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Surface Geochemical Exploration continues to progress global deepwater frontiers

N.R. Cameron (consultant to TDI-Brooks International, Inc. and GeoMark Research, Inc.),
James M. Brooks and Bernie B. Bernard (TDI-Brooks International, Inc.)
and John E. Zumberge and Stephen Brown (GeoMark Research, Inc.)

Introduction

This paper is an invited update relating to a presentation delivered to the 1998 IBC “Worldwide Deepwater Technologies” forum (Cameron *et al.*, 1998). Extensive use is also made of two other presentations to IBC, both given in 1999. These were to the Nigeria Energy Summit in June (Cameron *et al.*, 1999) and to the Oil and Gas Developments in West Africa meeting in October (Cameron and White, 1999).

In deepwater exploration a crucial, and arguably the most critical single issue, is whether oil has been generated, and if it has, what can be determined, before making costly decisions, regarding the quality, maturity and the age of the source succession. With the choicest deepwater acreage continuing to attract large signature bonuses and with wells in some cases costing in excess of $US 50-60 million, a reliable means of assessing source rock risk is required.

Whilst trap geometry details and reservoir horizons can be predicted from seismic with increasing degrees of confidence, no fail proof method exists for remotely predicting the composition of reservoir fluids and gases. AVO theory provides some degree of control, but continuing dry holes show that serious interpretational issues persist. Fortunately, since oil and gas accumulations are invariably leaky, Surface Geochemical Exploration (SGE) can be used to recover and type migrant hydrocarbons before committing to either blocks or wells. The goal is to initially high-grade open acreage and subsequently rank prospects by means of gas and high molecular weight hydrocarbon screening of piston-cored samples. Heatflow surveys and the collection of geological samples for age, source quality (Total Organic Carbon, etc.) and maturity determinations (Tmax etc.) are also permitted, together with a wide variety of geotechnical programmes.

The traditional onset of the deepwater is the 200-metre (660-feet) shelf edge isobath. Increasingly, the deepwater commences at the 500 metres (1640 feet) isobath with the ultra-deepwater commencing at 1500 metres (4920 feet). Now, as the exploration and technology horizon advances oceanwards, terms such as ultra-ultradeepwater are emerging for the 2500 metres (8200 feet) plus frontier. These distinctions are not utilised in this review and all water depths greater than 200 metres are referred to as deepwater.

Since its formation in 1996 TDI-Brooks has conducted SGE surveys in the following countries, Angola, Gabon, São Tome, Equatorial Guinea, Nigeria, Brazil, Trinidad, Barbados, Colombia, the USA (Gulf of Mexico) and Mexico. A total of 3500 cores have been collected, almost exclusively from deepwater settings. Additionally, TDI-Brooks has acquired about 500 deepwater heatflow measurements as part of their multiclient and private programmes.

Why can the deepwater be so rewarding?

As knowledge of the geology of the continental margins advances it is evident that sands are widely present in deepwater settings, notably oceanwards of the major river mouths. However, source rocks, source rock maturity and structural traps need not be present. Fortunately, many of the world's great producing shelf and onshore basins were quickly found to be associated with prolific deepwater plays. Why this should be so is outside the scope of this presentation, but ultimately it relates to two commonly occurring factors:

1) many productive shallow water basins either developed above source rock rich, deepwater provinces or are greatly influenced by them, and
2) the oceanwards build-out of basins into deepwater creates load induced structuring in the deepwater.

Examples are the Gulf of Mexico, the Niger Delta, northern Angola (the Congo Fan) and the Campos Basin.

The answer to "Why can the deepwater be so rewarding" question is, as in all of the world's great fairways, the simplicity of the resulting play elements. These are: 1) an abundance of rich, commonly oil-prone source rocks, 2) the frequent presence of thick clean sands, 3) young structuring and 4) ongoing hydrocarbons generation.

The application of seabed sampling to frontier basin exploration

The primary objective of Surface Geochemical Exploration (SGE) is to reduce risk by defining the regional distribution and origin of oil, condensate and gas seepages (Brooks *et al.*, 1997). The goal is to firstly to high-grade open acreage and subsequently prospects by locating foci of active oil migration and charge using gas and high molecular weight hydrocarbon screening of cored samples. The assumption is that active migration will have previously charged the underlying reservoirs occupying the same compartments of a Petroleum System. The value of piston-core programmes to frontier basin exploration is illustrated in **Figure 1**. The question at issue here is the prospectivity of the compound closure labelled A. This hypothetical closure is positioned in the extensional portion of the Congo Fan (Henry *et al.*, 1995) and structures of this type were the primary targets in the 1996 and 1998 TDI-Brooks work programmes in Angola. Currently the targets are the more oceanwards positioned compressional portion of the fan and the undeformed sequence beyond the limit of the salt. For the illustrated example, the primary drilling objective is a sand positioned just above the regional Mid-Tertiary break. Examination of the figure shows that five source units could supply the objective sands. Success at Site 1 would determine the origin of the oil and so permit a much improved assessment of the potential of the target structure. In this example, the optimum charge would be from the Tertiary aged Malembo Formation since this source horizon is interbedded with the reservoir objective. Least preferable are the two Pre-Salt sources due to inefficient migration pathways through the salt seal section.

The methodology

The piston-coring procedures and laboratory techniques to be described are those practised by TDI-Brooks International, Inc. The procedural and geochemical observations are based on the work of B&B Laboratories (Bernard, 1999) and GeoMark Research, Inc. The presented methodology is equally applicable to mature basin studies.

Selecting targets

Core sites are chosen by TDI-Brooks and/or participant companies, usually from regional 2-D seismic lines. When cores are collected from optimally located sites, for example those associated with the seabed intersection of deep faults, surface amplitude anomalies, wipe-out zones, and *Lophelia* mounds, it is often possible, especially from leaky regions such as the Gulf of Mexico, to obtain 5% or more of the cores with visible oil-staining from which biomarkers are routinely discovered . Macroseepages are also characterised by gas expansion pockets in the cores and by authigenic carbonates produced from the bacterial breakdown of seepage oil and gas. Microseepages of oil and gas have been identified by the geochemical techniques outlined in the following paragraphs. Identical procedures are used to confirm the macroseep indications.

Enhanced selection is permitted where 3-D seismic and/or swath bathymetry is available. An excellent illustration of the additional return from 3-D data is provided by Haskell *et al.* (1999) who include TDI-Brooks piston-core locations on time slices from deepwater Nigeria.

The optimum targets are deep cutting faults that link the source succession to the seabed. These are best developed where there is ongoing tectonism. However, even in tectonically quiet regions breaks are usually present, especially where the section is thick and/or where there has been differential movement and reactivation across basement features such the Benue and Charcot Fracture Zones of the Nigeria region. The ideal faults are those associated with: (1) amplitude anomalies (“flags”) and/or Bottom Simulating Reflectors (BSRs) associated with gas hydrates, (2) seabed constructional features such as carbonate accumulations and mud-gas mounds, (3) gas vent pits and (4) thermogenic gas chimneys. **Figure 2** illustrates a typical site, this one is positioned on an active sea bed feature associated with a shale diapir. Further information on the geology of seeps and slicks (the sea surface manifestation of a seep) may be found in MacDonald (1998).

Acquiring piston-cores

Core sites are positioned with differential GPS positioning to a precision of ± 5 metres and generally within ± 30 metres of the pre-selected locations.

Cores are acquired with a heavy-duty, 2000 lb. piston-corer with a collapsible piston and six metres of pipe plus core liner. Although a more expensive technique, piston-coring offers several advantages over gravity coring, including: (1) greater penetration depths, (2) better core recovery, and (3) higher quality (less disturbed) samples. Using piston-coring to sample depths of up to six metres significantly reduces intracore variability due to bioturbation, loss by near surface diffusion of gases, and mixing of natural hydrocarbon seepage or pollution in the top metre of sea floor sediments. The length of section allows three sections from each piston-core to be analysed and depth trends for measured parameters to be reliably determined and evaluated. **Figure 3** illustrates the coring procedure.

Often either precision bathymetric or subbottom (3.5 kHz or Chirp sonar) profiling is used to further refine core positions in the field. These techniques, which can also detect venting trains of gas bubbles, permit cores to be directly placed on to the seabed features previously identified from the seismic. After retrieval on deck, the cores are processed in a clean hydrocarbon sampling laboratory on the vessel. Samples are immediately frozen (-20° C) for dispatch by airfreight to Houston for laboratory analyses. Ancillary programmes such as palaeontology (age determinations of the cored section), sedimentology/geotechnical, and heat flow measurements are run as requested. Heatflow techniques are reviewed in the final section of this paper.

The normal operational window is water depths between 10-3000 metres. Sampling to depths of up to 4500 metres is possible, but the core acquisition rate is much lower than the 8-10 cores/day regularly achieved for shallower depths.

Surface Geochemical Exploration screening procedures

A three stage investigative procedure is used for examining piston-cores for migrant, thermally sourced oils and gases. The first stage is the visual examination of the cores on site for oil staining and related phenomena. Hydrocarbons are suspected when dark stained section is present or gas expansion pockets and authigenic carbonates are observed. However, visually obvious oil staining is not always present. In some cases, dark, oil-like staining and fluids are found by the subsequent testing procedures not to be of thermal origin. Gas hydrates have been recovered by TDI-Brooks from the Niger Delta (Brooks *et al.*, in press) and the Gulf of Mexico.

Upon receipt in the United States, the frozen cores are sectioned into three portions for the second investigative phase. This is handled entirely by TDI-Brooks. Three analytical procedures are utilised: (1) the total scanning fluorescence intensities of sediment extracts, (2) the C_{15+} hydrocarbons by gas chromatography in the sediment extracts, and (3) the light hydrocarbons in separately canned sediment sections by headspace extraction and gas chromatography.

The third and final stage comprises GC-MS studies by GeoMark Research Inc. for those samples where one or more of the TDI-Brooks screening procedures indicates the presence of oil. Here the objectives are also threefold: (1) to confirm the occurrence of oil, (2) characterise in terms of biomarkers the nature of the source rock supplying the oil, and (3) to determine the maturity of the oil.

Total scanning fluorescence (TSF)

TSF provides semi-quantitative measures of petroleum-related aromatic hydrocarbons. Increasing TSF intensity (expressed in arbitrary units) generally corresponds to enhanced aromatic hydrocarbon concentrations in the sediment extracts. Migrant oil samples contain a higher concentration of larger aromatic compounds (3 or more benzene rings) and fluoresce at longer wavelengths, whereas, extracts containing upward-migrated gas or condensate fluoresce at shorter wavelengths. TSF patterns are insensitive to bacterial alteration, except in the most severely situations. Additional information on TSF methodology is provided by Brooks *et al.* (1986).

Figure 4 compares the spectral features of background material with a sample subsequently proven by gc-ms analysis to contain oil.

Gas chromatography

Gas chromatography (GC) provides a separate means of detecting and characterising petroleum-related hydrocarbons. The output, the gas chromatogram, is a plot on which the vertical axis records abundances and the horizontal axis positions the hydrocarbon components of the sample. Background samples produce a flat basal trace with scattered peaks unrelated to thermogenic products. Fresh oil, which is only rarely recovered from seabed settings, is characterised by a regular train of peaks all related to known thermogenic products and which rise from a flat baseline. Most of these peaks are formed by alkanes (normal paraffins). They, together with lesser components, such as pristane and phytane, are used to study the origin and maturity of the source succession (Brooks *et al.*, 1986).

Almost all seabed oils are moderately to severely modified by bacterial attack. In a few cases, sufficient alkanes and related compounds remain to demonstrate the thermogenic origin of the sample. However, in most examples all the molecular components of the oil are lost and the sample acquires properties akin to modern seabed organic matter.

The process of bacterial attack is termed biodegradation. Biodegraded oils are characterised by the increasingly “moth-eaten” appearance of the alkane peaks and the appearance of a pronounced hump below the initially flat base of the trace. The hump represents the by-products from the bacterial attack. These are termed the Unresolved Complex Mixture or UCM.

Figure 5 presents an example of gas chromatograms for: (1) a background sample and (2) a severely biodegraded oil. Gc-ms analysis (see below) was used to type the origin of the oil. Barnard *et al.* (2000) include a TSF-UCM cross-plot that distinguishes, for the Niger Delta, background from anomalous samples.

Headspace gas analysis

Headspace gas analysis relates to the determination of interstitial light hydrocarbon gases. Various gas parameters such as total alkanes, total non-methane alkane gases (C_{2+}) and ethane/ethene ratios are used to separate thermogenic from biogenic gas seepages. Methane can be thermal or bacterial origin. Ethane is a stable thermogenic product, ethene is formed by bacterial fermentation and does not persist at depth. Thus the higher the ethane/ethene ratio the more likely is the thermal origin o f the sample.

Figure 6 relates, for a large (n=363) data set, the ethane/ethene ratio to the maximum TSF intensity. The linkage with enhanced ethane/ethene ratios to migrant oils is readily apparent. The less pronounced ethane/ethene peak in the central region of the plot is associated with migrant thermogenic gas.
+

Biomarker analysis

Biomarkers are organic molecules whose chemistry is specific to life. Most originate from the thermal degradation of bacteria, algae and vegetal debris. The resulting biomarker suites are diagnostic, provided that a sample is either not too severely affected by biodegradation by bacterial action or is a condensate, of the depositional setting of source rocks, their relative thermal maturity, and, in some cases, the geological age of the source. Biomarkers are routinely analysed by Gas Chromatography-Mass Spectrometry (gc-ms). In this technique, a mass spectrometer is used to split the biomarker portion of a gas chromatograph’s output into diagnostic molecular fragments. **Figure 7** demonstrates how the resulting ratios of biomarkers may be used in the form of cross-plots to determine oil source environments. **Figure 8** shows two examples of the biomarker traces used to build the cross-plots.

Locations containing confirmed oil are termed macroseeps, locations containing probable oil are termed microseeps. Macroseep and most microseep samples contain sufficient quantities of biomarkers to allow them to be readily typed to their source rocks. It is often helpful to compare, for example when building play maps, the piston-core samples with oils from producing shallow water or onshore fields. **Figure 9** compares the gc-ms trace of a macroseep oil with a produced oil. In this case, a common Tertiary source is indicated by the enhanced amounts of the age diagnostic biomarker oleanane. Bacteria have attacked the piston-core oil and many of the peaks on the right hand portion of the trace represent remnants of the original biomarkers. In addition, new peaks, labelled with stars (*), have appeared in the field occupied in fresh oils by biomarkers known as pentacyclic terpanes – the starred peaks are related to seabed products. Fortunately, the left portion of the trace, which is occupied by biomarker compounds unpalatable to bacteria and known as the tricyclic terpanes, has not been affected. The pattern of the tricyclic peaks indicates derivation from a marine claystone containing terrestrially derived detritus. More on this subject may be found in Brooks *et al.* (1986). In some frontier basins the piston-core oils may provide the first evidence of entirely new Petroleum Systems.

Multivariant statistics

Multivariant statistics provide a powerful means of compiling Oil Families from suites of biomarker environmentally diagnostic components that best explain the geological variation in the data. The effectiveness of this approach is illustrated on **Figure 10**, which presents a cluster analysis dendrogram prepared by Schiefelbein *et al.* (1999) for a GeoMark oils set from the South Atlantic region. This methodology clearly separates marine from lacustrine sourced oils. The data set does not include the deepwater oils from the South Atlantic. Most of these are marine oils, but lacustrine oils are the source in the deepwater Campos. For much of Brazil and in West Africa north of the Namibia/Angola border many of the Cretaceous and older Tertiary marine sources are richly oil prone and since they are regional in their extent they will generate hydrocarbons wherever there is sufficient cover for maturity.

Oil quality: determining from seeps the commercial value of deepwater oils

Provided the recovered oil is not too severely biodegraded, it is possible to determine the ultimate commercial value of many deepwater oils from their seep geochemistry. Thus in relation to Closure A on **Figure 1**, it may be possible by sampling Site 1 to determine the API, the ppm metals content, the saturate/aromatic ratio, the wax content and the sulphur content of the migrating oil. Once again a Malembo source would be ideal, though there is risk, if the reservoir is too shallow, of biodegradation of the type present in Elf’s Block 17 lowering the oil’s value. Biodegraded oils have high TAN (Total Acid Number) values and require more expensive pipework and topside facilities than pH neutral oils. The origins of acidic biomarkers are described, in a timely paper on this topic, by Nascimento *et al.* (1999).

In the Gulf of Mexico many deepwater oils originate from late Jurassic shale sources with carbonate-marl affinities (Zumberge *et al.*, 1998 and 1999). Typical products are low maturity and, therefore, low API oils high in sulphur. These contrast with the more valuable, higher API, low sulphur oils derived from the Cretaceous and Tertiary shale succession that supplies the shallower water fields. **Figure 11** summarises the relative commercial value of Jurassic and Cretaceous/Tertiary oils in terms of their APIs and sulphur contents.

The definition of slicks from radarsat imagery and other techniques

Identification of surface slicks using radar satellite images or other sensing methods offers an alternative and substantially cheaper method for initially screening seepage in a frontier basin. However, slick supply is not necessarily continuous, calmish waters are required for their development and slick-like features can result from dry gas plumes.

Slick surveys are an important initial screening tool that requires subsequent ground truthing using the piston-coring techniques previously outlined. Sophisticated add-ons such as heat flow measurements are rarely practical in surface slick programmes.

Even after seeps have been located at sea it can be difficult to locate the source. For example, in Angola a seep could not be tracked to its source despite two days of Chirp subbottom surveying and the recovery of fifteen cores from potential leakage features. Interestingly, slick oils, because they are the frequently the product of transient events, tend to be fresher than seep oils. Thus slick oils should always be sampled.

Heatflow programmes

Of at least equal importance to the previously described SGE work in deepwater exploration evaluations is the determination of heatflow. Unless reference DSDP (Deep-Sea Drilling Project) sites are present, the information needed to control basin models is not available until the first wells have been drilled. The maturity and origin of a recovered oil provides clues to the heatflow, but since biodegradation frequently affects the biomarker ratios used for maturity studies, direct determinations of heatflow at the pre-bid stage are highly desirable.

Heatflow information is obtained by implanting up to eleven outrigger-style thermistors along the core barrel. Temperature measurements are recorded in-situ using a digital thermograd. Ambient temperatures below the seabed are derived by tracking for ten minutes the heat decay induced by the frictional energy of the core barrel and mathematically projecting the resulting decline curve to infinity. A known heat pulse is then applied to the thermisters enabling the conductivity of each section to be calculated using an identical ten minute sampling procedure. Heatflow (HF) is determined by combining the site thermal conductivity (k) with the geothermal gradient (G) determined from the thermistors according to the relationship HF = kG. Water depth is measured by pressure and the angle of tilt of the core barrel is monitored to obtain true vertical depths. Heatflow measurements are possible in water depths of up to 6000 metres. More details on the technology may be found in Hutchison and Owen (1989).

Once criticism of the technique is that the six metre maximum penetration may not permit measurements below the water saturated bottom coating oozes so commonly seen on seismic. This problem can be minimised by selecting sites from the seismic where these oozes are of minimal thickness such as on the crests of an active shale diapir or along the walls of fault scarps. During the later stages of exploration, direct well becomes possible.

Cost benefits

Given the necessity of mobilising an ocean going vessel and operating safely and efficiently in remote settings, the cost of mounting piston-core surveys approaches those of seismic operations. As each core requires to be treated as potentially hydrocarbon bearing at all stages of the TDI-Brooks screening programme, the total cost of acquisition and analysis varies from $3,000 to $5,000/core. Using an overall 5% success rate for biomarker typed oils, each success or “hit” will cost on average between $60,000 and $100,000. Though these are sizeable sums, a $100,000 hit represents 0.2% of the cost of a $50,000,000 deepwater well. Multiple oil “hits” and the availability of oil analyses from wells permit the source risk to be further refined through the supply of corroborative detail.

Since their initiation SGE programmes have exercised significant impact on the progress of deepwater exploration in West Africa and the Gulf of Mexico. This is because of their ability to delineate areas of active migration in undrilled acreage almost regardless of water depths. **Figure 12** illustrates a success – in this case the recovered oil was typed to it source. Thus dollars were initially saved, for example by getting the value of the bid correct, and potentially earned, for example by setting the scene for a future commercial discovery.

References

Bernard B.B., J.M. Brooks, T. McDonald and N. Cameron, 2000. Threshold vs anomalous concentrations of near-surface hydrocarbons in the ultradeepwater, offshore Nigeria. Petroleum Systems and Evolving Technologies in African E&P, Geological Society/PESGB, Burlington House, London, May 16-18, 2000, extended abstract, p.3.

Bernard B. B., 1999. Core Sampling – Summary Methodology. B&B Laboratories, Inc., pp. 20.

Brooks J.M., M.C. Kennicutt II and B.D. Carey Jr., 1986, Offshore surface geochemical exploration. Oil and Gas Journal, 20 October, pp. 6.

Brooks J.M., W.R. Bryant, B.B. Bernard and N.R. Cameron, in press. The nature of gas hydrates on the Nigerian continental slope. The New York Academy of Sciences. Third International Conference of Gas Hydrates, Park City, Utah, July 18-22 1999.

Brooks J.M., B.B. Bernard, J.D. Stonebraker, C. F. Schiefelbein, K.A. Allen, and T.J. McDonald, 1997. Design of multidisciplinary surface geochemical exploration surveys to identify active Petroleum Systems offshore West Africa, Hedberg Research Symposium, "Petroleum Systems of the South Atlantic Margin", Rio de Janeiro, 16-19 November, extended abstract, pp. 3.

Cameron N.R., C.F. Schiefelbein, J.M. Brooks and M.G.P. Brandão, 1998. The application of seabed sampling and organic geochemistry to frontier basin exploration in Angola. 3rd Annual Forum Worldwide Deepwater Technologies, London, 17-18 February 1998, pp. 8.

Cameron N.R., Brooks J.M. and J.E. Zumberge, 1999. Deepwater Petroleum Systems in Nigeria: their identification and characterisation ahead of the drill bit using SGE technology. IBC Nigeria Energy Summit, London, 15-16 June 1999, pp. 20.

Cameron N.R. and K. White, 1999. Exploration opportunities in offshore deepwater West Africa. Oil and Gas Developments in West Africa, IBC, 25-26 October 1999, pp. 28.

Haskell N., S. Nissen, M. Hughes, J. Grindhaug, S. Dhanani, J. Kantorowicz, L. Antrim, M. Cubanski, R. Nataraj, M. Schilly and S. Wigger, 1999. Delineation of geologic drilling hazards using 3-D seismic attributes. The Leading Edge, 18, 3, p. 373-374, 376, 378, and 381-382.

Henry S.G., W.D. Brumbaugh and N.R. Cameron, 1995. Pre-salt source rock development on Brazil's conjugate margin: West African examples. 1st Latin American Geophysical Conference, Rio de Janeiro, August, extended abstract, pp.3.

Hutchison I. and T. Owen, 1989. A microprocessor heat flow probe. *In*: Handbook of Seafloor Heat Flow. J.A. Wright and K.E. Louden (editors), CRC Press, Baton Rouge, USA.

MacDonald I.R., 1998. Natural Oil Spills. Scientific American, November 1998, p. 31-35.

Nascimento L.R., L.M.C. Rebouças, L. Kolke, F. de A.M. Reis, A.L. Soldan, J.R. Cerqueira and A.J. Marsaiola, 1999. Acidic biomarkers from Albacora oils, Campos Basin, Brazil. Organic Geochemistry, 30, p. 1175-1191.

Schiefelbein C.F., J.E. Zumberge, N.R. Cameron and S.W. Brown, 1999. Petroleum Systems in the South Atlantic Margins. *In*: Cameron N.R., R.H. Bate, and V.S. Clure (editors). The Oil and Gas Habitats of the South Atlantic. Special Publication of the Geological Society No. 153, p. 169-180.

Zumberge J., H. Illich, C. Pratsch, S. Brown and N. Cameron, 1998. Origin of oil in the Gulf of Mexico: exploration significance. Petroleum Exploration Society of Great Britain, PETEX 98 Conference and Exhibition, London, 1-3 December 1998, Paper E5, pp. 2 (abstract).

Zumberge J., H. Illich, C. Pratsch, S. Brown and N. Cameron, 1999. Origin of oil in the Gulf of Mexico: exploration significance. Bulletin of the American Association of American Petroleum Geologists, 83, 8, p. 1346 (abstract).

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Contacts

Nick Cameron is the UK representative for TDI-Brooks International, Inc. and GeoMark Research, Inc. Contact options include: +44-(0)1494-776850 (telephone/fax) and nick@topaz.primex.co.uk. Information relating to TDI-Brooks International 1996, 1998, and 1999-2000 coring programmes may be obtained from either Dr. Jim Brooks [+1-409-695-3634 (telephone), +1-409-695-5168 (fax), Drjmbrooks@aol.com] or Dr. Bernie Bernard [+1-409-693-3446 (telephone), +1-409-693-6389 (fax), bbb@txcyber.com].

The GeoMark Research, Inc contacts are: Stephen Brown and Dr. John Zumberge, +1-281-856-9333 (telephone), +1-281-856-2987 (fax), or <biomarkers@aol.com>.

The figures and the talk graphics were prepared by Steve King (+44-(0)1442-825128 and steve@topaz.primex.co.uk).

Figures

Figure 1. Source options for a hypothetical SGE site located in the eastern Congo Fan of Angola (based on Henry *et al.*, 1995). Multiple sources could have charged the closure labelled A. and supplied oil to seep site 1. The objective is to determine the Petroleum Systems before the acreage is awarded.

Figure 2. A typical piston-core site. This example is from the Niger Delta. The target is an active clay diapir. The horizon marked BSR (Bottom Simulating Reflector) defines the base of a gas hydrate layer. The line was acquired by Mabon Limited.

Figure 3. Piston-coring methodology.

Figure 4. Total scanning fluorescence (TSF) spectra. The upper illustration shows a background sample, the lower illustration depicts a sample confirmed by gc-ms analysis to contain migrant oil. Perylene, present only in the background sample, originates in modern seabed settings. The parameter R1 provides a qualitative estimate of the nature of the fluorescence. Values in excess of 2 typically indicate the presence of mature hydrocarbons. The oil sample was diluted 7000 times for analysis.

Figure 5. Gas chromatograms. The upper illustration shows a background sample, the lower illustration depicts a biodegraded macroseep oil. Bacterial by-product compounds collectively termed UCM (Unresolved Complex Mixture) create the hump shaped area below the base of the trace.

Figure 6. Ethane/ethene and TSF maximum intensity cross-plot. The macro and microseep oil samples have TSF intensities in excess of 1,000,000 units. Possible migrant thermogenic gases form the small population of samples grouping around the 10:1 ethane/ethene line.

Figure 7. Examples of biomarker cross-plots used to determine source rock environments. Similar procedures are used to assess oil maturities. The cross-plot are for the tricyclic terpanes, a family of biomarkers that are particularly useful in environmental work as they are resistant to biodegradation.

Figure 8. Examples of the range of biomarker abundances. The top trace is for a marine source, the lower trace is for a lacustrine source. Note how the peak heights used to prepare Figure 7 vary between the two types of source rocks. For example, C21 is

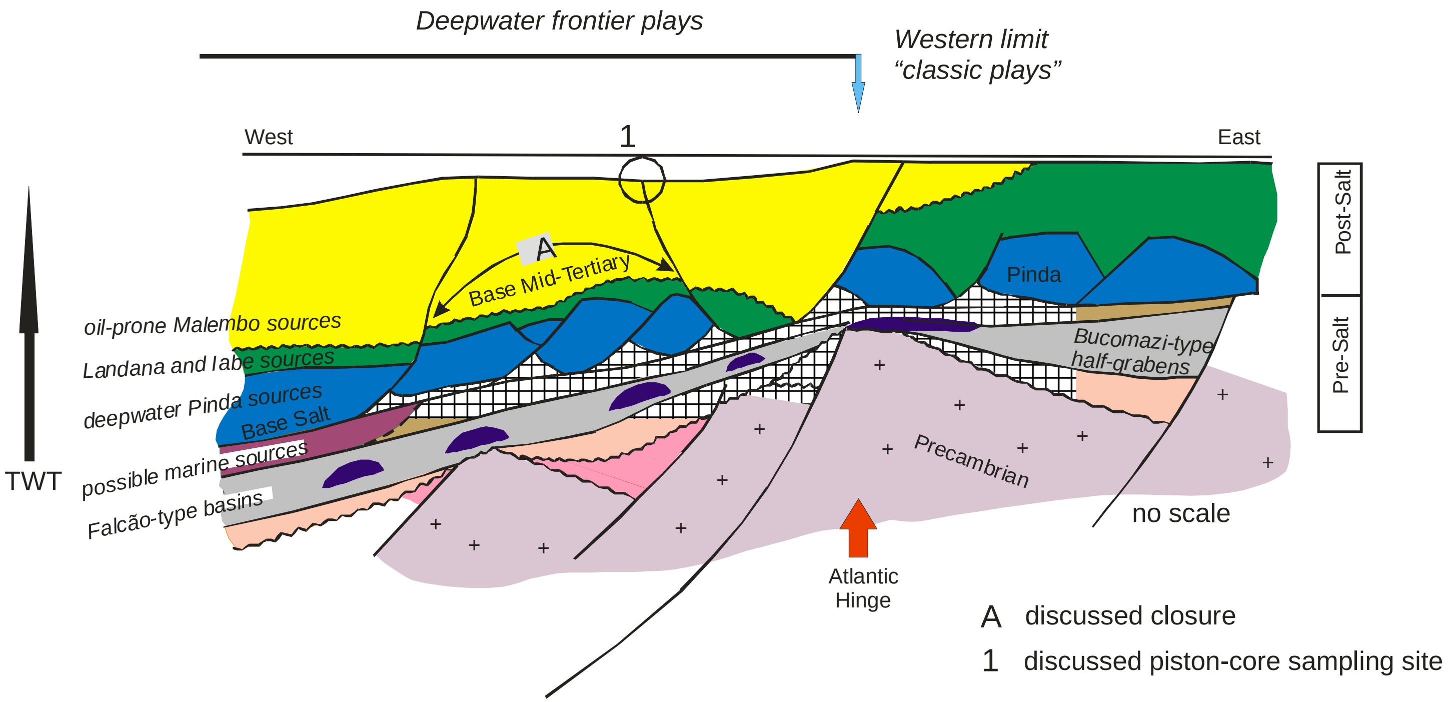
much higher in lacustrine than in marine sources. The C26/C25 ratio is >1 in lacustrine sources and <1 in marine sources.

Figure 9. Gc-ms traces from Nigeria. Comparison for the terpanes of a piston-core macroseep with a nearshore field oil. Both these oils, because of the abundance of the biomarker oleanane, were derived from Tertiary aged sources. Selected biomarkers used in environmental and maturity studies are shown. These include the age diagnostic molecule oleanane. The starred (*) peaks on the macroseep trace are biodegradation products. Terpanes are biomarkers derived from bacteria and vegetation. They are depicted using the m/z 191 mass chromatogram.

Figure 10. Dendrogram illustrating the variety of the South Atlantic Oil Families (after Schiefelbein *et al.*, 1999).

Figure 11. Cross-plot comparing in terms of API and % sulphur the relative commercial value of two offshore GOM Oil Families. The most valuable oils have high APIs and low sulphur contents.

Figure 12. A deepwater macroseep success from the Niger Delta.



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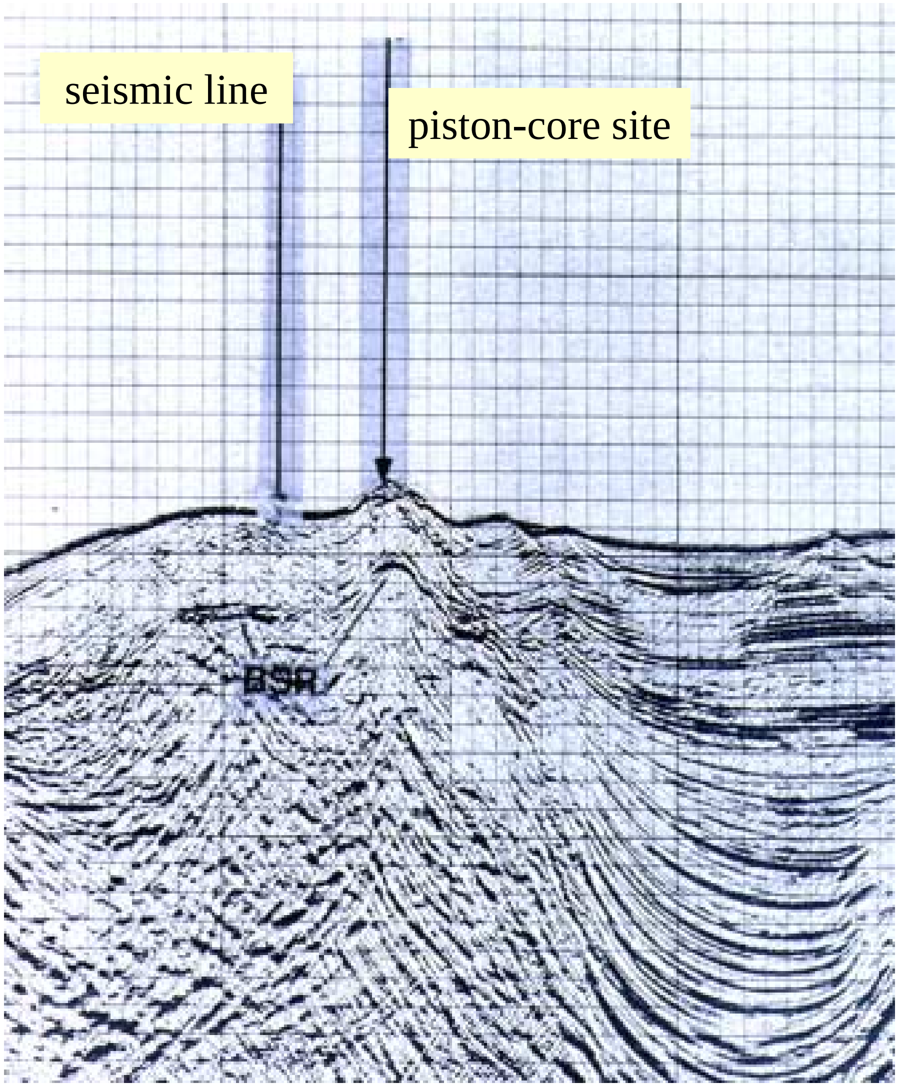


Figure 2. A typical piston-core site. This example is from the Niger Delta. The target is an active clay diapir. The horizon marked BSR (Bottom Simulating Reflector) defines the base of a gas hydrate layer. The line was acquired by Mabon Limited.

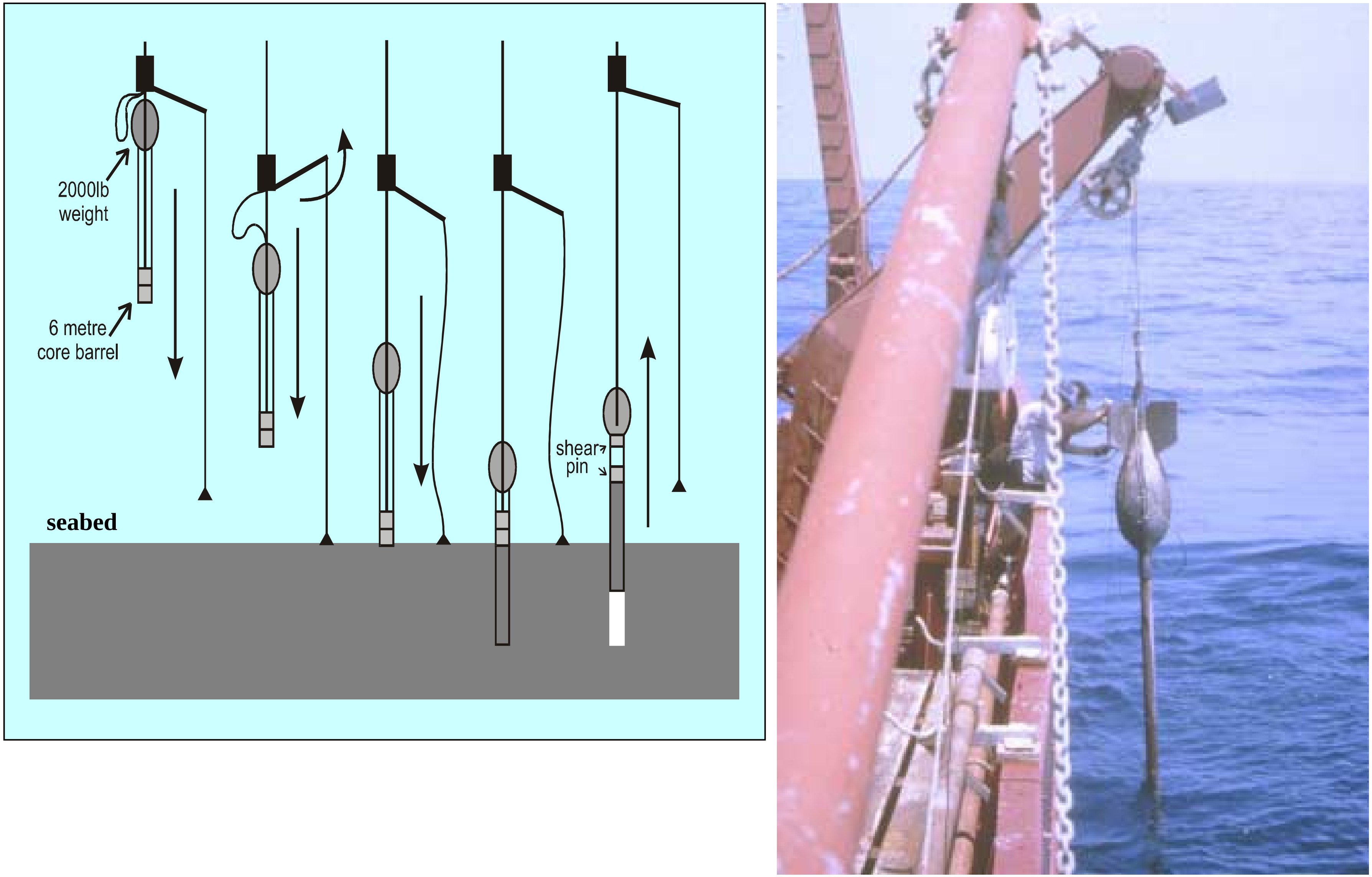
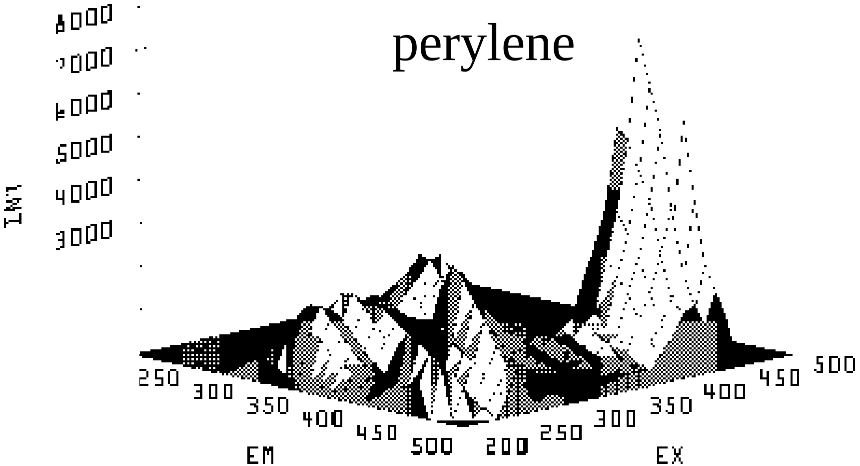


Figure 3. Piston-coring methodology.

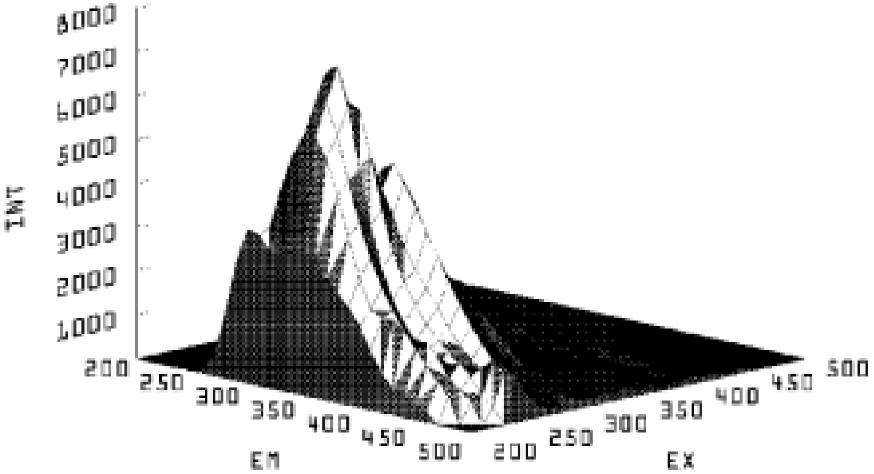
background



perylene

R1 2.02

macroseep oil



R1 2.41, dilution x7000

Figure 4. Total scanning fluorescence (TSF) spectra. The upper illustration shows a background sample, the lower illustration depicts a sample confirmed by gc-ms analysis to contain migrant oil. Perylene, present only in the background sample, originates in modern seabed settings. The parameter R1 provides a qualitative estimate of the nature of the fluorescence. Values in excess of 2 typically indicate the presence of mature hydrocarbons. The oil sample was diluted 7000 times for analysis.

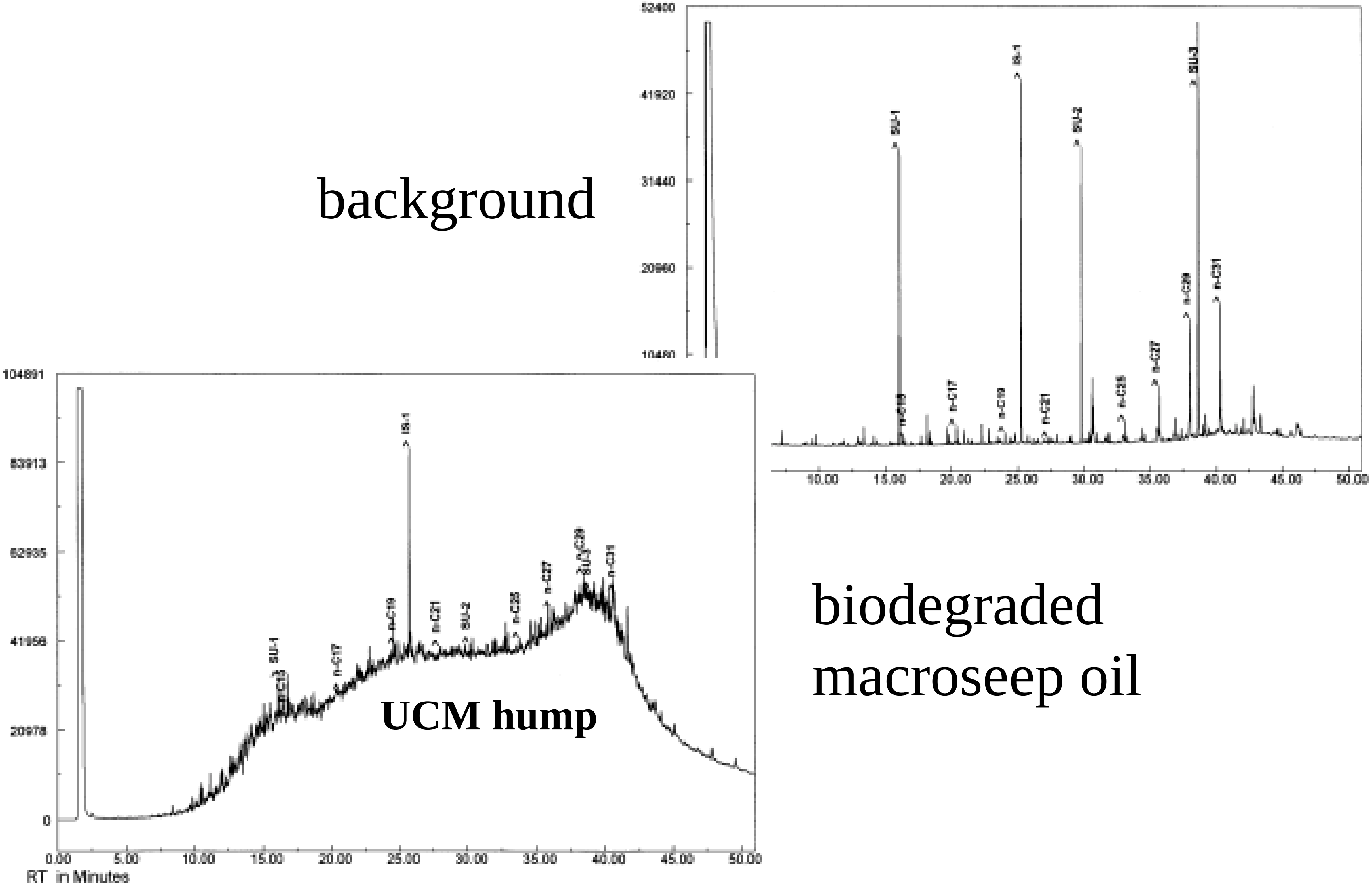


Figure 5. Gas chromatograms. The upper illustration shows a background sample, the lower illustration depicts a biodegraded macroseep oil. Bacterial by-product compounds collectively termed UCM (Unresolved Complex Mixture) create the hump shaped area below the base of the trace.

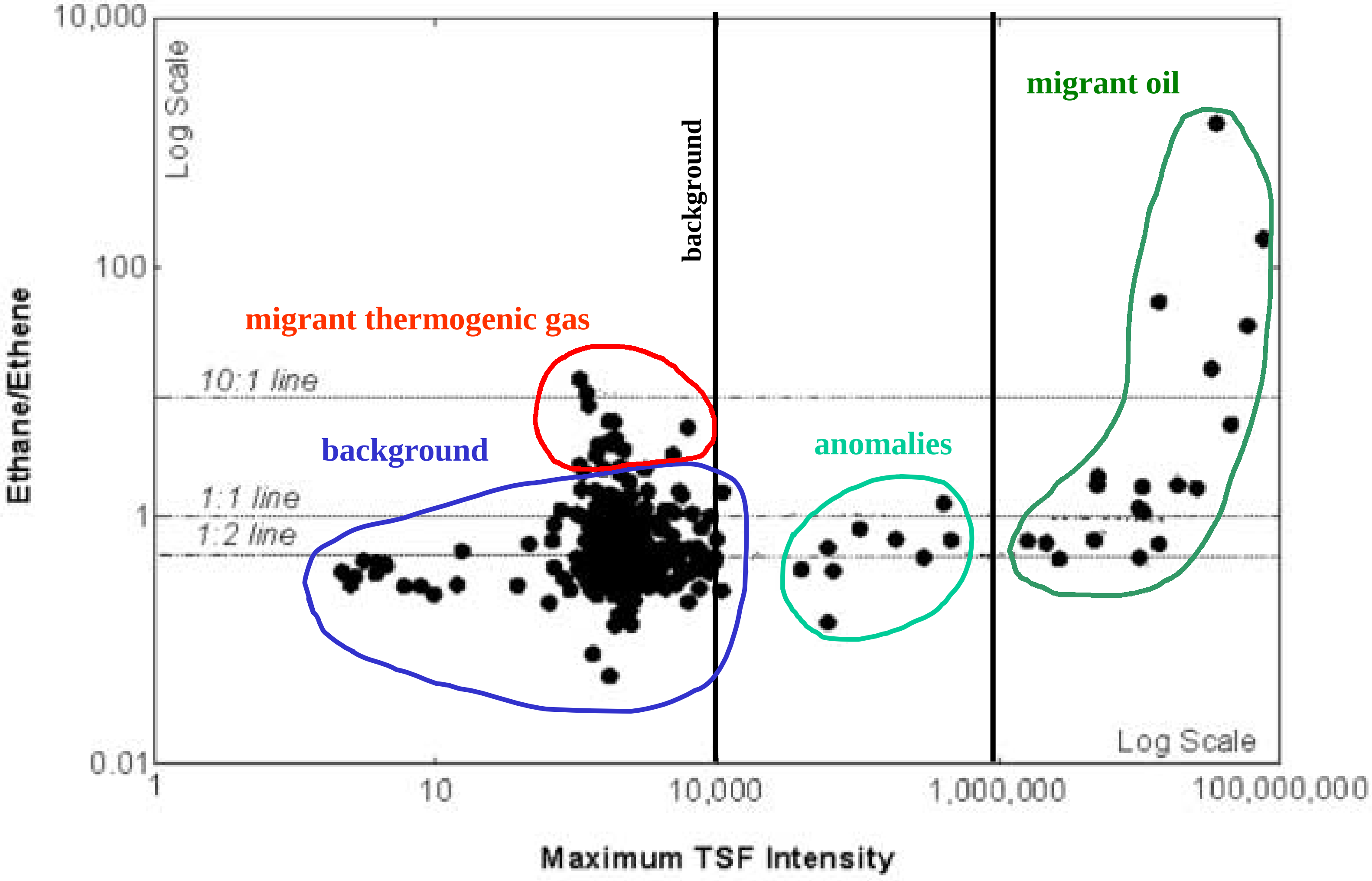


Figure 6. Ethane/ethene and TSF maximum intensity cross-plot. The macro and microseep oil samples have TSF intensities in excess of 1,000,000 units. Possible migrant thermogenic gases form the small population of samples grouping around the 10:1 ethane/ethene line.

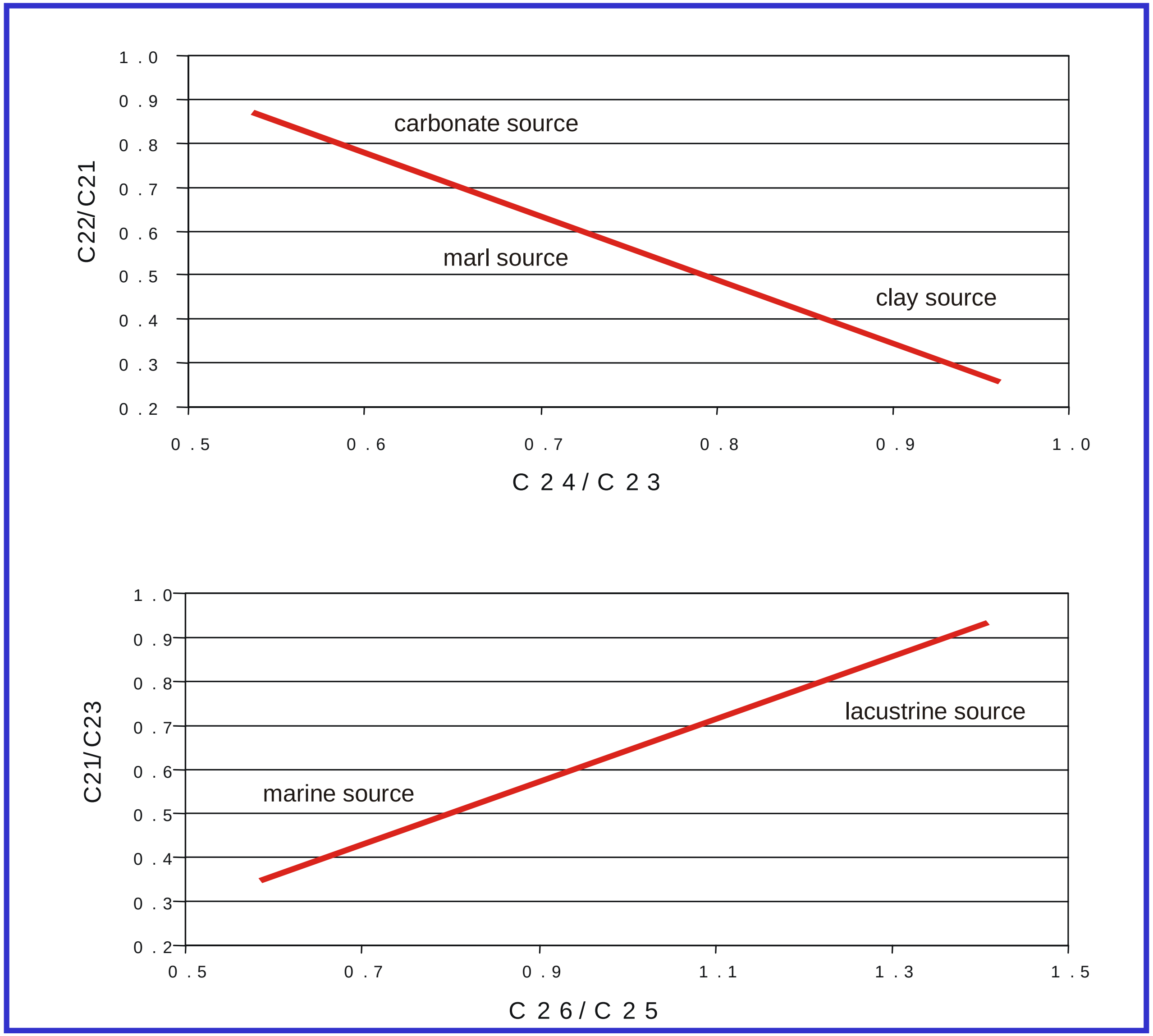


Figure 7. Examples of biomarker cross-plots used to determine source rock environments. Similar procedures are used to assess oil maturities. The cross-plot are for the tricyclic terpanes, a family of biomarkers that are particularly useful in environmental work as they are resistant to biodegradation.

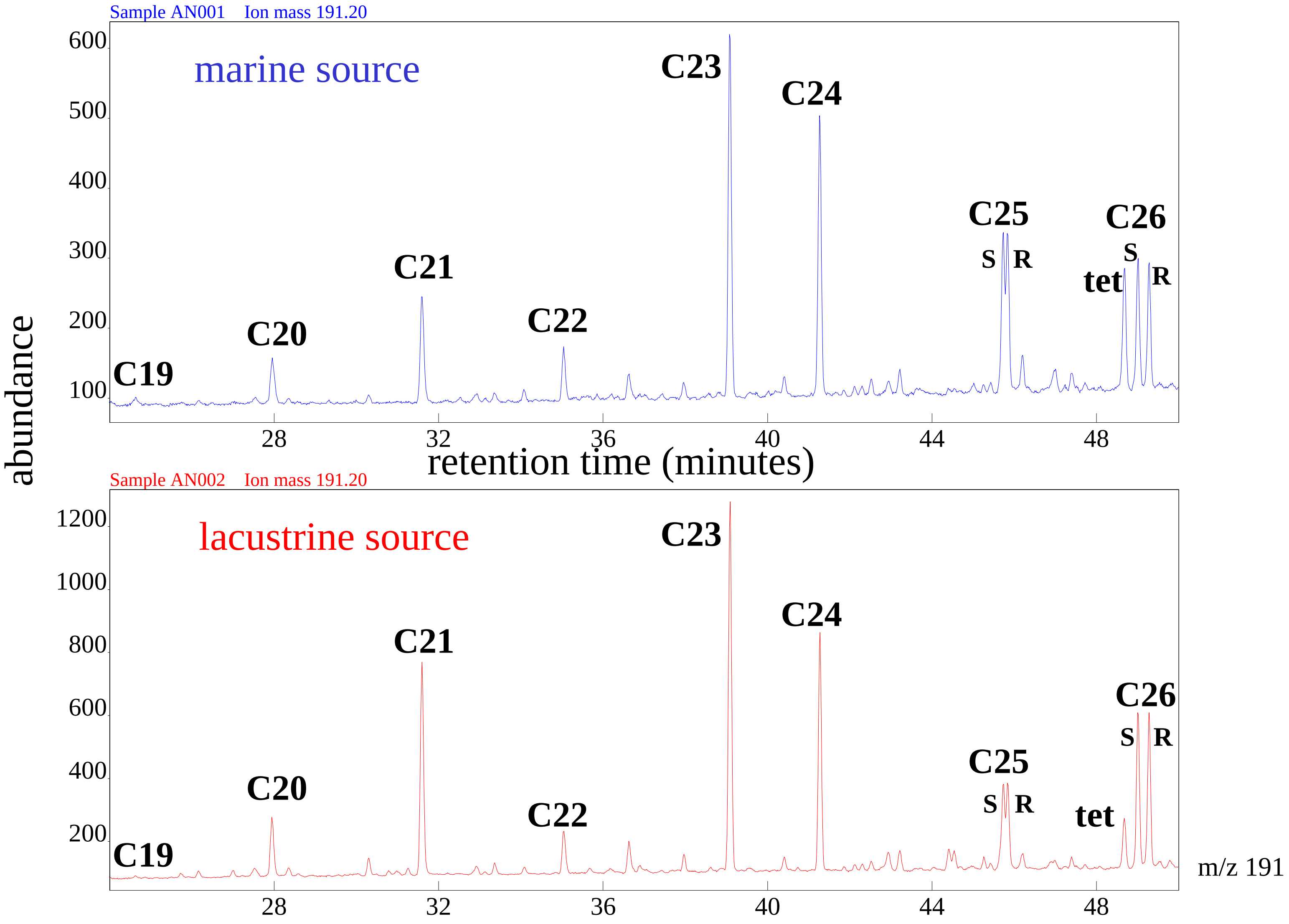


Figure 8. Examples of the range of biomarker abundances. The top trace is for a marine source, the lower trace is for a lacustrine source. Note how the peak heights used to prepare Figure 7 vary between the two types of source rocks. For example, C21 is much higher in lacustrine than in marine sources. The C26/C25 ratio is >1 in lacustrine sources and <1 in marine sources.

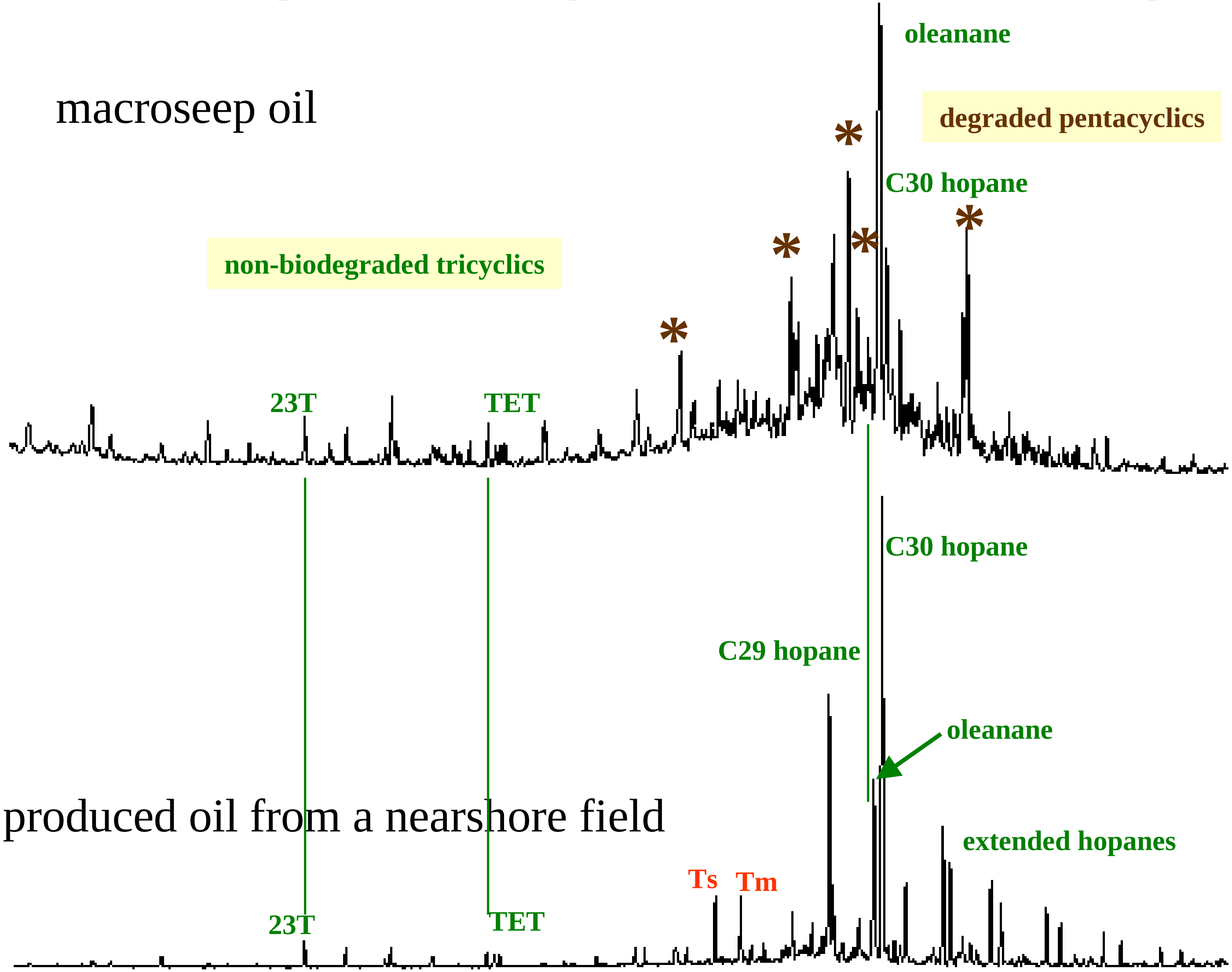


Figure 9. Gc-ms traces from Nigeria. Comparison for the terpanes of a piston-core macroseep with a nearshore field oil. Both these oils, because of the abundance of the biomarker oleanane, were derived from Tertiary aged sources. Selected biomarkers used in environmental and maturity studies are shown. These include the age diagnostic molecule oleanane. The starred (*) peaks on the macroseep trace are biodegradation products. Terpanes are biomarkers derived from bacteria and vegetation. They are depicted using the m/z 191 mass chromatogram.

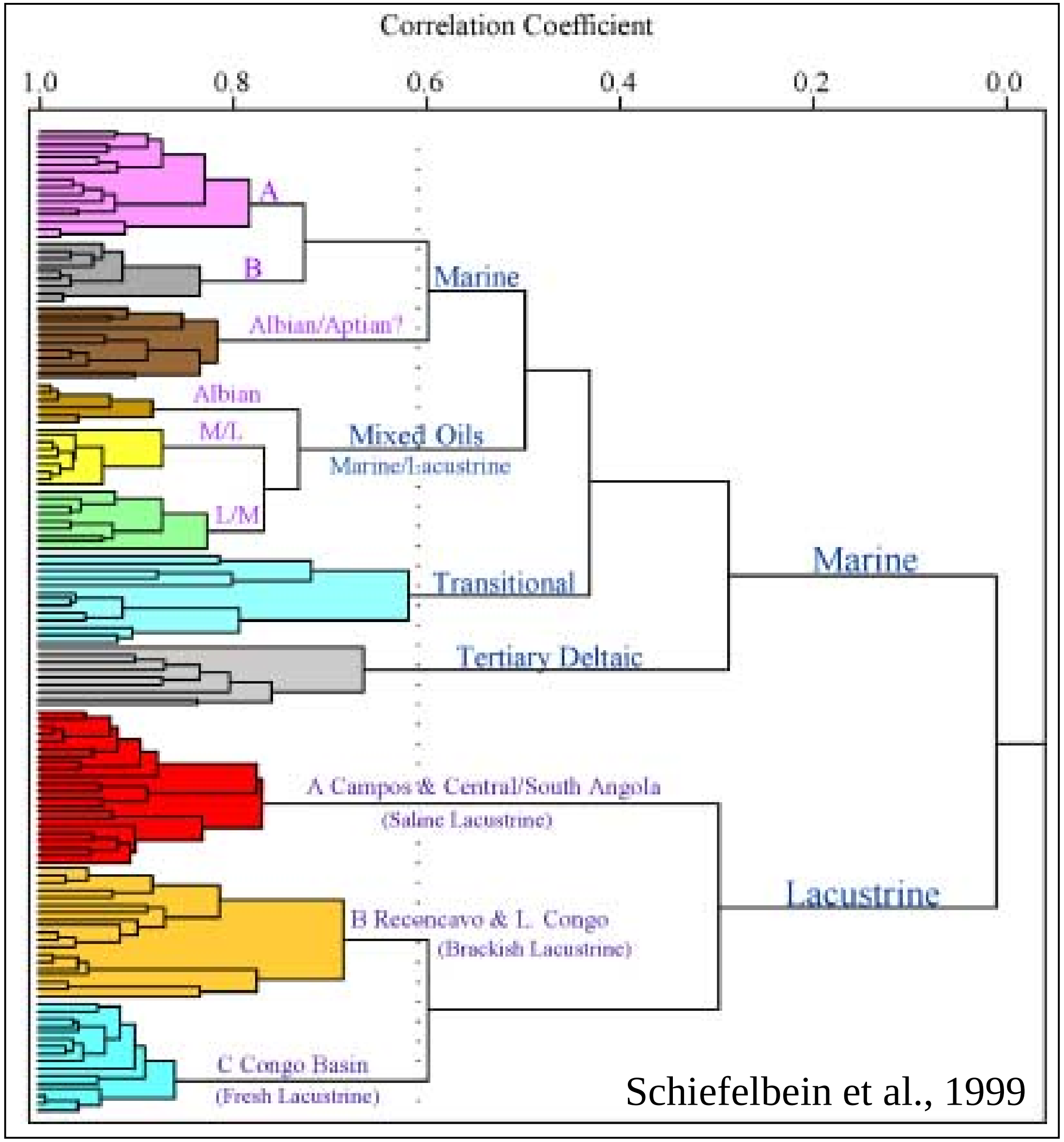


Figure 10. Dendrogram illustrating the variety of the South Atlantic Oil Families (after Schiefelbein *et al*., 1999).

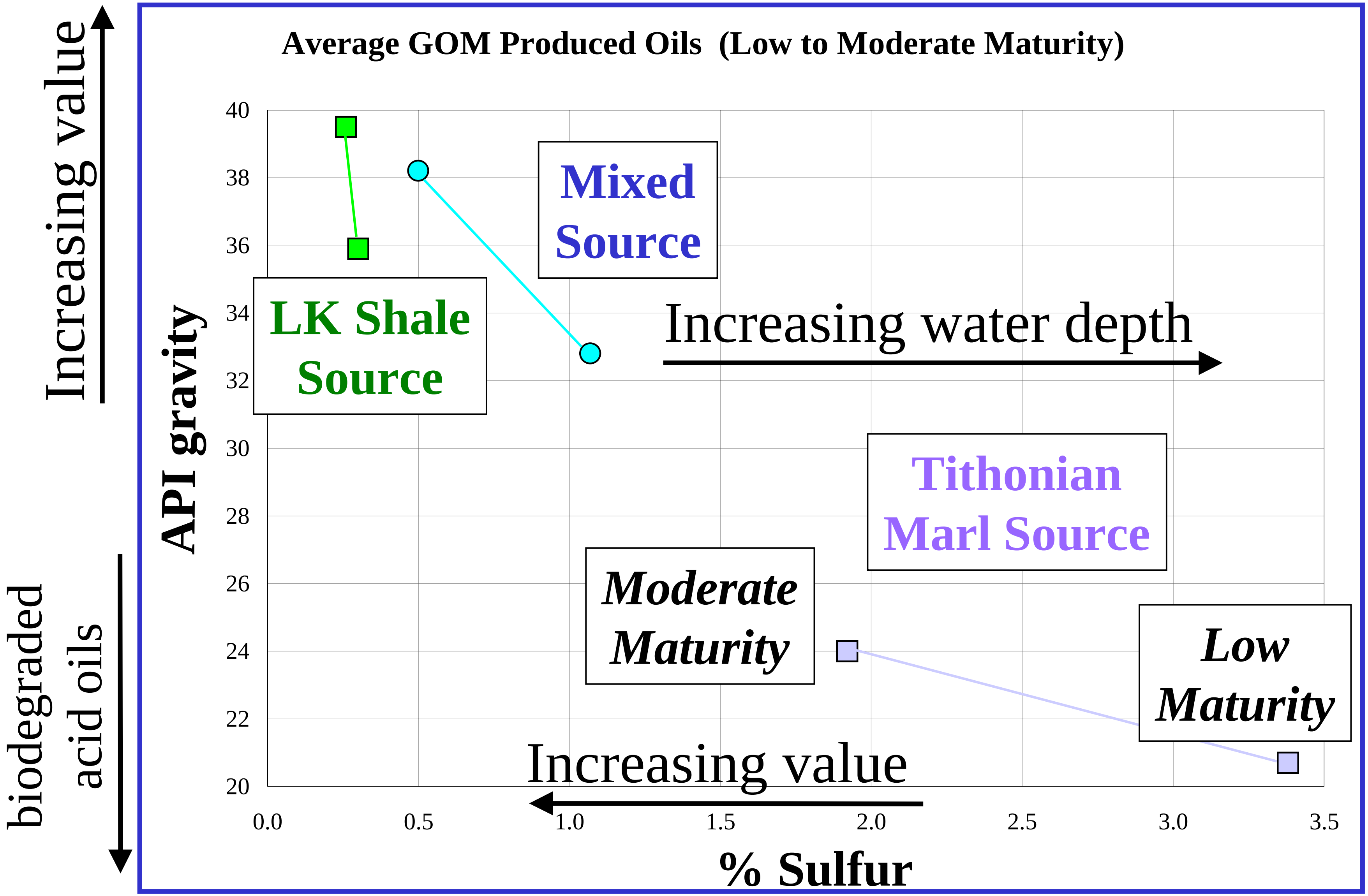


Figure 11. Cross-plot comparing in terms of API and % sulphur the relative commercial value of two offshore GOM Oil Families The most valuable oils have high APIs and low sulphur contents.

Figure 12. A deepwater macroseep success from the Niger Delta.