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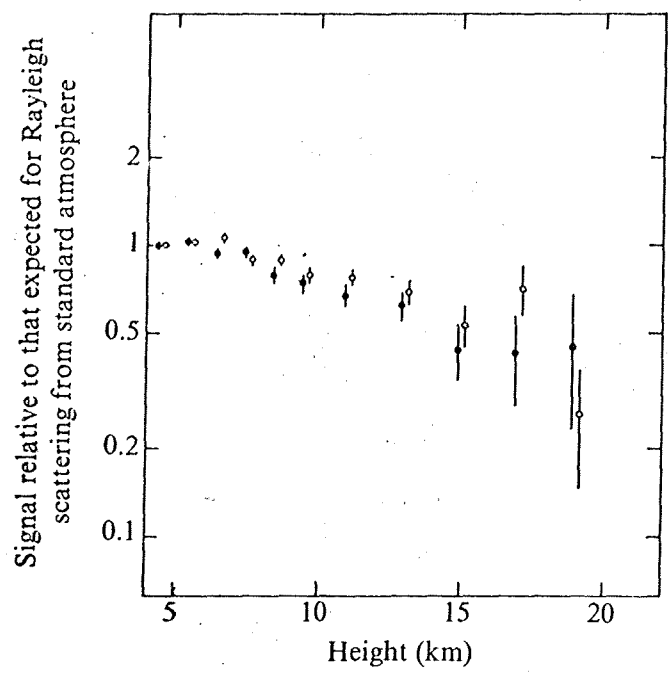


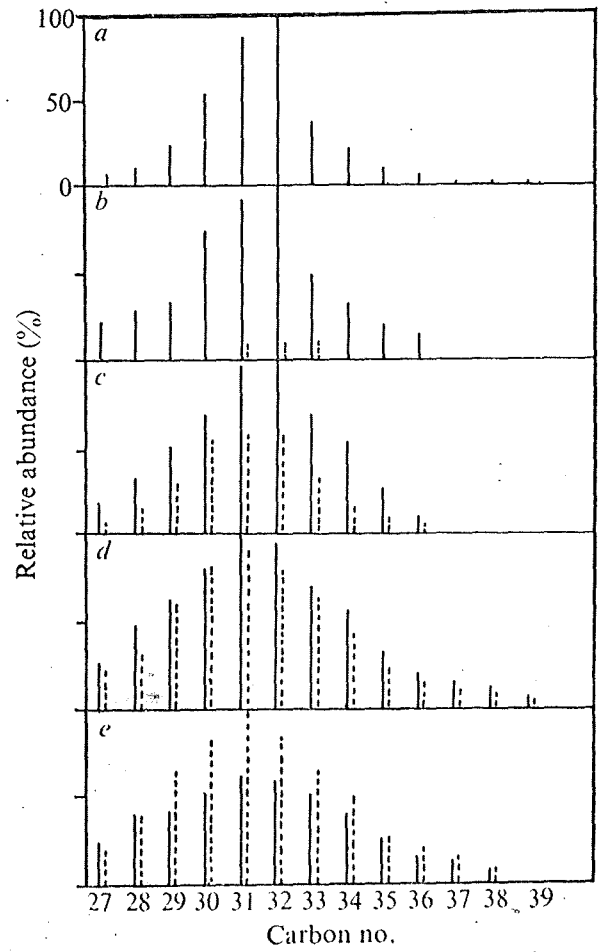
Fig. 2 Observed signals at 303.5 nm (●) and 308.0 nm (○) for February 27, 1975, relative to those expected for Rayleigh scattering. Error bars indicate the standard deviations corresponding to the photon count for each height channel.

Petroporphyrins as indicators of geothermal maturation

We report here two new sets of data which provide evidence of the occurrence of the postulated conversion of deoxyphyloerythroetioporphyrin (DPEP) to etioporphyrin. Simulated geothermal maturation in the laboratory demonstrates that DPEP-etio conversion occurs proportionally to the severity of the treatment, and an analysis of petroporphyrins from a suite of genetically related petroleum and their source rocks reveal that the DPEP:etio ratio is inversely proportional to the presumed severity of the geothermal history of the sample.

Alkyl petroporphyrins occur in a wide range of geological materials^{1,2} where they are usually present as two major homologous series of the deoxyphyloerythroetioporphyrin (DPEP) and etio type. Initially, the DPEP compounds containing the isocyclic ring were thought to be representative of, and derived from, chlorophylls, whereas the etio homologues, with no isocyclic ring, were considered to be remnants of the haem type pigments³. But though chlorophyll pigments exist in far greater abundance than haem pigments in the biosphere⁴, DPEP and etio porphyrins⁵ frequently occur in similar amounts in geological samples, and Corwin suggested⁴ that the conversion of

Fig. 1 Relative abundance of metallopetroporphyrins (VO) from thermally altered (210 °C for 0 (a), 50 (b), 100 (c), 150 (d) and 385 (e) h) La Luna (Mara) extract obtained by mass spectrometric determination of M⁺ at the following masses: DPEP (solid line) = (457+n14) a.m.u.; etio (dashed line) = (459+n14) a.m.u.; where n = 1 to 13 (C₂₇ to C₃₉). The mass spectra were collected by computer controlled gas chromatography-mass spectrometry; because of instrument background low abundance ions are occasionally not recorded (for example, C₃₇, C₃₈, and C₃₉ in the 50-h (b) and 100-h (c) heating experiments).



results can be better interpreted in terms of absorption by water vapour in the height range 0-5 km; a difference in absorption cross section of about 10⁻²⁷ m² between 297 and 308 nm would be required for that to occur, but no accurate measurements of cross section are available for this range of wavelengths.

There is considerable scope for the further development of this technique of ultraviolet laser sounding of the atmosphere. With the production of new frequency-doubling materials suitable for 90° phase-matching¹⁵, it should become possible to increase substantially the available ultraviolet pulse energies. The accuracy and height resolution of the present type of measurement should thereby be improved, and the height range extended. In addition, measurements of the concentrations of certain constituents by resonance scattering or fluorescence should become possible.

A. J. GIBSON
L. THOMAS

Science Research Council,
Appleton Laboratory,
Ditton Park,
Slough SL3 9JX, Berkshire, UK

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Table 1 Characteristics of petroporphyrins and source rocks from the Maracaibo Basin

Sample	Current geological setting				Petroporphyrins			
	Type	Age*	Depth (m)	Temperature (°C)	Content† (p.p.m.)	Carbon no. of most abundant molecular ion		DPEP/etio
						DPEP	etio	
a La Luna (Mara)	Source rock	Cretaceous	outcrop	< 30†	55,900	32	—	≥ 100
b Boscan (BN-4)	Petroleum	Eocene reservoir	2,050–2,230	71	3,540	32	31	1.56
c La Paz (P187-Z)	Petroleum	Jurassic fracture	3 300–3,450	95	628	31	30	0.56
d La Luna (36E-2)	Source rock	Cretaceous	4,410–4,550	135	2,730	31	30	0.56

*The two oils are believed to have originated in the La Luna Formation (Cretaceous) but are currently found in the host formations indicated¹².

†No information concerning maximum depths of burial or temperature history is available but low reflectivity ($R_{av} = 0.19$) of vitrinite suggests a mild geothermal history. (We thank Dr M. Jones, Organic Geochemistry Unit, University of Newcastle, for this measurement.)

‡Metalloporphyrin content (p.p.m.) in oil or organic extract.

DPEP to etio homologues must occur in the geological environment. Indirect evidence of the conversion of DPEP to etio has been obtained from a comparison between petroporphyrins recovered from a retorted shale oil and those from the original shale⁶. The retorted oil contained a large proportion of etio type homologues, suggesting that conversion did occur during the retorting. The drastic temperatures required for the retorting process are, however, significantly higher than those (about 50–180 °C) normally experienced in deeply buried sediments, which effect the geothermal maturation of entrapped or dissolved petroporphyrins and other organic materials. Evidence of the conversion has also been provided by the thermal alteration, in the laboratory, of a crude petroleum containing metalloporphyrin to which etio porphyrin III had been added as an internal reference compound⁷. Other studies which have simulated geothermal maturation^{8–11} have been restricted to porphyrins of the etio skeleton; they could not, therefore, provide information about the fate of the isocyclic ring of DPEP homologues or about the occurrence of the DPEP to etio conversion.

The geological materials used (Table 1) in this study are from, or are genetically related to, the Cretaceous La Luna formation of the Maracaibo Basin in western Venezuela. This formation is extensive and source beds in it are believed to have generated the major part of the oil produced in the Maracaibo area¹². One of the most remarkable characteristics of these shaly limestones is the high porphyrin content (up to 55,000 p.p.m. of the organic extract); it has, in fact, been used to establish source rock–crude oil relationships for the oils from the Maracaibo Basin¹³.

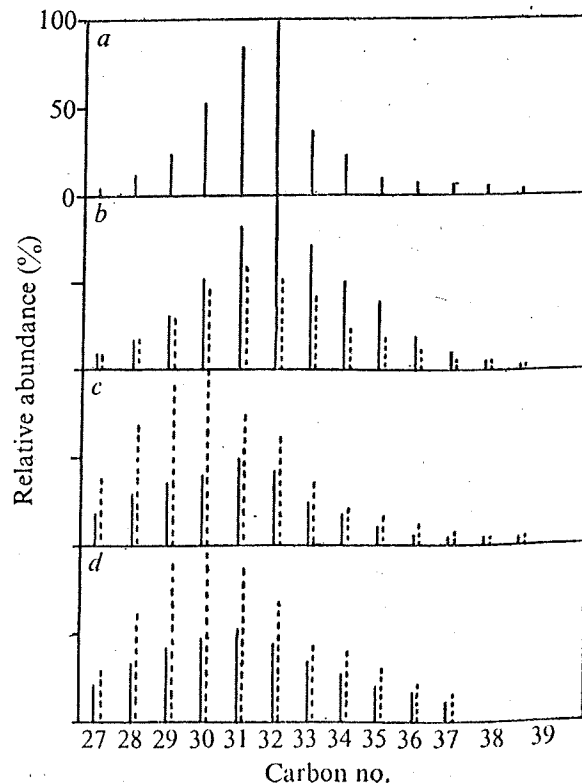
The simulated geothermal maturation was performed on the total organic extract of the least mature shale (Table 1a). The toluene–methanol (3:1) extract was deposited on prewashed (redistilled hexane B.D.H.) and vacuum-dried bentonite to give a concentration of about 2,790 p.p.m. of metalloporphyrin (98% vanadyl). Bentonite, a montmorillonitic clay mineral was chosen as the organic free matrix for thermal alteration experiments. Results obtained using this material rather than limestone should be more generally applicable to the geothermal fate of porphyrins in argillaceous sediments.

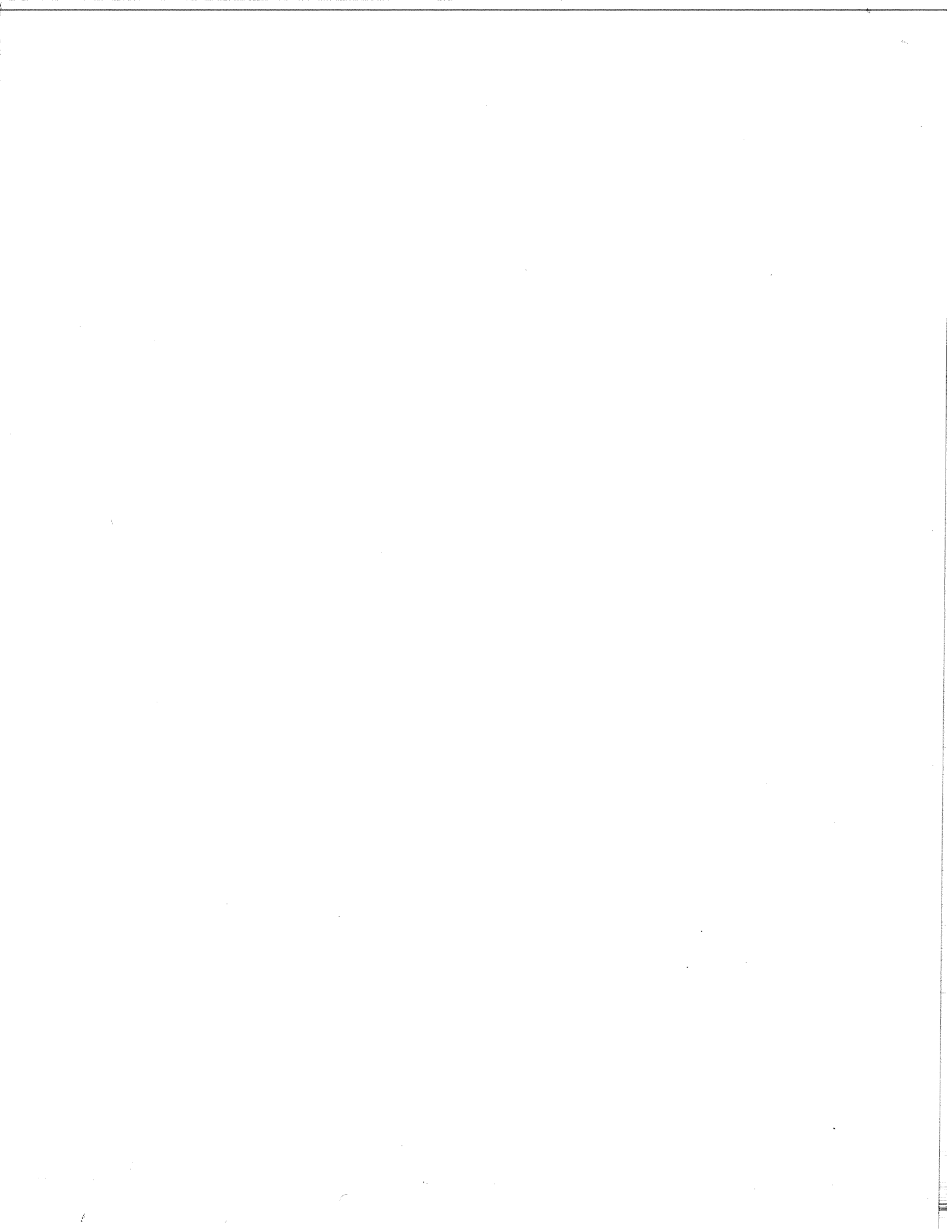
Aliquots of coated bentonite were placed in heavy-walled glass tubes (15×150 mm), flushed with oxygen-free nitrogen and sealed under vacuum. The sealed tubes were stored in the dark at 210 °C; individual tubes were removed at successively longer time intervals from 0 to 385 h. After cooling, the bentonite was extracted with toluene–methanol (3:1) and the metalloporphyrins were isolated, and purified using thin-layer chromatography (silica gel H, 0.5 mm, toluene–methylene chloride, 1:1). Recoveries of total metalloporphyrins after thermal treatment varied from 81% (0 h) to 19% (385 h experiment). The thermal degradation of metalloporphyrins was found to be first order ($t_{1/2} = 166$ h). The extracts were examined using mass spectrometry; a computerised data handling system¹⁴ monitored and collected the spectra in real time.

Bar diagrams (Fig. 1) show the relative abundance of the molecular ions of metalloporphyrins isolated after various times of thermal treatment. The zero-time extract exhibits a single homologous DPEP series of carbon number C_{27} – C_{39} , maximising at C_{32} . After 50 h an etio series could just be detected, after 100 h this was prominent and after 385 h the abundance of this series exceeded that of the now much-diminished DPEP compounds. Thus, the DPEP series seems to have undergone extensive thermal conversion to the etio series. The most abundant DPEP homologue remaining was then C_{31} , indicating that a second maturational process involves loss of alkyl groups. Dealkylation is a well known feature of geothermal maturation of other geolipids¹⁵ and has been recorded following the laboratory thermal alteration of etio-porphyrins^{8–11}.

In the second part of this study petroporphyrins from two crude oils and from the toluene–methanol (3:1) extracts of two

Fig. 2 Relative abundance of petroporphyrins isolated from geological samples described in Table 1. Mass spectrometric determination of M^+ occurring at the following masses: DPEP (Solid line) = $(392+n14)$ a.m.u.; etio = $(394+n14)$ a.m.u.; where $n = 1-13$ (C_{27} – C_{39}). a, La Luna (Mara); b, Boscan BN4; c, La Paz P187-Z; d, La Luna 36E-2.





different samples of their presumed source rock (Table 1) were isolated using demetallation-extraction with methanesulphonic acid (4 h at 110°C) and were analysed using mass spectrometry¹⁶. Figure 2 presents the relative abundances of the petroporphyrins of these samples; the samples increasing in maturity (based on geological information) from top to bottom of the diagram. As the geothermal maturity increases there is an increase in the relative abundance of the etioporphyrins and a shift to the lower carbon number of the most abundant petroporphyrin observed (Table 1). The decrease in the DPEP : etio ratio would suggest that during geothermal maturation DPEP species are converted into etio homologues. A general trend observed¹⁷ within a group of non-genetically related geological materials suggests that the DPEP : etio ratio decreases with the depth of burial.

The DPEP-etio conversion suggested for the Maracaibo Basin samples parallels the conversion observed in the thermal alteration experiment. In each case the maxima of the two homologous series occur either at the same carbon number or with the abundance of etio homologues maximising one carbon atom lower than the DPEP homologues. Similar distributions have been observed in a wide range of naturally occurring petroporphyrins¹. The thermally induced conversion of DPEP to etio porphyrins may be widespread in the geological environment and could account for the abundance of etio homologues in crude oils and sedimentary rocks. The decrease in the DPEP : etio ratio with increasing maturation could be a useful measure of the extent of maturation of genetically related geological materials.

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BORYS M. DIDYK
YOUSIF I. A. ALTURKI
COLIN T. PILLINGER
GEOFFREY EGLINTON

Organic Geochemistry Unit,
School of Chemistry,
University of Bristol,
Bristol BS9 1TS, UK

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or goethite (α -FeOOH) to the ferrimagnetic form, maghaemite (γ -Fe₂O₃). He also proposed two possible mechanisms involving a reduction process followed by reoxidation to maghaemite. In the first (fermentation mechanism), the reduction occurs as a result of the decay of organic matter in the soil in anaerobic conditions achieved during wet periods, and reoxidation to maghaemite occurs in the aerobic conditions prevailing during subsequent dry periods. In the second (heating mechanism) the burning of organic material produces the temperature increase and reducing atmosphere necessary for the reduction to magnetite (Fe₃O₄) in a thin layer of soil underlying the fire and reoxidation occurs during the cooling down of the fires when air enters the system.

On the basis of the heating mechanism, the percentage of the iron oxide in the soil which has been converted *in situ* to maghaemite (that is, the percentage conversion) is given by the ratio of the observed magnetic susceptibility (χ_o) to the susceptibility (χ_N) after heating the soil in a laboratory furnace at 550°C in an atmosphere of nitrogen followed by air³. Although pure maghaemite converts to haematite at temperatures above 350°C, maghaemite doped with, for example, sodium, aluminium or magnesium is stable up to very much higher temperatures⁴. Therefore, since the iron oxides in soils are in a finely divided form and in intimate contact with the clay minerals, it is assumed that the laboratory heating converts the iron oxides to a thermally stable, impure maghaemite. Support for this hypothesis has been provided by Le Borgne¹ who has shown that soils with a high magnetic susceptibility exhibit an exothermic DTA peak, characteristic of maghaemite, at about 700°C. Furthermore, X-ray diffraction measurements on the laboratory heated soils have established that either maghaemite or magnetite is present, and in view of the final oxidising stage in the heating, the latter alternative is unlikely.

Magnetic susceptibility measurements (Table 1) were undertaken, using an a.c. bridge system⁵ operating at 1 kHz, on soils (0-20 cm; A horizon) derived from a wide range of sedimentary rock deposits (Triassic-Miocene) in England and Italy, as well as on a small selection of soils from other parts of the Mediterranean zone and from various tropical regions.

Table 1 Magnetic susceptibility ranges for soils

Region	Geology	Magnetic susceptibility ($\times 10^{-8}$ kg ⁻¹)	
		Observed (χ_o)	After heating (χ_N)
England	Limestone	15-90	1,000-5,000
England	Sandstone, clay	10-180	600-8,000
Italy	Marly limestone, marl	10-80	600-3,000
Italy	Sandstone, clay	5-30	600-2,000
Italy	Limestone	30-500	200-4,000
Mediterranean	Limestone	150-600	1,500-3,000
Mediterranean	Calcareous alluvium	30-400	500-6,000
Tropics		15-500	200-8,000
(wet and dry)			
Tropics (rainy)		5-15	700-1,000

The percentage conversions (that is, $100\chi_o/\chi_N$) observed for the English soils were normally less than 5%, irrespective of the type of sedimentary rock from which they were derived (Fig. 1a). In contrast, the percentage conversions observed for the Italian soils differed widely depending on the associated rock-type. Soils developed on marly limestones, marls, sandstones and clays, again normally exhibited percentage conversions of less than 5% (Fig. 1b) whereas those developed on hard, as opposed to marly, limestones exhibited significantly higher percentage conversions extending up to 50% (Fig. 1c). These differences in percentage conversion cannot be satisfactorily explained in terms of the heating mechanism as it is extremely unlikely that the limestone soils from Italy have been consistently subjected to more extensive burning than either the other

Effect of climate on the magnetic susceptibility of soils

The magnetic susceptibility of soils derived from sedimentary rocks is normally significantly higher than that of the parent rock. Le Borgne^{1,2} has suggested that this enhanced susceptibility of the soil is due to the *in situ* conversion of the iron oxides from an antiferromagnetic form such as haematite (α -Fe₂O₃)

