C.S.I.R.O.

PETROLEUM STUDIES IN MRL.

OIL and GAS DIVISION

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Petroleum studies in MRL

Some of the methods used by MRL when examining samples of oil and rocks from exploration wells are described. The information gained is used to establish the history of any hydrocarbons present and hence act as a guide to further exploration.

The major emphasis of the MRL Energy Program is on the greater use of Australia's fossil fuel resources. Coal reserves are being characterized and methods of converting certain coals to oil are being investigated. One method – the flash pyrolysis of coal – has been developed to the technical scale.

Equal attention is being given to naturally-occurring liquid and gaseous hydrocarbons, with studies of their genesis, migration and accumulation. The aim of this research is to provide an understanding of the processes that have occurred at various localities around Australia, as a basis for optimizing the results of future petroleum exploration.

Australia's crude oil reserves are small and at the present time can only supply 70 per cent of the country's requirements. Within 10 years this proportion will be nearer 30 per cent and Australia could be spending $2000 million each year on imported oil unless new sources of liquid fuel are found. The search for oil in Australia has been expensive, only occasionally successful, and rather intermittent. The current level of exploration is very low but there are indications of some improvement.

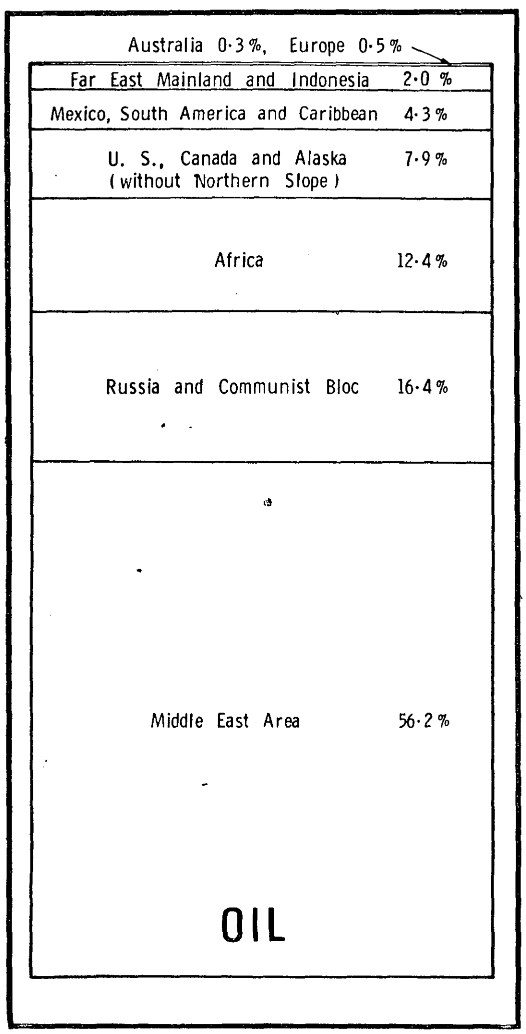


Fig. 1
Who has the oil?

In the national interest, it is essential that companies searching for petroleum here achieve the highest possible success rate and MRL's work is intended to complement their activities. MRL's research is important for two reasons – first, because oil discoveries made so far in Australia do not conform completely to most overseas experience; and second, because all the largest company-operated laboratories carrying out such research are in the northern hemisphere.

The formation of hydrocarbons

Both liquid and gaseous hydrocarbons are believed to have been formed from solid organic matter, for the most part finely dispersed in sedimentary rocks. The "sedimentary basins" in and around Australia are the regions in which the search for oil and gas takes place. Many of the thickest sequences of sedimentary rocks occur off-shore, a factor that adds greatly to the hazards and expenses of drilling and recovery.

The type of organic matter in the sediments greatly influences the kind of hydrocarbons produced. Natural gas can be formed from many organic materials, but petroleum is most likely to be formed from those rich in hydrogen, such as algae.

The maturity of the organic matter is important too. Petroleum is generated when the organic matter has matured to a certain degree; that is, when the rocks in which the organic matter occurs are heated to temperatures of 100°C or more as a result of geothermal heat. The process is usually slow and requires geological time for completion. After release, any liquid or gaseous hydrocarbons may migrate, usually upwards, to form accumulations. However, if any petroleum that is generated remains *in situ* and the rocks become warmer as they are buried at increasingly greater depths, the oil molecules "crack" and ultimately only gas will remain. It is therefore very important to know the maturity likely to have been attained at a given level.

Thus the main questions asked when studying hydrocarbon generation are:

How much organic matter exists in the

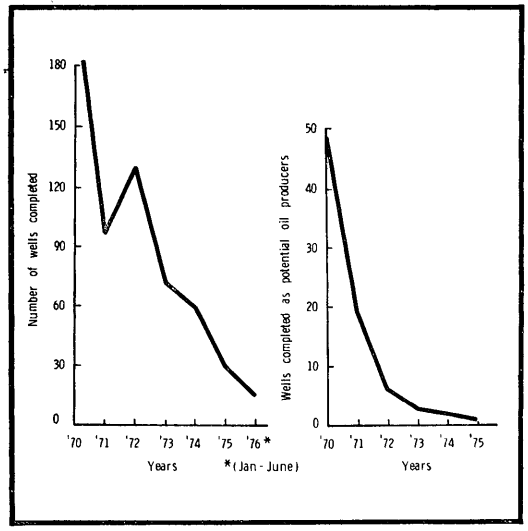


Fig. 2
Oil exploration activity in Australia (figures courtesy of BMR). The curve on the left shows the number of wells drilled each year, that on the right, how many actually produced oil.

various sedimentary rocks of a sequence?
What is its type?
What is its maturity at various depths?

MRL is attempting to answer these questions for many Australian oil deposits. Samples from the North-west Shelf, Bonaparte Gulf, Bass Strait, the Cooper Basin, the Perth Basin and the Galilee Basin are being examined by microscopic and chemical techniques. The type and maturity of the organic matter is established, the oils are characterized and genetic histories and relationships investigated. This detailed research is of particular importance in areas where no discoveries have been made and decisions on further exploration depend on information which can be gained from the very limited samples obtained from drilling.

Type of organic matter

Much solid organic matter in sedimentary rocks can be divided into three groups, each containing material of broadly similar characteristics. These groups, which are of importance as constituents of coal, are called "macerals" and are named vitrinite, exinite and inertinite.

Vitrinite is composed from the wood and bark of plants when these are deposited relatively unaltered. Exinite represents the portions of plants such as spores, leaf cuticles and resins, and also includes algal bodies. If the plant material, such as wood and bark, is chemically or biologically attacked *before* burial, a degree of oxidation may occur, and the material then becomes the precursor of the third maceral type, inertinite. Somewhat comparable material is formed from marine animal organisms, but, so far, most Australian source rocks appear to contain predominantly plant, rather than animal, remains.

These macerals can usually be distinguished under the microscope. If a very thin section of the sediment containing the organic material is made, so that it is transparent, light passing

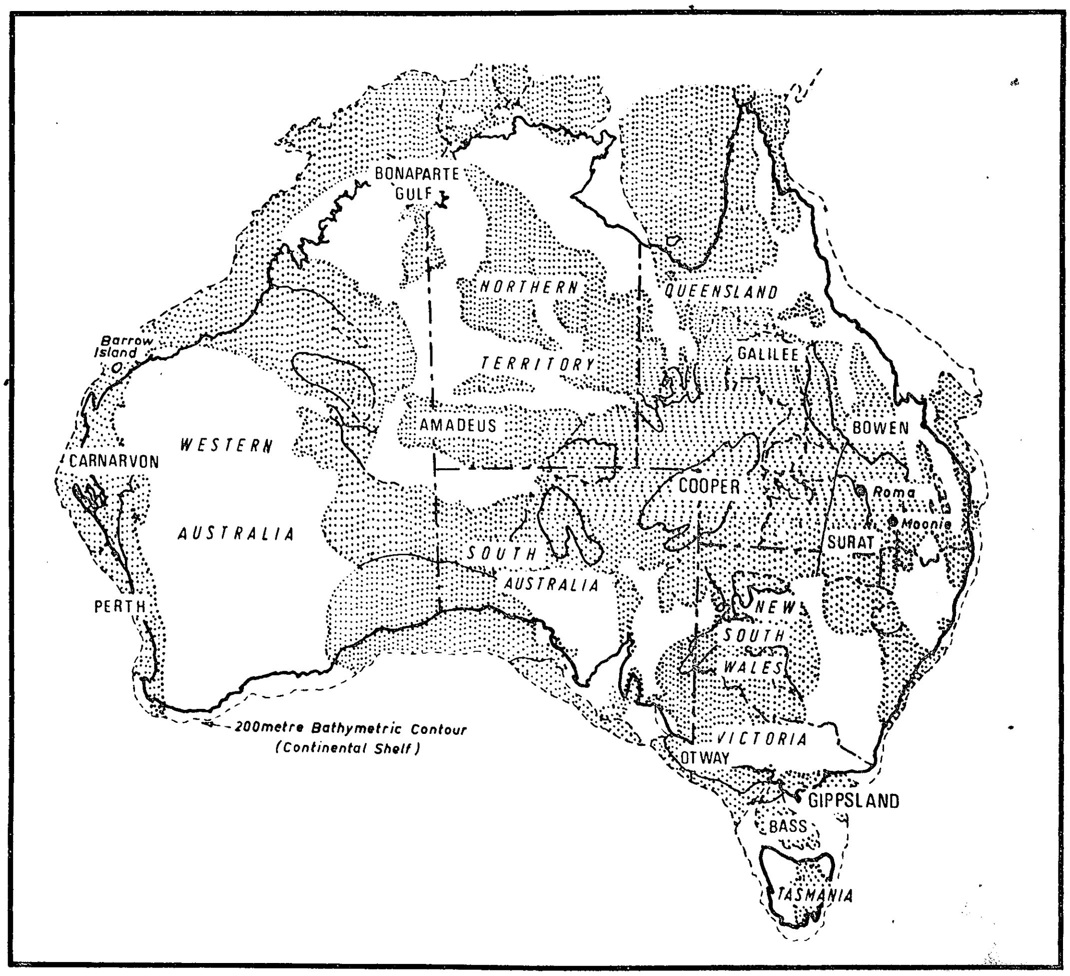


Fig. 3
Oil-bearing sedimentary basins in Australia.

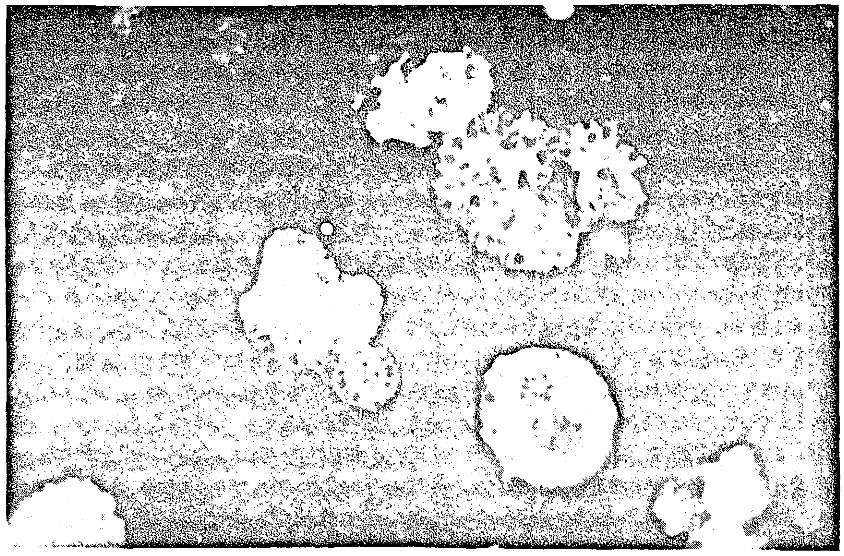


Fig. 4
Algae such as this, found in shales from the Cooper Basin, could be the source of hydrocarbons in that area.

through it (transmitted light) helps an observer to distinguish the three types. In potential petroleum source rocks, vitrinite is coloured orange-red, red or reddish brown; exinite is yellow; and inertinite is black or almost opaque.

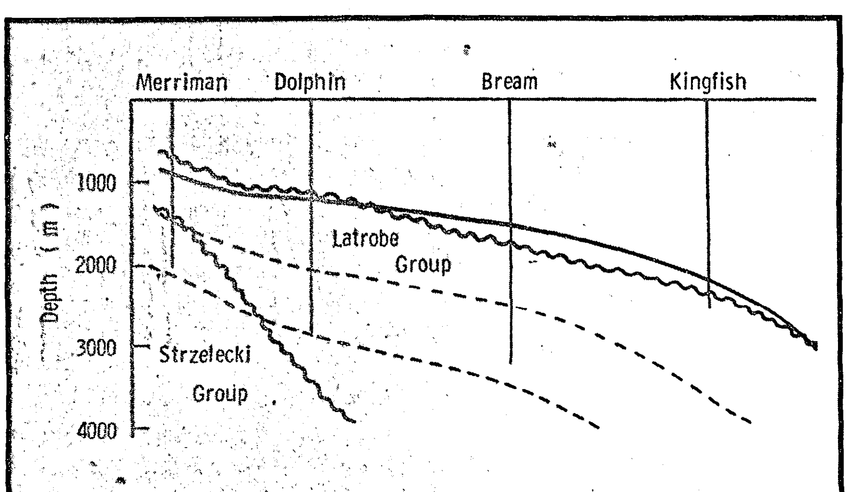
A complementary technique uses reflected, instead of transmitted, light. If the surface of a rock sample is polished so that light is reflected back from it into the microscope, vitrinite appears grey, exinite dark grey and inertinite pale grey to bright white.

One area from which MRL has examined many rock samples is the Gippsland Basin in Victoria. Many people now accept that the hydrocarbons found there originated from plant-derived organic matter within the Latrobe Group in this Basin. (While examples from the Gippsland Basin are used in this article, the procedures described are of general application.)

Microscopic examination of cores from the upper part of the Latrobe Group has shown that they contain a comparative abundance of exinitic material. Overall, the main component in these core samples was vitrinite, but in some samples, components of the exinite group (spores, leaf cuticles, resins) comprised up to 28 per cent of the organic matter. Exinite is known to give comparatively large amounts of oily products under both natural and artificial conditions of maturation, with only a small amount of non-volatile residue.

Recently, MRL has been using fluorescence microscopy to examine such core samples. This technique depends on the fact that exinite components fluoresce with green, orange or yellow light when the sample is irradiated with blue light and ultraviolet radiation. The exinite in samples from the upper part of the Latrobe Group fluoresces strongly and this is evidence that these samples are immature from the point of view of oil or gas generation, which means that most of the potential for generating hydrocarbons has not yet been realized. Exinite of similar type but of greater maturity (i.e. at greater depth) would fluoresce weakly or not at all.

Fig. 5
Simplified cross-section of offshore Gippsland Basin.



Maturity of organic matter

Several methods may be employed to determine the maturity of organic matter in samples; reference has already been made to fluorescence microscopy.

One of the most useful measurements that can be carried out on carbonaceous rock samples recovered during drilling is the reflectance of dispersed particles of vitrinite. Usually, the organic material is concentrated from the crushed rock by froth flotation or chemical demineralization. After setting in plastic and polishing, vitrinite grains are identified microscopically and the amount of light reflected under specific conditions is measured photoelectrically.

In general, reflectance values increase systematically with depth and are a direct measure of the maturity of the organic matter. Most interest centres around the reflectance range 0.5-2.0 per cent, since most oil and gas is evolved over that range of maturity. Vitrinite of the Latrobe Group in on-shore areas is very low in reflectance (about 0.3-0.5 per cent) but higher values (0.7-1.0 per cent) are observed in some off-shore wells where samples are more mature because their depths of burial, and so their bed temperatures, are greater.

The chemical composition of the organic matter separated from a sedimentary rock can also be used as a measure of maturity. A diagram is used, in which the atomic hydrogen/carbon ratio of the organic matter is plotted against its atomic oxygen/carbon ratio. A typical diagram is shown on the next page; on this, values are plotted for on-shore and off-shore samples of organic material from near the top of the Latrobe Group. Several pieces of information can be gleaned from this diagram:

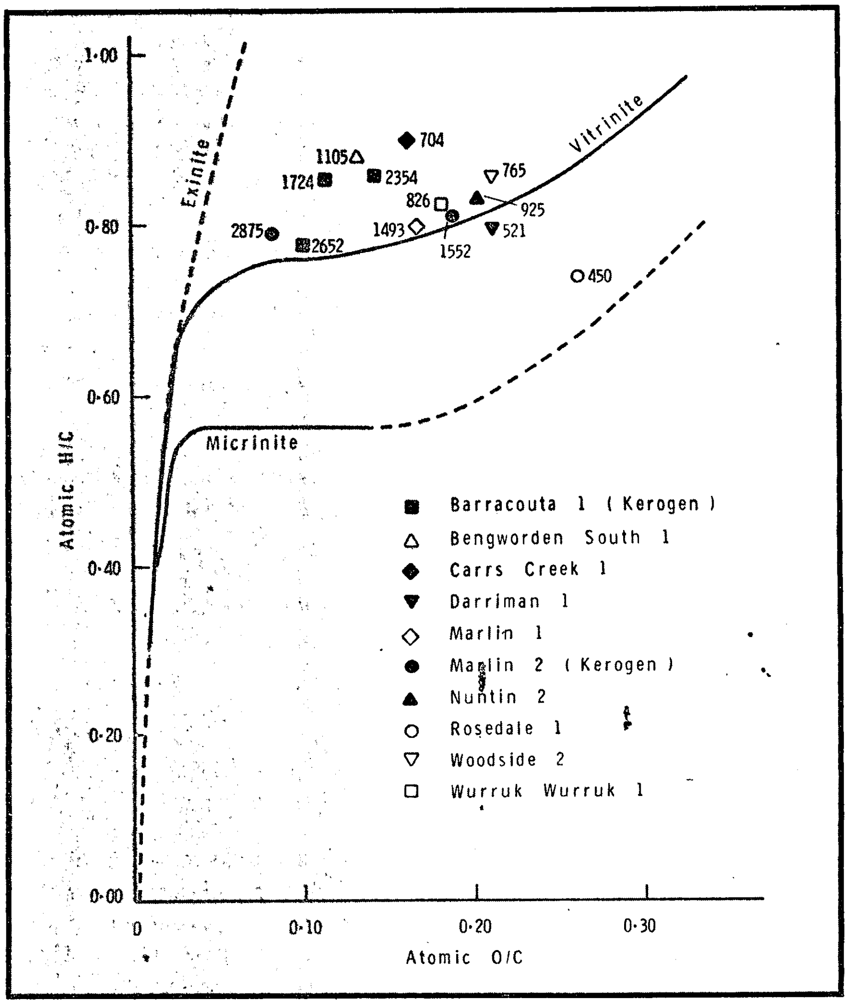


Fig. 6
Atomic H/C versus O/C for Gippsland Basin coals and kerogens. Depths in metres are shown beside each point.

(i) the plotted points are all fairly well to the right of the diagram, that is, in the region of immaturity,
(ii) nearly all the points lie between the composition lines for vitrinite and exinite, consistent with the composition found by microscopic examinations,
(iii) the more deeply buried samples have been at higher temperatures and are hence more mature; they tend to lie on the left of the diagram.

Where the source is

Knowing the depth at which oil or gas generation could occur is vital to companies in planning the maximum depth to be reached by an exploration well. It would certainly be wasteful to drill below the zone at which generation can occur, since it is very rare for hydrocarbons to migrate downwards, and in any case, the larger hydrocarbon molecules would be thermally cracked, mostly to methane.

For the Gippsland Basin, the evidence of the type and maturity of the organic matter in the Latrobe Group indicates that most exploration wells have barely, or have not yet, reached the main source rocks for the oil and gas deposits. The organic matter in the upper part of the Latrobe Group is rich in oil-producing exinites but is not yet mature enough to have produced the quantities of oil and gas present in the Basin. It seems likely that the organic material in the lower part of the Latrobe Group is also rich in exinite. At the temperatures encountered at this depth (over 130°C at 4000 m) exinite would yield a considerable amount of oil with a small amount of residue; vitrinite would yield mainly gas and a considerable amount of solid residue.

Barrow Island is another area where research pointed to a zone of generation considerably deeper than the oil accumulations and recent exploration has confirmed the presence of natural gas, over a thousand metres below the oil reservoirs.

Characterization of oil and extracts

Crude oils contain hundreds of different chemical compounds and separation of these components is best achieved by gas chromatography. In this technique, a small oil sample (10^{-6} g or less) is passed through a long column in an oven whose temperature is carefully controlled. Each compound is separated according to its boiling point and other properties, and a detector at the end of the column registers a peak for each component.

Similar distributions are obtained for oily material extracted from shale and other rocks with solvents such as chloroform. Even though such hydrocarbons may be present in amounts of only one part per million of the rock, their compositions may be highly characteristic.

Chromatograms can be used as fingerprints for different types of petroleum, or the content of a particular component, such as pristane, can be examined to give evidence as to the source of the hydrocarbons. If extracts from a representative series of cores in a basin are small and show distributions unlike those in any known crude oil, further exploration may not be warranted. If, however, there are large volumes of potential source rocks, extracts are comparatively big, with a petroleum-like chromatogram, the indications may be favourable providing suitable traps exist.

Genetic relationships of oils

Within an oil field, there may be several reservoirs of oil and to guide further exploration in that area it is important to know how these oils relate to one another in their genesis and history.

One of the methods MRL is using in this work is the measurement of stable isotope ratios with a mass spectrometer. The small differences in the masses of isotopes of light elements (especially carbon, oxygen, sulphur and hydrogen) are sufficient to influence chemical, physical and biological behaviour. Over geological time, this has led to distinct patterns in the distributions of the isotopes,

Fig. 7
Typical gas chromatograms from Gippsland Basin samples

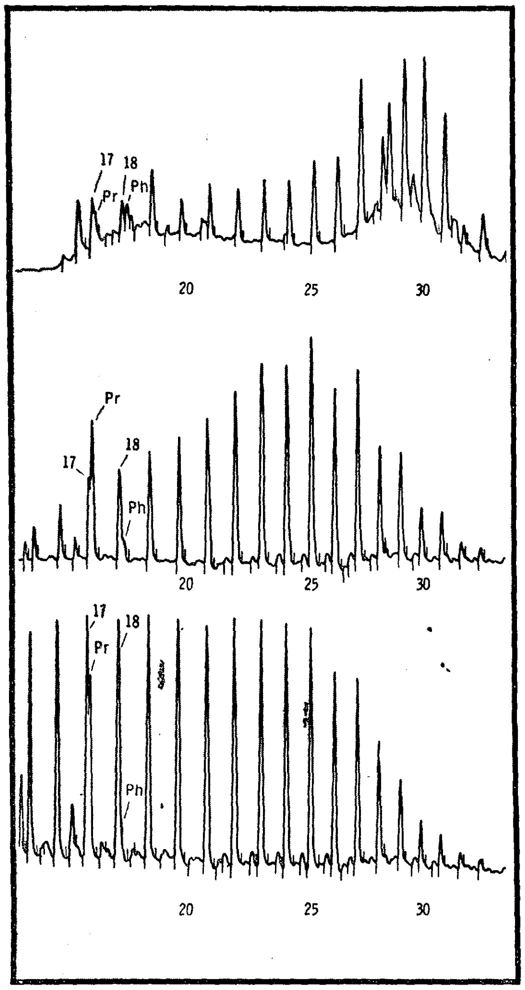
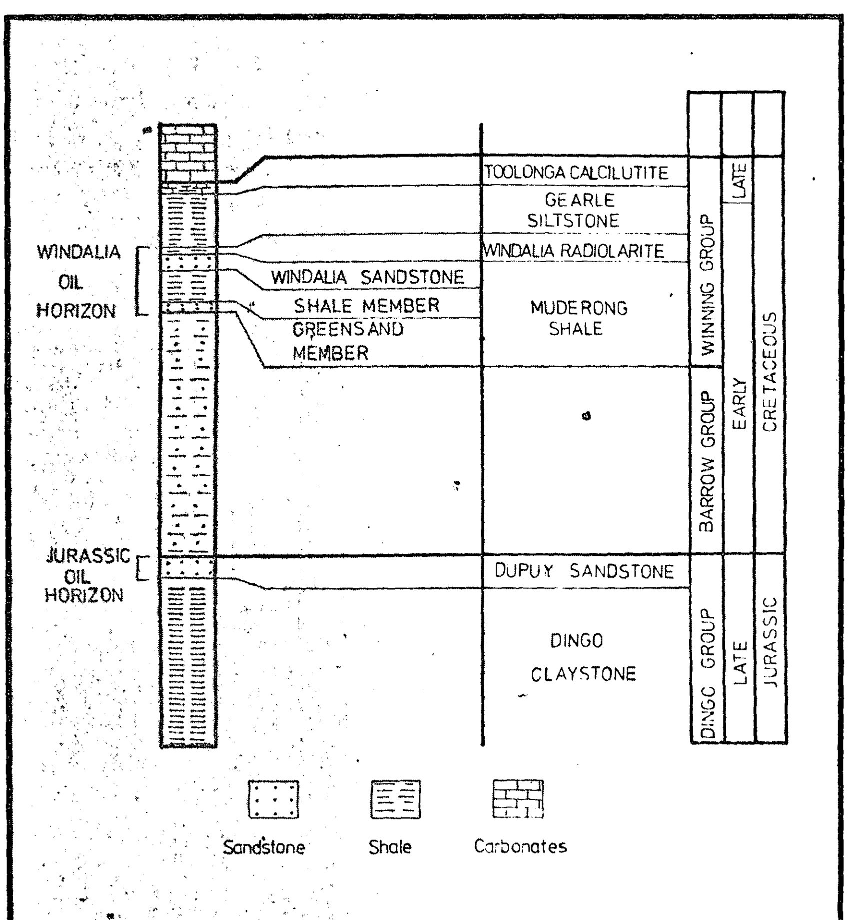


Fig. 8
General stratigraphy of the Barrow Island Oil Field.



which can reveal much about the history of mineral and hydrocarbon deposits.

MRL has recently applied measurements of stable isotope fractionation patterns to the petroleum geochemistry of the Barrow Island Oil Field, in an effort to understand the genetic relationships of its oils.

In the Barrow Sub-basin of the North-west Shelf, crude oils of different chemical compositions are recovered from different stratigraphic levels. The main crude is obtained at a depth of 1000 m; it occurs in Cretaceous rocks, is aromatic in character and contains virtually no paraffin hydrocarbons. Smaller yields of a waxy, paraffinic crude are produced from Jurassic horizons, 1000 m below.

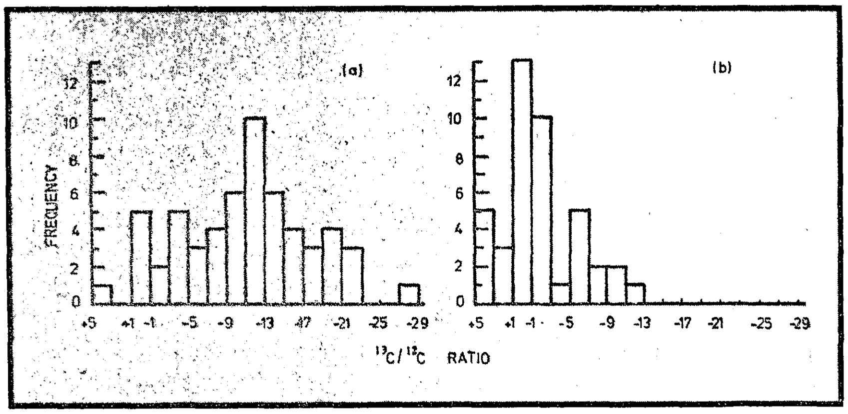
As the main crude is produced from a shallow reservoir, it would be expected to be fairly immature if the oil had not migrated far from its source. However, this Cretaceous oil has many mature characteristics; consequently, its origin is the subject of much speculation.

A possibility is that the Cretaceous crude could have been formed from the deeper Jurassic oil. This could have happened in one of two ways — by geothermal alteration or by biodegradation; MRL believes the latter process is the more likely. The lack of paraffinic hydrocarbons in the Cretaceous oil could well be the result of bacterial attack since bacteria are known to oxidize straight-chain paraffinic hydrocarbons in preference to other hydrocarbons.

If bacterial oxidation had occurred, the carbon dioxide so generated could well have led to the formation of new carbonate minerals. Consequently, one of the main measurements made was that of the carbon isotope ratios in the carbonates in rock samples from nine exploration wells in the Barrow Island area.

Fortunately, carbonates formed in this way can be distinguished from marine carbonate minerals. Ocean waters are in equilibrium with atmospheric carbon dioxide, and the carbonates which deposit from this interaction (marine carbonates) have very uniform $^{13}C/^{12}C$ ratios. However, when atmospheric carbon dioxide is fixed by photosynthesis, the heavier ^{13}C isotope is discriminated against and thus biological materials and their geologically preserved residues, such as coal and petroleum, are comparatively enriched in the lighter isotope, ^{12}C. Microbiological oxidation of such material then results in the formation of carbon dioxide that is similarly depleted in ^{13}C. Part or all of this carbon dioxide may accumulate as sedimentary biogenic carbonates by reacting with existing carbonates or metal ions in circulating groundwaters.

The measurements made showed a clear distinction in the isotopic compositions of the two



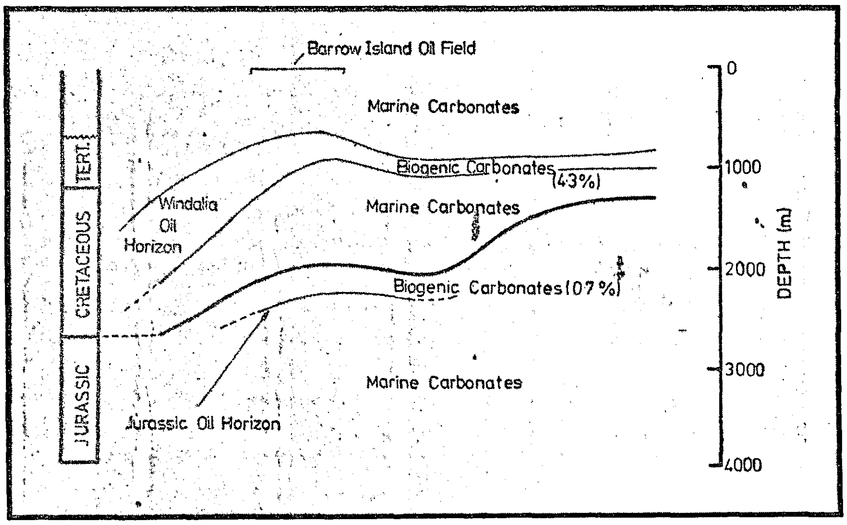


Fig. 9 (top)
Isotopic compositions of carbonates from the Barrow sub-basin (a) from oil-producing horizons (b) from other strata.

Fig. 10
Regional stratigraphic distribution of carbonate types within the Barrow sub-basin.

types of carbonate in the Barrow Island sediments examined. With the aid of this information, the distribution of the two carbonate types throughout the sequence can be plotted.

This distinction between carbonates of differing origin, which has important implications for the porosity and permeability of rocks, can be made only with a mass spectrometer and not with normal analytical methods.

If normal geothermal and diagenetic maturation processes, rather than microbiological oxidation, were responsible for the formation of all the biogenic carbonates in the Barrow Island samples, then similar or greater amounts of biogenic carbonates might be expected to accompany those crude oils found at greater depths. This proves not to be the case, when the average biogenic carbonate contents of the sediments associated with each crude oil are compared. At a depth of 1000 m this value is 4.33% w/w (as calcium carbonate) in the Cretaceous sediments, and in the deeper oil-bearing Jurassic horizons at 2000 m, it is 0.73% w/w.

The close and restricted association of biogenic carbonates with oil-rich horizons can thus be regarded as evidence of microbiological attack upon the crude oils. The data from MRL analyses of samples from exploration wells have led to the conclusion that both Jurassic and Cretaceous crude oils in the Barrow Island Oil Field may have had similar sources, or even a single source.

Future petroleum studies

The examples given indicate the ways in which MRL research can help in gaining a greater understanding of the factors controlling the occurrence of hydrocarbons. Petroleum exploration is very expensive, especially when the drilling is off-shore, as much future drilling in the Australian region is likely to be. When a single off-shore well may cost several million dollars, its siting and planning require the greatest amount of relevant information and understanding of processes that have occurred in that particular area. If this understanding is not available before drilling commences, then an early aim of the drilling program should be to recover samples that will enable the necessary insights to be gained.

Since Australian sedimentary basins have been very inadequately sampled by some overseas standards, MRL hopes to keep its work in this area at a high level for the next few years. It is during this time that the question of where Australia's future liquid fuel supplies will come from must be answered.

In addition to the work already described, MRL is also carrying out research aimed at developing and applying geochemical methods of exploration which will supplement the geological and geophysical methods now widely used.