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The significance and variation characteristics of interlay water in smectite of hydrocarbon source rocks

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To investigate variation characteristics of interlayer water bound up with organic matter in smectite, organo-clay complexes extracted from grinded source rock samples were determined using thermo-XRD, DTA and PY-GC. The d_{001} diffraction peak of organo-clay complexes is postponed from 250 to 550°C before reaching 1.00 nm and accompanied by exothermal peaks on DTA and organic matter with abundant C_{20}–C_{30} carbon detected by PY-GC, which is different from single smectite and indicates the existence of organic matter in the interlayer of smectite. Water desorption characteristics of organo-clay complexes are in consistent with smectite at 100 and 600°C, but different from smectite at 550°C with an additional dehydration peak and a remaining d_{001} diffraction peak, suggesting the water removed at 550°C is interlayer adsorption water rather than constituent water of clay minerals. Comparing the dehydration order and water loss, we conclude that part of interlayer water of smectite may act as the "bridge" that binds organic matter and smectite, which results in water-expelled lag beyond 250°C and may provide a good medium for hydrocarbon migration and oil pool formation.

source rocks, organo-clay complexes, interlayer water, organic matter

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Sorption of organic matter (OM) to clay minerals is a common phenomenon at natural settings [1]. Organo-clay interaction occurs everywhere including water, soil, and sediments [2–5]. Many recent studies show that in marine sediments, organic matter content increases with the increase of the surface area (SA) of the sediments [6–10]. In muddy hydrocarbon source rocks, more than 80% organic matter is bound tightly with clay minerals, forming organo-clay complexes [11–14].

Smectite group is one of the most common minerals in sedimentary rocks with a 2∶1 layered structure, which is created from two tetrahedral sheets sandwiched by a dioctahedral type or trioctahedral type octahedral sheet. In clay minerals, smectite is the most capable of adsorption organic matter [15], and also is enhydrite with the highest water content. The adsorbed water amount by smectite is around 50% of the total mineral in terms of bulk and 22% in terms of weight. Three states of clay hydration have been identified: adsorption water, interlamellar water, and constitution water [16]. Nuclear magnetism and neutron scanning studies showed that interlamellar hydration includes 3-layered water. When dehydration occurred, the construction unit of smectite was not destroyed but only the interlamellar spacing reduced [17–21]. During deposition and burial, dehydration of adsorption water and the first hydration layer occur at 1000 m, and the other two hydration water layers

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dehydrate at greater depths [22, 23], as supported also by calorimetric analysis [24]. In addition, the depth of H_2O dehydration of smectite is close to the hydrocarbon generation depth of hydrocarbon source rocks in many oil fields [25]. All this indicates that dehydration of smectite is related to the generation and migration of petroleum, a topic that has received growing interests and concerns from sedimentologists, petroleum geologists, and geochemists.

Dehydration of smectite is not a simple process of adsorption water being removed, but a function between interlayer actions, charge density, vapour pressure, temperature and solution medium, and a complex process of smectite illitization [24, 26, 27]. In the smectite-organic matter interaction system, hydration of smectite has a great influence on organic molecular adsorption. Synthesis studies [28–33] showed that carboxylic acid, alcohol, and nitrogenous compounds can intercalate smectite through water bridges when examined using infrared spectroscopy in combination with thermoanalysis [34–44]. In hydrocarbon source rocks, however, clay minerals and organic matters are much more complicated. Therefore, the evolution of organo-clay complexes in source rocks, especially the smectite interlayer water evolution, is the focus of our attention. In this study, <2 μm organo-clay complexes were extracted from hydrocarbon source rocks for analysis of the characteristics of interlayer water in smectite bound organic matter using thermo-XRD, DTA and TG in combination with PY-GC, aiming to extrapolating hydrocarbon generation and expulsion mechanisms of source rocks.

1 Materials and methods

1.1 Sampling

Samples were taken from organic matter-rich hydrocarbon rocks in the Oligocene Shahejie Formation with a depth range of 1000–3500 m, Jiyang sag, Bohai bay basin, China. Samples were powdered, then steeped in distilled water and further dispersed by agitation with a mortar and pestle. Stable suspension liquid was then prepared by agitation with ultrasonic dispersion repeatedly. Clay-size (<2 μm) fractions of all samples were extracted by sedimentation and allowed to dry at room temperature.

1.2 Analyses

Clay fractions of samples were analyzed for multiple properties: total organic carbon (TOC), thermogravimetric-differential thermal analysis (TG-DTA), X-ray diffraction (XRD), and pyrolysis-gas chromatography (PY-GC).

1.2.1 TOC

Test conditions: oxygen pressure 0.17 MPa, burning pressure 0.055 MPa. Total bulk was determined by combustion in a Leco CS-444 instrument after eliminating inorganic carbon with 5% hydrochloric acid.

1.2.2 TG-DTA

Test conditions: ±250 μV, span: 5 mg, rate: 20°C/min, room temperature ~800°C. TG-DTA curves were obtained on a Rigaku TAS-2000 instrument at the treating rate of 20°C/min under air and α-alumina as the standard.

1.2.3 XRD

Instrument model: Panalytical Xpert-MPD diffractometer, Test conditions: copper butt, pipe pressure 30 kV, conduit flow 40 mA, scanning speed 2° (2θ)/min. XRD analysis was performed after air drying (25°C for 24 h), ethylene glycol saturation (exposing the oriented clay slides to ethylene-glycol vapor at 60°C for 8 h), and heating at 250°C for 2 h and 550°C for 2 h to study clay minerals composition. The oriented clay slides were measured from 50 to 550°C at 100°C intervals for variations in the interlayer spacing of smectite.

1.2.4 PY-GC

Instrument model: Shimadzu GC-14B with SE-54 column. Water detection: Total bulk was putted in a pyrolysis oven and successively heated at a specific temperature in the range of 50–650°C between 50°C intervals. Each temperature setting was held for 5 min to allow organic matter totally pyrolysed. Gas chromatography (GC) analyses were carried out using a PORAPAK.Q chromatography (on-column injection, 5m long, He as carrier gas, oven programmed from 60 to 180°C at 12°C min^{-1}). Hydrocarbon detection: Total bulk was putted in a pyrolysis oven and successively heated at a specific temperature in the range of 50–650°C with 50°C or 100°C intervals.

2 Results

2.1 Bulk characteristics

Organo-clay complexes were dominated by I/S mixed-layer mineral and illite with minor kaolinite and chlorite (Table 1). The abundance of smectite in sample 26 is the highest, whereas illite is the most abundant in sample 53. TOC of all complexes samples were relative high, suggesting organic matter is enriched in clay minerals.

2.2 TG and DTA

Figure 1 shows the TG and DTA curves for samples 26 and 53. Two endothermal valleys below 200°C provide the evidence of interlayer water desorption of clay minerals, whereas an endothermal valley above 600°C may signal water dehydration. These features are similar with pure smectite and illite [16]. However, several exothermal peaks between 250–550°C and an endothermal valley at 550°C distinguish them from pure smectite and illite.

Table 1 Clay mineral composition and TOC of organo-clay complexes

Sample No.	Lithology	I/S mixed-layer (%)	Illite (%)	Kaolinite (%)	Chlorite (%)	I/S ratio	TOC (%)
1	dark grey mudstone	61	26	5	8	45	3.09
3	dark grey mudstone	75	19	3	3	70	4.42
5	dark grey mudstone	70	24	2	4	30	3.68
6	dark grey mud stone	58	28	10	4	20	2.62
11	light grey mud stone	69	16	10	5	60	1.62
26	dark grey mudstone	83	9	6	2	60	9.78
31	red mudstone	87	10	2	1	55	0.05
53	dark grey mudstone	20	70		10	5	1.00

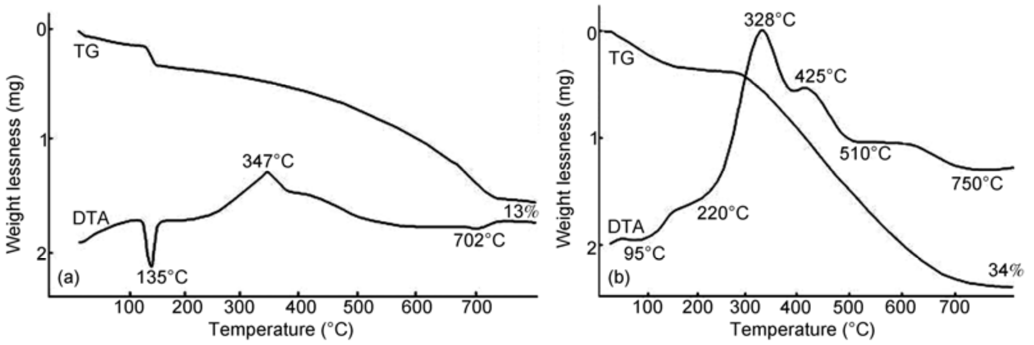

Figure 1 TG and DTA curves of organo-clay complexes sample No. 53 (a) and No. 26 (b).

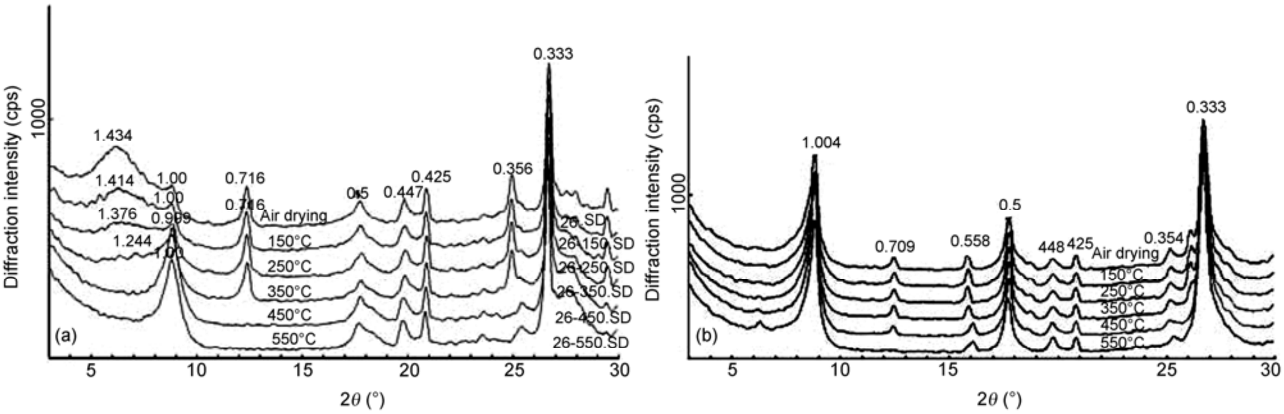

Figure 2 XRD patterns of sample No. 53 (a) and No. 26 (b) at different temperature settings.

2.3 XRD

The XRD patterns of sample No. 26 shown in Figure 2 differ from those of pure smectite, especially in the positioning of the d_{001} diffraction peak. Instead of forming a d_{001} peak at 1.0 nm near 250°C as in pure smectite, sample No. 26 shows a wide platform at 1.4–1.5 nm. The d_{001} diffraction peak did not move to 1.0nm with symmetry enhancing until being heated up to 450–550°C. In contrast, the XRD patterns of sample 53 are similar to pure illite in keeping the distinct d_{001} diffraction peak at 1.0 nm regardless of temperature changes (Figure 2).

2.4 PY-GC

2.4.1 Dehydration of clay minerals

In order to compare the dehydration features of organo-clay complexes, an analysis of pure clay minerals is necessary (Figure 3). For smectite, the amount of water loss was large at 50–150°C, minor at 250–550°C, and slightly increased after 550°C. With respect to illite, the amount of water loss was much smaller initially but increased dramatically after 550°C and reached a maximum near 600°C.

2.4.2 Dehydration of organo-clay complexes

Dehydration of organo-clay complexes was analyzed using

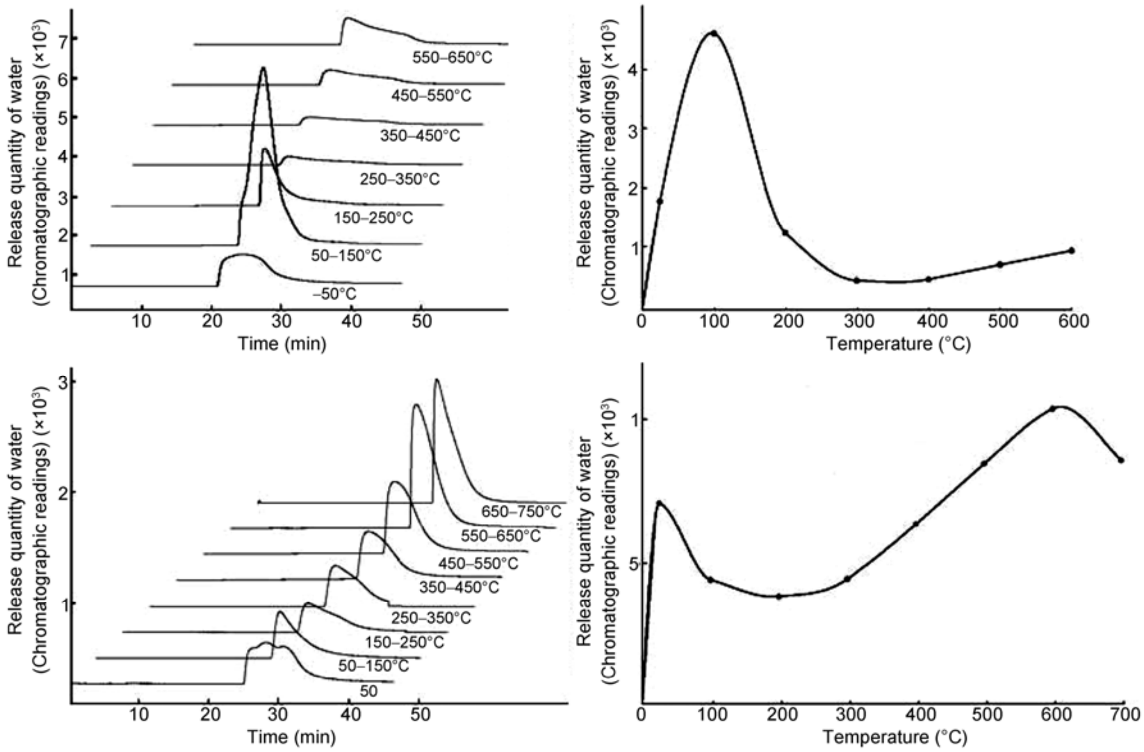

Figure 3 The dehydration curves by PY- GC for pure smectite (upper) and illite (lower).

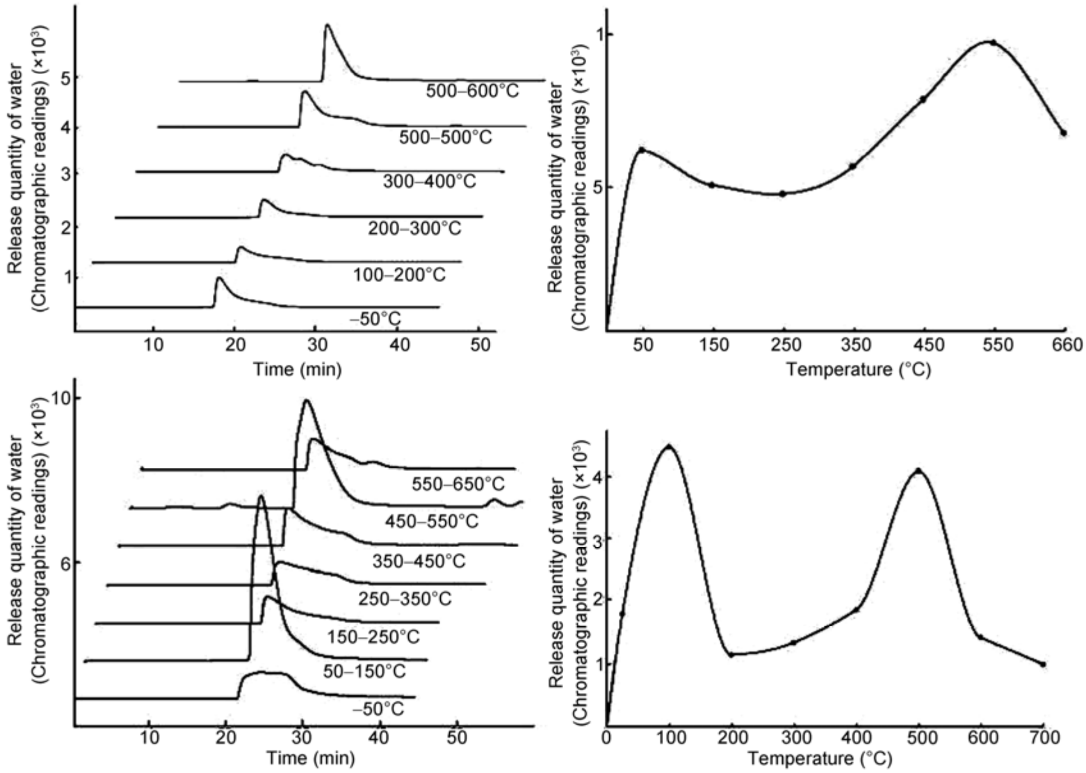

Figure 4 The dehydration curves of sample No. 53 (upper) and No. 26 (lower) by PY-GC/MS analysis.

PY-GC and the results are shown in Figure 4. For sample 26, two water loss peaks of similar amplitude occur at 50–150°C and near 550°C respectively. For sample 53, the water loss peak at 50–150°C is relatively weak, whereas the water loss peak near 550°C is pronounced. These dehydration characteristics of organo-clay complexes were different from those of pure smectite and illite as discussed above.

2.4.3 Organic matter pyrolysis of organo-clay complexes

The results of PY-GC analysis (Figure 5) indicate that the amount of organic matter released was relatively minor before 250°C and after 550°C, but increased significantly at 250–550 °C.

3 Discussion and conclusions

3.1 Occurrence of organic matter

TOC of <2 μm organo-clay complexes was relatively high whereas smectite abundances were different, confirming that clay minerals in all samples have enrichment of organic matter [10]. Comparison with XRD patterns of pure smetite shows differences of d_{001} diffraction peaks at 250 and 550°C on XRD curves of organo-clay complexes, which are similar to artificially synthesized organo-clay complexes [39], indicating organic matter intercalated smectite [14]. DTA curves of organo-clay complexes and pure smectite at 200 and 600°C were similar, while an exothermal peak developed at 350°C on organo-clay complexes (Figure 6), resembling the one on synthesized organo-clay complexes [45]. The exothermal peak at 350°C was the reflection of burning of bonded organic matter by clay minerals.

Figure 7 shows the amount of pyrolyzed products of organo-clay complexes released at different temperature settings. At 50–150°C, the amount of organic matter released was small and carbon number was less than C_{15}. It increased slightly at 250°C (Figure 5), with carbon dominated by C_1–C_{30}. When heated to 350°C, pyrolyzed organic matter increased evidently, with carbon number ranging from C_1 to C_{35}. Heated up to 450°C, pyrolyzed organic matter increased dramatically, consisted mainly of C_1–C_{10} and C_{25}–C_{30}. At 550°C, the released amount of organic matter is reduced slightly, which was composed chiefly of C_5–C_{15} and C_{20}–C_{30}. To 650°C, organic matter detected was drastically reduced with carbon of C_1–C_{10}. The maximum amount of pyrolyzed organic matter was obtained at 250–550°C and organic matter was middle to long chain, which suggests that they were bound by clay minerals.

XRD features reflect the variations of interlamellar spacing of clay minerals, and DTA curves reflects the pyrolytic process of organic matter whereas PY-GC reveals the composition of organic matter. At 250–550°C, interlamellar spacing of clay minerals is reduced gradually, with exothermal and C_{20}–C_{30} organic matter detected, which are totally different from pure smectite. Taken together, it is clear that organic matter intercalated the interlayers of smectite in forming organo-clay complexes.

3.2 Variations of interlayer water

Dehydration characteristics of organo-clay complexes are in good agreement with pure smectite and illite at 100 and

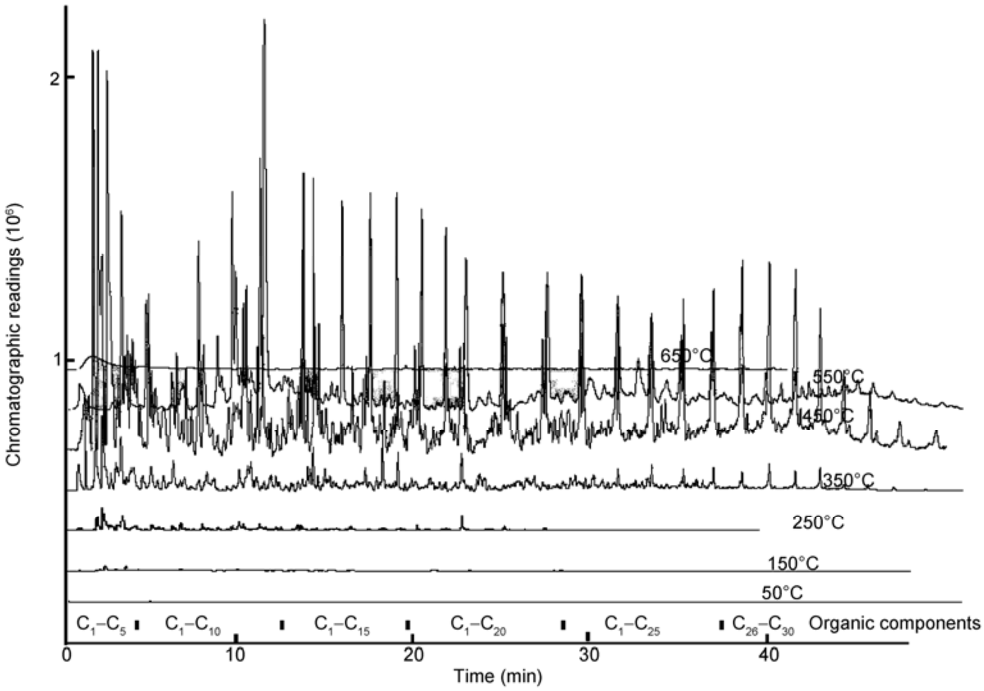

Figure 5 The PY- GC/MS curves of sample No. 26.

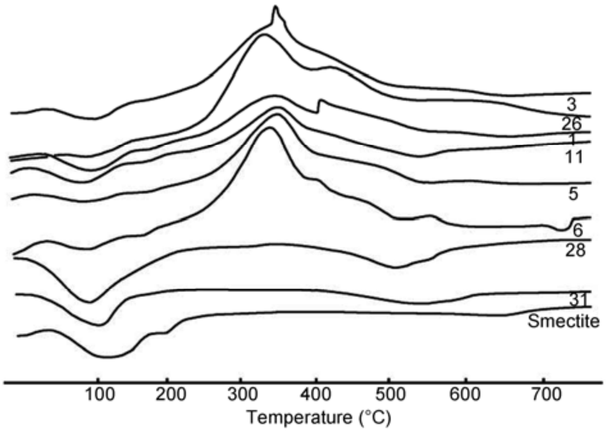

Figure 6 Comparation of DTA curves between organo-clay complexes and smectite.

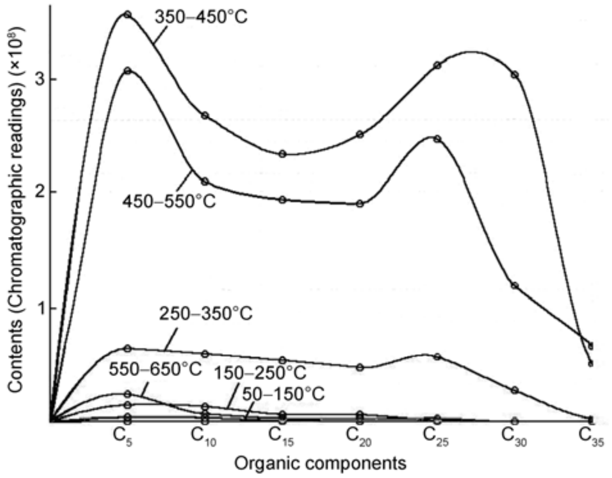

Figure 7 Organic matter releasing curves of sample 26 at different temperature settings.

600°C (Figure 6). However, the endothermic valley at 550°C on organo-clay complexes indicates the changing existence of interlayer water as organic matter intercalated into the interlayers of clay minerals. XRD of organo-clay complexes at 550°C shows a clear d_{001} diffraction peak of smectite with enhanced acuity, suggesting that crystal structure of complexes was intact. Accordingly, the dehydration peak at 550°C represents the interlayer water rather than the constitution water of clay minerals.

PY-GC curves (Figure 8) show dehydration peaks at 50–200°C and near 600°C for pure smectite and illite, and an additional peak at 550°C for organo-clay complexes, which was in accordance with DTA results.

Table 2 and Figure 9 show the water loss from smectite, illite, and organo-clay complexes in different temperature ranges as calculated from PY-GC results. Water losses from smectite and illite at 50–150°C were 44% and 10% respectively, corresponding to adsorption water and interlayer water. The constitution water was removed near 800°C, which caused lattice disturbance [16]. Water loss from organo-clay complexes was totally different from that from pure smectite and illite, regardless of their TOC and smectite contents. For instance, for samples with similar clay

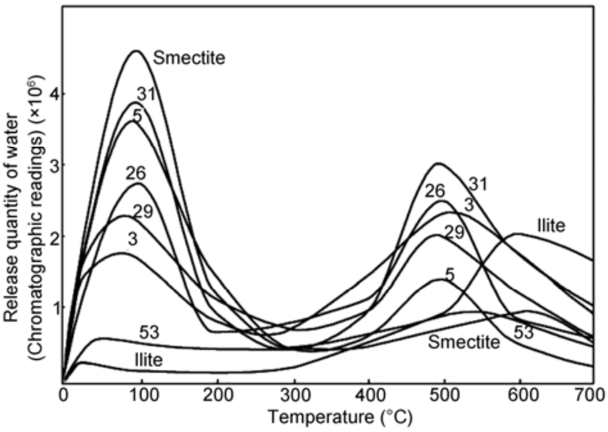

Figure 8 The dehydration curves of organo-clay complexes and clay minerals by PY- GC/MS.

Table 2 Water loss in smetite, illite, and organo-clay complexes according to the peak intensity of PY-GC

Temperature (°C)	Sample No. (integrated area of water peak)							
	Smectite	26	31	3	29	5	53	Illite
25–50	1602948	1802798	593345	3141436	6589344	8034883	230128	709887
50–150	4067787	4453416	1429900	3806630	9004035	17618800	376002	438296
150–250	1132917	1151754	370250	1940523	4772428	7443353	280976	379269
250–350	433605	1346258	170016	1657998	3060316	2369024	312282	441364
350–450	451721	1863378	353916	3246817	3978957	3131028	504858	634800
450–550	664134	4069968	1118796	5177099	8193866	7050926	694687	849703
550–650	870710	1427462	660068	4019334	5078356	2732268	663010	1043907
Total	9223822	16115034	4696291	22989837	40677302	48380282	3061943	4497226
Water loss at 50–150°C/total water loss (%)	44	28	30	17	22	36	12	10
Water loss at 450–550°C/total water loss (%)	7	25	24	23	20	14	23	19
Total water loss at 50–150°C and 450–550°C (%)	51	53	54	40	42	50	35	29

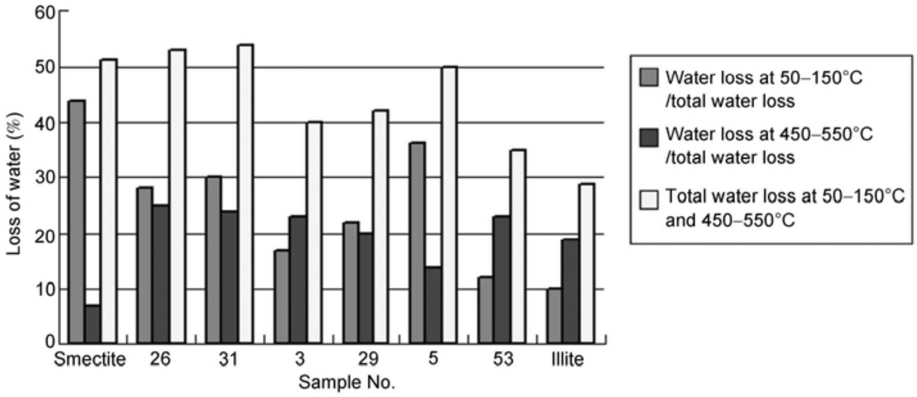

Figure 9 The dehydration diagram of organo-clay complexes and clay minerals by PY-GC analysis.

mineral composition and different TOC, water loss from samples 31 (TOC, 0.05%) and 26 (TOC, 9.78%) were 30% and 28% at 50–150°C, and 24% and 25% at 450–550°C respectively, very close to each other. For samples with similar TOC and different clay mineral composition, water loss from sample 3 (S/I, 70) and 5 (S/I, 30) were 17% and 36% at 50–150°C and 23% and 14% at 450–550°C respectively, showing very large differences between each other. Either way, if there was smectite in organo-clay complexes, part of interlayer water would delay to expel.

3.3 Significance of interlayer water delayed expulsion

The desorption order in smectite is sorption water, interlayer water, and constitution water, whereas the order in organo-clay complexes is sorption water, interlayer water, interlayer water bound by interlayer organic matter, and constitution water, indicating a tight association between the interlayer organic matter and the interlayer water. Studies have showed that interlayer water acts as "bridges" binding smectite and organic matter together, called water bridges [35, 37, 46]. Because of this water bridge mechanism, dehydration temperature and water loss in organo-clay complexes were totally different from that in pure smectite. Only after interlayer organic matter was expelled was the interlayer water as bridges desorbed to cause a dehydration peak at 550°C on DTA curves and a dehydration peak on PY-GC curves. This was also the reason why part of interlayer water delayed to dehydrate, revealing a close association among smectite, interlayer water, and interlayer organic matter.

In sediments, smectite transforms to illite with depth accompanied by interlayer water dehydration, as supported by calorimetry study [24]. For organo-clay complexes of source rocks, some interlayer water may be expelled during illitization of smectite, and some would remain as water bridges in association with intercalated organic matter. Simulation experiments for hydrocarbon generation have proved that hydrocarbon amounts increased in hydrous pyrolysis [47]. Therefore, sequential desorption of interlayer organic matter and water from organo-clay complexes in source rocks improved hydrocarbon generation efficiency, resulting in a hydrocarbon generation threshold of source rocks being close to the water desorption depth of smectite in many oil fields [25]. Expulsion by compaction plays an important role in petroleum migration. However, as organic matter intercalated into smectite interlayer, some interlayer water delayed to expel at 550°C. Consequently, smectite of organo-clay complexes is capable of releasing part of interlayer water in deep stratum, which provides a good medium for hydrocarbon migration.

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