Clay diagenesis in the Kimmeridge Clay Formation, onshore UK, and its relation to organic maturation

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Abstract

Conversion of randomly ordered illite–smectite to ordered illite–smectite in the Upper Jurassic Kimmeridge Clay Formation from the North Sea has been recorded in the literature as occurring within the 'oil window' and has been suggested as an indicator of oil source rock maturity. Studies of authigenic clay minerals in the fine fraction ($>0.5\ \mu m$) of the Kimmeridge Clay Formation mudstones from fourteen locations along the UK onshore outcrop between Dorset and North Yorkshire show that they comprise mainly ordered illite–smectites. The onshore Kimmeridge Clay section is organically immature, suggesting that the illite–smectite ordering reaction cannot be extrapolated between basins as an inorganic indicator of 'oil window' levels of maturity. These results also have important implications in source rock hydrocarbon expulsion and migration models which involve shale dewatering as a flushing agent. However, dewatering of shales may aid migration as it could cause fracturing of the shale bands separating the organic-rich layers within the source rock, prior to hydrocarbon generation.

KEYWORDS: clay diagenesis, Kimmeridge Clay Formation, illite, smectite, organic maturation.

Introduction

THE Upper Jurassic Kimmeridge Clay Formation from the onshore United Kingdom is an ideal subject for geochemical study of burial diagenesis in organic-rich mudstones. The formation shows remarkable continuity along the whole of the 200 km outcrop strip from the Dorset coast type section to North Yorkshire (Fig. 1) and has a well-known stratigraphy (Chadwick, 1985), being subdivided into 48 beds defined on palaeontological and lithological changes within the standard ammonite zones (Gallois and Cox, 1976; Gallois, 1979a; Cox and Gallois, 1981). Deposition took place during a period of eustatic rise (Hallam, 1984), which, coupled with tectonic subsidence (Sellwood et al., 1986), gave rise to a relatively uniform depositional environment over the whole outcrop. Localized facies variations in the mudstones resulted from: (i) variations in detrital clay and carbonate inputs relative to organic input giving changes in overall lithology from organic-rich to carbonate-rich mudstones; (ii) sedimentation rate variations reflecting the overall Jurassic basin and swell subsidence pattern (Hallam, 1958; Hallam and Sellwood, 1976), resulting in variable dilution and preservation of the organic matter flux; and (iii) maximum burial depth variations affecting the level of both clay diagenesis and organic maturation. The organic matter content of the mudstones appears to be independent of the lithology, being determined by detrital dilution by clay and carbonate minerals and by subsequent diagenesis (Williams and Douglas, 1983; Farrimond et al., 1984).

By studying the mineralogy of a particular bed along the outcrop, the interaction of these parameters and their effects on the diagenetic reactions can be assessed. The aim of this paper is to study the clay diagenesis of four beds of differing lithology in the onshore Kimmeridge Clay outcrop and subcrop and make comparison with the more deeply buried Kimmeridge Clay section from the North Sea, where it is the major oil source rock (Fuller, 1975; Barnard and Cooper, 1981; Reeder and Scotchman, 1985).

Studies of the clay mineralogy from several

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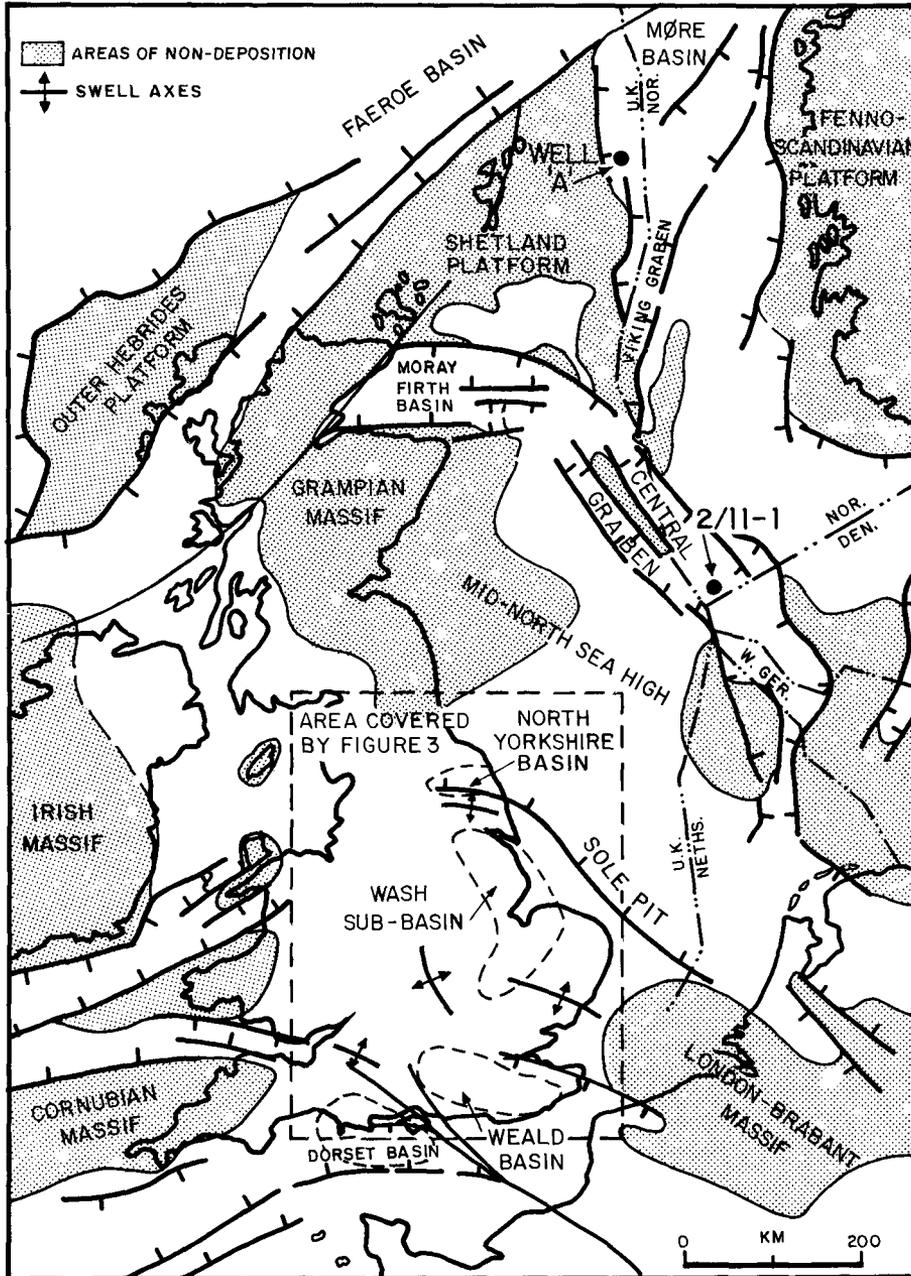
FIG. 1. Location map showing Upper Jurassic tectonic setting of the North Sea area (adapted from Ziegler, 1982).

sedimentary basins have established the progressive illitization of smectite with depth as the dominant clay reaction during diagenesis, with the formation of chlorite at greater depths (Burst, 1969; Hower et al., 1976; Jennings and Thompson, 1986). The illitization reaction is therefore a potentially sensitive indicator of thermal maturation (Castano and Sparks, 1974; Smart and

Clayton, 1985) and as such has been proposed as an inorganic indicator of oil maturity (Heroux et al., 1979; Foscolos and Powell, 1980).

To compare clay diagenesis and organic maturation in the onshore Kimmeridge Clay and test the applicability of this relationship, study was made of stratigraphically laterally continuous Bed 32; also investigated were the effects of sedimentation rate, burial depth and porewater chemistry on clay mineral diagenesis and associated kerogen maturation to gain some insight into controls on these reactions. The bed, which lies at the top of the A. Eudoxus Zone (Fig. 2), comprises an
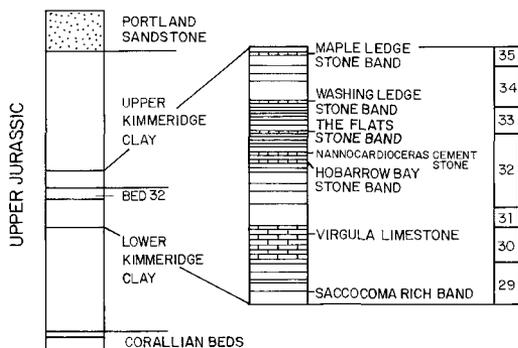

FIG. 2. Kimmeridge Clay type section from Dorset showing position of Bed 32.

oil shale with in intercalated beds of medium grey, sparsely shaly mudstones (Gallois and Cox, 1976; Gallois, 1979a) and represents a minor transgressive phase in the Lower Kimmeridgian, being deposited when sedimentation rates were at a maximum (Penn et al., 1986). Bed thickness was used to gain comparison of sedimentation rate between locations as the bed is a time unit assuming compaction effects are equivalent while maximum burial depths for the Kimmeridge Clay have been estimated (Fig. 3). The overall lithology of the bed, which ranges from calcareous in the thinner, swell sections to organic-rich and carbonate-poor in the thicker, basinal sections, gives an indication of pore-water chemistry, with the former tending to be alkaline and the latter acidic.

Geological background

The Kimmeridge Clay Formation comprises a cyclic mudstone sequence (Gallois, 1979b) which shows considerable variations in thickness and in facies along the length of the outcrop. The maximum thickness of about 500 m is attained in the
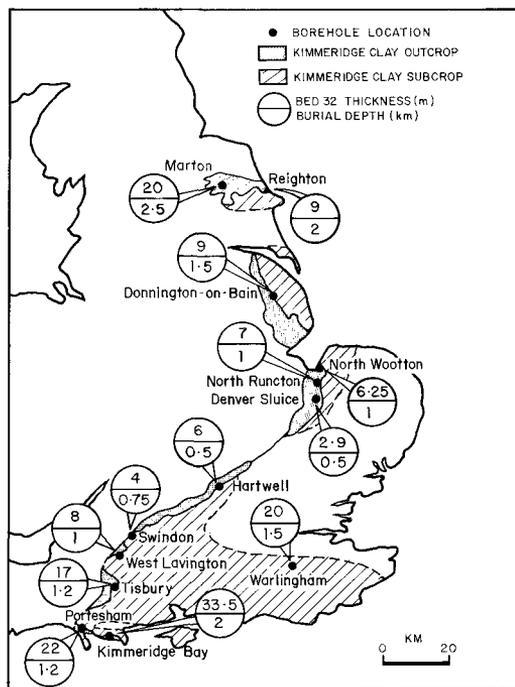

FIG. 3. Location map showing the Kimmeridge Clay distribution.

Kimmeridge Bay area (Arkell, 1947) with dramatic thinning over the flanks of the London landmass to about 40 m in South Norfolk (Gallois, 1979b). This attenuation reflects both tectonic control on subsidence and post-Jurassic erosion. A thick section of about 300 m is preserved in the North Yorkshire Basin, north of the Market Weighton swell, where the mudstones are silty and very organic-rich (Gallois, 1979b).

The effect of tectonic control on both thickness and mudstone facies is evident, the former being expressed as lateral thickness variations within the time-equivalent beds, reflecting real variation in sedimentation rate between the basinal and swell areas and the latter as gross lithology changes. These lithology changes are from the overall organic-rich, carbonate-poor facies with thick oil shale seams of the basins to the carbonate-rich, generally organic-poor mudstones with thin, poor quality oil shale bands which typify the swell areas. The thinner sections also contain numerous erosional breaks and condensed sequences within the overall calcareous mudstone facies (Gallois, 1979c). The Kimmeridge Clay displays a cyclic sequence in the onshore section, generally from organic-rich to calcareous and from less to more silty. This cyclic character can be recognized from

gamma ray and sonic logs (Gallois, 1973; Whit-taker *et al.*, 1985; Penn *et al.*, 1986) and can be used to aid correlation between boreholes along the outcrop. The cyclic sequence appears to repre-sent a relatively shallow water depositional envir-onment with the overall calcareous mudstone facies representing the more marginal sequence. In comparison, the much thicker 'Kimmeridge Clay' of the Central and Viking Grabens of the North Sea does not appear to display this charac-teristic cyclic log sequence. Caution must be used when correlating between the onshore and the offshore sections as the 'Kimmeridge Clay Forma-tion' offshore is not a rigidly defined chronostrati-graphic unit, comprising the equivalent of the Oxford Clay through to the top of the Lower Cre-taceous Ryazanian Zone (Dore *et al.*, 1985).

Burial depth is also a major control on both diagenesis and organic maturation in the Kimmer-idge Clay. It follows the overall pattern of Jurassic basin and swell topography although Tertiary Alpine-age inversion tectonics and consequent erosion have dramatically affected Southern Eng-land and North Yorkshire (Whittaker, 1985).

Sampling

Core samples were analysed from fourteen onshore cored boreholes (Fig. 3), ten of which were drilled for the Institute of Geological Sciences (now British Geological Survey)/De-partment of Energy Oil Shale Resource Study in 1975 to 1978 (Gallois, 1976*a*; 1978; 1979*b*) and from two offshore wells: well 2/11-1 in the Norwe-gian section of the Central Graben (Norwegian Petroleum Directorate, 1977) and well 'A' in the East Shetland Basin.

Four beds were studied in the onshore section: Bed 18, a calcareous mudstone with a band of concretions near the top; Bed 24, a silty calcar-eous mudstone; Bed 32, an alternating sequence of calcareous mudstone and organic-rich mud-stone with oil shale bands and Bed 44, a calcar-eous mudstone. Representative samples were taken from the top, middle and bottom of each bed (where present) in each borehole. A more complete study was made of Bed 32 from the Har-twell Borehole and Beds 32 and 44 from the Mar-ton Borehole.

Methods

The samples were prepared for X-ray diffrac-tion analysis by first crushing in a pestle and mor-tar to 1–2 mm size followed by disaggregation in distilled water and separation of the 0.5–8.0 μm size fraction using a sedimentation tube. The

<0.5 μm size fraction was collected by centrifug-ing the supernatant liquid and the clays were saturated with Mg cations to unify and optimize the basal expansion of smectite minerals. Simple orientated smear mounts on glass slides were then prepared. X-ray diffraction analysis was per-formed over the range 4 to 31° 2θ using Cu-$K\alpha$ radiation of wavelength of 1.521838 Å (Brown, 1980) with a nickel filter and scan rate of 1° 2θ per minute.

To aid in mineral identification, three diffracto-grams were made from each sample, the first in the air-dried state, the second following glycola-tion with ethylene glycol at 60 °C for 1 hour and the last after heating in a furnace for an hour at 550 °C. In addition, geochemical analyses involv-ing virtinite reflectance, visual kerogen analysis and Rock–Eval pyrolysis were carried out on the central sample from Bed 32 in each borehole and from the offshore wells.

Interpretation of X-ray diffractograms

Relative percentages of the major clay minerals present, illite, mixed-layer illite–smectite and kaolinite were determined from the peak areas using a planimeter. While the peak area approxi-mates to the amount of the mineral present it is only a semi-quantitative measure, depending on the intensity of reflection (Johns *et al.*, 1954) but as the procedure was standardized, the method indicates internally consistent compositional var-iations within the sample set (Schultz, 1964).

The illite and kaolinite (001) peak areas were measured between 7.5° and 10.5° 2θ and 10.5° and 13.0° 2θ respectively, the latter also incorpor-ating the chlorite (002) peak. The smectite peak area was determined from the change in areas of the basal (001) peak between 5.5°, and 9° 2θ between the glycolated and air dried diffracto-grams. This comparison is possible as the glycola-tion treatment does not affect the surface and orientation factors of the mounted samples leav-ing the baseline unaffected, allowing the peak area changes to be directly measured.

Results

The analyses show that the Kimmeridge Clay is composed of mixed layer illite–smectite, vari-able amounts of kaolinite and minor chlorite (Table 1), the percentage of smectite in the illite–smectite varying both between the beds and later-ally and vertically within them. Two types of illite–smectite pattern can be recognized from the glycolated diffractograms. The majority of sam-ples show a strong, well defined illite peak at

about 9.8 Å with a 'tail' and minor peak at 13–14 Å, representing the smectite component and an illite content of over 50%.

Using the definitions of Reynolds and Hower (1970) and Pearson *et al.* (1982) and comparison with diffractograms published by Hower *et al.* (1976) and Foscolos and Powell (1979) these were identified as ordered illite–smectites (Fig. 4*a*). The second type is illustrated by a small number of samples, particularly those from Marton borehole which have an illite content of less than 50%, a weaker illite peak at 9.8 Å and a weak 'bulge' at 17 Å. These were identified as randomly ordered illite–smectites (Fig. 4*b*). Only one sample, that from Well 'A' in the East Shetland Basin, has a strong 17 Å peak indicating a very high smectite content and a very low illite content of 6% (Fig. 5*a*). The most 'mature' clay mineral assemblage is seen in samples from Norway 2/11-1 well in the North Sea Central Graben which have very little smectite (16%) in ordered illite–smectites (Fig. 5*b*). Chlorite is present only in minor amounts and occurs largely as an amorphous phase as it is destroyed in most cases on heating to 550 °C.

Variations in the proportion of smectite in the illite–smectite occur not only between beds but also within them. The majority of samples comprise ordered illite–smectites with less than 50% smectite, as illustrated by the sample from Warlingham borehole Bed 44 at 736 m (Fig. 4*b*). Random ordered illite–smectites with more than 50% smectite predominate in the Marton Borehole while several samples from Bed 32 at Reighton and Bed 44 from the Hartwell and Donnington-in-Bain boreholes show random ordering. The sample from Marton borehole Bed 32 at 127.15 m (Fig. 4*a*) shows a random ordered illite–smectite pattern typical of many of the samples. The amount of smectite varies considerably with depth in all locations but generally shows no overall systematic variation, with relatively large variations in smectite content occurring within the bed. The exception appears to be Bed 32 at Marton where smectite decreases with depth.

The amount of kaolinite present in the samples, as reflected by the illite:kaolinite ratio, varies between 0.06 and 2.40. The majority of samples are illite-rich but in the Marton and Reighton boreholes kaolinite becomes dominant, particularly in the former. As with smectite content, a wide variation in the illite:kaolinite ratio is apparent within the beds.

Vitrinite reflectance (%Ro), the T_{max} and total organic carbon values from Rock-Eval pyrolysis and the kerogen compositions from Bed 32 are presented in Table 2. Vitrinite reflectance and T_{max} show no apparent trend with smectite content. No trends in organic maturity are seen between basins and swells in the onshore section although maturity is increased in the samples from the North Yorkshire basin at Marton and from the North Sea Central Graben. In the former case, the smectite content increases to 60% while in the latter it is low at 16%.

Discussion

Clay mineralogy. The results show that the clay mineralogy of the Kimmeridge Clay Formation mudstones from both the onshore and offshore sections comprises dominantly mixed layer illite–smectites with variable amounts of kaolinite and minor chlorite. The illite and smectite end members are not present, although a wide compositional range of 16 to 94% smectite in illite–smectite can be seen. The mixed layer illite–smectites exhibit random and ordered structures, often in adjacent samples interspersed within the same bed unit.

Within Bed 32, ordered illite–smectite is dominant along the outcrop except in the Marton borehole where random ordering predominates. The other beds show larger variations in the degree of ordering with more widespread occurrence of interspersed random ordered illite–smectite, probably in response to the more varied lithologies present (Smart and Clayton, 1985).

The smectite percentage in the illite–smectites from Bed 32 shows no relationship with either sedimentation rate as represented by bed thickness or with burial depth. With burial depth, the majority of samples are grouped between 45 and 65% illite (Fig. 6) except for the Marton and offshore well samples which appear to lie on a positive trend. This indicates that illitization in the majority of samples has proceeded to similar levels regardless of burial depth, only the deeply burial Central Graben sample showing a strong degree of illitization. This interpretation of the results may indicate either: (i) a detrital source mineralogy of mixed layer composition illite 40%: smectite 60%, or (ii) an original smectite input which has been illitized due to burial diagenesis, as suggested from Bed 18 of the North Wootton borehole (Merriman and Strong, 1979) where the original smectite input has been preserved from further illitization within a concretion.

The strong group of samples in Fig. 6 is probably partly due to poor geological control on burial depth as evidenced by the poor correlation of illite composition with Jurassic basin topography, wells with good depth control (offshore North Sea and Marton borehole) lying on the same trend. The
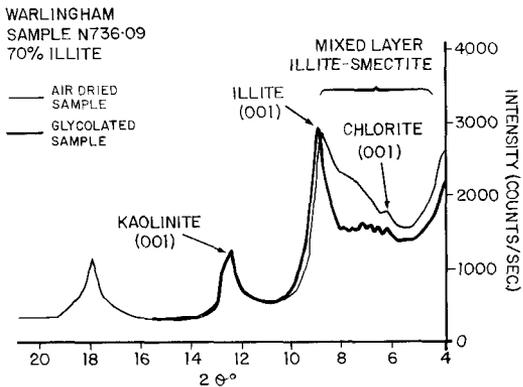
TABLE 1. Mineral analyses of Kimmeridge Clay

LOCATION	SAMPLE	% ILLITE	MEAN	% SMECTITE	MEAN	ILLITE:KAOLINITE	MEAN
BED 44							
ENCOMBE	M97.00 / M105.50 / M114.50	67 / 57 / 67	64	33 / 43 / 33	36	0.49 / 0.42 / 0.70	0.54
PORTESHAM	K25.5 / K34.5 / K44.5	66 / 61 / 62	63	34 / 39 / 38	37	0.37 / 0.52 / 0.71	0.53
TISBURY	F130.40 / F142.00 / F154.50	68 / 58 / 69	65	32 / 42 / 31	35	0.79 / 0.88 / 0.60	0.76
HARTWELL	B33.25 / B35.75 / B39.50	40 / 25 / 51	39	60 / 75 / 49	61	0.95 / 1.56 / 0.80	1.10
WARLINGHAM	N736.09 / N745.45 / N754.09	70 / 54 / 68	64	30 / 46 / 32	36	0.30 / 0.58 / 0.38	0.42
NORTH RUNCTON	H15.25 / H17.25 / H19.50	54 / 42 / 70	62	46 / 58 / 30	38	0.66 / 0.96 / 0.24	0.62
NORTH WOOTTON	A27.30 / A29.40 / A33.00	45 / 52 / 45	47	55 / 48 / 55	53	1.06 / 0.84 / 0.55	0.82
DONNINGTON-ON-BAIN	D34.50 / D37.50 / D41.50	50 / 44 / 47	43	50 / 56 / 53	53	0.65 / 0.81 / 0.60	0.69
MARTON	C13.80 / C16.40 / C18.65 / C20.85 / C27.80 / C29.15 / C31.70 / C33.50	23 / 50 / 38 / 45 / 53 / 53 / 35 / 47	43	77 / 50 / 62 / 55 / 47 / 47 / 65 / 53	57	2.40 / 1.22 / 1.53 / 0.88 / 0.86 / 0.54 / 1.52 / 0.71	1.21
BED 32							
KIMMERIDGE BAY	C59.25 / C61.75 / C64.75	61 / 69 / 63	64	39 / 31 / 37	36	0.77 / 0.56 / 0.60	0.64

LOCATION	SAMPLE	% ILLITE	MEAN	% SMECTITE	MEAN	ILLITE:KAOLINITE	MEAN
PORTESHAM	K134.49 / K139.24 / K144.49	62 / 63 / 65	63	38 / 37 / 35	37	0.78 / 0.72 / 0.71	0.74
TISBURY	F228.0 / F231.5 / F237.5	64 / 61 / 71	65	36 / 39 / 29	35	0.71 / 0.72 / 0.66	0.70
WEST LAVINGTON	J153.25 / J156.25 / J159.5	46 / 46 / 53	49	54 / 54 / 47	51	0.99 / 0.93 / 0.59	0.84
SWINDON	L77.25 / L81.35	61 / 62	61	39 / 38	39	0.52 / 0.39	0.46
HARTWELL	B48.25 / B48.75 / B49.25 / B49.75 / B50.25 / B50.75	51 / 51 / 43 / 37 / 54 / 55	48	49 / 49 / 57 / 63 / 46 / 45	52	0.74 / 0.60 / 0.85 / 0.69 / 0.66 / 0.66	0.70
WARLINGHAM	N829.06 / N830.58 / N834.06	65 / 67 / 68	67	35 / 33 / 32	33	0.42 / 0.36 / 0.43	0.42
DENVER SLUICE	I16.70 / I17.40 / I19.30	61 / 57 / 71	63	39 / 43 / 29	37	0.69 / 0.48 / 0.57	0.58
NORTH RUNCTON	H45.25 / H48.25 / H51.50	59 / 52 / 60	57	41 / 48 / 40	43	0.44 / 0.60 / 0.46	0.50
NORTH WOOTTON	A60.30 / A63.00 / A66.30	59 / 50 / 62	57	41 / 50 / 38	43	0.61 / 0.79 / 0.48	0.63
DONNINGTON-ON-BAIN	D86.25 / D90.25 / D94.75	47 / 52 / 61	53	53 / 48 / 39	46	1.03 / 1.14 / 0.57	0.91
REIGHTON	E116.43 / E120.25 / E124.75	45 / 49 / 60	51	55 / 51 / 40	49	1.06 / 0.95 / 0.54	0.85

TABLE 1 (cont.)

LOCATION	SAMPLE	% ILLITE	MEAN	% SMECTITE	MEAN	ILLITE:KAOLINITE	MEAN
MARTON	C122.30	21		79		2.29	
	C126.30	35		63		1.30	
	C127.15	39	40	61	60	1.29	1.35
	C128.63	39		61		0.75	
	C132.28	39		61		1.30	
	C134.05	46		54		1.81	
	C135.85	46		54		1.47	
	C137.28	39		61		1.31	
	C139.29	57		43		0.61	
BED 24							
PORTESHAM	K203.00	56		44	-	0.82	-
TISBURY	F268.75	61	-	39	-	0.60	-
WEST LAVINGTON	J185.75	52	-	48	-	0.66	-
SWINDON	L89.75	50	-	50	-	0.53	-
HARTWELL	B60.68	55	-	45	-	0.50	-
DENVER SLUICE	133.90	48	-	52	-	0.55	-
NORTH RUNCTON	H73.75	55	-	45	-	0.44	-
NORTH WOOTTON	A86.60	50	-	50	-	0.49	-
DONNINGTON-ON-BAIN	D113.75	32	-	68	-	1.60	-
BED 18							
WEST LAVINGTON	J195.75	66		34		0.29	
	J197.25	56	67	44	33	0.41	0.34
	J199.75	79		21		0.31	

LOCATION	SAMPLE	% ILLITE	MEAN	% SMECTITE	MEAN	ILLITE:KAOLINITE	MEAN
HARTWELL	B62.25	53		47		0.20	
	B62.75	52	56	48	44	0.28	0.24
	B63.50	63		37		0.24	
WARLINGHAM	N900.50	63		37		0.25	
	N905.56	44	55	56	45	0.06	0.15
	N908.50	59		41		0.13	
DENVER SLUICE	143.40	38		62		1.00	
NORTH RUNCTON	H85.25	56		44		0.36	
	H87.25	51	53	49	47	0.42	0.32
	H89.50	53		47		0.19	
NORTH WOOTTON	A96.00	66		34		0.25	
	A97.80	54	61	46	39	0.50	0.36
	A100.2	64		36		0.32	
DONNINGTON-ON-BAIN	D150.25	49		51		0.36	
	D154.75	43	51	57	49	0.70	0.48
	D159.50	60		40		0.37	
REIGHTON	E150.25	64		36		0.32	
	E152.25	44	54	56	46	0.66	0.46
	E154.75	53		47		0.39	
NORTH SEA							
WELL A	1920.2	2	-	98	-	0.38	-
NORWAY 2/11-1	3863.9	86		14		0.26	
	3871.0	75	82	25	18	0.57	0.24
	3875.5	84		16		0.21	

A. ORDERED ILLITE-SMECTITE

WARLINGHAM
SAMPLE N736·09
70% ILLITE

A. RANDOM ORDERED ILLITE-SMECTITE

WELL A
1920.2m (6300')
6% ILLITE

B. RANDOM INTERLAYERED ILLITE-SMECTITE

MARTON
SAMPLE C127·15
39% ILLITE
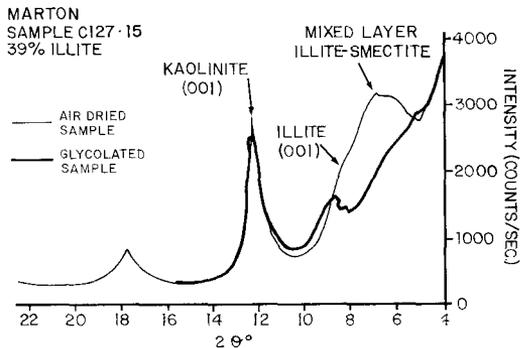
FIG. 4. Clay mineral diffractograms from the onshore Kimmeridge Clay.

B. ORDERED ILLITE-SMECTITE
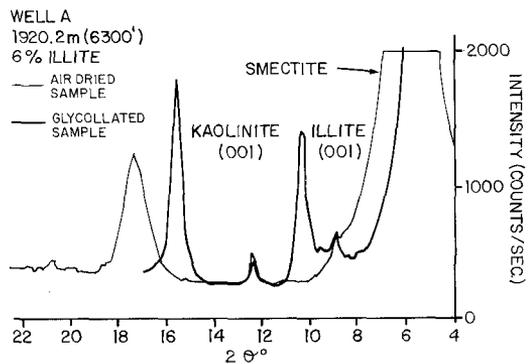
NORWAY 2/11-1
3875.5 (12,715')
84% ILLITE
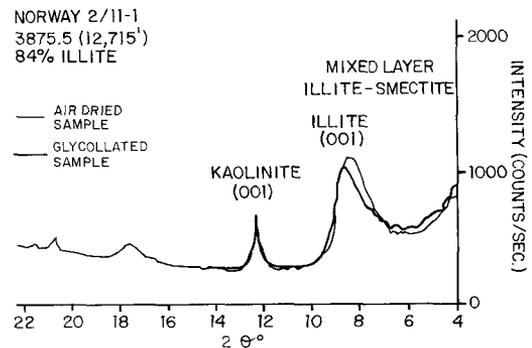
FIG. 5. Clay mineral diffractograms from the offshore Kimmeridge Clay.

two offshore wells are probably currently at maximum burial depth while at Marton the amount of post-depositional uplift has been estimated from shale sonic log velocities (Marie, 1975; Whittaker *et al.*, 1985) and from mineralogical evidence (Hemingway and Riddler, 1982). In the other locations the maximum burial depth is much more poorly controlled and has been estimated from the probable thickness of post-Jurassic sediments in each location. As much of southern and eastern England has suffered basin inversion in the early Tertiary (Whittaker, 1985), with consequent erosion of much of the post-Jurasssic section, these estimates probably represent minimum burial depths.

Small-scale variations in the degree of illitization are apparent within beds as illustrated by Bed 32 at Marton where illite increases with depth over the 20 m interval from 21% to 57% (Fig. 7). The illite : kaolinite ratio shows also great variability, ranging from 0.61 to 2.24. Similar small-scale variations in the illite content have been observed

in other shale sequences such as the Tertiary of the Gulf Coast of the USA (Gorsline, 1985) while Velde and Nicot (1985) report fluctuations in mixed-layer clay compositions of up to 20% smectite. It is therefore apparent that very fine controls can greatly affect the progress of the illitization reaction.

A further diagenetic reaction noted in all samples, except those from Marton, is the disappearance of kaolinite as burial depth increases and the appearance of chlorite. In particular, the Bed 18 samples have a very small kaolinite peak. Similar trends have been reported by Van Moort (1971) while Jennings and Thompson (1986) note the appearance of chlorite as kaolinite disappears, suggesting a probable diagenetic reaction pathway.

Similar results have been obtained by other workers who have studied the mineralogy of the onshore Kimmeridge Clay (Tank, 1964; Perrin, 1971; Merriman and Strong, 1979; Merriman and Jeans, 1979). Parker (1974) and Dypvik (1984)

TABLE 2. BED 32: ORGANIC GEOCHEMISTRY RESULTS

SAMPLE	% Ro	T_{max} (°C)	TOTAL ORGANIC CARBON (Wt%)	KEROGEN COMPOSITION (%)		
				AMORPHOUS	HUMIC[1]	INERTINITE
G59.25	0.49	425	5.8	60	30	10
K139.49	0.46	427	2.3	50	39	11
F237.50	0.54	418	4.6	65	25	10
J153.25	0.47	418	5.9	65	25	10
L77.25	0.46	413	1.8	55	25	20
B50.75	0.44	417	8.1	60	30	10
N830.58	0.53	429	1.7	53	36	12
I19.30	0.59	412	4.4	65	30	5
H45.25	0.52	418	2.0	59	30	12
A66.30	0.58	418	4.0	65	24	12
D94.75	0.45	424	1.8	60	27	13
E124.75	0.52	426	2.1	56	34	11
C132.75[2]	0.46	437	9.4	55	40	6
WELL A	0.49	411	5.5	47	42	11
N2/11-1	0.58	430	4.7	68	23	9

1. Includes spores, pollen, plant, tissue, vitrinite, etc.
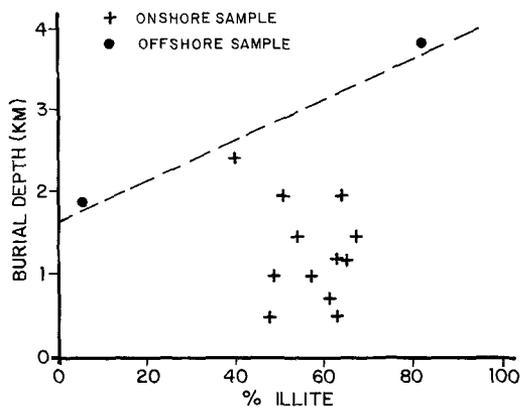
2. Bitumen present in sample.

FIG. 6. Bed 32—relation of illite % to burial depth.

FIG. 7. Variation of clay mineralogy with depth—Bed 32, Marton.

both report a broadly similar clay mineralogy in the Early Cretaceous Speeton Clay which overlies the Kimmeridge Clay in the North Yorkshire section. Kaolinite increases with depth in the section while illite decreases and the mixed-layer clays become more smectitic, suggesting that the clay mineralogy trends observed in the Kimmeridge Clay continue up into the Speeton Clay.
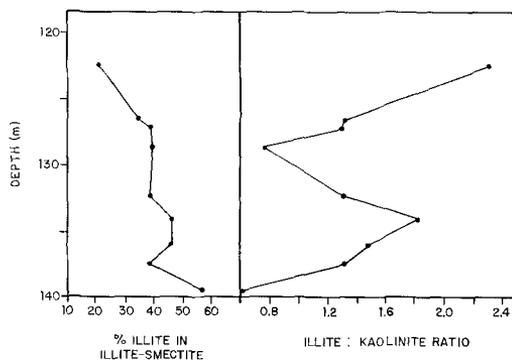
In the offshore Kimmeridge Clay section Bjørlykke *et al.* (1975) report a similar illite, kaolinite and mixed layer illite-smectite composition to the onshore samples. In the Viking Graben, where the mudstones range from over 1200 m thick in the basin centre to less than 150 m in the graben flanks, they found the kaolinite content as shown by the kaolinite : illite ratio to be lower in the graben samples than in those from the flank,

indicating a decrease in kaolinite with respect to illite with burial depth as seen in the onshore samples.

Comparable diagenetic trends, in particular the decreasing expandable content of illite–smectite with increasing burial depth and the change from random to ordered illite–smectite, have been well documented in the literature (Burst, 1969; Perry and Hower, 1970; Hower et al., 1976), suggesting that the reaction is commonplace in deeply buried shales.

Palaeotemperatures and palaeogeothermal gradients

The dominant mineralogy of ordered illite–smectite of the Kimmeridge Clay samples can be used to estimate temperatures attained during burial. The disappearance of smectite and the formation of ordered illite–smectites have been reported over a wide temperature range. The loss of smectite commonly occurs over the 65–75 °C range (Heling, 1974; Dypvik, 1983) with ordering at 80–100 °C (Hower et al., 1976; Pearson et al., 1982; Dypvik, 1983). Much wider temperature ranges have also been reported with smectite disappearance over the 50–150 °C range (Weaver, 1978), in excess of 150 °C (Bruce, 1984) or over the very large 70 to 210 °C range (Jennings and Thompson, 1986). Therefore, by analogy and assuming an authigenic mineralogy (discussed below), the onshore Kimmeridge Clay must have attained a minimum palaeotemperature of 45–75 °C to account for the lack of pure smectite in the shallowest buried parts of the section and, more likely, 80–90 °C to attain the dominant ordered illite–smectite assemblage.

This suggests that, assuming the average present-day geothermal gradient of 30 °C/km for the onshore UK (Richardson and Oxburgh, 1978), burial depth must have attained 2.5 to 3 km over the whole section, which appears rather high, particularly for the South Midlands area. Therefore the palaeogeothermal gradient in the Early Cretaceous and Tertiary must have been somewhat higher than that of today, such as the 45 °C/km of the Kimmeridge Clay in the Winterborne Kingston Borehole, Dorset (Bloomer et al., 1982) or the 45–50 °C/km found in the present-day Viking Graben flanks in the Northern North Sea (Carstens and Finstad, 1981). Assuming an average surface temperature of 20 °C this would give a maximum burial depth of 1400 m which is a more reasonable estimate on geological grounds (Gallois, 1979b).

Origin of ordered illite–smectites

Two sources of the ordered illite–smectites are possible: authigenic or detrital. Due to the very fine grained fraction of the samples studied (<0.5 μm) the ordered illite–smectites are likely to be authigenic as diagenetic reaction products predominate in the very finest fractions of mudstones (C. D. Curtis, pers. comm.). This has been confirmed by age determination studies on various size-fractions of mudstones by several workers. Perry (1974) and Aronson and Hower (1976), using the K–Ar method, showed that detrital illites in Tertiary mudstones from the Gulf Coast of the USA were largely confined to the coarser size fractions of greater than 1 μm in size with authigenic mixed layer illite–smectites dominating the <0.5 μm and <0.1 μm fractions respectively. Rb—Sr studies by Morton (1985a,b) on Oligocene Shales from the Gulf Coast and on Upper Devonian shales from Texas again showed the fine fraction (<0.2 μm) illites to be authigenic by their much younger ages than coarse fraction (2–1 μm) illites. A high, detrital ordered illite–smectite input would therefore only be apparent in the coarser size fractions of a shale (Gibbs, 1977). Finally, and perhaps more circumstantially, very fine grained authigenic illites are common in sandstones (Almon et al., 1976; Hancock and Taylor, 1978; McHardy et al., 1982). This evidence also appears to support the hypothesis that fine fraction illite–smectites are authigenic in origin.

The ordered illite–smectites in the <0.5 μm fraction studied are therefore likely to be authigenic in origin, suggesting that deep burial diagenesis of the mudstones has taken place. Nevertheless, a small, fine-grained detrital illite–smectite component is apparent in many of the ordered illite–smectite samples as shown by the distinct illite peak on the diffractograms. Therefore, while a detrital origin for the ordered illite–smectites are suggested by the strong grouping of illite composition cannot be ruled out, from the evidence cited above an authigenic origin appears more likely. Resolution of the problem can only be made by resorting to age-determination methods.

Controls on the illitization reaction

While temperature has been cited in the literature as the main control on the illitization reaction (Perry and Hower, 1972; Foster and Custard, 1983; Hower et al., 1976; Weaver, 1978), the high smectite content and random ordered structure of the illite–smectites from the deeply buried Marton section, which indicate that the illitization

reactions has been retarded or even reversed, suggest a further fundamental control on the reaction. The random ordered illite–smectites at Marton are associated with higher kaolinite contents than in other samples. Mechanisms such as (i) sediment age; (ii) pressure; (iii) burial rate; (iv) sedimentation rate; (v) smectite composition; (vi) increased detrital smectite input; (vii) residence time at elevated temperatures or (viii) porewater chemistry could be invoked to account for the observed anomalous smectite content:

(i) McCubbin and Patton (1981) found sediment age to be a possible control on the illitization reaction, but this can be discounted as the samples from Bed 32 are of the same age and show a wide range of smectite contents.

(ii) Increased pressure through burial is a further possible control on the illitization reaction. Velde and Nicot (1985) have shown that differences between hydrostatic and lithostatic pressures could explain variations in clay-mineral assemblages. This mechanism cannot be used to explain the high smectite contents of the Marton section as both shallower and more deeply buried sections contain ordered illite–smectites.

(iii) McCubbin and Patton (1981) also cite burial rate as a control. Burial rate is unlikely to have retarded the illitization reaction as samples from the Central Graben with a higher burial rate than at Marton contain ordered illite–smectites with little smectite.

(iv) Howard (1980) has cited high sedimentation rates as an influence on the rate of diagenetic conversion of smectite to illite. High sedimentation rates cause strong fluid migration from rapidly compacting mudstones, lowering the temperature and causing the random interlayered illite–smectites to react towards illite at a lower rate than in similar composition sediments deposited under a lower sedimentation rate regime. Fluctuations in the sedimentation rate could be invoked to explain the alternation of more ordered to more random interlayering seen in boreholes such as Marton, but this seems unlikely within the confines of a single bed. Sedimentation rate appears unlikely as an important control as the Central Graben mudstones from Norway well 2/11-1 probably had a higher rate than at Marton but contain ordered illite–smectites.

(v) Differences in the composition of the smectite could also have resulted in the low illite content of the Marton samples. Compositional variations have been shown to affect the degree of conversion to illite (Foster and Custard, 1983), low enthalpy smectites being converted to illite much more slowly than volcanic-origin smectites. This

appears unlikely as the detrital smectites would have had a grain size greater than 0.5 μm and so would not have affected the very fine fraction being studied. Also the diffractograms show that the smectite in the Marton samples have a similar composition to that from other locations.

(vi) An increased detrital smectite input into the North Yorkshire basin could account for the high smectite content of the Marton samples. Although this would probably only affect the coarser fractions of the mudstone, source effects have been noted in the fine fractions of Upper Jurassic mudstones of the Moray Firth (M. Pearson, pers. comm.) and from Tertiary mudstones of the Norwegian North Sea (Carstens and Karlsson, 1980), so this mechanism cannot be discounted.

(vii) Ramseyer and Boles (1986) suggest that residence time at elevated temperatures may be a controlling factor as they report a positive relationship between the smectite content in illite–smectite and the Time Temperature Index of Waples (1980).

(viii) The most likely mechanism for the retardation of the illitization reaction, with the preservation of random interlayered illite smectite and a high kaolinite content and localized variations in the smectite content, is a chemical one.

Chemical control on illitization

The illitization reaction requires an input of potassium ions and a lack of these ions will retard the reaction and favour kaolinite growth (Keller, 1964; Ramseyer and Boles, 1986). A lack of potassium ions is postulated for the North Yorkshire basin as strongly leaching and acidic conditions were prevalent in the deeply buried section as evidenced by the lack of carbonate in shell fragments and the large amounts of pyrite present in the black, very organic-rich mudstones. The strongly acidic conditions would have caused the rapid dissolution of potassium feldspars, which supply K ions to the illitization reaction, early in burial, leaving the porewaters K-depleted. With an insufficient potassium supply the conversion of random illite–smectite to ordered illite–smectite was 'frozen'. A similar retardation of the illitization of smectite has been documented in the Eocene of the North Sea Southern Viking Graben by Pearson et al. (1983) which they correlate with a lack of detrital feldspars and therefore K ions. The acidic conditions in the North Yorkshire Basin appear, therefore, to have favoured kaolinite authigenesis and caused the illitization reaction to cease: consequently the mudstones

retain an unusually high amount of expandable clay and are kaolinite-rich.

The preservation of random ordered illite–smectite and the predominance of kaolinite in the Marton section strongly suggests that porewater chemistry is an important control on the illitization reaction as a supply of K and Al ions are necessary for the conversion to take place. This is supported in the literature by the numerous observations of the disappearance of potassium feldspars over the zone of the active illitization (Hower *et al.*, 1976; Jennings and Thompson, 1986). Work by Velde (1985) also implies reduction of iron as an influence on the smectite content of mixed-layer minerals. In the onshore section, the illitization reaction appears to be most advanced in the carbonate-rich mudstones, where the porewaters were dominantly alkaline and potassium-rich.

Therefore, the illitization reactions appears to be both temperature and chemically controlled, the reaction apparently occurring earlier in the alkaline, potassium-rich porewaters of the calcareous mudstones than in the very acidic, potassium-poor porewaters of the very organic rich mudstones where it appears to have been retarded or even reversed: under the latter conditions much higher temperatures are required before the reaction can proceed, which could explain Bruce's (1984) results from the Niger Delta. The small scale vertical and lateral variations of smectite content within a bed can probably also be explained by changes in porewater chemical composition. However, caution must be used when applying this hypothesis to the Marton section as the lack of feldspar and hence K has not been demonstrated. Indeed, work by Dypvik (1984) shows the coarse fraction of a 10 m section of the Lower Kimmeridge Clay at Speeton to be rich in feldspar. Nevertheless, these results serve to illustrate the dependence of the illitization reaction on factors such as pore-water chemistry as well as burial temperature. A detrital source for the smectite in this section therefore cannot be overruled.

Kaolinite authigenesis in the North Yorkshire Basin

The higher kaolinite content of the North Yorkshire Basin mudstones was probably due to conditions which favoured the diagenetic growth of kaolinite rather than illite, causing the trend between these two minerals to be the reverse of that seen elsewhere. Keller (1964) and Staub and Cohen (1978) report that kaolinite forms in a high Al:Si ratio, acidic environment with extensive leaching causing potassium, magnesium, and iron to be absent. The North Yorkshire mudstones had a strong acidic, leached diagenetic environment due to the strong organic matter degradation taking place. Dissolution of feldspars provided Al and Si, while the leaching action of the porewaters removed Fe, Mg, and K, providing the ideal environment for kaolinite authigenesis. The relationship between carbonate dissolution and kaolinite precipitation, as seen in the North Yorkshire samples, has been discussed by Curtis (1983*a* and *b*), kaolinite being precipitated as the porewaters become less acidic. In the other areas onshore carbonate precipitation favoured illite authigenesis due to alkaline pore-water conditions which followed the cessation of organic matter degradation in the shallow buried mudstones (Scotchman, 1984). The replacement of illite by kaolinite in interlaminated sandstones and shales has been reported by Bucke and Mankin (1971), suggesting that the illitization could have been reversed in the North Yorkshire Basin with 'kaolinitization' of illite and preservation of smectite.

Kerogen composition

The kerogen compositions of the samples are very similar, comprising mainly amorphous kerogen with a variable amount of humic material (spores, pollen, plant fragments and vitrinite) and about 10% inertinite. The samples from the swells and basin margins contain larger amounts of humic kerogen and inertinite as would be expected, the basinal samples containing the most amorphous organic matter. These results suggest that the organic matter input was relatively constant across the basin, the majority being derived from marine sources. Similar kerogen compositions have been reported for the Kimmeridge Clay by Gallois (1979*b*) and Ebukanson and Kinghorn (1985).

The dominant kerogen facies is amorphous material as indicated by the small amount of vitrinite present: this would be expected on environmental grounds as the mudstones were deposited in relatively deep water with anoxic bottom conditions (Gallois, 1976*b*; Tyson *et al.*, 1979; Scotchman, 1984). The kerogen facies appears to be related to the organic richness, indicating control by the fluctuating oxic/anoxic boundary in the depositional waters (Scotchman, 1984; Ebukanson and Kinghorn, 1985). These conditions favoured the deposition and preservation of Type II amorphous kerogens, the Type III virtinites being relatively rare except in the marginal areas due to the distance from shore. The virtinites are

therefore allochthonous and of detrital origin, probably being reworked from older sediments as well as from Kimmeridgian land plants.

The organic geochemistry results show that the samples have a vitrinite reflectance range of 0.44 to 0.59% Ro indicating that the mudstones are immature. The results are problematic as some of the shallow buried mudstones, such as at Denver Sluice, have a similar vitrinite reflectivity to that from the deeply buried sample from the Norway 2/11-1 well.

The sample from Marton borehole contains bitumen filaments and appears to show the highest maturity levels although the vitrinite reflectivities measured were generally low. This is perhaps due to the vitrinite reflectivity being retarded by the presence of bitumen in the sample (Price and Barker, 1985).

In the North Sea, the well 'A' sample is immature with a vitrinite reflectivity of 0.49% while the shale from the Norway 2/11-1 well is of higher maturity at 0.58% Ro as befits its basinal location.

Similar vitrinite reflectivity values have been reported in the literature for the onshore Kimmeridge Clay (Williams and Douglas, 1981). Gallois (1979b) gives a range of 0.3 to 0.4% Ro for the oil shale bands with similar values of 0.31 to 0.36% Ro being reported for Kimmeridge Bay Section (Farrimond et al., 1984). Gallois (1979b) and Williams and Douglas (1979) report a trend of increasing organic maturity northwards from Dorset through Lincolnshire which is not supported by this study, the organic matter being immature over this section of the outcrop. Higher maturities are reported to the north from South Humberside (Dypvik et al., 1979) and North Yorkshire (Barnard and Cooper, 1983). Higher maturity levels are also postulated for the basinal area in the English Channel south of the Purbeck—Isle of Wight fault zone (Colter and Harvard, 1981).

The Rock-Eval pyrolysis T_{max} results range from 411–413 °C for the swell area mudstones and East Shetland Basin flank well 'A' to 424° to 437 °C for the basinal samples, the Marton sample showing the highest maturity at 437 °C. The deepest buried sample from the Norway 2/11-1 well shows a lower maturity with a T_{max} of 430 °C.

Analysis of the vitrinite reflectance and pyrolysis T_{max} values in a basinal context shows that neither is a satisfactory measure of organic maturity as they do not clearly reflect differences in burial depths (Fig. 8). The vitrinite reflectance results in particular were difficult to measure as only very small, often partially oxidized particles were present. Also, a very wide reflectivity range was obtained between 0.3 and 1.2% Ro from each

sample which could be divided into several populations. The most likely population was based on visual kerogen evidence and lay between 0.4 and 0.6% Ro. The small size of the vitrinite particles, their often partially oxidized state and the wide range of reflectance values obtained, suggests that much of the material is reworked from older sediments and therefore does not reflect the true level of maturity of the Kimmeridge Clay.

The T_{max} values show a much closer fit with basin topography (Fig. 8), the values from the swell areas being lower than those from the basins, as would be expected. The Marton sample has the highest maturity of 437 °C, higher than the 430 °C value from well 2/11-1 even though the burial depth is much greater than at Marton. This clearly illustrates that use of T_{max} as a maturity indicator is unreliable as it is affected by the presence of high maturity detrital humic kerogens which probably influenced the Marton result. Clearly, a measure of maturity is required for rocks with a dominant amorphous sapropel composition which will not be affected by the humic kerogen content which appears to reflect the maturity of the sediment source rather than the host mudstone.

The organic content of the Kimmeridge Clay samples studied are largely amorphous with potential for oil generation, the maturity based on vitrinite reflectance, T_{max}, and spore colour ranging from immature to the early oil generation stage with bitumen formation. The samples therefore appear to lie within the incipient oil generation zone as defined by Lewan (1985).

Comparison of clay diagenesis and organic maturation

The results of this study show a variable relationship between clay diagenesis and organic maturity both within the onshore Kimmeridge Clay section and between the onshore and offshore sections (Fig. 8).

In the onshore section the organically immature carbonate-rich and organic-rich mudstones of the Southern England and East Midland sections contain a mature assemblage of ordered illite–smectite with some chlorite. This contrasts with the North Yorkshire basin where the clay minerals, which comprise random ordered illite–smectite, are immature but the section is organically more mature, attaining marginal to early peak oil generation levels of maturity.

In the offshore Kimmeridge Clay sections, the East Shetland Basin Well 'A' sample is immature with respect to both clay minerals, where random
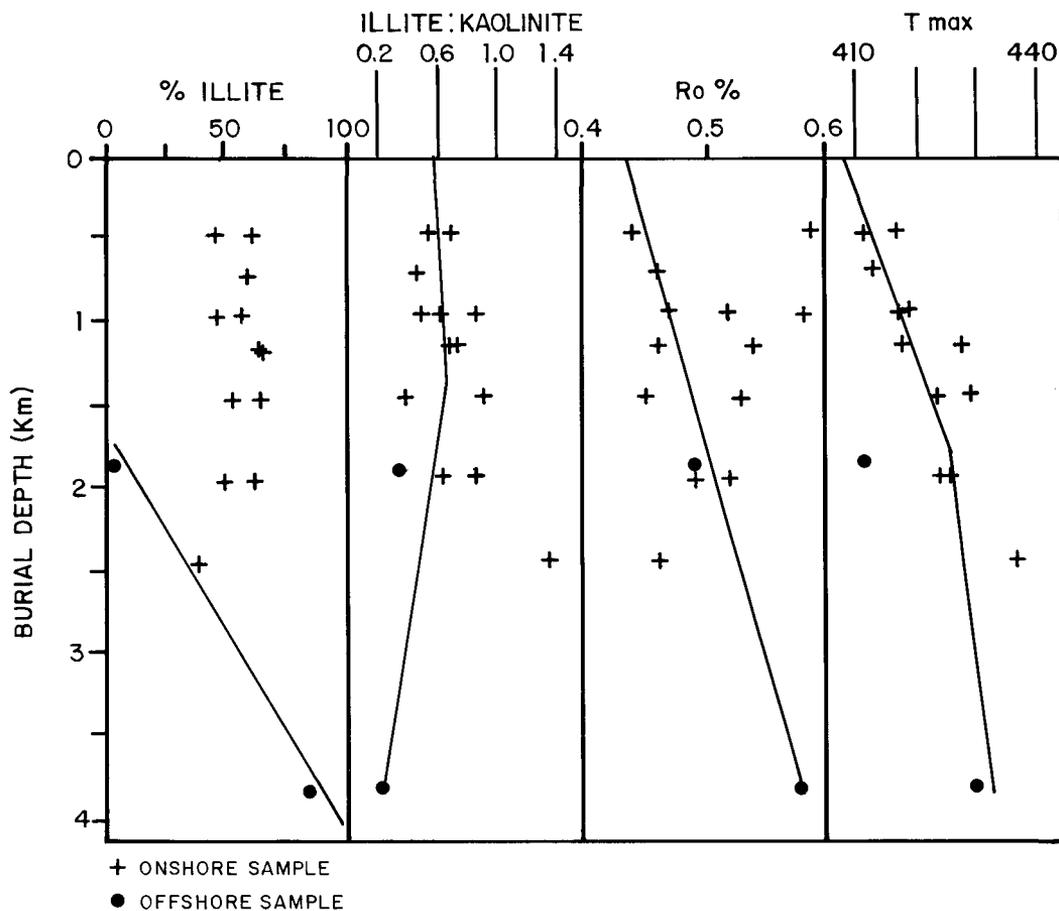
FIG. 8. Comparison of maturation parameters for the Kimmeridge Clay.

ordered illite–smectite predominates and to organic maturity. The deeper burial section from the Central Graben Norway 2/11-1 well contains mature ordered illite–smectites and exhibits an early peak oil generation level of organic maturity.

Therefore in the onshore section the illitization reaction has occurred at below 'oil window' levels of organic maturity except in the North Yorkshire basin where it has not taken place in a section which has reached the 'oil window'. The offshore mudstones exhibit the more 'classical' picture with the illitization reaction occurring within the 'oil window'. This latter relationship has been recorded by workers from several parts of the world (Heroux et al., 1979). Pearson et al. (1982, 1983) report a similar relationship from Mesozoic mudstones of the North Sea Southern Viking Graben, the illitization reaction beginning at 0.4%

Ro and being completed at 0.6% Ro. Powell et al. (1978) and Foscolos and Powell (1979; 1980) report the conversion of random ordered illite–smectite to the ordered variety as occurring at a vitrinite reflectivity of 0.5% in the Sverdrup Basin of N.W. Canada. Higher vitrinite reflectivities are reported by Pevear (1983) who found that regular interstratified illite–smectite were related to a reflectivity of 0.9% Ro in Tertiary sediments of the Northwest Pacific while Mackenzie et al. (1983) report a value of 0.7% Ro for the ordering point in a Brazilian sand–shale sequence. That the conversion of random ordered illite–smectite to ordered illite–smectite occurs within the 'oil-window' was clearly shown by Burtner and Warner's results (1983) from the Cretaceous Mowry Shale of North Dakota. Hydrocarbon generation has only occurred in the most deeply buried sections in the basin centre which coincides

with the appearance of ordered illite–smectite. On the basin flanks the shales are immature source rocks and contain only randomly ordered illite–smectites.

It can therefore be seen that, while there is much evidence for the illitization reaction occurring place at 'oil-window' levels of organic maturity, the presence of authigenic ordered illite–smectites within a shale cannot be used to imply a specific level of organic maturity or that organic maturity is sufficiently advanced to generate oil as has been suggested and used by Monnier (1982). Although both reactions are temperature dependent, the relationship breaks down when other factors such as pore-water chemistry either advance or retard the illitization reaction as in the carbonate-rich or very organic-rich mudstone facies of the onshore section respectively. The importance of parameters other than temperature is shown by the effect of residence time at elevated temperatures on the reaction progress, as defined by the Time-Temperature Index of Waples (1980). Ramseyer and Boles (1986) report very short residence times at high temperatures and conclude that once the reaction has begun it goes to completion or near completion over a narrow temperature range. Morton (1985a) also found illitization to be a punctuated, discrete event which occurred rapidly over a short depth interval, confirming the importance of chemical controls on illitization. Therefore, once the required burial temperatures have been attained, the reaction appears to take place rapidly when the chemical environment is favourable, explaining the wide range of temperatures over which illitization has been reported in the literature.

Conclusions

The present study has shown that the major clay phases in the mudstones of the Kimmeridge Clay Formation comprise mixed layer illite–smectites and kaolinite with minor chlorite, illite and smectite. The illite–smectites from the onshore section are largely of the ordered variety with illite dominant over kaolinite, with the exception of the Marton section from the North Yorkshire basin where random ordered illite–smectite and kaolinite predominate. The majority of the onshore clay assemblages are therefore mature but, in contrast, they are organically immature, being in the incipient zone of oil generation (Lewan, 1985). While commonly occurring within the 'oil-window', the illitization reaction can therefore occur above or below it, reflecting the additional control on the reaction by pore-water chemistry and, in particular, the supply of

K ions. Both organic maturation and the illitization of smectite appear to reflect the regional temperature distribution patterns encountered during burial but the illitization reaction can only proceed if an adequate K supply is present. Although other effects such as the composition of the initial smectite or errors in the estimation of the illite content of the illite–smectites may occur, it can be seen that the presence of authigenic ordered illite–smectite does not necessarily indicate 'oil-window' levels of organic maturity. Therefore caution must be used when using the illitization reaction as an organic maturity indicator as, while may be applicable locally, the relationship may not hold basin-wide, due to the sensitivity of the reaction to K supply and probably other chemical factors.

Applications

Water expelled during the illitization of smectite into the pore system of the host mudstone has been postulated as a vehicle for hydrocarbon migration as both illitization and oil generation had been observed to occur at similar burial depths (Powers, 1967; Burst, 1969; Perry and Hower, 1972; Bruce; 1984). This expelled water would not be available for hydrocarbon migration when the illitization of smectite takes place above the 'oil-window': nevertheless, water released prior to hydrocarbon generation could aid the expulsion and migration of oil by creating microfractures in the source rock.

Acknowledgements

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