Palaeoclimatic implications of high-resolution clay mineral assemblages preceding and across the onset of the Palaeocene–Eocene Thermal Maximum, North Sea Basin

SIMON J. KEMP1,* , MICHAEL A. ELLIS1, IAN MOUNTENEY1 AND SEV KENDER1,2

1 British Geological Survey, Environmental Science Centre, Nicker Hill, Keyworth, Nottingham NG12 5GG, UK
2 Centre for Environmental Geochemistry, School of Geography, University of Nottingham, University Park, Nottingham NG7 2RD, UK

ABSTRACT: Understanding the composition of clay-rich sediments and their transportation into proximal marine basins allows us to better decipher hydroclimatic changes before and within the Palaeocene–Eocene Thermal Maximum (PETM). Only a limited number of such studies exists from the North Sea Basin, which was proximal to the volcanic activity and early rifting hypothesized to have triggered the PETM. The present study examines core material from well 22/10a-4, UK North Sea, as it exhibits an exceptionally expanded and almost stratigraphically complete fine-grained sedimentary sequence suitable for high-resolution analysis.

Quantitative Newmod-for-WindowSTM-modelled clay mineral assemblages, rather than traditional semi-quantitative estimates, are dominated by smectite-rich, interlayered illite-smectite that probably developed from volcanogenic deposits on continental landmasses. Soil development before the PETM is consistent with the existence of a seasonal tropical climate with a prolonged dry season. A striking rise and fall of kaolinite content within the PETM onset, prior to the principal carbon-isotope excursion, is reported here. This variation is interpreted as a signal of an enhanced hydrologic cycle producing an increase in erosionally derived kaolinite, followed by a dampening of this detrital source as sea-levels rose. Global variations in PETM kaolinite concentrations are consistent with a latitudinal shift in patterns of precipitation in models of global warming.

KEYWORDS: Palaeocene–Eocene Thermal Maximum (PETM), clay minerals, kaolinite, erosion, North Sea, 22/10a-4.

The Palaeocene–Eocene Thermal Maximum (PETM), at ∼56 Ma, represents arguably the most rapid and significant global warming event in the Cenozoic era. The warming is associated with a carbon isotope excursion (δ13C, CIE) of at least 5‰ consistent with a massive, 2000–12,000 Gt, exogenic pulse of isotopically light carbon to the atmosphere-ocean system and over a time-scale on the order of 100 ky (Röhl et al., 2007; Murphy et al., 2010). The rates of carbon release during the CIE are comparable to the 9 Gt/y produced by current anthropogenic sources (CO2.Earth, 2016). Consequently the PETM has undergone intensive study as an analogue, or at least a lesson in Earth system behaviour, for anthropogenic climate change. The PETM carbon release was sufficient to raise surface and deep ocean water temperatures by ∼5°C (Zachos et al., 2003; Tripati & Elderfield, 2005), with eustatic sea-level estimated to have risen by 3–5 m,
probably as a result of thermal expansion of seawater (Sluijs et al., 2008).

Extensive evidence of an intensified hydrological cycle during the PETM is provided by highly seasonal rainfall, enhanced river discharge and terrestrial input into the oceans (Bowen et al., 2004; Kelly et al., 2005; Pagani et al., 2006; Schmitz & Pujalte, 2007; Sluijs et al., 2007; McInerney & Wing, 2011). In particular, worldwide oceanic records show increased proportions of the clay mineral, kaolinite (Gibson et al., 1993, 2000; Clechenko et al., 2007). Kaolinite develops from the intense weathering of aluminosilicate minerals and generally provides an indication of a warm, humid climate (Chamley, 1989; White & Brantley, 1995; Thiry, 2000). However, as kaolinite may have taken 1–2 My to form during the peak warmth and CO$_2$-rich atmospheric conditions of the Cretaceous (Thiry, 2000), some authors have questioned whether its appearance during the PETM signifies concomitant warming and precipitation (e.g. Gawenda et al., 1999), but instead points to seasonal erosion of pre-existing deposits during the PETM (e.g. Thiry, 2000; Berggren et al., 2012; John et al., 2012). Although these phenomena have been described widely, geographic variability is still poorly understood, even for the circum-North Atlantic region from where several datasets exist (e.g. Schmitz & Pujalte, 2003; John et al., 2008, 2012; Dypvik et al., 2011; Kender et al., 2012).

A significant and outstanding question is the relative timing of the major carbon release and an intensified hydrological cycle. This is an important issue because it speaks to the cause of carbon release and to the existence of possible early warning signals of global environmental instability. The rate of sedimentation represented in most PETM cores is insufficient to resolve this relative timing at the time scale on the order of $10^3$ y, and so it has been assumed that the release of carbon triggered global warming and the subsequent change in hydrology. Increasing evidence, however, suggests that the onset of environmental change, including an intensified hydrological cycle, occurred prior to the CIE by several thousand years (Sluijs et al., 2007; John et al., 2012; Kender et al., 2012).

Here, the nature of the clay mineralogy across the PETM transition from a cored interval in the central North Sea Basin is reported (22/10a-4; Fig. 1), in particular to examine any hydrologically associated variations during the onset of the PETM. Knox (1996) previously presented low-resolution clay mineral data from 22/10a-4 and his detected increase in kaolinite was later shown to coincide approximately with the onset of the CIE (Kender et al., 2012). Kender et al. (2012) also used palynological, geochemical and sedimentological proxies to reveal enhanced halocline stratification and terrigenous deposition well before ($10^3$ y), at the onset of, and within the earliest CIE. The present study takes advantage of high-resolution sampling of the same core as investigated by Knox (1996) and Kender et al. (2012), and improvements to clay mineral quantification, to reconstruct a higher-fidelity record that uncovers the details of its lead/lag relationship with carbon release.

**GEOLOGICAL SETTING**

The North Sea Basin first developed as an extensional basin through rifting along the axes of the Central, Viking and Witch Ground grabens during the Late Permian/Triassic (Glennie, 1986) (Fig. 1). Further rifting and block faulting occurred during the Late Jurassic and Early Cretaceous with subsidence continuing to the present day. Cretaceous and Tertiary sediments represent the majority of the sedimentary fill. The basin is bounded by the major landmasses of Scotland, the Fenno-Scandian shield and, until the Eocene, Greenland. A marine connection existed periodically to the south but has generally been continually open to the north, to the Boreal Ocean. A restricted, marine depositional environment, characterized by siliciclastic sedimentation and high terrigenous input, has therefore prevailed with the exception of delta progradation in the Middle Jurassic and locally during the Late Jurassic and Palaeocene (Pearson, 1990; Knox, 1998).

The provenance of the sediment, including clay minerals, supplied to the North Sea Basin has varied over time as tectonics have exposed different land areas and drainage patterns have changed. Initially, the granitic and metamorphic terrains of Scandinavia and northern Scotland together with the Devonian sedimentary rocks of the East Shetland Platform are likely to have made substantial contributions (Pearson, 1990). Northward supply is more uncertain and variable with Devonian and Carboniferous sources through much of the Jurassic and Cretaceous (Ziegler, 1982) and erosion of basic Forties volcanics in the Middle Jurassic. However, during the early Tertiary, airfall volcanic ash probably covered land areas to a large extent and is likely to have dominated erosion products (Pearson, 1990). Sediment movement southwards into the northern North Sea Basin from Greenland was probably impeded by the Faeroe–Shetland Trough which may have existed since the Carboniferous (Haszeldine & Russell, 1987), though fine detritus may have been unobstructed.
Well 22/10a-4 is situated in the central part of the
North Sea Basin (Fig. 1), distant from land masses and
marginal-marine processes (e.g. river, wave, current or
tidal effects) that could disguise oceanographic indica-
tors (Kender et al., 2012). Palaeo-ecological micro-
palaeontology methods (Gillmore et al., 2001)
combined with 2D structural restoration (Kjennerud &
Sylta, 2001) suggest that the central parts of the northern
North Sea have experienced palaeodepths of >0.5 km
during the earliest Eocene (Kjennerud & Gillmore,
2003). Owing to its depocentre location, the core
obtained from 22/10a-4 exhibits an exceptionally
expanded and almost stratigraphically complete
Palaeocene–Eocene transition sequence. Minor
erosion at the base of thin turbidite sandstones (typically
<10 cm) provides the only evidence for breaks in the
succession (Kender et al., 2012). A lack of diagenetic
alteration suggests that the sequence has only undergone
shallow burial (e.g. Nielsen et al., 2015).

Late Palaeocene regional uplift, associated with the
proto-Iceland mantle plume in the North Atlantic
(Knox, 1996), led to a sea-level fall of the order of
100 m and the basin becoming more restricted. This
drop in sea level produced a lithological change from
pale greyish green, waxy bioturbated claystones to
medium to dark-grey laminated mudstone and demar-
cation of the boundary between the lower Lista and
upper Sele formations (Figs 2 and 3). Basin restriction
also stagnated bottom waters, and led to a change in the
benthic foraminiferal assemblages to low-diversity, low-
oxygen-tolerant agglutinated species (Knox, 1996;
Kender et al., 2012).

Relative sea-level rise within the early PETM has
been inferred from sections in the Atlantic, Pacific,
Tethyan and Arctic oceans and the Turgay Strait (Harding et al., 2011). However, clay mineral assemblage and oxygen-isotope records from the New Jersey margin (John et al., 2012) suggests that the onset preceded the PETM by 20–200 ky, and is supported by further data from Spitsbergen (Harding et al., 2011). Sluijs et al. (2008) suggested the thermal expansion of seawater, melting from small-scale Antarctic alpine glaciers and/or a decrease in ocean-basin volume (caused by tectonics/volcanism associated with the North Atlantic Igneous Province, NAIP) as possible mechanisms for the pre-CIE sea-level rise.

Previous North Sea Tertiary clay mineral studies

Despite the wide extent and substantial thickness (up to 3500 m) of the UK offshore Tertiary succession, published clay mineralogical data for these sedimentary rocks are limited (Huggett & Knox, 2006) but have recently been augmented by a further review of the Norwegian and Danish sectors (Nielsen et al., 2015).

Pearson & Small (1988) and Pearson (1990) analysed shale cuttings from six wells from the East Shetland Basin, Viking Graben, Inner and Outer Moray Firth Basin, to the north and northwest of the present study area. They found that the Palaeocene to Eocene succession is composed predominantly of smectite-rich R0-ordered interlayered illite-smectite (I-S) with minor illite, kaolinite and variable amounts of chlorite. However, they failed to distinguish between kaolinite and chlorite in many of the studied wells.

Similarly, in the very southwest of the Norwegian sector and south-east of 22/10a-4, the clay mineralogy of Palaeocene shales in well 2/11-1 (Fig. 1) is dominated by smectite with only minor amounts of kaolinite and illite (Karlsson et al., 1979). Eocene shales show a gradual upwards increase in illite and kaolinite (Karlsson et al., 1979). Elsewhere in the Norwegian sector, the Palaeocene and lower Eocene sedimentary rocks in well N15/12-1 are also dominated by smectite with only minor amounts of illite, kaolinite and chlorite, the latter being distinctly Fe-rich (Berstad & Dypvik, 1982). Clay assemblages in well 30/1-1 (Fig. 1), to the south of the present study area, exhibit similar trends to those described for the Norwegian sector. Large smectite contents have also been observed in Tertiary mudrocks from onshore Denmark (Nielsen, 1974).

The low-resolution study of Knox (1996) was the first to note the kaolinite-free nature of the clay mineral assemblages in the Lista Formation, which are dominated by smectite or chlorite and initially persist into the lower part (Unit 1a) of the Sele Formation in 22/10a-4 (Fig. 3). Kaolinite appears about half way up Unit 1a, reaching a low peak within a turbidite sandstone unit. After a slight decrease in the lower
part of Unit lb, kaolinite increases rapidly, paralleling an overall increase in grain size.

**MATERIALS AND METHODS**

Core samples from the Sele and Lista formations from well 22/10a-4 (57°44'3.87"N; 1°50'26.59"E) consist of variably fissile claystone with interbedded fine- to coarse-grained sandstone layers interpreted as turbidites, with occasional mm-thick ash layers (Fig. 3). In total, 100 samples were collected for clay mineralogical X-ray diffraction (XRD) analysis from claystone horizons only, avoiding sandstone beds. The section of 22/10a-4 analysed in this study is from 2596.5 to 2651.6 m (core depth), chosen because this part of the core is predominantly in claystone facies and provides a greatly expanded section over the onset of the CIE (Fig. 3). Between core depths of 2609 and 2613 m the claystone becomes finely laminated with alternately pale and dark laminae couplets ranging from 1 to 25 per mm. The pale laminae consist of clay and silt, and the dark laminae are rich in organic carbon and pyrite inclusions (Kender *et al.*, 2012).

There is some debate about the placement of the boundaries between the Lista and Sele formations and the subdivision of the Sele Formation into units 1a and 1b. On the basis of geophysical log response, Knox (1996) placed the former at 2636.5 m and the latter at 2617.5 m (Fig. 3). In a later paper (Huggett & Knox, 2006), the Sele Unit 1a-1b boundary was moved higher to beneath the lowermost sandstone at 2609.5 m, presumably using core-depth data. Kender *et al.* (2012) placed the core boundary between the Lista and Sele formations at 2630.5 m, proposing a −6 m offset between log and core depths. Excluding Fig. 3 which shows geophysical log depth, core depths including the Lista-Sele formation boundary (2630.5 m) and Sele Unit 1a-1b boundary (2609.5 m) have been used throughout this study.

The XRD methodology employed here broadly follows that used in two previous PETM clay mineral studies (Harrington & Kemp, 2001; Harrington *et al.*, 2004). However, in order to initially compare results with those obtained previously from well 22/10a-4 (Knox, 1996), a nominal <4 µm size fraction was isolated and analysed, rather than the more traditional <2 µm size fraction employed in most studies. On sedimentological grounds, <4 µm reflects clay-grade particles (Wentworth, 1922). Because smectite is typically composed of finer-grained particles than other clay minerals (Moore & Reynolds, 1997), the finer the fraction isolated, the greater
the proportion of smectite that will be recorded. Therefore, where smectite is common, analysis of the <4 µm fractions enables more sensitive monitoring of changes in the clay mineral assemblage composition. For this study, the desire for such sensitive monitoring outweighed the requirement to compare directly with previous <2 µm fraction regional data.

Sample preparation

In order to reduce the proportion of non-clay minerals present in isolated fine-size fractions for clay mineral XRD analysis, these should ideally be prepared from crushed (not milled) material. We therefore targeted crushed material, apart from when only milled material was available (24 samples). Approximately similar particle-size and XRD results from juxtaposed milled and crushed materials suggest that, in this case, the different sample forms do not appear to have adversely affected the analytical results produced.

A representative ∼4 g portion of each core sample was removed and crushed in a pestle and mortar to pass a 2 mm sieve. The <2 mm (or in some cases milled) material was then dispersed in deionized water using a reciprocal shaker combined with treatment with ultrasound. The resulting suspensions were then sieved on a 63 µm aperture sieve and the >63 µm (or in some cases milled) material was then dispersed in deionized water using a reciprocal shaker combined with treatment with ultrasound. The <2 mm (or in some cases milled) material was then dispersed in deionized water using a reciprocal shaker combined with treatment with ultrasound. The resulting suspensions were then sieved on a 63 µm aperture sieve and the >63 µm (‘sand’) material was dried at 55°C and bagged. The <63 µm material was placed in a 250 mL measuring cylinder with a few drops of 0.1 M sodium hexametaphosphate (‘Calgon’) solution to disperse the individual clay particles and prevent flocculation.

After standing for a period determined by Stokes’ Law, a nominal <4 µm fraction was removed in a single extraction. The <4 µm (‘clay’) material and remaining 4–63 µm (‘silt’) material were then dried at 55°C and stored in glass vials.

So that similar amounts of material were mounted and exposed to the X-ray beam, ∼100 mg of the <4 µm material was re-suspended in a minimum of deionized water and pipetted onto a ceramic tile in a vacuum apparatus to produce an oriented mount. In order to remove the effects of the ‘Calgon’ addition and/or possible seawater interaction, homionic Ca-saturated mounts were produced by adding 2 mL of 0.1 M CaCl₂·6H₂O solution, washing twice to remove excess reagent before drying at room temperature.

Clay mineral analysis

The XRD analysis was carried out using a PANalytical X’Pert Pro series diffractometer equipped with a cobalt-target tube, X’Celerator detector and operated at 45 kV and 40 mA. The <4 µm oriented mounts were scanned from 2 to 40°2θ at 1.02°2θ/min after air-drying, ethylene glycol-solvation (16 h) and heating at 550°C (2 h). Clay mineral species were then identified from their characteristic peak positions and intensities and their reaction to the diagnostic testing program.

With the exceptions of Harrington & Kemp (2001) and Harrington et al. (2004), previous palaeoclimatic and PETM clay mineralogical studies have all employed relatively simple XRD peak area/height measurements and correction multipliers to determine semi-quantitative estimates of the clay minerals present (e.g. Pearson & Small, 1988; Pearson, 1990; Harding et al., 2011; John et al., 2012; Bornemann et al., 2014; Hermoso & Pellenard, 2014; Lombardi, 2014). Such semi-quantitative methods (most commonly based on Biscaye, 1965), are objective, reproducible and have been used extensively by sedimentologists to provide fit-for-purpose comparisons of regional datasets.

However, as acknowledged by Biscaye (1965), the intensity of a clay mineral’s characteristic XRD peaks cannot be used as a direct measure of its abundance because of variations due to machine conditions, sample-mount thickness, the degree of clay mineral preferred orientation and the variable ‘diffractability’ of different clay minerals. Critically, the Biscaye (1965) method only provides rough estimates of interlayered clays and takes no account of variations in the crystal order and chemical composition of different species of the same mineral. The latter also mean that pure mineral standards (Huggett, 1992, 1996) have limited use in this regard. Weighted peak-area percentages are constructs and, at best, are untestable approximations of real percentages (Biscaye, 1965) with precision estimated to be ±5 to 10% of the amount present at percentages >15% (Schultz, 1964). For detailed clay mineralogical studies, therefore, a more rigorous methodology producing quantitative data is clearly desirable.

Although quantitative evaluation of clay mineralogy was not achievable in the 1960s (Biscaye, 1965), more recent advances, particularly in the computer modelling of XRD profiles (e.g. Newmod-for-Windows™, Reynolds & Reynolds, 1996; SYBILLA, Zeelmaekers et al., 2007) have helped to deliver realistic quantitative data (Zeelmaekers et al., 2015).

The modelling-based methodology used in the present study (and previously by Harrington & Kemp, 2001; Harrington et al., 2004) holds several key advantages over the peak area/height techniques. Importantly, modelling allows changes in both the crystal order (crystallite-size
FIG. 4. Comparison of a composite modelled XRD profile with an experimental ethylene glycol-solvated XRD trace; sample depth 2612.35 m, Sele Formation Unit 1a (upper figure). Modelled XRD traces for each clay mineral component (illite-smectite, illite, kaolinite and chlorite) with peak positions (Å) are shown in the lower four figures. Note the different intensity scales for the component traces.
(distribution) and chemistry of clay mineral species to be taken into account on a sample-to-sample basis. The pattern fitting/deconvolution approach employed during modelling also facilitates the more accurate interpretation of peak overlaps, a particularly important feature when distinguishing and quantifying kaolinite in the presence of chlorite, critical for this study.

Modelling of the <4 µm glycol-solvated XRD profiles was carried out using Newmod-for-Windowstm (Reynolds & Reynolds, 1996) software on all the samples. The modelling process requires the input of diffractometer, scan parameters and a quartz intensity factor (instrumental conditions), and the selection of different sheet compositions and chemistries. In addition, an estimate of the crystallite-size distribution of the species may be determined by comparing peak profiles of calculated diffraction profiles with experimental data. By modelling the individual clay mineral species in this way, ‘mineral reference intensities’ were established and used for quantitative standardization following the method outlined by Moore & Reynolds (1997).

An example of the excellent fit of a modelled profile with that produced by one of the samples is shown in Fig. 4.

**RESULTS**

**Particle-size distribution**

As part of the preparation procedure for XRD analysis, approximate particle-size data were produced (% ‘sand’, ‘silt’ and ‘clay’). Note, however, that as full recovery of <4 µm material was not achieved, the particle-size data overestimate the ‘silt’ fraction and underestimate the ‘clay’ fraction proportions of the samples and should only be regarded as indicative. Our previous experiments suggest that >70% of the <4 µm material present in a typical mudstone sample is removed in a single extraction, >95% after two extractions.
The particle-size data show a marked upwards fining through the 22/10a-4 sampled sequence (Fig. 5). Using the classification of Shepard (1954), the two deepest samples from the Lista Formation are relatively coarse-grained sands/silty sands while the shallower samples are much finer, clayey silts. The overlying Sele Formation Unit 1a is also composed predominantly of silty sands/sandy silts/sand silt-clays with occasional clayey silts. In comparison, the Sele Formation Unit 1b is composed of silts, clayey silts and rarely sandy silts.

Berstad & Dypvik (1982) present approximately similar particle-size distributions from the Palaeocene and Eocene sediments of a Norwegian sector well (N15/12-1, Fig. 1) to those found in 22/10a-4. The generally silty clays show an overall fining-up sequence with decreasing sand content similar to the present study.

Clay mineralogy

The XRD analysis revealed that the clay mineral assemblages of the deepest samples from the coarse-grained lithologies of the Lista Formation (below 2650 m), are dominated by an interlayered illite-smectite (I-S, mean 70%) with moderate amounts of chlorite (mean 23%) and minor amounts of illite (mean 7%) (Fig. 6). No kaolinite was detected in these samples (Fig. 7a).

The XRD peak positions for the Ca-saturated mounts together with Newmod-for-Windows™-modelling of the glycol-solvated XRD profiles suggests that the I-S is an R0-ordered 40% illite: 60% smectite species, in which the illite layers have a 0.1 Fe, 0.7 K per (Si, Al)$_3$O$_4$(OH)$_2$ chemistry and which has a crystallite-size distribution with a mean defect-free distance of four layers and a range of 1–15 layers. The lack of kaolinite in these samples enables more accurate characterization...
of the chlorite, which is very Fe-rich with a mean defect-free distance of four layers and a crystallite-size range of 1–14 layers. The illite has a composition 0.05 Fe, 0.7 K per (Si, Al)$_4$O$_{10}$(OH)$_2$, a crystallographic range of 1–60 layers and a mean defect-free distance of 19 layers.

The clay mineral assemblages of samples from the upper Lista Formation and the base and middle of the Sele Formation Unit 1a (2635–2620 m) are also dominated by I-S with minor amounts of illite and chlorite together with the appearance of traces of kaolinite (Figs 6 and 7b). The illite and I-S detected in these samples is generally similar to that found in the lower Lista Formation; the I-S again being identified as an R0-ordered 40%I species. Newmod-for-Windows™ deconvolved kaolinite $d_{001}$ XRD peak widths (full width at half maximum, FWHM, mean 0.38°2θ), isolated from the chlorite $d_{002}$ input, indicate moderate crystal order with a mean defect-free distance of 15 layers and a crystallite-size distribution range of 1–60, 7 Å layers. The chlorite has a more intermediate Fe/Mg chemistry compared to that identified in the deeper Lista Formation samples.

The upper part of Sele Formation Unit 1a (from 2620 to 2609.5 m) shows clay mineral assemblages with decreasing proportions of I-S, increasing proportions of kaolinite with minor illite and only traces of chlorite (Figs 6 and 7c). Towards the base of this interval the I-S retains a similar R0-ordered 40%I composition but from ~2618 m upwards, the I-S increasingly exhibits a more smectitic character (R0-ordered 30%I). While the illite and chlorite retain similar characteristics to those detected in the base and middle of the Sele Formation Unit 1a, the increased kaolinite exhibits sharper, deconvolved XRD peaks ($d_{001}$ FWHM, mean 0.30°2θ) indicative of a more highly ordered nature. Newmod-for-Windows™-modelling suggests that kaolinite crystallite-size distributions reach mean defect-free distances of 40 layers and a range of 1–80, 7 Å layers.

Above 2609.5 m, the clay mineral assemblages of Sele Formation Unit 1b continue to be dominated by I-S. An R0-ordered 30%I species is most prevalent at the base of the interval but considerably more variable and illite-rich species with up to 80%I were detected in the shallowest samples. Minor proportions of kaolinite

![Fig. 7. Sample XRD traces (air-dry, ethylene glycol-solvated and heated 550°C) to illustrate the clay mineral assemblages identified in the 22/10-a4 samples: (a) Lista Formation, 2651.46 m; (b) Sele Formation Unit 1a base and middle, 2624.51 m; (c) Sele Formation Unit 1a upper, 2612.84 m; and (d) Sele Formation Unit 1b, 2608.20 m.](image-url)
and illite were also detected together with traces of chlorite in these samples (Figs 6, 7d). Kaolinite crystal order \( (d_{001} \text{ FWHM, mean } 0.33^\circ 2\theta) \) and chlorite chemistries generally appear similar to the upper part of Unit 1a.

Clay mineral indices

The PETM studies that include clay mineralogical analyses frequently determine clay mineral ratios \( (e.g., \text{kaolinite/smectite, K/S and kaolinite/illite, K/I}) \) in order to provide indices for estimating environmental change \( (\text{e.g. Robert & Kennett, 1994; Bolle & Adatte, 2001; John et al., 2012}) \). Chamley (1989) advocates the use of relative variations in the abundance of different clay minerals rather than absolute values in palaeoclimatic reconstructions, in order to differentiate their erosion from soil or rocky substrates. However, different authors have determined these apparently similar ratios in different ways. Bolle & Adatte (2001) calculated their K/S index using a ratio of ethylene glycol-solvated XRD peaks (kaolinite \( \sim 7.1 \) Å and smectite \( \sim 16.9 \) Å); although they provide no indication of whether peak heights or areas were measured. Robert & Kennett (1994) used peak-height data for the same peaks. More recently, John et al. (2012) measured XRD background-subtracted peak heights adjusted by form-factors for the different clay minerals. Comparison of these semi-quantitative values and ratios with the more accurate, quantitative clay-mineral data and ratios that can now be routinely produced, are clearly restricted to trend commentaries.

We also present clay mineral indices for kaolinite/illite-smectite (K/(I-S)) and K/I to aid comparison with previous studies. However, rather than simply ratioing peak-area measurements (raw or adjusted) from XRD traces, the present indices were calculated from modelled clay mineral proportions and therefore more accurately reflect actual clay mineral variation.

Both K/(I-S) and K/I values are consistently low and close to zero through the Lista Formation and older part of the Sele Formation Unit 1a (below \( \sim 2620 \) m, Fig. 8). Both indices show single-point peaks (\( \sim 2617 \) and \( \sim 2615 \) m) prior to complex multi-peaked maxima at \( \sim 2612-2613 \) m), after which they fall to background levels during the bulk of the CIE excursion (\( i.e. \) above \( 2611.5 \) m). Importantly, the rise and fall of the clay indices occurs prior to the principal CIE (\( i.e. \) carbon release). The transition from Sele Formation Unit 1a to 1b is marked by further, minor K/(I-S) and K/I spikes. Decreasing depth within the Sele Formation Unit 1b is characterized by a gradual overall K/(I-S) increase together with a much more pronounced increase in K/I (Fig. 8) reflecting a reduction in the relative proportion of illite in the youngest rocks (Fig. 6).

DISCUSSION

This study indicates the predominance of smectite-rich I-S in the PETM sequence of 22/10a-4 and differs from many previous North Sea studies where discrete smectite has been described. These include that by Knox (1996) who examined the same core interval, albeit at a much lower resolution and included coarser-grained lithologies. Sedimentologists have frequently used the term ‘smectite’ to include smectite-rich I-S (\( e.g. \) Chenot et al., 2016) but in most cases, including Knox (1996), this simplification is not detailed and therefore ambiguous. The XRD responses of discrete smectite and smectite-rich I-S are similar in terms of peak position behaviour, and speciation can be difficult where assemblages are complex and severe peak-overlap issues occur in the diagnostic low-angle region. However, the current authors contend that accurate speciation, significantly aided by modelling approaches, is critical. Newmod-for-\textit{Windows} TM mod-elling suggests that peak areas for the lowest-angle basal spacing, the sole basis for traditional semi-quantitative estimates, can vary dramatically between discrete smectite and smectite-rich I-S and therefore yield very different concentrations and clay mineral indices. Comparison of data produced from semi-quantitative peak areas (Knox, 1996) and Newmod-for-\textit{Windows} TM modelling concentrations (this study) in Figs 3 and 6 indicates that Knox (1996) substantially underestimated the proportion of smectite-rich I-S present in the sequence.

Further comparison between the two datasets highlights that the Newmod-for-\textit{Windows} TM-modelling approach is more successful in detecting kaolinite in the presence of chlorite (Figs 3 and 6).

Clay mineral provenance

The highly smectitic nature of the Tertiary sedimentary sequence in the North Sea (and onshore in Denmark) is considered to be the end-result of episodes of explosive volcanic activity \( (\text{e.g. Malm et al., 1984; Pearson, 1990; Nielsen et al., 2015}) \). Petrographic and mineralogical identification of glass, plagioclase, anatase, zeolites and carbonates provide further evidence for a significant volcaniclastic component in these sediments \( (\text{e.g. Karlsson et al., 1979; Huggett, 1992}) \).

Volcanic material was available from two phases of volcanic activity associated with the opening of the NE
Fig. 8. Downhole variation in clay mineral indices for the 22/10a-4 samples: K/(I-S) and K-I and %‘sand’ compared to total organic carbon (TOC) isotopic and micropalaeontological proxies from the same core (from Kender et al., 2012). The carbon isotope excursion (CIE) can be correlated to the global CIE of the PETM.
Atlantic and with the Faeroe–Shetland rift (Fig. 2). Firstly, 1–3 m thick tholeiitic basalt ash beds (Knox & Morton, 1988) are interbedded with mudrocks in lower Palaeocene deposits in the northeastern Atlantic region (Huggett, 1992). Secondly, >200 ashfalls have been recorded from more acidic volcanoes in Early to Mid-Eocene deposits in the Faroes–Greenland area (Huggett, 1992). On the basis of uranium, thorium and potassium geochemistry, Berstad & Dypvik (1982) estimated that Palaeocene and lower Eocene sediments in well N15/12-1 have a 60–80% pyroclastic origin. Post-Mid-Eocene sediments have greater concentrations of these elements and produce an increased gamma-ray response reflecting a decreasing pyroclastic (~20%) and increased terrestrial input (Berstad & Dypvik, 1982). However, there is debate about whether volcanic material was initially deposited in the North Sea, on adjacent landmasses, or in both locations (Nielsen et al., 2015).

Marine development. Early workers favoured an in situ development of smectite via the halmyrolitic alteration of volcanic glass and ash (e.g. Karlsson et al., 1979). Volcanism was further evidenced by the presence of sponge spicules and radiolarian tests representing organism blooms, stimulated by high-pH, silica brines (Berstad & Dypvik, 1982). We note that smectite and I-S may also develop by direct precipitation from the mixing of marine waters and hydrothermal fluids on the sea floor (e.g. Alt & Jiang, 1991; Inoue, 1995). Previous workers have discounted this mechanism, presumably due to the large geographical extent of the smectite in the Tertiary sediments and the lack of other hydrothermal influences (Huggett & Knox, 2006). Nielsen et al. (2015) suggest that differences they noted in smectite interlayer cations indicate different development paths. Monovalent (Na+) types reflecting direct formation from volcanic ash in the depositional environment while divalent (Ca2+) types infer smectite supplied from surrounding land areas. However, such differences in XRD peak positions may again reflect the mis-identification of I-S or alternatively the differential interaction of smectite with seawater/soluble salts. The clay mineral assemblages in the present study were dispersed using ‘Calgon’ and subsequently saturated with Ca2+ and their in situ interlayer cation chemistry therefore cannot be identified.

Continental development. Continental authigenesis of precursor smectite is limited to two possible environments: relatively common soil development, or rarer precipitation in saline, alkaline lakes. On the basis of its rarity and a lack of lacustrine facies, the latter environment is discounted in this case.

Widespread soil authigenesis of smectite-group clay minerals is typically associated with vertisols, formed in seasonal tropical climates with a dry season of 4–8 months, such as that found in present day India, eastern Australia, Sudan, Ethiopia, Kenya, Chad and the lower Parana River in South America (Chamley, 1989; Righi & Meunier, 1995; Bergaya et al., 2006). On Fe-Mg-rich parent rocks such as basalt or volcanic ash, leaching of cations (Ca, Mg) is minimized and with favourable high pH, smectite develops. Vertisols typically exhibit wide and deep cracks due to seasonally-induced, alternate shrinking and swelling. Such processes cause self-mulching and the development of an extremely deep A horizon (the surface mineral soil) and no B horizon (subsoil).

It is likely that sufficient volumes of volcanic products were deposited on the landmasses supplying the Cenozoic North Sea basin (the East Shetland Platform was extensive after the Palaeocene uplift), so that smectite remained the main clay product of weathering for a significant period (Pearson, 1990). Alternatively, intrabasinal reworking of lavas or recycling of clays (of volcanic origin) during reworking of exhumed sedimentary rocks may have been contributory. A lack of abrupt changes in the clay mineralogy supplied suggests an homogeneous source area and/or good mixing in the basin (Karlsson et al., 1979). Petrographic evidence provides further tentative evidence for a detrital origin for I-S in Tertiary sediments from Norwegian block 34/10 on the basis of the ragged appearance of flat to undulose platelets under Field Emission Scanning Electron Microscopy (FESEM) (Huggett, 1996).

We suggest that continental soil authigenesis produced the 22/10a-4 smectite before weathering and transport. A detrital, but different source is therefore also most probable for the kaolinite component of the mudstones. Relatively broad kaolinite XRD peaks (mean FWHM 0.38°2θ) noted throughout the lower sequence would also appear to favour a detrital, soil-derived source (Wilson, 1999; Tye et al., 2009). In terms of soil development, kaolinite, along with iron and aluminium oxyhydroxides, is regarded as the typical product of laterites (Ferrosols) and humid, tropical climatic zones such as those found in modern-day Africa, South America and Indonesia (Righi & Meunier, 1995; Bergaya et al., 2006). Significant kaolinite forms throughout the profile as a result of
high rainfall, distributed throughout the year, which produces soil solutions with low concentrations of SiO₂ and basic cations.

**Burial authigenesis.** As well as debate about whether the clay assemblage initially developed in the marine or continental environment, there is also disagreement over whether the North Sea Tertiary sediments have undergone significant burial authigenesis. The illitization of smectite, or progressive transformation of smectite to illite via a series of intermediate mixed-layer I-S species was first recognized in shale diagenetic studies of the Gulf Coast (e.g. Hower et al., 1976). Changes in the proportion of illite and smectite and ordering in the I-S have since been correlated and an empirical relationship established with changes in temperature due to burial depth (e.g. Pollastro, 1993). These depth-dependent reaction changes in clay minerals have been compared to changes observed in organic materials to construct a Basin Maturity Chart (Merriman & Kemp, 1996). Assuming a ‘typical’ geothermal gradient of ~25°C/km, the Chart and predominant I-S composition (R0 40% I) suggest maximum burial of ~2.5 km for the 22/10a-4 sequence, similar to the present burial depth. The temperatures and pressures experienced under such shallow burial would be insufficient to alter detritally supplied kaolinite (Merriman & Kemp, 1996). Greater geothermal gradients (40°C/km) and an average reservoir temperature of 107°C for the overlying Forties Sandstone Member suggested by Huggett (1995) cannot have been sustained for a significant period of time. As first highlighted by Ramsever & Boles (1986), residence time at elevated temperatures is critical in determining the extent of the smectite-to-illite reaction. Although limited burial transformation of smectite to illite would therefore appear plausible, no direct evidence has previously been provided to the base of the Tertiary (Karlsson et al., 1979; Nielsen et al., 2015). Huggett (1995) also argues that regional, unpublished oil-company XRD data indicate no correlation between I-S composition and depth. However, the marginal, overall increase (30–40%) in illite interlayering in the I-S species with increasing depth through the 22/10a-4 sampled interval, may reflect some limited degree of diagenetic alteration.

**Palaeoclimate and palaeohydrology**

As stated above, although there are a number of factors affecting clay mineral assemblages (climate, time, parent material, topography, soil-profile type, transport processes, burial diagenesis) (Singer, 1984; Hillier, 1995), palaeoclimate information in the 22/10a-4 sequence is likely to have been preserved as it represents a broad catchment area, is remote from land masses and has undergone relatively shallow burial. By comparison with modern settings, continental soil authigenesis of precursor smectite (I-S) suggests that a seasonal tropical climate with a prolonged dry season was in place during the latest Palaeocene and earliest Eocene in the landmasses surrounding the North Sea Basin. Erratic droughts and floods combined with the dry, deeply cracked vertisol profiles may have led to enhanced erosion and transport to the marine environment (e.g. Freebairn et al., 1996).

Increases in kaolinite content in mudstone sequences (frequently evidenced by an increase in the K/S ratio) have often been interpreted to reflect a change to warm and humid conditions and intensified chemical leaching (e.g. Robert & Kennett, 1994; Gawenda et al., 1999; Bolle & Adatte, 2001). On this basis, the low K/(I-S) and K/I values recorded in this study (through the Lista Formation and lower Sele Formation Unit 1a, Fig. 8) are interpreted to indicate a seasonal, tropical climate, supplying a smectite-dominated clay mineral assemblage, and increased kaolinite (like the K/(I-S) and K/I ‘kicks’ and major deflection in the upper Sele Formation Unit 1a) interpreted to indicate a transition to a hot, humid climate. Thiry (2000) argues, however, that the formation of mature, thick kaolinitic soils in equilibrium with the environment requires long-lasting landscape stability of at least 1 Ma. The arrival of soil-clay assemblages in the basin inevitably lags behind their continental formation. John et al. (2012) showed, using oxygen isotopes (δ¹⁸O), that clays arriving on the New Jersey Margin at the onset of the PETM were most likely to have been reworked from Cretaceous laterites. Therefore, sequential changes in sedimentary clay mineral assemblages with durations of ~1 Ma cannot be caused by climatic changes acting on soil mineralogy, but rather on physical transport processes.

The observed short-term kaolinite anomaly detected in 22/10a-4 is, therefore, more likely to be explained by enhanced fluvial erosion of the pre-existing kaolinite-bearing soils and regolith column rather than chemical weathering and soil formation (cf. Schmitz et al., 2001; Foreman et al., 2012; John et al., 2012). Earlier pulses of kaolinite recorded in 22/10a-4 may indicate brief, wetter episodes. These authors argue that a ‘kaolinite spike’ associated with the PETM reflects an increase in erosion and fluvial discharge, with important implications for hydrology and sediment transport to continental margins.
Fig. 9. Comparison of kaolinite (this study) and sediment carbon isotope (from Kender et al., 2012) from 22/10a-4 with recent studies from Arctic Spitsbergen (Harding et al., 2011), New Jersey Margin (John et al., 2012) and the Eastern North Atlantic (Barneman et al., 2014).
Evidence for such an origin may be provided by the measured crystal order of the kaolinite. The XRD peak widths for the kaolinite-rich samples detected during the CIE onset are significantly sharper (mean FWHM 0.30° ± 20) than those lower in the sampled sequence (mean FWHM 0.38° ± 20). Such increased crystal order is consistent with erosion and winnowing from lithologies with more advanced diagenetic development, possibly porous sandstones, rather than the more poorly crystalline forms typically produced during soil development (Parry et al., 2015).

Although in some regions the PETM is preceded by a brief (<20 ky) period of aridity (Wing et al., 2005; Kraus & Riggins, 2007; Jaramillo et al., 2010), the PETM is more generally characterized by a humid climate (e.g. Robert & Kennett, 1994; Bowen et al., 2004; Adatte et al., 2014) and subsequent hydrological change. Increased sedimentation rates indicate increased precipitation and/or continental erosion, plant- and aquatic-derived biomarker δD compositions indicate increased precipitation and decreased seawater salinity, respectively (Pagani et al., 2006), and surface-water freshening may be indicative of higher river discharge (John et al., 2012; Kender et al., 2012).

Sedimentologically, increased kaolinite in marine sediments is frequently linked with sea-level lowstand deposits as it is typically formed of coarser grain-sizes than other clay minerals, particularly smectite or I-S deposits as it is typically formed of coarser grain-sizes than other clay minerals, particularly smectite or I-S deposits. However, benthic foraminifera extinction, as opposed to a discrete pulse, was identified following the initial CIE (Bornemann et al., 2014) (Fig. 9), and non-existent in some regions e.g. Bighorn Basin, Wyoming (Gibson et al., 1999). For example, a very significant (~75%) increase in kaolinite precedes the benthic foraminifera extinction (BFE) by ~270 ka and the CIE by ~325 ka in the Zumaia section, Spain (Gawenda et al., 1999). Similarly in Tawanui, New Zealand (Kaiho et al., 1996) the proportion of kaolinite increases just below the CIE, ~3 ky before the BFE and lasted >~40 ky. John et al. (2012) found a three-fold increase in K/S starting 40 cm below the CIE, peaking 2–3 m above the CIE and returning to pre-CIE values <10 m above the CIE in boreholes from the New Jersey margin (Fig. 9). However, in the Dababiya section, Egypt, a kaolinite spike follows the initial CIE (Soliman et al., 2011). Similarly at the DSDP site 401, eastern North Atlantic, a gradual kaolinite increase, as opposed to a discrete pulse, was identified following the initial CIE (Bornemann et al., 2014) (Fig. 9). A prominent kaolinite spike during the CIE recovery period corresponds with the A. subsphaerica acme in the Weddell Sea, near Antarctica, at ODP Site 690 (Kelly et al., 2005). In marked contrast to other studies, kaolinite content declines within the CIE onset in Spitsbergen (Harding et al., 2011) (Fig. 9).

Such variable behaviour in the proportion of kaolinite present in sediments before, during and after the PETM, lends further weight to their origin from increased erosion of soils and/or sedimentary-rock sequences rather than generation by soil-formation processes, as a change to warm and humid conditions might be expected to occur across similar latitudes approximately simultaneously, and...
throughout the PETM rather than only in one part of it. In contrast, the variable record in kaolinite content is likely to indicate a combination of: (1) the extent of pre-existing kaolinite deposits; (2) enhanced periods of physical erosion related to intense precipitation (either seasonal or annual changes); and (3) the gradual erosion of available kaolinite. The increases in kaolinite may mark the onset of such precipitation patterns, but subsequent decreases may not signify the termination of intense rainfall if the kaolinite was completely eroded (with no time to form new kaolinite). Overall, the elevation in kaolinite at the PETM noted in this study and in other locations is consistent with an increased hydrological cycle (Pagani et al., 2006) probably taking place immediately before the PETM (Kender et al., 2012). Global variations in PETM kaolinite concentrations are expected, as earth system modelling (Caballero & Langen, 2005) and sediment geochemical studies (Pagani et al., 2006) suggest migrating storm tracks and hydrological cycling with global warming.

**CONCLUSIONS**

A high-resolution study of clay mineral assemblages from mudstones sampled across the PETM transition and carbon isotope excursion (CIE) onset in North Sea well 22/10-a4 has provided new sedimentological and palaeoclimatic data for this intensively studied sequence. Particle-size data show a marked upwards-fining trend through the sampled sequence, commensurate with an overall eustatic rise. Newmod-for-WindowSTM, modelling of XRD profiles provides improved clay mineral quantification and generally indicates smectite-rich I-S (previously discussed as smectite)-dominated assemblages, the final product of episodes of explosive volcanic activity (Pearson, 1990). It is likely that the smectite-rich I-S formed due to both continental erosion of pedogenic horizons and marine alteration of volcanic ash. I-S development in vertisol soil profiles suggests a prevailing dry, seasonal tropical climate.

Dramatic increases in kaolinite content (∼1–50% of the clay assemblage) and K/(I-S) values were detected in the upper part of Sele Formation Unit 1a, prior to the principal CIE but during what now appears to be a complex onset of the PETM, associated with palynological fluctuations (Kender et al., 2012). Previous studies associate such increased kaolinite concentrations in the PETM interval with a change to warm and humid conditions producing intensified chemical leaching. However, the length of time taken to form kaolinite (10⁶ years), and isotopic evidence from New Jersey (John et al., 2012), suggest that these were the result of physical weathering of ancient clays by enhanced runoff associated with a more humid climate. The kaolinite anomaly is more likely to be the result of an intensified hydrological regime that caused extensive erosion of pre-existing kaolinite-bearing soils and regolith. Comparisons between the precise timing, magnitude and nature of the kaolinite deviation and other worldwide PETM sequences are consistent with a complex geography of a shifting climate pattern.

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