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SMECTITE TO ILLITE CONVERSION RATES: EFFECTS OF SOLUTION CHEMISTRY

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Abstract—Mixed-layer illite/smectite (I/S) was formed by reacting the Chambers or Polkville montmorillonite hydrothermally at 270° and 350°C from several hours to more than 15 weeks. Reactions were conducted in closed vessels containing K or mixed K-Na, K-Ca, or K-Mg solutions of varying concentrations. The reaction rate and the rate of ordering of I/S for the reaction smectite + $K^+ \rightarrow$ mixed-layer I/S + SiO_2 was inhibited by the addition of Na^+, Ca^{2+}, and Mg^{2+}; the inhibitory strength of Na^+, Ca^{2+}, and Mg^{2+}, on an equivalent basis, increased approximately in the ratio 1:10:30. The first order reaction-rate constants for the reactions at 270° and 350°C indicate an activation energy of about 30 kcal/mole.

In the experimental system studied, the reaction smectite → mixed-layer I/S appeared to proceed by solid state transformation, as suggested by: (1) rapid dissolution of large amounts of silica, probably creating an Al-enriched residue; (2) similarity of particle size and morphology of the mixed-layer products to those of the original montmorillonite, implying no extensive dissolution of Al^{3+}; and (3) relatively high activation energy compared to published values for silicate dissolution.

Key Words—Hydrothermal, Illite, Mixed layer, Reaction rate, Silica dissolution, Smectite.

INTRODUCTION

The conversion of smectite to mixed-layer illite/smectite (I/S) commonly occurs as a response to the burial of clayey sediments. If mixed-layer I/S in a deeply buried shale is at equilibrium at a given temperature, pressure, and pore solution, a sensitive measure of diagenesis or metamorphism exists. If it is not at equilibrium, but, instead, is a product of reaction kinetics, the factors affecting the reaction kinetics need to be identified and quantified. Eberl and Hower (1976) determined the rate of illite formation from smectite at elevated temperatures. Their rate constants indicated that the conversion of smectite to illite was sufficiently rapid to be compatible with either an equilibrium or a kinetic interpretation for the range of mixed layering found in Gulf Coast shales of Tertiary age. These authors recognized that their reaction rates were probably greater than conversion rates in a natural setting because most of their hydrothermal runs were conducted in the absence of excess Na^+, and all were conducted in the absence of Ca^{2+} and Mg^{2+}, ions which could be expected to impede significantly the conversion (Blatter, 1975).

The primary purpose of the present experiments was to determine the effect of the presence of Na^+, Ca^{2+}, and Mg^{2+} on the rate of the reaction smectite + $K^+ \rightarrow$ illite/smectite + SiO_2 and to gain insight into the reaction mechanism.

PROCEDURE

The <0.5-μm fractions of montmorillonites from Polkville, Mississippi (A.P.I. No. 21), and Chambers, Arizona (A.P.I. No. 23), obtained from Ward's Natural Science Establishment, Rochester, New York, were concentrated by centrifiguation after the clay was saturated with either Na^+ or Ca^{2+}. Saturation was effected by repeatedly washing the bulk clay with 1 N $CaCl_2$ or NaCl. The clays were then washed with distilled water until free of Cl^- ($AgNO_3$ test).

Ten milligrams of the 0.5-μm clays was heated with 1 ml of solution in a sealed gold capsule within a closed hydrothermal vessel. Internal pressure was the vapor pressure of H_2O at the temperature of the experiment. All solutions contained 280 ppm HCO_3^-, either as the Na^+ or K^+ salt. Additional Na^+, K^+, Ca^{2+}, or Mg^{2+} was added as the chloride salt. Following heating at 270° or 350°C for the desired length of time, the samples were quenched, and solid products were separated by centrifugation, washed free of chloride, suspended in water, and allowed to settle on a glass slide. The phases in the solid products were identified with a Philips X-ray diffractometer using Ni-filtered CuKα radiation. The oriented clay minerals on the glass slides were X-rayed in the air-dried state and after solvation with ethylene glycol. Initial scans were at 2°2θ/min. Spacings of the $(001)_{10}/(002)_{17}$[2] and the $(002)_{10}/(003)_{17}$ reflections of the mixed-layer phases were determined at scan speeds of

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[2] $(001)_{10}$ = a 001 reflection occurring at ~10 Å, and so forth.

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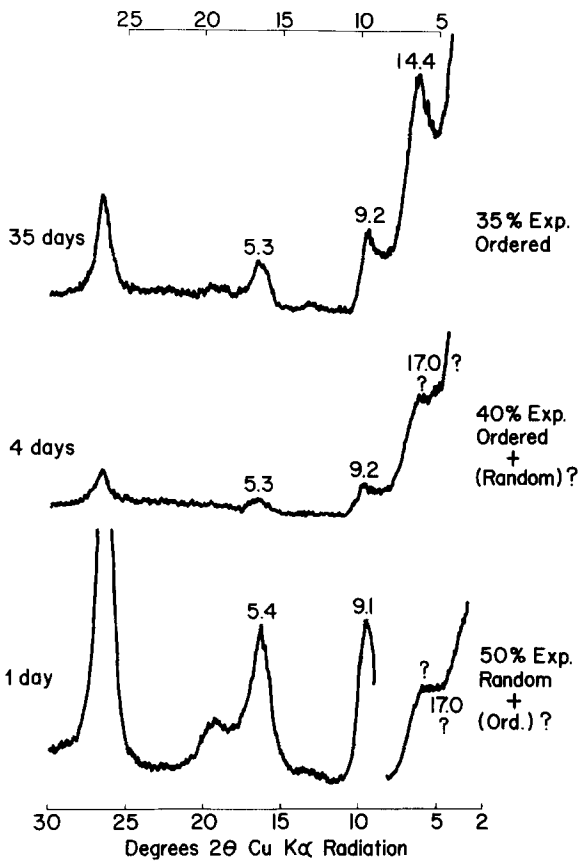


Figure 1. X-ray powder diffraction patterns of I/S reaction products when Na-saturated Chambers montmorillonite was reacted with 400 ppm K^+ starting solution at 270°C. (d-spacings in Å shown for critical peaks)

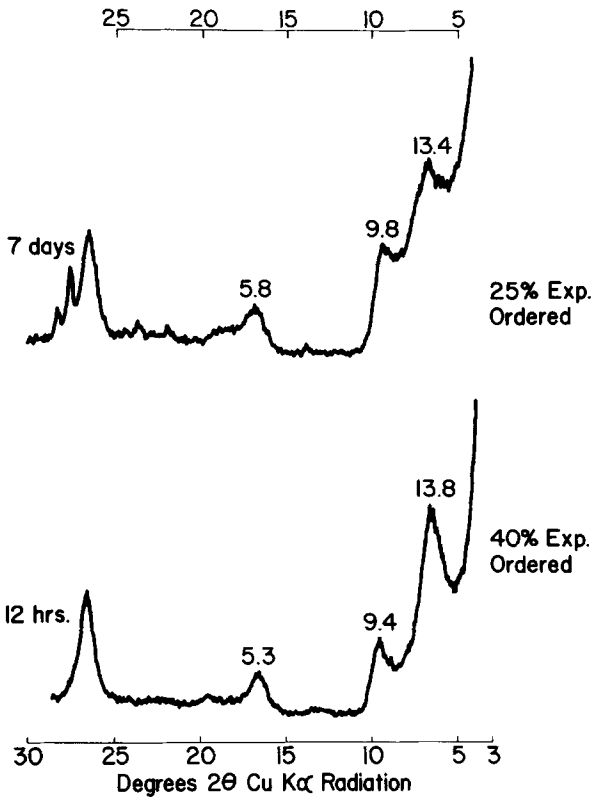


Figure 2. X-ray powder diffraction patterns of I/S reaction products when Na-saturated Chambers montmorillonite was reacted with 400 ppm K^+ starting solution at 350°C. (d-spacings in Å shown for critical peaks)

0.4°2θ/min. The proportion of smectite layers (% expandability) in the mixed-layer phase was determined using the Reynolds and Hower (1970) technique. The expandabilities reported are thought to be accurate to ±5%.

Plots of expandability vs. time are shown in Figures 4–7. Plots of both random and ordered mixed-layer phases indicate that expandability decreased linearly with time at a given temperature. First-order kinetics were, therefore, assumed. The first-order rate constant k was calculated using the equation

$$\ln x = kt$$

where x = % expandability and t is time in days.

After removal of the clay, the fluids were analyzed for Na^+, Ca^{2+}, Mg^{2+}, and K^+ by atomic absorption spectrophotometry employing a Perkin Elmer 303 instrument. Soluble silica was analyzed spectrophotometrically by the molybdenum-blue method, following depolymerization in $NaHCO_3$ solution. Cation-exchange capacities were determined by repeated exchange with 1 N $BaCl_2$ in a buffered, pH 8 solution.

RESULTS

Figure 1 shows the X-ray powder diffraction pattern (XRD) tracings of Na-saturated Chambers montmorillonite (Na-Chambers) after reaction with 400 ppm K^+ solution for varying lengths of time at 270°C. The Na-Chambers clay (originally 100% expandable), after having reacted for only one day, decreased in expandability to 50%. It is impossible to determine whether a single, broad, first order maximum at 15–17 Å is present or whether the peak consists of two unresolved maxima, one at 17 Å and the other at a somewhat lower value (15–16 Å). Higher order reflections are also somewhat ambiguous in determining whether the mixed layering is ordered or whether both random and ordered mixed layering are present. At 350°C (Figure 2), expandability decreased significantly within hours, as did the degree of ordering. After 7 days at 350°C, the expandability of the clay decreased to 25%.

The effect of adding a large amount of Na^+ to the reaction solution is shown in Figure 3. The Na-Chambers clay that had been treated with both Na^+ and K^+ (9400 ppm Na^+, 400 ppm K^+) at 270°C converted to an I/S with only 65% expandability after 7 days, and to an I/

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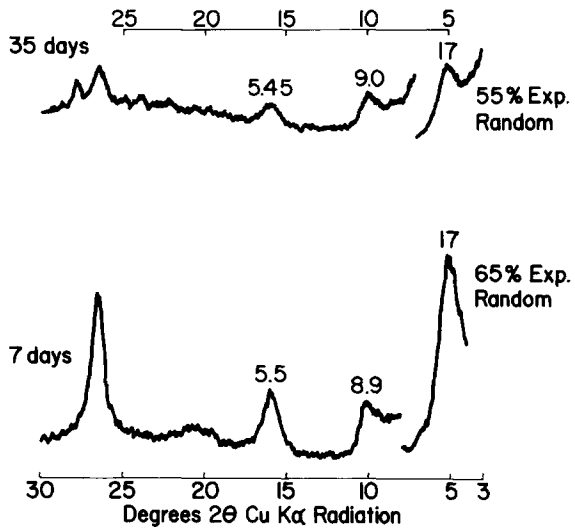


Figure 3. X-ray powder diffraction patterns of I/S reaction products when Na-saturated Chambers montmorillonite was reacted with 400 ppm K^+, 9400 ppm Na^+ starting solutions at 270°C. (d-spacings in Å shown for critical peaks)

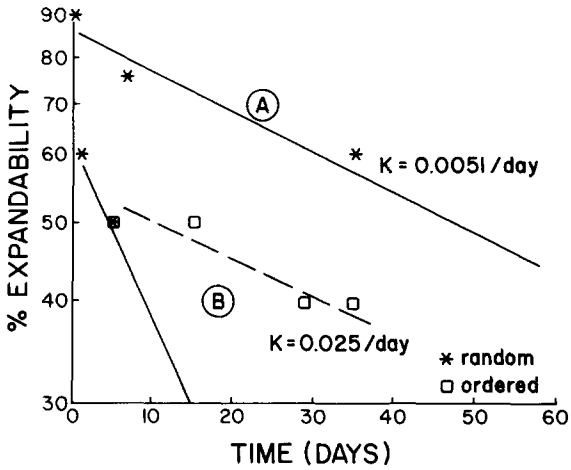


Figure 4. Expandability of reaction products as a function of time when Na-saturated Chambers montmorillonite reacted at 270°C with (A) 400 ppm K^+/9400 ppm Na^+ and (B) 400 ppm K^+ starting solutions.

S with 55% expandability after 35 days. All products showed only random mixed layering. The addition of Na^+ obviously slowed the rate of mixed-layer formation.

Figure 4, a plot of expandability vs. time, illustrates well how the addition of Na^+ impedes illite formation at 270°C. Solid lines have been drawn through expandability values for random mixed layering only so that a valid comparison can be made. The rate of formation of ordered mixed layering in 400 ppm K^+ starting solution is distinctly slower than that of the random mixed-layer clay. Figure 5 shows how expandability changes with time at 270° and 350°C when clays are reacted in a solution having an initial concentration of 400 ppm K^+ and 9400 ppm Na^+. When plotted on an Arrhenius plot the rate constants at each of these temperatures (calculated using the slopes of the lines shown in Figure 5) indicate an activation energy on the order of 30 kcal/mole. Because activation energies based on two temperatures are of questionable validity, a short error analysis was performed. Five percent error in determination of expandability of the reaction products could lead to calculated activation energies ranging from 25–35 kcal/mole. The activation energy for this experimental system is therefore 30 ± 5 kcal/mole.

Figure 6 shows the reaction products when the Na-Polkville and Ca-Polkville clays were reacted in 400 ppm K^+ solution at 270°C. Ordered mixed-layer clays developed within 14 days in the Na-Polkville sample; however, even after 60 days, no ordering was observed in the Ca-Polkville material. It is also apparent from Figure 6 that Ca^{2+} more effectively impeded illite formation than did Na^+. When additional Ca^{2+} was added to the solution, loss of expandability took place at even slower rates, as expected. When 800 ppm K^+ solution was added to Ca-Polkville sample, expandability was lost rapidly, as is shown in Figure 7. However, when only 100 ppm Mg^{2+} was added to the 800 ppm K^+ solution, expandability of the initial Ca-Polkville clay was still 90% after 35 days, demonstrating how effectively Mg^{2+} impedes the rate of illite formation.

Reaction rate constants are plotted in Figure 8 as a function of system chemistry, specifically, the ratio of K^+ to all other alkali-alkaline earth cations. Reaction rate constants were plotted on a logarithmic scale to

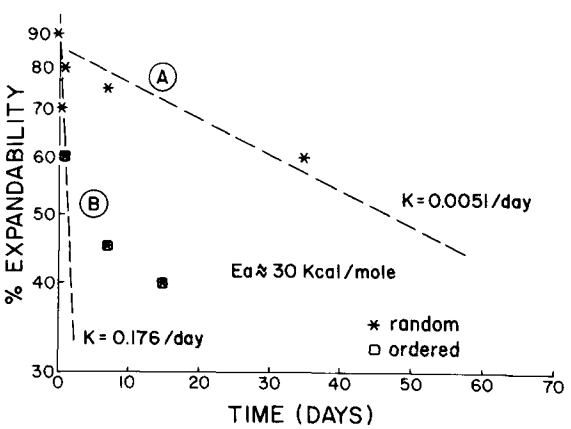


Figure 5. Expandability of reaction products as a function of time when Na-saturated Chambers montmorillonite reacted with 400 ppm K^+, 9400 ppm Na^+ starting solution at (A) 270°C and (B) 350°C.

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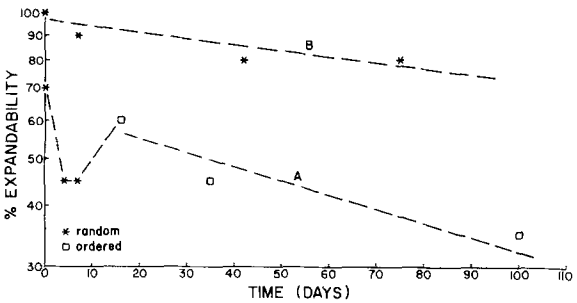


Figure 6. Expandability of reaction products as a function of time comparing effect of starting with (A) Na-saturated Polkville montmorillonite vs. starting with (B) Ca-saturated Polkville montmorillonite in 400 ppm K^+ starting solution at 270°C.

incorporate all data on a single illustration. In calculating the $K/(Na^+ + Ca^{2+} + Mg^{2+})$ ratio, octahedral Mg^{2+} was ignored. Thus, the Na^+, Ca^{2+}, and Mg^{2+} in the system is the sum of the ions initially in solution and the initial exchange population of the clay. For example, at the solid:solution ratio employed in this study, a 400 ppm K^+ solution has sufficient K^+ to exchange 85% of the initial exchange population of the clay. Thus, the Na-Chambers, the Na-Polkville, and the Ca-Polkville samples have a $K/(Na^+ + Ca^{2+} + Mg^{2+})$ ratio at 0.85/1.0 = 0.85 when the starting solution has a concentration of 400 ppm. In all cases (see Figure 8), increasing the inhibitor ion concentration ($Na^+ + Ca^{2+} + Mg^{2+}$) reduced the value of the rate constant, and increasing the K concentration increased the value of the rate constant. This illustration (note log scale) demonstrates the dependence of reaction rate on the presence and nature of inhibitor ions.

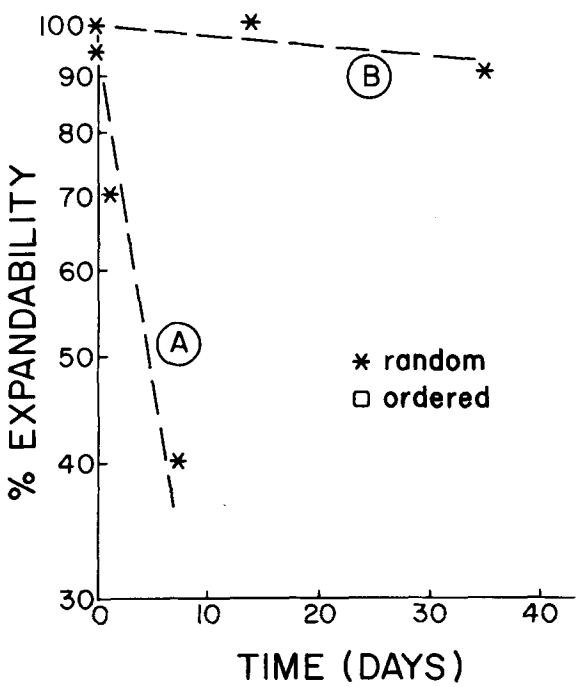


Figure 7. Expandability of reaction products when Ca-saturated Polkville montmorillonite reacted at 270°C in two different starting solutions (A) 800 ppm K^+ and (B) 800 ppm K^+ + 100 ppm Mg^{2+}.

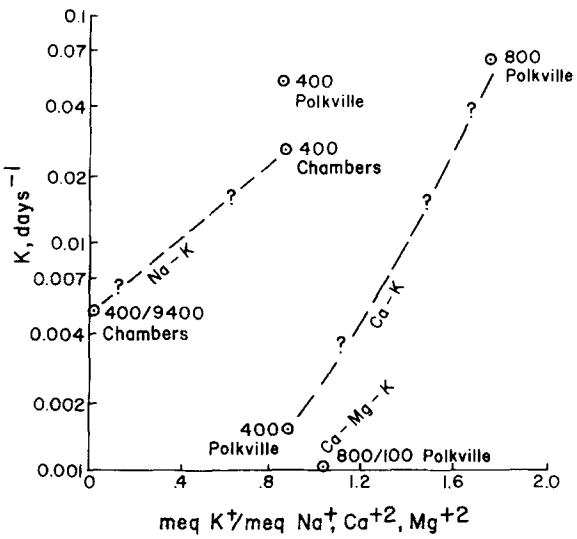


Figure 8. Reaction rate constants for 270°C run as a function of system chemistry, expressed as a ratio of K to all other alkali-alkaline earth cations.

DISCUSSION

Examination of Figures 4 and 6 indicates that the apparent initial expandability (by extrapolating to time zero) of the Na-Polkville and Na-Chambers samples in contact with a solution having an initial concentration of 400 ppm K^+, was approximately 70–75%, not 100%, as was found for the same clays when saturated with Ca^{2+} or when placed in contact with a solution having an initial concentration of 400 ppm K^+ and 9400 ppm Na^+. This observation raises two questions: (1) should the expandability data be treated as a first order reaction, and (2) what is the mineralogical meaning of the low "initial" expandability values?

For a reaction to be first order, it must satisfy the differential equation

$$dX/dt = K_1X \quad (1)$$

where X is the percent expandable/100, t is time, and K_1 is a constant. For those samples with "initial" expandabilities of 100%, the equation of the line fitting the data would be of the form

$$\ln X = K_1t \quad (2)$$

where X is the percent expandability/100, and K_1 the slope of the line. Differentiation of Eq. (2) with respect to X yields

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$$d \ln X/dt = d(K_1 t)/dx \quad (3)$$

from which it follows that

$$dX/dt = K_1 X.$$

For those samples for which "initial" expandability is not 100%, the form of the line fitting the data is

$$\ln X = K_1 t + K_2 \quad (4)$$

where K_2 is a constant equal to the natural logarithm of the "initial" expandability (in percent)/100. Differentiation of Eq. (4) with respect to X yields

$$\frac{d \ln X}{dx} = \frac{dk_1 t}{dx} + \frac{dK_2}{dX} \quad (5)$$

from which it follows that

$$dX/dt = K_1 X.$$

Thus, the rate constants derived for all systems may be compared directly, and the lines fitting the expandability data need not pass through 100% expandable at time zero in order for the reaction to be first order.

The first reaction to occur after immersion of a clay sample in the ionic fluids employed in the present experiments appears to be the establishment of cation-exchange equilibrium between interlayer-exchange sites and solution. It is significant that the only clay-solution systems to display the low "initial" expandability phenomenon were those with the greatest K^+/Na^+ ratio (i.e., Na-saturated clay, 400 ppm K solution). Lahann and Roberson (1980) indicated that under these solution conditions after 24 hr at 270°C, K^+ occupies about 80–85% of the exchange sites on the clay. The sample is effectively K-saturated, and any clay layers with sufficient charge to dehydrate K will appear as nonexpandable layers. It is therefore proposed that the low "initial" expandability of the clay formed by placing the Na-saturated clay in 400 ppm K^+ solution resulted from the fixation of K by high-charged layers present in the natural unheated clay.

To test the above hypothesis, samples of both Na-saturated clays were suspended in 400 ppm K^+ solution at the solid/solution ratio employed in the hydrothermal experiments, and allowed to equilibrate at room temperature for 3 hr. XRD of these clays showed that expandabilities of about 70% were obtained. These data suggest that the natural, untreated clay samples possess layers with sufficient charge to fix K^+ from solution without heating.

The results reported herein demonstrate that the addition of either Na^+, Ca^{2+} or Mg^{2+} to a solution with an initial K^+ concentration of 400 ppm will retard the rate of illite formation at 270° and 350°C. However, the question arises of whether these data are helpful in determining the origin of mixed-layer I/S in moderately to deeply buried sediments. An apparent weakness of the experimental design which might limit the applicability of the results to natural systems, is the initial high K^+ concentration employed, usually 400 ppm. A value of 400 ppm K^+ represents a compromise among the need to have a sufficiently high K^+ concentration so that significant illite will form before the fluid becomes depleted in K, the need to employ a sufficiently large clay sample so that analyses of products are reliable, and the desire to keep the total sample volume within reasonable limits for gold tubes in hydrothermal vessels. A 10-mg clay sample at 10 mg/ml requires a minimum of 400 ppm K^+ if available K^+ is to approximate the exchange capacity of the clay. A lower solid/liquid ratio would allow a lower K^+ concentration to be employed, but it would create a problem of expense because larger capsules would be required, and would resemble the solid/liquid ratio of pore systems even less than the current ratio. In any case, the problem of high initial K^+ concentration is more apparent than real. The final concentration of K in the fluid phase was always less than the initial value, indicating that either exchange or fixation of K^+ had occurred.

Lahann and Roberson (manuscript in preparation) calculated that in a solution with a 9400 ppm Na^+, 400 ppm initial concentration, smectite will convert to mixed-layer illite/smectite between 20° and 120°C at a rate that is within an order of magnitude of that observed in buried Gulf Coast shales, although the predicted conversion is always more rapid than observed. Rates of illite formation should be significantly lower when Ca^{2+} and/or Mg^{2+} co-exist in the reacting solution, as has been shown above. It is well established that pore solutions in buried shales of the Gulf Coast (Schmidt, 1973) contain appreciable amounts of one or both of these ions. The presence of these ions is probably the main cause of the slower kinetics in the natural system. Figure 8 may be used in a semiquantitative manner to estimate the relative inhibitory strength of Na^+, Ca^{2+}, and Mg^{2+} ions. For example, at $K^+/(Na^+ + Ca^{2+} + Mg^{2+})$ ratio of 0.85, the rate constant for illitization of the Ca-Polkville sample is roughly an order of magnitude lower than that of the Na-Polkville sample. Similarly, the data for Ca-Polkville may be used to compare the inhibitory strength of Ca^{2+} and Mg^{2+}. It is assumed that a system with a K^+/Ca^{2+} ratio between 0.85 (400 ppm K^+ and Ca-saturated clay) and 1.7 (800 ppm K and Ca-saturated clay) would have a rate constant intermediate to those determined for systems where solutions had initial concentrations of 400 ppm K^+ or 800 ppm K^+. The shape of the curve connecting the 400 ppm K^+ and 800 ppm K^+ data points is not known; a linear relationship is the simplest assumption. The 800 ppm K^+-100 ppm Mg^{2+}-Ca-Polkville system has a reaction rate constant lower than that of the 400 ppm K^+ system, despite a higher K^+/inhibitor ion ratio. This relationship suggests greater inhibitor strength for Mg^{2+} relative to Ca^{2+}. If a linear relation between log K and the K^+/inhibitor ratio is assumed for the Ca^{2+}-K^+ sys-

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tem, the 800 ppm K^+-100 ppm Mg^{2+} system has a rate constant about ⅓ that predicted for a Ca^{2+}-K^+ system at the same K^+/inhibitor ion ratio. For experimental systems described herein, the inhibitory strength of Na^+, Ca^{2+}, and Mg^{2+}, on an equivalent basis, appears to increase approximately in the ratio 1:10:30.

A second question relating to the smectite/illite conversion is the mechanism by which smectite converts to illite. To convert a smectite to illite, it is necessary to increase the layer charge on the smectite. The relationship between K^+ fixation and increased layer charge is uncertain. As the negative charge on the silicate layer builds up, so does the selectivity of the clay for K^+ (Sawhney, 1970). Lahann and Roberson (1980) showed that increasing the proportion of K^+ exchange ions on a montmorillonite increases the rate of Si removal. It is possible that K^+ uptake precedes and accelerates layer charge development. In any case, a critical charge is developed in the presence of K^+ exchange ions, the clay becomes dewatered, and illite is formed.

It should be noted that increased tetrahedral Al does not require an external source (from K-feldspar or mica) of Al. In the present experiments and in those of Eberl and Hower (1976), there was no external source of Al. Al which became incorporated in tetrahedral layers in the I/S structures was derived from the breakdown of other smectite layers. Eberl and Hower (1976) produced both kaolinite and illite at the expense of smectite. This reaction must be reconciled with the observation by Hower *et al.* (1976) that kaolinite does not increase with depth as does illite in Gulf Coast shales. A possible explanation for the kaolinite not forming diagenetically in natural systems was offered by Boles and Franks (1979) who suggested that illite formation proceeds in a "constant Al" system and that excess octahedral ions and silica are released to solution and ultimately precipitate as authigenic cements. Presumably, the mechanism for mobilization of the Al in these systems is via dissolution and reprecipitation. Such a reaction pathway is consistent with the activation energy of 19.4 Kcal/mole for illite formation observed by Eberl and Hower (1976). This activation energy also compares favorably with the activation energy values of 18.4 Kcal/mole and 19 Kcal/mole for dissolution of layer silicates reported respectively by Abdul-Latif and Weaver (1969) and Thompson and Hower (1973). A dissolution-reprecipitation process is also consistent with the solution conditions in the experiments of Eberl and Hower (1976) in which the pH after quenching was in the range 4–5. Significantly, kaolinite was found as a reaction product, most likely in response to the low pH. Whether such a mechanism could function at the pH and temperature of clay diagenesis in natural systems is not known.

Solutions in the present experiments were buffered by carbonate ions which kept the pH at higher values; pH values measured in solutions quenched to 25°C ranged between 6 and 7. No kaolinite was found in the products. No changes in particle morphology or size of I/S reaction products were detected by electron microscopy when compared with the starting material, not inconsistent with a solid state transition of smectite to mixed-layer I/S.

Dissolved silica in reaction solutions frequently reaches a maximum value within the first 24 hr of the experiment (Lahann and Roberson, 1980). Either no further change in dissolved silica was observed or silica concentration declined and then rose again. The silica concentration appeared to vary independently of the formation of non-expandable layers. In addition, the activation energy for silica dissolution was found to be on the order of 10 Kcal/mole, whereas illite formation had an activation energy on the order of 30 Kcal/mole. It appears that within the first 24 hr of an experiment, a silica-depleted montmorillonite formed. With time, octahedral Al migrated to occupy tetrahedral sites, a process having the activation energy observed in this study. In the natural system additional chemical changes may take place within the octahedral layer depending on the chemistry of the starting materials and the chemistry of the reacting solution. Such changes are probably not as critical in these experiments as the compositional change in the tetrahedral layer.

Two factors in the present experimental system appear to favor solid-state reorganization as opposed to solution-reprecipitation: (1) The pH-buffered solution minimized the solubility of Al^{3+} and prevented the acid-dissolution of the clay; and (2) the presence of excess alkali and alkaline earth cations may have inhibited Al^{3+} uptake from solution. In short, the lower activation energy (~20 Kcal/mole) dissolution-reprecipitation pathway was "blocked" by the nature of the reaction solution, and a higher activation-energy (~30 Kcal) pathway resulted.

It is possible that in nature illite might form by either solid-state reorganization or by dissolution-reprecipitation. It is also possible that Al^{3+}, as well as K^+, could be supplied by the breakdown of detrital K-feldspar, as has been suggested by Hower *et al.* (1976).

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Резюме—Смешано-слойный иллит/смектит (И/С) был получен при гидротермической реакции Чамберского или Польквилового монтмориллонита при температурах 270° и 350°С, в течение от нескольких часов до более чем 15 недель. Реакции проводились в замкнутых сосудах, содержащих растворы K или смешанные растворы K-Na, K-Ca, или K-Mg с изменяющимися концентрациями. Скорость реакции и скорость упорядочнения И/С для реакции смектит + K → смешанно-слойный И/С + SiO_2 замедлялись добавлением Na^+, Ca^{2+}, и Mg^{2+}; замедлительная сила Na^+, Ca^{2+}, и Mg^{2+}; на эквивалентной основе, приблизательно увеличивалась как соотношение 1:10:30. Постоянные скорости реакции первого порядка для реакции при температурах 270° и 350°С указывают на то, что энергия активации есть порядка 30 ккал/моль.

Вероятно, в рассматриваемой системе, реакция смектит → смешанно-слойный И/С происходит путем преобразования твердого состояния. На это указывают: (1) быстрое растворение большого количества двуокиси кремния с вероятным образованием резидуума обогащенного алюминием, (2) подобие размеров частиц и морфологии смешанно-слойных продуктов с исходным монтмориллонитом, указывающее на небольшое растворение Al^{3+}, и (3) относительно большая энергия активации по сравнению с литературными данными для растворения силикатов. [E.C.]

Resümee—Eine Illit/Smektit-Wechsellagerung (I/S) wurde bei der hydrothermalen Reaktion des Chambers- oder Polkville-Montmorillonites bei 270° und 350°C und Reaktionszeiten von einigen Stunden bis mehr als 15 Wochen gebildet. Die Reaktionen wurden in geschlossenen Gefäßen durchgeführt, die K- bzw. K-Na-, K-Ca-, oder K-Mg-Lösungen unterschiedlicher Konzentration enthielten. Die Umwandlungsgeschwindigkeit und der Ordnungsgrad von I/S der Reaktion Smektit + K^+ → Wechsellagerung I/S + SiO_2 wurde durch die Zugabe von Na^+, Ca^{2+} und Mg^{2+} verzögert; der Verzögerungseffekt durch Na^+, Ca^{2+} und Mg^{2+} nimmt, bezogen auf die gleiche Menge, im Verhältnis 1:10:30 zu. Die Reaktionsgeschwindigkeitskonstanten erster Ordnung für die Reaktionen bei 270° und 350°C sprechen für eine Aktivierungsenergie von etwa 30 kcal/Mol.

Im untersuchten experimentellen System scheint die Reaktion Smektit → I/S-Wechsellagerung durch eine Umwandlung im festen Zustand abzulaufen. Dies geht hervor: (1) aus der raschen Lösung einer großen SiO_2-Menge, die wahrscheinlich die Bildung eines Al-reichen Restes verursacht; (2) aus der Ähnlichkeit der Teilchengröße und der Form der Wechsellagerung mit der des ursprünglichen Montmorillonites, was für kein starkes Inlösunggehen des Al^{3+} spricht; und (3) aus der relativ hohen Aktivierungsenergie im Vergleich zu den publizierten Werten für die Silikatauflösung. [U.W.]

Résumé—De l'illite/smectite à couches mélangées (I/S) a été formée en faisant réagir de la montmorillonite Chambers ou Polkville hydrothermalement à 270° et 350°C pour une durée de plusieurs heures à plus de quinze jours. Les réactions ont été entreprises dans des vaisseaux fermés contenant K ou un mélange K-Na, K-Ca, ou des solutions K-Mg à concentrations variées. L'allure de la réaction et l'allure du rangement d'I/S pour la réaction smectite + K^+ → I/S à couches mélangées + SiO_2 étaient inhibées par l'addition de Na^+, Ca^{2+}, et Mg^{2+}; la force inhibante de Na^+, Ca^{2+}, et Mg^{2+}, sur une base équivalente, a augmenté approximativement dans la proportion 1:10:30. Les constantes d'allure de réaction de premier ordre pour les réactions à 270° et 350°C indiquent une énergie d'activation d'à peu prés 30 kcal/mole.

Dans le système expérimental étudié, la réaction smectite → I/S à couches mélangées semblait avoir procédé par transformation à l'état solide, suggéré par (1) la dissolution rapide de larges quantités de silice, créant probablement un résidu enrichi d'Al; (2) la similarité de la taille de particule et de la morphologie des produits à couches mélangées à celles de la montmorillonite originale, impliquant aucune dissolution extensive d'Al^{3+}; et (3) une énergie d'activation relativement haute comparée aux valeurs publiées pour la dissolution silicate. [D.J.]

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