

Non-hydrocarbons of significance in petroleum exploration: volatile fatty acids and non-hydrocarbon gases

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Abstract

Non-hydrocarbon gas species (CO₂, N₂, H₂) are locally important in exploration for gas, and there is a growing body of evidence that acid water originating in shales materially affects the diagenesis of nearby sandstones. These gases have been studied by analysing the products of closed-vessel hydrous pyrolysis of known petroleum source rocks, and comparing the results with field observations. Alteration of petroleum source rocks at temperatures >250 °C yields a significant amount of non-hydrocarbon components. Ethanoate and higher acid anions are liberated in substantial quantities; the yield appears to be related to the oxygen content of the sedimentary organic matter present.

The non-hydrocarbon gases CO₂, H₂ and N₂ are frequently the dominant gaseous products from hydrous pyrolysis: in the natural environment the same rock sequences at a higher maturity preferentially generate hydrocarbon gases—mainly methane. This discrepancy may be attributed to reaction and phase thermodynamic effects between laboratory and natural systems, behaviour that has important implications in the prediction of gas generation and composition in nature by source rock pyrolysis in the laboratory.

KEYWORDS: hydrous pyrolysis, kerogen, petroleum generation, simulated maturation, source rock, volatile fatty acids.

Introduction

PETROLEUM geochemistry has necessarily concentrated on the hydrocarbon products of the thermal alteration of sedimentary organic matter (kerogen). This is partly because of the analytical techniques usually used to measure the products, and partly because of the obvious importance of hydrocarbon generation. However, breakdown of kerogen at elevated temperatures has also been observed to yield significant amounts of non-hydrocarbon components (e.g. Harwood, 1977; van

de Meent *et al.*, 1983). This report investigates non-hydrocarbon materials which are: (1) generated directly from kerogen; (2) formed elsewhere in the subsurface but which partition into, or become associated with, the same phases as the hydrocarbons. We concentrate on two issues of significance for petroleum exploration: volatile fatty acids and non-hydrocarbon gases.

Volatile fatty acids (VFAs) have been cited as the likely cause of inferred secondary porosity, believed to be produced by etching with appropriate solutions (e.g. Surdam *et al.*, 1984). This increased porosity may be a major contribution to the economic viability of a potential petroleum

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TABLE 1. ROCK SAMPLES

SAMPLE	TOC (%wt)	Ro (%)	ANALYSIS
HRZ, North Slope Alaska	5.7	0.5	Gases
Kimmeridge Clay, Dorset, UK	12.0	0.36	Gases & VFAs
Australasian brown coal	54.0	0.4	VFAs
Marl Slate, Durham, UK	10.4	0.4-0.45(e)	VFAs
Green River shale, USA	14.3	0.4-0.45(e)	VFAs

TOC = Total Organic Carbon content

Ro = Vitrinite reflectance (oil immersion)

(e) = equivalent %Ro from distributions of biological marker compounds in rock extract.

reservoir. When associated with petroleum discoveries, non-hydrocarbon gases, such as carbon dioxide, nitrogen, hydrogen and hydrogen sulphide, lead to deterioration in the value of the accumulation. With the exception of hydrogen, they do not combust, and they must be disposed of, or produced for alternative uses. Also, the presence of quite minor amounts of non-hydrocarbons in a petroleum system can strongly influence the phase behaviour of the system at different pressures and temperatures. This can dramatically alter the economic worth of a petroleum discovery during its production life.

With these points in mind, several non-hydrocarbons were studied in the products of hydrous laboratory pyrolysis of organic-rich rocks. The results are compared with field observations, and some guidelines are formulated for both petroleum geochemists and exploration geologists.

Experimental

Samples. A suite of five different petroleum source rocks was examined; they are all predominantly oil-prone, and originate from as far afield as Alaska, mid-USA, England and Australia. Samples and analyses are summarised in Table 1.

HRZ is an oil-prone marine mudstone of Cretaceous age. Its name derives from its gamma-ray logging tool response ('high radioactivity zone') and is considered to be a major oil source rock on the Alaskan North Slope. At the location from which the borehole sample was taken, the HRZ is immature, but is at a maturity close to the onset of significant oil generation. The Kimmeridge mudstone was sampled from an outcrop on the

south Dorset coast, UK. This oil-prone source rock is Jurassic (Kimmeridgian) in age and is too thermally immature to have generated significant oil. The Australasian brown coal sample from the Gippsland Basin is of late Cretaceous-Palaeogene age, and is an immature example of a possible major source of the waxy crude oils found in the region offshore south-east Australia.

Our laboratory study concentrated mainly on the above three source rocks, although two further source rocks were examined in less detail. Marl Slate is a potential oil source rock of Permian age, sampled from an outcrop in County Durham, northern England. The Colorado oil shale (Green River Formation) is an immature oil shale of Eocene age, from the Uinta Basin, USA.

The hydrous pyrolysis technique. Numerous *anhydrous* pyrolysis techniques are used to estimate the generating potential, thermal maturity and organic input of petroleum source rocks, but they invariably generate products which do not closely resemble natural crude oils. Lewan *et al.* (1979) demonstrated that, by sealing a source rock with water inside a closed vessel and heating for periods of several days at temperatures between 300 °C and 360 °C, they could generate an oil-like pyrolysate which in overall composition, *n*-alkane distribution and $\delta^{13}\text{C}$ ratio, bore a close resemblance to oils sourced naturally from the same rock.

Hydrous pyrolysis conditions more closely resemble the natural geological setting of actively generating petroleum source rocks than most *anhydrous*, inert gas-sweep pyrolysis techniques. Provided the temperature remains below that of the critical point of water (374 °C) the water remains in the liquid phase providing an approximation to pore water. The higher pressure and

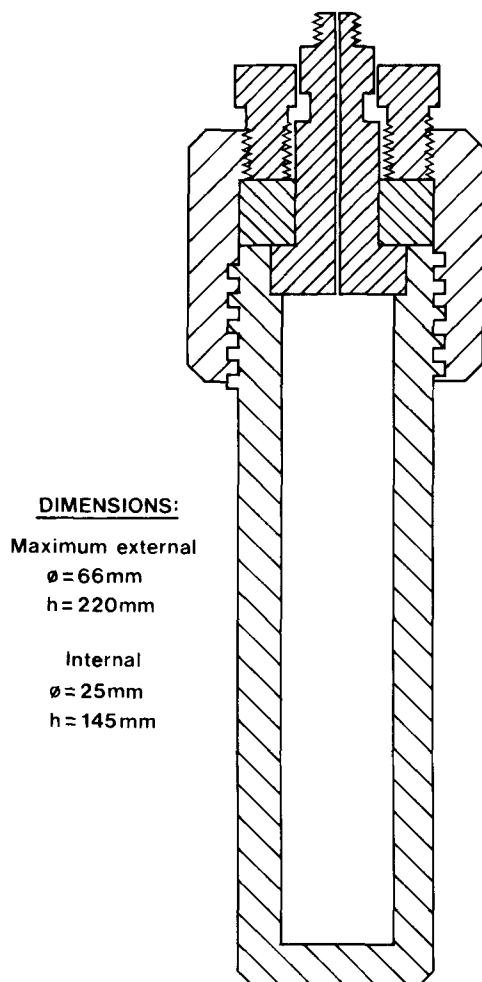


FIG. 1. Closed-vessel pyrolysis autoclave.

longer pyrolysis period (compared with inert gas-sweep experiments) mean that kerogen breakdown products are confined to the proximity of the rock for longer periods. This permits intimate contact, and thereby allows any further chemical interaction between the source rock and generated products, which is undoubtedly the case in nature.

Procedure. All source rocks were pyrolysed in the presence of water inside a stainless steel autoclave (Fig. 1). Approximately 20 g of rock, accurately weighed, were sealed inside the autoclave (72 cm³ capacity) with 20 cm³ water. This water volume was calculated to expand to almost fill the autoclave at the experimental temperatures. The remaining volume of the autoclave (c. 40 cm³)

was occupied by air. The rocks were heated to temperatures of 250–360°C for 3 days (72 hours). Oven temperature varied by only $\pm 2.5^\circ\text{C}$ of the stated temperature after the initial heat-up period (c. 3 hours). Samples and conditions for each experiment are listed in Table 2.

During these pyrolysis experiments the pressures inside the autoclave could not be measured and they are difficult to estimate accurately. Over the temperature range 300–360°C, pressure probably varied between 11.5 and 30 MPa, being composed of the vapour pressure of water (which is very high just below its critical point of 374°C) plus the pressure of the enclosed air and the generated gases which are contained in a volume of approx. 15–30 cm³ due to the expansion of water. The presumed pressure range (11.5–30 MPa) assumes that none of the air or generated gas dissolves in the water, which is certainly not the case. According to Henry's Law, the solubilities of most gases increase with increasing pressure but decrease with increasing temperature. If the contribution of dissolved gases to the pressure of the vessel is removed, the estimated pressure range becomes c. 8–20 MPa.

After cooling, the autoclave was connected to a gas syringe at room temperature and pressure; the volume of gas was recorded and transferred to an evacuated gas bottle for subsequent analysis. The autoclave was then opened and a sample of the water collected and immediately frozen. The heated rock sample was also removed for analysis but is not discussed further here. The gas syringe was gas-tight to 0.2–0.3 MPa pressure. As the maximum pressure inside the autoclave was probably no more than 0.7–0.8 MPa once cooled, and the gas residence time in the syringe was short (<1 minutes) it is unlikely that any significant gas leakage occurred at this point.

Gas analyses. Pyrolysate gas samples were separated by gas chromatography; the components were determined by thermal conductivity detection and quantified on an air-free basis. This corrects for nitrogen gas trapped as air in the autoclave and associated pipework by assuming that all the determined oxygen entered the system in this manner. If oxygen is either consumed or produced during the experiment this correction is not valid. Undoubtedly, some oxygen will indeed react with nickel in the autoclave; this may reduce the accuracy of other gas determinations to a minor degree.

Water analyses. Frozen water samples from the autoclave were analysed for VFA species by ion-exclusion chromatography (Parkes and Taylor, 1983), which is particularly suited to samples containing large amounts of both inorganic anions

TABLE 2. PYROLYSATE PRODUCTS (mmol kg⁻¹ rock)

No.	SAMPLE	PYROLYSIS TEMP. (°C)	GAS							VFAs	
			C ₁	C ₂	C ₃	C ₄₊	CO ₂	H ₂	N ₂	CH ₃ COOH	C ₂ H ₅ COOH
1	HRZ	300°	1	0.5	0.2	1	200	65	80		
2	-	310°	3	1.3	0.6	2	170	191	90		
3	-	320°	4	2	0.8	3	160	225	100		
4	-	340°	14	6	2.6	7	195	310	115		
5	-	350°	17	8	4.6	18	275	350	190		
6	-	360°	28	13	6.8	14	225	575	255		
7	Kimm. Clay	250°								5.7	1.6
8	-	300°	15	5	3	6	415	155	240	8.3	1.8
9	-	310°	31	16	9	20	620	200	335	9.9	1.9
10	-	320°	20	11	6	12	695	315	230	14.6	4.0
11	-	330°	47	27	15	23	870	415	265	19.9	4.8
12	-	340°	66	37	20	31	860	465	135	21.9	5.1
13	-	350°	140	76	42	56	675	605	260	18.9	4.2
14	Brown coal	300°								209	54
15	-	310°								228	56
16	-	320°								231	58
17	-	350°								268	68
18	Marl slate	320°								21.5	5.4
19	G.R. shale	320°								13.7	3.4

and hydrocarbons. The technique is based on addition of phosphoric acid to the water sample, followed by vacuum distillation of the resultant solution to allow separation from salts which would otherwise interfere with the analysis. Distillates were injected directly into an ICE (ion chromatography exclusion) liquid chromatograph. VFAs in the eluents were determined by conductometric detection and the identities of the major monofunctional carboxylic acids were confirmed by co-injection with reference compounds. Quantification was performed by calibration with external standard solutions.

Ethanoate (acetate) and propanoate (propionate) assignments were confirmed, independently, by gas chromatographic (GC) analysis. Water samples were acidified with solid oxalic acid (after Henderson and Steedman, 1982) and the products were chromatographed through a 2 m by 2 mm i.d. glass-packed column coated with SP1000 stationary phase (0.1%). Eluents were detected by flame ionisation detection and VFAs

were identified by comparison with external standards. Limited semi-quantitative VFA determinations by GC were encouragingly close to those obtained by ICE.

Results

Volatile fatty acids are a class of short chain monocarboxylic acids containing six or fewer carbon atoms. Perhaps the most exciting discovery of this study is that ethanoate and higher VFA species are indeed liberated from known hydrocarbon source rocks (Table 2); until now their production from hydrocarbon source rocks in substantial quantity has remained rather speculative.

VFAs appear in the residual pyrolysate waters as free species in solution and it is this that makes their detection rather difficult. At all pyrolysis temperatures for all the source rocks examined, ethanoate production consistently exceeds propanoate production by about four times. Butanoate

and isobutanoate (higher homologues to propanoate) are also liberated in smaller quantities.

Ethanoate yields from the pyrolysis of the Australasian brown coal are very high: values greater than 250 millimoles per kg rock were recorded (Fig. 2). This is equivalent to production of *c.* 30 g

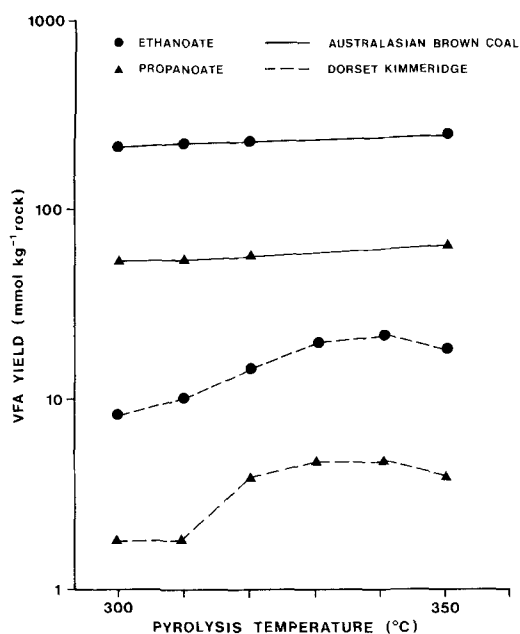


Fig. 2. Volatile fatty acid (VFA) yields.

ethanoate per kg carbon in the rock or almost 3% of the original total organic carbon (TOC) content of the coal (Fig. 3). Likewise, the Kimmeridge mudstone yielded a maximum of *c.* 10 g ethanoate per kg carbon in the rock, equivalent to *c.* 1% of the original TOC of the mudstone. The production of VFA species from source rocks may be related to the oxygen content of kerogen; the brown coal has a relatively high oxygen content and yielded the highest ethanoate (per unit mass of carbon). The Kimmeridge kerogen has a lower oxygen content and yielded less ethanoate.

VFA yields recorded in the Marl Slate and Green River shale pyrolysates are consistent with the above observations. The Green River shale liberated *c.* 0.6% of its original TOC as ethanoate—it has a lower oxygen content than that of the Marl Slate, which evolved just over 1% of its original TOC as ethanoate. The Marl Slate and Kimmeridge mudstone kerogens have similar oxygen contents per unit mass of carbon.

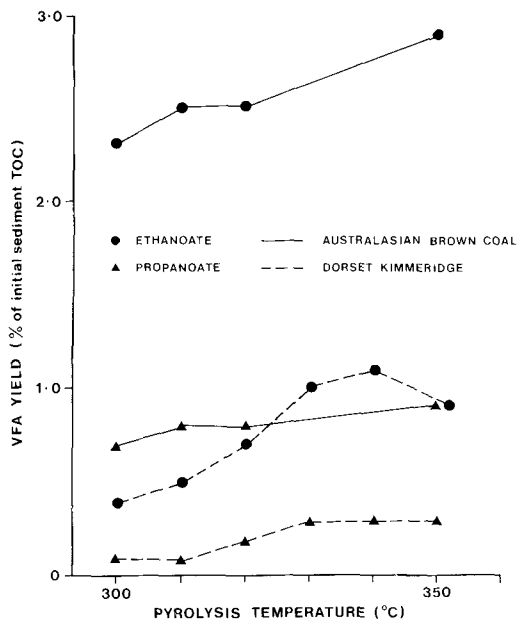


Fig. 3. Volatile fatty acid (VFA) yields normalised to initial sediment TOC.

Unpublished work at Sunbury has shown that up to approximately 5% of evolved volatile carbon-containing species are not detected by conventional flow-through pyrolysis equipment (e.g. 'Rock Eval'). This equates fairly well with the level of VFA production from the brown coal and Kimmeridge mudstone; flame ionisation detectors usually fitted to pyrolysis units are relatively insensitive to fatty acid species.

Gases. The hydrocarbon gases methane, ethane and propane (CH_4 , C_2H_6 , C_3H_8) were determined individually; higher hydrocarbons in the gas phase were determined as a composite measurement. Of the non-hydrocarbons, carbon dioxide, nitrogen and hydrogen (CO_2 , N_2 and H_2 respectively) were determined; neither carbon monoxide (CO) nor hydrogen sulphide (H_2S) were detected in any of the gas samples.

Gases were analysed on an air-free basis, to which a correction has also been applied to account for the solubility of CO_2 in water at room temperature and pressure (20°C , 1 Atmosphere). At room temperature and pressure approximately one volume of CO_2 dissolves in an equivalent volume of distilled water. In comparison, the solubilities of the other gases examined (H_2 , N_2 and hydrocarbons) are not significant (Table 3) and no solubility corrections for these gases were applied.

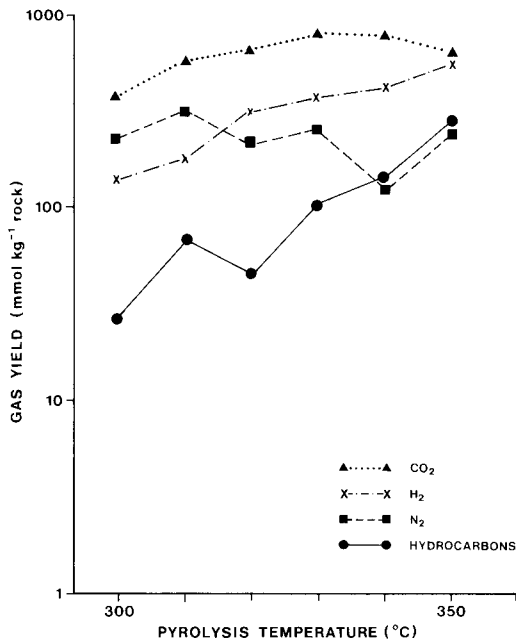


Fig. 4. Pyrolysis gas yields—Kimmeridge source rock.

TABLE 3. GAS SOLUBILITIES IN DISTILLED WATER

(Temperature = 25°C ; Pressure = 1 atmosphere)

GAS SPECIES	SOLUBILITY (cm ³ 100cm ⁻³ water)	DATA SOURCE*
CO ₂	88	1
H ₂	1	1
N ₂	1.6	1
CH ₄	3.7	2
C ₂ H ₆	4.8	2
C ₃ H ₈	3.4	2

*1. Merck Index, 1976

2. McAuliffe, 1963.

The immediate striking feature of the gas data (Table 2) is that the majority of the gases produced from hydrous pyrolysis of these petroleum source rocks are not hydrocarbons. Although the production of gaseous hydrocarbons from the

source rocks increases with pyrolysis temperature, the yields are always subordinate to that of non-hydrocarbon gases (Figs. 4 and 5).

Yields of CO₂, N₂ and H₂ in the pyrolysate gases are large but variable, both between source rocks, and for a single source rock pyrolysed at different temperatures. In general, H₂ was the most abundant gaseous product from pyrolysis of the HRZ shale; CO₂ was the most abundant gas from the Kimmeridge mudstone. Neither H₂ or CO₂ are the major gaseous product from such petroleum source rocks in their natural subsurface habitat (Hunt, 1979).

Pyrolyses between 300 and 360°C result in an increased yield of hydrocarbon gases of over one order of magnitude from the HRZ shale and Kimmeridge mudstone. In these experiments, however, the yield of hydrocarbon gases never exceeded production of non-hydrocarbon gases at the same temperature.

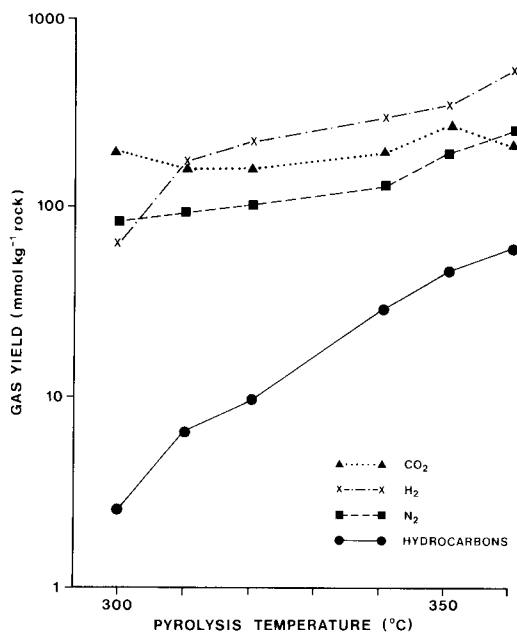


Fig. 5. Pyrolysis gas yields—HRZ source rock.

As in the natural production of hydrocarbons from these source rocks, the molar yields of methane exceeded ethane, and ethane exceeded propane in all the experiments (Table 2). For HRZ and Kimmeridge samples, the molar proportions of these three hydrocarbon gases does not seem to vary appreciably with pyrolysis temperatures above *c.* 320°C. At temperatures below *c.* 320°C,

the proportion of methane is considerably higher. Production of all three gases increases with pyrolysis temperature.

Discussion

Volatile fatty acids. The origin of VFAs in sediments is undoubtedly organic; anaerobic sulphate-reduction has been shown to play a major role in the degradation of organic matter within marine sediments (Jørgensen, 1982), and the main organic substrates for the bacteria involved in these reactions are VFAs—particularly ethanoate (Sørensen *et al.*, 1981). VFAs are also metabolic intermediates in other oxygen-poor habitats, such as anaerobic digesters (Jeris and McCarty, 1965), rumen systems (Hungate, 1966), and freshwater sediments (Lovley and Klug, 1982).

Free carboxylic acids are highly susceptible to decarboxylation during early stages of rock diagenesis; they can readily undergo biodegradation and their high water solubility suggests that they are also very susceptible to water washing in the free state. Carboxylic acids bound into the sediment matrix or actually bonded into the kerogen structure will be much more resistant to alteration. The ability of carboxylic acids to be preserved in rocks until maturities at which the onset of significant petroleum generation occurs suggests that these components are stabilised by incorporation within the rock structure.

Work at the Scottish Marine Biological Association has suggested that marine bottom sediments have higher VFA concentrations than the surrounding pore waters—perhaps upward of one order of magnitude higher. This appears to be supported by a comparison of VFA studies by Parkes and Taylor (1983) and Sansone and Martens (1981) on marine pore waters and marine bottom sediments respectively. These suggest an ability of marine bottom sediments to accumulate and incorporate VFAs dissolved in the surrounding pore waters.

VFAs may be bound directly to sedimentary organic matter or held within the forming rock network, such as occlusions, or in pores by adsorption. In this state the acids are more resistant to thermal decarboxylation or biodegradation, to be liberated only at much higher temperatures close to the onset of petroleum generation. Our current prejudice is that the majority of VFA species are probably desorbed by heating rather than by covalent bond cleavage from kerogen macromolecules. This is supported by the significant yields of ethanoate and propanoate anions from pyrolysis of Kimmeridge clay

at 250°C; it is likely that the rate of covalent bond fission is relatively low at this temperature. An increase in the rate of covalent bond fission at higher pyrolysis temperatures does not result in significantly greater VFA yields (Figs. 2 and 3). Also, the relative abundances of VFA homologues liberated by hydrous pyrolysis of the brown coal and Kimmeridge mudstone closely resemble that of present day marine pore waters (Parkes and Taylor, 1983), recent sediments (Sansone and Martens, 1981), and encouragingly in view of relationships between natural and laboratory VFA generative processes, oil-field formation brines (Carothers and Kharaka, 1978). Generation of free VFA species directly from kerogen exclusively via covalent bond fission seems unlikely to specifically promote ethanoate production in preference to lower (methanoate) or higher (propanoate, butanoate, etc.) VFA homologues. An observation that mineral acid digestion of carbonates and silicates from pre-extracted petroleum source rocks also yields long chain (n -C₁₆, n -C₁₈) carboxylic acids also points towards these species being bound or adsorbed onto the rock matrix, rather than bound directly to kerogen (Cooles, unpublished data).

Carothers and Kharaka (1978), working primarily with oil-field brines in the San Joaquin valley in California and the Texas Gulf coast, found an abrupt increase in VFA concentration in formation brines at subsurface temperatures around 80°C. Above this temperature they observed that the concentration of subsurface aqueous VFA anions generally decreased with higher temperatures. The concentrations of acid anions that they measured were as much as *c.* 5000 mg l⁻¹ in oil-field brines at about 100°C. In addition, for 95 formation waters from relatively young (Eocene–Miocene) oil and gas fields, it was shown that the carboxylic acid anions contribute 50–100% of the measured alkalinity over the 80–140°C temperature range. The carboxylic acid dominance with respect to alkalinity is particularly pronounced in the 80–120°C range. This suggests that major VFA production from organic-rich rocks in the subsurface starts at a temperature of around 80°C—some 20–40° lower than that at which most petroleum source rocks start to generate significant volumes of oil and gas (Cooles *et al.*, 1986). Once liberated inside the source rock, the aliphatic VFA species, being highly water soluble, partition into *in situ* pore waters where they may be expelled from the source rock. The expulsion process may be related to clay dehydration. Thus, VFAs may be released and expelled at around, or before, the major phase of petroleum generation and expulsion from the same source rocks.

TABLE 4. COMPOSITION OF SELECTED NATURAL GASES (% VOLUME)

AREA / FIELD	C ₁	C ₂	C ₃	C ₄	C ₅₊	N ₂	CO ₂	H ₂ S
Algeria / Hassi-R'Mel	83.5	7.0	2.0	0.8	0.4	6.1	0.2	-
France / Lacq	69.3	3.1	1.1	0.6	0.7	0.4	9.6	15.2
Holland / Groningen	81.3	2.9	0.4	0.1	0.1	14.3	0.9	Trace
New Zealand / Kapuni	46.2	5.2	2.0	0.6	0.1	1.0	44.9	-
North Sea / West Sole	94.4	3.1	0.5	0.2	0.2	1.1	0.5	-
North Sea / Brent	82.0	9.4	4.7	1.6	0.7	0.9	0.7	-

Source of data: British Petroleum, 1977.

Source rock-derived VFAs may, therefore, reach potential reservoir rock horizons before the major influx of petroleum.

In aqueous solution, the electrochemistry of VFA dissolution is undoubtedly more complex than a simple ionic equilibrium between ethanoic acid, ethanoate anions and hydronium ions (hydrated protons). The presence of many ionic species in pore waters and surrounding rock surfaces will buffer the solutions and resist any dramatic pH changes. VFAs, however, may be capable of dissolving carbonates and feldspars in mineral-cemented sandstones. Another substrate from essentially the same source has also been suggested as an acid capable of subsurface mineral cement dissolution—that is carbon dioxide forming a carbonic acid solution (Lundegard *et al.*, 1984). Carbon dioxide can be produced by decarboxylation or oxidation of organic matter—especially carboxylic acids.

At present, there is no unequivocal substrate known to be responsible for dissolving and transporting carbonate and feldspar minerals from cemented sandstone sequences in the subsurface. However, acid solutions derived from the liberation of carboxylic acids from sedimentary organic matter and/or CO₂ by defunctionalisation of these acids at higher temperatures, are available (if not responsible) substrates of the observed phenomenon of secondary porosity in reservoir rocks adjacent to organic-rich sediment horizons.

Gas production on sediment pyrolysis—comparison with nature. The major portion of all evolved gases from our sediment pyrolyses are non-hydrocarbons, mainly CO₂ and H₂ with smaller quantities of N₂ (Figs. 4 and 5). Natural gas accumulations, however, are usually dominated by hydrocarbon gas components, usually

methane, with subordinate proportions of higher (C₂–C₄) hydrocarbon constituents (Table 4). Thus, there is a direct conflict between gaseous products generated from petroleum source rocks during laboratory pyrolysis, and the composition of gas accumulations sourced from similar source rocks in the subsurface.

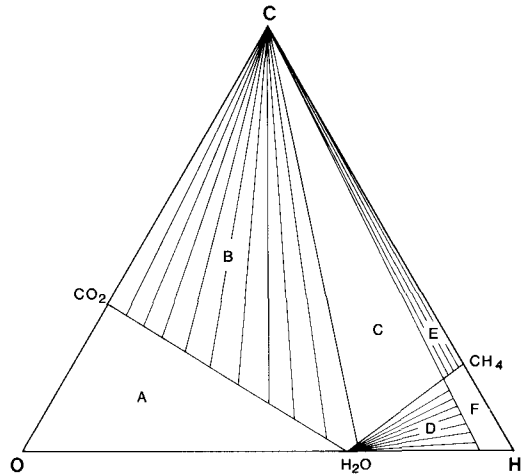
Hydrocarbon and non-hydrocarbon gases produced in both nature and in the laboratory probably have multiple sources. In nature, the dominant source for the major gaseous components (hydrocarbons, CO₂ and N₂) is thought to be the thermal degradation of organic constituents in sedimentary rocks. Some of the CO₂ produced on pyrolysis may be 'inorganic' in origin—that is, formed by the decomposition of labile carbonate minerals in the rock matrix. Harwood (1977), however, pyrolysed thermally immature, dry, mineral-free kerogens between 250 and 450 °C and found significant amounts of CO₂, H₂ and N₂ in the gaseous products. This suggests that the major source of the carbon dioxide formed during closed vessel rock pyrolysis is sedimentary organic matter, although the oxygen may be either organic (CO₂ generated by e.g. decarboxylation of fatty acid species) or water derived.

Thermodynamic considerations. Closed vessel sediment pyrolyses in this study took place at between 250 and 360 °C over 3 days—necessarily higher temperatures than that encountered by source rocks while generating petroleum in the subsurface (c. 100–250 °C over Ma). Other variants of the closed vessel pyrolyses and nature are that water was added to the sediments prior to pyrolysis at concentrations over and above natural pore water levels in petroleum producing sediments, and that the pyrolyses took place in a stainless steel autoclave.

Recent work published by Saxby *et al.* (1985) has demonstrated that carbon dioxide is a major product of the artificial maturation of an Australian torbanite and brown coal (the latter analogous to the brown coal of this study). The experiments of Saxby *et al.* used demineralised and chloroform-extracted sediments which were dried and then heated extremely slowly (1 °C per week, from 100 °C up to a maximum 400 °C) in an open glass tube sealed inside a stainless steel autoclave under nitrogen. These latter experiments are possibly as slow as can be realistically planned within a human time-scale, and are the longest source-rock pyrolysis experiments reported in the literature to date. The sediments, when pyrolysed at low temperatures (<250 °C) evolved small amounts of CO and, although the yields were not quantified, there were indications that H₂ gas was present in the higher temperature experiments. Harwood's (1977) analogous (anhydrous) pyrolysis experiments inside evacuated glass tubes also produced major amounts of H₂ and CO₂ gas. Thus, it appears that water is not the controlling influence on the production of CO₂ and H₂ in hydrous rock pyrolysis.

Holloway (1984) has used thermodynamic calculations of fluid compositions co-existing with graphite to show that for fluids in a carbon-hydrogen-oxygen (C-H-O) system, the important species are CO₂, H₂O, CH₄ and H₂. At temperatures above 400 °C, Holloway demonstrated that these species mix to form a single, homogeneous supercritical fluid—while at lower temperatures such a single phase partitions into a carbonic fluid (either CO₂ or CH₄-rich) and a fluid rich in H₂O. Such fluid partitioning has important implications for chemical equilibria in fluids generated in closed vessel hydrous pyrolysis apparatus.

An example of one of Holloway's phase diagrams for a C-H-O system at 300 °C and 1000 bar/c. 100 MPa (the closest to experimental conditions inside our autoclaves) illustrates the effect that pressure (*P*), temperature (*T*) and composition can have on the stability of fluid compositions in a closed hydrous pyrolysis system (Fig. 6). Three different phases are apparent on the phase diagram: a CO₂-H₂O fluid, a CH₄-rich fluid, and graphite. These co-exist according to the elemental composition of the system, and are described by various regions of the diagram, whose boundaries are fixed at a given *T* and *P*. To the left of the diagram (high percentage of C and O), the thermodynamically preferred species is a CO₂-H₂O fluid mixture (Fig. 6, regions A and B). A system that plots to the right of the diagram, toward higher proportions of hydro-



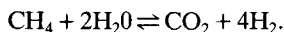
- A : (CO₂ - H₂O) FLUID
- B : GRAPHITE + (CO₂ - H₂O) FLUID
- C : GRAPHITE + (CO₂ - H₂O) + CH₄ FLUID
- D : (CO₂ - H₂O) + CH₄ FLUID
- E : GRAPHITE + CH₄ FLUID
- F : CH₄ - rich FLUID

FIG. 6. C-O-H system at 300 °C and 1000 bar, after Holloway (1984).

gen, has a CH₄-rich fluid as the thermodynamically stable phase (regions E and F). The intermediate regions (C and D) describe mixed CO₂-H₂O/CH₄ fluid stabilities.

The distribution of products generated by hydrous closed-vessel pyrolysis of petroleum source rocks is similarly controlled by reaction and phase equilibria thermodynamics. The chemical potential or thermodynamic stability of gaseous species varies as a function of *P*, *T* and the overall composition of a closed system. Methane is thermodynamically stable at geologically common oxidation conditions and temperatures (Holloway, 1984). Within pyrolysis autoclaves, however, the conditions are such that the relative stability of a CO₂-rich fluid is greater than that of hydrocarbon-rich fluids. This is an artefact of differential gas fugacities for individual gas species varying as a function of *P* and *T*. Thus, although hydrocarbon species are the dominant gaseous products generated from pyrolysis of a source rock, the prevalent pyrolysis conditions inside the closed vessel promotes chemical partitioning that achieves the lowest chemical potential. The result is that in the presence of water, CH₄-rich fluids convert to, and partition

with, a CO₂-rich fluid. A very simplified chemical representation of this conversion is:



On a mass balance basis, it is extremely unlikely that CO₂ is generated naturally from kerogen in the amounts suggested by the yields of this gas from hydrous pyrolyses: insufficient carbon would remain within source rocks to produce the volumes of hydrocarbons found in nature.

Thus, in summary, methane is a stable species at geologically common temperatures and oxidising conditions. Closed-vessel source rock pyrolysis promotes the equilibrium stability of CO₂-H₂O fluids with respect to CH₄-rich fluids; this may be the mechanism by which the high concentrations of CO₂ and H₂ and concordant low yields of hydrocarbon gases are formed in laboratory closed vessel pyrolysis experiments. The message is clear: detailed gas data obtained by closed vessel source rock pyrolysis should not be extrapolated directly to the prediction of gas generation in nature. The ultimate calibrant, of course, is nature itself.

Summary and conclusions

Water-soluble VFA species are generated from petroleum source rocks in significant quantity during the course of artificial maturation experiments by closed-vessel hydrous rock pyrolysis. Hydrous pyrolysis of Kimmeridge clay and Australasian brown coal samples yielded significant amounts of aliphatic VFAs; c. 1 and 3% of the total organic carbon contents of the original sediments were converted to VFA species respectively. Greater amounts of VFA were generated from the relatively oxygen-rich coal than the oxygen-poor clay; production of these species from petroleum source rocks may, therefore, be related to the oxygen content of the sediment. Although the most abundant VFA species generated from these source rocks are not the most acidic organic acids in nature (viz: formic and oxalic acids), these water-soluble VFA species may be possible agents of observed subsurface porosity enhancement by etching of carbonate and feldspar grains and cements in sandstone sequences. If this is proved to be the case, the association of organic acids with petroleum source rocks will have a major influence on predicting and defining locations of previously cemented sandstone sequences which may be economically viable petroleum reservoirs due to secondary porosity enhancement.

The unnaturally large yields of CO₂ and H₂ generated in hydrous rock pyrolyses may be rationalised by the high temperature and pressure pyr-

olysis conditions increasing fugacities for each gas component to a different degree. Individual gas fugacities control the chemical potential (and, therefore, thermodynamic stability) of each gaseous product such that, under laboratory pyrolysis conditions, the stability of a CO₂-H₂O phase is greater than that of gas phase hydrocarbons. Thus, although bulk yields and carbon number distributions generated from subsurface petroleum source rocks may be duplicated under laboratory conditions, a more detailed inspection of pyrolysate products shows that petroleum production by closed vessel pyrolysis and nature are not truly comparable, particularly for gas phase products.

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