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GEOLOGICAL FACTORS CONTROLLING CRUDE OIL COMPOSITION IN AUSTRALIA AND PAPUA NEW GUINEA[1]

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ABSTRACT

A geochemical survey of both commercial and non-commercial crude oils in Australia has shown them to be predominantly paraffinic or paraffinic-naphthenic in composition. High wax contents are common.

A close stratigraphic control on crude oil type operates in the Perth and Carnarvon Basins of Western Australia. The chemical character of Australian oils can be related to their sedimentary environments, which range from lacustrine to near-shore marine. Spores, pollen, and cuticles derived from land plants have been a major source for the hydrocarbons.

Apart from changing the relative proportions of the different boiling fractions, maturation has had little effect on the basic composition of the oils. Alteration of crude oil by water-washing and microbial activity in the reservoir is rare but, in several oil accumulations, light fractions are thought to have been mobilized by gas invasion of the oil reservoir.

Other differences in crude oil composition can be attributed to variations in microbial activity during early diagenesis of the organic source material.

INTRODUCTION

Petroleum is a complex mixture of hydrocarbons and other compounds; its composition is governed by the interaction of many geological processes such as sedimentation and decay of organic detritus, burial diagenesis (involving thermal alteration and catalytic activity), migration, etc. The relative significance of these processes will vary from one reservoir to another and it is unlikely that any two crudes will be identical in composition. Classification of petroleums on the basis of the various parameters which have determined their composition is therefore extremely difficult. Many early workers attributed variations in crude oil quality to thermal effects related to age, depth of burial, and catalytic activity (Barton, 1937; Brooks, 1952; McNab et al., 1952). Other authors have demonstrated a relation between crude oil composition and source environment (Neumann et al., 1947; Hlaucshek, 1950; Bornhauser, 1950; Haeberele, 1951; Hunt, 1953; Jones and Smith, 1965; Barbat, 1967). By examining single-source petroleums, Hunt (1953) and Barbat (1967) found that the role of maturation in determining crude oil type was not as great as had previously been thought. Spencer and Koons (1970), in a study of Canadian oils, have shown that distinctions between oil families are maintained over a wide depth range, indicating that source-rock environment is the primary control of oil composition. More recently Evans et al. (1971), whilst acknowledging the influence of source effects, have demonstrated that alteration processes in the reservoir are important in controlling the commercial quality of petroleum in western Canada.

Petroleum exploration has had a comparatively short history in Australia (Rudd, 1967). Although hydrocarbon shows have been encountered in many sedimentary basins, commercial accumulations are few. The present geochemical survey is an attempt to characterize all commercial and most non-commercial crude oils in Australia in terms of the factors which may have influenced their compositions.

LOCATIONS OF HYDROCARBON ACCUMULATIONS

The locations of the commercial or potentially commercial hydrocarbon-bearing areas are shown in Figure 1. Their stratigraphic distribution and estimated reserves are given in Figure 2. The major oil-bearing region is the offshore Gippsland Basin of southeast Victoria (Fig. 3), where two oil fields and two gas/condensate fields are in production; these accumulations lie within the Latrobe Group of Cretaceous-Eocene age. The Cooper Basin in the northeast corner of South Australia has developed into a significant gas/condensate province with some oil (Fig. 4); the reservoirs are located in several formations of the Gidgealpa Group of Permian age. The main gas and oil-bearing regions of Queensland occur in the southern part of the Bowen Basin and the overlying Surat Basin (Fig. 5), where gas is the major commercial product on the Roma Shelf and oil has been produced from small fields in the Mimosa Syncline; the deposits are found in sediments ranging in age from Devonian to Jurassic. To the northwest an oil show has been encountered in non-marine Permian sediments of the Galilee Basin. In the centre of the continent, oil and gas have been discovered in the Amadeus Basin (Fig. 6), where the main reservoir for the Mereenie oil and gas field and the Palm Valley gas field is the Ordovician Pacoota Sandstone.

In the Perth Basin of Western Australia, dry gas is produced from basal Triassic sands in the northern part of the Dandaragan Trough (Fig. 7); small accumulations of oil have also been found in these sands as well as in Permian and Jurassic sediments in the area. Farther south, in the cental part of the Dandaragan Trough, gas is produced from Jurassic sands in the Gingin and Walyering fields. Oil and gas discoveries have been made in the Barrow and Dampier Sub-basins of the Carnarvon Basin (Fig. 8). In the Barrow Sub-basin, oil is produced from the Cretaceous Windalia Sand and to a lesser extent from the underlying Barrow Group (Jurassic-Cretaceous) and Dingo Claystone (Jurassic). Within the Dampier Sub-basin several gas/condensate fields have been delineated in Jurassic-Cretaceous and Triassic sediments; some oil has also been found. Finally gas/condensate has been found both onshore and offshore in the Papuan Basin, and a minor oil accumulation was located onshore at Puri (Fig. 9).

ANALYSIS OF OILS

The analytical procedures outlined below are in part based on a scheme for the geochemical analysis of crude oils devised by Rogers et al. (1971) and modified to suit the facilities available in the Bureau of Mineral Resources (BMR).

The API gravities of the oils were measured according to method IP 160/68. Sulphur analyses were carried out by the Commonwealth Scientific and Industrial Research Organization (CSIRO) Microanalytical Service, Melbourne. Carbon-isotope measurements on selected crudes were made by Geochron Laboratories Inc., Cambridge, Massachusetts, using the PDB standard. The extract pour points were not determined; instead, distinctions were drawn as to whether the pour points fell above or below 50°F. Since the asphalt content of Australian oils discovered to date is negligible, a pour point of greater than 50°F (Hedberg, 1968) was taken to indicate a high-wax oil. Where the pour point fell between 30°F and 50°F, a cloud point of about 25°F for US Bureau of Mines distillation fraction 11, or a cloud point of above 35°F for fraction 15, was also used as evidence of a high wax content (Hedberg 1968). This additional information was obtained from US Bureau of Mines and company analyses. The wax content was thus determined as high or low and was not measured in condensates.

Preliminary distillation was carried out according to method IP 24/55 and cuts were made at intervals of 50°C. The specific gravity of each cut was measured, and the data was used to calculate US Bureau of Mines Correlation Indices (Smith, 1964). Values below 10 indicate ultra-paraffinic fractions; 10 to 20, highly paraffinic; 20 to 30, paraffinic; 30 to 40, naphthenic; and above 40, aromatic (Barbat, 1967). The indices represent a series from paraffinic at low values to aromatic at high values, but the division between naphthenic and aromatic is somewhat arbitrary since these fields overlap considerably.

The fractions boiling above 250°C were combined, and the asphaltenes were separated according to method IP 143/57. The asphaltene-free residue was then chromatographed on alumina by eluting successively with petroleum ether (40-70°C), benzene, and methanol to obtain the saturated hydrocarbons, the aromatic hydrocarbons, and the oxygen, nitrogen and sulphur (ONS) compounds respectively. The saturated hydrocarbons were analysed by gas chromatography using a 50 m x 0.25 mm ID capillary column coated with Apiezon L and nitrogen as a carrier gas. The column was temperature-programmed from 100°C to 250°C at 4°C per minute and held at 250°C until all hydrocarbons had been eluted. Normal alkanes, pristane, and phytane were identified by co-injection of authentic standards and by comparison of retention times with published data.

COMPOSITION OF CRUDE OILS FROM AUSTRALIA AND PAPUA NEW GUINEA

GROSS PROPERTIES

The API gravities and sulphur contents of Australian oils are plotted in Figure 10. They are similar to the most frequent values that Smith (1968) determined for several thousand samples, viz. API 35°-40°, sulphur 0.1%. The wax content of crude oils has been used by Hedberg (1968) to distinguish crude oils of non-marine origin, or, more precisely, those derived from the debris of higher plants. Many of the samples examined in this study were condensates to which Hedberg's definition of a high wax content cannot be readily applied. However, of the 43 crude oils examined, all but six have a high wax content (Fig. 10).

Selected samples of crude oil have been analyzed for their stable carbon-isotope ratios and the results are listed in Table 1. With the exception of the Mount Horner and Mereenie oils, they all fall in a narrow range (δC^{13}_{PDB} -26.6 to -28.1)

CORRELATION INDICES

Average correlation indices of oils from the major hydrocarbon areas of Australia are given in Figure 11. The crude oils which occur in the northern Dandaragan Trough of the Perth Basin are highly paraffinic. Oils and condensates found in the Amadeus, Bowen-Surat, Cooper, Gippsland, and Perth (central Dandaragan Trough) Basins have correlation indices between 20 and 30, which signifies an appreciable paraffin component. Hydrocarbons from onshore Papua and pre-Cretaceous sediments of the Carnarvon Basin are slightly more naphthenic. Only the Cretaceous oils of the Carnarvon Basin and a Miocene condensate from offshore Papua (200-250°C fraction, correlation index 56) have high correlation indices indicative of a low paraffin content.

COMPOSITION OF FRACTIONS BOILING ABOVE 250°C

The compositions of the combined fractions boiling above 250°C as determined by liquid chromatography are shown in Figure 12. A characteristic feature is their high proportion of saturated hydrocarbons. Furthermore there is only a slight decrease in the percentage of saturated hydrocarbons with increasing correlation index (Fig. 13). The high correlation indices of the Cretaceous oils from the Carnarvon Basin must, therefore, be due to a high naphthene content. This feature is illustrated in Figure 14, where gas chromatograms of the saturated hydrocarbons obtained from one Cretaceous oil and one Jurassic oil from the Carnarvon Basin are compared. The hydrocarbon distribution of the Barrow-Jurassic oil is dominated by n-paraffins, but the saturated hydrocarbons from the Windalia crude are an extremely complex mixture of naphthenic components with n-paraffins forming only a small proportion of the total.

The isoprenoid hydrocarbon, pristane, is a major component in the majority of these oils (see e.g. Fig. 14) and phytane is a relatively minor component. There is considerable variation in the ratio of pristane to phytane in oils from the different sedimentary basins (Fig. 15). Oils from the Bowen-Surat, Cooper, and Gippsland Basins generally have high ratios. Those with low ratios are confined to the Amadeus, Carnarvon, and Perth Basins. Oils with intermediate values occur in the Carnarvon, Cooper, Papuan, and Perth Basins.

RELATIONSHIP OF CRUDE OIL COMPOSITION TO GEOLOGY

STRATIGRAPHIC CONTROL

Usually, oils in a given province of Australia are essentially of the same type, but a notable exception exists in the Carnarvon Basin (Fig. 8), where oil and gas/condensate of varying composition are found in sediments ranging in age from Triassic to Cretaceous (Fig. 16). In the Barrow Sub-basin, oil has been recovered from both Jurassic and Cretaceous formations, but only that in the Cretaceous at Barrow Island is a significant commercial accumulation. Samples have been examined from the Windalia Sand and the Muderong Greensand (both Cretaceous) and at three levels from the Barrow Group and underlying Dingo Claystone at Barrow Island (viz. 2042 m, 2012 m, and 1890 m in the Barrow No. 1 well). In addition, oils from the Birdrong Sand (Cretaceous) in the Flinders Shoals No. 1 well, and from two levels within the Jurassic (viz. 1737 m and 1798 m) in the Pasco No. 1 well, were analyzed. The correlation curves (Fig. 17) clearly indicate that the oils of the Barrow Sub-basin fall into two families: those in Cretaceous reservoirs are predominantly naphthenic and those from the Barrow Group and Dingo Claystone are mainly paraffinic.

Within the Dampier Sub-basin, gas/condensate and oil are known from Triassic, Jurassic, and Cretaceous formations. The major gas/condensate discoveries, viz. North Rankin, Goodwyn, and Rankin, were made in Triassic sediments on the Rankin Trend (Fig. 8). A thin oil column was encountered in the Rankin No. 1 well beneath the gas/condensate and an oil leg has been located in the Goodwyn field. Oil has also been discovered in Triassic sands in the Eaglehawk No. 1 well, and in the Barrow Group in the Egret No. 1 well. In the Rankin No. 1 well a small amount of oil was recovered from the Cretaceous Toolonga Calcilutite. Gas/condensate has been found in the Barrow Group (Jurassic-Cretaceous) at the Angel location, and a non-commercial oil discovery was made in the same group in the Legendre No. 1 well. The correlation curves (Fig. 18) reveal a basic similarity in the composition of the oils and condensates from both the Barrow Group and the Triassic reservoirs (Eaglehawk excepted). The close resemblance of the condensates from the Rankin Trend and the Angel field is particularly striking and a common source is likely.

The Rankin Platform is an uplifted Triassic fault block overlain unconformably by Cretaceous sediments. To the southeast (Fig. 8) a fault with up to 2.4 km of throw separates it from a trough of Jurassic sediments (Kaye <u>et al</u>., 1972). Within this trough are located the Legendre structure and the Madeleine-Dampier anticlinal trend containing the Angel field. Chemical evidence suggests that the hydrocarbons in all these structures were generated from Jurassic sediments. Subsequent migration led to accumulation in Triassic sediments on the Rankin Platform and in sands of the Barrow Group at the Angel and Legendre locations. The oils and condensates of Jurassic origin in the Dampier Sub-basin are slightly more naphthenic than the Jurassic oils in the Barrow Sub-basin.

The small amount of oil recovered from the Toolonga Calcilutite in the North Rankin No. 1 well and the oil which flowed from the Triassic at Eaglehawk No. 1 are very similar in composition. They are of the naphthenic type and, as such, strongly resemble the oils found in the Cretaceous at Barrow Island. The main difference is that the two oils from North Rankin and Eaglehawk have a larger proportion of high boiling fractions. If both these oils had a Cretaceous source it follows that the oil at Eaglehawk must have migrated into the Triassic sands from overlying Cretaceous sediments. Thus the division of oils into a paraffinic-naphthenic type with a Jurassic source and a naphthenic type with a Cretaceous source is a feature of both the Barrow and Dampier Sub-basins, yet the occurrences are about 160 kilometres apart and at contrasting depths.

The stable carbon-isotope ratios of four oils from the Carnarvon Basin provide supporting evidence for the foregoing conclusions. The δC^{13} values for the Barrow-Windalia and Eaglehawk oils are almost identical (-27.3 and -27.4 respectively), but differ from the value (-28.1) for Jurassic-source soils, viz. Rankin and Legendre.

Another area where stratigraphic control of crude oil composition can be demonstrated is the central part of the Dandaragan Trough in the Perth Basin. Here gas/condensate is produced from the Gingin and Walyering fields, which are 55 km apart (Fig. 7). The producing units are several unconnected sands within the Cockleshell Gully Formation (Jurassic). Two samples of condensate from different levels within the Gingin field were compared with two samples from approximately equivalent stratigraphic intervals in the Walyering field; the two condensates from the greater depths contain the higher proportion of heavy hydrocarbons. The correlation curves (Fig. 19) show that samples from equivalent horizons are similar in composition, but that there are marked differences between the upper and lower levels within the same field.

MARINE OR NON-MARINE?

Geological Evidence

Hedberg (1968) has suggested that high-wax oils are of non-marine origin and cited many examples where such oils are associated with paralic and non-marine sediments. In Australia and Papua New Guinea there are numerous examples of high-wax oils, notably those from the Gippsland, Bowen-Surat, Cooper, Galilee, Perth, Carnarvon (Jurassic-source), and Papuan Basins. In each case the oils are of paraffinic to paraffinic-naphthenic composition and their geological environment is predominantly non-marine.

In the Gippsland Basin the major hydrocarbon accumulations lie within the Latrobe Group (Cretaceous-Eocene), which comprises quartz sand, coal, mudstone, siltstone, and shale. It is considered to represent a lacustrine and fluviatile environment although small amounts of marginal marine coarse clastics are also present.

The hydrocarbons of the Cooper Basin occur in various formations of the Gidgealpa Group (Permian). The major lithologies are siltstone, mudstone, coal, and sandstone of various types. The environment of deposition ranges from lacustrine to deltaic (Thornton, 1973).

In the Bowen Basin, where oil and gas are found in Devonian-Triassic reservoirs, the sediments are again largely non-marine with some marginal marine beds in the lower part of the Upper Permian (Allen, 1973). In the Surat Basin (Jurassic-Cretaceous), which overlies the southern part of the Bowen Basin, oil and gas are produced from the basal Precipice Sandstone and the overlying Evergreen Formation. Both are non-marine sequences although there is some evidence of a minor marine incursion in the upper part of the Evergreen Formation (Allen, 1973).

Oils discovered in the northern part of the Dandaragan Trough, Perth Basin, are extremely waxy and are solid at room temperature. They occur in Upper Permian, Triassic, and Jurassic sands. The Kockatea Shale (Triassic) is considered to be the source of these oils, and although this formation was deposited in a marginal marine environment (Jones and Pearson, 1972) its organic content mainly comprises the debris of land plants. The gas/condensate accumulations at Gingin and Walyering are located in the Jurassic Cockleshell Gully Formation, comprising coal-bearing sandstone, siltstone, and shale, which were deposited in a continental to marginal marine environment (Jones and Pearson, 1972).

In the Barrow Sub-basin the Upper Jurassic Dingo Claystone is considered to be the source for the high-wax oils; it consists of alternating siltstone and glauconitic sandstone deposited in a marginal marine environment. The sequence grades up into the predominantly deltaic succession of the Barrow Group (Crank, 1973). The Jurassic is likewise considered to be the source for the major gas/condensate discoveries in the Dampier Sub-basin. Here the Lower and Middle Jurassic sediments are fluviatile to deltaic in character (Kaye et al., 1972). A marine transgression during the Upper Jurassic resulted in the deposition of thick marine shales, but deltaic conditions persisted marginal to the Pilbara Block (Fig. 8). All the Jurassic-source oils in the Barrow Sub-basin have a high-wax content, whereas in the Dampier Sub-basin only the Legendre oil has this character.

In the Papuan Basin waxy condensate was recovered from near-shore marine sandstones of Jurassic age at the Omati No. 1 well. The high-wax oil at Puri was recovered from a Lower Miocene limestone, overlying Mesozoic sediments of near-shore origin.

Chemical Evidence

Further evidence for a non-marine origin of many Australian oils is given by their pristane to phytane ratios (Powell and McKirdy, 1973b). Pristane and phytane are usually considered to be the products of the diagenesis of the phytol side-chain of chlorophyll, although other sources are possible. The presumed mode of derivation of pristane and phytane is illustrated in Figure 20. In coals, pristane is formed by decarboxylation of phytanic acid, and phytane by dehydration and hydrogenation of phytol (Brooks et al., 1969). Differences in the ratio of pristane to phytane may reflect variations in the degree of oxidation during the early stages of chlorophyll degradation. Thus the formation of phytanic acid should occur to a greater extent on land during the initial aerobic stages of plant decay than in an aquatic environment, where totally anaerobic decay is more likely. High pristane to phytane ratios as found in bituminous coals (Brooks et al., 1969) indicate a source from land-derived organic matter or organic materials which have passed through an oxygenated phase in their decomposition. From Figure 15 it is evident that those oils which are thought to have a non-marine source also possess high pristane to phytane ratios (above 4.5). Notable exceptions are the high-wax oils from the Galilee and northern Perth Basins. These oils, however, show evidence of immaturity, viz. poor gasoline yield and a relative lack of naphthenic components. A possible explanation for the low pristane to phytane ratios is that these oils were derived from terrestrial organic matter which had undergone little thermal alteration during burial diagenesis. Brown and sub-bituminous coals have low pristane to phytane ratios (1-3) in contrast to high volatile bituminous coals (Brooks et al., 1969), which have higher values (7-10). Clearly the generation of pristane from phytanic acid is incomplete at the brown coal stage. The variation in pristane to phytane ratio with extent of diagenesis of the source beds, as indicated by gasoline yield, is illustrated in Figure 21 for oils and condensates of presumed non-marine origin. Of course any process that changes the proportion of gasoline in these oils during or after migration (e.g. maturation and fractionation) would tend to disrupt this relationship.

Oils from the Carnarvon Basin (Jurassic source), Perth Basin (central Dandaragan Trough), and Papuan Basin have intermediate pristane to phytane ratios (3.0-4.5). They are generally slightly more naphthenic than the previous group. The differences probably reflect the greater marine affinity of the host sediments and the possible contribution to the source material of detritus from micro-organisms that has escaped extensive oxidation during its decay. Unpublished studies by the authors on the probable source sediments for the hydrocarbons in the Triassic and Jurassic reservoirs in the Dampier Sub-basin have shown that the organic matter is of mixed terrestrial and marine origin.

Only seven oils from Australia have an unequivocal marine source: the Cretaceous-source oils in the Carnarvon Basin, the Uramu condensate occurring in a Miocene reef in the offshore Papuan Basin, and the Mereenie oil of the Amadeus Basin. They are all characterized by low pristane to phytane ratios (below 3) and, with the exception of the Mereenie oil, are naphthenic to aromatic in composition (Fig. 22). The Mereenie oil is paraffinic but its occurrence in an Ordovician marine sequence precludes the contribution of higher plants to its source material.

Geochemical Classification

A geochemical classification of Australian crude oils has been derived from the evidence discussed above. The classification is based on the composition of the oils as indicated by wax content, the correlation indices and pristane to phytane ratio, and the geological environment in which they are found. The oils have been divided into three groups, which are illustrated in Figure 22, where the pristane to phytane ratios are plotted against the average correlation index of the distillation fractions boiling in the range 250-300°C.

Group A: High-wax and predominantly paraffinic oils and condensates generally with high pristane to phytane ratios (above 4.5), and occurring in lacustrine, fluviatile, or deltaic sequences with little or no marine influence.

Group B: Paraffinic-naphthenic oils with intermediate pristane to phytane ratios (3.0-4.5), occasionally a high wax content, and associated with marginal marine clastic sediments or deltaic sequences showing some marine influence.

Group C: Low-wax, predominantly naphthenic oils possessing low pristane to phytane ratios (below 3.0), and associated with marine shales and carbonates.

The first group is the most common and includes oils from the Gippsland, Bowen-Surat, Cooper, and Perth Basins. Oils from the northern Perth Basin and the Galilee Basin are anomalous in that they have low pristane to phytane ratios, which, as we have seen, may be attributed to the immaturity of the source organic material.

Oils found in marginal marine sediments of the Papuan, Perth and Carnarvon Basins fall into the second category.

The third group comprises the oils which have an undoubted marine source, the Cretaceous-source oils in the Carnarvon Basin, the Uramu condensate from the offshore Papuan Basin, and the Mereenie crude from the Amadeus Basin.

Representative samples from these groups were analyzed for their stable carbon-isotope ratios (Table 1). Little or no distinction can be drawn between the three groups on the basis of their δC^{13} values. This is perhaps not surprising in the light of the wide stratigraphic and geographic distribution of the samples. However, several observations can be made. The non-marine Mount Horner oil shows the greatest degree of fractionation (δC^{13}_{PDB}-32.8) and consequently falls in the non-marine group of oils defined by Silverman (1964). It originates in Triassic sediments, and oils of this age characteristically show a high degree of fractionation (δC^{13}_{PDB}-28 to -33; Degens, 1969). The Mereenie oil of Ordovician age has a similar value (δC^{13}_{PDB}-31.0). This is also in agreement with the published figures for oils of Lower Palaeozoic age (δC^{13}_{PDB}-24 to -35; Degens, 1969).

EFFECTS OF MATURATION

It has not been possible within Australia to examine the effects of maturation on single-source petroleums. Nevertheless the oils from the northern Perth, Galilee, Gippsland, and Cooper Basins appear to have been derived from the debris of higher plants, and yet compositional differences do occur. In Figure 23 the average yields of the various distillation fractions of the oils from each of these basins are plotted together with their pristane to phytane ratios and the ranks of coals in associated sediments. A regular increase in the relative yield of the lower boiling fractions can be seen if the basins are considered in the following order: northern Perth, Galilee, Gippsland, and Cooper. This change in distillation behaviour is accompanied by an increase in the rank of associated coals (80-86% carbon DAF). In the Cooper Basin, where gas/condensate is the major product, there is a local area of high-rank coals (89% carbon DAF) near the Moomba field (Fig. 4), from which only dry gas is obtained. It may also be significant that the δC^{13}_{PDB} values listed in Table 1 for the Perth (-32.8), Gippsland (-28.1), and Cooper (-26.9) Basin oils appear to increase in a regular manner.

Apart from these differences, which can be reasonably attributed to differing degrees of diagenesis of the source beds, there is little variation in the gross composition of the oils and condensates in this non-marine series. Whereas the oils from the northern Perth and Galilee Basins are generally more paraffinic than those from the Gippsland Basin (Fig. 24), the correlation curves of the Cooper Basin oils and condensates cover the whole paraffinic range.

CHANGES DURING MIGRATION AND ACCUMULATION

Evans _et al._ (1971) have recently documented a number of changes that can take place during migration and accumulation of crude oil: namely, gas-deasphalting, water-washing, and biodegradation. The sparsity of petroleum occurrences in Australia has mitigated against comparative studies of crude oil composition in local areas. Nevertheless there are some instances where alteration during or after migration is suspected.

Considerable variation exists in the composition of the lighter ends of oils found on the Roma Shelf in the Bowen-Surat Basin (Fig. 25). The Roma Shelf is an extremely complex structure, and is considered to be a dissected basement ridge against and over which successively younger sediments onlap (Swindon, 1968). The oils occur in small pools in sediments ranging in age from Devonian basement to Jurassic and are confined to the southwestern part of the shelf. The sand bodies are locally discontinuous and in many instances permeability barriers contribute to the trapping mechanism. Location of the oil pockets on the updip sides of commercial gas accumulations suggests that the migration has occurred by Gussow's differential entrapment mechanism (Swindon, 1968). In addition the Surat Basin is part of the hydrodynamically active Great Artesian Basin, and flushing may have occurred in many areas (Power and Devine, 1970). The oils on the Roma Shelf are thought to have a common or related source. This supposition is based on the similarity in composition of the fractions boiling above 250°C and the uniformly high wax content and pristane to phytane ratios. A complex migration process, then, has presumably caused the observed differentiation of the light fractions.

The main evidence for water-washing and bacterial modification of the crude oil in the reservoir is loss of light fractions, absence of n-paraffins, and invasion of the reservoir by meteoritic waters (Evans et al., 1971). The Conloi oil (Fig. 25) from the Surat Basin seems to satisfy these criteria. Less than 10 percent of the oil distills below $200^{\circ}C$, and gas chromatography of the saturated hydrocarbons shows that n-paraffins are not present, in marked contrast to the remaining oils in the area (Fig. 26). Fresh water (about 3000 ppm total solids) is a feature of most of the reservoirs throughout the Surat Basin.

Absence of low-boiling fractions does not necessarily mean that water-washing has occurred. In the northern part of the Perth Basin, crude oil occurs in the same reservoir as dry gas (97% methane) in the Dongara, Mondarra, and Yardarino fields (Fig. 7). Three additional oil shows have been discovered in which dry gas is not present, viz. Erregulla, North Erregulla, and Mount Horner. Distillation data for the Dongara, Mondarra, and Yardarino oils show that they are stripped of light ends (Table 2) compared with the other oils in the area. Condensates recovered during gas production are similar in composition to the oils. A possible explanation for the absence of light ends is that the oils were derived from Triassic sediments, whereas dry gas originated in more thermally altered Permian Coal Measures downdip of the present hydrocarbon accumulations; migration of the gas into the Dongara, Mondarra, and Yardarino reservoirs may have resulted in the mobilization of light fractions from the oils.

Similarly the absence of n-paraffins from crude oils does not by itself indicate that microbial degradation has occurred. Oils of Cretaceous origin throughout the Carnarvon Basin are characterized by an absence of n-paraffins and it has been shown that their composition is related to the depositional environment of their source beds. Obviously the criteria for water-washing and microbial degradation are not clear-cut and each case must be considered on its merits.

RELEVANCE OF AUSTRALIAN OILS TO THEORIES OF PETROLEUM GENESIS

Most of the crude oils so far found in Australia are paraffinic or paraffinic-naphthenic and it has been demonstrated that many are derived from the remains of higher plants. These conclusions strongly contradict the claims that sediments rich in ligno-humic compounds derived from terrestrial sources are the principal source of aromatic oils (Hlauschek, 1950). In Australia at least, it is rather the leaf, pollen, and spore cuticles of higher plants which have been the major precursors for petroleum hydrocarbons, but of a waxy paraffinic type (Brooks and Smith, 1969; Hedberg, 1968).

Australian crude oils become more naphthenic as the contribution of the detritus of higher plants to the source organic matter diminishes. However, the occurrence of paraffinic crudes in Lower Palaeozoic sediments (e.g. Mereenie oil, Amadeus Basin) deposited before the advent of land plants, demonstrates that the type of source material is not the sole determinant of crude oil composition. Barbat (1967) has shown that maturation of aromatic petroleums does not lead to the generation of paraffinic crudes, but simply changes the relative proportions of the distillation fractions. Thus the paraffinic character of certain Lower Palaeozoic petroleums is probably in part a function of environment. Again Barbat (1967) has suggested that highly paraffinic oils were formed in predominantly oxidizing conditions, but it is noteworthy that the examples quoted by him were largely from environments where debris of higher plants could be expected to have formed a large proportion of the source organic matter. Thus in clastic sediments deposited after Devonian time it is difficult to distinguish the effect of environment on crude oil composition from that of primary source material since such sediments inevitably contain spore, pollen, and leaf cuticles from higher plants.

The question remains, therefore, as to what conditions in the source environment could control crude oil composition.

Although the catalytic activity of mineral surfaces (particularly clays) is thought to play a significant role in the generation of petroleum hydrocarbons, it is unlikely that wide variations in crude oil composition could be achieved by this means. Louis (1966) has shown that aromatic hydrocarbons are converted to heavier asphaltic substances when heated to 180°C in the presence of montmorillonite, whereas saturated hydrocarbons after similar treatment are virtually unaffected. However this process is probably only confined to maturation (Louis, 1966) and is not a factor in determining the initial composition of the oil.

Zobell (1959), Emery and Rittenberg (1952), and Baas-Becking (1959) have demonstrated the importance of microbial activity during the early stages of diagenesis, but comparative studies of its effect in different sedimentary environments are few. Lindblom and Lupton (1961) found a marked contrast between bacterial activity in recent carbonate muds and deltaic clastic sediments. In carbonate muds from Florida, heterotrophic bacterial activity was not detected below 0.9 m, whereas in sediments from the Orinoco Delta, viable bacteria were detected to a depth of 46 m, although most were found above 15 m. The carbonates were highly reducing owing to a high hydrogen sulphide content which may also have limited bacterial growth. In contrast, the deltaic sediments had a positive Eh, even at great depth, and both aerobic and anaerobic bacteria were present. Lindblom and Lupton observed that in the deltaic sediments, the concentrations of protein, carbohydrate, and lipid decreased rapidly to a depth of 3 m. Below 3 m, the protein and carbohydrate content continued to decline, but the lipid content began to increase.

Nissenbaum and Kaplan (1972) found that humic compounds formed in a marine environment had a high sulphur content compared with humic compounds formed under freshwater or subaerial conditions. Kaplan et al. (1963) noted that the sulphur of organic compounds trapped in recent sediments differed in isotopic composition from that in sulphur-bearing compounds of organisms in the overlying water column. These results suggest that sulphur is incorporated into organic matter during decay in the marine environment. Clearly comparative studies of the mechanisms of organic decay will be fundamental to our further understanding of the variations in petroleum composition.

CONCLUSIONS

1. Australian oils in general have API gravities greater than 35° and low sulphur and asphalt values. They range from paraffinic to naphthenic in composition.
2. The major factors controlling the composition of Australian crude oils are the depositional environment of the source rock and the relative contribution to the source organic matter of the cuticles of pollen, spores, and leaves derived from higher plants.
3. Australian oils may be classified into three groups on the basis of composition and geological environment. These groups are:
    - (i) Paraffinic oils associated with non-marine sediments.
    - (ii) Paraffinic-naphthenic oils associated with marginal marine and deltaic sediments.
    - (iii) Naphthenic oils associated with marine shales and carbonates.

However the distinctions are not reflected in the stable carbon-isotope ratios.

4. For oils of non-marine origin, differences in the degree of diagenesis of the source beds lead to variations in the relative proportions of the distillation fractions. The ratio of pristane to phytane, and possibly δC^{13} value also, increases, but no fundamental change in overall chemical composition results.

5. Alteration of crude oil in the reservoir by processes such as water-washing and biodegradation is not common in Australia. However, mobilization of light fractions by invasion of dry gas into oil reservoirs has occurred in the northern Perth Basin.

6. Bacterial activity during the early diagenesis of source organic material is thought to be important in determining crude oil composition.

ACKNOWLEDGEMENTS

We wish to thank the following companies which generously supplied samples: BOC of Australia Ltd, West Australian Petroleum Company Ltd, Delhi International Oil Corporation, Australasian Petroleum Company Pty Ltd, and Broken Hill Pty Ltd. We are also indebted to Z. Horvath and R. Moon of BMR for technical assistance. This paper is a synthesis of results presented at two recent conferences of the Australian Petroleum Exploration Association (Powell and McKirdy,1972, 1973a).

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Table 1. Carbon-isotope ratios of selected crude oils (values relative to PDB standard)

BASIN	OIL SAMPLE	RESERVOIR AGE	δC^{13}
Gippsland	Kingfish	Cret.-Eocene	-28.1
Cooper	Yanpurra	Permian	-26.9
Surat	Moonie	Jurassic	-26.6
Perth	Mount Horner	Triassic	-32.8
Carnarvon	Rankin	Triassic[+]	-28.1
Carnarvon	Legendre	Jurassic	-28.1
Papuan	Puri	Miocene	-27.6
Amadeus	Mereenie	Ordovician	-31.0
Carnarvon	Barrow-Windalia	Cretaceous	-27.3
Carnarvon	Eaglehawk	Triassic*	-27.4

+ Jurassic source
* Cretaceous source

Table 2. Gasoline yield of oils from the north Dandaragan Trough, Perth Basin

Well or Field	Fraction	100°C	100-200°C
		percent of oil by volume	
Dongara		2.5	3.5
Erregulla		3.0	12.0
Mondarra		2.5	2.5
Mount Horner		4.0	17.0
North Erregulla		3.5	12.5
Yardarino		2.0	2.5

FIGURES

14. Gas chromatograms of saturated hydrocarbons isolated from the Barrow-Windalia and Barrow-Jurassic oils, Carnarvon Basin

15. Frequency distribution of pristane to phytane ratios in Australian oils and condensates

16. Stratigraphic distribution of hydrocarbon discoveries in the Carnarvon Basin

17. Correlation curves for oils from the Barrow Sub-basin

18. Correlation curves for oils and condensates from the Dampier Sub-basin

19. Correlation curves for oils and condensates from the central Dandaragan Trough, Perth Basin

20. Mode of derivation of pristane and phytane from phytol

21. Variation of the ratio of pristane to phytane with gasoline yield for non-marine oils and condensates

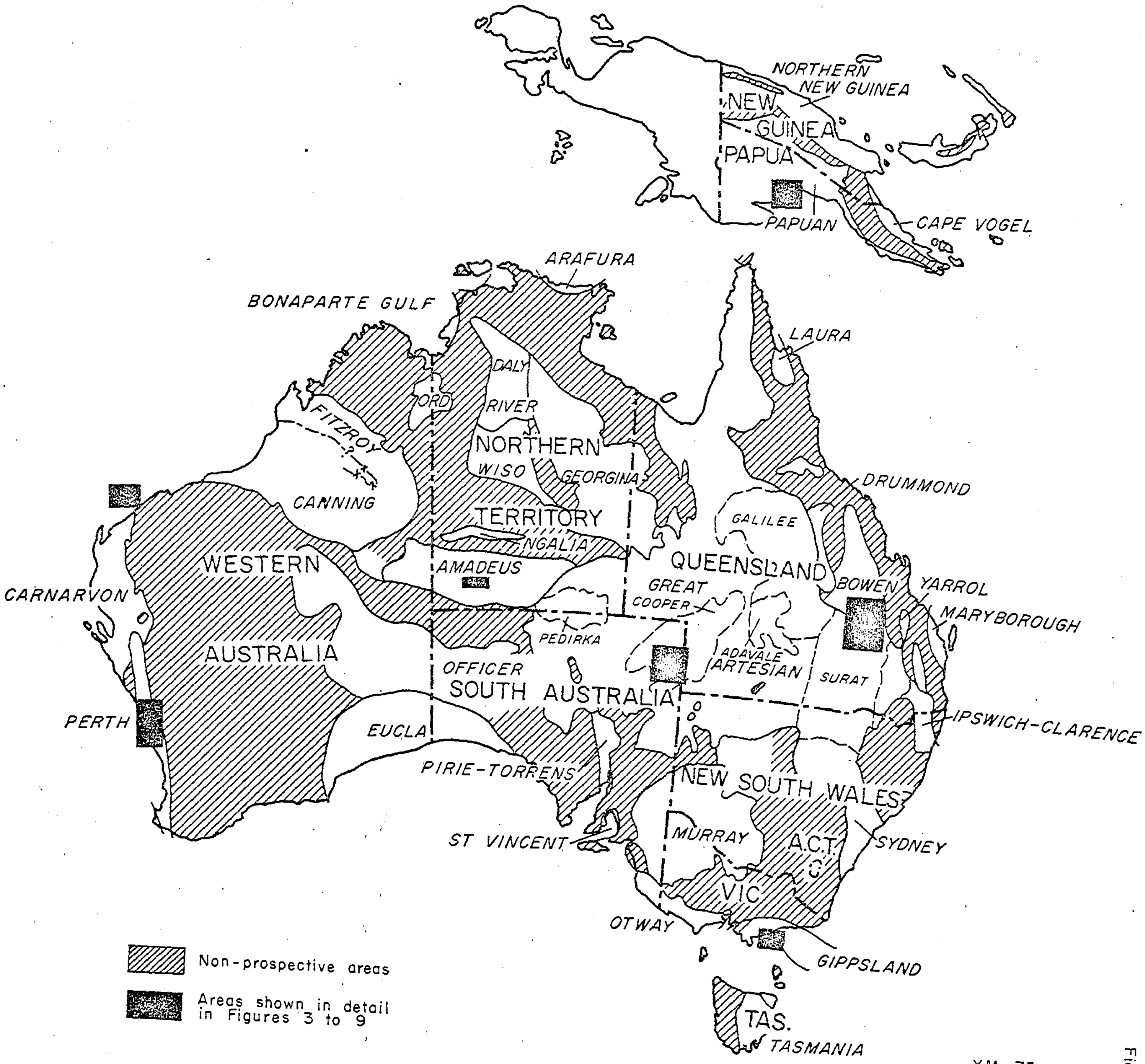
22. Variation of the ratio of pristane to phytane with correlation index

23. Effects of maturation on yield of distillation fractions in non-marine oils and condensates. *Data courtesy West Australian Petroleum Pty Ltd

24. Correlation curves for oils and condensates from the North Dandaragan Trough, Perth Basin; the Gippsland Basin; and the Cooper Basin

25. Correlation curves for oils and condensates from the Bowen and Surat Basins

26. Gas chromatograms of the saturated hydrocarbons obtained from the Moonie and Conloi oils, Surat Basin


NORTHERN NEW GUINEA
NEW GUINEA
PAPUA
PAPUAN
CAPE VOGEL
ARAFURA
BONAPARTE GULF
LAURA
DALY RIVER
ORD
FITZROY
NORTHERN TERRITORY
WISO
GEORGINA
CANNING
DRUMMOND
GALILEE
NGALIA
WESTERN AUSTRALIA
AMADEUS
QUEENSLAND
GREAT COOPER
BOWEN
YARROL
MARYBOROUGH
CARNARVON
PEDIRKA
ADAVALE
ARTESIAN
SURAT
OFFICER
SOUTH AUSTRALIA
IPSWICH-CLARENCE
PERTH
EUCLA
PIRIE-TORRENS
NEW SOUTH WALES
SYDNEY
ST VINCENT
MURRAY
A.C.T.
VIC
OTWAY
GIPPSLAND
TAS.
TASMANIA
▨ Non-prospective areas
▩ Areas shown in detail in Figures 3 to 9

XM-75

Fig. 1

Fig. 2

PERIOD	GIPPSLAND	COOPER	BOWEN	SURAT	GALILEE	AMADEUS	PERTH	CARNARVON	PAPUAN
MIOCENE									✸ ☼ ◒
OLIGOCENE	◒								
EOCENE	✸ ●								
PALAEOCENE	✸ ●								
CRETACEOUS							✺	◒ ✹ ✸	
JURASSIC				✸ ●			✸ ◒		✸
TRIASSIC			☼ ◒				☼ ◒	✸ ●	
PERMIAN		✸ ●	✺ ☼		◒		◒ ☼		
CARBONIFEROUS									
DEVONIAN									
SILURIAN									
ORDOVICIAN						✹ ✸ ☼			
INITIAL RESERVES									
Gas x 10^{12} cu ft	8·0	3·5	0·2		nil	1·9	0·6	15·1	1·8
Gas Liquids x 10^{6} bbls	637·5	269·2	1·4		nil	15·0	0·9	423·9	152
Oil x 10^{6} bbls	1738·4	44·1	21·6		nil	60·0	1·3	261·3	nil

☼ Gas well or field
✸ Condensate well or field
✺ Gas and oil show
◒ Oil show
● Oil well or field

XM – 76

Fig. 3

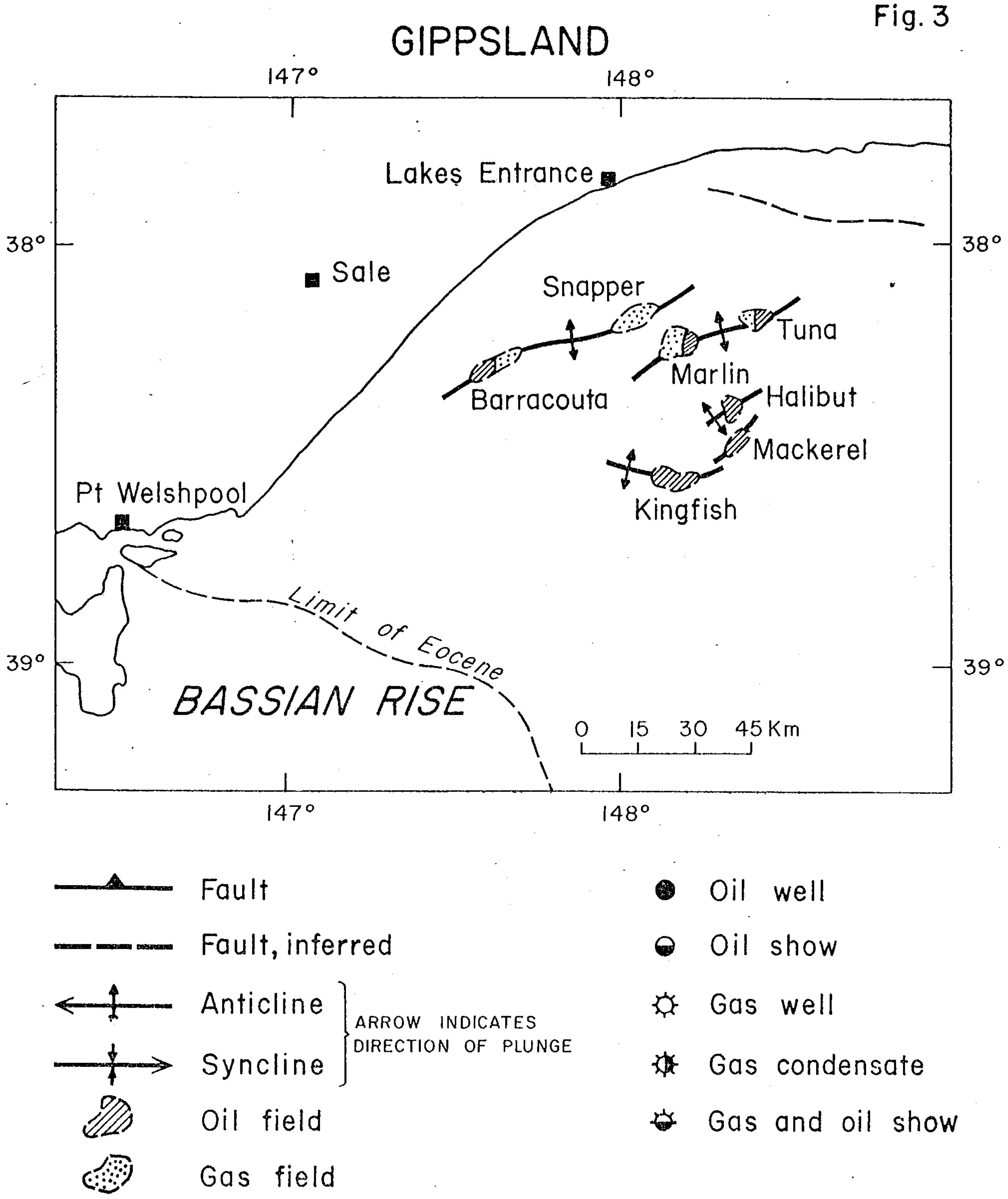
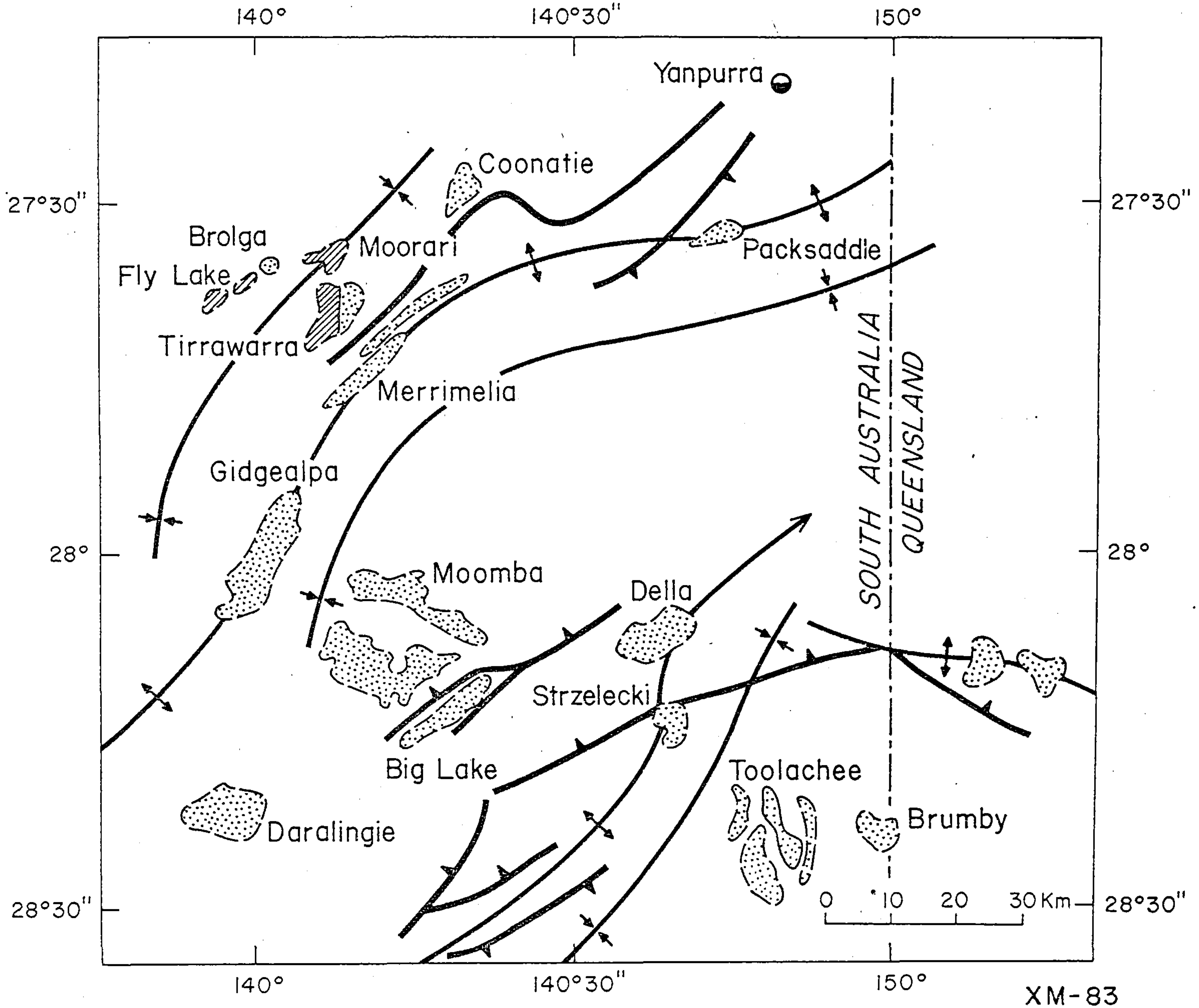

GIPPSLAND
147°
148°
38°
39°
Lakes Entrance
Sale
Snapper
Tuna
Marlin
Barracouta
Halibut
Mackerel
Kingfish
Pt Welshpool
Limit of Eocene
BASSIAN RISE
0 15 30 45 Km
Fault
Fault, inferred
Anticline
Syncline
ARROW INDICATES DIRECTION OF PLUNGE
Oil field
Gas field
Oil well
Oil show
Gas well
Gas condensate
Gas and oil show

Fig.4

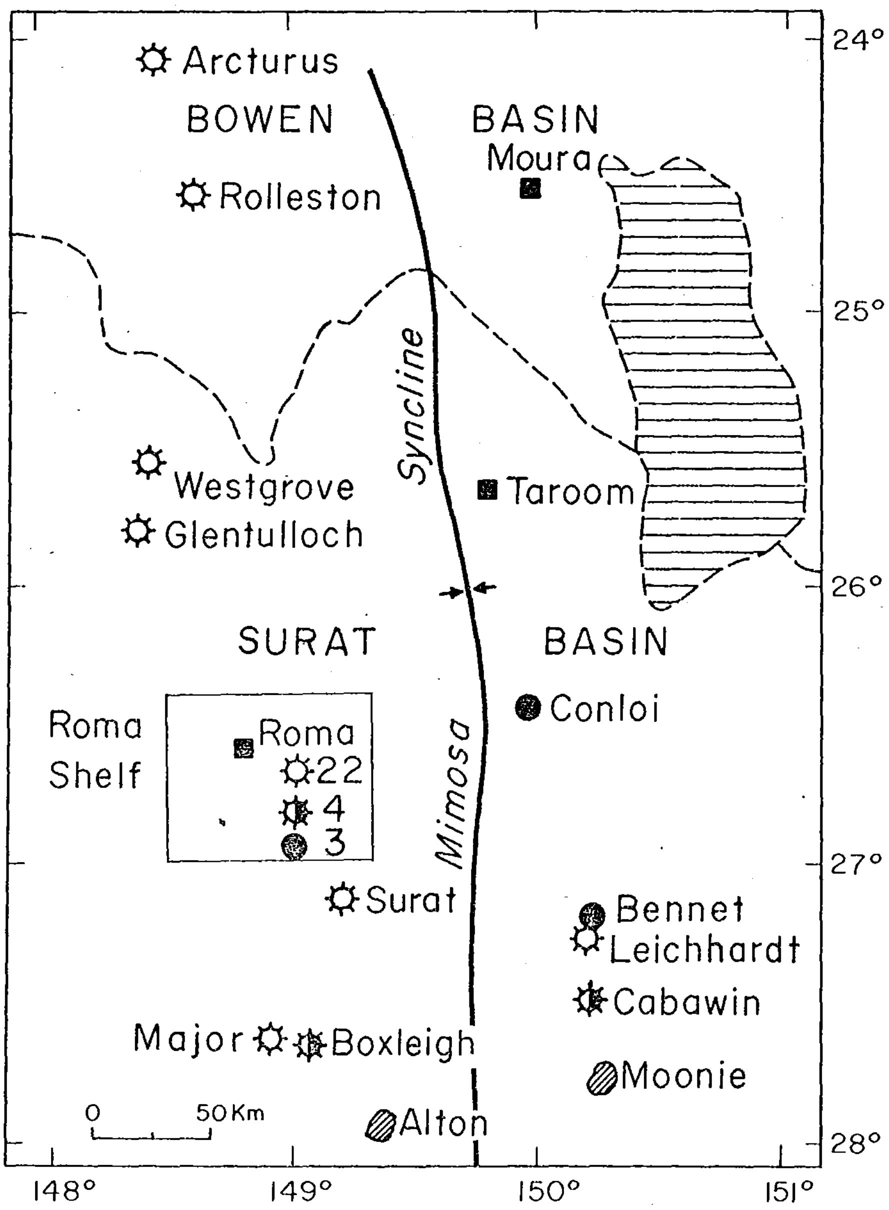
COOPER



XM-83

Fig.5

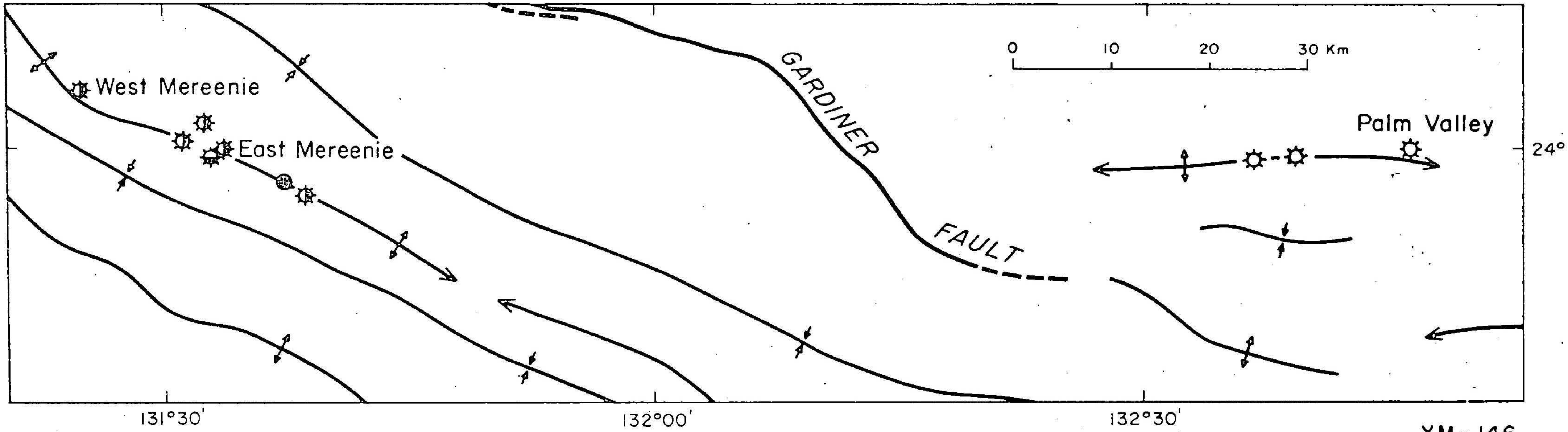
BOWEN – SURAT



XM-145

Fig. 6

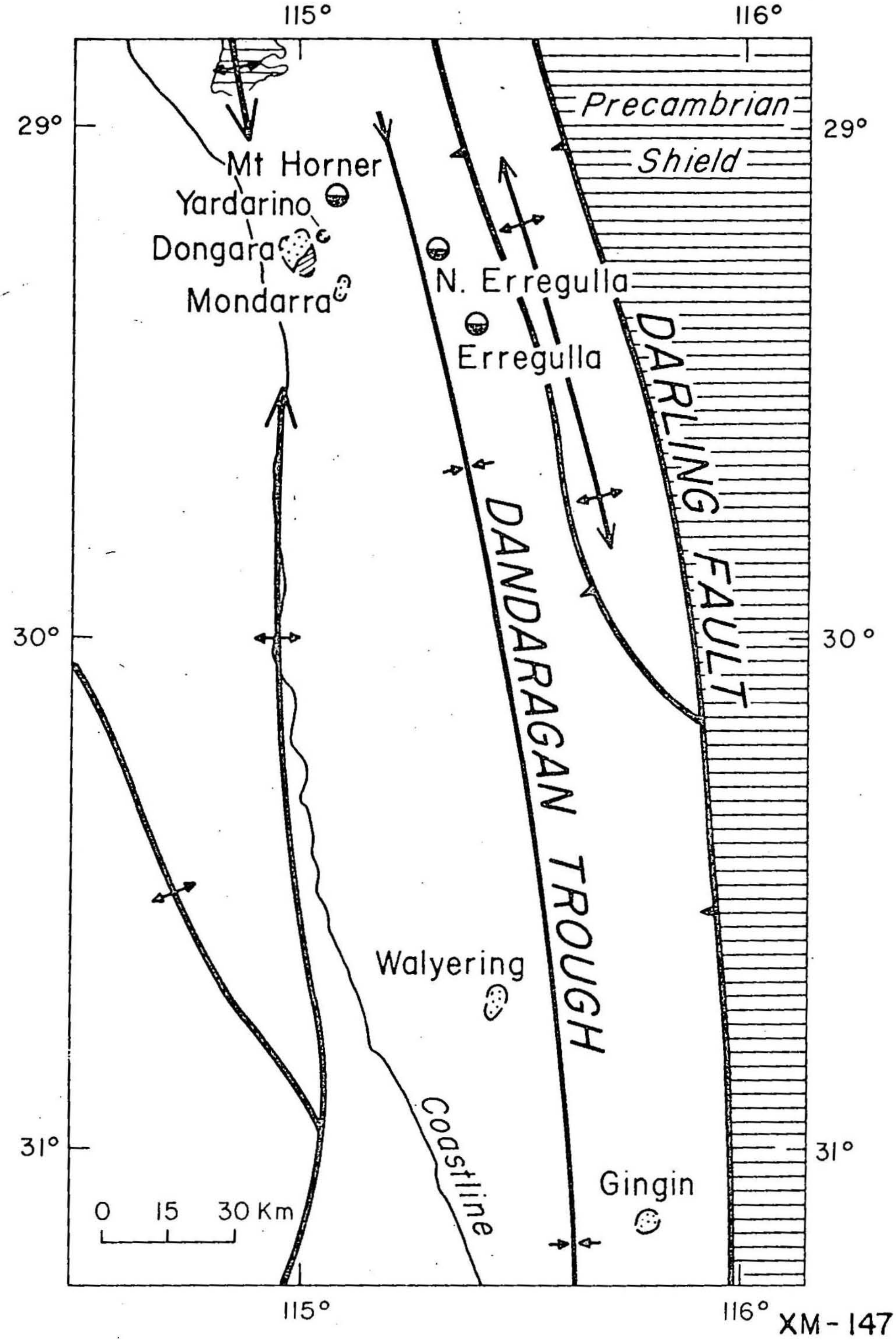
AMADEUS



XM-146

Fig.7

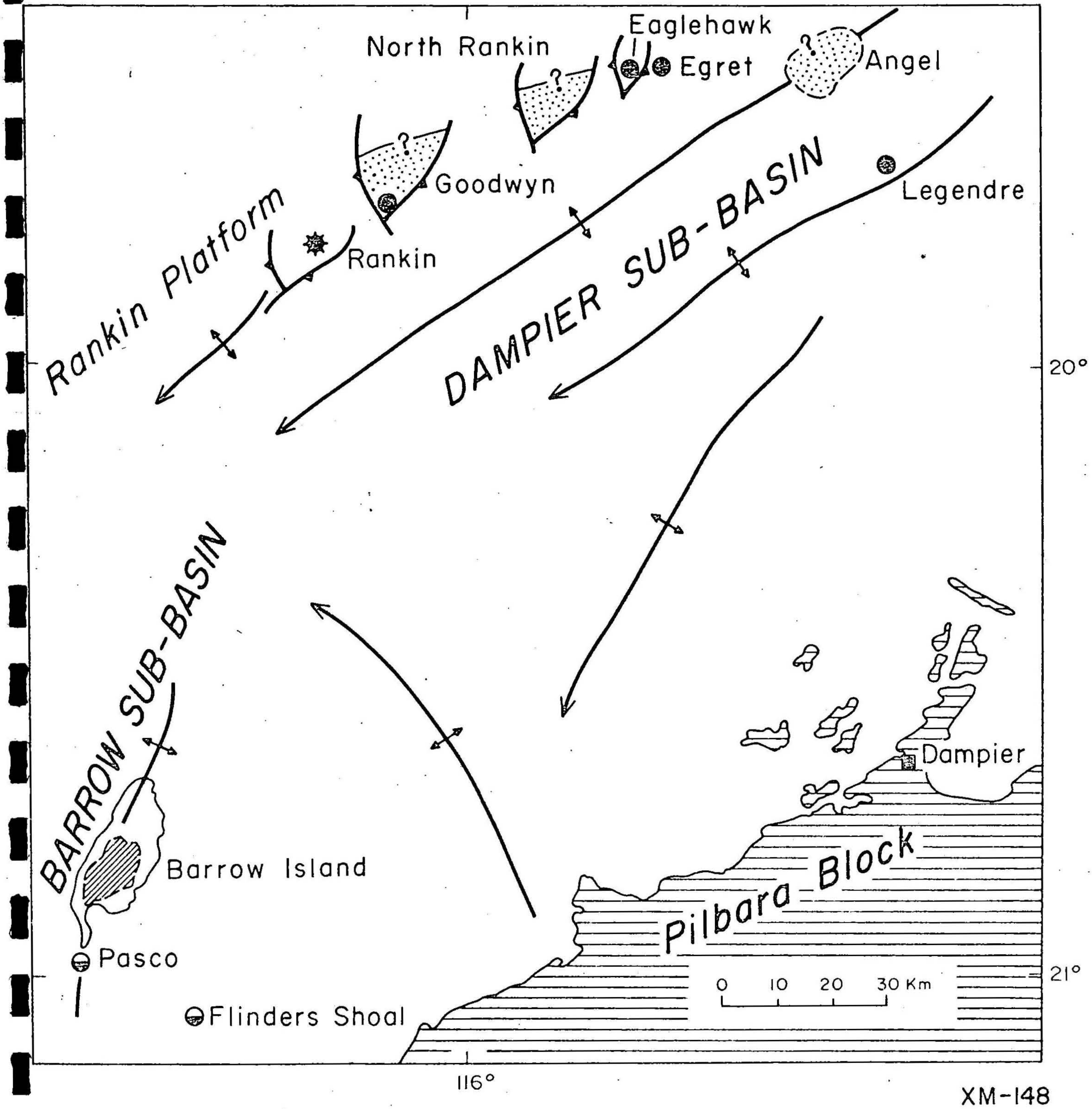
PERTH



XM-147

Fig. 8

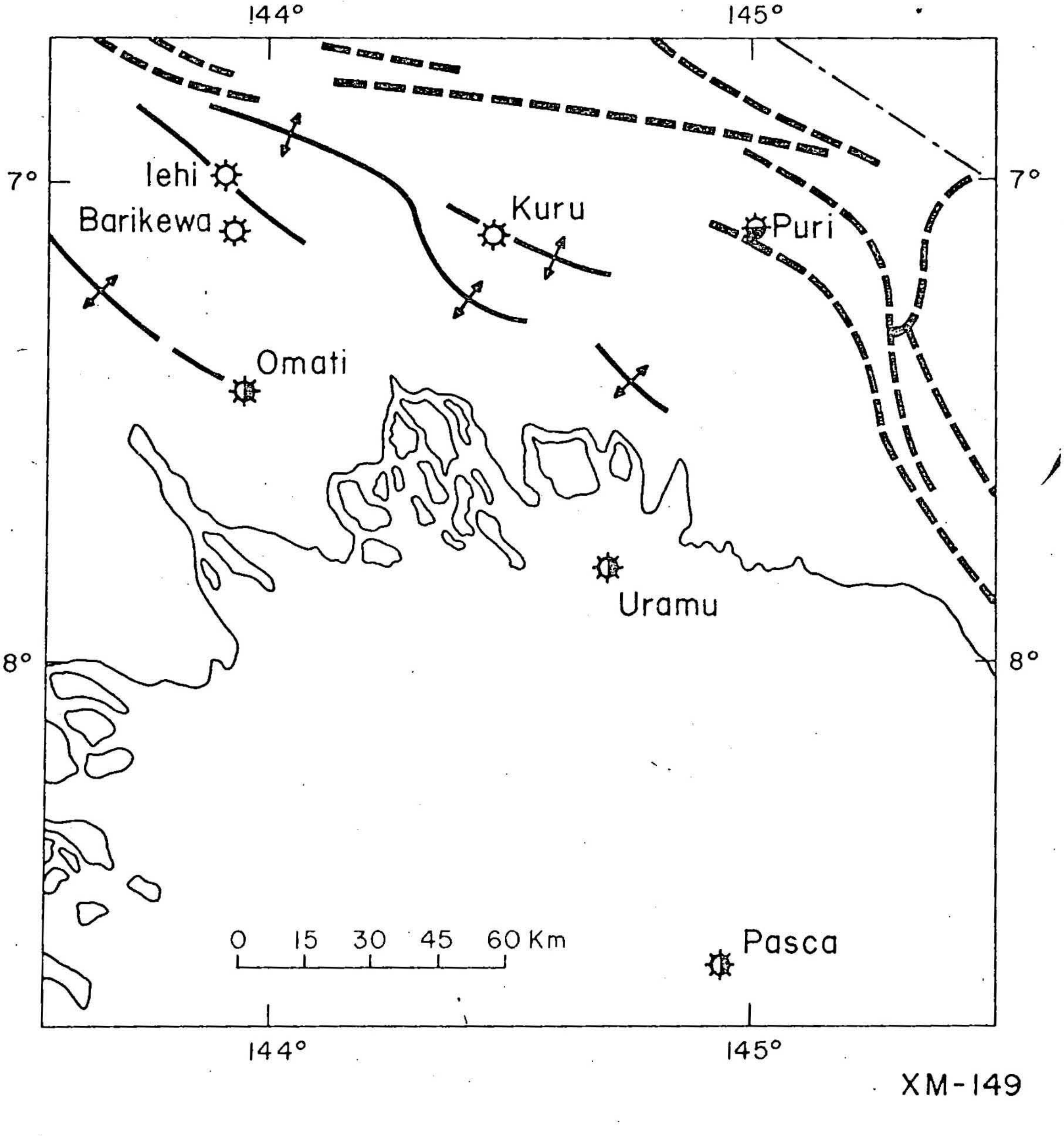
CARNARVON



XM-148

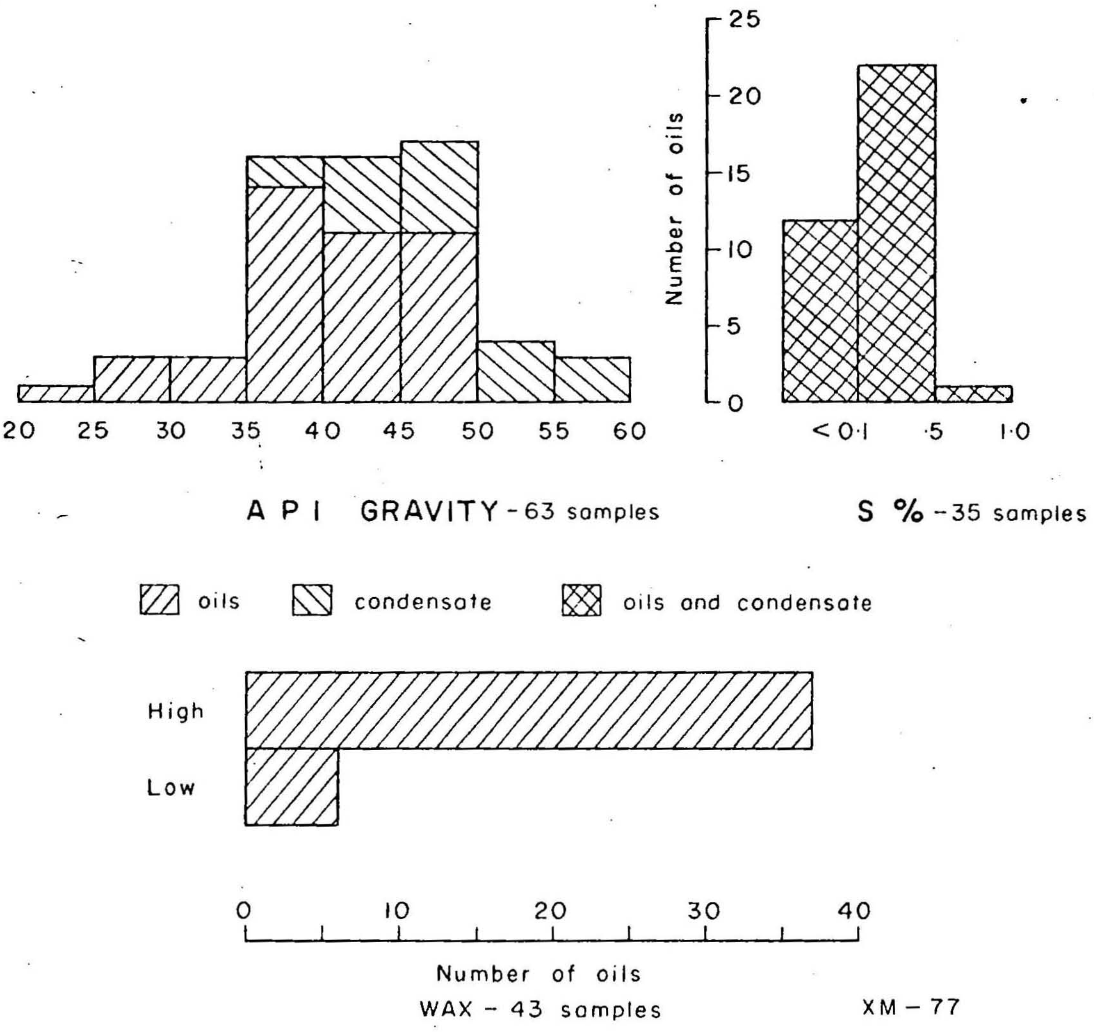
Fig. 9

PAPUAN



XM-149

Fig. 10



25
20
15
10
5
0
Number of oils
20
25
30
35
40
45
50
55
60
< 0·1
·5
1·0
A P I GRAVITY - 63 samples
S % - 35 samples
▨ oils
▧ condensate
▩ oils and condensate
High
Low
0
10
20
30
40
Number of oils
WAX - 43 samples
XM - 77

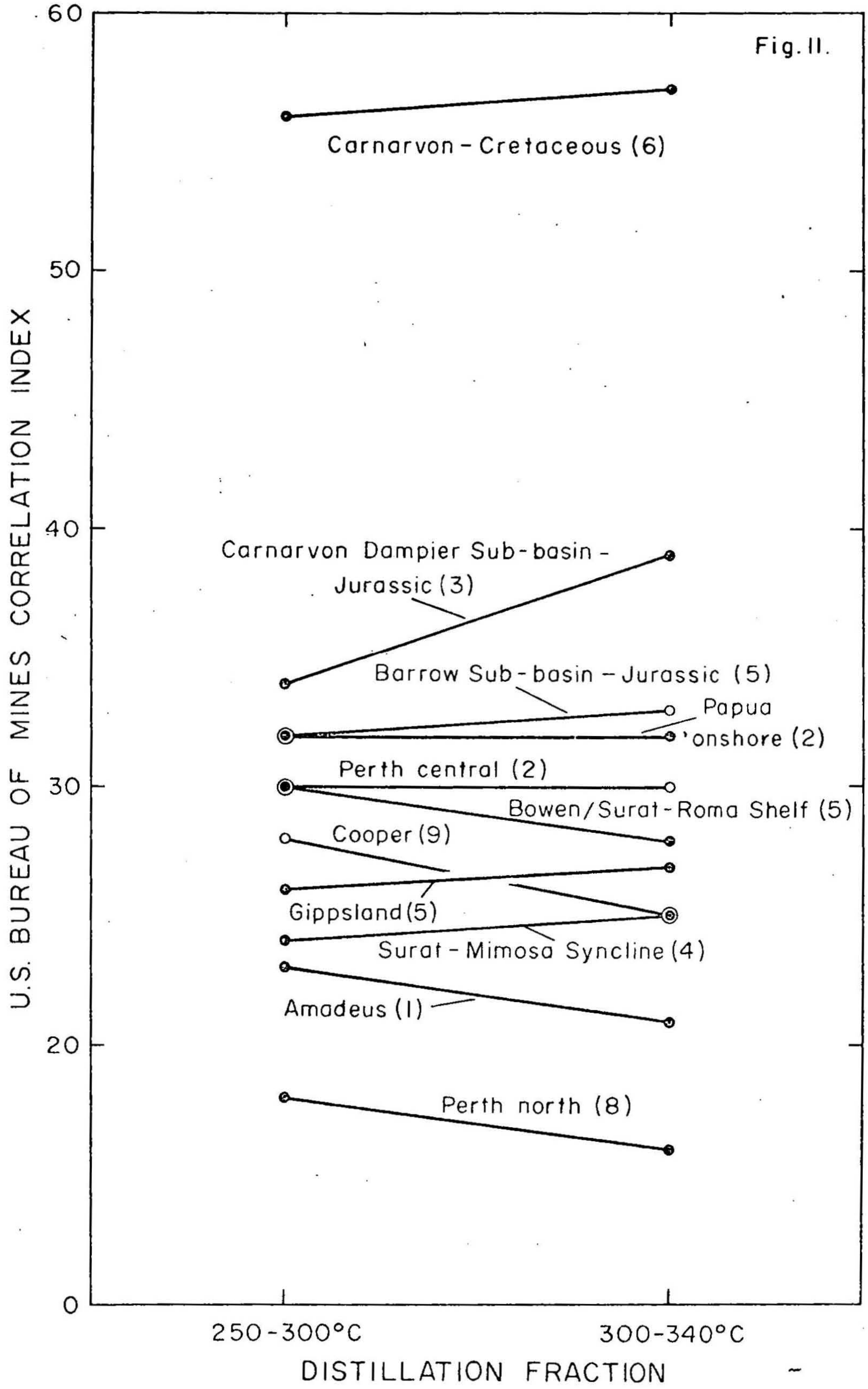
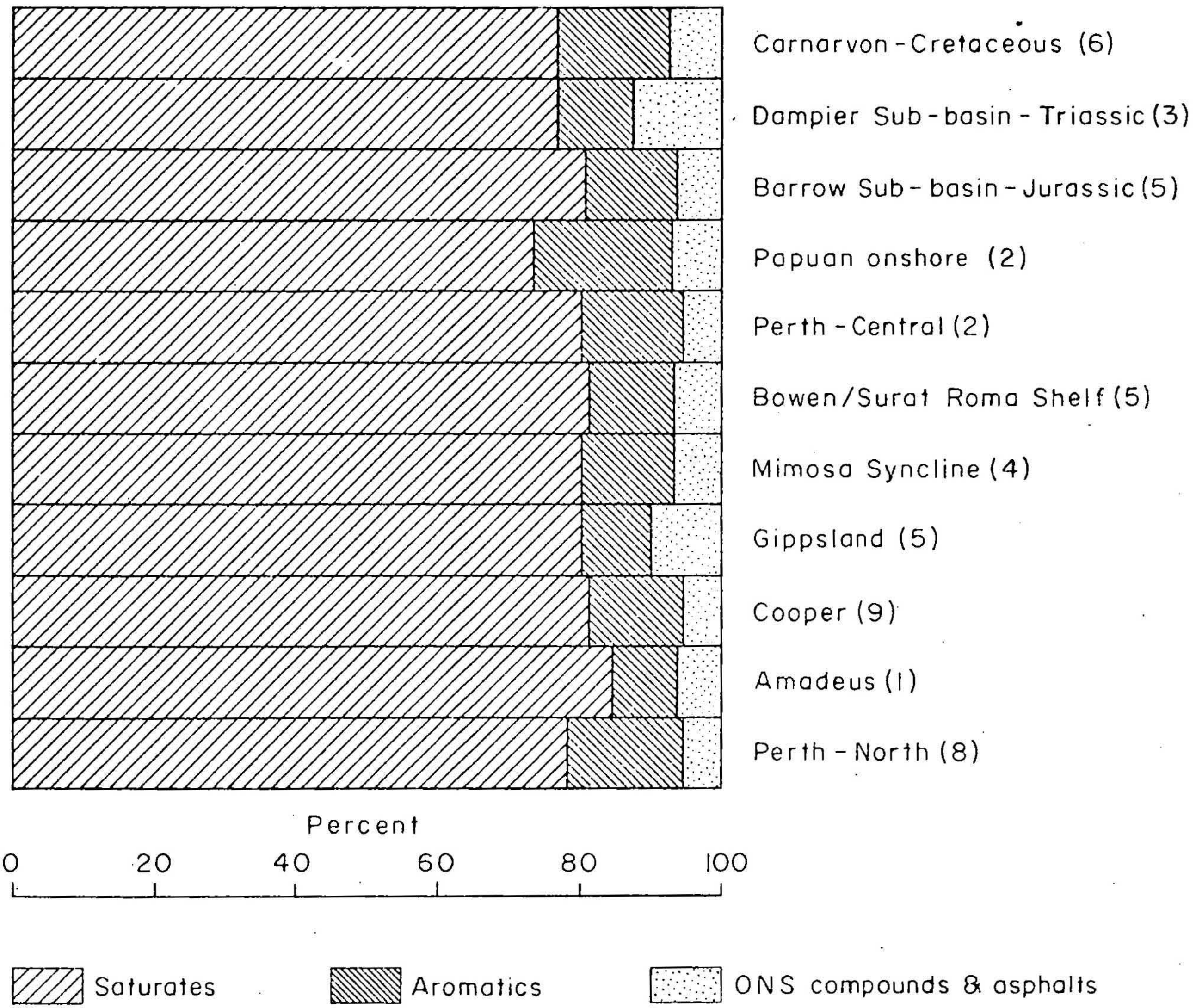

60
50
40
30
20
0
U.S. BUREAU OF MINES CORRELATION INDEX
Carnarvon - Cretaceous (6)
Carnarvon Dampier Sub-basin - Jurassic (3)
Barrow Sub-basin - Jurassic (5)
Papua onshore (2)
Perth central (2)
Bowen/Surat - Roma Shelf (5)
Cooper (9)
Gippsland (5)
Surat - Mimosa Syncline (4)
Amadeus (1)
Perth north (8)
250-300°C
300-340°C
DISTILLATION FRACTION

Fig. 11.

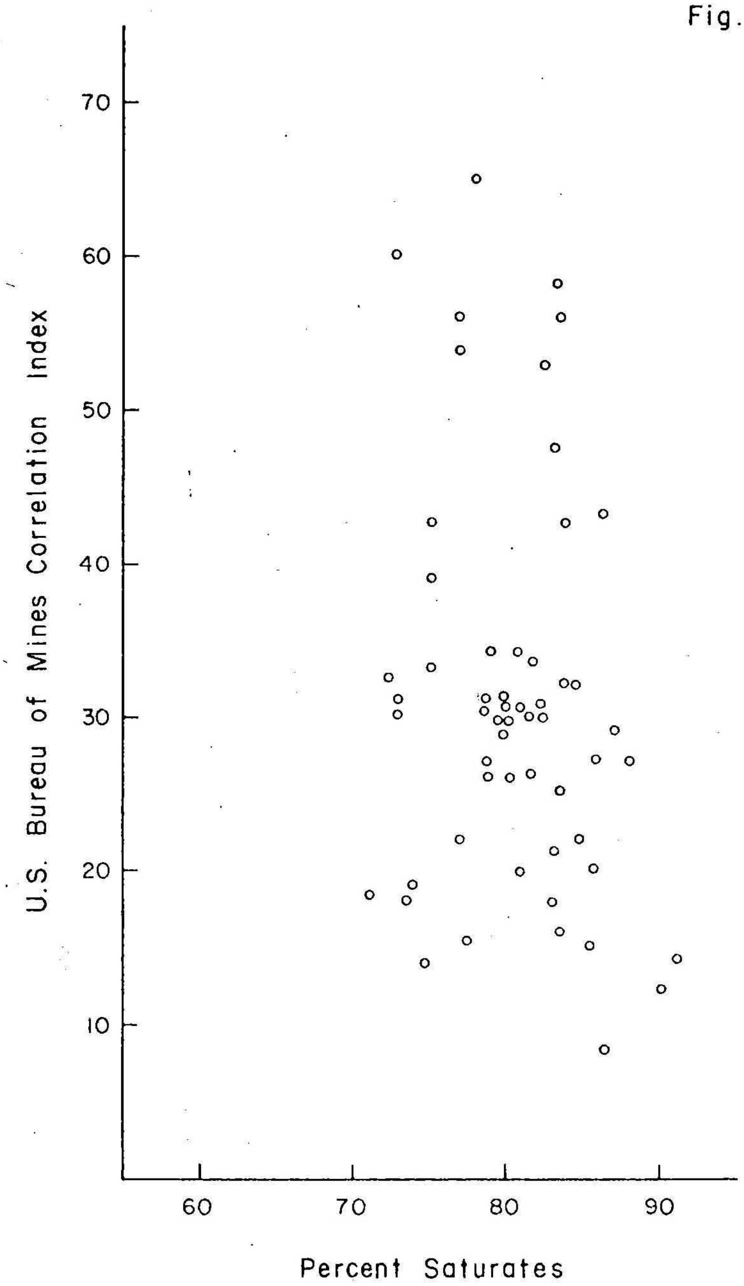
XM - 78

Fig. 12.


Carnarvon - Cretaceous (6)
Dampier Sub-basin - Triassic (3)
Barrow Sub-basin - Jurassic (5)
Papuan onshore (2)
Perth - Central (2)
Bowen/Surat Roma Shelf (5)
Mimosa Syncline (4)
Gippsland (5)
Cooper (9)
Amadeus (1)
Perth - North (8)
Percent
0
20
40
60
80
100
Saturates
Aromatics
ONS compounds & asphalts

XM — 73

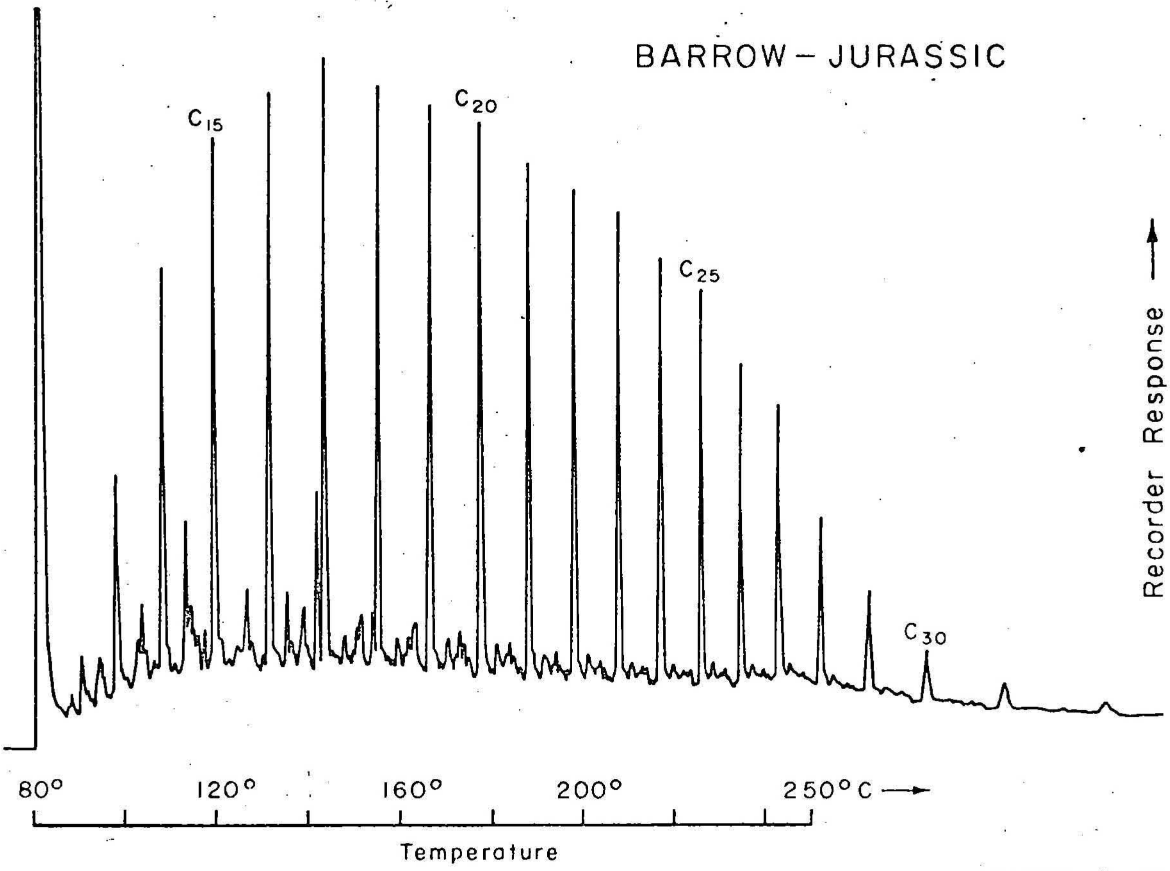
Fig. 13



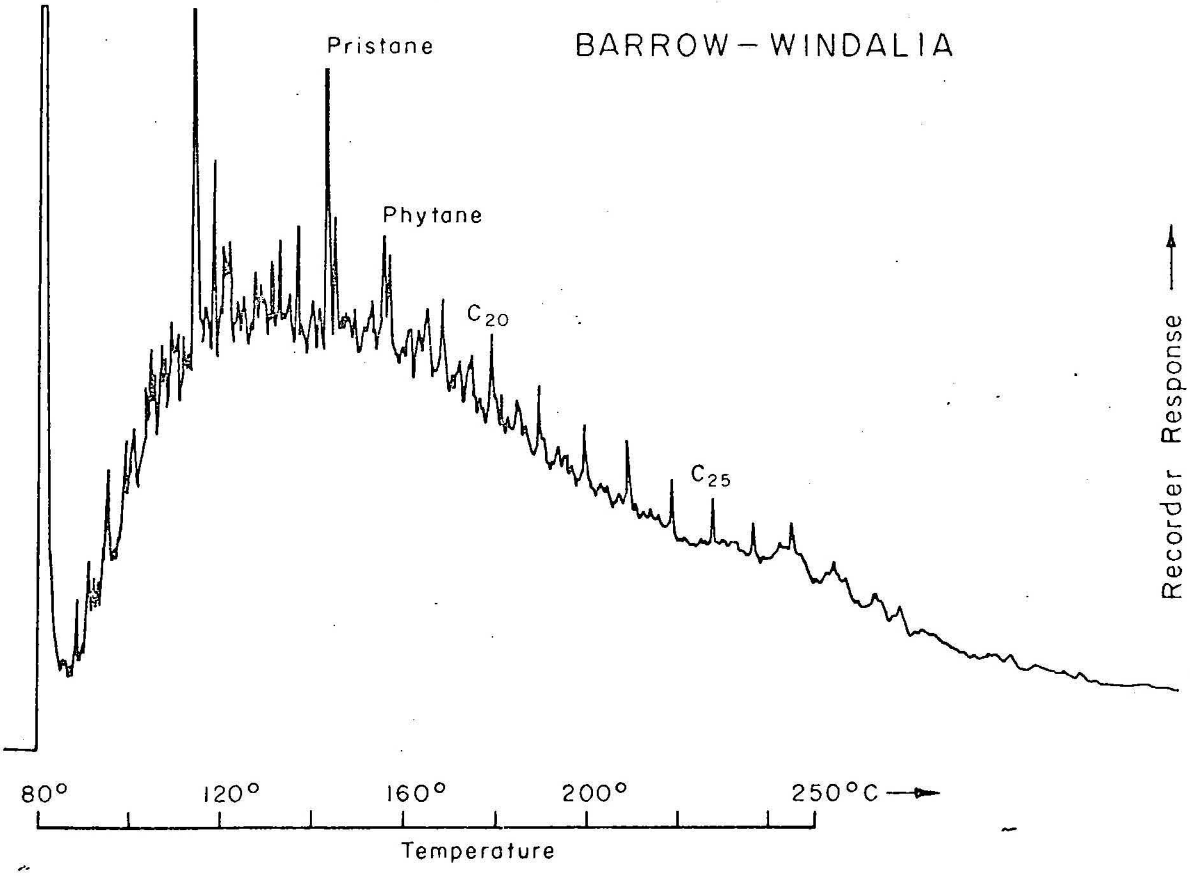
U.S. Bureau of Mines Correlation Index
70
60
50
40
30
20
10
60
70
80
90
Percent Saturates

XM - 71

Fig. 14

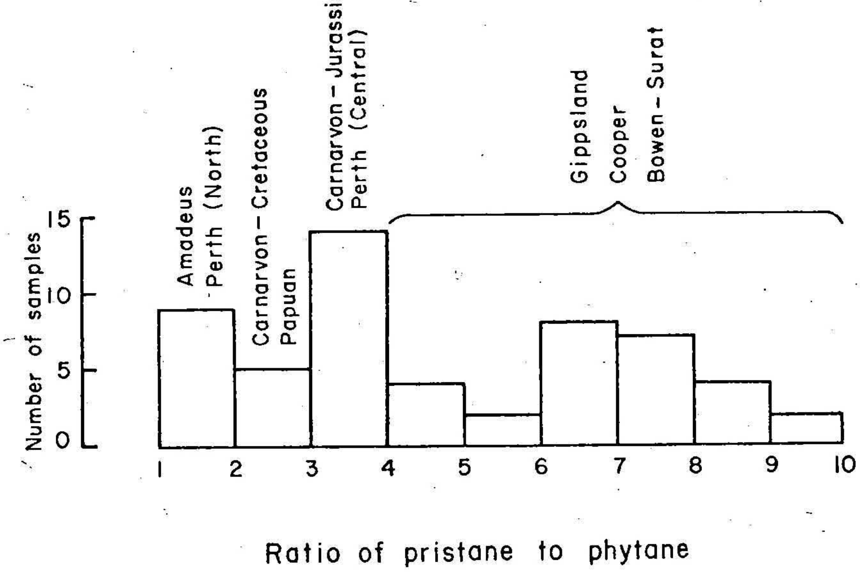


XAUS-2-156L



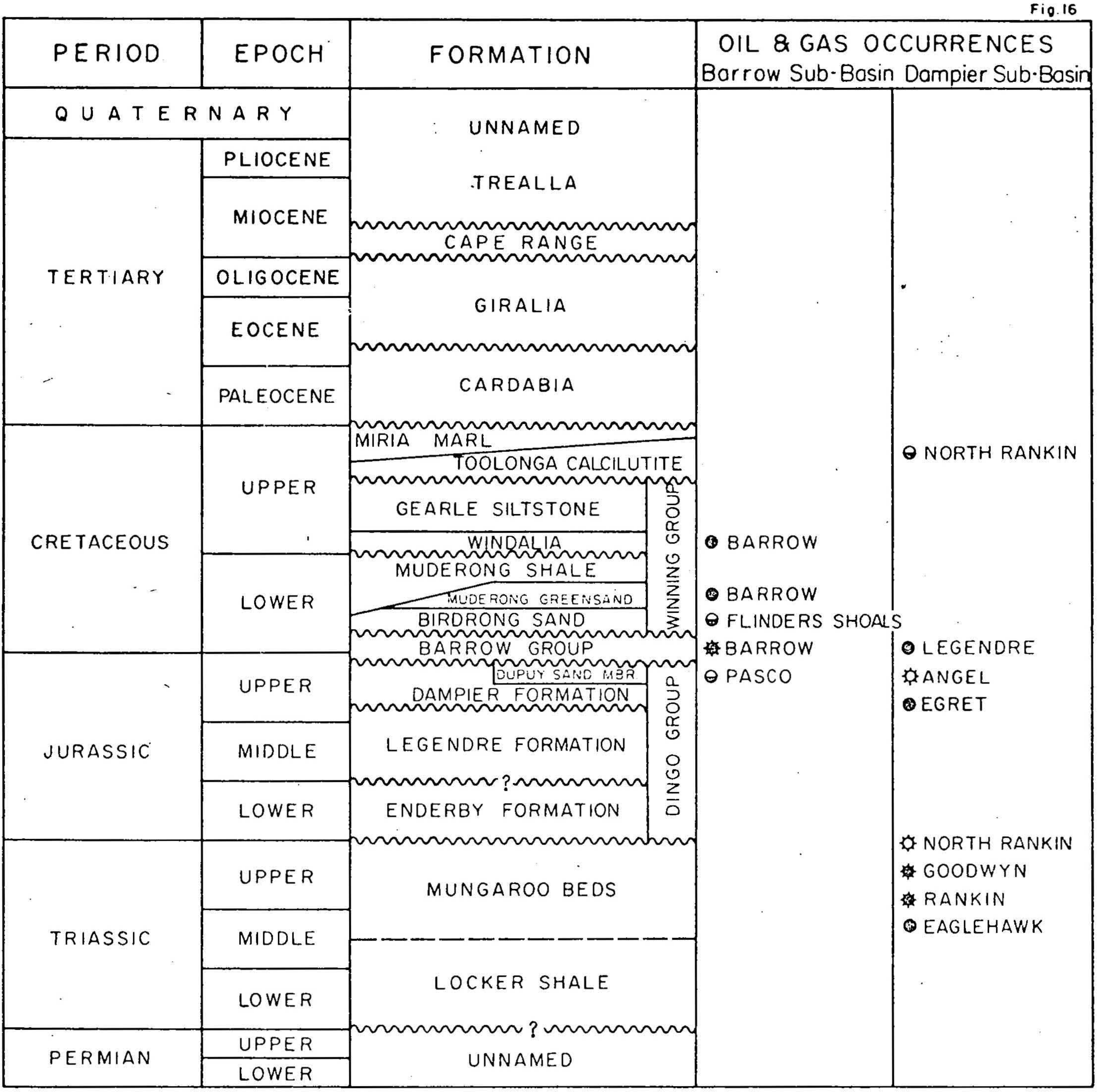
XAUS-2-156M

Fig. 15


Number of samples
15
10
5
0
Amadeus
Perth (North)
Carnarvon - Cretaceous
Papuan
Carnarvon - Jurassic
Perth (Central)
Gippsland
Cooper
Bowen - Surat
1
2
3
4
5
6
7
8
9
10
Ratio of pristane to phytane

XM - 72

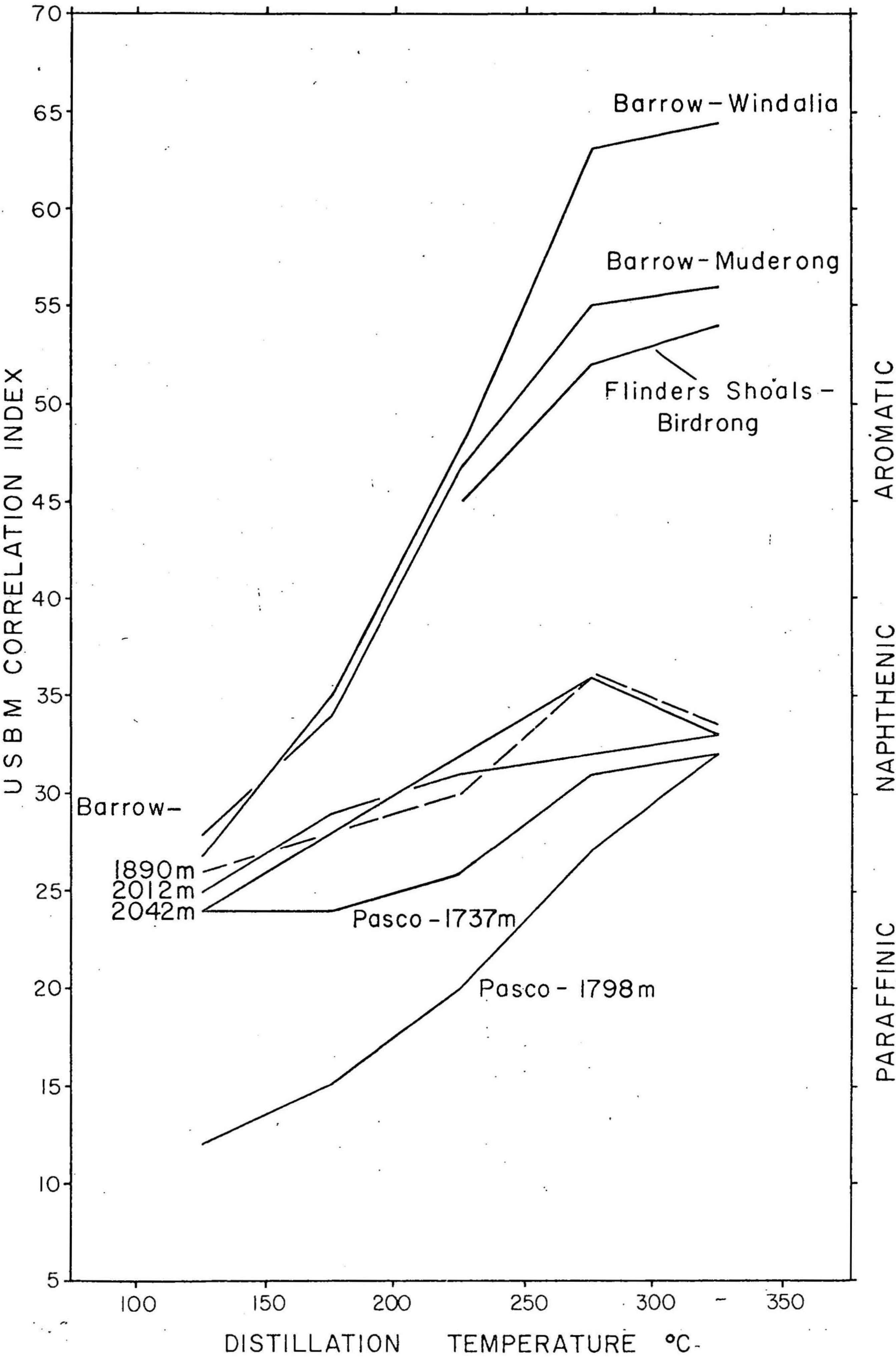
Fig.16



X-M-55

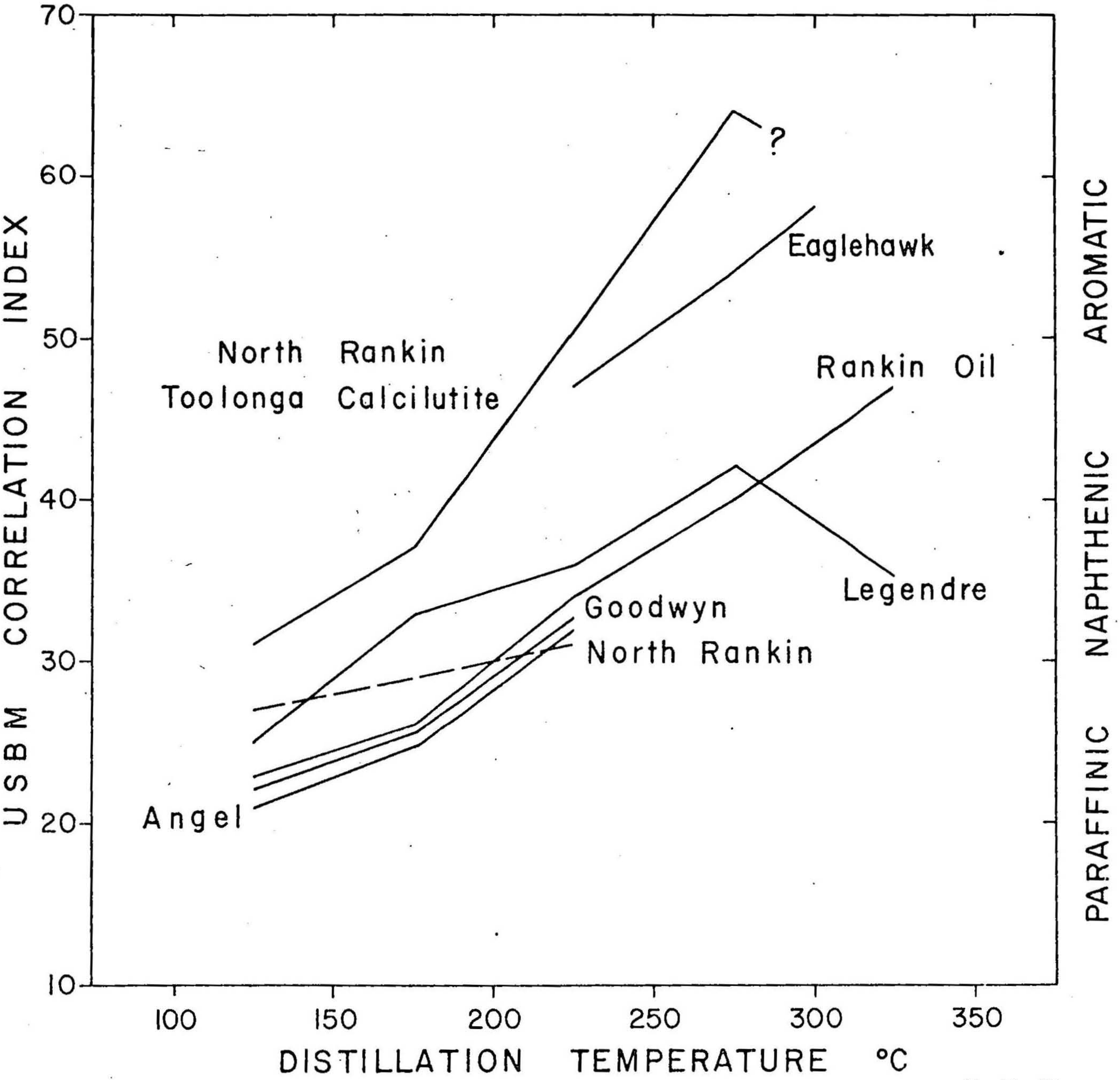
Stratigraphic distribution of hydrocarbon occurrences in the Carnarvon Basin

Fig. 17


USBM CORRELATION INDEX
70
65
60
55
50
45
40
35
30
25
20
15
10
5
100
150
200
250
300
350
DISTILLATION TEMPERATURE °C
Barrow - Windalia
Barrow - Muderong
Flinders Shoals - Birdrong
Barrow-
1890m
2012m
2042m
Pasco - 1737m
Pasco - 1798m
AROMATIC
NAPHTHENIC
PARAFFINIC

XM - 66D

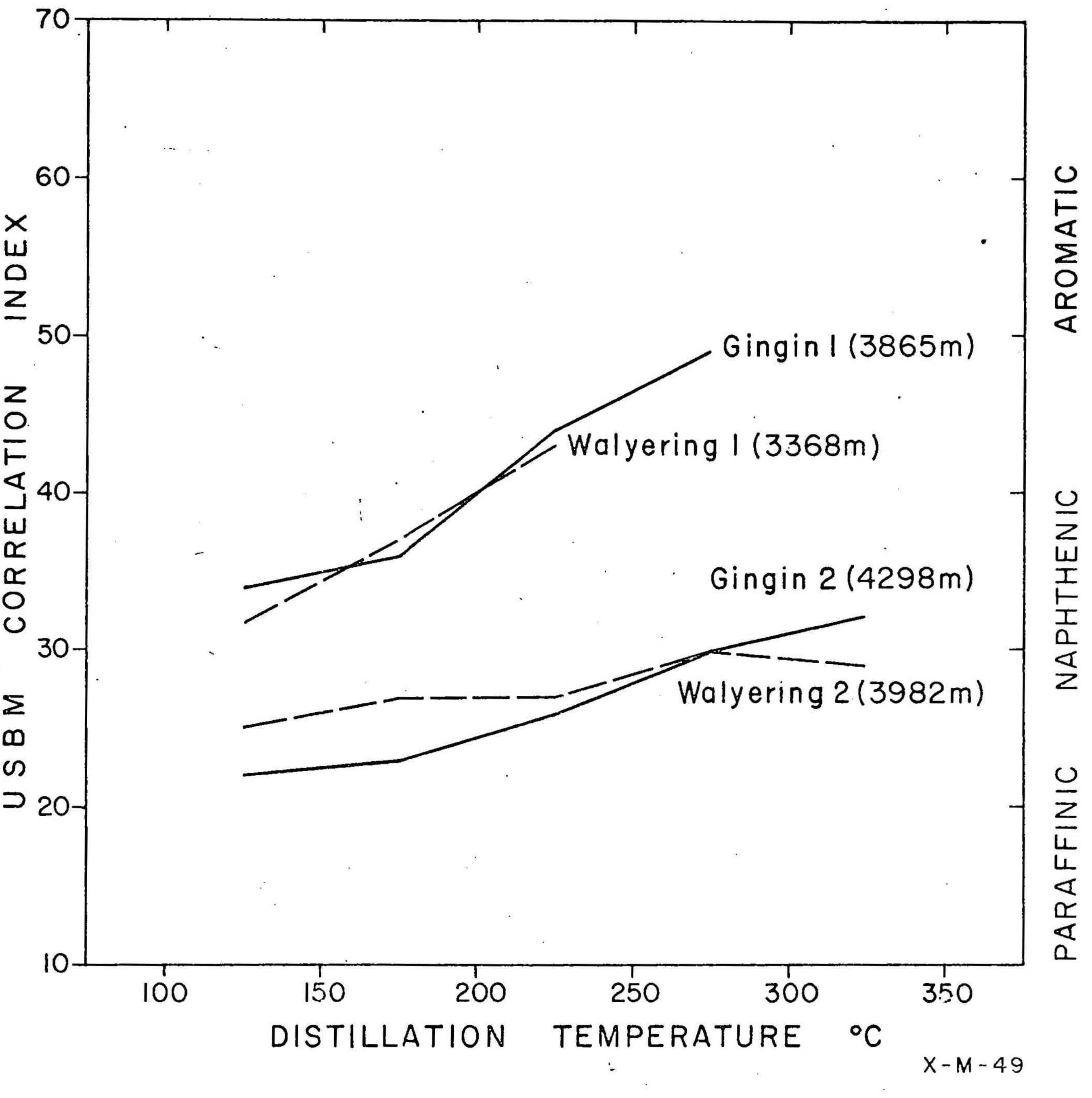
Fig. 18



70
60
50
40
30
20
10
USBM CORRELATION INDEX
100
150
200
250
300
350
DISTILLATION TEMPERATURE °C
?
Eaglehawk
North Rankin
Toolonga Calcilutite
Rankin Oil
Legendre
Goodwyn
North Rankin
Angel
AROMATIC
NAPHTHENIC
PARAFFINIC

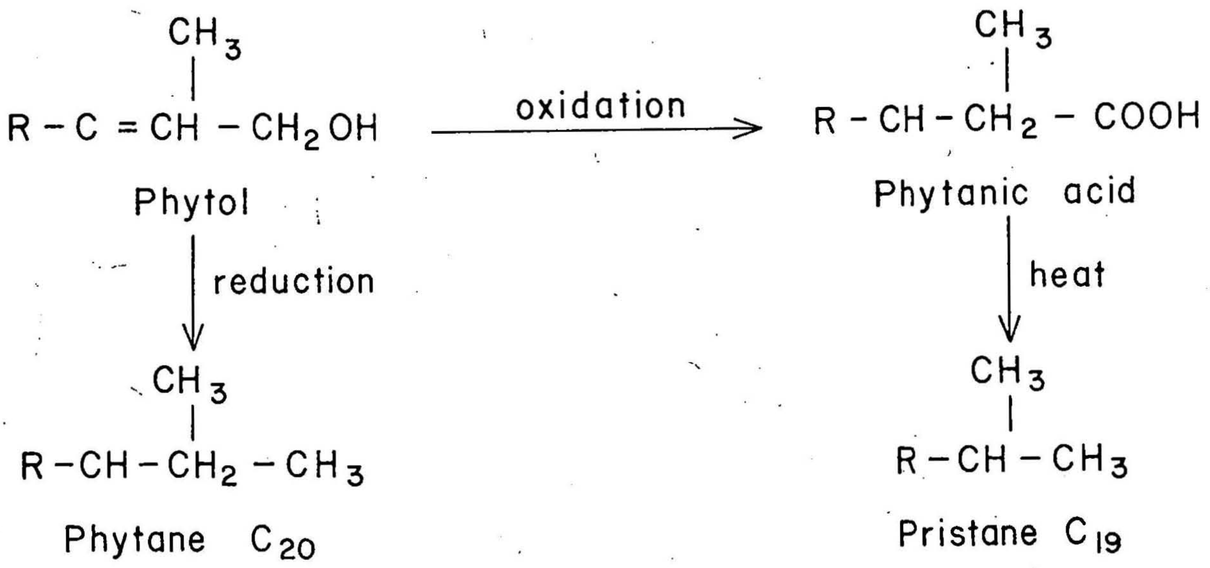
X-M-51

Fig. 19


70
60
50
40
30
20
10
USBM CORRELATION INDEX
100
150
200
250
300
350
DISTILLATION TEMPERATURE °C
AROMATIC
NAPHTHENIC
PARAFFINIC
Gingin I (3865m)
Walyering I (3368m)
Gingin 2 (4298m)
Walyering 2 (3982m)

X-M-49

Fig.20



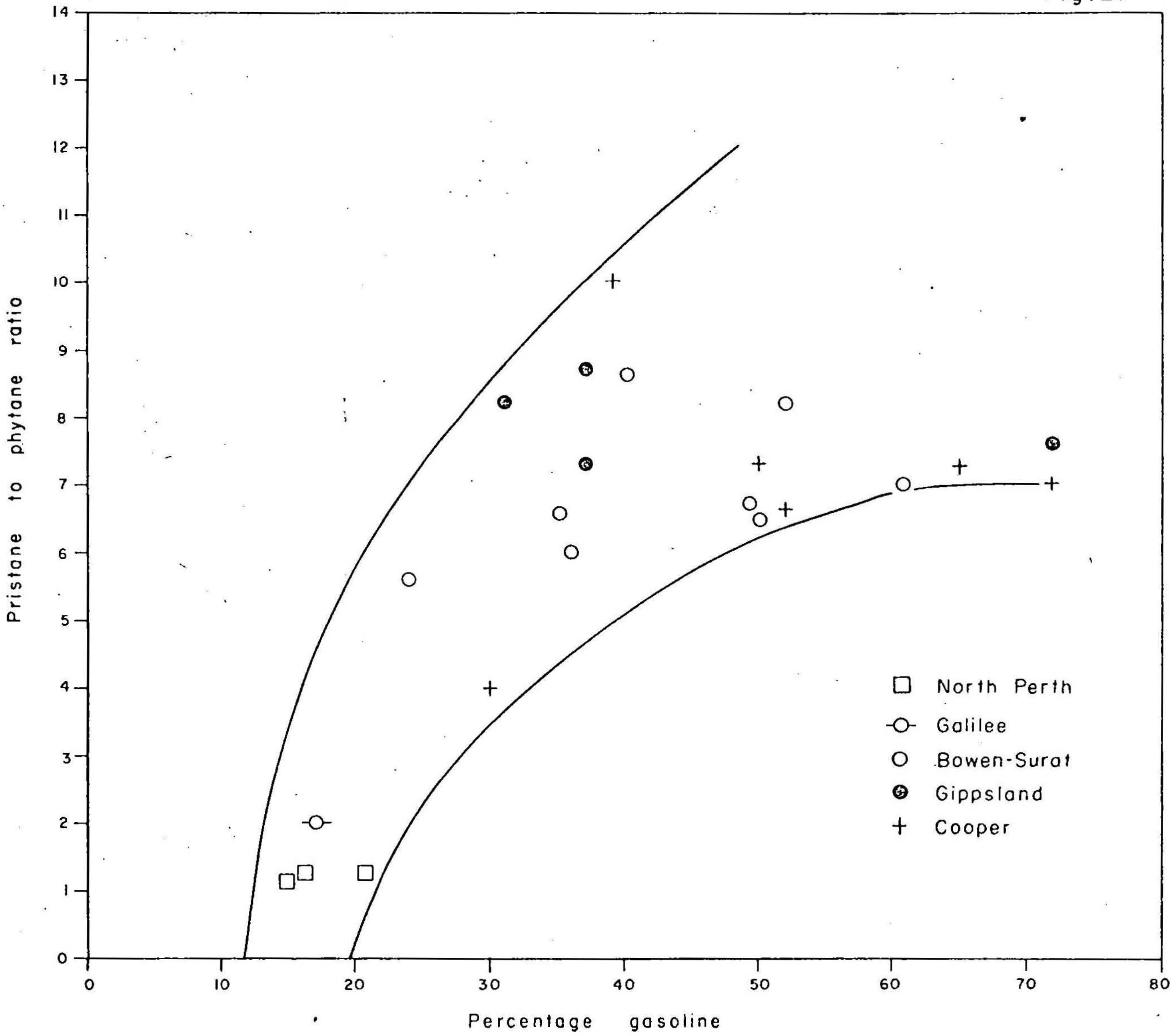
$R-\overset{\overset{CH_3}{|}}{C}=CH-CH_2OH \xrightarrow{\text{oxidation}} R-\overset{\overset{CH_3}{|}}{CH}-CH_2-COOH$

$R-\overset{\overset{CH_3}{|}}{CH}-CH_2-CH_3$ Phytane C_{20}

$R-\overset{\overset{CH_3}{|}}{CH}-CH_3$ Pristane C_{19}

XM-80

Fig.21



Pristane to phytane ratio
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
Percentage gasoline
0
10
20
30
40
50
60
70
80
□ North Perth
-○- Galilee
○ Bowen-Surat
● Gippsland
+ Cooper

XM - 74

Fig. 22

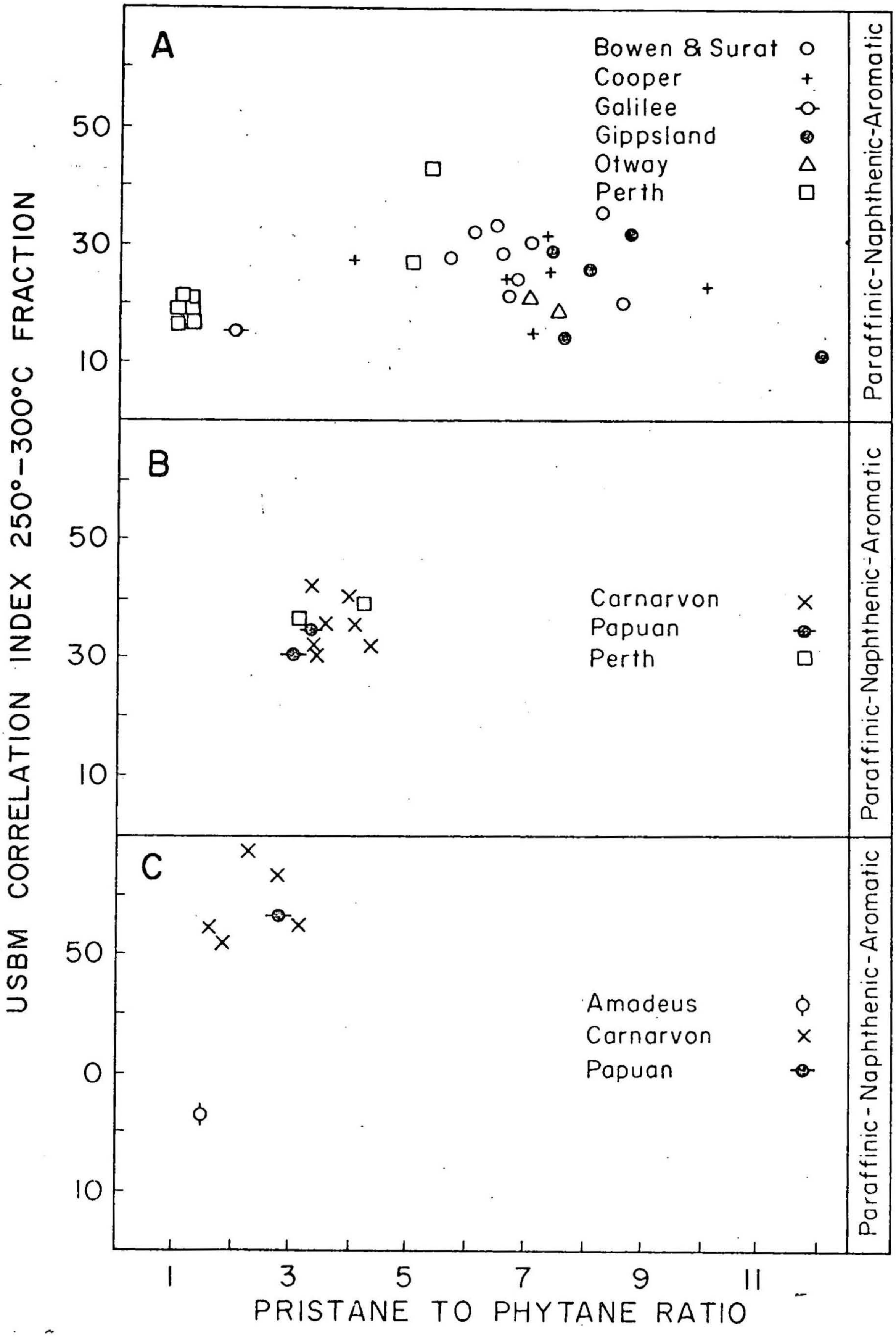
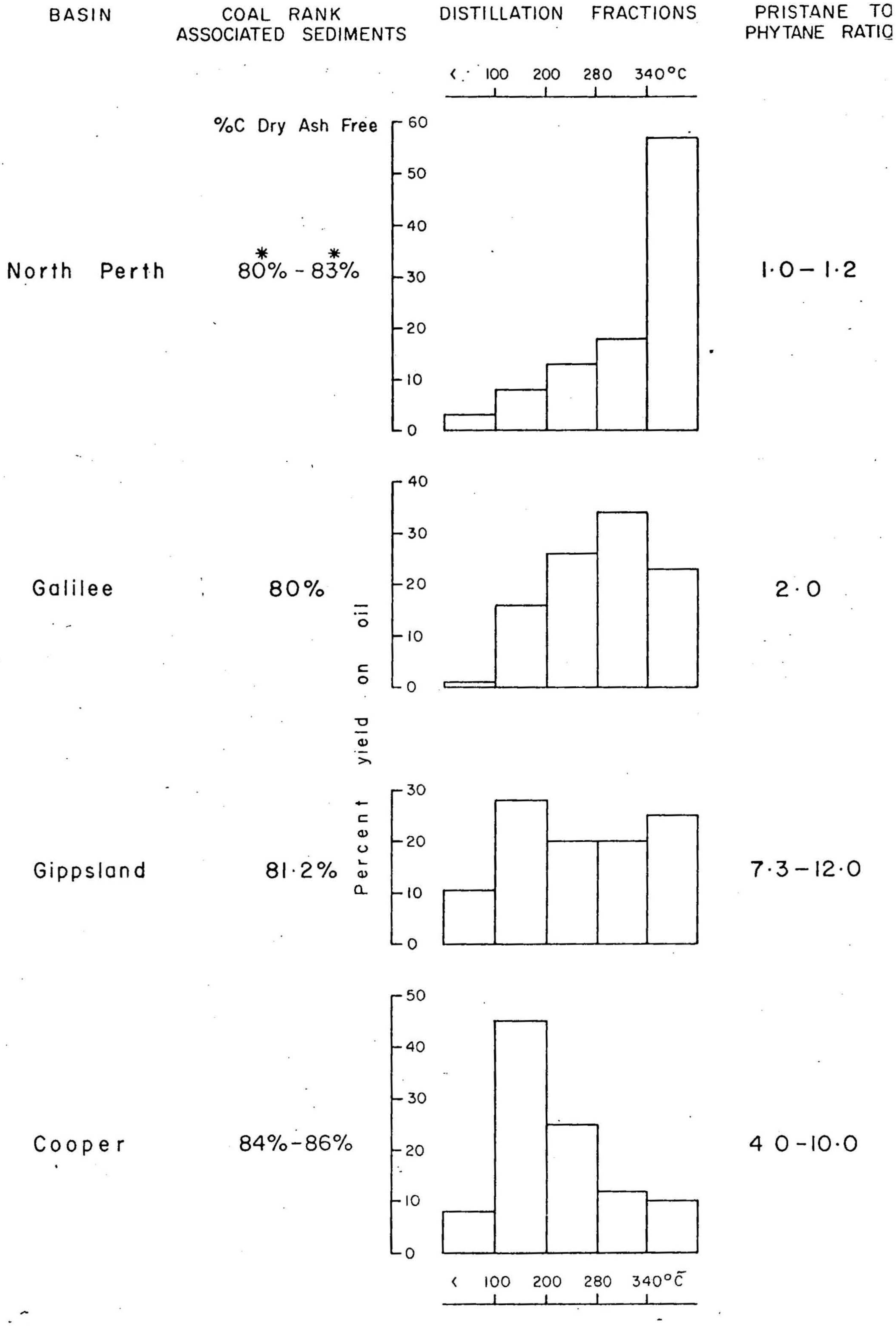

A
Bowen & Surat ○
Cooper +
Galilee -○-
Gippsland ●
Otway △
Perth □
Paraffinic-Naphthenic-Aromatic
B
Carnarvon ×
Papuan -●-
Perth □
Paraffinic-Naphthenic-Aromatic
C
Amadeus ф
Carnarvon ×
Papuan -●-
Paraffinic-Naphthenic-Aromatic
50
30
10
50
30
10
50
0
10
USBM CORRELATION INDEX 250°-300°C FRACTION
1
3
5
7
9
11
PRISTANE TO PHYTANE RATIO

Fig. 23


BASIN
COAL RANK
ASSOCIATED SEDIMENTS
DISTILLATION FRACTIONS
PRISTANE TO
PHYTANE RATIO
< 100 200 280 340°C
%C Dry Ash Free
60
50
40
30
20
10
0
North Perth
80%* - 83%*
1·0 – 1·2
40
30
20
10
0
Galilee
80%
2·0
Percent yield on oil
30
20
10
0
Gippsland
81·2%
7·3 – 12·0
50
40
30
20
10
0
Cooper
84%–86%
4 0 – 10·0
< 100 200 280 340°C

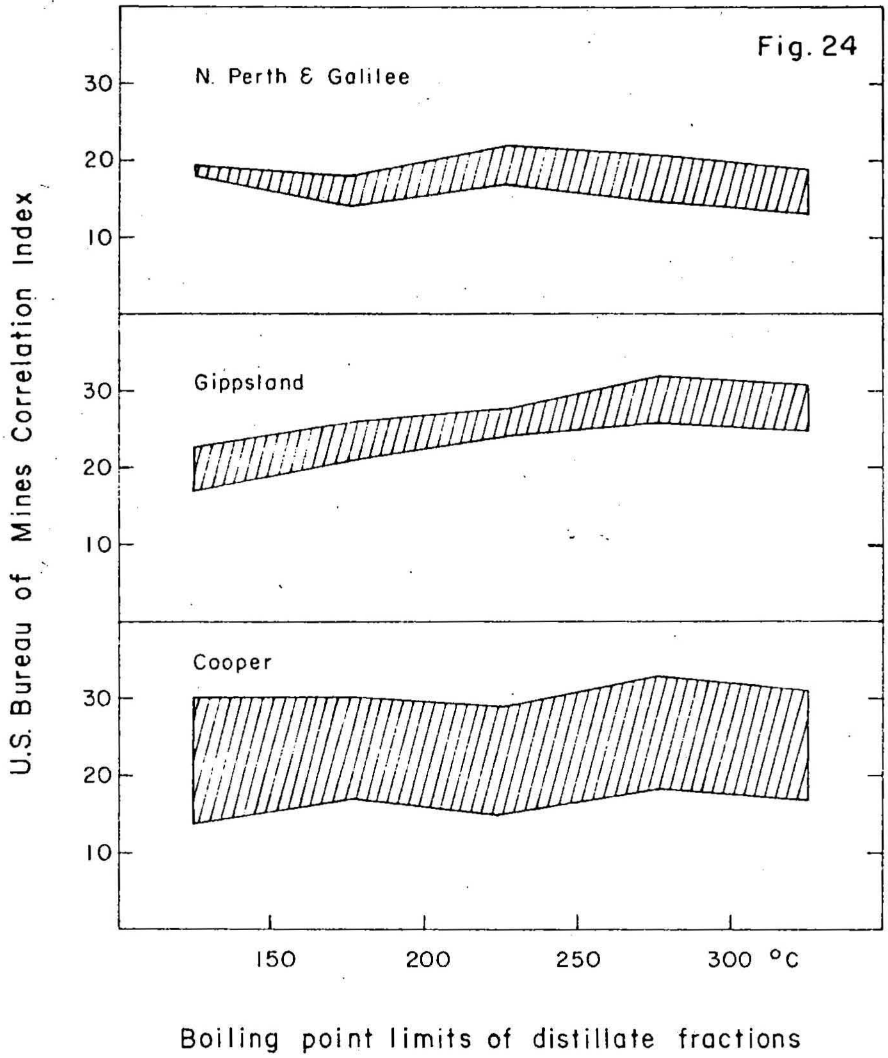
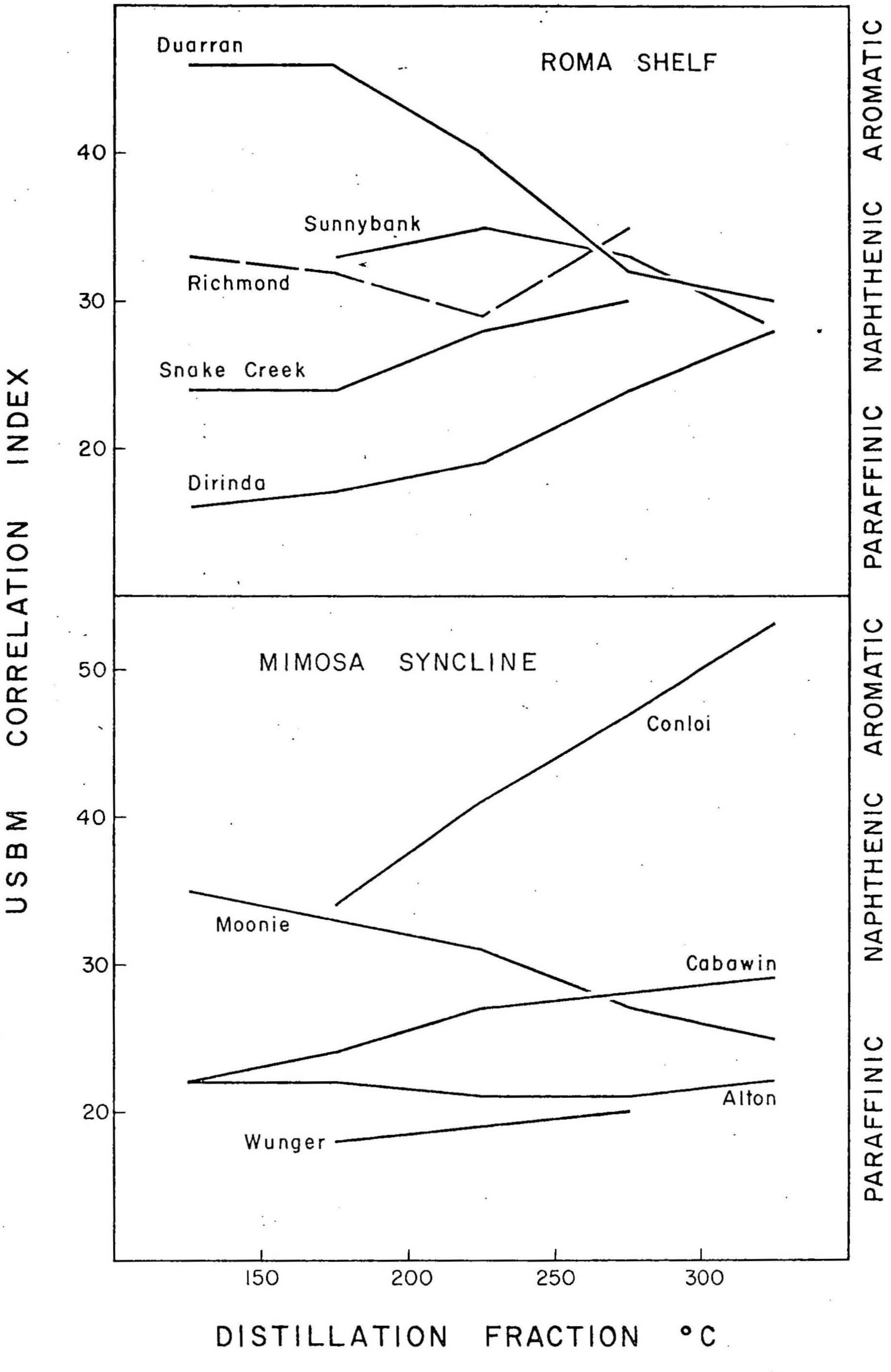


Fig. 24
N. Perth & Galilee
Gippsland
Cooper
U.S. Bureau of Mines Correlation Index
30
20
10
30
20
10
30
20
10
150
200
250
300 °C
Boiling point limits of distillate fractions

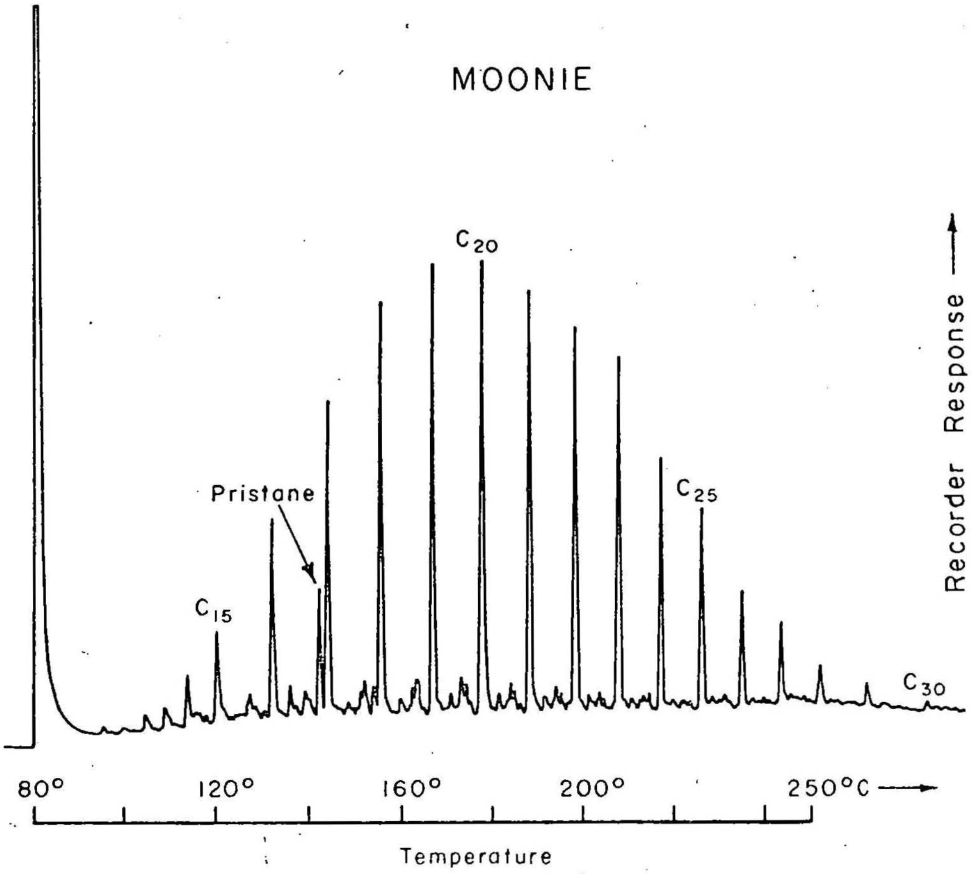
XM-79

Fig. 25

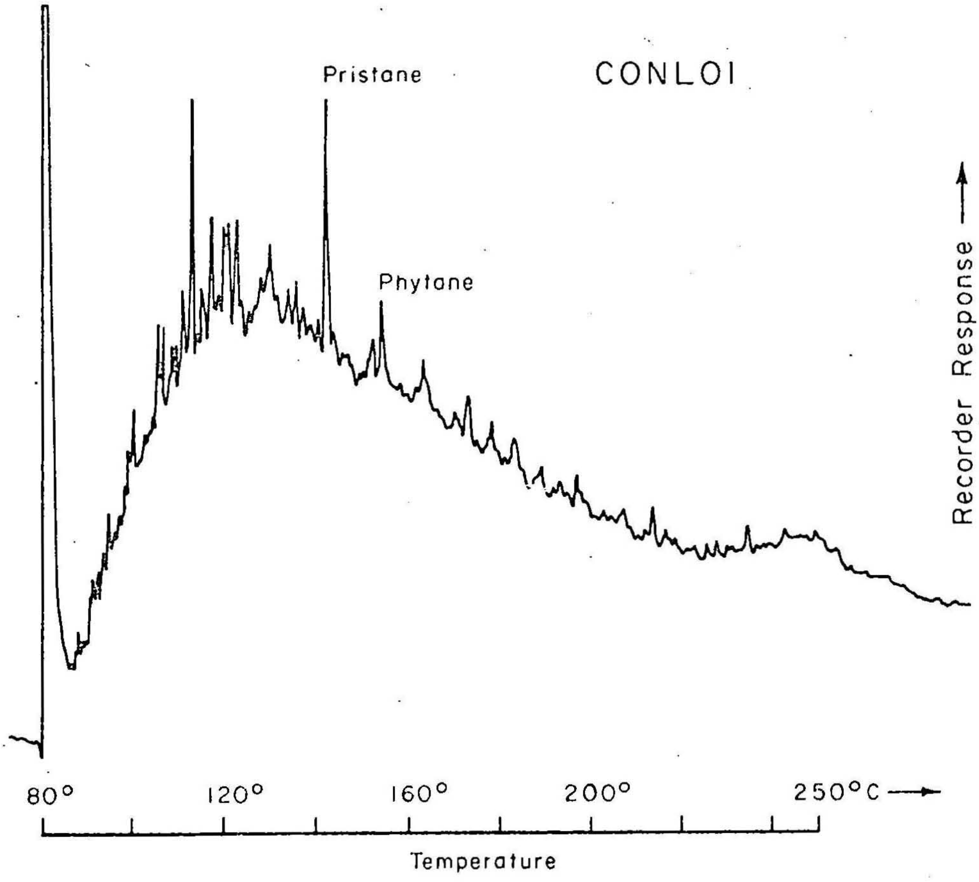

ROMA SHELF
Duarran
Sunnybank
Richmond
Snake Creek
Dirinda
MIMOSA SYNCLINE
Conloi
Moonie
Cabawin
Alton
Wunger
40
30
20
50
40
30
20
150
200
250
300
USBM CORRELATION INDEX
DISTILLATION FRACTION °C
PARAFFINIC NAPHTHENIC AROMATIC
PARAFFINIC NAPHTHENIC AROMATIC

XM-66B

Fig. 26



X AUS-2-156N



X AUS-2-156O