# LOWER PALAEOZOIC SOURCE ROCKS IN SOUTHERN BALTOSCANDIA

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The most interesting source rock interval in the Lower Palaeozoic sedimentary succession in Baltoscandia is the Middle Cambrian to Lower Ordovician Alum Shale Formation. The unit has high TOC-values, contains oil-prone organic matter and is widespread. Major oil generation took place in connection to the Caledonian orogeny in Late Silurian and Early Devonian time. However, no hydrocarbons remain from this event. Other source intervals include parts of the Middle to Upper Ordovician *Dicellograptus* Shale and the Lower Silurian *Rastrites* Shale.

## INTRODUCTION

In Northern Europe, Lower Palaeozoic rocks are known from outcrops in Britain, Denmark, Norway, Sweden, Estonia and Germany, and from deep wells in Denmark, northeasternmost Germany, northern Poland, the Kaliningrad District, Lithuania, Latvia and the southern Baltic Sea (see Fig. 1). Deposition was controlled by the development and subsequent closing of the Iapetus Ocean and Tornquist Sea west and south of the Balto-Russian Continent (Baltica). The present-day occurrences of these rocks include deposits from at least two different continents or continental fragments (Avalonia and the Balto-Russian Continent), and direct comparison between these areas is difficult. In the present study, emphasis has been placed on the black shales in Baltoscandia. Here, several organic-rich horizons have been identified as potential or exhausted source rocks for oil and gas. Their possible continuation across the Danish-German-Polish Caledonian Deformation Front into northern Germany is a matter of debate.

## THE CAMBRO-ORDOVICIAN ALUM SHALE

The Middle Cambrian to Lower Ordovician (Tremadocian) in Baltoscandia is represented by widespread deposits of black, organic-rich shales. In Scandinavia, these shales have traditionally been termed Alum Shales reflecting their former exploitation as a source for alum salt ($KAl(SO_4)\cdot 12H_2O$). The term is now formally used to describe the black shale succession between the Lower and Middle Cambrian coarse clastic deposits and the Lower Ordovician (Upper Tremadocian to Arenigian) calcareous rocks (Gee, 1972; Andersson et al., 1985; Buchardt et al., 1997).

The Alum Shale Formation comprises organic-rich laminated mudstones and mudshales with subordinate beds of limestone and siltstone. It is thick (up to 150 metres) at the western margin of the Baltoscandian Platform and thins out towards the east and southeast. No Alum Shale has been reported from easternmost Poland, Kaliningrad District, Lithuania and Latvia. The shale is enriched in organophilic metals (V, Mo, Ni) and contains anomalously high concentrations of organically bound syngenetic uranium (up to 400 ppm U at some stratigraphic levels in Sweden). Black, early diagenetic calcareous concretions of pre-compactional origin (anthraconites) are common throughout the formation (Bjørlykke, 1973; Buchardt and Nielsen, 1985).

In southern Scandinavia, the Alum Shale rests on sandstones and siltstones of Early to Middle Cambrian age or directly on the Precambrian basement and is covered by limestone and shale of Late Tremadocian and Arenigian age (Martinsson, 1974). The Alum Shale equivalent in northern Estonian is of Late Tremadocian age (Türisalu Formation, Kaljo et al., 1986; Pukkonen and Buchardt, 1994) and of Late Cambrian age in deep wells in northeast Poland (Piaśnicka Formation, Bednarczyk 1984) and in the G14-well off Rügen (Rempel, 1992).

The distribution of the Alum Shale reflects the shape and slope of the southwestern margin of the Balto-Russian Continent in Cambrian time. The initial Cambrian transgression took place from west and south onto a deeply eroded and peneplaned Precambrian surface, where minor variations in sea level lead to major fluctuations in coast lines. Late Cam-

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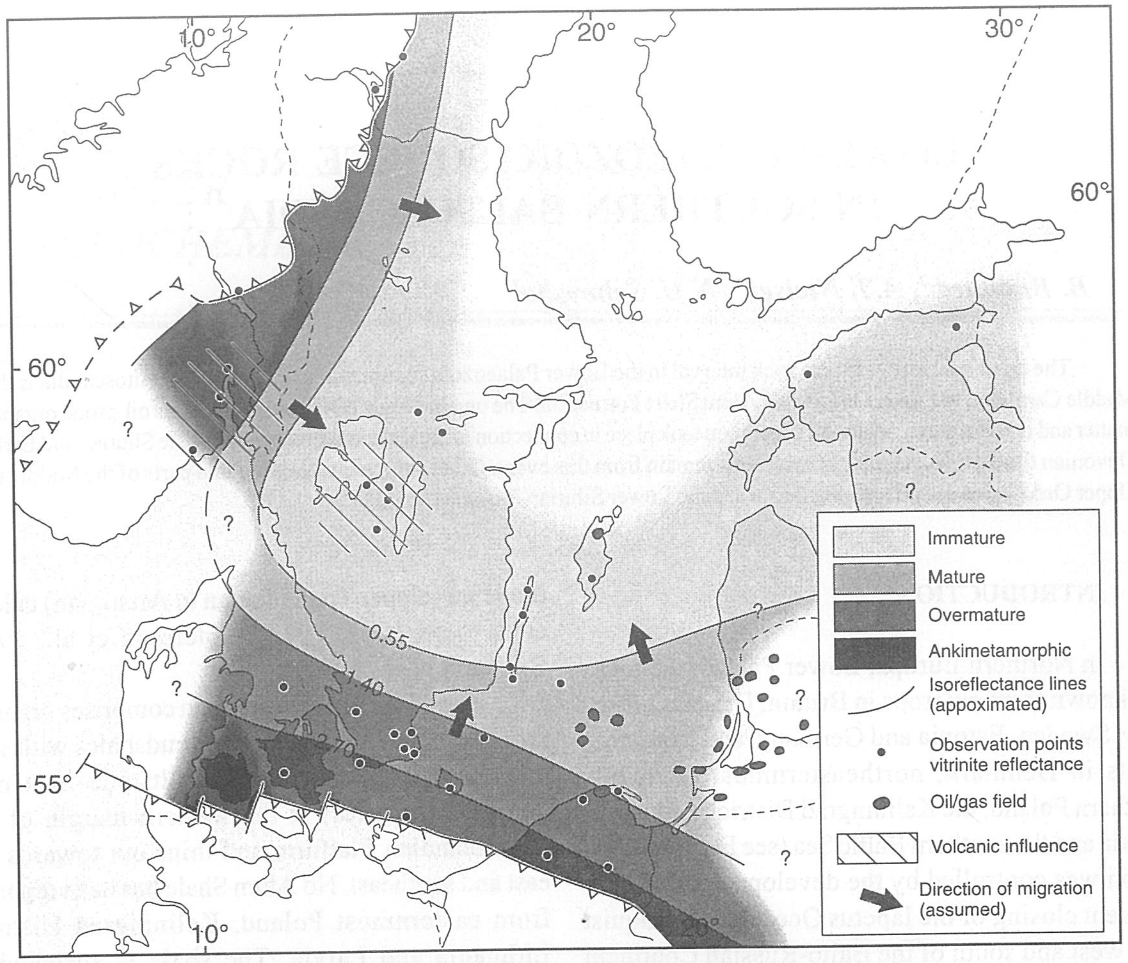


**Fig. 1.** Distribution of Lower Palaeozoic deposits In southern Baltoscandia outside the Swedish-Norwegian Caledonides. The Distribution of the Alum Shale Formation is the same except for the southeastern area from Latvia to easternmost Poland and for the Siljan area.

brian was a period of sea level high stands, and most of the Baltoscandian Platform was submerged. No direct evidence of a coastal facies has been reported. However, the general thinning-out of the formation towards the east and northeast and the lack of Alum Shale in the subsurface in the eastern Baltic points to a coastline following the eastern and northern margins of the present Baltic Syneclise.

The shale was deposited under anoxic to euxinic conditions lasting for more than 15 million years (Thickpenny, 1984). Water depths probably never exceeded 200 metres. Sedimentation rates were low (1-10 mm/1000 years) and reflected eolian processes as the major supplier of terrigenous, clastic material. Low organic carbon accumulation rates (0.02 to 0.5 gram/cm$^2$/10$^3$ yr.) exclude high productivity as major course for the anoxia, and no other present-day models for anoxic environments seem to match the Alum Shale scenario. Probably, a combination of sluggish ocean circulations, extremely stable tectonic conditions and lowered atmospheric oxygen pressures controlled the development and pertinacity of the Alum Shale anoxia.

## ORGANIC GEOCHEMISTRY OF ALUM SHALE

Organic carbon in the Alum Shale ranges from 2 to 25 wt. % with the majority of the formation having TOC-values between 8 and 15 wt. %. The distribution of organic matter is determined by stratigraphic levels. TOC content is low (below 6 wt. %) in the Middle Cambrian and gradually increases to high values (between 12 and 25 wt. %) in the Upper Cambrian *Olenus* and *Peltura* Zones. The uppermost Cambrian and the Tremadocian are characterized by lower TOC-values (5 to 15 wt. %). Based on the content of organic matter, the Alum Shale can be characterized as an extremely rich source rock.

The high-TOC intervals are associated with anomalously high concentrations of uranium reaching levels of 200 to 500 ppm in the *Peltura* Zone in Västergötland. These values correspond to enrichments of 10 to 100 times compared to other black shales. The uranium is evenly distributed within the shale and closely associated with the organic matter.



The extreme uranium enrichment can be explained by the very low sedimentation rates combined with the general anoxic conditions (Lewan and Buchardt, 1989). Leaching of exposed granitic bedrock of Precambrian age on the Baltic Shield and the East European Platform may have caused local enrichment in the sea water of dissolved uranium, which subsequently was absorbed and precipitated by the organic matter under reducing conditions.

The Alum Shale was formed before the evolution of terrestrial vascular plants, and organic matter in the shale is exclusively of marine origin. Optical analyses of the shale prove a high dominance of amorphous organic matter with minor constituents of structured kerogen. Vitrinite-like particles of unknown origin and Tasmanites-like algal bodies have been observed in all investigated samples (Buchardt et al., 1986; Buchardt and Lewan, 1990). In the TOC-rich samples, the organic matter forms discrete lamellae, probably reflecting bacterial mats on the sea-floor. The abundant occurrence of pyrite points to intensive sulphate reduction in the bottom environment. Buchardt et al. (1986) characterized the organic matter as a liptinitic, alginite B type lamalginite.

Elemental analyses of the Alum Shale kerogen classify the organic matter as a type II kerogen as defined by Durand and Monin (1980). Atomic H/C ratios from immature samples are between 1.10 and 1.20, defining the Alum Shale as an oil-prone source rock. Corresponding Rock Eval HI-values are between 400 and 600 mg HC/g TOC. In the high-uranium intervals, organic matter composition has been modified by the long-term radiation damage from alpha particles generated by decay of uranium (Lewan and Buchardt, 1989; Dahl et al., 1989). The radiation is believed to cause cross-linking and polymerization of especially the paraffinic hydrocarbons, drastically changing the character of the organic matter and the expelled oil. Aromatic hydrocarbons, on the other hand, are less susceptible to radiation damage and their relative amount will increase in the high-uranium intervals.

The kinetics of Alum Shale oil generation has been evaluated by isothermal hydrous pyrolysis (Lewan and Buchardt, 1989). Activation energy and pre-exponential factor for a typical type II kerogen from Västergötland were 201 kJ/mol and $1.77 \cdot 10^{15}$ h$^{-1}$ respectively. These values fall within the range of younger sulphur-poor type II kerogen (Lewan and Buchardt, 1989), indicating that oil generating kinetics is not significantly different for the Alum Shale despite its higher age and extreme uranium enrichment.

Oil yields from the Alum Shale were strongly influenced by uranium concentration. The high-uranium samples had yields two to three times lower (70 mg/g TOC for a 440 ppm uranium sample) than normal samples under the same experimental conditions. The expelled oils had considerable variability ranging from normal oils with *n*-alkane distributions between $C_7$ and $C_{31}$ and acyclic isoprenoids to oils with a condensate-like composition very low in normal paraffins above *n*-$C_{15}$ and lacking acyclic isoprenoids (Lewan and Buchardt, 1989).

Generation of hydrocarbon gas during the hydrous pyrolysis experiments was synchronous with the oil generation, and maximal gas generation took place within the first half of the primary oil generation stage. Gas yields from immature samples ranged from 97 mg/g TOC to 118 mg/g TOC. Postmature samples still had a gas potential at reflectance values of 2 % (10 to 20 mg/g TOC), which dropped almost to zero for the anchimetamorphic samples. Methane content of the total hydrocarbon gas increased from about 50 % for the immature samples to close to 90 % for the anchimetamorphic samples. However, even the strongest modified samples at $R_o$-values of 5.3 % had a considerable $C_{2+}$ component. Carbon isotope composition of the generated methane was between -42 and -35 ‰ PDB typical for oil-associated gases.

## SOURCE POTENTIAL OF THE ALUM SHALE

The Alum Shale has good source rock qualities. The formation contains high amounts of oil-prone organic matter of type II kerogen and has reaction kinetics comparable to well-documented source rocks. Generation characteristics have been modified by radiation damage from decay of uranium. The effect is distinguishable only in rocks with uranium concentrations above 100 ppm. Here, the hydrocarbon potential has changed to more gas prone characteristics.

Thermal maturity conditions are unfavourable in most of the studied areas, where the Alum Shale is either immature or postmature with regard to hydrocarbon generation (see Fig. 2 and Buchardt et al., 1997). The only area where the Alum Shale may have reached hydrocarbon generative stages in connection with favourable reservoir conditions is in the southeastern Baltic Sea between Sweden and Poland. The oil fields in the Kaliningrad District in the easternmost Baltic probably were sourced by other organic-rich units.

The major hydrocarbon generation took place

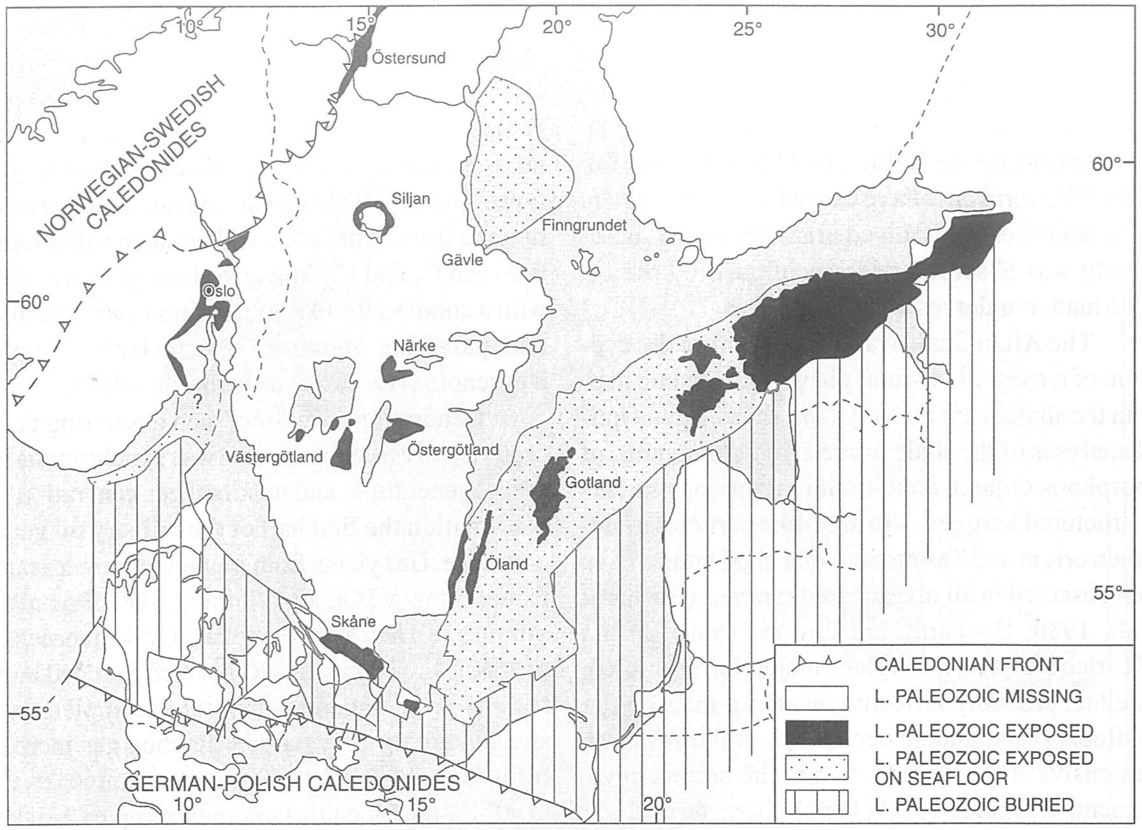


**Fig. 2.** Tentative map of the thermal maturity distribution of the Lower Palaeozoic deposits in southern Baltoscandia. Maturity determined from vitrinite-like particles in the Alum Shale Formation.

during the Late Silurian and earliest Devonian. Deep burial of the Lower Palaeozoic rocks in a foreland basin formed in connection with the main Caledonian deformation phase led to an almost total exhaustion of the Alum Shale in Denmark, southern Sweden, northern Poland and the southern Baltic Syneclise. Only a small gas potential remains in these areas. Alum Shales deposited on the Baltic Platform itself were not affected by this episode and remains immature with regard to hydrocarbon generation to this very day.

The palaeogeographic distribution of the Alum Shale in southern Baltoscandia indicates that the strike of the Caledonian Deformation Front in southern Denmark, northern Germany and northern Poland is not congruent with the former southern continental margin of the Balto-Russian continent. Probably, the shelf extended several hundred kilometres further to the south and west. Therefore, rocks equivalent to the Alum Shale may have been overridden by Caledonian thrusts during the Avalonian (?) - Baltic plate collision in Late Silurian time. If this scenario holds true, highly over matured source rocks may be found at great depths buried below Caledonian rocks in northern Germany.

## OTHER POTENTIAL LOWER PALAEOZOIC SOURCE ROCKS IN BALTOSCANDIA

Apart from the Alum Shale, two other levels in the Lower Palaeozoic succession in Baltoscandia are characterized by TOC-enrichment and widespread geographic occurrence (Buchardt et al., 1994). In Scandinavian stratigraphic terminology, these levels include the Middle to Upper Ordovician Upper *Didymograptus* and *Dicellograptus* Shales and the Lower Silurian *Rastrites* Shale. Similar levels have been identified in the eastern part of the Baltic Syneclise. Moreover, the Estonian kukersite represents a local development of high-TOC rocks. The kukersite of northern Estonia is an algal limestone highly enriched in organic carbon (20 to 60 % TOC) found at three stratigraphic levels in the Lower and Middle Ordovician. Kukersite covers an area of more than 50.000 km$^2$ with a cumulative thickness of up to 20 m and represents the most important Estonian fossil fuel resource (21 billion t). Geographically, the kukersite is restricted to northeast Estonia, where it crops out in an east-west band. The thickness of the kukersite beds decreases downdip towards the south, and no kukersite has been reported from the Baltic Syneclise further to the south. Thermal modification of the kukersite has been small as indicated by the low reflectance values of vitrinite-like macerals in the underlying Türisalu Formation (R° 0.53 %). None of the kukersite has thus reached hydrocarbon generation stages, and the kukersite is of no interest as a source rock in the region.

The Upper Ordovician Dicellograptus Shale is known from most of Baltoscandia and probably represents a regional sea-level high stand. The facies is present in the southern and southwestern part of the Baltic Syneclise and along the Caledonian Deformation Front in Poland. It probably constitutes an important source rock in areas in the southern Baltic where the Alum Shale is missing.

During the Early Silurian, a strong facies differentiation developed in the eastern and southern Baltoscandia between platform and deep water deposits, the latter generally being enriched in organic matter. Of interest is the Lower Silurian *Rastrites* Shale known from most of southern Scandinavia, where TOC enrichments up to 8 % have been recorded. Equivalent beds are widespread in the Baltic Syneclise and in Latvia and Lithuania. Since the TOC-enriched intervals most likely represent sedimentary condensation caused by raising sea-level, these intervals may be conjectured to be of regional distribution.

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