*Clays and Clay Minerals*, Vol. 41, No. 2, 119–133, 1993.

# CONSIDERATIONS AND APPLICATIONS OF THE ILLITE/SMECTITE GEOTHERMOMETER IN HYDROCARBON-BEARING ROCKS OF MIOCENE TO MISSISSIPPIAN AGE

RICHARD M. POLLASTRO

U.S. Geological Survey, Box 25046, Mail Stop 960
Denver Federal Center, Denver, Colorado 80225

**Abstract**—Empirical relationships between clay mineral transformations and temperature provide a basis for the use of clay minerals as geothermometers. Clay-mineral geothermometry has been applied mainly to diagenetic, hydrothermal, and contact- and burial-metamorphic settings to better understand the thermal histories of migrating fluids, hydrocarbon source beds, and ore and mineral formation.

Quantitatively, the most important diagenetic clay mineral reaction in sedimentary rocks is the progressive transformation of smectite to illite via mixed-layer illite/smectite (I/S). Changes in both the illite/smectite ratio and ordering of I/S, as determined from X-ray powder diffraction profiles, correlate with changes in temperature due to burial depth. Although the smectite-to-illite reaction may be influenced by several factors, reaction progress appears to be strongly controlled by temperature. Studies show that the model proposed by Hoffman and Hower in 1979 is applicable in burial diagenetic settings from about 5 to 330 Ma, and includes most rocks about Miocene to Mississippian in age. Reliability of the I/S geothermometer is, however, dependent upon a good understanding of the rock's original clay-mineral composition.

Changes in the ordering of I/S are particularly useful in the exploration for hydrocarbons because of the common coincidence between the temperatures for the conversion from random-to-ordered I/S and those for the onset of peak, or main phase, oil generation. Here, the utility of the I/S geothermometer is reviewed in hydrocarbon-bearing rocks of Miocene to Mississippian age. Using three common applications, the I/S geothermometer is compared to other mineral geothermometers, organic maturation indices, and grades of indigenous hydrocarbons. Good agreement between changes in ordering of I/S and calculated maximum burial temperatures or hydrocarbon maturity suggests that I/S is a reliable semiquantitative geothermometer and an excellent measures of thermal maturity.

**Key Words**—Geothermometer, Hydrocarbons, Illite/smectite, Illitization, Smectite diagenesis, Thermal maturity.

## INTRODUCTION

Clay minerals provide information on the burial and thermal history of sedimentary rocks that is useful in the exploration, evaluation, and production of hydrocarbons. The use of mixed-layer illite/smectite (I/S) as a geothermometer and indicator of thermal maturity in petroleum geology studies is based on concepts of shale diagenesis that were first described in detail from studies of the Gulf Coast (Powers, 1957, 1967; Burst, 1959, 1969; Perry and Hower, 1970; Weaver and Beck, 1971; Hower *et al.*, 1976). Quantitatively, the most important diagenetic clay reaction in shale is the progressive transformation of smectite into illite via mixed-layer illite/smectite (I/S) because smectite plus I/S account for 30% of the total sediment/rock mass (Środoń, 1989). This reaction is also commonly referred to as *smectite diagenesis* or *smectite illitization* (Bethke and Altaner, 1986). The reaction is irreversible under progressive burial conditions.

Changes in the proportion of illite, smectite (also referred to as expandability), and ordering of I/S, interpreted from X-ray powder diffraction (XRD) profiles, correlate with changes in temperature due to burial depth (Figure 1). An empirical relationship between these changes in I/S and subsurface temperature was first demonstrated by Perry and Hower (1970, 1972). Models applying temperatures to clay minerals for their use as geothermometers in burial diagenetic or low-grade metamorphic settings were first proposed by Hoffman and Hower (1979) and Weaver (1979). Similar empirical clay mineral-to-temperature relations have been demonstrated for hydrothermal fluid systems and contact metamorphic situations (Hoffman and Hower, 1979). However, temperatures initiating change in the illite/smectite ratio and ordering of I/S differ between relatively short-lived geothermal systems and long-term burial settings. These specific changes in I/S, therefore, indicate maximum temperatures provided that the proper temperature model is used (Pytte and Reynolds, 1989; Pollastro, 1989, 1990). It is the purpose of this paper to briefly describe some important assumptions, considerations, and applications of I/S geothermometry, and to demonstrate its utility as a reliable indicator of maximum temperature and/or thermal maturity from five case-history studies of petroleum-bearing rocks from Miocene to Mississippian in age.




https://doi.org/10.1346/CCMN.1993.0410202 Published online by Cambridge University Press

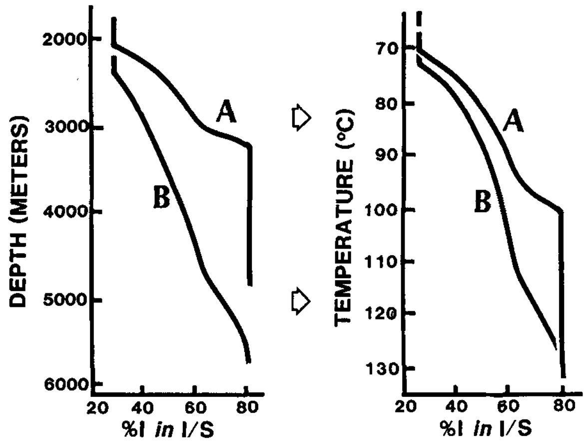


Figure 1. Proportion of illite (I) layers in mixed-layer illite/smectite (I/S) *vs* depth (left) and temperature (right) for samples from A) Oligocene well and B) Miocene well in Gulf Coast region. Modified from Hower, 1981.

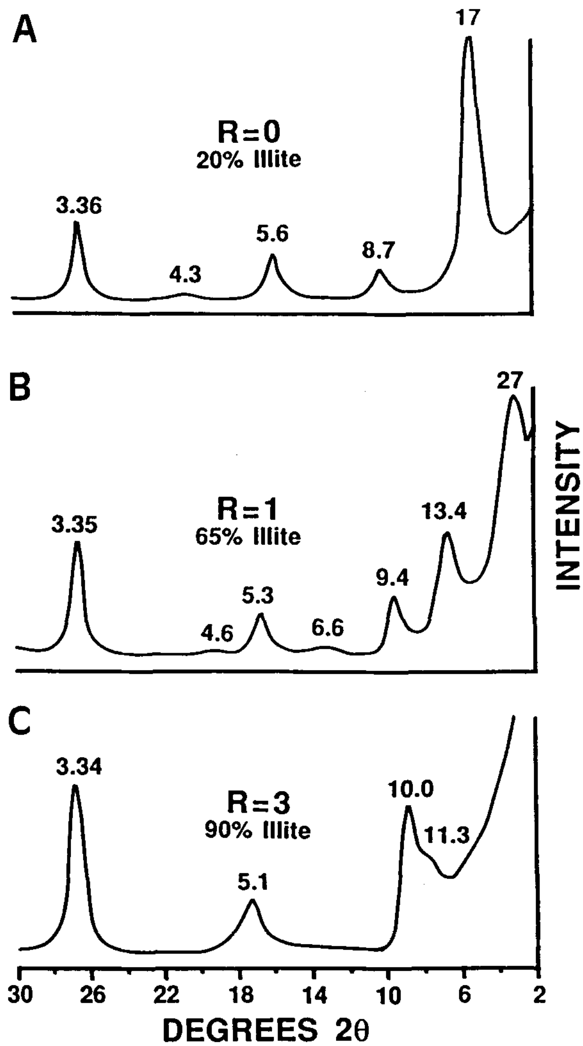


Figure 2. Calculated X-ray powder diffraction patterns of mixed-layer illite/glycol-smectite (I/S) with different expandability and Reichweite (R) ordering using the modeling program *NEWMOD*™. A) random I/S (R = 0) with 20% illite; B) short-range ordered I/S (R = 1) with 65% illite; C) long-range ordered I/S (R = 3) with 90% illite. Copper $K_\alpha$ radiation.

## MODELS AND APPLICATIONS

### *Temperature models for I/S geothermometry*

I/S is commonly interpreted from XRD profiles of oriented, glycol-saturated specimens of the <2 $\mu$m or finer fraction(s) (see Moore and Reynolds, 1989, for review). Trends in I/S with depth were first defined in detail by Reynolds and Hower (1970), who compared XRD profiles of natural materials with calculated profiles. They defined three interstratification forms of I/S using the "Reichweite" (R) notation (Reynolds, 1980): random (R = 0), short-range (R= 1) ordered, and long-range (R ≥ 3) ordered (Figure 2).

Two simple time-temperature models are used for I/S geothermometry studies (Table 1). These simple time-temperature models are based primarily on the duration of heating (or residence time) at critical I/S reaction temperatures (Pollastro, 1990). The first model was proposed by Hoffman and Hower (1979) who cautioned that its usage be restricted to rocks of Tertiary and Cretaceous age because the appearance or disappearance of an index mineral may be dependent also on reaction time. In this report, the *Hoffman and Hower* model applies to long-term, burial diagenetic settings where geothermal gradient is the primary heat source and rocks are subjected to increased temperatures due to burial (commonly in excess of 100°C) typically for tens to hundreds of millions of years. Minimum heating time for the *Hoffman and Hower* model is about 2 my (Pollastro, 1990). Thus, the *Hoffman and Hower* model applies to most geologic and petroleum studies of sedimentary rocks and basins of Miocene age or older.

Table 1. Approximate temperatures for changes in mixed-layer illite/smectite (I/S) in Hoffman and Hower and short-life geothermal I/S geothermometry models.

| Change in I/S | Hoffman and Hower model (5–300 m.y.) | Short-life geothermal model (<3 m.y.) |
|---|---|---|
| Smectite-to-R = 0 I/S | 50°–60°C | variable |
| R = 0 to R = 1 | 100°–110°C | 120°–140°C |
| R = 1 to R = 3 | 170°–180°C | 170°–180°C |

The second model, the *short-life geothermal* model, applies to short-lived heating events and is also based primarily on empirical relations between changes in I/S and temperature due to burial depth. Studies of well samples from the Colorado River Delta in California by Jennings and Thompson (1986) and analysis of the submarine fan deposits, San Joaquin Basin, by

https://doi.org/10.1346/CCMN.1993.0410202 Published online by Cambridge University Press

Ramseyer and Boles (1986) are good examples of the *short-life geothermal* model. In these studies, residence time at critical reaction temperatures for I/S is about 3 my or less, commonly 0.5 to 1 my. Geological settings for the *short-life geothermal* model are those where relatively young rocks were subject to progressive burial temperatures in excess of 100°C for <3 my, such as young basins, areas of relatively recent thermal activity producing elevated geothermal gradients, and/or a recent or short-lived hydrothermal environment or event. The 3 my age or heating period separating the two models, however, is somewhat arbitrary because some variability in temperatures for smectite diagenesis is documented for rocks <5 my in age.

Comparison of the two models is shown in Table 1. In the *Hoffman and Hower* model, the major change from R = 0 to R = 1 ordering of I/S occurs at about 100°–110°C (Hoffman and Hower, 1979). In the *short-life geothermal* model, the temperature for R = 0 to R = 1 I/S is about 120°–140°C (Jennings and Thompson, 1986; Ramseyer and Boles, 1986). The temperature for the conversion from R = 1 to R ≥ 3 ordering, however, is about 170°–180°C for both models.

### Common applications

The most common approaches utilizing the I/S geothermometer in diagenetic studies are: 1) vertical profiles from wells or outcrops, where I/S is studied through several hundred or thousand feet of sedimentary rock (samples from either well core or cuttings are used in well-profile studies); 2) paleotemperature or thermal maturity mapping on local or regional scale, where I/S of a particular unit or bed of interest (e.g., a potential hydrocarbon source bed) is studied using both outcrop and well samples to produce a geothermal history map of the unit in the study area; and 3) unit-specific cross-sectional profiles, where I/S in well core or cuttings of a particular unit or bed of interest is studied in the subsurface from a series of wells, or on the surface from a series of outcrops, or both, commonly along a line of section at various depths and (or) outcrop localities within a basin or region.

Well-profile studies are the most widely used and simplest application of I/S geothermometry in basin history studies and petroleum exploration, producing an "illitization reaction profile" that is compared to the present geothermal gradient profile, organic maturation profiles (commonly vitrinite reflectance), and types and grade of hydrocarbon produced in the well or field. The I/S geothermometer can be used to determine temperature points or profiles versus depth in wells. Temperatures for changes in I/S ordering are assigned using the established temperature models. Combination of two or more points produces a depth versus temperature profile that corresponds to a maximum temperature. The temperatures determined from I/S geothermometry are then compared to those constructed from present-day measured well temperatures, present geothermal gradients, or geothermal gradients inferred for a particular time in the past.

Several applications of I/S paleotemperature mapping were also published from late 1970's to mid-1980's, many of which produced thermal maturity or source-rock hydrocarbon-potential maps for a particular unit (Schultz, 1978; Hoffman and Hower, 1979; Nadeau and Reynolds, 1981; Rettke, 1981; Pollastro and Scholle, 1986; Burtner and Warner; 1986). Examples for each of the three applications are given later in this paper where case-history studies are presented.

## INTERPRETIVE CONSIDERATIONS

### Factors controlling smectite illitization

Primary factors controlling the smectite illitization reaction are temperature and potassium availability. If potassium is available, as it is in most natural systems containing I/S, temperature appears to be the main driving force for the reaction. Secondary factors include time (Pytte and Reynolds, 1989; Pollastro, 1990), rock/water ratio (Whitney and Northrop, 1987; Whitney, 1990), fluid and rock composition (Eberl, 1978; Nadeau and Reynolds, 1981; Roberson and Lahann, 1981), starting composition of I/S (Schultz, 1978; Rettke, 1981; Pollastro and Scholle, 1986; Freed and Peacor, 1989; Pollastro, 1990), and pressure (Bruce, 1984; Colton-Bradley, 1987).

Perhaps the most controversial of the secondary factors is the effect of time on the reaction. Because most hydrocarbon generation models involve time-temperature calculations (Waples, 1980; Tissot and Welte, 1984), the effect of time should be considered when I/S geothermometers are used as thermal maturity indicators for petroleum source rocks. Time was first recognized by Perry and Hower (1972) as a possible factor affecting illitization (Figure 1). Subsequently, several laboratory and case-history studies have suggested that time is an important consideration (Eberl and Hower, 1976; McCubbin and Patton, 1981; Środoń and Eberl, 1984; Jennings and Thompson, 1986; Ramseyer and Boles, 1986; Pytte and Reynolds, 1989; Freed and Peacor, 1989; Pollastro, 1990).

In contrast, Weaver (1979) reviewed published data and plotted the temperature of conversion of random I/S to ordered I/S (the disappearance of the 17 Å glycol reflection) as a function of time (Weaver, 1979, Figure 2). He found good correlation between the composition and degree of ordering of I/S and temperature, but no apparent relation to age. Weaver concluded that time had little effect on the smectite-to-illite reaction in samples from about 10 to 350 my in age. Similarly, studies by Foster and Custard (1983), Pearson and Small (1988), Velde and Iijima (1988), Pollastro and Schmoker (1989), and Elliott *et al.* (1991), among others, con-

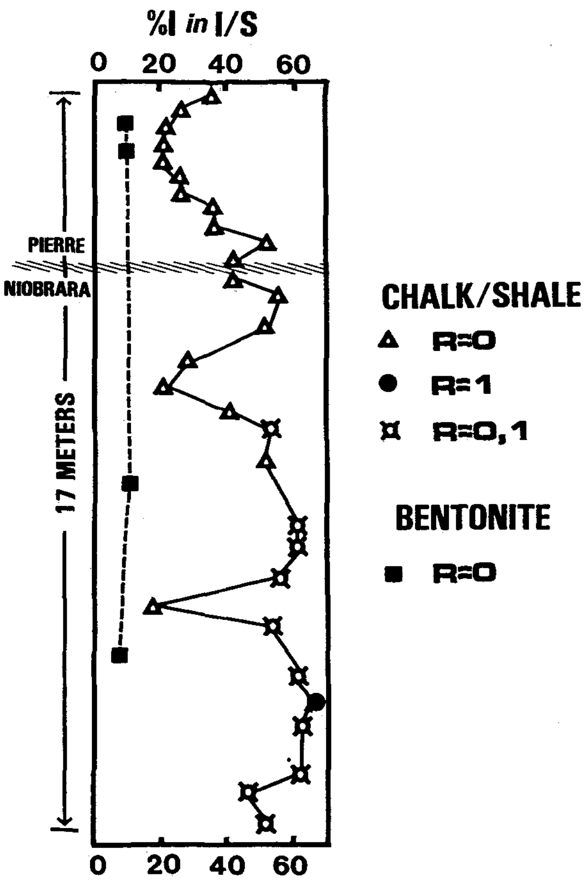


Figure 3. Percent illite layers (%I) in mixed-layer illite/smectite (I/S) of shale, chalk, and bentonite from the Pierre Shale and Niobrara Formation sampled from core of the Whomble No. 1 well, Denver Basin, Colorado. Note heterogeneity in both percent illite layers in I/S and ordering of I/S.

cluded that the smectite-to-illite reaction is largely dependent upon temperature.

*Interpretive problems and other important considerations*

Several important considerations are recommended before any reliable interpretations in I/S geothermometry can be made. Perhaps the most important consideration is to first establish, if possible, the original composition(s) of the I/S within the units of interest because many rocks contain a heterogeneous assemblage of I/S. Additionally, detrital I/S deposited in a sediment may contain a high proportion of illite layers. Commonly, the illite/smectite ratio and ordering type of I/S are heterogeneous within any one sample due to multiple origins of the clay (Figure 3). Heterogeneity of I/S may be caused by multiple source areas, detrital (depositional) versus authigenic (diagenetic) origins, hydrothermal alteration, recycling, and more rarely, weathering.

Major variations in I/S commonly occur in sedimentary rocks (Figure 3) over vertical and (or) horizontal intervals of meters, centimeters, or millimeters (Pollastro and Scholle, 1986; Owen *et al.*, 1989; Elliott *et al.*, 1991). Therefore, it is important to analyze several samples from different lithologies in vertical and horizontal profiles on a local, or perhaps regional, scale to establish trends related to factors other than temperature, such as provenance, lithology, stratigraphy, eustacy, paleoenvironment, paleoclimate, etc. For example, commonly only ordered I/S may be present in the samples, and a trend in I/S on XRD profiles is not recognized from random sampling or sample profiles. Sufficient evidence must then be established by controlled sampling that illitization occurred from a precursor smectite or random I/S. Only then can the I/S be used as an absolute geothermometer. Indeed several workers have been disappointed in their attempts to apply I/S geothermometry because the rocks studied lack crucial components such as smectite or highly smectitic I/S. It is critical, therefore, to establish the original clay-mineral composition of such rocks because detrital I/S may have undergone extensive illitization during a previous burial cycle (Rettke, 1981; Nadeau and Reynolds, 1981; Pollastro, 1981; Pollastro and Scholle, 1986).

Control samples are important and aid in evaluating the diagenetic extent of I/S used for determining paleotemperature. Control samples with a known starting composition are the most favorable. I/S in thin altered volcanic ashes, particularly bentonites and tonsteins, are very useful for determining diagenetic extent and paleotemperatures of the enclosing rocks. The subaqueous alteration of vitric volcanic ash to pure or nearly pure smectite commonly occurs rapidly after deposition in the relatively low temperatures of the marine or peat swamp environments. Thus, a known starting composition—nearly pure smectite—that is essentially unreacted (i.e., has not been illitized) provides a control or base for studying subsequent smectite diagenesis. Altered ashes composed almost entirely or partly of smectite may subsequently be subjected to increased temperature due to depth of burial or proximity to intrusion or other local thermal events causing progressive illitization. Maximum temperature can thus be interpreted from the I/S product. Additionally, type, amount, and extent of illitization of I/S in the bentonite compared to I/S in adjacent lithologies can aid in establishing the diagenetic and detrital extent of adjacent beds (Schultz, 1978; Pollastro, 1981; Rettke, 1981, Pollastro and Scholle, 1986).

In the case of well profiles, core samples are preferred over cuttings. Although it is more difficult to obtain core than cuttings, the latter introduce uncertainty in specific sample depth and lithology, as well as in quality. Cuttings are originally sampled and bagged during drilling; their reliability, therefore, is strongly dependent upon the experience of the logger and other well-site personnel. More importantly, cuttings may become contaminated. Contamination is common from caving of material at shallower depth in the well and by drilling muds, both of which can introduce higher expandable I/S into the sample. A relatively small amount of highly expandable I/S washed or mixed into samples recovered deeper in the well can overprint more illitic I/S upon XRD examination. This is particularly important if one is tracing the disappearance of the 17 Å glycol phase.

Freed and Peacor (1989) found agreement between depth and temperatures for the onset of smectite-to-illite reaction in samples of cuttings and core from the same Gulf Coast well, but depths and corresponding calculated temperatures for the transition from random to ordered I/S were different. They questioned the discrepancy because the lower temperature value for the transition was determined from core samples and the higher temperature determined from cuttings. These authors recognized the possibility of contamination from shallower depths in the well where the analysis was based on only cuttings.

Other fine-grained mineral geothermometers, particularly other clay minerals, zeolites, or metastable silica, may coexist with I/S. For example, the presence of corrensite and changes in diagenetic silica-phase (opal-A-to-opal-CT; opal-CT-to-quartz) are commonly observed in oriented clay-sized specimens prepared for I/S analysis. Other useful geothermometers include vitrinite reflectance, fluid inclusions, and Rock-Eval pyrolysis.

Petrographic analysis or other analytical techniques should be used to characterize I/S. Thin section and SEM analysis can help determine detrital *vs* authigenic origins of clays and other minerals. In addition, it is important to determine the bulk-rock mineralogy before any geologic interpretations are made from the clay mineralogy (Towe, 1974). Finally, it is important to compile other pertinent information for the study area, such as burial history, geothermal gradient, present-day well temperatures, or the possibility of other local thermal events that may have promoted or inhibited smectite diagenesis.

## RELATION AND APPLICATION TO HYDROCARBON GENERATION AND EXPLORATION

The relations between the I/S geothermometers and stages of hydrocarbon generation are summarized in Figure 4. The relations shown in Figure 4 are documented best for rocks of Tertiary and Cretaceous age, however, may also apply to those from Miocene to Mississippian in age. The *Hoffman and Hower* model is applicable to most hydrocarbon exploration plays, as it includes sedimentary rocks and basins older than about 2 to 5 my. This paper will concentrate primarily on studies where the *Hoffman and Hower* model is applicable. Perhaps the most important relation of I/S to hydrocarbons is the transition from random I/S (R = 0) to ordered I/S (R = 1). The temperature range of 100°–110°C for the ordering change of I/S from R = 0 to R = 1 in the *Hoffman and Hower* model is roughly coincident with the temperatures generally designated for the "oil window" and approximates the temperatures for the onset of peak (or main phase) oil generation in rocks of Tertiary through Cretaceous age (Tissot and Welte, 1984). For example, if upon examination of I/S in a potential source rock a distinct 17 Å glycol XRD peak is present, the rock would be designated as immature or marginally mature with respect to oil generation. Thus, the simplest application of the I/S geothermometer in burial diagenetic settings of petroleum rocks is to interpret or record the 100°C point or isotherm, or the 100°–110°C isoband, using the R = 0 to R = 1 transition.

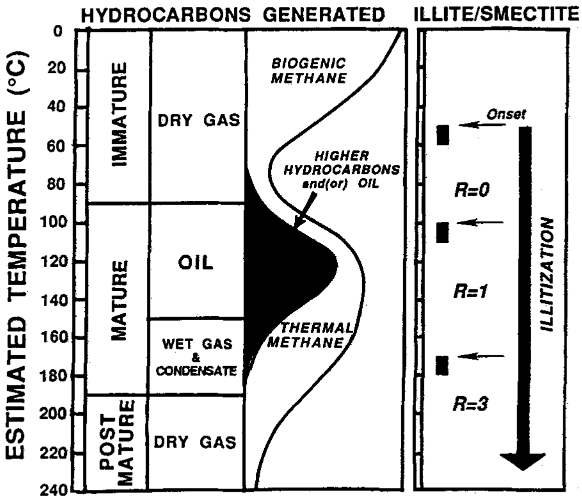


Figure 4. Generalized relationships between temperature, hydrocarbon generation, and changes in mixed-layer illite/smectite. Figure and data modified and compiled from Hoffman and Hower (1979), Waples (1980), Rice and Claypool (1981), and Tissot and Welte (1984). Relations documented best for rocks of Tertiary and Cretaceous age, however, may also apply to those from Miocene to Mississippian in age.

The I/S geothermometer provides a maximum burial temperature relative to basin history that can be used as a maturation indicator for hydrocarbon generation. This method is particularly valuable for samples lacking vitrinite or other indicators from which the maturity level of organic matter can be estimated directly. Temperatures determined from I/S correlate well with coal rank and mean vitrinite reflectance (Środoń, 1979; Pevear *et al.*, 1980; Nadeau and Reynolds, 1981; Pollastro and Barker, 1986; Connolly, 1989), and "$T_{max}$" (Burtner and Warner, 1986; Glassman *et al.*, 1989; Velde and Espitalié, 1989). Other studies have related changes in I/S to particular stages of oil generation (Weaver, 1979; Foscolos and Powell, 1980; Dypvik,

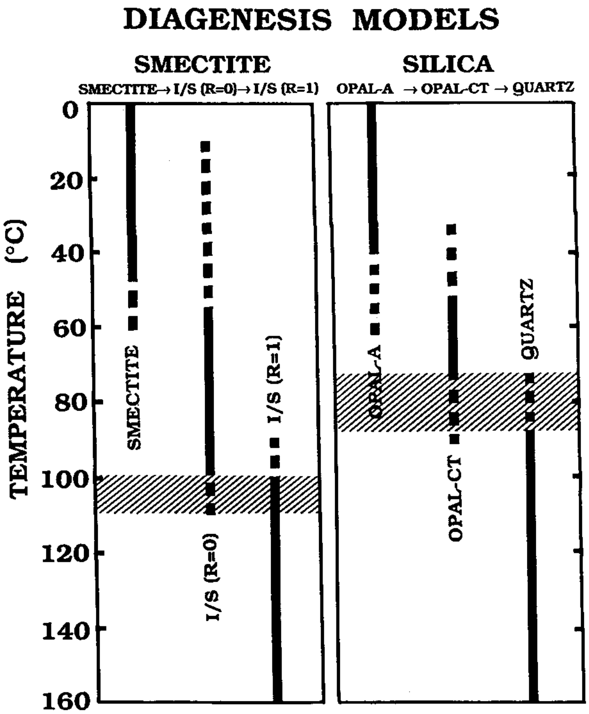


Figure 5. Comparison of temperature for smectite and silica diagenesis. Data from Hoffman and Hower (1979) and Keller and Isaacs (1985). Diagonal patterns indicate temperature ranges for R = 0 illite/smectite (I/S) to R = 1 I/S, and opal-CT to quartz transitions.

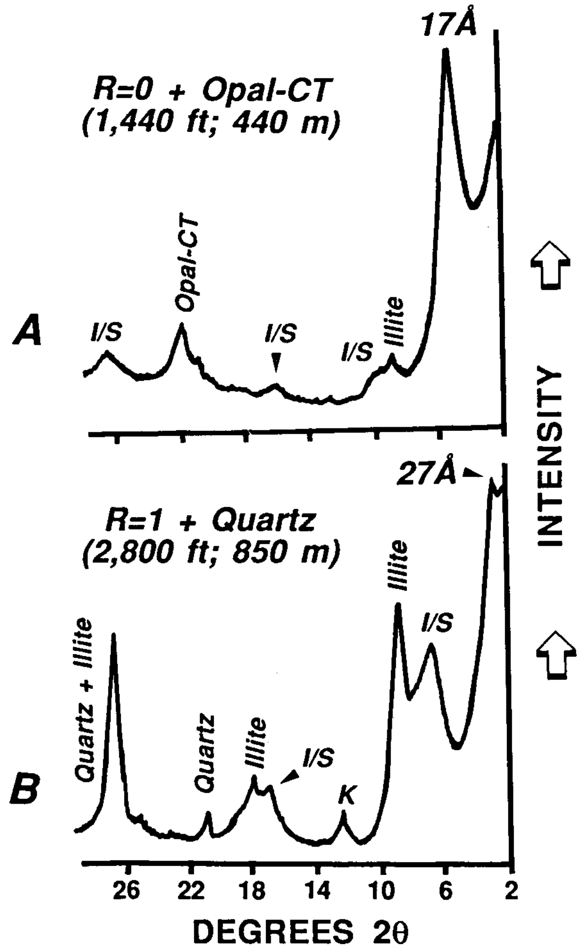


Figure 6. X-ray powder diffraction profiles of oriented, <2-μm glycol-saturated specimens of diatomaceous rocks from the Union Newlove 51 well, Orcutt field, Santa Maria Basin, California showing transition from random illite/smectite (I/S) to ordered I/S and transition from opal-CT to quartz. A) Sample at 1440 ft (440 m) containing random I/S (R = 0) and opal-CT. B) Sample at 2800 ft (850 m) containing ordered I/S (R = 1) and quartz. K = Kaolinite. Copper $K_\alpha$ radiation.

1983; Edman and Surdam, 1986; Hagen and Surdam, 1989; Pollastro and Schmoker, 1989).

Similarly, the conversion of I/S from R = 1 to R = 3 ordering, indicating a temperature of transition of about 175°–180°C, may document the upper limit of oil generation for a potential source rock (Figure 4). For example, a rock containing only R ≥ 3 I/S would be classified as overmature with respect to oil generation and would indicate that the source rock may have potential to generate only thermal methane. Again, this interpretation can only be made if there is evidence that the I/S had undergone illitization during burial within the current basin.

## CASE-HISTORY EXAMPLES OF I/S GEOTHERMOMETRY

Five case histories are presented here where changes in I/S are used to: 1) demonstrate and test the I/S geothermometry model established by Hoffman and Hower (1979), and 2) determine the thermal history and thermal maturity of sedimentary basins and hydrocarbon source beds. Additionally, these studies demonstrate the three common applications of I/S geothermometry in rocks ranging in age from about 3 to 330 my (Pliocene to Mississippian).

### *Case #1*

The first example is that of well profiles of I/S with a coexisting silica-phase geothermometer in a study of the siliceous, organic-rich, Pliocene and Miocene, Sisquoc, and Monterey Formations (3–18 my). These inherently fine-grained, diatomaceous rocks are prolific producers of indigenous, immature, low-gravity oils (particularly the Monterey Formation) in numerous onshore and offshore basins along the coast of California. In both the Monterey and Sisquoc Formations, diatoms were originally composed of amorphous opal-A, and clay-rich detritus comprised mostly smectite and I/S. Thus, the utility of both I/S and silica-phase geothermometers may be applied and compared to constrain the thermal histories of these petroleum source

https://doi.org/10.1346/CCMN.1993.0410202 Published online by Cambridge University Press

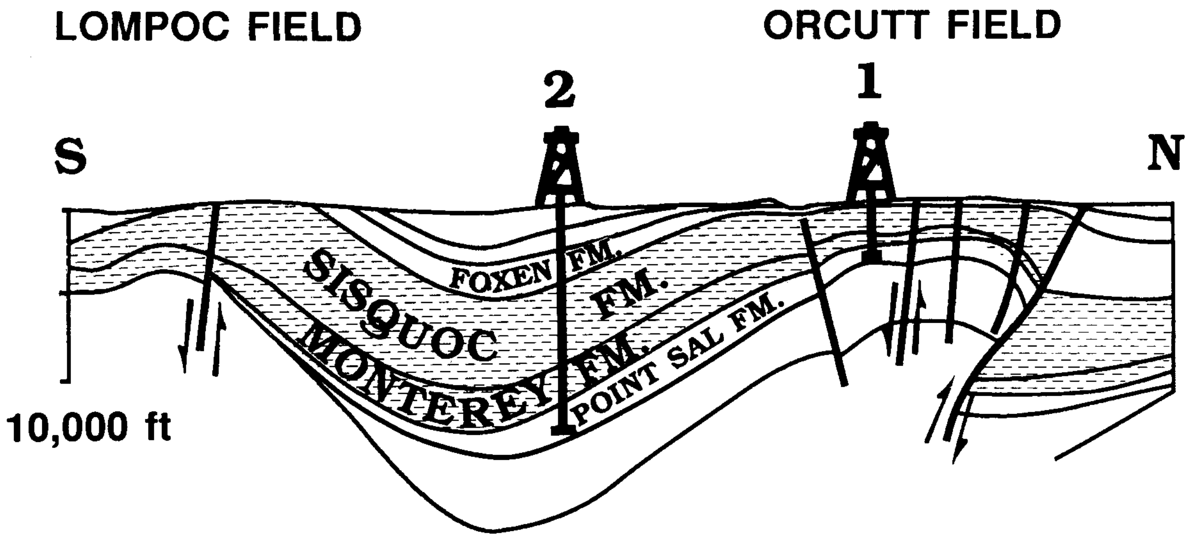


Figure 7. Generalized south-to-north cross section from the Lompoc to Orcutt fields, Santa Maria Basin, California, showing location and structure for Union Oil Corporation, Newlove 51 (1) and Coastal Oil and Gas, Hunter-Careaga No. 3 (2) wells. Dashed pattern designates Sisquoc and Monterey Formations.

and reservoir rocks (Pollastro, 1989). The I/S and silica-phase geothermometers are compared in Figure 5. The opal-CT to quartz transition temperature, commonly about 75–85°C, is the primary silica-phase geothermometer used here (Figure 5).

I/S and silica phases were studied and compared in two wells from two fields with different tectonic and thermal histories in the Santa Maria Basin, California. The two wells, located in Santa Barbara County, are the Union Oil Co. Newlove 51 (sec. 25, T. 9 N. R. 34 W.) well and the Coastal Oil and Gas, Hunter Careaga No. 3 well (sec. 18, T. 8 N., R. 33 W.). About 80 samples of core from the Newlove well and 60 samples of cuttings from the Hunter Careaga well were analyzed by XRD for whole-rock and clay mineralogies. The fine-grain size of both I/S and biogenic silica mandates monitoring of both geothermometers using XRD profiles of the $<2$ $\mu$m fraction (Figure 6) or finer. The Newlove 51 well is located in the Orcutt field on a faulted anticlinal structure with a relatively high ($\sim$55°C/km) geothermal gradient, whereas the Hunter Careaga No. 3 well is located about halfway between the Orcutt and Lompoc fields in a synclinal valley with a much lower ($\sim$35°C/km) geothermal gradient (Figure 7). Burial-history reconstructions indicate about 2500 ft (750 m) of uplift and erosion for the Newlove 51 well at Orcutt field (Pisciotto, 1981) and $<330$ ft (100 m) for the Hunter Careaga No. 3 well.

There is an overall progressive increase in percent illite in I/S with increased burial depth from about 15% at 500 ft (150 m) to about 70% at 3600 ft (1100 m) in the Union Newlove 51 well (Figure 8). The change from random I/S (R = 0) to ordered I/S (R = 1) occurs over a short depth interval beginning at about 2500 ft (750 m); the reaction converting all R = 0 to R = 1 (as can be measured by XRD) is complete at about 2625 ft (800 m) in the well (Figures 8 and 9). Because of considerable uplift and erosion in the Orcutt area, no original opal-A exists in core from shallowest samples at about 500 ft (150 m); thus, the opal-CT zone occurs very near the surface. The progressive diagenesis of opal-CT to quartz in Newlove 51, however, can be well documented between about 2000 ft (600 m) and 2130 ft (650 m); quartz is the only silica phase present in samples below 2130 ft (650 m) (Figure 8).

Similarly, a progressive illitization reaction profile is shown in the Hunter Careaga well over a much larger depth interval (Figure 9). The percent illite layers in I/S increased from about 10% at 2500 ft (750 m) to about 80% at 12,000 ft (3650 m). The transition of R = 0 to R = 1 I/S occurs at about 9000 ft (2750 m) in the Hunter Careaga No. 3 well, whereas the opal-CT-to-quartz transition occurs at about 6000 ft (1800 m).

The utility of the I/S- and silica-phase geothermometers can now be tested in the Union Newlove 51 and Hunter Careaga No. 3 wells from the established profiles. Assuming a constant geothermal gradient of 55°C/km since maximum burial, a mean average surface temperature of 14°C, and a 2500 ft (750 m) correction for uplift and erosion, the calculated maximum paleotemperature is 100°–105°C for the depth in Newlove 51 where random I/S (R = 0) is converted to ordered I/S (R = 1) and 85°–90°C for the depth of the opal-CT to quartz conversion (Figure 8). The temperatures calculated for the Hunter Careaga well, assuming a 35°C/km geothermal gradient since maximum burial and no correction for uplift and erosion, are about 105°–115°C for the R = 0 to R = 1 I/S conversion and about 75°C

https://doi.org/10.1346/CCMN.1993.0410202 Published online by Cambridge University Press

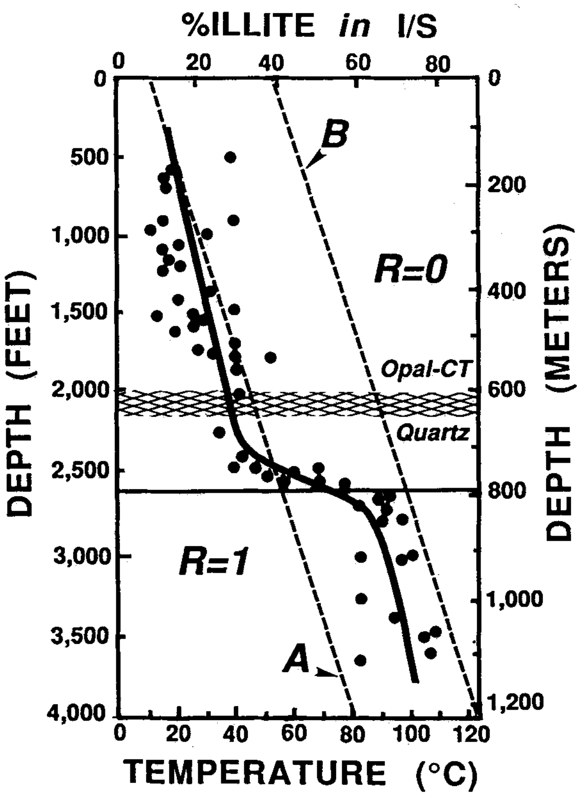


Figure 8. Superimposed plots of depth versus percent (%) illite layers and ordering type in interstratified illite/smectite (I/S) (solid dots and horizontal line) and depth *vs* temperature from <0.25 $\mu$m fraction of core samples of diatomaceous rocks of the Sisquoc and Monterey Formations in the Union Oil Corporation, Newlove 51, well, Orcutt field, Santa Maria Basin, California. Zones of random I/S (R = 0), ordered I/S (R = 1), opal-CT, and quartz also shown. Cross-hatch pattern indicates reaction zone for opal-CT-to-quartz transition. Bold line approximates smectite-to-illite reaction profile. Dashed lines indicate: A) geothermal gradient at present burial depths and B) reconstructed temperatures at maximum burial. Note that opal-CT-to-quartz transition on gradient line B occurs at about 90°C and R = 0 to R = 1 I/S change occurs at about 105°C.

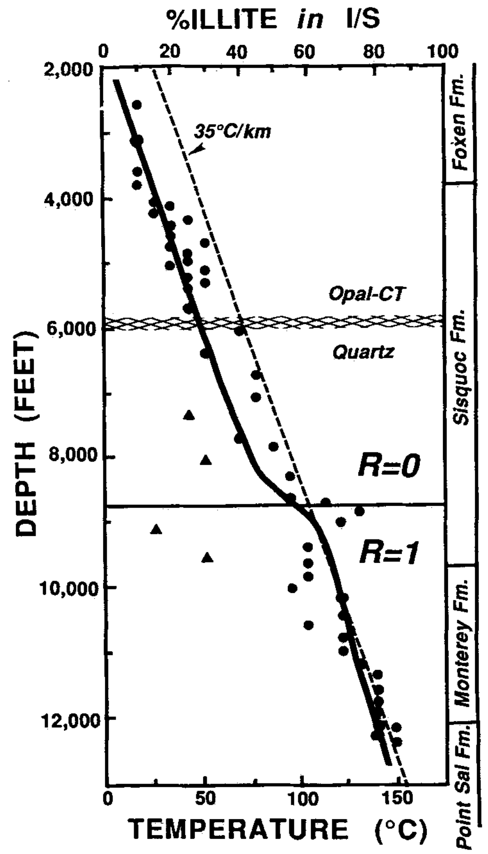


Figure 9. Superimposed plots of depth *vs* percent (%) illite layers and ordering type in interstratified illite/smectite (I/S) line and solid symbols and depth *vs* temperature from <0.25 $\mu$m fraction from cuttings of the Foxen, Sisquoc and Monterey, and Point Sal Formations in the Coastal Oil and Gas, Hunter-Careaga No. 3 well, Santa Maria Basin, California. Figure also designates zones of random I/S (R = 0), ordered I/S (R = 1), opal-CT, and quartz. Cross-hatch pattern indicates approximate reaction zone for opal-CT-to-quartz transition. Bold line approximates smectite-to-illite reaction profile. Dashed line approximates present geothermal gradient. Solid triangles indicate cutting samples contaminated by cavings from shallower depths, probably from about 4000 to 6000 ft. Note opal-CT-to quartz transition occurs at about 75°C and R = 0 to R = 1 I/S transition occurs at about 110°C. Formations in well designated on right side of figure.

for the opal-CT to quartz transition (Figure 9). These temperatures calculated for smectite diagenesis are in good agreement with the 100°–110°C for the *Hoffman and Hower* model. Although studies have shown that the temperature for the conversion of opal-CT to quartz varies, it commonly occurs at about 75°–85°C (Keller and Isaacs, 1985). Thus, temperatures of 85°–90°C and 75°C calculated for opal-CT to quartz in the wells are also in good agreement with established silica diagenesis models. In summary, the temperatures derived from I/S geothermometry are consistent with the *Hoffman and Hower* model and, furthermore, are supported by temperatures determined from silica-phase geothermometry. Moreover, I/S and silica-phase geothermometry demonstrate their potential use in providing thermal histories of the economically important Monterey Formation in the tectonically complex Santa Maria Basin.

The data for I/S from cuttings in the Hunter Careaga No. 3 well show some discrepancy in the reaction profile of Figure 9. The solid triangles in Figure 9 are intervals with illite layer contents lower than expected, as compared to the illitization pathway generally represented by the bold line. This deviation in I/S suggests contamination, perhaps by caving of beds at shallower depths in the well as cuttings at the drill bit were being carried to the surface. The well-site geologist confirmed that caving was a serious problem in the Hunter Careaga No. 3 well while drilling through the Sisquoc For-

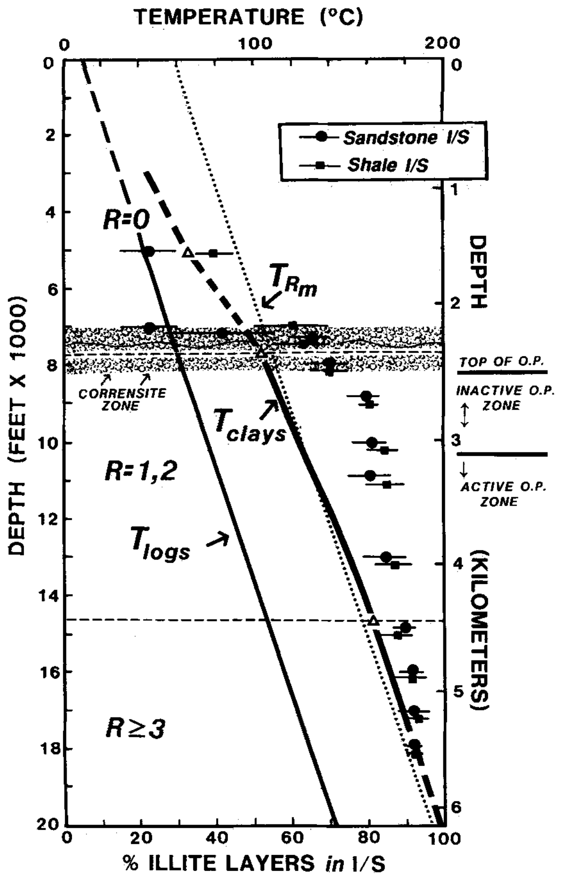


Figure 10. Depth *vs* percent (%) illite layers and ordering (R) of mixed-layer illite/smectite (I/S) and depth *vs* temperature for sandstone and shale samples from the El Paso Natural Gas, Wagon Wheel No. 1 well, Pinedale area, Wyoming. $T_{logs}$, present-day temperatures from logs; $T_{clays}$, maximum burial temperature from I/S geothermometers: $T_{Rm}$, maximum burial temperature from vitrinite reflectance. Note zones of active and inactive overpressuring (O.P.) at right of diagram relative to present and maximum temperature curves. Modified from Pollastro and Barker (1986) and Law *et al.* (1986).

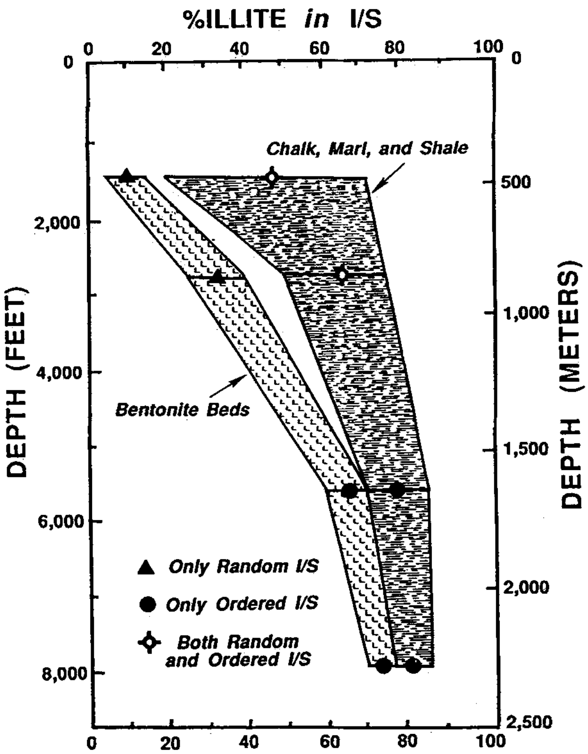


Figure 11. Percent illite layers and ordering of mixed-layer illite/smectite (I/S) in chalk, marl, and shale, and in bentonite *vs* present depth in samples from core of the Niobrara Formation in six wells, Denver Basin, Colorado. Modified from Pollastro and Scholle (1986).

mation and that the contamination of cuttings, particularly those from lower in the unit, was very likely (C. E. Katherman, personal communication, 1991). A later and more careful sampling of the cuttings from these intervals yielded I/S with much higher illite content consistent with those represented by the bold line of Figure 9.

### *Case #2*

Another example of the well profile application is a study of low-permeability gas reservoirs from core of the Wagon Wheel No. 1 well, northern Green River Basin, Wyoming (Pollastro and Barker, 1986). Present-day temperatures for lower Tertiary and Upper Cretaceous (about 40–85 my) rocks of the Pinedale anticline are significantly cooler than maximum temperatures determined from I/S and corrensite (C/S) geothermometers, mean vitrinite reflectance ($R_m$), and fluid inclusions. The profiles of I/S and $R_m$ are also used to help determine the amount of uplift and erosion in the area of the Pinedale anticline. The percent illite in I/S and ordering of I/S versus depth for about 180 samples of sandstone and shale from the Wagon Wheel well are shown in Figure 10.

Application of the *Hoffman and Hower* model for I/S and C/S (minimum temperature of formation at about 90°C) in Wagon Wheel samples, produced a maximum burial temperature profile ($T_{clay}$) for the well (Figure 10). Similarly, a temperature profile was calculated from $R_m$. Calculated maximum temperatures from both clay and $R_m$ geothermometry are about 30°–50°C hotter than present-day temperatures in the Wagon Wheel well; however, slopes of the maximum temperature curves are similar to that of present measured well temperatures (Figure 10). These relations suggest that about 5600 ft (1700 m) of uplift and erosion has occurred in this area of the Pinedale anticline; however, geothermal gradient has probably remained constant since maximum burial.

Paleotemperatures determined by clay geothermometry also help explain active and inactive zones of overpressuring in these low permeability rocks. Overpres-

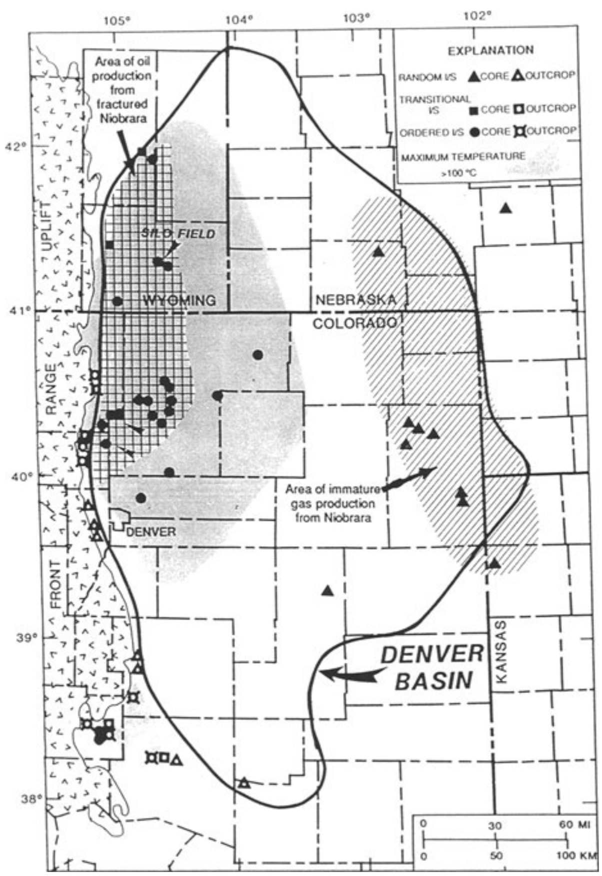


Figure 12. Geothermometry map as an indicator of maximum burial temperature and thermal maturity of hydrocarbons for the Niobrara Formation, Denver Basin. Temperatures determined from ordering of mixed-layer illite/smectite (I/S) in bentonite from core (solid symbols) and outcrop (open symbols). Shaded pattern indicates areas of maximum burial >100°C. Areas of current microbial gas (diagonal pattern) and oil (grid pattern) from the Niobrara are shown. Small arrows point to areas targeted for horizontal wells.

suring in the area of the Pinedale Anticline is believed to be caused by generation of thermal methane from coals (Law *et al.,* 1986). Well temperatures are insufficient at the present depths in Wagon Wheel to explain residual overpressuring from thermal gas generation. Maximum temperatures calculated from I/S and $R_m$ geothermometry at time of maximum burial (about 3–37 Ma), however, are sufficient to explain a paleothermal gas generation window at present depths coincident with inactive or residual overpressuring. The zone of active overpressuring, however, is at a depth where present temperatures are sufficient for active methane generation (Figure 10).

*Case #3*

I/S geothermometry has been uniquely applied in a study of surface and subsurface samples of chalk, chalky shale, and bentonite from the organic-rich, Upper Cretaceous Niobrara Formation (about 75–85 my), Denver Basin and adjacent areas because 1) the Niobrara is both a petroleum source and reservoir rock in these areas; 2) well-documented, progressive diagenetic changes occur relative to increased depth of burial and temperature in I/S (Figure 11) and in the chalk that affect both reservoir quality of the chalks and the type of indigenous hydrocarbons (microbial gas versus oil) produced (Pollastro and Scholle, 1986); and 3) within the past five years, the overall success of the many horizontal wells drilled, particularly in fractured, organic-rich, thermally mature chalk or chalky shale reservoirs, has rekindled interest in the Niobrara Formation throughout the Rocky Mountain region as an exploration target for oil.

Chalk and chalky shale of the Niobrara contain I/S with a heterogeneous illite-layer content and ordering of I/S before any significant burial and illitization (Figure 3). Percent illite in I/S and ordering of I/S in bentonite, however, is relatively homogeneous in multiple samples from any one location and/or depth (Figures 3 and 11). In this study, I/S in bentonite beds from the Niobrara Formation and basal Pierre Shale is used as an indicator of thermal maturity of hydrocarbons sourced by organic-rich chalk and chalky shale of the Niobrara. Applying the *Hoffman and Hower* model, only random I/S (R = 0) exists in bentonite below temperatures of about 100°C; thus, only ordered (R = 1 or greater) I/S is present in bentonites that have been buried to temperatures above this range (>110°C). A transitional R = 0-to-R = 1 type I/S (or imperfect? R1 I/S), i.e., I/S that is in an initial or transitional stage of converting from random to ordered I/S (Pollastro and Martinez, 1985; Whitney and Northrop, 1988), has been identified and is interpreted as forming at temperatures just below the 100°–110°C conversion. Transitional type I/S commonly contains about 45–55% illite layers.

The relations between the temperatures for changes in I/S and those for hydrocarbon generation in Cretaceous rocks (Figure 4) provide a basis for predicting hydrocarbon maturity within the Niobrara form I/S geothermometry. Additionally, biogenic methane (an immature gas generated at low temperatures from the decomposition of organic matter by anaerobic microorganisms) is produced from the Niobrara in areas where burial temperatures never exceeded 75°C (Rice and Claypool, 1981). The I/S geothermometer is, therefore, especially useful for Niobrara rocks because it outlines areas of different degrees of thermal maturity as related to the type of hydrocarbon generated. Areas of lesser potential, for example, areas where maximum burial temperature is estimated between about 75° to 100°C and thus too high for biogenic gas and too low for thermogenic oil and(or) gas production, can also be interpolated from I/S ordering and well production data. Areas that are potential targets for horizontal

https://doi.org/10.1346/CCMN.1993.0410202 Published online by Cambridge University Press

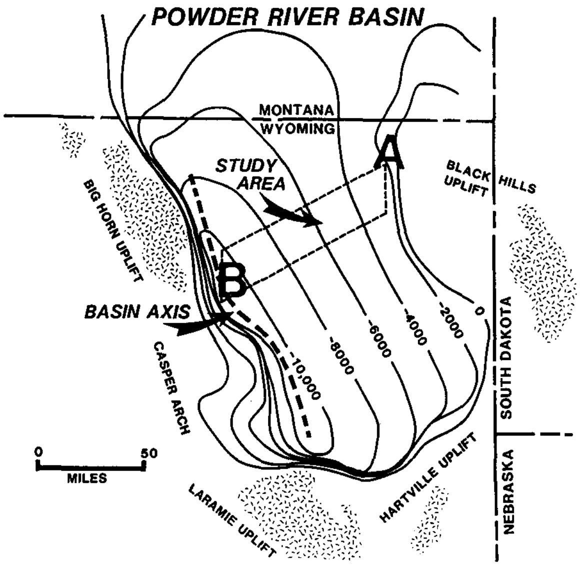


Figure 13. Map showing general area for well-core study (dashed-in area) from sixteen wells of the Permian upper part of the Minnelusa Formation, Power River Basin, Wyoming, and adjacent states. Shallowest core were samples from wells at about 1500 ft (*location A*) along a general southwest trend to about 15,000 ft (*location B*) and near basin's axis (bold dashed line).

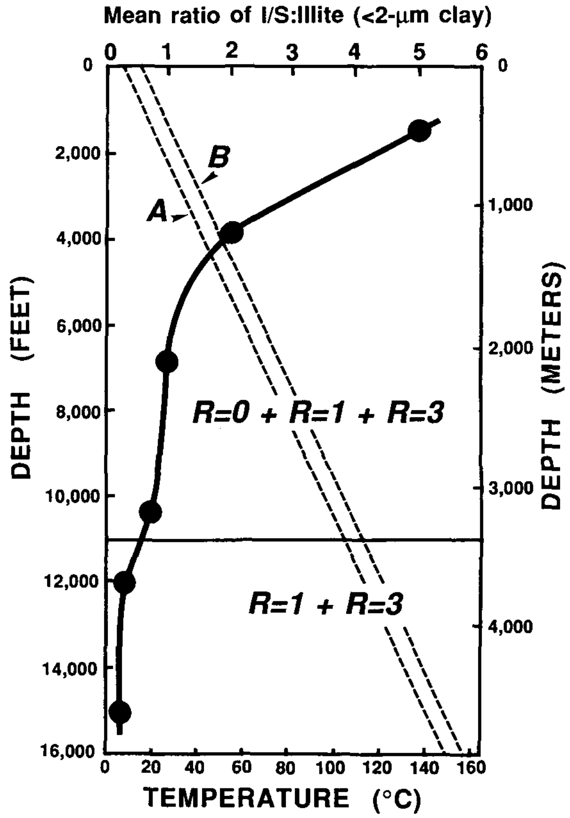


Figure 14. Depth versus mean ratio of relative weight amount of discrete illite to mixed-layer illite/smectite (I/S) in the <2-μm clay (solid dots and line) and depth *vs* temperature (dashed lines) for core samples of eolian sandstones from the Permian upper part of Minnelusa Formation, Powder River Basin, Wyoming. Ordering (R) of I/S is also noted. A) geothermal gradient at present depths and B) after correction for maximum burial. Note the absence of R = 0 I/S in samples >11,000 ft and maximum burial temperature of about 110°C.

wells in thermally mature, fractured, Niobrara oil reservoirs should, therefore, contain only ordered I/S in bentonites.

Figure 12 is an I/S geothermometry map applied to maturity of hydrocarbons generated within the Niobrara Formation. Random (R = 0) I/S in bentonite indicates areas of maximum burial temperatures for Niobrara rocks <100°C, whereas ordered I/S indicates areas where the Niobrara has been buried to temperatures >110°C and is thermally mature with respect to oil generation. Similarly, transitional I/S probably indicates maximum burial temperatures near 100°C (perhaps about 90°–100°C) and can be interpreted as marginally mature with respect to oil generation. The areas of current biogenic gas and oil production from Niobrara rocks are also indicated on Figure 12.

*Case #4*

The line-of-section application is demonstrated in a study of the hydrocarbon-productive, Permian upper part (~290–305 my) of the Minnelusa Formation, Powder River Basin, Wyoming. About 110 samples of eolian sandstone, dolomite, and shale were collected from cores of 16 wells at depths ranging from about 1500 to 15,000 ft (460–4600 m) forming a general northeast-southwest trend toward the basin axis (Figure 13). Smectitic clays are present in the sandstones mostly as grain coatings both as early allogenic infiltrates and as authigenic cement (Pollastro and Schenk, 1991). In samples from core recovered at depths <10,000 ft (3100 m), the amount, ordering, and expandability of I/S is variable. The mean ratio of I/S to discrete illite (I/S:illite) in the <2 μm fraction, however, decreases progressively with increasing depth (Figure 14), suggesting that illitization has occurred with increased burial (Pollastro, 1985). Although random I/S is present to depths of 10,000–11,000 ft (3050–3350 m) it is particularly abundant in core recovered from <4000 (1200 m). In core recovered from >11,000 ft (3350 m), however, only ordered I/S is present (Figure 14).

Burial-history reconstructions by Schenk (1990) indicate about 800 ft (250 m) of uplift and erosion for "fairway" Minnelusa fields at depths of about 7000–8000 ft (2100–2400 m). Using the 800 ft (250 m) uplift and erosion correction, a mean annual surface temperature of 7°C, and the present geothermal gradient of 30°C/km, the maximum burial temperature calculated at 11,000 ft (3600 m) for the approximate R =

https://doi.org/10.1346/CCMN.1993.0410202 Published online by Cambridge University Press

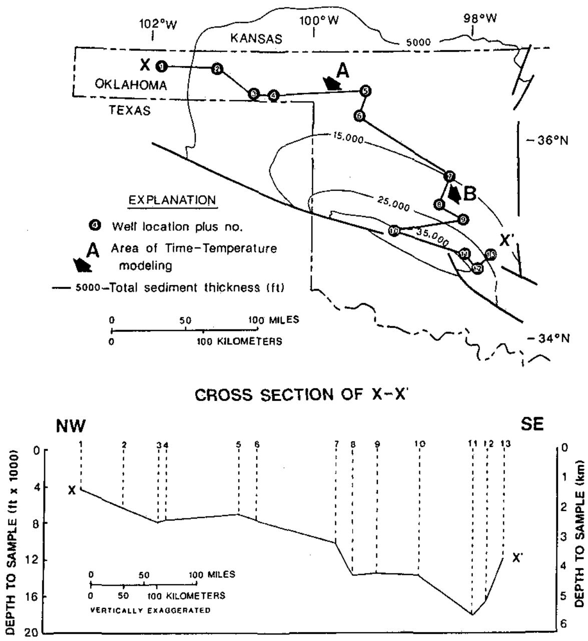

Figure 15. Index map and sediment thickness of Anadarko Basin, Oklahoma, showing locations, line of section (X-X'), and cross section of wells sampled. *A* and *B* on map locate areas of burial reconstruction in Figure 17. Modified from Pollastro and Schmoker (1989).

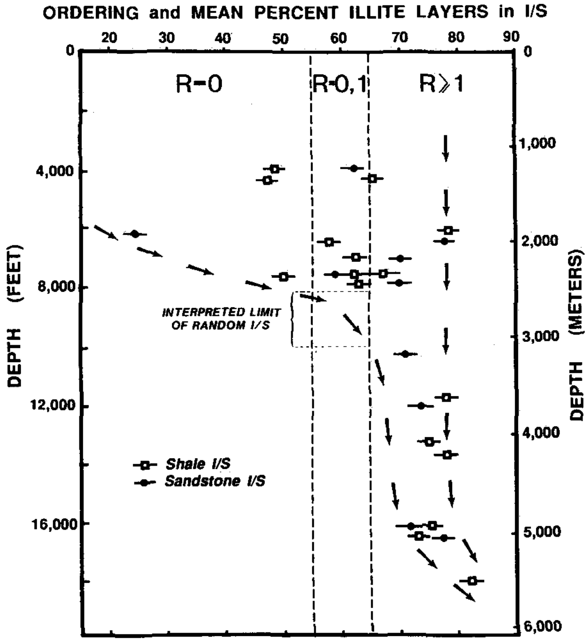

Figure 16. Percent illite layers and ordering of interstratified illite/smectite (I/S) in sandstone and shale of Springer and Morrow age, Anadarko Basin, Oklahoma. Arrows define composition "window" for I/S *vs* depth. Samples from core of 13-well profile (see Figure 15). R = 0, random I/S; R = 0, 1 both random and ordered I/S; R ≥ 1, only ordered I/S. Modified from Pollastro and Schmoker (1989).

0 to R = 1 I/S transition is 110°C, again in agreement with *Hoffman and Hower* model.

*Case #5*

A slightly different example of the line-of-section application is demonstrated by a study of I/S in sandstone and shale of Springer and Morrow age (320–330 my), Anadarko Basin, Oklahoma (Pollastro and Schmoker, 1989). Here, changes in ordering of I/S are combined with Lopatin's (1971) time-temperature index of thermal maturity (TTI) and burial history reconstructions, 1) to test the dependence of the smectite-to-illite reaction on temperature and time, and 2) to relate smectite diagenesis to burial history and stages of hydrocarbon generation.

Expandability and ordering of I/S was determined on about 80 core samples of sandstone and shale from 13 wells forming a general northwest-southeast trend across the Anadarko Basin (Figure 15) and spanning a present depth range from about 4000–18,000 ft (1200–5500 m) (Figure 15). Randomly interstratified I/S (R = 0) disappears at about 9000–10,000 ft (2750–3050 m); only R ≥1 is found below 10,000 ft (3050 m) (Figure 16). Assuming a constant geothermal gradient of 24°C/km, a mean annual surface temperature of 18°C, 2600 ft (800 m) of uplift and erosion, and the burial history reported by Schmoker (1986), calculated maximum burial temperature is about 102°–109°C at maximum burial depth (about 60 Ma). We concluded that all randomly interstratified I/S (R = 0) disappears, and thus was probably converted to ordered I/S (R = 1) in Morrow and Springer age rocks at essentially the same maximum temperature (100°–110°C) as that for rocks of Tertiary and Cretaceous age, as suggested from the model of Hoffman and Hower (1979).

Figure 17 relates the changes in I/S ordering to stages of oil generation from Lopatin reconstruction in the Anadarko Basin. The nonparallelism between the 100°–110°C temperature band and stages of oil generation reflects the different time dependence assumed for clay diagenesis and kerogen maturation. The burial histories in Figure 17 relate smectite illitization in two areas (*locations A* and *B* on Figure 15) of the basin to geologic time, show the states of tectonic development at which clays entered critical temperature windows, and also show the length of time spent at or above critical temperatures. The burial curve for *location A* illustrates that Morrowan rocks in this area have never reached the temperatures required for conversion of randomly interstratified I/S to ordered I/S. XRD profiles confirm this conclusion by showing a well-developed 17 Å reflection in Morrowan samples from wells near *location A*. Thus, although these rocks have been deeply buried and remained at temperatures slightly cooler for some 250 my, all I/S has not been converted to the short-range ordered variety. In contrast, the burial curve in

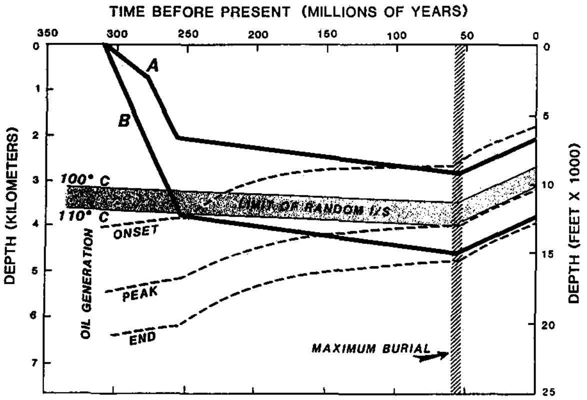


Figure 17. Lopatin, burial, and temperature reconstructions for Morrow rocks, Anadarko Basin, Oklahoma, relating ordering changes in interstratified illite/smectite (I/S) to burial history and stages of oil generation. Solid lines are burial reconstructions for top of Morrow near wells with A) randomly interstratified I/S and B) only ordered I/S (see Figure 15). Dashed lines are time-depth reconstructions for oil generation based on Lopatin modeling. Mottled zones shows 100°–110°C temperature band and represents predicted upper limit for randomly interstratified I/S. Modified from Pollastro and Schmoker (1989).

Figure 17 for *location B* indicates that Morrowan rocks in this area reached temperatures required for the ordering of I/S about 265 my ago; these rocks have remained at burial temperatures >110°C to the present time. XRD profiles show that only ordered I/S is present in Morrowan samples from wells near *location B*. In addition, the burial curve for *location B* (Figure 17) suggests that the conversion of randomly interstratified I/S to ordered I/S occurred just prior to the onset of oil generation (i.e., a large proportion of smectite was converted to illite). Such relations and interpretations may provide insight into the effects of the smectite-to-illite reaction on petroleum migration, reservoir cementation (Boles and Franks, 1979), and geopressures (Bruce, 1984).

## SUMMARY

Empirical relations suggest that the illitization of smectite appears to be controlled primarily by temperature. In particular, changes in I/S as documented on XRD profiles can be a reliable maximum recording geothermometer only after the starting composition of I/S is established through sufficient analysis and control samples. Moreover, the geothermometry model proposed by Hoffman and Hower (1979) seems to apply to rocks of Miocene through Mississippian in age, a period of about 5–330 my.

I/S geothermometry can greatly assist in evaluating the thermal and tectonic history of a sedimentary basin. Specific I/S geothermometers are approximately coincident with temperatures for hydrocarbon "windows" and, therefore, are useful in energy exploration for determining the hydrocarbon-generation potential and thermal maturity of petroleum source rocks.

## ACKNOWLEDGMENTS

I would like to thank Gene Whitney, Bruce Bohor, Paul Nadeau, and Crawford Elliott for their reviews of the manuscript. Their comments and suggestions greatly improved the final paper. Any use of trade names is for descriptive purposes only and does not imply endorsement by the USGS.

## REFERENCES

Bethke, C. M. and Altaner, S. P. (1986) Layer-by-layer mechanism of smectite illitization and application to a new rate law: *Clays & Clay Minerals* **34,** 136–145.

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

Bruce, C. H. (1984) Smectite dehydration—Its relation to structural development and hydrocarbon accumulation in northern Gulf of Mexico: *Amer. Assoc. Petrol. Geol. Bull.* **68,** 673–683.

Burst Jr., J. F. (1959) Post diagenetic clay mineral-environmental relationships in the Gulf Coast Eocene: *Clays & Clay Minerals* **6,** 327–341.

Burst Jr., J. F. (1969) Diagenesis of Gulf Coast clayey sediments and its possible relation to petroleum migration: *Amer. Assoc. Petrol. Geol. Bull.* **68,** 73–93.

Burtner, R. L. and Warner, M. A. (1986) Relationship between illite/smectite diagenesis and hydrocarbon generation in Lower Cretaceous Mowry and Skull Creek shales of the northern Rocky Mountain area: *Clays & Clay Minerals* **34,** 390–402.

Colton-Bradley, V. A. (1987) Role of pressure in smectite dehydration-effects on geopressure and smectite-to-illite transformation: *Amer. Assoc. Petrol. Geol. Bull.* **71,** 1414–1427.

Connolly, C. A. (1989) Thermal history and diagenesis of the Wilrich Member shale, Spirit River Formation, northwest Alberta: *Bull. Canadian Petrol. Geology* **37,** 182–197.

Dypvik, H. (1983) Clay mineral transformations in Tertiary and Mesozoic sediments from North Sea: *Amer. Assoc. Petrol. Geol. Bull.* **67,** 160–165.

Eberl, D. D. (1978) Reaction series for dioctahedral smectites: *Clays & Clay Minerals* **26,** 327–340.

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

Edman, J. D. and Surdam, R. C. (1986) Organic-inorganic interactions as a mechanism for porosity enhancement in the Upper Cretaceous Ericson Sandstone, Green River basin, Wyoming: *Roles of Organic Matter in Mineral Diagenesis,* D. L. Gautier, ed., SEPM Spec. Publ. **38,** 85–109.

Elliott, W. C., Aronson, J. L., Matisoff, G., and Gautier, D. L. (1991) Kinetics of the smectite to illite transformation in the Denver Basin: Clay mineral, K-Ar data, and mathematical model results: *Amer. Assoc. Petrol. Geol. Bull.* **75,** 436–462.

Foscolos, A. E. and Powell, T. G. (1980) Mineralogical and geochemical transformation of clays during catagenesis and their relation to oil generation: in *Facts and Principles of World Petroleum Occurrence,* A. D. Miall, ed., Canadian Soc. Petrol. Geol. Memoir **6,** 153–172.

Foster, W. R. and Custard, H. C. (1983) Role of clay composition on extent of illite/smectite diagenesis: *Amer. Assoc. Petrol. Geol. Bull.* **67,** 462.

https://doi.org/10.1346/CCMN.1993.0410202 Published online by Cambridge University Press

Freed, R. L. and Peacor, D. R. (1989) Variability in temperature of the smectite/illite reaction on Gulf Coast sediments: *Clay Miner.* **24,** 171–180.

Glassman, J. R., Larter, S., Briedis, N. A., and Lundegard, P. D. (1989) Shale diagenesis in the Bergen High area, North Sea: *Clays & Clay Minerals* **37,** 97–112.

Hagen, E. S. and Surdam, R. C. (1989) Thermal evolution of Laramide-style basins: Constraints from the northern Bighorn basin, Wyoming and Montana: in *Thermal History of Sedimentary Basins,* N. D. Naeser and T. H. McColloh, eds., Springer-Verlag, New York, 277–295.

Hoffman, J. and Hower, J. (1979) Clay mineral assemblages as low grade metamorphic geothermometers: Application to the thrust faulted disturbed belt of Montana: in *Aspects of Diagenesis,* P. A. Scholle and P. S. Schluger, eds., SEPM Spec. Publ. **26,** 55–79.

Hower, J. (1981) Shale diagenesis, in *Clays and the Resource Geologist,* F. J. Longstaffe, ed., Mineral. Assoc. of Canada, Short Course Handbook **7,** 60–80.

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

Jennings, S. and Thompson, G. R. (1986) Diagenesis of Plio-Pliocene sediments of the Colorado River delta, southern California: *J. Sed. Petrol.* **56,** 89–98.

Keller, M. A. and Isaacs, C. M. (1985) An evaluation of temperature scales for silica diagenesis in diatomaceous sequences including a new approach based on the Miocene Monterey Formation, California: *Geo-Marine Letters* **5,** 31–35.

Law, B. E., Pollastro, R. M., and Keighin, C. W. (1986) Geologic characteristics of low-permeability gas reservoirs in selected wells, Greater Green River basin, Wyoming, Colorado, and Utah: in *Geology of Tight Gas Reservoirs,* C. W. Spencer and R. F. Mast, eds., Amer. Assoc. Petrol. Geol. Special Studies in Geology **24,** 253–270.

Lopatin, N. V. (1971) Temperature and geologic time as factors in coalification: *Akademiya Nauk SSSR Izvestiya, Seriya Gweologicheskaya* **3,** 95–106 (in Russian).

McCubbin, D. G. and Patton, J. W. (1981) Burial diagenesis of illite/smectite: The kinetic model: *Amer. Assoc. Petrol. Geol. Bull.* **65,** 956.

Moore, D. M. and Reynolds Jr., R. C. (1989) *X-ray Diffraction and the Identification and Analysis of Clay Minerals:* Oxford University Press, New York, 332 pp.

Nadeau, P. H. and Reynolds Jr., R. C. (1981) Burial and contact metamorphism in the Mancos Shale: *Clays & Clay Minerals* **29,** 249–259.

Owen, D. E., Turner-Peterson, C. E., and Fishman, N. S. (1989) X-ray diffraction studies of the $<0.5$-$\mu$m fraction from the Brushy Basin Member of the Upper Jurassic Morrison Formation, Colorado Plateau: *U.S. Geological Survey Bulletin* **1808-G,** 25 pp.

Pearson, M. J. and Small, J. S. (1988) Illite-smectite diagenesis and paleotemperatures in northern North Sea Quaternary to Mesozoic shale sequences: *Clay Miner.* **23,** 109–132.

Perry, E. A. and Hower, J. (1970) Burial diagenesis in Gulf Coast pelitic sediments: *Clays & Clay Minerals* **29,** 165–177.

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

Pevear, D. R., Williams, V. E., and Mustoe, G. (1980) Kaolinite, smectite, and K-rectorite in bentonites: Relation to coal rank at Tulameen, British Columbia: *Clays & Clay Minerals* **28,** 241–254.

Pisciotto, K. A. (1981) Diagenetic trends in the siliceous facies of the Monterey Shale in the Santa Maria region, California: *Sedimentology* **28,** 547–571.

Pollastro, R. M. (1981) Authigenic kaolinite and associated pyrite in chalk of the Cretaceous Niobrara Formation, eastern Colorado: *J. Sed. Petrol.* **51,** 553–562.

Pollastro, R. M. (1985) Mineralogical and morphological evidence for the formation of illite at the expense of illite/smectite: *Clays & Clay Minerals* **33,** 265–274.

Pollastro, R. M. (1989) Clay minerals as geothermometers and indicators of thermal maturity—Application to basin history and hydrocarbon generation: *Amer. Assoc. Petrol. Geol. Bull.* **73,** 1171.

Pollastro, R. M. (1990) The illite/smectite geothermometer—Concepts, methodology, and application to basin history and hydrocarbon generation: in *Applications of Thermal Maturity Studies to Energy Exploration,* V. F. Nuccio and C. E. Barker, eds., Rocky Mountain Section, SEPM, 1-18.

Pollastro, R. M. and Barker, C. E. (1986) Application of clay-mineral, vitrinite reflectance, and fluid inclusion studies to the thermal and burial history of the Pinedale anticline, Green River basin, Wyoming: in *Roles of Organic Matter in Sediment Diagenesis,* D. L. Gautier, ed., Society of Economic Paleontologists and Mineralogists Special Publication **38,** 73–83.

Pollastro, R. M. and Martinez, C. J. (1985) Whole-rock, insoluble residue, and clay mineralogies of marl, chalk, and bentonite, Smoky Hill Shale Member, Niobrara Formation near Pueblo, Colorado—Depositional and diagenetic implications: in *Fine-grained Deposits and Biofacies of the Cretaceous Western Interior Seaway: Evidence of Cyclic Sedimentary Processes,* L. Pratt, E. G. Kauffman, and F. B. Zelt, eds., SEPM Field Trip Guidebook **4,** 215–222.

Pollastro, R. M. and Schenk, C. J. (1991) Origin and diagenesis of clay minerals in relation to sandstone paragenesis: An example in eolian dune reservoirs and associated rocks, Permian upper part of the Minnelusa Formation, Powder River Basin, Wyoming: *Amer. Assoc. Petrol. Geol. Bull.* **75,** 1136.

Pollastro, R. M. and Schmoker, J. (1989) Relationship of clay-mineral diagenesis to temperature, age, and hydrocarbon generation—An example from the Anadarko basin, Oklahoma: in *Anadarko Basin Symposium, 1988,* K. S. Johnson, ed., Oklahoma Geological Survey Circular **90,** 257–261.

Pollastro, R. M. and Scholle, P. A. (1986) Diagenetic relationships in a hydrocarbon-productive chalk—The Cretaceous Niobrara Formation: in *Studies in Diagenesis,* F. A. Mumpton, ed., Geological Survey Bulletin **1578,** 219–236.

Powers, M. C. (1957) Adjustment of clays to chemical change and the concept of the equivalence level: *Clays & Clay Minerals, Proceedings of the Sixth National Conference,* 309–326.

Powers, M. C. (1967) Fluid release mechanisms in compacting marine mudrocks and their importance in oil exploration: *Amer. Assoc. Petrol. Geol. Bull.* **51,** 1240–1254.

Pytte, A. M. and Reynolds Jr., R. C. (1989) The thermal transformation of smectite to illite: in *Thermal History of Sedimentary Basins,* N. D. Naeser and T. H. McColloh, eds., Springer-Verlag, New York, 133–140.

Ramseyer, K. and Boles, J. R. (1986) Mixed-layer illite/smectite minerals in Tertiary sandstones and shales, San Joaquin basin, California: *Clays & Clay Minerals* **34,** 115–124.

Rettke, R. C. (1981) Probable burial diagenetic and provenance effects on the Dakota Group clay mineralogy, Denver basin: *J. Sed. Petrol.* **51,** 541–551.

Reynolds Jr., R. C. (1980) Interstratified clay minerals: in *Crystal Structures of Clay Minerals and Their X-ray Identification,* G. W. Brindley and G. Brown, eds., Mineralogical Society, London, 249–303.

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

Rice, D. D. and Claypool, G. E. (1981) Generation, accumulation, and resource potential of biogenic gas: *Amer. Assoc. Petrol. Geol. Bull.* **64,** 5–25.

Roberson, H. E. and Lahann, R. W. (1981) Smectite to illite conversion rates: Effect of solution chemistry: *Clays & Clay Minerals* **29,** 129–135.

Schenk, C. J. (1990) Overview of eolian sandstone diagenesis, Permian upper part of the Minnelusa Formation, Powder River Basin, Wyoming: in *Modern and Ancient Eolian Deposits: Petroleum Exploration and Production,* S. G. Fryberger, L. F. Krystinik, and C. J. Schenk, eds., Rocky Mtn. Sec. SEPM, Denver, 15-1–15-10.

Schmoker, J. W. (1986) Oil generation in the Anadarko Basin, Oklahoma and Texas: Modeling using Lopatin's method: *Oklahoma Geol. Surv. Spec. Pub.* **86-3,** 40 pp.

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.

Środoń, J. (1979) Correlation between coal and clay diagenesis in the Carboniferous of the Upper Silesian coal basin: *Proceedings International Clay Conference,* Oxford, 251–260.

Środoń, J. (1989) Mechanism of illitization of smectite: A review of current concepts: *Abstracts of the 9th International Clay Conference,* Strasbourg, France, 367 pp.

Środoń, J. and Eberl, D. D. (1984) Illite: in *Micas,* S. W. Bailey, ed., Reviews in Mineralogy **13,** 495–544.

Tissot, B. P. and Welte, D. H. (1984) *Petroleum Formation and Occurrence:* Berlin, Springer-Verlag, 539 pp.

Towe, K. M. (1974) Quantitative clay petrology: The trees but not the forest?: *Clays & Clay Minerals* **22,** 2871–2876.

Velde, B. and Espitalié, J. (1989) Comparison of kerogen maturation and illite/smectite composition in diagenesis: *Jour. Petrol. Geol.* **12,** 103–110.

Velde, B. and Iijima, A. (1988) Comparison of clay and zeolite mineral occurrences in Neogene age sediments from several deep wells: *Clays & Clay Minerals* **36,** 337–342.

Waples, D. W. (1980) Time and temperature in petroleum formation: Application of Lopatin's method to petroleum exploration: *Amer. Assoc. Petrol. Geol. Bull.* **64,** 916–926.

Weaver, C. E. (1979) Geothermal alteration of clay minerals and shales: Diagenesis: *Office of Nuclear Waste and Isolation Technical Report* **21,** 176 pp.

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

Whitney, G. (1990) Role of water in the smectite to illite reaction: *Clays & Clay Minerals* **38,** 343–350.

Whitney, G. and Northrop, H. R. (1987) Experimental investigations of factors affecting rates of illitization: Rock/water ratio, potassium availability, ionic strength, and Na/K ratio [abs:]: *Clay Minerals Society, 24th Annual Meeting, Program and Abstracts,* 145 pp.

Whitney, G. and Northrop, H. R. (1988) Experimental investigations of the smectite to illite reaction: Dual reaction mechanisms and oxygen-isotope systematics: *Amer. Mineral.* **73,** 77–90.


*(Received 18 February 1993; accepted 3 March 1993; Ms. 2331)*