

FRIO SHALE MINERALOGY AND THE STOICHIOMETRY OF THE SMECTITE-TO-ILLITE REACTION: THE MOST IMPORTANT REACTION IN CLASTIC SEDIMENTARY DIAGENESIS

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Abstract—Burial diagenesis of shales of the Frio Formation resulted in an increase in the abundance of mixed-layer illite–smectite (I–S), albite and chlorite, and a decrease in the abundance of K-feldspar, illite and kaolinite. Some of the mineralogic trends determined in this study contrast with the results of Hower et al. (1976) and other studies of Frio shales. The differences are due to improvements in laboratory and clay quantification techniques since the time of the earlier research. I–S composition changed from ~20% to ≥80% illite, and mineralogic and chemical reaction of I–S continued throughout burial. Shale diagenesis was an open-system process that required addition of K₂O and Al₂O₃, and resulted in loss of SiO₂. The amount of SiO₂ made available by shale diagenesis is sufficient to be the source of the quartz-overgrowth cements in the associated Frio sandstones. The relationships between I–S diagenesis and fluid flow from shales into sandstones, generation of abnormal formation-water fluid pressure, onset of sandstone diagenesis and distribution of authigenic phases in sandstones indicate that reaction of the I–S in shales is one of the most important components of the sandstone/shale/formation water diagenetic system.

Key Words—Diagenesis, Illite–Smectite, Mass Balance, Mineralogy, Shale.

INTRODUCTION

The Oligocene Frio Formation was deposited along the northwest margin of the Gulf of Mexico sedimentary basin. It is underlain by the Oligocene Vicksburg Formation and overlain by the Oligocene/Miocene Anahuac Formation. Deposition of the Frio Formation began 33.5–31.5 m.y.b.p., and continued until approximately 25 m.y.b.p. (Galloway et al. 1982). It is one of the major Cenozoic clastic wedges that prograded into the Gulf in response to increased sediment influx derived from the Tertiary volcanic terrain in west Texas and Mexico and from the Laramide orogeny (Martin 1978; Galloway 1989).

The burial-diagenetic reaction of smectite to illite through an intermediate mixed-layer clay in Gulf Coast shales has been described by Powers (1957, 1967); Burst (1959, 1969); Perry and Hower (1970); Weaver and Beck (1971); Hower et al. (1976); Freed (1981, 1982); and others. The reaction has been shown to take place in the high-temperature regime of contact metamorphism (Kramer 1981; Nadeau and Reynolds 1981; Pytte 1982; Lynch and Reynolds 1984; Lynch 1985), and has been the focus of numerous laboratory experiments (Eberl and Hower 1975, 1976, 1977; Eberl 1978; Lahann and Roberson 1980; Roberson and Lahann 1981; Inoue and Utada 1983; Bethke et al. 1986; Guven and Huang 1991; and many others). In burial-diagenetic settings, the reaction takes place over the same temperature interval as hydrocarbon maturation (Perry and Hower 1970; Johns and Shimoyama 1972). The release of interstitial water during the transforma-

tion may cause zones of overpressure and aid in petroleum migration (Hower 1981; Bruce 1984). The conversion of smectite to illite has been proposed as a major source of cements in sandstones (Hower et al. 1976; Boles and Franks 1979), and the extent of the reaction has been applied as a geothermometer (Hoffman and Hower 1979; Weaver 1979; Pollastro 1993; Huang et al. 1993).

Hower et al. (1976) showed that mixed-layer I–S is the most abundant mineral in Frio Formation shales. Inasmuch as the shale-to-sandstone ratio of the Frio Formation (and other Cenozoic units) is greater than 8:1 (Sharp et al. 1988), and since I–S is relatively common in sandstones from all but the highest-energy environments (Lynch 1996), I–S is probably the most abundant mineral in the entire unit. In fact, endmember illite, endmember smectite and their mixed-layer I–S intermediates comprise 30% of *all* sedimentary rocks (Garrels and Mackenzie 1971; Środoń 1990). Considering the abundance and very labile composition of I–S, depth-related reactions involving it must be important in the burial diagenesis of the Tertiary section of the Gulf of Mexico basin, and in other sedimentary basins throughout the world.

The goals of this investigation are: to use the most accurate X-ray diffraction (XRD) techniques available to determine the clay and whole-rock mineralogy of shale cuttings from the Frio Formation, to delineate the changes in mineralogy during burial diagenesis, to perform mass-balance calculations in an attempt to determine if shales act as open or closed systems during diagenesis and to better define the mechanism for the smectite-to-illite reaction.

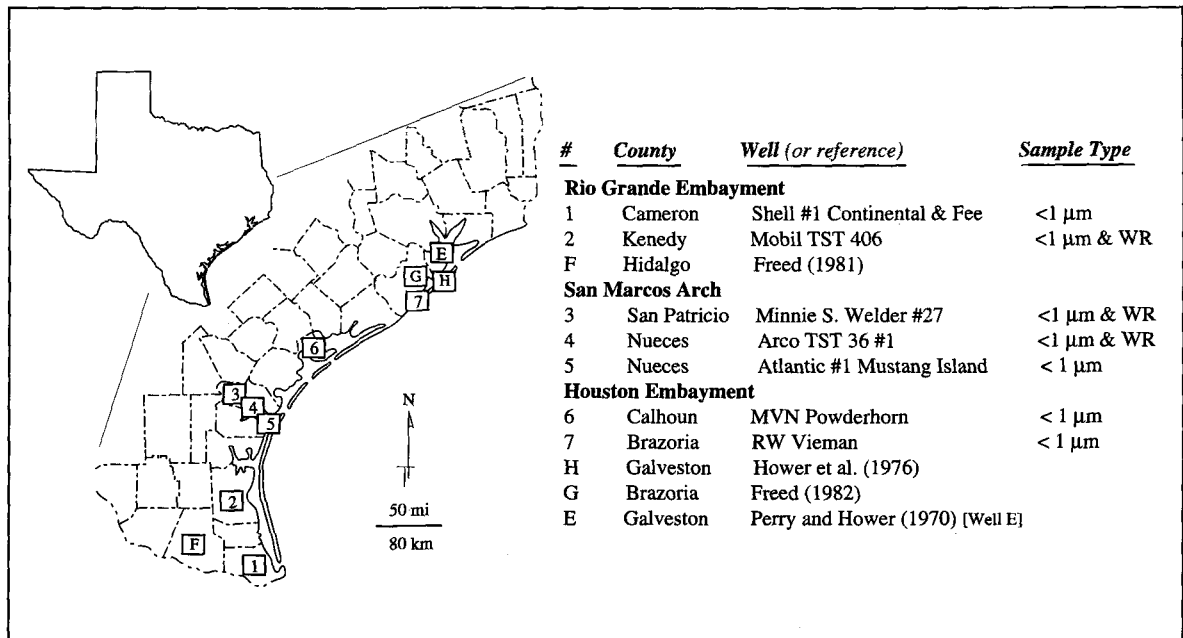


Figure 1. Location of shale cuttings samples. Frio Formation depositional systems from Galloway et al. (1982).

SAMPLE PREPARATION AND DATA INTERPRETATION

The <1- μm fraction of 102 shale cuttings collected from 7 wells was analyzed by powder XRD to determine clay mineralogy (Figure 1). The depth interval sampled was 3005 to 18,085 ft (2346 to 5512 m). Additionally, 43 cuttings samples from 3 wells (depth interval 7765 ft (2367 m) to 18,085 ft (5512 m)) were analyzed by powder XRD to determine whole-rock mineralogy. Cuttings were obtained from the collection of the Core Research Center, University of Texas at Austin. Each sample represented material hand-picked from a 30- to 90-ft (~10- to 30-m) interval; the depths reported represent the average depth for the interval. During picking, sampling was biased intentionally toward material that appears as uniform gray mudrock under binocular magnification of 10 \times to 30 \times . The samples were thoroughly washed to remove drilling mud contamination.

Samples used for clay analyses were ultrasonically disaggregated with the aid of a sodium pyrophosphate dispersant. The <1- μm fraction was removed by centrifugation and was saturated with 1 M MgCl₂. Oriented samples for XRD were prepared by the Millipore filtration technique (modified method of Drever 1973) as described in Moore and Reynolds (1989), taking great care to prevent particle-size segregation. Air-dry and glycol-solvated XRD spectra were collected using Cu radiation, 0.02 $^{\circ}2\theta$ step size, and 2-s count time (Figure 2). Quantitative analyses of the samples were determined on glycol-solvated patterns using the techniques of Reynolds (1989) and Moore

and Reynolds (1989). The characteristic XRD peak value for a mineral was corrected by dividing its area by its mineral intensity factor (MIF). The relative mineral proportions in a sample were based on the ratio of the MIF-corrected characteristic peak areas. Only samples that met the requirements for good quantitative analysis as outlined in the above references were included in this study.

Characteristic peaks used for quantification of the <1- μm fraction (Figure 2) were the I-S 002/003 peak (\blacklozenge), the illite 002 peak at 17.7 $^{\circ}$ (I), the chlorite 003 peak at 18.8 $^{\circ}$ (C) and the kaolinite 003 peak at 37.7 $^{\circ}$ (Moore and Reynolds 1989). The MIFs used to correct the I-S characteristic peaks were modified for Frio I-S chemistry (Lynch et al. 1997) by application of the NEWMOD $\text{\textcircled{C}}$ modeling program of Reynolds (1985). The percent illite (%I) layers in the I-S is based on the position of the I-S 002/003 (\blacklozenge) (Reynolds and Hower 1970).

Samples for whole-rock analysis were powdered in a ball mill in order to produce an approximately 20- to 50- μm powder, which was back loaded into sample holders. XRD data were collected using a 0.02 $^{\circ}2\theta$ step and 2-s count time (Figure 3). Quantitative analyses were performed using a method similar to that applied to the <1- μm fraction. The MIF correction factors used in the quantification of these whole-rock samples (Figure 3) were originally from Schultz (1964) and have been modified based on tests on standard mixtures, chemical analyses and computer models, and have been determined as being appropriate for quantifying the mineralogy of shales.

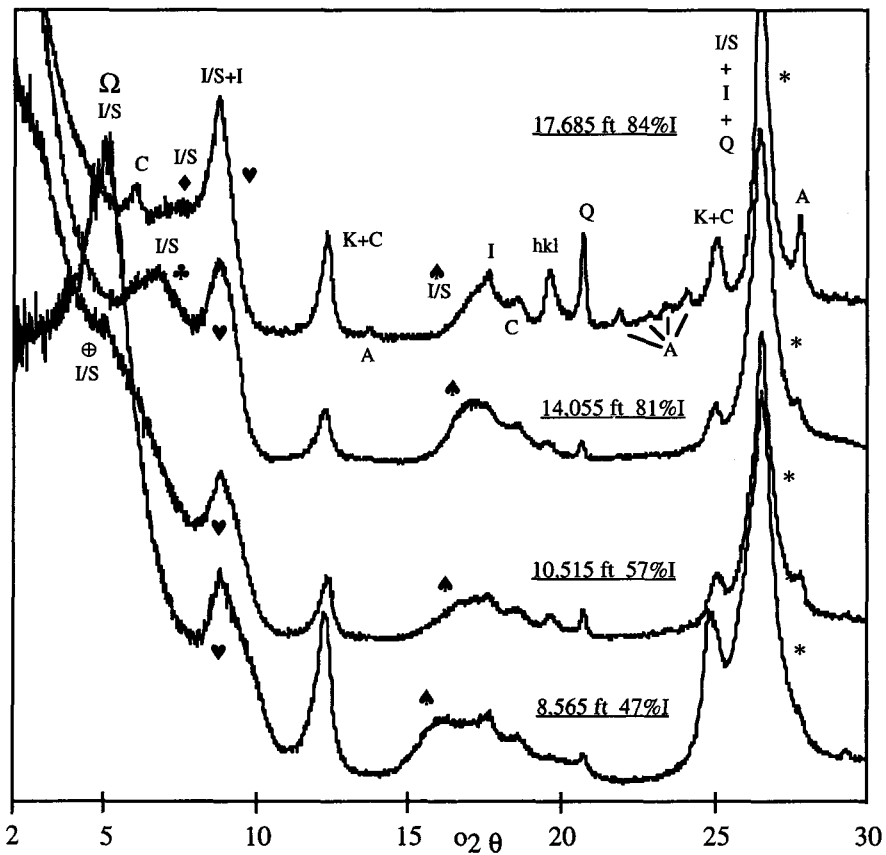


Figure 2. XRD patterns of oriented, glycol-solvated $<1\text{-}\mu\text{m}$ fraction samples. I/S=mixed-layer illite-smectite, I=illite, C=chlorite, K=kaolinite, Q=quartz, A=albite, hkl=non-basal peak common to most clays. See text for other symbols.

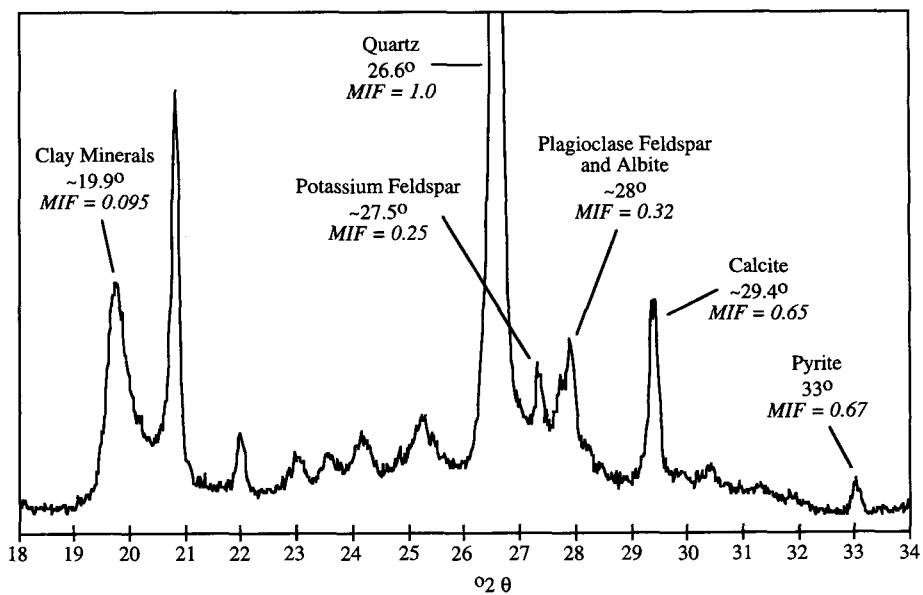


Figure 3. XRD pattern of a randomly oriented, powdered, whole-rock (WR) sample.

The I-S chemistry used in the mass-balance calculations is from analyses of nearly monomineralic $<0.1\text{-}\mu\text{m}$ fraction samples of Frio Formation shale whole cores. The laboratory procedures and XRD quantification techniques used were the same as employed in this study (Lynch et al. 1997).

The XRD techniques used to quantify both the clay mineralogy and the whole-rock mineralogy yield results that are the relative mineral proportions within the analyzed sample. This procedure forces the analysis to total 100%. For example, if the results of a clay mineral analysis of the $<1\text{-}\mu\text{m}$ fraction of shale A is 25% chlorite and 75% illite, that means that 100 g of the $<1\text{-}\mu\text{m}$ fraction of shale A is composed of 25 g chlorite and 75 g illite. It does *not* mean that shale A is 25% chlorite and 75% illite, only that the $<1\text{-}\mu\text{m}$ fraction is composed of those phases in those relative abundances, and that no other clay mineral phases can be detected in that size fraction.

Similarly, if the results of the whole-rock XRD analysis of shale A are 65% clay, 25% quartz and 10% plagioclase and albite (which are not easily differentiated by the XRD techniques employed in this study), that means that 100 g shale A contains 25 g quartz, 10 g plagioclase and albite and 65 g clay.

If we assume that the relative proportions of the different clay minerals in the total shale are the same as in the $<1\text{-}\mu\text{m}$ fraction (Hower et al. (1976) showed that the most abundant size-fraction of their samples of Frio shale cuttings was the $<2\text{-}\mu\text{m}$ fraction, and that this size-fraction was composed predominantly of clay minerals. Clay mineral analyses of the $<1\text{-}\mu\text{m}$ and $<2\text{-}\mu\text{m}$ fractions of 8 of the samples used in this study are nearly identical (Lynch 1994); therefore, the assumption that the clay mineralogy of the $<1\text{-}\mu\text{m}$ fraction approximates the clay mineralogy of the total shale, while not entirely correct, is at least a reasonable supposition), then the amount of chlorite in 100 g of shale A is 16.25 g (65 g total clay \times 25% chlorite in the fine fraction), and the amount of illite is 48.75 g (65 g total clay \times 75% illite in the fine fraction). The complete mineralogy of shale A is 49% illite, 16% chlorite, 25% quartz and 10% plagioclase and albite. The XRD analyses are listed in Tables 1 and 2.

Factors Affecting Quantitative Analysis of Clay Minerals

Some of the mineralogic data presented here, and the conclusions drawn from them, differ from earlier studies of Frio shale mineralogy (Perry and Hower 1970; Hower et al. 1976; Freed 1981, 1982). The quantitative XRD techniques used in those earlier studies are those of Johns et al. (1954) and Perry and Hower (1970). Since those methods were developed, the factors influencing XRD of clay minerals, and especially how they affect the quantitative

interpretation of XRD patterns, have been extensively investigated, principally by Reynolds (1983, 1985, 1986, 1989). Computer modeling of XRD patterns using his conventions very closely match measured XRD data. Quantitative analytical techniques summarized by Moore and Reynolds (1989), and applied in this study, take into account variables in both sample preparation and interpretation that were overlooked in the older methods. Specifically, the older quantification techniques were based on diffraction peaks now known to suffer from multiphase interferences, and used MIF values that have since been shown to be greatly in error. Also, laboratory procedures routinely applied in the 1970s and early 1980s involved settling of the clays on glass slides (Hower et al. 1976), a procedure Reynolds (1989) has shown can result in size (and therefore mineralogic) fractionation that can produce quantitative errors greater than 50% relative. The quantitative clay mineralogy techniques applied in this study yield results accurate to 10% relative for phases in abundance, and 20% relative for minor phases (Reynolds 1989).

The clay mineral abundance data in Table 1 are calculated for I-S that has 2-glycol layers in the smectite interlayer space. Although 2-glycol smectite I-S is not a natural mineral, it is what is produced during sample preparation, and what is analyzed during data collection. Application of the NEWMOD© program (Reynolds 1985) shows that, depending on the silicate-layer chemical composition, 2-glycol layers can account for $\sim 24\%$ of the weight of 2-glycol smectite. A rock that is 50% 2-glycol smectite and 50% chlorite in the laboratory is, in nature, actually composed of 43% deglycolated smectite and 57% chlorite: (50 g 2-glycol smectite/100 g laboratory sample \times 0.76 = 38 g deglycolated smectite; 38 g deglycolated smectite + 50 g chlorite = 88 g "natural" sample; 43 wt% (38 g deglycolated smectite/88 g sample) of the "natural" sample is deglycolated smectite.

A similar correction must be made for the glycol component of smectite layers in mixed-layer I-S. The dashed lines in Figure 4 are the regression lines through the Rio Grande embayment and San Marcos arch samples after correction for the glycol content of I-S. The correction is obviously much larger for low %I I-S. This correction is necessary when calculating accurate "natural" weight percents (or moles) of clay from glycol-solvated analyses performed in the laboratory. Clay mineral proportions based on the deglycolated (dashed) regression lines in Figure 4 are used to calculate the whole shale mineralogy (Table 3), and in the mass-balance calculations (Table 4). Actually, in nature, smectite interlayers are hydrated to a varying degree, depending on interlayer cation, pressure and temperature (Colten-Bradley 1987; Huang et al. 1994). However,

Table 1. Clay mineralogy of the <1- μ m fraction of Frio shales. Relative wt%. In each well, samples more shallow than depth marked "F" are Miocene.

Well	Depth (ft)	Order	%I	I-S%	Ill%	Ch%	Ko%	Well	Depth (ft)	Order	%I	I-S%	Ill%	Ch%	Ko%	
1	3,005	R = 0	0	70	9	4	16	3	14,967	R > 0	82	61	8	5	26	
	3,586	R = 0	0	42	26	8	23		15,506	R > 0	72	61	13	12	14	
	4,192	R = 0	0	18	35	16	31		16,052	R > 0	71	47	8	5	40	
	4,768	R = 0	9	59	21	7	12		16,531	R > 0	72	70	12	7	11	
	5,347	R = 0	31	54	24	8	13		17,182	R > 0	71	56	17	7	20	
	5,876	R = 0	50	66	21	10	2		17,752	R > 0	66	64	13	3	20	
	6,568	R = 0	48	63	25	9	4		4 F	5,910	R = 0	4	58	21	0	21
	7,085	R = 0	59	55	26	14	4			6,450	R = 0	21	44	13	1	42
	7,662	R = 0	56	70	19	6	4			7,080	R = 0	18	52	18	2	28
	8,180	R = 0	46	49	33	11	6			7,710	R = 0	31	61	15	1	22
	8,740	R = 0	58	59	29	7	5			8,270	R = 0	34	42	19	3	36
	9,377	R = 0	53	69	17	6	8			8,810	R = 0	45	58	13	2	27
	9,931	R = 0	56	78	13	5	4			9,350	R = 0	31	67	27	0	6
	10,482	R = 0	69	79	7	5	9			9,950	R = 0	69	75	14	0	11
	11,107	R = 0	55	66	20	1	13			10,700	R > 0	81	64	9	2	25
	11,703	R = 0	46	80	11	1	8			11,420	R > 0	74	56	22	2	21
	12,285	R = 0	69	75	13	2	10			12,620	R > 0	88	64	8	1	28
14,484	R > 0	84	45	22	6	26	13,320	R > 0		86	60	10	0	30		
14,984	R = 0	73	64	17	14	5	13,830	R > 0		77	49	21	3	27		
2	7,145	R = 0	13	48	28	7	17	14,490		R > 0	83	66	7	5	23	
	7,560	R = 0	32	64	13	5	18	5 F		12,671	R > 0	79	72	11	3	14
	8,565	R = 0	47	69	17	3	11			13,376	R > 0	79	77	7	4	12
	9,045	R = 0	61	66	22	6	5			13,960	R > 0	75	65	11	4	19
	9,525	R = 0	46	76	12	6	7		14,544	R > 0	78	77	7	5	12	
	10,035	R = 0	63	69	19	5	6		15,230	R > 0	75	69	10	4	16	
	10,515	R = 0	57	74	14	4	8		15,837	R > 0	77	80	9	4	7	
	11,055	R > 0	81	84	9	3	3		16,434	R > 0	77	79	7	4	10	
	11,670	R > 0	73	72	17	8	3		17,034	R > 0	81	90	3	3	4	
	12,135	R > 0	74	65	22	6	7		6 F	8,010	R = 0	8	54	10	1	35
	13,065	R > 0	81	79	12	4	5			10,026	R = 0	23	58	19	1	22
	14,055	R > 0	81	74	18	5	3			11,053	R = 0	56	70	8	2	20
	14,265	R > 0	81	68	24	5	3			12,050	R > 0	65	64	6	2	28
	14,715	R > 0	82	83	12	3	2			13,650	R > 0	69	68	6	3	23
	15,135	R > 0	83	79	10	8	3			14,062	R = 0	45	58	7	0	35
	15,645	R > 0	81	72	17	4	6			7 F	6,972	R = 0	23	72	10	0
	16,215	R > 0	77	77	16	3	4		7,472		R = 0	27	78	8	0	14
16,725	R > 0	82	74	13	6	6	7,965		R = 0		36	68	9	0	23	
17,145	R > 0	83	68	14	9	9	8,460	R = 0	41		69	10	0	21		
17,685	R > 0	84	82	9	6	3	9,018	R = 0	28		59	19	0	22		
18,085	R > 0	84	80	10	5	5	9,579	R = 0	33		67	10	0	24		
3 F	8,507	R = 0	10	46	23	6	26	10,135	R = 0		55	71	9	0	20	
	9,090	R = 0	46	59	10	2	29	10,624	R = 0	42	66	15	0	18		
	9,936	R > 0	75	58	7	1	35	11,120	R > 0	66	66	16	0	18		
	10,517	R > 0	73	80	7	5	9	11,654	R > 0	59	71	8	1	21		
	11,119	R > 0	81	50	12	3	35	13,000	R > 0	84	89	3	0	8		
	11,693	R > 0	72	58	11	4	27	13,600	R > 0	87	79	7	2	11		
	12,270	R > 0	80	67	8	7	18	14,035	R > 0	88	91	4	0	5		
	12,787	R > 0	79	68	11	2	18	14,605	R > 0	81	76	9	1	14		
	13,271	R > 0	74	55	10	6	29	15,175	R > 0	74	64	12	2	21		
	13,844	R > 0	82	66	8	5	21	15,704	R > 0	78	73	9	2	17		
	13,844	R > 0	82	69	7	4	20									
	14,419	R > 0	77	70	7	3	20									

the weight difference between dehydrated smectite and hydrated smectite is <10%, so errors introduced by disregarding this exchangeable water are of significantly less magnitude than those due to ignoring the glycol contribution. This correction for the glycol content of I-S was not made in the earlier studies of Frio shales.

RESULTS

Whole-Rock Mineralogy

The whole-rock abundances of clay minerals, quartz, K-feldspar and plagioclase feldspar and albite from 3 wells (from the San Marcos arch and Rio

Table 2. Whole-rock mineralogy of the silicate fraction of Frio shales. Relative wt%.

Well	Depth (ft)	Total clay%	Quartz%	K-feld.%	Plag. feld. & albite%
2	9,525	60	26	7	7
	10,035	60	26	5	9
	10,515	73	19	3	5
	11,055	72	21	0	7
	11,670	73	20	0	7
	12,615	70	21	3	6
	13,065	69	22	2	7
	14,055	64	26	2	7
	14,265	75	19	0	6
	14,715	76	18	0	5
	15,135	72	23	0	5
	15,645	69	21	3	7
	16,215	70	24	0	7
	16,725	71	22	0	6
	17,145	74	20	0	5
	17,685	78	17	0	5
17,685	76	19	0	5	
18,085	64	26	0	9	
3	9,090	63	31	2	5
	9,936	70	26	1	3
	11,119	72	24	1	4
	11,693	72	22	1	5
	12,270	73	22	1	4
	12,787	74	22	1	4
	13,271	73	22	1	4
	13,844	71	23	0	5
	14,419	71	24	1	5
	14,967	69	26	0	5
	16,052	71	23	0	5
	16,531	71	25	2	2
17,182	72	26	1	2	
4	7,710	76	18	2	3
	8,270	75	19	3	4
	8,810	80	15	3	3
	9,350	79	16	2	3
	9,950	78	17	2	2
	10,700	75	19	2	4
	11,420	76	19	2	3
	11,975	73	22	0	4
	12,620	74	22	0	4
	13,190	71	23	2	3
	13,830	70	25	0	4
14,490	66	29	0	5	

Grande embayment depocenters, (Figure 1, Table 2) are shown in Figure 5. There is little change in the quartz or total clay content of the shales with depth. The amount of K-feldspar decreases, and the amount of albite increases with depth. The relative changes in the feldspar content of the shales are the same as reported by Milliken (1992), based on scanning electron microscopy (SEM) and microprobe analyses of some of the same samples used in this study. The same relative changes in feldspar content are also seen in Frio sandstones (Loucks et al. 1984; Milliken 1989). Calcite is present in extremely variable amounts (absent to >10%) in samples from all 3 wells. Pyrite is a ubiquitous, minor (usually <1%), component of all the samples.

Clay Mineral Abundances

I-S is the most abundant clay in the <1- μ m fraction of all but a few samples (Figure 4). The abundance of I-S increases from ~55% at 5000 ft (1524 m) to ~70% at 18,000 ft (5486 m). The illite and kaolinite contents of Frio shales decrease with depth (Figure 4), though neither phase is completely absent even in the deepest samples. The greater abundance of kaolinite in shales from the San Marcos arch vs. shales from the Rio Grande embayment is probably due to a larger kaolinite-rich cratonic source contribution to the San Marcos arch shales, compared to the exclusively volcanogenic-derived source for the more southern shales (Galloway et al. 1982). Differences in the detrital composition of sandstones (feldspar- and quartz-rich sandstones in the Houston embayment, volcanic rock fragment-rich sandstones in the Rio Grande embayment, and mixed-composition sandstones in the San Marcos arch) from these depocenters are also due to provenance differences (Loucks et al. 1984; Lynch 1994; Milliken et al. 1994). Chlorite is the least abundant clay in Frio Formation shales. The abundance of chlorite increases with depth in shales from south Texas. Frio shales from the Houston embayment and especially Miocene age shales contain anomalously large amounts of chlorite, probably due to provenance differences.

Depth-related mineralogical trends observed in these shales are best explained as the result of diagenetic modification rather than preservation of initial variation in sediment composition (Perry and Hower 1970; Land et al. 1997). Some of the downhole mineralogical trends observed in this study are different than the results of earlier studies of Frio shale mineralogy and diagenesis (Table 5). Although detrital compositional differences surely existed between shales from the different depocenters (most of the previous analyses were of shales from the Houston embayment, Figure 1), data from well 7, which is located within the Houston embayment depocenter and close to the sites of the previous studies, show the same relative mineralogical trends with depth as the shales from the San Marcos arch and Rio Grande embayment (Table 1). Because of improvements in sample preparation and quantification techniques (described above), it is likely that the mineralogical data determined in this study more accurately reflect the correct composition of Frio shales.

%I in I-S

The most significant and striking diagenetic change with depth in the clay mineralogy of the samples is the increase in the %I of the mixed-layer clay (Figure 6). Figure 2 shows examples of XRD patterns of oriented, glycol-solvated, <1- μ m fraction samples. The large 17-Å (marked Ω) peak in the pattern from 8565

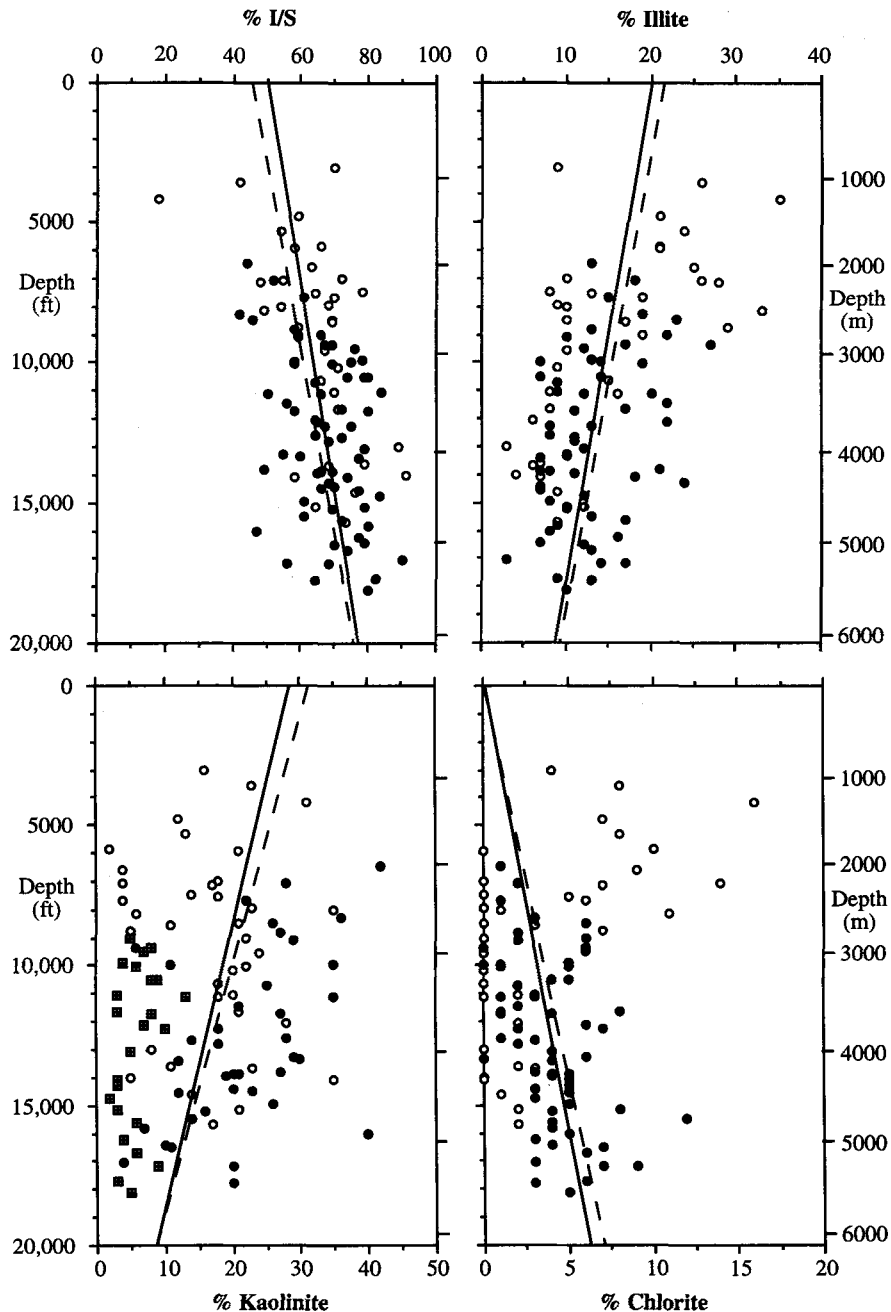


Figure 4. Clay mineral abundances in the $<1\text{-}\mu\text{m}$ fraction. Relative wt%. For kaolinite, ● indicates Frio shales from the San Marcos arch and ⊞ indicates Frio shales from the Rio Grande embayment. For I-S, illite and chlorite, ● indicates Frio shales from the San Marcos arch and Rio Grande embayment. For all clays, ○ indicates Frio shales from the Houston embayment and Miocene-age shales from all regions. The solid line is the regression line through the Rio Grande embayment and San Marcos arch samples (Table 1). The dotted line is explained in the text.

ft indicates random I-S interstratification. The intensity of this peak is diminished and its position has moved to slightly higher 2θ (marked ⊕) in the pattern from 10,515 ft, which indicates a less-random arrangement of the component smectite and illite layers in this sample. The position of the 002/003 peak (marked ◆

in all patterns) corresponds to 47%I in I-S in sample 8565 ft and 63%I in sample 10,515 ft. In the pattern from 14,055 ft, the 17-Å random interstratification peak is replaced by an I-S 002* superlattice peak at $\sim 13\text{ \AA}$ (marked ♣) indicating R1 (ISIS) ordering. The position of the 001/004* superlattice peak (marked ◆

Table 3. Shale mineralogy. Weight percent of the silicate fraction of Frio Formation shales at 7000 ft (2133 m) and 15,000 ft (4572 m). Calculated from regression lines in Figures 4 and 5. I-S at 7000 ft is ~20%I, I-S at 15,000 ft is $\geq 80\%I$.

Mineral	7000 ft	15,000 ft	Relative change
Quartz	20.7	22.6	+9%
K-feldspar	3.1	0.7	-77%
Plagioclase feldspar	3.9	0.0	-100%
Albite	0.0	5.2	+100%
I-S	41.3	49.3	+19%
Illite	12.4	8.8	-29%
Kaolinite	16.8	9.7	-42%
Chlorite	1.8	3.7	+105%

at $\sim 11 \text{ \AA}$ in the pattern from 17,685 ft denotes the presence of a large component of R3 (ISII) ordering in the I-S. Kalkberg (R3) ordering is present in samples deeper than $\sim 12,000 \text{ ft}$ ($\sim 3257 \text{ m}$).

Figure 6 shows that I-S composition remains constant after reaching $\sim 80\%I$. Perry and Hower (1970), Hower et al. (1976), and others have interpreted similar increasing %I trends as evidence that I-S reaction ceases at 80%I composition; however, there are several lines of evidence that suggest that I-S continues to react throughout burial.

The I-S in the sample from 14,055 ft is 81%I (Figure 2). The I-S in the sample from 17,685 ft is 84%I. These %I values are essentially the same; however, the stacking order of the component layers in the 2 samples is greatly different. This change in I-S order type from $R = 1$ to $R = 3$ indicates that the I-S continued to react, at least structurally, throughout burial. More evidence for continuous reaction of I-S is XRD peak-width measurements that show crystallographic annealing (Klug and Alexander 1974; Moore and Reynolds 1989) in samples deeper than $\sim 11,000 \text{ ft}$ (3353 m), the depth where I-S composition became $\sim 80\%I$ (Figure 7).

More compelling evidence of I-S reaction past 80%I composition comes from analyses of I-S sam-

ples from Frio Formation shale whole core. Figure 8 shows that the %I in I-S in both the $<0.1\text{-}\mu\text{m}$ fraction and 0.1- to $<2\text{-}\mu\text{m}$ fraction increases past 80%I to almost 100%I. Chemical analyses of the same, essentially monomineralic, $<0.1\text{-}\mu\text{m}$ fraction samples also show changes (increased K_2O , Al/Si, Fe^{2+}/Fe^{3+} and decreased $\delta^{18}O$) throughout burial (Lynch et al. 1997). How can these data be reconciled with the XRD analyses of I-S in the $<1\text{-}\mu\text{m}$ fraction samples from shale cuttings (Figures 2 and 6)?

Why shale cuttings behave differently from shale core is one of the great unanswered questions of clay mineralogy (personal communication D. Pevear 1995). The most important reason for the 80%I limit of I-S from shale cuttings is probably the nature of the cuttings samples themselves. The analyzed samples are a mixture of materials from an interval as large as 90 ft ($\sim 30 \text{ m}$), and, as such, contain a heterogeneous combination of I-S with different %I, order type and companion mineralogies, all of which affect the diffraction characteristics of the samples in a dissimilar way. As pointed out by Hower (1981), "Cuttings yield data that allow a simpler, more straightforward interpretation of diagenetic changes . . . but it should be kept in mind that the data are averages of a more variable set." Still, why this "average" value remains more or less constant at 80%I, and does not increase, even at depths as great as 18,000 ft ($\sim 5500 \text{ m}$) remains unclear. Nevertheless, the data presented here (ordering changes and crystallinity increases in I-S from the deeper cuttings, and XRD and chemical analyses of pure I-S separates) indicate that the mixed-layer clay does not simply stop reacting at 80%I.

Temperature is considered to be the primary factor controlling the smectite-to-illite reaction (Eslinger and Pevear 1988; Eslinger and Glasmann 1993). In these Frio Formation shales, I-S became ordered between 60%I and $\sim 75\%I$, at depths between ~ 9500 and 12,000 ft (~ 2900 and 3657 m), and temperatures between 110 and 130° C (Figure 6; Table 1). This temperature range is similar to that reported in previous

Table 4. Mass-balance calculation. Δ is the change in shale mineralogy between 7000 ft (2133 m) and 15,000 ft (4572 m) from Table 3 (as $10^{-2} \text{ mol}/100 \text{ g}$ shale). Chemical changes are calculated from Δ and the mineral chemistry in Table 6. Difference values in parentheses are g/100 g shale.

Mineral	Δ	SiO_2	Al_2O_3	K_2O
Quartz	3.16	3.16	—	—
K-feldspar	-0.86	-2.59	-0.43	-0.43
Plagioclase feldspar	-1.46	-3.94	-0.95	—
Albite	1.98	5.95	0.99	—
I-S ($\sim 20\%I$)	-10.93	-42.42	-8.36	-0.66
I-S ($\sim 85\%I$)	12.59	42.94	14.29	4.09
Illite	-0.91	-3.10	-1.07	-0.34
Kaolinite	-2.75	-5.50	-2.75	—
Chlorite	0.27	0.79	0.39	—
Difference		-4.70 (-2.82)	2.11 (2.15)	2.66 (2.51)

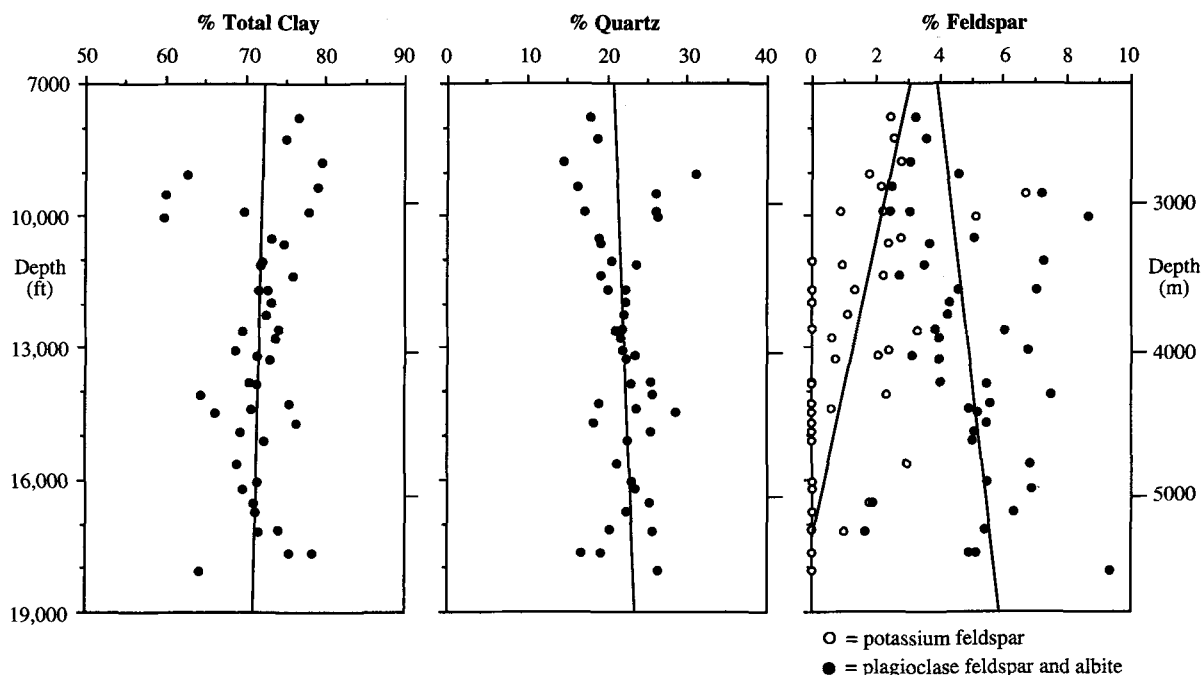
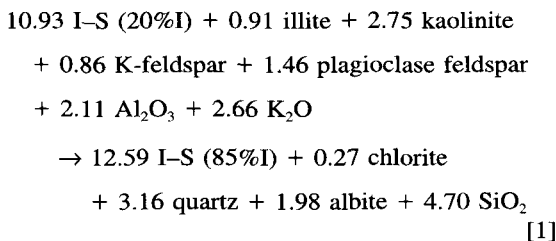


Figure 5. Whole-rock abundances in the silicate fraction of Frio shales. Relative wt%. Regression lines through the data from Table 2.

studies of I-S in Frio shales (Hower et al. 1976; Freed 1981, 1982).

SHALE MASS BALANCE AND BASIN DIAGENESIS

Table 3 shows the calculated mineralogic composition of the silicate fraction of Frio Formation shales at 7000 ft (2133 m) and 15,000 ft (4572 m). Table 4 shows the molar changes in shale mineralogy, and the SiO_2 , Al_2O_3 and K_2O mass balance over the same burial depth range. The data show that the diagenetic mineralogic changes in Frio shales result in an excess of SiO_2 , and require additional Al_2O_3 and K_2O . Equation [1], (which disregards Ca, Na, Mg, Fe and H_2O) shows this data:



Are these mineralogic and chemical changes reasonable? Whole-rock chemical analyses of many south Texas Frio shales show a K_2O increase of the same order of magnitude as predicted by Equation [1] (Land et al. 1995, 1997). Milliken et al. (1994) show that K_2O is lost from Frio sandstones during diagenesis due

to K-feldspar dissolution. However, given the relative proportions of the 2 rock types, there must be an additional source for the K_2O required by the mineralogic changes in the shales. A K_2O increase with depth has also been identified in Wilcox shale of the Texas Gulf Coast (Awwiller 1993).

Petrographic and chemical analyses of Frio sandstones indicate that they lose Al_2O_3 during diagenesis due to feldspar and rock fragment framework grain dissolution (Loucks et al. 1984; Land et al. 1987; Milliken et al. 1994). If this Al is exported to the shales, where a gain of Al is required for the mineralogic changes therein (Table 4, Equation [1]), then chemical data for both of these elements show that the diagenesis of sandstones and shales is closely related and that, during diagenesis, shales act as sinks for K_2O and Al_2O_3 .

Equation [1] shows that shale diagenesis results in a loss of SiO_2 (irrespective of the small increase in the quartz content of deep shales), and, in fact, whole-rock chemical analyses of Frio Formation shales do show a decrease in SiO_2 with depth (Land et al. 1997). The amount of SiO_2 made available by loss from shales is more than the amount of diagenetic quartz found in the associated Frio sandstones (2.82 g $\text{SiO}_2/100$ g shale divided by 2.65 g/cc = 1.06 cc SiO_2 available per 100 g shale). Also, 12.5 g Frio sandstone/100 g Frio shale (the shale-to-sandstone ratio of the Frio Formation is 8:1 (Sharp et al. 1988)) divided by 2.65 g/cc = 4.72 cc Frio sandstone per 100 g shale. Continuing,

Table 5. Analyses of Frio shale diagenesis. Downhole mineralogic trends from this study and previous analyses of Frio Formation shales (Figure 1). "+" = increase with depth, "-" = decrease with depth, "nc" = no change.

Reference	I-S	Illite	Kaolinite	Chlorite	Quartz	K-spar	Plag./albite
This study	+	-	-	+	nc	-	+
Hower et al. (1976) CWRU 6	-	-	-	+	+	-	+
Perry and Hower (1970) Well E	nc	-	nc				
Freed (1981) Dixie Mortgage	-	-	+	+	nc	nc	+
Freed (1981) A. A. McAllen	-	-	+	+	nc	nc	+
Freed (1982) Pleasant Bayou	+	-	nc		+	-	+
Freed (1982) #2 Tx state lease	-	nc	+		+	nc	+

1.06 cc SiO₂ available/100 g shale divided by 4.72 cc Frio sandstone/100 g shale = 22 vol% SiO₂/cc Frio sandstone. Petrographic analyses indicate that the diagenetic-quartz content of south Texas Frio sandstones (which do not have an autochthonous SiO₂ source) averages ~3 vol%, though distal-shelf-facies sandstones, which are surrounded by large amounts of shale, sometimes contain >10 vol% (and as much as 26%) authigenic quartz overgrowths (Loucks et al. 1984;

Lynch 1996). This relationship again suggests that the diagenesis of the sandstones and shales is closely related, and that during diagenesis the shales act as the sources of SiO₂ for diagenetic quartz in the sandstones.

Mud weight data from well log headers, and regional information from Bebout et al. (1975, 1978), indicate that "hard" overpressure is reached between ~8500 and 12,000 ft (2591 and 3657 m) in most of these wells. This is approximately the same depth interval over which I-S structure changed from random-interstratified to ordered-interstratified (Figure 6, Table 1). Maximum water expulsion, and therefore maximum dissolved-elemental transport from the shales, also occurred when the I-S structure changed from random-interstratified to ordered-interstratified (Burst 1969; Perry and Hower 1972; Hower et al. 1976). In these wells the minimum depth to I-S ordering corresponds to a burial temperature of ~110 °C.

Most of the diagenesis of Frio Formation sandstones occurred in what currently is the high-pressure-gradient transition zone between formation-water hydro-pressure and lithopressure (Lynch 1996). The δ¹⁸O composition of authigenic quartz overgrowths in the sandstones indicates that this diagenetic mineral precipitated from formation water with a temperature of ≥ 110 °C. This temperature is significantly hotter than the burial temperature of the sandstones at the depth at which quartz overgrowths become abundant (75 °C at 6000 ft (~1830 m)), implying that the diagenetic quartz precipitated from hot water derived 1 km or more deeper in the section, at approximately the depth and temperature that the I-S became ordered (≥9500 ft, ~2900 m), and the maximum amount of water (and dissolved Si) was released from the shales (Lynch 1996).

The coincidence of the relationships between I-S structural change and 1) maximum water expulsion (and dissolved Si transport) from shales; 2) diagenetic quartz (in sandstones) with isotopic evidence of upward fluid flow; and 3) the development of formation-water overpressure (and the commencement of diagenesis in the sandstones), indicates that reaction of the I-S in the shales is not only the source of the authigenic SiO₂ in the sandstones (Table 4), but is probably also largely responsible for the variable pres-

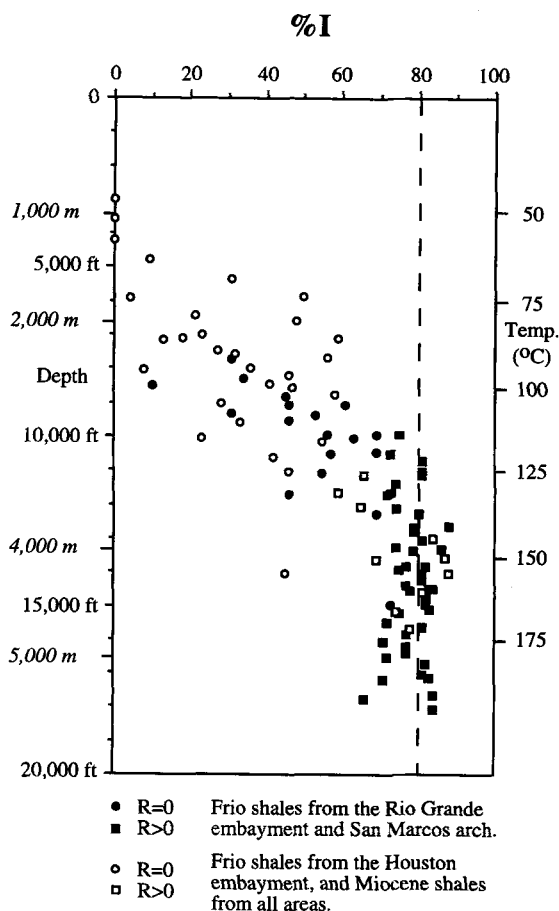


Figure 6. I-S composition (%I) of the <1- μ m fraction of shale cuttings. Temperatures are based on well-log header data from wells in the San Marcos arch area, and have been corrected according to the technique of Kehler (1971).

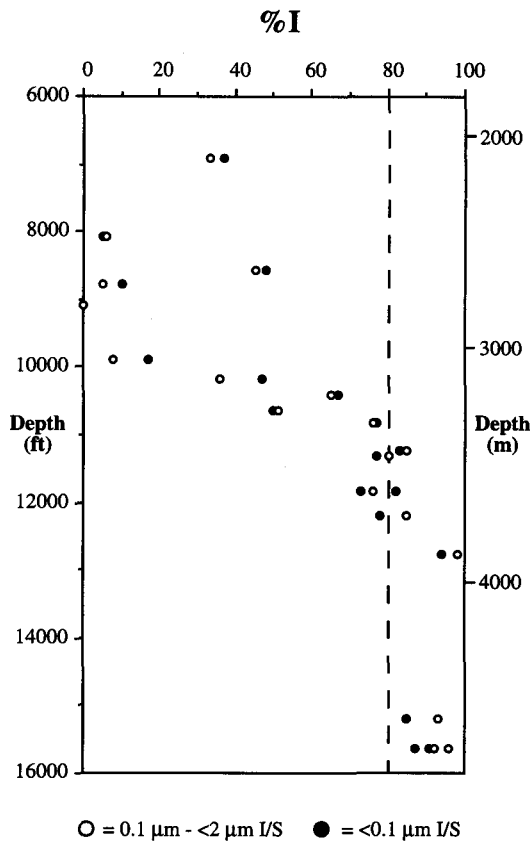
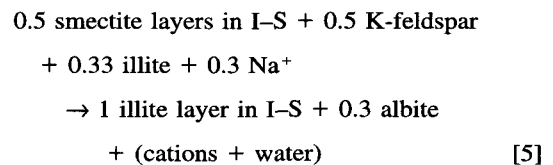


Figure 8. I-S composition (%I) of shale core samples. Samples from Lynch et al. (1997).

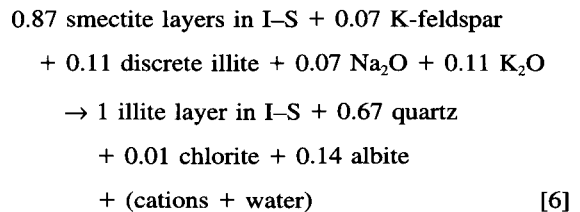
icate layers (Table 6), as well as in the oxygen isotopic composition of the mineral, imply that the conversion of smectite layers to illite layers in I-S is a dissolution and reprecipitation (and $\delta^{18}\text{O}$ re-equilibration) reaction, and not a simple transformation (Lynch et al. 1997). The Al-conservative, smectite-cannibalization reaction of Equation [4] calls for significantly less I-S after the conversion of smectite layers to illite layers; however, Figure 4 and Table 3 show that the amount of I-S in Frio shales increased as the composition of the I-S became more illitic. Additionally, there is no evidence, in the shales or the sandstones, for the very large amount of diagenetic quartz produced by this reaction.

Both the reaction of Equations [3] and [4], and the I-S chemistry calculated by Boles and Franks (1979), are based on the quantitative data of Hower et al. (1976), which have been shown to be suspect (Table 5). It is interesting that, in a discussion of the reaction proposed by Boles and Franks (1979), Hower himself had doubts about the accuracy of that data: "The points plotted on this graph are the relative I-S concentration that Boles and Franks have derived from the data of Hower et al. Assuming that the analyses are sufficiently accurate to draw a conclusion, their suggestion may be correct" (Hower 1981).

The mineralogic changes determined in this study do not support either Equation [3] or [4], and are similar to the illite neoformation reactions proposed by Lynch (1985) for contact metamorphic shales:



and Awwiller (1993) for the burial diagenesis of Wilcox shales:



CONCLUSIONS

State-of-the-art quantitative XRD analyses of shale samples of the Frio Formation show that burial diagenesis of the rocks resulted in an increase in the abundance of I-S, albite and chlorite, and a decrease in the abundance of K-feldspar, illite and kaolinite. The mineralogic data show that the transformation of smectite layers to illite layers in I-S is a neoformation reaction, and neither a simple transformation (Hower et al. 1976), or an I-S volume-reducing Al-conservative reaction (Boles and Franks 1979). There is min-

Table 6. Mineral chemistry used in mass-balance calculations. Plagioclase chemistry from Milliken (1989), chlorite from Genuise (1991), illite modified after Hower and Mowatt (1966). I-S chemistry is from Lynch et al. (1997).

Quartz	SiO_2
K-feldspar	KAlSi_3O_8
Plagioclase feldspar	$\text{Na}_{0.7}\text{Ca}_{0.3}\text{Al}_{1.3}\text{Si}_{2.7}\text{O}_8$
Albite	$\text{NaAlSi}_3\text{O}_8$
I-S ~20%I (at 7000 ft)	$\text{K}_{0.12}\text{Na}_{0.25}(\text{Al}_{1.41}\text{Fe}_{0.22}\text{Mg}_{0.41})(\text{Si}_{3.88}\text{Al}_{0.12})\text{O}_{10}(\text{OH})_2$
I-S ~85%I (at 15,000 ft)	$\text{K}_{0.65}\text{Na}_{0.08}(\text{Al}_{1.68}\text{Fe}_{0.14}\text{Mg}_{0.20})(\text{Si}_{3.41}\text{Al}_{0.59})\text{O}_{10}(\text{OH})_2$
Illite	$\text{K}_{0.75}(\text{Al}_{1.75}\text{Fe}_{0.1}\text{Mg}_{0.2})(\text{Si}_{3.4}\text{Al}_{0.6})\text{O}_{10}(\text{OH})_2$
Kaolinite	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$
Chlorite	$(\text{Al}_{1.77}\text{Fe}_{3.27}\text{Mg}_{0.96})(\text{Si}_{2.89}\text{Al}_{1.11})\text{O}_{10}(\text{OH})_8$

eralogical and chemical evidence that I-S does not stop reacting when it reaches ~80%I composition.

Combined with chemical analyses of I-S from Frio shale core samples (Lynch et al. 1997), the data presented here show that shale diagenesis is an open-system process that requires addition of K_2O and Al_2O_3 to the shales, and results in a loss of SiO_2 from the shales. The amount of SiO_2 made available by shale diagenesis is sufficient to be the source of the quartz-overgrowth cements in the associated Frio sandstones.

The relationships between I-S diagenesis and fluid flow from shales into sandstones, generation of abnormal formation-water fluid pressure, onset of sandstone diagenesis and distribution of authigenic phases in sandstones, indicate that reaction of the I-S in shales is one of the most important components of the sandstone/shale/formation-water diagenetic system.

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