LITHIUM AND POTASSIUM SATURATION OF ILLITE/SMECTITE CLAYS FROM INTERLAMINATED SHALES AND SANDSTONES

JAMES J. HOWARD[1]

Department of Geological Sciences, State University of New York at Binghamton
Binghamton, New York 13901

Abstract—Mixed-layer illite/smectite (I/S) clays in lower Eocene sediments of the Texas Gulf Coast decrease in expandability with depth as found in previous studies of clay diagenesis, but at the same depth the I/S clays from sand laminae tend to be more expandable than clays from adjacent shales. The I/S clays with greater expandability from sands collapse to phases with very low expandabilities after saturation with K. This non-ideal smectite behavior indicates that many of the expandable layers in I/S clays from sand laminae possess an illite-level negative layer charge on the structure. The Greene-Kelley Li-saturation test of the I/S clays also reveals that a considerable portion of the increased layer charge deficiency is created by tetrahedral substitution. The illitization of individual smectite layers in an I/S clay is envisioned to be a two step process instead of the single step rapid transformation implied in many earlier studies. The first rate-limiting step is the creation of sufficiently large negative layer charge in the lattice, primarily by Al for Si substitution in the tetrahedral sheet. The second rate-limiting step is the supply of K to the high-charged expandable layers. The abundance of high-charged expandable layers in I/S clays from sand laminae suggests that the K supply is influenced more by competing ions in the interstitial waters than by the absolute activity of K.

Key Words—Diagenesis, Expandability, Illite, Interstratification, Smectite.

INTRODUCTION

In the past ten years research on mixed-layer illite/smectite (I/S) clays has included studies on the application of equilibrium assemblages as paleotemperature indicators (Schultz, 1978; Hoffman and Hower, 1979; Weaver, 1979), the likelihood of illitization reactions as a source of silica in sandstone cementation (Boles and Franks, 1979; Lahann, 1980), and the consideration of the various environmental factors which influence illitization (Eberl and Hower, 1976; Eberl, 1978). Hydrothermal experiments have emphasized the kinetic nature of I/S clay assemblages, which suggests that the degree of measured I/S expandability is not necessarily in equilibrium with ambient temperature and pressure conditions (Eberl and Hower, 1976). A recent study of I/S clays from the Texas Gulf Coast supports the idea that I/S clays are merely intermediate steps in the transformation of smectite to illite during diagenesis, and that measured expandabilities are not simply a function of temperature conditions alone (Howard, 1980).

The transformation of a highly expandable I/S clay to illite has been studied extensively in terms of the various environmental factors that influence reaction rates, but the mechanism of the actual transformation of a smectite layer to a collapsed illite layer has not evolved beyond that used in earlier equilibrium models.

In these earlier studies the illitization of each layer in the I/S clay involved the increase in negative layer charge by tetrahedral Al for Si substitution and the concomitant fixation of K in the interlayer position when the charge deficiency became large enough (Perry and Hower, 1970; Hower *et al.*, 1976; Schultz, 1978). Implicit in the equilibrium interpretation of I/S clay assemblages was that the steps in this reaction were essentially continuous, i.e., the uptake of readily available K occurred as soon as the high-charged layers were created (Hower *et al.*, 1976). Instead of individual layers being "instantaneously" transformed from smectite to illite, a kinetic interpretation of illitization suggests a mechanism that involves numerous steps, i.e., in accordance with Ostwald's mechanism (Chai, 1974).

The problem in the past has been the identification of such intermediate steps in the illitization reaction. The purpose of this study is to identify any layer in the I/S clays that behaves differently under the scrutiny of X-ray powder diffraction than an ideal smectite or illite after standard Li, K, and ethylene glycol treatments.

DEFINITIONS

Various types of clay layers are defined on the basis of the interlayer cation, the magnitude of the layer charge deficiency created by lattice substitution, and the location of this ionic substitution in either the octahedral or tetrahedral sheets (Grim, 1968). An illite layer is thus defined as a layer in which a higher lattice charge deficiency is located primarily in the tetrahedral

---

[1] Current address: Materials Research Laboratory, Pennsylvania State University, University Park, Pennsylvania 16802.

Table 1. Mineralogical and chemical analyses of I/S clays.

Depth (ft)	Lithology	% Expandable layers	% Expandable layers K-saturated	SiO$_2$	TiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$[1]	MgO	CaO	Na$_2$O	K$_2$O
C-157 interval											
6931	Sand	51	35	58.0	0.55	25.84	4.63	3.24	1.52	2.21	3.97
6963	Shale	40	35	57.5	0.80	27.17	4.15	3.17	1.50	0.57	5.17
6964	Shale	45	40	58.4	0.81	26.45	4.64	3.28	1.16	0.73	4.53
6969	Shale	45	40	57.4	0.75	27.18	4.99	3.23	0.83	0.78	4.70
7038	Shale	43	45	59.6	0.69	26.23	4.59	3.10	1.14	0.12	4.50
7038	Sand	45	30	58.4	0.53	26.65	3.60	2.93	2.13	1.03	4.75
T-30 interval											
9022	Sand	35	25	55.9	0.72	29.48	5.09	2.34	0.66	0.17	5.66
9039	Sand	24	10	52.7	0.87	30.75	5.48	2.59	0.68	0.38	6.54
9047	Shale	20	15	55.2	0.75	29.10	4.50	2.37	0.47	1.03	6.56
9047	Sand	32	0	52.6	0.74	28.59	6.26	2.88	0.91	1.05	6.88
9058	Shale	18	20	54.6	0.80	28.27	4.82	2.49	0.84	1.23	6.93
9156	Sand	26	10	55.6	0.73	27.84	5.08	2.31	0.90	1.06	6.51
9162	Shale	20	15	54.8	0.94	30.16	4.47	2.30	0.54	0.72	6.11
9162	Sand	32	15	52.7	0.83	28.46	6.20	2.52	0.83	2.38	6.10
9183	Shale	18	10	54.5	0.94	29.93	4.21	2.10	0.46	1.12	6.75
9183	Sand	35	20	52.7	0.71	29.67	6.47	2.58	0.99	0.58	6.32
9194	Shale	22	15	54.6	0.88	28.70	3.92	2.32	1.36	1.59	6.62
9207	Shale	22	15	53.4	0.82	31.99	3.67	2.05	0.43	1.57	6.06
9207	Sand	32	10	55.0	0.77	30.29	4.39	2.18	0.42	0.95	5.96
9266	Shale	18	10	54.4	0.87	30.94	4.73	2.43	0.38	0.56	5.73

[1] Fe$_2$O$_3$ = total iron.

sheet, approximately -0.75 equivalents per O$_{10}$(OH)$_2$, and has K$^+$ present in the interlayer positions. The combination of high negative lattice charge and low dehydration energies for K$^+$ results in the dehydration of K within these interlayer spaces and the collapse of the layer to a 10-Å basal spacing (Eberl, 1978).

Smectite layers are defined as having a lower layer charge deficiency, roughly -0.33 equivalents per O$_{10}$(OH)$_2$. This layer charge is insufficient to overcome hydration energies of most of the major interlayer cations, and it is the hydrated nature of interlayer cations that produces the characteristic expandable behavior. Two types of smectite layers are distinguishable by use of the Greene-Kelley Li-saturation test. Montmorillonite-type smectite layers are defined as those having a layer charge deficiency located primarily in the octahedral sheet, in contrast with a layer charge deficiency restricted to tetrahedral sheets as found in beidellite-type smectite layers.

EXPERIMENTAL

Samples

Two cored intervals of interlaminated shales and sandstones from lower Eocene sediments in the Texas Gulf Coast were studied. The C-157 interval is from the lower Eocene Queen City Formation at a depth of 2 km and is distinguished by thin shale laminae between thicker laminae of coarse silt and very fine sand. The T-30 interval is from a nearby well and contains Wilcox Formation sands and shales from a depth of 3 km.

These intervals were chosen because of their distinct sand-shale laminae which enabled a clean separation of the two lithologies to be made.

Methods

Sand and shale laminae were separated by hand from each other prior to grinding with mortar and pestle. An ultrasonic probe was used to continue the gentle disaggregation of the shales and sands. The clay-size fraction from each lithology, <0.25 μm, was separated from the bulk by centrifugation and settling methods.

Mineralogy of the predominately I/S clay samples was determined by X-ray powder diffraction (XRD) methods using a Philips-Norelco diffractometer with stripchart readout. X-rays were produced with a copper target and collimated with a quartz monochromator. A slurry of the <0.25-μm fraction was pipetted onto a glass slide and allowed to dry overnight. The air-dried slides were solvated with ethylene glycol for at least 6 hr at 60°C in order to measure I/S expandability (Reynolds and Hower, 1970).

A portion of the fine fraction of each sample was saturated with 3 N KCl solution for several hours and then washed with distilled water until all excess chloride was removed. An oriented slide of the K-saturated clay was prepared, solvated with ethylene glycol, and X-rayed. The behavior of expandable smectite layers after K saturation gave an estimate of the magnitude of the layer charge deficiency; those expandable layers with sufficiently high negative charge collapsed to 10 Å when K was introduced into the interlayer.
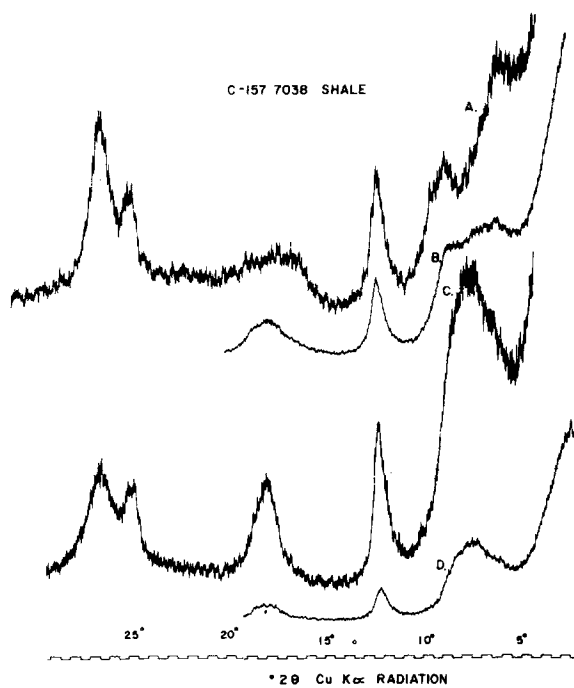
Figure 1. Diffractograms from C-157 interval, 7038 shale sample, CuKα radiation. A. Fully expanded with ethylene glycol. B. K-saturated, ethylene glycol. Basal reflection (001/001) shifted slightly towards higher angles. C. Li-saturated, heated to 200°C, glycerol. Basal reflection (001/001) shows little change in I/S expandability compared to unexpanded Li-treated I/S clay. D. Li-saturated, heated to 200°C, air-dried. Most expandable layers are collapsed.

Figure 2. Diffractograms from C-157 interval, 7038 sand sample, CuKα radiation. A. Fully expanded with ethylene glycol. B. K-saturated, ethylene glycol. 001/001 and 002/003 reflections have shifted towards higher angles, i.e., 5.9° to 7.1°2θ. C. Li-saturated, heated to 200°C, glycerol. Shift in basal reflection (001/001) indicates an increase in I/S expandability from unexpanded Li-treated I/S clay. D. Li-saturated, heated to 200°C, air-dried. Most expandable layers are collapsed.

Another portion of each fine fraction was saturated with 1 N LiCl solution and washed (Greene-Kelley, 1955; Schultz, 1978). The Greene-Kelley Li-test is useful in distinguishing between tetrahedral and octahedral charge deficiencies in smectites. An oriented slide was prepared and allowed to dry overnight. The Li was then fixed into available interlayer and octahedral vacancies by heating the slide to 200°C for 6 hr. The slide was X-rayed after cooling and then again after treatment with glycerol.

The chemistry of the clay-size fraction was determined by rapid wet chemical methods modified from Shapiro and Brannock (1962). Samples were fluxed with lithium metaborate and placed into solution with sulfuric acid. Colorimetric techniques were used for SiO_2, Al_2O_3, and TiO_2 using a Beckman DU spectrophotometer. K_2O, total iron, CaO, MgO, and Na_2O were analyzed by atomic absorption spectroscopy. The analytical error was estimated to be ±0.5% for SiO_2, 0.1% for Al_2O_3, 0.05% for total iron, 0.03% for MgO and K_2O, and 0.01% for CaO and Na_2O.

RESULTS

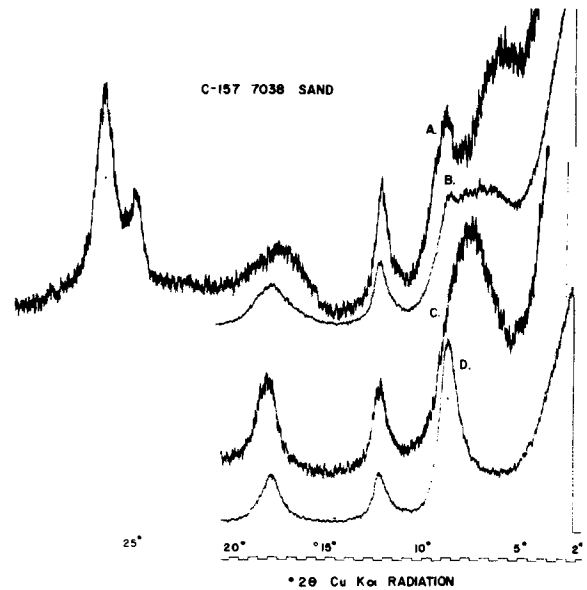The I/S clays from this study show the same pattern of decreasing expandability with depth that was found in other Gulf Coast mixed-layer clays (Perry and Hower, 1970, 1972; Hower *et al.*, 1976; Weaver and Beck, 1971; van Moort, 1971). I/S clays from the C-157 interval have expandabilities of 40–50% (Table 1). The T-30 samples contain I/S clays that are characterized by expandabilities of 18–35%.

Within the T-30 interval the lithology of the host rock from which each I/S clay sample was obtained influences the expandability of the clay. I/S clays from sand laminae all contain more than 30% expandable layers, in contrast to the I/S clays from shale laminae which have expandabilities of less than 20%. A t-test indicates that at a 95% confidence interval the mean I/S expandability for clays from shale laminae, 22%, does not come from the same population that produced the 32% mean expandability found in I/S clays from sand laminae. This contrast in I/S expandability between the two types of host lithology is not apparent in the C-157 interval clays.

K-saturated I/S clays from the shale C-157 samples show little evidence of expandable layer collapse; the I/S expandabilities decrease no more than 5% (Figure 1). This absence contrasts with a significant collapse of expandable layers in I/S clays from C-157 sand laminae. As much as half of the original expandability of these samples was destroyed by the K treatment. An example of this alteration is a decrease in expandability from 45% to 25% in the 7038 sand sample (Figure 2).
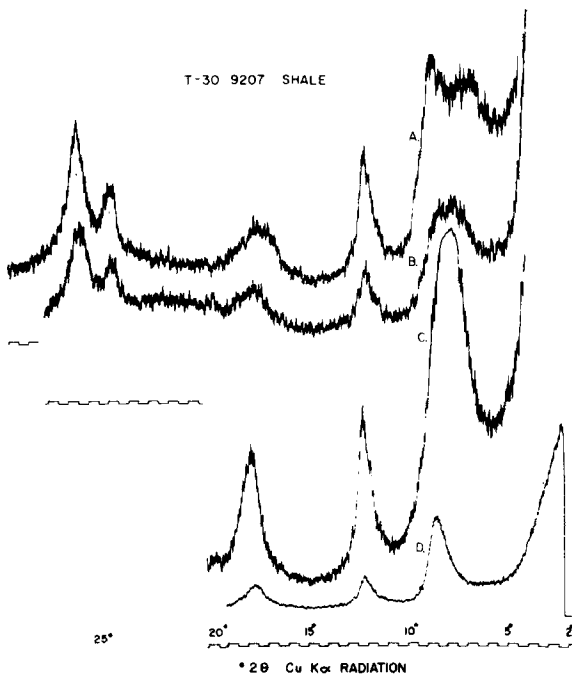
Figure 3.   Diffractograms from T-30 interval, 9207 shale sample, CuKα radiation. A. Fully expanded with ethylene glycol. B. K-saturated, ethylene glycol. Slight shift in 001/001 reflection to higher angles. C. Li-saturated, heated to 200°C, glycerol. Basal reflection (001/001) differs little from unexpanded Li-treated I/S clay. D. Li-saturated, heated to 200°C, air-dried. Most expandable layers are collapsed.

Figure 4.   Diffractograms from T-30 interval, 9207 sand sample, CuKα radiation. A. Fully expanded with ethylene glycol. B. K-saturated, ethylene glycol. 001/001 and 002/003 reflections have shifted towards higher angles, i.e., 7.1° to 7.9°2θ. C. Li-saturated, heated to 200°C, glycerol. Shift in basal reflection indicates an increase in I/S expandability from unexpanded Li-treated I/S clay. D. Li-saturated, heated to 200°C, air-dried. Most expandable layers are collapsed.

I/S clays from the T-30 interval respond to K saturation in a manner similar to the C-157 clays. I/S clays from T-30 shale laminae show little evidence of expandable layer collapse after K treatment. The I/S clay from the 9207 shale lamina loses approximately only 5% of its expandable layers after K treatment (Figure 3). In contrast to shale I/S clays being relatively unaffected by K saturation, the I/S clays from sand laminae show almost complete expandable layer collapse after K treatment. The I/S clay from the 9207 sand sample is an example of the large scale collapse of expandable layers, a decrease in expandability from 30% to less than 10% (Figure 4).

Results of the Greene-Kelley Li-saturation test indicate that the I/S clays from C-157 shale laminae are characterized by the collapse of expandable layers after saturation with Li, heating, and treatment with glycerol (Figure 1). In contrast, I/S clays from C-157 sand laminae retain diffraction maxima that indicate the presence of expandable layers after the Li treatment (Figure 2).

The I/S clays in the T-30 interval are similarly affected by the Greene-Kelley Li test. Clays from the shale laminae show no evidence of any expandable layers after treatment with Li and glycerol (Figure 3). In contrast, some of the expandable layers in the I/S clays from T-30 sand laminae re-expand after the Li treatment (Figure 4).
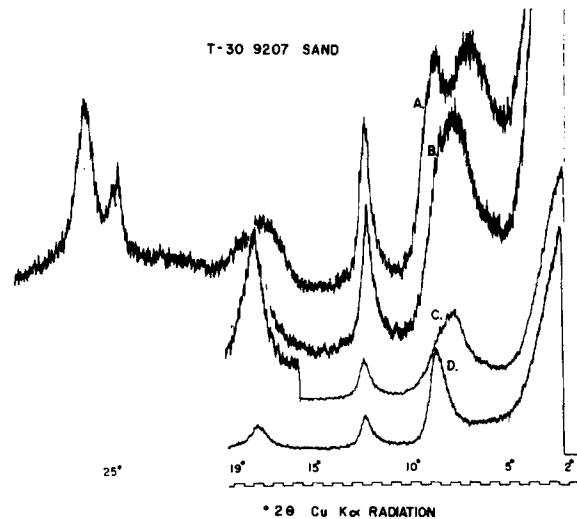
Chemical analyses of the fine fraction clays support the concept of progressive illitization with depth. The chemical analyses in Table 1 have been recast to remove the contribution of the small amounts of kaolinite and discrete illite determined by semi-quantitative XRD methods, the result being an approximate analysis of the I/S clay. Within each interval there is no discernible trend between the calculated chemical analyses of the I/S clays and their measured expandabilities. However, between the C-157 and T-30 intervals the differences in I/S chemistry are more pronounced, corresponding to the larger difference in I/S mineralogy. The most significant differences in I/S clay chemistry are the increase in K_2O content and the decrease in the Si/Al ratio with progressive illitization. Other previously reported depth-related trends, such as a decrease in Fe (Foscolos and Kodoma, 1974; Hower et al., 1976) and an increase in Mg (Weaver and Beck, 1971), are not evident in these clays.

Structural formulae of the I/S clays were calculated for many of the samples in the C-157 and T-30 sections, covering a wide range of expandabilities (Table 2). No distinction was made between ferrous and ferric iron in this study; the total iron was treated as ferric for structural formulae determinations. The structural formulae produced for these samples are similar to those of I/S clays in other studies, with an overall layer charge deficiency of −0.55 to −0.70 equivalents per $O_{10}(OH)_2$,

along with a summation of octahedral structural components of about 2.0 equivalents (Weaver and Pollard, 1973).

DISCUSSION

The most significant result of this study is that the I/S clays from sand laminae tend to be more expandable than I/S clays from adjacent shale laminae. Not only is the overall expandability different for the two lithologies, but the expandable layers in the I/S clays seem to possess different characteristics in the sand laminae than in the shale. This difference in I/S expandability is more pronounced in the deeper T-30 section, but other studies of Gulf Coast mixed-layer clays reveal the same relationship over a wider range of depths (Boles and Franks, 1979).

The identification of high-charged expandable layers by means of K-saturation tests suggests that the illitization reaction is at least a two-step process. First, low-charged smectite layers develop a sufficiently large negative charge deficiency by substitution within the lattice. After a suitably large layer charge is created, K ions in the interlayer positions are dehydrated by the attractive bonding forces between the ion and lattice, and fixed into the interlayer position. The creation of layer charge and subsequent fixation of potassium are not simultaneous and interdependent events; rather, they are two independent events, both of which have their own rate-limiting steps.

The presence of high-charged expandable layers in these I/S clays suggests that K is not immediately fixed into interlayer spaces after a sufficiently large charge is created. Previous studies of illitization presumed an abundant and readily available supply of K from the dissolution of feldspar, discrete illite, or other potential K source (Perry and Hower, 1970; Weaver and Beck, 1971; Hower *et al.*, 1976; Weaver, 1979). The high-charged expandable layers in the I/S clays from this study suggest that the supply of K to interlayer vacancies may be an important rate-limiting step in illitization.

The Greene-Kelley Li-saturation results indicate that much of the increased layer charge deficiency in the expandable layers that is required for K fixation is created in the tetrahedral layer. A greater proportion of the expandable layers in I/S clays from sand laminae in this study have a tetrahedral charge deficiency as evidenced by expansion of the basal reflection. The association of both high-charged expandable layers and a tetrahedral layer charge deficiency in these layers of I/S clays from sand laminae suggests that tetrahedral substitution is a key step in the illitization process.

Structural formulae of the I/S clays show an increase in tetrahedral Al with progressive illitization, while octahedral Al remains essentially constant. This implies that Al does not simply diffuse from the octahedral to the tetrahedral sheet where it substitutes for vacant Si;

Table 2. I/S structural formulae.

Depth (ft)	Lithology	Structural formulae based on $O_{10}(OH)_2$
C-157 interval		
6931	Sand	$(Si_{3.58}Al_{0.42})(Al_{1.46}Fe_{0.22}Mg_{0.30})_{1.98}Ca_{0.10}Na_{0.26}K_{0.31}$
6963	Shale	$(Si_{3.56}Al_{0.44})(Al_{1.54}Fe_{0.19}Mg_{0.29})_{2.02}Ca_{0.10}Na_{0.07}K_{0.41}$
6964	Shale	$(Si_{3.60}Al_{0.40})(Al_{1.52}Fe_{0.21}Mg_{0.30})_{2.03}Ca_{0.08}Na_{0.09}K_{0.36}$
6969	Shale	$(Si_{3.55}Al_{0.45})(Al_{1.53}Fe_{0.23}Mg_{0.30})_{2.06}Ca_{0.06}Na_{0.09}K_{0.37}$
7038	Shale	$(Si_{3.65}Al_{0.35})(Al_{1.53}Fe_{0.21}Mg_{0.28})_{2.02}Ca_{0.08}Na_{0.01}K_{0.35}$
7038	Sand	$(Si_{3.60}Al_{0.40})(Al_{1.53}Fe_{0.17}Mg_{0.27})_{1.97}Ca_{0.14}Na_{0.12}K_{0.37}$
T-30 interval		
9022	Sand	$(Si_{3.46}Al_{0.54})(Al_{1.61}Fe_{0.24}Mg_{0.22})_{2.05}Ca_{0.04}Na_{0.02}K_{0.45}$
9039	Sand	$(Si_{3.31}Al_{0.69})(Al_{1.59}Fe_{0.26}Mg_{0.24})_{2.09}Ca_{0.05}Na_{0.05}K_{0.52}$
9047	Shale	$(Si_{3.45}Al_{0.55})(Al_{1.59}Fe_{0.21}Mg_{0.22})_{2.02}Ca_{0.03}Na_{0.12}K_{0.52}$
9047	Sand	$(Si_{3.34}Al_{0.66})(Al_{1.47}Fe_{0.30}Mg_{0.27})_{2.04}Ca_{0.07}Na_{0.13}K_{0.56}$
9058	Shale	$(Si_{3.44}Al_{0.56})(Al_{1.53}Fe_{0.23}Mg_{0.23})_{1.99}Ca_{0.06}Na_{0.15}K_{0.55}$
9162	Shale	$(Si_{3.41}Al_{0.59})(Al_{1.63}Fe_{0.21}Mg_{0.21})_{2.05}Ca_{0.04}Na_{0.04}K_{0.49}$
9162	Sand	$(Si_{3.34}Al_{0.66})(Al_{1.47}Fe_{0.30}Mg_{0.24})_{2.01}Ca_{0.06}Na_{0.29}K_{0.49}$
9156	Sand	$(Si_{3.48}Al_{0.52})(Al_{1.54}Fe_{0.24}Mg_{0.21})_{1.99}Ca_{0.06}Na_{0.13}K_{0.52}$
9183	Shale	$(Si_{3.41}Al_{0.59})(Al_{1.62}Fe_{0.20}Mg_{0.20})_{2.01}Ca_{0.03}Na_{0.14}K_{0.54}$
9183	Sand	$(Si_{3.32}Al_{0.68})(Al_{1.52}Fe_{0.31}Mg_{0.24})_{2.07}Ca_{0.07}Na_{0.07}K_{0.51}$
9194	Shale	$(Si_{3.43}Al_{0.57})(Al_{1.55}Fe_{0.18}Mg_{0.22})_{1.95}Ca_{0.09}Na_{0.19}K_{0.53}$
9207	Shale	$(Si_{3.33}Al_{0.67})(Al_{1.68}Fe_{0.17}Mg_{0.19})_{2.04}Ca_{0.03}Na_{0.12}K_{0.48}$
9207	Sand	$(Si_{3.42}Al_{0.58})(Al_{1.64}Fe_{0.20}Mg_{0.20})_{2.04}Ca_{0.03}Na_{0.12}K_{0.47}$
9266	Shale	$(Si_{3.38}Al_{0.62})(Al_{1.65}Fe_{0.22}Mg_{0.22})_{2.04}Ca_{0.02}Na_{0.07}K_{0.45}$

rather, an external source of Al is required for illitization, such as the concomitant dissolution of feldspar, discrete illite, or kaolinite or the cannibalization of I/S clay edges during burial (Perry and Hower, 1970; Hower *et al.*, 1976; Weaver, 1979).

The interstitial water of sand lithologies in deep sedimentary basins is commonly significantly more saline than that in shales (Schmidt, 1973; Merino, 1975). Despite the presumed greater activity of K in the sand layers of the two intervals of the present study, the I/S clays in these sands are more expandable than those I/S clays from shales with lower K activity. K appears to be more readily fixed by the I/S clays in shale laminae, as noted by the overall greater percentage of illite

layers and the smaller percentage of high-charged expandable layers present.

This apparent contradiction in K fixation and K activities in the interstitial waters can be explained by observing that absolute K contents are not as important in the illitization reaction as the amount of K that actually comes in contact with the high-charged interlayer. In the higher salinity waters in sand laminae, larger K activities have to compete with extremely large abundances of other major cations for the interlayer spaces. An estimate of the K to total cation ratio is approximately 2×10^{-3} (Schmidt, 1973). In shale waters the competition between K and other cations is less; the K to total cation ratio is approximately 1×10^{-2} (Schmidt, 1973). Thus, in the shale laminae there is a greater likelihood of a high-charged expandable layer being filled with K and collapsing to a 10-Å illite spacing.

The illitization of expandable layers in an I/S clay seem to follow a step-wise process which suggests a kinetic control of observed I/S expandability, rather than a process in equilibrium with ambient temperature and pressure conditions. The illitization reaction is envisioned to include the creation of a large layer-charge deficiency in the expandable layers by substitution within the lattice and subsequent fixation of K in the interlayers. The creation of a sufficiently large layer charge deficiency does not appear to guarantee K fixation and illite formation. The supply of K to the proper interlayer vacancies is likely an important rate-limiting step in the illitization of smectite layers.

ACKNOWLEDGMENTS

REFERENCES

Boles, J. R. and Franks, S. G. (1979) Clay diagenesis in Wilcox sandstones of southwest Texas: Implications of smectite diagenesis on sandstone cementation: *J. Sediment. Petrology* **49**, 55–70.

Chai, B. (1974) Mass transfer of calcite during hydrothermal recrystallization: in *Geochemical Transport and Kinetics*, A. Hofmann, B. Giletti, H. Yoder, and R. Yund, eds. Carnegie Instit. Washington Publ. **634**, 353 pp.

Eberl, D. D. (1978) The reaction of montmorillonite to mixed-layer clay: The effect of interlayer alkali and alkaline earth cations: *Geochim. Cosmochim. Acta* **42**, 1–7.

Eberl, D. D. and Hower, J. (1976) Kinetics of illite formation: *Bull. Geol. Soc. Amer.* **87**, 1326–1330.

Foscolos, A. E. and Kodoma, H. (1974) Diagenesis of clay minerals from lower Cretaceous shales of northeastern British Columbia: *Clays & Clay Minerals* **22**, 319–336.

Greene-Kelley, R. (1955) Dehydration of the montmorillonite minerals: *Mineral. Mag.* **30**, 604–615.

Grim, R. (1968) *Clay Mineralogy:* 2nd ed., McGraw-Hill, New York, 576 pp.

Hoffman, J. and Hower, J. (1979) Clay mineral assemblages as low grade metamorphic geothermometers: Application to the thrust faulted disturbed belt of Montana, U.S.A.: in *Aspects of Diagenesis,* P. Scholle, and P. Schulger, eds., Soc. Econ. Paleon. Mineral. Spec. Pub. **26**, 55–80.

Howard, J. (1980) Diagenesis of mixed-layer illite/smectite in interlaminated shales and sandstones: Ph.D. Dissertation, State Univ. New York at Binghamton, 158 pp.

Hower, J., Eslinger, E., Hower, M., and Perry, E. (1976) Mechanism of burial metamorphism of argillaceous sediment: I. Mineralogical and chemical evidence: *Bull. Geol. Soc. Amer.* **87**, 725–737.

Lahann, R. (1980) Smectite diagenesis and sandstone cement: The effect of reaction temperature: *J. Sediment. Petrology* **50**, 755–760.

Merino, E. (1975) Diagenesis in Tertiary sandstones from Kettleman North Dome, California. II. Interstitial solutions: Distribution of aqueous species at 100°C and chemical relation to the diagenetic mineralogy: *Geochim. Cosmochim. Acta* **39**, 1629–1645.

Perry, E. and Hower, J. (1970) Burial diagenesis in Gulf Coast pelitic sediments: *Clays & Clay Minerals* **18**, 165–178.

Perry, E. and Hower, J. (1972) Late-stage dehydration in deeply buried pelitic sediments: *Amer. Assoc. Petrol. Geol. Bull.* **56**, 2013–2021.

Reynolds, R. J., Jr. and Hower, J. (1970) The nature of interlayering in mixed layer illite-montmorillonites: *Clays & Clay Minerals* **18**, 25–36.

Schmidt, G. (1973) Interstitial water composition and geochemistry of deep Gulf Coast shales and sandstones: *Amer. Assoc. Petrol. Geol. Bull.* **57**, 321–337.

Schultz, L. G. (1978) Mixed-layer clay in the Pierre Shale and equivalent rocks, Northern Great Plains region: *U.S. Geol. Surv. Prof. Pap.* **1064-A**, 28 pp.

Shapiro, L. and Brannock, W. (1962) Rapid analysis of silicate, carbonate, and phosphate rocks: *U.S. Geol. Surv. Bull.* **1144-A**, 56 pp.

van Moort, J. (1971) A comparative study of the diagenetic alteration of clay minerals in Mesozoic shales from Papua New Guinea, and in Tertiary shales from Louisiana, U.S.A.: *Clays & Clay Minerals* **19**, 1–20.

Weaver, C. E. (1979) Geothermal alteration of clay minerals and shale: Diagenesis: *Tech. Rept.* **ONWI-21**, Georgia Inst. Tech., Battelle Off. Nucl. Waste Isolation, 176 pp.

Weaver, C. E. and Beck, K. (1971) Clay-water diagenesis during burial: How mud becomes gneiss: *Geol. Soc. Amer. Spec. Pap.* **134**, 96 pp.

Weaver, C. E. and Pollard, L. (1973) *The Chemistry of Clay Minerals:* Elsevier, New York, 205 pp.

Резюме—Смешанно-слойные глины, иллит/смектит (И/С), в осадках нижней Эоценовой формации на побережьи Техаского залива характеризуются уменьшающейся способностью к расширению с глубиной, как это было обнаружено в предыдущих исследованиях диагенеза глин. На одинаковой глубине, тем не менее, И/С глины из песчаной плоскости отслоения имеют большую тенденцию к расширению, чем глины из соседних сланцев. И/С глины, из песков, с большей способностью к расширению обваливаются на фазы с очень низкой способностью к расширению после насыщения калием. Это неидеальное поведение смектита указывает на то, что многие расширяющиеся слои в И/С глинах из песчаной плоскости отслоения имеют отрицательный слойный заряд решетки на уровне иллита. Проба Грина-Келлея по насыщению И/С глин литием также показывает, что значительная часть увеличивающейся недостаточности заряда слоев воздается тетраэдрическим замещением. Иллитизация индивидуальных слоев смектита в И/С глине является двуступенчатым процессом вместо одноступенчатой быстрой трансформации, предполагаемой во многих ранних исследованиях. Первая ограничивающая скорость ступень—это создание достаточно большого отрицательного слойного заряда решетки, в основном, замещением кремния алюминием в тетраэдрических пластах. Вторая ограничивающая скорость ступень—это снабжение калием расширяющихся слоев в высоким зарядом. Избыток этих слоев в И/С глинах из песчаной плоскости отслоения указывает на то, что конкурирующие ионы промежуточных вод влияют на доставку калия более, чем его абсолютная активность. [E.C.]

Resümee—Die Expandierbarkeit der Illit/Smektit-Wechsellagerungen (IS) in den Untereozänen Sedimenten der Golfküste von Texas nimmt mit der Tiefe ab, wie aus früheren Untersuchungen zur Diagenese von Ton hervorgeht. Die I/S-Tone aus den Sandlagen der gleichen Tiefe sind jedoch mehr expandierbar als die Tone der benachbarten Tonschiefer. Die I/S-Tone mit der größeren Expandierbarkeit aus den Sanden kontrahieren nach einer Kalium-Sättigung zu Phasen mit einer sehr geringen Expandierbarkeit. Dieses nicht-ideale Smektit-Verhalten deutet darauf hin, daß viele der expandierbaren Lagen in den I/S-Tonen aus den Sandschichten eine dem Illit entsprechende negative Schichtladung haben. Der Lithiumsättigungs-Test nach Greene und Kelley der I/S-Tone zeigt ebenfalls, daß ein beträchtlicher Anteil des erhöhten Schichtladungsmangels durch Substitution auf den Tetraederplätzen hervorgerufen wird. Es wird angenommen, daß die Illitisierung einzelner Smektit-Lagen in einem I/S-Ton in zwei Schritten vor sich geht anstatt durch eine rasche Umwandlung in einem Schritt, wie es in vielen, früheren Untersuchungen angenommen wurde. Der erste geschwindigkeitsbestimmende Schritt ist die Bildung einer genügend großen negativen Schichtladung im Gerüst, die vor allem durch die Substitution von Si durch Al in den Tetraederlagen hervorgerufen wird. Der zweite geschwindigkeitsbestimmende Schritt ist die Kaliumzufuhr zu den hoch geladenen expandierbaren Lagen. Der Überschuß an hochgeladenen expandierbaren Lagen in den I/S-Tonen aus den Sandschichten deutet darauf hin, daß die Kaliumzufuhr in größerem Maße durch die konkurrierenden Ionen im Wasser der Zwischenschicht als durch die absolute Kalium-Aktivität bestimmt wird. [U.W.]

Resumé—L'expansion des argiles illite/smectite (I/S) à couches mélangées dans les sédiments du bas éocène de la Côte du Golfe du Texas décroit à mesure que la profondeur croit, ainsi qu'on l'a montré dans des études précédentes de la diagénèse des argiles, mais à la même profondeur, les argiles I/S dans les lames de sable tendent à être plus expansibles que les argiles dans les shales adjacents. Les argiles I/S ayant la plus grande expansion s'effondrent en des phases avec des expansions très basses après avoir été saturées de K. Ce comportement non-idéal de smectite indique que beaucoup de couches expansibles dans les argiles I/S des lames de sable possèdent une couche à charge négative au niveau illite sur l'édifice cristallin. Le test de saturation-Li Greene-Kelley des argiles I/S révèle aussi qu'une portion considérable de la plus grande déficience de charge de couche est crée par la substitution tétraèdre. L'illitisation de couches individuelles de smectite dans une argile I/S est vue comme un procédé à deux étapes plutôt qu'une transformation rapide à une étape impliquée dans beaucoup d'études précédentes. La première étape limitant l'allure est la création d'une charge négative suffisemment grande dans l'édifice cristallin, principalement par la substitution d'Al pour Si dans la feuille tétraèdre. La deuxième étape limitant l'allure est la fourniture de K aux couches expansibles hautement chargées. L'abondance de couches expansibles à haute charge dans les couches des argiles I/S des lames de sable suggère que la fourniture de K est plus influencée par la compétition d'ions dans les eaux interstitiales que par l'activité absolue de K. [D.J.]