. 2006. Post-Chicxulub depositional and diagenetic history of the northwestern Yucatan Peninsula, Mexico. *Sediment. Geol*. 183: 51–70.

McArthur, J.M., Howarth, R.J., Bailey, T.R. 2001. Strontium isotope stratigraphy: LOWESS Version 3: best fit to the marine Sr-isotope curve for 0–509 Ma and accompanying look-up table for deriving numerical age. *J. Geol.* 109: 155–170.

Miller, K.G., Kominz, M.A., Browning, J.V., Wright, J.D., Mountain, G.S., Katz, M.E., Sugarman, P.J., Cramer, B.S., Christie-Blick, N., Pekar, S.F. 2005. The Phanerozoic Record of Global Sea-Level Change. *Science* 310(5752): 1293-1298.

Ocampo, A.R., Pope, K.O., Fischer, A.G. 1996. Ejecta blanket deposits of the Chicxulub crater from Albion Island, Belize. In Ryder, G., Fastovsky, D., Boulder, Gartner S. (eds), *The Cretaceous-Tertiary event and other catastrophes in Earth history*: 75-88. Boulder: Geological Society of America.

Perry, E.C., Velazquez-Oliman, G., Marin, L. 2002. The hydrogeochemistry of the karst aquifer system of the northern Yucatan Peninsula, Mexico. *Int. Geol. Rev.* 44: 191–221.

Perry, E.C., Paytan, A., Pedersen, B., Velazquez-Oliman, G. 2009. Groundwater geochemistry of the Yucatan Peninsula, Mexico: constraints on stratigraphy and hydrogeology. *J. Hydrogeology*. 367: 27-40.

Perry, E.C., Velazquez-Oliman, G., Wagner, N. 2010 (in press). Groundwater and surface water geochemistry of Cl, SO_4, and Sr in Campeche and southern Quintana Roo. To be published in *Water Research in México: Scarcity, Degradation, Stress, Conflicts, Management and Policy*. New York: Springer.

Servicio Geológico Mexicano 2007. Carta Geológico-Minera, Estados de: Campeche, Quintana Roo, y Yucatán. Escala 1:500,000. <http://portaljsp.sgm.gob.mx/cartas_impresas/productos/cartas/estados/geologia/pdf/Peninsula.pdf>

ACKNOWLEDGEMENTS

Parts of this study were funded by NOAA NA05OAR4311117 and by grants from the NIU Latino Center (to E.P.), the NIU Graduate School (to E.P.) and by the NIU Goldich Fund to Niklas Wagner. Dra Rosa Leal Bautista graciously provided transportation, and Nina Slack and Mark Howland provided technical assistance. The authors also gratefully acknowledge assistance by personnel of the Mexican National Water Commission (CONAGUA), particularly Ing. Jose Luis Acosta and Ing. Ivan Gamboa.