

THE EFFECTS OF EARLY DIAGENETIC BACTERIAL SULPHATE REDUCTION UPON THE PETROLOGY AND CHEMISTRY OF COAL

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1. INTRODUCTION

Sulphur in coal has been the subject of many studies with respect to industrial use and environmental implications. However, the occurrence of sulphur in the coal matrix is only one specific expression of a general process that affects the coal structure and chemistry during early diagenesis. The most important physical parameter for the description of rank is vitrinite reflectance (%Rm). The progressive increase of %Rm appears to be governed mainly by increasing temperature. However, recent data clearly indicate that reflectance values are also affected by factors other than the geothermal history of the depositional area [e.g. 1, 2, 3].

It is hypothesized that %Rm and the presence of sulphur both depend in part on early diagenetic processes. In the present study the correlation of the occurrence of sulphur with physical (optical) and chemical characteristics of coal will be discussed to test possible relationships between sulphur and %Rm.

2. SAMPLE DESCRIPTION

Within the continuously cored coal-bearing Westphalian sequence of well Kemperkoul-1 (S. Netherlands), deviations in reflectance values from the general trend were observed at particular depths. A sequence including a fresh-water coal seam (XXIV) above the Aegir marine band (Westphalian B/C boundary) and a coal seam immediately underlying this marine horizon (XXV) has been studied. A series of samples was selected for detailed coal petrological, Rock-Eval and organic geochemical analysis. The two coal seams have an approximate thickness of 1 m. The sequential development of the coal seams shows that peat formation generally has not been a continuous process. This is demonstrated by several clastic intervals. The coal bed below the marine band is characterized by a high sulphur content (5.4 % total S).

3. RESULTS

3.1 Coal petrology

Above the Aegir marine band the general vitrinite reflectance value is approximately 0.95 %Rm (Table 1). The coal seam immediately underlying the marine band shows a %Rm value of 0.82. Maceral/mineral analyses of the coal beds show no significant differences with respect to the abundances of the three maceral groups vitrinite (VIT), liptinite (LIPT), inertinite (IN) and minerals (MIN). The analysis of the individual vitrinite macerals from both seams shows that the seam below the Aegir marine band contains elevated proportions of framboidal pyrite incorporated in the vitrinite matrix [3].

3.2 Rock-Eval

Rock-Eval parameters revealed only minor differences between the two seams. However, it was noted that the Tmax values from the coal seam underlying the marine horizon generally are lower than those of the fresh-water seam (Table 1). The hydrogen index (HI) shows a positive correlation with the liptinite content. No correlation could be established between vitrinite reflectance and hydrogen index. The large fluctuations in total organic carbon content (TOC) within seam XXV are due to the clastic intervals.

Table 1. Summary of coal petrological results and Rock-Eval data

No.	%Rm	VIT	LIPT	IN	MIN	Tmax	S1	S2	S3	TOC	HI	OI
SEAM XXIV												
1	0.96	64.8	18.2	17.0	0.0	442	2.13	195.90	2.29	71.74	273	3
2	0.93	74.9	14.0	11.1	0.0	445	4.69	203.74	2.44	68.54	279	3
3	0.96	71.0	15.4	13.2	0.4	448	2.46	180.68	2.32	72.42	249	3
4	0.99	76.6	16.6	6.6	0.2	448	4.63	195.04	2.52	74.75	260	3
5 (*)	1.00	80.4	13.4	5.6	0.6	448	5.86	199.60	2.33	82.58	241	2
6	0.98	80.9	12.3	5.2	1.6	448	5.38	193.84	2.53	82.07	236	3
7	0.94	75.2	17.2	4.6	3.0	447	2.43	186.08	1.82	61.74	301	2
8	0.95	26.0	0.8	0.2	73.0	445	0.51	29.43	0.31	13.03	225	2
SEAM XXV												
9 (*)	0.79	71.8	10.4	7.0	10.8	446	2.43	181.48	1.21	80.79	224	1
10	0.87	63.2	3.0	1.4	32.4	447	2.09	116.62	1.28	55.43	210	2
11	0.86	11.6	0.4	0.0	88.0	446	0.51	6.14	0.43	3.53	173	12
12	0.80	56.7	5.0	6.5	31.8	446	0.65	34.64	0.57	27.15	127	2
13	0.85	14.8	1.4	0.2	83.6	447	0.16	7.83	0.21	5.03	155	4
14	0.85	81.6	8.0	8.8	1.6	448	2.76	196.64	2.46	69.70	282	3
15	0.89	82.6	10.0	5.6	1.8	447	2.86	188.18	2.30	61.15	307	3
16	0.88	20.0	0.6	1.0	78.4	446	0.24	17.75	0.40	11.12	159	3
17	0.91	82.2	9.2	6.2	2.4	446	5.24	202.05	3.12	82.73	244	3
18	0.87	79.9	8.6	10.8	0.9	447	6.71	213.97	3.01	57.88	369	5
19	0.84	77.0	10.2	10.3	2.5	445	1.24	160.80	2.26	63.77	252	3
20	0.83	7.0	0.4	0.0	92.6	363	2.29	10.10	0.86	2.99	337	28

3.3 Pyrolysis-Gas chromatography-Mass Spectrometry

Curie point pyrolysis-gas chromatography (Py-GC) and Curie point pyrolysis-gas

chromatography-mass spectrometry (Py-GC-MS) were performed on two samples, one from each coal seam. In table 1 these samples are marked with an asteriks. The analytic procedures are described in ref. [5]. The pyrolysates of both samples are characterized by the presence of n-alkene/n-alkane doublets, alkylbenzenes, alkylphenols, alkyl-naphthalenes and alkylphenanthrenes/anthracenes. Relative differences between the two pyrolysates were observed in the abundance of a.o. the alkylated naphthalenes, phenanthrenes and anthracenes. Though internal distribution patterns of these series of compounds show no distinct differences their relative abundance in sample 9 is higher.

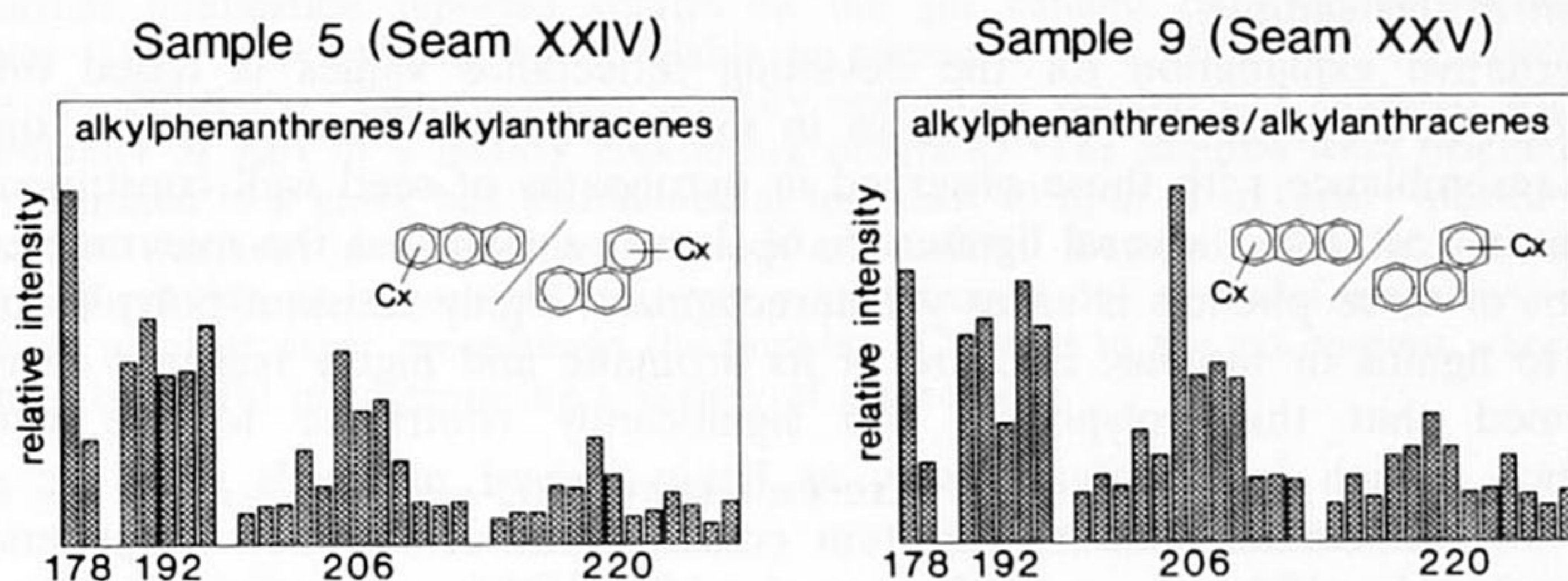


Figure 1. Internal distribution pattern of C₀-C₃ alkylated phenanthrenes and anthracenes in a sample with reduced reflectance values (9) compared to a 'normal' sample (5). The values at the X-axis refer to the molecular weights of the compounds.

4. DISCUSSION AND CONCLUSIONS

The presence of sulphur substances within the vitrinite matrix is likely the consequence of the activity of sulphate reducing bacteria in the depositional environment [3, 4]. During a transgression period sulphate-rich seawater will penetrate into the surface peats and induce the growth of sulphate reducing bacteria. If the duration and intensity of this bacterial activity is significant, inorganic sulphur compounds such as pyrite as well as organic sulphur compounds (OSC) are produced whereby the chemical composition of the peat can undergo considerable changes. Upon coalification many diagenetic transformations will occur but the ultimate molecular structure of the resulting coal will still reflect the original sulphur incorporation. The relatively higher amounts of framboidal pyrite observed in the seam directly underlying the Aegir marine band probably reflects the above described process. The presence of dibenzothiophenes, benzonaphthothiophenes and other condensed sulphur-containing aromatic components in the pyrolysates of the samples investigated also indicate the sulphur incorporation despite their relatively low amounts. The deviating vitrinite reflectance values of the 'marine-influenced' coal seam XXV may be ascribed to two phenomena related to sulfur chemistry: i) highly condensed aromatic moieties containing one or more thiophenic sulphur atoms have a lower vitrinite reflectance value than their

corresponding non-sulphur containing moieties at the same degree of coalification; ii) the presence of certain inorganic sulphur species catalyse the aromatisation of saturated polycyclic moieties at an early stage of coalification resulting in relatively stable and small aromatic units thus hampering the genesis of higher condensed aromatic systems later on. Comparison of the pyrolysates of both seams appears to support this latter possibility; although the internal distribution patterns of the alkylbenzenes, alkyl-naphthalenes, alkylanthracenes and phenanthrenes is similar to some extent in both pyrolysates (Fig. 1 shows these distributions for the alkylated phenanthrenes and anthracenes) these aromatic pyrolysis products are more abundant in the marine-influenced sample. This could imply that the more highly condensed aromatic moieties, which do not undergo pyrolysis, are relatively less abundant in this sample.

An alternative explanation for the deviating reflectance values is based on the distribution patterns of the alkylphenols in the pyrolysates. These patterns show a striking resemblance with those observed in pyrolysates of seed wall constituents of waterplants (testa) and several lignites [5, 6]. It was shown that the macromolecular precursor of these phenols is an as yet unrecognized highly resistant polyphenol not related to lignins or tannins. Because of its aromatic and highly resistant nature it is assumed that this polyphenol can significantly contribute to the vitrinite reflectance though in a different way as lignin-derived materials with the same degree of coalification. Relative different contributions of this new polyphenol to the samples investigated may thus explain the difference in their vitrinite reflectances.

5. REFERENCES

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