

Effects of irradiation from uranium decay on extractable organic matter in the Alum Shales of Sweden*

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Abstract—Extractable organic matter in the Alum Shales of Sweden is believed to have been altered by irradiation from the natural decay of uranium. The amount of extractable bitumen is inversely proportional to uranium concentration suggesting conversion of extractable bitumen by irradiation. The ratio of aromatic to saturated hydrocarbons increased with increasing uranium concentration, presumably because aromatic hydrocarbons are more stable in the presence of radiation than saturated hydrocarbons. Bitumen from samples with high uranium concentrations tends to be relatively enriched in aromatic hydrocarbons and contains a larger percentage of polars, asphaltenes and resins.

Acyclic isoprenoid hydrocarbons are absent in extracts and kerogen pyrolysates of samples with high uranium concentrations. They therefore appear more susceptible to irradiation induced alteration than normal alkanes, which are present in almost all extracts and kerogen pyrolysates. Parent/alkylated polyaromatic hydrocarbon (PAH) ratios are highest in shallow samples with high uranium concentrations. Extracts from samples low in uranium concentration contain C₂₀, C₂₁, C₂₆, C₂₇ and C₂₈ triaromatic steroids, whereas extracts from samples of high uranium concentration contain only C₂₀ and C₂₁. Alkyl side chain cleavage by irradiation is the mechanism presumed responsible. Ratios of pyrene/phenanthrene and pyrene/chrysene are highest whereas ratios of 1 + 9/2 + 3 methylphenanthrenes are lowest in shallow samples with high uranium concentrations.

Key words: alum shales, organic geochemistry, uranium, irradiation, Sweden

INTRODUCTION

Studies have shown that sedimentary organic matter associated with uranium may be altered by irradiation from natural decay. For example, kerogen H/C ratios have been found to be inversely proportional to irradiation dosages (Pierce *et al.*, 1958), which explains why organic matter associated with uranium tends to be hydrogen poor (Zumberge *et al.*, 1978; Rouzaud *et al.*, 1979; Leventhal *et al.*, 1986; Sassen, 1984). Furthermore, an increase in reflectivity, decrease in fluorescence (Sassen, 1984), polyaromatization (Zumberge *et al.*, 1978), and an increase in ¹³C/¹²C ratio (Leventhal and Threlkeld, 1978) have been documented. These studies have been made on insoluble organic matter, or kerogen, with the exception of a gas chromatographic-mass spectrometric study of kerogen pyrolysates of Witwatersrand organic matter (South Africa) by Zumberge *et al.* (1978).

The Alum Shales of Sweden, which are Middle Cambrian to Early Ordovician in age, contain both abundant organic matter and uranium. Shale samples used in this study contained from 7 to 250 ppm uranium and had total organic carbon contents from 1 to 16%. The organic matter is believed to be algal

in origin (Buchardt *et al.*, 1986), and samples used in this study are known to be of roughly the same thermal maturity; immature to marginally mature with respect to petroleum generation. Thermal maturation was determined from conodont color in the overlying limestone (Bergstrom, 1980), from "Rock-Eval" pyrolysis and reflectance measurements (Buchardt *et al.*, 1986) and from biomarker and kerogen H/C ratios (Dahl *et al.*, 1988a). It has been observed (Dahl *et al.*, 1988b) that irradiation from uranium decay has affected the Alum Shale kerogen elemental ratios. Because these shales vary in uranium concentration and have solvent extractable organic matter, they offer an opportunity to study natural irradiation effects on the extractable organic matter (bitumen). This work compares the amount and characteristics of extractable bitumen in the Alum Shale with varying uranium concentrations. A location map is shown in Fig. 1.

SAMPLES

Samples of shales were obtained from five different cores: Hynneberg, in the country of Närke; Bårstad in Östergötland; Kinnekulle in Västergötland; Segerstad on the island of Öland; and from the island of Gotland. The stratigraphy of the location where two of the cores were taken is shown in Fig. 2. Stratigraphy at the site of the Kinnekulle core has not been

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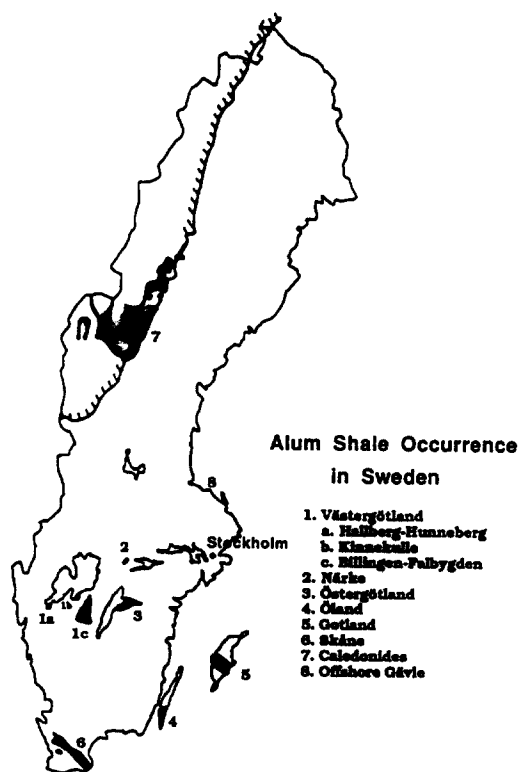


Fig. 1. Location map showing Alum Shale occurrences in Sweden (adapted from Andersson *et al.*, 1985).

worked out. It is inferred from Andersson *et al.* (1985) that the Middle Cambrian–Upper Cambrian boundary for the Kinnekulle core is at about 97 m. For the Segerstad core, the Middle Cambrian–Upper Cambrian boundary is at approximately 39 m and the Upper Cambrian–Ordovician boundary at 32 m. Sample nomenclature designates the core from which the sample was taken and the depth.

EXPERIMENTAL

Core samples were first surface cleaned in a sonic bath in CH_2Cl_2 prior to powdering with a rotary disc mill. An aliquot of crushed shale was sent to the nuclear reactor at Essbo, Finland for uranium determination by neutron activation. Another was analyzed for total organic carbon using a Leco Carbon Analyzer following removal of carbonates. The remainder of the powdered sample was solvent extracted in a sonic bath in CH_2Cl_2 at least 3 times, and if necessary, extraction continued until the extract was colorless. The extracted powdered shale was then demineralized with HF and HCl, followed by HCl treatment to remove fluorides, to obtain kerogen concentrate. The kerogen was re-extracted and pyrolyzed dry at 300°C for 48 h in an evacuated tube according to the method of Tannenbaum and Kaplan (1985). Extracts and pyrolysates were separated into

saturate, aromatic and polar fractions by column chromatography over silica gel according to the methods of Tannenbaum *et al.* (1986), and the fractions weighed on a microbalance following solvent evaporation under N_2 at room temperature. Aliphatic fractions of the extract and pyrolysate were analyzed by gas chromatography using a Varian 3700 Model interfaced with a Spectra Physics SP4270 integrator.

The aromatic fraction was analyzed using a Finnigan 4000 quadrupole mass spectrometer interfaced with a Finnigan 9610 gas chromatograph and an INCOS 2300 data system. Separations were performed on a $30\text{ m} \times 0.25\text{ cm}$, J & W, DB-5, fused silica capillary column. GC conditions were 6 min at 35°C , $4^\circ\text{C}/\text{min}$ to 280°C , and $2^\circ\text{C}/\text{min}$ to 310°C . Phenanthrenes were identified using mass fragments m/z 178, 192, 206 and 220; pyrenes using 202, 216, 230 and 244; chrysenes and triphenylenes (which co-eluted) with 228, 242 and 256; and benzo [e]pyrenes using 252, 266 and 280; all in combination with retention times of injected standards. Triaromatic steroids were identified using mass fragment m/z 231, spectra and relative retention times giving in the literature (Philp, 1985; Mackenzie *et al.*, 1985; Mackenzie and McKenzie, 1983).

RESULTS

Results of the extractions are presented in Table 1 and plotted graphically against uranium concentration in Figs 3 and 4. Chromatograms of the extracts are shown in Fig. 5 and of the pyrolysates in Fig. 6. As seen in Table 1 and Figs 3 and 4, samples with low uranium concentration tend to have the greatest amount of extractable bitumen. This is especially true if bitumen/% Total Organic Carbon (or TOC) ratios are used as in Fig. 4.

The saturate and aromatic fractions of the extract decrease with increasing uranium concentration. Saturated hydrocarbons decrease most rapidly. The ratio of aromatic to saturate hydrocarbons increases with increasing uranium concentration (see Fig. 7).

The two samples from Gotland, G382 and G385 (see Table 1) are from a much deeper core than the other samples, and therefore are less likely to have been subjected to weathering. The sample with 35 ppm uranium, had over three times the extractable bitumen of the sample with 250 ppm uranium. Furthermore, the extract from the sample with 250 ppm uranium consisted almost entirely of polars, resins and asphaltenes. It contained less than 0.01 mg hydrocarbons/g shale.

Gas chromatograms of the aliphatic fraction of Alum Shale extract (Fig. 5) and pyrolysate (Fig. 6) contain a large hump, representing an unresolved complex mixture, for most of the high uranium samples, and generally, to a lesser extent, for some low uranium samples. Normal alkanes are present in all samples. Relatively short ($n\text{-C}_{15}$) n -alkanes predominate. Isoprenoids, including pristane and

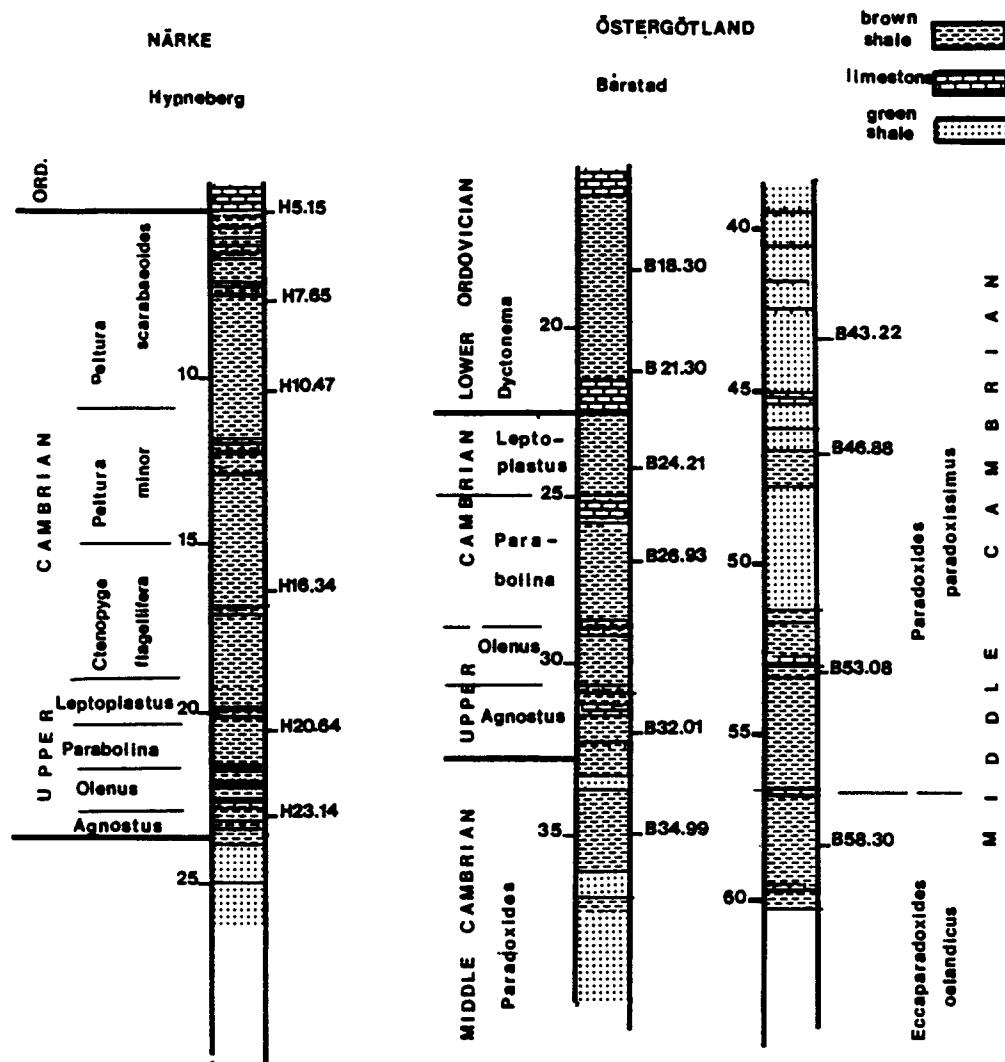


Fig. 2. Stratigraphy of Närke and Östergötland cores.

phytane, are present only in some samples with low uranium concentrations, usually those from the greatest depth. Some shallow samples with low uranium concentrations (H23 and S22) also have low ratios of isoprenoids to *n*-alkanes. Table 2 and Fig. 8 compare uranium concentration to *n*-alkane length. They suggest little correlation between the two.

C₂₀, C₂₁, C₂₆, C₂₇ and C₂₈ triaromatic steroids are present in extracts from relatively deep samples with low uranium concentrations, whereas only C₂₀ and C₂₁ triaromatic steroids are present in extracts from shallow samples with high uranium concentrations (see Fig. 9).

Ratios of phenanthrene/pyrene and chrysene/pyrene are lowest in near surface samples with high uranium concentrations (see Table 3 and Fig. 10). In almost all extracts and pyrolysates, alkylated PAHs are relatively more abundant than parent PAHs.

Extracts and pyrolysates from shallow samples with high uranium concentrations tend to have the highest ratios of parent/alkylated PAHs (see Figs 11 and 12). In the one core where the sample lowest in uranium was nearest the surface (Öland), the parent/alkylated PAH ratios are about the same for the shallow and deep samples. The pyrolysis of a relatively deep sample low in uranium yielded no benzo[*e*]pyrenes, no parent chrysene triphenylene and relatively little parent pyrene. The ratio of 1 + 9/2 + 3 methylphenanthrenes is lower in shallow samples with high uranium concentration (see Table 3).

DISCUSSION

There are many factors which can influence the nature of extractable organic matter. These include source, thermal maturity, migration, weathering (oxidation by ground water and biodegradation). Each

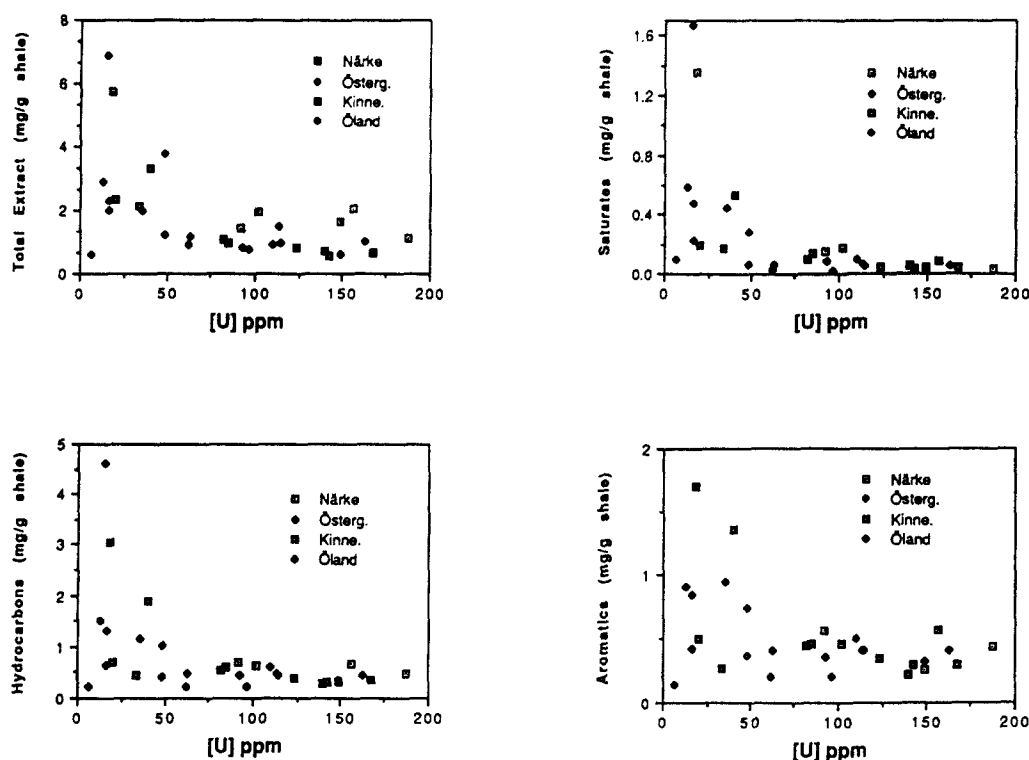


Fig. 3. The amount of extractable bitumen is compared to whole rock uranium concentration.

of these factors, in addition to the effects of uranium decay, must be considered with respect to variations in the composition of extractable organic matter in the Alum Shales. Whereas source, migration, weathering and biodegradation may have played some part in determining bitumen characteristics in the Alum Shale, we believe, from the data presented and the following arguments, that many characteristics cannot be explained without taking into account irradiation induced effects.

It has been suggested by Armands (1972) that organic complexation at the site of deposition may have in part been responsible for the high uranium concentration of the Alum Shale. Figure 13 plots TOC versus uranium concentrations, and shows a relatively good correlation ($R = 0.71$).

Highly aromatic bitumen such as that from the Alum Shale, where aromatic/saturate ratios are generally greater than one, might be considered to result from vascular plant input. However, deposition of the Alum Shale preceded the evolution of vascular plants by about 100 Myr. Marine source rocks, like the Alum Shale, which contain organic matter which is believed to be predominantly algal in origin (Buchardt *et al.*, 1986), generally are not sources of bitumen with aromatic/saturate ratios greater than 1. Some Alum Shale bitumens have aromatic/saturate ratios over 10.

The amount of extractable bitumen in a source rock is a function of, among other things, thermal

maturity. Because the bitumen from these cores is of roughly the same thermal maturity (with the exception of bitumen from Öland which according to Dahl *et al.* (1988a) is slightly less mature), thermal maturation is not considered to be the cause of variations in the extractable bitumen within each individual core, or from region to region.

Weathering (chemical and bacterial oxidation and water washing) has been shown to significantly reduce the amount of extractable organic matter (Forsberg and Bjorøy, 1983). Most of the cores studied here are taken at shallow depth. The large unresolved complex mixture hump in the gas chromatograms of saturated hydrocarbons from Alum Shale extracts indicate that weathering may have affected the organic matter in the Alum Shale. However, all samples, with the exception of the Gotland sample (which was devoid of hydrocarbons), contain normal alkanes which are generally removed by extensive biodegradation.

If weathering were the predominant factor affecting the amount of extractable bitumen in the Alum Shale, then the amount of extractable bitumen should generally be a function of the depth from which the sample was taken. Porosity differences due to sedimentology and fracturing may be important, but Alum Shale (the dark shale itself) from these three cores generally displays the same lithology and shows no evidence of vertical fracturing. Horizontally, there are zones on the order of several mm thick

Table 1. Extractable bitumen in mg extract/g shale of Middle Cambrian–Early Ordovician Alum Shale is given along with TOC in % and whole rock uranium concentration

Sample ^a	[U] (ppm)	TOC ^b	Total extract	Tot _c TOC	Hydro- carbons	Hydro ^d TOC	Saturates	Sat _c TOC	Aromatics	Aro TOC	Arom Sat
H5.15	102	10.25	1.93	18.8	0.63	6.1	0.17	1.6	0.46	4.5	2.5
H7.65	156	14.25	2.03	14.2	0.66	4.6	0.09	0.6	0.57	4.0	6.1
H10.47	187	15.94	1.14	7.1	0.47	2.9	0.03	0.2	0.44	2.8	16.3
H16.34	149	15.96	1.66	9.6	0.31	1.9	0.04	0.3	0.26	1.6	5.8
H20.64	92	11.36	1.42	12.5	0.71	6.2	0.15	1.3	0.56	4.9	3.8
H23.14	18	8.12	5.75	70.1	3.05	37.6	1.35	16.6	1.70	20.9	1.2
B18.30	110	12.68	0.93	7.3	0.60	4.7	0.10	0.8	0.50	3.9	5.0
B21.30	114	10.56	1.47	13.9	0.47	4.5	0.06	0.6	0.41	3.9	7.1
B24.21	115	10.88	0.96	8.8	0.46	4.2	0.05	0.5	0.41	3.8	8.2
B26.91	163	14.65	1.02	6.9	0.46	3.1	0.05	0.3	0.41	2.8	8.5
B32.01	48	8.19	3.80	46.4	1.02	12.4	0.28	3.4	0.74	9.0	2.6
B35.00	15	4.43	6.86	154.8	4.61	104.1	1.67	37.7	2.94	66.4	1.8
B43.22	16	4.15	1.98	47.7	1.33	32.0	0.48	11.6	0.85	20.5	1.8
B46.88	13	4.38	2.92	66.7	1.50	34.2	0.59	13.5	0.91	20.8	1.5
B53.08	7	1.09	0.60	55.0	0.24	22.0	0.10	9.2	0.14	12.8	1.3
B58.30	16	4.01	2.32	57.8	0.65	16.2	0.23	5.7	0.42	10.5	1.8
K85.23	85	11.91	0.95	7.9	0.61	5.1	0.14	1.2	0.46	3.9	3.3
K87.42	140	8.77	0.72	8.2	0.27	3.1	0.05	0.6	0.22	2.5	4.0
K89.51	124	12.49	0.80	6.4	0.38	3.0	0.04	0.3	0.34	2.7	8.1
K91.42	167	13.95	0.68	4.9	0.34	2.4	0.04	0.3	0.30	2.2	7.4
K93.60	82	13.26	1.07	8.1	0.56	4.2	0.10	0.8	0.45	3.4	4.4
K95.12	143	16.72	0.56	3.3	0.33	2.0	0.03	0.2	0.30	1.8	11.2
K97.21	40	10.41	3.33	32.0	1.90	18.2	0.53	5.1	1.36	13.1	2.5
K99.74	20	4.72	2.35	49.8	0.70	14.8	0.20	4.2	0.50	10.6	2.5
K101.68	33	9.23	2.13	23.1	0.44	4.7	0.17	1.8	0.27	2.9	1.6
S22.44	35	9.63	2.02	20.9	1.14	11.8	0.45	4.7	0.95	9.9	2.1
S25.61	93	9.17	0.81	8.8	0.45	4.9	0.09	1.0	0.36	3.9	4.6
S28.21	149	11.24	0.64	5.6	0.36	3.2	0.04	0.4	0.32	2.8	7.4
S31.27	97	10.95	0.75	6.8	0.23	2.1	0.03	0.3	0.21	1.9	4.5
S33.94	48	8.33	1.21	14.5	0.43	5.2	0.06	0.7	0.37	4.4	6.1
S34.88	62	11.43	0.91	8.0	0.23	2.0	0.03	0.3	0.20	1.7	6.6
S38.30	63	8.79	1.17	13.3	0.48	5.5	0.07	0.8	0.41	4.7	2.7
G382.0	250	10.70	1.74	16.3	0.00	0.00	0.00	0.0	0.00	0.0	—
G385.0	35	11.23	5.33	47.5	0.50	4.7	0.18	1.6	0.32	2.8	1.8

^aSample. H samples are from Hynneberg Närke; K from Kinnekulle Västergötland; B from Bårstad Östergötland; S from Segerstad Öland; G from Gotland. The numbers following the letter symbol gives the depth in m at which the sample was taken (the center of a 2–5 cm chunk).

^bTotal organic carbon (%).

^c[(mg hydrocarbon/g sediment)/% Total organic carbon] × 100.

^d[(mg saturates/g sediment)/% Total organic carbon] × 100.

^e[(mg aromatics/g sediment)/% Total organic carbon] × 100.

occurring at intervals of several tens of cm which may represent oxidation by ground waters (these zones were avoided in this study). However, as a whole, one might expect that samples taken nearest the surface should, on the average, contain the least extractable bitumen (normalized to TOC), which is not the case. In the Östergötland and Västergötland cores, the greatest amount of extractable bitumen comes from samples in the middle of the core. On Öland, the greatest amount of extractables are at the top of the core even though it is only 22 m deep. In Närke, the greatest amount of bitumen is from the bottom of the core. For all of the cores, the greatest amount of extractables are found in samples with relatively high TOC values and low uranium concentrations. On Gotland, where the Alum Shale is found at a depth of 380 m, and where one might expect much less extensive weathering as a result of the depth, the inverse relationship between uranium concentration and bitumen content also applies. Therefore, if weathering is important in determining the amount of extractable bitumen, the amount of weathering cor-

relates strongly with uranium concentration and not with depth. We see no reason for such a correlation unless irradiation was facilitating oxidation of the bitumen. Although chemical oxidation by meteoric waters may have affected organic matter in the Alum Shale cores examined, it seems to be a less important factor in determining the amount of extractable bitumen than is uranium concentration.

Furthermore, Forsberg and Bjorøy, (1983), in a study of the effects of weathering on organic matter, found that aromatic hydrocarbons were removed prior to saturates. The aromatic hydrocarbon fraction of Alum Shale bitumen is greater by weight than the saturate fraction for all samples studied; it shows no correlation with depth; but the aromatic/saturate ratio increases with increasing uranium concentration (see Fig. 7).

It was found by Clayton and King (1986) and Wardroper (1984) that low molecular weight triaromatic steroids were preferentially removed by weathering. Figure 9 shows that only low molecular weight triaromatic steroids are present in Alum Shale

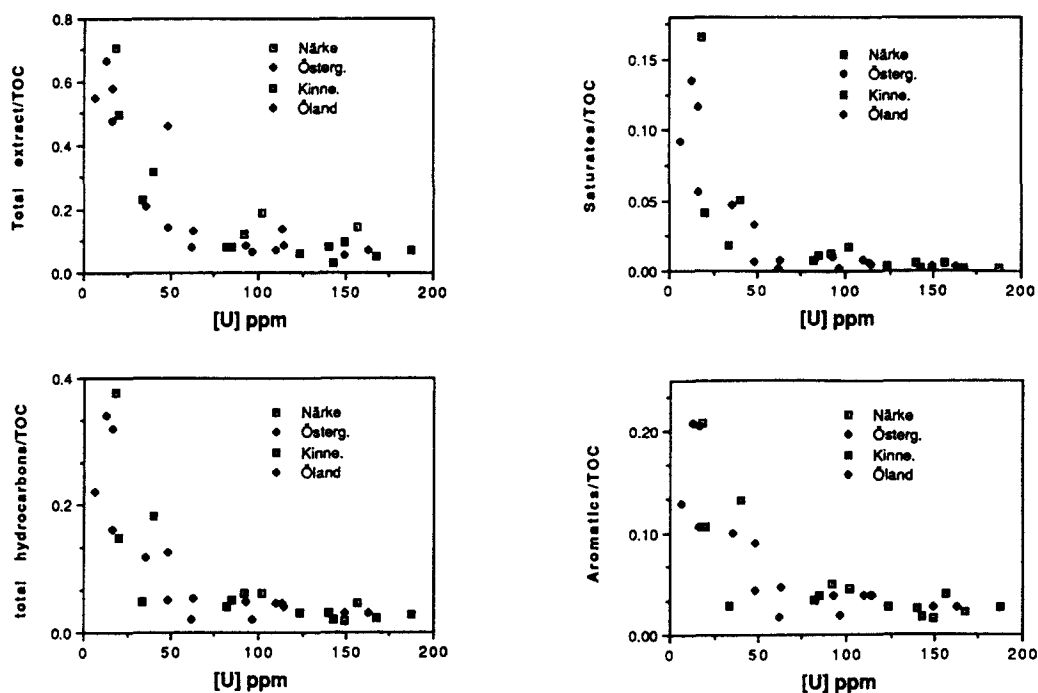


Fig. 4. The amount of extract/TOC is compared to whole rock uranium concentration.

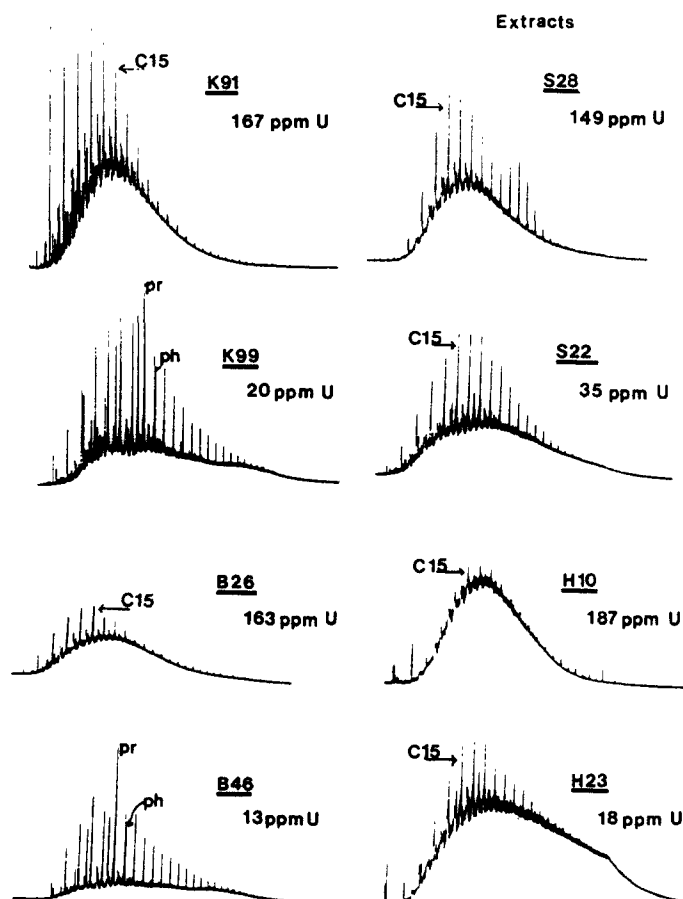


Fig. 5. Gas chromatogram of saturate fractions of extracts from samples with high and low uranium concentrations from each core.

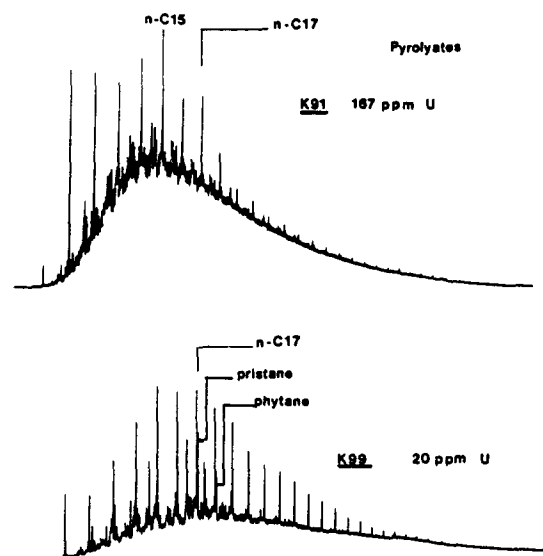


Fig. 6. Gas chromatograms of the saturate fractions of kerogen pyrolysate from samples from the Västergötland core with high and low uranium concentrations.

extracts from a relatively shallow depth, which is the opposite of what one would expect if weathering determined the distribution of triaromatic steroids in the Alum Shale. C_{26} , C_{27} and C_{28} triaromatic steroids occur only in extracts from samples with low uranium concentrations. It is known that aromatic hydrocarbons are more stable in the presence of ionizing radiation than aliphatic hydrocarbons (Bovey, 1958) and it may be that the aliphatic side chains are being cleaved by irradiation from uranium decay.

Parent/alkylated PAH ratios have been shown to increase as a result of weathering (Clayton and King, 1986). Parent/alkylated PAH ratios in Alum Shale extract are higher in extracts from shallow samples high in uranium concentration (Figs 11 and 12). In the Öland sample, where the shallowest core sample has a lower uranium concentration than the deeper sample, the parent/alkylated PAH ratio is about the same for the deep and the shallow samples. This

Table 2. Relationship of normal alkane length to uranium concentration in the Alum Shale of Sweden. Data are from GC peak areas

Sample	[U] (ppm)	R_1	R_2
<i>Närke</i>			
H5	102	38.5	0
H7	156	—	—
H10	187	6.9	0.10
H16	149	3.3	0.06
H20	92	8.6	0.04
H23	18	4.8	0
<i>Östergötland</i>			
B18	110	16.3	0
B21	114	13.9	0
B24	115	14.4	0
B26	163	11.0	0
B32	48	5.9	0
B35	16	3.0	0.80
B43	16	2.7	0.18
B46	13	3.0	0.16
B53	7	1.6	0.10
B58	16	2.4	0.10
<i>Kinneulle</i>			
K85	85	14.0	0
K87	140	9.4	0
K89	124	18.7	0
K91	167	10.7	0.03
K93	82	12.3	0
K95	143	5.7	0.06
K97	39	8.4	0
K99	20	6.0	0.10
K101	33	7.5	0.20
<i>Öland</i>			
S22	35	4.2	0
S25	93	9.0	0
S28	149	1.9	0
S31	97	11.6	0
S33	48	—	—
S34	62	5.4	0
S38	63	4.1	0

$$R_1 = \frac{[C_{15} + C_{16} + C_{17}]}{[C_{21} + C_{22} + C_{23}]}, \quad R_2 = \frac{[C_{25} + C_{26} + C_{27}]}{[C_{15} + C_{16} + C_{17}]}$$

suggests that both weathering and uranium concentration may play a part in determining parent/alkylated PAH distribution in Alum Shale extract. As with triaromatic steroids, alkyl side-chain cleavage may be partly responsible for parent/alkylated PAH ratios in Alum Shale extract and pyrolysate.

Ratios of methylphenanthrene isomers have been used to determine the maturity of organic matter

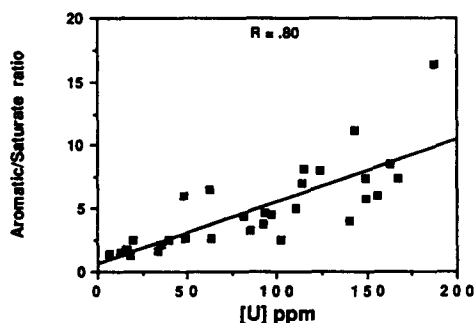


Fig. 7. Aromatic/saturate hydrocarbon ratio of Alum Shale extract compared with uranium concentration.

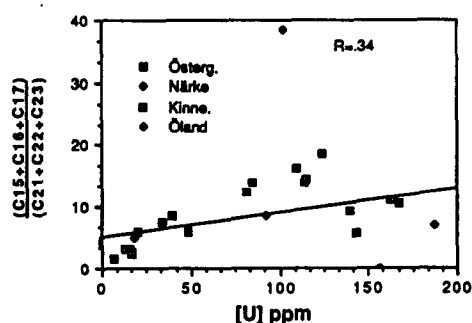


Fig. 8. Relationship of n -alkane length to uranium concentration.

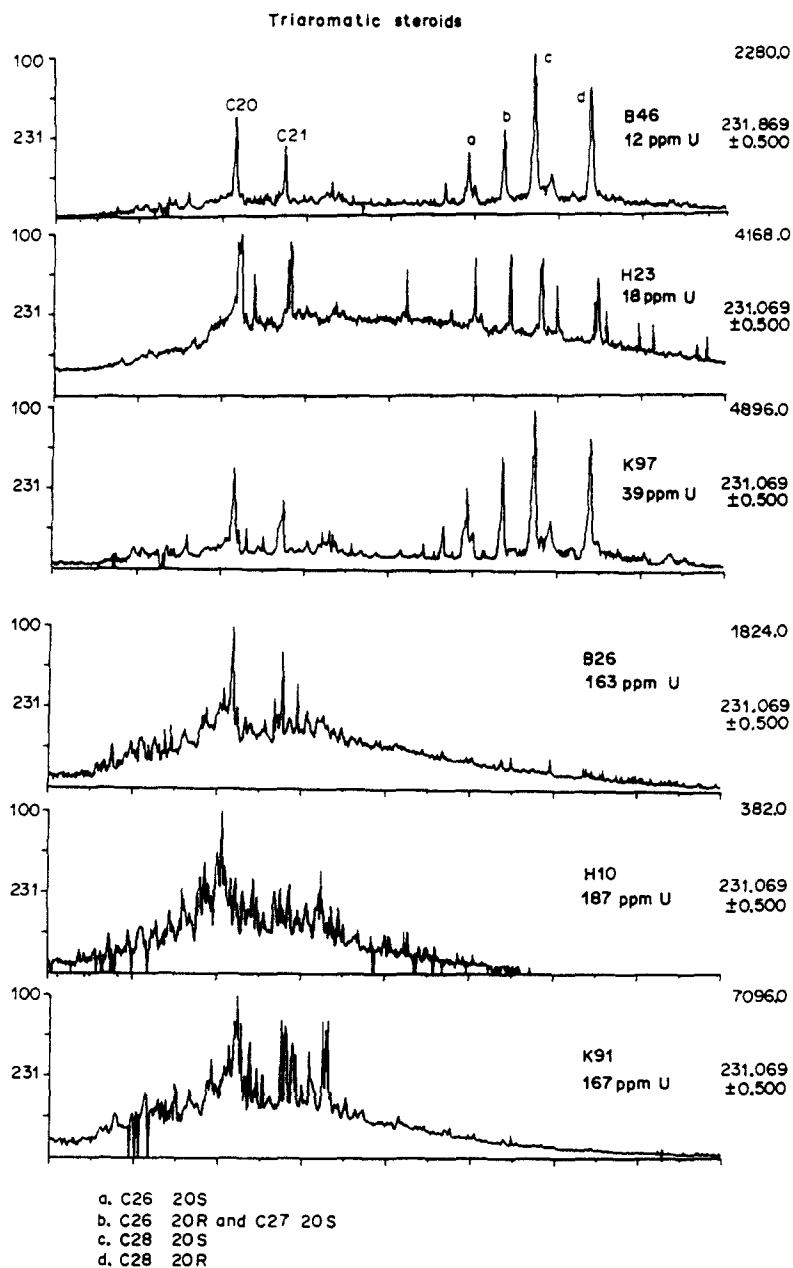


Fig. 9. Triaromatic steroid distribution from samples with high and low uranium concentrations.

(Radke *et al.*, 1982; Kvalheim *et al.*, 1986). These studies utilize the fact that 2 and 3 methylphenanthrene isomers are thermally more stable than the 1 and 9 methyl isomers. Clayton and King (1986) investigated possible weathering effects on isomeric ratios of methylphenanthrenes, and found no effect. Data from Table 3 of this study suggest that samples with high uranium concentrations taken near the surface tend to have lower ratios of 1 + 9/2 + 3 methylphenanthrenes than deeper samples with lower uranium concentrations. The Öland sample nearest the surface, which has a relatively low uranium

concentration, has about the same 1 + 9/2 + 3 ratio as a deeper sample with a relatively high uranium concentration. This would again suggest that both irradiation and weathering may have altered the distribution of methylphenanthrene isomers in Alum Shale extract, contrary to Clayton and King (1986).

Kerogen pyrolysates of a relatively deep sample with low uranium concentration generated no parent chrysene-triphenylene, a relatively small amount of parent pyrene and no benzo[e]pyrenes. A shallower, more uranium rich sample, generated all of the above. The difference in the 1 + 9/2 + 3 methyl-

Table 3. Ratios of parent and alkylated phenanthrenes, chrysenes-triphenylenes, pyrenes and benzofluoropyrenes. Values were obtained by ratioing GC-MS peak area

Extract	[U](ppm)	%1	%2	%3	%4	%5	%6	%7	%8	9	%10	%11	%12	%13	14	%15	%16	%17
B46	12	16.9	23.3	29.3	30.4	1.51	17.3	23.1	59.5	3.8	0.0	13.1	35.6	51.3	14.2	23.5	40.7	35.8
B26	163	14.1	23.1	32.8	30.0	1.34	27.1	30.2	42.8	0.9	16.1	16.8	28.6	38.5	5.1	33.9	34.4	31.7
K97	39	12.8	25.6	32.8	28.8	1.41	20.4	21.2	58.2	2.3	0.0	12.8	32.6	54.7	11.9	15.4	43.7	40.8
K91	167	17.8	19.4	25.0	37.8	1.32	23.1	32.6	44.3	1.0	10.1	19.3	33.3	37.2	4.2	21.6	32.5	45.9
H23	18	7.8	18.7	33.3	40.2	1.63	20.4	27.2	52.3	3.2	0.0	20.6	42.3	37.1	10.3	8.9	41.9	32.9
H10	187	15.7	26.8	33.3	24.2	1.31	22.2	38.3	39.5	0.5	16.1	22.3	32.1	29.5	3.1	25.3	51.0	40.1
S22	35	13.5	25.1	34.4	27.0	2.06	29.2	31.8	39.0	1.5	9.9	18.4	33.1	38.4	4.2	27.1	34.1	38.8
S28	149	15.6	37.2	27.7	19.6	2.03	32.6	30.0	37.4	1.4	9.9	18.1	34.6	37.2	6.0	26.0	31.3	42.6
<i>Pyrolysates</i>																		
K99	19	8.0	24.4	31.5	36.1	2.17	0.0	29.3	70.7	1.0	2.5	11.1	35.7	50.7	6.1	0.0	0.0	0.0
K91	167	8.0	26.4	35.2	30.4	1.13	11.5	33.6	54.9	0.8	10.4	15.7	40.3	33.6	4.5	24.8	42.5	32.7

(1) Phenanthrene; (2) methylphenanthrene; (3) dimethylphenanthrene; (4) trimethylphenanthrene; (5) ratio of (1 + 9)/(2 + 3) methylphenanthrene; (6) chrysene and triphenylene; (7) methylchrysene and methyltriphenylene; (8) dimethylchrysene and dimethyltriphenylene; (9) chrysene-triphenylene/pyrene ratio; (10) pyrene; (11) methylpyrene; (12) dimethylpyrene; (13) trimethylpyrene; (14) phenanthrene/pyrene ratio; (15) benzofluoropyrene; (16) methylbenzofluoropyrene; (17) dimethylbenzofluoropyrene.

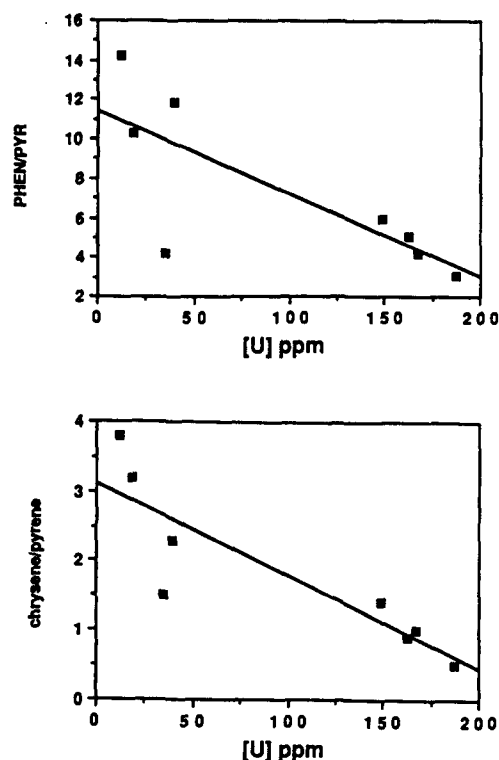


Fig. 10. Phenanthrene/pyrene and chrysene/pyrene ratios in Alum Shale extract are plotted against whole-rock uranium concentration.

phenanthrene ratios of the pyrolysates of kerogen from samples with high and low uranium concentrations is also considerably larger than that of the extracts. It is suggested that the reason for the larger differences seen in the pyrolysates than the extracts may be the result of bitumen migration and weathering. Migration would tend to even out differences in extracts as bitumen sourced from samples high in uranium concentration may mix with bitumen sourced from samples low in uranium concentration. Mixing due to migration would have little effect on kerogen pyrolysate, as kerogen cannot migrate. Weathering is known to degrade bitumen more readily than kerogen. Therefore, kerogen pyrolysates may tend to show relatively less weathering and more irradiation effects in comparison to extracts.

It is not clear why samples relatively near the surface with high uranium concentrations have low phenanthrene/pyrene and chrysene/pyrene ratios.

Dahl *et al.* (1988a) have suggested that some of the bitumen contained in the Alum Shales of Central Sweden (Närke, Västergötland, and Östergötland) is migrated. This may explain several of the relatively high bitumen ratios (i.e. H23 and B35) and be part of the reason for the scatter in Figs 3 and 4. However, migration cannot explain the correlation between uranium concentration and the amount and aromaticity of the extractable bitumen.

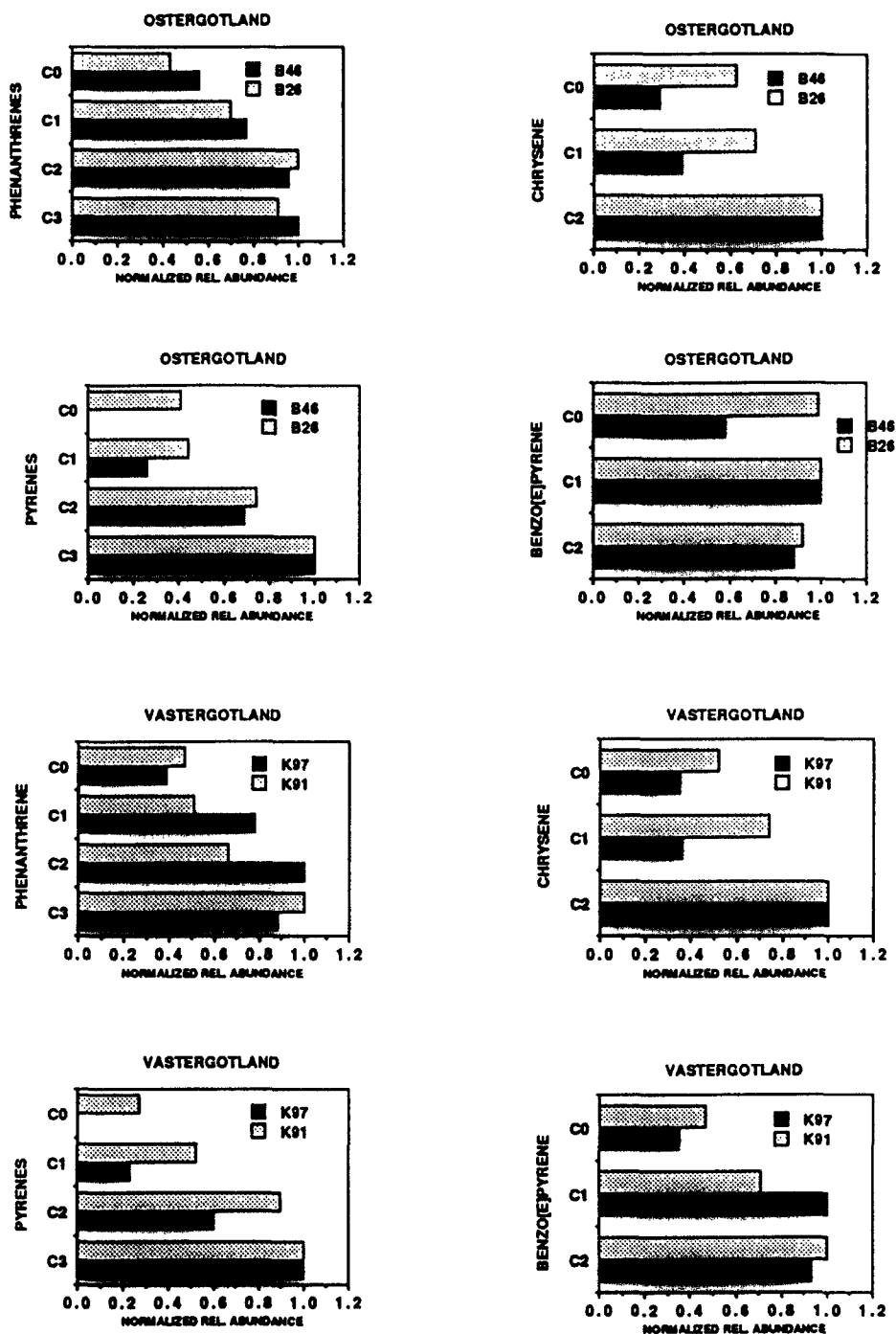


Fig. 11. Parent/alkylated PAH ratios tend to be higher in extracts from Alum Shale samples with high uranium concentrations, which are shown by the light colored bars. Samples with low uranium concentrations are designated by black bars. Samples from Västergötland and Östergötland are shown here.

Gas chromatographic analyses of extracts pyrolyses (Figs 5 and 6) show isoprenoids present only in samples with low uranium concentrations. Pristane (C_{19} isoprenoid)/ n - C_{17} ratios have been used to show migration (Leythauser and Schwarzkopf, 1986). Low pristane/ n - C_{17} ratios may be indicative of

migration. Therefore it could be interpreted that the bitumen in many of the high uranium samples has migrated into the Alum Shale. Kerogen is however indigenous to the rock from which it is extracted. Pyrolyses of solvents extracted kerogen from samples of high and low uranium concentrations yielded

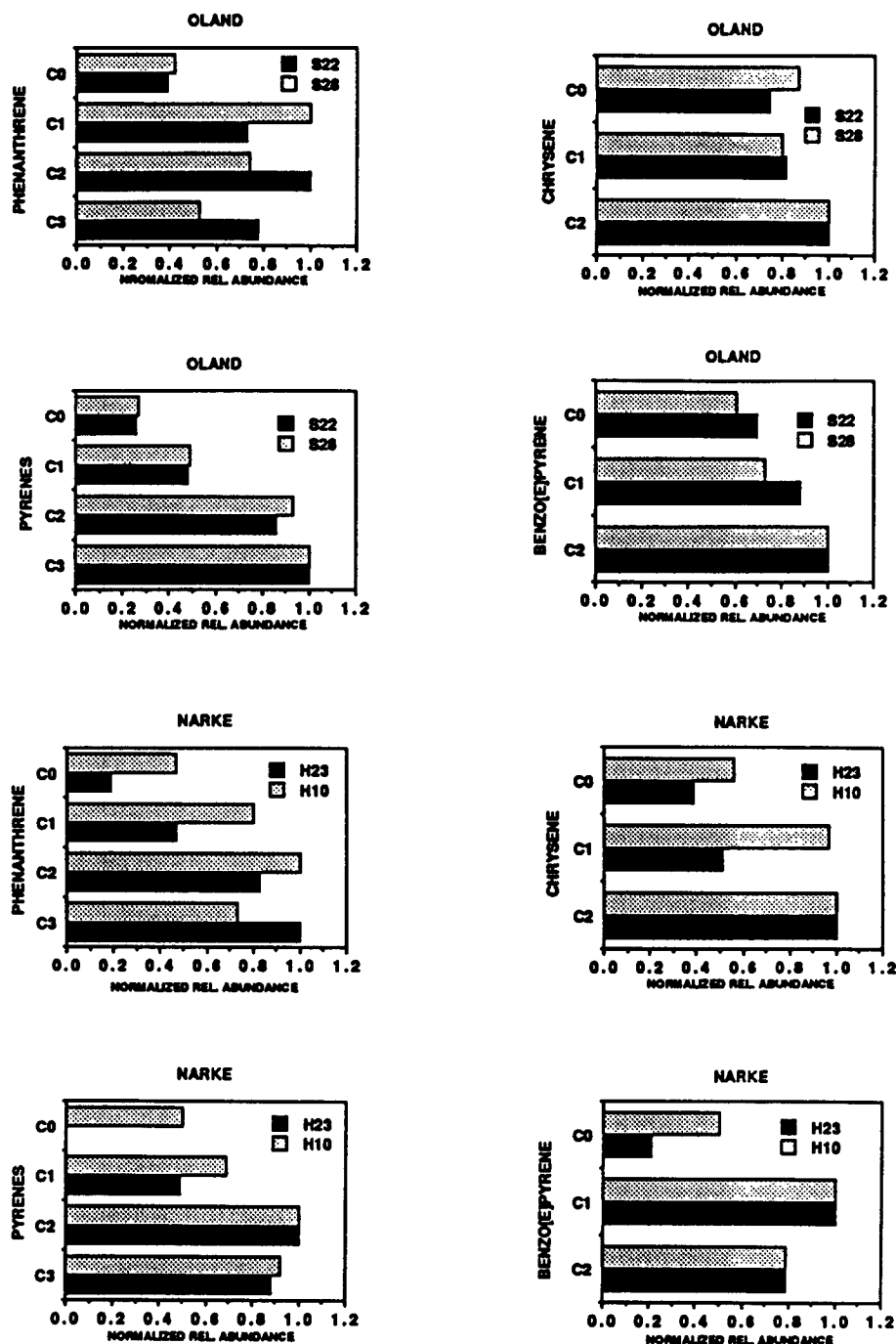


Fig. 12. Parent/alkylated PAH ratios from Närke and Öland are given. The Öland core is the only one in which the sample relatively highest in uranium concentration is stratigraphically below the sample in the core with the lowest uranium concentration.

bitumens closely resembling extracts from the whole rock samples. This suggests that pristane/*n*-C₁₇ ratios are generally a property of the kerogen in the Alum Shale and not the result of migration.

The relationship between uranium concentrations and extractable bitumen in the Alum Shales suggests that bitumen is being altered by irradiation. Figures

5, 6 and 7 and Table 1 suggests that isoprenoids are most easily removed, followed by *n*-alkanes, and finally by aromatics, which is in agreement with experimental work which shows that saturated hydrocarbons are more susceptible to irradiation damage than are aromatics (Desrosier and Rosenstock, 1960). In the sample with the highest uranium

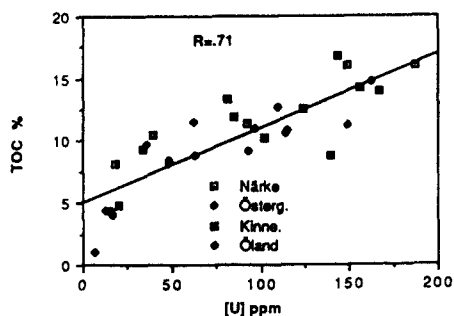


Fig. 13. Alum Shale TOC in % plotted against whole-rock uranium concentration.

concentration (from Gotland), C_{15+} hydrocarbons have been completely removed, leaving only polar heteromolecules, referred to as polars, resins and asphaltenes. It is not known how hydrocarbons are lost, but from experimental irradiation of organic matter (i.e. Bovey *et al.*, 1958) possible mechanisms include polymerization, aromatization, cleavage and formation of free radicals and subsequent oxidation.

SUMMARY

The data presented suggest that irradiation from the natural decay of uranium within the Alum Shale of Sweden has reduced the amount and changed the nature of C_{15+} saturate and aromatic hydrocarbons in the extractable bitumen. The greater the radiation dosage (i.e. the higher the uranium concentration), the more aromatic the extractable bitumen tends to be. Aliphatic isoprenoids appear more susceptible to removal than normal alkanes, which are in turn less stable than aromatic hydrocarbons. The pathway of hydrocarbon alteration in the Alum Shale may be from saturated to aromatic hydrocarbons, and finally, perhaps with the addition of oxygen, to formulation of large, insoluble polyaromatic heteromolecules similar to kerogen.

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REFERENCES

- Andersson A., Dahlman B., Gee D. G. and Snäll S. (1985) *The Scandinavian Alum Shales*, 50 pp. Sveriges Geologiska Undersökning. Avhandlingar och Uppsatser 1 A4 No. 56, Uppsala.
- Armands G. (1972) Geochemical studies of uranium, molybdenum and vanadium in a Swedish Alum Shale. *Stockholm Contr. Geol.* **27**, 2–45.
- Bergstrom S. M. (1980) Conodonts as paleotemperature tools in Ordovician rocks of the Caledonides and adjacent areas in Scandinavia and the British Isles. *Stockholm Contr. Geol.* **102**, 377–392.
- Bovey F. A. (1958) *The Effects of Ionizing Radiation on Natural and Synthetic Polymers*, 287 pp. Wiley Interscience, New York.
- Buchardt B., Clausen J. and Thompson E. (1986) Carbon isotope composition of lower Paleozoic kerogen: Effects of maturation. In *Advances in Organic Geochemistry 1985* (Edited by Leythaeuser D. and Rullkötter J.). *Org. Geochem.* **10**, 127–135. Pergamon Press, Oxford.
- Clayton J. L. and King J. D. (1987) Effects of weathering on biological marker and aromatic hydrocarbon composition of organic matter in Phosphoria shale outcrop. *Geochim. Cosmochim. Acta* **51**, 2153–2157.
- Dahl J., Chen R. L. and Kaplan I. R. (1988a) Bitumen migration associated with the Alum Shales of Central and Eastern Sweden. *A.A.P.G. Bull.* Submitted.
- Dahl J., Hallberg R. and Kaplan I. R. (1988b) The effects of uranium decay on elemental and isotopic ratios of Alum Shale kerogen. *Appl. Geochem.* Submitted.
- Desrosier N. W. and Rosenstock G. M. (1960) *Radiation Technology in Food Agriculture and Biology*, 401 pp. AVI, Westport, Conn.
- Forsberg A. and Bjørøy M. (1983) A sedimentological and organic geochemical study of the Botneheia Formation Svalbard, with special emphasis on the effects of weathering on the organic matter in shales. In *Advances in Organic Geochemistry 1981* (Edited by Bjørøy M. *et al.*), pp. 60–68. Wiley, Chichester.
- Kvalheim O. M., Christy A. A., Telnaes N. and Bjørseth A. (1987) Maturity determination of organic matter in coals using methyl-phenanthrene distribution. *Geochim. Cosmochim. Acta* **51**, 1883–1888.
- Leventhal J. S. and Threlkeld L. N. (1978) Carbon-13/carbon-12 isotope fractionation of organic matter associated with uranium ores induced by alpha radiation. *Science* **202**, 430–432.
- Leventhal J. S., Daws T. A. and Frye J. S. (1986) Organic geochemical analysis of sedimentary organic matter associated with uranium. *Appl. Geochem.* **1**, 241–249.
- Leythaeuser D. and Schwarzkopf T. (1986) The pristane/n heptadecane ratio as an indicator for recognition of hydrocarbon migration effects. In *Advances in Organic Geochemistry 1985* (Edited by Leythaeuser D. and Rullkötter J.). *Org. Geochem.* **10**, 191–197. Pergamon Press, Oxford.
- Mackenzie A. S. and McKenzie D. (1982) Isomerization and aromatization of hydrocarbons in sedimentary basins formed by extension. *Geol. Mag.* **120**, 417–528.
- Mackenzie A. S., Rullkötter J., Welte D. H. and Manikiewicz P. (1985) Reconstruction of oil formation and accommodation in North Slope, Alaska, using quantitative gas chromatography-mass spectrometry. In *Alaskan North Slope Oil/Rock Correlation Study* (Edited by Magoon L. B. and Claypool G. E.), pp. 319–377. *AAPG Stud. Geol.* No. 20.
- Philp R. P. (1985) *Fossil Fuel Biomarkers: Applications and Spectra*, 294 pp. Elsevier, Amsterdam.
- Pierce A. P., Mytton J. W. and Barnett P. R. (1958) Geochemistry of uranium in organic substances in petroliferous rocks. In *Proceedings of the Second Conference on the Peaceful Uses of Atomic Energy*, Vol. 2, p. 192. United Nations, New York.
- Radke M., Welte D. H. and Willsch G. (1982) Geochemical study on a well in the Western Canada Basin: relation of the aromatic distribution pattern to maturity of organic matter. *Geochim. Cosmochim. Acta* **46**, 1–10.
- Rouzaud J. N., Oberlin A. and Trichet F. (1979) Interaction of uranium and organic matter in uraniumiferous sediments. In *Advances in Organic Geochemistry 1979* (Edited by Douglas A. G. and Maxwell J. R.), pp. 505–516. Pergamon Press, Oxford.
- Sassen R. (1984) Effects of radiation exposure on indicators of thermal maturity. *Org. Geochem.* **5**, 183–186.
- Tannenbaum E. and Kaplan I. R. (1985) Role of minerals in the thermal alteration of organic matter—I: Gener-

- ation of gases and condensates under dry condition. *Geochim. Cosmochim. Acta* **49**, 2589–2604.
- Tannenbaum E., Ruth E., Huizinga B. J. and Kaplan I. R. (1986) Biological marker distribution in coexisting kerogen, bitumen and asphaltenes in Monterey Formation diatomite, California. In *Advances in Organic Geochemistry 1985* (Edited by Leythaeuser D. and Rullkötter J.) *Org. Geochem.* **10**, 531–536. Pergamon Press, Oxford.
- Wardroper A. M. K., Hoffman C. F., Maxwell J. R., Barwise A. J. G., Goodwin N. S. and Park P. J. D. (1984) Crude oil biodegradation under simulated and natural conditions—II. Aromatic steroid hydrocarbons. In *Advances in Organic Geochemistry 1983* (Edited by Schenck P. A., Leeuw J. W. de and Lijmbach G. W. M.) *Org. Geochem.* **6**, 605–617. Pergamon Press, Oxford.
- Zumberge J. E., Sigleo A. C. and Nagy B. (1978) Molecular and elemental analyses of the carbonaceous matter in the gold and uranium bearing Vaal Reef carbon seams, Witwatersrand Sequence. *Minerals Sci. Eng.* **10**, 223–246.