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### Organic Geochemistry of Permian Organic-rich Sediments from the Sudetes Area, SW Poland

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**Organic geochemistry of Permian organic-rich sediments  
from the Sudetes area, SW Poland**

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**Abstract**

Lacustrine and marine sediments from the Permian rift-basins of southwestern Poland were analysed using GC-MS and petrographic techniques. High Pr/Ph ratios,  $\gamma$ - and  $\beta$ -carotanes and gammacerane in the lacustrine sediments indicate deposition under elevated water salinities. The primary organic matter is represented by bacterial and algal lipids with variable terrestrial input. Marine algal lipids with minor bacterial and cyanobacterial lipids are the primary source of organic matter in the marine sediments. Extended hopanes, n-alkanes with even-odd predominance and low Ts/Tm ratios are consistent with deposition in a closed, evaporitic basin with substantial carbonate sedimentation.

**Keywords:** lacustrine;  $\gamma$ -carotanes;  $\beta$ -carotanes; gammacerane; saline-water environment

**INTRODUCTION**

The Sudetes area of southwestern Poland consists of two major rift basins of Permian age: the Intrasudetic Basin and the North Sudetic Basin (Mastalerz and Wojewoda, 1988; Fig. 1). The basins, which now occur as small NW-SE trending synclinal units, are a result of Variscan orogenic movements on the periphery of the Bohemian Massif. The Permian sediments analysed are from the continental Rotliegendes deposits of the Intrasudetic Basin and the Zechstein marine transgressive sequence from the Fore-Sudetic Monocline (Mastalerz and Wojewoda, 1988; Fig. 2a,b).

<Figure 1>

<Figure 2>

The Lower Rotliegendes within the Intrasudetic Basin have three fining-upward sequences at its base, each capped by organic-rich shales of lacustrine origin, with some intercalations of limestones and coals. These lacustrine shales are known as the Lower Anthracosia, Upper Anthracosia and Walchia shales, with the Walchia being the youngest of the three (latest Autunian-earliest Saxonian). In the North Sudetic Basin, only two fining-upward sequences are present: the Walchia shales are absent.

Previous organic geochemical work on the lacustrine shales in the Sudetes region is limited to organic petrographic studies based on a small number of samples of the Anthracosia shales (Mastalerz, 1988). The Kupferschiefer has, however, been more extensively studied using gas-chromatographic techniques (Puttman et al., 1988).

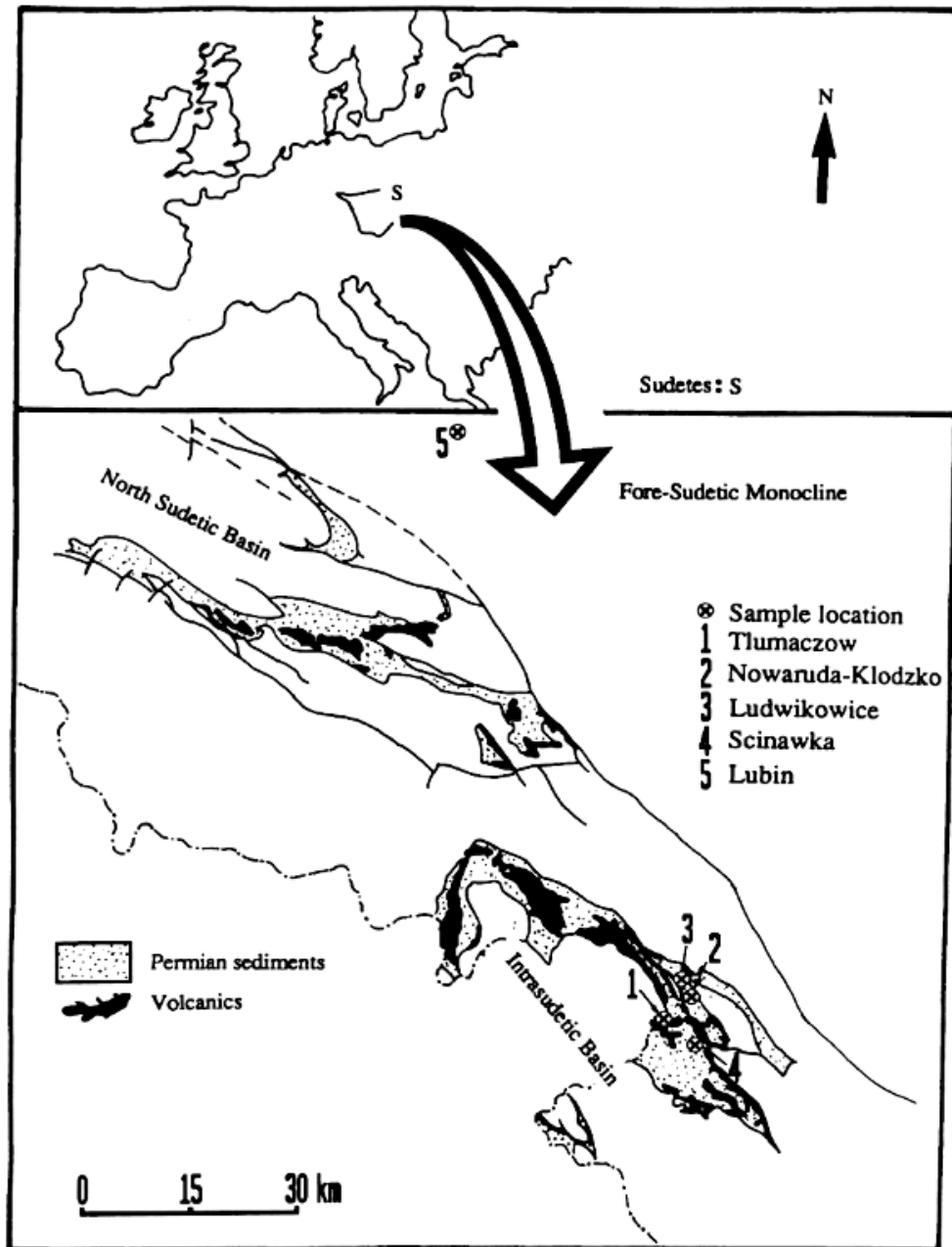


Fig. 1. Location map and simplified geologic map of the study area in the Sudetes region of southwestern Poland . Modified from Mastalerz and Wojewoda (1988).

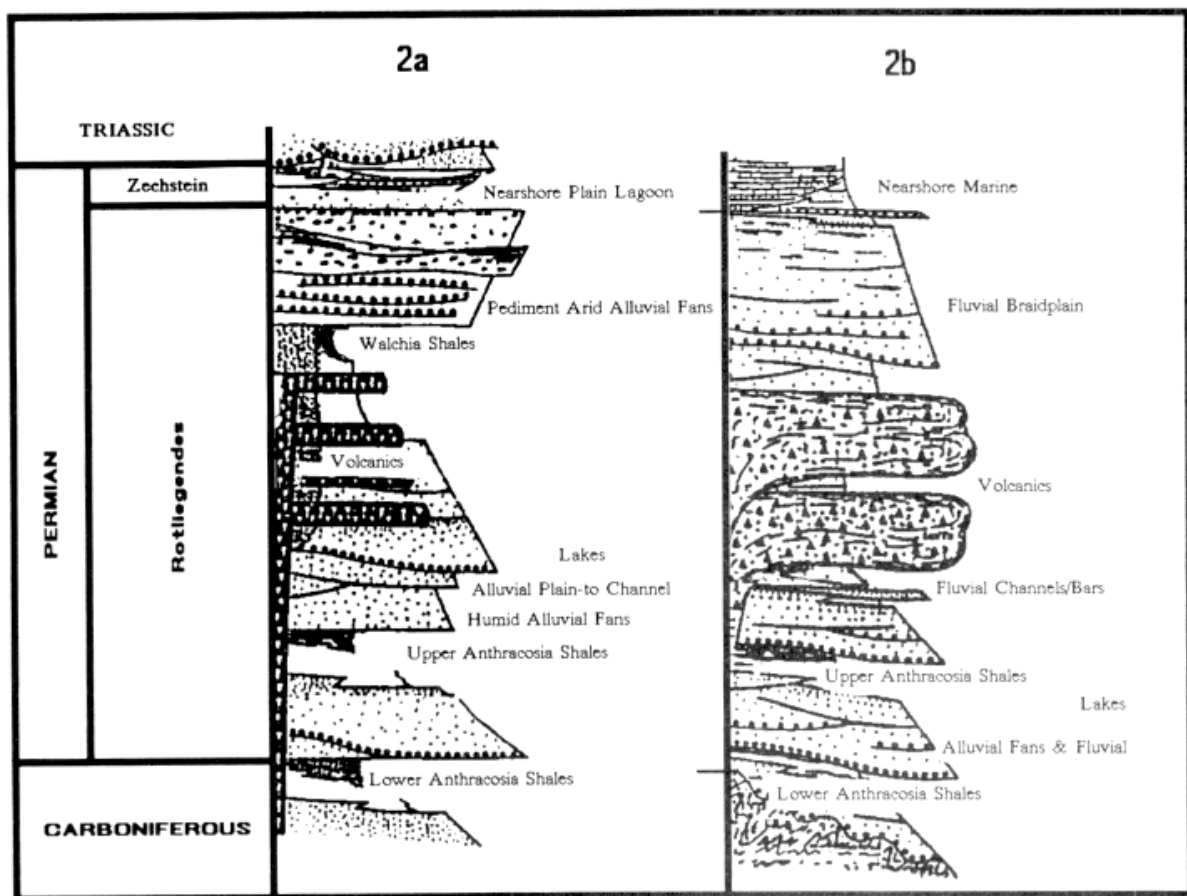


Fig. 2. Stratigraphic column of the Permo-Triassic interval within the Intrasudetic Basin (a) and the North Sudetic (b). Kupferschiefer interval occurs only in the North Sudetic Basin, at the base of the Zechstein. After Mastalerz and Wojewoda (1988) .

## SAMPLE DESCRIPTION

Organic geochemical analyses were carried out on 19 organic-rich rock samples taken from four locations in the Intrasudetic Basin and 1 location in the Fore-Sudetic Monocline (Fig. 1). The sediments sampled were the black shales of the Upper Anthracosia and Walchia lacustrine sequences, the copper-bearing marine Kupferschiefer black shales and the dolomitic limestone underlying the Kupferschiefer, known locally as the Border Dolomite (Table 1). The rock samples of the Upper Anthracosia and Walchia Shales were collected from outcrop locations while the Kupferschiefer shales and dolomitic limestone were obtained at Lubin copper mine from a depth of approx. 600 m.

<Table 1>

## METHODS

All 19 samples were pulverized and extracted by sonication at room temperature (15 min with dichloromethane until solvent runs clear). The extracted bitumen was then separated by liquid chromatography into saturate, aromatic and polar fractions (silica gel, activated at 300 °C for 3 h), with *n*-C<sub>6</sub>H<sub>14</sub>, 9:1 *n*-C<sub>6</sub>H<sub>14</sub>:CH<sub>2</sub>Cl<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub> and 1:1 CH<sub>2</sub>Cl<sub>2</sub>:CH<sub>3</sub>OH as the respective elutants. The saturate and aromatic fractions were analyzed for biological markers by gas chromatography mass spectrometry (GC-MS), with a 25 m OV-1 column (0.2 mm i.d., film thickness 0.33 μm), initially held at 100 °C for 10 min, then programmed from 100 to 300 °C at 3°C min<sup>-1</sup>, then held for 18 min, using a Hewlett Packard 5890A GC coupled to an HP 5970B Mass Selective Detector run in selected ion monitoring mode. Peak area quantitations were done on *m/z* 99 mass chromatograms of the saturate fractions and *m/z* 182, 178, 192, 198 and 231 mass chromatograms of the aromatic fractions.

Seven whole rock samples were prepared according to coal standard preparation techniques for organic petrological studies. A Leitz MPV II microscope was used for optical examination both in reflected white and blue light excitation modes.

## MOLECULAR GEOCHEMICAL RESULTS

### *Lacustrine samples*

The lacustrine samples show variations in isoprenoid/*n*-alkanes ratios, proportions of steranes and triaromatic steroid ratios, distribution of triterpane isomers and relative abundance of tricyclic terpanes. The *n*-alkanes are detectable usually up to the C<sub>35</sub> compounds with a pronounced odd-even predominance in the C<sub>22</sub>-C<sub>33</sub> range (Fig. 3). Overall there is a fairly high concentration of the long chain alkanes relative to the short chain compounds, especially within the Walchia Shale profile. The distribution of isoprenoids relative to *n*-alkanes varies widely (Table 2, for example). The Pr/Ph ratio varies from 0.29 to 1.72.

<Figure 3>

<Table 2>

Of particular interest is the presence of the high molecular weight carotenoid components that are clearly discernible in the black shale samples. The carotanes are present in small amounts or not at all in the mudrock samples. The carotanes are characterised by strong *m/z* 83 and 123 fragments with β-carotane eluting just after *n*-C<sub>37</sub> and γ-carotane, just after *n*-C<sub>36</sub> under the gas chromatographic conditions employed in this study (Jiang and Fowler, 1986; Fig. 4). In both the black shales and mudrock samples, β-carotane is present in medium to high abundance relative to *n*-C<sub>37</sub> while γ-carotane is present in low abundance, or

Sample number	Location	Age	Series	Description
PL9028	Ludwikowice	Permian	L. Rotliegendes	Lacustrine; Anthracosia black shales
PL9029	Nowaruda-Klodzko	Permian	L. Rotliegendes	Lacustrine; mudrocks and
PL9030				Anthracosia black shale (PL9030).
PL9031				4.6 m thick sequence, sampling
PL9032				interval of between 0.4 and 2.0 m
PL9033				
PL9034				
PL9035				
PL9036	Tlumaczow	Permian	L. Rotliegendes	Lacustrine; mudrocks and
PL9037				Walchia black shale (PL9038).
PL9038				5.2 m thick sequence, sampling
PL9039				interval of between 0.5 and 2.5 m.
PL9040				
PL9043	Scinawka	Permian	L. Rotliegendes	Lacustrine; Anthracosia black shale
PL9050	Lubin mine	Permian	Zechstein	Marine; dolomitic limestone
PL9051				(PL9050) and Kupferschiefer
PL9052				black shales 0.6 m thick
PL9053				sequence, sampling interval of
PL9054				0.1 m.

Table 1. Description of the samples analysed.

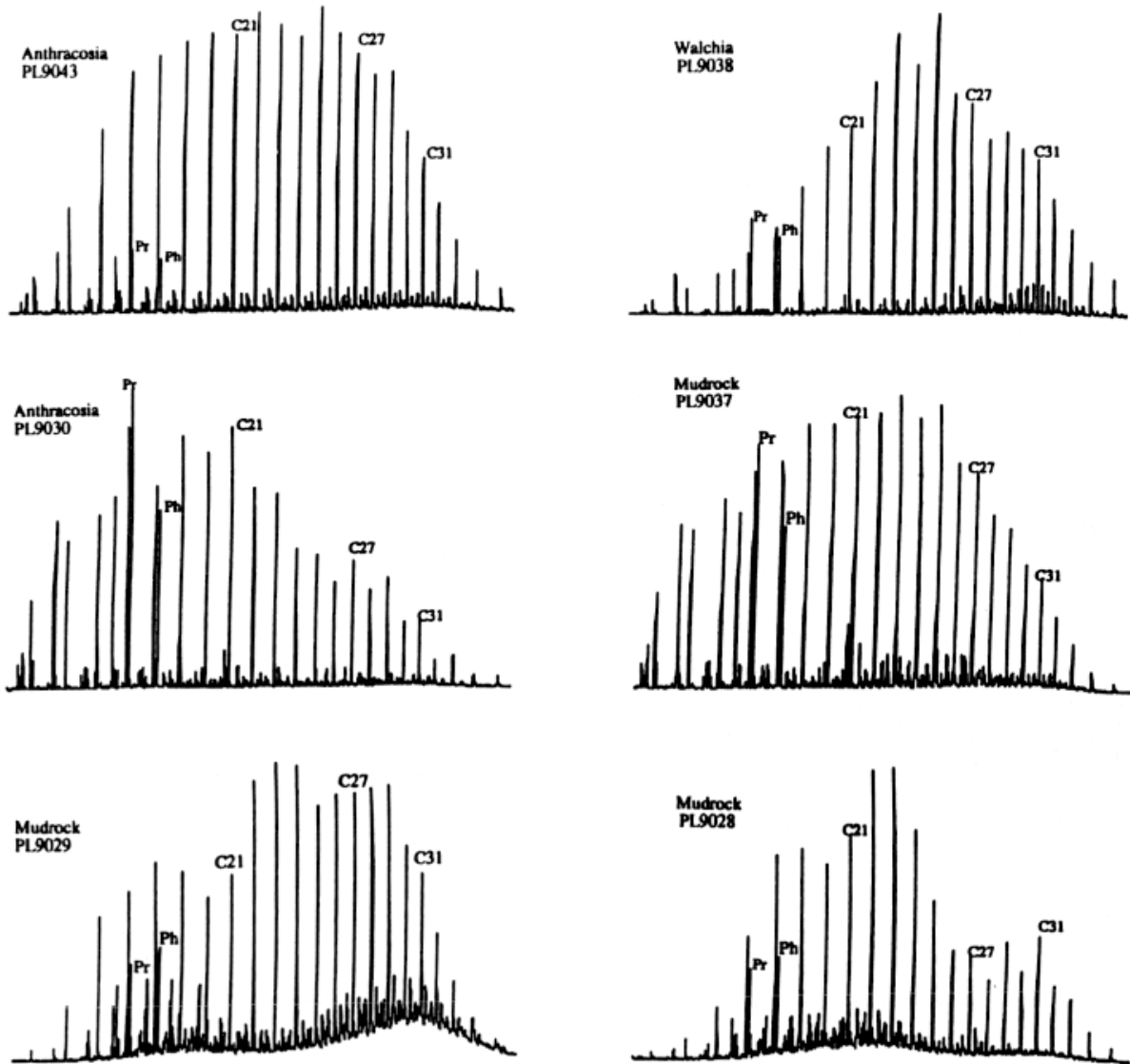


Fig. 3.  $m/z$  99 mass chromatograms that show the normal alkane and isoprenoid distributions of selected lacustrine shales and mudrocks from the Intrasudetic Basin.  $n$ -Alkanes are labelled according to their carbon numbers. Pr = pristane, Ph = phytane.

Sample	Pr/ <i>n</i> -C17	Ph/ <i>n</i> -C18	Pr/Ph	CPI	MPI	TRS
PL9028	0.54	0.49	0.88	1.14	0.89	1.00
PL9029	0.56	0.51	0.90	1.20	0.87	N/A
PL9030	1.15	0.86	1.72	1.34	0.14	0.06
PL9031	0.54	0.35	1.26	1.36	0.88	N/A
PL9032	0.55	0.63	0.63	1.18	0.89	N/A
PL9033	0.46	0.53	0.35	1.33	0.87	N/A
PL9034	0.44	0.51	0.29	1.21	0.89	N/A
PL9035	0.31	0.50	0.33	1.19	0.87	N/A
PL9036	0.48	0.44	0.95	1.16	0.90	1.00
PL9037	1.10	0.71	1.44	1.64	0.21	0.10
PL9038	1.62	0.90	1.30	1.08	0.24	0.12
PL9039	0.82	0.44	1.44	1.15	0.83	0.62
PL9040	0.89	0.35	0.89	1.33	0.91	0.98
PL9043	0.38	0.21	1.16	1.16	0.50	0.83
PL9050	2.08	1.33	1.73	1.02	0.35	0.09
PL9051	1.04	0.63	1.73	1.02	0.44	0.81
PL9052	0.88	0.53	1.72	1.00	0.43	0.81
PL9053	0.89	0.60	1.65	1.00	0.44	0.79
PL9054	0.91	0.57	1.71	1.00	0.44	0.80

Table 2. Molecular geochemical parameters calculated. Abbreviations Pr/*n*-C<sub>17</sub> = pristane/*n*-C<sub>17</sub> ratio; Ph/*n*-C<sub>18</sub> = phytane/*n*-C<sub>18</sub> ratio; Pr/Ph = pristane/phytane ratio; CPI = carbon preference index; MPI = Methylphenanthrene Index (Radke et al., 1982, 1986); TRS = (C<sub>20</sub> + C<sub>21</sub>) / (C<sub>20</sub> + C<sub>21</sub> + C<sub>26</sub> + C<sub>27</sub> + C<sub>28</sub>)



not at all, relative to  $n$ -C<sub>36</sub>. Where present, the  $\gamma$ -carotanes are greatly subordinate to the  $\beta$ -carotanes. Both  $\beta$ - and  $\gamma$ -carotanes were found to be most prominent in the Walchia shale sample (PL9038) and the organic-rich mudrock sample lying directly below it in the Walchia profile (PL9037). The presence of both these compounds is concurrent with higher Pr/ $n$ -C<sub>17</sub> and Ph/ $n$ -C<sub>18</sub> ratios, which was also reported by Duncan and Hamilton (1988) in their study of the Middle Devonian of the Orcadian Basin. Carotenoids are C<sub>40</sub> compounds occurring in continental plants and algae (Tissot and Welte, 1984). They have been reported from a variety of ancient lacustrine sediments which include, apart from the Middle Devonian of the Orcadian Basin (Duncan and Hamilton, 1988; Hall and Douglas, 1983), the Green River shale (Murphy *et al.*, 1967) and the Lower Jurassic East Berlin Formation of the Hartford Basin (Pratt and Burruss, 1988; Kruge *et al.*, 1990). The presence of carotanes has been suggested to be an indicator of saline environments (Hall and Douglas, 1983).

<Figure 4>

Sterane and diasterane content in the lacustrine samples can only, at best, be described as being low relative to both  $n$ -alkanes and hopanes (Fig. 5). The C<sub>29</sub> steranes, both regular and rearranged, seem to be more prominent in samples PL9043, PL9038 and PL9037. The other samples have a dominant C<sub>27</sub> peak. The predominance of C<sub>29</sub> steranes has been used as evidence for the presence of terrigenous organic matter and as characteristic of terrestrial environments (e.g. MacKenzie *et al.*, 1984; Moldowan *et al.*, 1985). While it is true that certain C<sub>29</sub> sterols are common in higher land plants, it is now known that certain varieties of algae or cyanobacteria are also important sources for C<sub>29</sub> sterols (Tissot and Welte, 1984; Volkman, 1986, 1988). Thus, the mere presence of the C<sub>29</sub> sterols should not be used, in isolation, as indicative of terrestrially derived organic matter since there are examples of oils and sediments having high amounts of this compound which are not the result of land plants (McKirdy *et al.*, 1983, 1985). Apart from source implications, the overall low relative concentration of steranes could also reflect the extent of sterane isomerization in response to thermal stress although it is thought that this is unlikely in this case especially since the thermally unstable  $\beta$ -carotanes (Jiang and Fowler, 1986) are present in increased amounts relative to the more resistant  $\gamma$ -carotanes. The aromatic steroids on the other hand, are present in greater abundance when compared to the steranes. Triaromatic steroids in the C<sub>26</sub>-C<sub>28</sub> range predominate over the C<sub>20</sub> and C<sub>21</sub> triaromatics in samples PL9030, PL9037, PL9038 and PL9043 (Table 2). The triaromatics in the black shales are subordinate to the monoaromatic steroids in relative abundance.

<Figure 5>

The terpane distribution shows that the C<sub>29</sub> ( $\alpha\beta$ )-norhopane in all the samples is subordinate to the C<sub>30</sub> ( $\alpha\beta$ )-hopanes and the C<sub>32</sub> homologues are barely detectable. The C<sub>29</sub> and C<sub>30</sub> moretanes are present in the entire sample suite (Fig. 6), with sample PL9043 having the highest relative concentrations. The Walchia Shale profile shows an upward increasing trend in the concentrations of moretane relative to the hopanes, from a minimum in PL9036 to a maximum in PL9040. The terpanes are believed to be derived from either bacterial activity or from higher plants while one kind, the hopane series, is found in relatively large concentrations in bacteria and blue-green algae (Tissot and Welte, 1984). They are useful as indicators of thermal maturity (MacKenzie, 1984), but because of their occurrence in a wide variety of sediments have limited use as paleoenvironmental indicators unless their proportions relative to other compounds, steranes for instance, are considered (Volkman, 1988; MacKenzie *et al.*, 1982).

<Figure 6>

Of interest is the presence of the C<sub>31</sub> triterpane gammacerane which is observed in the mudrocks and shale samples of the Walchia profile and within the Anthracosia shales (Fig. 6). It is conspicuously absent in the mudrock samples associated with the Anthracosia shales.

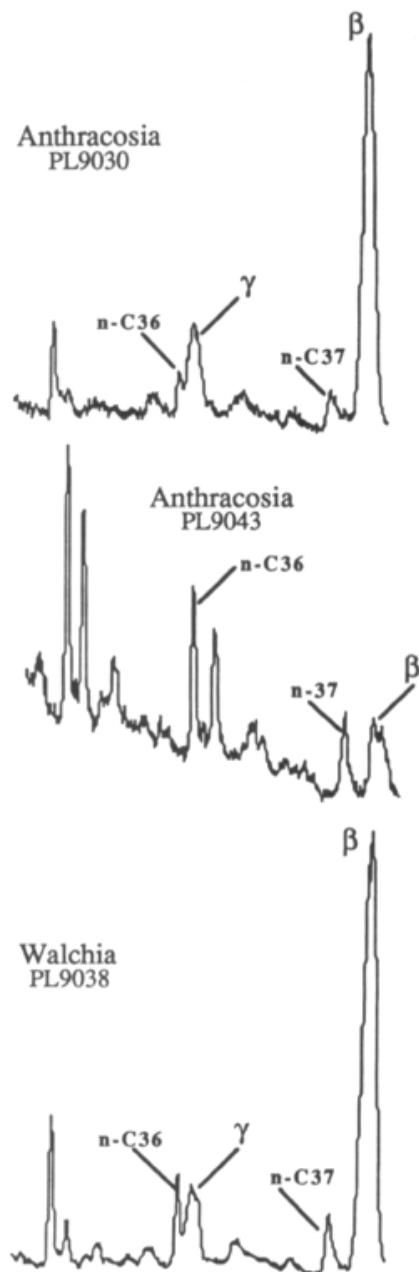


Fig. 4. Partial  $m/z$  83 mass chromatograms showing carotane peaks with corresponding *n*-alkane peaks.

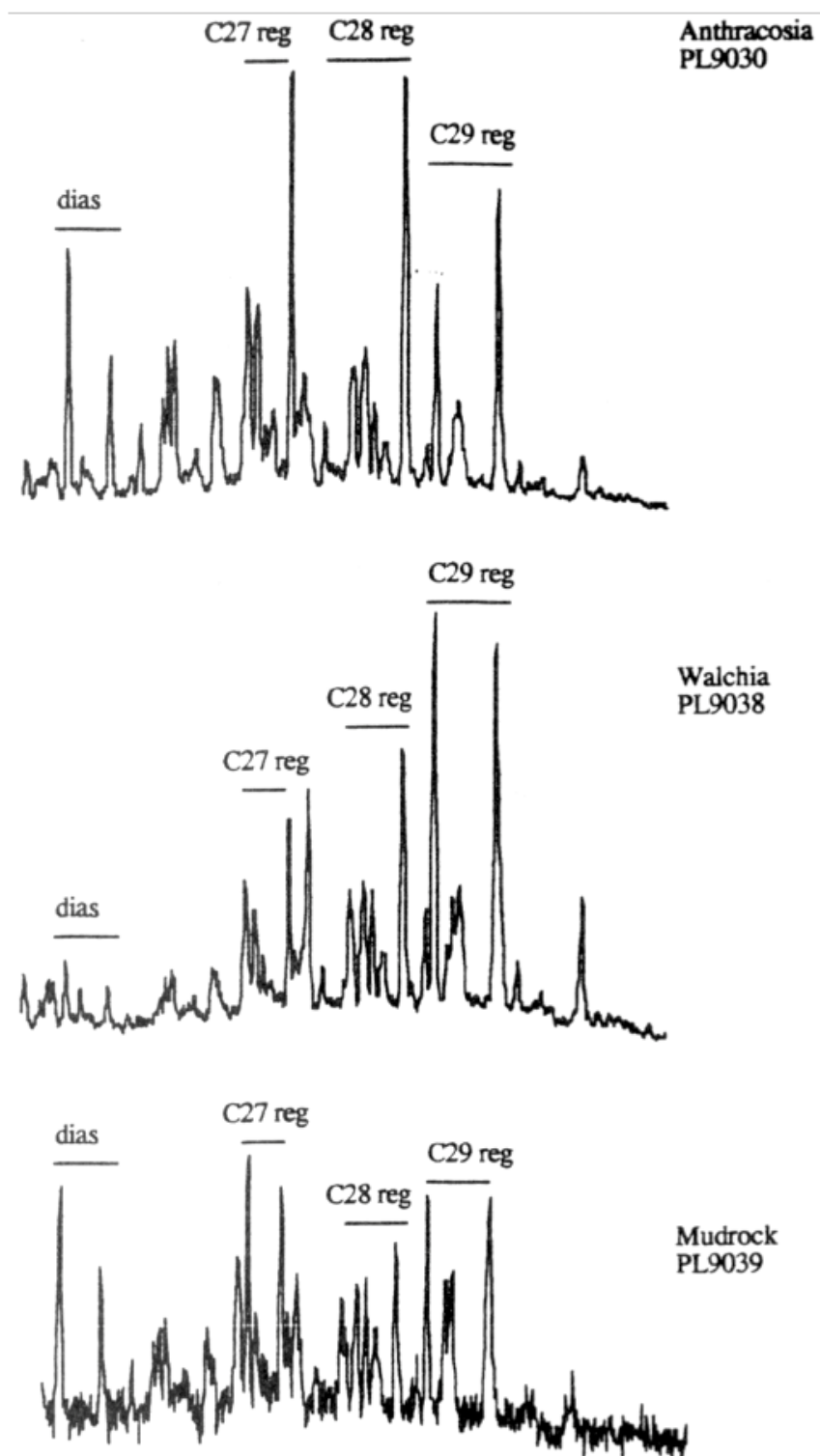


Fig. 5. Partial m/z 217 mass chromatograms of selected, representative lacustrine samples with steranes labelled according to carbon number (reg = regular steranes, dias = diasteranes).

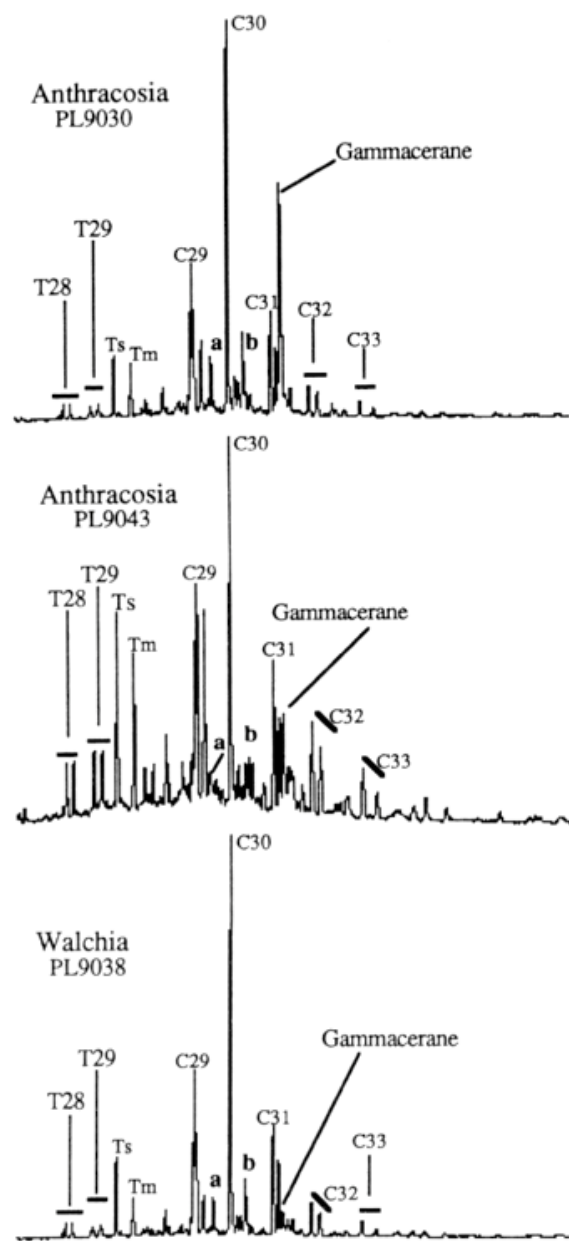


Fig. 6. Partial  $m/z$  199 mass chromatograms of lacustrine black shale samples containing gammacerane. Selected tricyclic terpanes labelled with a "T" and their carbon numbers; hopanes according to their carbon numbers. Peak a =  $C_{29}$  moretane, peak b =  $C_{30}$  moretane .

In the black shale samples, the gammacerane content is observed to have an overall low to medium abundance relative to the C<sub>31</sub>  $\alpha\beta$  hopanes and is more abundant within the Anthracosia shales, with a maximum in PL9030. In the Walchia profile, the compound shows an increase in concentration from a minimum in the mudrock sample at the bottom of the profile to a maximum in the Walchia shale sample (PL9038), after which the concentration decreases again in the overlying mudrocks. It has been suggested that gammacerane is a result of the degradation of tetrahymanol, which is found in protozoans (Brassel and Eglinton, 1983). The compound has been reported as a marker of saline and hypersaline sediments of both lacustrine and marine origin (e.g. Moldowan et al., 1985; ten Haven et al., 1988).

A strong tricyclic terpane concentration relative to the hopanes is consistent throughout the sample suite. These compounds are detectable from C<sub>19</sub> up to C<sub>29</sub>, with the C<sub>23</sub> compound being the major peak in all but the Walchia shale sample, in which the C<sub>21</sub> compound is the predominant peak. The C<sub>19</sub> tricyclics are present in low concentrations in the black shale samples and are often absent in the mudrocks. Also present in all the samples are the C<sub>24</sub> tetracyclic terpanes, believed to originate from microbial activity either during diagenesis or catagenesis (Tissot and Welte, 1984). The tetracyclics are subordinate to the C<sub>26</sub> tricyclics in the black shale samples but the reverse holds true for the mudrock samples.

Other differences observed in the terpane distribution relates to the ratio of 18 $\alpha$  trisnorneohopane to 17 $\alpha$  trisnorhopane (Ts/Tm) which may be used as a maturity indicator due to the fact that molecular ratios based on isomeric pairs change systematically with maturity, provided the technique is used with samples with similar organic matter source (Seifert and Moldowan, 1978). Higher Ts/Tm ratios indicate greater maturity. In the samples analysed, the thermally unstable Tm is found to be either subordinate to Ts or not present at all (Fig. 6). There is no real maturity trend observed within the individual profiles and there appears to be no correlation between these ratios and other maturity parameters used. Thus, the variation is presumed to be a result of changes in the organic matter input.

Standard biomarker maturity parameters based on sterane isomerization were not employed due to the very low sterane concentrations. Triaromatic steroid ratios (TRS), methylphenanthrene indices (MPI) and isoprenoid to *n*-alkanes ratios were determined instead (Table 2). The MPI does not always correlate well with the other maturity parameters. It is known however that this parameter was initially developed for use in coals and rocks containing type III kerogen (Radke et al., 1982, 1986). The TRS ratios range from a maximum value of 1.0 in the mudrock samples PL9028 and PL9036 where only the C<sub>20</sub> and C<sub>21</sub> triaromatic steroids are present, to a minimum of 0.06 in the Anthracosia sample PL9030. The MPI values which range from 0.14 to 0.91 and the isoprenoid to *n*-alkane ratios of between 0.21 and 1.62.

### *Marine samples*

The Kupferschiefer and Border Dolomite samples show simple *n*-alkane distributions that are biased towards the lower molecular weight compounds in the black shale samples (Fig. 7). The Border Dolomite (PL9050) and the overlying calcareous Kupferschiefer shale sample (PL9051) have a higher proportion of the long chain *n*-alkanes relative to the short chain alkanes. The Border Dolomite shows a slight even-odd predominance in the C<sub>24</sub>-C<sub>30</sub> range while the calcareous Kupferschiefer shale shows an even-odd predominance in the C<sub>20</sub>-C<sub>28</sub> range. This is a common feature in carbonate or evaporitic sediments (Tissot and Welte, 1984). However, the Pr/Ph ratio is high throughout the profile (1.65-1.73; Table 2). There is no even-odd predominance observed in the overlying black shale samples nor is there an appreciable odd-even predominance within the high molecular weight region. All five

samples however show a predominant C<sub>15</sub> and/or C<sub>17</sub> peak relative to the C<sub>14</sub>, C<sub>16</sub> and C<sub>18</sub> peaks which is indicative of marine algal organic matter (Tissot and Welte, 1984). A dominant C<sub>27</sub> and/or C<sub>35</sub> peak is normally seen in carbonate source rocks (McKirdy *et al.*, 1983, 1985); this feature is absent however in the Border Dolomite. The distribution of branched alkanes relative to the *n*-alkanes is fairly consistent with the exception of the Border Dolomite. The Border Dolomite contains a larger proportion of isoprenoids relative to the *n*-alkanes. The Pr/Ph ratios are, however, consistent throughout the profile and indicate deposition in an anoxic, marine environment.

<Figure 7>

Concentrations of both steranes and triterpanes are low relative to the normal and branched alkanes. The carbon number distributions of the steranes show the C<sub>28</sub> steranes to be subordinate to the C<sub>27</sub> and C<sub>29</sub> steranes (Fig. 8). Diasteranes are abundant throughout the profile. The triaromatic steroids are more abundant, relative to the steranes, in the Kupferschiefer shales than in the Border Dolomite. The triaromatic steroids predominate over the monoaromatic steroids except in the dolomite where the former appear to be slightly subordinate.

<Figure 8>

The m/z 191 chromatograms show that the marine samples possess low concentrations of triterpanes and tricyclic terpanes, relative to steranes, with the preeminent peak being C<sub>30</sub> hopanes. Of interest is the presence of the extended hopanes detectable up to C<sub>35</sub> with the C<sub>35</sub> homologues being subordinate to the C<sub>34</sub> (Fig. 9). It is believed that the C<sub>35</sub> prokaryotic precursor (Ourisson *et al.*, 1979) may yield a series of alkanes and acids extending to C<sub>35</sub> in confined anoxic environments, and C<sub>32</sub> in more open environments (Tissot and Welte, 1984). The  $\alpha\beta$  hopanes (C<sub>29</sub>-C<sub>35</sub>) generally occur in greater amounts relative to the moretanenes. The Ts/Tm ratios are low despite other evidence indicating elevated maturity levels of these sediments. However, the Tm compound has been proposed as a carbonate-specific biomarker (McKirdy *et al.*, 1983, 1985; Rullkotter *et al.*, 1985). The tricyclic terpane content appears to be fairly consistent within the profile with the C<sub>23</sub> tricyclics being the most abundant. The C<sub>24</sub> tetracyclic terpanes are clearly detectable and are present in almost equal abundance to, or slightly predominant over, the C<sub>26</sub> tricyclics in the first three samples at the bottom of the profile. In samples PL9053 and PL9054 the C<sub>24</sub> tetracyclics are subordinate to the C<sub>26</sub> tricyclics.

<Figure 9>

Maturity levels for the marine samples were determined from triaromatic steroid ratios (0.09-0.81), methylphenanthrene indices (0.35-0.44) and isoprenoid to *n*-alkane ratios (0.53-2.08; Table 2). The extent of sterane isomerisation was too advanced to allow calculations of sterane ratios. A disparity is observed between the MPI values and that of the other maturity parameters in that the former are anomalously low for samples that appear to be well within the oil window. Again, this could be the result of the fact that the MPI was initially developed for use in coals and rocks with type III kerogen (Radke *et al.*, 1982, 1986).

## ORGANIC PETROGRAPHY RESULTS

Seven whole rock samples were available for qualitative petrographic observations: samples PL9043 (Anthracosia Shale), PL9037, PL9038 (Walchia Shale), PL9039, PL9040, PL9050 (Border Dolomite) and PL9052 (Kupferschiefer Shale).

The results reveal that the lacustrine samples can be differentiated in terms of the microscopically observable amount and type of organic matter present. Alginite appears to be the dominant organic matter type in the Anthracosia and Walchia Shale samples as well as

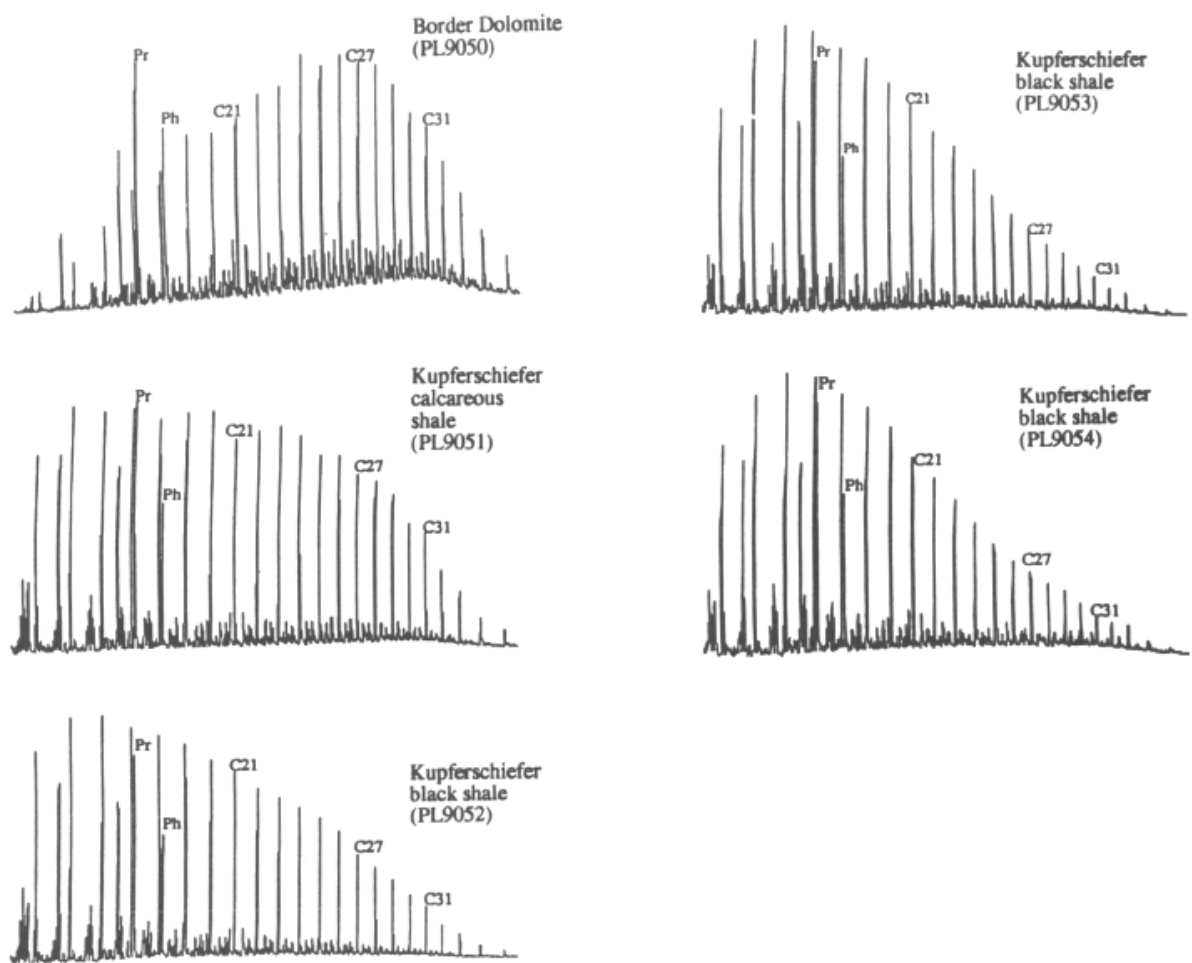


Fig. 7.  $m/z$  99 mass chromatograms that show the normal alkane and isoprenoid distributions of the Kupferschiefer profile with  $n$ -alkanes labelled according to carbon number. The Border Dolomite sample is located at the bottom of the profile.

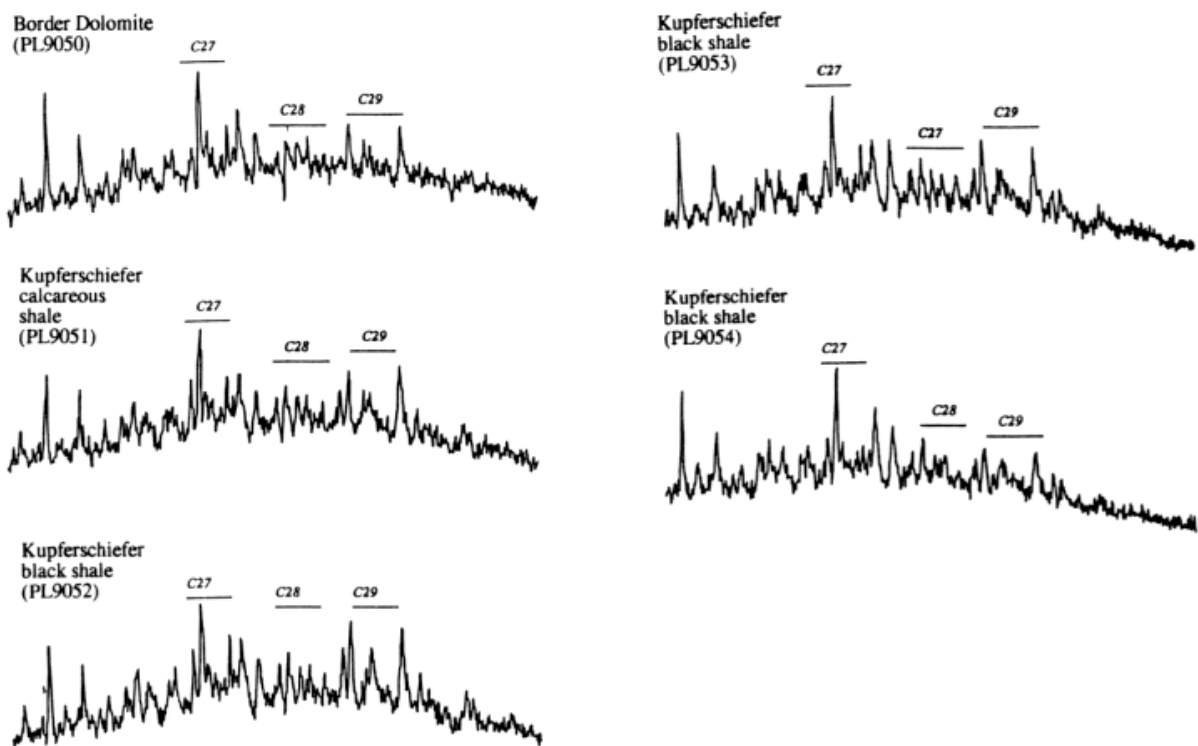


Fig. 8. Partial m/z 217 mass chromatograms of the Kupferschiefer profile with steranes labelled according to carbon number.



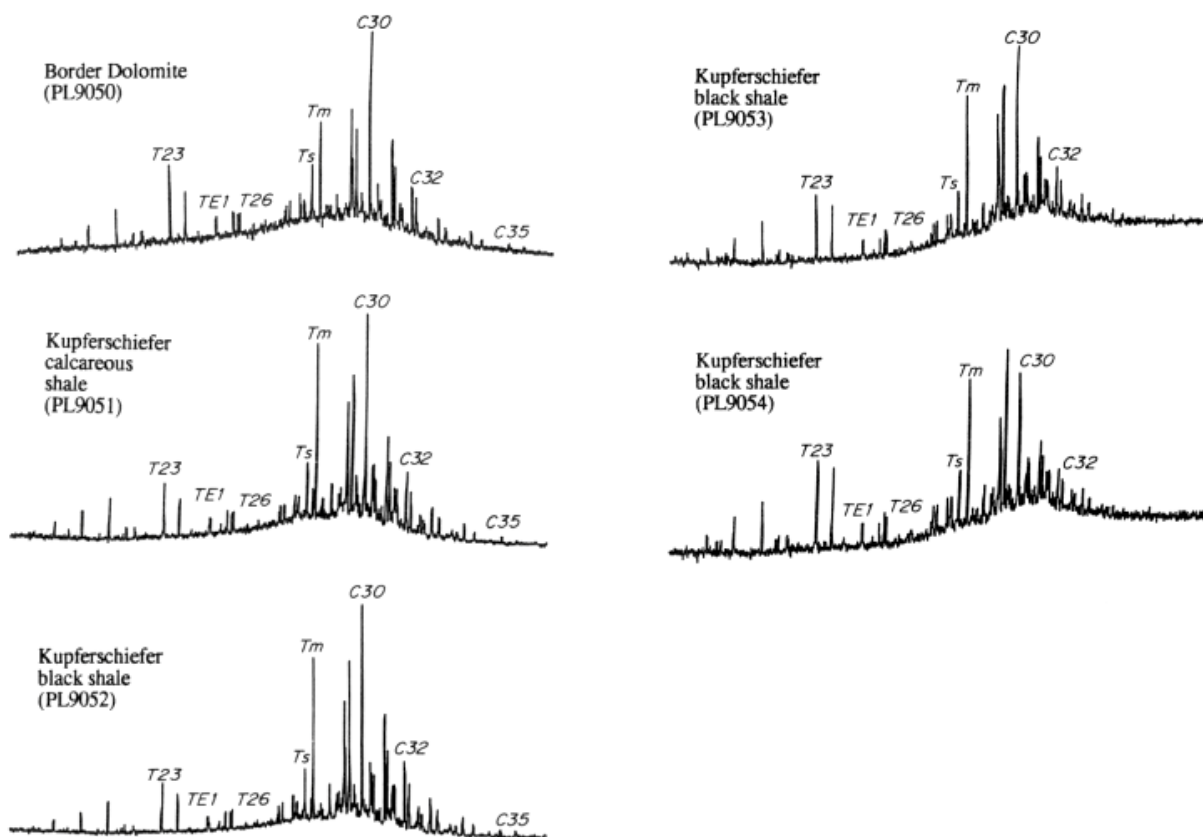


Fig. 9. Distributions of terpanes as seen in the partial  $m/z$  191 mass chromatograms of the Kupferschiefer profile. Selected tricyclic terpanes labelled with a "T" and their carbon numbers; hopanes according to their carbon numbers. TE1 =  $C_{24}$  tetracyclics.

the organic-rich mudrock sample PL9037. Three different types of algal material were observed namely: (1) single elongated and oval bodies, (2) rarely *Botryococcus*, and (3) lamalginite layers. Sporinite is also relatively common in these samples. Exudatinite is observed in association with sulphides or as vug fillings. In the samples studied, the mineral-bituminous groundmass strongly fluoresced either yellow or yellow-brown depending on the maturity and relative concentrations of the organic matter present. Vitrinite is relatively rare and occurs as angular, oxidized fragments. The presence of reworked material is evident. Inertinite is present in the form of semifusinite and oxidized megaspores which are fairly common. In general, the Anthracosia Shale sample shows a lower abundance of lamalginite than the Walchia. There is very little fluorescing material observed in the PL9039 and PL9040 mudrock samples from the Walchia profile and what little there is occurs as liptodetrinite and exudatinite. Vitrinite is again rare in these samples.

In the marine samples studied, alginite is the dominant organic matter. It is relatively abundant and occurs as single elongate algal bodies some of which are probably *Campania*, or as layers of lamalginite. The groundmass of the samples fluoresces green or yellow-green which is suggestive of relatively high organic matter content. Exudatinite is also common and it is always associated with the sulphides bornite and marcasite. The Border Dolomite sample (PL9050) contains less organic matter when compared to the shale (PL9052). Vitrinite is rare in these samples and where present occurs as angular fragments. The above characteristics are all indicative of organic matter of marine origin with very little terrestrial input.

Vitrinite reflectance measurements were obtained on angular vitrinite particles with random reflectance values taken on 25 readings for all but sample PL9038, in which 10 readings were taken (Table 3). In terms of maturity, all the lacustrine samples studied appear to be within the conventional window of oil generation with mean values of between 0.70 and 0.74. The mean values from the marine samples range from 0.78 to 0.81, indicating that their maturity corresponds to either the marginal or middle part of the oil window.

<Table 3>

## DISCUSSION

### *Organic matter and depositional environment*

The bitumen extracts of the lacustrine black shales are rich in *n*-alkanes with no evidence of biodegradation. While not being dominated by long chain alkanes, the medium to high molecular weight alkanes are certainly present in greater amounts than are the short chain alkanes. Long chain *n*-alkanes are derived from higher plant waxes and some varieties of algae. The Pr/Ph ratio of between 0.29 and 1.72 and the sterane distribution pattern, which shows a slight but distinct predominance of C<sub>29</sub> and/or C<sub>27</sub> compounds over C<sub>28</sub> compounds, are consistent with the above premise. The wide variability of the Pr/Ph ratios, while falling within the expected range for sediments deposited under anoxic conditions, suggests that there was variable intensity in lake water anoxia. It has been also suggested that high Pr/Ph ratios could reflect the relationship between contributing organisms and chemistry of the environment, for example, low salinity, rather than simply the anoxic/oxic conditions (Didyk *et al.*, 1978; Mello and Maxwell, 1990). However, the results obtained in this study contrast with the above premise in that the high Pr/Ph ratios correspond to the samples containing high salinity indicators such as carotenoid compounds and gammacerane.

The presence of  $\gamma$ - and  $\beta$ -carotenes is prominent in the black shales and the more organic-rich mudrock samples and their general absence in the leaner mudrock samples is believed to indicate that these compounds represent a sensitive monitor of the relative amounts of terrestrially derived organic matter and/or primary source input.  $\beta$ -Carotene was

Sample number	Romean	Sd
PL9043	0.924	0.154
PL9037	0.716	0.102
PL9038	0.698	0.097
PL9039	0.742	0.216
PL9040	no measurements possible	
PL9050	0.813	0.263
PL9052	0.777	0.202

Table 3. Vitrinite reflectance measurements of selected lacustrine and marine samples, based on 25 readings for all samples except PL9038 where only 10 readings were taken.

first identified in the Green River shale (Murphy *et al.*, 1967) and the presence of these high-molecular weight compounds generally appears to be representative of saline or hypersaline terrestrial environments. The variable concentrations of these compounds in the Anthracosia shales could be a reflection of subtle changes in the organic matter input and lake water salinities in response to changes in the depositional environments, that is, whether the sediments were deposited near to or away from the ancient lake shoreline. The presence of gammacerane in conjunction with carotanes is believed to be indicative of enhanced salinity levels within the lake waters. The inconsistency observed in the relative amounts of gammacerane and carotane present in the Walchia sample does not necessarily mean a salinity decrease in the waters of Walchia Lake relative to Anthracosia Lake. It may imply instead that primary source input, and not environment, may be the controlling factor in determining the amount of carotanes preserved. The presence of both biomarkers suggests enhanced salinity levels, but not to the extent associated with hypersaline environments, which contain high concentrations of both (Mello *et al.*, 1989).

The high Pr/Ph ratios, low to high relative abundance of  $\gamma$ - and  $\beta$ -carotanes and low to medium relative abundance of gammacerane suggest that water salinity in both the Anthracosia and Walchia Lakes was not high enough to achieve the ratios and relative abundances found in hypersaline environments (Mello and Maxwell, 1990). It is therefore believed that the sediments were deposited in waters that had experienced salinity increases over normal fresh-water lake conditions and that had fluctuated with time. The low sterane concentration, high C<sub>30</sub>  $\alpha\beta$  hopane concentrations, high hopane/sterane ratios, abundant tricyclics and the presence of the C<sub>24</sub> tetracyclics are all indicative of a bacterial origin for a significant proportion of the extractable organic matter. Furthermore, Mello and Maxwell (1990) report that these features are also consistent with deposition in lake-waters of enhanced salinity. The lack of extended hopanes, however, suggests that deposition occurred in a relatively open basin (Tissot and Welte, 1984).

The organic remains preserved in the lake sediments are consistent with the above molecular chemical characteristics. With the exception of the mud rock samples PL9039 and PL9040, the predominance of alginite in the samples analysed confirms an algal origin for a large proportion of the organic matter input. The presence of alginite also reflects deposition under deeper water conditions for the black shales and organic-rich mudrocks while the presence of liptodetrinite in the leaner mudrock sample indicates shallower water conditions. The occurrence of *Botryococcus* at first seems incompatible with the high salinity biomarker indicators since these blue-green algae are indicative of deposition in a fresh-water environment. It is conceivable, however, that the salinity levels of both the Anthracosia and Walchia Lakes had increased during the last stages of lacustrine sedimentation. This is believed to be a result of drastic reduction in lake water levels in the regression that followed the period of maximum transgression that was coincident with black shales deposition (Mastalerz and Wojewoda, 1988). The presence of sporinite and vitrinite in all the samples is evidence of some terrestrial organic matter input.

The marine sediments analysed show molecular geochemical characteristics that are clearly distinct from those of the lacustrine sediments discussed earlier. The *n*-alkane distribution seen in all five samples analysed is typical of marine source rocks with predominantly marine organic matter input. The presence of larger amounts of the long-chain lipids relative to the short-chain lipids in samples PL9050 and PL9051 indicates that these samples have a higher proportion of reworked terrestrial organic matter when compared to the Kupferschiefer black shales. The even-carbon number predominance observed in the middle molecular weight region in both these samples is a common feature in carbonate or evaporitic sediments although pristane predominates over phytane in all five samples. The absence of an even-carbon number predominance in the overlying Kupferschiefer black

shales could be a function of the maturity levels of these samples, the original organic matter input or the lithological changes involved. The dominant C<sub>15</sub> and/or C<sub>17</sub> peak within the low molecular weight range, which is observed throughout the profile, is evidence of mainly marine algal organic matter input. The predominance of the C<sub>27</sub> steranes in the sterane distribution and low hopane/sterane ratios is consistent with marine organic matter, in particular marine phytoplankton, being the main contributors to the organic matter content in these samples. The overall low concentrations of steranes relative to the *n*-alkanes and the abundant diasteranes present indicate elevated maturity levels for these sediments. The C<sub>29</sub> steranes were most likely sourced by marine algae but the presence of some reworked terrestrial organic matter cannot be ruled out. Organic petrography, however, confirms that marine organic matter is predominant in these samples and that there is very little terrestrial input.

Extended hopanes indicate deposition in a confined anoxic basin and their presence in all the marine samples is in agreement with the generally accepted sedimentary setting for the Zechstein Basin. That this was an evaporitic basin with substantial carbonate sedimentation is demonstrated also in the even carbon number predominance observed in the Border Dolomite and calcareous Kupferschiefer samples and the high T<sub>m</sub> values, relative to T<sub>s</sub>, obtained for the entire profile. In the case of the Border Dolomite, there is considerable doubt as to whether the extractable organic matter in the sample analysed is indigenous to the unit. Based on the carbonate-specific biomarker features proposed by McKirdy *et al.*, (1983, 1985), the absence of a dominant C<sub>27</sub> and/or C<sub>35</sub> *n*-alkane peak, the presence of abundant diasteranes, and C<sub>35</sub> hopanes which are subordinate to its C<sub>34</sub> homologues mitigate against the presence of a carbonate source rock. Thus, the extracted organic matter in the dolomitic sample is believed to represent migrated material from an as yet unknown source.

### *Maturity*

Optical and molecular maturity parameters show that large variations in maturity occur both laterally and vertically over very short distances in the lacustrine samples while the marine samples display a more consistent maturity level. There appears to be a lack of correlation between the chemical maturity parameters employed, in particular the MPI, and optical indicators of maturity. The paucity of vitrinite in type I and type II kerogen could place an important limitation on the use of reflectance as maturity indicators in rocks containing these kerogen types (Alpern, 1980). By nature of the fact that the organic matter found in source rocks is amorphous, only random reflectance values can be determined and this can result in a wide range of values. Furthermore, marine or lacustrine kerogens may also contain gelified particles resembling vitrinite, although their chemical composition and the evolution of reflectance may be different (Alpern *et al.*, 1978). The above situations and the presence of reworked material and/or nonindigenous vitrinite could account for the wide range of reflectance values obtained in this study.

The assessment of the thermal maturation of organic matter by monitoring the extent of isomerization and aromatization reactions has been proven to be reliable (MacKenzie, 1984; Radke *et al.*, 1982). Methylphenanthrenes are often among the most abundant compounds in the aromatic fraction of fossil fuels. The validity of the MPI as a maturity parameter is demonstrated through the observed strong correlation between the MPI and vitrinite reflectance data (Radke *et al.*, 1982). However, the original calibration between MPI and vitrinite reflectance was on coaly organic matter (Radke *et al.*, 1986). However, from the data obtained in this study, it appears entirely possible that this correlation is only viable when applied to rocks containing mainly type III kerogen and that in fact the MPI is significantly influenced by changes in organic matter input. Sterane isomerization was not

used as a maturity parameter in this study due to the low sterane concentrations in the lacustrine samples which might have affected the results. Also, the advanced stage of isomerization in the marine sediments would have rendered the results from these samples meaningless. Furthermore, it was felt that a consistent set of parameters should be used in both the lacustrine and marine samples in order to make comparisons between the two types of sediments. Triaromatic steroid ratios appear to work best in this study as they cover the entire range of diagenesis to peak oil generation (MacKenzie et al., 1981). However, no triaromatic steroids were detected in the m/z 231 mass chromatograms of the lacustrine mudrocks due, presumably, to their very low organic-matter content.

In general, conventional interpretation of the data suggests that the lacustrine mudrocks appear to be at a higher maturity level compared to the shales and that both the Anthracosia and Walchia Shales are within the oil window. The differences in maturity levels between samples from different locations could be a result of local variations in heat flow values (Dowgiallo, 1987), or differences in the thermal conductivities of particular lithologies. The vertical variations are however more difficult to explain especially since they occur within depth intervals of less than 6 m. One possible explanation for these apparent changes could be that the original organic matter input in the different lithologies analysed is being reflected in the maturity parameters calculated. In any event it is clear that maturity parameters based on aromatic hydrocarbons (e.g. MPI), calibrated in terrestrial coal sequences, should not be used in isolation and indiscriminately in lacustrine sequences.

Vitrinite reflectance and TRS ratios obtained indicate that the Kupferschiefer shale samples are well within the oil window. The MPI values are anomalously low but fairly consistent, suggesting that this geochemical parameter may not be suitable for use in carbonate environments. TRS ratio value for the Border Dolomite is inconsistent because it indicates marginal maturity, while the vitrinite reflectance value places it at a similar maturity level as the Kupferschiefer shales. The maturity of the shales could be related to the Rotliegendes brines responsible for mineralization of the Kupferschiefer horizon (Jowett, 1986). The brines are believed to have reached temperatures of up to 90 °C in the subsurface and at these temperatures could very well have affected the thermal maturation of the preserved organic matter (Tissot and Welte, 1984).

## CONCLUSIONS

1. The primary organic matter input into both the Anthracosia and Walchia Lakes is represented by algal lipids. There is evidence also for bacterial lipids as well as varying amounts of land plant debris and some protozoan lipids.
2. The prominence of carotanes and gammacerane in some samples suggests that enhanced salinity in the water column existed intermittently although the high Pr/Ph ratios and the absence of extended hopanes are not in keeping with this salinity enhancement. Variability within each lacustrine sequence suggests that anoxia in both lakes appears to have fluctuated with time.
3. The lacustrine sediments are not all at the same maturity levels possibly due to the influence of organic matter type on maturity parameters and/or due to variations in heat flow rates within the region. Most maturity parameters indicate that the samples are at the marginal to middle mature stage of oil generation.
4. The primary organic matter input in the Zechstein marine samples analysed is represented by marine algal lipids with some bacterial and cyanobacterial lipids. Reworked terrestrial material is probably also present, especially in the Border Dolomite and calcareous Kupferschiefer shale samples.

5. The occurrence of an even carbon number predominance and extended hopanes, as well as low Ts/Tm ratios in the marine sediments, indicates deposition under anoxic bottom waters conditions in a restricted, evaporitic basin with substantial carbonate sedimentation.

6. Maturity parameters based on aromatic hydrocarbons and vitrinite reflectance indicate that the Border Dolomite and Kupferschiefer shales are presently at the middle mature region of oil generation. The high maturity levels of the marine sediments are believed to be related to the presence of mineralization fluids.

7. The absence of carbonate-specific biomarkers indicates that the Border Dolomite is not a carbonate source rock. The organic matter present represents migrated material from an as yet unknown source.

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