Elemental and structural changes in illite/smectite mixed-layer clay minerals during diagenesis in Kimmeridgian- Volgian (- Ryazanian) clays in the Central Trough, North Sea and the Norwegian-Danish Basin

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The literature on the diagenetic conversion of smectite layers to illite layers in mixed-layer illite/smectite is reviewed. According to this smectite layers are converted to illite layers during diagenesis at temperatures above 55°C and illite/smectites become IS ordered at about 100°C and at illite percentages of about 80%. Charge and elemental composition seem, beside temperature, to be of importance in the process. Investigations from metamorphic and hydrothermal areas have also found a conversion of smectite to illite layers with increasing temperature. In hydrothermal experiments, the process has been found to occur at temperatures of 250°C and above. Investigations from metamorphic areas have shown that the increase in amount of illite layers in illite/smectite during short lived heating events is very slow compared to the increase in vitrinite reflectancy. The elemental changes during illite layer formation are a substitution of Al^{3+} for Si^{4+} in the tetrahedral sheet and a fixation of K^+ between 2:1 units. Some investigations have also found substitution of Al^{3+} for Mg^{2+} and Fe and a reduction of Fe^{3+} in the octahedral sheet. The changes seen during the hydrothermal experiments and in hydrothermal areas are different from the diagenetic changes in that higher negative charges are created and Na^+ and Ca^{2+} are fixed under hydrothermal conditions. Two models have been proposed for the diagenetic formation of illite layers from smectite layers: 1) A solid-state Al^{3+} for Si^{4+} substitution in the tetrahedral sheets of smectite layers and sub-sequent fixation of K^+ and interlayer collapse, giving illite layers; and 2) A dissolution of smectite layers and crystallization and growth of illite crystals. K^+ supply is the main control on the formation of illite layers from smectite. Even in systems with sufficient K^+ available, other cations such as Mg^{2+}, Ca^{2+}, and Na^+ may inhibit K^+- fixation and illite layer formation.

The release of clay transformation water and its possible role in petroleum migration has been the subject of several investigations. There seems in most cases to be a coincidence between collapse of interlayer space (assumed to release interlayer water) and the generation of petroleum. But the role of the water released during clay diagenesis is not clear.

The geology of the Central Trough and the Norwegian-Danish Basin is shortly reviewed. The source of the Upper Jurassic clays was probably mainly the Fennoscandian Shield. In addition volcanic material including ash has probably been sedimented in the North Sea region during Upper Jurassic.

Cores and hand-picked cuttings samples from the Mandal, Farsund and Haugesund Formations in the Central Trough and from the Sauda, Tau, Børglum and Bream Formations in the Norwegian-Danish Basin have been investigated. Intact bulk rock samples were ion-milled and investigated by high resolution transmission electron microscopy (HRTEM). The samples were also ultrasonically and chemically treated and the mixed-layer illite/smectite isolated by centrifuging. The illite/smectite samples thus obtained were investigated by HRTEM, by transmission electron microscopy (TEM) on shadowed specimens, by X-Ray diffraction (XRD), by ^{27}Al and ^{29}Si magic angle spinning, nuclear magnetic resonance spectroscopy (mas-nmr), by infrared spectroscopy (IR), and by chemical analysis for elements and NH_4^+. Illite percentages and ordering in illite/smectite were estimated by computer simulation of XRD patterns by the NEWMOD program for two-component systems and by a program for three component systems. The interpretations of the HRTEM images of illite/smectite structures in intact bulk rock were supported by computer simulations.

The results of XRD on coarse clay fractions indicated that the main source area for the Upper Jurassic claystones was the Fennoscandian Shield.

XRD supported by computer simulations showed that the amount of illite layers in illite/smectite was between 40% and 80% illite layers in randomly ordered or I-S segregated illite/smectite, between 80% and 90% in mainly IS ordered illite/smectite, and about 95% illite layers in ISII ordered illite/smectite.

10–14 Å distances were seen in lattice fringes by HRTEM on intact bulk rock and are probably due to smectite layers with non-contracted interlayer space, whereas 10 Å lattice fringes can be due to illite or collapsed smectite and 14 Å distances to chlorite or non-collapsed smectite. 10 Å lattice fringes with periodically enhanced contrast were observed by HRTEM on intact bulk rock in all Central Trough samples investigated. Regular 20 Å period sequences of such enhanced contrast were most frequent but also 30 Å period sequences and sequences with enhanced contrast occurring randomly along c* were seen. These particles are MacEwan illite/smectite particles. The specimens prepared for HRTEM from dispersed illite/smectite contained a large amount of thin particles with 10 Å period in contrast but also, in IS ordered illite/smectite, a large number of particles with 20 Å periodically enhanced contrast, MacEwan particles. It is concluded that the thin particles seen by HRTEM and TEM on specimens prepared from dispersed illite/smectite have probably formed by dispersion of the thick particles seen by HRTEM in intact bulk rock.

The illite/smectite from the Norwegian-Danish Basin, with 65–75% illite layers and randomly ordered or I-S segregated, is probably detrital. Similar illite/smectite at shallow depth (less than about 3 km) and low temperatures (less than about 100°C) in the Central Trough is probably also detrital, but at larger depths and higher temperatures it is diagenetically changed to predominantly IS ordered illite/smectite with 80–95% illite layers. This change occurs at a vitrinite reflectancy of about 0.65%, i.e. at about oil generation.

Chemical analysis and mas-nmr showed that the formation of illite layers is accompanied by an increase in tetrahedral Al and a minor increase in octahedral Al, by a decrease in tetrahedral Si and by a minor decrease in octahedral Mg and Fe. Analysis of pore water from Upper Jurassic claystone cores gave ratios for K^+/NH_4^+ in pore water similar to those in illite/smectite from the same depth, indicating that the relative amounts of K^+ and NH_4^+ control the fixation of these cations in illite/smectite.

The ordering of illite and smectite layers in MacEwan particles in intact bulk rock, observed in images as 20 Å (and sometimes 30 Å) periods of enhanced contrast, can only have formed during solid-state smectite to illite formation, the polarization effect probably being responsible. The chemical analyses show that the illite layers have charges of about −0.8, less than the ideal −1.0 of mica. Such low charge illite layers can form during a solid-state transformation. It is concluded that the formation of illite layers from smectite layers in the Upper Jurassic claystones is a solid-state transformation.

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Introduction

The key to the development in clay mineralogy has been the development of analytical equipment in this century. X-ray diffraction supported by computer simulation furnishes information on clay mineral groups present in samples and on the presence of mixed-layer clays and the statistics of mixing. This is essential in investigation of mixed-layer illite/smectite diagenesis. High resolution transmission electron microscopy and electron diffraction can give information on the layering and layer types present in intact bulk rock. Chemical analyses of mixed-layer clays furnish their elemental composition. ^{27}Al and ^{29}Si nuclear magnetic resonance magic- angle spinning spectroscopy and ^{57}Fe Mössbauer spectroscopy give information on the coordination of Al, Si, and Fe and on the valency of Fe, information which is essential in investigations on diagenesis, as an important diagenetic process is Al for Si substitution in the clay mineral layers. In addition, infrared spectroscopy can supply information on the types of bonds between elements present in the sample. An up-to date investigation of diagenesis of clay minerals is therefore dependant on the availability of these techniques.

The exploration for oil and gas in the Danish area was initiated late in the 1930's and drilling continued onshore after the Second World War. Several wells were drilled but only traces of oil and gas have been found onshore. In the Central Trough of the North Sea, drilling discovered several oil and gas reservoirs. Oil and gas are formed in source rocks and migrate out of these rocks to the reservoirs. An important part of the evaluation of the oil and gas potential is therefore an investigation of the source rock potential. This is determined by the amount of source rock present, its content and type of organic material, and its degree of maturity. Combined organochemical, coal petrographical and clay mineralogical investigations of the source rock potential in the Danish concession area were carried out in the Source Rock Project, which started in April 1981 and was funded by the Danish Energy Research Council. Organochemistry and coal petrography are well established methodologies in source rock evaluations. The publications of Hower and co–workers on the clay mineralogy of the U.S. Gulf Coast Tertiary shales, of Foscolos and co–workers on Canadian Tertiary to Jurassic shales, of Heling and Teichmüller on the Tertiary shales of the Rhine Graben, and of Środoń on the Silesian
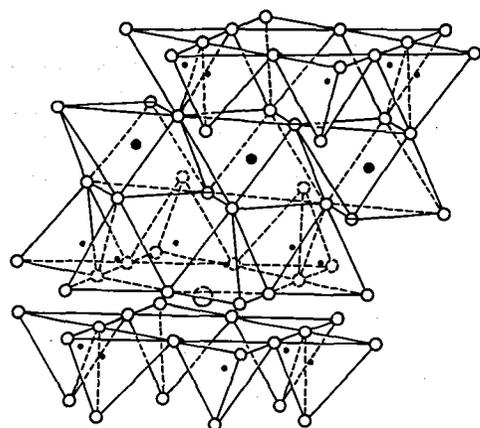
O: Oxygen   •: tetrahedral cation
⊖: hydroxyl   •: octahedral cation or
                    vacancy
O: fixed interlayer cation

Fig. 1. Simplified model for mica. Modified from Goodman (1976, fig. 2). Originally from Grim (1953, fig. 14).

of Poland have shown that the percentage of illite layers and the degree of ordering in mixed-layer illite/smectite increase during diagenesis. Coal petrography and organochemistry showed that the main source rocks in the Danish area are of Upper Jurassic age and that they are mature in large parts of the Central Trough and pre-mature in the Danish Subbasin. The X-ray diffracto-grams of clay fractions (< 2 µm) from these rocks were dominated by discrete illite and kaolinite and investigation of mixed-layer illite/smectite was therefore difficult. The mineralogical part of the source rock evaluations of Upper Jurassic rocks dealt therefore mainly with correlations be-tween non-clay mineralogy and maturity of the organic matter.

This left the question of clay mineralogical changes during diagenesis in the Upper Jurassic source rocks unanswered. Late in the project, X-ray diffraction, Mössbauer spectroscopy and chemical elemental investigations on fine-clay fractions (< 0.2 µm) from these rocks showed that ordering of the mixed-layer illite/smectite was roughly coincident with oil generation. The opportunity came to investigate in detail the structural changes of the mixed layers during di-agenesis when I obtained a senior scholarship at the Institute of Mineralogy, University of Copen-hagen. I carried out X-ray diffraction at the In-stitute of Mineralogy, chemical elemental deter-

minations at the Department of Chemistry and the Department of Physics at the Royal Veter-inary and Agricultural University, infrared spec-troscopy at the H.C.Ørsted Institute, and Möss-bauer spectroscopy at the Geological Survey of Denmark. Programs for computersimulation of diffractograms of two-component mixtures were kindly placed at my disposal by R.C.Reynolds and for three-component mixtures by P.D.Crad-wick. These investigations were combined with results of solid-state ^{27}Al and ^{29}Si NMR carried out at the Department of Chemistry, University of Aarhus by lektor Hans Jørgen Jakobsen and cand. scient. Hans Jacobsen, and with results from high resolution transmission electron mi-croscopy and diffraction carried out at the Lab-oratory of Applied Physics, Technical University of Denmark, by cand. scient. Poul Lenvig Han-sen. Professor Harry Micheelsen investigated the coarse fractions (> 10 µm) of the rocks by light microscopy and spent several months to make the three component program of P.D.Cradwick oper-ative on a computer at the Institute of Mineralo-gy.

The structure of clay minerals

Terminology

The clay crystal terminology adopted by AIPEA (Bailey 1980) will be used in the following. Thus, the term "structure" means a physical arrange-ment of atoms or ions, "plane" means a single plane of atoms in a structure, "sheet" is used as in an octahedral or a tetrahedral sheet, and "layer" is used as in a 1:1 layer or a 2:1 layer. The terms "plane", "sheet" and "layer" refer to increasingly thicker arrangements; a sheet is a combination of planes, and a layer is a combination of sheets. In addition, layers may be separated from one an-other by "interlayer" material, such as cations.

The structure of clay mineral layers

A simplified mica model is shown in fig. 1. Clay minerals are sheet silicates composed of tetra-hedral and octahedral sheets. The tetrahedral sheets are built up with a central cation, mainly Si^{4+}, with four oxygen anions at the apices. The formula for the tetrahedral sheet alone is thus,

Table 1. Classification scheme for phyllosilicates related to clay minerals, Bailey (1980, p.74).

Layer type	Group ($\times$ = charge per formula unit)	Subgroup	Species[1]
1:1	Kaonite-serpentine $\times^- 0$	Kaonite Serpentine	Kaonite, dickite, halloysite Chrysotile, lizardite, amesite
2:1	Kaolinite-serpentine $\times^- 0$	Pyrophyllite Talc	Pyrophyllite Talc
	Smectite $\times^- 0,2$–0.6	Dioctahedral smectite Trioctahedral smectite	Montmorillonite, beidellite Saponite, hectorite, sauconite
	Vermiculite $\times^- 0.6$–0.9	Dioctahedral vermiculite Trioctahedral vermiculite	Dioctahedral vermiculite Trioctahedral vermiculite
	Mica[2] $\times^- 1$	Dioctahedral mica Trioctahedral mica	Muscovite, paragonite Phlogopite, biotite, lepidolite
	Brittle mica $\times^- 2$	Dioctahedral brittle mica Trioctahedral brittle mica	Margarite Clintonite, anandite
	Clorite $\times$ variable	Dioctahedral chlorite Di,trioctahedral chlorite Trioctahedral chlorite	Donbassite Cookeite, sudoite Clinochlore, chamosite, nimite

[1] Only a few examples are given

[2] The status of illite (or hydromica), sericite, etc. must be left open at present, because it is not clear whether or at what level they should enter the table; many materials so designated may be interstratified.

with one hydroxyl group available at each tetrahedron for bonding to the octahedral sheet: $Si_2O_3(OH)_2$. The octahedral sheets are built up with a central cation, usually Al^{3+}, Fe^{3+}, Fe^{2+} or Mg^{2+}, with 6 anions at the apixes. With Al^{3+} as the cation the formula for the octahedral sheet can be written: $Al_2(OH)_6$. Bonding of one octahedral sheet to one tetrahedral sheet as in the 1:1 or 2-layer silicates results in the formula: $Al_2Si_2O_5(OH)_4$, and bonding of two tetrahedral sheets to one octahedral sheet as in the 2:1 or 3-layer silicates results in the formula: $Al_2Si_4O_{10}(OH)_2$. Only 2/3 of the octahedral vacancies are filled in sheets with trivalent cations, dioctahedral sheets, whereas octahedral sheets of divalent cations like Mg^{2+} or Fe^{2+}, trioctahedral sheets, have all vacancies filled and the corresponding formulae are: for 1:1 or 2-layer silicates: $Mg_3Si_2O_5(OH)_4$ and for 2:1 or 3 layer silicates: $Mg_3Si_4O_{10}(OH)_2$. So far the layers have no charge. The 2:1 layers obtain a permanent, negative charge, if Si^{4+} in the tetrahedral sheet is substituted by Al^{3+} or Fe^{3+} and/or if an octahedral Al^{3+} or Fe^{3+} in the octahedral sheet is substituted by Mg^{2+} or Fe^{2+}. This negative charge is balanced by cations clustering around or fixed at the surface of the layers. Substitution degrees are low in 1:1 layer silicates and also in 2:1 layer silicates with interlayered octahedral sheets (the chlorites) or with alternat-

ing 2:1 layers (sepiolites and palygorskites). The degree of substitution is the basis for the classification into groups within the remaining 2:1 layer silicates (talc pyrophyllites, smectites, vermiculites, micas and brittle micas); see table 1. The classification of the sheet silicates into subgroups is based on whether the octahedral sheet is di- or trioctahedral.

It is noteable that the status of illite is left open in the classification of the International Mineralogical Association shown in table 1 and that many of the materials so designated may be interstratified according to the footnote in table 1. Illite was proposed as a general term for mica-like clay minerals by Grim, Bray & Bradley (1937). Grim (1953) concluded that by then the term illite had been widely accepted for a mica-type clay mineral with a 10 Å c–axis spacing and which shows substantially no expanding lattice characteristics. He furthermore proposed a classification of clay minerals according to which three layer types with non-expanding lattice belong to the illite group. It should be noted that the group level in Grim's classification for three-layer silicates is based on expandability. However, the Clay Minerals Society's Nomenclature Committee concluded (Brindley 1966) that a classification of clay minerals cannot be independant of a classification of layer silicates (phyllosili-

cates). Therefore the classification scheme later adopted (shown in table 1) omitted some commonly used clay mineral terms because their nature was considered to be such that they do not fall within this classification scheme. Bailey (1984) wrote that illite is predominantly dioctahedral but differs from ideal muscovite in having on the average more silicon, magnesium, and water but less interlayer potassium. Bailey noted that although many clays termed illite in the literature are known to contain expandable layers in addition to micaceous layers illite should be used to designate only non-expandable 10 Å mica. This designation will be followed in the present work.

Mixed-layer clay minerals

In mixed-layer or interstratified clay minerals two or more different layers are interstratified in a more or less random or in a regular way. In this chapter I will denote illite layers and S smectite layers. In later chapters reviewing the literature M can also be used for montmorillonite layers by the cited authors. Montmorillonite was earlier used as a group name, but was later substituted by the term smectite and montmorillonite was thereafter only smectites with negative layer charges from octahedral substitutions, see table 1. In mixed-layer or interstratified minerals two or more different layers are interstratified in a more or less random or in a regular way. Ideally IS ordered illite/smectite with 50% illite layers have alternating layers of illite and smectite giving a superlattice of I + S along c*. Ideally ISI and ISII ordered illite/smectite consist of I + S + I and I + S + I + I superlattices, respectively. In order to describe less ideally ordered illite/smectite also, Reynolds (1984) has given a statistical treatment of sequences with two types of layers. He used statistical parameters to describe the sequences of layers in interstratified crystallites. One parameter is the probability of finding one of the components in the layer sequence of principal infinite thickness along c*. The other parameters are junction probabilities giving the probabilities of a layer following another layer (e.g. $P_{A,B}$) or following a sequence of specified layers (e.g. $P_{AA,B}$ or $P_{AAA,B}$). Ordering implies accordingly that the minor of the two components is always found as a component of the superlattice structure. For example, in IS ordered illite/smectite with more than 50% illite layers all smectite layers are found in IS units and the remaining illite layers are then distributed among these units. Consequently it is characteristic for IS ordered illite/smectite with more than 50% illite layers that a smectite layer can *never* follow a smectite layer in the sequence and for ISI ordered illite/smectite with predominantly illite layers that each smectite layer is separated by at least two illite layers.

The XRD patterns of mixed-layer clay minerals have basal reflections from one or both components together with scatter interference maxima ("compromise diffractions" (Brindley 1981)) between basal reflections from each of the two components, when these reflections occur close to each other (Brindley 1981). As soon as these characteristics were known, mixed-layer clay minerals were observed in many different geological materials. In randomly ordered or I-S segregated mixed-layers dominated by one of the components, the XRD pattern is dominated by the (00l) reflections from that component and mixed-layering can therefore only be identified by comparing intensities in the experimental pattern and intensities in computer modelled patterns (see below). Thus, identification of discrete minerals based on the presence of the (00l) reflections of these minerals may be erroneous. For example, the presence of discrete smectite cannot be deduced from the presence of a 17 Å peak in glycolated specimens, as done by Heling (1978, 1979), because randomly ordered or I–S segregated illite/smectite with up to 70% illite layers give such a peak (Reynolds 1984). Higher order reflections from ordered mixed-layer minerals may be mistaken for first order reflections of single clay minerals. Thus, a 14 Å peak in glycolated specimens may be due to a vermiculite component, as proposed by Foscolos, Powell & Gunther (1976), but may also be a (002) from a regularly interstratified illite/smectite. These interpretation difficulties may result in different results from different investigators, see later. Computer modelling of XRD patterns from mixed layer clays with two components was carried out by MacEwan (1956, 1958) for randomly ordered mixed-layers and by Reynolds & Hower (1970) both for randomly ordered and I-S segregated and for ordered two-component mixed-layers. Computer modelling

Fig. 2. Markovian and fundamental particle models in illite/smectite.

for three-component illite/vermiculite/smectite was done by Cradwick & Wilson (1978).

The mixed-layering in these calculations was assumed to occur as layers of one component interstratified with layers of the other component (or components) in the same particle, the Markovian model (see fig. 2), and particle thicknesses of 5–15 elementary layers produced satisfactory computer simulated patterns. However, TEM on dispersed sodiumsaturated smectites showed that the particles in these specimens were 1–2 elementary layers thick (Mering & Oberlin 1971).

Similarly, Weir, Nixon & Woods (1960) found by TEM on specimens prepared from dispersed allevardite that the dispersion had produced suspended flakes two 2:1 unit layers thick. Nadeau, Tait, McHardy & Wilson (1984) showed that interparticle diffraction in very thin illite particles (one to more than five unit layers thick) in oriented XRD specimens gives rise to mixed-layer illite/smectite XRD patterns which resemble those modelled with a mean particle thickness in the range 5–15 unit layers. Nadeau et al. (1984) viewed mixed-layer illite/smectite to be composed of elementary illite layers (random distribution in thicknesses: randomly ordered illite/smectite) and regularity to arise from uniformity in thicknesses of the elementary particles (see fig. 2) (one unit layer: smectite; two unit layers: IS ordered illite/smectite; three unit layers: IIS ordered illite/smectite; four unit layers: IIIS ordered illite/smectite). The smectite spacing of 17 Å after this model is due to one interparticle spacing of 7 Å plus one illite layer of 10 Å (fig. 2). It should be noted that the interparticle diffraction model has so far only been applied to diagenetic illites from sandstone reservoirs or originating from bentonites. Both the Markovian model and the interparticle diffraction model are based on investigations on dispersed clay specimens. These specimens were saturated with specific cations and/or with ethylene glycol or glycerol so that the d(001) could be correlated to layer charge; this is the criterion for distinguishing between the 2:1 layer clay minerals (table 1). Ahn & Peacor (1986a) investigated by high resolution transmission electron microscopy (HRTEM) ion-milled rock specimens from Gulf Coast Tertiary well sections. These same samples had been investigated by XRD by Reynolds & Hower (1970). Ahn & Peacor found mainly 10 Å thick lattice fringes in 2:1 layer minerals and concluded that the smectite layers had collapsed to 10 Å during specimen preparation and in the vacuum of the microscope and that illite and smectite layers therefore not could be distinguished from their d(001). Ahn & Peacor observed in intact rock only thick particles and not the thin particles found by Nadeau et al. (1984) in specimens prepared from dispersed clay. Ahn & Peacor found only two types of particles: one with a wavy appearance identified as smectite, and one with straight layers (packets) identified as illite. The

identifications were based on the depth-dependant variations in amounts of these particle types and on the amount of potassium determined from analytical electron microscopy (AEM). The absence of thin particles did not conform to the fundamental particle model of Nadeau et al. (1984), and the occurrence of illite and smectite layers in illite and smectite particles, respectively, was against the Markovian particle model (see fig. 2). Klimentidis & Mackinnon (1986) and Ahn & Peacor (1986b) used HRTEM on mixed-layer clays and concluded that particles composed of different layers with different interlayer spacings were present in samples prior to dispersion for preparation of oriented X-ray specimens. Ahn & Peacor proposed therefore that the dispersion technique may be responsible for disruption of interstratified clay particles at smectite layer positions. This conforms with the results of Mering & Oberlin (1971) and Weir et al. (1960) who found that smectite and allevardite disaggregate into elementary layers when deflocculated in suspension with sodium as the dominating cation. Therefore, interstratified particles with both illite and smectite layers are expected to be present in sediments with interstratified minerals, but they disperse easily at smectite spacings during cation saturation and preparation for X-ray diffraction oriented specimens.

Methods applied to study of mixed-layer clay minerals

As mentioned above, the existence of mixed-layer clay minerals and the nature of mixed-layering was demonstrated by XRD. The clay mineral definitions based on layer structure and charge (Bailey 1980) have been correlated to XRD on clay specimens saturated with specific cations and intercalated with specific organic compounds (MacEwan & Wilson 1984). Therefore, most of the investigations of clay mineral diagenesis have been carried out by XRD, supplemented in some cases by chemical dissolution of the clays and calculation of an ideal mineral formula from the elemental composition of the resulting solution. Supplementation of XRD by TEM on shadowed specimens prepared from dispersed clays has, as mentioned above, given rise to the neoformation theory of Nadeau et al. for

Table 2. Classification of diagenetic stages based on chemical and mineralogical indicators derived from the study of clay minerals. From Foscolos et al. (1976, Table 7).

Diagenetic Stages		Occurrence of Hydrocarbons (HC)	Chemical indicators					Mineralogical indicators				Discrete layers	
			Per cent K$_2$O in the mixed layers	Molar ratio of K$_2$O content of the mixed layers to adsorbed water on the expandable portion	Per cent adsorbed water (H$_2$O) – in the mixed layers*	Ratio of K$_2$O to C.E.C. of the mixed layers	Molar ratio of SiO$_2$+FE$_2$O$_3$+MgO/Al$_2$O$_3$ in the mixed layers*	Crystallinity index of illites in mm	Sharpness ratio of illites	Per cent 2M illite Polymorphs	Per cent illite in illite-2:1 expandables in the mixed layers	Expandables	Kaolinite
Eodiagenesis (Early diagenesis)		Expulsion of pore water and indigenous HC retention and decarboxylation of fatty acids by clays	<4	<.50	>8	<.10	>5.5	N/A**	N/A	N/A	<25	Present	Present
Mesodiagenesis (Middle diagenesis)	Early	1st Interlayer water removal from smectite, inducing acid properties which enchance catalytic cracking of hydrocarbons	4–5	0.50–1.00	6.7	0.10–0.15	4.5–5.5	N/A	N/A	N/A	25–50	Usually absent	Present
	Late	2nd Interlayer water removal flushing of hydrocarbons from clay surfaces	5–6	1.00–3.00	5–6	0.15–0.20	3.5–4.5	N/A	N/A	N/A	50–75	Absent	Usually absent
Telodiagenesis (Late diagenesis)		Production of non-liquid hydrocarbons	>6	>3.00	<5	>.20	<3.3	<15	>2.3	>50	>75	Absent	Absent

* Results calculated on air-dry basis
** N/A – not applicable

illite layer formation in mixed-layer illite/smectite. HRTEM investigations on bulk rock led Ahn & Peacor to discuss the extent to which the XRD and TEM results on dispersed clays can be applied to the mixed-layers in intact bulk rock (see above). The ideal formulae for mixed-layers may be calculated from total elemental analysis of clay fractions. However, spectroscopy (NMR, Mössbauer and IR) yields information on the elemental substitutions in 2:1 layers of illite/smectite. Spectroscopy of illite/smectites with different amounts of illite layers can therefore indicate which elemental substitutions have taken place during the formation of illite layers from smectite layers. Thus, Eslinger, Highsmith, Albers & DeMayo (1979) applied Mössbauer spectroscopy to study the role of iron reduction in the increase in negative charge of the 2:1 layer, and Altaner, Weiss & Kirkpatrick (1988) applied ^{29}Si NMR to investigate the importance of tetrahedral Al for Si substitution during illite layer formation. Altaner et al. (1988) furthermore correlated the NMR results with XRD and discussed the tetrahedral Al substitution in illite and smectite layers. Altogether, it can be seen that a combination of HRTEM on intact bulk rock with

XRD and TEM on dispersed clays yields important information on the layer-by-layer structure of the mixed-layers in a specimen. The overall elemental composition of illite/smectite is determined by total elemental analysis, but Mössbauer and NMR spectroscopy, although sparsely used so far, yield important information on the substitution pattern of Fe, Al and Si in illite/smectite.

Mixed-layer illite/smectite diagenesis

Diagenetic stages

According to Grim (1958) "diagenesis in general terms refers to the changes which may take place when a sediment passes from one environment into a second environment, in which it accumulates". Grim wrote that "opinions differ about the place in the sedimentary cycle where diagenesis should be considered to begin and where it should end, and further changes should be considered metamorphic in nature". Frey (1970) investigated the step from diagenesis to metamorphism (greenschist facies) and found that illite/smectite disappeared and 1Md illite changed to 2M$_1$ illite in the transition zone, the anchizone. Foscolos et al. (1976) discussed burial diagenetic staging in relation to clay mineralogical transformations. Their conclusions for occurrence and mineralogy of discrete clay minerals and for the amount of expandable layers, interlayer potassium and water are seen in table 2. This staging has, however, not been used widely later, and the distinction between discrete, expandable layers and expandable layers in mixed layers as seen in XRD is not generally valid, see paragraph on interstratified clay minerals. Diagenesis in the following will cover the interval from sedimentation to the beginning of the anchizone.

Investigation of the formation of illite layers from smectite layers

The conversion of smectite layers to illite layers with increasing depth of burial was studied in an Eocene Gulf Coast formation by Burst (1959). Since then several investigations of burial sequences, e.g. Perry & Hower (1970), Hower, Eslinger, Hower & Perry (1976), Bruce (1984), found the same conversion of smectite layers with depth. This conversion has also been found to occur during relatively short-lived heating during overthrusting, e.g. Hoffman & Hower (1979) and in hydrothermally altered material, e.g. Horton (1985). It is difficult to deduce the composition of the starting material and the role of time, temperature and pressure in the geological processes. Laboratory tests have therefore been carried out with well defined mineralogical and chemical reagents, at specified temperatures and for a specified time, e.g. by Eberl & Hower (1976, 1977). The temperatures in these experiments were 250° to 500°C, at least 100°C more than the temperatures of the smectite to illite layer conversion during burial diagenesis (see below). At a lower experimental temperature, reaction rates were insignificant. The temperatures during overthrusting and during hydrothermal smectite-to-illite layer reactions are also higher than the normal temperatures of burial diagenesis. The mixed-layer conversions in the Central Trough and the Norwegian-Danish Basin have occurred during burial diagenesis. Therefore, the literature on the burial diagenetic reaction for conversion of smectite layers to illite layers in mixed-layer illite/smectite will be reviewed in the following together with some of the results from hydrothermal and metamorphic areas and from experiments.

Illitization of illite/smectite during burial diagenesis

Use of the X-ray diffractometer revealed that mixed-layer minerals are common clay constituents in burial sequences. When the data from clay mineralogical analysis are presented the question each time is: what minerals are detrital (or inherited) and what changes have they undergone? Or alternatively: how liable are the clay minerals to diagenetic alterations and can they be used as diagenetic indicators? Weaver (1958 a and b) went so far as to suggest that shales and clay minerals are largely detrital in nature and have not suffered a great deal of chemical modification. He discussed the clay petrology of Upper Mississippian-Lower Pennsylvanian sediments of Central United States and considered the clay mineralogy of these sediments, even variations
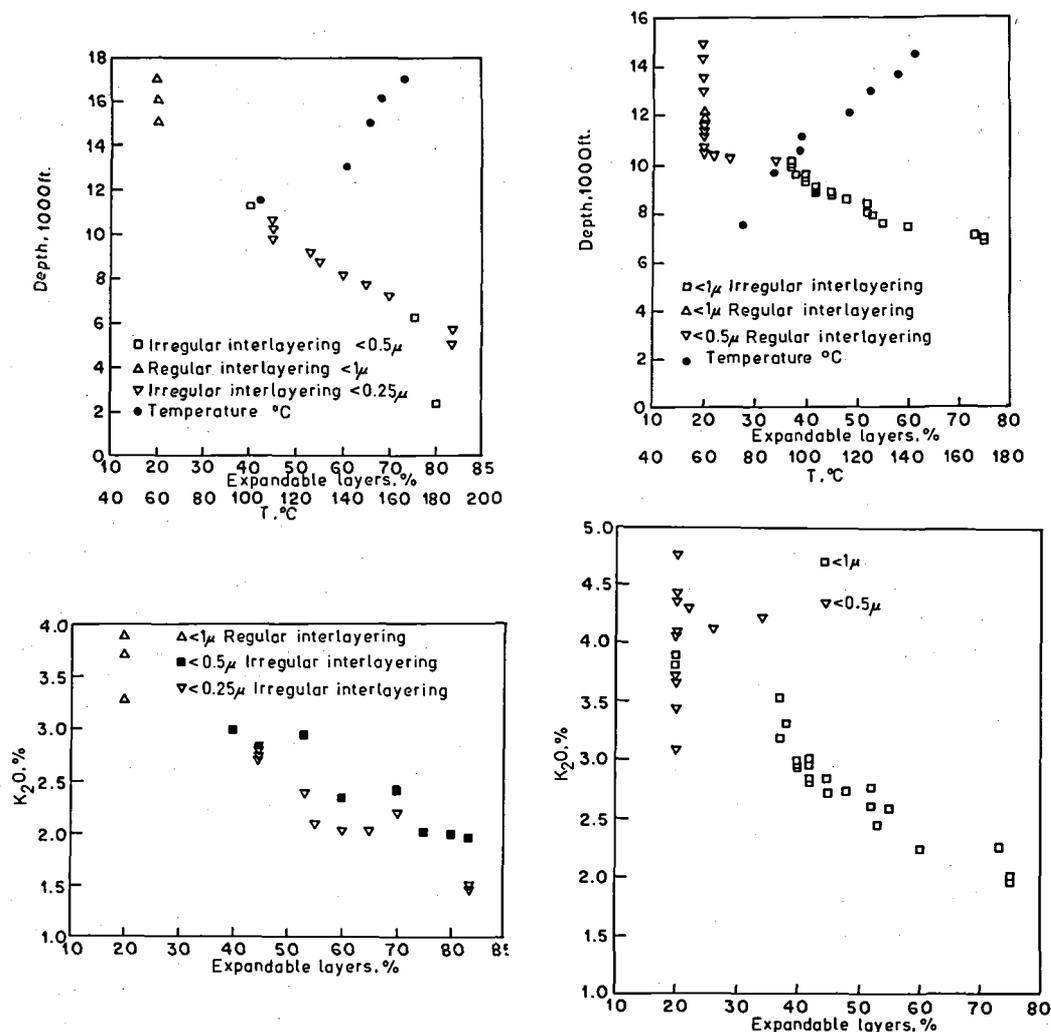
Fig. 3. Illitization of illite/"montmorillonite" (smectite) in U.S. Gulf Coast sediments. After Perry & Hower (1970, figs. 6 and 7). a: The relationship between % expandable layers in illite/montmorillonite and sample depth and temperature in Gulf Coast Oligocene to Eocene sediments in well B. b: The relationship between %K$_2$O in clay-size fraction and % expandable layers in illite/montmorillonite in well B. c: Relationship between % expandable layers in illite/montmorillonite and sample depth and temperature in Gulf Coast Oligocene sediments in well E. d: The relationship between %K$_2$O in clay size fraction and % expandable layers in illite/montmorillonite in well E.

with depth in proportions of illite in illite/smectite mixed-layers, to be due solely to different sources and to different weathering conditions.

The first indication of a diagenetic change in mixed–layers was noted by Burst (1959) in Eocene Gulf Coast sediments. He found that montmorillonite became less evident below 10000 ft, but was interspersed (mixed-layered) with illite at depths between 3000 ft and 14000 ft. In general he noted a progressive loss of expandable material with depth. Weaver (1959) reviewed the literature on clay mineralogy of recent sediments and considered most of the clay mineral changes to be due to detrital variations. He also discussed the depth related changes in clay mineralogy in Gulf Coast Miocene and Oklahoma Upper Mississippian shales and found it probable that montmorillonite below a depth of 10000 ft gave way to mixed-layer illite/montmorillonite with the proportion of illite increasing with depth. Weaver argued that this increase could be related to environment as well as to depth of burial.

The modelling of MacEwan (1956, 1958) and of MacEwan & Amil (1959) made it possible to

deduce structural layer changes in mixed-layer minerals from XRD patterns. The results of this modelling were applied by Burst (1969) to analysis of the 002/003 illite/smectite peak migration with change in composition of smectite/illite mixed-layers. He calculated that Gulf Coast Eocene sediments contained about 15–20% illite in mixed-layers in the depth interval: 2600 ft – 8500 ft. The illite percentage then increased to 65% at 12500 ft, and from that depth no further reduction in expandable layers was apparent. The temperature at 8500 ft was 210°F (99°C) and at 12500 ft 275°F (135°C). Weaver (1960) compared clay mineral data with log values for density and velocity from two Tertiary sections of the Texas Gulf Coast and from an Upper Mississippian shale of Oklahoma and found a similar clay suite and a similar diagenetic change with depth in all three sections. He concluded that time does not appreciably influence the rate of conversion of montmorillonite to illite.

Weaver & Beck (1971) investigated Pliocene-Miocene Gulf Coast muds and found that the percentage of illite layers and the ordering of the illite/montmorillonite increased with depth. They concluded from XRD and chemical investigations that the mixed-layers had a third component, chlorite, which increased in amount with depth. The well investigated bottomed at 16450', where the temperature was 119°C. In the interval 1000'-16450' there was a minor increase in the proportion of 10 Å layers in the mixed layers, but the major change appeared to be an increase in the regularity of mixed-layering. They found similar trends with increasing depth in Mississippian shales (Carboniferous) from Oklahoma, but these shales showed a more advanced stage of diagenesis (more illite and chlorite layers in the deeper samples). The deepest Mississippian shales, from 23800' and at a temperature of 170°C, still contained mixed-layers with some montmorillonite layers.

Perry & Hower (1970) investigated Gulf Coast Pleistocene to Eocene shales by XRD and chemical analysis and found a monotonous decrease from 80% to 20% of expandable layers in illite/montmorillonite with depth and that the interstratification changed from random to ordered at about 35% expandable layers (fig. 3). However, in one well discrete illite decreased with depth in the whole rock, whereas potassium in illite/mont-

morillonite increased. They found in well E (fig. 3c) that the decrease of expandable layers from 75% to 35% took place from 55°C to 95°C and that expandability decreased from 35% to 20% expandable layers over a short depth interval when the ordering temperature was reached. The composition of random illite/smectite changed rapidly with temperature, but IS ordered illite/ smectite persisted over a broad temperature range (fig. 3). Dunoyer de Segonzac (1970) considered the transformation of montmorillonite to be mainly influenced by depth of burial because of the role of pressure in the dehydration process, but he stressed the importance of the chemical composition of the interstitial solutions. Heling & Teichmüller (1974) reported the first mixed-layers in the Tertiary of Oberrheingraben at a vitrinite reflectance of 0.4%R_o. For comparison they also carried out analyses on samples from the Tertiary of Louisiana, where they found that montmorillonite disappeared at a vitrinite reflectance of 0.5% R_o and at a depth of about 1000 m. They concluded that, besides temperature and potassium availability, the duration of heating was also important, whereas the depth of burial was of no importance, and that mixed-layer transformations were slower than the coalification process. However, Heling & Teichmüller (1974) based their mixed layer investigation on (001) reflections or $(001)_I/(001)_S$ scatter interference peaks in glycolated specimens. Thus a 17 Å reflection was assigned to montmorillonite and a high background between 10 Å and 17 Å to disordered mixed-layer illite/montmorillonite. A discrete 10 Å peak was thus probably assigned to discrete illite. But 10 Å and 17 Å peaks are, in accordance with Reynolds & Hower (1970), also due to illite and montmorillonite layers in mixed layers. Therefore, the results of Heling & Teichmüller (1974) may be due to an increasing amount of illite layers in mixed-layers which, for the temperature range 40°C to about 175°C, is more in accordance with the results discussed below.

Foscolos & Stott (1975) investigated Lower Cretaceous Formations in Canada and proposed 3 diagenetic stages (early, middle, and late) based on the illite crystallinity index of Kubler, the illite sharpness ratio of Weaver, %2M$_t$ illite and on %illite in mixed-layers. The early diagenetic stage had less than 20–25% illite in mixed-

Temp.°C   Clay mineral R_o
                 transformations   %

30

40   30%.ILL.

50

60   50%.ILL.   SMECTITE
                          DISAPPEARS   0.5
70
80   70%.ILL.
90
100   0.8
110
120

130   1.3

140
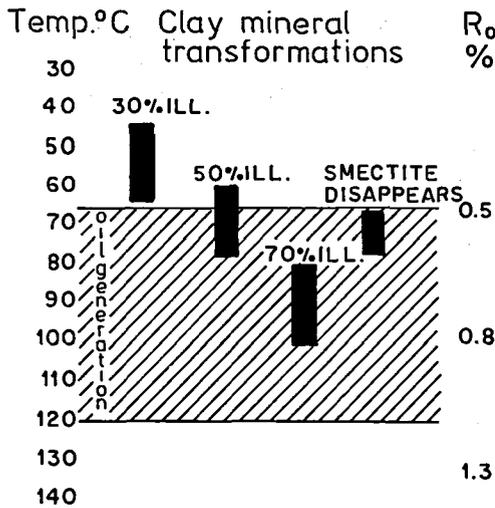
Fig. 4. Clay mineral transformations and their relationship to temperature and vitrinite reflectance values in Tertiary and Mesozoic sediments in 10 North Sea wells. After Dypvik (1983, fig. 4).

layers, the middle diagenetic stage less than 80–90% illite in mixed layers, and the randomly interstratified minerals were absent in the late diagenetic stage. Powell, Foscolos, Gunther & Snowdon (1978) found the onset of changes in mixed-layers in Tertiary to Jurassic sediments to correspond to a vitrinite reflectancy of 0.5% R_o. An elaborate subdivision of the diagenetic stages based on clay mineralogy was proposed by Foscolos et al. (1976) and is presented above in table 2.

Hower et al. (1976) investigated Gulf Coast Oligocene– Miocene sediments by XRD and chemical analysis. They found with increasing depth: a) a conversion of smectite layers to illite layers in mixed-layer illite/smectite (see fig. 6a), b) an appearance of chlorite and c) a disappearance of potash feldspars. They suggested that the chlorite had formed from magnesium and iron released by the formation of illite layers from smectite, and that released silica had formed quartz. Their results confirmed the persistence from 100°C to 175°C found by Perry & Hower (1970) of IS ordered illite/smectite with 80% illite layers. Hower et al. (1976) used bottom hole temperatures, and corrections of these temperatures by Freed & Peacor (1989) increased the value from about 100°C to about 115°C. Freed & Peacor found that the depth for occurrence of the ordered illite/smectite was larger for cuttings alone than for a mixture of cuttings and cores

from the same well. They attributed this to mixing of silt and sandstone cuttings with the shale cuttings, because sandstone and siltstone layers are common in the Tertiary Gulf Coast shales and illite/smectite in coarse lithologies tend to have larger illite layer percentages than in adjacent shales (Boles & Franks 1979). Hower et al. (1976) reported from deeper Gulf Coast Wells that non-interlayered illite formed at about 200°C. Investigations by Maxwell & Hower (1967) and Eslinger & Savin (1973) of metamorphic sequences in Montana and Idaho showed that recrystallization to a $2M_1$ dioctahedral mica took place at 200°C to 300°C giving the argillite to phyllite transition.

Dypvik (1983) correlated clay mineral changes with temperature for Tertiary and Mesozoic North Sea samples. The illite/smectite mixed-layer composition changed as follows in 10 wells (see fig. 4): more than 30% illite layers above temperatures ranging from 45° to 65°C, more than 50% above 60° to 75°C, and more than 70% above 80° to 100°C.

Środoń (1984) investigated low-temperature diagenesis in samples from the Carpathian foredeep (0–200 m depth) and concluded that the rate of illitization of expandable clay during subsurface diagenesis is too low to produce detectable variation of illite/smectite over a time scale of millions of years, and that smectite and smectite-illite are stable in marine sediments until the high temperatures of deep diagenesis are reached. Środoń cited Perry & Hower (1970), Hower et al. (1976), and Pearson, Watkins & Small (1982) that diagenetic illitization begins at about 50°C, usually more than 1000 m below surface.

Środoń & Eberl (1984, fig. 21) plotted literature data for the smectite to illite transformation in shales from different sedimentary basins as a function of temperature. The basins were: Central Poland (Carboniferous); Douala Basin (Cretaceous); North Sea (Lower Tertiary through Cretaceous); and US Gulf Coast (Tertiary). Weaver (1988) concluded that these curves for the different basins clustered fairly well, except for the data from Central Poland. He received, however, personal communication (in 1988) from Środoń that 1.7 km of Cretaceous rocks lately were found to have been eroded and then the curve for Poland falls on trend with the others. "This illustrates the type of pitfalls that exist in

interpretative shale petrology" (Weaver, 1988, p. 426, l. 15).

Ramseyer & Boles (1986) investigated mixed-layers in the Tertiary of the San Joaquin Basin in California. Relative to what was found in the Gulf Coast shales at the same temperature they found a high amount of smectite in mixed-layers and explained it by the shorter duration of heating in the San Joaquin Basin compared to the Gulf Coast. They also found that when the reaction forming illite from smectite layers begins it goes to completion within a relatively short temperature interval (80–140°C).

Primmer & Shaw (1987) analysed Gulf Coast Tertiary samples and North Sea Lower Cretaceous and Upper Jurassic samples from the Magnus and Brae Fields by XRD of clay fractions and by scanning electron microscopy (SEM) and microprobe analysis on polished thin sections. They found abrupt changes in the degree of ordering in illite/smectite with stratigraphic position and proposed that the compositional changes in the North Sea could be due to differences in source material. They noted that the Gulf Coast Basin has undergone a much simpler and more rapid subsidence than the North Sea Basin and that such differences may manifest themselves in the diagenetic history of the sediments. They concluded from the SEM and microprobe investigations that closed microenvironments existed within the shales. Different diagenetic processes had taken place in these microenvironments, e.g. the formation of authigenic chlorite and kaolinite but also changes in feldspar, carbonate and sulfide phases. In two Gulf Coast samples they calculated structural formulae for chlorite and illite/smectite from the microprobe data. These formulae must, however, be considered of limited value because 1) The single mineral phases are much smaller in dimensions (see e.g. Ahn & Peacor (1987), who found kaolinite a few hundred Å thick in illite crystals) than the smallest spot dimensions of the microprobe; 2) No distinction can be made between elements in the mineral phase and in the fluid phase; and 3) The accuracy of tetrahedral Al is low, as it is obtained from the amount of tetrahedral Si (which is about 5 times larger) and an ideal tetrahedral cation population of 4 per 10 oxygen atoms.

Burtner & Warner (1986) investigated Lower Cretaceous Rocky Mountain shales by XRD.

They cited Rettke who in an investigation from 1981 of adjacent Cretaceous shales found ordered, low-expandable illite/smectite in many samples that had never experienced significant heating. Rettke also found according to Burtner & Warner that a wide range in expandabilities at low borehole temperatures was significantly reduced above 60°C and that only low expandable illite/smectite was present above 90°C. Burtner & Warner found an abrupt change from randomly to IS ordered illite/smectite at about 100°C, at about 80% illite layers. They also cited Foster and Costard who in investigations from 1982 and 1983 found that burial diagenetic sequences with abrupt changes in percent smectite layers in illite/smectite contain smectite layers with a low charge produced by divalent cation substitutions in the octahedral sheet. Burtner & Warner wrote that this type of illite/smectite is common in Tertiary strata of the Gulf Coast, and that profiles marked by a more gradual increase in the illite/smectite ratio with depth possess a higher lattice charge produced by tetrahedral Al for Si substitution. Burtner & Warner concluded that the abrupt change in illite/smectite in their samples could be due to smectite layers of predominantly low charge, but that such an abrupt change in illite/smectite expandability might also be due to a high geothermal gradient. They correlated percentage of expandable layers in illite/smectite to T_{max} from Rock Eval analysis and found that the samples above T_{max} of 437°C only contained ordered low expandable illite/smectite (T_{max} of 435^C being the top of the oil generative zone for type II and type III kerogen (Espitalie, Madec, Tissot, Menig & LePlat 1977)).

Chang, Mackenzie & Schoonmaker (1986) investigated Cretaceous shales and sandstones from offshore NE Brazil by XRD, SEM, and chemical analysis. They concluded that dioctahedral illite/smectite became ordered between 90°C and 110°C and trioctahedral chlorite/smectite at 70°C in shales. They calculated that chlorite formation in chlorite/smectite occurred through Al for Si substitution in the tetrahedral sheets of the trioctahedral saponite layers and a loss of interlayer cations, and that the resulting charge was balanced by fixation of hydroxide sheets. Anjos (1986) investigated Cretaceous shales from offshore SE Brazil by XRD. She interpreted from the XRD patterns the smectites
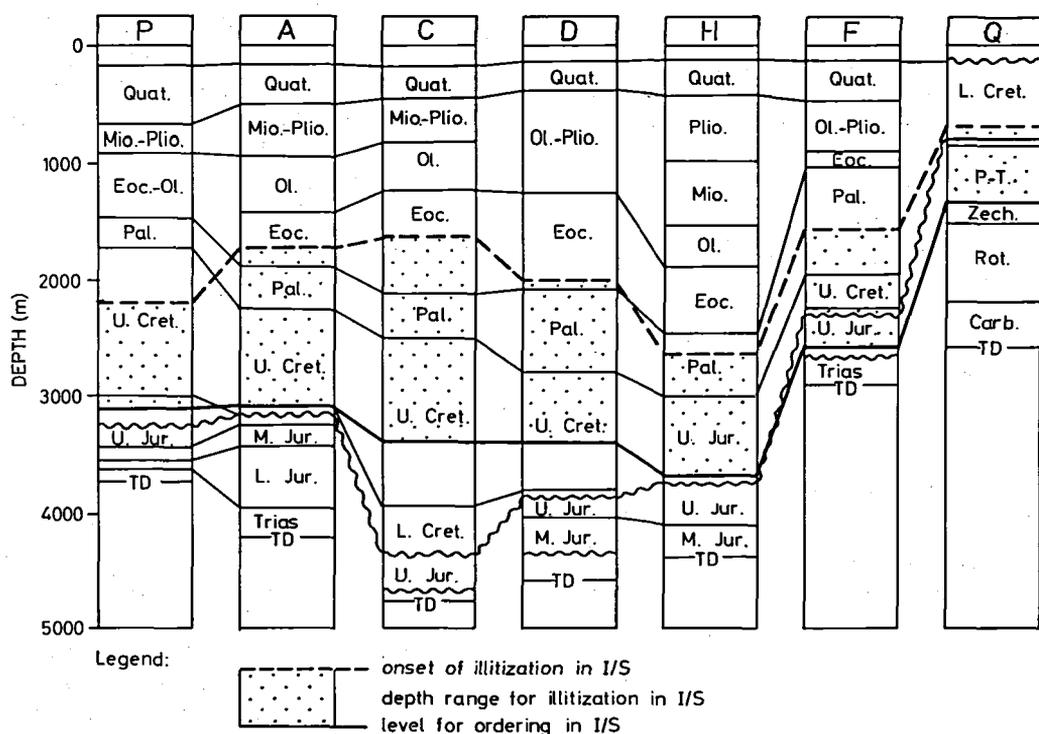
Fig. 5. Comparison of stratigraphy with the depth ranges of illitization south through the Viking Graben (wells A – H) and then east through the Moray Firth Basin (wells F – Q). After Pearson & Small (1988, fig. 13).

in illite/smectite to be Fe-rich and proposed that this property retarded the illitization of the illite/smectite.

Pearson & Small (1988) investigated Quarternary to Triassic shales from the Viking Graben and the Moray Firth by XRD and chemical analysis. They found only randomly ordered or I-S segregated illite/smectite in the shallow buried sediments irrespective of age. The temperatures for the depth where randomly ordered or I-S segregated illite/smectite became IS ordered were 87°C to 100°C, except for one well where it was 125°C, and vitrinite reflectancy values were 0.54–0.72% R_o. Pearson & Small observed that the ordering levels southwards through 5 wells in the Viking Graben and then eastwards through 2 wells in the Moray Firth Basin ran parallel to the Paleocene-Eocene boundary (fig. 5). They interpreted this to mean that the illite/smectite ordering was the result of a Paleocene-Eocene heating event.

Hillier & Clayton (1989) investigated illite/smectite diagenesis and organic maturity in lacustrine mudrocks from Northern Scotland. All the illite/smectites contained more than 75% illite

layers and many of them more than 90%. At the same vitrinite reflectancy (0.8–1.0 %R_o), they found different amounts of illite layers in the Caithness- Orkney region (90–95%) and in the Moray Firth region (75–80%) and tentatively attributed the different trends in vitrinite vs. %illite layers to different burial histories for the two regions.

These various investigations have shown that smectite layers are converted to illite layers in mixed-layer illite/smectite at burial diagenesis, at temperatures above 55°C, and that illite/smectite become IS ordered at about 100°C and at illite percentages of about 80% in mixed layers. There are, however, indications that the charge and elemental composition of the smectite layers influence the reaction mechanism. An increase in percent illite layers in mixed-layer illite/smectite with increasing temperature has also been found in investigations from metamorphic areas (Hoffman & Hower 1979, Eslinger et al. 1979, and Šrodoń 1979) and from hydrothermal areas (Aoyagi & Kazama 1980, Aoyagi & Asakawa 1984, and Horton 1985) and mixed-layer illite/smectite has been synthesized in experiments at

temperatures of 250°C and above. Investigations from metamorphic areas have shown that the increase in percent illite layers in mixed-layer illite/smectite with increasing temperature is very slow compared to the increase in vitrinite reflectancy (Środoń 1979, and Smart & Clayton 1985). They have furthermore shown that the increase in percent illite layers is larger in shales than in adjacent bentonites (Eslinger et al. 1979), whereas the ordering occurred in the bentonites earlier than in the shales and at a lower illite content than in the shales (Nadeau & Reynolds 1981a).

Elemental changes in the 2:1 unit during illite layer formation

The formation of illite layers from smectite layers during diagenesis has in many cases only been investigated by XRD.

In the terminology of Millot (1970) the illite may have formed by:

1) an aggradation (fixation of K^+ between high charge layers);
2) a transformation (formation of high charge by solid-state substitution in smectite layers followed by a K^+ fixation); or
3) a neoformation (dissolution of smectite layers and recrystallization of illite layers).

Weaver (1958a) postulated that "no mixed layer illite-montmorillonite has been reported, which has a basic lattice character near that of montmorillonite, that is, predominantly octahedral substitution" (p. 261, l. 16). He believed that mixed-layer clays with a higher charge (than montmorillonite), a larger amount of tetrahedral substitution, and commonly formed in continental deposits, contain hydrated Ca^{2+}, Mg^{2+} or Na^+ as interlayer cations and therefore usually are referred to as montmorillonites or beidellites. The decrease in expandability should then take place when these clays are transported to a marine environment and the high charge layers exchange their Ca^{2+} for K^+ and contract to mica-like layers, whereas the lower and octahedrally charged layers remain expanded. Weaver emphasized that, due to the character of the basic lattice, they were mixed-layers irrespective of expansion features. Syngenetic alterations, according to Weaver, oc-

cur while the clay is still in contact with sea water; epigenetic alterations occur later and eventually pass into low-grade metamorphism. Weaver then reviewed the literature on clay mineralogy of Recent sediments and explained most clay mineral changes found in these to be due to detrital variation. He suggested that montmorillonite type clay predominantly forms from volcanic ash under fresh-water conditions and that in a marine environment, in the presence of potassium, the ash would in many instances, as in Ordovician K-bentonites, go directly to a mixed-layer clay rather than to beidellite. Weaver (1959) stressed that, since no change in basal lattice occurs during the potassium fixation, such fixation should not be termed diagenesis but rather adsorption or exchange. As mentioned above he argued that the decrease of montmorillonite and increase of illite, chlorite and mixed-layer illite-montmorillonite with depth in the Gulf Coast Miocene and Upper Mississippian shales of Oklahoma can be related to environment as well as depth of burial, but concluded that time does not appreciably influence the rate of conversion of montmorillonite to illite. The former support of a sole aggradation process during burial was, however, modified to include the possibility of a transformation: "it remains to be proved whether this (the increase in amount of illite layers in mixed-layers with depth) is caused by chemical modification of the basic lattice with burial or if the detrital clay lattice has the inherent ability to contract without chemical rearrangement when buried to sufficient depth" (p.182, l.4 from bottom).

Burst (1959) supported an aggradation mechanism in Gulf Coast Tertiary clays. He proposed that the loss of montmorillonite swelling capacity and a simultaneous perfection of chlorite crystal development with depth were the benefications of degraded and fragmental mineral lattices by gradual fixation of potassium and magnesium to form illite and chlorite, respectively.

Powers (1959) proposed two alternatives for the change of montmorillonite to illite: 1: adsorbed Mg^{2+} and Fe^{2+} may move into the octahedral sheet and replace Al^{3+}, which possibly moves into the tetrahedral sheet expelling Si^{4+}, and K^+ moves into interlayer positions. 2: a slow interlayer replacement of interlayer Mg by K. Powers favoured the first possibility, because he believed that an increase in tetrahedral charge of
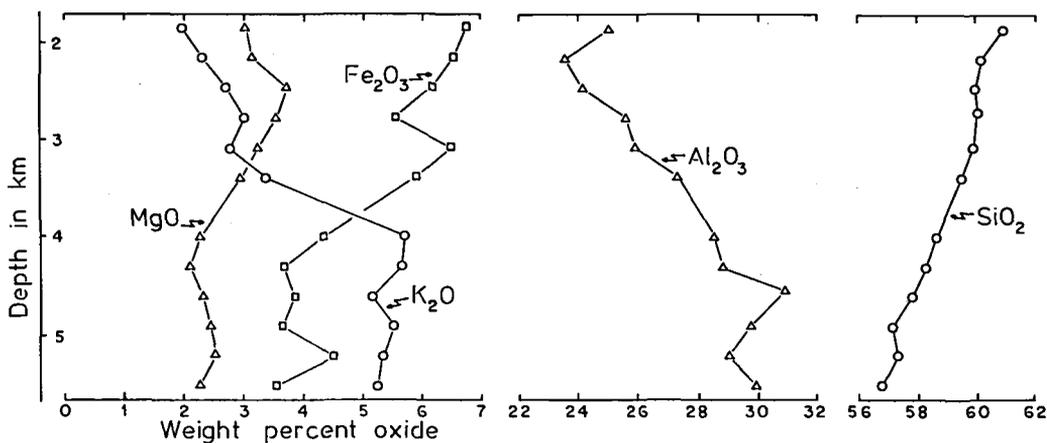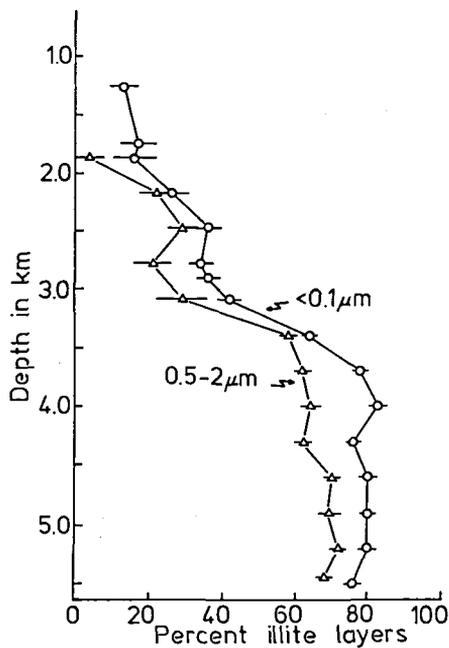
Fig. 6. Illitization of illite/smectite in U.S. Gulf Coast Miocene to Oligocene sediments, Case Western Reserve University Gulf Coast well 6, after Hower et al. (1976). a: Percent of illite layers in illite/smectite as a function of depth in the finest and coarsest clay fractions, after fig. 3 of Hower et al. (1976). b: Depth-dependance of the K_2O, MgO, Fe_2O_3, Al_2O_2, and SiO_2 content of the less than 0.1 µm fraction, after Hower et al. (1976, fig. 9 and 10).

the montmorillonite layers is necessary for K-fixation. Thus Ross & Hendricks (1945) wrote that the number of non-exchangeable interlayer ions in montmorillonites, essentially of K^+, increases with degree of tetrahedral substitution of Si by Al. Hower & Mowatt (1966) and Weaver & Pollard (1973) noted that illite and smectite layers in mixed-layers may well differ in composition. Hower (1967) found that a mixed-layer illite/montmorillonite of a given bulk composition can have a wide range of expandabilities depend-

ing on the amount of ordering. Burst (1969) proposed, however, that the change of montmorillonite layers to illite layers was a physical process, during which interlayer water with depth acquired sufficient thermal energy to be released.

Then followed a series of publications, mostly based on XRD and chemical investigations of illite/smectite from burial sequences. Their conclusions were generally in support of the transformation mechanism. Dunoyer de Segonzac (1970) proposed that, during the montmorillonite

→ mixed-layer illite/montmorillonite → illite transition, Al^{3+} should leave octahedra and be replaced in octahedra by Mg^{2+}. Pollard (1971) found that the transformation of montmorillonite to illite involved an increase in tetrahedral substitution of Al for Si from about 0% to 20% and that the degree of Al substitution is ⅙ of Si at the time when the illite type lattice is formed. Weaver & Beck (1971) investigated samples from shallow depths (less than 1000') in areas with relatively low geothermal gradients. They found indications that K had migrated into the highly charged expandable layers and caused contraction of these layers to 10 Å at shallow depths of burial and concluded that it was unlikely that much structural rearrangement occurred at these depths. Weaver & Beck proposed that interlayer Al^{3+} at larger depths of burial (> 10000') could migrate into the tetrahedral sheet of montmorillonite layers to substitute for Si^{4+} and increase layer charge when the temperature becomes high enough. They proposed alternatively that Al and Si tetrahedra might form illitic rims at the edges of montmorillonite flakes but they considered this alternative unlikely. According to Weaver & Beck, the Al required for tetrahedral substitution might originate from kaolinite and/or feldspar. Hower et al. (1976) found in their investigation of Eocene-Pleistocene Gulf Coast shales that the formation of illite from smectite layers in illite/smectite was accompanied by a gain in Al and K and a loss of Si and, to a minor degree, of Fe and Mg (fig. 6). They believed the process to be a solid-state transformation with a tetrahedral charge increase through Al for Si substitution accompanied by interlayer fixation of K:

$$smectite + Al^{3+} + K^+ = illite + Si^{4+}$$
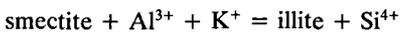
and also accompanied by octahedral Al for Fe and Mg substitution. Foscolos et al. (1976) concluded from chemical analysis and XRD that Al substituted for Si and Fe and the content of K increased in the mixed-layers with increasing depth of burial, whereas adsorbed H_2O decreased.

The transformation mechanism was then further supported by the results of hydrothermal experiments by Eberl (1978a, 1978b) and by Eberl & Hower (1976, 1977). Eberl & Hower (1976) concluded that the rate limiting step in formation of illite layers from smectite was probably an increase in layer charge by tetrahedral substitution of Al for Si. In their opinion, a significant reaction rate for this step was only obtained at the elevated temperatures during burial diagenesis. Eberl & Hower (1977) proposed a polarization effect in a 2:1 layer by tetrahedral substitution of Al for Si and increase in negative charge of one tetrahedral sheet in the 2:1 unit. This polarization should, according to their proposal, create 50% expandability, since subsequent tetrahedral substitution in the other tetrahedral sheet of the 2:1 unit should be more difficult. However, the effect on the tetrahedral sheet adjacent to the substituted layer should be less due to the positive interlayer cations.

Investigations of little transformed and of metamorphosed illite/smectite from the disturbed belt of Montana are of interest in relation to structural changes in illite/smectite during diagenesis. Eslinger et al. (1979) found a positive correlation between the percentage of iron as Fe^{2+} and the amount of fixed K^+. The percentage of iron as Fe^{2+} and the amount of illite layers were not correlated because of the low amount of iron in the samples and the relatively low importance of iron reduction compared to tetrahedral substitution of Al for Si in increasing layer charge. They calculated that octahedral iron reduction might have contributed as much as 10–30% of the increase in total structural charge that occurred during metamorphism of bentonites. Eslinger et al. believed that iron reduction might become more important compared to tetrahedral substitution of Al for Si in samples having high percentages of illite layers, since access to a tetrahedral site would be more difficult once the adjacent interlayer space has collapsed. All of their bentonites had, however, been in an "oxidising outcrop" environment for some years. Hoffman & Hower (1979) found a much higher Al for Si substitution in smectites from the metamorphic area (0.56 Al tetrahedral) compared to the little transformed smectites (0.09 Al tetrahedral).

Brockamp (1979) found that the conversion of smectite layers into illite layers involved a change of d(001) in Mg-glycolated specimens, from 17 Å over 14 Å to 10 Å, a corresponding increase of tetrahedral Al from 0.10 to 1.05 per $(OH)_4O_{20}$, and a corresponding increase in fixed K^+ from

0.24 to 1.00. Brockamp placed about 0.20 fixed Mg per $(OH)_4O_{20}$ in the illite layers of the 14 Å and 10 Å phases.

Frank-Kamenetski, Kotelnikova, Kotov & Starke (1979) found from hydrothermal experiments that montmorillonites with practically no tetrahedral substitution formed illite only at elevated temperatures and believed the process to take place by transition of Al from octahedral to tetrahedral positions.

Eberl (1980) proposed that cation selectivity should be a function of layer charge and different cations should therefore segregate into separate interlayers in smectites that have an inhomogeneous layer charge distribution (low and high charge interlayers).

Boles & Franks (1979) investigated interbedded shales and sandstones of Eocene age from the Gulf Coast by XRD and electron microprobe. Mass balance calculations based on their own data and on those of Hower et al. (1976) led Boles & Franks to propose that the more aluminous smectite layers should transform into illite layers by Al for Si substitution and K-fixation during the increase in amount of illite layers in randomly ordered illite/smectite. The more Mg- and Fe- containing smectite layers should during this stage either dissolve and thereby release Al for the smectite to illite transformation of the more aluminous layers and Fe, Mg, and Si for growth of other minerals or they should not undergo transformation to illite until the temperature of ordering. If this is correct, the amount of mixed-layer illite/smectite will decrease during diagenesis. Hower (1981b, p.68, 1.29) commented on the calculations as follows: "Assuming that the analyses are sufficiently accurate to draw a conclusion, their (Boles and Franks) suggestion may be correct."

Howard (1981) investigated shales and adjacent sandstones and found high-charge expandable layers in the shale laminae. From the Greene-Kelley test, the charge of these layers was probably due to tetrahedral substitution. Tetrahedral Al increased with progressive illitization, whereas octahedral Al remained essentially constant. He concluded that the illitization reaction probably was a step-wise process, first a creation of a high layer charge in the expandable layers by lattice substitutions and subsequently a fixation of K^+ within the interlayers. He believed, therefore, that creation of a high layer charge did not guarantee K^+-fixation and illite formation.

Pearson et al. (1982) compared two shallow Upper Jurassic samples from the Inner Moray Firth with two deeply buried Upper Jurassic samples from the Viking Graben and took a greater content of K and Al and a lower content of Si in the Viking Graben samples as indicating that a pronounced depletion of Si and enrichment of K and Al occurred during burial.

Ireland, Curtis & Whiteman (1983) investigated glauconites and illite in mudstones and sandstones of low diagenetic to greenschist facies and concluded that both groups evolved during diagenesis into phengite by tetrahedral Al for Si substitution together with octahedral Al for Fe^{3+} substitution. Inoue & Utada (1983) found in a hydrothermal area that degrees of ordering changed discontinuously from R0 ordering (100–55% expandable layers) to R1 (45–20% expandable layers) and from R1 to R2 (<20% expandable layers). This was different from the published transformations in burial sequences, where a continuous change in ordering type is seen in illite/smectite. Compared to the published results of burial diagenetic mixed-layers, the hydrothermal mixed-layers had a greater layer charge at a given amount of expandable layers, and Inoue & Utada proposed that both smectite and illite layers should have a greater charge compared to the same layer types in burial diagenetic samples. These comparatively higher charges for the hydrothermal samples cause dehydration of interlayer Na and Ca (these require a larger charge than K for dehydration, Eberl (1980)), and influence the degree of ordering at a given expandability. Inoue & Utada suggested from the data that the development of the hydrothermal mica/smectite zone and the progress of the conversion reaction were controlled by the cation composition of hydrothermal solutions as well as by temperature.

Howard & Roy (1985) found from hydrothermal experiments at both relatively high (250°C) and relatively low (150°C) temperature that the creation of a layer charge sufficient to lead to transformation of smectite to illite required no K. Illitization proceeded when K was introduced to layers with a sufficiently high charge. Analysis of resulting solutions indicated that the substitution

reaction at 150°C proceeded by congruent dissolution of octahedral and tetrahedral sheets. Howard & Roy suggested that different reaction mechanisms might occur at 150°C compared to those at the higher temperatures experimentally investigated earlier.

Horton (1985) found a poor correlation between the amount of illite/smectite and the composition of illite/smectite in a hydrothermal vein. It should be noted that the vein was alkaline and that K feldspars were present even at 80% illite in illite/smectite. This means that K availability was not a limiting factor in illite layer formation.

Pearson & Small (1988) concluded from chemical analysis of fine-clay fractions (< 0.4 μm) from the Viking Graben that increasing K fixation in interlayer sites of illite/smectite mixed-layers was accompanied by increasing substitution of Al for Si in tetrahedral sites.

These various investigations have shown that Al^{3+} substitutes in the tetrahedral sheet for Si^{4+} and that K^+ is fixed during the diagenetic formation of illite layers from smectite layers. Some of the investigations have also found changes in the octahedral sheet (Al substituting for Mg and Fe; reduction of Fe^{3+}). The changes seen during hydrothermal experiments and in hydrothermal areas seem to differ from those seen during burial diagenesis in that higher negative charges are created and that Na^+ and Ca^{2+} also are fixed under hydrothermal conditions.

Changes in interlayer cations and potassium fixation during illite layer formation

The hydrothermal experiments mentioned above have shown that specific interlayer cations are dehydrated and fixed when the negative charge of the 2:1 layer becomes sufficiently high. The concentration and type of the cations in the interlayer are therefore important and several investigations have dealt with this subject.

Powers (1959) emphasized the role of chemical composition of interstitial water in clay diagenesis, especially the role of the Mg/K-ratio, and proposed a model according to which preferential adsorption of Mg to K should decrease with depth in marine sediments due to decreasing amounts of Mg with depth of burial, from the 5:1 ratio found in sea water. Dunoyer de Segonzac

(1970) wrote that the most important process during formation of non expandible layers occurred in the interlayer where water and exchangeable cations should be replaced by non-exchangeable Na^+ and K^+. He predicted mica sheets in regular mixed layers to be rich in Na^+ relatively to K^+ because of the dominance of Na^+ in most interstitial solutions. Powell et al. (1978) found that K^+ was adsorbed on the surface of the clay during the first dehydration of the interstratified clays (illite/vermiculite/smectite). (They probably mean fixed instead of adsorbed). In one well they found a sharp decrease in the molar ratio of $SiO_2 + Fe_2O_3 + MgO$ to Al_2O_3 at the depth where a change in the d_{001} spacing was observed. Eberl & Hower (1977) concluded from hydrothermal experiments that potassium as interlayer cation was more readily fixed than sodium because of the lower hydration energy of potassium and that the formation of sodium mica layers therefore required a larger layer charge than did potassium mica-layers. Eberl (1978a) found from further hydrothermal experiments that the greater the hydration energy of the interlayer cation, the greater the charge that must develop in the 2:1-layers to cause dehydration, layer contraction and cation fixation, and therefore the slower the dehydration rate. Eberl (1978a) also found that monovalent cations resulted in a gradual transformation of smectite layers into illite layers. Divalent cations resulted in direct formation of a rectorite-like phase from smectite (there was no gradual increase in amount of illite layers). Potassium fixation is, however, preferred both because dehydrated potassium fits into the hexagonal holes of the tetrahedral sheet and because potassium has the lowest hydration energy (Eberl 1978a). Heling (1978, 1979) investigated the illite/smectite mineralogy, the potassium minerals, the specific surface (N_2), and the pore dimensions (by mercury intrusion) of Tertiary samples from the Rhine Graben. He concluded that although tetrahedral substitution should be important, the major process in the formation of illite layers from smectite is the diffusion of K^+ ions into the interlayer space of smectite.
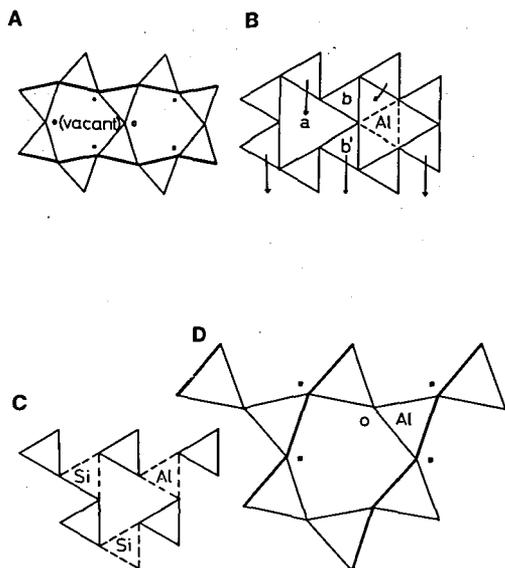
Fig. 7. Model for a solid-state transformation of a single tetrahedral sheet, as proposed by Pollard (1971). Figure and figure captions slightly modified from Pollard (1971, fig. 1).
A: Projection on (001) of the basal faces of tetrahedra in one sheet and of occupied (■) and vacant (○) octahedral sites for a "montmorillonite" (smectite) layer. Tetrahedral rotation is approximately 12°, and tetrahedra are tilted approximately 5.5° about the bolder edge. This is the bottom tetrahedral sheet, so that the basal oxygen in each tetrahedron that is not on the bolder edge is slightly elevated.
B: Aluminum has entered some of the "a" sites, causing full rotation of the tetrahedra (30°) and creating the possibility that silicon can be expelled either from the tetrahedral "b" or "b'" sites. The "b'" expulsion is schematically depicted here. The expelled silicon can migrate along easy paths either to empty "a" sites (straight arrows) or to the interlayer volume (curved arrow), if the neighbouring "a" sites are occupied by aluminum.
C: Previous "b'" sites are depicted as empty and previous "a" sites are depicted as occupied either by aluminum or by silicon that has migrated from previous "b'" sites. These new (Al, Si) tetrahedra are outlined by dashed lines. The previous "b" tetrahedra are unchanged, still occupied by silicon, and outlined in solid lines. Relaxation from extreme rotation has not occurred yet at this stage.
D: Continued tetrahedral rotation and retilting of tetrahedra yield the bottom tetrahedral sheet of the alteration product, where the corrugations in the basal oxygen plane trend at 120° from those in the original tetrahedral sheet. The distribution of aluminum over the tetrahedral sites in the alteration product is ordered, and the ratio Al/Si in the (Al, Si) tetrahedra varies from 0 to ⅓ (as depicted) to infinity, depending on the occupancy of the original "a" sites by aluminum when increased tetrahedral rotation was initiated.

Mechanisms for formation of illite layers from smectite layers

Possible mechanisms for formation of illite layers were mentioned in the chapter on elemental changes in the 2:1 layers during illite layer formation. These mechanisms will now be discussed in

more detail, in relation to different materials and reaction conditions.

Weaver (1958a) advocated the formation of illite layers as solely aggradation (K^+- fixation between high-charge, K^+- depleted layers). This involves no changes in the substitution pattern of the 2:1 layers and is termed aggradation by Millot (1970).

Van Olphen (1966) investigated the collapse of the interlayer space after heating K^+- saturated montmorillonite clays. He found that the ease and degree of this collapse was high for a high degree of tetrahedral substitution and for a high K^+ population on the unit layer surface. He also found that a highly crystalline bentonite, probably originating from weathering of mica, showed a higher degree of collapse than did a poorly crystalline bentonite, probably originating from weathering of volcanic ash. After the AIPEA classification, see table 1, the amount of layer charge determines whether the 2:1 clay layers are smectitic, vermiculitic or micaceous (illitic), and the decrease in expansion following K^+–fixation between high-charge layers is therefore a K^+–fixation in illitic layers. The investigations cited above show that the cations in the 2:1 layers are changed during diagenesis and this ruled out the theory of pure aggradation. Therefore, the smectite to illite reaction must occur either as a transformation or a neoformation after the terminology of Millot (1970) (see above).

Pollard (1971) described the formation of illite layers from smectite layers through a transformation. He proposed the following mechanism for solid-state Al for Si substitution in tetrahedral sheets (see fig. 7): A slight rotation, approximately 12°, positions 3 of the 6 oxygens of the ditrigonal holes closer to the middle of these holes (fig. 7A). They are therefore attracted by one entering Al cation and this attraction causes tetrahedral rotation of 30° so that the basal plane of the tetrahedral sheet looks like in fig. 7B. One Si^{4+} is then expelled from neighbouring site b, and ordered substitution of Al^{3+} for Si^{4+} is obtained by repeating this procedure throughout the tetrahedral sheet. Continued tetrahedral rotation and tilting results in a tetrahedral sheet with ditrigonal holes like those before substitution but with tetrahedra rotated 120° with respect to the octahedral sheet (fig. 7D). As "a" sites become Al tetrahedra and "b'" sites are vacated

by Si^{4+} ions, protons have to be exchanged from the apical oxygen of the "b" sites to the hydroxyl groups coordinated to the "a" sites. Pollard proposed that Al from breakdown of kaolinite or feldspar is present as a dissolved species in the interlayer volume of clays and therefore present for migration into the "a" sites. He proposed that the presence of ⅓ Al per "a" site may result in an illite layer after one operation of the proposed mechanism. However, if the ratio of Al atoms per "a" site is less than one third, the mechanism would be required to operate more than once during diagenesis, such that tetrahedral Al in one sheet would increase with each operation. Pollard wrote that "in this sense, the montmorillonite-to-illite alteration may represent a segment of the larger metamorphic alteration from montmorillonite to mica, the total process being constructed of smaller semidisplacive steps" (p. 90, l. 14 from bottom).

Hower et al. (1976) investigated cuttings from Oligocene-Miocene sediments from the Gulf Coast, USA. They found that the chemical changes in the illite/smectite generally fit the reaction: smectite + Al^{3+} + K^+ → illite + Si^{4+}, as suggested by Pollard (1971). Hoffman & Hower (1979) investigated outcrop samples from Cretaceous shales and bentonites from the Distorted Belt, Montana. They concluded that the reaction during the low metamorphic process in the shales appeared to be the same as that which had been proposed by Hower et al. (1976) for burial diagenetic sequences. In the bentonites, they proposed three different reaction schemes depending on the amount of available potassium and aluminum:

1) No K^+: X-smectite → kaolinite + quartz + X^+
2) Limited K^+: K^+ + X-smectite → illite/smectite + quartz + K^+ + kaolinite
3) Unlimited K^+: K^+ + X-smectite → illite/smectite + quartz + X^+
   (X-smectite is smectite with the exchangeable cation X^+)

Hoffman & Hower (1979) did not discuss the mechanisms in these reactions. However, the initial formation of smectite from the volcanic ash in the bentonites must have occurred through dissolution of the ash and crystallization of the smectite layers. The formation of kaolinite and quartz under conditions of limited or no available potassium must also occur from aluminum and silicon dissolved from the smectite layers. The complete conversion of smectite to kaolinite when no potassium is available is therefore a complete neoformation mechanism. The conversion of smectite to illite in shales during burial diagenesis (Hower et al. 1976) or metamorphism (Hoffman & Hower 1979) was considered a transformation mechanism, mainly occurring through Al^{3+} for Si^{4+} substitution in the tetrahedral sheet.

Eberl & Hower (1976) carried out hydrothermal experiments on the smectite → illite reaction. They concluded that the activation energy calculated for the reaction probably represented the energy required to break chemical bonds in the tetrahedral sheet so that Al^{3+} can substitute for Si^{4+}. Eberl & Hower (1977) concluded that in nature the mechanism of illite layer formation can be related to the hydration energy of potassium. The mechanism proposed to occur in nature is that Al^{3+} substitutes for Si^{4+} in the tetrahedral sheet at high temperatures in the sediments. When the layer charge during this reaction has become sufficiently high, interlayer potassium dehydrates, the interlayer space contracts irreversibly and illite layers have formed. Sawhney (1967) suggested that polarization of electron densities in the 2:1 layer towards the mica interlayer should take place because of the shorter distance between a dehydrated cation and the surface of the tetrahedral sheet in the 2:1 layer facing the adjacent interlayer. This polarization would then make the tetrahedral sheets adjacent to the expanded interlayers effectively less negative. Such less effectively negative tetrahedral sheets will, according to Eberl & Hower (1977), require more substitution of Al^{3+} for Si^{4+} to develop sufficient negative charge to dehydrate the interlayer cation. Furthermore, the polarization effect may make Al^{3+} substitution in the other tetrahedral sheet of a 2:1 layer more difficult when one tetrahedral sheet has acquired a negative charge through Al^{3+} for Si^{4+} substitution. Thus, the polarization effect may, according to Eberl & Hower (1977), favour ordering of illite and smectite layers in illite/smectite. Depending on the degree of substitution in a tetrahedral sheet, ordering may be IS (high charge

from tetrahedral substitution) or ISI (lower charge from tetrahedral substitution, so that polarization from two layers is required to prevent Al^{3+} for Si^{4+} substitution in adjacent 2:1 layers) (Eberl & Hower 1977). The reactions at the elevated temperatures (260°–490°C) of the hydrothermal experiments together constitute a solid-state transformation mechanism and the polarization from such a solid-state Al^{3+} for Si^{4+} substitution can result in ordering (IS or ISI) of the formed illite/smectite.

Roberson & Lahann (1981) found that K^+ saturation of natural montmorillonites resulted in a decrease in the amount of expandable layers and suggested that these minerals possessed layers with sufficient charge to fix K^+ from solution without heating. Roberson & Lahann treated the montmorillonites hydrothermally at 270°C and 350°C. TEM showed that the formed illite/smectite did not differ in morphology or size from the starting montmorillonites and this was taken by Roberson & Lahann to be "not inconsistent with a solid-state transition of smectite to illite". Initially, there was no Al in the solution so Roberson and Lahann concluded that the Al necessary for illite layer formation was derived from the breakdown of other smectite layers.

Howard & Roy (1985) heated a sodium saturated bentonite hydrothermally at 150°C and 250°C to investigate the importance of K^+- deficiency for creation of charge in the 2:1 layers during hydrothermal conversions. They found in the 150° experiment that Al, Si and Mg appeared to be released stoichiometrically with respect to the original smectite composition. They took this to indicate the formation of high-charge layers through a dissolution mechanism. No illite layers were formed in the reactions, but only high-charge layers which contracted to 10 Å after K^+-saturation and glycolation. This was contrary to the solid-state transformation previously proposed for interlaminated sandstones and shales by Howard (1981).

Whitney & Northrop (1988) carried out hydrothermal experiments on the smectite to illite reaction. K^+- saturated standard smectites from the Clay Minerals Society were treated at 250–450°C. The products were examined by XRD and for oxygen isotope composition. Whitney & Northrop concluded that the formation of randomly ordered illite/smectite was accompanied by incomplete isotopic resetting and could be considered a transformation reaction, whereas the formation of ordered illite/smectite was accompanied by complete isotopic resetting and could therefore be considered a neoformation reaction. They found, however, that the "illite" layers reexpanded after Na^+–saturation and were therefore to a large extent not true illite layers. Furthermore, Whitney & Northrop stressed that, according to results of Yeh & Savin (1977), isotopic exchange occurs increasingly with increasing temperature and may have reached equilibrium above 100°C. Thus, the isotopic resetting of the ordered illite/smectite may have been an isotopic exchange, and they concluded that the interpretation of the isotopic composition of illite/smectite must be done cautiously.

The above mentioned investigations of the illite/smectites were all carried out by XRD and chemical analysis supplemented in one case (Eslinger et al. 1979) by Mössbauer spectroscopy. Nadeau, Wilson, McHardy & Tait (1985) investigated the conversion of smectite to illite during diagenesis in bentonite and sandstone samples by XRD and transmission electron microscopy (TEM) on dispersed clay particles. The neoformation mechanism, which previously had been agreed to for sandstone illites and substantiated by scanning electron microscopy (SEM), was extended to include bentonites by Nadeau et al. (1985). They considered the particle thickness distributions observed by TEM to arise from dissolution of smectite particles and neoformation and growth of thin (from 10 Å to more than 50 Å thick) illite particles. The IS ordered illite/smectites were explained to be 20 Å thick illite particles, with an interparticle space of 7 Å (when glycolated), which by the interparticle diffraction effect should give (10 Å + 10 Å + 7 Å) regular d(001) spacings. Nadeau & Bain (1986) investigated smectites from Cretaceous bentonites and illitic clays from Cretaceous, Devonian and Ordovician bentonites and from Jurassic and Permian sandstones. Nadeau & Bain used XRD, chemical analysis (including infrared spectroscopy (IR)) and TEM on dispersed clay particles. The negative octahedral charges were 0.2–0.4 in the smectites and in some of the Cretaceous illitic clays but smaller than 0.12 in the other illitic clays. The negative tetrahedral charges were about 0.1 in the smectites and 0.4–0.8 in the illitic

clays. All figures were per $O_{10}(OH)_2$. Four of the illitic clays from Cretaceous bentonites had a higher Al and a lower Mg content in octahedral sheets than the "parent" smectites. Nadeau & Bain concluded that all the data suggested that the illitic clays in bentonites, like those in sandstones, are neoformed, diagenetic products. They mentioned that the expandable layers in many of the illitic clays had negative charges significantly greater than 0.6 per $O_{10}(OH)_2$, i.e. charges usually found for vermiculite layers (table 1).

Środoń, Morgan, Eslinger, Eberl & Karlinger (1986) investigated illite/smectites from Silurian (from U.K.), from Carboniferous (from Poland), and from Cretaceous (from Montana) by XRD, chemical analysis and surface area measurements. They calculated that the R0 ordered illite/smectites required a charge of −0.55 in the illite layers to dehydrate and fix potassium. Once about 50% of the layers had collapsed, the clay ideally was composed of 20 Å thick particles. They proposed that a further decrease in expandability occurred by joining together of these 20 Å thick illite particles to form 40 Å thick particles and calculated that a charge of −1.0 was required for this dehydration. They attributed this higher charge compared to the −0.55 to the polarization from adjacent illitic substituted tetrahedral sheets in the same unit. They concluded therefore that the smectite to illite reaction in their samples proceeded as a transformation, in agreement with their finding that the octahedral charge was stable throughout the mixed layer series.

Ahn & Peacor (1986a) investigated samples from the Tertiary Gulf Coast clays by HRTEM on intact bulk rock. These samples had been investigated chemically and by XRD by Hower et al. (1976). Ahn & Peacor did not find the very thin illite particles predicted by the neoformation theory of Nadeau et al. but deduced that smectite crystals were dissolved and that illite crystals (packets) grew both laterally and in thickness (along c*). They did not detect mixed-layering of illite and smectite. They also investigated (Ahn & Peacor 1986b) a standard Clay Minerals Society rectorite. Grains of this rectorite had a 20 Å contrast in lattice images in HRTEM. Some of the packets seen in ground rectorite were very thick and others only 20 Å thick. Ahn & Peacor concluded that grinding and dispersion of clays

prior to XRD investigation might have caused disrupture of illite/smectite and thereby resulted in the very thin particles seen in TEM by Nadeau et al. These thin particles are accordingly not present in intact bulk rock.

Altaner et al. (1988) used XRD and ^{29}Si NMR to investigate samples of illite/smectite with 90–100% illite layers and one rectorite with 50% illite layers. The percentage of smectite layers as calculated from the ^{29}Si NMR was significantly higher than the percentage obtained by XRD (the percentages given above). They concluded that tetrahedral sheets with a low degree of Al for Si substitution, the smectitic substitution pattern, must be present in the illite particles and that these particles therefore had probably formed by a transformation process by Al for Si substitution, as proposed by Hower et al. (1976), and not by a neoformation and growth of fundamental particles, as proposed by Nadeau et al. (1985).

The solid-state transformation proposed by Pollard (1971) and Hower et al. (1976) from investigations of shales was thus substantiated by the hydrothermal experiments of Eberl & Hower (1976, 1977). The solid-state transformation was opposed by Nadeau and co-workers in their theories of interparticle diffraction and of illite particle neoformation, through a smectite dissolution followed by illite precipitation and growth of very thin illite particles. They assumed that the thin particles seen in dispersed illite/smectite are present in intact bulk rock and that the illite/smectite diffraction patterns represented structures formed during specimen preparation. The solid-state transformation was also opposed by Ahn & Peacor in their theory of dissolution of smectite layers and growth of thick illite particles. However, the chemical calculations of Środoń et al. and Altaner et al. and the observations of Nadeau & Bain indicate that variation in charge is present among the smectite layers seen in XRD or among the terminating layers of the fundamental particles seen in TEM of dispersed clay specimens. A neoformation of illite should result in particles where all layers have an illitic charge. Thus, these findings of different charges in the smectitic layers can best be considered to result from a solid state transformation.

Chemical controls

The above mentioned investigations have shown that the formation of illite layers from smectite layers requires an input of an interlayer cation for fixation. It has hitherto been believed that this cation in burial diagenesis was predominantly K^+. It also requires a supply of Al and a release of Si to increase tetrahedral substitution, and perhaps a supply of Al and a release of Fe and Mg to modify the octahedral sheet. The chemistry of migrating solutions can control clay diagenesis (kaolinite or illite formation) in sandstones (Millot 1970; Hancock & Taylor 1978) and in pores and microfractures in the claystone formations investigated here (Lindgreen 1985, 1987a). The mineralogy of the pores and veins in Upper Jurassic claystones from the North Sea (Lindgreen 1985, 1987a) showed that there has been at least two phases of fluid migration from these claystone oil source rocks. In the following it is discussed to what extent claystones are open or closed systems, and to what extent illite/smectite diagenesis in claystones is influenced by pore water composition and bulk rock composition.

Lai & Mortland (1960) showed that ions can diffuse rapidly through mud without water movement and proposed that self-diffusion of cations in a clay-water system occurred by cations jumping from the exchange site on one particle to a site on another particle. Hanshaw (1964) demonstrated for compacted montmorillonite that ion mobility is more important than ion charge for ion exchange in compacted clays and that the more mobile monovalent cations are therefore adsorbed in preference to the divalent cations.

Powers (1959) emphasized the role of chemical composition of interstitial water in clay diagenesis, especially the Mg/K ratio, and proposed a model according to which preferential adsorption of Mg to K should decrease with depth in marine sediments due to decreasing amounts of Mg, from the 5:1 ratio found in sea water.

Long & Neglia (1968) investigated the content of K^+, Na^+, and Cl^- in clay pore waters of Tertiary (from Italy), Triassic (from Tunisia) and Carboniferous (from the North Sea) age and the diagenesis of clay minerals in these samples. They found that the content of K^+ increased from 9–13% to 18–22 meq% (as $100K^+/(CEC + Cl^-)$) at the same depth where illite/smectite changed

from randomly ordered to ordered in the Italian Miocene clays. They explained this increase in K^+ to be due to an invasion of the claystones by alkaline fluids rich in potassium. They concluded that the pore waters were in chemical equilibrium with the minerals and that the increase in K^+ had resulted in formation of the ordered illite/smectite from the randomly ordered illite/smectite. In the Triassic clays they found montmorillonite at shallow depth, changing to randomly ordered mixed-layers, further to ordered mixed-layers, and finally to illite, with increasing depth, and they explained this similarly to be due to the increase in amount of K^+ in pore waters with depth.

Dunoyer de Segonzac (1970) estimated that the transformation of montmorillonite is mainly influenced by depth of burial because he believed in the role of pressure in the dehydration process, but he stressed the importance of the chemical composition of the interstitial solutions. Weaver & Beck (1971) found in a Gulf Coast well in Eocene Pliocene strata that Na^+ was the major cation in the interstitial water ($> 90\%$ of the cations) and K^+ was second in abundance, followed by Mg^{2+} and Ca^{2+}. The cation ratios in the well were approximately constant to 12000' depth, where Ca^{2+}/Na^+ decreased and K^+/Na^+ and Mg^{2+}/Na^+ increased. HCO_3^- was the dominant anion, SO_4^{2-} next in abundance, and Cl^- present in lower amounts. They deduced the existence of a permeability seal causing high water pressures at about 9800', and proposed that the upward migration was therefore hindered, mainly for water and Cl^- and to a lesser extent for the other ions. In the deeper samples, they found that K^+ and Mg^{2+} increased in the interstitial water with increasing depth and temperature and attributed this to the increased solubility of the silicate minerals at high temperature. They proposed from the chemical data that K^+, Mg^{2+} and Fe migrated upwards to react with K^+-, Mg^{2+}-, and Fe- deficient clays to form an illite-chlorite suite and that deeply buried shales are accordingly "autocannibalistic".

Schmidt (1973) investigated sidewall cores from Oligocene shales from the US Gulf Coast. He found that the content of Na^+, K^+, Ca^{2+} and Cl^- increased downwards, whereas the content of Mg^{2+} did not vary with depth and he proposed that the increase in K^+ was caused by feldspar

dissolution. In the interstitial water of abnormally pressured clays, the Ca^{2+} concentration was low and the Mg^{2+} concentration high. He found that SO_4^{2-} increased in concentration with depth and dominated over HCO_3^- and Cl^-. Furthermore he found a large difference in composition between water in the clays and in adjacent sandstones, in that the water in the sandstones was notably low in sulfate and bicarbonate. He found that, shallower than 10000', the water in the sandstones had a concentration of dissolved solids of more than 150000 mg/l, whereas deeper sandstones had a concentration of only 20000 mg/l in wells with abnormally high pressure but increased up to 180000 mg/l in normally pressured wells. The total dissolved solids in the interstitial water of normally pressured shales increased gradually with depth, ranging between 10000 and 70000 mg/l. In the zone with high pressures, the salinity of the interstitial water was about the same in the shales and in the sandstones. Schmidt concluded that the data seemed to support a selective membrane-filtration process in the shales. Furthermore, that a diagenetic release of interlayer water from smectite layers could explain the low salinities of the interstitial water in the sandstones and shales in the zone with high pressures. In the zones with normal pressure, Schmidt's finding of higher salinities in the sandstone waters than in the shale interstitial water is surprising, since membrane filtration effects of the shale should concentrate ions in the shale interstitial water. Heling & Teichmüller (1974) found, from investigations in the Tertiary of Oberrheingraben in three wells, an unexpectedly high amount of illite layers in mixed-layers relative to temperature and thought it was due to the influence of high-saline thermal solutions probably with a high content of K. They noted that the diffusion of K^+ ions into the interlayers of smectite is dependent on temperature, time and K^+- concentration gradients. Hower et al. (1976) proposed that the K^+ for illite layer formation originated from dissolution of feldspar or detrital mica in the rock. Eberl & Hower (1976) found that kaolinite and quartz were additionally formed during formation of illite/smectite from K^+- saturated smectite in hydrothermal experiments, because Al and K for illite layer formation had to be supplied from breakdown of some smectite layers. They proposed, however, that

excess Al and K in natural systems could result in the reaction:

$$Al^{3+} + K^+ + smectite \rightarrow illite/smectite + SiO_2$$
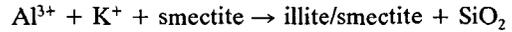
Eberl & Hower (1977) concluded from hydrothermal experiments between 260° and 490°C that sodium saturated smectite must develop a full mica charge of -1.0 equivalents per $O_{10}(OH)_2$ to form a non-expanding layer, whereas potassium smectite needs only to develop an illite charge of -0.8 equivalents per $O_{10}(OH)_2$. Thus, the formation of paragonite from sodium smectite yielded more kaolinite than did the formation of illite from potassium smectite. Eberl & Hower (1977) found that the rate-limiting control in formation of illite from smectite is tetrahedral Al for Si substitution. They reasoned that the greater negative charge developed during transformation of sodium saturated smectite is necessary for sodium dehydration prior to its fixation. Eberl (1978a) concluded from hydrothermal experiments at 300°C and 400°C that alkali saturated clays reacted by means of a gradual transformation of smectite into mixed layer clay, and that alkaline earth cation saturated clay led to a reaction in which the smectite disappeared and a rectorite-like phase emerged fully formed. Eberl (1978b) investigated the following reaction series for dioctahedral smectites by hydrothermal experiments at 300°C and 500°C, with variable interlayer and solution chemistry:

1) gel → K-beidellite → random illite/smectite → K-rectorite → illite
2) K-montmorillonite → K-rectorite → illite
3) Na-montmorillonite or beidellite → Na-rectorite → paragonite
4) Li-montmorillonite → Li-tosudite → Li-rectorite → cookeite(?)
5) Mg-montmorillonite → Mg-rectorite → tosudite → sudoite(?)
6) Ca-montmorillonite → Ca-rectorite → margarite(?)
7) (at 150°C) Al-Ca-montmorillonite → kaolinite/smectite → kaolinite
8) (at 320°C) Al-Ca-montmorillonite → pyrophyllite/smectite → pyrophyllite

Heling (1978, 1979) believed potassium supply from external sources to be unlikely "because of

the very low permeability of compacted shales" (Heling 1978, p.219, 1.8), and favoured K-feldspar as the potassium source because he could not believe in the simultaneous decomposition of muscovite and formation of illite. He wrote that as increasing pressure decreased pore radii and thereby lowered diffusion rates, the pressure factor in depth of burial should decrease illite formation rates. Środoń (1979) found from the Silesian coal basin that illite/smectite in pyroclastics are always more smectitic than in surrounding shales, at least by 10%, and that the illite content in pyroclastics decreases more, even down to pure smectite, towards the centres of the beds. This kind of variation within a bed is, according to Środoń who cites pers.com. with Hower and with Brusewitz, a general phenomenon; it is thought by Środoń and Hower to be due to deficiency of K within bentonite beds. Środoń proposed a triple control (of temperature, K-supply and starting material) on the formation of illite/smectite and concluded that clay diagenesis proceeds more slowly than the coalification process and that the increase of illite content of illite/smectite is much faster for the IS than for the ISII structure. Lahann & Roberson (1980) found in hydrothermal experiments that an increasing concentration of K^+ accelerated Si removal. They inferred that most of the silica dissolution and transport occurred in the interlayer space and proposed that, because of the greater hydration energies of Mg^{2+}, Ca^{2+} and Na^+ relatively to K^+, the movement of silica through the interlayer space was restricted by Mg^{2+}, Ca^{2+} and Na^+ in the interlayer space. They wrote that this role of K^+ in clay diagenesis implied the importance of pore water chemistry. Roberson and Lahann (1981) wrote that no external source was required for increased tetrahedral Al and concluded that the Al, which became incorporated in tetrahedral sheets in illite/smectite in hydrothermal experiments, was derived from breakdown of other smectite layers. They also showed that rates of illite formation were significantly lower when Na^+, Ca^{2+} or Mg^{2+} were present in addition to K^+ compared to when K^+ was present alone. They wrote that the presence of these ions is probably the main cause for slower kinetics in natural systems. Petukhov, Zvereva & Tikhomirova (1981) found indications in Caspian oil fields that hydrocarbons have a protective effect on clay minerals

and may result in "montmorillonite caps" over hydrocarbon pools. They also proposed that acidification of pore water through catalytic breakdown of hydrocarbons (producing CO_2) on clay mineral surfaces might result in reversal of the illitization process in caprocks. Eslinger & Sellars (1981) proposed from investigations on the Precambrian Belt Supergroup in Idaho that K for the smectite to illite reaction originated from detrital K feldspar and that K can be derived from breakdown of detrital mica, when insufficient K feldspar is present for the smectite to illite reaction. They suggested that illite is generally formed from smectite, which is formed during orogenic volcanism, and that much of the illite then originate from metamorphism of smectite.

Nadeau & Reynolds (1981a) found in shales and bentonites that calcium carbonate inhibits the formation of ordered illite/smectite, particularly during the incipient stages of the reaction. The data of Inoue & Utada (1983) suggested that the development of the hydrothermal mica/smectite zone and the progress of the conversion reaction were controlled by the cation composition of the hydrothermal solution as well as by temperature. Bruce (1984) tabulated data from Tertiary shales from three basins and concluded that the threshold temperature to initiate smectite diagenesis ranged from 71 to 150°C, it may be retarded by lack of potassium feldspars or inhibited by calcium, sodium or magnesium, and that the reaction apparently ceased when the potassium feldspars were absent. Time and pressure were, according to Bruce, of no importance in the basins investigated. Środoń (1984) concluded that the salinity of the basin (up to extreme basins such as K-Mg salt basins) did not influence the rate of illitization of expandable clay. Smart & Clayton (1985) found that illite/smectite in sandstones generally has a higher percentage of smectite layers than in the surrounding mudrocks although the reverse is sometimes the case. They concluded that the sand laminae acted as pathways for the migration of ions to and from the system, whereas they believed that the mudrocks with K feldspar and discrete illite as a K^+ source acted as a closed system. Velde (1985) compared results of the investigations of Hower et al. (1976), Boles & Franks (1979) and Velde on clay mineralogical transformations in the Gulf Coast Tertiary and proposed that an isothermal transi-

tion of smectite layers to illite layers in the investigation of Hower et al. could be due to differences in sediment chemical composition at the transition position in the sediments, whereas the gradual transformation of smectite to illite layers (of Boles & Franks) should be due to a chemical control in the sediment affecting the clay composition. Velde proposed from data on the composition of chlorites that the oxidation stage of iron should be such a chemical control.

Pearson & Small (1988) calculated for Quaternary to Triassic shales from the Viking Graben and Moray Firth that the amount of K feldspar in Lower Tertiary sediments with a high content of smectite would be sufficient to allow complete illitization of the smectite layers. They concluded therefore that destruction of K feldspar during burial (it was absent in most wells beyond 2500m depth) was a major source of K for illitization of deeper sediments.

According to the above mentioned investigations, K^+ supply is the main chemical control for the formation of illite layers from smectite. Even in systems with sufficient K^+ available, other cations such as Mg^{2+}, Ca^{2+} and Na^+ may inhibit K^+ fixation and illite layer formation. It has been proposed by several authors that this inhibition may be the cause for the slower reaction rates in natural systems where these cations are present in significant amounts. It was calculated from hydrothermal investigations that the rate limiting step in illite layer formation is tetrahedral Al for Si substitution. Therefore, the formation of the negative charge by Al for Si substitution is not necessarily inhibited by Mg^{2+}, Ca^{2+} or Na^+. This may be the cause in formation of high-charge expandable layers during diagenesis.

The investigations give examples of K^+ supply from pore water, from breakdown of K feldspar or from breakdown of detrital mica. However, the last possibility was questioned by Heling who did not believe in simultaneous decomposition of muscovite and formation of illite.

The oxidation state of iron may, according to Velde, be another chemical control. The Al required for tetrahedral substitution has been proposed by some authors to originate from dissolution of some smectite layers. It has been documented by several investigations that clays can be open systems, but also that the elements necessary for the smectite to illite layer transition can

be supplied from breakdown of minerals in the clay rock. The possible role of NH_4^+ as a fixed interlayer cation has not been investigated, but NH_4^+ has been found in illites by Higashi (1978) and Sterne, Reynolds & Zantop (1982).

Release of clay transformation water

Weaver (1960) found for two Tertiary well sections and one Upper Mississippian well section in USA that log velocity values and density values increased with increasing age whereas the amount of expandable clay layers at a given depth was the same regardless of age. He suggested that the expulsion of pore water is not related to the collapse of montmorillonite as one would expect and that the contraction of expandable layers has little effect on the overall density of the sample. He noted, however, that the small amounts of water released by contraction of montmorillonite layers may be important in moving hydrocarbons from between the expanded clay layers (if formed there) to the pores.

Powers (1967) used a clay colloid chemical approach and proposed from clay mineralogical variations with depth in wells that water is expelled by compaction of marine mudrocks to about 3000', except for montmorillonite clays (fig. 8). Powers applied the adsorption isotherms of van Olphen (1963) according to which moderate overburden pressure alone cannot remove the last four layers of adsorbed water from interlayer positions in montmorillonite. Powers proposed, therefore, that these last water layers are released when K is adsorbed and montmorillonite is transformed into illite and mixed-layers in the depth interval 6000' to 10000', the "no-montmorillonite level". The release of this "high-density" water may, according to Powers, create overpressuring of the source rock and flush hydrocarbons suspended in water out of the source rock through fractures and other avenues of escape. Powers calculated that only small amounts of water were released from conversion of montmorillonite layers in mixed-layers to illite, from the "no-montmorillonite level" and down to a depth of 14000' in the Gulf Coast.

Burst (1969) distinguished 3 dehydration stages (fig. 8):

1. dehydration (release of pore water and excess interlayer water)

WATER ESCAPE CURVES

PERRY AND HOWER
High geothermal   Low geothermal
gradient ~.94°C/100'   gradient ~.74°C/100'

POWERS(1967) BURST(1969)

SUBSURFACE DEPTH

stage I

stage II

No montmo-
rillonite level

stage I

stage II

stage III

stage I

stage II

stage III

stage IV

stage I

stage II

stage III

stage IV

WATER AVAILABLE FOR MIGRATION
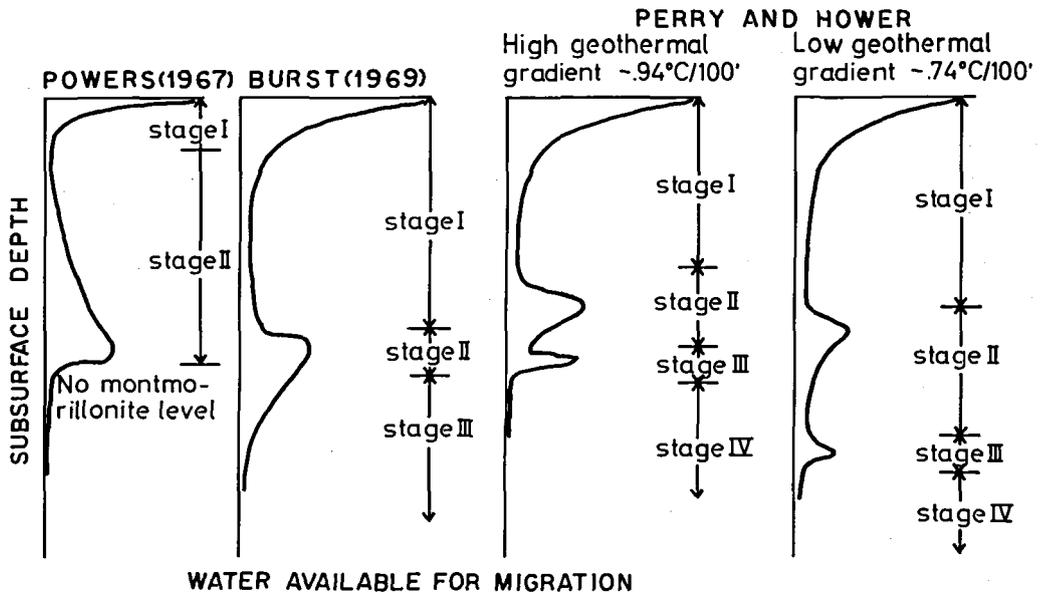
Fig. 8. Dehydration of illite/smectite in U.S. Gulf Coast sediments. The relation between burial depth and illite/smectite dehydration as proposed by Perry & Hower (1972), Powers (1967) and Burst (1969). After Perry & Hower (1972, fig. 8).

2. dehydration (release of one of the two water layers between silicate layers)
3. dehydration (release of the last water layer)

He found that the hydrocarbon production depths in Gulf Coast sediments were distributed in a statistically consistent relation to the calculated second clay dehydration contour surface. Burst based his calculation of this second clay dehydration on the loss of the 17 Å montmorillonite peak in glycolated specimens and on a model for conversion of montmorillonite to illite via stages with 2 and 1 water layers.

Perry & Hower (1972) calculated the water release from the amount of montmorillonite layers in the samples (they based their calculations on the presence of two water layers in montmorillonite as determined by the adsorption isotherms of van Olphen (1963)) and proposed 4 stages as follows (fig. 8):

Stage 1: The removal through pressure of interstitial water and of interlayer water in excess of two water layers.
Stage 2: Random collapse of montmorillonite layers until c. 65% montmorillonite lay-

ers have collapsed via chemical conversion to illite layers. Stage 2 was initiated in Gulf Coast shales at about 75% smectite. This stage began with a very high dehydration rate corresponding to an initially rapid decrease in the amount of smectite layers, which then decreased.

Stage 3: Transition from random to ordered interlayering. Perry and Hower calculated that a second, rapid dehydration rate took place at this stage. This stage lasted until c. 80% of the layers had collapsed, and then a reduction of the reaction rate was calculated to take place.

Stage 4: Loss of last interlayer water during collapse of the last expandable layers. This was assumed by Perry & Hower to be quite slow and was not observed in the Gulf Coast.

Heling & Teichmüller (1974) concluded that the first dehydration step of Burst (1969) occurred in the Tertiary of the Oberrheingraben above the oil generating zone and therefore assumed it to be of

little importance in oil migration in Oberrhein-graben. But they inferred from temperature de-terminations that the water released during the later dehydration stages was probably released during significant oil formation and was therefore of importance in assisting oil migration.

Foscolos et al. (1976) concluded from their investigation of Tertiary to Jurassic sediments that early mesodiagenesis (table 2) coincided with the first dehydration of water from the mixed-layers (stage 2 of Perry & Hower (1972)) and late mesodiagenesis (with 50–75% illite in mixed-layers) with the second dehydration of the mixed-layers (stage 3 of Perry & Hower (1972)). Powell et al. (1978) calculated that only one de-hydration took place during diagenesis in rocks where vermiculite in a smectite/vermiculite/illite mixed-layer was an intermediate product in the formation of illite layers from smectite layers. They believed that the second dehydration step due to the formation of illite layers from vermicu-lite layers was retarded because of a Ca-vermicu-lite component in mixed-layers, and they cited work by Kittrick which indicated that Mg and Ca vermiculites undergo the second dehydration step at around 230°C. Foscolos & Powell (1979) identified chlorite as a fourth component in the smectite/vermiculite/illite mixed-layers and be-lieved it to have formed by interlayering of Fe_2 $(OH)_6$ and/or $Al_2(OH)_6$ in expandable layer sil-icates. Foscolos & Powell (1979) concluded that the first clay dehydration step took place above and the second dehydration step below the main phase of oil generation in North Canadian wells because vermiculite was an intermediate product in the illite layer formation. They therefore con-cluded that clay dehydration water did not have a role to play in oil migration in the wells investi-gated.

Pearson et al. (1982) found that illitization was initiated at a depth of 2000–2500 m at 65–80°C in shales in the Viking Graben of the North Sea and proceeded via randomly interlayered minerals to a depth of 3200–3800 m at 100–120°C, where a change to the IM ordered structure was seen. They concluded that clay dehydration in the Vik-ing Graben took place in sediments which were either immature or at most early mature with respect to oil generation. The Kimmeridge clay in the wells was close to or below the level for illite/smectite ordering.

Bruce (1984) discussed the timing of the water release from claystones during diagenesis in rela-tion to oil migration and suggested that the water released from a smectite diagenesis occurring during or after oil generation was more effective in moving thermally generated oil and gas than water released early and above the hydrocarbon generating interval. He emphasized the addi-tional role of the released water in forming over-pressured shales and in microfracturing.

The water released during diagenesis of smec-tite layers has so far been calculated only from the number of smectite layers transformed into illite layers. However, Davidtz & Low (1970), Ravina & Low (1972) and Ravina & Low (1977) showed for different smectites that the degree of free swelling depends on the b-dimension, on the degree of tetrahedral rotation and on the valence of the cation. They suggested that the clay sur-face acts as a template for the adsorbed water molecules and therefore that the degree of free swelling depends mainly on the degree of tetra-hedral substitution of Al for Si. Ross & Rich (1973) showed that the b-dimension of a biotite decreased after oxidation of Fe^{2+} and that the tetrahedral rotation decreased with replacement of K by Ca. Odom & Low (1978) showed that the swelling of montmorillonite, at least at low water tensions, depends linearly on the fraction of lay-ers that fully expand and that this fraction, in turn, depends linearly on the b-dimension of the montmorillonite. Stucki, Low, Roth & Golden (1984) investigated the effects of iron oxidation state on clay swelling because of the decrease of the b-dimension with oxidation of octahedral iron. They concluded that increase in the amount of Fe^{2+} enhanced the relative stability of the un-expanded and/or partially expanded layers and thereby decreased the clay swelling.

The main points of the above cited literature are: Powers proposed a mechanism whereby clay dehydration aids in oil migration out of the source rock, primary oil migration. Burst demon-strated a statistical relation between clay dehy-dration levels and hydrocarbon production depths. Perry & Hower revised the dehydration stages proposed by Burst and these revised de-hydration stages have been used since then. Sub-sequent investigations have largely confirmed the statistical relation found by Burst, although ex-ceptions are reported. This statistical relation has
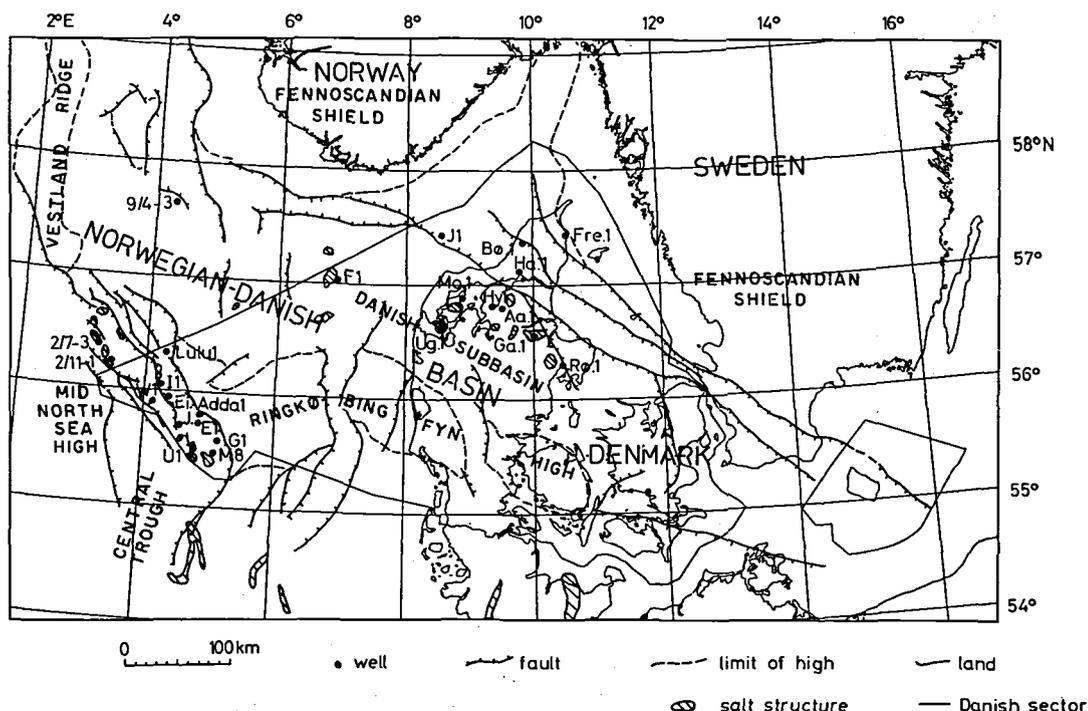
Fig. 9. Location of wells examined in the Central Trough and the Norwegian-Danish Basin. Main structural elements from Michelsen (1978) and O. V. Vejbæk (pers. com.).
Abbreviations: Bø. 1: Børglum 1; Fre. 1: Frederikshavn 1; Ga. 1: Gassum 1; Ha. 1: Haldager 1; Hy. 1: Hyllebjerg 1; Mo. 1: Mors 1; Rø. 1: Rønde 1; Ug. 1: Uglev 1; Aa. 1: Aars 1.

been interpreted to mean that clay dehydration aids in primary oil migration. But this has not been demonstrated, even if the creation of over-pressures (which are often seen in oil generating clay source rocks) has been taken as a clue about the "flushing out" mechanism. As a majority of the pores in the compacted clays are very fine (Lindgreen 1987b), a "flushing out" mechanism involving Darcy flow is unlikely to play a major role in oil expulsion. The statistical relation between oil production and clay dehydration may therefore be a coincidence, so that oil maturation and expulsion on one side and illitization and clay dehydration on the other side simply occur at the same temperature. Clay dehydration was investigated from adsorption isotherms by van Olphen (1963), and his work was the basis for the clay dehydration calculations based on XRD data. The correlation between the b-dimension in the 2:1 layer and water adsorption on smectites appears to be important for investigation of the diagenetic clay dehydration because the fraction of smectite that fully expands depends linearly on the b-dimension (Odom & Low 1978). In addi-

tion, since the degree of free swelling depends mainly on the degree of tetrahedral substitution of Al for Si (Ravina & Low 1977), the diagenetic illite layer formation by Al for Si substitution should influence the water release, even if K^+ is not fixed between the illitic substituted layers.

Geology of the Central Trough and the Norwegian-Danish Basin

The structural outline of the area is shown in fig. 9 and the structural outline of the Central Trough in fig. 10. The troughs in the area, the North Sea and Danish troughs, probably formed during Permo-Triassic instability of a Pangean megacontinent (Ziegler 1981). The following geological information is from Ziegler (1981). During the late Middle and Upper Jurassic, the Viking Graben and the Central Trough developed into the dominant rift system in the North Sea. During the Late Jurassic, subsidence rates in the Viking and Central grabens considerably exceeded sedimentation rates resulting in the development of

2°E 3° 4° 5°

57°N

Søgne Basin

Mandal High

Lulu1 RINGKØBING·

2/7-3

Feda

Grensen

2/11-1

FYN

HIGH

Graben

Tail End Graben

Nose

I1

Elin1

MID

56° NORTH

SEA

HIGH

Outer Rough Basin

Heno Plateau

W1

Adda1

Jens1

Salt Dome

G1

U1

M8

Province

• well

fault

salt structure

national sector
boundary

0 100km
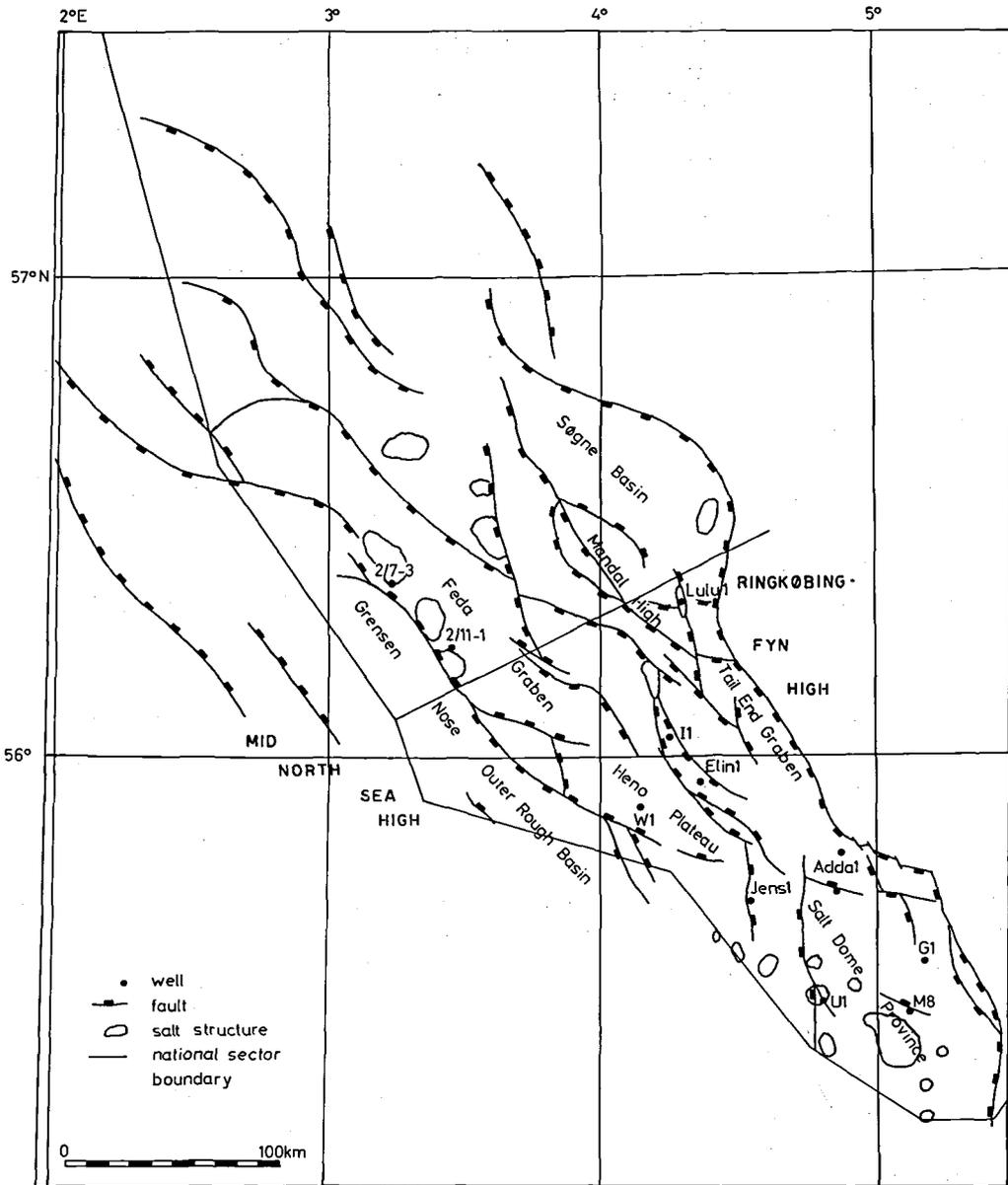
Fig. 10. Location of wells examined from the Central Trough. Main structural elements from Gowers & Sæbøe (1985) and O. V. Vejbæk (pers. com.).

deep water conditions. Upper Jurassic strata consist in these grabens of organic rich shales and local deeper water fan deposits; the Upper Jurassic strata display rapid lateral thickness variations due to the differential subsidence of individually rotated fault blocks. The highly organic Upper Jurassic shales represent the principal source rock for hydrocarbons occurring in the Central and Northern North Sea. In the Danish Trough

these source rocks are, however, replaced by low-organic shales. In large parts of onshore and offshore Europe, Middle and Upper Jurassic strata were deeply eroded during Cretaceous and Tertiary times. This renders it virtually impossible to reconstruct their original thickness and to obtain an impression of the overall subsidence patterns on the basis of a regional isopach map. Moreover, isopachs of the Upper Jurassic strata

do not reflect the true subsidence pattern in areas where sedimentation rates lagged behind subsidence rates.

During most of the Tertiary and the Mesozoic, the Fennoscandian shield and other highs were the source area for clastic sediments in the North Sea (Dypvik 1983) and in the Danish Subbasin (Michelsen 1978). Gowers & Sæbøe (1985) took the presence of immature erosion products of early Jurassic age in 2/7–3 and in the Fulmar and Clyde fields as an indication of emergent highs (Dogger High and the Mid North Sea High) in part of Upper Jurassic. Christensen (1974) investigated the Danish Jurassic ostracod fauna and concluded that the Northwest Danish Embayment was a part of a larger North Sea Basin with ostracod faunas closely related to the faunas in English deposits.

Rawson & Riley (1982) discussed the latest Jurassic to early Cretaceous events and the "Late Cimmerian Unconformity" in the North Sea. The transition from the Heather Formation to the Kimmeridge Clay Formation in deeper parts of the North Sea graben systems appears, according to Rawson and Riley, to mark the late Oxfordian transgression. By the early Kimmeridgian, the Kimmeridge Clay Formation and the Bream Formation organic-rich shales were accumulating over most of the offshore area with "hot" radioactive shales accumulating in parts of the Central Trough and Egersund Subbasin. In the central and northern North Sea, deposition of organic-rich shales continued through the Volgian and much of the Ryazanian, and middle Volgian to early Ryazanian "hot shales" are widespread through the graben system. However, the late Cimmerian movement had, according to Rawson & Riley, some profound effects in the offshore area though, as in the onshore region, many events were localized and not synchronous. In the basins flanking the central graben systems, regressive facies developed. In the graben systems, fault movement was renewed. Here, structural discordancy induced by step faulting and rotational slipping caused middle Volgian to Early Cretaceous sediments to transgress over a complex surface of tilted fault blocks. Rawson & Riley interpreted the Kimmeridge Clay- Valhall boundary to represent not a regional unconformity but a major isochronous environmental change and suggested that the shales of the Kimmeridge Clay Formation were deposited under a stratified water column. They believed that these shales formed during periods of fluctuating aerobic and/or anaerobic conditions with the consequent preservation of abundant organic matter. The "hot shales" should thus result from a restriction of water circulation, coupled with minimal clastic input, due to tectonically controlled "basin enclosure". They concluded that the Kimmeridge Clay- Valhall boundary represents a flushing out of the anaerobic Kimmeridge Clay basins and a breakdown of the stratified water column as a result of the late Ryazanian transgression.

Tentative isopach maps of the Cretaceous Series (Ziegler 1981, figs. 15b and 16b) show that the sediments deposited in both the Central Trough and the Norwegian- Danish Basin attained 200–1000 m in Early Cretaceous and 1000 to 2000 m in Late Cretaceous. An isopach map of the Cenozoic series (Ziegler 1981, fig. 17) shows that about 2000 m of sediments were deposited in the Central Trough during Cenozoic time, but that the thicknesses of Cenozoic sediments decrease from the Central Graben eastwards through the Norwegian-Danish Basin to become about nil in the north-eastern part of Denmark.

According to Nielsen, Sørensen, Thiede & Skarbø (1986) the subsidence of the Norwegian-Danish Basin seems to have been great in Miocene and part of the Oligocene. The subsidence of the Danish Subbasin in early Palaeocene was, from the isopach maps presented by Nielsen et al., up to 200 m and then practically ceased. The subsidence of the Central Trough increased through Tertiary time and sediments of 1300–3000 m accumulated.

Several investigations indicate that during Jurassic Cretaceous there was a supply of volcanic material in addition to the detrital material supplied from the highs in the area. Jurassic volcanics (lavas and tuffaceous material) from the Forties and Piper fields were investigated by Howitt, Aston & Jaqué (1975). They concluded that basaltic volcanism connected with rifting occurred during Jurassic times, probably commencing in the Bathonian and petering out in the Kimmeridgian. In some wells the tuffaceous material reached thicknesses of more than 120 m, interbedded with layers of basaltic lava. Aptian and Bathonian Fuller's Earth of Southern England

was studied by Hallam & Sellwood (1968). Their analysis indicated it to be an almost pure montmorillonite. They concluded from the total or almost total absence of illite, kaolinite and quartz which are ubiquitous in other Mesozoic sediments that terrestial derivation of the Fuller's Earth was improbable, and that it was produced by in situ alteration of volcanic ash. Cretaceous Fuller's Earth of Southern England was studied by Cowperthwaite, Fitch, Miller, Mitchell & Robertson (1972). They found that detrital minerals and other evidence of sedimentary transport and deposition occur in the Fuller's Earth. Moreover they believed that true bentonites of the thicknesses described by Hallam & Sellwood (1968) could only have accumulated very close to source vents. Cowperthwaite et al. inferred from studies on the structure of Fuller's Earth that argillization of what must have been glassy volcanic ash was mainly post-depositional. The lower seam in the Cretaceous Lower Greensand deposit was, according to Cowperthwaite et al., a true ashfall, whereas the main seam was mainly ash brought in as fine, sandy material from the neighbouring land mass during a rapid transgressional episode. In discussing occurrences of Fuller's Earth of Bathonian to Aptian age, Cowperthwaite et al. suggested that volcanic episodes associated with the Jurassic to Recent rifting of the North Atlantic might have affected Southern England. They considered the English Mesozoic Fuller's Earth to be mainly montmorillonite-rich deposits derived both directly from crystal-vitric ashfalls that accumulated in small lagoons and indirectly from the rapid penecontemporaneous erosion of ashfalls covering adjacent landmasses. Knox & Fletcher (1978) investigated samples from the Ryazanian part of the Yorkshire Speeton Clay and found four beds of volcanic clays in this formation. Jeans, Merriman, Mitchell & Bland (1982) described Ryazanian to Albian volcanic clays from southern England and found indications for an easterly source probably in the southern North Sea area. Dixon, Fitton & Frost (1981) found two sequences of igneous rocks of earliest Cretaceous age in well 29/25–1 at the edge of the Mid North Sea High, very close to the Auk Field. They summarized data for igneous activity in the North Sea Basin and concluded that the Jurassic phase of stretching activity in the North Sea Graben System resembles early Miocene activity in

the Kenyan segment of the East African Rift, except that the erupted volumes in the North Sea are negligible by comparison with those in Kenya.

Millot (1970) concluded that montmorillonite commonly results from weathering of volcanic glass, either in situ or as ash accumulated in sedimentary beds, and that this occurs only if the drainage is moderate enough to maintain an alkaline environment. Nadeau & Reynolds (1981b) proposed from clay mineral and K-Ar data for Cretaceous marine shales from North America that illite/smectite in these rocks originated from volcanic debris. They argued that high sedimentation rates of volcanic debris, resulting in the formation of distinct bentonite beds, means that the material has a much shorter marine residence time and is therefore essentially smectitic. Consequently, bentonite clay alteration should primarily occur below the sediment water interface, and this can explain the very low illite content of illite/smectite in bentonites.

Sedimentation of volcanic material in the North Sea region is, from the literature cited above, likely to have occurred during the period when the claystones of the present investigation were deposited. Such volcanic material will, after Millot (1970) and Nadeau & Reynolds (1981b), form montmorillonite and illite/smectite with a high amount of smectite layers. Diagenesis of such material is likely to be different from diagenesis of illite/smectite originating from weathering.

Material

Chrono- and lithostratigraphy

Burial stage terminology is used in accordance with Jensen, Holm, Frandsen & Michelsen (1986). Thus "the Upper Jurassic- Cretaceous boundary coincides with the boundary between the Volgian and Ryazanian or between the *Lamplughi* and the *Runctoni* ammonite zones. The base of the Volgian stage coincides with the base of the *Elegans* ammonite zone. The Middle- Upper Jurassic boundary is regarded as coincident with the Callovian- Oxfordian boundary" (Jensen et al. 1986, p.11, 1.13). The Kimmeridgian- Ryazanian claystones in the Danish part of the Cen-

Table 3. Chronostratigraphy of Central Trough samples, according to Hoelstad (1986), Myhre (1977) and Ofstad (1981).

Well	Depth	Stratigraphy	Formation
E1	2983 m	Late Ryazanian	Farsund
	3444 m	Early Volgian	Farsund
	3828 m	Early Volgian	Farsund
	3938 m	Early Volgian	Farsund
G1	2609 m	Middle Volgian	Farsund
	3441 m	Kimmeridgian	Farsund
M8	2368 m	Middle Volgian	Farsund
	2387 m	Early Volgian	Farsund
	2588 m	Kimmeridgian	Farsund
	2725 m	Kimmeridgian	Farsund
U1	2542 m	Early Volgian	Farsund
	2716 m	Kimmeridgian	Farsund
	2899 m	Kimmeridgian	Farsund
I1	3371 m	Ryazanian	Farsund
	3441 m	Late Volgian	Farsund
	3688 m	(Volgian?)	Farsund
	3908 m	(Volgian?)	Farsund
2/11–1	3633 m	Kimm-Early Volgian	Farsund
	3877 m	Kimm-Early Volgian	Farsund
	4548 m	Kimm-Early Volgian	Haugesund
2/7–3	3365 m	Late Volgian	Mandal
	3502 m	Middle Volgian	Farsund
	3789 m	Early Volgian	Haugesund
	4178 m	Early Volgian?	Haugesund
Lulu 1	3420 m	Early Volgian	Farsund
W1	3816 m	Middle Volgian	Farsund
	4051 m	Kimmeridgian	Farsund
Adda 1	2633 m	Ryazanian	Farsund
	2917 m	Middle Volgian	Farsund

tral Trough belong to the Farsund Formation and in the Norwegian Central Trough to the Mandal, Farsund and Haugesund Formations. The investigated Upper Jurassic claystones from the Danish Subbasin belong to the Børglum Formation which is synchronous with the oldest part of the Farsund Formation and of Kimmeridgian- Middle Volgian age (Olaf Michelsen, pers. com.; Niels Poulsen, pers. com.).

Formations and samples

Claystones during Kimmeridgian – Volgian were sedimented in a probably deeper shelf environment in the Central Trough and are here found at present with a depth to top Jurassic of 2100 to 4000 m (Michelsen & Andersen 1983). In the same period, claystones were sedimented on a more shallow shelf in the Danish Subbasin and are here presently found with a depth to top Jurassic of 400 to 2400 m (Michelsen & Andersen

1983 and Michelsen 1978). In the Central and Northern North Sea, deposition of organic-rich shales continued through the Volgian and much of the Ryazanian, and Middle Volgian to Early Ryazanian "hot shales" are widespread through the graben system, but regressive facies developed in the basins flanking the central graben systems (Rawson & Riley 1982). The claystones of Kimmeridgian- Volgian- (Lower Ryazanian) age in the Central Trough and the Norwegian-Danish Basin have been selected for the present investigation. Selection of one or a few equivalent formations found over a wide range of burial depths will minimize the variability of parent material and makes it easier to reconstruct diagenetic processes. The variation in burial depth of these claystones is similar to the variation seen in the Tertiary US Gulf Coast clays and the variation in maturity of the organic material in the selected formations is from minimum oil generation to peak oil generation (Thomsen, Lindgreen & Wrang 1983). The thicknesses of the Farsund plus Mandal formations vary widely in different wells because of differential subsidence in the Central Trough during Upper Jurassic. Very thick sections are present in the wells from the Tail End Graben and the Feda Graben (Michelsen, Frandsen, Holm, Jensen, Møller & Vejbæk 1986). Jensen et al. (1986) proposed that these thick sections may be explained by redeposition into deeper parts of the basin and Myhre (1977) proposed that the thick sequence in 2/11–1 may be partly due to repeated sections in a fault zone. According to Michelsen et al. (1986), salt movements in wells M8, U1 and Lulu 1 may have been responsible for the deposition of relatively thin Farsund Formation sequences in these wells and for the absence of Volgian to Ryazanian sediments in U1 because of non-deposition. The variation in the thicknesses of the Børglum Formation in the Danish Subbasin and of the combined, equivalent Sauda and Tau formations in 9/4–3 are mainly due to the development of regressive, sandy or silty facies during Volgian and Ryazanian. Relatively thick sections in the Danish Subbasin are found in the wells in the centre of the basin (in Aars 1 65 m), but the member is very thin or absent in wells at the margin of the basin, e.g. 4 m in Skagen 1, because of the regression.

The lithostratigraphical units of Vollset & Doré (1984) and Jensen et al. (1986) have been

used. From the Central Trough, material was se-
lected from the Haugesund Formation in wells
2/7-3 and 2/11-1, from the Farsund Formation in
wells Adda 1, E1, G1, I1, Lulu 1, M8, W1, 2/7-3
and 2/11-1, and from the Mandal Formation in
2/7-3. The Haugesund Formation is of Kimme-
ridgian age in wells 2/7-3 and 2/11-1 (Ofstad 1981
and Myhre 1977), the Farsund Formation is of
Kimmeridgian-Ryazanian age in wells Adda 1,
E1, G1, I1, Lulu 1, M8, W1, 2/7-3 and 2/11-1
(Jensen et al. 1986 and Birkelund, Clausen, Han-
sen & Holm 1983) and the Mandal Formation is
of Portlandian-Ryazanian age in 2/7-3 (Ofstad
1981). Chronostratigraphy of the samples is
shown in table 3.

Two conventional cores from the Farsund For-
mation were available for sampling, one from E1
and one from 2/11-1. The amounts of side-wall
core material available were too small for clay
mineralogical analysis. The other samples are
from drill cuttings. They represent large inter-
vals, 30 feet in M8 and in G1 (2609 m), 20 feet in
E1 and 10 feet in the other wells in the Central
Trough. In the cutting samples, lithologies of the
depth interval in question are mixed and thus
give an average value for the interval. A draw-
back is that errors in depth may occur because
the rate of circulation of the drilling mud (which
brings up the cuttings) may differ from the calcu-
lated value. Caving may occur in non-cased parts
of the hole and caving from other formations may
then mix with the sample material. Unconsoli-
dated and/or highly smectitic clays may disin-
tegrate during the drilling and be mixed with the
drilling mud. Prior to analysis, the cuttings mate-
rial was cleaned of drilling mud by soaking and
washing in distilled water. After drying, the dom-
inating rock type (dark grey from the Haugesund
Formation in 2/7-3 and 2/11-1, dark grey from
the Farsund Formation, and dark grey from the
Mandal Formation in 2/7-3) was hand-picked for
analysis.

In the Norwegian-Danish Basin, conventional
cores were available from the Børglum Forma-
tion in the wells Børglum 1, Frederikshavn 1,
Gassum 1 and Haldager 1, and from the Bream
Formation in Uglev 1. Cuttings were available
from the Børglum Formation in Aars 1, F1, Hyl-
lebjerg 1, Mors 1 and Rønde 1 and from the
Sauda and Tau Formations in 9/4-3. The cuttings
intervals are 30 feet except in Rønde 1 and Aars 1

(15 feet), and Hyllebjerg 1 (10 feet). The cuttings
material from the Norwegian-Danish Basin wells
was also washed and the dark grey cuttings hand-
picked for analysis.

The depth figures given for the samples are
depth in m below kelly bushing. The depth fig-
ures for cuttings samples are the bottom figures
of the interval given by the drilling company.

Preparation procedures

The mixed-layer illite/smectite should be sepa-
rated from the other minerals in the sample prior
to XRD and chemical analysis, so that the in-
terference from other minerals is minimized. This
separation is difficult in well-compacted, highly
organic claystone where the mineral particles are
aggregated by organic matter. Hower et al.
(1976) wrote that the coarse clay fractions in the
deeper burial diagenetic samples from the Oligo-
cene-Miocene Gulf Coast contained a significant
amount of clay, mainly mixed-layer illite/smec-
tite, that could not be separated (their max.
depth was 5500 m). Except for the specimens for
HRTEM, the samples in the present investiga-
tion were therefore given a combination of ultra-
sonic and chemical pretreatment prior to analy-
sis. The NaOCl procedure of Anderson (1963)
was applied to destroy the fairly large amount of
organic matter in the claystones. Removal of the
organic matter aids in particle dispersion and de-
struction of possible clay interlayered organic
matter (indicated to be present by gas adsorption
experiments on these clays (Lindgreen 1987b)).
Interlayered organic matter may furthermore
prevent the characteristic swelling of smectite
layers following cation exchange and glycol/gly-
cerol intercalation. The NaOCl treatment was
continued until the reaction ceased (sometimes
simultaneously with the appearance of a violet
colour from MnO_4^-). In most cases 4 to 5 treat-
ments, each lasting 15 min, were sufficient, but
the treatment had to be repeated up to 10 times
with samples containing large amounts of organic
matter.

The dithionite-citrate procedure of Mehra &
Jackson (1960) was then used for removal of iron
and aluminium oxides and hydroxides. The red-
dish colour of the core sample Gassum 1, 1191.2
m, showed that iron oxides were present in this
sample. In most of the other samples, especially

those from the Central Trough, Fe^{2+} in pyrite in the samples was oxidized during the NaOCl treatment and formed reddish iron oxides-hydroxides at the high pH (9.0) used during this treatment. The aggregating role of the iron and aluminium oxides made their removal an important step in the disaggregation procedure. The solution/sample ratio was about 5 in both the NaOCl procedure and the dithionite-citrate procedure. Dithionite was added in portions of 100 mg per g sample until the reddish colour of the sample had changed to greyish-bluish. One treatment with dithionite-citrate, lasting 15 min., was sufficient for most samples, but two treatments were necessary to reduce the iron oxides in samples from the Central Trough with large amounts of organic matter and pyrite.

To check a possible breakdown of clay minerals during the treatment, Al_2O_3, SiO_2, Fe_2O_3 and K_2O dissolved during the NaOCl and dithionite-citrate treatments were measured by atomic absorption spectrometry for some of the samples. The NaOCl treatment dissolved less than: 0.3% K_2O, 0.02% Fe_2O_3, 0.01% Al_2O_3 and less than 0.2% SiO_2. The dithionite citrate treatment dissolved less than: 0.02% K_2O, 0.2% SiO_2 and less than 0.05% Al_2O_3 and from 0.2 to 3.3% Fe_2O_3. This Fe_2O_3 was probably due to pyrite and iron carbonates in the samples. The clay minerals therefore seem stable to the chemical treatments, in accordance with pretreatment experiments on soil clays by Follett, McHardy, Mitchell & Smith (1965) and on a microcrystalline soil clay by Lindgreen & Rasmussen (1978). A Palaeozoic glauconite from Sweden and a Clay Minerals Society ripidolite were subjected to the treatments and Mössbauer spectroscopy showed that their Fe^{3+}/Fe^{2+} ratios were not changed by the treatment. Furthermore, less than 0.01% Al_2O_3, 0.01% Fe_2O_3 and 0.2% SiO_2 were dissolved from the ripidolite by NaOCl and 0.1% Fe_2O_3, 0.7% Al_2O_3 and 0.4% SiO_2 by the dithionite citrate treatment. It may therefore be deduced that the treatments as described above have minimal effect on the structural elements of the clay minerals of the samples. However, even the combination of chemical and ultrosonic dispersion could not disaggregate the samples totally, as optical microscopy showed that clay aggregates were present in the sand- and silt fraction (H. Micheelsen, pers. com.).

The chemically and ultrasonically treated samples were divided into sand plus silt and into clay by centrifugation or elutriation. Thereafter, the coarse (2–0.2 µm) and fine clay (<0.2 µm) fractions were separated in a continuous flow centrifuge. As 10 Å and 5 Å XRD reflections from discrete illite were present in the fine clay fraction, and as discrete illite makes a detailed XRD and chemical mixed layer investigation difficult, the fine clay fraction was subdivided into the mixed-layer fraction and a fraction dominated by discrete illite and/or kaolinite by the ethanol procedure, as described by Hansen & Lindgreen (1989).

Investigation of discrete clay minerals and non-clay minerals

Mg^{2+}- saturated and air-dried or glycolated specimens and K^+- saturated and heated (to 250°C) specimens were analysed from the fine (< 0.2 µm) fraction dominated by discrete clay minerals. Mg^{2+}- saturated, air-dried or glycerolated specimens, and K^+- saturated, heated (to 250°C) specimens were analysed from the coarse clay fraction. Reflection areas (in % of the total peak area of (001) reflections in the diffractogram of the K^+-saturated specimen heated to 250°C) were calculated as follows: The illite/kaolinite area ratio was calculated from the diffractogram of the Mg^{2+}-saturated, glycerolated specimen. The relative areas for kaolinite, for illite+vermiculite+smectite+illite/smectite, and for chlorite were then calculated from the diffractogram of the K^+-saturated specimen heated to 250°C. The ratio between areas of vermiculite and kaolinite was calculated from the diffractogram of the Mg^{2+}-saturated, glycerolated specimen, taking into account the contribution of chlorite to the 14 Å peak in this diffractogram. The (area) ratios:
(mixed-layer illite/smectite)/kaolinite and smectite/kaolinite were then calculated from the diffractogram of the Mg^{2+}-saturated, air-dried specimen, taking into account the contribution of chlorite and vermiculite to the 14 Å peak in this diffractogram. Results are given in table 6a and b.

Na^+- saturated, randomly oriented specimens were prepared from the fine (< 0.2 µm) clay fraction dominated by discrete clay minerals and

from the coarse clay fraction for investigation of possible (hkl) reflections from clay minerals and the possible presence of other minerals. Na$^+$-saturated, randomly oriented specimens were prepared from the sand plus silt fraction to investigate the total mineralogy of this fraction.

XRD characterization of mixed-layers

Identification of layers at group level

The clay mineral classification was mentioned in the chapter on the structure of clay mineral layers. The negative charge of mica layers is sufficient to keep the layers together with cations, usually K$^+$, in between, and the layer thickness is fixed at 10 Å. The negative layer charge of vermiculite and smectite is so low that the layers can be separated and cation exchange and sorption of organic compounds can occur in the interlamellar space. The uptake of water and organic compounds depends on the exchangeable cation. With Mg^{2+} as exchangeable cation, standard smectites and vermiculites form 2-layer hydrates between 52% and 79% relative humidity, i.e. the normal humidity range in the laboratory (MacEwan & Wilson 1984, table 3.1). Two organic compounds are widely used as interlamellar sorbents for identification of smectite and vermiculite layers: ethylene glycol and glycerol. They generally give one and two layered complexes with vermiculite and smectite layers, respectively (MacEwan & Wilson 1984). However, ethylene glycol may give two layered complexes with some vermiculites. Generally, neither high charge smectites nor vermiculites will expand with ethylene glycol when they are K$^+$- saturated (MacEwan & Wilson). MacEwan & Wilson (1984) concluded that glycerol solvation of Mg^{2+}- saturated specimens is the best basis to distinguish empirically between vermiculites and smectites as classified in table 1. However, the structure of the ethylene glycol interlayer complex is well established (MacEwan & Wilson 1984), and ethylene glycol has therefore been used in computer modelling, also because ethylene glycol is more commonly used than glycerol. This may partly be due to the fact that ethylene glycol can fairly easily be introduced in interlamellar spaces of air-dried specimens if the specimens are exposed to ethylene

glycol vapour at 50–60°C for two or more days (MacEwan & Wilson 1984). Therefore, one specimen can be investigated air-dried and later be ethyleneglycolated and may even then be heated and investigated again, making the specimen preparation easier.

The mentioned relation between the clay mineral classification criteria (amount of layer charge) and layer thickness plus interlayer spacing makes XRD a routine method for clay mineral identification. The basal reflections originating from layer and interlayer spacings, d(00l), are enhanced if the clay minerals are oriented with their 001 parallel to the specimen surface. This orientation is favoured if a clay film prepared by 1) suction of a clay in suspension onto a porous, ceramic plate or 2) by smearing a thick suspension or 3) pipetting a thin suspension on a glass slide and leaving the water to evaporate. Gibbs (1965) compared these methods and found that the pipette method resulted in marked differential sedimentation in a mixture of coarse and fine clay particles but that it gives the highest degree of preferred orientation. As the mixed layers investigated in the fine-clay fraction are microcrystalline (according to the TEM investigations from one to several elementary layers thick) the pipette method for preparation of oriented XRD specimens was used in the present investigation. They were prepared with 2.5 mg sample per cm^2. This is a very thin specimen for XRD in the range 1.5°–30° 2θ when compared to the amount of material required for specimens "infinitely thick" to the XRD radiation as calculated by Brown & Brindley (1984, table 5.2). Comparison between diffractograms from the 2.5 mg/cm^2 specimens and diffractograms from thicker specimens showed, however, that the 2.5 mg/cm^2 specimens were infinitely thick to Cu-radiation in the range 1.5°–30° 2θ. The use of thin specimens should minimize the effect of differential sedimentation during specimen preparation.

Mg^{2+}- saturated, air-dried and oriented specimens were investigated because of the stability of the two-layer water complex for both vermiculites and smectites of such specimens over a wide range of relative humidities. Smectite and vermiculite layers have therefore basal spacings d(001) at about 15 Å and illite layers at 10 Å. These specimens were then glycolated at 60°C in

three days and then investigated by XRD. Mg^{2+}-saturated and glycerolated specimens were also prepared, in accordance with the applicability of this specimen type to the clay mineral classification as discussed above. These specimens were prepared by mixing two drops of 10% glycerol in water with 1 ml of clay-water suspension and leaving this suspension to dry on the glass slide. A set of specimens were saturated with K^+, air dried, and afterwards analysed by $CuK\alpha$ and $CrK\alpha$ radiation. These specimens were later glycolated at 60°C for 3 to 9 days and analysed with $CuK\alpha$ radiation. The diffractograms did not change with 3 to 9 days duration of glycol treatment. Another set of specimens saturated with K^+ were heated to 250°C for one hour to dehydrate the smectite and vermiculite layers and cause a decrease of d(001) for these mineral layers to about 10 Å. The K^+ saturation diminishes the possibility for rehydration after cooling (MacEwan & Wilson 1984).

Lindgreen & Rasmussen (1978) found that Mg^{2+}- saturated specimens compared to Na^+- saturated specimens gave much lower reflection intensities. Therefore, Na^+- saturated, oriented specimens were also prepared and examined by XRD before and after glycolation. However, the reflection intensities were about the same as for Mg^{2+}- saturated specimens. To obtain information about the layer charge of the expandable mixed-layer component, K^+- saturated and oriented specimens were prepared and glycolated prior to XRD investigation.

Randomly oriented powder specimens were prepared of the Na^+- saturated mixed-layer fractions for investigation of (hkl) reflections.

Mixed-layer terminology

The symbols and nomenclature of Reynolds (1984) are used in the following. The fraction of illite layers (I) in the illite/smectite (illite/smectite) is given by P_I, which is the probability for a given layer in the mixed-layer crystal to be an illite layer. $P_{S.I}$ is the probability that an illite layer succeeds a smectite layer, $P_{SI.I}$ is the probability that an illite layer succeeds a SI unit, and $P_{SII.I}$ is the probability that an illite layer succeeds a SII unit. Ordering can be: a) random ordering or I-S segregation (which means that illite and smectite layers have a tendency to be segregated;

b) IS ordering or rectorite ordering (including IS-I segregation, i.e., that IS units and I layers have a tendency to be segregated); c) ISI ordering (including ISI-I segregation); and d) ISII ordering or Kalkberg ordering. The Reichweite ordering values used by Lindgreen & Hansen (1991) and by Lindgreen et al. (1991) were incorrect as follows: a) for random ordering or I-S segregation was used R0; b) for IS ordering or IS-I ordering was used R1; and c) for ISII ordering was used R3.

Estimation of illite percentages and ordering

In the following, $(00a)_I/(00c)_S$ means the composite peak from the reflections (00a) from illite layers and (00c) from smectite layers in mixed-layer illite/smectite. $(00a)_I/(00b)_V/(00c)_S$ means the composite peak from the reflections (00a) from illite layers, (00b) from vermiculite layers and (00c) from smectite layers in mixed-layer illite/vermiculite/smectite. $(00d)_{IS}$ means the (00d) reflection from IS ordered I/S.

For Mg^{2+}- saturated and glycolated specimens the degree of ordering was estimated by visual inspection of the diagrams. Random ordering or I-S segregation was assessed to be dominant, when smectite peaks at 17 Å (001) and 2.83 Å (006) and illite peaks at 10 Å (001) and 1.98 Å (005) were present. IS ordering was disclosed by peaks between 14.5 Å $(002)_{IS}$ and 10 Å $(001)_I$ and by the presence of a peak at 2.7 Å $(0.0.10)_{IS}$. ISII ordering was deduced from a shoulder at about 11 Å (004) and a peak at 2.6 Å (0.0.18). To start with, the percentages of illite layers were then calculated by the following methods:

a) For glycolated specimens (Mg^{2+}- saturated or Na^+- saturated) the percentages of illite layers in the mixed layers were calculated from peak migration of $(001)_I/(002)_S$ and $(002)_I/(003)_S$ from the tables of Hower (1981a).
b) For Mg^{2+}- saturated, air-dried specimens the percentages of illite layers in the mixed-layers were calculated from peak migration of (001) $_I/(002)_S$ for random ordering or I-S segregation and of $(002)_{IS}/(001)_I$ for IS ordering from table 3.5 of Hower (1981a).

The P_I values for illite/smectite were then estimated from computer modelling as follows:

Table 4a: Mixed-layer illite/smectite from wells in the Central Trough. Statistical parameters obtained from comparison between recorded and computer simulated X-ray diffraction patterns. From Lindgreen et al. (1991, table 1).

Well Depth, meters	Mg^{2+}- saturated specimens				Ordering	K^+- saturated specimens (glycolated)	
	P_I	$P_{S.I}$	$P_{SI.I}$	$P_{SII.I}$		P_I	$P_{S.I}$
E1							
2983	0.65	0.45	0.76	0.76	I-S segregated	0.82	0.82
3444	0.80	1.00	0.55	0.82	IS		
3828	0.80	1.00	0.45	0.85	IS	0.95	0.95
3938	0.85	1.00	0.55	0.88	IS	0.85	0.85
G1							
2609	0.75	0.65	0.78	0.78	I-S segregated		
3441	0.70	3-component(0.10V, 0.20S)				0.85	
M8							
2368	0.65	0.55	0.70	0.71	I-S segregated	0.82	0.82
2387	0.70	0.50	0.79	0.79	I-S segregated	0.80	0.70
2588	0.75	0.55	0.82	0.82	I-S segregated	0.90	0.90
2725	0.82	1.00	0.50	0.86	IS	0.90	0.90
U1							
2542	0.70	0.60	0.74	0.74	I-S segregated	0.80	0.80
2716	0.60	0.30	0.80	0.80	I-S segregated	0.80	0.60
2899	0.70	0.60	0.74	0.74	I-S segregated	0.90	0.90
I1							
3371	0.82	1.00	0.60	0.83	IS	0.90	0.90
3441	0.82	1.00	0.60	0.83	IS	0.95	0.95
3688	0.82	1.00	0.60	0.83	IS		
3908	0.85	1.00	0.65	0.86	IS	0.95	0.95
2/11–1							
3633	0.82	1.00	0.60	0.83	IS	0.90	0.90
3877	0.85	1.00	0.55	0.88	IS	0.95	0.95
4548	0.85	1.00	0.65	0.86	IS	0.95	0.95
2/7–3							
3365	0.40	0.40	0.40	0.40	random	0.75	0.75
3502	0.40	0.30	0.55	0.55	I-S segregated		
3789	0.95	1.00	1.00	1.00	ISII	0.95	0.95
4178	0.90	1.00	0.70	0.91	IS	0.95	0.95
Lulu 1							
3420	0.85	1.00	0.55	0.88	IS	0.95	0.95
W1							
3816	0.50	0.40	0.60	0.60	I-S segregated	0.75	0.55
4051	0.80	1.00	0.45	0.85	IS		
Adda 1							
2633	0.65	0.45	0.76	0.76	I-S segregated		
2917	0.70	0.50	0.79	0.79	I-S segregated	0.85	0.85

The diffractograms showed that the $d(001)_S$ was 17.0 Å in glycolated specimens. In Mg^{2+}-saturated, air-dried specimens the $d(001)$ of smectite was calculated to be 14.5 Å from the (001) values of higher orders. Computer modelling with the two component NEWMOD program, which was kindly placed at my disposal by R.C.Reynolds, was carried out for Cu radiation with the (001) values for smectite from above and for Mg^{2+}- saturated specimens with following parameters: 0.8K per illite layer, 0.3 octahedral Fe per layer in both illite and smectite, and a cation exchange capacity (CEC) of 0.4 per smectite layer, all layers as $O_{10}(OH)_2$. Particle thicknesses in computer models were 3–14 2:1 layers. The values for percentages of illite obtained from peak migration calculations were first used in the models and then the models were refined for each specimen by varying P_I, $P_{S.I}$ and $P_{SI.I}$. The final results of the modelling were compared to the actual diffractograms for both air-dried and glycolated Mg^{2+}- saturated specimens and the independent results for both specimens finally compared. In all cases the maximum difference between the results for the two specimens agreed within 0.05 in P_I.

Table 4b: Mixed-layer illite/smectite from wells in the Norwegian-Danish Basin. Statistical parameters obtained from comparison between recorded and computer simulated X-ray diffraction patterns.

Well	Depth,m	P_I	$P_{S,I}$	Ordering
Frederikshavn 1	649	0.70	0.50	I-S segregated
Uglev 1	821	0.70	0.50	I-S segregated
	862	(0.80)	(3 comp.?)	
Børglum 1	986	0.65	0.45	I-S segregated
J1	1012	0.75	0.55	I-S segregated
Haldager 1	1049	0.70	0.50	I-S segregated
Gassum 1	1190	(0.80)		
	1191	(0.80)		
	1191	(0.85)		
F1	1734	0.75	0.55	I-S segregated
Hyllebjerg 1	1850	0.70	0.50	I-S segregated
Mors 1	1899	0.70	0.50	I-S segregated
Rønde 1	2115	(0.85)	(3 comp.?)	
Aars 1	2425	0.70	(3 comp., 0.15S, 0.15V)	
	2465	0.70	(3 comp,. 0.15S, 0.15V)	
9/4–3	2377	0.70	0.50	I-S segregated
	2435	0.75	0.55	I-S segregated

Note: It was difficult to determine the mixed-layering in Rønde 1, Gassum 1 and in Uglev 1, 862 m because of the large amounts of kaolinite in the illite/smectite fraction and because of broad mixed-layer peaks, probably due to three component mixed layering.

In three cases of random or I-S segregated mixed layering, the modelling of the low-angle region (5°2θ to 10°2θ) indicated significantly higher smectite percentages than the position of the $(003)_S/(002)_I$. This can be explained by the presence of vermiculite layers so that the $(003)_S/(002)_I$ becomes a $(003)_S/(002)_I/(003)_V$ and moves towards higher angles, due to the interference with the 4.7 Å $(003)_V$. For these samples, the diffractograms for Mg^{2+}- saturated, air-dried specimens were modelled with the NEWMOD program, because smectite and vermiculite in this type of specimen have about the same d(001) and the system may therefore be modelled as two-component. For the same samples, the diffractograms for the Mg^{2+}- saturated, glycolated specimens were modelled with the three-component program kindly placed at my disposal by P. D. Cradwick. The three-component program generally produces less satisfactory fits in the low-angle region since, in the version applied, it only operates with a narrow particle distribution of about 10 2:1 layers which produces a series of additional (001) interferences due to particle thickness. Therefore, the result of applying the three-component model is less accurate than of applying the NEWMOD program when only two components

are present. However, the three-layer modelling strongly indicated both illite, vermiculite and smectite layers to be present in the mixed-layers from G1, 3441 m, and Aars 1A, 2425 m and 2465 m, and maybe in Rønde 1 and Uglev 1, 862 m. Large amounts of kaolinite in the illite/smectite fractions from Gassum 1, Rønde 1 and Uglev 1, 862 m, made the interpretation of the diffractograms uncertain.

After plots of chemical composition versus P_I had been made (Lindgreen, Jacobsen & Jakobsen 1991), the end-member smectite and illite compositions were calculated. These end-members contained 0.2Fe (illite) and 0.7Fe (smectite) and 0.6 (K plus equivalent NH_4^+ × 10/18) (illite) and had a CEC of 0.7 (smectite), all figures per $O_{10}(OH)_2$. New computer simulations with these figures and based on particle thicknesses 3–7 or 3–14 unit layers (2:1 units) were made and again compared to the diffractograms. Some mixed-layers fitted best to the 3–7 unit layer and others best to the 3–14 unit layer simulations. However, the new chemical data did not change the simulated curves significantly.

The P_I values obtained from simulations of Mg^{2+}- saturated, air-dried specimens agreed within 0.05 with the P_I values obtained for the
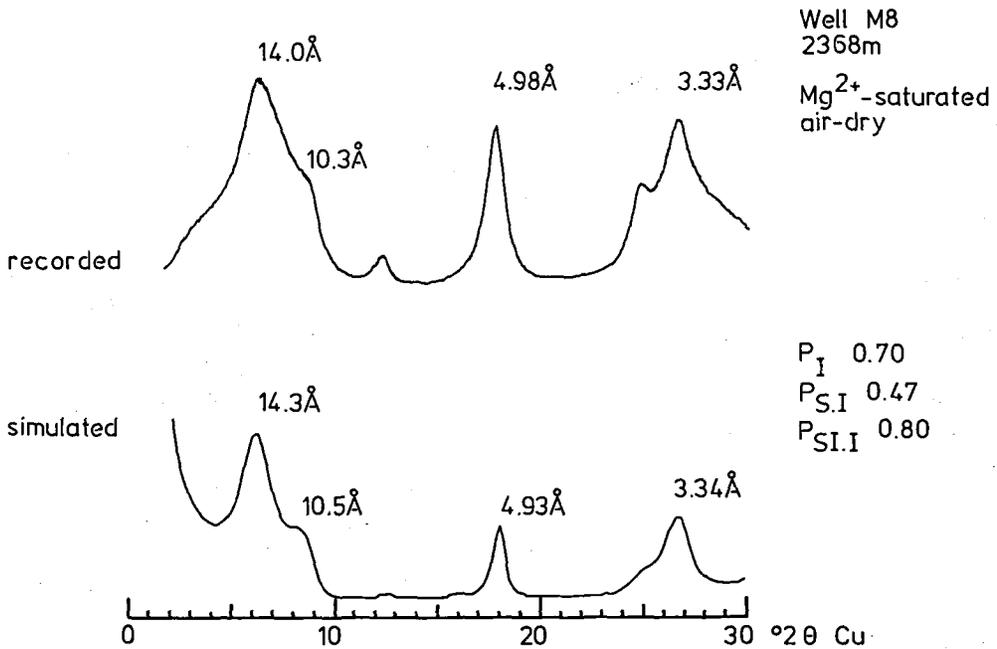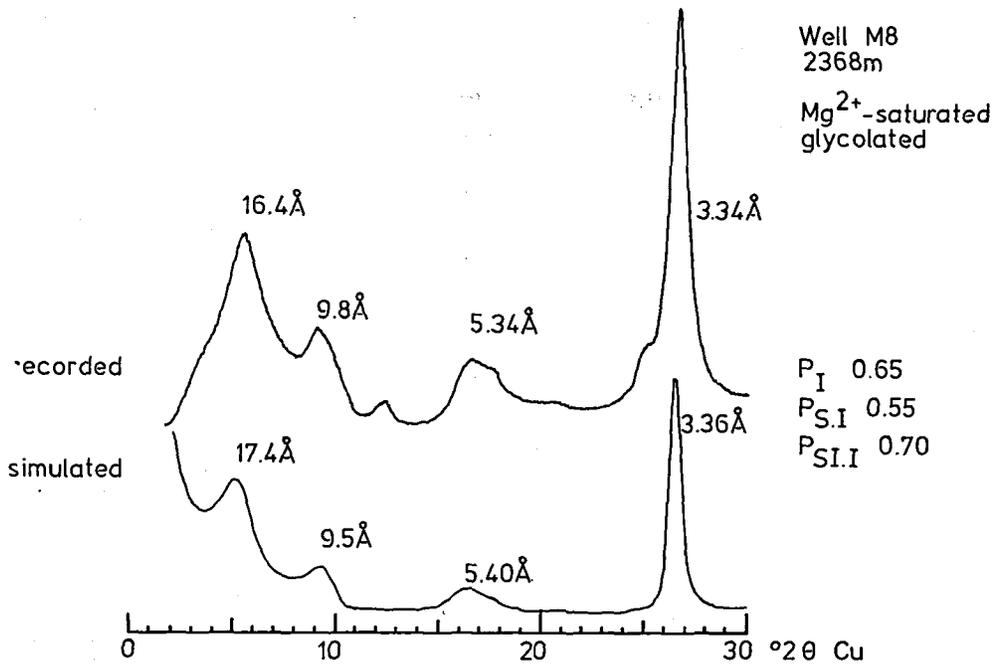
Fig. 11a. Illite/smectite from the Central Trough, well M8, 2368 m depth. Recorded X-ray diffractograms of oriented specimens prepared from illite/smectite fractions, shown together with diffractograms computer simulated with the NEWMOD program of R. C. Reynolds. Mg^{2+}- saturated and glycolated (1) and Mg^{2+}- saturated and air-dried (2).
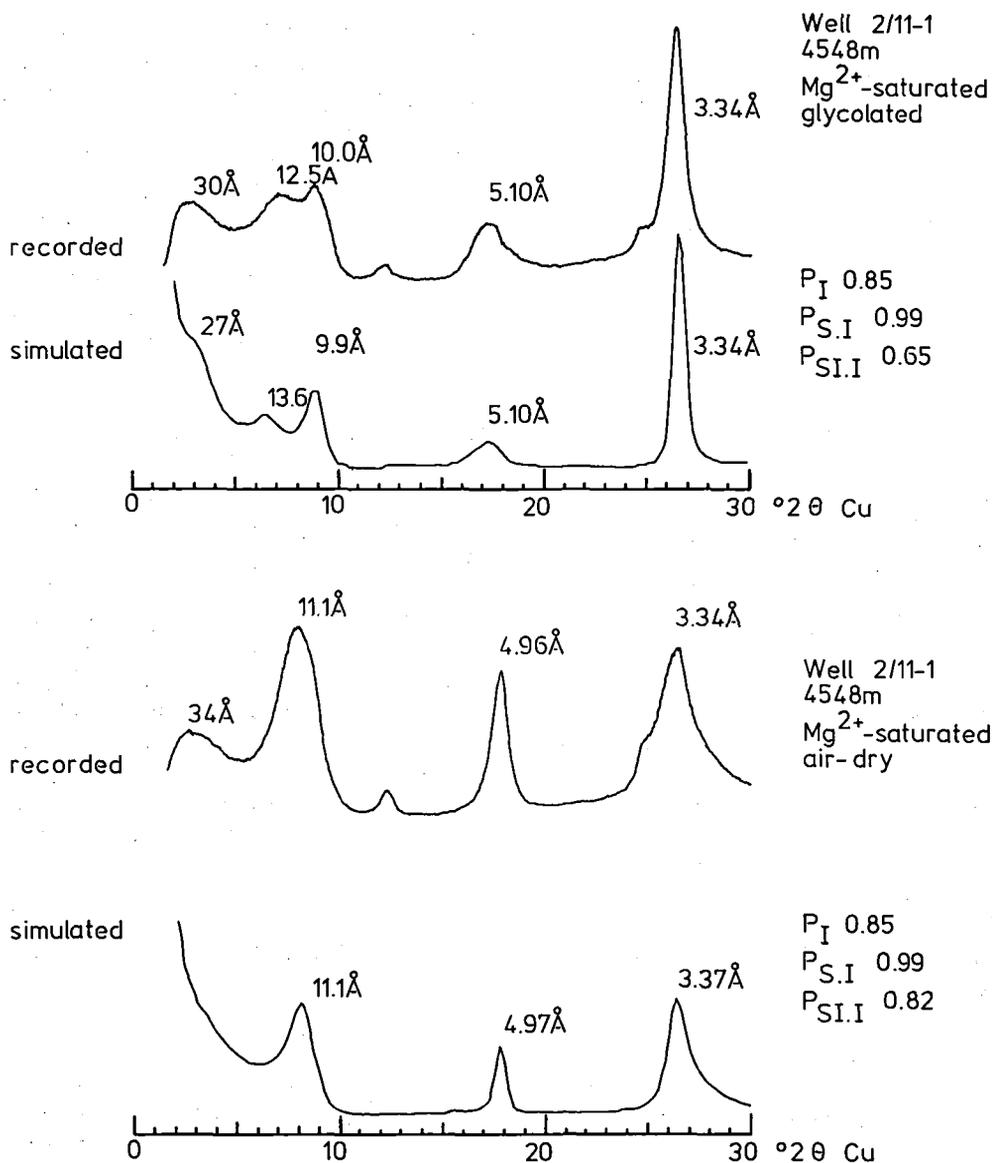
Fig. 11b. Illite/smectite from the Central Trough, well 2/11–1, 4548 m depth. Recorded X-ray diffractograms of oriented specimens prepared from illite/smectite fractions, shown together with diffractograms computer simulated with the NEWMOD program of R. C. Reynolds. Mg^{2+}- saturated and glycolated (1) and Mg^{2+}- saturated and air-dried (2).

Mg^{2+}- saturated, glycolated specimens. The degrees of ordering obtained by simulation were for some samples slightly higher for air-dried illite/ smectite than for glycolated illite/smectite. For example, the experimental pattern for the sample from well G1, 2609 m, in the air-dried specimen was close to the modelled pattern with $P_{S.I}$ 0.88, i.e. half IS ordered, whereas the experimental pattern of the glycolated illite/smectite from the

same sample resembled the modelled pattern with $P_{S.I}$ 0.65, i.e. I-S segregation.

The result of the modelling of the glycolated patterns is seen in tables 4a and b and selected modelled patterns with the corresponding, measured diffractograms in figs. 11a and b.

As mentioned above, MacEwan & Wilson (1984) concluded that glycerol solvation of Mg^{2+}- saturated specimens is the best basis for distinguishing between vermiculites and smectites. The
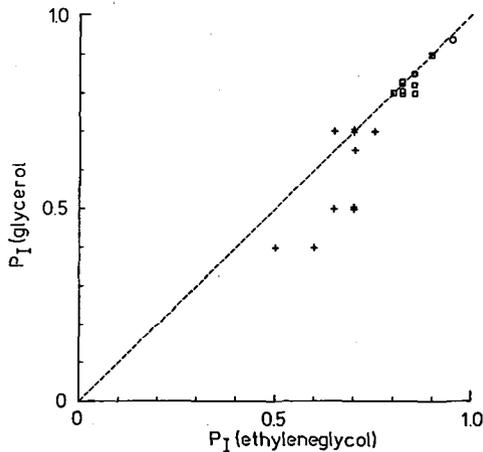
Fig. 12. Illite/smectite from the North Sea and onshore Denmark. X-ray diffraction of oriented specimens of illite/smectite fractions. CuKα radiation. The P_I values obtained from Mg^{2+}-saturated and glycerolated specimens vs. the P_I values obtained from Mg^{2+}-saturated and ethyleneglycolated specimens. (+) = randomly ordered or I-S segregated, (□) = IS ordered and (○) = ISII ordered illite/smectite.

diffractograms of the Mg^{2+}-saturated and glycerolated specimens were therefore investigated for ordering and amount of illite in illite/smectite by comparison with computermodelled diffractograms calculated for Mg^{2+}-saturated illite/smectite with ethyleneglycol in the smectite interlayers (because the structure of the glycerol complex is not known). A d(001) of 17.8 Å as seen in the experimental diffractograms of glycerolated specimens was used. The error arising from using the 2-layer ethyleneglycol complex instead of a 2-layer glycerol complex should be small because of the low scattering power from the light atoms in the organic compounds. The P_I values and ordering of illite/smectite obtained by comparing such simulated patterns with the patterns of Mg^{2+}-saturated, glycerolated specimens of Central Trough illite/smectite fractions are plotted in fig. 12 versus the P_I and ordering values obtained for the same illite/smectite samples from Mg^{2+}-saturated and ethyleneglycolated specimens (given in table 4a). This plot shows that 0.1–0.2 higher values for P_I are obtained from ethyleneglycolated specimens than for glycerolated specimens for four samples with low P_I (0.5–0.7) in ethyleneglycol, but that the agreement between P_I for ethyleneglycolated specimens and for glycerolated specimens is otherwise good (≤ 0.05 P_I). The P_I values for Mg^{2+}-saturated and air-dried

specimens and for Mg^{2+}-saturated and ethyleneglycolated specimens of the same sample agreed within 0.05 P_I (see above). The higher P_I values obtained for the four samples for ethyleneglycolated or air-dried specimens than for glycerolated specimens show that glycerolation has kept some layers expanded at a d(001) of 17.8 Å, whereas these layers were contracted to a d(001) of 10 Å in ethyleneglycolated or air-dried specimens. None of the standard minerals of MacEwan & Wilson (1984) showed a similar behaviour. The layers showing this behaviour must have a high charge to keep them contracted in Mg^{2+}-saturated, air-dried or ethyleneglycolated specimens. On the other hand, a vermiculitic charge should only allow uptake of one glycerol layer giving a d(001) of 14 Å according to MacEwan & Wilson (1984). A high charge of a layer may, however, keep layers contracted to 10 Å when air-dried and the subsequant exposure to ethyleneglycol vapours may then be unable to expand the interlayer space, whereas glycerol under wet condition may be able to intercalate these layers and keep them expanded during and after drying. The different behaviour when exposed to ethyleneglycol vapour and to glycerol may therefore be due to a high charge of the layers.

Discrete clay minerals and non-clay minerals

Bulk rock samples

XRD on randomly oriented specimens showed that the claystones contained the following minerals: quartz, plagioclase feldspar, illite and kaolinite. Potassium feldspars were neither detected by optical microscopy (H. Micheelsen, pers.com.) nor by XRD in the samples from the Central Trough. Quartz was determined quantitatively (accuracy estimated to $^{\pm}2\%$) from XRD on randomly oriented specimens with quartz 4.5–45 µm size as external standard and measurement of peak areas for the (10$\bar{1}$0), (10$\bar{1}$1) and (11$\bar{2}$0) reflections. The ratio between calcite and (dolomite + ankerite) was determined from the ratio between the areas of the (10$\bar{1}$4) reflections of these minerals. The contents of gypsum, calcite + dolomite + ankerite, siderite, pyrite and organic carbon were determined by differential

Tab. 5a. Quantitative mineralogy (except for clay minerals) of samples from the Central Trough. Determined by X-ray diffraction plus differential thermal analysis with quantitative detection of evolved H_2O, CO_2 and SO_2.

Well, depth, m	Organic Carbon	Quartz	Pyrite	Gypsum	Calcite	Dolomite + ankerite	Siderite
	%	%	%	%	%	%	%
E1							
2983 m	8.2	25	3.8	0.1	2	–	–
3938 m	2.0	25	0.8	–	10	5	1
G1							
2609 m	1.6	25	1.7	–	9	3	–
3441 m	1.4	20	0.9	–	5	16	1
M8							
2368 m	3.3	20	0.3	–	5	5	–
2387 m	1.7	20	1.4	–	6	4	–
2588 m*	2.1	20	0.5	–	4	5	–
2725 m	1.9	15	1.1	–	2	14	–
U1							
2542 m	2.3	20	1.3	–	11	11	–
2716 m	2.1	15	0.4	–	8	11	–
2899 m	2.1	15	0.8	–	4	6	–
I1							
3371 m	8.0	30	3.8	–	12	4	–
3908 m	3.2	20	2.8	–	3	9	–
2/11–1							
3633 m*	5.5	15	0.3	–	12	–	1
3877 m	4.9	30	1.0	–	–	–	–
4548 m	4.5	15	1.0	–	6	2	1
2/7–3							
3365 m	1.2	15	–	–	4	–	–
3789 m*	7.4	15	1.2	0.1	11	5	–
4178 m	5.3	20	1.1	–	4	3	–
Lulu 1							
3420 m	3.5	20	2.4	–	3	7	–
W1							
3816 m	2.5	30	1.0	–	–	–	–
Adda 1							
2917 m	3.5	20	0.8	–	3	3	1

*Sample 2/11–1, 3633 m contains 20% barite and samples M8, 2588 m and 2/7–3, 3789 m contain each 5% barite.

thermal analysis with determination of evolved CO_2, H_2O and SO_2. The thermal analysis instruments are described by Morgan (1977). The results of these quantitative determinations are given in tables 5a and 5b. The total clay fraction constituted about 50% of the samples, and the ratio of coarse clay to fine clay was about 0.5. The isolated illite/smectite fraction constituted about ¾ of the fine clay fraction. Optical microscopy (H. Micheelsen, pers. com.) showed, however, that the coarse clay and the sand plus silt fractions were dominated by clay aggregates. The persistency of aggregation despite chemical and physical pretreatments has been found in several other investigations, one of them being Hower et al. (1976).

Cox & Gallois (1981) described the lithologies of the Kimmeridge Clay in Dorset. In the Central Trough, the hand picked dark-grey lithologies which have been analysed in the present investigation and the two core samples (E1, 2983 m and 2/11–1, 3877 m) belong, from their content of organic carbon, to the lithologies of Cox and Gallois as follows: either oil shale (10–45% kerogen)(E1, 2983 m; I1, 3371 m; and 2/7–3, 3789 m); dark grey mudstone (< 2% kerogen) (2/7–3, 3365 m); or to the bituminous mudstones (2–10% kerogen)(the remaining samples). It is noteworthy that sample 2/7–3, 3365 m, contains a markedly lower amount of organic carbon (1.2%) than the other Central Trough samples analysed. This could be due to a bentonitic origin. The carbon-

Tab. 5b. Quantitative mineralogy (except for clay minerals) of samples from wells in the Norwegian-Danish Basin. Determined by X-ray diffraction plus differential thermal analysis with quantitative detection of evolved H_2O, CO_2 and SO_2.

Well, depth, m	Organic Carbon %	Quartz %	Pyrite %	Gypsum %	Calcite %	Dolomite + ankerite %	Siderite %
Frederikshavn							
1							
649 m	1.1	25	0.8	0.5	–	–	–
Uglev 1							
821 m	1.0	25	0.5	–	6	15	–
862 m	1.6	15	2.6	0.1	–	–	3
Børglum 1							
986 m	0.9	40	0.4	0.1	1	1	–
J1							
1012 m	0.7	15	3.4	3.2	1	–	–
Haldager 1							
1049 m	1.0	20	0.7	0.4	–	–	–
Gassum 1							
1190 m	0.4	30	–	–	–	–	–
1191 m	0.4	15	–	–	–	–	–
1191.2 m	0.4	20	–	–	–	–	–
Hyllebjerg 1							
1850 m	1.0	30	2.3	0.1	4	3	–
Mors 1	0.5	20	3.2	–	6	2	–
Rønde 1							
2115 m	2.8	20	1.2	–	4	–	1
Aars 1							
2425 m	2.7	30	2.3	0.2	7	4	–
2465 m	0.9	25	3.5	–	2	2	0.3
9/4–3							
2377 m	2.2	25	1.2	0.5	3	5	1
2435 m	5.7	15	2.1	0.3	9	2	–

ate content of the investigated samples (0–16%) is low compared to the range of 10–25% calcium carbonate given by Cox & Gallois for the oil shale and the bituminous mudstone. Gallois (1976) proposed that coccolith blooms, in an environment between open ocean and an enclosed marine basin, formed the Kimmeridge Clay oil shales. Tyson, Wilson & Downie (1979) suggested, however, that the bituminous shale–oil shale – coccolith limestone lithologic association characteristic of the type Kimmeridge Clay can be attributed to the vertical movement of the O_2:H_2S interface in a temporarily stratified water column. Wignall (1989) proposed that during deposition of the Kimmeridge Clay storms caused oxygenation of anoxic bottom layers. The generally low amounts of pyrite (exceptions are: E1, 2983 m; I1, 3371 m; and Lulu 1, 3420 m) could indicate that anoxic conditions have not prevailed for a long time in the sediments in-

vestigated. Diagenesis may, however, have caused a later dissolution of pyrite. The samples from the Norwegian-Danish Basin are low in organic carbon (exceptions are the samples from 9/4-3) compared to the Central Trough samples. The quartz content is generally the same (15–30%), indicating that near-shore sediments are not present. The samples from Gassum 1 have markedly low contents of organic carbon and do not contain pyrite or carbonates. This could be the result of uplift and weathering during Upper Jurassic, as is also indicated by the clay mineralogy (see below).

Carbonate bands in the claystone

Sonic and gamma ray logs of Upper Jurassic sections in the Central Trough have several sharp peaks. X-ray diffraction of side-wall cores from wells G1 and E1 showed that the peaks in these

Tab. 6a. Clay mineralogy of 2 – 0.2 µm fraction from wells in the Central Trough as determined by X-ray diffraction of oriented specimens.

Well depth, m	% reflection area				
	kaolinite	illite	I/S	vermiculite	chlorite
E1					
2983 m	38	23	38 (x)	–	–
3444 m	27	48	25 (y)	–	–
3938 m	17	37	46 (y)	–	–
G1					
2609 m	30	30	38 (x)	–	1
3441 m	16	48	36 (x)	–	–
M8					
2368 m	24	27	50 (x)	–	–
2387 m	31	24	43 (x)	–	1
2588 m	28	23	48 (x)	–	1
2725 m	33	31	29 (y)	–	7
U1					
2542 m	20	21	58 (x)	–	–
2716 m	13	26	61 (x)	–	–
2899 m	14	30	56 (x)	–	1
I1					
3371 m	45	14	40 (z)	–	–
3441 m	40	28	32 (z)	–	–
3688 m	20	46	33 (z)	–	–
3908 m	19	41	41 (z)	–	–
2/11–1					
3633 m	24	15	61 (z)	–	–
3877 m	12	32	56 (z)	–	–
4548 m	13	26	61 (z)	–	–
2/7–3					
3502 m	15	3	82 (x)	–	–
3789 m	27	51	22 (y)	–	–
4178 m	17	35	48 (y)	–	–
Lulu 1					
3420 m	43	37	21 (y)	–	–
W1					
3816 m	12	8	77 (x)	–	2
4051 m	14	20	67 (y)	–	–
Adda 1					
2633 m	33	12	55 (x)	–	–
2917 m	26	28	46 (x)	–	–

(x): random ordering or I-S segregated
(y): IS, ISI, or ISII ordered
(z): IS ordered

wells are caused by carbonate bands in the claystone. Similar log peaks were present in the cored well section of the Norwegian well 2/11–1. Investigation of this cored section (Lindgreen 1985) showed that the carbonate bands consisted of claystone fragments, coarse grains of dolomite, quartz, and siderite, and of diagenetic layer silicates, all cemented by ankerite. The diagenetic layer silicates were kaolinite being neoformed into muscovite. This neoformation is similar to the process seen in the Cambrian sandstone of Sahara by Millot (1970) and in Middle Jurassic Brent sandstone by Hancock & Taylor (1978). In these rocks, formation of kaolinite was related to an early infiltration of fresh, neutral to weakly acid solutions and a later formation of mica from kaolinite was linked to infiltration of alkaline, saline solutions. Lindgreen (1985) concluded by analogy that the kaolinite in the carbonate bands had formed during an early release of fresh, neutral solutions from the claystone and the subsequant neoformation of mica from kaolinite dur-

Tab. 6b. Clay mineralogy of 2 – 0.2μm fraction from wells in the Norwegian Danish Basin as determined by X-ray diffraction of oriented specimens.

Well depth, m	% reflection area				
	kaolinite	illite	I/S	vermiculite	chlorite
Frederikshavn 1					
649 m	54	17	26 (x)	2	–
Uglev 1					
821 m	16	27	57 (x)	–	1
862 m	50	16	32 (x)	1	1
Børglum 1					
986 m	51	31	18 (x)	–	–
J1					
1012 m	47	17	33 (x)	2	1
Haldager 1					
1049 m	33	21	46 (x)	–	–
Gassum 1					
1190 m	67	15	17 (x)	–	–
1191 m	88	3	9 (x)	–	–
1191.2 m	67	13	21 (x)	–	–
F1					
1734 m	40	14	44 (x)	2	–
Hyllebjerg 1					
1850 m	43	31	24 (x)	–	2
Mors 1					
1899 m	31	24	43 (x)	–	1
Rønde 1					
2115 m	56	12	27 (x)	5	–
Aars 1					
2425 m	35	21	42 (x)	–	3
2465 m	44	31	24 (x)	–	2
9/4–3					
2377 m	27	25	48 (x)	–	–
2435 m	36	25	39 (x)	–	–

(x): random ordering or I-S segregated

ing a later release of alkaline, saline solutions. Lindgreen (1985) proposed that the carbonate bands had formed through fracturing of the claystone. Scotchman (1988) questioned this and suggested that they were silty beds resembling the thin sandstone layers in the Northern North Sea. Lindgreen (1988) rejected Scotchman's explanation because of the carbonate lithology of the bands and because extremely thin bands (~0.1 mm wide) of the same lithology in the claystone of E1 (Lindgreen 1987a) clearly cannot have a detrital origin. Also, diagenetic quartz formation was observed in very thin bands in the claystone from M8 (Lindgreen 1987a). The claystone was later cored in well Elin 1 and this core has inclined fractures filled with ankerite. Wignall

(1989) discussed the influence of tempests and earthquakes on the Kimmeridge Clay of Dorset. He proposed that silt laminae and thin graded mud horizons were storm produced events and that fissures were earthquake-induced. The carbonate bands and the fractures in Elin 1 may well have been induced by earthquakes. Whatever the origin, the carbonate bands present beautiful examples of clay neoformation in coarse lithologies, mainly controlled by the chemistry of the migrating solutions, like shown by Hancock & Taylor (1978), whereas the claystone itself shows illite/ smectite diagenesis mainly controlled by the chemical composition of the rock (see below).

Discrete clay minerals

It is beyond the scope of this publication to give a detailed description of discrete clay mineralogy and of the origin of these minerals. The mineralogy of the coarse clay fraction will be discussed below under the assumption that it is largely of detrital origin because of the large grain size. The composition of this fraction should then reveal the mineralogy of the source rocks for the illite/smectite. Furthermore, detrital illites may release potassium for formation of illite layers in illite/smectite (Hower et al. 1976).

Clay mineralogical data for the coarse clay fraction are given in tables 6a and 6b and were discussed by Hansen & Lindgreen (1989). Traces of chlorite were found by XRD in the sand-and silt fraction, in the coarse clay fraction and in the remaining part (remaining from the isolation of the illite/smectite fraction) of the fine-clay fraction of most samples from the Norwegian-Danish Basin. Exceptions were the samples from the wells Gassum 1 and Rønde 1 and from the Tau Formation in 9/4–3, where chlorite was not found. Traces of chlorite were also found by XRD in the corresponding fractions from the Central Trough samples in wells M8, G1 and U1 and in the sample W1, 3816 m. In the deepest sample in M8, from 2725 m, the (001) chlorite peak was sharper and a little larger relatively to the samples above as described for diagenetic chlorite in the Mesozoic shales from the Sleipner field by Hurst (1982). Chlorite was not detected by XRD in the deepest samples with the highest vitrinite reflectancy and degree of ordering in mixed-layers such as in wells 2/11–1, I1 (except in one sample from 3908 m), 2/7–3 and E1. Therefore, a general diagenetic formation of chlorite as described in the Gulf Coast Tertiary sediments (Hower et al. 1976; Ahn & Peacor 1985 and 1987) and in the North Sea Mesozoic sediments from the Sleipner Field (Hurst 1982) is not found by XRD in the present investigation of the Kimmeridgian-Volgian(-Ryazanian) claystones in the Central Trough and the Norwegian-Danish Basin. Diagenetic chlorite formation may, however, have taken place in M8. The traces of chlorite found in the other wells are probably detrital as proposed by Hurst (1985a) for some of the chlorites from the Sleipner Field. Diagenetic chlorite was, however, found by optical microscopy of the sand and silt fraction from all Central Trough wells (Micheelsen & Lindgreen, in prep.), even if in too small amounts to be seen in XRD.

Traces of vermiculite were found in the coarse clay fractions of Rønde 1, F1, J1, Frederikshavn 1 and in the deepest sample from Uglev 1 but not in the Central Trough (tables 6a and b). Its occurrence in these onshore well samples with a high kaolinite/illite peak area ratio (see below) makes a detrital origin probable.

Two factors determine the composition of the detrital clays: 1) the clay mineralogy of the source area; and 2) clay mineral segregation in the depositional environment. The importance of the source area was demonstrated by Milne & Earley (1958) for Recent sediments and by the review of Weaver (1959).

Delfaud (1983) discussed the Jurassic sedimentary facies of Western Europe and concluded from the character of the sediments that the climate was relatively hot during Lower Lias, Dogger and Upper Portlandian and was more temperate in Upper Lias and Kimmeridgian. The end of the Jurassic and the beginning of the Cretaceous showed an increase in temperature and in humidity. The climate was Mediterranian in the North Sea region. Francis (1984) discussed climate of Volgian (Purbeck) fossil forests in Dorset, UK, and concluded that the climate was of the Mediterranian type with warm, wet winters and hot, arid summers. Hurst (1985b) investigated the clay mineralogy of the Jurassic sediments from Brora, NE Scotland and discussed the implications of clay mineralogy to palaeoclimate and provenance. Brora was close to a landmass, lying within a semi-enclosed marine basin, and therefore the effect of clay particle segregation, according to Hurst, could be assumed to be minimal. The clay mineralogy was dominated by illite, kaolinite and (mostly ordered) illite/smectite. The source of the illite/smectite, according to Hurst, was Devonian rocks, whereas he proposed that the kaolinite probably originated from erosion of Carboniferous regoliths. His arguments were that the kaolinite had formed prior to the Jurassic, since erosion and sedimentation of the ordered illite/smectite could not have taken place in a climate with kaolinite formation during weathering. He proposed therefore that the climate during Upper Jurassic was sub-tropical.

Porrenga (1965) investigated the clay mineralogy of recent sediments of the Niger Delta and found that montmorillonite increased and kaolinite decreased in amount with distance from the shore. Illite was only present in small amounts in the samples and variation in the illite content with distance from shore was not apparent. Porrenga carried out settling experiments with the Niger Delta clays in samples of ocean water and found that kaolinite increased slightly in proportion during early sedimentation and montmorillonite later. He attributed this to differential flocculation such that illite and kaolinite flocculate and settle faster than montmorillonite when they come into salt water. Parham (1966) reviewed the literature on coastal lateral variation of clay minerals in modern and ancient sediments. He concluded that the direction of sediment transport can be indicated by lateral variations in clay mineral assemblages as follows: kaolinite decreases outwards from the shore, whereas montmorillonite increases in the same direction. Illite and chlorite increase initially outwards from the shore but then decrease at greater distances from the shore. Parham noted exceptions from these patterns. Some of these exceptions could be due to the fact that sediment contributions from different source areas can overlap and mix irregularly, e.g. in the Gulf of Mexico. But Parham noted that the correlation between clay mineralogy and shore distance, even if seen in the majority of studies, could neither be detected in investigations from recent sediments off the North Carolina coast nor off the coast of California. Gibbs (1977) investigated clay mineral segregation in Amazon River sediments deposited in the Atlantic Ocean. He found that differential flocculation was not important, and that this was probably because of natural coatings of oxides and organic matter on the clays. Instead he found that the dominant clay mineral segregation mechanism was a physical sorting by size. The results of Porrenga (1965), Parham (1966) and Gibbs (1977) indicate then that not only is the type of clay mineral important for sedimentation in the ocean water but also the sizes of the minerals in the clay fraction and an eventual coating of the clay minerals by oxides and organic matter.

Sellwood & Sladen (1981) argued that the volume of mud deposited in the Kimmeridgian was too large to have been derived from local source lands in the British area. They therefore proposed that the clays originated to a large extent from the more distant hinterlands of Greenland-N.America and Scandinavia. Sellwood (1972) found that the predominating clay minerals in Liassic shales from Britain are illite and kaolinite. He concluded that these minerals probably reflect the nature of the source areas in the region and that decreasing kaolinite contents in these sediments reflect greater distance from source areas. Bjørlykke, Dypvik & Finstad (1975) found in well 2/11–1 an average increase in the kaolinite/illite peak area ratio by a factor of about 3 from 4100 m to 3500 m depth and thought that this increase reflected a higher degree of proximity to deltaic or shoreline facies in a regressional sequence. They alternatively proposed that this increase in the kaolinite/illite peak area ratio may be due to a climatic change towards more humid conditions at the end of Upper Jurassic. Wignall & Ruffell (1990) calculated kaolinite/illite ratios from clay mineralogical data given by Deconinck, Chamley, Debrabant & Colebeaux (1983) for Upper Jurassic marine strata marginal to the Boulonnais shore in Northern France. Wignall & Ruffell found that high kaolinite/illite ratios reflected shallow water and low distance to the shore. Wignall & Ruffell (1990) found that onset of aridity in the middle of the *Hudlestoni* ammonite zone (in Early Volgian) produced a low kaolinite/illite peak area ratio in Kimmeridge clay from Kimmeridge Bay, Southern England, but that the ratio then fluctuated during the arid times later in the *Hudlestoni* zone and in the *Pectinatus* ammonite zone (at the end of Early Volgian). Wignall & Ruffell could not explain these fluctuations.

In the present investigation, illite was found in all coarse clay fractions (tables 6a and b) and may be largely considered detrital because of its grain size and because the illite reflection area does not vary with sample depth. It probably originated from erosion of parent rocks which were little weathered. It should be noted, however, that overgrowths of authigenetic mica were seen by optical microscopy of the sand and silt fractions from the Central Trough (Micheelsen & Lindgreen, in prep.).

Kaolinite was found in all fractions and the amount did not vary with diagenesis in any fraction. It is therefore most probably detrital and
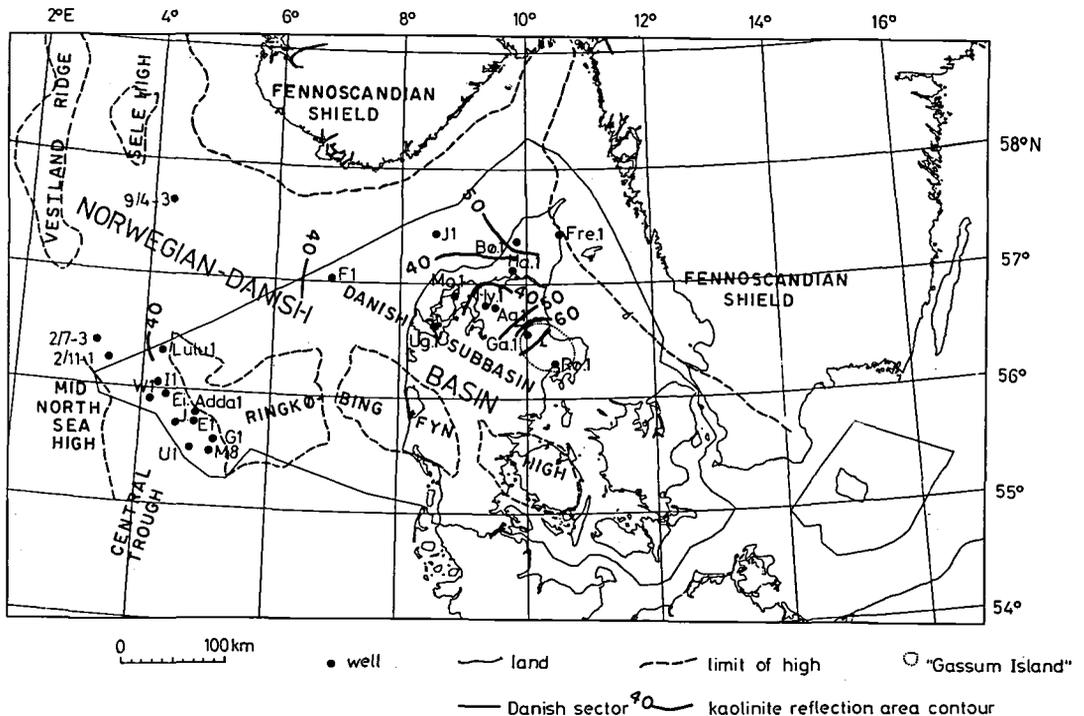
Fig. 13. Kaolinite reflection area contours for samples from the Norwegian-Danish Basin and from the Central Trough. X-ray diffraction of oriented samples of the coarse clay fraction.
(Lower part in well Uglev 1 (862 m) is higher in kaolinite than the upper part (representing the well in the contour map). This may be due to uplift and weathering of the lower part of the Bream Formation in this well during Upper Jurassic (salt movements)). Abbreviations: Bø. 1: Børglum 1; Fre. 1: Frederikshavn 1; Ga. 1: Gassum 1; Ha. 1: Haldager 1; Hy. 1: Hyllebjerg 1; Mo. 1: Mors 1; Rø. 1: Rønde 1; Ug. 1: Uglev 1; Aa. 1: Aars 1.

results from erosion of land surfaces which in earlier times had undergone weathering in a semi-humid tropical climate, in agreement with the proposals of Hurst (1985b). The kaolinite reflection area (%) for the coarse clay fractions from the Bream, Børglum, Sauda and Tau formations from the Norwegian-Danish Basin is given in table 6b and plotted on the map in fig. 13. The samples from Rønde 1 and Gassum 1 are very high in kaolinite and this will be discussed below. For the other wells, a decrease in the amount of kaolinite with distance from the Fennoscandian Shield can be seen. This may be taken to indicate that the main source area for the Upper Jurassic claystones is the Fennoscandian Shield, in agreement with Larsen (1966), who concluded from a heavy mineral study that transport in the Danish Embayment (the Danish Subbasin) was predominantly from the north or north-east. A climatic change can not be the explanation for the variation in the ratio for the samples from the Norwegian-Danish Basin. Firstly, because samples

from the top of the Børglum Formation (in Aars 1, 2425 m (17 m from the top of a 71 m thick formation) and in J1 (21 m from the top of a 101 m thick formation) and from the bottom of the same formation (in F1 (17 m from the bottom in an 83 m thick formation) and in Aars 1, 2465 m (14 m from the bottom of the 71 m thick formation) have about the same kaolinite reflection areas. Secondly, because two samples with high reflection areas, Frederikshavn 1 and Børglum 1, are taken from the bottom of a 7 m thick Børglum Formation and 6 m from the top of a 34 m thick Børglum Formation, respectively.

The kaolinite/illite peak area ratios for the Central Trough samples do not vary with distance from the local highs, the Mid North Sea High and the Ringkøbing-Fyn High (fig. 13). Therefore, these highs were not significant source areas during the Upper Jurassic. The kaolinite reflection areas are generally smaller for the Central Trough samples than for the samples from the NorwegianDanish Basin. This fits with the pro-
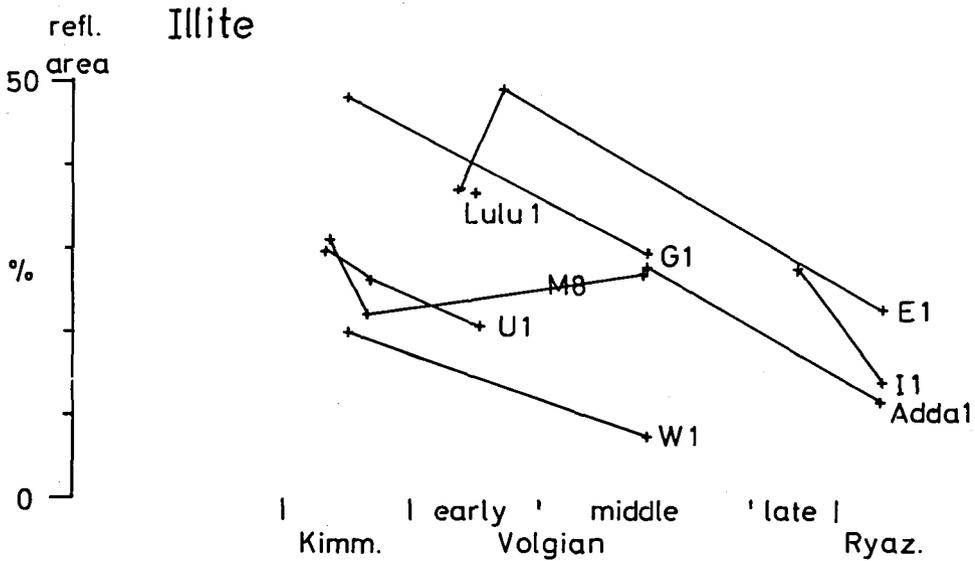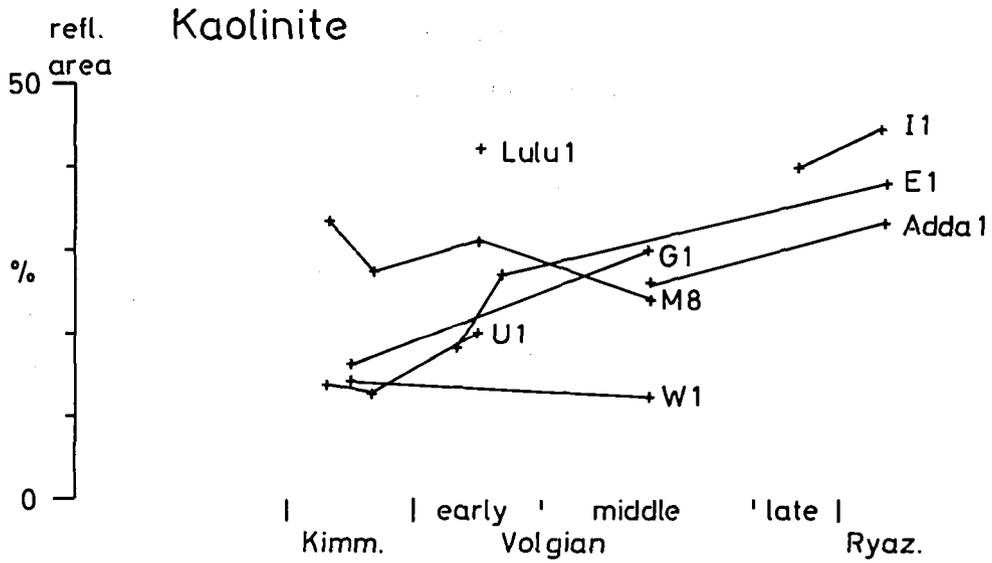
Fig. 14. Discrete clay minerals from the Central Trough. Kaolinite and illite reflection areas vs. chronostratigraphy of sampled intervals. X-ray diffraction of oriented samples of the coarse clay fraction from Central Trough wells.

posal of Sellwood & Sladen (1981) that the distant hinterlands (Scandinavia in the case of the Central Trough samples) are the main source areas. The time span for the Central Trough deposition (Kimmeridgian – Ryazanian) is larger than for the deposition of the Børglum Formation in the Norwegian-Danish Basin (Kimmeridgian–Middle Volgian). Therefore the reflection areas for illite and kaolinite in the coarse clay fraction are plotted vs. time in fig. 14. This figure shows a general increase in kaolinite and a decrease in illite reflection areas from the Kimmeridgian to

the Ryazanian. This increase is much less than the variation during the more limited time span for the Børglum Formation in the Norwegian-Danish Basin and may be due to a change in climate as proposed by Bjørlykke et al. (1975). The decrease in the kaolinite/illite peak area reported at the end of Early Volgian by Wignall & Ruffell (1990) can not be seen in the present investigation (fig. 14). The large intervals represented by the cuttings samples, however, would make detection of such narrow variations impossible.

The kaolinite peaks at 7.4 Å are broad in the diffractograms from the Rønde 1 and Gassum 1 wells (relatively to the peaks from diagenetic kaolinite reservoirs and in the carbonate bands in 2/11–1) and the samples, especially from Gassum 1, have a large kaolinite content and a low content of mixed-layer illite/smectite in all fractions; see the diffractograms for the illite/smectite fraction in Hansen & Lindgreen (1989). This composition is similar to the soil type clay XRD pattern of Hughes, DeMaris, White & Cowin (1987) for clays from Pennsylvanian strata of the Illinois Basin. Hughes et al. found that this clay assemblage resulted from soil processes during deposition. Soil weathering in emergent sediments may therefore have formed the clays from Gassum 1 and Rønde 1. The clay mineralogical results thus support the finding of Larsen (1966) that a "Gassum Island" (fig. 13) existed during part of the Upper Jurassic.

Hower et al. (1976) found a higher percentage (about 10% higher) of illite layers in illite/smectite from the fine clay fraction than in the coarse clay fraction. The large amounts of discrete illite in the present coarse clay fractions made estimation of illite fractions in illite/smectite difficult. But the illite/smectite in the coarse clay fraction appeared similar to the illite/smectite isolated from the corresponding fine clay fraction. There are no indications of a diagenetic change in the discrete minerals of the coarse clay fraction as seen in tables 6a and b. Detrital mica can furnish potassium for the formation of illite layers in the illite/smectite (Hower et al., 1976). Potassium felspars were not detected by microscopy of the silt fractions in the present investigation, and therefore potassium from detrital illite may have played an important role in illite layer formation in illite/smectite also in the North Sea samples.

But the documented presence of significant amounts of ammonium and its fixation together with potassium limit the requirements for potassium from detrital mica.

Layer structure of mixed-layer illite/smectite

Variability of illite/smectite in the claystone

Nine samples were investigated from the core of well 2/11–1, 3863.9 m–3877.7 m, in order to assess the variability of illite/smectite in the claystone. The diffractograms were essentially similar in appearance and were dominated by IS ordered illite/smectite with P_I 0.85. Illite/smectite isolated from the carbonate bands (see above) contained in addition small amounts of randomly ordered or I-S segregated illite/smectite. This may be drilling mud contamination. The uniformity of the illite/smectite patterns from the 2/11–1 core indicates that the illite/smectite mineralogy of the cuttings samples is not the result of mixing of very different lithologies in the intervals sampled and that the amount of illite layers in illite/smectite is fairly constant over short depth intervals.

The nature of segregation

The MacEwan and the fundamental particle models for illite/smectite are shown in fig. 2. Segregation means that a sequence of illite layers will statistically be more probable in an illite/smectite sequence than in an ideal randomly, IS, ISI, or ISII ordered sequence. According to the interparticle diffraction concept for illite/smectite (Nadeau et al. 1984), illite/smectite diffraction patterns are the result of interparticle and intraparticle diffraction in samples consisting of very thin illite particles and eventually single layers of smectite. Diffraction in such a mixture of illite particles will have to be simulated either as a segregation of illite layers or as very thin illite particles.

Simulation of experimental XRD patterns of Mg^{2+}- saturated, air-dried and of Mg^{2+}- saturated, glycolated specimens showed that illite layers in most samples were segregated, as I-S and IS-I segregation in illite/smectite. This is in contrast to information from Bethke & Altaner
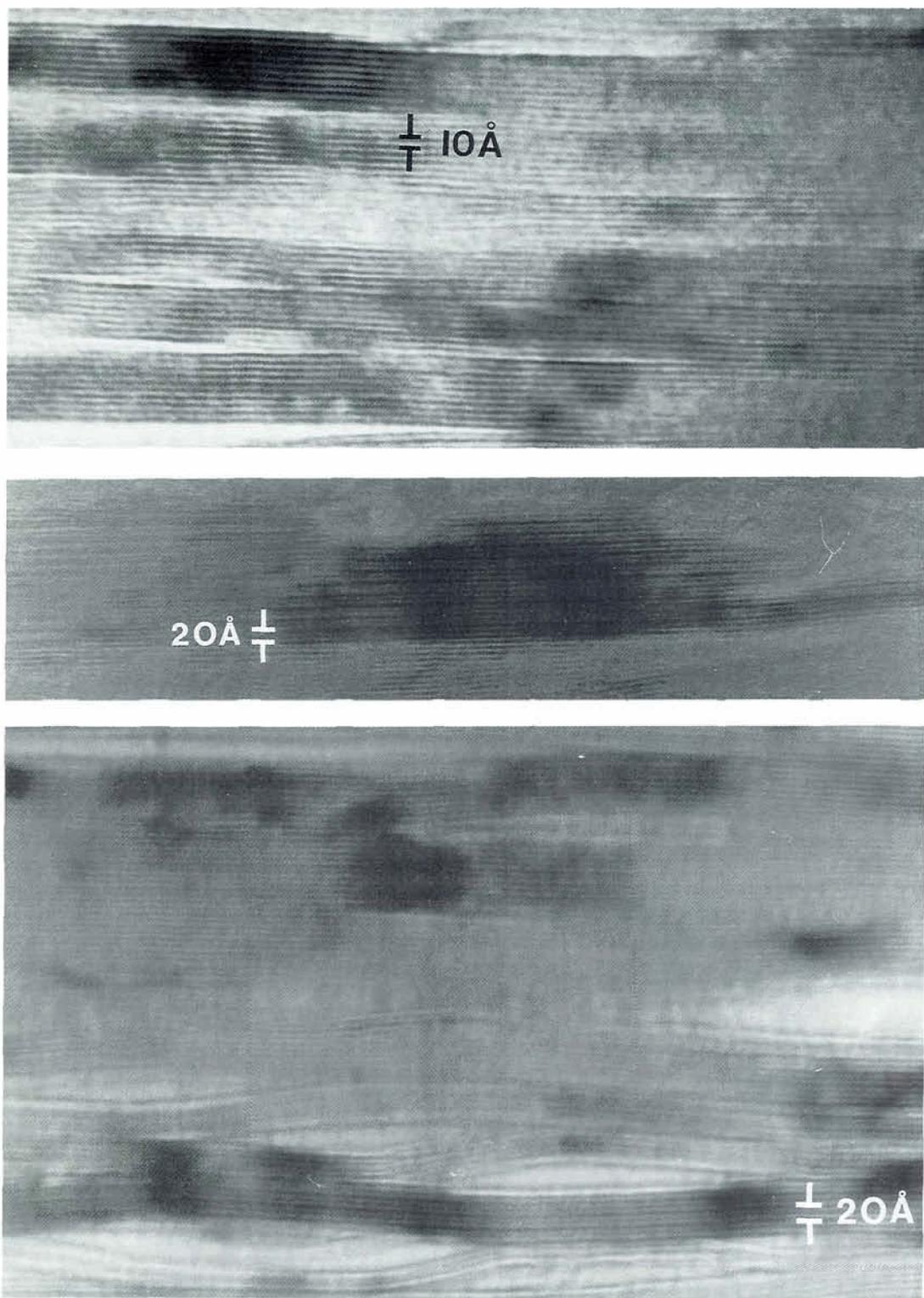
Fig. 15. Bulk rock clays from the Central Trough. High resolution electron microscopy of intact bulk rock samples. a: Well M8 (2387 m); lattice image of lagre crystal with 10 Å period in contrast; from Lindgreen & Hansen (1991, fig. 5). b) Well M8 (2387 m); enhanced contrast is seen in every second lattice fringe giving 20 Å periodicity; from Lindgreen & Hansen (1991, fig. 6). c) Well 2/11–1 (3877 m); short sequences of 20 Å periods are observed in all specimens investiged from this sample.
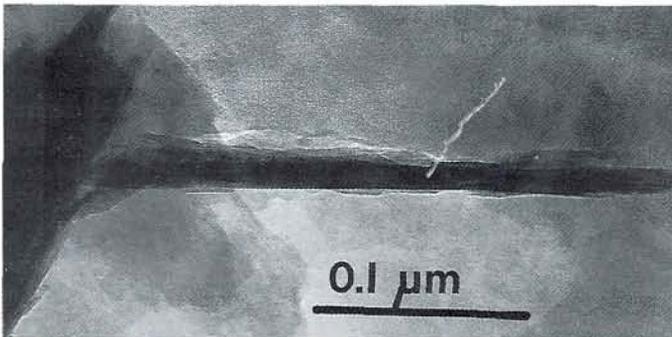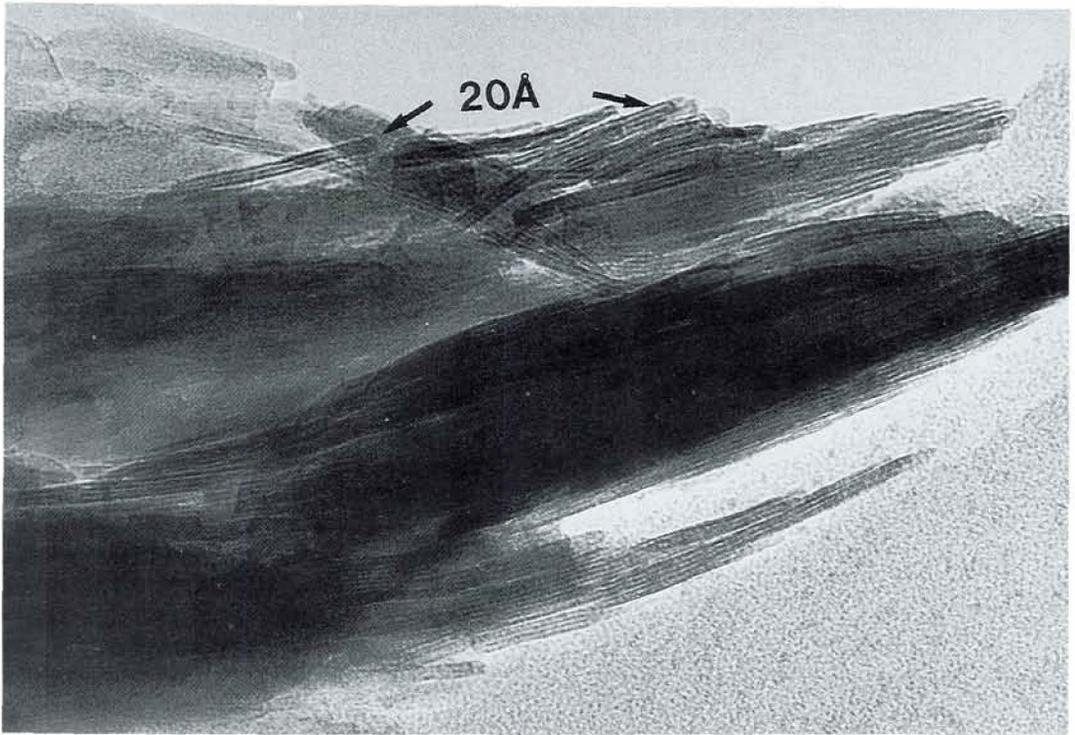
Fig. 16. Illite/smectite from the Central Trough. High resolution electron microscopy of specimens prepared from dispersed illite/smectite which is sedimented along holes in a holed carbon film. a: Well 2/11-1 (3877 m); edge-on view of thin particles, which do not show periods in enhanced contrast of more than 10 Å; from Lindgreen & Hansen (1991, fig. 12). b: Well 2/11-1 (4548 m); single particle. c: Lattice image of the particle in Figure 16b; short 20 Å periods of enhanced lattice fringe contrast; from Lindgreen & Hansen (1991, fig. 13).
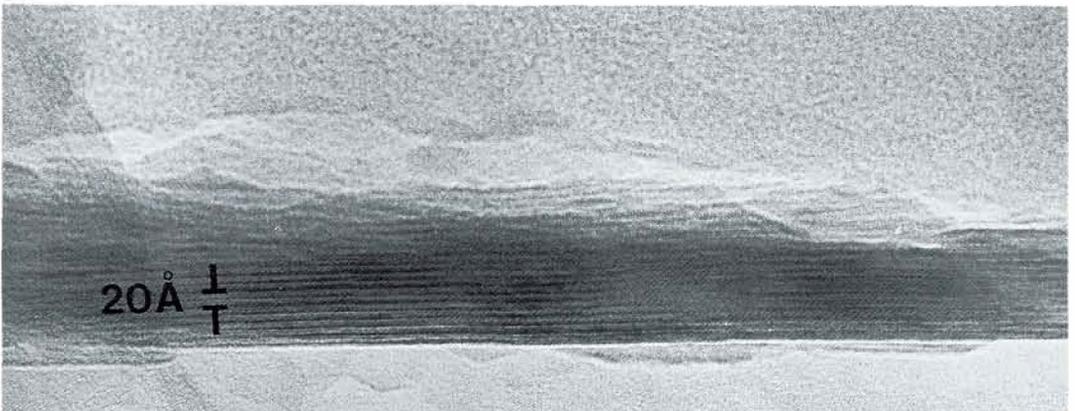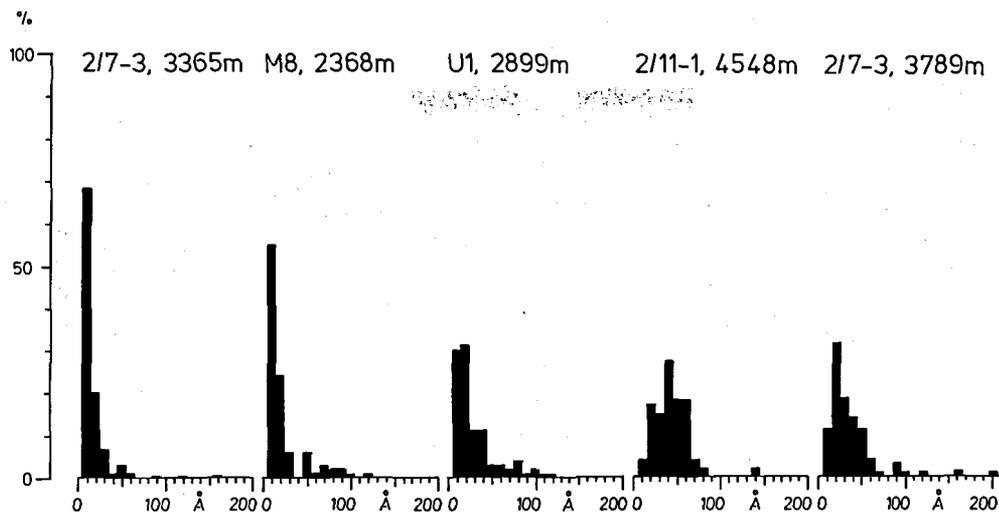
Fig. 17. Illite/smectite from the Central Trough. Particle thickness distributions as calculated from particle thicknesses measured from shadow lengths in transmission electron microscope pictures. Specimens prepared from dispersed illite/smectite fractions.

(1986) that natural illite/smectite is normally not segregated. HRTEM of the present illite/smectite prepared from dispersed Na^+- saturated samples and viewed edge-on showed a large number of particles with only 10 Å period in contrast (see later), probably the fundamental illite particles of Nadeau et al. (1984). Such particles were, however, not observed in intact bulk rock and must therefore have been formed by disrupture along smectite layers in larger particles in the bulk rock (see below). Such 10 Å period particles should give segregation in XRD patterns of dispersed samples, as is observed.

Layer structures in intact bulk rock and in dispersed illite/smectite

Ordering of illite and smectite layers in illite/smectite in intact bulk rock and in dispersed illite/smectite were investigated and discussed by Lindgreen & Hansen (1991).

Illite and smectite layers are distinguished in XRD by the constant d(001) of 10 Å of illite and the swelling of smectite after Mg^{2+}- saturation and glycerolation to 18 Å (MacEwan & Wilson 1984). Smectite layers are expanded in natural rocks even at great depths of burial (van Olphen 1963). The preparation of thin sections of intact bulk rock for HRTEM often involves ion milling at vacuum, and a removal of interlayer water in smectite and a subsequent contraction of inter-

layers between smectite layers to 10 Å is then highly probable. Even if ball-milling is used for preparation of thin sections, a contraction of smectite interlayers will be very probable in the high vacuum of the electron microscope (Klimentidis & Mackinnon 1986; Ahn & Peacor 1986a). Guthrie & Veblen (1989) showed that lattice fringe d(001) values are only reliable in perfectly oriented specimens. Perfect orientation is, however, difficult to achieve, as illite/smectite crystals are easily destroyed by the electron beam.

Particles showing lattice fringes with only 10 Å period in enhanced contrast were very frequent in bulk rock samples, and an example is shown in fig. 15a. These particles may be illite particles but may also contain contracted smectite layers (see below). Larger lattice fringe d(001) values were occasionally seen in packets with 10 Å lattice fringes. The d(001) values of more than 10 Å may be due to interlayered organic matter in the organic-rich Upper Jurassic source rocks. Crystals with lattice fringe d(001) values of 14 Å were observed (Hansen & Lindgreen 1989). These crystals are probably chlorite as only one spacing (14 Å) in lattice fringes was observed. It can be concluded that few or single lattice fringes with a d(001) of more than 10 Å in crystals with 10 Å lattice fringes are probably smectite or chlorite, whereas lattice fringes with d(001) of 10 Å are due to illite or collapsed smectite.

10 Å lattice fringes with periodically enhanced contrast were observed by HRTEM on intact bulk rock in all Central Trough samples investigated. Regular 20 Å period sequences of such enhanced contrast were most frequent, but also 30 Å period sequences and sequences with enhanced contrast occurring randomly along c* were seen (Hansen & Lindgreen 1989). Particles with 20 Å period in enhanced contrast are shown in fig. 15b and 15c. Computer modelling (Hansen & Lindgreen 1989) showed that such enhanced contrast in underfocus can be due to alternating interlayers of K^+ and Na^+. Therefore, Na^+- saturated smectite layers between K^+- saturated illite layers can show such contrast under appropriate instrumental conditions which involve near perfect orientation of the crystals (Guthrie & Veblen 1989) and preferentially overfocus (Guthrie & Veblen 1989), even if enhanced contrast could also be seen in the present investigation in underfocused images. 2M and 3T mica polytypes can also show 20 Å and 30 Å periods of enhanced contrast, respectively, in lattice fringes. The abundance of 20 Å period particles in HRTEM images in the present investigation and the finding of only 1M mica by XRD of sand+silt, coarse-clay and fine-clay fractions (including the illite/smectite fraction) show that 2M mica cannot be responsible for most of the 20 Å period particles seen in HRTEM. Stacking of thin illite particles can not be the cause of the enhanced lattice fringe contrast, as dislocations would have occurred frequently in such stacked aggregates. Most of the enhanced lattice fringes seen in intact bulk rock by HRTEM are therefore due to interlayered smectite and illite in illite/smectite (MacEwan) particles. It is important that the enhanced contrast can be caused by interlayering of the lighter cation Na^+ instead of K^+ (present in most illites) (Hansen & Lindgreen 1989). Periodically enhanced contrast can also be caused by the lower amount of cations present between smectite layers than between illite layers (Guthrie & Veblen 1989), but it must then be more weak. For ammonium illite layers interlayered with smectite, the contrast difference between illite and smectite layers must be neglegible, as the larger number of NH_4^+ between illite layers compared to the smaller number of Na^+ between smectite layers is counterbalanced by the lower scattering power of NH_4^+ compared to Na^+. Na^+

is the dominating cation in pore waters of the claystones investigated here, and this explains why illite/smectite particles with lattice fringes of enhanced contrast are so frequent in the samples. These particles are, according to the arguments above, illite/smectite or MacEwan particles. However, MacEwan particles with NH_4^+ illite layers and Na^+- saturated smectite layers will almost certainly show 10 Å period particles resembling illite. Besides, non-perfectly oriented crystals which show 10 Å periods in contrast (like in fig. 15a) may both be illite/smectite and illite, and (contracted) smectite crystals, because near-perfect orientation is required for obtaining the enhanced periods in contrast (Guthrie & Veblen 1989). Na^+ was the dominating cation in the Gulf Coast Tertiary shales investigated by Schmidt (1973). The failure of Ahn & Peacor (1986a) to observe lattice fringes with more than 10 Å periodicity can therefore be attributed to the focusing of their microscope during lattice imaging or to imperfect orientation, according to the computermodelling carried out by Guthrie & Veblen (1989). Ahn & Peacor (1989) have later reexamined their pictures and found that slightly overfocused images of the sample with 80% illite layers and IS ordering (from XRD) had 20 Å periods in enhanced contrast. Ahn & Peacor modified accordingly their former conclusion (Ahn & Peacor 1986a) so that the results of XRD on dispersed illite/smectite and of TEM (HRTEM) on intact bulk rock were not incompatible. Veblen, Guthrie, Livi & Reynolds (1990) examined two ordered illite/smectites of hydrothermal origin by XRD on dispersed samples and by HRTEM on intact bulk rock. They examined strongly overfocused HRTEM images showing larger than 10 Å periods in enhanced contrast and calculated the amount of smectite layers from the number of extra dark fringes. The amount of smectite layers obtained in this way for the two samples agreed well with the amounts obtained from XRD. These results conform with those of the present investigation in that ordering of illite/smectite can be seen by HRTEM on intact bulk rock.

Attempts to disperse the samples and isolate illite/smectite resulted in a fraction dominated by illite/smectite from almost all samples. However, kaolinite, perhaps interlayered with illite and smectite, dominated the illite/smectite fractions
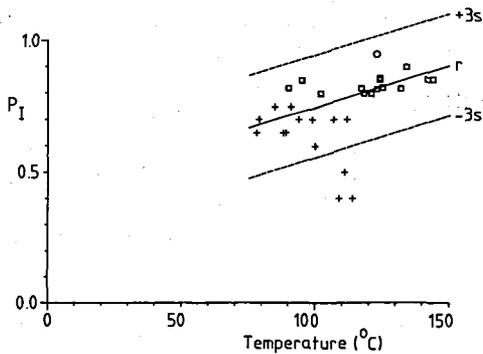
Fig. 18. Illite/smectite from the Central Trough. P_I values vs. formation temperatures. (+) = randomly ordered or I-S segregated, (□) = IS ordered and (○) = ISII ordered illite/smectite. Dotted lines delimit three standard deviations.

Tab. 7. Dispersed illite/smectite from Central Trough samples. Fractions of illite layers and average particle thicknesses (calculated from TEM) and P_I values and ordering (obtained from XRD).

I/S fraction	TEM		XRD	
	Fraction of I	Average thickness	P_I	Ordering
2/7–3, 3365 m	0.42	17 Å	0.40	random
M8, 2368 m	0.62	23 Å	0.65	I-S segr.
U1, 2899 m	0.76	30 Å	0.70	I-S segr.
2/11–1, 4548 m	0.89	41 Å	0.85	IS
2/7–3, 3789 m	0.84	35 Å	0.95	ISII

from the Gassum 1 and Rønde 1 wells (Hansen & Lindgreen 1989). Even when the isolation was successful, some of the illite/smectite remained in the coarse clay and coarser fractions during the dispersion and isolation procedure.

Illite/smectite crystals may rupture along smectite layers, as these can disperse and float apart during hydration (Mering & Oberlin 1971; Altaner et al. 1988; Ahn & Peacor 1986b). Ahn & Buseck (1990) showed by HRTEM on ion-milled illite/smectite samples that packets having coherent stacking arrangements were thicker than the fundamental particles in such illite/smectite. They concluded therefore that the "fundamental particles" of Nadeau et al. (1984) are artefacts of sample preparation. If all smectite layers float apart, the illite/smectite crystals will be changed into a mixture of thin illite particles like those seen in a HRTEM picture of dispersed illite/ smectite from well 2/11–1, 3877 m depth (fig. 16a). Such a mixture of very thin illite particles can then give, by combined inter- and intraparticle diffraction, diffraction patterns resembling those from fundamental illite given by Nadeau et al. (1984). When complete dispersion of smectite layers has been achieved, illite/smectite layer composition can be calculated from a particle thickness distribution measured from TEM as follows: half a bottom and half a top layer of each particle are smectite, the remaining part of each particle is illite (similar to the calculation of Nadeau (1985)), see also fig. 2. The result of such a calculation on the present material is shown in table 7 together with the results of XRD on the same samples and the particle thickness distribu-

tions (shown in fig. 17) of the illite/smectite fractions as calculated from TEM of the shadowed illite/smectite fractions.

It can be seen from table 7 that the fractions of illite layers calculated from TEM particle thicknesses agree fairly well with the P_I values obtained by XRD. The poorest agreement is seen for 2/7–3, 3789 m. For this sample the lack of correspondence between TEM and XRD may be due to the difficulty in assessing a small number of smectite layers by XRD. On the other hand, the sedimentation of thin suspensions of particles on cleaved mica for TEM may have separated layers with a high, smectitic or vermiculitic charge, which may be collapsed in Mg^{2+}-saturated, glycolated specimens and therefore re-
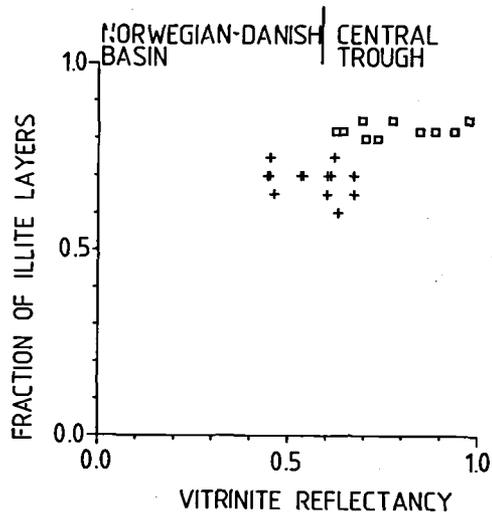
Fig. 19. Illite/smectite from the Norwegian-Danish Basin and the Central Trough. Fraction of illite layers (P_I values) vs. vitrinite reflectancy values. (+) = randomly ordered or I-S segregated illite/smectite, and (□) = IS ordered illite/smectite. From Hansen & Lindgreen (1989, fig. 9).
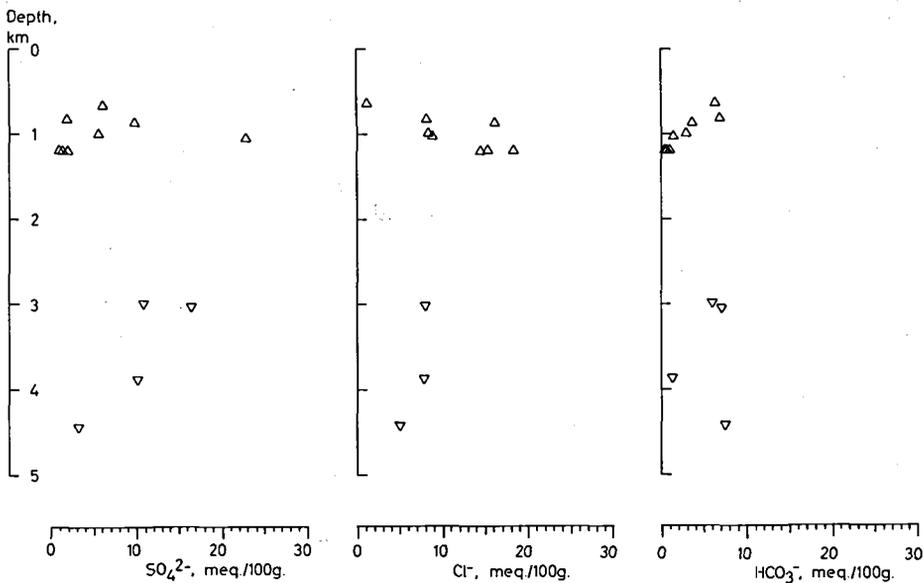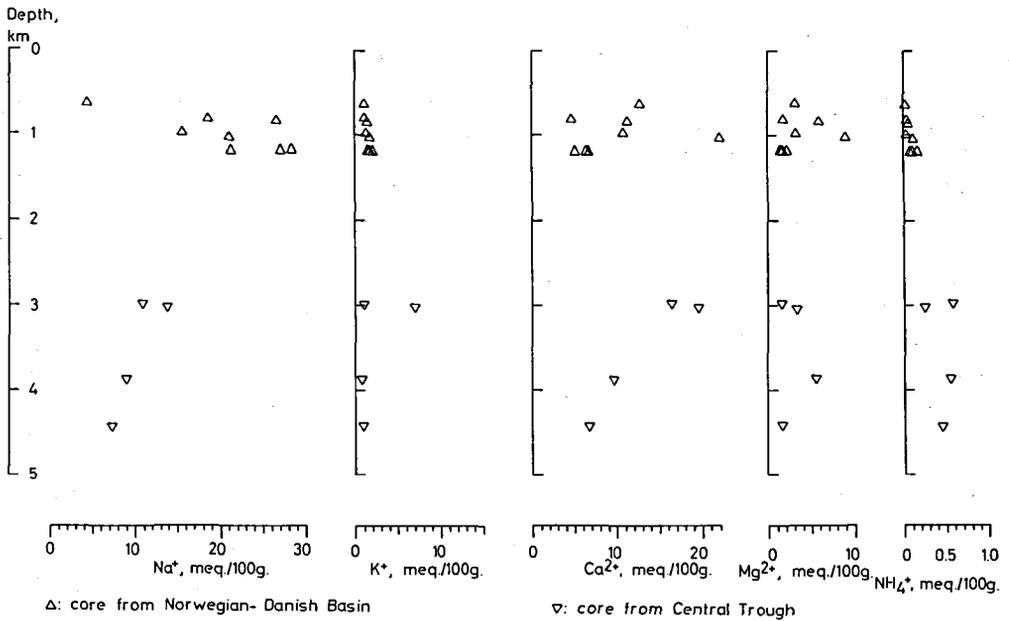
Fig. 20. Bulk rock clays from the North Sea and onshore Denmark. Amount of soluble ions in core material vs. depth of samples.

corded by XRD as illite. When illite is the major component, IS ordering, ISI ordering and ISII ordering require that smectite layers are separated by at least one, two and three illite layers, respectively. According to the interparticle diffraction concept, IS, ISI and ISII ordering require that only particles at least 20 Å, 30 Å and

40 Å thick, respectively, are found in the illite/smectite. This contrasts with the finding of about 15% 10 Å thick particles and about 30% 20 Å thick particles in the ISII ordered illite/smectite from 2/7-3, 3789m. The discrepancy could be due to collapse of some interparticle spacings to 10 Å in Mg-glycolated specimens, but could also be

due to misinterpretation of the ordering degree from XRD. This last possibility is probable because Reynolds (1984) mentioned that computer simulations using R3 ordering and Markov theory give good agreement with experimental patterns with next-to-next neighbour ordering, but that the agreement anyway is not as good as for less distant ordering. Correspondingly, Altaner & Bethke (1988) found that TEM on shadowed dispersed specimens indicated lower P_I values than the simulated XRD patterns did.

The three, randomly ordered or I-S segregated illite/smectites are either dominated by 10 Å thick particles (2/7–3, 3365 m; M8, 2368 m) or have a large amount of particles of different thicknesses (fig. 17), both of which after the interparticle concept of Nadeau et al. (1984) should give random ordering or I-S segregation in XRD. The predominantly IS ordered sample 2/11–1, 4548 m, is composed mainly of particles with a uniform thickness distribution, from 20 Å to 60 Å (fig. 17), where IS ordering according to the interparticle diffraction idea should be due to predominance of 20 Å thick particles. However, HRTEM on the dispersed samples showed that 20 Å period particles, most probably IS ordered MacEwan illite/smectite particles as discussed above, are abundant in this and other IS ordered illite/smectite fractions (an example is shown in fig. 16 b and 16c). Therefore the particles seen in shadowed TEM are not all illite particles and complete dispersion of the smectite layers has accordingly not been achieved. Assuming that all 40 Å and 60 Å thick particles seen in TEM of shadowed specimens are IS ordered illite/smectite particles leads to a fraction of illite layers for 2/11–1, 4548 m, of 0.79. This agrees, as does the value from TEM given in table 7, with the P_I value from XRD and illustrates that a fair agreement between XRD and TEM values can not be taken as proof for the occurrence of only "fundamental" illite particles in a sample. It should be noted that even those particles showing only 10 Å period in contrast in HRTEM images (like those in fig. 16a) may well contain smectite layers. This is because near-perfect orientation of the particles is required for observation of periodically enhanced contrast (Guthrie & Veblen 1989 and 1990) and such near-perfect contrast is difficult to achieve in the loosely sedimented particles viewed edge-on.

Illite/smectite diagenesis

Illitization of illite/smectite during burial diagenesis

The conclusion of the literature review on illitization of illite/smectite was that smectite layers are converted to illite layers during burial diagenesis. The conversion is initiated above 55°C, and the illite/smectite becomes IS ordered at about 100°C when it contains about 80% illite layers.

Diagenesis of the Upper Jurassic illite/smectite of the present investigation was discussed by Hansen & Lindgreen (1989). For Central Trough samples, a plot of P_I and ordering values versus temperature is shown in fig. 18. The present day temperatures of the samples were derived from the calculated formation temperature gradients of Evans & Coleman (1974) and Jensen (1982). Scattering of the points is considerable, probably to a large degree because of uncertainties in the calculated formation temperatures. Ordering in illite/smectite begins at about 90°C and randomly ordered or I-S segregated illite/smectite is absent above 115°C. Three samples, from wells W1 (3816 m) and 2/7–3 (3365 m and 3502 m) deviate from the general trend (see below). For the other samples, correlation between temperature and P_I is low (0.69) and ordering in illite/smectite accompanied by an increase in P_I from 0.65–0.75 for randomly ordered or I-S segregated illite/smectite to 0.80–0.95 for ordered illite/smectite was the most obvious response of the illite/smectite to increasing temperature. The ordering temperature interval, 90–115°C, agrees well with the ordering temperature of 1) 95°C for an Oligocene-Miocene Texas Gulf Coast well (Hower et al. 1976); 2) 115 −125°C for the Miocene-Pliocene Texas Gulf Coast well E (Perry & Hower 1970), which has a high geothermal gradient (30.5°C/km); and 3) 99°C for the Lower Cretaceous shales of the Rocky Mountain area, which have an even higher geothermal gradient of 41°C (Burtner & Warner 1986). But it is lower than the 130–160°C for the Miocene Pliocene well C with a low geothermal gradient (24.0°C/km) (Perry & Hower 1970).

The samples from the Norwegian-Danish Basin contain randomly ordered or I-S segregated illite/smectite with P_I 0.65–0.75 at formation temperatures of 24–68°C. This extends then the tem-

NH₄/K molar ratios vs. depth

Figure:

Depth, km — **Clay pore fluid (cores)** — **I/S minerals**
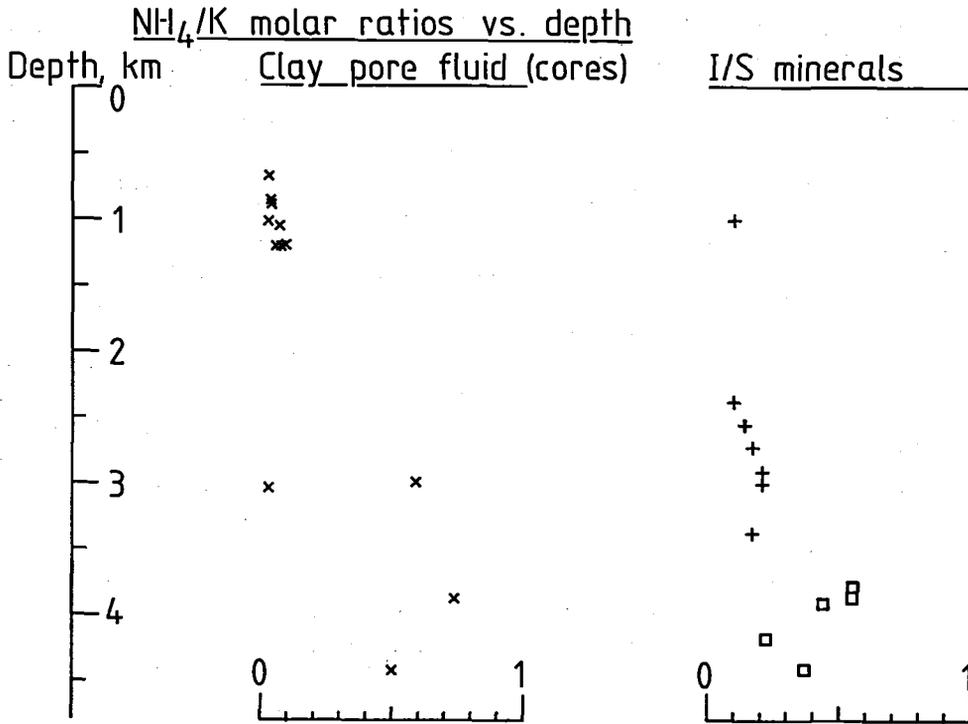
Fig. 21. Bulk rock clays from the North Sea and onshore Denmark. NH₄/K molar ratios in core pore fluids and in illite/smectite fractions vs. depth. (+) = randomly ordered or I-S segregated, and (□) = IS ordered illite/smectite (I/S).

perature range for these illite/smectites down to 24°C, far below the 55°C required for illite layer formation and the c. 70°C found by Perry & Hower (1970) to be required for formation of illite/smectite with a similar amount of illite layers. These illite/smectites must therefore be detrital in the Norwegian-Danish Basin. This conclusion, together with their occurrence in the Central Trough wells at temperatures ranging from 80°C to 90–115°C, makes it likely that they are also detrital in the Central Trough, even if they could have formed at the temperatures in the Central Trough according to the data of Perry & Hower (1970).

Besides temperature several investigations (e.g. Eberl & Hower 1976; Ramseyer & Boles 1986) have shown the importance of time to the illitization process. Vitrinite reflectancy is also a result of both time and temperature and it is the standard parameter in source rock maturation evaluations. Because it has been shown that illite/smectite react slower to heating than do vitrinite (Heling & Teichmüller 1974; see literature review), the comparison of illitization in illite/smectite with vitrinite reflectancy will show an eventu-

al influence of long-lived paleothermal events. Vitrinite reflectancy values, R_o, are available for wells E1, M8, U1 and I1 (down to 3885 m) from Thomsen et al. (1983) and for well 2/11–1 from Thomsen (1984), but not from G1, W1 and 2/7–3. Vitrinite reflectancy values from Danish onshore wells are available from Thomsen et al. (1983) and Schmidt (1985). A plot of P_I versus R_o is shown in fig. 19. The immature onshore well sections from the Danish Subbasin all contain randomly ordered or I-S segregated illite/smectite. In the Central Trough, the plotted randomly ordered or I-S segregated mixed-layers are only found in the interval 0.60–0.67% for R_o, whereas IS and ISII ordered mixed-layers are found above R_o values of 0.63%. A regression analysis for the IS and ISII ordered mixed-layers shows that P_I is not increasing significantly with R_o, and that the correlation coefficent is 0.26. Vitrinite reflectancy values were not available for the three samples deviating in the P_I – T plot in fig. 18. The plot of P_I and ordering in illite/smectite vs. vitrinite reflectancy thus confirmed the finding from the plot of P_I and ordering vs. present temperature, i.e. that the randomly ordered or I-S segre-

gated illite/smectite with P_I 0.65–0.75 become ordered in response to an increase in temperature, which is reflected in an increase in vitrinite reflectancy also. Furthermore, the finding of randomly ordered or I-S segregated illite/smectite with P_I 0.65–0.75 at vitrinite reflectancies down to 0.4 shows that these illite/smectites have not formed during paleoheating events, especially because vitrinites react faster to short-lived heating events than do illite/smectite (Środoń 1979; Smart & Clayton 1985). These illite/smectites must therefore be detrital.

Parent material for illite/smectite

The source for the illite/smectite of the present investigation was discussed by Hansen & Lindgreen (1989). Pearson et al. (1982) proposed that randomly ordered or I-S segregated illite/smectite in Viking Graben wells at vitrinite reflectancies lower than 0.60 were detrital and Hurst (1982) proposed a detrital origin (in this case from the northern part of Scotland) for randomly ordered or I-S segregated illite/smectite in Jurassic shales from Brora, NE Scotland, with "in general" 35–60% illite layers. This fits well with the conclusion above that the parent material for illite/smectite diagenesis (except for illite/smectite in wells W1(3816 m) and 2/-3 (3365 m and 3502 m)) in the Central Trough and the Norwegian-Danish Basin is randomly ordered or I-S segregated illite/smectite. On the other hand, Hurst (1982) also found ordered illite/smectite in the same area, but he related it to Devonian sandstone as parent rock. Both ordered and randomly ordered illite/smectite may form during weathering in soils (Eberl 1984). In the present investigation the detrital illite/smectite with P_I 0.65–0.75 originate probably from weathered material on the highs, notable the Fennoscandian Shield, conforming with the arguments of Sladen & Sellwood and with the conclusion on origin of discrete clay minerals in the coarse clay fraction, see above.

The three illite/smectites deviating from the general P_I–T trend in fig. 18, from wells W1 (3816 m) and 2/7–3 (3365 m and 3502 m) are from samples which contain large amounts of these mixed-layers, such that the mixed-layers are also found in aggregates in the other clay subfractions and in the sand and silt fraction. According to

Lindgreen et al. (1991), the detrital randomly ordered or I-S segregated illite/smectites and the IS and ISII ordered illite/smectite follow the same trend in chemical composition with P_I, whereas the I/S from 2/7–3, 3365m (the only one of these three samples investigated for all elements) deviated significantly from this trend in containing less Mg and Fe and more Al and in having more tetrahedral Al. The three mixed-layer clays are therefore assumed to have a particular parent material, very rich in smectite. This is probably a bentonite, which is a rock dominated by smectite (Grim & Güven 1978). Bentonites usually originate from volcanic ash (Grim & Güven 1978), they show lower P_I values than surrounding shales (Hoffman & Hower 1979; Środoń 1979) and they have, at a given temperature, low P_I values compared to detrital illite/smectite (Velde & Brusewitz 1986). The hypothesis of a bentonitic and possibly volcanic origin explains the drastic change in well 2/7–3 from a P_I value of 0.40 and random ordering or I-S segregation at 3502 m to a P_I value of 0.95 and ISII ordering at 3789 m, and in well W1 from a P_I value of 0.50 and I-S segregation at 3816 m to a P_I value of 0.80 and IS ordering at 4051 m. The interpretation agrees with the reported volcanic activity in the region (see literature review). It is furthermore supported by the results of Pearson & Small (1988). They found that the mineralogical variation in fine fractions of Quaternary to Triassic shales from the Viking Graben and the Moray Firth exhibited a strong source control and attributed particularly the very high abundance of randomly ordered or I-S segregated illite/smectite to alteration of volcanic ash.

Chemical controls

Cores from the Børglum Formation in the Danish Subbasin (wells Børglum 1, Frederikshavn 1, Gassum 1, Haldager 1 and Uglev 1) and from the Farsund Formation in the Central Trough (wells 2/11–1, E1, Jens 1 and Elin 1) were investigated. Cleaned core samples were crushed to pass a 0.25 mm sieve and two samples were washed four times with 1M $MgCl_2$ and 0.5M $RbNO_3$, respectively. The pH was ~6 in the extracts from Gassum 1, ~7 in the extracts from 2/11–1, 3877 m and from Haldager 1, 1049 m and ~8 in the extracts from the other core samples. It is prob-
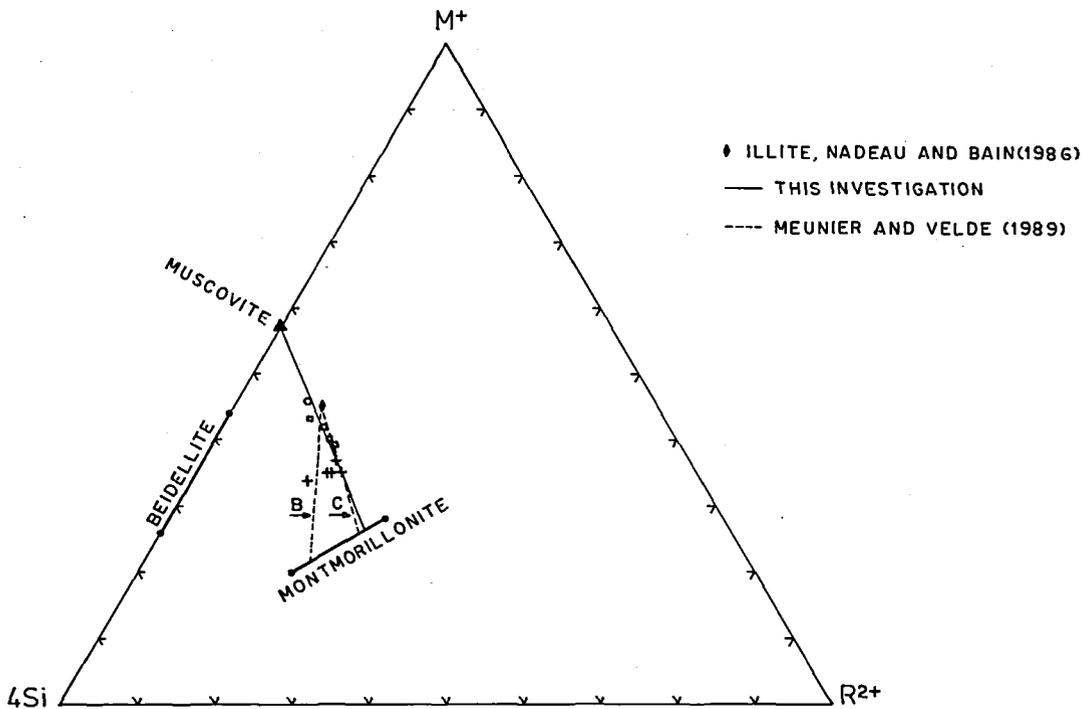
Fig. 22. Illite/smectite from the Central Trough plotted in a ternary M$^+$-4Si-R^{2+} system used by Meunier & Velde (1989). M$^+$ is equivalent of fixed plus adsorbed interlayer cations, 4Si is the number of silicon atoms, R^{2+} is the number of divalent octahedral cations, all per $O_{10}(OH)_2$. The three coordinates are: 1): M$^+$: M$^+$/(M$^+$+Si+R^{2+}); 2): 4Si: Si/(M$^+$+Si+R^{2+}); and 3): R^{2+}: R^{2+}/(M$^+$+Si+R^{2+}); it should be noted that Si is *one fourth* of the number of tetrahedral silicon atoms per $O_{10}(OH)_2$. (+) = randomly ordered or I-S segregated, ($\square$) = IS ordered, and (○) = ISII ordered illite/smectite.

able that some NH$_3$ has escaped from the core fluids with pH 8 and that the NH$_4$ values determined are lower than in the formations sampled, even if the content of NH$_4$ was determined the day after the extraction and the maximum NH$_4$ concentration in the extracts was 2 ppm. The contents of soluble + exchangeable cations are shown in fig. 20. The dominating cations are Na$^+$ and Ca^{2+}, there are minor amounts of Mg^{2+}, and very small amounts of K$^+$ and NH$_4^+$. An exception is Jens 1, 3034 m, where K$^+$ is present in relatively large amounts. The contents of Mg^{2+} and K$^+$ do not change with depth. The content of Na$^+$ is low in the most shallow core from Frederikshavn 1, 649 m, but decreases for the other samples with depth. The content of NH$_4^+$ is relatively high in three deep samples: Elin 1, 4418 m; E1, 2983 m; and 2/11-1, 3877 m, but is lower in Jens 1, 3034 m and in samples from less than 1500 m depth. The Cl$^-$, HCO$_3^-$ and SO$_4^{2-}$ anions are present in varying amounts in the samples (fig. 20). They do not vary in amount with depth even though three deep samples: E1, 2983 m; 2/11-1,

3877 m; and Jens 1, 3034 m, have a high content of sulphate.

Weaver & Beck (1971) and Schmidt (1973) found that Na$^+$ is the dominating cation in pore waters from the US Gulf Coast shales, K$^+$, Mg^{2+} and Ca^{2+} being of minor importance. This predominance of Na$^+$ was also observed by Jones, Hughes & Tomkins (1989) for Lower Cretaceous shales from the Witch Graben of the North Sea. The addition of pore water cations and exchangeable cations in the present investigation cannot account for the high amounts of Ca^{2+} relative to Na$^+$ in the present investigation, even if Ca^{2+} (because of its divalent charge) is adsorbed on the exchange sites preferentially to Na$^+$. Gypsum was detected in several samples (tables 5a and b) and the solubility product for CaCO$_3$ is exceeded by dissolved Ca^{2+} and HCO$_3^-$. Thus the relatively high amounts of Ca^{2+} in the present investigation are due to dissolution of calcite and gypsum during laboratory leaching. In US Gulf Coast shales, Weaver & Beck (1971) found that HCO$_3^-$ generally was the dominating anion,
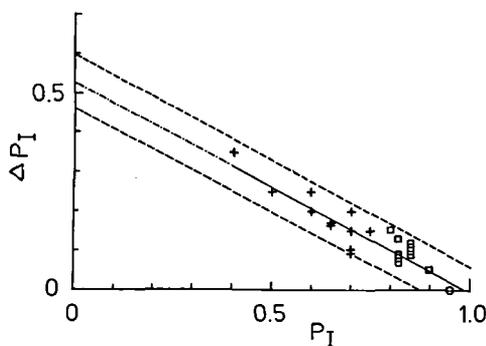
Fig. 23. Illite/smectite from the Central Trough. ΔP_I vs. P_I. ΔP_I is the fraction of all illite/smectite which is smectite but remains contracted to 10 Å after K^+- saturation and glycolation. (+) = randomly ordered or I-S segregated, (□) = IS ordered, and (○) = ISII ordered illite/smectite. From Lindgreen et al. (1991, fig. 9).

SO_4^{2-} next in abundance, followed by Cl^-, whereas Schmidt (1973) found that SO_4^{2-} generally was dominating, HCO_3^- next, followed by Cl^-. In North Sea Cretaceous shales, Jones et al. (1989) found that Cl^- was dominating, CO_3^{2-} next, followed by SO_4^{2-}. The general dominance of SO_4^{2-} over Cl^- and HCO_3^- in the present investigation is thus in accordance with the results for the shales investigated by Schmidt but disagrees with the data of Weaver & Beck and especially the data of Jones et al. (1989). Weaver & Beck (1971) reported their data in ppm, but a correction for equivalent weight does not change the relative abundances of either cations or anions by more than a factor two.

The contents of sodium and chloride are both markedly high in the four shallow samples from the wells Gassum 1, 1190 and 1191 m (3 samples) and Uglev 1, 862 m (fig. 20). These two wells are the only onshore wells drilled on salt structures and the high contents of sodium and chloride must be due to salt solutions migrating upwards from the Zechstein, in Gassum 1 through Triassic sandstone (700 m) and shale (1200 m) and Lower Jurassic clays (300 m), and in Uglev 1 through Middle Jurassic sandstone (60 m) (both wells are drilled on top of the structures). Of the Central Trough wells for which pore water chemistry has been investigated, only one (2/11–1) is drilled on a possible Zechstein salt structure, but salt water from the Zechstein has not infiltrated the Upper Jurassic claystones in this well to any measurable extent. Cayley (1987) mentioned that produced

formation waters from the Tertiary sandstones in the Central Trough are salt saturated and that this indicates that waters associated with the Zechstein have migrated vertically. Schmidt (1973) found a constant amount of exchangeable potassium and an increasing amount of potassium in interstitial water of shale with depth. He explained the increasing amount in interstitial water to be the result of breakdown of detrital feldspar, and the constant amount of exchangeable potassium to be due to potassium fixation in interlayer positions of illite. Potassium feldspars could not be detected in the sand and silt fraction of the North Sea claystones. This may explain the lack of variation of potassium with depth in this investigation. Bogomolov, Kudel'skiy & Kozlov (1970) analysed groundwaters in various oil and gas basins in USSR and found that ammonium is a direct indicator of a present or past occurrence of oil below the surface. They attributed this to ammonium being one of the conversion products of oil. A similar origin can explain the high content of ammonium in the oil generating Central Trough claystones rich in organic material compared to the immature onshore claystones with less organic material or a more terrestrial origin.

The absence of potassium feldspars in samples from the Central Trough indicates that the potassium for illite layer formation must be supplied by pore water migrating from deeper layers (as proposed by Long & Neglia (1968), Weaver & Beck (1971), and by Hay, Lee, Kolata, Matthews & Morton (1988)) or from breakdown of detrital mica (as proposed by Hower et al. (1976)). Both processes should give an increase in the amount of pore water potassium with depth. The constant amount of potassium in pore waters in the present investigation must be due to the fact that the supply of potassium is small compared to the fixation in illite/smectite. Long & Neglia (1968) found that illite/smectite diagenesis is influenced by pore water chemistry. In the present investigation the parallelism is obvious between 1: the NH_4^+/K^+ ratio in pore waters vs. depth and 2: the NH_4^+/K^+ ratio in illite/smectite vs. depth (fig. 21). This shows that the NH_4^+/K^+ ratio in pore water controls the fixation of NH_4^+ and K^+ in illite/smectite during diagenetic illite layer formation and illite/smectite ordering in our samples.

Moles of fixed K per $O_{10}(OH)_2$ vs. % illite in I/S

Moles of fixed NH_4 per $O_{10}(OH)_2$ vs. % illite in I/S
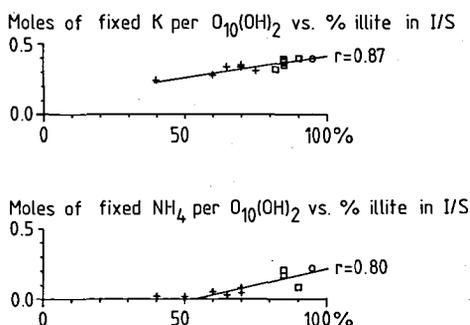
Fig. 24. Illite/smectite from the Central Trough. Moles of fixed K (a) and fixed NH_4 (b) per $O_{10}(OH)_2$ vs. % illite in illite/smectite (equal to 100 · P_I). (+) = randomly ordered or I S segregated, (□) = IS ordered and (○) = ISII ordered illite/smectite (I/S).

Elemental composition of illite/smectite

Fine-clay fractions (< 0.2 μm) of the Upper Jurassic claystones were investigated by ^{27}Al and ^{29}Si MAS NMR spectroscopy by Jakobsen, Jacobsen & Lindgreen (1988).

For the Upper Jurassic illite/smectites, structural arrangements of major elements (Fe, Al and Si) were investigated by ^{57}Fe Mössbauer spectroscopy, by ^{27}Al and ^{29}Si MAS NMR spectroscopy and by infrared (IR) spectroscopy (Lindgreen et al. 1991). For details of IR spectroscopy, see App. 1. Furthermore, the elemental composition of the illite/smectite fraction was determined by total dissolution ($HF-H_3BO_3$) followed by atomic absorption spectrometry (AAS) of dissolved elements. NH_4 was determined by degassing at 600°C and isotope dilution. From these data, the diagenetic structure transformations were discussed by Lindgreen et al. (1991).

Lattices of illite and smectite layers

The composition of illite/smectite at P_I 1.0 was calculated by prolongation of the lines of elemental composition vs. P_I, of Al(4)/Al(6) vs. P_I, of Al(4)/(Al(4) + Si) vs. P_I (Lindgreen et al. 1991), and of Fe^{2+}/Fe^{3+} vs. P_I. The corresponding formula is:

$$Na_{0.45}K_{0.42} (NH_4)_{0.22}$$
$$(Mg_{0.13}Al_{1.67}Fe^{2+}_{0.04}Fe^{3+}_{0.12})(Al_{0.68}Si_{3.32}) O_{10}(OH)_2$$
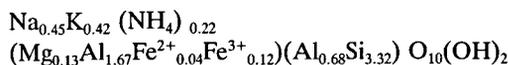
and this may therefore be the composition of illite layers in illite/smectite. Prolongation of the

lines to P_I 0 would then give the composition of the smectite layers, but such a prolongation is not justified as the data are only statistically reliable above P_I 0.6, also because NH_4^+ vs. P_I and Al(4)/(Al(4) + Si) vs. P_I cannot be extrapolated below P_I 0.55. The calculated illite layer composition shows the same, small content of Mg and Fe in the octahedral sheet. This and the tetrahedral Al content of 0.68 is normal for illites (Weaver & Pollard 1973, table V).

Meunier & Velde (1989) plotted previously published chemical data on illite/smectite in a $4Si-M^+-R^{2+}$ triangular diagram, where M^+ and R^{2+} are the layer charge and the number of divalent, octahedral cations, respectively. They noted that Cretaceous and Tertiary samples were characterized by a strong dispersion of chemical compositions bounded by ideal beidellite (having only tetrahedral substitutions) and ideal montmorillonite (having only octahedral substitutions). The Silurian and Ordovician samples showed on the contrary a linear relationship between illite and montmorillonite components. For these samples, the lines joined an illite/smectite component having a constant layer charge of −0.75 with montmorillonites having an octahedral sheet charge between −0.33 and −0.66. This smectite layer charge was lowest in bentonites from Poland and highest in bentonites from Sweden. The chemical composition of illite/smectite from the Upper Jurassic of this investigation are similarly plotted in fig. 22. They fall on a line between muscovite and a montmorillonite with an octahedral sheet charge of 0.54, i.e. a high-charge montmorillonite. This line is close to the one for the samples from the United Kingdom plotted in Meunier & Velde's fig. 2C (line C in fig. 22). The illite/smectite of probably volcanic origin and for which chemical composition was determined plots away from this line and slightly to the left of the line shown in Meunier & Velde's fig. 2B (line B in fig. 22) for Silurian bentonites from Poland. The illite/smectite from 2/7–3, 3789 m, with 95% illite layers and ISII ordering, plots closer to muscovite than does the end-member of Meunier and Velde, a Rotliegende sandstone reservoir illite from the North Sea. Meunier & Velde attributed the determinations by several authors of 0% expandable layers at values below -0.87 layer charge to incorrect estimations from X-ray diffractograms. In this respect the illite/

MODELS FOR MIXED-LAYERING IN I/S
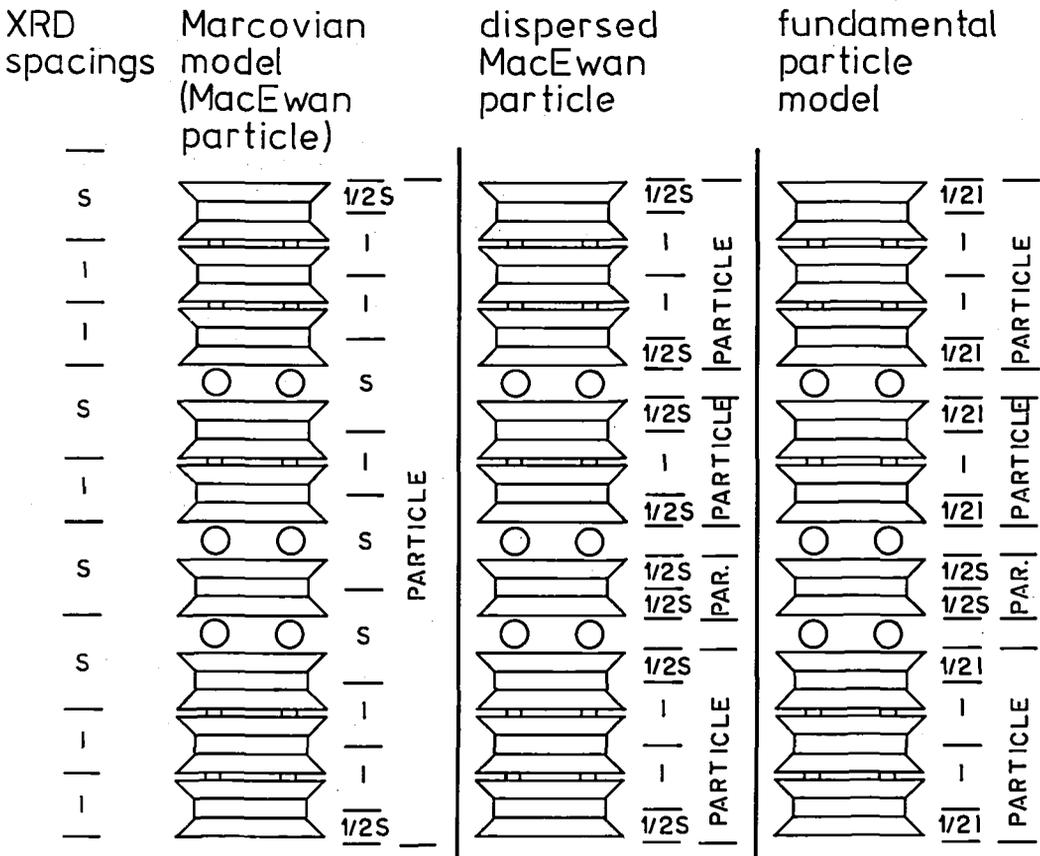
Fig. 25. Models for mixed-layering in illite/smectite and implications for composition of particle terminating layers. Model for randomly ordered illite/smectite with P_I 0.8 (or with 80% illite layers).

smectite from 2/7–3, 3789 m, with a layer charge of −0.85 and 5% illite layers, is closer to the expectations of Meunier & Velde. The discrepancies between the amount of expandable layers predicted by the plots of Meunier & Velde on the one hand and the expandabilities calculated from X-ray diffractograms on the other hand are more likely to be due to the fact that Meunier & Velde plot ideal layer compositions, whereas natural illite/smectites probably contain illite sites in smectite layers and smectite sites in illite layers.

Elemental changes in illite/smectite during diagenesis

It was concluded in the literature review that Al^{3+} substitutes for Si^{4+} and that K^+ is fixed during the diagenetic formation of illite layers. Some of the investigations also found substitution of Al^{3+} for Fe and Mg in the octahedral sheet and reduction of Fe^{3+}. In most of these investigations, however, the accuracy of the figures for tetrahedral Al^{3+} is low (because it has been calculated from tetrahedral Si, which is about five times larger) and fixed NH_4^+ has not been determined.

Środoń et al. (1986) suggested from their investigation on diagenetic illite/smectites that illitization proceeded by a transformation mechanism in their bentonites from the Silurian of Wales, from the Carboniferous of Silesia, and from the Cretaceous of Montana. This was because their calculations showed a stable octahedral charge and stability of early formed illite layers throughout the series. The samples of Środoń et al. covered almost the whole illite/smectite compositional range, from about 10% to about 100% illite layers. The Upper Jurassic mixed-layers of the present investigation cover only the interval 40–95% illite layers. Furthermore, the three mixed-layers with 40–50% illite (of which the elemental composition was determined for only one) probably originate from bentonites, whereas the others are largely of continental origin. Therefore, only the interval between 60–95% illite layers (0.60–0.95 P_I) is statistically reliable. This interval covers the randomly ordered or I-S segregated, IS and ISII ordered illite/smectite. However, the upper part of the P_I interval for randomly ordered or I-S segregated illite/smectite, 0.6–0.75 P_I, is so narrow that the trends for the randomly ordered or I-S segregated mixed-layers cannot be relied upon. The elemental composition of the mixed-layers was plotted vs. P_I (Lindgreen et al. 1991, fig. 7). All plots were fitted with one regression line, but it cannot be excluded that two or more lines would have been more appropriate, if the whole range of P_I values, also below P_I 0.6, had been represented in the material. Thus, for randomly ordered or I-S segregated illite/smectite, a line segment parallel to the P_I axis will fit in most plots (exceptions are: fixed cations vs. P_I and SiO_2 vs. P_I) if the mixed-layers of bentonitic origin shall

conform to a general trend for randomly ordered or I-S segregated illite/smectite. Such a trend, however, is not probable, since it means a constant Al(4)/Al(6) ratio and a constant Al(4)/(Al(4)+Si) ratio for randomly ordered or I-S segregated illite/smectite and thus implies a layer charge constancy over the range 0.4–0.75 P_I. Illite layer formation by aggradation, i.e. fixation of cations between high-charge layers, conforms with charge constancy in this interval. However, comparison between K^+- saturated and glycolated specimens and Mg^{2+}- saturated and glycolated specimens showed that the ratio between high charge and low charge smectite layers is constant, about 1, irrespective of P_I (fig. 23). Therefore a larger amount of high-charge layers is not present in the randomly ordered or I-S segregated illite/smectites. Accordingly the narrow interval of 0.6–0.75 P_I for randomly ordered or I-S segregated illite/smectite has been analysed statistically together with the IS and ISII ordered illite/smectite as one group. The two illite/smectites with P_I 0.4 and 0.5 fit, in the plots of Al(4)/Al(6) and Al(4)/(Al(4)+Si) vs. P_I, a line through the origin and parallel to the line for the other samples. This indicate that these two samples formed from a smectite starting material with no tetrahedral Al for Si substitution and is compatible with formation from a pure smectite formed from volcanic ash (an origin for smectite proposed by Millot (1970) and by Nadeau & Reynolds (1981b)).

Moles of fixed K^+ increase with P_I (fig. 24), whereas CEC (here as moles of adsorbed Na^+) decrease with P_I by about the same amount. Moles of fixed NH_4^+ increase with P_I from P_I 0.55 and the increase is then about twice the increase in moles of K^+ with P_I (fig. 24).

The increase in P_I during diagenesis (figs. 18 and 19) is thus correlated with an increase in K, NH_4 and Al, and a decrease in Fe, Mg and Si in illite/smectite. Lindgreen et al. (1991) from Mössbauer spectroscopy on 5 samples could not detect any trend in the ratio $Fe^{2+}/(Fe^{2+} + Fe^{3+})$ with P_I. Mössbauer spectroscopy on a larger number of samples (14) has later shown that the ratio $Fe^{2+}/(Fe^{2+} + Fe^{3+})$ increases with P_I, from a value of 0.15 at $P_I = 0.6$ to a value of 0.23 at $P_I = 0.95$, but that the correlation coefficient is low (0.63). The values for elemental composition, for the amount of tetrahedral (4) and octahedral (6)

Tab. 8. Elemental composition of illite/smectite calculated from plots in Lindgreen et al. (1991, Fig. 7).

	P_I 0.60	P_I 1.00
Na_2O	4.7%	3.7%
K_2O	3.7%	5.3%
$(NH_4)_2O$	0.17%	1.53%
MgO	3.4%	1.35%
Fe_2O_3	7.7%	3.3%
Al_2O_3	23.2%	32.2%
SiO_2	57%	54%
Al (4)/(Al (4) + Si)	0.059	0.172
Al (4)/Al (6)	0.142	0.392
$Fe^{2+}/(Fe^{2+} + Fe^{3+})$	0.149	0.244

Al, and for Fe^{2+} and Fe^{3+} have been calculated at P_I 0.60 and 1.00 from the data given by Lindgreen et al. (1991) and from the data for the $Fe^{2+}/(Fe^{2+} + Fe^{3+})$ ratio given above and are shown in table 8. The content of CaO is low (average 0.23%) and does not vary with P_I.

Full formulae were calculated from these figures for a tetrahedral lattice cation number of 4 (corresponding to $O_{10}(OH)_2$ and 2 octahedral cations). This calculation, the method of fixed cationic numbers (Grim & Güven 1978), resulted in reasonably well correspondance between the increase in net negative charge and the increase in interlayer cations (Lindgreen et al. 1991). The figures for total octahedral cations were calculated from the ideal number of octahedral cations (2) but then corrected according to nmr. This means that the accuracy relies on ^{29}Si and ^{27}Al nmr data. The figures from nmr and the content of Al_2O_3 and SiO_2 fit into the same formula for P_I 1.00. At P_I 0.60, the content of Al_2O_3 and the nmr data from ^{29}Si and ^{27}Al nmr correspond well, whereas the content of Si must be increased by 0.18 to 3.77 to fit into the Al_2O_3 and nmr data. This corresponds to an error of 5% in the SiO_2 determination which is about the analytical error for Si determinations by AAS and the assumption of this error is therefore reasonable. The resulting formulae are shown in table 9. The content of Ca is 0.02 per $O_{10}(OH)_2$.

It can be seen that if the numbers of tetrahedral cations are 4.00 (the ideal value) then the numbers of octahedral cations at P_I 0.6 are 2.18 and at P_I 1.0 1.95.

The increase from P_I 0.6 to 1.0 and the ordering thus involves an increase in tetrahedral charge of 0.45 by Al for Si substitution and a decrease in octahedral charge of 0.20 by an increased amount of octahedral Al (0.18) and a decreased amount of Fe^{3+} (0.20) and of Mg^{2+} (0.19). This results in a decreased number of octahedral cations, from 2.18 to 1.95. The content of Fe^{2+} is approximately the same at P_I 0.6 and 1.0. The net increase in charge, of 0.45–0.20 = 0.25, is accompanied by fixation of 0.19 NH_4^+ and 0.12 K^+, totalling 0.31. This slightly higher figure can be due to analytical inaccuracy, since it is calculated from so many figures. Alternatively the slightly higher figure for fixed cations, 0.31, than for net increase in charge, 0.25, can be due to the decrease in octahedral charge of 0.20 and the corresponding increase in tetrahedral charge. This migration towards the interlayer of a charge of 0.20 gives stronger coulomb forces and can therefore result in increased fixation of K^+ and NH_4^+.

Eberl (1986) carried out thermodynamic calculations for sodium/potassium exchange during smectite diagenesis occurring as a solid-state transformation. He concluded that a cation in a smectite interlayer dehydrates in response to increasing interlayer charge and that, for the same charge, the smallest ion is fixed preferentially. The cation with the smallest radius in the dehydrated state becomes the largest cation in the hydrated state. Accordingly, he concluded for the sodium-potassium exchange that potassium is greatly preferred compared to sodium when the layer charge required for potassium dehydration has been exceeded. In the present investigation, NH_4^+ also became fixed. The ionic radii for dehydrated NH_4^+, K^+ and Na^+ are 1.43 Å, 1.33 Å and 0.98 Å, respectively (Sterne et al. 1982 and

Tab. 9. Elemental composition per $O_{10}(OH)_2$ of illite/smectite, corresponding to 6 cations.

	P_I 0.60	P_I 1.00
Na	0.57	0.45
K	0.30	0.42
NH_4	0.025	0.22
	0.90	1.09
Mg	0.32	0.13
Al(6)	1.49	1.67
Fe^{2+}	0.054	0.037
Fe^{3+}	0.31	0.12
	2.18	1.95
Al(4)	0.23	0.68
Si	3.77	3.32
	4.00	4.00

Eberl 1986). The smallest cation is, according to Eberl (1986), fixed preferentially. Therefore, the cations NH_4^+, K^+ and Na^+ are fixed preferentially during increase of smectite interlayer charge as follows: At low smectite interlayer charge, all three cations are hydrated and $NH_{4\ aq.}^+$ is adsorbed with slight preference over $K_{aq.}^+$ ($_{aq.}$ denotes a hydrated ion). When the interlayer charge increases, $NH_{4\ aq.}^+$ is dehydrated first and then fixed with stronger preference over $K_{aq.}^+$ and $Na_{aq.}^+$. When the interlayer charge is slightly increased further, $K_{aq.}^+$ is also dehydrated and is then fixed slightly preferentially over NH_4^+ (the radius of dehydrated K^+ is slightly smaller compared to NH_4^+). When the interlayer charge is increased sufficiently to dehydrate $Na_{aq.}^+$, Na^+ is fixed with clear preference over K^+ and NH_4^+. The charge for Na^+ dehydration is apparently not achieved in the North Sea illite/smectites, whereas the increase in NH_4^+ fixation at about P_I 0.7 (fig. 24) may be explained by dehydration of $NH_{4\ aq.}^+$ at this P_I level. NH_4^+ fixation is not increasing significantly with P_I until this P_I level, even if it should have a slight coulomb preference. But this is due to the fact that the cations are only adsorbed when hydrated and have to be dehydrated before fixation takes place. On the other hand, NH_4^+ increases in pore waters at about the P_I level 0.7, and the increase in fixed NH_4^+ may therefore be due to increase in the NH_4^+/K^+ ratio (see above).

The mechanism for formation of illite layers from smectite layers

The most distinct, depth-dependent clay mineralogical changes in the present investigation are the formation of illite layers from smectite layers and the ordering of these in mixed-layers. According to the literature review, illite layer formation can take place through a solid-state substitution or through a neoformation. The mechanism for the solid-state transformation is a tetrahedral substitution of Al^{3+} for Si^{4+} followed by K^+ fixation and layer contraction (Eberl & Hower 1976; Eberl 1978a). Eberl & Hower (1977) proposed that IS ordering can be explained by an electrical polarization effect during the solid-state transformation: tetrahedral substitution of Al for Si and the resulting increase in

the negative charge takes place in one of the tetrahedral sheets of the 2:1 layer. Substitution in the other tetrahedral sheet in the same unit should then be less probable, and the resulting polarization effect should result in IS ordering. The activation energy for transforming two IS units to one SIII unit is then so much higher than that for IS unit formation that all smectite layers have to be present in IS units before SIII units are formed. According to this theory, ISI ordering is less likely to occur if polarization is strong enough to influence substitution in the tetrahedral sheet in the same 2:1 unit. If, however, the polarization power of illitic substituted layers is low then it may take two 2:1 illite layers to develop enough polarizing power to inhibit the formation of neighbouring illite layers (Eberl & Hower 1977), and IIS units and ISI ordering may then be the result.

The alternative mechanism, proposed by Nadeau et al. (1985), is a neoformation of illite layers. By this mechanism, smectite layers dissolve and illite layers crystallize from solution and grow in thickness. This mechanism is linked to the interparticle diffraction model of Nadeau et al. (1984) (see literature review) which considers the illite/smectite XRD patterns to be due to inter- and intra- particle diffraction in a specimen with such thin illite particles, perhaps also with some elementary smectite layers. Ordering is according to the interparticle diffraction model due to a mixture of thin illite particles with one, dominating particle thickness.

HRTEM investigations on intact bulk rock did not detect the thin illite particles of the neoformation theory of Nadeau et al. The thick particles with 10 Å periods in contrast may, as discussed above, be MacEwan illite/particles and their smectite layers may be undergoing a solid-state transformation to illite layers, but they may also be illite particles. It was seen by HRTEM that each particle in intact bulk rock had its specific degree of ordering. This can be explained by the polarization effect operating in a solid-state transformation. The particles seen in HRTEM on intact rock are not aggregates, as dislocations are largely absent. The crystallization and growth of illite particles according to the neoformation theory cannot explain an occurrence of ordered MacEwan particles. Even if the particles with 20 Å (or with 30 Å) period in contrast were interpreted

as a stacking of thin illite particles, a crystallization and growth of thin illite particles can not be expected to form exactly equally thin illite particles within an aggregate. The observations by HRTEM on intact bulk rock therefore support the solid-state mechanism and are not compatible with the neoformation model of Nadeau et al. (1985).

XRD on specimens prepared from dispersed illite/smectite showed that randomly ordered or I-S segregated illite/smectite dominates the samples with P_I less than 0.8, and that IS ordered illite/smectite dominates the samples with P_I in the interval 0.8–0.9, whereas ISII ordering was found to dominate the single sample with P_I of 0.95. Although ISI ordered illite/smectite was detected by HRTEM on intact rock and was indicated by XRD by CuKα radiation, it is not present in large amounts. This dominance of IS ordering in dispersed illite/smectite can be explained by the polarization effect in the solid-state transformation but could, according to the interparticle diffraction theory, also arise from a mixture of predominantly 20 Å thick illite particles formed by neoformation. HRTEM on specimens prepared from dispersed illite/smectite showed predominantly thin particles, which may be illite or elementary layers of smectite, and thus could be the result of a neoformation of illite. They may, however, equally well have formed from dispersion of MacEwan particles in intact bulk rock and this is probably the case, as thin particles were not observed in intact bulk rock by HRTEM. Specimens prepared for HRTEM from IS ordered illite/smectite also contained particles, which have 20 Å periods in contrast and which, from the absence of Fresnel fringes in defocused images and from the absence of dislocations are true particles and not aggregates of thin particles. These true particles must then be IS ordered illite/smectite MacEwan particles according to the paragraph on Layer Structures in Intact Bulk Rock and in Dispersed Illite/ smectite. The occurrence of these particles is incompatible with the neoformation theory but fully compatible with a solid-state transformation.

The elemental composition per $O_{10}(OH)_2$ of an end-member illite in the mixed-layer illite/smectite series (table 9) shows that this end member has 0.64 fixed cations, 0.29 octahedral Fe plus Mg, and 0.68 tetrahedral Al. The total octahedral charge is −0.17 and the tetrahedral charge is −0.68, summing to a charge of −0.85. This is low compared to an ideal mica charge of −1.0, and the number of fixed cations, 0.64, is also low compared to a mica. Extrapolation of the plots of %MgO vs. P_I and of %Fe_2O_3 vs. P_I resulted in intercepts with the horizontal axis at P_I 1.3 in both plots (Lindgreen et al. 1991). This corresponds then to zero octahedral charge. Extrapolation to P_I 1.3 from the data in table 9 results in 0.88 fixed cations (NH_4^+ plus K^+) and 0.98 Al(4), i.e. 0.98 tetrahedral charge. This is close to an ideal mica after the AlPEA classification (table 1). The finding of an ideal mica composition at P_I 1.3 (Lindgreen et al. 1991) indicates that the illite layers contain about (1.3–1.0)/1.3 (i.e. 25%) smectitic sites, which means sites of smectitic chemical composition. The end-member illite/ smectite must therefore contain smectitic sites, either in the illite layers or as terminal layers in each particle. If the smectitic sites are due to smectitic terminal layers in particles then the 25% smectitic sites correspond to particles about 4 layers thick, and this agrees well with the data in table 7 for samples with high P_I values. Środoń et al. (1986) calculated that the necessary charge for layer contraction was −0.55 for randomly ordered or I-S segregated illite/smectite and −1.0 for IS ordered illite/smectite. 20% of the layers in our illite/smectite have thus needed −1.0 and 15% of the layers a charge of −0.55, giving a mean of −0.80 to increase P_I from 0.65 to P_I 1.00 or overall a change of −0.32 from P_I 0.60 to 1.00. This compares well with the −0.45-(-0.20)= −0.25 as calculated from table 9. Thus, the data in table 9 agree fairly well with the figures calculated by Środoń et al. (1986) for a solid-state transformation. Contraction at a layer charge of −0.55 means that smectitic sites must be present in the layers seen in XRD as illite. Eberl (1978a) calculated that illite formed from smectite by a solid state tetrahedral Al for Si substitution and K- fixation will have a layer charge of −0.77. The charge of −0.85 of the illite layers in the present illite/smectites (see above) is compatible with the −0.77 of Eberl and with the contraction at layer charges of −0.55 (random ordering or I-S segregation) and −1.0 (IS ordering) after Środoń et al. (1986).

Formation of illite layers from smectite layers

by a solid-state Al for Si transformation as pro-
posed by Eberl & Hower (1976) and Eberl
(1978a) means that mixed layer illite/smectite will
have tetrahedral sheets with different degrees of
Al for Si substitution, i.e. the Markovian particle
model of fig. 25. This agrees well with the tetra-
hedral substitutions calculated above for illite
layers and the values of Środoń et al. (1986)
required for layer contraction, which can give the
values in the present illite/smectites. On the con-
trary, formation of illite layers from smectite lay-
ers by neoformation (from solution) as proposed
by Nadeau et al. (1985) means that the illite
layers all have the same, illitic degree of tetra-
hedral substitution (fig. 25), as inferred by Al-
taner et al. (1988). According to the neoforma-
tion model, separate smectite layers may be pre-
sent together with the neoformed illite particles
but only in very small amounts at high P_I values,
and the implications for 25% smectitic sites in the
illite are incompatible with an occurrence of only
illite particles. The composition of the 2:1 layer
of the Jurassic illite/smectites of the present in-
vestigation therefore agrees well with what would
result from a solid-state transformation but not
with an ideal, illitic composition expected in thin
illite particles.

Inoue, Watanabe, Kohyama & Brusewitz
(1990) tentatively concluded that, in the bento-
nites from Kinnekulle, Sweden, illitization was a
solid-state transformation and proposed that this
mechanism should take place in rocks with low
porosity and permeability, such as bentonites and
shales. According to Inoue et al. (1990), a low
supply of the elements for illite layer formation
should favour a transformation mechanism in low
permeable rocks. In the present investigation,
the increase in the amount of illite layers, from c.
60% to c. 85%, requires only one half of the
aluminum and potassium required for the in-
crease in illite layers, from c. 25% to 80%, in the
US Gulf Coast illite/smectite (Perry & Hower
1970 and Hower et al. 1976). Furthermore, the
significant amount of ammonium available at the
depth of ordering means that smaller amounts of
potassium are necessary for illite layer formation.
The more limited amounts of aluminum and po-
tassium for illite layer formation in the North Sea
than in the US Gulf Coast illite/smectite makes a
solid-state illite layer transformation more likely
in the North Sea, because only few (if any) smec-

tite layers have to dissolve to provide aluminum
(the model of Roberson & Lahann 1981).

In summary, the illite/smectite structures seen
by HRTEM in intact bulk rock and in dispersed
illite/smectite are only compatible with the solid-
state transformation but cannot have formed by a
neoformation of thin illite particles. The charge
of the contracted 2:1 layers is far from ideal mica
and indicates that layer contraction at a charge of
-0.77 has taken place and not a crystallization of
mica layers with about -1.0 charge.

Thus the conclusion is that the formation of
illite layers from smectite layers in the Upper
Jurassic illite/smectites is a solid state transforma-
tion.

during atomic absorption spectrophotometry at the Chemistry Department, Royal Veterinary and Agricultural University.

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Dansk sammendrag

Der indledes med en kort gennemgang af lermineralernes opbygning med specielt henblik på veksellagsmineralernes struktur. Lermineralerne er opbyggede af tetraeder- og oktaederplader (eng.: sheets): i to-plademineralerne (kaolinit-serpentin gruppen) af en oktaederplade og en tetraederplade (1:1 lag), i tre-plademineralerne (pyrophyllit-talk, smektit, vermikulit, glimmer, sprødglimmer, og chlorit) af to tetraederplader og en oktaederplade (2:1 lag). I henhold til klassifikationen vedtaget af IMA (International Mineralogical Association) bestemmes grupperingen indenfor 2:1 phyllosilikaterne af ladningen pr. 2:1 enhed, dog adskiller chlorit sig ved at have en oktaederplade mellem 2:1 lagene. Opdelingen og klassifikationen af lermineralerne er af IMA vedtaget at følge klassifikationen for phyllosilikater, derfor er kvældningsegenskaber ikke medtaget i IMA klassifikationen. Flere af de mineraler, der tidligere er betegnet som illit, indeholder lagenheder af andre mineraler, oftest smektit, og er derfor veksellagsmineraler. Illit er derfor ikke anvendt som mineralnavn i IMA klassifikationen. Illit vil i nærværende arbejde blive brugt som betegnelse for et mineral i glimmergruppen, som har en fast d(001) på 10 Å. Den af IMA vedtagne klassifikation af phyllosilikater (og lermineraler) er vist i tabel 1 og opbygningen af et tre plademineral i fig. 2. Veksellagsmineraler indeholder lag af forskellige mineraler. To modeller for veksellagsmineralernes opbygning har været fremsat: 1) Markov modellen, ifølge hvilken veksellagsmineral partiklerne er relativt tykke og indeholder lag af alle de mineraler, der indgår i veksellagsmineralet (MacEwan partikler); og 2) fundamental-partikel modellen, ifølge hvilken veksellagsmineral partiklerne er tynde, ned til enkelte lag, og hver partikel kun indeholder lag af det ene af mineralerne i veksellagsmineralet. De to modeller er skitseret i fig. 2.

Der gives herefter et kort sammendrag af litteraturen om den diagenetiske omdannelse af smektitlag til illitlag i veksellagsmineralet af illit og smektit (illit/smektit).

Markov modellen var til at begynde med (i slutningen af 1960'erne og i 1970'erne) den almindeligt anerkendte model og blev grundlaget for de computer simuleringer af diagrammer fra røntgendiffraktion (XRD), som bl.a. Reynolds & Hower (1970) viste. Sådanne computer simulerede diagrammer blev anvendt i undersøgelser af veksellagsmineralernes diagenetiske ændringer. Disse undersøgelser viste, at smektitlag i illit/smektit omdannes til illitlag ved temperaturer over 55°C, samt at illit- og smektitlagene i illit/smektit var tilfældigt ordnede op til et illitindhold på 60–70% og derover IS ordnede (d.v.s. ordnede i enheder på 1 illitlag + 1 smektitlag), ISI (d.v.s. enheder på 1 smektitlag + 2 illitlag) ordnede, eller ISII (d.v.s enheder på 1 smektitlag + 3 illitlag) ordnede (Perry & Hower 1970; Reynolds & Hower 1970), se fig. 3. Ordningen af illit/smektit sker ved temperaturer på ca. 100°C. Udover temperaturen synes ladning og kemisk sammensætning af smektitlagene samt mængden af kalium i porevæsken at være bestemmende for processen. Undersøgelser fra områder med højere temperaturgradienter, ved metamorfose og hydrotermale betingelser, har også vist en omdannelse af smektitlag til illitlag med stigende temperatur. I hydrotermale eksperimenter er omdannelsen foregået ved 250°C og derover. Undersøgelse af bjergarter, der har undergået kortvarige, kraftige opvarmninger, har vist, at omdannelsen af smektitlag til illitlag er meget langsom sammenlignet med forøgelsen af vitrinits reflektionsevne.

Kalium indholdet stiger med indholdet af illit i illit/smektit (Perry & Hower 1970; Hower et al. 1976). Endvidere fandt

flere undersøgelser (Weaver & Beck 1971; Hower et al. 1976; Foscolos et al. 1976) at dannelsen af illitlag ledsages af en forøgelse af mængden af aluminium i illit/smektit og et fald af indholdet af jern, magnesium, og silicium, se fig. 6. Hower et al. (1976) konkluderede, at dannelsen af illitlag fra smektitlag er en fast-fase transformation, en tetraedrisk substitution af aluminium for silicium og en påfølgende fiksering af kalium i mellemlaget mellem 2:1 lagene. Denne hypotese blev støttet af hydrotermale eksperimenter (Eberl & Hower 1976 og 1977). Dannelsen af illitlag i hydrotermale experimenter og i hydrotermale områder adskiller sig fra den diagenetiske omdannelse ved at der skabes højere negative ladninger i 2:1 lagene. Under hydrotermale betingelser kan natrium og calcium udover kalium dehydratiseres og fikseres, i modsætning til de diagenetiske omdannelser, hvor kun kalium dehydratiseres og fikseres.

Imidlertid udførte Nadeau, Wilson, McHardy & Tait kombinerede undersøgelser med XRD og transmissions elektron mikroskopi (TEM) af skyggede præparater af disaggregeret illit/smektit fra sandsten og bentoniter (Nadeau et al. 1984, 1985). De opstillede herudfra fundamental partikel teorien, se ovenfor. Endvidere argumenterede de for, ud fra partikeltykkelses fordelinger af illit/smektit med forskelligt indhold af illitlag, at med stigende grad af diagenese opløses smektitlagene, og illitlagene dannes ud fra de opløste ioner og vokser i størrelse (Nadeau et al. 1985). Undersøgelser med højopløsende transmissions elektronmikroskopi (HRTEM) udført af Ahn & Peacor (1986a) på intakte bjergarter fra de prøver, Perry & Hower (1970) og Hower et al. (1976) havde undersøgt med XRD, kunne ikke påvise tynde, fundamentale partikler i de intakte bjergarter, men kun tykke "pakker". Disse pakker var enten regelmæssige og blev af Ahn og Peacor ud fra morfologi og EDAX analyse vurderet til at være illit, eller de var bølgende og blev af Ahn og Peacor vurderet til at være smektit. Ahn og Peacor mente ud fra forløbet af lagenes kontraststriber i HRTEM, at smektitpartiklerne opløstes og illitpartiklerne voksede langs partikelkontakter mellem illit og smektitpartiklerne. Ahn og Peacor har dog senere (Ahn & Peacor 1989) reevalueret deres resultater og anerkendt eksistensen af illit/smektit partikler i deres materiale. Mængden af tilgængeligt kalium er den begrænsende faktor i dannelsen af illitlag fra smektitlag. Dog kan andre kationer, såsom af magnesium, calcium, og natrium, i systemer med tilstrækkeligt tilgængeligt kalium forhindre kaliumfikseringen og dermed dannelsen af illitlag.

Frigivelsen af vand fra omdannelsen af smektit til illit og betydningen af dette vand for migrationen af kulbrinter fra kildebjergarter har været genstand for flere undersøgelser. Der synes at være et sammenfald mellem omdannelsen af smektitlag til illitlag og dannelsen af olie og gas. Men betydningen af det frigjorte vand for olie-gas migrationen er ikke afklaret.

Geologien af Det danske Centraltrug og af Det norsk danske Bassin gennemgås kort. Tykke lerlag blev i Øvre Jura aflejret i Det norsk-danske Bassin og især i Centraltruget, hvor de er rige på organisk stof (algemateriale). Indsynkning i Kridt og især i Tertiær resulterede i oliedannelse i lerlagene i Centraltruget. De Øvre Jurassiske lersten har nok overvejende Det fennoskandiske Skjold som kildeområde. Derudover er der sandsynligvis sket en sedimentation af vulkansk materiale indbefattende aske i Nordsøregionen i Øvre Jura.

Lerbjergarter fra Mandal, Farsund, og Haugesund formationerne i Centraltruget og fra Sauda, Tau, Børglum og Bream formationerne i Det norsk-danske Bassin er blevet undersøgt. Det undersøgte materiale er fra dansk landområde kerner, suppleret med cuttingsmateriale, og fra Nordsøen cuttingsmateriale, suppleret med to kerner fra boringerne 2/11–1 og E1. Fra cuttings er fra hver prøve udsorteret den grå-mørkegrå Øvre Jurassiske lersten.

På prøver af intakte bjergarter (tyndslib, indstøbt i epoxy og ionætset) er anvendt højopløsende transmissions elektronmikroskopi (HRTEM). På forbehandlede og fraktionerede prøver

er anvendt røntgendiffraktion (XRD), og på isoleret illit/smektit er anvendt XRD, HRTEM, transmissions elektronmikroskopi af skyggede præparater (TEM), faststof ^{27}Al og ^{29}Si kernemagnetisk resonans spektroskopi (MAS-NMR), Mössbauer spektroskopi, og infrarød spektroskopi, samt bestemmelse af K, Na, Mg, Ca, Al, Fe, Si, og NH_4^+. K, Na, Mg, Ca, Al, Fe, og Si bestemtes ved atomabsorptions spektrofotometri efter HF oplukning i teflonbomber og efterfølgende kompleksdannelse med H_3BO_3. NH_4^+ bestemtes i illit/smektit, efter opvarmning af ca. 1 mg prøve ved 600° og oxidation af nitrogen til N_2, ved emissionsspektroskopi og beregning ud fra en isotopfortyndingsmetode. Tolkningen af resultaterne fra XRD og HRTEM blev støttet af computer modelleringer, for XRD med NEWMOD programmet udviklet af R.C.Reynolds for tokomponent veksellagsmineraler og med et program udviklet af P.D.Cradwick for trekomponent veksellagsmineraler. Med XRD blev illitindholdet i og ordningen af illit/smektit vurderet ud fra sammenligninger mellem simulerede og kørte diffraktogrammer. Eksempler på simulerede og kørte diffraktogrammer er vist i fig. 11a og b. I visse illit/smektit prøver synes der udover illit og smektit at være en tredje komponent, vermikulit.

Lermineralogien i grovlersfraktionerne (2–0.2 µm) støtter ideen om, at leret i Centraltruget og Det norsk danske Bassin i overvejende grad stammer fra forvitring og jordbundsdannelse på Det fennoskandiske Skjold, og at der under denne forvitring er dannet tilfældigt ordnet eller illit-smektit segregeret illit/smektit med ca. 70% illitlag. (Illit-smektit segregering vil sige, at illitlag har en tendens til at følge illitlag og smektitlag en tendens til at følge smektitlag.) Dog er der i to boringer i Centraltruget, W1 og 2/7–3, fundet lerlag af sandsynlig vulkansk oprindelse. Den detritale, tilfældigt ordnede eller illit-smektit segregerede illit/smektit med ca. 70% illitlag er under diagenesen i Centraltruget omdannet til IS ordnet illit/smektit med 80–90% illitlag og til ISII ordnet illit/smektit med ca. 95% illitlag. Den formodet bentonitiske illit/smektit er blevet omdannet til tilfældigt ordnet eller illit-smektit segregeret illit/smektit med 40–50% illitlag. I Det norsk-danske Bassin er temperaturerne under indsynkningen ikke nået så højt op, at den detritale, tilfældigt ordnede eller illit-smektit segregerede illit/smektit er blevet ændret. I K^+-mættede og glycolerede prøver er ca. halvdelen af smektitlagene (bestemt ud fra Mg^{2+}-mættede og glycolerede eller lufttørre prøver) kontraherede til ca. 10Å, se fig. 23. Dette forhold gælder for alle prøver og kan forklares med, at ca. halvdelen af smektitlagene har en høj ladning som gør, at de i K^+- mættet tilstand forbliver sammenklappede. XRD af præparater med partiklerne i tilfældig orientering viser, at d(060) er tilnærmelsesvis konstant (1.495–1.501Å) for varierende illitindhold i illit/smektit, mens halvliniebredden falder med stigende indhold af illit; altså har de dannede illitlag tilnærmelsesvis samme d(060) som smektitlagene. At d(060) ikke ændres under den tetraedriske ombytning af Si med Al (se nedenfor) kan forklares ud fra en øget grad af rotation af tetraedrene i illitlagene.

Undersøgelsen af intakte bjergartsprøver med HRTEM viser, at partikler med 10 Å, 20 Å, og 30 Å periode i billedkontrast findes i alle prøver, i enkelte prøver tillige partikler med forskellige perioder (op til 40 Å) i samme partikel, se fig. 15. Computer simuleringer viser, at ordnede lag af illit plus Na-smektit (IS ordning) kan give 20 Å perioder. 2M glimmer kunne også give 20 Å perioder under specielle instrumentbetingelser, men kan ikke detekteres med XRD i prøverne. Det konkluderes derfor at der i de intakte bjergarter findes veksellags illit/smektit partikler (MacEwan partikler). HRTEM på dispergeret illit/smektit fra de samme prøver viser, at partiklerne i dispergerede prøver gennemgående er tyndere end i de intakte bjergarter. Dette indicerer, at partiklerne ved dispergeringen er gået i stykker. Partikeltykkelses fordelinger beregnet ud fra TEM på skyggede præparater af dispergeret illit/smektit (se fig. 17) viser, at tilfældigt ordnet og illit-smektit segregeret illit/smektit består overvejende af 10 Å og 20 Å

tykke partikler, mens ordnet illit/smektit med større mængde illitlag er kendetegnet ved en bredere fordeling af 10 Å–60 Å tykke partikler. Dog findes der i henhold til HRTEM stadig partikler med 20 Å perioder, MacEwan partikler, i de dispergerede illit/smektit prøver, som derfor ikke, som antaget af Nadeau et al. (1984, 1985), består alene af "fundamentale" illitpartikler og enkeltlags smektitpartikler, se fig. 16.

Si/Al forholdet i illit/smektit fraktionerne bestemt med ^{27}Al og ^{29}Si MAS-NMR på den ene side og med totalkemisk analyse på den anden side viser god overensstemmelse. Derimod er bestemmelserne af tetraedrisk og oktaedrisk Al ved ^{27}Al og ^{29}Si MAS-NMR betydeligt nøjagtigere end beregningen ud fra totalkemisk analyse. Mens der i det ene af de foreliggende arbejder (Lindgreen et al. 1991) ikke med Mössbauer spektroskopi kunne konstateres en sammenhæng mellem Fe^{3+}/Fe^{2+} forholdet i illit/smektit og mængden af illitlag, synes dette forhold, efter analyse af et større antal prøver, at falde ved omdannelsen af smektitlag til illitlag. Den betydelige linieforbredning af Fe^{3+} linierne for illit/smektit i Mössbauer spektrene gør det ikke muligt at drage mere detaljerede slutninger om de diagenetiske omdannelser i oktaederpladen. Derimod giver ^{27}Al og ^{29}Si MAS-NMR nøjagtige data for fordelingen af Si og Al i oktaeder- og tetraederpladen. Under omdannelsen af den detritale, tilfældige tilfældigt ordnede eller illit-smektit segregerede illit/smektit med 70% illitlag til ordnet illit/smektit med 80–95% illitlag er hovedprocessen en ombytning af Si med Al i tetraederpladerne og en dehydratisering og fiksering i mellemlaget af K^+ og NH_4^+. Det skal her bemærkes, at NH_4^+ ikke tidligere er blevet bestemt i kemiske undersøgelser af veksellagsmineraler. Forholdet NH_4^+/K^+ i illit/smektit begynder at stige ved den dybde, hvor dannelsen af illitlag i illit/smektit begynder. I samme dybde stiger forholdet mellem de to ioner adsorberet på leret og i porevæsken, se fig. 21. Udover hovedprocessen sker en mindre ombytning af Fe og Mg i oktaederpladen med Al. For en stigning i illitindholdet i illit/smektit fra 60% til 100% kan ombytningerne pr. $O_{10}(OH)_2$ beregnes at medføre en stigning i tetraederpladens negative ladning på 0.45, et fald i oktaederpladens negative ladning på 0.20, og en stigning i mængden af fikseret K^+ på 0.12 og af fikseret NH_4^+ på 0.19. En illit/smektit med 100% illitlag indeholder dog stadig væsentlige mængder Fe og Mg i oktaederpladen og ladningen er −0.85 pr. $O_{10}(OH)_2$. Ekstrapoleres plottene for kemisk sammensætning versus mængden af illitlag i illit/smektit, fås, ved et illitindhold på 130%, et mineral med kun Al i oktaederpladen og med en negativ ladning på 0.98 stammende alene fra ombytning af Si med Al i tetraederpladen, altså en glimmer i henhold til IMA klassifikationen (tabel 1). Dette tyder på, at illitlagene indeholder ca. 25% smektit positioner, d.v.s. positioner med smektits kemiske sammensætning. Dette, og den regelmæssige ordning i 20 Å (og i ringe grad 30 Å) periode i kontrast (svarende til henholdsvis en IS ordning (20 Å) og en ISI ordning (30 Å)) i illit/smektit partiklerne i den intakte bjergart, samt den konstante b-dimension bestemt ud fra (060) i XRD, tyder på, at dannelsen af illitlag ud fra smektitlag i illit/smektit i de undersøgte prøver er en fastfaseomdannelse, en transformation.

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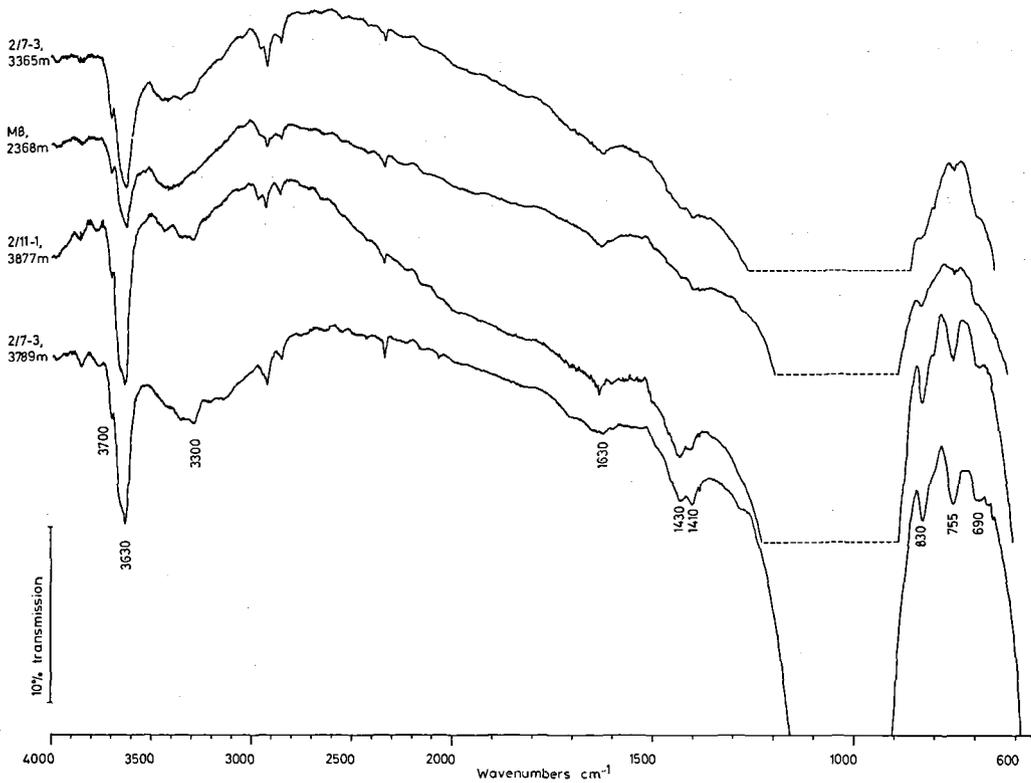
Fig. A1. Transmission FT-IR spectra of illite/smectite fractions. The section 4000 cm⁻¹ to 600 cm⁻¹. 3 mg sample per 300 mg KBr.

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Appendix

Infrared spectroscopy

Infrared spectroscopy was made on a Bruker 113V FT IR spectrometer at Chemical Laboratory V, H.C.Ørsted Institute, University of Copenhagen, by Daniel Christensen. KBr pellets heated overnight at 150°C for dewatering were analysed.

IR spectra are shown in figs. A1-A3. The peaks at 1630 cm⁻¹ and at about 3400 cm⁻¹ are due to water left after heating at 150°C. One, sharp band at 3700–3705 cm⁻¹ is due to a small content of kaolinite (fig. A1). In illite/smectite, the strong hydroxyl band at 3630 cm⁻¹, the Al-Mg-OH deformation band at 830 cm⁻¹ and the Al-O-Si in plane vibration at 755 cm⁻¹ are almost certainly diagnostic for illite (Russell 1988). A weaker band at 3650 cm⁻¹ may be due to beidellite. However, beidellite bands at 818 cm⁻¹ and 770 cm⁻¹ (Russell 1988) are not seen in any sample. The band at 910–930 cm⁻¹ (fig. A2) is due to Al-
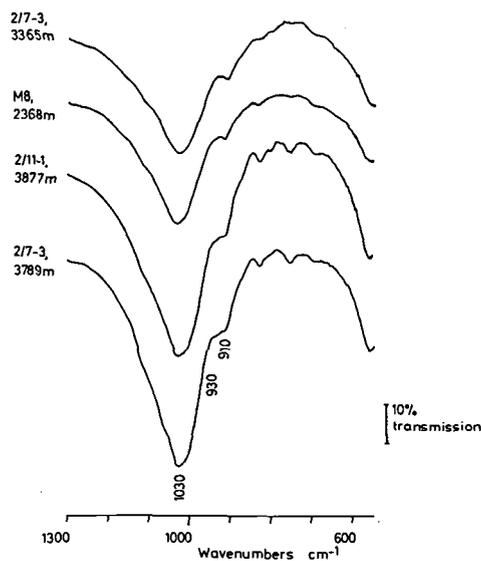
Fig. A2. Transmission FT-IR spectra of *illite/smectite fractions.*
The section 1300 cm^{-1} to 600 cm^{-1} with smaller amounts of
sample in pellets (0.3 mg/300 mg KBr).

Fig. A3. Transmission FT-IR spectra of illite/smectite fractions.
The section 700 cm^{-1} to 200 cm^{-1} with 3 mg sample per 300 mg
KBr.

Al-OH deformation. *It broadens to 910–930 cm^{-1}*
with increasing amount of illite layers in illite/
smectite. This is probably due to an increasing
amount of layers with a lower amount of octa-
hedral Mg and Fe, as muscovites show a shift of
this absorption band from 930 cm^{-1} to 908 cm^{-1}
with increasing amount of Fe and Mg in the octa-
hedral sheet (Sayin & Reichenbach 1978). The
strong band at 1030 cm^{-1} is due to Si-O stretching
(Farmer & Russell 1964). It is not split into two
bands as in rectorite (Farmer 1974). The bands at
1410 cm^{-1}, 1430 cm^{-1} and 3360 cm^{-1} are due to
interlayer NH$_4^+$ (Vedder 1965; Chourabi & Fri-
piat 1981; Sterne et al. 1982).

The strong absorption bands in the region be-
low 550 cm^{-1} have been assigned to in-plane vi-
bration of the octahedral ions and their adjacent
oxygen planes and to Si-O bending, and sub-
stitution of Al^{3+} for Si^{4+} does not greatly shift the

main absorption bands in this region (Farmer &
Russell 1964). Farmer & Russell concluded that
the pattern in this region is largely determined by
the nature and the distribution of the octahedral
cations. The absorption patterns for the investi-
gated illite/smectites appear similar to each other
in this region (fig. A3) with absorption bands at
570 cm^{-1} (weak), 534 cm^{-1}, 475 cm^{-1}, 428 cm^{-1},
and 358 cm^{-1}(weak). This indicates that the octa-
hedral sheet is little changed during diagenetic
illite layer formation in illite/smectite, in contrast
to the indications of the 910–930 cm^{-1} peak. With
increasing amount of illite layers in illite/smec-
tite, the main change of the infrared spectra (fig.
A1) is an increase in intensity of the illite bands at
3630 cm^{-1}, 830 cm^{-1} and 755 cm^{-1}. The ammo-
nium bands also increase in intensity with in-
creasing amount of illite layers in illite/smectite.