Stratigraphy and geochemical composition of the Cambrian Alum Shale Formation in the Porsgrunn core, Skien–Langesund district, southern Norway

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The fully cored BHD-03-99 borehole (hereafter referred to as the Porsgrunn borehole and core) penetrated Ordovician and Cambrian strata in the Skien–Langesund district, southern part of the Oslo region in Norway. Hand-held X-ray fluorescence (HH-XRF) measurements combined with spectral gamma ray and density core scanning of the Middle Cambrian – Furongian Alum Shale Formation have been made and compared with similar measurements obtained on Alum Shale cores from Scania (southernmost Sweden) and Bornholm (Denmark). The Porsgrunn drill site is located in an area that was only mildly overprinted by Caledonian tectonics and represents one of the few sites in the Oslo area where a nearly untectonised sedimentary succession can be studied in terms of thickness and geochemistry. The Alum Shale Formation is 28.8 m thick in the Porsgrunn core, excluding the thickness of five 0.9–5.5 m thick dolerite sills of assumed Permian age.

In the Alum Shale Formation the bulk densities are around 2.7 g/cm^3 with a slightly decreasing trend up through the formation. The shale has total organic carbon (TOC) values up to 14 wt%, which is comparable to the TOC levels for the Alum Shale elsewhere in the Oslo area and for dry gas matured Alum Shale in Scania and Bornholm. The basal Furongian is characterised by a gamma ray low and an increase in Mo interpreted to reflect the Steptoean Positive Carbon Isotope Excursion (SPICE) event. The Porsgrunn core data suggest that the Mo concentration remained high also after the SPICE event.

Characteristic, readily identified features in the gamma log motif are named the Andrarum gamma low (AGL), base Furongian gamma low (BFGL), *Olenus* triple gamma spike (OTGS) and the *Peltura* gamma spike (PGS). No Lower Ordovician Alum Shale is present. The 14.8 m thick Furongian part of the Alum Shale represents the *Olenus*, *Parabolina*, *Leptoplastus*, *Protopeltura* and *Peltura* trilobite superzones judging from log-stratigraphic correlations to Scania and Bornholm. The Middle Cambrian interval is 14.0 m thick and includes the Exsulans Limestone Bed and 1.4 m of quartz sandstone. A 0.3 m thick primary limestone bed may be an equivalent to the Andrarum Limestone Bed. The succession represents the *Paradoxides paradoxissimus* and *P. forchhammeri* superzones. The Alum Shale Formation rests atop the 13.0 m thick Lower Cambrian Stokkevannet sandstone (new informal name) that in turn directly overlies the basement. Overall, the stratigraphic development of the comparatively thin Alum Shale Formation resembles the condensed sequence seen on Bornholm.

Keywords: Porsgrunn, Alum Shale, Cambrian, Correlation, Scandinavia, Geochemistry.

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Nowhere in the Oslo region are the Palaeozoic sedimentary rocks more dramatically displayed than in the Skien–Langesund area. High cliffs and local fjord sections expose fossiliferous Cambrian and Ordovician rocks preserved in a series of fault-controlled horsts, which fascinated Brøgger (1884) and his predecessors such as Forbes (1856), Dahl (1856) and Kjerulf (1857). All produced local stratigraphic schemes that were followed in subsequent years by Kiær (1897, 1906), Strand (1934) and Størmer (1953). The succession includes a comparatively thin Alum Shale Formation, briefly referred to by Henningsmoen (1957), based on a cored shallow borehole at Rognstranda (Fig. 1).

Investigation of the Alum Shale Formation in Norway is hampered by the fact that the unit is strongly tectonised in most areas, as the shale acted as decollement level during the Caledonian Orogeny (Ramberg & Bockelie 1981; Bockelie & Nystuen 1985; Nilssen 1985; Owen *et al.* 1990). As a consequence few areas exist where a detailed undeformed stratigraphy can be studied. The aim of this paper is to examine the cored Porsgrunn borehole that penetrated the entire Alum Shale in the Skien–Langesund district. The examination is based on hand-held X-ray fluorescence (HH-XRF) measurements and spectral gamma and density logs derived from scanning of the core (Figs 1, 2). The paper also demonstrates that long-distance correlation of the Alum Shale is possible, based on consistent gamma log-patterns.

In this paper we use the traditional terms Early/Lower Cambrian (≈Terreneuvian and Cambrian provisional series 2) and Mid/Middle Cambrian (≈Cambrian provisional series 3), pending the introduction of formal names for the new Cambrian global series. The Furongian corresponds to the traditional Late/Upper Cambrian except that the *Agnostus pisiformis* Zone is now assigned to the Middle Cambrian.

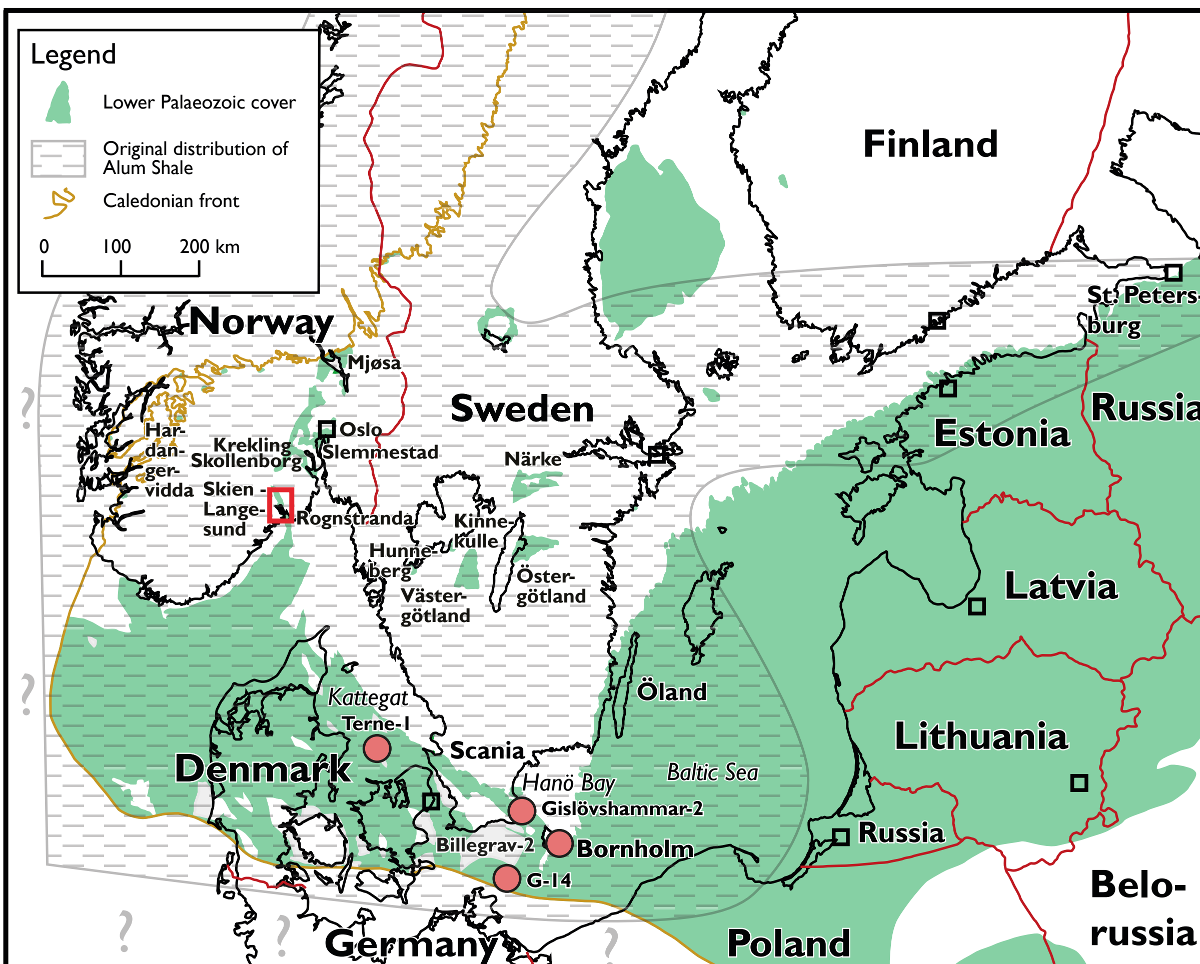

Fig. 1. Outline of approximate original distribution of the Alum Shale Formation and present day occurrence of lower Palaeozoic strata in southern Scandinavia. Boreholes referred to in this work are indicated with red dots. Red square outlines the Eidanger peninsula where the Porsgrunn core is drilled (Fig. 2). The occurrence of lower Palaeozoic strata is modified from Nielsen & Schovsbo (2015) with respect to interpretation of the Hanö Bay area as presented by Sopher *et al.* (2016).

Geological Setting

During the Cambrian, Baltica was positioned at intermediate latitudes in the southern hemisphere, and siliciclastic deposition prevailed (Torsvik *et al.* 1991; Nielsen & Schovsbo 2011). The sea level rose stepwise through the Early Cambrian and eventually all of Scandinavia became covered by a relatively shallow epicontinental sea (Nielsen & Schovsbo 2011, 2015). From the early Mid Cambrian through to the Tremadocian (Early Ordovician), the offshore parts of this epicontinental sea became characterised by low-oxygen conditions, i.e. from about the storm wave base and deeper. Here the slowly accumulating Alum Shale mud was deposited, comprising dark organic-rich mudstone with abundant disseminated pyrite (for a general discussion of the Alum Shale facies, see Nielsen & Schovsbo 2015 and references therein). Deposition of the Alum Shale took place in an area that extended for more than 800 000 km^2 across the

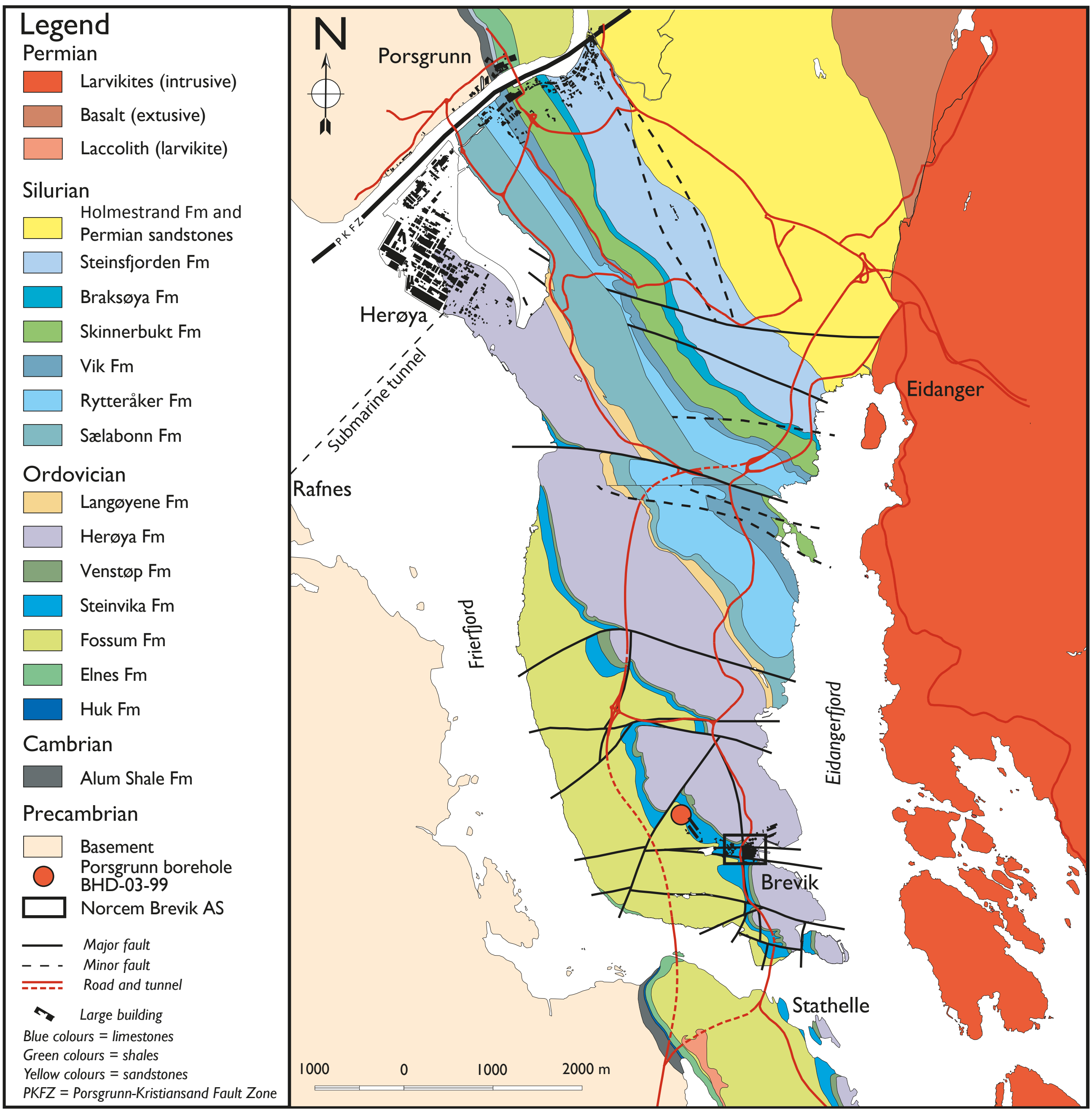

Fig. 2. Geological map of the Eidanger peninsula with the location of the Porsgrunn borehole (BHD-03-99). The surface coordinates for the borehole are 59°03′59.63″ N, 9°40′37.19″ E and the elevation is 63 m above sea level. Modified from Harstad (2005). Location of tunnel from Lien et al. (1978).

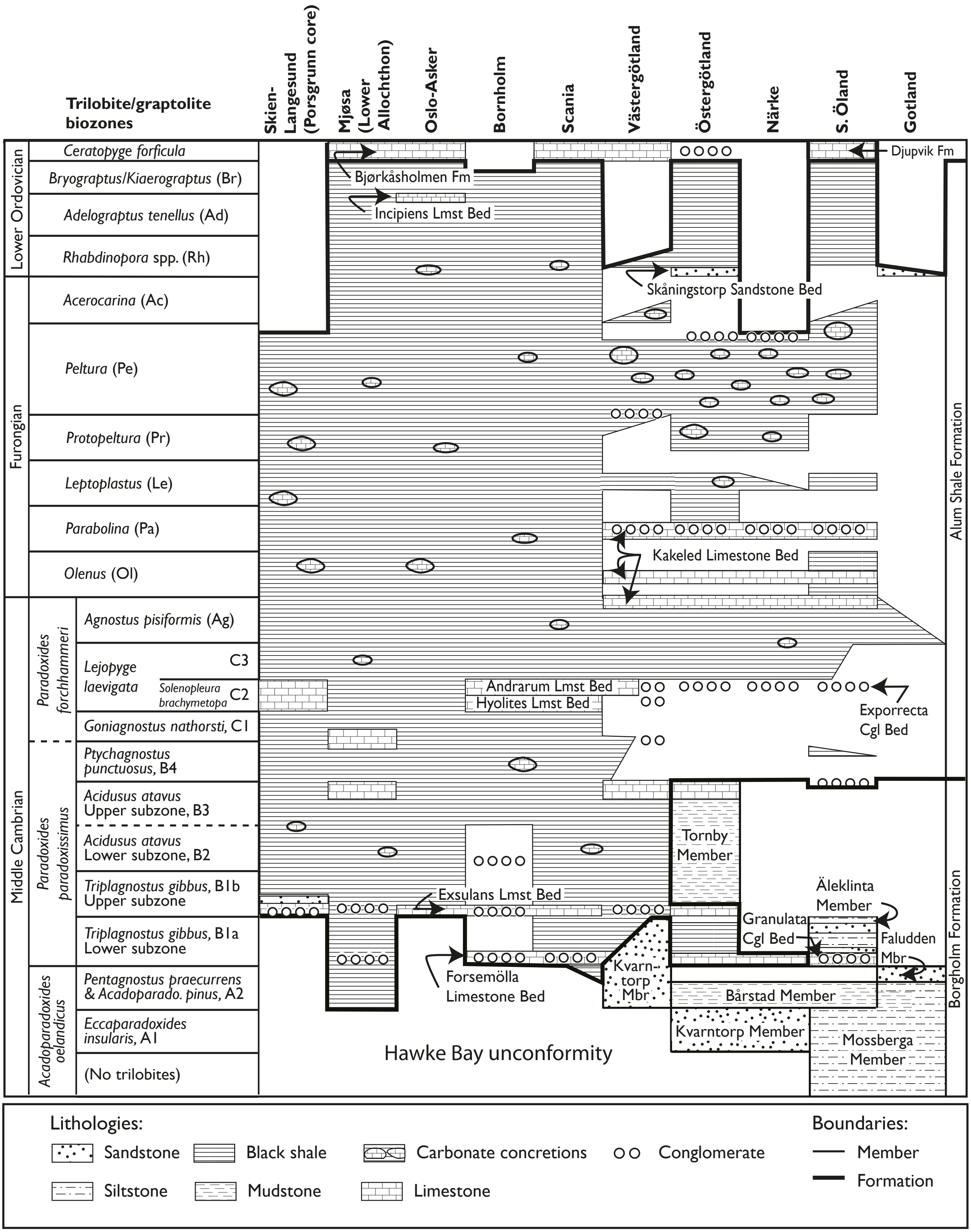

Fig. 3. Stratigraphic development of the Alum Shale in various districts of Scandinavia. For locations, see Fig. 1. The Furongian trilobite stratigraphy is updated according to Nielsen *et al*. (2014). Modified from Nielsen & Schovsbo (2007).

western part of Baltica (Fig. 1; Nielsen & Schovsbo 2015). Throughout this vast area the Alum Shale lithology is remarkably uniform although a mid shelf and an outer shelf facies (termed platform and shelf facies, respectively, by Buchardt *et al.* 1997) have been recognised, based on the abundance of carbonate concretions and stratigraphic completeness (Buchardt *et al.* 1997; Schovsbo 2002; Nielsen & Schovsbo 2007). Buchardt *et al.* (1997) assigned the Alum Shale in the Skien–Langesund area to the platform facies whereas the Alum Shale in the Oslo–Asker area was assigned to the shelf facies. They inferred a local south Norwegian topography referred to as the Telemark Shoal and the Oslo Trough (cf. Buchardt *et al.* 1997, fig. 9). The assignment of the Skien–Langesund Alum Shale to the platform facies was at the time only based on the local thinness of the unit. However, it does not contain much limestone (c.. 12%) and no intraformational limestone conglomerate levels and is here considered as a thin outer shelf facies type.

The unit varies considerably in thickness across Scandinavia. In south-central Sweden the Alum Shale is mostly around 20–25 m thick, whereas in Scania and the central Oslo area it varies between 80 and 100 m. The greatest thickness, 178 m, has been encountered in the Danish offshore well Terne-1 (Nielsen & Schovsbo 2007; Schovsbo *et al.* 2016). The shale thins towards the southern margin of Baltica and measures only some 27–34 m on Bornholm (Schovsbo *et al.* 2011, 2015b) and 32 m in the offshore German well G-14 (Piske & Neumann 1993). The Alum Shale apparently also thins towards the western margin of Baltica, being some 30–40 m thick in the Hardangervidda area (Andresen 1978). As reported in the present paper the unit is only 29 m in the Skien–Langesund district located in the southernmost part of the Oslo area (excluding the combined thickness of 15 m of dolerite sills intruded into the formation). The thickness variation reflects repeated erosive events in south-central Sweden linked to sea level lowstands in combination with uplifts of the margins of Baltica. The latter condition may have created a silled basin leading to poor ventilation of the Alum Shale sea (Nielsen & Schovsbo 2015).

The Alum Shale deposited on the southern and western fringes of Baltica became deeply buried in the Caledonian foreland basin during the late Silurian – Early Devonian (e.g. Buchardt & Lewan 1990; Samuelsson & Middleton 1998; Pedersen *et al.* 2007). The Alum Shale acted as decollement level during Caledonian thrusting and the unit is usually strongly tectonised in the Caledonides, including most of the Oslo area. However, the southern part of the Skien–Langesund area, where the Porsgrunn borehole was made, is located outside the Caledonian deformation zone (Bruton *et al.* 2010), but here the lower Palaeozoic strata have been affected by igneous larvikite intrusions and dolerite sills during the Permian rifting that created the Oslo Graben (Jamtveit *et al.* 1997; Fig. 2).

Despite being deposited under low oxygen conditions, the Cambrian part of the Alum Shale contains a low-diverse, but highly abundant trilobite fauna. This fauna has facilitated the definition of a high-resolution biostratigraphic zonation comprising three Middle Cambrian superzones subdivided into eight zones and six Furongian superzones subdivided into 26 zones (Fig. 3); for review and latest updates, see Terfelt *et al.* (2008), Weidner & Nielsen (2014), Nielsen *et al.* 2014) and Rasmussen *et al.* (2016).

The Alum Shale lithology is remarkably uniform across Scandinavia with a fairly simple lithostratigraphy including several widespread thin event beds (Fig. 3). The unit is enriched in a variety of trace elements, notably U, V and Mo (Armands 1972; Andersson *et al.* 1985; Leventhal 1991; Buchardt *et al.* 1997; Schovsbo 2001, 2002; Dahl *et al.* 2013; Hammer & Svensen 2017). Of these elements the radioactive U has been especially studied both for economic reasons and stratigraphic purposes (Gee 1972; Edling 1974; Hessland & Armands 1978; Andersson *et al.* 1985; Schovsbo 2002).

The gamma ray (Gr) log pattern of the Alum Shale is readily correlated between boreholes (Pedersen & Klitten 1990; Michelsen & Nielsen 1991; Erikson 2012; Schovsbo *et al.* 2015a, 2016; Nielsen *et al.* manuscript in submission 2018). The unique nature of the gamma response of the formation has been used for lithostratigraphic correlation within local areas such as the Oslo Region (Siggerud 1955; Skjeseth 1958; Elvebakk 2011), Bornholm (Pedersen & Klitten 1990; Schovsbo *et al.* 2016), central Sweden (Armands 1972; Hessland & Armands 1978, Andersson *et al.* 1985; Dypvik 1993) and the Caledonian mountain chain (Snäll 1988).

The Porsgrunn core

The investigated core was made available by Norcem Brevik AS. The company is Norway's largest producer of cement and part of the Heidelberg Cement Group. It is situated in the community of Porsgrunn, Telemark County (Fig. 2). The core was drilled in 1999 as part of a work program associated with the establishment of a regional geological stratigraphic reference model. Brevik is situated in the southern end of the Oslo region (Størmer 1953; Bruton *et al.* 2010). Palaeozoic rocks in the area outcrop in a NNW–SSE belt delimited by Precambrian rocks to the west and Permian igneous rocks to the east (Fig. 2). A series of dolerite sills of assumed Permian age intruded into the lower Palaeozoic strata have given rise to low-grade contact metamor-

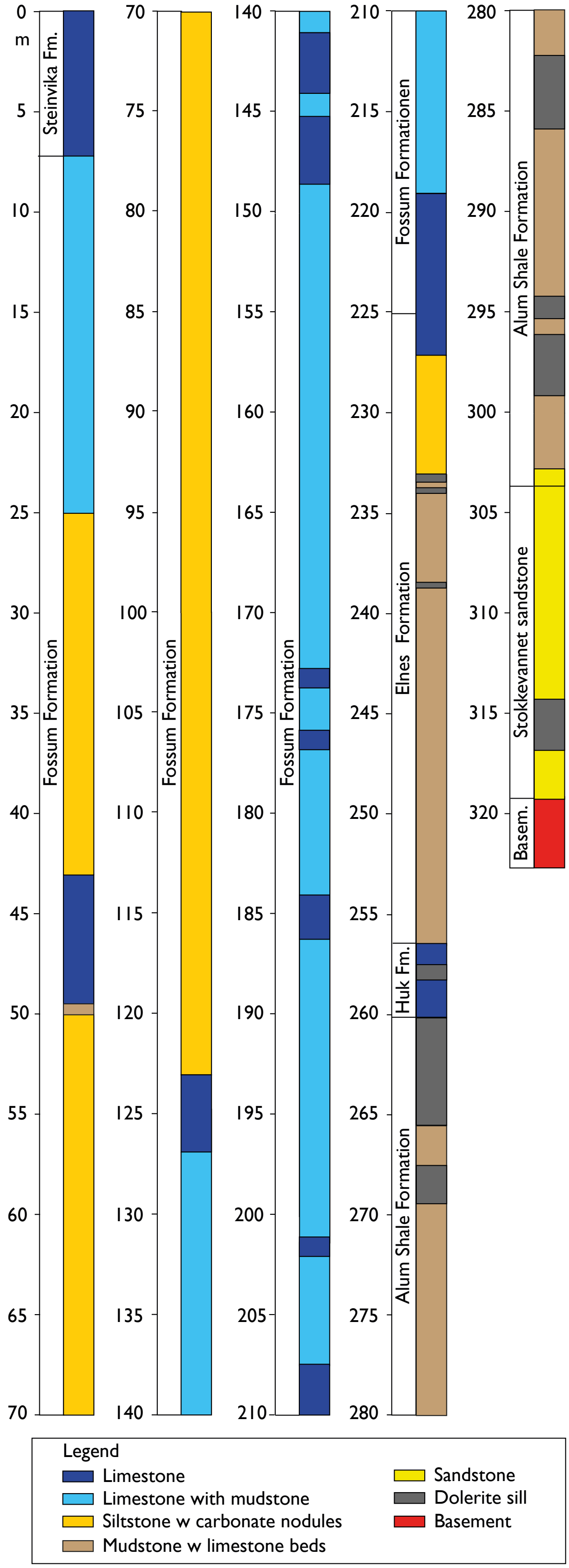

Fig. 4. Overview log of the Porsgrunn (BHD-03-99) core. Based on unpublished log provided by Norcem Brevik AS.

phism. Tectonism caused a general regional tilting to the east; for local details, see Ramberg & Bockelie (1981), Bockelie & Nystuen (1985) and Nilssen (1985).

The Porsgrunn borehole was drilled using conventional mining exploration equipment which provided a continuous 1 inch diameter core. The surface borehole location is in the northern part of the Dalen open pit limestone mine some 900 m north-east of the Norcem cement plant in Brevik, on the southern part of the Eidanger Peninsula (Fig. 2). The borehole was drilled to a total depth of 322.6 m with full core recovery (Fig. 4). Sedimentological logging of the core suggested that none of the known faults in the area intersected the well. Thus, it is assumed that the borehole represents the true stratigraphic thickness of the penetrated rock units. Stratigraphically, the surface location of the borehole is situated 7.2 m above the base of the Middle Ordovician Steinvika Formation (see Owen *et al.* 1990). Below the Steinvika Formation the borehole encountered the Fossum, Elnes, Huk and Alum Shale formations (Fig. 4). The Alum Shale rests on Lower Cambrian sandstone, here informally referred to as the Stokkevannet (named so after Stokkevannet, South of Brevik) sandstone, which in turn overlies the Precambrian gneiss basement (Fig. 4).

Methods

Hand-held XRF core measurements

Concentrations of elements were determined at 365 levels in the core, corresponding to approximately every 15 cm in the interval 322.6–260.0 m. Measuring was done using a hand held Niton™ Xl3t Goldd+ XRF device (HH-XRF) at the Geological Survey of Denmark and Greenland (GEUS's) Core Analysis Laboratory in Copenhagen, Denmark. The device is equipped with an Ag anode that measures at 6–50 kV and up to 200 μA and provides semi-quantitative element concentrations. The measuring area is about 5 mm in diameter, and the measuring time was 2 minutes per measuring point, applying the "test all geo filter" that measured dually on low and high filters. Measurements were performed both directly on the curved core surface and on bedding planes where the core had split. Measurements of both in-house and certified powder samples were made to ensure data quality and reliability.

The HH-XRF has proved to be a reliable and stable tool (Dahl *et al.*, 2013; Hammer & Svensen 2017), provided that matrix effects are eliminated by comparison with reference samples with similar matrix (Esbensen & Johansson 2013). For this study the HH-

XRF element concentrations of Si, Al, Ca, Fe, K, Mg, Mn, P, Ti, S, As, Ba, Cu, Mo, Nb, Ni, Pb, Rb, Sr, Th, U, V, Zn, and Zr were compared to element concentrations determined by ICP-MS (inductively coupled plasma mass spectrometry) analysis of a set of eleven representative in-house lower Palaeozoic shale samples. The ICP-MS analyses were carried out on an Elan 6100 ICP-MS instrument at GEUS. Crushed samples were dissolved in HF and HNO_3 acid for two days at 130°C and element concentrations were determined using the Perkin Elmer TotalQuant software that provides semi-quantitative concentrations for 66 elements.

The element concentrations determined by HH-XRF and ICP-MS methods are highly correlated, as reflected in Pearson correlation coefficient (r^2) values generally >0.9 (n=11, Table 1, Fig. 5). Lowest correlation coefficients between the two methods are seen for Mg (no relationship could be established) and for Al (not statistically significant at the calculated probability < 0.1, Table 1). For comparison with literature data, the HH-XRF element concentrations were recalculated using the regression lines for the interdependence of the HH-XRF and ICP-MS results; nine examples are presented in Fig. 5.

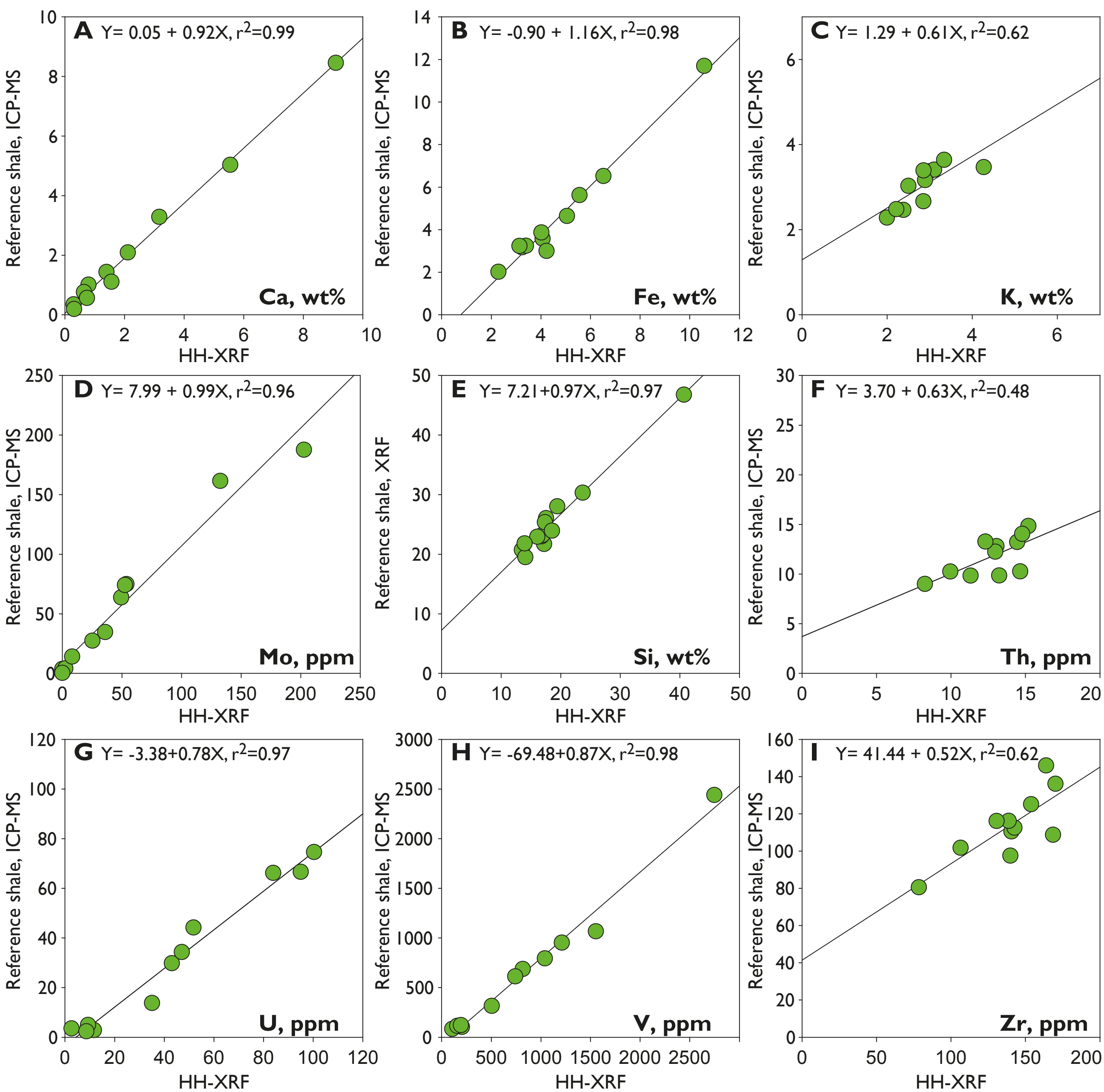

Fig. 5. HH-XRF *vs* ICP-MS (Total Quant method) comparison for powdered samples.

Table 1. Correlation coefficients and statistical significance levels for correlations between elements determined by HH-XRF and ICPMS analysis of 11 Palaeozoic shale samples from Denmark.

Element	R^2 for linear regression line*	Significant at $p < 0.10$
Al	0.19	no
As	0.99	yes
Ba	0.52	yes
Ca	0.99	yes
Cu	0.98	yes
Fe	0.98	yes
K	0.62	yes
Ni	0.96	yes
Nb	0.23	no
Mn	0.97	yes
Mo	0.96	yes
P**	0.93	yes
Pb	0.91	yes
Rb	0.70	yes
Si***	0.97	yes
Sr	0.99	yes
Th	0.48	yes
Ti	0.48	yes
U	0.97	yes
V	0.98	yes
Zn	0.98	yes
Zr	0.62	yes

* linear conversions used. see Fig. 5 for selected elements.

** for P >200 ppm; N=4.

*** Determined by conventional XRF.

Formation bulk density

The Porsgrunn core interval between 322.6 and 260.0 m was scanned at the GEUS Core Analysis Laboratory using a density scanner equipped with a Cs source for determining the bulk density. The vertical resolution is 1 cm core length. The scanning was performed at a speed of 1 cm/min. Calibration of the scanner was made by running in-house standards with known densities. The scanned density measurements are very sensitive to imperfections such as cracks, fractures, drilling- induced damages, and to poor alignment of the core within the scanner. Generally the core is in very good condition and extra care was taken to align it directly under the sensor and to fit the core pieces together to minimise any effects on the measurements.

Determination of the bulk density was done on 33 core samples, each consisting of an approximately 1 cm long full core. Measurements were done by normalising the weight of the sample relative to the bulk volume measured by submersion of the sample in a Hg bath using Archimedes' principle. The porosity was determined on the same samples by subtraction of the measured grain volume from the measured bulk volume. The He technique, employing Boyle's Law, was used for grain volume determination, applying a double-chambered helium porosimeter with digital readout. For each measurement stable He volumes were reached in more than 15 minutes to ensure complete filling of the pore volume. For more detailed descriptions of methods, instrumentation and principles of calculation, see American Petroleum Institute (API)'s recommended practice for core analysis procedure (API 1998).

Spectral gamma ray scanning

Spectral gamma ray scanning of the core was done at the GEUS Core Analysis Laboratory in a scanner equipped with two 15 cm NaI (Tl) crystals. Due to the size of the crystals, the U, K, and Th signals are averaged over 15 cm core lengths. Calibration of the spectral gamma ray scanner was made by running in-house standards with known U, K and Th concentrations. After calibration, the core measurements of U, K and Th were rescaled by comparing with the HH-XRF measurements. The gamma ray activity measured by the scanner (counts per second) was converted to Sum gamma ray (SGr) in American Petroleum Institute (API) units according to the algorithm by Ellis & Singer (2007): Sum gamma ray (API units) = 4 × Th (ppm) + 8 × U (ppm) + 16 × K (wt%).

Carbon and sulphur core measurements

Total organic carbon (TOC), total carbon (TC) and total sulphur (TS) contents were measured on 63 acid treated samples in a LECO CS-200 carbon/sulphur analyser at GEUS's Source Rock Laboratory. Dissolution of carbonate was done by treating 0.05 g dried sample with 2M HCl solution at 65°C for 2 hours. The powdered samples were placed together with iron accelerator material in an induction furnace and heated to 1300°C, and the evolved gases were measured by infrared absorption.

Results

Lithostratigraphy

Dolerite sills intrude the section from the basement and up to the base of the Middle Ordovician Huk Formation with an accumulated thickness of 17.5 m. The true thickness of the Alum Shale Formation is

Table 2. Stratigraphic depths and thicknesses of intervals and dolerite sills in the Porsgrunn well

	Depth in core. m	Restored depth below top Alum Shale. m	Thickness. m
Base Huk Formation	260.0	0.0	
Top Alum Shale / base dolerite	265.5	0.0	
Peltura gamma spike (PGS)	275.0	7.5	
Top *Olenus* triple gamma spike (OTGS)	280.0	12.5	
Base *Olenus* triple gamma spike (OTGS)	281.3	13.8	
Base Furongian gamma low (BFGL)	282.3	14.8	
? Andrarum Lmst Bed gamma low (AGL)	296.0	24.0	
Base Exsulans Lmst Bed	303.7	28.8	
Base Alum Shale Formation	303.7	28.8	
Base Stokkevannet sandstone	319.2	41.7	
Alum Shale. restored			28.8
Furongian. Alum Shale			14.8
Middle Cambrian. Alum Shale			14.0
Stokkevannet sandstone			13.0
Dolerite in Furongian (2.00 + 3.54 + 5.50 m)			11.0
Dolerite in M. Cambrian (0.93 + 2.91 m)			3.8
Dolerite in Stokkevannet sst (2.58 m)			2.6

The borehole was terminated at 322.6 m in basement gneiss

thus 28.8 m (Table 2). Due to magmatic heating the cored rock is very hard and brittle. The basal 3.4 m of the core (322.6–319.2 m) consist of gneissic basement, in turn overlain by 13.0 m of fine-grained quarzitic sandstone (319.2–303.7 m) intruded by a 2.6 m thick dolerite sill (Fig. 6). The fine-grained sandstone is here informally termed the Stokkevannet sandstone. It likely represents a tongue of the Swedish File Haidar Formation (Nielsen & Schovsbo 2007, 2011) and for simplicity it could be contemplated using that term in Norway also.

The topmost part of the Stokkevannet sandstone between 303.7–304.9 m is dark stained and includes a matrix-supported conglomerate between 304.7–304.5 m. The matrix consists of fine-grained quartz sand; the clasts are up to 3 cm in diameter, typically around 1 cm, sub-angular to sub-rounded, dark coloured and probably consist of phosphorite. Unfortunately, none of the HH-XRF measuring points covered these clasts. The upper boundary of the conglomerate may represent an unconformity; here a crust of assumed phosphorite is developed with a sharp upper boundary. The sandstone between 304.5–303.7 m is very fine-grained and bioturbated (dark-stained mottled).

The basal 6 cm of the Alum Shale Formation (303.67–303.61 m) is developed as a conglomeratic limestone with a primary bioclastic fabric, and this horizon likely represents the Exsulans Limestone Bed (Fig. 3). The lower boundary to the Stokkevannet sandstone is sharp but irregular and is overlain by phosphorite nodules up to 1×1.5 cm in size. The limestone grades into very fine to fine-grained sandstone, in part carbonate cemented (303.6–302.2 m). The upper boundary is sharp. The overlying interval (302.2–265.5 m) is developed as black shale with limestone beds and concretions that in total amount to about 3.6 m or approximately 12% of the formation thickness. Macroscopic pyrite occurs in veins. In the interval 299.0–294.3 m, 0.4 m of shale and a 0.30 m thick limestone bed are sandwiched between two dolerite sills (Fig. 6). The carbonate bed (296.0–295.7 m) has in part a clear limestone texture and does not resemble the diagenetic limestone commonly present in the shale. The interval above the dolerite sill at 294.3–265.5 m represents the main upper part of the Alum Shale Formation and consists of shale with scattered black limestone nodules. Dolerite sills with sharp boundaries to the Alum Shale occur at 285.8–282.2, 269.4–267.4 and 265.5–260.0 m. The top dolerite sill is directly overlain by the Middle Ordovician Huk Formation at 260.0 m, suggestive of a major unconformity at this level.

Formation bulk density

The formation bulk density ranges between 2.0 and 3.3 g/cm^3 with the lowest values measured in the shales and the highest in the dolerite sills (Fig. 6). The bulk density of the Lower Cambrian sandstone is close to 2.65 g/cm^3 in the interval 314.0–309.0 m, which is the density of pure quartz (Ellis & Singer 2007). Slightly higher densities occur in the interval 307.0–305.5 m where also the K_2O content is slightly raised, suggest-

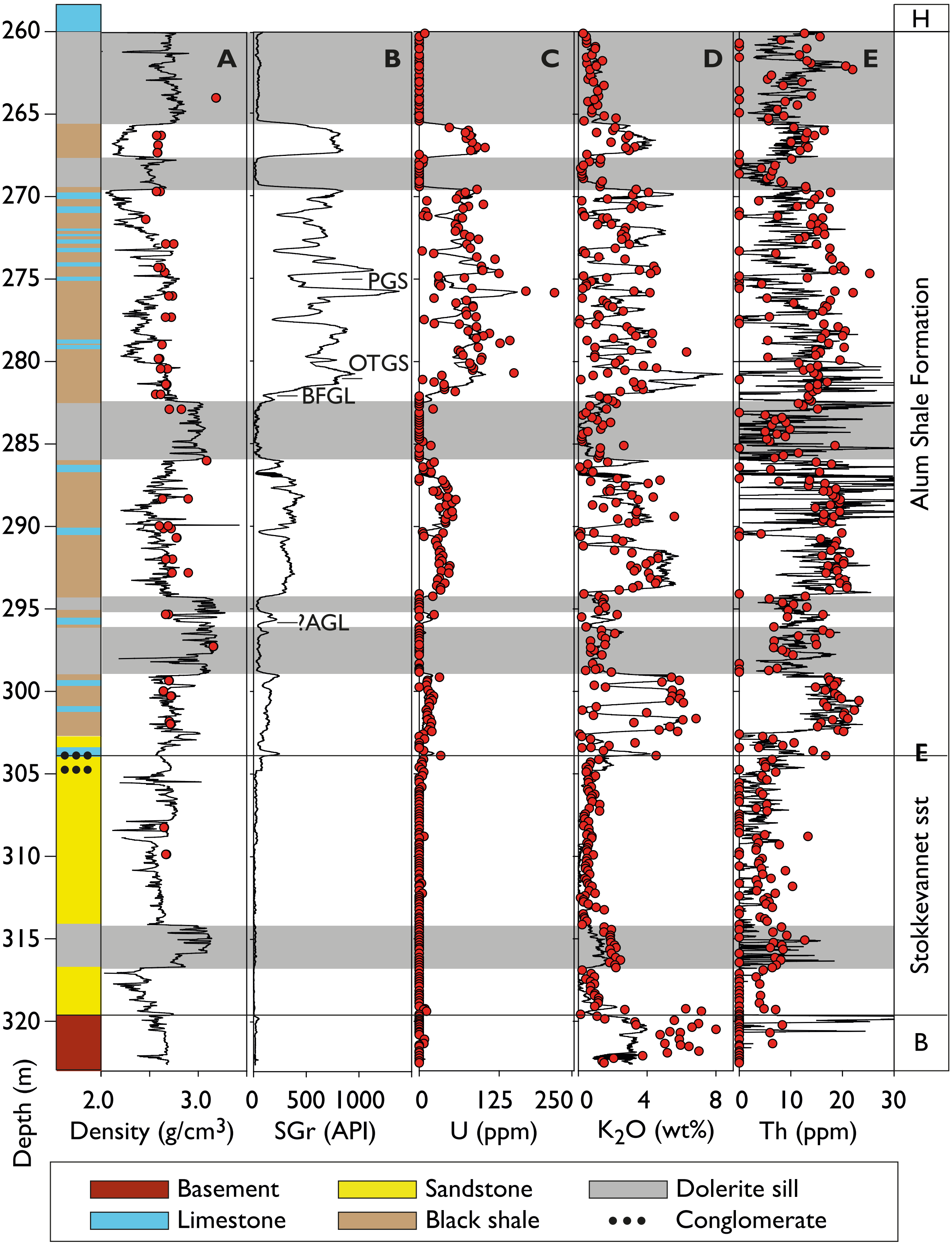

Fig. 6. Lithology, core scanning and core measurements of the Porsgrunn core (BHD-03-99) in the interval 322.6–260.0 m. A 5 cm running average was calculated through the density data. U, K_2O and Th determined by HH-XRF. Black lines: core scanning measurements. Red dots: core sample measurements. H: Huk Formation. B: Basement. E: Exsulans Limestone Bed. Sst: sandstone. PGS: *Peltura* gamma spike (central position). OTGS: *Olenus* triple gamma spike (central position). BFGL: Base Furongian gamma low. AGL: Andrarum gamma low.

ing the presence of other components besides quartz in the sand (Fig. 6). The low bulk values in the interval 320.0–316.7 m may reflect poor alignment of the core in the scanner.

In the Alum Shale Formation the bulk densities are around 2.7 g/cm^3 with a slightly decreasing trend up through the formation. The highest densities in the Alum Shale (>2.7 g/cm^3) are associated with carbonate beds (Fig. 6). Very low densities were measured by the scanner in the intervals 279.3–276.0, 271.6–269.6, and 267.4–265.5 m that cannot be reproduced by the core bulk density measurements (Fig. 6), and we suspect that the measured densities reflect poor alignment of the rather slim core (diameter 2.5 cm) in the scanner.

The dolerite sills have a density of about 2.8–3.2 g/cm^3. The highest densities were measured in the dolerite sills in the basal part (316.7–314.1 m) and the lowest in the topmost part of the core (265.5–260.0 m).

Spectral gamma scanning

The Sum gamma ray (SGr) log ranges from 0 to 1500 API units with the highest readings in the Alum Shale and the lowest in the dolerite sills and the Stokkevannet sandstone (Fig. 6). The latter unit has <40 API units in agreement with the general non-radioactive mineralogy present here. A slight increase in API units is seen from 310.0 m and upwards and again in the topmost part of the sandstone around 305 m. In both cases the increase is related to higher K_2O and Th contents suggesting that clay minerals are present in the sand.

In the Alum Shale the API values increase in a stepwise manner from 230 API units in the interval 305.0–300.0 m, to 420 API units in the interval 294.0–286.0 m, and to about 800 API values in the interval 282.0–265.0 m which shows a quite fluctuating pattern (Fig. 6). The high API values in the Alum Shale reflect the U content with concentrations up to 220 ppm in parts of the core (Fig. 6). Low API values were measured in intervals with carbonate beds as these are characterised by low U, K_2O and Th concentrations. The K_2O content in the Alum Shale varies between 0 and 8 wt%. The K_2O content exhibits an overall upwards decrease in concentrations from around 7 wt% at the base of the shale to about 4 wt% in the topmost part. A similar decrease in Th concentrations can be seen from about 20 ppm in the basal part of the formation to about 15 ppm in the topmost parts.

The SGr response of the dolerite sills varies between 50 and 100 API units and is thus slightly higher than the SGr response of the basal sandstone. The K_2O content varies around 1–2 wt% with the highest content in the basal dolerite sills and the lowest content in the topmost sill (Fig. 6). This, together with the differences in densities of the sills, may indicate compositional differences caused either by primary variation or differences in reactions between the sills and the surrounding sediment.

The U, K and Th concentrations measured by HH-XRF were used to rescale the spectral gamma log readings (see section on methods), and thus they have similar ranges in values (Fig. 6). The core scanning and the HH-XRF measurements generally track each other quite well despite the fact that the core-scanner readings were measured with a 15 cm wide crystal sensor where the radioactive signal is representative for the whole core volume, whereas the HH-XRF measurements are representative of only discrete spots. The Th variation seen in Fig. 6 even suggests that the HH-XRF measured a more stable signal in the Alum Shale, which implies that the Th calibration of the core-scanner drifted slightly during measurement.

Mo, V, TOC and SiO_2 content

In the Stokkevannet sandstone and the dolerite sills, only a few samples have a measurable Mo content (Fig. 7). In the Alum Shale, the Mo concentrations increase in a stepwise manner that tends to follow the pattern exhibited by the U concentrations (Fig. 6). In the Alum Shale the section between 304.0 and 295.0 m has 0–20 ppm Mo, the section between 294.5 and 286.0 m has on average 150 ppm Mo and the section above 280.0 m has up to 450 ppm Mo. The Mo content decreases from about 290.0 m and upwards to the sill contact at 285.7 m and increases again above the sill contact at 282.1 m up to about 280 m (Fig. 7A). No decrease in Mo concentration is observed near any other contact to sills, i.e. at 294.0 m, 269.2 m and 265.5 m, suggesting that the Mo variation is not controlled by the occurrence of sills.

The Stokkevannet sandstone has V contents generally lower than 20 ppm (Fig. 7). The V content in the dolerite sill in the sandstone ranges up to 800 ppm. In the dolerite sills in the Alum Shale the V content is slightly lower, in the range 500–800 ppm. The V content in the Alum Shale is in the range of 100–500 ppm for most of the section, without a clear stratigraphic trend (Fig. 7). This enrichment pattern thus deviates from the stepwise upwards increase in U and Mo concentrations.

The TOC content has only been measured in the shale lithology of the Alum Shale Formation (Fig. 7). The TOC content varies between 1 and 14 wt%, with the lowest content in the basal section between 304.0 and 300.0 m where values of 1–4 wt% are found. Higher up in the formation the TOC content varies between 7 and 14 wt% with the highest values measured in the interval between 275.0–272.0 m. In the intervals 294.0–288.0 m and 275.0–272.0 m, the TOC content exhibits upward increasing trends (Fig. 7).

The SiO_2 content in the Stokkevannet sandstone is overall very high, as expected for a pure sandstone (Fig. 7). The SiO_2 concentrations exceed, however, 100 wt% because a powdered quartz standard was used for calibration (see section on methods), and thus the denser nature of the core resulted in a slightly higher content. The dolerite sills have SiO_2 contents around 40 wt% with no clear stratigraphic variation.

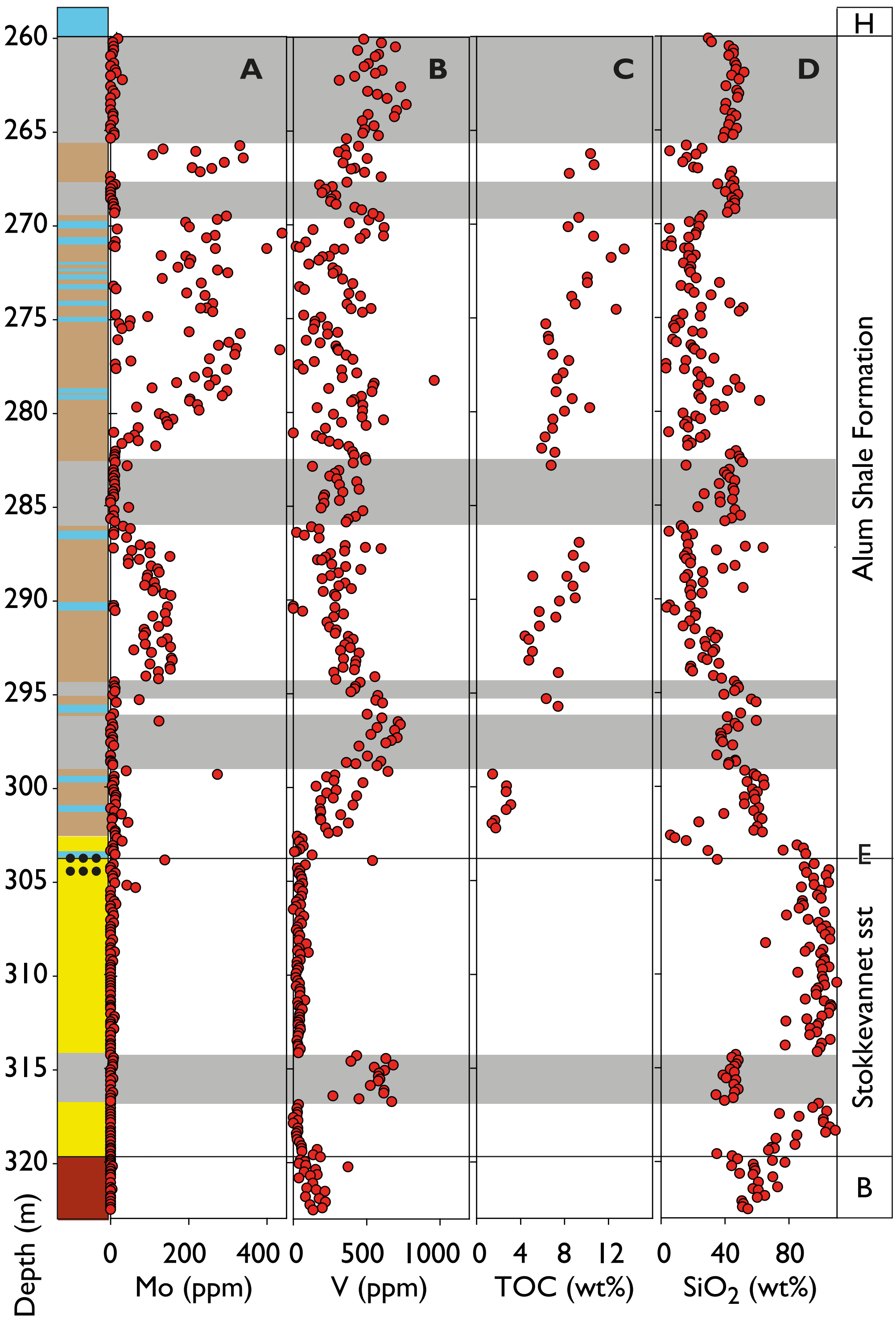

Fig. 7. Measurements of the Porsgrunn core (BHD-03-99) in the interval 322.6–260.0 m. Mo, V and SiO_2 by HH-XRF. Other explanations as in Fig. 6.

The basal Alum Shale Formation in the interval 303.6–302.7 m has a SiO_2 content >80 wt%, similar to the Stokkevannet sandstone and in agreement with the sandy to silty lithology of the interval. Above this level the SiO_2 content decreases up to the 290.0 m level; at higher levels the SiO_2 content is stable around 20 wt% (Fig. 7). However, a few samples in the shale show SiO_2 concentrations exceeding 40 wt%.

Discussion

Correlation

The stratigraphic motif of the restored SGr log (excluding the sills) compares well with results from boreholes through the Alum Shale in Scania and on Bornholm, where the log intervals to some extent have been dated based on the occurrence of trilobites (Fig. 8) (Nielsen & Buchardt 1994; Pedersen & Klitten 1990; Lauridsen 2000; Christensen *et al.* 2002; Schovsbo 2002).

In the Gislövshammar-2 well, located in southeastern Scania (Fig. 1), the Andrarum Limestone Bed is identified on the gamma ray log as a characteristic low peak termed the Andrarum gamma low (AGL) (Fig. 8). The AGL separates higher Gr active shale belonging to the *Lejopyge lavigata* Zone (C3) from rather low Gr active parts of the underlying shale belonging to the *Goniagnostus nathorsti* (C1) and *Paradoxides paradoxissimus* (B1-B4) superzones (Fig. 8). In the Porsgrunn core the AGL level is not unequivocally identified but may be located at either 296.0 m, corresponding to 24.0 m (restored) below the top of the Alum Shale, or at 290.2 m, corresponding to 19.1 m (restored) below the top of the Alum Shale (Fig. 8). At 296.0 m a limestone bed with a primary bio-clastic fabric occurs that may be a representation of the Andrarum Limestone Bed, whereas the limestone at 290.2 m is clearly of diagenetic origin. Hence, the 296.0 m level is the most likely candidate for the AGL.

In the Gislövshammar-2 and in the Billegrav-2 wells located in Scania and on Bornholm, respectively (Fig. 1), the base of the Furongian is characterised by a transient minimum in the Gr log (termed base Furongian gamma low, BFGL) underlying an interval with very high responses that characterises the upper part of the *Olenus* Superzone (termed *Olenus* triple gamma spike, OTGS; see also Schovsbo 2002). In the Porsgrunn core the BFGL log pattern is observed at 282.3 m in the core (14.8 m below top of the Alum Shale) and the OTGS is observed between 280.0–281.3 m in the core (13.8–12.5 m below the top of the Alum Shale), see Fig. 8 and Table 2. This interpretation is also supported by the stratigraphic distribution of Mo in the Porsgrunn core (Fig. 7) which is known to increase in the lower part of the *Olenus* Superzone accociated with the Steptoean Positive Carbon Isotope Excursion (SPICE) event (Gill *et al.* 2011). The increase in Mo content seen at 283.3–281.0 m (15.8–13.5 m below top of the Alum Shale) in the Porsgrunn core (Fig. 7) is suggested to reflect this event. The Porsgrunn core data suggest that the Mo concentration remained high also after the SPICE event at least to the mid-Furongian *Peltura* Superzone (see below). Dahl *et al.* (2013) observed that the Mo content remained high at least until the *Parabolina* Superzone at Andrarum in SE Scania they did not investigate higher levels.

The most prominent gamma-ray spikes in the Furongian occur at 274.2 and 276.3 m core depth (at 6.7 m and 8.8 m below the top of the Alum Shale, respectively). However, the lowering of the U content between these peaks reflects the presence of a diagenetic carbonate concretion and thus the original spike was not twinned. This spike is easily identified as the gamma ray spike that occurs in the lower part of the *Peltura* Superzone (termed the *Peltura* gamma spike, PGS) in the Gislövshammar-2 core (Fig. 8). This horizon is one of the most characteristic of all gamma ray spikes within the Furongian. The PGS can thus be identified in wells penetrating the Alum Shale Formation in Denmark and Sweden (Andersson *et al.* 1985; Pedersen & Klitten 1990; Michelsen & Nielsen 1991; Schovsbo 2002; Eriksson 2012; Schovsbo *et al.* 2011, 2015a, b, 2016) as well as in Norway (Skjeseth 1958; Elvebakk 2011; present study).

Compared with the Gislövshammar-2 and Billegrav-2 cores there is no suggestion that the Porsgrunn core contains any Lower Ordovician Alum Shale. This would have been seen as consistent lower gamma ray readings compared to those of the Furongian. This interpretation is corroborated by the absence of a V anomaly in the topmost part of the Alum Shale in the Porsgrunn core, which is elsewhere characteristic of the topmost Furongian and Lower Ordovician Alum Shale (Andersson *et al.* 1985; Berry *et al.* 1986; Schovsbo 2001; Gautneb & Sæther 2009). The Furongian is thus interpreted to be 15.8 m thick in the Porsgrunn core (Table 2).

Effect of diagenesis

The Alum Shale Formation in the Skien–Langesund district has experienced early diagenetic, catagenetic and contact metamorphic effects during the Palaeozoic. This caused changes in the mineralogy and may possibly also have led to mobilisation of certain elements. Thus the original trace element signature may in theory have been altered in the Porsgrunn core. However, the Alum Shale is known to retain its

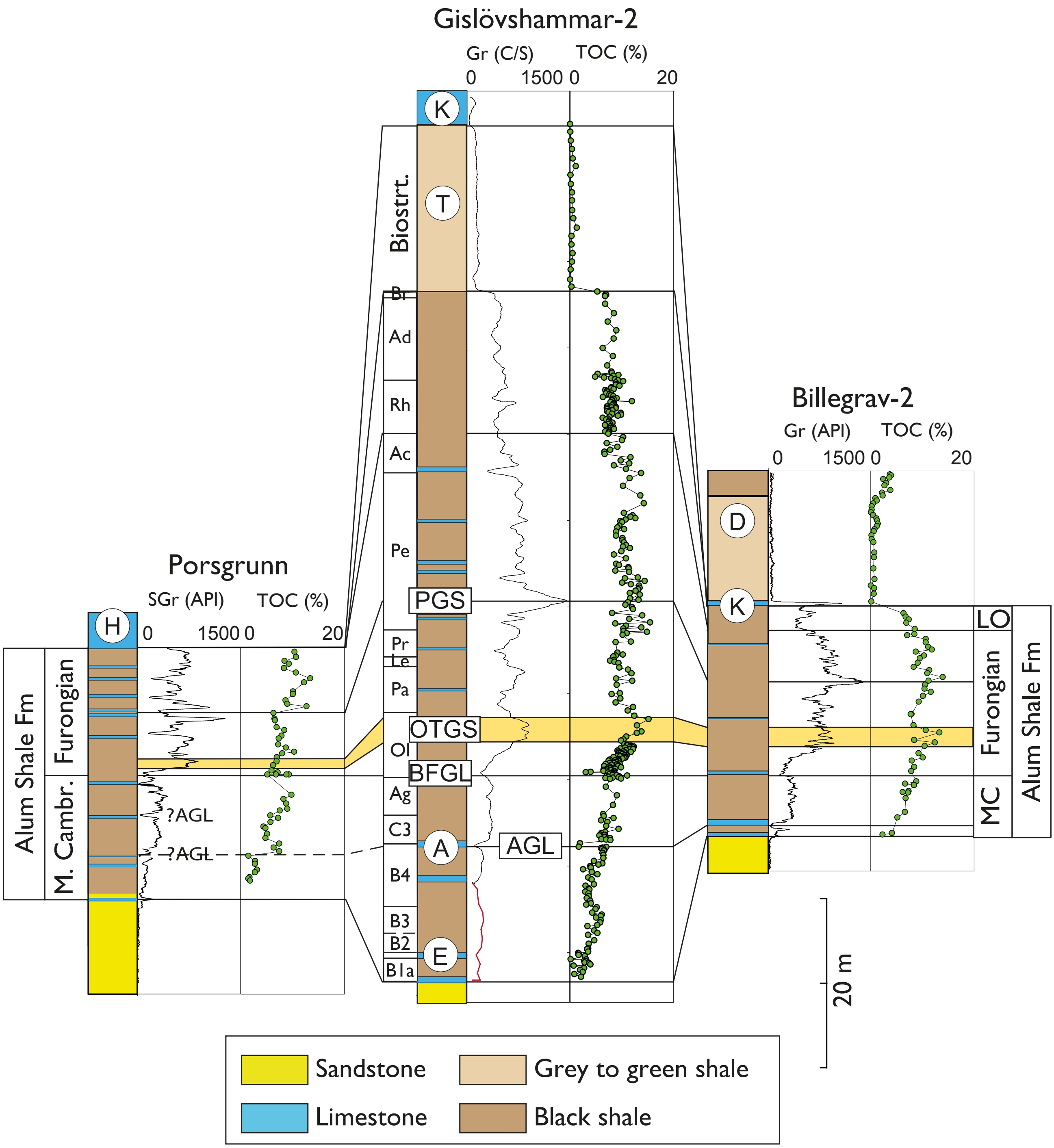

Fig. 8. Gamma ray log and TOC correlation between the Porsgrunn, Gislövshammar-2 and Billegrav-2 cores, including data from Schovsbo (2001, 2002) and Schovsbo *et al.* (2011). The biostratigraphy of Gislövshammar-2 is based on Nielsen & Buchardt (1994) and modified according to Nielsen *et al.* (2014). The lowest part of the Gr curve (in red) in the Gislövshammar-2 core is calculated from core measurements. Abbreviations: TOC: Total Organic Carbon. SGr: Spectral gamma ray. Gr: Gamma ray. API: America Petroleum Institute units. C/S: counts pr second. K: Komstad Limestone. T: Tøyen Shale. D: Dicellograptus Shale. H: Huk Formation. MC: Middle Cambrian. M. Cambr.: Middle Cambrian. LO: Lower Ordovician (Tremadocian). A: Andrarum Limestone Bed. E: Exsulans Limestone Bed. PGS: *Peltura* gamma spike. OTGS: *Olenus* triple gamma spike (interval shown with pale orange colour). BFGL: Base Furongian gamma low. AGL: Andrarum gamma low. Biostr.: Biostratigraphy in the Alum Shale Formation. For biostratigraphical abbreviations, see Fig. 3. Two possible positions for the AGL are shown; the preferred correlation is shown with a dashed line.

geochemical characteristics even in metasediments, and radioactive elements such as K, Th and U are in general considered to be immobile during diagenesis (Gee 1981; Olerud 1984; Snäll 1988, Lecomte *et al.* 2017). The presence of high concentrations of U and V in Alum Shale of presumed Furongian and Early Ordovician age in the Caledonian Mountain belt (Gee 1981; Sundblad & Gee 1985) also suggest that the trace element signature is very robust.

The new data from the Porsgrunn core compare rather well with previous geochemical studies of the Alum Shale in the Oslo area presented by Gautneb & Sæther (2009) and Pabst *et al.* (2016). The U values found in the Porsgrunn core are also comparable to those observed elsewhere in other outer shelf Alum Shale facies, see Schovsbo (2002). Hence we do not anticipate a significant tectonic overprint on the geochemistry in the core.

The organic carbon levels are lowered as thermal maturation increases due to hydrocarbon generation and expulsion, and it is expected that the TOC content is lowered in the Porsgrunn core. Thermal maturation probably took place during deep burial of the shale and/or thrust loading during the Caledonian Orogeny, but subsequent local heating also occurred in association with Permo–Carboniferous magmatic activity during the extensional phase of the Oslo Graben (Buchardt & Lewan 1990; Samuelsson & Middleton 1998; Pedersen *et al.* 2007). Any organic carbon originally present is now converted to graphite. Due to the proximity to the sills the maturity of the Alum Shale in the Porsgrunn core is assumed to correspond to at least 5 % graptolite reflectance values (cf. Buchardt & Lewan 1990; Olsson 1999).

The Alum Shale kerogen is a type II with hydrogen index of about 500 mg HC per g TOC, capable of generating hydrocarbons (Dahl *et al.* 1989; Więcław *et al.* 2010; Sanei *et al.* 2014). In the Porsgrunn core, TOC values up to 14 wt% occur, which is comparable to the TOC levels reported by Gautneb & Sæther (2009) for the Alum Shale elsewhere in the Oslo area. This level is also similar to the values seen in dry gas matured Alum Shale sections (graptolite reflectance values of 2–2.3 %; Petersen *et al.* 2013) in Scania and Bornholm (Fig. 8). The TOC content in immature Alum Shale may exceed 20 wt% (Schovsbo 2002) and it is likely that the TOC content has been somewhat reduced in all thermally mature Alum Shale sections throughout Scandinavia. In Scania and on Bornholm the TOC content increases in a step-wise manner up though the Alum Shale Formation to the *Peltura* Superzone from where it gradually decreases again (Fig. 8). In the Porsgrunn core this trend can still be recognised although in a rather scattered condition, which suggests that some remobilisation of C has occurred.

Stratigraphy

The established gamma ray log-stratigraphy of the Porsgrunn core is in good agreement with previous knowledge of the Cambrian succession in and around the Skien–Langesund district. In the Slemmestad and Krekling areas farther north and northeast (Fig. 1), an up to 3 m thick, basal interval of conglomerates, sand, silt and shale overlies the basement and marks the regional Early Cambrian transgression (Høyberget & Bruton 2008; Nielsen & Schovsbo 2011). This basal succession is thicker in the Skien–Langesund district; Vogt (1929) reported a section of 15.5–17.5 m of sandstone at Stokkevannet, and this interval was *c.* 6 m thick in a borehole at Rognstranda c. 5 km south of Porsgrunn studied by Henningsmoen (unpublished). The Lower Cambrian is 13.0 m thick in the Porsgrunn core, i.e. essentially intermediate in thickness between the two previous reports. It is likely that some of the thickness variation of the basal strata reflects undulations of the Subcambrian Peneplane, but a general thickening southwards is anticipated. We here informally refer to this unnamed succession as the Stokkevannet sandstone, but it may be envisaged as a tongue of the File Haidar Formation in south-central Sweden and this term could perhaps also be used in Norway (cf. Nielsen & Schovsbo 2011). These beds are unconformably overlain by Middle Cambrian shales with a phosphorite-bearing limestone at the base. This basal limestone is assumed to represent the Exsulans Limestone Bed, as in the classical outcrop just south of the centre of Slemmestad described by Spjeldnæs (1955, 1962). At Slemmestad a very thin arkosic sandstone bed occurs intercalated in the Alum Shale a few centimetres above the Exsulans Limestone Bed (Høyberget & Bruton 2008); in the Porsgrunn core there is intercalated 1.4 m of quartz sandstone, in part with lime cement, between the assumed Exsulans Limestone Bed and the base of the shale (Fig. 6 at 303.6–302.2 m). It may be discussed whether this sandstone should be separated as a member of its own within the Alum Shale Formation. Thin sandstone units of similar thickness are known to overlie the Hawke Bay unconformity farther north in the Caledonian Mountain chain, see Marklund (1952) and Nielsen & Schovsbo (2015).

The trilobites reported by Brøgger (1878) from the lower part of the Alum Shale in the Skien–Langesund area (see alternatively Strand 1929) are characteristic of the Middle Cambrian *Aciducus atavus* Zone (upper part equivalent to the *Hypagnostus parvifrons* Zone sensu Westergård 1946), the *Ptychagnostus punctuosus* Zone and the *Goniagnostus nathorsti* Zone. According to Brøgger's measurements the *Paradoxides paradoxissimus* Superzone is 5 to 6 m thick and overlain by *c.* 6

m of shale belonging to the *P. forchhammeri* Superzone, whereupon follow the "upper" Cambrian shales. In the Porsgrunn core the Middle Cambrian is 14.0 m thick, i.e. in good accordance with Brøgger's measurements; note that we here assign the pre-Furongian *Agnostus pisiformis* Zone to the Middle Cambrian.

According to Henningsmoen (1957) the thickness of the Upper Cambrian (~ Furongian) is not more than 12 m in the Skien–Langesund area owing to the absence not only of the *Acerocarina* Superzone but also of the upper part of the *Peltura* Superzone. The 12 m thickness derives from a borehole at Rognstranda where the Alum Shale is penetrated by numerous sills (unpublished), and it is uncertain whether the succession includes the *A. pisiformis* Zone. The Furongian is close to 15 m thick in the Porsgrunn core. Conglomeratic levels of possible regional distribution as observed in Sweden (see e.g. review by Martinsson 1974) have not been described from the Furongian of the Skien–Langesund district and are not identified in the Porsgrunn core. The biostratigraphy of the Furongian in the district was investigated by Henningsmoen (1957, 1958), but due to the intense Permian heating fossils are difficult to extract from the baked Alum Shale which is hard and splintery.

The Cambrian-Ordovician hiatus

Central to work in the area has been a discussion of the local unconformity between the Cambrian and Ordovician. In the borehole at Rognstranda the Furongian part of the Alum Shale Formation consists of only 12 m of strata lacking parts of the *Peltura* Superzone and all of the *Acerocarina* Superzone (Henningsmoen 1957; Strand & Henningsmoen 1960). The Alum Shale is here directly overlain by the Middle Ordovician Rognstranda Member of the Huk Formation (Owen *et al.* 1990).

Rønning (1976, 1978; personal communication 1/12/2014 to D. Bruton) identified the Tremadocian Zone of *Rhabdinopora* in a submarine tunnel used for a pipeline for Norsk Hydro from their chemical plant at Rafsnes to Herøya, extending under Frierfjord (see also Lien *et al.* 1978; for location see Fig. 2). Rønning made collections of well-preserved dendroid graptolites (*Rhabdinopora*) and obolid brachiopods, proving beyond doubt the presence of Tremadocian Alum Shale in the now flooded tunnel.

The interpretation of the local unconformity is controversial; it was interpreted as a thrust contact by Ramberg & Bockelie (1981, fig. 2) and Bockelie & Nystuen (1985) and as an erosional unconformity by Nilssen (1985). The former authors suggested that a sole thrust might be present within the Alum Shale Formation to explain the lack of Lower Ordovician at almost all localities in the district.

Bockelie & Nystuen (1985, p. 76, fig. 4I), referring to Rønning's work, preferred to invoke a frontal ramp to explain the absence of Tremadocian Alum Shale, rather than local non-deposition or erosion as favoured by Strand & Henningsmoen (1960). The Alum Shale is stratigraphically complete at Krekling some 75 km to the north (Høyberget & Bruton 2008) where it includes the Tremadocian followed by the Bjørkåsholmen Formation (0.6 m thick) and a thin Tøyen Shale (ca. 5 m), while further west, south of Skollenborg and near Flata, these units are absent and the Alum Shale (middle part of the *Peltura* Superzone) is directly overlain by the Huk Formation (see Fig. 1 for locations). Elsewhere in Scandinavia are also seen gaps between the Furongian and the Tremadocian. A classic example is Hunneberg in Västergötland, south-central Sweden, where pockets of thin Tremadocian Alum Shale directly overlie the *Peltura* Superzone (Westergård 1922). Reworked trilobites from the *Peltura* Superzone were recorded in the *Acerocarina* Superzone at nearby Kinnekulle by Weidner & Nielsen (2013), which is taken to indicate late Furongian uplift and erosion of Västergötland. Tremadocian Alum Shale is absent across most of this district. On southern Öland only the middle part of the Tremadocian is represented (Westergård 1922). We conclude that there appears to have been widespread crustal unrest in Scandinavia in the late Furongian associated with local uplift. As a result the terminal Furongian *Acerocarina* Superzone has a rather limited distribution (see recent map in Weidner & Nielsen 2013). We thus support Strand & Henningsmoen (1960) in proposing the local absence of the Tremadocian in most of the Skien–Langesund district to be the result of non-deposition.

Conclusions

The described core section represents the interval 322.6–260.0 m (TD) in the BHD-03-99 Porsgrunn borehole. This drill site is located in an area of southern Norway that did not undergo Caledonian tectonic deformation and thus represents one of the few sites in the Oslo region where it is possible to study a nearly untectonised sedimentary sequence in terms of thickness and geochemistry. The succession is, however, penetrated by numerous sills of assumed Permian age. The Alum Shale Formation is 28.8 m thick in the Porsgrunn core, excluding the thickness of five 0.9–5.5 m thick dolerite sills.

The Middle Cambrian interval is 14.0 m thick and includes the Exsulans Limestone Bed (0.06 m thick) and 1.4 m of quartz sandstone immediately overlying this limestone. A 0.3 m thick primary limestone at

296.0–295.7 m may represent the Andrarum Limestone Bed but interpretation of the gamma log-motif in this interval is ambiguous. The Alum Shale Formation rests atop a 13.0 m thick lower Cambrian sandstone, informally referred to as the Stokkevannet sandstone, that in turn rests directly on the basement.

The upper 14.8 m thick Furongian part of the Alum Shale represents the *Olenus*, *Parabolina*, *Leptoplastus*, *Protopeltura* and *Peltura* trilobite superzones, judging from log-stratigraphic correlations to Scania and Bornholm. No Ordovician Alum Shale is present and the *Acerocarina* Superzone also appears to be absent. This is ascribed to local uplift as also seen elsewhere in Scandinavia at that time.

The stratigraphic development of the comparatively thin Alum Shale Formation resembles the condensed sequence seen on Bornholm except for the absence of Ordovician strata.

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