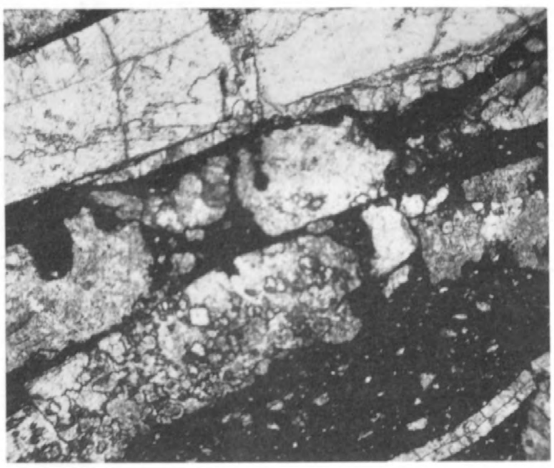
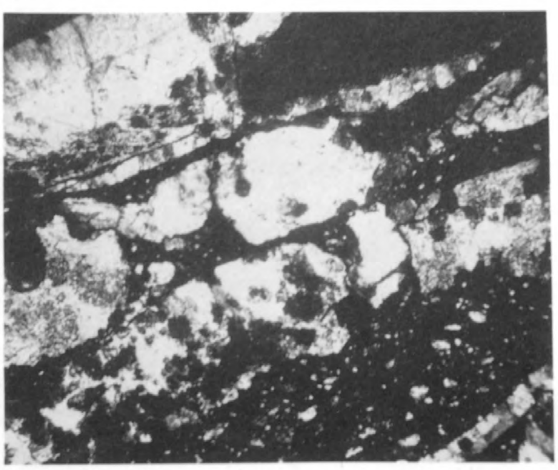
Comparative Petrology of Cores from Two Test Wells in the Eastern Part of the Edwards Aquifer, South-Central Texas





U.S. Geological Survey
Water-Resources Investigations
Report 87-4266

Cover

Core sample from Randolph well, leached and collapsed members, that is finely layered with petroliferous organic material and fine laminae of calcite and fluorite. In thin section, the fluorite is isotropic (black) under crossed polarizors and in plane light note that it follows cleavage planes in the calcite, hence it is a secondary replacement.

Comparative Petrology of Cores from Two Test Wells in the Eastern Part of the Edwards Aquifer, South-Central Texas

by Ruth G. Deike

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Water-Resources Investigations Report 87-4266

Reston, Virginia
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CONVERSION FACTORS

For use of readers who prefer to use metric (International System) units, conversion factors for inch-pound terms used in this report are listed below:

Multiply Inch-Pound Unit	By	To Obtain Metric Unit
foot (ft)	0.3048	meter (m)
foot squared per day (ft^2/d)	0.0929	meter squared per day (m^2/d)
cubic foot per second (ft^3/s)	0.02832	cubic meter per second (m^3/s)
gallon per minute (gal/min)	0.06309	liter per second (L/s)
million gallons per day (Mgal/d)	0.04381	cubic meter per second (m^3/s)
inch (in)	25.4	millimeter (mm)
inch per year (in/yr)	25.4	millimeter per year (mm/yr)
mile (mi)	1.609	kilometer (km)
square mile (mi^2)	2.590	square kilometer (km^2)

Temperature in degrees Fahrenheit (°F) can be converted into degrees Celsius (°C) as follows:

$$\text{Temp °F} = 1.8 \text{ Temp °C} + 32$$

<u>Sea level</u>: In this report "sea level" refers to the National Geodetic Vertical Datum of 1929 (NGVD of 1929)--a geodetic datum derived from a general adjustment of the first-order level nets of both the United States and Canada, formerly called Sea Level Datum of 1929.

COMPARATIVE PETROLOGY OF CORES FROM TWO TEST WELLS
IN THE EASTERN PART OF THE EDWARDS AQUIFER, SOUTH-CENTRAL TEXAS

By Ruth G. Deike

ABSTRACT

Two continuous cores from wells about 6 miles apart and vertically displaced by normal faults were stratigraphically correlated to compare latest early-Cretaceous rocks from the Edwards aquifer, south-central Texas, with stratigraphically equivalent rocks that have not been subjected to mixing-zone dedolomitization. The stratigraphic correlation was possible because sediments were deposited simultaneously at both well sites and datum horizons consisting of unaltered rocks could be correlated between pervasively altered aquifer units. The aquifer rock is composed of recrystallized calcite containing evidence for dolomite replacement (dedolomitization). The comparison indicates that the aquifer units (characterized by cavernous porosity) are equivalent to permeable dolomitic tidal flat facies, which also are the regionally significant petroleum-producing units of the Person and the Kainer Formations of the Edwards Group. Isotopic and petrologic differences between these dolomitic facies and aquifer rock show that during formation of the aquifer, dolomite dissolved, followed by precipitation of the calcite from solutions that were a mixture of calcium sulfate brine and dilute meteoric recharge water. This conclusion is supported by extensive discussion of lithologic and petrographic differences between all members of the early Cretaceous rocks cored in both wells.

Examination of the Kainer Formation of the Edwards Group in the study area shows that it can be divided into members that are correlative with members of the Fort Terret Formation on the Edwards Plateau. It is suggested, therefore, that these members in the study area in the Balcones Fault Zone probably are extensions of members in the Edwards Plateau.

All core samples were analyzed using x-ray diffraction complemented with thin-section observations. Differences in mineral abundance and mineral occurrence are discussed with respect to late-stage diagenesis during dedolomitization. Mineral and chemical comparisons of stratigraphically equivalent samples of calcite and dolomite include discussions of differences in magnesium carbonate content and cation substitution. Many core samples were analyzed by emission spectroscopy and the distribution of minor and trace elements within and between cores is discussed with reference to the environment of deposition, association with specific minerals, and stratigraphic associations.

INTRODUCTION

The Edwards aquifer discussed in this report is located in the Balcones Fault Zone in south-central Texas, and the wells studied are near San Antonio. In this area, the aquifer is contained in the Edwards Group of Early Cretaceous age described by Rose (1972) and its stratigraphic equivalents and the Georgetown Formation of Early Cretaceous age. More than 500,000 acre-feet of dilute, calcium bicarbonate water per year flow through part of this confined artesian system. Downdip and downfaulted from the freshwater part of the system, the Edwards aquifer contains saline water (up to 8,000 mg/L (milligrams per liter) total dissolved solids).

BACKGROUND

Since 1970, the U.S. Geological Survey, in cooperation with the Texas Department of Water Resources, has collected data on the Edwards aquifer in an effort to understand the hydrogeologic system in this area. This report is based on observations of rock cores obtained from the Edwards aquifer in the two different hydrochemical environments (Deike, 1984). One set of cores is from the Selma test hole, which penetrated the aquifer within the freshwater zone, and the other set is from the Randolph test hole, which penetrated the aquifer within the saline zone. Geologic descriptions of these rock cores indicate that: (1) some stratigraphic units in the freshwater zone are highly cavernous and other units are not, (2) the cavernous units could be stratigraphically correlated with dolomitic units within the saline zone, and (3) cavernous units in the freshwater zone are composed of recrystallized calcite and do not contain any dolomite. It was evident from these observations that the rock in major aquifer units had been significantly altered compared to rock in the nearby Randolph core.

Dedolomitization, or the dissolution of dolomite and replacement by calcite, is a geochemical reaction taking place in the Edwards aquifer (Abbott, 1974; Deike and Pearson, 1978; Deike, 1984; Ellis, 1985). It is suspected that the process of dedolomitization creates interconnected cavernous porosity and provides conduits for rapid flow of large volumes of freshwater.

PURPOSE AND SCOPE

This report presents the results of a study that compared zones of cavernous porosity where dolomite has been removed by alteration and zones where stratigraphically equivalent strata still contain dolomite in order to determine the causes of dedolomitization in the Edwards aquifer.

The comparison is based on detailed sampling of well-documented, continuous core from the two wells. Enough information is available to place these samples in a regional paleogeographic and diagenetic context so that the results of this comparison are applicable to major parts of the rocks containing the Edwards aquifer.

In addition to changes in carbonate lithology, the dedolomitization reactions involved changes in noncarbonate minerals, stable carbon-isotope ratios, and minor and trace elements. In an effort to define these changes, comparative data from x-ray diffraction, mass spectrometry and emission spectroscopy of stratigraphically equivalent samples are presented in this report, along with preliminary interpretation.

APPROACH

The general method of investigation was first, to establish a detailed stratigraphic correlation between the rocks of the freshwater zone, as represented by the Selma core and rocks of the saline-water zone as represented by the Randolph core; and second, to describe and compare the petrographic, mineralogic, and isotopic character of the rocks from these zones. In the course of the study, it became apparent that rocks deposited under certain conditions were more likely to become cavernous aquifer units. The investigation, therefore, focused on depositional environment and diagenesis of rocks in the Randolph core in order to determine what factors contributed to the development of cavernous porosity in stratigraphically equivalent rocks in the Selma core.

DESCRIPTION OF STUDY AREA

Location and Physical Setting

The area including the two wells is 6 miles long and is located in the Balcones fault zone in south-central Texas, 15 miles northeast of San Antonio and 100 miles from the Gulf of Mexico (fig. 1). The surface topography of the area surrounding the wells includes the broad valley of Cibolo Creek and bordering buttes and mesas with a relief of roughly 300 feet. The wells are 12 miles south of the Balcones escarpment where land surface is 1,000 feet lower than the Edwards plateau.

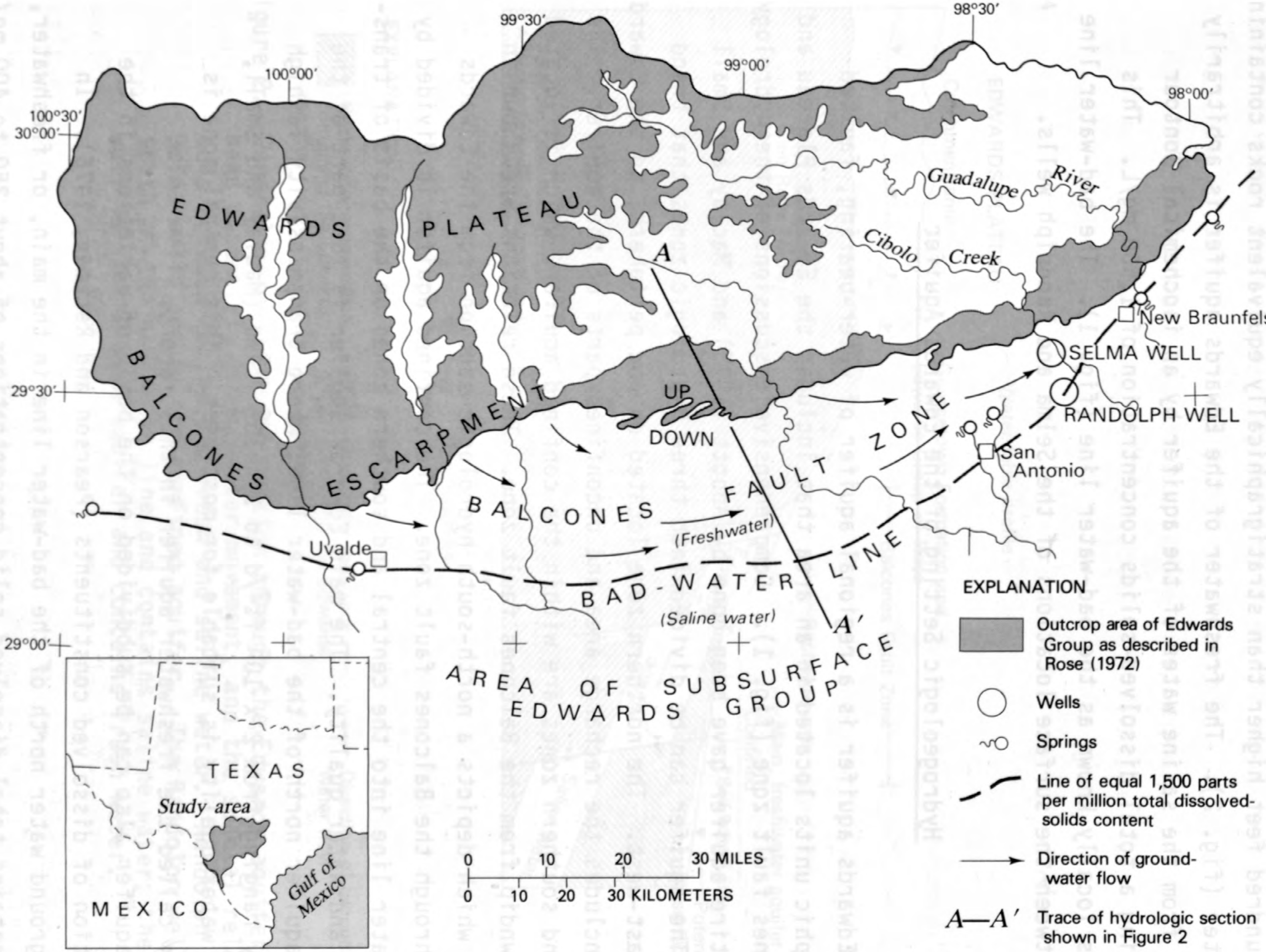


Figure 1.--The study area includes the Edwards Plateau and outcrop area of the Edwards Group, of Rose (1972) the Balcones escarpment; and the Balcones fault zone where the main aquifer is located. Recharge to the aquifer occurs along the escarpment, and major discharge is from springs in the eastern part of the fault zone. Relative fault movements are generalized as up (northern blocks) and down (southern blocks), as shown in figure 2.

The wells are located in the northeastern end of the Balcones fault zone and are separated by faults that place the rocks of the freshwater zone several hundred feet higher than stratigraphically equivalent rocks containing saline water (fig. 2). The freshwater of the Edwards aquifer is arbitrarily separated from the saline water of the aquifer by an isochemical contour representing a total dissolved-solids concentration of 1,500 mg/L. This contour is locally known as the bad-water line (fig. 1). The bad-water line passes between the surface locations of the Selma and Randolph wells.

Hydrogeologic Setting of the Edwards Aquifer

The Edwards aquifer is a regional aquifer of water-bearing, faulted stratigraphic units located in an area that includes the Edwards Plateau and the Balcones fault zone (fig. 1). Comprehensive discussions of the hydrology of the entire aquifer have been done by Abbott (1975) and Maclay and Small (1976). The aquifer can be divided into three hydrologic zones that trend roughly east-west. The northern zone located on and peripheral to the Edwards Plateau includes the recharge area and unconfined parts of the aquifer. The central and southern zones are within the confined aquifer, which is located in and downdip from the Balcones fault zone. These relations are shown in figure 2, which depicts a north-south hydrologic section from the Edwards Plateau through the Balcones fault zone. The confined aquifer is divided by the bad-water line into the central and southern zones on the basis of transmissivity and water quality. The main Edwards aquifer is that part of the confined aquifer north of the bad-water line, where transmissivity is high (typically ranging from 2×10^5 ft^2/d to 2×10^6 ft^2/d (Maclay and Small, 1984) and water quality is suitable for most uses. This central zone is informally called the freshwater aquifer in this report.

The aquifer also can be subdivided on the basis of variations in the concentration of dissolved constituents (Pearson and Rettman, 1976). In general, ground water north of the bad-water line in the main, or freshwater, aquifer contains total dissolved solid concentrations of about 250 to 400 mg/L, whereas to the south, concentrations of total dissolved solids range from 700 to as high as 8,000 mg/L. These southern waters are informally referred to

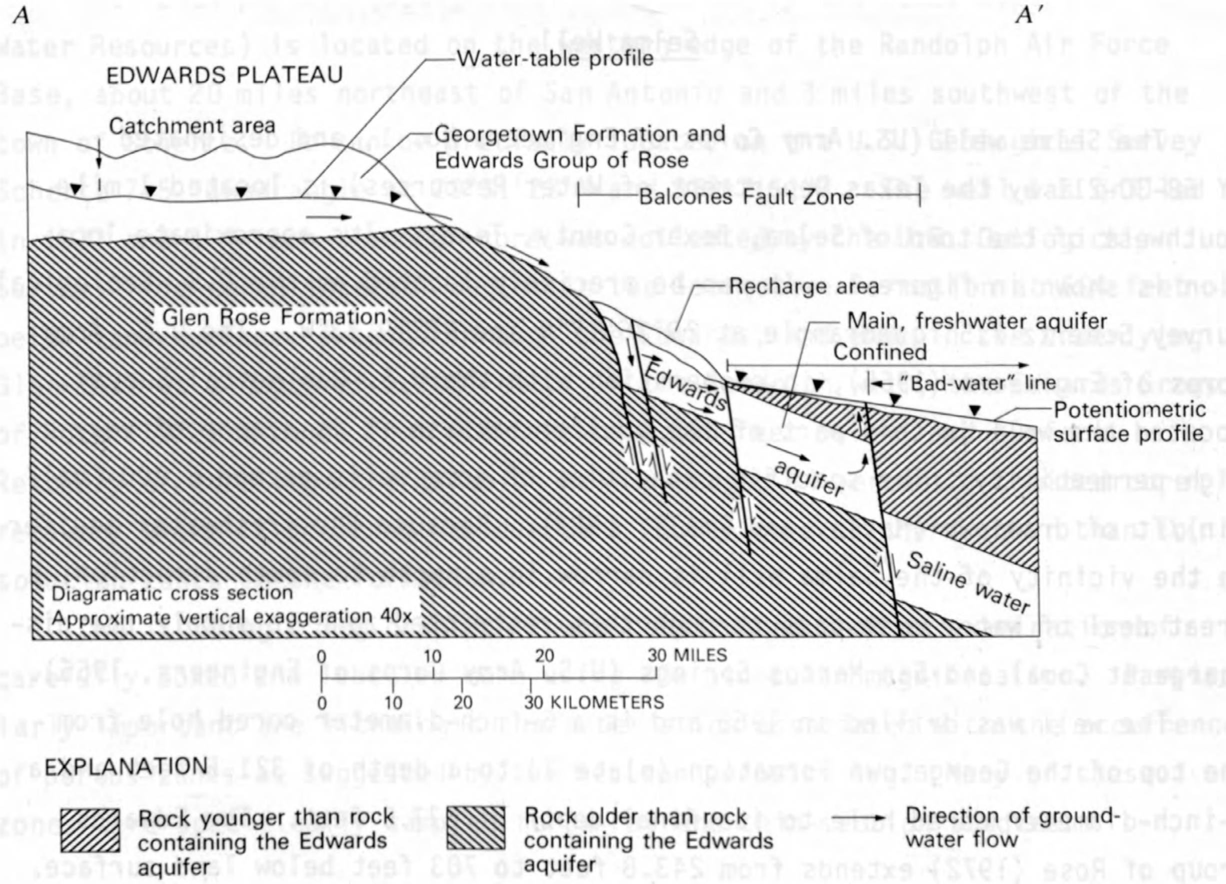


Figure 2.--Generalized hydrologic section through the Edwards aquifer showing head potential, ground-water movement, and the spatial relationship between faults and fresh and saline water. Randolph and Selma wells are in the confined aquifer. The Randolph well is south of the bad-water line and contains saline water; the Selma well is in the main aquifer and contains fresh water.

as saline in this report. This more saline ground water underlies a much larger area than the freshwater, and regional equipotential contours (Maclay and Small, 1976) indicate that it is moving generally toward the Gulf of Mexico.

DESCRIPTION OF WELLS

Selma Well

The Selma well (US. Army Corps of Engineers No. 1, and designated AY 68-30-211 by the Texas Department of Water Resources) is located 1 mile southwest of the town of Selma, Bexar County, Texas. Its approximate location is shown in figure 1. It can be precisely located on the U.S. Geological Survey Schertz 7.5' quadrangle at 29°36'17"N and 98°19'33"W. The U.S. Army Corps of Engineers (1965), in cooperation with the U.S. Geological Survey, located the well in this part of the aquifer because it is a zone of very high permeability. The specific capacities of some wells exceed 6,000 (gal/min)/ft of drawdown (Maclay and Small, 1984). Because the freshwater aquifer in the vicinity of the Selma well is narrow in a north to south direction, a great deal of water must pass through this restricted zone to supply the discharge at Comal and San Marcos Springs (U.S. Army Corps of Engineers, 1965).

The well was drilled in 1963 and is a 6-inch-diameter cored hole from the top of the Georgetown Formation (plate 1) to a depth of 321.5 feet and a 3-inch-diameter cored hole to its final depth of 777.5 feet. The Edwards Group of Rose (1972) extends from 243.8 feet to 703 feet below land surface. Core from the Edwards limestone generally is highly broken and shows evidence of rounding from rock dissolution. Core recovery averaged 65 percent and, in any given interval, ranged from 0 to 100 percent.

In their report on the well, the U.S. Army Corps of Engineers (1965) provide evidence that lack of core recovery reflects open voids in the limestone. The driller estimates that, throughout the Edwards rock section, approximately 80 percent of the available rock from cavernous zones was recovered. The zone yielding the most highly solution-rounded and broken core extends from about 486 to 598 feet below land surface. In this interval, the core recovery was very poor and the driller logged cavities up to 2 feet in diameter.

Randolph Well

The Randolph well (designated AY 68-30-807 by the Texas Department of Water Resources) is located on the western edge of the Randolph Air Force Base, about 20 miles northeast of San Antonio and 3 miles southwest of the town of Schertz. It can be precisely located on the U.S. Geological Survey Schertz 7.5' quadrangle at 29°31'27"N and 98°17'51"W. The well was drilled in 1972 and a 4-inch-diameter core was collected by the U.S. Geological Survey. The cored interval begins in the Georgetown Formation at 604 feet below land surface, extends through the Edwards, and ends in the underlying Glen Rose at a depth of 1,202 feet. In the Randolph well, the Edwards Group of Rose (1972) extends from 614 feet to 1,156 feet below land surface. Recovery of core from the Randolph well averaged 94 percent. Limited core recovery where it occurred was due to a faulty core catcher rather than to solution zones in the formation.

The lithologic log on plate 1 was constructed from an examination of carefully boxed and labelled core using 20x binocular magnification. Particularly important are lithologic characteristics associated with the occurrence of porous zones as suggested by the neutron porosity log. Many of these zones were specifically sampled for x-ray and thin-section studies.

STRATIGRAPHIC CORRELATION OF THE WELL CORES

The proximity of these two continuous cores from two distinctly different hydrogeochemical environments within the Edwards carbonate sequence provides a unique opportunity to study mineral changes that have been associated with observed changes in pore-fluid composition. To compare mineralogy, it is important to be certain that the samples selected are stratigraphically correlative. This section summarizes the techniques and assumptions used to correlate these two cores (Deike, 1984).

Sediments of the Edwards Group of Rose (1972) were deposited simultaneously at both well sites, and, therefore, many stratigraphic units are identical in both cores. These identical stratigraphic units can be used as datum horizons to correlate intervening units that have apparently been subjected to pervasive late diagenetic changes. Correlation of altered units in the aquifer zone in the Selma core with their unaltered counterparts in the Randolph core (fig. 3) was based on remnants of unaltered sedimentary textures and structures, nonsoluble mineralogy (silicified shell material and chert-bearing zones), and the order of sedimentary sequences.

The best evidence for alteration is the open and vacant zones shown on the stratigraphic log of the Selma core (fig. 3). These zones represent loss of rock mass, as cavernous porosity. The loss of rock mass has resulted from rock dissolution. Significantly, these same stratigraphic units are zones of high transmissivity in the Edwards aquifer (Maclay and others, 1981; Maclay and Small, 1984, p. 30). In the Selma well, these zones were defined where the driller reported less than 10 percent core recovery. The few core samples recovered from these zones all show the effects of rock dissolution. The caliper log (plate 1--in pocket) at these same depths indicates abundant cavernous porosity, and borehole photographs show large vugs (U.S. Army Corps of Engineers, 1965).

The framework for the detailed correlation within stratigraphic members and informal sedimentary subunits of the Edwards carbonate sequence was based on contacts between members and formations established by the stratigraphic mapping of previous workers. The general stratigraphy of the Edwards Group in the Selma core was described by the U.S. Army Corps of Engineers (1965), Rose (1972), Abbott (1973) and Maclay and Small (1976). Abbott (1973) and Maclay and Small (1976) have described the stratigraphy of the Randolph core. In addition, H. B. Kozik (Shell Oil Company, written commun., 1973) divided the Randolph-well lithologic log that he compiled and constructed (plate 1) into zones correlative with those found in the petroleum-producing Edwards carbonate rocks a short distance to the south by Kozik and Richter (1974, p. 24). Using these contacts as guidelines, individual member and informal unit boundaries were further clarified by examining continuous core from both wells and by comparing sample analyses to lithologic and geophysical logs.

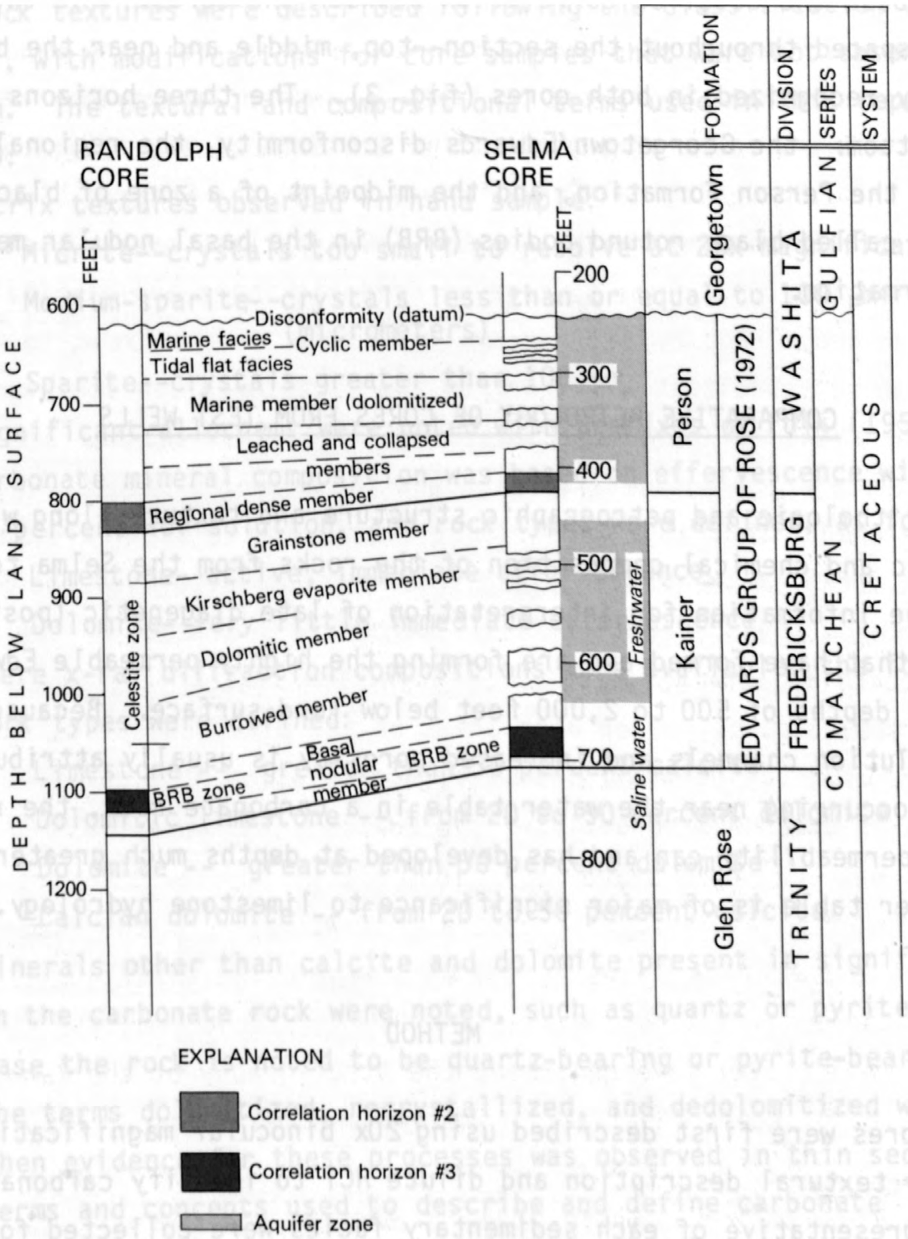


Figure 3.--Generalized stratigraphic logs of the Edwards Group continuously cored in the Randolph and Selma wells showing zones of core loss and inferred alteration in the Selma well, and major unaltered beds in both wells upon which the stratigraphic correlation was based.

Lithologic descriptions of members and formations are presented in the section on comparative petrology of the cores. Plate 1 shows the petrography, mineralogy, and selected borehole logs of the Randolph and Selma core holes.

From this stratigraphic framework, three datum horizons were chosen upon which to base the detailed correlation between the cores. The three horizons are well spaced throughout the section--top, middle and near the bottom--and are easily recognized in both cores (fig. 3). The three horizons are, from top to bottom: the Georgetown/Edwards disconformity, the regional dense member of the Person Formation, and the midpoint of a zone of black, pyrite pisoliths called black rotund bodies (BRB) in the basal nodular member of the Kainer Formation.

COMPARATIVE PETROLOGY OF CORES FROM TEST WELLS

The lithologic and petrographic structure and texture along with the mineralogic and chemical composition of the rocks from the Selma test well contain the information for interpretation of late diagenetic (post-Miocene) processes that have formed and are forming the highly permeable Edwards aquifer at depths of 500 to 2,000 feet below land surface. Because development of solution channels and increased porosity is usually attributed to processes occurring near the water table in a carbonate rock, the recognition that high permeability can and has developed at depths much greater than that of the water table is of major significance to limestone hydrology.

METHOD

The cores were first described using 20x binocular magnification for sedimentary textural description and dilute HCl to identify carbonate minerals. Samples representative of each sedimentary facies were collected for thin-section study and for x-ray diffraction analysis to determine carbonate and noncarbonate mineral composition. Particular attention was given to the sampling of sedimentary contacts where lithologies differed significantly in an effort to separate depositional textures from textures due to rock/water reactions in the aquifer. Secondary alteration features, such as recrystallization, solution pitting, and crystalline intergrowths, were specifically noted and sampled to verify stratigraphic placement.

The classification of Archie (1952) was used to estimate porosity. Carbonate-rock textures were described following the classification of Folk (1959, 1965), with modifications for core samples that were not observed in thin section. The textural and compositional terms used in this report are listed below:

1) Matrix textures observed in hand sample:
   - Micrite--crystals too small to resolve at 20x magnification
   - Medium-sparite--crystals less than or equal to 100 μm (micrometers)
   - Sparite--crystals greater than 100 μm
2) Significant allochems were noted with prefixes of Folk (1959)
3) Carbonate mineral composition was based on effervescence with 10-percent HCl solution, and rock types were defined, as follows:
   - Limestone--active, immediate effervescence
   - Dolomite--very little immediate effervescence
4) Where x-ray diffraction compositions were available, the following rock types were defined:
   - Limestone -- greater than 50 percent calcite
   - Dolomitic limestone -- from 20 to 50 percent dolomite
   - Dolomite -- greater than 50 percent dolomite
   - Calcian dolomite -- from 20 to 50 percent calcite

   Minerals other than calcite and dolomite present in significant amounts in the carbonate rock were noted, such as quartz or pyrite, in which case the rock is noted to be quartz-bearing or pyrite-bearing.
5) The terms dolomitized, recrystallized, and dedolomitized were used when evidence for these processes was observed in thin section.

For terms and concepts used to describe and define carbonate depositional environments, the reader is referred to Scholle and others (1983) and, for carbonate-rock diagenesis, to Bathurst (1975).

LITHOLOGIC AND PETROGRAPHIC COMPARISONS

The chronostratigraphic relations of the units described in the cores are shown on figure 4 along with their relations to equivalent units to the south in the deep subsurface and to the north on the Edwards Plateau. The lithologic descriptions are shown graphically on plate 1 and mineral composition of all samples is listed on table 1. Nomenclature for informal members and units containing the aquifer are defined according to Rose (1972). The U.S. Geological Survey divisions of the Edwards Limestone differ from Rose's. The Survey recognizes the Edwards Limestone as part of the Fredericksburg Group. Rose's usage of Fredericksburg and Washita Divisions (designated Group rank by the Survey) introduces another rank in stratigraphic nomenclature that differs from the North American stratigraphic code followed by the Survey. Rocks containing the Edwards aquifer are part of a thick sequence of carbonates deposited on the Comanche Shelf. Regional tectonic elements that influenced deposition over the shelf are shown in figure 5. Rocks in the Balcones Fault Zone accumulated over the San Marcos Platform behind the Stuart City Reef. Carbonate sediments of the aquifer, therefore, are a back-reef assembledge in which similar lithologies are deposited simultaneously over wide areas of the platform (Rose, 1972, fig. 33, p. 64). In general, sediments accumulating on tidal flats correlate with zones of cavernous porosity.

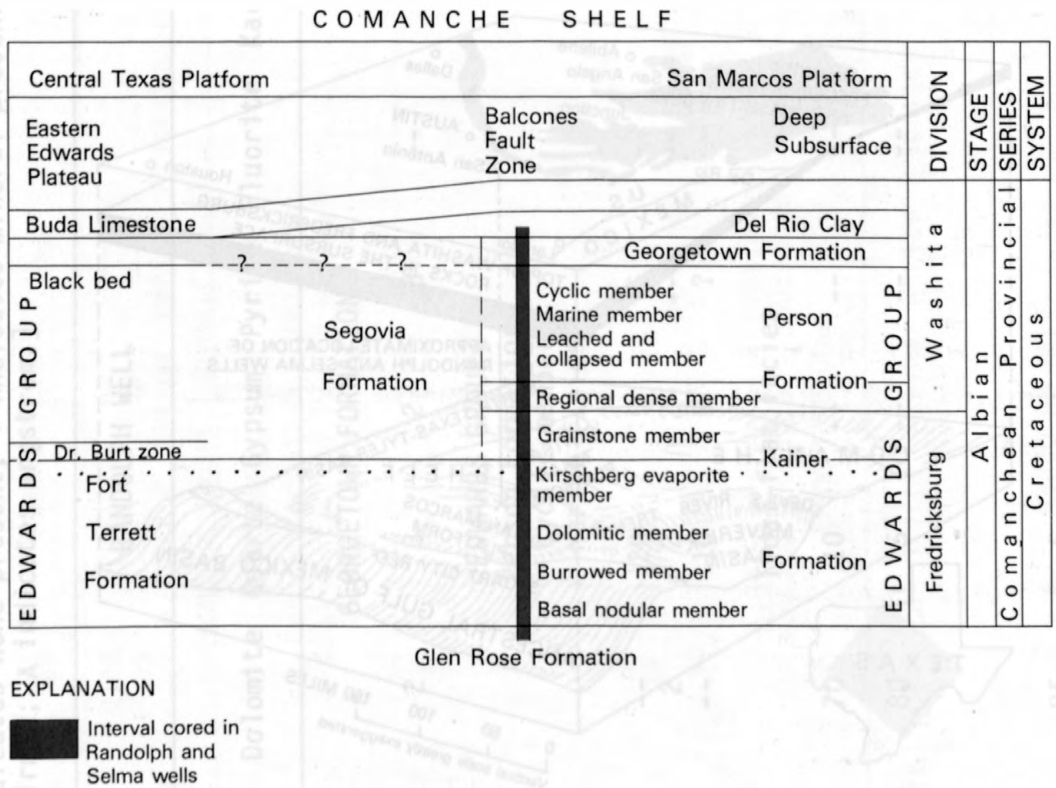


Figure 4.--Generalized stratigraphic correlation of the Edwards Group, from surface outcrops on the Edwards Plateau to subsurface cores in the the Balcones fault zone. Cored interval studied in Randolph and Selma wells is shown. The Edwards Group and associated rocks are approximately 600 feet thick and the distance from the Edwards Plateau into the subsurface is about 80 miles. Note that in the Balcones fault zone the Kainer Formation in this report has been redefined and includes the dolomitic, burrowed and basal nodular members that are recognized in the Randolph core.

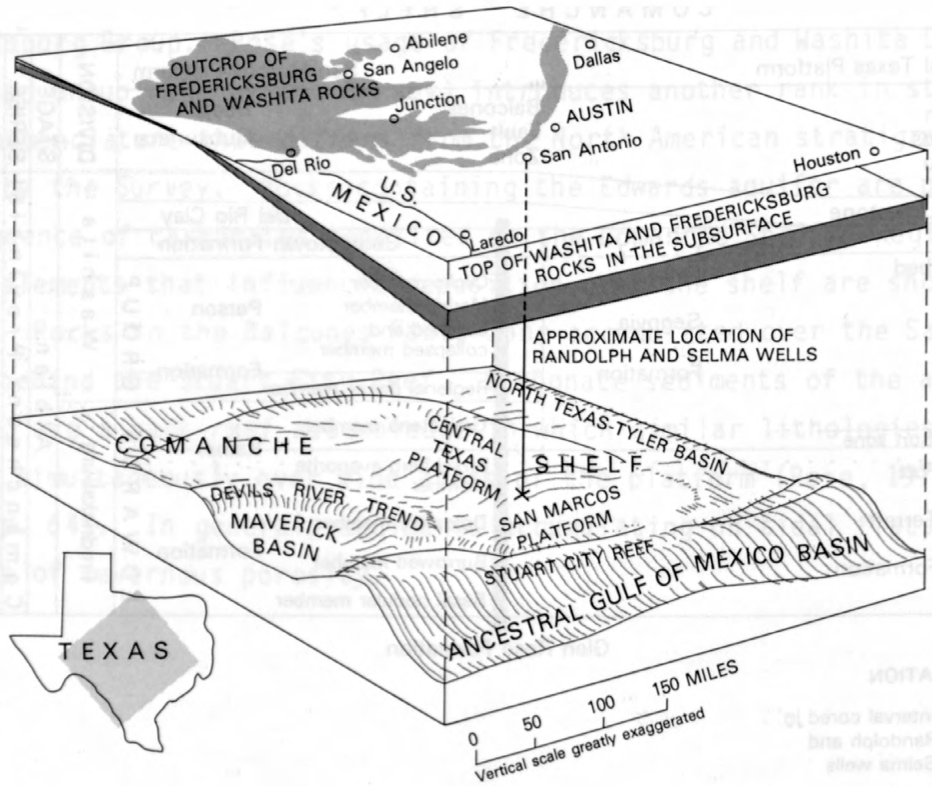


Figure 5.--Regional tectonic elements that influenced deposition of the Edwards Group during latest Early Cretaceous (late Albian) time.

Table 1.--Estimates of relative weight, in percent, of inorganic minerals in core samples from Randolph and Selma wells based on results of X-ray diffraction analyses. [Estimates are as much as ±10 percent of value indicated. A double dash indicates none present; + indicates mineral present but not quantified; ? indicates mineral not confirmed; Å indicates angstrom.]

RANDOLPH WELL

Depth, in feet[1]	Lithology	Calcite	Dolomite	Quartz	Gypsum	Pyrite	Fluorite	Kaolinite	Celestite	Other
	GEORGETOWN FORMATION									
611(606)	Biomicrite	80	2	3	2	8	--	5	--	Marcasite
	EDWARDS GROUP[2] Person Formation Cyclic member Marine facies									
626(621)	Pelmicrite	65	--	20	5	5	--	5	--	--
641(634.5)	Biopelmicrite	94	2	2	2	--	--	--	--	--
645(639.4)	Biopelsparite	85	--	10	5	?	--	--	--	--
	Tidal-flat facies									
650(658.5)	Dolomite, medium crystalline	20	70	10	--	--	--	--	--	--
665(664)	Breccia, dolomite, fine crystalline clasts cemented with calcite spar	15	80	5	--	--	--	--	--	--
668(671)	Dolomite, medium crystalline	10	85	5	--	--	--	--	--	--

Table 1 (continued)

Depth, in feet[1]	Lithology	Calcite	Dolomite	Quartz	Gypsum	Pyrite	Fluorite	Kaolinite	Celestite	Other
RANDOLPH WELL										
EDWARDS GROUP Person Formation, continued Tidal-flat facies, continued										
676.3	Intraclastic micrite with organic-rich dolomite and quartz-bearing whisps	50	40	10	--	?	--	2	--	--
Marine member										
678	Dolomite, medium crystalline with micrite laminae	5	93	2	--	--	--	--	--	--
679.5	Dolomite, medium crystalline	3	95	2	--	--	--	--	--	Organics
Marine member (dolomitized)										
689(691.5)	do	10	90	?	--	--	--	--	?	--
727(722)	Dolomite, fine crystalline	2	98	--	--	--	--	--	--	--
727.8(722.8)	do	2	98	--	--	--	--	--	--	--

Table 1 (continued)

					RANDOLPH WELL					
Depth, in feet[1]	Lithology	Calcite	Dolomite	Quartz	Gypsum	Pyrite	Fluorite	Kaolinite	Celestite	Other
					EDWARDS GROUP Person Formation, continued Leached and collapsed members Tidal-flat facies					
731.5	Dolomite, very fine crystalline, with petroliferous organic matrix and radiating masses of chalcedony	2	78	10	5	--	--	5	--	Goethite?, talc
739(740)	Dolomite, medium fine crystalline, breccia with organic-rich laminated layers	10	69	5	2	2	2	10	--	Talc?
745.5	Dolomite, coarse crystalline	20	62	5	--	--	3	10	--	--
755(758)	Dolomite, fine crystalline	1	96	3	--	--	--	--	--	--
768(771)	Limestone, medium-sparite, porous	73	20	5	--	?	?	2	--	--
					Marine facies					
772(776)	Biosparite	70	18	10	--	?	--	2	--	Marcasite
779(788)	Biosparite	73	20	5	2	--	--	--	--	--

Table 1 (continued)

RANDOLPH WELL

Depth, in feet[1]	Lithology	Calcite	Dolomite	Quartz	Gypsum	Pyrite	Fluorite	Kaolinite	Celestite	Other
	EDWARDS GROUP Person Formation, continued Regional dolosparite									
795(795.5)	Dolomite, aphanocrystalline with quartz-spar-filled vugs and chalcedony	2	78	20	--	--	--	?	--	--
	Regional dense member									
810(811)	Foram biomicrite with dolomite, very fine crystalline	45	33	5	5	5	2	5	--	Organics
811(812)	Limey micrite	45	5	25	5	10	--	10	--	Biotite?
	EDWARDS GROUP Kainer Formation Grainstone member									
837(839)	Biopelmicrite	86	--	5	2	2	?	5	--	Organics, talc
850(853)	Foram biomicrite	75	--	10	5	?	--	10	--	--
871(881)	Oolitic biosparite	100	--	--	--	--	--	--	--	Talc?

Table 1 (continued)

RANDOLPH WELL

Depth, in feet[1]	Lithology	Calcite	Dolomite	Quartz	Gypsum	Pyrite	Fluorite	Kaolinite	Celestite	Other
	EDWARDS GROUP									
	Kainer Formation									
	Kirschberg evaporite member (including the celestite zone)									
890(898.5)	Dolomite, very fine crystalline, petroliferous, whispy	5	90	5	--	--	--	--	--	--
894(904)	Biomicrite with fine crystalline dolomite	84	16	--	--	--	--	--	--	Biotite?
902(912.5)	Dolomite, very fine and fine crystalline	2	77	3	3	--	--	--	15	Talc?
915(933.5)	Milliolid and Eoradiolites biomicrite with scattered dolomite, fine-medium crystalline and celestite spar	65	15	?	3	--	--	2	15	Biotite?
922(939)	Dolomite, medium crystalline	10	80	?	--	?	?	--	10	--
928(951)	Calcic dolomite, medium crystalline	35	54	?	2	--	2	2	5	Talc?

Table 1 (continued)

RANDOLPH WELL

Depth, in feet[1]	Lithology	Calcite	Dolomite	Quartz	Gypsum	Pyrite	Fluorite	Kaolinite	Celestite	Other
	EDWARDS GROUP Kainer Formation, continued Dolomitic member									
944(962)	Dolomite, medium crystalline	2	96	--	--	--	--	2	--	Talc?
947(968.5)	Dolomitized quartz biosparite	15	63	20	--	--	--	2	1?	--
948(969.4)	Dolomitized biomicrite with hollow rhombs and celestite spar fracture filling	35	55	--	3	--	--	--	7	Apatite?
948(969.5)	Burrowed biomicrite	95	5	--	--	--	--	--	--	--
969(992.5)	Dolomite, fine crystalline	5	80	3	2	--	--	--	10	--
975(998)	Recrystallized slightly dolomitic biosparite	95	5	--	--	--	--	--	--	Biotite?
982(1005)	Dolomite, medium crystalline	5	85	2	2	--	--	1	5	Biotite
991(1015.5)	do	5	85	--	--	--	--	--	10	--
1002(1026.5)	Dolomite, fine crystalline	5	90	5	--	--	--	--	?	--
1003(1028)	Dolomite, medium crystalline	5	90	5	--	--	--	--	?	Talc?

Table 1 (continued)

RANDOLPH WELL

Depth, in feet[1]	Lithology	Calcite	Dolomite	Quartz	Gypsum	Pyrite	Fluorite	Kaolinite	Celestite	Other
	EDWARDS GROUP									
	Kainer Formation, continued									
	Dolomitic member, continued									
1003(1028)	Dolomitized biomicrite	70	20	10	--	?	?	--	--	--
1007(1031)	do	80	10	6	2	?	--	2	--	Biotite?
	Burrowed member									
1014(1039.5)	Dolomitized biomicrite with celestite-filled fossil molds	80	13	5	--	--	--	2	?	--
1019(1044.5)	Biosparite with chert nodules	60	30	8	--	--	--	2	--	--
1048(1068)	Dolomite, medium crystalline	5	85	3	--	?	--	--	5	Goethite (2)
1057(1080)	Biosparite	90	5	3	--	--	--	2	--	--
1058(1081)	Organic-rich laminated foram biomicrite	45	5	10	25	5	--	10	--	--
1073(1094.5)	Dolomitized Milliolid biosparite	75	25	?	--	--	--	--	--	--
1078(1101.5)	Dolomite, medium crystalline	25	75	5	--	--	--	--	--	--
1082(1105)	do	25	75	5	--	--	--	--	--	--

Table 1 (continued)

RANDOLPH WELL

Depth, in feet[1]	Lithology	Calcite	Dolomite	Quartz	Gypsum	Pyrite	Fluorite	Kaolinite	Celestite	Other
	EDWARDS GROUP Kainer Formation, continued Basal nodular member									
1095(1125)	Dolomitized biosparite	50	40	10	--	--	--	--	--	--
1100(1128)	do	50	40	10	--	--	--	--	--	--
1108(1134)	Dolomitized biomicrite	50	40	5	--	--	--	5	--	--
1115(1140.5)	do with Black Rotund Bodies (BRB's)	45	35	10	5	2	--	3	--	--
1126(1146.5)	Dolomite-bearing bio-micrite with BRB's	50	20	20	5	?	--	5	--	Chlorite?
1130(1158)	Dolomitized biomicrite	35	50	10	--	--	--	5	--	--
1130(1158)	Dolomitized biosparite	60	20	20	--	--	--	--	--	--
1146(1172)	Biomicrite	90	5	5	--	--	--	--	--	--
1146(1172)	Dolomitized biomicrite	20	70	8	--	--	--	2	--	--
1152(1180)	do	10	63	15	10	--	--	2	--	Biotite?

Table 1 (continued)

RANDOLPH WELL

Depth, in feet[1]	Lithology	Calcite	Dolomite	Quartz	Gypsum	Pyrite	Fluorite	Kaolinite	Celestite	Other
GLEN ROSE FORMATION										
1161.5(1189.5)	Dolomite, medium crystalline	20	65	15	--	?	--	?	--	--
1162(1190)	do	--	95	5	--	--	--	--	--	--
1166(1196)	do	2	89	4	?	--	--	5	--	--

Table 1 (continued)

SELMA WELL

Depth, in feet[1]	Lithology	Calcite	Dolomite	Quartz	Total Clay	Other
			GEORGETOWN FORMATION			
241	Biopelmicrite	83	--	6	9	10Å clay, kaolinite(?), pyrite (2)
			EDWARDS GROUP[2] Person Formation Cyclic member, marine facies			
248.7	Pelsparite recrystallized	95	--	4	--	Goethite (1)
256.5	Biosparite, recrystallized, and micrite, grumulous	100	--	+	--	--
269	Sparite, recrystallized	98	--	2	--	--
280	Micrite	98	--	2	--	--
287	Nodule, medium-sparite, recrystallized	99	1	+	--	--
			Marine member (dolomitized)			
301.8	Biosparite	100	--	--	--	--
314	Biomicrite, iron stain	98	--	2	--	--
338.9	Medium-sparite with sponge spicules	50	--	50	--	--

Table 1 (continued)

SELMA WELL

Depth, in feet[1]	Lithology	Calcite	Dolomite	Quartz	Total Clay	Other
			EDWARDS GROUP Person Formation, continued Leached and collapsed members			
357.2	Dolomite mudstone laminated with organics	2	78	21	+	Goethite(+), 10Å clay, kaolinite(?), gypsum, pyrite
361.1	Micrite, sparry with chert	60	15	25	+	
366.1	Sparite with soft, chalky calcite	90	--	10	--	
			Marine facies			
394.6	Sparite coarse crystalline, solution-pitting	90	?	10	--	
			Regional dense member			
411	Biomicrite, dense with organic whisps	94	1	4	+	Pyrite, kaolinite, gypsum

Table 1 (continued)

SELMA WELL

Depth, in feet[1]	Lithology	Calcite	Dolomite	Quartz	Total Clay	Other
	EDWARDS GROUP[2] Kainer Formation Grainstone member					
460	Sparite coarse crystalline, recrystallized, vuggy	95	5	+	--	--
474	Pellet and Milliolid biosparite	100	--	+	--	--
485.5	Microcrystalline quartz with sponge spicules	20	--	80	--	--
	Altered zone--Equivalent to Kirschberg evaporite member, dolomitic member, burrowed member					
495.4	Sparite, medium crystalline, dense	85	5	10	--	--
507.5	Sparite, dense, hard	98	?	2	--	--
522	Medium-sparite, dense with spar-filled fossil molds, spar-lined vugs	99	1	+	--	--
544	Colliform quartz with micrite and spar boxwork	23	1	76	--	--

Table 1 (continued)

SELMA WELL

Depth, in feet[1]	Lithology	Calcite	Dolomite	Quartz	Total Clay	Other
	EDWARDS GROUP[2]					
	Kainer Formation, continued					
	Altered zone--Equivalent to Kirschberg evaporite member, dolomitic member, burrowed member, continued					
547	Travertine sparite	100	--	--	--	--
563.8	Pelsparite, micritic pellets surrounded with coarse spar	93	2	5	--	
570.8	Medium-sparite, dense, aggrading recrystallization	100	--	+	--	Goethite
577.5	Medium-sparite, dense, vuggy, aggrading recrystallization	100	--	+	--	--
591	Micrite, dense with large vugs	98	1	1	+	Kaolinite (?), gypsum(?)
606	Gastropod biomicrite and biosparite	100	--	--	--	--
624	Medium-sparite, chalky,	100	--	--	--	--
642.5	Foram biomicrite with displacive and rhombic pore-fill spar	93	2	5	--	--

Table 1 (continued)

SELMA WELL

Depth, in feet[1]	Lithology	Calcite	Dolomite	Quartz	Total Clay	Other
	EDWARDS GROUP[2] Kainer Formation, continued Basal nodular member					
658	Biomicrite	90	--	10	--	Kaolinite(?)
664.5	Dolomite medium crystalline with coarse calcite and quartz spar	20	70	10	--	--
670.2	Dolomitic lime-stone, nodular, whispy	70	20	10	+	Kaolinite (?), gypsum (?)
677.4	Dolomite medium crystalline with medium-sparite	50	40	10	+	Kaolinite (?), gypsum (?)
680.2	Dolomitic lime-stone, with BRB's	69	10	7	11	Kaolinite(?), gypsum (+), pyrite (3%)
	GLEN ROSE FORMATION					
716.5	Dolomite sucrosic	5	85	10	+	Kaolinite (+)
730.5	Siltstone, gray-green	--	40	60	+	Kaolinite (+), 10Å clay
743.3	Quartz and celestite-bearing dolomite, very-fine crystalline, chalky, with organic laminae	--	50	40	--	Celestite (10), Kaolinite (?), pyrite

Table 1 (continued)

SELMA WELL

Depth, in feet[1]	Lithology	Calcite	Dolomite	Quartz	Total Clay	Other
GLEN ROSE FORMATION, continued						
754	Dolomite, fine crystalline	1	87	4	8	Kaolinite (+)
763.6	Quartz-bearing dolomite, fine crystalline, dense	--	95	5	--	Kaolinite (?)

[1] Two depths are reported for Randolph well samples: corrected (uncorrected) feet below land surface.

[2] According to Rose (1972)

Georgetown Formation

The lower Georgetown Formation is part of the Edwards aquifer and, thus, is included in the comparison. Seventeen feet of the Georgetown Formation were examined in the Randolph core and nearly 10 feet in the Selma core (plate 1). In the study area, the Georgetown Formation apparently was deposited on a submarine discontinuity that had never been exposed and eroded. In both the Randolph and Selma cores, the Georgetown consists of a nodular, mollusc biomicrite--a facies typical of subtidal deposition (Wilson, 1975; Scholle and others, 1983). The early Georgetown carbonate muds are clay-mineral free suggesting that carbonate production was taking place far from the influence of siliceous terrestrial sediments.

If the sediments now observed in the Selma core were, at one time, similar to those of the Randolph core, then the differences can be studied and related to the effects of late diagenesis. To illustrate similarities and differences, the predominant lithologies of Randolph and Selma cores from the Georgetown Formation are described below. In the Randolph core, the description is of rock above the Georgetown/Edwards contact at a depth of 626 feet; and in the Selma core, the rock described lies above the contact at a depth of 248 feet.

RANDOLPH	SELMA
609 to 626 feet below land surface	238.8 to 248 feet below land surface
Limestone, dense, blue-gray, mollusc-bearing biomicrite, nodular, wispy, locally pelleted, organic-rich, slightly dolomitized; pyrite + marcasite replace mollusc shells.	Limestone, soft, limey, light gray and tan, mollusc and foram-bearing biopelmicrite, (II, A-D), large vugs (mollusc shell molds?). Euhedral pyrite disseminated in chalky matrix; blocky calcite spar filling matrix voids and replacing molluscs; sparry rims on pellets.

The facies examined in both cores is a pelleted, mollusk-bearing biomicrite. Similar sedimentary structures are found in both cores. Pyrite is present in both, indicating common deposition in a reducing environment. In unaltered parts of the Selma core, the matrix is dense-gray micrite similar to that in the Randolph core. Fossil fragments in both cores include mollusc, large pelecypods, possibly Exogyra, and miliolids, including dictyoconus.

The major differences between Selma and Randolph lithologies are the color and texture. Local oxidation of organic matter in the matrix of Selma rocks imparts a tan color; and leaching of the dense biomicrite produces a chalky, soft, earthy texture. In the Randolph core, organic material has not been oxidized and the rock is gray. The pelleted micritic muds of the Randolph core are dense and fracture concoidally.

The effect of late-diagenetic processes on rocks of the lower Georgetown Formation in the Selma part of the study area was less severe than the effect of alteration of the underlying Edwards Group of Rose (1972). There is little core loss and no cavernous porosity in the Georgetown rocks. Iron sulfides in the Georgetown have not been oxidized, even though found in matrix that has been leached. Some pyrite persists in the soft, limey, calcite matrix of the Selma core where biomicritic matrix has been altered to a chalky texture. This association suggests leaching by pore fluids in equilibrium with pyrite. Pyrite also is present locally in nonaltered parts of the Selma core along with kaolinite and unoxidized organic matter in thin layers similar to those in the Randolph core. In Selma core samples from underlying rocks of the Edwards limestone, such layers are absent. In tan matrix zones where micrite has been leached from Georgetown rocks, pellets are preserved indicative of only partial recrystallization of the finer-grained calcite matrix. In the highly altered beds of the underlying Edwards Group farther below land surface, the calcite is completely recrystallized, and sedimentary textures have been obliterated.

Georgetown/Edwards Contact Zone

There is no evidence for subaerial exposure and associated Cretaceous weathering in the contact zone; however, lithologic differences between the cores several feet below the contact suggest late diagenetic ground-water alteration of the upper Edwards limestone in the Selma part of the study area. In the Selma core, beds several feet below the contact are oxidized and leached and contain calcite with stable carbon-isotope ratios that indicate alteration by meteoric water (see discussion later in report, and table 4). The fluids that caused alteration of these beds could not have moved downward from a Cretaceous surface exposed to the atmosphere, because lithology of the contact zone suggests that the depositional regime from the Edwards into the Georgetown was continuously marine. Edwards rock beneath the contact is a subtidal facies that shows no subaerial weathering, and the contact appears to be submarine.

In the Randolph core, Abbott (1973) finds evidence for submarine etching of upper Edwards Group rocks. Abbott locates the Georgetown/Edwards contact at 626 feet below land surface where the upper surface of the Toucasia-bearing Edwards Group of Rose (1972) is etched, presumably by submarine dissolution. The etched surface has a relief of 1/4 to 1/2 in.; pyritic Georgetown material fills the troughs.

In the Randolph and Selma cores, the Edwards rock immediately below the contact shows no effects of subaerial epigenesis or erosion. In the Randolph core, the bed beneath the contact is a calcitic, dense, burrowed biopelmicrite. The Selma core is unaltered immediately beneath the Georgetown/Edwards contact as identified by Rose (1972). The upper Edwards Group rocks in the Selma core are composed of unaltered marine facies of dense, gray, nonporous biofragmental microspar showing no evidence of karsting or extreme subaerial erosion. The contact itself is missing, but Rose (1972) recognizes a change from Georgetown to Edwards rocks at 246 feet beneath a Gryphaea-bearing bed of the Georgetown Formation. Rose's placement of the contact here has been accepted by Maclay and Small (1976).

The first intensely altered Edwards rocks of the Selma core lie beneath several feet of dense, calcitic microspar. This alteration consists of (1) oxidation of iron sulfides to iron oxyhydroxides (goethite), which impart a tan color to the rock; and (2) leaching of the dense, gray micrite to a yellowish, chalky texture. Randolph core samples from the same depth beneath the Georgetown/Edwards contact show no oxidation of iron sulfides or leaching of matrix micrite. Alteration of Selma rocks, therefore, appears to have been from beneath--a characteristic of ground-water diagenesis, rather than from above--a characteristic of subaerial erosion.

Edwards Group

Person Formation

Based on facies changes, Rose (1972) divided the Person Formation in the subsurface of south-central Texas into five informal members, which in descending order, are: the cyclic, marine, leached, collapsed, and regional dense members. These members are the result of facies changes that occurred nearly simultaneously over wide areas of the San Marcos Platform (fig. 5). Rose's interpretation of the depositional environments of the members of the Person Formation in the subsurface were applied to sequences in both the Selma and Randolph cores.

Comparison of Randolph and Selma cores suggests that permeable facies within the carbonate rock body in the study area probably provided access of dilute ground water to the developing freshwater aquifer. Laterally extensive zones of permeability in the Person Formation are present in sediments deposited over the San Marcos Platform (Rose, 1972; Kozik and Richter, 1974). South of the Balcones fault zone, these permeable rock units are of great importance as oil reservoirs. In a study of the Person complex of oil fields in Karnes County, 60 miles to the south of the study area, Kozik and Richter (1974) divided the Person Formation of Rose (1972) into five zones of porosity based on acoustic-log correlations. They were also able to show that these zones matched Rose's (1972) facies subdivisions. For the study reported on here, Kozik (Shell Oil Company, written commun., 1973) approximately located his five porosity zone boundaries on neutron-porosity and lithologic logs of the Randolph well, making it possible to correlate results of petrographic studies on the Randolph core in this study to Rose's facies and subdivisions and to the results of extensive petrographic analyses of the porosity of the Person Formation in the subsurface.

In response to changing sea levels over the San Marcos Platform, sediments of the Person Formation (extending upward from the base of the regional dense member to the Georgetown/Edwards contact inclusive) were deposited in two sedimentary cycles (fig. 3 and plate 1). Each cycle is initiated by a transgressive marine phase (deepening water) and each cycle is completed by regressive (shallowing water) intertidal and supratidal deposition (Kozik and Richter, 1974). The first cycle includes the rock sequence from the regional dense member upward to the top of the leached member. The second cycle includes the sequence upward from the marine member (dolomitized) to the middle of the cyclic member. The remaining beds of the cyclic member just below the Georgetown/Edwards contact may represent a third transgression.

Cyclic member

The cyclic member lies directly beneath the Georgetown/Edwards contact and, in the Randolph core, is composed of two facies units. The upper unit is a marine facies (the result of a possible third transgression as noted above), and the lower unit is a tidal flat facies. The marine facies also can be recognized in the Selma core, where it consists of two calcitic rock types deposited on an open shelf or bank.

The lower unit of the cyclic member is found only in the Randolph core, but is of regional significance as a petroleum reservoir. This facies unit consists of a predominantly dolomitic series of tidal-flat cycles that can be correlated with oil-producing Zone II (Kozik and Richter, 1974) in the Fashing-Person complex of oil fields 60 miles to the south of the study area (fig. 6).

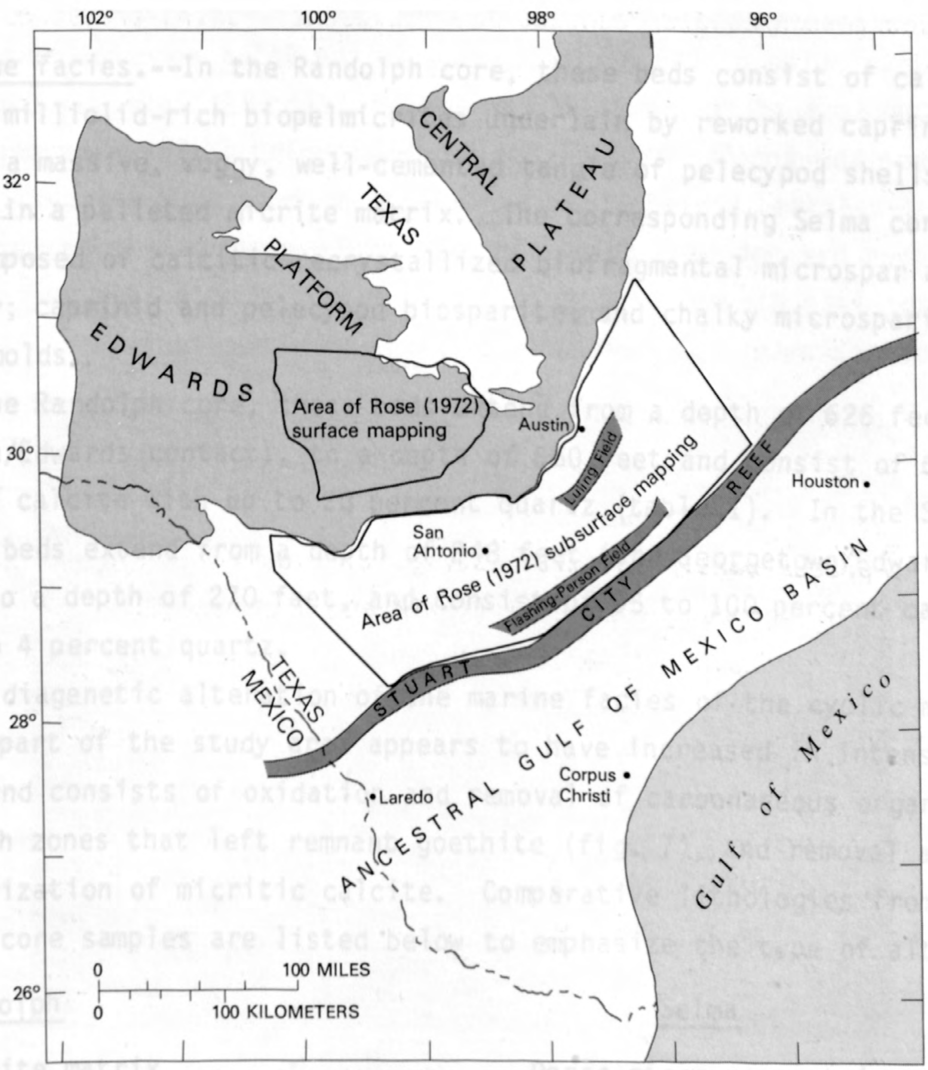


Figure 6.--Map of southern Texas showing regional depositional systems during lower Cretaceous time; the mapping areas of Rose (1972); and the locations of the Luling and Fashing-Person oil fields. Modified from Figure 1, p.4, Rose (1972).

In the Selma core, rocks equivalent to this lower dolomitic, tidal-flat facies of the cyclic member are of calcitic composition; have been highly altered; and significantly, this interval is a major unit of the confined freshwater aquifer. As shown in plate 1, the alteration has resulted in cavernous porosity at the top and bottom of the unit.

Marine facies.--In the Randolph core, these beds consist of calcitic, burrowed, milliolid-rich biopelmicrites underlain by reworked caprinid reef debris in a massive, vuggy, well-cemented tangle of pelecypod shells and caprinids in a pelleted micrite matrix. The corresponding Selma core interval is composed of calcitic recrystallized biofragmental microspar and pseudospar; caprinid and pelecypod biosparite; and chalky microsparite with caprinid molds.

In the Randolph core, these beds extend from a depth of 626 feet (the Georgetown/Edwards contact), to a depth of 650 feet and consist of 65 to 94 percent calcite with up to 20 percent quartz (table 1). In the Selma core, the beds extend from a depth of 248 feet (the Georgetown/Edwards contact) to a depth of 270 feet, and consist of 95 to 100 percent calcite with up to 4 percent quartz.

Late diagenetic alteration of the marine facies of the cyclic member in the Selma part of the study area appears to have increased in intensity downward and consists of oxidation and removal of carbonaceous organic and pyrite-rich zones that left remnant goethite (fig. 7), and removal along with recrystallization of micritic calcite. Comparative lithologies from Randolph and Selma core samples are listed below to emphasize the type of alteration.

Randolph	Selma
Dense micrite matrix	Dense microspar matrix
Caprinids contain pyrite in inner parts	Caprinids are vugs surrounded by silicified shell material and lined with goethite (FeOOH)
Few vugs	Many irregular vugs filled with soft, chalky calcite
Wispy, black organic-rich laminae just below Georgetown/Edwards contact	Fine laminae (200 µm thick) of goethite just below Georgetown/Edwards contact
No goethite	Abundant goethite

Selma core samples from 256 feet below land surface, in a vuggy caprinid zone were examined in thin section. The matrix in these samples has been recrystallized into blocky, intermeshed calcite crystals (fig. 7). Ghosts of prealteration pellets and fossil fragments are outlined as fine microspar surrounding blocky calcite spar. The spar crystals within pellets range in size from 30 to 150 micrometers across.

The alteration of the marine facies in the Selma core has resulted in only limited loss of rock mass (few zones yielding little or no core), probably because the prealteration lithology as sampled in Randolph core was composed of calcite. Samples from the Randolph core indicate that this marine facies has not been dolomitized. Samples from the Selma core contain evidence for late diagenetic alteration, but unlike dolomitic units, there is no core loss or extensive honeycomb formation in this facies.

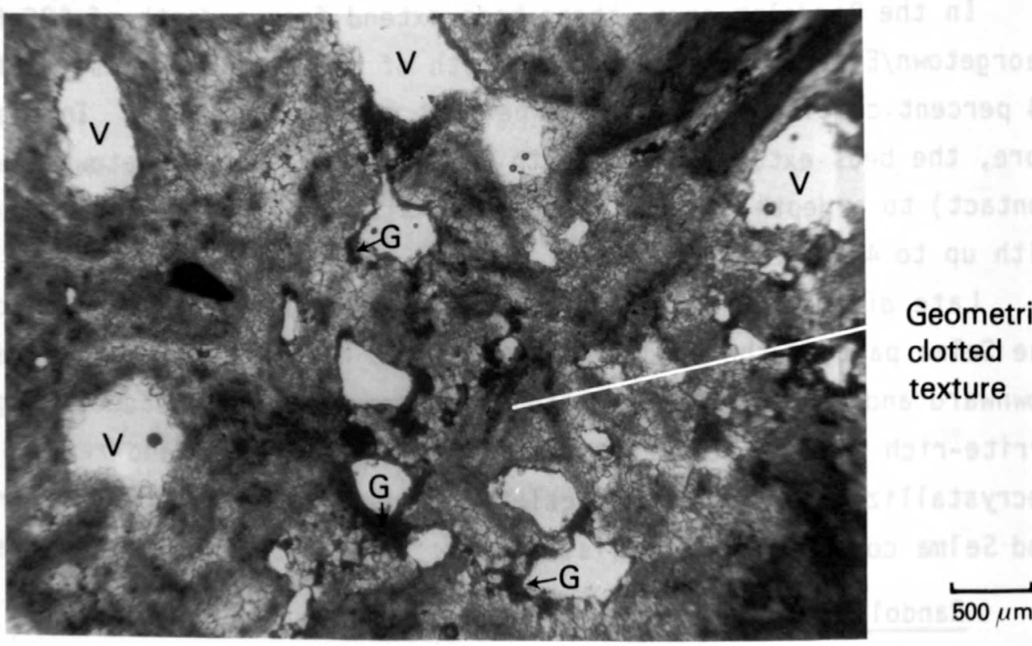


Figure 7.--Sample from Selma well, 256 feet below land surface, marine facies, Person Formation. The recrystallized calcite matrix shown in this photomicrograph is typical of white to tan, vuggy zones of intense alteration found in aquifer zones in the Selma well. The matrix is microspar to pseudospar with a geometrically clotted texture often defining rhombic areas. White areas are vugs (V) that generally do not contain sparry calcite but are lined with a reddish to opaque mineral (G), probably goethite. Vugs appear to have been produced by oxidation, then removal of either organic material or micrite without subsequent infilling of pore-filling spar. Neomorphism of matrix probably preceded formation of vugs.

For purpose of this report, the base of the marine facies of the cyclic member is an informal boundary placed where the facies changes from open marine to a series of tidal-flat cycles in the Randolph core shown on plate 1. This position also was chosen because the Randolph core rocks change to a dolomitic composition and are more permeable. The overlying marine facies is composed predominantly of calcite, whereas the tidal-flat beds are composed of sucrosic dolomite.

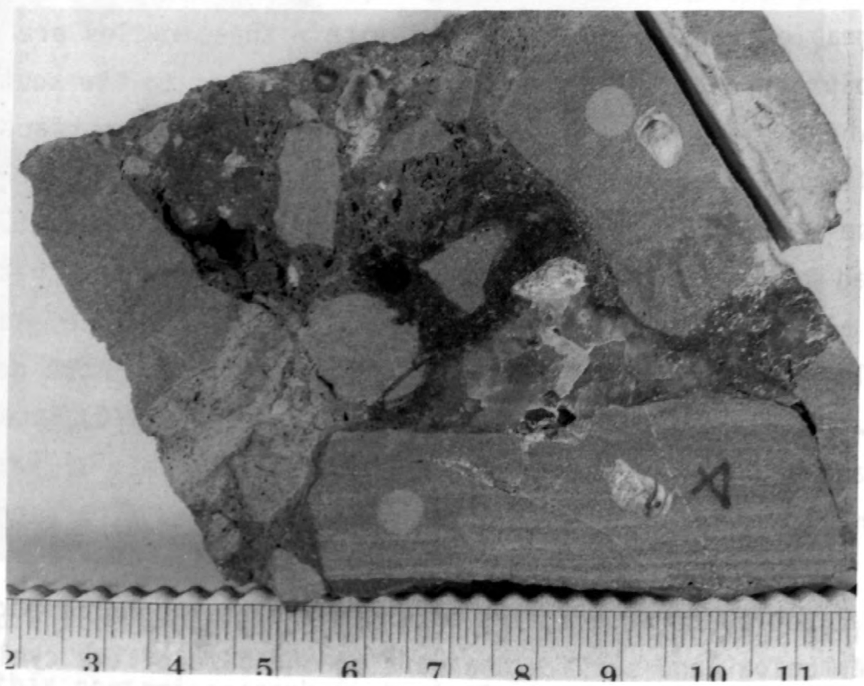
In the Selma core, the base of the marine facies is just above a zone of poor core recovery (plate 1). The depth of this zone with respect to the Georgetown/Edwards datum horizon corresponds to caprinid beds just above the tidal-flat cycle in the Randolph core.

Tidal-flat cycles.--This cyclic member was named in the subsurface by Rose (1972) who recognized cycles composed of reworked tidal-flat sediments that alternate with intertidal and undisturbed, laminated tidal-flat sediments. Permeable sucrosic dolomite beds within these cycles are recognized in the Randolph core and also are found in oil fields to the south of the study area where the Edwards Group is deeper beneath land surface. In the Person Complex of oil fields, Karnes County, Texas, core from the unit containing these beds is referred to as petroleum-producing Zone II. Zone II was described by Kozik and Richter (1974, p. 31). They note that Zone II "is composed of alternating thin intervals of dolomitic limestone and calcitic dolomite. The best development of porosity occurs in the more dolomitic intervals..." Kozik (Shell Oil Company, oral commun., 1973) located Zone II on neutron and lithologic logs of the Randolph well (plate 1) based on intervals of highly variable porosity that can be correlated with sucrosic dolomite units.

In the Randolph core, a series of three cycles extend as shown on plate 1 from 650 feet below land surface downward to the base of the cyclic member at 680 feet below land surface. The upper beds of this series of cycles are massive, sucrosic, pelleted, biofragmental dolomites overlain by a laminated organic-rich layer; and the lower beds are composed of two dolomitic breccia zones, each of which also is overlain by laminated organic-rich layers.

The upper cycle represents a period of intertidal, carbonate-bank deposition followed by deposition of algal laminations. The two lower breccias, together with overlying organic layers, are cycles that suggest two periods of brecciation as sea level deepened and the shoreline transgressed landward, reworking previous tidal-flat beds (Rose, 1972). Each brecciation was followed by a short period of stability that deposited laminations and algal crusts.

The permeable dolomite, particularly in the brecciated parts of these cycles in the Randolph core (fig. 8) are zones of alteration in the Selma core. As shown on plate 1, a major zone of cavernous porosity is present in the Selma core about 20 feet below the Edwards/Georgetown disconformity in nearly the same interval as the reworked and brecciated facies of the tidal-flat cycle recognized in the Randolph well approximately 660 feet below land surface.



Metric scale shown (cm)

Figure 8.--Handspecimen of breccia from Randolph well, 665 feet below land surface, tidal flat facies, cyclic member, Person Formation. Clasts of laminated, medium-grained dolomite "float" in extremely porous matrix composed of sucrosic dolomite and secondary calcite spar. X-ray diffraction carbonate composition of whole sample is 97 percent dolomite, 3 percent calcite.

These permeable dolomites in the cyclic member are regionally extensive. As noted, these same beds are found at least 60 miles south of the study area where this dolomitic part of the cyclic member is petroleum-producing Zone II. These cycles probably were deposited over much of the San Marcos Platform and probably were found to the north in the prealtered rocks of the early Edwards aquifer.

These permeable dolomites are a significant factor in regional layering of ground-water flow. In sucrosic dolomite samples from the cyclic member in the Randolph well, Maclay (U.S. Geological Survey, San Antonio, Texas, written commun., 1981) calculated a matrix porosity of 28 percent. Thin-section examination of core from the cyclic member in the Randolph core reveals that the high matrix porosity in these dolomitic beds reflect intergranular pores between dolomite rhombs and intragranular pores within the rhombs (fig. 9). Selective dissolution of the centers of these dolomite rhombs is common in other Edwards Group members in the Randolph core that also can be correlated with cavernous porosity in the Selma core.

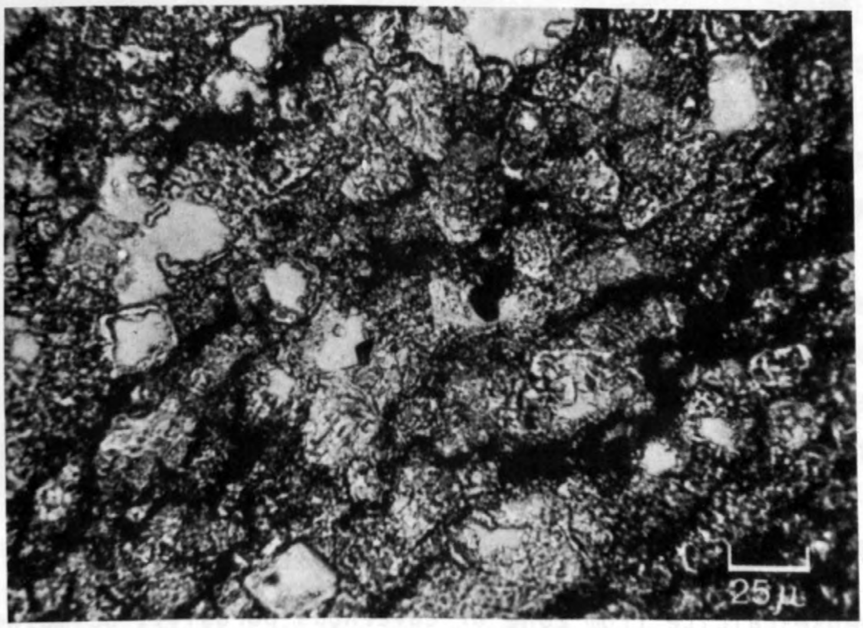


Figure 9.--Permeable dolomite and associated algal organics from Randolph well, 678 feet below land surface, tidal flat facies, cyclic member, Person Formation. Partially dissolved dolomite rhombs occur in laminae of micrite (calcite) which includes finely disseminated organic material together with quartz and kaolinite. Porosity is developed by removal of central portions of dolomite rhombs. Carbonate composition from x-ray diffraction is 57 percent calcite, 43 percent dolomite.

Laminated beds rich in carbonaceous organic matter and pyrite associated with sucrosic dolomites in these tidal-flat cycles are repeatedly correlative with zones of missing core and dolomite removal in freshwater aquifer rocks. These organic-rich zones produce a pronounced natural-gamma-log response in the Randolph well that is missing in gamma logs from the Selma well. Rose (1972) notes that the cyclic member ordinarily cannot be detected from core logs in the Balcones fault zone because of secondary alteration. Samples of the Selma core recovered from these intensely altered zones (fig. 10) are fragments lacking organic matter and composed entirely of calcite. The calcite is present as dense micrite and microspar matrix containing small rhombic pores filled with bladed spar suggestive of removal of dolomite and replacement by calcite.

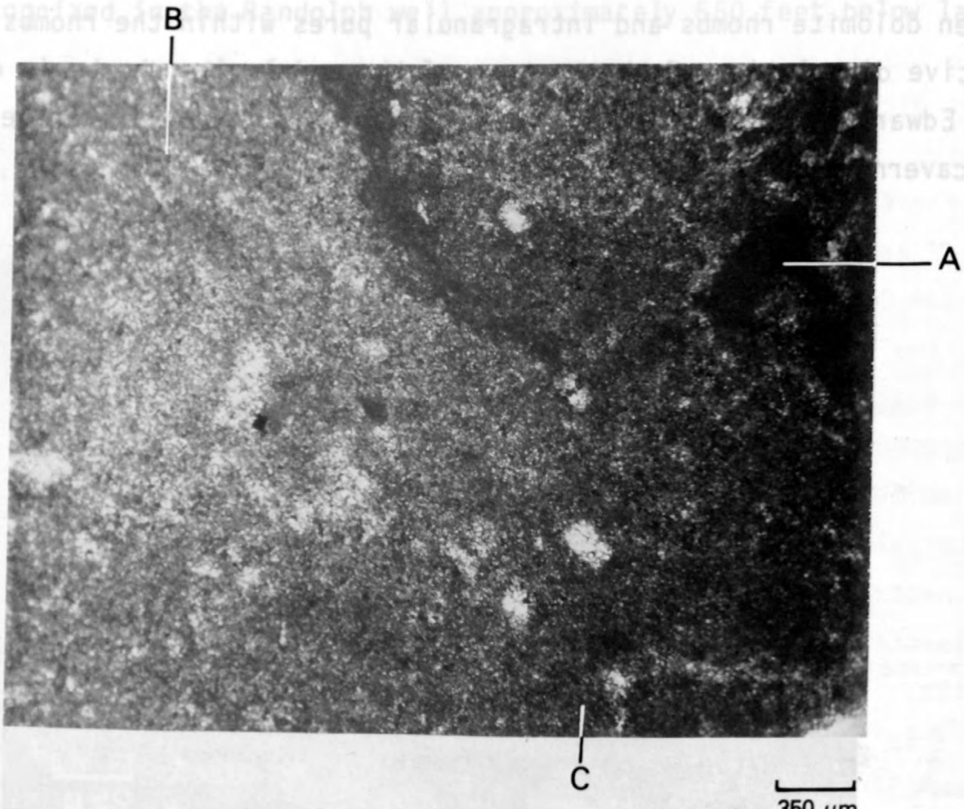


Figure 10.--Dense calcite from zone of cavernous porosity, Selma well, 287 feet below land surface, cyclic member, Person Formation. Dense micrite (A) (grains averaging 2 micrometers) along with densely packed neomorphic, or newly recrystallized grains of microspar (B) (5 to ~30 micrometers) are typical in zones of cavernous porosity. Note also occasional rhombic-shaped pores (C) where pore-filling calcite has filled molds possibly left as dolomite rhombs dissolved. X-ray diffraction composition of sample is 100 percent calcite.

Marine member

In the Selma well, much of the interval corresponding to this member is cavernous pore space, and the caliper log (plate 1) indicates full extension of the calipers. In the Randolph core, this member is composed of permeable dolomite. By contrast, the Selma core is composed of calcite and many samples are coated with travertine, indicating that it was severely altered by late diagenetic processes. This is strong evidence that prior to alteration, these Selma beds were composed of permeable dolomite.

High-permeability zones in the marine member are present throughout the San Marcos Platform, and dolomitization of the member is believed to be widespread. Rose (1972) found that the marine member deposited on the San Marcos Platform (which includes the study area) has undergone massive dolomitization.

In the Randolph core, the marine member is a complex assemblege of dolomitized and eroded tidal-flat deposits and very shallow-water intertidal to subtidal beds. The upper half of the marine member is characterized by dolomitized and locally silicified, laminated algal beds, erosional contacts, and intraclastic, earthy, chalky fossiliferous limestones. The lower half of the member is chert-nodule-bearing sucrosic-to-marly, dolomitized caprinid biosparites and recrystallized foram biomicrites.

Subaerial exposure during deposition of the marine member in the study area did not result in significant loss of rock section. Thickness of the member in both wells is nearly identical and close to that found on the rest of the Platform (40 to 60 feet, according to Rose (1972)). Correlation of the marine member in Randolph and Selma cores was obtained on the basis of chert layers and beds containing silicified _Toucasia_ valves. These siliceous horizons are found in similar vertical positions in the section from both wells.

In comparing the Randolph marine-member sequence with the Selma core sequence, the following differences were noted:

1. Randolph-core lithologies, such as organic layers, erosional contact zones, sucrosic dolomites, stylolites, breccia zones, and most micritic dolomite zones, are absent from the Selma core.

2. Lithologies remaining in the Selma core include marly (soft, chalky) limestones, calcitic biosparites and biomicrites, dense, horizontally

laminated and dolomite-streaked micrites, chert nodules, and silicified *Toucasia* shell material in calcitic pelleted micrite matrix.

3. The rest of the Selma lithologies are coarsely recrystallized calcite and travertine-like layered precipitates with a smooth iron-stained outer surface that presumably was exposed in a fluid-filled open cavity. There are no rocks like these in the Randolph core.

Erosional contacts and brecciated horizons increase in number at the base of the marine member. These sedimentary structures indicate longer periods of subaerial exposure and erosion, which, in turn, suggest the down-core change in depositional regime toward the restricted-circulation and evaporite-mineral-precipitating conditions of the underlying leached member defined by Rose (1972).

Leached and collapsed members

Large differences in permeability and mineral composition characterize the facies in these two members in the Randolph core. These differences can be related to aquifer units in the Selma core. These members extend from the base of the marine member to the top of the regional dense member. In the Randolph part of the study area, rocks equivalent to the leached and collapsed members of Rose (1972) extend from 728 feet to 810 feet below land surface (plate 1). Major parts of both of these members accumulated on a broad topographic surface of low relief, usually under hypersaline conditions because of restricted circulation over the entire Commanche Shelf (fig. 5). These two members in the Randolph core contain four facies. These facies differ in depositional setting; this, in turn, has caused differences in permeability and mineral composition. The facies units are, in descending order: tidal-flat facies, with several intervening interclastic breccia layers; open marine-shelf biomicrite facies; regional permeable dolomicrosparite; and dolomitized intertidal marine facies.

Although altered, the sequence of facies units in the leached and collapsed members in the Selma core resembles the sequence of facies in the Randolph core (plate 1). The stratigraphically equivalent Selma-core interval extends from 347.3 feet to 404 feet below land surface. The Selma sequence suggests three facies. In descending order, they are: tidal flat, intertidal to subtidal, and a zone that is intensely altered beyond recognition. Tidal-flat beds in the Selma core can be recognized by the rare occurrences of dolomitized carbonate mud in fine horizontal laminae that suggest settle-out deposition by tidal sheets of water on a surface of very low relief (Shinn, 1983). Dolomitization associated with the low relief of an upper tidal flat may have resulted from subsequent exposure to evaporation and concentration of pore fluids. Underlying this tidal flat is an intertidal and subtidal facies that was deposited under subaqueous conditions. The criteria used to distinquish the intertidal or subtidal facies in the Selma core are the presence of burrowing (or honeycombed) zones (Rose, 1972) reworked by a prolific benthic community; the presence of the oyster, Gryphaea (Moore and others, 1952); and the presence of chert nodules that commonly form as a result of solution of sponge spicules in subtidal-shelf environments.

Generalized lithologic descriptions of these facies in Randolph and Selma core are listed in table 1a below:

Table 1a.--Lithology of the Person Formation, leached and collapsed members

Randolph core		Selma core	
Depth, in feet	Lithology	Depth, in feet	Lithology
	Tidal-flat facies		Tidal-flat facies
728-770	Chalky limestone, fossil-poor micrite, and biomicrite; erosional contacts upon which are deposited clastic layers of sucrosic dolomite clasts in organic-rich dolomite and calcite spar matrix; laminated organic-rich sucrosic dolomite; dolomitic burrowed micrite; and dolomitized megashell biosparite	347.3-350.5	Limestone, sparse micrite, hard, gray to black, non-porous and dense, some grainy interbeds
		350.5-357.2	Limestone, very argillaceous and marly, brown-gray; dolomicrite, fine horizontal laminations. 7 FEET MISSING
		357.2-359.2	Dolomitic biomicrite, dense, banded, core whole

Table 1a.--Lithology of the Person Formation, leached and collapsed members, continued.

Randolph core		Selma core	
Depth, in feet	Lithology	Depth, in feet	Lithology
	Open marine-shelf facies		Intertidal to subtidal facies
770-782	Gastropod, *Toucasia* and miliolid-bearing recrystalized biomicrosparite (80-90% calcite)	359.2-379.4	Limestone, chalky, soft, light gray; at 366.1, bands of black chert and cobbles, clay fillings, 5.6 FEET MISSING; at 375.6, 4.2 FEET MISSING
	Regional dolosparite	379.4-386.2	Limestone, white, limey and soft, to gray, dense hard micrite, burrowed, vuggy, argillaceous lenses, pelecypods; at 382, vugs filled with porous lime; at 386, contact with yellow, silty layer
782-797	Dolomite, medium-fine grained, very porous; quartz spar common toward base	386.2-387.5	Dolomitic biomicrite, hard horizontal partings
	Dolomitized intertidal facies	387.5-394.6	Limestone, honeycombed (burrowed) vuggy, *Gryphaea*; at 387.5, 3 FEET MISSING; at 392.6, recrystallized hard, argillaceous,
797-810	Dolomitic micrite, wispy, nodular, interclastic, with sparry rims around clasts		Intensely altered zone
		394.6-403	Biomicrite, dense; solution pitting common; at 394.6, 2 FEET MISSING; at 397.4, dolomitic, 4 FEET MISSING
		403-404	Micrite, dense, solution pitting intense, pieces coated with travertine, vuggy, only pieces left

There are many aquifer units within the leached and collapsed member, and in the Selma core, the rock from these units invariably contains evidence of dissolution, reprecipitation, and cavernous porosity. Roughly 45 percent of the Selma core is missing in the interval equivalent to the leached and collapsed members, indicating intense late-diagenetic dissolution in the Selma part of the study area. All Selma-core remnants from zones of core loss show petrographic evidence for neomorphic mineral changes and/or dissolution. Minerals common in the Randolph core, such as dolomite, sulfates, sulfides and fluorite, are mostly gone, and calcite textures have been altered, leaving a dense, hard matrix composed of microsparite and pseudospar. All organic material and iron-bearing minerals are oxidized, and the rock color is reddish tan. Silicified rudistid shell and, as noted above, fine-grained, dense, laminated beds from tidal-flat sequences have been preserved, whereas units equivalent to the brecciated zones from tidal-flat cycles in the Randolph core are missing.

The caliper log of the Selma well (fig. 3 and plate 1) confirms that zones of missing (unrecovered) core are the result of cavernous porosity. Further, the cavernous porosity must be interconnected, because rocks equivalent to these members in the Selma part of the study area constitute a major subdivision of the freshwater Edwards aquifer (Maclay and Small, 1976). These observations suggest that much of the rock composing these members was dissolved and removed during late-diagenetic reactions, and that this process ultimately led to formation of this part of the aquifer.

The regional permeability of prealtered beds in these members was a significant factor that led to the development of aquifer units. Like overlying members of the Person Formation of Rose (1972), the leached member contains units that are regionally permeable throughout the San Marcos Platform. In the study area, thin sections from the leached member indicate abundant intergranular and intragranular porosity. The collapsed member defined by Rose (1972) also is a permeable unit. On the San Marcos Platform the collapsed member is characterized by a series of collapse breccias containing fragments of laminated, dolomitized stromatolitic crusts (Rose, 1972). The porosity was developed by the leaching of allochems and gypsum as occurred in the leached member.

Comparison of neutron and lithologic logs of the leached and collapsed members of both wells (plate 1) show a precise correspondence between zones of high porosity in the Randolph core, and altered zones in the Selma core from which there was little core recovered. Three of these high porosity zones are located in dolomitic rocks of the tidal-flat facies in the upper half of the leached and collapsed members. These are separated from the lower two zones of high porosity by a unit with lower porosity that is calcitic in composition. This unit is an open shelf, subtidal facies that has not been dolomitized. Below this, the lower two zones of high porosity in the Randolph well are in dolomitic rocks. These zones in the Randolph well correspond to high-porosity zones in the Selma well defined by low-core recovery. On the Selma-well lithologic and neutron logs (plate 1), the upper zone of high porosity in the upper part of the leached and collapsed members is a zone in which 7 feet of core is missing. Below this, as in the Randolph well, there is a section of lower porosity, and no core is missing. The base of the collapsed member in the Selma well shows two more neutron-log highs, and a zone of low core recovery is associated with each.

Based on the correlation from neutron and lithologic logs, stratigraphically equivalent samples can be selected from Randolph zones of high porosity and Selma core zones of alteration. A comparison of these samples shows that before alteration the Selma core was composed of organic-rich, dolomitized and permeable tidal-flat beds. An excellent example of the effect of alteration is a comparison of the upper part of the leached member in the Selma core with the uppermost zone of high porosity on the Randolph-well neutron log (plate 1) from 731.5 to 734 feet below land surface. In the Randolph core, this zone is organic-rich and dolomitic. The corresponding section of the Selma core is located just beneath the top of the leached and collapsed members and is characterized by cavernous porosity and limited core recovery.

The dolomitic bed in the Randolph core in this zone is 2.5 ft thick and contains a permeable tidal-flat sedimentary sequence composed of reactive minerals. The lower half of the bed is vuggy due to molds of both clasts and fossils, indicating a clastic predolomitization limestone precursor. Such clastic beds suggest shoal sediments that often underlie a tidal-flat sequence. The upper half of the dolomite bed contains black-to-brown, organic-rich laminae that resemble algal mats. The organic-rich laminae increase in abundance and their composition becomes petroliferous toward the top of the bed. The top of the zone consists of black, organic-rich laminae broken and reworked in a sucrosic dolomite matrix. In the reworked zone, gypsum and radiating masses of length-slow chalcedony were precipitated from pore fluids presumably concentrated by evaporation from the exposed surface of the tidal flat (Folk and Pittman, 1971). A thin section cut in the reworked zone at the top shows the main mass of the zone is composed of anhedral to euhedral dolomite crystals roughly 15 μm in longest dimension. The dolomite grains are homogeneously surrounded with black organic material. This entire sequence is missing from the Selma core.

Many minerals are associated with organic material in these zones in the Randolph core. These minerals are missing in corresponding Selma core zones which suggests that they are prime candidates for reaction with meteoric pore fluids (Pearson and Rettman, 1976). A few feet farther down in the Randolph core (740 feet below land surface) is an organic-rich tidal flat unit that is not found in the Selma core. This unit is the next lowest zone of high porosity on the neutron log (Plate 1), and consists of tidal-flat sediments reworked and overlain by a massive, very permeable, sucrosic dolomite. The tidal flat sediments are composed of petroliferous, pyrite-bearing organic layers, finely laminated with calcite and fluorite (fig. 11). In these laminae, the fluorite (visible as isotropic dark patches under crossed nicols) is replacing calcite. The replacement of calcite or aragonite by fluorite indicates the presence in the early history of this rock of pore fluids enriched in fluoride (Jones and others, 1977). There is no fluorite in corresponding parts of the Selma core, and goethite ($FeOOH$) rather than pyrite is the iron species found in Selma core samples.

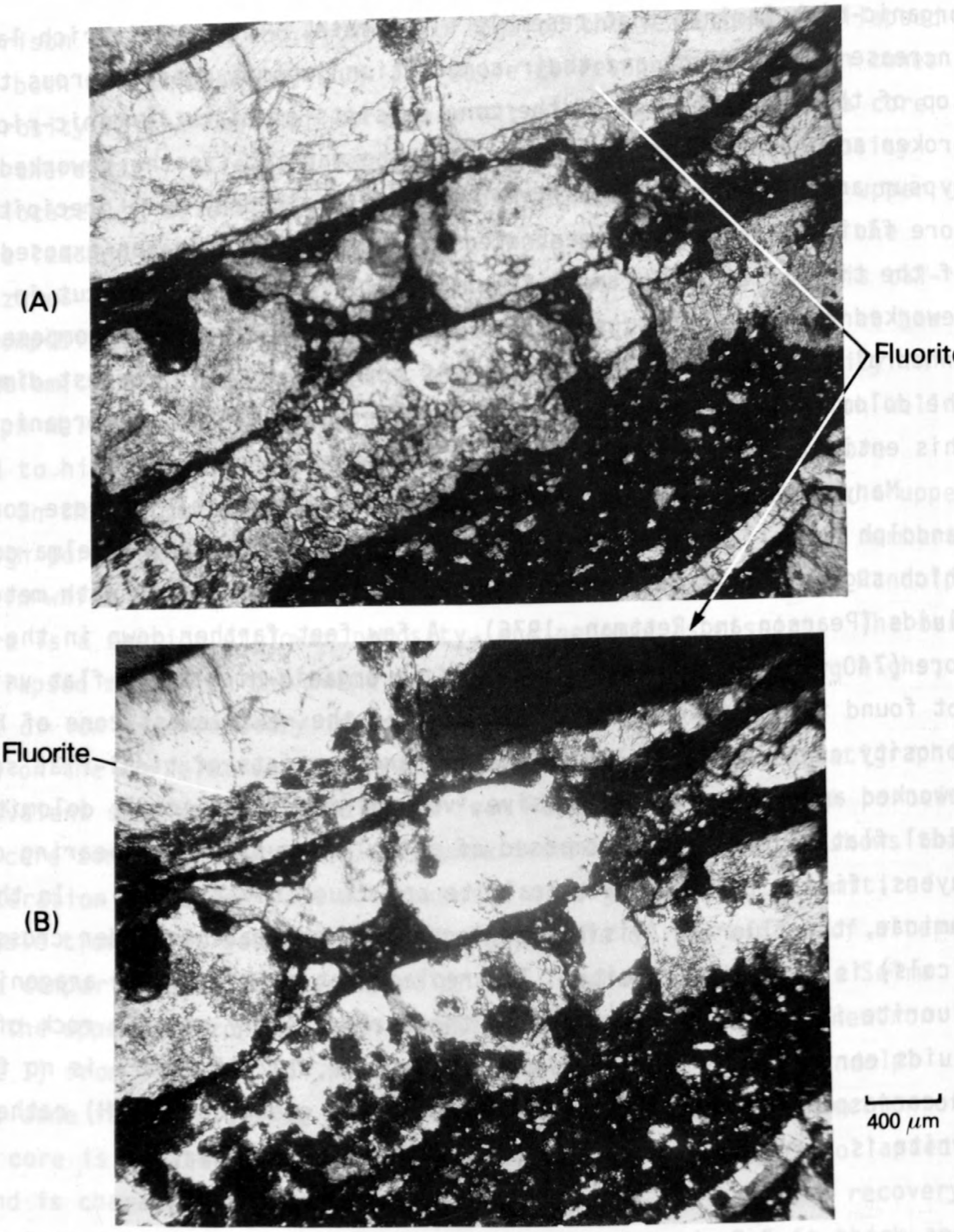


Figure 11.--Sample from Randolph well, 740 feet below land surface, showing secondary fluorite in the leached and collapsed members, Person Formation. (11A) In plane polarized light, a petroliferous, pyrite-rich organic layer contains several laminae of calcite partially replaced with fluorite (CaF_2). (11B) The isotropic fluorite appears black when the same area is shown with cross polarized light. The fluorite follows cleavage planes in the calcite, and, therefore, it may be pseudomorphic. This mineral assembledge is not found in the leached and collapsed members sampled in the Selma core.

Permeable rocks continue beneath the tidal-flat facies. The laminated fluorite-bearing beds grade downward into an organic-rich layer in which burrows are filled with very fine permeable dolomite. Shortly after the burrowed muds were exposed, they apparently were rapidly covered by an influx of fine carbonate sand that filled the burrows and that was subsequently dolomitized. The texture of the burrow filling is sucrosic, with permeability due to partial dissolution of many dolomite rhombs (fig. 12). Again, as in the overlying facies, the net result of these depositional and diagenetic processes was the association of permeable rocks composed of soluble minerals, including dolomite, pyrite, fluorite, and organic matter.

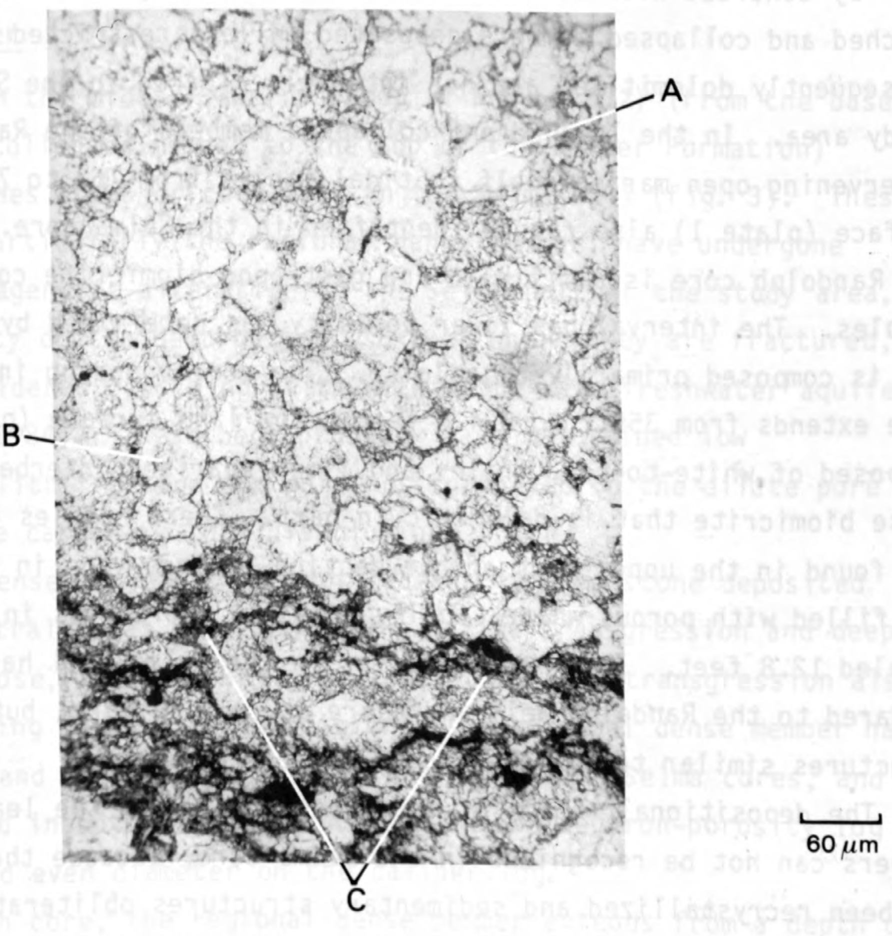


Figure 12.--Sample from Randolph well, 740 feet below land surface, leached and collapsed members, Person Formation. Dolomite rhombs with dissolved (A) and granular (B) centers provide permeability, and occur along with organic layers (C) containing pyrite. Oxidation of organic matter and pyrite during alteration lowers pH of the pore fluid and provides conditions for dolomite dissolution.

The lithologies found in the next-lower permeable zone in the Randolph core present just above a depth of 760 feet also are missing from the Selma core. In the Randolph core, this zone grades downward from a very porous, chalky dolomite, to an extremely porous and permeable dolomitic microsparite, and then to a burrowed zone composed of dolomitized pelecypod-bearing biomicrite. This burrowed zone is almost pure dolomite, and is marly and composed of friable, loosely packed sucrosic dolomite grains with very high permeability. Recovery of the Selma core from the equivalent interval is very poor and samples consist of dominantly chalk, calcarenite, and microsparite--all of calcitic composition.

By contrast with dolomitic tidal-flat facies, calcitic sediments of the leached and collapsed members deposited in less restricted settings and not subsequently dolomitized are not intensely altered in the Selma part of the study area. In the leached and collapsed members of the Randolph core, an intervening open marine-shelf subtidal facies from 762 to 786 feet below land surface (plate 1) also can be identified in the Selma core. This facies in the Randolph core is a miliolid and gastropod biomicrite containing chert nodules. The interval has lower porosity, as determined by the neutron log, and is composed primarily of calcite. The corresponding interval in the Selma core extends from 359.2 to 394.6 feet below land surface (plate 1) and is composed of white-to-tan, grainy and limey sparites interbedded with thin, dense biomicrite that is dolomitic in part. Chert nodules and clay fillings are found in the upper part of the section. Large vugs in the biomicrite are filled with porous white, chalky calcite. Core loss in this facies totaled 12.8 feet. This marine facies in the Selma well has been altered compared to the Randolph well and there is core missing, but sedimentary structures similar to Randolph rocks can be recognized.

The depositional regime of the lowest facies in the leached and collapsed members can not be recognized in the Selma core, because the remaining rock has been recrystallized and sedimentary structures obliterated. This altered zone, however, is in nearly the same stratigraphic position as the very permeable regional dolomitic facies at the base of the collapsed member in the Randolph core, as discussed below.

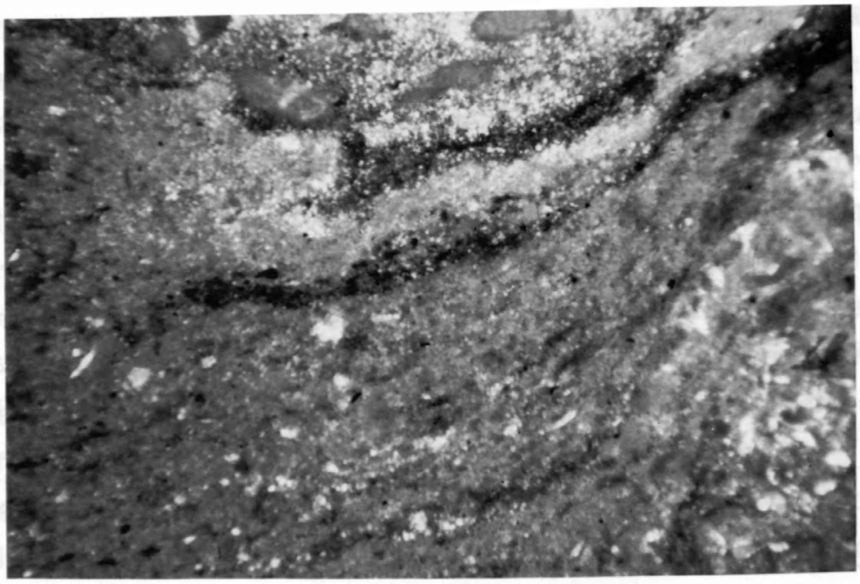
The lowest major solution zone in the Selma core is stratigraphically equivalent to the regional dolosparite which is the most consistent oil-producing bed in the subsurface. The solution zone is located from 394.6 to 404 feet below land surface, just above the regional dense member. The caliper log shows that the Selma hole here exceeds 16 inches (plate 1) and 6 of 10 feet of core are missing. Pieces recovered are solution pitted, and many are coated with travertine. Eroded vugs are common, and, occasionally, the matrix has been coarsely recrystallized. This zone in the Randolph core contains the two lowest very permeable units, as indicated by the neutron log (plate 1).

Regional dense member

Marine units in the middle Edwards Group of Rose (1972) (from the base of the leached and collapsed member to the top of the Kainer Formation) separate the two zones of major core loss in the Selma well (fig. 3). These open-marine beds, particularly the regional dense member, have undergone relatively minor diagenetic alteration in the Selma part of the study area, and show low porosity on the neutron log. Except where they are fractured, these beds are considered confining units within the main freshwater aquifer (Maclay and Small, 1984). These beds probably have maintained low permeability since lithification and were not subjected to the dilute pore fluids that initiate carbonate rock dissolution.

The regional dense member is an argillaceous lime mudstone deposited over the entire Central Texas Platform during marine transgression and deep-water conditions (Rose, 1972 and Bay, 1977, p. 20). This transgression also signaled the beginning of Washita deposition. The regional dense member has the same lithology and mineral assemblage in Randolph and Selma cores, and it is easily identified in both cores as a trough in the neutron-porosity log and by its small and even diameter on the caliper log.

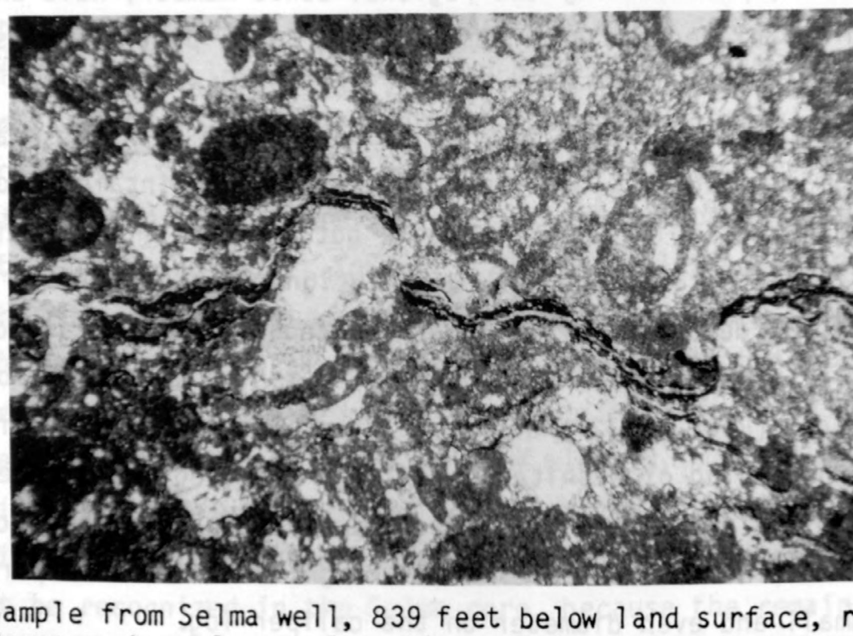
In the Randolph core, the regional dense member extends from a depth of 810 to 836 feet (plate 1); it is a massive, medium-gray, wispy micrite with low porosity, interbedded in the upper half with dolomitic microspar and relatively nonporous limey biomicrite (fig. 13). In the lower half, massive intraclastic micrite layers grade into a medium- to fine-grained foram biosparmicrite (fig. 14).



400 μm

1 cm = 400 μm

Figure 13.--Sample from Randolph well, 811 feet below land surface, regional dense member, Person Formation shows a massive predominantly calcitic micrite of densely packed grains (less than 4 micrometers) with wisps of organic matter containing kaolinite and quartz.



400 μm

1 cm= 400μm

Figure 14.--Sample from Selma well, 839 feet below land surface, regional dense member, Person Formation. This unaltered member is easily recognized in the Randolph well (fig. 11). The fragmental micrite to microspar (2 to 10 micrometers) matrix is texturally different than dedolomite, and soluble minerals, gypsum, kaolinite and pyrite are concentrated along the stylolite. This member is preserved in the Selma core because it is composed of dense, relatively impermeable calcite.

In the Selma well, the regional dense member extends from a depth of 404 to 427 feet (plate 1). The core recovery is complete, and evidence for solution activity and oxidation is lacking. Kaolinite and sulfide-bearing organic stringers are preserved, as are euhedral pyrite grains scattered throughout very fine-grained micrite that show no signs of late-stage neomorphism.

Kainer Formation

The Kainer Formation was the name proposed by Rose (1972) for the "Edwards B-zone" in the Fashing-Person trend of oil fields (fig. 6) in the subsurface, 60 miles south of the study area. In the subsurface, the Kainer extends from the base of the overlying regional dense member of the Person Formation to the contact with the underlying Glen Rose Formation. In the type section, Rose (1972, pl. 3) divided the Kainer Formation, in descending order, into the grainstone member and dolomitic member. Using the Selma core, Rose (1972, pl. 3) extended both members into the Balcones fault zone. In the fault zone, Rose implies that the Kirschberg evaporite unit is located in the upper part of the dolomitic member.

Examination of the Randolph core has shown that, in this part of the Balcones fault zone, Rose's dolomitic member of the Kainer Formation is equivalent in descending order to the Kirschberg evaporite, dolomitic, burrowed, and basal nodular members of the Fort Terrett Formation of the Edwards Group of Rose (1972) in the eastern part of the Edwards Plateau. Small and Maclay (1982) recognized the Kirschberg evaporite and basal nodular members in the Randolph core, but left the remainder of the dolomitic member undivided. Except for the Kirschberg evaporite unit, Rose probably could not recognize his members of the Fort Terrett Formation within the undivided dolomitic member of the Kainer Formation in the study area, because the lower part of the Kainer is intensely altered in the Selma core. However, the Randolph core drilled nearby after Rose completed his work clearly shows that the members of the Fort Terrett Formation can be recognized in the Kainer Formation of the study area. Therefore, in the Randolph core, the Kainer Formation is divided, in descending order, into five members: the grainstone member; the Kirschberg evaporite member; the dolomitic member; the burrowed member; and the basal nodular member, which includes an important mapping unit containing aggregates of pyrite that are well known to subsurface geologists as the black rotund bodies, or BRB, zone (Small and Maclay, 1982). The boundaries of these members are shown on the lithologic log of the Randolph core on plate 1.

Recognition of these members in the Randolph core requires the following changes in the Kainer Formation in the study area (and possibly throughout the Balcones fault zone):

1) The Kirschberg evaporite is assigned member rank in the Kainer Formation, because the upper and lower boundaries of Rose's Kirschberg evaporite unit (emended)[1] can be recognized in the Randolph core.

2) The dolomitic member of the Kainer Formation is stratigraphically restricted to beds equivalent to the dolomitic member of the Fort Terrett Formation.

3) The burrowed and basal nodular members of the Fort Terrett Formation are extended into the subsurface of the study area as the two lower members of the Kainer Formation.

Grainstone member

In the Randolph and Selma cores, the grainstone member is a complete and preserved zone 54 feet and 57 feet thick, respectively. In the upper part, it consists of a limey, chalky, foram and gastropod biomicrite, and in the lower parts it is an oolitic foram biosparite. The only significant lithologic difference in the grainstone member between Randolph and Selma cores is the presence of calcite that was precipitated in interpore areas in the Selma core.

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1 (emended) refers to the fact that Rose's Kirschberg evaporite unit includes an interval of altered recrystallized limestone, dolomite and travertine that contains two zones of breccia and in addition the few remaining feet of dolomite and limestone between the upper breccia horizon and the top of the Fort Terrett Formation (or bottom of the grainstone member of the Kainer Formation).

The similarity of lithology of the grainstone member cores indicates that no major alteration of this rock has taken place in the Selma part of the study area. It is proposed here that the grainstone member has not been altered because of its lack of permeability and its calcitic mineral composition. The grainstone member in the Randolph core differs in two important respects from other members of the Edwards Group in the Randolph core that correlate with altered parts of the Selma core: (1) The neutron porosity log (plate 1) shows a homogeneous lack of high porosity except for a zone at the base, and (2) the carbonate composition is dominantly calcitic.

In the Randolph core, the grainstone member extends from 836 to 890 feet below land surface. Thin sections suggest a porosity of 5 to 7 percent because of unconnected fossil molds and pore spaces within a predominantly sparry matrix. Samples from depths of 850 feet and 871 feet show a low magnesium-calcite composition (2 to 3.7 mol percent $MgCO_3$) and an absence of dolomite. Dolomite streaks in other parts of the core were noted, but not sampled. Stylolite surfaces are thinly coated with black organic material containing gypsum and kaolinite. The latter sample (depth, 871 feet) is from an interclastic oolitic foram biosparite. Miliolids are surrounded by concentric rings of micite and spar. Clasts containing oolites in a micrite matrix form interclasts along with the miliolid allochems. Nearly all of the interclasts are rounded and have been coated with tiny isopachous spar. The interfragment area is partially filled with fine-grained sparry cement. Chert nodules appear in the middle and base of the member.

In the Selma core, the grainstone member extends from 427 to 490 feet below land surface. The upper half consists of a limey, chalky foram biomicrite, occasionally interbedded with dense, nonchalky micrite and coarse-grained, locally vuggy recrystallized calcite. The recrystallized calcite near the middle of the member in the Selma core is apparently a localized alteration. In thin section, formation of the blocky crystals has forced the gray micritic matrix into blebs, presumably during a localized dissolution/reprecipitation process.

In two samples from the Selma core, dolomite amounts to slightly more than 10 percent of the total carbonate content. A dolomite rhomb with a dissolved center was identified within a large crystal of calcite spar in the recrystallized calcite described above.

Comparative semiquantitative x-ray diffraction of the relative abundance of calcite and dolomite in Selma and Randolph samples from the grainstone member combined with thin-section evidence indicate that more calcite has precipitated in interpore areas in the Selma core than in the Randolph core. Forams increase greatly in proportion to the matrix in the lower part of the grainstone member in the Selma core and it closely resembles the lower part of the member in the Randolph core. However, in the Selma core, calcite spar cement is much more coarse-grained and more abundant than in the Randolph core. A typical sample of the Selma core at 474 feet below land surface is a dense, heavy biosparite composed of miliolids, pellets, and eliptical, concentrically ringed oolites. The allochems are well sorted, surrounded by a small amount of micrite, and cemented with coarse, blocky calcite spar. X-ray diffraction analysis of this sample indicates that the carbonate composition is 84 percent calcite (3.7 mol percent $MgCO_3$) and 16 percent dolomite. The spar locally replaces the fossil fragments. Pore space of about 1 to 2 percent is developed mostly within the miliolids. Calcite precipitation and the resulting lower porosity would reduce circulation in this member and possibly prevent ground-water solution during late diagenesis.

Porcelaneous limestone bed.--A bed of porcelaneous limestone at the base of the grainstone member in the Selma core helps to mark the boundary between the open marine facies of the grainstone member and the underlying beds that were deposited under conditions of restricted circulation in the Kirschberg evaporite member. The porcelaneous limestone bed extends from 484 to 492.1 feet below land surface. Rose (1972, p. 34) notes that this siliceous bed also is present above the Kirschberg evaporite member of the Fort Terrett Formation in outcrops on the eastern Edwards plateau. In the Selma well, Rose places the boundary between the grainstone member and the Kirschberg evaporite member at the base of a bed containing Toucasia located just beneath the porcelaneous limestone bed.

Where present, this porcelaneous-limestone bed may prevent the upward flow of water and force water flow and subsequent solution into lateral channels. It is evident from x-ray diffraction analysis that this bed has been preserved, because about two-thirds of the virtually nonporous micrite consists of quartz (table 1). In thin section, a felted, siliceous porcelanite matrix surrounds elongated, brownish, microgranular sponge spicules. The sponge spicules are arranged subhorizontally, suggestive of bedding (fig. 15). Ten feet of Selma core are missing (by dolomite dissolution) from the 20 feet of core just beneath this bed, which suggests that, before alteration, beds beneath the porcelaneous layer were permeable and soluble. A porcelaneous limestone was not observed in the Randolph core; however, beds just below the grainstone member are dolomitized and permeable.

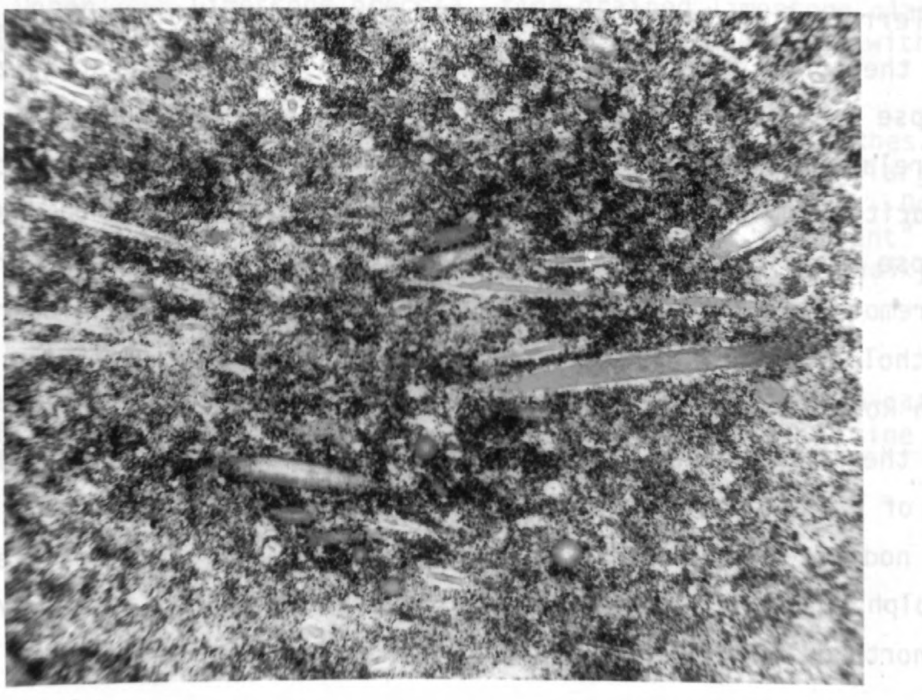

Figure 15.--Sample from Selma well, 485.5 feet below land surface, porcelaneous limestone bed, Kainer Formation. Dense siliceous matrix surrounds sponge spicules that are arranged subhorizontally. This lithologic structure results in a bed which is nearly nonporous and could act locally as an aquiclude between the upper and lower parts of the Edwards aquifer.

The new members of the Kainer Formation (Kirschberg evaporite, dolomitic, and burrowed) are described only for the Randolph core. These members can not be recognized in the Selma core; therefore, this "altered part" of the Kainer Formation in the Selma core is described later in the report.

Kirschberg evaporite member (emended)

The Kirschberg evaporite member (emended) in south-central Texas is characterized by gypsum deposits or collapse breccia. During late Fredericksburg time, thick gypsum deposits of the Kirschberg evaporite accumulated on the Commanche Shelf, including the Central Texas Platform north and west of the Randolph/Selma area (Fischer and Rodda, 1969; Bay, 1977, fig. 19, p. 26). The gypsum was deposited under restricted, evaporitic conditions produced as regional shoaling restricted open circulation of marine water over the Platform. Thick widespread gypsum deposits are not found today in the Kainer or Fort Terrett Formations over the entire postulated area of accumulation. Instead, the stratigraphically correlative position is characterized by beds of collapse breccia.

Correlation of the Kirschberg evaporite member in the Randolph core with the evaporite member in the Fort Terrett Formation is based on the presence of collapse breccia beds. Two thin breccia layers in the Randolph core suggest removal of a limited amount of gypsum--the upper and lower breccias; their lithology is described in table 1b. The correlation of the Randolph core with Rose's Kirschberg evaporite member of the Fort Terrett Formation is based on the stratigraphic position of these two breccia layers along with the type of facies found above and between the breccia layers and the presence of chert nodules in the upper part of the member. The two breccia layers in the Randolph core are in the same stratigraphic position as the gypsum beds present northwest of the study area.

Table 1b.--Lithology of the Randolph core, Kainer Formation, Kirschberg evaporite member (emended)

Depth, in feet below land surface		Lithology
890-917		Dolomite, very fine-grained, very permeable, sugary with black chert nodules toward the top. Interbedded with vuggy recrystallized biomicrite, locally intraclastic and locally thinly laminated. Dolomite, wispy, brown, fine-grained with organic layers. Dolomite, limey, sucrosic with porosity. Limestone, medium-fine, "limey". Dolomite, fine-grained, limey, vuggy, very porous, with chert nodules toward base.
902		Top of celestite zone
917-920	Upper Breccia	Limestone breccia, fine-grained limestone clasts, vuggy, with soft vug fillings; recemented with calcite spar.
920-937		Highly variable lithologies over a few inches. Limestone, very fine grained, earthy with large bivalves; calcite spar-cemented fractures. Dolomite, very fine-grained, punky, sucrosic, "instant" porosity. Calcilutite, light blue. Calcimicrite, chalky, vuggy.
937-940		Dolomite, intraclastic, dense.
940-942	Lower Breccia	Dolomite breccia, very fine grained, intra- and interclastic, vuggy, recrystallized, abundant fine spar cement.
942		Sharp contacts

The middle Kirschberg rocks above the gypsum beds on the Edwards Plateau consist of cyclic facies that can be recognized above the breccia layers in the study area. The gypsum beds in the type section on the plateau are overlain by chert-bearing and burrowed beds consisting of subtidal mollusk biomicrites and biosparites that have been dolomitized. In both areas, these middle beds are characterized by recurring highly variable lithologies that are similar to Rose's cycles in the overlying Person Formation.

Comparison of Randolph core and Selma core suggests that the permeability of dolomitic units in the Kirschberg evaporite member was high enough to provide a path for the movement of meteoric water in the Selma part of the study area. Note that on the neutron-porosity log of the Randolph core (plate 1), the Kirschberg is a zone (approximately 890 to 920 feet below land surface) with very high porosity. These permeable units correlate with zones of unrecovered core and cavernous porosity in the Selma well (plate 1). The correlation suggests that these units provided lateral movement of freshwater, which initiated late-diagenetic reactions that led to formation of highly transmissive units in the Selma part of the study area.

The permeability of the sucrosic dolomite beds in the Kirschberg member in the Randolph well is the result of partial solution of the dolomite. Like the cyclic member dolomites described in the Person Formation, many rhombs have granular and apparently more soluble central parts (fig. 16) that have been removed (fig. 17), leaving hollow centers. Rhombic pores also are common in thin sections from the Kirschberg member (fig. 17). These pores indicate complete removal of dolomite.

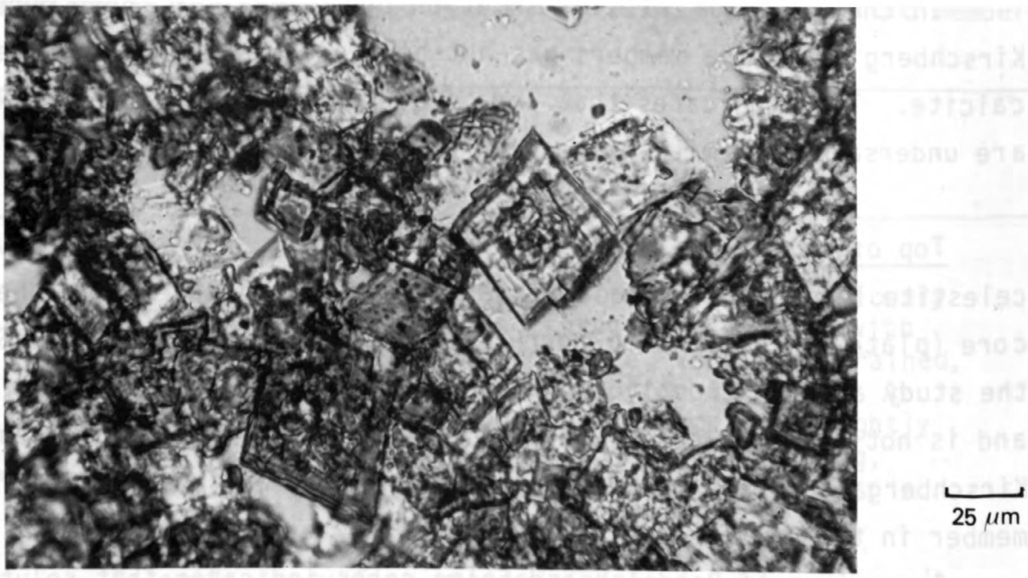

Figure 16.--Samples from Randolph well, 895.5 feet below land surface of a porous, petroliferous dolosparite from the top of Kirschberg Evaporite, Kainer Formation, showing dolomite rhombs with granular centers that are selectively more soluble than the rims. Much core is missing in equivalent zones in the Selma well.

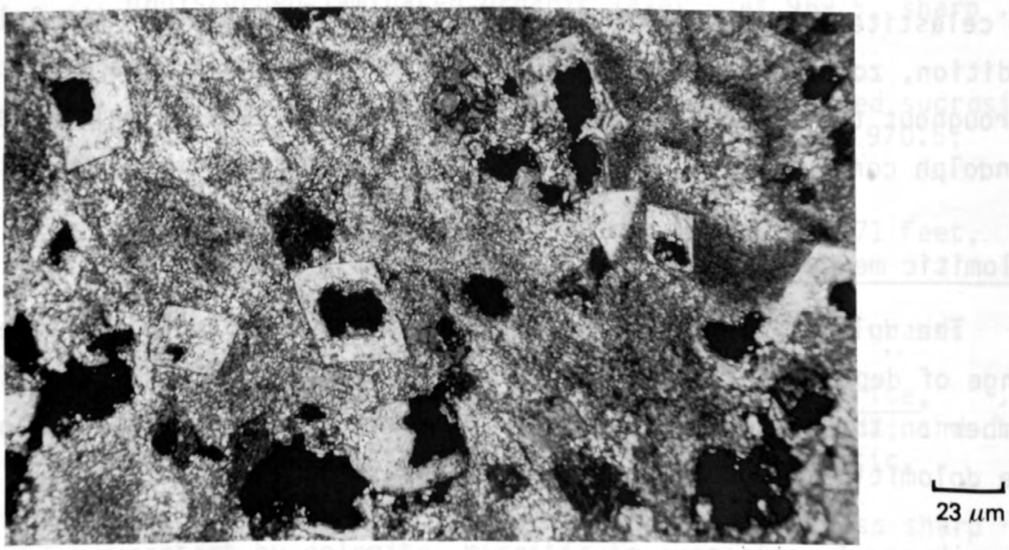

Figure 17.--Sample from Randolph well, 940 feet below land surface, taken from the top of the Kirschberg Evaporite, Kainer Formation. Hollow centers imply selective dissolution of impure, early dolomite. These hollow rhombs cause zones of high porosity on the neutron log, which are stratigraphically equivalent to zones of dolomite dissolution in Selma well.

In the Randolph core, dissolution of dolomite in these beds in the Kirschberg evaporite members has not been accompanied by the precipitation of calcite. This indicates that pore fluids in these beds in the Randolph core are undersaturated with respect to both dolomite and calcite.

Top of celestite zone.-- A zone containing significant amounts of celestite ($SrSO_4$) provides a large, well-defined interval in the Randolph core (plate 1) that can be correlated with altered beds in the Selma part of the study area. Celestite appears abruptly at 902 feet beneath land surface and is not found below 1,048 feet. It is, thus, a significant mineral in the Kirschberg evaporite member, dolomitic member, and upper part of the burrowed member in the downfaulted part of the study area.

Comparison of Randolph and Selma cores indicates that solution of celestite along with accompanying minerals has contributed significantly to the development of cavernous porosity in the freshwater aquifer. Celestite is undersaturated with respect to the composition of modern freshwater in the Edwards aquifer (Pearson and Rettman, 1976) and, consequently, there is no celestite in the upper half of the Kainer Formation in the Selma core. In addition, zones of limited core recovery are common in the Selma well throughout the depth interval equivalent to the zone of celestite in the Randolph core.

Dolomitic member

The dolomitic member facies in the study area suggest a somewhat wider range of depositional conditions than the restricted tidal flat facies of the member on the eastern Edwards plateau. The lithology of the major units of the dolomitic member in the Randolph core are described in table 1c.

Table 1c.--Lithology of the Randolph core, Kainer Formation, dolomitic member

Depth, in feet below land surface	Lithology
942-951	Biosparite and biomicrite, dolomitized and variously silicified, gastropods and forams; recemented with celestite. At 943-944, Dolomite, very fine-grained, sucrosic, intraclasts, wispy, burrowed, vuggy. At 948.5-951, Biomicrite, very fine grained, slightly dolomitized, *Eoradiolites* or *Monopleura*-bearing, celestite filling fractures, apatite inclusions in calcite.
951-958	Dolomite, very fine grained, sucrosic, wispy, organic-rich, with sparse fossils. At 958, chert layer.
958-969.5	Biomicrite, partially dolomitized, medium to light gray, massive, fossil hash, porous, limey, and chalky; very fine-grained micrite matrix locally recrystallized to microspar. Calcite crystals on fracture faces. At 967, undisturbed laminated organic layer. At 969.5, sharp contacts.
969.5-970.5	Dolomite, dense, aphanitic to very fine grained sucrosic; High angle fractures healed with calcite. At 970.5, sharp contacts.
970.5-971	Dolomite, sucrosic, brown, moldic vugs. At 971 feet, band of organic-rich carbonate, 1-inch thick.
971-972	Dolomite, medium-fine crystalline, blue-gray, grades downward into variable lithologies including, biosparite, medium-fine, tan; micritic biosparite, intraclastic, with organic layer 3/4-inch thick; and biosparite, coarse-grained, tan and intraclastic.
972-973	Dolomite, sucrosic, laminated; underlain across sharp contact by dolomite, micritic to sucrosic, clastic, blue, with fine organic-rich laminae. At 973 feet, undulating contact.

Table 1c. (continued)

Depth, in feet below land surface	Lithology
Kainer Formation, dolomitic member, Randolph core, continued	
973-980.5	Biosparite, dolomitized, medium-coarse grained, light gray, recrystallized and calcite-cemented, locally very porous, abundant fossil allochems include forams, ostracods, and possibly Monopleura. Locally organic-rich or vuggy, very porous. Calcite spar in fractures. At 980.5 feet is abrupt contact.
980.5-1003	Dolomite, fine to medium crystalline, highly variable thin beds that are: aphanitic; organic-rich; inter-clastic; limey and solution-pitted; blue-gray to light gray and brown. At 982.5-985 feet, sucrosic, brown, horizontal laminae, "instant" porosity, moldic vugs, earthy. At 994 feet, sucrosic, tan to gray, recrystal-lized. At 995 feet, medium crystalline, sucrosic, gray-brown, with moldic vugs, burrowed, celestite-bearing.
1003-1013	Biomicrite, nodular, wispy organics. At 1,003 feet, intraclasts, squeezed and flattened.

Open fractures in the topmost unit of the dolomitic member are an obvious source of high permeability and would provide fresh recharging ground water easy access to soluble minerals in this part of the Kainer Formation. Many of these fractures are partially filled with celestite--a mineral that, as noted previously, is unsaturated with respect to the composition of modern water in the main Edwards aquifer (Pearson and Rettman, 1976). Early in the formation of the freshwater aquifer, in response to the initial dilution of pore fluids, this celestite would dissolve, enlarging the fracture and providing even higher permeability; this, in turn, leads to further dilution of pore fluids. Ultimately the wall rock became involved in this progressive process.

The Selma core from the altered zone, Kainer Formation, illustrates the end products of reactions between dilute pore fluids and what were probably dolomitized and fractured biomicrites. Matrix in the Selma core is microspar and pseudospar. Fossil shell material, all sedimentary texture, and secondary dolomite rhombs have been obliterated. Fractures in these Selma core samples are filled with blocky calcite spar representative of the final event in the late-diagenetic reaction series.

Quartz is a significant mineral in the upper unit of the dolomitic member and is also found in a stratigraphically equivalent horizon in the Selma core. The quartz appears to have been dissolved and reprecipitated during the same late diagenetic reactions that resulted in neomorphic calcite. This is discussed below in the section on mineralogic comparisons.

High porosity and permeability is found in the medium-grained dolomites of the dolomitic member in the Randolph core. Mud-free and well-washed foraminiferal sands of the dolomitic member have been completely dolomitized; the fossil foram material has dissolved, leaving foram-shaped pores. The resulting rock is usually sucrosic, brown, earthy dolomite.

Adjacent sedimentary layers in the Randolph-core dolomitic member have had different diagenetic histories, possibly because of variations in grain size and permeability. Mineral replacements, such as dolomite for calcite and calcite for dolomite, have occurred in adjacent layers in upper units of the dolomitic member. Dolomite has replaced calcite and, in turn, has been replaced by quartz in the topmost unit. This unit is a permeable biosparite, allowing easy access to pore fluids. The biosparite has been first dolomitized and then silicified. In an adjacent layer, only 1-foot lower, dolomite has been replaced by calcite. The calcite has replaced small dolomite rhombs in a very finely crystalline, burrowed and vuggy dolomitized biomicrite. The calcite is in the form of blocky spar that fills rhombic pores and fossil molds. Both of these beds are permeable, but the biomicrite shows the replacement of dolomite by calcite, whereas the biosparite does not.

Burrowed member

The dolomitic member in the Randolph core is underlain by massive, burrowed foraminiferal and pellet-rich mudstones that contain chert nodules and beds of porous sucrosic dolomite. Within the Fort Terrett Formation on the eastern Edwards plateau, these burrowed mudstones were named the burrowed member by Rose (1972, p. 32). Burrowed structures several centimeters in diameter are prominent throughout the sequence. The base of this sequence and its relationship to the underlying member are the same in both the study area and on the plateau. Rose defines the base of the burrowed member at the first appearance of the organic-rich nodular structures of the underlying basal nodular member. This lower boundary of the burrowed member and the underlying nodular beds are easily recognized in the Randolph core. The burrowed member of the Fort Terrett Formation can, therefore, be extended from the plateau into the study area as a member of the Kainer Formation.

The major units of the burrowed member in the Randolph core are described in table 1d.

Table 1d.--Lithology of the Randolph core, Kainer Formation, burrowed member.

Depth, in feet below land surface	Lithology
1013-1018	Limestone, biomicrite, partially dolomitized, dark gray, mottled, burrowed lithographic limestone. Matrix is composed of less than two micron grains in which celestite fills molds left as fossil shell disolved. Dictyoconus and monopleura common and not recrystallized; burrowed mud shows fine vertical cracks (evaporative shrinking?); becomes chalky toward base of unit. Burrows are filled with lighter gray limey, very porous dolomitic biomicrite in which dolomite rhombs are partially dissolved, and bioclasts are more intensely reworked than host mud.
1018-1045	Limestone, biomicrite, chalky, locally fossil hash (packstone), very fine grained, hard, quartz-cemented. At 1018-1022 feet, chert pebbles (1-inch diameter); at 1022 feet, contact with dolomitic reworked layer; at 1034 feet, organic-rich; at 1039 feet, chert, large nodule with irregular surface; at 1041-1042 feet, excellent porosity, 1/2-2-inch chert fragments; at 1042-1045 feet, nodular structures, organic wisps.
1045	Base of celestite zone
1045-1052	Dolomite, fine-grained, sucrosic, brown, earthy, "instant porosity"[1], large chert nodules, variously limey. At 1050 feet, hard, recrystallized; at 1051 feet, vuggy zone; at 1051.3-1052 feet, reworked, interclasts; at 1053 feet, horizontal bedding with 1/2-inch organic layer.
1052-1089	Limestone, biopelmicrite, variably dolomitized, miliolids, pellets, ostrocods, very fine-grained to medium-grained in dolomites, good[2] porosity, moldic vugs, variously earthy and soft, to hard and recrystallized. Highly variable lithologies: 1) Organic layers 1/2-1-inch thick, composed of organic laminae and micrite, 2) burrowed zones with limey, sucrosic dolomite filling burrows, 3) fossil-rich biomicrite (packstone) layers, variously dolomitized with large rhombs growing in micrite, 4) heavily dolomitized sucrosic zones with "instant porosity".

1 A droplet of acid disappears instantly.

2 A droplet of acid disappears within 1 minute.

These massive, burrowed mudstones suggest a subtidal to intertidal facies, and compared to the overlying dolomitic member, the down-core sequenc is indicative of deposition in a deepening-water environment. Conversely, up-core to the Kirschberg evaporite member, the depositional sequence is a regressive one, indicative of deposition in shallowing waters.

The burrowed member of the Kainer Formation is the deepest member to be highly altered by freshwater in the Edwards aquifer. These beds form a porous and permeable unit in the downfaulted Randolph core part of the study area. In the Selma core, depositional structures, such as burrowing, are unrecognizable, but highly permeable honeycombed zones are common. These are zones in which soft, permeable burrow fillings have been removed by dissolution, leaving a rock that is possibly 50-percent pore space.

Base of celestite zone.-- Within the burrowed member is the base of a zone in which celestite is a significant mineral (table 1). As noted previously, this interval can be correlated with the altered zone within the Kainer Formation in the Selma part of the study area. The celestite zone has sharply defined upper and lower limits. Its upper limit is in the Kirschberg evaporite member, at 902 feet below land surface, and the lowest occurrence of celestite is at 1,048 feet below land surface (plate 1). Stratigraphic correlation of the Selma core with the Randolph core indicates that the base of the zone of intense alteration in the Selma core is present within the burrowed member and closely corresponds to the base of the celestite-bearing interval.

In order to correlate within the Kainer Formation the zone of core loss in the Selma core with the celestite zone in the Randolph core, the top of the regional dense member (Person Formation) and the black rotund bodies zone in the basal nodular member are used as a planes of reference. Then, assuming that the thickness of the Kainer Formation in the Selma core can be reconstructed to match that of the Randolph core (see fig. 3), the base of the interval of extensive core loss in the Selma core is 196 feet below the top of the regional dense member. This depth is comparable to the base of the celestite zone. In the Randolph core, the base of the zone of abundant celestite is 204 feet below the top of the regional dense member. Zones of dissolution therefore, appear to be associated with the presence of celestite.

Altered zone, Selma core, equivalent to Kirschberg, dolomitic, and burrowed members

It is very difficult to recognize Kirschberg, dolomitic, and burrowed-member lithologies or member boundaries in the Selma core. It is possible, however, to delineate the upper and lower boundaries of the zone of intense alteration in the Selma core stratigraphically, because unaltered units are present above and below the altered zone. These unaltered units can easily be correlated with their counterparts in the Randolph core. The grainstone member, which lies above the altered zone and the lower part of the burrowed member, together with the complete basal nodular member below the altered zone, are nearly identical to corresponding units in the Randolph core. Thus, the zone of heaviest core loss incorporates the Kirschberg evaporite, dolomitic, and upper burrowed members of the Kainer Formation. Selective alteration of certain units continues downward into the basal nodular member, but the zone of intense alteration ends in the burrowed member.

This alteration is defined by five major characteristics: (1) There is a nearly total absence of dolomite, celestite, and carbonaceous organic matter; (2) calcite is neomorphosed by late diagenetic reactions and shows petrographic evidence for dedolomitization; (3) much of the core is missing due to cavernous porosity; (4) altered rock is cream to white, stained red, and contains oxidized iron minerals (predominantly goethite); and (5) most sedimentologic textures and structures are obliterated.

Beds with all five of these characteristics appear in the Selma core at 485.9 feet below land surface within the porcelaneous limestone, just beneath the grainstone member. The lower boundary of alteration is not as abrupt as the upper boundary. Intense alteration ends at a depth of 600 feet below land surface where sedimentary structures become more recognizable, zones of missing core are less common, and recrystallized, neomorphosed calcite or dedolomite occurs in specific and limited zones beneath this depth. From 660 feet below land surface downward, the abrupt appearance of dolomite, recognizable sedimentary structures, and nearly 100-percent core recovery indicate the presence of the base of the altered zone in the basal nodular member (plate 1). The lithology of the basal nodular member is described in the next section.

The lithologies of Kainer units in the Selma core from the porcelaneous limestone to the base of the burrowed member are described in table 1e. These units include the intensely altered zone and bordering unaltered units with contacts that can be recognized in the Randolph core.

Table 1e.--Lithology of the Selma core, altered zone, Kainer Formation.

Depth, in feet below land surface	Lithology
Kainer Formation	
Grainstone member, porcelaneous limestone bed	
484.2-485.9	Porcelaneous limestone, fine-grained with sparry grains, cream-color, dense, quartz to calcite = 1:1, siliceous sponge spicules arranged horizontally, porosity very low.
485.9	Top of altered zone
485.9-492.1	Porcelaneous limestone, dense, solution-pitted and vuggy, core broken in small fragments
Kirschberg evaporite member, dolomitic member, burrowed member	
492.1-495.9	3 feet of unrecovered core Limestone, coarse, recrystallized, small pores and vugs, secondary crystal growth. Biomicrite, 3-inch layer, dense, spar-filled vugs.
495.9-503	7 feet of unrecovered core Limestone, Biomicrite, pellets at base. Solution zone leaves 1-inch pebbles in core box. Sample S-495.4.
503-504	Limestone, coarse, recrystallized, micropores
504-506	Limestone, fine-grained, hard, dense, chalky, may be argillaceous.
506-507.5	Limestone, medium-coarse (200 to 400 microns), sucrosic, recrystallized, visible pores greater than 100 microns, many small pieces at 507.5.

Table 1e. (continued)

Depth, in feet below land surface	Limnology
Kainer Formation	
Kirschberg evaporite member, dolomitic member, burrowed member (cont.)	
507.5-520.8	10 to 11 feet of unrecovered core Limestone, Pellet-bearing medium-sparite, 6-inch layer, dense, hard; Biomicrite, dense; Pelmicrite, tan to gray, nodular, burrowed, vugs filled with chalky, sugary, very porous cream-colored calcite.
520.8-547	22.5 feet of unrecovered core Limestone, Travertine, transluscent; Medium-sparite, dense, light tan-gray, secondary calcite crystals and boxwork; at 531.85 feet only few pebbles left in core box.
547-552	2 feet of unrecovered core Limestone, Biomicrite, dense, heavy, pinpoint vugs creating good porosity; Limestone, chalky, recrystallized, very fine grained, pinpoint vugs creating good porosity.
552-554	Limestone, Biomicrite, dense, moldic vugs filled with white limey, sugary, soft calcite.
554-555	Limestone, recrystallized, soft, limey with good[1] porosity.
555-557.5	Limestone, Biomicrite, dense, moldic vugs.
557.5-562.2	1.5 feet of unrecovered core Limestone, recrystallized; Biomicrite, gray, burrowed, and vugs filled with chalky to sugary, white, soft calcite.
562.2-570.8	5 feet of unrecovered core Limestone, Biomicrite, dense, pinpoint porosity is poor to fair. Pellet-bearing medium-sparite, dolomite- and quartzbearing, some goethite, tan, recrystallized, pellet diameter is 200 microns, matrix pore space is 10 percent, pellets well sorted.

Table le. (continued)

Depth, in feet beneath land surface	Lithology
Kainer Formation	
Kirschberg evaporite member, dolomitic member, burrowed member (cont.)	
570.8-577.5	5 feet of unrecovered core Limestone, Medium-sparite, tan, vuggy--vugs filled with chalky, cream-colored, soft, sugary calcite, solution pitting, red clay streaks.
577.5-583.5	4 feet of unrecovered core Limestone, Medium-sparite, pinpoint vugs, only pebbles left in core box; Sparite, finely crystalline, recrystallized.
583.5-589.8	5 feet of unrecovered core Limestone, Medium-sparite, dolomite-bearing, honeycomb structures, burrowed layer, red clay containing coarse crystal-spar masses, core in pieces.
589.8-593.3	Limestone, Fossil-bearing medium-sparite, dense, cream-colored, locally sugary, vug fillings.
593.3-608	Approximately 3 feet of unrecovered core
600	Base of intensely altered zone Limestone, Fossil-bearing, medium sparite; dense, small gastropods; limey with low porosity toward base.
608-617.3	2.5 feet of unrecovered core Limestone, Biomicrite, limey to dense, light gray; core fractured but no solution pitting.
617.3-624.4	1 foot of unrecovered core Limestone, Fossil-bearing medium sparite; dense to porous, chalky, light gray.
624.4-629.5	4 feet of unrecovered core Limestone, Medium sparite, recrystallized, dense, sugary, cream-gray; vuggy toward bottom with coarse calcite crystals in vugs; nodular toward base; micrite matrix forms nodules.

Table 1e. (continued)

Depth, in feet beneath land surface	Lithology
Kainer Formation	
Kirschberg evaporite member, dolomitic member, burrowed member (cont.)	
629.5-636.1	2 feet of unrecovered core Limestone, Biomicrite, dense, cream-white, chalky, hard, very poor porosity, gray chert nodule; becomes dense, gray, nodular and bioclastic toward the base and is both harder and heavier.
636.1-642.5	1 foot of unrecovered core Limestone, Biomicrite, dense, blue-gray, burrowed, with very permeable, light gray, chalky micrite and microsparite filling burrows.
642.5-646	1 foot of unrecovered core Limestone, Medium sparite; chalky, earthy, soft, cream-tan, argillaceous.
646	Base of burrowed member

[1] A droplet of acid disappears within 1 minute.

Like the altered members of the overlying Person Formation, lithologies recovered from the altered part of the Kainer Formation in the Selma core are characterized by dense, neomorphic calcite. This calcite is the product of late diagenesis (Ellis, 1985). This neomorphic calcite matrix is illustrated in Selma-core thin sections (figs. 18-19).

Fractures in Selma-core samples are filled with calcite spar, and blocky calcite spar fills rhombic areas once occupied by dolomite. Organic material that forms algal laminations in the Randolph core, particularly throughout the dolomitic member, is totally absent from the Selma altered section where elongate pores (fig. 18) or goethite-filled laminae (fig. 19) are present instead.

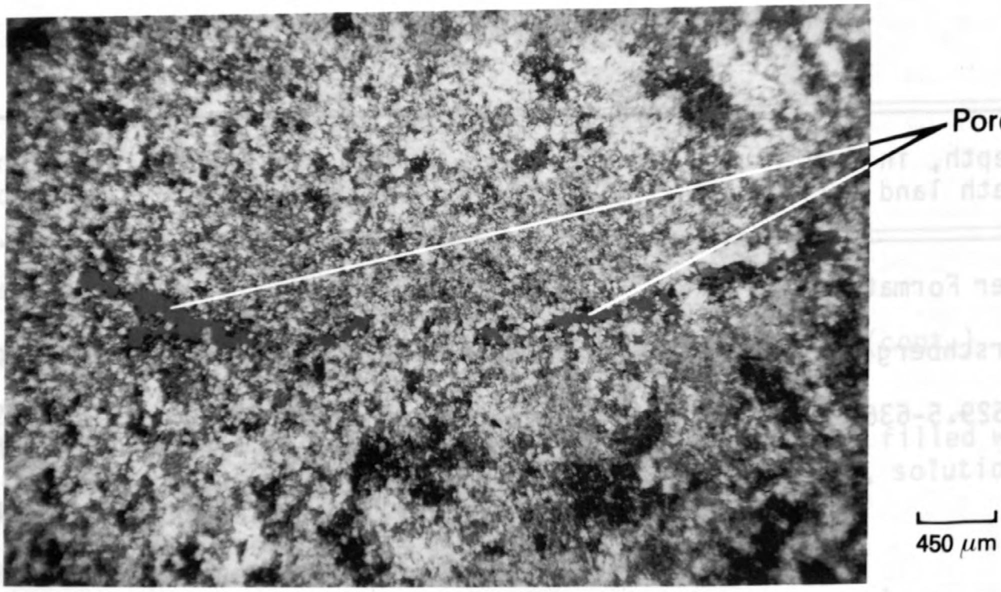

Figure 18.--Sample from Selma well, 570 feet below land surface, Kirschberg Evaporite, Kainer Formation. The dense microspar matrix is composed of interlocking grains of late-stage neomorphic calcite with crenulate grain boundaries. Elongate pores have developed by dissolution of organic-rich laminae, perhaps of an algal origin.

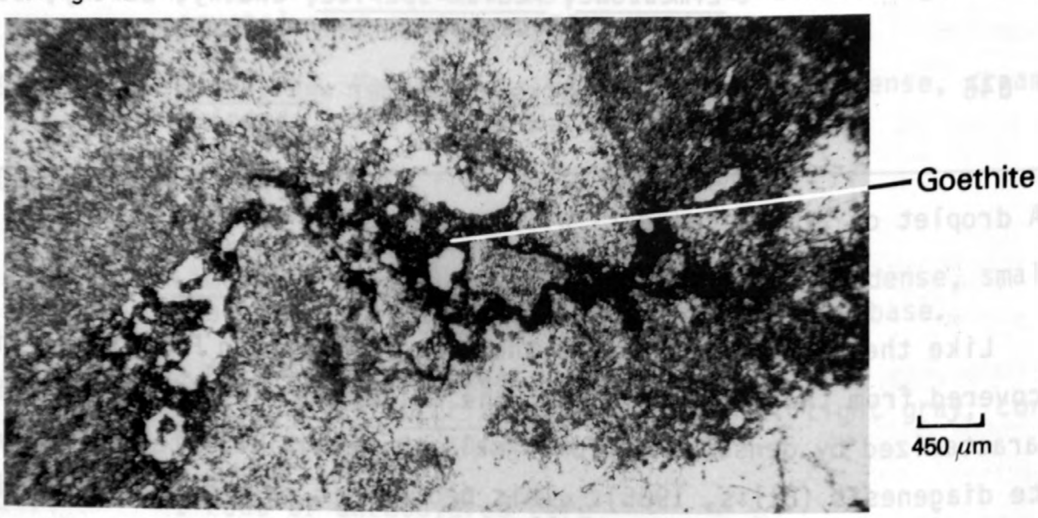

Figure 19.--Sample from Selma well, 577 feet below land surface, Kirschberg evaporite, Kainer Formation. In the freshwater part of the aquifer, goethite is found in laminae in dense microspar of recrystallized calcite. These laminae were originally composed of iron sulfide-bearing organic material that has been oxidized during the dedolomitization reaction, which left remnant iron oxyhydroxide.

Sediments of the Kirschberg evaporite member in the Selma part of the study area have been intensely altered by dilute meteoric water. The most cavernous (see caliper log, plate 1) and water-bearing (Maclay and Small, 1976) zones of the Selma well are present in the 60-foot interval below the porcelaneous limestone bed. This interval (490 to 550 feet below land surface) corresponds almost exactly to the Kirschberg evaporite member (fig. 3) as defined in the Randolph core. At least 40 of the 60 feet of core were not recovered. Most of the recovered core samples show evidence of rock removal by solution. Randolph-core lithologies from this zone indicate that this dissolution has taken place in sediments deposited under tidal-flat conditions. During deposition, the minerals in this facies were in equilibrium with pore fluids that were far more concentrated with respect to total dissolved solids than the dilute ground waters that gained access to these rocks after Miocene faulting.

Rock/water interaction during formation of the freshwater aquifer unit in the Kirschberg evaporite has had a complex geochemical history. Travertine coatings on samples from this solution zone indicate that calcite precipitation followed the major dissolution. Core fragments from the interval from 520.8 to 547 feet below land surface are coated with transluscent travertine, similar to that of some cavern formations. This event obviously involved ground waters supersaturated with respect to calcite. The extensive recrystallization of micrite matrix found in the altered zone of the Selma core indicates an earlier event involved pore fluids capable of dissolving calcite. Siliceous veins associated with the recrystallized neomorphic calcite are exposed on the surfaces of other core fragments from this interval. The veins were left in relief as the intervening calcite dissolved. In the earliest event of the sequence, microcrystalline quartz associated with these veins appears to have precipitated along with neomorphic microsparite. All three of these events postdate Miocene faulting, inasmuch as Randolph rocks do not have any of these characteristics. The quartz is discussed further in a later section on the comparison of specific mineral phases in Selma and Randolph parts of the study area.

In beds below the Kirschberg evaporite, burrowed facies also are vulnerable to alteration by freshwater as noted by Abbott (1975). In the lower part of the altered zone at a depth of 583.5 to 589.8 feet, honeycomb structures are common, indicative of selective dissolution of burrowed zones that characterize the burrowed member of the Kainer Formation. Burrow fillings examined in the Randolph core are composed of dolomite more permeable than that of the interburrow muds (see lithology of Randolph core burrowed member). During freshwater invasion, these permeable zones were preferentially dissolved; this left the muds relatively intact.

The zone of unrecovered Selma core that corresponds to the celestite zone ends abruptly at a depth of 594 feet, and, except for some smaller solution zones and two honeycomb zones within the basal nodular member, the Selma core is more or less intact throughout the lower Kainer and into the Glen Rose Formation (fig. 3). Dolomite is the predominant carbonate mineral in these lower Kainer beds in the Selma core. The sedimentary structures are preserved, as is pyrite-bearing organic material; thus, the color of the core is grey, in contrast with the tan and white color of the overlying altered parts of the Kainer Formation.

Basal nodular member

This lowest member of the Kainer Formation can be used to define the lower limit of alteration stratigraphically. In the Selma part of the study area, this is the first member beneath the altered zone that also can be recognized in the Randolph core. The basal nodular member is characterized by nodular sedimentary structures and by dense, gray, partially dolomitized biomicrites. A distinctive zone of BRB's ("black rotund bodies", pyrite pisoliths) is present in the middle of the basal nodular member in core from both wells. The midpoint of this BRB zone in both cores is the lower datum horizon used in this report for correlating the Edwards Group across the barrier fault. In the Randolph core, the basal nodular member extends from the base of the burrowed member at a depth of 1,089 feet to the Glen Rose Formation contact at a depth of 1,156 feet. In the Selma core, the basal nodular member extends from 646 feet to 710 feet below land surface. Lithologic and petrographic descriptions of major units from the member in both Randolph and Selma cores, respectively, are listed below.

Table 1f.--Lithology of the Kainer Formation, basal nodular member.

Depth, in feet below land surface	Lithology of the Randolph core
1089-1092	Dolomitic limestone, recrystallized, light gray, limey, porous, microvugs
1092-1102	Dolomitic limestone, gray and brown sucrosic dolomite matrix surrounding nodules of blue-gray, dense biomicrite at 1,093-1,095, variously limey matrix and nodules locally densely packed. Core broken in places along sides of nodules.
1102-1119	Limestone, burrowed biomicrite with white and chalky to brownish, limey burrow fillings. Becomes more nodular downward, with blue-gray biomicrite nodules, and matrix ranges from tight and dense to chalky and soft. At 1,109 rock contains pisoliths (many black masses of tightly packed, tiny pyrite grains, called BRB's or "black rotund bodies").
1109	Top of BRB zone
1119-1128	Dolomitic limestone, gray, tight, massive intraclastic clam shell (Exogyra?) and gastropod biomicrite. Reworked light gray clasts in dark gray (organic-rich) matrix. BRB's scattered throughout matrix. Becomes tan, limey and more dolomitic toward base of unit.
1128	Base of BRB zone
1128-1133	Dolomitic limestone, light to dark gray, massive, tight, wispy to nodular gastropod biomicrite. Stylolitic. Contact at 1,133 with organic-rich, clastic micrite in thin-bedded zone, clasts are flattened, possibly by compaction

Table 1f. (continued)

Depth, in feet below land surface	Lithology of the Randolph core
1133-1156	Dolomitic limestone, variable lithologies often separate by sharp contacts. Sucrosic and recrystallized sparite, earthy, argillaceous, vuggy. Blue-gray, massive biomicrite, becoming wispy and limey. At 1,135-1,138, blue-gray massive biomicrite, small clasts, stylolitic At 1,139-1,140, stylolites around large, irregular blue-gray nodules in light gray, vuggy, limey matrix At 1,143-1,154, medium-fine grained recrystallized biomicrite, intraclastic, stylolitic At 1,154-1,155.5, dense organic-rich biomicrite with many small, nodular intraclasts At 1,155.5-1,156, horizontal organic-rich beds, limey argillaceous matrix, core broken
1156	Contact with Glen Rose Formation
Glen Rose Formation	
1156-1163	Dolomite, brown, sucrosic, tightly cemented, earthy with large vugs; and limey with angular and nodular clasts of blue micrite, locally vuggy
1163-1165	Dolomite, blue, massive, limey micrite; and, tan, medium crystalline with moldic vugs; some organic layers with white, fossiliferous clasts
1165	Angular erosional contact cuts across depositional boundaries
1165-1168	Dolomite, brown to blue-gray, medium crystalline, indurated, appears vesicular, vuggy
1168-1172	Dolomite, medium gray, finely crystalline, chalky with organic wisps

Table 1f. (continued)

Depth, in feet below land surface	Lithology of the Selma core
646-658.2 (3 feet missing)	Limestone, dense medium-sparite, nodular with blue-gray micrite nodules; locally chalky and earthy; pinpoint and moldic pores suggesting bioclasts toward base of unit; local horizontal fracturing
658.2-660	Limestone, gray, dense micrite with red clay wisps, burrowed with limey fillings in burrows At 660, loose nodules with dissolved and rounded surfaces, partially coated with boxwork of calcite spar
660-665.9 (1 foot missing)	Dolomite, medium-fine grained dolomitized biosparite, sucrosic, IIIB, quartz and calcite-bearing, pin-point vugs; core broken by horizontal fractures At 664-665.9, few nodules left in core box; nodules show B vugs filled with calcite spar and red sandy clay
665.9-672.7	Dolomitic limestone, dolomitized biomicrite with sedimentary structures as follows At 665.9-667?, light gray, burrowed, nodular biomicrite with red, silty sand between nodules; spar-filled veinlets At 667?-669, tan to blue, well-cemented biomicrite, B vugs At 669-672.7, rudist biomicrite, blue, burrowed, wispy, limey, organic laminae, very poor porosity
672.7	Top of "black rotund bodies" (BRB) zone
672.7-677.4	Dolomite, gray, very fine grained dolomitized whole mollusk and gastropod biomicrite, tight, dense, contains many round, black masses (BRB's) composed of tightly packed tiny pyrite grains
677.4-691.6 (2 feet missing)	Dolomitic limestone, gray-blue dolomitized biomicrite, nodular with nodules flattened; wispy, speckled with BRB's; harder and stylolitic downward At 689.6-691.6, burrowed, with BRB's concentrated in burrow fillings
691.6-699 (2.4 feet missing)	Marly limestone, light gray gastropod biomicrite, wispy At 696-699, burrowed, with BRB's in burrow-fillings, organic-rich

Table 1f. (continued)

Depth, in feet below land surface	Lithology of the Selma core
699	Base of "black rotund-bodies" zone
699-710	Marly limestone, medium gray mollusk-fragment and whole mollusk biomicrite, dense, nodular, wispy At 702-705, burrowed At 705-706.5, dolomitic layer overlying squeezed organic-rich layer At 706.5-710, laminated and thick organic layers
Glen Rose Formation	
710-723.2	Dolomite, brown to yellowish, very fine to fine crystalline, sucrosic, earthy, vesicular, with micritic and organic-rich layers

The base of the altered zone in the Selma part of the study area is transitional in that only the most permeable parts of the sediments are altered. The deepest evidence for altered rock in the Selma core lies 3 feet above the BRB zone at 669 feet below land surface. Here, across a sharp contact, the matrix between dense, micritic nodules changes abruptly from red, iron-oxide-stained, vuggy sparite to blue, dense micrite with organic wisps preserved. This change is attributable to oxidation of iron sulfides to iron oxides and recrystallization (neomorphism) of micrite to larger spar crystals. Below this zone, Selma- and Randolph-core material is mineralogically and petrographically very similar.

The basal nodular member provides the two lower datum horizons used to correlate Randolph and Selma wells and complete the rock column. The datum horizons used for the correlation are the midpoint of the BRB zone and the base of the Edwards Group, as defined by geophysical logs and mineralogic changes.

The basal nodular member is a mappable unit throughout the San Marcos Platform and is nearly identical in both wells in the study area. Comparison of Randolph and Selma core material from the basal nodular member indicates that the same facies units were deposited at both locations and that their thickness is comparable. The BRB zone provides strong evidence for similar depositional environment throughout the study area. The BRB's, or their prediagenetic precursors, appear to have been deposited simultaneously over a wide area. Small and Maclay (1982) document the presence of BRB's in cores from the basal nodular member throughout the San Marcos Platform. In both the Randolph and Selma cores, the BRB zone is of the same mineral composition and lithology (figs. 20 and 21) and nearly the same thickness--19 feet in the Randolph core and 26.3 feet in the Selma core. An increase in the gamma log coincides with the BRB zone in both wells. This increase in gamma radiation may reflect the presence of radioactive elements associated with organic material and/or sulfides (see discussion of minor elements to follow). The pisoliths press against and contort organic laminae as though the laminae and mud were soft when these masses were deposited. A similar sedimentary unit overlies the BRB zone in both cores. This unit is composed of burrowed and nodular dolomitized biomicrites, with distinctive burrow fillings of brown (Randolph) and red (Selma) silty carbonate mud.

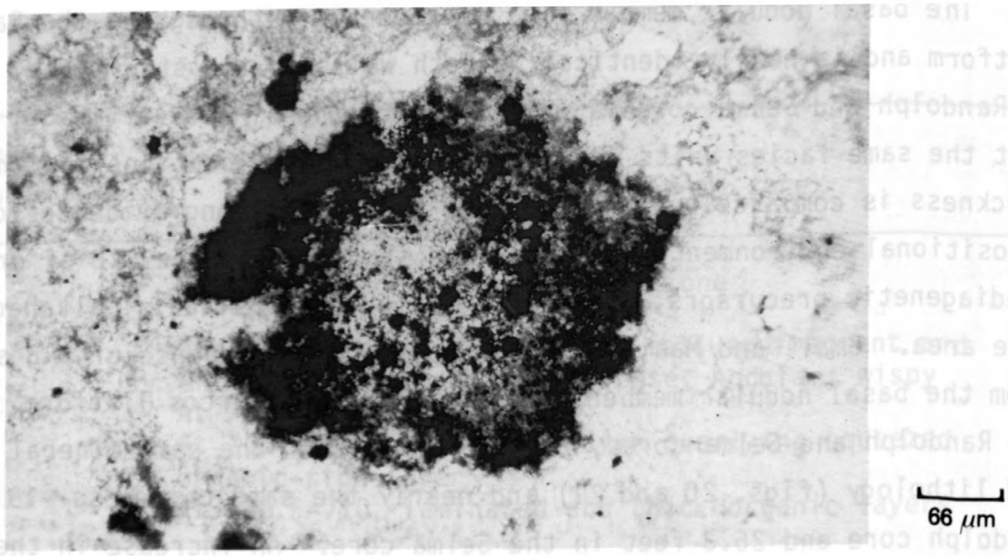

Figure 20.--Sample from Randolph well, 1,146 feet below land surface, basal nodular member, Kainer Formation. Enlarged view of black rotund body (BRB) shows that it is composed of fine-grained pyrite. This same zone in the Selma well provides a useful horizon for correlating the lower Edwards aquifer (fig. 19). Note dolomite rhombs in the matrix. Carbonate composition in this sample is 72 percent calcite, 28 percent dolomite.

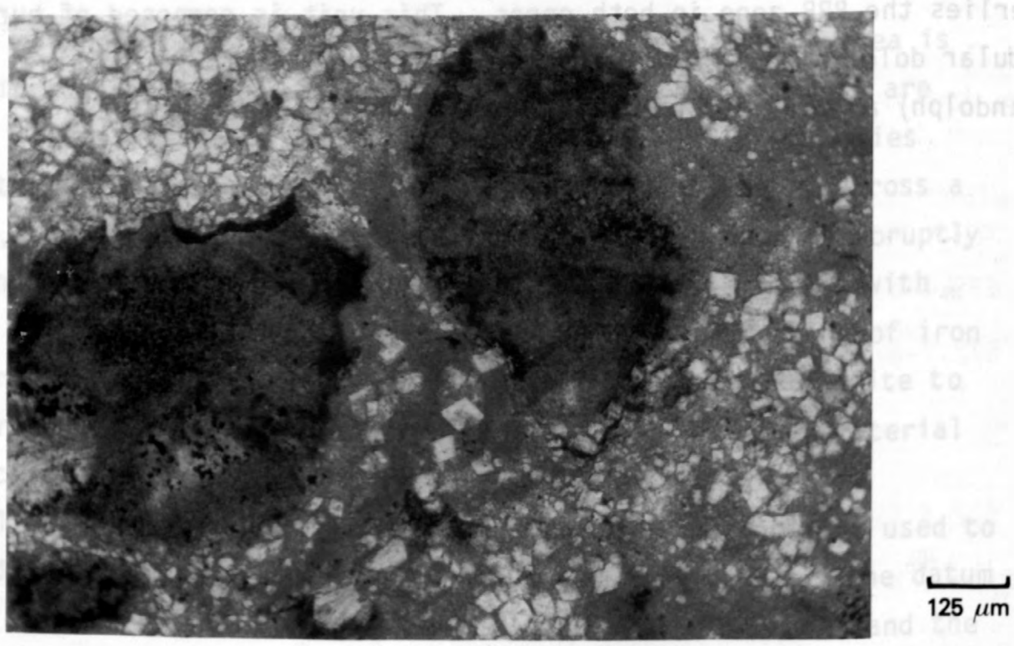

Figure 21.--Sample from Selma well, 680 feet below land surface, basal nodular member, Kainer Formation. Black rotund body (BRB) composed of pyrite is preserved along with dolomite in lower Edwards below zones carrying freshwater. Survival of pyrite in BRB's and dolomite rhombs in the matrix indicate that this zone has not undergone alteration by ground water. Carbonate composition here is 76 percent calcite and 24 percent dolomite--comparable to that of the Randolph core.

Glen Rose Formation

The intensely dolomitized and arenaceous beds of the upper Glen Rose Formation in Randolph and Selma cores have similar lithologies. The sucrosic dolomites are porous and contain many moldic vugs, but, in the Selma core, they have not been invaded by fresh ground water.

MINERALOGIC AND CHEMICAL COMPARISONS

Carbonate mineral phases in the two cores were analyzed for the following: (1) the relative abundance of calcite and dolomite by semiquantitative x-ray diffraction; (2) the amount of $MgCO_3$ incorporated in calcites and dolomites; (3) the ($^{12}C/^{13}C$) ratio of the stable isotopes of carbon within the calcites and dolomites; and (4) the comparative abundance of the cations, Sr, Fe, Mn, and Cu as cations other than Ca and Mg associated with the carbonate phases.

The noncarbonate mineral phase comparisons between the cores were based on the following analyses: (1) Semiquantitative abundance of gypsum, celestite, kaolinite, quartz, pyrite and goethite (determined by x-ray diffraction); and (2) comparative amounts of organic matter.

The whole-rock chemical analyses by emission spectrography are treated separately in order to discuss minor and trace-element associations with depositional environment, mineralogy, and mobility of elements during the alteration process.

Analytical Methods

X-Ray Diffraction

Using a dental drill equipped with a variety of bits, parts of core samples were separated for x-ray-diffraction (XRD) analyses. The resulting powder was hand ground until homogeneous and mounted as a water smear on glass slides. Diffractometer patterns were obtained with a diffractometer using CuK_α radiation discriminated with a graphite-crystal monochrometer; patterns were recorded using pulse-height analysis. Most runs were made at 40 kilovolts, 20 milliamps, and 1°2θ (1 degree, 2 theta) per minute scan speed. Relative weight percentages (proportion of mineral in a unit mass of rock) of calcite and dolomite were calculated from the intensity of their 211 (104) hkl x-ray reflections (Royse and others, 1971). In addition, the abundance of such major noncarbonate minerals as kaolinite, quartz, gypsum, celestite, pyrite and goethite was estimated from peak intensity.

$MgCO_3$ Content of Calcite and Dolomite

The molar proportion of $MgCO_3$ in calcites and dolomites can be approximated with XRD measurements of the size, or d-spacing (in angstroms) of the unit cell. Because Mg is a smaller atom than Ca, the unit cell becomes correspondingly smaller as Mg content increases. Incorporation of other atoms, like Fe^{+2}, also can affect the size of the unit cell, but these atoms are present in small amounts, and, thus, Mg was assumed to be the major cation present other than Ca.

The amount of $MgCO_3$ was determined in more than 100 samples from both cores. The XRD measurements of °2θ (degrees 2 theta) for the 211 crystal plane were first converted to d-spacings (d_{211}). Using the spacing of the 111 crystal plane of annealed CaF_2 provided by D. R. Wones (Virginia Polytechnic Institute, written commun., 1966) as an internal standard[2] in 20 randomly chosen samples, a correction factor was determined and applied to more than 100 d_{211}-spacing measurements of calcite and dolomite in samples without an internal standard. The molar proportion (mol percent) $MgCO_3$ could then be determined directly from curves empirically measured by Goldsmith and Graf (1958).

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2 Wones measured the CaF_2 cell edge ($\underline{a}$ = 5.4620 ±0.0005Å) against that of gem diamond measured by Parrish (1960).

The correction factor was required for two types of error. First, the uncorrected samples were run at a fast goniometer scan rate (1°θ per minute) and second, they were run without internal standard. The correction factor was determined by comparing slow scans of samples that included an internal standard with fast scans of the same samples.

The 20 samples chosen for determination of the correction factor were prepared by hand grinding the CaF_2 powder along with the sample in a mortar. A water-paste smear on a glass slide was made from the mixture and scanned from 28° to 31°2θ at 1/4°2θ per minute to determine d-spacings of CaF_2, calcite, and dolomite. The amount of correction required for calcite compared to dolomite is a good measure of machine and sample preparation errors. For calcite, the difference between CaF_2 corrected and uncorrected spacings had a standard deviation of 0.8 mol percent $MgCO_3$ and, for dolomite, 0.6 mol percent $MgCO_3$.

The corrected 1/4°2θ runs were compared to uncorrected 1°2θ measurements from the same samples to determine the precision of the 1°2θ data. For calcite, the average difference between fast and slow scans was +2.7 mol percent $MgCO_3$ and, for dolomite, the difference was +2.5 mol percent $MgCO_3$. Because the differences for both minerals are nearly the same, there is apparently a consistent difference between the 1/4° and 1° runs. In addition, the internal error of 0.2 mol percent is the same as the internal error between 0.8 mol percent (calcite) and 0.6 mol percent (dolomite) in the 1/4° runs themselves, further implying that there is a consistent error between the 1/4° and 1° runs and that the error is not random.

This error (+2.7 mol percent $MgCO_3$ for calcite, and +2.5 mol percent $MgCO_3$ for dolomite) is the correction factor subtracted from the 1°2θ calcite and dolomite measurements, respectively.

Stable Carbon-Isotope Ratios

Twenty-three samples from Randolph and Selma cores were analyzed for stable carbon-isotope ratios. The samples were carefully selected from defined stratigraphic intervals, and the selection included 10 pairs of samples that are stratigraphically equivalent. Each sample was analyzed for calcite and dolomite content by x-ray diffraction. The dissolution scheme for carbon-isotope analysis was designed to analyze sequentially for carbon associated with calcite and then for that associated with dolomite.

The measurements were made in the U.S. Geological Survey laboratory at Reston, Virginia. Calcite and dolomite samples were prepared for measurements of stable-isotope abundance by reacting with 100 percent phosphoric acid at 25°Celsius (McCrea, 1950).

The difference in absolute ratios of stable isotopes of carbon-13 (^{13}C) to carbon-12 (^{12}C) is sufficient for comparison of substances containing carbon atoms. This difference is expressed as δ. The δ value for an unknown substance (x) is defined (Friedman and O'Neil, 1977, p. KK1) as follows:

$$\delta_x = \frac{R_x - R_{Std}}{R_{Std}} 10^3,$$

where $R_x = (^{13}C/^{12}C)_x$, and R_{Std} is the corresponding ratio in a standard. The δ value is thus the difference in isotope ratio between a sample and a standard, expressed in parts per thousand, or per mil (°/oo). Negative δ values indicate depletion of the heavy isotope relative to the standard, and positive values indicate enrichment. The δ value is the quantity actually measured on isotope mass spectrometers. The standard for carbon-isotope ratios in marine carbonate rocks is the Pee Dee Belemnite (PDB) (Cretaceous, South Carolina); compared to PDB, the $\delta^{13}C$ of most marine calcites cluster near 0 °/oo.

Chemical Analysis by Emission Spectroscopy

Thirty-three whole-rock samples were analyzed by emission spectrography for a total of 64 major and minor elements. A minicomputer-based scanning microphotometer system is used routinely for these analyses.

Standards were diluted to provide six evenly spaced logarithmic divisions per decade of concentration desired. When available, natural-rock standards were preferred over synthetic standards and were diluted to correspond to the six steps: 1: 1.47: 2.15: 3.16: 4.64: 6.81. The nature of the standards used limited the expected accuracy to plus or minus one step, which corresponds to roughly +50 percent or -33 1/3 percent. The computerized procedure is semi-quantitative, because it calculates concentrations using prestored coefficients calculated from these previously arced standards. Analytical curves are not established from standards arced on the same plate as the samples.

Dilution with graphite increases the uniformity of the species arced; thus, the effects on the arcing of the great variety of sample matrices are minimized. The spectrograph has been modified to include a mask near the focal plane. In one position, the mask allows only the wavelength regions around 2748 and 4415 angstroms to be exposed. When the mask is in this position, two Cd spectral lines from a Cd discharge lamp are exposed on each spectrum of sample lines. These lines serve as fiducial lines for wavelength calibration. In the other mask position, the Cd windows are masked, but the rest of the spectrum is exposed. Thus, Cd and sample spectra are coexposed. An argon/oxygen atmosphere minimizes cyanogen band formation and, thus, frees the wavelength region from approximately 3500 to 4200 angstroms for analytical use.

The basis of the system is a scanning microphotometer. The optics are designed to sample a part of the spectrum 1 mm high by 7 μm wide (about a quarter of the width of a spectral line). The signal from light passing through the plate and detected by a solid-state detector is sampled by an analog-to-digital converter.

The heart of the signal processing system is a 2100S Hewlett-Packard[3] minicomputer with 32K of memory. Within 5 minutes of recording the last sample, the necessary number of two-page report forms containing the concentrations of 64 elements for as many as 10 samples are printed on a line printer. Information about effective arc temperature and electron pressure during each arcing and the calculated total oxides (considering only major constituents) for each sample also are available.

The computer algorithm calculates the coefficients of first- and second-degree polynomials for the analytical curve of the natural log of intensity as a function of the natural log of concentration. It evaluates the curve for range, goodness of fit, and slope and suggests a working concentration range for the line such that a lower limit defined by a signal/noise ratio of 2 is maintained.

Generalized interference routines are of two types: subtraction and line changing. The subtraction routine allows gross corrections by subtracting an equivalent concentration contributed by the interfering line. This subtraction routine uses prestored coefficients, relating the concentration of interference to apparent concentration of analyte. This interference concentration and the coefficients have been predetermined in the absence of the analyte. For samples having elevated concentrations of Ca, corrections for this elemental interference with Na, Gd, Sc, Th, and Tb, and many of the rare earths had to be made based on spectral lines from the National Bureau of Standards (NBS) Standard Reference Materials 1b, Argillaceous Limestone.

Each photoplate contains spectra from several standard reference materials in addition to spectra from a suite of samples and an iron, two-step calibration spectrum. The computer program recognizes these rock standards and compares the results calculated for Si, Al, Fe, Ca, Mg, Ti, Co, Pb, and Zr with accepted values in these standards. These nine elements were chosen, because they include the major rock constituents, have a wide range in volatility, and enable checks for loss of refractory elements if a molten bead pops from the anode during the arcing procedure.

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[3]Use of trade, brand, or firm names in this report is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

Along with these carbonates, residue from a dental drill used in sampling also was analyzed. The drill residue contained significant amounts of B, Co, Cu, and Ni. Two samples showing anomalously high values for some or all of these elements were resampled without using the drill and analyzed by induction-coupled argon plasma (ICAP) spectrometry (see table 2). The ICAP analyses confirmed contamination of dental drill residue in the emission spectrograph samples.

The two samples (table 2) are the only ones showing anomalous values for all of these elements, and it is believed that contamination of other samples is minimal.

The comparison of emission spectrograph and ICAP analyses for the elements shown in table 2 reflects the different sample preparation procedure used for ICAP work. The ICAP samples were digested at room temperature in 5 percent concentrated HCl (500 milligrams of sample in 20 mL (milliliters) of HCl), filtered, and brought to 50 mL volume with distilled water.

From U.S. Geological Survey standards prepared in the same manner as the sample solution, the ICAP spectroscopy instrument was standardized for 23 elements. The ICAP is a multielement instrument using hollow cathode lamps to detect absorption of energies from a solution aspirated into an argon flame, creating a plasma.

Table 2:--Comparison of chemical analyses by emission spectrograph and induction coupled plasma for two samples from Selma core [values in milligrams per liter].

	Sample S-287		Sample S-544	
Element	Emission spectrograph	Induction coupled argon plasma	Emission Spectrograph	Induction coupled argon plasma
Al	< 460	309 368	< 460	170 216
**Fe	270	268	130	339
Mg	7400	4674 4584	980	1577 1533
**Mn	52	29	17	8.3
**Ba	3.7	3.5	35	30.0
**Cd	< 32	0.52	< 32	0.75
Ce	< 63	< 3.2	< 63	< 1.5
**Co	8.5*	<0.27	17*	<0.12
Cr	< 1.0	0.19	< 1.0	1.5
Cu	9.1*	4.4	46*	3.9
Er	< 10	0.06	< 10	0.32
Li	< 68	0.33	< 68	0.26
Mo	< 1.0	<0.17	< 1.0	< .12
Ni	250*	1.9	560*	0.80
**Pb	< 6.8	3.9	< 6.8	0.48
Pr	< 68	19.5	< 68	15.8
Sc	4.2	0.11	< 1.0	0.09
Sr	150	36.6	26	30.5
V	3.8	1.9	3.1	3.5
Y	< 1.5	0.66	< 1.5	0.47
Yb	<0.15	0.038	<0.15	0.06
Zn	< 15	1.9	53	1.6
Zr	7.2*	0.06	< 3.2	< .23
K	1100	96	< 680	215

*Contamination from dental drill burr suspected
**Elements that give results with less than 5 percent standard deviation (Carol Skeen, U.S. Geological Survey, written commun., 1982)

Organic-Carbon Analysis

Organic carbon in percent by weight was analyzed with a Leco DC-12 carbon analyzer. Samples were weighed, treated with 30-percent phosphoric acid to remove inorganic carbon, then combusted and the organic-carbon CO_2 volume measured. The residue was acid-treated, rinsed, and dried and mixed with vanadium pentoxide, then combusted in a continuous flow of ultra-pure grade O_2 for 3 minutes. Initial combustion was through an induction furnace at 750 amperes (~1000°C) and through a secondary combustion furnace at 800°C. CO_2 and CO were passed through a series of traps for moisture, sulfur, SO_2, Cl, Fl, and then through a platinum catalytic heater at 400°C that converted CO to CO_2.

The CO_2 sample was collected on a vacuum line on a fitted glass disk using liquid nitrogen, and the water was removed using a dry ice isopropanol slush before measurement in a calibrated manometer.

Comparison of carbonate phases

Calcite

Calcite is present throughout the Randolph core (table 1) in limestone facies that have undergone normal early diagenesis, as well as in dolomitized facies. Facies deposited under open marine conditions are generally all calcitic, whereas dolomite is more common in the hypersaline facies. In the Selma core, these dolomitic facies are absent, with the result that calcite is far more abundant than in the Randolph core. Only scattered streaks and pods are dolomitic in Selma rocks. Calcite in the Selma core is petrographically very different from calcite in the Randolph core. Calcite in the Selma core has been recrystallized, particularly in beds stratigraphically comparable to the dolomitic facies.

Dolomite

Dolomite is abundant in the Randolph core (table 1). An average (from all samples) of roughly 50 percent by weight of the carbonate mineralogy is dolomitic, and many sedimentary units are composed entirely of dolomite. This is particularly true of supratidal facies deposited under hypersaline conditions and underlying permeable sandy carbonate facies that have been secondarily dolomitized. By contrast, comparable sedimentary units in the Selma core are composed of calcite. Only one dolomitic sample was recovered from parts of the Selma core collected from the freshwater aquifer.

$MgCO_3$ Content

Average values of mol percent $MgCO_3$ in calcite and/or dolomite are listed in table 3 for all stratigraphic units studied. These averages were calculated from more than 100 samples.

Calcite in the Selma well averages 0.3 mol percent $MgCO_3$ and this is less magnesium than the measurement error of 0.8 mol percent. Dolomites from the Selma core average 45.2 mol percent $MgCO_3$ and, thus, also are depleted in Mg compared to a stoichiometric composition of 50 mol percent.

Some loss of magnesium also is evident in Edwards Group carbonates from the Randolph core, because they are depleted in $MgCO_3$ compared with carbonates in formations above and below the Edwards Group. Calcite in the Edwards Group contains less $MgCO_3$ than both the overlying Georgetown and underlying Glen Rose Formations, and, with the exception of the regional dense member, the dolomite in the Randolph core suggests the same trend. Wet chemical analyses would be required to verify this small, but consistent loss of Mg from the Edwards Group carbonates.

Table 3.--Average corrected mol percent $MgCO_3$ of samples within zones, calculated from d_{211} spacings measured against CaF_2 as an internal standard. [Composition as a function of d spacing from Goldsmith and Graf (1958). Both calcite and dolomite in Selma core samples contain less Mg than corresponding Randolph core samples. Dash means mineral not present.]

Stratigraphic Units	Randolph core	($MgCO_3$, in mol percent)	Selma core	
	Calcite	Dolomite	Calcite	Dolomite
GEORGETOWN FORMATION	2.4	49.4	0.0	----
EDWARDS GROUP, of Rose (1972)				
Person Formation				
Upper members[1]	1.3	48.7	0.3	45.7
Regional dense member	1.0	50.0	0.0	----
Kainer Formation				
Grainstone member	0.1	----	0.7	37.7
Celestite zone[2]	1.1	48.2	0.9	----
Lower burrowed member[3]	1.0	48.1	0.0	----
Basal nodular member	1.0	47.4	0.4	44.7
GLEN ROSE FORMATION	2.5	49.5	----	46.5

1 All members except regional dense member.

2 Celestite zone includes Kirschberg evaporite, dolomitic and upper burrowed members of Kainer Formation.

3 Lower burrowed member includes beds from the base of the celestite zone to the top of the basal nodular member.

Stable Carbon-Isotope Ratios

The stratigraphic position, mineralogy, and lithology of samples analyzed for stable carbon-isotope ratios is listed in table 4. The stratigraphic position of the samples can be seen graphically on the lithologic log, plate 1.

The 23 samples of calcite and dolomite selected for stable carbon-isotope analysis represent eight stratigraphically correlative comparisons between the cores. Five of these comparisons represent isotope ratios before and after diagenetic reactions in which dolomite and calcite dissolve and new calcite precipitates. The three remaining comparisons are made among three stratigraphic units in which very little or no late diagenesis has taken place in the Selma part of the study area.

The major petrologic criteria for selecting samples from unaltered Randolph core and equivalent altered stratigraphic units in the Selma core for isotope analysis are listed below along with the contrasting results:

Randolph core	Selma core
Permeable dolomite facies	Cavernous porosity
Core recovery complete	Minor amounts of core recovered
Sedimentary structures intact	Vuggy and unrecognizable structures
Dolomite and/or normal calcite are the major carbonates	Neomorphic (recrystallized, replacement, or pore filling) calcite is the major carbonate
Results	
Dolomite and calcite enriched in ^{13}C	Calcite depleted in ^{13}C

Table 4.--Stratigraphic position, lithology and mineralogy of samples analyzed for stable carbon isotope ratios [Analyses by Joan Woodward, U.S. Geological Survey, Reston, Va.]

Randolph Core				Selma Core			
Depth, in feet	Major Carbonate	Lithology	$\delta^{13}C$	Depth, in feet	Major Carbonate	Lithology	$\delta^{13}C$
			EDWARDS GROUP[1]				
			Person Formation				
			Cyclic member, marine facies				
				256	Calcite	Microspar and pseudospar, recrystallized	+0.06
			Cyclic member, tidal flat cycles				
665	Dolomite	Fine crystalline, sucrosic, porous, breccia clasts, see fig. 8	+2.8	287	Calcite	Recrystallized, travertine?	-6.6
668	Dolomite	Medium crystalline, porous	+2.4				
678	Dolomite	Medium crystalline, porous, with moldic vugs	+3.2				
			Leached and collapsed members, tidal flat cycles				
755	Dolomite	Fine crystalline, porous, with moldic vugs	+3.2	357.2	Dolomite	Very fine crystalline	+2.9

Table 4. (continued)

Randolph Core				Selma Core			
Depth, in feet	Major Carbonate	Lithology	$\delta^{13}C$	Depth, in feet	Major Carbonate	Lithology	$\delta^{13}C$
EDWARDS GROUP[1] Person Formation Leached and collapsed members, continued Dolomitized intertidal facies							
				394.6	Calcite	Recrystallized	-5.9
Regional dense member							
837	Calcite	Biopelmicrite, wispy with kaolinite and quartz	+2.7	411	Calcite	Biomicrite	+2.0
EDWARDS GROUP[1] Kainer Formation Grainstone member							
871	Calcite	Biosparite, with oolites and milliolids	+2.4	474	Calcite	Biosparite, Milliolid grainstone	-1.0

Table 4. (continued)

Randolph Core				Selma Core			
Depth, in feet	Major Carbonate	Lithology	$\delta^{13}C$	Depth, in feet	Major Carbonate	Lithology	$\delta^{13}C$
			EDWARDS GROUP[1]				
			Kainer Formation, continued				
			Kirschberg evaporite member				
902	Dolomite	Very fine and fine crystalline, porous, horizontal laminae, celestite-bearing	+4.1	522(A)	Calcite	Spar lining vugs in 522(B)	-7.1
				522(B)	Calcite	Hard, recrystallized, vuggy, microspar, and pseudospar	-6.6
			Dolomitic member				
944	Dolomite	Medium crystalline, porous with light gray intraclasts, moldic vugs	+3.1	544(A)	Calcite	Secondary spar filling fractures and coating inside solution cavities	-4.0
				544(B)	Calcite	Microspar and pseudospar, dense, cherty, vuggy	-3.2
				547	Calcite	Travertine? spar coating of tangled crystals	-7.7

Table 4. (continued)

Randolph Core				Selma Core			
Depth, in feet	Major Carbonate	Lithology	$\delta^{13}C$	Depth, in feet	Major Carbonate	Lithology	$\delta^{13}C$
EDWARDS GROUP[1]							
Kainer Formation, continued							
Burrowed member							
991	Dolomite	Medium crystalline, sucrosic, dark brown, with moldic vugs, burrowed, celestite-bearing	+2.4	577(A)	Calcite	Soft, orange, vug filling	-0.8
Basal nodular member, black rotund bodies (BRB) zone							
1126	Calcite and Dolomite	Detrital dolomite-bearing Biomicrite, gray, wispy, nodular, pyrite-bearing	+2.9	680	Calcite and Dolomite	Biomicrite, gray wispy, nodular, pyrite-bearing	+2.3

[1] of Rose (1972)

Description of samples and results

The stratigraphically highest sample is S-256 (see photomicrograph, fig. 7) from the marine facies of the Person Formation in the Selma core. There is no stratigraphically equivalent sample from the Randolph core. This partially recrystallized sample shows a carbon-isotope ratio of +0.06 $^{o}/oo$, which suggests contributions from both normal marine and late stage calcite.

The next samples are a stratigraphically equivalent pair from the tidal-flat facies of the cyclic member. Below these are samples of two permeable dolomites from lower in the cyclic member of the Randolph core. All three of the Randolph core samples are enriched in ^{13}C. The highest Randolph core sample (R-664) is stratigraphically equivalent to Selma core sample, S-287. Randolph sample, R-664, is dolomite from the tidal-flat facies, and it is isotopically heavier than normal marine carbonates ($\delta^{13}C$ = +2.8 $^{o}/oo$). This dolomite is from a clast in an intraformational breccia (fig. 8). The clast is disk shaped, suggesting an origin during the breakup and reworking of a dolomitic crust on the tidal flat. Enrichment of ^{13}C is common in dolomitic tidal-flat surfaces as a result of evaporative fractionation. Core is missing in the stratigraphically equivalent zone in the Selma core, and there is ample evidence for cavernous porosity. The remaining rock is composed of recrystallized and newly precipitated calcite. The Selma-core sample (S-287) resembles travertine--a late-stage calcite that may have precipitated after the dissolution that resulted in cavernous porosity. The isotopic ratio of the Selma-core sample indicates that this late-stage calcite contains light-isotope carbon from bicarbonate contained in meteoric water (Mench and others, 1980). The isotopic ratio of the Selma core sample (S-287) is -6.6 $^{o}/oo$, indicating that it is depleted in ^{13}C. By contrast, the two samples of permeable dolomites from the cyclic member in the Randolph core are enriched in ^{13}C. R-668 and R-678 show ratios of +2.4 $^{o}/oo$ and +3.2 $^{o}/oo$, respectively.

In the leached and collapsed member, a pair of stratigraphically equivalent dolomite samples from both cores were chosen as a check on the original prediagenetic isotopic composition of Selma-core dolomite. The two samples are isotopically very similar. The stable carbon-isotope ratio of the Randolph core sample (R-755) is +3.2 °/oo and that of the Selma sample is +2.9 °/oo. The similarity in the isotopic composition of these dolomites supports the concept of using Randolph-core material as the starting, or reactant, mineral composition.

In contrast to dolomite from the leached and collapsed member in the Randolph core, recrystallized calcite from the Selma core is depleted in ^{13}C. Sample S-394.6 is a tan to white recrystallized calcite composed of microspar and pseudospar. Its $\delta^{13}C$ (-5.9 °/oo) is similar to that of the other recrystallized calcites and much lighter than the dolomites from the Randolph and Selma cores.

The sample pair in the unaltered regional dense member are petrologically and isotopically similar. Both are calcitic biomicrites, and the $\delta^{13}C$ of the Randolph sample, R-837, is +2.7 °/oo, whereas that of the Selma sample is +2.0 °/oo.

In the grainstone member of the Kainer Formation, the samples in the pair are similar petrologically but differ isotopically. Both are calcitic biosparites, and the Randolph sample R-871 is enriched in ^{13}C (+2.4 °/oo), whereas the Selma sample (S-474) is somewhat depleted in ^{13}C ($\delta^{13}C$ = -1.0). A possible explanation for light-isotope carbonate in the Selma core is the precipitation of pore-filling calcite spar that was derived from meteoric water. Such late stage calcite spar fills voids and pore spaces in the Selma grainstone member.

In the Kirshberg evaporite member, a sample pair was selected to compare celestite-bearing porous dolomite (R-902) from the Randolph core with two Selma samples--calcite spar (S-522(A)) and recrystallized microspar and pseudospar (S-522(B)). The dolomite from the evaporite facies is the heaviest Randolph sample analyzed--$\delta^{13}C$ = +4.1. The calcite spar from the correlative Selma interval is isotopically very light in contrast; it is $\delta^{13}C$ = -7.1 °/oo. The $\delta^{13}C$ of the recrystallized calcite sample from the Selma core is -6.6 °/oo, also indicating that it also is depleted in ^{13}C. It is interesting to note that recrystallized matrix calcite in the Selma core contains somewhat less ^{13}C than pore-filling spar and spar coatings. These latter calcites were the last to precipitate. This suggests that as the dedolomitization reaction proceeded, pore fluids became more meteoric and contained less ^{13}C, resulting in calcites that were also depleted in ^{13}C.

A similar comparison was made in the dolomitic member of the Kainer. The Randolph sample (R-944) is a permeable dolomite with a carbon-isotope ratio of $\delta^{13}C$ = +3.1. This sample was compared with three Selma samples: a secondary calcite spar (S-544(A)) filling fractures and coating solution cavities; a dense microsparite matrix with calcite-replaced dolomite rhombs (S-544(B), see fig. 25 below); and a late-stage calcite coating of tangled crystals (S-547) resembling travertine. These samples are all depleted in ^{13}C; their $\delta^{13}C$ ratios are -4.0 $^{o}/oo$, -3.2 $^{o}/oo$, and -7.7 $^{o}/oo$, respectively. Note that the travertine-like coating is the isotopically lightest sample analyzed and is isotopically similar to the secondary spar in the Kirshberg and cyclic members of the Selma core.

The lowest pair in the dolomitic member of the Kainer Formation also is the lowest pair in the altered part of the Edwards Group. Here again a permeable dolomite (R-991) is compared to a late diagenetic calcite (S-577(A)) from the Selma core. The dolomite $\delta^{13}C$ = +2.4 $^{o}/oo$, whereas that of the calcite is -0.8 $^{o}/oo$, which is considerably lighter isotopically. This calcite is unusual in that it is a soft, damp powder that fills vugs in a dense pseudospar.

The lowest pair of samples were collected from the BRB zone of the basal nodular member of the Kainer Formation to see if unaltered Selma core below the solution zone is isotopically similar to that of the Randolph core. The samples are similar mineralogically and isotopically. Both samples are dolomite-bearing biomicrite with $\delta^{13}C$ = +2.9 $^{o}/oo$ (Randolph) and $\delta^{13}C$ = 2.3 $^{o}/oo$ (Selma).

Cation Substitution for Ca and Mg in Dolomite and Calcite

Cation substitution in dolomites from the Randolph core reflect diagenesis before dedolomitization, whereas cation substitution in neomorphosed calcite after alteration reflects late-diagenetic processes. The abundance of four elements, Fe, Mn, Cu, and Sr, that can substitute for calcium was examined to determine whether substitution in neomorphic calcite tends to differ from that in precursor dolomite.

Stratigraphically equivalent sample pairs of pure calcite (Selma) and pure dolomite (Randolph) (to the limit of x-ray-diffraction analysis) were analyzed by replicate ES and a few by ICAP (see methods discussion). The two analytical techniques gave slightly different results; however, except for iron, the difference between methods is smaller than the arithmetic mean difference in concentration between calcite and dolomite pairs analyzed by ES alone. Thus, the ES results can be regarded as trends, but inasmuch as the amounts are small and both ES and ICAP data are semiquantitative, the trends should be verified by more quantitative techniques. Samples and ES data are listed in table 5. Lithologic descriptions of the samples are found in table 6.

Table 5.--Composition of selected elements in dolomites from the Randolph core and stratigraphically correlated calcites from the Selma core, in milligrams per liter. [Analyses by emission spectrograph, Carol Skeen, U.S. Geological Survey, Reston, Va.] [nd = not determined]

Sample	Depth in feet	Element: Iron	Manganese	Copper	Strontium
Randolph core					
R-3	665	220	63	6.6	370
R-4	678	360	30	3.9	380
R-6	758	180	28	12.0	340
R-7	795	530	29	6.1	410
R-10	902	190	60	3.2	530
R-11	944	250	30	2.6	400
R-12	991	890	33	4.2	nd
Arithmetic Means		374	39	5.5	405
Selma core					
S-3	287	268	29	4.4	150
S-4	301.8	96	59	4.6	260
S-6	366.1	310	47	2.2	360
S-7	394.6	410	38	3.3	210
S-10	522	160	50	2.5	290
S-11B	547	120	53	3.9	250
S-12A	570.8	440	78	2.7	nd
S-12B	570.8	910	150	3.9	nd
S-12C	577.5	190	63	2.4	nd
Arithmetic Means		322	63	3.3	253

Table 6.--Lithology and mineralogy of stratigraphically equivalent pairs of samples analyzed by emission spectrography.

[Mineral composition in weight percent by x-ray diffraction; --, mineral not present; nd, not determined; emission spectrographic analyses by Carol Skeen and organic carbon analyses by Sharon S. Lindsay, both of the U.S. Geological Survey, Reston, Va.]

Sample	Depth, in feet	Lithology[1]	Calcite	Dolomite	Quartz	Gypsum	Organic carbon	Pyrite	Total clay	Other
			GEORGETOWN FORMATION							
R-1	611	Limestone, pellet-bearing mollusk biomicrite, dense, light gray	84	--	3	--	nd	8	5	Marcasite
S-1	241	Limestone, pellet-bearing foram and mollusk biomicrite, chalky, soft, marly, with moldic vugs, green chamosite(?) peloids	83	--	6	--	0.171	2	9	10Å clay, Kaolinite
			EDWARDS GROUP[2] Person Formation Cyclic member, marine facies							
R-2	645	Limestone, caprinid coquina, biosparite, gray	99	--	2	--	nd	--	--	--
S-2	256	Limestone, caprinid coquina, recrystallized, buff, moldic pores	100	--	--	--	nd	--	--	--
			Cyclic member, tidal flat cycles							
R-3	665	Dolomite, dolomite mudstone clasts in calcite spar matrix. Clasts only.	3	97	--	--	nd	--	--	--

Table 6. (continued)

Sample	Depth, in feet	Lithology[1]	Calcite	Dolomite	Quartz	Gypsum	Organic carbon	Pyrite	Total clay	Other
		Person Formation, continued								
		Cyclic member, tidal flat cycles, continued								
S-3	287	Limestone, medium sparite, rounded pieces of core, dense, vuggy, hard, light gray	99	1	Trace	--	nd	--	--	Kaolinite
		Marine member (dolomitized)								
R-4	678	Dolomite, sparite, fine to medium crystalline, moldic pores	1	99	--	--	nd	--	--	--
S-4	301.8	Limestone, biomicrite to medium sparite, buff, creme, soft, chalky, "ropey" structure	100	--	--	--	nd	--	--	--
		Leached and collapsed members								
R-5A	740	Limestone, carboniferous layer, laminated, petroliferous, black. Sample A (740-2,3,4,5) See fig. 9	63	18	5	2	1.24	2	10	Fluorite
R-5B	740	Dolomite, sparite, brown sucrosic, porous. Sample B (740-6) See figs. 9, 21	5	76	4	--	0.917	--	15	Fluorite
S-5	357.2	Dolomite, very fine crystalline, gray, porous	2	78	21	--	nd	--	--	--

Table 6. (continued)

Sample	Depth, in feet	Lithology[1]	Calcite	Dolomite	Quartz	Gypsum	Organic carbon	Pyrite	Total clay	Other
		Person Formation, continued								
		Leached and collapsed members, continued								
R-6	758	Dolomite, fine crystalline, homogeneous, chalky, porous	1	96	3	--	nd	--	--	--
S-6	366.1	Limestone, fine grained, dense, chalky, buff	100	--	--	--	nd	--	--	--
		Leached and collapsed members, marine facies								
S-7	394.6	Limestone, coarse crystalline, solution-pitted with eroded vugs	99	1	--	--	nd	--	--	--
		Leached and collapsed members, regional dolosparite facies								
R-7	795	Dolomite, sparite, brown, sucrosic, homogeneous, porous, petroliferous	2	97	1	--	nd	--	Trace	--
		Regional dense member								
R-8	837	Limestone, intramicite, biofragmental, wispy, gray	90	--	4	--	nd	1	5	--
S-8	411	Limestone, biomicrite, wispy, dense, gray	94	1	4	--	nd	3	Trace	--

Table 6. (continued)

Sample	Depth, in feet	Lithology[1]	Calcite	Dolomite	Quartz	Gypsum	Organic carbon	Pyrite	Total clay	Other
		Kainer Formation Grainstone member								
R-9	871	Limestone, biosparite, porous	100	--	--	--	0.109	--	--	--
S-9	474	Limestone, biosparite	100	--	--	--	nd	--	--	--
		Kirschberg evaporite member								
R-10	902	Dolomite, horizontally laminated, fine to medium crystalline. Celestite-bearing. Sample = dolomite only	1	99	--	--	nd	--	--	--
S-10	522	Limestone, medium-sparite, very dense	99	1	--	--	nd	--	--	--
		Dolomitic and burrowed members								
R-11	944	Dolomite, fine crystalline, with gray intraclasts, porous, moldic vugs	1	99	--	--	nd	--	--	--
S-11A	544	Calcite-bearing quartz, sparite, tan-creme, "ropey" structure.	23	1	76	--	nd	--	--	--

Table 6. (continued)

Sample	Depth, in feet	Lithology[1]	Calcite	Dolomite	Quartz	Gypsum	Organic carbon	Pyrite	Total clay	Other
		Kainer Formation, continued Dolomitic and burrowed members, continued								
S-11B	547	Travertine (popcorn) very dense, aphanitic with megaspar. Pitted, vuggy.	100	--	--	--	nd	--	--	--
R-12	991	Dolomite, medium fine crystalline, sucrosic, homogeneous, porous, dark gray	2	98	--	--	nd	--	--	--
S-12 A,B	570.8	Limestone, recrystallized, very dense, buff, vuggy. Vugs filled with soft yellowish calcite.								
		A) Dense microspar	99	1	--	--	nd	--	--	--
		B) Soft vug filling	99	1	Trace	--	nd	--	Trace	--
S-12 C,D	577.5	Limestone, recrystallized, very dense, blue-gray, fractured with soft yellowish calcite in cracks between clasts and in vugs.								
		A) Dense microspar and pseudospar	97	2	1	--	nd	--	Trace	--
		B) Soft vug filling	100	Trace	--	--	nd	--	--	--

Table 6. (continued)

Sample	Depth, in feet	Lithology[1]	Calcite	Dolomite	Quartz	Gypsum	Organic carbon	Pyrite	Total clay	Other
		Kainer Formation, continued Basal nodular member, black rotund bodies (BRB) zone								
R-13	1126	Dolomitic limestone, gray, vuggy, nodular with ~20 BRBs/cm[2]	72	9	7	--	0.419	3	9	--
S-13	680.2	Dolomitic limestone, kaolinite-bearing, gray, wispy, nodular with BRBs	69	10	7	Trace	nd	3	11	Kaolinite
		GLEN ROSE FORMATION								
R-14	1166	Dolomite, sucrosic with moldic pores	2	89	4	--	0.181	--	5	--
S-14	754	Dolomite, sucrosic, dense, layered	1	87	4	Trace	0.138	--	8	--

[1] Sample chosen for emission spectrographic analyses was representative of whole sample unless stated otherwise.

[2] After Rose (1972)

Based on the ES data, the difference in arithmetic means for each element in all pairs (table 5) suggests that the alteration process has resulted in changes in the elemental composition of the carbonates. The ES results indicate that, at the 98-percent confidence level, the neomorphic calcite contains significantly less Sr than dolomite precursors. The Sr may be present in unaltered dolomites as either a lattice cation substituting for Ca within the dolomite structure or as $SrSO_4$ (celestite) coexistant with dolomite. The loss of Sr because of freshwater alteration suggests that Sr^{+2} in the solution phase was unavailable to substitute for Ca in the solid phase.

Most of the freshwater calcite samples have lost iron compared to their dolomitic precursors, but several calcite samples have increased iron. The difference between the maximum loss and maximum gain exceeds 800 mg/L, suggesting that some precursor dolomite samples contained minute amounts of iron minerals, such as sulfides and oxyhydroxides. For this reason, a statistical test was not applicable. Verification of iron loss must, therefore, await analytical techniques, such as use of the electron microprobe, to examine the cation composition of individual carbonate crystals.

The neomorphic calcite samples from the Selma core also may contain less copper than their dolomitic equivalents, because comparison of all but two sample pairs shows a loss of copper. The amounts of copper in all samples are small, generally less than 5 ppm, and within the error band of emission spectrographic analysis. In any case, the calcite appears to have lost 20 to 80 percent of the original amount present in precursor dolomites.

The ES analyses of manganese concentration suggest possible increases in neomorphic calcite compared to the original composition of the dolomite. Comparison of the arithmetic means of manganese concentration in calcite and dolomite indicates that the increase may be 50 percent higher than the original amount present. Manganese content, like iron, must be analyzed by a technique that will exclude sources of contamination from noncarbonate minerals, and, for this same reason, a statistical test was not used.

If there has been a gain in manganese incorporated in the freshwater calcite lattice, then pore fluids at the time the calcite precipitated may have been locally enriched in the concentration of Mn^{+2} (Oglesby, 1976). At the same time, pH, redox, and HCO_3^--activity[4] conditions may have prevented formation of manganese oxides (Hem, 1970).

On the other hand, the lack of iron (Fe^{+2}) within the calcite along with XRD evidence for goethite in many samples from the freshwater part of the core indicate that reduced-iron species were not present in the freshwater part of the aquifer at the time the calcite precipitated. If reduced iron were present, it too, would have been incorporated in the carbonate structure. Redox conditions in the solutions from which the calcite precipitated therefore may have been poised between manganese reduction and iron oxidation.

Comparison of Noncarbonate Phases

Gypsum

Gypsum is disseminated throughout the Edwards Group of Rose (1972) in the Randolph part of the study area but is rare in the Selma area (table 1). Samples from the Randolph core (table 1) contain up to 25 percent gypsum by weight and average roughly 5 percent by weight. Only three samples from the Selma core contain gypsum.

In the Randolph core, gypsum is common along depositional partings, such as bedding surfaces, particularly those rich in organic material, and along tectonic surfaces, such as joint faces and slickensides. Gypsum is also typically found on stylolitic surfaces. Gypsum is rare in micrite (mud) matrix, except in the presence of mud-filled burrows.

The most abundant occurrence of gypsum is in the Kirschberg evaporite member of the Kainer Formation, where it is found in pores and along veins, commonly accompanied by celestite. Where gypsum is present in organic layers and laminae, it is nearly always accompanied by pyrite, kaolinite, and quartz.

In the Georgetown Formation, gypsum is present with pyrite in small pisoliths. In addition, gypsum is found on fracture faces and in the matrix

---

4 Activity is a geochemical term based on concentration that quantifies the tendency for a dissolved species to take part in a specified reaction.

in pelleted micrite. Just beneath the Georgetown/Edwards Group contact, in the marine facies of the cyclic member, Person Formation, gypsum is found in burrow fillings and fine, organic-rich laminae. In petroliferous, black, organic layers of the leached and collapsed members, gypsum is found with calcite, fluorite, pyrite, kaolinite, and quartz. In the lower Person Formation (base of the collapsed member), gypsum is found on slickenside surfaces. In the regional dense member, gypsum is found in organic layers with kaolinite, an unidentified 10-angstrom clay mineral species, and pyrite.

In the Kainer Formation, Kirschberg evaporite member, gypsum and celestite spar (visible, well-formed crystals) are present in layers parallel to the bedding and in secondary vein fillings. Both minerals also are found as fillings in round to oval fossil molds in the Kirschberg. In the burrowed member of the Kainer, gypsum is found in burrows and, with celestite, in laminated organic layers and on stylolite surfaces. In the basal nodular member, organic layers contain gypsum in association with kaolinite, pyrite, and quartz. In the BRB zone, gypsum and organic material are found on fracture faces and in stylolitic layers.

Gypsum is rare in the Selma core from stratigraphic units that have been altered by mineral dissolution. In one dolomitic sample from the Person Formation in the leached and collapsed member, gypsum is present in organic layers. In the regional dense member, gypsum is found along with pyrite and kaolinite in organic-rich laminae similar to those in Randolph core from the same stratigraphic location.

In Selma core from the lower part of the Kainer Formation, gypsum was found in a burrowed horizon eroded into a honeycomb zone. In the basal nodular zone, gypsum is present with organic material in a burrowed zone and on slickensides. In the black rotund bodies zone, gypsum is found with pyrite in the pisoliths.

Celestite

As noted in the section on stratigraphic correlation of the cores, celestite is present in a sharply defined zone in the Randolph core from the Kainer Formation (table 1). Where present, celestite averages roughly 10 percent by weight. It is most abundant in the Kirschberg evaporite member of the Kainer, but also is found in the dolomitic and burrowed members. Only one sample from the Person Formation contained celestite; that sample was from the dolomitized marine member.

Typically, celestite in the Kainer Formation is present in open veins, vugs, and in pores left after dissolution of fossil shell. Commonly, the host sediments have been dolomitized and are permeable. In the upper part of the dolomitic member, large blocky euhedral celestite partially fills a tension fracture (fig. 22) in a partially dolomitized biomicrite and microsparite. Dark mineral inclusions in calcite microspar in this same bed appear to be a strontium-rich apatite. In the burrowed member, celestite fills fossil molds in dolomitized biomicrite.

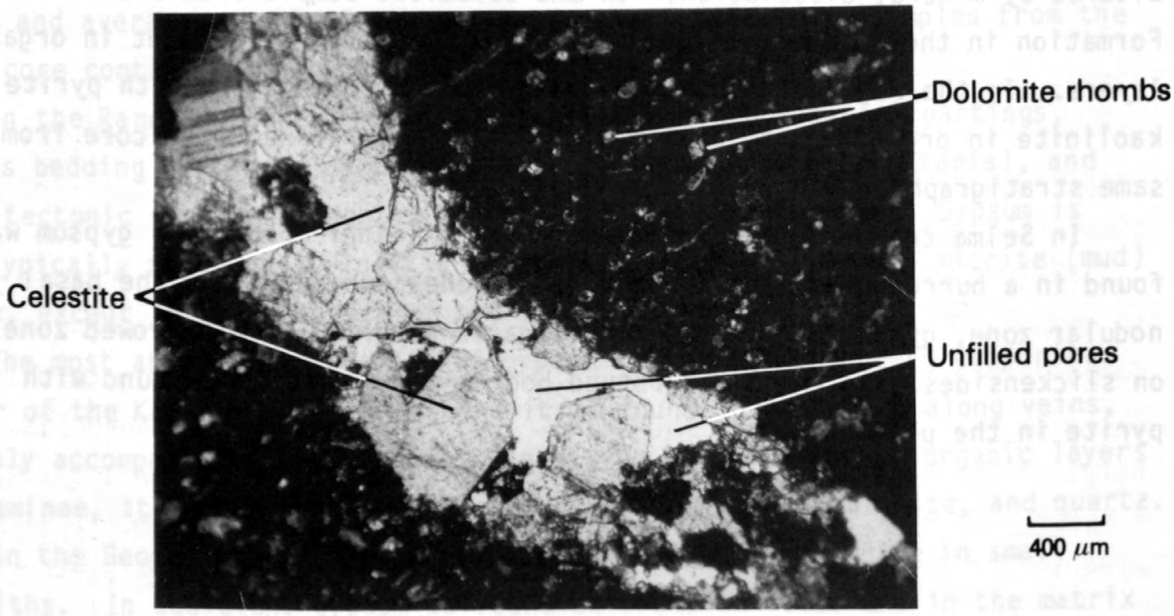

Figure 22.--Sample from Randolph well, 948 feet below land surface, dolomitic member, Kainer Formation, showing celestite that partially fills a large fracture. Note unfilled pores and dolomite rhombs in matrix. Matrix is 92 percent calcite, 8 percent dolomite.

The celestite in supratidal and tidal-flat sediments of the Kirschberg evaporite member is thought to be a byproduct of the dolomitization of strontium-rich aragonitic muds (Rose, 1972). In a sequential reaction process, strontium released from the aragonite combines with sulfate in hypersaline pore fluids (Rose, 1972) and precipitates celestite in pores left as aragonitic shell material dissolved.

The presence of celestite in intervening intertidal sediments of the dolomitic (fig. 22) and burrowed members may be the result of the deeper circulation of concentrated pore fluids generated on overlying tidal flats. Olaussen (1981) for example, describes the occurrence of anhedral to euhedral celestite prismatic crystals that fill intrapores and interpores of a low intertidal to subtidal facies in the Silurian Steinsfjord Formation (Norway). He attributes the celestite to precipitation from pore fluids enriched in SO_4^{2-} derived from solution of gypsum from overlying supratidal sediments. The Sr^{2+} also was released from the overlying supratidal sediments during transformation of aragonite to either dolomite or calcite. These geochemical processes in pore fluids result when an evaporative depositional environment follows a more open marine setting. Such a sequence is characteristic of deposition in a back-reef environment, such as once occupied the San Marcos Platform.

Celestite is absent in Selma-core samples, suggesting that the celestite was dissolved along with dolomite and gypsum. Pearson and Rettman (1976) found that water in the main Edwards aquifer is unsaturated with respect to celestite, and Longman and Mench (1978) report calcite "molds" pseudomorphous after celestite and/or gypsum in rock samples from the main freshwater aquifer. The petrographic occurrence of celestite in precursor rocks indicate that it is associated with permeable facies. Where the celestite in Randolph core partially fills open vugs and veins (fig. 22), it is vulnerable to solution by ground water. In the freshwater-aquifer zone, the loss of celestite from beds equivalent to the Kirschberg Evaporite dolomitic and burrowed members is one of the most significant stratigraphic differences between the two wells (see plate 1).

Carbonaceous Layers and Iron-Bearing Minerals

The light-buff to brown color of the Selma core is in sharp contrast to the dark-gray to black color of the Randolph core. The black tint in the Randolph core is the result of the presence of carbonaceous material. The organic-carbon content of the layers shown in figure 23 is 1.24 percent,

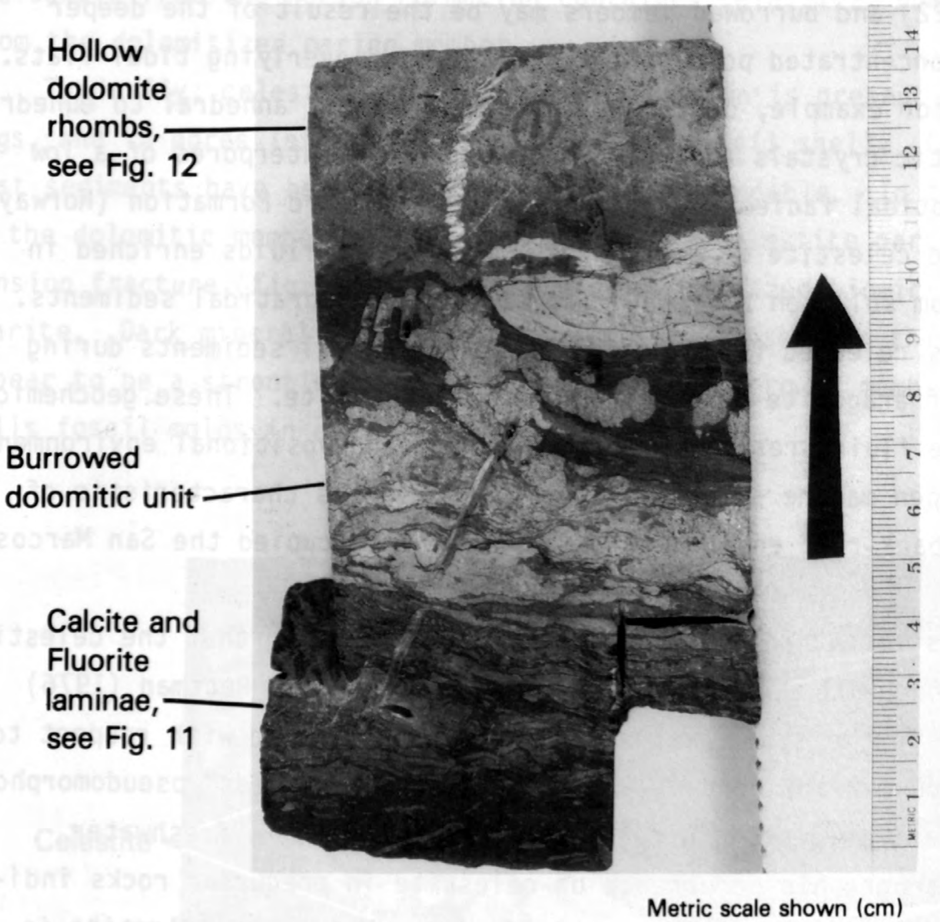

Figure 23.--Handspecimen from Randolph well, 739 feet below land surface, leached and collapsed members, Person Formation. This sample is typical of beds that react rapidly with oxidizing recharge water. The layers shown here are (from left): petroliferous organic material containing the minerals pyrite, gypsum, and fine laminae of calcite and fluorite (fig. 11); a burrowed dolomitic unit; and a unit of extremely porous, sucrosic, hollow- and granular-centered dolomite rhombs (fig. 12). None of these lithologies are found in the Selma core where this is a zone of recrystallized calcite and poor core recovery.

which probably is typical of organic-rich zones throughout the Randolph core. Organic material is nearly ubiquitous in core from the Randolph well. It is found as wisps or laminae gently reworked in a typically gray micritic matrix. Thin but persistent organic-rich material coats stylolite surfaces and fracture faces. A suite of minerals that commonly includes pyrite, gypsum, quartz, and kaolinite is associated with the organic material in nearly every sample.

The morphology of the organic remains from Randolph core sample R-739 was examined to determine its origin. This sample was composed of cellulose-type fragments, possibly from trees; shreds of unidentified material that may have derived from matt-like stromatolitic algal layers; and fecal pellets containing remains of phytoplankton (Eleanora Robbins, U.S. Geological Survey, oral commun., 1985).

Scattered layers of this carbonaceous material remain in the altered parts of the Selma core--a strong indication that previous to alteration, lithology in the altered Selma section resembled that found in the Randolph section. Where unaltered, the presence of organic matter in the Selma core is nearly identical to that in the Randolph core. For example, organic laminae and wispy, nodular structures are found in Selma core from the regional dense member and continuously throughout the lower burrowed and basal nodular members of the Kainer Formation. Dolomite is present in all of these rock sections.

Although carbonaceous layers generally are absent from the altered parts of the Edwards Group in the Selma core, their presence before alteration can be inferred from laminae of ferric oxyhydroxide minerals, chiefly, goethite and limonite (fig. 7 and table 1), which impart the yellowish to red color in the recrystallized calcite zones in the Selma core. The goethite apparently remains after pyrite and organic compounds have been oxidized.

The carbonate matrix in Selma-core samples from zones containing goethite is distinctly different from matrix associated with organic matter in the Randolph core. The texture of Selma-core samples is limey, chalky and commonly soft, whereas the Randolph-core samples have a dense texture and commonly contain pyrite.

Kaolinite

Kaolinite is distributed throughout the Edwards Group in the Randolph core, where it is particularly abundant in organic layers. Note in table 1 that larger quantities of kaolinite generally are accompanied by pyrite, gypsum, and quartz. These samples also are either organic-rich or clearly siliclastic. Longman and Mench (1978) suggest that kaolinite formed authigenically, perhaps in response to slightly acidic ground water, such as that reported by Pearson and Rettman (1976) in the saline water part of the Edwards system. In the Selma core, kaolinite is not present in highly permeable and altered members of the Person Formation and the Kirschberg Evaporite, implying, but not proving, its loss by dissolution. Where the Selma core is unaltered, kaolinite is preserved in unoxidized organic layers that are particularly common in the regional dense member of the Person Formation and in the basal nodular member of the Kainer Formation.

Quartz

In the Randolph core, quartz commonly is associated with pyrite, gypsum, and kaolinite in organic layers. None of these organic-rich and quartz-bearing beds remain in altered zones in the Selma core.

In core from both wells, there is abundant quartz precipitation in the middle part of the Kirschberg evaporite member of the Kainer Formation. In the Randolph core, quartz fills rhombic pores (as a result of dolomite dissolution) and fossil molds (produced by dissolution of calcite and possibly aragonite) in a porous, dolomitized foram biosparite. The quartz is optically length-slow--a crystallographic characteristic associated with precipitation from concentrated pore fluids (Folk and Pittman, 1971). The presence of this quartz indicates that carbonate-mineral dissolution occurred prior to development of the freshwater flow system. Permeability was developed concurrent with this process because of dissolution of calcite bioclasts and dolomite rhombs.

There is petrographic evidence for the dissolution and reprecipitation of quartz early in the formation of the freshwater aquifer. In the Selma core, the Kirschberg evaporite is a zone of intense alteration, as indicated by poor core recovery and neomorphic calcite. In Kirschberg samples from the Selma core, colloform layers of quartz (fig. 24) occur that may have precipitated along with recrystallized calcite. The quartz is associated with boxwork (a rectangular network of fractures that have filled with spar). The boxwork veins are composed of a core of monocrystalline calcite spar surrounded by a dense recrystallized microsparite containing colloform siliceous zones (fig. 24) indicative of coprecipitation of quartz and calcite. The siliceous material is extremely fine grained and shows spherulitic extinction.

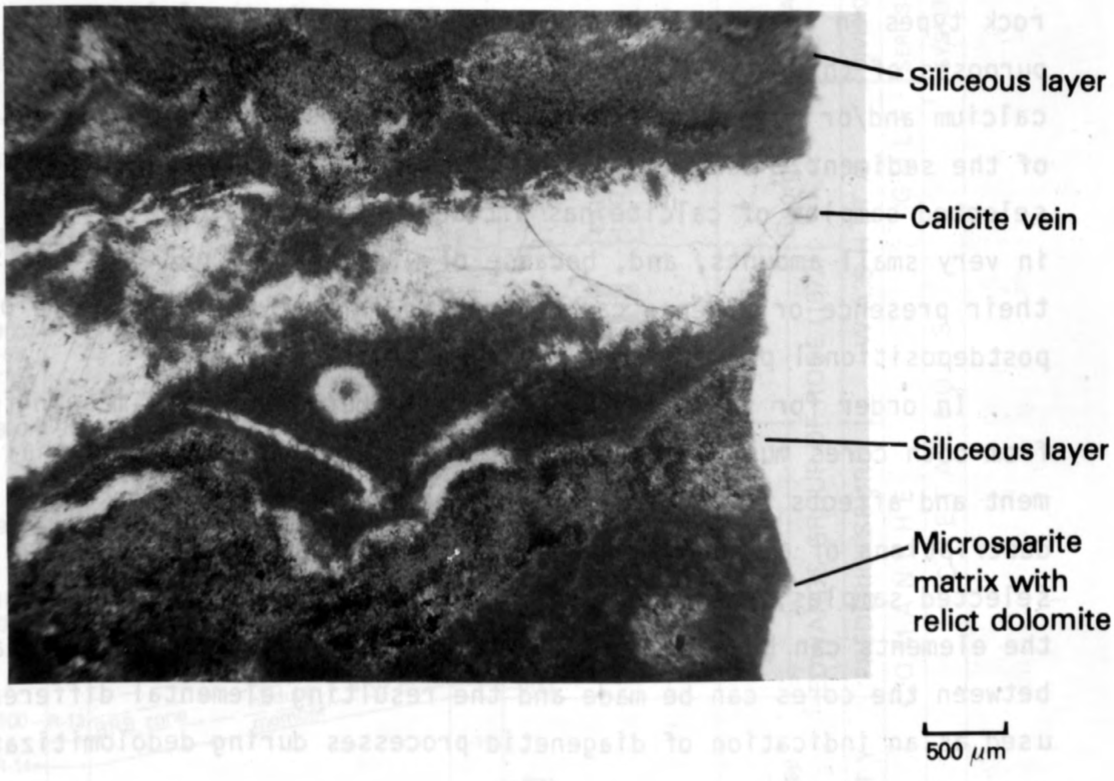

Figure 24.--Samples from Selma well, 544 feet below land surface, Kirschberg Evaporite member, Kainer Formation. In this intensely altered zone, microcrystalline quartz layers flank sparry calcite boxwork vein that cuts through and thus postdates neomorphic calcite matrix of microspar, pseudospar and pore-filling spar containing relict dolomite rhombs.

Microsparite and the colloform siliceous zones line both sides of the veins and, therefore, must be part of the secondary alteration that followed the fracturing. Microcrystalline quartz was not found in stratigraphically equivalent samples from the Randolph core. This suggests that silica has been mobilized during freshwater movement along fractures in the Kirschberg evaporite member. This silica then reprecipitated during the development of boxwork.

Comparison of Minor and Trace-Element Chemical Composition

Study of the occurrence and distribution of minor and trace elements provides additional information about the processes that have altered the rock types in the Randolph core to rock types in the Selma core. For purposes of this study, minor elements are those that can substitute for calcium and/or magnesium in the carbonate minerals that constitute the bulk of the sediment. Substitution of the minor elements Fe, Mn, Cu, and Sr in selected samples of calcite has already been discussed. Trace elements occur in very small amounts, and, because of wide variations in atomic structure, their presence or absence can be used to infer types of depositional and postdepositional processes.

In order for variation in elemental abundance to be meaningful, samples from both cores must be carefully selected and their depositional environment and affects of dedolomitization reasonably well understood. Therefore, descriptions of all samples analyzed are included. By use of the analyses of selected samples, the general factors affecting prealteration abundance of the elements can be determined. Finally, comparison of paired analyses between the cores can be made and the resulting elemental differences can be used as an indication of diagenetic processes during dedolomitization.

Description of Whole-Rock Samples

Fourteen pairs of stratigraphically correlated whole-rock samples were analyzed by DC arc-emission spectrograph (U.S. Geological Survey Analytical Laboratory, Reston, Va.) for differences in their minor and trace element composition. The following descriptions include, for each sample: (1) the depositional environment, and where understood, the early diagenesis; (2) co-existing mineralogy; (3) its relationship to the stratigraphically eqivalent sample in the sample pair; and (4) late diagenesis in the case of Selma core samples. The lithology of the samples is summarized in table 6, and the stratigraphic location of the sample pairs is shown on figure 25.

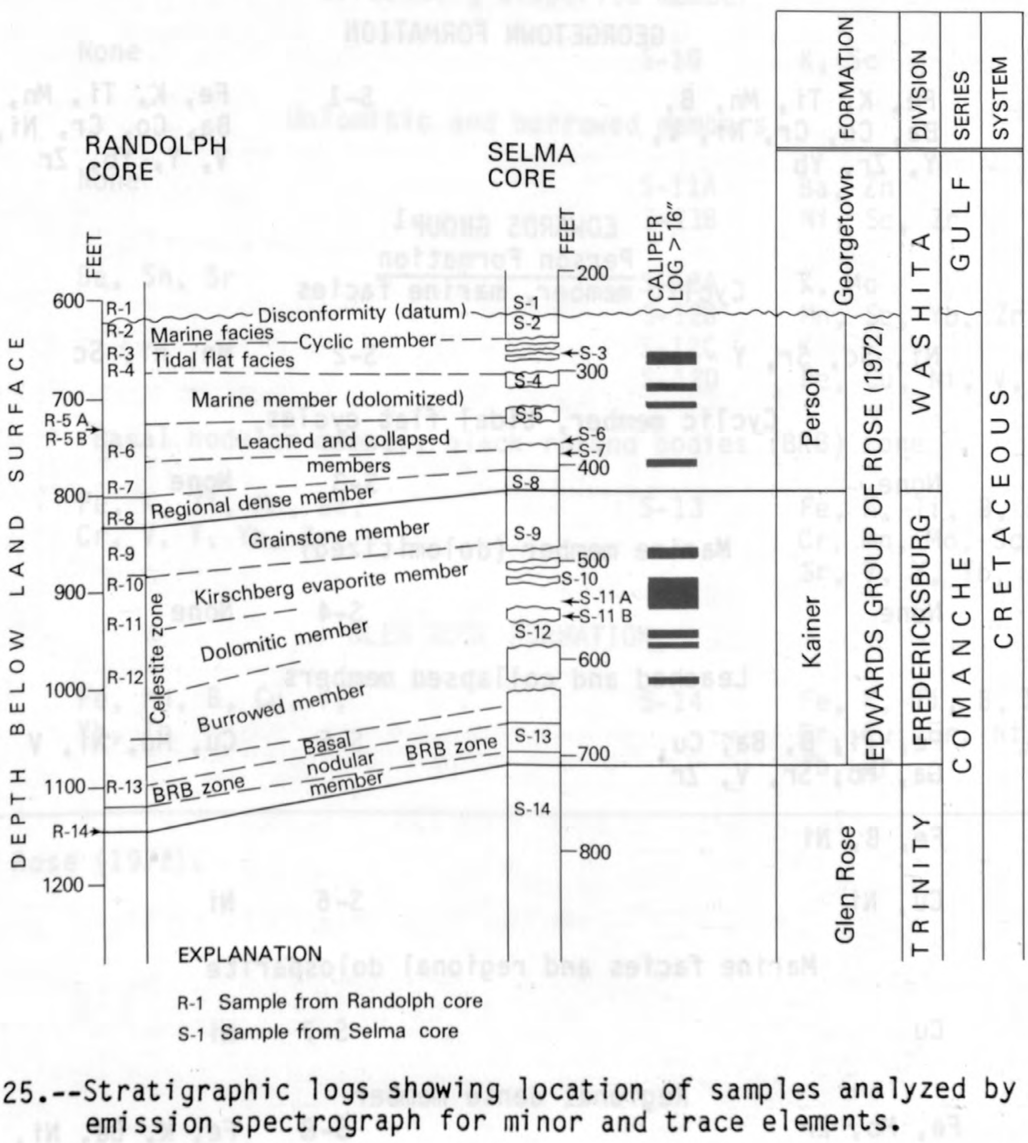

Figure 25.--Stratigraphic logs showing location of samples analyzed by emission spectrograph for minor and trace elements.

For each sample, the elements that show relatively high values compared to values for those same elements in all other samples are listed in table 7, and concentrations of all elements are listed in table 8.

Table 7.-- Abundant elements (relative to all other samples) in stratigraphically equivalent pairs of samples from Randolph (R) and Selma (S) cores.
[Analyses by emission spectrograph, Carol Skeen, U.S. Geological Survey, Reston, Va.]

Randolph core: Sample	Randolph core: Element	Selma core: Sample	Selma core: Element
GEORGETOWN FORMATION			
R-1	Fe, K, Ti, Mn, B, Ba, Co, Cr, Ni, V, Y, Zr, Yb	S-1	Fe, K, Ti, Mn, B, Ba, Co, Cr, Ni, Sn, V, Y, Yb, Zr
EDWARDS GROUP[1] Person Formation Cyclic member, marine facies			
R-2	Ni, Sc, Sr, Y	S-2	Mn, Ni, Sc
Cyclic member, tidal flat cycles			
R-3	None	S-3	None
Marine member (dolomitized)			
R-4	None	S-4	None
Leached and collapsed members			
R-5A	Fe, Ti, B, Ba, Cu, Ga, Mo, Sr, V, Zr	S-5	Cu, Mo, Ni, V
R-5B	Fe, B, Ni		
R-6	Cu, Ni	S-6	Ni
Marine facies and regional dolosparite			
R-7	Cu	S-7	Ni
Regional dense member			
R-8	Fe, Mo, Zr	S-8	Fe, K, Ba, Ni, Sr, Yb, Zr

Table 7.-- Abundant elements (relative to all other samples) in stratigraphically equivalent pairs of samples from Randolph (R) and Selma (S) cores.
[Analyses by emission spectrograph, Carol Skeen, U.S. Geological Survey, Reston, Va.]

Randolph core		Selma core	
Sample	Element	Sample	Element
	Kainer Formation Grainstone member		
R-9	K, Zr	S-9	None
	Kirschberg evaporite member		
R-10	None	S-10	K, Sc
	Dolomitic and burrowed members		
R-11	None	S-11A	Ba, Zn
		S-11B	Ni, Sc, Zr
R-12	Ba, Sn, Sr	S-12A	K, Mo
		S-12B	Mn, Sc, Yb, Zr
		S-12C	K
		S-12D	Fe, Cu, Ni, V, Zr
	Basal nodular member, black rotund bodies (BRB) zone		
R-13	Fe, K, Ti, Mn, Ba, Cr, V, Y, Yb, Zr	S-13	Fe, K, Ti, B, Ba, Cr, Mn, Mo, Sc, Sr, V, Y, Yb, Zr
	GLEN ROSE FORMATION		
R-14	Fe, Mn, B, Cu, Y, Yb, Zr	S-14	Fe, K, Ti, B, Mn, Cr, Cu, Er, Ni, Yb, Zr

1 After Rose (1972).

Table 8.--Emission spectrographic data, in parts per million for stratigraphically equivalent pairs of samples from Randolph (R) and Selma (S) cores. [Analyses by Carol Skeen, U.S. Geological Survey, Reston, Va.; <, less than; >, more than; *, contamination from dental drill burr suspected.]

Sample	Fe	K	Ti	B*	Ba	Co*	Cr	Cu*	Er	Ga	Mn	Mo	Ni*	Sc	Sn	Sr	V	Y	Yb	Zr*
R-1	21,000	1,600	180	9.2	18	3.1	7.2	7.2	<10	<1.5	880	7.4	13	5.6	<1.5	500	27	5.7	0.26	39
S-1	9,600	2,300	380	11	190	4.6	12	3.7	<10	<1.5	610	6.2	36	6.7	6.3	580	38	9.1	0.57	69
R-2	140	1,100	32	<4.6	3.5	1.1	<1.0	5.5	<10	<1.5	59	6.0	14	8.7	<1.5	1,900	5.0	2.3	<0.15	8.6
S-2	130	1,000	<32	<4.6	<2.2	1.6	<1.0	3.5	<10	<1.5	99	<1.0	39	9.2	<1.5	280	3.7	<1.5	<0.15	6.9
R-3	220	1,100	<32	6.7	<2.2	<1.0	<1.0	6.6	<10	<1.5	63	6.1	9.6	2.6	<1.5	370	5.9	1.8	<0.15	5.8
S-3	270	1,100	<32	<4.6	3.7	8.5*	<1.0	9.1*	<10	<1.5	52	<1.0	250*	4.2	<1.5	150	3.8	<1.5	<0.15	7.2*
R-4	360	950	<32	5.2	<2.2	1.7	1.4	3.9	<10	<1.5	30	4.3	22	5.5	<1.5	380	4.3	<1.5	<0.15	6.5
S-4	96	1,200	<32	<4.6	<2.2	3.9	<1.0	4.6	<10	<1.5	59	<1.0	5.7	4.6	<1.5	260	5.8	2.1	<0.15	8.5
R-5A	8,000	1,300	410	14	21	2.1	3.6	12	<10	2.2	60	30	8.9	4.3	<1.5	1,200	34	1.9	<0.15	69
R-5B	1,500	870	41	30	2.6	1.5	2.3	3.8	<10	<1.5	34	7.5	13	2.2	<1.5	300	15	<1.5	<0.15	15
S-5	1,100	1,100	63	<4.6	3.8	1.6	1.4	7.1	<10	<1.5	36	8.7	34	1.6	<1.5	390	26	2.1	<0.15	8.3
R-6	180	940	<32	<4.6	<2.2	1.1	<1.0	12	<10	<1.5	28	5.5	13	2.7	<1.5	340	11	<1.5	<0.15	3.8
S-6	310	1,300	37	<4.6	2.6	1.7	<1.0	2.2	<10	<1.5	47	4.0	20	4.8	<1.5	360	16	<1.5	<0.15	11
R-7	530	990	33	<4.6	<2.2	<1.0	<1.0	6.1	<10	<1.5	29	2.5	3.6	5.8	<1.5	410	7.9	<1.5	<0.15	4.3
S-7	410	1,300	<32	<4.6	5.9	1.5	1.2	3.3	<10	<1.5	38	<1.0	24	6.5	<1.5	210	5.8	<1.5	<0.15	7.0
R-8	3,300	1,200	51	<4.6	5.9	1.2	2.0	2.8	<10	<1.5	50	11	2.8	4.3	<1.5	620	18	<1.5	<0.15	22
S-8	4,300	1,500	97	<4.6	21	1.6	2.8	2.2	<10	<1.5	50	7.6	13	5.6	<1.5	1,200	15	<1.5	0.16	34
R-9	200	1,500	34	<4.6	3.1	<1.0	1.4	1.8	<10	<1.5	29	7.1	1.6	3.7	<1.5	590	11	<1.5	<0.15	11
S-9	<74	1,400	50	<4.6	<2.2	1.4	<1.0	1.7	<10	<1.5	23	<1.0	5.4	6.5	<1.5	490	9.2	<1.5	<0.15	5.2
R-10	190	1,000	<32	<4.6	<2.2	<1.0	<1.0	3.2	<10	<1.5	6.0	6.2	6.2	2.4	<1.5	530	5.0	<1.5	<0.15	<3.2
S-10	160	1,800	<32	<4.6	3.3	2.0	1.9	2.5	<10	<1.5	50	<1.0	5.9	13	<1.5	290	7.4	<1.5	<0.15	6.3
R-11	250	1,100	<32	<4.6	<2.2	4.7	<1.0	2.6	<10	<1.5	30	6.2	3.7	6.3	<1.5	400	10	<1.5	<0.15	4.3
S-11A	130	<680	<32	75*	35	17*	<1.0	46*	<10	<1.5	17	<1.0	560*	<1.0	<1.5	26	3.1	<1.5	<0.15	<3.2
S-11B	120	<680	<32	<4.6	3.7	1.7	<1.0	2.7	<10	<1.5	53	<1.0	17	11	<1.5	250	5.5	<1.5	<0.15	12
R-12	890	1,100	32	<4.6	240	1.0	2.7	4.2	<10	<1.5	33	4.4	6.7	2.5	3.6	33,000	15	3.3	<0.15	3.9
S-12A	440	1,600	40	<4.6	6.2	1.2	1.1	2.7	<10	<1.5	78	8.1	1.9	5.9	<1.5	520	16	<1.5	<0.15	8.0
S-12B	910	1,400	<32	<4.6	6.5	1.8	<1.0	3.9	<10	<1.5	150	<1.0	7.4	9.5	<1.5	500	14	3.4	0.16	11
S-12C	190	1,500	<32	<4.6	2.2	1.0	<1.0	2.4	<10	<1.5	63	7.8	2.6	6.1	<1.5	640	18	2.5	<0.15	7.4
S-12D	6,800	1,400	40	<4.6	3.9	2.7	2.3	12	<10	<1.5	81	<1.0	15	4.6	<1.5	650	36	<1.5	<0.15	12
R-13	7,900	1,500	390	<4.6	23	2.0	4.6	3.4	<10	<1.5	160	6.2	6.9	6.6	<1.5	540	32	6.3	0.46	110
S-13	12,000	2,400	360	19	76	2.9	11	4.3	<10	<1.5	240	12	9.4	9.6	<1.5	750	50	11	0.92	130
R-14	4,000	<680	78	9.3	9.3	1.1	1.6	12	<10	<1.5	320	3.2	8.7	2.8	<1.5	310	9.5	8.7	0.58	28
S-14	5,700	2,900	260	15	8.5	2.2	4.9	6.9	12	<1.5	170	4.2	32	2.9	<1.5	290	12	3.2	0.16	30
Drill Burr	<74	<680	<32	21	<2.2	680	1.9	26	<10	<1.5	<1.0	<1.0	>15,000	<1.0	<1.5	<1.0	<1.0	<1.5	<0.15	34

Samples R-1 and S-1 from the Georgetown Formation are pellet-bearing biomicrites. The Randolph sample is from a nodular subtidal facies and includes pyrite and marcasite, both of which have replaced mollusc remains. It is dense, blue gray, and organic rich. The corresponding sample from the Selma core is composed of several types of fossil fragments, including forams and molluscs in a dense, limey micrite matrix. Pyrite is present as tiny crystals disseminated throughout the matrix. The Randolph sample is 15 feet above the Georgetown/Edwards Group contact, and the Selma sample is 7 feet above the contact.

The stratigraphically highest samples (R-2, S-2) from the Edwards Group of Rose (1972) are from the cyclic member of the Person Formation. Both samples are coquina biosparites, composed of caprinid shell debris cemented with calcite spar. In the Randolph sample, the caprinids have been partially silicified and pyritized, and the matrix includes micrite pellets. In the Selma sample, much of the caprinid shell material has dissolved, leaving large molds, many of which are lined with geothite. The matrix in the Selma sample is recrystallized to microspar and pseudospar. The Randolph sample was collected from 18 feet beneath the Georgetown/Edwards contact; the Selma sample is from 8 feet beneath the contact.

The next pair of samples (R-3, S-3) also are from the cyclic member of the Person Formation. Both are samples from the tidal-flat cycles; the Randolph sample is from a transgressive dolomite breccia, and the Selma sample is from a zone where very little core was recovered. The Randolph sample is from a rectangular clast composed of finely crystalline dolomite (2.5 to 10 μm) with a mat-like structure and fine laminated bedding suggestive of an algal crust. The Selma sample is from a nodular piece of core about 3 inches in diameter from a 7-foot zone where the core was recovered in rounded and solution-pitted pieces. The sample is composed of densely packed, interlocking calcite crystals about 10 μm across that make the rock very hard. For this reason, Ni and Co contamination from the dental drill was found in the analysis. (See analysis of drill burr, table 8.) The outer surface of the sample is rounded from ground-water solution, and fine coliform iron-oxide laminae noted in thin section suggest that the sample may be partially composed of travertine.

The next set of samples (R-4, S-4) are from the marine member (dolomitized) of the Person Formation. The Randolph sample is a massive, porous fine-to-medium crystalline dolomite from a porous and permeable upper tidal facies. The sample also contains micrite concentrated along horizontal laminae suggestive of an algal crust. The Selma sample is from a limey, chalky biomicrite, recrystallized to microgranular spar. Both samples are located near the top of the member.

Seven samples represent the leached and collapsed members of the Person Formation. Two Randolph samples (R-5A and (R-5B) were collected a few inches apart from the sample shown in figure 23. Sample R-5A is from a laminated, organic-rich bed (see fig. 11) overlying a sucrosic, porous, and permeable dolosparite (see fig. 12). These samples were chosen to compare the trace-element composition of the organic-rich laminae with that of the underlying dolomitized and permeable rock. Replacement of some carbonate by fluorite was noted in both of these samples. These samples are located in the tidal-flat facies in the upper third of the leached and collapsed members.

The Selma-core sample (S-5), also from a tidal-flat facies in the upper third of the leached and collapsed members, is a quartz-bearing, finely crystalline dolomite. It was chosen to compare the trace-element composition of dolomitic samples from the Selma core with that of samples from the dolomitic Randolph core in order to establish the prealteration composition of Selma rock.

Another pair of samples (R-6, S-6) selected from the leached and collapsed members contrasts the trace-element composition of Randolph-core dolomite with Selma-core neomorphosed calcite. The Randolph sample is a homogeneous fine crystalline, chalky dolomite with high porosity. This sample is probably a dolomitized shallow subtidal, sparsely bioclastic mud. The sample is located near the middle of the members. The corresponding Selma sample also is chalky, porous, and finely crystalline but is composed of calcite.

The remaining two samples (S-7 and R-7) are from the lower part of the leached and collapsed members. The Selma-core sample is a coarsely crystalline calcite from a zone of poor core recovery. The outer surface of the sample is pitted by solution, and vugs in the sample have been enlarged. A honeycombed bed a few feet beneath the sample is indicative of the dissolution of a burrowing zone and suggests a shallow subtidal facies for the sample. The corresponding Randolph sample is a very finely crystalline dolomite (approximately 5 µm grain size) containing length-slow chalcedony and petroliferous organic material. The mud from which this sample was collected was deposited in an organic-rich environment. Subsequent to deposition, coarse secondary quartz precipitated in bands and masses in a 5-foot-thick zone that includes the sample.

Samples R-8 and S-8 from the regional dense member in both cores are similar in mineralogy and petrology. Both are calcitic and contain sparse quartz, kaolinite, and pyrite. The Randolph-core sample is located near the middle of the member; it is a foraminiferal pellet-bearing intramicrite. The Selma core sample is located near the top of the regional dense member; it is a dense, pyrite-bearing biomicrite.

Samples R-9 and S-9 from the grainstone member of the Kainer Formation from both wells are calcitic biosparites. The Randolph sample consists of miliolids, ooloids, and micrite clasts in grain-to-grain contact, and patches of finely crystalline sparry matrix. The Selma-core sample is a miliolid and pellet-bearing biosparite. Both the Randolph and Selma samples are from the lower part of the member.

Samples R-10 and S-10) are from the Kirschberg evaporite member of the Kainer Formation. The Randolph sample is a laminated fine-to-medium crystalline dolomite. It is a dolomitized, finely bedded miliolid biomicrite. Many of the forams have been micritized and many have dissolved, leaving microvugs lined with micrite. The dolomite is calcic, (that is, the Ca:Mg ratio is greater than 1) and many rhombs show granular centers that are interpreted by Ellis (1985) as being calcic zones. A layer of celestite spar about 1 cm thick is present a few centimeters below the sample. The corresponding Selma-core sample is a very dense, brownish-gray calcite microspar. Vugs in the sample core are partially filled with soft, limey calcite spar. Blocky calcite spar has grown into fossil molds and fractures.

The Randolph-core sample (R-11) from the dolomitic member of the Kainer Formation is compared with two intensely altered samples from a stratigraphically correlative zone of the Selma core (S-11A and S-11B). The Randolph-core sample is a gray, finely crystalline, porous, dolomitized, intraclastic biomicrite. The uppermost Selma-core sample (S-11A) is a dense, tan-to-cream-colored calcite-bearing quartz sparite. The sample piece was one of the very few pieces recovered at that depth, and it is pitted and vuggy probably as a result of dissolution. A few feet lower, Selma-core sample S-11B is covered with travertine that was selectively sampled for its trace-element composition. The travertine is a knobby type similar to the cavern deposit called "popcorn". It is very dense and aphanitic (grains too small to distinguish at 20X). The core sample coated with popcorn is pitted and vuggy on uneven surfaces and contains calcite spar in the matrix.

In the next set of samples, the Randolph sample (R-12) from the lower part of the dolomitic member was compared with two Selma-core samples, (S-12A and S-12B), located 30 feet below the base of the intensely altered zone. The Randolph sample is a finely crystalline, sucrosic dolomite that is homogeneous, dark gray, very vuggy, and porous. The sample is from an intensely dolomitized sequence of variable lithologies that possibly were deposited in an upper intertidal setting. The Selma-core samples are vuggy recrystallized calcite from a zone of poor core recovery that is evidence for cavernous porosity. The upper sample (S-12A) is a very dense, buff, microspar (see fig. 16). All original sedimentary structure has been obliterated. Trace-element analysis of the microspar was done on sample S-12A. Vugs in this core sample are filled with soft, yellowish calcite that XRD analysis suggests may be accompanied by ankerite ($Ca(Mg,Fe^{+2},Mn)(CO_3)_2$). This vug filling (S-12B) was removed and analyzed for comparison with the host microspar.

Seven feet lower, Selma samples S-12C and S-12D were selected for comparison with the Randolph-core sample from the lower dolomitic member (R-12). These Selma samples, like samples S-12A and S-12B, are from an intensely altered vuggy zone and are from dense, host rock (S-12C) and soft vug-filling (S-12D). The four Selma samples, S-12A and B and S-12C and D provide two pairs of samples that can be compared within the Selma core. These samples show a significant comparison of the trace element composition of neomorphosed host rock and soft calcite vug-fillings. These filled vugs are relatively common in the Selma core where alteration has been severe. The host rock (S-12C) is dense, buff, vuggy recrystallized calcite composed of interlocking microspar and pseudospar (20 to 50 μm crystal size) with calcite spar vein fillings and iron oxide lining pore space. Vugs in this host rock are filled with soft, yellowish calcite that was sampled separately (S-12D).

In the basal nodular member, samples of similar lithologies from both cores (R-13 and S-13) were selected from the BRB zone. Both of these samples are gray, nodular, dolomite-bearing limestones, with minor pyrite, quartz, and clay (see figs. 20 and 21). Both samples contain BRB's and both are dolomitized biomicrites. In the Randolph-core sample, some of the dolomite is detrital.

A pair of samples (R-14 and S-14) were collected from the Glen Rose Formation to (1) compare their trace-element composition with that of the Edwards samples and (2) compare Glen Rose samples from the two wells. The Randolph-core sample (R-14), located 16 feet beneath the Edwards/Glen Rose contact, is a sucrosic dolomite. The rock is brown to blue gray, porous, and vuggy (almost "vesicular" in places). The corresponding Selma-core sample (S-14), located 44 feet below the contact, is a dense, dark-gray-to-tan, sucrosic dolomite with interbedded micrite that was not included in the trace-element sample.

Factors Affecting Elemental Abundance Within the Cores

The abundance of trace elements varies several orders of magnitude from sample to sample (table 8). For some elements, variations in abundance can be related to the environment of deposition. Some variation can be related to specific minerals in the sample. Abundance of groups of elements varies, sometimes dramatically, across major stratigraphic boundaries, suggesting that elemental abundance is affected by major changes in environment related to events that caused the stratigraphic contact. Abundance of some elements varies directly with abundance of others, suggesting common elemental characteristics and a similar reaction to environment of deposition or diagenetic changes; whereas variation of specific elements can be related to unusual depositional or mineralogic characteristics of that setting.

Environment of deposition

The three major depositional environments represented by the Edwards carbonates are subtidal, intertidal, and upper tidal flat; samples were collected from all three. There is no single environment that contains a characteristic suite of trace elements. The important factor appears to be oxidation or reduction within any of the above three major settings. Invariably, where the depositional conditions were reducing and both organic matter and pyrite are present, there also is an abundance of trace elements.

Samples of the Georgetown Formation, leached and collapsed members and regional dense member (Person Formation), and basal nodular member (Kainer Formation) all contain trace elements associated with reducing conditions. Nodular subtidal facies from the Georgetown Formation and the BRB zone of the basal nodular member, Kainer Formation, contain elevated concentrations of more trace elements than were detected in samples from any other facies except for the organic-rich layers in the Person Formation. The nodular sediments contain pyrite, clay minerals, and organic matter; this suggests that many of the elements are associated with sulfides (Fe, Ti, Ba, Cr, Mn, Mo, V, Zr); adsorbed onto or exchanged into clay minerals (Y, Yb in addition to possible sulfide-associated elements); or complexed with organics (Fe, V, B?, Ba?). The subtidal sediments are biomicrites that are calcitic or only partially dolomitized; this suggests that the trace elements originally deposited have not been mobilized and removed by dolomitizing pore fluids. Subtidal sediments of the regional dense member (Person Formation) contain an abundance of Fe, Mo, and Zr in the Randolph core and, in addition, K, Ba, Ni, and Yb in the Selma core.

Well-washed shoal or patch reef sediments composed of nondolomitized caprinid shell fragments or a mix of foram tests and oolites with little micrite matrix are enriched in Sr, Sc, and Ni and impoverished in Fe, Ti, and the other siderophile elements.

Elements associated with specific minerals

Large amounts of Sr in certain of the carbonates are associated with celestite or gypsum detected elsewhere in the core sample from XRD analysis. These samples include R-5 (1,200 mg/L Sr) from the leached and collapsed members and S-9 (1,200 mg/L Sr) from the regional dense member, where the Sr may be substituting for Ca in gypsum; and R-2 (33,000 mg/L Sr), where celestite was present in the sample. In this latter celestite-bearing facies, the highest value for Ba (240 mg/L) was reported, suggesting Ba substitution in the celestite. High Ba also is associated with the other samples (R-5 and S-8) containing high Sr where Sr is present as the sulfate. High values for Sr (1,900 mg/L) in the caprinid biosparite sample (R-2), however, was not accompanied by high Ba (3.5 mg/L), suggesting that the Sr was sited not in sulfate, but in the calcareous shell material and the depositional setting did not favor Ba concentration.

Samples in which the largest amounts of Fe were reported contain pyrite, indicating the Fe is present as the sulfide. One exception is a goethite-bearing sample S-12C obtained from vugs in the host rock. The goethite is accompanied by high Cu, Ni, and V (table 8), which probably also are present as oxides.

Samples enriched in K (S-1, R-13, S-13, and S-14) also contain appreciable amounts of clay minerals (table 1), probably including illite. High values for Ti (260 to 390 mg/L) also appear to reflect abundance of clay minerals--an association reported by other investigators (Degens, 1965; Gross, 1967; and Tourtelot, 1962). By comparing the mineral composition on table 1 with the ES data on table 8, it can be seen that samples enriched in clay minerals also contain high amounts of Fe (5,700 to 12,000 mg/L), B (11 to 19 mg/L), Ba (8.5 to 190 mg/L), Cr (4.6 to 12 mg/L), Mn (160 to 610 mg/L), V (12 to 50 mg/L), Y (3.2 to 11 mg/L), Yb (0.16 to 0.92 mg/L), and Zr (30 to 130 mg/L).

The presence of more than 20 weight percent quartz (R-7, R-13, S-11A) does not seem to be consistently associated with a relative abundance of any one element. Concentrations of organic matter appear to be associated with Fe and V and, to a lesser extent, Cu, Mo, B, and Ba. Zirconium (15 to 130 mg/L) appears to reflect the abundance of 2-5 weight percent pyrite (R-5A, R-8; S-1, S-8, S-13). In these samples, molybdenum abundance (7.5 to 30 mg/L) also varies with that of pyrite.

Stratigraphic differences

The Georgetown Formation samples are significantly enriched (one to two orders of magnitude) in Fe, K, Ti, B, Ba, Co, Cr, Mn, V, Y, Yb, and Zr compared to the underlying Edwards Group samples. The only sample containing Er came from the Glen Rose Formation. In general, Glen Rose samples were enriched in many elements but not more so than Edwards Group samples.

Concentration of specific elements

The highest value for B (30 mg/L) was found in sucrosic dolomite clasts in the tidal-flat breccia of the Person Formation. High values (11 to 19 mg/L) also are found in the organic-rich, fluorite-bearing, laminated sample R-5; in the calcitic pellet-bearing biomicrites, Georgetown Formation; in the calcitic BRB zone, Kainer Formation; and in the dolomitic Glen Rose Formation. There does not appear to be any one mineral or depositional or diagenetic factor that could explain the high B. There is a rough correlation of B with high values of K, that suggests that some B may be present in clay-mineral lattice as a substitute for tetrahedral Al.

The abundance of Co is low (1.0 to 4.7 mg/L). High values for Co associated with high Ni and B (shown with asterisk on table 8) are assumed to be contamination from the dental drill burr. Four samples (R-1, S-1, S-4, and R-11) contain more than 3 mg/L Co. The first two samples are pyrite-bearing biomicrites; S-4 is a chalky biomicrite, and R-11 is a dolomitized intraclastic biomicrite. These samples are all biomicrite, and that is the only obvious common factor, but other biomicritic samples are not enriched in Co. It may be that low levels of Co are ubiquitous and variations are a function of analytical error.

The amount of Cr is generally low, but values of 4 to 12 mg/L were found. The two samples (S-1, S-13) with highest Cr (12 and 11 mg/L) are both enriched in pyrite, suggesting the Cr is present as the sulfide. Alternatively, these samples also are high in Mn (610 and 240 mg/L, respectively), suggesting the possibility of Cr incorporation in manganese oxide (Degens, 1965, p. 82).

In three samples (R-5A, R-14, S-12D), high values for Cu (12 mg/L) are accompanied by low Co and Ni, suggesting that Cu is probably not from the drill burr. The Cu is associated with high Fe (4,200 to 8,000 mg/L) and the presence of pyrite, suggesting that Cu coprecipitates with iron. In sample R-6, a pure (96 weight percent) microcrystalline, soft, porous, chalky, dolomite, the siting of high (12 mg/L) Cu is uncertain.

Gallium was present (2.2 mg/L) above the detection limit (< 1.5 mg/L) in only one sample. This is R-5A, the organic-rich sample from the leached and collapsed members. The Ga may be associated with clay minerals as a substitute for Al during a combination of high temperature and acid-leaching conditions that prevailed on the tidal flat.

The largest amounts of Mn (610 and 880 mg/L) were found in two samples from the Georgetown Formation. This was true of samples from both the cores, indicating that some factor favored the greater concentration and subsequent retention of manganese during Georgetown deposition and subsequent diagenesis. Both samples contain high Fe (9,600 and 21,000 mg/L), along with pyrite. Therefore, Mn may be present as the sulfide. However, some Edwards samples (R-5A, R-8, S-8) that contain pyrite and high Fe (3,300 to 8,000 mg/L) contain an order-of-magnitude less of Mn (50 to 60 mg/L). Other Edwards samples (R-13, R-14; S-13, S-14) with high Mn (160 to 240 mg/L) are from a subtidal depositional facies similar to the facies sampled from the Georgetown. These Edwards samples are from the BRB zone, Kainer Formation. However, the amount of Mn in these samples is roughly one-third to one-half that of the Georgetown samples. This suggests that there were factors during deposition of the Georgetown that may have contributed to the concentration of Mn. As noted above, several other elements are abundant in the Georgetown compared to the underlying Edwards. Of these elements, Fe and Cr are more abundant in Georgetown samples than in any others. This suggests that these elements were all concentrated together by the same process.

Mn may be present as a carbonate in neomorphosed sample S-12B. The Mn concentration in this sample (150 mg/L) is an order of magnitude higher than that in most samples from the Edwards Group. Ankerite (an Mn-bearing carbonate) was observed on the x-ray diffraction pattern of this sample as well as in thin section.

High concentrations of Mo (11 to 30 mg/L) are associated with organic material and a reducing depositional setting (see samples R-5A, R-8, S-13).

Molybdenum is found in the highest amount (30 mg/L) in the organic-rich, tidal-flat algal sample R-5A. This is roughly 10 times the concentration of Mo in normal marine sediments (Gross, 1967, p. 280). Some of the organic matter in R-5A appears to be cellulose from terrestrial plant remains, and Hem (1985, p. 216) notes that Mo may accumulate in plant tissue. The high concentration of Mo in R-5A may be related to the reducing capacity of the tidal-flat sediments (Gross, 1967) where bacterialy mediated sulfide (from sulfate reduction) would lead to coprecipitation of Mo with iron as a colloidal sulfide (Koralev, 1958). In an oxidizing environment, Mo appears to be removed in solution. In Edwards samples containing pyrite (R-5A, R-8, S-13), the Mo concentration ranges from 11 to 30 mg/L; however, in most samples where iron has been oxidized to goethite (S-2, S-3, S-10, S-11B), the Mo concentration is below the detection limit (< 1.0 mg/L).

In comparing Mo concentration in Randolph- and Selma-core samples from aquifer units of the Edwards carbonates, there is a nearly consistent trend of Mo "loss" in Selma samples. That is, in pairs of samples, the Randolph sample will contain Mo, whereas the Selma sample will contain Mo in amounts reported as below the detection limit. This suggests that Mo is present in unaltered carbonates in a form that is soluble and mobilized during the alteration. This idea is further strengthened by the presence of Mo in unaltered Selma-core samples. Two Selma samples, S-12A and S-12C, are exceptions--both are dense microspar, obviously neomorphosed, and both contain detectable Mo.

High uncontaminated Ni concentrations (32 to 39 mg/L) are all in Selma-core samples, but otherwise these samples have nothing in common. Very high values for Ni (250 to 560 mg/L, see asterisks on table 8) are certainly contaminated by material from the dental burr, as these samples are also noticeably high in B, Co, and Cu, and replicate analyses of chunks broken from the same sample are very low in these elements and in Ni. Because Ni varies somewhat randomly, small amounts of drill contamination are probably swamping the natural concentrations in many cases.

Scandium concentrations are highest (9 to 13 mg/L) in five samples, all from the Selma core and all but one composed of neomorphosed calcite. Acidic conditions at the onset of alteration, due possibly to pyrite dissolution, may have fixed and enriched Sc in iron oxyhydroxides (Degens, 1965).

Tin concentrations occur in only two samples, S-1 and R-12 (6.3 and 3.6 mg/L, respectively). S-1 is a partially recrystallized biopelmicrite, and R-12 is a finely crystallized dolomitized biomicrite(?). Sn can substitute for Ca in calcite, but the cause for enrichment in these two samples is unknown.

Samples containing the highest concentrations of V (26 to 50 mg/L) include organic-rich, sulfide-rich, and iron oxide-rich associations. The V may be complexed with petroleum-bearing organic components (Degens, 1965); associated with sulfides; adsorbed onto clay minerals (Gross, 1967); and associated with both Fe and Mn oxides. Vanadium can be mobilized in an oxidizing alkaline environment, but its activity may be controlled by metal vanadates and, in particular, ferrous vanadate (Hem, 1985, p. 138).

Two samples from the BRB zone, R-13 and S-13, contained an order of magnitude more Zr than was found in any other sample. These same two samples also were high in Ti, Mn, and V. Adsorption by clay minerals may be the concentration mechanism, because both of these samples are clay rich.

Elemental Differences Between the Cores

In general, it is apparent that the Randolph-core samples and unaltered Selma-core samples contain a wider variety of elements than neomorphosed calcite in the Selma core (table 7). Where relatively unaltered Selma samples are compared to their stratigraphic equivalents in the Randolph core, the minor and trace-element abundances are similar. This is the case in samples from the Georgetown Formation (R-1, S-1); in the unaltered Selma dolomite sample in the leached and collapsed member (S-5 compared to R-5A, 5B); in sample pairs from the regional dense member (R-8, S-8); and in all sample pairs below the altered zone (R-13, R-14 and S-13, S-14) from the basal nodular member and the Glen Rose Formation.

In the following samples, where neomorphosed calcite from the Selma core is compared with equivalent Randolph samples, there are significant differences in the minor and trace elements (table 8). Recrystallized calcite (S-2) with vugs of caprinid molds in the marine facies of the Selma cyclic member shows losses of Ba and Sr, possibly during recrystallization of caprinid shell that is intact in the Randolph sample. The Selma sample has also lost Mo, compared to its Randolph counterpart, but gained larger amounts of Mn and Ni. The Mn in this case could be incorporated in matrix calcite. Both samples are rich in Fe, but it has been oxidized during the alteration of the Selma sample, because the Randolph sample contains pyrite, whereas the Selma sample contains goethite. In the underlying tidal-flat facies, an intraclastic dolomite breccia from the Randolph core (R-3) contains less B, Mo, and Si compared to an equivalent dense microspar sample from the Selma core (S-3). The Selma microspar has apparently gained B and, possibly, Si, during late-stage diagenesis.

Losses of Fe, B, Ni, and Sr were noted in limey microspar in the Selma core (S-4) that represents recrystallized, dolomitized intertidal sediments (R-4). The recrystallized microspar has gained K and Mn. During late diagnesis, chalky, porous, finely crystalline calcite (S-6) in the Selma core has gained Fe, K, Ti, Mn, Ni, V, and Zr compared with unaltered chalky, porous, finely crystalline dolomite (R-6) from the lower leached and collapsed members in the Randolph core. The Randolph dolomite is rich in Cu, whereas the Selma calcite is depleted in Cu. Loss of Cu also is noted in the lowest Selma sample (S-7) from the leached and collapsed member. This coarsely crystalline calcite is from an altered zone and shows depletion of Sr as well. The corresponding Randolph sample (R-7) that still contains Cu (6.1 mg/L) and Sr (410 mg/L) is a very finely crystalline dolomite. There is little difference in the Fe content of this pair of samples, suggesting that Fe has been retained in the alteration process. However, compared to the Randolph sample, the coarse Selma calcite (S-7) has gained K, Ba, and Mn.

Alteration of finely crystalline dolomite (R-11) in the upper dolomitic member has resulted in losses of some Fe, K, Mo, Sr, and V. Ba apparently has been concentrated in calcite microspar and quartz sparite (S-11A), and Mn, Ni, Sc, and Zr have been increased in travertine (S-11B) relative to the prealteration composition of the dolomite. In the lower part of the dolomitic member, finely crystalline dolomite (R-12) has lost large amounts of both Ba and Sr, whereas dense calcite microspar (S-12A) has gained K, Ti, Mn, Mo, Sc, and Zr. Soft vug fillings of ankeritic calcite (S-12B) in the microspar contain increased amounts of Mn, thus substantiating the ankerite component. Like the surrounding microspar, the vug fillings also have gained K, Sc, and Zr, but, unlike the microspar, the soft calcite contains more Fe and Yb and less Mo compared to the prealteration dolomite. This suggests that during late-diagenetic alteration of the dolomite, the vug fillings retained (or gained) Fe and Yb but lost Mo compared to the surrounding microspar.

In summary, alteration of dolomite in the Randolph core to calcite in the Selma core generally has been accompanied by losses of Sr and Mo (and possibly Cu and B) from the system, whereas Mn, Sc, K, and Zr have been gained or concentrated in the altered rocks. Ba, Ni, and Ti also show more tendency toward increases than decreases as a result of alteration, and Fe is more likely to be retained than decreased or increased.

Diagenetic processes indicated by elemental differences

Loss of Sr from the solid phase during diagenetic alteration may be attributed to both dissolution of celestite and release of Sr from prealteration calcite during recrystallization. The Sr apparently is leaving the site of alteration in solution. Loss of Mo from the site of alteration may be the result of oxidation of Mo as the sulfide and/or release of Mo associated with organic matter, possibly also by oxidation.

Retention of Mn in neomorphosed calcite suggests substitution of Mn^{2+} for Ca. Sc in altered rocks may be associated with the iron oxyhydroxide, goethite. Increases in K because of alteration are generally small but consistent, suggesting an enrichment in clay-mineral residue as carbonate minerals dissolve. This same mechanism may explain relative increases in Zr that may have been adsorbed by the clay minerals prior to alteration.

Loss of Ba as a result of alteration probably is due to its mode of occurrence in prealtered rocks. During alteration, rocks containing high Ba and Sr lose both elements, and indicating that, like Sr, Ba stayed in solution and left the site of alteration. Where Ba has increased in altered rocks, it is associated with secondary late-diagenetic precipitation of quartz.

Increases in Ni in altered rocks need to be regarded with caution because of contamination by the dental burr used to extract samples for ES analysis. Increases in Ti, as with Zr and K, may have resulted from enrichment of clay residue to which the Ti was adsorbed before the alteration.

CONCLUSIONS

It is possible to stratigraphically correlate dolomitic rocks from the latest Early Cretaceous Edwards Group with Edwards aquifer units characterized by cavernous porosity. The aquifer units are equivalent to regionally permeable tidal flat facies rich in pyrite, celestite, kaolinite, and organic material. Rock from the aquifer units shows petrographic evidence for dedolomitization--the replacement of dolomite with calcite and recrystallization of preexisting calcite. Pyrite, kaolinite, and organic matter are not present in aquifer units, but goethite is found. Celestite has been dissolved and/or replaced by calcite. Dolomite in rocks that have not been altered is enriched in ^{13}C, whereas calcite in altered rock that contains the aquifer units is depleted in ^{13}C. Depletion of ^{13}C in recrystallized calcite provides significant evidence for the influx of soil-CO_2-derived HCO_3^- in meteoric recharge water. Minor and trace-element data indicate that calcite in the aquifer units precipitated from dilute, mildly oxidizing solutions. Alteration has resulted in losses of Sr and Mo and increases in Mn, Sc, K and Zr. It is concluded that the Edwards aquifer developed by mixing-zone dedolomitization, which resulted in mineral alteration and increased the porosity in regional and permeable dolomitic units of the Edwards limestone.

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