

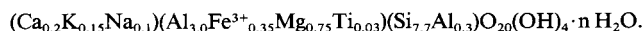
MIXED-LAYER ILLITE/SMECTITE MINERALS IN TERTIARY SANDSTONES AND SHALES, SAN JOAQUIN BASIN, CALIFORNIA

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Abstract—The southern San Joaquin Valley contains more than 7 km of sedimentary fill, largely Miocene and younger in age. Ancient depositional environments ranged from alluvial fans at the basin margins to turbidite fans toward the basin center. Mixed-layer illite/smectite (I/S) dominates the <2- μm fraction of Miocene shales, and kaolinite is abundant in Miocene sandstones. I/S from carbonate-cemented sandstones contains 5–20% more smectite layers than I/S from uncemented sandstones. The timing of cementation correlates with the proportion of smectite layers in the I/S, suggesting that cementation slowed the illitization process. Smectite and I/S with >80% expandable layers occur at present burial temperatures of 120°–140°C in Miocene sandstones and shales. This highly expandable I/S is restricted to areas covered by thick deposits (1000–2500 m) of Pleistocene sediments. Rocks of similar age and at equivalent temperatures, but covered by <900 m of Pleistocene sediments, contain I/S having low expandabilities (<30%).

Microprobe analyses of 16 discrete smectite and smectite-rich I/S clays indicate an average montmorillonite composition of:



Smectite in I/S-rich clays of Gulf Coast shales has a similar composition except for lower octahedral Al/Fe ratios ($\text{Al}/\text{Fe}^{\text{VI}} = 3.1$), compared with the San Joaquin samples ($\text{Al}/\text{Fe}^{\text{VI}} = 8.6$).

Residence time at different temperatures appears to be an important influence on the percentage of smectite layers in I/S from the San Joaquin basin. Areas containing I/S with high expandabilities (e.g., 95% smectite layers) have a time-temperature index (TTI) of 4.0–4.5 at 120°C, whereas areas containing I/S with low expandabilities (e.g., 30% smectite layers) have a TTI of 5.0. Present data suggest that highly expandable I/S changed to slightly expandable I/S over a narrow temperature interval (10°–20°C). Differences in the potassium availability from detrital components and in the K^+/H^+ activity ratios of pore water do not appear to be related to the differences in the percentage of smectite layers of these I/S clays.

Key Words—Carbonate cementation, Illite/smectite, Microprobe analysis, Mixed layer, Smectite, Time-temperature index.

INTRODUCTION

Mixed-layer illite/smectite (I/S) is dominant in the clay-size fraction of many shales from Tertiary basins. The reaction of smectite to illite in these clays has received considerable attention because of its potential for (1) flushing hydrocarbons from the shales (Burst, 1969; Bruce, 1984), (2) catalyzing hydrocarbon generation (Johns and Shimoyana, 1972), (3) producing high pore-fluid pressures (Powers, 1967), and (4) providing cementation agents to sandstones (Towe, 1962; Boles and Franks, 1979; Lahann, 1980).

Most detailed studies of the smectite-to-illite transformation have focused on the Tertiary section of the Gulf Coast where the expandability of the I/S clay changes from high (i.e., a large percentage of smectite layers) to low with increasing burial depth (see, e.g., Perry and Hower, 1970; Hower *et al.*, 1976; Boles and Franks, 1979). Burial temperature and K^+ availability have long been emphasized as controls on the reaction. The age of the rocks, or *residence time* at temperature, has also been recognized as an important factor (Eberl

and Hower, 1976); for example, the reaction appears to begin as low as 50°C in Eocene rocks (Perry and Hower, 1970; Boles and Franks, 1979), and probably as high as 90°–100°C in younger sediments (Bruce, 1984). No studies to date have shown the effect of residence time at temperature within the same age sediment.

For all the great interest in the illitization reaction, it is surprising that little is known about the composition of the phases involved, particularly the smectites. The illitization reaction requires the addition of potassium and, perhaps, aluminum ions to the smectite reactant, suggesting that rock permeability may control reaction progress. The composition of the smectite determines the type and proportion of components released by illitization and, hence, may indirectly influence the proportion and type of components released (Boles and Franks, 1979). Eberl *et al.* (1978) showed experimentally that Al-rich smectite reacts more readily to illite than Al-poor smectite, suggesting that smectite compositions may be an important control on the

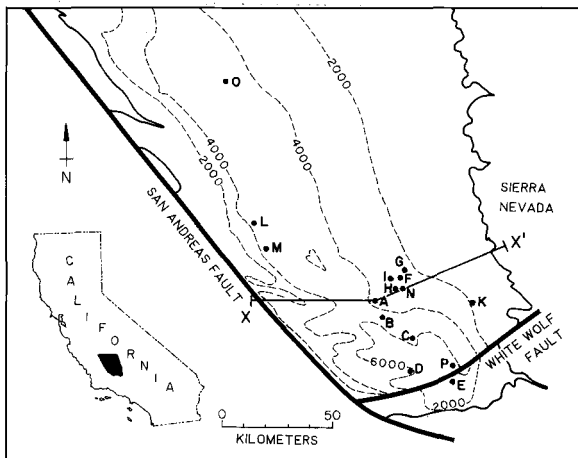


Figure 1. Location of oil fields (A-M) and wildcat wells (N-P) studied in the southern San Joaquin Valley (see Table 1). Dashed lines show Tertiary sedimentary rock thickness (m) from Callaway (1971). Cross section line X-X' shown in Figure 2.

illitization reaction (see also, Bruce, 1984). In addition, experimental studies of Roberson and Lahann (1981) have shown that the reaction rate of illitization is slowed by the presence of Ca^{2+} and Mg^{2+} .

The preliminary results of the present study of sedimentary rocks from the southern San Joaquin Valley indicate that I/S clays dominate the clay fraction of the shales and many of the sandstones. In this paper we demonstrate the importance of burial history, including residence time and cementation, in controlling smectite diagenesis and the smectite-to-illite reaction.

GEOLOGIC SETTING

The study area is in the southern part of the San Joaquin Valley (Figure 1). Here, the Tertiary section comprises more than 7 km of basin-fill sediments. The rocks conformably overlie the Sierra Nevada plutonic complex to the east, and are faulted on the west and to the south by the San Andreas and White Wolf faults, respectively (Figure 2). Local uplifts during deposition of the Tertiary sediments resulted in minor disconformities and unconformities, but, by and large, the region subsided throughout the Tertiary and has not been uplifted significantly since that time (see, e.g., Callaway, 1971). The southern San Joaquin Valley ba-

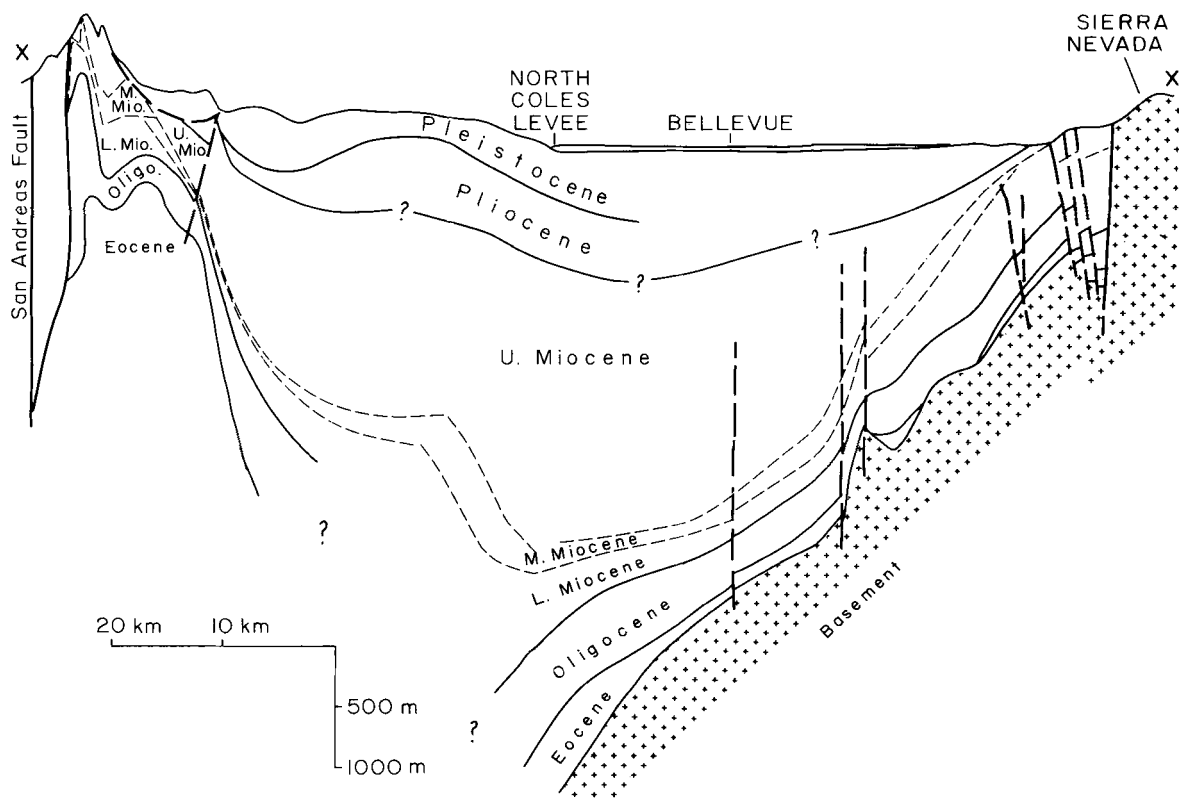


Figure 2. Cross section of the southern San Joaquin basin. See Figure 1 for cross section location. Modified from *California Oil and Gas Fields* (1982 publication, California Division of Oil and Gas) using new age determinations from Bartow and McDougall (1984).

sin-fill, therefore, represents a first-cycle burial sequence. The sediments were deposited in a nonmarine environment on the eastern edge of the basin and grade westward into a shallow marine facies. The uppermost Tertiary section is largely nonmarine throughout the region. Most of the basin-fill material is shale; isolated deep-water turbidite sand bodies are also present, many of which are prolific producers of oil and gas.

Lithology

The sandstones are arkosic and contain subequal proportions of quartz and feldspar (Figure 3). Facies analysis demonstrates that the sediment came from the Sierra Nevada to the east and, to a lesser extent, the south (Webb, 1981). Overall, the sandstones contain more or less equal proportions of quartz, plagioclase, and K-feldspar (except for a slight quartz enrichment), modally similar to their granodiorite source. Volcanic rock fragments are generally minor in these sandstones, except in Oligocene (Figure 3) and, locally, Eocene rocks.

Subsurface temperature and pressure

The most reliable subsurface temperatures have been obtained from "shut-in" wells, especially if the temperatures were measured during the early production history of the oil field. Shut-in well temperatures were obtained from the North Coles Levee, Paloma, and San Emidio Nose field (see Table 1). In other areas, the subsurface temperatures were estimated from a geothermal gradient map of the region (American Association of Petroleum Geologists portfolio Map No. 22, 1974), assuming a mean surface temperature of 18°C.

The subsurface fluid pressure of the North Coles Levee Field is 269 bars at 2590 m depth, or slightly more than the hydrostatic pressure. Fluid-pressure data were not acquired for other areas in the region, although fluid pressures throughout the southern San Joaquin Valley are generally near the hydrostatic gradients of about 0.5 psi/ft (personal communication, ARCO, Bakersfield, California).

EXPERIMENTAL

Clay minerals from sandstones and shales were concentrated in the <2- μm size fraction by centrifuge techniques. Calgon was used as a deflocculation agent for a few samples, usually sandstones, where flocculation was a problem. A Norelco X-ray diffractometer operated at $1^\circ 2\theta/\text{min}$ and using $\text{CuK}\alpha$ radiation generated XRD patterns for clay identification. After ethylene glycolation, the proportion of smectite layers in I/S clays was estimated using the method of Środoń (1980). This method results in errors in the percentage of expandable layers of less than 5%, whereas the Reynolds and Hower method (1970) is reliable only to $\pm 15\text{--}20\%$ (see Środoń, 1980). The principal reflection of quartz

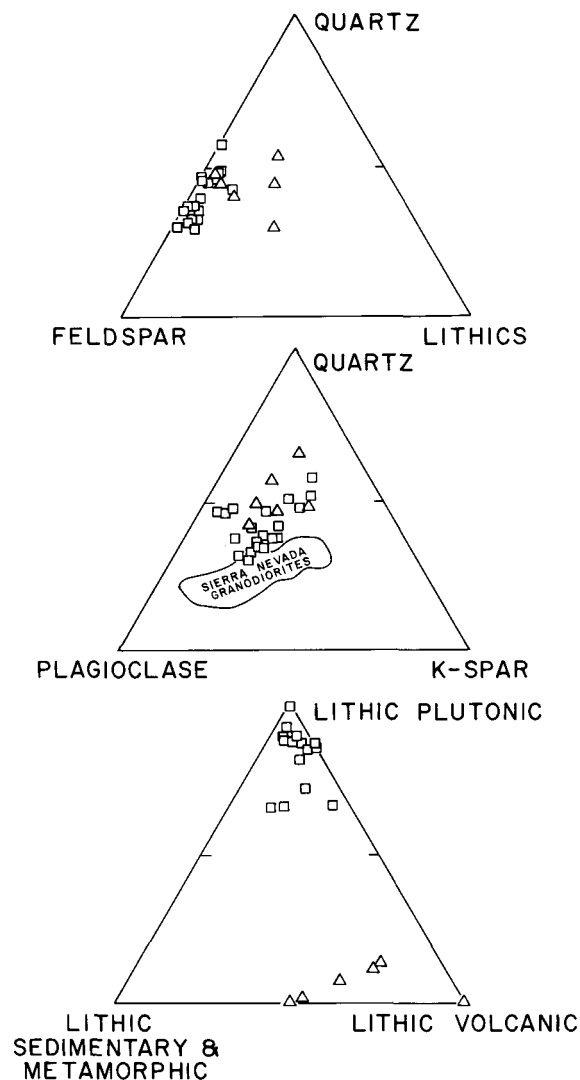


Figure 3. Modal proportions of selected components in sandstones from the San Joaquin basin. Square = Miocene; triangle = Oligocene sediment. Sierra Nevada granodiorite field from Bateman *et al.* (1963).

($26.67^\circ 2\theta$) overlaps the I/S peaks used in Środoń's method; hence, for samples containing appreciable quartz, the Reynolds and Hower method was used to estimate the proportion of smectite layers in the clay.

For clays in sandstones, chemical analyses were obtained by electron microprobe of either conventional polished thin sections or carbon disks smeared with the <0.1- μm size fraction (see description of technique in Peters and Hofmann, 1984). Carbon disk mounts were used exclusively for shale separates. On the basis of XRD analyses, the <0.1- μm fraction contains only highly expandable I/S clay.

Microprobe analyses were made on an ARL Model EXM-SM electron microprobe equipped with three spectrometers (WDS) and a Tracor Northern TN4000

Table 1. List of oil fields and wildcat wells used in this study.¹

Field name	Number of samples		Depth range of samples (m)	Present burial temperature range of samples ² (°C)	
	Sandstone	Shale			
A	North Coles Levee	21	11	2605–4232	103–156
B	South Coles Levee	2	2	2656–3020	103–116 ²
C	Paloma	12	3	3288–3669	129–142 ³
D	San Emidio Nose	8	4	3497–4314	113–134 ³
E	North Tejon	5	3	2642–3444	94–117 ⁶
F	Rosedale	2	3	1815–3323	66–107 ⁵
G	Rosedale Ranch	10	6	1039–3089	45–101 ⁵
H	Bellevue	11	5	1767–2366	66–83 ⁵
I	Greeley	8	1	2338–3528	80–112 ⁵
K	Edison	1		1401	56 ⁶
L	North Belridge	5	2	2565–2933	102–114 ⁴
M	South Belridge		4	2195–2787	94–115 ⁷
Wildcat wells					
N	Ohoi KCL G-1	17	2	1447–3212	56–104 ⁵
O	Tennaco Schutte #1	10	3	3541–4529	113–139 ⁵
P	Tenneco Sand Hills 64X34	2	2	5573–6765	162–193 ⁸

¹ For sample locations see Figure 1.

² Present burial temperatures based on shut-in well temperatures or calculated from AAPG Geothermal Gradient Map No. 22 (1974), assuming a mean surface temperature of 18°C.

³ Shut-in well temperatures.

⁴ 33°C/1000 m.

⁵ 27°C/1000 m.

⁶ 29°C/1000 m.

⁷ 35°C/1000 m.

⁸ 26°C/1000 m.

energy-dispersive X-ray analysis system. Analyses were made at 100-s counting intervals, using a 10-kV acceleration potential and an 8-nA sample current. The following standards were used: albite for Na; K-feldspar for Si, Al, and K; hematite for Fe; rhodonite for

Mn; rutile for Ti; andesine for Ca; Mg-olivine for Mg; and troilite for S. Concentrations were corrected for absorption, fluorescence, and atomic number with the ZAF computer program written by F. Schamber, N. Wodke, and J. McCarthy and supplied by Tracor Northern (Version 11, November 1981). Precision for the major elements is about $\pm 5\%$ of the amount present.

Totals of the above elements ranged between 57 and 90% and reflect the high amount of water in smectite

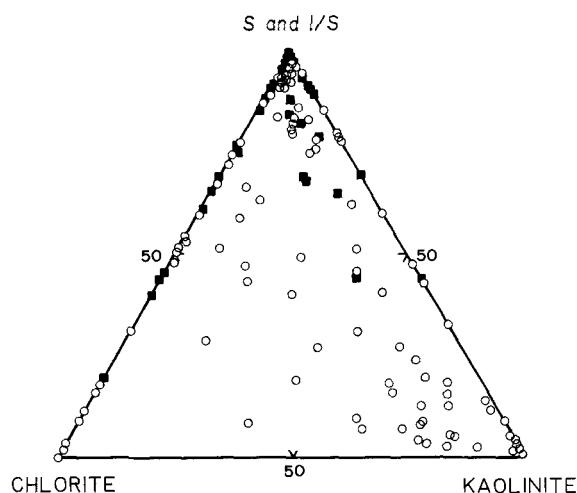


Figure 4. Relative X-ray powder diffraction peak intensities from $<2\text{-}\mu\text{m}$ size fractions of San Joaquin sandstone (circle) and shale (solid square). Peak heights were taken from chlorite ($25.2^\circ 2\theta$), kaolinite ($24.8^\circ 2\theta$), and ethylene glycolated smectite (S) and/or illite/smectite (I/S) clay (5° to $8^\circ 2\theta$), and $\text{CuK}\alpha$ radiation, and recalculated to 100 for plotting.

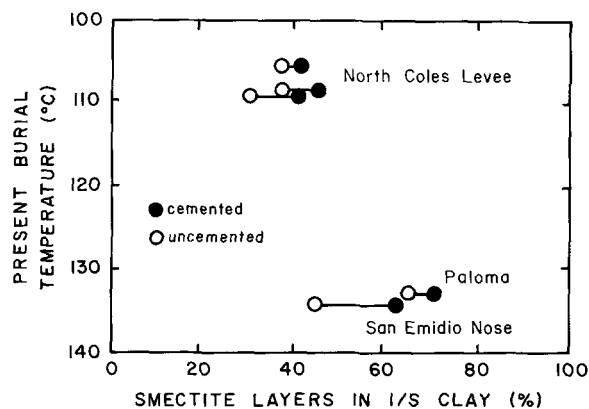


Figure 5. Present burial temperature plotted against percentage of smectite layers in $<2\text{-}\mu\text{m}$ size illite/smectite (I/S) from cemented and uncemented sandstones, San Joaquin basin. Note higher percentage of smectite in cemented compared with subjacent uncemented sandstones.

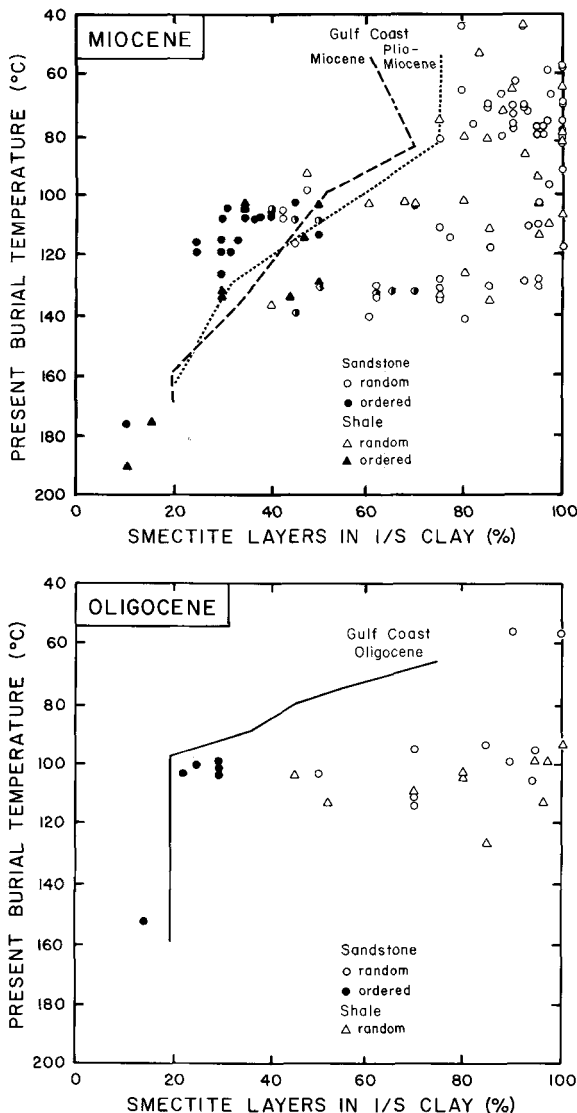


Figure 6. Present burial temperature vs. percentage of smectite layers in $<2\text{-}\mu\text{m}$ illite/smectite (I/S) from the San Joaquin basin. Present burial temperature is based on data in Table 1. Ordered interstratification is based on presence of 002 reflection between 5.2° and $8.9^\circ 2\theta$ (see Środoń, 1980). Figure 6a is from Miocene Gulf Coast data from Bruce (1984), and Gulf Coast Plio-Miocene data from Perry and Hower (1972). Figure 6b is from Oligocene Gulf Coast data from Perry and Hower (1970).

(as much as 22% by weight) and the porosity between individual clay particles. A formula for the highly expandable I/S clay was calculated on the basis of an anhydrous, 22-oxygen unit cell. Iron was corrected for the presence of pyrite from the amount of sulfur detected in the analyses. The quantity of pyrite calculated by this method was $<3\%$ in each sample. All remaining Fe was assumed to be ferric iron. Fe, Mg, and Ti were assumed to be in octahedral sites. Al was assigned to

Table 2. Calculated residence time, time-temperature indexes (TTI) values and average percentage of smectite layers in illite/smectite (I/S) from upper Miocene samples, San Joaquin Basin.¹

Field	Residence time between 100° and 120°C (my)	TTI at 120°C	Smectite layers in I/S at 120°C (%)
San Emidio Nose	2.0	4.0	95
Paloma	2.1	4.5	95
North Coles Levee	2.5	5.0	30

¹ Calculations based on method of Waples (1980) using present geothermal gradients (see Table 1); stratigraphy from California Division of Oil and Gas (California Oil and Gas Fields compilation, 1982); formation ages given by Bartov and McDougall (1984).

tetrahedral sites such that $\text{Si} + \text{Al} = 8$ atoms per 22 oxygens; the remaining Al was assigned to octahedral sites.

RESULTS

Mineralogy of the $<2\text{-}\mu\text{m}$ fraction

The $<2\text{-}\mu\text{m}$ size fractions of the sandstones and shales contained chiefly one or more of the following: illite, smectite, chlorite, kaolinite, illite/smectite (I/S) and chlorite/smectite (Ch/S). Minor amounts of quartz and feldspar were also present. The different proportions of the various clay minerals in these fractions is undoubtedly due to different source materials and to different degrees of diagenesis. Figure 4 shows that the $<2\text{-}\mu\text{m}$ fraction contains *relatively* more kaolinite than this same fraction from the shales, the latter being rich in I/S. These differences are even more pronounced if coarser fractions are compared, because relatively coarse-grain kaolinite tended to be excluded from the finer fractions.

Smectite component in I/S clays from carbonate-cemented and uncemented sandstones

Cemented sandstones contained 10–25% carbonate cement, usually calcite. Oxygen isotope values ($\delta^{18}\text{O}$) for cements from the North Coles Levee and San Emidio Nose areas suggest crystallization temperatures of $50^\circ\text{--}70^\circ\text{C}$ and $25^\circ\text{--}35^\circ\text{C}$, respectively (unpublished data). I/S in cemented sandstones consistently contained 5 to 20% more expandable layers than that in adjacent uncemented (porous) sandstones (see Figure 5). Within cemented sandstones, the timing of the cementation appears to correlate with the percentage of smectite layers in the I/S; e.g., I/S from the San Emidio Nose material contained about 63% smectite layers, whereas I/S from the North Coles Levee material contained about 40–50% smectite layers. Thus, early cementation appears to have retarded the illitization process, probably by impeding the transport of Al and K to and from the reaction sites.

Table 3. Unit-cell contents¹ from microprobe analyses of San Joaquin smectite and illite/smectite (I/S) in sandstones (ss) and shales (sh).

	Field name	Rosedale			Rosedale Ranch			Wildcat	
	Edison Well	J.A.C. 8-8	Humble KCL C-3		Texaco CWL #1	Continental KCL B-1		OHIO KCL G-1	
Rock type	ss*	sh	sh	sh	ss	ss	ss*	ss	ss
Depth (m)	1401	1663	2579	3322	2494	2728	2825	1448	1982
Present burial temperature (°C)	59	62	87	107	84	87	93	56	67
Smectite layers in I/S (%)	100	100	95	85	100	100	85	100	95
Si	7.85	7.86	7.78	7.58	7.86	7.94	7.71	7.93	7.56
Al ^{IV}	<u>0.15</u>	<u>0.14</u>	<u>0.22</u>	<u>0.42</u>	<u>0.14</u>	<u>0.06</u>	<u>0.29</u>	<u>0.07</u>	<u>0.44</u>
Sum	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00
Al ^{VI}	2.74	2.85	3.10	2.92	3.17	3.16	2.95	2.66	3.00
Fe ³⁺	0.45	0.51	0.30	0.24	0.20	0.17	0.31	0.54	0.37
Mg ²⁺	0.86	0.64	0.68	0.89	0.63	0.77	0.85	0.67	0.71
Mn ²⁺	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ti ⁴⁺	<u>0.03</u>	<u>0.07</u>	<u>0.05</u>	<u>0.05</u>	<u>0.03</u>	<u>0.00</u>	<u>0.06</u>	<u>0.07</u>	<u>0.04</u>
Sum	4.11	4.07	4.13	4.10	4.03	4.10	4.17	3.94	4.12
Ca	0.25	0.19	0.13	0.34	0.09	0.14	0.09	0.34	0.30
K	0.14	0.07	0.05	0.26	0.15	0.04	0.25	0.12	0.06
Na	0.03	0.02	0.13	0.02	0.33	0.14	0.11	0.04	0.08
Wt. % oxide, from mi- croprobe analysis	75	78	82	83	67	84	70	83	77

¹ Unit-cell calculations are based on a 22 oxygen, anhydrous unit cell. All iron was treated as ferric. All iron and magnesium was assigned to octahedral sites. Alumina was assigned to tetrahedral sites so that Si + Al = 8. The remaining alumina was assigned to octahedral sites.

² Continental KCL B-1 (2825 m) and Tennaco Schutte #1 (4058 m) samples are Oligocene. All other samples are Miocene. Analyses from thin section shown as ss*; other analyses are from <0.1- μ m size fractions mounted on carbon blocks. See text for analytical details.

Relation of smectite component in I/S clay and burial history

The I/S in the San Joaquin basin varies widely in its expandability (Figure 6). The sandstone suite shown in Figure 6 included about 80% uncemented samples, and, in general, the large differences in expandability cannot be attributed solely to the degree of cementation of these rocks. I/S in shales tended to show a slightly higher content of smectite layers (about 5–10%) than the I/S in closely spaced sandstones, although considerable overlap in smectite layer content was noted. These data contrast with those found in studies of Gulf Coast rocks (Boles and Franks, 1979; Howard, 1981).

Many I/S samples at burial temperatures of 100°C showed substantially more smectite layers than the I/S in age-equivalent samples from the Gulf Coast. For example, at about 130°C, I/S in Miocene samples from the Gulf Coast (Perry and Hower, 1972; Bruce, 1984) typically contain about 30% smectite layers, whereas some I/S in San Joaquin samples contained 60–90% smectite layers (Figure 6a). Samples at burial temperatures greater than 140°C were few in number, but what data were collected suggest that these samples contained low percentages of smectite layers.

Studies of Gulf Coast samples have indicated that the smectite-to-illite reaction does not proceed beyond

an expandability of about 10–20% smectite (see, e.g., Hower *et al.*, 1976). This limit was reached in the San Joaquin basin at temperatures greater than 150°C, similar to those found for Gulf Coast Miocene wells (see Figure 6a). The San Joaquin data, however, suggest that the reaction took place over a few tens of degrees (i.e., 120°–140°C in Miocene rocks; 100°–120°C in Oligocene rocks), whereas in the Gulf Coast the transition in comparable age sediment took place over a temperature range of 80° (Miocene) to 40°C (Oligocene).

Samples with highly expandable I/S clays at temperatures >120°C have been found in the San Emidio Nose, Paloma, and Schutte wells, located in areas overlain by a thick section of Pleistocene rocks (1000–2500 m), implying that the residence time at temperature in these areas was less than in areas containing only a thin cover of young Tertiary rock (<900 m) (Figure 7). The TTI index is a function of both residence time and temperature (Waples, 1980). $TTI = \Sigma$ (residence time \times temperature) within 10°C burial intervals. Table 2 shows calculated residence times and TTI values for areas containing highly expandable I/S (Paloma, San Emidio Nose), compared with an area containing only slightly expandable I/S (North Coles Levee). Table 2 shows that relatively small differences in residence time (for the 100°–120°C temperature interval) and in TTI

Table 3. Continued.

Wildcat	North Coles Levee		Paloma				Wildcat		
OHIO KCL G-1	NCL 21-33		Benco 36-28		Superior Anderson 18-35		Tennaco Schutte #1		
sh	ss	ss	ss*	ss*	ss*	ss*	ss	ss*	sh
3198	3006	3298	3318	3409	3288	3354	3557	3803	4058
104	116	129	130	133	129	131	113	120	127
95	80	75	85	62	95	90	90	25	88
7.66	7.56	7.38	7.68	7.43	7.76	7.65	7.42	6.99	7.66
<u>0.34</u>	<u>0.44</u>	<u>0.62</u>	<u>0.32</u>	<u>0.57</u>	<u>0.24</u>	<u>0.35</u>	<u>0.58</u>	<u>0.01</u>	<u>0.34</u>
8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00
2.66	3.38	3.05	3.17	3.23	3.18	3.28	2.62	2.59	3.02
0.64	0.17	0.27	0.35	0.28	0.24	0.20	0.56	0.61	0.30
0.72	0.55	0.98	0.67	0.70	0.62	0.66	0.09	0.96	0.83
0.00	0.00	0.00	0.00	0.00	0.01	0.03	0.00	0.00	0.00
<u>0.08</u>	<u>0.02</u>	<u>0.02</u>	<u>0.00</u>	<u>0.02</u>	<u>0.04</u>	<u>0.00</u>	<u>0.05</u>	<u>0.08</u>	<u>0.03</u>
4.10	4.12	4.32	4.19	4.23	4.09	4.17	4.32	4.24	4.18
0.23	0.21	0.23	0.07	0.08	0.09	0.18	0.22	0.09	0.13
0.14	0.11	0.12	0.18	0.33	0.33	0.14	0.14	0.78	0.17
0.06	0.06	0.03	0.07	0.06	0.02	0.05	0.05	0.17	0.13
79	81	78	70	75	68	57	78	80	90

correlate with widely different proportions of smectite in I/S. If the differences in expandability between areas is a result of differences in residence time, these data suggest that the smectite-to-illite reaction may have taken place over a very small depth interval. A residence time difference of about 0.5×10^6 yr between areas may have resulted in large differences in I/S composition (Table 2). These and other variables affecting the smectite-to-illite reaction will be discussed later.

Chemical composition of smectite and I/S

Microprobe compositions of smectite and highly expandable I/S clays are listed in Table 3, along with analyses of I/S clays containing 25–75% smectite layers. The average chemical composition of the 16 smectites and I/S clays containing >80% smectite layers from Table 3 yields the following formula:

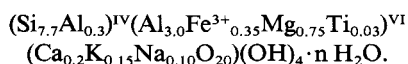
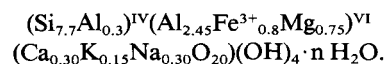


Table 3 and the Experimental section of this paper describe the assumptions used for assigning elements to various structural sites in the above formula.

The composition of these smectites and nearly pure smectites is similar to published analyses of montmorillonite (Figure 8). In general, the San Joaquin smectites have compositions similar to the compositions of smectite components calculated by Boles and Franks (1979) for the I/S clays analyzed by Hower *et al.* (1976) from Gulf Coast shales (Figure 8). The mean composition of the smectite components in the I/S

from the Gulf Coast samples (averaged from Table 5 of Boles and Franks, 1979) is:



the same assumptions were used in assigning elements to structural sites of the Gulf Coast clays as for the San Joaquin materials.

The Fe content and Al/Fe^{VI} ratio of the Gulf Coast and San Joaquin smectite compositions are different. The Gulf Coast smectites have Al/Fe^{VI} ratios of about 3.1, whereas the Al/Fe^{VI} ratio of the San Joaquin smectites is about 8.6. The effect of different iron contents on smectite stability is uncertain, but Boles and Franks (1979) and Bruce (1984) suggested that different smectite compositions affect the illitization reaction. In particular, Boles and Franks (1979) suggested that the Al-rich smectite reacted before Fe- and Mg-rich smectites, based on compositional differences of *residual* smectite layers at various stages of the reaction. The present analyses are based essentially on unreacted smectites and I/S clays.

DISCUSSION

One of the most important findings of the present study is the presence of highly expandable I/S (>80% smectite) at relatively high temperature (>120°–140°C). The effect of various parameters on the smectite-to-illite reaction are discussed below:

Temperature. Perry and Hower (1972) and Hower *et al.* (1976) showed a strong correlation between the ill-

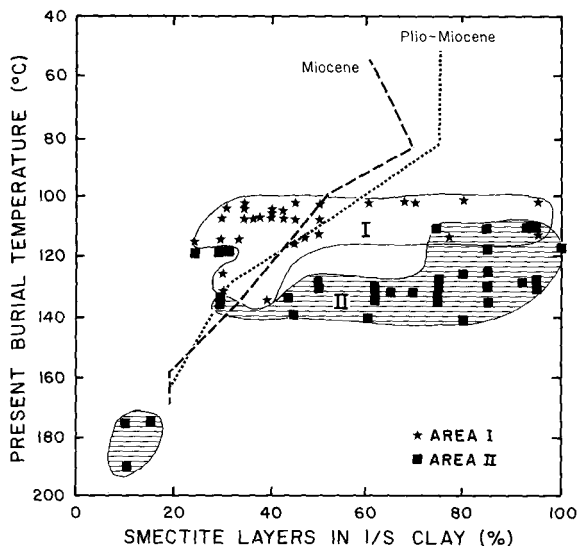


Figure 7. Present burial temperature vs. percentage of smectite layers in $<2\text{-}\mu\text{m}$ illite/smectite (I/S) from Miocene rocks of the San Joaquin basin. San Joaquin basin data from Figure 6a are grouped into two areas: (1) Pleistocene thickness <900 m (North Coles Levee, South Coles Levee); and (2) Pleistocene thickness = $1000\text{--}2500$ m (Paloma, San Emidio Nose, and Schutte and Sand Hills wildcat wells). Gulf Coast data are from Figure 6. Note relatively high percentage of smectite at high temperature in area containing thick Pleistocene cover.

litzation reaction and temperature. Temperature is probably one of the most important variables controlling the reaction; however, the data presented here clearly show that a measurement of maximum burial temperatures in first-cycle burial sequences is by itself inadequate to predict reaction progress.

Potassium availability. Reactions in which natural smectites are largely converted to illite require the addition of K ion. The source of this K is commonly the dissolution of detrital K-feldspar or micas (see Hower *et al.*, 1976). In the rocks studied in the present investigation, K-feldspar and micas (largely biotite) are significant detrital components in the sandstones and shales but do not appear to decrease in abundance or disappear with burial depth. Hence, the presence of highly expandable smectite in some areas cannot be attributed to a lack of potassium availability. Likewise, K^+/H^+ log activity ratios of pore fluids from two fields in the basin that contain different proportions of smectite layers in I/S are similar (Table 4). In the North Coles Levee area, the K^+/H^+ log activity ratio pore fluids is about 4.4 ± 0.2 at 100°C , and at San Emidio Nose the ratio is 4.6 ± 0.2 at 125°C .

Inhibitor ions. Hydrothermal studies indicate that the stability of K-exchanged dioctahedral Mg-rich smectite is less than that of Ca-, Mg-, and Na-exchanged smectite (Eberl *et al.*, 1978). Roberson and Lahann (1981)

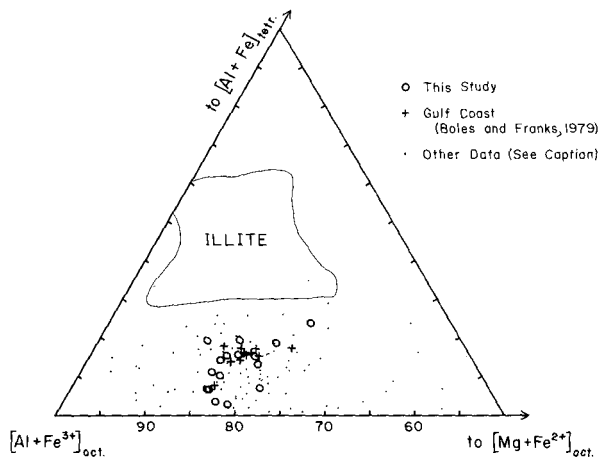


Figure 8. Microprobe analyses (moles) of smectite and illite/smectite ($>80\%$ smectite layers) in San Joaquin basin sandstones and shales (open circle). See text for analytical methods and assumptions. Data from Table 3. + = smectite compositions in Gulf Coast shale (see Boles and Franks, 1979). Montmorillonite compositions taken from Aoki *et al.* (1974), Brigatti (1983), Brigatti and Poppi (1981), Brindley and Brown (1980), Deer *et al.* (1963), Mattigod and Sposito (1978), Nemezc (1981), Ross and Hendricks (1945), Tardy and Garrels (1974), and van Olphen and Fripiat (1979). Illite compositions from Deer *et al.* (1963), Merino and Ransom (1982), and van Olphen and Fripiat (1979).

showed experimentally that Ca^{2+} and Mg^{2+} inhibit the smectite-to-illite reaction rate by an order of magnitude compared with Na^+ , at a fixed K^+ content in solutions.

Table 4 shows that the $\log a_{\text{Ca}^{2+}}/a_{\text{H}^+}^2$ and $a_{\text{Mg}^{2+}}/a_{\text{H}^+}^2$ ratios of pore waters in the San Emidio Nose area is about an order of magnitude greater than those from the North Coles Levee area. In accord with Roberson and Lahann's (1981) conclusions, the relative high Ca and Mg content of San Emidio Nose waters probably is responsible for the highly expandable I/S in that area, compared with the North Coles Levee area. We are reluctant to explain all of the observed data in this way,

Table 4. Log activity ratios of ions in pore waters from North Coles Levee and San Emidio Nose areas.¹

Field name	North Coles Levee	San Emidio Nose
N	5	2
Sample depth (m)	2590–2780	3660–3980
Temperature ($^\circ\text{C}$)	100	120–125
$\text{Log}(a_{\text{K}^+}/a_{\text{H}^+})$	4.4 ± 0.2	4.6 ± 0.2
$\text{Log}(a_{\text{Ca}^{2+}}/a_{\text{H}^+}^2)$	11.4 ± 0.4	12.1 ± 0.1
$\text{Log}(a_{\text{Mg}^{2+}}/a_{\text{H}^+}^2)$	10.2 ± 0.5	11.5 ± 0.5
$\text{Log}(a_{\text{Na}^+}/a_{\text{H}^+})$	6.2 ± 0.2	6.5 ± 0.1

¹ Activity ratios calculated from well-head pore-water samples using the EQ3 computer program (Woolery, 1979) by G. Thyne, ARCO Geoscience Group, Dallas, Texas.

however, because Roberson and Lahann's data suggest slower *reaction rates* in the presence of abundant Ca and Mg, yet it appears that the illitization reaction occurs rapidly (i.e., over a narrow depth range) at suitable burial conditions (see Figure 6).

Effect of permeability. As discussed above, early permeability of a rock relative to reaction sites can affect the progress of the illitization reaction. As shown above, carbonate cements in sandstones appear to slow the illitization reaction relative to that in subjacent sandstones; however, on a regional scale the widespread nature of highly expandable I/S in both cemented and uncemented samples from a given area (Figure 6) suggests that the inhibiting effect of cementation is not solely responsible for the overall differences in the smectite content of I/S clays between areas.

Smectite composition. Few empirical data are available in the literature on the reactivity of smectite of different composition, in particular, Fe-bearing varieties. The stability of smectite with respect to illite or chlorite depends on, among other variables, the composition of the smectite. For example, Dunoyer de Segonzac (1970) showed that in Mg solutions montmorillonite forms chlorite at 350°C. K-montmorillonites react more readily to illite than Na or Ca varieties (Eberl, 1978). Hydrothermal studies indicate that Mg-rich (trioctahedral) smectite is stable at 300°–400°C, whereas Al-rich (dioctahedral) smectite reacts to form I/S + kaolinite (Eberl *et al.*, 1978).

Our microprobe analyses indicate generally similar smectite compositions in the San Joaquin basin, irrespective of geographic or stratigraphic positions; e.g., the composition of a smectite from more volcanogenic Oligocene sandstones (Continental KCl B-1 well, 2825 m, Table 3) is not significantly different from a smectite from less volcanogenic Miocene sandstones.

The composition of San Joaquin basin smectites are generally similar to those from the Gulf Coast, aside from the lower octahedral Al/Fe content of the latter. The effect of this difference in composition on the observed differences in the proportion of smectite layers in I/S in the two regions is, however, not clear. The slightly higher Al content of the San Joaquin smectites should make them more reactive (see Boles and Franks, 1979), but their preservation in the San Joaquin basin does not support this contention. On the other hand, the apparent narrow transition interval from highly expandable to slightly expandable I/S may be due to this aluminous composition.

Residence time. Experimental studies have shown the effect of time on the smectite-to-illite reaction (Eberl and Hower, 1976); however, Bruce (1984) recently concluded that geologic age is not important to the reaction. The present work shows that residence time within a specific temperature window or range of TTI values

correlates with the percentage of smectite layers in I/S. The importance of residence time to the I/S reaction has come to light in the San Joaquin samples due to their very short residence times at elevated temperatures. The data indicate that after a reaction begins, it goes to completion (or near completion) over a narrow temperature interval (Figure 7).

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