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## COMPUTERISED CAPILLARY GAS CHROMATOGRAPHIC-MASS SPECTROMETRIC STUDIES OF THE PETROPORPHYRINS OF THE GILSONITE BITUMEN (EOCENE, U.S.A.)

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### SUMMARY

Computerised capillary gas chromatographic-mass spectrometric analysis of the petroporphyrins [as their bis(*tert.*-butyldimethylsiloxy)Si(IV) derivatives] of Gilsonite (an Eocene bitumen, Uinta Basin, UT, U.S.A.) has revealed 123 components in the C<sub>26</sub>-C<sub>36</sub> carbon number range, demonstrating the complexity of such mixtures. Four structural classes have been recognised: (i) the A class comprising 43 components with alkyl  $\beta$ -pyrrole substituents (formerly aetioporphyryns), (ii) the major A-2 class (one further degree of unsaturation; 57 components) containing compounds bearing an exocyclic ring, (iii) the A-4 class (two further degrees of unsaturation; 13 components), and (iv) the A-6 class (three further degrees of unsaturation; 10 components). Co-chromatography of *n*-alkanes, allowing computer-aided calculation of Kováts retention indices, has enabled further classification into homologous or pseudo-homologous series. Co-chromatography of derivatised porphyrins of known structure has allowed structural assignment of 9 components; at least 24 other compounds are assumed to be structurally related to these components by extrapolation on Kováts plots.

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### INTRODUCTION

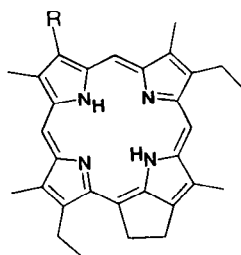
Recent structural studies of deoxyphylloerythroaetio(DPEP)-type porphyrins (1-3)<sup>1-5</sup> from a range of geological samples (in which they occur as metal complexes) have provided evidence consistent with the hypothesis that alkyl petroporphyrins are derived largely from chlorophyll *a*<sup>6</sup>. The structures of less abundant petroporphyrins bearing exocyclic rings of varying size, some with methyl-substitution, have also been determined (4-6<sup>7,8</sup>, 7-8<sup>9</sup>, 9<sup>11</sup>, 10<sup>12</sup>, 11<sup>13</sup>), as have a number of aetio-type structures (12-15<sup>2,10,14-16</sup>). Other structures more tentatively assigned include the tetrahydro-

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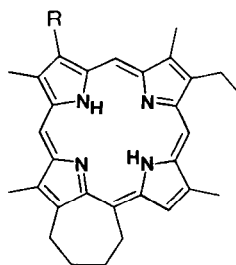
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benz-DPEP (21<sup>17</sup>), benz-aetio (22<sup>18</sup>) and benz-DPEP types (23<sup>18,19</sup>). Several porphyrins bearing carboxylic acid substituents have also been identified in an immature (Eocene) shale<sup>20,21</sup>.

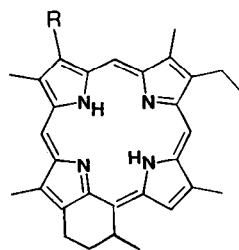
The discovery of structures other than the DPEP (1) and aetio-III (13) proposed by Treibs<sup>6,22,23</sup> has required extension of his original hypothesis. In addition to the pheophytinisation, hydrolysis, decarboxylation and reduction steps originally proposed<sup>6</sup>, other types of reaction may significantly affect the sedimentary alkyl porphyrin distributions. The discovery of structure 11, believed to be related to chlorophyll *b*<sup>13</sup> and structure 9, related to chlorophyll *c*<sup>11</sup>, means that inputs other than chlorophyll *a* should not be discounted. An origin for aetioporphyryns in haem type precursors<sup>6</sup>, largely discounted by Corwin<sup>24</sup> on the basis of the vastly greater relative



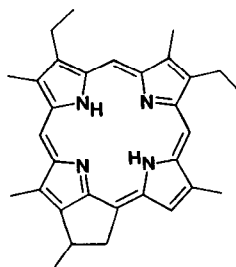
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 2 R = CH<sub>3</sub>  
 3 R = H



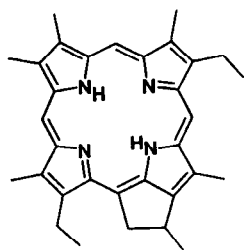
- 4 R = C<sub>2</sub>H<sub>5</sub>  
 5 R = CH<sub>3</sub>  
 6 R = H



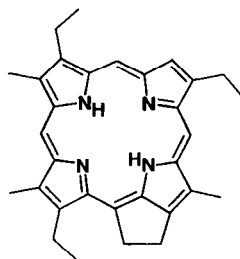
- 7 R = C<sub>2</sub>H<sub>5</sub>  
 8 R = CH<sub>3</sub>



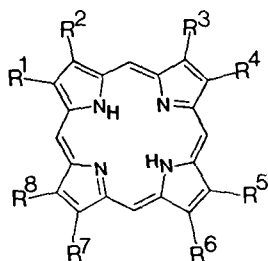
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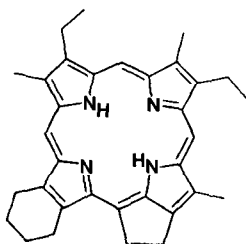
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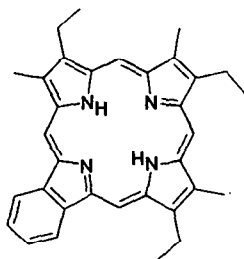
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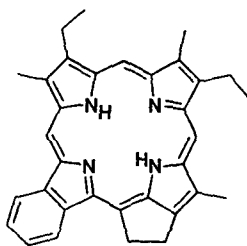
- 12  $R^{1-6,8} = \text{CH}_3$ ,  $R^7 = \text{C}_2\text{H}_5$
- 13  $R^{1,3,5,8} = \text{CH}_3$ ,  $R^{2,4,6,7} = \text{C}_2\text{H}_5$
- 14a  $R^{1-3,5-7} = \text{CH}_3$ ,  $R^{4,8} = \text{C}_2\text{H}_5$  or
- 14b  $R^{1-3,5,6,8} = \text{CH}_3$ ,  $R^{4,7} = \text{C}_2\text{H}_5$
- 15  $R^{1,3,5,8} = \text{CH}_3$ ,  $R^{2,4,7} = \text{C}_2\text{H}_5$ ,  $R^6 = \text{H}$
- 16  $R^{1-8} = \text{CH}_3$
- 17  $R^{1-8} = (\text{C}_2\text{H}_5)_2(\text{CH}_3)_5\text{H}$ , order unknown; at least two isomers present
- 18a  $R^{2,4,5,7,8} = \text{CH}_3$ ,  $R^{1,3,6} = \text{C}_2\text{H}_5$  or
- 18b  $R^{2,4,6,7,8} = \text{CH}_3$ ,  $R^{1,3,5} = \text{C}_2\text{H}_5$  or
- 18c  $R^{2,3,4,5,8} = \text{CH}_3$ ,  $R^{1,6,7} = \text{C}_2\text{H}_5$  or
- 18d  $R^{1,3,4,5,8} = \text{CH}_3$ ,  $R^{2,6,7} = \text{C}_2\text{H}_5$  } at least two isomers present
- 19  $R^{1-8} = \text{C}_2\text{H}_5$
- 20  $R^{1-7} = \text{CH}_3$ ,  $R^8 = \text{H}$



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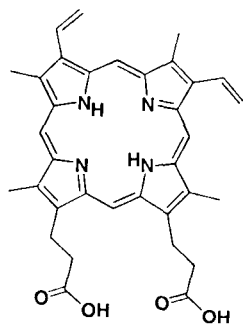


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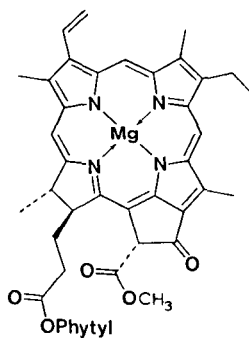


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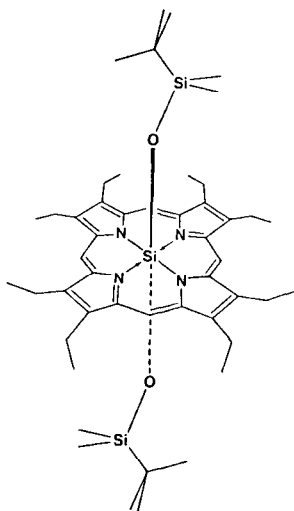
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abundance of plant over animal-derived tetrapyrrole pigments, may be significant on account of the greater stability of the porphyrin system (24) in haem relative to the reduced, chlorin structure of chlorophyll *a* (25). Furthermore, the cytochromes produced by most living organisms, especially micro-organisms, may be significant precursors of aetio-type porphyrins<sup>25</sup>.

As with other biological marker compounds, the distribution of petroporphyrin structures in a given sedimentary material may reflect: (i) the nature of the original input of organic matter to the sediment, (ii) the palaeoenvironment of deposition, and (iii) subsurface effects, such as biodegradation, thermal stress and migration. While a certain amount of information relating to these fundamental geochemical effects can be obtained from petroporphyrins, their full potential as biological marker compounds has yet to be realised. Progress has been hampered by the lack of an analytical technique capable of providing an effective qualitative and quantitative assessment of petroporphyrin composition. <sup>1</sup>H NMR spectroscopy has been

important in establishing the structures of many of the key components and direct-insertion probe mass spectrometry (MS) is important in providing evidence of the carbon number range of the mixtures. Neither of these techniques can, however, be readily employed in the quantitative and qualitative analysis of petroporphyrins. High-performance liquid chromatography (HPLC) has been employed and provides an approximate relative abundance profile for the components<sup>26-28</sup>. However, with so few compounds of known structure available for co-injection studies many of the assignments of peak identity are inevitably tentative, as co-elutions, which certainly occur, are not readily detected. The use of combined LC-MS would provide a solution, but is not widely available.

We have recently developed a computerised capillary gas chromatography (GC)-MS technique for the analysis of alkyl porphyrins. The bis-(*tert*-butyldimethylsilyloxy)Si(IV) [abbreviated to (TBDMSO)<sub>2</sub>Si(IV)] derivative (*e.g.* 26) was found to be by far the most amenable to GC-MS analysis<sup>29,30</sup>, and has been effectively applied to the analysis of complex alkyl petroporphyrin mixtures<sup>31,32</sup>. The technique, employing both manual<sup>31</sup> and automated<sup>33</sup> data interpretation, affords detailed compositional information of both a qualitative (through mass spectra, mass chromatograms, co-injections and relative retention indices) and quantitative (relative at this stage, via ion intensity data) nature.

We report here the first detailed computerised GC-MS investigation of petroporphyrins. The sample chosen is the bitumen Gilsonite (Eocene, Uinta Basin, UT, U.S.A.) which has a well-defined origin, geological and depositional history and a relatively high porphyrin content (*ca.* 100 ppm as nickel chelates).

Furthermore, much is known of its petroporphyrin content from previous MS, thin-layer chromatographic (TLC), UV-VIS, HPLC and NMR studies. The earliest investigation of the porphyrins of Gilsonite was that of Sugihara and McGee<sup>34</sup>. On the basis of UV-VIS and IR spectroscopy and elemental analyses they proposed that DPEP (1) or an isomer, as its nickel(II) complex, was the major component. Direct-insertion probe MS provided the first evidence that the porphyrins of Gilsonite comprise a mixture of aetio and DPEP (13,15-ethano)-type porphyrins in the C<sub>29</sub> to C<sub>34</sub> carbon number range, with the DPEP series predominant, and C<sub>31</sub> DPEP porphyrin the major component<sup>18,35</sup>. That the mixture was more complex than previously supposed, by way of the presence of structural isomers and pseudo-homologous series of DPEP and aetio classes, was shown by use of liquid chromatography (preparative TLC<sup>14,36</sup>, semipreparative HPLC<sup>37</sup>) in combination with probe MS analyses, at least six series being separable as free-bases by TLC<sup>36</sup>. Hodgson *et al.*<sup>38</sup> reported the presence of aetioporphyryns yielding 3-ethyl-4-methylpyrrole-2,5-dione and 3-ethyl-pyrrole-2,5-dione on oxidation. The findings of Alturki *et al.*<sup>36</sup> were subsequently confirmed by <sup>1</sup>H NMR, MS and UV-VIS investigations of TLC and HPLC fractions obtained from the demetallated porphyrins<sup>1,10,12,14,15,37</sup>. The work of Quirke *et al.*<sup>14</sup> and Quirke and Maxwell<sup>15</sup> on Gilsonite provided the first structural elucidations of petroporphyrins, full structures being determined for fully alkylated C<sub>29</sub> (12) and C<sub>32</sub> (aetio-III; 13) aetio-components (A class). A number of partial structures were also determined. Amongst these was that of DPEP (1) which, although not unambiguously proven, was shown by <sup>1</sup>H NMR and nuclear Overhauser effect (nOe) studies<sup>1</sup> to possess the necessary exocyclic ring (13,15-ethano) and adjacent alkyl groups to be consistent with it having a biogenic origin in chlorophyll

$a^6$ . Continued investigations<sup>10,39</sup> afforded further partial structures including an unusual A-2 class porphyrin proposed to bear a 13,15-propano ring system. However, more recent work<sup>12</sup> has shown the structure to be 10, with a 13<sup>1</sup>-methyl-13,15-ethano system. In the present study, derivatised aliquots of the majority of the above compounds isolated from Gilsonite have been included in the co-injection programme in addition to five further compounds obtained from Serpiano oil shale and three from other sources (Table I).

## EXPERIMENTAL

### *Extraction of free-base porphyrins*

The porphyrins were extracted as their free-bases by demetallation with methanesulphonic acid<sup>41</sup>. Typically, powdered Gilsonite (10 g) was heated (100°C, 2 h) with at least a five-fold excess (50 ml) of methanesulphonic acid (98%, Aldrich). The reaction was quenched by pouring the mixture into distilled water (100 ml). After allowing to cool, the coagulated organic material was removed by filtration. The aqueous filtrate, containing the porphyrins as dications, was extracted with dichloromethane (3 × 15 ml), neutralised (sodium hydrogencarbonate) and dried (sodium sulphate). The free-bases were purified by TLC (silica gel) or Sep-pak (Waters Assoc., silica gel) using dichloromethane as eluent.

### *Friedel-Crafts acetylation*

Acetylation<sup>42</sup> was performed on the copper(II) derivatives<sup>43</sup> of an aliquot of the free-base porphyrins obtained above. Subsequent TLC [silica gel; eluent, acetic acid-dichloromethane (1:99)] afforded separation of the fully  $\beta$ -alkyl substituted components ( $R_F = 0.95$ ) from the  $\beta$ -acetylated components ( $R_F = 0.3$ ). Separation was confirmed by UV-VIS spectrophotometry and probe MS. Repeated attempts to deacetylate<sup>44</sup> microgram quantities of the derivatives were ineffective, resulting in degradation of the porphyrins. After demetallation, the fully  $\beta$ -alkyl substituted porphyrin fraction was submitted to derivatisation and GC-MS analysis, along with an aliquot of the total porphyrins.

### *Derivatisation*

Insertion of silicon into an aliquot of the free-bases, was carried out by a modification of the method of Marriott *et al.*<sup>29</sup>. The porphyrins (0.5 mg) were dissolved in dry toluene (1 ml) in a screw-topped vial and Si<sub>2</sub>Cl<sub>6</sub> (Aldrich) (1 drop) added. Quantitative formation of the dichlorosilicon(IV) porphyrins occurred at room temperature (2 h) as indicated by the presence of visible absorption maxima at 535 and 574 nm (dichloromethane) and absence of absorbance bands corresponding to porphyrin free-bases or dications.

Hydrolysis to the dihydroxysilicon(IV) porphyrin complexes was performed as described previously<sup>31</sup>. N-Methyl-N-(*tert.*-butyldimethylsilyl)trifluoroacetamide (Regis) (1% in dry pyridine) was used in place of Corey's reagent<sup>45</sup> to form the TBDMS derivatives of the dihydroxy silicon(IV) porphyrins (*e.g.* 26).

### *Computerised gas chromatography-mass spectrometry*

The GC-MS system comprised a Finnigan 9610 gas chromatograph equipped

TABLE I  
CO-CHROMATOGRAPHY OF STANDARD PORPHYRIN DERIVATIVES WITH GILSONITE PETROPORPHYRIN DERIVATIVES  
Abbreviations: OMP = 2,3,7,8,12,13,17,18-octamethylporphyrin; aetio-III = aetioporphyrin III; OEP = 2,3,7,8,12,13,17,18-octaethylporphyrin.

Porphyrin	Structure	KRI	$m/z$ $/M-131$ <sup>+</sup>	Co-chromatographs?	Source of compound
C <sub>28</sub> A (OMP)	16	3455	579	yes	P.S. Clezy <sup>***</sup>
C <sub>29</sub> A*	17	3528	593	yes	Gilsonite bitumen <sup>1,4,39</sup>
C <sub>30</sub> A	14	3540	593	yes	Gilsonite bitumen <sup>10,39</sup>
C <sub>31</sub> A**	18	3541	607	yes	Gilsonite bitumen <sup>39</sup>
C <sub>32</sub> A (aetio-III)	13	3583	621	yes	J. G. Erdman <sup>***</sup>
C <sub>36</sub> A (OEP)	19	3624	635	no	Porphyrin Products Inc. <sup>***</sup>
C <sub>31</sub> 13,15-ethano	2	3715	619	yes	Serpiano shale <sup>40</sup>
C <sub>32</sub> 13,15-ethano	1	3754	633	yes	Serpiano shale <sup>40</sup>
C <sub>32</sub> 13 <sup>1</sup> -methyl-13,15-ethano	10	3715	633	yes	Gilsonite bitumen <sup>12,39</sup>
C <sub>32</sub> 15 <sup>1</sup> -methyl-15,17-propano	7	3795	633	no	Serpiano shale <sup>9</sup>
C <sub>31</sub> 15,17-butano	5	3842	619	yes (trace)	Serpiano shale <sup>10,40</sup>
C <sub>32</sub> 15,17-butano	4	3894	633	no	Serpiano shale <sup>7,40</sup>

\* At least two components, partially resolved into two peaks.

\*\* At least two components, not resolved.

\*\*\* Synthetic compound.

with a modified SGE OCI-2 on-column injector. The column was a flexible fused-silica capillary (Hewlett Packard, "Ultra" series; 25 m × 0.31 mm I.D.) coated with cross-linked methylsilicone (0.17 μm film thickness). Helium carrier gas at a pressure of 0.8 kg cm<sup>-2</sup>, produced a linear flow-rate of *ca.* 50 cm s<sup>-1</sup>. All analyses were programmed from 50 to 225°C at 20°C min<sup>-1</sup> then to 300°C at 3°C min<sup>-1</sup> followed by an isothermal period (40 min) at 300°C.

The column was led directly into the source of a Finnigan 4000 quadrupole mass spectrometer operating under the following conditions: source temperature, 250°C; emission current, 350 μA; electron energy, 35 eV. Multiple ion detection (MID) was used to increase sensitivity. The MID cycle allowed 13 ms to monitor *m/z* 113 (a characteristic ion for the *n*-alkane retention index standards) and 1.314 s to scan the range *m/z* 545–850 necessary to detect the porphyrin derivatives. All data acquisition and processing was under the control of an INCOS 2300 data system. Co-chromatography of *n*-alkanes with the porphyrin derivatives permitted subsequent computer calculation of relative retention indices (RRI) for the alkyl porphyrin derivatives. Relative retention indices were calculated in a manner similar to the Kováts method<sup>46</sup> and are referred to as pseudo-Kováts retention indices (KRI)<sup>31</sup>.

### Qualitative analysis

Interpretation of the GC-MS data has been described in detail elsewhere<sup>31</sup>. Briefly, assignments are based on single ion mass chromatograms and spectra, the intense [M - 131]<sup>+</sup> ion of the TBDMS derivative being used to assign carbon number (C<sub>n</sub>) and structural class. Care is taken to ensure that the mass chromatogram peaks correspond to genuine [M - 131]<sup>+</sup> ions and do not arise from isobaric ions produced by some alternative fragmentation. More precise assignments are made by co-chromatography of derivatised alkyl porphyrins of known structure (Table I).

### Quantitative analysis

Quantification is relative rather than absolute. The relative abundance (%) of a given component (X) is determined on the basis of the proportion of its ion current (IC<sub>X[M-131]</sub>), in the single ion [M - 131]<sup>+</sup> mass chromatograms, relative to the sum of the ion currents for all genuine [M - 131]<sup>+</sup> chromatograms (IC<sub>all[M-131]</sub>), *i.e.*

$$\text{Relative abundance (\%)} \text{ of X} = \frac{\text{IC}_{\text{X[M-131]}}}{\text{IC}_{\text{all[M-131]}}} \cdot 100$$

where X is the petroporphyrin the abundance of which is required.

## RESULTS

The reconstructed ion current profile for the total petroporphyrins analysed as their (TBDMSO)<sub>2</sub>Si(IV) derivatives is shown in Fig. 1a; 25 fully or partially resolved peaks are visible in the KRI range 3400 to 4000. As at least 35 peaks can be fully or partially resolved by HPLC (Fig. 2a), co-elution must be occurring in the GC-MS analysis. In order to check for this, single-ion mass chromatograms were produced.



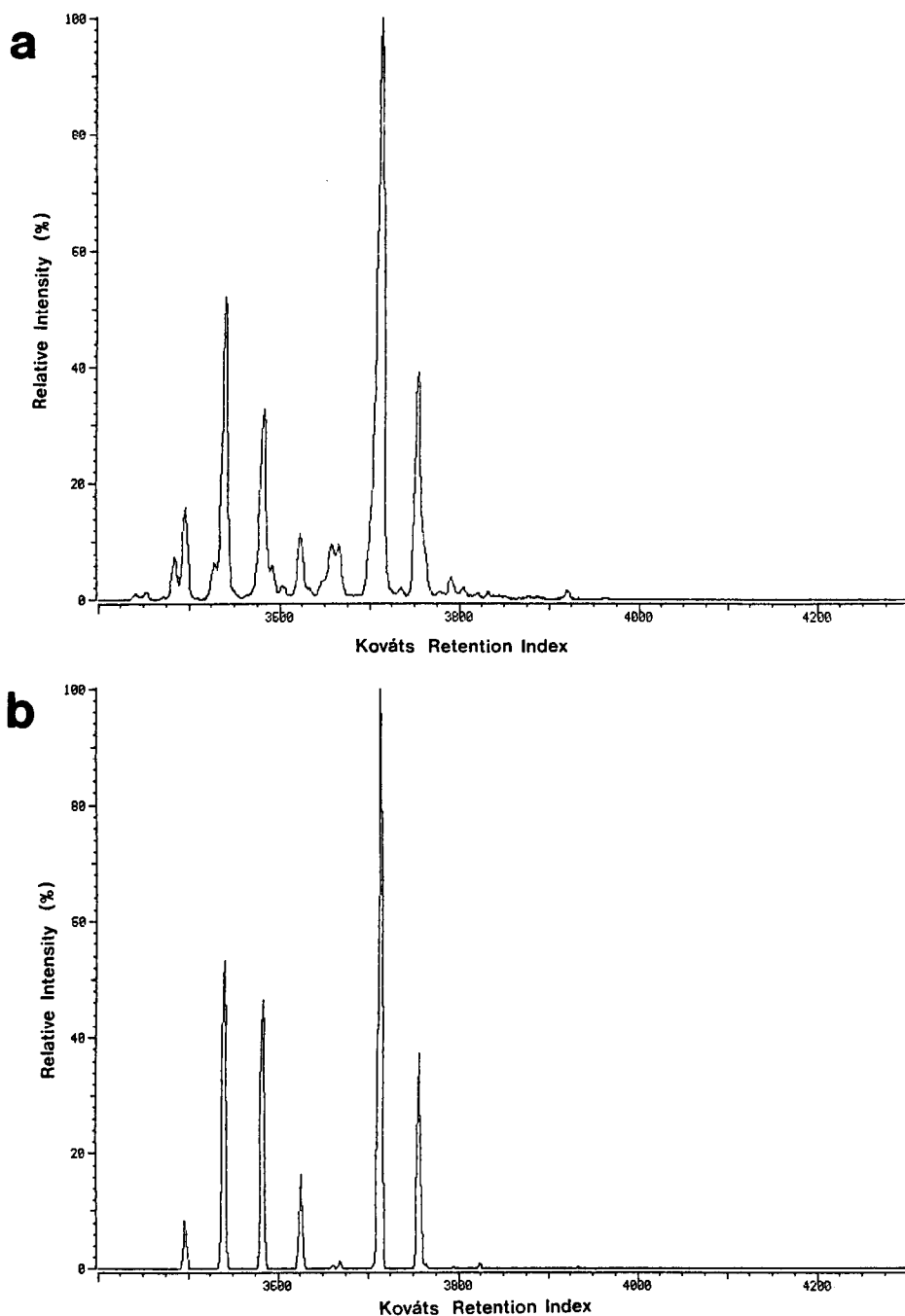


Fig. 1. The reconstructed ion current traces for the total petroporphyrins of Gilsonite (a) and the fully  $\beta$ -alkyl substituted components (b). The traces were produced by multiple ion detection and show only those peaks produced by ions in the  $m/z$  range 545–850. This mass range covers that required to detect the intense  $[M - 131]^+$  ion of the eluting porphyrin TBDMS derivatives. The retention time scale has been converted to KRI by computer interpolation from co-injected  $n$ -alkanes (the  $n$ -alkane peaks do not appear in these profiles). The analyses were performed on a  $25 \text{ m} \times 0.31 \text{ mm}$  I.D. cross-linked methyl silicone coated ( $0.17 \text{ }\mu\text{m}$  film thickness) flexible fused-silica capillary (Hewlett Packard, "Ultra" series) column. Helium was the carrier at a flow-rate of  $50 \text{ cm s}^{-1}$ . The analyses were temperature programmed, following on-column injection, from ambient to  $225^\circ\text{C}$  at  $20^\circ\text{C min}^{-1}$  then at  $3^\circ\text{C min}^{-1}$  to  $300^\circ\text{C}$  followed by a 40-min isothermal hold.

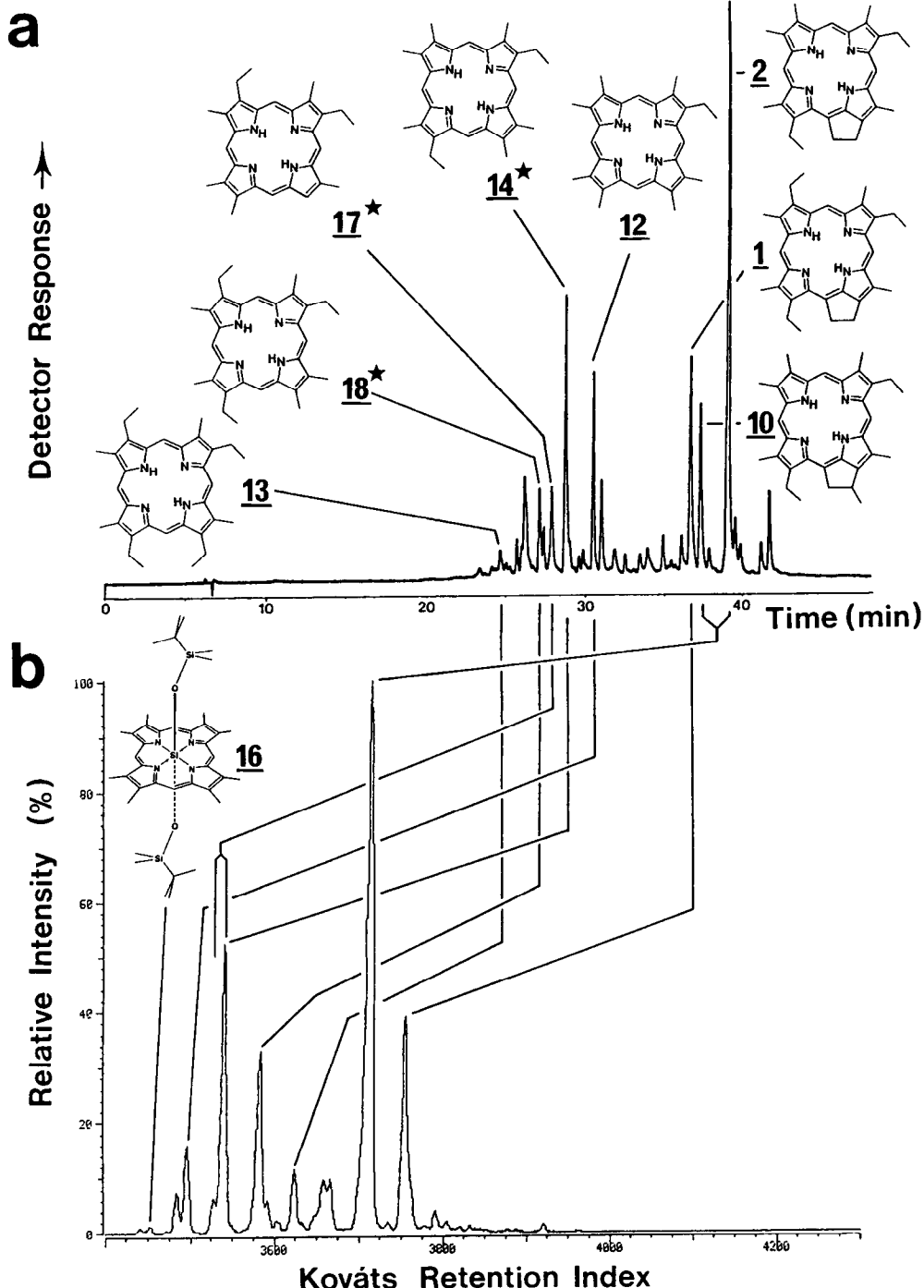


Fig. 2. The upper trace (a; modified from ref. 39) shows normal-phase ( $\text{SiO}_2$ ) HPLC of free-base (de-metallated nickel) porphyrins of Gilsonite with spectrophotometric detection at 400 nm. Compounds of known or partially known structure are shown (Table I). The lower trace (b) is the GC-MS RIC, showing the results of co-injection studies with the marked compounds [after  $(\text{TBDMSO})_2\text{Si}(\text{IV})$  derivatisation]. The derivative of 16 was also found to co-chromatograph with a Gilsonite component. 17 separates into two peaks by GC, but 18a-d co-elute. ★, Structure shown is one of several possible isomers.

TABLE II  
CLASSIFICATION OF PETROPORPHYRINS\*

Porphyryns are grouped according to the degree of unsaturation in their  $\beta$ -alkyl substituents.

Class	Empirical formula	Structural type**	Structure No.**	Molecular formula
A	$C_{(20+n)}H_{(2n+14)}N_4$	Aetio	13	$C_{32}H_{38}N_4$
A-2	$C_{(20+n)}H_{(2n+12)}N_4$	DPEP (13,15-ethano)	1	$C_{32}H_{36}N_4$
A-4	$C_{(20+n)}H_{(2n+10)}N_4$	Tetrahydrobenz-DPEP	21	$C_{33}H_{36}N_4$
A-6	$C_{(20+n)}H_{(2n+8)}N_4$	benz-aetio***	22	$C_{33}H_{34}N_4$
A-8	$C_{(20+n)}H_{(2n+6)}N_4$	benz-DPEP***	23	$C_{33}H_{32}N_4$

\* Based on the system of Yen *et al.*<sup>47</sup>

\*\* Example: thus, for the A-2 class, other types include 13<sup>1</sup>-methyl-13,15-ethano (10), 15,17-butano (4), 15<sup>2</sup>-methyl-15,17-ethano (9), 15<sup>1</sup>-methyl-15,17-propano (7).

\*\*\* Tentative structural assignments, yet to be proved unambiguously.

### Mass chromatography

The single-ion mass chromatograms were selected on the basis of masses predicted for the intense  $[M - 131]^+$  ion for  $(TBDMSO)_2Si(IV)$  alkyl porphyrin derivatives containing varying degrees of unsaturation in their  $\beta$ -alkyl substituents. The procedure has been described and exemplified<sup>31</sup>. The various structural types of petroporphyrin have previously been assigned as aetio (fully saturated  $\beta$ -alkyl substituents), DPEP (one degree of unsaturation in the  $\beta$ -alkyl substituents), di-DPEP (recently reassigned tentatively as tetrahydrobenz-DPEP<sup>17</sup>; two degrees of unsaturation), rhodo-aetio (benz-aetio; three degrees of unsaturation) and rhodo-DPEP (benz-DPEP; four degrees of unsaturation). In the light of recent discoveries of four distinct structural types of porphyrin (1, 4, 7 and 10) isomeric with DPEP (1) it is obvious that this nomenclature is misleading for compounds for which only the molecular mass is known (from MS). Only in the case of the aetio series where  $\beta$ -alkyl substituents are fully saturated is the nomenclature acceptable. To avoid confusion a system of nomenclature is adopted (A, A-2, A-4, A-6 and A-8; Table II, based on that of Yen *et al.*<sup>47</sup>) to relate compounds of similar empirical formulae. Only when co-injection provides assignment of structural type is more precise nomenclature adopted.

The mass chromatograms for the A, A-2, A-4 and A-6 class components (no A-8 class components were observed), have been screened to identify the genuine  $[M - 131]^+$  peaks<sup>31</sup>. Conversion of retention times (scan numbers in MS file) to Kováts retention indices is facilitated by co-chromatography of homologous *n*-alkanes.

The quantification adopted was simply to use the peak areas of the characteristic  $[M - 131]^+$  ions in the GC-MS data. These areas were obtained from RI lists (see Fig. 7 of ref. 31) produced by program RRI<sup>48</sup>. The KRI values and peak areas may be read directly from the list, and the areas are then expressed as fractions (%) of the area of the major component, the C<sub>31</sub> A-2 porphyrin (KRI = 3715), read from the *m/z* 619 list.

Table III lists each porphyrin detected, its class, carbon number, retention index (KRI), and abundance (relative to the C<sub>31</sub> A-2 porphyrin of KRI = 3715, and also as a percentage fraction of the total petroporphyrins). Every assignment was made on the basis of the  $[M - 131]^+$  fragment ion and the components characterised further by their KRI values.

TABLE III

## RETENTION INDEX AND RELATIVE ABUNDANCE\* FOR THE PETROPORPHYRINS OF GILSONITE

tr = Less than 0.1% of total petroporphyrins.

Class	Carbon number									
	26	27	28	29	30	31	32	33	34	35
A	3429 (0.2:tr)	3441** (2:0.4)	3455** (2:0.4)	3496** (23:4)	3541** (55:10)	3583** (38:7)	3624** (14:3)	3666** (0.1:tr)	3756** (0.2:tr)	3842 (0.1:tr)
		3447** (0.7:0.1)	3485** (13:2)	3528** (9:1.6)	3572** (1.4:0.2)	3627** (1:0.2)	3648 (1:0.2)	3688 (0.4:tr)	3803 (0.3:tr)	3858 (0.1:tr)
		3472 (1:0.2)	3495** (5:0.9)	3540** (28:5)	3581** (5:0.9)	3633 (2:0.4)	3673** (0.6:0.1)	3716** (0.7:0.1)	3820 (0.1:tr)	3886 (0.1:tr)
		3484 (1:0.2)	3527 (3:0.5)	3582 (2:0.4)	3591 (2:0.4)	3666 (1:0.2)	3715 (10:1.8)	3755 (4:0.7)	3832 (0.1:tr)	
		3491 (0.1:tr)	3539 (3:0.6)		3620 (0.4:tr)			3791 (1:0.2)	3845 (0.2:tr)	
								3804 (0.4:tr)		
A-2		3520 (0.1:tr)	3539** (2:0.4)	3530 (0.2:tr)	3582 (1:0.2)	3636 (1:0.2)	3715** (59:10)	3756** (17:3)	3802** (0.3:tr)	3880 (0.1:tr)
		3540** (0.3:tr)	3564 (1:0.2)	3541 (2:0.4)	3593 (3:0.6)	3666** (10:2)	3754** (35:6)	3791** (5:0.8)	3832 (1:0.2)	3890 (0.1:tr)
			3581** (0.5:tr)	3550 (0.4:tr)	3602 (2:0.3)	3715** (100:18)	3762 (5:0.8)	3806 (1:0.3)	3838** (0.2:tr)	3919 (0.1:tr)
			3601 (0.5:tr)	3577** (8:1.4)	3621** (3:0.6)	3735 (1:0.3)	3779 (0.3:tr)	3821 (0.7:0.1)	3863 (0.1:tr)	
			3623 (0.2:tr)	3604 (0.5:tr)	3658 (12:2)	3754 (4:0.7)	3789 (0.7:0.1)		3922 (0.1:tr)	
			3628 (0.1:tr)	3625** (1:0.2)	3667** (6:1.1)	3761 (3:0.7)	3805 (0.1:tr)			
			3645 (0.2:tr)	3650 (5:0.9)	3704 (12:2)	3803 (0.5:tr)	3813 (0.4:tr)			
				3661 (1:0.2)	3713 (6:1.1)	3842 (0.2:tr)	3836 (0.1:tr)			
				3679 (0.4:tr)	3759 (3:0.5)		3851 (0.4:tr)			
				3715 (1:0.2)			3863 (0.1:tr)			
	A-4						3791 (0.2:tr)	3791 (0.2:tr)	3877 (0.2:tr)	3953 (0.1:tr)
						3804 (0.1:tr)	3820 (0.1:tr)	3908 (0.1:tr)	3962 (0.7:tr)	
							3852 (0.1:tr)	3921 (2.4:0.4)		
							3877 (0.7:0.1)			
							3914 (0.3:tr)			

TABLE III (continued)

Class	Carbon number										
	26	27	28	29	30	31	32	33	34	35	
A-6						3889 (0.2:tr)	3921 (0.1:tr)	3935 (0.3:tr)	3962 (0.1:tr)	3977 (0.2:tr)	4016 (0.1:tr)
							3945 (0.1:tr)	3953 (0.1:tr)	3995 (0.1:tr)		
							3973 (0.1:tr)				

\* 1st relative to C<sub>31</sub> A-2 (KRI = 3715) = 100%; 2nd relative to total petroporphyrins = 100%.

\*\* Component co-chromatographed with standard or identified by extrapolation from standards on Kováts plots.

### Kováts plots

Table III lists 123 components in the C<sub>26</sub>-C<sub>36</sub> carbon number range. These include 43 A class (aetio), 57 A-2 class, 13 A-4 class and 10 A-6 class components. Further classification was achieved by generating Kováts plots of KRI vs. C<sub>n</sub> for the four classes. These plots are complex (Figs. 3-5) wherein, as found previously<sup>31,32</sup>, certain of the data points appear to be related as linear series. Several of the standards (Table I) are related as pseudo-homologous series rather than truly homologous series, *i.e.* the additional methylene unit in each member is not necessarily added to the same position. Nonetheless, straight-line relationships are observed for the pseudo-homologous series among these standards. The per-carbon increments of KRI were 43 for the fully alkylated aetio series (16, 14, 18, 13 and 19), 40 for the fully alkylated 13,15-ethano series (2 and 1), and 51 for the mono  $\beta$ -unsubstituted 15,17-butano series (5 and 4). It seems, therefore, that if the points on the Kováts plots for Gilsonite (Figs. 3-5) are joined by straight lines with gradients of *ca.* 40-50 KRI units per carbon number, then these lines represent homologous, or more likely, pseudohomologous, series of structurally related porphyrins.

### Co-injection

The electron impact (EI) spectra of the (TBDMSO)<sub>2</sub>Si(IV) derivatives, although allowing classification on the basis of empirical formula through the intense [M - 131]<sup>+</sup> ion, give no detailed structural information. Consequently, structural assignments rely on co-chromatography of alkyl porphyrins of known or partly known structure. The standards are listed in Table I together with their measured KRI values. Where co-chromatography of a component of Gilsonite occurred this is indicated in the Table and on the Kováts plots (Figs. 3 and 4). The linear relationship between homologous or pseudo-homologous components is well recognised; hence, the identities of further A (aetio; 12 components) and A-2 (12 components) class components are assumed by extrapolation from the 9 co-chromatographed compounds. Consequently, the identities of 33 components (18 A and 15 A-2 class) have

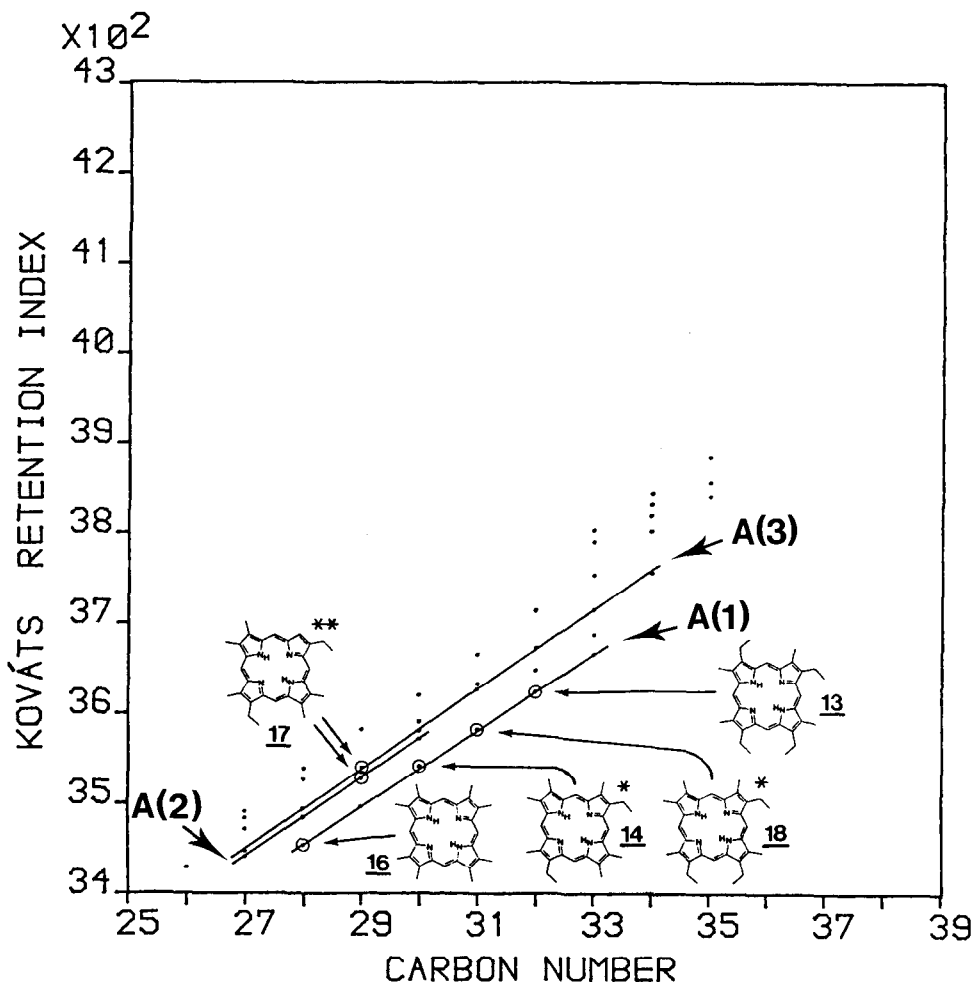


Fig. 3. A plot of KRI vs. carbon number for the A class porphyrins of Gilsonite as their TBDMS derivatives. Parallel or near-parallel lines can be drawn linking individual components in presumptive homologous or pseudo-homologous  $C_n$  series. Those components which co-chromatograph with derivatised standards of known structure are indicated. The co-injection data are summarised in Table I. The relative intensity distribution profiles for the series presumed by extrapolation to be related to the co-injected standards are presented in Fig. 7. Experimental details as for Fig. 1. \*, Structure shown is one of several possible isomers (Table I); \*\*, at least two isomers, partially resolved into two peaks.

been adduced on the basis of co-chromatography and extrapolation using linear Kováts plots. The fully-alkylated  $C_{29}$  aetioporphyryn (12)<sup>14</sup> was not available for co-injection, but by consideration of relative abundances and of the KRI values for two  $\beta$ -unsubstituted  $C_{29}$  aetioporphyryns (17), it was concluded that the component of KRI = 3496 represents its  $(\text{TBDMSO})_2\text{Si(IV)}$  derivative.

Under the conditions employed, certain positional isomers are not resolved, e.g. actios I and III co-elute<sup>29</sup>. However, the  $C_{29}$  aetio compound (17; known to be a mixture from partial resolution by HPLC<sup>39</sup>) is also partially resolved by GC. NMR

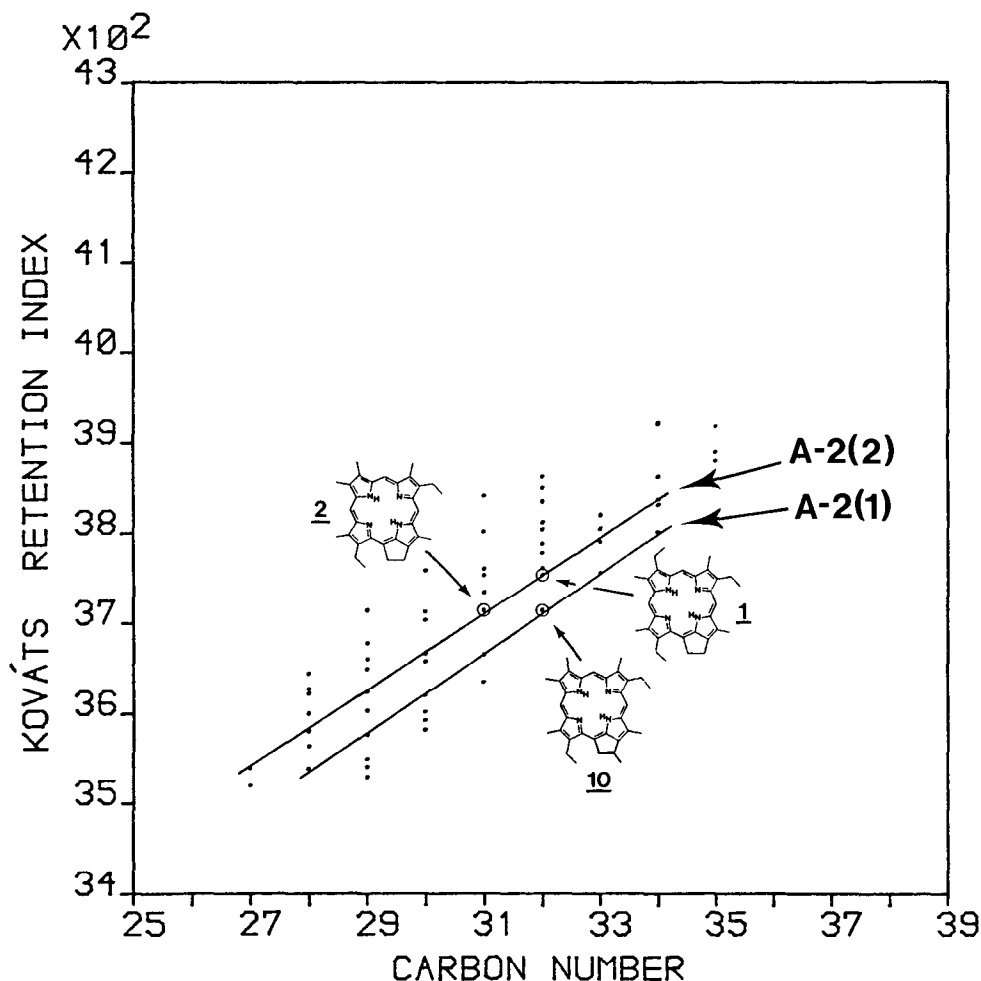


Fig. 4. A plot of KRI vs. carbon number for the A-2 class porphyrins of Gilsonite. The distribution profiles for the identified series are presented in Fig. 7. All other details are the same as for Figs. 1 and 3.

studies of the mixture 17 have shown<sup>14</sup> that these two C<sub>29</sub> aetio compounds have an unsubstituted  $\beta$ -position (unlike the fully substituted aetios I and III). Evidently, this structural feature confers sufficient difference in GC behaviour to allow partial separation of the two isomers. Thus, while confident assignment of structural type can be made (e.g. differentiation of 13,15-ethano-, 13<sup>1</sup>-methyl-13,15-ethano-, and 15,17-butano-members of the A-2 class), positional isomers may be indistinguishable in some instances. However, due to our knowledge of the composition of Gilsonite from previous investigations, we are able to state with confidence that many of the peaks for which assignments have been made by GC-MS co-injection are those of single compounds and not mixtures of positional isomers.

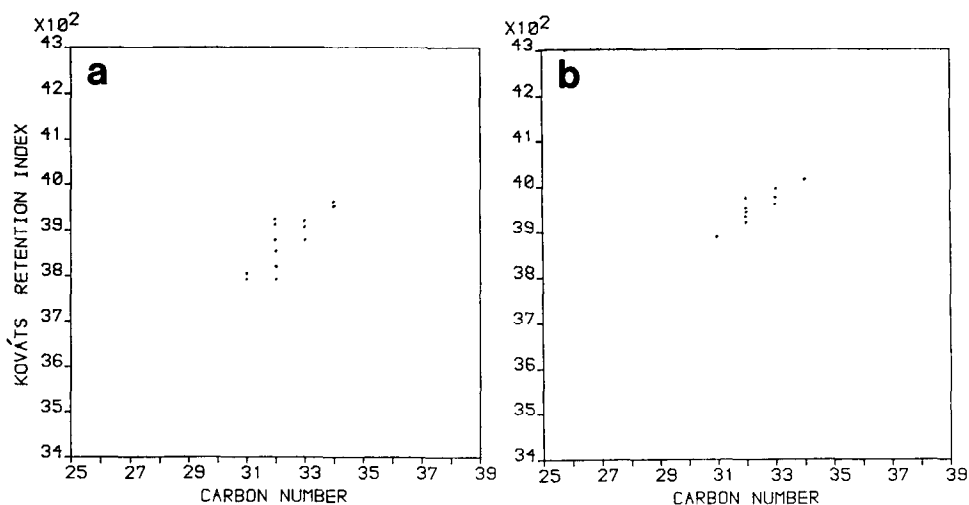


Fig. 5. A plot of KRI vs. carbon number for the A-4 class (a) and A-6 class porphyrins (b) of Gilsonite. All other details are the same as for Figs. 1, 3 and 4.

#### *Friedel-Crafts acetylation*

Further structural information relating to the remaining unassigned components, and confirmatory evidence for the co-injections and extrapolations on the Kováts plots has been obtained following Friedel-Crafts acetylation of the copper(II) derivatives of the total free-base components. Separation of the fully alkylated (non-acetylated) porphyrins from the acetylated species, and derivatisation and GC-MS of the fully alkylated fraction gave the RIC profile shown in Fig. 1b. The RIC profiles for the total derivatised porphyrins and the fully  $\beta$ -alkylated fraction are strikingly similar, as expected since the major components of Gilsonite are known to be fully  $\beta$ -alkyl substituted. Similar data processing, *i.e.* KRI calculations and plots for the fully  $\beta$ -alkylated components (Fig. 6), as for the total porphyrins, shows that only 37 of the original 123 components remain after acetylation. The A-6 class components, *i.e.* those proposed to possess a fused benz-system<sup>18,19</sup> are greatly reduced in number and abundance. Hence, it can be concluded that the majority of the 123 component petroporphyrins of Gilsonite possess sites facile to Friedel-Crafts acetylation. Table III summarises the petroporphyrin composition of Gilsonite.

#### DISCUSSION

The first detailed GC-MS analyses of the Gilsonite petroporphyrins have shown their composition to be much more complex than previously realised. More than 100 components have been characterised on the basis of their mass spectra. Of these, 33 have been further characterised by co-chromatography of nine derivatised standards, and extrapolation from these by use of Kováts plots. They contribute *ca.* 80% of the total porphyrin content and comprise five pseudo-homologous series of four structural classes.

Three aetio (A class) series were identified. The most abundant [A(1); 24% of the total] is made up of six fully  $\beta$ -alkyl substituted components in the C<sub>28</sub>-C<sub>33</sub>



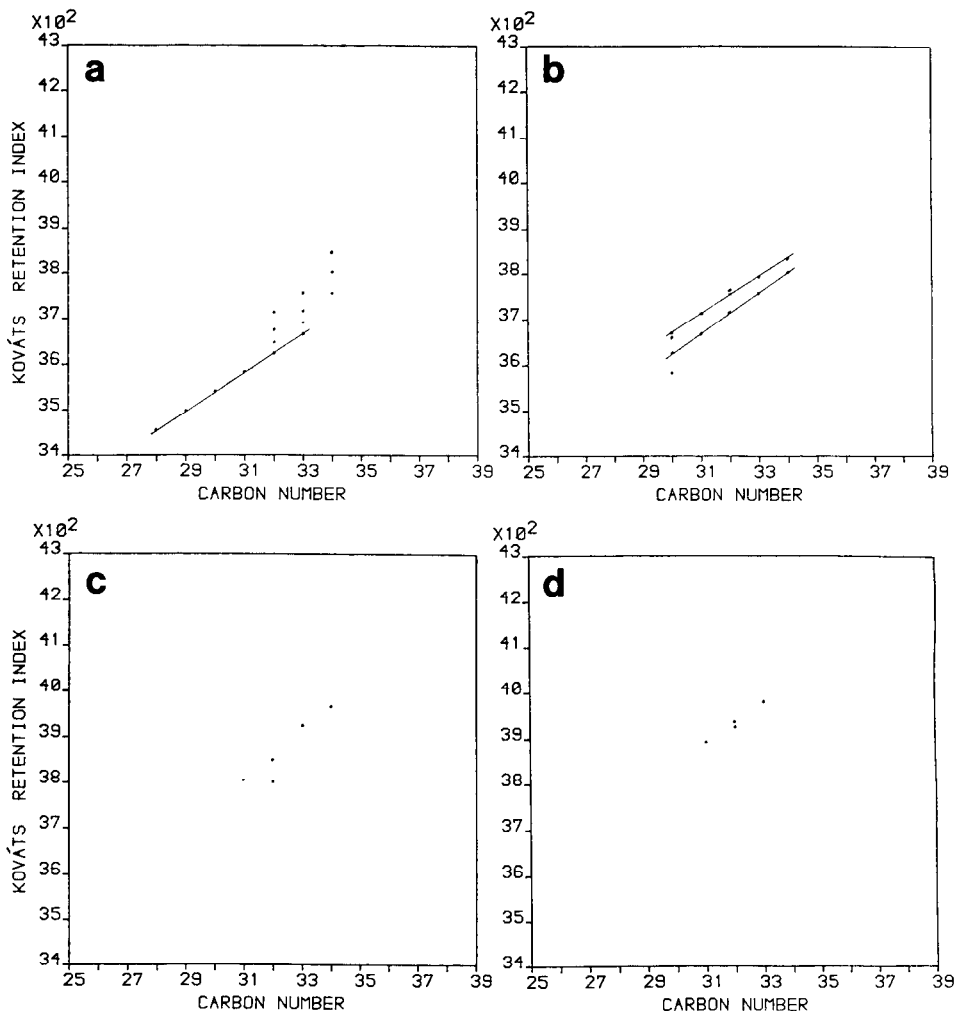


Fig. 6. Plots of KRI vs. carbon number for the A class (a), A-2 class (b), A-4 class (c) and A-6 class (d) porphyrins in the fully alkylated fraction of Gilsonite, as their  $(\text{TBDMSO})_2\text{Si}$  (IV) derivatives. The simplification which has ensued from removal of  $\beta$ -unsubstituted porphyrins is evident by comparison with Figs. 3–5; however, such removal may not be complete, see text. Experimental conditions were as for Figs. 1 and 3–5.

carbon number range and is dominated by the  $\text{C}_{30}$  component (14; Fig. 7a). In the two other A series [A(2) and A(3)], the  $\text{C}_{29}$  components co-chromatographed with two  $\text{C}_{29}$  aetioporphyryns (17), each of which is known to possess five methyl and two ethyl substituents at the  $\beta$ -positions, *i.e.* they are mono  $\beta$ -unsubstituted. Both series were largely removed upon acetylation, though the higher  $\text{C}_n$  members of the later-eluting series, A(3), remained (*cf.* Figs. 3 and 6a). The A(3) series forms 7.5% of the total, extends from  $\text{C}_{27}$  to  $\text{C}_{34}$ , and maximises at  $\text{C}_{29}$  (Fig. 7c). The earlier-eluting of the two mono  $\beta$ -H series, A(2), extends from  $\text{C}_{27}$  to  $\text{C}_{30}$ , maximises at  $\text{C}_{28}$  (Fig. 7b) and comprises 4.5% of the total. Two A-2 class series were identified. The major

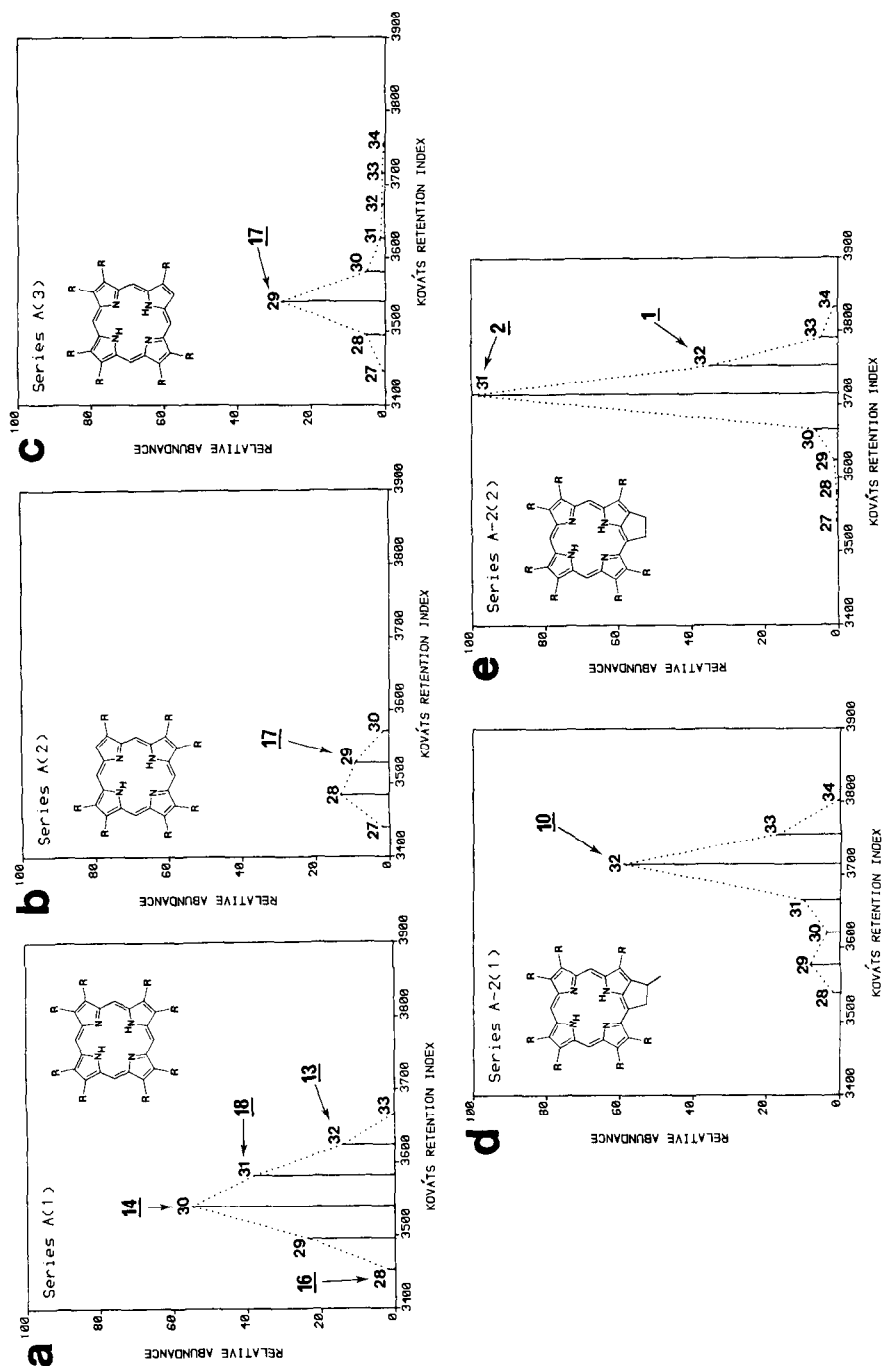


Fig. 7. (a) Distribution profile for the A class "fully  $\beta$ -alkyl substituted" pseudo-homologous series of porphyrins. (b) Distribution profile for an A class " $\beta$ -unsubstituted" pseudo-homologous series. (c) Distribution profile for a second A class " $\beta$ -unsubstituted" pseudo-homologous series, eluting later than b. (d) Distribution profile for the A-2 class 13<sup>1</sup>-methyl-13,15-ethanopseudo-homologous series. (e) Distribution profile for the A-2 class 13,15-ethanopseudo-homologous series.

TABLE IV

## PSEUDO-HOMOLOGOUS SERIES OF PETROPORPHYRINS IN GILSONITE BITUMEN

tr = Less than 0.1% of total petroporphyrins.

Carbon number	Series (abundance, %)*				
	A(1)	A(2)	A(3)	A-2(1)	A-2(2)
27		0.4	0.1		tr
28	0.4	2	0.9	0.4	tr
29	4	1.6	5	1.4	0.2
30	10	0.2	0.9	0.6	1.1
31	7		0.2	2	18
32	3		0.1	10	6
33	tr		0.1	3	0.8
34			tr	tr	tr

\* As percentage of total petroporphyrin content.

series is composed of eight components in the C<sub>27</sub>-C<sub>34</sub> carbon number range which are structurally related to DPEP (1) (*i.e.* they bear a 13,15-ethano system) and contributes 26% of the total. As can be seen from the distribution profile for this series (Fig. 7e) the C<sub>31</sub> member (2) is the major component, with DPEP (1) the second most abundant. The second A-2 class pseudo-homologous series (18% of the total) comprises components in the C<sub>28</sub>-C<sub>34</sub> carbon number range. The major component is a C<sub>32</sub> compound (10) which bears a methyl-substituted five-membered exocyclic ring (Fig. 7d). The compositions of these series are summarised in Table IV.

TABLE V

## HPLC AND GC-MS CHARACTERISTICS OF KNOWN GILSONITE PORPHYRINS\*

GC-MS conditions as for Fig. 1; HPLC conditions as for Fig. 2a.

Carbon number	Type	Structure	HPLC retention time (min)	GC-MS	
				KRI	m/z**
28	Aetio	16	?	3455	579
29	Aetio	12	30.5	3496***	593
29	Aetio	17	27.9	3528	593
29	Aetio	17	27.9	3540	593
30	Aetio	14	28.9	3541	607
31	Aetio	18	27.2	3583	621
32	Aetio	13	25.7	3624	635
36	Aetio	19 <sup>§</sup>	?	3800	691
31	13,15-Ethano	2	39.2	3715	619
32	13,15-Ethano	1	36.7	3754	633
32	13 <sup>1</sup> -Methyl-13,15-ethano	10	37.2	3715	633

\* HPLC data from ref. 39.

\*\* m/z of [M - 131]<sup>+</sup> ion.

\*\*\* GC-MS assignment on basis of intensity (see text).

§ Not found in Gilsonite, included for reference.

TABLE VI  
PETROPORPHYRIN ANALYSES OF GILSONITE BITUMEN

n.d. = Not detected; n.r. = not reported. NiP = Nickel(II)porphyrin chelates.

Reference	Porphyrin content (ppm)	A class (Aetio-porphyrins)		A-2 class porphyrins	
		Range	Max	Range	Max
Sugihara and McGee <sup>34</sup>	300	n.d.	n.d.	C <sub>32</sub>	C <sub>32</sub>
Baker <sup>35</sup>	n.r.	n.d.	n.d.	C <sub>32</sub>	C <sub>32</sub>
Baker <i>et al.</i> <sup>18</sup>	40	C <sub>29</sub> –C <sub>34</sub>	C <sub>31</sub>	C <sub>29</sub> –C <sub>34</sub>	C <sub>32</sub>
Alturki <i>et al.</i> <sup>36</sup>	100	C <sub>27</sub> –C <sub>34</sub>	C <sub>30</sub>	C <sub>25</sub> –C <sub>36</sub>	C <sub>31</sub>
Hodgson <i>et al.</i> <sup>38</sup>	n.r.	C <sub>27</sub> –C <sub>32</sub>	C <sub>31</sub>	n.d. <sup>§</sup>	n.d. <sup>§</sup>
Didyk <sup>51</sup>	99	C <sub>27</sub> –C <sub>33</sub>	C <sub>30</sub>	C <sub>27</sub> –C <sub>34</sub>	C <sub>31</sub>
Quirke <i>et al.</i> <sup>14</sup>	100	C <sub>27</sub> –C <sub>32</sub> <sup>§§</sup>	C <sub>30</sub>	C <sub>27</sub> –C <sub>33</sub>	C <sub>31</sub>
This paper	200	C <sub>26</sub> –C <sub>35</sub>	C <sub>30</sub>	C <sub>27</sub> –C <sub>35</sub>	C <sub>31</sub>

\* Description or characterization given for Gilsonite.

\*\* No data on metalloporphyrins given, only demetallated pigments reported.

\*\*\* As calculated from mass spectrometric data.

§ The lack of DPEP (A-2 class) porphyrins is surprising and may arise either from differences in the composition of the Gilsonite examined or from selectivity in the extraction process.

§§ Further work<sup>37</sup> revealed three pseudo-homologous series of aetioporphyryns, the X, Y and Z series.

§§§ Trace only. VOP = Oxovanadium(IV)[vanadyl]porphyrin chelates.

The A-4 (13 components) and A-6 (10 components) class compounds, in sum, comprise only 0.9 and 0.3% of the total porphyrins, respectively. Linear series are less in evidence than for the A and A-2 classes. Owing to lack of compounds of known structure for co-injection the A-4 and A-6 compounds cannot be more precisely assigned. The presence of 2 and 3 additional degrees of unsaturation compared to the aetio (A class) porphyrins means that the A-4 components might be related to the tetrahydrobenz-DPEP and the A-6 components to the benz-aetio (formerly rhodo-aetio) structures proposed previously<sup>18,19</sup>. The large number of possible isomeric structures precludes further speculation. It is notable that both the A-4 and A-6 components are largely removed by acetylation, though some remain, at much reduced abundance (Fig. 6c and d, respectively), possibly as a result of incomplete acetylation.

As a result of GC-MS co-injection studies, it is possible to compare directly the traces obtained by HPLC and GC-MS analysis of Gilsonite petroporphyrins [as their free-bases and (TBDMSO)<sub>2</sub>Si(IV) derivatives, respectively]. Fig. 2a shows the HPLC trace, with components of known structure marked. Fig. 2b shows the GC-MS RIC, with the same compounds (after derivatisation) marked. It should be noted that in the GC-MS case, as a result of co-elutions, certain of the marked peaks contain other components. Table V details the known Gilsonite porphyrins, their structures, their HPLC retention times and their GC-MS KRI values.

The power of the GC-MS technique for petroporphyrin analysis is clearly demonstrated. The data extend greatly the number of porphyrin components detected in Gilsonite (to 123). The carbon number ranges over which they occur are also extended. In addition, previously undetected minor A-4 and A-6 class components,

<i>A-4 class porphyrins</i>		<i>A-6 class porphyrins</i>		<i>A-2/Aetio</i>	<i>Metallo-porphyrins</i>	<i>Gilsonite*</i>
<i>Range</i>	<i>Max</i>	<i>Range</i>	<i>Max</i>			
n.r.	n.r.	n.r.	n.r.	—	NiP	Cowboy
n.r.	n.r.	n.r.	n.r.	—	n.r.**	Cowboy
n.r.	n.r.	n.r.	n.r.	1.50***	n.r.**	Cowboy
n.r.	n.r.	n.r.	n.r.	1.32***	n.r.**	Little Bonanza
n.r.	n.r.	n.r.	n.r.	—	n.r.**	Bonanza
n.r.	n.r.	n.r.	n.r.	1.60***	NiP	Barber selects
n.r.	n.r.	n.r.	n.r.	1.60***	NiP	Barber selects
C <sub>31</sub> –C <sub>34</sub>	C <sub>33</sub>	C <sub>31</sub> –C <sub>34</sub>	C <sub>32</sub>	1.36	NiP/VOP <sup>§§§</sup>	Selects

known to occur in samples from other locations, are also present in Gilsonite, albeit in low abundance. A summary of the data obtained is presented in Table VI, together with those obtained by previous investigators.

#### *Assignment of pseudo-homologous series*

GC-MS analysis reveals that the petroporphyrins, when their KRI values are plotted against their carbon numbers, form many straight-line relations, which are proposed to represent pseudo-homologous series. Five series have been partially identified by extrapolation from co-chromatographed standards.

Earlier, HajIbrahim *et al.*<sup>37</sup> analysed the porphyrins of Gilsonite by isocratic HPLC and produced Kováts plots of  $\log_{10}$  retention time against carbon number. These plots revealed three pseudo-homologous series of aetioporphyryns in this sample, which were termed X (fully alkylated), Y (with one unsubstituted  $\beta$ -position), and Z (suggested as having two unsubstituted  $\beta$ -positions). Due to the larger number of series discovered in the present work, a different nomenclature has been adopted. It is clear, nonetheless, that the X series of HajIbrahim *et al.*<sup>37</sup> is the A(1) series (Fig. 7a). The other series are less clear; it seems likely that the Y (mono-unsubstituted) series is split by GC into the series A(2) and A(3); the correspondence between the Z series and the GC-MS data is speculative. From knowledge of the GC retention behaviour of fully alkylated and mono-unsubstituted aetioporphyryns, it is proposed that the porphyrins falling above series A(3) on the Kováts plot (Fig. 3) are compounds with two unsubstituted  $\beta$ -positions. It is, of course, possible that GC has further separated the Z series of HajIbrahim *et al.*<sup>37</sup>.

By consideration of the five series in Gilsonite, structures have been postulated

for certain of the unknown members. A number of factors have been taken into account in the considerations of structures for these compounds (Fig. 8). In Boscan oil<sup>49</sup> and in Gilsonite<sup>50</sup>, the major pyrrole-2,5-diones produced by oxidation of the porphyrins are the 3-methyl-4-*n*-alkyl series. In Boscan oil, a second series is observed<sup>49</sup> with methyl branching at the 1-position of the 4-alkyl substituent. In contrast, Messel oil shale contains, as significant components, porphyrins of bacteriochlorophyll origin<sup>21</sup>, several of which have an ethyl substituent at C-12 and one an iso-butyl substituent at C-8 (*i.e.* with a methyl branch at the 2-position of the side-chain). Decarboxylation of the C-17 propionic acid substituent is readily envisaged, giving alkyl petroporphyrins of similar substitution patterns. As yet, however, there is no evidence to suggest that such petroporphyrins are significant constituents of Gilsonite. It seems reasonable that the 33 compounds (Table IV) found in the present work to account for *ca.* 80% of the total porphyrin content of the bitumen possess only *n*-alkyl substituents.

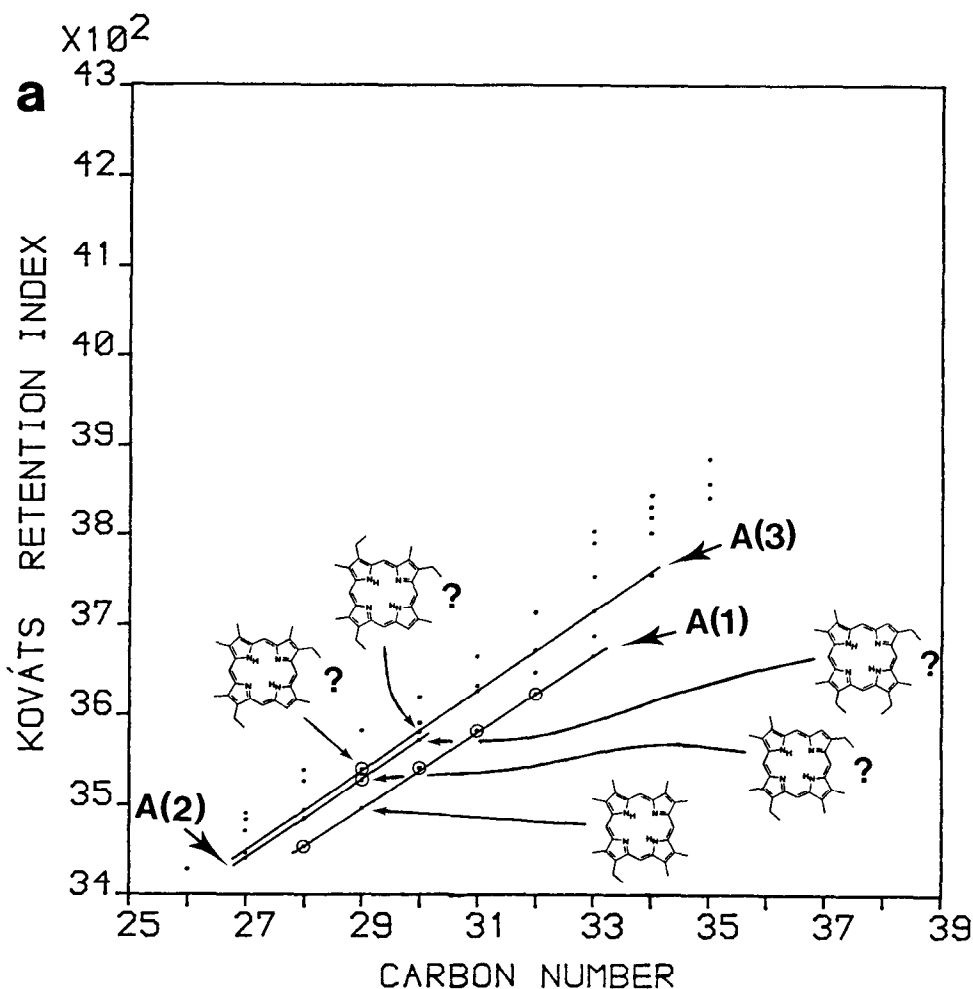


Fig. 8.

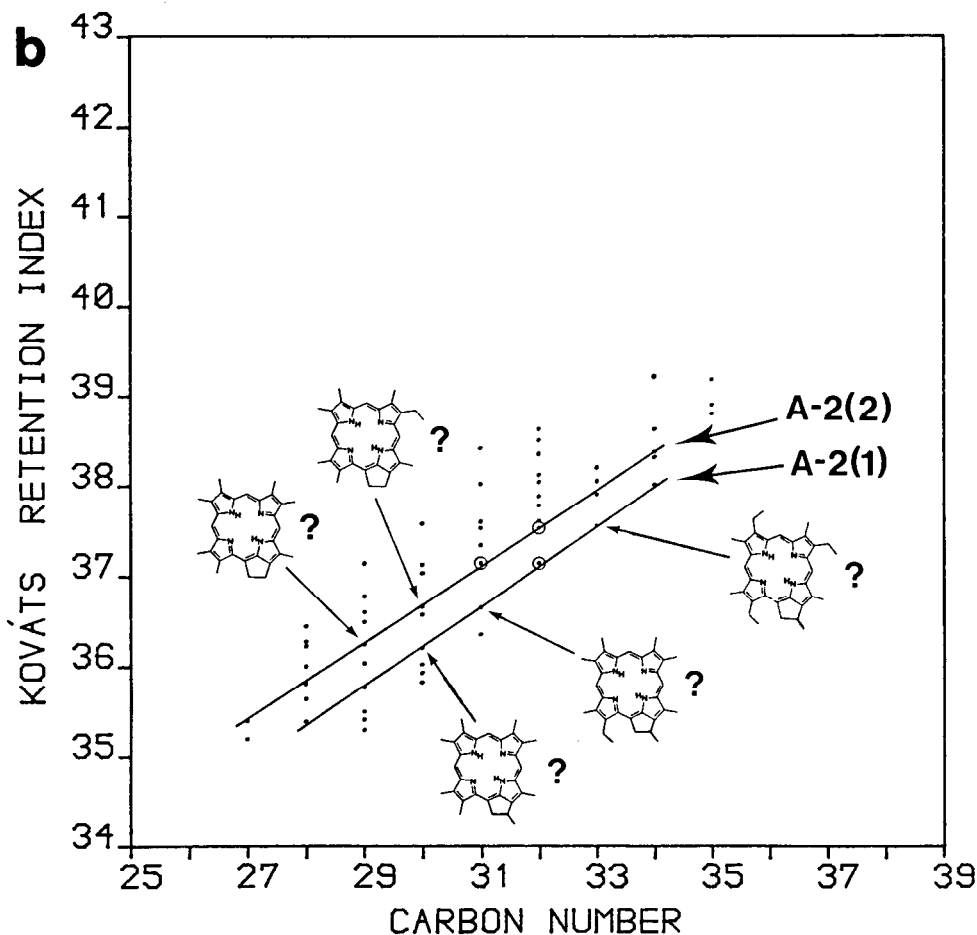


Fig. 8. Kováts plots for A class (a) and A-2 class (b) porphyrins of Gilsonite as  $(\text{TBDMSO})_2\text{Si}$  (IV) derivatives with homologous (or pseudo-homologous) series marked, and with structures proposed for some members of these series on the basis of GC behaviour, and by comparison with known structures in the same series (*cf.* Figs. 3 and 4).

The site of the unsubstituted  $\beta$ -position of series A(3) is tentatively assigned as C-13 on the basis of structure 15, found to be a major aetioporphyrin of Serpiano shale<sup>16</sup>. The earlier-eluting series A(2) also has one unsubstituted position (at least the  $\text{C}_{29}$  member, 17). This may be either C-3 or C-7, since precedents exist for sedimentary alkyl porphyrins unsubstituted at either of these positions<sup>13,20</sup>. It is not known why members of A(2) were not detected above  $\text{C}_{30}$ ; such compounds are readily envisaged, being structural isomers of A(3), which does have members above  $\text{C}_{30}$ .

The apparent occurrence of two  $\text{C}_{27}$  aetioporphyryns with one unsubstituted  $\beta$ -position is an anomaly. Only one isomer is possible (20), so that one of these compounds must possess two unsubstituted positions, and yet falls adventitiously in the same straight line relation as a  $\text{C}_{29}$  compound with only one unsubstitution (17).

Similarly, it is difficult to suggest structures for the  $C_{28}$  and  $C_{29}$  members of series A-2(1); only one compound was available for co-injection, a fully alkylated 13<sup>1</sup>-methyl-13,15-ethanoporphyrin (10). However, a  $C_{29}$  13<sup>1</sup>-methyl-13,15-ethanoporphyrin must contain one (or more) unsubstituted  $\beta$ -positions, and so would not be expected to fall in the same series. An analogous situation arises in series A-2(2), where the presence of  $C_{27}$  and  $C_{28}$  species is not easily rationalised.

A further complication is that the higher carbon number members ( $\geq C_{32}$ ) of series A(3) are not removed by Friedel-Crafts acetylation, implying that these compounds have no unsubstituted  $\beta$ -position, or that their acetylation is somehow inhibited. It is known, from co-injection, that the  $C_{29}$  member does have one unsubstituted position. Thus, either the acetylation, under the conditions employed, does not affect the  $\beta$ -H positions of higher members, or series A(3) contains both fully alkylated and mono-unsubstituted aetioporphyrins.

## CONCLUSIONS

GC-MS analysis of the petroporphyrins of Gilsonite as  $(TBDMSO)_2Si(IV)$  derivatives has revealed 123 individual porphyrins with abundances  $\geq 0.1\%$  of the major  $C_{31}$  13,15-ethanoporphyrin. Each has been assigned a KRI value by co-chromatography of *n*-alkanes, and its carbon number and unsaturation class on the basis of its molecular mass.

These 123 points have been plotted on a scale of KRI vs. carbon number, in groups according to their class. Within the two major classes (A; A-2), and possibly the minor classes (A-4; A-6), there is evidence for straight-line relationships, indicating the presence of pseudo-homologous series.

Co-injection of 12 porphyrin standards, one of which is partially resolved into two components, revealed that 10 co-chromatograph with components of the Gilsonite petroporphyrin suite (one, a  $C_{31}$  15,17-butanoporphyrin, co-chromatographs with a component present in only trace amount). Thus, the identities of nine Gilsonite petroporphyrins have been assigned by co-chromatography. Certain of these are structurally related, confirming that the straight lines on the Kováts plots do indeed contain pseudo-homologous series.

By extrapolation from the structures of the co-injected standards, five series of petroporphyrins have been assigned (Fig. 7):

- A(1), a series of fully-alkylated aetioporphyrins
- A(2) and A(3), two series of mono  $\beta$ -unsubstituted aetioporphyrins
- A-2(1), a series of 13<sup>1</sup>-methyl-13,15-ethanoporphyrins
- A-2(2), a series of 13,15-ethanoporphyrins.

In Gilsonite, these have carbon number ranges as follows: A(1),  $C_{28}$ - $C_{33}$ ; A(2),  $C_{27}$ - $C_{30}$ ; A(3),  $C_{27}$ - $C_{34}$ ; A-2(1),  $C_{28}$ - $C_{34}$ ; A-2(2),  $C_{27}$ - $C_{34}$ .

Other standards, especially of higher ( $> C_{32}$ ) carbon number, are needed for further work, but the relatively low abundances of such porphyrins in geological samples will obviously restrict their availability.

The 33 compounds contained by these series constitute *ca.* 80% of the abundance of porphyrins in Gilsonite bitumen. Since it is to be expected that they will be major components of other samples, they will provide useful comparative data for geochemical studies of porphyrins.



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