

BURIAL DIAGENESIS IN GULF COAST PELITIC SEDIMENTS

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(Received 16 December 1969)

Abstract—Subsurface samples of shales ranging in age from Pleistocene to Eocene obtained from five Gulf Coast oil wells were examined mineralogically and chemically to determine the nature and extent of burial diagenesis in pelitic sediments. Illite/montmorillonite dominates the mineralogy and undergoes a monotonic decrease in expandability from about 80 to a limit of 20 per cent montmorillonite layers with increasing depth. The interstratification changes from random to ordered at about 35 per cent expanded layers. Discrete illite and kaolinite phases are ubiquitous and judged detrital. The discrete illite (mica) content of the whole rock decreases with depth, while the kaolinite shows no systematic variation. Chlorite occurs in appreciable amounts in only one well and there only in samples from the shallow water facies. This chlorite is also considered detrital.

Whole rock chemical analyses show no systematic variation with depth except for a decrease in calcium and magnesium caused by solution of carbonate. In contrast, potassium increases progressively with depth in the clay-size fraction, indicating a redistribution of potassium within the rock. Detrital illite (mica) seems to break down with increasing depth, thereby supplying potassium for interlayer fixation in illite/montmorillonite as the proportion of illite layers increases. The diagenetic reaction is independent of the geologic age of the sediments and of stratigraphic boundaries. Temperature seems to be more important than pressure in governing the reaction.

INTRODUCTION

THE PETROLOGIC interpretation of clay mineral assemblages in ancient sediments depends strongly on our understanding of the effects of burial diagenesis. Of particular interest is the proposed diagenetic conversion of montmorillonite to illite under conditions of deep burial. Burst (1959, 1969), in studying Gulf Coast sediments, noted a progressive modification in the structure of montmorillonite and its eventual disappearance with increasing burial depth. In his earlier paper, the proposed mechanism was a benification of degraded and fragmental mineral lattices by gradual fixation of potassium and magnesium to form illite and chlorite respectively. Powers (1959, 1967) considered the loss of montmorillonite with depth in Gulf Coast sediments as a conversion to illite by the substitution of Mg^{+2} for Al^{+3} in the silicate structure, with the consequent fixation of interlayer potassium. Burst (1969) has since re-interpreted his data and concluded that montmorillonite is compositionally unchanged by burial, the structural conversion involving only dehydration to one water layer.

Dunoyer de Segonzac (1965) in a study of 4000 m section of Upper Cretaceous shales in the African Cameroun concluded that with increasing

depth of burial montmorillonite is converted to illite through an intermediate mixed-layered phase. Kaolinite decreases in abundance and is eventually lost, while chlorite appears and then increases in abundance. Other workers have noted the lack of non-interlayered montmorillonite in deeply buried sediments (Powers, 1959; Weaver, 1960, 1961).

Virtually all of the earlier studies consisted only of X-ray diffraction determinations of the distribution of clay minerals as a function of depth. Dunoyer de Segonzac (1965) does include some chemical analyses of unfractionated sediments, but unfortunately omits the alkalis. Furthermore, as will be seen below, a re-interpretation of the X-ray diffraction characteristics of mixed-layered clays leads to a somewhat different understanding of the mineralogical changes involved. Nevertheless, there is in the literature substantial evidence that deep burial results in the diagenetic conversion of montmorillonite to illite; other diagenetic changes may include the destruction of kaolinite and the formation of chlorite. This research represents an attempt to examine the validity of these conclusions by a detailed mineralogical and chemical study of deeply buried pelitic sediments.

SAMPLES STUDIED

Subsurface, washed well cutting samples from five Gulf Coast oil wells were supplied by the Pan American Petroleum Corp. Well *E* is in Galveston

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County, Texas, and contains Oligocene sediments from the Anahuac and Frio formations. Well *B* is in Harris County, Texas, with sediments ranging in age from Lower Oligocene to Middle Eocene, encountering the Vicksburg through the Wilcox formations. Wells *A*, *C* and *D* are Louisiana offshore wells whose locations must remain classified. Well *A* contains mostly Pleistocene sediments; Well *C*, mostly Miocene. All the cuttings were shales, often calcareous, and more than 120 individual samples were examined.

ANALYTICAL TECHNIQUES

The well cuttings were ultrasonically disaggregated and oriented diffraction specimens of the $<1\ \mu$ and smaller size fractions prepared by the method of Kinter and Diamond (1956). Air-dried and ethylene-glycol solvated samples were analyzed by X-ray diffraction; only the latter are presented here for they provide the most readily interpretable patterns of the mixed-layered phase. In addition, most samples were heated to 550°C and 400°C for 1 hr; potassium saturated samples were prepared with 1N KCl.

Nineteen whole rock and six $<1\ \mu$ fraction Well *E* samples were analyzed for major constituents by vacuum X-ray emission spectroscopy, except for sodium and magnesium, which were done by atomic absorption spectrophotometry. The samples for X-ray analysis were fused with a light element dilutant, $\text{Li}_2\text{B}_4\text{O}_7$, and pelletized; a computer program was employed for matrix corrections. In addition, potassium analyses were carried out on all the oriented diffraction specimens. Here no matrix correction was employed and values averaged about 0.3 per cent lower for the same samples prepared by the fusion technique.

Eight Well *E* samples were treated to destroy potassium dioctahedral micas in order to determine the portion of whole rock potassium bound in the alkali feldspar (Reynolds, 1963). Samples were prepared for potassium analysis by the fusion technique.

X-RAY DIFFRACTION RESULTS

Representative X-ray diffraction patterns from two of the five wells (*E*, *B*) are shown in Figs. 1, 3, 4, 9 and 10; all are oriented specimens, and except for a few specially treated samples, are ethylene-glycol solvated. The general mineralogy of samples from all of the wells is quite similar and dominated by illite/montmorillonite, with lesser amounts of kaolinite and discrete illite, and, occasionally, small amounts of quartz, feldspar and calcite. Some samples are unavoidably too thin (see Fig. 3, *E*-7418 ft) and the quartz and feldspar peaks arise from the ceramic plate on which the sample

is mounted. Chlorite is generally not present in amounts detectable by acid removal or heat treatments. Notable exceptions are the deeper samples of Well *B* which are discussed below. Potassium saturation treatment indicated no detectable interlayered vermiculite present.

In order to determine the amount of material in the clay size fraction and mineralogic variations with particle size, Well *E* samples from depths of 8450, 9580, 11360 and 14365 ft were quantitatively size fractionated into the >20 , 5–20, 1–5 and $<1\ \mu$ ranges (Table 1 and Fig. 1). About 70 per cent of the rock by weight is in the $<1\ \mu$ fraction, and this fraction is dominated by illite/montmorillonite. Illite, quartz and feldspar increase in abundance with increasing grain size, the latter two minerals dominating the 5–20 and $>20\ \mu$ fractions. Discrete illite (mica) in the $<1\ \mu$ fractions decreases in abundance with increasing samples depth; no other variations were correlative with depth except for the nature of the illite/montmorillonite.

A quantitative estimation of the absolute amounts of each clay mineral species is notoriously difficult and unreliable (Johns, Grim and Bradley, 1954; Schultz, 1964; Weaver, 1958; Freas, 1962). However, relative and absolute abundances are of considerable importance to this study, and determinations were attempted using the calculations described below. We decided to use the relative

Table 1. Well *E* size fractionation results

	Wt. %	%K ₂ O	Total %K ₂ O in 1–20 μ
<i>E</i> -8450':			
> 20 μ	6.4	n.d.	1.57
5–20 μ	5.5	1.07	
1–5 μ	12.8	1.83	
< 1 μ	75.3	2.55	
<i>E</i> -9580':			
> 20 μ	2.4	n.d.	1.66
5–20 μ	9.6	0.97	
1–5 μ	19.1	2.10	
< 1 μ	69.0	2.55	
<i>E</i> -11,360':			
> 20 μ	4.5	n.d.	1.35
5–20 μ	11.8	0.84	
1–5 μ	20.9	1.64	
< 1 μ	62.3	3.79	
<i>E</i> -14,335':			
> 20 μ	3.1	n.d.	1.36
5–20 μ	8.1	1.03	
1–5 μ	21.6	1.48	
< 1 μ	67.2	3.66	

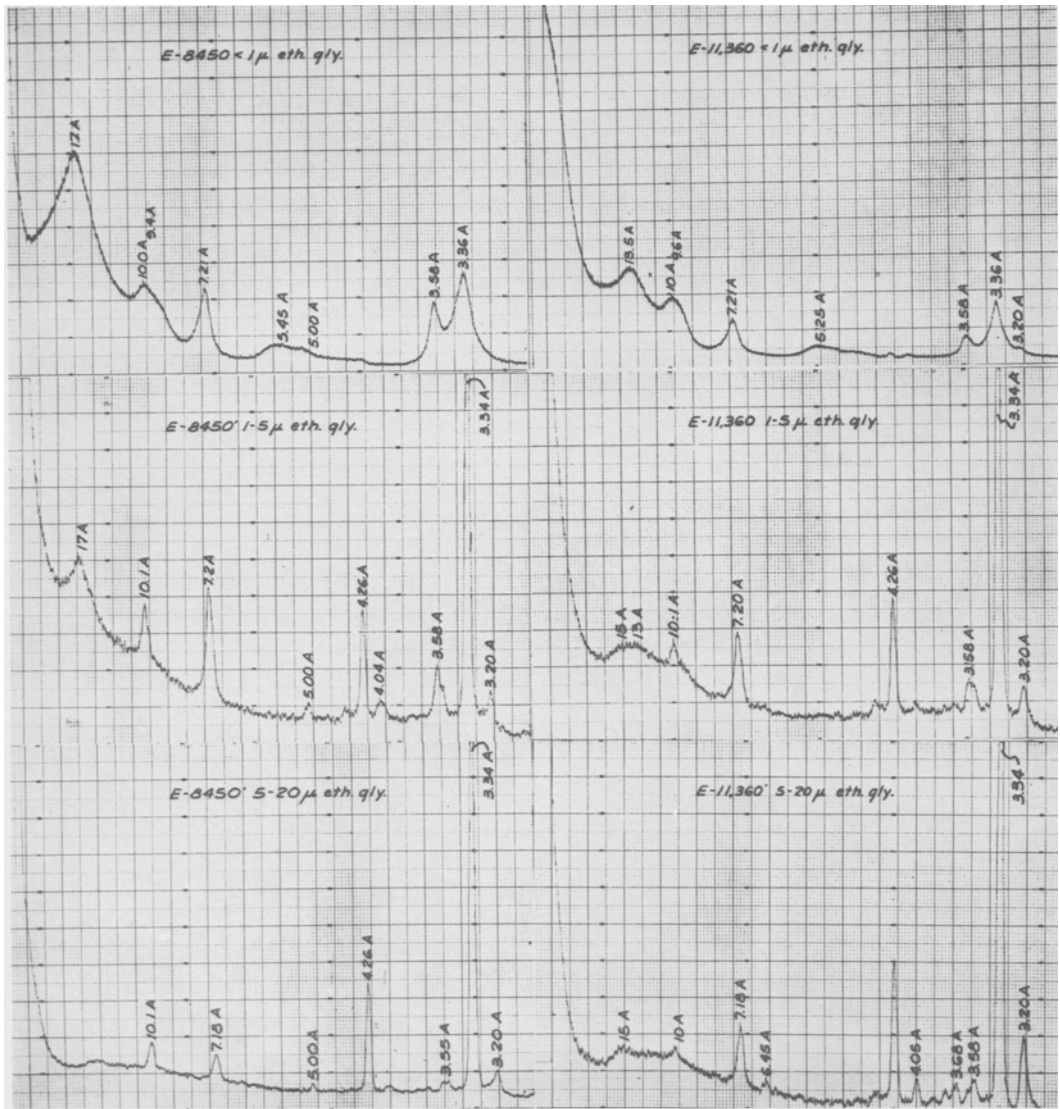


Fig. 1. X-ray patterns of well E. Size fractionated samples.

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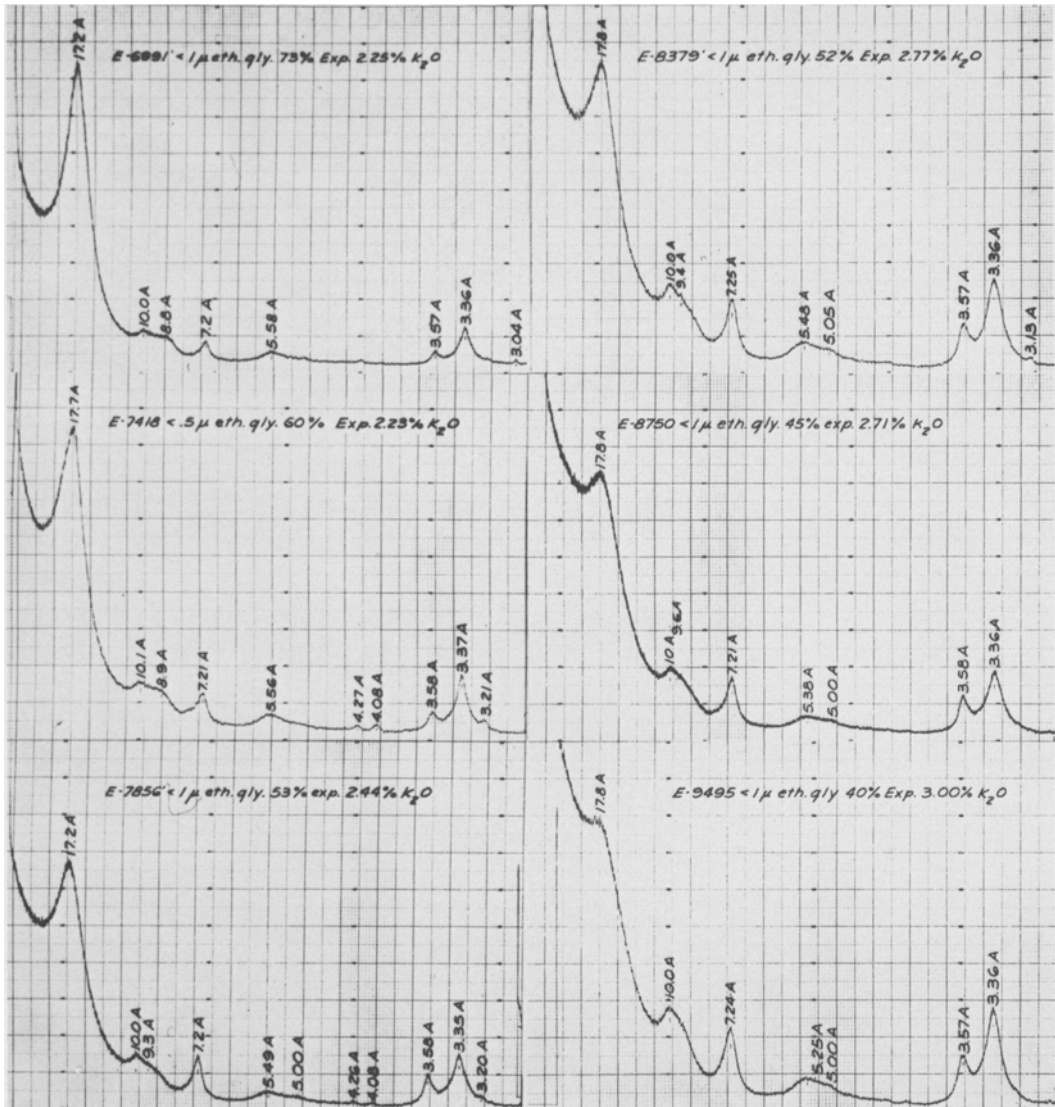


Fig. 3. X-ray patterns of well E depth sequence.

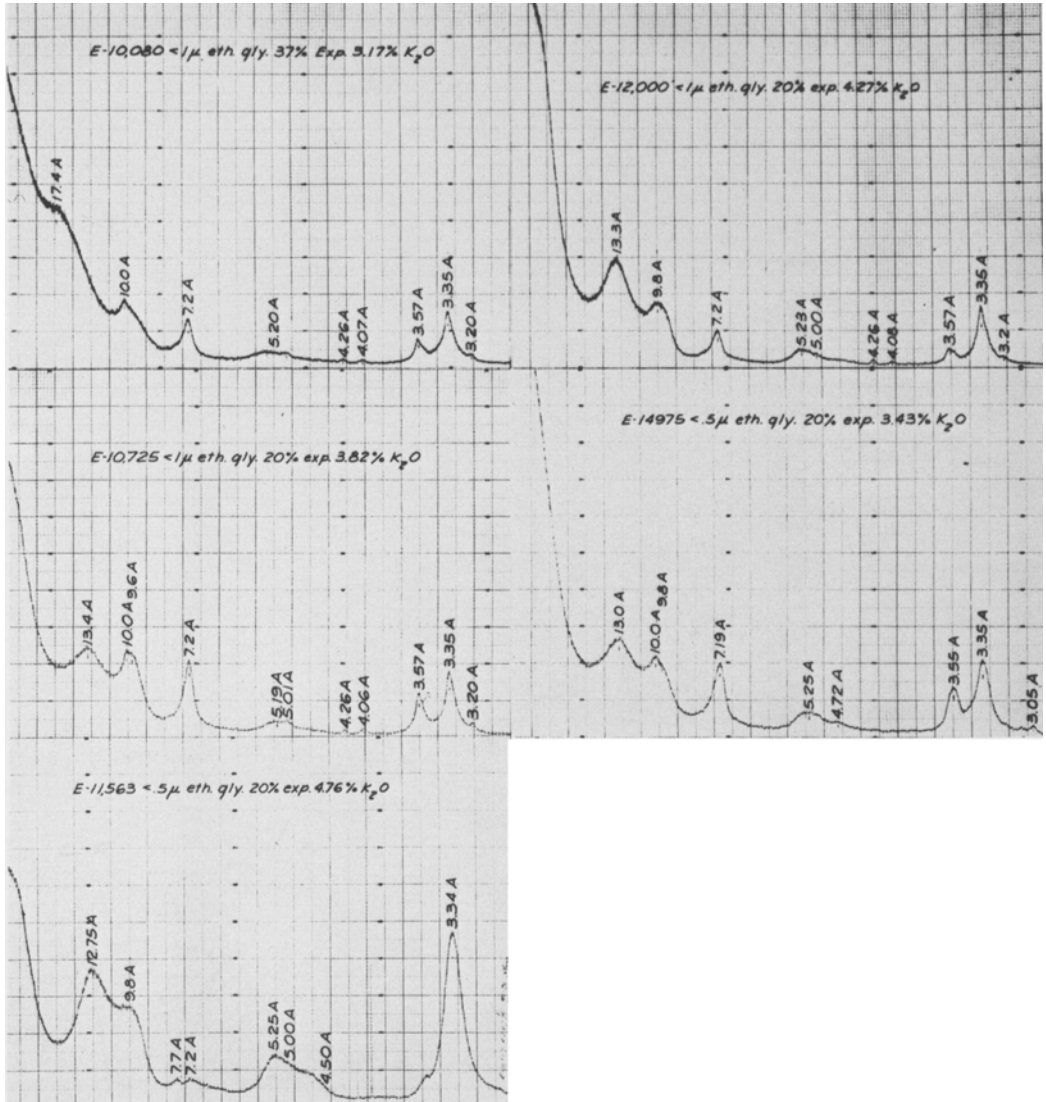


Fig. 4. X-ray patterns of well E depth sequence (cont.).

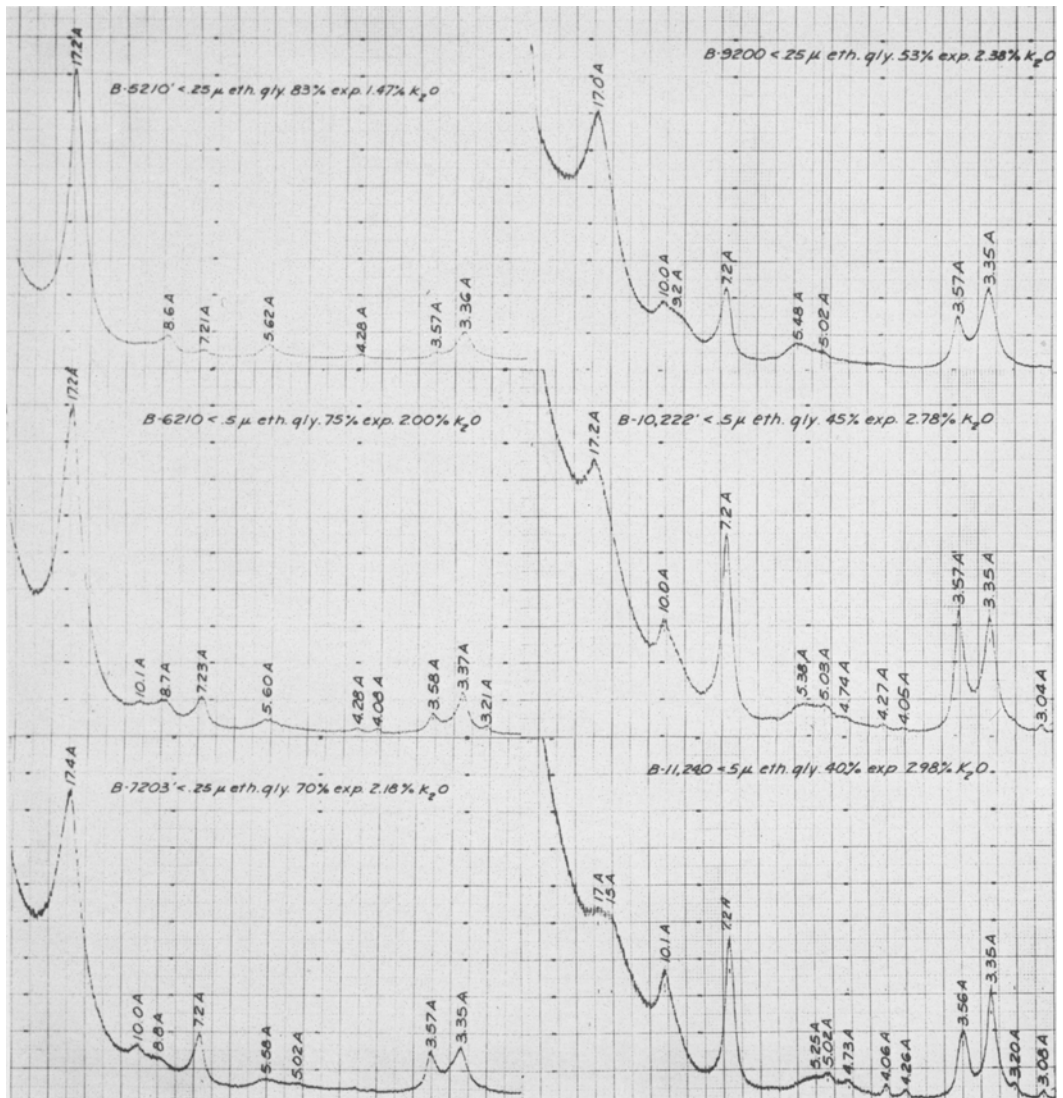


Fig. 9. X-ray patterns of well B depth sequence.

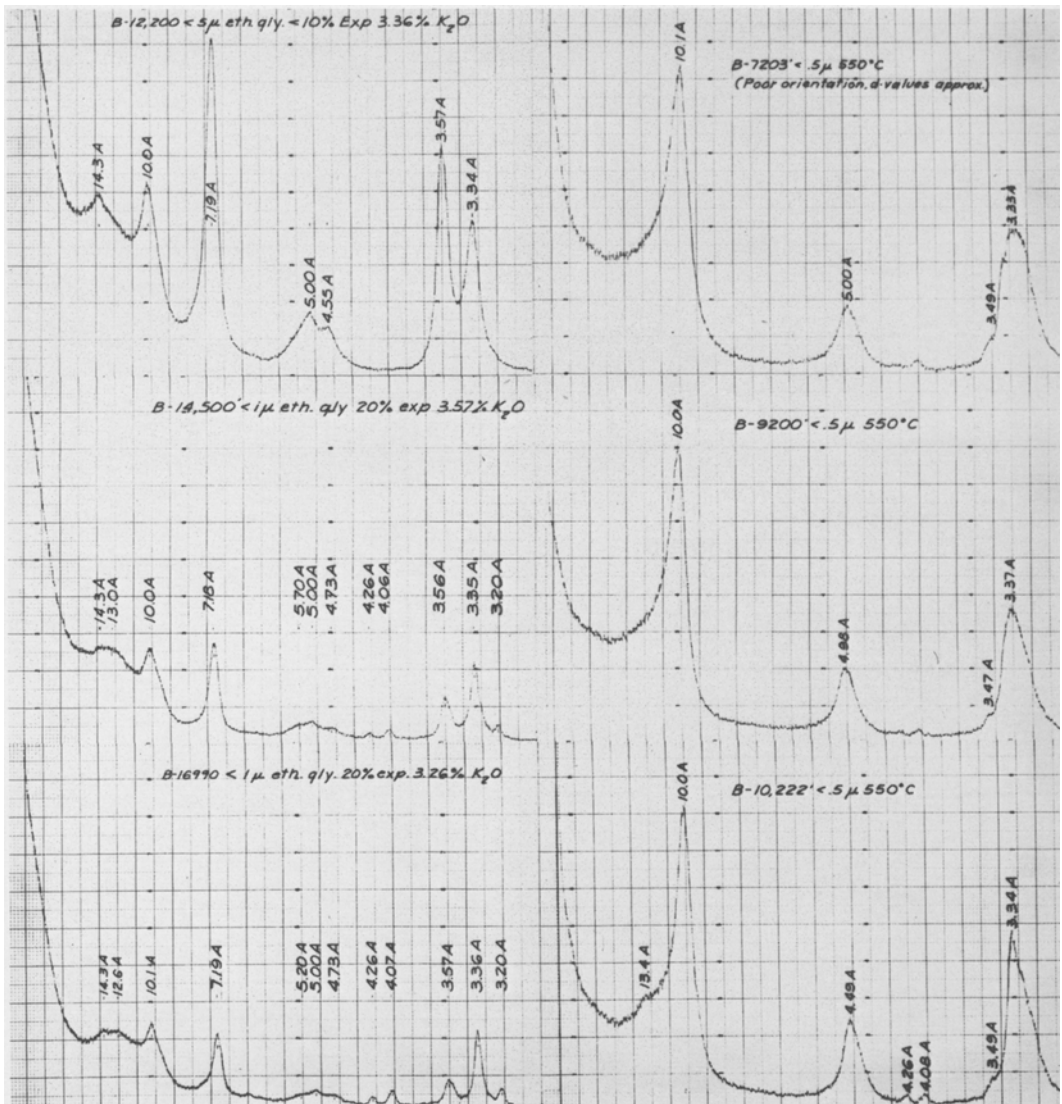


Fig. 10. X-ray patterns of well B depth (*cont.*) and heat treated samples.

intensity of the kaolinite (002) and illite/montmorillonite (003)/(005) to determine relative abundances. From consideration of the data of Weaver (1958), Freas (1962), and Schultz (1965) a value of 3 was assigned the kaolinite (001)/illite (001) intensity ratio. The kaolinite (002)/(001) and illite (002)/(001) intensity ratios can be determined for the pure minerals, both averaging about 0.75. Therefore the kaolinite (002)/illite (003) is also about 3. This value must be modified because the mineral is not pure illite, but an illite/montmorillonite ranging from almost pure montmorillonite to 20 per cent montmorillonite layers. The intensity of the 3.3 Å (003/005) 10/17 Å peak varies with the proportion of montmorillonite layers. The relationship is shown in Fig. 2, taken from calculations by

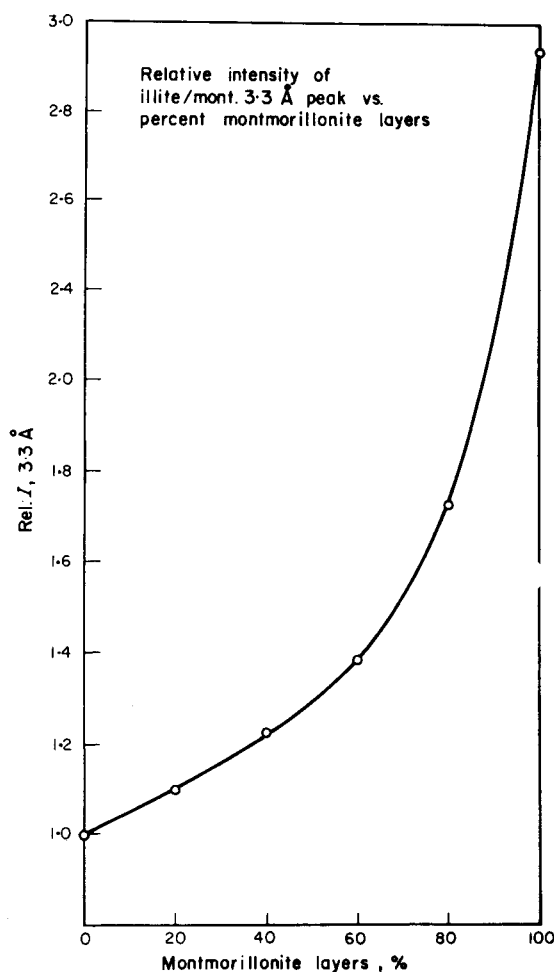


Fig. 2. The relationship between the relative intensity of the illite/mont. 3.3 Å peak and per cent montmorillonite layers.

Reynolds (personal communication, 1969). The kaolinite (002)/M(003/005) intensity ratio is then modified according to the proportion of montmorillonite layers in the mixed-layered phase. Using these assumptions, the following abundances were determined for $E = 8379$ ft (Fig. 3): illite/montmorillonite = 85 per cent, kaolinite = 9 per cent and illite = 6 per cent. The determination for illite is susceptible to error because of interference by the illite/montmorillonite diffraction peaks.

The proportion of montmorillonite layers in illite/montmorillonite was determined by the methods of Reynolds and Hower (in press) assuming a glycol-montmorillonite spacing of 17 Å and illite 10 Å. For random interstratification, the relative intensity of the 17 Å peak and adjacent low angle scattering intensities were compared to calculated diffraction patterns. The position of the (200/033)_{10/17 Å} peak was also determined. Both vary as a function of the proportion of montmorillonite layers. The (002/005)_{10/27 Å} peak position was measured for ordered illite/montmorillonites, those involving a glycol-montmorillonite-illite 27 Å superlattice. Discrete illite could be distinguished from mixed-layered illite/montmorillonite by the presence of distinct 10 Å and 5 Å diffraction peaks.

Mineralogic variations with depth—Well E. From forty samples examined in detail, a representative depth sequence of the $<1\mu$ fractions is shown in Figs. 3 and 4, covering a stratigraphic interval of 6991–14,975 ft. Illite/montmorillonite, kaolinite and discrete illite are present in all samples. Illite comprises an approximately constant small amount of about 5 per cent. Kaolinite ranges in abundance from about 25 per cent to virtually none in $E-11,563$ ft. The kaolinite to illite/montmorillonite abundance ratio as a function of depth is shown in Fig. 5. In the Anahuac formation, a shale section, the kaolinite content remains about constant, but in the Frio formation, a mixed sand-shale, the kaolinite content fluctuates considerably, the mean value being significantly less than in the Anahuac.

In contrast to the unsystematic variation of the kaolinite and discrete illite components, the composition of the illite/montmorillonite is directly related to the sample depth. This variation can readily be seen in Figs. 3 and 4. The shallowest sample illustrated has an illite/montmorillonite containing slightly more than 70 per cent expandable (montmorillonite) layers with random interstratification. The proportion of montmorillonite layers decreases monotonically to 37 per cent at 10,080 ft. The interstratification then becomes ordered (see patterns of Reynolds and Hower, in press), and the expandability rapidly decreases to 20 per cent by 10,518 ft. The illite/montmorillonite

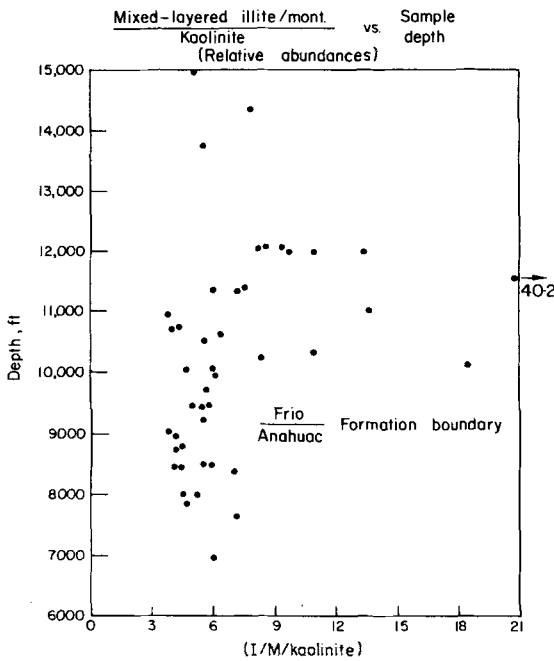


Fig. 5. The relationship between the relative abundances of illite/mont. and kaolinite and sample depth in well E.

then remains unchanged to the total depth of 14,975 ft. The relationship between expandability and depth for all Well E samples is shown in Fig. 6. Table 2 lists the expandability and K₂O contents of the clay size fractions.

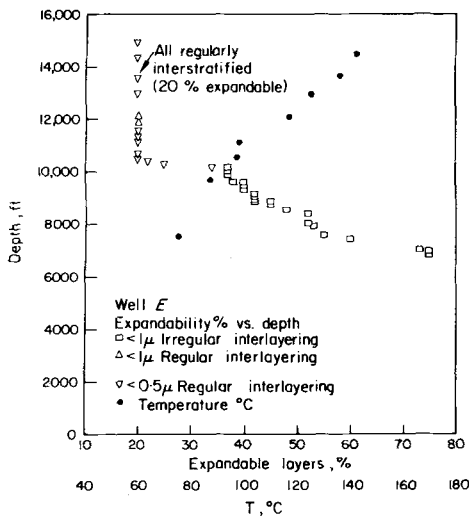


Fig. 6. The relationship between per cent expandable layers in illite/mont. and sample depth in well E.

Table 2. Well E, per cent montmorillonite (expandable) layers in illite/montmorillonite and per cent K₂O in clay-size fraction

Sample depth (ft)	Size	exp. (%)	K ₂ O (%)
6811	< 1 μ	75	1.94
6932	< 1 μ	75	2.02
6991	< 1 μ	73	2.25
7418	< 1 μ	60	2.23
7514	< 1 μ	55	2.57
7856	< 1 μ	53	2.44
8005	< 1 μ	52	2.60
8379	< 1 μ	52	2.77
8501	< 1 μ	48	2.74
8750	< 1 μ	45	2.71
8781	< 1 μ	45	2.84
8936	< 1 μ	42	2.84
8962	< 1 μ	42	3.01
9030	< 1 μ	42	2.79
9090	< 1 μ	42	2.96
9244	< 1 μ	40	2.97
9464	< 1 μ	40	2.93
9495	< 1 μ	40	3.00
9715	< 1 μ	38	3.42
9982	< 1 μ	37	3.53
10,080	< 1 μ	37	3.17
10,137	< 0.5 μ	34*	4.22
10,235	< 0.5 μ	26*	4.12
10,325	< 0.5 μ	20-24*	4.29
10,518	< 0.5 μ	20*	3.67
10,674	< 0.5 μ	20*	3.71
10,725	< 1 μ	20*	3.82
10,922	< 1 μ	20*	3.89
11,055	< 0.5 μ	20*	4.06
11,375	< 0.5 μ	20*	4.35
11,563	< 0.5 μ	20*	4.76
11,755	< 1 μ	20*	4.18
12,000	< 1 μ	20*	4.27
12,061	< 0.25 μ	20*	4.44
12,092	< 1 μ	20*	4.09
12,955	< 0.5 μ	20*	4.44
13,761	< 0.5 μ	20*	3.08
14,365	< 0.5 μ	20*	3.66
14,975	< 0.5 μ	20*	3.43

*Ordered interlayering.

As indicated on the diffraction patterns, there is a concomitant increase in the potassium content of the clay size fractions with decreasing expandability. This increase would be expected if the increased proportion of non-expandable 10 Å layers are of a normal illite composition. The relationship between the per cent K₂O in the clay size fraction and the proportion of expandable layers for all Well E samples is shown in Fig. 7. The correlation is quite good for samples in the Anahuac formation, to about 40 per cent expandable layers, but quite

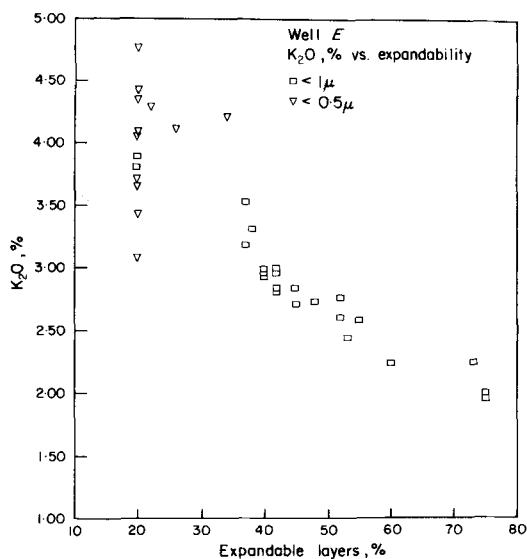


Fig. 7. The relationship between % K_2O in clay-size fraction and per cent expandable layers in illite/mont., well E.

irregular in the Frio formation. Figure 8 displays the relationship between the $I_{7\text{\AA}}/I_{10\text{\AA}}$ ratio—the kaolinite to illite/montmorillonite ÷ illite intensity ratio—and the per cent K_2O for all samples below 10,725 ft which have a constant 20 per cent expandability. The scatter in potassium values in Fig. 7 appears to be caused by the variable kaolinite content rather than a variation in the potassium content of the illite/montmorillonite. The curve shown in Fig. 8 extrapolates to a potassium value close to that which would be expected for a pure illite/montmorillonite of the same expandability (Hower and Mowatt, 1966).

Wells B, A, C and D. These four wells show the same diagenetic trend as Well E, a decrease in

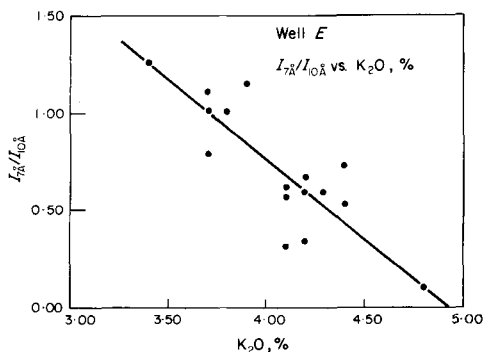


Fig. 8. The relationship between $I_{7\text{\AA}}/I_{10\text{\AA}}$ peak ratio and % K_2O clay size fractions having 20 per cent expandable layers illite/mont., well E.

expandability of the illite/montmorillonite and concomitant increase in potassium content of the clay size fraction as a function of depth. Well B (Figs. 9–12) is very similar to Well E except for an increased abundance of kaolinite, chlorite and discrete illite in some of the deeper samples. The illite/montmorillonite decreases from 85 to 40 per cent expandable layers over the depth interval 5,210 to 11,240 ft, over which interval the interstratification is random. The lower samples generally contain little illite/montmorillonite, which is replaced by kaolinite, chlorite and illite. However, some of the deeper Well B samples do contain a significant amount of illite/montmorillonite (see B-14,500 ft, B-16,990 ft, Fig. 10) which at these

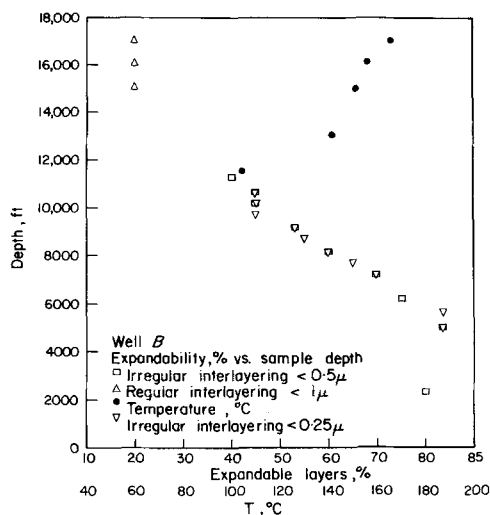


Fig. 11. The relationship between expandable layers in illite/mont. and sample and samples depth, well B.

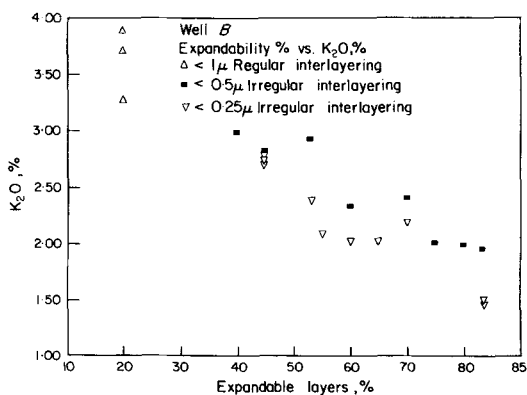


Fig. 12. The relationship between % K_2O in clay-size fraction and per cent expandable layers in illite/mont., well B.

depths has about 20 per cent expandable layers and ordered interstratification.

The response of the illite/montmorillonite to burial depth in Well *B* appears the same as in Well *E*, but it is masked over a considerable depth interval by the presence of the large amounts of discrete illite as well as chlorite and kaolinite. The burial depth effect on the illite/montmorillonite is evident below about 11,000 ft only when this detrital assemblage is present in lesser amounts.

The proportion of kaolinite, discrete illite, and chlorite begins to increase at 9200 ft and completely dominates the assemblage by 11,240 ft. Figure 10 illustrates the factor of increasing chlorite content with depth in heat treated samples. The presence of large amounts of discrete illite, chlorite, and kaolinite appears to be related to the depositional environment. Water depth zone data derived from paleontologic evidence interpreted by the Pan American Petroleum Corp. show that the samples

high in illite, chlorite and kaolinite are from near-shore and continental facies of the Wilcox formation. It seems very likely that this clay mineral assemblage represents original unaltered detritus resulting from differential sedimentation, as described by Parham (1966). When deeper water facies are encountered in the Wilcox sediments, illite/montmorillonite increases in abundance. The shallow water clay mineral assemblage mask less the mineralogical variations caused by burial diagenesis which are otherwise similar to Well *E*.

Table 4 reports the data for all samples from Louisiana Wells *A*, *C* and *D*. The general mineral-

Table 3. Well *B*, per cent montmorillonite (expandable) layers in illite/montmorillonite and per cent K₂O in clay-size fraction

Sample depth (ft)	Size	exp. (%)	K ₂ O (%)
3364	< 0.5 μ	80	1.98
5210	< 0.5 μ	83	1.85
5210	< 0.25 μ	83	1.47
5710	< 0.25 μ	83	1.50
6210	< 0.5 μ	75	2.00
7203	< 0.5 μ	70	2.41
7203	< 0.25 μ	70	2.18
7704	< 0.25 μ	65	2.02
8215	< 0.5 μ	60	2.32
8215	< 0.25 μ	60	2.01
8711	< 0.25 μ	55	2.08
9200	< 0.5 μ	53	2.92
9200	< 0.25 μ	53	2.38
9707	< 0.25 μ	45	2.71
10,222	< 0.5 μ	45	2.78
10,222	< 0.25 μ	45	2.72
10,712	< 0.5 μ	45	2.80
10,712	< 0.25 μ	45	2.79
11,240	< 0.5 μ	40	2.98
12,200	< 0.5 μ	†	3.36
13,700	< 0.5 μ	†	4.80
14,000	< 1 μ	†	4.36
14,500	< 1 μ	*20*†	3.57
15,000	< 1 μ	†	4.20
15,500	< 1 μ	†	4.20
16,000	< 1 μ	*20+†	3.38
16,500	< 1 μ	†	4.56
17,000	< 1 μ	*20+†	3.26

*Ordered interlayering.

†Illite, kaolinite and chlorite assemblage—near-shore and continental facies.

Table 4. Per cent montmorillonite (expandable) layers in illite/montmorillonite and per cent K₂O in clay-size fraction wells *A*, *C*, and *D*

Sample depth (ft)	Size	exp. (%)	K ₂ O (%)
Well A:			
1000	< 1 μ	60	3.04
1000	< 0.25 μ	50-55	2.45
3000	< 1 μ	70	3.08
3000	< 0.25 μ	55-60	2.37
5000	< 1 μ	60	3.01
7000	< 1 μ	60	3.24
7000	< 0.25 μ	55	2.91
8000	< 1 μ	55	3.55
8000	< 0.25 μ	50	3.32
9000	< 1 μ	55	3.09
10,000	< 1 μ	53	3.20
11,000	< 1 μ	53	3.50
11,000	< 0.25 μ	53	3.23
12,000	< 1 μ	43	3.87
13,000	< 1 μ	43	3.33
13,456	< 1 μ	43	3.97
13,456	< 0.25 μ	35	3.56
Well C:			
3754	< 0.5 μ	75	1.94
6517	< 0.5 μ	75	2.27
7452	< 0.5 μ	75	2.04
9504	< 0.5 μ	60	2.72
13,504	< 0.5 μ	42	2.81
15,509	< 0.5 μ	37	3.14
17,398	< 0.5 μ	23*	3.79
18,402	< 0.5 μ	20*	3.49
Well D:			
410	< 0.5 μ	75	2.38
2010	< 0.5 μ	70	2.65
5975	< 0.5 μ	70	2.64
8020	< 0.5 μ	70	2.60
10,020	< 0.5 μ	55	3.08
11,995	< 0.5 μ	50	3.37
13,985	< 0.5 μ	48	3.67

*Ordered interlayering.

ogy is the same as in the Texas wells, and the illite/montmorillonite phase shows the monotonic decrease in the proportion of montmorillonite layers with increasing sample depth. Also, there is a similar increase in the potassium content of the clay size fraction as the illite/montmorillonite decreases in the proportion of montmorillonite layers. The potassium values are higher here due to a greater amount of discrete illite.

In the Louisiana wells, the decrease in expandability does not begin until at least 8000 ft vs. 6000–7000 ft in the Texas wells. At a given depth, the strata in the Louisiana wells have an illite/montmorillonite with a greater proportion of montmorillonite layers and the change to ordered interstratification occurs only in samples from Well C and there at a depth much greater than in the Texas wells. The Louisiana wells have significantly lower geothermal gradients than the Texas wells (see Tables 2, 3 and 4). Within the limits of accuracy of the temperature measurements, the expandability of the illite/montmorillonite seems to be more closely related to temperature than to burial depth.

Summary of depth-dependent mineralogical variations. The only qualitative mineralogical variation common to all five wells investigated that shows a serial relationship with depth is the expandability of the illite/montmorillonite, which decreases monotonically with increasing depth. Chlorite is present in detectable amounts only in Well B in the Wilcox formation. The appearance of chlorite is associated with an increasing abundance of discrete illite and kaolinite at the expense of illite/montmorillonite. The origin of the assemblage discrete illite, chlorite, and kaolinite appears to be explained most logically as detritus unaltered by burial diagenesis.

In Well E, which was investigated in the most detail, the amount of discrete illite in the whole rock decreases progressively with depth.

CHEMICAL RESULTS

It has been shown that the clay mineralogical variation common to all wells is a progressive change in the nature of the illite/montmorillonites with increasing depth. The question now arises as to whether the physical changes might be accompanied by chemical changes in the whole rock or clay-size material. The kinds of chemical data taken in this study are:

1. Potassium analyses of each X-ray diffraction specimen, made of the same plate used to obtain the diffraction pattern. These analyses are reported in the diffraction section.

2. Complete major constituent analyses for

sixteen whole rock Well E specimens, covering a stratigraphic interval of 7203 to 11,969 ft.

3. Analyses of all major constituents except for sodium and magnesium in six $<1\mu$ fraction samples from Well E, covering a stratigraphic interval of 6991 to 12,092 ft.

4. Potassium analyses of the four size fractionated Well E samples.

5. A determination of the amount of potassium bound in the feldspar for eight whole rock Well E samples.

Major constituent chemical analyses. The major constituent analyses are reported in Table 5. In general, the compositions are surprisingly similar over the whole depth range covered; Fe, Ti, Si, Al and Na do not show any significant trend as a function of depth. Below 8500 ft the Ca content decreases with increasing depth (Fig. 13), as does Mg, although not as markedly. Both decreases can most reasonably be explained by the progressive solution of carbonate.

The role and source of potassium is very critical to the interpretation of the mineralogical variations. As reported in the diffraction section, there is a progressive increase in the potassium content of the clay-size fraction with increasing depth. This increase is directly related to the proportion of illite layers in the illite/montmorillonite phase. The systematic increase in potassium on the clay size fraction does not seem to be reflected in the potassium count of the whole rock, as would be expected if potassium were being gained from the pore fluids.

Both the whole rock and clay-size fraction potassium contents are shown as a function of

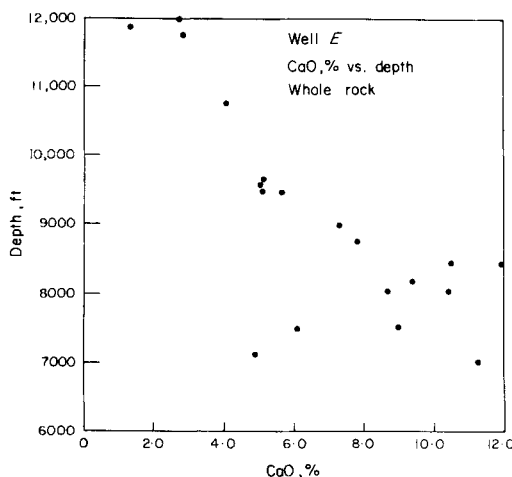


Fig. 13. The relationship between %CaO in whole rock and sample depth well E.

Table 5. Well *E*, major constituent chemical analyses

Sample depth (ft)	Whole rock									
	FeO+Fe ₂ O ₃	TiO ₂	CaO	K ₂ O	SiO ₂	Al ₂ O ₃	MgO	Na ₂ O	K ₂ O/Al ₂ O ₃	SiO ₂ /Al ₂ O ₃
7023	6.04	0.91	11.27	2.66	58.87	16.45	1.33	1.89	0.162	3.58
7100	5.93	0.83	4.93	2.65	63.62	16.50	1.70	1.98	0.161	3.86
7490	6.10	1.98	6.15	2.62	62.11	17.87	1.34	1.34	0.160	3.48
7514	5.32	0.85	9.02	2.48	61.58	15.93	1.48	2.60	0.156	3.87
7514	5.54	0.84	9.02	2.52	60.41	15.54	1.47	2.66	0.162	3.89
8036	5.66	1.18	8.77	2.44	59.64	17.37	1.33	1.80	0.140	3.43
8036	6.24	0.81	10.43	2.36	58.90	16.84	1.33	1.80	0.140	3.50
8190	5.79	0.88	9.37	2.39	61.10	16.18	1.33	1.10	0.148	3.78
8409	6.45	0.89	10.69	2.40	58.86	17.12	1.32	1.11	0.140	3.44
8501	6.17	0.88	11.99	2.28	58.49	17.09	1.37	1.10	0.133	3.42
8750	6.53	0.97	7.79	2.45	59.83	18.59	1.38	1.39	0.132	3.22
8899	5.98	1.16	7.26	2.25	61.28	16.48	1.26	1.22	0.137	3.72
9464	5.91	0.92	5.72	2.40	62.51	17.69	1.19	1.55	0.136	3.53
9464	5.98	0.93	5.02	2.47	61.68	18.43	1.19	1.55	0.134	3.35
9580	6.33	0.94	5.04	2.58	62.97	18.04	1.25	1.08	0.143	3.49
9616	6.51	1.02	5.15	2.76	62.82	18.92	1.10	1.11	0.146	3.32
11,718	5.02	1.02	2.88	3.09	65.37	17.83	0.74	1.22	0.173	3.67
11,876	5.41	1.01	1.37	3.40	63.33	19.31	0.79	1.18	0.176	3.30
11,969	4.62	0.83	2.77	3.21	65.10	18.17	0.79	1.71	0.177	3.58
				<u>< 1 μ Size fraction</u>						
6991	6.39	0.89	1.52	2.52	59.89	22.46	n.d.	n.d.	0.103	2.67
8450	6.70	1.01	tr.	3.08	59.62	26.01	n.d.	n.d.	0.118	2.29
9580	6.06	1.06	tr.	3.33	53.60	25.40	n.d.	n.d.	0.131	2.31
9982	5.56	0.97	0.50	3.91	57.94	25.18	n.d.	n.d.	0.155	2.30
11,375	4.47	1.06	tr.	4.42	57.91	25.33	n.d.	n.d.	0.175	2.29
12092	4.30	0.98	0.40	4.71	59.25	26.31	n.d.	n.d.	0.179	2.25

depth in Fig. 14. It is obvious that in the Anahuac formation there is no sensible regular depth-dependent gain in whole rock potassium while clay-size fraction shows a progressive increase. The Frio formation rocks from depths close to 12,000 ft are higher in potassium but also contain about 10 per cent less kaolinite (see Fig. 13), resulting in a sufficient concentration of the potassium bearing minerals to account for the difference. Therefore, it appears that there is a re-distribution of potassium within the rock giving an increasing concentration of illite/montmorillonite as the depth increases, rather than an abstraction of new potassium from the formation waters.

The major constituent analyses of six <1 μ Well *E* samples are reported in Table 5. Sodium and magnesium were not determined. As might be expected, Al is concentrated in the clay fraction; Ca is not. The lower Fe content in the deeper Frio formation samples correlates with the generally lower Fe in the whole rock analyses. The potassium contents confirm the mineral trends as determined from the numerous diffraction specimens.

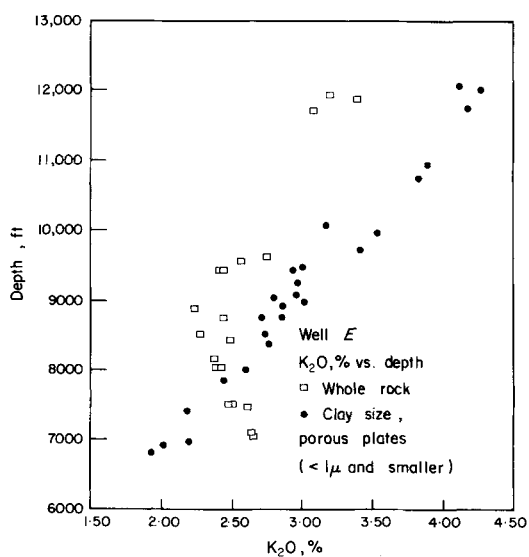


Fig. 14. The relationship between %K₂O in whole rock and clay-size fraction and sample depth, well *E*.

Distribution of potassium within the total rock. There does not appear to be a progressive increase in the potassium available to the illite/montmorillonite, despite the fact that the clay size fraction clearly gains potassium, presumably due to increased potassium fixation by the illite/montmorillonite. Therefore, there must be a progressive decrease in potassium bearing minerals other than the illite/montmorillonite. The minerals containing appreciable potassium are discrete illite (mica), alkali feldspar and illite/montmorillonite.

The potassium held in the feldspar was determined for eight Well *E* samples, covering a stratigraphic interval of 7514 to 11,969 ft (Table 6). Although there is less potassium feldspar in the deeper samples, the amount of potassium feldspar contributes to the whole rock is about 0.1 per cent and is of little significance.

Both the X-ray diffraction data (Fig. 1) and the potassium analyses (Table 1) of the Well *E* size fractionated samples indicate a lower discrete illite (mica) content in the $\geq 1\mu$ fraction with increasing depth. It is important to note that the potassium in the $>1\mu$ fraction of the deeper samples is significantly lower than that of the shallower samples, despite the presence of a significant amount of illite/montmorillonite with a high potassium content in the coarser sizes and a greater amount of potassium in the whole rock.

The authors conclude that the increasing potassium content of the illite/montmorillonite with increasing depth in rocks of essentially constant total available potassium is correlated with a decreasing discrete illite (mica) content in the whole rock. There appears to be sufficient potassium derived from the breakdown of the discrete illite (mica) to account for all of the potassium gain in the illite/montmorillonite.

DISCUSSION

It has been shown for the five wells studied that the consistent mineralogical variation with depth is

a monotonic decrease in the proportion of montmorillonite layers in the illite/montmorillonite. Furthermore, the progression has no respect for the geologic age or formation boundaries of the sediments. Outcropping rocks of correlative age have a clay mineral assemblage dominated by montmorillonite and kaolinite and are noticeably lacking in illite and illite/montmorillonites of low expandability (Simmons and Taggart, 1954). The writers therefore conclude that the mineralogical change represents burial diagenesis.

Temperature appears to be more important than pressure in controlling the diagenetic conversions. The decrease in expandability with depth is more rapid in the Texas wells than the Louisiana wells, the former having higher geothermal gradients. Burst (1969) gives further applicable evidence and discussion against pressure dehydration.

It is instructive to compare this study to Burst (1959, 1969) as similar sediments and conditions are involved. In his 1959 paper dealing with the Wilcox formation, Burst concluded that the illite/montmorillonite becomes a completely non-expandable illite and that chlorite appears to increase in abundance or crystallinity with increasing depth. In all five wells studied here, the illite/montmorillonite never becomes a pure illite. In Well *B*, which also encounters the Wilcox formation, discrete illite and chlorite are present in large amounts in many samples, but as shown previously, their presence is attributable to original mineralogy rather than diagenesis. Several Wilcox samples from deeper water facies contain lesser amounts of detritus and have a 20 per cent expandable illite/montmorillonite present. Even the deepest Well *B* sample (*B*-17,000 ft) has a mixed-layered phase with about 20 per cent montmorillonite layers. One must conclude that there are no detectable gains or losses of chlorite and kaolinite that are a result of diagenesis, and that a pure illite phase has not been formed.

Burst (1969) has re-interpreted the mineralogical

Table 6. Potassium present in feldspar, Well *E*

Sample depth (ft)	Whole rock	Mica	Feldspar
	K ₂ O (%)	K ₂ O (%)	K ₂ O (%)
<i>E</i> - 7514	2.20	2.06	0.14
<i>E</i> - 8036	2.17	2.07	0.10
<i>E</i> - 8409	2.13	2.03	0.10
<i>E</i> - 8750	2.17	2.07	0.10
<i>E</i> - 9464	2.13	2.07	0.06
<i>E</i> - 9580	2.29	2.20	0.09
<i>E</i> -11,718	2.74	2.66	0.08
<i>E</i> -11,969	2.84	2.79	0.05

data and now calls upon thermal dehydration to explain the observed structural changes in the illite/montmorillonites. His prime example, as in this paper, is a section that includes the Anahuac and Frio formations. In explaining the mechanism of collapse of the montmorillonite layers, Burst interprets the diffraction patterns of glycol-solvated illite/montmorillonites as showing a progressive loss of the next to last water layer so that the ultimate product in the subsurface is a homogeneous one water layer montmorillonite. This interpretation apparently comes about because of the following assumptions: (1) the number of glycol layers an expandable layer absorbs is equal to the number of water layers it had in the subsurface, and (2) the weakening of the 17 Å peak from samples of increasing depth is the result of a mixed two glycol layer and one glycol layer montmorillonite, with the appearance of a 13 Å peak indicating a pure one glycol layer montmorillonite.

In the writers' opinion, there seem to be three inconsistencies in Burst's interpretation of the diffraction patterns. First, if they actually represent a mixed-layered two glycol-one glycol layer montmorillonite, a continuous peak migration from 17 Å to 13.5 Å should occur in the same manner as mixed-layered montmorillonites/chlorites (MacEwan, *et al.*, 1961). Instead, the patterns are readily interpretable in terms of a mixed-layered illite (non-expanded)/two-glycol layer montmorillonite. Second, if the final product were actually a one glycol layer = one-water layer montmorillonite, the diffraction pattern should show an integral sequence of basal reflections of the 13 Å spacing, which it does not. Third, there is no evidence for the irreversible formation of a one water layer montmorillonite. If this were to happen in the subsurface, the montmorillonite would rapidly re-hydrate to two-water layers on being raised to the surface. At atmospheric pressure, there is complete irreversible removal of interlayer water at temperatures only above 300°C, and even then the structure will still expand when glycol solvated (Brown, 1961).

It should be emphasized that although the writers disagree with Burst's mechanism giving rise to the collapse or dehydration of montmorillonite layers, this in no way negates Burst's conclusions as to the significance of this reaction as a water-drive for petroleum accumulation.

POSSIBLE MINERALOGIC REACTIONS GIVING USE TO INCREASING ILLITIC LAYERS

The question now arises as to the nature of the chemical changes that produce a progressive increase in the proportion of illite layers in the illite/montmorillonite. Hower and Mowatt (1966)

have demonstrated a compositional continuum between pure illite and montmorillonite consisting of the illite/montmorillonites of varying expandabilities. A given structure, i.e., proportion of montmorillonite layers as determined by X-ray diffraction, has compositional significance in that the composition determines the amount of charge deficiency on the 2:1 aluminosilicate sheets which in turn allows for the fixation of a suitable amount of interlayer cations, mainly potassium, so as to give an electrostatically neutral structure. The potassium gain in the clay-size fraction, which has been related to the collapse of montmorillonite layers, must therefore involve compositional changes in the 2:1 sheets to maintain charge balance.

The charge deficiency on the 2:1 aluminosilicate sheets can be increased in three ways: (1) substitution of Al^{3+} for Si^{4+} in the tetrahedral layer, (2) substitution of Mg^{2+} and/or Fe^{2+} for Al^{3+} in the octahedral layer, and/or (3) reduction of Fe^{3+} which proxies for Al^{3+} , to Fe^{2+} . Most of the potassium increase will come from the breakdown of the detrital illite, but the remaining alumina and silica from the illite must be accounted for, such as in mineralogical reactions involving (1) and (2) which require the formation of additional amounts of either illite/montmorillonite or kaolinite, depending if some external introduction of potassium is called upon or not. Within the limits of detection, there is no apparent systematic change in the relative abundance of either phase. Reduction of iron has the advantage of not requiring the formation of additional material, but Fe^{2+}/Fe^{3+} ratios could not be reliably determined because of interference by organic material. No definite conclusion can be reached as to the nature of the mineralogical reactions involving the chemical changes in the illite/montmorillonites.

Stability of the illite/montmorillonite. The problem of the thermodynamic stability of mixed-layered silicates is one that has been little considered but is of prime importance to the petrologic interpretation of pelitic sediments (Zen, 1963). If they are truly stable, then one can deduce diagenetic grade with confidence. If the apparent destruction of mica and concomitant formation of illite/montmorillonite observed in this study and by Dunoyer de Segonzac (1965) represents a real diagenetic reaction, it constitutes the first definite evidence for the thermodynamic stability of mixed-layered silicates.

It is of interest to examine the response of illite/montmorillonite to increasing temperature in more detail. Figure 15 shows the structural variations as a function of temperature in Well E. The conversion of an illite/montmorillonite from 75

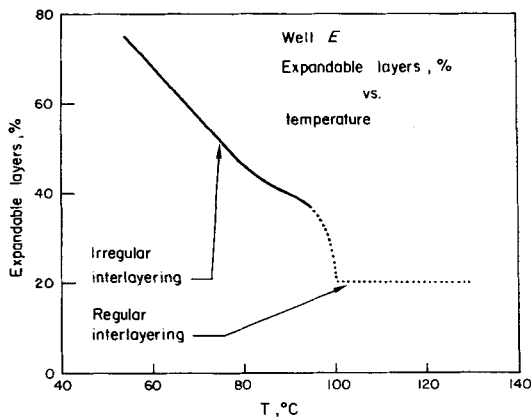


Fig. 15. The relationship between per cent expandable layers in illite/mont. and subsurface temperature, well E.

per cent to 35 per cent expandable layers takes place over a 40°C range (55–95°C). When the temperature is reached at which ordered interlayering occurs the expandability decreases at an almost discontinuous rate, a feature predicted by the type of transformation (Hower, 1967). Once reaching 20 per cent expandable layers, there is no further detectable change to the highest temperature reached, 130°C. The upper stability of this phase can logically extend to 166°C at a depth of 17,000 ft, the highest temperature reached in Well B.

Velde (in press) carried out experimental studies on the system muscovite–pyrophyllite which contains the beidellite composition and the compositional intermediates between montmorillonite and muscovite. Although the reaction temperatures are considerably higher than those in the Gulf Coast subsurface, the general sequence of development of illite/montmorillonite at the potassium poor side of the system with increasing temperature is remarkably similar to that in Gulf Coast sediments. The proportion of montmorillonite layers decreases rapidly to 30–40 per cent in a randomly interstratified illite/montmorillonite, and then ordered interstratification occurs with expandability decreasing slowly to its upper stability. Thus, the temperature dependence of the illite/montmorillonite structure is almost identical in the synthetic system and Gulf Coast sediments.

SUMMARY OF CONCLUSIONS

The mineralogy of Gulf Coast Tertiary and Pleistocene pelitic sediments is being altered by burial diagenesis. The diagenetic changes involve the conversion of illite/montmorillonite near montmorillonite in composition (80 or more per cent expandable layers) to an illite/montmoril-

lonite of low expandability. The rate of decrease in expandability is proportional to the geothermal gradient, rather than depth of burial.

Where the geothermal gradient is highest the sequence consists of a decrease in expandability of a randomly interstratified illite/montmorillonite to about 35 per cent montmorillonite layers, alleverdite-like ordering of the interlayering and a reduction in expandability to about 20 per cent expandable layers over a short depth interval, and persistence of this phase to maximum depth. Where the geothermal gradient is low the deepest wells penetrate only the upper part of this sequence.

The diagenetic reaction also appears to involve the breakdown of detrital illite (mica) which serves as the major source of potassium in the illite layers being produced in the illite/montmorillonite. There is no detectable progressive gain or loss of kaolinite or chlorite which can be attributed to burial diagenesis. Calcium carbonate and, to a lesser extent, potassium feldspar are lost with increasing burial.

Acknowledgments—Robert C. Reynolds, Jr. supplied much stimulation and assistance in the X-ray diffraction interpretations. Robert Duschatko and Roger Ames of Pan American Petroleum Corp., Tulsa, were especially helpful in furnishing the necessary samples and geological information. Robert Martin and John F. Burst critically reviewed the manuscript. The research has been aided by an NSF Traineeship and NSF Grant GA-1269.

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Résumé—Des échantillons souterrains de schistes variant en âge du Pléistocène à l'Eocène, prélevés dans 5 puits de pétrole de la côte du golfe du Mexique ont été examinés minéralogiquement et chimiquement afin de déterminer l'étendue de la diagenèse "en terre" dans les sédiments pélitiques. L'illite/montmorillonite domine la minéralogie et subit une décroissance monotonique de l'expandabilité de 80 à 20% des couches de montmorillonite au fur et à mesure que la profondeur augmente. L'interstratification passe de hasardeuse à ordonnée à peu près aux couches étendues à 35%. De discrètes phases d'illite et de kaolinite sont présentes partout et considérées détritiques. Le contenu discret d'illite (mica) du roc diminue avec la profondeur, alors que celui de la kaolinite ne subit pas de variation. Le chlorite n'apparaît en quantité appréciable que dans un puit et seulement dans les échantillons des facies d'eau peu profondes. Ce chlorite est également considéré détritique.

Les analyses chimiques du roc entier ne montrent pas de variations systématiques avec la profondeur, à part une diminution du calcium et magnésium due à la dissolution de carbonate. Par contre, le potassium augmente progressivement avec la profondeur dans la fraction argileuse indiquant une redistribution du potassium à l'intérieur du roc. L'illite (mica) détritique semble se décomposer avec l'augmentation de la profondeur, fournissant ainsi du potassium pour la fixation en inter-couche dans l'illite/montmorillonite, comme la proportion des couches d'illite augmente. La réaction diagénétique est indépendante de l'âge géologique des sédiments et des limites stratigraphiques. La température semble, plus que la pression, déterminer les réactions.

Kurzreferat—Es wurden Untergrundproben von Schiefen, deren Alter sich vom Pleistozän bis zum Eozän erstreckte, und die aus fünf Mineralölbohrlöchern an der Golfküste erhalten worden waren, mineralogisch und chemisch untersucht um die Art und das Ausmass von unterirdischer Diagenese in pelitischen Ablagerungen zu bestimmen. Mineralogisch vorherrschend ist Illit/Montmorillonit, der mit zunehmender Tiefe eine monotone Abnahme im Schwellvermögen von etwa 80 bis zu einem Grenzwert von 20 Prozent Montmorillonitschichten erfährt. Die Zwischenlagerung verändert sich von unregelmässig zu geordnet bei etwa 35 Prozent aufgeblähten Schichten. Getrennte Illit und Kaolinit Phasen sind allgegenwärtig und werden als Geröll angesehen. Der Gehalt des Vollgesteins an getrenntem Illit (Glimmer) nimmt mit der Tiefe ab, während der Kaolinit keine systematische Veränderung zeigt. Chlorit kommt in bedeutenden Mengen nur in einem Bohrloch vor und auch hier nur in Proben aus den Seichtwasserfazies. Der Chlorit wird ebenfalls als Geröll angesehen.

Chemische Analysen von Vollgestein zeigen keine systematische Veränderung mit zunehmender Tiefe mit Ausnahme einer Abnahme von Calcium und Magnesium infolge einer Auflösung von Carbonat. Umgekehrt nimmt der Kaliumgehalt mit zunehmender Tiefe in der Tongrösserfraktion zu, was auf eine Neuverteilung des Kaliums innerhalb des Gesteins hinweist. Der aus Geröll bestehende Illit (Glimmer) scheint mit zunehmender Tiefe zu zerfallen und so Kalium für eine Zwischenschichtfixierung in Illit/Montmorillonit zu liefern während sich der Anteil an Illitschichten erhöht. Die diagenetische Reaktion ist unabhängig vom geologischen Alter der Ablagerungen und von stratigraphischen Grenzen. Die Temperatur scheint für die Reaktion in höherem Masse bestimmend zu sein als der Druck.

Резюме — Образцы глинистых сланцев из нефтяных скважин Галф Коуст, возраст которых колеблется от плейстоценового до эоценового, подверглись минералогическому и химическому изучению для выяснения природы и степени диагенеза в погребенных пелитовых осадках. Преобладающим минералом сланцев является иллит-монтмориллонит; его способность к набуханию однообразно уменьшается при падении содержания монтмориллонита с 80 до 20% по мере возрастания глубины. Характер смешаннослойных образований меняется от неупорядоченного до упорядоченного (при приблизительно 35% набухающих слоев). Обычны также иллит и каолинит так таковые, которые рассматриваются как детритные. Содержание иллита как такового в породе уменьшается с глубиной, тогда как для каолинита данные не определены. Хлорит встречен в значительных количествах только в образцах из одной скважины и притом лишь в отложениях мелководной фации; он также рассматривается как детритный. Водовые анализы пород не указывают на определенные вариации с глубиной за исключением уменьшения содержания кальция и магния, которое вызвано растворением карбонатов. В противоположность этому содержание калия в глинистой фации прогрессивно возрастает с глубиной, указывая на его перераспределение в пределах породы. Детритный иллит, по-видимому, разрушается с возрастанием глубины, освобождая калий, который фиксируется в смешаннослойном иллит-монтмориллоните (с глубиной в последнем содержание иллитовых слоев увеличивается). Диагенетические реакции не зависят от геологического возраста осадков и их стратиграфической приуроченности. Температура, вероятно, в диагенетических реакциях играет большую роль, чем давление.