

Regional controls on the geochemical evolution of saline groundwaters in the Edwards aquifer, central Texas

Gregg C. Oetting, Jay L. Banner*, John M. Sharp, Jr.

Department of Geological Sciences, University of Texas, Austin, TX 78712, USA

Received 19 September 1994; revision accepted 20 August 1995

Abstract

Geochemical and isotopic parameters are used to evaluate models for the evolution of saline groundwaters in the Edwards aquifer, which lies on the northwestern margin of the Gulf of Mexico sedimentary basin. Saline groundwaters, termed 'badwaters', range in salinity from 1000 to 12 500 mg l⁻¹ total dissolved solids. Models for badwater evolution must account for complexities owing to: (1) the range in compositions of saline basinal fluids that may migrate into the Edwards aquifer from its down-dip section and from underlying hydrostratigraphic units; (2) the range of depositional, diagenetic, and mineralogic variations in the host aquifer rocks; (3) volcanic and intrusive igneous rocks that locally crosscut the aquifer; (4) extensive faulting, which in places juxtaposes Edwards aquifer units with adjacent hydrostratigraphic units.

Calcium, Mg, Na, SO₄, Cl, and HCO₃ variations define six badwater hydrochemical facies. Strontium isotope values of freshwaters (⁸⁷Sr/⁸⁶Sr = 0.7077–0.7086), badwaters (0.7076–0.7094), and brines from aquifer rocks down-dip (0.7078–0.7097) are nearly all higher than the range of most Edwards aquifer rocks (0.7074–0.7077) and volcanic and intrusive igneous rocks that crosscut the aquifer (0.7032–0.7055). Argillaceous carbonate rocks that underlie the Edwards aquifer are likely sources of Sr with high ⁸⁷Sr/⁸⁶Sr values.

Transitions between the hydrochemical facies in some locations correspond to changes in depositional environments in aquifer rocks and to changes in the intensity of faulting through the aquifer. Major element, mineral saturation state, and Sr/Ca–⁸⁷Sr/⁸⁶Sr variations in badwaters of the westernmost aquifer region indicate that incongruent dissolution of gypsum and recrystallization of calcite control the geochemical evolution of these badwaters. Sr/Ca–Na–Cl–⁸⁷Sr/⁸⁶Sr variations in badwaters of extensively faulted areas to the east of the westernmost aquifer region are consistent with fluid mixing processes involving at least five endmember

* Corresponding author.

fluids, including (1) saline groundwaters from two underlying hydrostratigraphic units, (2) two endmember brines from down-dip Edwards aquifer equivalent units, and (3) freshwaters that have interacted extensively with aquifer rocks. The compositions of badwaters from the northeasternmost region reflect fluid mixing between freshwaters and saline groundwaters from underlying hydrostratigraphic units.

1. Introduction

The development of aquifers in large-scale carbonate platforms is governed by depositional, tectonic, hydrodynamic, and chemical processes. The geochemical and isotopic evolution of groundwaters in carbonate aquifers reflects processes of fluid–rock interaction and fluid mixing that occur along migration pathways within and external to their present aquifer. Regional fluid mixing processes involving freshwaters and formation brines influence the evolution of saline groundwaters found on the margins of major sedimentary basins (Land and Prezbindowski, 1981; Toth, 1988; Long et al., 1988; Musgrove and Banner, 1993). An understanding of the effects of this mixing on saline fluid geochemistry and mineral saturation states has implications for the hydrodynamics of sedimentary basins, hydrocarbon migration and entrapment, ore formation, and the regional dynamics of groundwater quality in aquifers. Previous investigations provide this study with a well-characterized framework in which to test hypotheses for the origin and evolution of saline groundwaters in the Edwards aquifer, a regional carbonate aquifer in central Texas (Fig. 1).

The Edwards aquifer developed from karstification of a large-scale carbonate platform on the northwestern margin of the Gulf of Mexico sedimentary basin. Previous studies have addressed tectonic, depositional, and geomorphic controls on aquifer development, hydrodynamics, carbonate rock compositions, and groundwater geochemistry (Longman and Mench, 1978; Woodruff and Abbott, 1979; Maclay and Small, 1983, 1986; Maclay et al., 1985; Clement and Sharp, 1987, 1988; Maclay and Land, 1988; Clement, 1989; Ogden and Collar, 1990). A review of previous studies has been provided by Sharp (1990). Geochemical studies of groundwaters in the Edwards aquifer have delineated a Ca–HCO₃ freshwater zone and a number of distinct hydrochemical facies, or groups, in a ‘badwater’ zone (Figs. 1(B) and 1(C)): Ca–SO₄ (Facies A), Ca–Mg–SO₄ (low Na–Cl; Facies B), Ca–Mg–SO₄ (high Na–Cl; Facies C), Na–Cl (Facies D), Na–SO₄–Cl (Facies E), and Na–Cl–SO₄–HCO₃ (Facies E’; Pearson and Rettman, 1976; Clement and Sharp, 1987, 1988; Clement, 1989; Sharp, 1990). The badwater line is the down-dip limit of freshwaters in the Edwards aquifer (Figs. 1(A) and 1(B)). At this down-dip limit, groundwater salinities rise rapidly to more than 1000 mg l⁻¹ total dissolved solids (TDS) and the major element geochemistry of groundwaters varies regionally (Figs. 1(B) and 1(C)). Multiple hypotheses have been suggested for the origin of these badwater hydrochemical facies, including: fluid–rock interaction involving carbonates, evaporites, siliciclastics, and volcanics within or adjacent to the Edwards aquifer; fluid mixing between local meteoric recharge, water from aquifers and confining units adjacent to

the Edwards; up-dip migration of oil field brines from Edwards equivalent units deeper in the Gulf of Mexico sedimentary basin (Table 1; Groschen, 1988). These hypotheses are constrained by major element variations and geochemical modeling of ion speciation and mineral saturation states (Maclay et al., 1980; Groschen, 1988; Clement, 1989). This work by previous researchers provides a framework in which to examine both local and regional groundwater evolution processes through detailed geochemical study. In this study, we focus on the integration of Sr isotope variations and quantitative geochemical modeling with previously established major element variations. In addition, badwater geochemical evolution is examined in the context of variations in structural and depositional settings within the aquifer.

Strontium isotopes have been applied to studies of regional fluid flow and have provided significant insight into the origin and evolution of saline groundwaters (Stueber et al., 1984, 1987; Chaudhuri et al., 1987; Banner et al., 1989; McNutt et al., 1990). Argillaceous carbonate rocks and shales that underlie and overlie the Edwards aquifer and igneous rocks that locally crosscut the aquifer are potential sources of groundwater Sr with $^{87}\text{Sr}/^{86}\text{Sr}$ values that are distinctly different from each other and from values for aquifer carbonate and evaporite rocks. Previous studies of formation brines in Edwards Group carbonate and evaporite rocks down-dip of the badwater line (Land and Prezbindowski, 1981; Land and Macpherson, 1992) provide constraints on the major and trace element, and O, H, and Sr isotopic composition of these down-dip fluids. Major and trace element, and O and H isotopic data from previous studies of freshwaters and badwaters are integrated with geochemical and Sr isotopic data from this study to trace geochemical evolution processes in the Edwards aquifer (Pearson and Rettman, 1976; Prezbindowski, 1981; Land and Prezbindowski, 1981; Ellis, 1985; Clement and Sharp, 1987, 1988; Senger et al., 1990). Quantitative modeling of this data provides evidence for (1) fluid mixing processes involving at least five fluid endmembers that migrate up-dip from aquifer rocks down-dip of the badwater line or along faults and fractures from underlying hydrostratigraphic units, and (2) extensive interaction with both carbonate and evaporite Edwards aquifer host rocks. Fluid–rock interaction processes may involve (1) dissolution, precipitation, and recrystallization of aquifer carbonate and evaporite minerals, and (2) ion exchange with clay minerals disseminated through aquifer carbonate and evaporite rocks, and along contacts between the aquifer and its confining units. Regional geochemical and isotopic variations suggest that fluid–rock interaction and fluid mixing processes, which influence the evolution of badwaters, vary in their nature and/or extent as a function of regional tectonic and depositional settings.

2. Structural and stratigraphic setting

Post-depositional development of the Edwards aquifer can be summarized by four events: (1) Cretaceous karstification; (2) Miocene uplift and faulting; (3) plateau dissection; (4) continuing localized karstification and dissolution. A more complete summary of the aquifer's development is discussed in the Edwards aquifer

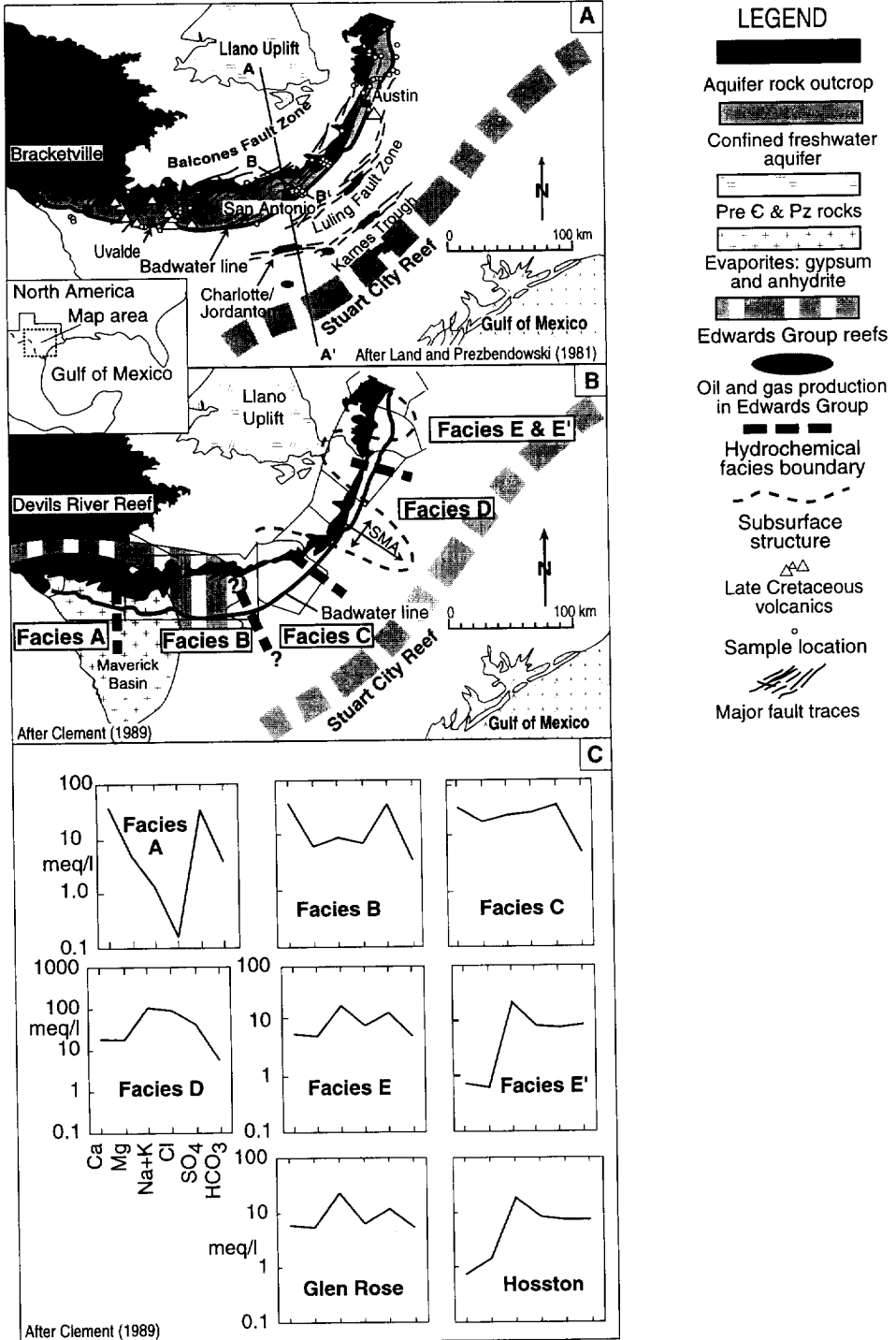


Table 1
Summary of geochemical processes proposed for evolution of badwaters

	Hydrochemical facies					
	A	B	C	D	E	E'
Gypsum dissolution	◆	◆	◆	◆		
Mixing with Edwards Fm. brines		?	◆	◆		
Mixing with groundwaters from underlying units	?	?		?	◆	◆
Sulfate reduction	◆	◆	◆	◆		
Interaction with volcanics and/or intrusives		?				
Na/Ca exchange with clays	◆	◆		◆	◆	◆
Halite dissolution				◆		
Dedolomitization			◆	◆		

Modified from Clement (1989).

development section below. The carbonate rocks that make up this hydrostratigraphic unit, as defined by Seaber (1988), are the Edwards Group and Georgetown Formation (Fig. 2(A)). These rock units extend from outcrops in central Texas coastward and down-dip to the Stuart City Reef Trend, which formed the Lower Cretaceous shelf margin (Fig. 1(A)). The Edwards Group caps the Lower Cretaceous section in central and southern Texas, which is underlain by Paleozoic rocks in the Balcones and Luling Fault Zone areas (Figs. 3(A) and 3(B); Culotta et al., 1992). South of the Luling Fault Zone (Fig. 1(A)) Lower Cretaceous rocks are underlain by Middle Jurassic evaporites and Lower Jurassic–Upper Triassic ‘red beds’ (Fig. 3(A)). Deformation of Middle Jurassic evaporites resulted in major areas of faulting south of the Balcones Fault Zone (Karnes Trough, Charlotte–Jordanton, and Luling Fault Zones; Figs. 1(A) and 3(B); Reid and Boyer, 1975; Salvador, 1991). Prezbindowski (1981) suggested that these areas of faulting are important pathways of large-scale fluid migration in the Gulf of Mexico sedimentary basin. Balcones faulting terminates in the western part of the aquifer (Fig. 1(A)) and the main structural elements are gradual anticlinal and synclinal features related to Cordilleran tectonics to the northwest.

3. Regional hydrogeology: shelf to basin

The Del Rio Clay and Glen Rose Limestone are clay-rich, low-permeability units that confine the Edwards aquifer (Fig. 2(A)). Structural and tectonic elements in the

Fig. 1. (A) Map showing the unconfined (aquifer rock outcrop) and confined zones of the Edwards aquifer and important tectonic features. Cross-sections A–A' and B–B' are in Fig. 3. (B) Regional extents of the six badwater hydrochemical facies and locations of structural features and depositional settings (Rose, 1972; Clement, 1989) ‘SMA’, San Marcos Arch. Facies B–C boundary is shown with ‘?’s because data are not available for a precise delineation. (C) The Schoeller diagrams depict type examples of badwaters and saline groundwaters from underlying hydrostratigraphic units. Delineation of facies is based on published analyses of over 200 badwaters (Clement, 1989).

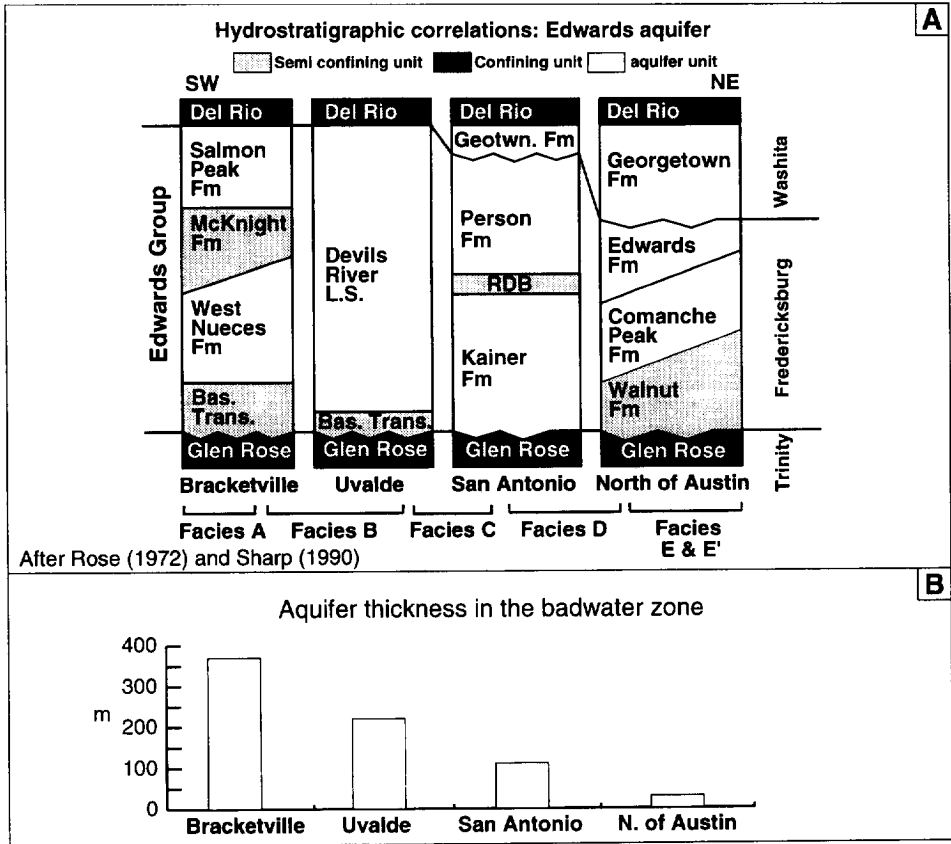


Fig. 2. (A) Southwest–northeast hydrostratigraphic correlations in the Edwards Group. Local chronostratigraphic subdivisions are shown on the right and the regional distribution of badwater hydrochemical facies at the bottom. RDB, Regional Dense Bed; Bas. Trans., Basal Transgressive Unit. (B) Aquifer thickness in the four regions represented by the hydrostratigraphic columns in (A).

Edwards aquifer affect both local and regional hydrodynamics. High-angle normal faults of the Balcones Fault Zone crosscut and in some places completely offset the aquifer. Faults and fractures provide both vertical and horizontal pathways for the migration of extraformational fluids into the Edwards aquifer (Figs. 3(B) and 3(C); Maclay and Small, 1983, 1986; Maclay et al., 1985; Maclay and Land, 1988; Clement, 1989; Sharp, 1990). Permeable and impermeable units juxtaposed by faulting may result in flow along fault traces in the aquifer (Fig. 3(C); Abbott, 1975; Maclay and Small, 1986; Maclay and Land, 1988). Groundwaters that migrate along these fault traces may interact with aquifer rocks and with rocks of both underlying and overlying confining units (Fig. 3(C)). Two areas of Late Cretaceous intrusion and volcanism crosscut the aquifer and may form local barriers to groundwater flow (Fig. 1(A); Welder and Reeves, 1962; Ewing, 1986; Barker et al., 1987; Clement and Sharp, 1987, 1988; Clement, 1989). Groundwaters flowing along contacts between permeable

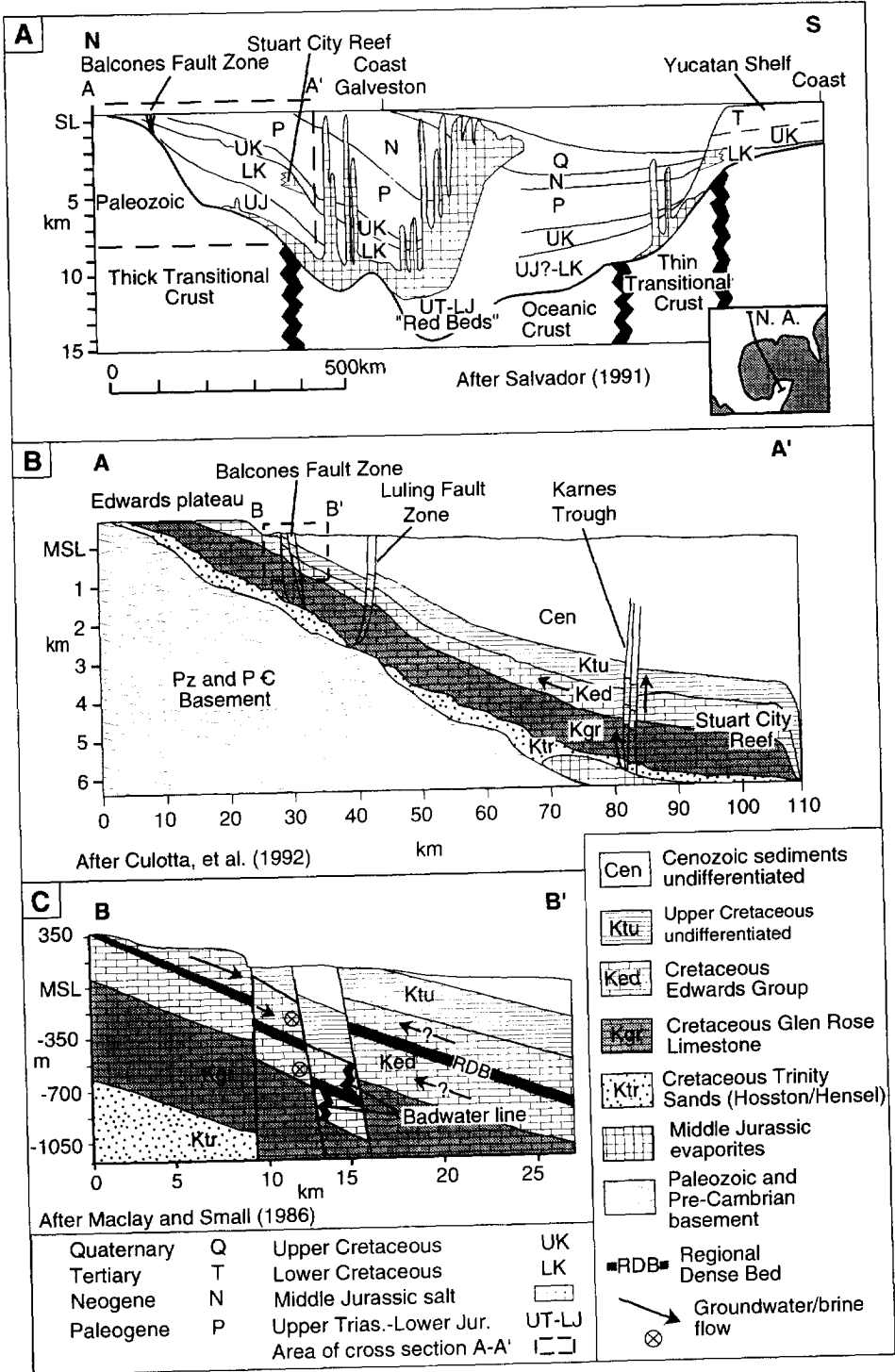
aquifer rocks and less permeable volcanic and intrusive igneous rocks may interact with both rock types.

The 'badwater line' represents a narrow transition zone from a rapidly circulating freshwater system up-dip to slowly migrating basinal fluids down-dip (Figs. 1(A) and 3(C); Abbott, 1975; Sharp and Clement, 1988; Clement, 1989). Estimated rates of flow up-dip and down-dip of the badwater line range from 90 to 900 cm day⁻¹ and from 1 to 2 cm day⁻¹, respectively, reflecting a sharp decline in permeability (Maclay and Small, 1986; Maclay and Land, 1988; Clement, 1989; Sharp, 1990). Freshwater flow in the confined aquifer is generally subparallel to the badwater line, which implies that only diffuse freshwater flow crosses the badwater line (Fig. 3(C); Abbott, 1975; Maclay and Small, 1986; Maclay and Land, 1988; Sharp, 1990).

Basinal fluids in Edwards Group rocks are Na–Ca–Cl saline groundwaters and brines that have increasing salinities down-dip from the Luling Fault Zone (TDS 13 000–24 000 mg l⁻¹) to the Stuart City Reef (TDS 30 000–290 000 mg l⁻¹; Land and Prezbindowski, 1981; Land and Macpherson, 1992). Previous studies of Edwards Group brines along the Stuart City Reef Trend indicate a source of salinity derived from underlying Middle Jurassic evaporites (Land and Prezbindowski, 1981; Land and Macpherson, 1992). Regional trends in salinity and $\delta^{18}\text{O}$ values in Edwards Group brines from the Stuart City Reef Trend to the Luling Fault Zone suggest that brines migrate up-dip from the Stuart City Reef Trend and mix with freshwaters (Figs. 3(B) and 4; Land and Prezbindowski, 1981). Hydrodynamic models of compaction-driven flow in sedimentary basins support the hypothesis of Land and Prezbindowski (1981) and further suggest that compaction-driven fluids migrate to discharge points marginal to the basin (Bethke, 1985; Blanchard, 1987).

4. Edwards aquifer development

A topographic high formed by the San Marcos Arch controlled the distribution of depositional environments and early porosity development in the Edwards Group (Fig. 1(B); Rose, 1972; Longman and Mench, 1978; Ellis, 1985; Sharp, 1990). Dolomitization and early karstification are focused in shallow subtidal, intertidal, and supratidal environments (Rose, 1972; Woodruff and Abbott, 1979; Ellis, 1985; Sharp, 1990). Cretaceous paleokarst in the Edwards Group extends an unknown distance down-dip of the badwater line along the axis of the San Marcos Arch (Longman and Mench, 1978; Ellis, 1985). Dolomitization of the Edwards Group extends down-dip along the San Marcos Arch to the Stuart City Reef Trend (Rose, 1972). Karstification and dolomitization of the Edwards Group proximal to the San Marcos Arch result in greater permeabilities down-dip of the badwater line in the Facies C and D regions (Fig. 1(B)) relative to Edwards Group rocks down-dip of the badwater line in other regions. A second episode of karstification and phreatic dolomite dissolution began in the late Cenozoic, when stream entrenchment and normal faulting in the Balcones Fault Zone formed discharge sites in the uplifted Edwards Plateau (Abbott, 1974, 1975; Woodruff and Abbott, 1979; Sharp, 1990). This sequence of diagenetic and tectonic events forms two regional trends in the



transmissive characteristics of aquifer rocks: (1) more porous, permeable, and dolomitic aquifer rocks down-dip of the badwater line proximal to the San Marcos Arch relative to Edwards group carbonates down-dip of the badwater line in other regions; (2) much greater porosity and permeability up-dip of the badwater line.

Previous studies have not focused on hydrodynamic and geochemical effects of changes in depositional and structural settings within the Edwards Group. We discuss below geochemical and isotopic variations in badwater hydrochemical facies regions that correspond to specific depositional and structural settings on the northwestern margin of the Gulf of Mexico sedimentary basin. The discussion of badwaters involves several water types in addition to the six hydrochemical facies. To simplify discussion, the additional water types are defined as follows:

(1) freshwaters: waters of the freshwater Edwards aquifer. These occur up-dip of the badwater line;

(2) evolved meteoric waters: groundwater composition resulting from extensive freshwater interaction with carbonate and evaporite rocks of the Edwards aquifer;

(3) Luling Fault Zone brines: saline groundwaters of the Edwards Group in the Luling Fault Zone (Fig. 1(A));

(4) Edwards Group brines: deep formation waters of the Edwards Group including brines of the Stuart City Reef, Karnes Trough, and Charlotte–Jordanton Fault Zones (Fig. 1(A)).

(5) Saline groundwaters from underlying hydrostratigraphic units: saline groundwaters from the Glen Rose and Hosston Formations, which underlie the Edwards aquifer.

5. Analytical methods

Surface waters and groundwaters were collected using acid-cleaned filtration and collection apparatus. pH, Eh, conductivity, and alkalinity were determined by electrochemical and titrimetric methods in the field. All analyses of major and trace elements and Sr isotopes were conducted at the University of Texas at Austin. Major cations and anions were determined by single column ion chromatography (IC). Inductively coupled plasma atomic emission spectrometry (ICP-AES) was used to determine Sr concentrations and to verify the accuracy of cation concentrations measured by IC. Analytical uncertainty for the methods used (determined as $\pm\%$ of mean replicate sample and standard values) are as follows: cations (IC) 3.0% or less; anions (IC) 5.0% or less; Sr (ICP-AES) 3.0% or less. Oxygen and H isotopes were analyzed at Southern Methodist University using the standard mass spectrometric

Fig. 3. (A) Gulf of Mexico sedimentary basin cross-section. Inset indicates line of section. Dashed box (A–A') is approximate scale of cross-section in (B). (B) Cross-section A–A' through central and southern Texas; location shown in Fig. 1(A). The dashed box labeled B–B' represents the approximate scale of cross-sections B–B' in (C). (C) Line of section B–B' in Fig. 1(A). The RDB (Regional Dense Bed) is a regional semiconfining unit that extends from the eastern edge of the Devils River Reef to the axis of the San Marcos Arch (SMA; Fig. 1(B)).

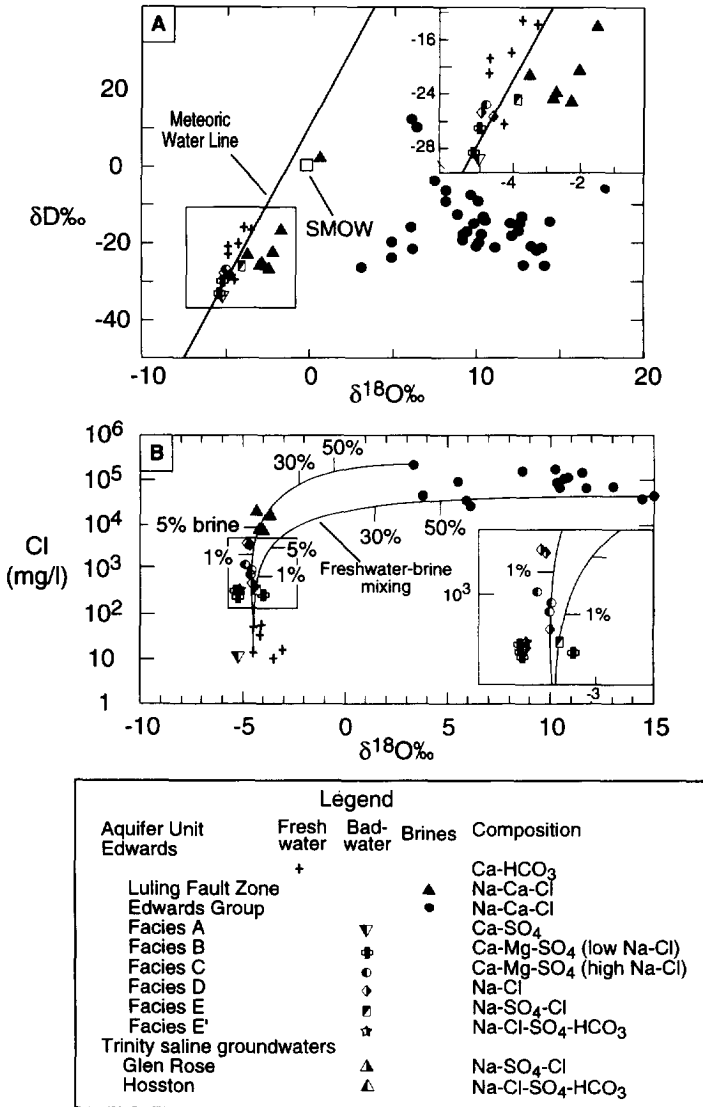


Fig. 4. (A) Groundwater and brine $\delta^{18}\text{O}$ and δD values are plotted relative to Standard Mean Ocean Water (SMOW) and the global Meteoric Water Line of Craig (1961). The inset (upper right) is an enlargement of the area at the lower left. (B) $\delta^{18}\text{O}$ and Cl variations in groundwaters and brines. Model fluid mixing calculations in this and all succeeding figures follow method of Banner and Hanson (1990) and are contoured (tick marks) for percentage of brine in the mixtures. In this and all succeeding figures, Edwards Group brine data are from Land and Macpherson (1992) and Luling Fault Zone brine data and two analyses of each Facies B, C and D water are from G. Groschen (unpublished data, 1990).

techniques outlined by Epstein and Mayeda (1953) and Copeland and Clayton (1973). Analytical errors determined from replication of samples are as follows: $\delta D \pm 1.3\text{‰}$; $\delta^{18}\text{O} \pm 0.2\text{‰}$. Strontium separation was conducted using ion exchange chemistry. Analyses for Sr isotopes were conducted using a Finnigan-MAT (San Jose, CA) 261 thermal ionization mass spectrometer in static multicollection mode. $^{87}\text{Sr}/^{86}\text{Sr}$ values are normalized to $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$ using an exponential fractionation law. Multiple analyses of the NBS-SRM 987 standard conducted over four time intervals during the course of this study yielded average values ranging from 0.710228 to 0.710264 and external errors (2σ) ranging from ± 0.000018 to ± 0.000029 (Table 2). $^{87}\text{Sr}/^{86}\text{Sr}$ values for samples reported in Table 2 have been adjusted to correspond to an NBS-SRM 987 value of 0.710250. Strontium blanks determined for total collection procedure, including filtration in the field, were less than 500 pg l^{-1} . Blanks for the ion exchange procedure ranged from 900 pg at the beginning of the study to 10–15 pg at the end. These blanks were negligible for the samples analyzed.

6. Results

Forty-seven water samples were collected from wells, springs, and streams. Analytical results for major and trace element concentrations, and O, H, and Sr isotopes are presented in Table 2. No significant variation in the concentrations of Na, K, Mg, Ca, and Sr, or $^{87}\text{Sr}/^{86}\text{Sr}$ compositions was observed between analyses of filtered and unfiltered aliquots. Analyses of Facies D and E' badwaters from previous studies (Senger et al., 1990; Brown et al., 1991; G. Groschen, unpublished data, 1990) and from localities collected for this study indicate no significant seasonal variation in major or trace elements.

Regional major element variations in badwaters sampled for this study are consistent with six regionally extensive hydrochemical facies that have been defined from previous geochemical analysis of over 200 badwaters (Clement, 1989; Fig. 1(C)). A west to east transect along the badwater line defines a progression from Facies A to D of increasing Na, Mg, and Cl concentrations (Fig. 1(C); Table 2). Calcium and SO_4 concentrations in Facies A, B, C, and D badwaters are significantly higher than freshwater concentrations (Table 2). Major element variations in Facies E badwaters are very similar to those of saline groundwaters of the underlying Glen Rose Formation, whereas Facies E' badwater major element variations are similar to those of saline groundwaters of the Hosston Sand, as noted by Clement (1989; Fig. 1(C)).

Calculations of ion speciation and mineral saturation states using the computer program WATEQ4F (Ball and Nordstrom, 1991) indicate that all fresh groundwaters and badwaters are saturated with respect to calcite, but generally undersaturated with respect to gypsum and dolomite. Three trends are observed in mineral saturation states: (1) freshwaters are highly undersaturated with respect to gypsum and anhydrite, whereas Facies A, B, C, and D badwaters either approach saturation or are saturated with respect to gypsum and anhydrite; (2) saturation with respect to gypsum progressively decreases in badwaters from values at saturation in Facies A

Table 2
Geochemical and isotopic analyses of Edwards aquifer groundwaters

Sample	Na (mg l ⁻¹)	K (mg l ⁻¹)	Mg (mg l ⁻¹)	Ca (mg l ⁻¹)	Sr (mg l ⁻¹)	Cl (mg l ⁻¹)	SO ₄ (mg l ⁻¹)	HCO ₃ (mg l ⁻¹)	⁸⁷ Sr/ ⁸⁶ Sr ^a	δ ¹⁸ O (‰)	δD (‰)
<i>Freshwaters</i>											
14 sample average ^b	3–19	0.2–3	5–24	37–114	0.04–1.4	4.5–45	7.5–60	130–370	0.70769–0.70872	-4.4 to -3.0	-29 to -16
<i>Facies A</i>											
A-1	29	1.3	57	732	14.3	10	1566	225	0.707569 ± 13	-5.2	to -34
A-2	90.2	-	141	685	15.5	18.4	1878	355	0.707532 ± 12		
A-2 Rep.	90.3	-	140	684	-	-	-	-	0.707572 ± 12		
A-3	28.2	0.6	52	689	12.9	13.3	1560	212	0.707560 ± 13		
<i>Facies B</i>											
B-1	93.4	-	22	202	0.94	244	101	275	0.708008 ± 16	-4.9	to -25
B-2	51.4	-	25	168	3.53	104	224	276	0.707984 ± 13		
B-2 Rep.	-	-	-	-	-	-	-	-	0.708003 ± 13		
B-3	183	4	34	138	4.43	301	215	227	0.709182 ± 10	-5.3	to -29
B-3 (UF)	-	-	-	-	-	-	-	-	0.709180 ± 12		
B-4 (UF) Rep.	-	-	-	-	-	-	-	-	0.709191 ± 12		
B-4	168	22	72	696	13.5	242	1594	211	0.708602 ± 14	-5.4	to -33
<i>Facies C</i>											
C-1	340	13	144	428	11.1	649	1272	276	0.708296 ± 13		
C-2	504	19	210	614	14.6	883	1642	303	0.708303 ± 12		
C-3	568	46	244	601	14.9	1100	1836	304	0.708314 ± 13	-4.8	to -26
C-3 Rep.	565	33	243	604	-	1040	1890	-	0.708307 ± 12		

<i>Facies D</i>												
D-1	342	13	106	175	14.3	512	491	344	0.708352 ± 11			
D-2	156	7.8	62	101	28.6	238	271	287	0.707851 ± 13	-5.1	to	-26
D-3	2466	54	220	376	18.2	3240	2020	350	0.708345 ± 13	-4.8	to	-28
<i>Facies E</i>												
E-1	443	2.2	66	120	1.70	295	683	326	0.709458 ± 12	-3.8	to	-20
E-1 Rep.	432	2.3	67	123	1.74	-	-	-	0.709460 ± 11			
E-2 ^c	156	5.9	25	37	1.30	81	135	350	0.709314 ± 16			
E-3 ^c	430	25.6	50	65	7.55	255	617	436	0.709423 ± 16			
<i>Facies E'</i>												
E'-1	491	5.0	7.5	14.6	2.13	284	357	511	0.708753 ± 17	-5.1	to	-28
E'-2	514	6.1	8.1	13.6	2.10	296	390	481	0.708903 ± 21			
E'-3 ^c	225	14	10	15.0	7.36	111	125	391	0.708633 ± 18			
<i>Trinity wells</i>												
T-1	424	7.6	21	15.0	1.84	295	348	447	0.708842 ± 14	-5.0	to	-27
T-1 Rep.	-	-	-	-	-	-	-	-	0.708846 ± 15			
T-2 ^c	484	4.0	5.6	11.8	1.50	316	270	453	0.708903 ± 21			
T-3 ^c	665	45	98	119	7.10	326	1160	433	0.709713 ± 18			
<i>Edwards Formation brines</i>												
Endmember I ^d	6397	3570	1840	1850	2030	14000	79	250	0.7095	8.6		
Endmember II ^d	1824	590	539	5440	1520	40343	32	174	0.7078	3.8		
Luling Fault	3300-	130-	350-	840-	35-	6700-	710-	500-	0.70794-	-3.6	to	-25
Zone (range) ^e	6700	270	580	1900	45	14000	1700	860	0.70879	-4.2	to	-26

^a Sr isotope data for filtered (less than 0.22 μm) samples, except those noted as UF (unfiltered).

^b Data from Oetting (1995).

^c Major and trace ion data from Senger et al. (1990).

^d Data from Land and Macpherson (1992).

^e Data from four samples from G. Groschen (unpublished data 1990). Analysis by L.S. Land, University of Texas.

Reported errors are $2\sigma_{\text{mean}}$ of $^{70-110} \text{Sr}/^{87}\text{Sr}$ ratios measured for each sample, and correspond to the last two significant figures reported. 'Rep', complete analytical replicate. Complete sample information and well locations given by Oetting (1995).

badwaters to undersaturated values in Facies D badwaters; (3) saturation with respect to dolomite progressively increases from undersaturated values in Facies A badwaters to values approaching saturation in Facies D badwaters. Previous workers have noted a similar regional trend in the saturation state of dolomite in badwaters using similar geochemical models (Pearson and Rettman, 1976; Clement, 1989). No significant variations in calcite, dolomite, and gypsum saturation states were observed between the analyses of this study and those of previous studies.

The O and H isotopic values of badwaters range from -5.4 to -4.0 ‰ and from -34 to -24 ‰, respectively, and plot along the global meteoric water line (Fig. 4(A)). Oxygen and H isotopic values in Edwards Group brines from previous investigations plot in two distinct groups that correspond to deep oil fields along the Stuart City

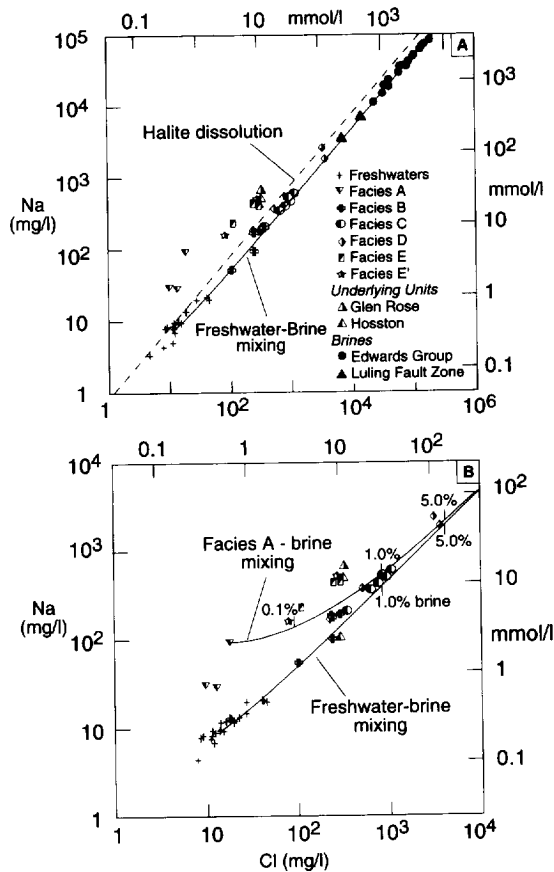


Fig. 5. Na and Cl variations in freshwaters, Facies A–E' badwaters, saline groundwaters from underlying hydrostratigraphic units and Luling Fault Zone and Edwards Group brines. (A) Halite dissolution (molar Na/Cl = 1 : 1). Freshwater–brine mixing refers to mixing of average freshwater and average Edwards Group brine. (B) Enlargement of the scale in (A). Mixing lines are contoured for percentage of average Edwards Group brine. For Figs. 5(A) and (B) and Figs. 6(A) and (B), the lower x-axis is Cl in mg l^{-1} and the upper x-axis is Cl in mmol l^{-1} in each figure.

Reef, Karnes Trough, and Charlotte–Jordanton Fault Zones, and shallow oil fields along the Luling Fault Zone (Fig. 4(A)). It should be noted that the brine $\delta^{18}\text{O}$ values are up to 20‰ higher than badwater values.

Sodium and Cl concentrations in Edwards freshwaters, badwaters, and Edwards Group brines span more than four orders of magnitude in range (Figs. 5(A) and 6). Sodium and Cl variations in badwaters plot in a range between freshwaters and Edwards Group brines, and span the Na/Cl ratios represented by model curves for

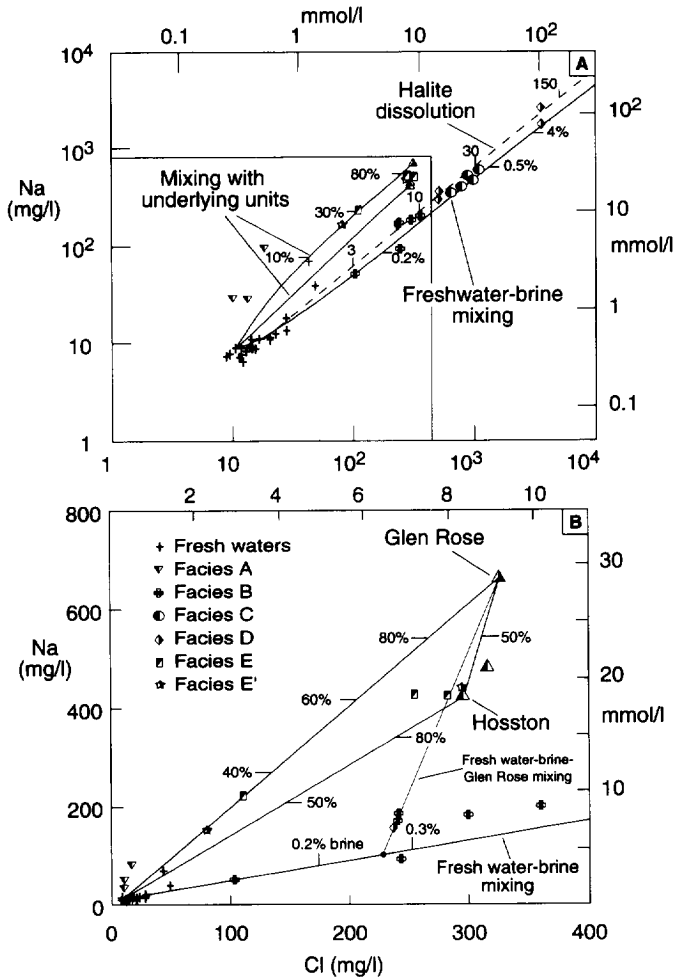


Fig. 6. Na and Cl variations in freshwaters, Facies A–E' badwaters and saline groundwaters from underlying hydrostratigraphic units. The continuous lines are model fluid mixing lines contoured for percentage of saline groundwater from underlying units and average Edwards Group brine. The dashed line in (A), molar Na/Cl = 1 : 1, is contoured for millimoles of halite dissolved. The box in the lower left of (A) is the Na and Cl range of (B).

freshwater–brine mixing and halite dissolution (Fig. 5(A)). Edwards freshwaters, badwaters, and Luling Fault Zone brines have a narrow range of $\delta^{18}\text{O}$ values over a wide range of Cl concentrations (Fig. 4(B)). A broad range of $\delta^{18}\text{O}$ values occurs only in deeper Edwards Group brines (Fig. 4(B)).

$^{87}\text{Sr}/^{86}\text{Sr}$ values of badwaters (0.70753–0.70946) span the range of freshwater values (0.70769–0.70872) and span nearly the entire range of Edwards Group brine values (0.7078–0.7097; Fig. 7). Nearly all freshwater and badwater $^{87}\text{Sr}/^{86}\text{Sr}$ values are higher than most Edwards carbonate and evaporite rocks analyzed to date (0.70742–0.70773; Koepnick et al., 1985; Oetting, 1995; Fig. 7). $^{87}\text{Sr}/^{86}\text{Sr}$ values of saline groundwaters from underlying units are similar to the highest values for Edwards Group brines and Glen Rose carbonate and evaporite rocks (Fig. 7).

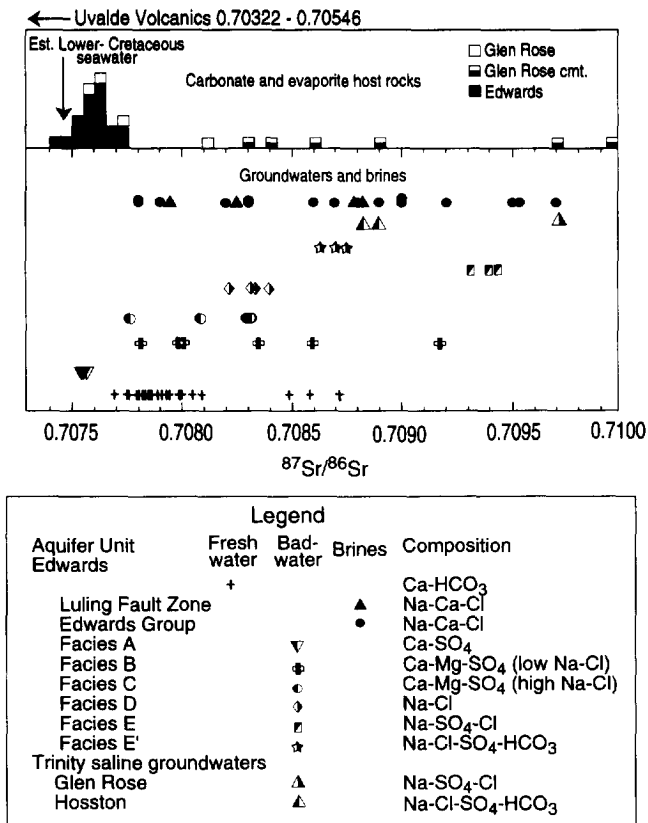


Fig. 7. Histogram at the top of the diagram shows Edwards Group and Glen Rose Limestone whole-rock $^{87}\text{Sr}/^{86}\text{Sr}$ values from Koepnick et al. (1985) and Oetting (1995), and Glen Rose carbonate and evaporite cement (cmt) values from Woronick (1985). Range of Uvalde volcanic rocks from Wittke and Mack (1993). The lower part of the diagram depicts $^{87}\text{Sr}/^{86}\text{Sr}$ variations in freshwaters, Facies A–E' badwaters, saline groundwaters from underlying hydrostratigraphic units and Luling Fault Zone and Edwards Group brines. Three samples of Facies A are shown.

7. Discussion

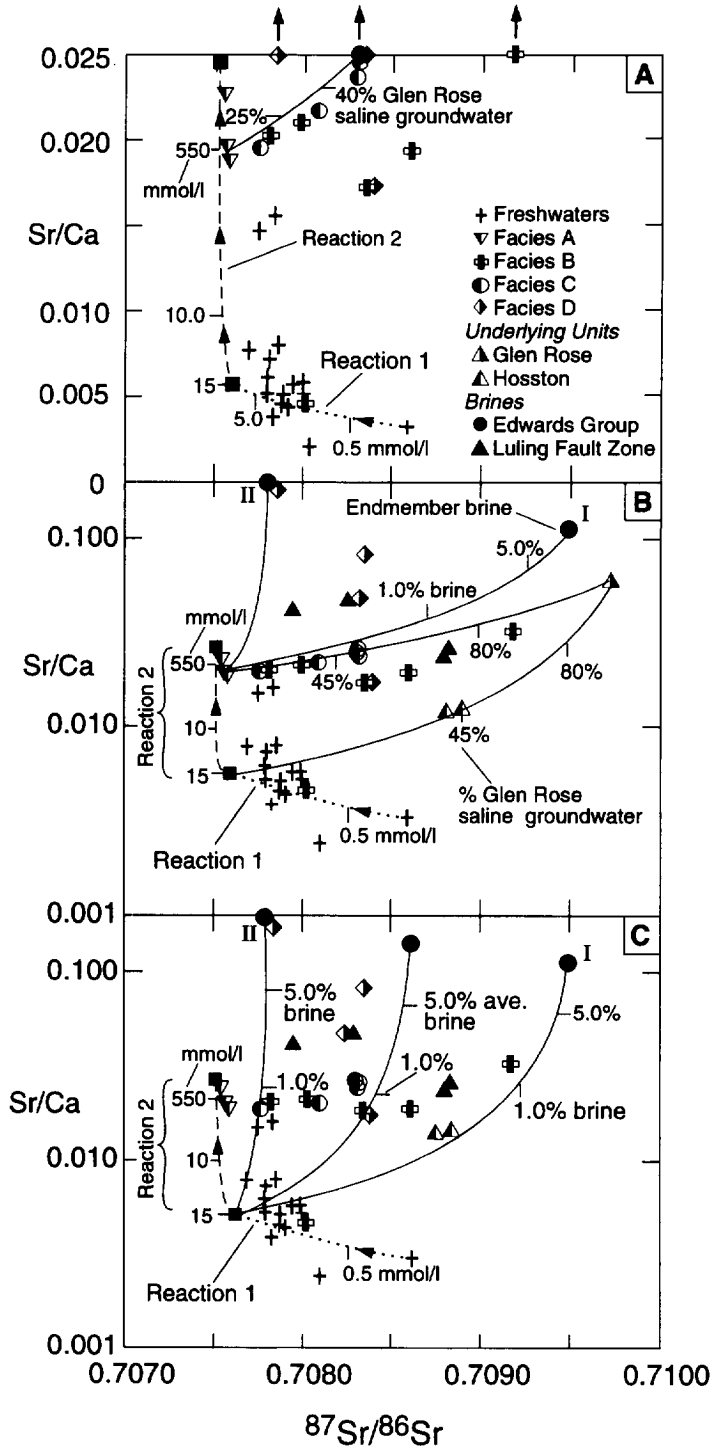
Previous studies have identified fluid mixing and fluid–rock interaction processes that can account for many of the major element variations in badwaters. Quantifying the role of these processes in the evolution of badwaters, however, has been limited by the non-unique results of major element geochemical modeling (Table 1). To gain a greater understanding of the geochemical evolution of badwaters, quantitative geochemical models are presented below that account for the simultaneous variations of major and trace elements, mineral saturation states, and O, H, and Sr isotopes in badwaters.

Variations in O and H isotopes and Na and Cl concentrations are consistent with two alternative origins for badwaters: (1) fluid–rock interaction involving freshwater and carbonate and evaporite rocks (i.e. evolved meteoric water model); (2) saline–freshwater mixing processes (Figs. 4(A) and 5(A)). Fig. 4(B) illustrates modeled variations in Cl and $\delta^{18}\text{O}$ values that occur during fluid mixing processes between freshwaters and Edwards Group brines. Chloride vs. $\delta^{18}\text{O}$ variations during freshwater–brine mixing processes are governed by the large disparity between Cl concentrations in freshwaters and Edwards Group brines, and the very narrow range of oxygen contents in these two fluids. As a result, major element variations are a more sensitive tool for evaluating fluid mixing processes involving small percentages of brine (Fig. 4(B)).

This mixing calculation is consistent with the proposal of Prezbindowski (1981) that both Edwards badwaters and Luling Fault Zone brines result from mixing between Edwards freshwaters and Edwards Group brines. The wide range of $^{87}\text{Sr}/^{86}\text{Sr}$ values in badwaters relative to aquifer rocks indicates an extraformational source or sources of Sr. The ranges of $^{87}\text{Sr}/^{86}\text{Sr}$ in Glen Rose carbonate and evaporite rocks, saline groundwaters from underlying hydrostratigraphic units, and Edwards Group brines suggest that multiple extraformational sources may contribute to the wide range of $^{87}\text{Sr}/^{86}\text{Sr}$ values in badwaters (Fig. 7). In the following sections, geochemical variations in facies that occur in specific structural and depositional settings are examined separately, so that depositional and structural effects on geochemical and isotopic variations can be evaluated.

7.1. Facies A badwaters

Aquifer rocks of the facies A region were deposited on the northern margin of the evaporitic Maverick Basin and are predominantly composed of calcite, gypsum, and anhydrite. The aquifer is thickest in this region, which lies west of the Balcones Fault Zone (Figs. 1(B), 2(A) and 2(B)). Few major faults crosscut the aquifer, and volcanic and intrusive igneous rocks are absent in the Facies A region. Consequently, groundwater contact with extraformational strata in the Facies A region is more limited than in other aquifer regions. Major element variations in Facies A badwaters suggest an evolution involving freshwater dissolution of carbonate and evaporite minerals (Clement, 1989). $\delta^{18}\text{O}$ and δD values of a Facies A badwater indicate a meteoric origin (Fig. 4(A)). $^{87}\text{Sr}/^{86}\text{Sr}$ variations in Facies A badwaters suggest that nearly



all Sr in these badwaters is derived from aquifer carbonate and evaporite rocks (Fig. 7). The geochemical and isotopic evidence cited above strongly suggests a Facies A badwater evolution that involves meteoric water interaction with aquifer carbonate and evaporite rocks. This is consistent with the conclusions of a previous major element geochemical study of badwaters (Clement, 1989). Freshwater evolution involving fluid–rock interaction with Edwards carbonate and evaporite rocks may be reflected in the high concentrations of Ca and SO_4 and calcite and gypsum saturation indices (SI_{cal} and SI_{gyp}) in several badwater facies, as discussed in later sections.

Further constraints on Facies A badwater evolution are obtained from application of quantitative geochemical modeling of simultaneous variations in mineral saturation states, major and trace element concentrations, and $^{87}\text{Sr}/^{86}\text{Sr}$ values. Geochemical modeling using PHREEQE (Parkhurst et al., 1980) of incongruent dissolution of gypsum and precipitation of calcite, which assumes an initial fluid similar to fresh groundwaters in the Edwards aquifer, can account for Facies A badwater Ca, SO_4 and HCO_3 concentrations, and pH, SI_{cal} , and SI_{gyp} values. However, Sr concentrations and Sr/Ca ratios in Facies A badwaters are significantly higher than values that can be obtained from this equilibrium model (Fig. 8(A)). Fluid–rock interaction processes involving recrystallization of aquifer calcite can account for Facies A Sr/Ca and $^{87}\text{Sr}/^{86}\text{Sr}$ variations (Fig. 8(A)). A geochemical model that involves incongruent dissolution of aquifer gypsum and precipitation of calcite followed by recrystallization of aquifer calcite can account for simultaneous variations in Facies A badwater major and trace element concentrations, and pH, SI_{cal} , SI_{gyp} and $^{87}\text{Sr}/^{86}\text{Sr}$ values.

Sodium and Cl variations in Facies A badwaters indicate a source of Na in addition to that derived from either halite dissolution or freshwater–brine mixing (Fig. 5(A); Clement, 1989). The low Cl concentrations ($10\text{--}20\text{ mg l}^{-1}$; $0.282\text{--}0.564\text{ mmol l}^{-1}$) and high Na concentrations ($28\text{--}90\text{ mg l}^{-1}$; $1.22\text{--}3.91\text{ mmol l}^{-1}$) in Facies A badwaters relative to freshwaters suggest that the source of excess Na in these waters is not also a source of Cl (Fig. 5(A)). The high concentrations of Cl in saline groundwaters from underlying hydrostratigraphic units make them unlikely sources of Na in Facies A badwaters. Ion exchange processes involving clay minerals disseminated through aquifer rocks, or along contacts between the aquifer and its confining units, could contribute excess Na to Facies A badwaters (Clement, 1989). This source of Na, however, is also a likely source of Sr with very high $^{87}\text{Sr}/^{86}\text{Sr}$ values relative to

Fig. 8. Sr/Ca and $^{87}\text{Sr}/^{86}\text{Sr}$ variations in freshwaters, Facies A–E' badwaters, saline groundwaters from underlying hydrostratigraphic units and Luling Fault Zone and Edwards Group brines. Samples with upward pointing arrows at the top of (A) have Sr/Ca values that plot off the diagram. The dotted line in (A)–(C) (Reaction 1) leading in the direction of the arrows to the first black square represents incongruent dissolution of gypsum with 1800 ppm Sr and precipitation of calcite. The dashed line leading in the direction of the arrows to the second black square (Reaction 2) represents recrystallization of calcite containing 450 ppm Sr. Both the calcite and gypsum have an $^{87}\text{Sr}/^{86}\text{Sr}$ value of 0.70755. The continuous lines are model fluid mixing curves contoured for percentages of endmember (I, II) Edwards Group brines and saline groundwater from underlying hydrostratigraphic units.

carbonate and evaporite aquifer rocks. High $^{87}\text{Sr}/^{86}\text{Sr}$ values expected for clay minerals stem from (1) high $^{87}\text{Sr}/^{86}\text{Sr}$ values associated with older continental sources of terrigenous material in the region, and (2) the in-situ decay of ^{87}Rb to ^{87}Sr in clay minerals, which typically have high Rb/Sr ratios relative to carbonate and evaporite minerals. The essentially invariant and low $^{87}\text{Sr}/^{86}\text{Sr}$ values in Facies A badwaters (similar to aquifer carbonate and evaporite rocks) suggest that interaction with clay minerals is negligible.

Previous studies indicate that Edwards carbonate rocks may contain significant concentrations of Na, which suggests another source of Facies A badwater Na (Mueller, 1975; Clement, 1989). If Edwards carbonate rocks have similar Na/Cl ratios to the wide range found in other studies of modern and ancient carbonate rocks from non-burial settings, then Facies A badwater Na concentrations and Na/Cl ratios could reflect recrystallization of aquifer carbonate and perhaps evaporite rocks (Land and Hoops, 1973; Staudt et al., 1993). Sodium and Cl analyses of carbonate and evaporite rocks in the Facies A region are required to test this model.

If the concentrations of Ca and SO_4 in Facies B, C, and D badwaters reflect fluid–rock interaction processes that occur before fluid mixing processes, then fluid mixing models should require an evolved meteoric water endmember that is similar to Facies A badwaters. Previous studies have demonstrated calcite undersaturation in saline–freshwater mixing zones of coastal aquifers and on the margins of major sedimentary basins (Wigley and Plummer, 1976; Back et al., 1986; Toth, 1988; Long et al., 1988). Geochemical modeling, using SOLMINEQ88 (Kharaka et al., 1988), of changing mineral saturation states during fluid mixing predicts saturated or supersaturated SI_{cal} values and undersaturated SI_{gyp} values in mixtures of 70–100% evolved meteoric water and 1–30% Edwards Group brine for most Edwards Group brine compositions. Sensitivity analysis of SI_{cal} values in fluid mixing models indicates that the high temperature of Edwards Group brines (126–174°C; Land and Macpherson, 1992), and the high concentrations of Ca in both evolved meteoric waters and Edwards Group brines significantly contribute to saturated–supersaturated SI_{cal} values in model mixtures.

7.2. Facies B badwaters

Aquifer rocks in the Facies B region were deposited on the margin of the evaporitic Maverick Basin and along the Lower Cretaceous Devil's River Reef, and are composed of calcite, dolomite, gypsum and anhydrite (Fig. 1(B)). The facies boundary between the Facies A and B regions (Fig. 1(B)) corresponds to a transition zone known as the Frio River Line, which delineates the boundary between easternmost Cordilleran fold and thrust tectonics and westernmost salt deformation-related Gulf of Mexico Basin style tectonics (Ewing, 1987). The aquifer in the Facies B region is crosscut in several locations by volcanic and intrusive igneous rocks, and by faults in the Balcones Fault Zone (Fig. 1(A)). We evaluate below the extent to which the geochemistry of badwaters in the Facies B region is affected by both faulting and volcanic and intrusive igneous rocks that crosscut the aquifer.

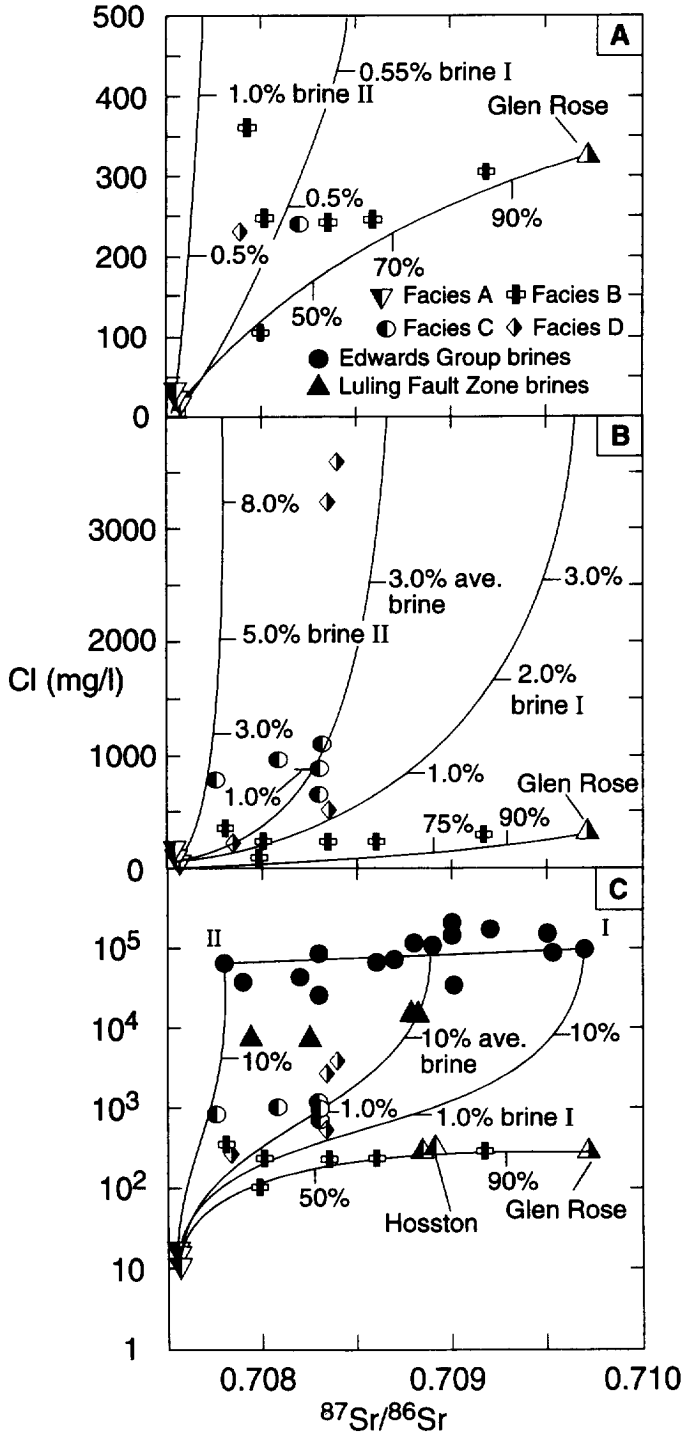
Although the Facies B badwater shown in Fig. 1(C) is typical of badwaters from

this region with TDS values greater than 2000 mg l⁻¹, badwaters from the Facies B region that have salinities from 1000 to 2000 mg l⁻¹ TDS have lower Ca and SO₄ concentrations (Table 2; see Clement (1989) for a more complete listing of Facies B badwaters). The Ca and SO₄ concentrations in Facies B badwaters suggest significant fluid–rock interaction with aquifer rocks that is apparently more extensive in Facies B badwaters with TDS greater than 2000 mg l⁻¹ (Table 2). The increase in SI_{gyp} values and near constancy of SI_{cal} values between freshwaters and Facies B badwaters suggest that these fluid–rock interaction processes involve gypsum dissolution and precipitation or recrystallization of carbonates. An increasing west to east trend in Mg concentrations and the saturation state of dolomite from the Facies A to the Facies B region may reflect fluid–rock interaction with more dolomitic aquifer rocks east of the Maverick Basin or with crosscutting volcanic and intrusive igneous rocks in the Facies B region, as suggested by Clement (1989; Figs. 1(A) and 1(B)).

Chloride concentrations in Facies B badwaters are more than an order of magnitude higher than in Facies A badwaters (Fig. 1(C), Table 2). Sodium and Cl variations in Facies B badwaters plot along two trends: (1) a freshwater–brine mixing trend; (2) a trend approximately centered between freshwater–brine mixing and endmember Facies A–brine mixing curves (Fig. 5(B)). These trends may reflect differences in the extent of fluid–rock interaction with aquifer rocks that occur before fluid mixing between evolved meteoric waters and Edwards Group brines. Alternatively, Na and Cl variations in Facies B badwaters that cannot be accounted for by evolved meteoric water–brine mixing may reflect a third component of saline groundwater from underlying hydrostratigraphic units (Fig. 6(B)).

⁸⁷Sr/⁸⁶Sr variations in badwaters of the Facies B region suggest a source of Sr with ⁸⁷Sr/⁸⁶Sr values that are much higher than those of either Late Cretaceous volcanic rocks in the region or carbonate and evaporite aquifer rocks (Fig. 7; Koepnick et al., 1985; Wittke and Mack, 1993). ⁸⁷Sr/⁸⁶Sr variations in Facies B badwaters indicate an extraformational source or sources of Sr that may be derived from underlying units, Edwards Group brines migrating out of the Gulf of Mexico sedimentary basin, or contributions from both sources (Fig. 7). Evidence from major element variations for fluid–rock interaction processes indicates that these extraformational sources of Sr in Facies B badwaters are additional to Sr derived from carbonate and evaporite aquifer rocks. To evaluate the role of both fluid–rock interaction and fluid mixing processes in Facies B badwater evolution, simultaneous variations in Cl, Sr/Ca, and ⁸⁷Sr/⁸⁶Sr in Facies B badwaters are compared with results of geochemical models of these processes.

Chloride and ⁸⁷Sr/⁸⁶Sr variations during fluid mixing between freshwaters and Edwards Group brines can be significantly affected by fluid–rock interaction processes between the freshwater endmember and aquifer carbonate and evaporite rocks. Strontium added to endmember freshwaters from fluid–rock interaction processes changes the shape of model fluid mixing curves. Given the major element geochemical evidence for both fluid–rock interaction and fluid mixing processes in the evolution of Facies B badwaters, geochemical models of fluid mixing between evolved meteoric waters and Edwards Group brines may account for Cl and ⁸⁷Sr/⁸⁶Sr variations in Facies B badwaters.



Fluid mixing models involving evolved meteoric waters and (1) endmember Edwards Group brines and (2) saline groundwater from the underlying Glen Rose Formation can account for Cl, Sr/Ca, and $^{87}\text{Sr}/^{86}\text{Sr}$ variations in Facies B badwaters (Figs. 8(A), 8(B), 9(A) and 9(B)). Sr/Ca and $^{87}\text{Sr}/^{86}\text{Sr}$ variations in Facies B badwaters help place constraints on the extent of fluid–rock interaction between freshwaters and aquifer carbonate and evaporite rocks that define the evolved meteoric water endmember in fluid mixing models. The two fluid mixing curves leading to the Glen Rose saline groundwater reveal the importance of calcite-crystallization in elevating Sr/Ca ratios in the evolved meteoric water endmember (Fig. 8(B)). Facies B badwater Sr/Ca variations can be accounted for by varying the extent fluid–rock interaction that occurs before mixing with Glen Rose saline groundwaters (Figs. 8(A) and 8(B)). Model fluid mixing curves between Edwards Group brines and evolved meteoric waters can also account for Sr/Ca and $^{87}\text{Sr}/^{86}\text{Sr}$ variations in Facies B badwaters, but do not require recrystallization of aquifer calcite subsequent to incongruent reaction (Fig. 8(C)).

Fluid mixing models involving (1) evolved meteoric waters and Glen Rose saline groundwater (Fig. 8(B)) and (2) evolved meteoric waters and Edwards Group brines (Fig. 8(C)) both appear to account for Sr/Ca and $^{87}\text{Sr}/^{86}\text{Sr}$ variations in Facies B badwaters. A large disparity in Na/Cl ratios between saline groundwaters from underlying hydrostratigraphic units (relatively high Na/Cl) and Edwards Group brines (relatively low Na/Cl) provides an additional tool to distinguish between these two sources. Models of fluid mixing between Facies A badwaters, which approximate evolved meteoric waters, and Edwards Group brines can account for Na/Cl and $^{87}\text{Sr}/^{86}\text{Sr}$ variations in only those Facies B badwaters with relatively low $^{87}\text{Sr}/^{86}\text{Sr}$ values (Fig. 10(A)). Saline groundwaters from underlying hydrostratigraphic units, which have high Na/Cl ratios and $^{87}\text{Sr}/^{86}\text{Sr}$ values, are a likely source for the high Na/Cl ratios and $^{87}\text{Sr}/^{86}\text{Sr}$ values in the other Facies B badwaters (Fig. 10(A)).

No single geochemical model evolution path can account for simultaneous variations in Sr/Ca, Cl, Na/Cl, and $^{87}\text{Sr}/^{86}\text{Sr}$ variations in all Facies B badwaters (Figs. 8–10). However, two distinct evolution paths can be identified from quantitative geochemical models: (1) fluid mixing between evolved meteoric waters and Edwards Group brines; (2) fluid mixing between evolved meteoric waters and saline groundwaters from the underlying Glen Rose Formation.

7.3. Facies C and D badwaters

Aquifer rocks in the Facies C and D regions are primarily limestones and dolostones that were deposited in shallow subtidal, intertidal and supratidal

Fig. 9. Cl and $^{87}\text{Sr}/^{86}\text{Sr}$ variations in Facies A–E' badwaters, saline groundwaters from underlying hydrostratigraphic units and Luling Fault Zone and Edwards Group brines. The continuous lines in (A)–(C) are model fluid mixing curves that are contoured for percentages of Edwards Group brine endmembers (I, II), average Edwards Group brine and saline groundwater from underlying hydrostratigraphic units.

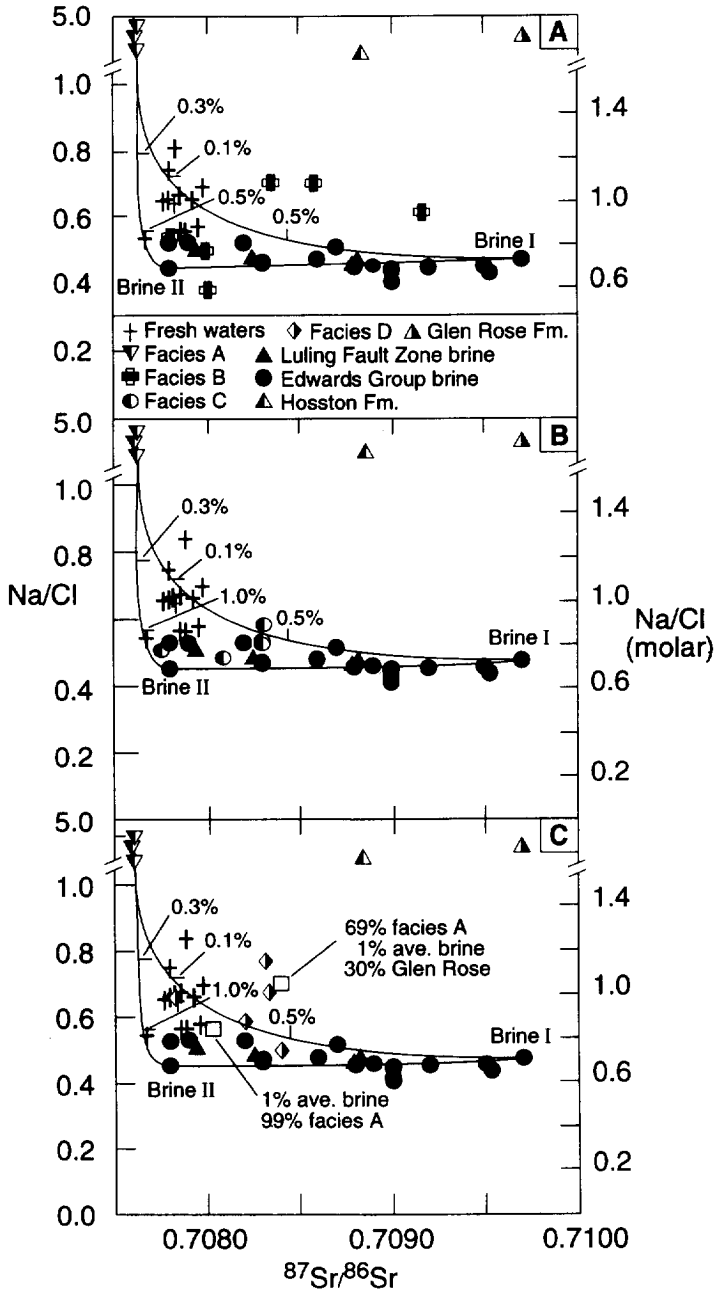


Fig. 10. Na/Cl and $^{87}\text{Sr}/^{86}\text{Sr}$ variations in freshwaters, Facies A–E' badwaters, saline groundwaters from underlying hydrostratigraphic units and Luling Fault Zone and Edwards Group brines. The continuous lines in (A)–(C) are model fluid mixing curves that are contoured for percentages of endmember Edwards Group brines (I, II). (Note that the top of the scale is compressed.) Open squares represent compositions of two- and three-component fluid mixtures.

environments that developed over the San Marcos Arch (Fig. 1(B); Rose, 1972; Clement, 1989). Aquifer rocks become increasingly dolomitic from west to east within the Facies C and D regions along the badwater line and down-dip to the Stuart City Reef (Rose, 1972; Longman and Mench, 1978; Ellis, 1985; Deike, 1987, 1990). The cumulative displacement across the Balcones Fault Zone and displacement on individual faults increase from west to east across the Facies C and D regions. Aquifer rocks in the Balcones Fault Zone and in areas down-dip are faulted with increasing intensity from west to east across the Facies C and D badwater regions (Fig. 1(A)). In the Facies D region faults may completely offset the aquifer locally and thereby (1) exclude hydraulic contact in the Edwards aquifer between fault blocks and (2) place underlying hydrostratigraphic units in extensive hydraulic contact with groundwaters in the Edwards aquifer (Fig. 3(C); Abbott, 1974, 1975; Maclay and Small, 1983, 1986; Maclay et al., 1985; Clement, 1989). Faults of lesser displacement in the Facies C and D regions may increase hydraulic contact between hydrostratigraphic intervals within the Edwards aquifer by placing units above and below semiconfining units in hydraulic contact (Fig. 3(C)). Regional changes in the intensity and displacement on faults through the Edwards aquifer and in the carbonate mineralogy of Edwards Group rocks down-dip of the badwater line may be reflected in major and trace element and $^{87}\text{Sr}/^{86}\text{Sr}$ variations in Facies C and D badwaters.

Geochemical and isotopic variations in Facies C and D badwaters provide evidence for both fluid–rock interaction and fluid mixing processes. The high Ca and SO_4 concentrations in most Facies C and D badwaters relative to freshwaters suggest substantial fluid–rock interaction with carbonate and evaporite aquifer rocks (Fig. 1(C), Table 2). Magnesium concentrations and Mg/Ca ratios in Facies C and D badwaters are higher than in Facies B badwaters, which may reflect (1) groundwater evolution in more dolomitic aquifer rocks down-dip of the badwater line or (2) fluid mixing involving evolved meteoric waters and extraformational fluids that have high Mg/Ca ratios (Fig. 1(C)). Facies A badwater and Edwards Group brine Mg/Ca ratios are lower than those of Facies C and D badwaters, indicating that fluid mixing between these fluids cannot account for Facies C and D badwater Mg/Ca ratios. However, Mg/Ca ratios in saline groundwaters from underlying hydrostratigraphic units are very high relative to values for Facies A, B, C, and D badwaters (Fig. 1(C)). This suggests that both saline groundwaters from underlying hydrostratigraphic units and the dolomitic composition of aquifer rocks down-dip of the badwater line in the Facies C and D regions may both contribute to the increasing trend in badwater Mg/Ca ratios from the Facies A to the Facies D badwater regions.

Sodium and Cl concentrations in Facies C and D badwaters are as much as an order of magnitude higher than in Facies B badwaters (Table 2). Chloride and $^{87}\text{Sr}/^{86}\text{Sr}$ variations in Facies C and D badwaters suggest that these high Na and Cl concentrations result from fluid mixing between evolved meteoric waters and Edwards Group brines (Figs. 9(B) and 9(C)). An Edwards Group brine source of Cl can account for the high Cl concentrations in most Facies B, C, and D badwaters (Figs. 9(B) and 9(C)). $^{87}\text{Sr}/^{86}\text{Sr}$ and Cl variations from the Facies B region to the Facies C and D regions along the badwater line indicate a regional increase in the contribution of Edwards Group brine (Figs. 9(B) and 9(C)). Greater permeability

associated with more dolomitic rocks down-dip of the badwater line proximal to the San Marcos Arch may account for this regional trend.

Geochemical models of fluid mixing between evolved meteoric waters (represented by Facies A badwaters) and Edwards Group brines can account for Na/Cl and $^{87}\text{Sr}/^{86}\text{Sr}$ variations in essentially all Facies C badwaters. Some Facies D badwaters, however, plot above the model mixing curves (Fig. 10(C)). Processes that may contribute to these elevated Na/Cl ratios include: (1) dissolution of accessory halite within Edwards aquifer rocks; (2) mixing with saline groundwaters from underlying units, which have high Na/Cl ratios; (3) Na–Ca exchange with clay minerals. Although accessory halite has been described in Edwards Group rocks down-dip of the badwater line in the Facies D region (Ellis, 1985; Deike, 1987), Cl and Br systematics in Facies C and D badwaters are more consistent with fluid mixing between freshwaters and Edwards Group brines than with the dissolution of halite in the Facies D badwater region (Oetting, 1995). Facies D badwaters have a narrow range of $^{87}\text{Sr}/^{86}\text{Sr}$ values and a relatively wide range of Na/Cl ratios (Fig. 10(C)), indicating that either the source of Na in Facies D badwaters has a similar $^{87}\text{Sr}/^{86}\text{Sr}$ to Facies D badwaters or that the source of Na contributes negligible Sr. Although Na–Ca exchange in clay minerals is a possible source of Na, as discussed above for Facies A, clay mineral Sr is expected to have very high $^{87}\text{Sr}/^{86}\text{Sr}$ values. The lack of a positive correlation between $^{87}\text{Sr}/^{86}\text{Sr}$ and Na/Cl suggest that ion exchange with clay minerals is not a likely source for the high Na/Cl ratios in some Facies D badwaters (Fig. 10(C)).

Quantitative modeling of geochemical and $^{87}\text{Sr}/^{86}\text{Sr}$ variations in Facies C and D badwaters suggests that fluid mixing between evolved meteoric waters and Edwards Group brines controls the evolution of Facies C and D badwaters. Given a hypothetical Facies C or D badwater consisting of a mixture of 30% saline groundwater from the underlying Glen Rose Formation, 69% evolved meteoric water, and 1% average Edwards Group brine, the Sr contributed from the Glen Rose saline groundwater is 2.1 mg l^{-1} of the total mixture Sr of 19.7 mg l^{-1} . The addition of Sr from saline groundwaters of the Glen Rose Formation changes an evolved freshwater–average Edwards Group brine mixture $^{87}\text{Sr}/^{86}\text{Sr}$ value by 0.00019. This shift in $^{87}\text{Sr}/^{86}\text{Sr}$ is negligible relative to the range of possible $^{87}\text{Sr}/^{86}\text{Sr}$ values that could result from 99% evolved meteoric water–1% Edwards Group brine fluid mixtures (Fig. 8(C)). However, Na/Cl ratios in mixtures of evolved meteoric waters and Edwards Group brines could be significantly affected by the addition of saline groundwater from underlying hydrostratigraphic units (Fig. 10(C)).

A trend of increasing Mg/Ca from the Facies A to the Facies D regions suggests either an aquifer dolomite source of Mg, or an extraformational source from underlying hydrostratigraphic units. The Glen Rose signature observed in some Facies D badwaters (high Na/Cl–high $^{87}\text{Sr}/^{86}\text{Sr}$), however, is not reflected in Facies C badwaters (Figs. 10(B) and 10(C)). This suggests that badwaters in the Facies D region are in more extensive hydraulic contact with the underlying Glen Rose Formation and that both Facies C and D badwaters reflect fluid–rock interaction with more dolomitic aquifer rocks. These geochemical trends across the Facies C and

D regions are consistent with (1) an increase in the displacement on major faults in the Balcones Fault Zone, which provides more extensive contact between the Edwards aquifer and saline groundwaters of the underlying Glen Rose Formation (Fig. 3(C)), and (2) an increasing abundance of dolomite in Edwards Group rocks along the badwater line and down-dip to the Stuart City reef.

Increased intensity of faulting and displacement on major faults should increase communication between the Edwards aquifer and saline groundwaters of the underlying Glen Rose Formation. The permeability of Edwards aquifer rocks, however, may dictate how uniformly Glen Rose saline groundwaters mix with badwaters in the Edwards aquifer. The lower permeability of Edwards aquifer rocks down-dip of the badwater line in the Facies B region relative to the Facies C and D regions may result in locally significant plumes of unmixed Glen Rose saline groundwaters adjacent to fault contacts in the Facies B region. This localized control on the geochemistry of badwaters should result in a broad range of geochemical and $^{87}\text{Sr}/^{86}\text{Sr}$ compositions among badwaters from a single region, much like badwaters from the Facies B region. These apparent relationships between badwater geochemical trends and regional trends in the intensity and displacement on faults in the Balcones Fault Zone remain a topic for further investigation, given the limited number of badwater analyses from individual regions.

7.4. Facies E and E' badwaters

Aquifer rocks of the Facies E–E' (northern) region were deposited in open shallow marine environments and are composed of limestones and dolostones (Rose, 1972). Faults in the Balcones Fault Zone with smaller displacements than faults in the Facies D region may completely offset the Edwards aquifer, which is thinner in the northern aquifer region (Fig. 2(B); Baker et al., 1986; Clement, 1989; Senger et al., 1990). The hydraulic head of underlying units in the Facies E–E' region is locally above the base of the aquifer, indicating that vertical flow from underlying units may occur along faults and fractures (Clement, 1989). Major element variations in Facies E and E' badwaters are very similar to those for saline groundwaters from underlying hydrostratigraphic units (Fig. 1(C)). Clement (1989) suggested that these geochemical similarities are the result of fluid mixing between Edwards freshwaters and saline groundwaters from underlying units. $^{87}\text{Sr}/^{86}\text{Sr}$ values of saline groundwaters from underlying units and Facies E and E' badwaters are also similar, which supports evidence from major elements for these fluid mixing processes (Fig. 7).

Quantitative fluid mixing models indicate that some Facies E and E' badwaters may represent mixtures of Edwards freshwater and greater than 80% saline groundwater from underlying units (Figs. 6 and 11). These high percentages of non-Edwards groundwater in Facies E and E' badwaters can be accounted for by changes in stratigraphic thickness and the presence of faults and fractures that occur in the northern region of the aquifer. The volume of groundwater stored in the Edwards aquifer becomes smaller as the aquifer thins northward, whereas the volume stored in thickened underlying units increases. Horizontal flow along faults, and vertical flow along faults and fractures from thick underlying units into a relatively thin Edwards

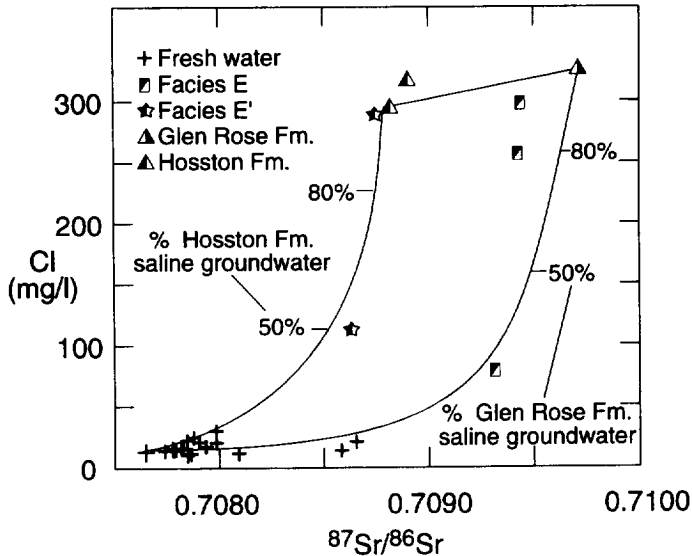


Fig. 11. Cl and $^{87}\text{Sr}/^{86}\text{Sr}$ variations in freshwaters, Facies E and E' badwaters and saline groundwaters from underlying hydrostratigraphic units. The continuous lines are model fluid mixing curves that are contoured for the percentage of saline groundwater from the Glen Rose and Hosston formations in mixtures with freshwaters. Some Cl data (see Table 2) from Senger et al. (1990).

aquifer could result in the high non-Edwards groundwater fractions portrayed by the quantitative geochemical models.

8. Summary

Geochemical and isotopic variations in badwaters of the Edwards aquifer suggest that structural features and depositional settings of regional significance marginal to the Gulf of Mexico sedimentary basin influence (1) migration of Edwards Group brines up-dip from the Cretaceous shelf margin and (2) vertical migration of fluids along faults and/or fractures into the Edwards aquifer. These structural features coincide with the occurrence of and trends in the intensity of faulting in the Balcones Fault Zone and major areas of faulting down-dip (Figs. 1(A) and 1(B)).

The geochemistry of badwaters in the Edwards aquifer reflects meteoric water interaction with Edwards carbonate and evaporite rocks and fluid mixing between these evolved meteoric waters and (1) saline groundwaters from underlying hydrostratigraphic units and (2) Edwards Group brines. The brines that mix with evolved meteoric waters in the badwater zone may reflect a history of interaction with evaporites and siliciclastics and may have migrated up-dip or along faults from depths greater than 5 km (Prezbindowski, 1981; Land and Prezbindowski, 1981). Regional geochemical and isotopic variations in Edwards aquifer badwaters suggest the following: (1) relatively isolated regions in which badwaters show little or no

geochemical evidence for large-scale fluid mixing processes; (2) regions in which badwaters show evidence for fluid mixing between evolved meteoric waters and Edwards Group brines migrating up-dip from the Cretaceous shelf margin; (3) regions in which badwaters show evidence for three-component mixing between evolved meteoric waters, Edwards Group brines, and saline groundwaters from underlying hydrostratigraphic units; (4) regions in which badwater geochemistry may be dominantly influenced by migration along faults and fractures of saline groundwaters from underlying hydrostratigraphic units into the Edwards aquifer.

9. Conclusions

Geochemical and isotopic variations in saline groundwaters of the regionally extensive Edwards aquifer reflect a diversity of geochemical evolution pathways within a narrow saline–freshwater mixing zone on the northwestern margin of the Gulf of Mexico sedimentary basin. This diversity of geochemical evolution pathways results in six regionally extensive hydrochemical facies: Ca–SO₄ (Facies A), Ca–Mg–SO₄ (low Na–Cl; Facies B), Ca–Mg–SO₄ (high Na–Cl; Facies C), Na–Cl (Facies D), Na–SO₄–Cl (Facies E), and Na–Cl–SO₄–HCO₃ (Facies E'). The geochemical evolution of these hydrochemical facies is apparently controlled by (1) tectonic settings marginal to the Gulf of Mexico basin and (2) the mineralogy, thickness, and depositional setting of carbonate and evaporite rocks within the Edwards aquifer. Quantifying the geochemical effects of individual aquifer characteristics on fluid evolution is complicated by the regional concurrence of changes in these characteristics and in tectonic settings. Given these complexities, geochemical and isotopic trends within saline–freshwater mixing zones marginal to the basin suggest that migration of brines out of the basin is significantly influenced by the combined effects of faulting related to salt movement deeper in the basin and greater permeability of dolomitic aquifer rocks along the San Marcos Arch (Prezbindowski, 1981; Clement, 1989). Vertical migration of fluids between hydrostratigraphic units appears more significant where aquifer thickness is reduced and fault displacements are greatest.

The evolution of meteoric waters from extensive interaction with carbonate and evaporite aquifer rocks is reflected in saline groundwaters in the westernmost region of the Edwards aquifer. Equilibrium geochemical models of incongruent dissolution of gypsum and precipitation of calcite can account for major element variations and mineral saturation states in Facies A badwaters, but fail to account for Facies A badwater Sr/Ca and ⁸⁷Sr/⁸⁶Sr variations. Recrystallization of aquifer calcite following incongruent gypsum dissolution and calcite precipitation is required to account for the simultaneous variations of major elements, Sr, calcite and gypsum saturation states, and ⁸⁷Sr/⁸⁶Sr values in Facies A badwaters.

Although numerous volcanic and intrusive igneous rocks crosscut the Edwards aquifer in the Facies B region, interaction with these volcanic and intrusive igneous rocks is of little significance in evolution of Facies B badwaters. The geochemical and isotopic evolution of these badwaters appears more significantly affected by fluid

mixing processes involving evolved meteoric waters and either Edwards Group brines or saline groundwaters from the underlying Glen Rose Formation, or some contribution from both fluids.

Fluid mixing processes between evolved meteoric waters and Edwards Group brines apparently exert a dominant control over major and trace element and $^{87}\text{Sr}/^{86}\text{Sr}$ variations in Facies C and D badwaters. However, Facies D Na/Cl and $^{87}\text{Sr}/^{86}\text{Sr}$ variations are accounted for only in three-component mixtures of evolved meteoric water, Edwards Group brine, and saline groundwater from the underlying Glen Rose Formation. A regional west to east increase in the apparent contribution of saline groundwaters from the underlying Glen Rose Formation from the Facies C to the Facies D badwater region corresponds to an increasing trend in displacement of major faults through the aquifer that place underlying hydrostratigraphic units in extensive hydraulic contact with the Edwards aquifer.

In the aquifer's northernmost region badwaters reflect fluid mixing between groundwaters in the Edwards aquifer and saline groundwaters from two underlying hydrostratigraphic units. The fraction of saline groundwaters from underlying units in mixtures with fresh groundwaters in the Edwards aquifer can exceed 80%. The extent of fluid mixing with saline groundwaters from underlying units is consistent with the reduced thickness of the Edwards aquifer and increased thickness of underlying units in this region.

Geochemical modeling of saline groundwater evolution in the Edwards aquifer suggests that regional geochemical and isotopic variations within a narrow saline–freshwater mixing zone on the northwestern margin of the Gulf of Mexico sedimentary basin reflect variations in the nature and extent of fluid–rock interaction and fluid mixing processes. These fluid mixing processes apparently involve (1) dilute meteoric waters that have interacted extensively with aquifer carbonate and evaporite rocks, (2) saline groundwaters from underlying hydrostratigraphic units that migrate into the aquifer across fault contacts, or vertically along faults and fractures, and (3) brines from aquifer rocks that migrate up-dip from the Lower Cretaceous shelf margin.

Acknowledgments

This project was supported by the National Science Foundation (EAR 9204980), the Geological Society of America, and the Geology Foundation of the University of Texas. We thank G. Groschen (USGS San Antonio), who provided this study with additional groundwater and brine geochemical and isotopic data, which significantly contributed to the interpretation of some badwater hydrochemical facies. Three anonymous reviewers, P. Bennett, and M. Musgrove provided constructive reviews of the manuscript. We also thank the following individuals and organizations for their technical assistance and cooperative efforts: M. Thomas and P. Rettman (USGS San Antonio); T. Housh, C. Wolfson, N. Walker, P. Bennett, J. Grubb, C. Dreschel, and T. Rasbury (University of Texas); numerous individuals at city offices, Soil Conservation Service offices, and land owners in central and southern Texas.

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