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ORIGINAL PAPER

Petroleum source rock evaluation of the Alum and Dictyonema Shales (Upper Cambrian–Lower Ordovician) in the Baltic Basin and Podlasie Depression (eastern Poland)

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Abstract We present geochemical characteristics of the Lower Palaeozoic shales deposited in the Baltic Basin and Podlasie Depression. In the study area, this strata are represented by the Upper Cambrian–Lower Ordovician Alum Shale recognized in southern Scandinavia and Polish offshore and a equivalent the Lower Tremadocian *Dictyonema* Shale from the northern Estonia and the Podlasie Depression in Poland. Geochemical analyses reveal that the Alum Shale and *Dictyonema* Shale present high contents of organic carbon. These deposits have the best source quality among the Lower Palaeozoic strata, and they are the best source rocks in the Baltic region. The bituminous shales complex has TOC contents up to ca. 22 wt%. The analysed rocks contain low-sulphur, oil-prone Type-II kerogen deposited in anoxic or sub-oxic conditions. The maturity of the Alum and *Dictyonema* Shales changes gradually, from the east and north-east to the west and south-west, i.e. in the direction of the Tornquist-Teisseyre Zone. Samples, located in the seashore of Estonia and in the Podlasie region, are immature and in the initial phase of "oil window". The mature shales were found in the central offshore part of the Polish Baltic Basin, and the late mature and overmature are located in the western part of the Baltic Basin. The Alum and *Dictyonema* Shales are characterized by a high grade of radioactive elements, especially uranium. The enrichment has a syngenetic or early diagenetic origin. The measured content of uranium reached up to 750 ppm and thorium up to 37 ppm.

Keywords Alum Shale · *Dictyonema* Shale · Baltic Basin · Podlasie Depression · Source rock evaluation

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Introduction

Investigation of Alum and *Dictyonema* Shales (Upper Cambrian–Lower Ordovician) in the Baltic region and adjacent areas (Fig. 1a) as source of hydrocarbons has been performed for over 200 years (Andérsson et al. 1985). The first attempts were connected with solvent extraction of bitumen and before World War II up to 1966 these rocks were retorted for its oil in Sweden (Dyni 2006). Interest in these strata is also connected with their potential source for hydrocarbons accumulations and multi-elements, especially radioactive elements enrichment (e.g. Schovsbo 2002; Lippmaa et al. 2009). These strata, especially the Alum Shale, are considered as forming hydrocarbon accumulations in Polish and Russian offshore and onshore parts of the Baltic Basin (Kanev et al. 1989, 1994; Brangulis et al. 1992; Karnkowski 1999; Więcław et al. 2010; Sliaupa and Hoth 2011) and Southern Scandinavia (Pedersen et al. 2007). Generated oils are accumulated mostly in *Paradoxides paradoxissimus* Zone of Middle Cambrian strata (Karnkowski et al., 2010). Apart from the Cambrian, oil accumulations and shows were also discovered in the Precambrian, Ordovician, Silurian and Devonian strata in Russia, Lithuania, Latvia and Sweden (Zdanaviciute and Bojesen-Koefoed 1997; Zdanaviciute and Lazauskiene 2004, 2007; Pedersen et al. 2006). Generation of these oils from a source different than the Upper Cambrian–Tremadocian complex, especially Lower Silurian rocks, is not excluded (Zdanaviciute and Lazauskiene 2004, 2007).

As a source of uranium and rare metals, Alum and *Dictyonema* Shales were partially exploited (Andérsson et al. 1985; Brangulis et al. 1992; Bergh 1994; Lippmaa et al. 2009). Because of low maturity, the *Dictyonema* Shale has low potential for thermogenic hydrocarbons, but is interesting from the point of view of the content of radioactive elements and their influence on hydrocarbon generation (Bergh 1994; Lippmaa and Maramäe 1999; Dyni 2006).

Research on these bituminous shales was carried out in the western part of the Baltic Basin–Västergötland region (south-central Sweden), Skåne region (south Sweden), Öland and Götland (Sweden), and Bornholm (Denmark) islands and the Polish offshore of the Baltic Basin (Fig. 1b). Moreover, the study was also conducted in the eastern part of the basin—on the seashore of Estonia and the northern part of Podlasie Depression (Fig. 1a, b).

Bituminous shales were also examined for the presence of organic matter. These studies showed that these deposits have the best source quality among the Lower Palaeozoic strata and they are the best source rocks in the Baltic region. The Alum and *Dictyonema* shales show high contents of organic carbon and presence of radioactive elements. The bituminous shales complex has TOC contents up to ca. 22 wt% and contains oil-prone Type-II kerogen. The maturity of the Alum and *Dictyonema* Shales changes from immature phase in the east and north-east to the postmature in the west and south-west of the study area. The Alum and *Dictyonema* Shales are characterized by a high grade of radioactive elements, especially uranium. The enrichment has a syngenetic or early diagenetic origin. The measured content of uranium reached up to 750 ppm and thorium up to 37 ppm.

In the present study, organic matter (OM) quantity, genetic type, maturity and its hydrocarbon potential dispersed in Alum and *Dictyonema* Shales are discussed on the basis of results of wide-range geochemical techniques (Rock-Eval, stable carbon isotopes, biomarkers, kerogen elemental composition). The relation of uranium with OM properties and forms of this element occurrence are presented as well. The study area encompasses the Polish offshore of the Baltic Basin and adjacent onshore area: southern Sweden, Bornholm

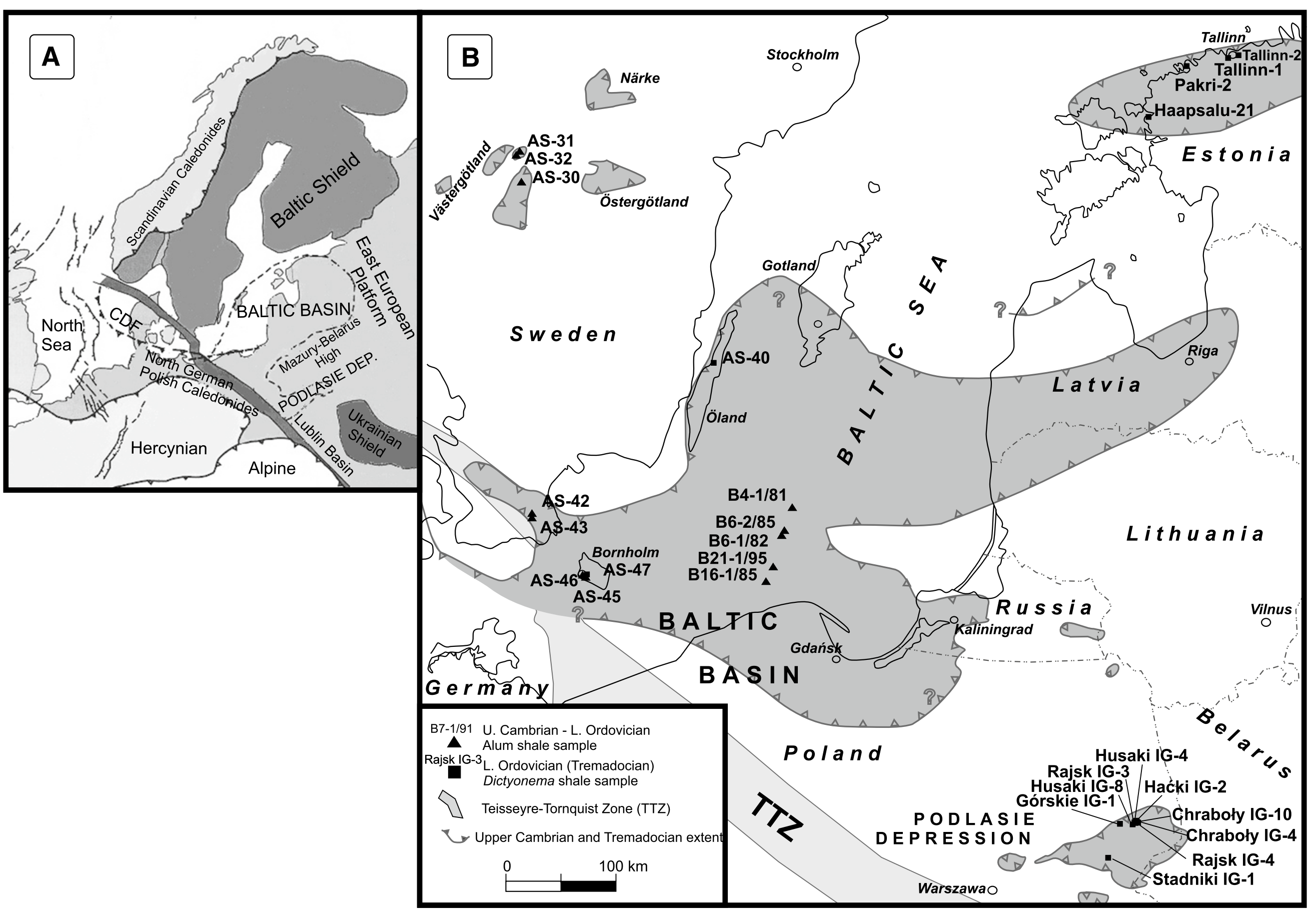

Fig. 1 **a** Location of main tectonic units and **b** location of sampled wells and outcrops in the Polish and Estonia part of the Baltic Basin, and Podlasie basin. *CDF* Caledonian Deformation Front, *Podlasie Dep.* Podlasie Depression

(Denmark) and northern Estonia, and the Podlasie Depression which is the northern part of the Lublin-Podlasie Basin (Tomczykowa and Tomczyk 1976, 1978; Ulmishek 1990) (Fig. 1).

Geological setting

The Baltic Basin (BB) and Podlasie Depression (PD) are tectonic units located in the western margin of the East European Craton (EEC; Ulmishek 1990). Development of the BB was started in the Ediacaran after breakup of Rodinia. At that time, the basin formed a passive continental margin on the western slope of the palaeocontinent of Baltica (Torsvik et al. 1992; Andréasson 1994; Torsvik 2003). The BB was affected by Proterozoic tectonism (early Ediacaran rifting) as well as by Caledonian orogenesis (closure of the Tornquist Ocean), Permo-Triassic rifting, late Jurassic and late Cretaceous uplifts (Flodén 1980; Ulmishek 1990; Poprawa et al. 1997, 1999; Poprawa 2006a, b; Karnkowski 1999). The early Cambrian to early Devonian sedimentary cycle was terminated with an erosional event, which is observed as a regional unconformity, coinciding with a global low-stand of sea level (House 1983; Johnson et al. 1985).

The early to middle Cambrian evolution of the western margin of Baltica was controlled by progressive opening of the Iapetus and Tornquist oceans (Nikishin et al. 1996). These oceans began to close again during middle and late Cambrian times. The early Ordovician mild tensional tectonics may have controlled the development of the linear depocentres of the Baltic Basin (Mäannil 1965; Kaplan and Suveizis 1970; Rotenfeld et al. 1974; Flodén 1980; Suveizis 1982). In the course of the Caledonian orogeny, the western and south-western passive margins of Baltica were destroyed and foreland basins superimposed on their proximal parts during the Silurian (Nikishin et al. 1996). Compressional deformations of the early Devonian (Lochkovian) ended the Caledonian stage of the BB development (Gee and Sturt 1985; Andréasson 1994). During the Devonian and late Carboniferous to late Permian periods, the BB was eroded in some parts, and the Permian-Mesozoic complex was deposited directly on the Lower Palaeozoic strata (van Balen and Heeremans 1998). During the late Permian to Cretaceous time, the western part of the BB constituted an eastern flank of the Polish Trough. The main phases of subsidence and burial took place during late Permian–early Triassic time and were associated with rifting in the Polish Trough. During the late Cretaceous, in relation to the compressional regime, uplift and erosion occurred. The intensive tectonic movements and related activities have increased thermal maturity of organic matter (Poprawa et al. 2010).

In the BB, the Cambrian profile begins poorly sorted sandstones (quartz and arkosic wackes) and conglomerates of Żarnowiec Formation (Fig. 2). In the middle part of profile are observed fine-grained sandstones, siltstones and sandstone–mudstone heterolithic deposits (Kluki and Łeba formations), and black claystones, dark grey mudstones and mudstone–sandstone heterolithic deposits (Sarbsko Formation). The Upper Cambrian strata are represented by bituminous shales with thin interbeds and lenses of dark, often bioclastic limestones (Słowiński and Piaśnica formations; Fig. 2). The total thickness of these deposits reaches about 35 m. The shales represent shelf muds deposited in anoxic conditions, and they correspond to the Alum Shale of Scandinavia (Andérsson et al. 1985; Bauert 1994). The lowermost Ordovician (Tremadocian) is represented by the topmost part of black bituminous shales of Piaśnica Formation (Fig. 2). On Bornholm, Scania, Öland islands and in Estonia, its equivalents are lower Tremadocian bituminous shales traditionally referred to as the *Dictyonema* Shale (Lippmaa and Maramäe 1999, 2000, 2001; Bergström et al. 2004) (Fig. 2). Their thickness ranges between a few metres to 10 m. The bituminous shales are covered by transgressive shales with glauconite, marly limestones and limestones of the Słuchowo Formation (Modliński and Podhalańska 2010) (Fig. 2). Above this formation, marly limestones of Kopalino Formation, and black and grey shales often bituminous of Sasino Formation occur. The uppermost part of the Ordovician is assigned to the Prabuty Formation. The Silurian deposits, with an erosional unconformity, are represented by a thick monotonous claystones, and mudstones' succession belongs to Pasłek, Pelplin, Kociewie and Puck formations (Modliński and Podhalańska 2010) (Fig. 2).

In the south-eastern of the Baltic Basin, along the TTZ and by the Mazury–Belarus High, the Lublin-Podlasie Basin (L-PB) is located. The analysed basin is divided into Lublin and Podlasie zones. Like the BB, it developed in the Ediacaran following the breakup of Rodinia on the western slope of the palaeocontinent of Baltica. The basin was formed as a result of the NW–SE peri-Tornquist depression rotated into the NE–SW direction, so-called Orsha-Volyn Aulacogen (Poprawa et al. 1999; Nawrocki and Poprawa 2006). It consists of two structural sub-basins: the Podlasie Depression in the north and the Lublin Slope in the south.

In the L-PB, four main tectonic episodes of the Lower Palaeozoic strata evolution can be distinguished (Poprawa and Pacześna 2002). The first was connected with the Late Neoproterozoic syn-rift and the second episode with transition from a syn-rift to post-rift phase at the latest Neoproterozoic to Early Cambrian. The third was related to post-rift thermal subsidence of the passive continental margin in the late Early Cambrian to the Middle Ordovician. The last episode was related to late Ordovician to late Silurian flexural bending.

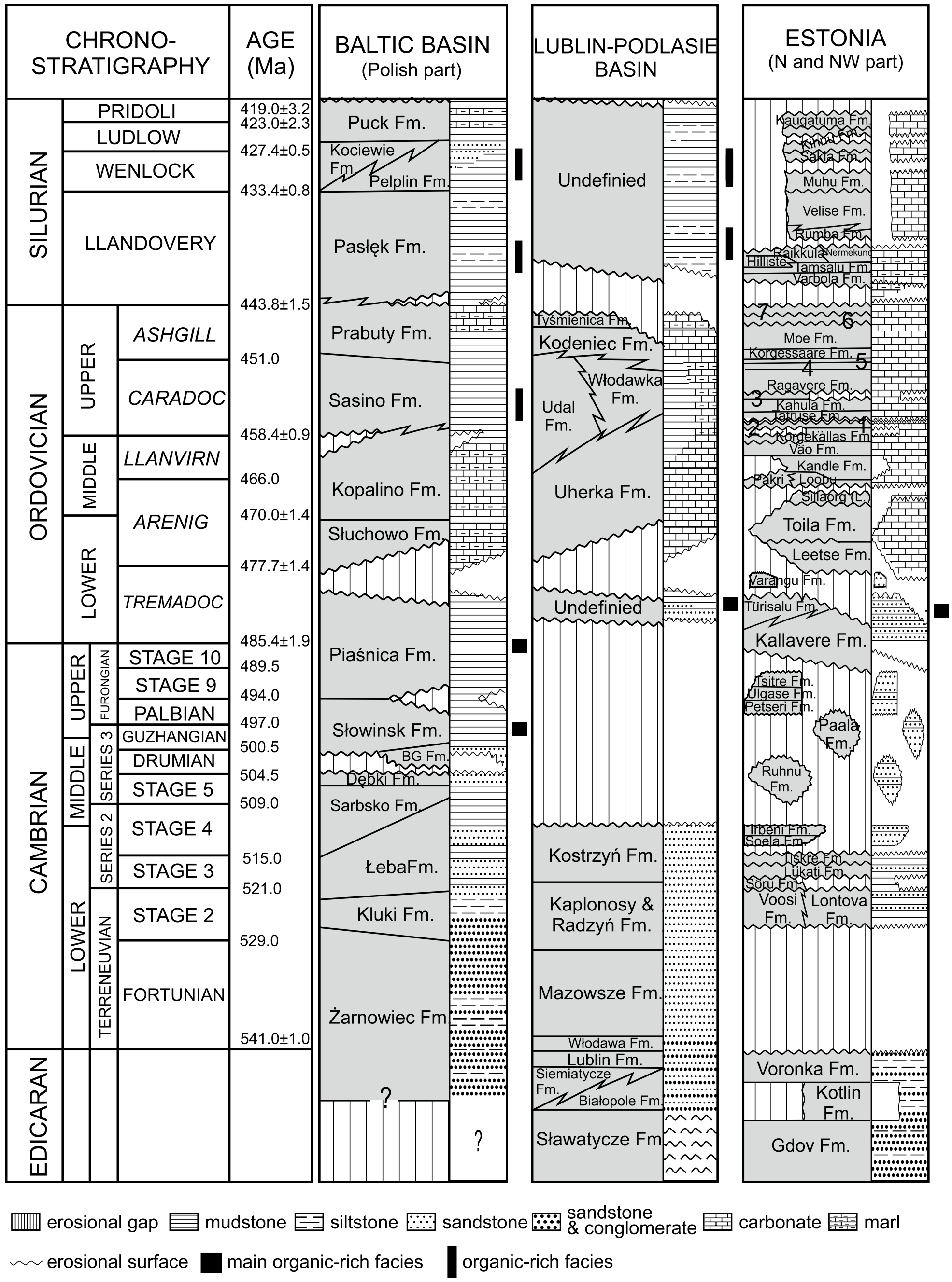

Fig. 2 Lower Palaeozoic generalized stratigraphy Polish part of the Baltic Basin, Podlasie Depression and N and NW part of Estonia (based on Pacześna and Poprawa 2005; Drygant et al. 2006; Podhalańska and Modliński 2010). *BG Fm.* Bałogóra Formation, *1* Viivikonna Fm., *2* Pihla Fm., *3* Vasalemma Fm., *4* Paekna Fm., *5* Saunja Fm., *6* Adila Fm., *7* Arina Fm

Continuous sequences of the Lower Palaeozoic strata occurred in both sub-basins, from Ediacaran to the Silurian, except for an erosional gap comprising the upper Middle and Late Cambrian (Nawrocki and Poprawa 2006). The uppermost Ediacaran–Middle Cambrian are represented by continental–marginal marine and open marine coarse-grained sandstones, and conglomerates belong to Polesie, Siemiatycze, Białopole, Lublin and Włodawa formations, and basalts and tuff with conglomerates of Sławatycze Formation (Areń 1982; Lendzion 1983; Pacześna 1996; Bogdanova et al. 1997; Poprawa and Pacześna 2002) (Fig. 2). The uppermost part of the Middle Cambrian and Upper Cambrian deposits does not occur in the studied basin. Probably, these strata were removed during erosion.

The Cambrian deposits are unconformably overlain by Ordovician clastic, and carbonate deposits belong to

Uherka, Udal/Włodawka, Kodeniec and Tyśmienica formations (Modliński 1982; Drygant et al. 2006) (Fig. 2). The lowermost of that complex forms the *Dictyonema* Shale. Characteristic of the Podlasie Depression is the development of shallow neritic facies sediments (Tomczykowa and Tomczyk 1978).

The Silurian strata begin with a distinct erosional unconformity at the base. The deposits, as in the Baltic Basin, are represented by a thick undefined claystones and mudstones succession.

Alum and *Dictyonema* shales

The Alum Shale is a unit of black organic-rich mudstones, originally containing iron sulphide (pyrite and marcasite), about 20–60 m thick, which were deposited in a shallow marine shelf environment on the tectonically stable Baltoscandian Platform in middle and late Cambrian to earliest Ordovician time (lowermost Tremadocian) (Thickpenny 1984; Dyni 1990, 2006). Black mudstones, equivalent in part to the Alum Shale, are present on the islands of Öland and Götland (Andérsson et al. 1985; Dahl et al. 1989; Falk et al. 2006). The bituminous black shales of early Ordovician (Tremadocian) age are called *Dictyonema* Shale in the outcrops along the north shore of Estonia and Podlasie Depression (Modliński et al. 2007; Modliński and Szymański 2008). The Alum Shale represents slow deposition in shallow, near-anoxic waters that were little disturbed by wave- and bottom-current action. The Alum Shale is remarkable for its high content of metals including uranium, vanadium, nickel and molybdenum (e.g. Andérsson et al. 1985; Bergh 1994; Falk et al. 2006; Dyni 2006; Lippmaa et al. 2009).

The organic carbon content of Alum Shale ranges from a few per cent to more than 20 per cent, being highest in the upper part of the shale sequence (Dyni 2006; Falk et al. 2006). Thermal maturity of organic matter in Alum Shale increases to the TTZ zone direction. In southern Scandinavia (Skåne in southern Sweden), Denmark (e.g. Bornholm island) and Jämtland in west-central Sweden, the Alum Shale is overmature. In the Polish offshore, as in central Sweden, the organic matter is thermally mature and low mature. The Upper Cambrian–Lower Ordovician complex of black shales is considered as the main source rock in the Baltic Basin (Bharati et al. 1992; Schleicher et al. 1998; Więcław et al. 2010; Kosakowski et al. 2010). Lewan and Buchardt (1989) evidenced in the Swedish Alum Shales the mid-reactive kerogen described S/(S + C) atomic ratio of 0.035. In the Polish and Estonian Alum and Dictyonema Shales, only low-reactive kerogen was recorded.

Dictyonema Shale is a formation of the Tremadoc stage (Pakerort and Varangu regional stages) of the Early Ordovician (Veski and Palu 2003). The name *Dictyonema* was given after the benthic root-bearing *Dictyonema flabelliforme*, which turns afterwards to a planktonic nema-bearing *Rhabdinopora flabelliformis* (Erdtmann 1986). In the western part of the Baltic Basin, *Dictyonema* Shale, similarly to Alum Shale, is metalliferous and has a high content of uranium (Loog et al. 1995; Lippmaa et al. 2009). The extreme selectivity of enrichment favouring Mo, U, Sb, As and Zn, even Re, does not correlate with adsorption on clays (Lippmaa et al. 2009). The organic content of *Dictyonema* Shale is very high, up to 20 % TOC, with a 15 % average (Althaus 1992; Veski and Palu 2003).

Data and methods

Sample description

The samples for this organic geochemical study were collected from outcrops and wells from the northern part of Estonia, offshore part of the Polish Baltic region, southern Scandinavia and the Polish Podlasie region (Fig. 1). The Alum Shale rock samples were taken from cores and outcrops representing Upper Cambrian as well as Lower Ordovician (Tremadocian) strata from outcrops in Sweden and the Danish island of Bornholm and from wells located in the Polish offshore area (Fig. 1). A total of 13 Upper Cambrian samples were collected: 7 onshore (southern Sweden and Bornholm island) and 6 offshore from B16-1/85, B21-1/95 and B6-1/82 wells (Polish Exclusive Economic Zone of the Baltic Sea; Table 1). From the Tremadocian (Lower Ordovician) strata, 9 samples were collected. Two AS-40 and AS-47 samples were taken from outcrops on Öland and Bornholm islands, respectively (Fig. 1). The remaining 7 samples came from wells in the Polish offshore: B21-1/95 (1 sample), B4-1/81 (2 samples), B6-1/82 (3 samples) and B6-2/85 (1 sample) (Table 1; Fig. 1).

Four samples of the *Dictyonema* Shale were collected from the Estonian part of the Baltic Basin: one from Haapsalu-21 well, one from the cliff near the Pakri village and two in Tallin (Fig. 1). From the Podlasie Depression, eighteen samples were collected from 9 wells: Chraboły IG-10 (2 samples), Chraboły IG-4 (1 sample), Górskie IG-1 (2 samples), Haćki IG-2 (1 sample), Husaki IG-4 (4 samples), Husaki IG-8 (2 samples), Rajsk IG-3 (1 sample), Rajsk IG-4 (3 samples) and Stadniki IG-1 (2 samples) (Table 1; Fig. 1).

Methods

Screening pyrolysis analyses of rock samples were carried out with a Rock-Eval 6 instrument equipped with an

Table 1 Rock-Eval data and bitumen extract content and composition of the Upper Cambrian–Lower Ordovician complex

Well/sample	Depth (m)	Strat.	Rock-eval analysis							Bit. ext.	Fractions (wt. %)				BR	HR
			TOC	$S_1 + S_2$	S_1/S_3	T_{max}	PI	HI	OI		sat.	aro.	res.	asph.		
Baltic Basin																
Alum Shale																
AS-30	Surface	Cm3	19.9	34.8	47.6	431	0.04	167	4	0.52	5	28	35	32	3	1
AS-31	Surface	Cm3	21.9	102.6	38.9	423	0.02	459	12	1.39	6	20	31	43	6	2
AS-32	Surface	Cm3	18.4	39.0	12.2	424	0.03	205	17	1.44	4	11	18	67	8	1
AS-42	Surface	Cm3	12.8	0.20	0.03	n.ap.	n.ap.	0	5							
AS-43	Surface	Cm3	11.1	0.10	0.04	n.ap.	n.ap.	0	4							
AS-45	Surface	Cm3	9.30	0.10	0.00	n.ap.	n.ap.	0	11							
AS-46	Surface	Cm3	9.46	0.30	0.00	n.ap.	0.50	1	0							
B16-1/85	1847.50	Cm3	9.49	14.4	27.0	436	0.14	131	5	1.17	29	33	23	15	12	8
B16-1/85	1850.30	Cm3	3.09	9.70	35.6	434	0.23	242	7							
B16-1/85	1857.60	Cm3	8.03	14.5	51.5	441	0.15	154	3	1.59	32	31	21	16	20	13
B21-1/95	1731.70	Cm3	14.6	40.0	54.9	438	0.11	245	4	1.94	39	31	20	10	13	9
B21-1/95	1734.35	Cm3	9.01	35.0	57.3	437	0.10	350	4	2.37					26	
B6-1/82	1432.75	Cm3	13.0	37.3	46.5	431	0.07	268	6	1.96	33	38	22	7	15	11
AS-40	Surface	Otr	8.36	42.3	23.2	426	0.03	488	21	1.86	8	21	37	34	22	6
AS-47	Surface	Otr	7.82	0.40	7.67	n.ap.	0.47	3	0	0.21					3	
B4-1/81	1103.70	Otr	10.8	40.5	141.3	440	0.06	353	2	2.28	23	34	25	18	21	12
B4-1/81	1105.70	Otr	11.4	38.3	56.8	434	0.05	318	6							
B6-1/82	1416.15	Otr	8.50	29.9	84.6	436	0.10	318	4	3.96	34	31	26	9	47	30
B6-1/82	1420.00	Otr	11.8	43.9	80.3	434	0.07	347	4	3.53	33	34	25	8	30	20
B6-1/82	1425.00	Otr	10.2	36.1	72.4	434	0.08	326	5	3.72	31	30	31	8	36	22
B6-2/85	1432.10	Otr	9.03	30.4	57.6	433	0.07	313	5							
B6-2/85	1437.40	Otr	8.19	38.9	129.2	434	0.07	442	3							
Dictyonema Shale																
Haapsalu-21	165.0	Otr	12.7	22.6	3.99	413	0.04	171	43	2.39	1	5	20	74	19	1
Pakri-2	Surface	Otr	13.6	80.5	48.1	411	0.01	586	12	2.70	1	10	23	66	20	2
Tallinn-1	Surface	Otr	13.4	80.3	46.3	415	0.01	592	13	3.60	3	10	27	60	27	4
Tallinn-2	Surface	Otr	7.16	40.0	27.0	420	0.01	555	21	3.04	7	10	29	54	42	7
Podlasie Depression																
Dictyonema Shale																
Chraboły IG-10	590.45	Otr	7.44	17.9	6.29	425	0.05	228	36	1.89					25	
Chraboły IG-10	592.34	Otr	11.6	27.0	6.22	418	0.05	222	36	2.28	2	12	24	62	20	3
Chraboły IG-4	581.65	Otr	6.34	17.0	6.63	422	0.05	255	38	1.30					21	
Górskie IG-1	724.90	Otr	8.89	21.9	11.7	426	0.04	237	20	1.62					18	
Górskie IG-1	725.30	Otr	6.97	10.5	2.60	427	0.09	137	29	1.05					15	
Haćki IG-2	590.56	Otr	7.7	24.3	8.31	425	0.04	303	36	2.52					33	
Husaki IG-4	630.57	Otr	12.7	27.4	5.09	423	0.04	206	40	2.87					23	
Husaki IG-4	631.06	Otr	12.2	24.3	5.06	421	0.05	190	38							
Husaki IG-4	631.16	Otr	13.7	25.8	4.39	422	0.04	180	41	2.67	5	7	21	67	20	2
Husaki IG-4	631.26	Otr	11.0	20.7	4.19	424	0.05	178	43							
Husaki IG-8	634.62	Otr	4.33	15.1	10.2	423	0.05	333	33	1.26					29	
Husaki IG-8	634.74	Otr	4.85	15.2	9.16	422	0.04	300	33							
Rajsk IG-3	618.24	Otr	12.8	36.5	8.25	421	0.04	272	33	5.08	3	11	19	67	40	6
Rajsk IG-4	637.30	Otr	6.79	25.7	9.09	420	0.04	363	40	2.84					42	
Rajsk IG-4	638.24	Otr	11.0	23.2	5.06	421	0.05	201	40							
Rajsk IG-4	638.70	Otr	11.7	33.8	6.39	421	0.08	266	42	8.85	42	7	18	33	76	37

Table 1 continued

Well/sample	Depth (m)	Strat.	Rock-eval analysis							Bit. ext.	Fractions (wt. %)				BR	HR
			TOC	$S_1 + S_2$	S_1/S_3	T_{max}	PI	HI	OI		sat.	aro.	res.	asph.		
Stadniki IG-1	1192.40	Otr	10.5	48.0	9.76	422	0.03	441	45	3.12	2	13	19	66	30	5
Stadniki IG-1	1192.85	Otr	13.1	29.9	3.41	429	0.07	212	62	1.99	6	11	29	54	15	3

Strat., Stratigraphy; TOC, total organic carbon (wt%); S_1, S_2, hydrocarbons content (mg HC/g rock); T_{max}, temperature of S_2 peak (oC); PI, production index; HI, hydrogen index (mg HC/g TOC); OI, oxygen index (mg CO2/g TOC); Bit. ext., bitumen extract (mg/g); sat., saturates; aro., aromatics; res., resins; asph., asphaltenes; BR, bitumen ratio (mg bitumens/g TOC); HR, hydrocarbon ratio [mg (sat + aro)/g TOC]; blank space, not detected or not determined; n.ap., not applicable due to traces of hydrocarbons; Cm3, Upper Cambrian; Otr, Ordovician–Tremadocian

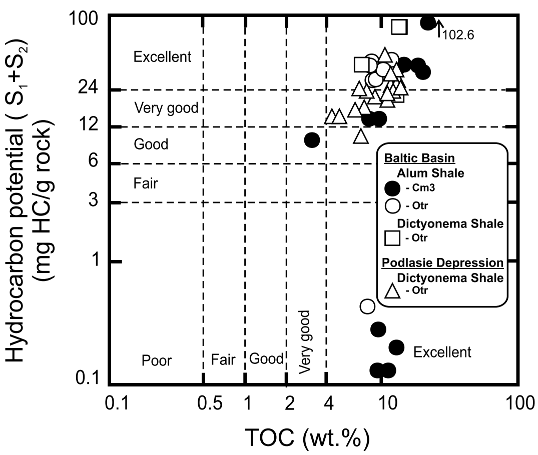

Fig. 3 Petroleum source quality diagram for the Upper Cambrian–Lower Ordovician organic matter. Classification after Peters and Cassa (2002). *Cm3* Upper Cambrian, *Otr* Tremadocian (Ordovician)

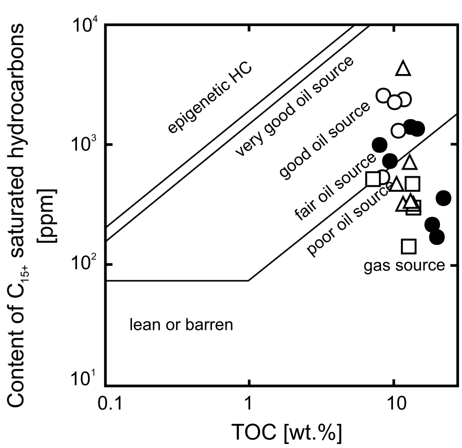

Fig. 4 Correlation of C_{15} saturated hydrocarbons versus total organic carbon contents. Classification after Hunt (1979) and Leenheer (1984). For explanation of symbols, see Fig. 3

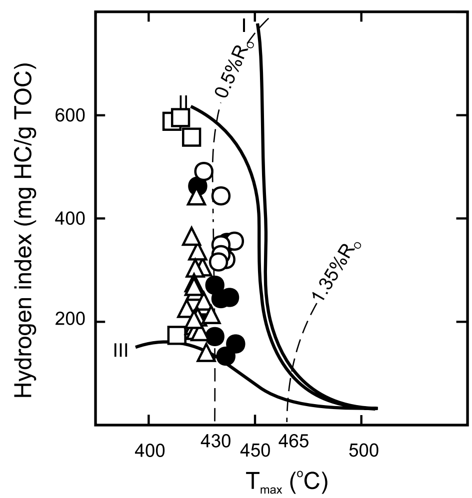

Fig. 5 Hydrogen index versus Rock-Eval T_{max} temperature for diagram for Upper Cambrian–Lower Ordovician organic matter. Maturity paths of individual kerogen types after Espitalié et al. (1985). For explanation of symbols, see Fig. 3; line 0.5 % R_o and 1.35 % R_o—range of "oil window"

organic carbon module. Aliquots of the pulverized samples were extracted with dichloromethane/methanol (93:7 v/v) in a SOXTEC™ apparatus. The asphaltene fraction was precipitated from bitumens with *n*-hexane. The remaining maltenes were then separated into compositional fractions of saturated hydrocarbons, aromatic hydrocarbons and resins by column chromatography, using alumina/silica gel (2:1 v/v) columns (0.8 × 25 cm). The fractions were eluted with *n*-hexane, toluene and toluene/methanol (1:1 v/v), respectively. After removal of carbonates with hydrochloric acid and extraction of bitumens, rock samples selected for stable carbon isotope analysis of kerogen were combusted in an online system. Preparation of previously extracted bitumens and their fractions was performed by the same procedure. Stable carbon isotope analyses were performed using a Finnigan Delta Plus mass spectrometer. The stable carbon isotope data are presented in the δ-notation relative to VPDB standard, with an analytical precision estimated to be ±0.2 ‰. Elemental analysis of isolated kerogen (C, H, N and S) was determined with an EA 1108 elemental analyser. The quantity of pyrite contaminating the kerogen was analysed as iron, on a Perkin-Elmer Plasma 40 ICP-AES instrument after digesting the ash from burned kerogen (815 °C, 30 min.) with hydrochloric acid. The organic

Table 2 Main contents of oxides, sulphur and radioactive elements of the Upper Cambrian–Lower Ordovician complex

Well/sample	Depth (m)	Strat.	(wt%)								(ppm)	
			Al_2O_3	CaO	FeO	K_2O	MgO	Na_2O	P_2O_5	S	Th	U
Baltic Basin												
Alum Shale												
AS-30	Surface	Cm3	12.1	0.8	6.48	4.8	0.8	0.2	0.2	6.8	11.5	261
AS-31*	Surface	Cm3	11.3	0.6	7.41	4.4	0.7	0.1	0.2	6.8	12.0	190
AS-32*	Surface	Cm3	12.1	0.6	7.27	4.8	0.8	0.1	0.2	6.9	8.0	440
AS-42	Surface	Cm3	16.3	0.5	2.5	4.9	1.0	0.1	0.0	2.5	10.3	25
AS-43	Surface	Cm3	15.6	0.6	4.5	4.5	0.9	0.1	0.0	4.3	9.3	24
AS-45	Surface	Cm3	12.9	0.1	8.2	4.0	0.8	0.1	0.1	8.0	11.5	74
AS-46	Surface	Cm3	13.8	0.2	5.7	4.8	0.9	0.1	0.1	4.4	15.1	77
B16-1/85	1847.50	Cm3	8.1	1.8	11.6	4.3	1.0	0.2	0.1	9.5	9.5	124
B16-1/85	1857.60	Cm3	7.5	0.9	13.9	4.1	1.4	0.3	0.1	10.8	8.7	57
B21-1/95	1731.70	Cm3	7.6	0.8	6.5	5.7	1.7	0.4	0.2	4.9	9.6	117
AS-40*	Surface	Otr	14.0	0.4	4.4	6.0	1.5	0.3	0.2	1.5	12.0	60
AS-47	Surface	Otr	13.3	0.2	3.5	4.3	1.3	0.1	0.2	2.1	14.9	57
B4-1/81	1103.70	Otr	7.4	0.5	4.4	5.0	1.8	0.4	0.1	2.1	11.6	41
Dictyonema Shale												
Haapsalu-21	165.00	Otr	13.7	0.3	4.0	7.4	1.3	0.1	0.1	2.7	16.8	305
Pakri-2	Surface	Otr	13.9	0.3	3.8	6.0	1.2	0.1	0.1	2.9	22.0	125
Tallinn-1	Surface	Otr	14.3	0.2	4.8	5.6	1.2	0.1	0.1	2.9	21.4	78
Podlasie Depression												
Dictyonema Shale												
Chraboły IG-10	590.45	Otr	9.4	1.0	6.0	2.3	0.4	0.1	0.5	6.1	13.7	128
Chraboły IG-10	592.34	Otr	12.1	0.3	2.8	3.1	0.5	0.1	0.2	2.8	15.1	84
Chraboły IG-4	581.65	Otr	14.2	0.4	2.7	3.9	0.6	0.1	0.2	2.0	19.5	81
Górskie IG-1	724.90	Otr	13.6	0.7	2.6	2.2	0.6	0.1	0.2	2.0	14.1	33
Haćki IG-2	590.56	Otr	14.2	0.5	2.5	3.3	0.6	0.1	0.2	2.2	18.5	42
Husaki IG-4	630.57	Otr	14.2	0.3	3.7	3.1	0,8	0.1	0.2	2.3	24.5	124
Husaki IG-4	631.06	Otr	9.1	0.2	3.1	2.9	0,4	0.1	0.1	2.5	23.5	105
Husaki IG-4	631.16	Otr	12.0	0.3	3.4	2.8	0.7	0.1	0.1	2.1	24.9	84
Husaki IG-4	631.26	Otr	13.5	0.3	2.3	2.8	0.6	0.1	0.1	1.6	24.6	83
Husaki IG-8	634.62	Otr	14.9	0.4	3.1	3.6	0.6	0.1	0.1	2.3	28.9	31
Husaki IG-8	634.74	Otr	15.6	0.3	2.8	3.7	0.7	0.1	0.1	1.8	28.6	42
Rajsk IG-3	618.24	Otr	13.9	0.2	2.9	3.6	0.6	0.1	0.1	2.5	23.3	45
Rajsk IG-4	637.30	Otr	16.0	0.3	2.6	4.1	0.7	0.1	0.2	1.6	28.5	37
Rajsk IG-4	638.24	Otr	13.2	0.3	3.3.	3.1	0.6	0.1	0.2	2.9	24.0	141
Rajsk IG-4	638.70	Otr	11.4	0.3	3.4	3.5	0.5	0.1	0.2	2.9	25.9	108
Stadniki IG-1	1192.40	Otr	14.4	0.4	3.6	2.8	0.7	0.1	0.2	3.0	26.3	150
Stadniki IG-1	1192.85	Otr	19.1	0.5	2.6	3.8	1.1	0.1	0.2	1.1	37.0	754

Strat., Stratigraphy; * data from Lewan and Buchardt (1989); Cm3, Upper Cambrian; Otr, Ordovician–Tremadocian

sulphur content in kerogen was calculated as the difference of total and pyritic sulphur. The oxygen content was calculated as difference to 100 % taking into account C, H, N, S, moisture and ash contents. Biomarker distributions were determined by analysing the maltene fraction on a computerized GC-mass spectrometer (MS) system using a Hewlett-Packard 6890 GC with a DB-1701 60 m × 0.31 mm column (0.25 µm film thickness, bonded phase: 14 % cyanopropylphenyl–86 % dimethylpolysiloxane copolymer) directly interfaced to a JEOL GC-Mate magnetic sector MS. The aromatic hydrocarbon fractions of the extracted bitumens were analysed by GC for phenanthrene and its derivatives. Analysis was carried out with a Hewlett-Packard type 5890 Series II gas chromatograph equipped

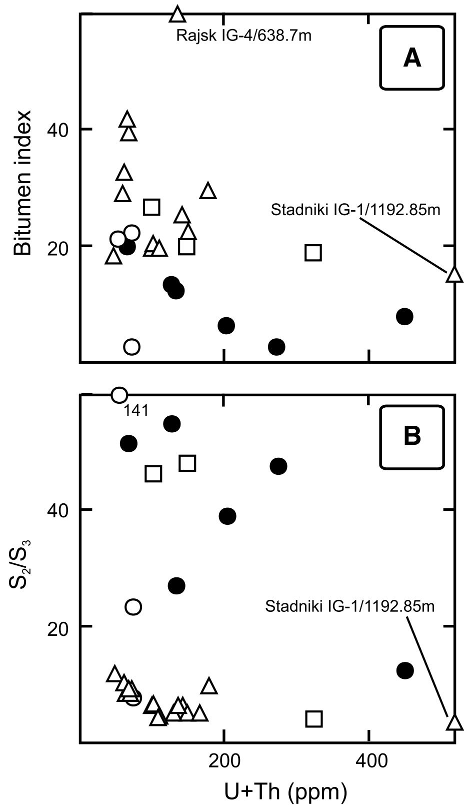

Fig. 6 **a** Bitumen index and **b** S_2/S_3 index versus uranium and thorium contents. For explanation of symbols, see Fig. 3

with fused silica capillary column (60 m × 0.25 mm i.d.) coated with 95 % methyl/5 % phenylsilicone phase (DB-5, 0.25 µm film thickness) and flame ionization detector. Nitrogen was used as a carrier gas. The GC oven was programmed from 80 to 315 °C at a rate of 3 °C min-1. Analyses of organic matter and other minerals were carried out using an EDS (energy-dispersive spectroscopy) system combined with an electron scanning microscope FEI Quanta-200 FEG (20 kV acceleration voltage). Microchemical analyses of organic matter were carried out without carbon coating. All analysed samples were carefully investigated in reflected light of an ore microscope.

The geochemical analyses and electron scanning microscope were performed at the Faculty of Geology, Geophysics and Environmental Protection (AGH-UST).

The uranium and thorium contents in rocks were determined by instrumental neutron activation analysis (INAA) by Actlab Laboratories®, Canada. Chemical analyses on the original and recovered rocks were conducted by ICP-OES for oxides (Al_2O_3, CaO, FeO, K_2O, MgO, Na_2O and P_2O_3). Total sulphur was analysed with a Leco SC-132 sulphur analyser and Polish Standard PN-90/G-04514.16.

Results and discussion

Upper Cambrian–Lower Ordovician Alum Shale

The results of geochemical investigations are presented below in an order corresponding to principal indicators: organic carbon content, type of kerogen and its thermal maturity. The source rock potential was evaluated in accordance with the criteria proposed by Espitalié and Bordenave (1993), Hunt (1996) and Peters and Cassa (1994).

In the analysed samples, the organic carbon content, described by TOC parameter, is highly variable. Measured TOC contents in the Upper Cambrian–Lower Ordovician black Alum Shale vary from 3 to 22 wt% (Table 1). Despite such high variability, the median of TOC values is very high—10 wt%. A similarly wide range of values is observed for hydrocarbon contents. The petroleum potential ($S_1 + S_2$) is also very high too, up to 103 mg HC/g rock, with a median 35 mg HC/g rock (Table 1), indicating the excellent hydrocarbon potential of this stratigraphic division (Fig. 3). Results of extractable hydrocarbon content analyses reveal Alum Shale mainly as fair to good source rocks (Fig. 4). This assessment is probably reduced and modified due to irradiation of organic matter by radiogenic elements, mainly uranium decay (Lewan and Buchardt 1989; Court et al. 2006). The hydrogen index (HI), which describes the hydrocarbon potential, also shows high variability. The calculated HI values for Alum Shale range from 0 to 488 mg HC/g TOC (Table 1; Fig. 5). The lowermost values of HI are observed in overmature samples from Skåne and Bornholm island (southern Scandinavia). The immature samples collected from Öland island and Västergötland region (south-central Sweden) show much higher values, up to 488 mg HC/g TOC (Table 1). The whole samples present very low oxygen indices, usually several mg CO_2/g TOC (Table 1). These results are similar to those given by Buchardt et al. (1986, 1998), Dahl et al. (1988a, b) and Leventhal (1991). The high TOC concentration is accompanied by anomalously high contents of uranium and thorium. Those radioactive elements reach levels of tens to about 450 ppm (Tables 1, 2). Equally high results were observed in Swedish Alum Shale (Andérsson et al. 1985; Dahl et al. 1988a, b; Lewan and Buchardt 1989; Leventhal 1991; Buchardt et al. 1998; Schovsbo 2002), where measured uranium concentrations were up to 500 ppm. These sediments were probably enriched in organic matter as well as radioactive elements due to low sedimentation rates and anoxic conditions. The high concentrations are associated with the high content of organic matter (Fig. 6a), and correlation of some basic geochemical parameters (i.e. bitumen ratio and S_2/S_3 ratio) is observed (Fig. 6b, c). These ratios inversely correlate

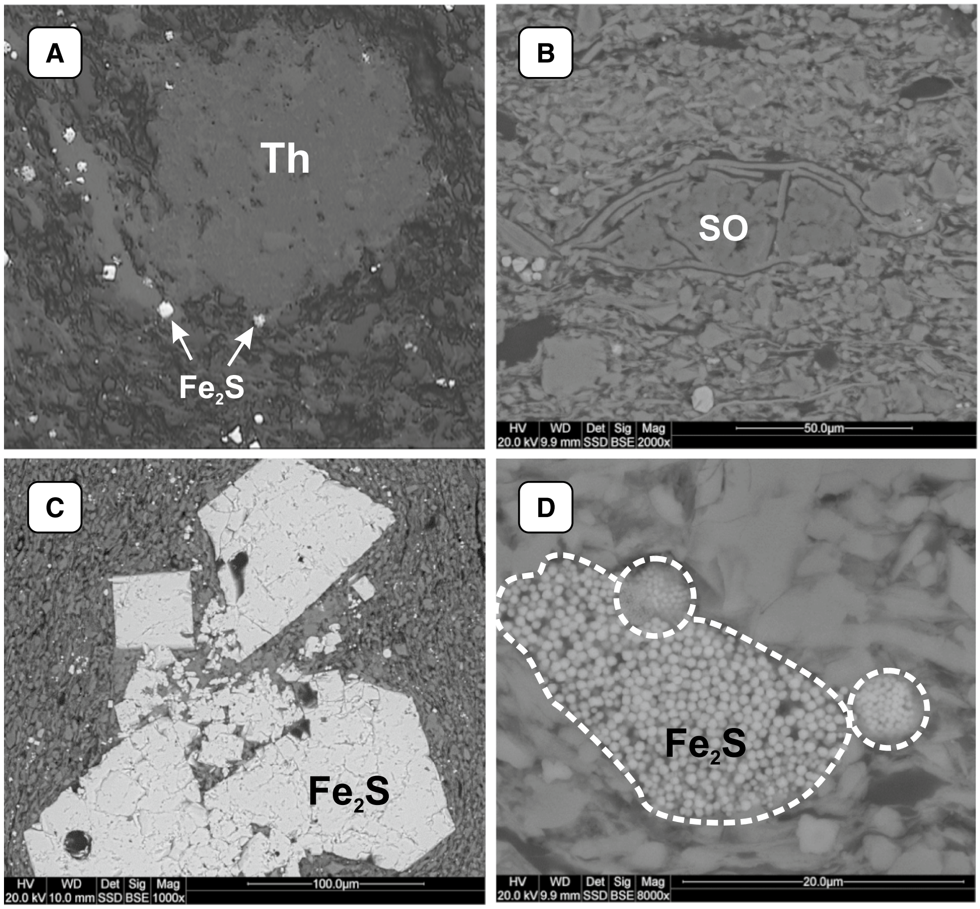

Fig. 7 **a** Backscattered electron (BSE) image thucholite type of organic matter (well B21-1/95), **b** organogenic structure composed of apatite (sample AS-40), **c** pyrite framboids (*black* is organic matter; sample AS-40), **d** euhedral crystals of pyrite (well B4-1/01)

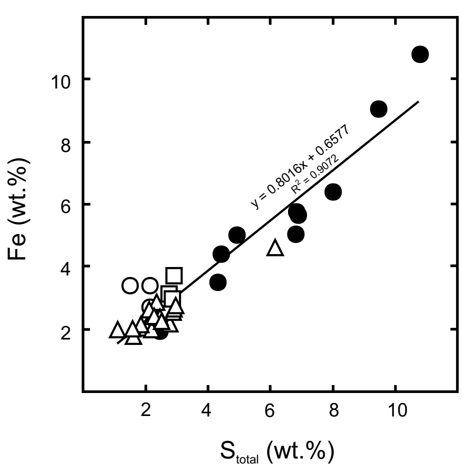

Fig. 8 Iron versus sulphur content. For explanation of symbols, see Fig. 3

with uranium and thorium content, because decay of radioactive elements induces polymerization of organic structures and oxidation of them (Fig. 6) (Court et al. 2006). This oxidation effect is also recorded in stable carbon isotope composition of saturates and aromatics. It manifests often in higher $\delta^{13}C$ value of saturates than aromatics (Fig. 6d). Light isotopes of saturates are preferentially oxidized resulting in increase of $\delta^{13}C$ value. Comparable effect, but induced by migration of oxidizing fluids, was earlier described for Kupferschiefer strata by, for example, Kotarba et al. (2006).

The results of electron scanning microscope, performed in the AS-32, AS-40 samples and samples from B21-1/95 and B4-1/01 wells (Fig. 1), showed that organic matter is occurring as thin, several micrometres thick, laminae composed of clay and sapropelic type of organic matter (Fig. 7a), probably over 10 wt%. Thucholite type of organic matter also has been observed (Fig. 7b). These micro-concretions are relatively big in size, up to 1 mm. Some of them show differences in reflectivity, that is probably a result of the organic matter maturation. Xenomorphic crystals of rutile and anatase and pyrite have also been identified. Euhedral and framboidal pyrite crystals are very common (Fig. 7c, d).

Table 3 Selected biomarker ratios and indices for bitumen from the Upper Cambrian–Lower Ordovician complex

Sample	Depth (m)	CPI	Pr/Ph	Pr/n-C_{17}	Ph/n-C_{18}	Gam/Hop	C_{27}	C_{28}	C_{29}	DBT/Phen.	Dia/Hop	Bis/Hop	C_{26}/C_{24}	Mor/Hop	H_{31}S/(S+R)	H_{32}'S/(S+R)	C_{29}SR	C_{29} (ββαα)	C_{29}Ts/C_{29}H	Ts/Tm	Gam/C_{31}Hop	Dia/Reg
Baltic Basin																						
Alum Shale																						
AS-30	Surface	0.86	0.17	0.83	0.27	n.c.	n.c.	n.c.	n.c.	1.10	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.
AS-32	Surface	0.81	0.49	1.75	0.63	n.c.	n.c.	n.c.	n.c.	0.63	n.c.	n.c.	n.c.	0.15	0.58	n.c.	n.c.	n.c.	n.c.	0.66	n.c.	n.c.
B16-1/85	1847.50	0.88	0.44	0.23	0.38	0.24	0.51	0.29	0.21	n.c.	0.15	0.17	2.06	0.19	0.57	0.59	0.42	0.46	0.84	1.04	0.58	2.71
B16-1/85	1857.60	0.95	0.47	0.32	0.30	0.06	0.50	0.25	0.25	n.c.	0.19	0.32	1.95	0.17	0.62	0.62	0.47	0.34	1.35	1.26	0.16	1.86
B21-1/95	1731.70	0.91	0.86	0.37	0.28	n.c.	0.58	0.27	0.16	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	0.50	n.c.	n.c.	n.c.	n.c.	3.90
B4-1/81	1103.70	0.96	0.86	0.24	0.21	n.c.	0.48	0.27	0.26	n.c.	0.18	0.25	1.80	0.24	0.52	0.50	0.51	0.59	1.30	1.01	0.00	2.42
Dictyonema Shale																						
Haapsalu-21	165.00	0.83	n.c.	n.c.	0.56	n.c.	n.c.	n.c.	n.c.	0.20	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.
Pakri-2	Surface	0.95	0.07	2.10	0.64	n.c.	n.c.	n.c.	n.c.	0.26	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.
Tallin-1	Surface	0.96	0.26	0.77	0.68	0.61	n.c.	n.c.	n.c.	0.15	n.c.	n.c.	n.c.	0.51	0.34	n.c.	n.c.	n.c.	n.c.	0.30	0.63	n.c.
Podlasie Depression																						
Dictyonema Shale																						
Chraboły IG-10	592.34	0.99	0.19	0.54	0.75	0.15	n.c.	n.c.	n.c.	0.03	n.c.	n.c.	n.c.	0.12	0.60	n.c.	n.c.	n.c.	0.17	0.43	0.23	n.c.
Husaki IG-4	631.16	0.97	0.23	0.52	0.73	0.10	n.c.	n.c.	n.c.	0.03	n.c.	n.c.	n.c.	0.14	0.66	n.c.	n.c.	n.c.	0.35	0.63	0.21	n.c.
Rajsk IG-3	618.24	0.92	0.48	0.68	0.81	0.40	n.c.	n.c.	n.c.	0.02	n.c.	n.c.	n.c.	0.51	0.31	n.c.	n.c.	n.c.	0.50	0.27	0.49	n.c.
Stadniki IG-1	1192.40	0.95	0.18	0.62	0.44	n.c.	n.c.	n.c.	n.c.	0.09	n.c.	n.c.	n.c.	0.17	0.51	n.c.	n.c.	n.c.	0.08	0.92	n.c.	n.c.
Stadniki IG-1	1192.85	0.92	0.31	n.c.	0.48	n.c.	n.c.	n.c.	n.c.	0.08	n.c.	n.c.	n.c.	n.c.	0.50	n.c.	n.c.	n.c.	0.10	0.79	n.c.	n.c.

$CPI_{(Total)} = [(C_{17} + C_{19} + \cdots + C_{27} + C_{29}) + (C_{19} + C_{21} + \cdots + C_{29} + C_{31})]/2(C_{18} + C_{20} + \cdots + C_{28} + C_{30})$; Pr, Pristane; Ph, Phytane; Gam/Hop = gammacerane/17α-hopane; $C_{27} = C_{27}$ααα20R sterane/($C_{27} + C_{28} + C_{29}$)ααα20R steranes; $C_{28} = C_{28}$ααα20R sterane/($C_{27} + C_{28} + C_{29}$)ααα20R steranes; $C_{29} = C_{29}$ααα20R sterane/($C_{27} + C_{28} + C_{29}$)ααα20R steranes; DBT/Phen, dibenzothiophene/phenanthrene; Dia/Hop = 15α-metylo-27-nor-17α-hopane/17a hopane; Bis/Hop = 28,30-bisnorhopane/17α-hopane; $C_{26}/C_{24} = C_{26}$(S + R) tricyclic terpanes/C_{24} tetracyclic terpane; Mor/Hop = (normoretane + moretane)/(norhopane + 17a-hopane); H_{31}S/(S + R) = homohopane 22S/(22S + 22R); H_{32}S/(S + R) = bishomohopane 22S/(22S + 22R); C_{29}SR = epimerization of regular steranes C_{29} ratio; C_{29}ββαα = ratio of ββ-epimeres of regular steranes C_{29} to their total quantity; $C_{29}Ts/C_{29}H = C_{29}$ 18α norneohopane/C_{29} norhopane; Ts/Tm = C_{27} 18α trisnorhopane/C_{27} 17α trisnorhopane; Gam/C_{31}Hop = gammacerane/C_{31} 22R hopane; Dia/Reg = C_{27} βα 20S diasterane/C_{29} ααα 20R sterane; n.c., not calculated due to lack of biomarkers

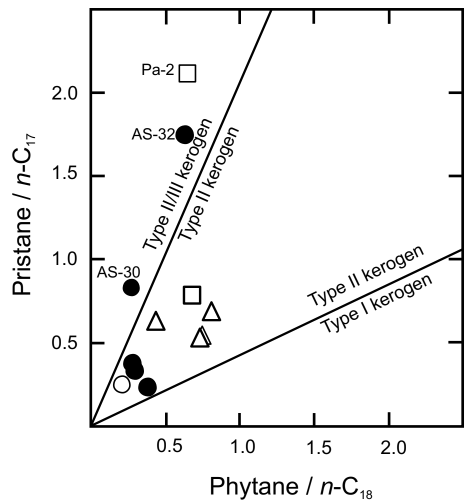

Fig. 9 Genetic characterization of bitumen from Upper Cambrian and Tremadocian strata of the Polish part of Baltic Basin in terms of pristane/n-C_{17} and phytane/n-C_{18} according to the categories of Obermajer et al. (1999). For explanation of symbols, see Fig. 3

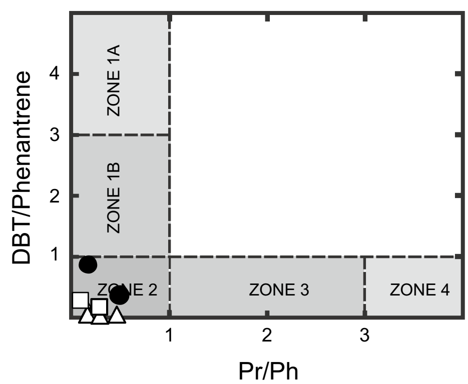

Fig. 10 Genetic characteristic of depositional environment of the Upper Cambrian–Lower Ordovician organic matter based on dibenzothiophene/phenanthrene (DBT/Phen) and pristane/phytane (Pr/Ph) correlation. The zone of depositional environment after Hughes et al. (1995); Zone 1A—marine carbonates; Zone 1B—marine and lacustrine (carbonates, marls) enriched in sulphates; Zone 2—lacustrine deposits weakened in sulphates or marine carbonates lean in organic carbon; Zone 3—marine (lacustrine) shale; Zone 4—fluvial/deltaic deposits (carbonaceous shale, coal). For explanation of symbols, see Fig. 3

The genetic type of organic matter dispersed in the Upper Cambrian–Lower Ordovician strata is determined by the age of rocks and environment conditions of sedimentation (Andérsson et al. 1983). Sapropelic matter, predominant algae and sulphide bacteria are present there (Buchardt et al. 1986, 1998; Buchardt and Lewan 1990). The correlation between iron and sulphur and their contents (Table 2; Fig. 8), suggesting occurrence of pyrite, points to anoxic conditions of deposition and sulphate reduction. The reduced and sub-oxic conditions of deposition are also indicated by values of the pristane/phytane ratio (Table 3; Figs. 9, 10). Results of geochemical investigations including Rock-Eval (Table 1; Figs. 3, 4, 5), distribution of biomarkers (Tables 2, 3; Figs. 8, 9, 10), elemental composition of kerogen and stable carbon isotopes (Table 4; Figs. 11, 12) show the presence of oil-prone Type-II kerogen. In the n-alkane distribution, maximum intensities at 20–22 carbon atoms are noted. Dominance of short-chain n-alkanes speaks for their generation from algal kerogen (Peters et al. 2005). The high proportion of C_{27} regular steranes, from 0.48 to 0.58, in the regular steranes distribution confirms an algal source of extracted bitumens (Table 3; Czochanska et al. 1988), and very high values of diasterane to regular sterane ratios, up to 3.9 (Table 3), evidence shaly environment of organic matter deposition (Peters et al. 2005). In some samples, as AS-30 and AS-32, only traces of steranes and hopanes were noted, not allowing calculation of most indices (Table 3).

The maturity level of the Upper Cambrian–Lower Ordovician strata was determined mainly based on results of Rock-Eval T_{max} (Table 1). These results were verified by maturity indices calculated from distribution of biomarkers and aromatic hydrocarbons (Table 5). The T_{max} values show the changeable maturity of Alum Shale, from immature and the initial phase of "oil window" up to the overmature phase (Table 1; Fig. 5). The T_{max} values refer only to maturity corresponding to the "oil window" stage, because sufficient quantities of residual hydrocarbons present only in samples of such transformation level for a correct T_{max} value reading. For the higher maturing samples, the T_{max} values were unreliable due to only trace amounts of residual hydrocarbons (S_2 peak). The previous published vitrinite-like macerals reflectance data (e.g. Buchardt and Lewan 1990) and re-calculated R_o values (after Jacob and Hiltmann 1985) show maturity up to 6.3 % in the Upper Cambrian strata in Västergötland region. The highest maturities are noted along TTZ, in deeply buried strata (over 4000 m) (Buchardt et al. 1986, 1998; Grotek, 2006). The biomarker and aromatic hydrocarbon distributions (Tables 3, 5) confirm previous data. Sterane and hopane isomerization indices are near to equilibrium. The calculated biomarker indices could be affected by radiation of radiogenic elements (Tables 1, 2). The uranium and thorium decay influences the hydrocarbons distribution as radiation-induced polymerization of the side chains or cross-linking of longer n-alkane precursors in the kerogen matrix (Lewan and Buchardt 1989). Więcław et al. (2010) revealed that this decay influenced especially the n-alkane and isoprenoid distributions, and led to the characteristic "hump" of unresolved complex mixture (UCM) composed of polymerized species on the GC chromatogram. The Upper Cambrian–Lower Ordovician black Alum Shale is the unit having the

Table 4 Stable carbon isotope composition of bitumen, its individual fractions and kerogen as well as elemental composition of kerogen separated from the Upper Cambrian–Lower Ordovician complex

Sample	Depth (m)	$\delta^{13}C$ (‰)						S_{TOTAL} (wt%)	Fe_{TOTAL} (wt%)	Elemental composition (daf, wt. %)					Atomic ratio			
		Sat	Bit	Aro	Res	Asph	Ker			C	H	O	N	S	H/C	O/C	N/C	S/C
Baltic Basin																		
Alum Shale																		
AS-30	Surface	−27.6	−28.2	−28.4	−27.7	−28.8	−28.6	12.9	9.0	81.5	5.4	8.1	1.8	3.4	0.79	0.10	0.02	0.02
B16-1/85	1847.50	−26.9	−27.7	−28.0	−28.2	−28.1	−29.2	16.9	13.5	84.7	5.2	5.2	2.6	2.3	0.74	0.05	0.03	0.01
B16-1/85	1857.60	−27.8	−27.4	−27.6	−27.2	−27.2	−27.3	17.5	14.1	84.7	5.3	4.8	2.8	2.4	0.75	0.04	0.03	0.01
B21-1/95	1731.70	−28.3	−28.4	−28.7	−28.6	−28.4	−29.4	10.4	7.9	86.6	6.2	3.0	2.3	1.9	0.87	0.03	0.02	0.01
B4-1/81	1103.70	−29.7	−29.5	−29.7	−29.3	−29.3	−30.0	6.9	5.6	86.0	7.2	3.4	2.5	0.8	1.01	0.03	0.03	0.00
B6-1/82	1432.75	−28.7	−28.9	−29.1	−29.1	−28.9	−29.8	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
B6-1/82	1425.00	−28.7	−28.9	−29.2	−29.0	−29.0	−30.1	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Dictyonema Shale																		
Haapsalu-21	165.00	−28.2	−28.9	−28.7	−28.5	−29.0	−29.5	2.5	0.3	71.2	5.5	19.0	2.0	2.3	0.93	0.20	0.02	0.01
Pakri-2	Surface	−28.5	−28.1	−27.7	−28.1	−28.2	−29.2	7.4	4.4.	71.2	6.4	17.3	2.4	2.7	1.08	0.18	0.03	0.01
Tallin-1	Surface	−30.3	−29.1	−28.5	−29.4	−29.0	−29.8	6.2	3.2	71.4	6.8	16.5	2.4	2.9	1.14	0.17	0.03	0.02
Podlasie Depression																		
Dictyonema Shale																		
Chraboły IG-10	592.34	−28.2	−28.5	−28.2	−28.7	−28.7	−29.6	3.5	1.0	70.8	5.9	18.4	2.4	2.5	1.01	0.20	0.03	0.01
Husaki IG-4	631.16	−28.0	−28.6	−27.6	−28.3	−28.6	−29.4	2.2	0.2	69.7	5.5	20.3	2.5	2.1	0.94	0.20	0.03	0.01
Rajsk IG-3	618.24	−28.2	−28.5	−28.2	−28.7	−28.7	−29.6	3.2	1.1	70.1	5.9	19.3	2.5	2.1	1.01	0.20	0.03	0.01
Stadniki IG-1	1192.40	−28.03	−28.9	−29.3	−28.6	−29.0	−29.7	6.5	4.3	72.1	6.0	17.9	2.2	1.8	1.00	0.20	0.03	0.01

Daf, dry, ash-free basis; Sat, saturated hydrocarbons; Bit, bitumen extract; Aro, aromatic hydrocarbons; Res, resins; Asph, asphaltenes; Ker, kerogen; n.a., not analysed

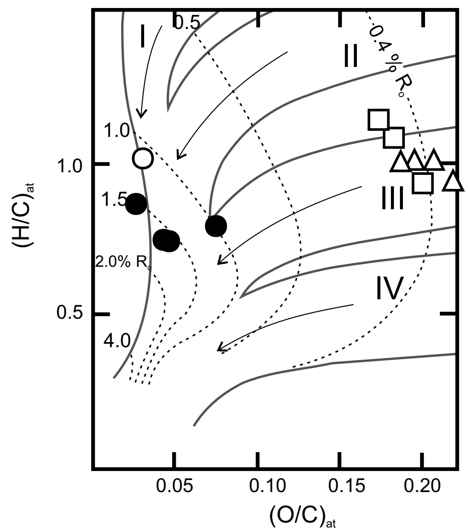

Fig. 11 Genetic characterization and thermal maturity of the Upper Cambrian–Lower Ordovician organic matter. Fields representing natural maturity paths for kerogen after Hunt (1996); at—atomic. For explanation of symbols, see Fig. 3

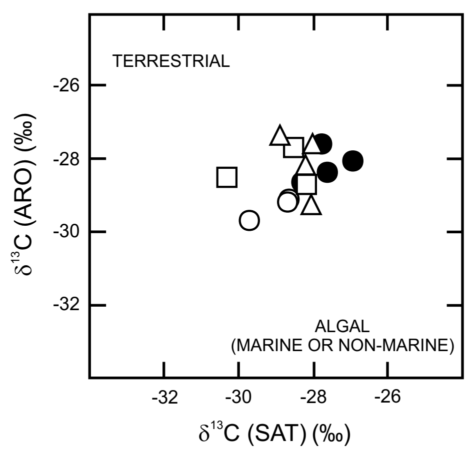

Fig. 12 Genetic characteristic of organic matter from of the Upper Cambrian–Lower Ordovician strata based on stable carbon isotope composition of saturated and aromatic hydrocarbons Genetic fields after Sofer (1984). For explanation of symbols, see Fig. 3

best hydrocarbon potential of the entire Lower Palaeozoic strata in the Baltic Basin.

Tremadocian *Dictyonema* Shale

The Tremadocian *Dictyonema* Shale, the coeval of Alum Shale, was collected on the seashore of Estonia and Podlasie Depression. The Rock-Eval pyrolysis results show high amounts of organic carbon, up to 13.7 wt% and high hydrocarbon potential (S_1 and S_2), up to 80 mg HC/g rock, indicating very good to excellent hydrocarbon potential of *Dictyonema* Shale in the Tremadocian black shales (Table 1; Fig. 3). Hydrogen index values, mainly from 300 to 400 mg HC/g TOC with exceptionally high values in the Estonian part (Table 1; Fig. 5), confirm their excellent petroleum potential. The extractable hydrocarbons content indicates that the Tremadocian shales are poor to fair oil source rocks (Fig. 1). This “low” assessment of these deposits is caused by the influence of radioactive elements on organic matter—reduction in bitumen quantity by polymerization of structures (Lewan and Buchardt 1989).

In the *Dictyonema* Shale, comparable to the Alum Shale, oil-prone Type-II kerogen was deposited. This was proved by analysis of pyrolytic (Table 1; Fig. 5), biomarker (Tables 3, 5; Fig. 9), kerogen elemental composition (Table 4; Fig. 11) and stable carbon isotope (Table 4; Fig. 12) data. The results of elemental analysis, showing the presence of Type-III kerogen in some samples, are unreliable due to the influence of radioactive elements decay on organic matter (oxidation and polymerization of biomarkers, lowering of H/C ratio; Fig. 11). The depositional environment described by biomarker indices (Tables 3, 5) was mainly anoxic (reduced). The single values of pristane/phytane ratio over unity (Table 3) suggest the presence of sub-oxic conditions in local areas of sedimentary basin (Didyk et al. 1978). The influence of radiogenic radiation is also not excluded (Lewan and Buchardt 1989). As in Alum Shales, no simple relationships were found between the TOC and the U and Th contents.

Similar to the Cambrian, the maturity of the Ordovician strata was determined from results of Rock-Eval T_{max} (Table 1), distribution of biomarkers (Table 3), elemental composition of kerogen (Table 4) and aromatic hydrocarbons (Table 5). The thermal maturity values show maturity from immature to initial phase of the “oil window” (Fig. 5). The immature *Dictyonema* Shale is located in the Podlasie Depression and low maturing in the seashore of Estonia. The biomarker indices calculated for the *Dictyonema* Shale, comparable to the Alum Shale, could be affected by radiation of radiogenic elements (Lewan and Buchardt 1989).

The electron scanning microscope study performed in the Stadniki IG-1 and Chraboły IG-10 wells revealed that the clay-organic black shale with mudstone and sandstone occurs in thin, several micrometres thick, laminae composed of clay and sapropelic type of organic carbon content up to 20 wt% (Fig. 13). The organic matter of the thucholite type has also been identified. It forms rounded micro-concretions characterized by higher reflectivity in comparison with sapropelic O.M. (Fig. 13a). Xenomorphic crystals of rutile and anatase and pyrite have also been noted. Pyrite content is on the level of 0.1–0.2 wt% (Table 6). In the Chraboły IG-10, the routine examination using electron microscope

Table 5 Maturity indices calculated from distribution of phenanthrene and dibenzothiophene and their methyl derivatives in bitumens of the Upper Cambrian–Lower Ordovician complex

Sample	Depth (m)	MPI1	MPR	MPR1	R_{cal} (%)	$R_{cal(MPR)}$ (%)	MDR	$R_{cal(MDR)}$ (%)	DBT/P
Baltic Basin									
Alum Shale									
AS-30	Surface	0.76	1.13	0.43	0.83	0.79	3.47	0.76	1.10
AS-32	Surface	0.65	1.01	0.42	0.76	0.78	1.68	0.63	0.65
B16-1/85	1847.50	1.17	1.31	0.48	1.07	0.90	2.68	0.71	n.c.
B16-1/85	1857.60	0.98	1.05	0.42	0.96	0.77	5.43	0.91	n.c.
B21-1/95	1731.70	1.01	1.27	0.42	0.97	0.79	5.65	0.92	n.c.
B6-1/82	1432.75	1.44	2.23	0.55	1.23	1.06	4.1	0.81	n.c.
B4-1/81	1103.70	0.58	0.80	0.32	0.72	0.55	3.33	0.75	n.c.
B6-1/82	1425.00	1.17	1.78	0.47	1.07	0.88	2.89	0.72	n.c.
Dictyonema Shale									
Haapsalu-21	165.00	0.84	1.10	0.46	0.87	0.86	1.33	0.61	0.20
Pakri-2	Surface	0.76	1.30	0.49	0.83	0.94	1.40	0.61	0.26
Tallin-1	Surface	0.61	1.23	0.48	0.74	0.91	1.62	0.63	0.15
Podlasie Depression									
Dictyonema Shale									
Stadniki IG-1	1192.40	0.46	1.14	0.47	0.65	0.88	1.94	0.65	0.09
Stadniki IG-1	1192.85	0.44	1.29	0.50	0.63	0.95	2.38	0.68	0.08
Chraboły IG-10	592.34	0.24	1.68	0.59	0.51	1.16	0.99	0.58	0.03
Husaki IG-4	631.16	0.23	1.67	0.59	0.51	1.16	1.01	0.58	0.03
Rajsk IG-3	618.24	0.19	2.19	0.67	0.48	1.33	1.81	0.64	0.02

MPI1 = 1.5(2-MP + 3-MP)/(P + 1-MP + 9-MP); P, phenanthrene; MP, methylphenanthrene; MPR = 2-MP/1-MP; Rcal = 0.60 MPI1 + 0.37 for MPR <2.65 (Radke 1988); MPR1 = (2-MP + 3-MP)/(1-MP + 9-MP + 2-MP + 3-MP); $R_{cal(MPR)} = -0.166 + 2.242(MPR1)$ (Kvalheim et al. 1987); MDR = 4-MDBT/1-MDBT; MDBT, methyldibenzothiophene; $R_{cal(MDR)} = 0.51 + 0.073*MDR$ (Radke 1988); DBT, dibenzothiophene; n.c., not calculated

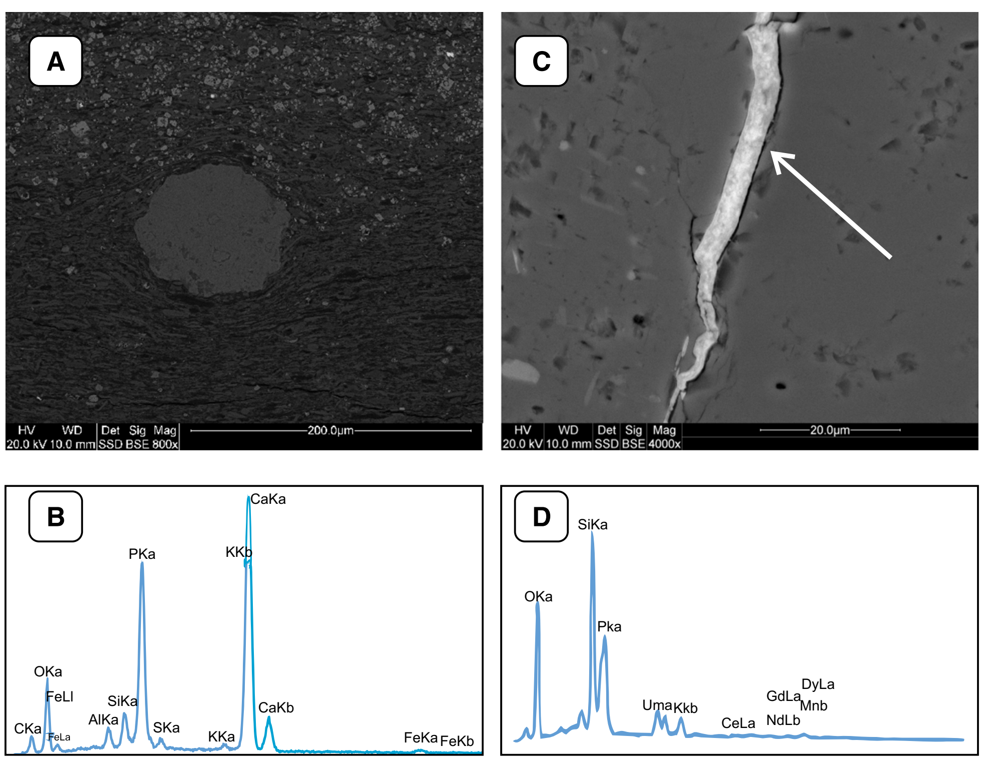

Fig. 13 Sample from Stadniki IG-1 well **a** BSE image and **b** EDS spectra, and sample from Chraboły IG-10 well **c** BSE image of secondary uranium–yttrium minerals (*white arrow*) and **d** EDS spectra of secondary U–Y minerals sample

Table 6 Secondary uranium minerals (in wt%), in the sample from Chraboły IG-10 (xenotime) and B4-1/81 wells, and sample AS-40 from outcrop

Element	Chraboły IG-10	B4-1/81	AS-40
O Kα	38.23	12.62	19.53
Na Kα	0.66	n.a.	n.a.
Al Kα	1.88	1.52	2.35
Si Kα	15.70	3.46	7.57
Y Lα	15.03	n.a.	n.a.
P Kα	6.57	0.06	0.33
U Mα	9.27	0.23	0.28
K Kα	0.37	0.67	1.51
Ca Kα	2.35	n.a.	n.a.
Ce Lα	1.39	n.d.	n.d.
Nd Lα	1.46	n.d.	n.d.
Mn Kα	0.23	n.d.	n.d.
Gd Lα	1.89	n.d.	n.d.
Tb Lα	0.70	n.d.	n.d.
Fe Kα	1.13	0.75	1.25
Dy Lα	2.50	n.d.	n.d.
Co Kα	0.64	n.a.	0.36
S Kα	n.a.	0.93	0.97
C Kα	n.a.	79.75	65.85

n.a., not analysed; n.d., not data

led to identified secondary veinlets containing mixture of uranium mineral (probably coffinite) and xenotime (Table 6; Fig. 13b). Uranium-containing minerals are 1-3 µm in size. Inclusions of U-mineral are randomly distributed in xenotime (Fig. 13c), which makes EDS analyses more complicated (Fig. 13d). Apart from yttrium, traces of other REE (rare earth elements) have also been measured (Fig. 13c).

Generally, the geochemical characteristic of Tremadocian *Dictyonema* Shale is very similar to the Upper Cambrian–Lower Ordovician Alum Shale.

Conclusions

In the Baltic Basin, Podlasie Depression, the best source rock parameters are observed for the Upper Cambrian–Tremadocian complex. This complex is represented by black shales with high organic carbon and radiogenic contents termed Alum and *Dictyonema* Shales. Their thickness varies from a few metres up to ca. 40 m. Present TOC contents reach ca. 22 wt% and 103 mg HC/g rock. Although the highest contents are observed in immature samples collected in south-central Sweden and the seashore of Estonia, high contents are also measured in overmature samples from the Skåne region and Bornholm. Results of Rock-Eval pyrolysis analyses as well as biomarker, stable carbon isotope and elemental compositions of kerogen reveal that Upper Cambrian–Tremadocian strata of the Baltic Basin and Podlasie Depression contain oil-prone Type-II kerogen. The organic matter has been identified also in the thucholite micro-concretions. It has low organic sulphur and is deposited in anoxic or sub-oxic conditions. The maturity of investigated strata is changeable and depends on position in sedimentary basin. The immature samples are observed in marginal parts of the basin—in Estonia and the Podlasie region. The maturity increases in the SW direction, to T–T zone.

The high TOC concentration is accompanied by anomalously high contents of uranium and thorium. Those radioactive elements reach levels of tens to 440 ppm, in the Baltic Basin, and to 750 ppm, in the Podlasie Depression. SEM study showed the presence of mixture of uranium mineral and xenotime. Pyrite framboids and euhedral pyrite crystals are very common too.

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