Source rock characterisation and correlation with oils using free and macromolecularly-bound biomarkers (Offshore Angola).

By

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DECLARATION

I hereby certify that the work described in this thesis is my own, except where otherwise acknowledged, and has not been submitted previously for a degree at this, or any other university.

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ABSTRACT

This study addresses the information potential of biological marker compounds of the free aliphatic hydrocarbon fraction and the biomarkers bound into the macromolecular organic matter fractions of oils and source rocks, within an exploration framework of Offshore Angola. Bound biomarkers are released by hydropyrolysis, and applied to overcome problems of drilling mud contamination and biodegradation, and are also investigated from the context of being an additional quantitatively significant 'pool' of source information to enhance oil to source rock correlations.

Early Cretaceous rift and drift events associated with the separation of the African and South American continents led to the development of palaeo-depositional centres for organic-rich lacustrine sediments (Burwood, 1999). This rifting later evolved into the drift phase opening of the South Atlantic (Burwood *et al.*, 1995) which led to the development of highly prolific petroleum systems involving deposition of extensive marine source rocks in the Cretaceous and Tertiary (Cole *et al.*, 2000). This study addresses a suite of oils from the Angolan Margin, and source rock samples from four wells covering almost the whole stratigraphic section. Bulk geochemical analysis shows that almost the entire Cretaceous/Tertiary section is composed of source rocks with oil or gas-prone hydrocarbon potential, although lateral variations in hydrocarbon potential occur between wells.

Quantitative analysis of the biomarkers in the macromolecular fractions of the oils and source rocks compared to the free fractions, shows that the bound biomarkers are quantitatively less important, representing 10 - 45% for kerogens (proportional to the thermal maturity of the well) and typically less then 1% in the asphaltene and polar fractions. The biomarkers released from the macromolecular fractions of both the oils and source rocks show evidence for compositional fractionation of biomarkers between the free and bound biomarker fractions. This is illustrated by the absence of certain compounds in the bound fractions which can be found in the free fractions (e.g. oleanane and BNH), and also variations exist in the percentage of bound hopanes relative to steranes. From an oil-source rock correlation perspective the asphaltene-bound fraction of the oils appears to be most comparable to the kerogen-bound biomarkers of the source rocks, at least in terms of maturity parameters. The biomarkers released from the macromolecular fractions (particular the kerogen-bound) provide a good replacement for the free biomarkers, and from an exploration perspective may prove useful where contamination by drilling mud has occurred. Although absolute values of individual ratios calculated for the biomarkers in the kerogen-bound and bitumen fractions are not directly comparable, the values do not differ greatly.

The biomarkers in the free hydrocarbon fraction of the marine oils and source rocks show good correlation, as do those for the lacustrine samples. The kerogen-bound biomarkers in the source rocks show good correlation with the asphaltene-bound biomarkers in the oils for the marine facies; however, the lacustrine oil does not correlate well with the lacustrine source rocks possibly as a result of poor sample representation. To determine the specific marine stratigraphic group(s) from which the marine oils are sourced is more difficult. On the basis of their higher $C_{35}\alpha\beta$ hopane and C_{29} sterane abundances the Pinda and Malembo Gps. have been ruled out as contributing to the marine oils. Detailed oil-source rock correlation using biomarkers in both the free and bound fractions of the marine oils and source rocks shows that the oils are most likely derived from either a pure Iabe or pure Landana source, or a source rock section comprised of both Iabe and Landana source rocks.

1 Introduction

This Ph.D. thesis addresses the information potential of biological marker compounds bound within the macromolecular organic matter fractions of oils and their source rocks, within an exploration framework of Offshore Angola. Accordingly, this chapter introduces the topics of macromolecular organic matter fractions, how biomarkers within these fractions can be analysed, and the nature and importance of such bound biomarkers. The aims and scope of the study are outlined at the end of the chapter.

1.1 Macromolecular organic matter fractions

1.1.1 Kerogen

1.1.1.1 Definition

The widely accepted definition of kerogen is the "fraction of organic matter dispersed in sediments which is insoluble in organic solvents" (Durand, 1980, p.24). It should be noted that different workers use different solvents or solvent mixtures during kerogen preparation therefore, variations in the specific fraction termed kerogen must exist.

1.1.1.2 Origin and formation

The nature of kerogen varies considerably as a result of organic matter inputs and palaeoenvironmental depositional conditions, e.g. redox potential (Chappe *et al.*, 1979). Despite kerogen comprising of 90-95 wt% of organic matter within sediments, there is no clear consensus on its formation. There are three main theories; in the first Tissot and Welte (1984) advocate a classical condensation and polymerization model. Secondly, Tegelaar *et al.* (1989) proposed the selective preservation model. Thirdly the process of 'natural sulphurization' also requires consideration (Tegelaar *et al.*, 1989).

1.1.1.2.1 The classical condensation and polymerization model

The classical condensation and polymerization model or so called 'classical pathway' of kerogen formation (outlined by Tissot and Welte, 1984), comprises three stages. Biochemical degradation and polycondensation occur simultaneously in the water column and top layer of sediment, and insolubilization occurs during diagenesis, extending over a greater depth and time period. During biochemical degradation and polycondensation, macromolecular substances such as proteins and polysaccharides are enzymatically degraded by microorganisms to smaller units (*i.e.* amino acids and sugars), which may escape mineralization by a series of random polymerization and condensation reactions (Fig. 1). The reaction products are fulvic and humic acids termed 'geopolymers'. During the insolubilization phase, insoluble humin predominates over fulvic and humic acids with increasing depth by sequential polycondensation and loss of functional groups, creating increasingly insoluble macromolecular material to finally yield kerogen. The terms fulvic and humic acids and also humin are soil science terminology; the collective term used by organic geochemists for these fractions is protokerogen.

This pathway allows for the incorporation of lipid hydrocarbons into kerogen and its macromolecular precursors during various stages of diagenesis. Lipid hydrocarbons may also survive as 'free' bitumen compounds (Fig. 1; Tissot and Welte, 1984). The 'classical pathway' of kerogen formation results in a minor fraction of the initial organic matter finally forming kerogen, and leads to kerogen having an amorphous structure (Largeau *et al.*, 1990).

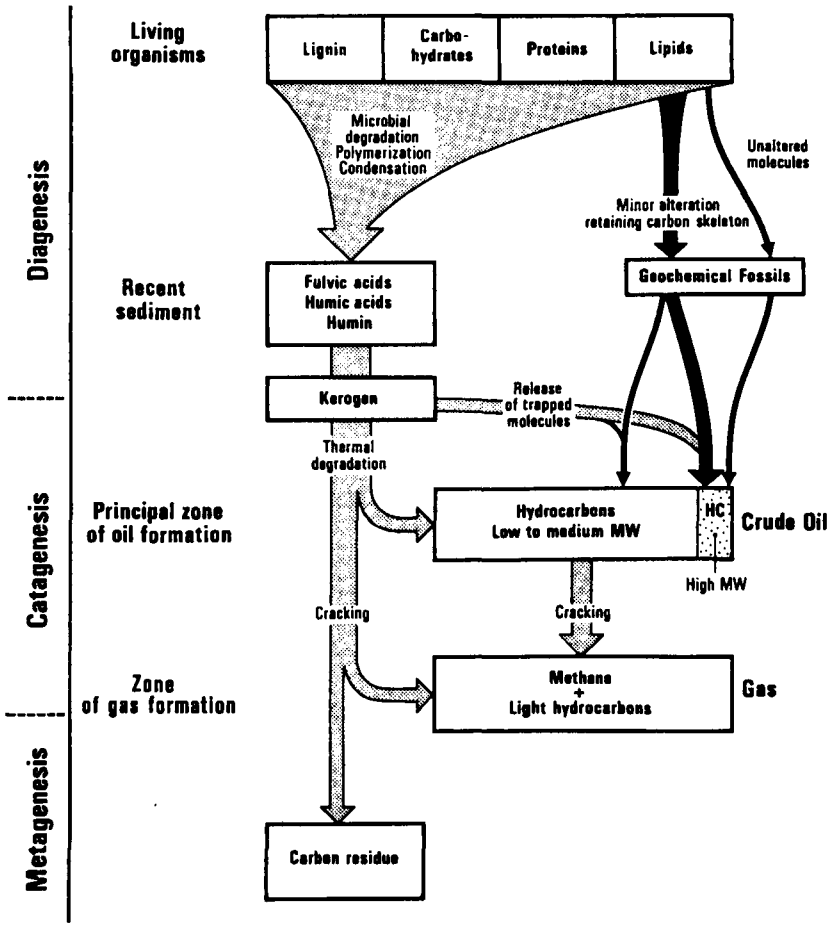


Fig. 1 The 'classical pathway' of kerogen formation (from Tissot & Welte, 1984).

The discovery that mineral surfaces can play a role in polycondensation reactions supports this model of kerogen formation. A linear relationship between mineral surface area and organic carbon concentrations in soils and modern sediments has been observed (Kiel *et al.,* 1994; Mayer 1994a, 1994b). The relationship is attributed to a monolayer of adsorbed organic carbon on mineral surfaces, indicating a surface area control upon the stabilization and burial of organic matter (Mayer, 1994a). The association with mineral surfaces provides a possible mechanism to explain the protection of reactants from biodegradation, the concentration of reactants and incorporation *via* condensation of labile organic compounds into macromolecules (Collins *et al.,* 1995). It is the adsorption into pores in the mineral surface which are too small to allow access by enzymes of the decay process which protects biopolymers from biodegradation (Mayer, 1994a). Condensation and adsorption reactions occurring simultaneously can overcome criticisms of the classical condensation mechanism; adsorption of organic matter

onto mineral surfaces concentrates reactants and thermodynamically favours condensation (Collins *et al.,* 1995). Condensation reactions between adsorbed organic compounds will further strengthen binding to mineral surfaces. Essentially, adsorption promotes condensation and condensation enhances adsorption of other reactants (Collins *et al.,* 1995).

1.1.1.2.2 Selective preservation of resistant biopolymers

The identification of insoluble and non-hydrolyzable macromolecular structures derived from the protective envelopes of extant organisms has led to a reappraisal of kerogen formation (Tegelaar *et al.,* 1989). A detailed scanning electron microscopy study of the Messel oil shale kerogen revealed small structures considered to be the cell-wall remains of unicellular algae (*Tetraedron* algae), the labile components having been degraded (Goth *et al.,* 1988). Despite forming a relatively small fraction of their source organism, through selective preservation they become enriched in kerogen (de Leeuw *et al.,* 1991; de Leeuw & Largeau, 1993). This alternative to the 'classical condensation' model considers kerogen as a physical mixture comprised primarily of selectively preserved and sometimes partly altered resistant biomacromolecules (Fig. 2) (Tegelaar *et al.,* 1989). A study of 40 kerogens previously considered as having an amorphous structure using light and UV microscopy supports the selective preservation theory (Largeau *et al.,* 1990). Of the studied kerogens 22 were recognized to have 'ultra-laminar' structures when viewed under transmission electron microscopy (TEM), identified as the resistant outer walls of microalgae, thought to have survived *via* the 'selective preservation' pathway. The selective preservation model also requires some form of 'geopolymerisation'. This may be either *via* the process of 'natural sulphurisation' or the 'classical condensation pathway' as a method of formation of high molecular weight (HMW) organic matter and a means of incorporation of lipid hydrocarbons into the macromolecular matrix (Section 1.1.1.2.3) (Tegelaar *et al.,* 1989).

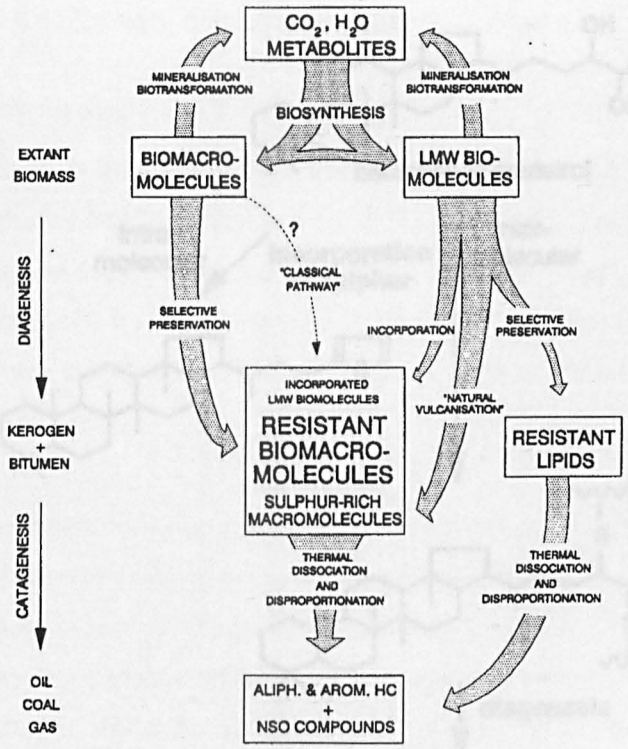


Fig. 2 The selective preservation model of kerogen formation (from Tegelaar *et al.*, 1989).

1.1.1.2.3 Natural sulphurization

The intramolecular reaction between inorganic sulphur species (H_2S and/ or polysulphides) and functionalized lipids forms low molecular weight (LMW) organic sulphur compounds. This reaction happens not only on an intramolecular basis but also intermolecular, giving rise to high molecular weight (HMW) substances which ultimately form kerogens and other macromolecular fractions (Fig. 3) (Sinninghe Damsté *et al.*, 1988; Sinninghe Damsté & de Leeuw, 1990). This method is restricted to specific depositional environments and leads to the formation of amorphous organic matter.

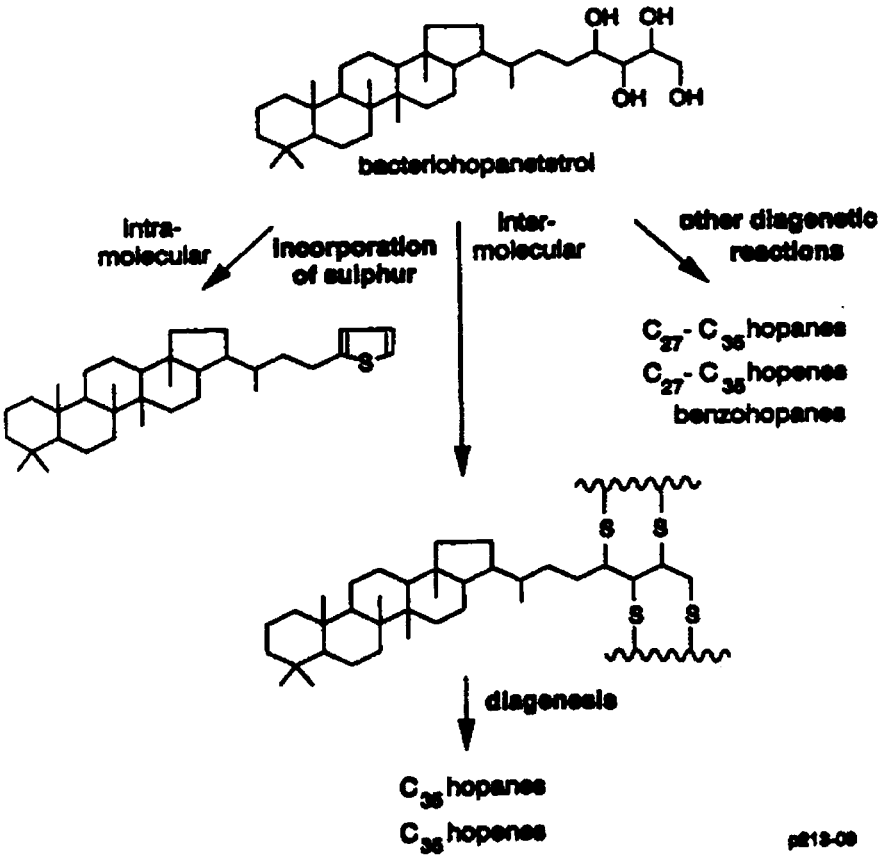


Fig. 3 The early diagenetic pathway for intra and intermolecular sulphur incorporation of bacteriohopanetetrol (from Sinninghe Damsté *et al.,* 1990).

The process of natural sulphurisation was first considered due to the identification of organic sulphur compounds (OSC) in sediments and oils which differed from previously identified OSCs and showed a structural similarity to well known geologically occurring hydrocarbons and their precursors (Sinninghe Damsté *et al.,* 1988). Identification of a novel diagenetic pathway for acyclic isoprenoids involving intramolecular incorporation of inorganic sulphur species into lipids to form OSC led to the suggestion that sulphur cross-linking may also occur in an intermolecular fashion (Brassell *et al.,* 1986). This sulphur quenching process is now known to form an important trapping mechanism for free lipids (e.g. Sinninghe Damsté & de Leeuw, 1990), leading to the formation of macromolecular compounds.

1.1.2 Asphaltenes and other macromolecular fractions

1.1.2.1 Origin and formation

The bitumen fraction of oils and source rocks contain two main macromolecular fractions that are soluble in organic solvents; asphaltenes and the resin fraction of maltenes (which together make up "polars"). The origin and formation of these fractions have been studied in the literature in detail and are shown to form *via* similar mechanisms, they will therefore be considered together in this section.

Asphaltenes are considered as secondary products released from the thermal cracking of kerogen during cata- and meta- genesis, whereby oil asphaltenes can be considered as reservoired kerogen moietes (Pelet *et al.,* 1986). Essentially, asphaltenes are considered as intermediates in the reactions leading from kerogens to hydrocarbons, although hydrocarbons may be produced directly from kerogen (Pelet *et al.,* 1986). At lower thermal maturities asphaltenes may be formed via condensation of smaller entities (i.e. resins & hydrocarbons). In this theory, asphaltenes and kerogens originate from the same precursors but asphaltenes contain fewer cross-linkages. This process occurs during early diagenesis but becomes quantitatively less important with maturation as asphaltenes are released from kerogen by thermal cracking during cata- and meta- genesis.

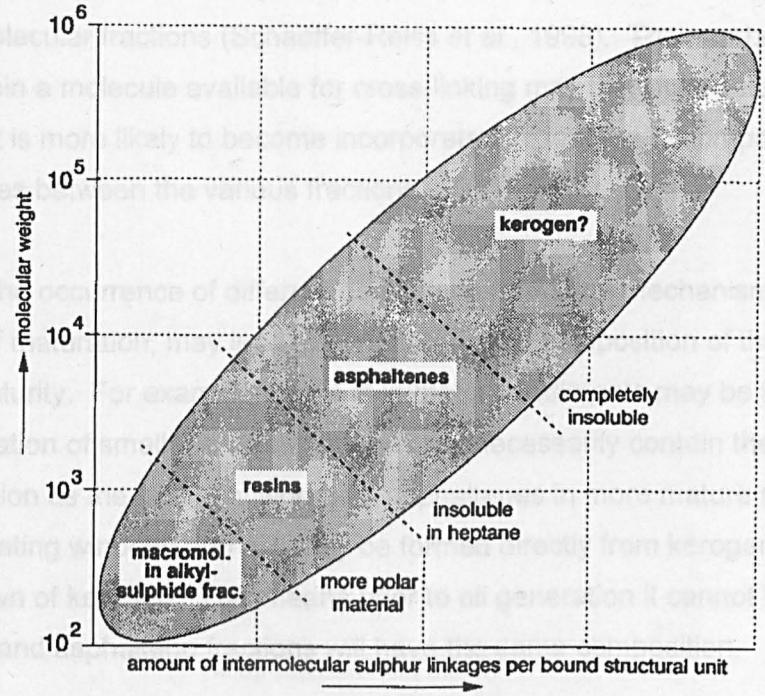


Fig. 4. The relationship between extent of intermolecular sulphur cross-linking and molecular weight of various macromolecular fractions (Kohnen *et al.,* 1991a).

The second formation mechanism is *via* intermolecular incorporation of reduced sulphur into low molecular weight functionalized biological lipids *i.e.* the process of 'natural vulcanization' (Section 1.1.1.2.3; Brassell *et al.,* 1986; Sinninghe Damsté *et al.,* 1988; Sinninghe Damsté & De Leeuw, 1990, Kohnen *et al.,* 1991a, 1991b;). Different macromolecular fractions are considered as on the basis of differences in solubility in organic solvents as opposed to differences in chemical structure (Kohnen *et al.,* 1991a; Schaeffer *et al.,* 1995). A direct linear relationship is said to exist between the degree of inter-molecular cross-linking and the molecular weight and solubility of macromolecules (Fig. 4; Sinninghe Damsté *et al.,* 1990; Kohnen *et al.,* 1991b). Sulphur-rich fractions of highest molecular weight contain a higher abundance of cross-linkages and hence more C-S bonds per carbon skeleton (Schouten *et al.,* 1995). Analysis of macromolecular fractions from the Vena del Gesso shale has yielded hydrocarbons with only small variations in their lipid distributions, suggesting the sulphur-bound structural units of the fractions are similar (Kohnen *et al.,* 1991a). An alternative study of the Vena del Gesso shale considered polar compounds to be 'building blocks' of kerogen; and heterogeneity was observed in the composition of the macromolecules (Schaeffer-Reiss *et al.,* 1998). This was proposed to be the result of variations in the extent of cross-linking, in turn determined by the number of functionalities available on certain lipid compound

classes liable to react with reduced sulphur and thus become incorporated into macromolecular fractions (Schaeffer-Reiss *et al.,* 1998). The number of potential sites within a molecule available for cross-linking may therefore determine which fraction it is more likely to become incorporated in, leading to compositional differences between the various fractions.

The occurrence of different asphaltene formation mechanisms at different stages of maturation, may lead to variations in the composition of the fractions at a given maturity. For example, those in immature sediments may be formed *via* condensation of smaller entities and may not necessarily contain the same lipid composition as the kerogen, whereas, asphaltenes in more mature sediments (in the oil-generating window) and oils may be formed directly from kerogen *via* thermal breakdown of kerogen. This means prior to oil generation it cannot be assumed kerogen and asphaltene fractions will have the same composition.

1.1.3 Occurrence of biomarkers in macromolecular fractions

Biological marker compounds (biomarkers) are compounds present in geological samples which show little or no change in structure from their parent molecules in living organisms (Peters & Moldowan, 1993). In petroleum geochemical studies, biomarkers are routinely examined within the hydrocarbon fractions of oils, and the equivalent fractions of the solvent soluble organic matter (bitumen) of source rocks. However, it is known that biomarker compounds are also found within polar and asphaltene fractions of oils and source rocks (Rubinstein *et al.,* 1979; Durand, 1980), and in kerogens e.g. Seifert, 1978).

Biomarkers may be simply entrapped in macromolecular networks or chemically bound through the sites of functional groups (Tissot & Welte, 1984). Incorporation may occur *via* C-S, C-S_n, S-S and C-O (*i.e.* ether and ester) bonds. Biomarker incorporation most likely starts during very early diagenesis (Hoffman *et al.*, 1992; Richnow *et al.,* 1993; Kok *et al.,* 2000; Werne *et al.,* 2000) and could begin to occur in the overlying water column (Adam *et al.,* 1993; Innes, 1993;). Bacteriohopanetetrol (BHT), a widely presumed biological precursor of fossil hopanoids, has been released from the Messel Oil Shale kerogen by selective chemical degradation (see Section 1.2; Mycke *et al.,* 1987). The Eocene Messel Oil Shale kerogen is approximately 50 x 10^6 years old, demonstrating that intact labile

compounds can survive early diagenesis by binding into stable macromolecules. The presence of four hydroxyl groups in BHT would make it highly unlikely to survive diagenesis in its free form, but make it amenable to binding (Mycke *et al.,* 1987). Biomarker binding into macromolecular fractions will be discussed in greater detail in Section 1.3.

1.2 Analysis of bound biomarkers

Macromolecular fractions cannot be analysed using routine analytical techniques, *i.e.* gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS), but must first be degraded either thermally or chemically to compounds more amenable to these routine analytical procedures. Pyrolysis techniques thermally cleave bonds to degrade macromolecular fractions and generate hydrocarbons and non-hydrocarbons, whereas, chemical degradation techniques chemically cleave specific types of bonds. The quality of information obtained is dependent on the type of cleavage method employed and the product analysis method. Key considerations are the degree of secondary alteration of the products (pyrolysis) and product yields (chemical degradation; Rullkötter & Michaelis, 1990).

1.2.1 Chemical degradation

1.2.1.1 Methods

During chemical degradation specific bonds are cleaved by chemical reagents leading to the breakdown of macromolecular material and the release of lower molecular weight compounds (LMW), yielding information on both the composition of bound lipids and the nature of the bonds linking them to macromolecules (Sinninghe Damsté & De Leeuw, 1990). Carbon-sulphur bonds have been successfully cleaved using Raney nickel (RaNi), nickel boride (Ni_2B; Schouten *et al.,* 1993) and lithium in ethylamine ($Li/EtNH_2$) reagents (Kohnen *et al.,* 1991a; Hoffman *et al.,* 1992). Di-sulphide and polysulphide bonds have been cleaved by treatment with methyl lithium/methyl iodide (MeLi/MeI; Kohnen *et al.,* 1991a). Oxygen bonds have been cleaved using boron trichloride (BCl_3; Richnow *et al.,* 1993), whereas potassium hydroxide and methanol (KOH/ MeOH) is specifically used to cleave ester bonds, and hydrogen iodide/lithium aluminium tetrahydride ($HI/LiAlH_4$) to cleave ether bonds (Schaeffer-Reiss *et al.,* 1998). Ruthenium tetroxide

has been successfully applied to the oxidative cleavage of double bonds and aromatic moieties (e.g. Schaeffer-Reiss *et al.,* 1998). Yields from chemical degradation of macromolecules are typically lower than from pyrolysis techniques (Bishop *et al.,* 1998) partly due to problems of reagent access (Rullkötter & Michaelis, 1990).

1.2.1.2 Sequential or stepwise chemical degradation

During sequential or stepwise chemical degradation reagents are applied to cleave successively different chemical bond types (Schaeffer-Reiss *et al.,* 1998). The technique indicates the importance of different bond types and has provided evidence that sub-units of macromolecular material can be linked simultaneously by different bond types (Richnow *et al.,* 1992, 1993; Schaeffer-Reiss *et al.,* 1998). Chemical reagents should not be applied in a strict order, as with successive reagent treatments previously inaccessible sites may become more accessible (Rullkötter & Michaelis, 1990).

1.2.1.3 Incorporation of deuterium

Several chemical degradations studies have involved incorporation of deuterium on the sites of bond cleavage (Mycke & Michaelis, 1986; Hoffman *et al.,* 1992; Adam *et al.,* 1993; Richnow et al., 1993; Schouten *et al.,* 1993; Schaeffer *et al.,* 1995). Evidence regarding the number and specific location of sites of attachment of lipid compounds has been determined during deuterium labelling experiments (Mycke & Michaelis, 1986; Adam *et al.,* 1993; Richnow *et al.,* 1993; Schaeffer *et al.,* 1995), intern providing evidence for intermolecular incorporation of biomarkers *via* reduced sulphur species at the original sites of functional groups (Hoffman *et al.,* 1992). There are several criticisms of chemical degradation experiments involving deuterium, including long preparation and reaction times (Schouten *et al.,* 1993) and excessive numbers of deuterium atoms attaching to products (Rullkötter & Michaelis, 1990).

1.2.2 Pyrolysis

1.2.2.1 Methods

Several pyrolysis methods have been used for the structural elucidation of kerogen and other macromolecular fractions. Anhydrous pyrolysis involves heating samples in closed reactors or "bombs" in an inert atmosphere in the absence of water (at approximately 250-330°C for 72 hours; Jones & Douglas, 1987). Hydrous pyrolysis studies involve heating in a closed reactor for similar times and temperatures to anhydrous pyrolysis but in the presence of distilled water (Hoering, 1984; Jones & Douglas, 1987; Eglinton & Douglas, 1988; Stalker *et al.,* 1998). An alternative method, flash pyrolysis, involves rapid heating of samples to high temperatures in an open reactor for only limited time period (*i.e.* approximately 610°C for 10 seconds; Sinninghe Damsté *et al.,* 1989).

Some pyrolysis methods (particularly sealed-vessel hydrous and anhydrous pyrolysis) have been used in attempts to simulate natural burial and maturation processes. However, it is difficult to replicate organic matter maturation in the laboratory on a reasonable timescale, as elevated temperatures must be used to compensate for the short reaction times (*i.e.* days, months or years instead of millions of years). Consequently, although artificial maturation techniques assume that reaction pathways and rates will be similar to natural conditions, in reality this is an oversimplification of a very complex process (Hoering, 1984).

1.2.2.2 Hydrous versus anhydrous pyrolysis

There are conflicting views in the literature with regard to the role of water in pyrolysis methods. The ubiquitous occurrence of water in sediments in the natural environment has led to suggestions that hydrous pyrolysis experiments are more realistic in simulating the maturation effects of natural burial (Lewan, 1993; Hoering, 1984; Stalker *et al.,* 1998). Hydrous pyrolysis is suggested to have the advantage over anhydrous pyrolysis in that it cannot only generate oil similar to that produced under natural conditions but also expel oil, suggesting that water plays a role also in expulsion from source rocks (Lewan, 1993). The absence of water in anhydrous experiments is therefore suggested to significantly reduce the total pyrolyzate yield (Lewan, 1993). Anhydrous pyrolysis has also been reported to produce products not found in petroleum generated under natural conditions, suggesting that it may not be considered as a good simulator of natural conditions (Koopmans, 1997). However, a

study comparing yields and distributions of lipids generated under closed-system hydrous and anhydrous conditions observed similar products (Jones & Douglas, 1987).

1.2.2.3 Incorporation of deuterium

A further development in the application of hydrous pyrolysis studies (as with chemical degradation) is the use of deuterited reagents, in this case heavy water (D_2O), involving substitution of deuterium at the points of hydrocarbon cleavage, thus enabling determination of binding sites of molecules (Stalker *et al.,* 1998). A disadvantage of deuterium labelling in hydrous pyrolysis compared to chemical degradation is that hydrous pyrolysis is not bond specific, and therefore deuterium may become incorporated into any bond type (*i.e.* C-O, C-S etc.; Stalker *et al.,* 1998).

A further disadvantage is that a larger number of deuteriums may also become incorporated per cleaved bond than during chemical degradation through hydrogen exchange due to thermal effects of the pyrolysis procedure (Stalker *et al.,* 1998).

1.2.2.4 Online/offline pyrolysis

In general the severity of pyrolysis experiments leads to secondary rearrangement reactions, resulting in structural units that are not present in the original material. This can be minimised by rapid removal of products; e.g. where the pyrolyzer is connected to an 'on-line' detector (Sinninghe Damsté *et al.* 1989; Rullkötter & Michaelis, 1989). Offline pyrolysis has the advantage that large quantities of sample can be collected prior to further analysis; the disadvantage however is that volatile components may be lost (Sinninghe Damsté & De Leeuw, 1990). An alternative technique to online pyrolysis to preserve volatile components is micro-sealed vessel pyrolysis (MSSV), in which samples are artificially matured in micro sealed glass tubes in an inert atmosphere. The glass tube is then cracked in a special device allowing direct 'online' entry of products into the detector (e.g. Sinninghe Damsté *et al.,* 1998).

1.2.2.5 Hydrogen pyrolysis: A novel technique.

This technique is an open pyrolysis system which involves high pressure hydrogen flushing a reactor, ensuring that generated products are rapidly removed to a cold trap (Bishop *et al.,* 1998). The technique overcomes many problems associated with conventional pyrolysis and chemical degradation techniques. The hydrogen has two roles; firstly as a purely physical carrier to flush the reactor furnace quickly and secondly, as a reagent, to cap the cleaved bonds and minimize secondary reactions. A combination of slow heating rate (5°C/min), a high hydrogen pressure (15MPa) and a dispersed sulphided molybdenum catalyst achieves maximum yields of products and minimum structural rearrangement (Love *et al.,* 1997). The role of the sulphided molybdenum catalyst is to improve the selectivity of which bonds are cleaved under high pressure hydrogen pressures i.e. in this case, the temperatures at which reductive cleavage of heteroatom (C-O and C-S) bonds are achieved (typically below 400°C for ether bonds and below 350°C for sulphides) are significantly lower in comparison to that required to achieve cracking of C-C bonds (typically above 400°C). This technique also does not involve significant change in aromaticity compared to other pyrolysis methods (Marto-Valer *et al.,* 1997). Bishop *et al.* (1998) pyrolyzed a hopanoid-producing bacterium using hydrogen pyrolysis. The pyrolysate showed evidence of side-chain cleavage (a shift to lower homologue hopanes) which is inevitable with any pyrolysis method, however only minor isomerisation occurred which was not sufficient to obscure the original isomeric composition. The high product yields of C_{35} ββ hopanes illustrated the potential of hydrogen pyrolysis to maximize yields without significantly affecting stereochemistries (Love *et al.,* 1995). Hydrogen pyrolysis can pyrolyze extracted sediments loaded directly into the reactor, or other macromolecular fractions such as asphaltenes and polars adsorbed on to silica. Sample quantities required are approximately 20-30 mg of organic carbon for kerogens and 20-30 mg of polars or asphaltenes, and the approximate run time for each sample is 40 minutes.

1.3 Nature and importance of bound biomarkers

1.3.1 Nature and location of linkages

1.3.1.1 Type of linkages

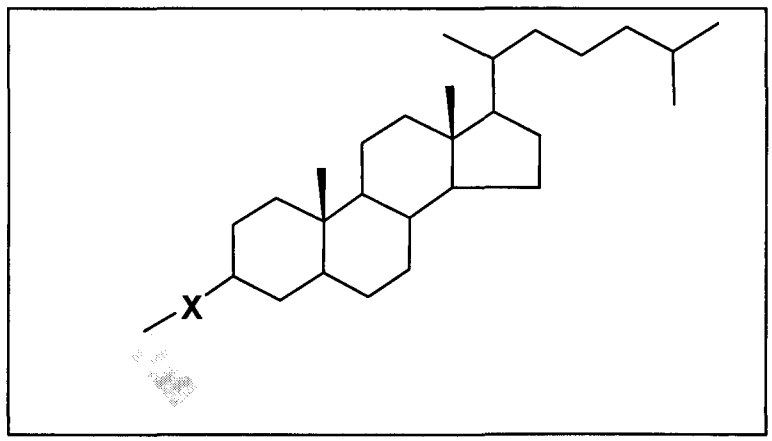
Depending on the existing geochemical conditions during early diagenesis functionalized biomarker precursors may become incorporated into macromolecular organic matter by reaction with inorganic sulphur species *via* C-S, C-S_n, S-S bonds (Hoffman *et al.,* 1992; Richnow *et al.,* 1993;Adam *et al.,* 1993; Putschew *et al.,* 1998; Kohnen *et al.,* 1991b; Sinninghe Damsté *et al.,* 1989), or by condensation reactions with oxygen and carbon *via* ether or ester bonds (Tissot & Welte, 1984; Mycke *et al.,* 1987; Rullkötter & Michaelis, 1990; Richnow *et al.,* 1993; Richnow *et al.,* 1993; Schaeffer-Reis *et al.,* 1998; Section 1.3.2). The relative strengths of the bonds are from weakest to strongest, S-S < C-S < C-O ≈ C-C (Putschew *et al.,* 1998). As C-S and particularly S-S bonds are considerably weaker than C-O and C-C bonds, the presence of such linkages in macromolecular organic matter may be important for the early release of biomarkers (into the hydrocarbon fraction) during source rock burial.

1.3.1.2 Number and location of linkages

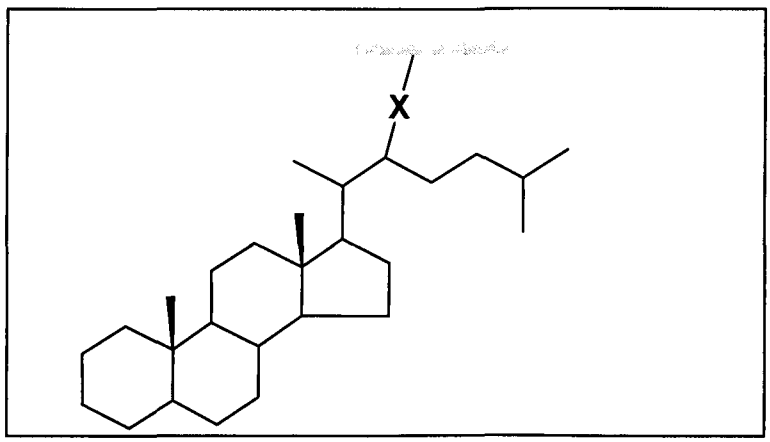
The location of linkages between biomarkers and macromolecular organic matter is determined by the position(s) of functionality(ies) in the precursor compound (Kohnen *et al.,* 1991a; Richnow *et al.,* 1993). Cleavage of specific bonds using chemical degradation techniques and incorporation of deuterium into the released products at the sites of bond cleavage has allowed greater knowledge of the number and location of binding sites (Mycke & Michaelis, 1986; Kohnen *et al.,* 1991a; Hoffman *et al.,* 1992; Adam *et al.,* 1993; Richnow *et al.,* 1993; Schouten *et al.,* 1993; Schaeffer *et al.,* 1995). The results suggest attachment of *n*-alkanes *via* 1 or 2 sites at terminal positions, hopanes *via* multiple attachments in the side chain, and steranes *via* one attachment in the A or B ring, fully consistent with our knowledge of functionality of the precursors (Mycke & Michaelis, 1986; Adam *et al.,* 1993; Richnow *et al.,* 1993; Fig. 5). Evidence has since been proposed for multiple attachments of steroids *via* C-3 or C-2 in the A-ring (related to the original hydroxyl group of sterol precursors) and an additional linkage at C-22 in accordance with the location of a double bond in some sterols (Kohnen *et al.,* 1991a). Additionally, evidence has been presented for 3 points of attachment, in the A-ring, the side chain

and possibly in the C-ring (Hoffman *et al.,* 1992). Multiple attachment sites in steroids provide evidence they can act as cross-linking units (Richnow *et al.,* 1993). Certain lipids (*i.e. n*-alkanes, hopanoids and steroids) may be bound simultaneously by different linkages (e.g. C-S and C-O; Richnow *et al.,* 1992, 1993).

a)



b)



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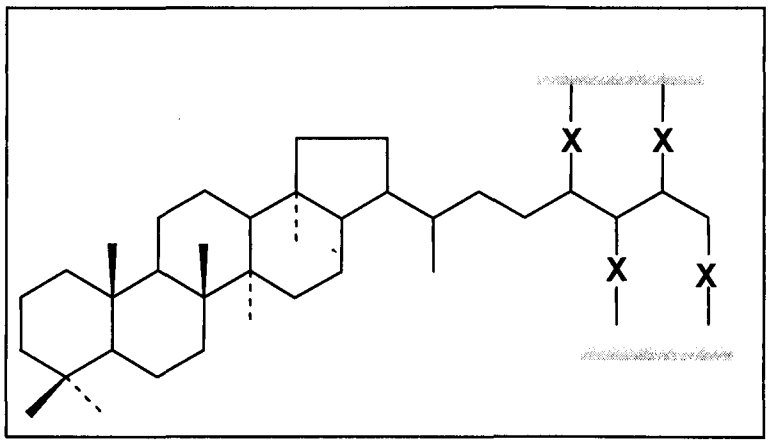

Fig. 5 Diagram to illustrate the location of linkages between hopanoid and steroid skeletons and macromolecules (shaded) at the site of functional groups via a) A or B ring of steroids, b) C-22 *i.e.* the location of a double bond in some steroids, and c) multiple attachments in the side chain of hopanoids. Note, X shown in this figure indicates S or O linking.

1.3.2 Mechanisms and controls on binding

Lipids can be considered to have general fates in the depositional and diagenetic environments; degradation (remineralisation), conversion (to form more stable diagenetic products) and incorporation (binding into macromolecular organic matter). Degradation of lipids may occur mainly in the water column, especially if this is long and /or well oxygenated, resulting in only a minor proportion (potentially modified in composition) of the originally produced lipids reaching the sediment. Diagenetic conversion of lipids to more stable products occurs both within the water column and the sediment, and includes defunctionalisation (tending to form hydrocarbons), isomerisation, rearrangement and aromatisation. Finally, the incorporation of lipids into sedimentary macromolecular organic matter (primarily kerogen) has been recognized as an important diagentic pathway for the preservation of biomarkers in sediments, and is the focus of this thesis.

Although the nature of the linkages between biomarkers and macromolecular structure are generally well characterized (C-S-C, C-S_n-C, ether, ester), the precise mechanisms involved in their formation, and the environmental/geological factors influencing the processes, are relatively poorly understood. This section presents a brief overview of current understanding.

1.3.2.1 Sulphur linkages

The mechanisms of sulphur incorporation into macromolecules have been discussed in the literature in detail. Aizenshtat *et al.* (1995) propose two mechanisms to explain the incorporation of reduced sulphur into organic matter *via* electrophilic addition under acidic conditions and nucleophilic addition under basic conditions. However, it has been suggested that an ionic addition reaction with H_2S is unlikely as it requires strong acidic catalysis, which is unlikely to occur under natural conditions (Adam *et al.,* 1993). The reaction under basic conditions is suggested to have the potential to occur (also referred to in the literature as the Michael-type addition reaction) where the reactivity of double bonds are increased by the presence of unsaturated ketones or carboxylic acid functions, but not where double bonds are simply isolated or conjugated (Adam *et al.,* 1995). An alternative mechanism proposed to explain the formation of cross-linked macromolecules is *via* a radical type reaction (Adam *et al.,* 1993; Fig. 6).

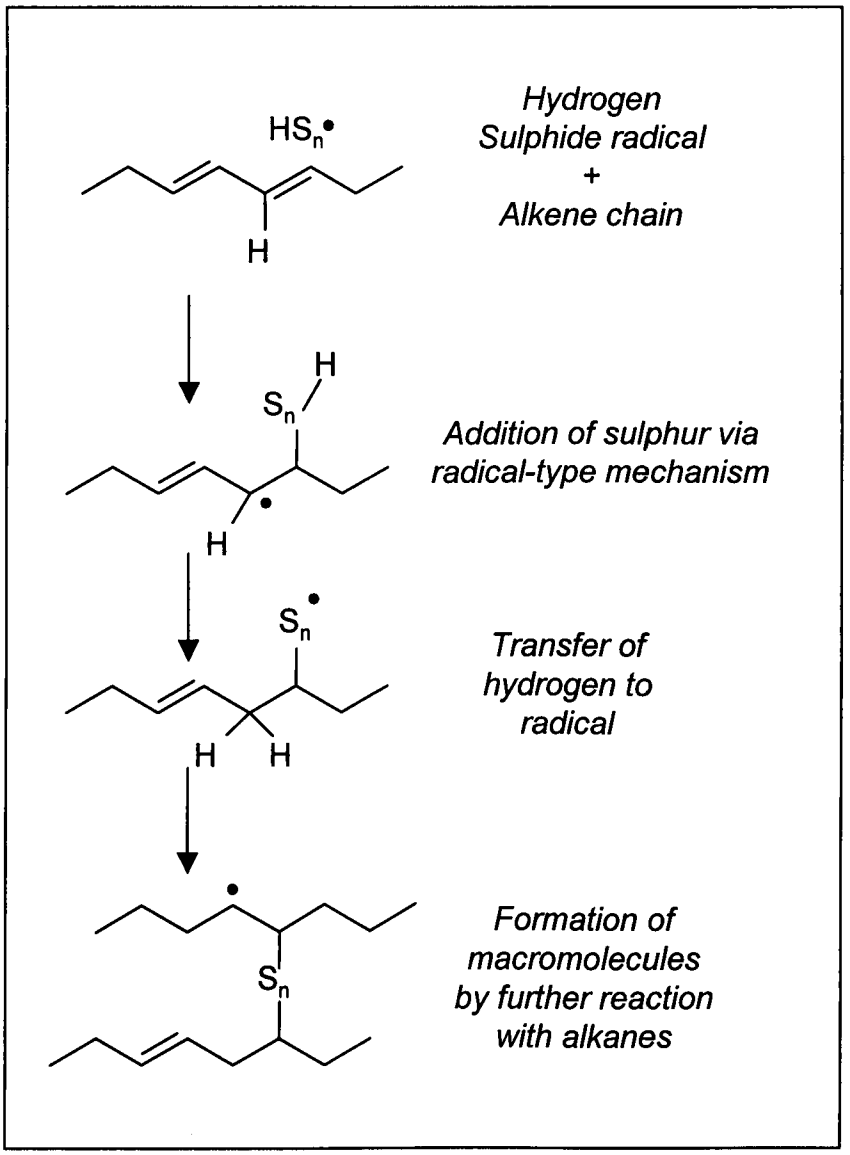

Fig. 6 Mechanism for radical-type addition of sulphur to organic molecules (after Adam *et al.*, 1993).

1.3.2.1.1 Availability of reduced sulphur species and iron minerals

Reduced sulphur species react more readily with iron than with organic matter, therefore sulphur-rich kerogens are most likely to form in anoxic environments low in iron, *i.e.* non-clastic carbonate and evaporitic environments (Sinninghe Damsté *et al.*, 1988, 1990; Sinninghe Damsté and de Leeuw, 1990; Adam *et al.*, 1993). Availability of reactive iron minerals in marine siliciclastic environments therefore plays a role in the incorporation of biomarkers in competing with organic matter in reacting with reduced sulphur species (i.e. H_2S, polysulphidies) (Sinninghe

Damsté *et al.,* 1988, 1990; Sinninghe Damsté & de Leeuw, 1990; Kok *et al.,* 2000). Although sulphurisation is more important in non-clastic settings it is still important in clastic settings with extreme sulphide contents. For example, Innes (1998) observed a much higher proportion of kerogen-bound hopanoids in a sulphidic fjord environment compared with a lacustrine environment of similar age. The variability between the two environments was suggested to be a result of the different sulphur levels; *i.e.* in the sulphur-rich fjord environment more rapid and extensive binding of hopanoids via C-S bonds may have occurred. A study by Holba *et al.* (2000) also effectively demonstrates the impact that environmental diagenetic conditions may play in the incorporation of lipids into kerogen. A high abundance of C_{30} tetracyclic polyprenoids was observed in the bitumen fraction of source rocks from a non-marine low sulphate environment and low abundance in sediments from an anoxic sulphate-rich marine environment. Natural sulphurisation is suggested to have occurred in the sulphate-rich environment, preferentially binding the precursors into the kerogen fraction and resulting in a low abundance in the bitumen fraction (Holba *et al.,* 2000).

1.3.2.2 Oxygen linkages

Esters are formed by the reaction of an acid and an alcohol with the loss of water (Mundy *et al.,* 1993). This concept can be applied to the incorporation of lipids into macromolecular material, whereby an acid functional group on a lipid (e.g. a hopanoic acid) can react with an alcohol group (*i.e.* hydroxyl group) on the macromolecular material, or vice versa. In both cases the loss of a hydroxyl group as water (H_2O) is from the acid not the alcohol (Fig. 7).

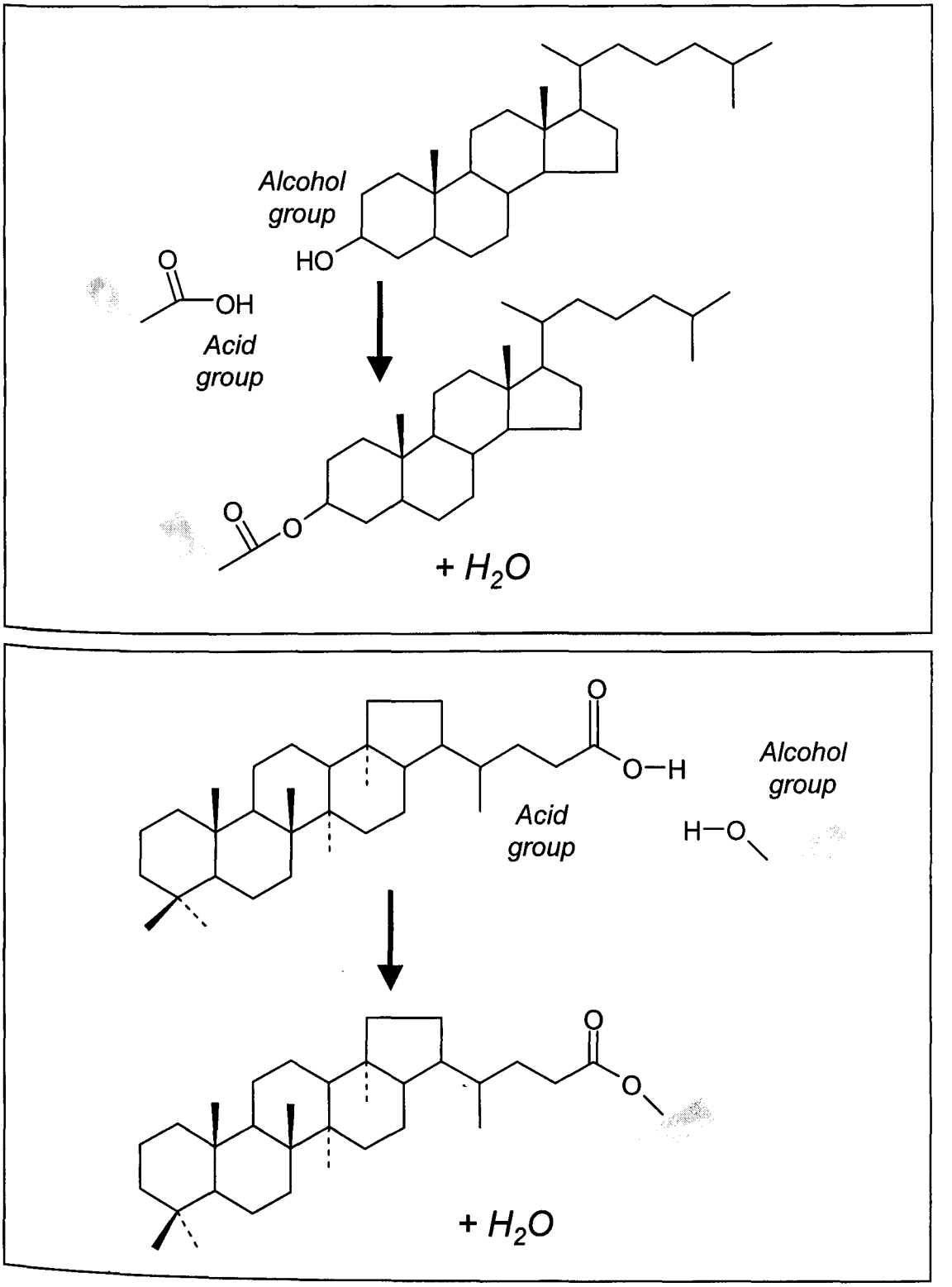

Fig. 7 Generalized mechanisms of formation of ester linkages for the incorporation of biomarkers into macromolecular material shown as a shaded bar.

An ether bond is one in which an oxygen atom forms a bridge between two hydrocarbon groups (Mundy *et al.*, 1993). Ethers are formed by elimination of one molecule of water from two alcohol units. This reaction can again be applied to the incorporation of lipids into macromolecular material whereby an alcohol functional group on a lipid (e.g. a sterol or hopanol) reacts with an alcohol (hydroxyl) group on the macromolecular material (Fig. 8).

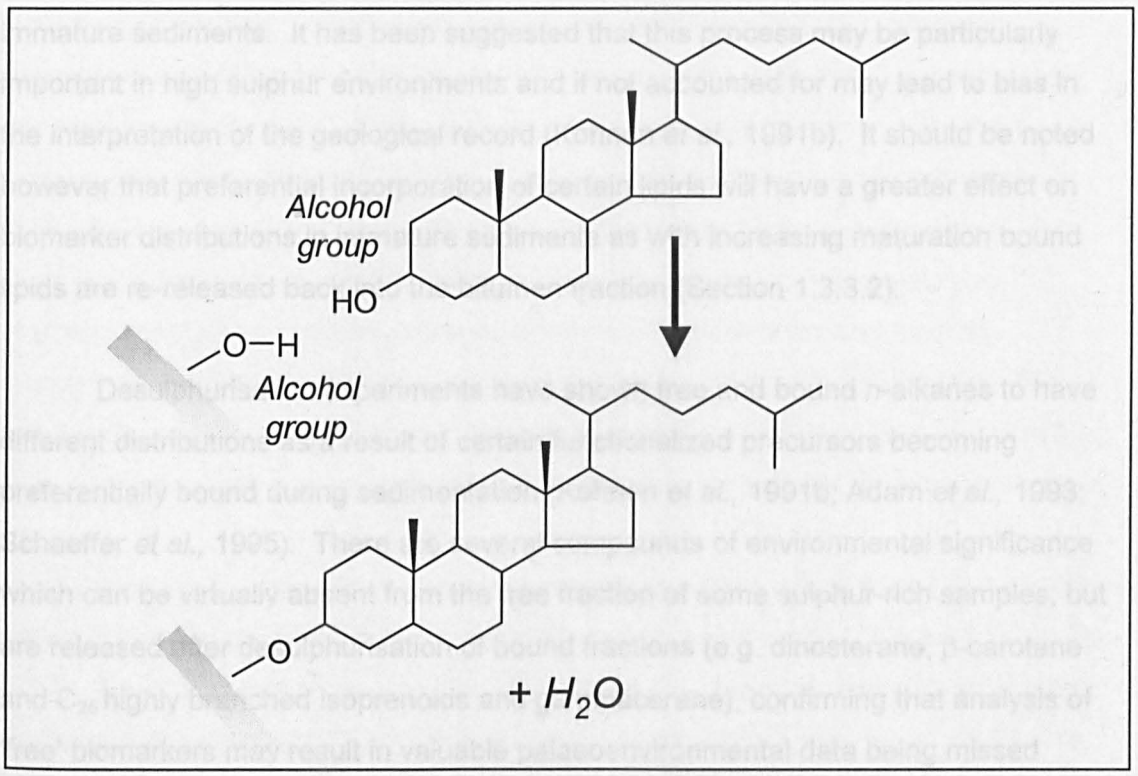

Fig. 8 General mechanism for the formation of ether linkages for the incorporation of biomarkers into macromolecular material.

1.3.3 Compositional fractionation of bound biomarkers

Higher abundances of terpanes relative to steranes have been observed in pyrolyzates than bitumens, suggesting that compositional fractionation may occur between the free and bound 'pools' of biomarkers (Seifert, 1978; Eglinton & Douglas, 1988). Variations in the absolute concentrations of kerogen-bound compounds, and abundance relative to free compounds may be a result of maturity (see Section 1.3.3.2) but depositional environment and diagenetic conditions also exert controls (Bishop *et al.*, 1998).

1.3.3.1 Compositional fractionation through incorporation of biomarkers

Natural sulphurisation during early diagenesis is important for the incorporation, and hence enrichment of specific lipids which may otherwise be prone to microbial transformations and mineralization into macromolecular fractions (Schaeffer *et al.,* 1995). Note, the 'classical condensation pathway' also allows for incorporation of lipid biomarkers into macromolecular fractions during diagenesis. Preferential incorporation of certain hydrocarbon precursors into macromolecular fractions will alter the distribution of biomarkers remaining in the bitumen fraction of immature sediments. It has been suggested that this process may be particularly important in high sulphur environments and if not accounted for may lead to bias in the interpretation of the geological record (Kohnen *et al.,* 1991b). It should be noted however that preferential incorporation of certain lipids will have a greater effect on biomarker distributions in immature sediments as with increasing maturation bound lipids are re-released back into the bitumen fraction (Section 1.3.3.2).

Desulphurisation experiments have shown free and bound *n*-alkanes to have different distributions as a result of certain functionalized precursors becoming preferentially bound during sedimentation (Kohnen *et al.,* 1991b; Adam *et al.,* 1993; Schaeffer *et al.,* 1995). There are several compounds of environmental significance which can be virtually absent from the free fraction of some sulphur-rich samples, but are released after desulphurisation of bound fractions (e.g. dinosterane, β-carotane and C_{25} highly branched isoprenoids and gammacerane), confirming that analysis of 'free' biomarkers may result in valuable palaeoenvironmental data being missed (Kohnen *et al.,* 1991b; Schaeffer *et al.,* 1995). Alternatively, compounds present in the 'free' fraction are not always bound into macromolecular fractions. For example, 28,30-bisnorhopane only occurs in the 'free' aliphatic hydrocarbon fraction of oils and source rocks, and not bound into macromolecular fractions (Jones *et al.,* 1987; Jones *et al.,* 1988; Eglinton & Douglas, 1988; Richnow *et al.,* 1992). The as yet unidentified precursor of bisnorhopane has been suggested to lack and reactive functionality (although it may have a sterically hindered double bond) that would allow binding reactions to occur.

Diasteranes are also not generally observed to be covalently-bound constituents of macromolecular organic matter and these compounds appear to exist exclusively in free hydrocarbon form in bitumen phases (Seifert, 1978; Philp & Gilbert, 1985; Fowler & Brooks, 1987). There are two theories to explain this; firstly,

the formation of rearranged sterenes (diasterenes) by acidic clay catalysis at an early stage of diagenesis, followed by rapid reduction, may exclude the possibility of having a reactive functional group available for binding into macromolecular organic phases. The rapid reduction would reduce the diasterenes to diasteranes; hence, the diasteranes would lack the reactive double bond available for attachment. Secondly, steric hindrance of the alkene bond in diasterenes reduces the reactivity at this site of unsaturation (Seifert, 1978) i.e. diasterenes are unlikely to become incorporated into bound fractions due to the shielded position of the double bond at C-13 and 17 position. Another important factor preventing the occurrence of rearranged steroids in bound fractions may be due to the high molecular weight of macromolecular fractions. Clay catalysis requires intimate interaction between organic molecules and clays and this is not possible with larger macromolecular units. Peters *et al.* (1990) have observed diasteranes in hydrous pyrolysates. It is more likely, in this instance, that diasteranes were generated from acidic clay rearrangement of free regular steranes which had just been cleaved from the kerogen as an oil product. Hydrous pyrolysis involves the heating of samples with liquid water over a period of days in the closed system, and this cooking of generated oil in interaction with source rock minerals will lead to rearranged biomarker products

Similarly to rearranged steroids, rearranged hopanes (e.g. C_{27}Ts and C_{29}Ts) are not generally observed within macromolecular organic matter (Fowler & Brookes, 1987). Rearranged hopanes are though to derive *via* chemical mechanisms during diagenesis of unrearranged hopanoid natural products (Moldowan *et al.,* 1991). The chemical mechanism by which the rearranged hopane Ts is formed is thought to be catalysed by clay. As with diasteranes this may also explain the absence of Ts from macromolecular fractions. A hydropyrolysis study be Murray *et al.* (1998) observes very low amounts of diasteranes and Ts in hydrogen pyrolysates; this may be explained as free biomarkers which were trapped within the physical macromolecular network and hence not extracted prior to the pyrolysis procedure when the sediments were pre-extracted to remove the bitumen fraction.

Pristane, C_{20} highly branched isoprenoid alkanes and squalane have also been observed to be low in the desulphurised fraction of sulphur-rich sediments, suggesting they did not react with sulphur during early diagenesis, possibly because they were synthesized without the necessary functionality for attachment (Kohnen *et al.,* 1991b).

1.3.3.2 Release of biomarkers during maturation

A reversal of the above biomarker binding processes occurs with burial depth and increasing maturation. A minor fraction of bitumen in deeply buried sediments may be inherited directly from biomass, but the main proportion is released from kerogen during burial and maturation due to thermal stress and associated bond cleavage (Rullkötter and Michaelis, 1990). In immature source rocks, the concentration of kerogen-bound hopanoids has been shown to be typically higher than that of the bitumen extract (Bishop *et al.,* 1998). A five fold increase in bitumen hopanoid concentration has been observed with increasing proximity to a dyke (and associated maturity increase) demonstrating this concept; with increasing maturation hopanoids were generated from the macromolecular fraction to the bitumen fraction (Farrimond *et al.,* 1996). Another study of the effects of thermal maturation on the abundance of tricyclic terpanes with proximity to an igneous dyke, showed an increase in tricyclic terpane concentrations towards or within the effective 'oil window', thought to record generation of the compounds from the kerogen- and asphaltene-bound fractions (Farrimond *et al.,* 1999). Farrimond *et al.* (1998) in a study of natural burial maturation effects in a Barrent Sea well also observed increased concentrations of steranes and hopanes with depth, interpreted to represent generation from mainly kerogen and also other macromolecular fractions. A hydrous pyrolysis study of the immature Monterey Shale kerogen showed that the kerogen-bound fraction of the biomarkers in source rocks is quantitatively significant. The analysis demonstrated that the kerogen-bound fraction had the potential to 'swamp' the original free biomarker fingerprint (Eglinton & Douglas, 1988). A hydrogen pyrolysis study by Bishop *et al.* (1998) has shown the abundance of kerogen-bound hopanes varies as a result of maturity however their results show that; depositional environment and diagenetic conditions also play a role in controlling kerogen-bound hopane concentrations.

It is also important to note that biomarker compounds found only in the 'free' fraction (due to lack of the necessary functionality for attachment) that are utilized in biomarker ratios will have their ratios altered with maturation. For example, the ratio of BNH to hopanes will decrease as hopanes are released from kerogen with increasing maturity.

1.3.3.3 Bias in routine biomarker analysis

Biomarker skeletons in the aliphatic fraction of oils can be derived from a whole range of organic matter fractions in the source rock, as heteroatomic linkages are cleaved with increasing maturation (Fig. 9). In consequence, the composition of the aliphatic fraction may change with increasing maturation due to release of bound biomarkers. Indeed, the changes in isomerisation of free biomarkers with increasing maturity has been suggested to be at least partly due to the release of biomarkers from macromolecular fractions (e.g. Farrimond *et al.,* 1996, 1998). Such overprinting of the free biomarker signal by compounds generated from the kerogen may also cause changes in molecular parameters routinely employed to interpret organic matter sources and environmental conditions of source rock deposition.

Biomarker skeletons from all organic matter fractions of a source rock may contribute to the aliphatic fraction of oil, but only the source rock aliphatic fraction is routinely analysed for correlation purposes. Analysis of the kerogen fraction and also the polar and asphaltene fraction of source rocks to supplement the bitumen fraction should give a more complete picture of source rock biomarker composition, enabling more accurate oil-source rock correlation.

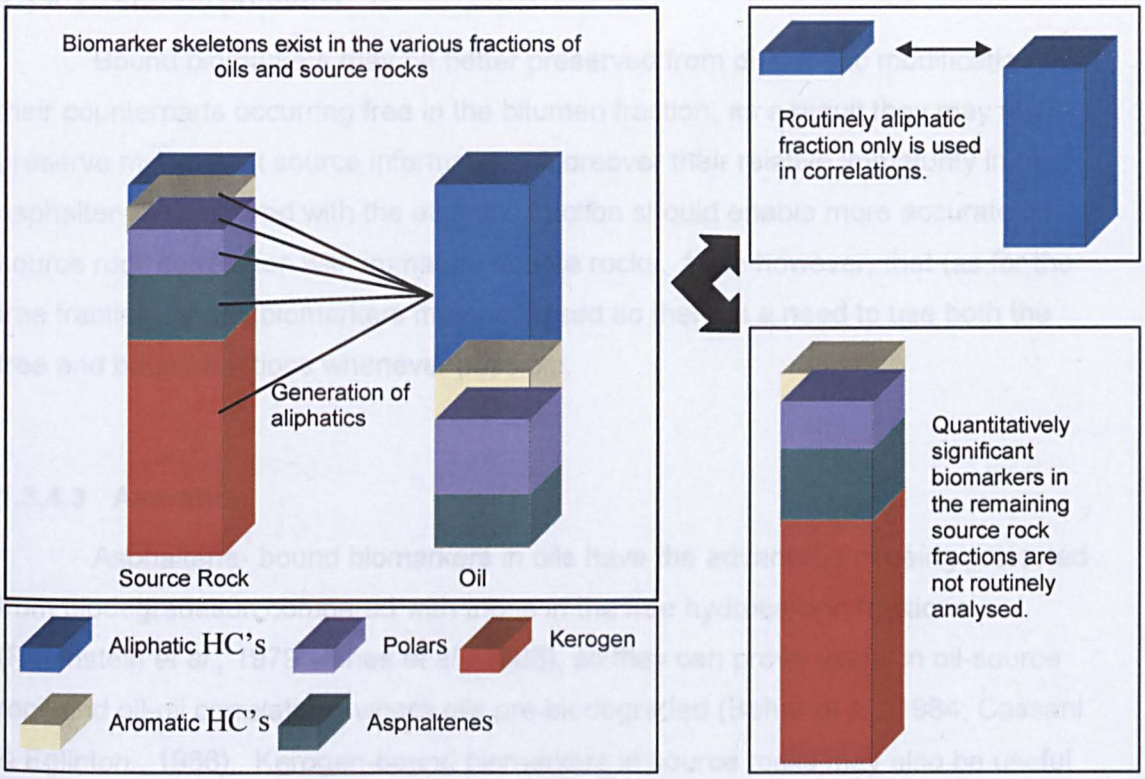

Fig. 9 Biomarker bias in routine oil to source rock correlation.

1.3.4 Advantages of analysing bound biomarkers

1.3.4.1 Maturity

Binding into kerogen and asphaltenes provides steric protection; thus bound biomarkers are relatively immature (i.e. less extensively isomerized) compared to biomarkers free in the bitumen (e.g. Rocha *et al.*, 1997). There are two theories to explain this; firstly, attachment to macromolecules may prevent mineral catalysis at certain sites and secondly, the relative stability of the bound R isomers (at C-20 in steranes and at C-22 in hopanes) is within covalently bound molecules (Richnow *et al.*, 1992 Adam *et al.*, 1993). Due to this steric hindrance the thermally less stable 17β(H), 21α(H) moretanes are relatively more abundant in the bound fractions and the moretane/hopane maturity parameter is below equilibrium and therefore still responding to changes. As a result the moretane maturity ratio of bound biomarkers extends over a greater maturity range than in the bitumen and has a greater sensitivity at higher levels of maturity to small maturity changes (Murray *et al.*, 1998).

1.3.4.2 Source potential

Bound biomarkers may be better preserved from diagenetic modification than their counterparts occurring free in the bitumen fraction; as a result they may also preserve more intact source information. Moreover their relative immaturity in oil asphaltenes compared with the aliphatic fraction should enable more accurate oil-source rock correlation with immature source rocks. Note however, that (as for the free fraction) bound biomarkers may be biased so there is a need to use both the free and bound fractions whenever possible.

1.3.4.3 Alteration

Asphaltene- bound biomarkers in oils have the advantage of being protected from biodegradation compared with those in the free hydrocarbon fractions (Rubinstein *et al.,* 1979; Jones *et al.,* 1988), so they can prove useful in oil-source rock and oil-oil correlations where oils are biodegraded (Behar *et al.,* 1984; Cassani & Eglinton., 1986). Kerogen-bound biomarkers in source rocks may also be useful where the bitumen fraction has been altered by contamination with an oil-based drilling mud or crude oil (Murray *et al.,* 1998).

1.4 Aims and scope of this study

This thesis addresses the application of biomarkers, including those bound into macromolecular fractions, from an exploration context in Offshore Angola. Bound biomarkers will be released by hydropyrolysis, and applied to overcome problems of drilling mud contamination and biodegradation, and will also be investigated from the context of being a quantitatively significant 'pool' of additional source information to enhance oil to source rock correlations.

1.4.1 Context: Angola

The West-African Atlantic margin from Cabinda to Mid-Angola consists of two major basins, the Lower Congo and the Kwanza Basins (see Geology and Sample Framework Chapter for more details). The basins are passive pull-apart basins related to Early Cretaceous rifting events later evolving into the drift phase opening of the South Atlantic (Burwood, 1999). This research will focus for an exploration perspective on the Lower Congo Basin, although some source rock and oil samples from the Kwanza Basin are also included.

Successive rift and drift events throughout the Early Cretaceous associated with the separation of the African and south American continents led to the development of palaeo-depositional centres for organic-rich lacustrine sediments (Burwood *et al.*, 1995). During this period of lacustrine sedimentation (Neocomian - Barremian) the regions premier oil-forming source rock, the Bucomazi Formation, was deposited (Burwood et al., 1990, 1992, 1995; Burwood, 1999). During the late Barremian subsidence rates were reduced and the lacustrine depo-centres merged together occasionally forming an inland sea giving more oxygenated waters which limited organic-rich sedimentation (Burwood *et al.*, 1995). Following an Early Aptian drift phase regional subsidence led to increasingly persistent marine incursions. The Aptian Loeme salt deposit, a desiccation event, marks the boundary after which permanent marine conditions occurred. The Loeme salt acts as a regional marker essentially separating the stratigraphy into a predominantly lacustrine 'pre-salt' section and a marine 'post-salt' section. Following the Loeme salt deposition sedimentation involved deposition of several thick marine organic-rich sediment packages with significant hydrocarbon potential. The sediment packages are the Late Cretaceous (Cenomanian-Maastrichtian) Iabe Group, the Tertiary (Paleogene) Landana Group, and the Tertiary (Oligocene/ Miocene) Malembo Group. Detailed

biomarker characteristics of these Upper Cretaceous black shales, described as having "unproven possible offshore potential" (Burwood, 1999, p181), and the marine Tertiary source rocks will be the main focus of this research, although the whole stratigraphic section both pre- and post- salt will be covered.

The plentiful supply of potential source rocks in Angola leads to a common problem in petroleum exploration: linking oils to their source rocks. This problem of oil-source rock correlation is further complicated in Angola by the concept of 'poly' and 'hybrid' petroleum systems where multiple sourcing exists (Burwood, 1999). Through a range of geochemical techniques, both standard and novel, I intend to develop a detailed biomarker stratigraphy of the organic matter changes throughout the sedimentary succession with some emphasis on the Late Cretaceous to Tertiary section, identifying distinguishable features that may enable oil-source rock correlation. To my knowledge the geochemistry of this particular section has not been documented in the literature in great detail to date. The geological history of the Offshore Angola region will be considered in more detail in the 'Geology and Sample Framework' chapter.

1.4.2 Aims

1. To characterise the source rock stratigraphy in terms of hydrocarbon potential.
2. To characterise the molecular characteristics (both free and bound) of the source rocks in terms of maturity and facies, and identify biomarker characteristics that can be used to distinguish individual sections, and thus be applied as age-specific biomarkers of individual units in this region.
3. To conduct (free and bound) biomarker analysis and isotopic studies of the oils in the region and identify source rock contributions to the oils.
4. To analyse oil and source rock free and bound biomarkers to determine the quantitative importance of bound biomarkers.

From an exploration context the focus of this research is the Tertiary - Cretaceous section of the Lower Congo Basin as a potential source rock for Block 17 oils. Details of the sample suite employed (i.e. Stratigraphic and regional coverage) will be given in the 'Geology and Sample Framework' chapter.

2 Methods

Fig. 10 shows a schematic diagram to illustrate the methods of analysis employed for the analysis of the biomarkers in both the free and bound oil and source rock fractions. The remainder of the chapter provides a more detailed description of these techniques. The methods carried out for this thesis were completed at either Newcastle University, Norsk Hydro research laboratories in Bergen, Norway, or Nottingham University. Technicians at Norsk Hydro in Bergen carried out the majority of the free biomarker analysis, although some extra samples were selected at a later date for analyses, and completed by myself at Norsk Hydro. The preparation of oil and source rock samples for hydrogen pyrolysis was carried out by myself at Newcastle University. I also carried out the hydrogen pyrolysis of these samples at Nottingham University. Finally, the fractionation and analysis of the hydrogen pyrolysates was completed by myself at Norsk Hydro in Bergen.

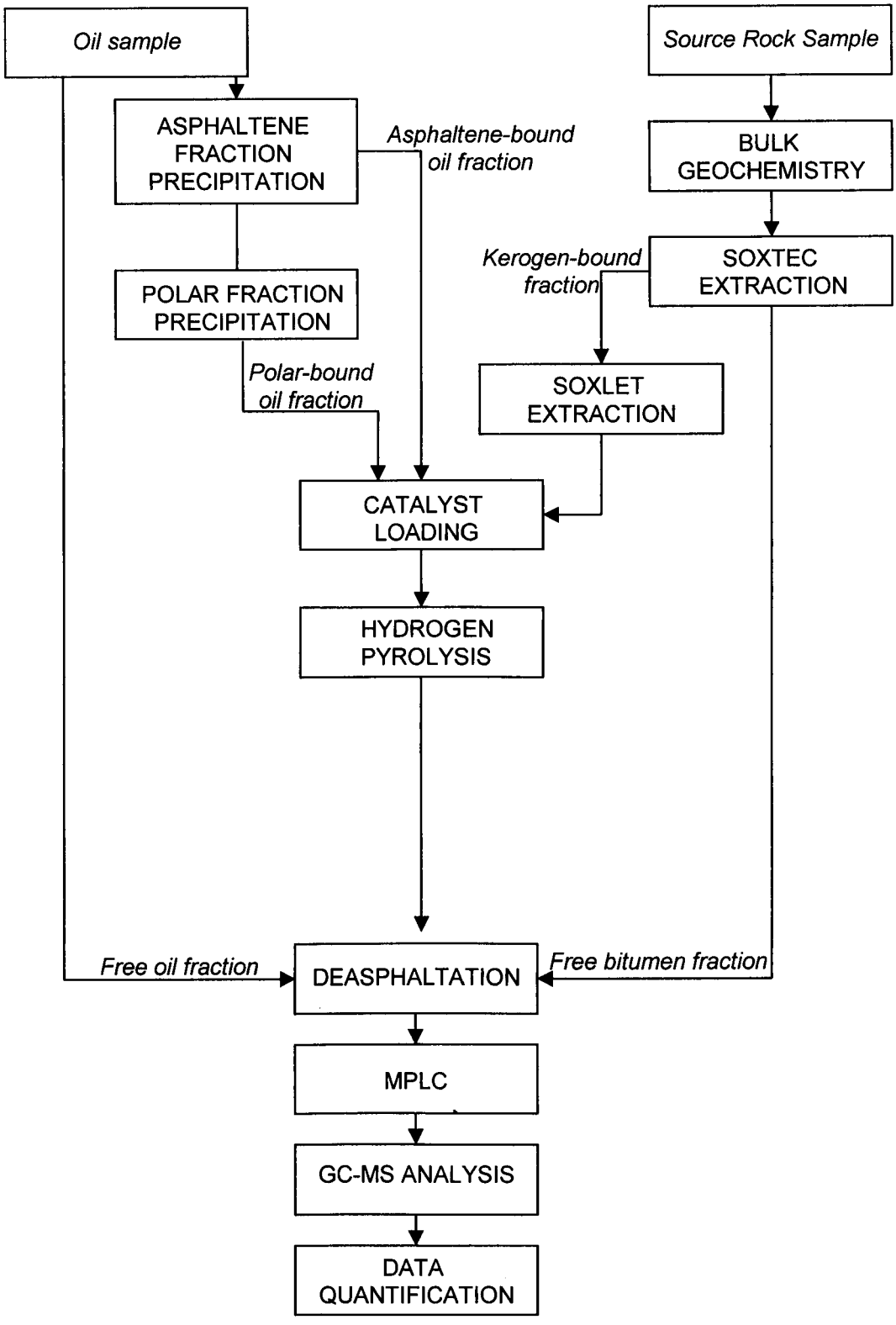

Fig. 10 Schematic representation of methods used in the analysis of the biomarkers in both the free and bound fractions of the oils and source rocks.

2.1 Bulk Geochemistry

A 50mg aliquot of powdered sediment were submitted for Rock Eval Pyrolysis to determine Total Organic Carbon (TOC) content (in wt%), S_0 (in mg HC/g sediment (gas)), S_1 (in mg HC/g sediment (oil)) and S_2 (in mg HC/g sediment (oil)) and T_{max} (°C). From these values, Production Index (PI) and Hydrogen Index (HI) were calculated using the formula below:

$$PI = (S_0 + S_1)/ (S_0 + S_1 + S_2)$$

$$HI = (100 \times S_2)/ TOC$$

2.2 Analysis of free hydrocarbons

2.2.1 Soxtec Extraction of source rock samples

Prior to extraction procedures, selected source rock samples were powdered in a pestle and mortar. Sample aliquots required for extraction were determined from Table 1 using the Rock Eval Pyrolysis parameter S_1. Samples were solvent extracted for 4 hours using a Soxtec auto advanti 2050 system and dichloromethane (DCM - CH_2Cl_2): methanol (CH_3OH); 93:7. Samples were initially immersed in boiling solvent for 1 hour followed by drip rinsing (or refluxing) for 3 hours. Elemental sulphur was removed by the addition of copper turnings. Extract volumes were reduced automatically using the Soxtec equipment to approximately 5 -10ml and transferred to centrifuge tubes for deasphaltation procedures (Section 2.2.2). A known aliquot of each extract was removed and dried under a stream of nitrogen in a weighed vial to obtain a weight. From this weight the extractable organic matter contents (EOM) of the sample was calculated.

S_1 (mg HC/ g sediment)	Sample Weight (g)
< 0.5	100
0.5 - 1.0	50 - 30
1 - 2	25 - 15
2 - 3	10 - 5

Table 1 Sample aliquots (in mg) required for analysis of the free hydrocarbon fraction of source rocks determined from the Rock Eval pyrolysis parameter S_1.

2.2.2 Deasphaltation of oils and source rock extracts

Prior to deasphaltation an internal standard of 5β(H)-cholane was added to each sample (100µl of standard (concentration, 12 micrograms per ml) per 50mg EOM). Source rock extracts (from Section 2.2.1) and oil samples were reduced in centrifuge tubes using a stream of nitrogen to *ca.* 0.3 - 0.4 ml of sample in DCM (CH_2C1_2):methanol (CH_3OH); 93:7. An excess of *n*-pentane ($CH_3(CH_2)_3CH_3$) was added to increase the volume to 12mls. The centrifuge tubes containing the samples were then placed in an ultrasonic water bath for 10 minutes and allowed to settle overnight. Samples were then centrifuged for 5 minutes and the maltene fraction (i.e. the *n*-pentane soluble fraction) decanted and collected. The precipitated asphaltene fractions were rinsed with *n*-pentane and the process repeated a further 3 times to remove any residual maltenes. The asphaltene fractions were then dissolved in minimal DCM and transferred to weighed vials and weights obtained and the percentage asphaltene calculated. Maltene fractions were reduced under a stream of nitrogen and made up to a concentration of 100mg per ml. A 200µl aliquot was then transferred to a glass vial with an insert and fractionated by medium pressure liquid chromatography (MPLC) (see Section 2.2.3).

2.2.3 Medium Pressure Liquid Chromatography (MPLC)

Extracts were fractionated into saturate, aromatic and NSO fractions using an automated MPLC system. The saturate fraction was collected between 0.2 – 3.3 minutes using hexane ($CH_3(CH_2)_4CH_3$), the aromatic fraction between 3.3 and 10 minutes using hexane, and the NSO fraction between 10–14 minutes in methyl tert-butyl ether ($(CH_3)_3COCH_3$). The aliphatic fraction was subsequently reduced in volume using a stream of nitrogen and made to a concentration of 10mg per ml in isooctane ($(CH_3)_3C.CH_2CH(CH_3)_2$) and added to a vial insert for analysis by GC-MS (see Section 2.2.4). The aromatic and polar fractions were reduced using a stream of nitrogen and stored in isooctane in a refrigerator.

2.2.4 Gas Chromatography Mass spectrometry (GC-MS) analysis

Due to a change in the type of column used at Norsk Hydro during the course of this PhD the GC-MS analysis was completed using two different columns.

GC-MS column method 1: The aliphatic hydrocarbon fractions were analysed by gas chromatography-mass spectrometry (GC-MS) in selected ion monitoring mode using a HP5971 mass selective detector. The HP5890 GC was fitted with two flexible silica capillary columns (25m x 0.2mm id. 5% phenyl methyl silicone (HP-5): 0.33µm film thickness), one leading to the mass spectrometer, and the other to the flame ionisation detector. The carrier gas was helium. The oven temperature program was 80°C (5mins) to 310°C at 4°C/min, with a hold at 310°C for 20 minutes.

GC-MS column method 2: The aliphatic hydrocarbon fractions were analysed by gas chromatography-mass spectrometry (GC-MS) in selected ion monitoring mode using a HP1901A-105 mass selective detector. The HP6890 GC was fitted with two flexible silica capillary columns (50m x 0.2mm id. % phenyl methyl silicone (HP-1): 0.33µm film thickness), one leading to the mass spectrometer, and the other to the flame ionisation detector. The carrier gas was helium. The oven temperature program was 70°C (2min) to 150°C at 5°C/min, with a hold at 150°C for 1 minute followed by an increase 2°C/min to 325°C with a hold at 325°C for 10 minutes.

Biomarker compounds were identified on the basis of mass fragmentographic responses and relative retention times and by comparison with a standard North Sea oil. Quantification was conducted automatically by peak height responses in specific mass chromatograms: hopanes were integrated on the m/z 191, methylhopanes on the m/z 205, steranes on the m/z 217 (excluding αββ steranes which were integrated on the m/z 218 mass chromatogram). A response factor of 1.32 was applied to all hopanes, excluding C_{30} compounds where a response factor of 2.05 was applied, and a response factor of 0.91 was applied to all sterane compounds. Biomarker concentrations for the free and bound source rock fractions are expressed in ng/mg of rock. Biomarker concentrations for free and bound oil fractions are expressed in ng/mg of oil.

2.3 Analysis of bound hydrocarbons

2.3.1 Kerogen preparation for hydrogen pyrolysis

2.3.1.1 Soxlet extraction

Approximately 30mg of organic carbon is desirable from source rock samples for hydropyrolysis to yield sufficient quantities of pyrolyzates for further GC-MS analysis. The weight of sample required to yield this amount was determined using the source rock TOC values (from Section 2.1). Pre-extracted source rock samples were added to cellulose thimbles and exhaustively soxlet extracted for 48 hours in dichloromethane (DCM)/methanol; 93:7 (250ml)). Although the samples were previously extracted at Norsk Hydro (see Section 2.2.1) the samples were re-extracted at Newcastle to ensure that no residual maltenes remained. The re-extracted source rock samples were dried in a fume cupboard and then recovered from the soxlet thimbles. The resulting extract was discarded and the source rock samples catalyst loaded (see Section 2.3.4).

2.3.2 Oil asphaltene precipitation and purification for hydropyrolysis

The asphaltene- and polar-bound oil fractions analysed in this thesis were not those prepared in Section 2.2.3 by Norsk Hydro but were precipitated from crude oil samples at NRG, Newcastle. This was performed in order to obtain sufficient quantities of asphaltene and polars.

Ideally a minimum amount of 10mg of asphaltene was required for hydropyrolysis. The weight of oil required to yield such quantities was determined from the asphaltene percentages for the oils. Crude oils were transferred to conical flasks using minimal DCM. Samples were magnetically stirred in a 40-fold excess of chilled *n*-heptane ($CH_3(CH_2)_5CH_3$) for 30 minutes. Samples were transferred to centrifuge tubes and spun for 5 minutes at 2200rpm. The *n*-heptane fraction (containing the maltene fraction) was decanted from the centrifuge tubes. The remaining precipitated asphaltene fractions were re-dissolved in minimal DCM and the process repeated 3 times. A final weight for the asphaltene fraction was obtained; ideally this was greater than 10mg of asphaltene, however, for certain oils sufficient amounts could not be obtained. Samples were then loaded onto silica (2g) using minimal DCM and allowed to dry at room temperature.

2.3.3 Oil Polar fraction precipitation and purification for hydropyrolysis

Approximately 100mg of deasphaltened oil (maltene fraction) were loaded on to pre-extracted silica (~2g) using minimal dichloromethane. The silica loaded samples were dried at room temperature and then added to a silica column for liquid chromatography separation. A small plug of extracted cotton wool was placed between the sample and the column of silica to enable later recovery of the silica loaded polar fraction. The columns were eluted with 30mls light petroleum ether to removed the saturated aliphatic hydrocarbon fraction, and 70ml 3:1 light petroleum ether:DCM to remove the aromatic hydrocarbon fraction. The silica loaded polar fraction was then recovered from the column and loaded with catalyst for hydropyrolysis (see Section 2.3.4).

2.3.4 Catalyst loading of kerogen, asphaltene and polar fractions

Source rock kerogens and silica-adsorbed oil asphaltene and polar fractions were loaded with a sulphided molybdenum catalyst (ammonium dioxythiomolybdate – $(NH_4)_2MoO_2S_2$) to improve the selectivity of hetero-atom bond cleavage under high pressure hydrogen pyrolysis. Catalyst quantities (3% weight of source rock samples and 3% weight of silica for asphaltene and polar fractions) were weighed into 3ml vials and approximately 2mls of DCM was added then decanted off to clean the catalyst. A 20% methanol: aqueous solution was then added to each vial and the catalyst transferred using a pipette to 250ml round bottom flasks which contained either the extracted source rock samples (i.e. from Section 2.3.1.1) or the silica adsorbed polar or asphaltene samples (i.e. from Sections 2.3.2 and 2.3.3). A further 20mls of 20% methanol:aqueous (H_2O) solution was added to each flask. Samples were then stirred on a shaker stirrer for 30 minutes then rotary-evaporated to remove excess solution, samples were then transferred to 10ml vials and freeze dried to total dryness.

2.3.5 Hydrogen pyrolysis (or hydropyrolysis)

A schematic of the hydrogen pyrolysis rig is shown in Fig. 11. Catalyst-loaded sediments or silica-adsorbed oil asphaltene and polar fractions were placed directly into a hydropyrolysis reactor tube between two solvent-extracted wire wool plugs. A small plug of solvent-extracted silica wool was placed into the outflow of the trap. The reactor and trap (see below for trapping methods) were then connected to the hydropyrolysis rig. The hydrogen pyrolysis rig was then pressure tested at 50MPa to test for hydrogen leaks. If the pressure drop during testing was less than or equal to 2 bar over a minute the pressure test was accepted and the sample ran if the leakage was greater than two bar any appropriate alterations made to the rig to tighten the leak and the rig pressure tested again. Electronic connectors were then connected to the rig and a protective screen secured around the rig. Samples were heated under high hydrogen pressure of 15MPa from ambient to 520°C at a heating rate of 5°C per minute. Hydrogen was flushed through the system at 4-5 litres per minute. Initially samples were collected in a coiled metal trap cooled with dry ice and recovered through rinsing with DCM. Following method development at Nottingham University hydropyrolysis tars were later collected in a short trap containing a bed of extracted silica.

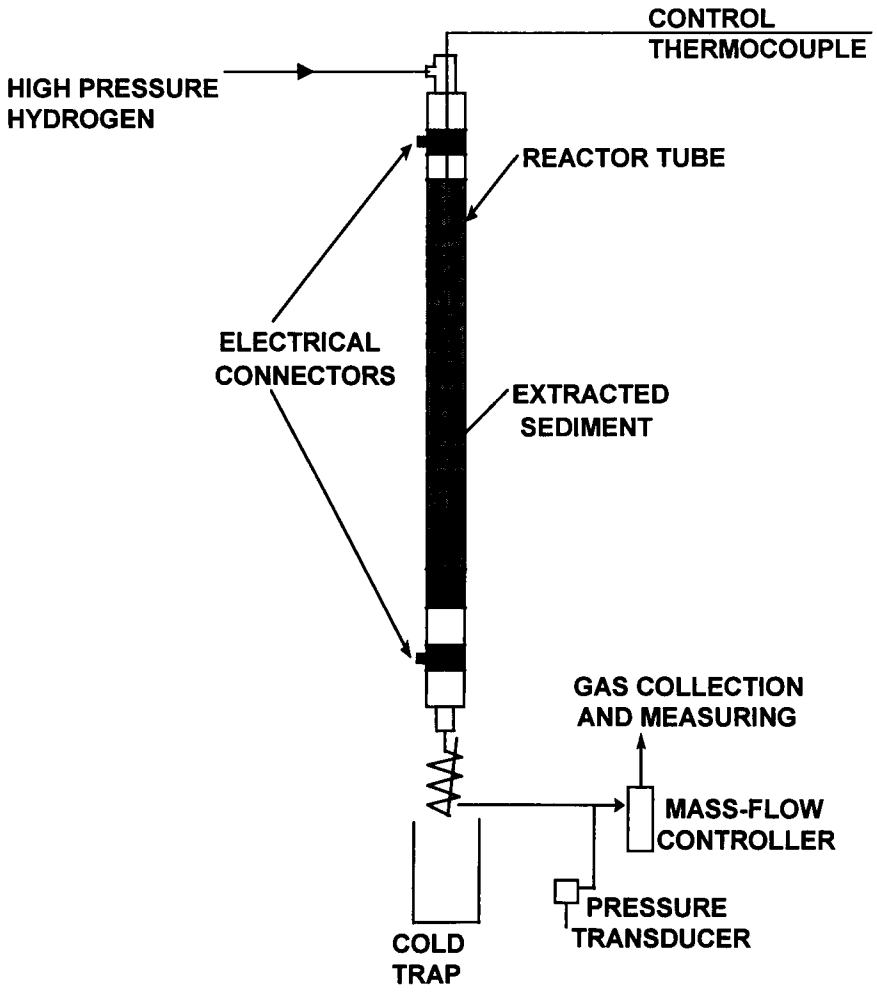

Fig. 11 Schematic representation of the hydropyrolysis apparatus.

2.3.6 Separation and Analysis of hydropyrolysis Tars

Hydropyrolysis tars were analysed using the same procedure outlined for free biomarker fractions involving deasphaltation (Section 2.2.2), MPLC (Section 2.2.3) and GC-MS analysis (Section 2.2.4; column method 2) by myself at Norsk Hydro laboratories in Bergen, Norway. Bound biomarker peak quantification was conducted by the same techniques used as at Norsk Hydro for the free biomarker fractions, although peak height measurements and quantifications were conducted manually by myself at NRG, Newcastle.

3 Geology and sample framework

This chapter introduces the regional geology of Angola and illustrates the thesis' geographical and stratigraphical source rock sample coverage. The chapter also includes bulk geochemical interpretations of organic richness and source rock quality in terms of the hydrocarbon potential of each stratigraphic unit.

3.1 3.1 Geological introduction

3.1.1 Separation of the Southern Atlantic

West Africa and Brazil difted apart during the Mesozoic, due to the extensional opening of the southern Atlantic. Early Cretaceous rift events later evolved into drift phase opening (Burwood *et al.*, 1999). The resulting tectonic and depositional regime throughout the remaining Mesozoic and Tertiary led to the development of highly prolific petroleum systems. This involved deposition of extensive source rocks in the Cretaceous and Tertiary, deposition of reservoirs in the Tertiary and also salt tectonics during Cretaceous and Tertiary leading to the development of salt traps (Cole *et al.*, 2000). The stratigraphy is divided into two distinct sedimentary and tectonic regimes: the Pre- and Post-salt. These are separated by a regional stratigraphic marker, the Aptian Loeme salt, an extensive evaporite (Fig. 12; Burwood *et al.*, 1999).

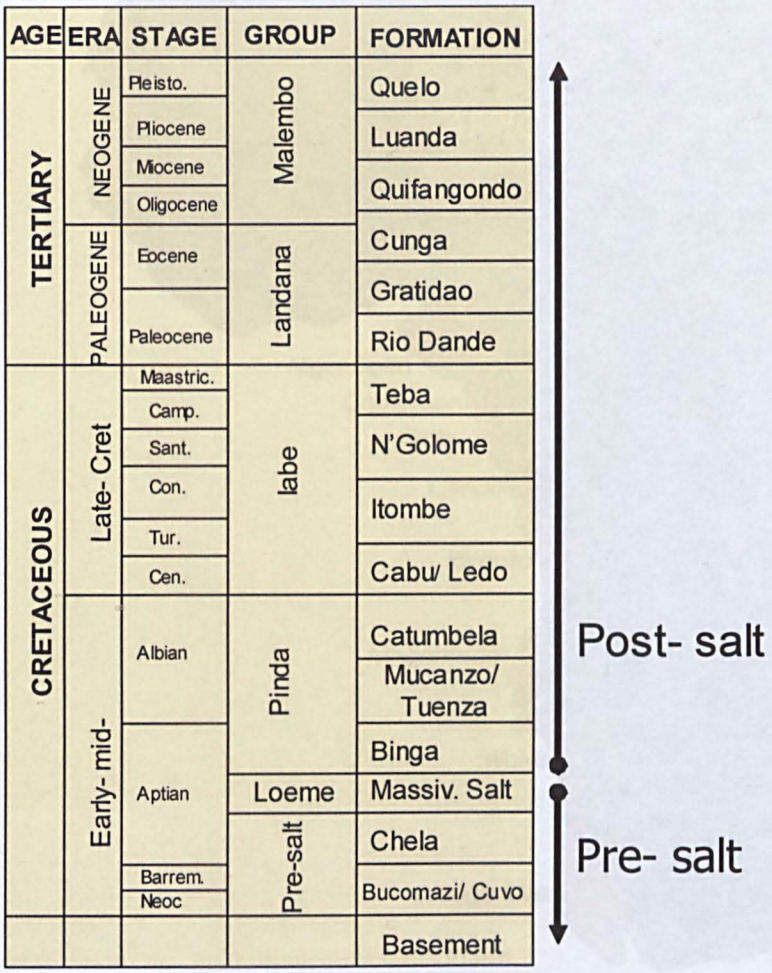

Fig. 12 Stratigraphy of the Lower Congo Basin (from Norsk Hydro internal report).

3.1.2 Location of study area

The West-African Atlantic margin from Cabinda to Mid-Angola consists of two major passive pull-apart basins: the Lower Congo and Kwanza Basins (Burwood, 1999). From an exploration perspective, the focus of this thesis is on the Lower Congo Basin although source rock and oil samples from the Kwanza Basin will also be included (Fig. 13).

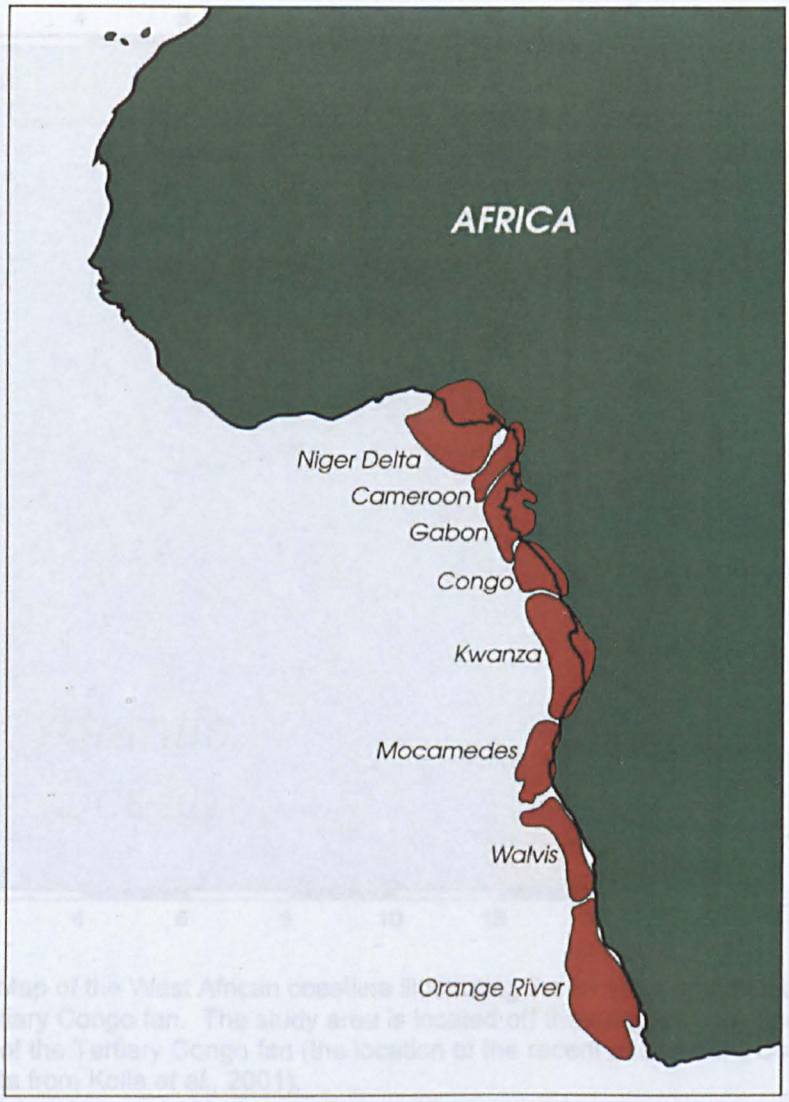

Fig. 13 Distribution of basins along the eastern South Atlantic margin (basins are shown in red; Katz & Mello, 2000).

A particular exploration focus of this study will be the oils and source rocks from block 17. This study area is located on the Tertiary Congo Fan in a transitional zone between an eastern extensional regime, containing rifts and grabens and a compressional regime to the west characterized by salt diapirs and compressional structures (Fig. 14; Sperrevik *et al.*, in press (a)). Several of the oils in this thesis (e.g. Dalia and Girassol fields) have their stratigraphic targets in the Malembo Fm. of the Lower Congo Basin Tertiary Congo Fan (Kolla *et al.*, 2001) source rock samples from Girassol-1 well are also included in this thesis.

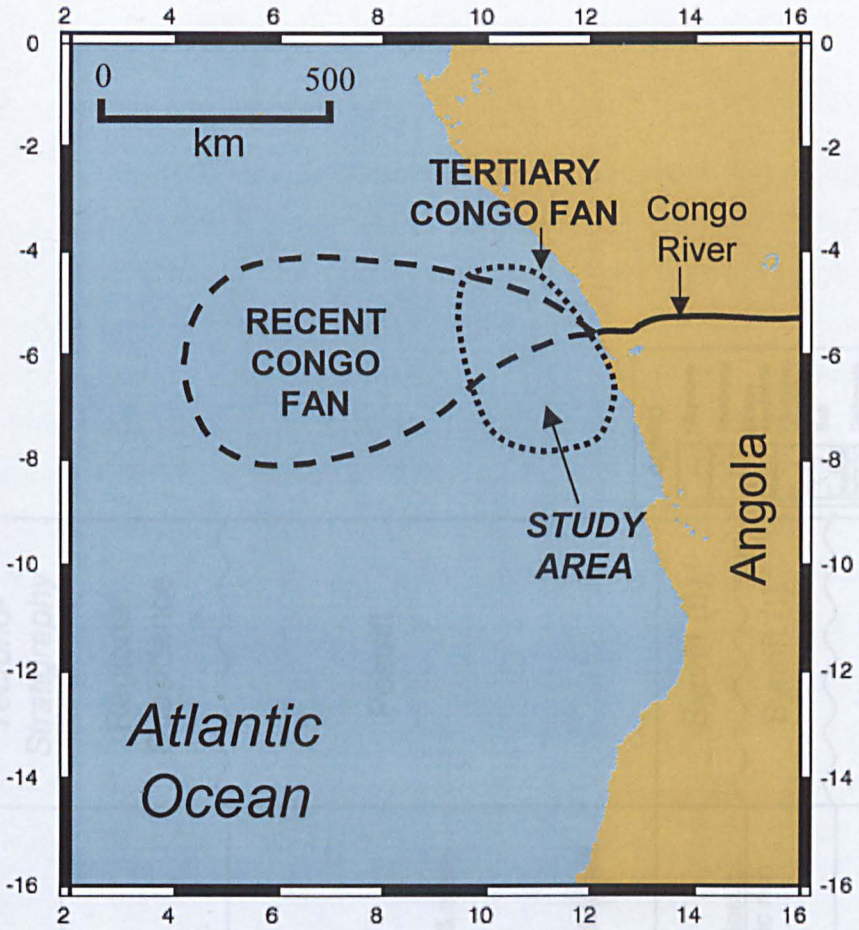

Fig. 14 Map of the West African coastline illustrating the location of the Quaternary (recent) and Tertiary Congo fan. The study area is located off the Angolan coastline on a small section of the Tertiary Congo fan (the location of the recent and ancient Congo Fan is taken from data from Kolla *et al.*, 2001).

3.1.3 Tectono-stratigraphy

Five tectonic regimes, which significantly influenced the stratigraphy of Angola during the separation of the South Atlantic, can be recognized (Fig. 15; Brice *et al.*, 1982). Each of the tectonic regimes listed below will be discussed in more detail in Section 3.1.3.2.

1. Prerift
2. Synrift (I)
3. Synrift (II)
4. Postrift
5. Regional subsidence.

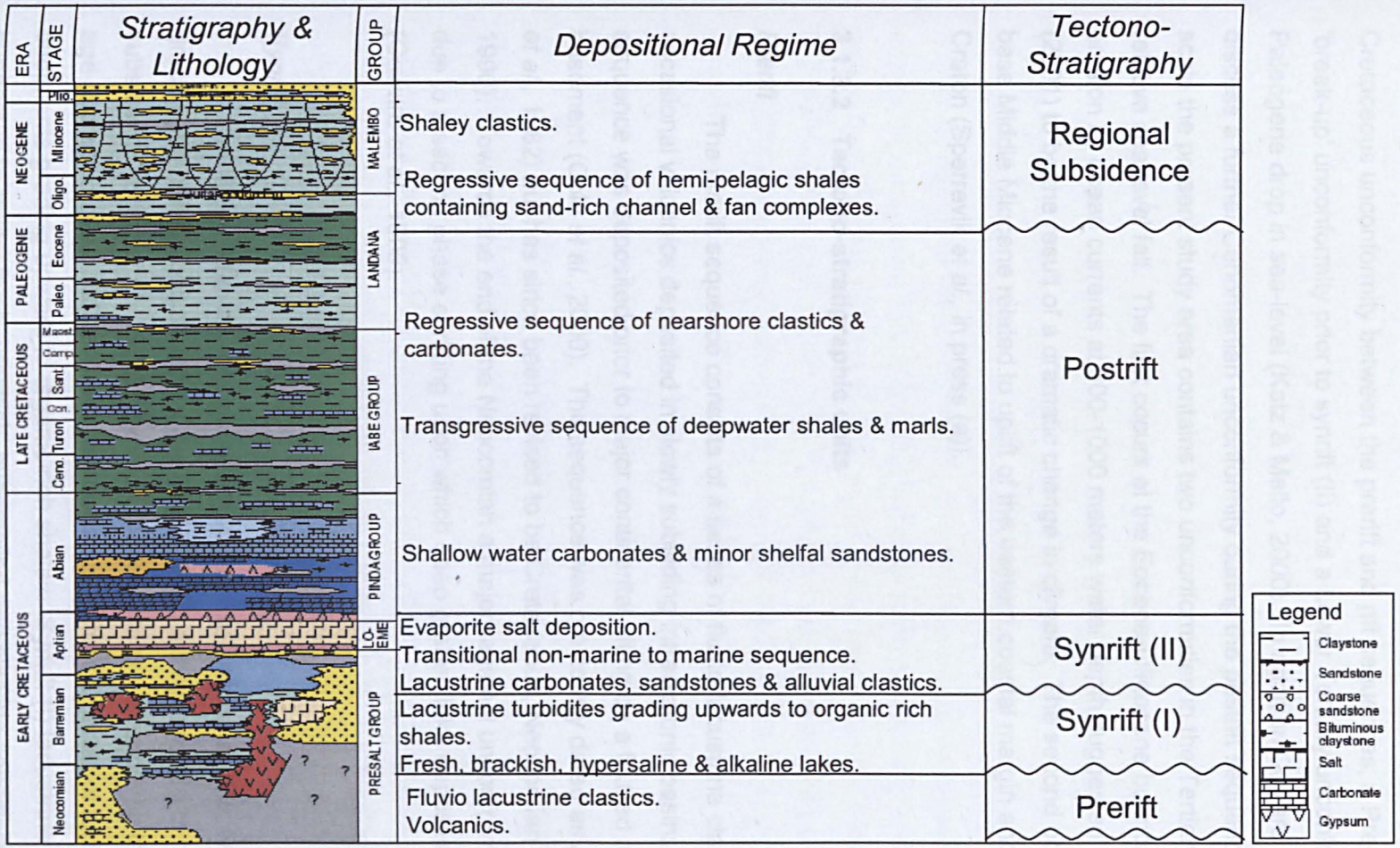

Fig. 15 Stratigraphy of the Lower Congo Basin showing the five tectono-stratigraphic units and their respective depositional environments (tectono-stratigraphic data from Brice *et al.,* 1982; stratigraphic section from Sperrevik *et al.,* in press (a)).

3.1.3.1 Unconformities

The five tectonic regimes are separated by four major regional unconformities with the exception of the synrift (II) and postrift sequences (Brice *et al.,* 1982). These include from oldest to youngest: an Upper Jurassic unconformity separating the Paleozoic section from the prerift Mesozoic sections; a Lower Cretaceous unconformity between the prerift and rift sequences; a Pre-Aptian or 'break-up' unconformity prior to synrift (II) and a Lower Tertiary unconformity due to a Paleogene drop in sea-level (Katz & Mello, 2000). In addition Coward *et al.* (1999) discuss a further Cenomanian unconformity during the postrift sequence. On a local scale the present study area contains two unconformities in the Tertiary related to a relative sea-level fall. The first occurs at the Eocene-Oligocene boundary, a result of erosion by ocean currents at 500-1000 meters water depth suggested by Lavier *et al.* (2001) to be the result of a dramatic change in climate. The second occurs at the base Middle Miocene related to uplift of the eastern coastal margin and the African Craton (Sperrevik *et al.,* in press (a)).

3.1.3.2 Tectono-stratigraphic units

Prerift

The prerift sequence consists of a series of fluvio-lacustrine clastics with occasional volcanics deposited in slowly subsiding intracratonic basins. The sequence was deposited prior to major continental rifting on a faulted metamorphic basement (Cole *et al.*, 2000). The sequence was previously dated as Jurassic (Brice *et al.,* 1982) but has since been revised to be Cretaceous, Neocomian (McHargue, 1990). Towards the end of the Neocomian a major regional unconformity developed due to a second phase of rifting upon which deep graben lake deposits formed (Coward *et al.,* 1999).

Synrift (I)

Synrift (I) sediments consist of organic-rich lacustrine shales, which infilled, graben and half-graben troughs (Cole *et al.,* 2000), during a phase of rapid subsidence (Brice *et al.,* 1982). Synrift (I) sediments are Neocomian to Barremian in age (Burwood *et al.,* 1992). The lakes began to infill by a series of lacustrine turbidite sediments grading upward to organic-rich shales. Synrift (I) lacustrine sediments are suggested to reflect fresh, brackish, hypersaline and alkaline conditions (Burwood *et*

al., 1990). Freshwater lakes were restricted geographically to the deepest basins, whereas saline lakes appear to be shallower and more aerially extensive and strongly influenced by intermittent marine transgressions introducing fresh nutrients leading to blooms of cyanobacteria (Katz & Mello, 2000). In the Lower Congo Basin this sequence of bituminous shales is termed the Bucomazi Formation and its geochemical properties are documented in great detail by Burwood *et al.* (1990, 1992, 1995) and Burwood (1999). The closure of the synrift (I) phase is marked by a major regional unconformity (Brice *et al.,* 1982).

Synrift (II)

The Synrift (II) sequence is Barremian to Aptian in age and began with a phase of major basement movement with re-activation of earlier faults followed by erosion of high-standing fault blocks and a period of westward subsidence (Brice *et al.,* 1982). The sediments are characterised by transitional sequences from non-marine to marine conditions consisting of lacustrine carbonates, sandstones and alluvial clastics (Cole *et al.,* 2000). Marine incursions were initially constrained to the sub-basins, however towards the end of the Aptian they extended over the majority of the area (Brice *et al.,* 1982). The first marine incursion occurred towards the end of Synrift II and by the Aptian marine incursions had formed a thick evaporite sequence, the Loeme salt (Brice *et al.,* 1982).

Postrift

Following the evaporite deposition of synrift (II) stage, permanent marine conditions and carbonate deposition characterised the postrift sediments (Cole *et al.,* 2000). Postrift sedimentation was dominated by a major marine transgression followed by a regression. Initially widespread carbonate sedimentation dominated during the Albian to Cenomanian consisting of shallow water to platform carbonate facies containing minor shelfal sandstones (Cole *et al.,* 2000). Due to the transgressive phase (a result of subsidence) sediments graded to deepwater shales and marls in the Campanian. This sequence involved deposition of a major Upper Cretaceous source rock interval in the Iabe Gp. The Iabe Gp. sediments represent outer shelf to slope facies with an upward increase in source quality as a result of the transgressive nature of the unit (Katz & Mello, 2000). Towards the end of the Campanian subsidence slowed down and the regressive phase followed which extended to the Paleogene depositing a sequence of near-shore marine clastics and

carbonates (the Landana Gp.; Brice *et al.*, 1982). The Post-salt source rock deposition is thought to be a result of either coastal upwelling (a process occurring at the present day on the West African coastline) or the result of an ocean anoxic event (OAE) whereby the oxygen minimum layer is extended (the Iabe Gp. encompassing a period during which ocean anoxic event source rocks were deposited; Cole *et al.*, 2000).

The structural style of the Post-salt sequence in the Lower Congo Basin is greatly influenced by salt tectonics, forming pillows, diapirs and rafts (Sperrevik *et al.*, In press (a)). In particularly, the structural style of the Congo Fan resulted from sediment loading, updip extension and downdip compression and related immobilisation of the salt (Kolla *et al.*, 2001).

Regional subsidence

At the end of the Paleogene the continent experienced strong westward tilting and regional subsidence (Brice *et al.*, 1982; Cole *et al.*, 2000). Large volumes of sediment were delivered to the Angolan margin during the Tertiary *via* the Congo River system, resulting in a basinward shift of the margin and the creation of the Tertiary Congo Fan (Fig. 14; Kolla *et al.*, 2001). This thick (Oligocene-Miocene) regressive sequence is unconformably deposited on the older shelf sequence (Cole *et al.*, 2000). Large sediment volumes were a result of the cumulative effects of uplift of the African craton, the westward tilting mentioned earlier plus sea-level changes and increased river runoff (Kolla *et al.*, 2001). The sequence is composed of hemipelagic shale successions containing sand-rich channel and fan complexes, the main transport mechanism for coarser grained sediments being turbidity currents (Sperrevik *et al.*, In press (b)). As mentioned in section 3.1.3.1 there are two unconformities in this zone at the Eocene-Oligocene boundary and the base Middle Miocene. From the Miocene to the present day there was a large increase in terrigenous clastic inputs causing the shelf to prograde across the Eocene ramp (Lavier *et al.*, 2000). The increase in sediment volume from the River Congo is suggested to be related to a period when large permanent ice sheets formed on Antarctica and is therefore linked to the associated global climate shift influencing the African tectonic and climatic zones across which the Congo River drained (Lavier *et al.*, 2001).

3.1.4 The South Atlantic conjugate margins (Brazil Analogy).

Traditionally the sedimentary basins along the Atlantic margins of South America and Africa were considered as independent basins; this was mainly a result of lack of common stratigraphic nomenclature and regional integration. A recent study by Coward *et al.* (1999) considers the basins of the South Atlantic as having one large-scale tectono-stratigraphy that can be recognised across all basins. the purpose being to study similarities across the South Atlantic and study differences between adjacent sectors on the same margin. Improved understanding and knowledge of the petroleum systems in operation has enabled consideration as a single region with a structural, stratigraphic and geochemical style upon which local characteristics can be overlain (Katz & Mello, 2000). The oils of the South Atlantic margin basins have been classified as containing a number of compositionally distinct oil families based on their geochemical properties reflecting source palaeoenvironment, age and source rock effectiveness e.g. lacustrine brackish to fresh water, lacustrine hypersaline, marine hypersaline and marine carbonate oils (Fig. 16; Schiefelbein *et al.,* 1999; Katz & Mello, 2000). From an exploration perspective, similarities between the margins can prove useful; for example, knowledge gained during exploration of the deep and ultra deep regions of Brazil can be applied to enable more effective exploration of the outer regions of the Angolan Basins (Katz & Mello, 2000). However, differences in individual basin development mean the distribution of oil fields across the two margins should not be considered simply as 'mirror images' (Katz & Mello, 2000). The nature of original rifting in the Southern Atlantic has given an asymmetric distribution where productive and non-productive sections alternate across the Atlantic related to alternating polarity of rifting (Szatmari, 2000). Work by Mello *et al.* (1988a, 1988b, 1989) on the geochemistry of the oils and source rocks of the Brazillian Marginal basins has proven a useful basis for later geochemical studies of the Angolan Basins such as Burwood *et al.* (1990, 1992, 1995) and Scheifelbein *et al.* (1999) and also for this thesis.

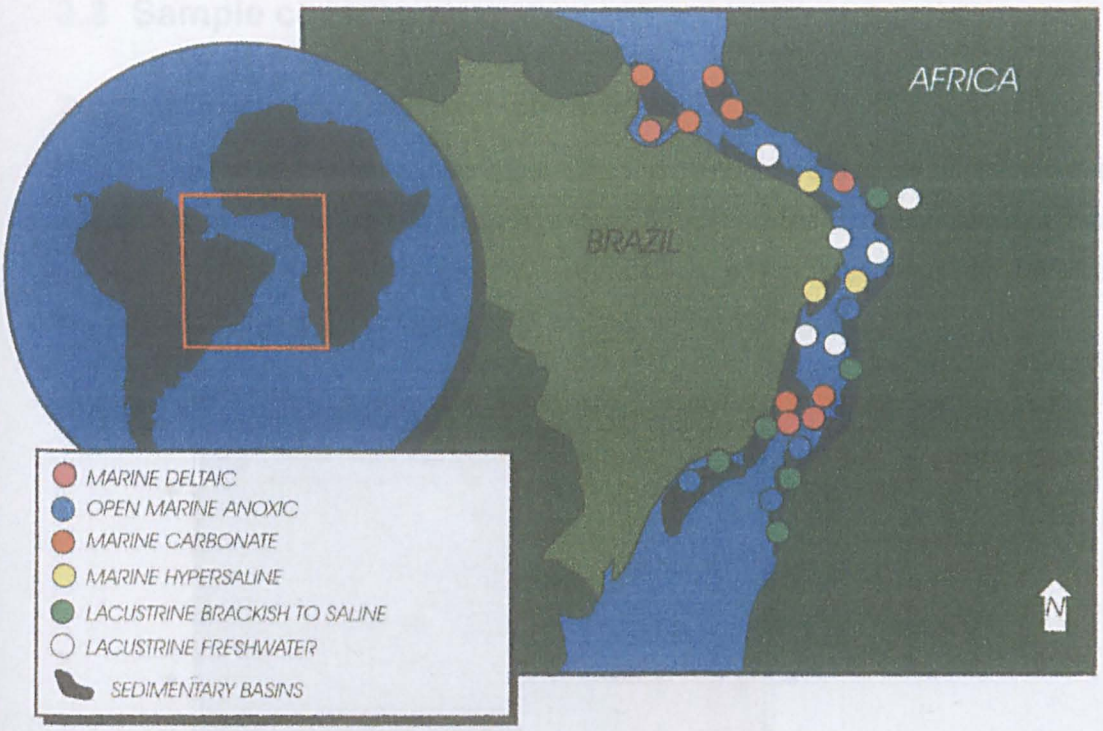

Fig.16 Oil types along the South Atlantic margins (Katz & Mello, 2000, p.5).

3.2 Sample coverage

3.2.1 Geographical sample coverage

The present study contains source rock samples from three offshore wells in blocks 4, 9 and 17 (4-26-1AT, Abacaxi-1and Girassol-1 respectively) and one well onshore of block 6 (Funda-3) (Fig. 17). In addition, oil samples were obtained from several additional wells covering both on and offshore Angola.

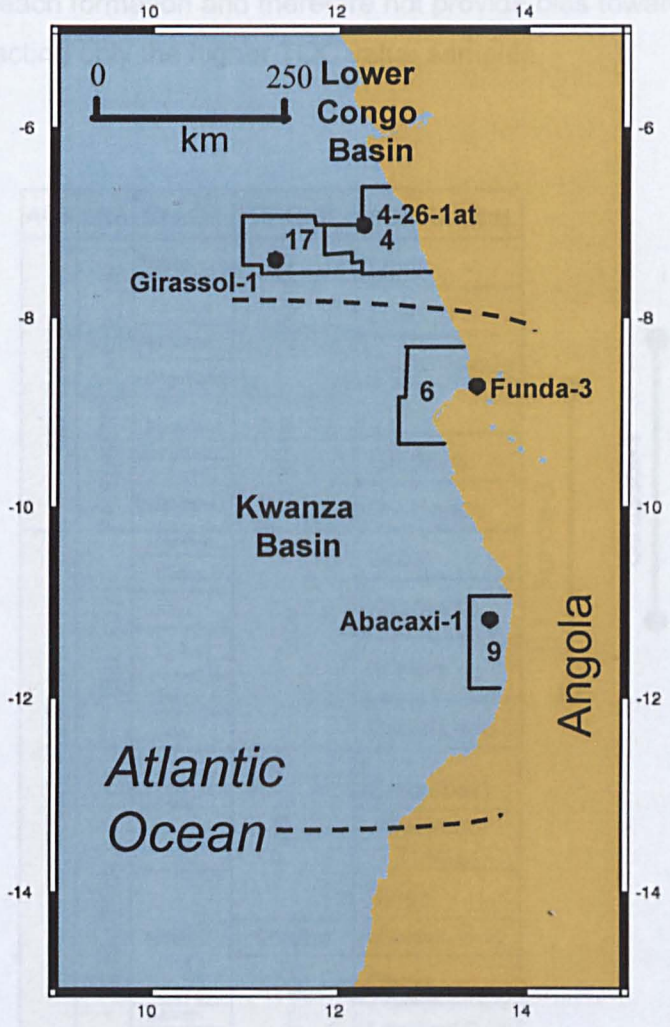

Fig. 17 Map of the Angolan margin illustrating the locations of the four wells from which source rock samples were studied.

3.2.2 Stratigraphic sample coverage

Between the 4 wells the majority of the Angolan Cretaceous/ Tertiary section will be covered although not every formation is represented in each well. The stratigraphic coverage of the 4 wells is illustrated in Fig. 18. The source rock samples are cuttings samples selected to include a range of both high and low TOC value samples, selected to include each stratigraphic formation. Samples of both high and low TOC values were included in an attempt to cover facies variations within each formation and therefore not provide bias towards 'black shale' samples by selecting only the higher TOC value samples.

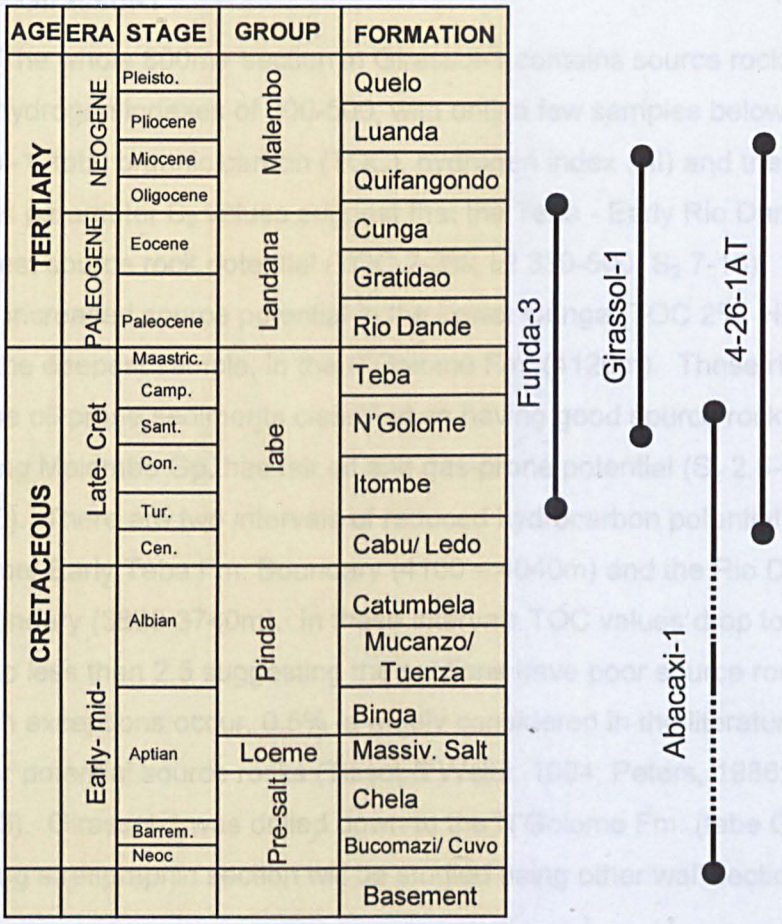

Fig. 18 Stratigraphy of the Lower Congo Basin to illustrate stratigraphic sample coverage (dashed lines indicate gaps in sample coverage).

3.3 Bulk Geochemical characterisation

Within this section the kerogen type of the source rocks from the 4 wells studied are classified. Also the hydrocarbon potential of the different kerogen types is defined as either fair, good or excellent is according to Bordenave *et al.,* (1993) using the TOC and S_2 values of the sediments. On the basis of this classification potential candidate source rocks for the Angolan oils will be determined.

3.3.1 Stratigraphic variability in organic richness and source rock quality by well.

3.3.1.1 Girassol-1

The whole 800m+ section in Girassol-1 contains source rock, up to 2.7%, typical hydrogen indexes of 300-500, with only a few samples below 1% TOC. In Girassol-1, total organic carbon (TOC), hydrogen index (HI) and the Rock Eval pyrolysis parameter S_2 values suggest that the Teba - Early Rio Dande section has the richest source rock potential (TOC 2-3%, HI 330-500, S_2 7-13). There is also a zone of increased source potential in the Lower Cunga (TOC 2%, HI 300-400, S_2 4-6) and the deepest sample, in the N'Golome Fm. (4120m). These rich intervals comprise oil-prone sediments classified as having good source rock potential. The remaining Malembo Gp. has fair oil and gas-prone potential (S_2 2.5-5, TOC 1-2%, HI 200-300). There are two intervals of reduced hydrocarbon potential around the N'Golome/ Early Teba Fm. Boundary (4100 – 4040m) and the Rio Dande - Gratidao Fm. boundary (3820-3740m). In these intervals TOC values drop to ca. 0.5% and S_2 values to less than 2.5 suggesting the sections have poor source rock potential. Although exceptions occur, 0.5% is widely considered in the literature as the cut-off value for potential source rocks (Tissot & Welte, 1984; Peters, 1986; Bordenave *et al.*, 1993). Girassol-1 was drilled down to the N'Golome Fm. (Iabe Gp.); the remaining stratigraphic section will be studied using other well sections.

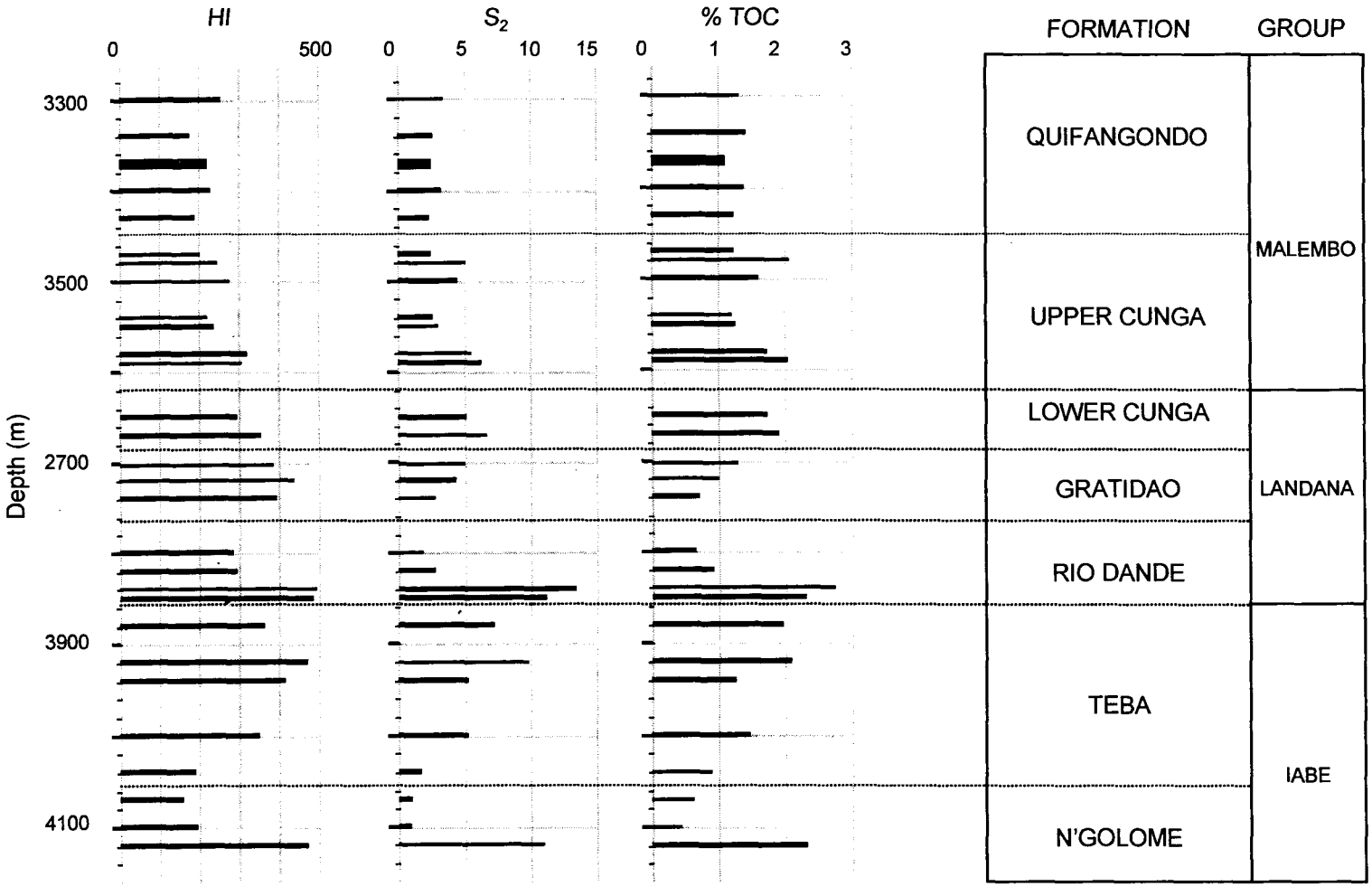

Fig. 19 Stratigraphic variation in source rock quality illustrated by hydrogen Index (HI in mg HC/g TOC), total organic carbon (TOC) and the Rock Eval Pyrolysis parameter S_2 (mg HC/ g rock) for Girassol-1 source rocks.

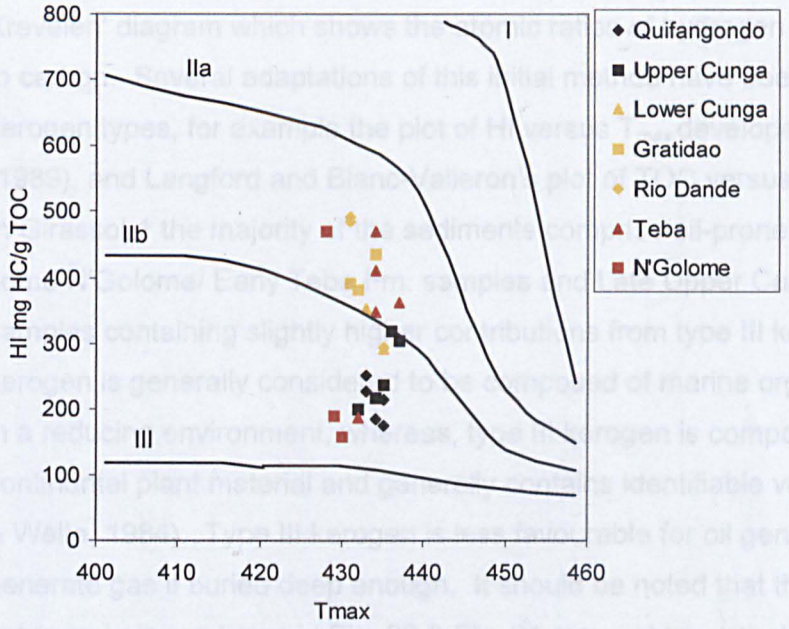

Fig. 20 Hydrogen Index and T_{max} data for Girassol-1 source rocks plotted on the diagram of Delvaux *et al.* (1989). The trend lines approximate to the following kerogen types: I = lacustrine, IIa = marine, IIb = mixed, III = terrestrial.

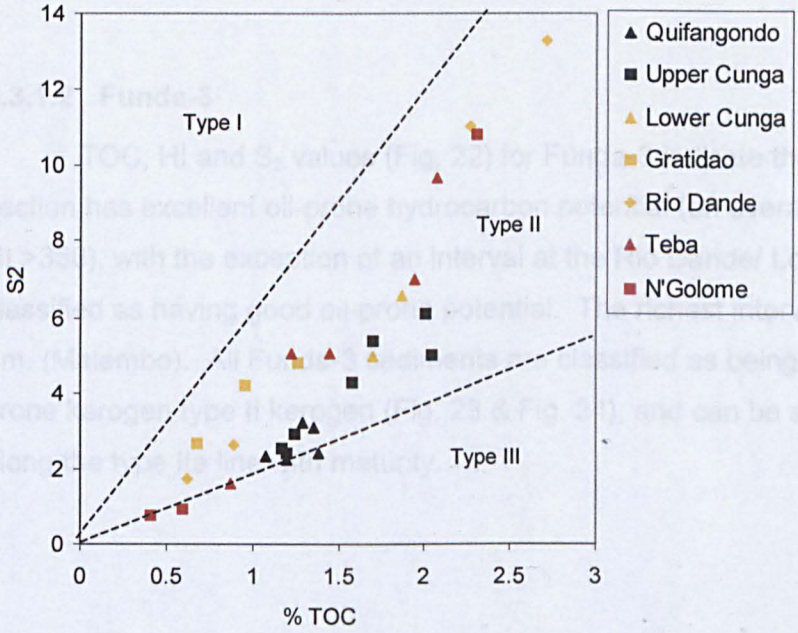

Fig. 21 Total Organic Carbon and Rock Eval pyrolysis parameter S_2 data for Girassol-1 source rocks plotted on the diagram of Langford and Blanc-Valleron (1990). The lines represent a transition between kerogen types, they do not define exact kerogen types (i.e. the line representing type II kerogen would lie half way between the I-II and II-III transition lines).

Kerogen types were first introduced by Tissot *et al.* (1974) on a 'Van Krevelen' diagram which shows the atomic ratios of hydrogen to carbon and oxygen to carbon. Several adaptations of this initial method have been developed to define kerogen types, for example the plot of HI versus T_{max} developed by Delvaux *et al.* (1989), and Langford and Blanc-Valleron's plot of TOC versus S_2 (Fig. 20 & Fig. 21). In Girassol-1 the majority of the sediments comprise oil-prone type II kerogen, with some N'Golome/ Early Teba Fm. samples and Late Upper Cunga/ Quifangondo Fm. samples containing slightly higher contributions from type III kerogen. Type II kerogen is generally considered to be composed of marine organic matter deposited in a reducing environment, whereas, type III kerogen is composed predominantly of continental plant material and generally contains identifiable vegetable debris (Tissot & Welte, 1984). Type III kerogen is less favourable for oil generation but can generate gas if buried deep enough. It should be noted that the differentiation between kerogen types in Fig. 20 & Fig. 21 may not be entirely a result of varying organic matter inputs but a result of varying preservation of marine and amorphous organic matter. To help determine whether organic matter preservation has affected the results microscopic analysis of the kerogen could be conducted.

3.3.1.2 Funda-3

TOC, HI and S_2 values (Fig. 22) for Funda-3 indicate that the entire >1200m section has excellent oil-prone hydrocarbon potential (on average S_2 >12, TOC >3%, HI >350), with the exception of an interval at the Rio Dande/ Lower Cunga boundary classified as having good oil-prone potential. The richest interval is the Upper Cunga Fm. (Malembo). All Funda-3 sediments are classified as being comprised of oil-prone kerogen type II kerogen (Fig. 23 & Fig. 24), and can be seen in Fig. 23 to fall along the type IIa line with maturity.

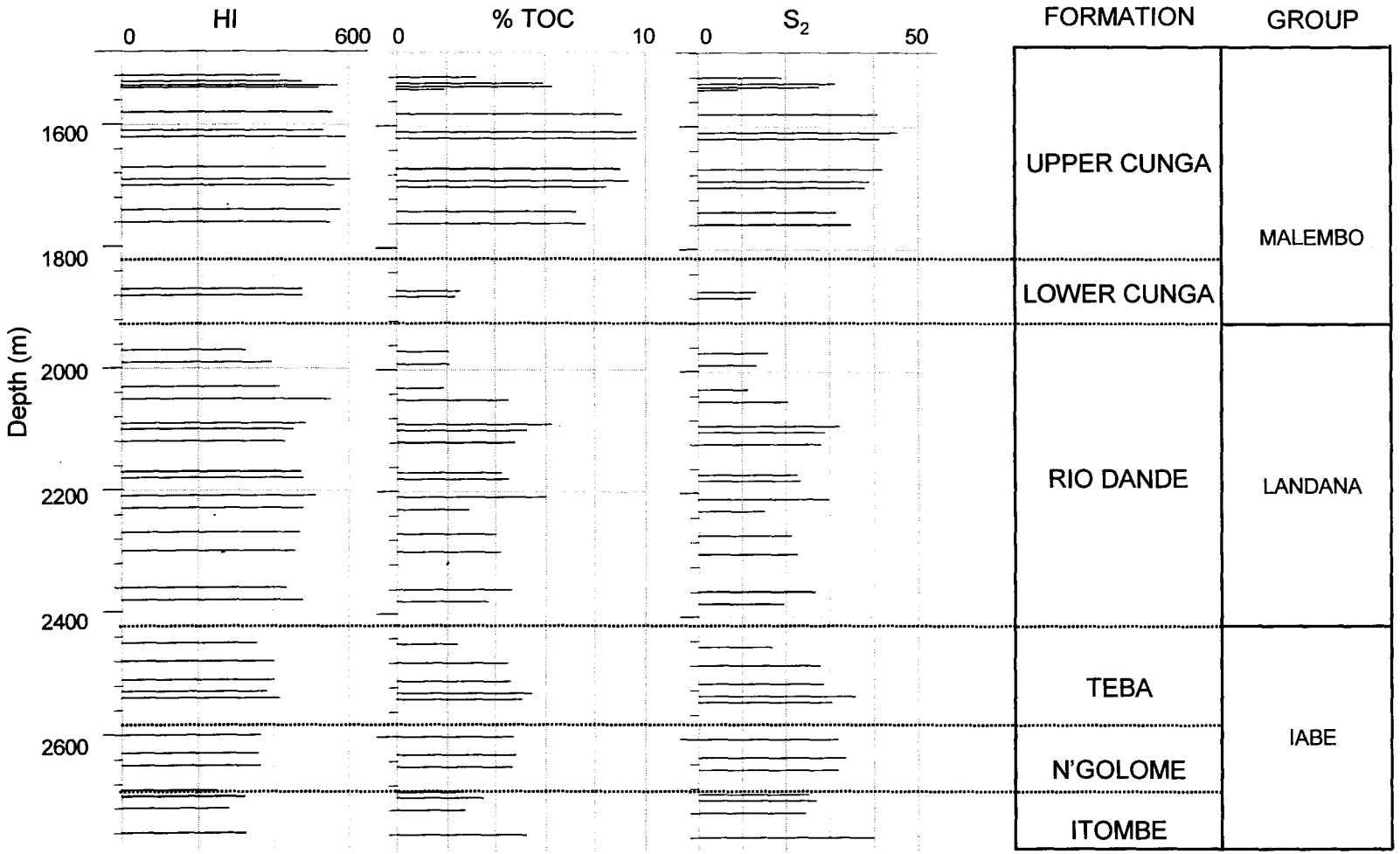

Fig. 22 Stratigraphic variation in source rock quality illustrated by hydrogen Index (HI in mg HC/g TOC), total organic carbon (TOC) and the Rock Eval Pyrolysis parameter S_2 (mg HC/g rock) for Funda-3 source rocks.

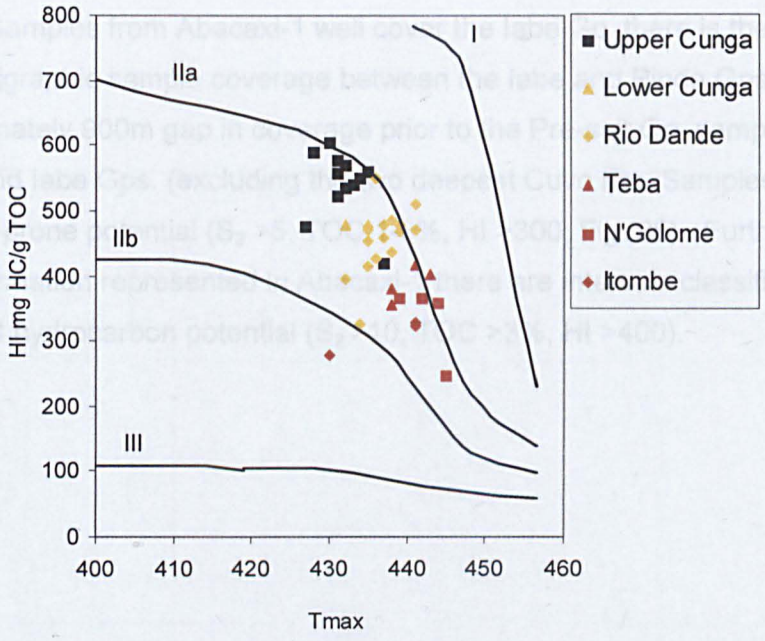

Fig. 23 Hydrogen Index and T_{max} data for Funda-3 source rocks plotted on the diagram of Delvaux *et al.* (1989). The trend lines approximate to the following kerogen types: I = lacustrine, IIa = marine, IIb = mixed, III = terrestrial.

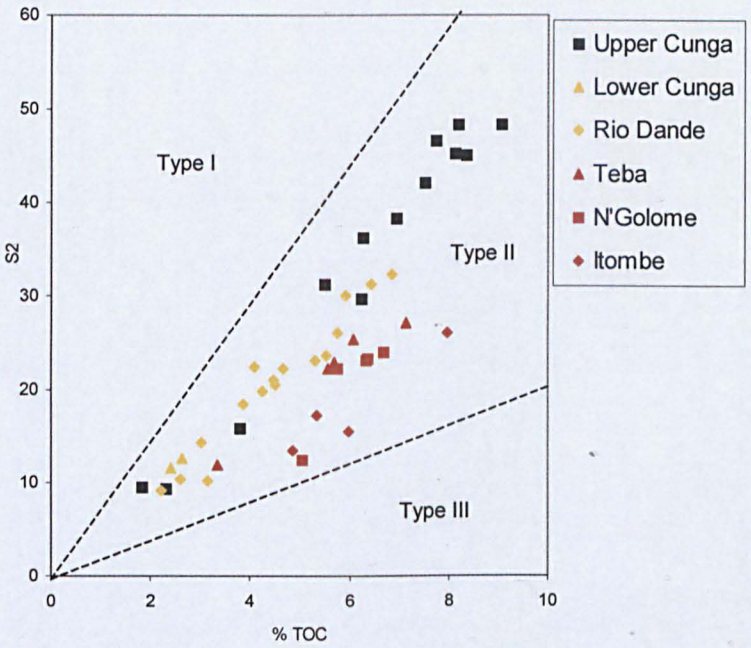

Fig. 24 Total Organic Carbon and Rock Eval pyrolysis parameter S_2 data for Funda-3 source rocks plotted on the diagram of Langford and Blanc-Valleron (1990). The lines represent a transition between kerogen types, they do not define exact kerogen types, and i.e. the line representing type II kerogen would lie half way between the I-II and II-III transition lines.

3.3.1.3 Abacaxi-1

Samples from Abacaxi-1 well cover the Iabe Gp. there is then a short gap in the stratigraphic sample coverage between the Iabe and Pinda Gps. followed by an approximately 900m gap in coverage prior to the Pre-salt Gp. samples. The Pre-salt, Pinda and Iabe Gps. (excluding the two deepest Cuvo Fm. Samples) have fair to good oil-prone potential (S_2 >5, TOC 1-3%, HI >300; Fig. 25). Furthermore within every formation represented in Abacaxi-1 there are intervals classified as having excellent hydrocarbon potential (S_2 >10, TOC >3%, HI >400).

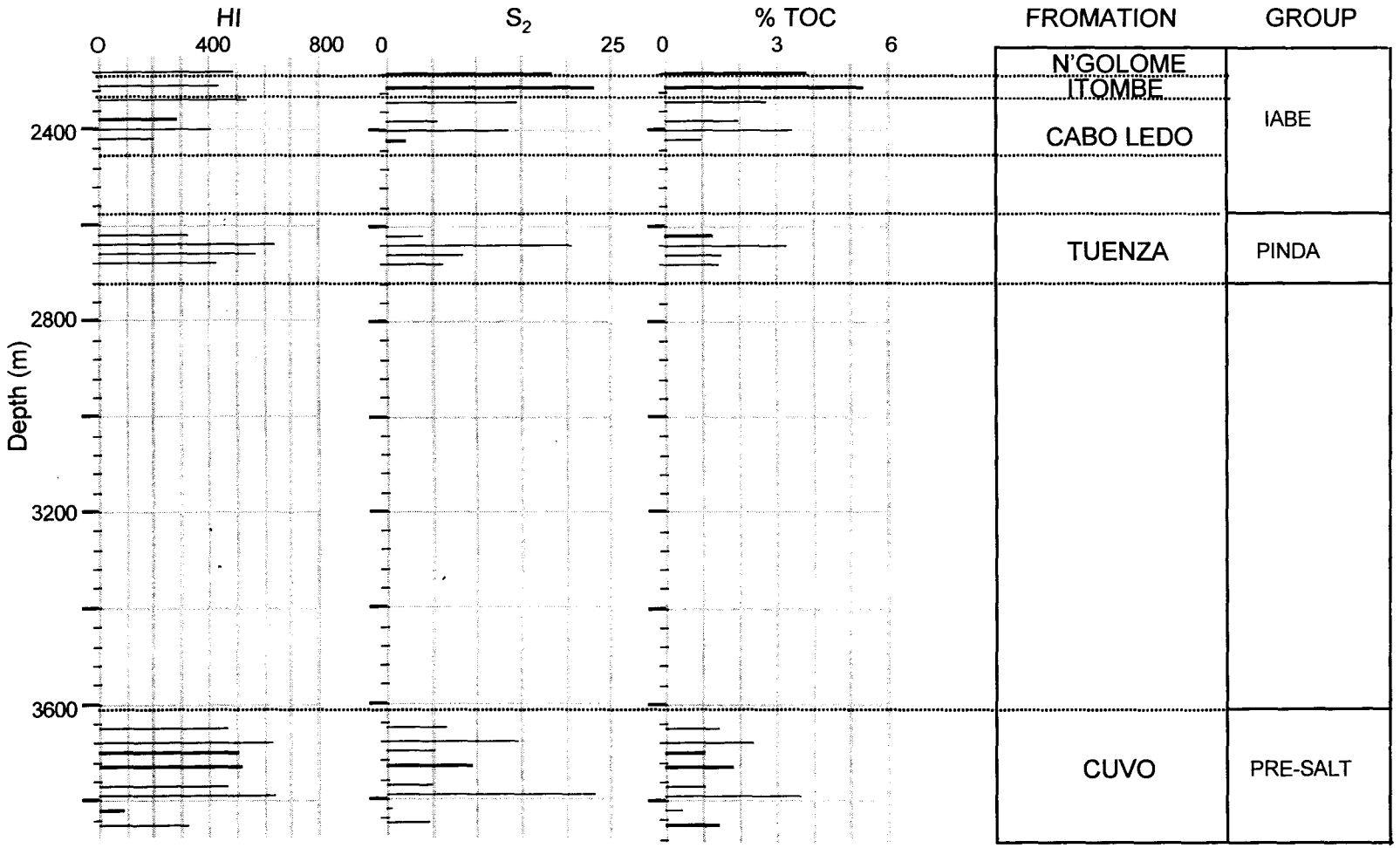

Fig. 25 Stratigraphic variation in source rock quality illustrated by hydrogen Index (HI in mg HC/g TOC), total organic carbon (TOC) and the Rock Eval Pyrolysis parameter S_2 (mg HC/g rock) for Abacaxi-1 source rocks.

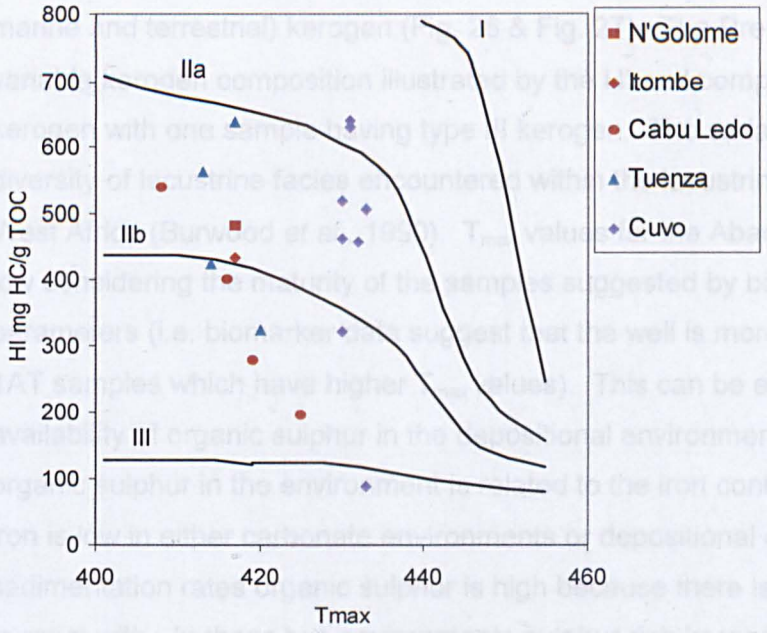

Fig. 26 Hydrogen Index and T_{max} data for Abacaxi-1 source rocks plotted on the diagram of Delvaux *et al.* (1989). The trend lines approximate to the following kerogen types: I = lacustrine, IIa = marine, IIb = mixed, III = terrestrial.

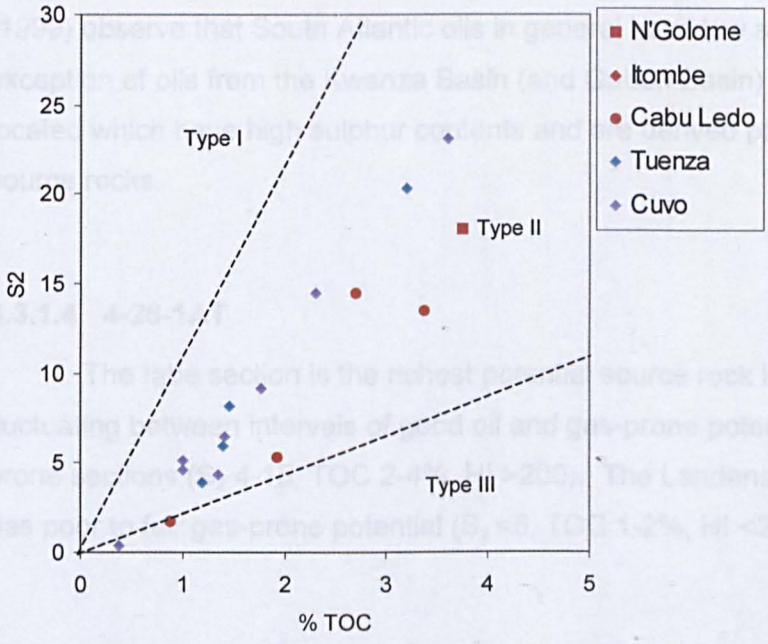

Fig. 27 Total Organic Carbon and Rock Eval pyrolysis parameter S_2 data for Abacaxi-1 source rocks plotted on the diagram of Langford and Blanc-Valleron (1990). The lines represent a transition between kerogen types, they do not define exact kerogen types, i.e. the line representing type II kerogen would lie half way between the I-II and II-III transition lines.

The Post-salt section comprises marine type IIa and b (marine to mixed marine and terrestrial) kerogen (Fig. 26 & Fig. 27). The Pre-salt Cuvo Fm. has variable kerogen composition illustrated by the HI and comprises type IIa and b kerogen with one sample having type III kerogen. The variability may be due to the diversity of lacustrine facies encountered within the lacustrine source rock sections in West Africa (Burwood *et al.,* 1990). T_{max} values for the Abacaxi-1 source rocks are low considering the maturity of the samples suggested by biomarker maturity parameters (i.e. biomarker data suggest that the well is more mature than the 4-26-1AT samples which have higher T_{max} values). This can be explained by the availability of organic sulphur in the depositional environment. The amount of organic sulphur in the environment is related to the iron content of sediments; where iron is low in either carbonate environments or depositional environments with low sedimentation rates organic sulphur is high because there is less free iron for sulphur to react with. In these two environments sulphur-rich kerogens may form which contain abundant sulphur bonds. Sulphur bonds are weaker than other bond types, and therefore break at lower thermal maturites, hence, generating at lower Tmax values (Tyson, R.V., pers comm.). To support this interpretation Scheifelbein *et al.* (1999) observe that South Atlantic oils in general have low sulphur contents with the exception of oils from the Kwanza Basin (and Gabon Basin) in which Abacaxi-1 is located which have high sulphur contents and are derived predominantly from marine source rocks.

3.3.1.4 4-26-1AT

The Iabe section is the richest potential source rock interval in 4-26-1AT fluctuating between intervals of good oil and gas-prone potential to excellent oil-prone sections (S_2 4-15, TOC 2-4%, HI >200). The Landana and Malembo section has poor to fair gas-prone potential (S_2 <5, TOC 1-2%, HI <200; Fig. 28).

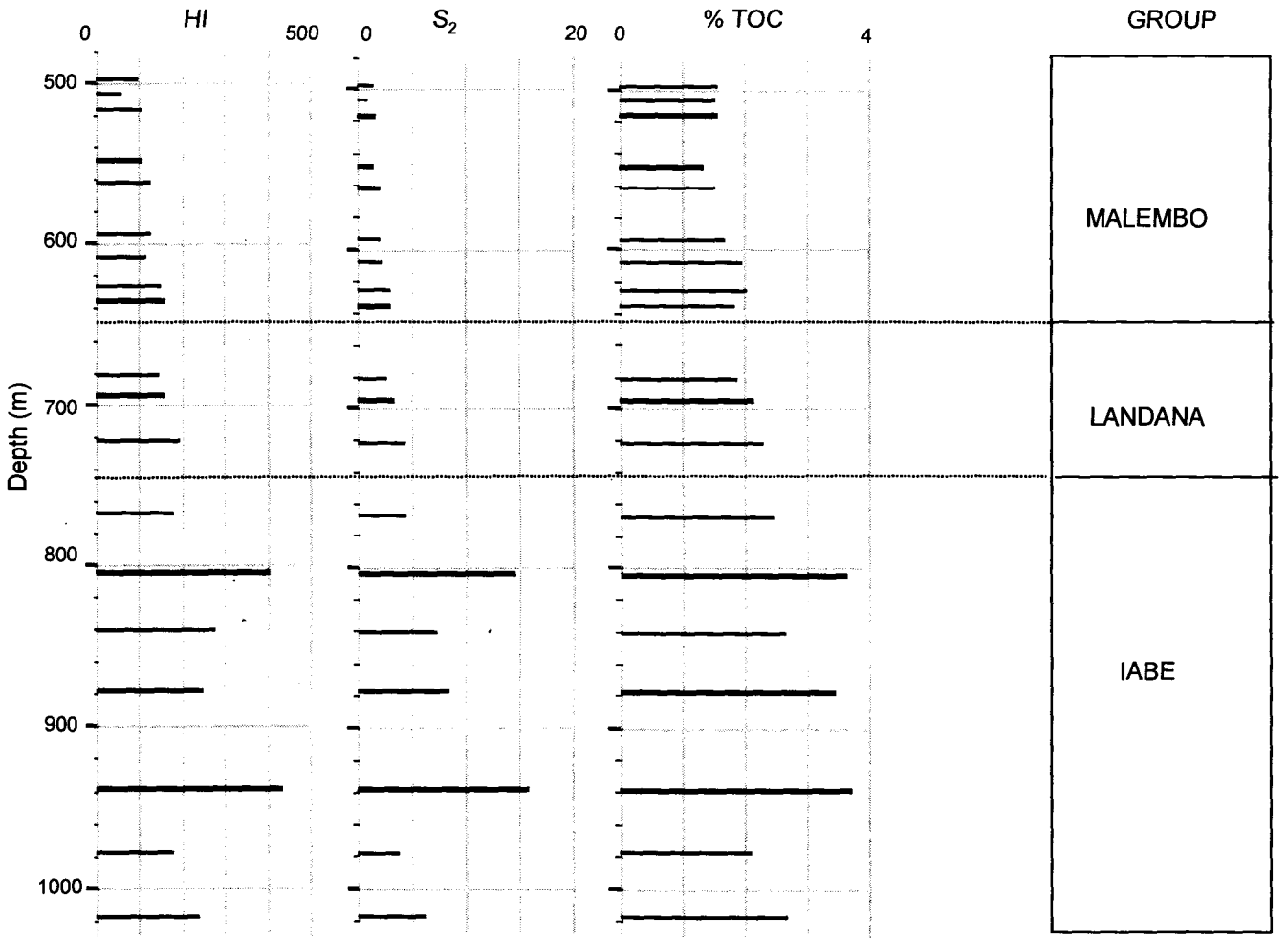

Fig. 28 Stratigraphic variation in source rock quality illustrated by hydrogen Index (HI in mg HC/g TOC), total organic carbon (TOC) and the Rock Eval Pyrolysis parameter S_2 (mg HC/g rock) for 4-26-1AT source rocks (only source rock group data are available for 4-26-1AT).

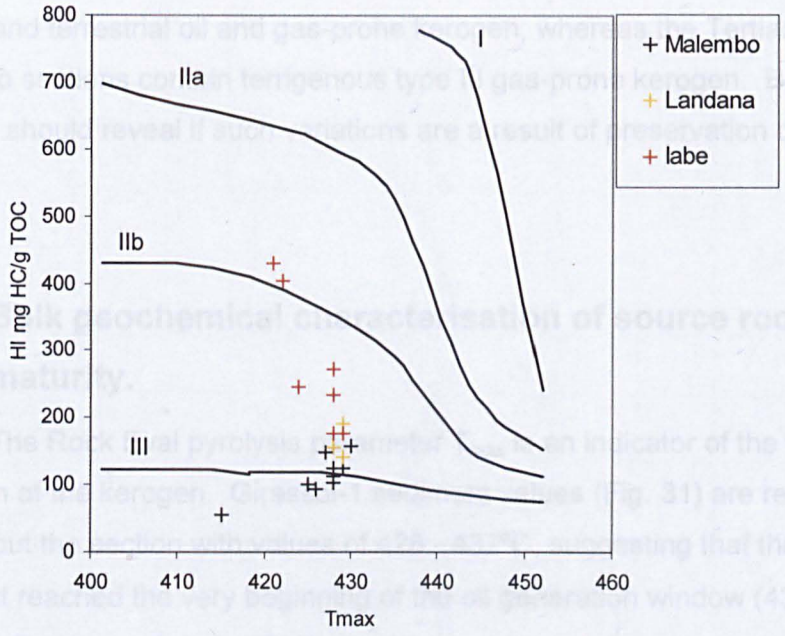

Fig. 29 Hydrogen Index and Tmax data for 4-26-1AT source rocks plotted on the diagram of Delvaux *et al.* (1989). The trend lines approximate to the following kerogen types: I = lacustrine, IIa = marine, IIb = mixed, III = terrestrial.

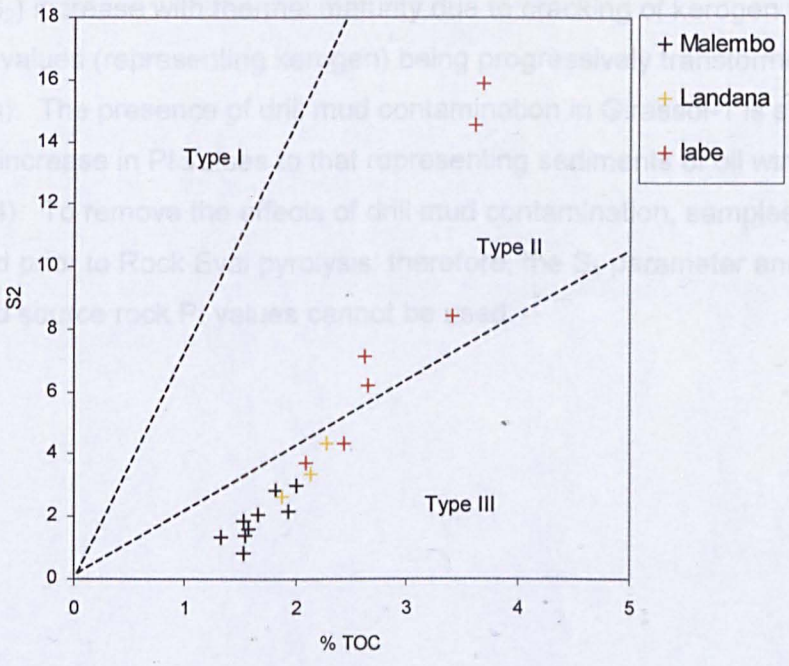

Fig. 30 Total Organic Carbon and Rock Eval pyrolysis parameter S_2 data for 4-26-1AT source rocks plotted on the diagram of Langford and Blanc-Valleron (1990). The lines represent a transition between kerogen types, they do not define exact kerogen types, i.e. the line representing type II kerogen would lie half way between the I-II and II-III transition lines.

Fig. 29 and Fig. 30 illustrate that the labe section comprises type IIb mixed marine and terrestrial oil and gas-prone kerogen, whereas the Tertiary Landana and Malembo sections contain terrigenous type III gas-prone kerogen. Biomarker analysis should reveal if such variations are a result of preservation or organic source inputs.

3.3.2 Bulk geochemical characterisation of source rock thermal maturity.

The Rock Eval pyrolysis parameter T_{max} is an indicator of the thermal evolution of the kerogen. Girassol-1 sediment values (Fig. 31) are relatively constant throughout the section with values of 428 - 437°C, suggesting that the source rocks have just reached the very beginning of the oil generation window (435°C for type II kerogen; Bordenave *et al.*, 1993).

Typical production index (PI) values for samples just prior to the oil window such as in Girassol-1 would be less than or equal to 0.1. Source rock PI values (S_1/S_1+S_2) increase with thermal maturity due to cracking of kerogen which results in S_2 peak values (representing kerogen) being progressively transformed into S_1 (bitumen). The presence of drill mud contamination in Girassol-1 is shown by the artificial increase in PI values to that representing sediments of oil window maturity (0.1 - 0.4). To remove the effects of drill mud contamination, samples were solvent extracted prior to Rock Eval pyrolysis; therefore, the S_1 parameter and hence the extracted source rock PI values cannot be used.

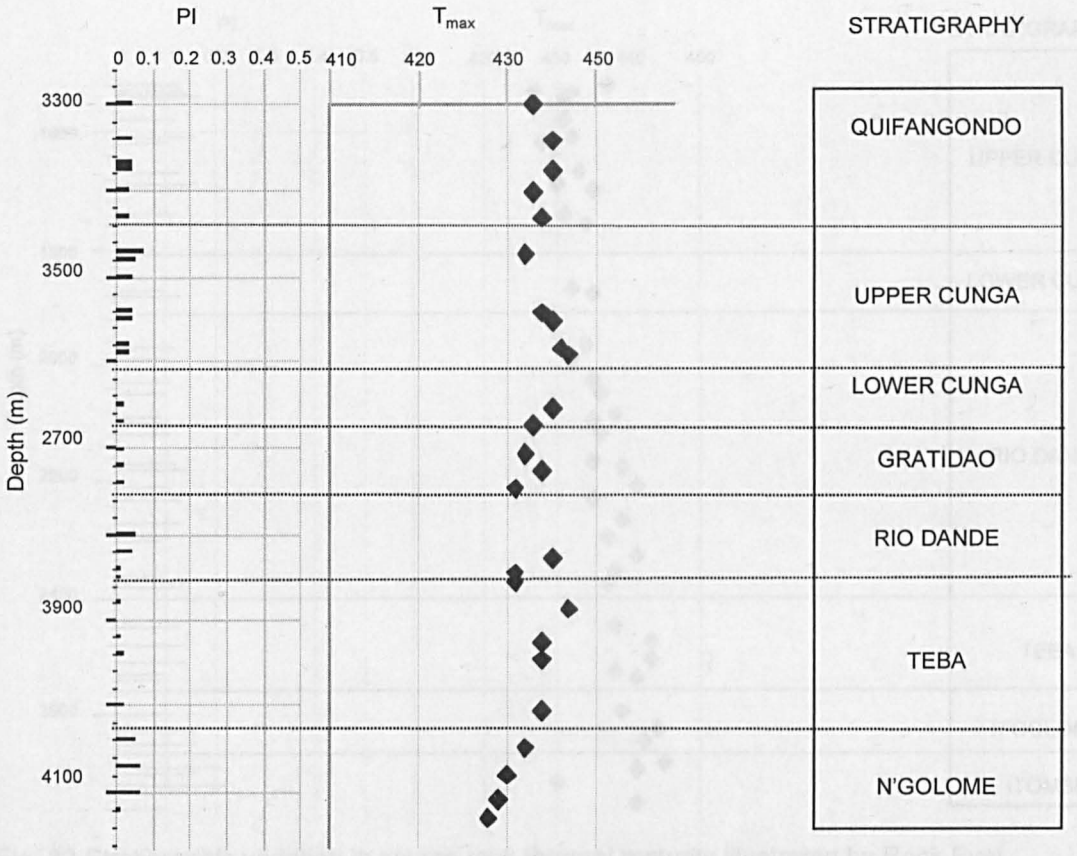

Fig. 31 Stratigraphic variation in source rock thermal maturity illustrated by Rock Eval pyrolysis parameter Tmax (°C) and production index (PI) for Girassol-1 source rocks.

T_{max} values for Funda-3 source rocks (Fig. 32) show a gradual increase with depth as a result of increasing thermal maturity during burial. The source rocks have reached earliest oil window maturity within the Rio Dande Fm. (~2050m). Production index values for the Funda-3 section lie between 0.1 and 0.2, typical of early mature sediments (Miles, 1994).

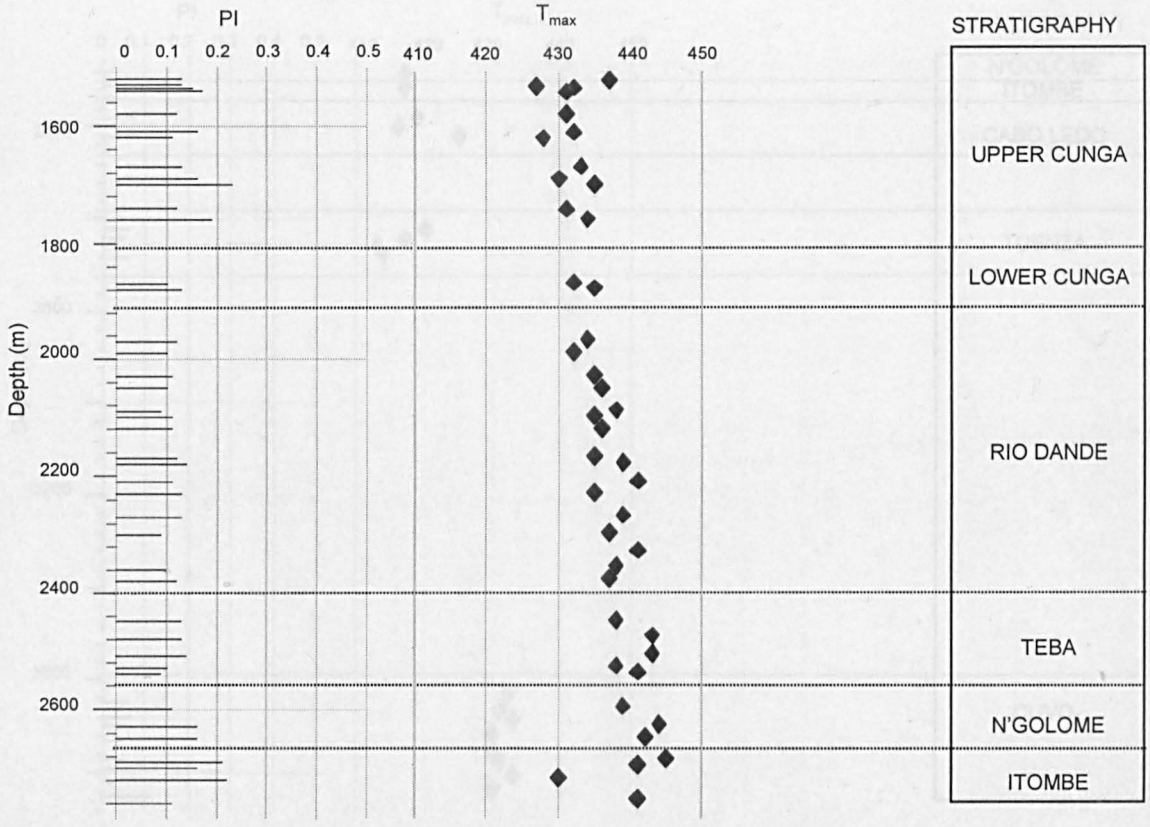

Fig. 32 Stratigraphic variation in source rock thermal maturity illustrated by Rock Eval pyrolysis parameter T_{max} (°C) and production index (PI) for Funda-3 source rocks.

Source rock PI and T_{max} values for Abacaxi-1 suggest that the entire Pre-salt and Post-salt section is immature (Fig. 33) (i.e. P I <0.1, Tmax <435°C). This interpretation contrasts with biomarker data for the Pre-salt section which suggests the section has oil window maturity (see Section 4.1.2).

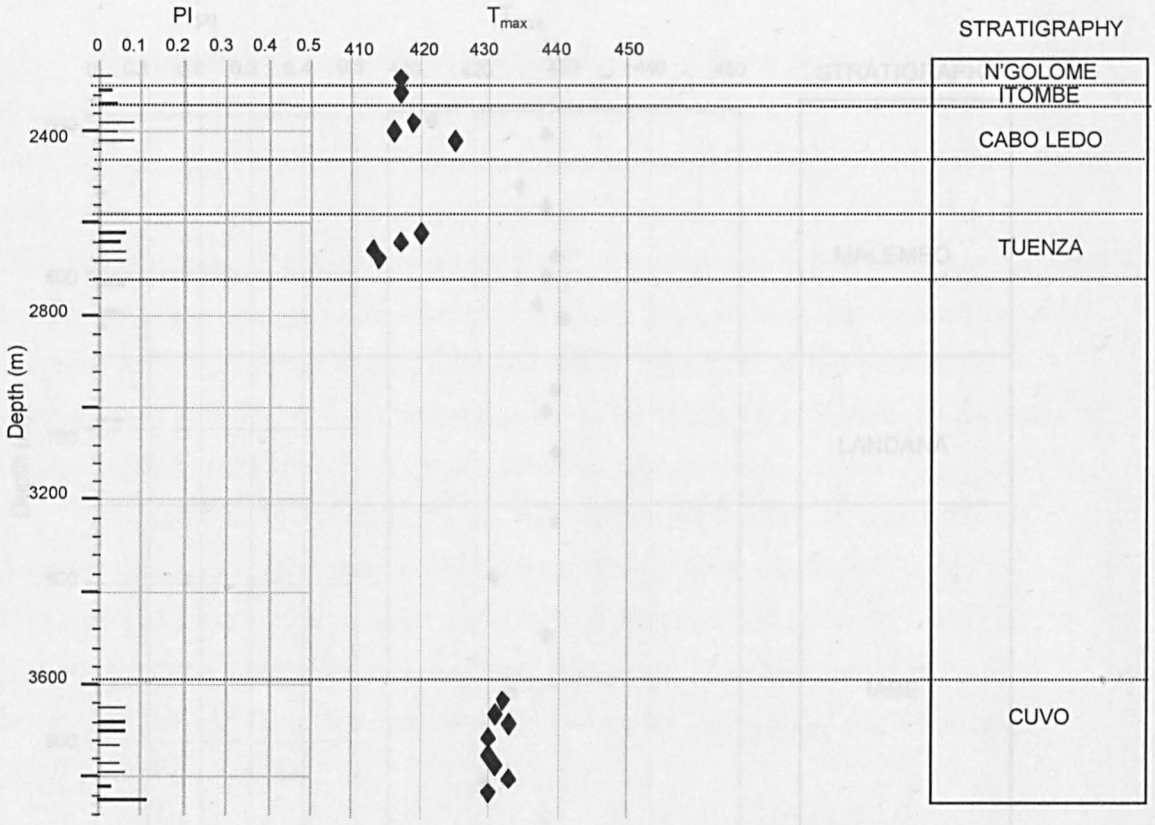

Fig. 33 Stratigraphic variation in source rock thermal maturity illustrated by Rock Eval pyrolysis parameter T_{max} (°C) and production index (PI) for Abacaxi-1 source rocks.

Well 4-26-1AT T_{max} values (<435°C) and PI values (<0.1) suggest the sediments are immature (Fig. 34).

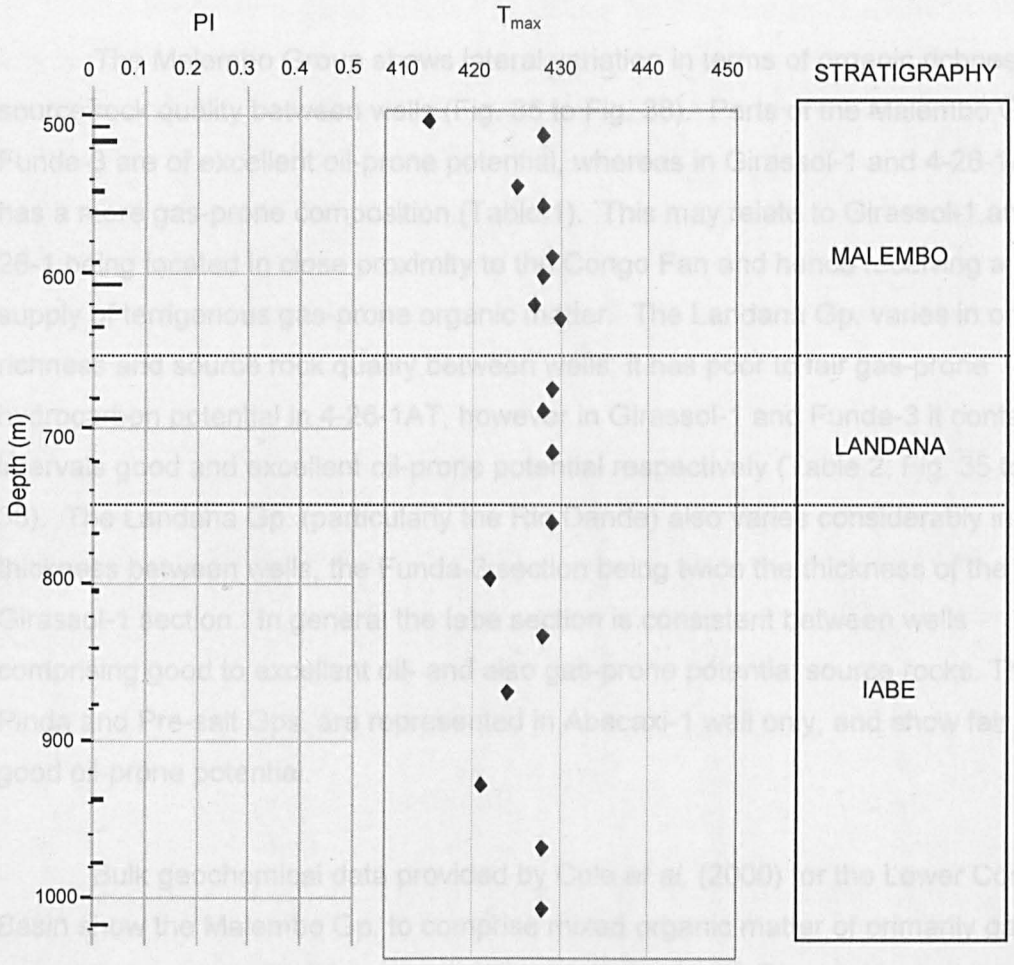

Fig. 34 Stratigraphic variation in source rock thermal maturity illustrated by Rock Eval pyrolysis parameter T_{max} (°C) and production index (PI) for 4-26-1AT source rocks (source rock group data only available for 426-1AT).

3.3.3 Overview

3.3.3.1 Comparison of source rock organic richness and quality by stratigraphy.

This section aims to summarise the overall characteristics of the five stratigraphic groups and to make comparison of the groups between wells in order to identify lateral variations in character. Comparisons for the Pinda and Pre-salt Groups cannot be made between wells due to their occurrence in only Abacaxi-1. A summary of the range of TOC and HI values used in this chapter to interpret the organic richness and quality of the different stratigraphic groups are shown in Table 2 and have been grouped by well. The table clearly shows Funda-3 well is the richest well analysed.

The Malembo Group shows lateral variation in terms of organic richness and source rock quality between wells (Fig. 35 to Fig. 38). Parts of the Malembo Gp. in Funda-3 are of excellent oil-prone potential, whereas in Girassol-1 and 4-26-1AT it has a more gas-prone composition (Table 1). This may relate to Girassol-1 and 4-26-1 being located in close proximity to the Congo Fan and hence receiving a greater supply of terrigenous gas-prone organic matter. The Landana Gp. varies in organic richness and source rock quality between wells; it has poor to fair gas-prone hydrocarbon potential in 4-26-1AT, however in Girassol-1 and Funda-3 it contains intervals good and excellent oil-prone potential respectively (Table 2; Fig. 35 to Fig. 38). The Landana Gp. (particularly the Rio Dande) also varies considerably in thickness between wells, the Funda-3 section being twice the thickness of the Girassol-1 section. In general the Iabe section is consistent between wells comprising good to excellent oil- and also gas-prone potential source rocks. The Pinda and Pre-salt Gps. are represented in Abacaxi-1 well only, and show fair to good oil-prone potential.

Bulk geochemical data provided by Cole *et al.* (2000) for the Lower Congo Basin show the Malembo Gp. to comprise mixed organic matter of primarily gas-prone composition with TOC values of approximately 1%. The Landana Gp. is reported to have oil-prone hydrocarbon potential with TOC values of about 4%, whereas the Iabe Gp. is reported to have excellent oil-prone potential with intervals with TOC values in excess of 10%. Of the wells in this thesis Girassol-1 and 4-26-1 are from the Lower Congo Basin. In general the TOC values for the Malembo Gp. are similar to those given by Cole *et al.,* (2000) however the Landana and Iabe Gps. have lower TOC values than those in the literature. This suggests lateral variations within the Lower Congo Basin have given rise to richer intervals than those studied herein.

Values for the Lower Congo Basin Pre-salt section by Cole *et al* (2000) are highly variable with TOC values of less than 1% and up to 10%, however, this thesis does not contain any Pre-salt samples from the Lower Congo Basin. The Pre-salt samples in this thesis are from the Kwanza Basin penetrated in Abacaxi-1. Burwood (1999) studied the Pre-salt Cuvo Fm. and found TOC values to be about 2.5% and HI values of 292. The Cuvo Fm. Samples in this thesis are therefore slightly richer than the samples studied by Burwood (1999).

An important point to note is T_{max} values for the Abacaxi-1 source rocks are low considering the maturity of the samples (i.e. as suggested by biomarker maturity parameters). This may be related to high organic sulphur in the depositional environment and hence the formation of sulphur-rich kerogens, containing abundant weak sulphur bonds. The sulphur bonds would break at lower thermal maturites, hence, generating at lower T_{max} values. In general Angolan oils are low in sulphur with the exception some oils from the Kwanza Basin in which Abacaxi-1 is located, where high sulphur oils can be found (Scheifelbein *et al.*, 1999).

Group	Well	Total Organic Carbon	Hydrogen Index*
Malembo	4-26-1AT	1.3-2.0	60-160
	Girassol-1	1.2-2.0	180-320
	Funda-3	1.8-9.1	400-600
Landana	4-26-1AT	1.9-2.3	140-190
	Girassol-1	0.7-2.7	290-490
	Funda-3	2.3-6.9	330-550
Iabe	4-26-1AT	2.1-3.7	180-430
	Girassol-1	0.4-2.0	160-490
	Funda-3	3.4-8.0	250-420
	Abacaxi-1	0.9-5.3	200-490
Pinda	Abacaxi-1	1.2-3.2	330-640
Pre-salt	Abacaxi-1	1.0-3.6	320-640

(*to nearest 10 mg HC/g TOC)

Table 2 Organic richness and quality for Angola source rocks grouped by well.

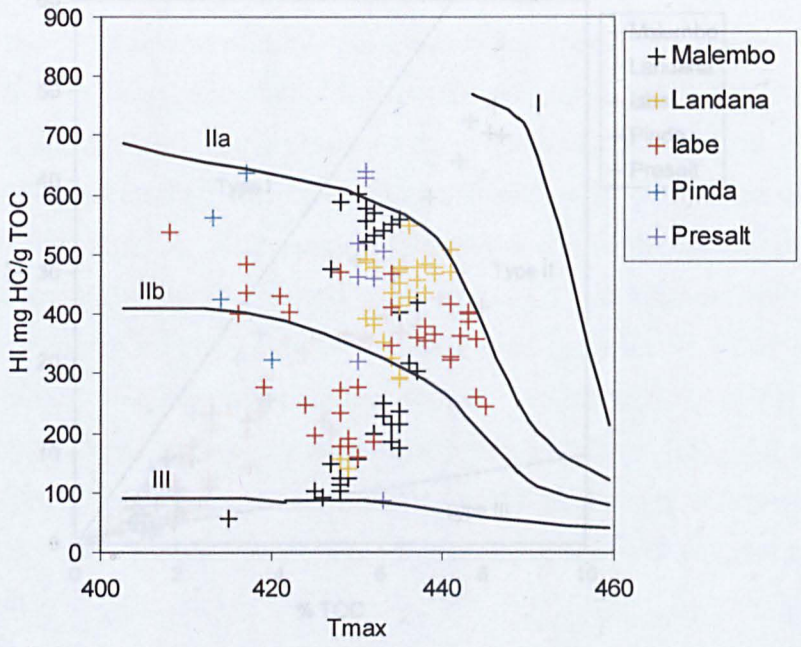

Fig. 35 Hydrogen Index and Tmax data for all source rocks plotted on the diagram of Delvaux *et al.* (1989) plotted by stratigraphic Group. The trend lines approximate to the following kerogen types: I = lacustrine, IIa = marine, IIb = mixed, III = terrestrial.

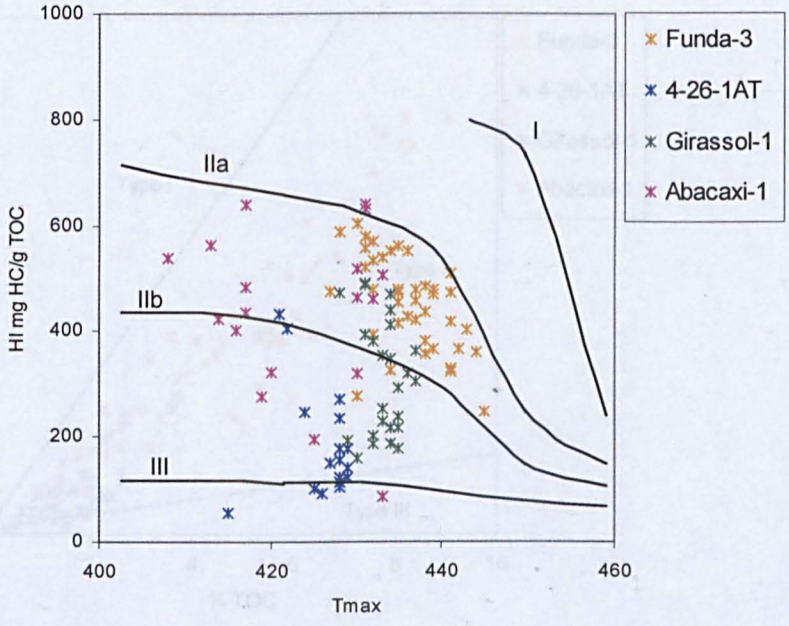

Fig. 36 Hydrogen Index and Tmax data for all source rocks plotted on the diagram of Delvaux *et al.* (1989) plotted by well. The trend lines approximate to the following kerogen types: I = lacustrine, IIa = marine, IIb = mixed, III = terrestrial.

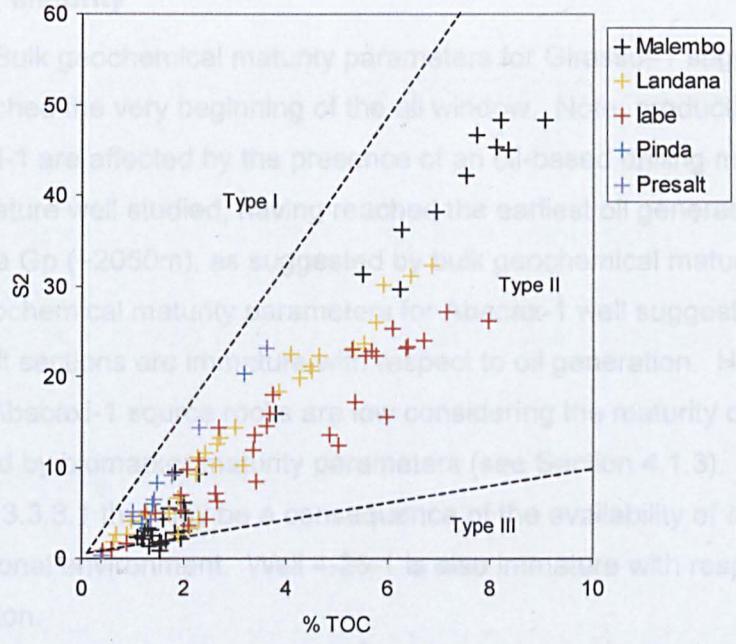

Fig. 37 Total Organic Carbon and Rock Eval pyrolysis parameter S_2 data for all source rocks plotted by stratigraphic Group on the diagram of Langford and Blanc-Valleron (1990). The lines represent a transition between kerogen types, they do not define exact kerogen types, i.e. the line representing type II kerogen would lie half way between the I-II and II-III transition lines.

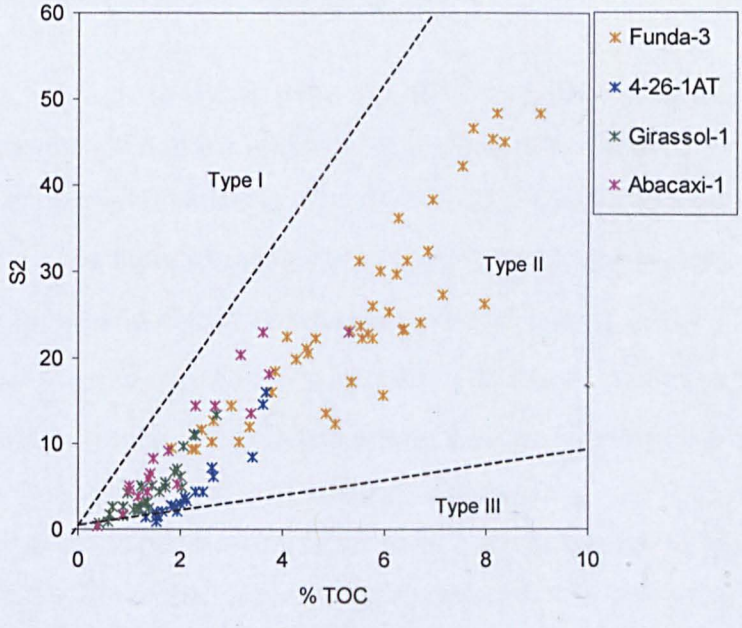

Fig. 38 Total Organic Carbon and Rock Eval pyrolysis parameter S_2 data for all source rocks plotted by well on the diagram of Langford and Blanc-Valleron (1990). The lines represent a transition between kerogen types, they do not define exact kerogen types, i.e. the line representing type II kerogen would lie half way between the I-II and II-III transition lines.

3.3.3.2 Maturity

Bulk geochemical maturity parameters for Girassol-1 suggest the section has just reached the very beginning of the oil window. Note, production Index values for Girassol-1 are affected by the presence of an oil-based drilling mud. Funda-3 is the most mature well studied, having reached the earliest oil generation window by the Landana Gp (~2050m), as suggested by bulk geochemical maturity parameters. The bulk geochemical maturity parameters for Abacax-1 well suggest both the Pre- and Post-salt sections are immature with respect to oil generation. However, T_{max} values for the Abacaxi-1 source rocks are low considering the maturity of the samples indicated by biomarker maturity parameters (see Section 4.1.3). As explained in Section 3.3.3.1 this may be a consequence of the availability of organic sulphur in the depositional environment. Well 4-26-1 is also immature with respect to oil generation.

4 Molecular analysis of source rock free hydrocarbons.

This chapter will address the molecular composition of the biomarkers free in the bitumen fraction i.e. in the aliphatic hydrocarbon fraction, of the Angolan source rock in terms of thermal maturity and variation in facies between stratigraphic groups.

4.1 Maturity analysis.

4.1.1 Girassol-1

Carbon preference index (CPI), a measure of the thermal maturity of sedimentary organic matter, calculates the relative abundance of odd to even *n*-alkanes (Bray & Evans, 1961). With increasing maturity the odd carbon number predominance inherited from the biological origin is lost, and hence values trend towards approximately 1. Girassol-1 samples have values greater than 1 suggesting the samples are immature (Fig. 39).

Fig. 40 shows three m/z 191 mass chromatograms illustrating progressive changes in hopane and tricyclic terpane composition with increasing depth and hence thermal maturity. Ts (18α(H)-22,29,30-trisnorneohopane) increases relative to the more thermally stable Tm (17α(H)-22,29,30-trisnorhopane). The 17α(H), 21β(H) 22S hopane also increase relative to the 17α(H), 21β(H) 22R isomer, and the 17β (H), 21α(H) hopanes (or moretanes) decrease relative to the more stable 17α(H), 21 β(H) hopanes. Fig. 40 also shows that the abundance of tricyclic terpanes relative to hopanes increases with maturity, although this may also vary as a reflection of organic facies. Several ratios have been calculated to represent graphically the stratigraphic changes in hopane composition with thermal maturity and depth (Fig. 41). The $\%C_{27}$Ts parameter does not gradually increase with depth as expected, but fluctuates at lower values (20-30%) down to 3580m then increases to a constant value of 30-35%. The ratio is known to vary with both source and maturity differences (Seifert & Moldowan, 1978) and is therefore a more useful maturity parameter in evaluating oils from a common source or source rocks consistent in facies (Peters & Moldowan, 1993). The $\%C_{29}$Ts (not shown) has been shown to be a

more effective maturity parameter within the oil window (Farrimond *et al.,* 1998) and does not increase with depth in Girassol-1. The $\%C_{30}\beta\alpha$ parameter gradually decreases with depth from 3300m to 3600m, and then stabilizes at *ca.* 15%. The $\%C_{32}\alpha\beta S$ parameter values at depths greater than 3700m in Girassol-1 are 50-54% suggesting the source rocks have barely entered the oil generation window. The deepest labe sample (56%) has almost reached equilibrium (57-60%) suggesting it may have reached early oil generation phase (Peters & Moldowan, 1993). Bulk geochemical data for Girassol-1 suggest that the whole source rock section has just reached the very beginning of the oil generation window, hence suggesting the beginning of the oil generation window is reached at shallower depths than biomarker data suggest (see Section 4.1.1).

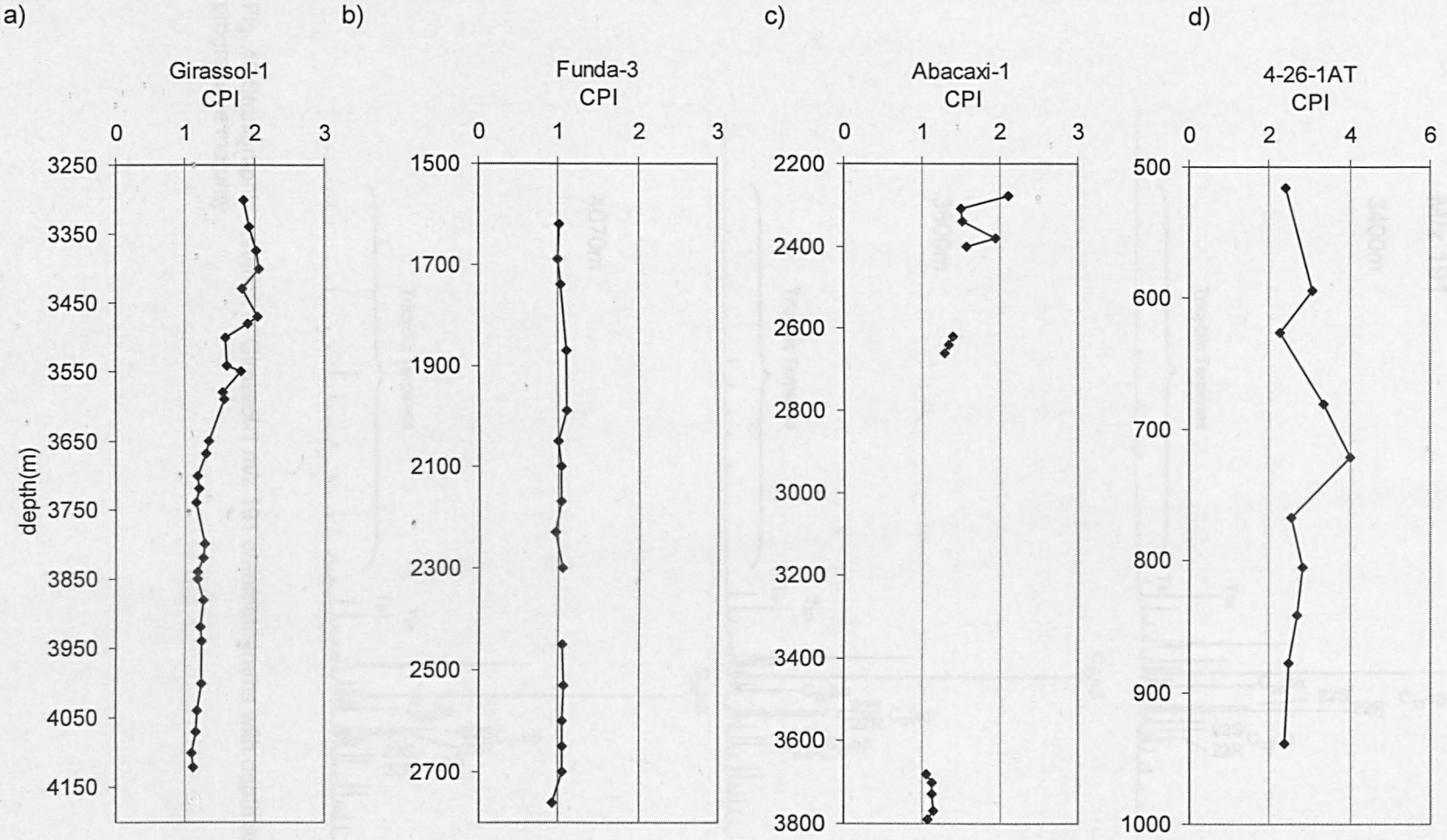

Fig. 39 Stratigraphic variation in carbon preference index (CPI) with depth for a) Girassol-1, b) Funda-3 and c) Abacaxi-1 d) 4-26-1AT wells.

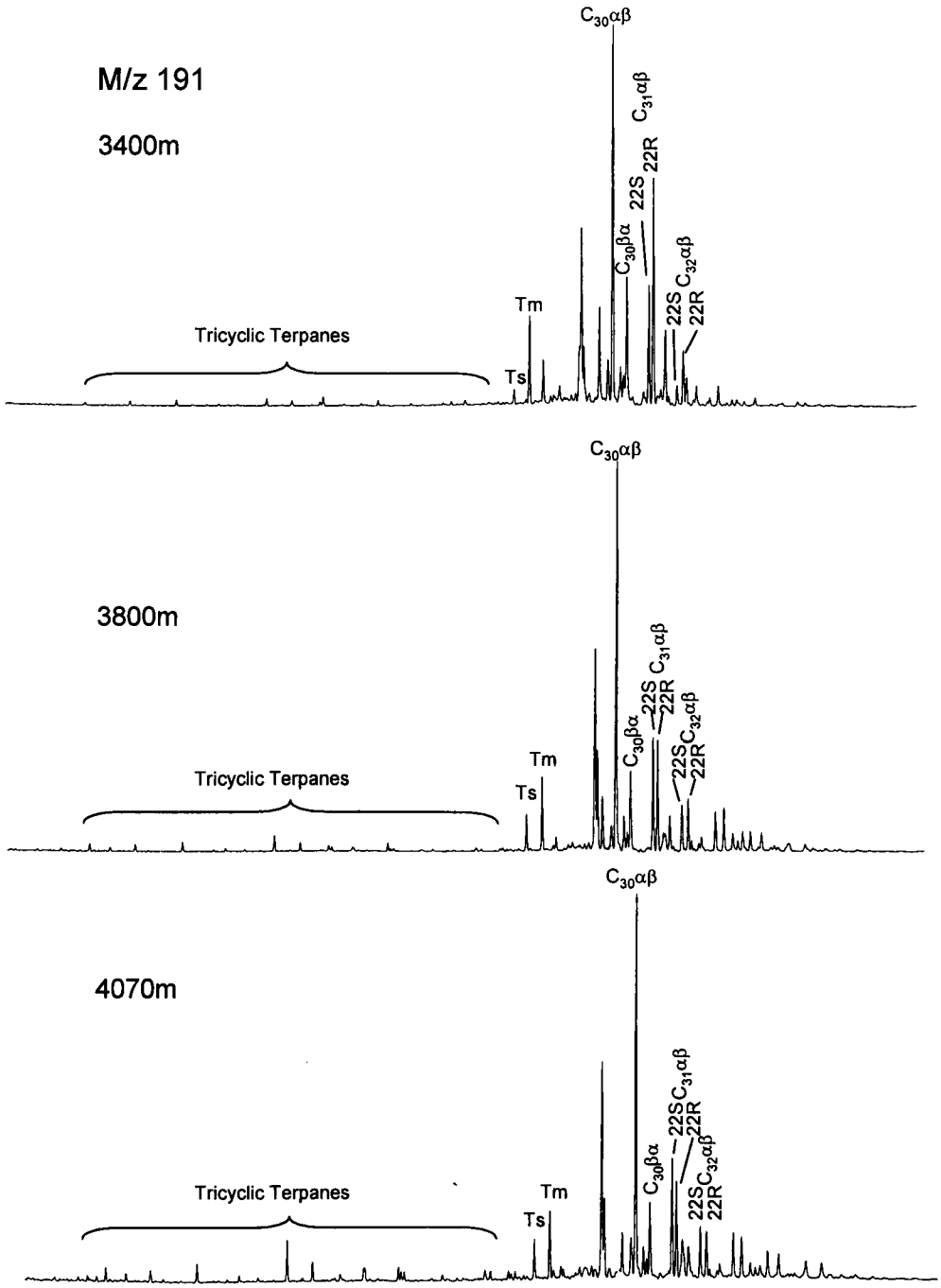

Fig. 40 Stratigraphic variation in Girassol-1 m/z 191 chromatograms with depth and progressive maturity.

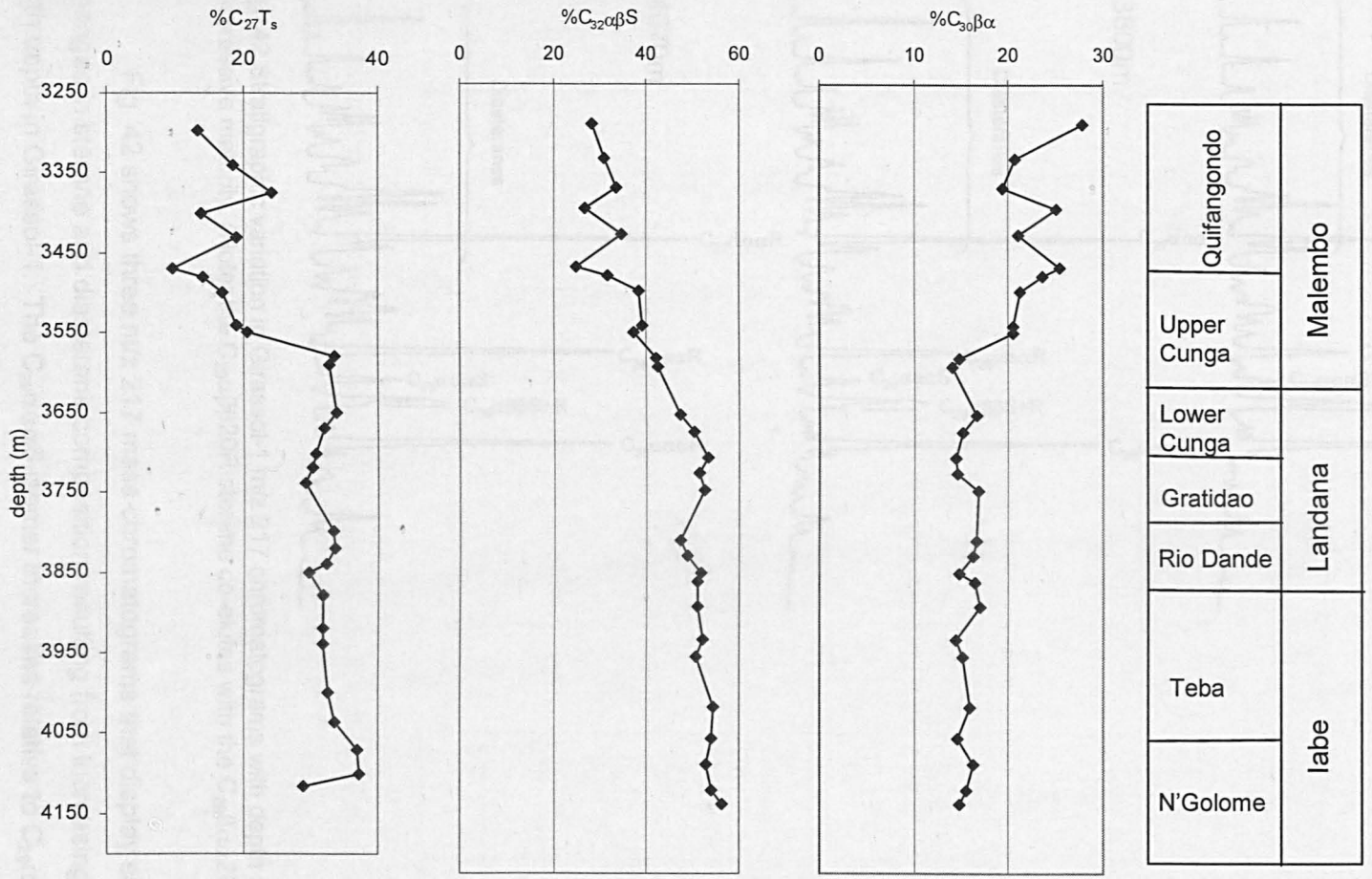

Fig. 41 Maturity parameters $\%C_{27}Ts$, $\%C_{32}\alpha\beta S$ and $\%C_{30}\beta\alpha$ versus depth and progressive maturity for Girassol-1 source rocks (stratigraphic formations and groups shown).

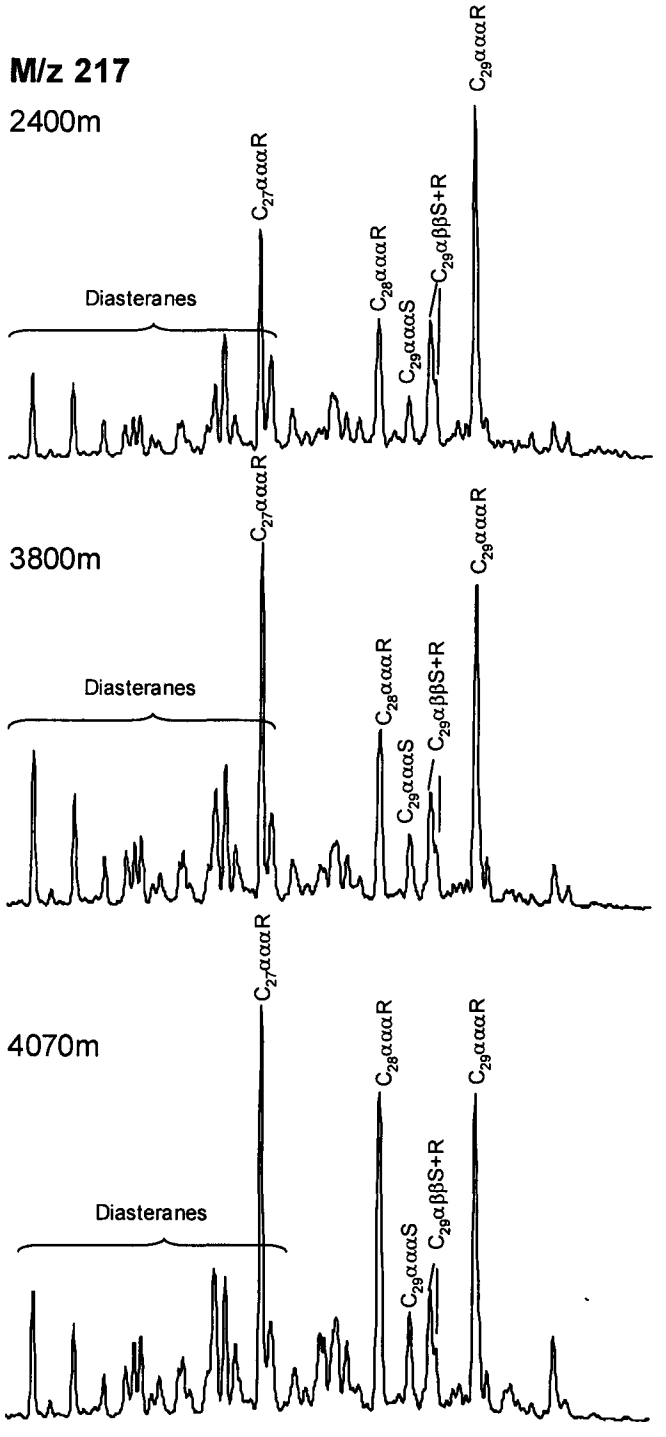

Fig. 42 Stratigraphic variation in Girassol-1 m/z 217 chromatograms with depth and progressive maturity. (Note: the $C_{29}\alpha\beta\beta$20R sterane co-elutes with the $C_{29}\beta\alpha\alpha$20R sterane.)

Fig. 42 shows three m/z 217 mass chromatograms that display some changes in sterane and diasterane composition resulting from increasing maturity with depth in Girassol-1. The $C_{29}\alpha\alpha\alpha$S isomer increases relative to $C_{29}\alpha\alpha\alpha$R as a function of maturity. The $\%C_{29}\alpha\alpha\alpha$S parameter has been calculated to show this structural isomerisation (Fig. 43). The end point for this parameter, representing

peak oil generation (50-55%), has not been reached (Mackenzie *et al.,* 1980; Peters & Moldowan 1993). The $\%C_{29}\alpha\beta\beta$ parameter records the relative abundance of C_{29} 5α(H), 14β(H), 17β(H) 20 S and R isomers to the less thermally stable C_{29} 5α(H), 14 α(H), 17α(H) 20 S and R isomers (Seifert & Moldowan, 1986). In Girassol-1 the parameter does not record an increase in maturity with depth. Values are initially high due to co-elution of $C_{29}\beta\alpha\alpha R$ steranes with the $C_{29}\alpha\beta\beta S$ and R doublet in the more immature samples. The $C_{29}\beta\alpha\alpha R$ would be lost with depth possibly leading to the apparent fall in the parameter.

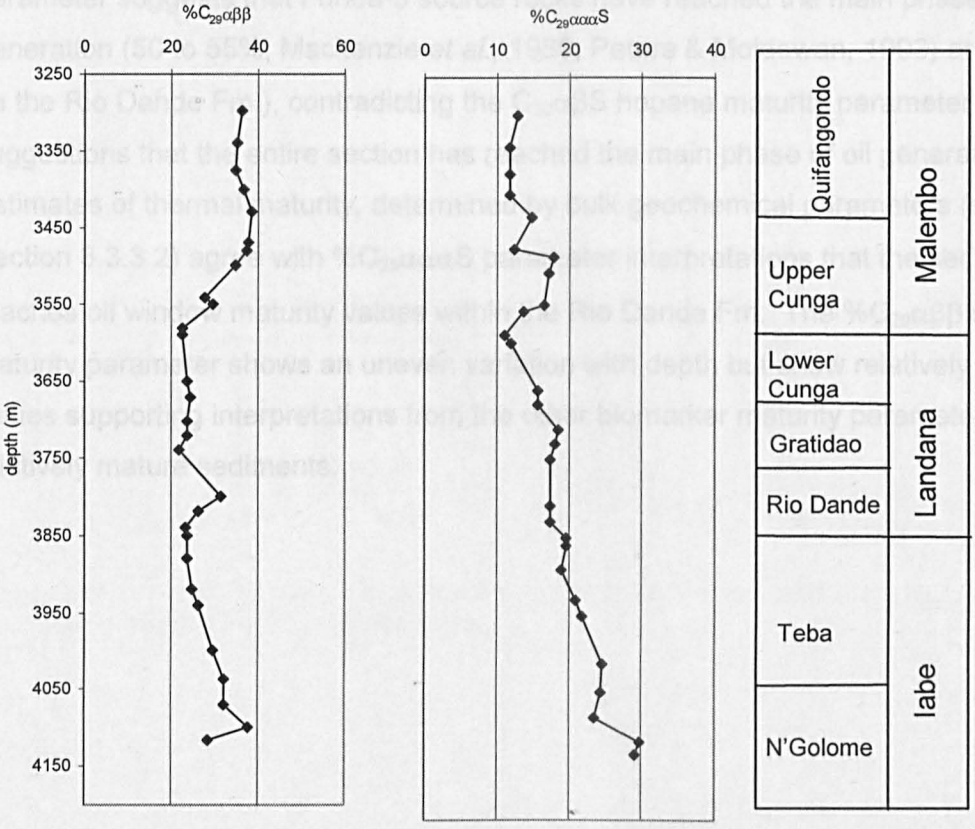

Fig. 43 Maturity parameters $\%C_{29}\alpha\alpha\alpha S$ and $\%C_{29}\alpha\beta\beta$ versus depth and progressive maturity for Girassol-1 source rocks (stratigraphic formations and groups shown).

4.1.2 Funda-3

CPI values for Funda-3 source rocks are approximately 1, suggesting the sediments are thermally mature (Fig. 39). Source rocks do not reach values of 1 unless they are mature to late mature (Miles, 1994). The $\%C_{27}Ts$ (Fig. 45) and $\%C_{29}Ts$ (not shown) parameters show a gradual increase in maturity with depth in Funda-3. The ratio of moretanes (βα hopanes) to hopanes (αβ hopanes) decreases

with increasing thermal maturity; values of 80-85% are found in immature bitumens decreasing to values of less than 15% in mature oils and source rocks, to a minimum of 5% (Mackenzie *et al.,* 1980; Peters & Moldowan, 1993). Fig. 44 illustrates the mature hopane and sterane biomarker profile of the Funda-3 source rocks. Values for this parameter (%$C_{30}\beta\alpha$) in Funda-3 show the conversion of $C_{30}\beta\alpha$ hopane to the more thermally stable $C_{30}\alpha\beta$ hopane to be almost complete, having reached values of 5%. The %$C_{32}\alpha\beta S$ parameter values for the section have reached end point (57-62%), suggesting that the entire section has reached the main phase of oil generation (Peters & Moldowan, 1993). The sterane maturity parameter %$C_{29}\alpha\alpha\alpha S$ parameter suggests that Funda-3 source rocks have reached the main phase of oil generation (50 to 55%; Mackenzie *et al.,* 1980; Peters & Moldowan, 1993) at 2100m (in the Rio Dande Fm.), contradicting the $C_{32}\alpha\beta S$ hopane maturity parameter suggestions that the entire section has reached the main phase of oil generation. Estimates of thermal maturity, determined by bulk geochemical parameters (see Section 3.3.3.2) agree with %$C_{29}\alpha\alpha\alpha S$ parameter interpretations that the section reaches oil window maturity values within the Rio Dande Fm. The %$C_{29}\alpha\beta\beta$ sterane maturity parameter shows an uneven variation with depth but show relatively high values supporting interpretations from the other biomarker maturity parameters of relatively mature sediments.

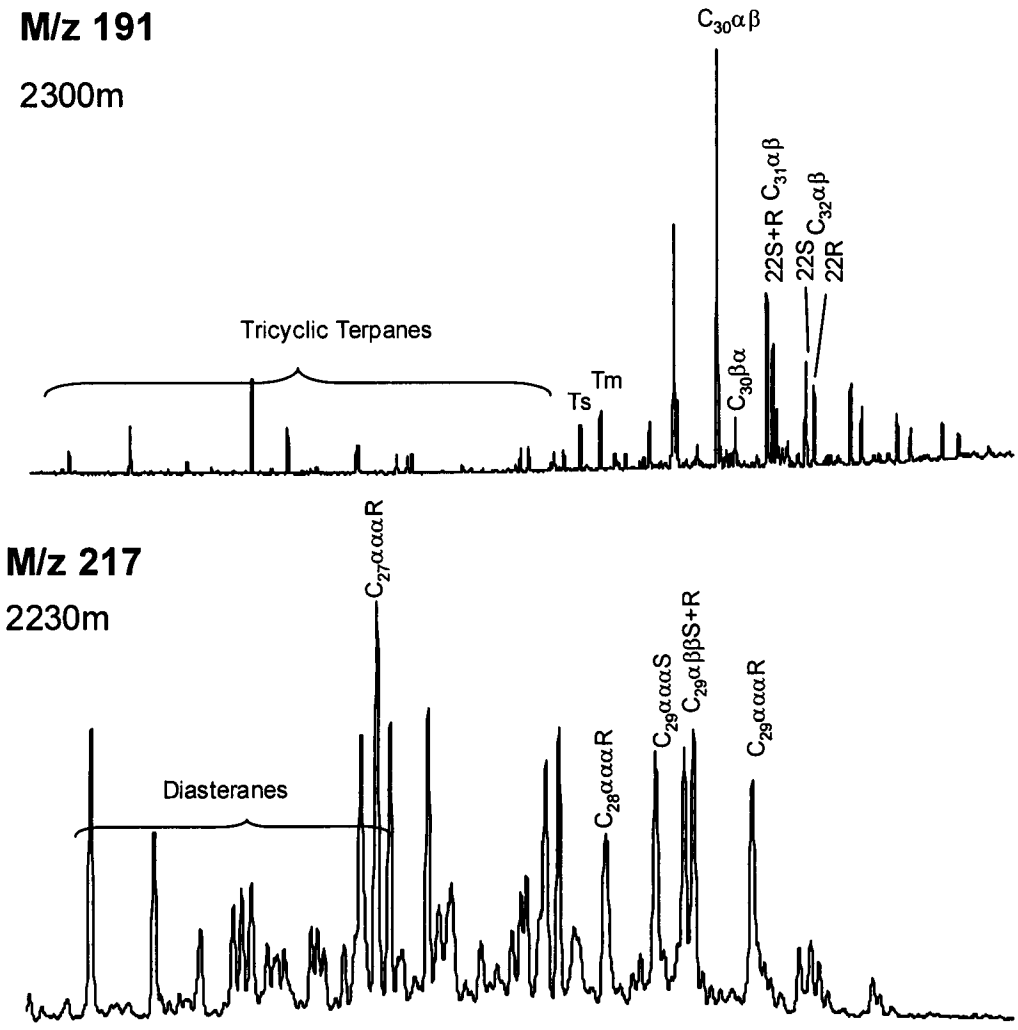

Fig. 44 M/z 191 and 217 mass chromatograms to illustrate the mature hopane and sterane biomarker profiles in Funda-3 source rocks.

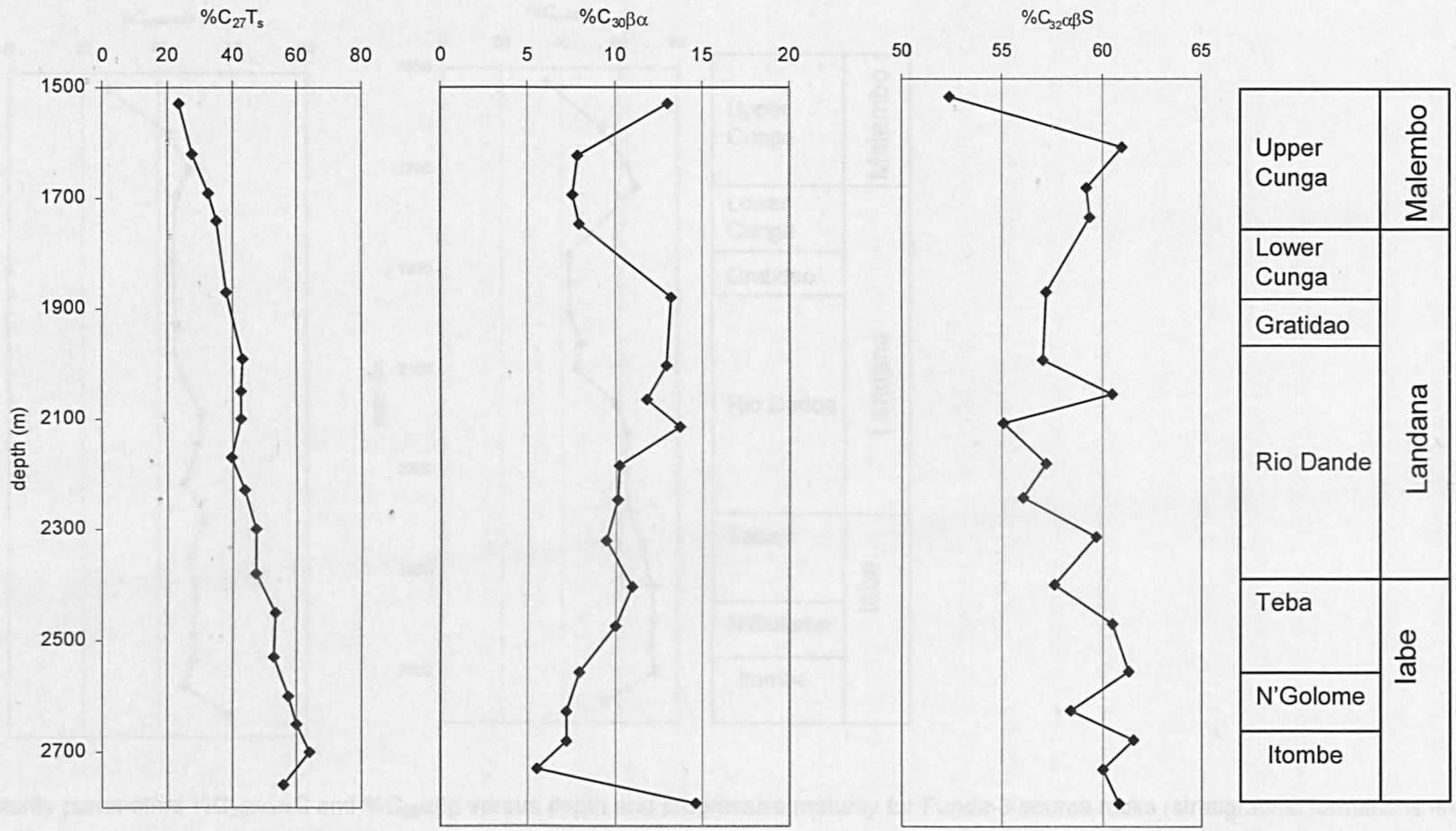

Fig. 45 Maturity parameters $\%C_{27}Ts$, $\%C_{32}\alpha\beta S$ and $\%C_{30}\beta\alpha$ versus depth and progressive maturity for Funda-3 source rocks (stratigraphic formations and groups shown).

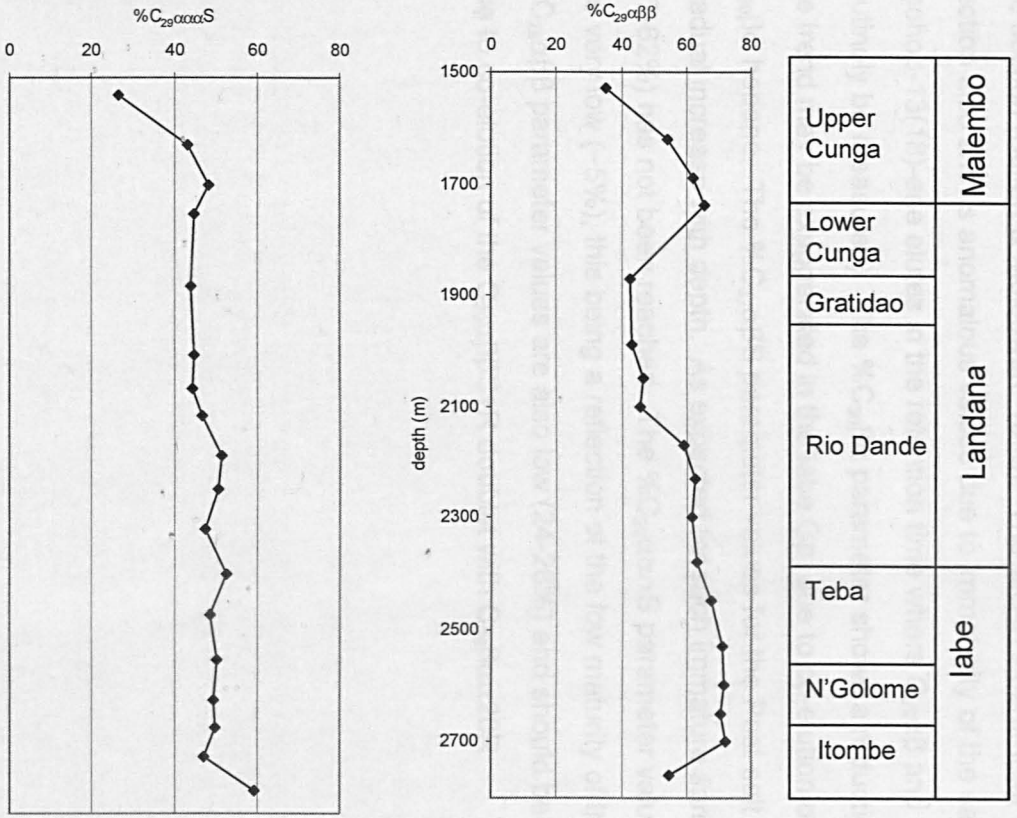

Fig. 46 Maturity parameters $\%C_{29}\alpha\alpha\alpha S$ and $\%C_{29}\alpha\beta\beta$ versus depth and progressive maturity for Funda-3 source rocks (stratigraphic formations and groups shown).

4.1.3 Abacaxi-1

Source rock CPI values for the Abacaxi-1 Post-salt section (Fig. 39) are greater than 1 and show a gradual decrease with increasing depth and thermal maturity. Values for the Pre-salt section are approaching but still greater than 1.

The immaturity of the Abacaxi-1 Post-salt source rock samples is illustrated (Fig. 47) by the presence of the immature rearranged neohop-13(18)-enes (C_{27}, C_{29} and C_{30}) and the regular hop-17(21)-enes (C_{27}, C_{30} and C_{31}). Also present in the Iabe Gp. but not the Pinda Gp. are the immature C_{29} to C_{35} 17β(H), 21β(H) hopanes. The 17β(H), 21β(H) hopanes are less thermally stable than other hopanes and are thought to isomerise to their more stable counterparts well ahead of the hydrocarbon generation zone (Mackenzie *et al.*, 1980). The $\%C_{27}$Ts parameter in Abacaxi-1 shows anomalous values (Fig. 48) possibly as a result of facies variations throughout the section (Seifert & Moldowan, 1978). The $\%C_{29}$Ts parameter for the Post-salt section also shows anomalous values due to immaturity of the samples (i.e. the C_{29} neohop-13(18)-ene elutes in the retention time where $C_{29}\alpha\beta$ and C_{29}Ts would routinely be measured). The $\%C_{30}\beta\alpha$ parameter shows a reduction with depth but the trend may be exaggerated in the Iabe Gp. due to co-elution of $C_{29}\beta\beta$ hopane with $C_{30}\beta\alpha$ hopane. The $\%C_{32}\alpha\beta$S parameter values for the Post-salt section shows a gradual increase with depth. As expected for such immature samples the end point (57-62%) has not been reached. The $\%C_{29}\alpha\alpha\alpha$S parameter values for the Post-salt are very low (~5%), this being a reflection of the low maturity of the samples. The $\%C_{29}\alpha\beta\beta$ parameter values are also low (24-28%) and should be possibly lower still due to co-elution of the $C_{29}\alpha\beta\beta$S+R doublet with $C_{29}\beta\alpha\alpha$20R.

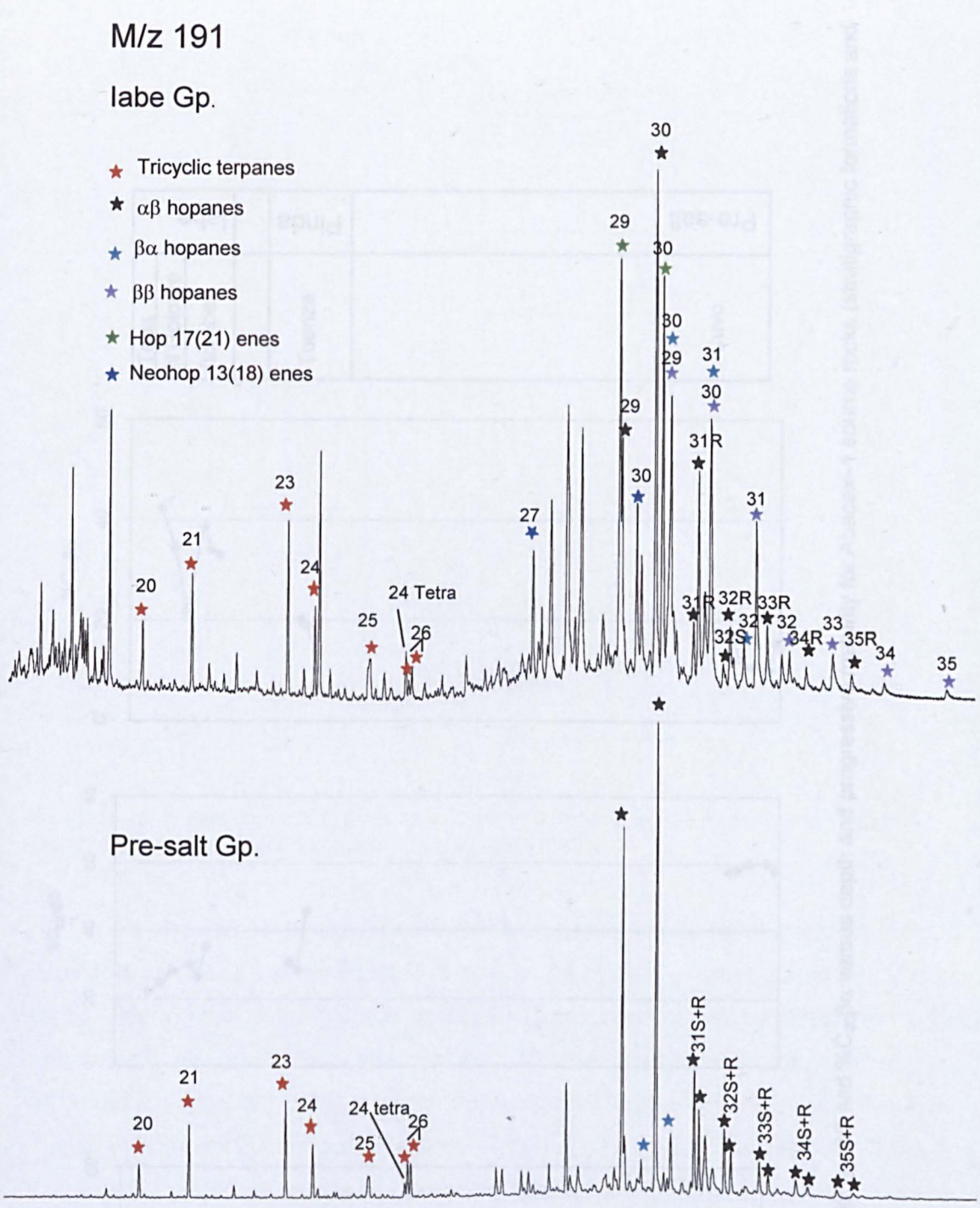

Fig. 47 M/z 191 chromatogram for Abacaxi-1 Iabe Gp. and Pre-salt Gp. source rock. Note the presence of the less thermally mature 17β(H), 21β(H) hopanes, regular hop-17(21)-enes and rearranged neohop-13(18)-enes (isomers represented by coloured symbols, carbon numbers marked) in the less mature Iabe Gp. sample.

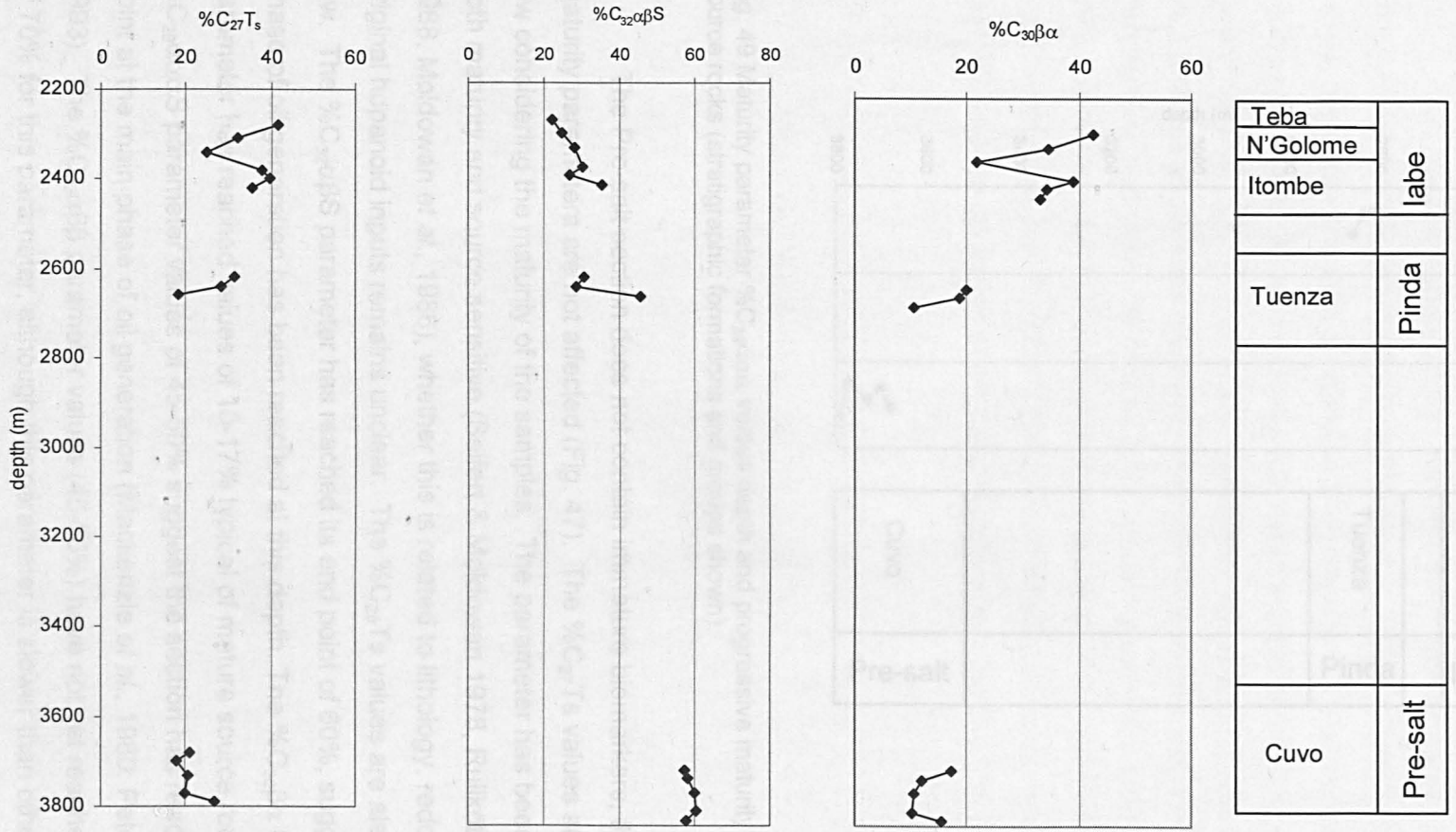

Fig. 48 Maturity parameters $\%C_{27}Ts$, $\%C_{32}\alpha\beta S$ and $\%C_{30}\beta\alpha$ versus depth and progressive maturity for Abacaxi-1 source rocks (stratigraphic formations and groups shown).

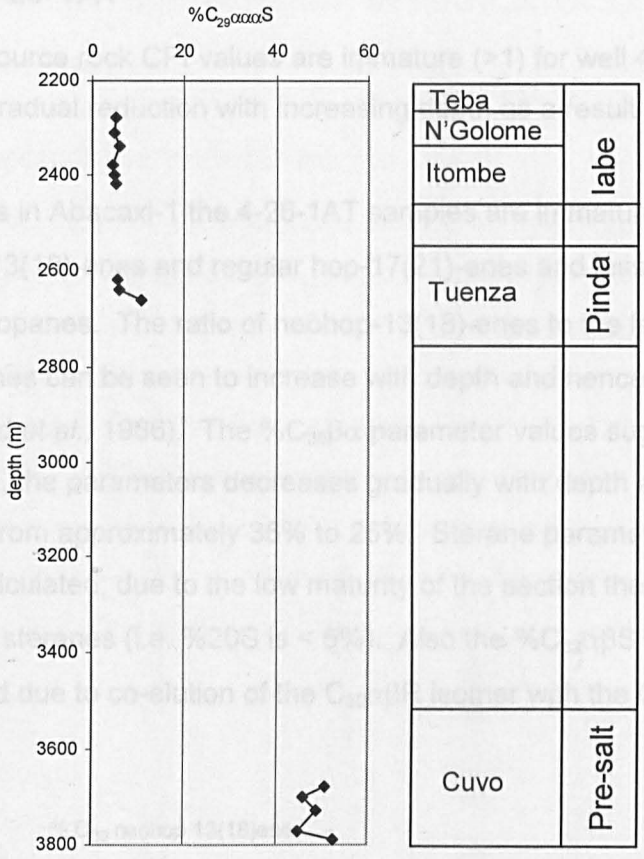

Fig. 49 Maturity parameter $\%C_{29}\alpha\alpha\alpha$ versus depth and progressive maturity for Abacaxi-1 source rocks (stratigraphic formations and groups shown).

The Pre-salt section does not contain immature biomarkers, therefore the maturity parameters are not affected (Fig. 47). The $\%C_{27}$Ts values are anomalously low considering the maturity of the samples. The parameter has been reported to be both maturity and source sensitive (Seifert & Moldowan 1978, Rullkötter & Marzi, 1988, Moldowan *et al.,* 1986), whether this is related to lithology, redox conditions or original hopanoid inputs remains unclear. The $\%C_{29}$Ts values are also unusually low. The $\%C_{32}\alpha\beta$S parameter has reached its end point of 60%, suggesting the main phase of oil generation has been reached at this depth. The $\%C_{30}\beta\alpha$ hopane maturity parameter has reached values of 10-17% typical of mature source rocks. The $\%C_{29}\alpha\alpha\alpha$S parameter values of 45-50% suggest the section has reached the end point at the main phase of oil generation (Mackenzie *et al.,* 1980; Peters & Moldowan 1993). The $\%C_{29}\alpha\beta\beta$ parameter values (45-55%) have not yet reached the end point of 70% for this parameter, although this parameter is slower than other maturity parameters to reach equilibrium and is therefore more effective at higher maturities (Peters & Moldowan, 1993).

4.1.4 4-26-1AT

Source rock CPI values are immature (>1) for well 4-26-1AT (Fig. 39) but show a gradual reduction with increasing depth as a result of increasing maturity.

As in Abacaxi-1 the 4-26-1AT samples are immature containing rearranged neohop-13(18)-enes and regular hop-17(21)-enes and less thermally stable 17β(H), 21β(H) hopanes. The ratio of neohop-13(18)-enes to the less thermally stable hop-17(21)-enes can be seen to increase with depth and hence maturity (Fig. 50; Farrimond *et al.,* 1986). The $\%C_{30}\beta\alpha$ parameter values suggest the source rocks are immature, the parameters decreases gradually with depth a result of increasing maturity from approximately 35% to 25%. Sterane parameters for 4-26-1AT could not be calculated; due to the low maturity of the section the distributions contain only ααα 20R steranes (i.e. %20S is < 5%). Also the $\%C_{32}\alpha\beta S$ parameter could not be calculated due to co-elution of the $C_{32}\alpha\beta R$ isomer with the C_{33} 17(21) hopene.

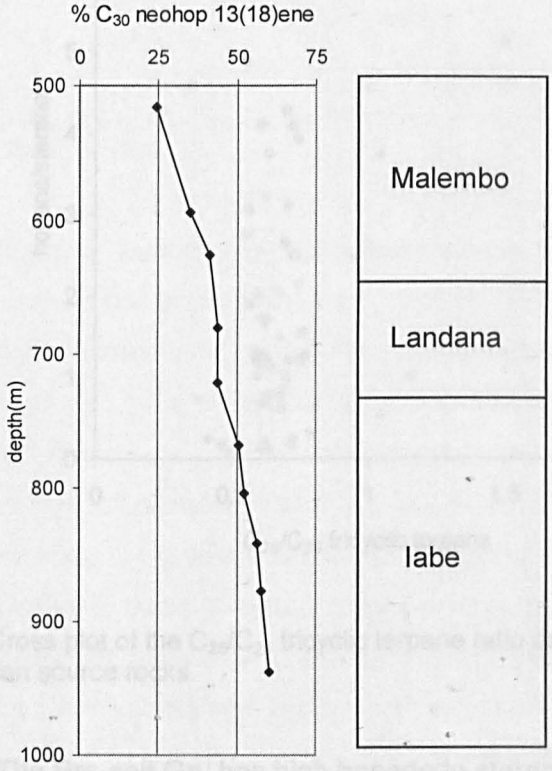

Fig. 50 Stratigraphic variation in the % neohop 13(18) enes (C_{30} neohop-13(18)-ene/($_{30}$ neohop-13(18)-ene + C30 hop-17(21)-ene) with depth and progressive thermal maturity (stratigraphic groups shown, stratigraphic formations are unknown).

4.2 Stratigraphic variation in source rock depositional environment.

4.2.1 Lacustrine versus marine

The lacustrine Pre-salt facies and the marine Post-salt source rock facies can be distinguished using the C_{26}/C_{25} tricyclic terpane ratio and the hopane to sterane ratio (Fig. 51). These ratios have been used in the literature on Angolan oils and source rocks to differentiate oils and source rocks of lacustrine and marine origin (Burwood, 1999; Schiefelbein *et al.,* 1999; Cole *et al.,* 2000). It is not known in the literature why the C_{26}/C_{25} tricyclic terpane parameter behaves in this way. Lacustrine-derived oils have C_{26}/C_{25} tricyclic terpane ratio values >1 whereas marine-derived oils have values <1. The ratio has also been used to identify marine incursions within the lacustrine Bucomazi Fm. source rocks (Burwood *et al.,* 1992).

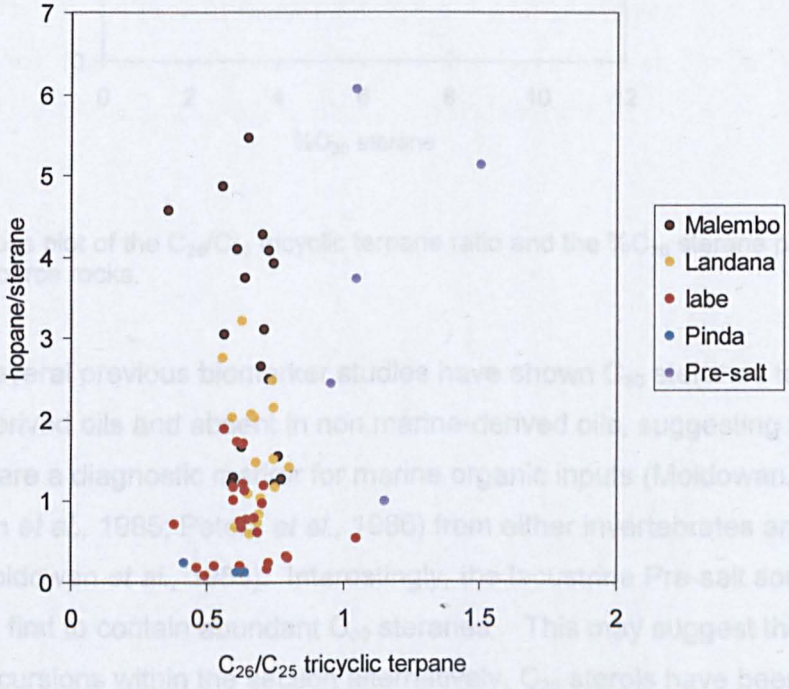

Fig. 51 Cross plot of the C_{26}/C_{25} tricyclic terpane ratio and the hopane/sterane parameter for all Angolan source rocks.

The Pre-salt Gp. has high hopane to sterane ratios characteristic of type I kerogens from lacustrine environments. The lacustrine samples cover only 110m of section but show a wide spread of hopane to sterane ratio values; this may reflect the greater complexity of lacustrine environments. The low hopane to sterane ratios encountered in the Pinda, Iabe and Landana Gps. are interpreted as characteristic of

marine type II kerogens deposited in distal marine and carbonate environments (Cole *et al.*, 2000). The Malembo Gp. has high hopane to sterane ratio characteristic of type II/III kerogens from marine deltaic environments.

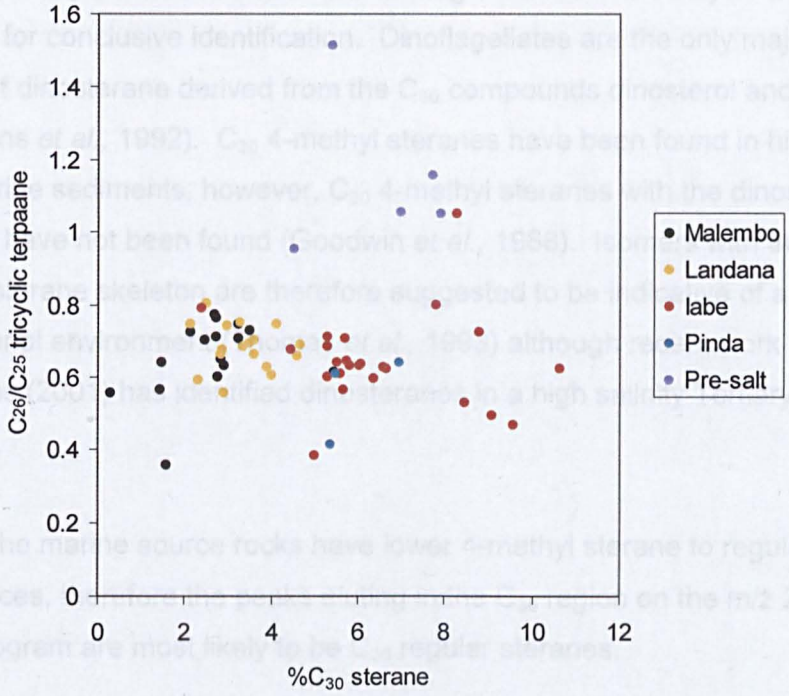

Fig. 52 Cross plot of the C_{26}/C_{25} tricyclic terpane ratio and the $\%C_{30}$ sterane parameter for all Angolan source rocks.

Several previous biomarker studies have shown C_{30} steranes to be present in marine-derived oils and absent in non marine-derived oils, suggesting that C_{30} steranes are a diagnostic marker for marine organic inputs (Moldowan, 1984; Moldowan *et al.*, 1985; Peters *et al.*, 1986) from either invertebrates and/or marine algae (Moldowan *et al.*, 1985). Interestingly, the lacustrine Pre-salt source rocks appear at first to contain abundant C_{30} steranes . This may suggest the presence of marine incursions within the section alternatively, C_{30} sterols have been suggested to have potential to occur in certain phytoplankton which may occur in lakes (Volkman, 1988). However, examination of the m/z 231 mass chromatogram reveals that the lacustrine source rocks also have a high abundance of 4-methyl steranes relative to steranes (Fig. 53). Analysis of the m/z 231 mass chromatogram shows the peaks eluting at the C_{30} regular sterane region (in the m/z 217) are actually C_{30} 4α methyl steranes; 4-methyl steranes have a m/z 217 ion in their mass spectra they therefore may occur in m/z 217 if present in high abundance, which is the case here. The origin of 4-methyl steranes is debated in the literature but in general thought to derive

mainly from the phytoplankton dinoflagellates found in both marine and lacustrine environments (Thomas *et al.,* 1993). The m/z 231 mass chromatogram has a complex distribution of compounds in the C_{30} region, suggesting the source rocks may potentially contain dinosteranes although GC-MS-MS analysis would be required for conclusive identification. Dinoflagellates are the only major proven source of dinosterane derived from the C_{30} compounds dinosterol and dinostanol (Summons *et al.,* 1992). C_{30} 4-methyl steranes have been found in high abundance in lacustrine sediments; however, C_{30} 4-methyl steranes with the dinosterane skeleton have not been found (Goodwin *et al.,* 1988). Isomers with the presence of the dinosterane skeleton are therefore suggested to be indicative of a marine palaeo depositional environment (Thomas *et al.,* 1993) although recent work by Chen & Summons (2001) has identified dinosteranes in a high salinity Tertiary lacustrine dolomite.

The marine source rocks have lower 4-methyl sterane to regular sterane abundances, therefore the peaks eluting in the C_{30} region on the m/z 217 mass chromatogram are most likely to be C_{30} regular steranes.

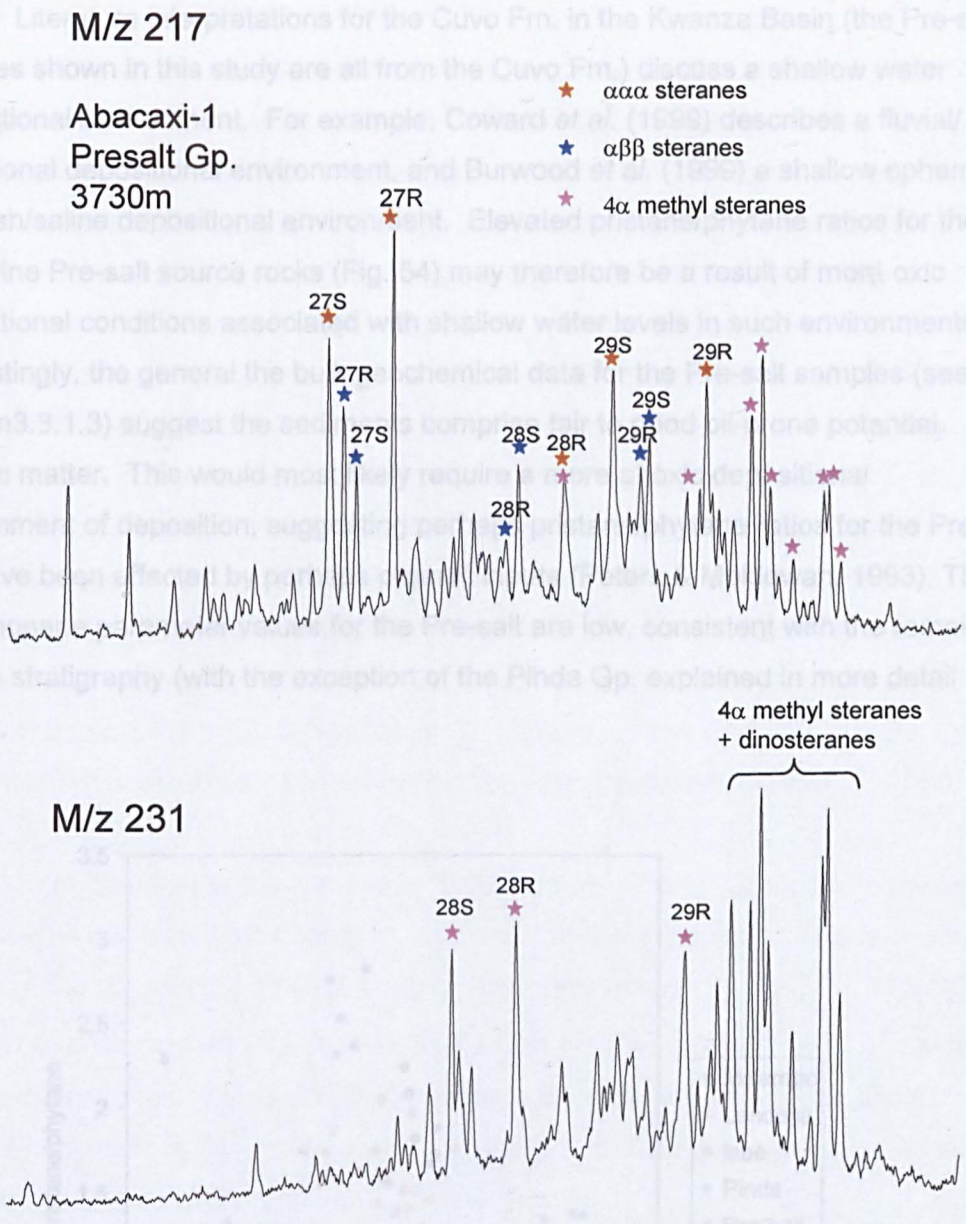

Fig. 53 M/z 231 chromatogram for Abacaxi-1 source rock to illustrate presence of methyl steranes occurring in the m/z 217 chromatogram at the retention time of C_{30} regular steranes within the Pre-salt section (isomers represented by coloured symbols, carbon numbers marked).

4.2.2 Redox conditions

4.2.2.1 Pre-salt source rocks

Pristane to phytane ratios have been used to provide information regarding the redox potential of source rock depositional environments (Didyk *et al.*, 1978). In general, pristane/phytane ratios < 1 indicate anoxic deposition and ratios >1 more oxic deposition. Note, however that the ratio should be used with caution and in conjunction with other environmental biomarker parameters (Peters & Moldowan,

1993). Literature interpretations for the Cuvo Fm. in the Kwanza Basin (the Pre-salt samples shown in this study are all from the Cuvo Fm.) discuss a shallow water depositional environment. For example, Coward *et al.* (1999) describes a fluvial/ transitional depositional environment, and Burwood *et al.* (1999) a shallow ephemeral brackish/saline depositional environment. Elevated pristane/phytane ratios for the lacustrine Pre-salt source rocks (Fig. 54) may therefore be a result of more oxic depositional conditions associated with shallow water levels in such environments. Interestingly, the general the bulk geochemical data for the Pre-salt samples (see Section3.3.1.3) suggest the sediments comprise fair to good oil-prone potential organic matter. This would most likely require a more anoxic depositional environment of deposition, suggesting perhaps pristane/phytane ratios for the Pre-salt have been affected by perhaps organic inputs (Peters & Moldowan, 1993). The $\%C_{35}$ hopane parameter values for the Pre-salt are low, consistent with the remaining marine stratigraphy (with the exception of the Pinda Gp. explained in more detail below).

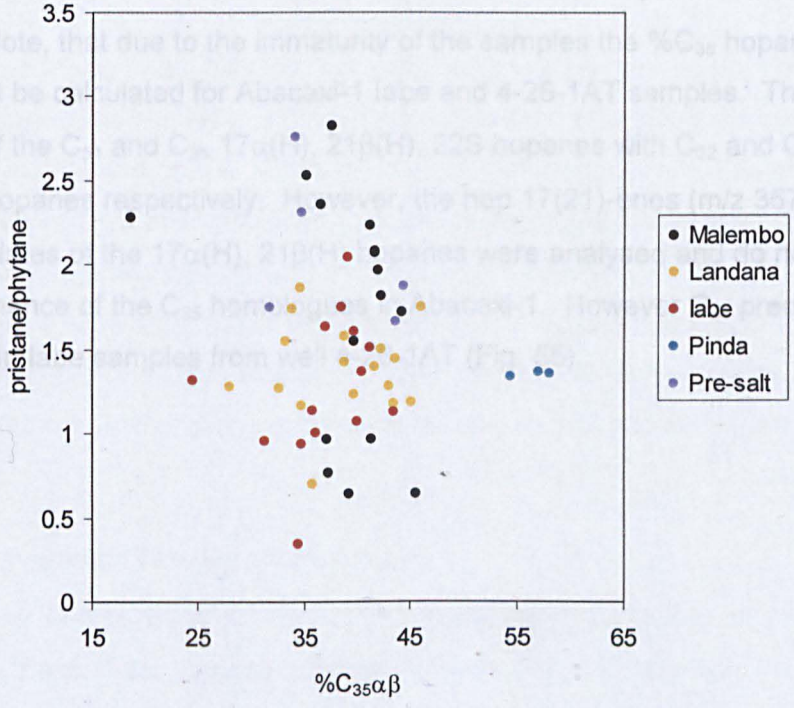

Fig. 54 Cross plot of the pristane/phytane ratio and the $\%C_{35}\alpha\beta$ parameter ($100*C_{35}\alpha\beta(S+R)/(C_{34} + C_{35}\alpha\beta(S+R))$ for all Angolan source rocks.

4.2.2.2 Post-salt Cretaceous source rocks

The Pinda Gp. can be clearly distinguished from the remaining stratigraphy by elevated levels of C_{35} hopanes (Fig. 54). The $\%C_{35}\alpha\beta$ hopane parameter (comparable to the homohopane index) is used to indicate the redox conditions of ancient depositional environments. High values are typical of anoxic marine conditions (Ten Haven *et al.*, 1988; Peters & Moldowan, 1991), specifically sulphur-rich environments (Bishop & Farrimond, 1995). An elevated abundance of C_{35} hopanes and hop-17(21)-enes may also result from hypersaline environments (Peters & Moldowan, 1991). High C_{35} homohopane index values are thought to result from the selective preservation of C_{35} bacteriohopanetetrol, most likely though incorporation of sulphur into the sidechain during diagenesis (Peters & Moldowan, 1991). Reduced sulphur species react more readily with iron than with organic matter, hence incorporation of sulphur is most likely to occur in anoxic environments low in iron; i.e. non-clastic carbonate or evaporitic environments (Adam *et al.*, 1993). This may explain the high abundance of C_{35} hopanes in the Pinda Gp. source rocks which were deposited during a period of carbonate deposition (Cole *et al.*, 2000).

Note, that due to the immaturity of the samples the $\%C_{35}$ hopane parameter could not be calculated for Abacaxi-1 Iabe and 4-26-1AT samples. This is due to co-elution of the C_{34} and C_{35} 17α(H), 21β(H), 22S hopanes with C_{32} and C_{33} 17β(H), 21β(H) hopanes respectively. However, the hop 17(21)-enes (m/z 367), diagenetic intermediates of the 17α(H), 21β(H) hopanes were analysed and do not show predominance of the C_{35} homologues in Abacaxi-1. However C_{35} predominance can be seen in Iabe samples from well 4-26-1AT (Fig. 55).

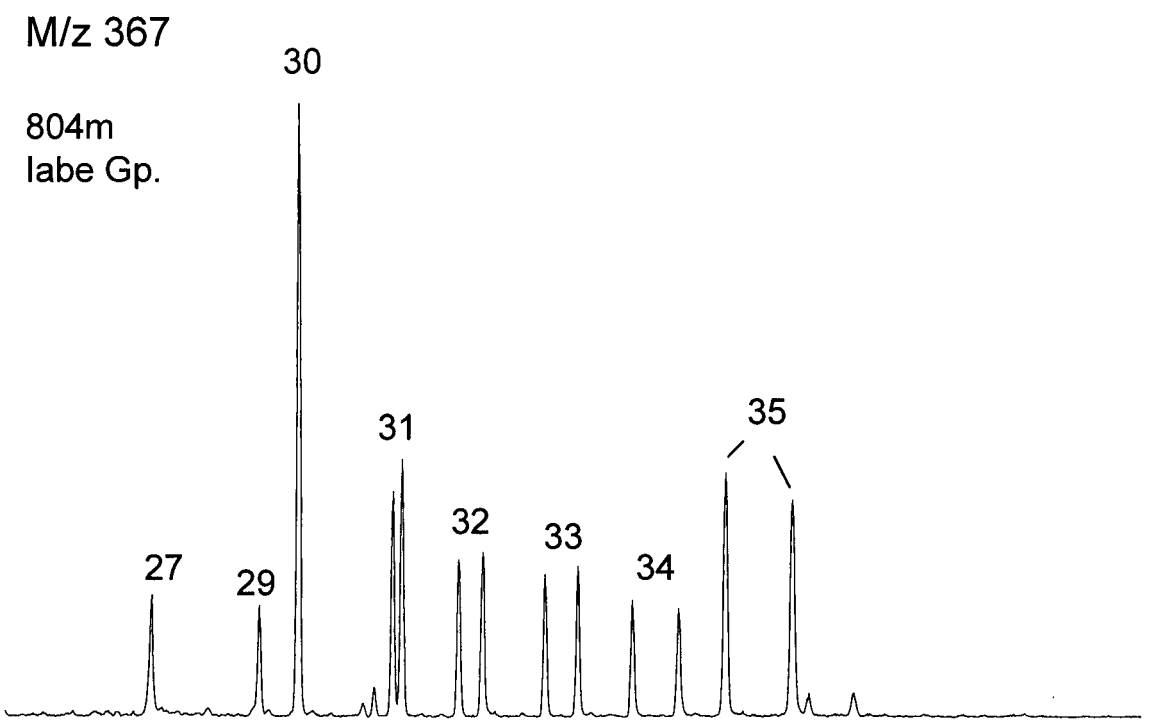

Fig. 55 M/z 367 chromatogram for a 4-26-1AT source rock sample showing hop 17(21) enes (carbon numbers marked).

The Pinda and labe Gps. have relatively low pristane to phytane ratios (~0.5 to 1.7) suggesting that less oxic conditions prevailed during their deposition than the Pre-salt and Malembo Gps. Post-salt source rock deposition is thought to be a result of either coastal upwelling or ocean anoxic events (OAE; Cole *et al.,* 2000); both depositional regimes permitting the development of anoxic or oxygen-depleted conditions. In upwelling areas remineralization of high concentrations of organic matter may lead to oxygen-depleted bottom waters and anoxic surface sediments leading to increased phytane production relative to pristane (Volkman, 1988).

4.2.2.3 Post-salt Tertiary source rocks

The Tertiary Landana Fm. source rocks have pristane to phytane values similar to those of the Cretaceous Post-salt source rocks, whereas the Malembo Gp. samples have higher pristane to phytane ratios suggesting a more oxic depositional environment. The higher proportion of type III kerogen (inferred from Section 3.3.2) in the Malembo Gp. source rocks may be in part a result of organic matter inputs, but also due to reduced preservation of marine organic matter in a more oxic environment. This would lead to relative enrichment of more resistant terrigenous organic matter. The Malembo Gp. is a regressive sequence (Cole *et al.,* 2000), and

shallower water depths may lead to less stratified conditions making it less likely for anoxic conditions to develop, although this would be dependent upon the actual water depths involved.

It should be noted that, with the exception of the sterane composition, the Malembo Gp. samples from Funda-3 have biomarker compositions (in terms of their hopane/sterane, C_{27}/C_{29} sterane, $\%C_{24}$ tetracyclic terpane, %tricyclic terpane and % gammacerane parameters) most similar to the Iabe Gp. (sometimes Landana Gp.) as opposed to the remaining Malembo Gp. samples. They also differ in their hydrocarbon potential from other Malembo samples, comprising excellent type II oil-prone organic matter. This geographical variation in depositional environment may be a reflection of varying organic inputs, with increasing distance from the Tertiary Congo Fan. From an exploration perspective it is important to note that, oils sourced from the Malembo Gp. in this region may have a biomarker composition similar to the Iabe Gp.

4.2.3 Algal versus terrestrial indicators

4.2.3.1 Pre-salt source rocks

Fig. 56 shows sterane compositional data plotted on the ternary diagram originally devised by Huang and Meinschein (1976) to distinguish ecosystems on the basis of sterol compositions, based on the principle that C_{27} and C_{28} sterols are most abundant in plankton and marine invertebrates, the principal contributors to marine organic matter, whereas, C_{27} and particularly C_{29} sterols are the predominant sterols in higher plants and animals which are characteristic of terrestrially influenced environments (Huang & Meinschein, 1979). Note, however that exceptions to this general trend occur, most notably that C_{29} sterols are known to be produced by some algae (Moldowan *et al.,* 1985; Volkman, 1986). The Pre-salt lacustrine source rocks show C_{27} steranes as the most abundant sterane (Fig. 56 & Fig. 57); this contrasts with reports of non-marine environments having high C_{29} steranes interpreted as such environment having greater exposure to terrigenous organic matter (Huang & Meinschein, 1979; Moldowan *et al.,* 1985). Note, this pattern of high C_{27} in non-marine environments is also observed in Brazilian freshwater and saline lacustrine-derived oils (Mello *et al,* 1988a).

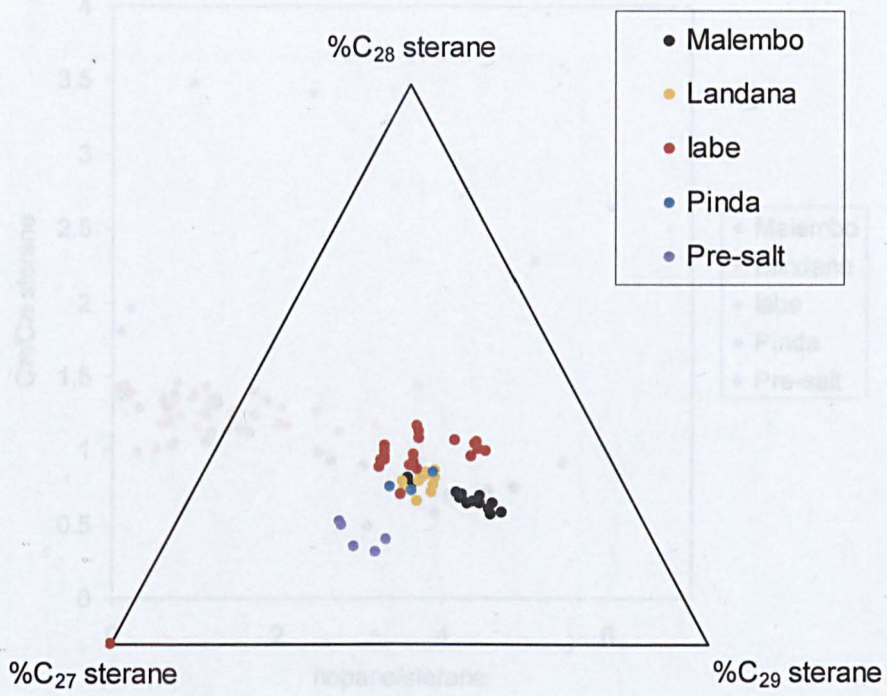

Fig. 56 Ternary diagram of all Angolan source rock C_{27}, C_{28} and C_{29} α(H), 14β(H), 17β(H), 20 S + R sterane distributions from the m/z 218 mass chromatogram (note due to the low maturity and absence of $\alpha\beta\beta$ steranes 4-26-1AT well samples are not included). The $\alpha\beta\beta$ steranes have been used as opposed to the $\alpha\alpha\alpha$ steranes because the Norsk Hydro automatic quantification system does not measure the C_{28}aaaR.

High hopanes relative to steranes are indicative of terrigenous and/or microbially reworked organic matter, whereas low hopane to sterane ratios are interpreted to reflect marine organic matter with major algal contributions (Peters & Moldowan, 1993). The lacustrine Pre-salt section is characterised by a high proportion of hopanes relative to steranes, this perhaps being a reflection of high bacterial reworking in the lacustrine sediments. Biomarkers characteristic of terrigenous organic matter (i.e. C_{29} steranes, waxy *n*-alkanes and $\%C_{24}$ tetracyclic terpane (Fig. 56, Fig. 57 & Fig. 59)) are not in abundance in the lacustrine section and therefore do not support an interpretation of high hopane concentrations resulting from terrigenous organic matter.

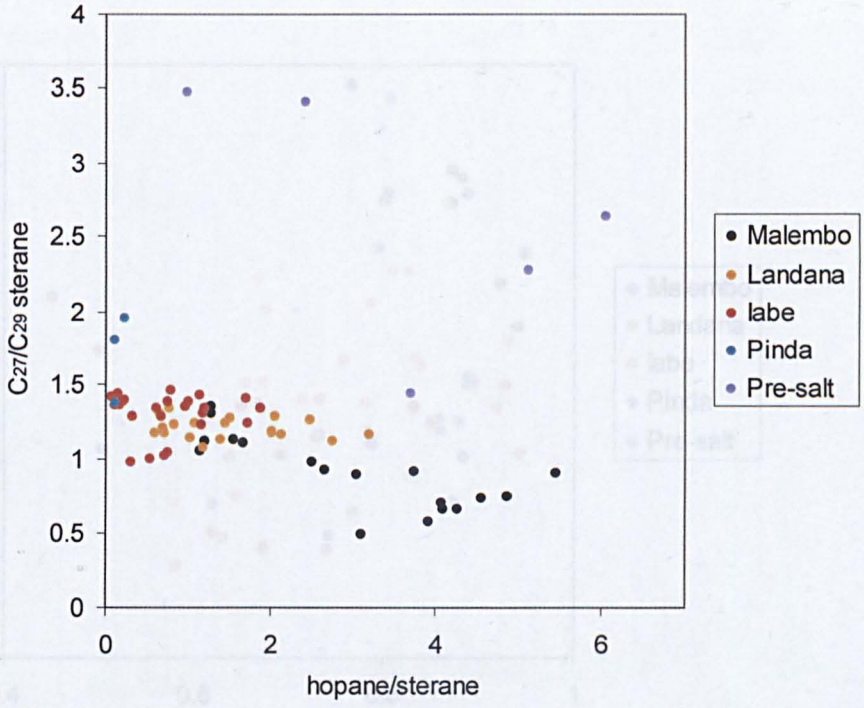

Fig. 57 Cross plot of the C_{27}/C_{29} sterane parameter and the hopane/sterane parameter for all Angolan source rocks.

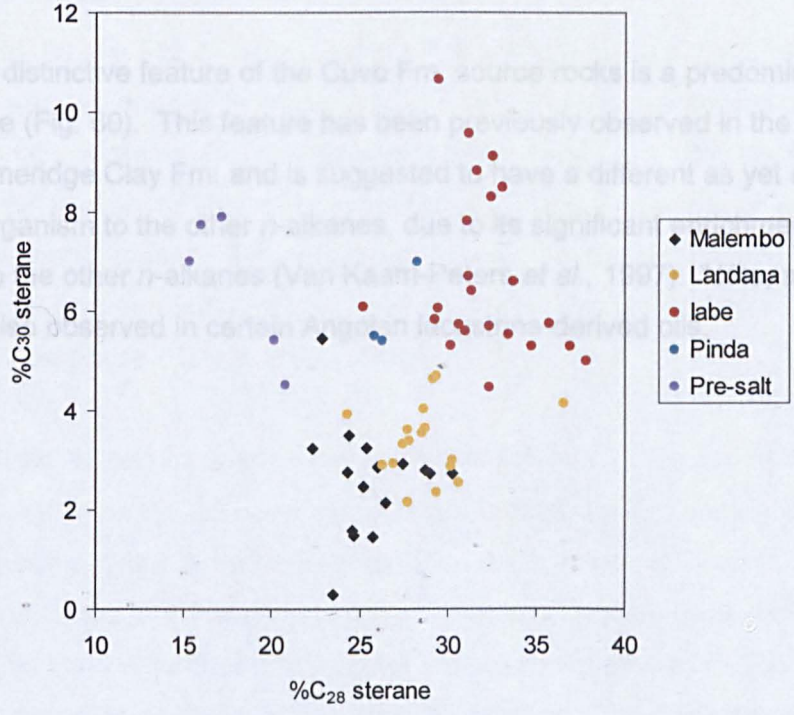

Fig. 58 Cross plot of the $\%C_{30}$ sterane parameter and the $\%C_{28}$ sterane parameter for all Angolan source rocks.

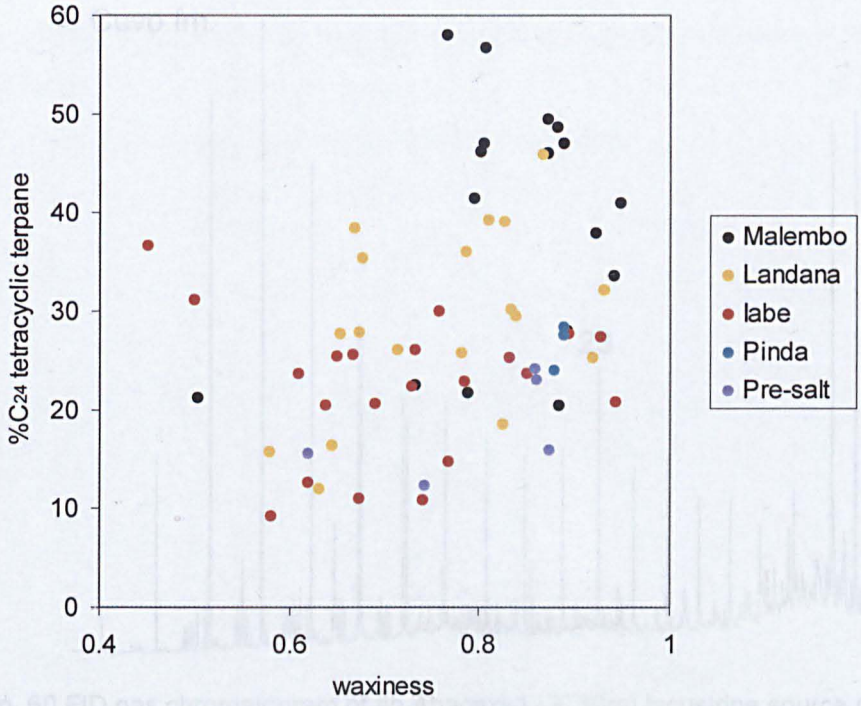

Fig. 59 Cross plot of the $\%C_{24}$ tetracyclic terpane parameter and the $nC_{17}/(nC_{17}+nC_{27})$ (or waxiness) parameter for all Angolan source rocks.

A distinctive feature of the Cuvo Fm. source rocks is a predominance of the *n*-C_{23} alkane (Fig. 60). This feature has been previously observed in the marine North Sea Kimmeridge Clay Fm. and is suggested to have a different as yet unidentified source organism to the other *n*-alkanes, due to its significant enrichment in ^{13}C relative to the other *n*-alkanes (Van Kaam-Peters *et al.*, 1997). Note, a predominant *n*-C_{23} is also observed in certain Angolan lacustrine-derived oils.

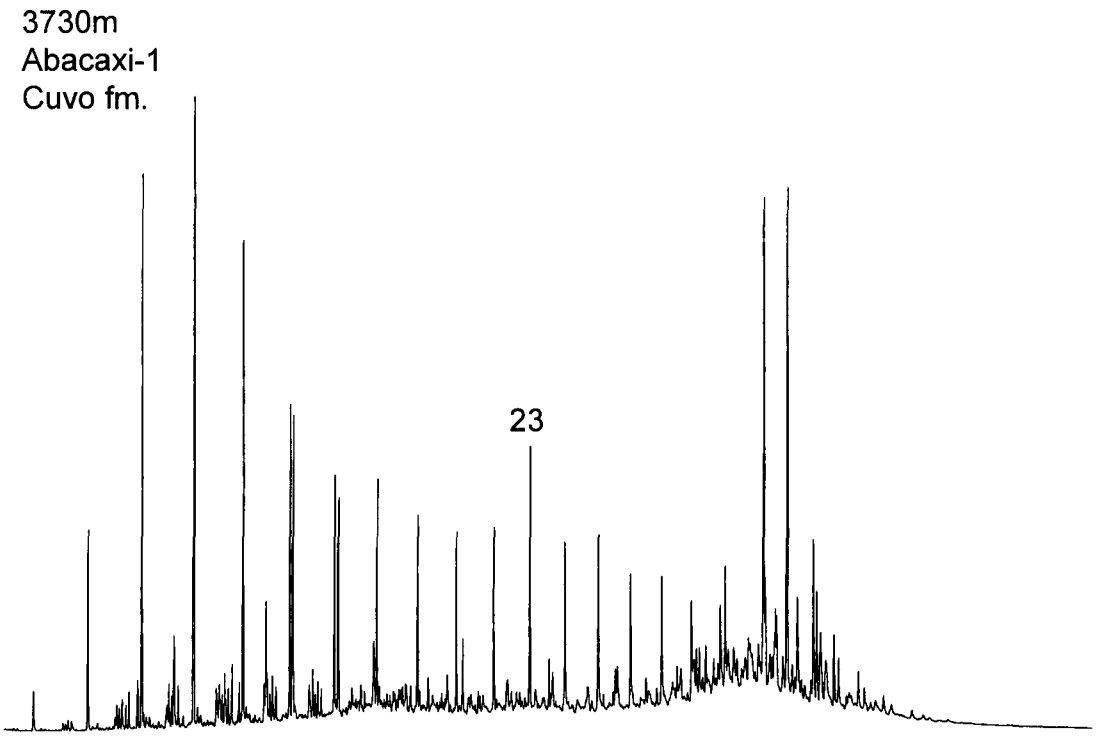

Fig. 60 FID gas chromatogram of an Abacaxi-1 (3730m) lacustrine source rock to illustrate the elevated abundance of *n*-C_{23} alkane.

4.2.3.2 Post-salt Cretaceous source rocks

Fig. 58 and Fig. 57 show that the Pinda and Iabe Gps. have high %C_{30} steranes and low hopane to sterane ratios, reflecting the marine nature of the depositional environment. They also have lower %C_{24} tetracyclic terpane ratios (Fig. 59) than the remaining Post-salt source rocks. This is perhaps a reflection of the low terrestrial contributions to the marine basin due to increased distance of the depositional environment from the coastline, during this period known to be a marine transgressive phase (Katz & Mello, 2000). .

Changes can be seen in the distribution of the C_{27}, C_{28} C_{29} and C_{30} 5α(H), 14α(H), 17α(H), 20R steranes throughout the Post-salt section (Fig. 61). The sterane distributions can be broadly separated into three main sterane facies types. Fig. 61 shows m/z 217 mass chromatograms from Girassol-1 well, but comparable variability in carbon number distributions are seen in other wells. The variability in carbon number facies occur at the group boundaries. The Cretaceous Iabe Gp. has a distinctive high C_{28} sterane (and also as mentioned earlier a high C_{30} sterane) representing high contributions from marine algae, this probably being a reflection of the more open marine nature of the depositional environment. The Landana and

Malembo sterane facies will be discussed in section 4.2.3.3. Fig. 58 shows that the Iabe Gp. (excluding some well 4-26-1AT samples) is clearly distinguished from the remaining stratigraphy by high abundance of C_{28} steranes relative to the C_{27} to C_{30} steranes.

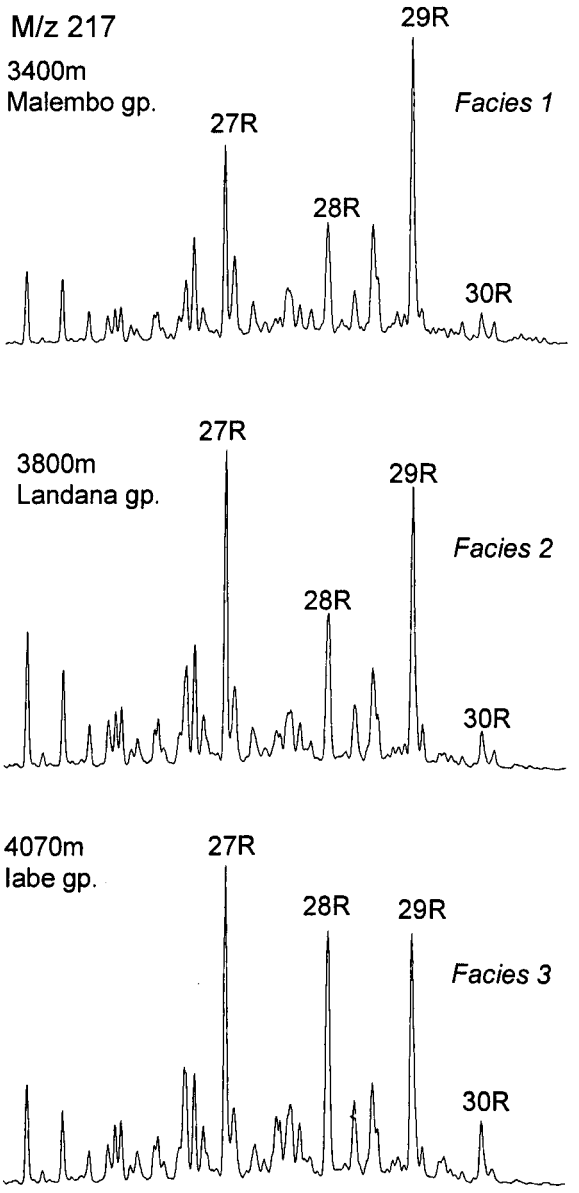

Fig. 61 M/z 217 chromatograms showing variation in the distribution of C_{27}, C_{28} C_{29} and C_{30} 5α(H), 14α(H), 17α(H), 20R steranes between the Post-salt marine Iabe, Landana and Malembo Gp. source rocks. These data are from Girassol-1, but comparable variability in carbon number distribution are seen in other wells. Facies 1 is characterised by high C_{29} to C_{27} sterane ratio, facies 2 has high C_{27} relative to C_{29} sterane, and facies 3 has abundant C_{28} and C_{30} steranes relative to facies 1 and 2.

4.2.3.3 Post-salt Tertiary source rocks

The Landana Group represents a regressive interval during the transition from the marine-dominated Iabe to the more terrestrially-influenced Malembo Gp., and comprises near-shore clastics and carbonates (Brice *et al.,* 1982). The molecular biomarker signature of the Landana Gp. reflects this transition, essentially comprising intermediate biomarker composition between the Malembo and Iabe Gps. (Fig. 57 to Fig. 59). The sterane facies of the Landana Gp. shows a low relative abundance of C_{28} and C_{30} steranes and a C_{27} sterane greater then C_{29} sterane.

The Malembo Gp. sterane facies (Fig. 61) has a distinctive high relative abundance of C_{29} sterane compared to C_{27} sterane and a low relative abundance of C_{28} and C_{30} steranes. The higher abundance of C_{29} steranes in the Malembo Gp. (Fig. 56 & Fig. 57) suggests higher terrestrial contributions to the depositional environment, and is consistent with bulk geochemical and other biomarker indicators for terrestrial organic matter [(e.g. a high abundance of C_{24} tetracyclic terpane relative to tricyclic terpanes (Fig. 59), and a higher abundance of oleanane relative to C_{30} 17α(H), 21β(H) hopane (Fig. 62)]. There is little stratigraphic variation in the *n*-C_{17}/(*n*-C_{17}+*n*-C_{27}) parameter which is a measure of the short to long chain *n*-alkanes. Distributions skewed towards medium to high molecular weight *n*-alkanes, especially with predominant C_{27}, C_{29} and C_{31} homologues, have been described as an indication of long-chain lipid contributions from higher plants (Tissot & Welte, 1984; Mello *et al.,* 1988). Due to the high terrestrial inputs to the Malembo Gp. it might therefore have been expected to contain an abundance of waxy *n*-alkanes. A high abundance of C_{24} tetracyclic terpane seen in the Malembo Gp. Is suggested be to be related to a significant input of higher plant material occurring in oils of terrestrial origin (Philp & Gilbert, 1986; Czochanska *et al.,* 1988), including the Brazilian marine deltaic derived oils (Mello *et al.,* 1988a). It should be noted that a high abundance of tetracyclic terpanes has also been reported in the literature as indicators of carbonate and evaporite environments. For example, Connan *et al.* (1986) proposes a halophilic bacterial cell wall source.

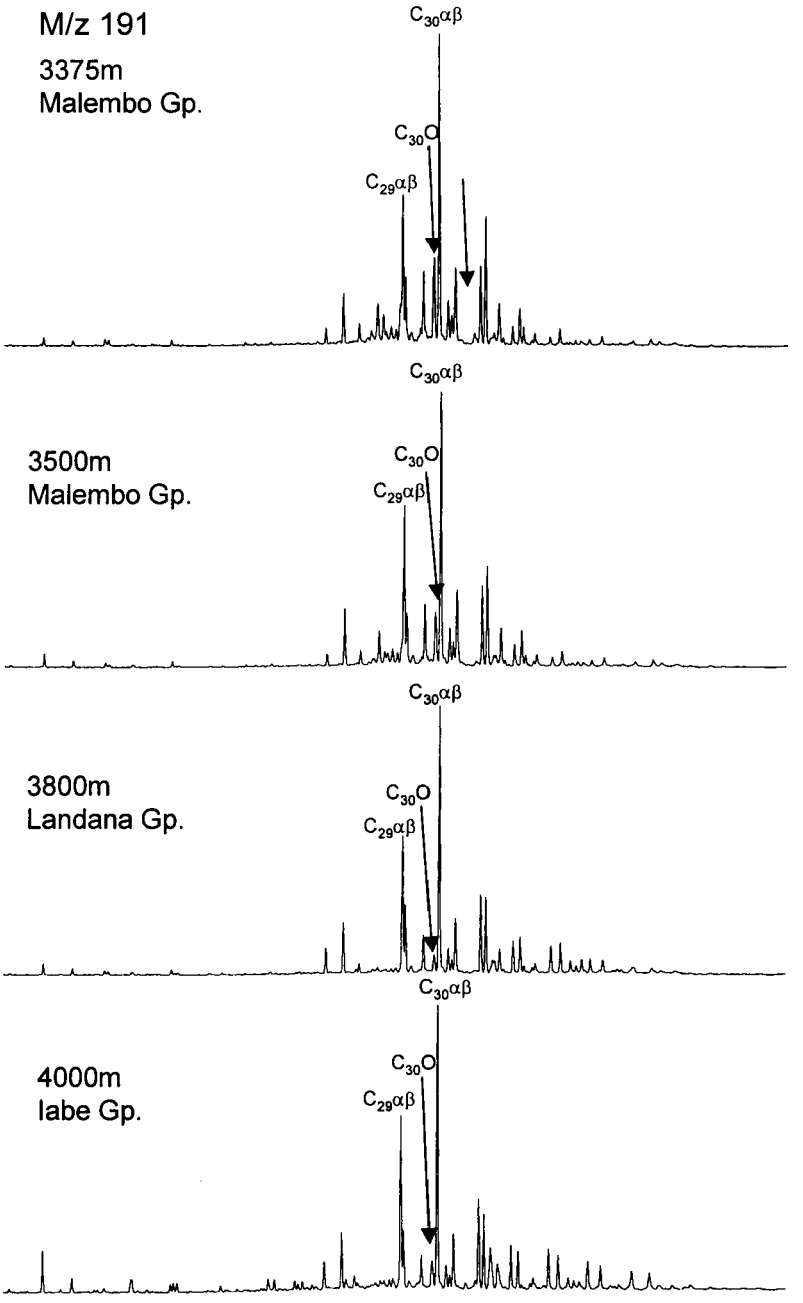

Fig. 62 M/z 191 mass chromatogram of Girassol-1 source rocks from the labe, Landana and Malembo Gps. illustrating the high relative abundance of oleanane in the Malembo Gp.

Oleanane, which is found in high relative abundance in the Malembo Gp. (Fig. 62), is thought to be derived from angiosperms (flowering plants) and has been observed in various oils and source rocks globally of Cretaceous or Tertiary age. In a study of 103 source rocks from Jurassic to Tertiary age the highest relative abundance of oleanane to 17α hopane was observed in a source rock sample from the Malembo Gp. of the Lower Congo Basin (Moldowan *et al.*, 1994). This was attributed to an unusually high biomass of angiosperms in this region during the Late Oligocene (Moldowan *et al.*, 1994).

In support of the Malembo Gp. containing higher contributions from higher plants the it has a high ratio of hopanes to steranes which may result from either, a higher contribution to the sediments of higher plant inputs and/or a more oxic depositional environment. A more oxic depositional environment would lead to preferential degradation of marine organic matter which more suceptive to degradation and hence relative enrichment of terrigenous organic matter.

4.2.4 Water column stratification and salinity

4.2.4.1 Pre-salt source rocks

High abundances of low molecular weight (C_{20}-C_{26}) tricyclic terpanes relative to hopanes are observed in the Pre-salt Gp. samples (Fig. 63). A depositional environment control on tricyclic terpane abundances (including extended tricyclic terpanes up to C_{54}) has been suggested whereby organisms contributing tricyclic terpane precursors are said to thrive in moderate salinity (e.g. saline lacustrine and marine carbonate) environments and are suppressed by hypersaline and freshwater conditions (de Grande *et al.,* 1993). Although the specific source of tricyclic terpanes is unknown, their ubiquitous occurrence in oils and sediments is suggested to imply a microbial or algal origin (Aquino Neto *et al.,* 1983). Tricyclic terpane abundances are known to increase with maturity due to their generation from kerogen at higher thermal maturity (Peters & Moldowan, 1993; Kruge *et al.,* 1990) and their greater thermal stability than hopanes, therefore the ratio should be applied with caution. High concentrations of both low and high molecular weight tricyclic terpanes have been observed in Tasmanite oil shales inferring the unicellular green alga *tasmanites* as one possible origin (Greenwood *et al.,* 2000). Note, however that high molecular weight tricyclic terpanes (>C_{26}) have been observed in abundance in source rocks where no identifiable tasmanites have been found (Perez-Infante *et al.,* 1996) suggesting that alternative sources must exist.

Gammacerane was originally thought to be an indicator of hypersalinity but is now understood to suggest stratification of the water column during sediment deposition (Sinninghe Damsté *et al.,* 1995). Higher salinity is often accompanied by density stratification (Peters and Moldowan, 1993). Fig. 63 shows that the Pre-salt and Post-salt samples have relatively low % gammacerane values of approximately 10-30%, with the exception of the Malembo Gp. which has very low values mainly

less than 5%. This may suggest that the Pre-salt and the remaining Post-salt sediments were deposited under more stratified conditions than the Malembo Gp.

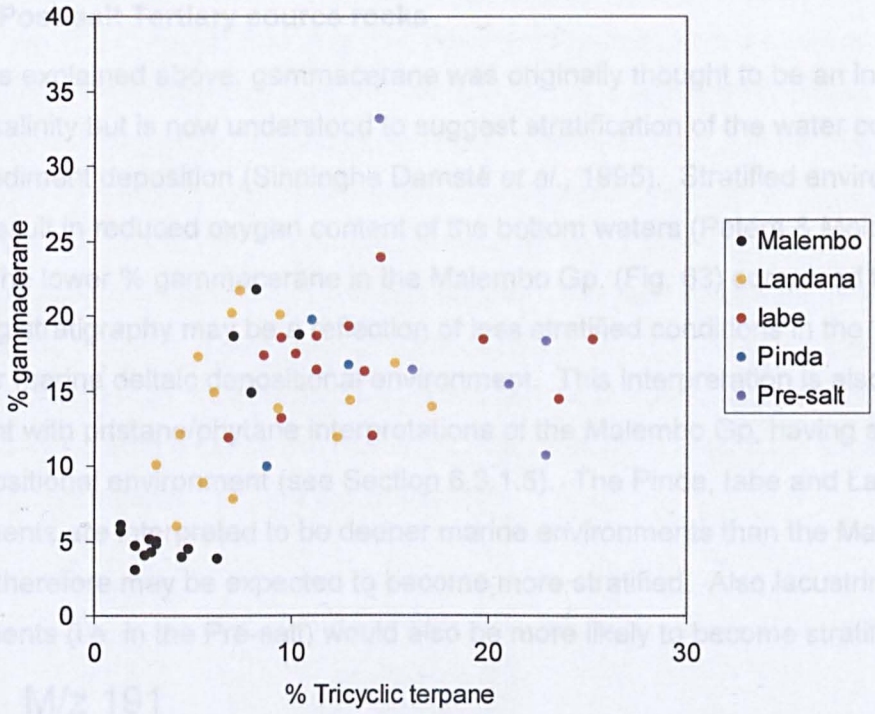

Fig. 63 Cross plot of the % gammacerane parameter and the % tricyclic terpane parameter for all Angolan source rocks.

Pregnane has been associated with hypersaline environments (Peters & Moldowan, 1993). Hypersaline lacustrine source rocks have been reported in Angola (Burwood *et al.,* 1990), and it might therefore be expected that if the Cuvo Fm. source rock samples in this thesis were deposited in a hypersaline lacustrine environment the samples would contain elevated levels of pregnane compared to the remaining stratigraphy. However, there is no significant stratigraphic variation in pregnane, implying that the samples are not from hypersaline environments.

4.2.4.2 Post-salt Cretaceous source rocks

The Iabe Gp. source rocks also show high abundances of low molecular weight tricyclic terpanes (even at low maturity as in the Abacaxi-1 samples), suggesting that they were deposited in moderate salinity conditions (Fig. 63). The Iabe Gp. source rocks in Funda-3 also show high abundances of high molecular weight tricyclic terpanes ranging for C_{28}-C_{35} (Fig. 64). Extended tricyclic terpanes are also observed in certain Angolan oils (see Section 6.3.1.5), where they may

dominate the triterpane distribution. They are also found in Brazilian oils of moderate salinity (i.e. lacustrine saline and marine carbonate derived oils; Mello *et al.*, 1988a).

4.2.4.3 Post-salt Tertiary source rocks

As explained above, gammacerane was originally thought to be an indicator of hypersalinity but is now understood to suggest stratification of the water column during sediment deposition (Sinninghe Damsté *et al.*, 1995). Stratified environments usually result in reduced oxygen content of the bottom waters (Peters & Moldowan, 1993). The lower % gammacerane in the Malembo Gp. (Fig. 63) compared to the remaining stratigraphy may be a reflection of less stratified conditions in the shallower marine deltaic depositional environment. This interpretation is also consistent with pristane/phytane interpretations of the Malembo Gp, having a more oxic depositional environment (see Section 6.3.1.5). The Pinda, Iabe and Landana environments are interpreted to be deeper marine environments than the Malembo Gp. and therefore may be expected to become more stratified. Also lacustrine environments (i.e. in the Pre-salt) would also be more likely to become stratified.

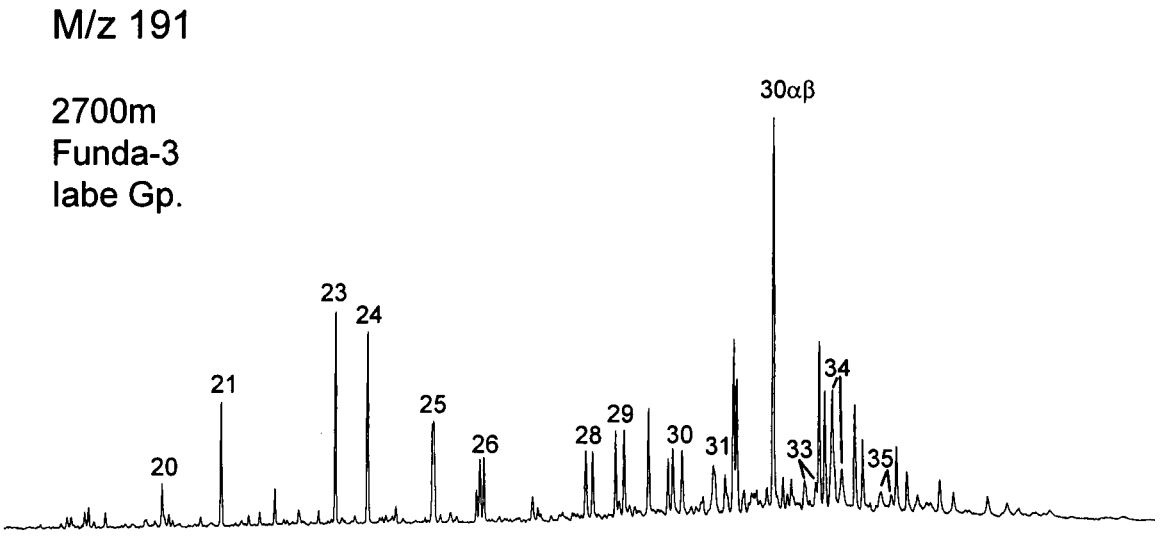

Fig. 64 M/z 191 chromatogram of a Funda-3 source rock sample to illustrate the high abundance of low molecular weight tricyclic terpanes and the occurrence of extended tricyclic terpanes (tricyclic terpane carbon numbers marked).

4.2.5 Freshwater lacustrine indicators

The presence of the 2α-methyl and 3β-methyl hopanes represents particular bacterial inputs to the sediments; 2-methyl hopanes are most likely but not exclusively derived from cyanobacteria (Summons *et al.*, 1999), and are often abundant in carbonate environments (Farrimond *et al.*, 1990); 3-methylhopanoids are

found in methane oxidizing bacteria (i.e. methylotrophic and methanotrophic bacteria important in freshwater lacustrine settings where methanogenesis dominates over sulphate reduction). Pre-salt enrichment of 3β- methyl hopanes in most Pre-salt samples (Fig. 65) suggests that they may have been deposited in a freshwater environment. The shallowest Cuvo Fm. sample, which is significantly poorer in 3-methylhopanes, may reflect a variation in facies. The use of the 2-methyl hopane contributions as a tool to determine carbonate environments seems to have limited use as there appears to be considerable overlap between the Post-salt groups in Fig. 65. Interestingly, the Tuenza Fm. which is suggested to be a carbonate facies (Brice *et al.,* 1982) is similar in methylhopane composition to the Pre-salt Cuvo samples, showing enrichment in 3-methylhopanes characteristic of fresh water environments. As it is a derived from a carbonate rich unit it might therefore have been expected to contain high abundances of 2-methyl hopanes.

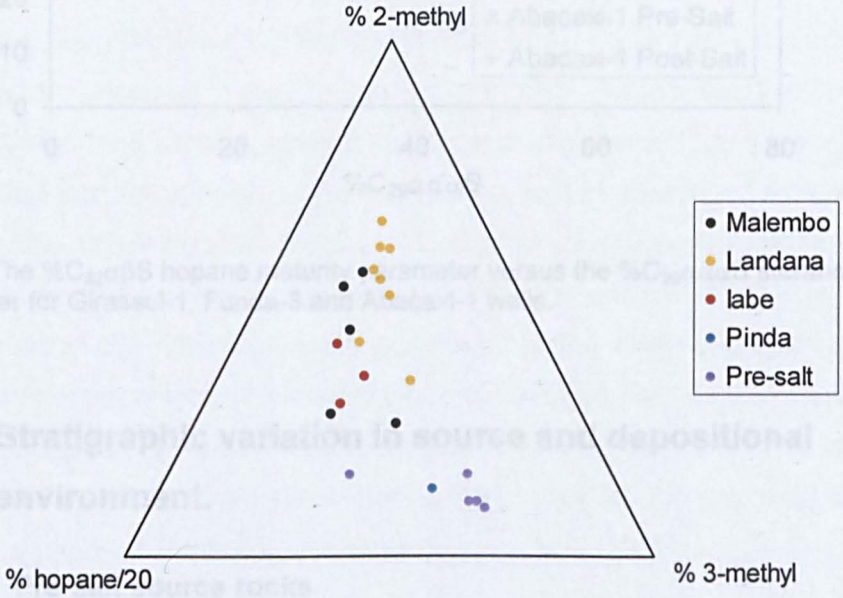

Fig. 65 Ternary plot of 2 α-methyl- αβ-hopane, 3 β-methyl- αβ-hopane and αβ-hopane (divided by 20) for the Angolan source rocks.

4.3 Overview

4.3.1 Maturity

Fig. 66 is a cross plot of two maturity parameters to summarize the relative maturities of the wells studied. Due to the low thermal maturity of 4-26-1AT the parameters could not be calculated for this well. Funda-3 samples and the Abacaxi-1

Pre-salt samples are most mature, having reached (or nearly reached) the end point for both parameters, with both sets of samples being interpreted as having reached the main phase of oil generation. Girassol-1 is immature with respect to oil generation but is approaching early oil generation values in the lower part of the well. Abacaxi-1 Post-salt samples and samples from 4-26-1AT are considerably less mature than the remaining source rocks, and are immature with respect to oil generation.

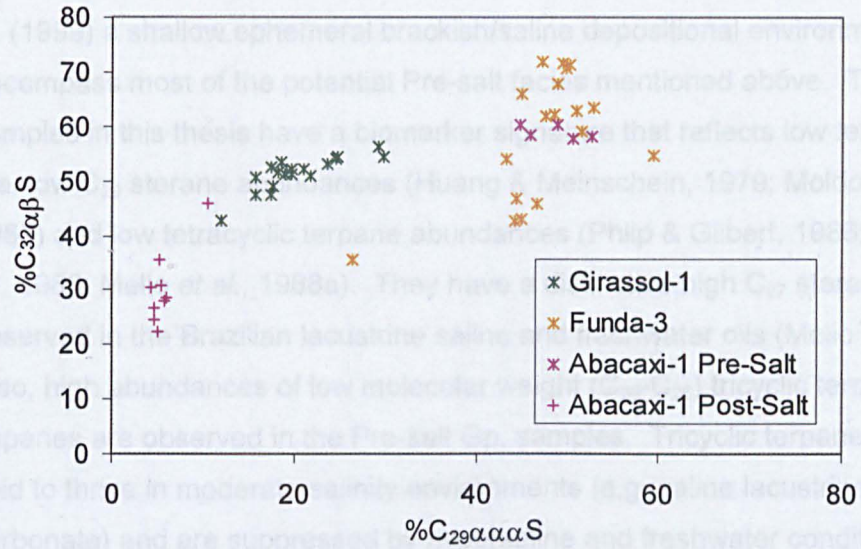

Fig. 66 The $\%C_{32}\alpha\beta S$ hopane maturity parameter versus the $\%C_{29}\alpha\alpha\alpha S$ sterane maturity parameter for Girassol-1, Funda-3 and Abacaxi-1 wells.

4.3.2 Stratigraphic variation in source and depositional environment.

4.3.2.1 Pre-salt source rocks

The lacustrine Pre-salt facies and the marine Post-salt source rock facies can be distinguished using the C_{26}/C_{25} tricyclic terpane ratio and the hopane to sterane ratio (Fig. 51). In general the lacustrine source rocks have high hopane/sterane ratios (>2) and C_{26}/C_{25} tricyclic terpane ratios > 1, and the marine source rocks have low hopane/sterane ratios (<2) and C_{26}/C_{25} tricyclic terpane ratios < 1. These ratios have been previously applied in the literature to differentiate oils and source rocks of lacustrine and marine origin in this region (Burwood, 1999; Schiefelbein *et al.*, 1999; Cole *et al.*, 2000).

Literature reports regarding the depositional environment of lacustrine Pre-salt sections in Angola suggest fresh, brackish, hypersaline and alkaline conditions may occur (Burwood *et al.,* 1990; Katz & Mello, 2000). In the Lower Congo Basin this sequence is termed the Bucomazi Formation and its geochemical properties are documented in great detail by Burwood *et al.* (1990, 1992, 1995) and Burwood (1999). However, the Pre-salt samples in this study are from its lateral equivalent the Cuvo Fm. of the Kwanza Basin. There is limited literature on this formation, Coward *et al.* (1999) describe a fluvial/ transitional depositional environment and Burwood *et al.* (1999) a shallow ephemeral brackish/saline depositional environment, which encompass most of the potential Pre-salt facies mentioned above. The particular samples in this thesis have a biomarker signature that reflects low terrestrial inputs, (i.e. low C_{29} sterane abundances (Huang & Meinschein, 1979; Moldowan *et al.,* 1985) and low tetracyclic terpane abundances (Philp & Gilbert, 1986; Czochanska *et al.,* 1988; Mello *et al.,* 1988a). They have a distinctive high C_{27} sterane a feature also observed in the Brazilian lacustrine saline and freshwater oils (Mello *et al.,* 1988a). Also, high abundances of low molecular weight (C_{20}-C_{26}) tricyclic terpanes relative to hopanes are observed in the Pre-salt Gp. samples. Tricyclic terpane precursors are said to thrive in moderate salinity environments (e.g. saline lacustrine and marine carbonate) and are suppressed by hypersaline and freshwater conditions (de Grande *et al.,* 1993), providing evidence for a moderate salinity lacustrine environment. However, in contrast methylhopane data for the Pre-salt sections show an enrichment of 3β-methylhopanes suggesting that they may have been deposited in a freshwater environment. An interpretation of the Cuvo Fm. as a freshwater deposit is further supported by evidence in Section 6.4.1 whereby two oils interpreted as being freshwater-derived on the basis of their isotopic data are the only two oils enriched in 3β-methylhopanes (Maboque-1 and Seria-1).

4.3.2.2 Post-salt Cretaceous source rocks

The Pinda Gp. samples are reported in the literature to be deposited during a period of carbonate deposition (Cole *et al.,* 2000). The Pinda Gp. has elevated %$C_{35}\alpha\beta$ hopane abundances, high values are typical of anoxic marine conditions (Ten Haven *et al.,* 1988; Peters & Moldowan, 1991), specifically sulphur-rich environments (Bishop & Farrimond, 1995). In such environments C_{35} bacteriohopanetetrol skeletons are selectively preserved through incorporation of sulphur into the sidechain during diagenesis (Peters & Moldowan, 1991). This most likely occurs in anoxic environments low in iron; i.e. non-clastic carbonate or

evaporitic environments (Adam *et al.,* 1993). This may explain the high abundance of C_{35} hopanes in the Pinda Gp. source rocks, which were deposited in this period of carbonate deposition (Cole *et al.,* 2000). The Pinda Gp. samples also have a low pristane to phytane ratios consistent with interpretations of oxygen-depleted depositional conditions.

The Pinda and Iabe Gps. are known to represent a marine transgressive phase (Katz & Mello, 2000). For the Pinda and Iabe Gps. C_{24} tetracyclic terpane abundances are low, interpreted to represent low terrigenous contributions (Philp & Gilbert, 1986; Czochanska *et al.,* 1988; Mello *et al.,* 1988a). The interpretation of low terrestrial contributions to the marine basin may relate to the increased distance of the depositional environment from the coastline, during this period known to be a marine transgressive phase. The Iabe Gp. sediments are reported in the literature to represent outer shelf to slope facies (Katz & Mello, 2000). The Pinda and Iabe Gps also have high $\%C_{30}$ steranes and low hopane to sterane ratios, reflecting the marine nature of the depositional environment.

A distinctive feature of the Iabe Gp. is a high C_{28} sterane (and also as mentioned earlier a high C_{30} sterane) representing high contributions from marine algae, this probably being a reflection of the more open marine nature of the depositional environment. The Iabe Gp. source rocks also show high abundances of low molecular weight tricyclic terpanes (even at low maturity as in the Abacaxi-1 samples) suggesting they were deposited in moderate salinity conditions (de Grande *et al.,* 1993). The Iabe Gp. source rocks in Funda-3 also show high abundances of extended tricyclic terpanes observed in Brazilian oils of moderate salinity (i.e. lacustrine saline and marine carbonate derived oils).

4.3.2.3 Post-salt Tertiary source rocks

The molecular biomarker signature of the Landana Gp. reflects a transitional, group essentially comprising an intermediate biomarker composition between the Malembo and Iabe Gps. This is consistent with a literature report for the Landana Gp. which suggests that it represents a regressive interval during the transition from the marine-dominated Iabe to the more terrestrially-influenced Malembo Gp., and comprises near-shore clastics and carbonates (Brice *et al.,* 1982).

The Malembo Gp. contains higher pristane/phytane values than the remaining Post-salt samples and a very low abundance of gammacerane, interpreted as showing the Malembo Gp. to have been deposited under more oxic depositional conditions (Didyk *et al.,* 1978) and a less stratified environment of deposition (Sinninghe Damsté *et al.,* 1995). This is consistent with literature interpretations of the Malembo Gp. representing a regressive sequence (Brice *et al.,* 1982; Cole *et al.,* 2000). The shallower water depths as a result of the regressive nature of the unit may lead to less stratified conditions making it less likely for anoxic conditions to develop. This is also consistent with bulk geochemical interpretation (in Section3.3.2) for the Malembo Gp. suggesting it contains higher abundances of terrestrial organic matter. The biomarker composition of the Malembo Gp. can also be seen to suggest higher terrigenous contributions compared to the remaining Post-salt units. These features include a high abundance of C_{29} steranes (Huang & Meinschein, 1979; Moldowan *et al.,* 1985), higher hopane/sterane ratio, higher abundance of C_{24} tetracyclic terpane (Philp & Gilbert, 1986; Czochanska *et al.,* 1988; Mello *et al.,* 1988a), and in Girassol-1 higher oleanane abundances (Moldowan *et al.,* 1994). From an exploration perspective an important point to note is that with the exception of the sterane composition the Malembo Gp. samples from Funda-3 have biomarker compositions most similar to the Iabe Gp. (and sometimes the Landana Gp.) as opposed to the remaining Malembo Gp. samples (e.g. hopane/sterane, C_{27}/C_{29} sterane, $\%C_{24}$ tetracyclic terpane, % tricyclic terpane and % gammacerane parameters). It should be noted that they also differ in their hydrocarbon potential from other Malembo samples (see Section 3.3.2), comprising excellent type II oil-prone organic matter.

Ratio/ Parameters	Stratigraphic Groups				
	Pre-salt (5)	Pinda (3)	Iabe (25)	Landana (19)	Malembo (19)
C_{26}/C_{25} tricyclic terpane	>1	<1	<1	<1	<1
hopane/ sterane	1.0-6.0	0.1-0.2	0.1-1.9	0.6-3.2	1.2-5.5
$\%C_{28}$ sterane	15-21	26-28	25-40	24-37	22-30
$\%C_{30}$ sterane	8-5	5-7	2-11	2-5	<5
pristane/phytane	1.7-2.8	1.3-1.4	0.3-2.0	0.7-3.0	0.6-2.8
C_{27}/C_{29} sterane	1.4-3.5	1.4-2.0	1.0-1.5	1.1-1.3	0.5-1.3
$\%C_{35}\alpha\beta$	32-44	54-58	24-43	28-46	19-48
% tricyclic terpane	14-23	9-13	7-38	3-17	1-10
$\%C_{24}$ tetracyclic terpane	12-24	24-28	9-43	12-46	16-58
% gammacerane	11-33	10-20	12-49	6-22	3-22
waxiness	0.6-0.9	0.9-0.9	0.2-0.9	0.5-0.9	0.2-0.9
% 2-methyl	26-55	34-65	30-41	12.7	9-16
% 3-methyl	15-39	16-38	20-28	51.9	35-64
comments	predominant n-C23 alkane		abundant extended tricyclic terpanes		

* only one sample analysed

Table 3 Summary table for Angolan source rock biomarker parameters. (Number of samples analysed indicated in brackets. Note, for certain samples not all parameters could be calculated.)

5 Molecular analysis of the kerogen-bound hydrocarbons in source rocks.

This chapter will address the information potential of the biological marker compounds in the kerogen-bound fraction of the Angolan source rocks. It will involve both quantitative and qualitative analysis of the hydrocarbons in the aliphatic fractions of the hydropyrolysates. A total of 31 source rock samples have been selected for analysis from the 65 samples that were analysed for free (bitumen faction) biomarkers.

5.1 Maturity analysis.

Fig. 1 and Fig. 2 compare the distribution of the free (bitumen fraction) and kerogen-bound biomarkers, for the same source rock sample. The biomarkers released by hydropyrolysis from the kerogen fraction of the source rocks preserve a less mature biomarker profile than the corresponding free biomarkers, consistent with previous literature reports (Love *et al.,* 1995; Bishop *et al.,* 1998; Murray *et al.,* 1998) this is also been previously observed in studies using other methods of pyrolysis, (e.g. Seifert, 1978; Peters *et al.,* 1990). They appear to undergo the same epimerisation reactions as free biomarkers but at a retarded rate, hence they have a more immature biomarker profile (Murray *et al.,* 1998). The immaturity of the kerogen-bound fraction hopanes compared to the free fraction can be seen by the higher relative abundances of the 17β(H), 21α(H) hopanes (or moretanes) compared to the more thermally stable 17α(H), 21β(H) hopanes. The kerogen-bound biomarkers also include the thermodynamically unstable 17β(H) hopane, which is either not found in the free biomarker fractions or found in negligible amounts. The free and kerogen-bound sterane biomarkers both contain ααα and αββ isomers; however, only the kerogen-bound biomarkers contain the less thermodynamically stable βαα steranes, and the αββ isomers are less prominent.

Diasteranes which are known to increase in concentration in the bitumen with maturity (Peters & Moldowan, 1993) are present in the free biomarkers but frequently absent in the bound. Diasteranes are also not generally observed within macromolecular organic matter, thought to be due to the products not being incorporated into the macromolecular material (Seifert, 1978; Philp & Gilbert, 1985;

Fowler & Brooks, 1987). There are two theories to explain absence of diasteranes in bound fractions; firstly, the formation of rearranged sterenes by acid catalysis at an early stage of diagenesis followed by rapid reduction, may thus prevent the possibility of incorporation into the carbon skeleton (Seifert, 1978) i.e. the diasteranes would lack the double bond for attachment. Secondly, excessive steric hindrance of the rearranged sterenes, may result in the lack of ability to become incorporated for reasons of lack of reactivity with other functional groups (Seifert, 1978) i.e. due to the shielded position of the double bond at the C-13-17 position in diasterenes. Another important factor preventing the occurrence of rearranged steroids in bound fractions may be due to the size of the particles in macromolecular fractions, clay catalysis may require interaction between organic molecules and clays and access may not be possible with larger macromolecular units. The presence of diasteranes in the samples may therefore indicate the occurrence of free steranes trapped within the physical macromolecular network, which were not removed during extraction of sediments to eradicate the bitumen fraction prior to hydrogen pyrolysis.

Comparison of the kerogen-bound fraction to free fraction shows a relative increase in the proportion of $C_{29}\alpha\beta$ hopane to $C_{30}\alpha\beta$ hopane in the pyrolysate of the samples (Fig. 1). This can also be observed in previous hydropyrolysis studies whereby, the free fractions show higher C_{30} *versus* C_{29} $\alpha\beta$ hopanes, whereas in the corresponding pyrolysates the reverse can be found (Bishop *et al.,* 1998; Murray *et al.,* 1998). This is thought to be a result of the high temperature employed. Alternatively this may be a result of the bound and free hopanes having different carbon number distribution.

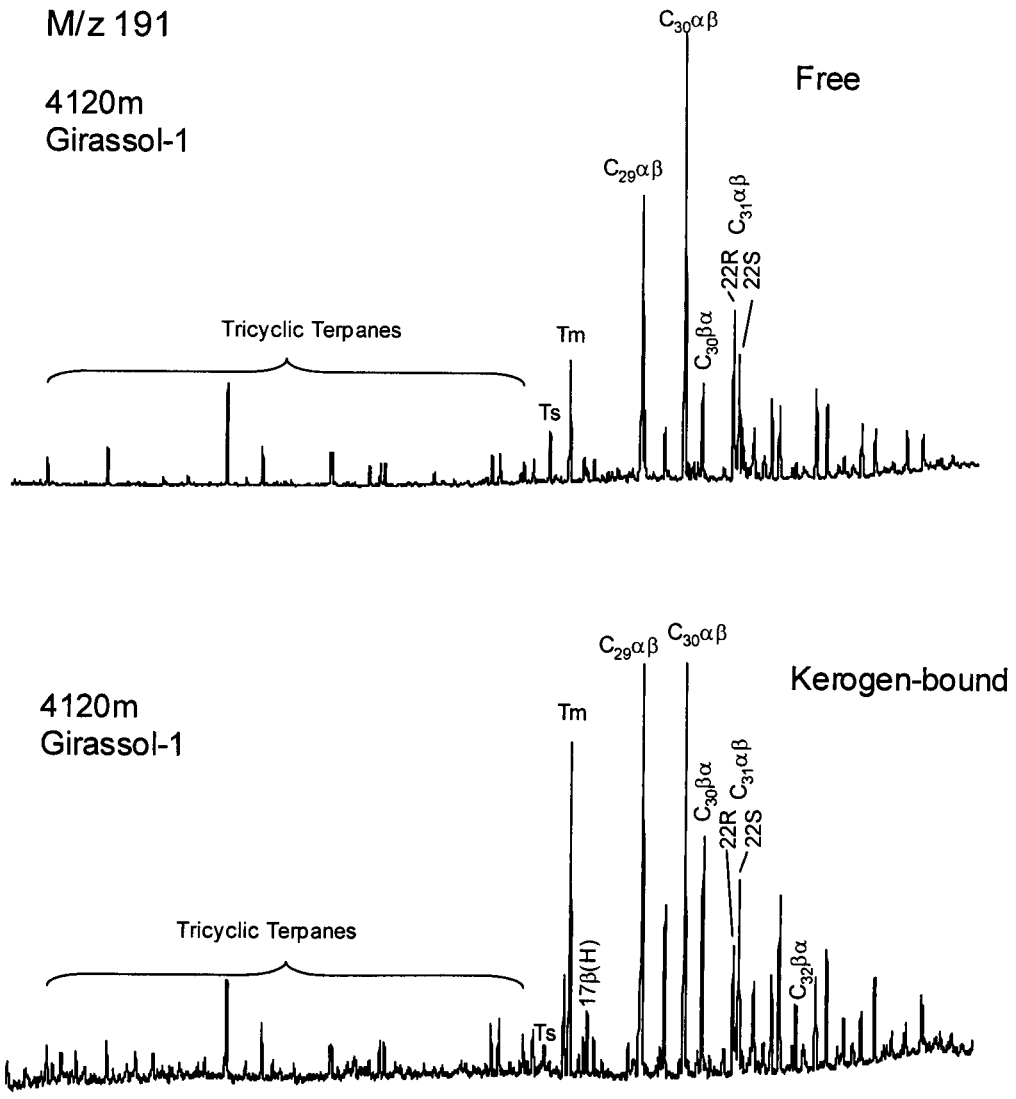

Fig. 1 Comparison of a) kerogen-bound and b) free triterpane biomarkers in a Girassol-1 source rock.

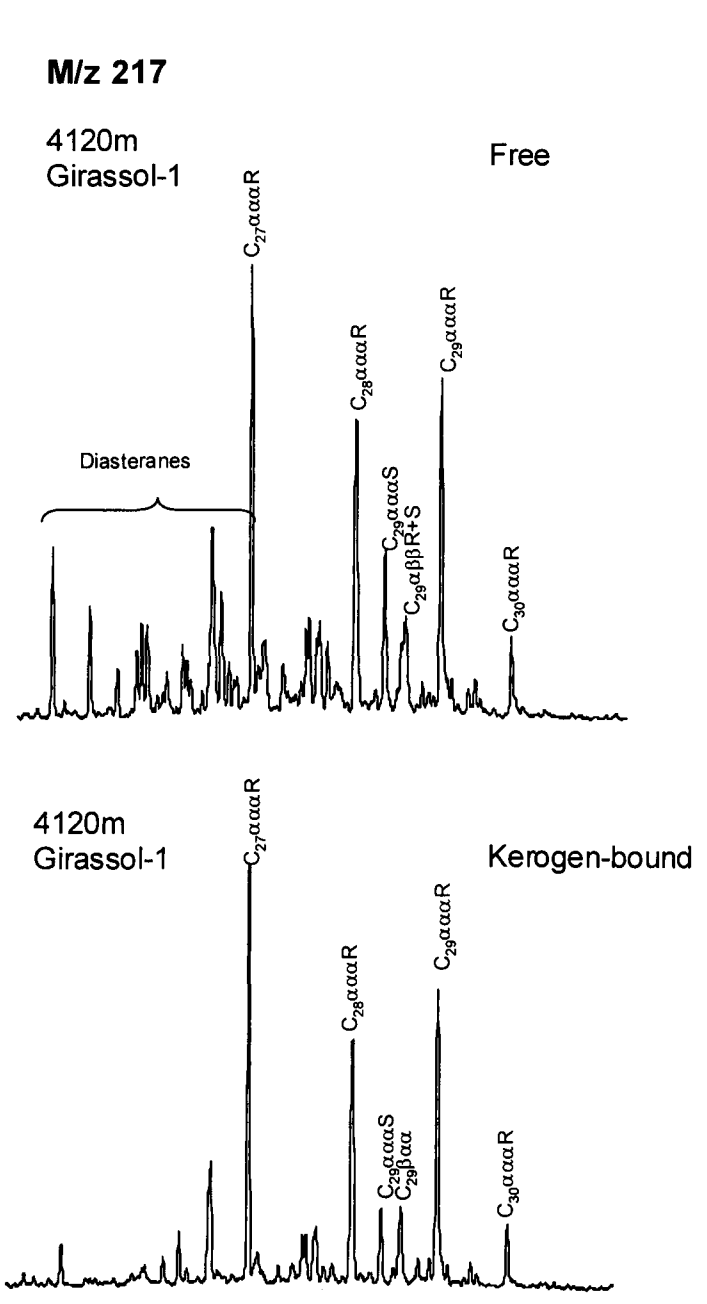

Fig. 2 Comparison of a) kerogen-bound and b) free sterane biomarkers in a Girassol-1 source rock.

Fig. 3 to Fig. 5 show selected free and kerogen-bound hopane and sterane maturity parameters plotted versus depth, and hence progressive maturity for Girassol-1, Funda-3 and Abacaxi-1 wells. The same data for all three wells is combined in maturity parameter cross-plots in Fig. 6 and Fig. 7. The figures confirm that the kerogen-bound biomarkers are consistently less mature than the free biomarkers. The bound $\%C_{30}\beta\alpha$ maturity parameter values are considerably less mature than their free counterparts, and specifically in Girassol-1 and Funda-3 the bound parameter operates over a greater depth range and to higher maturities (i.e. once the free parameter has stopped responding to changing maturity the bound

parameter continues to change). This is a result of biomarker binding into kerogen, which provides steric protection (e.g. Love *et al.,* 1995; Rocha *et al.,* 1997, Murray *et al.,* 1998). This steric hindrance retards isomerisation. As a result of this steric hindrance the thermally less stable 17β(H), 21α(H) hopanes are relatively more abundant in the bound fractions, therefore the moretane (βα)/ hopane (αβ) ratio has not yet reached equilibrium, and is therefore still responding to maturity changes. Data from the most mature well Funda-3 suggests the moretane ratio does not have a less mature end point than the free but instead the free and bound moretane/hopane ratio parameters converge. The greater maturity range covered by the βα/αβ hopane ratio for the bound biomarker fractions compared to the free fractions has been previously observed by Murray *et al.* (1998). Girassol-1 is the only well to show a good gradient with depth for the $\%C_{30}\beta\alpha$ parameter. Variability in the remaining wells may result from facies/input variability. The $C_{30}\beta\alpha/\alpha\beta$ ratio has been previously observed to be affected by facies/ input variations (Rullkötter & Marzi, 1988), which may explain the variability in the remaining wells.

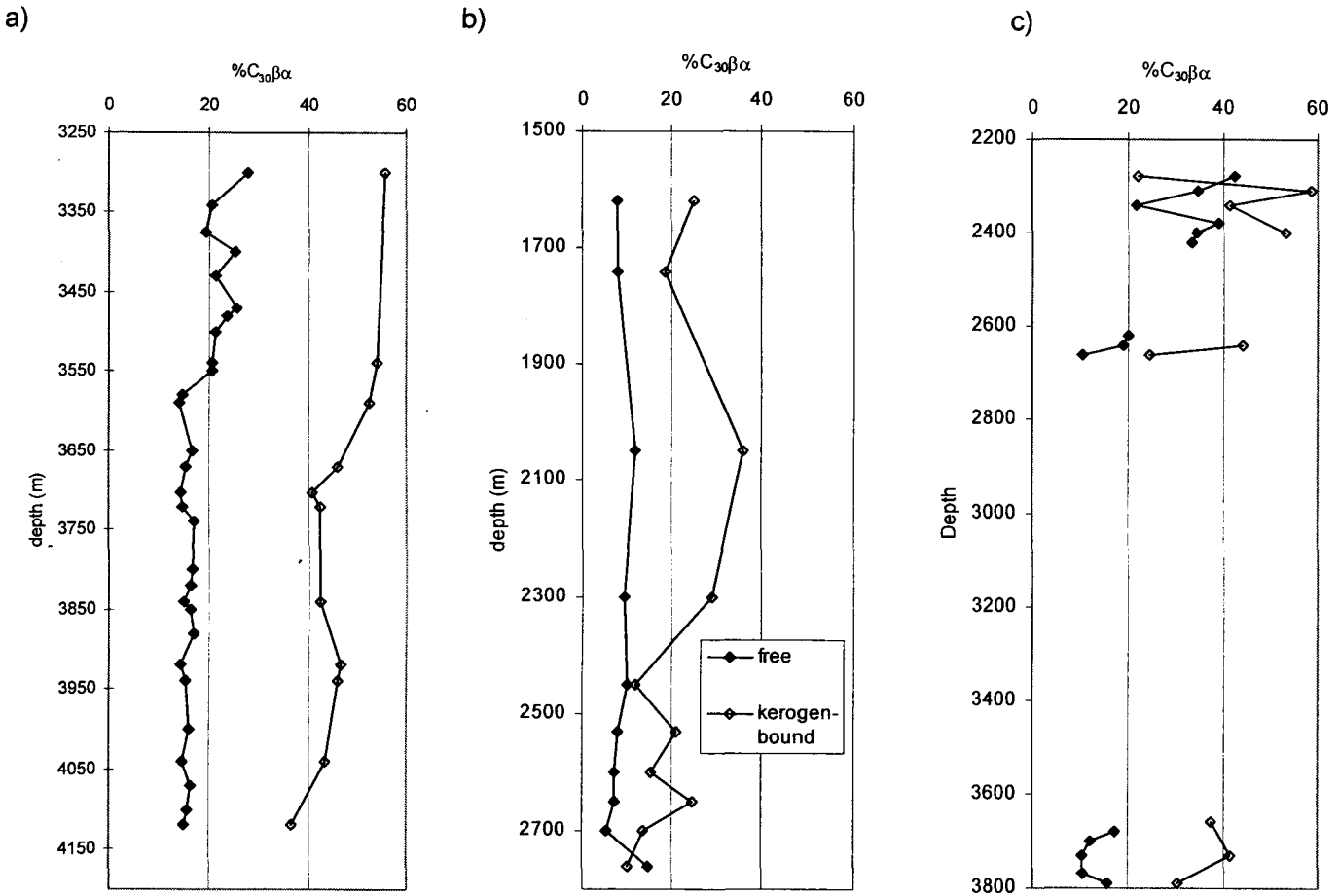

Fig. 3 Maturity parameter $\%C_{30}\beta\alpha$ versus depth and progressive maturity for the kerogen-bound and free hopanes for a) Girassol-1 b) Funda-3 and c) Abacaxi-1 source rocks.

The %$C_{32}\alpha\beta$S maturity parameter for Girassol-1 kerogen-bound biomarkers as with the %$C_{30}\beta\alpha$ parameter operates over a greater depth range and to higher maturites than the free parameter (Fig. 4 & Fig. 7). This may in part be due to steric hindrance in bound biomarkers preventing mineral catalysis at certain sites, or results from the greater stability of the stereoisomer at C-22 in kerogen-bound hopanes; particular as C-22 located on the side-chain of hopanes one of the principal sites of attachment for hopanes to kerogen (Richnow *et al.,* 1992: Adam *et al.,* 1993). Funda-3 well shows the %$C_{32}\alpha\beta$S parameter has reached an endpoint in both the free and kerogen-bound biomarkers. The free biomarkers have reached an end point at approximately 60%, whereas the kerogen-bound biomarkers have reached their end point at the lower value of approximately 50 to 55% (Fig. 4). This is in contrast to Murray *et al.* (1998) where the values for the 22S/(S+R) for the $C_{32}\alpha\beta$ hopanes for the free and bound biomarkers were seen to converge with increasing maturity as equilibrium was reached.

The %$C_{29}\alpha\alpha\alpha$S parameter for the kerogen-bound biomarkers in Girassol-1 appears to be less mature than for the free steranes, and increases with maturity at a similar rate (Fig. 5 & Fig. 7). However in Funda-3, which is a more mature well, there appears to be little difference between the free and bound parameter values.

There is clearly a difference in behaviour between hopanes and steranes. The bound hopanes appear far more retarded in isomerisation than the bound steranes. This may be a result of the closer location of the centres of isomerisation in hopanes (at C-17 C-21 in the ring systems and C-22 in the side chain) to the binding sites (predominantly in the side chain of hopanes) providing greater steric hindrance, whereas in steranes attachment is mainly in the A or B ring which is further away from the majority of the isomeric centres (at C-5, C-14, C-17 and C-20).

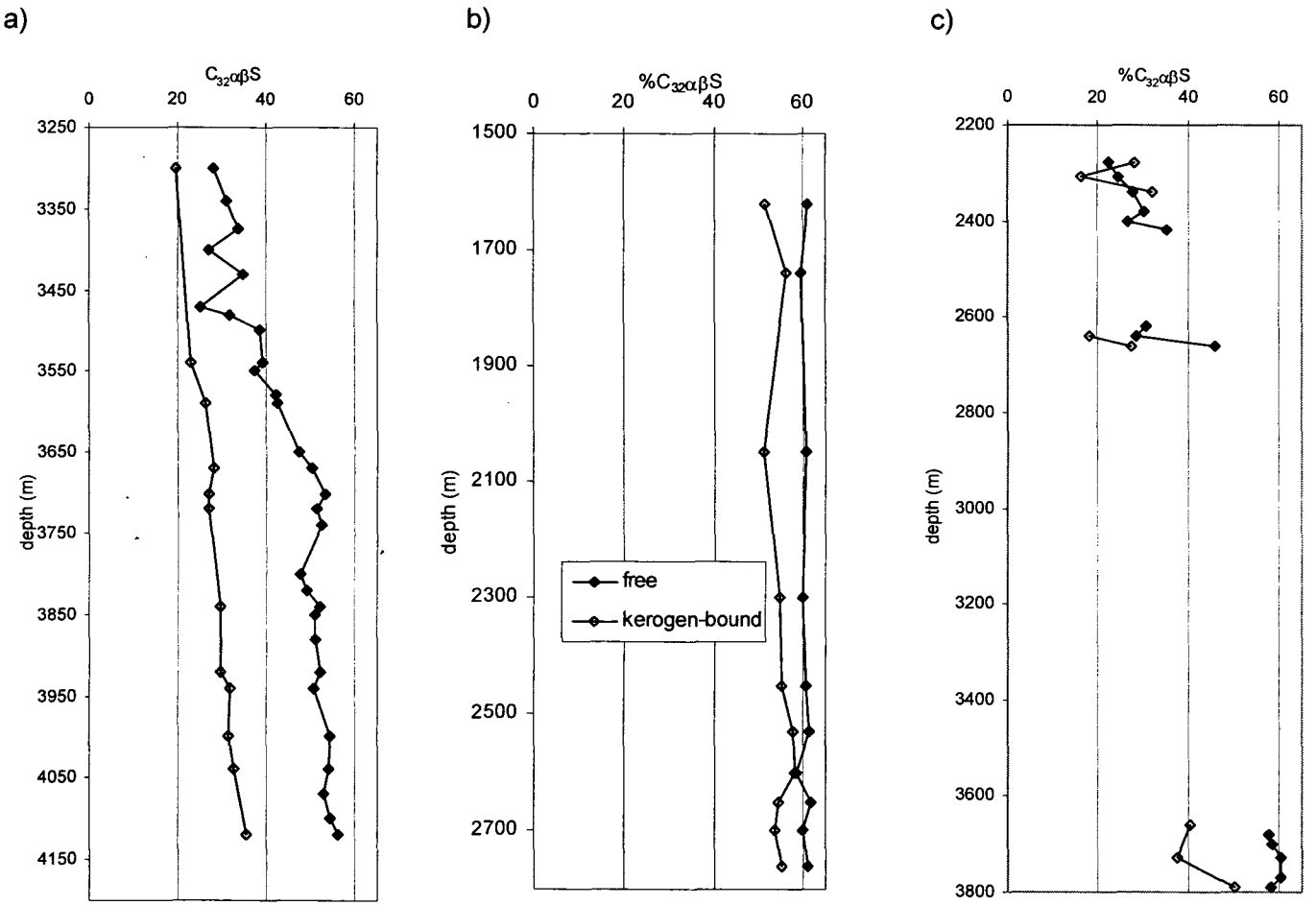

Fig. 4 Maturity parameter $\%C_{32}\alpha\beta S$ versus depth and progressive maturity for the kerogen-bound and free hopanes for a) Girassol-1 b) Funda-3 and c) Abacaxi-1 source rocks.

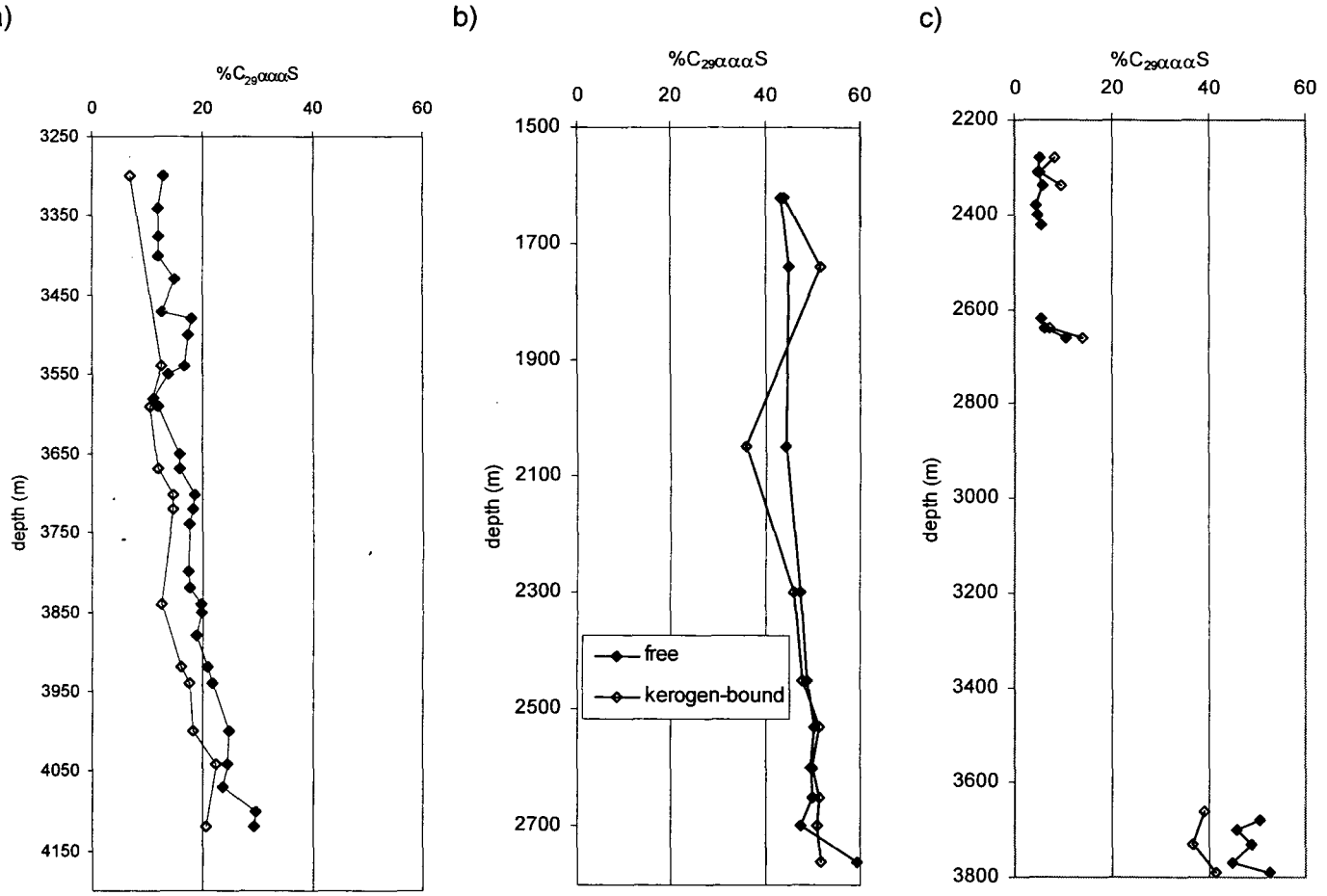

Fig. 5 Maturity parameter $\%C_{29}\alpha\alpha\alpha S$ versus depth and progressive maturity for the kerogen-bound and free steranes for a) Girassol-1 b) Funda-3 and c) Abacaxi-1 source rocks.

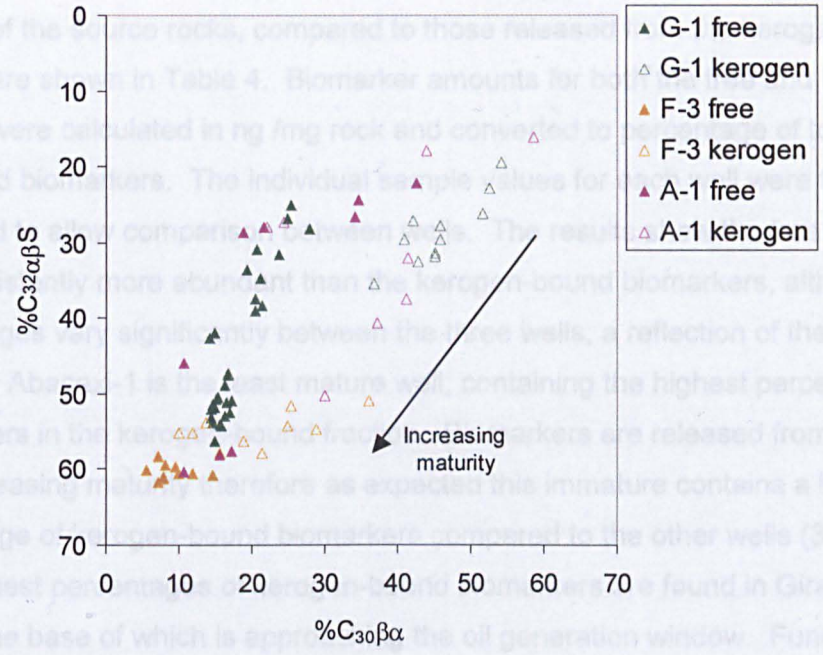

Fig. 72 The free and kerogen-bound $\%C_{32}\alpha\beta S$ hopane maturity parameter versus the $\%C_{30}\beta\alpha$ hopane maturity parameter for Girassol-1 (G-1), Funda-3 (F-3), and Abacaxi-1 (A-1) wells.

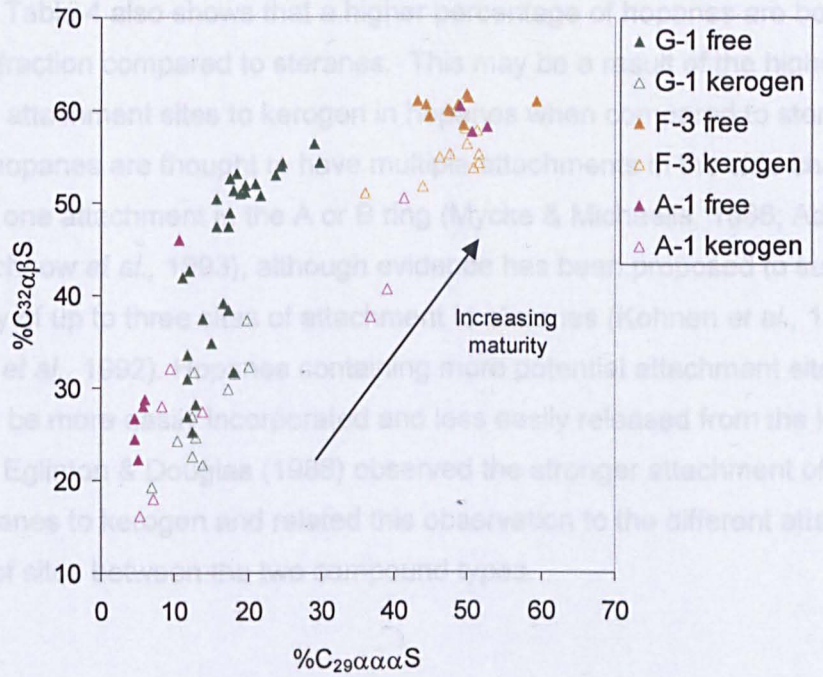

Fig. 73 The free and kerogen-bound $\%C_{32}\alpha\beta S$ hopane maturity parameter versus the $\%C_{29}\alpha\alpha\alpha S$ sterane maturity parameter, for Girassol-1 (G-1), Funda-3 (F-3), and Abacaxi-1 (A-1) wells.

Results of quantitative analysis of the biomarkers found free in the bitumen fraction of the source rocks, compared to those released from the kerogen-bound fraction are shown in Table 4. Biomarker amounts for both the free and bound fraction were calculated in ng /mg rock and converted to percentage of total quantified biomarkers. The individual sample values for each well were then averaged to allow comparison between wells. The results show the free biomarkers are consistently more abundant than the kerogen-bound biomarkers, although percentages vary significantly between the three wells, a reflection of the maturity of the well. Abacaxi-1 is the least mature well, containing the highest percentage of biomarkers in the kerogen-bound fraction. Biomarkers are released from kerogen with increasing maturity therefore as expected this immature contains a higher percentage of kerogen-bound biomarkers compared to the other wells (35%). The next highest percentages of kerogen-bound biomarkers are found in Girassol-1 (22%), the base of which is approaching the oil generation window. Funda-3 well is the most mature well, having reached the main phase of oil generation and contains the smallest percentage of biomarkers in the kerogen fraction (10%). By the stage of oil generation the majority of the biomarkers have been released into the free fraction. Table 4 also shows that a higher percentage of hopanes are bound into the kerogen fraction compared to steranes. This may be a result of the higher number of available attachment sites to kerogen in hopanes when compared to steranes. In general hopanes are thought to have multiple attachments in the side chain, and steranes one attachment in the A or B ring (Mycke & Michaelis, 1986; Adam *et al.*, 1993; Richnow *et al.*, 1993), although evidence has been proposed to support the possibility of up to three sites of attachment to steranes (Kohnen *et al.*, 1991a; Hoffman *et al.*, 1992). Hopanes containing more potential attachment sites would therefore be more easily incorporated and less easily released from the kerogen fraction. Eglinton & Douglas (1988) observed the stronger attachment of hopanes than steranes to kerogen and related this observation to the different attachment number of sites between the two compound types.

well	% Total	
	Free fraction	Kerogen Fraction
Selected biomarkers (hopanes + steranes*)*		
Girassol-1	77.7	22.3
Funda-3	90.2	9.8
Abacaxi-1	65.0	35.0
*Selected steranes**		
Girassol-1	84.3	15.7
Funda-3	90.7	9.3
Abacaxi-1	75.5	24.5
*Selected hopanes**		
Girassol-1	74.0	26.0
Funda-3	89.8	10.2
Abacaxi-1	54.8	45.2

NB. The selected biomarkers used are those provided by Norsk Hydro automatic peak quantification system i.e. those used in the calculation of set ratios.

* hopanes = sum of TS + Tm + 17β(H) + $C_{29}\alpha\beta$ + $C_{29}\beta\alpha$ + $C_{30}\alpha\beta$ + $C_{30}\beta\alpha$ $C_{31\text{-}35}$ ($\alpha\beta$ S+R).

* steranes = sum of C_{27}-C_{29} ($\alpha\beta\beta$ R+S) + $C_{27}\alpha\alpha\alpha$R +$C_{29}\alpha\alpha\alpha$S +C29$\alpha\alpha\alpha$R

Table 4 Comparison of the percentage yields (in ng/mg rock) of selected biomarkers from the free bitumen fraction and the kerogen-bound fraction of the Angolan source rocks shown by well.

5.2 Stratigraphic variation in source rock depositional environment.

Comparison between the free and kerogen-bound m/z 191 and 217 mass chromatograms for the Angolan source rocks provides evidence for compositional fractionation of biomarkers between the free and kerogen-bound biomarker fractions. Gammacerane, which can be relatively abundant in the free biomarker fraction of certain samples is present in either low or negligible amounts in the corresponding kerogen-bound fractions. Contrary to this, chemical degradation experiments by Schaeffer *et al.* (1995) released gammacerane from the bound fraction where the compound was found absent from the free fraction. Also, the compounds oleanane and 28,30 bisnorhopane (BNH) which are present in the free fractions are absent from the kerogen-bound fractions. The absence of BNH in bound biomarker fractions has been previously explained in the literature as a result of the precursor compound of BNH (unidentified as yet) lacking the functionality for attachment (Jones *et al.*, 1987; Eglinton & Douglas, 1988; Richnow *et al.*, 1992). Note that compositional fractionation has been previously observed whereby biomarker compounds may be preferentially incorporated into the kerogen-bound fraction and are absent from the free biomarker fraction (Kohnen *et al.*, 1991a; Schaeffer *et al.*, 1995). This is essentially the reverse of the above process.

Within this study the ratio of pristane to phytane has not been calculated for the kerogen-bound fractions. Due to the lower relative maturity of bound biomarker fractions unsaturated pristenes and phytenes are also still present and therefore complicate use of this parameter.

5.2.1 Pre-salt

The application of the C_{26}/C_{25} tricyclic terpane ratio to distinguish the lacustrine Pre-salt (values >1) from the marine Post-salt (values <1) source rocks using the free biomarkers (Burwood, 1999; Schiefelbein *et al.*, 1999; Cole *et al.*, 2000), does not follow for the bound biomarkers. The C_{26}/C_{25} ratio for the kerogen-bound terpanes in the lacustrine source rocks analysed consistently have values >1, but several marine source rocks also have values greater than 1 (Fig. 74).

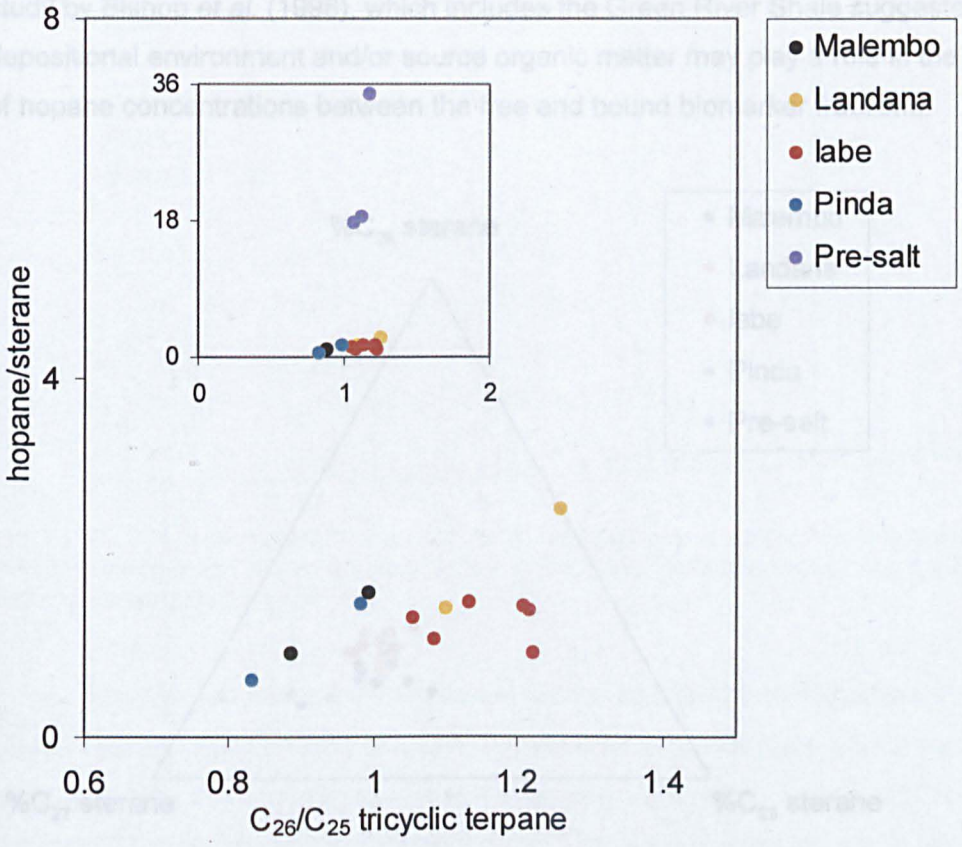

Fig. 74 Cross plot of the kerogen-bound C_{26}/C_{25} tricyclic terpane ratio and the hopane/sterane parameter for all Angolan source rocks. Note, the Girassol-1 Malembo Gp. samples have not been included due to the low maturity of samples tricyclic terpanes were not present in the kerogen-bound fraction.

As found in the free biomarkers, the lacustrine Pre-salt kerogen-bound biomarkers have high hopane/sterane ratio values, characteristic of lacustrine Type I kerogens. However, the kerogen-bound hopane/sterane ratios are greater than the free by a factor of approximately 5. Previous studies have shown that kerogen-bound hopane contents can be highly variable (e.g. Bishop *et al.*, 1998). This has in part been explained as a result of maturity, with progressive generation of hopanoids from kerogen with increasing maturity. However, the large factor difference between the hopane/sterane ratio found between the free and kerogen-bound fraction of the lacustrine source rocks is not seen in the marine Angolan source rocks, of similar maturity (i.e. oil generation maturity range). This suggests that the higher

hopane/sterane ratio found in the lacustrine samples is most likely due to a depositional or source organic matter control as opposed to maturity. A previous hydrogen pyrolysis study by Bishop *et al.* (1998), which includes the Green River Shale suggested that depositional environment and/or source organic matter may play a role in the variability of hopane concentrations between the free and bound biomarker fractions.

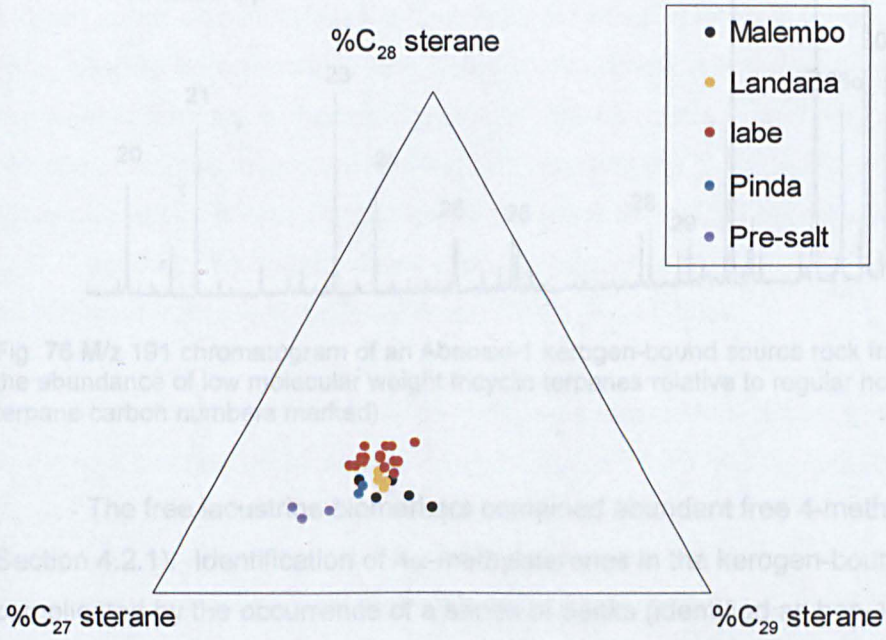

Fig. 75 Ternary diagram of the Angolan source rock C_{27}, C_{28} and C_{29} 5α(H), 14α(H), 17α(H), 20 R kerogen-bound sterane distributions.

Fig. 75 shows sterane compositional data plotted on the ternary diagram originally devised by Huang and Meinschein (1976) to distinguish ecosystems (primarily algal input) on the basis of sterol compositions. The diagram shows the Pre-salt Gp. kerogen-bound source rocks to have the same distinctive pattern of C_{27} steranes as the most abundant sterane seen in the free biomarker fractions (Section 4.2.3). Another distinctive feature of the lacustrine source rocks in the free fraction was an elevated *n*-C_{23} alkane, but this is not seen in the kerogen-bound *n*-alkanes. The kerogen-bound lacustrine source rock fractions contain abundant low molecular weight tricyclic terpanes relative to hopanes (% tricyclic terpane ratio values ~ 20%), a feature also see in the free biomarker fraction of the lacustrine source rocks (Fig. 76; see also section 4.2.4).

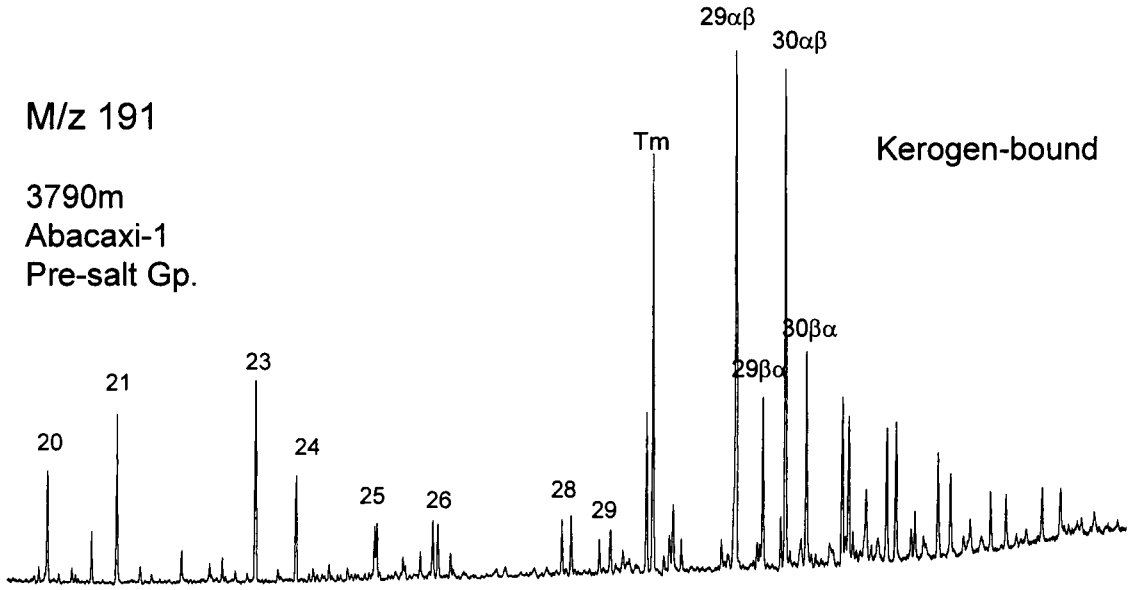

Fig. 76 M/z 191 chromatogram of an Abacaxi-1 kerogen-bound source rock fraction to illustrate of the abundance of low molecular weight tricyclic terpanes relative to regular hopanes, (tricyclic terpane carbon numbers marked).

The free lacustrine biomarkers contained abundant free 4-methylsteranes (see Section 4.2.1). Identification of 4α-methylsteranes in the kerogen-bound fractions is complicated by the occurrence of a series of peaks (identified as hop-17(21) enes using the m/z 367 mass chromatogram) in the m/z 231 mass chromatogram at similar retention times to the methyl steranes. The peaks have a high intensity and therefore the 4α-methylsteranes may be obscured beneath appearing as background noise in the trace; 4α-methylsteranes are found in the kerogen-bound fraction of the marine source rocks. Considering that the free fractions of the lacustrine source rocks contain a higher abundance of 4α-methylsteranes to regular steranes than the free fraction of the marine source rocks, it is most probable they are also present in the kerogen-bound lacustrine samples but obscured by the hopenes.

5.2.2 Post-salt Cretaceous

A distinctive feature of the Pinda Gp. free biomarker samples is a high $C_{35}\alpha\beta$ hopane, interpreted to represent an anoxic marine, sulphur rich depositional environment, most likely non-clastic (i.e. low iron; Ten Haven *et al.,* 1988; Peters & Moldowan 1991; section 4.2.2.2). Elevated $C_{35}\alpha\beta$ hopanes can also be seen in the

kerogen-bound biomarker fractions, although it should be noted only two samples have been analysed (Fig. 77). The C_{35} hopanes are thought to result from the selective preservation of the C_{35} bacteriohopanetetrol, most likely though incorporation of sulphur into the side-chain during diagenesis (Peters & Moldowan, 1991). In anoxic environments high in organic sulphur, binding of hopanoids into kerogen is more likely through C-S bonds than C-O bonds. Carbon-sulphur bonds are weaker than carbon-oxygen bonds and therefore the possibility of releasing intact C_{35} side-chains is more likely (Bishop & Farrimond, 1995). Also of importance is that the carbon-sulphur bonds are weaker than the carbon-carbon bonds making up the side chain; therefore the release of sulphur incorporated skeletons retaining the C_{35} side chain is more likely. In more oxic environments oxygen bonds are more likely; C-O bonds are of similar strength to C-C bonds in the hopanoid side-chain so intact hopane side-chains are less likely to be released from the kerogen with maturation (Innes, 1998).

The Pinda and Iabe Gps. as mentioned above have similar hopane/sterane ratio in the free and kerogen-bound biomarker fraction (~ 0.5 to 3.0), suggesting limited compositional fractionation between the free and bound biomarker 'pools' for these marine source rocks (Fig. 74 & Fig. 77). The kerogen-bound fractions of the Iabe and Pinda Gp. source rocks also have a high abundance of C_{30} steranes (Fig. 78) compared to the remaining marine stratigraphy. This is also seen in the free steranes and along with a relatively low hopane/sterane ratio consistent with the marine nature of their respective depositional environments. Fig. 78 appears useful for distinguishing the Post-salt marine sediments (particularly the Iabe Gp.) from the Post-salt Tertiary (Malembo and Landana Gps.) on the basis of their $\%C_{30}$ and $\%C_{28}$ sterane abundances.

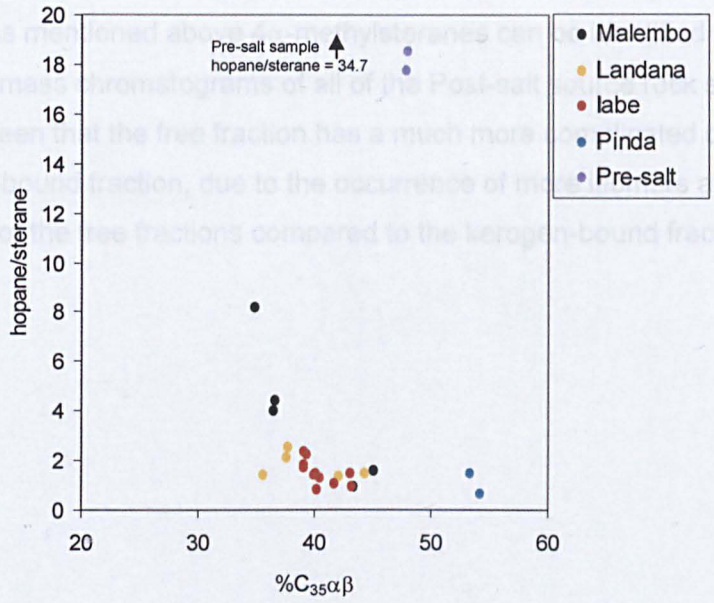

Fig. 77 Cross plot of the kerogen-bound %$C_{35}\alpha\beta$ parameter and the hopane/sterane parameter for all Angolan source rocks.

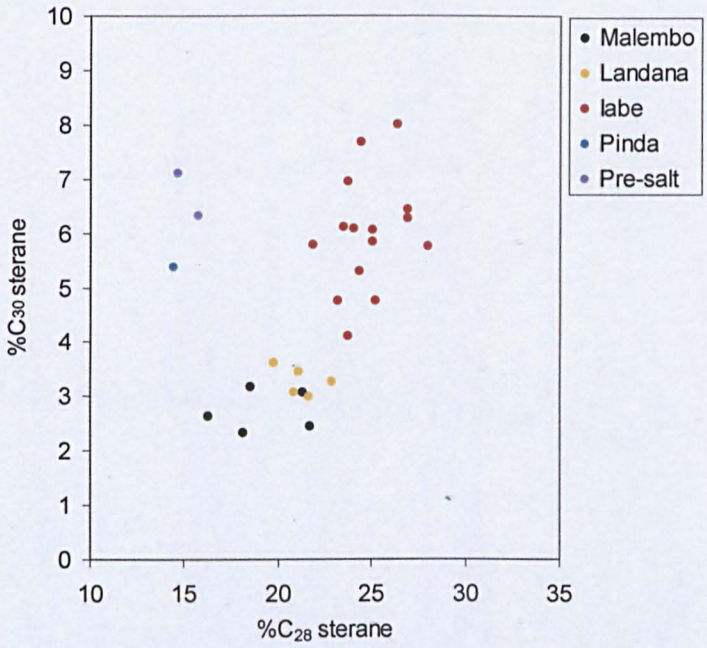

Fig. 78 Cross plot of the kerogen-bound %C_{30} sterane parameter and the %C_{28} sterane parameter for all Angolan source rocks. A peak eluting at the retention time of C_{30} sterane for the lacustrine source rocks has been used in the %C_{30} ratio. However analysis of the free hydrocarbon m/z 231 revealed this compound was a 4α-methylsterane . This is also possible for the bound fraction, however due to the lower maturity of the bound fractions the m/z 231 mass chromatograms are dominated by hopenes. The hopenes may be obscuring the 4α methylsteranes, thus preventing identification

As mentioned above 4α-methylsteranes can be identified in the kerogen-bound m/z 231 mass chromatograms of all of the Post-salt source rock samples (Fig. 79). It can be seen that the free fraction has a much more complicated distribution than the kerogen-bound fraction, due to the occurrence of more isomers as a result of the higher maturity of the free fractions compared to the kerogen-bound fractions.

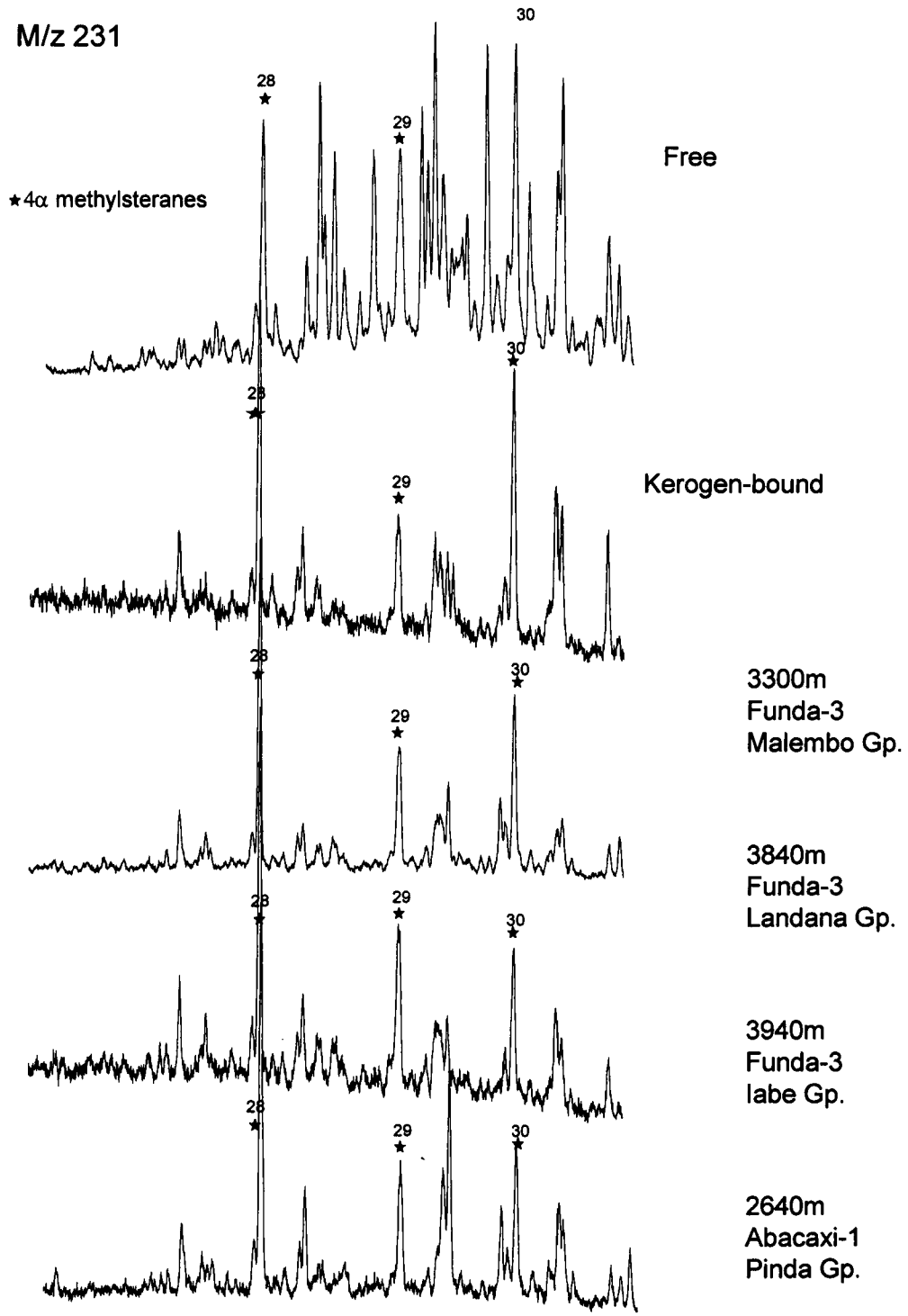

Fig. 79 M/z 231 mass chromatograms of kerogen-bound source rock fractions to illustrate the presence of 4α-methylsteranes in the Post-salt marine a) Malembo, 2) Landana, 3) Iabe and 4) Pinda Gps. A m/z 231 mass chromatogram from a Funda-3 free Post-salt source rock has also been included for comparison to the kerogen-bound fractions.

Fig. 80 shows changes in the distribution of the C_{27}, C_{28}, C_{29} and C_{30} 5α(H), 14α(H), 17α(H), 20R kerogen-bound steranes through the Post-salt section. As in the free source rock biomarkers the sterane distributions can be broadly separated into three main sterane facies types. The Iabe Gp. kerogen-bound source rocks have the same distinctive high C_{28} sterane (and also a C_{30} sterane mentioned earlier; Fig. 78), seen in the free Iabe Gp. source rocks. The Landana and Malembo Gps. sterane distributions will be discussed in Section 5.2.3.

The Iabe Gp. kerogen-bound biomarkers contain abundant low molecular weight tricyclic terpanes relative to hopanes (Fig. 81). High tricyclic terpane ratios are also observed in the free fractions (~10 to 20%), but are less abundant than in the kerogen-bound fraction (~20 to 40%). Tricyclic terpanes are generated from kerogen at higher thermal maturities relative to the hopanes (Peters & Moldowan, 1993). This may be because they are more tightly bound into macromolecular fractions than the hopanes and hence explain the higher abundance relative to hopanes in the kerogen-bound fraction of the source rocks. Another characteristic of the Iabe Gp. free biomarkers is the occurrence of significant amounts of extended tricyclic terpanes ranging from C_{28}-C_{35}. Analysis of the kerogen-bound chromatograms shows that extended tricyclic terpanes do occur in the kerogen-bound fractions of the Iabe Gp. samples although they can only be clearly identified up to C_{33} (Fig. 81).

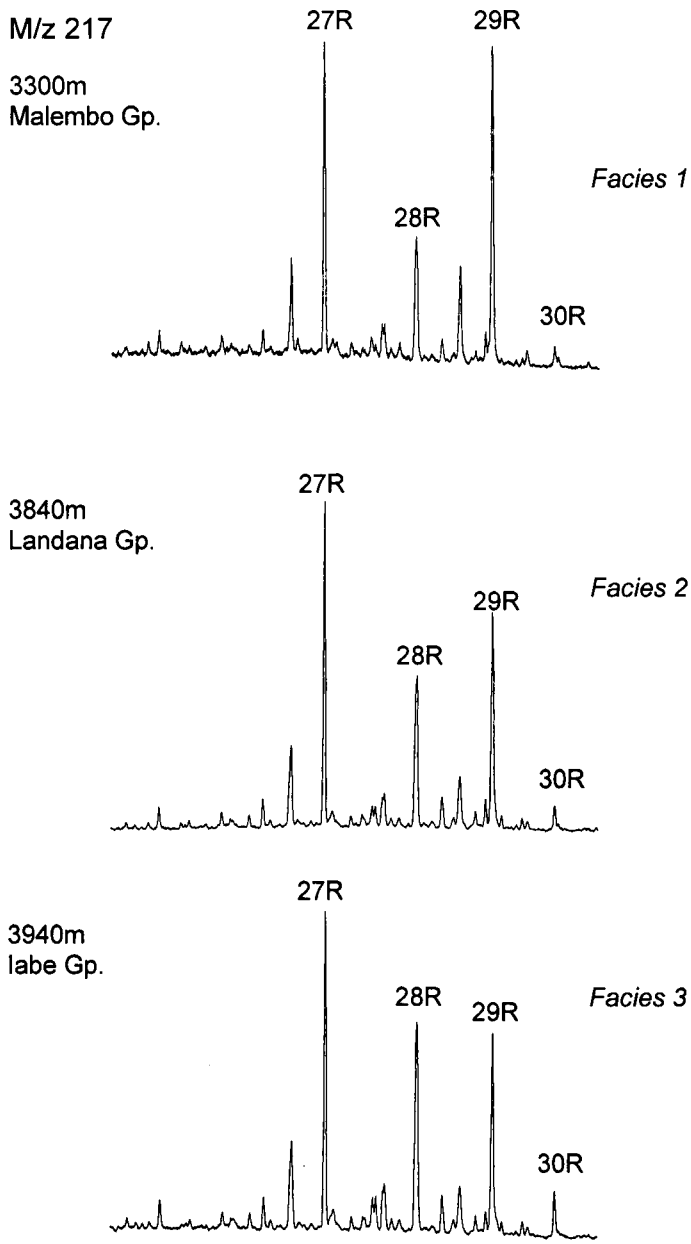

Fig. 80 M/z 217 mass chromatograms to illustrate distribution of C_{27}, C_{28} C_{29} and C_{30} 5α(H), 14α(H), 17α(H), 20R kerogen-bound sterane distribution facies of the Post-salt marine Iabe, Landana and Malembo Gp. source rocks. The data are from Girassol-1, but comparable variability in carbon number distributions are seen in Funda-3 and Abacaxi- wells. Facies 1 is characterised by high approximately equal C_{29} to C_{27} sterane, facies 2 has high C_{27} relative to C_{29} sterane, and facies 3 has abundant C_{28} and C_{30} steranes relative to facies 1 and 2.

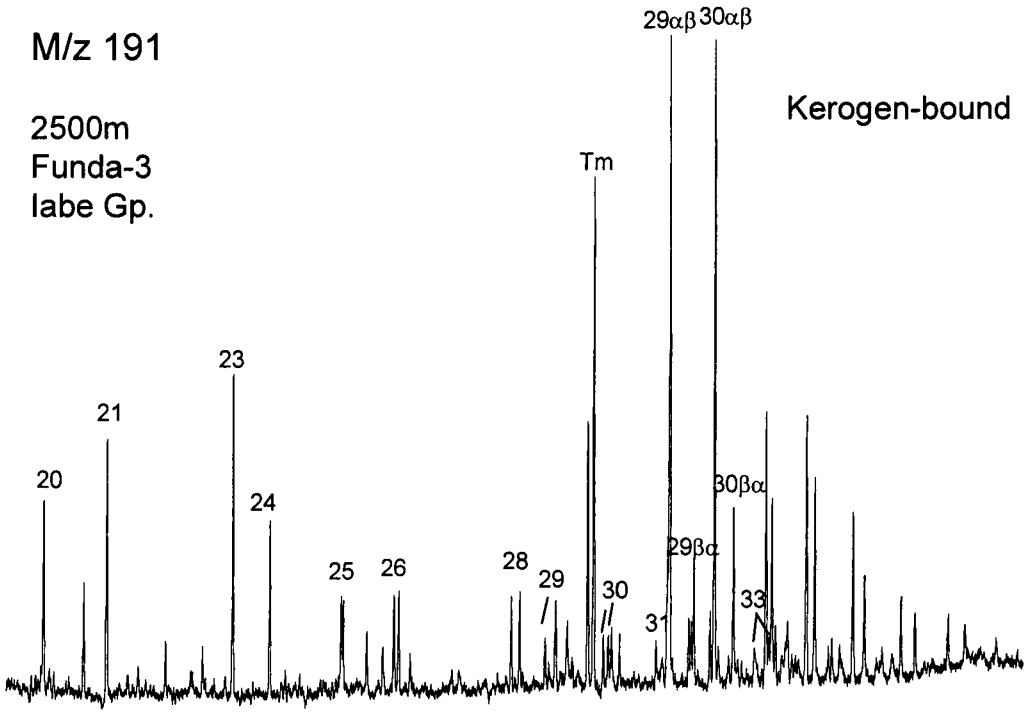

Fig. 81 M/z 191 mass chromatogram of the kerogen-bound fraction of a Funda-3 source rock sample to illustrate the presence of a high abundance of low molecular weight tricyclic terpanes and the occurrence of extended tricyclic terpanes which can be clearly identified up to C_{33} (tricyclic terpane carbon numbers marked). Note, the second eluting C_{31} isomer co-elutes with the $C_{29}\alpha\beta$ hopane.

5.2.3 Post-salt Tertiary

Free biomarker analysis (see Section 4.2.3.3) revealed that the Landana Gp. has generally intermediate biomarker compositions between the marine Iabe and Malembo Gps. This reflects the regressive nature of the Landana Gp. deposited during the transition from a marine-dominated Iabe Gp. to the more terrestrially-influenced Malembo Gp. (Brice *et al.*, 1982). The kerogen-bound biomarkers from the Landana Gp. samples also have an intermediate biomarker composition between the Malembo and Iabe Gps (Fig. 75, Fig. 77, Fig. 78, Fig. 82 & Fig. 83).

Several of the Malembo Gp. samples analysed by hydrogen pyrolysis were taken from Funda-3. It is important to note that the free biomarker composition of these

samples was more similar (excluding the sterane composition) to the Iabe Gp. than other Malembo Gp. samples analysed. This pattern can also be seen in the kerogen-bound biomarkers whereby some of the Malembo Gp. samples plot within the Iabe Gp. samples (Fig. 77 and Fig. 82).

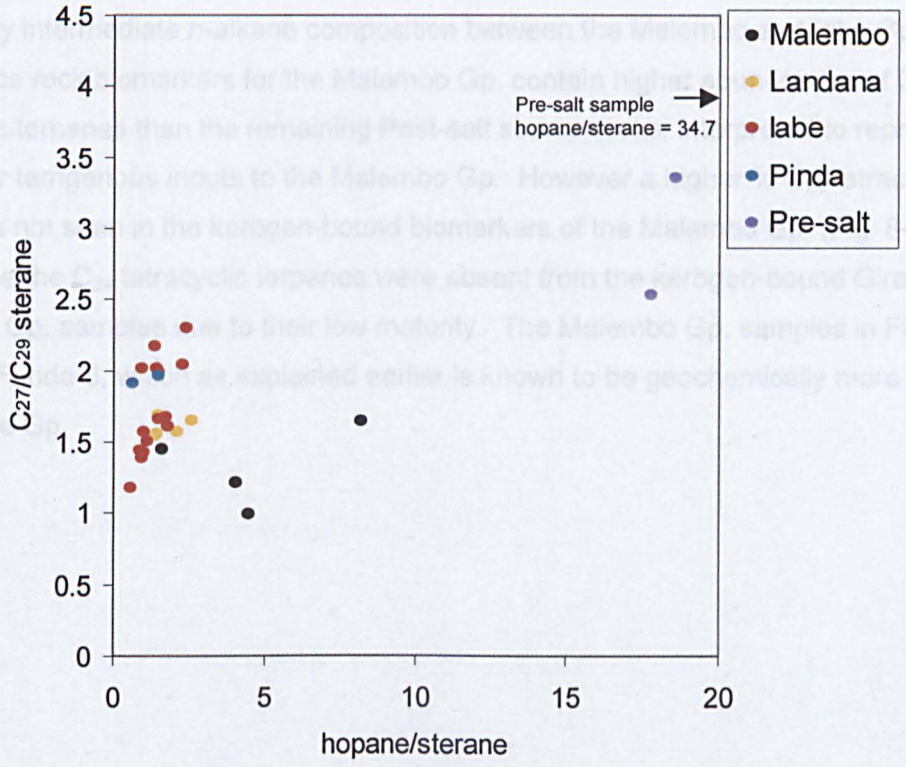

Fig. 82 Cross plot of the kerogen-bound C_{27}/C_{29} sterane parameter and the hopane/sterane parameter for all Angolan source rocks.

Fig. 82 shows the Malembo Gp. samples (excluding those mentioned above) to have higher kerogen-bound hopane/sterane ratios than the other Post-salt marine source rocks and also a higher average abundance of C_{29} steranes. These features were also observed in the free biomarkers for the Malembo Gp. and are interpreted to represent high contributions of terrigenous organic matter to the depositional environment. The kerogen-bound fraction mass chromatograms for Girassol-1 provide additional evidence for the terrestrial depositional environment and have the advantage that they are not affected by drill mud contamination which can be seen in the free hydrocarbons. The Malembo Gp. samples have broad *n*-alkane distributions, with a high

abundance of the waxy (C_{23-30}) *n*-alkanes (Fig. 83). In contrast, the kerogen-bound *n*-alkanes of the Iabe Gp. samples begin to tail off after approximately *n*-C_{18} to a more marine *n*-alkane distribution. Gas chromatogram distributions skewed towards medium to high molecular weight *n*-alkanes, especially with predominant C_{27}, C_{29}, C_{31} homologues, have been described as an indication of long-chain lipid contributions from higher plants (Tissot & Welte, 1984; Mello *et al.*, 1988). The Landana Gp. has an essentially intermediate *n*-alkane composition between the Malembo and Iabe Gps. The free source rock biomarkers for the Malembo Gp. contain higher abundances of C_{24} tetracyclic terpanes than the remaining Post-salt source rocks, interpreted to represent the higher terrigenous inputs to the Malembo Gp. However a higher % C_{24} tetracyclic terpane is not seen in the kerogen-bound biomarkers of the Malembo Gp. (Fig. 84). This is because the C_{24} tetracyclic terpanes were absent from the kerogen-bound Girassol-1 Malembo Gp. samples due to their low maturity. The Malembo Gp. samples in Fig. 84 are from Funda-3, which as explained earlier is known to be geochemically more similar to the Iabe Gp.

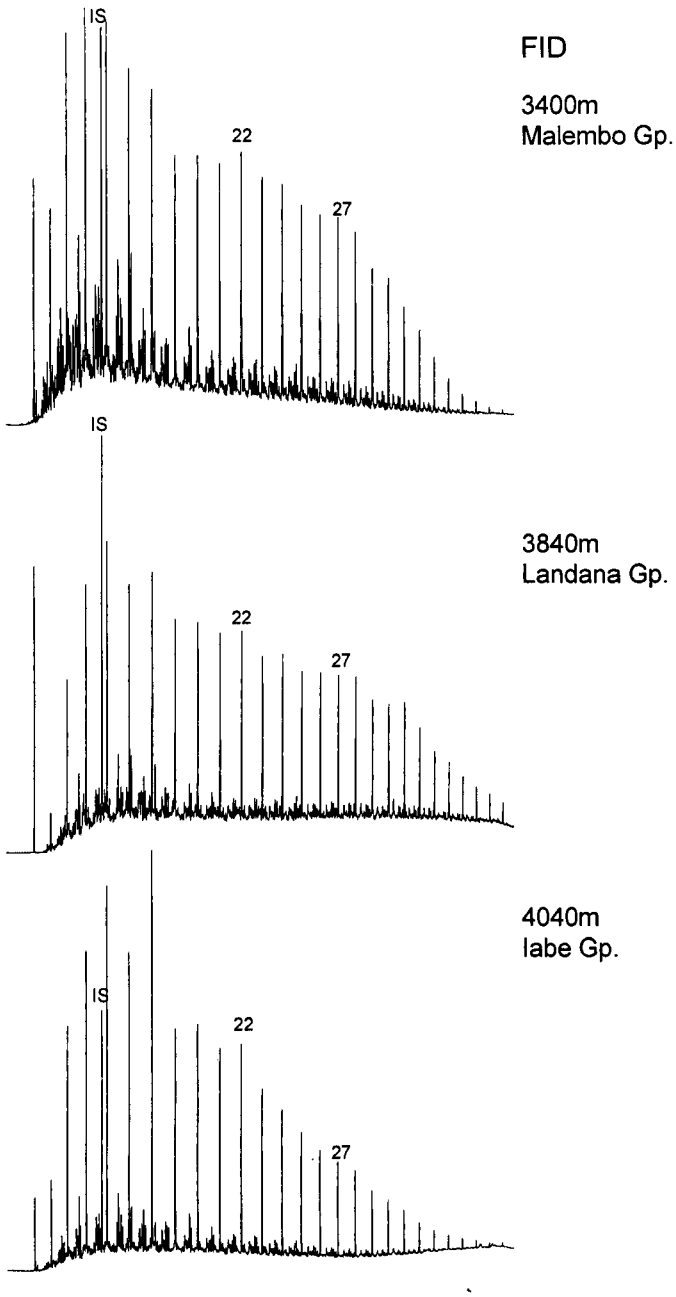

Fig. 83 Stratigraphic variation in Girassol-1 kerogen-bound *n*-alkane distributions. Note the higher abundance of high molecular weight waxy *n*-alkanes in the Malembo Gp (carbon numbers marked; IS = internal standard).

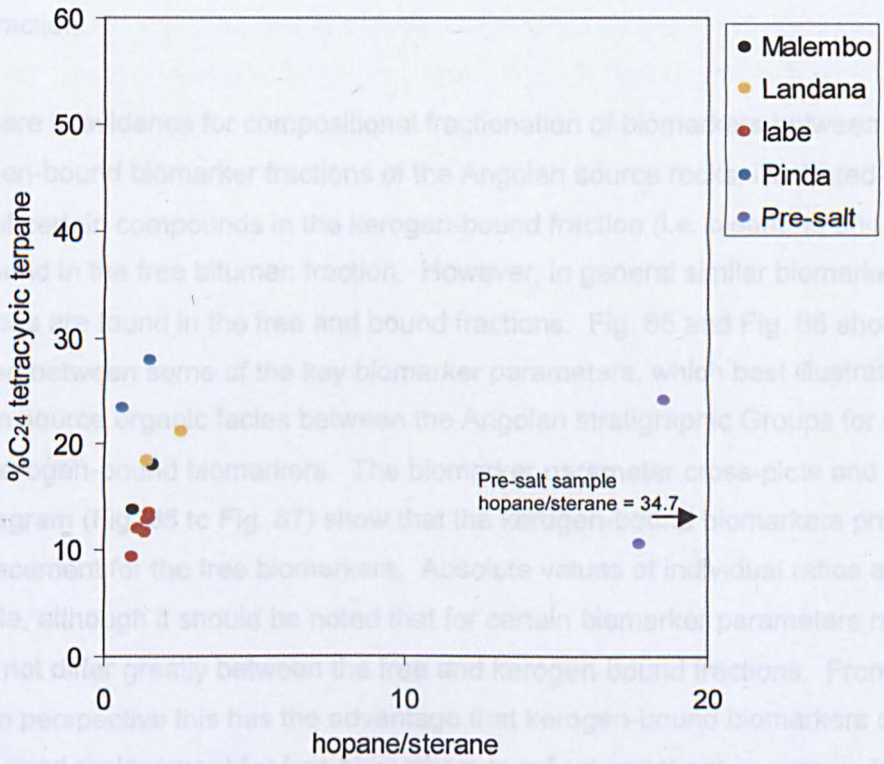

Fig. 84 Cross plot of the kerogen-bound $\%C_{24}$ tetracyclic terpane parameter and the hopane/sterane ratio for all Angolan source rocks.

5.2.4 Overview

The Angolan source rock kerogen-bound biomarkers are consistent with previous literature reports that they undergo the same epimerisation reactions as free biomarkers but at a retarded rate, and therefore have a more immature biomarker profile (Love *et al.*, 1995; Bishop *et al.*, 1998; Murray *et al.*, 1998). Due to steric hindrance, kerogen-bound biomarkers can operate over greater depth ranges and to higher maturities.

The biomarkers in the bitumen fraction of the source rocks are consistently more abundant than the kerogen-bound biomarkers, although percentages of kerogen-bound biomarkers increase in the less mature samples. A higher percentage of hopanes is bound into the kerogen fraction compared to steranes. This may be a result of the higher number of attachment sites to kerogen in hopanes when compared to steranes.

Hopanes would therefore be more easily incorporated and less easily released from the kerogen fraction.

There is evidence for compositional fractionation of biomarkers between the free and kerogen-bound biomarker fractions of the Angolan source rocks, illustrated by the absence of certain compounds in the kerogen-bound fraction (i.e. oleanane and BNH) that are found in the free bitumen fraction. However, in general similar biomarker compositions are found in the free and bound fractions. Fig. 85 and Fig. 86 show a comparison between some of the key biomarker parameters, which best illustrate variation in source organic facies between the Angolan stratigraphic Groups for both the free and kerogen-bound biomarkers. The biomarker parameter cross-plots and sterane ternary diagram (Fig. 85 to Fig. 87) show that the kerogen-bound biomarkers provide a good replacement for the free biomarkers. Absolute values of individual ratios are not comparable, although it should be noted that for certain biomarker parameters ratio values do not differ greatly between the free and kerogen-bound fractions. From an exploration perspective this has the advantage that kerogen-bound biomarkers could be used as a good replacement for free biomarkers to reflect variations in organic facies within a source rock section. This would be particularly useful where free biomarkers have been contaminated by use of a crude oil as a drilling mud. Kerogen-bound biomarkers can also provide additional source information to supplement free biomarker interpretations, as has been shown by analysis of the Girassol-1 kerogen-bound *n*-alkanes. The Malembo Gp. shows a higher abundance of waxy *n*-alkanes than the remaining Post-salt stratigraphy, supporting biomarker interpretations of a more terrestrially influenced depositional environment, a feature not seen in the free *n*-alkanes.

The only biomarker parameter to differ greatly in terms of absolute ratio values between the free and kerogen-bound biomarker is the hopane/sterane ratio for the lacustrine source rocks. Hopane to sterane ratio values for the marine source rocks of similar maturity to the lacustrine samples, have comparable ratios between the free and kerogen-bound fractions. This suggests most likely that depositional environment and/or source organic matter may also play a role in controlling biomarker fractionation between the free and bound biomarker fractions.

Fig. 85 shows in terms of the $\%C_{30}$ steranes and $\%C_{28}$ steranes the different startigraphic groups are most clearly distinguished in the bound biomarkers than the free and therefore might prove more useful in correlations. However, due to the fewer number of samples analysed this may be an artifact of the smaller data set.

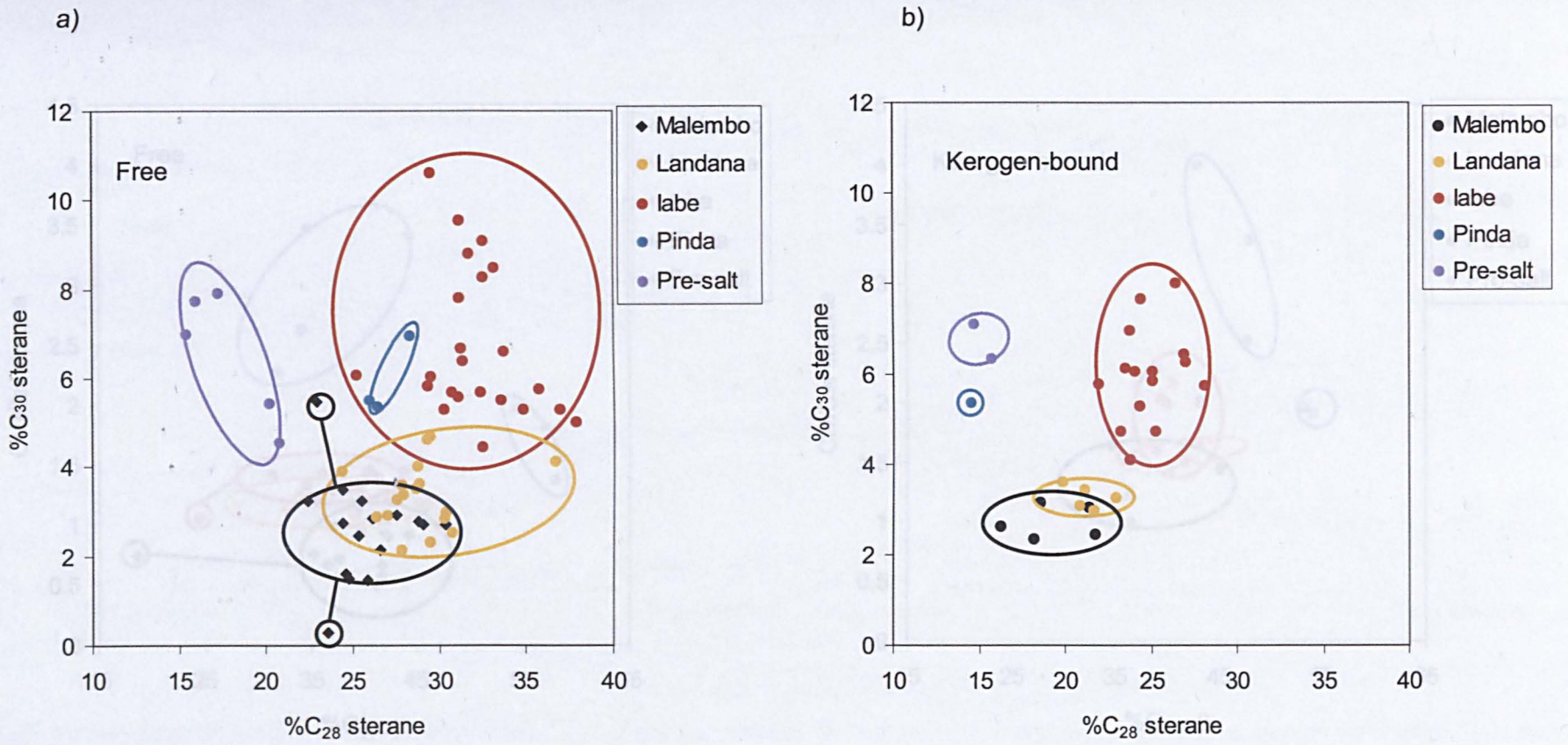

Fig. 85 Cross plot of the $\%C_{30}$ sterane parameter and the $\%C_{28}$ sterane parameter for a) free and b) kerogen-bound Angolan source rocks. A peak eluting at the retention time of C_{30} sterane in the Pre-salt lacustrine has been used in the $\%C_{30}$ ratio. However analysis of the free hydrocarbon m/z 231 revealed this compound was a 4α-methylsterane. This is also possible for the bound fraction, however due to the lower maturity of the bound fractions the m/z 231 mass chromatograms are dominated by hopenes. The hopenes may be obscuring the 4α methylsteranes, thus preventing identification.

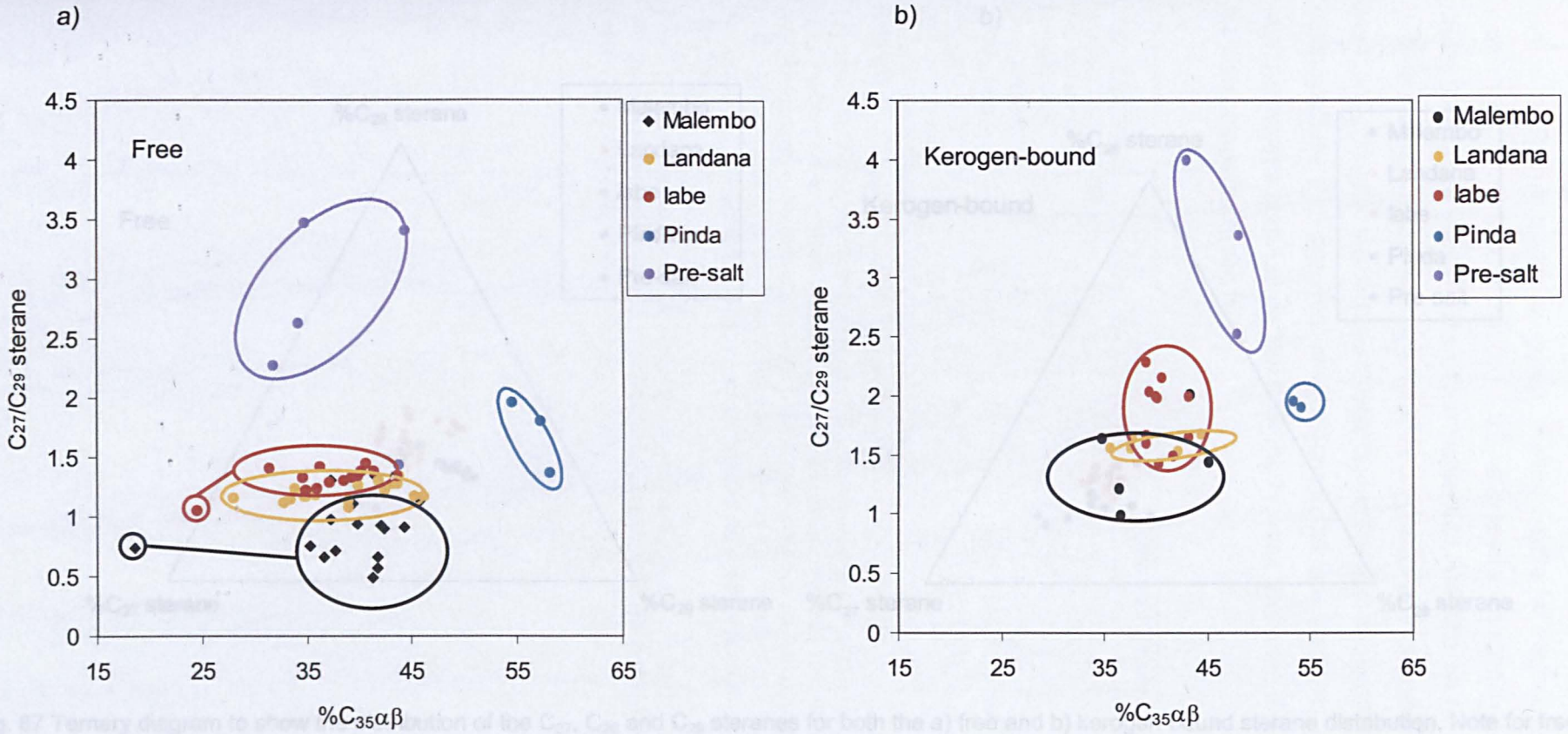

Fig. 86 Cross plot of the C_{27}/C_{29} ratio and the $\%C_{35}\alpha\beta$ parameter for a) free and b) kerogen bound Angolan source rocks.

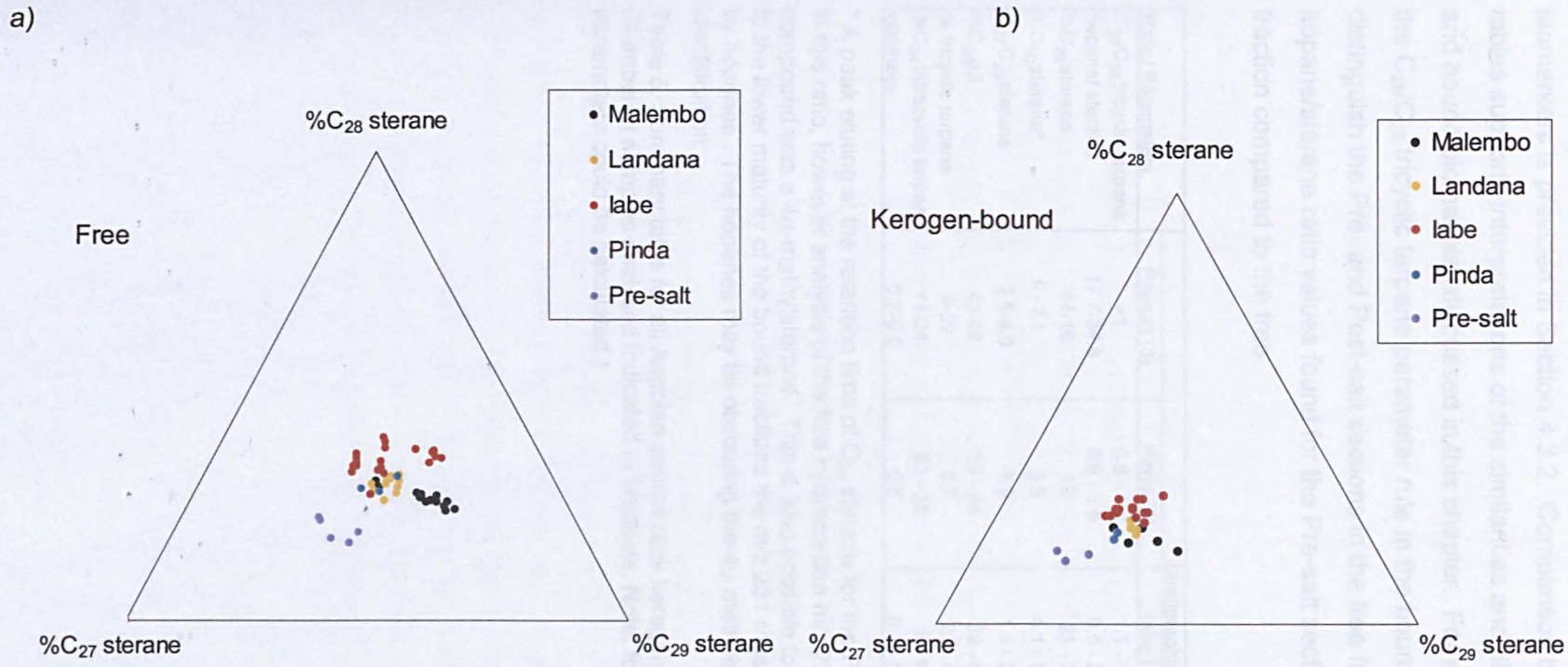

Fig. 87 Ternary diagram to show the distribution of the C_{27}, C_{28} and C_{29} steranes for both the a) free and b) kerogen-bound sterane distribution. Note for free biomarker the distribution of the 5α(H), 14β(H), 17β(H), 20 S + R steranes have been used. Due to the lower maturity of the kerogen-bound fraction and hence absence of αββ steranes the 5α(H), 14α(H), 17α (H) R compounds have been used.

Table 5 provides a summary of the kerogen-bound biomarker parameter values for each stratigraphic group. A similar table for the free source rock biomarkers is provided in Section 4.3.2. Comparison between the values in the two tables supports interpretations of the similarities and differences between the free and bound biomarkers discussed in this chapter. For example, the inconsistency of the C_{26}/C_{25} tricyclic terpane parameter rule in the bound biomarkers, which is used to distinguish the Pre- and Post-salt sections in the free fractions. Also the much higher hopane/sterane ratio values found for the Pre-salt section in the kerogen-bound fraction compared to the free.

	Stratigraphic Groups				
Ratio/ Parameters	Pre-salt (3)	Pinda (2)	Iabe (15)	Landana (6)	Malembo (5)
C_{26}/C_{25} tricyclic terpane	>1	0.8 - 1.0	1.1 - 1.2	1.1-1.3	<1
hopane/ sterane	17.7-34.8	0.6 - 1.5	0.5 - 2.4	1.4-2.5	0.9-8.2
$\%C_{28}$ sterane	14-16	19	21 - 28	20-23	16-22
$\%C_{30}$ sterane*	0 - 7.1	5.3	4.1 - 8.0	3.0-3.6	2.3-3.2
C_{27}/C_{29} sterane	2.5-4.0	1.9	1.1 - 2.2	1.5-1.7	1.0-2.0
$\%C_{35}\alpha\beta$	43-48	53 - 54	39 - 43	36-44	35-45
% tricyclic terpane	9-22	8.7	23 - 40	12-13	12-17
$\%C_{24}$ tetracyclic terpane	11-24	23 - 28	9 - 14	18-21	14-18
waxiness	0.7-0.8	0.7	0.7 - 0.8	0.5-0.7	0.5-0.8

* A peak eluting at the retention time of C_{30} sterane for the Pre-salt lacustrine has been used in this ratio, however analysis of the free hydrocarbon m/z 231 chromatogram revealed this compound was a 4α-methylsterane. This is also possible for the bound fraction, however due to the lower maturity of the bound fractions the m/z 231 mass chromatograms are dominated by hopenes. The hopenes may be obscuring the 4α methylsteranes, thus preventing identification.

Table 5. Summary table for all Angolan source rock kerogen-bound biomarker parameters. (Number of samples analysed indicated in brackets. Note, for certain samples not all parameters could be calculated.)

6 Molecular and isotopic analysis of saturated hydrocarbons in oils

This chapter will address the molecular composition of the biomarkers in the aliphatic hydrocarbon fraction of several Angolan oils and also the isotopic composition of the oils. A total of 34 oils were analysed and the results are interpreted in terms of their degree of biodegradation, thermal maturity and source organofacies.

6.1 Biodegradation

The Angolan oils (with the exception of the block 17 oils) have undegraded *n*-alkane, isoprenoid, hopane and sterane distributions. However, several of the oils contain abundant demethylated 25-norhopanes (Fig. 88 & Fig. 89). 25-norhopanes are thought to be the biotransformation products of the corresponding 17α(H) hopanes (Moldowan & McCaffrey, 1995). The process occurs at a late stage of biodegradation, after removal of the steranes has taken place (Volkman *et al.,* 1983), equivalent to a biodegradation ranking of level 6 (Peters & Moldowan, 1993). However, it has also been suggested that demethylated hopanes appear abundant in biodegraded crude oils solely because the less resistant compounds have been removed (Goodwin *et al.,* 1982). The presence of demethylated hopanes in oils, which otherwise appear undegraded, is suggested to result from residues of previously biodegraded oil in a reservoir with subsequent entry of a fresh undegraded oil (Volkman *et al.,* 1983). For the oils with low % 25nor $C_{30}\alpha\beta$ values (<4%) analysis of the m/z 177 mass chromatogram reveals small peaks where the 25-norhopane compound elute; however, they are so small they could simply represent background noise in the traces as opposed to 25-norhopanes. Table 6 shows the biodegradation rank of the Angolan oils (the block 17 oils are shown separately in Table 7) classified according to the Peters & Moldowan (1993) biodegradation scale.

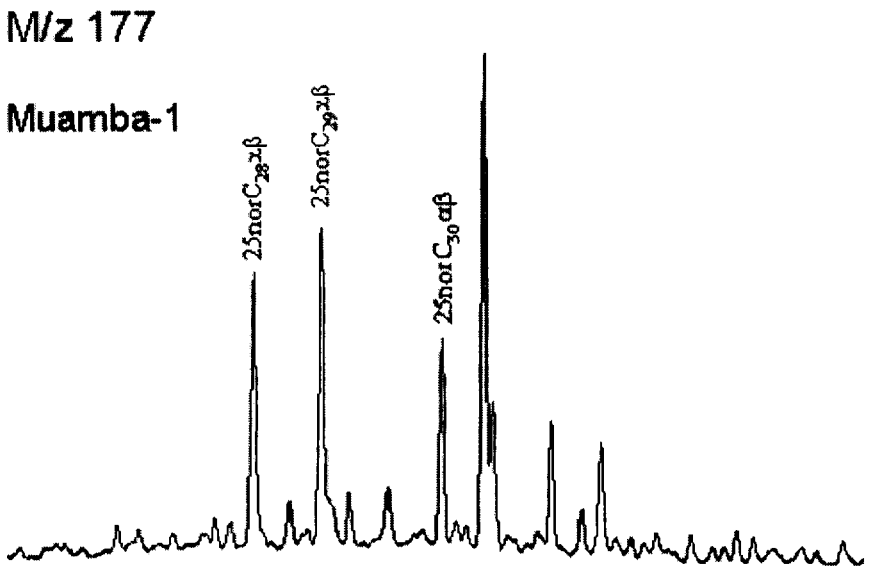

Fig. 88 M/z 177 mass chromatogram for Muamba-1 to illustrate the presence of the C_{28}-C_{30} 25- norhopanes.

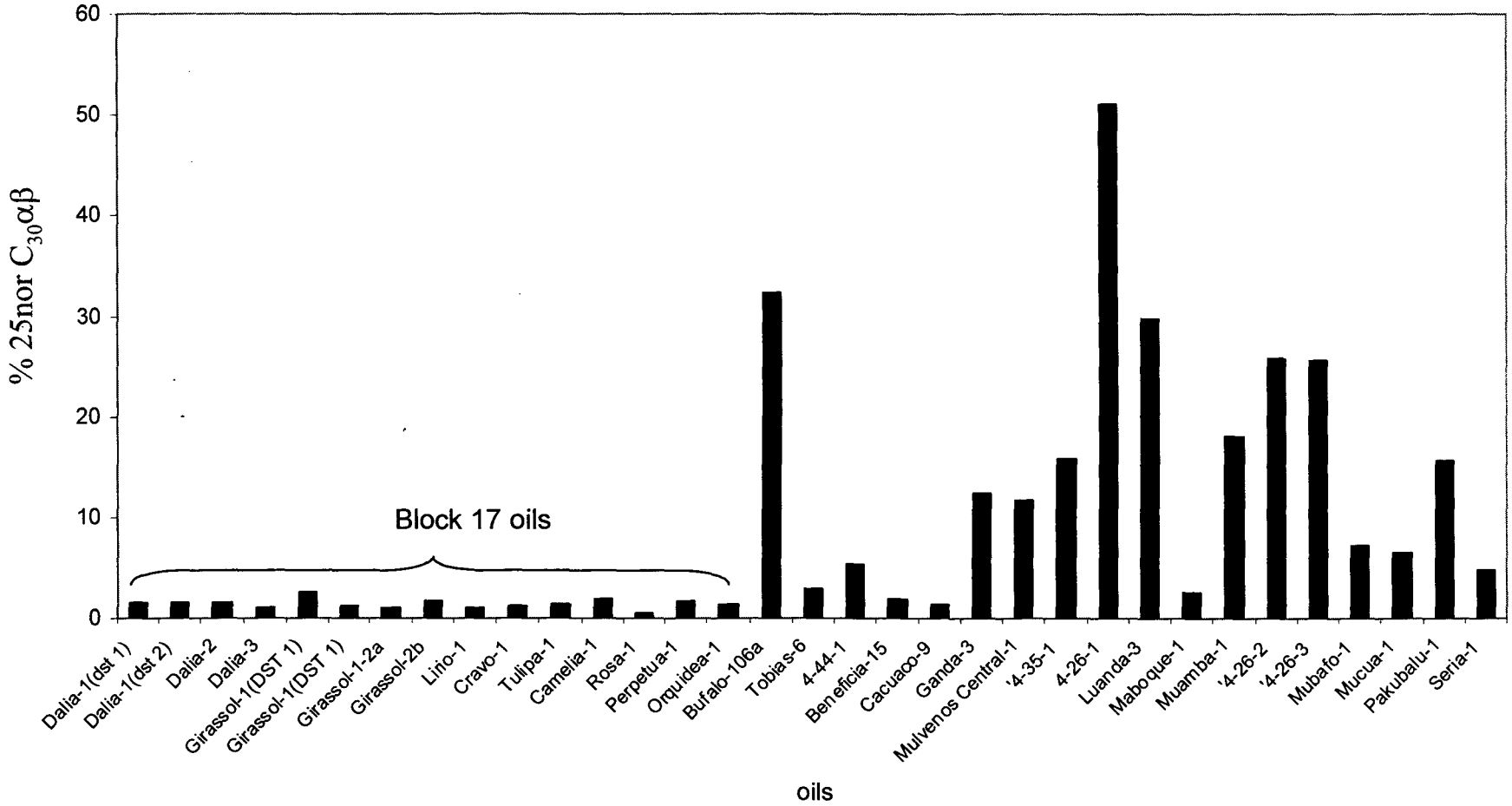

Fig. 89 %25nor$C_{30}\alpha\beta$ parameter (100*(25nor$C_{30}\alpha\beta$/(25nor$C_{30}\alpha\beta$ + $C_{30}\alpha\beta$)) values for all Angolan oils.

Sample	Block	Biodegradation Rank
Bufalo-106a	3	1 (1- 6)
Tobias-6	Onshore of block 6	1
4-44-1	4	1 (1- 6)
Benficia-15	Onshore of block 6	1
Cacuaco-9	6	1
Ganda-3	2	1 (1- 6)
Mulvenos Central-1	6	1 (1- 6)
'4-35-1	4	1 (1- 6)
4-26-1	4	1 (1- 6)
Luanda-3	6	1 (1- 6)
Maboque-1	9	1
Muamba-1	5	1 (1- 6)
'4-26-2	4	1 (1- 6)
'4-26-3	4	1 (1- 6)
Mubafo-1	5	1 (1- 6)
Mucua-1	9	1 (1- 6)
Pakubalu-1	5	1 (1- 6)
Seria-1	2	1 (1- 6)

Table 6 Biodegradation rank for Angolan oils (excluding block 17) classified according to Peters & Moldowan (1993). Note, biodegradation level 1(1– 6) represents a reservoired oil previously degraded to at least biodegradation rank 6 with fresh entry of a non-biodegraded oil. Block locations are illustrated in Fig. 90.

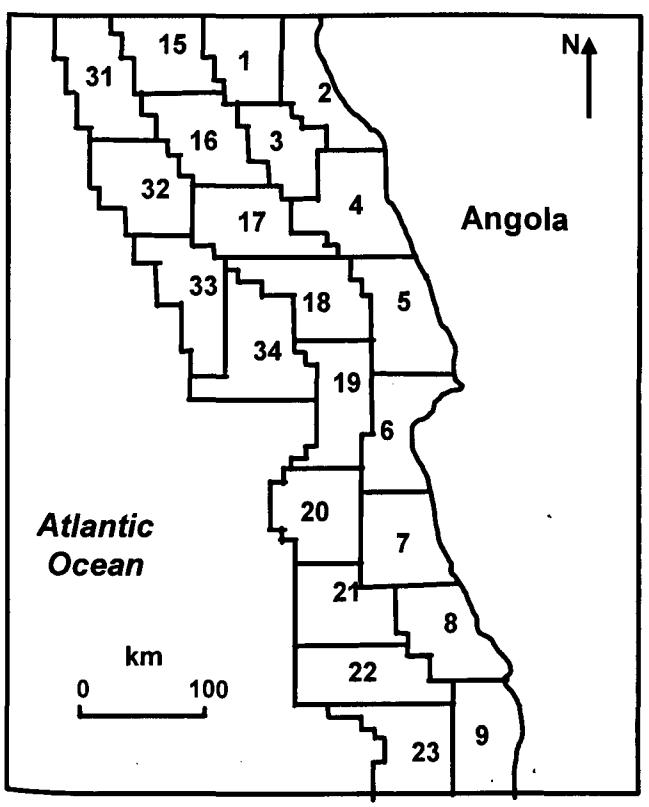

Fig. 90 Map to show the Angolan coastline exploration blocks.

Table 7 shows the biodegradation rank for each of the block 17 oils classified according to the biodegradation scale developed by Peters and Moldowan (1993). The block 17 oils range from biodegradation level 1 (degradation of the lower homologue *n*-alkanes) up to level 6 (partial degradation of the steranes) for two samples. Examples of the sterane distributions are illustrated in Fig. 91. Steranes are typically degraded in the order ααα steranes prior to αββ steranes (Peters & Moldowan, 1993). Interestingly in Orquidea-1 the ααα steranes have been preferentially degraded prior to the αββ steranes. Sterane biodegradation in Perpetua-1 follows the typical order of ααα steranes prior to the αββ steranes (Fig. 91). This difference may be due to a preference of certain bacteria for different compounds. Biodegradation typically decreases the API gravity of oils (Connan, 1984). Table 7 shows in general the block 17 oils with higher levels of biodegradation have lower API values. Molecular parameters for the block 17 oils calculated in this thesis may be affected by biodegradation of the *n*-alkanes, isoprenoids and steranes but are noted when this occurs.

Sample	API	Reservoir Temperature °C	Crude Description	Biodegradation Rank
Dalia-1 (DST1)	22.4	40	heavy	3
Dalia-1 (DST2)	22.6	39	heavy	5
Dalia-2	23	38	heavy	5
Dalia-3	23	NR	heavy	5
Girassol-1	35	62	light	1
Girassol-2a	32	62	light to medium	1
Girassol-2b	31	68	medium	1
Rosa-1	28	63	medium	2
Rosa-2	27	58	medium	3
Lirio-1	31	63	medium	2
Orquidea-1	22.4	44	heavy	6
Perpetua-1	20	65	heavy	6
Camelia-1	23	NR	heavy	3
Cravo-1	34	NR	heavy	1
Tulipa-1	24.1	59	heavy	3

NR = not recorded

Table 7 API gravity, reservoir temperature and biodegradation rank (Peters & Moldowan, 1993) for block 17 oils.

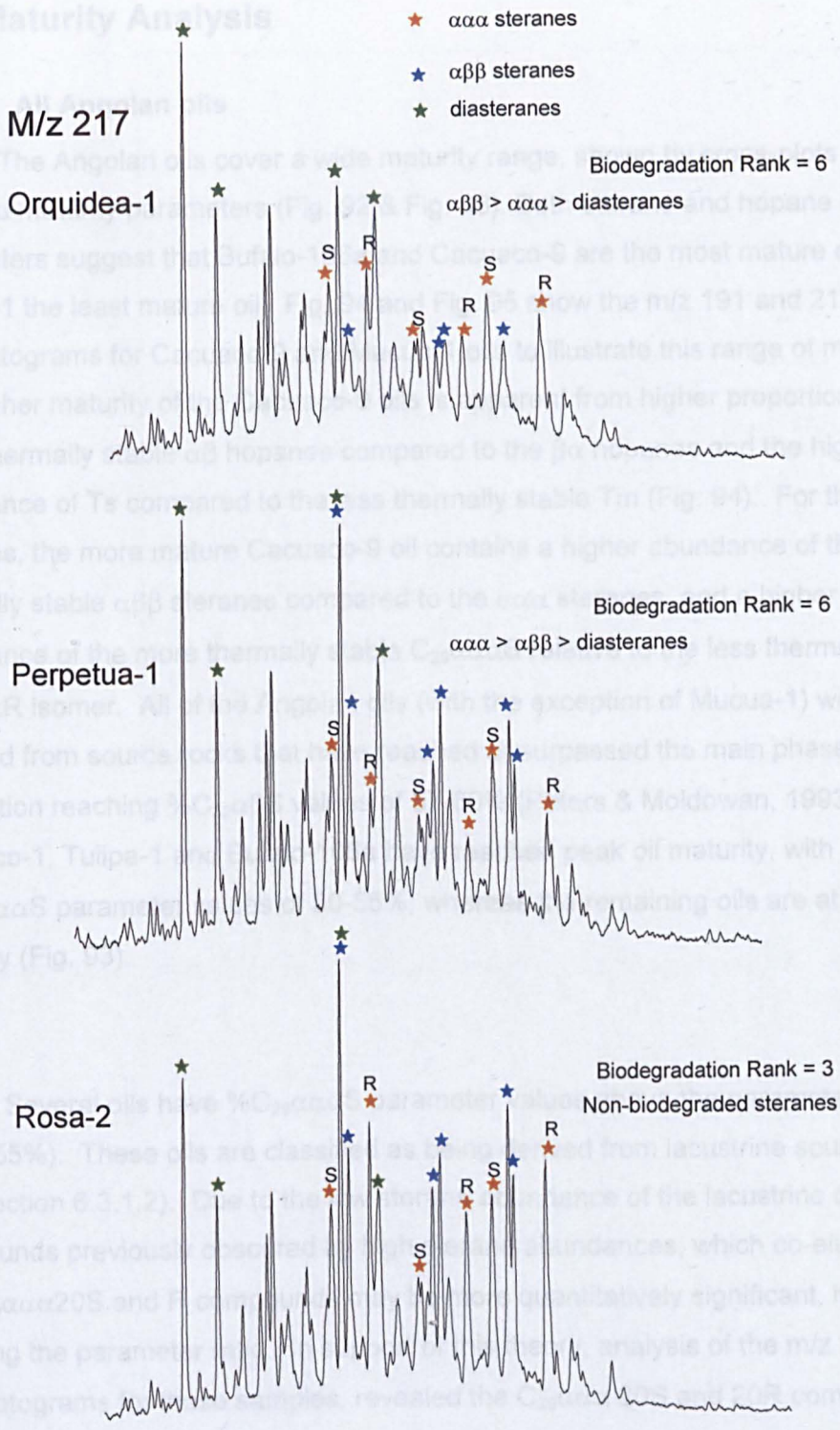

Fig. 91 M/z 217 mass chromatograms for Orquidea-1, Perpetua-1 and Rosa-1. Note, the unusual order of biodegradation of compounds in Orquidea-1 (αββ > ααα), as opposed to the more regular ordering in Perpetua-1 (ααα > αββ). Oil biodegradation rankings are according to Peters & Moldowan (1993).

6.2 Maturity Analysis

6.2.1.1 All Angolan oils

The Angolan oils cover a wide maturity range, shown by cross-plots of selected maturity parameters (Fig. 92 & Fig. 93). Both sterane and hopane maturity parameters suggest that Bufalo-106a and Cacuaco-9 are the most mature oils, and Mucua-1 the least mature oil. Fig. 94 and Fig. 95 show the m/z 191 and 217 mass chromatograms for Cacuaco-9 and Mucua-1 oils to illustrate this range of maturity. The higher maturity of the Cacuaco-9 oils is apparent from higher proportions of the more thermally stable αβ hopanes compared to the βα hopanes and the higher abundance of Ts compared to the less thermally stable Tm (Fig. 94). For the steranes, the more mature Cacuaco-9 oil contains a higher abundance of the more thermally stable αββ steranes compared to the ααα steranes, and a higher relative abundance of the more thermally stable C_{29}ααα**S** relative to the less thermally stable C_{29}ααα**R** isomer. All of the Angolan oils (with the exception of Mucua-1) were expelled from source rocks that have reached or surpassed the main phase of oil generation reaching %C_{32}αβ**S** values of 57-60% (Peters & Moldowan, 1993). Cacuaco-1, Tulipa-1 and Bufalo-106a have reached peak oil maturity, with %C_{29}ααα**S** parameter values of 50-55%, whereas the remaining oils are at early oil maturity (Fig. 93).

Several oils have %C_{29}ααα**S** parameter values above the parameter end point (55%). These oils are classified as being derived from lacustrine source rocks (see section 6.3.1.2). Due to the low sterane abundance of the lacustrine oils, compounds previously obscured by high sterane abundances, which co-elute with the C_{29}ααα20S and R compounds may be more quantitatively significant, hence affecting the parameter ratio. In support of this theory, analysis of the m/z 217 chromatograms for these samples, revealed the C_{29}ααα 20S and 20R compounds have broadened peaks suggesting co-elution of compounds.

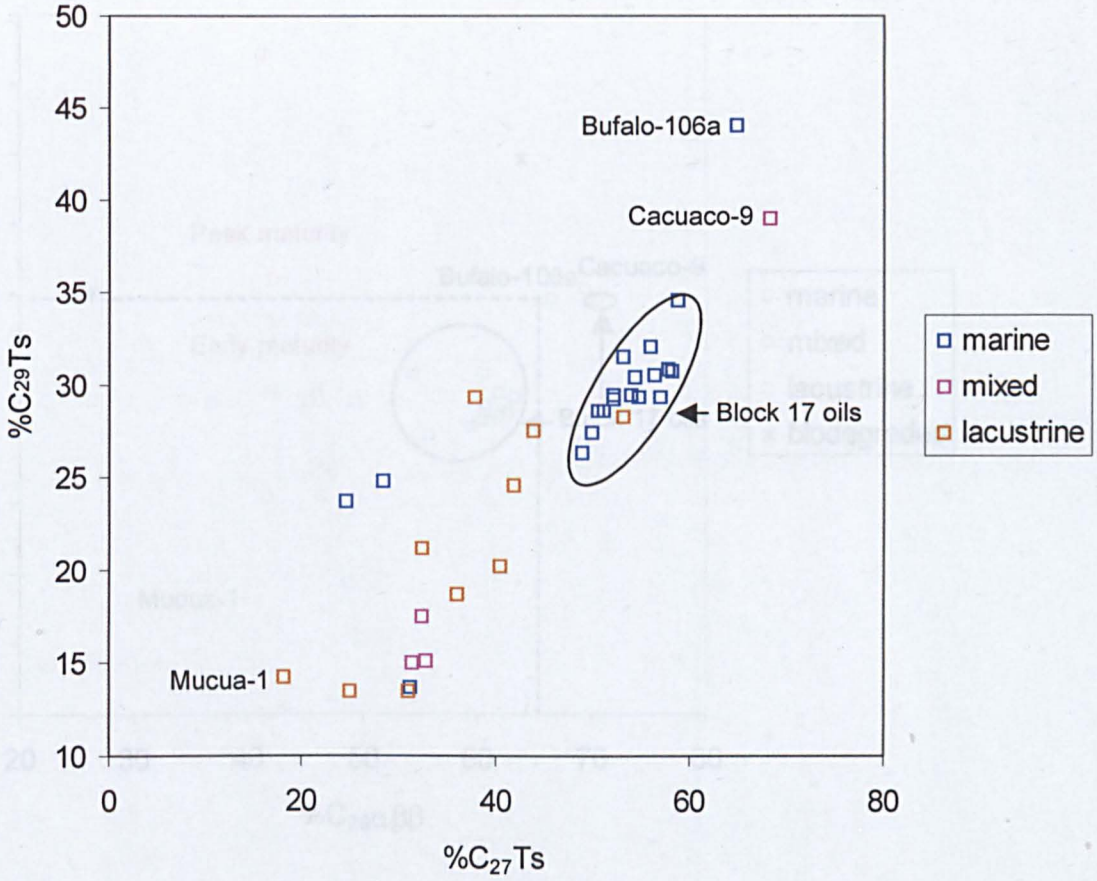

Fig. 92 Cross plot of the $\%C_{27}Ts$ versus $\%C_{29}Ts$ hopane maturity parameters for all Angolan oils.

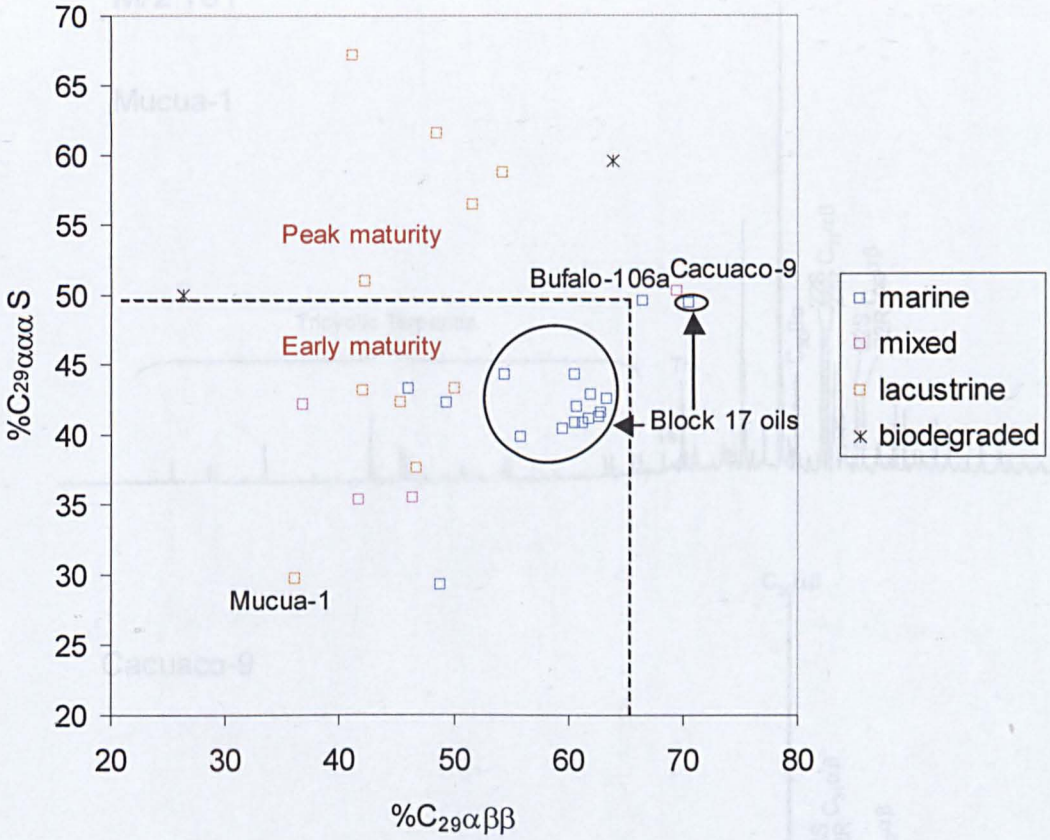

Fig. 93 Cross plot of the $\%C_{29}\alpha\alpha\alpha S$ versus $\%C_{29}\alpha\beta\beta S$ sterane maturity parameters for all Angolan oils. Peak and early mature oils are classified according to Mackenzie *et al.,* 1980; Peters & Moldowan, 1993).

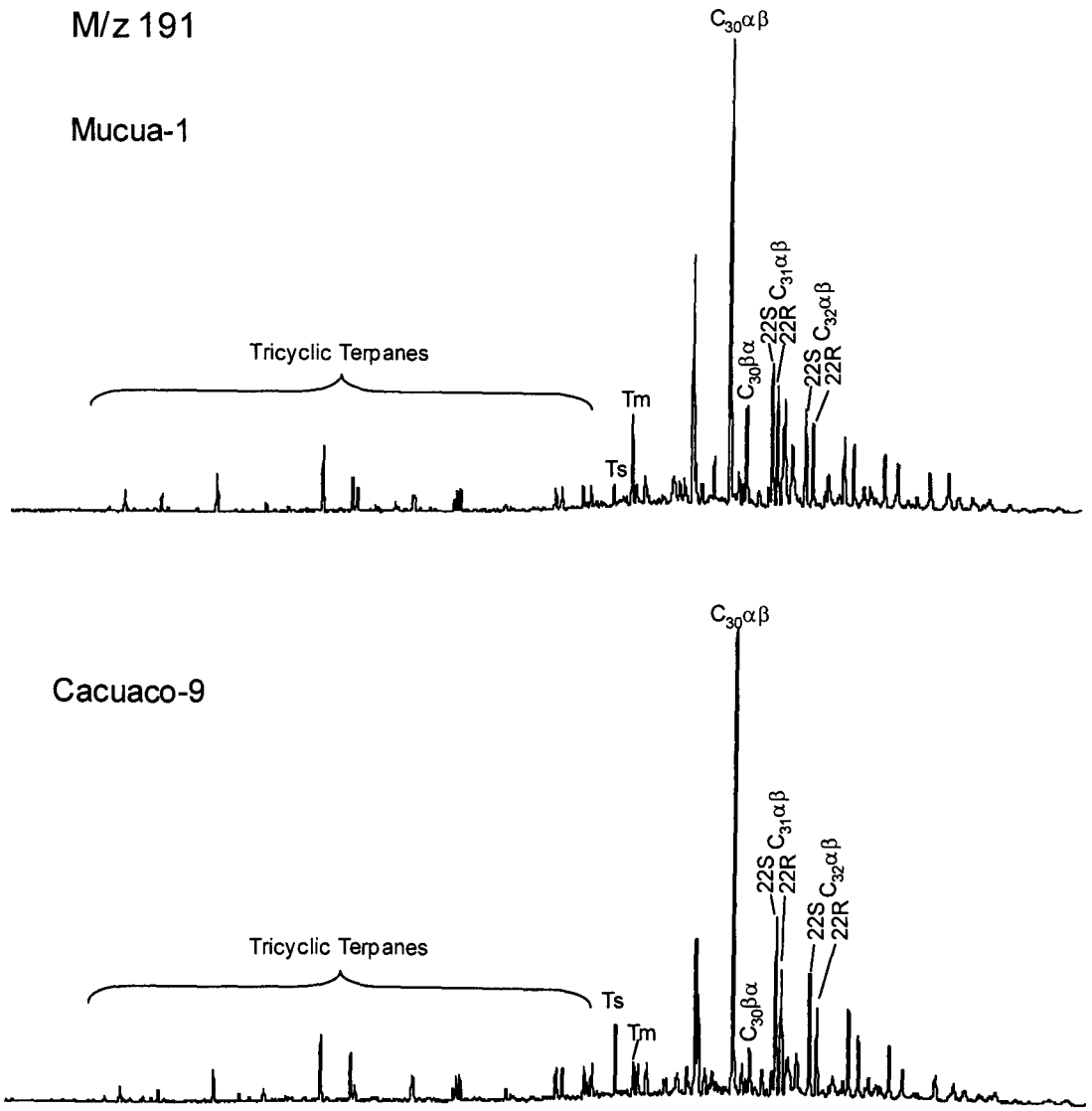

Fig. 94 M/z 191 mass chromatograms of the early mature oil, Mucua-1 and peak mature oil, Cacuaco-1.

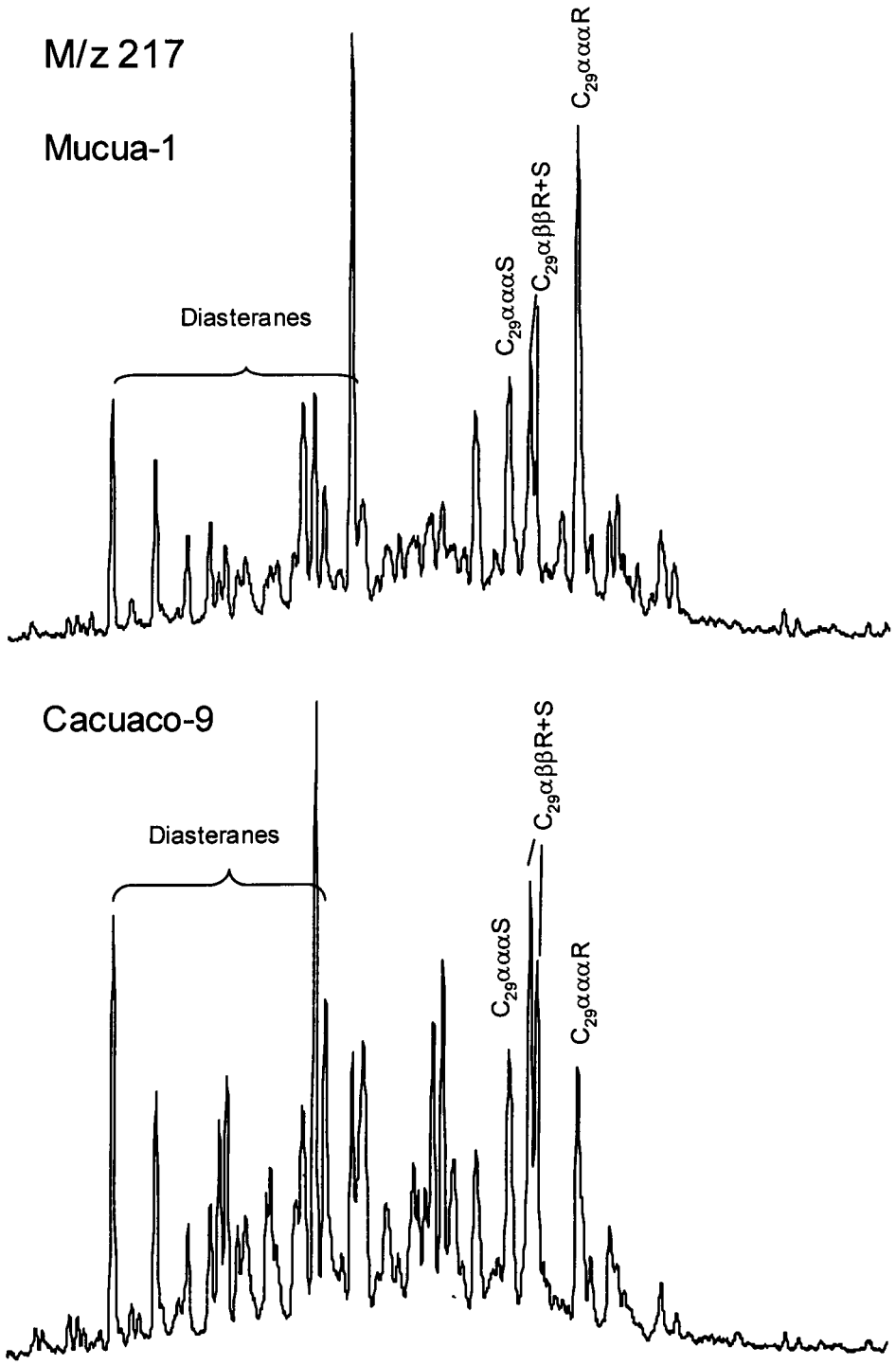

Fig. 95 M/z 217 mass chromatograms of the early mature oil, Mucua-1 and peak mature oil, Cacuaco-1.

6.2.1.2 Block 17 oils

The block 17 oils fall within a narrow maturity range compared to the other Angolan oils (Fig. 92 & Fig. 93). Slight maturity differences (Fig. 96) can be seen

between the oils determined using the hopane maturity parameters $\%C_{27}Ts$ and $\%C_{29}Ts$ (see below):

Tulipa > Lirio = Orquidea = Cravo > Rosa > Girassol = Perpetua > Camelia = Dalia.

With the exception of Tulipa-1, which is at peak maturity the block 17 oils are all early mature (Fig. 97). Perpetua-1 and Orquidea-1 steranes are biodegraded and therefore show anomalous sterane maturity parameter values. The sterane maturity parameters show the same general sequence to the hopanes (see below):

Tulipa > Girassol = Rosa = Lirio = Cravo > Dalia > Camelia.

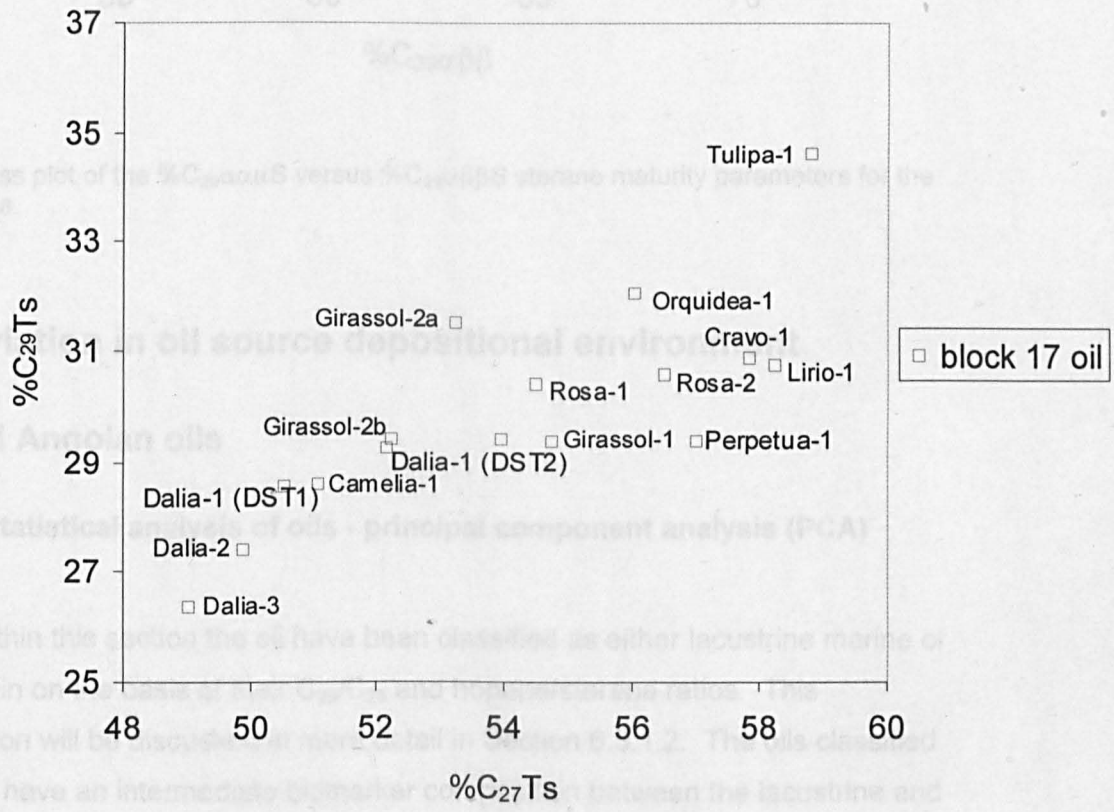

Fig. 96 Cross plot of the $\%C_{27}Ts$ versus $\%C_{29}Ts$ hopane maturity parameters for the block 17 oils.

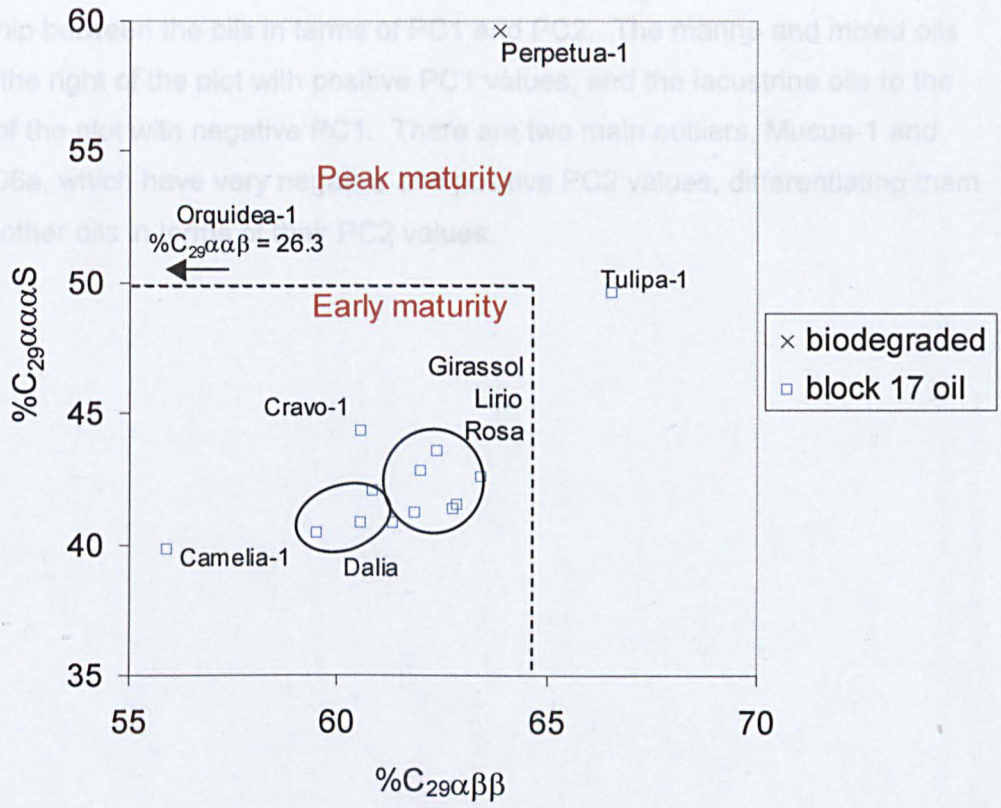

Fig. 97 Cross plot of the $\%C_{29}\alpha\alpha\alpha S$ versus $\%C_{29}\alpha\beta\beta S$ sterane maturity parameters for the block 17 oils.

6.3 Variation in oil source depositional environment

6.3.1 All Angolan oils

6.3.1.1 Statistical analysis of oils - principal component analysis (PCA)

Within this section the oil have been classified as either lacustrine marine or mixed origin on the basis of their C_{26}/C_{25} and hopane/sterane ratios. This classification will be discussed in more detail in Section 6.3.1.2. The oils classified as 'mixed' have an intermediate biomarker composition between the lacustrine and marine oils in terms of their C_{26}/C_{25} and hopane/sterane ratios which may be derived from either two or more oils from different sources, or comprise an oil derived from a source rock section composed of mixed marine and lacustrine organofacies. Principal component analysis (PCA) was performed on a data set of 56 biomarker peaks from 30 Angolan oils. In the analysis PC1 explained 48% of the variance in

the normalized data set and PC2, 28% of the variance. Fig. 98 shows the relationship between the oils in terms of PC1 and PC2. The marine and mixed oils group to the right of the plot with positive PC1 values, and the lacustrine oils to the left side of the plot with negative PC1. There are two main outliers, Mucua-1 and Bufalo-106a, which have very negative and positive PC2 values, differentiating them from the other oils in terms of their PC2 values.

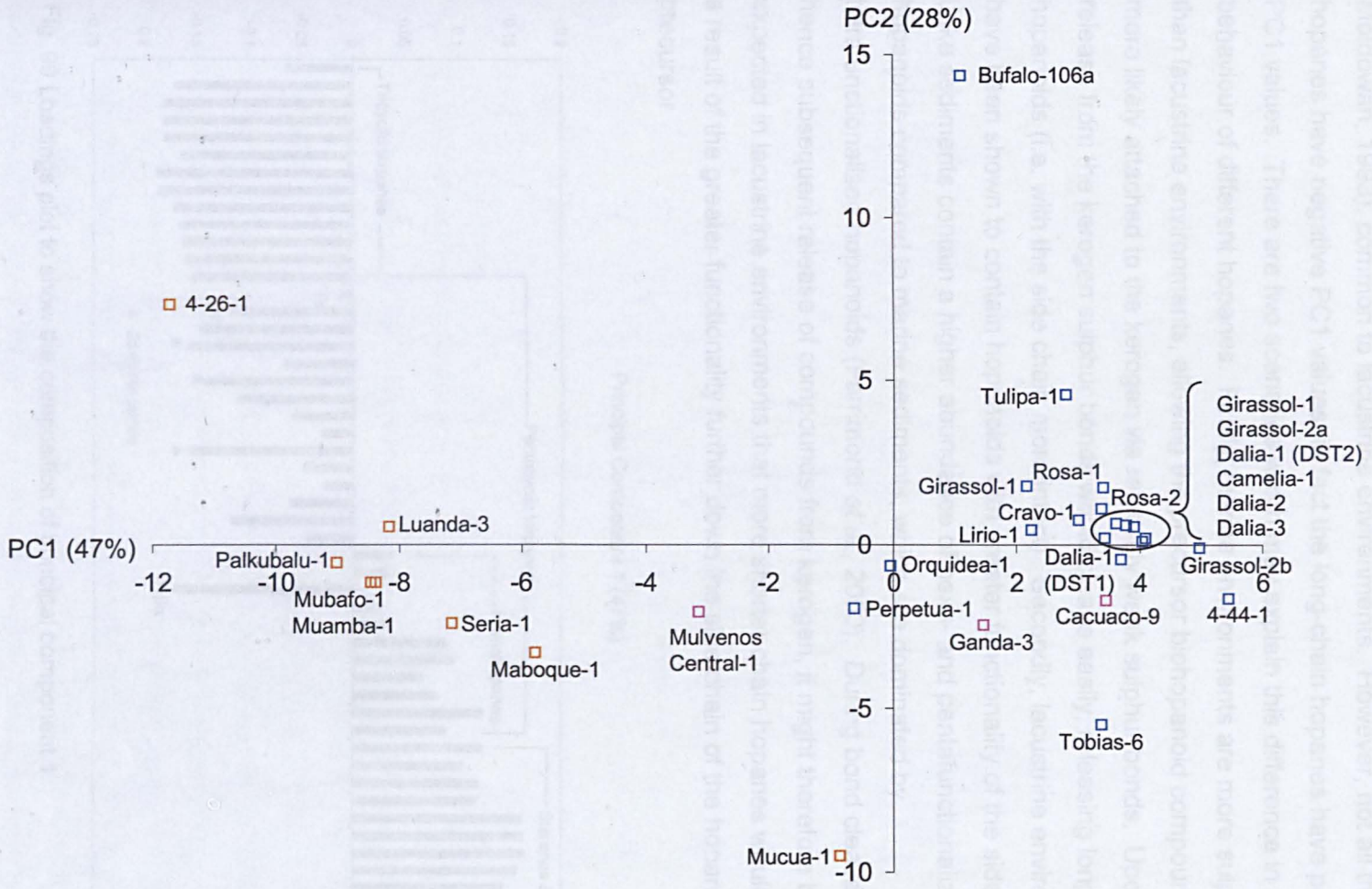

Fig. 98 A scores plot (PC1 *vs.* PC2) showing the relationships between the Angolan oils in terms of the first and second principal components. PC1 explains 48% of the variance and PC2 explains a further 28% (samples are coloured as follows, marine = blue, lacustrine = orange & mixed = pink).

PC1 reflects the proportion of steranes, diasteranes and long-chain hopanoids (homohopanes) relative to short-chain hopanes and tricyclic terpanes (Fig. 98). This may reflect variations in organic matter supply; marine environments have high abundances of steranes interpreted to represent contributions from marine algal organic matter (Peters & Moldowan, 1993). In contrast, high abundances of hopanes relative to steranes indicate contributions to the source depositional environment from terrigenous and/or microbial reworked organic matter (Peters & Moldowan, 1993), common to lacustrine environments. However, not all the hopanes have negative PC1 values; in fact the long-chain hopanes have positive PC1 values. There are two scenarios which may explain this difference in apparent behaviour of different hopanes. Firstly, marine environments are more sulphur rich than lacustrine environments, allowing the precursor biohopanoid compounds to be more likely attached to the kerogen via relatively weak sulphur bonds. Upon their release from the kerogen sulphur bonds would cleave easily, releasing longer chain hopanoids (i.e. with the side chain more intact). Secondly, lacustrine environments have been shown to contain hopanoids with greater functionality of the side chain. Lake sediments contain a higher abundance of hexa- and pentafunctionalized hopanoids compared to marine sediments, which are dominated by tetrafunctionalised hopanoids (Farrimond *et al.*, 2000). During bond cleavage and hence subsequent release of compounds from kerogen, it might therefore be expected in lacustrine environments that more shorter chain hopanes would occur as a result of the greater functionality further down the side chain of the hopanoid precursor.

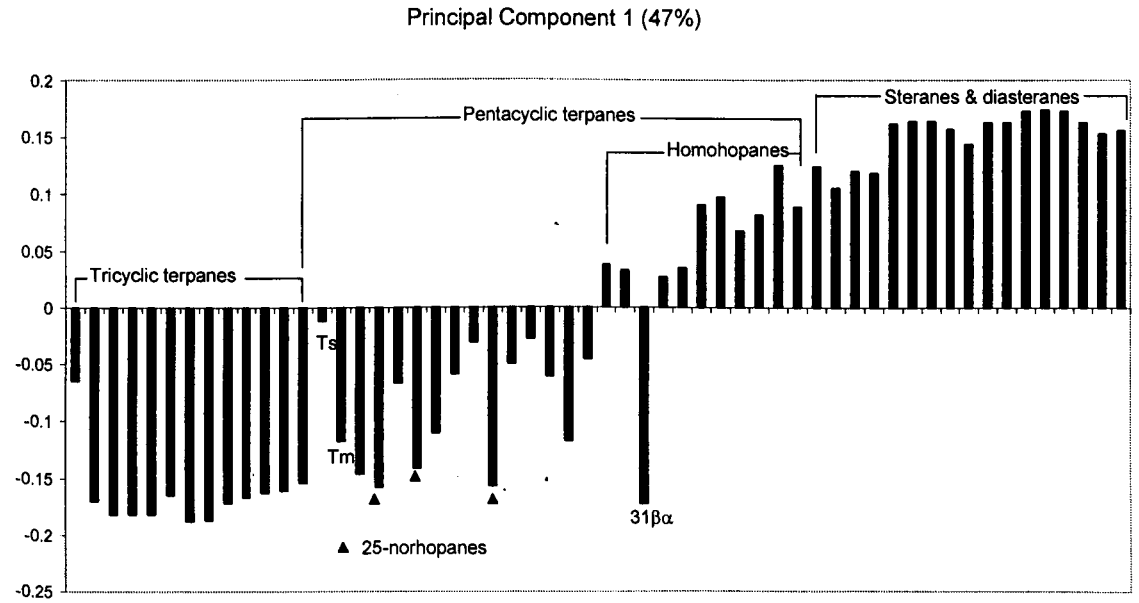

Fig. 99 Loadings plot to show the composition of principal component 1.

PC2 is again a source-related principal component, essentially relating to algal (positive PC2, steroids and tricyclic terpanes) versus bacterial input (negative PC2, pentacyclic terpanes) (Fig. 100). However, there are some maturity influences within PC2; for example, the less thermally stable ααα20R steranes plot with a negative PC2 compared to the more thermally stable steranes and diasteranes with a positive PC2. Also, Tm has a negative PC2 loading whereas the more thermally stable Ts has a positive loading on PC2. Thus, Bufalo-106a (the most mature oil in this study) has the most positive PC2 value and Mucua-1 (the least mature oil in this study) has the most negative PC2 value.

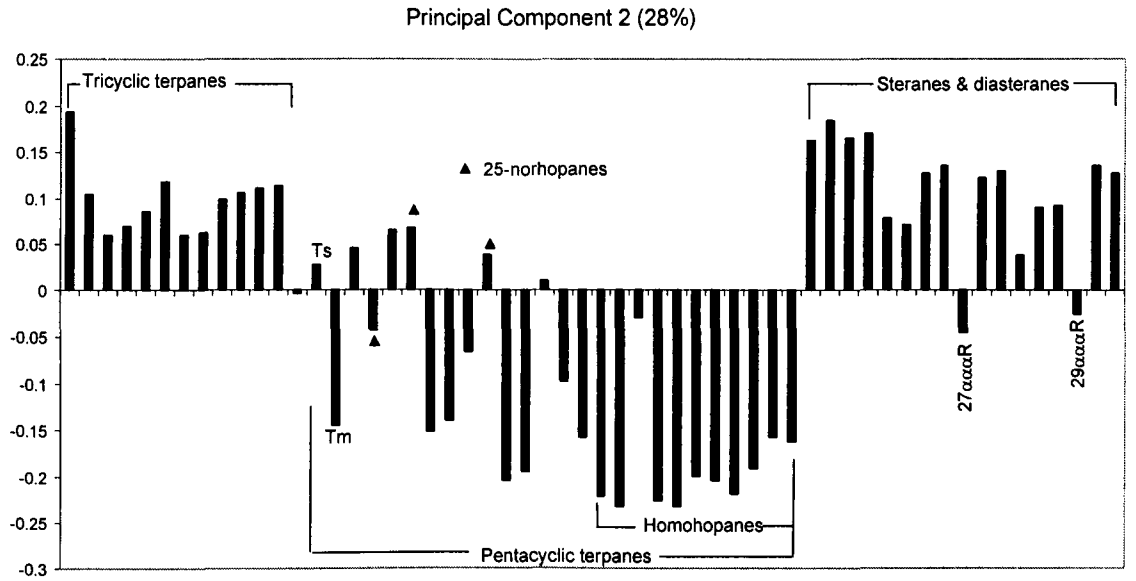

Fig. 100 Loadings plot to show the composition of principal component 2.

6.3.1.2 Lacustrine versus marine

The Angolan oils, like the source rocks (Section 4.2.1), are classified on the basis of their C_{26}/C_{25} tricyclic terpane and hopane/sterane ratios as marine, lacustrine or 'mixed' (Burwood, 1999; Schiefelbein *et al.*, 1999, Cole *et al.*, 2000). Lacustrine-derived oils have high hopane/sterane values (>2) and C_{26}/C_{25} tricyclic terpane ratio values greater > 1, whereas marine-derived oils have low hopane/sterane values (<2) and C_{26}/C_{25} tricyclic terpane values < 1. The term 'mixed' may be applied to an oil composed of two or more oils from different sources, or an oil derived from a source rock section composed of mixed marine and lacustrine organofacies; for example, lacustrine source rocks with marine incursions. The mixed oils have

intermediate C_{26}/C_{25} and hopane/sterane values between the marine- and lacustrine-derived oils (Fig. 101). Biomarker analysis shows they have a molecular composition most similar to the marine oils, suggesting they are derived predominantly from marine source rocks with only minor lacustrine contributions. However, the oil-source rock correlation chapter of this thesis will critically evaluate the use of the C_{26}/C_{25} tricyclic terpane ratio and hopane/sterane ratios to define the source rocks and oils in this thesis as either marine or lacustrine, and investigate the applicability of these parameters to further characterise oils as mixed on the basis of these parameters.

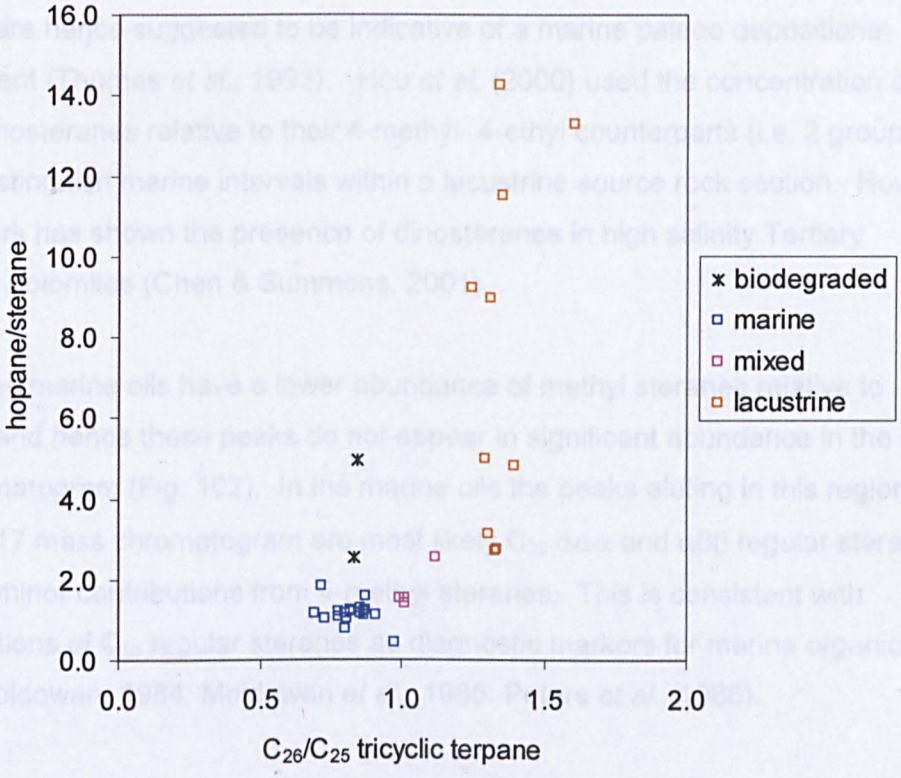

Fig. 101 Cross plot of the C_{26}/C_{25} tricyclic terpane ratio and the hopane/sterane parameter for all Angolan oils.

Examination of the m/z 217 mass chromatograms for the lacustrine oils shows they appear to have abundant C_{30} $\alpha\alpha\alpha$ and $\alpha\beta\beta$ steranes. However the lacustrine oils have a high abundance of 4-methyl steranes relative to steranes (Fig. 102), and examination of the m/z 231 mass chromatogram reveals that the peaks eluting in the C_{30} regular steranes region in the m/z 217 mass chromatogram are actually C_{30} 4α- methyl steranes (Fig. 102). This is explained by the presence of an m/z 217 ion in the mass spectra of 4-methyl steranes which means that if they occur in high abundance they may also appear in the m/z 217 chromatogram. Although the

origin of 4-methyl steranes is debated in the literature, they are thought to derive primarily from the phytoplankton dinoflagellates found in both marine and lacustrine environments (Thomas *et al.,* 1993). The distribution of compounds in the C_{30} region of the m/z 231 mass chromatogram for the marine and lacustrine oils appears complex and may potentially contain dinosteranes (Fig. 102). Further confirmation would require GC-MS-MS analysis. Dinoflagellates are the only major proven source of dinosterane derived from the C_{30} compounds dinosterol and dinostanol (Summons *et al.,* 1992). C_{30} 4-methyl steranes have been found in high abundance in lacustrine sediments; however, C_{30} 4-methyl steranes with the dinosterane skeleton have not been found (Goodwin *et al.,* 1988). Isomers with the presence of the dinosterane skeleton are hence suggested to be indicative of a marine palaeo depositional environment (Thomas *et al.,* 1993). Hou *et al.* (2000) used the concentration of 4-methyl dinosteranes relative to their 4-methyl- 4-ethyl counterparts (i.e. 2 groups at C-4) to distinguish marine intervals within a lacustrine source rock section. However, recent work has shown the presence of dinosteranes in high salinity Tertiary lacustrine dolomites (Chen & Summons, 2001).

The marine oils have a lower abundance of methyl steranes relative to steranes and hence these peaks do not appear in significant abundance in the m/z 217 chromatogram (Fig. 102). In the marine oils the peaks eluting in this region of the m/z 217 mass chromatogram are most likely C_{30} $\alpha\alpha\alpha$ and $\alpha\beta\beta$ regular steranes, with only minor contributions from 4-methyl steranes. This is consistent with interpretations of C_{30} regular steranes as diagnostic markers for marine organic inputs (Moldowan, 1984; Moldowan *et al.,* 1985: Peters *et al.,* 1986).

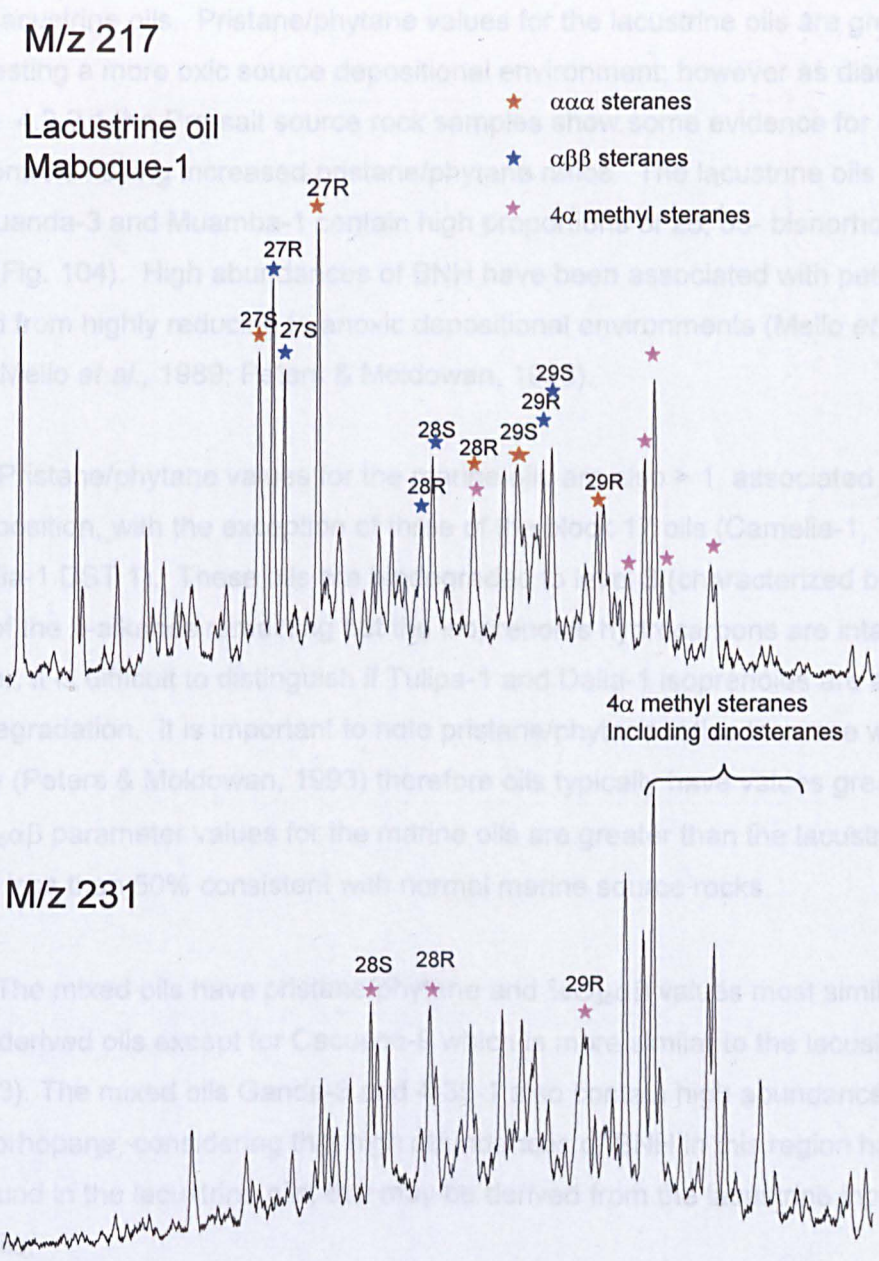

Fig. 102 M/z 217 and 231 mass chromatograms to illustrate the sterane and 4-methyl sterane distributions for the lacustrine oil Maboque-1. Note, the 4-methyl steranes also have an m/z 217 ion and hence can be seen in the m/z 217 chromatogram due to their high abundance in the lacustrine oil.

6.3.1.3 Redox conditions

The $\%C_{35}\alpha\beta$ parameter ($(100*C_{35}\alpha\beta(S+R)/(C_{34}+C_{35}\alpha\beta(S+R))$; comparable to the homohopane index) has been used to infer the redox conditions of ancient depositional environments; high values are typical of anoxic marine conditions (ten Haven *et al.,* 1988; Peters & Moldowan, 1991). The lacustrine oils have relatively low values; however high C_{35} abundances rely upon sulphur (Peters & Moldowan, 1991), which is generally low in lacustrine sediments and may explain the low values

for the lacustrine oils. Pristane/phytane values for the lacustrine oils are greater than 1 suggesting a more oxic source depositional environment; however as discussed in Section 4.2.2.1 the Pre-salt source rock samples show some evidence for organic input controls having increased pristane/phytane ratios. The lacustrine oils 4-26-1, 4-26-2, Luanda-3 and Muamba-1 contain high proportions of 28, 30- bisnorhopane (BNH) (Fig. 104). High abundances of BNH have been associated with petroleum sourced from highly reducing to anoxic depositional environments (Mello *et al.,* 1988a; Mello *et al.,* 1989; Peters & Moldowan, 1993).

Pristane/phytane values for the marine oils are also > 1, associated with more oxic deposition, with the exception of three of the block 17 oils (Camelia-1, Tulipa-1 and Dalia-1 DST 1). These oils are biodegraded to level 3 (characterized by only traces of the *n*-alkanes remaining but the isoprenoids hydrocarbons are intact). However, it is difficult to distinguish if Tulipa-1 and Dalia-1 isoprenoids are affected by biodegradation. It is important to note pristane/phytane ratios increase with maturity (Peters & Moldowan, 1993) therefore oils typically have values greater than 1. $\%C_{35}\alpha\beta$ parameter values for the marine oils are greater than the lacustrine oils and are less than 50% consistent with normal marine source rocks.

The mixed oils have pristane/phytane and $\%C_{35}\alpha\beta$ values most similar to the marine-derived oils except for Cacuaco-9 which is more similar to the lacustrine oils (Fig. 103). The mixed oils Ganda-3 and 4-35-1 also contain high abundances of 28, 30 bisnorhopane; considering that high abundances of BNH in this region have only been found in the lacustrine oils, this may be derived from the lacustrine inputs to the mixed oils.

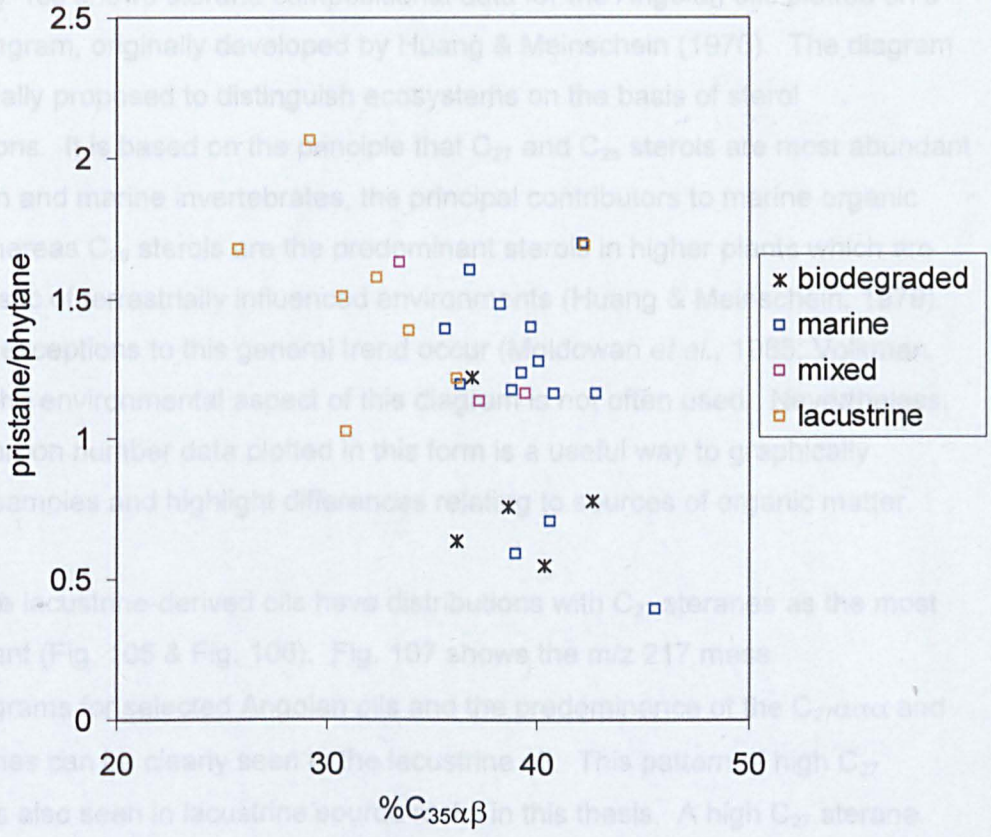

Fig. 103 Cross plot of the pristane/phytane ratio and the $\%C_{35}\alpha\beta$ parameter for all Angolan oils. The $\%\ C_{35}\alpha\beta$ parameter is calculated as follows $100*(C_{35}\alpha\beta S+R/((C_{35}\alpha\beta S+R)+(C_{34}\alpha\beta S+R))$.

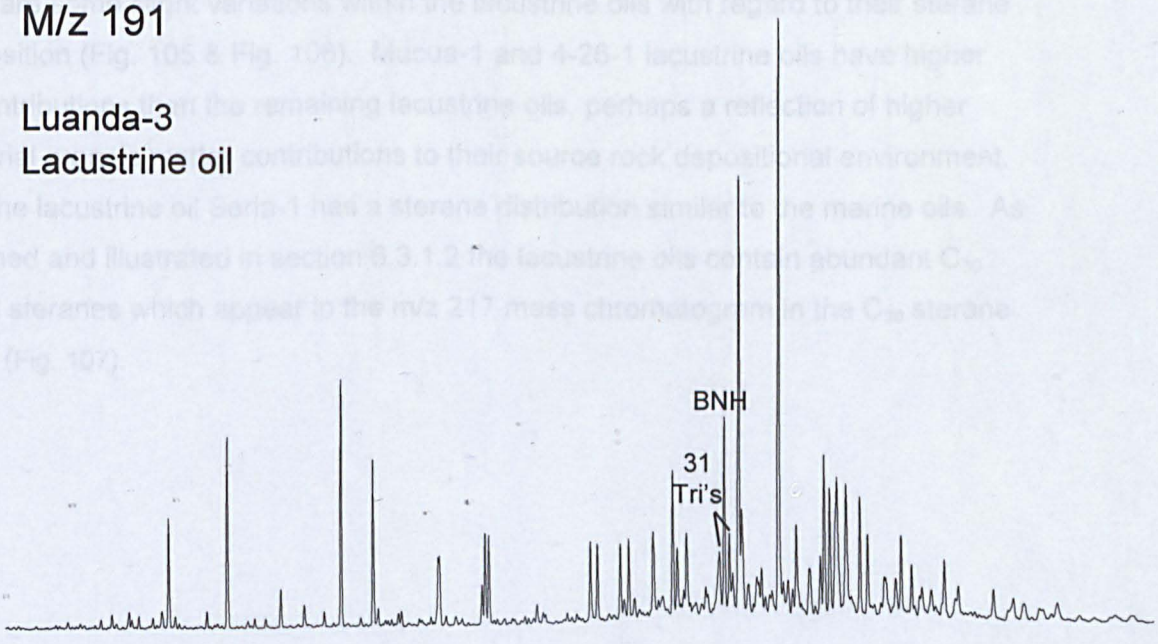

Fig. 104 M/z 191 chromatogram of Luanda-3 oil to illustrate the high abundance of 28, 30-bisnorhopane.

6.3.1.4 Algal versus terrestrial indicators

Fig. 105 shows sterane compositional data for the Angolan oils plotted on a ternary diagram, originally developed by Huang & Meinschein (1976). The diagram was originally proposed to distinguish ecosystems on the basis of sterol compositions. It is based on the principle that C_{27} and C_{28} sterols are most abundant in plankton and marine invertebrates, the principal contributors to marine organic matter, whereas C_{29} sterols are the predominant sterols in higher plants which are characteristic of terrestrially influenced environments (Huang & Meinschein, 1979). However, exceptions to this general trend occur (Moldowan *et al.*, 1985; Volkman, 1986) so the environmental aspect of this diagram is not often used. Nevertheless, sterane carbon number data plotted in this form is a useful way to graphically compare samples and highlight differences relating to sources of organic matter.

The lacustrine-derived oils have distributions with C_{27} steranes as the most predominant (Fig. 105 & Fig. 106). Fig. 107 shows the m/z 217 mass chromatograms for selected Angolan oils and the predominance of the $C_{27}\alpha\alpha\alpha$ and $\alpha\beta\beta$ steranes can be clearly seen in the lacustrine oil. This pattern of high C_{27} steranes is also seen in lacustrine source rocks in this thesis. A high C_{27} sterane abundance is also observed in the Brazilian oils of lacustrine origin (Mello *et al.*, 1988a). Non-marine environments are more commonly associated with higher C_{29} contributions, a reflection of such environments experiencing greater exposure to terrigenous organic matter (Huang & Meinschein, 1979; Moldowan *et al.*, 1985). There are some slight variations within the lacustrine oils with regard to their sterane composition (Fig. 105 & Fig. 106). Mucua-1 and 4-26-1 lacustrine oils have higher C_{29} contributions than the remaining lacustrine oils, perhaps a reflection of higher terrestrial organic matter contributions to their source rock depositional environment. Also, the lacustrine oil Seria-1 has a sterane distribution similar to the marine oils. As explained and illustrated in section 6.3.1.2 the lacustrine oils contain abundant C_{30} methyl steranes which appear in the m/z 217 mass chromatogram in the C_{30} sterane region (Fig. 107).

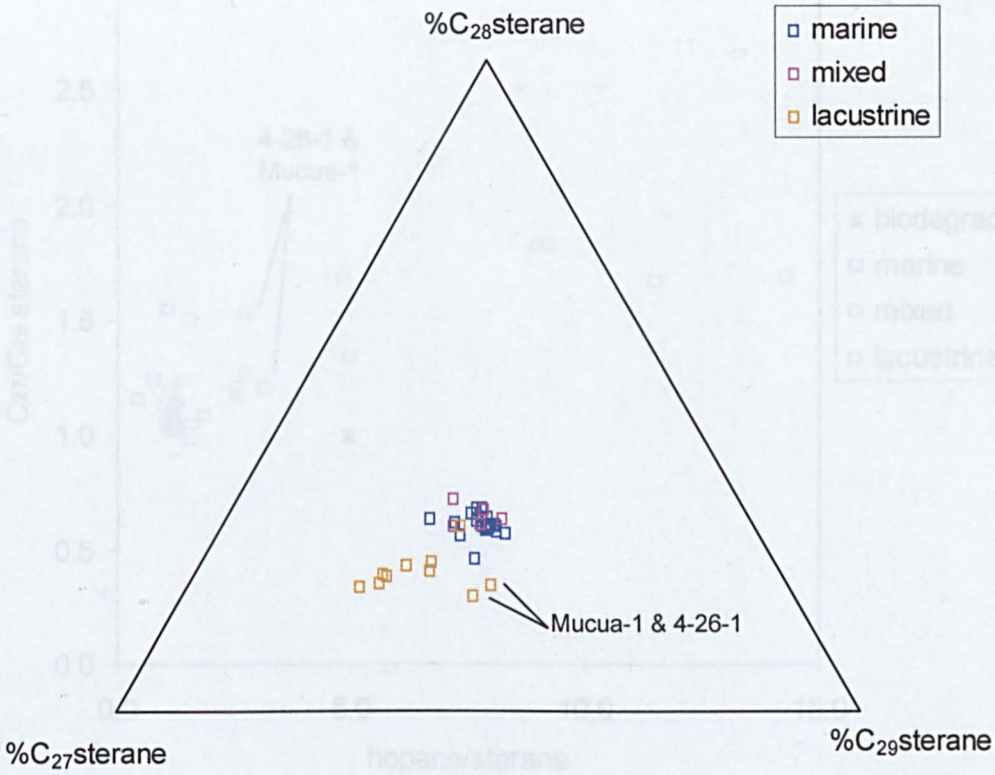

Fig. 105 Ternary diagram of all Angolan oil C_{27}, C_{28} and C_{29} α(H), 14β(H), 17β(H), 20 S + R sterane distributions. The $\alpha\beta\beta$ steranes have been used as opposed to the $\alpha\alpha\alpha$ steranes because the Norsk Hydro automatic quantification system does not measure the C_{28}aaaR. Note, the two lacustrine oils with higher C_{29} steranes are Mucua-1 and 4-26-1.

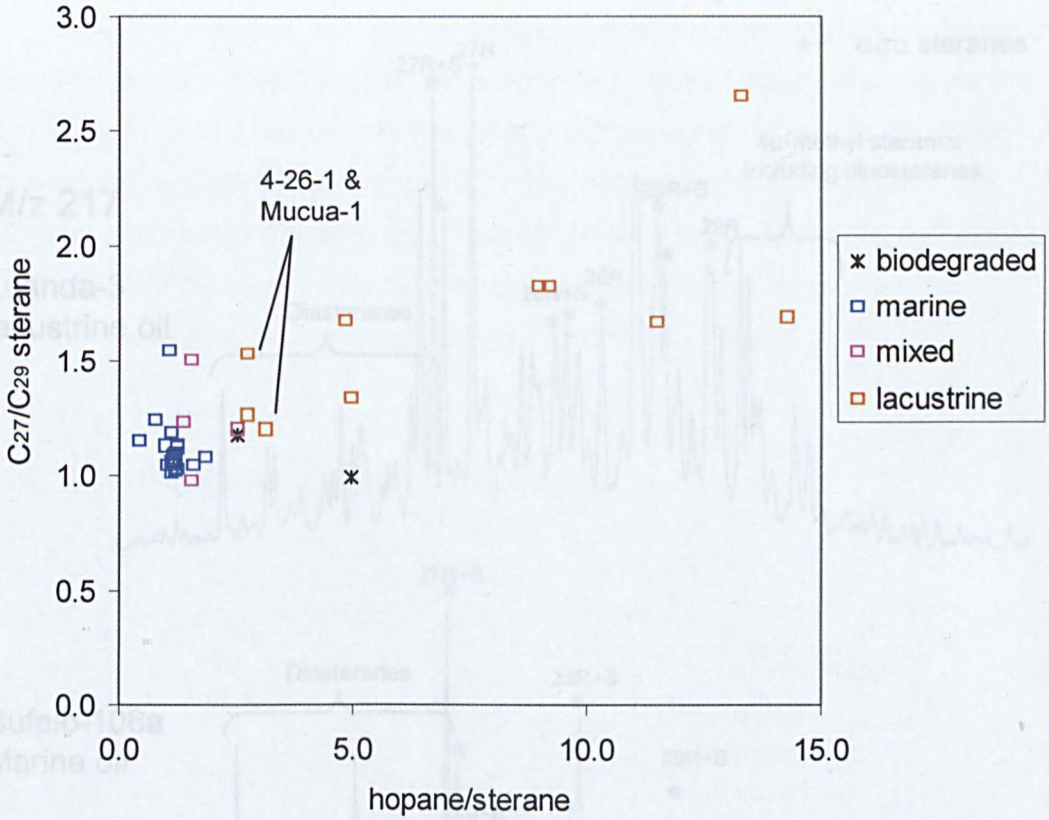

Fig. 106 Cross plot of the C_{27}/C_{29} sterane parameter and the hopane/sterane parameter for all Angolan oils.

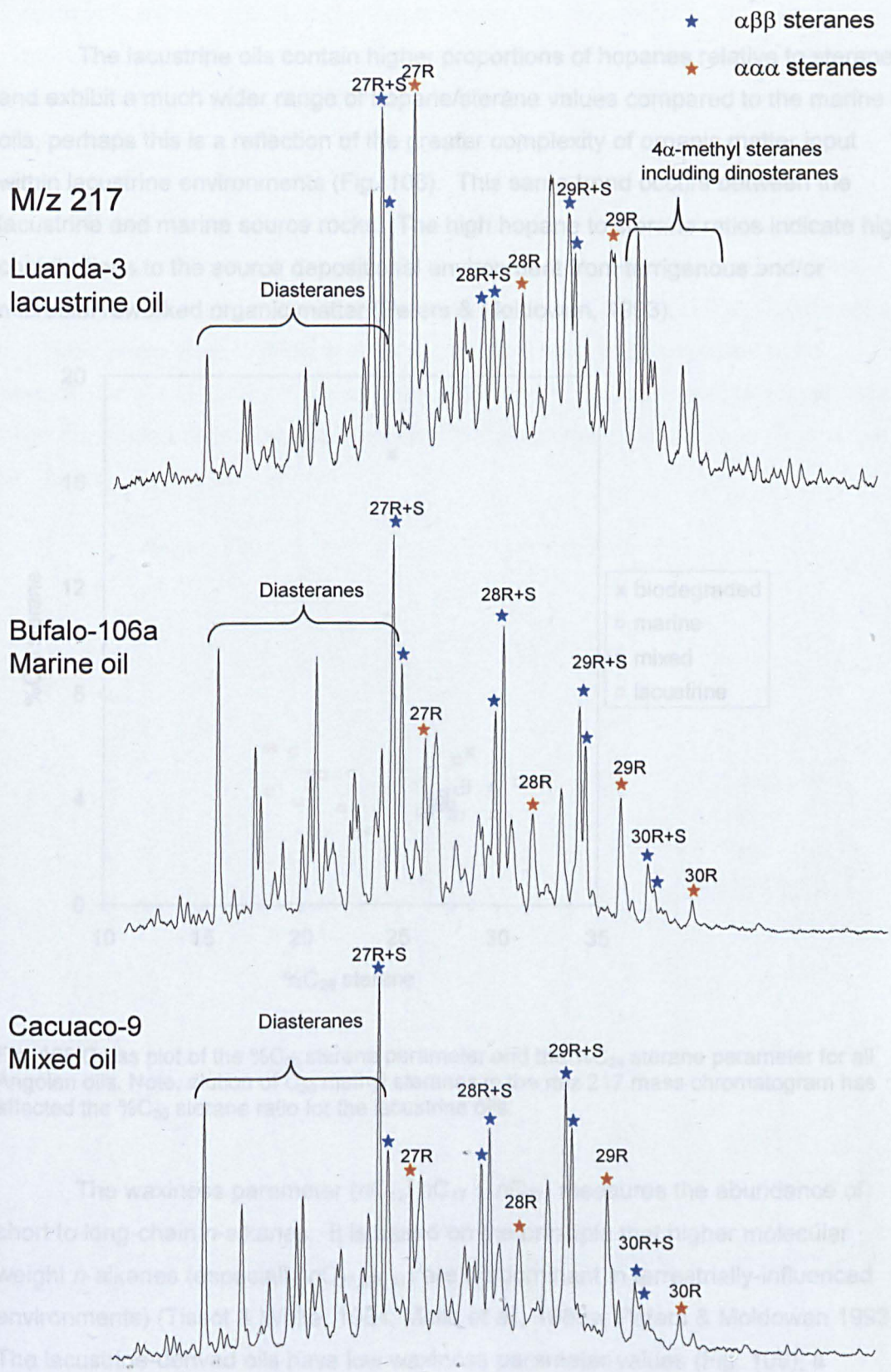

Fig. 107 M/z 217 mass chromatograms to illustrate distribution of C_{27}, C_{28} C_{29} and C_{30} 5α(H), 14α(H), 17α(H), 20R sterane distributions facies of the lacustrine, marine and mixed oils.

The lacustrine oils contain higher proportions of hopanes relative to steranes and exhibit a much wider range of hopane/sterane values compared to the marine oils; perhaps this is a reflection of the greater complexity of organic matter input within lacustrine environments (Fig. 106). This same trend occurs between the lacustrine and marine source rocks. The high hopane to sterane ratios indicate high contributions to the source depositional environment from terrigenous and/or microbial reworked organic matter (Peters & Moldowan, 1993).

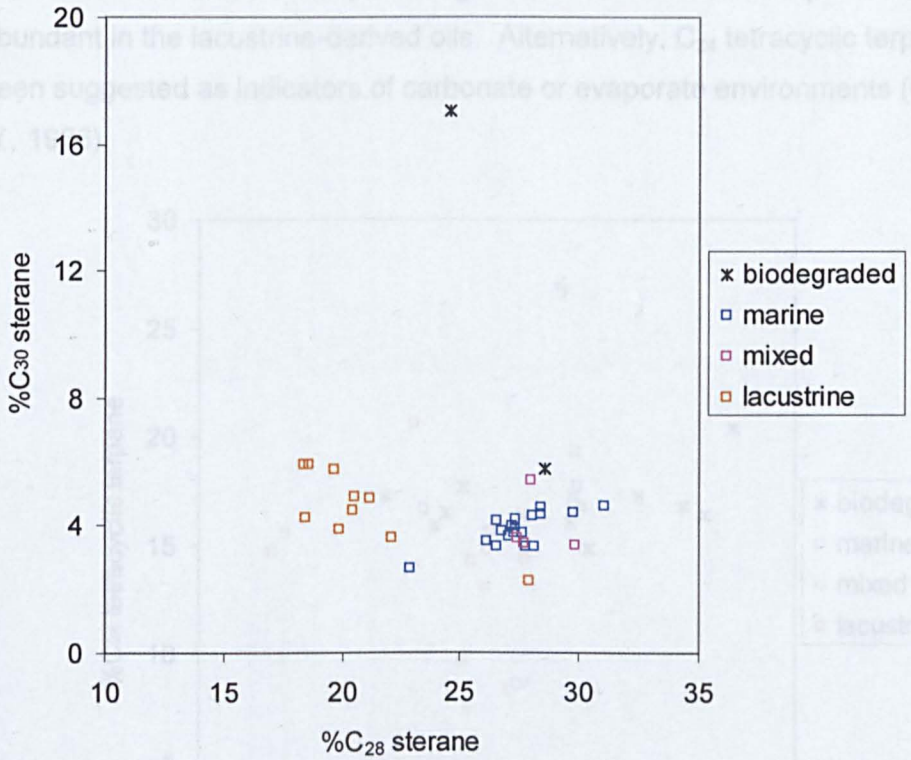

Fig. 108 Cross plot of the $\%C_{30}$ sterane parameter and the $\%C_{28}$ sterane parameter for all Angolan oils. Note, elution of C_{30} methyl steranes in the m/z 217 mass chromatogram has affected the $\%C_{30}$ sterane ratio for the lacustrine oils.

The waxiness parameter (nC_{17}/ nC_{17} + nC_{27}) measures the abundance of short to long-chain *n*-alkanes. It is based on the principle that higher molecular weight *n*-alkanes (especially $nC_{27, 29, 31}$) are predominant in terrestrially-influenced environments) (Tissot & Welte, 1984; Mello *et al.*, 1988a; Peters & Moldowan 1993). The lacustrine-derived oils have low waxiness parameter values (Fig. 109), a reflection of their broad *n*-alkane distributions (Fig. 110). This is consistent with lacustrine environments containing higher amounts of terrigenous-derived organic matter. The lacustrine oils Maboque-1, Mubafo-1, Muamba-1, Palkubalu-1, Luanda-3 show a predominance of the nC_{23} alkane (Fig. 111), a feature also observed in the

lacustrine Cuvo Fm. source rocks in this thesis. An elevated nC_{23} alkane has previously been noted in the marine Kimmeridge Clay Fm. and is suggested to derive from a different (as yet unidentified) source to the other *n*-alkanes (Van Kaam-Peters *et al.*, 1997).

The lacustrine oils have low values of the C_{24} tetracyclic terpane parameters covering a narrow range (~7-20%). C_{24} tetracyclic terpanes have been suggested to represent inputs from terrestrial organic matter (Philp & Gilbert, 1986; Czochanska *et al.*, 1988: Mello *et al.*, 1988a) and might therefore have been expected to be abundant in the lacustrine-derived oils. Alternatively, C_{24} tetracyclic terpanes have been suggested as indicators of carbonate or evaporate environments (Connan *et al.*, 1986).

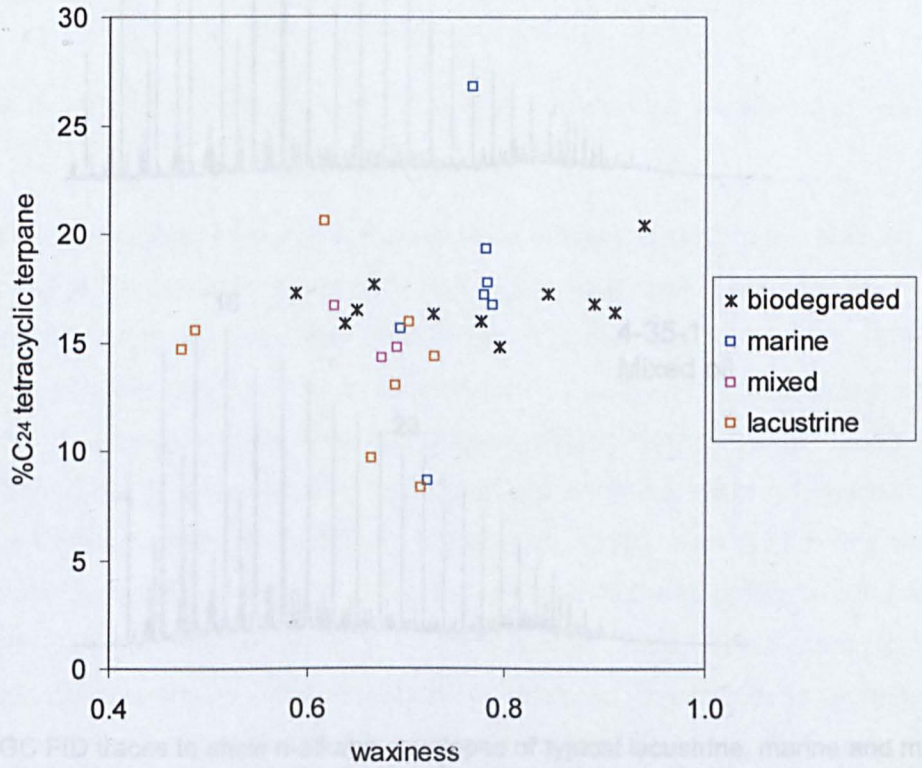

Fig. 109 Cross plot of the $\%C_{24}$ tetracyclic terpane parameter and the $nC_{17}/(nC_{17}+nC_{27})$ (or waxiness) parameter for all Angolan oils. Note biodegradation has only affected the waxiness parameter; values for the $\%C_{24}$ tetracyclic terpane values are valid.

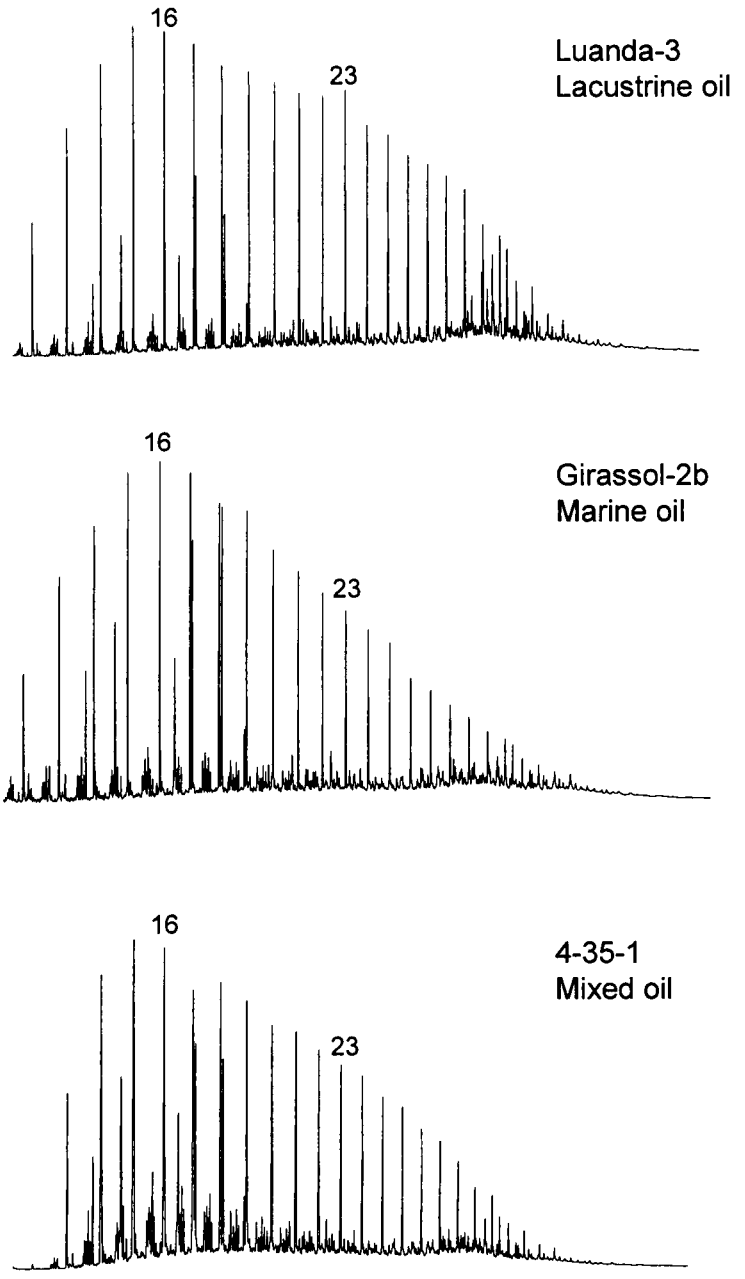

Fig. 110 GC FID traces to show n-alkane envelopes of typical lacustrine, marine and mixed Angolan oils (carbon numbers marked). Note the predominance of high molecular weight (> nC_{23})components for the lacustrine oils and a predominance of the low molecular weight n-alkanes for the marine oils maximising at $nC_{16\text{-}17}$.

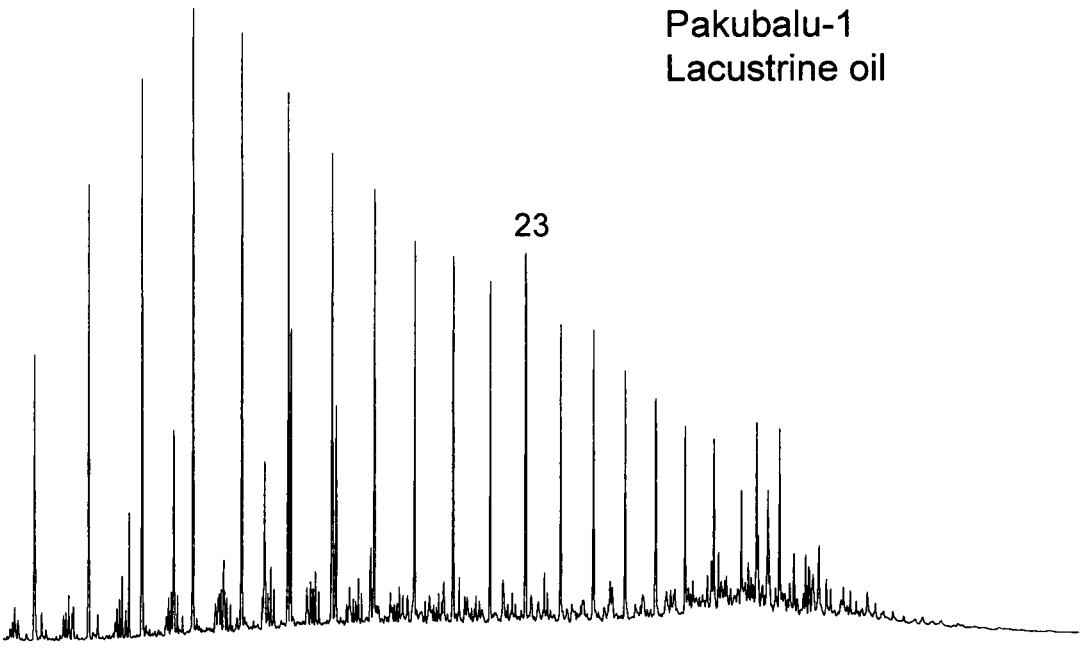

Fig. 111 A GC FID trace of a lacustrine oil to illustrate the elevated abundance of n-C_{23} alkane (carbon number marked).

The marine oils, as with the marine source rocks, display high relative abundances of C_{28} steranes, consistent with inputs from marine plankton and invertebrates (Huang & Meinschein, 1979) (Fig. 105, Fig. 107 & Fig. 108). The C_{28} sterane in some oils can be of equal abundance to the C_{27} and C_{29} homologues. This pattern has been seen in those oils of the Brazilian Atlantic Margin thought to be derived from a highly anoxic source facies with a predominance of calcareous mudstone lithology (Mello *et al.,* 1988b, Mello *et al.,* 1989). The marine Angolan oils also contain C_{30} steranes, thought to derive from invertebrates and/or marine algae (Moldowan, 1984; Moldowan *et al.,* 1985: Peters *et al.,* 1986). The marine oils contain low abundances of hopanes relative to steranes, interpreted to represent dominant contributions from marine algal organic matter (Peters & Moldowan, 1993). The marine-derived oils have higher waxiness parameter values than the lacustrine-derived oils due to their higher abundance of low molecular weight *n*-alkanes (Fig. 109 and Fig. 110. The marine oils, like the lacustrine oils, have low abundances of C_{24} tetracyclic terpanes , with the exceptionof the 4-44-1.

Examination of the m/z 191 chromatograms of all the Angolan oil show that the block 17 marine oils contain a significant quantity of oleanane (Fig. 112). Oleanane is thought to be derived from Angiosperms (flowering plants) that first became predominant in the Late Cretaceous (Peters & Moldowan, 1993). The mixed

oil Mulvenos Central-1 also contains a significant quantity of oleanane. This suggests that the marine oils are derived from or contain contributions from oils sourced from source rocks of Cretaceous or younger age. Note, an absence of oleanane from the other Angolan oils does not infer they do not contain contributions from a source rock of Cretaceous age or younger. However, it is worth noting that the m/z 191 chromatograms for all the Post-salt source rocks in this study contain identifiable quantities of oleanane; it might therefore be expected that the marine oils would show the same characteristics.

The mixed oils have a sterane composition and hopane/sterane ratio most similar to the marine oils. This may suggest that lacustrine contributions are the minor component and is discussed further in the oil-source rock correlation chapter. It should be noted that steranes in the lacustrine facies are in low abundance and therefore may not be expected to greatly influence the sterane distribution of a mixed oil derived from both marine and lacustrine oils, whilst the high abundances of hopanes from a lacustrine-derived oil would significantly influence the hopane/sterane ratio. The *n*-alkane distributions of mixed origin oils do not tail off after nC_{16-17} as quickly the marine oils but contain an intermediate distribution between the marine and lacustrine oils (Fig. 110).

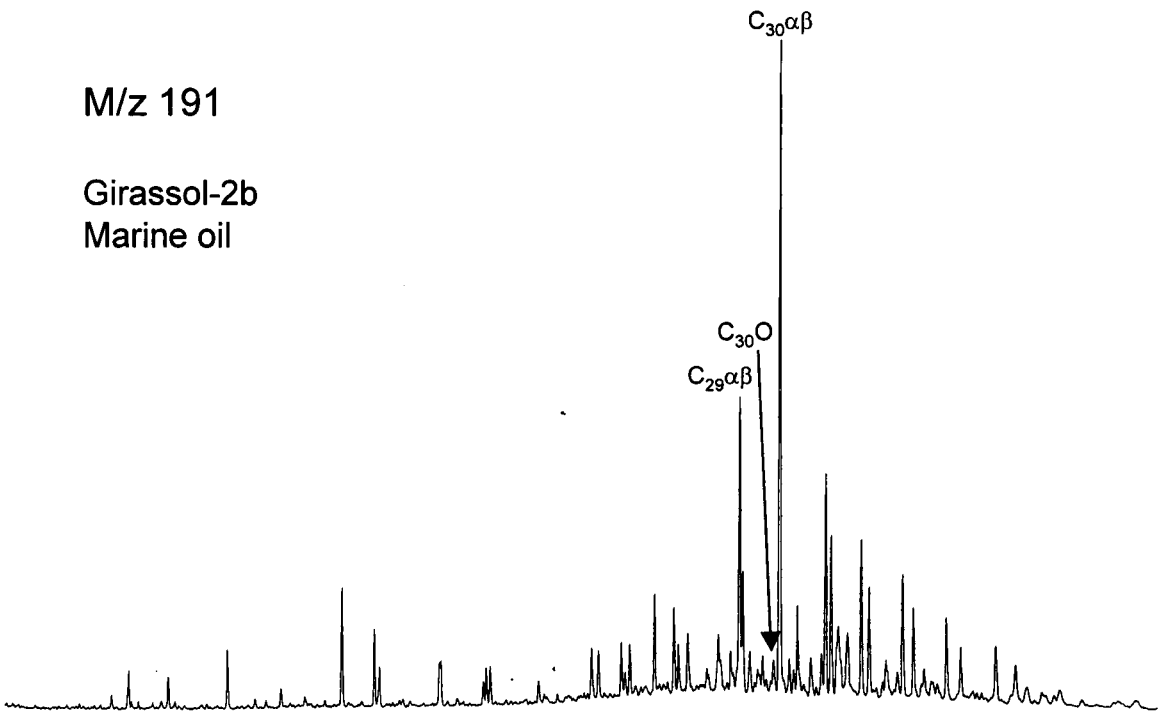

Fig. 112 M/z 191 mass chromatogram to show significant quantities of oleanane in the marine block 17 oils.

6.3.1.5 Water column stratification and salinity

The lacustrine samples Seria-1, Pakubalu-1, Muamba-1, Mucua-1, 4-26-1AT have high relative ratios of gammacerane. Gammacerane was originally thought to be an indicator of hypersalinity, but is now understood to suggest stratification of the water column during sediment deposition (Sinninghe Damsté *et al.,* 1995). However, hypersaline environments are commonly stratified. It is important to note that in the m/z 191 mass chromatogram the C_{34} tricyclic terpane co-elutes with gammacerane, therefore in samples also containing high extended tricyclic terpanes, gammacerane values will be artificially enhanced (i.e. 4-26-1AT and Seria-1).

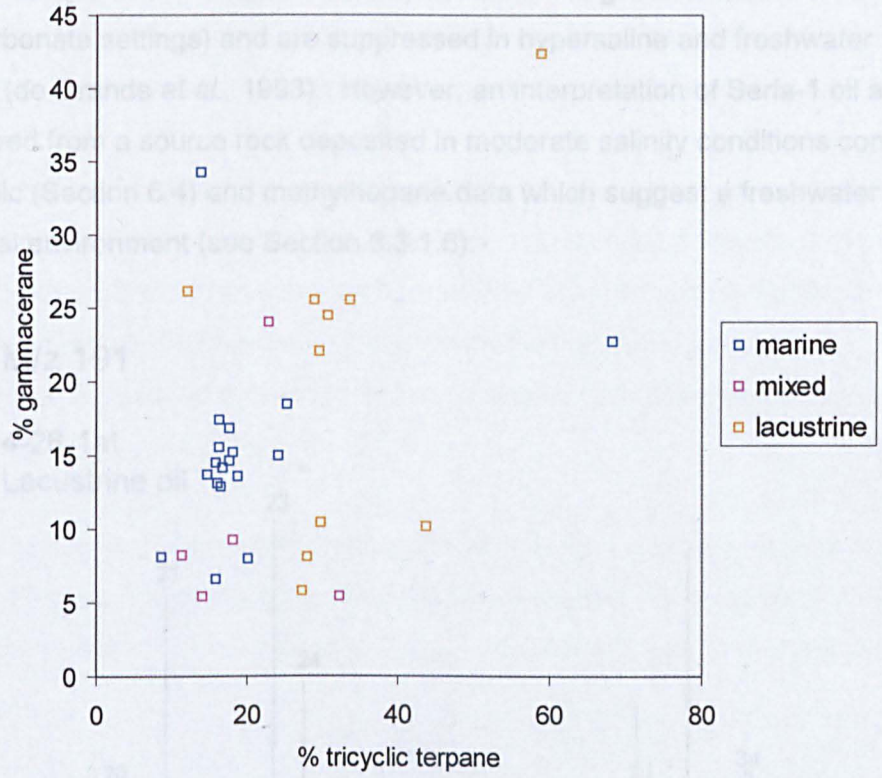

Fig. 113 Cross plot of the % gammacerane parameter and the % tricyclic terpane parameter for all Angolan oils.

In general the lacustrine oils have elevated levels of tricyclic terpanes compared to the marine and mixed oils (Fig. 113). Although the specific source of tricyclic terpanes is unknown, their ubiquitous occurrence in oils and sediments is reported to imply a microbial or algal origin (Aquino Neto *et al.,* 1993). Specifically, the unicellular green alga, *Tasmanites* has been suggested as one possible source (Greenwood *et al.,* 2000). The only lacustrine oil with low tricyclic terpanes is Mucua-1 (the least mature oil in this study). The low abundance of tricyclic terpanes in this

sample may in part be a result of its low thermal maturity, since tricyclic terpane abundances are known to increase with thermal maturity due to their generation from the kerogen (Kruge *et al.,* 1990) and greater stability compared with hopanes.

In general all of the Angolan oils appear to contain extended tricyclic terpanes (C_{28}-C_{35}), although often in low abundance. The lacustrine oils, 4-26-1, 4-26-2, 4-26-3, Seria-1and Luanda-3 have very high extended tricyclic terpanes, such that they can dominate the triterpane distribution (the low molecular weight tricyclic terpanes are also very high in these samples; Fig. 114). A depositional environment control on the abundance of tricyclic terpanes (up to C_{54}) has been proposed, whereby the precursors survive under moderate salinity conditions (e.g. saline lacustrine and marine carbonate settings) and are suppressed in hypersaline and freshwater conditions (de Grande *et al.,* 1993). However, an interpretation of Seria-1 oil as being derived from a source rock deposited in moderate salinity conditions contrasts with isotopic (Section 6.4) and methylhopane data which suggest a freshwater depositional environment (see Section 6.3.1.6).

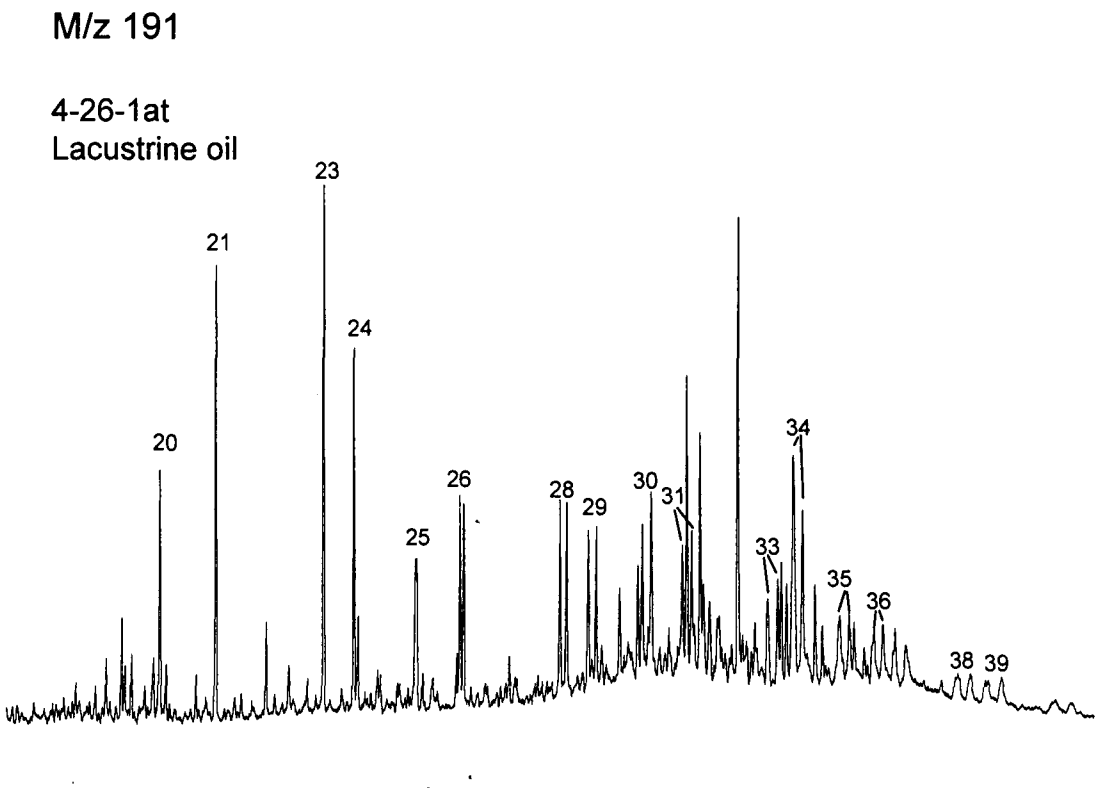

Fig. 114 M/z 191 chromatogram of 4-26-1 lacustrine oil to illustrate the high abundance of low molecular weight tricyclic terpanes and the occurrence of extended tricyclic terpanes (tricyclic terpane carbon numbers marked).

The marine oils show a lower relative abundance of gammacerane than the lacustrine oils, with the exception of Bufalo-106a and Tobias-6. Note however, that Bufalo-106a also contains high abundances of extended tricyclic terpanes, therefore the parameter may be affected by co-elution, as mentioned earlier. Bufalo-106a is the only marine oil to contain high abundances of extended tricyclic terpanes, suggesting a possible source depositional environment of moderate salinity (e.g. marine carbonate; de Grande *et al.,* 1993).

A distinctive feature of the marine oil Tobias-6 (Fig. 115) is the occurrence of *n*-alkanes with an even over odd predominance a feature associated with carbonate or hypersaline environments (Peters & Moldowan, 1993). This sample also has a very high abundance of gammacerane thought to represent stratification of the water column in the depositional environment (Sinninghe Damsté *et al.,* 1995; Fig. 113).

The mixed oils generally have low relative abundances of gammacerane and tricyclic terpanes. The mixed oil 4-35-1 contains high extended tricyclic terpanes suggesting contributions from a source depositional environment of moderate salinity. The mixed oil Mulvenos Central-1 contain a high abundance of gammacerane, suggesting contributions from a source rock deposited in a stratified environment.

There appears to be a geographical cluster of the lacustrine, marine and mixed oils containing abundant extended tricyclic terpanes. With the exception of Luanda-3 these oils fall within blocks 2, 3 and 4, clustered together in the Lower Congo Basin.

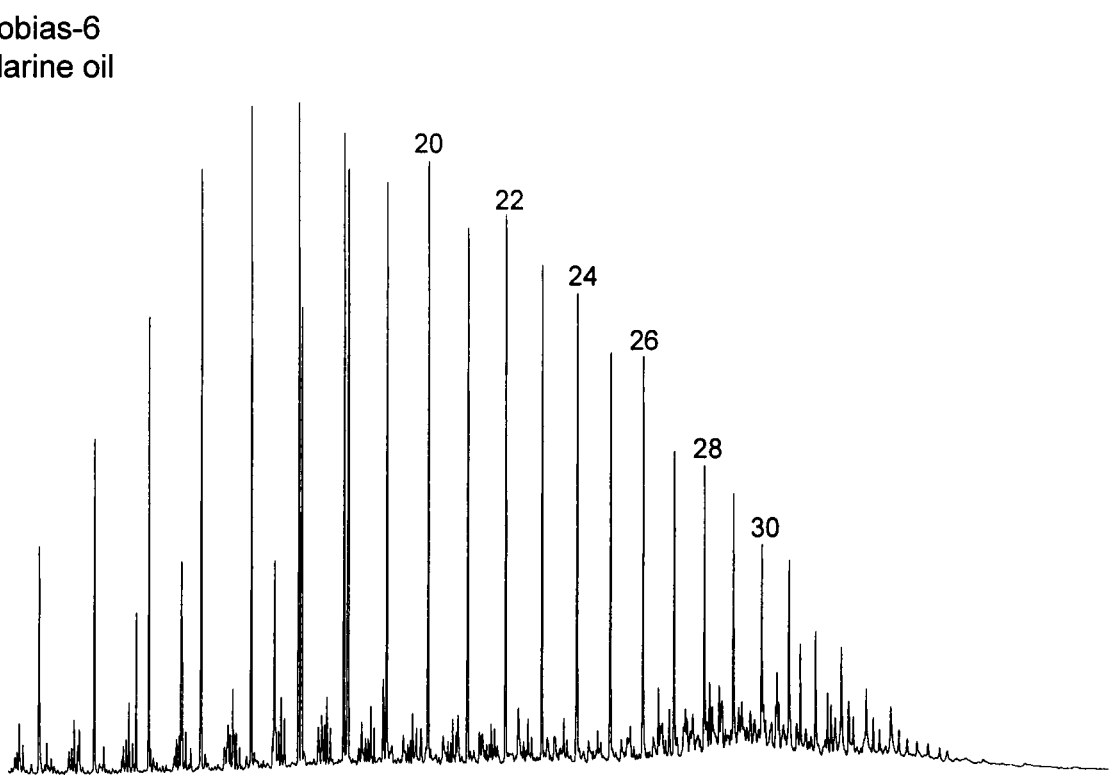

Fig. 115 FID trace for the marine oil Tobias-6 to illustrate the nC_{20-28} even/odd n-alkane predominance.

6.3.1.6 Fresh water lacustrine indicators

The presence of 2α-methyl and 3β-methyl hopanes represents the bacterial inputs to the sediments. The Angolan oils show considerable variability in terms of their 2-methyl hopane and 3-methyl hopane abundances (Fig. 116). However, with the exception of the oils Seria-1 and Maboque-1 the marine, mixed and lacustrine oils show significant overlap in Fig. 116 and therefore the relative proportions of 2α- and 3β-methylhoapnes cannot be used to differentiate the marine, mixed and lacustrine oils. The two samples Maboque-1 and Seria-1 show an enrichment of 3β-methyl hopanes; 3β-methylhopanoids are thought to derive from methanotrophic (methane oxidising) bacteria, which are found in freshwater lacustrine environments where little or no sulphate reduction occurs. It might therefore be implied that Maboque-1 and Seria-1 are of freshwater origin. In support of this theory, both Maboque-1 and Seria-1 have different isotopic signals to the other lacustrine oils (see Section 6.4). The remaining lacustrine oils may represent lacustrine brackish/saline source rocks. In such environments, if sulphate reduction predominates over methanogenesis, contributions from methanotrophic bacteria would be expected to be low (Farrimond, pers, comm., 2002).

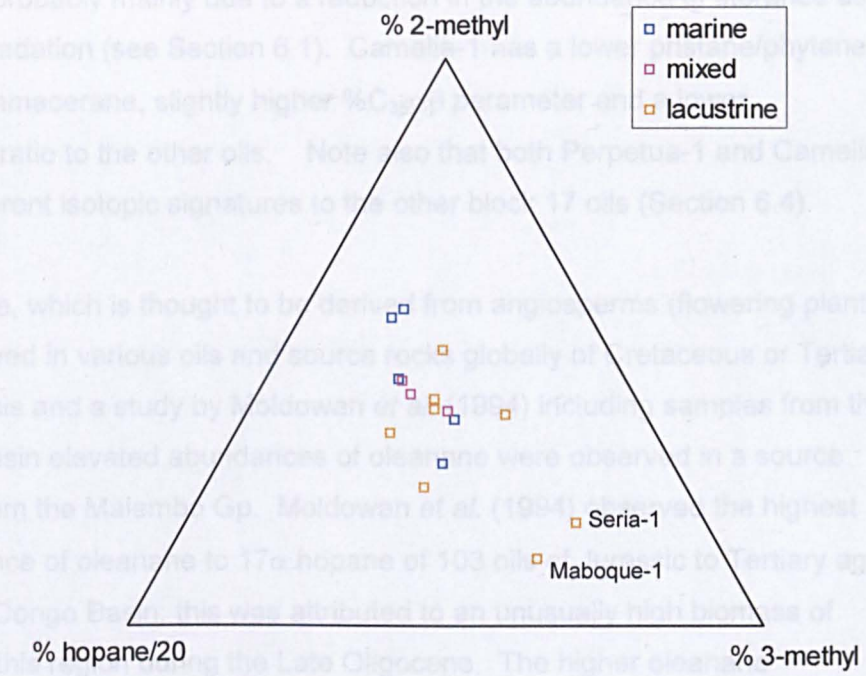

Fig. 116 Ternary plot of 2 α-methyl- αβ-hopane, 3 β-methyl- αβ-hopane and αβ-hopane (divided by 20) for a subset of Angolan oils analysed for their methylhopanes.

6.3.2 Block 17 oils

From an exploration perspective the oils from block 17 will be discussed in more detail to investigate if there are any variations in their source organofacies.

6.3.2.1 Detailed variations in oil source depositional environment

The block 17 oils are relatively similar in terms of their molecular composition (Fig. 117 to Fig. 121). However, Camelia-1 and Perpetua-1 have very slightly different biomarker properties to the other block 17 oils, suggesting that they are derived from a slightly different source rock organofacies or that they contain contributions from another oil. If so, from an exploration perspective this information would prove useful for basin modeling studies. Note they do not differ in the same way, suggesting they also differ from each other with respect to their source. Perputua-1 has a higher abundance of oleanane, lower gammacerane and slightly higher $\%C_{24}$ tetracyclic terpane abundance (Fig. 120 to Fig. 122), consistent with being derived from a source depositional environment with higher contributions from

terrestrial organic matter. Perpetua-1 also has a higher hopane/sterane ratio although this is probably mainly due to a reduction in the abundance of steranes as a result of biodegradation (see Section 6.1). Camelia-1 has a lower pristane/phytane ratio, higher gammacerane, slightly higher $\%C_{35}\alpha\beta$ parameter and a lower hopane/sterane ratio to the other oils. Note also that both Perpetua-1 and Camelia-1 also have different isotopic signatures to the other block 17 oils (Section 6.4).

Oleanane, which is thought to be derived from angiosperms (flowering plants) has been observed in various oils and source rocks globally of Cretaceous or Tertiary age. In this thesis and a study by Moldowan *et al.* (1994) including samples from the Lower Congo basin elevated abundances of oleanane were observed in a source rock samples from the Malembo Gp. Moldowan *et al.* (1994) observed the highest relative abundance of oleanane to 17α hopane of 103 oils of Jurassic to Tertiary age from the Lower Congo Basin; this was attributed to an unusually high biomass of angiosperms in this region during the Late Oligocene. The higher oleanane observed in Perpetua-1 oil may therefore suggest the oil contains contributions from Tertiary (Malembo and Landana Gps.) source rocks. Cole *et al.*, (2000) used the oleanane/C_{30} hopane ratio of several Lower Congo Basin oils and source rocks to identify oils derived from the Tertiary source rocks containing higher oleanane abundances. Unfortunately, until recently oleanane was not quantified on the Norsk Hydro automatic GC-MS quantification system so data amounts for oleanane are not available. Knowledge that the Tertiary source rocks would prove important for basin modelling studies as the Tertiary Landana and Malembo sections in the Lower Congo Basin are often burial-constrained with respect to maturity (Cole *et al.*, 2000).

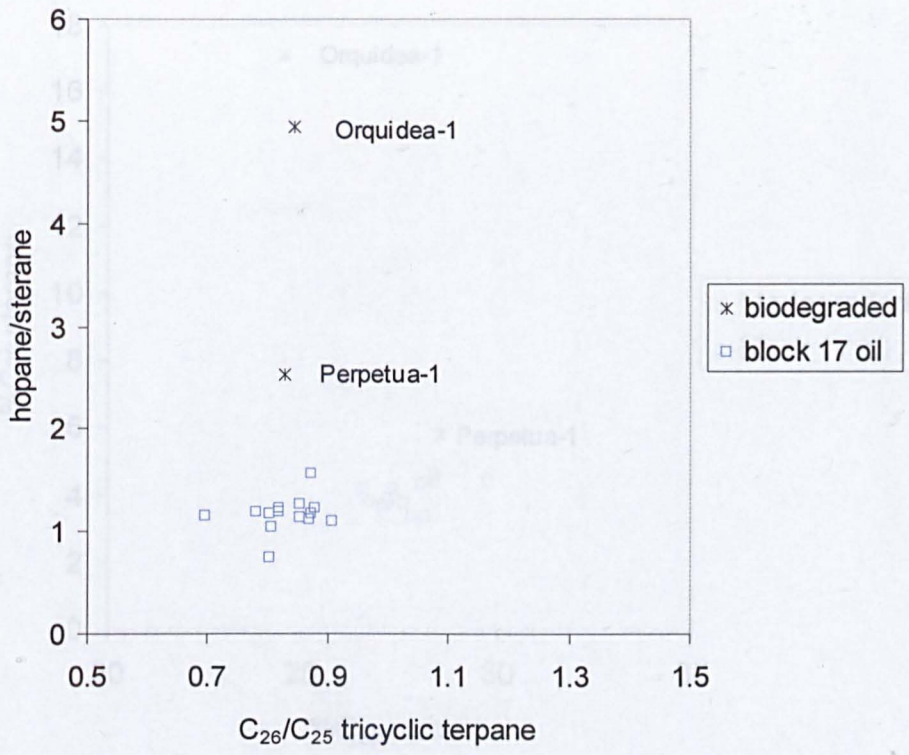

Fig. 117 Cross plot of the C_{26}/C_{25} tricyclic terpane ratio and the hopane/sterane parameter for Block 17 oils.

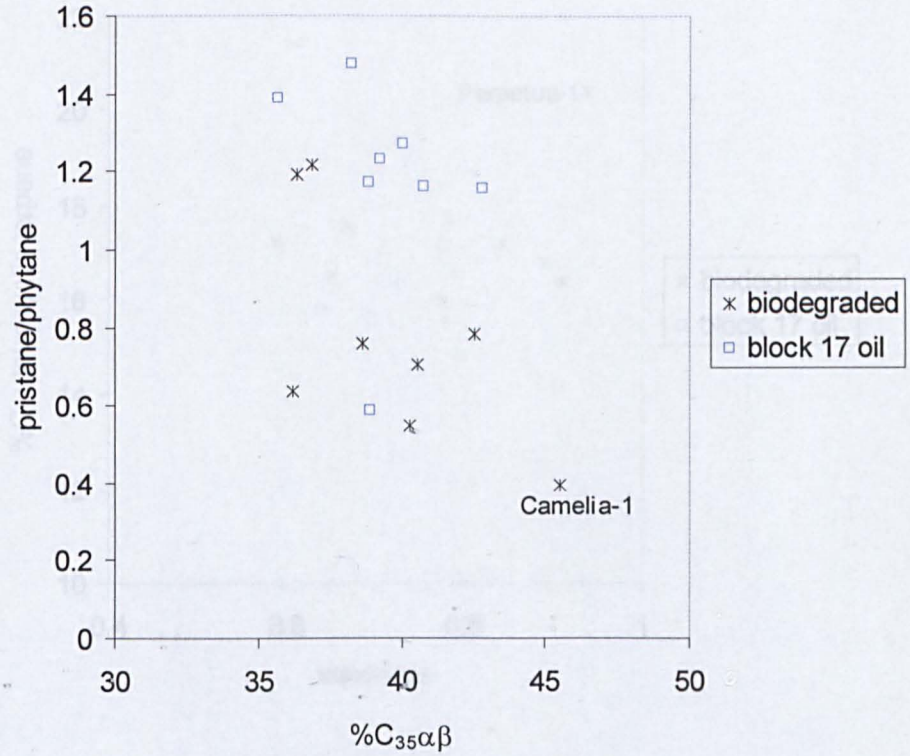

Fig. 118 Cross plot of the pristane/phytane ratio and the $\%C_{35}\alpha\beta$ parameter for block 17 oils. Note, the $\%C_{35}\alpha\beta$ parameter has not been affected by biodegradation.

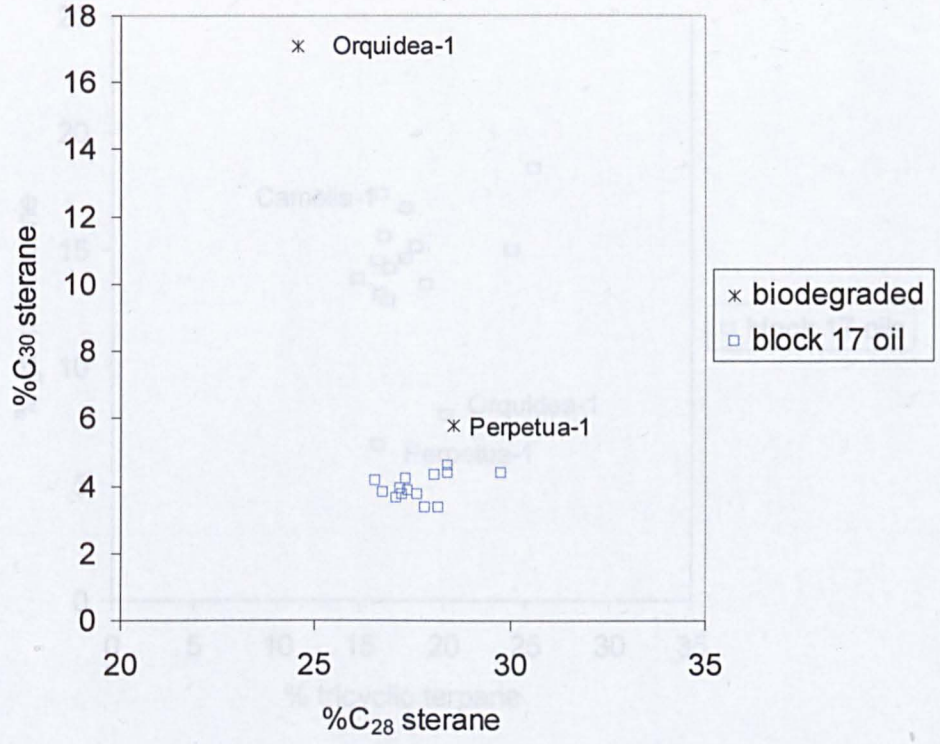

Fig. 119 Cross plot of the $\%C_{30}$ sterane parameter and the $\%C_{28}$ sterane parameter for block 17 oils.

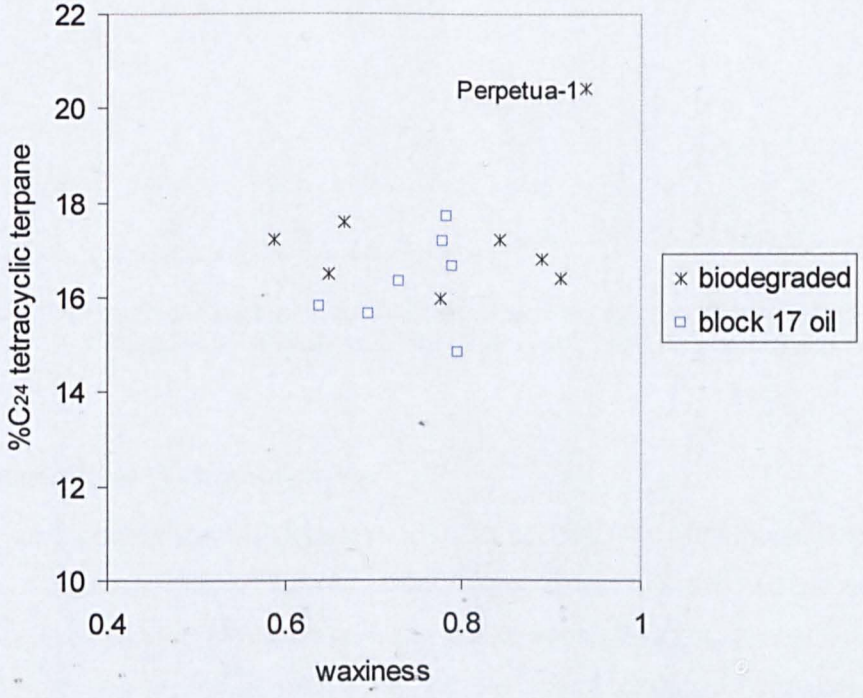

Fig. 120 Cross plot of the $\%C_{24}$ tetracyclic terpane parameter and the $nC_{17}/(nC_{17}+nC_{27})$ (or waxiness) parameter for block 17 oils. Note, the $\%C_{24}$ tetracyclic terpane parameter is not affected by biodegradation.

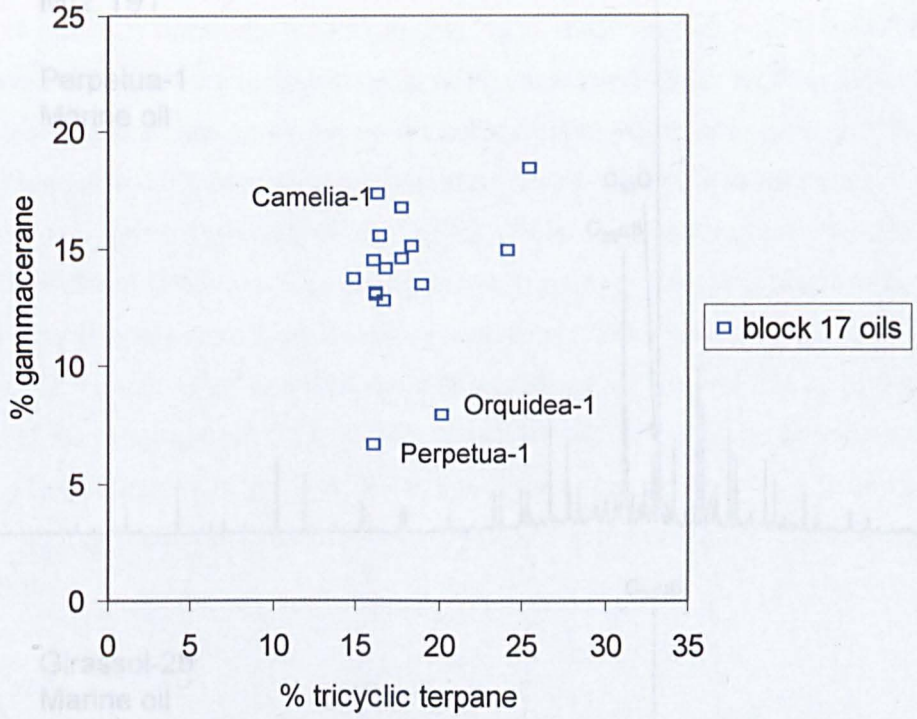

Fig. 121 Cross plot of the % gammacerane and the % tricyclic terpane parameters for block 17 oils.

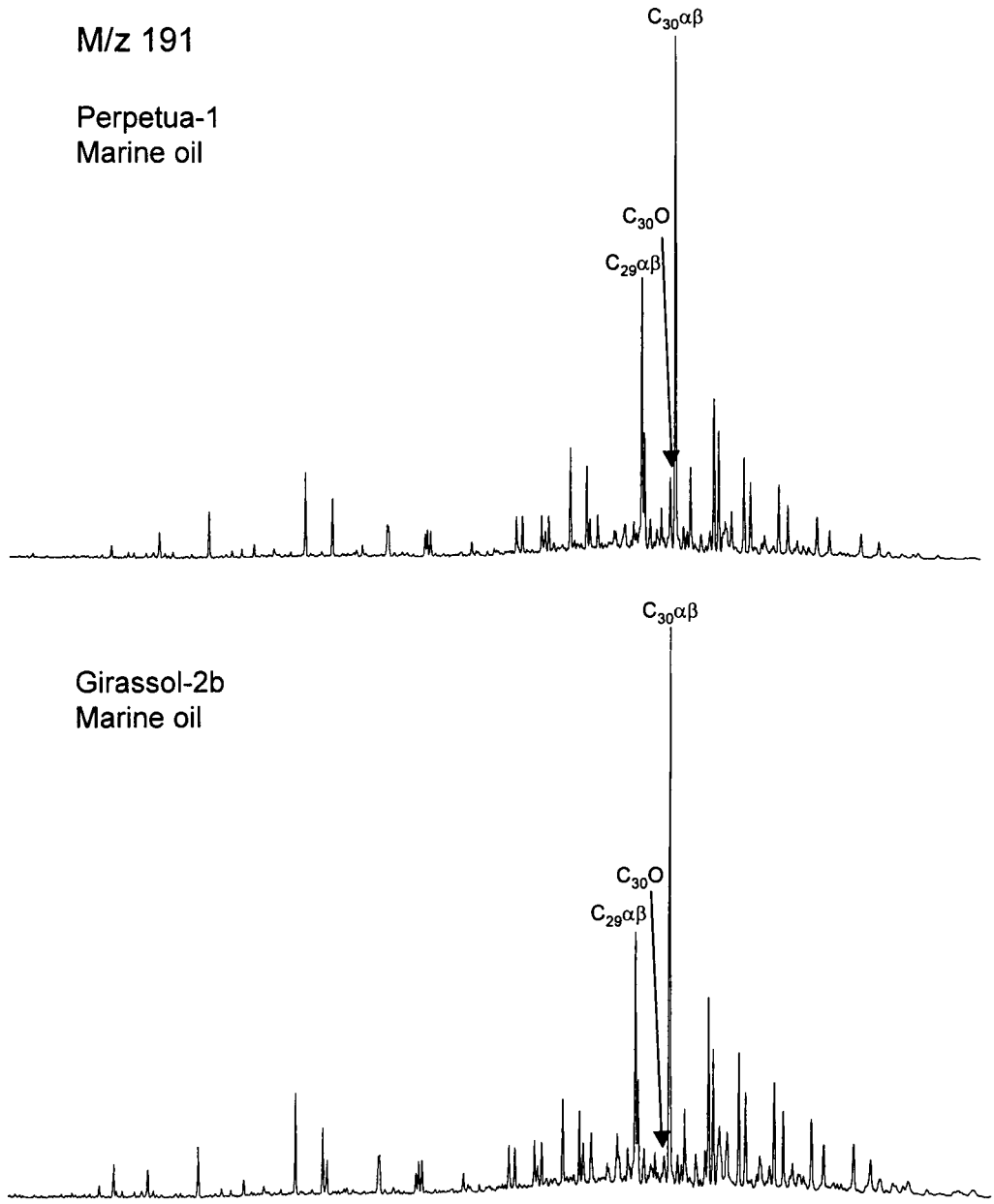

Fig. 122 M/z 191 mass chromatogram to show the higher abundance of oleanane in the marine block 17 oil Perpetua-1 compared to the other block 17 oil represented by Girassol-2b.

6.3.2.2 Variations in geological age

From an exploration perspective it would be useful to distinguish if any of the variations in biomarker characteristics in the block 17 oils are due to contributions form the Tertiary section. This would have important implications for basin modelling. 24- Norcholestanes can be used to constrain the age of geological samples, and are especially useful for petroleum (Holba *et al.,* 1998a, 1998b). The specific source of 24-norcholestanes is unknown, although evidence suggests that they may be derived from diatoms (Holba *et al.,* 1998a, 1998b). The nordiacholestane (NDR) and

norcholestane (NCR) ratios have been calculated to constrain the geological age of the block 17 oils (see appendix for ratios) (Fig. 123). NDR values > 0.20 (or NCR > 0.3) indicate a Jurassic or younger source, NDR values > 0.25 (or NCR values ≥ 0.40) suggest samples are derived from a Cretaceous or younger source, and NDR > 0.50 (NCR values ≥ 0.60) suggest samples are derived from source rocks of Oligocene or younger age (Holba *et al.*, 1998b). Note however, that samples derived from source rocks of Cretaceous or younger age in palaeo-upwelling areas where conditions may support increased diatom growth may have higher ratios (Holba *et al.*, 1998a). The block 17 oil samples have NCR values ranging from 0.29 to 0.40 and NDR values ranging from 0.14 to 0.29; these fall within the range of values for oils derived from Jurassic or younger source rocks and oils derived from Cretaceous or younger source rocks and are thus not very useful in the context of the Angolan source rocks.

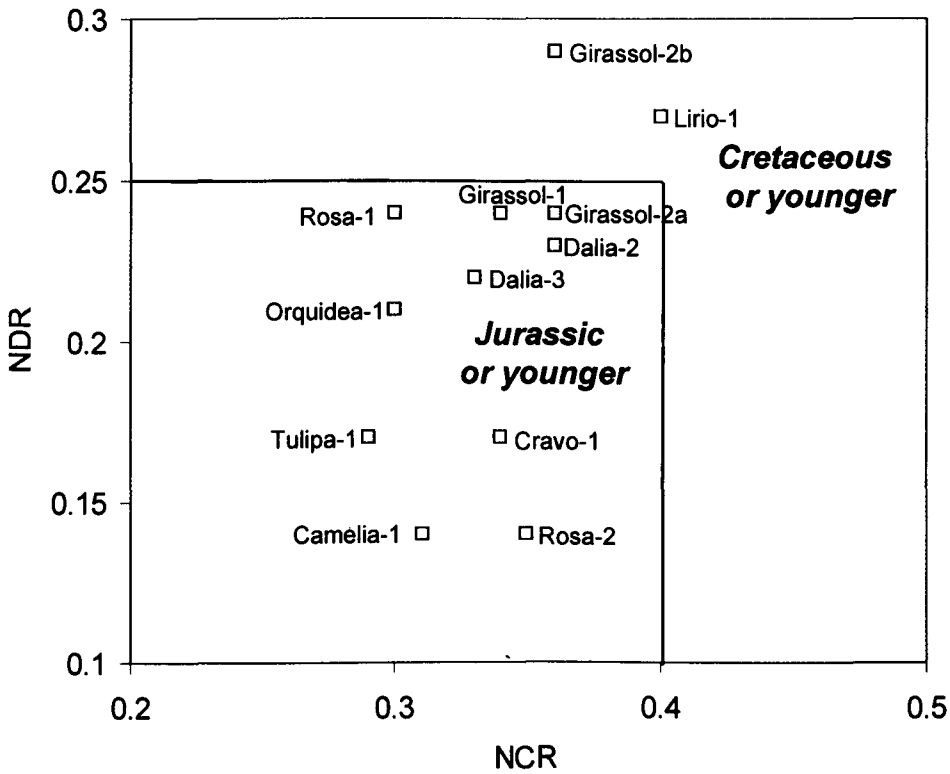

Fig. 123 Cross plot of the norcholestane ratio (NCR) versus the nordiacholestane ratio (NDR) for the block 17 oils. NDR values > 0.20 (or NCR > 0.3) indicate a Jurassic or younger source, NDR values > 0.25 (or NCR values ≥ 0.40) suggest samples are derived from a Cretaceous or younger source, and NDR > 0.50 (NCR values ≥ 0.60) suggest samples are derived from source rocks of Oligocene or younger age (Holba *et al.*, 1998b).

6.4 Oil Isotopic analysis

6.4.1 All Angolan oils

The lacustrine oils can be seen to have a much greater spread of $\delta^{13}C$ values for the saturate and aromatic fractions ($\delta^{13}C$ saturate fraction -23.3 to –25.9‰, $\delta^{13}C$ aromatic fraction –21.8 to –23.7‰) than the marine oils ($\delta^{13}C$ saturate fraction –25.8 to –28.91‰, $\delta^{13}C$ aromatic fraction –25.2 to –27.62‰) probably due to the greater diversity in environmental conditions and organic matter inputs in lacustrine environments (Fig. 124). The lacustrine oils Seria-1 and Maboque-1 have much lighter isotopic values than the other lacustrine oils (Fig. 124). Biomarker and isotopic analysis of the Brazilian oils which show many similar molecular characteristics to the Angolan oils, have shown the lacustrine oils to have either heavy or light isotopes dependent upon whether the oils are derived from a source rock deposited in a saline or freshwater environment (Mello *et al.*, 1988a). The freshwater-derived oils have light $\delta^{13}C$ isotopic values (-28.5 to –30.5‰ for the saturate fraction and values of –27 to –28‰ for the aromatic fraction). If the isotopes of the Angolan oils also show the same characteristics as the Brazilian oils it might therefore be implied that Seria-1 and Maboque-1 oils are derived from a source rock deposited in a freshwater environment. This is in agreement with methylhopane data for Maboque-1 and Seria-1, suggesting they are derived from source rocks deposited in freshwater environments (Section 6.3.1.6). The mixed oil 4-26-3 has isotopic values similar to the lacustrine oils, whereas Ganda-3 and Mulvenos Central-1 have isotopic signatures similar to the marine oils.

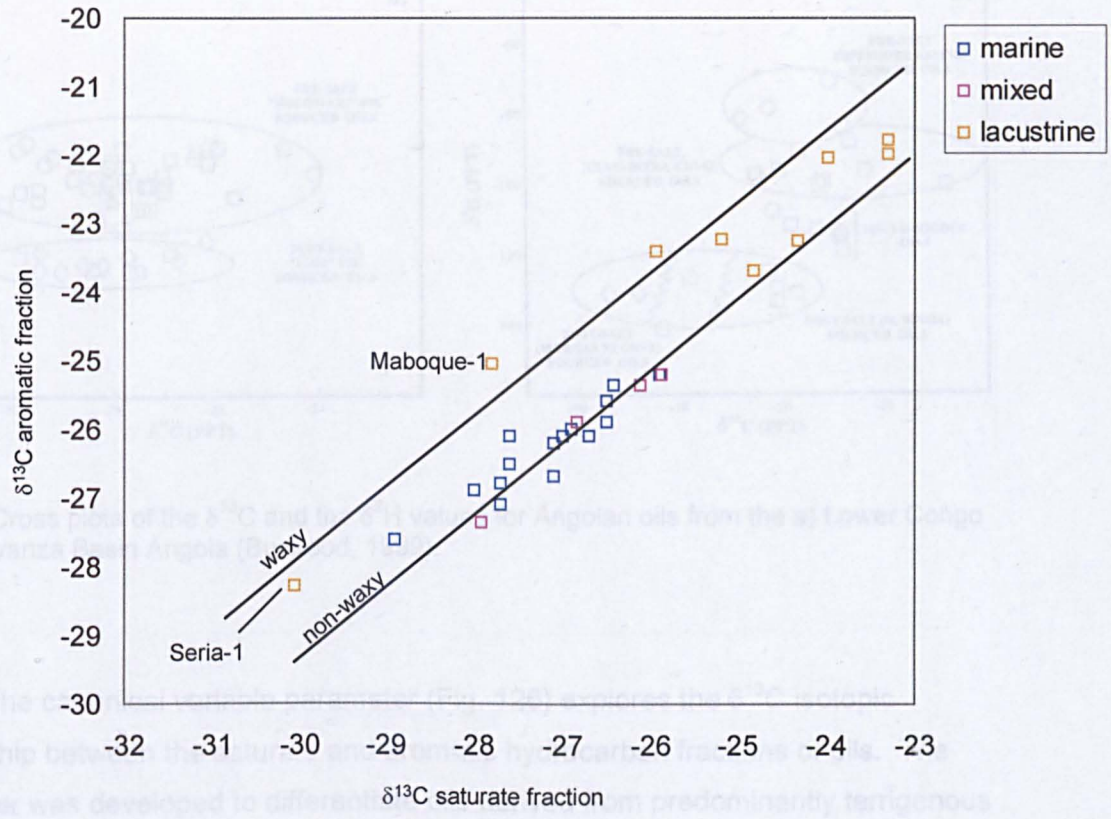

Fig. 124 Cross plot of the δ^{13} (in ‰) carbon isotopic compositions of saturate and aromatic hydrocarbons for all Angolan oils. The trend lines marked waxy and non-waxy are taken from Sofer *et al.* (1984). Oils falling on the waxy trend line are thought to be derived from predominantly terrigenous organic matter, deposited in lacustrine or deltaic environments and oils falling on the non-waxy trend line are derived from marine organic matter, deposited in open marine environments.

The δ^2H isotopic parameter has not been measured for the lacustrine oils in this thesis. However, Burwood (1999) has shown δ^2H parameter values for lacustrine sourced oils in the Lower Congo Basin Bucomazi Fm. to be approximately –80 to –110‰, and the Kwanza basin Cuvo/Infra-Cuvo Fm. oils to be –85 to –105‰ (Fig. 125). The Post-salt source rocks have considerably lighter δ^2H values than the lacustrine oils, -115 to –130‰ for the Lower Congo Basin Iabe source rocks, and –120 to –140 for the Kwanza Basin Middle Binga and Margas Negras Fms. The δ^2H values for the marine oils in this thesis have been measured and have values similar to those for the Post-salt oils presented in the literature. The marine block 17 oils will be discussed in more detail in Section 6.4.2.

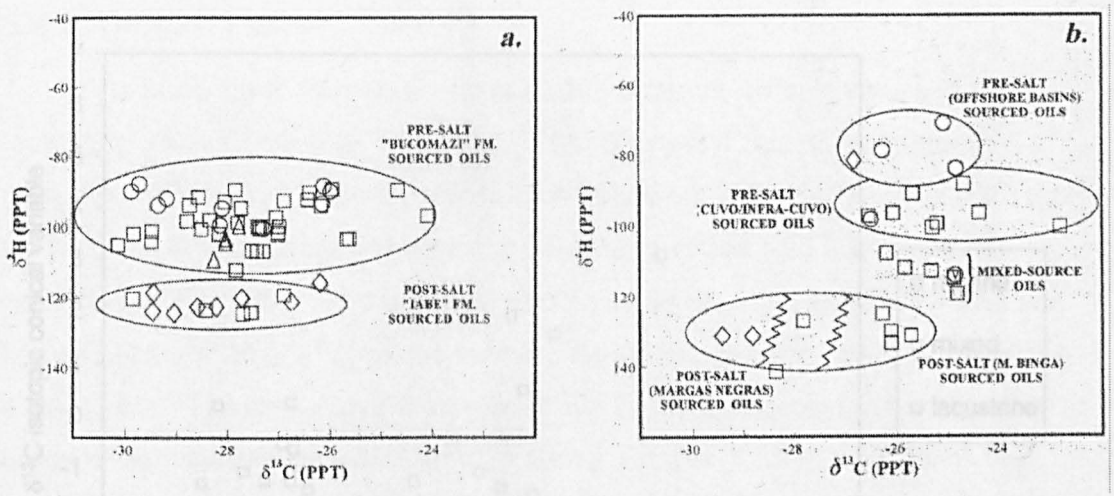

Fig. 125 Cross plots of the $\delta^{13}C$ and the $\delta^{2}H$ values for Angolan oils from the a) Lower Congo and b) Kwanza Basin Angola (Burwood, 1999).

The canonical variable parameter (Fig. 126) explores the $\delta^{13}C$ isotopic relationship between the saturate and aromatic hydrocarbon fractions of oils. The parameter was developed to differentiate oils derived from predominantly terrigenous organic matter, deposited in lacustrine or deltaic environments, termed waxy oils, and marine organic matter, deposited in open marine environments, termed non-waxy oils (Sofer, 1984). Fig. 124 classifies the Angolan oils as either waxy or non-waxy according to Sofer (1984). In agreement with Sofer (1984), in general the lacustrine oils fall either on the waxy trend line or between the waxy and non-waxy trend lines, and the marine oils on the non-waxy trend line. The canonical variable values for oils in this study (Fig. 126) are in agreement with the Angolan oils analysed in the literature by Cole *et al.* (2000) (Fig. 127). The lacustrine oils generally have more positive canonical variable values, and the marine oils more negative values. However, three lacustrine oils (4-26-2, Mubafo-1 and Palkubalu-1) and the mixed oil 4-26-2 have negative conical variable values, possibly due to a variation in facies.

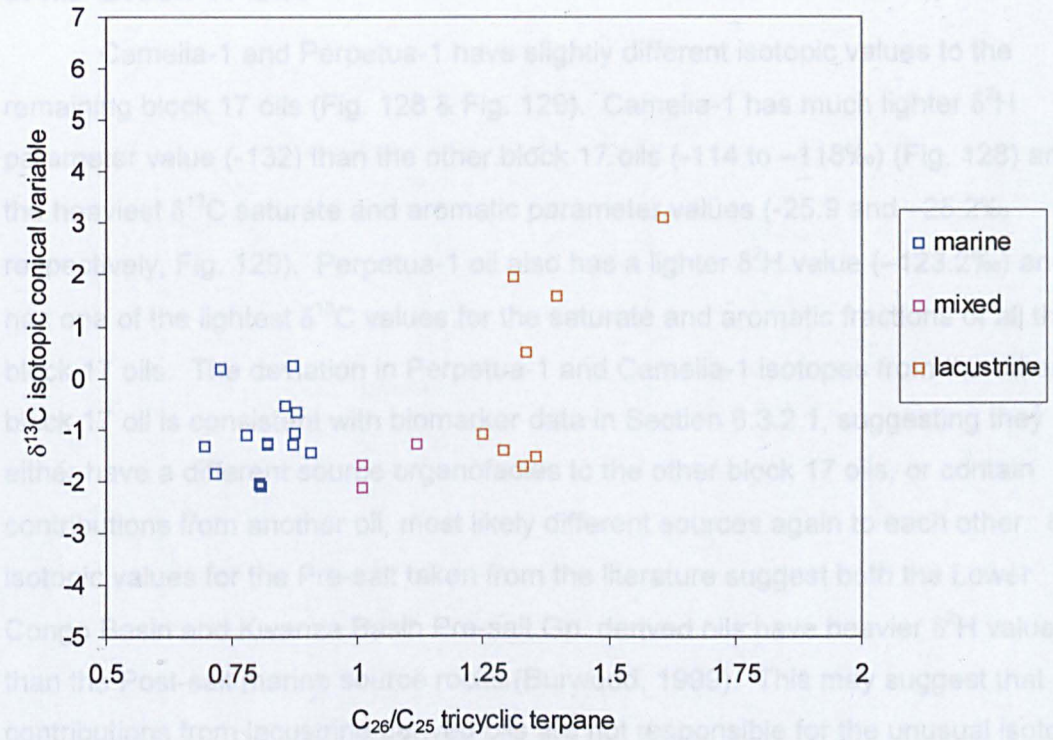

Fig. 126 Cross plot of the C_{26}/C_{25} tricyclic terpane versus the isotopic conical variable parameter for all Angolan oils.

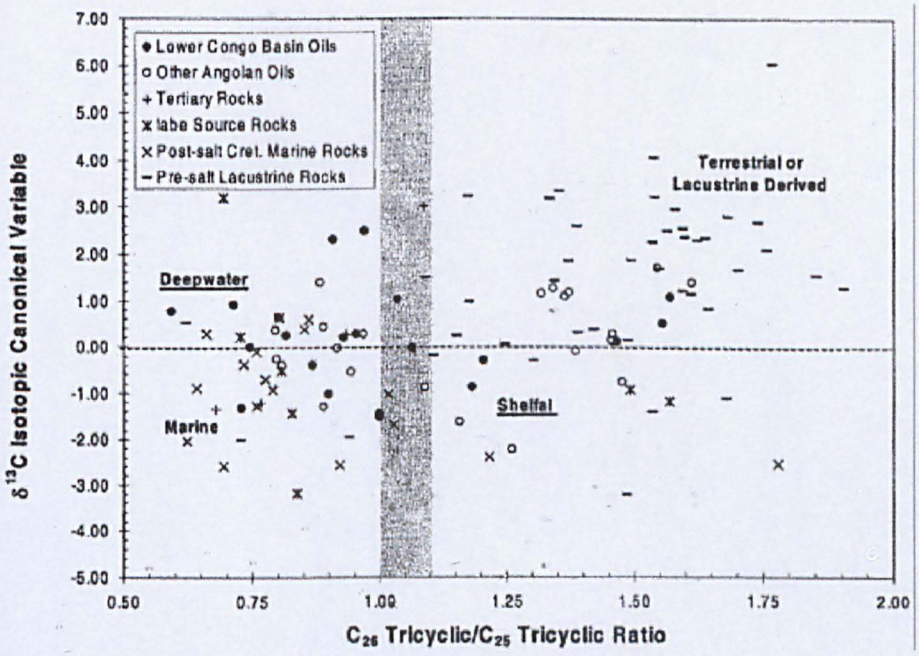

Fig. 127 Cross plot of the C_{26}/C_{25} tricyclic terpane ratio and the isotopic canonical variable for Angolan oils and source rock bitumens taken from Cole *et al.* (2000).

6.4.2 Block 17 oils

Camelia-1 and Perpetua-1 have slightly different isotopic values to the remaining block 17 oils (Fig. 128 & Fig. 129). Camelia-1 has much lighter δ^2H parameter value (-132) than the other block 17 oils (-114 to –118‰) (Fig. 128) and the heaviest $\delta^{13}C$ saturate and aromatic parameter values (-25.9 and –25.2‰ respectively, Fig. 129). Perpetua-1 oil also has a lighter δ^2H value (–123.2‰) and has one of the lightest $\delta^{13}C$ values for the saturate and aromatic fractions of all the block 17 oils. The deviation in Perpetua-1 and Camelia-1 isotopes from the other block 17 oil is consistent with biomarker data in Section 6.3.2.1, suggesting they either have a different source organofacies to the other block 17 oils, or contain contributions from another oil, most likely different sources again to each other. δ^2H isotopic values for the Pre-salt taken from the literature suggest both the Lower Congo Basin and Kwanza Basin Pre-salt Gp. derived oils have heavier δ^2H values than the Post-salt marine source rocks (Burwood, 1999). This may suggest that contributions from lacustrine derived oils are not responsible for the unusual isotopic compositions of Perpetua-1 and Camelia-1 oils, as lacustrine contributions would be expected to give heavier δ^2H isotopic values.

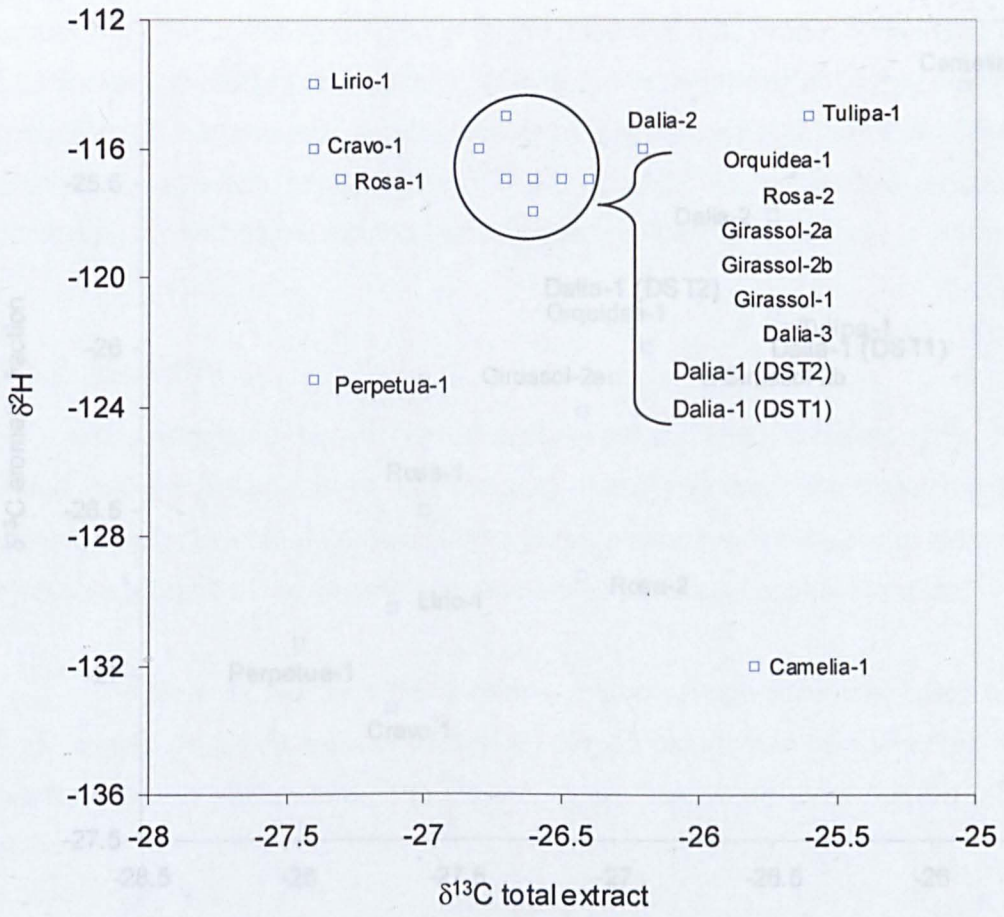

Fig. 128 Cross plot of the stable isotope δ^2H and δ^{13} total extract (saturate + aromatic) parameters for the block 17 marine oils.

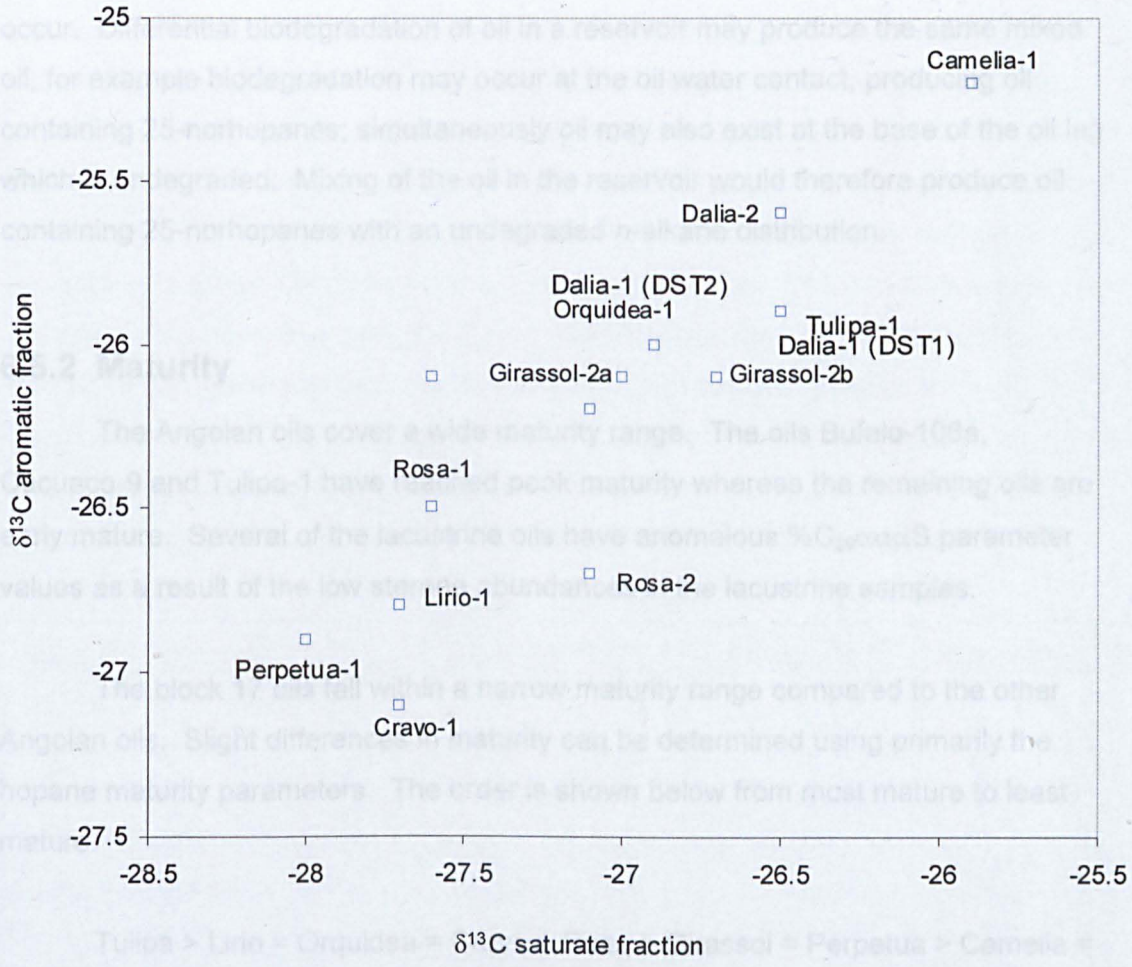

Fig. 129 Cross plot of the δ^{13} carbon isotopic compositions of saturate and aromatic hydrocarbons from block 17 marine oils.

6.5 Overview

6.5.1 Biodegradation

The Angolan oils cover a range of biodegradation levels (i.e. ranked according to the biodegradation scale developed by Peters and Moldowan (1993)). The block 17 oils range from biodegradation level 1, with degradation of only the lower homologue *n*-alkanes, up to level 6 in Perpetua-1 and Orquidea-1, whereby partial degradation of the steranes has occurred. Several of the remaining Angolan oils have apparently undegraded *n*-alkane, isoprenoid, hopane and sterane distributions but contain abundant demethylated 25-norhopanes. The presence of 25-nornopanes combined with undegraded *n*-alkane distributions is interpreted to result from residues of previously biodegraded oil in a reservoir with subsequent entry of a fresh undegraded oil (Volkman *et al.,* 1983). It should be noted a

secondary charge of oil may not be the only scenario whereby such mixed oils will occur. Differential biodegradation of oil in a reservoir may produce the same mixed oil, for example biodegradation may occur at the oil water contact, producing oil containing 25-norhopanes; simultaneously oil may also exist at the base of the oil leg which is undegraded. Mixing of the oil in the reservoir would therefore produce oil containing 25-norhopanes with an undegraded *n*-alkane distribution.

6.5.2 Maturity

The Angolan oils cover a wide maturity range. The oils Bufalo-106a, Cacuaco-9 and Tulipa-1 have reached peak maturity whereas the remaining oils are early mature. Several of the lacustrine oils have anomalous $\%C_{29}\alpha\alpha\alpha S$ parameter values as a result of the low sterane abundances in the lacustrine samples.

The block 17 oils fall within a narrow maturity range compared to the other Angolan oils. Slight differences in maturity can be determined using primarily the hopane maturity parameters. The order is shown below from most mature to least mature.

Tulipa > Lirio = Orquidea = Cravo > Rosa > Girassol = Perpetua > Camelia = Dalia

The fact that the Block 17 oils cover a narrow maturity range may suggest they have a common source. If a particular oil was more mature than the others this may have suggested it was source from a separate section, perhaps in a deeper basin.

6.5.3 Oil source depositional environment

Lacustrine-derived oils in this region are classified as having high hopane/sterane values and C_{26}/C_{25} tricyclic terpane ratio values greater > 1, whereas marine-derived oils have low hopane/sterane values and C_{26}/C_{25} tricyclic terpane values < 1. This is in agreement with classifications of the marine and lacustrine source rocks in this study (Section 4.2.1) and also oil and source rock data in the literature (Burwood, 1999; Schiefelbein *et al.*, 1999, Cole *et al.*, 2000). The mixed oils have intermediate C_{26}/C_{25} and hopane/sterane values, but generally their molecular composition is most similar to the marine oils. This suggests that they are

derived predominantly from marine source rocks with only minor lacustrine contributions, from either a lacustrine oil or from lacustrine intervals within a primarily marine source rock section. From an exploration perspective knowledge that the lacustrine Pre-salt has contributed to the block 17 oils would have significant explorational importance. It would imply the presence of an active lacustrine source rock system in the region this is important for both basin modelling for further exploration of Block 17 and its adjacent exploration blocks. The oils-source rock correlation chapter will investigate in more detail the applicability of the C_{26}/C_{25} tricyclic terpane ratio and the hopane/sterane ratio in assigning oils as either lacustrine or marine and investigate the applicability of these parameters to characterise oils as being of mixed origin. Table 8 provides a summary of the molecular characteristics of the Angolan marine, mixed and lacustrine oils.

Ratio/ Parameters	marine (19)	mixed (5)	lacustrine (10)
C_{26}/C_{25} tricyclic terpane	< 1	~1	>1
hopane/ sterane	0.4 - 1.6	1.4 - 2.5	2.7 - 14.2
$\%C_{28}$ sterane	26 - 31	23 - 30	18 -28
$\%C_{30}$ sterane	3 - 5	3 - 5	2 - 6
pristane/phytane	0.4 - 1.7	1.2 - 1.6	1.0 - 2.1
C_{27}/C_{29} sterane	1.0 - 1.5	0.8 - 1.2	1.2 - 2.6
$\%C_{35}\alpha\beta$	36 - 46	33 - 40	26 - 42
% tricyclic terpane	9 - 68	11 - 32	12 - 59
$\%C_{24}$ tetracyclic terpane	9 - 27	14 - 21	8 - 21
% gammacerane	7 - 34	5 - 23	6 - 42
waxiness	0.7 - 0.8	0.6 - 0.7	0.5 - 0.7
% 2-methyl	36 - 55	38 - 43	12 - 48
% 3-methyl	15 - 41	22 - 32	25 - 62

Table 8 Summary table for all Angolan oil biomarker parameters. (Number of samples analysed shown in brackets). Note that values affected by biodegradation of the biomarkers have been removed.

In terms of the redox conditions the marine and lacustrine oils have pristane/phytane ratios greater than one. A value greater than 1 for source rocks would imply a more oxic source depositional environment; however is important to note that pristane/phytane ratios increase with maturity (Peters & Moldowan, 1993) so oils typically have values greater than 1. The marine oils have slightly higher $\%C_{35}\alpha\beta$ parameter values (comparable to the homohopane parameter) for the marine oils suggesting they may be derived from a less oxic environment than the

lacustrine oils. However, a high %$C_{35}\alpha\beta$ parameter is dependent upon sulphur in the depositional environment, which is frequently low in lacustrine environments, therefore the usefulness of this parameter may only be for marine sourced oils and source rocks.

In terms of the organic inputs to the source rocks from which the oils derive, the lacustrine oils have a biomarker signature typical of source rocks deposited in a terrestrially-influenced lacustrine environment with possibly a high degree of bacterial reworking, whereas, the marine oils have a biomarker signature consistent with marine algal inputs. The lacustrine-derived oils have sterane distributions with C_{27} steranes predominant, a feature also seen in the lacustrine source rocks in this thesis and the Brazilian oils of lacustrine origin (Mello *et al.,* 1988a). The lacustrine oils contain higher proportions of hopanes relative to steranes, indicating high contributions to the source depositional environment from terrigenous and/or microbially reworked organic matter (Peters & Moldowan, 1993). They also have broad *n*-alkane distributions, consistent with lacustrine environments containing higher amounts of high molecular weight *n*-alkanes derived from terrestrial organic matter (Tissot & Welte, 1984; Mello *et al.,* 1988a; Peters & Moldowan 1993). A specific feature seen in some of the lacustrine oils, which is observed in the lacustrine source rocks in this thesis, is the presence of a dominant nC_{23} alkane. This is thought to derive from a different as yet unidentified source to the other *n*-alkanes (Van Kaam-Peters *et al.,* 1997).

The marine oils, as with the marine source rocks in this thesis, comprise a high abundance of steranes relative to hopanes and also high relative abundances of C_{28} and C_{30} steranes, consistent with inputs from marine plankton and invertebrates (Huang & Meinschein, 1979; Moldowan, 1984; Moldowan *et al.,* 1985: Peters *et al.,* 1986; Peters & Moldowan, 1993). The marine-derived oils have a higher abundance of low molecular weight *n*-alkanes, the distributions tailing off after $nC_{16\text{-}17}$ to a more marine *n*-alkane distribution.

In terms of the water column stratification and salinity of the source rock depositional environment from which the oils are derived, several lacustrine oils have higher levels of gammacerane than the marine oils, understood to suggest stratification of the water column during sediment deposition (Sinninghe Damsté *et al.,* 1995). In general the lacustrine oils have elevated levels of tricyclic terpanes compared to the marine and mixed oils. Also certain lacustrine oils contain very high

abundance of extended tricyclic terpanes, often dominating the triterpane distribution, interpreted to represent a source depositional environment of moderate salinity conditions (de Grande *et al.,* 1993; i.e. saline lacustrine settings).

A high abundance of extended tricyclic terpanes is not exclusive to the lacustrine oils, occurring in the marine oil Bufalo-106a. However, there appears to be a geographical cluster of the lacustrine, marine and mixed oils containing high extended tricyclic terpanes within blocks 2, 3 and 4 in the Lower Congo Basin.

The two lacustrine oils Maboque-1 and Seria-1 show an enrichment of 3β-methyl hopanes. 3β-Methylhopanoids are thought to derive from methanotrophic (methane oxidising) bacteria, which are found in freshwater lacustrine environments where little or no sulphate reduction occurs. It might therefore be implied that Maboque-1 and Seria-1 are of freshwater origin.

6.5.4 Oil isotopic analysis

Isotopic values for the lacustrine and marine oils are consistent with values in the literature for Angolan oils (Burwood, 1999; Cole *et al.,* 2000). The lacustrine oils can be seen to have a much greater spread of $\delta^{13}C$ values for the saturate and aromatic fractions than the marine oils a reflection of the greater complexity of lacustrine environments; this has been previously noted by Cole *et al.,* (2000). The lacustrine oils Seria-1 and Maboque-1 have much lighter isotopic values than the other lacustrine oils consistent with the Brazilian oils of freshwater origin. Methylhopane data for Seria-1 and Maboque-1 also support an interpretation of the two oils being derived from freshwater source rocks (Section6.3.1.6).

6.5.5 Block 17 oils

The block 17 oils are relatively similar in terms of their molecular composition, although Camelia-1 and Perpetua-1 have very slightly different biomarker properties, suggesting that they are derived from a different source rock organofacies or that they contain contributions from other oils. Note that they do not differ in the same way, suggesting they also differ from each other with respect to their source.

The age-related biomarker parameters for the block 17 oils have NCR and NDR values indicative of being derived from Jurassic or younger source rocks or

from Cretaceous or younger source rocks, neither of which is useful within our source rock context. The elevated abundance of oleanane in Perpetua-1 oil may however suggest the oil contains contributions form a Tertiary source rock. The Tertiary source rock (Malembo and Landana Gps.) is known from the source rock analysis in this thesis and also from literature reports to contain higher abundances of oleanane than the Cretaceous marine source rocks (Moldowan *et al.,* 1994).

Perpetua-1 and Camelia-1 have slightly different isotopes to the other block 17 oils, consistent with biomarker data that suggest they either have a different source organofacies to the other block 17 oils, or contain contributions from another oil. The oils have lower δ^2H values which may suggest that contributions from lacustrine-derived oils are not responsible for the differences seen for Perpetua-1 and Camelia-1, as lacustrine contributions would be expected to give heavier δ^2H isotopic values.

7 Molecular analysis of asphaltene- and polar-bound hydrocarbons in oils.

This chapter will address the information potential of the biological marker compounds in the asphaltene and polar fractions of Angolan oils; 8 oils have been selected for both quantitative and qualitative analysis of the biomarkers in the aliphatic hydrocarbon fractions generated by hydropyrolysis. Six of the oils are marine-sourced Block 17 oils and two of the oils are from Block 4, one of which is marine- and one lacustrine-sourced. Ideally a wider selection of oils would be analysed to cover the Angolan region geographically, and also to include more lacustrine oils. However no further oil samples were available to Norsk Hydro. Note, within this thesis the fraction referred to as the 'polar-bound' fraction is the polar fraction of the maltenes, often referred to in the literature as the resin fraction.

7.1 Biodegradation

The free block 17 oils range from biodegradation level 1 (degradation of the lower homologue *n*-alkanes) up to level 6 (partial degradation of the steranes) occurring in Orquidea-1 and Perpetua-1. Fig. 130 shows the FID traces for the free, asphaltene- and polar-bound *n*-alkane envelopes for Rosa-2 oil. The *n*-alkanes in the free fraction of Rosa-2 have been removed by biodegradation; however, the asphaltene- and polar-bound fractions have undegraded *n*-alkane distributions. Also Orquidea-1 and Perpetua-1 which have biodegraded free sterane distributions show undegraded distributions in the asphaltene- and polar-bound fractions. Bound biomarkers in oils have been previously reported to have the advantage of being protected from biodegradation compared to those in the free hydrocarbon fraction (Rubinstein *et al.*, 1979; Jones *et al.*, 1988), and can be used in oil-oil and oil-source rock correlations, where the free fraction biomarkers have been degraded (Behar *et al.*, 1984; Cassini & Eglinton, 1986).

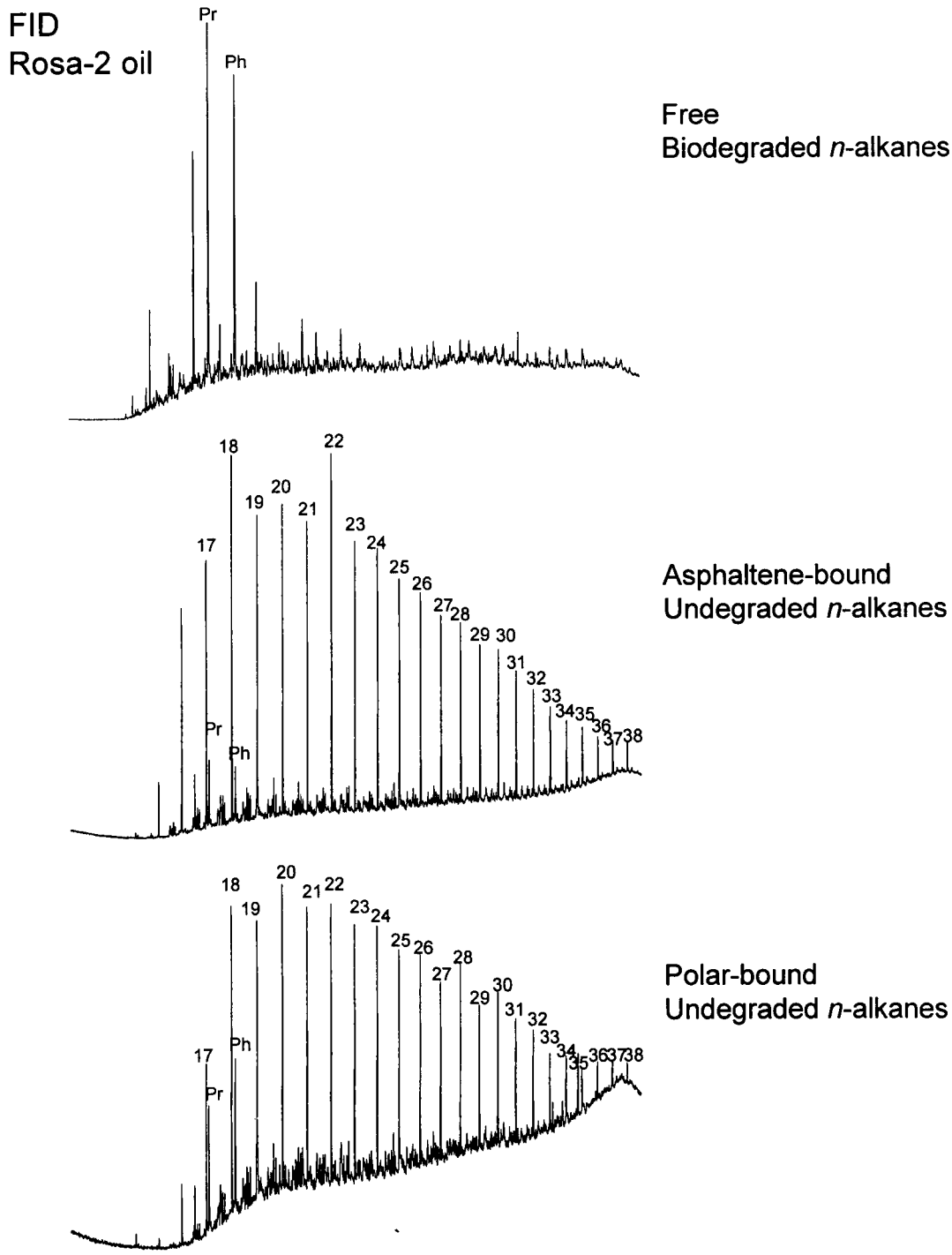

Fig. 130 FID traces to show free, asphaltene- and polar- bound *n*-alkane envelopes of the Block 17 oil Rosa-2.

7.2 Maturity analysis.

7.2.1 Gas chromatogram analysis and biomarker analysis (GC-MS).

Fig. 131 and Fig. 132 compare the free, asphaltene- and polar-bound sterane and triterpane biomarkers, for Rosa-2 oil. The data show that the biomarkers released by hydropyrolysis from the asphaltene- and polar-bound fractions of the oil are consistent with the kerogen-bound biomarkers in the source rocks, preserving a less mature biomarker profile than the free fraction. This is also consistent with the literature on bound biomarkers (Seifert, 1978; Peters *et al.,* 1990; Love *et al.*, 1995; Bishop *et al.,* 1998; Murray *et al.,* 1998). The bound fractions have a higher abundance of 17β(H), 21α(H) hopanes (or moretanes) compared to the more thermally stable 17α(H), 21β(H) hopanes, and also a lower abundance of the more thermally stable αβ22S to αβ22R hopanes. The bound fractions also contain higher proportions of ααα steranes, compared to the more thermally stable αββ steranes, than is found in the free fraction biomarkers, and also contain lower abundances of the more thermally stable ααα20S to 20R. The thermodynamically unstable β αα steranes are also found in the bound fractions co-eluting with the C_{29}αββS sterane.

Diasteranes, which are known to increase in concentration with maturity (Peters & Moldowan, 1993), are present in the asphaltene- and polar- bound fractions and are in lower relative abundance to the regular steranes than is found in the free fraction biomarkers. As explained in the kerogen-bound biomarker chapter, the literature reports diasteranes are generally not observed in macromolecular organic matter a result of the products not being incorporated into the macromolecular material (Seifert, 1978; Philp & Gilbert, 1985; Fowler & Brooks, 1987). The presence of diasteranes in the samples (as seen in the asphaltene-bound fraction of Rosa-2 in Fig. 132) may therefore indicate the occurrence of free steranes trapped within the physical macromolecular network, which were not removed during purification of the asphaltene and polar fractions prior to hydrogen pyrolysis. This presence of free biomarkers in the bound fractions would therefore affect biomarker maturity parameters for the fractions.

The rearranged hopane Ts is also absent from the bound-fractions. In the same way to rearranged steroids, rearranged hopanes (e.g. Ts) are not generally observed within macromolecular organic matter (Fowler & Brookes, 1987). They are though to derive *via* chemical mechanisms during diagenesis of unrearranged hopanoid natural products (Moldowan *et al.*, 1991). The chemical mechanism by which the rearranged hopane Ts is formed is though to be catalysed by clay. As with diasteranes this may also explain the absence of Ts macromolecular fractions.

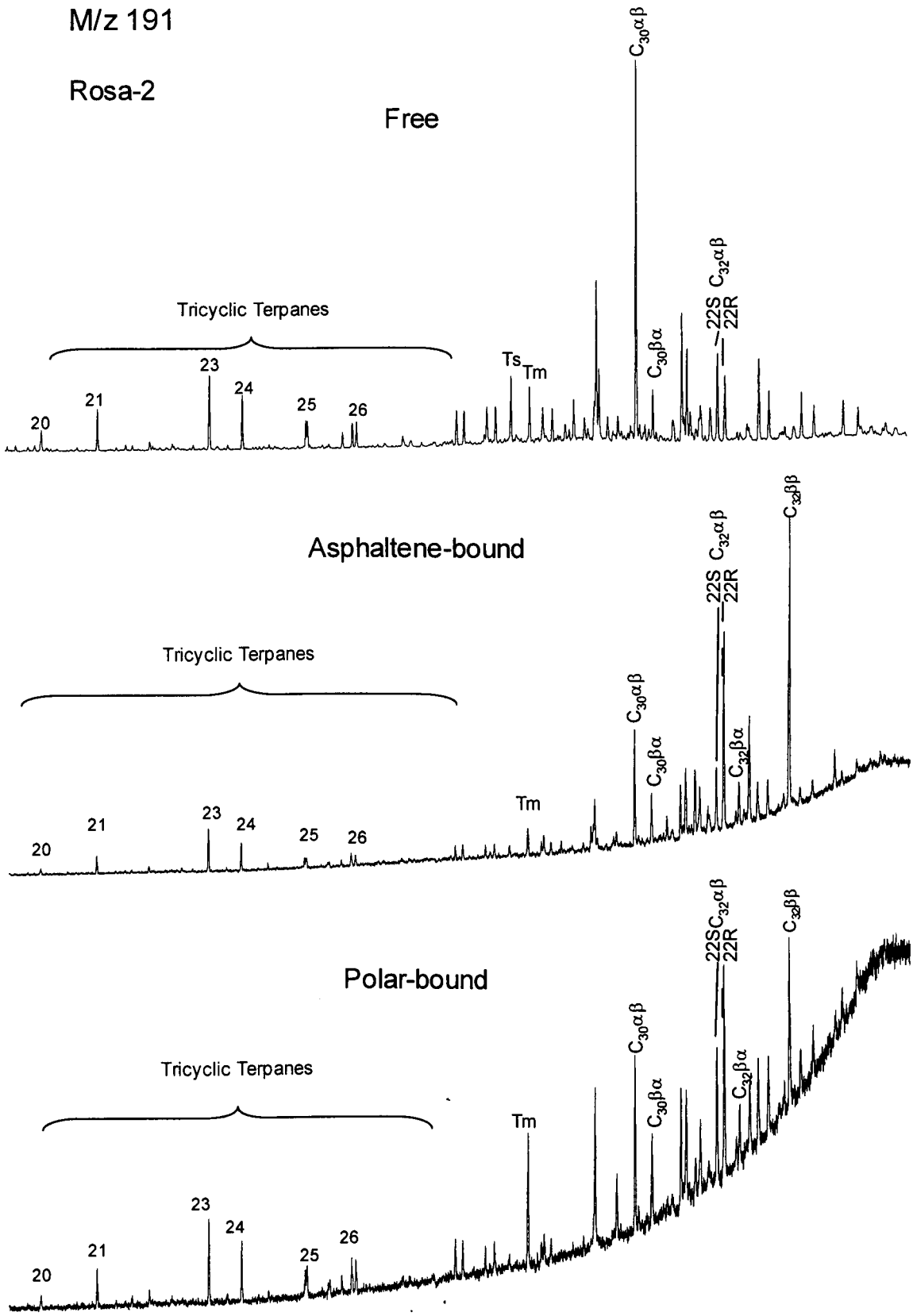

Fig. 131 Comparison of the free, asphaltene- and polar-bound triterpane biomarkers in the Block 17 oil Rosa-2.

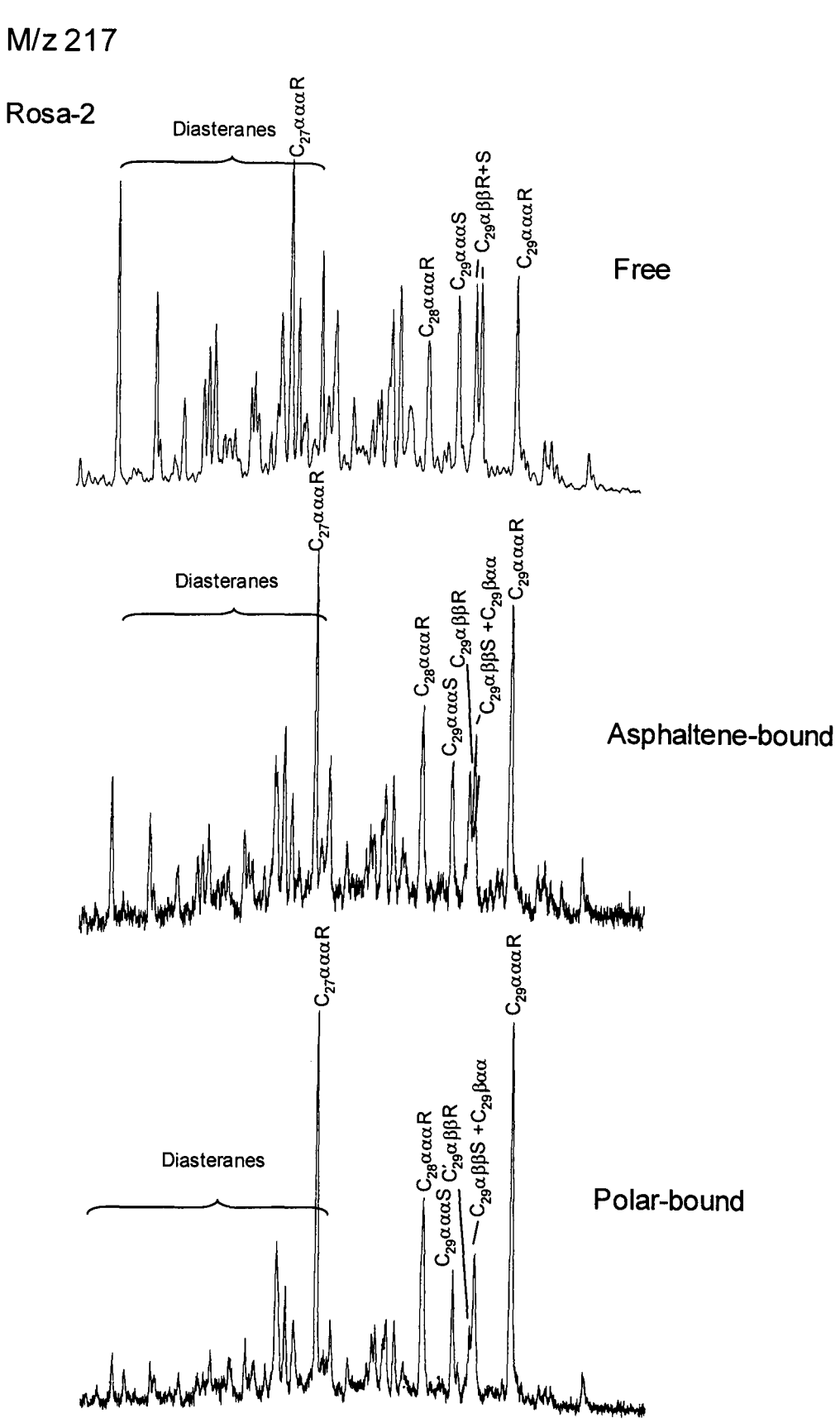

Fig. 132 Comparison of free, asphaltene- and polar-bound sterane biomarkers for the Block 17 oil Rosa-2.

Fig. 131 shows Rosa-2 and the other block 17 oils have an unusual hopane distribution. The hopane profile looks anomalously immature for C_{32} compounds (and relative to the sterane). There is a high abundance of these C_{32} hopanes compared with other carbon numbers in the m/z 191 ion chromatogram, and these largely possess immature stereochemistry (i.e. low 22S to R ratios (Table 9) and the presence of βα and, particularly, ββ hopanes). These strong C_{32} hopane signals may then be partially derived directly from hopanoid signals (such as bacteriohopanepolyols) from active or recently active (aerobic) bacteria, these microbes perhaps being involved in petroleum biodegradation (Note: after submission hopanoids have recently been reported to be formed in the deep black sea under anoxic conditions). In support of this theory, the block 17 oils all show some degree of biodegradation of the free biomarkers.

Oils	homohopane isomerisation				
	%31αβS	%32αβS	%33αβS	%34αβS	%35αβS
Asphaltene fractions					
Girassol-2b	41	30	46		
Orquidea-1	51	43	49	52	
Rosa-2	51	39	52	48	57
Perpetua-1	54	53			
camelia-1	55	49	54	52	51
Dalia-3	51	45	47	50	48
Polar fractions					
Girassol-2b	46	27	45	54	43
Orquidea-1	50	64	51	56	62
Rosa-2	45	24	50	47	45
Perpetua-1	51	37	54	50	50
camelia-1	50	37	51	48	47
Dalia-3	46	37	51	47	45

Table 9 Homohopane isomerisation for the biomarkers in the asphaltene- and polar-bound fractions of the Block 17 oils.

Fig. 133 and Fig. 134 show cross-plots of biomarker maturity parameters for the asphaltene- and polar-bound oil fractions. The kerogen-bound biomarkers from the source rocks have been included and fall in a relatively straight line; essentially a maturity gradient. The asphaltene-bound fractions of the oils show maturity parameter values that are more consistent with the kerogen-bound fractions of the source rocks. They plot within the source rock maturity gradient, particularly in Fig. 133, whereas the polar fraction values fall outside this maturity gradient.

Interestingly, quantitative analysis of the biomarkers, shown in Table 10 shows the polar fraction gives higher yields of biomarkers per mg oil than the asphaltene fraction. It might therefore have been expected to be more representative of the kerogen than the asphaltene fraction. However, it should be noted that % yields of biomarker from the asphaltene- and polar-bound fractions are both very low compared to the free fraction, and are generally less than 1% (with the exception of 4-44-1 oil). This may be due to low trapping efficiency of the hydropyrolysis runs; the trapping efficiency may also be proportional to the amount of sample (asphaltene or polar) initially pyrolysed. This may suggest lower quantities of asphaltene than polar fraction may have been pyrolysed, hence the lower total yields of biomarkers from the asphaltene fraction per mg of oil. The amounts of polar fraction pyrolysed were not recorded due to the method of polar isolation and purification used. Note, current work at Nottingham University is being conducted to improve trapping efficiencies. Regardless of the polar fraction yielding higher absolute amounts of biomarkers, from an exploration oil to source rock correlation perspective, the asphaltene-bound fractions of the oils appear most comparable to the kerogen-bound biomarkers of the source rocks, at least in terms of maturity parameters.

Table 10 shows that 4-44-1 oil has higher % yields of biomarkers from the asphaltene- and polar- bound fractions than the other oils. Several authors have noted an increase in biomarker concentration in the free hydrocarbon fraction of source rocks with increasing burial and maturation. This is interpreted to be result of release of compounds from the kerogen and/or asphaltene fractions (Eglinton & Douglas, 1988; Farrimond *et al.,* 1996; Bennet & Abbot, 1999; Bishop *et al.*, 1998; Bishop & Abbott, 1993; Farrimond *et al.,* 1998; Farrimond *et al.,* 1999) as a result of thermal stress and associated bond cleavage (Rullkötter and Michaelis, 1990). If this process is also true of the macromolecular fractions of oils (i.e. asphaltene and polar fractions), it might therefore be expected that 4-44-1 which is the most mature oil, would have lower amounts of biomarkers in the asphaltene and polar fractions as, with maturity, biomarkers would be released from the bound fractions.

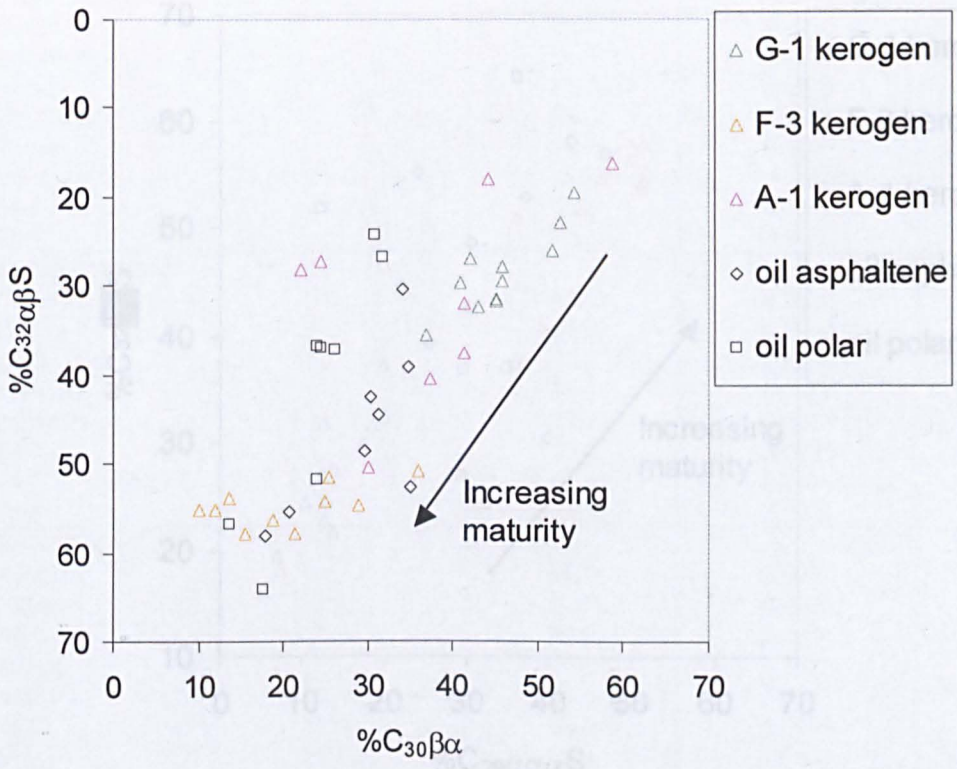

Fig. 133 The $\%C_{32}\alpha\beta S$ hopane maturity parameter versus the $\%C_{30}\beta\alpha$ hopane maturity parameter for kerogen-bound biomarkers from the source rock samples from Girassol-1 (G-1), Funda-3 (F-3), and Abacaxi-1 (A-1) wells and also the asphaltene- and polar-bound biomarkers of the oil fractions.

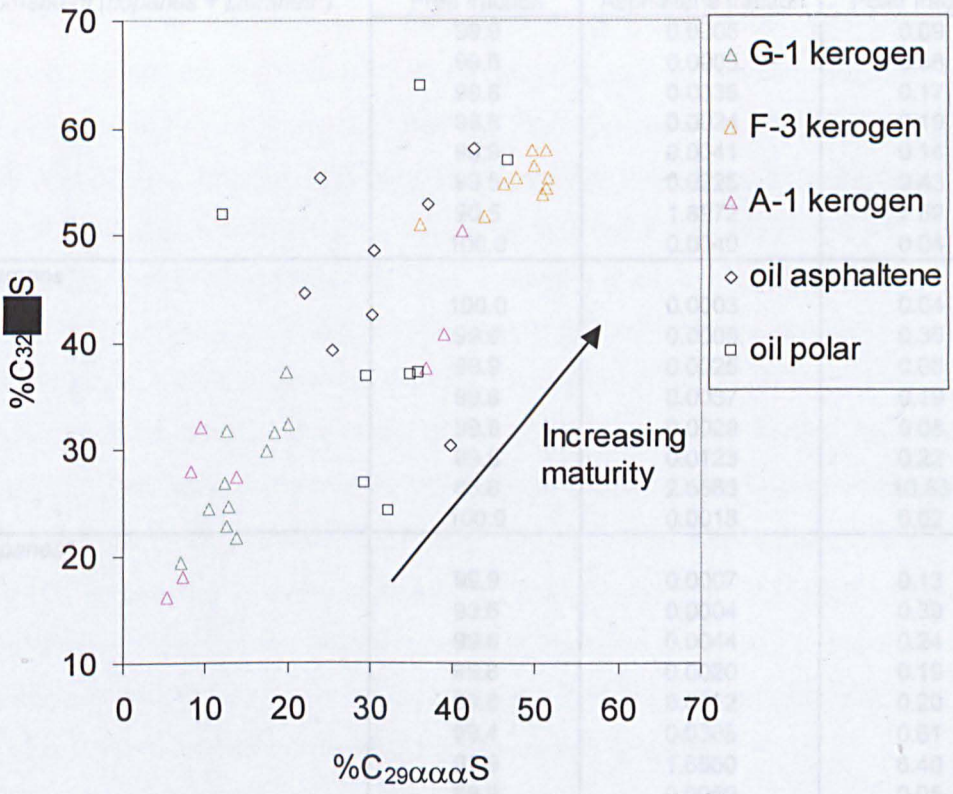

Fig. 134 The $\%C_{32}\alpha\beta S$ hopane maturity parameter versus the $\%C_{29}\alpha\alpha\alpha S$ sterane maturity parameter for kerogen-bound biomarkers from the source rock samples from Girassol-1 (G-1), Funda-3 (F-3), and Abacaxi-1 (A-1) wells and also the asphaltene- and polar-bound biomarkers of the oil fractions.

Oil	% Total		
Selected biomarkers (hopanes + steranes)*	Free fraction	Asphaltene fraction	Polar fraction
Girassol-2b	99.9	0.0005	0.09
Orquidea-1	99.6	0.0005	0.38
Rosa-2	99.8	0.0035	0.17
Perpetua-1	99.8	0.0024	0.19
Camelia-1	99.9	0.0041	0.14
Dalia-3	99.5	0.0225	0.43
'4-44-1	90.5	1.8972	7.59
'4-26-1	100.0	0.0040	0.04
*Selected steranes**			
Girassol-2b	100.0	0.0003	0.04
Orquidea-1	99.6	0.0008	0.35
Rosa-2	99.9	0.0025	0.08
Perpetua-1	99.8	0.0037	0.19
Camelia-1	99.9	0.0029	0.08
Dalia-3	99.8	0.0123	0.22
'4-44-1	86.6	2.5563	10.83
'4-26-1	100.0	0.0018	0.02
*Selected hopanes**			
Girassol-2b	99.9	0.0007	0.13
Orquidea-1	99.6	0.0004	0.39
Rosa-2	99.8	0.0044	0.24
Perpetua-1	99.8	0.0020	0.19
Camelia-1	99.8	0.0052	0.20
Dalia-3	99.4	0.0308	0.61
'4-44-1	91.9	1.6560	6.40
'4-26-1	99.9	0.0059	0.05

NB. The selected biomarkers used are those from the Norsk Hydro automatic peak quantification system i.e. those used in the calculation of set ratios.

* hopanes = sum of TS + Tm + 17β(H) + $C_{29}\alpha\beta$ + $C_{29}\beta\alpha$ + $C_{30}\alpha\beta$ + $C_{30}\beta\alpha$ + $C_{31\text{-}35}$ (αβ S+R).
steranes = sum of C_{27}-C_{29} (ααα R+S) + $C_{27}\alpha\alpha\alpha$R +$C_{29}\alpha\alpha\alpha$S +C29ααα R

Table 10 Comparison of the percentage yields (in ng/mg oil) of selected biomarkers from the free, asphaltene and polar fraction of the Angolan oils.

Fig. 135 and Fig. 136 show cross plots of the hopane and sterane maturity parameters for the free, asphaltene- and polar-bound oil fractions. Note, the %$C_{29}\alpha\beta\beta$ parameter could not be calculated for the bound fractions due to co-elution of $C_{29}\beta\alpha\alpha$ with $C_{29}\alpha\beta\beta$S. Also, the %$C_{29}T_s$ and %$C_{27}T_s$ could not be calculated due to the absence of $C_{29}T_s$ and $C_{27}T_s$ in the pyrolysate. As with rearranged steroids, rearranged hopanes (e.g. C_{27}Ts and C_{29}Ts) are not generally observed within macromolecular organic matter (Fowler & Brookes, 1987). Such rearranged hopanes are thought to derive *via* chemical mechanisms during diagenesis of unrearranged hopanoid natural products (Moldowan *et al.*, 1991). The chemical mechanism by which the rearranged hopane Ts is formed is thought to be catalysed by clay. As with diasteranes this may also explain the absence of C_{27}Ts and C_{29}Ts in macromolecular fractions, perhaps due to the shielded location of the double bond. For the Block 17 oils (i.e. all those in Fig. 135 & Fig. 136 excluding 4-26-1 and 4-44-

1) the biomarkers in the asphaltene and polar fractions are of similar maturity and are less mature than the free fraction biomarkers. The $\%C_{30}\beta\alpha$ parameter covers a greater spread of values in the bound fractions than the free and therefore appears to be a more sensitive measure of thermal maturity than the free biomarkers. The asphaltene- and polar-bound $\%C_{30}\beta\alpha$ maturity parameter values are considerably less mature than their free counterparts, and cover a greater maturity range (i.e. once the free parameter has stopped responding to changing maturity the bound parameter continues to change due to binding into macromolecular fractions, which provides steric protection (e.g. Love *et al.,* 1995; Rocha *et al.,* 1997, Murray *et al.,* 1998) retarding isomerisation. As a result of this steric hindrance the thermally less stable 17β(H), 21α(H) hopanes are relatively more abundant in the bound fractions; therefore the moretane (βα)/ hopane (αβ) ratio has not yet reached equilibrium, and is therefore still responding to maturity changes. The greater maturity range covered by the βα/αβ hopane ratio for the bound biomarker fractions compared to the free fractions was observed for the source rock kerogens in this thesis and has been previously observed in a source rock study by Murray *et al.* (1998).

The $\%C_{32}\alpha\beta S$ parameter also covers a greater spread of values in the asphaltene- and polar-bound fractions than the free and therefore appears a more sensitive measure of thermal maturity than the free biomarkers The $\%C_{32}\alpha\beta S$ maturity parameter for Girassol-1 kerogen-bound biomarkers was also observed to operate over a greater depth range and to higher maturites than the free parameter. This may in part be due to steric hindrance in bound biomarkers preventing mineral catalysis at certain sites, or results from the greater stability of the stereoisomer at C-22 in kerogen-bound hopanes particular, as C-22 located on the side-chain of hopanes is one of the principal sites of attachment for hopanes to kerogen (Richnow *et al.,* 1992: Adam *et al.,* 1993).

However, in the oils 4-44-1 and 4-26-1, which are more mature than the block 17 oils, there is less difference in maturity between the free and bound fractions; this may be because the isomerisation of the biomarkers which alter with maturity are approaching equilibrium, and/or be due to better steric protection of bound biomarker structure in macromolecular organic matter of the Block 17 oils compared to the Block 4 oils.

The maturity ordering of the block 17 oils derived from the free, asphaltene- and kerogen-bound hopanes and steranes are shown below. Note, not all Block 17 oils analysed for their free biomarkers were analysed for bound compounds. The free and bound fractions do not show agreement; in particular the bound fractions consistently show Rosa-2 and Girassol-2b as the least mature oils whereas, from the free biomarkers Dalia-2 and Camelia-1 are the least mature oils. Hydrogen pyrolysis tar recoveries from the asphaltene- and polar-bound fractions of the Block 17 oils were low (1.3 to 14.4 mg, and 0.7 to 7.3 mg respectively) which gave weak GC-MS signals. It might therefore be expected that peak amounts calculated may have a larger associated error. Therefore, the greater spread of maturity parameter values for bound fractions may not be entirely a real difference in maturity but in part due to scatter as a result of inaccuracy of quantification measurements.

Free fraction hopane maturity ordering:
Tulipa > Lirio = Orquidea = Cravo > Rosa > Girassol = Perpetua > Camelia = Dalia.

Free fraction sterane maturity ordering:
(Orquidea and Perpetua absent due to biodegradation of steranes):
Tulipa > Girassol = Rosa = Lirio = Cravo > Dalia > Camelia.

Asphaltene-bound hopane maturity ordering:
Orquidea = Dalia = Camelia = Perpetua-1 > Girassol = Rosa
Asphaltene-bound sterane maturity ordering:
Perpetua-1 = Girassol >Orquidea = Camelia > Rosa = Dalia

Polar-bound hopane maturity ordering:
Orquidea > Dalia = Camelia = Perpetua-1 > Girassol = Rosa
Polar-bound sterane maturity ordering:
Orquidea = Camelia = Perpetua-1 > Girassol = Rosa = Dalia

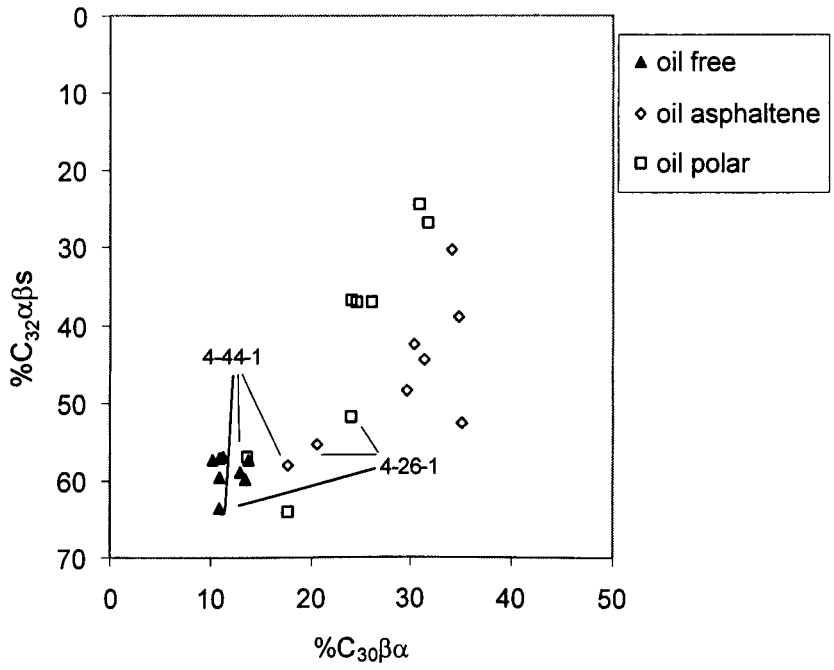

Fig. 135 The $\%C_{32}\alpha\beta S$ hopane maturity parameter versus the $\%C_{30}\beta\alpha$ hopane maturity parameter for free, asphaltene- and polar-bound fractions of the Angolan Block 17 oils plus the Block 4 oils 4-44-1 and 4-26-1.

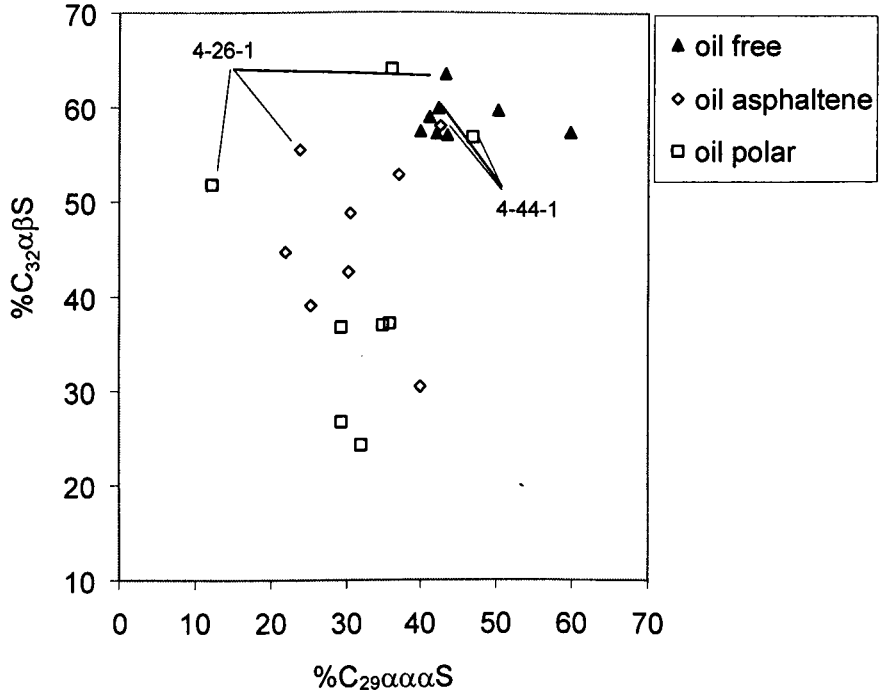

Fig. 136 The $\%C_{32}\alpha\beta S$ hopane maturity parameter versus the $\%C_{29}\alpha\alpha\alpha S$ sterane maturity parameter for the free, asphaltene- and polar-bound fractions of the Angolan Block 17 oils plus the Block 4 oils 4-44-1 and 4-26-1.

7.3 Identification of facies compositional information in the Angolan oils related to source rock depositional environment.

In the asphaltene- and polar-bound fractions the compounds oleanane and 28,30 bisnorhopane (BNH) which are found in the free fractions are not detectable. This was also observed in the kerogen-bound source rocks. The absence of BNH in bound biomarker fractions has been explained as a result of the precursor compound of BNH (which is unidentified as yet) lacking the functionality for attachment (Jones *et al.*, 1987; Eglinton & Douglas, 1988; Richnow *et al.*, 1992). Gammacerane is difficult to clearly identify due to the relatively weak GC-MS signal of the samples, which have a lot of background noise in the m/z 191 mass chromatogram. Gammacerane is present in the kerogen-bound fractions of the source rocks in either low or negligible amounts; therefore if GC-MS signals were stronger it may be more easily detectable in the asphaltene- and polar-bound fractions.

The application of the C_{26}/C_{25} tricyclic terpane ratio to distinguish oils sourced from the lacustrine Pre-salt (values >1) from the marine Post-salt (values <1) using the free biomarkers does not follow for the bound biomarkers. Although the asphaltene- and polar-bound biomarkers of the lacustrine oil analysed have a value greater than 1, several marine oils also have values greater than 1. The marine oils Perpetua-1 and Orquidea-1 have values much greater than 1 for their polar-bound fractions (8.8 and 16.8 respectively) this is due to the unusual tricyclic terpane distribution seen in these samples. They contain very high abundances of C_{21}, C_{24} and C_{26} tricyclic terpanes (Fig. 137). These tricyclic terpanes are also high in the asphaltene-bound fractions although are not as abundant as in the polar-bound fractions.

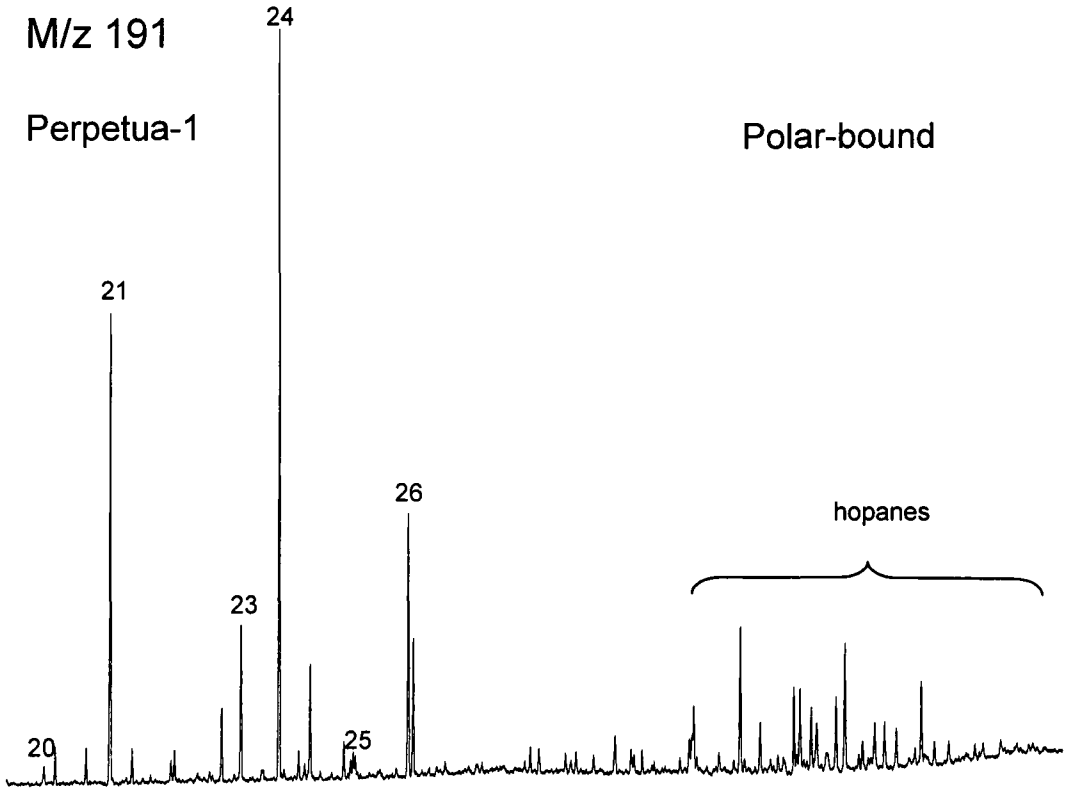

Fig. 137 Perpetua-1 m/z 191 chromatogram to illustrate of the unusually high abundance of C_{21}, C_{24} and C_{26} tricyclic terpanes in the polar-bound fraction (tricyclic terpane carbon numbers marked).

Several other characteristics of the free hydrocarbons that are used to differentiate the marine and lacustrine oils do not follow for the bound fractions, although it is important to note that only one lacustrine oil has been analysed for bound biomarkers due to sample availability. The lacustrine oils have a higher abundance of hopanes to steranes in the free hydrocarbons than do the marine oils. This can be seen in Fig. 138 where the lacustrine oil 4-26-1 has a higher hopane/sterane ratio than the marine oils. The asphaltene-bound fraction for this oil also has a higher hopane/sterane ratio; however, the polar-bound fraction does not. The bound fractions of the marine oils (all the samples in Fig. 138 excluding 4-26-1) cover a greater range of hopane/sterane ratio values than the free fractions. From an exploration perspective this might suggest that the bound fractions may be providing additional, more sensitive source information. However, this may also be a result of inaccuracy due to weak sample amounts for GC-MS analysis. Analysis of the free biomarkers in the lacustrine oils showed a distinctive predominance of C_{27} steranes (see Section 6.3.1.4). Analysis of the asphaltene- and polar-bound fraction of oil 4-26-1 shows this same characteristic for the asphaltene-bound fraction but not for the polar-bound fraction where C_{29} is the predominant sterane. These data

support interpretations that the asphaltene-bound fraction of oils may be a more reliable fraction for comparisons with kerogen-bound biomarkers in source rocks from an oil-source rock correlation perspective. The characteristic sterane pattern of the free biomarker fraction marine oils has a high C_{28} sterane which can often be found in equal abundance to the C_{27} and C_{29} steranes this rule does not follow for the bound oil fractions where C_{27} steranes dominate (Fig. 132).

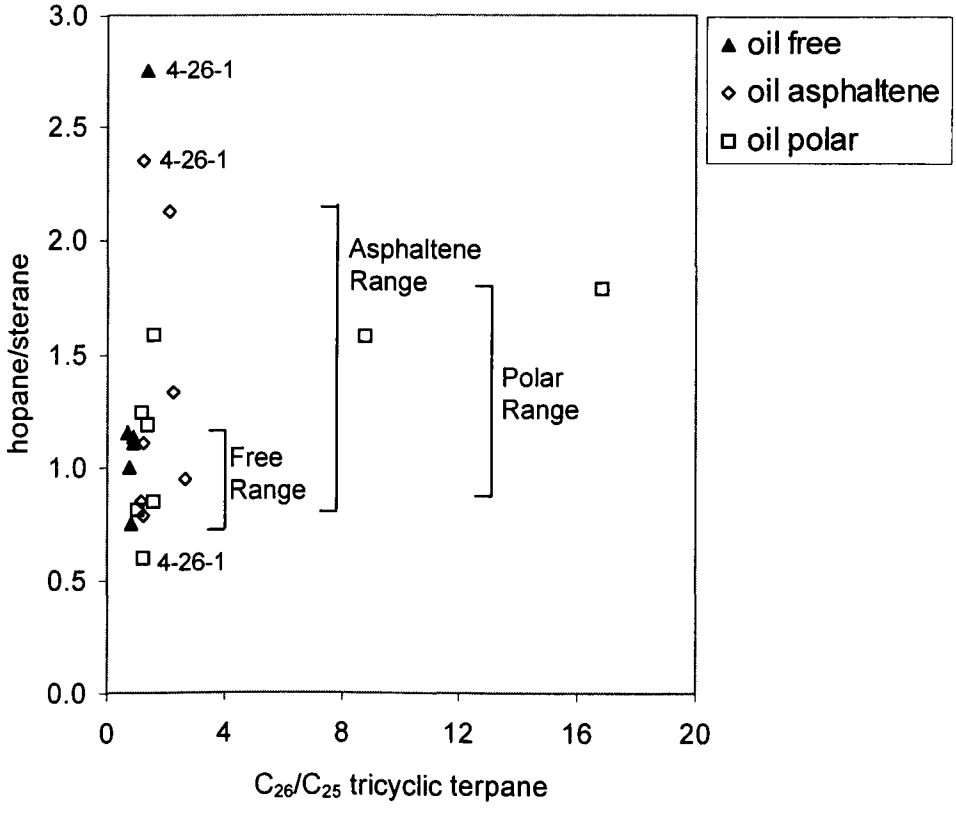

Fig. 138 Cross plot of the C_{26}/C_{25} tricyclic terpane parameter versus the hopane/sterane parameter for free, polar- and asphaltene-bound fractions of the Angolan. Note free biomarker values for Orquidea-1 and Perpetua-1 have been removed due to the hopane/sterane parameter being affected by biodegradation. The lacustrine oil 4-26-1 has been labelled; the remaining oils are Block 17 marine oils and the Block 4 marine oil 4-44-1. The range of values for the marine oil free, asphaltene and polar fractions have been illustrated.

Fig. 139 shows the m/z 191 mass chromatogram for the free, asphaltene- and polar-bound fractions for oil 4-26-1. The free hydrocarbon m/z191 trace is dominated by tricyclic terpanes, and extended homologues dominate the triterpane distribution. Analysis of the asphaltene and polar fractions reveals that the extended tricyclic terpanes are also present in the asphaltene-bound fraction identifiable up to C_{34} and in the polar-bound fraction up to C_{39}, and possibly higher. The tricyclic terpanes can be seen, occurring as doublets after C_{24} due to stereoisomerism at C-22 and hence

resolution of the 22S and 22R epimers, although the chromatographic elution order of the 22S and 22R epimers is unknown (Peters, 2000; Alberdi *et al.,* 2001). A second stereoisomer occurs at C-27 for the $\geq C_{30}$ tricyclic terpanes, giving additional 27S and 27R isomers; therefore C_{30} and higher homologues show four peaks for each homologue (22S27S, 22S27R, 22R27S, 22R27R) (Peters, 2000; Alberdi *et al.,* 2001). In Fig. 139 this resolution can be seen from C_{35} and higher homologues. Comparison of the two bound fractions reveals that the extended tricyclic terpanes are much higher relative to regular hopanes in the polar-bound fraction than in the asphaltene-bound fraction. The abundance of $C_{29}\alpha\beta$ (seen co-eluting with the second eluting C_{31} tricyclic) to $C_{30}\alpha\beta$ is much lower in the polar fraction than is commonly observed in bound fractions. This may suggest that the polar-bound fraction contains some free fraction biomarkers, hence containing the high extended tricyclics, although it should noted that in contrast to this the yield of biomarkers for this sample fraction is very low.

Fig. 139 shows a high abundance of $C_{35}\alpha\beta$ hopanes in the biomarkers released from hydropyrolysis of the polar fraction (prepared from the maltenes). This feature is not apparent in the hopane profile of the corresponding asphaltene fraction (which is, on average, composed of higher molecular weight organic structures than the polars) in the same samples. The C_{35} hopanes are thought to most likely result from the selective preservation of the C_{35} bacteriohopanetetrol, through natural vulcanisation reactions resulting in the incorporation of sulphur into the side-chain during early diagenesis (Peters & Moldowan, 1991, Bishop & Farrimond, 1995). The occurrence of high $C_{35}\alpha\beta$ hopanes in only the products generated from hydropyrolysis of the polar fraction (an *n*-pentane soluble fraction) though and not in the asphaltene products suggests that the precursor of these signals must be a low molecular weight (and *n*-heptane-soluble) polar compound. The most likely candidate is a hopane thiophene, formed during diagenesis or early catagenesis in the parent source rock, with the stable heterocyclic aromatic functionality present in the hopane side-chain preserving all the original carbon atoms in the hopanoid moiety. Hopane thiophenes are known to undergo fairly selective reductive desulphurisation without resulting in significant carbon-carbon bond cleavage (Köster *et al.,* 1997; van Kamm-Peters & Sinninnge Damsté, 1997) and this explains why hydropyrolysis generates C_{35} hopanes in high abundance from these precursors.

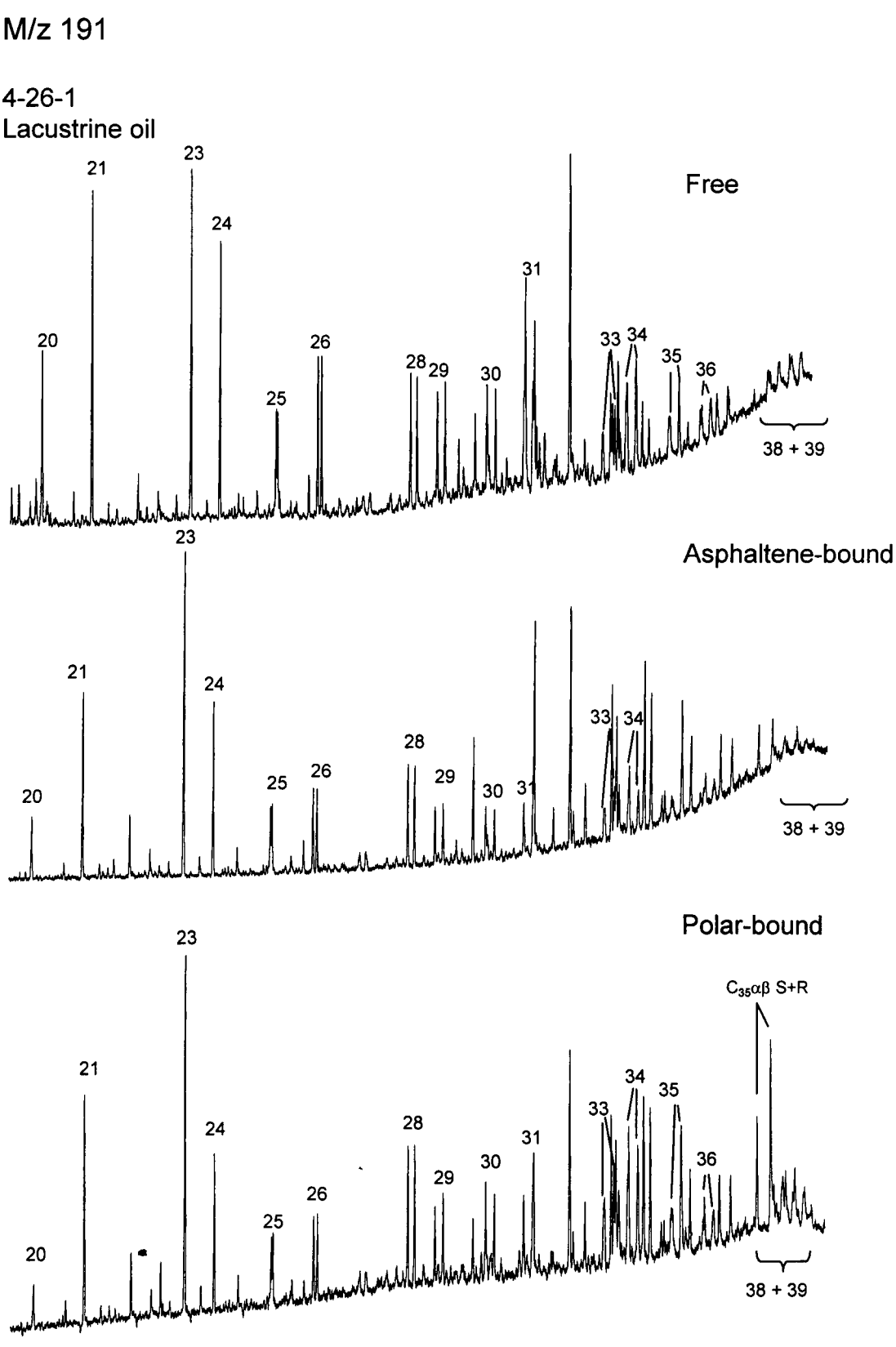

Fig. 139 M/z 191 mass chromatogram for 4-26-1 oil free, asphaltene- and polar-bound fractions to illustrate the high abundance of extended tricyclic terpanes in the free and polar-bound fractions. The second eluting C_{35} tricyclic terpane co-elutes with the $C_{33}\alpha\beta S$ hopane. Note the high abundance of $C_{35}\alpha\beta$ hopanes found in the polar-bound fraction.

7.4 Overview

Several of the oils analysed by hydrogen pyrolysis to release biomarkers from the asphaltene-and polar-bound fractions have suffered biodegradation of their free fractions. The asphaltene- and polar-bound fractions have the advantage of being protected from biodegradation, displaying undegraded *n*-alkane distributions.

The asphaltene- and polar-bound fractions of the oils show consistencies with the source rock kerogen-bound fractions and also the literature on bound biomarkers, in displaying less mature biomarker signals than the free biomarkers.

The asphaltene and polar-bound fractions of the oils comprise a very small percentage commonly less than 1% of the total biomarkers within the oil. However, they may be useful from an oil-source rock correlation perspective; the asphaltene-bound fraction appears more comparable to the kerogen-bound biomarkers of the source rocks. This is despite the fact that the polar fraction comprises a slightly higher % of total biomarkers in the oil than the asphaltene-bound fraction. The maturity parameters for the asphaltene- and polar-bound fractions display a greater range of values than the free fraction. These differences may be real maturity differences resulting from parameters not having reached their end point in the bound fractions, and therefore still responding to change. Alternatively, they may be the result of inaccuracy due to low hydrogen pyrolysis tar amounts from these oils giving weak GC-MS signals.

As found in the analysis of the kerogen-bound source rock fractions, there is evidence for compositional fractionation of biomarkers between the free and bound biomarker fractions. This is illustrated by the absence of certain compounds in the bound fraction (i.e. oleanane and BNH), which can be found in the free fraction. Several of the characteristics used to differentiate the marine and lacustrine oils in the free fractions (i.e. hopane/sterane ratio, C_{26}/C_{25} tricyclic terpane ratio, predominance of C_{27} steranes in lacustrine oils and C_{28} in marine), do not always follow for the bound fractions (see Table 11). However, of the bound fractions in the oils the asphaltene fraction is the more reliable fraction for distinguishing oil sources using these parameters and characteristics.

Ratio/ Parameters	Marine (7)		Lacustrine (1)	
	Asphaltene fraction	Polar Fraction	Asphaltene fraction	Polar Fraction
C_{26}/C_{25} tricyclic terpane	1.1 - 2.6	1.0 - 16.8	1.2	1.2
hopane/ sterane	0.7 - 2.1	0.8 - 1.8	2.3	0.5
$\%C_{28}$ sterane	18 - 24	16 - 24	20	16
$\%C_{30}$ sterane	3 - 6	4 - 8	5.6	6.9*
C_{27}/C_{29} sterane	0.9 - 1.7	1.1 - 1.8	1.5	0.8
$\%C_{35}\alpha\beta$	39 - 44	37 - 50	46	69
waxiness	0.5 -1.0	0.4 - 0.76	0.6	0.7
% tricyclic terpane	13 - 52	16 - 77	40	40
$\%C_{24}$ tetracyclic terpane	7 -12	1 - 10	8.8	8.3

* A peak eluting at the retention time of C_{30} sterane for the Pre-salt lacustrine has been used in this ratio, however analysis of the free hydrocarbon m/z 231 revealed this compound was a 4α-methylsterane . This is also possible for the bound fraction, however due to the lower maturity of the bound fractions the m/z 231 mass chromatograms are dominated by hopenes. The hopenes may be obscuring the 4α methylsteranes, thus preventing identification.

Table 11 Summary table, asphaltene- and polar-bound biomarker parameters for all Angolan oils. (Number of samples analysed indicated in brackets. Note, for certain samples not all parameters could be calculated.)

8 Oil-source rock correlation

This chapter presents results correlating the Angolan oils and source rocks using both the free and bound biomarkers. In this chapter I will also critically evaluate the parameters used in this thesis to define the source rocks and oils as being either marine or lacustrine. The section will also investigate the applicability of these parameters to further characterize oils that have been assigned on the basis of their hopane/sterane ratio and C_{26}/C_{25} tricyclic ratio as being of mixed origin.

8.1 Oil-source rock correlation using free and bound biomarkers.

Correlation will link the free biomarkers in the bitumen fraction of the source rocks to the free (aliphatic hydrocarbon) fraction of the oils, and also the kerogen-bound biomarkers of the source rocks to the asphaltene-bound biomarkers of the oils. Analysis of the asphaltene and polar bound fractions has shown that the asphaltene-bound biomarkers in the oils are more comparable with the kerogen-bound biomarkers of the source rocks, than are the polar-bound compounds. Bound biomarker comparisons in this chapter will therefore be made using only the asphaltene-bound oil biomarkers. It should be taken into consideration in bound biomarker correlations that the asphaltene fractions of oils gave weak GC-MS signals, in part due to the low recovery of asphaltenes from the oils, and also as a result of the low yields of biomarkers generated from the asphaltene fractions compared to the free fractions; therefore, the asphaltene-bound oil biomarker data may not be fully reliable. Section 5.2.4 showed that the kerogen-bound biomarkers can act as a good replacement for the free biomarker in the source rocks to distinguish between stratigraphic groups; however, absolute values of molecular parameters are not comparable. The free and bound biomarker source rock correlations will therefore be made separately in the following discussion. It is not practical for example to attempt correlations using the free biomarkers in oils with the kerogen-bound biomarkers in the source rocks.

Fig. 140 toFig. 144 show various plots of molecular parameters attempting to correlate between the free biomarkers of the marine oils and source rocks, and the free biomarkers of the lacustrine oils and source rocks. In general these show a

reasonably good correlation; the ternary diagram (Fig. 141) to show the distribution of the C_{27}, C_{28} and C_{29} steranes shows particularly good correlation between the marine oils and source rocks and the lacustrine oils and source rocks; also the $\%C_{28}$ parameter in Fig. 142 shows good correlations. The bound biomarkers of the marine oils generally correlate with the kerogen-bound biomarkers of the marine source rocks; however the asphaltene-bound biomarkers of the lacustrine oil do not show a good correlation with the kerogen-bound biomarkers in the lacustrine source rocks. It should be noted that due to restricted sample availability, one lacustrine oil has been analysed and may therefore not be representative of the lacustrine oils. The lacustrine oils in this thesis may be sourced from a range of lacustrine environments e.g. from saline to freshwater environments. It is therefore interesting to note the generally close correlation between the free biomarkers of the lacustrine oils and source rocks, considering that the source rocks shown represent only the freshwater facies. The reason the free biomarkers in the lacustrine source rocks and oils correlate well but the bound lacustrine fractions do not may be a result of poor source rock sample representation from the lacustrine section.

To determine which specific marine stratigraphic group is the source of the marine oils is more difficult. The possibility of an oil sourced from a source rock section containing more than one stratigraphic group may also occur. The free and bound biomarker data in Fig. 140 shows that the Pinda Gp. can be ruled out as a source of the marine oils on the basis of having higher $\%C_{35}\alpha\beta$ ratio values. The free biomarker sterane distribution shows that the Malembo Gp. can also be potentially ruled out as a source of the marine oils, having higher C_{29} sterane abundances than are found in the oils (Fig. 141). This interpretation is further confirmed by the higher $\%C_{24}$ tetracyclic terpane and hopane/sterane ratio of the free biomarkers in the Malembo Gp. compared with the free biomarkers in the marine oils (Fig. 143). However, the bound biomarkers are less distinctive for the Malembo Gp., as sterane distribution data shows that some of the marine oils have comparable C_{29} sterane abundances and hopane/sterane ratios. However, as mentioned above, the bound oil biomarkers may be a less reliable source of data than the free biomarkers in the oils.

The two remaining marine source rocks are the Landana and Iabe Gps. Several biomarker parameters show the oils to have a composition intermediate between the Iabe and Landana, e.g. the hopane/sterane ratio and $\%C_{24}$ tetracyclic terpane ratio (Fig. 143). The sterane distribution data for both the free and bound

data shown in Fig. 142 suggest a pure Landana source for the marine oils, whereas, the % tricyclic terpane parameter indicates a more likely labe source. The literature suggests certain parameters may be more reliable than others for use in biomarker oil and source rock correlation studies. For examples, this study and previous studies have observed the stronger attachment of hopanes into kerogen than steranes (Eglinton & Douglas, 1988). This is related to the higher number of attachment sites of hopanes compared to steranes (Mycke & Michaelis, 1986; Kohnen *et al.*,1991a; Hoffman *et al.*,1992; Adam *et al.*,1993; Richnow *et al.*,1993). If hopanes contain potentially more attachment sites than steranes they would therefore be more easily incorporated and less easily released from kerogen fraction. With generation biomarker compounds are released from kerogen and/or asphaltene fractions (Eglinton & Douglas, 1988; Farrimond *et al.*,1996; Bishop *et al.*,1998; Farrimond *et al.*,1998; Farrimond *et al.*,1999) as a result of thermal stress and associated bond cleavage (Rullkötter and Michaelis, 1990). Therefore correlation between an immature or less mature source rock with a more mature oil may be complicated by the fact the source rock may have lower hopane/sterane ratios than an oil generated from the source rock. The ratio of tricyclic terpanes to hopanes is also maturity dependent as tricyclic terpanes are generated from kerogen at higher thermal maturities relative to hopanes (Peters & Moldowan, 1993). This may be because they are more tightly bound into macromolecular fractions than the hopanes. This study has shown the higher abundance of tricyclic terpanes relative to hopanes in the kerogen-bound fraction of the source rocks compared to the bitumen fractions (see Section 5.2.2). This information implies an immature source rock may have a lower % tricyclic terpane ratio than an oil generated from it. In Fig. 144 the % tricyclic terpane ratio values for the marine oils could thus be potentially shifted to the left slightly and would therefore correlate more closely with the Landana Gp. source rocks.

To conclude, the source of the marine oils can be restricted to the labe and Landana source Gps., and may be purely one or the other (whereby the exact location of the source has not been sampled and therefore differs slightly in biomarker composition to the samples analysed in this study), or a contribution from both labe and Landana source rocks.

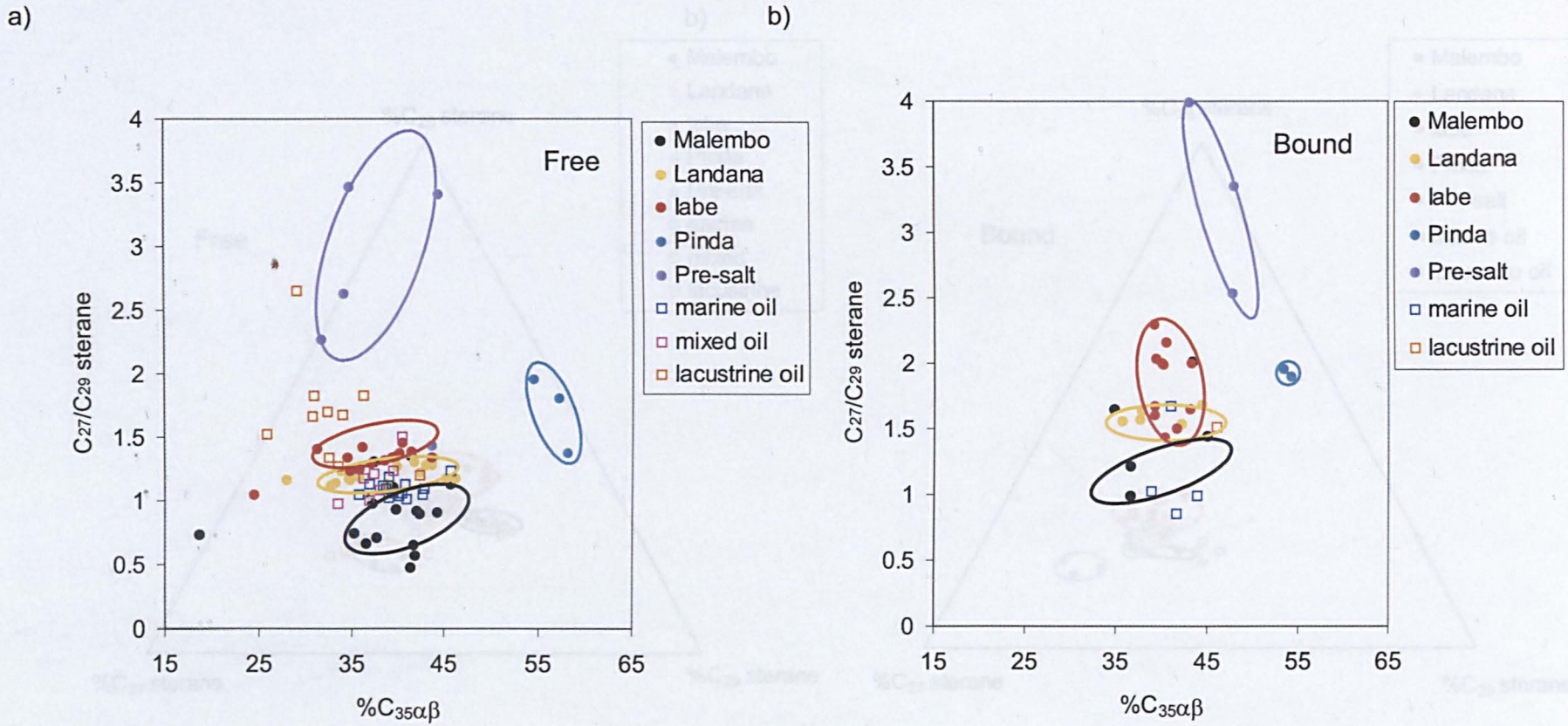

Fig. 140 Cross plot of the C_{27}/C_{29} ratio versus the $\%C_{35}\alpha\beta$ parameter for a) free source rocks and oils, and the b) kerogen-bound source rocks and asphaltene-bound oil fractions.

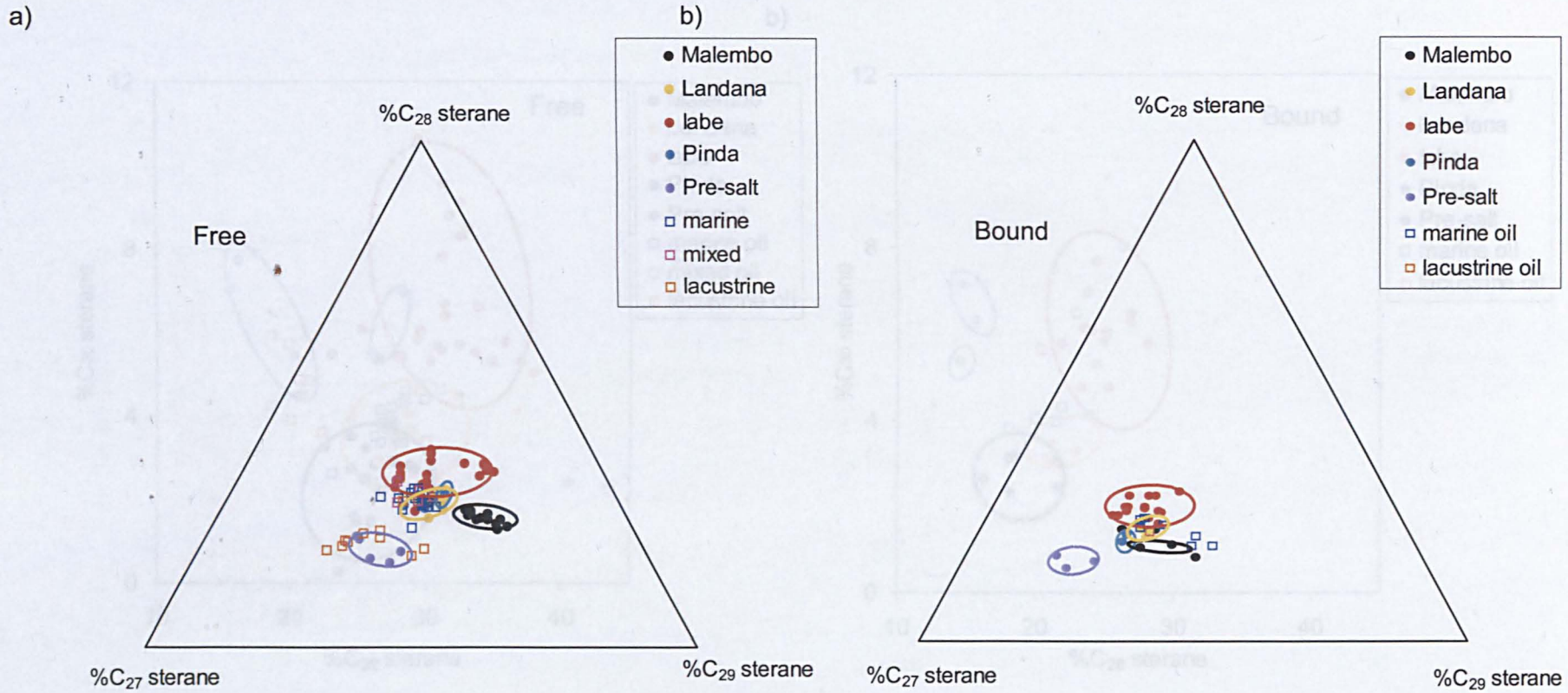

Fig. 141 Ternary diagram to show the distribution of the C_{27}, C_{28} and C_{29} steranes for both the a) free Angolan oils and source rocks, and the b) kerogen-bound source rocks and asphaltene-bound oil fractions. Note for free biomarker the distribution the 5α(H), 14β(H), 17β(H), 20 S + R steranes have been used. Due to the lower maturity of the kerogen-bound fraction and often absence of αββ steranes the 5α(H), 14α(H), 17α(H), 20 R compounds have been used.

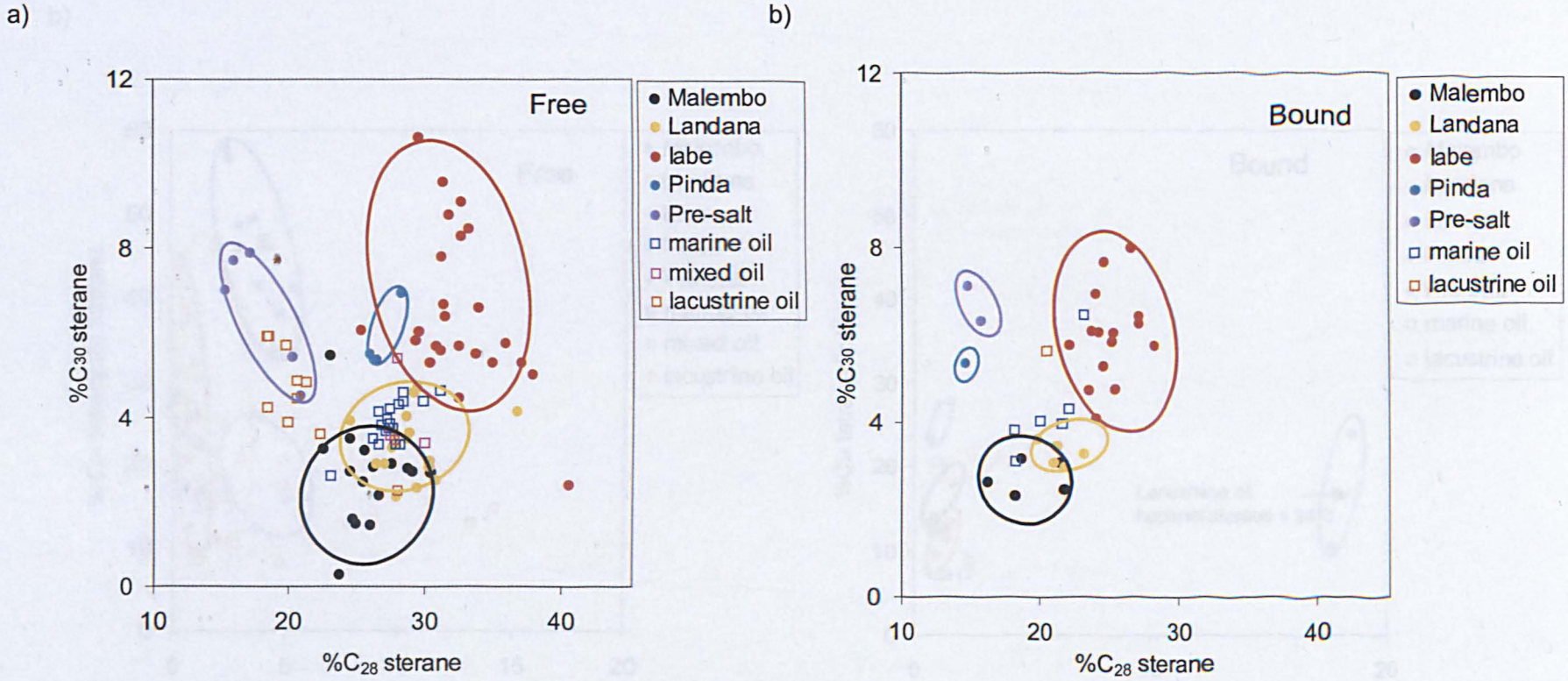

Fig. 142 Cross plot of the $\%C_{28}$ sterane ratio versus the $\%C_{30}$ sterane parameter for a) free source rocks and oils, and the b) kerogen-bound source rocks and asphaltene-bound oil fractions.

b)

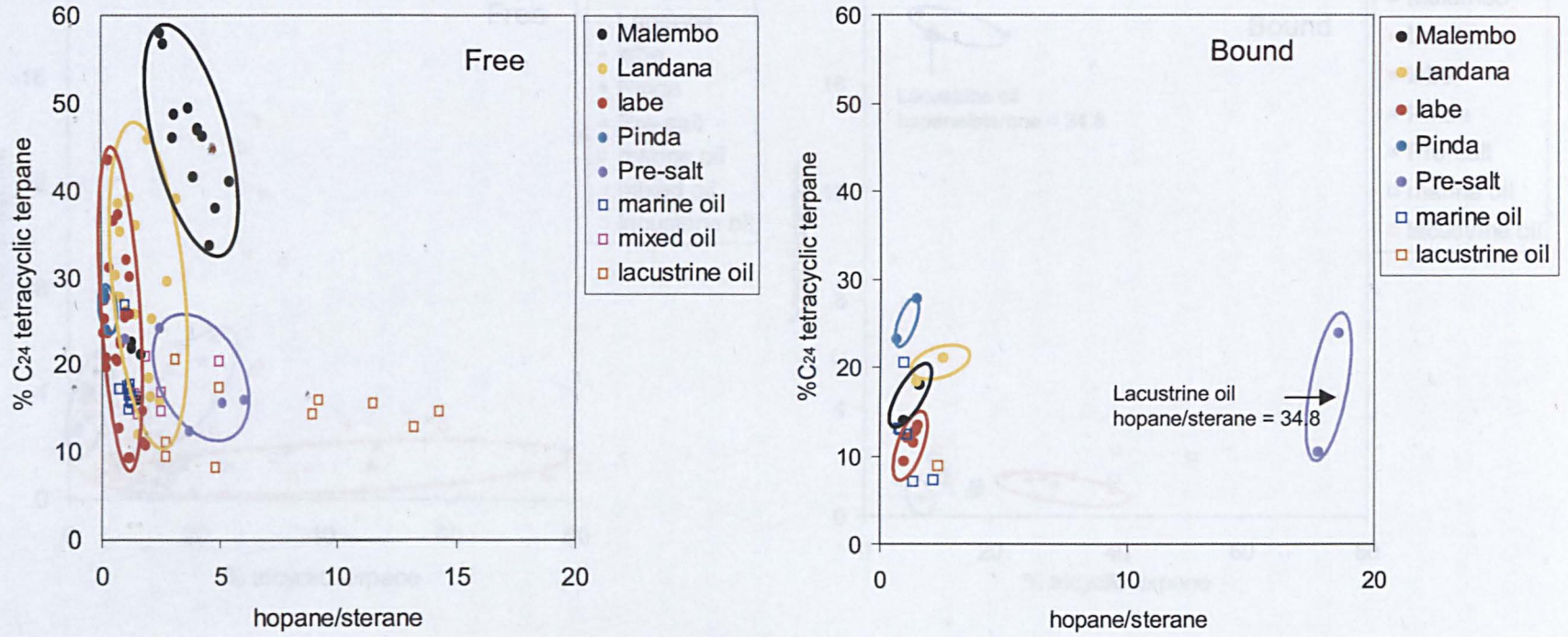

Fig. 143 Cross plot of the hopane/sterane ratio versus the $\%C_{24}$ tetracyclic terpane parameter for a) free source rocks and oils, and the b) kerogen- bound source rocks and asphaltene-bound oil fractions.

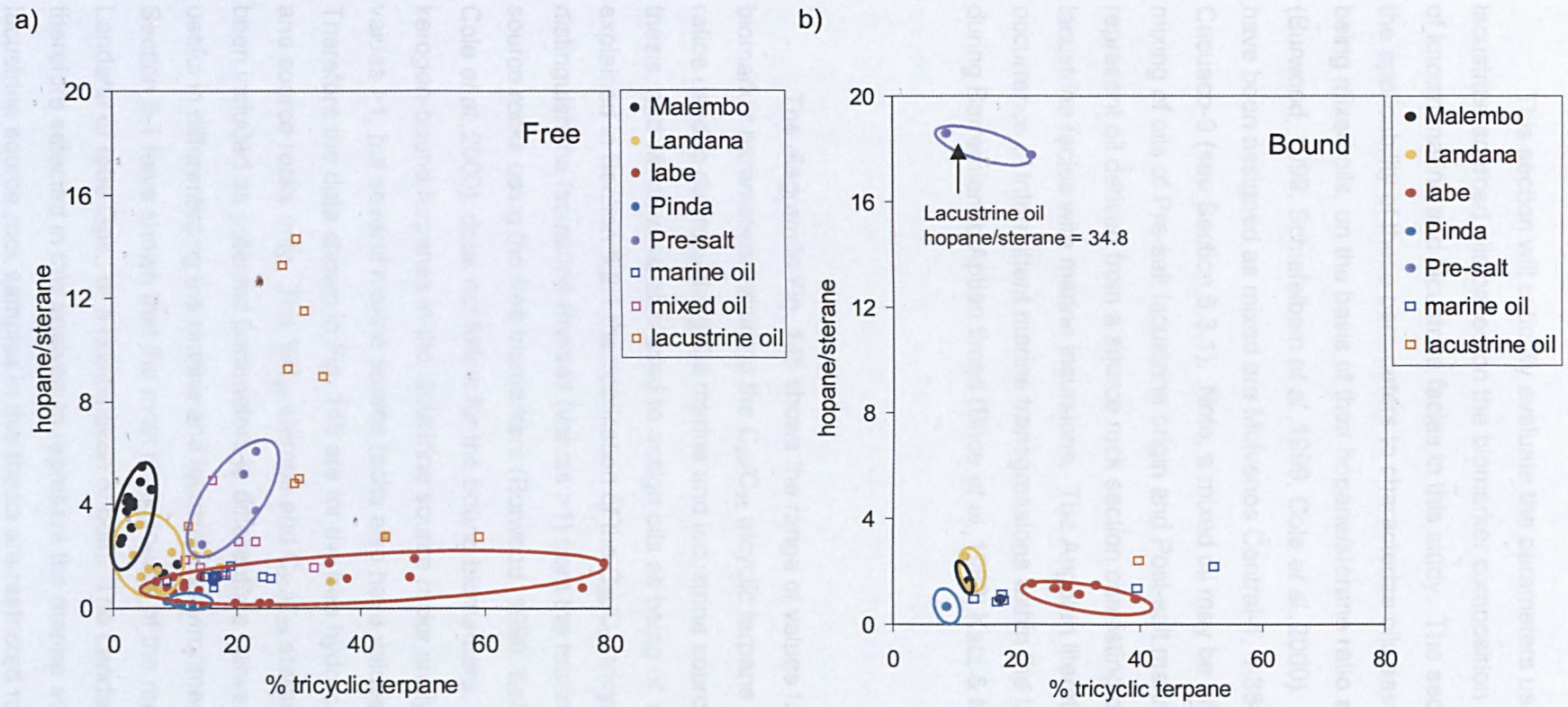

Fig. 144 Cross plot of the hopane/sterane ratio versus the %tricyclic terpane parameter for a) free source rocks and oils, and the b) kerogen-bound source rocks and asphaltene-bound oil fractions.

8.2 Mixing of oils.

This section will critically evaluate the parameters used to define marine vs. lacustrine sourced oils based on the biomarker composition of both the source rocks of known marine and lacustrine facies in this study. The section will also investigate the applicability of these parameters to characterize oils assigned in this thesis as being mixed oils, on the basis of their hopane/sterane ratio and C_{26}/C_{25} tricyclic ratio (Burwood, 1999; Schiefelbein *et al.*,1999, Cole *et al.*,2000). The Angolan oils that have been assigned as mixed are Mulvenos Central-1, 4-35-1, Ganda-3 and Cacuaco-9 (see Section 6.3.1). Note, a mixed oil may be an oil derived from the mixing of oils of Pre-salt lacustrine origin and Post-salt marine origin, or alternatively represent oil derived from a source rock section consisting of mixed facies, i.e. lacustrine facies with marine incursions. The Angolan literature discusses the occurrence of intermittent marine transgressions within the lacustrine Pre-salt section during Barremian to Aptian times (Brice *et al.*,1982; Katz & Mello, 2000).

The diagram in Fig. 145 shows the range of values found for various biomarker parameters including the C_{26}/C_{25} tricyclic terpane and hopane/sterane ratios used to distinguishing the marine and lacustrine source rocks and oils in this thesis, and which were also used to assign oils as being of 'mixed' origin. As explained in Section 5.2.1 the application of the C_{26}/C_{25} tricyclic terpane ratio to distinguish the lacustrine Pre-salt (values >1) from the marine Post-salt (values <1) source rocks using the free biomarkers (Burwood, 1999; Schiefelbein *et al.*,1999; Cole *et al.*,2000), does not follow for the bound biomarkers. The C_{26}/C_{25} ratio for the kerogen-bound terpanes in the lacustrine source rocks analysed consistently have values >1, but several marine source rocks also have values greater than 1. Therefore the data shown in Fig. 145 are for the free hydrocarbon fractions of the oils and source rocks only. The $\%C_{28}$ sterane and C_{27}/C_{29} sterane parameters have also been included as potential parameters to differentiate between the facies as they are useful in differentiating the marine and lacustrine environments. Data presented in Section 8.1 have shown that the most likely source of the marine oils is either the Landana or Iabe Gps., or a combination of both. The Landana and Iabe were therefore selected in this analysis to represent the marine source rocks. The lacustrine source rock samples in this thesis are restricted to the Cuvo Fm. from Abacaxi-1. Note, the Cuvo Fm. samples are interpreted (section **4.2.5**) to be

freshwater lacustrine source rocks. Literature reports regarding the depositional environment of lacustrine Pre-salt source rocks in Angola suggest fresh, brackish, hypersaline and alkaline conditions may occur (Burwood *et al.,*1990; Katz & Mello, 2000) so considering the lacustrine oils in this thesis are from several geographical locations in Angola they may therefore be derived from various environments. However, the data shown in Section 8.1 show a good correlation between the lacustrine oils (of potentially hypersaline, saline, alkaline or freshwater source) and the freshwater lacustrine source rocks.

Separation of oils into marine-derived and lacustrine-derived based on the C_{26}/C_{25} tricyclic terpane and hopane/sterane parameters has been made based on source rock results in this study and also comparable results and interpretations published in the literature (Burwood, 1999; Scheifelbein *et al.,*1999; Cole *et al.,*2000). Interpretations are also supported by isotopic evidence which differentiates oil as either marine and lacustrine. Isotopic values for the lacustrine and marine oils are consistent with values in the literature for Angolan oils (Burwood, 1999; Cole *et al.,*2000). The lacustrine oils can be seen to have a much greater spread of $\delta^{13}C$ values for the saturate and aromatic fractions than the marine oils a reflection of the greater complexity of lacustrine environments. The lacustrine oils Seria-1 and Maboque-1 have much lighter isotopic values than the other lacustrine oils consistent with the Brazilian oils of freshwater origin (Mello *et al.,*1988); this is in agreement with methylhopane data for Maboque-1 and Seria-1, suggesting they are derived from source rocks deposited in freshwater environments (Section 6.3.1.6).

Fig. 146 and

Fig. 147 illustrate the use of these biomarker parameters and isotopic data previously used in this study to characterize the oils as either being marine or lacustrine derived. A mixed marine/lacustrine origin has been assigned to the oils falling between the two clusters of marine and lacustrine oils. Fig. 145 has been compiled to assess the validity of this interpretation, and also to evaluate two other biomarker parameters that may be useful to distinguish the marine and lacustrine facies and hence determine if the oils in question are of mixed origin. Fig. 145 shows systematic separation of the marine and lacustrine oils and source rocks in terms of their C_{26}/C_{25} values. However there appears to be a difference in absolute values between the oils and source rocks, most likely due to maturity and generation effects. In terms of just the C_{26}/C_{25} tricyclic terpane ratio for the mixed oils, only Mulvenos

Central-1 has a truly intermediate value, the other three mixed oils, fall at the top end of the range for the marine oils. The hopane/sterane ratio also shows systematic separation of the marine and lacustrine oils and source rocks, but there is significant overlap in the source rock values. As for the C_{26}/C_{25} tricyclic terpane parameters the mixed oils plot within the top end of the range for the marine oils, with the exception of Mulvenos Central-1 which has a value approaching that of a lacustrine oil (Fig. 145). These data may suggest that the mixed oils, with the exception of Mulvenos Central-1, may in fact be marine oils with values at the extremes of the range of typical marine oils. They do in fact have isotopic values within the marine range (Fig. 147). However, it should be noted that mixing of oils would not necessarily be 50:50 marine:lacustrine. The oils may be predominantly marine but contain minimal lacustrine inputs which are pulling the values towards the top end of the marine range and hence towards lacustrine values, or indeed they may just contain higher marine quantities than the other marine oils. To be sure if mixing was occurring, a parameter would be required with a clearer separation difference between the marine and lacustrine values than is found with the C_{26}/C_{25} tricyclic terpane ratio and hopane/sterane ratio. A parameter that may prove useful for this distinction is a 4α-methylsterane/sterane ratio. Section 6.3.1.2 discusses the high abundance of 4α-methylsteranes compared to steranes in the lacustrine oils compared to the marine. However, due to the unavailability of complete data sets from Norsk Hydro this parameter has not been quantified. The parameters $\%C_{28}$ sterane and C_{27}/C_{29} sterane have also been used (Fig. 145), to attempt to differentiate between the marine and lacustrine facies and evaluate the assignment of mixed oils. The $\%C_{28}$ sterane parameter does show clear separation of the marine and lacustrine source rocks, although there is overlap between the marine and lacustrine oils. The C_{27}/C_{29} sterane ratio is less diagnostic, with some overlap between lacustrine and marine facies for both the oils and source rocks. For these two sterane parameters the mixed oils including Mulvenos Central-1 have a signal similar to the marine source rocks, or fall in the area of overlap (Fig. 145).

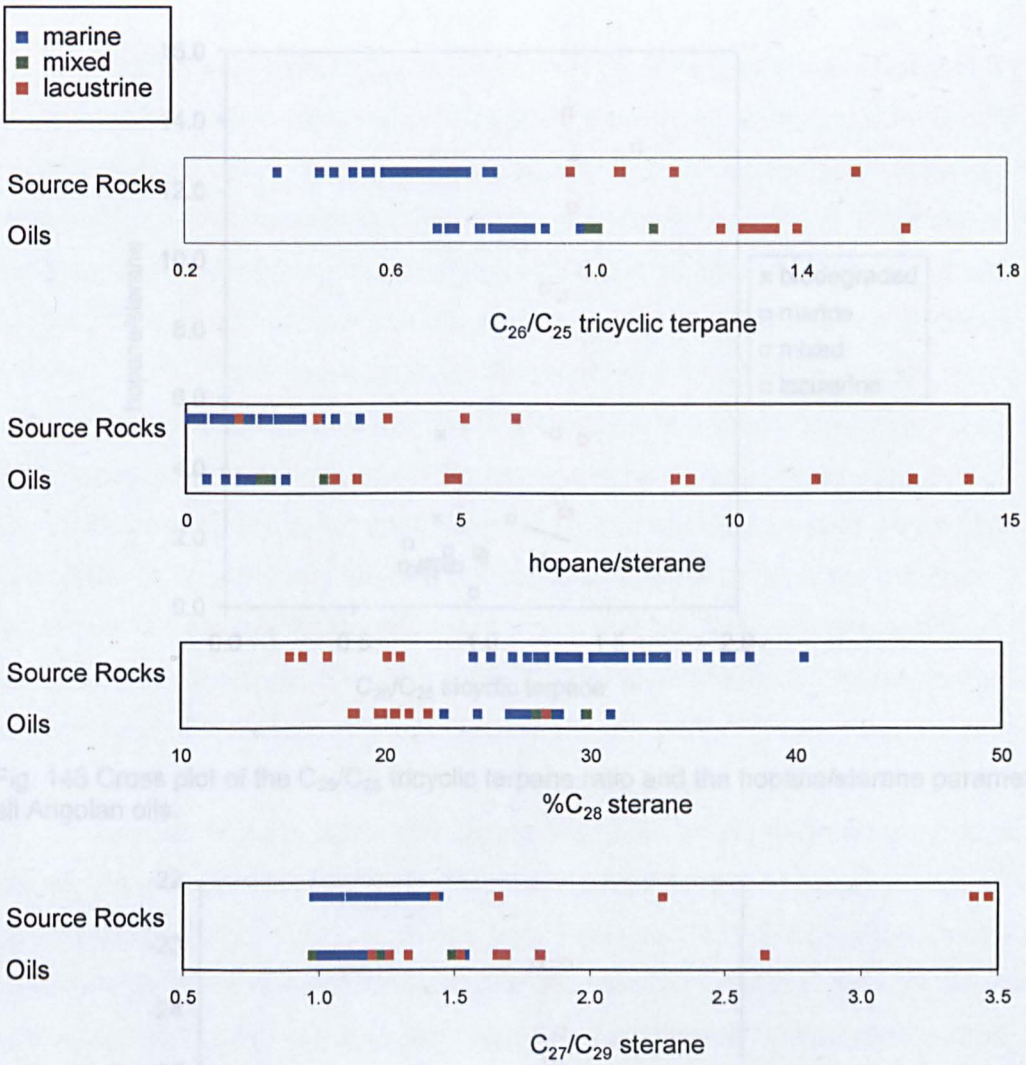

Fig. 145 Diagram to show the free hydrocarbon $\%C_{26}/C_{25}$ tricyclic terpane, hopane/sterane, $\%C_{28}$ sterane and $\%C_{27}/C_{29}$ sterane parameter range of values for the marine and lacustrine source rocks, and the oils proposed as marine, mixed or lacustrine origin.

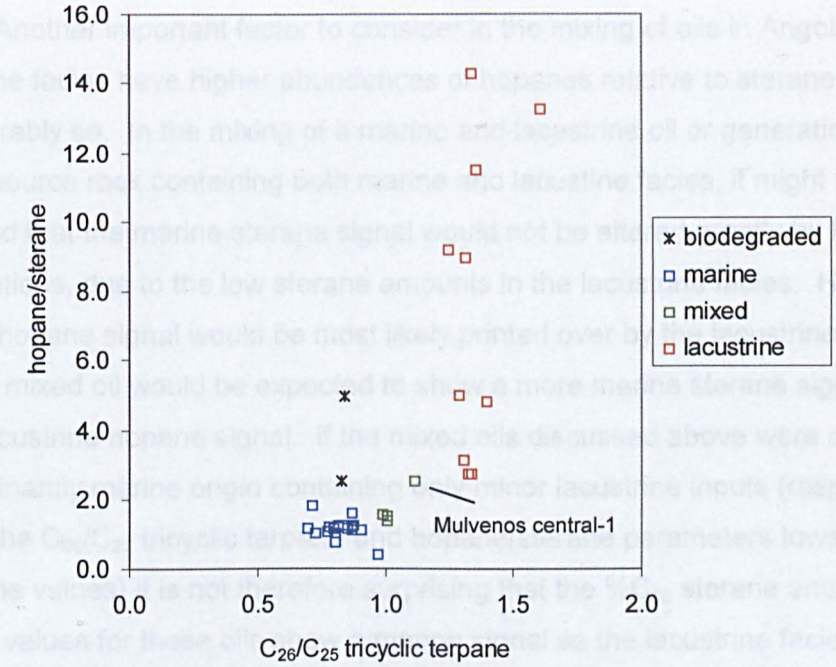

Fig. 146 Cross plot of the C_{26}/C_{25} tricyclic terpane ratio and the hopane/sterane parameter for all Angolan oils.

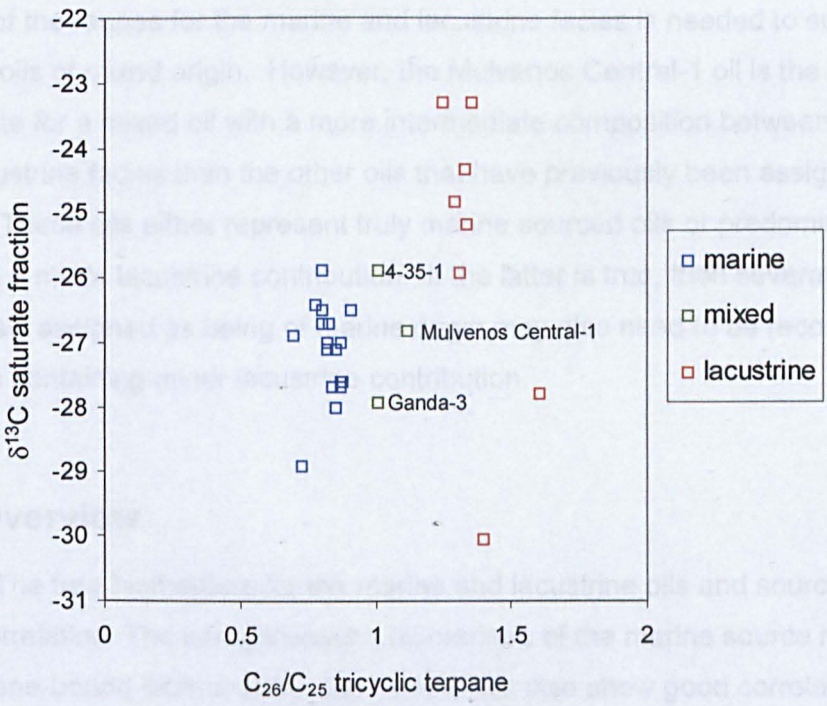

Fig. 147 Cross plot of the C_{26}/C_{25} tricyclic terpane versus the $\delta^{13}C$ of the saturate fraction (in ‰) for the Angolan oils for which isotope data are available.

Another important factor to consider in the mixing of oils in Angola is that the lacustrine facies have higher abundances of hopanes relative to steranes, often considerably so. In the mixing of a marine and lacustrine oil or generation of an oil from a source rock containing both marine and lacustine facies, it might therefore be expected that the marine sterane signal would not be altered greatly by lacustrine contributions, due to the low sterane amounts in the lacustrine facies. However, the marine hopane signal would be most likely printed over by the lacustrine signal. Thus, a mixed oil would be expected to show a more marine sterane signal and a more lacustrine hopane signal. If the mixed oils discussed above were of predominantly marine origin containing only minor lacustrine inputs (responsible for pulling the C_{26}/C_{25} tricyclic terpane and hopane/sterane parameters towards lacustrine values) it is not therefore surprising that the $\%C_{28}$ sterane and C_{27}/C_{29} sterane values for these oils show a marine signal as the lacustrine facies contains low amounts of steranes.

To summarise a parameter with greater differences between the end point values of the ranges for the marine and lacustrine facies is needed to successfully identify oils of mixed origin. However, the Mulvenos Central-1 oil is the most likely candidate for a mixed oil with a more intermediate composition between the marine and lacustrine facies than the other oils that have previously been assigned as mixed. These oils either represent truly marine sourced oils or predominantly marine oils with a minor lacustrine contribution. If the latter is true, then several other oils previously assigned as being of marine origin may also need to be reconsidered as perhaps containing minor lacustrine contribution.

8.3 Overview

The free biomarkers for the marine and lacustrine oils and source rocks show good correlation. The kerogen-bound biomarkers of the marine source rocks and asphaltene-bound biomarkers in the marine oils also show good correlation, but the lacustrine oil does not correlate well with the source rock samples studied on the basis of bound biomarkers. This may be a result of poor sample representation from the lacustrine oils and source rocks.

To determine which specific marine stratigraphic group(s) sourced the marine oils is more difficult. The Pinda and Malembo Gps have been ruled out on the basis

of their respectively higher $C_{35}\alpha\beta$ hopane and C_{29} sterane abundances, than are encountered in the marine oils. The most likely source is either a pure Iabe or pure Landana source, whereby the exact location of the source has not been sampled and therefore differs slightly in biomarker composition from the samples analysed in this study. Alternatively, the source of the marine oils may be a source rock section comprised of both Iabe and Landana source rocks.

Critical analysis of the biomarker parameters (primarily C_{26}/C_{25} tricyclic terpane and hopane/sterane ratio) used to assign the marine and lacustrine source rock and oil facies (Burwood, 1999; Schiefelbein *et al.*,1999, Cole *et al.*,2000) and to assign several oils as being of mixed origin has shown that Mulvenos Central-1 is the most likely candidate for a mixed oil. The remaining oils assigned as being of mixed origin may either represent marine oils with biomarker parameter values at the extreme end of the marine range of values, or marine oils with minor lacustrine inputs, essentially pulling the parameters to the top of the marine range, towards lacustrine oil values. To be confident of assigning oils as being of mixed origin a parameter would be required with a clearer separation difference between the marine and lacustrine values than is found with the C_{26}/C_{25} tricyclic terpane ratio and hopane/sterane ratio. Future work could consider use of a 4α-methylsterane/sterane ratio, which has been shown in this study (although not quantified) to be considerably higher in lacustrine oils than marine ones.

9 Conclusions and future work

In this section, conclusions to this research are drawn in relation to the original aims of this thesis outlined in Section 1.4.2.

Aim 1: To characterise the source rock stratigraphy in terms of hydrocarbon potential.

Analysis of the source rocks from the four wells studied in this thesis shows that almost the entire stratigraphic section (from Cretaceous to Tertiary) has oil or gas-prone hydrocarbon potential. However, both vertical variations, and lateral variations in hydrocarbon potential occur between wells. The Pre-salt and Pinda Gps. are represented in the Abacaxi-1 well only, and show fair to good oil-prone potential. The Iabe Gp. is fairly consistent between wells, comprising good to excellent oil- and also gas-prone potential source rocks. The hydrocarbon potential of the Iabe in the Lower Congo Basin wells, Girassol-1 and 4-26-1 is lower than Funda-3 and Abacaxi-1. However, literature reports suggest that richer Iabe Gp. source rock intervals exist within the Lower Congo Basin than those studied herein. The Landana Gp. varies in organic richness, source rock quality and thickness between wells; it has poor to fair gas-prone hydrocarbon potential in 4-26-1AT; however in Girassol-1 and Funda-3 it contains intervals with good and excellent oil-prone potential respectively. The Malembo Group shows lateral variation in organic richness and source rock quality between wells. In Funda-3 the Malembo Gp. has excellent oil-prone potential, whereas in the Lower Congo Basin wells Girassol-1 and 4-26-1AT it has a more gas-prone composition.

Bulk geochemical analysis has revealed that the T_{max} values for the source rocks in the Kwanza Basin well Abacaxi-1 are suppressed. This may be related to high organic sulphur in the depositional environment and hence the formation of sulphur-rich kerogens, containing abundant weak sulphur bonds. The sulphur bonds would break at lower thermal maturites, hence, generating at lower T_{max} values. The literature supports this interpretation reporting high sulphur oils to occur exclusively in the Kwanza Basin.

Aim 2: To analyse oil and source rock free and bound biomarkers to determine the quantitative importance of bound biomarkers.

The biomarkers in the macromolecular fractions of the Angolan oils (asphaltene and polar fractions) and source rocks (kerogen fractions) are consistent with previous literature reports in that they appear to undergo the same epimerisation reactions as free biomarkers but at a retarded rate, and therefore have a more immature biomarker profile. Due to this steric hindrance certain biomarker maturity parameters (%$C_{32}\alpha\beta S$ and %$C_{30}\beta\alpha$) determined from the macromolecular fractions can operate over greater depth ranges and to higher maturities.

Quantitative analysis of the biomarkers in the macromolecular fractions of the oils and source rocks compared to the free fractions, shows the bound fractions are quantitatively less important (representing 10 - 45% of the total biomarkers for kerogens and in oils the asphaltene and polar fractions are typically less than 1%). Kerogen-bound biomarker abundances are proportionately higher in the less mature wells due to their lower extents of hydrocarbon generation. Despite the low quantitative significance of the biomarkers in the oil asphaltene and polar fractions they have the advantage over their free equivalents in being protected from biodegradation. From an oil-source rock correlation perspective the asphaltene-bound fraction appears to be more comparable to the kerogen-bound biomarkers of the source rocks, at least in terms of maturity parameters, although they comprise a slightly smaller % of total biomarkers in the oil than do the bound biomarkers of the polar fraction.

The biomarkers released from the macromolecular fractions of both the oils and source rocks show evidence for compositional fractionation of biomarkers between the free and bound biomarker fractions. This is illustrated by the absence of certain compounds in the bound fractions (i.e. oleanane and BNH), which can be found in the free fractions. Also a higher percentage of the hopanes is bound into the kerogen-bound fraction compared to the steranes. This may be a result of the higher number of potential attachment sites to kerogen for hopanes when compared to steranes. Hopanes would therefore be more easily incorporated and less easily released from the kerogen fraction. However, in general similar biomarker compositions are found in the free and bound fractions. The biomarkers released from the macromolecular fractions (particularly the kerogen-bound ones) provide a

good replacement for the free biomarkers, and from an exploration perspective prove useful where contamination by drilling mud has occurred. Although absolute values of individual ratios are not directly comparable, the values do not differ greatly in most cases. The only biomarker parameter to differ significantly in terms of absolute ratio values between the free and bound fractions when samples of similar maturity are compared is the hopane/sterane ratio for the kerogen-bound lacustrine facies. This suggests most likely that depositional environment and/or source organic matter may also play a role as well as thermal maturation in controlling biomarker fractionation between the free and bound biomarker fractions.

The kerogen-bound biomarkers also provide additional source information to supplement free biomarker interpretations. They show more distinctive variations in the abundance of long-chain *n*-alkanes related to terrigenous inputs than is observed in the bitumen fraction.

Aim 3: To characterise the molecular characteristics (both free and bound) of the source rocks in terms of maturity and facies, and identify biomarker characteristics that can be used to distinguish individual sections, and thus be applied as age-specific biomarkers of individual units in this region.

Well 4-26-1AT is the least mature well containing thermally unstable hopenes in the m/z 191 mass chromatogram. Bulk geochemical maturity parameters for 4-26-1 (i.e. T_{max} and production index values) also suggest that this well too is immature with respect to oil generation. Biomarker data for Girassol-1 suggest the well is immature with respect to oil generation but is approaching early oil generation values in the lower part of the well. T_{max} values for Girassol-1 support this suggesting the lower part of the section has just reached the very beginning of the oil window. Note that estimates of maturity using Production Index values could not be made for Girassol-1 due to the presence of an oil-based drilling mud. Funda-3 is the most mature well studied; bulk geochemical and sterane biomarker parameters indicate the section has reached the earliest oil generation window in the Landana Gp., although hopane maturity parameters suggest the entire section has reached the main phase of oil generation. Abacaxi-1 Post-salt samples, like the 4-26-1 samples, have considerably less mature biomarker profiles than the remaining source rocks, and are also immature with respect to oil generation. Biomarker parameters for the Abacaxi-1 Pre-salt samples are mature, having reached (or nearly reached) the main phase of

oil generation. T_{max} values for the Abacaxi-1 source rocks are low considering the maturity of the samples indicated by biomarker maturity parameters. As explained above this may be a consequence of increased availability of reduced sulphur in the depositional environment, and formation of sulphur-rich kerogens.

In general the biomarkers in the bitumen fraction of the lacustrine source rocks in this thesis have high hopane/sterane ratios (>2) and C_{26}/C_{25} tricyclic terpane ratios > 1, and the marine source rocks have low hopane/sterane ratios (<2) and C_{26}/C_{25} tricyclic terpane ratios < 1. The use of the C_{26}/C_{25} ratio does not follow directly for the biomarkers in the kerogen-bound fractions, although the hopane/sterane ratio can be used in the same way although the lacustrine samples show values much greater than 2. These ratios have been previously applied in the literature to differentiate oils and source rocks of lacustrine and marine origin in this region.

Literature reports regarding the depositional environment of lacustrine Pre-salt sections in Angola suggest fresh, brackish, hypersaline and alkaline conditions may occur. The lacustrine samples in this thesis are from the Cuvo Fm. of the Kwanza Basin. The limited literature on this formation describes fluvial/ transitional and shallow ephemeral brackish/saline depositional environments. The particular samples in this thesis have a biomarker signature that reflects low terrestrial inputs. They also have high abundances of low molecular weight (C_{20}-C_{26}) tricyclic terpanes relative to hopanes interpreted to represent deposition in a moderate salinity environment. However, in contrast, methylhopane data for the Pre-salt sections show an enrichment of 3β-methylhopanes, suggesting the Cuvo Fm. section studied may have been deposited in a freshwater environment. An interpretation of the Cuvo Fm. as a freshwater deposit is further supported by isotopic evidence whereby two oils, interpreted as being freshwater-derived on the basis of their isotopic data have a methylhopane composition similar to the Cuvo Fm. source rocks.

The Pinda Gp. samples are reported in the literature to be deposited during a period of carbonate deposition (Cole *et al.,* 2000). In support of this, the Pinda Gp. has elevated %$C_{35}\alpha\beta$ hopane abundances in both the free bitumen and kerogen-bound fractions; high values are typical of anoxic marine conditions, specifically sulphur-rich environments. Preferential preservation of hopanoids with a C_{35} side-chain most likely occurs in anoxic environments low in iron; i.e. non-clastic carbonate or evaporitic environments. The Pinda and Iabe Gps. are described in the literature as being marine transgressive units. Biomarker and bulk geochemical

interpretations support high marine algal contributions, a reflection of the more open marine nature of the groups and also of low terrigenous contributions. The low terrestrial contributions may relate to the increased distance of the depositional environment from the coastline, during this marine transgressive phase.

Literature reports for the Landana Gp. suggest a regressive interval during the transition from the marine-dominated Iabe to the more terrestrially-influenced Malembo Gp. The transitional nature of this unit is reflected in the biomarkers in both the free and bound fractions, essentially comprising an intermediate biomarker composition between the Malembo and Iabe Gps.

The biomarker composition of the Malembo Gp. reflects higher terrigenous contributions compared to the remaining Post-salt units. The biomarkers released from the kerogen bound fraction also show a higher abundance of high molecular weight *n*-alkanes not seen in the biomarkers from the bitumen fraction, interpreted to represent higher contributions from terrigenous material. Bulk geochemical interpretation for the Malembo Gp. show that the sections (excluding Funda-3, see below) contain higher contributions of Type III organic matter which represent higher contributions from continental land plants, consistent with the biomarker interpretation above. It should be noted however that higher amounts of (Type III) terrigenous material may not solely be related to organic inputs, but can result from varying preservation of marine amorphous (Type II) organic matter. Literature interpretations of the Malembo Gp. suggest that it represents a regressive sequence. The shallower water depths, a result of the regressive nature of the unit, may lead to less stratified conditions, making it less likely for anoxic conditions to develop. Indeed pristane/phytane parameter values for the Malembo Gp. suggest a more oxic depositional environment. However, wells 4-26-1AT and Girassol-1 are in close proximity to the lower Congo Fan, therefore in this instance the higher proportions of Type III kerogen may be a result of both organic inputs and preservation potential.

From an exploration perspective an important point to note is that the Malembo Gp. samples in Funda-3 differ from their lateral equivalents in other wells in terms of their hydrocarbon potential, comprising excellent Type II oil-prone organic matter. With the exception of the sterane composition, the Malembo Gp. samples from Funda-3 have free and bound biomarker compositions most similar to the Iabe Gp. (and sometimes the Landana Gp.) as opposed to the remaining Malembo Gp. samples.

Aim 4: To conduct (free and bound) biomarker analysis and isotopic studies of the oils in the region and identify source rock contributions to the oils.

As with the source rocks the biomarkers in the free hydrocarbon fractions can classify the oils as being either lacustrine- or marine-derived according to their hopane/sterane and C_{26}/C_{25} tricyclic terpane ratios. As found with the biomarkers in the kerogen-bound fraction of the source rocks, use of these ratios does not always follow for the asphaltene and polar-bound fractions of the oils. In terms of the organic inputs to the source rocks from which the oils derive, the lacustrine oils have a biomarker signature typical of source rocks deposited in a terrestrially-influenced lacustrine environment with possibly a high degree of bacterial reworking, whereas the marine oils have a biomarker signature consistent with marine algal inputs. Isotopic values for the lacustrine and marine oils in this study are consistent with values in the literature for Angolan oils. The lacustrine oils have a much greater spread of $\delta^{13}C$ values for the saturate and aromatic fractions ($\delta^{13}C$ saturate fraction -23.3 to –25.9‰, $\delta^{13}C$ aromatic fraction –21.8 to –23.7‰) than the marine oils ($\delta^{13}C$ saturate fraction –25.8 to –28.91‰, $\delta^{13}C$ aromatic fraction –25.2 to –27.62‰), probably a reflection of the greater complexity of lacustrine environments.

Certain lacustrine oils contain very high abundance of extended tricyclic terpanes, which can dominate the triterpane distribution;this is interpreted to represent a source depositional environment of moderate salinity (i.e. saline lacustrine settings). A high abundance of extended tricyclic terpanes is not exclusive to the lacustrine oils, also occurring in the marine oil Bufalo-106a; however, there appears to be a geographical cluster of the lacustrine, marine and mixed oils containing high extended tricyclic terpanes within blocks 2, 3 and 4, in the Lower Congo Basin. Two of the lacustrine oils, Maboque-1 and Seria-1, show an enrichment of 3β-methyl hopanes, suggesting they may be derived from freshwater source rocks. These oils 1 have much lighter isotopic values than the other lacustrine oils, and are consistent with literature data for Brazilian oils of freshwater origin.

The biomarkers in the free hydrocarbon fractions correlate well between oils and source rocks for both the marine and lacustrine groups. The kerogen-bound biomarkers in the source rocks show good correlation with the asphaltene-bound

biomarkers in the oils for the marine facies, however the lacustrine oil does not correlate with the lacustrine source rocks possibly as a result of poor sample representation. To determine the specific marine stratigraphic group(s) from which the marine oils are sourced is more difficult. On the basis of their higher $C_{35}\alpha\beta$ hopane and C_{29} sterane abundances the Pinda and Malembo Gps. have been ruled out as contributing to the marine oils. Oil-source rock correlation using biomarkers in both the free and bound fractions of the oils and source rocks shows that the most likely source is either a pure Iabe or pure Landana source, whereby the exact location of the source has not been sampled and therefore differs slightly in biomarker composition to the samples analysed in this study, or a source rock section comprised of both Iabe and Landana source rocks.

The block 17 oils are relatively similar in terms of their molecular composition. Camelia-1 and Perpetua-1 have slightly different biomarker properties, suggesting that they are derived from a different source rock organofacies or that they contain contributions from other oils. However, they do not differ in the same way, suggesting they also differ from each other with respect to their source. The elevated abundance of oleanane in Perpetua-1 oil may suggest that the oil contains contributions form a Tertiary source rock. Perpetua-1 and Camelia-1 also have different isotopic signatures to the other Block 17 oils (lower δ^2H values). The literature suggests that lacustrine contributions to these oils would be expected to give heavier δ^2H isotopic values; therefore it can be concluded they do not differ from the other block 17 oils due to higher, if any contributions from a lacustrine oil or source rock.

Critical analysis of the biomarker parameters (primarily C_{26}/C_{25} tricyclic terpane and hopane/sterane ratio) used to assign oils and source rocks as being of either marine or lacustrine origin and to assign oils as being of mixed origin has shown that Mulvenos Central-1 is the most likely candidate for a mixed oil. A parameter with a clearer separation difference between the marine and lacustrine values (than is found with the C_{26}/C_{25} tricyclic terpane ratio and hopane/sterane ratio) would be required to confidently assigning oils as being of mixed origin.

9.1 Future Work

Mixed oils have important implication for exploration models, particularly the assessment of the % mixing of different oils would be useful. Quantification of the methylsteranes is recommended, as preliminary analysis has shown that this parameter may prove useful for differentiating the marine and lacustrine oils and source rocks and determining oils of mixed origin.

Future hydropyrolysis work should use greater weights of oil asphaltene and polar fractions, with an aim of higher yield of tars for subsequent fractionation and GC-MS analyses. Also obtaining analysis of the asphaltene and polar-bound fraction of the source rocks would provide a more complete view of the total biomarker population for use during oil-source rocks correlation.

To improve the study further increased sample representation from the Pre-salt and Pinda Gps. would be advantageous. These sections are represented only in Abacaxi-1 located in the Kwanza Basin. From the exploration perspective of determining source rock contributions to the Block 17 oils, it would be useful to have Pre-salt and Pinda Gp. samples from the Lower Congo Basin.

ADAM, P., SCHMID, J.C., MYCKE, B., STRAZIELLE, C., CONNAN, J., HUC, A., RIVA, A. & ALBRECHT, P. 1993. Structural investigation of nonpolar sulphur cross-linked macromolecules in petroleum. *Geochimica et Cosmochimica Acta,* **57**, 3395-3419.

ALBERDI, M., MOLDOWAN, J.M., PETERS, K.E. & DAHL, J.E. 2001. Stereoselective biodegradation of tricyclic terpanes in heavy oils from the Boliviar Coastal Fields, Venezuela. *Organic Geochemistry*, **32,** 181-191.

AQUINO NETO F.R., TRENDEL J.M., RESTLE A., CONNAN J. AND ALBRECHT P.A. 1983. Occurrence and formation of tricyclic and tetracyclic terpanes in sediments and petroleums. *In:* M. BJØROY *et al.* (eds), A*dvances in Organic Geochemistry 1981*, John Wiley & Sons, Ltd. 659-667.

BEHER, F., PELET, R. & ROUCACHE, J. 1984. Geochemistry of asphaltenes. *Organic Geochemistry*, **6**, 587-595.

BENNET, B. & ABBOTT, G.D. 1999. A natural pyrolysis experiment - hopanes from hopanoic acids? *Organic Geochemistry*, **30**, 1509-1519.

BISHOP A.N. & ABBOTT G.D. 1993. The interrelationship of biological marker maturity parameters and molecular yields during contact metamorphism. *Geochimica et Cosmochimica Acta,* 57, 3661-3668.

BISHOP A.N. & FARRIMOND P. 1995. A new method of comparing extended hopane distributions. *Organic Geochemistry.* **23**, 987-990.

BISHOP, A.N., LOVE, G.D., MCAULAY, C.E., SNAPE, C.E. & FARRIMOND, P. 1998. Release of kerogen-bound hopanoids by hydropyrolysis. *Organic Geochemistry*, **29**, 989-1001.

BORDENAVE, M.L., ESPITALIÉ, J., LEPLAT, P., OURDIN, J.L. & VANDENBROUCKE, M. 1993. Rock Eval Pyrolysis. Sreeening techniques for source rock evaluation. *In: Applied Petroleum Geochemistry.* (M.L. BOURDENAVE, ed.), Éditions Technip, Paris. 237-261.

BRASSELL, S.C., LEWIS, C.A., DE LEEUW, J.W., DE LANGE, F. & SINNINGHE DAMSTÉ. 1986. Isoprenoid thiophenes: novel products of sediment diagenesis? *Nature,* **320**, 160-162.

BRAY E.E. & EVANS E.D. 1961. Distribution of *n*-paraffins as a clue to recognition of source beds. *Geochimica et Cosmochimica Acta,* **22**, 2-15.

BRICE, S.E., COCHRAN, M.D., PARDO, G. & EDWARDS, A.D. 1982. Tectonics and sedimentation of the South Atlantic rift sequences: Cabinda, Angola. *In:* WATKINS, J.S. & DRAKE, C.L. (eds) *Studies in continental margin geology. American Association of Petroleum Geologists Memoirs,* **34**, 5-18.

BURWOOD, R. 1999. Angola: source rock control for Lower Congo Coastal and Kwanza Basin petroleum systems. *In:* CAMERON, N.R., BATE, R.H. and CLURE,

V.S. (eds) The Oil and Gas Habitats of the South Atlantic. Geological Society, London, Special Publications, 153, 181-194.

BURWOOD, R., CORNET, P.J., JACOBS, L. & PAULET, J. 1990. Organofacies variation control on hydrocarbon generation: A Lower Congo Basin (Angola) case history. *Organic Geochemistry*, **16**, 325-338.

BURWOOD, R., LEPLAT, P., MYCKE, B. and PAULET, J. 1992. Rifted margin source rock deposition: a carbon isotope and biomarker study of a West African Lower Cretaceous "Lacustrine" Section. *Organic Geochemistry*, **19**, 41-52.

BURWOOD, R., DE WITTE, S.M., MYCKE, B. & PAULET, J. 1995. Petroleum geochemical characterization of the Lower Congo Basin Bucomazi Formation. *In:* KATZ, B.J. (ed) *Petroleum source rocks.* Springer, 235-263.

CASSANI, F. & EGLINTON, G. 1986. Organic geochemistry of Venezuelan extra-heavy oils. 1. Pyrolysis of asphaltenes; A technique for the correlation and maturity evaluation of crude oils. *Chemical Geology*, **56**, 167-183.

CHAPPE, B., MICHAELIS, W. & ALBRECHT, P. 1979. Molecular fossils of Archaebacteria as selective degradation products of kerogen. In: DOUGLAS, A.G. & MAXWELL, J.R. (eds) *Advances in Organic geochemistry*, 265-274.

CHEN, J. & SUMMONS, R.E. 2001.Complex patterns of steroidal biomarkers in Tertiary lacustrine sediments of the Biyang Basin, China. *Organic Geochemistry*, **32**, 155-126.

COLE, G.A., REQUEJO, A.G., ORMEROD, D., YU, Z. & CLIFFORD, A. 2000. Petroleum geochemical assessment of the Lower Congo Basin. *In:* MELLO, M.R. & KATZ, B.J. (eds) *Petroleum systems of the South Atlantic. American Association of Petroleum Geologists Memoir*, **73**, 325-339.

COLLINS, M.J., BISHOP, A.N. & FARRIMOND, P. 1995. Sorption by mineral surfaces: Rebirth of the classical condensation pathway for kerogen formation? *Geochimica et Cosmochimica Acta*, **59**, 2387-2391.

CONNAN, J. 1984. Biodegradation of crude oils in reservoirs. *Advances in Organic Geochemistry,* **1**, 299-335.

COWARD, M.P., PURDY, E.G., REIS, A.C. & SMITH, D.G. 1999. The distribution of petroleum reserves in basins of the South Atlantic margin. *In:* CAMERON, N.R., BATE, R.H. & CLURE, V.S. (eds) *The oil and gas habitats of the South Atlantic. Geological society, London Special Publications,* **153**, 101-131.

CZOCHANSKA, Z., GILBERT, T.D., PHILP, R.P., SHEPPARD, C.M., WESTON, R.J., WOOD, T.A. & WOOLHOUSE, A.D. 1988. geochemical application of sterane and triterpane biomarkers to a description of oils from the Taranaki Basin in New Zealand. *Organic Geochemistry*, **12**, 123-135.

DE GRANDE, S.N.B., AQUINO NETO, F.R. & MELLO, M.R. 1993. Extended tricyclic terpanes in sediments. *Organic Geochemistry*, **20**, 1039-1047.

DE LEEUW, J.W. & LARGEAU, C. 1993. A review of macromolecular organic compounds that comprise living organisms and their role in kerogen, coal, and petroleum. *In:*

ENGEL, M.H. & MACKO, S.A. (eds) *Organic Geochemistry: principles and applications,* 23-72.

DE LEEUW, J.W. VAN BERGEN, P.F., VAN AARSSEN, G.K., GATELLIER, J.L.A., SINNINGHE DAMSTÉ, J.S. & COLLINSON, M.E. 1991. Resistant biomacromolecules as major contributors to kerogen. *Philosophical Transactions of the Royal Society of London,* **333**, 329-337.arious source rocks and oil shales. *Organic Geochemistry*, **16**, 889-895.

DELVAUX, D., MARTIN, H.., LEPLAT, P., & PAULET, J.1989. Geochemical characterisation of sedimentary organic matter by means of pyrolysis kinetic parameters. *Organic Geochemistry*, **16**, 175-187.

DIDYK, B.M., SIMONEIT, B.R.T., BRASSELL, S.C. & EGLINTON, G. 1978. Organic Geochemical indicators of palaeoenvironmental conditions of sedimentation. *Nature*, **272**, 216-222.

DURRAND, B. 1980. *Kerogen: Insoluble organic matter from sedimentary rocks.* Editions Technip, Paris, 519pp.

EGLINTON, T, I. & DOUGLAS, A.G. 1988. Quantitative study of biomarker hydrocarbons released from kerogens during hydrous pyrolysis. *Energy and Fuels*, **2**, 81-88.

EGLINTON G., BRASSELL S.C. & JENKYNS H.C. 1990 The Cenomanian/ Turonian anoxic event in Europe: an organic geochemical study. *Marine Petroleum Geology,* **7**, 75-89.

FARRIMOND P., EGLINTON, G. & BRASSELL, S.C. 1986. Geolipids of black shales and claystones in Cretaceous and Jurassic sediment sequences from the North American Basin. North Atlantic Palaeooceanography,In: SUMMERHAYES, C.P. & SHACKELTON, N.J. (eds) *Geological society, London Special Publications,* **21**, 347-360.

FARRIMOND, P., BEVAN, J.C. & BISHOP, A.N. 1996. Hopanoid hydrocarbon maturation by an igneous intrusion. *Organic Geochemistry*, **25**, 149-164.

FARRIMOND, P., TAYLOR, A. & TELNÆS,N. 1998. Biomarker maturity parameters: the role of generation and thermal degradation. *Organic Geochemistry*, **29**, 5-7.

FARRIMOND, P., BEVAN, J.C. & BISHOP, A.N. 1999.Tricyclic terpanematurity parameters; response to heating by an igneous intrusion. *Organic Geochemistry*, **30**, 1011-1019.

FARRIMOND, P., HEAD, I.M. & INNES, H.E. 2000. Environmental influence on the biohopanoid composition of recent sediments. *Geochimica et Cosmochimica Acta*, **64**, 2985-2992.

FARRIMOND P., EGLINTON G., BRASSELL S.C. & JENKYNS H.C. 1990. The Cenomanian/Turonian anoxic event in Europe: an organic geochemical study. *Marine Petroleum Geology,* **7**, 75-89.

FOWLER, M.G. & BROOKS, P.W. 1987. Organic geochemistry of Western Canada Basin tar sands and heavy oils. 2. Correlation of tar sands using hydrous pyrolysis of asphaltenes. *Energy & Fuels*, **1**, 459-467.

GOODWIN, N.S., PARK, P.J.D. & RAWLINSON, A.P. 1982. Crude oil biodegradation under simulated and natural conditions. In: BJORØY, M. (ed) *Advances in Organic Geochemistry 1981,* 650-658, John Wiley & Sons, Ltd, Chichester.

GOODWIN, N.S., MANN, A.L. & PATIENCE, R.L. 1988. Structure and significance of C_{30} 4-methylsteranes in lacustrine shales and oils. *Organic Geochemistry*, **12**, 495-506.

GOTH, K., DE LEEUW, J.W., PÜTTMANN, W. & TEGELAAR, E.W. 1988. Origin of the Messel Oil Shale kerogen. *Nature*, **336**, 759-761.

GREENWOOD P.F., AROURI K.R. AND GEORGE S.C. 2000. Tricyclic terpenoid composition of *Tasmanites* kerogen as determined by pyrolysis GC-MS. *Geochimica et Cosmochimica Acta,* **64**, 1249-1263.

HOERING, T.C. 1984. Thermal reactions of kerogen with added water, heavy water and pure organic substances. *Organic Geochemistry,* **5**, 267-278.

HOFFMAN, I.C., HUTCHISON, J., ROBSON, J.N., CHICARELLI, M.I. & MAXWELL, J.R. 1992. Evidence for sulphide links in a crude oil asphaltene and kerogens from reductive cleavage by lithium in ethylamine. *Organic Geochemistry,* **19**, 371-387.

HOLBA, A.G., DZOU, L.I.P., MASTERSON, W.D., HUGHES, W.B., HUIZINGA, B.J., SINGLETARY, M.S., MOLDOWAN, J.M., MELLO, M.R. & TEGELAAR, E.W. 1998a. Application of 24-norcholestanes for constraining source age of petroleum. *Organic Geochemistry,* **29**, 1269-1283.

HOLBA, A.G., TELGELAAR, E., ELLIS, L., SINGLETARY, M.S. & ALBRECHT, P. 2000. Tetracyclic polyprenoids: Indicators of freshwater (lacustrine) algae input. *Geology*, **28**, 251-254.

HOLBA, A.G., TEGELAAR, E.W., HUIZINGA, B.J., MOLDOWAN, J.M., SINGLETARY, M.S., MCCAFFREY, M.A. & DZOU, L.I.P. 1998b. 24-norcholestanes as age-sensitive molecular fossils. *Geology,* **26,** 783-786.

HOU, D., Li, M., & Huang, Q. 2000. Marine transgressional events in the gigantic freshwater lake Songliao: paleontological and geochemical evidence. *Organic Geochemistry*, **31**, 605-776.

HUANG, W.Y. & MEINSCHEIN, W.G. 1979. Sterols as ecological indicators. *Geochimica at Cosmochimica Acta*, **43**, 739-745.

INNES, H. E. 1998. Hopanoid distributions and diagenesis in recent sediments. PhD Thesis.

JONES, D.M. & DOUGLAS, A.G. & CONNAN, J. 1987. Hydrocarbon distributions in crude oil asphaltenes pyrolyzates. 1. Aliphatic compounds. *Journal of Energy and Fuels*, **1**, 468-476.

JONES, D.M. & DOUGLAS, A.G. & CONNAN, J. 1988. Hydrous pyrolysis of asphaltenes and polar fractions of biodegraded oils. *Organic Geochemistry*, **13**, 981-993.

KATZ, B.J. & MELLO, M.R. 2000. Petroleum systems of South Atlantic marginal basins – an overview. *In:* MELLO, M.R. & KATZ, B.J. (eds) *Petroleum systems of the South Atlantic. American Association of Petroleum Geologists Memoir*, **73**, 1-13.

KEIL, R.G., MOUTLUÇON, D.B., PRAHL, F.G. & HEDGES, J.I. 1994. Sorptive preservation of labile organic matter in marine sediments. *Nature*, **370**, 549-552.

KOHNEN, M.E.L., SINNINGHE DAMSTÉ, J.S., KOCK-VAN DALEN, A.C. & DE LEEUW, J.W. 1991a. Di- or polysulphide-bound biomarkers in sulphur-rich geomacromolecules as revealed by selective chemolysis. *Geochimica et Cosmochimica Acta*, **55**, 1375-1394.

KOHNEN, M.E.L., SINNINGHE DAMSTÉ, J.S. & DE LEEUW, J.W. 1991b. Biases from natural sulphurization in palaeoenvironmental reconstruction based on hydrocarbon biomarker distributions. *Nature,* **349**, 775-778.

KOK, M.D., RIJPSTRA, W.I.C., ROBERTSON, L., VOLKMAN, J.K. & SINNINGHE DAMSTÉ. J.S. 2000. Early steroid sulfurisation in surface sediments of a permanently stratified lake (Ace Lake, Antarctica). *Geochimica et Cosmochimica Acta*, **64**, 1425-1436

KOLLA, V., BOURGES, P., URRUTY, J.M. & SAFA, P. 2001. Evolution of deep-water Tertiary sinuous channels offshore Angola (West Africa) and implications for reservoir architecture. *American Association of Petroleum Geologists Bulletin,* **85**, 1373-1405.

KOOPMANS, M.P. 1997. Diagenetic and catagenetic transformations of sequested biomarkers. *PhD Thesis*. pp.304.

KÖSTER, J., VAN KAAM-PETERS,M.E., KOOPMANSS, M.P., DE LEEUW, J.W. & SINNINGHE DAMSTÉ, J.S. 1997. Sulphurisation of homohopanoids; Effects on carbon number distribution, speciation, and 22S/22R epimers ratios. *Geochimica et Cosomochimica Acta*, **61**, 2431-2452.

KRUGE, M.A., HUBERT, J.F., AKES, R.J. & MERINEY, P.E. 1990. Biological markers in Lower Jurassic synrift lacustrine black shales, Hartford basin, Connecticut, U.S.A. *Organic Geochemistry*, **15**, 281-289.

LANGFORD, F.F. & BLANC-VALLERON, M.M. 1980. Interpreting Rock Eval pyrolysis data using graphs of pyrolizable hydrocarbons vs. Total organic carbon. *American Association of Petroleum Geologists Bulletin*, **74**, 799-804.

LARGEAU, C., DERENNE, S., CASADEVALL, E., BERKALOFF, C., COROLLEUR, M., LUGARDON, B., RAYNAUD, J,F. & CONNAN, J. 1990. Occurrence and origin of "ultralaminar" structures in "amorphous" kerogens of various source rocks and oil shales. *Organic Geochemistry*, **16**, 889-895.

LAVIER, L.L., STECKLER, M.S. & BRIGAUD, F. 2000. An improved method for reconstructing the stratigraphy and bathymetry of continental margins: application to the Cenozoic tectonic and sedimentary history of the Congo margin. *American Association of Petroleum Geologists Bulletin,* **84**, 923-939.

LAVIER, L.L., STECKLER, M.S. & BRIGAUD, F. 2001. Climatic and tectonic control on the Cenozoic evolution of the West African Margin. *Marine Geology*, **178**, 63-80.

LEWAN, M.D. 1993. Laboratory simulation of petroleum formation: Hydrous pyrolysis. *In:* ENGEL, M.H. & MACKO, S.A. (eds) *Organic Geochemistry: Principles and applications,* 419-442.

LOVE, G.D., SNAPE, C.E., CARR, A.D. & HOUGHTON, C.H. 1995. Release of covalently-bound alkane biomarkers in high yields from kerogen via catalytic hydropyrolysis. *Organic Geochemistry*, **23**, 981-986.

LOVE, G.D., MCAULAY, A., SNAPE, C.E. & BISHOP, A.N. 1997. Effect of process variables in catalytic hydropyrolysis on the release of covalently bound aliphatic hydrocarbons from sedimentary organic matter. *Energy and Fuels,* **11**, 522-531.

MACKENZIE, A.S., PATIENCE, R.L. & MAXWELL,J.R. 1980. The molecular parameters of maturation in the Toarcian shales, Paris Basin, France –I. Changes in the configurations of acyclic isoprenoid alkanes, steranes and triterpanes. *Geochimica et Cosmochimica Acta,* **44**, 1709-1721.

MARTO-VALER, M.M., LOVE, G.D. & SNAPE, C.E. 1997. Close correspondence between carbon skeletal parameters of kerogen and their hydropyrolysis oils. *Energy and Fuels*, **11**, 539-545.

MAYER, L.M. 1994b. Relationships between mineral surfaces and organic carbon concentrations in soils and sediments. *Chemical Geology*, **114**, 347-363.

McHARGUE, T.M. 1990. Stratigraphic development of Proto-South Atlantic rifting in Cabinda, Angola – a petroliferous lake basin. *In:* KATZ, J.B. (ed) *Lacustrine Basin Exploration, American Association of Petroleum Geologists Memoir,* **50**, 307- 340.

MELLO, M.R., GAGLIANONE, P.C., BRASSELL, S.C & MAXWELL, J.R. 1988a. Geochemical and biological marker assessment of depositional environments using Brazilian offshore oils. *Marine and Petroleum Geology*, **5**, 205-223.

MELLO, M.R., TELNÆS, N., GAGLIANONE, P.C., CHICARELLI, M.I., BRASSELL, S.C & MAXWELL, J.R. 1988b. Organic geochemical characterisation of depositional palaeoenvironmnets of source rocks and oils in Brazilian marginal basins. *Organic Geochemistry,* **13**, 31-45.

MELLO, M.R., KOUTSOUKOS, E.A.M., HART, M.B., BRASSELL, S.C. & MAXWELL, J.R. 1989. late Cretaceous anoxic events in the Brazilian continental margin. *Organic Geochemistry,* **14**, 529-542.

MILES, J.A. 1994. *Illustrated glossary of petroleum geochemistry.* Clarendon Press, Oxford. 137pp.

MOLDOWAN, M. J. 1984. C_{30}-steranes, novel markers for marine petroleums and sedimentary rocks. *Geochimica et Cosmochimica Acta*, **48**, 2767-2768.

MOLDOWAN, M.J. & MCCAFFREY, M.A. 1995. A novel microbial hydrocarbon degradation pathway revealed by hopane demethylation in a petroleum reservoir. *Geochimica et Cosmochimica Acta,* **59**, 1891-1894.

MOLDOWAN, M.J., SEIFERT, W.K. & GALLEGOS, E.J. 1985. Relationship between composition and depositional environment of petroleum source rocks. *American Association of Petroleum Geologists Bulletin.* **69**, 1255-1268.

MOLDOWAN, J.M., SUNDARARAMAN, P. & SCHOELL. 1986. Sensitivity of biomarker properties to depositional environment and/or source input in the Lower Toarcian of SW-Germany. *Organic Geochemistry*, **10**, 915-926.

MOLDOWAN, M.J., DAHL, J., HUIZINGA, B.J., FAGO, F.J., HICKEY, L.J., PEAKMAN, T.M. & TAYLOR, D.W. 1994. The molecular fossil record of oleanane and its relationship to Angiosperms. *Science,* **265**, 768-771.

MOLDOWAN J.M., FAGO F.J., CARLSON R.M.K., YOUNG D.C., VANDUYNE G., CLARDY J., SCHOELL M., PILLINGER C.T. & WATT D.S. 1991. Rearranged hopane in sediments and petroleum. *Geochimica et Cosmochimica Acta*, **55,** 3333-3353.

MUNDY, B.P., ARMOLD, M.T. & AMEND, J.R. 1993. *Organic and biological chemistry.* Saunders College Publishing, 500pp.

MURRAY, I.P., LOVE, G.D., SNAPE, C.E. & BAILEY, N.J.L. 1998. Comparison of covalently-bound aliphatic biomarkers released via hydropyrolysis with their solvent-extractable counterparts for a suite of Kimmeridge clays. *Organic Geochemistry*, **29**, 1487-1505.

MYCKE, B. & MICHAELIS, W. 1986. Molecular fossils from chemical degradation of macromolecular organic matter. *Organic Geochemistry,* **10,** 847-858.

MYCKE, B., NARJES, F. & MICHAELIS, W. 1987. Bacteriohopanetetrol from chemical degradation of an oil shale kerogen. *Nature*, **326**, 179-181.

PELET, R., BEHAR, F. & MONIN, J.C. 1986. Resins and asphaltenes in the generation and migration of petroleum. *Organic Geochemistry.* **10**, 481-498.

PEREZ-INFANTE, J., FARRIMOND, P. & FURRER, M. 1996. Global and local controls influencing the deposition of the La Luna Formation (Cenomanian-Campanian), western Venezuela. *Chemical Geology*, **130**, 271-288.

PETERS, K.E. 2000. Petroleum tricyclic terpanes: predicted physiochemical behaviour from molecular mechanics calculation. *Organic Geochemistry,* **31**, 497-507.

PETERS, K.E. & MOLDOWAN, J.M. 1991. Effects of source, thermal maturity, and biodegradation on the distribution and isomerisation of homohopanes in petroleum. *Organic Geochemistry*, **17**, 47-61.

PETERS, K.E. & MOLDOWAN, J.M. 1993. *The Biomarker Guide: Interpreting molecular fossils in petroleum and ancient sediments.* Prentice Hall, Englewoods Cliffs, New Jersey. pp.363.

PETERS K, E., MOLDOWAN J.M. & SUNDARARAMAN P. 1990. Effects of hydrous pyrolysis on biomarker thermal maturity parameters – Montery Phosphatic and Siliceous Members. *Organic Geochemistry*, **15**, 249-265.

PETERS, K.E., MOLDOWAN, J.M., SCHOELL, M. & HEMPKINS, W.B. 1986. Petroleum isotopic and biomarker composition related to source rock organic matter and depositional environment. *Organic Geochemistry*, **10**, 17-27.

PHILP, R.P. & GILBERT, T.D. 1985. Source rock and asphaltene biomarker characterisation by pyrolysis-gas chromatography-mass spectrometry-multiple oin detection. *Geochimica et Cosmochimica Acta,* **49**, 1421-1432.

PHILP R.P. & GILBERT T.D. 1986. Biomarker distributions in Australian oils predominantly derived from terrigenous source material. *Organic Geochemistry.* **10**, 73-84.

PUTSCHEW, A., SCHAEFFER-REISS,C., SCHAEFFER, P., KOOPMANSS, M.P., DE LEEUW, J.W., LEWAN, M.D., SINNINGHE DAMSTÉ, J.S. & MAXWELL, J.R. 1998. Release of sulfur- and oxygen-bound components from a sulfur-rich kerogen during simulated maturation by hydrous pyrolysis. *Organic Geochemistry*, **29**, 1875-1890.

RICHNOW, H.H., JENISH, A. & MICHAELIS, W. 1992. Structural investigations of sulphur-rich macromolecular oil fractions and a kerogen by sequential chemical degradation. *Organic Geochemistry,* **19**, 351-370.

RICHNOW, H.H., JENISH, A. & MICHAELIS, W. 1993. The chemical structure of macromolecular fractions of a sulphur-rich oil. *Geochimica et Cosmochimica Acta*, **57**, 2767-2780.

ROCHA, J.D., BROWN, S.D., LOVE, G.D. & SNAPE, C.C. 1997. Hydropyrolysis: a versatile technique for solid fuel liquefaction, sulphur speciation and biomarker release. *Journal of Analytical and Applied Pyrolysis*, **40-41**, 91-103.

RUBINSTEIN, I., SPYCKERELLE, C. & STRAUSZ, O.P. 1979. Pyrolysis of asphaltenes: a source of geochemical information. *Geochimica et Cosmochimica Acta*, **43**, 1-6.

RULLKÖTTER, J. & MARZI, R. 1988. Natural and artificial maturation of biological markers in a Toarcian shale from Northern Germany. *Organic Geochemistry*, **13**, 639-645.

RULLKÖTTER, J. & MICHAELIS, W. 1990. The structure of kerogen and related materials - A review of recent progress and future-trends. *Organic Geochemistry*, **16**, 829-852.

SCHAEFFER, P., REISS, C. & ALBRECHT, P. 1995. Geochemical study of macromolecular organic matter from sulphur-rich sediments of evaporitic origin (Messinian of Sicily) by chemical degradations. *Organic Geochemistry,* **23**, 567-581.

SCHAEFFER-REISS, C., SCHAEFFER, P., PUTSCHEW, A. & MAXWELL, J.R. 1998. Stepwise chemical degradation of immature S-rich kerogens from Vena del Gesso (Italy). *Organic Geochemistry,* **29**, 1857-1873.

SCHIEFELBEIN, C.F., ZUMBERGER, J.E., CAMERON, N.R. & BROWN, S.W. 1999. Petroleum systems in the South Atlantic margins. *In*: CAMERON, N.R., BATE, R.H. & CLURE, V.S. (eds) *The oil and gas habitats of the South Atlantic. Geological society, London Special Publications,* **153**, 169-179.

SCHOUTEN, S., PAVLOVIĆ, D., SINNINGHE DAMSTÉ, J.S. & DE LEEUW, J.W. 1993. Nickel boride: an improved desulphurizing agent for sulphur-rich geomacromolecules in polar and asphaltenes fractions. *Organic Geochemistry,* **20**, 901-909.

SCHOUTEN, S., EGLINTON, T.I., SINNINGHE DAMSTÉ, J.S. & DE LEEUW, J.W. 1995. Influence of sulphur cross-linking on the molecular size distribution of sulphur-rich macromolecules in bitumen. *In:* VAIRAVAMURTHY, M.A. & SCHOONEN, M.A.A. (eds) *Geochemical transformations of sedimentary sulphur.* 80-92.

SEIFERT, W.K. 1978. Steranes and terpanes in kerogen pyrolysis for correlation of oils and source rocks. *Geochimica et Cosmochimica Acta*, **42**, 473-484.

SEIFERT, W.S. & MOLDOWAN, M. 1978. Applications of steranes, terpanes and monoaromatics to the maturation, migration and source of crude oils. *Geochimica et Cosmochimica Acta,* **42,** 77-95.

SEIFERT, W.S. & MOLDOWAN, M. 1986. Use of biological markers in petroleum exploration. *In:* JOHNS, N.R. (ed) *Methods in geochemistry and geophysics.* Elsevier, 261-290.

SINNINGHE DAMSTÉ, J.S. & DE LEEUW, J.W. 1990. Analysis, structure and geochemical significance of organically-bound sulphur in the geosphere: State of the art and future research. *Organic Geochemistry*, **16**, 1077-1101.

SINNINGHE DAMSTÉ, J.S., KOHNEN, M.E.L. & HORSFIELD, B. 1998. Origin of low-molecular-weight alkylthiophenes in pyrolysates of sulphur-rich kerogens as revealed by micro-scale sealed vessel pyrolysis. *Organic Geochemistry*, **29,** 1891-1903.

SINNINGHE DAMSTÉ, J.S., RIJPSTRA, I.C., DE LEEUW, J.W. & SCHENCK, P.A. 1988. Origin of organic sulphur compounds and sulphur-containing high molecular weight substances in sediments and immature crude oils. *Organic Geochemistry,* **13**, 593-606.

SINNINGHE DAMSTÉ, J.S., EGLINTON, T.I., DE LEEUW, J. W. & SCHENCK, P.A. 1989. Organic sulphur in macromolecular sedimentary organic matter: I. Structure and origin of sulphur-containing moieties in kerogen, asphaltenes and coal as revealed by flash pyrolysis. *Geochimica et Cosmochimica Acta*, **53,** 873-889.

SINNINGHE DAMSTÉ, J.S.,KENIG, F., KOOPMANSS, M.P., KÖSTER, J., SCHOUTEN, S., HAYES, J.M. & DE LEEUW, J.W. 1995. Evidence for gammacerane as an indicator of water column stratification. *Geochimica et Cosomochimica Acta,* **59**, 1895-1900.

SOFER, Z. 1984. stable carbon isotope compositions of crude oils: application to source depositional environments and petroleum alteration. *American association of Petroleum Geologists Bulletin*, **68**, 31-49.

SPERREVIK, S., VALLE, P.J. & GJELBERG, J.G. Structural impact on deep marine sedimentary systems in the Lower Congo Basin, Offshore Angola, part II: structural reconstruction. In press (b).

SPERREVIK, S., ZWACH, C., ERDMANN, M., TELNÆS, N. & VALLE, P.J. Modelling of secondary migration in tectonically active areas – a case study from the Lower Congo Basin. In press (a).

STALKER, L., LARTER, S.R. & FARRIMOND, P. 1998. Biomarker binding into kerogens: evidence from hydrous pyrolysis using heavy water (D_2O). *Organic Geochemistry*, **28**, 239-253.

SUMMONS, R.E., BOREHAM, C.J., THOMAS, j. & MAXWELL, J.R. 1992. Secular and environment constraint on the distribution of dinosterane in sediments. *Geochimica et Cosmochimica Acta,* **56**, 2437-2444.

SUMMONS R.E., JAHNKE L.L., HOPE J.M. & LOGAN G.A. 1999. 2-Methylhopanoids as biomarkers for cyanobacterial oxygenic photosynthesis. *Nature* **400**, 554-557.

SZATMARI, P. 2000. Habitat of petroleum along the South Atlantic margins. *In:* MELLO, M.R. & KATZ, B.J. (eds) *Petroleum systems of the South Atlantic. American Association of Petroleum Geologists Memoir*, **73**, 69-75.

TEGELAAR, E.W., DE LEEUW, S., DERENNE, S. & LARGEAU, C. 1989. A reappraisal of kerogen formation. *Geochimica et Cosmochimica Acta, **53**, 3103-3106.*

TEN HAVEN, H.L., DE LEEUW, J.S., SINNINGHE DAMSTÉ, J.S., SCHENECK, P.A., PALMER, S.E. & ZUMBERGE, J.E. 1988. *In:* FLEET, A.J., KELTS, K. & TALBOT, M.R. (eds), *Lacustrine Petroleum Source Rocks, Geological Society Special Publication*, **40**, 123-130.

THOMAS, J.B., MARSHALL, J., MANN, A.L., SUMMONS, R.E. & MAXWELL, J.R. 1993. Dinosteranes (4,23,24-trimethylsteranes) and other biological markers in dinoflagellate-rich marine sediments of Rhaetian age. *Organic Geochemistry*, **20**, 91-104.

TISSOT, B.P. & WELTE, D.H. 1984. *Petroleum Formation and Occurrence*. (2nd Edition), Springer, Berlin, 699pp.

TISSOT, B.P., DURAND, B., ESPITALIE, J.& COMBAZ, A. 1974. Influence of the nature and diagenesis of organic matter in formation of petroleum. American *Association of Petroleum Geologists Bulletin*, **58**, 449-506.

VAN KAAM-PETERS, H.M.E. & SINNINGHE DAMSTÉ, J.S. 1997. Characterisation of an extremely organic sulphur-rich, 150 Ma old carbonaceous rock: palaeoenvironmental implications. *Organic Geochemistry*, **27**, 371-397.

VAN KAAM-PETERS, H.M.E., SCHOUTEN, S., DE LEEUW, J.W. & SINNINGHE DAMSTÉ. 1997. A molecular and carbon isotope biogeochemical study of biomarkers and kerogen pyrolysates of the Kimmeridge Clay Facies: palaeoenvironmental implications. *Organic geochemistry*, **27**, 399-422.

VOLKMAN, J.K. 1986. A review of sterol markers for marine and terrigenous organic matter. *Organic Geochemistry*, **9,** 83-99.

VOLKMAN, J.K. 1988. Biological marker compounds as indicators of the deposit environments of petroleum source rocks. *In:* FLEET, A.J., KELTS, K. & TALBOT, M.R. (eds), *Lacustrine Petroleum Source Rocks, Geological Society Special Publication*, **40**, 103-122.

VOLKMAN, J.K., ALEXANDER, R., KAGI, R.I. & WOODHOUSE, G.W. 1983. Demethylated hopanes in crude oils and their applications in petroleum geochemistry. *Geochimica et Cosmochimica Acta*, **47**, 785-794.

WERNE, J.P., HOLLANDER, D.J., BEHRENS, A., SCHAEFFER, P., ALBRECHT, P. & SINNINGHE DAMSTÉ, J.P. 2000. Timing of early diagenetic sulfurization of organic matter: a precursor-product relationship in Holocene sediments of the anoxic Cariaco Basin, Venezuela. *Geochimica et Cosmochimica Acta*, **64**, 1741-1751

26/3(R+S)/25/3(R+S)	C_{26}/C_{25} tricyclic terpane
100*((sum20-25)/3+26/3(R+S))/	% tricyclic terpane
((sum20-25)/3+26/3(S+R)+27(Ts+Tm)+28αβ+sum29-30(αβ+βα)+sum31-35αβ(S+R)	
100*24/4(24/4+24/3+25/3)	$\%C_{24}$ tetracyclic terpane
100*Ts/(Ts+Tm)	$\%C_{27}$Ts
100*29Ts/(29Ts+29αβ)	$\%C_{29}$Ts
100*32αβS/(32αβ(S+R)	$\%C_{32}$αβS
100*30βα/(30βα+30βα)	$\%C_{30}$βα
100*29ααS/29αα(S+R)	$\%C_{29}$αααS
100*29βββ(R+S)/(29bb(R+S)+29αα(S+R)	C_{29}αββ
100*30G/(30G+30αβ)	% gammacerane
100*35αβ(S+R)/(34+35αβ(S+R))	$\%C_{35}$αβ
100*30Δ13(18)/(30Δ13(18))+30Δ17(21))	$\%C_{30}$neohop 13(18) ene
100*2Me/(2Me+3Me+(30αβ/20))	% 2-methyl
100*3Me/(2Me+3Me+(30αβ/20))	% 3-methyl
100*3Me/(2Me+3Me+(30αβ/20))	% hopane/20
100*(21+22)bb/((21+22)ββ+(27+28+29+30)ββ(R+S)	% pregnane
100*27ββ(S+R)/(27+28+29+30)ββ(R+S) (only cross plots)	$\%C_{27}$ sterane
100*28ββ(S+R)/(27+28+29+30)ββ(R+S) (only cross plots)	$\%C_{28}$ sterane
100*29ββ(S+R)/(27+28+29+30)ββ(R+S) (only cross plots)	$\%C_{29}$ sterane
100*30ββ(S+R)/(27+28+29+30)ββ(R+S) (only cross plots)	$\%C_{30}$ sterane
100*27ββ(S+R)/(27+28+29)ββ(R+S) (only ternary diagrams)	$\%C_{27}$ sterane
100*28bb(S+R)/(27+28+29)ββ(R+S) (only ternary diagrams)	$\%C_{28}$ sterane
100*29ββ(S+R)/(27+28+29)ββ(R+S) (only ternary diagrams)	$\%C_{29}$ sterane
27ααR/29ααR	C_{27}/C_{29} sterane
29(αβ+βα)/29αα(S+R)	hopane/sterane
Pr/Ph	pristane/phytane
nC17/(nC17+nC27)	waxiness
0.5*(nC(25+27+29+31+33)/nC(24+26+28+30+32)+	
(nC(25+27+29+31+33)/nC(26+28+30+32+34))	CPI
(-24-nor βα dia(R+S)/(24-nor βα dia(R+S)+27- nor βα dia(R+S))	NDR

24-nor αα(R+S)+ 24-nor ββ(R+S)/(24-nor αα(R+S)+ 24-nor ββ(R+S)+ 27-nor αα(R+S)+ 27-nor ββ(R+S))	NCR
2.53*13Csat)+(2.22*13Caro)-11.65	conical variable