

# The Thermal Transformation of Smectite to Illite

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## Abstract

Mixed-layered illite/smectite minerals composed of 80% illite layers have been identified from different argillaceous rocks that have been subjected to estimated peak temperatures that ranged from 250°C to 70°C, for durations of approximately 10 yr to 300 my. These observations strongly suggest that the reaction progress or extent is controlled by kinetic factors rather than by equilibrium factors. A sixth-order kinetic expression (first-order with respect to the pore-fluid activity ratio K/Na, and fifth-order with respect to the mole fraction of smectite) was successfully applied to the progressive illitization of smectite in the contact metamorphic zone adjacent to an 8.5-m-thick basalt dike that penetrates the upper Pierre Shale near Walsenberg, Colorado. The kinetic expression, together with its preexponential constant and activation energy (33 kcal/mol), provides a fair to good transformation model for a young geothermal sequence, and for burial diagenetic profiles that range in stratigraphic age from approximately a few million to 300 Ma.

The sixth-order model is an empirical device that explains the field evidence, but probably has little or no fundamental physical-chemical significance. The correct kinetic law is likely to be a chain of low-order reactions, each of which has kinetic constants that differ from the others.

## Introduction

The transformation of smectite to illite through an intermediate mixed-layered series is probably the most volumetrically important clay mineral reaction in sedimentary rocks. The reaction progress

correlates with hydrocarbon maturation (Perry and Hower, 1972); the transformation may cause zones of overpressure in shales which drive the expulsion of hydrocarbons and water to more permeable rocks (Burst, 1969; Bruce, 1984) and it may release ions that are responsible for cementation and other diagenetic reactions (Boles and Franks, 1979). Indeed, it appears that measurable mineralogical changes, correlated with temperature, occur over the continuum between room temperature (soils) and perhaps 300°C, which marks the beginning of greenschist facies metamorphism (Środoń and Eberl, 1984). In addition, the various representatives of this mineral reaction series are ubiquitous in sedimentary rocks and are major constituents of shales.

Evidence for the thermal transformation of smectite to illite comes from four distinct types of studies. The most convincing demonstration of smectite-illite diagenesis was provided by Perry and Hower (1970), who demonstrated a continuous increase, with respect to depth, in the proportion of illite layers in mixed-layered illite/smectite (hereafter designated as I/S) in shales from a Gulf Coast Tertiary well. Since that time, the Perry and Hower measurements have been repeated many times by numerous investigators. Few geologists these days doubt the essential validity of their conclusions.

Most bentonites are composed of smectite (usually montmorillonite) in young, shallow sedimentary sequences. Weaver (1953) noted, however, that clay layers whose stratigraphic characteristics certainly identify them as bentonites tend to be composed of I/S in older rocks. Indeed, the I/S

in such beds often consists of 80% or more illite in rocks older than middle Paleozoic. Originally, these so-called potash bentonites were thought to represent a chemical response to long residence times on the sea floor (Weaver, 1953), but the work of Hoffman and Hower (1979), in the Cretaceous of the disturbed belt of Montana, showed that burial temperatures were responsible for the high illite contents of the meta- or potash bentonites. They demonstrated that bentonites on the Sweetgrass arch are nearly pure smectite, whereas the same beds in the nearby disturbed belt are highly illitic due to increased temperatures associated with burial under accumulated thrust sheets. Nadeau and Reynolds (1981) studied Cretaceous bentonites in the southern Rocky Mountains and reported a wide range in illite content that correlated with regions of deep burial or proximity to igneous intrusives. One such bed contained I/S (75% illite) near the contact with an Oligocene intrusive, and yielded a K-Ar age that is nearly identical to the age of the intrusion (Aronson and Lee, 1986), yet an exposure approximately 20 km from the intrusive consists of essentially pure smectite for which the zircon fission-track age is 100 Ma (Kramer, 1981).

Contact metamorphosed Cretaceous shales, in proximity to igneous dikes, have been analyzed from southcentral Colorado (Reynolds, 1981; Pytte, 1982). The concentration of illite in I/S increases monotonically toward the dikes, demonstrating the compositional response of the mixed-layered phase to temperature. The reaction environment here consists of very high temperatures for short time durations, compared to the other geological settings described above.

Finally, I/S representing almost the entire compositional range has been prepared in the laboratory by means of hydrothermal synthesis (Eberl and Hower, 1976; Eberl, 1978a).

The major questions concern the reaction controls. What chemical and physical factors control the reaction progress or extent? Certainly temperature is important, and this fact makes the smectite-illite reaction interesting to geologists. The reaction extent ideally constitutes a diagenetic grade indicator or paleothermometer and could serve as a useful tool for tracing the thermal and burial history of sedimentary basins. Its utility, however, depends on the extent to which the effects of tem-

perature can be isolated from those of time, pore-fluid composition, and the composition of the mineral reactants. Nevertheless, the reaction extent correlates quite well with temperature and time for rock suites from different geological situations (Środoń and Eberl, 1984), suggesting that either many of the possible variables do not exert powerful influences on the reaction extent, or, on the other hand, that the ranges of such variables are fixed or buffered by geochemical systems that are widely extant in time and space.

Major questions concerning the smectite-illite reaction are as follows:

1. Is the reaction controlled by chemical equilibrium or kinetic principles, or both?
2. What are the relative molar quantities of illite and smectite that make up the reaction stoichiometry?
3. What are the effects of pore-fluid and mineral composition (smectite) on the reaction extent?
4. Does the reaction proceed as layer-by-layer transformation or by a dissolution reprecipitation mechanism?

This chapter presents evidence and arguments that support the role of kinetic factors in controlling reaction extent. The treatment is meant to apply to shales and perhaps carbonate rocks where solution chemistry is apt to be rock dominated. Clay diagenetic reactions in sandstones may be quite different due to the effects of chemically exotic fluids and temperatures that may or may not be controlled by the local geothermal gradient.

## Effects of Solution Composition on Reaction Progress

Pure illite, or its solid solution components celadonite or muscovite, may be stable in the presence of seawater and at surface temperatures. If so, montmorillonite and I/S are metastable and the composition of the mixed-layered material represents the reaction extent or progress caused by some combination of time and temperature effects, probably conditioned by pore-water chemistry (see Lippmann, 1982, for a discussion of the thermodynamic status of clays). Eberl and Hower (1976), Eberl (1978b), and Roberson and Lahann (1981)

TABLE 8.1. Approximate times at temperatures exceeding 90% of peak values for argillaceous rocks containing I/S with 80% illite.

Approximate time	Estimated peak temperature (°C)	Geological conditions	Reference
10 yr	250	Contact metamorphism	Reynolds (1981)
10,000 yr	150	Hydrothermal well	Jennings and Thompson (1986)
1 my	127	Burial diagenesis	Perry and Hower (1972)
10 my	100	Burial diagenesis	Perry and Hower (1972)
300 my	70	Burial diagenesis	Środoń and Eberl (1984)
450 my	70	K-Bentonite	Huff and Turkmenoglu (1981)

have studied the I/S reaction series by means of hydrothermal laboratory synthesis. Experimental results indicate that high potassium activity increases the reaction rate, and that magnesium, calcium, and sodium activities impede the reaction to diminishing degrees in the order given. Altaner et al. (1984) describe a 2.5-m-thick bentonite bed from Montana that is chemically and mineralogically zoned. The upper and lower contacts contain more illitic I/S than the core. Potassium diffusion from the enclosing shale is cited as the cause of the zonation. The role of potassium as either rate limiting or equilibrium controlling is demonstrated, whether or not kinetics are crucial here.

### Time-Temperature Associations

Field occurrences of I/S in rocks of different ages and subjected to different temperature regimes are best explained as reaction limits imposed by time-temperature conditions. Table 8.1 shows some of these data. They refer to the composition 80% illite because this is a common one in old or deeply buried rocks, and problems of potassium availability may become crucial for more illitic compositions. Thermal histories in any location may be complex, and time-at-temperature is difficult to estimate accurately, so Table 8.1 shows estimated maximum temperatures and rough approximations of the times that temperatures exceeded 90% of peak values. The data make the point that I/S has apparently formed over a wide range of temperatures, and that an inverse correlation exists between temperature and time for a fixed composition. The overwhelming importance of temperature is noteworthy, though potassium availability may have been a factor in controlling the composi-

tion of the Ordovician K-bentonite. For the fixed composition of 80% illite, the range in temperatures is only about 4-fold, whereas the time range is approximately a factor of  $10^7$ . The I/S reaction extent is thus a geothermometer for all practical purposes. Other variables may be involved that, for some reason or the other, were not operative during the reactions that produced the compositions shown here. But the most important point illustrated by the data in Table 8.1 is the likely role of kinetics in conditioning the reaction progress.

### Illite/Smectite in the Contact Metamorphic Environment

The transformation of smectite to illite at high temperatures provides strong evidence for kinetic control. Studies were made of the I/S reaction profile in the upper Pierre Shale where it is penetrated by a 8.5-m-thick basalt dike near Walsenburg, Colorado (Reynolds, 1981; Pytte, 1982). The discussion below is given in detail because the work has been published as a master's thesis and is not easily available. Samples from a single bed were collected at 0.3-m intervals starting at the contact and continuing to a distance of 12 m. The  $<0.5\text{-}\mu\text{m}$  fractions (equivalent spherical diameter) were separated, pipetted onto glass slides, and dried at 90°C. They were solvated by exposure to ethylene glycol vapor at 60°C for a minimum of 12 hr, and analyzed by means of a Siemens D-500 diffractometer equipped with a copper tube and a graphite monochrometer. Ordering in I/S was determined by peak positions in the low angle region, and composition was estimated from the angular position of the I/S diffraction peak near  $17^\circ 2\theta$  (Reynolds and Hower,

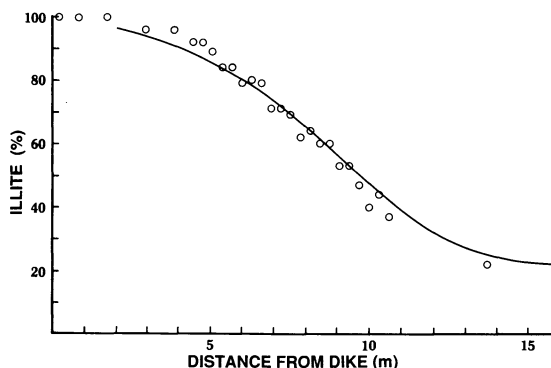


FIGURE 8.1. Composition of I/S in the Pierre Shale adjacent to a basalt dike near Walsenberg, Colorado. Curve is calculated from the kinetic model.

1970; Reynolds, 1980). The results are shown on Figure 8.1, which also illustrates (solid curve) a fit of the data to a kinetic scheme described below.

The reaction profile shows several interesting features. Unlike Gulf Coast profiles, the reaction progress continues smoothly through and beyond the composition of 80% illite to the end product, which is essentially pure illite. Here, K-feldspar diminishes in concentration toward the dike (Lynch and Reynolds, 1984), but is not eliminated. These data are consistent with the conclusion that the termination of the reaction in Gulf Coast shales is due to exhaustion of K-feldspar at that point (Hower et al., 1976). The transformation from random to ordered interstratification takes place at about 60% illite, just as it does in Gulf Coast and other burial sequences. The reason for ordering at this composition, instead of at 50% illite, is unknown, but its occurrence in both the burial and contact metamorphosed sequences suggests that the same reaction principles were in effect despite the very different time-temperature settings.

The time-temperature relation is very different for contact as opposed to burial metamorphism. The contact metamorphosed shales were affected by thermal pulses whose peak temperatures and durations increased with proximity to the dike. We assumed a simple conductive heat transfer process and computed the time-temperature functions by means of a model published by Jaeger (1964). A temperature-constant thermal diffusivity coefficient of  $0.0064 \text{ cm}^2/\text{s}$  was computed from data given by Tyler et al. (1978) and the effect of latent heat was incorporated by assuming a temperature

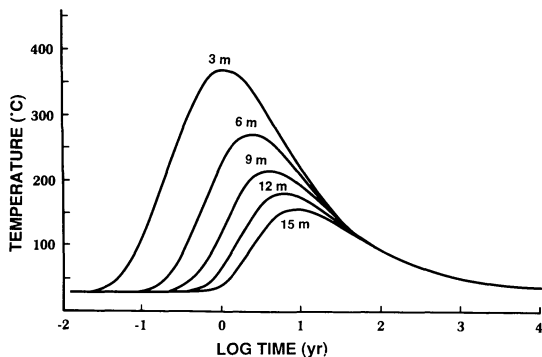


FIGURE 8.2. Temperature versus time curves in shale adjacent to an 8.5-m-thick dike, calculated for different distances from the contact.

of  $1200^\circ\text{C}$  for the intrusive. A low wall-rock temperature of  $30^\circ\text{C}$  was assumed quite arbitrarily because of the stratigraphically high position of the sequence and the late (Pliocene) date of emplacement of the dike. Figure 8.2 shows several time-temperature curves calculated for different distances from the contact. The curves are not expressible by a closed-form equation, but are easily utilized in computer calculations.

A kinetic expression was developed from chemical principles and the constants in it were optimized by adjustment so that the results conformed to those for the dike and for burial diagenetic reaction profiles. Let  $S$  be the mole fraction of smectite in I/S. Then

$$-dS/dt = k S^a \quad (1)$$

where  $t$  is the time,  $a$  is a constant that describes the order of the reaction, and  $k$  is the rate constant given by the Arrhenius equation

$$k = A \exp(-U/RT) \quad (2)$$

The constant  $A$  is the frequency factor,  $U$  is the activation energy for the reaction,  $R$  is the gas constant, and  $T$  is the temperature in  $^\circ\text{K}$ . A solution term is necessary to account for the effect of the activity of potassium on the reaction rate. We assumed equilibrium between albite and K-feldspar, and, using data from Robie et al. (1978), calculated the ratio of the activities of K/Na which increases with temperature. For these rocks, at least, this procedure seems justified because other work (Lynch and Reynolds, 1984) showed that the molar concentration of albite in the rocks increases

toward the dike and is antipodal to the molar concentration of K-feldspar. A general kinetic expression may be written

$$-dS/dt = S^a (K/Na)^b A \exp(-U/RT) \quad (3)$$

in which the form of  $K/Na$  has been arbitrarily selected. The superscripts  $a$  and  $b$  represent integers whose sum is the reaction order. Experimentation with Equation 3 revealed that many different sets of variables yielded excellent agreement with the data of Figure 8.1, but that only high-reaction orders allowed extrapolation to long duration, low-temperature conditions such as those that apply to burial diagenesis. The best compromise gave the parameters  $a = 5$ ,  $b = 1$ ,  $A = 5.2 \times 10^7 \text{ s}^{-1}$ , and  $U = 33 \text{ kcal/mol}$ . These results were used to construct the curve shown on Figure 8.1, and they are retained for the treatment below.

The quantity  $K/Na$  is given by the van't Hoff equation, which, after rearrangement and collection of constants, yields

$$K/Na = 74.2 \exp(-2490/T) \quad (4)$$

Equation 4 is substituted into Equation 3 for which  $a = 5$  and  $b = 1$ , the differential equation is integrated, the integration constant is inserted, and the result is

$$S^4 = \frac{S_0^4}{1 + 4 \times 74.2 t S_0^4 A \exp(-2490/T - U/RT)} \quad (5)$$

where  $S_0$  is the mole fraction of smectite in the initial mixed-layered clay and  $t$  is the time in seconds. Note that the van't Hoff equation, when expressed in this way (Equation 4), contributes to the exponential term as additional activation energy. For our study, the  $K/Na$  ratio could have been eliminated and the empirical analysis would have achieved identical results (so long as the  $K/Na$  ratio contributes a first-order effect) by the use of a higher activation energy.

## Kinetic Model and Time-Temperature Associations

The validity of the adjusted values for  $A$  and  $U$  was tested using the data of Table 8.1, though the fixed time and temperature approximations for these rocks represent thermal histories that have been

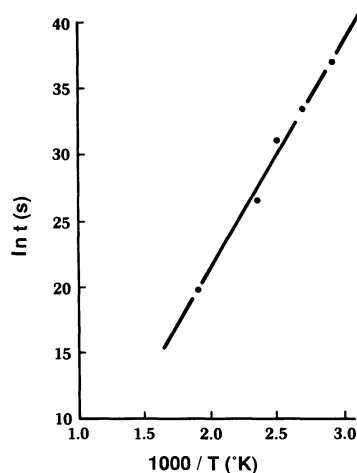


FIGURE 8.3. Plot of the time-temperature data of Table 8.1. The line was calculated by linear regression.

simplified and are, at best, only approximations. We assumed that  $S_0 = 1$  and substituted  $S = 0.2$  into Equation 5 because all of the compositions are 80% illite. Equation 5 was rearranged in the logarithmic form to give

$$\ln(t) = (1/T)(2490 + U/R) - \ln(A) + 0.743 \quad (6)$$

Figure 8.3 shows a plot of Equation 6 for which the values of time and temperature have been taken from the data of Table 8.1. The regression line has a slope of  $2,490 + U/R$ , an intercept of  $-\ln(A) + 0.743$ , with the correlation coefficient = 0.99. Solving for the kinetic parameters yields  $A = 5.6 \times 10^7 \text{ s}^{-1}$  and  $U = 33.2 \text{ kcal/mol}$ , in satisfactory agreement with the values deduced by trial-and-error methods from a more careful consideration of the time-temperature relations for the contact metamorphic reaction profile studied. Admittedly  $\ln(t)$  is imperfectly known, but it is noteworthy that an error in  $t$  by a factor of 2 would cause the displacement of a given data point by only the amounts shown by the two points of Figure 8.3 that do not lie on the regression line.

## Kinetics of Burial Metamorphism

The integrated form of Equation 3 cannot be used for modeling contact metamorphism and is cumbersome to use for burial diagenesis. The difficulty arises because temperature is a function of time,

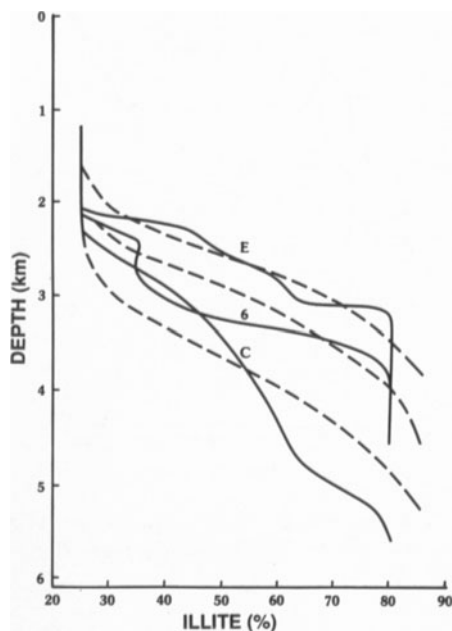


FIGURE 8.4. Burial diagenesis profiles for Gulf Coast Tertiary wells. Solid curves are smoothed observed data for Wells E and C (Perry and Hower, 1972) and Well 6 (Aronson and Hower, 1976). Dashed curves are calculated from the kinetic model.

and that function must be entered for  $T$  in Equation 3. The integration is easily accomplished by means of a digital computer and the replacement of the product  $t \exp(-2490/T - U/RT)$  in Equation 5 by  $Q$  where

$$Q = \exp(-2490/T(t) - U/RT(t)) dt \quad (7)$$

and the quantity  $T(t)$  is the temperature in  $^{\circ}\text{K}$  at time  $t$ . For contact metamorphism,  $T(t)$  is given, for example, by the curves of Figure 8.2, the lower limit of integration is zero and the upper limit is the time at which the temperature has fallen to the preintrusive value. For burial diagenesis, the upper limit is the stratigraphic age, and  $T(t)$  is equal to the surface temperature plus the product of the sedimentation rate, the geothermal gradient, and time. Proper attention must be given to the units to assure their consistency, and concentrations must be expressed as mole fractions.

Figure 8.4 shows calculated reaction profiles and measured I/S compositions with respect to depth for three Gulf Coast wells. Published values for I/S have been smoothed to give reasonably simple

curves. Well E is based on a final stratigraphic age of 40 Ma and a geothermal gradient of  $0.0308^{\circ}\text{C}/\text{m}$  and Well C on 10 Ma and  $0.0243^{\circ}\text{C}/\text{m}$  (Perry and Hower, 1972); both calculated profiles are based on continuous and constant sedimentation rates. Calculated data for Well 6 utilized the more complicated burial history summarized by Aronson and Hower (1976). A surface temperature of  $10^{\circ}\text{C}$  is assumed for all calculations, and kinetic constants are identical to those used to fit the dike reaction profile (Fig. 8.1).

The fit for Well E is good and Well 6 is adequately simulated by the model except for the strange reversal in the observed profile. The agreement for Well C is poor and suggests either inadequacies in the model or an imperfectly known burial history for this section.

The model is very sensitive to the uniformity and magnitude of the sedimentation rate, the geothermal gradient, and the surface temperature. So much so, in fact, that detailed agreement with burial diagenetic profiles may always be poor because these factors probably will never be known with the accuracy required for an exhaustive and convincing test. But the kinetic model proposed has generally proved extrapolatable over a wide range of time and temperature conditions. If the extrapolation is warranted, it demonstrates the dominating effect of temperature and the finite but small sensitivity of the reaction progress to time. Bruce (1984) has come to similar conclusions based on his study of Tertiary Gulf Coast reaction profiles of different ages.

## Comments on the Kinetic Model

The model proposed here is incomplete. It takes into account only one aspect of solution chemistry, the K/Na ratio, and no provision is included to provide for different reactivities of compositionally different smectites (Boles and Franks, 1979; Bruce, 1984). The fact that the model works as well as it does suggests that large variations in these quantities have not been operative for many of the reaction sequences studied to date. But there are exceptions. We cannot account for the composition of 90% illite in an Ordovician K-bentonite in New York State. Johnsson (1984) has shown that partial resetting of the zircon fission-track age in

this bentonite indicates a minimum temperature of approximately 175°C, and any sensible burial and uplift history for this region predicts a composition of 96+% illite. The difference between 90 and 96% may seem small, but the sharply reduced reaction rate at high illite contents means that the two compositions require very different temperatures. Potassium availability may have limited the reaction extent, but the illite in adjacent limestones is less than 5% expandable, suggesting that potassium deficiency may not account for the anomalous composition of the K-bentonite. Another difficulty exists with the Carboniferous reaction profile described by Środoń and Eberl (1984). Agreement is quite good for the latter portions of the reaction, but the model predicts significantly less illitization for the lower temperature samples.

A reaction order of five (with respect to smectite) is an empirical formulation that is difficult to reconcile with physical-chemical principles. Probably a very different kinetic law is operative that is approximated by a simple fifth-order equation. C. M. Bethke and S. P. Altaner (personal communication, 1984) have proposed a scheme consisting of three sequential first-order steps, each of which has a different activation energy, and their calculated results correlate well with several published Gulf Coast Tertiary reaction profiles.

## Conclusions

1. The correlation of I/S composition with temperature and time strongly suggests that the reaction progress is kinetically controlled.
2. A sixth-order kinetic expression, fifth-order with respect to smectite content and first-order with respect to the ratio of K/Na, describes the I/S reaction extent for conditions that range from contact metamorphism to low-temperature, long-term burial diagenesis.
3. The high reaction-order causes the reaction rate to slow drastically, for a given temperature, as the composition approaches that of pure illite.
4. Temperature is the dominant control on reaction progress; time is much less important.
5. Refinement of the proposed model requires that formulations be developed to account for the effects on reaction rate of the activities of magnesium and calcium in pore fluids, and the composition of prediagenetic smectite.

**Acknowledgments.** The authors gratefully acknowledge the National Science Foundation for supporting this research by means of grants EAR 79-03984 and EAR 84-07783.

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