Controls on the spatial and temporal variability of vadose dripwater geochemistry: Edwards Aquifer, central Texas

MaryLynn Musgrove[1,*] and Jay L. Banner[2]

[1]Department of Earth and Planetary Sciences, Harvard University, 20 Oxford Street, Cambridge, MA 01238, USA
[2]Department of Geological Sciences, The University of Texas at Austin, Austin, TX 78712, USA

Abstract—A 4-yr study of spatial and temporal variability in the geochemistry of vadose groundwaters from caves within the Edwards aquifer region of central Texas offers new insights into controls on vadose groundwater evolution, the relationship between vadose and phreatic groundwaters, and the fundamental influence of soil composition on groundwater geochemistry. Variations in Sr isotopes and trace elements (Mg/Ca and Sr/Ca ratios) of dripwaters and soils from different caves, as well as phreatic groundwaters, provide the potential to distinguish between local variability and regional processes controlling fluid geochemistry, and a framework for understanding the links between climatic and hydrologic processes.

The Sr isotope compositions of vadose cave dripwaters (mean $^{87}Sr/^{86}Sr = 0.7087$) and phreatic groundwaters (mean $^{87}Sr/^{86}Sr = 0.7079$) generally fall between values for host carbonates (mean $^{87}Sr/^{86}Sr = 0.7076$) and exchangeable Sr in overlying soils (mean $^{87}Sr/^{86}Sr = 0.7088$). Dripwaters have lower Mg/Ca and Sr/Ca ratios, and higher $^{87}Sr/^{86}Sr$ values than phreatic groundwaters. Dripwater $^{87}Sr/^{86}Sr$ values also inversely correlate with both Mg/Ca and Sr/Ca ratios. Mass-balance modeling combined with these geochemical relationships suggest that variations in fluid compositions are predominantly controlled by groundwater residence times, and water-rock interaction with overlying soils and host aquifer carbonate rocks. Consistent differences in dripwater geochemistry (i.e., $^{87}Sr/^{86}Sr$, Mg/Ca, and Sr/Ca) between individual caves are similar to compositional differences in soils above the caves. While these differences appear to exert significant control on local fluid evolution, geochemical and isotopic variations suggest that the controlling processes are regionally extensive. Temporal variations in $^{87}Sr/^{86}Sr$ values and Mg/Ca ratios of dripwaters from some sites over the 4-yr interval correspond with changes in both aquifer and climatic parameters. These results have important implications for the interpretation of trace element and isotopic variations in speleothems as paleoclimate records, as well as the understanding of controls on water chemistry for both present-day and ancient carbonate aquifers. *Copyright © 2004 Elsevier Ltd*

1. INTRODUCTION

Relatively little is known regarding how groundwaters evolve temporally (e.g., annual to decadal to millennial time scales), yet this knowledge provides a framework for assessing the controls of factors such as climatic variations on aquifer and karst development, long-term patterns of recharge, sources of dissolved constituents, and local vs. regional scale influences on groundwater. Although climate variability must play a fundamental role in hydrology (e.g., Barron et al., 1989; Gascoyne, 1992; Blum and Erel, 1995), the specific mechanistic interdependence of climatic, hydrologic, and geochemical processes is not well understood. Such links are particularly relevant for karst systems, which may respond rapidly to environmental and climatic conditions.

It has been previously demonstrated that soil water geochemistry may vary depending on fluid flow-routes through a soil zone (Trudgill et al., 1983). There has, however, been limited consideration of the role of soil compositions in controlling groundwater geochemistry. The influence of soils may be of particular relevance in karst aquifers due to the rapid and sensitive response of many karst groundwater systems to fluctuations in rainfall and recharge.

Many studies have investigated the major element chemistry of karst groundwater systems. In recent years there has been a growing interest in understanding controls on the geochemical evolution and spatial variability of fluids in the vadose zone of karst systems, such as cave dripwaters (e.g., Tooth and Fairchild, 2003). Previous work in the Edwards aquifer of central Texas (e.g., Oetting 1995) has investigated phreatic groundwater geochemistry and provides an understanding of regional scale controlling processes on groundwater evolution. That understanding provides an ideal framework within which to examine both spatial and temporal controls on vadose processes. This study integrates variations in trace elements (Mg/Ca and Sr/Ca ratios) and Sr isotopes in central Texas soils, vadose waters (i.e., cave dripwaters) and phreatic groundwaters to constrain hydrologic variables such as water-rock interaction, groundwater residence time, recharge, vadose flow-routes, the influence of soils on fluid geochemistry, and local vs. regional scale controls on cave dripwater evolution. We focus specifically on water samples collected from Natural Bridge Caverns in Comal County, Texas, and, to a lesser extent, Inner Space Cavern in Williamson County, Texas (Figs. 1 and 2).

Studies of fracture fill and cave calcite deposits (speleothems) using trace element and isotope geochemistry have yielded insight into Quaternary climate change (e.g., Harmon et al., 1978; Dorale et al., 1992; Winograd et al., 1992; Banner et al., 1996; Roberts et al., 1998; Musgrove et al., 2001). An
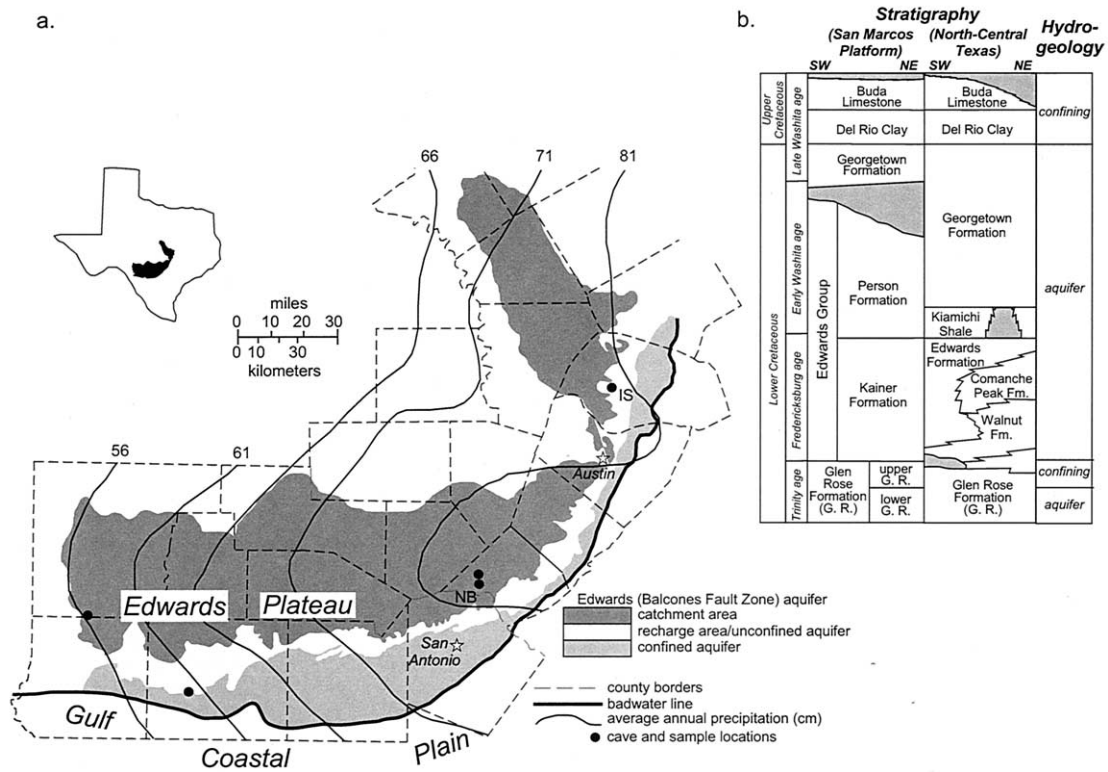
Fig. 1. (a) Hydrologic zones of the Edwards aquifer of central Texas, and cave locations. The badwater line defines the down-dip limit of potable water in the aquifer. Precipitation contours from Larkin and Bomar (1983). Temporal sequences of water samples were collected from Natural Bridge Caverns (NB) and Inner Space Cavern (IS). Caves are described in Figure 2, and in detail by Kastning (1983) and Elliott and Veni (1994). Samples from other cave locations (filled circles; detailed in Musgrove, 2000) are considered in evaluation of regional trends. Regional aquifer map after Burchett et al. (1986) and Brown et al. (1992). (b) Correlation of regional stratigraphic and hydrologic units from Rose (1972) and Maclay (1989). Natural Bridge Caverns is located in the upper member of the Glen Rose Formation (San Marcos Platform and North-Central Texas columns). Inner Space is developed within the Edwards Formation (North-Central Texas column). Note that although the upper member of the Glen Rose Formation is the regional basal confining unit of the Edwards aquifer, a cavernous lens (comprising the Upper Trinity Aquifer) exists in its upper 130 ft in Comal and Bexar counties in the San Antonio area. Shaded areas are locally absent. The Del Rio Clay, a gypsiferous and pyritic clay, is the upper confining unit of the Edwards aquifer, but is eroded over the Edwards Plateau aquifer catchment area and recharge area. The Kiamichi Shale is not present in the stratigraphic section near IS.

understanding of the sources and transport of geochemical constituents in modern aquifer systems is necessary to assess speleothem records that may preserve longer-term changes in water chemistry, sources of dissolved ions in groundwater, regional and local scale karst groundwater processes, and the links between hydrology and climate. The results of this study have implications for the interpretation of speleothem records, as well as the study of present-day and ancient carbonate aquifers, and provide insight into the fundamental role of soils in karst terrains.

2. HYDROGEOLOGIC SETTING

The Edwards aquifer region of central Texas is developed in Cretaceous limestone that is extensively karstified with many sinkholes and caves. The study area encompasses the Edwards (Balcones Fault Zone) aquifer, and includes portions of two other regional aquifer systems, the Edwards-Trinity (Plateau) aquifer, and the Trinity aquifer (Fig. 1). Late Cenozoic faulting of the predominantly flat-lying region along the Balcones Fault

Zone formed a series of high-angle normal en echelon faults, which display a-down-to-the-coast displacement (Clement and Sharp, 1988; Sharp, 1990). This faulting resulted in a series of blocks of Edwards aquifer rocks that are partially to completely offset, dividing the confined and unconfined portions of the aquifer (Maclay and Small, 1983). The Edwards Limestone is exposed on the Edwards Plateau, ranging between 350 to 500 ft in thickness (Burchett et al., 1986). Along the Fault Zone, the Edwards Limestone dips steeply to the south and southeast. Streams flowing south and east toward the Gulf of Mexico drain the Edwards Plateau and recharge the aquifer across the Balcones Fault Zone. Many studies have investigated the aquifer's development, fluid hydrodynamics, and groundwater geochemistry (e.g., Clement and Sharp, 1988; Sharp, 1990; Oetting et al., 1996; Sharp and Banner, 1997). Although the phreatic groundwater system is well characterized, only a few studies have addressed vadose zone geochemistry (Harmon, 1970; Oetting, 1995; Veni, 1997).

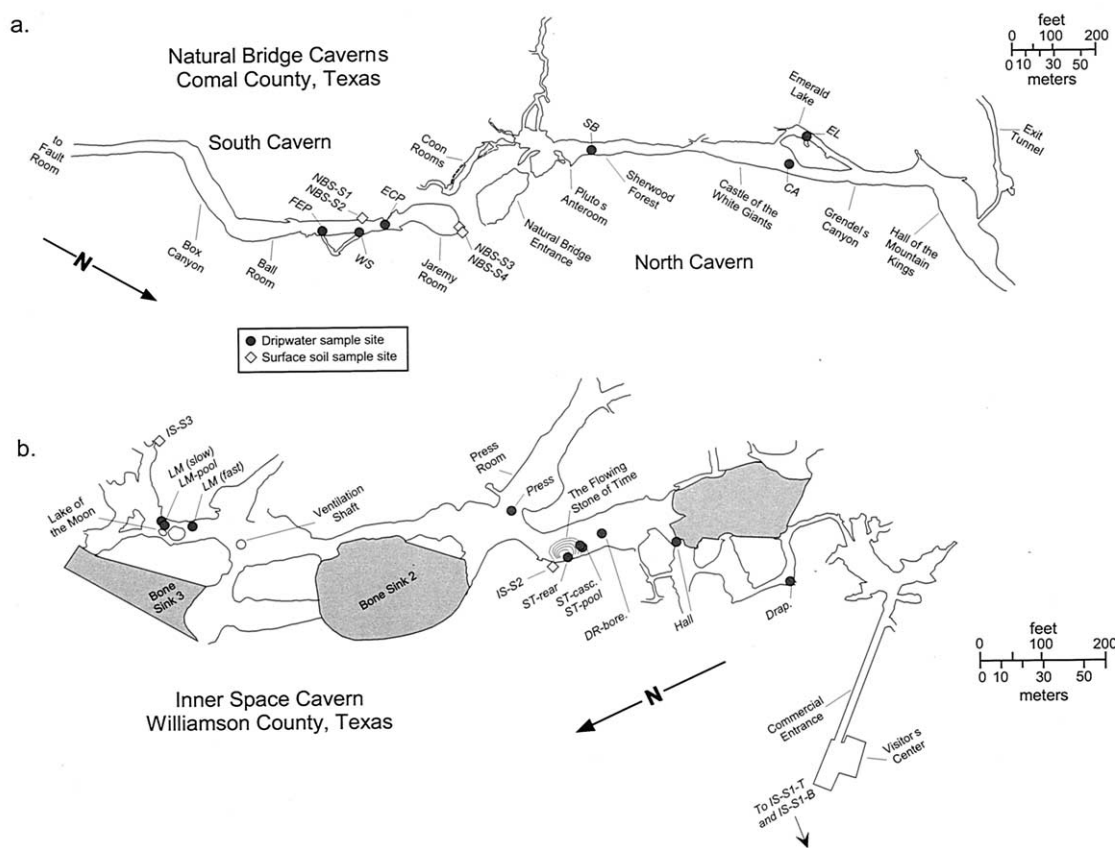Climatic and hydrologic extremes are common in this region

Fig. 2. Maps of Natural Bridge Caverns (a; NB) and Inner Space Cavern (b; IS) showing locations of cave dripwater samples and projections for surface soil sample sites. Soil samples IS-S1 (T and B) in (b) are located off the scale of the map to the west. Maps simplified from Elliott and Veni (1994). See text for lithologic description and geologic setting of caves.

(Griffiths and Strauss, 1985; Jones, 1991). Annual recharge to the Edwards aquifer varies markedly in response to regional precipitation. Effective moisture (i.e., precipitation less evaporation estimates) is strongly linked to precipitation (Musgrove, 2000). Approximately 85 to 90% of regional precipitation is lost through evapotranspiration (Maclay, 1995). Edwards Plateau soils, which are regionally characterized as mollisols, support grasses and live oak savanna vegetation with some mesquite and juniper (Godfrey et al., 1973; McMahan et al., 1984; Riskind and Diamond, 1986). Soils across the region as well as within the vicinity of the study areas are generally thin and stony. Soils are regionally characterized as dominantly calcareous, clayey, and loamy materials over indurated limestone, interbedded limestone and marls, and calcareous clayey outwash (Godfrey et al., 1973). Within this regional context, the gradual east-west decrease of moisture across the Plateau (Fig. 1) may contribute to local changes in soils and vegetation. A number of other factors, such as variations in the regional stratigraphy, as well as land use and development, may also contribute to differences in the soils. For example IS is located in a more urban area than NB, and a major highway crosses over IS. Assessing the impact of land use changes on soil compositions is complex, even in areas that appear undisturbed. Although the extent to which variations in soil geochemistry

are due to natural vs. anthropogenic factors is not certain, our results demonstrate that the soils vary compositionally.

The two caves that are the focus of this study, Inner Space Cavern (IS) and Natural Bridge Caverns (NB) are separated geographically by ~130 km, and stratigraphically by part of the Edwards Group limestones (Figs. 1 and 2). The local climate of the areas above the caves, however, is similar with respect to climatic conditions such as temperature and rainfall. Annual rainfall distribution is characterized by dry winters, and in particular, summers, and relatively wet conditions in the spring and fall. Descriptions of the geology and stratigraphy of the caves that follow are based on Kastning (1983). Both caves are overlain by relatively low or subdued topography. Although the exposed surface rocks above NB are the limestone Kainer Formation, the cave is largely formed within the upper member of the Glen Rose Formation, which contains interbedded limestone, marl, dolomite, and clay. Dripwater sites at NB are in a depth range of ~40 to 50 m below land surface.

IS is formed within a relatively pure horizon of the Edwards Limestone, although there are locally dolomitic and chert-rich units both above and below the cave. Dripwater sites are within the main level of the cave, between 12 and 18 m below land surface. Seepage of water into IS is locally pronounced, which is consistent with the fractured nature of the Edwards Forma-

Table 1. Mean groundwater and cave dripwater geochemistry.

	Cave dripwaters		Groundwaters
	Natural Bridge Caverns; NB	Inner Space Cavern; IS	
	Mean (n)	Mean (n)	Mean (n)
Geochemical parameter	Range (standard deviation)	Range (standard deviation)	Range (standard deviation)
$^{87}Sr/^{86}Sr$	0.7088 (61)	0.7083 (22)	0.7079 (49)
	0.7083–0.7091 (0.0002)	0.7080–0.7086 (0.0002)	0.7076–0.7086 (0.0002)
Mg/Ca	0.118 (81)	0.141 (48)	0.326 (27)
	0.015–0.359 (0.071)	0.057–0.268 (0.062)	0.119–0.752 (0.163)
Sr/Ca	0.26×10^{-3} (82)	0.63×10^{-3} (48)	2.07×10^{-3} (27)
	$[0.08–0.57 (0.08)] \times 10^{-3}$	$[0.24–0.84 (0.09)] \times 10^{-3}$	$[0.58–5.8 (1.1)] \times 10^{-3}$
HCO_3	261 (42)	241 (36)	230 (27)
	152–413 (66)	129–328 (53)	110–377 (50)
Ca	91 (84)	90 (49)	80 (27)
	38–320 (35)	60–125 (15)	54–150 (23)
Mg	5.7 (81)	7.6 (48)	17.5 (27)
	1.1–10.0 (2.0)	2.6–12.9 (3.1)	7.2–54 (9.7)
Sr	0.05 (82)	0.12 (48)	1.43 (27)
	0.03–0.07 (0.01)	0.05–0.16 (0.02)	0.09–3.2 (0.57)
Ba	0.03 (82)	0.04 (47)	0.04 (27)
	0.02–0.05 (0.007)	0.03–0.07 (0.010)	0.03–0.15 (0.02)
Na	5.25 (82)	6.26 (47)	11.73 (27)
	3.0–19.9 (2.1)	3.1–15.8 (3.5)	4.5–96.0 (17.5)
K	0.44 (71)	5.53 (48)	1.36 (27)
	0.08–3.3 (0.44)	0.20–48.0 (9.1)	0.70–3.4 (0.64)
Si	4.5 (69)	4.1 (48)	12.41 (27)
	3.7–5.8 (0.4)	2.3–5.1 (0.6)	10.0–22.0 (2.1)
U	0.44 (35)	0.79 (48)	1.4 (1)
	0.29–0.61 (0.08)	0.43–1.14 (0.19)	
Th	0.28 (13)	0.40 (21)	NA
	0.10–0.59 (0.17)	0.10–0.87 (0.22)	
Rb	0.48 (35)	1.95 (47)	NA
	0.26–1.82 (0.29)	0.39–20.1 (3.7)	

NB = Natural Bridge Caverns. IS = Inner Space Cavern. Units for all concentrations, except U, Th, and Rb, are in mg/L. U, Th, and Rb concentrations are in μg/L. Number in parentheses (n) following mean value = number of samples in mean calculation. Numbers in parantheses below mean value = range of values used in mean calculation and standard deviation. NA = not analyzed. Element ratios are molar concentrations. Detailed data for cave dripwaters available in Musgrove (2000) or from the authors. Groundwater data, excluding Sr and $^{87}Sr/^{86}Sr$, from Gandara and Barbie (1998). Groundwaters, collected by the Austin branch of the U.S. Geological Survey (NAWQA program), were analyzed for $^{87}Sr/^{86}Sr$ at the University of Texas at Austin, and for Sr concentration by ICP-AES at the University of California, Riverside, as detailed in Musgrove (2000).

tion. The Edwards Limestone is ~30 to 40 m thick in the vicinity of IS and is exposed at the surface above the cave. IS is wholly contained within a fault block of the Balcones Fault Zone. The Edwards Formation is also exposed in the adjacent block several hundred feet to the west of IS. The Georgetown Formation and Del Rio Clay are exposed in the adjacent block several hundred feet to the east. The Georgetown Formation is predominantly composed of limestone, but contains some beds of marl and shale.

3. METHODS AND RESULTS

Dripwater samples were collected periodically at NB from 1995 to 1999, and at IS during 1998 and 1999. Sampling procedures, sample locations and analytical methods are discussed in detail in Musgrove (2000). Table 1 summarizes the dripwater data by comparing mean elemental and isotopic values with regional phreatic groundwaters. The majority of elemental analyses for waters and soil leachates were determined by ICP-MS (Perkin Elmer/Sciex Elan 5000) at The University of Minnesota. Analytical uncertainties are generally < 5% for Ca, Mg, Sr, Ba, and Na analyses, and < 10% for

other elemental analyses. Replicate analyses on water samples are within analytical uncertainty.

Soil samples collected from above the caves were leached with 1 mol/L NH_4Ac to determine the composition of the exchangeable fraction (Suarez, 1996). Soil leachate analyses are summarized in Table 2. Reproducibility of soil leachates for Sr isotope values and trace element ratios (Mg/Ca and Sr/Ca) is generally within analytical uncertainty. Leachate elemental concentrations, however, for an equivalent weight of initial soil are more variable (by up to ~30%). These differences may result from heterogeneities in soil subsamples. The better reproducibility of isotopic values and trace element ratios in soil leachates, however, suggests that concentration differences may reflect differences in the net amount of material leached from the soils. X-ray diffraction analyses indicate that the soils are predominantly composed of variable mixtures of calcite, clay, and quartz (Table 3; Musgrove, 2000).

All strontium isotope values for dripwaters, groundwaters, and soils were measured at The University of Texas at Austin on a Finnigan-MAT 261 thermal ionization mass spectrometer using both static and auto-dynamic techniques. Results were

Table 2. Comparison of soil leachate geochemistry.

Geochemical parameter	Natural Bridge Caverns (NB) Mean (n = 4) Range (standard deviation)	Inner Space Cavern (IS) Mean (n = 4) Range (standard deviation)
$^{87}Sr/^{86}Sr$	0.7089 *0.7086–0.7093 (0.0003)*	0.7086 *0.7084–0.7089 (0.0002)*
Mg/Ca	0.037 *0.017–0.080 (0.030)*	0.086 *0.053–0.123 (0.033)*
Sr/Ca	0.21×10^{-3} *$[0.11–0.28 (0.07)] \times 10^{-3}$*	0.56×10^{-3} *$[0.40–0.91 (0.24)] \times 10^{-3}$*
Ca	265 *114–459 (172)*	235 *215–266 (22)*
Mg	7.6 *1.4–21.0 (9.0)*	12.1 *8.5–16.1 (3.9)*
Sr	0.153 *0.027–0.262 (0.112)*	0.296 *0.201–0.526 (0.155)*
Ba	0.670 *0.110–1.72 (0.726)*	0.740 *0.583–1.02 (0.201)*
Fe	0.139 *0.016–0.370 (0.167)*	0.198 *0.172–0.222 (0.021)*
Mn	0.029 *0.004–0.090 (0.041)*	0.010 *0.0005–0.026 (0.011)*
Na	0.897 *0.090–2.75 (1.249)*	0.378 *0.149–0.555 (0.175)*
K	11.54 *1.32–31.6 (13.8)*	11.97 *3.77–26.6 (10.1)*
Si	5.22 *2.28–8.16 (4.16)*	1.83 *0.97–2.78 (0.74)*
Rb	0.066 *0.059–0.072 (0.009)*	0.038 *0.012–0.059 (0.019)*
P	0.151 *0.098–0.204 (0.074)*	0.087 *0.072–0.102 (0.013)*

Units for all concentrations are mg/L. Element ratios are molar concentrations. Approximately 1.5 g of representative soil subsamples were leached with 10 mL of 1 molar NH_4Ac, buffered to a pH of between 7 and 8, for 1 h at 25°C. Samples were centrifuged and the supernatant collected and split for elemental and isotopic analysis. Detailed data available in Musgrove (2000) or from the authors.

normalized for fractionation to $^{86}Sr/^{88}Sr = 0.1194$ using an exponential fractionation law. A mean value of 0.710264 was determined for standard analyses of NIST-SRM 987 (external $2\sigma = \pm0.000026$ for auto-dynamic runs, $n = 79$, and external $2\sigma = \pm 0.000025$ for static runs, $n = 44$). Replicate analyses yielded a mean deviation of 0.000018 ($n = 26$). Blank values (3–40 pg) are negligible with respect to sample size (~200 ng Sr). $^{87}Sr/^{86}Sr$ values for Cretaceous

Table 3. Soil x-ray diffraction analyses.

Sample	Location	% Clay	% Quartz	% Potassium feldspar	% Plagioclase feldspar	% Calcite	Other (trace)
Natural Bridge Caverns; NB							
NBS-S1	Upper horizon, organic rich, 18 cm depth	61	20	Trace	Trace	19	
NBS-S2	Lower horizon, altered limestone at base, 29 cm depth	4	1	Trace	0	94	Goethite
NBS-S3	~0.6 m above base of South Cave entrance pit; lower karst fill	76	21	1	0	2	Goethite
NBS-S3	Replicate	71	22	2	0	4	Goethite
Inner Space Cavern; IS							
IS-S1-T[a]	Small thicket to west of visitor's center, upper horizon, 2.5 cm depth	36	61	2	1	0	—
IS-S1-B[a]	Small thicket to west of visitor's center, lower horizon, 18 cm depth	38	60	2	1	0	—
IS-S2	~40 ft N of I-35 overpass; halfway down slope of overpass, 7–10 cm depth	55	41	3	0	0	—
IS-S3	East of I-35, in thicket adjacent to parking lot north of IS wellshaft housing, upper horizon, 2.5 cm depth	57	30	3	1	9	—

Analyses are on whole soil fractions. Analytical methods are detailed in Lynch (1997). Locations shown on Fig. 2, excluding IS-S1.
[a] IS-S1 latitude and longitude coordinates are 30.61005°N and 97.68947°W.

carbonate rocks discussed in the text are from Koepnick et al. (1985) and Oetting (1995) and have been adjusted to a value for NIST-SRM 987 of 0.710264.

Total alkalinity was determined by titration for only a small number of samples due to sampling constraints. Correspondingly, saturation states for carbonate minerals were not determined on the majority of the dripwaters. The samples with complete data necessary to calculate saturation states are from widely spaced caves across the Edwards Plateau and are supersaturated with respect to calcite and undersaturated with respect to dolomite (Musgrove, 2000). A comparison of these limited saturation state values with previous studies of Edwards aquifer groundwaters shows no clear evolution in carbonate equilibrium relationships from dripwaters to groundwaters (Oetting, 1995). Similar to the phreatic groundwaters and cave waters from previous work in central Texas caves, the dripwaters of this study are dilute Ca-HCO$_3$ waters of meteoric origin (Harmon, 1970; Oetting, 1995; Veni, 1997). However, a comparison of dripwaters from specific caves and phreatic groundwaters reveals distinct differences (Table 1). For example, the mean Sr/Ca ratio of IS dripwaters is greater than NB dripwaters (Sr/Ca = 0.63×10^{-3} and 0.26×10^{-3}, respectively). Mean Mg/Ca ratios for NB and IS dripwaters (0.12 and 0.14, respectively) are less than values for phreatic groundwaters (0.33). Strontium isotope values of all dripwaters range from 0.7080 to 0.7091. The mean $^{87}Sr/^{86}Sr$ value for NB dripwaters (0.7088) is higher than that for IS dripwaters (0.7083). Dripwater $^{87}Sr/^{86}Sr$ values for both caves are offset to lower $^{87}Sr/^{86}Sr$ values than the range for soil leachates corresponding to the individual caves. Both temporal and spatial differences are present in the dripwater data.

4. DISCUSSION

4.1. Strontium Isotope Variations

Applications of Sr isotopes to natural waters have demonstrated their utility as a tracer for fluid evolution, weathering processes, and sources of dissolved constituents to fluids (e.g., Miller et al., 1993; Banner et al., 1994). Previous studies in the Edwards aquifer have applied Sr isotopes to constrain sources of dissolved constituents to phreatic groundwaters (Oetting, 1995; Oetting et al., 1996; Sharp and Banner, 1997). Strontium isotope values of Edwards cave dripwaters (0.7080–0.7091) are bracketed between (1) values for carbonate host rocks (0.7074–0.7081) and (2) values for soil leachates (0.7084–0.7093; Fig. 3). Values for fresh phreatic groundwaters of the Edwards aquifer range to more radiogenic $^{87}Sr/^{86}Sr$ than the aquifer host rocks (Fig. 3). The most likely source of Sr to the waters is the Cretaceous carbonate rocks that constitute the aquifer. The influence of the host carbonate rocks on regional groundwater geochemistry is well documented (Clement, 1989; Oetting, 1995; Oetting et al., 1996). Elevated $^{87}Sr/^{86}Sr$ values for both vadose and phreatic groundwaters relative to the host aquifer rocks are indicative of a source of more radiogenic $^{87}Sr/^{86}Sr$ to the waters. The migration of fluids from aquifer rocks located down-dip of the badwater line along faults and/or fractures has been demonstrated to be a source of radiogenic Sr to specific geochemical facies of Edwards phreatic groundwaters (Oetting et al., 1996). This is not a possible source of Sr to
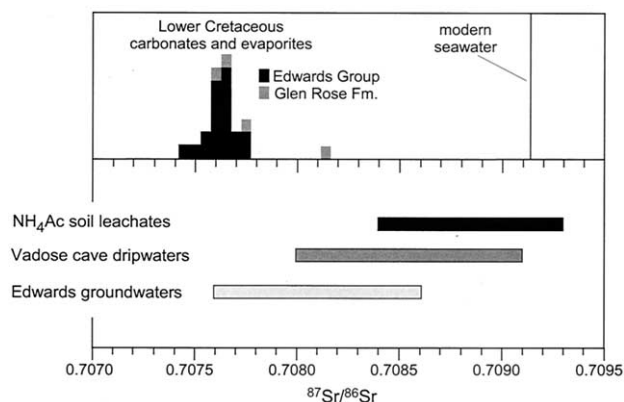

Fig. 3. Strontium isotope variations in regional Edwards aquifer system components. Histogram in the upper portion of the diagram represents twenty whole rock $^{87}Sr/^{86}Sr$ values determined for Lower Cretaceous carbonates and evaporites (18 from Koepnick et al., 1985, and 2 from Oetting, 1995). In the lower portion of the diagram are $^{87}Sr/^{86}Sr$ variations measured in different aquifer components. Data for soil leachates ($n = 12$) and dripwaters ($n = 100$) are from caves across the Edwards Plateau as shown in Fig. 1. Groundwater data are from Edwards aquifer wells across the region ($n = 49$). Soil leachates represent exchangeable Sr in soils near cave recharge zones. Modern seawater value ($^{87}Sr/^{86}Sr = 0.709173$) from Capo and DePaolo (1990).

vadose dripwaters, however, and cannot account for the regional trends in Sr isotope variations. Soil leachate $^{87}Sr/^{86}Sr$ values point to the overlying soils as this source.

The $^{87}Sr/^{86}Sr$ of soil leachates range to higher values than the ranges for host limestones, vadose dripwaters, and phreatic groundwaters. The exchangeable silicate/clay components of the soils are a likely source of radiogenic Sr. Airborne dust across the region, largely composed of mica and quartz (Rabenhorst et al., 1984), may also contribute a radiogenic component to the soils. One possible airborne source with high $^{87}Sr/^{86}Sr$ that may contribute to Texas soils is North African dust (Borg and Banner, 1996; Perry et al., 1997).

Several analyses of rainwaters in the Austin area have yielded $^{87}Sr/^{86}Sr$ values of 0.7088 to 0.7091 (Oetting, 1995). These values approach that of modern seawater. Limited analyses of central Texas rainwater suggest that Sr concentrations are generally not a significant source of Sr to the aquifer system (0.5–17 ppb; mean = 5.6 ± 8 ppb ; $n = 4$; Oetting, 1995). However, the highest value of this range approaches 20% of the Sr concentration for the most dilute dripwaters and precludes dismissing rainwater as a potential source of Sr to soils and/or dripwaters. Rainwater $^{87}Sr/^{86}Sr$ values are higher than values for the regionally extensive Cretaceous carbonates, and lie within the range of soil leachates. A lack of correlation between Na concentration and $^{87}Sr/^{86}Sr$ values for dripwaters (Musgrove, 2000), coupled with the distance of the region from the Gulf of Mexico, suggests that rainwater Sr is derived from airborne dust, rather than from sea salts.

The radiogenic/silicate component of the soils is likely derived from some combination of the insoluble residue of weathered underlying carbonate rocks and airborne dust. Regardless of the specific source of radiogenic strontium to the soils, regional strontium isotope values record a progression toward lower $^{87}Sr/^{86}Sr$ values from (1) soil leachates to (2) vadose cave dripwaters to (3) fresh phreatic groundwaters to (4) host

limestones (Fig. 3). This trend indicates that both dripwaters and groundwaters acquire Sr from two principal isotopically-distinct endmember sources: the soils and carbonate host rocks. As waters migrate through the aquifer system (e.g., from vadose to phreatic groundwaters), they acquire a larger component of Sr from interaction with the carbonate host rocks. This progression is consistent with the evolution of Sr isotope values of aquifer fluids toward limestone values with increased residence time, which allows for greater potential extents of water-rock interaction with the carbonate host rocks.

Within this regional context, spatial variability in $^{87}Sr/^{86}Sr$ values from different caves indicates that variations in the composition of host limestones and overlying soils exert a strong control on local scale fluid evolution. For example, both dripwaters and soil leachates at NB have more radiogenic $^{87}Sr/^{86}Sr$ values relative to IS. Yet, within each cave, soil leachates have more radiogenic $^{87}Sr/^{86}Sr$ values than corresponding dripwaters. These differences between NB and IS may reflect the caves' settings and the lithology of the local carbonate rocks. NB is primarily within the Glen Rose Formation. The argillaceous nature of this formation suggests the presence of a greater detrital, and therefore radiogenic Sr-rich component, in comparison with the Edwards Formation, which houses IS. In contrast, the Edwards Formation in the vicinity of IS is relatively pure limestone (Rodda et al., 1966). As proposed above, if dripwater $^{87}Sr/^{86}Sr$ values evolve from interaction with soils and limestones, then the higher $^{87}Sr/^{86}Sr$ range for NB dripwaters, relative to IS dripwaters, would be expected. It is, however, not clear from existing measurements that Glen Rose carbonates exhibit more radiogenic $^{87}Sr/^{86}Sr$ values (Fig. 3; Koepnick et al., 1985). These measurements were made for reconstruction of the paleoseawater Sr isotope curve and thus the data set is biased toward relatively pure samples. A more comprehensive study of cave host rocks would help clarify differences in whole rock strontium isotope compositions between the cave locations. As will be discussed below, the local control of soil and host rock geochemistry on dripwater $^{87}Sr/^{86}Sr$ values appears to be superimposed on broader regional controls.

4.2. Mg/Ca and Sr/Ca Variations

A fundamental influence of residence time on Mg/Ca ratios of carbonate groundwaters was illustrated in the Floridan aquifer where residence times may be thousands to tens of thousands of years (Plummer, 1977). Similarly, important controls on Mg/Ca ratios have since been demonstrated in carbonate groundwater systems with much shorter residence times (Langmuir, 1971; Cowell and Ford, 1980; Trudgill et al., 1980; Fairchild and Killawee, 1995; Fairchild et al., 1996). Proposed mechanisms for observed increases in groundwater Mg/Ca ratios with increasing residence time include progressive water-rock interaction processes such as the incongruent dissolution of dolomite, and calcite recrystallization (Wigley, 1973; Plummer, 1977; Lohmann, 1988). If these processes are also occurring in the vadose zone, then dripwater Mg/Ca ratios should also be strongly dependent on water residence time and the composition of the host aquifer rocks (Fairchild et al., 1996). The partitioning of trace elements such as Mg and Sr into a fluid during the recrystallization of either calcite or dolomite is largely controlled by the trace element's distribution coefficient (K_D value; e.g., $K_D^{Sr-Ca} = [Sr/Ca]_{mineral}/[Sr/Ca]_{solution}$) and the host rock composition (Banner and Hanson, 1990). For K_D values < 1, the trace element will generally be preferentially excluded from the mineral phase, and partition into the interacting fluid. Both Mg and Sr generally have K_D values < 1 and will therefore increase relative to Ca in a fluid progressively recrystallizing calcite or dolomite (Oomori et al., 1987; Banner and Hanson, 1990; Banner, 1995).

The observed variability in dripwater Mg/Ca and Sr/Ca ratios in this study indicates that water-rock interaction processes are neither spatially nor temporally constant, and that processes of water-rock interaction that control the evolution of phreatic groundwaters with long residence times also control vadose dripwater compositions. The range of Mg/Ca and Sr/Ca values for Edwards phreatic groundwaters overlaps with values for cave dripwaters, but extends to much higher values (Fig. 4). A correlation between Mg/Ca and Sr/Ca ratios is evident for different dripwater sites within a cave, as well for at different caves (Fig. 4). At NB there is a single positively correlated trend exhibited by the dataset, whereas at IS there are multiple positively correlated trends, each delineated by more than one dripwater site. Although each dripwater site has its own trend, the groupings of sites from the two caves are geochemically distinct. The spread in the data from site to site and cave to cave likely results from local variations in host limestone compositions, overlying soils, vadose flow-routes, and residence times.

Similar to the relationship of Mg/Ca and Sr/Ca ratios in the dripwaters, leachate values for soils from the two caves also overlap with respect to Mg/Ca, but exhibit distinct ranges for Sr/Ca (Fig. 4). This points to the importance of constituents derived from the soils in determining the "starting point" of dripwater geochemical evolution. The ranges of Mg/Ca and Sr/Ca values for individual dripwater sites also vary (Fig. 4). Dripwaters from IS appear to exhibit greater variability in their starting point than NB dripwaters. This may reflect the greater range of soil leachate geochemistry at IS relative to NB (Fig. 4). The relationship between Mg/Ca-Sr/Ca values for the soils and dripwaters at these two caves suggests that the spread in the dripwaters reflects variations in the soils. Soil differences, in turn, may reflect differences in the composition of underlying carbonate rocks. In spite of these local variations, the ranges of Mg/Ca and Sr/Ca values for all cave dripwaters are bracketed by regional values for soil leachates at their low end, and phreatic groundwaters at their high end (Fig. 4). These relationships suggest that the major controls on dripwater geochemistry are operating regionally across the Edwards Plateau.

4.3. Trace Element and Isotope Covariations

Mg/Ca and Sr/Ca ratios of central Texas vadose dripwaters and phreatic groundwaters covary inversely with Sr isotopes (Fig. 5). Low $^{87}Sr/^{86}Sr$ values, indicative of a large component of Sr derived from the limestones relative to the soils, correspond with high Mg/Ca and Sr/Ca ratios. High Mg/Ca and Sr/Ca ratios are indicative of greater extents of water-rock interaction that likely result from increased residence time in the limestone. Water-rock interaction processes, including both dissolution and progressive recrystallization of host limestones can be modeled based on mass-balance relationships, distribu-
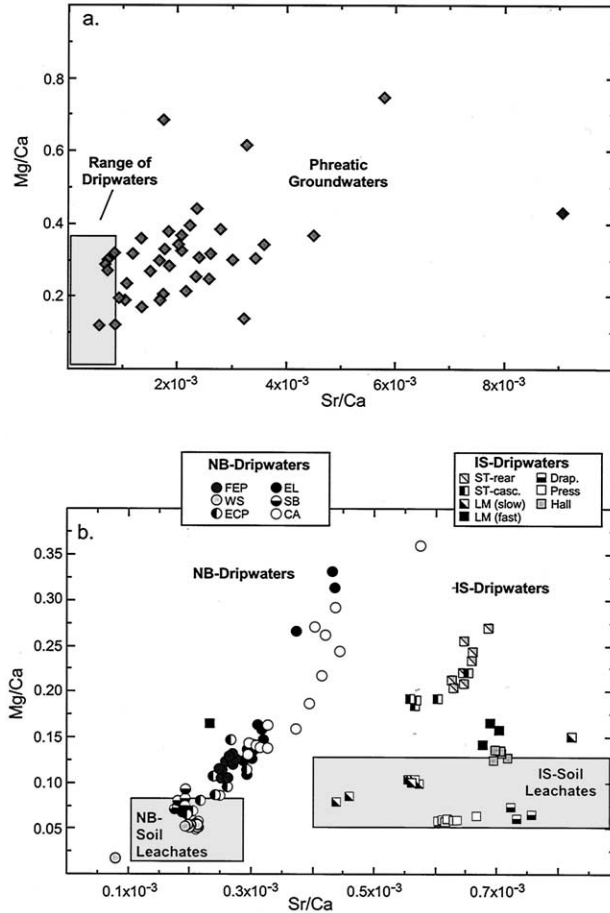
Fig. 4. Mg/Ca vs. Sr/Ca ratios for Edwards aquifer system components: (a) phreatic groundwaters (diamonds), and (b) dripwaters and soil leachates from Natural Bridge Caverns (NB) and Inner Space Cavern (IS). Note scale differences between (a) and (b). Shaded box in (a) marks area expanded in (b). Shaded boxes in (b) denote the range of Mg/Ca and Sr/Ca in soil leachates from the two caves. Soil leachates represent exchangeable Sr in soils near cave recharge zones. Symbols for NB (circles) and IS (squares) represent different dripwater sites within the caves (shown in Fig. 2), which were sampled periodically over the course of the study. Regional phreatic groundwaters (a) exhibit a similar trend as the dripwaters of increasing Mg/Ca with increasing Sr/Ca, but range to markedly higher values. Phreatic groundwater data from Oetting (1995), Gandara and Barbie (1998), and Musgrove (2000).

Fig. 5. $^{87}Sr/^{86}Sr$ vs. Mg/Ca (a) and Sr/Ca (b) ratios and carbonate mineral recrystallization models for regional phreatic groundwaters (triangles), and dripwaters and soil leachates from Natural Bridge Caverns (NB) and Inner Space Cavern (IS). Symbols for NB (circles) and IS (squares) represent different dripwater sites within the caves (shown in Fig. 2), which were sampled periodically over the course of the study. Shaded box in (a) and (b) represents range of values for exchangeable components of soils (combined NB and IS soils range). Average $^{87}Sr/^{86}Sr$ value for regional Cretaceous carbonate rocks = 0.7077 (Koepnick et al., 1985, and Oetting, 1995; n = 20). Phreatic groundwater data from Oetting (1995), Gandara and Barbie (1998), and Musgrove (2000). Model curves illustrate the evolution of $^{87}Sr/^{86}Sr$ and Mg/Ca (a), and $^{87}Sr/^{86}Sr$ and Sr/Ca (b) for a fluid that progressively recrystallizes either calcite or dolomite. Model curves labeled "calcite 1" and "dolomite 1" represent evolving composition of initial fluid 1 as it recrystallizes calcite or dolomite; model curves labeled "calcite 2" and "dolomite 2" represent evolving composition of initial fluid 2. Initial fluid compositions are based on range of values measured for soil leachates. Model calculations follow Banner et al. (1989) and Banner and Hanson (1990). Fluid 1 composition: Mg = 2 ppm, Sr = 0.04 ppm, Ca = 180 ppm, Mg/Ca = 0.02, Sr/Ca = 0.0001, $^{87}Sr/^{86}Sr$ = 0.7093. Fluid 2 composition: Mg = 10 ppm, Sr = 0.3 ppm, Ca = 150 ppm, Mg/Ca = 0.1, Sr/Ca = 0.0009, $^{87}Sr/^{86}Sr$ = 0.7093. Element ratios are molar concentrations. Initial composition of calcite (Sr = 250 ppm, Mg = 3000 ppm, $^{87}Sr/^{86}Sr$ = 0.7077) and stoichiometric dolomite (Sr = 1000 ppm, $^{87}Sr/^{86}Sr$ = 0.7077) is based on diagenetic studies and analyses of Edwards Group limestones (Fisher and Rodda, 1969; Rose, 1972; Petta, 1977; Ellis, 1985). Fluid-rock ratios (N = molar rock/water ratio) are given along the curves. Arrows indicate direction of increasing N values.

tion coefficients (K_D), porosity, and the composition of the interacting fluid and rock (Banner et al., 1989; Banner and Hanson, 1990). In this model a fluid (with an initial composition of that measured for the soil leachates) infiltrates into a limestone aquifer (with a constant composition and characteristics approximating central Texas carbonates). The fluid repeatedly dissolves and reprecipitates calcite or dolomite. An iterative calculation is used to simulate isotopic and trace-element exchange. Modeling results for the ongoing geochemical evolution ($^{87}Sr/^{86}Sr$, Mg/Ca and Sr/Ca) of two representative soil waters (with compositions similar to leachates from NB) that progressively recrystallize calcite or dolomite are shown in Figure 5. These results encompass the vadose and phreatic groundwater data, and demonstrate a clear progression
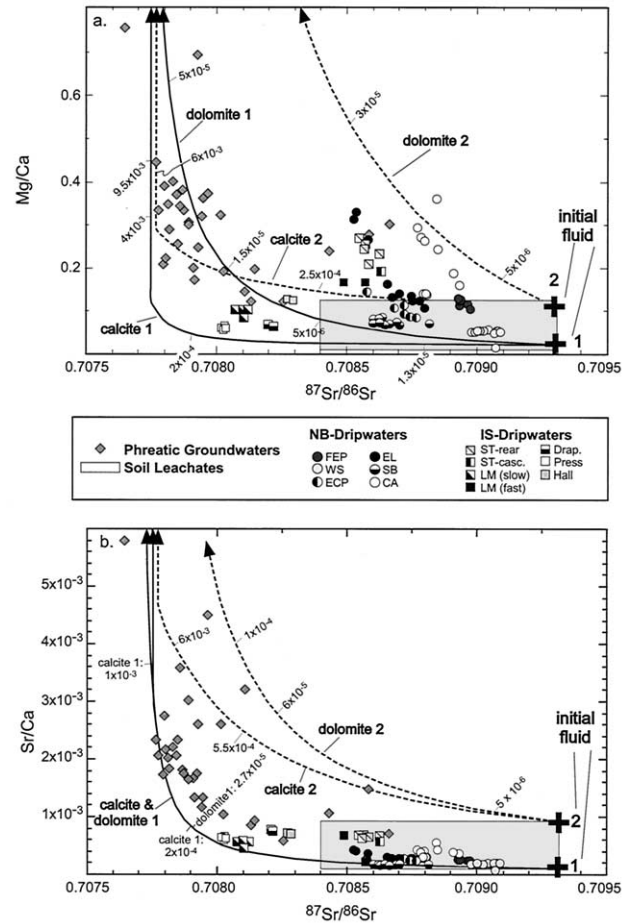
toward lower $^{87}Sr/^{86}Sr$ values and higher Mg/Ca and Sr/Ca ratios with increasing water-rock interaction. This progression is evident regionally, as well as at individual drip sites. Higher rock/water ratios, and therefore greater extents of water-rock interaction, are required to account for phreatic groundwater data (Fig. 5). This would be expected based on the longer residence and greater water-rock interaction potential of phreatic groundwaters relative to dripwaters. Dissolution of calcite and dolomite may also play a role in controlling water compositions. Dissolution reactions alone, however, cannot account for the range or pathway of data observed. For example, dissolution pathways in Sr/Ca vs. $^{87}Sr/^{86}Sr$ space would result in relatively flat horizontal trends from the initial fluid composition toward lower $^{87}Sr/^{86}Sr$ values.

It should be noted that for a given fluid and host rock composition (i.e., Mg, Sr, and Ca concentrations, and $^{87}Sr/^{86}Sr$ values) variations in the K_D value used in the model (for typical values < 1) will not affect the shape of the water-rock interaction pathway shown in Figure 5 (Banner, 1995). The relative rock/water ratio along the pathway, however, will vary in response to K_D values. Thus, although the absolute values of the rock/water ratios may not be quantitatively pertinent, the model approach allows us to evaluate the diagnostic trends of fluid evolution. Experimental determinations of K_D^{Mg-Ca} have shown a temperature dependence wherein K_D values, and correspondingly, Mg concentrations, increase with increasing temperature (Katz, 1973; Oomori et al., 1987; Mucci and Morse, 1990). While temperature may be a possible consideration for Mg/Ca changes in speleothems precipitated over thousands of years (e.g., the last glacial period in central Texas is proposed to have been on the order of 2 to 6°C cooler; Stute et al., 1992; Toomey et al., 1993), a more likely control is hydrologic variability (that is, variations in the chemical composition of the fluid precipitating the speleothems). Dripwater sites are within cave interiors where temperatures are relatively stable year-round. Thus, temperature variations at dripwater sites cannot account for Mg/Ca variations exhibited by the dripwaters in the modern aquifer system. Although little temperature dependence has been demonstrated for K_D^{Sr-Ca}, temperature may play a role in calcite precipitation rates and, thus, indirectly affect Sr partitioning into speleothem calcite (Katz et al., 1972; Baker et al., 1982; Banner, 1995). Experimental studies have demonstrated that mineral precipitation rates may have an important control on K_D values (Lorens, 1981; Banner, 1995).

In a discussion of controlling processes on dripwater geochemistry at two geographically separate European caves, Fairchild et al. (2000) call upon several potential factors that may contribute to elevated and covarying Mg/Ca and Sr/Ca ratios: (1) incongruent dolomite dissolution, (2) the initial faster dissolution of calcite over dolomite, which may lead to elevated Mg/Ca during drier conditions (i.e., increasing proportion of dolomite dissolution associated with longer residence times); and (3) the precipitation of calcite by vadose waters along a flow path, which will concentrate Mg and Sr in the fluid relative to Ca. Studies of Mg/Ca and Sr/Ca variations in speleothem calcite also support the importance of residence time in controlling vadose water geochemistry (Roberts et al., 1998; Musgrove, 2000). Precipitation of calcite along flow-routes within the Edwards aquifer has been called upon by previous workers

investigating phreatic groundwaters and discharging springwaters of the Edwards aquifer (Ogden and Collar, 1990).

The geochemistry of central Texas dripwaters suggests that multiple controls contribute to spatial geochemical variability; regionally, locally, and at individual dripwater sites. Mass-balance modeling and correlations between $^{87}Sr/^{86}Sr$, Mg/Ca, and Sr/Ca suggest that water-rock interaction with overlying soils and host limestones governs a regionally extensive fluid evolution pathway from soil waters, to vadose dripwaters, to phreatic groundwaters. Within this regionally extensive system, however, local variability in the soil composition accounts for the starting point of the evolution pathway. Although some component of fluid evolution occurs in the soil zone, the dripwater and groundwater data require subsequent modification by water-rock interaction with host limestones.

4.4. Temporal Variations in Dripwater Geochemistry

Regional monitoring of total dissolved solids concentrations in recharge and fresh groundwater wells in the Edwards aquifer indicates that small annual fluctuations may occur (Bader et al., 1993). These fluctuations are proposed to result from the response of the aquifer system to above- or below-average recharge conditions (Bader et al., 1993). Saturation states in spring discharge for central Texas springs also appear to change in response to aquifer recharge events (Ogden and Collar, 1990). For a suite of dripwaters collected from a central Texas cave (Cave Without a Name) over a 28-month period, Veni (1997) recognized seasonal geochemical variability, which may result from recharge variations. These studies collectively suggest that processes controlling spatial variations in dripwater geochemistry, such as water-rock interaction and evaporation, may also operate temporally to affect dripwater geochemistry. That is to say, if variations in these processes contribute to differences in dripwater geochemistry across the region, then changes in these process at a single site over time will also affect dripwater geochemistry. Such temporal changes may result from climatic and hydrologic variables (e.g., rainfall, recharge) that may affect the extent of these processes.

Dripwaters at NB that were sampled multiple times over a 4-yr period exhibit different amounts of variability in geochemical parameters such as $^{87}Sr/^{86}Sr$ values and Mg/Ca ratios. While some dripwater localities exhibit little geochemical variation, others change markedly (Fig. 6). For the latter group, changes in dripwater $^{87}Sr/^{86}Sr$ values and Mg/Ca ratios, which inversely correlate, appear to also correlate with variations in rainfall, effective moisture, and spring discharge at Comal Springs over the same time period (Fig. 7). Comal Springs is one of the major regional discharge points for the Edwards aquifer. Based on the short response time of the aquifer to precipitation variations, Comal Springs discharge is broadly indicative of the regional state of the aquifer. Most notably, a large drop in springflow occurred during the summer of 1996 in response to a regional drought. The temporal record of vadose dripwater geochemistry shows a corresponding decrease in $^{87}Sr/^{86}Sr$ values and increase in Mg/Ca ratios (Fig. 7) with the 1996 drop in springflow. The dripwater variations observed in $^{87}Sr/^{86}Sr$ values and Mg/Ca ratios at this time are in the direction that would be predicted (i.e., lower $^{87}Sr/^{86}Sr$ higher Mg/Ca) based on the potential increase in residence time and

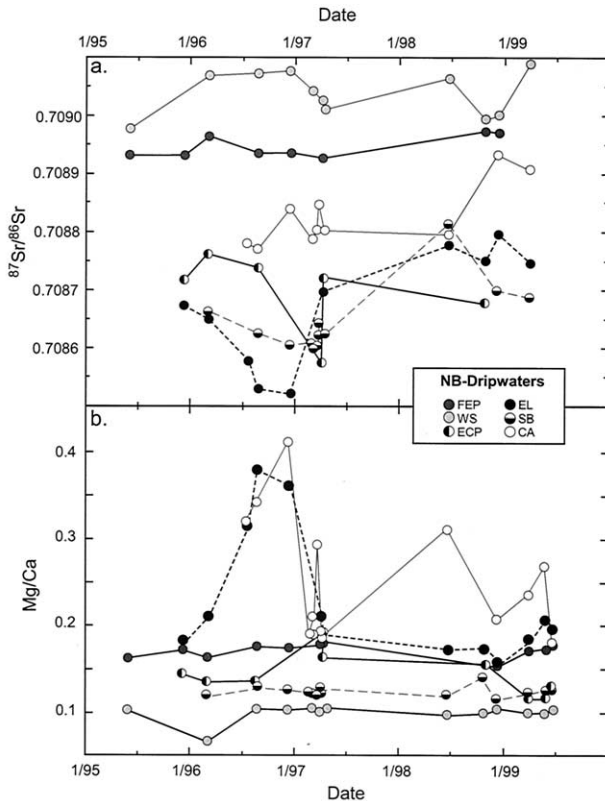Fig. 6. Temporal variations in $^{87}Sr/^{86}Sr$ values (a) and Mg/Ca ratios (b) for vadose cave dripwaters sampled from Natural Bridge Caverns between 1995 and 1999. Locations indicated by sample abbreviations are shown in Fig. 2.
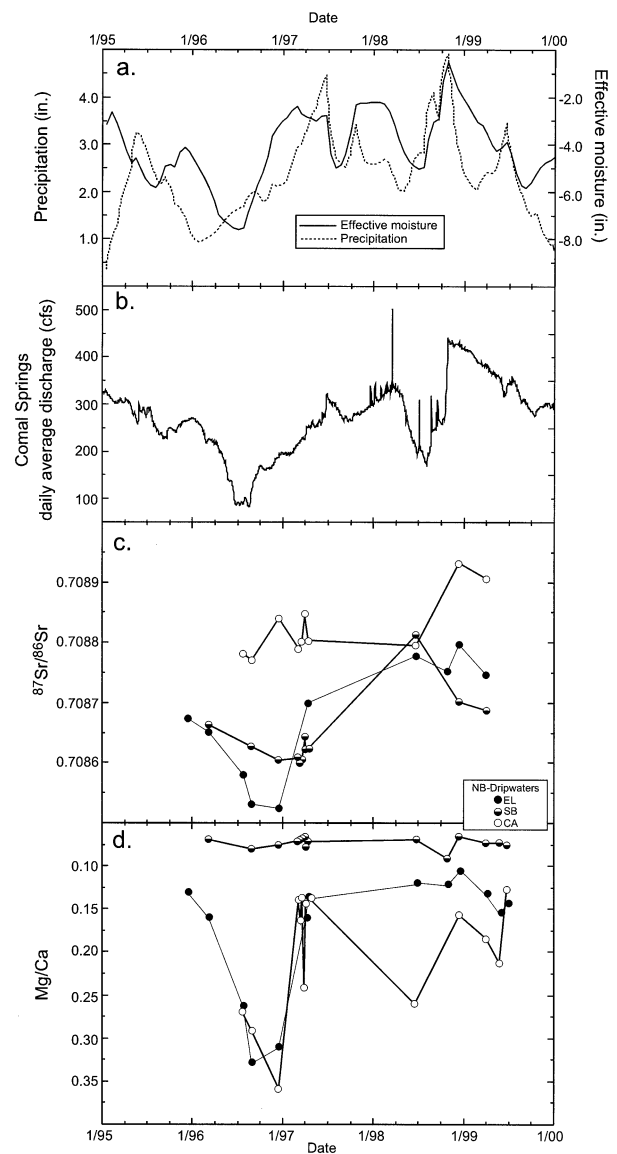

Fig. 7. Temporal variability between 1995 and 1999 in (a) central Texas precipitation and effective moisture, (b) springflow at Comal Springs, which is broadly representative of regional aquifer conditions (c) $^{87}Sr/^{86}Sr$ values for NB dripwaters, and (d) Mg/Ca ratios for NB dripwaters. Note inverted scale for Mg/Ca in (d). Effective moisture is the difference between monthly precipitation and evaporation data. Rainfall and evaporation data from the National Climatic Data Center (http://www.ncdc.noaa.gov) archive for San Antonio, TX—Seaworld (National Weather Service Cooperative Station Network—COOP ID # 418169). Note that effective moisture values are negative. This may reflect pan evaporation values that do not represent actual ground evapotranspiration values. In spite of the negative values, during a 5-yr observation period (1995–2000), drips in caves in the region remained active to varying degrees. Curves for rainfall and effective moisture are smoothed. Historical records for Comal Springs daily average discharge (cfs = cubic feet/s) from U. S. Geological Survey archives (station number #08168710; http://txwww.cr.usgs.gov/).

water-rock interaction accompanying drier conditions. Effective moisture trends for the period of 1995 to 2000 are similar to rainfall trends for this period, but also incorporate other factors (such as temperature and evapotranspiration) that may affect drip rates and the transport of water in the vadose zone.

Changes in dripwater geochemistry at some sites seem to lag temporally behind changes in rainfall, effective moisture, and spring discharge (Fig. 7). This lag time is not synchronous for different dripwater sites and may reflect residence time of dripwaters for different flow-routes in the vadose zone and different responses to antecedent conditions. This discussion focuses on samples from NB, because the temporal record for dripwaters sampled from IS is shorter. However, similar to the dripwaters from NB, only some of the sites sampled at IS exhibit temporal variability in $^{87}Sr/^{86}Sr$ values and Mg/Ca ratios. Nonetheless, the timing and direction of geochemical variability in IS dripwater geochemistry is similar to that observed for dripwater sites at NB (Musgrove, 2000). Although this discussion focuses on Mg/Ca ratios, data for Sr/Ca ratios exhibits similar temporal trends.

4.5. Mechanism for Spatial and Temporal Dripwater Geochemical Variations

Carbonate aquifers can be characterized as a mix of different permeability networks along a continuum from low-permeability diffuse flow pathways to high-permeability conduit flow pathways (Atkinson, 1977). Migration of fluid dominantly along high-permeability conduit pathways will limit both the residence time and reactivity (due to lower mineral-surface/

fluid-volume ratios) of that fluid with the limestone. Quantitative tracer studies in the Mendip Hills karst terrain of Great Britain support a model involving changes in the routes of vadose groundwater movement as a function of rainfall and resultant aquifer recharge (Smart and Friederich, 1987). In this model, groundwater migration is predominantly along low-permeability, diffuse flow-routes during periods of low rainfall and correspondingly, low recharge. As rainfall and recharge increase, the capacity of low-permeability diffuse flow-routes is exceeded and groundwater migration along pathways of high-permeability conduit flow-routes increases. Thus, during periods of high rainfall-recharge, the increase in high-permeability conduit flow will result in less interaction between vadose groundwaters and host limestones. Consequently, fluid $^{87}Sr/^{86}Sr$ values will reflect a soil signature (i.e., for the Edwards aquifer, high $^{87}Sr/^{86}Sr$) and Mg/Ca ratios will be low due to shorter residence times. Conversely, during periods of low rainfall-recharge both residence time and interaction between the groundwaters and host limestones will increase. As a result, $^{87}Sr/^{86}Sr$ values will shift toward limestone values (i.e., low $^{87}Sr/^{86}Sr$) and Mg/Ca ratios will increase as a result of increased residence time.

This rainfall/flow-route model has been applied to the karst groundwater system of Barbados in conjunction with Sr isotopes to demonstrate a climatic (i.e., rainfall-recharge) control on the temporal fluctuations between contrasting soil and limestone contributions to groundwater (Banner et al., 1996). Similar to the central Texas Edwards aquifer system, the soils and limestones in the Barbados Pleistocene aquifer exhibit contrasting Sr isotope signatures (Banner et al., 1994, 1996; Borg and Banner, 1996). The similarities in the behavior of Sr isotopes in response to changes in rainfall-recharge in both of these aquifer systems indicate that the application of this model may be valid in other karst aquifer systems. However, geochemical characterization of different aquifer components is necessary. For example, although Sr isotopes variations in both aquifer systems are controlled by fluxes from different reservoirs (e.g., soils vs. limestones) the age and purity of the limestones and the parent materials of the soils result in isotopically-distinct and aquifer-specific relationships. Central Texas limestones are less radiogenic than the overlying soils, whereas Barbados Pleistocene limestones are more radiogenic than overlying Barbados soils. Central Texas limestones and, correspondingly, groundwaters, exhibit a larger range of variation in $^{87}Sr/^{86}Sr$ values than Barbados limestones and groundwaters (Banner et al., 1994, 1996). In some groundwater systems other constituents in addition to soils and host carbonates, such as sea salts and dust, may contribute an important component of Sr and affect $^{87}Sr/^{86}Sr$ values (Bar-Matthews et al., 1999). Geochemical reservoirs or components that may influence fluid geochemistry must be delineated for specific aquifer systems.

As noted earlier, temporal variability in geochemical parameters is not observed at all locations (Fig. 6). This is consistent with dripwaters at these sites having a relatively long residence time. A study of the timing of vadose transport based on dripwater tritium ages and geochemistry in an arid karst system in Israel indicates that waters may be held in the vadose zone for long periods of time (e.g., decades; Ayalon et al., 1998). Tritium variations in Edwards aquifer groundwaters are consistent with residence times of 30 yr or less near the aquifer's recharge zone (Pearson et al., 1975). Mean phreatic groundwater ages in the Edwards aquifer have been estimated to range from 16 to > 130 yr based on a mixing-cell model and tritium analyses of rainwaters and groundwaters (Campana and Mahin, 1985). The behavior of cave dripwater sites with respect to both discharge and geochemistry is a reflection of the permeability network(s) contributing to that flow. An examination of cave inlets from the Mendip Hills indicates that dripwaters span a broad continuum from diffuse flow seepage, characterized by low flow volume of little variation, to conduit or shaft flow with a maximum higher flow volume but greater variability (Smart and Friederich, 1987). Based on these observations, central Texas dripwaters that exhibit little to no geochemical variability (Fig. 6) likely reflect cave inlets that are dominated by diffuse flow over the 4-yr study period. Similarly, the marked geochemical variability measured in some of the dripwaters may reflect a mixture of diffuse and conduit flow-routes that are responding to changes in flow-routing over the study period.

Dripwater geochemistry over the period of this study does not consistently vary with drip rate. Drip rates have been demonstrated to both increase and decrease non-linearly with increased precipitation and recharge, and both drip rate and dripwater chemistry are influenced by antecedent hydrologic conditions (Baker et al., 1997; Doctor and Alexander, 1998). We note that higher frequency sampling of dripwater sites, a focus of ongoing research in central Texas caves, may reveal more detailed information and/or important features of dripsite hydrology and geochemistry. The results of this study suggest that temporal variability in dripwater geochemistry may have multiple scales of variation. Discharge rates are influenced by many parameters including precipitation, evaporation, temperature, soil moisture, vadose storage, flow-routing, and limestone characteristics (Friederich and Smart, 1982; Smart and Friederich, 1987). The ultimate mix of these parameters affects recharge, and subsequently, the extent of processes such as water-rock interaction and residence time. Thus, dripwater sites that exhibit little to no geochemical variability over the study period may respond over longer periods of time and/or in response to more severe fluctuations in both the hydrologic system and climate. An understanding of these processes over seasonal, annual, and decadal timescales provides insight into the paleogroundwater system.

5. SUMMARY

Geochemical and isotopic variations in vadose groundwaters of the Edwards aquifer reflect interaction with overlying soils and host carbonate aquifer rocks along different geochemical evolution pathways. Small-scale spatial variability in soils, vadose flow-routes, recharge characteristics, and aquifer rocks contribute to geochemical differences between dripwaters from different sites within a single cave. On a larger scale these factors contribute to the geochemical disparity in dripwaters between different caves. Soil compositions exert a fundamental control on the starting point of fluid-rock evolution pathways. Despite the wide range of geochemical values for soils, limestones, and dripwaters both at the small-scale and aquifer-scale, geochemical and isotopic variations in $^{87}Sr/^{86}Sr$, Mg/Ca, and Sr/Ca suggest that controlling processes on fluid evolution are regionally extensive. Water-rock interaction modeling indi-

cates that shifts to lower $^{87}Sr/^{86}Sr$ values and higher Mg/Ca and Sr/Ca values are enhanced during periods of increased residence time, such as those associated with drier climatic periods. Changes in vadose flow-routes as a function of rainfall-recharge is a mechanism by which these parameters in groundwater geochemistry may vary temporally by receiving varying fluxes of dissolved constituents from geochemically distinct sources (i.e., soils vs. host limestones), changes in residence time, and different water-rock interaction pathways. High frequency sampling of dripwaters and continuous monitoring of drip rates will provide more detailed information regarding these processes in karst systems.

REFERENCES

Atkinson T. C. (1977) Diffuse and conduit flow in limestone terrain in the Mendip Hills, Somerset (Great Britain). *J. Hydrol.* **35**, 93–110.

Ayalon A., Bar-Matthews M., and Sass E. (1998) Rainfall-recharge relationships within a karstic terrain in the Eastern Mediterranean semi-arid region, Israel: $\delta^{18}O$ and δD characteristics. *J. Hydrol.* **207**, 18–31.

Bader R. W., Walthour S. D. and Waugh J. R. (1993) *Edwards Aquifer Hydrogeologic Status Report for 1992*. Edwards Underground Water District.

Baker P. A., Gieskes J. M., and Elderfield H. (1982) Diagenesis of carbonates in deep-sea sediments—Evidence from Sr/Ca ratios and interstitial dissolved Sr^{2+} data. *J. Sed. Petrology.* **52**, 71–82.

Baker A., Barnes W. L., and Smart P. L. (1997) Variations in the discharge and organic matter content of stalagmite drip waters in Lower Cave, Bristol. *Hydrol. Proc.* **11**, 1541–1555.

Banner J. L. (1995) Application of the trace element and isotope geochemistry of strontium to studies of carbonate diagenesis. *Sedimentology* **42**, 805–824.

Banner J. L. and Hanson G. H. (1990) Calculation of simultaneous isotopic and trace-element variations during water-rock interactions with applications to carbonate diagenesis. *Geochim. Cosmochim. Acta* **54**, 3123–3137.

Banner J. L., Wasserburg G. J., Dobson P. F., Carpenter A. B., and Moore C. H. (1989) Isotopic and trace-element constraints on the origin and evolution of saline groundwaters from central Missouri. *Geochim. Cosmochim. Acta* **53**, 383–398.

Banner J. L., Musgrove M., and Capo R. C. (1994) Tracing groundwater evolution in a limestone aquifer using Sr isotopes: Effects of multiple sources of dissolved ions and mineral-solution reactions. *Geology* **22**, 687–690.

Banner J. L., Musgrove M., Asmeron Y., Edwards R. L., and Hoff J. A. (1996) High-resolution temporal record of Holocene ground-water chemistry: Tracing links between climate and hydrology. *Geology* **24**, 1049–1053.

Bar-Matthews M., Ayalon, A., Kaufman A., and Wasserburg G. J. (1999) The Eastern Mediterranean paleoclimate as a reflection of regional events: Soreq cave, Israel. *Earth Planet. Sci. Lett.* **166**, 85–95.

Barron E. J., Hay W. W., and Thompson S. (1989) The hydrologic cycle: A major variable during earth history. *Palaeogeogr. Palaeoclim. Palaeoecol.* **75**, 157–174.

Blum J. D. and Erel Y. (1995) A silicate weathering mechanism linking increases in marine $^{87}Sr/^{86}Sr$ with global glaciation. *Nature* **373**, 415–418.

Borg L. E. and Banner J. L. (1996) Nd and Sr isotopic constraints on weathering processes and soil sources in Barbados, West Indies. *Geochim. Cosmochim. Acta* **60**, 4193–4206.

Brown D. S., Petri B. L. and Nalley G. M. (1992) Compilation of hydrologic data for the Edwards Aquifer, San Antonio area, Texas, 1991, with 1934-91 summary. *Edwards Underground Water District Bulletin* **51**.

Burchett C. R., Rettman P. L. and Boning C. W. (1986) *The Edwards Aquifer—Extremely Productive, But. . .A Sole-Source Water Supply for San Antonio and Surrounding Counties in South-Central Texas*. U. S. Geological Survey and Edwards Underground Water District, San Antonio, TX.

Campana M. E. and Mahin D. A. (1985) Model-derived estimates of groundwater mean ages, recharge rates, effective porosities and storage in a limestone aquifer. *J. Hydrol.* **76**, 247–264.

Capo R. C. and DePaolo D. J. (1990) Seawater strontium isotopic variations from 2.5 million years ago to the present. *Science* **249**, 51–55.

Clement T. J. (1989) *Hydrochemical Facies of the Badwater Zone of the Edwards Aquifer, Central Texas*. M.A. thesis, University of Texas at Austin.

Clement T. J. and Sharp J. M., Jr. (1988) Hydrogeochemical facies in the bad-water zone of the Edwards aquifer, Central Texas. In *Proceedings of the Ground Water Geochemistry Conference*, pp. 127–149. National Water Well Association, Dublin, OH.

Cowell D. W. and Ford D. C. (1980) Hydrochemistry of a dolomite karst: The Bruce Peninsula of Ontario. *Can. J. Earth Sci.* **17**, 520–526.

Doctor D. H. and Alexander E. C., Jr. (1998) Discharge, chemistry and stable isotope measurements of drip waters in Mystery Cave, Minn.: Records of hydrologic processes in the vadose zone. *SEPM Research Conference, Fluid Flow in Carbonates: Interdisciplinary Approaches*, September 20-24, 1998, Door County, Wisconsin, Program with Abstracts.

Dorale J. A., Gonzalez L. A., Reagan M. K., Pickett D. A., Murrell M. T., and Baker R. G. (1992) A high-resolution record of Holocene climate change in speleothem calcite from Cold Water Cave, northeast Iowa. *Science* **258**, 1626–1630.

Elliott W. R. and Veni G. (1994) *The Caves and Karst of Texas—1994 NSS Convention Guidebook*. National Speleological Society, Huntsville, AL.

Ellis P. M. (1985) *Diagenesis of the Lower Cretaceous Edwards Group in the Balcones Fault Zone Area, South-Central Texas*. Ph.D. dissertation, University of Texas at Austin.

Fairchild I. J. and Killawee J. A. (1995) Selective leaching in glacierized terrains and implications for retention of primary chemical signals in carbonate rocks. In *Water-Rock Interaction—Proceedings of the 8th International Symposium on Water-Rock Interaction, WRI-8* (eds. Y. K. Kharaka and O. V. Chudaev), pp. 79–82. A. A. Balkema, Rotterdam, the Netherlands.

Fairchild I. J., Tooth A. F., Huang Y., Borsato A., Frisia S., and McDermott F. (1996) Spatial and temporal variations in water and stalactite chemistry in currently active caves: A precursor to interpretations of past climate. In *Proceedings of the Fourth International Symposium on the Geochemistry of the Earth's Surface* (ed. S. H. Bottrell), pp. 229–233. University of Leeds, Ilkley, England.

Fairchild I. J., Borsato A., Tooth A. F., Frisia S., Hawkesworth C. J., Huang H., McDermott F., and Spiro B. (2000) Controls on trace element (Sr-Mg) compositions of carbonate cave waters: Implications for speleothem climatic records. *Chem. Geol.* **166**, 255–269.

Fisher W. L. and Rodda P. U. (1969) Edwards Formation (Lower Cretaceous), Texas: Dolomitization in a carbonate platform system. *Am. Assoc. Petrol. Geol. Bull.* **53**, 55–72.

Friederich H. and Smart P. L. (1982) The classification of autogenic percolation waters in karst aquifers; a study in G.B. Cave, Mendip Hills, England. *Proceedings–Univ. of Bristol Speleological Soc.* **16**, pp. 143–159.

Gandara S. C. and Barbie D. L. (1998) U.S. Geological Survey Ann. Data Report: Water Data Report TX-98-4: Water Resources Data, Texas, Water Year 1998 **4,** Groundwater.

Gascoyne M. (1992) Palaeoclimate determination from cave calcite deposits. *Quat. Sci. Rev.* **11,** 609–632.

Godfrey C. L., McKee G. S., and Oakes H (1973) *General Soil Map of Texas.* Texas Agricultural Experimental Station, Texas A & M University, in cooperation with the Soil Conservation Service, U. S. Department of Agriculture.

Griffiths J. F. and Strauss R. F. (1985) The variety of Texas weather. *Weatherwise* **38,** 137–141.

Harmon R. S. (1970) The chemical evolution of cave waters, Inner Space Cavern, Texas. *Caves Karst* **12,** 1–8.

Harmon R. S., Thompson P., Schwarcz H. P., and Ford D. C. (1978) Late Pleistocene climates of North America as inferred from stable isotope studies of speleothems. *Quat. Res.* **9,** 54–70.

Jones B. D. (1991) Texas; floods and droughts. In *National Water Summary 1988-89, Hydrologic Events and Floods and Droughts,* U. S. Geological Survey Water-Supply Paper 2375 (comps. R. W. Paulson, E. B. Chase, R. S. Roberts and D. W. Moody), pp. 513–520.

Kastning E. H., Jr. (1983) *Geomorphology and Hydrogeology of the Edwards Plateau Karst, Central Texas, Vols. 1 and 2.* Ph.D. dissertation, University of Texas at Austin.

Katz A. (1973) The interaction of magnesium with calcite during crystal growth at 25-95° C and one atmosphere. *Geochim. Cosmochim. Acta* **37,** 1563–1568.

Katz A., Sass E., Starinsky A., and Holland H. D. (1972) Strontium behavior in the aragonite-calcite transformation: An experimental study at 40-98° C. *Geochim. Cosmochim. Acta* **36,** 481–496.

Koepnick R. B., Burke W. H., Denison R. E., Hetherington E. A., Nelson H. F., Otto J. B., and Waite L. E. (1985) Construction of the seawater $^{87}Sr/^{86}Sr$ curve for the Cenozoic and Cretaceous: Supporting data. *Chem. Geol.* **58,** 55–81.

Langmuir D. (1971) The geochemistry of some carbonate ground waters in central Pennsylvania. *Geochim. Cosmochim. Acta* **35,** 1023–1045.

Larkin T. J. and Bomar G. W. (1983) *Climatic Atlas of Texas.* Texas Department of Water Resources, Austin.

Lohmann K. C. (1988) Geochemical patterns of meteoric diagenetic systems and their application to studies of paleokarst. In *Paleokarst* (eds. J. P. James and P. W. Choquette), pp. 58–80. Springer-Verlag, New York.

Lorens R. N. (1981) Sr, Cd, Mn, and Co distribution coefficients in calcite as a function of calcite precipitation rate. *Geochim. Cosmochim. Acta* **45,** 553–561.

Lynch F. L. (1997) Frio shale mineralogy and the stoichiometry of the smectite-to-illite reaction: The most important reaction in clastic sedimentary diagenesis. *Clays Clay Miner.* **45,** 618–631.

Maclay R. W. (1989) Edwards Aquifer in the San Antonio region: Its hydrogeology and management. *Bull. South Texas Geol. Soc.* **30,** 11–28.

Maclay R. W. (1995) *Geology and Hydrology of the Edwards Aquifer in the San Antonio Area, Texas.* U. S. Geological Survey Water-Resources Investigations Report 95-4186.

Maclay R. W. and Small T. A. (1983) Hydrostratigraphic subdivisions and fault barriers of the Edwards aquifer, south-central Texas, U.S.A. *J. Hydrol.* **61,** 127–146.

McMahan C. A., Frye R. G., and Brown K. L. (1984) *The Vegetation Types of Texas Including Cropland.* Texas Parks and Wildlife Department, Wildlife Division, Austin.

Miller E. K., Blum J. D., and Friedland A. J. (1993) Determination of soil exchangeable-cation loss and weathering rates using Sr isotopes. *Nature* **362,** 438–441.

Mucci A. and Morse J. W. (1990) Chemistry of low-temperature abiotic calcites: Experimental studies on coprecipitation, stability, and fractionation. *Rev. Aquat. Sci.* **3,** 217–254.

Musgrove M. (2000). *Temporal Links Between Climate and Hydrology: Insights From Central Texas Cave Deposits and Groundwater.* Ph.D. dissertation, University of Texas at Austin.

Musgrove M., Banner J. L., Mack L. E., Combs D. M., James E. W., Cheng H., and Edwards R. L. (2001) Geochronology of late Pleistocene and Holocene speleothems from central Texas: Implications for regional paleoclimate. *Geol. Soc. Am. Bull.* **113,** 1532–1543.

Oetting G. C. (1995) *Evolution of Fresh and Saline Groundwaters in the Edwards Aquifer: Geochemical and Sr Isotopic Evidence for Regional Fluid Mixing and Fluid-Rock Interaction.* M.A. thesis, University of Texas at Austin.

Oetting G. C., Banner J. L., and Sharp J. M., Jr. (1996) Geochemical evolution of saline groundwaters in the Edwards aquifer, central Texas: Regional stratigraphic, tectonic, and hydrodynamic controls. *J. Hydrol.* **181,** 251–283.

Ogden A. E. and Collar P. D. (1990) Interpreting calcite, dolomite, and gypsum saturation conditions in the Edwards aquifer, Texas. In *Selected Papers on Hydrogeology from the 28th International Geologic Congress, Vol. 1* (eds. E. S. Simpson and J. M. Sharp, Jr.), pp. 83–96. International Association of Hydrogeologists, Heise, Hannover, Germany.

Oomori T., Kaneshima H., Maezato Y., and Kitano Y. (1987) Distribution coefficient of Mg2+ ions between calcite and solution at 10-50 degrees C. *Mar. Chem.* **20,** 327–336.

Pearson F. J., Jr., Rettman P. L. and Wyerman T. A. (1975) *Environmental Tritium in the Edwards Aquifer, Central Texas, 1963-1971.* U. S. Geological Survey Open File Report 74-362.

Perry K. D., Cahill T. A., Eldred R. A., Dutcher D. D., and Gill T. E. (1997) Long-range transport of North African dust to the eastern United States. *J. Geophys. Res.* **102D,** 11225–11238.

Petta T. J. (1977) Diagenesis and geochemistry of a Glen Rose patch reef complex, Bandera County, Texas. In *Cretaceous Carbonates of Texas & Mexico: Applications to Subsurface Exploration* (eds. D. G. Bebout and R. G. Loucks), pp. 138–167. *Univ. of Texas at Austin, Bureau of Economic Geology, Report of Investigations* **89.**

Plummer L. N. (1977) Defining reactions and mass transfer in part of the Floridan Aquifer. *Water Resour. Res.* **13,** 801–812.

Rabenhorst M. C., Wilding L. P., and Girdner C. L. (1984) Airborne dusts in the Edwards Plateau region of Texas. *Soil Sci. Soc. Am. J.* **48,** 621–627.

Riskind D. H. and Diamond D. D. (1986) Plant communities of the Edwards Plateau of Texas: An overview emphasizing the Balcones Escarpment zone between San Antonio and Austin with special attention to landscape contrasts and natural diversity. In *The Balcones Escarpment—Geology, Hydrology, Ecology and Social Development in Central Texas* (eds. P. L. Abbott and C. M. Woodruff, Jr.), pp. 21–32. Geological Society of America.

Roberts M. S., Smart P. L., and Baker A. (1998) Annual trace element variations in a Holocene speleothem. *Earth Planet. Sci. Lett.* **154,** 237–246.

Rodda P. U., Fisher W. L., Payne W. R. and Schofield D. A. (1966) Limestone and dolomite resources, Lower Cretaceous rocks, Texas. *Univ. of Texas at Austin, Bureau of Economic Geology, Report of Investigations* **56.**

Rose P. R. (1972) Edwards Group, surface and subsurface, central Texas. *University of Texas at Austin, Bureau of Economic Geology, Report of Investigations* **74.**

Sharp J. M., Jr. (1990) Stratigraphic, geomorphic and structural controls of the Edwards aquifer, Texas, U. S. A. In *Selected Papers on Hydrogeology from the 28th International Geologic Congress, Vol. 1* (eds. E. S. Simpson and J. M. Sharp, Jr.), pp. 67–82. International Association of Hydrogeologists, Heise, Hannover, Germany.

Sharp J. M., Jr. and Banner J. L. (1997) The Edwards aquifer: A resource in conflict. *GSA Today* **7,** 1–9.

Smart P. L. and Friederich H. (1987) Water movement and storage in the unsaturated zone of a maturely karstified aquifer, Mendip Hills, England. In *Proceedings of the Environmental Problems in Karst Terrains and Their Solutions Conference,* pp. 57–87. NWWA, Bowling Green, KY.

Stute M., Schlosser P., Clark J. F., and Broecker W. S. (1992) Paleotemperatures in the southwestern United States derived from noble gases in groundwater. *Science* **256,** 1000–1003.

Suarez D. L. (1996) Beryllium, magnesium, calcium, strontium and barium. In *Methods of Soil Analysis, Part 3: Chemical Methods—SSSA Book Series No. 5,* Soil Science Society of America and American Society of Agronomy.

Toomey R. S., III, Blum M. D., and Smart P. L. (1993) Late Quaternary climates and environments of the Edwards Plateau, Texas. *Global Planet. Change* **7,** 299–320.

Tooth A. F. and Fairchild I. J. (2003) Soil and karst aquifer hydrological controls on the geochemical evolution of speleothem-forming drip waters, Crag Cave, southwest Ireland. *J. Hydrol.* **273,** 51–68.

Trudgill S. T., Laidlaw I. M. S., and Smart P. L. (1980) Soil water residence times and solute uptake on a dolomite bedrock—Preliminary results. *Earth Surf. Proc.* **5,** 91–100.

Trudgill S. T., Pickles A. M., Smettem K. R. J., and Crabtree R. W. (1983) Soil-water residence time and solute uptake. 1. Dye tracing and rainfall events. *J. Hydrol.* **60,** 257–279.

Veni G (1997) Geomorphology, hydrogeology, geochemistry and evolution of the karstic lower Glen Rose Aquifer, south-central Texas. *Texas Speleological Survey Monographs* **1**.

Wigley M. L. (1973) The incongruent solution of dolomite. *Geochim. Cosmochim. Acta* **37,** 1397–1402.

Winograd I. J., Coplen T. B., Landwehr J. M., Riggs A. R., Ludwig K. R., Szabo B. J., Kolesar P. T., and Revesz K. M. (1992) Continuous 500,000-year climate record from vein calcite in Devils Hole, Nevada. *Science* **258,** 255–260.