Clay content of a clayey diatomite, the Early Eocene Fur Formation, Denmark

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Pedersen, G.K., Pedersen, S.A.S., Steffensen, J. & Pedersen, C.S. 2004–12–15. Clay content of a clayey diatomite, the Early Eocene Fur Formation, Denmark. *Bulletin of the Geological Society of Denmark*, Vol. 51, pp. 159–177. © 2004 by *Geological Society of Denmark.* ISSN 0011–6297. https://doi.org/10.37570/bgsd–2004–51–11

The Early Eocene Fur Formation is a clayey diatomite interbedded with layers of volcanic ash. The diatomite is non-calcareous, laminated or structureless, and thin sections show that the proportion of clay-sized particles to diatom frustules varies between laminae. The clay mineral phase has been isolated and its chemical composition has been determined by X-ray fluorescence (XRF). Clay min-eralogical analyses based on X-ray diffraction (XRD) show that the dominant phase is smectite. A
general formula for the clay mineral phase is: $X_{0.1}K_{0.2}(Mg_{0.3}Fe(III)_{0.3-0.7}Al_{1.1-1.4})Si_4O_{10}(OH)_2$.

The investigation indicates that the clayey diatomite of the Fur Formation comprises three com-ponents: diatom frustules, clay minerals and volcanic dust. The chemical compositions of bulk sam-ples have been determined. The clay mineral content is calculated to be 30–45% (by weight). Vol-canic dust constitutes c. 10% of the diatomite, and the rest is diatoms (opal-A). The diatom frustules contain some Al_2O_3 that is either of primary or diagenetic origin.

Key words: Diatomite, clay minerals, chemical composition, Fur Formation, Early Eocene, Denmark.

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Modern diatomaceous oozes may be described as clayey, calcareous or pure (Hay, Sibuet *et al.* 1984). A similar subdivision of fossil diatomites may be possible provided that the relative amounts of diatom frustules, carbonates and clay minerals can be determined.

Determination of the carbonate content is simple and accurate. The content of biogenic opal may be determined from X-ray diffractograms, and the method is successful in diatomites with little or no content of clay minerals (Bish & Post 1989; Pedersen *et al.* 1999; Steffensen *et al.* 2000; Steffensen 2001). The amount of clay minerals is more difficult to determine as the clay fraction is a mixture of clay minerals, fine debris of diatom frustules and volcanic dust. An initial estimate was based on the assumption that all Al_2O_3 was located within clay minerals. Determination of the clay mineral composition combined with the sediment bulk chemistry can therefore form the basis for calculation of the clay mineral content in the diatomite (Pedersen 1978). The clay minerals contribute significantly to the technical properties of diatomites. It is consequently both of academic and industrial interest to identify the type of clay minerals, to determine their composition and to calculate their amount in specific samples in order to estimate the average clay mineral content of the formation. The Fur Formation is a raw material for various powders, heat-isolating bricks and cat litter.

In the present study we have identified the clay minerals through X-ray diffraction (XRD), analysed their composition by X-ray fluorescence (XRF) and determined the minimum clay mineral content by separating clay minerals. Subsequently we have calculated the theoretical composition of the diatomite. The calculated amount of opal-A is compared to the method of opal-quantification from X-ray diagrams.

The material originates from an Lower Eocene dia-

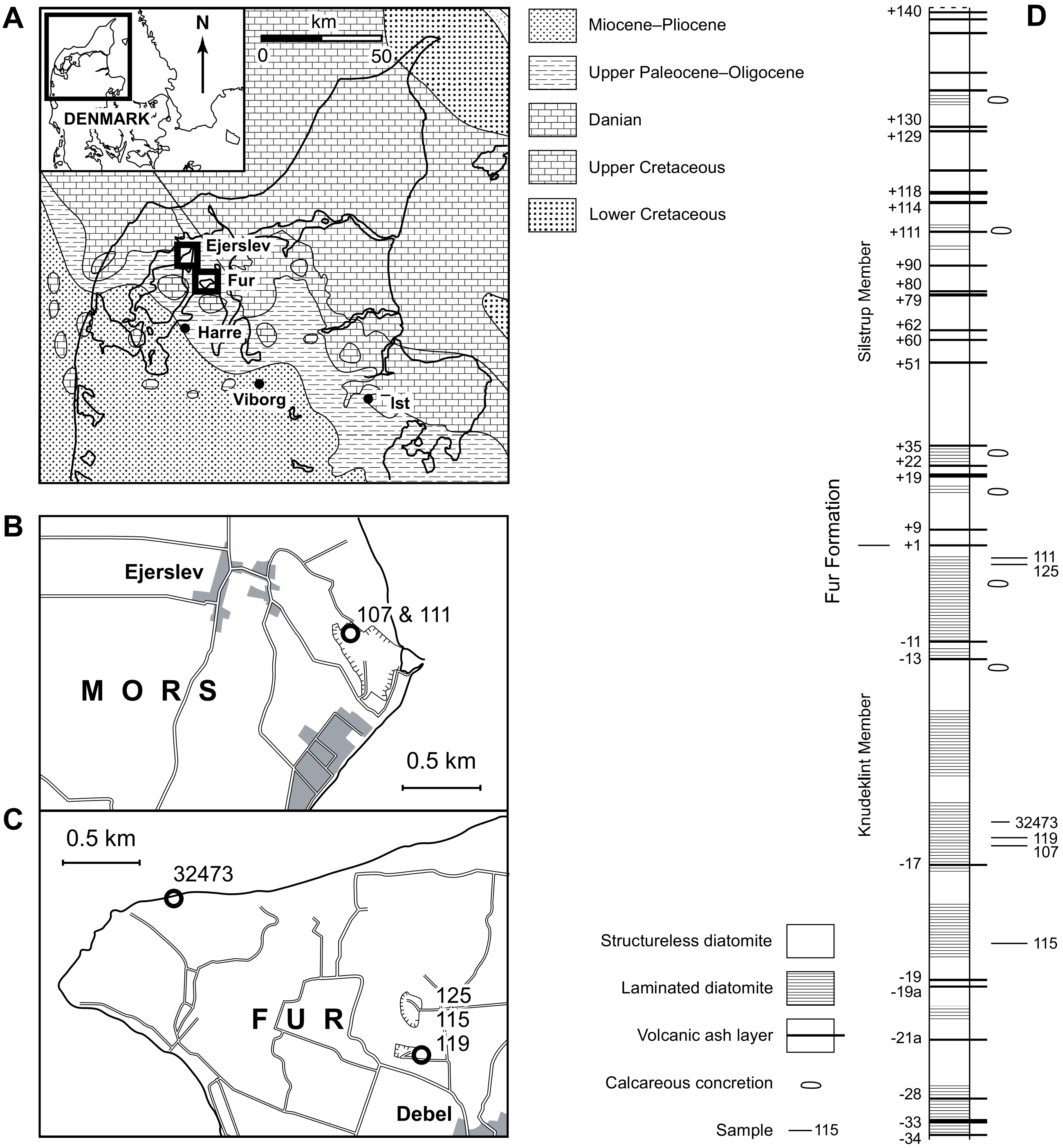

Fig. 1. A. Map showing the pre-Quaternary geology of northern Denmark. The Fur Formation is part of the Upper Paleocene – Oligocene clayey deposits. B. Location map of the pit at Ejerslev on the east coast of Mors; positions of samples 107 and 111 are circled. C. Location map of the northwest part of the island of Fur. Samples 115, 119, and 125 are from the pit north of Debel, and sample 32473 is from Knudeklint on the north coast of Fur. D. Sedimentological log through the Fur Formation showing the prominent ash layers, the alternation between laminated and structureless diatomite, and the stratigraphical position of the samples.

tomite, the Fur Formation in northern Jutland, Denmark. The Fur Formation consists of clayey, non-calcareous diatomite interbedded with relatively thin beds of volcanic ash and with calcareous concretions at certain stratigraphic levels (Bøggild 1918; Pedersen & Surlyk 1983; Pedersen & Buchardt 1996). The formation was deposited during intense activity of the North Atlantic Igneous Province and it is likely that volcanic dust was continuously added to the sediment. The clayey diatomite consists of detrital minerals (clay minerals, quartz and probably other minerals in amounts below limits of detection), volcanic dust, microfossils (biogenic opal, organic-walled), fragments of larger fossils, including plant debris and fish scales, and diagenetic minerals (pyrite, Fe-hydroxides, opal-C/T, gypsum, and calcite (in concretions)).

Geological setting

The Fur Formation comprises *c.* 60 m of diatomite interbedded with 179 numbered layers of volcanic ash (Pedersen & Surlyk 1983) (Figs 1, 2). The ash layers are distinct, 1–18 cm thick, with a sharp lower boundary and a sharp or gradual upper boundary, and consist of sand- and silt-sized particles (Bøggild 1918; Pedersen & Surlyk 1977; Pedersen 1981; Larsen *et al.* 2003). The volcanic ash layers have been studied as regards individual minerals, the composition and texture of the volcanic glass, as well as altered volcanic glass (Bøggild 1918; Pedersen *et al.* 1975; Rønsbo *et al.* 1977; Pedersen & Jørgensen 1981; Nielsen & Heilmann-Clausen 1988; Schmitz & Asaro 1996; Larsen *et al.* 2003; Schmitz *et al.* 2004). These studies have demonstrated that the ash layers below +1 vary in composition and include layers of tholeiitic, trachytic, rhyolitic, nephelinitic and phonolitic composition, whereas those above +1 are mostly enriched tholeiitic ferrobasaltic ash layers (Pedersen *et al.* 1975; Schmitz & Asaro 1996; Larsen *et al.* 2003).

Three phases of ash deposition are distinguished in the North Sea Basin (Knox & Morton 1988; Knox 1997). Their phases 2a and 2b comprise the ash layers in the Fur Formation, as well as those in the Sele and Balder Formations. Phase 2b is the phase of paroxysmal activity (Larsen *et al.* 2003). In Denmark, outside the study area, the ash layers are documented from the Ølst Formation (Bøggild 1918; Andersen 1937; Heilmann-Clausen *et al.* 1985; Nielsen & Heilmann-Clausen 1988). The Ølst Formation comprises clay with few, badly preserved diatoms and is subdivided into the Haslund and Værum Members (Andersen 1937; Heilmann-Clausen *et al.* 1985). The Haslund Member consists of a lower part of parallel-laminated, almost ash-free, greyish to olive-black clay overlain by dark clays interbedded with a few volcanic ash layers, mostly <1mm thick. The Værum Member consists of clays interbedded with volcanic ash beds that amount to almost half the thickness of the member.

On a regional scale the clayey diatomite of the Fur Formation passes laterally into clay both south eastwards (Ølst Formation) and westwards (Sele and Balder Formations). The transition between the lithologies is not gradual since an interfingering of the lithologies is observed in the Harre borehole (Nielsen *et al.* 1994) and the K-1, C-1 and Inez-1 wells (Danielsen & Thomsen 1997).

Pedersen & Surlyk (1983) indicated a transition from clay-rich diatomite to diatomite around ash layer –34 and stated that the succession below ash layer –34 was at that time neither exposed nor described in detail in older works. The succession with ash layers –39 to –34 was exposed for several years in the Hestegården pit on Fur and comprises *c.* 4.5 m of zeolite-bearing laminated clay (Pedersen 2000). Heilmann-Clausen *et al.* (1985) referred the black laminated clay (below ash layer –33) on Fur and Mors to the Haslund Member of the Ølst Formation. Later it was distinguished as a separate lithostratigraphic unit, the informal Stolle Klint Clay (Heilmann-Clausen 1995) or Stolleklint Clay (Beyer *et al.* 2001). It correlates with the lower part of the Sele Formation as this is defined by Schiøler *et al.* (2003), or to the lower to middle part of the Sele Formation according to Knox (1997).

Ash layers –17 and +19 are chemically distinct and have been traced regionally in much of the North Atlantic (Knox 1996a, b, 1997; Larsen *et al.* 2003). They have been dated radiometrically to 54.52 ±0.05 Ma (layer –17) and 54.04±0.14 Ma (layer +19) (Chambers *et al.* 2003). The biostratigraphy (Dinoflagellate zones 6–7) previously indicated a latest Paleocene or earliest Eocene age (Hansen 1979; Heilmann-Clausen 1985, 1994; Berggren *et al.* 1995; Knox 1997). On the basis of the diatoms the formation was interpreted as Lower Eocene (Fenner 1994). The uncertainty was due to the lack of an international definition of the Paleocene/Eocene boundary. Recently the global Paleocene/Eocene boundary has formally been placed at the base of the CIE (global carbon isotope excursion) (ISPS Newsletter No. 9, Nov. 2000). In Denmark the Paleocene/Eocene boundary is thereby placed between the Holmehus and Ølst Formations, and the Fur Formation entirely belongs in the earliest Eocene (Heilmann-Clausen & Schmitz 2000; Beyer *et al.* 2001; Schmitz *et al.* 2004).

The late Paleocene and early Eocene climate was warm (Buchardt 1978; Schmitz *et al.* 2000; Crouch *et al.* 2001) and the conditions were thus excellent for weathering of volcanic ash. The volcanic ash layers, which are recognized in the Ølst and Fur formations, probably also covered the terrestrial areas surrounding the North Sea Basin and there became weathered to clay. The same assemblage of detrital clay minerals is therefore expected in the Ølst and Fur Formations. Both formations are found to be rich in smectite (Unmack 1949; Tank 1963; Nielsen 1974; Pedersen 1981; Heilmann-Clausen *et al.* 1985; Mikkelsen & Andreasen 1985; Nielsen *et al.* 1986; Zhang 1987; Nielsen & Heilmann-Clausen 1988; Mikkelsen 1989; Thomsen 1992; Huggett 1993). Kaolinite is present in the Ølst Formation (Nielsen 1974; Pedersen & Petersen 1986; Zhang 1987) and has been recorded in the Fur Formation in small amounts (Pedersen *et al.* 1999). Small amounts of detrital mixed-layer minerals may also have derived from the chalk (Tank 1963; Håkansson *et al.* 1974; Lindgreen *et al.* 2002) exposed to the east of the study area.

Palaeogeographical reconstructions suggest that the Danish Basin and the North Sea Basin received most of the run-off (including clay minerals carried in suspension) from the terrains surrounding the semi-enclosed North Sea Basin (Ziegler 1990; Gibbard & Lewin 2003). A strong negative shift of $\delta^{13}C$ is recorded in the Stolle Klint Clay at Ølst and Storebælt corresponding to the global LPTM (late Paleocene thermal maximum) spike (Heilmann-Clausen & Schmitz 2000). The stratigraphic coincidence of three early basaltic ashes with the base of the CIE in the Ølst section suggests that the CIE may have been triggered by the basaltic volcanism associated with the opening of the Greenland-Norwegian sea (Schmitz *et al.* 2004).

Previous investigations

The Upper Paleocene and Eocene deposits of the Danish Basin are characterized by a high content of smectite. The mineralogy and chemical composition of the Holmehus Formation, the Ølst Formation and the clay at Holmstrup has been studied by Tank (1963), Nielsen (1974), Petersen & Buch (1974), Mikkelsen & Andreasen (1985), Zhang (1987), Nielsen & Heilmann-Clausen (1988), Mikkelsen (1989), Thomsen (1992), Huggett (1993) and Nielsen (1998).

The earliest XRD-studies of the Fur formation showed the presence of quartz, montmorillonite and, in few samples, kaolinite, and it was suggested that Na^+ is the exchangeable cation (Unmack 1949). A later study of bulk samples of the Fur Formation concluded that this is dominated by amorphous material, opaline diatom frustules and volcanic glass, in addition to which minor amounts of montmorillonite, illite and quartz are present (Tank 1963).

A sedimentological study of the Fur Formation included a small number of chemical analyses of sediment bulk composition as well as clay mineralogical analyses (Pedersen 1978). The bulk chemical composition was determined by atomic absorption spectrometry (AAS) after removal and determination of the amounts of Al and Fe occurring as 'free oxides'. These were insignificant compared to the compositional variance between the bulk samples. The clay mineralogical analyses showed that smectite is the dominant clay mineral and the diffractograms indicated very small amounts of illite (Pedersen 1978). The chemical composition of the clay minerals in the Fur Formation was proposed to be: $M^+_{0.4}(Al_{1.6}Fe^{3+}_{0.2}Mg_{0.2})(Al_{0.2}Si_{3.8}O_{10})(OH)_2$. This formula represents a dioctahedral mineral where the M^+-ions compensate for equal charge deficiencies in the octahedral and tetrahedral layers. On the basis of the formula above, and assuming that all Al_2O_3 was located in the clay minerals, the clay mineral content was calculated to range from 30–44% (Pedersen 1978).

The companies DAMOLIN A/S and SKAMOL A/S provided some of their own analyses from samples, which represent the best quality of a raw material, stratigraphically between ash layers –17 to +9 (S. Johansson, personal communication 1997). He assumed that the composition of the detrital clay minerals in the Fur and Ølst formations was similar (25% illite and 75% montmorillonite) and calculated that the average clay mineral content in the Fur Formation was c. 50% (by weight) on the assumption that all Al_2O_3 was located in the clay minerals (S. Johansson, personal communication 1997). A stratigraphic succession of Holmehus Formation, Ølst Formation and the lower part of the Fur Formation (between ash layers –19 and –13) has been cored in the shallow well Erslev-23 (Pedersen & Jørgensen 1989; Thomsen 1992). A total of 22 samples were examined; 18 of clayey diatomite, 1 of silicified diatomite and 3 of the clay underlying the Fur Formation. Thomsen (1992) studied the physical, chemical and mineralogical changes of the diatomite during heating, and the thermal stability of the diatomite was controlled primarily by the smectite content.

The Ølst Formation is contemporaneous with the Fur Formation. In the Ølst Formation the volcanic ash layers are strongly argillized. The volcanic glass in the ash beds from the Værum Member has been replaced by authigenic smectite, carbonates, and to a lesser extent, pyrite, titanite and zeolites. The authigenic clay is an iron-rich smectite (Huggett 1993).

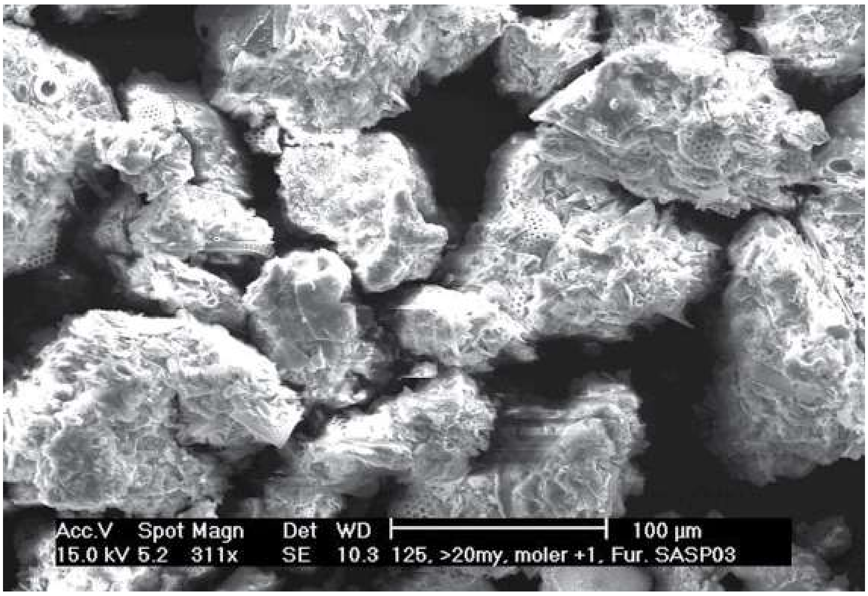

Fig. 2. SEM photomicrograph of aggregates in the fraction >20µm of the diatomite (sample 125). The aggregates are seen to consist of diatom frustules as well as fine particles that are not visually identifiable. Their chemical composition (Tables 4A–8A) compared to the bulk samples suggests that the aggregates may be held together by aluminium hydroxides.

Compared to Ølst the ash layers in the diatomite are distinct and alterations appear to be slight, probably due to different pore water chemistry. However, volcanic glass and diatom frustules are better preserved within the calcareous concretions than outside (Pedersen & Jørgensen 1981). This shows that the concretions have sealed the volcanic ash against diagenetic changes. If the volcanic glass undergoes diagenetic alterations it is possible that the diatom frustules might also react with circulating pore waters.

Materials and methods

The present study is based on five samples (No. 115, 107, 119, 125, 111) from the Knudeklint Member of the Fur Formation (Fig. 1). The samples were collected in clay pits (Pedersen *et al.* 1998). Joints coated with iron hydroxides were avoided during sampling. The pit at Fur (located on private property matr. nr. 29a) is no longer accessible. The pit at Ejerslev is accessible, but the sampled section no longer exists. Each sample has provided five or six sub-samples (Tables 1, 4–8), all of which have been chemically analysed, whereas X-ray diffraction or examination by scanning electron microscope has been restricted to some sub-samples. At a late stage of the investigation a large sample of diatom frustules was needed. Too little untreated material remained from the original samples, and an additional sample, No. 32473 from Fur Knudeklint 2 m above ash layer –17, was therefore included in the study.

Separation according to grain-size

The samples were gently crushed to particles finer than 250µm. This powder was split into four portions, two for XRF and XRD analyses of the bulk composition, and the third for isolation of particles <0.2µm using a separation flask and centrifuge (Slater & Cohen 1962). Later in the investigation the composition of the fractions >20µm, 20–2µm and <2µm were required and the fourth portion of the bulk sample was first split into these fractions. The clay minerals were isolated from the fraction <2µm, and the remaining clay fraction is referred to as the residual (Tables 1, 4–8). The clay minerals were isolated from the fraction <2µm by repeated resuspension and centrifugation. The clay particles in suspension were retrieved by flocculation through addition of 0.5 M NaCl, decantation of superfluous liquid, and were washed thrice with 50% ethanol to remove excess ions. The samples were dried at room temperature, weighed and the isolated amounts of clay minerals were determined (Table 1: isolate). However, an amount of clay minerals remained within aggregates in the fractions >20µm and 20–2µm, and the isolate is therefore the minimum amount of clay minerals in a sample. The measured Na_2O-values in Tables 4–8 are misleading except for the bulk-samples because of the addition of NaCl.

Table 1. Grain-size distribution of bulk samples of the diatomite. Each of these fractions has been analysed (Tables 4A–8A). The fine clay particles, <0.2μm, were separated from a different portion of the bulk sample and were not weighed.

Sample	> 20 μm		2–20 μm		< 2 μm, Residual		< 2 μm, Isolate		Total weight
	g	%	g	%	g	%	g	%	g
111	16.88	15.4	62.38	56.8	21.57	19.6	9.09	8.3	109.92
125	21.62	17.6	70.40	57.3	22.45	18.3	8.38	6.8	122.85
119	10.47	8.8	78.23	41.4	17.00	14.3	13.19	11.1	118.89
107	12.66	12.0	67.98	64.5	14.78	14.0	9.93	9.4	105.35
115	23.62	26.7	62.89	71.0	1.92	2.2	0.12	0.1	88.55

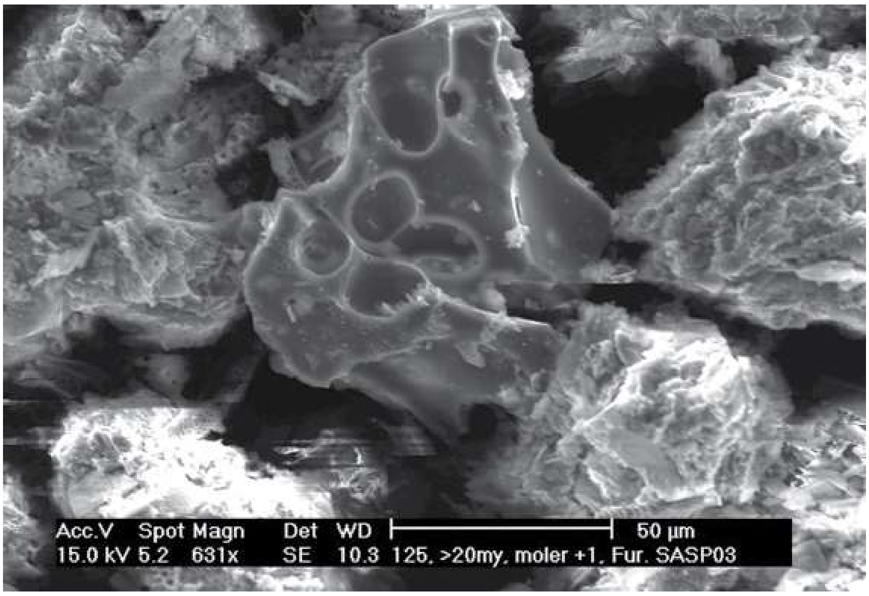

Fig. 3. SEM photomicrograph of volcanic glass in diatomite (sample 125). Diagnostic features such as vesicles are easier to observe on larger grains than on the silt- to clay-sized shards of volcanic glass.

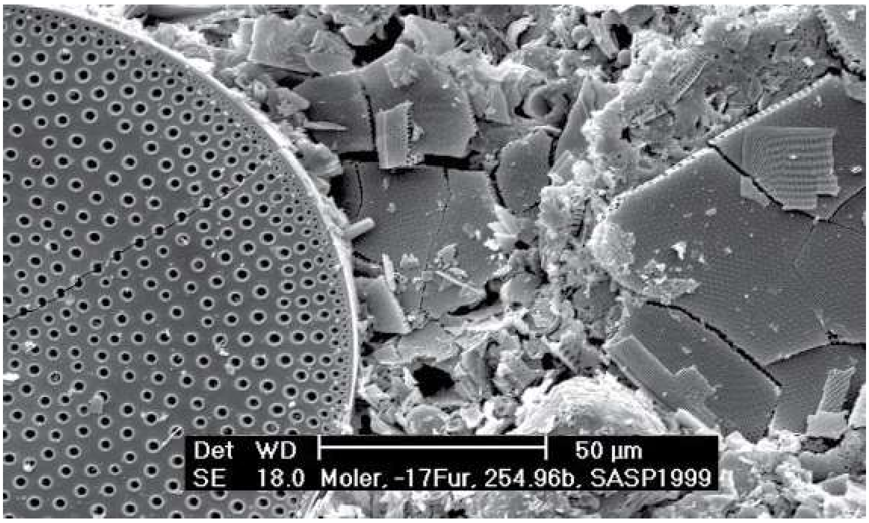

Fig. 4. Diatom frustules with well-preserved fine details, indicating that diagenetic alterations were minimal. SEM photomicrograph of sample stratigraphically below 115.

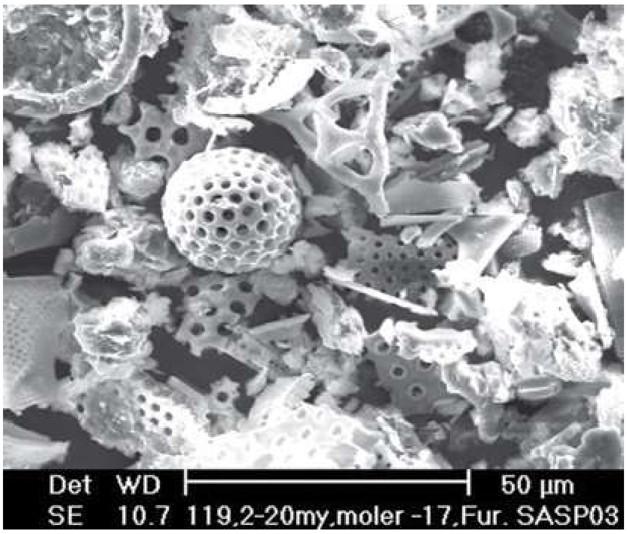

Fig. 5. The fraction 2–20µm is seen to contain both diatom frustules (complete or broken), silicoflagellates and aggregates. SEM photomicrograph of sample 119.

Scanning electron microscopy (SEM, EDAX)

All sub-samples of particles >20µm, 20–2µm and the residual<2µm were examined in a scanning electron microscope (SEM) for the types of particles present and their occurrence as individual particles or aggregates (Figs 2–5). The visual observations were supported by semi quantitative element analysis (EDAX), either as 'spot' analyses of individual particles (diameter of beam <3µm) or as area scanning analyses.

Quantification of opal (XRD)

The amount of opal (biogenic opal-A or recrystallized opal-C/T) may be determined in diffractograms of bulk samples (Bish & Post 1989; Pedersen *et al.* 1999; Steffensen *et al*. 2000; Steffensen 2001). Material from the bulk samples was analysed by X-ray diffraction in the interval 20–40° 2Θ at steps of 0.05° 2Θ. The volume of opal-A and opal-C/T was calculated as the area above the base line between 20.00–37.00° 2Θ (Fig. 6). The base line is defined as the average of 10 XRD-readings above and below the broad opal bulge. XRD-peaks, which overprint the opal bulge, were subtracted. The measured bulge was compared to a standard, chosen in a 2mm thick lamina dominated completely by *Coscinodiscus* frustules from the Fur Formation (Pedersen *et al.* 1999) (Fig. 6). The instruments used were a Philips 1050 goniometer with Co-Kα radiation, β-filter and pulse height selection, and a Philips 3050 goniometer with a monochromator.

Isolation of diatom frustules

Sample 32473 was crushed, suspended in distilled water and treated with ultrasonification for 15 minutes. The sample was left for *c.* 20 minutes to allow the frustules to settle, whereas the clay-sized particles remained in suspension. Water and suspended clay were decanted and the diatom frustules resuspended. After repeated washings the frustules were inspected under the microscope, and the sample was seen to consist entirely of diatoms frustules, apparently without impurities. A sample of the diatoms was analysed by XRF in order to determine their chemical composition (Table 3).

Chemical analyses (XRF)

The chemical composition, major as well as trace elements, for both bulk samples and the fine clay fractions was analysed by XRF according to the procedures described by Kystol & Larsen (1999). Only the major elements are shown in Tables 4–8. FeO was determined by dissolution and titration according to the method in Kystol & Larsen (1999).

Bulk mineralogy by (XRD)

The bulk samples were run from 5°–85° 2Θ at steps of 0.1° 2Θ. The analyses were performed with a Philips 1050 goniometer with Co-Kα radiation, β-filter and pulse height selection, as well as a Philips 3050 goniometer with a monochromator (Fig. 6, Table 2).

Clay mineralogy

Samples of the clay fraction were treated according to the standard method at the Clay Mineralogical Laboratory at GEUS. A portion of the bulk sample was selected. Calcite was removed by addition of acetic acid ($C_2H_4O_2$) until the pH of the suspension remained below 4.5 for more than a few seconds. Subsequently NaOH was added until pH=5 and the suspension was left overnight. After ultrasonification, particles >20µm were removed in a separation flask. The 2–20 µm fraction was removed from the suspension in a centrifugal particle size separator (Slater & Cohen 1962) with addition of demineralised water. After removal of sand- and silt-sized particles the clay fraction was retrieved from suspension by addition of NaCl. Excess water was removed by decantation and centrifugation. The samples were

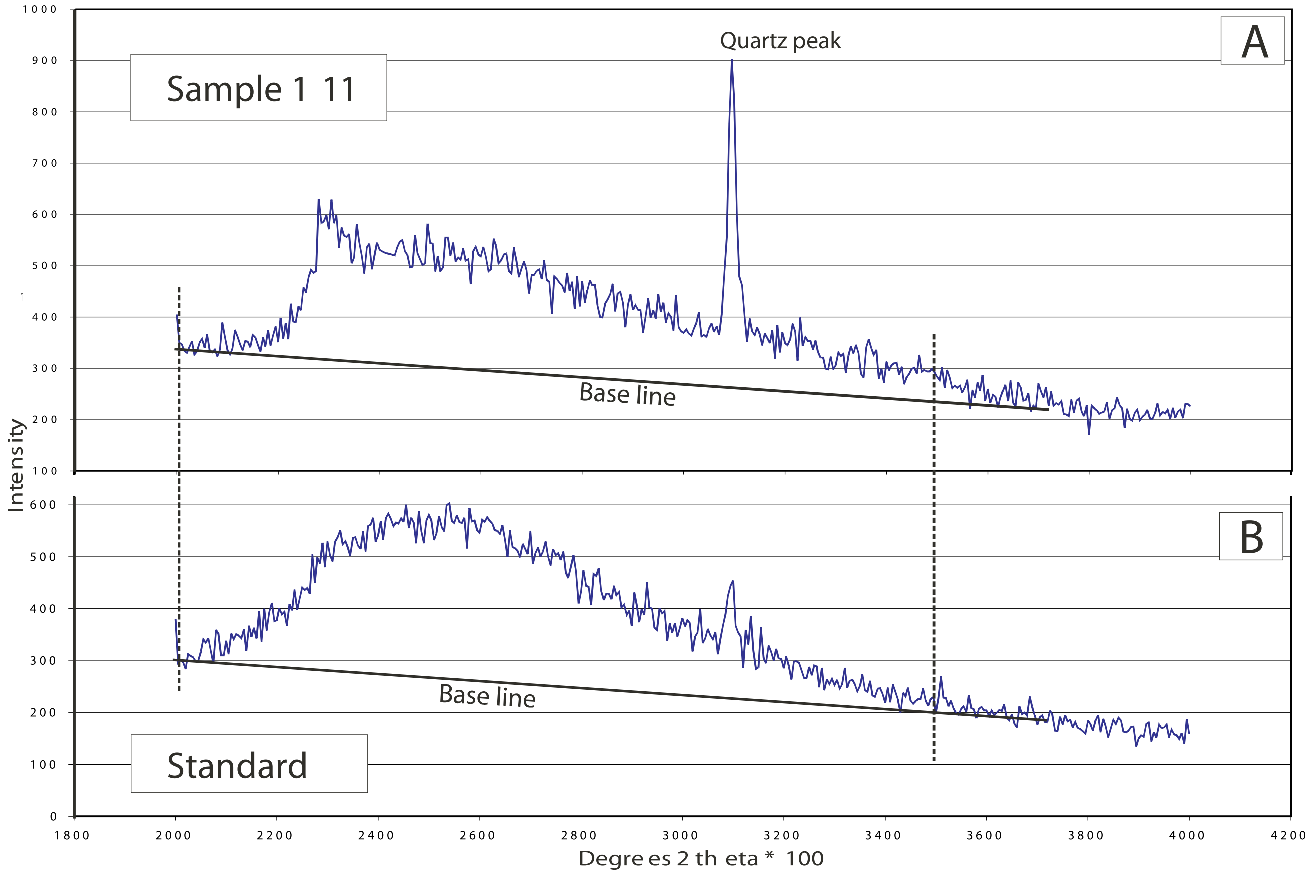

Fig. 6. X-ray diffractogram of randomly oriented powder, bulk sample 111, showing the presence of clay minerals and quartz (A). A standard of pure opal-A from the Fur Formation is shown for comparison (B). The opal content is proportional to the area between the base line and the 'opal bulge'. The contents of opal-A calculated by this method are given in Table 2.

washed thrice with 50% ethanol to remove excess ions, and the samples were left to dry. Finally the samples were saturated with Mg^{2+} and K^+ prior to XRD-analysis.

Oriented specimens were prepared by the pipette method, and the following specimens were analysed: Mg^{2+}-saturated and dried; Mg^{2+}-saturated and glycerolated; K^+-saturated and dried; and K^+-saturated and heated to 300° C to ensure identification of the clay minerals by XRD (Figs 7, 8). The instruments used were a Philips 1050 goniometer with Co-Kα radiation, β-filter and pulse height selection, and a Philips 3050 goniometer with a monochromator.

Calculation of sediment composition

Theoretically, biogenic opal, clay minerals and volcanic dust account for almost all the major elements of a bulk sample. The biogenic opal was only analysed once, and these values have been used in the calculations for all samples. The volcanic dust is presumed to be similar in composition to ash layer –13 (samples 107, 119) and ash layer +1 (samples 111, 125) from Larsen *et al.* (2003). The isolate (Tables 4A–8A) with subtraction of excess silicon represents the chemical composition of the clay minerals. The clay mineral composition varies slightly between the samples. The proportion of these three components was found by solving the appropriate mathematical equations (Tables 5B–8B). The 'Rest' indicates the amount by which the sum of the three components deviates from the bulk composition.

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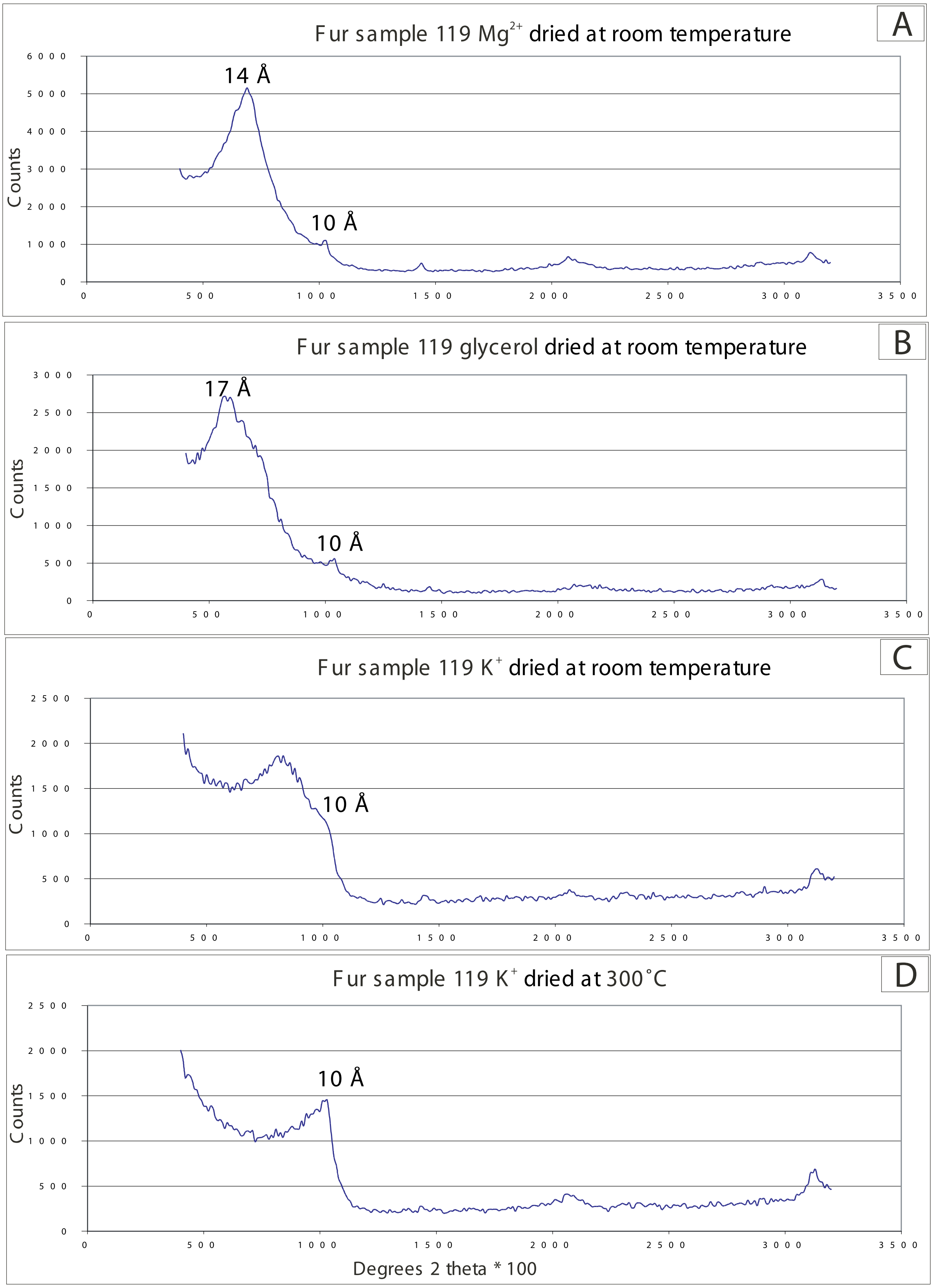
Fig. 7. Identification of the clay minerals in the Fur Formation (sample 119). Comparison of the four sub-samples A) Mg-saturated, B) Mg-saturated with glycerol, C) K-saturated, and D) K-saturated and heated to 300°C, indicates that smectite is dominant and that small amounts of illite are present.


A
Fur sample 119 Mg^{2+} dried at room temperature
Counts
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1000
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B
Fur sample 119 glycerol dried at room temperature
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C
Fur sample 119 K^{+} dried at room temperature
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Fur sample 119 K^{+} dried at 300°C
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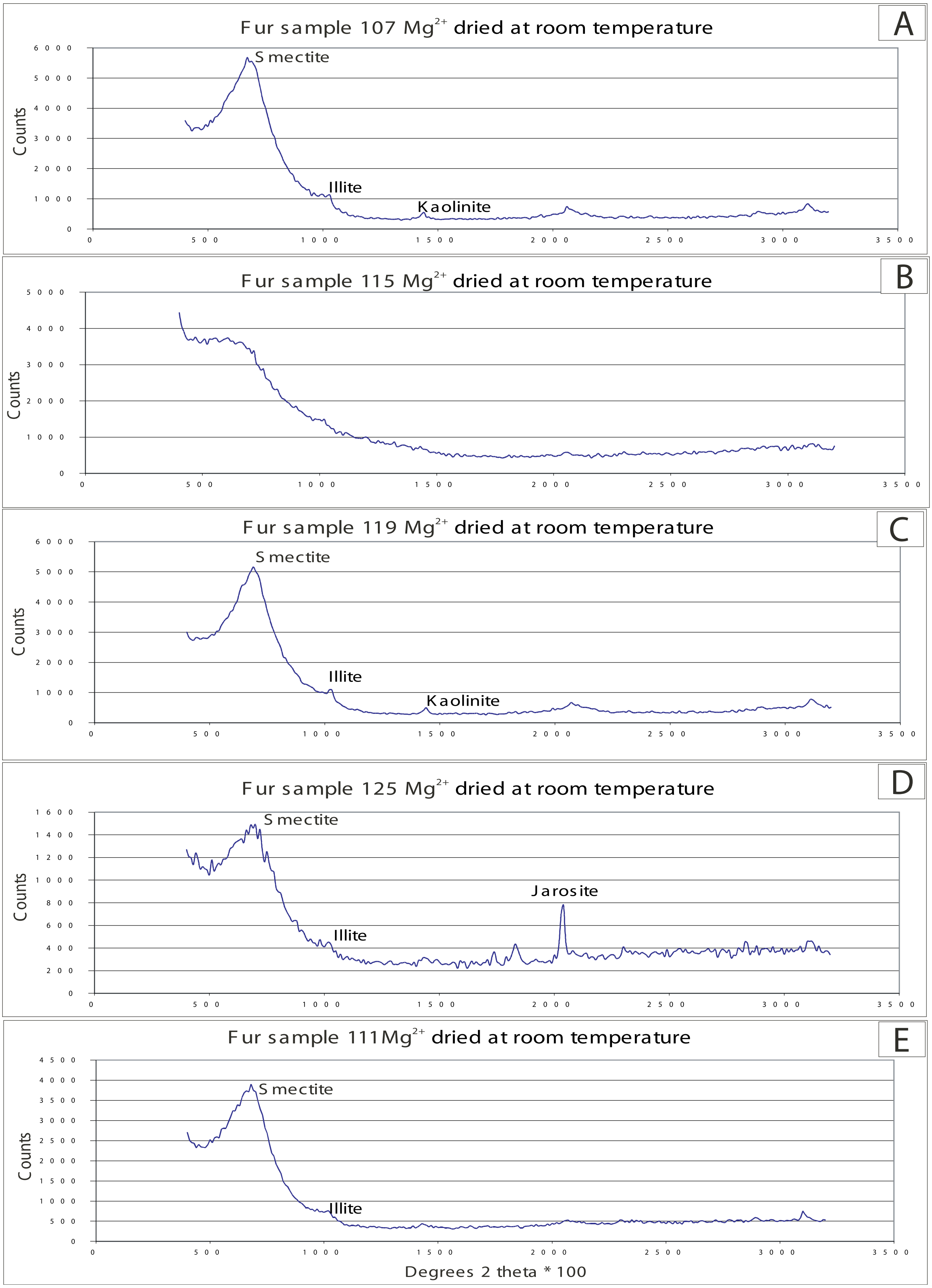
A
Fur sample 107 Mg2+ dried at room temperature
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Fur sample 115 Mg2+ dried at room temperature
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Fur sample 125 Mg2+ dried at room temperature
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Fur sample 111Mg2+ dried at room temperature
Counts
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Smectite
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Results

Bulk mineralogy and opal content (XRD)

The diffractograms of the bulk samples document the presence of clay minerals (peaks at 5–10° 2Θ, corresponding to *c.* 14Å and 10Å), opal-A (broad peak at 20–37° 2Θ, or 5.2–2.8Å) and quartz (strongest peak at 31° 2Θ, corresponding to 3.34Å) (Fig. 6). Jarosite, pyrite, and opal-C/T are present in some samples (Table 2). Additional minerals may be present in amounts below the detection limit of the diffractograms. Calculation of the opal content from the areas below the opal bulge indicate values from 65% (by weight) in sample 119 to 73% in sample 115 (Table 2). These values clearly differ from those calculated from the XRF–data, as is discussed below.

Bulk chemical composition (XRF)

The chemical analyses of the bulk samples of the clayey diatomite show that the quantitatively most important elements are silicon, aluminium and iron. The diatomite contains smaller amounts of titanium, magnesium, calcium, sodium and potassium, whereas manganese and phosphorus are negligible (Tables 4A–8A). The relatively large contents of volatiles are derived from opal-A and clay minerals.

The SiO_2 content reflects opal-A and silicates, especially clay minerals. The measured Al_2O_3 is primarily located in clay minerals. The measured amount of Fe_2O_3 varies considerably. It is attributed to clay minerals, volcanic dust, pyrite and diagenetic minerals including goethite? that coats joints, and which was probably leached from the volcanic ash layers or from pyrite in the diatomite. The bulk chemical composition varies considerably from one sample to another. Comparable variations are seen in analyses provided by S. Johansson (written communication 1997).

Silt- and sand-sized particles (SEM)

The SEM-inspection of particles >20µm showed that these, contrary to expectation, were not individual diatom frustules but were dominantly aggregates of diatomite (Fig. 3). The aggregates suggest that the diatomite is consolidated or weakly cemented. The fractions >20 µm and 2–20 µm comprise a small number of grains of volcanic glass (Fig. 4). The presence of silt-sized ash particles outside the ash layers supports the assumption that finer volcanic dust may also be present. The visual inspection of samples with numerous fine particles was problematical, as the SEM-images of particles smaller than 5 µm become increasingly blurred and make identification difficult.

Table 2. Bulk mineralogy of samples from the Fur Formation, determined from X-ray diffractograms. The amount of opal-A is calculated from the opal bulge. These values are higher than those calculated on basis of the chemical composition (Tables 5B–8B). It is suggested that volcanic dust, and possibly clay minerals, contributes to the opal bulge.

Sample	Opal-A %	Quartz	Opal-CT	Pyrite	Jarosite	Clay minerals
111	77	++	?	-	-	++
125	76	+	?	-	+++	+
119	59	++	?	-	+	+++
107	71	-	?	-	-	++
115	72	++	?	+	-	+++

Chemical composition of silt- and sand-sized particles and aggregates (XRF)

Analyses of the particles and aggregates that constitute the fraction >20 µm, 2–20 µm, and the residual of the clay fraction are presented in Tables 4A–8A. It is clearly seen that the chemical composition varies with the grain-sizes. The most surprising result is that the Al_2O_3-content is consistently high in the fraction >20 µm, intermediate in the 2–20µm fraction and low in the residual of clay-sized particles (Tables 4A–8A).

The SiO_2:Al_2O_3:Fe_2O_3 ratios for the various grain-size fractions of each sample are plotted in Fig. 9, which shows that the >20 µm fraction is depleted in SiO_2 and the 2–20 µm fraction is enriched in SiO_2 relative to the bulk samples. The highest SiO_2-contents are recorded for the residual (Fig. 9). The SEM photomicrographs show that most particles in the fraction >20µm are aggregates, and the Al_2O_3-enrichment is interpreted as reflecting cementation by Al-oxides or hydroxides, possibly initiated by the devitrification of volcanic glass. The fine silt fraction, 2–20 µm, is a mixture of fragments of diatom frustules and aggregates and its chemical composition is intermediate between those of the residual and the fraction >20 µm. The residual consists almost entirely of frag-

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Fig. 8. Comparison of XRD of Mg-saturated sub-samples from samples 107 (A), 115 (B), 119 (C), 125 (D) and 111 (E). It is seen that all samples are dominated by smectite, and that little illite is present. Locally kaolinite is present in trace amounts.

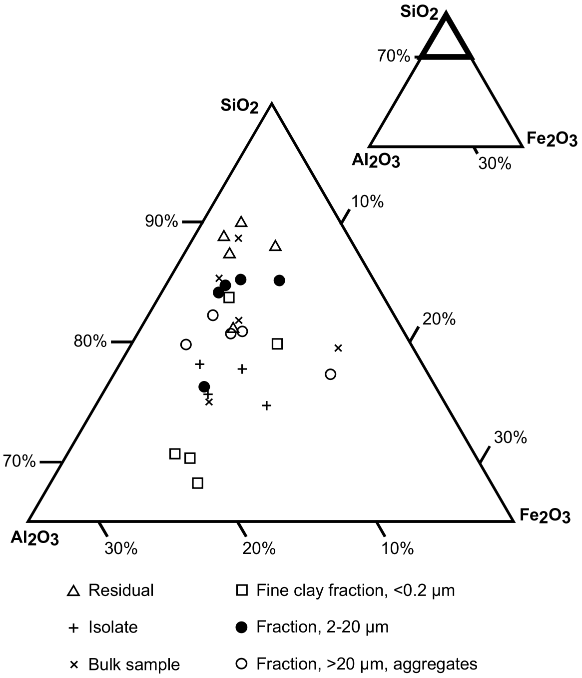

Fig. 9. Triangular plot of the Fe_2O_3:Al_2O_3:SiO_2 ratios of the studied samples. The highest SiO_2-content is found in the residual, the clay-sized fragments of diatoms. The highest Al_2O_3-content is found in the fraction <0.2µm, consisting of clay minerals and volcanic dust. The isolate consists of clay minerals <2µm, but its chemical analyses (Tables 5A–8A) show an excess of SiO_2 compared to the formula for the clay mineral phase. In this plot the isolate is seen to contain more SiO_2 than the fine-clay fraction, suggesting that 'excess SiO_2' in the isolate is present as fragments of diatom frustules.

ments of diatom frustules as shown by the chemical composition and the SEM photomicrographs. The high Al_2O_3-content of the fine clay fraction (<0.2 µm) is attributed to a mixture of clay minerals and volcanic dust (Fig. 9).

Chemical composition of the diatoms (XRF)

The diatom frustules were analysed by XRF. The single analysis shows that the diatom frustules are not pure $SiO_2{\cdot}nH_2O$ but that they contain 5% Al_2O_3 and small amounts of other elements (Table 3). Uptake of Al in diatom frustules is reported in studies of recent diatoms (Konno 1993; Hall *et al.* 1999). The possibility of the uptake of alumina being diagenetic may also be considered. However, opal-C/T has not been detected above trace amounts in the studied samples, and SEM photomicrographs document that very fine details in the diatom frustules are preserved (Fig. 4). It is therefore assumed that dissolution of opal-A was at a minimum. This is supported by observations of material from the Harre borehole, where the preservation of diatoms is better in diatom-rich material and where dissolution of diatoms leads to the formation of small amounts of clinoptilolite (Fenner 1994).

Table 3. Chemical composition of diatom frustules from sample 32473. Note especially their content of alumina, which contribute to the bulk chemical composition of the Fur Formation because the diatoms are volumetrically important. Sample 32473 is stratigraphically close to samples 107 and 119, but comparison shows that the bulk chemistries are different. This is probably due to various proportions of diatom-rich and more clay-rich laminae.

Sample 32473	Diatom frustules	Bulk sample
SiO_2	82.46	79.65
TiO_2	0.26	0.45
Al_2O_3	3.28	5.45
Fe_2O_3	0.84	1.28
FeO	0.00	0.00
MnO	0.00	0.00
MgO	0.19	0.48
CaO	0.05	0.14
Na_2O	0.31	0.73
K_2O	0.50	0.81
P_2O_5	0.02	0.04
Volatiles	7.64	7.91
Sum	95.55	96.94

Clay mineralogy (XRD)

The diffractograms of sub-samples of clay minerals document that smectite is the dominant phase (Figs 7, 8). Smectite is detected from the peak at 18 Å in the Mg-glycerol sub-sample, at 14 Å in the Mg sub-sample and at 10 Å in the K sub-sample heated to 300° (Fig. 7). The presence of small amounts of an illite phase is suggested by a small 10 Å peak in all sub-samples, except those from sample 115. The diffractograms show that smectite is by far the dominant mineral (Fig. 8). If illite is randomly interbedded with smectite, the relative proportion of the two phases may be difficult to determine from the X-ray diffractograms.

Chemical composition of the clay mineral phase (XRF)

The chemical compositions of the clay mineral phases ('isolate') have been determined by XRF (Tables 5A–8A). Sample 115 provided less material (isolate) than required for analysis. The analyses show that the iso-

Table 4. Chemical composition of various fractions of sample 115. The major elements were analysed by XRF. In this sample the amount of isolate is too small for analysis. In some sets of samples FeO was not determined (n.d.).

			Measured			
Sample 115	Bulk	<0.2 µm	Isolate	Residual	2–20 µm	>20 µm
SiO_2	62.18	55.23		69.11	63.01	66.93
TiO_2	1.27	1.71		1.38	1.48	1.53
Al_2O_3	14.10	17.08		10.33	13.92	13.66
Fe_2O_3	6.39	8.49		5.74	5.50	1.86
FeO	n.d.	n.d.		n.d.	n.d.	2.99
MnO	0.06	0.03		0.01	0.02	0.02
MgO	1.32	1.42		1.01	1.33	1.31
CaO	0.18	0.10		0.21	0.16	0.29
Na_2O	0.45	3.31		0.96	2.57	1.27
K_2O	1.24	0.71		0.97	1.23	1.73
P_2O_5	0.15	0.19		0.17	0.17	0.15
Volatiles	11.24	10.55		7.22	8.52	6.50
Sum	98.58	98.82		97.11	97.91	98.24

late varies in composition between the samples. This may reflect a variation in the composition of the smectite phase, or varying proportions of two phases (smectite and illite). A general formula for the clay mineral phase is proposed:

$$X_{0.1}K_{0.2}(Mg_{0.3}Fe(III)_{0.3-0.7}Al_{1.1-1.4})Si_4O_{10}(OH)_2$$

This formula indicates a clay mineral that is relatively poor in Al_2O_3 due to the relatively high contents of silicon and iron. The cation X is presumed to be mainly Na^+ or Ca^{2+}. The isolate contains small amounts of titanium, phosphorus and iron(II) (Tables 4–8). The presence of these elements is probably due to trace amounts of other minerals. The elements are therefore not included in the general formula for the clay mineral phase. Comparison between this formula and the composition of the isolate shows that the isolate contains an excess of SiO_2 of c. 20%.

Table 5. Chemical composition and calculated composition of sample 107. A. Measured composition (XRF) of the various fractions of sample 107. B. The calculated composition of the sample expressed as percentages of diatoms, clay minerals and volcanic dust. Prior to this calculation the bulk analysis was recalculated as free of volatiles and all iron was recalculated as Fe_2O_3. The 'Rest' is the difference between the sum of the three components and the recalculated bulk analysis.

	A: Measured						B: Calculated					
Sample 107	Bulk	<0.2 µm	Isolate	Residual	2–20 µm	>20 µm	Bulk recalc.	Clay minerals	Diatoms	Volc. dust	Sum	Rest
Composition								43.1%	48.5%	8.4%	100.0%	
SiO_2	73.46	52.14	57.50	78.45	70.56	70.28	80.90	31.78	45.49	4.72	81.99	−1.09
TiO_2	0.66	0.88	0.74	0.58	0.74	0.91	0.73	0.41	0.15	0.35	0.91	−0.18
Al_2O_3	9.57	15.99	11.65	8.00	9.78	11.33	10.54	6.46	1.81	1.12	9.39	1.15
Fe_2O_3	3.28	5.57	4.13	1.34	3.51	3.60	3.40	2.35	0.46	0.78	3.59	−0.19
FeO	n.d.	n.d.	0.27	0.82	n.d.	0.78						
MnO	0.01	0.02	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.01	0.00	0.01
MgO	1.40	2.51	1.81	0.79	1.28	1.46	1.54	1.00	0.10	0.37	1.47	0.07
CaO	0.42	0.21	0.12	0.19	0.19	0.29	0.46	0.07	0.00	0.76	0.83	−0.37
Na_2O	0.28	8.10	8.83	1.07	3.15	1.31	0.31	0.04	0.17	0.18	0.39	−0.08
K_2O	1.61	2.21	1.79	1.15	1.57	1.82	1.77	0.99	0.28	0.08	1.35	0.42
P_2O_5	0.11	0.06	0.12	0.06	0.08	0.10	0.12	0.07	0.01	0.04	0.12	0
Volatiles	6.99	10.42	12.15	4.87	7.45	5.97						
Sum	97.79	98.11	99.11	97.32	98.31	97.85	99.78	43.17	48.47	8.41	100.04	

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Table 6. Chemical composition and calculated composition of sample 119. A. Measured composition (XRF) of the various fractions of sample 119. B. The calculated composition of the sample expressed as percentages of diatoms, clay minerals and volcanic dust. Prior to this calculation the bulk analysis was recalculated as free of volatiles and all iron was recalculated as Fe_2O_3. The ‘Rest’ is the difference between the sum of the three components and the recalculated bulk analysis.

	A: Measured						B: Calculated					
Sample 119	Bulk	<0.2 µm	Isolate	Residual	2–20 µm	>20 µm	Bulk recalc.	Clay minerals	Diatoms	Volc. dust	Sum	Rest
Composition								44.0%	44.3%	11.7%	100.0%	
SiO_2	69.76	55.51	60.23	75.48	71.19	68.93	77.19	31.21	41.55	6.57	79.34	–2.15
TiO_2	0.79	1.10	0.95	0.81	0.77	0.93	0.87	0.49	0.13	0.49	1.11	–0.24
Al_2O_3	9.81	16.29	13.46	8.11	9.26	10.63	10.85	6.97	1.65	1.56	10.18	0.67
Fe_2O_3	5.82	7.10	5.91	2.65	3.46	5.37	6.44	3.12	0.42	1.09	4.63	1.81
FeO	n.d.	n.d.	0.23	0.50	0.51	0.58						
MnO	0.02	0.03	0.01	0.00	0.00	0.01	0.02	0.01	0	0.02	0.02	0.00
MgO	1.52	2.75	2.21	0.93	1.35	1.62	1.68	1.15	0.10	0.51	1.47	0.21
CaO	0.43	0.18	0.07	0.12	0.17	0.26	0.47	0.04	0.03	1.05	1.12	–0.65
Na_2O	0.26	5.57	4.48	0.96	2.06	0.98	0.29	0.25	0.16	0.25	0.65	–0.36
K_2O	1.87	2.19	1.79	1.43	1.53	1.80	2.07	0.93	0.25	0.11	1.23	0.84
P_2O_5	0.11	0.05	0.18	0.08	0.11	0.13	0.12	0.09	0.01	0.05	0.10	0.02
Volatiles	8.19	7.74	9.34	5.21	7.02	6.13						
Sum	98.58	98.51	98.86	96.28	97.43	97.37	100.00	44.26	44.30	11.70	99.85	

Table 7. Chemical composition and calculated composition of sample 125. A. Measured composition (XRF) of the various fractions of sample 125. Note the very high content of Fe_2O_3. B. The calculated composition of the sample expressed as percentages of diatoms, clay minerals and volcanic dust. Prior to this calculation the bulk analysis was recalculated as free of volatiles and all iron was recalculated as Fe_2O3. The Rest’ is significantly higher than in the other samples due to the very high Fe_2O_3–content.

	A: Measured						B: Calculated					
Sample 125	Bulk	<0.2 µm	Isolate	Residual	2–20 µm	>20 µm	Bulk recalc.	Clay minerals	Diatoms	Volc. dust	Sum	Rest
Composition								13.5%	76.5%	10.0%	100.0%	
SiO_2	62.47	64.87	56.80	76.64	71.66	66.39	74.84	9.46	71.75	5.46	86.68	–11.84
TiO_2	0.89	1.05	1.62	0.83	1.01	1.34	1.06	0.27	0.23	0.38	0.88	0.18
Al_2O_3	4.37	7.82	9.85	4.92	5.53	6.15	5.24	1.64	2.85	1.40	5.89	–0.65
Fe_2O_3	11.79	8.57	9.24	5.44	6.66	13.34	14.12	1.56	0.73	0.91	3.20	10.92
FeO	n.d.	n.d.	0.24	0.21	0.22	n.d.						
MnO	0.01	0.01	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.02	0.02	–0.01
MgO	0.65	1.08	1.49	0.44	0.68	0.76	0.78	0.25	0.16	0.49	0.91	–0.13
CaO	0.72	0.21	0.19	0.23	0.34	0.44	0.87	0.03	0.04	0.97	1.04	–0.17
Na_2O	0.83	3.20	6.50	1.07	2.67	1.02	0.99	0.00	0.29	0.26	0.53	0.46
K_2O	1.55	1.41	1.54	0.66	0.96	0.90	1.86	0.26	0.44	0.07	0.35	1.51
P_2O_5	0.19	0.13	0.19	0.10	0.12	0.25	0.23	0.03	0.02	0.04	0.07	0.16
Volatiles	14.53	10.71	11.81	5.34	8.01	7.03						
Sum	98.00	99.06	99.47	95.88	97.86	97.62	100.00	13.50	76.51	10.00	99.57	

Table 8. Chemical composition and calculated composition of sample 111. A. Measured composition (XRF) of the various fractions of sample 111. B. The calculated composition of the sample expressed as percentages of diatoms, clay minerals and volcanic dust. Prior to this calculation the bulk analysis was recalculated as free of volatiles and all iron was recalculated as Fe_2O_3. The 'Rest' is the difference between the sum of the three components and the recalculated bulk analysis.

	A: Measured						B: Calculated					
Sample 111	Bulk	<0.2 µm	Isolate	Residual	2–20µm	>20 µm	Bulk recalc.	Clay minerals	Diatoms	Volc. dust	Sum	Rest
Composition								27.8%	64.8%	7.4%	100.0%	
SiO_2	77.63	72.30	61.81	80.36	71.53	69.57	85.09	20.48	60.78	4.04	85.31	–0.22
TiO_2	0.41	0.81	1.00	0.58	0.81	0.97	0.45	0.33	0.19	0.28	0.81	–0.36
Al_2O_3	6.83	9.74	10.47	6.47	8.25	10.12	7.4	83.47	2.42	1.04	6.92	0.56
Fe_2O_3	3.01	4.27	7.07	2.30	4.13	6.2	33.33	32.38	0.62	0.67	3.67	–0.34
FeO	n.d.	n.d.	0.24	0.23	0.25	0.24						
MnO	0.01	0.01	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.02	0.02	–0.01
MgO	1.14	1.46	1.61	0.68	1.15	1.46	1.25	0.53	0.14	0.37	1.04	0.21
CaO	0.76	0.30	0.23	0.25	0.45	0.55	0.83	0.08	0.04	0.71	0.83	0.00
Na_2O	0.21	2.14	5.50	1.31	2.50	1.29	0.23	0.04	0.23	0.19	0.46	–0.23
K_2O	1.15	1.23	1.32	0.87	1.33	1.54	1.26	0.44	0.37	0.05	0.86	0.40
P_2O_5	0.09	0.10	0.27	0.07	0.12	0.19	0.10	0.09	0.01	0.03	0.13	–0.03
Volatiles	7.04	7.10	10.42	4.87	7.47	6.54						
Sum	98.28	99.46	99.94	97.99	97.99	98.70	100.03	27.84	64.80	7.40	100.05	

Composition of the diatomite

The principal components of the diatomite are:

(1) Diatom frustules, which range from c. 200 µm to fragments below 2 µm,
(2) Clay minerals (particles <2 µm),
(3) Volcanic dust (particles <2 µm),
(4) Detrital minerals other than clay minerals, and
(5) Diagenetic minerals (pyrite, jarosite, calcite, hydroxides of Fe and Mn, gypsum, opal-C/T, zeolite).

All of these five groups contribute to the bulk chemical composition of the diatomite, although some are only present in negligible amounts.

The silicon is located in opal-A, volcanic dust and detrital minerals, especially smectite and quartz. Aluminium is present mainly in clay minerals, volcanic dust, diatom frustules, and zeolites, which, however, are not detected by XRD (Table 2). Iron is located in volcanic dust, which has a composition similar to the coarser volcanic ash, in clay minerals and in a number of diagenetic minerals. A bulk sample may therefore contain a surplus of iron relative to the iron located in clay minerals or volcanic dust. Table 2 shows the presence of pyrite in sample 115 and jarosite in samples 119 and 125, which indicates that they are absent or present in negligible amounts in the remaining samples. Detrital minerals other than clay minerals and quartz have not been observed (Table 2). It is therefore concluded that the most important components of the clayey diatomite are diatom frustules, clay minerals and volcanic dust. Calculation of their relative proportions shows that the diatomite contains 30–45% clay minerals, 45–65% diatoms and c. 10% volcanic dust (Tables 5B–8B). The tables show that a reasonable fit is achieved between the sum of the three components and the bulk composition for samples 107, 111 and 119, whereas sample 125 contains a large surplus of iron and a deficit in silicon. This deviation from the bulk composition suggests that iron was added during diagenesis and possibly that silicon was simultaneously removed.

Discussion

This study has had three purposes: 1) to identify the clay mineral phases in the Fur Formation, 2) to determine their compositions and proportion, and 3) to compare two methods of determining the opal content of a clayey diatomite. These three topics are addressed below.

1) The dominant clay mineral phase of the Fur Formation is smectite, which is interpreted as being of detrital origin. Illite occurs as an independent phase in small amounts. Our results do not allow an estimate of the amount of illite or whether this varies between the samples. The smectite prob-

ably originated from weathering of volcanic ash which covered the terrestrial areas adjacent to the Palaeogene North Sea', since devitrification of the larger grains of volcanic glass in the ash layers in the diatomite is insignificant (Larsen *et al.* 2003). Illite is interpreted as a detrital mineral originating from weathering and erosion of crystalline rocks or older sediments. Small amounts of kaolinite are reported from this stratigraphic interval at other localities (Nielsen 1974; Pedersen & Petersen 1986; Zhang 1987) and kaolinite may occur in the Fur Formation as well, in amounts approaching the detection limit (Fig. 8 A, C).

2) Chemical analyses of the clay phase ('isolate') show that it varies in chemical composition (Tables 5A–8A). The variation may reflect the fact that the volcanic ash undergoing weathering had a variety of chemical compositions (Larsen *et al.* 2003). It is also possible that variation occurred in the proportion of smectite to illite, or that the ion exchange capacity of smectite led to reactions with pore water.

The initial hypothesis was that the clayey diatomite of the Fur Formation had two components: diatom frustules and clay minerals, and that the Al_2O_3-content reflected the content of clay minerals. The present investigation indicates a more complex relationship, reflecting compositional variance within the smectite phase as well as addition of a third component: volcanic dust. The presence of volcanic dust, settling more or less continuously from the atmosphere, is difficult to prove. The particles are too small to be seen in SEM and, being glass, they are not detected as peaks by XRD but form elevated background levels, a bulge. The outline of this is difficult to trace in the presence of abundant opal-A.

The bulk chemical composition of the Fur Formation has been analysed by Thomsen (1992), S. Johansson (personal communication 1997) and in the present study (Tables 4A–8A). All analyses show some variation between the samples, and we interpret this as reflecting varying proportions of smectite, opal-A, and volcanic dust. Inspection of laminated diatomite shows a mm-scale variation: laminae representing a continuous settling of clay minerals, volcanic dust and diatom frustules are interspaced with thin laminae rich in diatoms or clay, and interpreted as originating from blooms or increased run-off (Pedersen 1981). The variation encountered here is on a larger scale and suggests that longer-term variations may also be present. Additional analyses of the chemical composition of bulk samples are needed to document the range of this variation.

The isolated clay minerals constitute *c.* 10% of the bulk samples. They cannot account for more than a fraction of the Al_2O_3 in the bulk analyses. A significant amount of clay minerals must therefore be 'hidden', and we suggest that they are most likely contained within the aggregates. The chemical composition of the particles >20µm, which are almost exclusively aggregates, show that these contain, besides clay minerals, additional aluminium hydroxides, probably precipitated during diagenesis.

3) The opal content has been calculated successfully by XRD in pure diatomite and in calcareous diatomite with low contents of clay minerals (Bish & Post 1989; Pedersen *et al.* 1999; Steffensen 2001). In the present study we have measured the carbonate content by titration (nil in the Fur Formation), calculated the opal content (60–75%) from the opal bulge (Table 2) and calculated the opal content from the chemical analyses (45–65%). Comparison shows that the opal bulge is too large in the Fur Formation. We therefore suggest that dust-sized volcanic glass contributes to the bulge because of its non-crystalline, amorphous structure. The method of calculating the area of the opal bulge should therefore be applied with caution in diatomites containing volcanic dust.

Conclusions

The present study of the clay mineral composition and content of the Early Eocene Fur Formation has led to several conclusions:

- The diatomite is dominated by one clay mineral phase identified as smectite. An illite phase is present in subordinate amounts and kaolinite is locally present in small amounts.
- The chemical composition of the smectite phase varies, but a general formula is: $X_{0.1}K_{0.2}(Mg_{0.3}Fe\ (III)_{0.3–0.7}Al_{1.1–1.4})Si_4O_{10}(OH)_2$.
- The clay mineral content has been calculated as 30–45% by weight.
- Calculations of the opal content from diffractograms (area of opal bulge) appear to be affected by the presence of volcanic dust and possibly clay minerals.
- The diatomite was only slightly affected by diagenesis, but the deviation between bulk chemistry and the sum of three components suggests diagenetic changes, as do the precipitation of oxides and hydroxides of iron and manganese on joints, and the precipitation of calcite as calcareous concretions.

- The Fur Formation is classified as siliceous ooze to clayey siliceous ooze according to the definition of Hay, Sibuet *et al.* (1984).

Acknowledgements

The company SKAMOL A/S and Stig Johansson kindly placed their unpublished data at our disposal. The investigation was partly carried out as an activity within the EU–supported INCO-Copernicus project No. ERBIC15CT96 0712. Additional financial support was provided by Damolin A/S, Skamol A/S and Viborg Amt. Holger Lindgreen undertook the time–consuming work of isolating the clay minerals and participated in numerous discussions of the results. An early version of the manuscript was greatly improved by suggestions from Lotte Melchior Larsen, and Claus Heilmann-Clausen, Ole Bjørslev Nielsen and Richard Wilson provided helpful suggestions for improvements of the final text. Kirsten Fries kindly assisted in the Clay Mineralogical Laboratory and with the XRD-analyses. Morten Sparre Andersen assisted in the calculations of sediment composition. GEUS and the Geological Institute, University of Copenhagen, provided the SEM-analyses, and Jørgen Kystol and John Bailey the XRF-analyses. The paper is published with the permission of the Geological Survey of Denmark and Greenland. We are very grateful to all these persons and institutions for their help.

Dansk sammendrag

Fur Formationen er en eocæn, leret diatomit, som indeholder 179 nummererede lag af vulkansk aske. Diatomitten er kalkfri, strukturløs eller lamineret, og mængden af diatomeskaller og ler varierer fra lamina til lamina. Lermineralfasen er blevet isoleret. Lermineralogiske analyser, baseret på røntgendiffraktion, viser, at det dominerende lermineral er smektit. Den kemiske sammensætning af totalprøver, udvalgte kornstørrelser og lerfaser er bestemt ved røntgenfluorescens. En generel formel for smektitten er:

$X_{0.1}K_{0.2}(Mg_{0.3}Fe(III)_{0.3-0.7}Al_{1.1-1.4})Si_4O_{10}(OH)_2$.

Undersøgelsen viser, at diatomitten i Fur Formationen består af tre komponenter: diatomeskaller, lermineraler og vulkansk støv. Diatomittens lermineralindhold er beregnet som 30–45% (efter vægt). Vulkansk støv udgør ca. 10% og resten udgøres af diatomeskaller (opal-A). Den biogene opal har et lille indhold af Al_2O_3, som enten kan være primært eller diagenetisk.

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