Uranium enrichment shorewards in black shales: A case study from the Scandinavian Alum Shale

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Abstract: The Scandinavian Alum Shale Formation (Middle Cambrian to Lower Ordovician) contains high levels of organic carbon (up to 25 wt.%) and syngenetic enriched trace elements. A regional survey of the uranium and organic carbon content reveals that uranium is preferentially enriched in sections located palaeo-shorewards compared with sections located farther offshore. This type of enrichment mode is evident in the Upper Cambrian (above the *A. pisiformis* Zone) and Tremadoc interval. In the Middle Cambrian no significant regional variation in uranium level is present. In the most enriched Upper Cambrian biozone (*Peltura scarabaeoides* Zone) the average concentrations of uranium (100 to 300 ppm) are inversely correlated to zone thickness. The variable bed thicknesses are believed to represent primary differences in the rate of deposition and the relationship thus indicates a strong time-dependency in the enrichment processes governing uranium incorporation in sediments. The high uranium levels generally found shorewards are interpreted to reflect a more vigorous bottom water circulation that promoted higher rates of mass-transfer across the sediment/water interface relatively to the mud deposited farther offshore. Very high levels of uranium (1000 to 8000 ppm) concentrated in discrete beds (known as kolm) are interpreted to reflect resuspension of sediment in an anoxic water column that enhanced diffusive exchange between suspended particles and sea-water. A Late Silurian to Early Devonian thermal overprint towards the Caledonian Front affected the total organic carbon (TOC) content but appears to have no effect on the uranium distribution in the thermally mature sections.

Keywords: Alum shale, Cambrian, Tremadoc, anoxic environment, trace elements, uranium, diffusion, hydrodynamic.

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In modern dysoxic and anoxic environments, the major enrichment process of trace elements is by diffusion from seawater across the sediment/water interface (Francois 1988; Barnes & Cochran 1993; Anderson et al. 1989a, 1989b; Klinkhammer & Palmer 1991; Emerson & Huested 1991).

The importance of diffusion agrees poorly, however, with the general interpretation of how metals accumulated in ancient black shales (e.g. Hatch & Leventhal 1992; Nijenhuis et al. 1999). A large emphasis is given to scavenging of elements onto particles and to (co-)precipitation between elements and reduced sulphide compounds occurring in the water column. Significant enrichments of elements have, accordingly, been interpreted to reflect differences in water column anoxia as expressed in terms of the degree of water column stratification (e.g. Hatch & Leventhal 1992; Hoffman et al. 1998).

In contrast to this, diffusion of elements across the sediment/water interface depends on gradients in chemical potential. Profound enrichments of elements by diffusion thus reflect an environment in which effective removal of mobile elements from the pore water is combined with a high supply of elements. Since the volume of elements delivered to the seafloor depends on the replenishment of the water column, diffusion of elements will in theory cease if the bottom water gets stagnant leaving only scavenging processes in the water column to be effective. Profound enrichments of elements by diffusion across the sediment water interface is thus expected to occur between stagnant and oxic environments (see also Calvert & Pedersen 1993). In this situation, the bottom water oxygen levels are controlled by the supply of oxygenated bottom waters and by the microbial oxygen consumption in the water and the sediment. Within the sediment, different gradients in chemical potential exist for each element caused by their specific thermodynamic properties and kinetic differences with respect to the reduction and/or to the formation of insoluble compounds. Due to the instability of the bottom water oxygen levels (e.g. Jung et al. 1997), the mobility of the elements in the course of re-oxidation is also of great importance in determining the relative fluxes of elements to the sediment.

A possible link between bottom water circulation and enrichment of uranium by diffusion is therefore likely to exist. In order to investigate this further, a regional survey of the uranium variation in the Scandinavian Alum Shale (Middle Cambrian to Lower Ordovician) was made. A special feature of the Alum Shale depositional environment is that black shale was not restricted to the deeper part of the basin, but did also occur in shallow water areas, where the water column was more agitated (Dworatzek 1987; Buchardt et al. 1997; Eklöf et al. 1999). This setting appears similar to other Palaeozoic shales in which a characteristic shoreward enrichment of uranium has been described (Coveney et al. 1987, 1991; Leventhal et al. 1983; Hatch & Leventhal, 1992; Hoffman et al. 1998).

Geological frame

The Alum Shale Formation is an organic rich mudstone (up to 25 wt.% total organic carbon, TOC) with variable proportions of primary limestone and secondary carbonate concretions. The kerogen consists primarily of amorphous organic matter (>80 vol.%) probably having an algal origin (Buchardt & Lewan 1990; Guy-Ohlson & Lindqvist 1990; Bharati et al. 1995). The formation was deposited in a large, shallow epicontinental sea that covered substantial parts of Baltica at maximum sea-level stand (Fig. 1, Andersson et al. 1985).

Initial deposition of the shale took place in the early Middle Cambrian in ocean-facing areas. During the Cambrian and
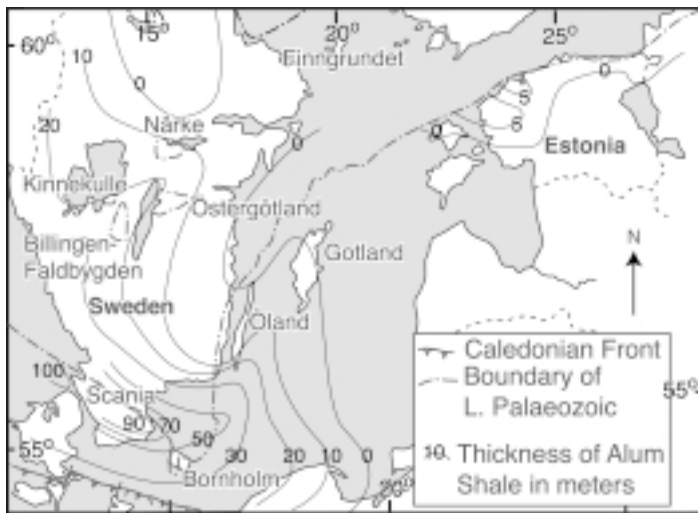
Fig. 1. Thickness and distribution of the Alum Shale in Baltoscandia. Modified from Buchardt et al. (1997).

Tremadoc a progressive widening of the Alum Shale facies is seen tracking shallow water deposits towards present day east and northeast i.e. towards the palaeo-shore line (Dworatzek 1987; Buchardt et al. 1997).

In the Upper Cambrian indications of the depositional energy at the sea bottom can be gained from the presence of coquinoid limestone horizons (Dworatzek 1987). These occur frequently in the whole Upper Cambrian succession in southern Sweden whereas they are lacking in the Scania-Bornholm area (Fig. 1). These lithological differences across the shelf are interpreted to reflect the water depth, i.e. they are caused by a closer position of the storm wave base on the 'inner-shelf' compared with the 'outer-shelf' (Buchardt et al. 1997). In addition to a high proportion of primary limestone and carbonate concretions the inner-

shelf (>30% of section thickness, Dworatzek 1987) is characterised by stratigraphically incomplete sections (Fig. 2A). The carbonate beds probably reflect a preferential removal of fine-grained siliciclastics by currents (Dworatzek 1987). This process is also reflected in the thickness variation of the shale that attains highest thicknesses on the outer-shelf and thins out on the inner-shelf towards the palaeo-shore line (compare Figs. 1 and 2).

The Tremadoc sediments differ from the Upper Cambrian sediments by having a low proportion of carbonate concretions. Instead, indications of the depositional energy at the sea floor can be inferred from the presence or absence of sandy intercalations in the shale (Fig. 2B). Hence sections on the 'inner-shelf' are characterised by such intercalations or reveal hiati (Westergård 1922; Thorslund & Axberg 1979; Andersson et al. 1985; Heinsalu & Viira 1997). In Estonia, a gradual transition can be seen from sandy intercalations in the shale to shaly intercalations in sand. Particularly thick sections of this facies have been included in the Kallavere Formation that represents the transitional beds between the Upper Cambrian *Acerocare* Zone and the lowermost Tremadoc (Mens et al. 1993; Heinsalu & Viira 1997).

Regional thermal maturation took place towards the Caledonian Front (Fig. 1), presumably because of foreland subsidence in the Late Silurian and Early Devonian (Buchardt & Lewan 1990; Samuelsson & Middleton 1998). At this time, Scania and Bornholm was buried to a depth of at least 3–4 km (Buchardt & Nielsen 1985). Volcanism in Late Permian to Early Carboniferous caused local thermal maturation of the shale on the Baltic Continent that elsewhere appear thermally immature (Bergström 1980; Buchardt et al. 1997).

Depositional controls on the uranium enrichment

Mass-exchange occurs along gradients in chemical potential, commonly coinciding with concentration gradients. In order for diffusion to be effective, such gradients must be established and maintained by effective removal of uranium from the pore water
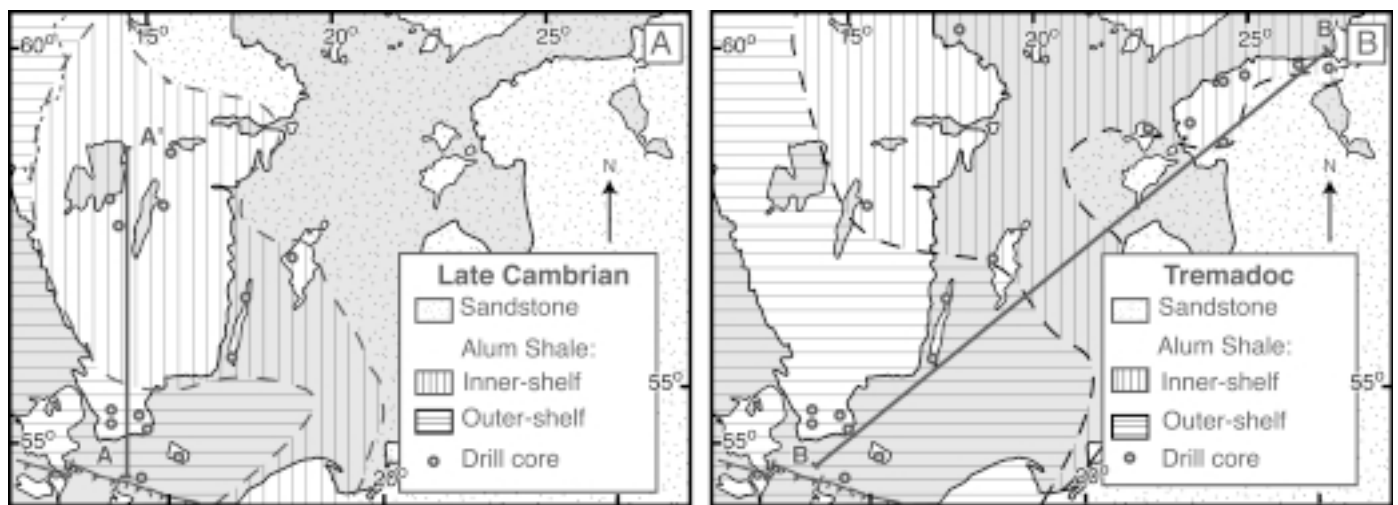

Fig. 2. Palaeogeographic reconstruction of; **A**, Late Cambrian; **B**, Early Tremadoc. The profile lines AA' and BB' extend from the outer-shelf towards the palaeo-shoreline. Data points indicate location of drill-cores. The Late Cambrian map is modified from Buchardt et al. (1997).
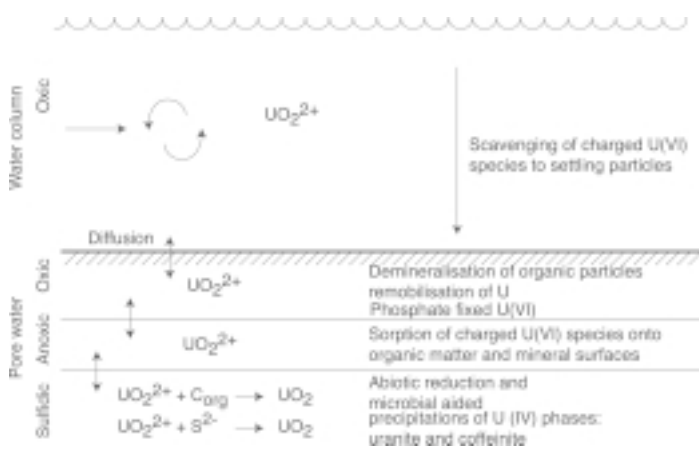
Fig. 3. Simplified aquatic geochemistry of uranium. Based on Murphy & Shock (1999) and references herein.

duction zone probably aided by a microbial pathway (Lovley et al. 1991; Barnes & Cochran 1993). Lowering of dissolved uranium concentrations can, however, take place above the sulphate reduction zone by sorption of uranium onto mineral surfaces or organic matter (Fig. 3).

The bottom water oxygen level creates some important boundary conditions. It is controlled by the supply of oxygen and consumption by microbes. If the supply of oxygen outmatches the microbial uptake the aerobic zone in the sediment can move downwards eventually resulting in a reoxidation of the sediment (a burn-down front, Jung et al. 1997) and loss of uranium to the bottom water (ten Haven et al. 1988). If the uptake of oxygen outmatches the supply, the redox boundary will eventually be situated close to the sediment/water interface or within the water column. Due to increased surface volume the effectiveness of the exchange between water and sediment is greatly enhanced if the sediment becomes resuspended (Shaw et al. 1994).

and by replenishment of uranium in the bottom water. The gradient can be established between an oxygenated environment where uranium is present in its soluble hexavalent form and a reducing environment where the insoluble tetravalent form is stable (Fig. 3).

The kinetics involved in the reduction is very sluggish and reduction of uranium appears first to take place in the sulphate re-

Results and discussion

Data collection

A compilation of data on uranium and total organic carbon (TOC) concentrations aimed towards a mapping of the basin-wide variations of uranium within well-defined biostratigraphical periods has been constructed from numerous sources (Table 1). An additional compilation of indicators of thermal stress

Table 1. Summary of uranium and TOC variation.

Area [1]	Agnostus pisiformis Zone						lower Olenus Zone [3] (upper Olenus Zone [4])					
	TOC (wt.%)	± [2] (wt.%)	n	U (ppm)	± [2] (ppm)	n	TOC (wt.%)	± [2] (wt.%)	n	U (ppm)	± [2] (ppm)	n
Rügen G14	4.7	4.0	3	27	n.d.	1	5.9	2.0	4	31	n.d.	1
Bornholm	7.18	1.16	5	38	90	2	7.0(10.4)	2.3(2.9)	3(6)	43(92)	150(33)	2(6)
Scania	8.5	0.8	15	31	4	6	8.5(11.2)	0.4(0.5)	48(62)	24(92)	25(33)	3(6)
S. Öland	8.9	1.5	5	40	5	5	12.1	13.8	2	78	516	2
N. Öland	8.6	0.6	3	28	46	3	-			-		
Gotland	11.2	n.d.	1	35	n.d.	1	-			-		
Billingen	9.1	0.7	10	56	30	2	-			-		
Östergötland	10.4	26.5	2	55	84	2	15.0	1.5	6	129	45	6
Kinnekulle	10.9	0.3	6	37	9	6	-			-		

Area	Peltura zones [5] (P. scarabaeoides Zone)						Tremadoc (Kallavere Fm.)					
	TOC (wt.%)	± [2] (wt.%)	n	U (ppm)	± [2] (ppm)	n	TOC (wt.%)	± [2] (wt.%)	n	U (ppm)	± [2] (ppm)	n
Rügen G14	not cored			not cored			4.0	2.0	8	58	246	2
Bornholm	11.1(11.7)	1.3(n.d.)	9(1)	113(100)	30(n.d.)	9(1)	8.0	1.2	5	73	10	5
Scania	11.5(11.6)	0.5(0.6)	87(56)	99(97)	13(14)	25(14)	7.5	0.3	143	53	9	28
S. Öland	14.5(15.3)	6.3(26.4)	3(2)	180(197)	86(205)	3(2)	9.9	0.8	13	66	20	13
N. Öland	-			-			9.7	0.5	17	43	12	16
Gotland	-			-			9.7	12.6	2	235	187	2
Billingen	14.4(14.7)	0.6(0.6)	76(69)	315(309)	56(56)	36(35)	-			-		
Östergötland	14.8 [6]	2.5	4	138 [6]	137	4	13.3	0.6	31	118	10	17
Kinnekulle	17.6(15.2)	2.1(3.2)	20(7)	168(176)	67(63)	11(3)	-			-		
Närke	15.6(14.4)	1.5(4.2)	13(5)	192(211)	48(148)	13(5)	-			-		
Finngrundet	-			-						216	301	2
W. Estonia [7]	-			-			10.9	1.5	8	120	14	31
C. Estonia [7]	-			-			8.9(10.4)	6.2(n.d.)	3 (1)	61(113)	22(101)	24(5)
E. Estonia [7]	-			-			9.7	6.1	3	225	54	10

[1]Combined data from cores and outcrops. [2]Confidence interval of the mean value (95%). [3]O. gibbosus to O. attenuatus Subzones. [4]O. dentatus to O. scanicus Subzones. [5]The Peltura zones include the P. scarabaeoides, P. minor and Protopeltura praecursor zones. [6]Only Protopeltura praecursor. [7]Area definition adopted from Pukkonen & Rammo (1992), n.d.: not defined. Data sources: Andersson et al. (1985); Bharati (1995); Buchardt et al. (1986, 1997); Dahl et al. (1988a); Dahlman (1962); Edling (1974); Leventhal (1990, 1991); Lewan & Buchardt (1989); Pukkonen & Buchardt (1994); Pukkonen & Rammo (1992); Schovsbo (1995, 2001); Thickpenny (1987); Thorslund & Axberg (1979); Warming et al. (1994). The stratigraphy of samples from Gotland in Dahl et al. (1988a) has been inferred from Andersson et al. (1985).
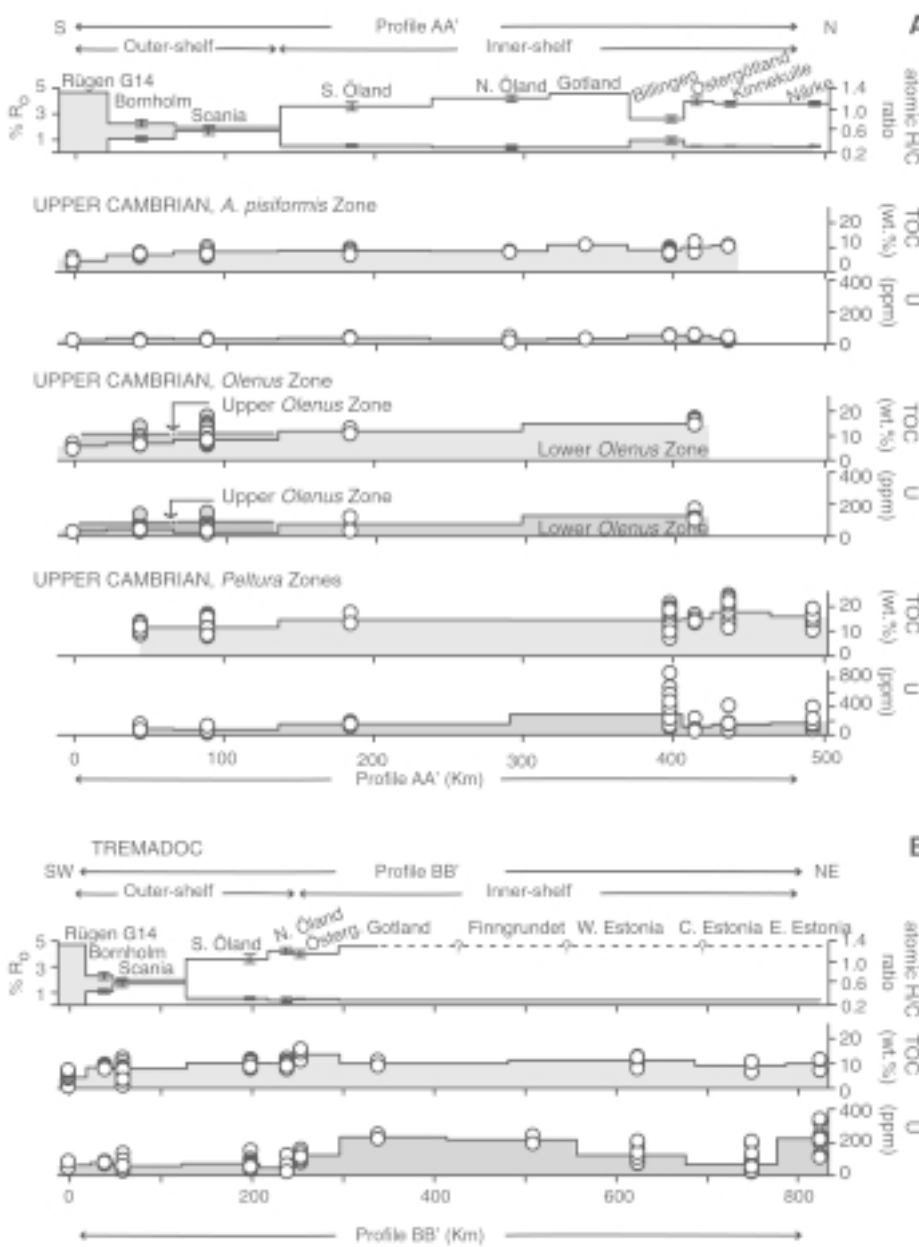
Fig. 4. Lateral variation in uranium and TOC concentrations along the two profile lines shown in Fig. 2. Area definition and stratigraphy are according to Table 1. Measurements of thermal stress level (%R$_o$) and stage of oil generation (atomic H/C ratio) are from Table 2.

level (%R$_o$) and stage of oil generation (atomic H/C ratio, Table 2) is included in order to evaluate possible thermally induced changes on the geochemical composition.

Lateral and vertical variation of uranium and TOC

The lateral variation of uranium and TOC concentrations at four stratigraphic levels are examined along two profile lines extending from the outer-shelf towards the palaeo-shoreline (Fig. 4). The stratigraphic levels includes the Upper Cambrian *Agnostus pisiformis* Zone, the *Olenus* Zone (divided into an upper and lower part, Table 1), the *Peltura* zones (the *P. scarabaeoides*, *P. minor* and *Protopeltura praecursor* Zones) and the Tremadoc interval. The down-core variation of uranium and TOC concentrations from six shallow cores is presented in Fig. 5 in order to illustrate the variation of uranium and TOC concentrations of the remaining stratigraphic levels.

In the Middle Cambrian (incl. the *Agnostus pisiformis* Zone) uranium concentrations are mostly identical throughout the basin (Fig. 5). In the *Olenus* Zone and onwards a preferential enrichment of uranium on the inner-shelf relative to the outer-shelf is evident (Fig. 5). Along both profile lines (Fig. 4) the average TOC content decreases towards south i.e. with increasing thermal stress levels and advancing stage of oil generation (Fig. 4). In a plot of the average TOC values versus the average H/C ratio (not shown) the average TOC level is inversely correlated to the H/C ratio (r^2=0.63–0.78, n=7–10, data from Table 1 and 2). Such relationship indicates that the initial TOC values have been modified during catagenesis. The amounts calculated from Table 1 yields a 20–40 % reduction at thermal stress levels

Table 2. Summary of thermal stress indicators.

Area	[1]Reflectance of vitrinite-like particles [2] (% R$_o$)						Atomic H/C ratio					
	mean	±[3]	Min	Max	range	n	mean	±[3]	Min	Max	range	n
N. Öland	0.40	0.19	0.32	0.47	0.15	3	1.21	0.06	1.16	1.26	0.10	5
Estonia	0.40[4]						–					
Gotland	0.40[4]						1.30					1
Finngrundet	0.40[4]						–					
Närke	0.47	0.06	0.44	0.51	0.07	4	1.11	0.04	0.98	1.27	0.29	15
Kinnekulle	0.49	0.03	0.43	0.52	0.09	6	1.11	0.05	0.99	1.26	0.27	13
Östergötland	0.50	0.05	0.46	0.53	0.07	4	1.16	0.07	1.01	1.31	0.30	10
S. Öland	0.61	0.09	0.40	0.77	0.37	9	1.09	0.09	1.00	1.25	0.25	7
Billingen	0.97	0.25	0.49	1.48	0.99	9	0.83	0.06	0.70	0.99	0.29	11
Scania	1.99	0.08	1.77	2.25	0.48	14	0.60	0.06	0.45	0.75	0.30	9
Bornholm	2.27	0.26	1.81	2.62	0.81	7	0.45	0.04	0.41	0.51	0.10	6
Rügen G14	4.70					1	–					

[1]Combined data from cores and outcrops. [2]Sensu Buchardt & Lewan (1990). [3]Confidence interval on mean value (95%). [4]Estimated from Buchardt et al. (1997),
Data sources: Assarsson & Grundulis (1961); Buchardt & Lewan (1990); Dahl et al. (1988b, 1989); Horsfield et al. (1992); Warming et al. (1994).
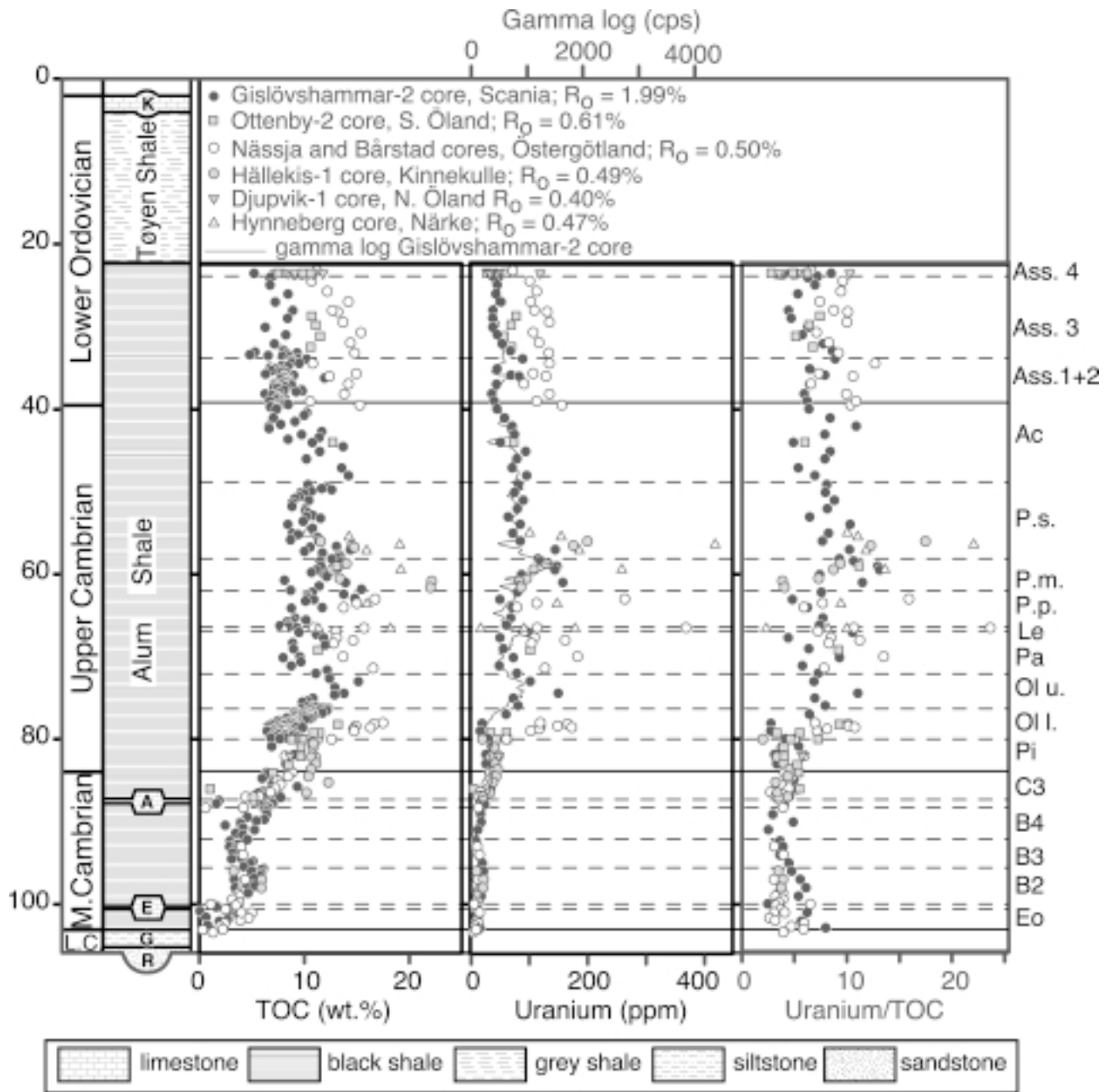
Fig. 5. Stratigraphical variation of uranium concentrations, TOC content and the U/TOC ratio in seven shallow cores from Sweden. The stratigraphical position of each sample has been assigned to approximately same level in the Gislövshammar-2 core. Data sources: Gislövshammar-2 (Buchardt et al. 1997; Nielsen & Buchardt 1994; Schovsbo 2001), Hällekis-1 and Djupvik-1 cores (Schovsbo 1995), Nässja core (Wikman et al. 1982; Dahlman 1962), Bårstad and Hynneberg cores (Dahl et al. 1988a; Lewan & Buchardt 1989). Note that stratigraphical assessment of samples from Hynneberg have been made according to log provided in Westergård (1941). Thermal maturation data are from Table 2. Lithological units: R = Rispebjerg Sandstone, G = Gislöv Formation, E = *Exsulans* Limestone, A = Andrarum Limestone, K = Komstad Limestone. Biostratigraphy (trilobite biozones according to Henningsmoen 1957; Westergård 1946) is shown on right: Eo = *Eccaparadoxides oelandicus*; B1 to B4 = *Paradoxides paradoxissimus*; C1 to C3 = *Paradoxides forchhammeri*; Ap = *Agnostus pisiformis*; Ol l = lower *Olenus* and Ol u = upper *Olenus* (see Table 1), Pa = *Parabolina,* Le = *Leptoplastus*, P.p. = *Protopeltura praecursor*, P.m. = *Peltura minor,* P.s. = *Peltura scarabaeoides*, Ac = *Acerocare*. Ass. 1-4: Tremadoc graptolite assemblages according to Cooper (1999).

approaching ankiometamorphic conditions, and are comparable to the estimates given in Buchardt et al. (1986) for the *P. scarabaeoides* Zone.

For uranium, no systematic relationship between the thermal stress level and content exists. This can be illustrated by the variation in the *Peltura* zones (Table 1). Here areas with highest

(Billingen, 315±56 ppm) and lowest (Scania, 99±13 ppm) average uranium concentrations are mature to post-mature with regard to oil generation (H/C < 0.80), whereas the thermally immature areas have intermediate average uranium levels (Table 1).

The increase in the average uranium content from <60 ppm in the *A. pisiformis* Zone to >80 ppm in the *Olenus* Zone is slightly
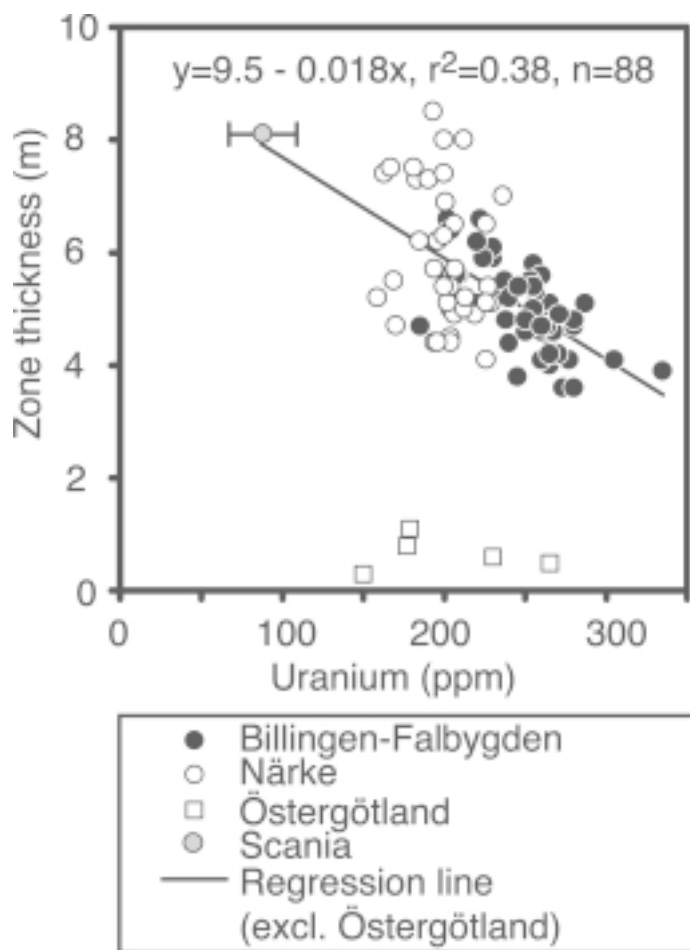
Fig. 6. Average uranium concentrations versus zone thickness of the Upper Cambrian *P. scarabaeoides* Zone. Data from localities in southern Sweden are from Dahlman (1962) and from Scania from Buchardt et al. (1997). Error bar indicates confidence level on the mean (95%).

diachronous and firstly initiated on the inner-shelf (Figs. 4 and 5). Here, the lower part of the zone is significantly more enriched than the *A. pisiformis* Zone (Table 1). Farther offshore, the lower *Olenus* Zone does not differ from the *A. pisiformis* Zone in uranium concentrations (Table 1). Instead the upper *Olenus* Zone has higher mean uranium and TOC contents compared with the underlying samples (Table 1). Judging from the gamma-log curve in Fig. 5 the increase in uranium levels is more gradual than reflected in the single sample analysis (Table 1).

   The *Olenus* Zone on the inner-shelf is partly developed as the 'Great Stinkstone Band', that is, an amalgamated limestone horizon composed of several generations of both primary and secondary carbonate beds (Dworatzek 1987). It is interpreted to reflect a lowering of the sea-level (Dworatzek 1987; Schovsbo 2001). The association of high uranium and U/TOC values related to a regressive event in the *Olenus* Zone might suggest that a uranium source in the hinterland started to erode. Equally high or higher U/TOC ratios are, however, also seen in the *Peltura* zones that probably mark the highest Cambrian sea-level stand (Leggett et al. 1981; Martinsson 1974). At this time potential basement highs occurred in northeastern Finland (Martinsson

1974). Likewise, the major phase of peneplain development by erosion of the basement took place before Alum Shale deposition was initiated, creating a discrepancy between enrichment and basement erosion.

   In the *P. scarabaeoides* Zone an inverse relationship between zone thickness and average uranium concentrations exist between individual localities in Närke, Billingen and Scania (Fig. 6). Localities in Östergötland deviate from this relationship (Fig. 6). The localities here are, however, stratigraphically less complete than those in Närke, Billingen, and Scania and have a higher proportions of primary carbonate beds (Dworatzek 1987). The underlying *P. minor* and *Protopeltura praecursor* Zones do not show any relationship between zone thickness and uranium concentrations (not shown, Dahlman 1962) and it is suggested that erosion rather than condensation controlled the variable thickness of these zones.

Uranium, TOC and phosphorus relationships

In the Middle Cambrian and in the *A. pisiformis* Zone uranium and TOC content are linearly correlated (Fig. 7A, B). Despite the differences in thermal maturation levels between Scania and the rest of southern Sweden (Table 2) the slope is nearly identical between the two areas (Fig. 7A, B). The proportionality between uranium and TOC concentrations might suggest that scavenging of uranium onto settling organic particles was the primary control of uranium enrichment in these periods. Data from modern environments do not suggest that constant U/TOC ratios in the sediment relates to the composition of the settling particles (Anderson et al. 1989a). Instead, it can only be inferred that the fluxes of uranium to the sediment were proportional to the preserved amounts of organic carbon. Lowering of the TOC contents in Scania related to hydrocarbon expulsion (e.g. Buchardt et al. 1986) suggests that the U/TOC ratio in Scania initially were lower compared with the rest of southern Sweden.

   In the Upper Cambrian and Tremadoc no linear correlation exists between uranium and TOC concentrations on the inner-shelf areas (Fig. 7A). Instead, a high degree of scatter in the data is seen with deviations towards higher U/TOC values more profoundly expressed on the inner-shelf areas compared with the outer-shelf areas (Fig. 7A, B). On the inner-shelf, highest U/TOC ratios are found in carbonaceous nodules known as kolm (Fig. 7C). These nodules that can form laterally persistent beds (600 meter long, <10 cm thick) occur at two levels in the *Peltura* zones and are found exclusively on the inner-shelf (Westergård 1922; Davidson 1961). Although kolm records the highest concentrations of uranium in the formation, intermediate values exist indicating a somewhat gradual transition from shale to kolm (Fig. 7C).

   In the Tremadoc large quantities of shell debris of the phosphatic brachiopod *Obolus* can be found in the sandy intercalations on the inner-shelf (Thorslund & Axberg 1979; Pukkonen & Rammo 1992). In Fig. 7D this is reflected by a higher normalised phosphor content than shown by the Cambrian samples although it does not appear that uranium is associated with this phase. In kolm, uranium has been associated with phosphate substances (Edling 1974; Parnell 1984). This association apparently was caused by early diagenetic mobilisation of uranium in the pore water (Edling 1974). From Fig. 7D kolm does not appear enriched in phosphorus compounds compared with the shale.
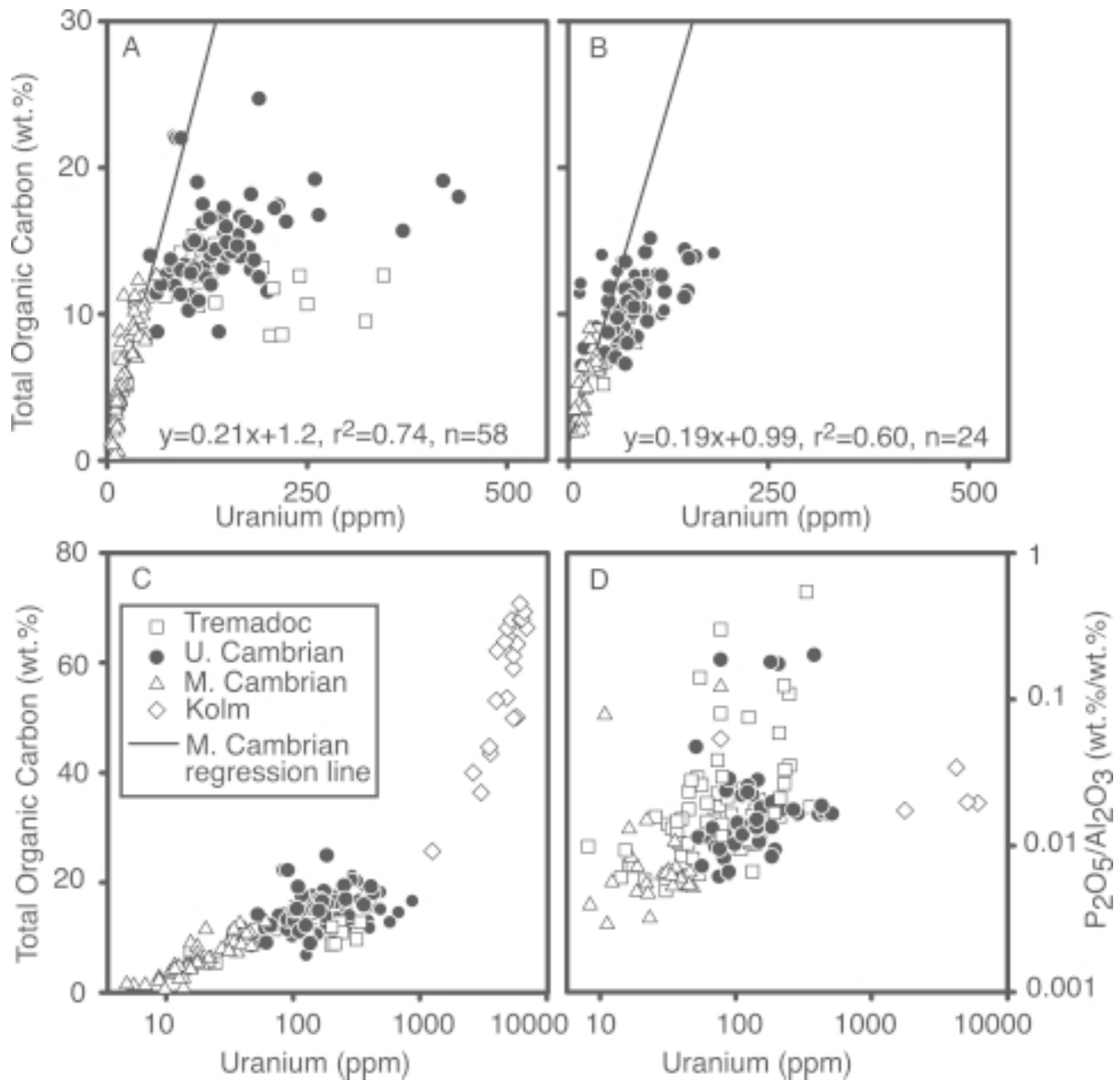
Fig. 7. Uranium versus TOC content in; **A**, thermally immature localities (%R_o < 0.6); **B**, thermally mature samples from Gislövshammar-2 (Buchardt et al. 1997) and Tosterup (Dahlman 1962) cores (Scania %R_o=1.99); **C**, thermally immature samples including samples from Billingen (%R_o=0.97) and kolm samples from Billingen and Närke; **D**, uranium versus the normalised phosphorus level of all samples.

Depositional controls on uranium

In both inner-shelf and outer-shelf areas, a preferential grouping of samples having high uranium concentrations is seen at sulphur contents of 7–8 wt.% (Fig. 8). This grouping of samples indicates that the optimal bottom water oxygen levels for enrichment were present in the lower dysoxic to anoxic environment using the environmental interpretation of the sulphur variation offered by Schovsbo (2001).

The environmental control might be explained by the sluggishness in the reduction of uranium (IV) to uranium (VI) which re-

sults in a deeply positioned redox front lying within the sulphate reduction zone (Barnes & Cochran 1993; Murphy & Shock 1999). Hence, profound enrichment of uranium by diffusion of ions through the seafloor is expected to take place when sulphate reduction occurs at or above the sediment/water interface.

Lowering of pore water uranium concentrations above the sulphate reduction zone occur as well (Fig. 3). This will also lead to an enrichment of uranium in the sediment. The uranium here is, however, more loosely bound and might be recycled to the bottom water in the course of an increase in the bottom water oxygen levels (e.g. ten Haven et al. 1988).
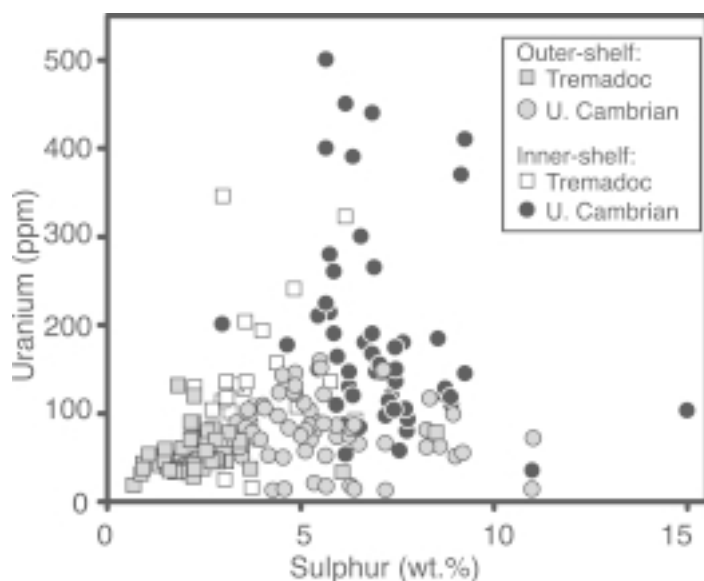
Fig. 8. Uranium versus sulphur content of samples (younger than *A. pisiformis* Zone) positioned on the inner-shelf and outer-shelf (see Fig. 2).

Inner-shelf versus outer-shelf areas

The inverse relationship between average uranium concentrations and zone thickness in the *P. scarabaeoides* Zone (Fig. 6) might suggest that the regional variation of uranium is the result of a constant rate of uranium being added to the sediment combined with a variable degree of dilution by siliciclastics (e.g. Anderson & Fleisher 1991).

The presence of uranium-enriched kolm and the highly variable uranium concentrations in the *Peltura* zones (Figs. 4 and 5) suggest that the mechanism for uranium enrichment was episodic. Episodic enrichment of uranium is possible when the redox boundary is positioned at the sediment/water interface or within the water column. The very high levels of uranium in kolm (Fig. 7C) might thus be explained if the kolm was derived from the shale by repeatedly being resuspended in an anoxic water column followed by addition of uranium by enhanced mass transfer of uranium from the sea water. This interpretation of kolm originating from the shale by means of current winnowing is in agreement with earlier models (e.g. Cobb & Kulp 1960). In contrast, the enrichment of uranium in the shale took place through a diffusive interlayer in the top part of the sediment or in the water column. Such enrichment is less efficient, yielding generally low uranium values and hence lower U/TOC ratios compared with kolm (Fig. 7C). Judged from Fig. 7a somewhat gradual transition exists between the most enriched shale samples and kolm, indicating that episodic enrichment of uranium in the shale also contributed to the total uranium level here.

Based on lithological variation on the shelf it appears reasonable to infer that the water column on the inner-shelf was more agitated than farther offshore (Dworatzek 1987; Buchardt et al. 1997; Eklöf et al. 1999). This higher depositional energy allowed less sediment to settle, but also enhanced the supply of uranium to the sea floor resulting in consistently higher enrichment levels compared with the shale deposited in deeper waters (Fig. 8).

Conclusions

High uranium concentrations in the sediment occur in environments in which uranium removal from the pore water takes place close to the sediment/water interface. In such environments the uranium fixation is bounded by the two end-member situations: A) the replenishment of oxygenated bottom water outmatches that of oxygen consumption, resulting in a 'burn-down' of the upper part of the sediment leading to loss of uranium, and B) the replenishment of bottom water ceases, resulting in a lack of uranium to be fixed in the sediment.

In a regional perspective, the model predicts that variations in concentrations reflect differences in the magnitude of the bottom water circulation given equal bottom water oxygen levels. A comparison with the uranium distribution in the Scandinavian Alum Shale indicates that the prediction works. Here a preferential enrichment is observed on the inner-shelf compared with farther offshore. Consistent with this facies interpretation the enrichment is explained by a higher degree of bottom water circulation resulting in enhanced supply of uranium, and hence enrichment of uranium by diffusion in the near-shore facies compared with the distal facies.

Very high levels of uranium concentrated in discrete beds (known as kolm) are interpreted to reflect resuspension of sediment in an anoxic water column in which enhanced diffusive exchange between suspended particles and the water column took place.

Thermal overprint of the initial TOC level in Late Silurian to Early Devonian might have lowered the TOC levels by 20–40% on localities that approaches ankiometamorphic conditions. No effect can be seen on the uranium levels.

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