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X-ray fluorescence (XRF) fingerprinting of Palaeogene deposits in Denmark

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Abstract

In this study, we test if cost-efficient X-ray fluorescence (XRF) analyses can be used to fingerprint Palaeogene clay and marl deposits in Denmark. A total of 67 samples from key sites in Denmark have been analysed. Our preliminary results indicate that it is possible locally within 10–30 km to distinguish between most of the Palaeogene units, but on a regional scale across Denmark, the units are not unique, and this probably reflects variations in clay mineralogy, grain size and calcareous content. Accordingly, we suggest that a comprehensive reference database is now needed if the full potential of the method is to be utilised, and this will ultimately result in more reliable geological models.

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Abbreviations:

EDXRF: Energy-Dispersive X-ray Fluorescence
GEUS: Geological Survey of Denmark and Greenland
Nr.: Nørre
PC: Principal Component
PCA: Principal Component Analysis
PETM: Paleocene–Eocene Thermal Maximum
XRF: X-ray fluorescence

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Introduction

In Denmark, the surficial deposits (<100 m) are of a large societal interest (farming, forestry, natural resources and geotechnical properties), and they also comprise a vital groundwater reservoir. The surficial deposits consist of Quaternary sediments (*c.* 10–30 m) above Palaeogene sediments in northern and eastern Denmark and Neogene sediments in south-western Denmark (Binzer & Stockmarr 1994; Fig. 1). Accordingly, pre-Quaternary deposits are often encountered in boreholes during large infrastructure projects and in connection with groundwater projects.

Knowledge about the surface deposits mainly derives from more than 260 000 boreholes drilled in Denmark in the last *c.* 125 years, and the data are available in the open-access Jupiter database hosted by the Geological Survey of Denmark and Greenland (GEUS; Hansen & Pjetursson 2011). The Jupiter database records the lithology and inferred age, whereas additional information that can be used to further discriminate sedimentary units (e.g. biostratigraphy) is only available for a very limited number of the boreholes. Another complicating matter when making geological models is that the surface deposits have often been disturbed by glaciotectonics (Jakobsen 2003). The heterogeneous surface geology in Denmark thus presents a serious challenge when trying to make a geological model based on borehole data. One way to produce more reliable geological models is to make additional analyses (e.g. biostratigraphy and clay mineralogy) to characterise and discriminate the deposits (Heilmann-Clausen *et al.* 1985; Nielsen *et al.* 2015). These procedures have, however, never been implemented routinely for geological investigations in Denmark because the analyses are very time-consuming.

In this study, we test a new cost-effective method to characterise and fingerprint Palaeogene deposits in Denmark using an X-ray fluorescence (XRF) analyser for discrete samples. We have analysed Palaeogene units (mainly

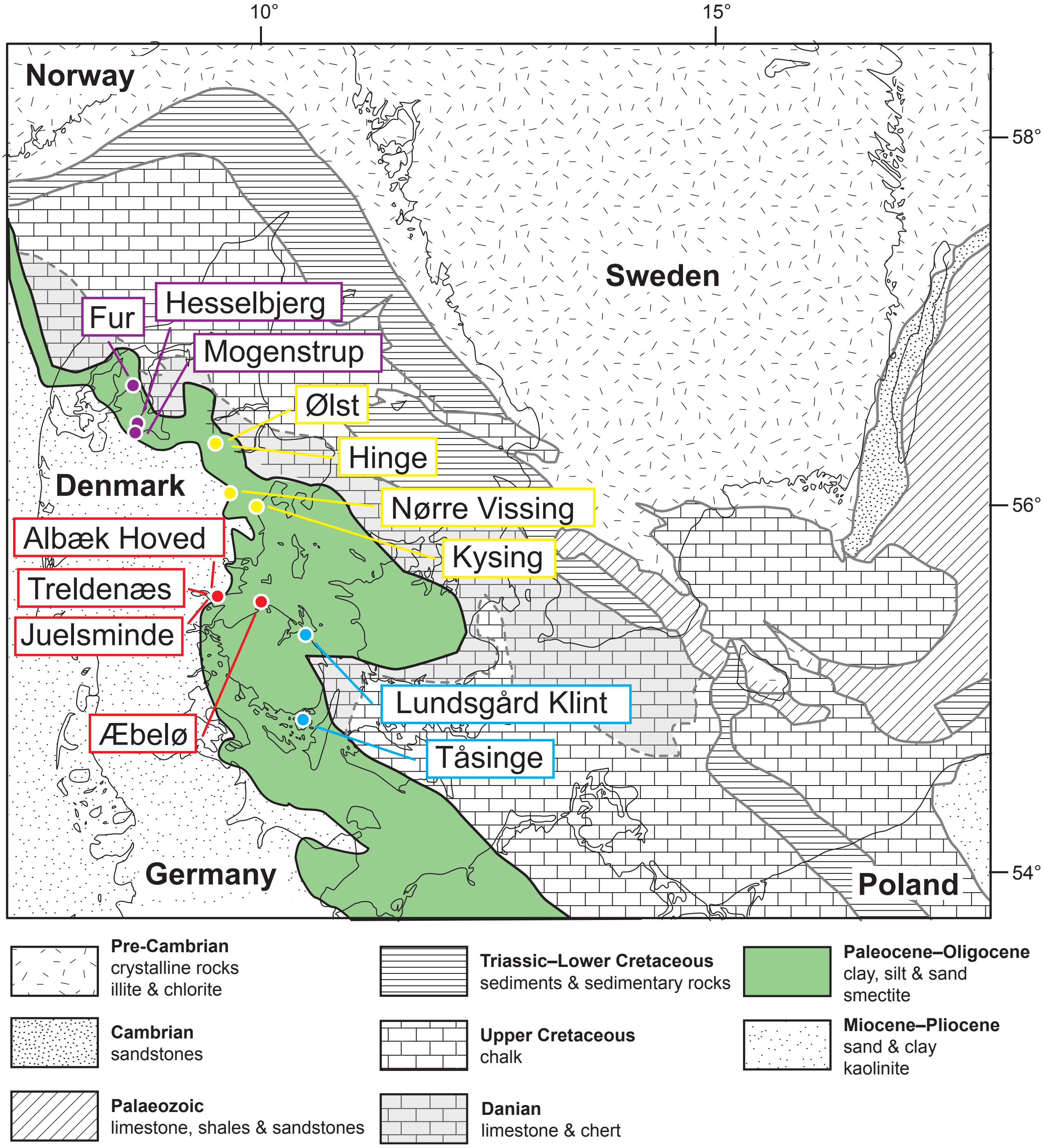

Fig. 1 Map of pre-Quaternary deposits in Denmark (based on Sorgenfrei & Berthelsen 1954). Sample sites are divided into four local areas: Limfjorden (**purple**), East Jylland (**yellow**), Lillebælt (**red**) and Fyn (**blue**).

marls and clays) from key localities (Fig. 1). Our results show that the method can be used to discriminate most Palaeogene units on a local scale (10–30 km) but lack the ability to differentiate the units on a regional scale across Denmark.

Palaeogene deposits in Denmark

Denmark is situated in the eastern part of the intracratonic Cenozoic North Sea Basin (Ziegler 1990). In most of Paleocene and Eocene times, the basin was inundated by relatively deep marine water that gradually became shallower and even subaerially exposed several times during the early Oligocene (Śliwińska *et al.* 2012; King *et al.* 2016). Overall, the Palaeogene succession comprises a series of lithologically distinct units composed of early Paleocene chalk, middle and late Paleocene and Eocene fine-grained clays and marls as well as Oligocene silty clays (Fig. 2).

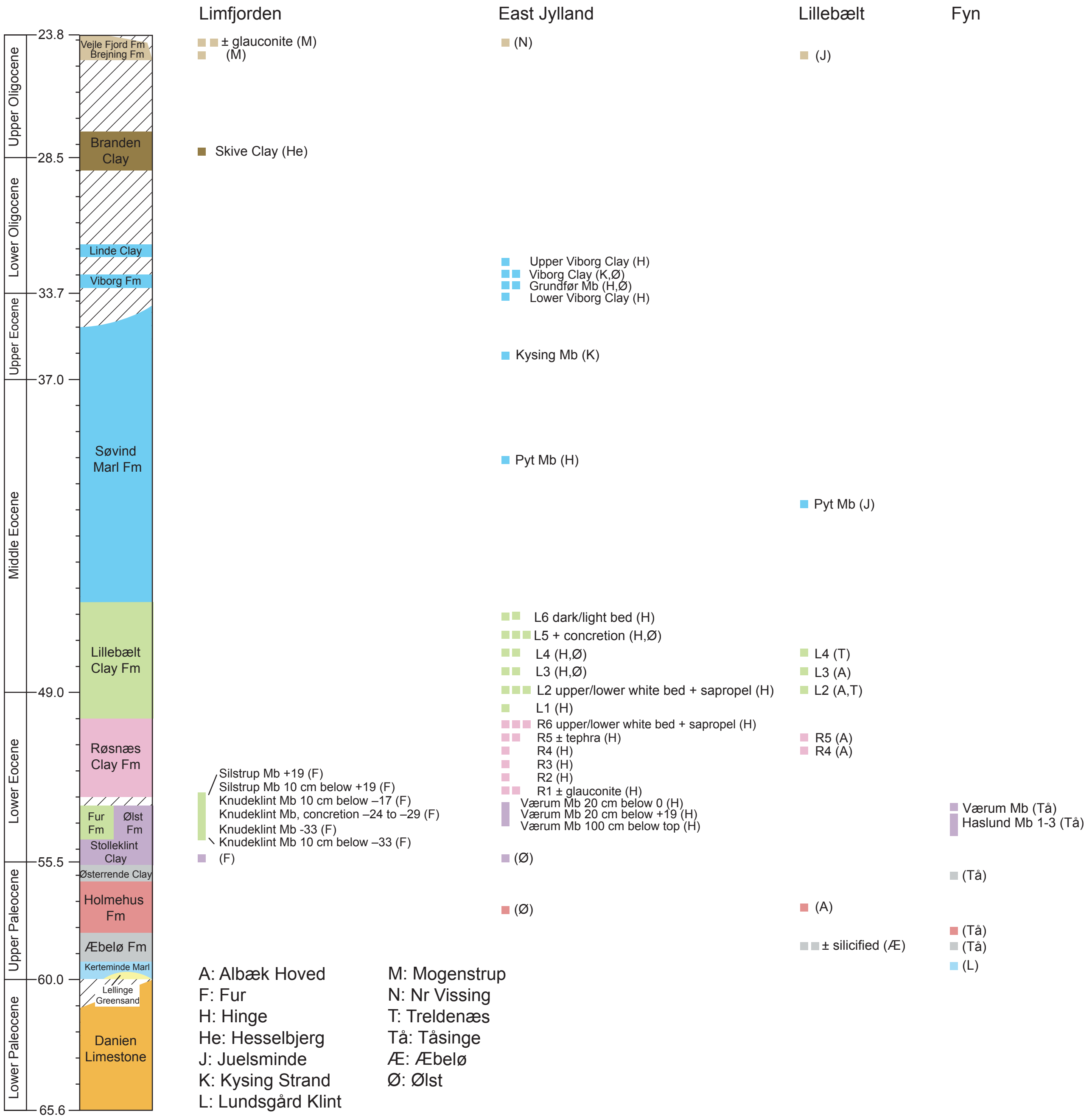

Fig. 2 Lithostratigraphy of the Palaeogene deposits in Denmark (after Schiøler *et al.* 2007) and distribution of the 67 analysed samples. Stratigraphy and ages of the lithostratigraphic units are based on Heilmann-Clausen (1995), Clemmensen & Thomsen (2005) and Rasmussen *et al.* (2010). Note that Knudeklint and Silstrup Members are part of the Fur Formation. Værum and Haslund Members are part of the Ølst Formation. Stolleklint Clay is a subunit of the Haslund Member. Skive Clay is a local facies of the Branden Clay.

During the late Cretaceous and early Paleocene (Danian), a chalk regime with the deposition of thick coccolithic chalk, bryozoan limestone and calcisiltite prevailed (Thomsen 1995). The oldest siliciclastic deposits in Denmark are the middle Paleocene (Selandian) Lellinge Greensand (up to 30 m) and the light grey Kerteminde Marl (*c.* 12–136 m), which in its upper part holds up to 50% reworked Cretaceous chalk (Thomsen 1995). Above this follows two units deposited under increasing water depth: the grey, partly silicified Æbelø Formation (*c.* 16–57 m) and the late Paleocene non-calcareous, varicoloured, very fine-grained Holmehus Formation (*c.* 12–40 m; Nielsen *et al.* 1986; Heilmann-Clausen 1995). In the latest Paleocene, the grey Østerrende Clay (up to 6 m) was deposited (Nielsen *et al.* 1986).

The Paleocene–Eocene transition coincided with a phase of intense activity in the Iceland mantle plume leading to major basaltic volcanism centred on the rift zone in the Norwegian–Greenland Sea (e.g. King *et al.* 2016; Ziegler 1990). During the Paleocene–Eocene Thermal Maximum (PETM), the laminated and in part organic-rich Stolleklint Clay (*c.* 15–24 m) was deposited

(Heilmann-Clausen 1995). Sometime after the PETM, the character of the volcanism in the rift zone changed from effusive, forming huge flood basalts in East Greenland and the Faroe Islands, to highly explosive, phreatomagmatic eruptions, spreading basaltic ash as far as 2000 km away in the northern Tethys (e.g. Stokke *et al.* 2020). In Denmark, more than 180 ash layers were deposited in probably outer neritic waters. The ash layers are a few mm to 20 cm thick and occur in the clayey Ølst Formation, all over the North Sea and most of Denmark. A remarkable exception is NW Jylland where the ashes occur in the diatomaceous Fur Formation (Pedersen *et al.* 2011).

After the deposition of the Ølst and Fur Formations, sea-level rise led to a high eustatic sea level and the opening of the English Channel and a marine connection across eastern Europe to the Peri-Tethys in western Asia (King *et al.* 2013). The hemipelagic, bathyal early Eocene, mainly red and calcareous Røsnæs Clay Formation (*c.* 3–28 m), and the early to middle Eocene, mainly non-calcareous Lillebælt Clay Formation (*c.* 40–100 m), were deposited in the present Danish land area. The two formations are each subdivided into 6 members based mainly on differences in calcareous content and colour (Heilmann-Clausen *et al.* 1985). The Røsnæs Clay Formation and lower members L1–L4 of the Lillebælt Clay Formation resemble the Holmehus Formation in being varicoloured, very fine-grained and condensed. Above these members follows the slightly siltier grey-green upper members L5 and L6 and the light grey middle to late Eocene Søvind Marl Formation (up to 90 m; Heilmann-Clausen *et al.* 1985).

The Søvind Marl Formation represents the last hemipelagic Eocene sedimentary unit (Thomsen *et al.* 2012) and is unconformably overlain by Oligocene deposits of variable age. In the central part of the Danish Basin, sedimentation of marl continued locally to the Eocene–Oligocene boundary, and here, the Søvind Marl Formation is usually overlain by the earliest Oligocene Viborg Formation composed of up to 85 m thick dark grey finely micaceous silty clay, coarsening upwards to sandy silt (Śliwińska *et al.* 2012; Thomsen *et al.* 2012). Above this formation usually follows the grey-green, silty, finely micaceous Skive Clay (80–90 m). The dark brown to nearly black, glauconitic and micaceous Brejning Formation was deposited in a marine, sediment-starved environment following a major fall in relative sea level during latest Oligocene (Rasmussen *et al.* 2010). On and south of the Ringkøbing–Fyn High, there is a major hiatus with only the oldest part of the Søvind Marl present, overlain by the Brejning Formation or younger units (Rasmussen *et al.* 2010).

Materials and methods

Samples have been collected in type and reference sections (Heilmann-Clausen *et al.* 1985; Heilmann-Clausen 1995) and other biostratigraphically controlled sections (Figs 1, 2). Four samples from Mogenstrup and Nørre (Nr.) Vissing (Supplementary File, Table S1) are tentatively assigned to Brejning and Vejle Fjord Formations. The samples are not equally distributed across Denmark or within the units but are the only samples available for this preliminary test of the method. From some units, we collected several samples if they were heterogeneous or contained, for example, concretions or ash layers. A total of 67 samples were analysed. Each analysis was repeated five times to estimate the analytical uncertainty.

After retrieval, the samples were dried in an oven at 90°C for 24 h. The dry samples were loosened in a mortar and sieved to 0–500 µm before they were poured into 40 mm XRF sample cups. The samples were analysed using a Bruker S2 PUMA Energy-Dispersive X-ray Fluorescence (EDXRF) spectrometer. The spectrometer was equipped with a 50 W X-ray tube with an Ag anode. For each analysis, three different tube settings were used: no filter, a 250 µm Cu filter and a 500 µm Al filter in front of the X-ray tube for a total time of 400 sec. Before each repeated analysis, the samples were gently stirred in the cup and lightly compacted. The analyses and data evaluation were performed using the Bruker SPECTRA.ELEMENTS software for standardless XRF analysis. The spectrometer was calibrated using a glass disc (FLX-K04 from FluXana) that was also used for drift monitoring. Elements with insufficient counts, including some of the trace elements, have been excluded from the data set.

Results

The XRF results show that the analytical uncertainty is minimal, and that there are variations in the abundance of elements between the Palaeogene units (Fig. S1 and Table S1). Elements like silicon (Si), potassium (K), aluminium (Al) and iron (Fe) are abundant in all units but because they vary little, and they cannot be used to discriminate the units. In contrast, some units are rather unique as they have a high content of sulphur (S), such as the ash-bearing Ølst, Fur and Stolleklint Formations. Other units contain higher amounts of calcium (Ca), such as the Kerteminde and Søvind Marl Formations as well as the calcareous parts of the Røsnæs Clay Formation (samples R3, R5 and R6 in Fig. S1). Barium (Ba) and manganese (Mn) are unique for the Lillebælt Clay and Røsnæs Clay Formations and less abundant in the other units. However, none of the elements is unique and cannot be used to fingerprint a unit alone.

Principal Component Analysis (PCA) of the data set groups the samples according to the formations that the samples come from (Fig. S2). The first Principal Component (PC) represents varying proportions of lime and clay having positive loading from elements associated with lime (Ca and Sr) and negative loading from elements associated with clay (Al, K, Rb and Si), whilst the second PC represents some diagnostic elements with positive loading from Ba and Ni that are diagnostic for the lower Lillebælt and upper Røsnæs divisions and negative loadings from S and Si that in high concentrations are diagnostic for ash layers and the Fur Formation, respectively. However, we do not consider PCA further as a tool for fingerprinting because the groups are not sufficiently distinct and because some very different units are grouped together by PCA. Thus, results from a PCA are not very useful to classify a new sample.

Instead, we have plotted the ratios between element concentrations for some of the most diagnostic elements in a 2D scatter plot, which makes it possible to differentiate most of the units (Fig. 3 and Fig. S3). We found that the ratios of K/Fe and Al/Si plotted against

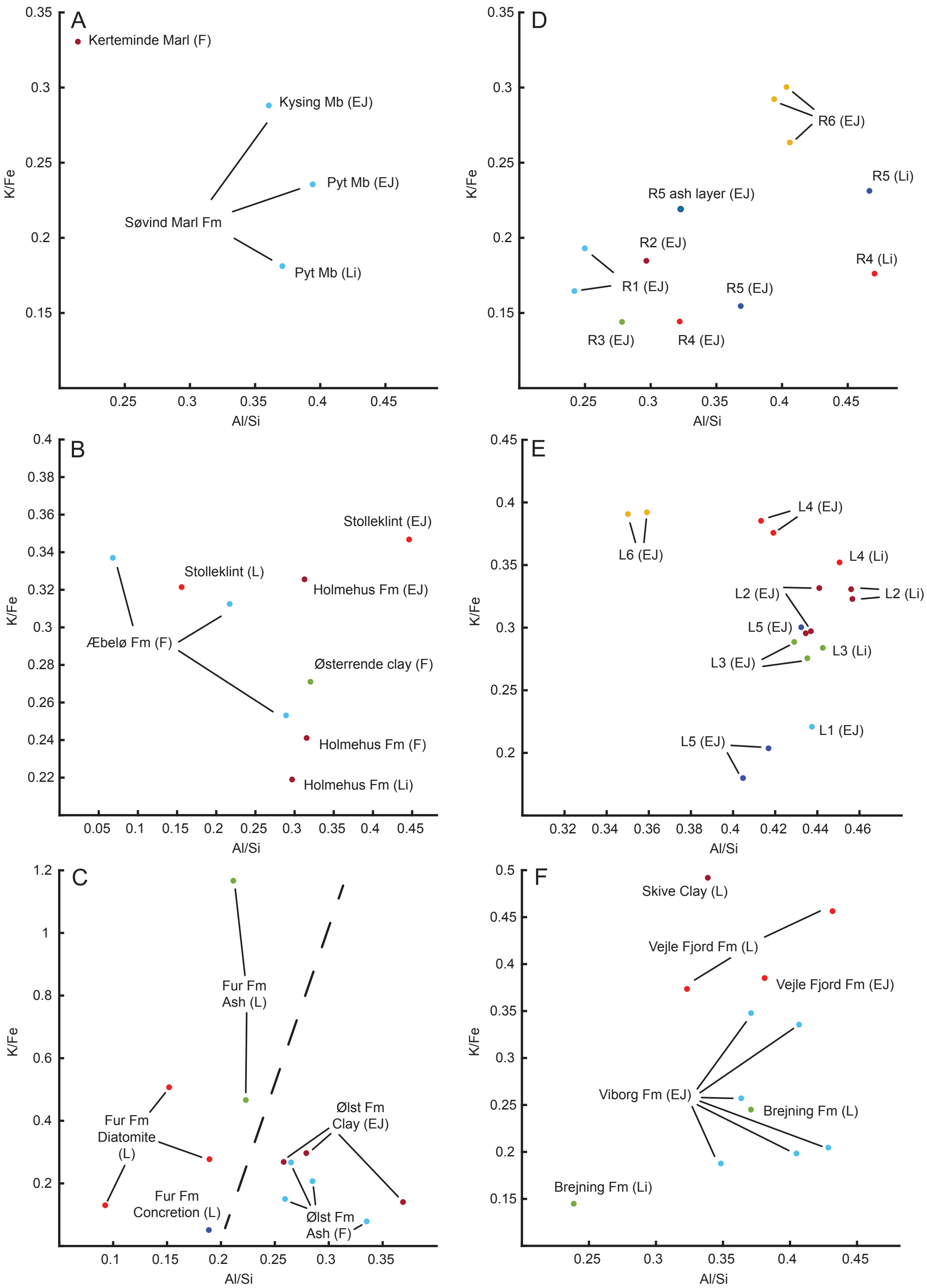

Fig. 3 XRF plot (ratios of Al/Si and K/Fe) from various Palaeogene deposits. **A**: Kerteminde Marl and Søvind Marl Fm. **B**: Æbelø Fm, Holmehus Fm, Østerrende Clay and Stolleklint Clay. **C**: Fur Fm and Ølst Fm. **D**: Røsnæs Clay Fm divided into members R1–R6. **E**: Lillebælt Clay Fm divided into members L1–L6. **F**: Viborg Fm, Skive Clay, Brejning Fm and Vejle Fjord Fm. **EJ**: East Jylland, **Li**: Lillebælt, **L**: Limfjorden and **F**: Fyn.

each other resulted in the best differentiation for Palaeogene units overall. In the Palaeogene, there are two marl units: the Paleocene Kerteminde Marl Formation and the Eocene Søvind Marl Formation (Fig. 3A). It is possible to differentiate the two formations, and it is even possible to distinguish between the two members, Pyt and Kysing, in the Søvind Marl Formation. The next units comprise Æbelø and Holmehus Formations, and Østerrende and Stolleklint clays from the Upper Paleocene and Lower Eocene, and it is also possible to distinguish between these (Fig. 3B). In the Æbelø Formation, the XRF data are scattered, and this probably reflects the heterogenous nature of the unit, which is composed of silicified and non-silicified clay. The more homogenous Stolleklint Clay and Holmehus Formation also have a scattered distribution, but this is probably because the samples were collected in different regions of Denmark. The XRF data from the contemporaneous Eocene ash-bearing diatomite (Fur Fm) and clay (Ølst Fm) are scattered, but the two formations can be clearly differentiated (Fig. 3C). The large scatter within the formations is probably due to the heterogenous nature of the units, which contain *c.* 180 ash layers as well as numerous barium carbonate and calcium carbonate concretions. The XRF data show that it is possible to distinguish between all members in the overlying Røsnæs Clay and Lillebælt Clay Formations within the same area, both in East Jylland and in the Lillebælt area (Fig. 3D–E). However, there are changes in the composition within the same member between the different regions. The youngest Palaeogene formations comprise the Viborg, Vejle Fjord and Brejning Formations and the informal Skive Clay. Within the different regions, the formations can be differentiated although there are significant inter-formational variations (Fig. 3F).

Discussion

Overall, our preliminary results suggest that it is possible to differentiate most of the Palaeogene units in the Danish area using XRF fingerprinting on a local scale (e.g. Limfjorden area) in combination with traditional facies analysis, whereas it is more difficult on a regional scale across Denmark. In the lithologically homogenous units (e.g. Holmehus, Røsnæs Clay, Lillebælt Clay and Søvind Marl Formations), there is very little variation in the XRF results locally, and the fingerprinting method is very promising. In contrast, there is more variability locally in some of the more heterogenous units (e.g. Fur, Ølst and Æbelø Formations), which contain ash layers and silicified or calcareous intervals that are in part modified by diagenetic processes (Fig. 3). On a regional scale across Denmark, we observe a variability within both the homogenous and less-homogenous units, which is greater than the differences between units. Accordingly, none of the Palaeogene units has a unique XRF signature across Denmark.

The regional XRF variability across Denmark probably reflects lateral facies variations in clay mineralogy, grain-size composition and calcareous content. In the Norwegian–Danish Basin, the clay mineralogy reflects the different composition of the source rock (Nielsen *et al.* 2015). For example, the high smectite content in Paleocene and early Eocene units reflects weathering of volcanic material, whereas abundant amounts of illite indicate a source area composed of metamorphic rocks. Sorting of the clay minerals also influences the composition where larger particles of kaolinite are more abundant close to the shore, whereas smectite often dominates the central part of the basin (Nielsen *et al.* 2015).

Conclusions

In this preliminary study, we have used XRF to analyse 67 samples of Palaeogene clayey and marly lithostratigraphic units from key sites in Denmark for their content of selected elements. We find that it is possible locally, within 10–30 km, to distinguish between most of the Palaeogene units, although some of them show large variability because of their content of ash, concretions and silicified intervals. On a regional scale across Denmark, the units are not unique, and this probably reflects basin-wide variations in grain size, clay mineralogy and calcareous content. By establishing a comprehensive reference database, the full potential of this cost-effective method could be realised, and this can ultimately be used to make better geological models. This is now planned by analysing more samples from repositories and future geotechnical boreholes.

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Author contributions

NKL and KHK conceptualised the study. NKL, KBRK, MLSA and CHC collected or supplied the material. KBRK and MLSA analysed the samples. All authors contributed to the interpretation of the data and in writing the manuscript.

Competing interests

The authors declare no competing interests.

Additional files

One supplementary file is available at *https://doi.org/10.22008/FK2/FCHYDQ* containing Table S1 and Figs S1–S3.

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