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ILLITE/SMECTITE DIAGENESIS AND ITS VARIABLE CORRELATION WITH VITRINITE REFLECTANCE IN THE PANNONIAN BASIN

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Abstract—The correlation between illite/smectite (I/S) diagenesis and mean vitrinite reflectance (R_o) data is examined in mudrocks from a hydrocarbon exploration well (geothermal gradient 35°C km^{-1}) from the Great Hungarian Plain of the Pannonian Basin System. The expandability of I/S decreases with depth and there is a change from random to ordered mixed-layering at about 2500 m depth. At this depth R_o is about 0.6%. Comparison of the correlation of expandability and R_o from this study to published data for the Vienna Basin and the Transcarpathian Basin, sub-basins of the Pannonian Basin System, shows that the correlation is systematically different for each sub-basin, according to their thermal histories. In the Vienna Basin (geothermal gradient 25°C km^{-1}), for any given value of R_o, the expandability of I/S is less than in the Transcarpathian Basin (geothermal gradient 55°C km^{-1}) and the sediments are older and more deeply buried. Data from the present study are intermediate. This variation is believed to be due to the effect of time on the smectite-to-illite reaction. Results of an optimization procedure to calculate the kinetics of the smectite-to-illite reaction, using as input the expandability depth profiles, and thermal histories constrained by comparison of observed and calculated R_o data, showed that I/S diagenesis in the Pannonian Basin System can be modelled by a single first order rate equation:

$$-dS/dt = e^{\log(A) - E/RT} \cdot S$$

where S = fraction of smectite layers in I/S, t = time (Ma), e = exponential function, log(A) = frequency factor = 7.5 (Ma^{-1}), E = activation energy = 31.0 kJ mol^{-1}, R = universal gas constant, and T is temperature in Kelvin. This result also suggests an important role for time. By combining the kinetics of the smectite-to-illite reaction with a kinetic model of vitrinite maturation it is possible to define a domain within which all 'normal' (burial diagenesis) correlations between R_o and I/S diagenesis should lie. Such diagrams can be used to identify different thermal histories related to different geotectonic settings and 'anomalous' data such as that affected by igneous intrusions.

Key Words—Illite/smectite, Kinetics, Pannonian Basin, Thermal history, Vitrinite reflectance.

INTRODUCTION

With increasing depth of burial in sedimentary basins there is a progressive conversion of smectite into illite and the extent of reaction is frequently used as an indicator of diagenetic grade (Hoffman and Hower 1979, Héroux *et al* 1979, Pollastro 1990, 1993, Price and McDowell 1993). However, besides the increase of temperature with depth, many other factors may influence the progress of this reaction complicating attempts to use it as a geothermometer. Nevertheless, the almost ubiquitous occurrence of this reaction in terrigenous sedimentary basins worldwide has assured a continued effort to use it as an indicator of diagenetic grade. Consequently, very general correlations of stages of the reaction with temperature, and with organic maturity indicators like mean vitrinite reflectance in oil (R_o), are reasonably well known (Kisch 1987, Kübler 1993). Indeed, it is perhaps surprising that, despite the great many variables that are suggested to influence the reaction, 'normal' correlations with temperature and with organic maturity indicators are established, and appear to be applicable to a wide variety of basins. In detail, however, there may be considerable variation in both the temperatures at which various stages of the reaction are reached, even within a single sedimentary basin (Freed and Peacor 1989), and in the correlation of the various stages with indicators such as R_o (Kisch 1987, Kübler 1993). Just how much of this variability is due to the geochemical peculiarities of different sequences and reaction mechanisms, and how much simply due to the relative kinetic roles of both temperature and time, remains unclear.

Recently, there have been several attempts to develop kinetic models of the smectite-to-illite reaction (Bethke and Altaner 1986, Pytte and Reynolds 1989, Velde and Vasseur 1992, Huang *et al* 1993). Such models provide insight into the potential roles of both temperature and geological time. In fact, several studies have documented an important effect of time on illitization by showing that its correlation with R_o data is considerably dependent on thermal history, and that

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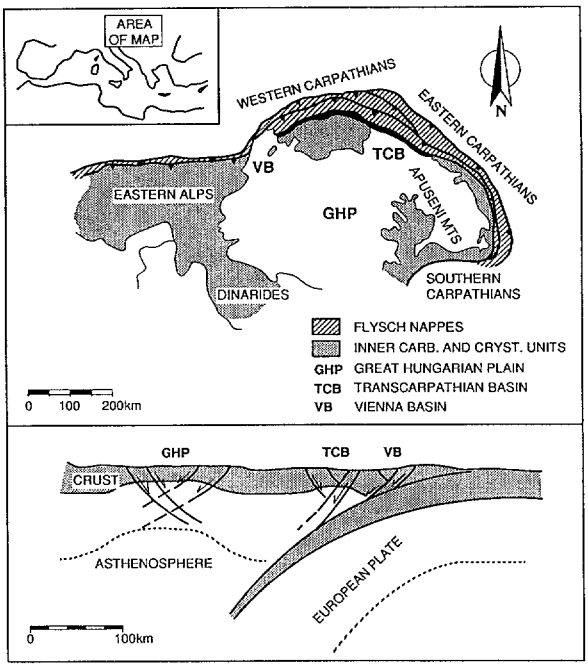


Figure 1. Geological setting and schematic tectonic cross section of the Pannonian Basin System. The samples investigated in the present study come from the well PB-2 located in the Great Hungarian Plain and are compared to published data for the Vienna and the Transcarpathian Basins.

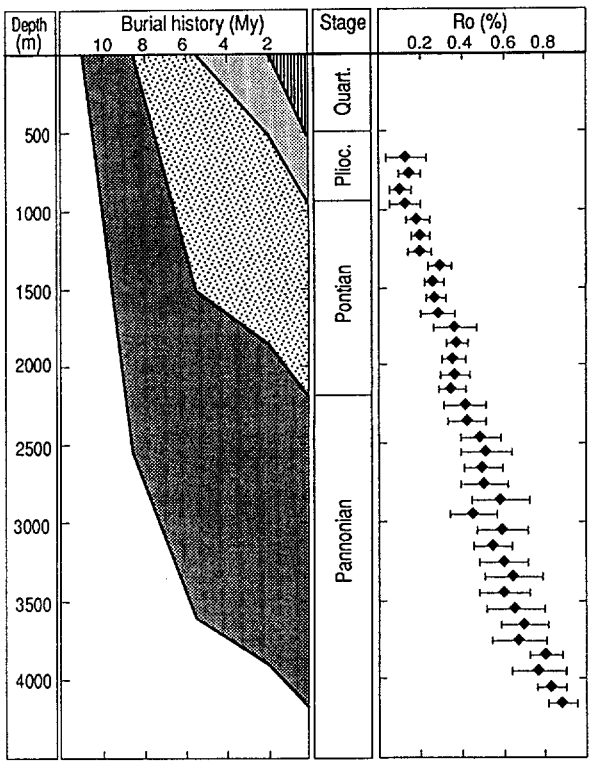


Figure 2. Burial history and mean vitrinite reflectance data (R_o%) for the well PB-2 located in the Great Hungarian Plain. Error bars on R_o indicate $\pm$ 1 σ.

it is not the illitization but R_o that behaves most like a true geothermometer, illitization 'lagging' behind the relatively more rapid response shown by R_o to increasing temperature (Wolf 1975, Smart and Clayton 1985, Robert 1985, Kisch 1987). Other factors being equal, such a relationship implies that in young hot sedimentary basins R_o should be more advanced relative to the smectite-to-illite reaction, whereas in older colder basins the reverse should be true.

The aim of this paper is to document the clay mineralogy, and an investigation of the smectite-to-illite reaction and its relationship to R_o data, for a deep hydrocarbon exploration well, PB-2 (the name of the well has been changed for proprietary reasons), located in the central depression (Great Hungarian Plain) of the Pannonian Basin System. These data are compared to other published data from other parts of the Pannonian Basin System where the thermal histories are very different, the purpose being to attempt to determine the kinetics of the smectite-to-illite reaction, and its potential range of correlation with R_o data due to kinetic (time, temperature) factors.

GEOLOGICAL SETTING

The Pannonian Basin System is a group of young sedimentary basins surrounded by the Eastern Alps, the Dinarides and the Carpathians (Figure 1). In the Great Hungarian Plain, basin formation began in the Middle Miocene. Two distinct periods of subsidence are recognised, the first (15–11.5 Ma) was dominated by a rifting phase, and was followed by a second phase of thermal subsidence. The subsidence history of the 4.2 km deep well PB-2 is shown in Figure 2, along with measured R_o data (provided by MOL Plc). Syn-rift sedimentation was dominantly marine and brackish, but the post-rift sedimentation gradually changed from deep-water lacustrine to deltaic and then to fluvial.

In general terms, the Pannonian Basin System formed as a Miocene back-arc basin, partly coeval with the thrusting of the Carpathians over the subducting European plate. However, within this framework individual sub-basins show considerable variation in their tectonic settings and, as a consequence, there is a wide range of thermal histories. A considerable amount of work has been devoted to determining the thermal history of various parts of the Pannonian Basin System, aided by a wealth of data accumulated from extensive hydrocarbon exploration (Royden *et al* 1983, Royden and Dövényi 1988). The outcome of this work is the division of the Pannonian Basin System into several different domains depending on the extent of mantle and lithosphere involvement during extension and basin formation. Basins close to the Carpathian thrust

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front are characterised by thin-skinned tectonics, whereby extension was accomplished along former thrust faults of the allochthonous cover. The Vienna Basin is the prime example of this type and is believed to have developed as a pull apart basin as a result of diachronous thrusting between the Eastern Alps and the Carpathians. In contrast, further from the Carpathian thrust front, in the Great Hungarian Plain, extension was achieved by heating and thinning of the lithosphere. These differences are believed to explain why the Vienna Basin is characterised by low heatflow (50 mW m^{-2}) and gentle organic maturation gradients, whereas the Great Hungarian Plain is characterised by high heatflow (80–110 mW m^{-2}) and steeper organic maturation gradients. Tectonically transitional regions include the Transcarpathian Basin, but in this particular case heat flow (105 mW m^{-2}) and organic maturation are anomalously high, probably due to immense local volcanic activity. This wide range of thermal conditions makes the Pannonian Basin System an excellent setting for a comparative study of the smectite-to-illite reaction and its correlation with organic maturation under different thermal regimes.

MATERIALS AND METHODS

Seventeen samples of mudrocks were obtained by hand picking fragments from washed cuttings, except for the deepest sample that was taken from a core. Samples were crushed and dispersed in de-ionised water using an ultrasonic probe and a few drops of sodium polymetaphosphate. The <2 μm fraction was separated by gravity settling, saturated with Mg, washed and concentrated by centrifugation and prepared for X-ray diffraction (XRD) by sedimentation onto a glass slide. Samples were examined by XRD in the air-dried state, after saturation with ethylene glycol (vapour pressure method), and after heating to 375°C for one hour. Semi-quantitative estimates of the relative abundance of clay minerals in the <2 μm fraction were made using the methods given in Moore and Reynolds (1989). Estimates of the percentage of expandable layers in mixed-layer illite/smectite (I/S) were made using the classical methods described by Reynolds and Hower (1970), Reynolds (1984), and Moore and Reynolds (1989), based on the entire character of the pattern and in particular the position of the peak that migrates between 5.6 and 5 Å. Although a consistent method of estimating the position of this peak was used, an accurate measurement of its position is difficult for samples where I/S is not the main component. However, this is typical of many clay mineral assemblages from shales, and the method is the most practicable due to the very weak intensity and/or overlap of the peaks required by more accurate methods. Because of these drawbacks, an attempt was also made to determine the position of this peak using an XRD peak decomposition program DECOMPXR (Lanson and Besson 1992, Lanson and Velde 1992).

RESULTS AND DISCUSSION

Clay mineralogy

The <2 μm fractions of all samples contain the clay minerals illite, chlorite, kaolinite and I/S. XRD patterns for the air-dried and glycolated preparations of five representative samples are shown in Figure 3. In all samples, a relatively well crystallised illite is identified by a peak at 10 Å with an integral series of higher orders. The presence of both chlorite and kaolinite throughout the sequence is indicated by the partial resolution of two peaks at about 3.5 Å. In the deepest sample (4140 m), these peaks are not resolved, but the shape of the 3.5 Å peak on its low angle side indicates the presence of a small amount of kaolinite. The I/S minerals which are present are of variable composition as shown by the changing position of low angle reflections in both the air-dried and glycolated traces (Figure 3).

Throughout the well the proportions of the various clay minerals in the <2 μm fraction are relatively constant. The only apparent change occurs at a depth of just over 2000 m and involves an abrupt increase in the relative amount of I/S, accompanied by a small decrease in the amount of kaolinite (Figure 4). However, the most abundant clay mineral is illite and none of the samples are particularly rich in I/S.

The clay mineralogy of mudrocks from the well PB-2 is very similar to that described by Viczián (1992) from the Doboz-I well located about 100 km to the northeast of PB-2. Furthermore, the results are comparable to those from several of the other Tertiary basins that surround the Alpine-Carpathian mountain chain (Kurzweil and Johns 1981, Monnier 1982, Viczián 1985, 1992, Francu *et al* 1990). Generally, in these basins, I/S is not the most abundant clay mineral in the <2 μm fraction of shales. Instead, the assemblages tend to be dominated by various combinations of illite and chlorite and kaolinite. Such assemblages are probably due to an origin dominantly by inheritance from the great variety of igneous, metamorphic, and sedimentary rocks exposed in the mountainous hinterlands. Much of the detritus supplied to these basins from the rapidly uplifting Alpine-Carpathian mountain chain probably avoided any significant chemical weathering throughout its transport history. The apparent increase in I/S and decrease in kaolinite at about 2000 m depth in PB-2 (Figure 4) could be interpreted as due to differential sorting during sedimentation associated with the change from pro-delta to delta-slope/front sediments that occurs at about this depth. However, the difference may be considered too small to attach any specific geological significance to it. Despite the relatively low abundance of I/S in shales from the PB-2

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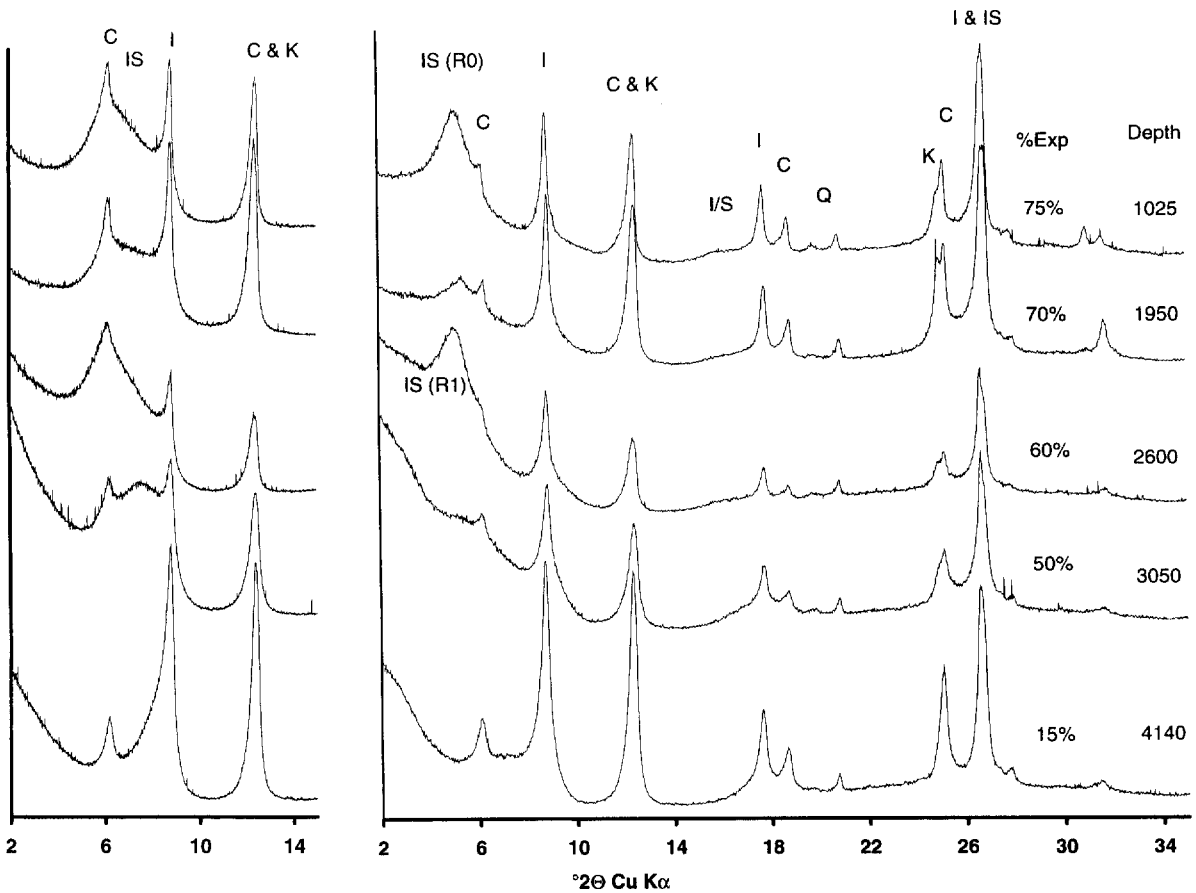


Figure 3. Mg saturated air-dried and glycolated XRD patterns of the <2 μm fraction of shales from the PB-2 well. Sample depth and estimated expandabilities (conventional methods) are indicated. I = illite, C = chlorite, K = kaolinite, IS = illite/smectite.

well, the most significant change in the clay mineralogy is the evolution of the mixed-layer composition of the I/S with respect to depth. This change is interpreted as due to the effect of burial diagenesis, i.e., the smectite-to-illite reaction, as has been documented elsewhere in the Pannonian Basin System (Viczián 1985, 1992, Francu *et al* 1990, Šucha *et al* 1993).

Expandability and ordering of illite/smectite

For the glycolated traces, estimates of expandability made by determining peak position by decomposition are generally within 10% of those made by conventional techniques and both sets of results show that expandability decreases from about 80% at less than 1 km depth to less than 20% at depths below 3.5 km (Figure 5). In general, the decomposition method gives values less expandable than those made by conventional evaluation. At depths shallower than 2.5 km the glycolated traces show that all the samples contain R0 I/S. Between about 2.5 and 3 km there is a rapid transition to ordered R1 structures. The largest discrepancies between the estimates of expandability made by conventional techniques and decomposition occur over this same depth interval. However, for the most part the values obtained by the conventional estimates are confirmed to within 10% expandability and the conventional estimates are those used in subsequent calculations since they are to be compared with the results of other workers made also in the conventional way. Overall, the results from the PB-2 well are comparable to those described previously in work by Viczián (1985, 1992) for other wells in the Makó Trough and in the Békés Basin of the Great Hungarian Plain.

Correlation of I/S expandability and ordering with vitrinite reflectance (R_o)

The change in ordering of I/S from R0 to R1 ordering in the well PB-2 correlates with a vitrinite reflectance of about 0.6% R_o, while in the deepest samples 20% expandability correlates with a vitrinite reflectance of about 0.8% R_o (Figure 6). In contrast, the data of Francu *et al* (1990) show that, in the Vienna and the Trans-

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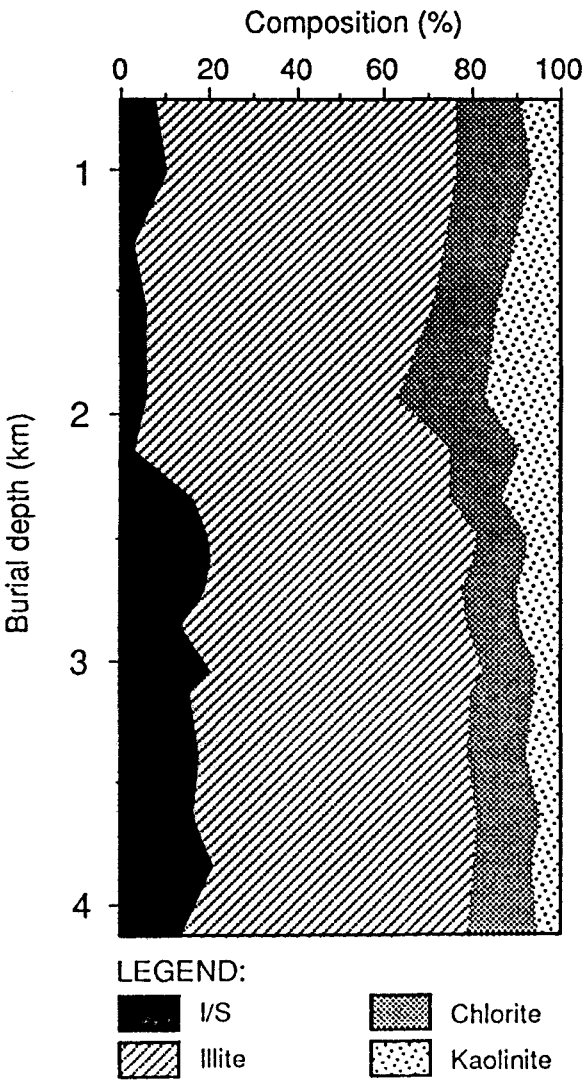


Figure 4. Changes in clay mineral abundance with depth in the <2 μm fraction of mudrocks from the well PB-2.

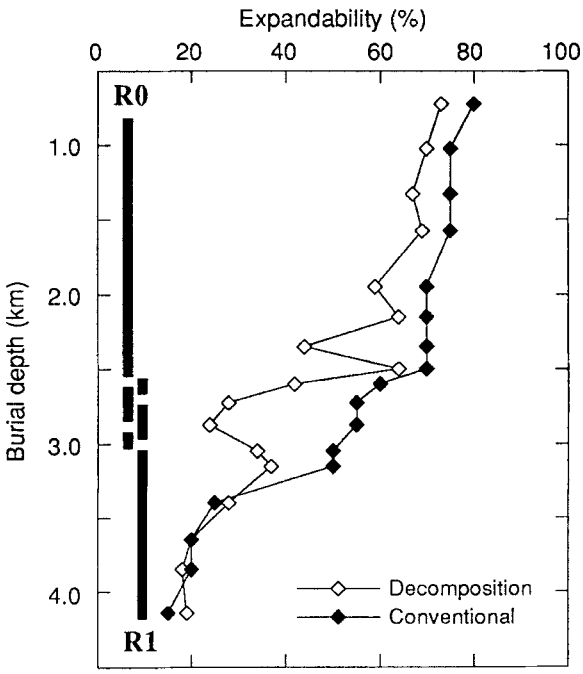


Figure 5. Estimates of expandability and change in ordering of illite/smectite versus depth in the PB-2 well. Estimates of expandability were made by two techniques, see methods section for details.

carpathian Basins of the Pannonian System the change from R0 to R1 occurs at about 0.5% and 0.65% R_o, respectively, whilst 20% expandability corresponds to about 0.6 and 1% R_o, respectively (Figure 6). Conversely, a vitrinite reflectance value of 0.5% R_o may correspond to an expandability of anywhere between about 35 to 75%, depending on which basin is considered (Figure 6). Such a comparison of the data set from the present study with those of Francu *et al* (1990) demonstrates that the correlation between R_o and I/S diagenesis varies from basin to basin within the Pannonian system. Even more important, however, overall the variation appears to be systematic. In the Vienna Basin, for any given value of R_o, the expandability of I/S is less than in the Transcarpathian Basin and in addition the sediments are older and more deeply buried. Data from the present study are intermediate. In detail, there is some considerable overlap of individual points, but the overall impression is that the correlation between R_o and illitization is systematically different from one sub-basin to another (Figure 6).

The general consensus of much recent work on R_o and organic maturation generally is that the maximum temperature to which sediments have been exposed is the prime control on the extent of reaction; time spent at temperature is much less important (Barker and Pawlewicz 1986, Quigley *et al* 1987, Burnham and Sweeney 1989). Indeed, in accordance with this view, the temperatures at which given R_o values are reached are comparable in all three of the sub-basins compared here. Therefore, the systematically different correlations apparent in Figure 6 are believed to be largely due to a kinetic effect on the smectite-to-illite reaction. In other words, it is vitrinite (R_o) not I/S that behaves most like a true (absolute) geothermometer, for I/S the duration of heating is relatively more important and can greatly affect reaction extent (Ramseyer and Boles 1986). The effect of time on the smectite-to-illite reaction is evident in the Pannonian data because of the very different thermal histories of the individual basins. The present geothermal gradients are about 25°C km^{-1} and 55°C km^{-1} for the Vienna and the Transcarpathian Basins, respectively, and about 35°C km^{-1} for the PB-2 well, from the Great Hungarian Plain. Previously, some workers have referred to this different

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Table 1. Geothermal gradients and burial history data used to calculate I/S kinetics and to calculate vitrinite reflectance profiles shown in Figure 7.

Vienna basin		Great Hungarian plain		Transcarpathian basin	
°C/km 25		35		55	
Depth (m)	Age (Ma)	Depth (m)	Age (Ma)	Depth (m)	Age (Ma)
190	7.0	556	1.7	1051	11.5
738	11.5	956	5.9	2116	13.7
1342	13.5	2197	8.5	3335	16.5
2708	16.5	4153	10.5	3758	17.5
4123	17.5				

behaviour of vitrinite and I/S as a tendency for the clay reaction to 'lag' behind R_o which responds relatively much more quickly to increasing temperature than does the smectite-to-illite reaction (Robert 1985, Kisch 1987).

Kinetics of illitization

Velde and Vasseur (1992) presented a method for calculating the kinetics of illitization by an optimization procedure that requires as input the thermal history and the measured values of expandability with depth from one or more different profiles. This method was applied to the data of the present study (conventional estimates of expandability in Figure 5) combined with the data published by Francu *et al* (1992) for the Vienna and Transcarpathian Basins, a total of 97 data points; but with the additional constraint that R_o calculated by the method of Burnham and Sweeney (1989) must also match the measured R_o data. This constraint was added in an attempt to ensure that the thermal histories used in the optimization of the clay kinetics are reasonable ones, at least in so far as measured R_o data are matched by values calculated using the thermal history of the basins and the kinetic model of Burnham and Sweeney (1989). This, of course, depends itself on the quality of the R_o data and on the validity of the vitrinite kinetic model of Burnham and Sweeney (1989), but at the very least it is believed to be better than no constraint on the thermal history at all. The model burial and thermal histories used for the three data sets are listed in Table 1, in all cases a constant mean surface temperature of 10°C was assumed. The results of the optimization showed that the data from these three different areas of the Pannonian Basin System can be modelled by a single first order reaction

$$-dS/dt = e^{\log(A) - E/RT} \cdot S$$

where S = fraction of smectite layers in I/S, t = time (Ma), e = exponential function, log(A) = frequency factor = 7.5 (Ma^{-1}), E = activation energy = 31.0 kJ mol^{-1}, R = universal gas constant, and T is temperature in Kelvin.

The fits of calculated to observed I/S expandability depth profiles given by this kinetic expression are shown in Figure 7, together with the fits of calculated to observed R_o depth profiles based on the vitrinite model of Burnham and Sweeney (1989). For the Vienna Basin and the Great Hungarian Plain the illitization reaction was started at a composition of 80% expandable layers and the Transcarpathian data are bracketed by curves with starting expandabilities of 80 and 100%. Starting expandabilities of about 80% seem to be common in unburied sediments from many basins (e.g., Środoń 1984), although clearly there may be considerable spatial and temporal variation of this value. Model calculations show that the effect of any initial variability in starting expandability is perpetuated longest in basins with high heating rates.

Overall, the agreement between measured and modelled values seems reasonable, the largest discrepancies for I/S being for the Transcarpathian data where expandabilities less than about 15% are not modelled successfully. The model values go to complete reaction whereas the measured values are 15 to 10% expandable layers. This may be due to a change in reaction mechanism such as from neoformation to recrystallisation and grain growth as in the scheme suggested by Eberl (1993). The calculated kinetic parameters predict too fast a rate of illitization for expandabilities less than 15% suggesting that the reaction mechanism has become much more temperature dependent. However, over the rest of the range of data the kinetic values given above appear to provide reasonable estimates of illitization over the wide range of thermal histories in the Pannonian Basin System.

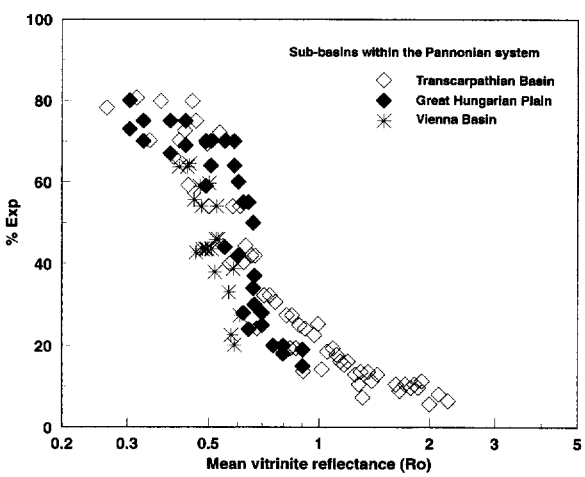
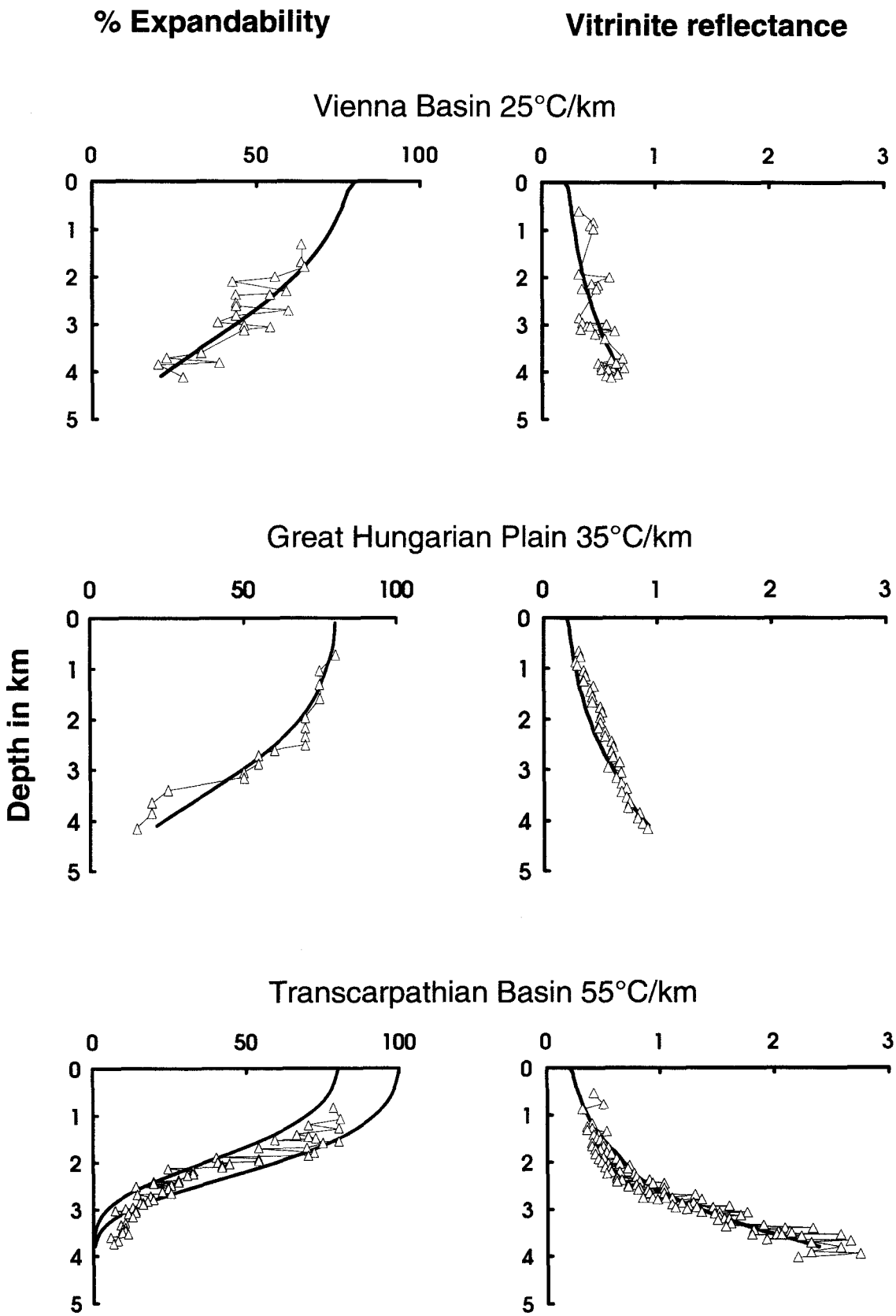


Figure 6. Correlation between expandability of I/S and vitrinite reflectance for the data from the well PB-2 in the Great Hungarian Plain (this study) compared to that from the Vienna Basin and the Transcarpathian Basin taken from Francu *et al* 1990. Vitrinite reflectance is plotted on a log scale because commonly there is a near linear relationship between log vitrinite reflectance and burial depth or temperature. The PB-2 data incudes both estimates of expandability made by conventional methods and those based on peak positions determined by decomposition.

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In contrast to the study by Velde and Vasseur (1992), only one reaction was necessary to model the Pannonian data. The reason for this is not known, but it might be due to differences in the kinetics of the smectite-to-illite reaction from one basin to another. For instance, changes in the composition of the starting smectite and the geochemical peculiarities of different sedimentary basins may affect both the mechanisms and the rate of reaction. To what extent such factors may play a role is difficult to assess. Velde (personal communication 1994) has suggested that the fact that expandability was determined using methods different to those used by Velde and Vasseur (1992) may also be a factor. In fact the kinetic description of illitization determined by Velde and Vasseur (1992) is not so very different to that found in this study. The second of their reactions (R1 ordered I/S) has almost identical kinetic parameters (log (A) = 7.2 Ma^{-1}, E = 37.4 kJ mol^{-1}) to those derived here. In both cases the low activation energies indicate that time at temperature will have a significant effect on reaction extent. The first of their reactions (R0 random I/S) (log (A) = 21.5 (Ma^{-1}) E = 69.7 kJ mol^{-1}), however, is much more temperature dependent.

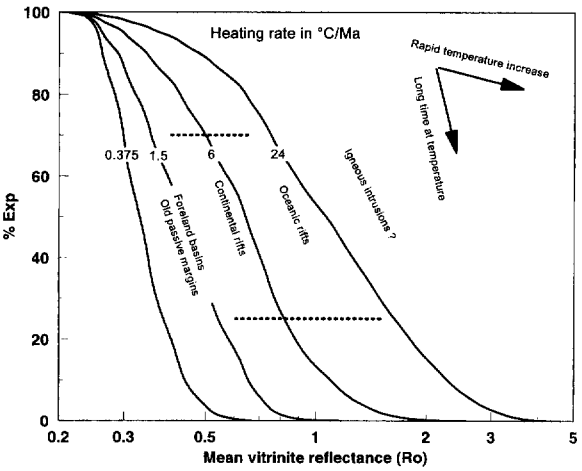


Figure 8. Theoretical range of potential correlations between vitrinite reflectance and I/S diagenesis based on the kinetics of the I/S reaction determined in this study and the kinetic model of vitrinite maturation of Burnham and Sweeney (1989). Horizontal dashed lines indicate the range of vitrinite reflectance values corresponding to expandabilities of 70 and 25% according to Kisch (1987). Also shown are suggested regions where data from different basin types and data affected by igneous intrusions might plot.

Correlations between vitrinite reflectance (R_o) and I/S expandability in relation to thermal history and sedimentary basin types

To a large degree different types of sedimentary basins are characterised by different mechanisms of formation and crustal settings that cause distinctly different types of thermal and burial histories. For example rift basins usually fill rapidly and have elevated thermal gradients whereas the basins of passive margins fill at lower rates and have lower thermal gradients. The usual range of geothermal gradients (20–50°C km^{-1}) and burial rates (20–400 m Ma^{-1}) encountered in sedimentary basins indicates that heating rates (the product of the two) normally lie within the range of 1–10°C Ma^{-1} (Gretner and Curtis 1982). By taking such a range of heating rates and a kinetic model for both I/S and vitrinite maturation it is possible to define a domain within which all 'normal' (burial diagenetic) correlations between expandability and R_o should lie.

A plot of this kind made using the kinetic parameters determined in this study to calculate expandability and the kinetic model of Burnham and Sweeney (1989) to calculate R_o is shown in Figure 8. The theoretical curves correspond to heating rates that range between 0.375 and 24°C Ma^{-1} so that the domain enclosed by them represents a vast spectrum of potential combinations of geothermal gradients and burial rates. That these values reasonably represent extremes for heating rates in sedimentary basins can be illustrated by considering a couple of examples. For instance, a heating rate of 0.375°C Ma^{-1} could result from the combination of a geothermal gradient of 30°C km^{-1} and a burial rate of 12.5 m Ma^{-1}, while for a heating rate of 24°C Ma^{-1} a combination of 60°C km^{-1} and a burial rate of 400 m Ma^{-1} is possible. For the low heating rate combination it would take 400 Ma of continuous sedimentation to accumulate a succession 5 km thick whereas for the high heating rate combination the same thickness would have to be deposited in only 12.5 Ma.

A comparable diagram of R_o versus illite crystallinity was presented by Robert (1985) in which he attempted to delineate a geodynamic classification of sedimentary basin types based on observed different relationships between organic maturation and clay mineral diagenesis. The present diagram can be used in a similar way but in addition it includes theoretical limits to correlations between R_o and clay mineral diagenesis (I/S) that might be observed in sedimentary basins simply because of their different kinetic response under variable heating rates. Whether or not the kinetic models are reasonable can be tested by plotting data from dif-

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Figure 7. Comparison of observed I/S and vitrinite reflectance data with calculated values. Calculated I/S trends are based on a first order rate equation for the I/S reaction with frequency factor = log(A) = 7.5 (Ma^{-1}) E = 31.0 kJ mol^{-1}), calculated vitrinite reflectance trends on the kinetic model of Burnham and Sweeney (1989). Both calculated I/S and vitrinite reflectance trends are in each case based on the same thermal histories as given in Table 1.

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ferent basin types, and if so the diagram can be used to identify hyper and hypo thermal histories, in the sense of Robert (1985), as well as anomalous relationships as might result from contact metamorphism (Smart and Clayton 1985). Some support that the domain is reasonable comes from the compilation of I/S versus R_o correlations compiled by Kisch (1987). The two horizontal lines in Figure 8 represent the range of R_o values that may correspond to 70% expandable layers and 25% expandable layers, according to the data of Kisch (1987). In both cases the ranges plot well within the theoretical domain, but they span a more conservative range of heating rates, a range within which most sedimentary basins would fall (Gretner and Curtis 1982). A similar domain (not shown) calculated using the kinetic scheme of Velde and Vasseur (1992) gives a much narrower range of potential correlations of I/S and R_o for random (R0) mixed-layer clay compositions. It also causes the domain covered by the second reaction (R1) to be shifted further to the right of Figure 8 so that much of the real Pannonian data plots, unreasonably, to the left of the lowest heating rate boundary of 0.375°C Ma^{-1}.

The actual trends of measured data within the diagram should not, however, be expected to follow the heating rate contours. The thermal history of individual units will be a complex summation of variable heating rates and in many cases cooling rates as well. Furthermore, variability in starting expandability may tend to blur distinction between different basin types at the lowest diagenetic grades. In general long times at temperatures close to maximum will drive the data points downwards towards the R_o axis, whilst short lived heating events such as caused by igneous dykes and sills will shift points towards the right-hand side along vectors more or less parallel to the R_o axis (Figure 8).

CONCLUSIONS

The clay mineral assemblages in mudrocks from the well PB-2 in the Great Hungarian Plain consist of illite, kaolinite, chlorite and I/S. The main change in clay mineralogy with depth is the change in composition of the I/S due to burial diagenesis. The change from random to ordered mixed-layering occurs at about 2500 m at which R_o is about 0.6%.

In the Pannonian Basin System as a whole, the correlation between the smectite-to-illite reaction and R_o varies from one sub-basin to another systematically in accordance with their different thermal histories. In areas with low heating rates the smectite-to-illite reaction is more advanced relative to R_o whereas in areas of high heating rates the reverse is true. This is believed to be due to the kinetics of the smectite-to-illite reaction that makes it relatively more sensitive to the length of time spent at temperature in contrast to vitrinite maturation, which behaves more like a true geothermometer. Kinetic parameters derived from the natural I/S data also suggest an important role for time. Combined with a kinetic model of vitrinite reflectance, they can be used to define a domain within which all burial diagenetic correlations between R_o and I/S expandability should fall. Using a range of heating rates typical for sedimentary basins, the domain encompasses the spread in the correlation of R_o with I/S expandability found in the literature. This suggests that much of this variability may be explained by the different kinetics of these two diagenetic reactions.

The data on which the present study is based are somewhat disparate and a more consistent study could no doubt improve on them. Nonetheless, what should really be emphasised is the potential of combining clay mineral and R_o data. In the modelling stage the R_o data provide a valuable constraint on the thermal histories used to derive the kinetics of the smectite-to-illite reaction. Without this constraint, the thermal histories may be very inaccurate, even totally unrealistic, especially for older basins. While for geological interpretation, diagrams such as Figure 8 can be used to identify different types of thermal histories and 'anomalous' data that might otherwise go unrecognised.

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