Thermal maturity of Oligocene oil-source rocks in the Cuu Long basin Vietnam: An approach using the illitization of smectite

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Abstract

The natural transformation of smectite-to-illite in Oligocene-Miocene sediments collected from an exploration well in Block 16-1, Cuu Long basin, has been examined in relation to quartz cementation and thermal maturity of source rocks. Evidences including X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM) data, identified that smectite is unstable with increasing burial temperature. Consequently, during the diagenesis stage, it was transformed to illite and released a significant amount of silica which formed micro-crystalline authigenic quartz within the clay matrix. The kinetic equation of the transformation of smectite to illite was utilized to evaluate the maximum paleotemperature for the first time; this indicated that the sediments had experienced a diagenesis episode in which the temperature was in a range of 100 - 140°C.

1. Introduction

The transformation of smectite to illite during diagenesis was first documented by studies of the Gulf Coast (Burst, 1959; John Hower, 1976). Some researchers have demonstrated that smectite transfers to illite via mixed-layer illite/smectite minerals (I/S) with increasing temperature due to burial depth. With the presence of potassium in solution, this reaction might start at about 50°C, and smectite completely transfers to illite when the exposed temperature is above 200°C (Huang et al., 1993; S. Hillier, 1995). Therefore in petroleum geology, studies of the illitization of smectite reaction occurring during digenetic processes have been of interest for several reasons. Firstly, the degree of the illitization of smectite is used as an indicator of geothermometry a geothermal indicater to construct the thermal history of sedimentary basins. A second reason is that authigenic clay minerals may grow to larger sizes and a significant amount of silica produced into solution, and consequently authigenic quartz will be crystallized caused changes in rock properties during the illitization of smectite. For that reason reservoir qualities are reduced by clay minerals coating on detrital grains.

Pollastro et al. (1993) have demonstrated that level of hydrocarbon-generation are linked to the stacking order of IS mineral in terms of the Reichweite index (R), which can be identified by analyzing the XRD patterns of IS mineral. In addition, many researchers have attempted to construct the kinetic equation of the smectite-to-illite reaction and then applied it to estimate paleotemperatures. However, due to geological diversity, there is not an exact kinetic equation that can be applied for every case. The two equations that most frequently appear in the literature are the first order equation (Huang et al., 1993) and the second order equation (S. Hillier, 1995). By choosing a range of activation energies and assigning is probability distribution, Susanne Gier et al, 2006, have successfully modeled the thermal history of Miocene sandstones in the Vienna basin, Austria. According to the research of Sorodon et al, 2002, measurements of K/Ar in fundamental illite particles are successfully used for dating of clay diagenesis. Although there are a numerous investigations of the smectite-to-illite reaction as mentioned above, many aspects of the kinetics and mechanisms of this reaction is still poorly understood (Douglas, 2008). That why the use of the kinetics of illitization of has not been widely used in interpreting the geothermal history in various places, e.g. Cuu Long basin. Other reasons are possible ambiguous interpretations of XRD patterns from clays containing a mixture of discrete clay minerals and mixed-layer phases.

Located in offshore Southern Vietnam, the Cuu Long basin is a typical rift basin, overlying heavily weathered Mesozoic basement (granites and granodiorites). The sedimentary succession consists of a Palaeogene syn-rift package different from a Neogene post-rift succession by an inversion unconformity of latest Oligocene to early Miocene age (Jørgen A. Bojesen-Koefoed, 2009). The syn-rift succession is made up of lacustrine sediments which are considered as the main source rock in the basin (Lee et al., 1996). One of the giant oil fields is the White Tiger field with estimated reserves of about 1.0 - 1.4 billion barrels of oil. Current daily production is 250,000 barrels, 90 percent of which is come from the fractured basement reservoirs with the remainder produced from Oligocene and Miocene classic reservoirs. However, there are not any papers reporting maturity and properties of the sediments in this basin based on analyses of alteration of clays**.** Nowadays, extensive explorations in this, present a good opportunity to investigate the relationship between the degree of illitization and thermal history of the basin as well as its effect on rock properties. Such a study also might help to appraise the prospectivity during exploration and the economic viability of potential petroleum discoveries.

In this paper, we report a study of smectite-to-illite transformation in a suite of Tertiary sediments from an exploration well in the Block 16-1, Cuu Long basin, Vietnam. The samples used for this study are cuttings collected down to about 3,500m. By choosing a suitable method to accurately estimate the percentage of illite in mixed-layer illite/smectite mineral, the first order kinetic equation of the smectite-to-illite reaction is utilized to evaluate the geothermal history of Tertiary sediments in the Cuu Long basin for the first time. The mechanism of this reaction is also discussed in relation to the presence of micro quartz cementation.

2. Methods

2.1. X-ray Diffraction (XRD)

Thirteen samples from an exploration well in the Western Block 16-1 (Fig. 1), Cuu Long basin, were collected from 2,460m down to 3,490m. All the cutting samples were analyzed by XRD for whole-rock mineralogy and clay mineralogy (< 0.2µm), using a Philip X'Pert X-ray diffractometer (Cu Kα, 40kV and 30mA).

2.1.1. Detrital mineralogy

For semi-quantitative analysis of whole-rock samples, the added internal standard reference intensity (RIR) method, modified from Moore and Reynolds (1997) and S. Hillier 2003, was utilized. Therefore, the finely gridded powders were mixed with 50% purified corundum (Al_2O_3) and then were analyzed by X-ray diffractometer. Semi-quantification is based upon calculation of the peak intensity divided by the measured peak intensity of the main corundum 113 peak and multiplied by weight percentage of added corundum divided by the RIR_{cor} (Table 1).

2.1.2. Clay mineralogy

Sample preparation: For the purpose of analysis of the clay fractions, the cutting samples were crushed into a fine powder, and organic materials removed by hydrogen peroxide, and disaggregated by ultrasonicator. The < 0.2µm fractions were obtained by sedimentation and then centrifugation, the settling time was calculated according to Stoke's law. Clay suspensions were treated by 0.1M calcium solution prior to orientation on glass slides and were analyzed after air-drying and after vapor saturation with ethylene glycol at 60°C for 4 hours. The exchanging cation is necessary because clay minerals absorb anions and cations and hold them in an exchangeable state. Additionally, the d-spacing of smectite or mixed-layer mineral illite/smectite depends on the type of cation held in the exchangeable sites. The technique for exchanging calcium is relatively uncomplicated, our laboratory experiments have demonstrated that cations

Table 1. *Reference intensity ratios (RIRs) used for semi-quantification (modified after S. Hillier, 2003)*

Mineral	Peak position	RIR_{cor}
Quartz	3.34	4.04
Calcite	3.03	2.73
Plagioclase	3.19	2.07
K-Felspar	3.24	1.00
Pyrite	2.72	1.70
Kaolinite	3.52	0.54
Chlorite	3.58	0.53
Corundum(standard)	2.08	1.00

in the interlayer of smectite are regularly exchanged with calcium if clays are twice treated with 0.1M $CaCl_2$ solution and carefully washed by distilled water. After treatments, the first peak of the XRD patterns of exchanged smectite identically shows at 15Å in d-spacing. That condition was repeatedly applied to all samples in this study.

Identification and quantitative analysis: The method to identify clay phases is modified from Moore and Reynolds (1997). In this study, both smectite and random mixed-layer illite/smectite is represented as an expendable mineral. Its quantity was determined by the integrated area of the expanded 17Å peak with ethylene glycol treatment, whereas the type of ordering (R0, R1 or R3) was determined by the location of 001/002 illite/EG-smectite peak. The normalized RIR method (Chung, 1974; Snyder, 1992) was applied for semi-quantitative analysis of clay fractions prepared as oriented mounts. The factors are 1, 4, 2 and 2 for the glycolated smectite 001, the illite 001, and the chlorite 002 and kaolinite 001, respectively. In order to apply the kinetics of the smectite illitization ratio, the percentage of illitic layers in the mixed-layer illite/smectite was determined upon estimating $\Delta 2\theta$ after careful calibration using the NEWMOD program (Moore and Reynolds, 1997).

2.2. Scanning Electron Microscopy (SEM)

The samples were embedded with epoxy resin before cutting, gridding, polishing and then coating with gold in order to obtain the cement textures on the Jeol 5,600 Scanning Electron Microscopy (SEM). To acquire a high quality backscattered scanning electron images (BSEIs), the acceleration voltage is adjusted to 30kV. However, it is adjusted down to 20kV at 20cm in walking distance prior to EDS analysis to identify the elemental composition and qualitative mineral identification.

3. Results and discussion

3.1. Detrital mineralogy

The general mineralogy of the Cuu Long basin within litho-stratigraphic frameworks is discussed in detail in Lee et al (1996) and in Nhuan T.V et al (2009 and 2010). Hence we only reexamined the detrital minerals in the research well by using XRD characterization and SEM prior to discussion of the mechanism of the smectite-to-illite reaction. The information about detrital mineralogy is desired because rock types are controls on occurrence and behavior of the smectite-to-illite transformation during diagenesis (J.M. McKinley, 2003). According to the XRD results, the major minerals of the collected sediment samples are quartz, plagioclase, K- feldspar, and minor calcite. BSEI images show the roundness of detrital grain varies from angular to subangular and also indicate partial dissolution of detrital K-feldspar grains (Fig. 4). The quantity of respective phases is calculated and shown in Table 2.

In the above table, only minerals having relatively high concentration were quantified, the other phases

Table 2. *Detrital mineralogy determined by the RIRs method*

Depth (m)	Quartz (%)	Calcite (%)	Plagioclase (%)	K-Feldspar (%)	Clays (%)	Rock type
2160	58.5	0.0	14.2	14.4	13.0	Fine sandstone
2395	50.5	0.0	26.0	9.5	14.0	
2550	57.6	0.0	27.6	14.4	0.3	
2645	47.5	0.0	19.2	21.3	12.0	
2715	45.9	2.8	11.2	7.6	32.5	Fine sandstone
2805	37.2	0.0	4.9	8.2	49.7	
2850	37.1	0.0	9.7	17.3	35.9	
2865	33.0	0.0	6.0	13.5	47.5	
2900	55.7	2.5	25.0	16.6	0.3	
2915	41.7	3.6	8.4	9.8	36.6	Mudstone
2965	38.8	15.4	6.8	13.3	25.7	
3395	44.5	3.7	15.2	11.6	25.0	
3490	44.8	0.0	7.4	12.8	35.0	

including clay minerals and organic compounds could not be included because of their relatively low concentration. Quantities of major phases (quartz, calcite, albite and K-feldspar) then were normalized after Chung (1974) before illustrating as a function of depth (Fig. 2). Generally, there is not a considerable change in the mineralogy pattern of sediments from 2,160m to 2,900m. A significant change in mineralogical components was observed from depths greater than 2,915m, which is marked by a dramatic increase in calcite content within a peak of 15.2% calcite at 2,965m depth (Table 2). In order to interpret changes in dispositional facies, the mineralogical data of the present research was plotted as a function of depth in comparison to studies of Nhuan T.V et al. (2009). The mineralogical data show similar patterns, a significant increase in the proportion of calcite with increasing depth of burial. These changes are presumed to be a result of changes in sedimentary composition or in depositional facies.

3.2. Clay mineralogy

Authigenic minerals are dominated by combinations of chlorite, kaolinite, illite, smectite, and mixed-layer illite-smectite mineral (IS) with a minor amount of quartz. The quantities of these minerals were determined and then listed in Table 3. Excepting smectite, the proportion (by weight) of other authigenic minerals do not show a clear tendency when moving down the drill hole, which might be controlled by differences in detrital mineralogy and depositional facies. Thus it is not reasonable if using the clay mineralogical pattern as a function of depth to evaluate the diagenesis degree. Meanwhile a number of previous studies have demonstrated that IS mineral is a valuable candidate for diagenesis study. Hence it is mainly discussed in this study; other clay minerals such as kaolinite and chlorite are of less concern, even they also influence rock properties.

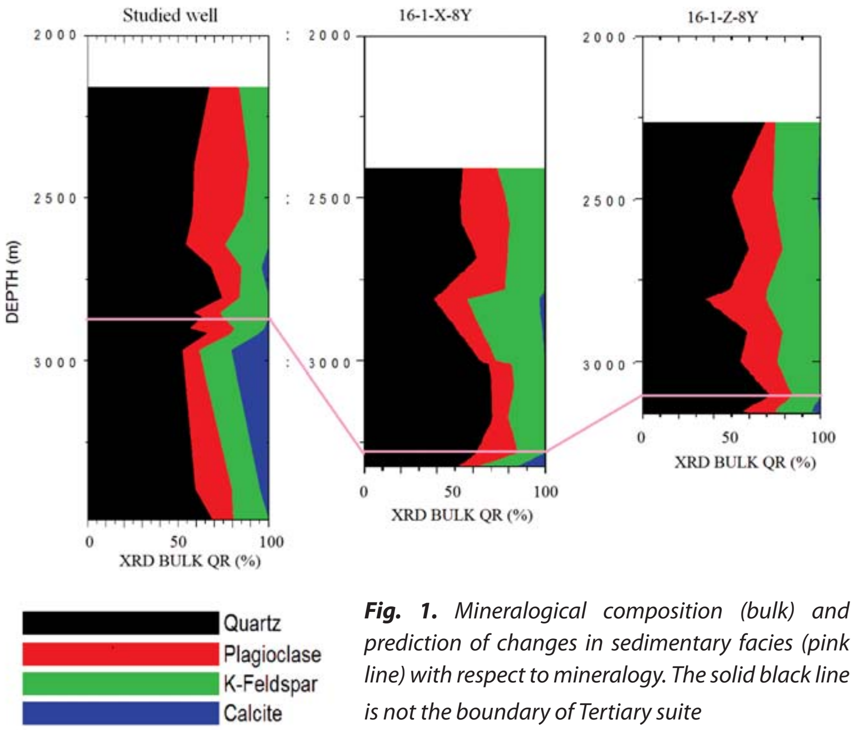

Fig. 1. *Mineralogical composition (bulk) and prediction of changes in sedimentary facies (pink line) with respect to mineralogy. The solid black line is not the boundary of Tertiary suite*

Table 3. *Clay mineralogical data determined by XRD of < 0.2µm factions*

Depth (m)	Chlorite (%)	Kaolinite (%)	Illite (%)	Illite-smectite (%)	Smectite (%)
2160	21.35	24.13	29.12	9.18	10.77
2395	15.30	19.28	35.08	10.05	16.76
2550	18.48	24.16	26.42	11.42	16.50
2645	21.89	23.16	23.90	10.49	18.06
2715	28.52	28.52	16.61	12.89	11.33
2805	28.61	29.83	22.73	8.64	8.23
2850	29.50	31.72	25.60	14.29	2.38
2865	34.12	35.17	18.38	16.61	0.98
2900	24.97	30.61	23.09	7.58	15.79
2915	32.37	35.10	13.77	14.97	1.72
2965	25.52	34.52	30.38	8.14	1.45
3395	31.85	27.74	40.42	0.00	0.00
3490	28.30	28.30	43.40	0.00	0.00

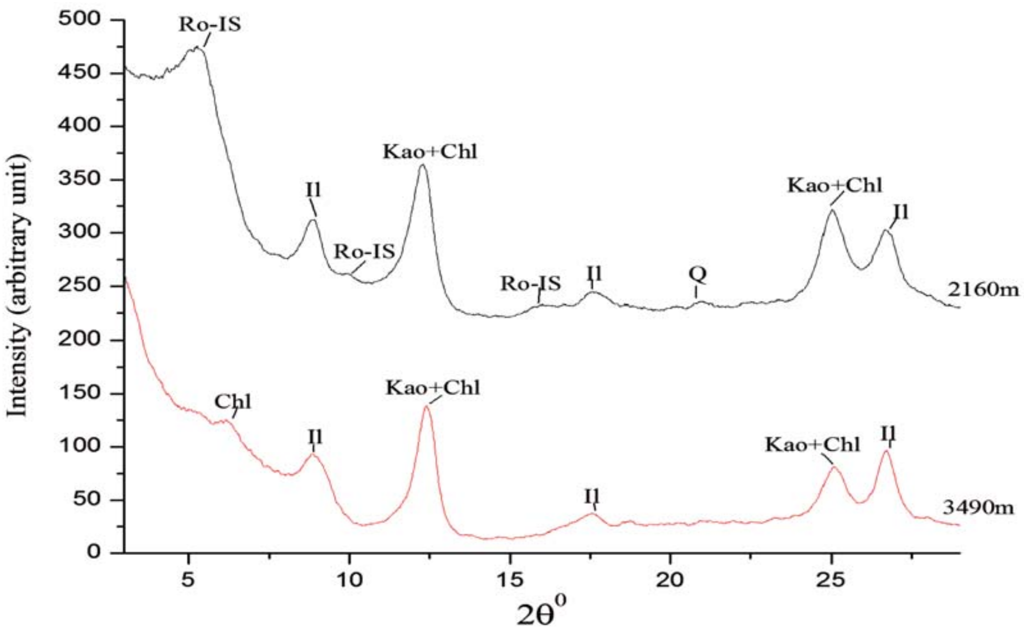

Fig. 2. *XRD patterns of EG-saturated < 0.2μm fraction cuttings from different depths. Ro-IS, random illite/smectite; Kao, kaolinite; Chl, chlorite; Il, illite; Q, quartz*

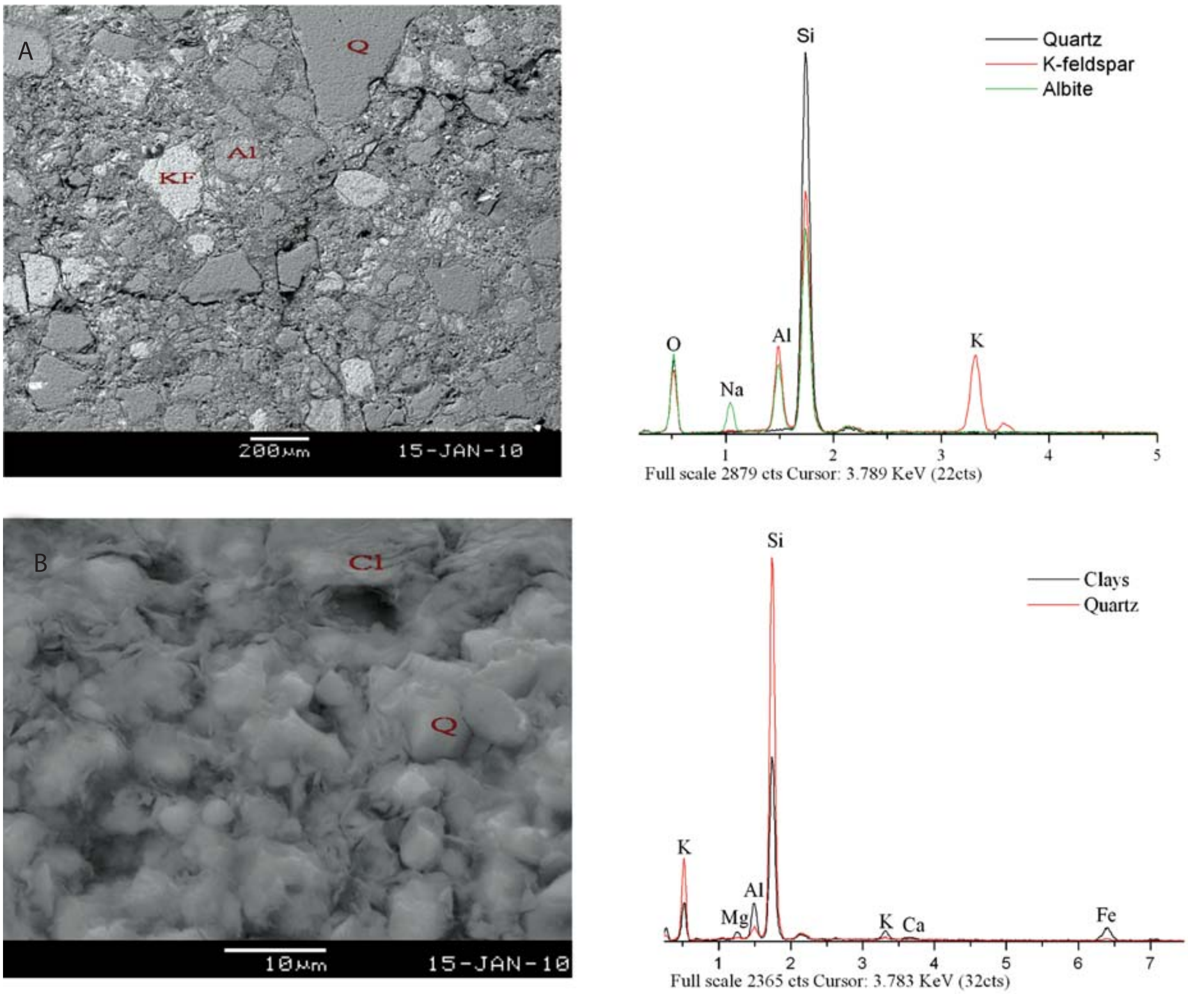

Fig. 3. *Backscatter electron image. (A) Rock texture and dissolution of primary K-feldspar. (B) Individual micro-quartz within fine clay matrix. Q, quartz; Al, albite; KF, K-feldspar; Cl, clays*

An absence of smectite and IS mineral at burial depths below 2,965m is fair evidence of the smectite-to-illite transformation with increasing burial depth. Occurrences of minor microcrystalline quartz incorporated with clays verify that a significant amount of silica is released into solution while smectite is converted to illite (Fig. 3 and Fig. 4). The release of silica during the transformation might result from substitution of Al for Si in the smectite structure (Hower et al., 1976). Therefore during diagenesis processes, the alteration of rich smectite sediments may influence their physical properties. One of the possible reasons may be the partial dissolution of detrital K-feldspars and occurrence of individual authigenic quartz crystal thus increasing pore sizes (Fig. 4). Additionally, the effect of micro-quartz cementation due to the release of Si from the smectite-to-illite alteration is not a single factor influencing the compaction of smectite rich sediments, but also increases in clay particle size and decreases in expendability resulting from S-I transformation may cause increasing rock permeability and reducing overpressure therefore increasing the rate of compaction (Peltonen et al., 2008).

3.3. Thermal history of Miocene-Oligocene sediments

The illite/smectite (IS) data reveal that the proportion of illite in interstratified illite/smectite steadily increases with increasing depths of burial (Fig. 4A). It starts at about 20% of illite at 2,160m, and the percentages of illite in IS are > 90% at depths below 2,800m. This observation demonstrates

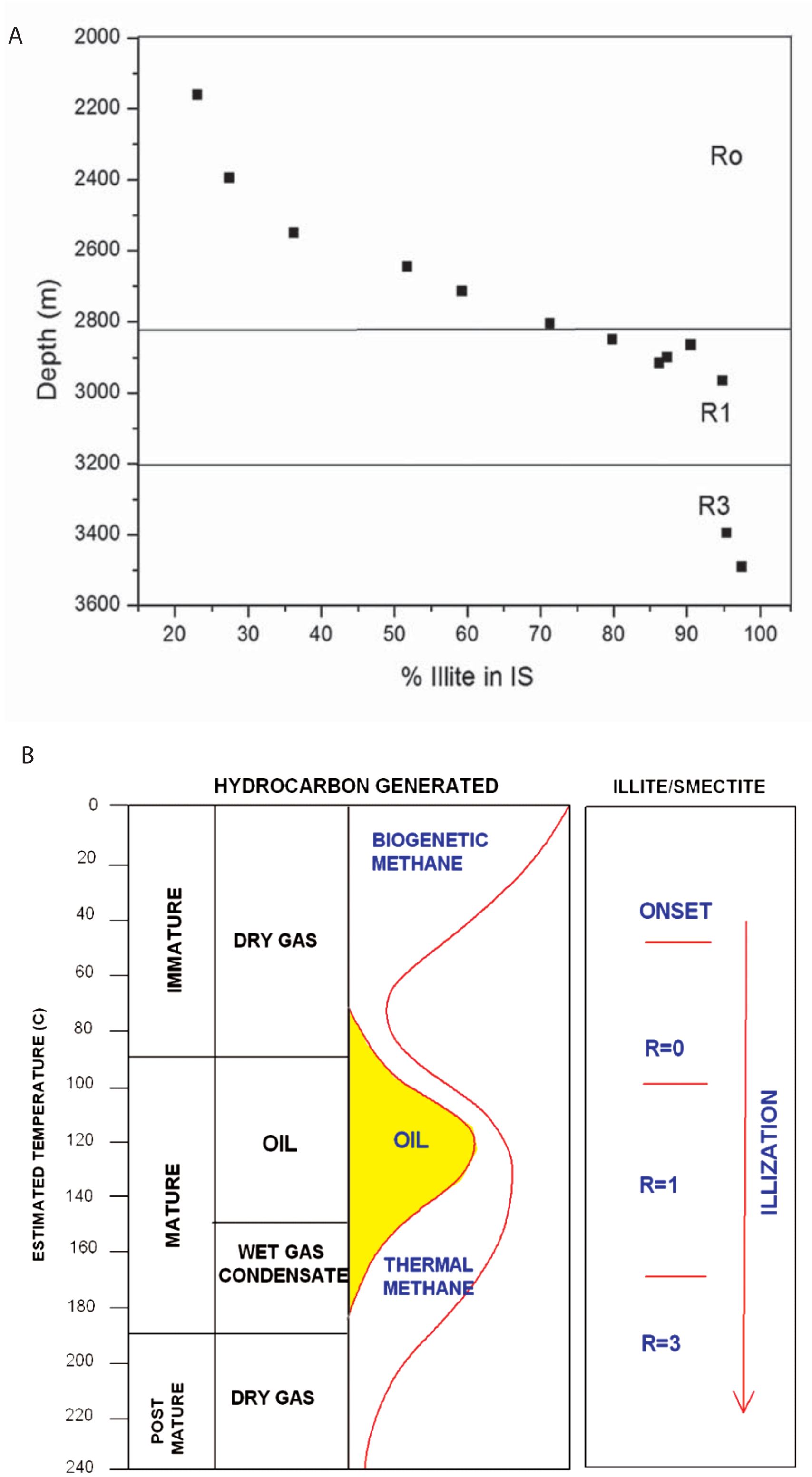

Fig. 4. *(A) The percentage of illite component in the interstratified illite–smectite (I/S) phase, plotted as a function of depths (R0, randomly interstratified I/S; R1and R3, ordered I/S). (B) The relation between smectite-to-illite conversion via mixed-layer I/S mineral and hydro-carbon generation (Richard M.R et al., 1993)*

that mixed-layer IS mineral is a precursor of authigenic illite. As discussed earlier, a major factor that controls the smectite-to-illite reaction is temperature, as confirmed by many observations both from nature and laboratory experiments (Huang et al., 1993; S. Hillier 1995; Reynolds et al., 1984, Hower et al., 1976). Therefore, IS mineral has been used as an indicator to predict the maturity of hydrocarbon source rocks. Based on Reichweite indices of IS mineral, determined by analyses of XRD profiles, the sedimentary succession in the researched well was classified into three different zones: R0, R1, and R3 corresponding to random illite/smectite, R1 ordered illite/smectite, and R3 ordered illite/smectite, respectively. Fig. 5 shows a comparison of the present observation in the Cuu Long basin to the theory of Richard et al., (1993). The sedimentary succession from 2,850 to 3,200m corresponds to the main oil-production phase, however sediments located at the depths greater than 3,200m are over matured thus only wet or dry gas is probably generated (Fig. 5).

Nevertheless, the transformation of smectite to illite is not only controlled by temperature but also by several other factors including burial rate, time, Na/K ratio, activation energy and the initial illite fraction in the IS mineral (Huang et al., 1993; S. Hillier, 1995). These factors reflect geological environments. Herein the kinetic equation of the smectite-to-illite reaction is utilized to predict the thermal history as well as other geological parameters of the Cuu Long basin for the first time. The aluminum (Al) required for the reaction is supplied by the destruction of additional smectite layers, and potassium (K) is produced by partial dissolutions of detrital F-feldspar grains (Eberl and Hower, 1976). It is reasonable because XRD results for bulk samples indicate that all collected samples contain a significant amount of K-feldspar, and SEM observation also shows dissolution and albitization of K-Feldspar. The reaction is simplified in Eq. (1).

$$\text{Smectite} + Al^{3+} + K^{+} \rightarrow \text{Illite} + SiO_2 \qquad (1)$$

The kinetic equation used herein is modified from Huang et al., (1993):

$$-dS/dt = k[K^{+}]S^{2}$$

Where: S is molar fraction (smectite %) of smectite in the illite-smectite mixed layer;

$[K^+]$ is concentration of the dissolved potassium; k is rate constant.

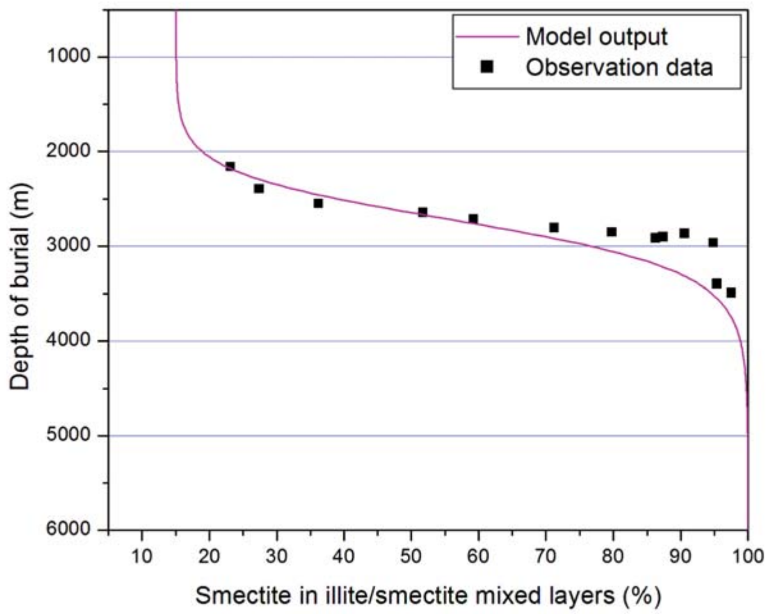

Fig. 5. *Kinetic modeling of smectite-to-illite transformation in comparison to clay mineral data from Oligocene-Miocene sediments in the Cuu Long basin*

In order to approach the kinetic modeling of the smectite-to-illite reaction for the present researched area, potassium concentration, geothermal gradient and burial rate were adjusted to get the optimum model. Fig. 6 shows the model of smectite to illite conversion in comparison to clay mineral data from Oligocene - Miocene sediments in the Cuu Long basin. The best fit model was constructed by using an initial smectite-illite ratio of 85%, geothermal gradient of 33°C/km, 250m/ma of burial rate, and 250ppm. Based on the kinetic modeling, the maximum temperature of sediments in the studied well is about 110°C, lower than the value estimated by comparing Reichweite indices to Richard M.R's model (1993). However in this research, the burial rate was adjusted arbitrarily to find out the best fit model therefore additional work, possibly K/Ar dating, may help to better estimate the thermal history. In addition, because this research is base on the limited data set, so larger data sets with better references about geological setting need to be carried out.

4. Conclusion

XRD results for clay fraction (< 0.2µm) in combination with SEM observation show a progressive illitization of smectite with increasing depth, which resulted in the release of significant amounts of silica into solution. Silica locally participated to form authigenic quartz within the clay matrix, thus it might cause changes in rock properties.

The smectite-to-illite conversion not only effects on quartz cementation but also may reflect on thermal history as well as geological environment of the basin. The IS data and the kinetic modeling demonstrate that the sediments at the depths of 2,160 to 3,200m are well matured, however these rocks at depths below 3,200m are probably over matured.

A dramatic increase in proportions of illite in the mixed-layers illite/smectite indicates a rapid dispositional environment. Most smectite in sediments at depths below 2,915m was converted to illite, a significant difference from that in its overlying sediments, which may reflect changes in temperature gradient over time.

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