COMPARISON OF I/S TRANSFORMATION AND MATURITY OF ORGANIC MATTER AT ELEVATED TEMPERATURES

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Abstract—Comparing the state of reaction advancement of I/S (illite content of illite/smectite mixed layer minerals) and organic matter (vitrinite reflectance) in instances of high temperature gradients allows one to observe the evolution of geologic materials under extreme conditions. In a geothermally heated sedimentary series (Salton Sea area, California), both clays and organics have reacted to completion in the temperature gradient range of 200°–400°C/km during heating episodes of 10^4 years. We observed an instance of rapid heating, through magmatic intrusion into the Meso-Paleozoic eastern Paris Basin sedimentary series in late Permian time, which induced changes in the organic material, but where clays are apparently unaffected.

Key Words—Illite/smectite, Kinetics, Vitrinite maturity.

INTRODUCTION

The evolution of organic matter, as recorded by vitrinite reflectance, has been the subject of much debate in the past (Price, 1983). A recent model given by Sweeney and Burnham (1990) demonstrates that the vitrinite reflectance of type III organic matter found in sediments can be predicted quite well using a kinetic model that uses a range of activation energies and pre-exponential factors. The predictions and observed vitrinite reflectances accord well.

Illite/smectite (I/S) evolution has been modeled for diagenetic sedimentary sequences by Dutta (1986) and Bethke and Altaner (1986), who propose one-step and two-step reaction models to fit clay composition data from wells in the Texas Gulf Coast. Velde and Vasseur (1992), on the other hand, propose a two-step reaction model for the smectite-to-illite transformation derived from a simultaneous fit of data from sedimentary basins of widely ranging ages. Kinetic data can be derived from laboratory experiments such as those of Eberl and Hower (1976), Roberson and Lahann (1981), and Howard and Roy (1985). Such data can be used to develop models of clay conversion such as that proposed in this issue by Huang *et al.* (1993). In the present paper, we wish to compare the effect of rapid heating in the evolution of natural materials by observing the change in clay composition and vitrinite reflectance of organic matter in two instances: in a series of very old rocks (Paleozoic) that have been subjected to a thermal pulse due to the intrusion of a granitic body; and in a geothermal area where heating occurred for periods of several tens of thousand years.

EXPERIMENTAL METHODS

Clay mineral identification

Estimations of the illite content of the I/S (illite/smectite) minerals were made using the position of the combined 001/001 peak of the mineral in the air-dried state (Velde *et al.*, 1986). The composition of the ordered R = 1 mineral is deduced from the peak position estimated from the Reynolds NewMod program, with the mean number of coherently diffracting layers being 6. Lanson (1990) has shown that minerals from different sedimentary series in the range of 30% to 5% smectite content show similar peak position/peak width characteristics and that these characteristics can be modeled as grains with near 8 coherently scattering layers (Moore and Reynolds, 1989). In the old Paleozoic samples studied here, no R = 0 disordered I/S mineral was encountered.

In our experience, young sediments have I/S-illite assemblages that are dominated by the I/S phase. In such samples, the position of the peak maximum (air-dried state) in the 14–10.5 Å range can be taken to indicate the average illite content of the interlayered (R = 0 or R = 1 structure) mineral assemblage as was done in the past by most authors studying these minerals. The maximum for each large band indicates the most common composition of the I/S mineral population. Such an estimation was undoubtedly used for the Salton Sea samples, although XRD diagrams are not published for these samples. A diffraction diagram is given in Figure 1a where the I/S phase (R = 1 ordering in this case) is much more intense than chlorite

or the illite bands at 14 and 10 Å. The peak maximum of this wide band can be used to estimate illite content of the I/S phases.

However, in mid-Cretaceous and older sediments, illite or a micaceous phase often becomes dominant (Figures 1b and 1c). In the Paleozoic samples from the Paris Basin, the illite bands are dominant as shown in Figures 1b and 1c for samples at two depths in the series studied. In order to estimate the clay mineral diffraction maxima of the lower intensity I/S mineral assemblage band in these samples, it was necessary to use a program to de-sum the complex band pattern of illite and I/S minerals (Lanson and Besson, 1992). Initial steps of background stripping were performed on the spectra in Figure 1. The diffraction maxima due to the illite material are de-summed as two bands, one (A in Figures 1b and 1c) representing the material of small (<10 layers) grain size fraction of the illitic material, and the other (B in the figure) of the larger grain sizes and detrital mica present. The justification of this de-summation is given in Lanson and Besson (1992).

Figure 1 indicates the problem and the results obtained in two typical cases from the study reported here where an I/S mineral assemblage is present with a larger amount of illite that can be decomposed into two bands, one for the small grain sized fraction and the other by the more coarse fraction. It can be seen that the I/S band is extremely large (Lanson and Besson, 1992), which indicates to a certain extent the dispersion of grain sizes in the I/S population.

De-summation is necessary, then, when there is a strong illite component in the clay assemblage. In using such techniques, we use the minimum number of bands to describe the mineral grain populations. This produces a larger band than would be predicted for a population with a limited grain size distribution. However, a single Gaussian band can represent a population of Gaussian bands that does not interfere with the interpretation of the most populous grain size and, hence, average smectite content of particle in the assemblage. We, thus, describe the I/S mineral assemblage by a single band indicated as I/S in Figure 1.

Organic matter maturity

Estimation of organic maturation was made using either vitrinite reflectance data (Salton Sea) or, in the Paris Basin, Tmax pyrolysis data converted to an equivalent value of vitrinite reflectance (Espitalié, 1986). The correspondence between pyrolysis and vitrinite reflectance values is derived from the data given by Durand *et al.* (1986). These data come from a Paleozoic sedimentary series in the same geologic area, which is so similar to that studied here that we feel a direct extrapolation from one series to the other is valid. All samples contained a great majority of type III organic material. The kinetic model used below necessitates this type of organic material.
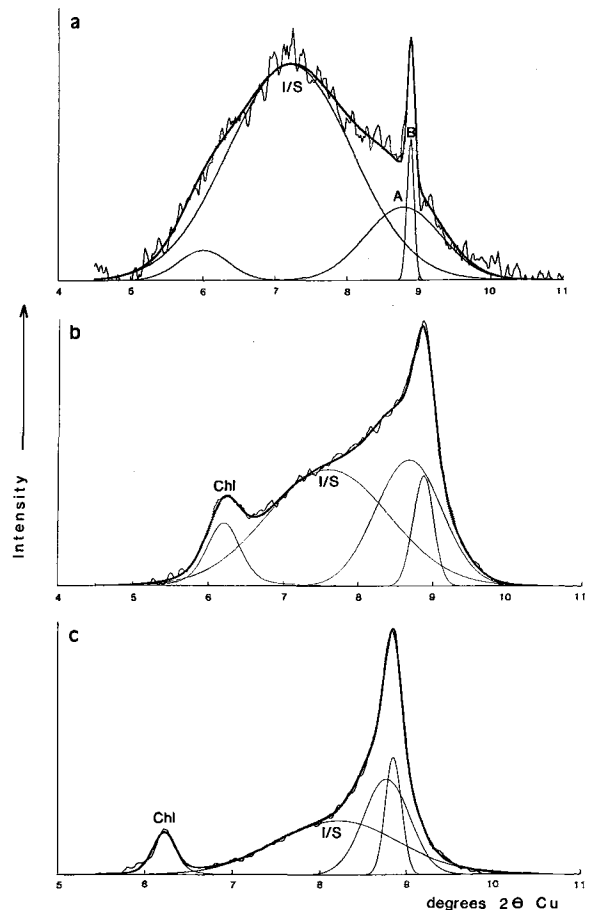

Figure 1. Illustration of multi-phase I/S assemblage in Paleozoic Paris Basin sediments. The experimental traces have been background subtracted and smoothed on a seven-point routine. The decomposition band indicated as I/S is attributed to the illite/smectite phase while the bands A and B are considered to show the small and larger grained size fraction of the illite component of the clay fraction. This follows the protocol established by Lanson (1990). The uppermost diagram (a) shows an I/S dominated assemblage (from a Cretaceous Paris Basin sample). Visual estimation of the peak maximum position will give a good idea of the smectite content of the I/S assemblage. Two samples from the Culey well are shown for different depths (b and c). Here, the I/S band is much less intense than the illite bands (a and b) making it necessary to de-sum the various components of the complex band structure in order to estimate smectite content of the I/S mineral assemblage present. Chl = chlorite.

Calculation of burial history and reaction progress

The progress of the two reactions, organic and clay mineral, is estimated for a given burial sequence using a program developed by G. Vasseur (Université Montpellier, France) where the individual stratigraphic layers are assigned thickness and a temperature gradient during their deposition. The thermal gradient that occurs during a deposition period is assumed to affect the entire sedimented pile present up to that point. It is also assumed that thermal conductivity and compac-
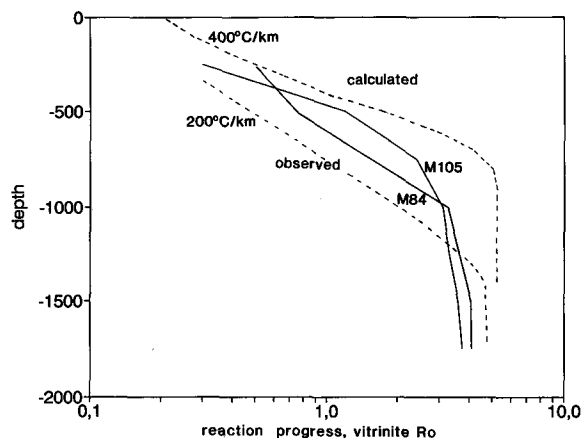
Figure 2. Vitrinite data for the Cerro Prieto field given in Barker and Elders (1981) for two wells, M-105 and M-84. Dashed lines show calculated vitrinite reflectance evolution for 400°C/km and 200°C/km thermal gradient (1Ma heating period) using the model proposed by Sweeney and Burnham (1990).
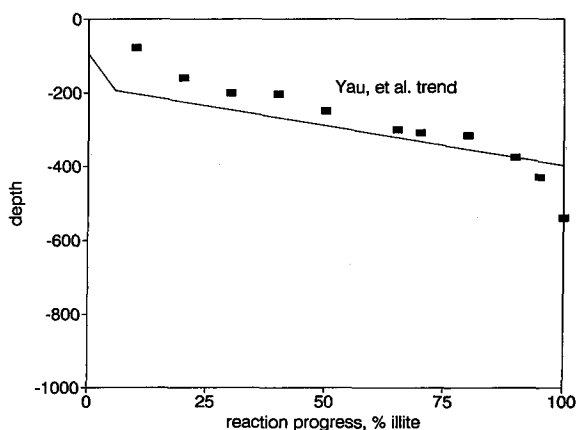

Figure 3. Trend of clay composition and maximum temperature (present day) given by Yau *et al.* (1987) shown as rectangles in the figure for clays in the Salton Sea area. Solid line shows calculated compositional trend using 78 kJ/mole activation energy and log A = 24 Ma[-1] in a one-step reaction model based upon the Yau *et al.* data.

tion effects for each sedimentary layer are negligible compared with the gradient of the intense thermal event. The burial history for each layer is then calculated as a function of time and temperature. Given these data, a kinetic formulation is applied that calculates the stage of reaction progression at the end of sedimentary burial. Either one-step or two-step reactions can be calculated, and the kinetic values can be optimized from the experimental data for either type of overall reaction.

Erosion is simulated in the program by negative deposition, using thickness and temperature gradient input as for sedimentation. The input in the program is sediment age and thickness for the different layers and the thermal gradient pertaining during the sedimentation. This last variable is the most important unknown for the problems treated here, since there is no significant erosion during the sedimentation sequence of the Paleozoic material as observed.

Extreme heating is imposed upon the entire sedimentary pile during a specified period where non-deposition is assumed.

EXPERIMENTAL RESULTS

Salton Sea

Vitrinite. Several wells in the Salton Sea area (Cerro Prieto field) reported by Barker and Elders (1981) and commented upon by Barker (1991) allow one to observe the effect of high gradient and rapid heating on vitrinite in sediments. Figure 2 gives the observed vitrinite-depth relations for two wells (M-105, M-84) where the present-day gradients are near 200°C/km, although there is a significant irregularity in the measured temperature profile of the M-105 well. These wells were used here because they have a vitrinite value

of 0.2 near the surface that seems in accord with the minimum values expected, e.g., Price, 1983.

According to Elders *et al.* (1984), the high temperature geothermal regime is of recent origin and would have persisted for 40,000 to 50,000 years. In using the Sweeney-Burnham model, there is little difference in reaction progress as determined by vitrinite reflectance between 0.001 and 1 Ma heating periods. If the geothermal gradient is variable from one site to the other and if it in fact can change rapidly over short periods of time (see the model proposed by Elders *et al.,* 1983), the time span of reaction is relatively unimportant compared with the maximum temperature attained in the sedimentary pile. As a result, we will assume that temperature is the most important factor in comparing model calculations of vitrinite reflectance (organic matter maturity) with the data available.

Figure 2 shows the calculations for an imposed gradient of 400°C/km and 200°C/km (dashed lines), which bracket the vitrinite data given in the figure for the Cerro Prieto field. The Sweeney and Burnham model seems to account for vitrinite reflectance under conditions of rapid and high level heating.

Clay minerals

The I/S clay mineral composition (percent illite or non-expanding layers in the illite/smectite interlayered minerals) shows a rapid progression in the present day temperature range to 200°C where the reaction is essentially complete. Yau *et al.* (1987) plot data from two different wells: one geothermal with a gradient of near 400°C/km and one non-geothermal where the present thermal gradient is not specified. The same type of data (composition and temperature) were reported by Jennings and Thompson (1986) for three non-geothermal wells. All of the temperature-clay composition
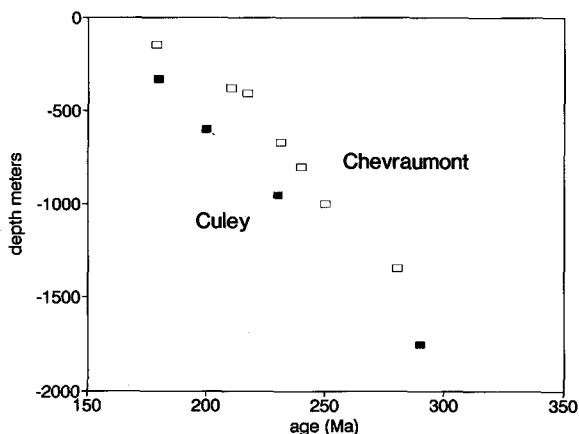
Figure 4. Depth-age relations for the two wells from the Paris Basin Meso-Paleozoic sequence.
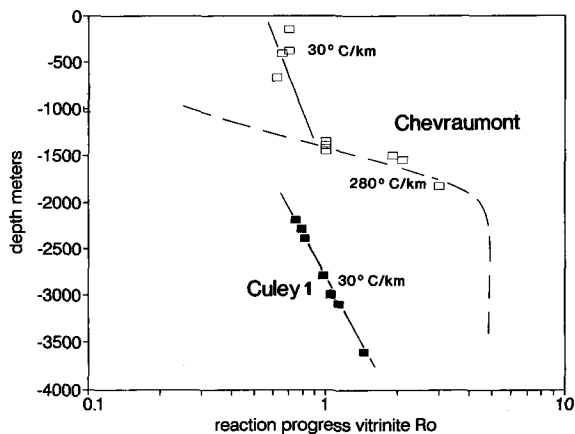

Figure 5. Vitrinite (Culey 1) and vitrinite equivalent (Chevraumont) reflectance data for the two wells in the Paris Basin. Calculated vitrinite trends are given: 30°C/km in the Culey and upper Chevraumont wells and 280°C/km in the lower portion of the Chevraumont well. The curve extrapolated to the paleo-surface vitrinite value of 0.2 indicates a present depth of 800 m. At this present-day depth, the series has a deposition age of 230 Ma (using Figure 4), which would have been the surface of the sedimentary pile at the time of the thermal event.

data follow approximately the same trends of composition and temperature. Figure 3 shows composition-depth relations for a 400°C/km gradient in the Salton Sea area as given by Yau et al. (1987).

These data indicate that the clays react rapidly to temperatures in geothermal areas and that thermal gradient does not greatly influence the reaction progress. Temperature is the most important variable for the processes in the span of 10^4–10^5 years reaction time.

The clay smectite-to-illite conversion reaction observed in the Salton Sea samples can be modeled reasonably well for these high temperatures using a single-step first-order reaction configuration with a 78 kJ/mole activation energy and a pre-exponential factor (log A) of 24 Ma^{-1}. Changing the heating period from 10^6 to 10^3 years does not significantly change the clay reaction advancement using this model.

In summary, the vitrinite and clay mineral data show a rapid change in maturity in the hydrothermal Salton Sea area and the Cerro Prieto field where temperature gradients of 400°/km can be found. Models for clay and organic matter maturity can be used to simulate these data.

Paris Basin Meso-Paleozoic series

Two series of samples from bore holes in the Lorraine area on the eastern edge of the Paris Basin in France were investigated for their clay mineral and organic matter composition. The depth-age relations are given in Figure 4. The wells have slightly different geologic histories as seen in depth-age plots. The sedimentation rate is nearly the same for the intervals observed, but the Chevraumont well shows slightly more erosion at the top of the section.

Vitrinite. In one well (Culey 1), the organic data are reported as both pyrolysis measurements (Tmax) and vitrinite reflectance. The second well (Chevraumont) has only Tmax pyrolysis measurements. Conversion

between the two estimations of organic matter maturity can be made according to the method outlined by Durand et al. (1986) and Espitalié (1986) for material in the same region. Data for the two wells are given in Figure 5.

The vitrinite (or equivalent vitrinite calculated from Tmax pyrolysis data) values show a significant change in maturity with depth in the Chevraumont well near the 1200 m level. This is due to an intrusion at greater depth in the late Paleozoic strata. The thermal gradient in the unaffected Culey well, using calculated values of vitrinite, is near 30°C/km and the same gradient is estimated for the upper portion of the Chevraumont well. The gradient calculated using Tmax to vitrinite conversion is near 280°C/km in the lower portion of the Chevraumont well. Tmax values of 560°C were recorded. Extrapolation of the vitrinite curve for the lower portion of the well to a value of 0.2 (assumed to be the starting point in vitrinite maturity) gives an estimate of the surface during the thermal event at a present depth of near 800 m. The age (using Figure 4) at 800 m current depth is 230 Ma in the Chevraumont well, or late Permian. We assume this to indicate the age for the thermal event of the intrusion. Subsequent burial has reactivated the maturation of the organic material down to the 1100 m depth, which is why one does not see values below 0.6 reflectivity.

Clay minerals. The smectite content of the I/S assemblage changes with depth in a regular manner in the Culey well over the sector investigated. The same is true of the clays in the Chevraumont well. However,
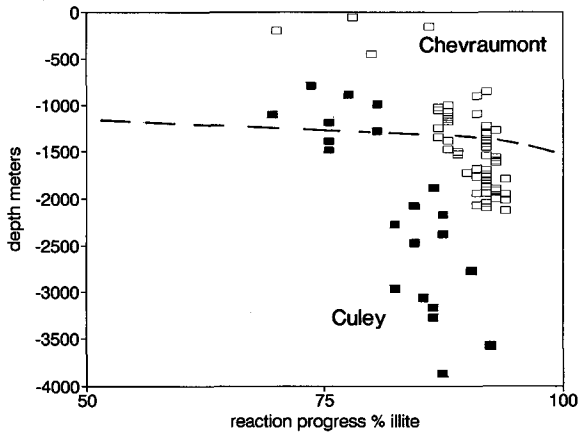
Figure 6. Clay composition data (I/S illite content) indicating reaction progress for the two Paris Basin wells. The trends seem to be quite parallel in the depth zone studied though offset by about 15% smectite content. The dashed curve indicates the compositional trend that would have been induced by the heating event had it been similar to the Salton Sea geothermal field. Subsequent burial and maturity would not have masked this trend entirely.

there is a difference in overall maturity between the two wells of about 15% smectite content of the I/S minerals for the same depth due to differences in age (Figure 4) or, perhaps, local thermal gradient. The clays in the Chevraumont well are about 15% more illitic for samples of the same age. This suggests the possibility of a slightly higher overall thermal gradient during diagenesis.

There is no significant rapid change in clay compositions in the Chevraumont well where the organics change radically in their maturity trend (vitrinite reflectance equivalent). Using the same kinetic model as that to describe the Salton Sea clay data, with an imposed thermal gradient of 280°/km as deduced from the vitrinite reflectance, one would expect to see a sharp change in clay composition near 1300 m depth in the Chevraumont well (Figure 6). Since there is none, this indicates that the clays in the Paris Basin sediments were less reactive during the high gradient (280°C/km) heating period than they were in the Salton Sea geothermal field. It is assumed that the high thermal gradient was due to an intrusion and, thus, would not have persisted for long periods of time.

CONCLUSIONS

The data presented here indicate that heating in recent and currently active geothermal fields induces a similar evolution in I/S clays and organic matter. However, the occurrence of the same type of event in the Permian time in sediments of the Paris Basin did not have the same effect. The organics changed, but the clays do not show the expected compositional trends.

This difference could be due to differences in dura-tion of the thermal event. However, this seems unlikely in that the models used to predict clay evolution do not show major differences in clay reaction advancement for periods of 1 and 0.001 Ma. Further, vitrinite data show thermal maturation over similar depth intervals (600 m or so) in the two cases and, therefore, one would not expect to have a significant difference in duration of the thermal event in the two regions.

In both sedimentary series studied, the sediments are pelitic in nature. Those in the Paris Basin are derived from acidic pyroclastic material in some portions of the section and thus could be expected to contain more potassium than those of the Salton Sea. Hence, one would not expect the lack of reactivity (formation of illite) in the Paris Basin sediments to be due to a lack of reactant.

A possible explanation of the slower reaction of the clays (or, in fact, inaction) would be in the water content of the two sequences of sediments. In the Salton Sea area, large amounts of water are available; hence, their interest as geothermal energy sources. If the Paleozoic sediments in the Paris Basin were less hydrous or the sequence was less permeable, it is possible that the reaction could not proceed as rapidly as in the case of the hydrous geothermal field in the Salton Sea area. Assuming that the observed clay reaction is due to a dissolution and precipitation mechanism (see Lanson and Champion, 1991), a situation of low free water content and low porosity and permeability would be less likely to respond quickly to a thermal impulse that would require rapid dissolution and precipitation from solution. Unlike the clays, the organics do not require a significant fluid/rock ratio to effect changes in maturity (vitrinite reflectance) and tend to indicate thermal conditions alone.

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