

# The geochemistry of Lower Palaeozoic sediments deposited on the margins of Baltica

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A regional survey of the geochemical composition of Lower Palaeozoic shales deposited on Baltica indicates that Llanvirn (Lower/Middle Ordovician) to Lower Silurian shales have higher concentrations of Na, Mg, Cr, Ni and Fe and lower concentrations of K, Rb and Ti compared to Arenig shales. This geochemical signature can be traced from Scania to the Oslo Region, i.e. in areas approximately 500 km apart, but is not present in Middle Ordovician sediments from Avalonia. The geochemical signature matches island arc tholeiites such as those in the Fundsjø Group within the Upper Allochthon of the Norwegian-Swedish Caledonides. Hence, these sediments were probably predominantly derived from island arcs formed during the end phase of closure of the Iapetus Ocean. Simple two component mixing calculations between oceanic and continental sediment sources suggest that the oceanic component diminishes towards the south where modifications related to longer sediment transport distances can be recognised. The introduction of sediment derived from island arcs coincides with increases in subsidence rates in the Oslo Region and may reflect an early stage in foreland basin development. The presence of the geochemical signature in Scania implies that island arcs systems were geographically widespread. The combined evidence indicates that the Arenig/Llanvirn boundary marks an important change in the continuing closure of the Iapetus Ocean. The data suggest that island arcs were obducted onto the outer margins of Baltica presumably during the Arenig. Continued obduction of island arcs in the Mid Ordovician and younger intervals is likely.

*Key words:* Provenance, Caledonides, Scania, Oslo, Lower Palaeozoic.

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The Iapetus Ocean and Tornquist Sea rimmed the western and southern margins of Baltica during Early Palaeozoic. These areas were created during Neoproterozoic to Cambrian Ocean floor spreading which followed the break-up of the supercontinent Rodinia. Closure of the seas commenced in the late Cambrian with the main phase of subduction in the Ordovician and final closure and continent-continent collision in latest Ordovician to early Silurian. The closure was two-sided involving subduction of Iapetus oceanic lithosphere between Baltica and Laurentia and subduction of Tornquist oceanic lithosphere between Baltica and Avalonia (Torsvik *et al.* 1996; Torsvik 1998).

The precise location and nature of the subduction zones are, however, unknown and highly controversial (Sturt & Ramsay 1999). For the Iapetus Ocean, models range from complete subduction solely along the Laurentian margin (Pedersen *et al.* 1992) to full subduction solely along the Norwegian margin (Sturt 1984). A consensus model of two-sided subduction

has been proposed by Grenne *et al.* (1999). Furthermore, the presence or absence of island arcs and micro-continents in these oceanic areas are also a matter of dispute. A large variety of models regarding island arcs have been proposed. The island arcs may have been created and subsequently accreted onto the margins of Baltica within a narrow time span in the Early Ordovician (Sturt 1984; Sturt & Roberts 1991). Others have claimed that isolated island arcs were a more long lasting phenomenon on which the faunas developed differently from those on the continents (Bruton & Harper 1981; Harper 1992). In the Tornquist Sea, micro-plates accreted to Baltica in the southeastern Polish region already in the Mid Cambrian (Belka *et al.* 2000). A general view is that the main phase of subduction occurred along the Avalonia plate (Giese *et al.* 1994; McCann 1998). Considerable oblique movements of Avalonia led to the docking of this continent rather than head-on collision. The Tornquist margin in the northwestern Mazury High of Poland

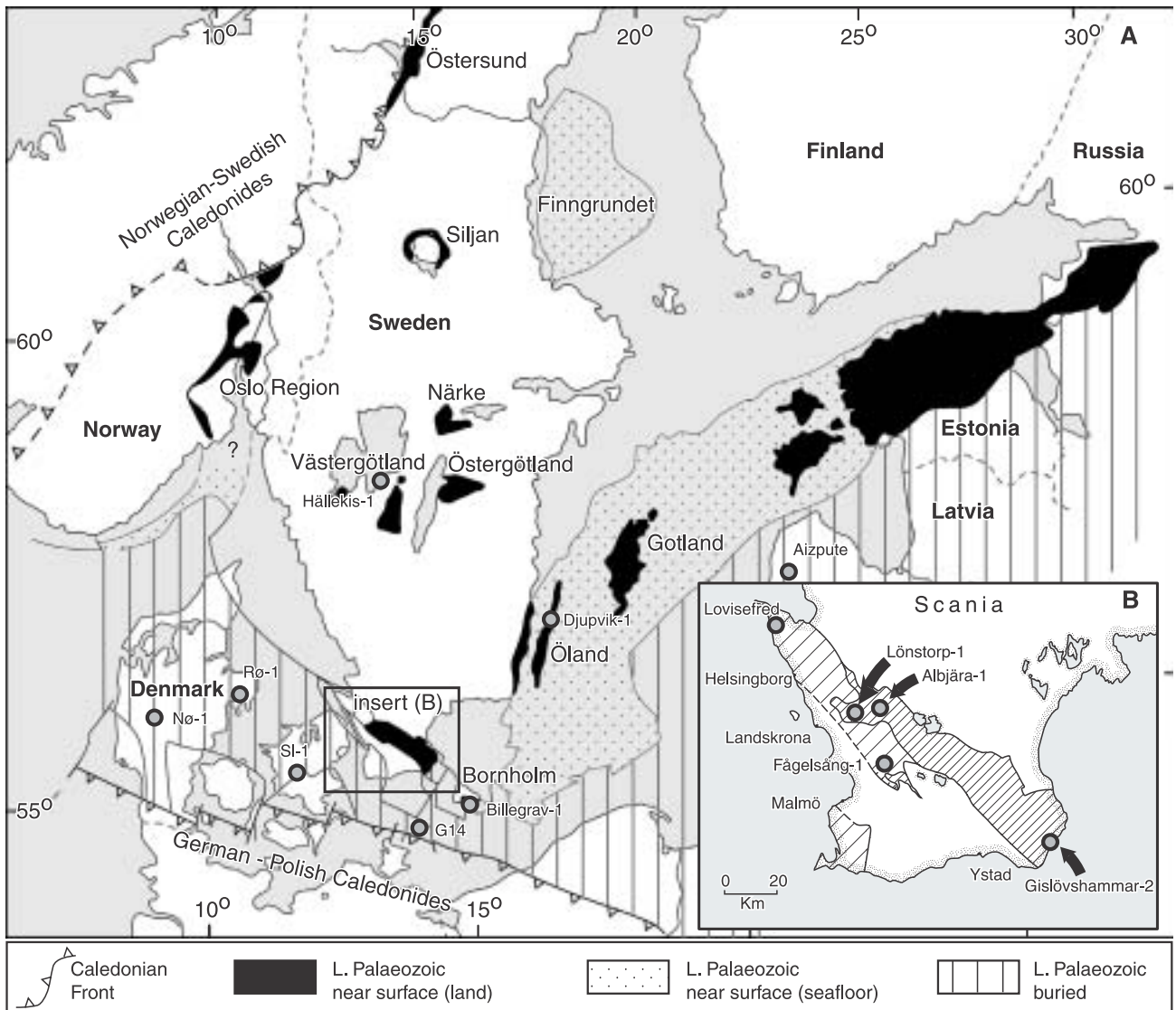


Fig. 1. A. Distribution of Lower Palaeozoic rocks in Baltoscandia and location of shallow wells (circles) mentioned in the text, B, close-up of Scania. Deep wells: Rø-1, Rønde-1; Nø-1, Nøvling-1; SI-1, Slagelse-1. Modified from Buchardt *et al.* (1997).

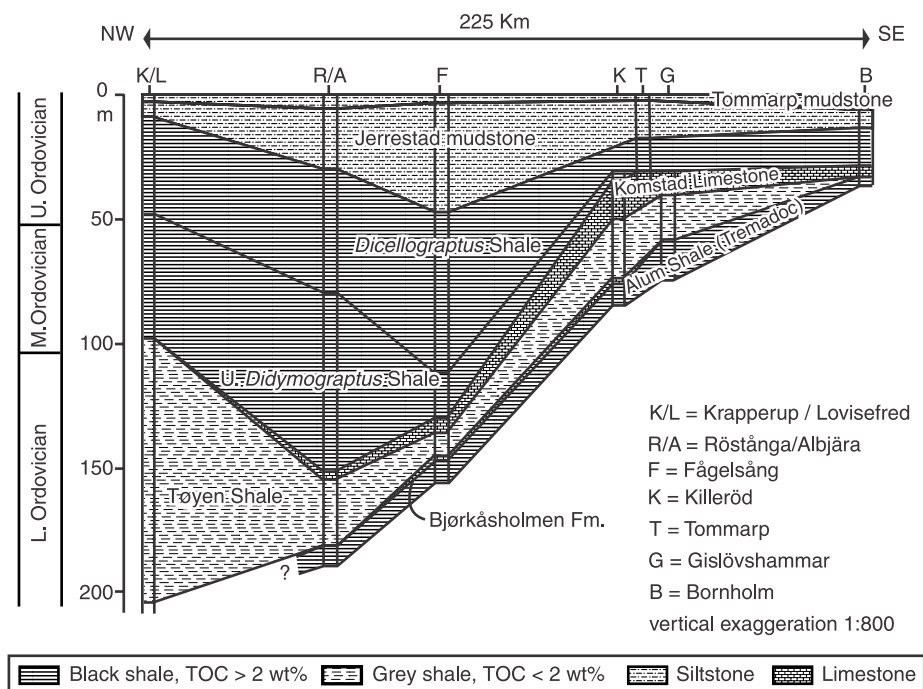
was developed as a passive margin (Poprawa *et al.* 1999).

One of the greatest uncertainties in establishing the chronology of the early phases of ocean closure in the Baltic area is the measurement of the relative distance between the different tectonic complexes within the Scandinavian Caledonides (Gee *et al.* 1985; Stephens & Gee 1989). These tectonic units contain different segments ranging from *in situ* Baltica cover sediments (Parautochthon) to Laurentian margin sediments (Uppermost Allochthon). Sandwiched between these are oceanic rocks within the Upper Allochthon. In order to unravel the relative movements of these complexes from west to east, Bjørlykke (1974a, b) made use of the contrasting geochemical signature of mafic to ultramafic rocks compared to average crustal com-

positions. The compositional differences arise from a higher degree of differentiation by fractional crystallisation of magmas during the generation of the continental crust. Over time this differentiation produced continental crust that was less enriched in ferromagnesian minerals and with lower contents of transitional elements (e.g. Cr, Ni, V) compared to rocks constituting the oceanic crust (Taylor & McLennan 1985). Sediment derived from these distinctly different source areas will thus vary markedly in their geochemical compositions.

The present paper is focused on a Middle Cambrian to Lower Silurian stratigraphic profile constructed from drill-cores in the Scania-Bornholm area of southern Scandinavia. The main objectives are to clarify the significance of a mafic source in this part

Fig. 2. Regional variation in thickness of Ordovician deposits across Scania to Bornholm. Modified from Nielsen (1995).



of the margin by examining the same stratigraphical interval as Bjørlykke (1974a, b). Aided by a detailed biostratigraphy, the relative depositional rate is used as a proxy for the relative stability of the crust. The outcome of this study is an estimate of the average composition of the source area as a function of time. Together with information on sediment transport between various parts of the craton, such data might form an alternative way to constrain the tectonical evolution during the early phases of the Caledonian orogeny.

## Geological settings

Lower Palaeozoic sediments are preserved in a broad belt along the German-Polish and the Norwegian-Swedish Caledonides (Fig. 1). The Neoproterozoic and Cambrian periods were characterised by ocean floor spreading and thermal subsidence of the margins of Baltica (Greiling *et al.* 1999; Poprawa *et al.* 1999). Sedimentation took place on the craton as the infilling of older pull-apart basins and in thermal contraction basins (Vidal & Moczyłowska 1995; van Balen & Heeremans 1998). Subsequent sedimentation assumed a more blanket-like distribution (Greiling *et al.* 1999) particularly in the condensed Middle Cambrian to Lower Ordovician (Tremadoc) organic-rich shales. These shales vary in thickness from ca 100 m in southern Sweden and in the Oslo Region to less

than 0.5 m in eastern Estonia and the St. Petersburg District (Artyushkov *et al.* 2000). The shales have a remarkably uniform lithology and contain distinctive event-like horizons traceable over large distances (Martinsson 1974; Bruton *et al.* 1989; Nicoll *et al.* 1992). The maximum extent of this facies was reached in the Tremadoc. Contemporaneous sand- and siltstones are not very thick reflecting the absence of major sediment source areas. Thus, the craton probably had a smooth topography created as a result of prolonged Proterozoic denudation.

Regional lithological differences were established in the Early Ordovician (Arenig) between the cold-water carbonate platform which developed on the craton interior and the relatively deep-water mud deposited along its margins (Nielsen 1995). Scania and Bornholm together with the Oslo Region were largely positioned within the belt of siliciclastic sedimentation during the Ordovician. Development of primary carbonate in these areas in the Late Arenig to Early Llanvirn (Huk/Komstad Limestone, Nielsen 1995) signalled a major lowering of sea level (Fig. 2). A direct link between ocean floor convergence and lithological development cannot be established. However, local thickness variations of the Ordovician deposits in the Scania-Bornholm area (Fig. 2) suggest crustal movements of the plate edge during the Ordovician (Vejbæk *et al.* 1994; Nielsen 1995).

Baltica collided with Laurentia in the Late Ordovician – Early Silurian and with Avalonia in the Early Silurian (Berthelsen 1992). Following collision with

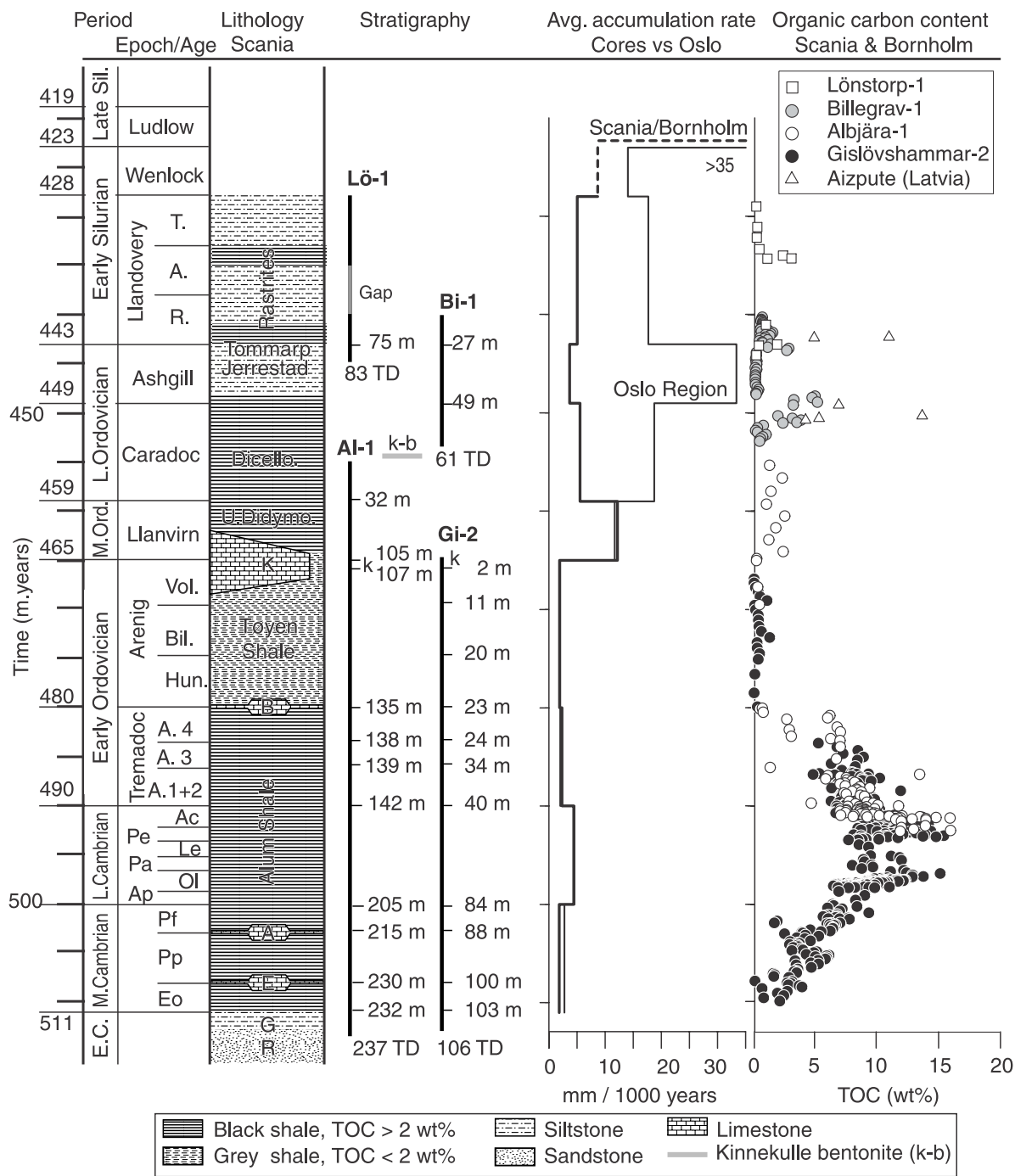


Fig. 3. Lithology, stratigraphy, average depositional rate and organic carbon content of the Lönstorp-1, Billegrav-1, Albjära-1 and Gislövshammar-2 cores (see Fig. 1 for location). Note that depths in the cores are converted to absolute dates assuming continuous deposition within each epoch. Equal duration of the Cambrian and Tremadoc biozones are assumed for simplicity. Biostratigraphical information is from Maletz (1995), Koren' & Bjerreskov (1997), Schovsbo (2001), Lauridsen (2000) and T. Koren' & A.T. Nielsen (unpublished). Time scale adapted from McKerrow & van Staal (2000). TOC content in the Billegrav-1 core is from Buchardt *et al.* (1986). Wenlock and Ludlow depositional rates are calculated from thicknesses in Vejrbæk *et al.* (1994). Average depositional rates in the Oslo Region (based on thicknesses in Bjørlykke 1974a and Owen *et al.* 1990) and TOC concentrations in the Baltic syncline (Aizpute core, Marshall *et al.* 1997) are included for comparison. Stage abbreviations: R.-Rhuddanian; A.-Aeronian; T.-Telychian. Lithological abbreviations: R, Rispebjerg Sandstone; G, Gislöv Formation; E, Exsulans Limestone; A, Andrarum Limestone; B, Björkåsholmen Formation; K, Komstad Limestone. Biostratigraphical abbreviations: Eo, *Eccaparadoxides oelandicus* Stage; Pp, *Paradoxides paradoxissimus* Stage; Pf, *Paradoxides forchhammeri* Stage; Ap, *Agnostus pisiformis* Zone; Ol, *Olenus* Zone; Pa, *Parabolina* Zone; Le, *Leptoplastus* Zone; Pe, *Peltura* Zone; Ac, *Acerocare* Zone; As 1-4, Tremadoc graptolite assemblages according to Cooper (1999).

Avalonia a rapidly subsiding foredeep developed along the SW margin (Eugeno-S Working Group 1988; Berthelsen 1992; Poprawa *et al.* 1999). High subsidence was initiated close to the Caledonian Front in the Early Silurian and later in distal areas (Vejbæk *et al.* 1994; Poprawa *et al.* 1999). In Scania, rapid subsidence occurred in the Late Silurian (Ludlow) with the development of the Colonius Shale Trough. During this period, thermal maturation of the organic carbon of the Lower Palaeozoic strata took place.

## Samples and analytical methods

Geochemical analyses have been conducted on samples from the Billegrav-1, Lönstorp-1, Albjära-1, Gislövshammar-2, Hällekis-1 and Djupvik-1 cores (Fig. 1). Geochemical analyses were obtained from 1-cm thick slices of half a core corresponding to 15 g. Prior to crushing, macroscopic calcite veins, pyrite and barite crystals were removed. The sample material was homogenised and crushed in an agate swing mill to a grain size below 60 µm. Total carbon (TC) and sulphur content was measured on a Metalyt 90S by combustion of 100 mg samples at 1250°C in an oxidising atmosphere. Measurements of CO<sub>2</sub> and sulphur gases were carried out with a TCD detector. Total organic carbon (TOC) content was either measured directly on acid-treated sample material or calculated from the total calcium content. Major elements were determined by XRF analysis of glass discs supplemented by atomic absorption (Mg, Na) and wet chemistry (FeO, H<sub>2</sub>O, LOI). Trace element concentrations were analysed directly on pressed powder pellets by X-ray fluorescence using a Phillips PW 1400 and the methodology of Norrish & Chappell (1977) at the University of Copenhagen. Trace element analyses from the Billegrav-1 core were measured by ICP-MS technique at the Geological Survey of Denmark and Greenland.

## Result and discussion

The Scania cores together with the Billegrav-1 core of Bornholm constitute a near continuous stratigraphic profile from the Lower Cambrian to the Lower Silurian (Fig. 3). The Lönstorp-1 core constitutes the uppermost part of the profile. It extends from the *Monograptus spiralis* graptolite Zone in the late Llandovery (Early Silurian) to the *Normalograptus persculptus* graptolite Zone in the latest Ordovician (Ashgill) (T. Koren' & A.T. Nielsen unpublished). A

hiatus corresponding to the upper part of the lower and lower part of the middle Llandovery is present in the core (Fig. 3). A similar development is also present in the Röstånga core (Bergström *et al.* 1999).

The Ordovician/Silurian boundary is located at 27 m in the Billegrav-1 core (Pedersen 1989; Koren' & Bjerreskov 1997; Fig. 3). The uppermost part of the Billegrav-1 core is represented by the *Cystograptus vesiculosus* graptolite Zone (Rhuddanian). The core was terminated approximately 6 m above the Komstad Limestone (Pedersen 1989). This interval is within the *Diplograptus multidentis* graptolite Zone (Caradoc). The precise boundaries of the Ashgill/Caradoc in the Billegrav-1 core are, however, poorly constrained. Based on the lithology, Pedersen (1989) assumed the boundary to be around 49 m in the core. If so the Ashgill is approximately 22 m thick in the Billegrav-1 core and the cored Caradoc interval is approximately 12 m thick. Since the core was terminated approximately 6 m above the Komstad Limestone the Caradoc interval at Billegrav is estimated at 18 m. As also noted by Pedersen (1989) these estimates are somewhat higher compared to thicknesses measured in outcrops within the Læså area (Poulsen 1966).

The Caradoc interval is also present in the Albjära-1 core (Maletz 1995; Fig. 3). The Albjära-1 and Billegrav-1 cores are, however, not believed to overlap stratigraphically. The reason for this is that the cores do not contain the Kinnekulle bentonite that was part of a 454 Ma major ash fall and serves as a chronostratigraphical marker bed (Huff *et al.* 1992). On Bornholm, the Kinnekulle bentonite is present within the basal part of the *Dicellograptus* Shale in the *D. multidentis* graptolite Zone. The Kinnekulle bentonite is not present in the Albjära-1 core (Fig. 3). The base of the Caradoc (*Nemagraptus gracilis* graptolite Zone; Fortey *et al.* 1995) is not well documented in the Albjära-1 core (Maletz 1995). Most reliable estimate for the Llanvirn/Caradoc boundary is at 32 m in the Albjära-1 core (Maletz 1995). The base of the Llanvirn is here placed above the Komstad Limestone at 105 m (Maletz 1995; Fig. 3).

The Lower Cambrian to Arenig is represented by the Gislövshammar-2 and Albjära-1 cores (Fig. 3). The Bjørkåsholmen Formation (Ceratopyge Limestone; Owen *et al.* 1990) is absent in the Gislövshammar-2 core, where there is a minor hiatus between the Alum Shale and Tøyen Shale formations. This interval is complete in the Albjära-1 core.

## Lithology

The lithologies of the Lower Palaeozoic shales range from mudstone to siltstones with variable amounts

of organic carbon (Fig. 3). Regionally-distributed primary limestone beds occur in the Middle Cambrian, the Upper Tremadoc and across the Arenig/Llanvirn boundary. In the Scania-Bornholm area TOC concentrations above 10 wt% are attained within the Upper Cambrian part of the Alum Shale Formation. The TOC concentrations are, however, affected by Late Silurian to Early Devonian deep burial resulting in a 30–50% relative lowering of carbon levels due to expelled hydrocarbons at maturation levels approaching ankiometamorphic conditions (Buchardt *et al.* 1986). Compared to thermally immature sites in south-central Sweden and Estonia, the thermally-induced lowering can account for the regional variation in southern Scandinavia of the TOC content suggesting that conditions for TOC accumulation were not substantially different within different parts of the Alum Shale sea basin (Schovsbo 2002).

In the post-Tremadoc shales, TOC concentrations are much lower (Fig. 3). Intervals with TOC below 2 wt% are present in the Arenig and middle Ashgill shales (Fig. 3). Concentrations above 5 wt%, i.e. comparable to those in the Alum Shale Formation, are present in the Caradoc and basal Ashgill interval in the Billegrav-1 core (Fig. 3). In the Billegrav core the TOC rich interval ends abruptly below a well-bioturbated interval at 46 m. In contrast to the Alum Shale Formation, the TOC-rich interval in the Billegrav-1 core represents a short time interval of a few million years (Fig. 3). In the Oslo Region, the Upper Ordovician and Lower Silurian shales have TOC concentrations below 1 wt% (Bjørlykke 1974a). Much higher TOC concentrations have been reported from the eastern part of the basin (Fig. 3), suggesting that more localised variations within the depositional environment controlled TOC accumulation in the post-Tremadoc shales.

### Average depositional rates

Estimates of average depositional rates have been reconstructed from the cores (Fig. 3). Depositional rates within the Oslo Region have been calculated based on data provided in Bjørlykke (1974a) and Owen *et al.* (1990). The time-scale used is adapted from McKerrow & van Staal (2000). The main difference between this time-scale and others, e.g. Tucker & McKerrow (1995), are minor corrections of the Cambrian and Early and Mid Ordovician dates. A notable change is a shortening of the Mid Ordovician interval due to improved correlation and re-evaluation of absolute ages (see McKerrow & van Staal 2000). Minor age corrections have been made to the

Llanvirn/Caradoc boundary in accordance with the revised stratigraphy (Fortey *et al.* 1995, 2000).

In Scania and the Oslo region, the Middle Cambrian to Lower Ordovician shales and limestones have broadly similar thicknesses (Fig. 3). These units were deposited at low depositional rates ranging from 2 to 4 mm/1000 years (Fig. 3, rates are all given as post-compactional values). Above the Huk/Komstad Limestone, a marked increase in the depositional rate to approximately 10 mm/1000 years occurs within the Llanvirn. In the Scania-Bornholm area, the average depositional rate decreases to lower values (approximately 5 mm/1000 years) in the Caradoc whereas the depositional rates in the Oslo Region remain high with peak values of 30 mm/1000 years in the latest Ordovician (Ashgill). A second increase in depositional rate occurs in the Scania-Bornholm area and the Oslo Region in the early Late Silurian (Ludlow; Fig. 3).

The relatively low Late Ordovician depositional rates in the Scania-Bornholm area might be an artefact related to gaps within the Bornholm sequences. Compared to Scania, however, comparable thicknesses of the Ashgill shales are preserved here, apart from the Fågelsång section, which is twice as thick (Bergström *et al.* 1999; Fig. 2). Adopting the thicknesses from the Fågelsång area (Fig. 1) do not, however, yield a depositional rate comparable to that in the Oslo Region. Instead, the Late Ordovician to Silurian depositional rates calculated here match estimates from the eastern part of the basin (Poprawa *et al.* 1999). Hence, local conditions alone cannot explain the differences in depositional rates between the Scania-Bornholm area and the Oslo Region. The difference in depositional rates between Scania and the Oslo region is thus likely to reflect different temporal developments within the Scandinavian and German-Polish Caledonides. In the Oslo Region, the increase in depositional rates in the Llanvirn most likely reflects the onset of foreland development in the Mid Ordovician as suggested by Bjørlykke (1974b).

In Scania, the increase in depositional rate during the Llanvirn would appear to reflect a minor uplift of the southern margin of Baltica (Vejbæk *et al.* 1994). This led to a thickening of the shales towards the northwest as exemplified by the Lovisefred core (Fig. 2). The re-establishment of reduced depositional rates in the Caradoc to Llandovery interval indicates, however, that the increase in depositional rate did not signal a change from passive to active margin. Hence, the inferred tectonically-induced transformation of the Norwegian Iapetus Ocean margin cannot be correlated to Scania.

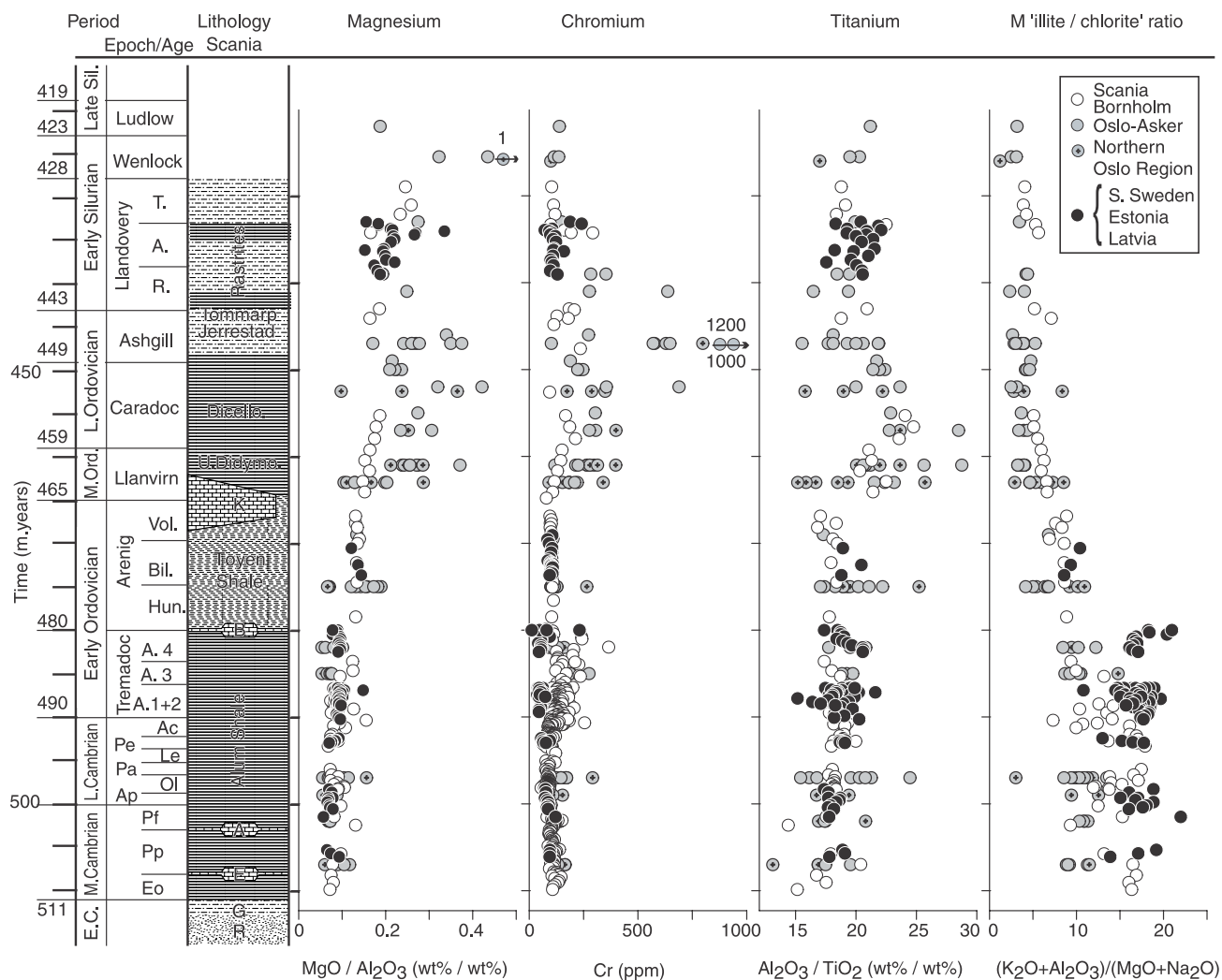


Fig. 4. Stratigraphical variations of  $\text{MgO}/\text{Al}_2\text{O}_3$  ratio, Cr concentrations,  $\text{Al}_2\text{O}_3/\text{TiO}_2$  ratio and the sediment maturity parameter M. See Figure 3 for legend and abbreviations. Data sources; Bornholm: Billegrav-1 core; Scania: Lönstorp-1, Albjära-1 and Gislövshammar-2 cores; southern Sweden: Hällekis-1 and Djupvik-1 cores; Oslo Region: Bjørlykke (1974c); Estonia (Tremadoc): Pukkonen & Rammo (1992) and Pukkonen & Buchardt (1994); Latvia (Llandovery, Aizpute core): Kiipli (1997). Only samples with  $\text{CaO} < 10 \text{ wt}\%$  are included. Major elements have been normalised to the  $\text{Al}_2\text{O}_3$  content in order to minimise matrix variation induced from variable amounts of TOC and reduced sulphur compounds. Note that no M-values are calculated from Latvia since Na values were not reported in Kiipli (1997).

## Magnesium and chromium

Magnesium concentrations increase above the Huk/Komstad Limestone in Scania and the Oslo Region. Below this level  $\text{MgO}/\text{Al}_2\text{O}_3$  ratios of ca 0.1 are found throughout the basin (Fig. 4). In Scania the ratio increases to 0.2 in the Upper Ordovician and approaches 0.3 in the Silurian. In the Oslo Region the Mg content is approximately twice that of the Ordovician shales whereas similar levels are present in the Silurian shales between Scania and the Oslo Region.

In Scania, chromium concentrations above 100 ppm are found within the Tremadoc and Middle Ordovi-

cian to lowermost Silurian shales (Fig. 4). In the Oslo Region, similar stratigraphical enrichment is found. Analogous to the variation in Mg content, the Cr concentrations in the Oslo Region are approximately twice that of the Upper Ordovician shales, with similar concentrations in the Silurian between the different areas. In the Oslo Region the highest Cr concentrations are measured in the Upper Ordovician (Ashgill) where detrital chromite grains are found (Bjørlykke 1974a).

According to Bjørlykke (1974b) the increase in Mg concentrations in the Oslo Region reflects the presence of chlorite in the shales. The chlorite was pre-

sumably derived from the weathering of basalts, implying proportional enrichments in for example Cr and Ni (Fig. 4). In the Slagelse-1, Nøvling-1, Rønde-1 and Billegrav-1 chlorite has been reported from the Ordovician to Silurian shales (Thomsen *et al.* 1983; Pedersen 1989; Fig. 1) and it is, therefore, likely that the increase in Mg and Cr concentrations also reflects the presence of chlorite in Scania. The chlorite type in the Danish cores is, however, of a species that is highly unstable during transport (Thomsen *et al.* 1983). Hence, Mg loss resulting from mineral re-equilibration during progressive burial might also be a controlling factor. The apparent similar enrichment levels of Mg and Cr may suggest that no substantial alteration of the Mg content has occurred. Limited mineral reactions due to burial diagenesis have also been inferred by Bergström *et al.* (1999) based on the presence of kaolinite in the K-bentonite beds in Scania.

The lack of Mg enrichment in the Tremadoc, where Cr concentrations above 100 ppm are reached reflects syngenetic enrichment of Cr in the TOC rich Alum Shale (compare Figs 3 and 4). The reason why the syngenetic Cr enrichment is profound in the Tremadoc part of the Alum Shale is currently unknown. Compared to some other syngenetic enriched trace elements this mode of enrichment is expected. Uranium is thus preferentially enriched in the Upper Cambrian whereas the Tremadoc interval is enriched in V (Armands 1972; Andersson *et al.* 1985; Buchardt *et al.* 1997).

The increase of Cr concentrations in the Ashgill far exceeds that of the Mg content in the Oslo Region. This suggests that physical fractionation of sediment particles occurred. High Cr concentrations are normally found proximal to an ultramafic source and primarily in the coarse-grained fractions (Garver *et al.* 1996).

## Titanium

$\text{Al}_2\text{O}_3/\text{TiO}_2$  ratios increase from less than 20 below the Komstad Limestone to 25 in the Caradoc (Fig. 4). The decrease in Ti concentrations, i.e. higher  $\text{Al}_2\text{O}_3/\text{TiO}_2$  ratios, is also a pronounced feature in the Middle and Upper Ordovician of the Oslo Region (Fig. 4). According to Bjørlykke & Englund (1979) the Ti concentrations in the shale are controlled by the transformation from biotite to illite since illite is not capable of accommodating Ti in its lattice structure. Accordingly, the shales deposited above the Huk/Komstad Limestone may have experienced a higher degree, or a different style, of weathering than the shales deposited below. Nevertheless, Bjørlykke (1974b) attributed the increase in Mg concentrations found

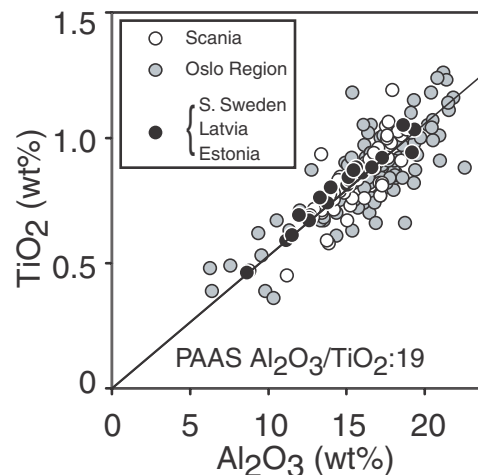


Fig. 5. Ti concentrations versus Al concentrations of samples in Figure 4. The  $\text{Al}_2\text{O}_3/\text{TiO}_2$  ratio of average continental derived sediments (PAAS, Taylor & McLennan 1985) is shown for comparison.

within the same period as a reflection of less intense weathering combined with rapid burial which allowed chlorite to be preserved in the deposited mud. Ti concentrations are closely correlated to the Al content (Fig. 5), which excludes the possibility that the Ti concentrations were controlled by mineral transformations.

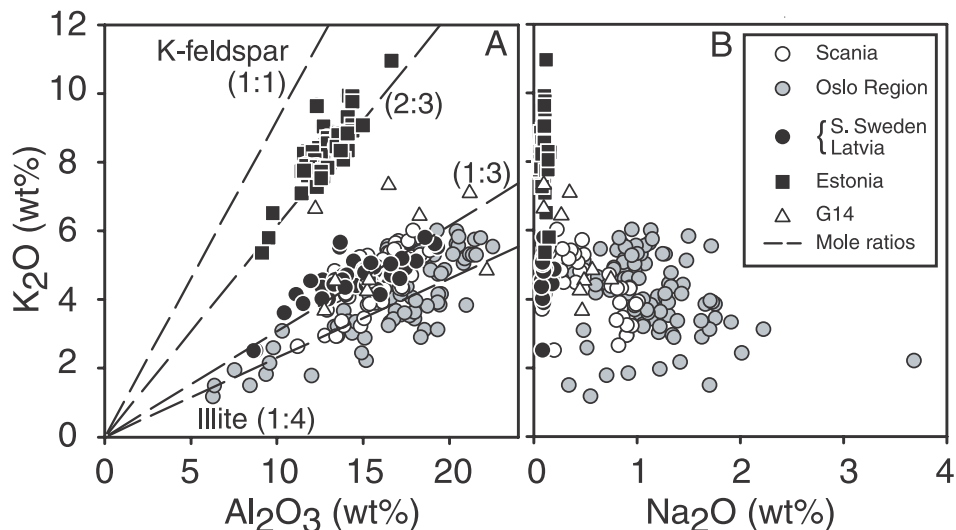
High  $\text{Al}_2\text{O}_3/\text{TiO}_2$  ratios have been used as a characteristic feature of continentally derived sediments (Fyffe & Pickerill 1993). In the Ordovician and Silurian such components are represented by calc-alkaline magmatics present in the Ordovician and Silurian sequences (Huff *et al.* 1992; Bergström *et al.* 1995, 1997). The bentonites have high  $\text{Al}_2\text{O}_3/\text{TiO}_2$  ratios compared to those of the average continental crust (Kolata *et al.* 1987; Huff *et al.* 1997) and were generated in a continental destructive plate-margin setting (Huff *et al.* 1992, 1997). Mixing calculations based on clay mineral content of the shale and bentonites indicate that material derived from the bentonites was subordinate (Bergström *et al.* 1999).

## Sedimentary maturity parameter

The M ratio  $[(\text{Al}_2\text{O}_3 + \text{K}_2\text{O})/(\text{MgO} + \text{Na}_2\text{O})]$  represents a geochemical proxy for the mineralogical composition of shale (Bjørlykke 1974b). M-values above 10 reflect a dominance of illite whereas values below 10 reflect dominance of chlorite and albite.

The Middle Cambrian to Arenig shales range in M-values from 10 to 20 whereas values below 10 characterise the Middle Ordovician to Silurian deposits (Fig.

Fig. 6. K concentrations versus Al (A) and Na concentrations (B) of samples in Figure 4. Molar ratios are included in (A) for comparison. Data from the G14 well (McCann 1998) are included for comparison.



4). The decrease in M-values above the Huk/Komstad Limestone reflects the presence of chlorite in the shales (Bjørlykke 1974b). In the Middle Cambrian to Tremadoc Alum Shale Formation, consistently higher M-values are calculated from the southern Swedish and equivalent shales in Estonia compared to those calculated from Scania and the Oslo Region. In the Middle Cambrian a decrease in M-values are seen in the *Paradoxides paradoxissimus* Stage whereas the opposite development in M-values are obtained in samples from southern Sweden (Fig. 4).

According to Lindgreen *et al.* (2000) the Alum Shale contains two illite types reflecting detrital illite and illite originating from the weathering of smectite derived from volcanic ash. Both types are present in the Upper Cambrian and Tremadoc samples from Scania, Southern Sweden and Estonia suggesting that there was no shift in source area during this period. The volcanic-derived illite possibly originated from the Vendian volcanic rocks formed during the break-up of Rodinia. A likely source area according to Lindgreen *et al.* (2000) could be in Poland, for example the Mazury High, which was uplifted during the Cambrian (Valverde-Vaquero *et al.* 2000).

In the Alum Shale, diagenetical K-feldspars have been described (Armands 1972). Diagenetical K-feldspars tend to be Na poor and are readily discriminated in a K vs Na plot due to its low Na content (Fig. 6B). Estonian samples (Tremadoc) have a high  $K_2O/Al_2O_3$  molar ratio approximating 2/3 (Fig. 6A). The high potassium content was attributed by Pukkonen & Rammo (1992) to reflect proximity to the Finnish basement. This setting allowed a short transport distance of the necessary ions either as metastable mineral phases or as fluids. Equally high, but more scattered,  $K_2O/Al_2O_3$  ratios are also present in the G14

well offshore Rügen (McCann 1998; Fig. 6) approximately 100 km south of the Gislövshammar-2 core (Fig. 1). Although these sample are of Cambrian age it nevertheless indicates that the  $K_2O/Al_2O_3$  ratios varied within this relatively short distance. More importantly, however, the proximity of the G14 well to the Caledonian Front clearly suggests that the  $K_2O/Al_2O_3$  ratio in the shale are not related to deep burial diagenesis but was established prior to deep burial and hence related to the depositional environment.

The variable  $K_2O/Al_2O_3$  ratio and the variability in the M-values of the Alum Shale might be the result of early diagenesis rooted in an initial difference in clay mineralogy across the shelf. According to Lindgreen *et al.* (2000) kaolinite was present in the Cambrian to Tremadoc source area. Due to its larger grain size this may have been preferentially deposited close to shore with more fine-grained clays being deposited farther off shore. In the Alum Shale the combination of low depositional rates and open anoxic porewaters might have allowed high levels of feldspars to develop at the expense of illite and other aluminium-bearing phases, such as kaolinite. This may account for the lack of kaolinite in Estonia as described by Lindgreen *et al.* (2000).

## Multi-element diagrams

Multi-element diagrams have been constructed in order to provide a geochemical signature based on several elements (Fig. 7). In the diagrams the geochemical composition is normalised to an average composition of the Tøyen Shale approximated by an average of 6 samples from the Gislövshammar-2 core (see Table 1 and 2).

Table 1: Major elements analysis of Ordovician and Silurian samples

Formation	Age/Stage	Sample #	Depth m	SiO <sub>2</sub> wt%	Al <sub>2</sub> O <sub>3</sub> wt%	Fe <sub>2</sub> O <sub>3</sub> wt%	MnO wt%	MgO wt%	CaO wt%	Na <sub>2</sub> O wt%	K <sub>2</sub> O wt%	TiO <sub>2</sub> wt%	P <sub>2</sub> O <sub>5</sub> wt%	LOI wt%	sum wt%
Lönstorp-1 core:															
Rastrites Sh.	Llandovery	79.008	9.90	51.2	12.8	6.2	0.33	3.1	9.1	0.90	2.94	0.68	0.10	12.7	100.0
Rastrites Sh.	Llandovery	79.007	31.50	50.3	13.4	4.3	0.14	3.4	9.1	0.90	2.92	0.70	0.11	12.4	97.6
Rastrites Sh.	Llandovery	79.006	42.50	61.2	14.8	7.3	0.06	3.4	0.9	0.95	3.22	0.81	0.09	6.7	99.5
Rastrites Sh.	Llandovery	79.004	54.60	64.0	15.1	6.3	0.03	2.7	0.5	0.86	3.45	0.67	0.05	6.4	100.0
Rastrites Sh.	Llandovery	79.003	64.30	58.6	16.1	6.1	0.04	2.6	0.7	1.01	3.93	0.76	0.08	10.1	100.1
Rastrites Sh.	Llandovery	79.005	75.00	58.8	15.2	5.8	0.15	2.8	2.1	0.99	3.84	0.73	0.06	9.2	99.7
Albjära-1 core:															
Dicellogr. Sh.	Caradoc	79.009	8.30	58.4	13.9	4.6	0.05	2.6	3.9	0.90	3.24	0.58	0.06	8.7	96.9
Dicellogr. Sh.	Caradoc	79.010	16.60	47.5	11.2	3.9	0.06	2.0	12.4	0.82	2.65	0.45	0.09	14.9	95.8
Dicellogr. Sh.	Caradoc	79.011	25.30	47.3	13.8	7.5	0.05	2.4	6.7	0.80	3.37	0.59	0.08	11.9	94.4
Dicellogr. Sh.	Llanvirn	79.012	35.20	57.5	17.1	4.5	0.04	2.8	2.1	0.93	4.34	0.82	0.30	7.0	97.4
Dicellogr. Sh.	Llanvirn	79.013	50.10	59.6	17.3	4.4	0.02	2.6	0.9	0.93	4.30	0.82	0.16	7.7	98.6
Dicellogr. Sh.	Llanvirn	79.014	65.00	63.1	15.4	3.7	0.03	2.5	0.9	0.84	3.87	0.76	0.14	7.5	98.6
Dicellogr. Sh.	Llanvirn	79.015	80.00	61.3	17.1	4.3	0.02	2.5	0.7	0.85	4.32	0.77	0.37	6.5	98.8
Dicellogr. Sh.	Llanvirn	79.016	94.90	56.4	17.2	4.7	0.04	2.6	2.2	0.75	4.37	0.81	0.18	8.4	97.6
Tøyen Shale	Arenig	79.019	110.00	57.7	17.8	3.7	0.03	2.3	3.0	0.73	4.70	0.98	0.10	6.4	97.5
Tøyen Shale	Arenig	79.020	130.70	65.4	16.2	3.6	0.02	2.2	0.5	0.81	4.30	0.90	0.28	4.6	98.9
Alum Shale	<i>R.flabelliforme</i>	109.380	140.65	56.5	15.3	4.8	0.01	1.2	0.3	0.49	5.28	0.85	0.14	13.8	98.7
Alum Shale	<i>R.flabelliforme</i>	109.374	141.56	54.5	17.0	4.8	0.01	1.2	0.3	0.47	5.70	0.96	0.18	13.7	98.8
Gislövshammar-2 core:															
Tøyen Shale	Volkhov	89.955	4.10	58.0	17.8	4.3	0.03	2.3	2.8	0.35	5.23	1.05	0.28	5.9	98.0
Tøyen Shale	Volkhov	89.952	7.00	58.9	17.5	3.5	0.04	2.3	2.6	0.43	5.06	1.05	0.23	6.3	98.0
Tøyen Shale	Billingen	89.948	11.04	59.6	18.5	3.8	0.03	2.5	1.0	0.35	5.26	1.01	0.12	5.0	97.2
Tøyen Shale	Billingen	89.944	15.02	59.5	18.3	3.8	0.03	2.4	1.3	0.40	5.30	1.03	0.33	6.6	99.0
Tøyen Shale	Billingen	89.940	19.06	60.2	18.9	3.6	0.03	2.5	0.8	0.36	5.41	1.03	0.26	5.3	98.3
Tøyen Shale	Hunneberg	89.937	22.09	61.3	17.6	3.9	0.02	2.3	0.9	0.34	5.17	1.00	0.49	4.9	97.9
Alum Shale	<i>R. norvegica</i>	91.743	23.49	62.5	14.6	3.8	0.02	1.8	0.7	0.29	4.47	0.84	0.34	9.6	98.9
Alum Shale	<i>A. tenellus</i>	89.932	26.98	50.8	14.8	4.3	0.06	1.8	4.1	0.19	4.84	0.83	2.04	14.0	97.7
Alum Shale	<i>A. tenellus</i>	89.930	28.95	54.5	16.4	3.9	0.02	1.5	0.6	0.15	5.35	0.88	0.14	14.0	97.5
Alum Shale	<i>A. tenellus</i>	109.141	33.15	55.5	16.9	3.5	0.02	1.3	0.5	0.08	5.64	0.90	0.28	14.4	99.0
Alum Shale	<i>R.flabelliforme</i>	109.161	35.61	54.5	17.6	4.8	0.01	1.3	0.3	0.08	5.66	0.92	0.15	13.4	98.7
Alum Shale	<i>R.flabelliforme</i>	89.923	36.00	55.0	16.6	4.3	0.02	1.3	0.8	0.10	5.37	0.91	0.22	14.1	98.7
Alum Shale	<i>R.flabelliforme</i>	109.170	36.68	54.4	16.2	4.7	0.04	1.4	1.6	0.08	5.16	0.87	0.15	14.4	99.0
Alum Shale	<i>R.flabelliforme</i>	109.180	37.35	53.2	15.8	5.5	0.07	2.0	2.0	0.07	4.95	0.85	0.13	14.1	98.7
Average of Tøyen Shale:															
Mean of 6 samples															
(Gislövshammar-2 core)				59.60	18.11	3.8	0.03	2.37	1.56	0.37	5.24	1.03	0.28	5.66	98.1
Standard derivation of mean				1.13	0.55	0.3	0.01	0.09	0.92	0.04	0.12	0.02	0.12	0.70	0.6

The Tøyen Shale in Scania is characterised by a flat pattern suggesting homogenous composition of the mud (Fig. 7B). The strata above and below show more variable spectras (Fig. 7A, C). The Tremadoc Alum Shale has profound V and Ni enrichments and low Na and Mg concentrations compared to the Tøyen Shale (Fig. 7A). The high V and Ni contents probably reflect syngenetic enrichment related to reducing conditions in the pore water. Syngenetic enrichment of Cr is also likely and may account for the higher con-

centrations of Cr in these TOC rich shales (Garver *et al.* 1996). Scatter in LREE (Ce, Nd, La) and Y might be related to preferential scavenging of monazite during early and late diagenesis (Milodowski & Zalasiewicz 1991; Lev *et al.* 1999). The Middle and Upper Ordovician shales in Scania show somewhat smoother patterns with consistent enrichments in Na and Mg and proportional enrichments in Cr and Ni when normalised to the Tøyen Shale (Fig. 7C). The Silurian shales exhibit similar Na and Mg enrichments when

Table 2: Selected trace elements analysis of Ordovician and Silurian samples

Formation	Sample #	Ba ppm	Ce ppm	Cr ppm	Cu ppm	Ga ppm	La ppm	Nb ppm	Nd ppm	Ni ppm	Rb ppm	Sc ppm	Th ppm	V ppm	Y ppm	Zn ppm	Zr ppm
Lönstorp-1 core:																	
Rastrites Shale	79.008	684	71	98			35		35		114	15		117			
Rastrites Shale	79.007	968	75	107			36		37		117	16		133			
Rastrites Shale	79.006	974	79	114	43	19	39	15	35	59	135	20	14	147	28	82	163
Rastrites Shale	79.004	1266	76	94	60	18	37	13	31	57	143	19	12	127	25	82	125
Rastrites Shale	79.003	1211	80	188	101	19	42	15	41	109	158	22	14	256	38	136	186
Rastrites Shale	79.005	1123	84	179	81	19	40	14	37	114	154	21	11	243	31	97	176
Albjära-1 core:																	
Dicellogr. Shale	79.009	1674	58	162	43	20	27	17	28	108	135	23	9	140	35	111	222
Dicellogr. Shale	79.010	1117	72	181	69	20	31	10	33	140	114	16	8	164	38	73	84
Dicellogr. Shale	79.011	1071	81	207	70	21	35	12	32	92	138	19	11	137	32	127	110
Dicellogr. Shale	79.012	1430	83	146	52	24	42	17	41	70	180	28	13	156	44	100	155
Dicellogr. Shale	79.013	1372	76	140	63	27	42	17	32	91	173	26	16	185	35	132	158
Dicellogr. Shale	79.014	1449	70	125	53	19	38	15	30	17	161	23	12	272	35	126	139
Dicellogr. Shale	79.015	1691	97	111	45	24	49	16	44	52	179	26	14	151	51	428	141
Dicellogr. Shale	79.016	1478	97	103	52	27	45	17	43	59	174	26	14	159	48	106	158
Tøyen Shale	79.019	1973	96	92	55	27	50	21	45	37	176	24	19	159	42	93	179
Tøyen Shale	79.020	1709	86	104	38	26	47	19	41	41	167	23	17	213	40	80	178
Alum Shale	109.380	2106	70	127	207	21	40	17	33	217	151	17	17	1535	29	273	142
Alum Shale	109.374	2211	71	135	209	25	41	19	36	185	167	17	18	1536	33	84	160
Gislövshammar-2 core:																	
Tøyen Shale	89.955	709	129	90	28	23	57	23	58	40	202	21	20	126	52	69	197
Tøyen Shale	89.952	1164	119	91	24	25	55	22	56	38	189	22	20	140	54	70	202
Tøyen Shale	89.948	1342	101	96	53	24	52	20	43	36	205	26	18	137	41	72	186
Tøyen Shale	89.944	1730	107	92	40	25	52	21	57	40	196	24	21	159	59	79	191
Tøyen Shale	89.940	1795	103	105	39	25	53	20	53	45	200	25	18	182	51	77	184
Tøyen Shale	89.937	1840	113	98	15	22	59	21	51	36	193	24	19	186	55	66	195
Alum Shale	91.743	2304	46	128	84	21	33	17	18	172	147	15	17	1893	23	80	157
Alum Shale	89.932	2648	113	117	140	20	56	15	75	355	156	19	16	3559	85	54	139
Alum Shale	89.930	5830	65	230	176	22	45	16	30	273	170	19	16	4738	25	1397	148
Alum Shale	109.141	2903	75	163	208	24	45	18	36	208	176	17	18	1990	34	25	159
Alum Shale	109.161	3480	84	113	176	28	45	19	43	139	177	19	17	832	43	23	161
Alum Shale	89.923	2761	90	98	170	24	49	17	47	162	170	18	17	1221	45	64	159
Alum Shale	109.170	2315	68	112	169	22	40	17	35	136	158	15	17	950	31	25	148
Alum Shale	109.180	2158	78	109	131	21	45	17	39	162	157	20	15	875	39	63	144
Average of Tøyen Shale:																	
Mean of 6 samples																	
(Gislövshammar-2)		1430	112	95	33	24	55	21	53	39	197	24	19	155	52	72	193
Standard derivation																	
of mean		445	11	5	13	1	3	1	6	3	6	2	1	25	6	5	7

compared to the Tøyen shale as seen in the Llanvirn and Caradoc shales (Fig. 7D). Two Silurian samples are enriched in V, Cr and Ni (Table 2) whereas the other Silurian samples have Cr values closer to that of the average Tøyen Shale. These enrichments might be partly related to syngenetic processes.

By normalising the Tøyen Shale of the Oslo Region against that of Scania marked differences in sodium and iron contents are evident (Fig. 7E). The higher V and Ni levels present in the Tøyen Shale of the Oslo

Region could indicate that these were deposited in slightly more reducing conditions allowing syngenetic enrichment of these elements. Differences in composition exist within the Oslo Region since shales from the northern part of the Oslo Region have higher average Cr concentrations compared to the southern parts (Fig. 7F). The high average Cr concentrations are, however, related to one sample having 260 ppm and it is not a general feature of the shales (Fig. 4). Higher V, Cr and Ni contents are also present in the

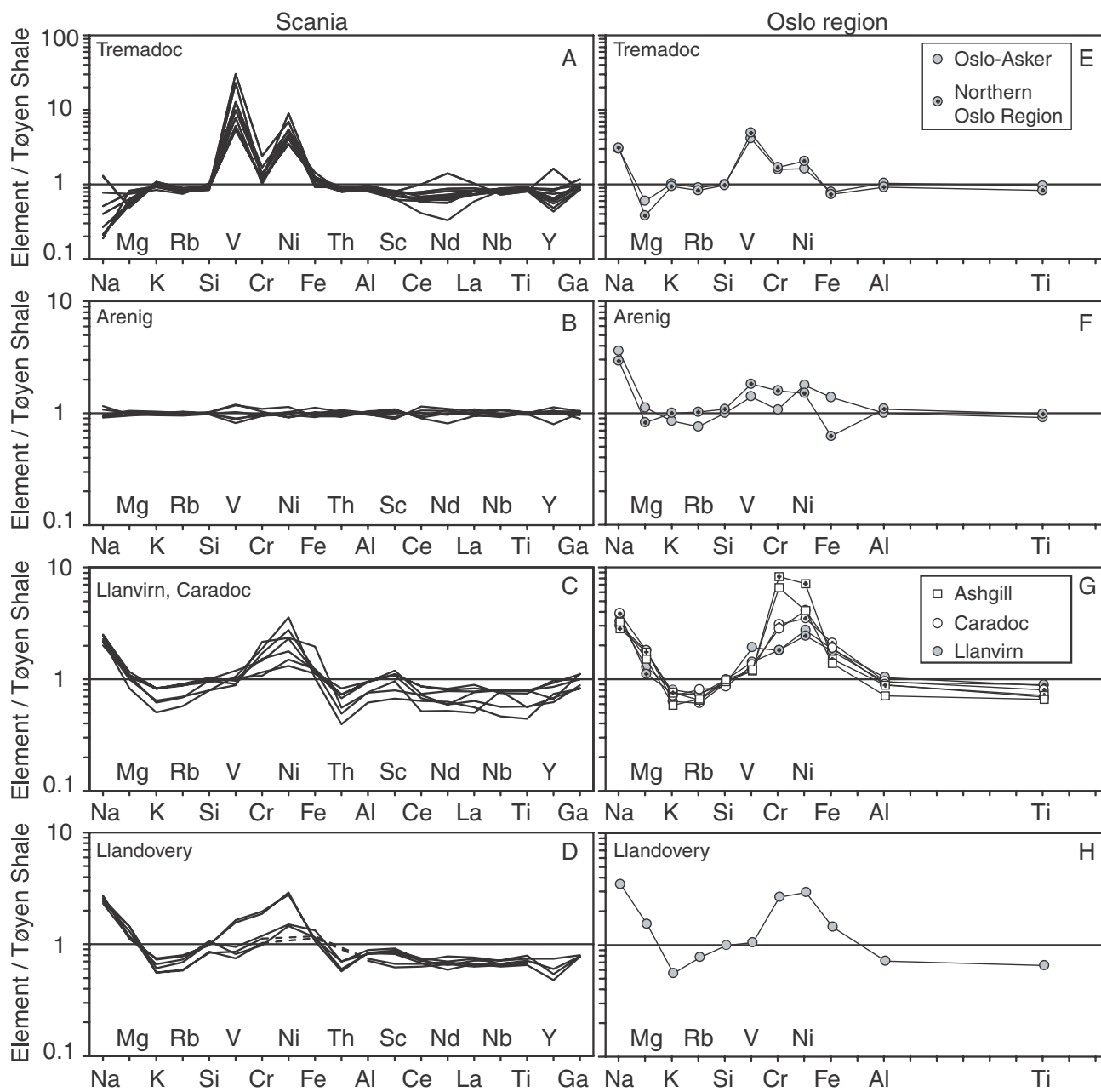


Fig. 7. Multi-element diagrams of samples from Scania (A to D) and an average of samples from the Oslo Region (E-H). Samples have been normalised to the average Tøyen Shale composition (Tables 1 and 2). With only slight modifications, the elements have been ordered by its seawater to crust partition coefficient that yields a crude approximation to the mobility of the element during weathering and subsequent transport (Taylor & McLennan 1985). Coefficient decreases from Na to Fe (decreasing mobility) and from Th to Y (generally immobile). Note scale for A and E (0.1 to 100).

Tremadoc Alum Shale from the Oslo Region (Fig. 7E). This pattern generally resembles that from Scania apart from higher Na content and less pronounced V and Ni anomalies. The difference in Na concentrations between Scania and the Oslo Region might reflect the variable early diagenetic control on the K and Na bearing phases. The areas have, however, also experienced different burial histories. Hence, the higher degree of sodium exchange reaction in the Oslo Region is likely to be related to fluid circulation.

A clear stratigraphical variation in the average enrichment level is present in the Middle to Upper Ordovician shales (Fig. 7G). On average the Ashgill shales show highest enrichments in Mg, Cr and Ni whereas the Llanvirn sediments exhibit the lowest enrichment levels of these elements. In the Upper Ordovician Cr is proportionally more enriched than the other elements, probably reflecting the presence of detrital chromite grains. Generally, the Ordovician and Silurian shales in the Oslo Region exhibit overall similar patterns to the shales in Scania (Fig. 7G, H).

## Origin of lower/middle Ordovician to lower Silurian geochemical signatures

Bjørlykke (1974a, b) and Bjørlykke & Englund (1979) proposed that the geochemical and mineralogical composition of the Ordovician and Silurian sediments was a function of the relative supply of materials from the Baltic shield and from island arc systems to the west. A likely source area for the oceanic sedimentary component was thought to be present in the Trondheim Region. Further examination of the Ordovician sediments and volcanic rocks in the Trondheim Region, however, suggested that the Oslo and Trondheim regions differed more in composition than expected if the sediments were derived from a single source area (Dypvik & Brunfelt 1976; Dypvik 1977). In the Trondheim Region, the Ordovician and Silurian sediments contain a minimum of 30–40% of greenstone debris, which was derived from localised erosion, and transport of the Støren greenstone (Dypvik 1977).

Within the group of mafic rocks two main types of basalts have been distinguished in the Scandinavian Caledonides, namely mid ocean ridge basalt (MORB) and island arc tholeiites (IAT; Grenne & Lagerblad 1985; Grenne 1988). These basalt types are represented by the Støren Group (MORB) and the Fundsjø Group (IAT). The Fundsjø Group of the Upper Allochthon

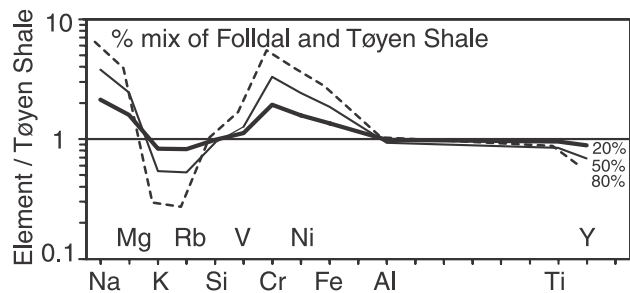


Fig. 8. Multi-element diagrams of a sedimentary signature produced by mixing between an average of metagabbros and metabasalts from Folldal (Bjerkgård & Bjørlykke 1994) and an average of Tøyen Shale (Tables 1 and 2). Mixing ratio indicates proportion of Folldal material in the calculations. The resulting composition has been normalised to the average Tøyen Shale composition.

represents one of the oldest preserved magmatic sequences with clear subduction affinities in the Scandinavian Caledonides (Grenne & Lagerblad 1985; Grenne *et al.* 1999). The IAT have formed by relatively high degree of melting of a primitive mantle source in accordance with their anomalous high Ni and Cr concentrations (Bjerkgård & Bjørlykke 1994). A primitive mantle source has also been proposed for the Feragen complex (Nilsson *et al.* 1997) that contains chromite grains with a composition similar to the chromite grains present in the Ordovician sediments of the Oslo Region (Bjørlykke 1974a).

Comparison between the IAT-component and the IAT-sedimentary signature is made from a simple two component mixing between an average of metagabbros and metabasalts from Bjerkgård & Bjørlykke (1994) with the average composition of the Tøyen Shale (Fig. 8). The mixing calculation appears to produce a pattern in the multi-element diagram that matches the patterns of the Lower to Middle and Upper Ordovician and Silurian shales (compare Figs 7 and 8). The mixing ratios indicate that the Middle Ordovician pattern present in the Oslo Region can be ascribed to 50–80% of an IAT-component. Only 20–50% of an IAT-component is needed to produce the signature present in Scania.

The geochemical signature of the Lower to Middle Ordovician sediments on Avalonia differ markedly by having lower Cr and Mg and higher Al and Fe concentrations than the equivalent beds in Scania and the Oslo Region (Fig. 9). The signature preserved in Avalonia reflects subduction-related volcanism on eastern Avalonia (McCann 1998) and the absence of a similar signature on the southern margins of Baltica suggests that Baltica and Avalonia were separated from each other in the Early to Mid Ordovician (McCann 1998). One single Upper Ordovician (Car-

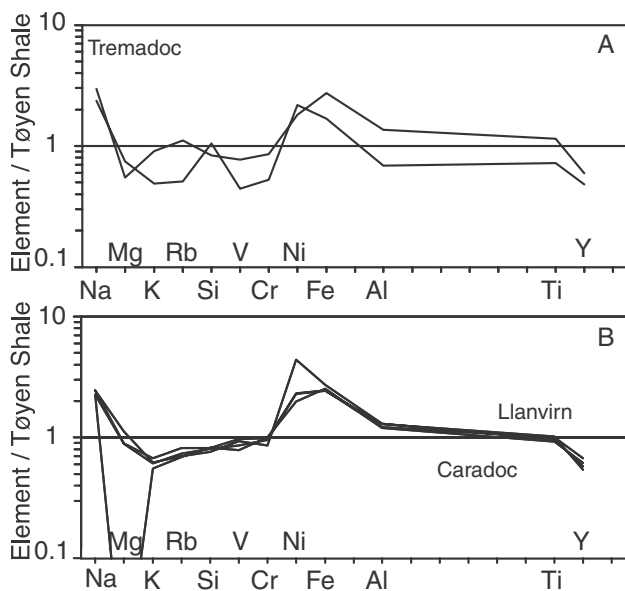


Fig. 9. Multi-element diagram of shales from northern Rügen (data from McCann 1998). Samples have been normalised to the average Tøyen Shale composition (Tables 1 and 2).

doc) shale sample does show similarities with the shale composition in Scania (compare Figs 7 and 9) suggesting that similar rock types were indeed present in the source area of both continents. However, the data are still too sparse to clarify whether the continents shared a common source area or if the source area evolved independently on Avalonia.

## Summary and conclusions

The appearance of a distinct IAT geochemical signature in the Oslo Region and Scania suggests that a major change in source area composition occurred on Baltica in Llanvirn times. The introduction of an IAT-component in the Oslo Region coincides with a marked increase in average accumulation rates suggesting that the change in source composition was tectonically induced. Mass-balance calculations indicate that the influence of oceanic sedimentary sources diminished towards the south probably reflecting longer transport distances.

The similarity of the Lower/Middle Ordovician signature with rocks belonging to the Upper Allochthon in the Scandinavian Caledonides suggests that these rocks were uplifted from the early Mid Ordovician possibly due to accretion onto the Baltic continent. Hence, IAT material and subduction of Iapetus oceanic crust was not restricted to the Laurentian side of the Iapetus Ocean but was also a feature of the

Baltica margin (Grenne *et al.* 1999). Moreover, the presence of the IAT-sedimentary signature both in the Oslo Region and Scania suggests that these areas produced considerable volumes of sediment.

Obduction of early Ordovician (pre-Arenig) ophiolite sequences during island arc accumulation has been related to the early Ordovician Finnmarkian subduction along the western margin of Baltica (Sturt & Roberts 1991). The time-lag between the accretion of oceanic material on the Baltic margin and the change in geochemical composition of the sediments in the Oslo Region and Scania might be explained by crustal shortening of the margins during the Arenig/Llanvirn. Estimates (Bruton & Harper 1988) suggest that the Early Ordovician margin might have extended some 750 km farther east. Sediments deposited here vary in thickness from less than 250 m in the Oslo Region to 1500 m west of the Oslo Region and exhibit a complex mosaic of sedimentary environments reflecting a pronounced basement topography and syn-depositional fault movement (Bruton & Harper 1988). Island-arc accumulations together with erosion products from these might not have reached the Oslo Region and Scania during the Early Ordovician. The introduction of sediments originating in the west might thus signal a phase of major crustal shortening and not the time of linkage of outboard terranes to Baltica.

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