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## CORRELATION OF CRUDE OILS AND SOURCE ROCKS IN THE GERMAN MOLASSE BASIN

### APPLICABILITY OF CHROMATOGRAPHIC TECHNIQUES

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#### SUMMARY

Chromatographic techniques can be applied successfully in organic geochemical research. Taking the oil-oil and oil-source rock correlations in the German Molasse basin as examples, it is demonstrated how classical column chromatography can help in oil-oil correlation work. Secondary alteration of oils can be detected by analysing the fraction of saturated hydrocarbons by means of capillary column gas chromatography. Aromatic hydrocarbons are less affected by biodegradation. The high-performance liquid chromatographic separation of this group of compounds is also demonstrated. Final conclusions in oil-oil correlations can be drawn from gas chromatographic-mass spectrometric (GC-MS) analyses of biomarker components (steranes, triterpanes).

Preliminary results of oil-source rock correlations were obtained by using thermochromatographic methods (pyrolysis-GC) for pre-selecting potential source rocks and GC-MS investigations of steranes.

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#### INTRODUCTION

Owing to the increasing demand for fossil fuels it is becoming more and more important to intensify exploration for crude oils and to investigate sedimentary basins with advanced geophysical and geochemical techniques. Organic geochemical methods are powerful tools for evaluating the hydrocarbon potential of a sedimentary sequence.

The aim of this paper is to show how chromatographic techniques can be used successfully in crude oil-crude oil and crude oil-source rock correlation work. Taking the South German Molasse basin as an example, it is demonstrated how the crude oils found in this region can be grouped together. Further, some preliminary results are presented on the correlation of these crude oils with possible source rocks. Such investigations may reveal important information on migratory pathways of crude oils, which in turn may lead to an increase (or decrease) in the exploration efforts in the basin investigated. Because drilling boreholes is very expensive, such analyses have a considerable economic importance.

## EXPERIMENTAL

### *Column chromatography*

Crude oils were topped at 40°C for 6 h. The deasphaltation procedure involved pouring the sample into a mixture of dichloromethane–light petroleum (b.p. 40–60°C) (1:30) and centrifugation at 1500 *g* for 20 min. After removal of the solvent the samples were redissolved in *n*-heptane and then chromatographed on a 50 cm × 4 mm I.D. column, of which the top one third was filled with alumina (neutral, activated at 700°C for 2 h) and the bottom two thirds with silica gel (activated at 400°C for 6 h, 70–230 mesh). The saturated hydrocarbons (SAT) were eluted using *n*-heptane, the aromatic hydrocarbons (ARO) with dichloromethane and the hetero-compound fraction (HET), containing N-, O- and S-substituted molecules, with dichloromethane–methanol (2:1). For a higher sample throughput an automated instrument was constructed using a desktop computer (Commodore PET 2001) as a controlling device, electrically controlled/pneumatically actuated Valco valves, a Waters M 45 solvent delivery pump and a fraction collector. A detailed description of the instrument, which is manufactured by R. Fromholz (Hannover, G.F.R.), is available from the authors on request.

Sedimentary material was ground to less than 100 μm, Soxhlet extracted with dichloromethane for 18 h and then deasphalted and fractionated as described above.

### *Gas chromatography and gas chromatography–mass spectrometry*

The SAT fraction was further investigated by gas chromatography (GC) using a Hewlett-Packard 5985 A instrument composed of a 5840 A gas chromatograph, a flame-ionization detector (FID), a quadrupole mass spectrometer and a 21 MXE computer. For separation a 30 m × 0.28 mm I.D. capillary column coated with SP-2100 was used. Samples were injected at 100°C and after 1 min the column temperature was programmed at 10°C/min to 170°C, then at 4°C/min to 250°C. After an isothermal period of 22 min the column temperature was further increased to 270°C at 2°C/min. The injector and detector temperatures were set at 220 and 280°C, respectively. Helium was used as the carrier gas. The column effluent was split in the ratio 1 (to the FID) to 2 (to the mass spectrometer). The coupling to the mass spectrometer was direct. For mass spectrometric (MS) analysis the selected-ion monitoring mode was preferred, measuring 200 msec at each mass point (*m/e* 191.2, 217.2 and two others) with an electron energy of 70 eV.

### *High-performance liquid chromatography*

The ARO fraction was further separated by means of high-performance liquid chromatography (HPLC) in the reversed-phase mode with a DuPont 830 instrument, equipped with a UV detector (254 nm), a 25 cm × 4.6 mm I.D. and a 15 cm × 4.6 mm I.D. Zorbox-ODS column and a 5 cm × 1 mm I.D. guard column packed with Spherisorb ODS. For elution of compounds a hyperbolic gradient from 65% aqueous methanol to pure methanol within 100 min was used. Working at constant pressure, the flow-rate at the initial composition was 0.9 ml/min. The column temperature was 65°C.

*Thermochromatography (pyrolysis-GC)*

The amount and composition of the sedimentary organic material was investigated with a Spex MP 3 thermochromatograph. A few milligrams of the sample were pyrolysed under helium in the temperature range 25–600°C at 40°C/min. An aliquot of the volatiles was measured with an FID and the remainder of the material was trapped on a 1 ft. × 1/8 in. O.D. column packed with 4% SE-30 on Porapak Q (80–100 mesh). Heating of the trap to 220°C transferred all volatiles on to a 6 ft. × 1/8 in. O.D. column packed with 3% Dexsil 300 GC on Chromosorb W HP (80–100 mesh). GC was then performed from 30 to 300°C at a rate of 12°C/min.

## RESULTS AND DISCUSSION

*Oil-oil correlation*

The column chromatographic separation of crude oils is shown in Table I. For comparison purposes these data are plotted in a triangular plot (Fig. 1b). This coarse separation allows the crude oils found in the German Molasse basin to be subdivided into three groups: firstly the oils found in reservoirs of Triassic age in the Western part of the basin (area I; Fig. 1a), secondly oils that have accumulated in reservoirs of Tertiary age (area II, Western part; area III, Eastern part; Fig. 1a), and thirdly oils that were found in the North-Eastern part of the Molasse basin (area IV; Fig. 1a). The differentiation of the oils is based mainly on the variation of the saturated hydrocarbon content.

The composition of crude oils may be altered by various factors. In addition to thermal destruction and removal of components by washing with water, biodegradation also has to be considered. Bacterial attack on a crude oil starts with the reduc-

TABLE I  
COLUMN CHROMATOGRAPHIC SEPARATION OF CRUDE OILS FROM THE GERMAN MOLASSE BASIN

Field	Area	Age of reservoir	Composition of deasphalted oil (%)		
			SAT	ARO	HET*
Ilmensee	I	Triassic	50.9	18.4	30.7
Pfullendorf	I	Triassic	48.7	20.2	31.1
Wald	I	Triassic	49.7	19.3	31.0
Mönchsrot	II	Tertiary	55.6	15.9	28.5
Heimertingen	II	Tertiary	56.4	18.0	25.6
Lauben	II	Tertiary	56.2	14.8	29.0
Lauberhart	II	Tertiary	55.6	11.9	32.5
Arlesried	II	Tertiary	56.7	21.1	22.2
Darching	III	Tertiary	55.8	15.5	28.7
Höhenrain	III	Tertiary	52.7	14.1	33.2
Assling	III	Tertiary	58.3	22.9	18.8
Mühdorf	IV	Tertiary	24.6	23.8	51.6
Teising	IV	Tertiary	29.2	38.5	32.3
Velden	IV	Tertiary	27.9	25.6	46.5
Ampfing	IV	Tertiary	31.9	31.2	36.9
Isen	IV	Tertiary	23.8	25.3	50.9

\* HET = 100% - SAT - ARO.

tion of aliphatic compounds, especially with the removal of *n*-alkanes<sup>1,2</sup>. Hence looking only at the triangular plot and neglecting the composition of the SAT fraction may lead to incorrect results.

Typical traces from the GC investigation of the SAT fraction are shown in Fig. 1c. The most abundant peaks represent *n*-alkanes. A direct correlation of the oils from areas II and III can clearly be seen. Triassic oils from area I possess a pronounced *n*-alkane pattern, but this pattern is completely different from the pattern of the area II/III oils, best deduced from the maximum of the *n*-alkane distribution. The gas chromatogram from crude oil from area IV shows a lack of *n*-alkanes. This trace is typical of a biodegraded oil.

Considering these results, there is no possibility of correlating the crude oils

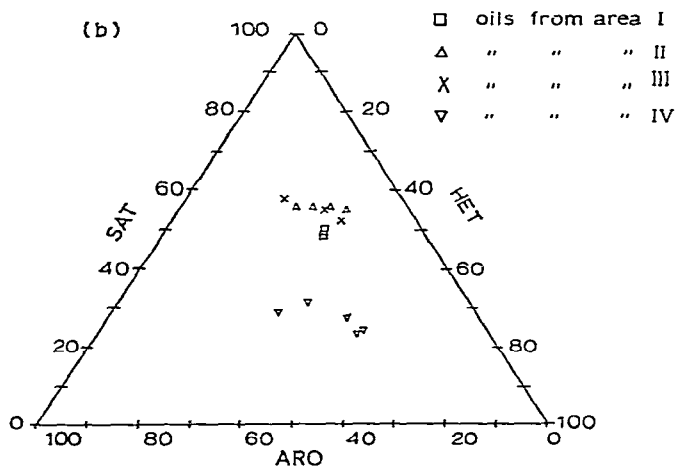
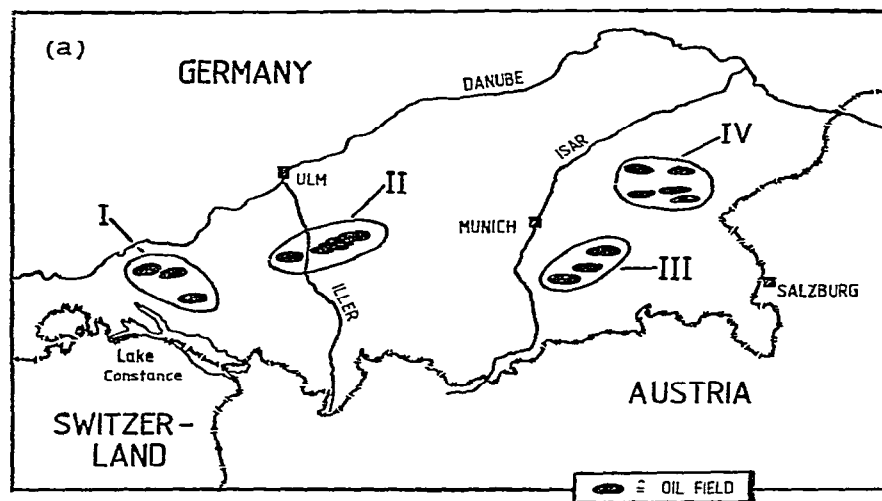


Fig. 1.

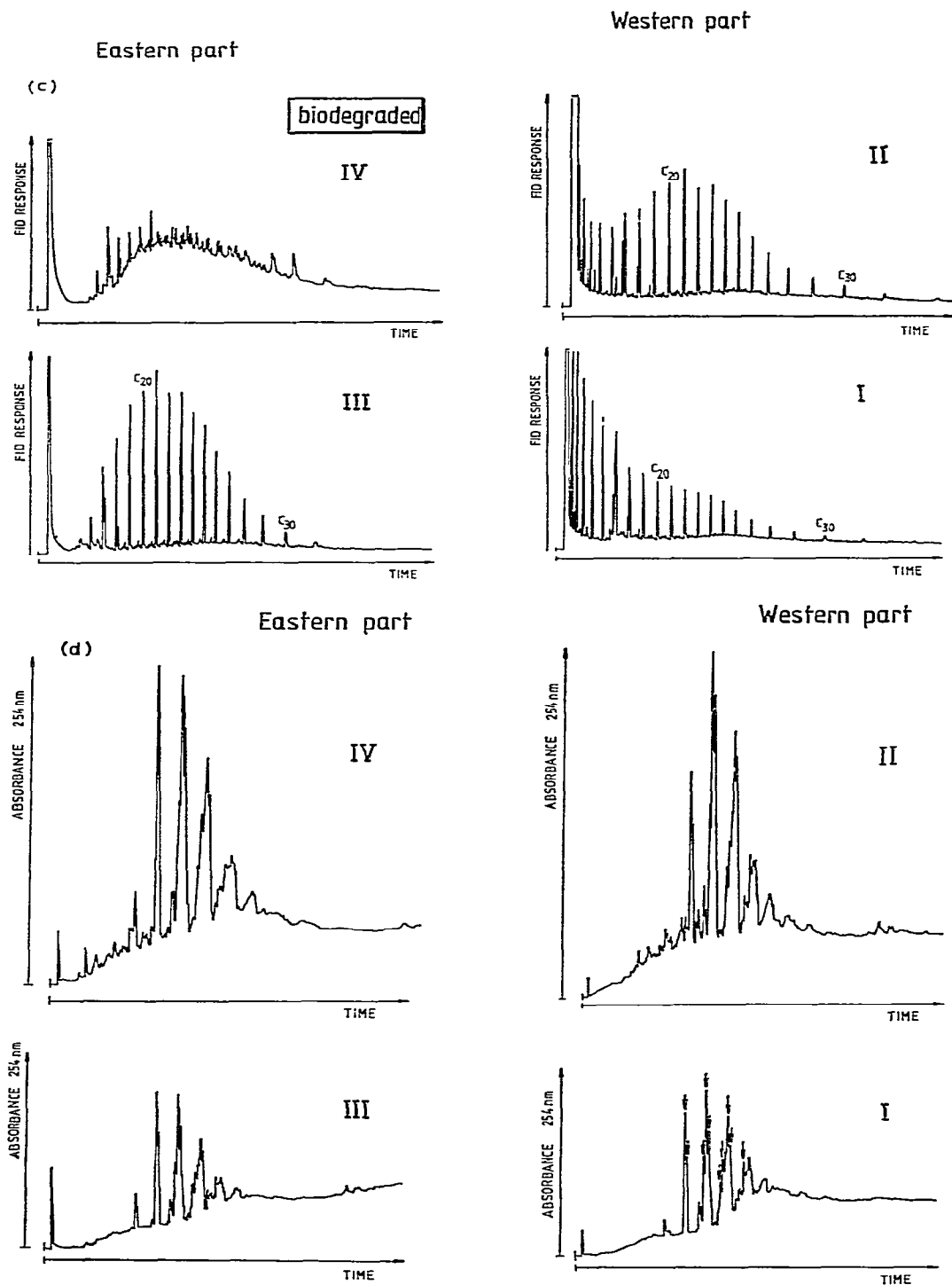


Fig. 1. (a) Map of the South German Molasse basin. (b) Triangular plot of the results of column chromatographic analyses of crude oils. (c) GC traces of SAT fractions of crude oils. (d) HPLC traces of ARO fractions of crude oils. Locations are indicated by I-IV.

from area IV with the other oil groups based only on the GC investigations. The aromatic hydrocarbon distribution is not so easily influenced by bacterial action because the nuclei are substituted with short alkyl substituents, mostly methyl groups, and direct action on the aromatic ring was observed only in some special cases<sup>3</sup>.

We investigated the distribution of aromatic hydrocarbons in the ARO fraction by means of HPLC. Typical traces for oils from all four areas are shown in Fig. 1d. These complex chromatograms without tracer compounds are easily compared with one another by using a simple equation derived in detail elsewhere<sup>4</sup>. Briefly, the heights of a set of peaks are measured and the height ratios of adjacent peaks are calculated, thus eliminating quantification problems. The set of ratios obtained is considered as a description of a vector. To compare two samples the distance of the vector tips,  $D$ , is then calculated by means of the equation

$$D = \left[ \sum_{a=1}^n (h_{ai} - h_{aj})^2 \right]^{1/2}$$

where  $h_{ai}$  and  $h_{aj}$  are corresponding peak-height ratios and  $n$  is the number of ratios. To deduce a positive correlation, this  $D$  value has to be less than, *e.g.*, 1.5 when using 10 heights in this calculation. In Table II the results for the four oils shown in Fig. 1d are presented. The heights taken for this calculation are indicated by arrows (compare Fig. 1d, bottom trace). All  $D$  values calculated indicate a positive correlation. In detail there are only slight differences between the chromatograms obtained. The findings of this investigation are contradictory to those of the GC and column chromatographic analyses. We feel that further conclusions can be drawn only by considering not only total fractions of a crude oil but also suitable substance classes within those fractions.

TABLE II

$D$  VALUES FOR THE HPLC SEPARATION OF CRUDE OILS FROM THE GERMAN MOLASSE BASIN (AREAS I-IV)

Field	Area	I	II	III	IV
Pfullendorf	I	0.00	1.30	0.86	1.42
Arlesried	II		0.00	0.91	1.02
Darching	III			0.00	0.65
Isen	IV				0.00

Biological markers are molecules synthesized by organisms. The molecules are found today in crude oils and sediments and are unchanged or have suffered only minor subsequent changes with preservation of the carbon skeleton. Tetracyclic steranes and pentacyclic triterpanes are suitable biomarkers<sup>5</sup>. Using GC-MS the distribution of these molecules can be analysed without prior separation from the SAT fraction by looking at the mass chromatograms of  $m/e = 217$  (steranes) and  $m/e = 191$  (triterpanes). In Fig. 2a mass fragmentograms are shown for crude oils from all areas of the German Molasse basin. For a positive oil-oil correlation these traces should be as similar as possible.

From Fig. 2a it can be deduced that there are only two oil groups in the Molasse basin. One consists of the crude oils found in Triassic reservoirs (area I;

Fig. 1a), and all of the other oils belong to the second group. Biodegradation seems to have little influence on the distribution pattern of steranes and triterpanes. Hence this technique is a real improvement in geochemical correlation work.

#### *Oil-source rock correlation*

The correlation of a crude oil with a sedimentary extract is difficult. First, sediments that may be possible source rocks are pre-selected according to the following rules: (1) the organic material, which is embedded in the sediments, must be of a type

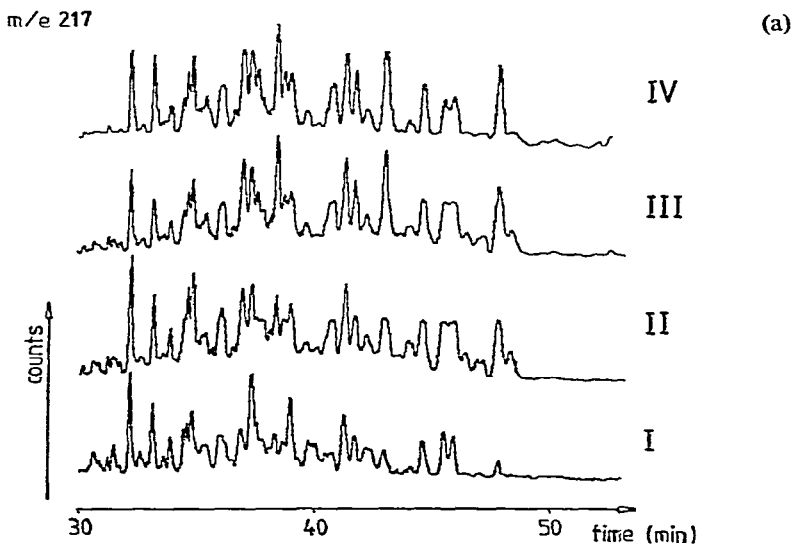
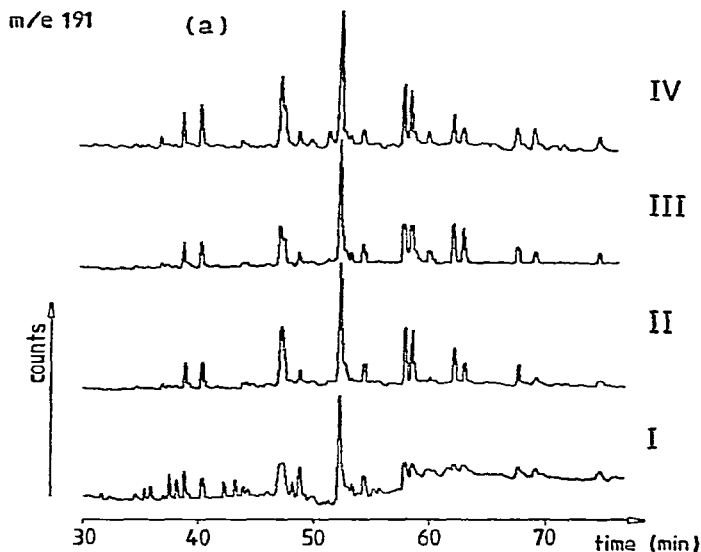


Fig. 2.

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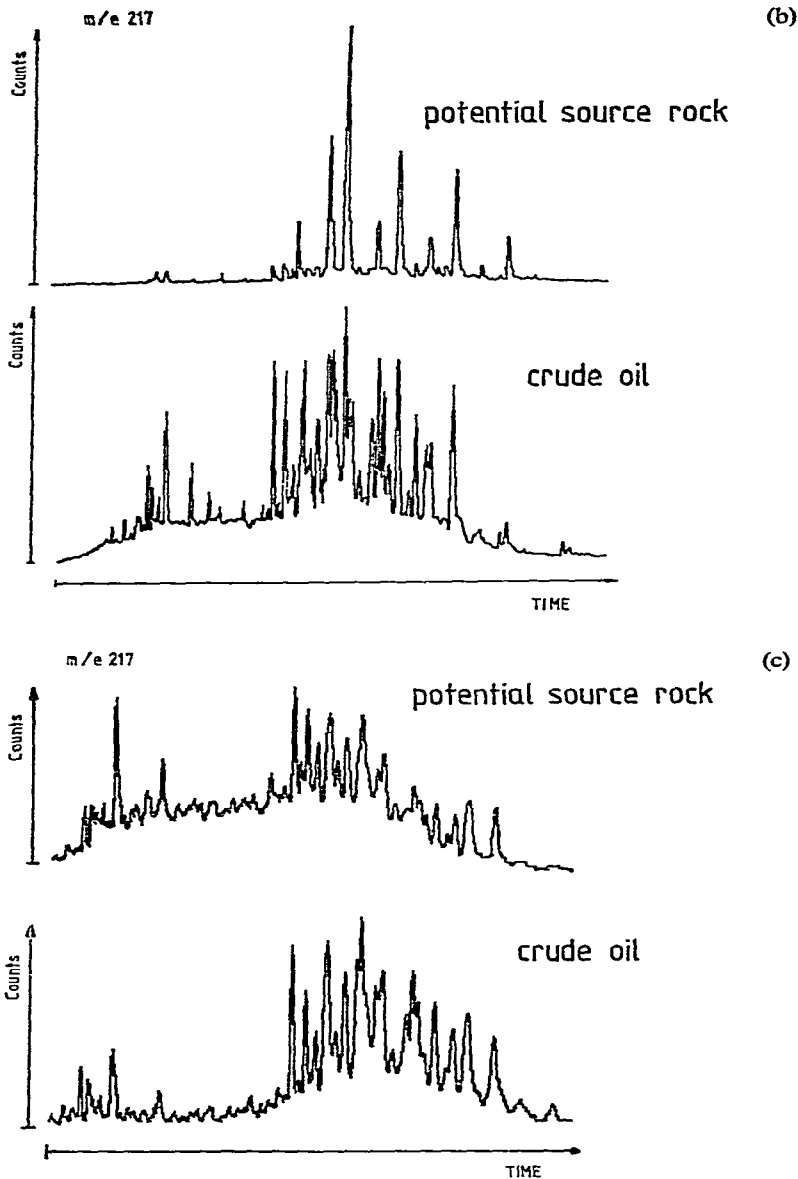


Fig. 2. (a) GC-MS investigation of crude oils; triterpane distribution pattern ( $m/e = 191$ ) and sterane distribution pattern ( $m/e = 217$ ). (b) Comparison of sterane distributions from a crude oil and a potential source rock in the Eastern part of the Molasse basin. (c) Comparison of sterane distributions from a crude oil and a potential source rock in the Western part of the Molasse basin.

that is able to generate oily material; (2) the sediment must be in a maturity stage that is suitable for oil generation, *i.e.*, it must have been buried deep enough; and (3) sediments that are only impregnated by an oil must be excluded. The maturity of a sediment is usually determined by petrographic methods, *e.g.*, measurement of the



vitrinite reflection<sup>6</sup>. Impregnated sediments may be detected by comparing the extract yield with the total organic carbon content.

The type of organic material can be determined by thermochromatographic methods<sup>7</sup>. Sediments containing bituminous material can act as a source rock for oils.

Such sediments show a larger amount of pyrolysable material in comparison with the total organic carbon content than do sediments with humic material, provided that the degrees of maturity are similar. Additionally, the GC trace of the volatiles is of importance<sup>8</sup>. In the Eastern part of the Molasse basin an organic-rich shale occurs at the base of Oligocene. In the past this "Fischschiefer" was considered as a potential source rock<sup>9</sup>. The degree of maturity of the organic material is just at the lower border of what is considered to be necessary for source rocks. However, considering the reconstructed mass chromatograms for steranes ( $m/e = 217$ , Fig. 2b), the distribution pattern is very different. For this reason the "Fischschiefer" must be ruled out as a source rock for the oils from area III of IV.

Another example can be shown from the Western part of the Molasse basin. Considering the degree of maturity of sediments, a strong increase is observed on going from the oil deposits in area II (Fig. 1a) to the South<sup>10</sup>. About 30 km from area II material was available from the "Elbsee" location. In Fig. 2c the  $m/e = 217$  mass fragmentogram of an extract of an Upper Jurassic shale is compared with that of an oil from area II. The traces show good agreement, indicating that this sedimentary layer may act as a source rock. A positive correlation of this sediment with an oil from area II has to be checked further, considering the geological situations in the past. Moreover, other potential source rocks in the Western part of the German Molasse basin have to be investigated. The results of our further studies will be published elsewhere.

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