GEOCHEMICAL AND PALYNOLOGICAL CHARACTERISTICS OF TERTIARY OIL SHALES AND LIGNITES OF THE MAE MOH BASIN, NORTHERN THAILAND

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Geochemical and Palynological Characteristics of Tertiary Oil Shales and Lignites of the Mae Moh Basin, Northern Thailand

by

Le van Minh

A thesis submitted to the
School of Graduate Studies
in partial fulfillment of the
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ABSTRACT

The sources of organic matter, the depositional conditions during lacustrine/swamp phases, the degree of post-depositional thermal alteration are examined for a Tertiary intermontane basin in northern Thailand, the Mae Moh Basin. Alternating oil shale and lignite layers in this basin also preserve a record of changing temperature and precipitation patterns, and variable contributions from swamp flora and lake primary producers.

Variations in molecular and isotopic geochemical characteristics (including compound-specific stable carbon isotope compositions) and spore and pollen assemblages (including thermal alteration index) across a 300 meter section of the Middle Mae Moh Formation are investigated. Samples collected are classified into: group I, lignite; group II, argillaceous lignite; and group III, oil shale. The saturate fraction for all samples is dominated by n-alkanes from C_{15} to C_{33}. Group I is characterized by a high abundance of the high molecular weight (HMW) C_{26} to C_{33} (up to 82%), and a low abundance of the low molecular (LMW) C_{15} to C_{19} (3 to 8%). Group III has a lower abundance of the HMW alkanes (29 to 66 %), and a greater abundance of the LMW homologues (13 to 43 %). Group II has n-alkane distribution that is intermediate between these end members. Although the dominance of higher plant contributions is indicated throughout the section, the oil shales clearly received substantial contributions from lake primary producers (algae). These molecular trends are consistent with the $\delta^{13}C$ values determined on bulk samples, which vary from -22.5 to -26.8‰. The $\delta^{13}C$ of n-alkanes in the HMW range, which are mostly lighter than -30‰, also substantiate a dominantly higher plant source. Algal contributions are suggested by the relative abundance of LMW alkanes with carbon isotopic compositions (about -24 to -30 ‰), which are somewhat enriched compared to the HMW homologues (-28 to -35‰).

Decomposition and settling conditions of organic particulates are inferred from the pristane/phytane ratios (Pr/Ph). Oil shale samples, having Pr/Ph ratios close to unity (0.95 to 1.58), were likely deposited during oxic-anoxic fluctuations on the bottom of lakes and bogs within the basin. Deposition and degradation of lignitic organic matter probably occurred in prevailing oxic conditions as indicated by their Pr/Ph values that range from 1 to 3.53.

The degree of thermal maturation given by thermal alteration index (TAI) values ranging from 2.0 to 2.4 and carbon preference index (CPI) from 0.63 to 3.77 (most values are > 1) indicate immature to early mature stages in terms of oil generation for Mae Moh source rocks. The spore and pollen assemblages are mainly palm (*Spinizonocolpites*, *Oncosperma*, *Calamuspollenites*, and *Cyrtostachys*), fern (*Verrucatosporites* sp. and *Polypodiidites* sp.), deciduous trees (*Quercoidites*, *Alnipollenites*, and *Trivestibulopollenites*), and other specimens of unknown affinity: *Crassoretitriletes* sp., *Trichanthera* sp., *Monosulcites*, *Cupuliferoipollenites*, *Biretisporites huonensis* and *Roipites* sp.. Their temporal variations suggest a dominant tropical paleoclimate with possible cooler conditions in the early stage of basin evolution.

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St. John's will be in my memory forever.

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Chapter 1

INTRODUCTION

Intermontane basins are common in Thailand and throughout southeast Asia. Recent exploration for energy resources is centred on intermontane basins where a number of oil, gas, and coal accumulations have been discovered. In Thailand, there are approximately 60 basins, both onshore and offshore, distributed in a nearly north-south direction, with sizes ranging from less than 10 km^2 to greater than 10,000 km^2 (Chinbunchorn *et al.*, 1989). Some of the basins contain liquid hydrocarbons (*e.g.*, Phitsanulok, Chumphon, Fang, and Pattani basins), whereas others are sources for coal, mostly lignite (*e.g.*, Krabi, Li). The Mae Moh Basin, the area selected for this study (Figure 1.1), is a lignite producing basin.

The International Symposium on Intermontane Basins held in Chiang Mai in February 1989 created an opportunity for geoscientists to share their experiences in intermontane sedimentary and tectonic settings. Much of the work reported there focused on the tectonics, stratigraphy, sedimentology, palaeontology and palynology of intermontane basins around the world, particularly in Thailand and eastern Asia. This study provides another reasearch on intermontane basins by a combination of geochemistry and palynology. It aims to characterize the sources of organic matter in one specific intermontane basin, the Mae Moh Basin, its depositional conditions,

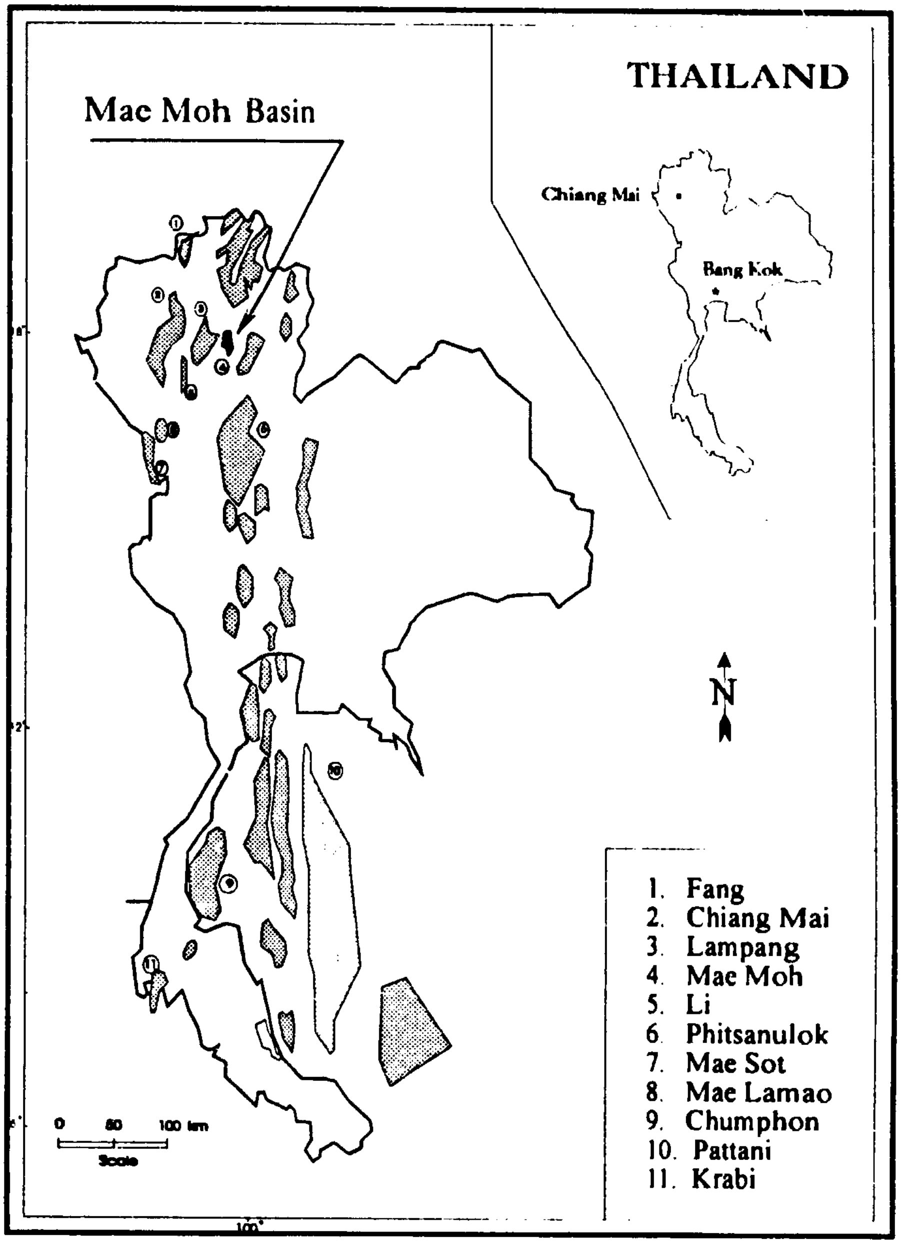


Figure 1.1 Distribution of significant Tertiary intermontane basins in Thailand (Chinbunchorn, 1989).

thermal alteration, and climatic changes as outlined in Section 1.2.

1.1 Organic Matter in Intermontane Basins

Intermontane basins form during orogenic mountain building in which subsidence, shape and size are controlled mainly by tectonic activities. Open and closed water conditions in these basins govern the relationship of lakes with surrounding lands, and to some extent by the climatic conditions (*i.e.*, precipitation rates, solar irradiation). Large lakes generally result in thick oil shale deposits, whereas small lakes with bog and swamps lead to the formation of coal deposits and oil shale (Tissot and Welte, 1984).

The sources for organic matter in the sediments, and the depositional conditions in intermontane basins are generally controlled by the tectonic regime and climate conditions (Gasse, 1990). These factors, in combination with local factors such as topography, determine the extent of the drainage area, the physical dynamics and chemical character of the water, and possibly the nature and distribution of biomass in and around the basins. They also likely determine, directly or indirectly, cycling and decomposition rates of organic matter in the water column, thus the degree of organic matter preservation (*i.e.*, net ecosystem productivity) within each basin.

Plants are broadly divided into two significant categories on the basis of biochemical compositions (Meyers and Ishiwatari, 1993). Nonvascular plants or lower plants are those which lack woody and cellulosic tissues (*i.e.*, algae); macrophytic vascular plants or higher plants are those constructed with tissue structure or self-supporting skeleton (*i.e.*, grasses, shrubs and trees).

Organic matter deposited in intermontane basins are mixtures of allochthonous and autochthonous sources. The allochthonous component usually consists of higher plant detritus and dissolved humic compounds brought in through the run-off and seepage network, and a small proportion from eolian sources. The autochthonous component is provided by algae and bacteria and the near-shore macrophytes. Upon their death, plants undergo microbial decay prior to being incorporated into the sediment. The main microbial agents are bacteria, actinomycetes, fungi and algae, which themselves are eventually deposited in the sediment (Moore, 1969). During burial, the organic matter can also be degraded by non-microbial mechanisms. Organic compounds such as carbohydrates and proteins are relatively easily broken down by degradation, while others such as waxes and resins have higher resistance to chemical and biological attack (Moore, 1969). More advanced diagenesis and catagenesis ultimately convert the organic matter into carbonized residues, partially destroying its original composition and detailed structure, but sometimes still preserving the primary morphological characteristics.

Numerous studies have shown that geochemical and biological markers can provide criteria for distinguishing the sources of organic matter in sedimentary rocks (Tissot and Welte, 1984; Hoffmann *et al.*, 1987; Hayes *et al.*, 1989). For example, the relative abundances of short-chain (or low molecular weight) and long-chain (high molecular weight) alkanes, and their odd to even ratios are believed to reflect the nature and extent of higher plants versus lower plants contributions (Meinschein, 1969; Clark and Blumer, 1967; Powell *et al.*, 1973; Cranwell, 1984; Tissot and Welte, 1984). Abundance of phytoplankton source material eventually leads to a dominance of low molecular weight (LMW) alkanes, whereas land plant cuticular waxes contribute to high molecular weight (HMW) alkanes. Specific HMW alkanes may also be indicative of certain types of land plants. For example, the predominance of n-C_{31} is related to marsh grasses, whereas n-C_{27} and n-C_{29} are abundant in deciduous trees (Cranwell *et al.*, 1987).

Delineation of diverse origins, biosynthetic pathways, and diagenetic fate of organic matter may be constrained by the combined use of molecular marker distribution and the stable carbon isotopic composition of organic matter and individual organic compounds (Freeman *et al.*,1990; Degens, 1969). N-alkanes are relatively resistant and tend to preserve the isotopic compositions of primary sources (Hayes *et al.*, 1987; Rieley *et al.*, 1991). Information regarding the biosynthetic pathways can also be indicated by the n-alkane isotopic composition (*e.g.* Rieley *et al.*, 1991). Hayes *et al.* (1987) have determined diverse origins of organic matter isolated from the Eocene Messel shale, where lower plants impart heavier isotopic composition such that eukaryotic algae, for example, have a $\delta^{13}C$ value of -22‰, green photosynthetic bacteria -24‰, and dinoflagellate lipids -25‰. As may be expected, higher plant components tend to have lighter values with some triterpenoid compounds showing values of -28 to -29‰. Rieley *et al.* (1991) also showed that the n-alkanes from higher plants grown in the surroundings of Ellesmere Lake have $\delta^{13}C$ values of -30.1 to -38.7‰, which are in the same range as those of extracted organic matter from the adjacent lake sediments. In the Eocene Messel shale, the isotopic compositions of leaf material in the sediment (-27.5‰) are similar to those of most modern plant leaf waxes.

Oxygen levels in aquatic and sedimentary environments influences the degree of degradation of organic matter. The oxic/anoxic conditions have been deciphered using pristane/phytane ratios (Cox, 1972; Brooks and Maxwell, 1974; Didyk *et al.*, 1978) in conjunction with other indicators (*i.e.*, sulphur or porphyrin contents), since pristane and phytane are presumed to derive from degradation of chlorophyll depending on the availability of oxygen (Brooks, 1969; Maxwell *et al.*, 1972, 1973). The environmental role of these ratios, however, should be applied with restrictions in hypersaline conditions (ten Haven *et al.*, 1987).

As the organic matter is buried in sediments, biochemical degradation is progressively replaced by geochemical degradation, where temperature and pressure are mainly responsible for biochemical structure rearrangement. With increasing depth, organic matter gradually changes its colour becoming darker. Thus, the degree of thermal maturation could be indicated by examining coloration of organic particulates, particularly spores and pollen. Thermal alteration and diagenetic degradation are also characterized by the ratios of odd versus even n-alkanes expressed as carbon preference index (Bray and Evans, 1961; Philippi, 1965). Ratios higher than 1 represent odd predominance and those less than 1 indicate an even predominance. Carbon preference index (CPI) is also used to characterize the molecular distribution of fatty acids and alcohols in fresh lipids and to illustrate the susceptibility of different fatty acids to diagenesis (Matsuda and Koyama, 1977).

Depending on the abundance of primary sources for plants, the resulting organic accumulations, which survive degradation, provide starting material for the generation of coal or hydrocarbon. Generally, coal is associated with abundance of higher plants and hydrocarbons are expected when lower plants and microorganisms predominate.

1.2. Purpose and Scope

Intermontane basins of Thailand contain significant coal and hydrocarbon deposits. Numerous geological, geochemical, seismic and structural, palynological and paleontological studies have been completed with the general aim of understanding the formation history, tectonic evolution, depositional environment, and petroleum source potential of the Tertiary sediments (Bunopas, 1981; Buffetaut, 1989; Ratanasthien, 1989c). In this study, an organic geochemical approach, using biological markers and stable carbon isotopes of specific organic compounds, combined with spore and pollen analysis, is tested on an intermontane basin in northern Thailand, the Mae Moh Basin, to:

1. Determine the relative contributions of biomass sources to the organic matter in sediments;

2. Assess the depositional conditions under which the organic matter was sequestered in the sediments (*i.e.*, swamp/lacustrine, oxic/anoxic conditions);

3. Evaluate the degree of post-depositional alteration of organic matter; and

4. Infer the climatic/depositional changes that occurred during the course of

basin evolution.

To address these objectives, samples are analyzed to:

1. Determine the total organic carbon content (TOC), the total extractable organic matter (EOM), and the total carbonate content;

2. Examine the distribution patterns of n-alkanes, and isoprenoids;

3. Analyze the carbon isotopic values ($\delta^{13}C$) of bulk organic matter and individual n-alkanes;

4. Identify the spore and pollen assemblages, and quantitatively evaluate their fossil coloration.

Although specifically focused on the Mae Moh Basin, the results of this study are expected to some extent, have implications on understanding other intermontane basins in Thailand and Indochina region.

1.3 Study Area.

The Mae Moh Basin is located in Lampang province, central part of northern Thailand between latitudes 18°15'40" and 18°23'10", and longitudes 99°40'45" and 99°45'42"(Figure 1.2). The basin, elongate shape and trending nearly north-south, occupies an area of approximately 150 km^2; the thickest section is approximately 1 km. The basin is surrounded by Triassic rocks of the Lampang Group. However, the southern margin of the basin is in contact with basalt of the Permian Ratburi Group. Granite of the Volcanic Formation is exposed a short distance west and northwest of the basin, where it forms a sill separating Mae Moh strata from most post-rift Pleistocene strata of the Mae Tang Group. A small outlier of Mae Tang

Figure 1.2 Geological Map of the Mae Moh Basin

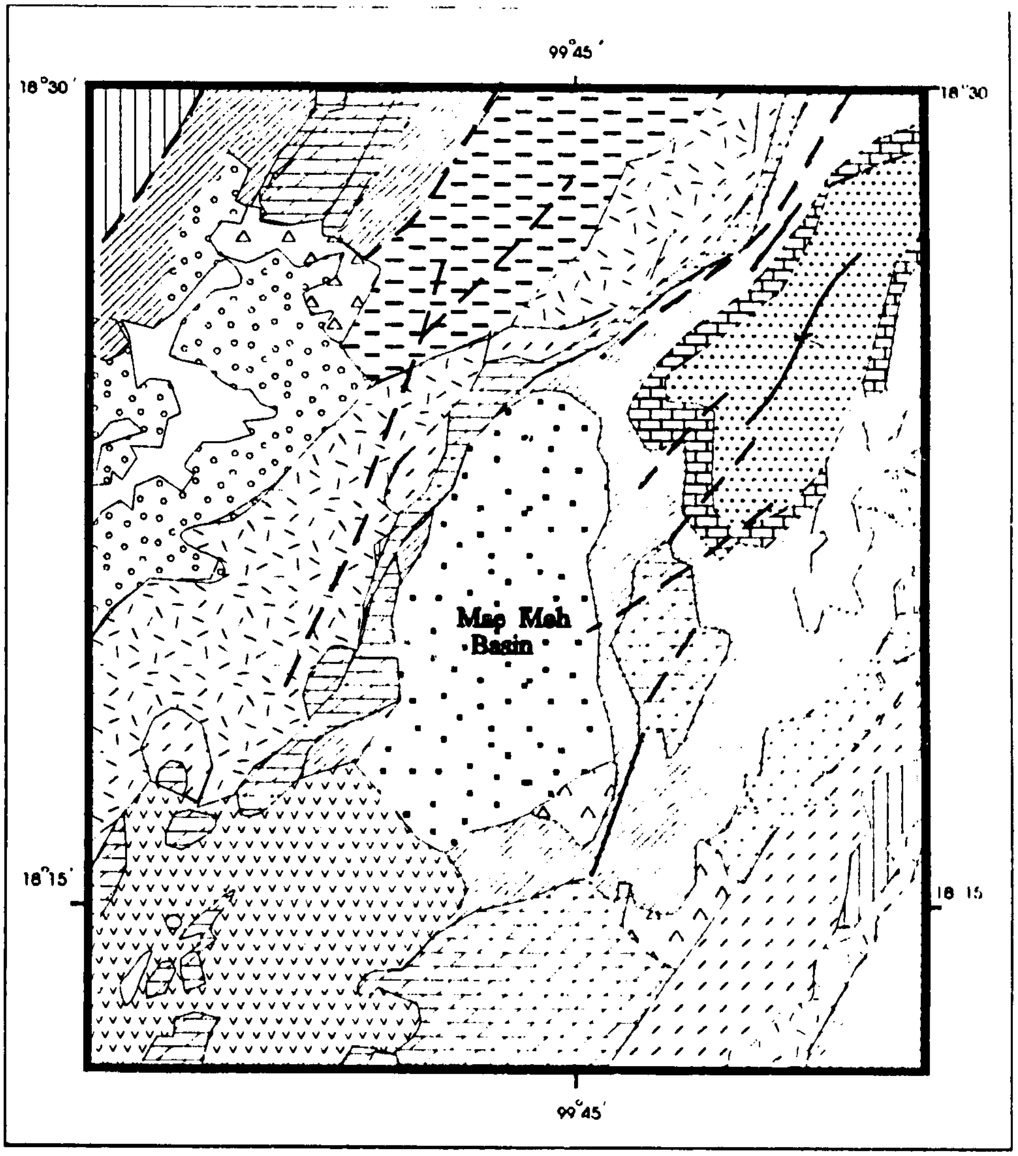
(Ratanasthien, 1989b)

LEGEND

Age	Symbol	Unit
Holocene	▭	1. River gravel and mud
		Mae Tang Group
Pleistocene	∘	2. Lower terraces unconsolidated gravel, sands, silt and clay
	^	3. High terraces unconsolidated gravel, sand, silt and clay
		Mae Moh Group
Miocene (?)	⁘	4. Claystone, siltstone, sandstone, and conglomerate containing fossils of gastropod, fish, mamal remains.
		Lampang Group
Triassic	▦	5. Limestone and conglomerate limestone containing gastropods and brachiopods.
	▨	6. Limestone, calcareous shale and sandstone containing brachiopods.
	⁄	7. Conglomerate, sandstone, and shale with intercalations of agglomerate and tuff.
	⁙	8. Pha Daeng Formation : sandstone, shale and conglomerate.
		Volcanic Formation
Permo-Triassic	⟋	9. Tuff and agglomerate of rhyolite and andesite.
		Ratburi Group
Permian	▤	10. Carbonaceous and tuffaceous shales, and sandstone with fossils.
	▤	11. Massive limestone, carbonaceous shale, tuffaceous sandstone.
	▥	12. Tuff and agglomerate of rhyolite and andesite.
	v	13. Vesicular and amygdaloidal basalt.

—+— Syncline Axes

- - - - - Faults


99°45′
18°30′
18°30
Mae Moh Basin
18°15′
18 15
99°45′

strata lies at the southeast margin of the Mae Moh Basin. The basin probably formed during the middle of the Tertiary as a result of extensional rifting related to the overall tectonic activities in the region (Jitapankul, 1985). Fault-controlled grabens associated with subsiding and filling phases are thought to be generally responsible for the alternating depositional environments including lacustrine, swamp, and fluviatile conditions.

Mae Moh is about 100 km southeast of Chiang Mai and 26 km east of Lampang. Route II connects Chiang Mai to Lampang, one of the oldest settlements in northern Thailand and famous for its temples, pagodas, handcrafts, and high quality ceramic products. The Mae Moh coal mine is accessed from Lampang through the local route. Coal exploration began on a small scale in 1957; it was not until 1980-1985 that the locality was recognized as host from an important lignite deposit estimated to be 1,317.4 million tonnes (Jitapankul, 1985).

Chapter 2

TERTIARY GEOLOGY OF THAILAND

2.1 Tectonic Evolution.

The formation of Tertiary intermontane basins in Thailand and southeast Asia is related to the tectonic history of the Indian, Australian, and Eurasian plates (Hutchison, 1989). As the Indian oceanic lithosphere moved northwards, it subducted under the Eurasian plate. Two significant episodes of collision were accounted. The first episode occurred in the early Eocene and the second one, believed to be more intense, occurred in the late Eocene (Xu *et al.*, 1985). The Himalayan Orogeny and the formation of the Gandise Transhimalayan volcano-plutonic arc are thought to relate to the second collision (Hutchison, 1989). Weak zones such as old sutures and shear-zones in Indochina were reactivated and divided into several independent plates such as the Southeast China plate, the Indochina plate, and the Central Sunda plate. Many of the major fault systems including the Red River, Thai-Burma, and Sumatra shears were probably produced by this collision (Figure 2.1). Fundamental features of the Indian- Eurasian collision, plate tectonic rotations and displacements are inferred from various studies, including the work of Tapponier *et al.* (1987).

The mechanism and timing of formation of most Tertiary basins throughout Indochina are accommodated within the framework of extrusion or escape tectonics,

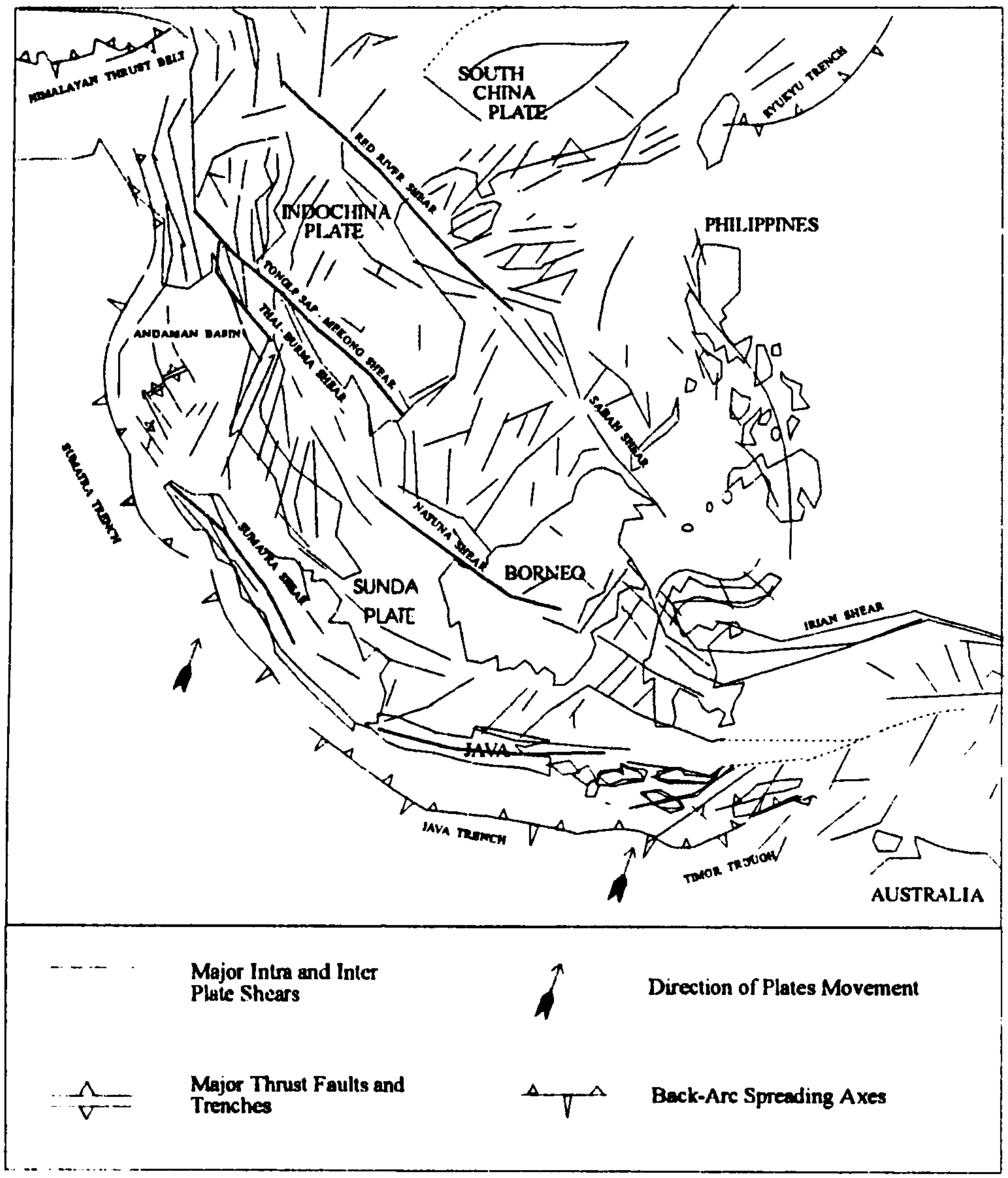


Figure 2.1 Main fault systems of southeast Asia illustrate sequential Tertiary deformations as a result of the Indian-Eurasian collision (Wood, 1985). Thai Tertiary intermontane basins distributed in a nearly north-south direction (Figure 1.1) likely link to this tectonic framework.

in most cases, rifting and subsidence phases of these basins occurred at about the same time (Hutchison, 1989). In Thailand, most workers presently believe that Tertiary intermontane basins of Thailand are either pure rift/back arc basins or conjugate strike-slip faulting basins (*e.g.*, Bunopas, 1981; Chinbunchorn *et al.*, 1989).

Intermontane basins in northern Thailand are likely accommodated within the regional tectonic framework. Initial rifting of these basins broadly coincides with the time frame of Eurasian collision. The occurrences of S-type granites along the west side of the Shan-Thai Craton (at Burma-Thailand border, and into the Malay Peninsula) are thought to be a product of this. Magmatic episodes constrained by K/Ar dates (18 to 40 Ma) suggest an active tectonic regime during this time (Ratanasthien, 1989c). The clockwise rotation of Thailand from early to middle Tertiary, and the westward movement and clockwise rotation of the western portion of Thailand and the Malay Peninsula are apparently responsible for the ultimate configuration of the intermontane depressions (Bunopas, 1981).

2.2 Intermontane Basin Stratigraphy.

The Tertiary intermontane basins of Thailand, including the Mae Moh Basin, possess generally analogous stratigraphic successions. Chinbunchorn *et al.* (1989) broadly divided them into a syn-rift and post-rift series based on geophysical data and well-log results. These Tertiary sedimentary sequences overlie a basement of different rock types and ages, including lower Palaeozoic metamorphic rocks, upper Palaeozoic clastic rocks and carbonates, Mesozoic clastic rocks, and upper Palaeozoic and Mesozoic granites.

The syn-rift series probably formed from late Oligocene to late middle Miocene (Chinbunchorn *et al.*, 1989). It is subdivided into lower, middle and upper units. The lower unit (late Oligocene-early Miocene) corresponds to the first phase of basin formation. In some basins (*e.g.*, Krabi) this phase might start earlier (probably Eocene) as suggested by mammal remains (Buffetaut *et al.*, 1989). The middle unit (early-middle Miocene/late-middle Miocene) is also very similar in each basin, where it contains considerable lacustrine and swamp sediments in the deeper parts of the basins. This unit is characterized by abundant organic shale with minor thin-bedded sandstone, especially in the shallow lacustrine facies. The upper unit (late middle to late Miocene) consists of fluvial sandstone deposits with some ephemeral lacustrine fine grained shale in the lower parts of the basins.

The post-rift series was deposited from late Miocene to Quaternary (Chinbunchorn *et al.*, 1989). This series unconformably overlies the syn-rift unit, and consists of fluviatile, fine to coarse grained sandstone and gravel conglomerate; thin layers of fine grained clay and lignite are also found. In some basins, such as the Pattani and the Malay basins in the Gulf of Thailand, the post-rift sequence is terminated with coastal and shallow marine deposits.

2.3 Stratigraphy of the Mae Moh Basin.

The stratigraphy of the Mae Moh Basin is shown in Figure 2.2. Here, Tertiary sequences overlie marine Triassic (limestone, shale and sandstone) rocks of the Lampang Group. Three Tertiary formations are defined for the Mae Moh Group. The Lower Formation consists of conglomerate, sandstone, siltstone and

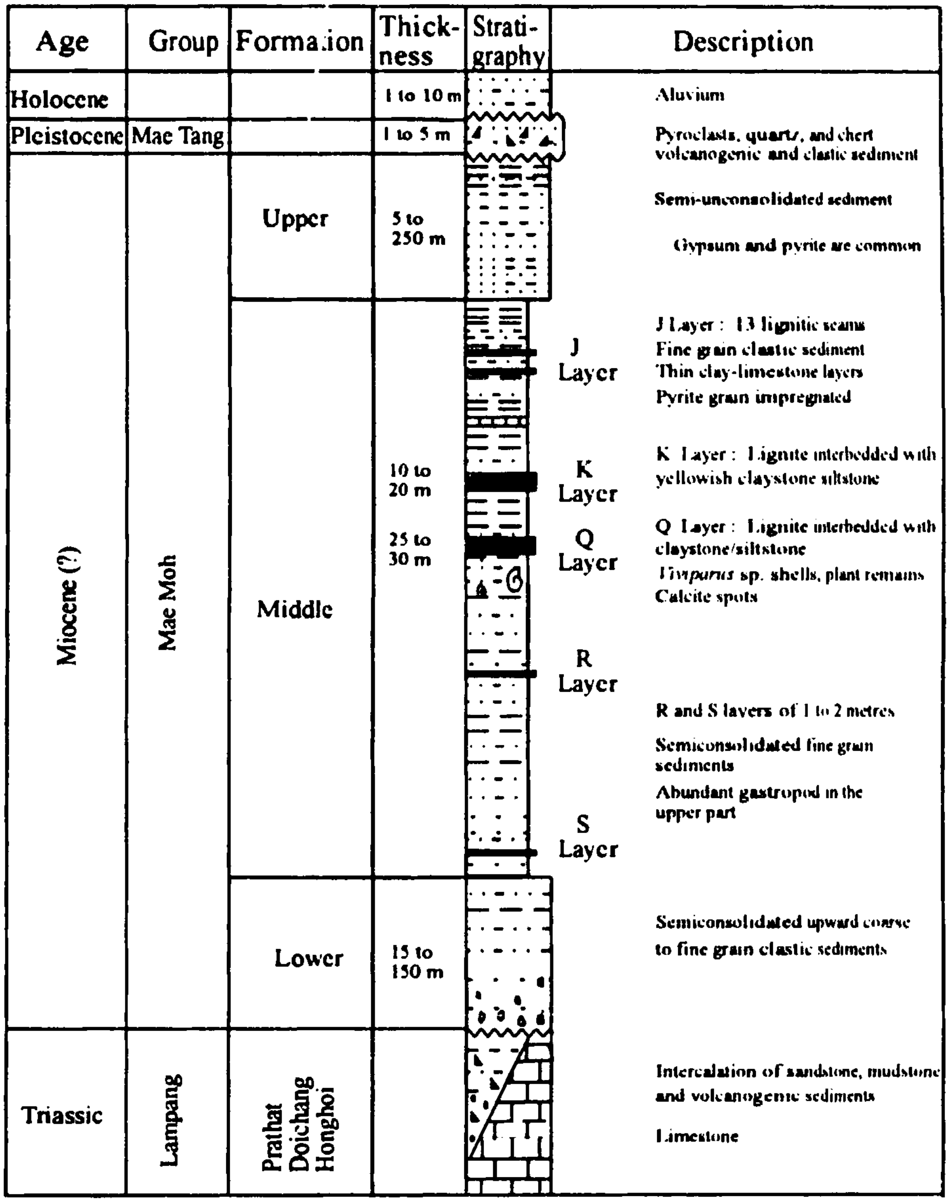


Figure 2.2 Stratigraphic column reconstructed on the basis of the general column by Jitapankul (1985) and descriptions by Ratanasthien (1989b). Samples were collected from the Middle Formation of the Mae Moh Group for analyses.

shale/mudstone reflecting fluviatile conditions. The thickness of this sequence varies from 15 to 150 metres. The Middle Formation is 300-500 metres of loosely consolidated shale and siltstone. Numerous lignite and oil shale layers occur in this formation. The five major lignite layers are labelled J, K , Q, R, and S in stratigraphically descending order. Fossils found in this formation include gastropods (*Viviparus* sp., *Millanoides* sp., *Physa* sp. etc.), ostracods, plants, fish and reptiles. Alternating swamp and lacustrine conditions are inferred from the lithology and paleontology. The Upper Formation consists of reddish semi-consolidated and unconsolidated claystone, siltstone and mudstone intercalated with sandstone and conglomerate lenses suggesting fluviatile depositional conditions. It is also called the "Red Bed or Huai Luang Formation" (Watanasak, 1989). The overall thickness varies considerably from 5 metres at the margin to 250 metres in deepest parts. Pleistocene strata contain volcanic pyroclasts, quartz and chert intercalated with clastic sediments. The exposure of coal seams and development of fault systems is linked to volcanic activities during Pleistocene (Ratanasthien, 1989b). Holocene strata occur as small outliers in the southern portion of the basin (Jitapankul, 1985).

2.4 Previous Palynological Studies.

Previous palynological studies aimed at determining the lithostratigraphic successions, depositional environments, and chronology of Tertiary intermontane basins of Thailand were conducted by Watanasak (1989, 1990) for mid-Tertiary of Thailand, and by Ratanasthien (1989b) for the Mae Lamao Basin, about 100 km southwest of the Mae Moh Basin (Figure 1.1).

In Watanasak's work, the mid-Tertiary pollen assemblages of the intermontane basins of Thailand are divided into 2 zones, Siam 1 and Siam 2 (Figure 2.3). Briefly, Siam 1 is characterized by the abundance of *Pinuspollenites* sp., *Piceaepollenites alatus* Potonié 1931, *Tsugaepollenites igniculus* Potonié ex Potonié 1958, *Quercoidites* sp., and *Alnipollenites verus* (Gemeraad *et al.*,1968). *Alnipollenites verus* is considered to have first appeared in the early Miocene. An age from late Oligocene to early Miocene was assigned to Siam 1. Siam 2 contains abundant *Polypodiisporites alienus* Potonié, *P. usmensis* Van Der Hammen, *Cyathidites minor* Couper 1953, *Quercoidites* sp., *Faguspollenites* sp., *Tiliaepollenites indubitabilis* Potonié 1931, *Tetracolporopollenites sapotoides* Pflug & Thomson, and *Pinuspollenites* sp. Other common taxa in the Siam 2 zone are *Zonocostites ramonae* and *Florschuetzia* sp., which reflect mangrove vegetation. *Zonocostites ramonae* appears in low frequency in the Palaeogene of Borneo, and significantly increases at the Oligocene-Miocene transition in the Caribbean, Nigeria, and Borneo (Gemeraad *et al.*, 1968). An age from early late to late Miocene is attributed to Siam 2.

Strata of the Mae Moh Group spans the interval from latest Siam 1 upward into Siam 2 (Watanasak, 1990). Characteristic species including *Alnipollenites verus*, *Caryapollenites simplex*, *Inaperturopollenites dubius*, *Piceaepollenites alatus* suggest more temperate conditions. Other species, such as *Quercoidites* sp., *Cupuliferiopollenites pusillus* and *Trivestibulopollenites betuloides* are also common. Tropical species occurring in smaller abundances include *Ammania* sp., *Bombacacidites annae* Hammen ex Leidelmeyer 1966, *Margocolporites vanroijhei*

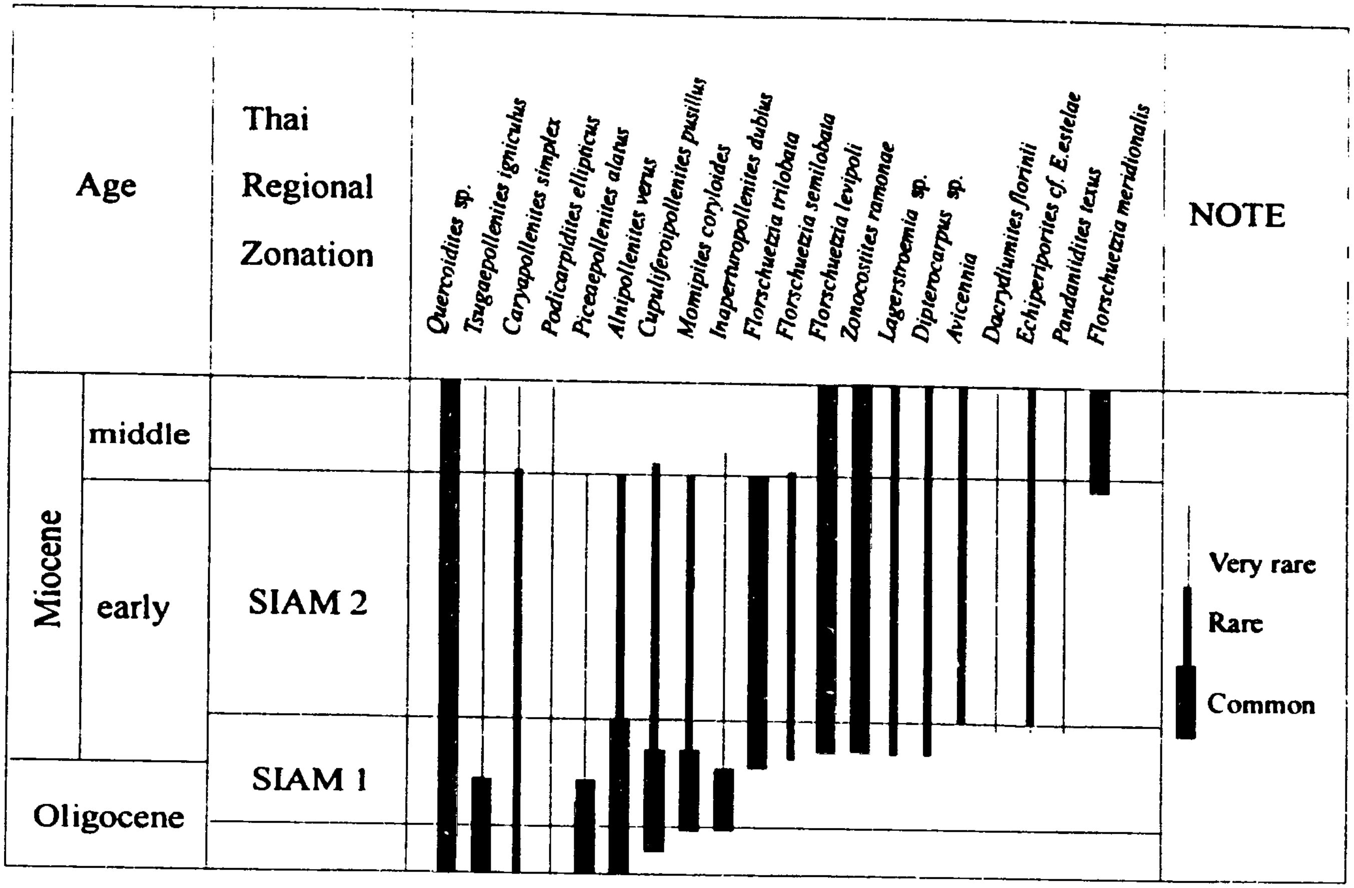


Figure 2.3 Selected Mid-Tertiary Spores and Pollen of Thailand (Watanasak, 1990)

Germeraad *et al.* 1968, and *Dipterocarpus* sp.. Climatic oscillations from cool in the lower part of the study section (Figure 2.3) to warm in the middle part of the section to cool at the top are recognised in the regional palynology (Watanasak, 1989).

Another palynological investigation by Ratanasthien (1989a) for the Mae Lamao Basin (see Figure 1.2 for location) shows abundant arboreal pollen. Among the palms, *Oncosperma, Cyrtostachys,* and *Calamus* pollen occur most frequently. *Oncosperma*, which was first described by Thanikaimoni (see Anderson and Muller, 1975), is common on the inland margin of the mangrove belt in northwestern Borneo. *Cyrtostachys* is also frequently identified in the transition between mangrove and peat. Among the pollen which characterize the swamp are *Durio* and *Calophyllum*. *Durio carinatus* is occasionally observed from northwest Borneo; it is more abundant in Malaya (Muller, 1975). Fern spores represent non-arboreal taxa. Among them, the genus *Verrucatosporites* is the most common in the Mae Lamao basin. This climbing fern has various taxonomic affinities. One of them is *Stenochlaena palustris*, an Indo-Malaysian climbing fern (Gemeraad *et al.*,1968). In this basin, the presence of *Florschuetzia trilobata* and *F. levipoli* suggests a late Oligocene to early Miocene age for Mae Lamao sediments (Ratanasthien, 1989a). Pollen and spore taxa suggestive of cool conditions (*i.e.*, *Alnus*, *Pinus* and *Betula*) are less frequently observed in this basin (Ratanasthien, 1989a).

2.5 Macro-Paleontological Studies.

Paleontological investigations also contribute towards understanding the chronostratigraphy of the Tertiary intermontane basins of Thailand. Unfortunately, the exact locations for many key fossils are poorly documented. In most, if not all the reports reviewed here, the fossils apparently were collected under, over or between lignite layers or oil shales, which correspond to deposition during the syn-rift sequence (Buffetaut *et al.*, 1989; Ginsburg, 1989).

The remains of rhinoceros and proboscideans were recovered from the Pong basin, a small feature located southeast of the Li basin, Figure 1.2 (Ginsburg, 1989). Among the fossils, a premolar of presumably *Deinotherium pentapotamiae* suggests a middle Miocene to early late Miocene age for the strata. In the same basin, Thai workers report other mammal fossils, including an elephantoid-like *Proboscidean*, a rhinoceros-like *Gaindatherium*, a chalicotheriid (*Chalicotherium*), a suid, and a tragulis (Buffetaut *et al.*, 1989). The assemblage also suggests a middle Miocene age. In the Li basin, a rodent fossil described as *Atemus thailandicus* and bird remains (herons, flamingoes, rail, and ducks) also suggest a middle Miocene age. The Phitsanulok basin (Figure 1.2) contains abundant bat remains (teeth, jaws, and limb bone fragments); fossils of the family Molossidae (*Mormopterus* or *Hydromops nonghenensis*) suggest a late early to middle Miocene age. The Krabi basin (Figure 1.1) is an exception amongst Thailand's intermontane basins in that significantly older mammal fossils are reported (Buffetaut *et al.*, 1989). These remains include skull and jaw of a small anthracothere (*Siamotherium krabiense)* and a much larger anthracothere (referable to the genus *Anthracothema*). The fossils are similar to those reported from the middle Eocene Xiangshan Formation of Yunnan in China, suggesting that the Krabi lignite is middle Eocene.

For the Mae Moh Basin, a mastodon molar belonging to the species *Stegolophodon praelatidens* was found and described by Von Koenigswald in 1959 (Buffetaut *et al.*, 1989). By analogy to similar findings in Burma, it suggests a late Miocene-early Pliocene age with uncertainties. Ginsburg and Tassy (Buffetaut *et al.*,1989) identified teeth and postcranial elements of the rhinoceros-like *Gaindatherium*, and attributed them to a middle to early late Miocene taxon .

In summary, paleontological and palynological studies delineate approximate ages for the Tertiary sequences, establish correlations between basins, and date a temporally restricted lacustrine phase of basin evolution lasting from late Oligocene to late Miocene - Pliocene. Although they are still in controversy, the fauna and flora reported in the Mae Moh Basin suggest a middle Miocene to Pliocene age. Palynological assemblages reported by Watanasak (1990), on the other hand, suggest climatic oscillations during basin evolution.

Chapter 3

ANALYTICAL PROCEDURES

3.1. Sampling Procedure.

Most of samples were collected from an open pit of the Mae Moh mine which currently is in production. The R and S layers are not exposed on the pit walls, and hence were selected from a drill core. All samples were collected by Ratanasthien and Abrajano (pers. comm.) in the summer of 1991. Samples were wrapped in aluminum foil and stored in zip lock plastic bags until ready for processing. Oxidized and weathered surfaces were carefully removed during sampling and prior to crushing.

3.2. Analytical Procedures

Samples were divided for different analyses following the flow-chart (Figure 3.1). Prior to being crushed, samples were trimmed and rinsed with distilled water to obtain fresh surfaces. They were then turned to pieces of about 0.3 to 0.5 cm using a maul and a plate, which were pre-cleaned with methanol. Crushed samples were pulverized in a shatter box to 50 to 70 μm grain size. Very short time intervals were selected for the shaking operation to prevent overheating. Coarse grained quartz was pulverized between samples to reduce contamination between samples. The bowl, the ring, and the puck were cleaned with methanol, then flushed with high pressure air

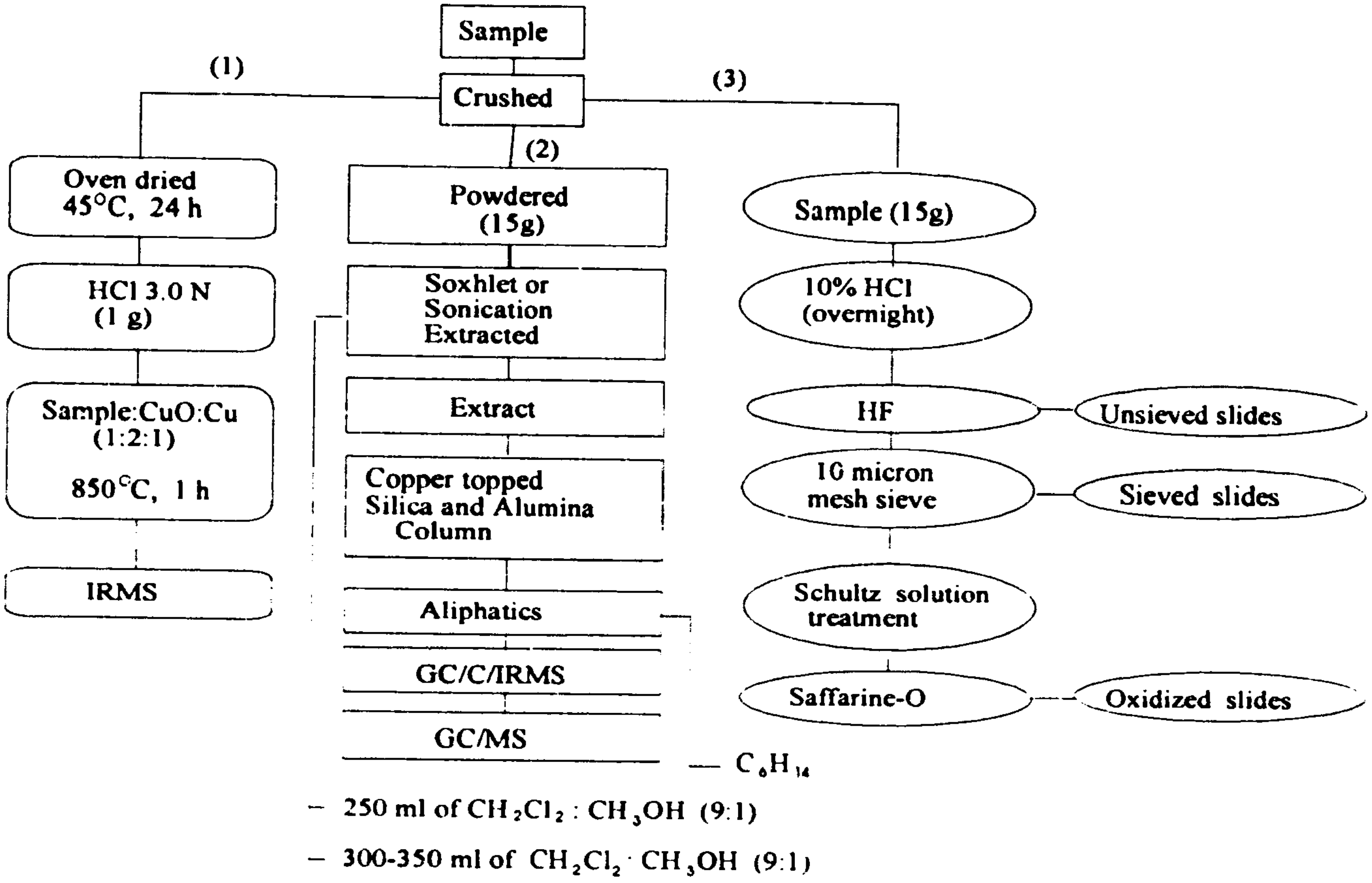


Figure 3.1 Flow-chart illustrating the analytical procedures; (1) carbon isotopic compositions of bulk samples; (2) n-alkanes and their individual carbon isotopic compositions; (3) spores and pollen preparation

for the next sample. Clean vials were used to store the powdered samples for later analysis.

3.3 Stable Carbon Isotope Analysis for Bulk Samples.

Line (1) of the flow-chart illustrates analytical steps for bulk isotopic composition. Total organic carbon (TOC) and CO_2 collection for isotopic analysis for bulk samples were carried out on a high vacuum line with a calibrated manometer (Sofer, 1980; Cauwet, 1975). Prior to removal of carbonate, samples were dried at 45°C for 24 hours to eliminate any free water. About 1 gram of sample was then treated with 3.0 N HCl for 24 hours. The solution was decanted and pre-weighed glass fibre filters were used to collect the acidified samples. The samples were rinsed through the filters using distilled water until the water wash reached neutral pH. The samples were then dried for 24 hours at 45°C and reweighed to calculate the total carbonate content (by weight loss).

Weighed carbonate-free samples were loaded into 9 mm internal diameter (ID) and 25-30 cm long quartz tubes. Coarsely ground copper oxide wire (BDH chemical) and granular copper metal (Alpha Resources Inc.) were added to the samples in volume ratio of 1:2:1 (sample:CuO:Cu). Quartz tubes and copper oxide granules were pre-combusted at 450°C, and 900°C, respectively for 1 hour. Quartz tubes containing samples were vacuumed and sealed on the high-vacuum line, then combusted in a furnace at 850°C for 1 hour.

Carbon dioxide formed from organic carbon was purified cryogenically using the high-vacuum line, and the amounts were measured manometrically. Initially, water and CO_2 were frozen out by liquid N_2 and the non-condensibles were measured and then pumped out. The liquid N_2 was replaced by a dry ice-methanol slurry releasing the CO_2 and trapping it in the manometer section by liquid N_2. The amount of CO_2 was measured manometrically, and the CO_2 collected in pre-evacuated sample containers for isotopic analyses. TOC was calculated by normalizing the measured CO_2 (in micromoles) to the dry rock weight.

The CO_2 obtained from the above procedure was injected into an isotope ratio mass spectrometer (Finnigan Mat 252). All carbon isotope results are reported in the δ-notation:

$$\delta^{13}C = \frac{(^{13}C/^{12}C)_{sample} - (^{13}C/^{12}C)_{standard}}{(^{13}C/^{12}C)_{standard}} \times 1000\ (‰)$$

where $^{13}C/^{12}C$ standard refers to accepted values for Pee Dee Belemnite. Machine precision is generally better than 0.01‰, although overall experimental precision based on duplicate sample preparation is 0.1‰.

3.4 Stable Carbon Isotope Analysis for N-alkanes.

This operation includes extraction of organic matter, preparation of column to isolate n-alkanes and determination of their isotopic compositions following line (2) of the flow-chart (Figure 3.1).

3.4.1 Organic Matter Extraction.

Samples were solvent extracted to isolate and quantify the amount of total extractable organic matter (EOM). Various extraction methods have been developed including sonication, shaking table, reflux, and Soxhlet. Sonication and shaker table techniques are based on physical agitation of samples in solvents. Soxhlet and reflux apparatus dissolve organic matter by refluxing warm solvents through the samples placed in a special filter (thimble).

Selection of the extraction methods and solvent mixture (azeotropic mixture) depends on the types of samples to be extracted (Weaver, 1988). In our study, both sonication and Soxhlet extraction were employed. These two methods have comparable yields, and are extremely efficient for the extraction of oil shales and lignitic samples.

A Vibra - Cell sonication apparatus was used to dissolve the organic matter. The main components of this apparatus are a frequency control panel which is connected with a cylindrical titanium horn. This horn is fitted with a replaceable tip and both are immersed into the solvent with sample. Ultrasonic vibrations of the horn will actually help dissolve the extractable organic matter part from the sample. In this study, about 15 g of powdered sample and 150 ml of solvent (dichloromethane : methanol with the volume ratio of 9 : 1) were mixed in a pre-cleaned glass beaker (250 ml). The horn was placed into the beaker, which was then covered with a pre-cleaned aluminum foil to reduce the evaporation of the solvents. Samples were sonicated for 2 hours with approximately 50 ml of new solvent added after every 1/2 hour.

After sonication, the solvent was decanted and filtered into a round-bottom flask. Successive washes of the solid residue were performed by adding the same solvent combination until the solution was clear. The combined solution (initial solvent plus washing) was rotary evaporated to reduce the solvent volume before transferring the extractant into a clean and pre-weighed vial. The vial containing the organic slush was dried under N_2 gas, and reweighed to calculate the total EOM.

In Soxhlet extraction, about 15 g of sample was weighed into a pre-cleaned thimble using a pre-cleaned spatula. The thimble was then carefully introduced into the Soxhlet concentrator. About 250 ml of solvent mixture (dichloromethane: methanol at 9:1 ratio) was placed in the bottom of the flask, and 24 to 30 hours of extraction was performed. A small volume of solvent was added after 12 hours depending on the observed loss. At the end of Soxhlet extraction, the EOM were treated as following the previous sonication step.

3.4.2 Column Preparation

The EOM consists of a series of different organic compounds. To isolate the alkane fraction from the aromatic and polar compounds, a separation column was utilized. It consists of a glass burette (50 cm long and 6 mm internal diameter) fitted with a 30 ml eluent reservoir and a stopcock to regulate flow rate. The burette is packed with activated silica gel and alumina. The general packing procedure is as follows: half of the column was initially filled with dichloromethane. Care was taken to ensure that the air bubbles that are usually formed around the stopcock were eliminated. About 10 g of activated silica gel was then stirred in a beaker with dichloromethane using a glass rod, and the slurry was gently packed at the bottom of the column. Approximately 5 g of activated alumina slurry was then added to the column. The top 1 cm of the column was packed with activated copper. Thin layers of sand are optionally used to separate the main layers.

3.4.3 N-alkanes Isolation

Prior to separating the compound fractions, the dichloromethane in the packed column was displaced with 50 ml of hexane. The EOM extract (from Sections 3.4.1) was dissolved in hexane and transferred to the top of the column. An initial 50 ml of hexane was allowed to flow through, and the aliphatic fraction alkanes were collected in a pre-weighed flask. Approximately 50 ml of azeotropic mixture of hexane and dichloromethane (1:1 volume ratio) was then allowed to flow through the column, and the resulting fraction containing unsaturated compounds was collected in another pre-weighed flask. The solvents of the saturated and unsaturated fractions were evaporated using the rotary evaporator, and small volumes of the remaining slush were dried off under N_2 gas. All fractions collected were then cold-stored in small vials for later analyses.

3.4.4 Gas Chromatography/Combustion/Isotope Ratio Mass Spectrometry (GC/C/IRMS)

The GC/C/IRMS is a relatively new instrument that allows compound-specific isotope analysis of complex organic mixtures. In this study, a GC/C/IRMS equipped with an HP 5890 gas chromatograph and a VG Optima IRMS were employed. Chromatographic separation was performed on a CP - Sil 5 silica capillary column (25 m x 0.25 mm ID x 0.12 m film thickness) on a splitless mode. Oven temperatures were programmed to hold at 35°C for 1.5 min. then increase at a rate of 10°C/min. to 150°C. This temperature is held for 1 min. then increased at a rate of

4°C/min. to the final temperature of 280°C. Where only the molecular distribution or compound identification are desired, the elutes from the capillary column are directed to the flame ionization detector (FID). During isotopic analysis, a combustion furnace between the GC and IRMS is used to convert the organic compounds in the GC effluent to CO_2. This CO_2 is cryogenically cleaned, and then detected by the IRMS. About 1 μl of sample in hexane was injected for each analysis. The amount of diluent hexane used ranges from 20 ml to 350 ml, depending on the amount of EOM.

3.5 Spore and Pollen Preparation.

This preparation is illustrated by line (3) of the flow-chart (Figure 3.1). Approximately 15 g of crushed sample was weighed into a 500 ml beaker, to which 100 ml of 10% HCl was added. The solution was stirred for about an hour and allowed to stand overnight, then transferred to 50 ml plastic test tubes. These were filled with deionised water, centrifuged (for approx. 3 minutes) and decanted. This procedure was repeated at least 3 times or until the solution was near-neutral. To digest the silicates, concentrated HF acid was added to the test tube and allowed to stand over night. The dissolved silicates and the remaining HF were cleaned with deionised water as in the previous steps.

A slide of the organic residue was made. The sample was then passed through a 10 μ mesh sieve and rinsed until the water passing became clear. Two sieved slides were made at this time. The remaining material was then divided into two parts: one part was stored in a vial labelled unoxidized residue; the other part was oxidized using Schultz solution, a mixture of 10 g potassium chlorate in 100 ml concentrated nitric acid. Depending on the colour of the organic slush, the treatment with Schultz solution varied from 3.5 min. (light brown) to 5-10 min. (brown) to 15 min. (black). The organic residue was then centrifuged and decanted. A second sieving was done first using potassium carbonate solution (50 g potassium carbonate and 500 ml of water), followed by deionized water until it again became clear. Two slides labelled as oxidized slides were made from this solution. For detailed spore and pollen identification, saffarine-O stain was added to the oxidized residue before the last slides were made. Residue remaining after this step was sealed in a vial and archived.

Chapter 4

RESULTS

4.1 Bulk Geochemical Measurements

Geochemical analyses of bulk samples include total organic carbon, total extractable organic matter, and carbonate content. Samples are from three different groups: group I consists of relatively pure lignites, group II includes argillaceous lignites, and group III contains oil shales. Results for each determination are plotted in tables (for different groups) and figures (for different layers).

4.1.1 Total Organic Carbon (TOC)

Total organic carbon (TOC) values vary considerably from 6.38% (MM91) to as high as 34.04% (MM73) with most of the values falling between 15% and 25% (Table 4.1). Both the lignitic samples of group I and the argillaceous lignites of group II have a wide range of TOC. The oil shale samples of group III contain high TOC concentrations and have a narrower range from 17.54% (MM38) to 31.11% (MM50).

Variations in TOC from different layers are presented in Figure 4.1. For the J layer, the TOC values range from 8.07% (MM81) to 30.74% (MM40). They vary from 15.62% to 23.67% for the K layer, from 16.83 to 34.04 for the Q layer, and from 6.38% to 27.54% for the R layer. All samples are very rich in terms of total

	Sample #	Location	TOC		EOM		$CaCO_3$	
			(wt%)	Mean	(wt%)	Mean	(wt%)	Mean
Group I	MM45	J1/1	10.98		3.56		0.26	
	MM47	J1/2	-		4.36		-	
	MM68	J1/3	14.64		1.60		11.46	
	MM71	J1/4	21.67		6.68		5.65	
	MM44	J2	19.02		5.27		3.03	
	MM67	J3B1	15.62	15.96	1.53	3.62	7.14	7.80
	MM80	J3B2	29.04		4.40		3.54	
	MM81	J4	8.07		1.26		5.70	
	MM77	J5B	18.06		4.19		17.45	
	MM46	J6	19.02		2.33		6.53	
	MM78	J6	19.40		4.60		25.08	
	MM85	K1	21.13	21.96	0.96	1.79	10.47	6.46
	MM36	K2	22.68		2.62		2.45	
	MM86	R1	18.26	22.90	2.32	2.72	6.16	6.83
	MM92	R3	27.54		3.12		7.50	
Group II	MM70	J2	-		5.60			
	MM40	J3A	30.74	22.00	6.75	4.46	16.81	13.16
	MM69	J3A	14.52		1.83		8.50	
	MM72	J5C	20.74		3.65		14.17	
	MM35	K1	15.62	18.54	1.77	2.95	12.00	8.85
	MM84	K2	21.45		4.13		5.70	
	MM41	Q1	16.83		3.02		10.46	
	MM73	Q1	34.04		1.38		6.19	
	MM49	Q2	20.37	23.12	2.33	3.33	6.53	6.90
	MM74	Q2	24.84		6.75		0.59	
	MM48	Q3	24.28		4.35		11.96	
	MM75	Q3	18.38		2.16		5.65	
	MM91	R2	6.38		0.85	0.85	18.56	18.56
	MM87	S1	15.56	15.56	1.85	2.30	7.15	5.70
	MM89	S2	-		2.75		4.25	
Group III	MM42	J4	15.98	22.75	1.20	3.57	24.57	16.66
	MM79	J5A	29.52		5.93		8.75	
	MM37	K3	23.67		1.08		10.15	
	MM38	K4	17.54	21.06	1.12	2 42	20.69	14.53
	MM82	K4	21.96		5.07		12.74	
	MM50	Q4	31.11	31.11	5.07	5.07	2.26	2.26

Table 4.1 Total organic carbon, total extractable organic matter and $CaCO_3$ contents.

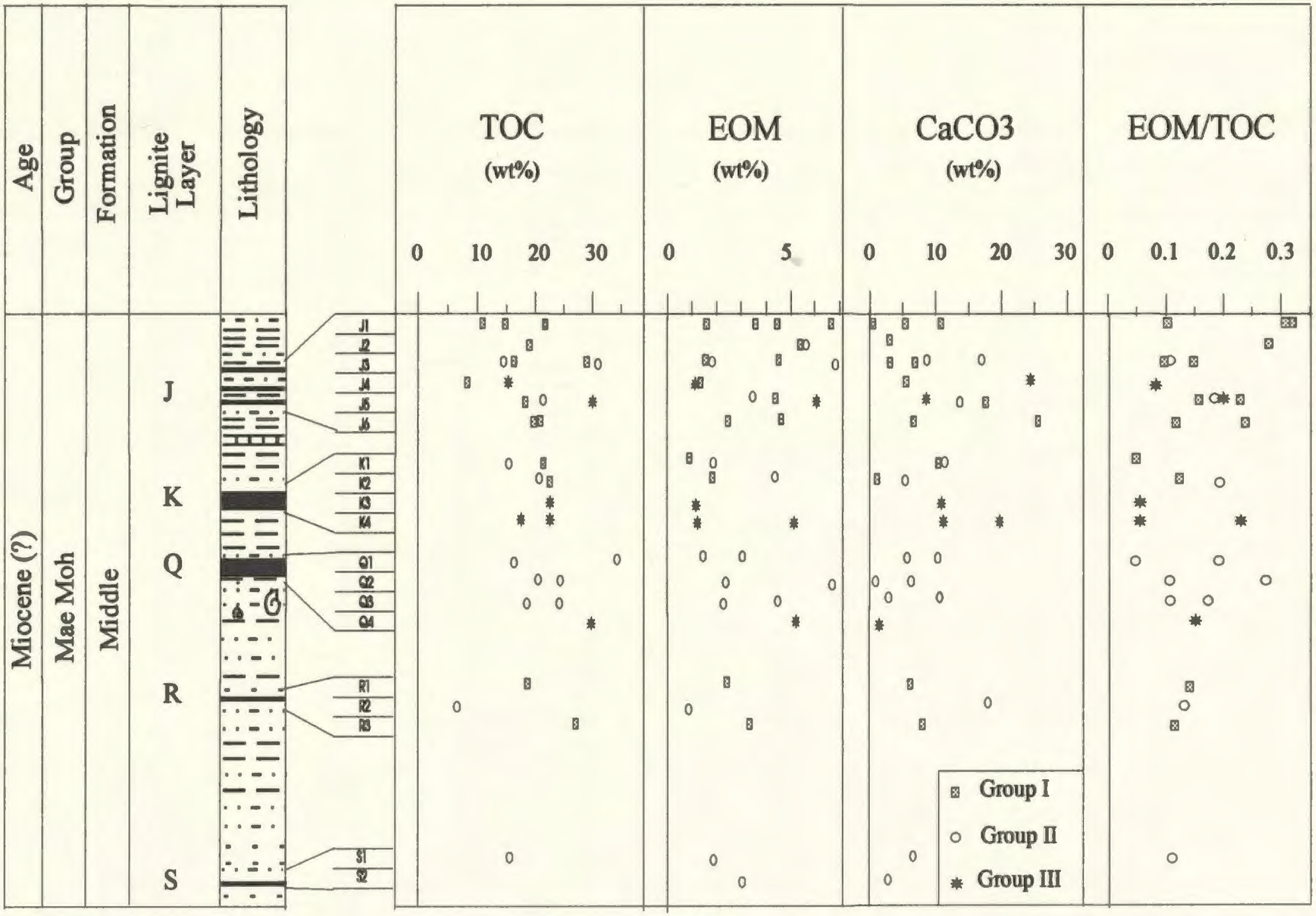


Figure 4.1 Variations of TOC, EOM, CaCO3, and EOM/TOC with depth

organic carbon content. No variation trend is observed for samples from the J, K, and Q layers. Only one sample (MM87) is analyzed for the S layer; it has a TOC value of 15.56%.

4.1.2 Total Extractable Organic Matter (EOM).

The amount of EOM in each sample is quantified following extraction. The values, ranging from 0.85 wt % to 6.86 wt %, are shown in Table 4.1. Most of the samples have EOM values within the range of 1% to 5%. Samples with the EOM values in excess of 5% include 2 from group I, 3 from group II and 3 from group III. Lignitic and argillaceous lignitic samples show the same EOM range: groups I and II have an EOM range of 0.85 wt% to 6.75 wt%, whereas the oil shale samples of group III are 1.08 to 5.93 wt %.

No clear EOM variation trend is observed for samples from the J, K, and Q layers (Figure 4.1). Samples from the R and S layers contain lower EOM concentrations compared to those from the upper layers. It should be noted that EOM is an operational definition that includes free molecules of asphaltenes, resins, and hydrocarbon fractions (Tissot and Welte, 1984). In the early stages of organic matter degradation, microbial degradation is believed to be largely responsible for generating extractable organic matter. At later stages of sediment maturation, thermal alteration is believed to predominate. The ratio of EOM versus TOC therefore may indicate the level of transformation of organic matter in the sediments. For Mae Moh Basin samples, this ratio ranges from 0.04 to 0.32.

4.1.3 Carbonate Content.

Carbonate contents vary considerably from 0.26 wt% to as high as 25.08 wt% (Table 4.1). Most lignitic samples have low concentrations of $CaCO_3$; oil shales of lignites J, K, and Q generally have a higher carbonate content with some samples in the J seam exceeding 20 wt%. Argillaceous lignitic samples of group II have a fairly high $CaCO_3$ content.

The $CaCO_3$ concentrations fluctuate considerably even within a thin sedimentary layer. For example, both MM45 and MM68 are from J1; their $CaCO_3$ contents are 0.26 wt% and 11.46 wt%, respectively. Likewise, MM46 and MM78 from J6 have $CaCO_3$ contents of 6.53 wt% and 25.08 wt%, respectively. No clear relationship between individual samples or sample groups in terms of $CaCO_3$, TOC, or EOM is determinable from these data.

4.2 Normal alkanes and Isoprenoids

Normal alkanes (n-alkanes) are members of an organic compound group consisting of linear saturated hydrocarbons. Isoprenoids such as pristane and phytane, and the n-alkanes are the most common compounds present in the saturate fraction of hydrocarbons. Individual n-alkane peaks in the FID chromatograms are labelled by carbon number (*e.g.*,"20" means 20 carbons in the carbon chain) and pristane and phytane are associated with n-C_{17} and n-C_{18}. In addition, minor peaks occur between the n-alkane peaks as "humps" that maximize at around C_{27}-C_{32} or, in some cases, around shorter chain length compounds C_{15}-C_{16}. Both the minor peaks and the "hump" are generally attributed to branched and cyclic compounds that elute with the saturate fraction during column chromatography.

4.2.1 N-alkane Distribution.

The n-alkane distributions of samples from the Mae Moh Basin are presented in Appendix 1, together with the carbon isotope compositions. These combined chromatograms show that all samples have n-alkanes ranging from n-C_{15} to n-C_{33}, which can be roughly divided into three compound series. The first series includes low molecular weight (LMW) components from n-C_{15} to n-C_{19}; medium molecular weight (MMW) components from n-C_{20} to n-C_{25} constitute the second series; whereas the third series consists of high molecular weight (HMW) components from n-C_{26} to n-C_{33}.

The oil shale samples of group III are characterized by a relatively high abundance of LMW series ranging from 13.0 to 42.9 wt% (Table 4.2). Most of the samples have maxima at n-C_{15} and n-C_{17}, with the n-C_{15} abundance usually exceeding that of n-C_{17}. The total abundance of MMW alkanes varies from 19.2 to 31.7 wt%, and that of HMW series range from 28.6 to 65.7 wt%. In contrast, group II samples have a lower abundance of LMW alkanes when compared to group III (9.2 to 15.5 wt%). None of the individual n-alkanes exceeds 5 wt%. The abundance of the MMW compounds in group II varies from 17.4 to 32.1 wt%. The high molecular weight compounds predominate in group II where they range from 52.4 to 72.3 wt%. The lignitic samples from group I are characterized by a significantly lower abundance of the LMW series (3 to 8.5 wt%) and a corresponding increase of HMW alkanes (53.6 to 82.3 wt%). The MMW alkanes in the lignitic samples range from

	Sample #	Location	Σ wt%		
			C_{15}-C_{19}	C_{20}-C_{25}	C_{26}-C_{11}
Group I	MM45	J1/1	3.21	14.72	82.06
	MM47	J1/2	4.11	17.98	77.91
	MM68	J1/3	4.95	23.74	71.30
	MM71	J1/4	5.21	20.28	74.51
	MM44	J2	6.31	40.08	53.61
	MM67	J3B1	6.44	29.51	64.05
	MM80	J3B2	3.02	23.34	73.64
	MM81	J4	8.46	19.25	72.29
	MM77	J5B	2.96	31.24	65.80
	MM46	J6	3.13	21.63	75.23
	MM78	J6	3.42	30.99	65.59
	MM85	K1	4.55	25.35	70.10
	MM36	K2	6.56	25.79	67.65
	MM86	R1	7.10	14.92	77.98
	MM92	R3	5.72	11.99	82.29
Group II	MM70	J2	9.15	24.74	65.75
	MM40	J3A	-	-	-
	MM69	J3A	7.53	34.45	58.02
	MM72	J5C	14.35	26.23	59.42
	MM35	K1	-	-	-
	MM84	K2	10.45	19.50	70.05
	MM41	Q1	11.20	23.10	65.62
	MM73	Q1	11.51	18.60	69.89
	MM49	Q2	13.75	28.44	57.81
	MM74	Q2	10.50	17.40	72.10
	MM48	Q3	9.50	20.45	70.05
	MM75	Q3	12.98	21.73	65.29
	MM91	R2	9.24	18.48	72.28
	MM87	S1	10.53	29.50	59.97
	MM89	S2	12.94	39.16	47.90
Group III	MM42	J4	13.04	22.76	64.20
	MM79	J5A	17.51	31.69	50.80
	MM37	K3	18.86	27.43	53.71
	MM38	K4	18.55	19.23	62.22
	MM82	K4	17.23	17.04	65.73
	MM50	Q4	42.89	28.49	28.62

Table 4.2 Group I and II samples are characterized by a high abundance of the LMW range and low abundance of the LMW, particularly those of group I. An increase in abundance of the LMW is observed for samples of group III.

14.7 to 40.1 wt%. HMW fractions predominate in all samples with maxima at n-C_{29} or n-C_{31}. The n-C_{27} component is less abundant than either n-C_{29} or n-C_{31}, except for MM44.

4.2.2 Carbon Preference Index (CPI)

CPI represents the ratio of relative abundance of odd versus even n-alkanes originally established by Bray and Evans (1961) to calculate the CPI over the C_{24}-C_{32} range. The formula :

$$\text{CPI 1} = \frac{C_{25}+C_{27}+C_{29}+C_{31}}{C_{24}+C_{26}+C_{28}+C_{30}} + \frac{C_{25}+C_{27}+C_{29}+C_{31}}{C_{26}+C_{28}+C_{30}+C_{32}}$$

has been modified and extended by various authors. For example, Philippi (1965) compared the odd predominance of three compounds: n-C_{28}, n-C_{29}, and n-C_{30} in the following relation:

$$\text{CPI 2} = \frac{2C_{29}}{C_{28} + C_{30}}$$

An odd carbon predominance of HMW alkanes (characterized by CPI 1 and CPI 2) in Mae Moh samples is observed (Table 4.3). CPI 1 varies from 0.9 to 3.0 with most of the values higher than 1, except MM48, MM49, and MM44. CPI 2 has a wider range from 0.6 to 3.8, with three samples (MM49, MM73, and MM44) having CPI 2 values less than 1. Only 4 out of the total 36 samples analyzed exhibit a CPI even preference. All oil shales have CPI higher than unity.

	Sample #	Location	CPI 1	Mean	CPI 2	Mean	CPI 3	Mean	CPI 4	Mean
Group I	MM45	J1/1	2.75	2.23	1.90	2.18	0.99	0.79	0.86	1.08
	MM47	J1/2	2.21		1.66		0.76		1.11	
	MM68	J1/3	2.30		1.66		0.79		1.09	
	MM71	J1/4	1.74		1.41		0.79		1.16	
	MM44	J2	0.95		1.00		0.91		1.05	
	MM67	J3B1	2.01		2.42		0.40		1.13	
	MM80	J3B2	2.66		2.87		0.70		1.05	
	MM81	J4	1.64		1.74		1.15		1.10	
	MM77	J5B	2.95		3.77		0.71		1.27	
	MM46	J6	2.43		1.81		0.80		1.20	
	MM78	J6	2.90		3.77		0.72		0.82	
	MM85	K1	1.96	2.03	2.05	2.09	1.34	0.94	1.53	1.33
	MM36	K2	2.09		2.13		0.53		1.12	
	MM86	R1	1.27	1.15	1.39	1.09	0.80	0.78	1.67	1.74
	MM92	R3	1.03		0.78		0.76		1.80	
Group II	MM70	J2	1.82	1.56	1.54	1.18	1.11	0.98	1.02	1.06
	MM40	J3A	1.02		1.11		1.42		1.25	
	MM69	J3A	2.03		-		0.42		-	
	MM72	J5C	1.35		0.90		0.95		0.92	
	MM35	K1	-	-	-	-	-	-	-	
	MM84	K2	-	-	-	-	-	-	-	-
	MM41	Q1	1.82	1.36	2.32	1.19	1.00	1.40	1.13	1.78
	MM73	Q1	1.52		1.22		1.23		1.09	
	MM49	Q2	0.87		0.64		1.52		1.26	
	MM74	Q2	1.67		1.03		1.75		1.52	
	MM48	Q3	0.97		0.72		1.41		4.62	
	MM75	Q3	1.29		1.15		1.49		1.04	
	MM91	R2	1.92	1.92	1.82	1.82	0.85	0.85	0.81	0.81
	MM87	S1	1.02	1.08	1.14	1.24	0.47	1.20	0.96	0.98
	MM89	S2	1.13		1.33		1.92		1.00	
Group III	MM42	J4	2.08	2.03	2.14	1.65	1.28	1.14	1.56	1.33
	MM79	J5A	1.97		1.16		1.00		1.09	
	MM37	K3	1.31	1.43	1.48	1.29	1.17	0.70	1.38	1.43
	MM38	K4	1.39		1.01		0.54		2.00	
	MM82	K4	1.60		0.38		0.40		0.92	
	MM50	Q4	1.98	1.98	-		1.33	1.33	5.62	5.62

Table 4.3 Carbon preference indices of Mae Moh samples. Most of the CPI 1 and CPI 2 values exceed unity showing an odd predominance for the HMW range. Some CPI 3 values are less than unity as a result of the abundance of the n-C_{24}. CPI 4 having most of the values higher than unity, also show an odd predominance of the LMW range.

In addition, the two equations

$$\text{CPI 3} = \frac{2C_{23}}{C_{22} + C_{24}} \qquad \text{and} \qquad \text{CPI 4} = \frac{2\ C_{17}}{C_{16} + C_{18}}$$

help characterize the LMW and MMW n-alkane series with respect to source changes and degradation. CPI 3 (MMW alkanes) have a narrower range (0.40 to 1.75). More samples have values less than 1 and those that exceed 1 still do not show a clear odd preference. The high concentration of the n-C_{24} component in many samples is the main reason responsible for the CPI 3 values being less than 1. CPI 4 show a clear odd predominance for the LMW alkanes. Two samples, which are exceptionally high, include MM48 (group II) and MM50 (group III). This is due to the abundance of C_{15} and particularly C_{17} (for MM50).

Figure 4.2 illustrates variation trends of CPI with increasing depth. Slight decreases towards unity from J towards S are observed for CPI 1 and CPI 2. It is more clearly seen for samples of groups I and III than those of group II. It is notable that CPI 1 values > 2 are only observed in the shallow samples of the J and K layers. Higher values for CPI 2 also tend to be restricted to shallower depths. Nevertheless, the stratigraphic pattern exhibited by CPI 2 is very similar to that of CPI 1. CPI 3 and CPI 4 do not follow the same pattern as in CPI 1 and CPI 2. CPI 3 tends to show a narrow range around unity. CPI 4, which represents the odd/even predominance for the LMW range, shows values that are generally higher than 1 for the entire stratigraphic section. MM50 and MM48 have high values of CPI 4; this is a result of abundant n-C_{15} and n-C_{17}, otherwise the records show a scattered

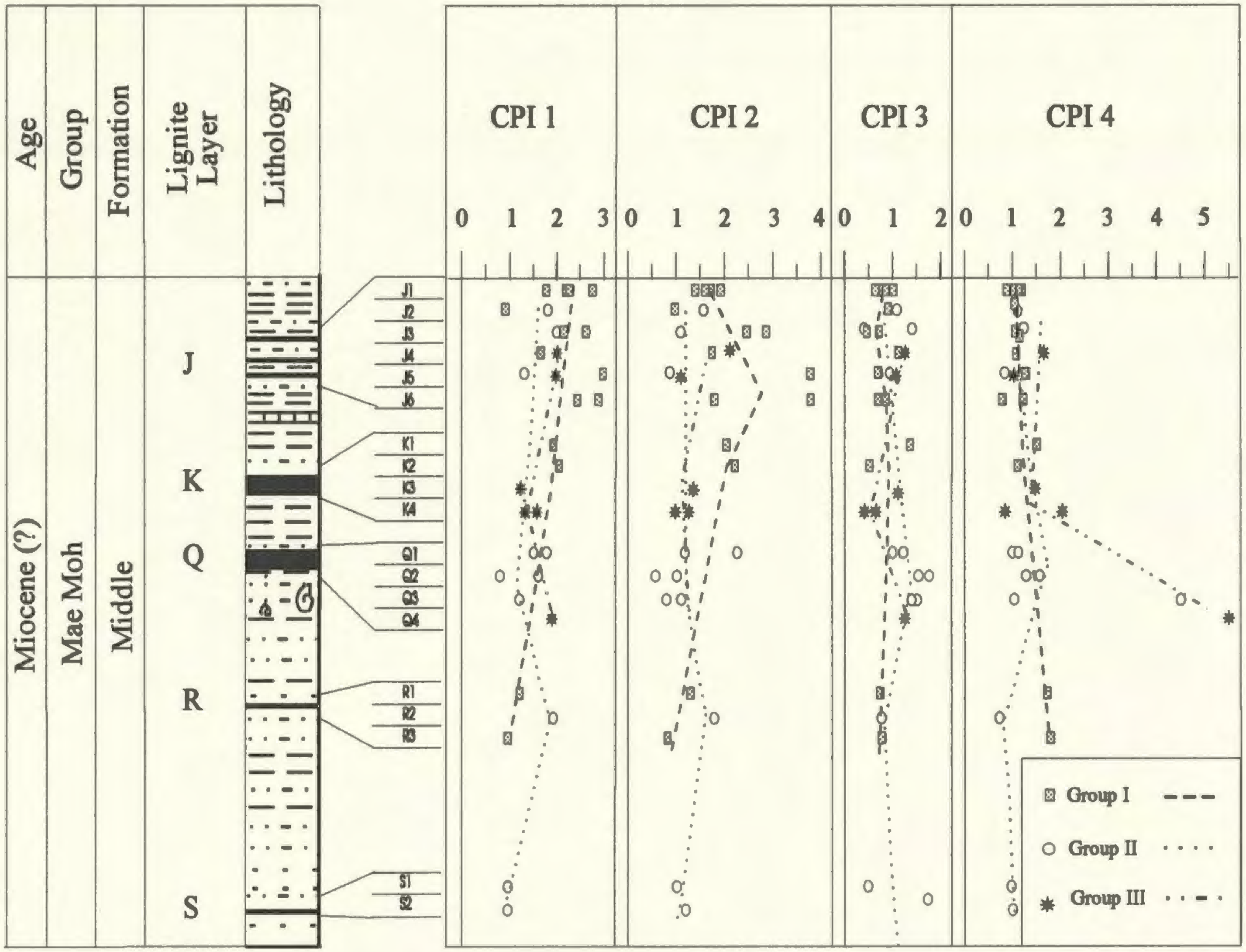


Figure 4.2 Interrupted lines illustrate variation tendencies of CPI values with increasing depth. CPI 1 and CPI 2 tend to decrease toward unity from J to S layers. CPI 3 having values less or close to unity shows an even dominance or diluted odd predominance for the C22 to C24 range. A large variation of odd predominance of the LMW range is indicated by CPI 4.

distribution (Figure 4.2). The traditional definition of CPI is only a partial representation of the n-alkane distribution, and unique patterns of distribution can be discerned from the distribution of MMW (CPI 3) and LMW (CPI 4) alkanes. It should be noted that the number of samples analyzed for each layer are not the same; variation trend presented may be biased from statistic view.

4.2.3 Pristane/phytane ratios.

Pristane (Pr) and phytane (Ph) occur in almost all Mae Moh samples, where their ratios vary from 1 to 3.53 (Table 4.4). They are absent in 4 samples (MM44, MM78, MM92, and MM50). MM35 and MM40 show "big humps" on FID chromatograms, therefore the Pr/Ph ratios are not calculated. In lignitic samples of group I, the Pr/Ph ratios range from 1.02 to 2.07. They have a wider range for samples of group II varying from 1.01 to 3.53. Oil shales of group III have values close to unity from 0.95 to 1.58.

Interrupted lines illustrate variations of Pr/Ph values at different layers for samples from different groups (Figure 4.3). Group I samples increase from 1 in the J layer to 2 in the K layer, and back to 1 in the R layer. Group II samples show a somewhat zigzag variation, where high values are found in the K,Q and S lignites and low values occur in the J and R lignites. Oil shales of group III have ratios close to 1 except MM37 (1.58), and do not change very much with depth.

	Sample #	Location	Pr/Ph	Mean
Group I	MM45	J1/1	1.32	
	MM47	J1/2	1.03	
	MM68	J1/3	1.40	
	MM71	J1/4	1.02	
	MM44	J2	-	
	MM67	J3B1	1.29	1.21
	MM80	J3B2	1.29	
	MM81	J4	1.17	
	MM77	J5B	1.06	
	MM46	J6	1.25	
	MM78	J6	-	
	MM85	K1	1.93	2.00
	MM36	K2	2.07	
	MM86	R1	1.27	1.27
	MM92	R3	-	
Group II	MM70	J2	1.21	
	MM40	J3A	-	1.18
	MM69	J3A	1.33	
	MM72	J5C	1.01	
	MM35	K1	-	
	MM84	K2	2.15	2.15
	MM41	Q1	3.53	
	MM73	Q1	3.33	
	MM49	Q2	3.10	2.72
	MM74	Q2	2.10	
	MM48	Q3	1.25	
	MM75	Q3	3.01	
	MM91	R2	1.06	1.06
	MM87	S1	1.91	1.66
	MM89	S2	1.40	
Group III	MM42	J4	1.09	1.02
	MM79	J5A	0.95	
	MM37	K3	1.58	
	MM38	K4	1.01	1.20
	MM82	K4	1.00	
	MM50	Q4	-	

Table 4.4 Most of the Pr/Ph ratios exceed unity. Those of group III samples are close to 1.

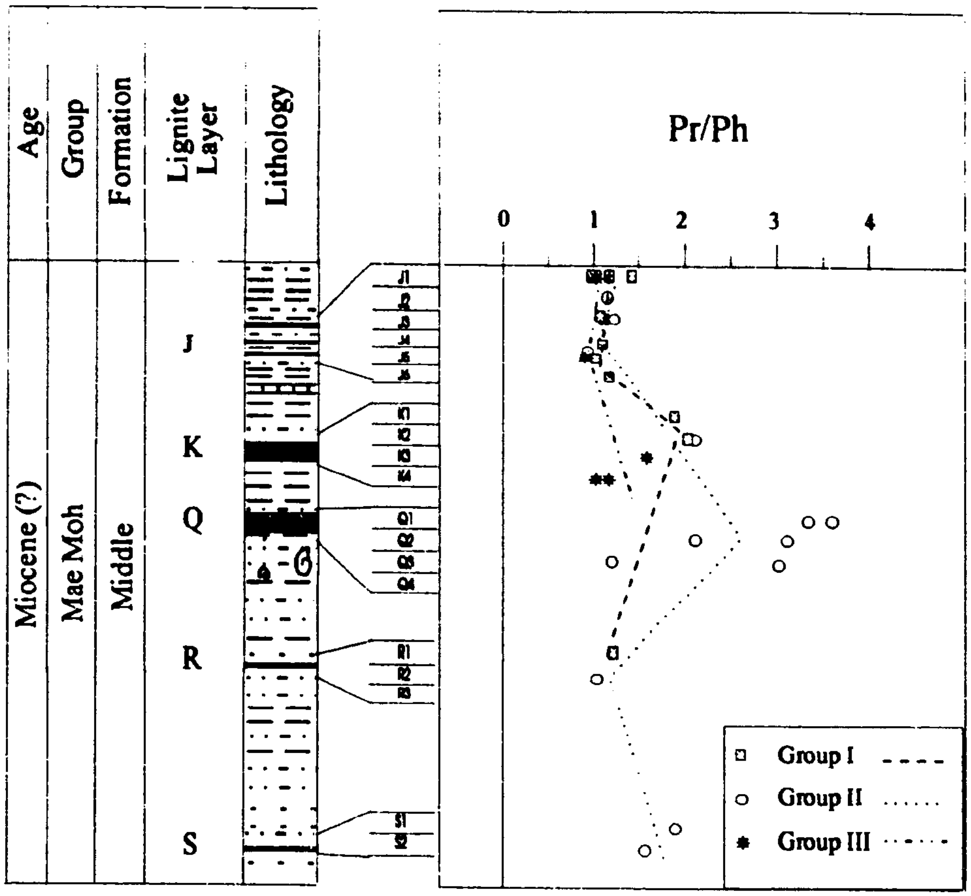


Figure 4.3 Variations of pristane/phytane ratios with depth are illustrated by interrupted lines. The Pr/Ph values of oil shale are close to unity. Groups I and II have high Pr/Ph values at the K and Q layers as shown by the zigzag shape.

4.3 Carbon Isotopic Composition of Bulk Samples.

The $\delta^{13}C$ bulk values fall in a narrow range from -22.5‰ to -26.8‰ (Table 4.5). No significant variations of the carbon isotopic composition between samples in the same layer were observed, and no systematic stratigraphic variations can be discerned. The highest $\delta^{13}C$ value (-22.5‰) belongs to the oil shale at the base of the K layer (MM82). This thin brown yellowish oil shale layer is intercalated with dark brown mudstone and overlain by a lignitic layer. The two samples which have low values are MM70 of the J layer (-26.1‰) and MM75 of the Q layer (-26.8‰). Both samples are black grey, yellowish argillaceous lignite in which woody tissues can be observed.

4.4 Carbon Isotopic Composition of Individual N-alkanes

The $\delta^{13}C$ values of the n-alkanes isolated from the Mae Moh Basin samples are shown in Table 4.5 and graphically presented together with the n-alkane distribution in Appendix A. The overall range of isotopic compositions varies from -24‰ to -39‰, much larger than the isotopic variations in bulk samples. However, most of the individual alkanes have values within the range of -27‰ to -32‰. Abundant land-plant samples are approximately 5 to 6‰ more depleted in ^{13}C compared with algal rich samples (Freeman *et al.*, 1990). Generally, the long-chain n-alkanes from the Mae Moh Basin are more depleted in ^{13}C compared to those of the shorter n-alkanes (*i.e.*, of the first and second series; see Appendix A). This tends to agree with the above suggestion that long-chain carbon compounds are derived primarily from higher plants and have more depleted ^{13}C values. Some oil shale samples of

	Location	$\delta^{13}C$			
		Bulk	N-alkanes		
			C15 - C19	C20 - C25	C26 - C33
<u>Group I</u>					
MM45	J1/1	-24.5	-29.5 to -31.9	-29.1 to -31.0	-30.3 to -35.0
MM47	J1/2	-25.4	-29.2 to -30.9	-29.9 to -30.4	-30.9 to -33.0
MM68	J1/3	-25.8	-28.2 to -30.8	-26.9 to -31.5	-29.4 to -36.1
MM71	J1/4	-25.3	-28.4 to -30.5	-27.8 to -31.4	-29.7 to -33.6
MM44	J2	-26.3	-30.5 to -31.9	-27.7 to -31.7	-30.0 to -35.0
MM67	J3B1	-24.3	-	-25.6 to -28.4	-29.4 to -33.7
MM80	J3B2	-23.6	-	-26.5 to -29.6	-28.2 to -29.9
MM81	J4	-24.4	-26.6 to -29.0	-27.4 to -33.0	-25.1 to -38.4
MM77	J5B	-23.8	-	-27.1 to -28.4	-28.2 to -30.8
MM46	J6	-25.7	-	-26.2 to -30.4	-26.5 to -32.2
MM78	J6	-23.1	-	-26.5 to -29.8	-28.5 to -33.2
MM85	K1	-23.8	-25.7 to -27.6	-26.7 to -29.9	-28.5 to -36.5
MM36	K2	-24.7	-28.2 to -30.9	-25.6 to -30.2	-30.1 to -33.0
MM86	R1	-23.6	-26.6 to -28.8	-28.7 to -29.6	-27.5 to -34.7
MM92	R3	-25.7	-	-	-27.3 to -35.5
<u>Group II</u>					
MM70	J2	-26.1	-28.8 to -30.5	-25.4 to -33.7	-30.3 to -34.6
MM40	J3A	-25.5	-	-	-
MM69	J3A	-23.8	-26.8 to -31.2	-26.0 to -29.4	-29.3 to -32.1
MM72	J5C	-23.4	-30.0 to -32.3	-27.7 to -30.6	-27.9 to -35.6
MM35	K1	-24.8	-	-	-
MM84	K2	-24.5	-	-26.4 to -28.7	-28.5 to -33.5
MM41	Q1	-23.9	-26.5 to -28.9	-27.1 to -28.8	-26.7 to -35.3
MM73	Q1	-25.8	-26.8 to -29.1	-27.7 to -29.3	-28.3 to -36.6
MM49	Q2	-25.4	-	-24.1 to -27.7	-27.9 to -35.0
MM74	Q2	-23.1	-28.2 to -29.8	-28.1 to -29.1	-28.1 to -30.7
MM48	Q3	-25.6	-	-27.4 to -31.5	-30.1 to -38.0
MM75	Q3	-26.8	-27.4	-26.1 to -29.9	-28.5 to -31.3
MM91	R2	-24.2	-29.6 to -31.6	-28.4 to -31.1	-30.1 to -34.9
MM87	S1	-24.4	-27.6 to -30.0	-26.3 to -29.3	-28.1 to -36.5
MM89	S2	-24.9	-	-25.0 to -28.5	-28.0 to -36.5
<u>Group III</u>					
MM42	J4	-23.8	-28.6 to -29.9	-27.8 to -30.7	-28.5 to -35.0
MM79	J5A	-23.4	-28.5 to -30.9	-29.1 to -30.3	-29.1 to -37.1
MM37	K3	-24.5	-24.9 to -29.4	-25.9 to -29.5	-28.6 to -39.0
MM38	K4	-23.8	-25.5 to -27.5	-21.7 to -27.9	-27.4 to -33.1
MM82	K4	-22.5	-24.7 to -28.3	-24.5 to -29.4	-25.4 to -35.1
MM50	Q4	-25.4	-28.4 to -28.9	-29.1 to -30.0	-29.7 to -30.4

Table 4.5 The bulk composition range is in agreement with that of lignites and oil shales elsewhere. It also suggests the C_3 biosynthetic pathways of plants. Individual n-alkanes show a depletion tendency in ^{13}C in the HMW range compared to those in the LMW. HMW alkanes are generally lighter than -30 ‰.

group III, having more algal material as indicated by higher abundance of shorter n-alkanes, exhibit slightly enriched values in ^{13}C in the first and second series compared to those of the same series in other groups. It is also noteworthy that the carbon isotopic values of n-alkanes tend to be more depleted compared to those of the bulk samples. This is consistent with the general observation that the saturated fractions of petroleum tend to be the most isotopically depleted EOM fractions.

4.5 Thermal Alteration Index (TAI)

Thermal maturation is reflected by progressive changes in the physical and chemical properties of spores, pollen and organic particulates. Such properties as colour, light transmission, index of refraction, and spectral fluorescence are widely used for evaluating the progress of thermal alteration due to burial (Staplin,1969). In this study, exinite (spores, pollen, "cuticle") and cutinite (degraded cellulosic woody fragments and leaf remains) examined under transmitted light are used to determine the degree of thermal maturation (TAI). The colours of 100 to 120 organic particles from each sample were matched with the standard colour charts of Staplin (1971) and Traverse (1988). Figure 4.4 shows the correlation between TAI, vitrinite reflectance (R_o), the oil window, and coal rank. TAI values range from 1 to 5 and correspond to the shift in colour from colourless, yellowish green, pale yellow, red, brown and black.

Spores and pollen of the same colour were counted and averaged for every layer from J to S. The average number of observations versus the colour values are presented in Figure 4.5. The palynomorphs of the Mae Moh Basin have colour

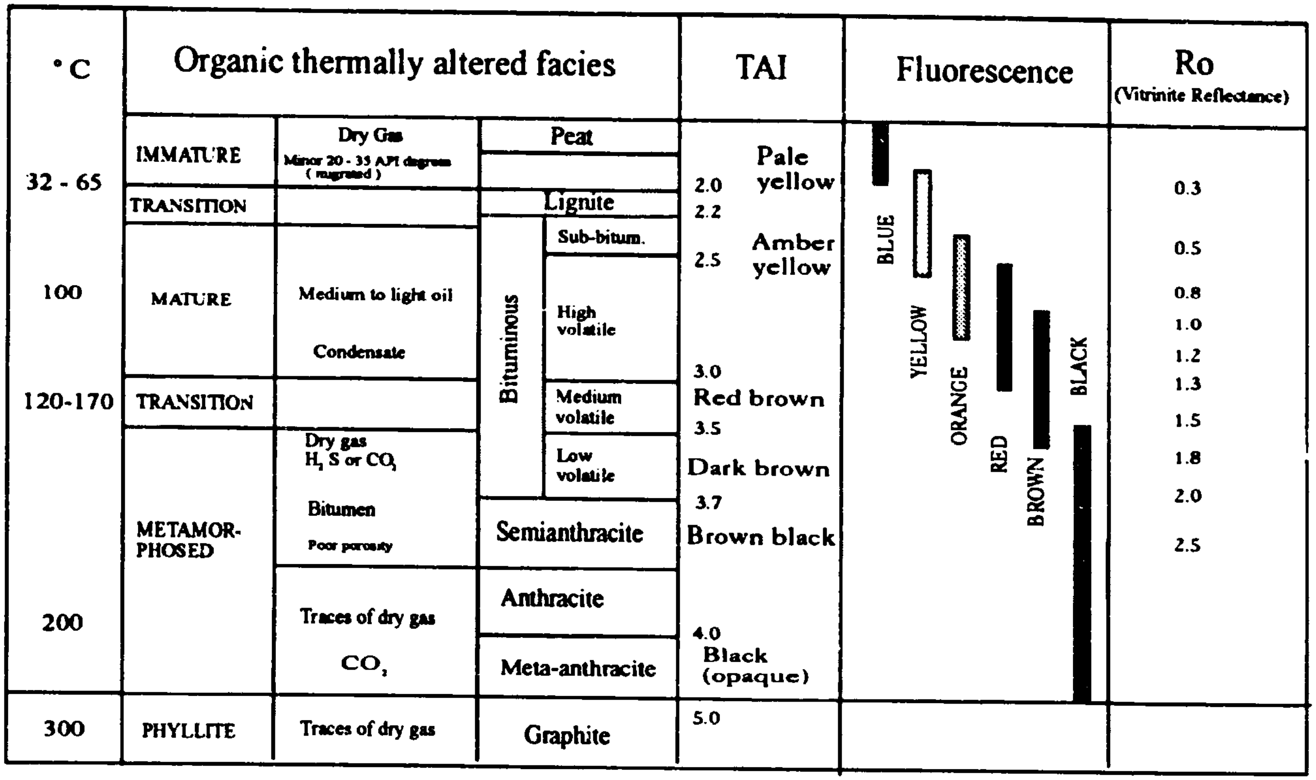


Figure 4.4 Correlation between TAI, vitrinite reflectance, and fluorescence was compiled by Staplin (1971) to show coal rank and oil generation evolution. The colour of spores, pollen, and organic particulates was matched with the TAI indices of Staplin (1971) and Traverse (1988).

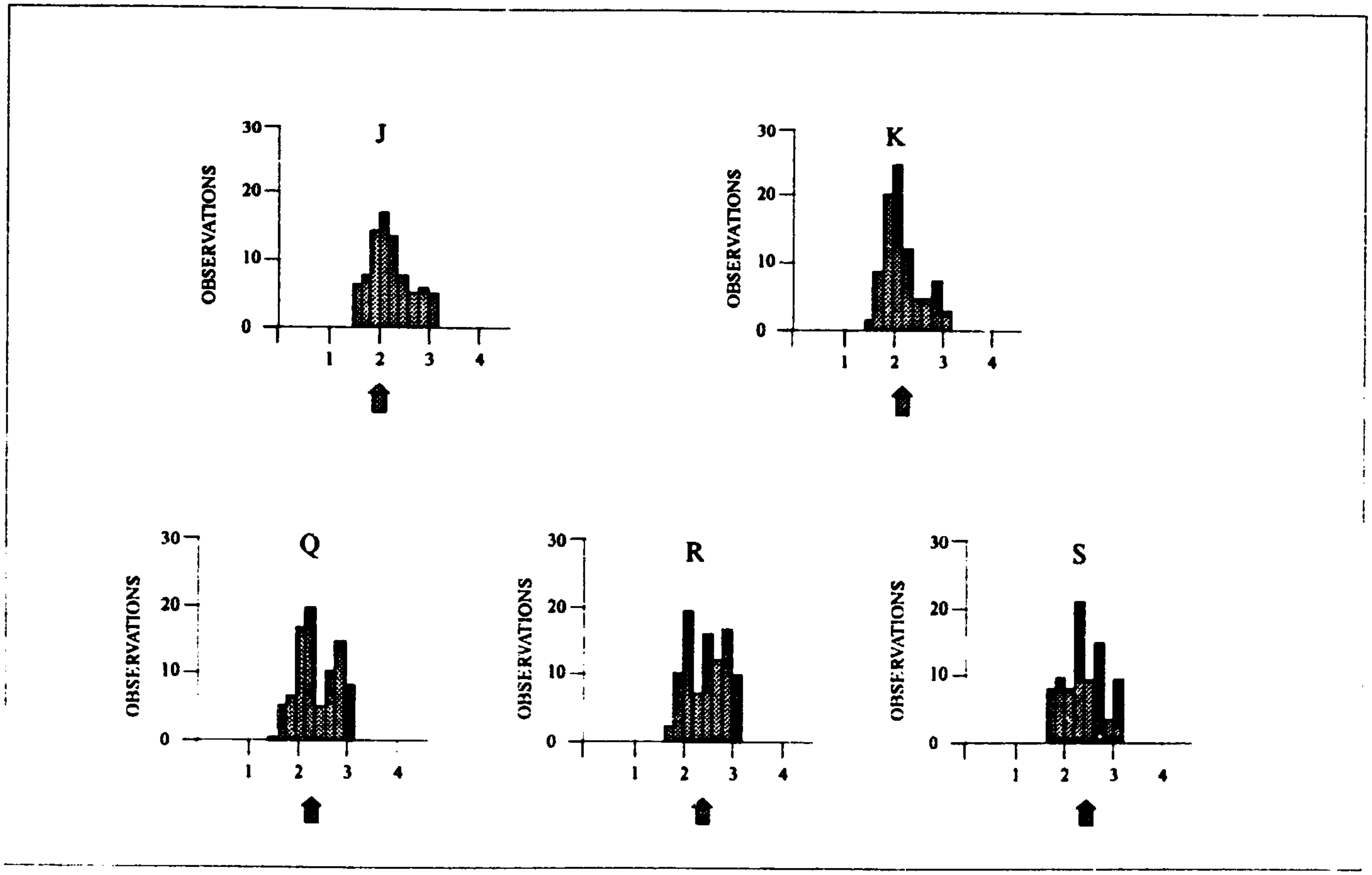


Figure 4.5 Maturation indicated by the TAI values are presented by the arrows below abscissas. The average values show a slight increase from the J to the S layer.

values ranging from 1.4 to 3.0. For the J layer, the majority of the observations have TAI values ranging from 1.8 to 2.2. For the K layer, TAI values of 1.4 and 1.6 are less common, but the maxima remain around 2.0; TAI values < 1.4 are still observed in the Q layer, but they are absent in the R and S layers. Here, more palynomorphs with TAI values of 2.6 to 3.0 are encountered.

4.6 Identification of spores and pollen

The Mae Moh Group is divided into 3 palynological units based on the appearance and abundance of specific spore-pollen assemblages (Figure 4.6). The first unit is defined by a greater abundance of deciduous trees and herbaceous taxa over palm and fern assemblages. The second unit is a transitional unit wherein deciduous trees are overwhelmed by palm, fern and other swamp forest species. The third unit is marked by a high frequency of fern, palm and swamp taxa. Photomicrographs of selected spores and pollen are shown in Appendix B.

Unit 1 is dominated by *Alnipollenites* and *Trivestibulopollenites* (Plate IV, Figure 4). Both specimens are produced by temperate deciduous trees, *Alnipollenites* by alder and *Trivestibulopollenites* by birch. Their frequency in this unit averages around 25 to 30 %. *Quercoidites*, oak pollen, is also present in a smaller amount (~3%). Specimens such as *Crassoretitriletes* sp. (Plate III, Figure 2) and *Trichanthera* sp. (Plate 3, Figure 4) account for around 10 to 15% of the assemblage. The presence of fern and palm palynomorphs are also notable. Among them, a palm specimen, *Spinizonocolpites* (Plate I, Figure 3), accounts for about 1 to 8% of the pollen assemblages. Pine pollen (*Pinus*) is found in small numbers in the S lignite at

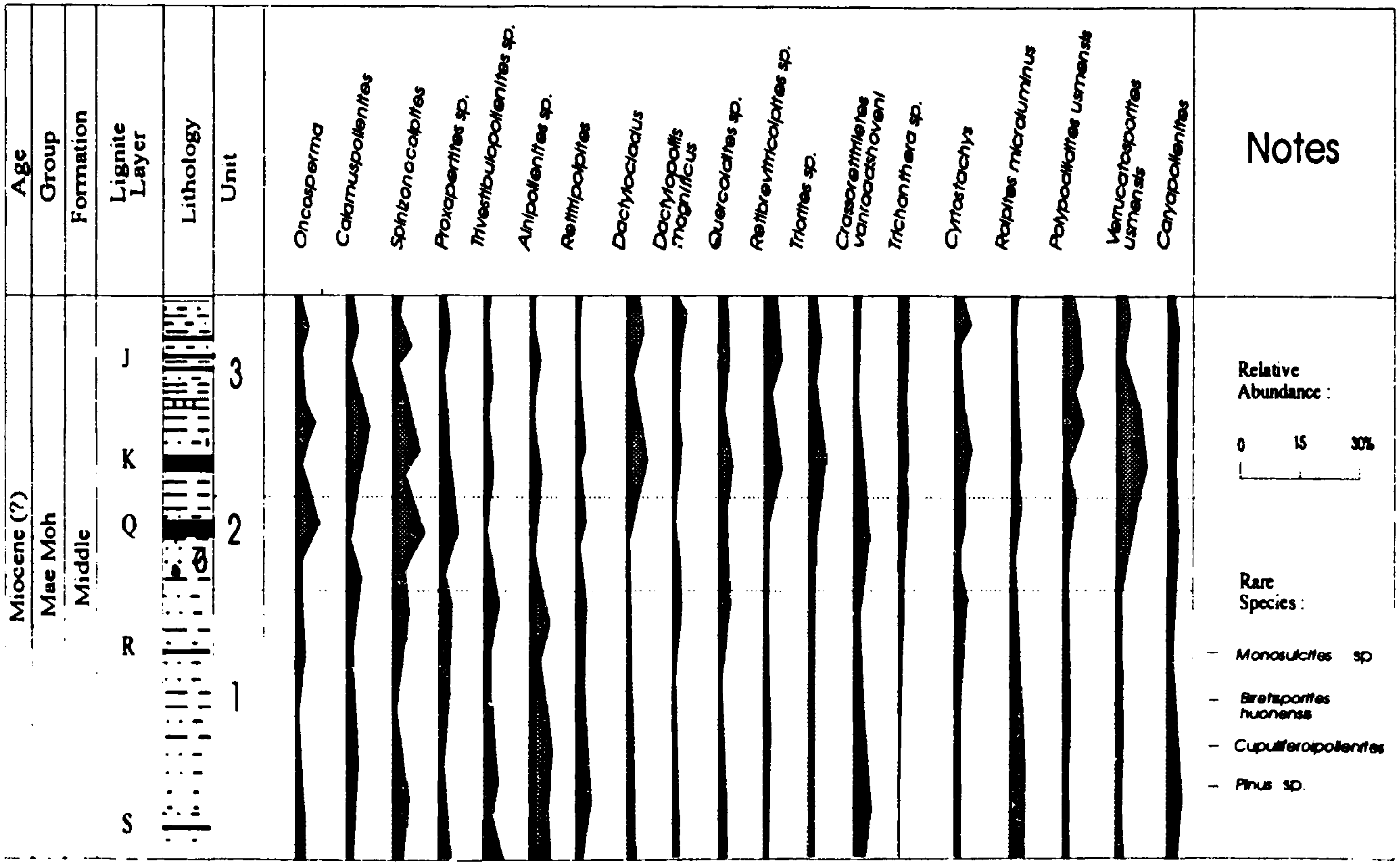


Figure 4.6 Spore and Pollen Diagram of the Mae Moh Basin. Shading parts show the abundances of identified species. Individual species are illustrated in Appendix B.

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Unit 2 is considered a transitional zone on the basis of the changes in abundance of warm and cool taxa. *Spinizonocolpites*, for example, is clearly more abundant (12%), as are *Oncosperma*, a mangrove swamp indicator (Anderson and Muller, 1975), and *Calamuspollenites*. The fern spore *Verrucatosporites* (Plate I, Figure 4) increases from about 2% at the base to nearly 10% at the top of unit 2. This transitional interval also marks the decline of deciduous trees.

Unit 3 is dominated by fern spores, palm pollen and other swamp forest taxa. *Verrucatosporites* shows peak abundances in this interval. Among palm taxa, *Oncosperma*, *Calamuspollenites*, *Spinizonocolpites* continue to be abundant. Other swamp forest forms such as *Dactylocladus*, *Dactilopollis magnificus*, and *Cyrtostachys* average around 10-12%. Some specimens with biostratigraphic significance are identified. *Roipites microluminus* Kemp (Plate IV, Figure 2) is also found in Oligocene - early Miocene strata of the Ninetyeast Ridge (Kemp *et al.*, 1977). Other rare species include *Pinus* sp. (Plate II, Figure 4), *Monosulcites* sp. (Plate IV, Figure 3), *Cupuliferoipollenites* and *Biretisporites huonensis* (Plate II, Figure 2).

In summary, analyses provide two principal set of data: geochemical and palynological measurements. In the first set of data, the bulk compositions include total organic carbon, total extractable organic matter, carbonate contents, and carbon isotopic compositions. N-alkanes distribution, carbon preference indices, pristane/phytane ratios, and carbon isotopic compositions of individual n-alkanes are provided by GC/C/IRMS and GC/MS equipments. In the second set of data, palynological evaluations help to construct the thermal alteration (TAI), and spores and pollen diagrams. Interpretations regarding the purpose and scope of the study are presented in the next chapter. Sources of the organic matter contributed are mainly inferred from the n-alkane distribution patterns and isotopic compositions of individual n-alkanes and bulk samples. Depositional conditions rely basically on the pristane/phytane ratios. Degree of thermal alteration of organic matter is provided by both carbon preference index and colour study of spores and pollen and organic particulates. Information on climatic changes comes from the spores and pollen assemblages identified with reference to the previous study for the area.

Chapter 5

DISCUSSION

5.1 Sources of Organic Matter to the Sediments.

Data obtained in this work contribute to understanding the relative contributions of different types of organic matter deposited in the Mae Moh Basin. Additional information contributing towards the history of burial and diagenesis of organic matter in the basin is provided by the preservation of tissue structure of organic particulates.

N-alkane distribution

The relative abundances of short-chain and long-chain n-alkanes have been used as source indicators of organic matter in both recent and ancient sediments (Tissot and Welte, 1984; Kawamura and Ishiwatari, 1985; Cranwell *et al.*, 1987). In ancient sediments, sedimentary organic matter has likely undergone two stages of transformation: an early stage of biochemical degradation and a later stage of geochemical alteration when the organic matter is buried. The likely order of susceptibility of organic compounds to degradation is protein, chlorophyll, carbohydrates (starch and cellulose), lignin, epidermis, pigments, cuticles, spore and pollen exines, waxes, and resin (*e.g*, Bustin et.al., 1983).

During biochemical degradation, the conversion to gases (CO_2, CH_4, NH_3,and

H_2O) of easily hydrolysable compounds such as protein and chlorophyll is accomplished through metabolism of microorganisms such as bacteria and fungi. Other materials such as starch, cellulose, and proteins are also hydrolysed to produce amino acids and sugar (Tissot and Welte, 1984). Lignin and other lipid compounds like fats, oils, waxes, resins, spores and pollen are relatively resistant, and are mainly transformed into humic acids, and later, kerogen. As burial progresses, the organic matter undergoes geochemical degradation where temperature and to a lesser extent, pressure are the main factors controlling the structural rearrangement of organic compounds, which lead to disintegration and polycondensation reactions. The main products are humic materials that may, in some cases, form up to 90% of the total organic matter, and in later transformations, produce kerogen (Huc and Durand, 1977). Other products, mainly composed of lipids and related compounds, are also retained with little or no structural change. These compounds may be partly bound to the kerogen as geochemical fossils (biomarkers).

Normal alkanes are included in this biomarker group. The transformation of biogenic n-alkanes together with n-alcohol and n-fatty acids from plant waxes have been widely discussed (Tissot and Welte, 1984). Biological degradation and early diagenetic processes influence their molecular distribution. For example, selective microbial reprocessing results in a general decrease in the short-chain n-alkane fraction (Meyers and Ishiwatari, 1993). Diagenesis at an early stage also reduces the concentration of short-chain alkanes. Such a case was clearly recorded, for example, in a decrease of n-C_{17} and n-C_{19} concentration from surface down to 30 cm depth of a sediment core from Lake Washington (Wakeham, 1976). Biotic or abiotic decarboxylation of n-fatty acids can also contribute to the long-chain n-alkane content in sediments (Kates, 1964; Jurg and Eisma in Powell and McKirdy, 1973). The content of the original n-alkanes is generally preserved in sediments which are at an immature stage of diagenesis. Thus, the relative abundances of n-alkanes can be used as indicators for the source of organic matter. In advanced stages of diagenesis, for example, at high volatile bituminous rank, the original n-alkane content is altered as n-alkanes (particularly short-chain fractions) and other related hydrocarbons are released from kerogen cracking (Radke *et al.*, 1980).

The relative abundances of n-alkanes from the Mae Moh Basin (Table 4.2 and Appendix A) show that the contributions of higher plants are significant in almost all samples, particularly those in groups I and II, where the relative abundances of the third series (HMW) n-alkanes are high. Organic matter contributed by algae and higher plants can be deduced by calculating ratios for both low and high molecular weight alkanes. For example, in a mixture of algae and higher plants in Eocene strata from the Uinta basin, the relative contributions were deduced from abundances of n-alkanes in two ranges, n-C_{15} to n-C_{17} and n-C_{27} to n-C_{29} (Tissot and Welte, 1984). In the present study, the relative abundances of the first (n-C_{15} to n-C_{19}) and third alkane series (n-C_{26} to n-C_{33}) show samples of group III have higher relative abundance of the LMW alkanes when compared to groups II and I. This supports the interpretation that the oil shale (group III) must have been deposited under lake conditions where algae make a significant contribution to organic matter. The overall contribution of algae may yet have been higher than indicated by the present alkane distribution; the LMW alkanes are more easily reduced by microbial reworking and early diagenesis (Meyers and Ishiwatari, 1993). Bacterial degradation also influences the distribution of n-alkanes by removing the LMW fractions during biochemical decomposition; higher molecular fractions follow at a later stage (Philp, 1985).

A feature which remains unclear is that an unusual abundance of the second series (MMW) components (nC_{20} - nC_{25}) was identified in many samples (*e.g.*, MM38, MM82, MM69, MM36, MM67, and MM87). The possibility exists that an exceptional abundance of certain type of plants may be responsible. For example, a similar unusual abundance of C_{24} n-alkanoic acid was reported by Cranwell (1974), who correlated this feature to the widespread occurrence of *Calluna* (heath pollen) in the study area. In another study, Schenk (1969) remarked on the unusual abundance of C_{22} compound but no explanation was given. Alternatively, this second series components may be degradation products of dehydroxylation reactions involving intact high molecular weight wax esters. For example, n-alkanols maximizing at C_{24} (presumably derived from land-plant epicuticular waxes) are quite common in modern lakes (*e.g.*, Meyers and Ishiwatari, 1993). The n-alkane diagenetic products of these compounds are likely to have an even predominance, because no carbon is lost during dehydroxylation of these compounds. An even predominance in the middle molecular weight range may therefore be expected as is observed in some Mae Moh samples.

The provenance of organic matter is also suggested by the textural observations on the organic particulates. Huminitic, vitrinitic, liptinitic and inertinitic components are readily recognized in almost all slides, although they are not specifically examined in this study. The remains of woody fragments, massive cellulosic tissues and to a lesser extent, the lipid-rich parts such as cuticles, resins, and waxes seem to be major components. Inertinite (relics of biological oxidation, forest fires or reworked material) is minor. Algal and fungal remains were also observed but were not identified nor quantified in this study.

Stable carbon isotopic composition

The isotopic compositions of organic carbon of both bulk samples and individual n-alkanes are suggestive of environments where organic matter is accumulated (*i.e.*, lacustrine, marine, fresh water etc.), and sources for individual hydrocarbons.

The $\delta^{13}C$ values of bulk samples from the Mae Moh Basin vary by about 4‰ from -22.5‰ to -26.8‰ (Table 4.5). The bulk composition falls within the range of lignites compiled by Deines (1980), and Eglinton and Murphy (1969) as shown in Figure 5.1. A difference of about 1‰ between samples of group III (from -22.5‰ to -25.4‰) and those of groups I and II (from -23.1‰ to -26.8‰ and to -26.3‰, respectively) may be broadly attributed to a higher content of algae in group III samples. This is consistent with the observed distribution of n-alkanes for group III samples, where LMW compounds are more abundant.

For a sedimentary pool where higher plants are the main contributor of organic matter, the bulk composition may also suggest the dominant biosynthetic pathway of the plants contributed. This assumption is based on the fact that bulk

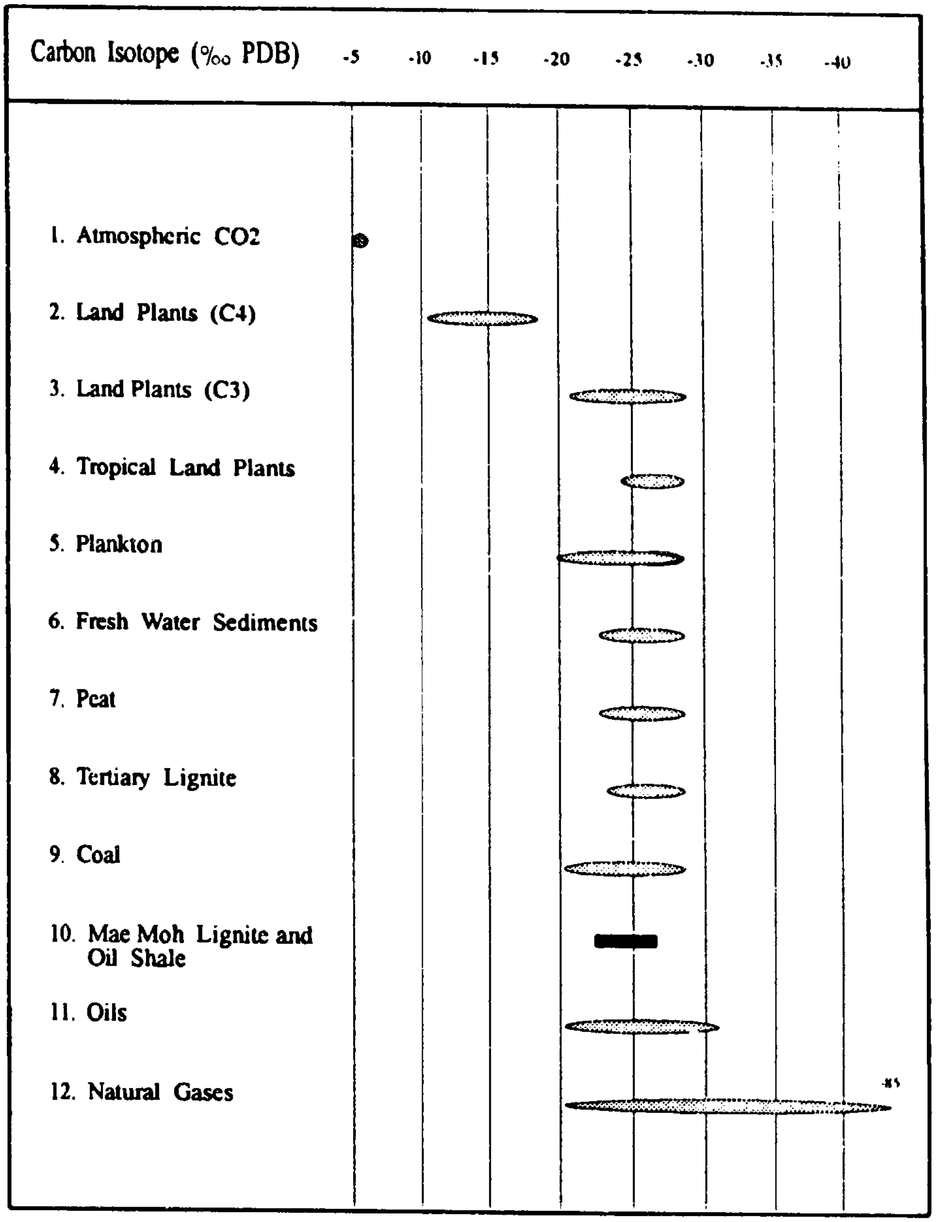

Figure 5.1 A comparison of isotopic compositions of carbon from diverse sources. Data are from Eglinton and Murphy (1969) and Deines (1980). Natural gases range from -20 to -85 ‰.

composition tends to be preserved up to the early stages of diagenesis (Macko *et al.*, 1993), although complex physical and chemical reactions occur during accumulation. For example, preference of bacteria to utilize ^{12}C (Kaplan and Rittenberg, 1964), release of CH_4 and inorganic oxidation of organic compounds (Sackett and Thompson, 1963) eventually lead to ^{13}C enrichment in the residual organic substrate. However, decarboxylation reactions (Macko *et al.*, 1993) and release of water-soluble compounds, which remove ^{13}C-heavy compounds, likely have a compensation effect on maintaining the bulk isotopic composition.

Sediments in the Mae Moh Basin are largely immature and organic matter is mainly from higher plants. The bulk carbon isotopic values may, therefore, also suggest compositions of the starting material or even the biosynthetic pathway the plants used to fix carbon from the atmosphere. Biosynthesis of plants proceeds through C_3, C_4, and CAM pathways (O'Leary, 1988). The isotopic composition fixed by the C_3 pathway averages at -28‰, that of the C_4 at -14‰, and the CAM generally covers the whole range of C_3 and C_4 (Deines, 1980). From the $\delta^{13}C$ values of Mae Moh samples in the range from -22.5‰ to -26.8‰, it can be assumed that plants contributed to the sedimentary organic matter mainly used the C_3 biosynthetic pathway. Figure 5.1 illustrates the isotopic range of the Mae Moh Basin, together with representative $\delta^{13}C$ values of bulk organic material from various sources including peat, selected Tertiary lignites, coal, oils, fresh water sediments, and land plants. The Mae Moh bulk isotopic composition is somewhat heavier than the range of tropical land plants, within the range of C_3 land plants , and lighter than that of C_4

land plants. The bulk composition may be enriched in ^{13}C by contributions from tropical grasses, which mainly use the C_4 pathway (Deines, 1980; O'Leary, 1988). This interpretation is based on the fact that tropical grasses were identified in some samples, albeit in minor proportion (Appendix B; Plate II; Figure 1). Alternatively, variable contributions of algal materials may also result in the observed isotopic range. N-alkane isotopic values from the Mae Moh Basin varies from -21.7‰ to -39‰ with most values in the range of -27‰ to -32‰ (Table 4.5). Samples of group III (oil shales), those containing abundant short-chain n-alkanes presumably derived from algae and microorganisms, record the most enriched in ^{13}C peaks in the LMW and MMW series (MM37, MM38, and MM82). However, isotopic compositions for many of the short-chain alkanes are depleted, even for samples of group III (for example, MM42 and MM50). From the data obtained for the n-alknanes, one can infer that: (i) HMW n-alkanes are more depleted in ^{13}C than those for LMW and MMW, and (ii) the general range from -27 to -32‰ is consistent with the bulk values for higher plants which utilize the C_3 metabolic pathway for carbon fixation (Trough, 1979). The general trend toward decreasing isotopic composition in the HMW range is recorded in almost all samples (Appendix A). Most values for HMW components are lighter than -30‰, indicating that they were indeed derived from higher plant waxes.

In summary, the stable carbon isotopic compositions for bulk organic matter and individual n-alkanes of the Mae Moh Basin are in agreement with the n-alkane distribution patterns. This indicates that the main contributors of organic matter to the sediments are higher plants. In some oil shale layers, contributions from aquatic biota are significant but still less than those from higher plants. The presence of woody tissue, leaf remains, together with pollen and spores support the dominance of higher plants in the organic matter. The isotopic compositions of bulk samples and the main isotopic range of n-alkanes suggest that most of the plants in Mae Moh sediments used the C_3 metabolic pathway to fix carbon during respiration. Isotopic and molecular studies involving specific biomarkers (*e.g.*, hopanes and steranes) are likely to further clarify our interpretations. Caution should be exercised, however, when interpreting the $\delta^{13}C$ values for the source for organic matter; for example, the isotopic composition of n-alkanes extracted from a single plant may, in some cases, vary by as much as 6‰ (Rieley *et al.*, 1993).

5.2 Environment of Deposition

Environmental conditions for sedimentation have a major influence on the degradation or preservation of organic matter. In aquatic environment, important parameters are degree of oxygen availability, pH and salinity. During burial, other parameters such as temperature, pressure, sediment grain size and stratification are dominant.

Several workers have attempted to indicate the degree of oxic/anoxic conditions by the use of pristane/phytane ratios (Powell and McKirdy, 1973; Didyk *et al.*, 1978). The formation of pristane (2,6,10,14 tetramethylpentadecane) or phytane (2,6,10,14 tetramethylhexadecane) from a chlorophyll-derived source with possible dependence on oxygen availability, has been widely discussed (Brooks and Maxwell, 1974; Cox, 1972; Ikan *et al.*, 1973). The pristane and phytane derivation reactions through two pathways are illustrated in Figure 5.2. In living organisms, pristane is found in planktonic algae and in some benthic algae (Clark and Blumer, 1967). It also occurs in animals, particularly zooplankton, which feed on the plants. In sediments, phytane is derived from phytol through dihydrophytol in the absence of oxygen. The reaction associated with microbial intervention was experimentally shown by Brooks and Maxwell (1974). Heating of chlorophyll to produce saturated isoprenoids including pristane and phytane have also been conducted. For example, Bayliss (1968) was able to isolate pristane, phytane and related isoprenoid hydrocarbons by hydrogenolysis of chlorophyll at high temperature and pressure.

The use of Pr/Ph ratios as a paleoenvironmental indicator in conjunction with other indicators has been applied to both recent and ancient sediments. In recent strata such as that found in the Black Sea, a shift of the Pr/Ph ratios from 1.43 to 0.85 is interpreted to reflect changes from lacustrine conditions when sediments were deposited in an oxygenated environment to marine condition when anoxic conditions prevailed (Didyk *et al.*, 1978). Oil shales of the Green River Formation have a Pr/Ph ratio of 0.56 (John, 1986) and those of Messel shales average at 0.68 (Arpino *et al.*, 1972); in both cases, anoxic conditions in a lacustrine setting are inferred for the sedimentary environment. Other studies using the Pr/Ph ratio as a paleoenvironmental indicator have been systematically summarised by Didyk *et al.* (1978). Generally, unity is the value which indicates the oxic/anoxic boundary. However, ten Haven *et al.* (1987) suggest that the application of Pr/Ph ratios as redox

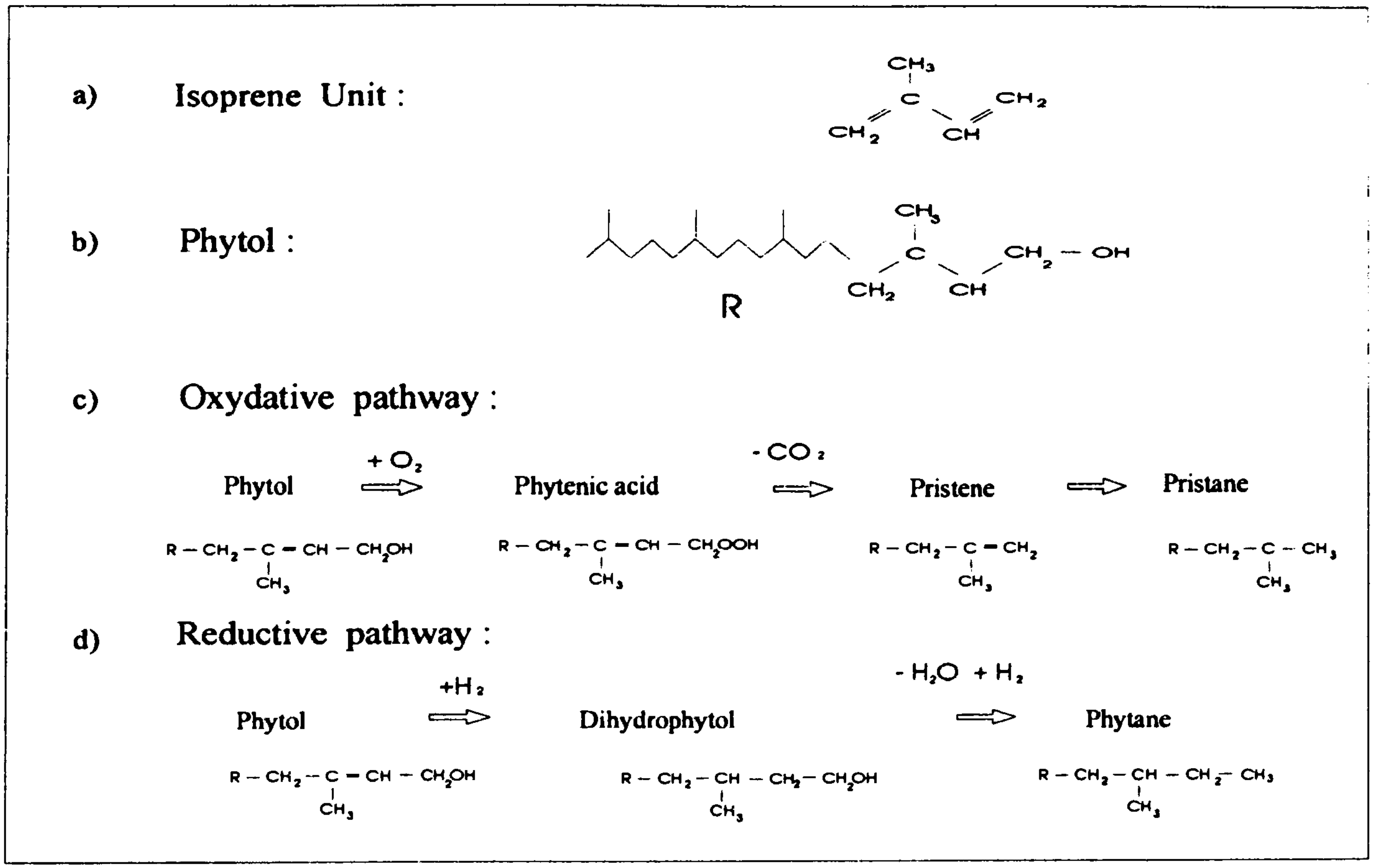

Figure 5.2 One of the possible reactions illustrates the formation pathways of pristane and phytane (Tissot and Welte, 1984).

indicators is only valid in hypersaline environments.

For the Mae Moh Basin oil shales, the Pr/Ph values are close to unity, whereas lignite and argillaceous lignite of groups I and II possess higher values (Table 4.4, Figure 4.3). The abundance of land-plants as indicated by the n-alkane distribution, carbon isotopic composition and fossil remains, suggests an overwhelming swamp forest ecosystem, which was responsible for the formation of the lignitic layers. It is not surprising therefore that the Pr/Ph ratios for lignitic samples (groups I and II) are also indicative of oxic conditions for the degradation of organic matter. Oil shale samples of group III having Pr/Ph ratios close to unity indicate less oxic conditions for deposition and degradation. It is likely that the difference in the redox conditions simply reflects water depth, as this is the main control over oxygen availability in these depositional environments. The thin oil shale layers were probably deposited in lakes and bogs adjacent to the forests. This is consistently suggested by the chemical signatures for algae and the carbonate content of the oil shales (Table 4.1). The presence of fish remains, ostracodes, *Millanoides* sp., and gastropods *Viviparus* sp., *Physa* sp. (Jitapankul, 1985), is also important indicator of lacustrine environments. The Pr/Ph found in oil shale deposits in the Mae Sot Basin, not far from the Mae Moh Basin, are generally less than unity (Curiale and Gibling, 1994). The authors seemed to attribute this to salinity, which created density-stratification, hydrodynamically stagnant water conditions, and an anoxic environment on the bottom. Depositional conditions in this lacustrine basin have been previously inferred from fish remains, rootless vegetation, and other geochemical characteristics (Gibling *et al.*, 1985a; 1985b). The dependence of the Pr/Ph ratio on high salinity, high productivity, and low diversity of organisms rather than on oxygen level was previously proposed by ten Haven *et al.* (1987). However, it is not likely that salinity-driven stratification occurred during the time of sedimentation of the Mae Moh Basin. No indications of such conditions (*i.e.*, gypsum, evaporites) were encountered for the Mae Moh Group. The degradation and deposition of oil shales in Mae Moh probably occurred at shallow water depths as suggested by fine intercalations with lignitic layers. Anoxic conditions may have prevailed in certain microenvironments as pyrite spots are found in some sediments (Jitapankul, 1985).

In summary, the lake and bog deposits of the Mae Moh Basin favoured the accumulation of both higher and lower plants with higher abundance of the former group. Degradation and deposition took place where anoxic and oxic conditions fluctuated; variations in oxygen availability are probably controlled by water depths and not by density stratification.

The overall mode of development of the Mae Moh Basin seems to be largely consistent with the model proposed by Schilische and Olsen (1990). When the tectonic subsidence rate is slow or the rate of sediment input is high, an extensional basin will fill with fluvial sediments; excess sediment and water will leave the basin. As subsidence and extension continues, a sediment-supply deficit occurs at some point and the basin may turn into a lake. In the Mae Moh Basin, fluviatile sediments were deposited in the initial phase of basin formation (Figure 2.4). Subsequently low subsidence rates and low sediment supply allowed deposition of the fine grained strata of the Mae Moh Group. Lakes and bogs of various sizes formed within the basin; the five major lignite layers reflect periodicity of vegetation growth, degradation, and burial.

5.3 Thermal Maturation

The degree of thermal maturation of Mae Moh sediments is reflected by the examination of colour changes of spores and pollen (TAI), and the carbon preference index (CPI).

The TAI values of Mae Moh Basin samples broadly fall on the boundary between largely immature and early mature levels (Figure 4.5). For the J, K, and Q layers, the average values range from 2.0 to 2.3. They become slightly higher at the R and S layers (2.4 to 2.5). The total thickness of the section is less than one kilometre. With a geothermal gradient of about 2.5 to 3 °C / 100 m, it is conceivable that low thermal maturities have been attained by burial. It is however, possible that volcanic activity during the Pliocene (*e.g.*, Ratanasthien, 1989b) may have resulted in the early attainment of a mature level in some of the sediments.

CPI is another parameter which has been used to indicate the degree of maturation. The CPI values of Mae Moh Basin samples (Table 4.3 and Figure 4.2) are consistent with the TAI values, showing an overall immature level of thermal alteration. With increasing depth, the CPI values tend to decrease (Figure 4.2); this too suggests a slight increase in maturation levels for the R and S layers.

5.4. Paleoclimatic Implications

The climatic regime in a region is controlled primarily by latitudinal position, altitude, and vegetation. Paleogeographical position determines the quantity of solar irradiation, a primary control for climatic parameters such as temperature, wind, and rain. The temperature and vegetation also change as a function of altitude (*i.e.*, a decrease of about 6.5 °C for every kilometre gained in height; Ruddiman and Kutzbach, 1991).

Three palynological units are identified from the spore and pollen assemblages (Section 4.4.2). Unit 1 (R and S layers) with abundant deciduous trees suggests rather temperate conditions. *Trivestibullopollenites* and *Quercoidites* are widely reported in high altitude areas throughout southeast Asia (Morley, 1982). In Thailand, the same assemblages were identified in Tertiary basins such as Li and Nong Ya Plong, where they were attributed to temperate vegetation (Watanasak, 1989). In unit 1, specimens such as *Crassoretitriletes vanraadshoveni*, *Trichanthera* sp. and other fern and palm species were also identified and account for up to one fifth of the palynological population. Units 2 and 3 (Q, K, and J layers) are dominated by fern, palm, and herb specimens indicating changes toward a warmer climate. *Spinizonocolpites*, a palm, which appears most frequently in units 2 and 3, is definitely a tropical climate indicator, since it is a dominant element in the microflora of Columbia, Venezuela, Nigeria, and Borneo (Muller, 1968). Amongst other related palm species, *Proxapertites*, was also found in Borneo and Venezuela (Muller, 1968). *Dactylocladus* pollen, which was described by Muller (1975), is not only a climatic but an environmental indicator as well. It is a common element in peat swamp in Kalimantan, Indonesia (Morley, 1981) and in northwest Borneo. This pollen type is easily confused with pollen of *Axinandra* (Crypteroniaceae) and of Melastomataceae (*Medinilia*, *Marumia*, and *Pogonanthera*), which also occur in the peat swamp of Borneo (Muller, 1975). *Dactylocladus*, *Cyrtostachys* and *Dactilopollis magnificus* account for about 10-12% in unit 3 with a particular abundance of *Dactylocladus*. *Oncosperma* and *Calamuspollenites* are also important elements in units 2 and 3. They were noted as common in Sarawak, Malaysia (Muller, 1968) and in the Mae Lamao Basin, Thailand (Ratanasthien, 1989a).

From the spore and pollen assemblages, it can be inferred that a climatic change, from rather cool conditions when the R and S layers were formed to warm conditions when the Q, K, and J layers were deposited, occurred during the deposition of the Mae Moh Group. In unit 1, besides the temperate elements, the palm, fern, and other herbaceous components are also present in considerable abundance. This indicates that, although the climatic conditions in the lower part (Unit 1) were relatively cooler, they were not dramatically different from the warm conditions in the upper part (Units 2 and 3). Generally, a cool climate is also characterized by a dry air mass, whereas a warm climate is associated with wetter conditions (Manabe and Hahn, 1977). This trend also appears to be reflected from the TOC and $CaCO_3$ contents in the area of this study (Table 4.1). $CaCO_3$ concentration, for example, is less than 7.5 %, except MM91 and the EOM/TOC ratios are less than 0.15 for the R and S layers, while they have a wider range of up to 0.3 in the upper layers. Wetter conditions may have favoured higher precipitation rates, and hence probably the water levels in the lakes. This in turn created conditions for carbonate deposition and algal production. However, higher water levels might also have been controlled by the tectonic regime (*i.e.*, open or close basin).

The slight climatic shift in the study area could be variously ascribed to the uplift of the mountain ranges of Tibet, the global warming during the early-middle Miocene, or even slight changes of paleogeographical position. The build-up of the Tibetan Plateau in the past 40 Ma may have altered the atmospheric circulation and hence the climatic pattern globally and more emphatically in the adjacent regions of southeast Asia (Ruddiman and Kutzbach, 1991). The computer simulations of Ruddiman and Kutzbach (1991), for example, showed that southeastern Asia and India became wetter as a result of the uplift. The climate in Tibet changed from tropical and subtropical forests about 30 Ma to temperate vegetation around 5 to 10 Ma ago (Ruddiman and Kutzbach, 1991). This computer model demonstrated a general cooling trend over the last 40 Ma. How and to what extent the uplift of the Tibetan Plateau affected the wind pattern over the nearby areas including southeast Asia goes beyond the scope of the present study. It is likely that disturbed atmospheric circulations caused by the tremendous uplift to the northwest resulted in changes of rainfall patterns at the flanks of the plateau, including the Mae Moh area. This monsoonal rain may have had an effect on the dispersal of spores and pollen as they can be transported by wind or rivers for long distances. The climatic changes of the study area may have been influenced by shorter term global climate fluctuations. For example, the global shift from cool in the late Oligocene to warm in the early-middle Miocene may have caused changes in local climate of Thailand (Watanasak, 1989). Finally, changes in paleogeographical position could also be a reason for regional climate change. However, Thailand has likely occupied its present position at least since the Eocene (Jurdy *et al.*, 1975; Audley-Charles *et al.*, 1988; Mitchell *et al.*, 1985), latitudinal changes are not thought to be a major factor for the climate shifts in the study area.

CONCLUSIONS

The main source of organic matter in the sediments of the Mae Moh Basin was higher plants as indicated by the n-alkane distribution where high molecular weight n-alkanes dominated the alkanes in almost all samples. Thin oil shale layers were deposited in lacustrine conditions in which additional organic matter was contributed by algal production as indicated by a higher abundance of low molecular weight n-alkanes. The $\delta^{13}C$ values of bulk composition and individual n-alkanes of organic matter in the Mae Moh Basin are consistent with the same dual origin, with little indication of any other sources (*e.g.*, bacteria). Bulk $\delta^{13}C$ values ranging from -22.5 to -26.8‰, are in the same range as previously measured lignite values. The $\delta^{13}C$ composition of most HMW n-alkanes (beginning from C_{26}) is lighter than -30‰ indicating their higher plant wax sources; the overall composition of individual n-alkanes, which mainly ranges between -27 to -32‰, also indicates the C_3 biosynthesis pathway utilized by higher plants.

The Pr/Ph ratios tend to be good depositional indicators in the Mae Moh Basin. They show that oxic-anoxic fluctuations persisted on the bottom of lakes and bogs where oil shales, which have the Pr/Ph ratios close to unity, were deposited. Higher plants, mainly composed of palms, ferns, herbs and other trees as suggested by spore and pollen identification, existed in the surrounding high-land and swamps.

Their deposition and degradation likely progressed in more oxic conditions as indicated by Pr/Ph ratios. The degradation and thermal alteration continued with further burial, although organic matter was largely immature throughout the section. The present depth of the basin varies from 500 metres to less than 1,000 metres, and the geothermal gradient is low. Specifically, the TAI values (2.0 to 2.4) and the CPI indices (mostly higher than 1) indicate an immature to early mature stage of alteration for Mae Moh sediments.

Finally, the climatic regime probably changed from somewhat cool at the early stages of basin formation to a tropical climate similar to the present time. The timing of the uplift of the giant plateau of Tibet and the global warming at the early-middle Miocene suggest a possible connection between the inferred climatic shift and these global climatic events.

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Appendix A

Distribution Patterns and

Carbon Isotopic Compositions of Individual N-alkanes

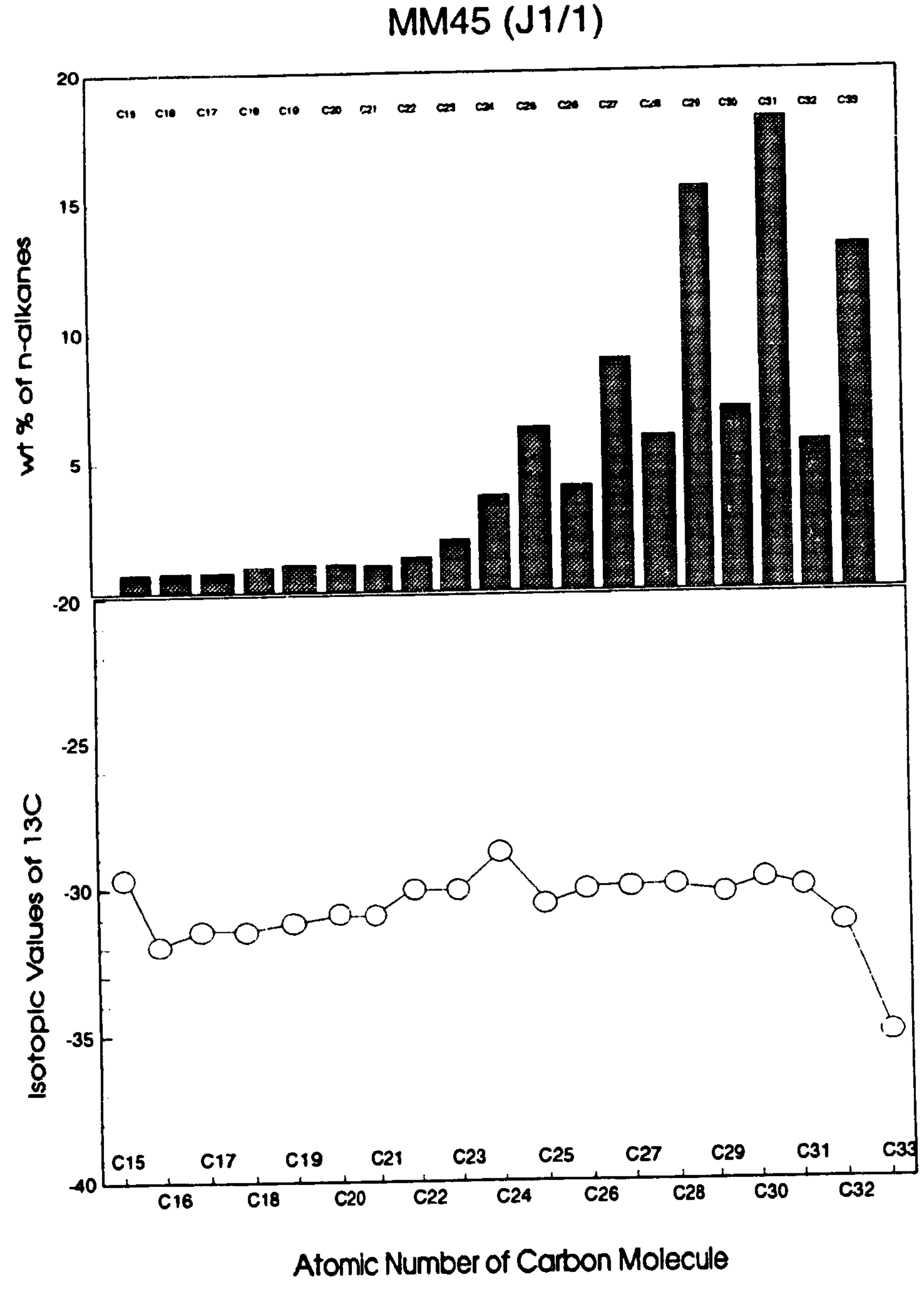
Relative abundances of individual n-alkanes and their carbon isotopic compositions recorded on the flame ionization chromatograms (FID) are plotted together for each sample.

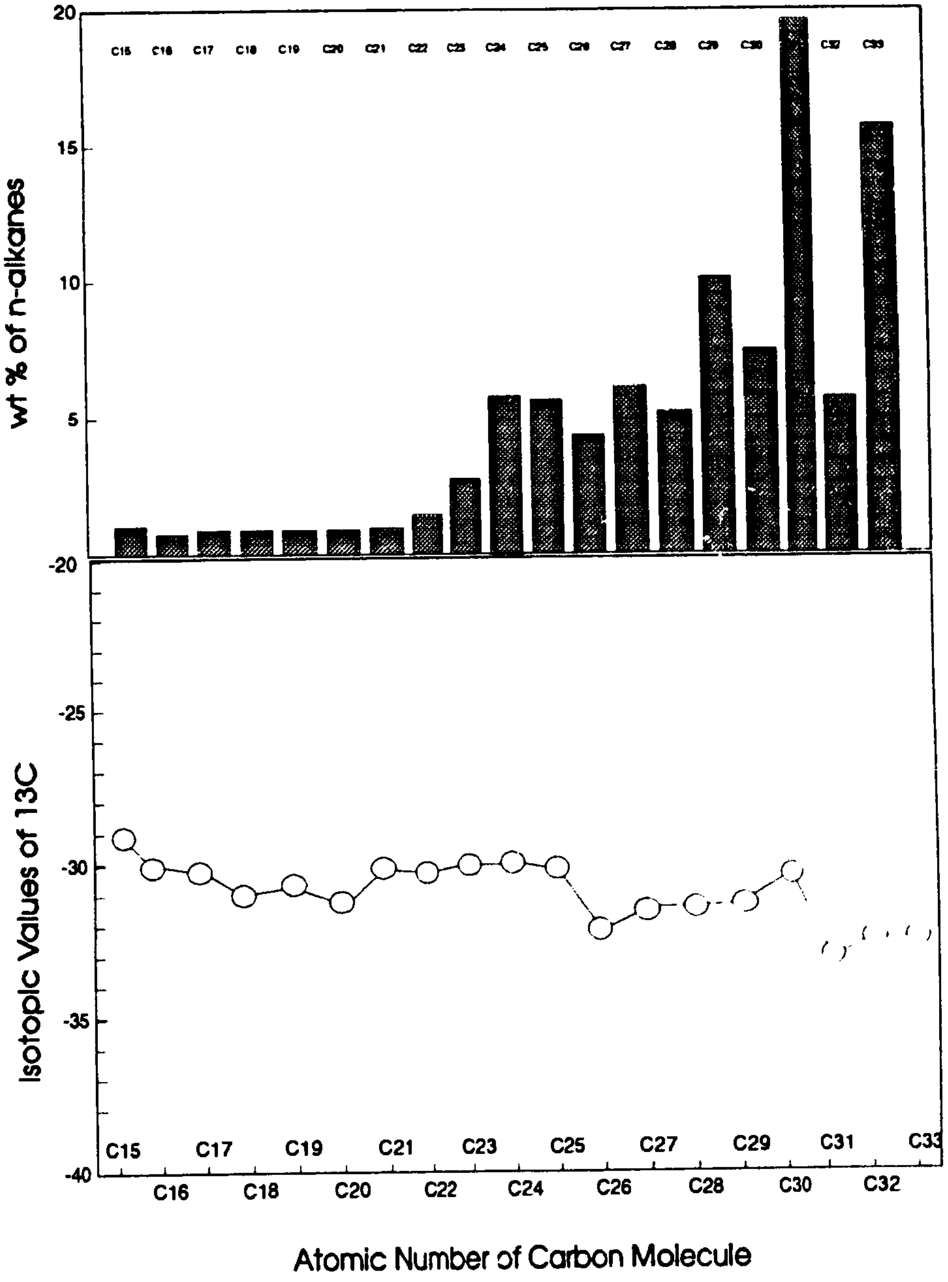
Orderly increased numbers of carbon molecules of n-alkanes from 15 to 33 are presented on abscissas.

Upper vertical scale shows the abundance of individual n-alkane quantified in percentage.

Lower vertical scale presents the carbon isotopic compositions. In some samples, particularly those of groups II and III, the isotopic compositions of the LMW series peaks were not recorded as the respective peaks height was below the detection limit.

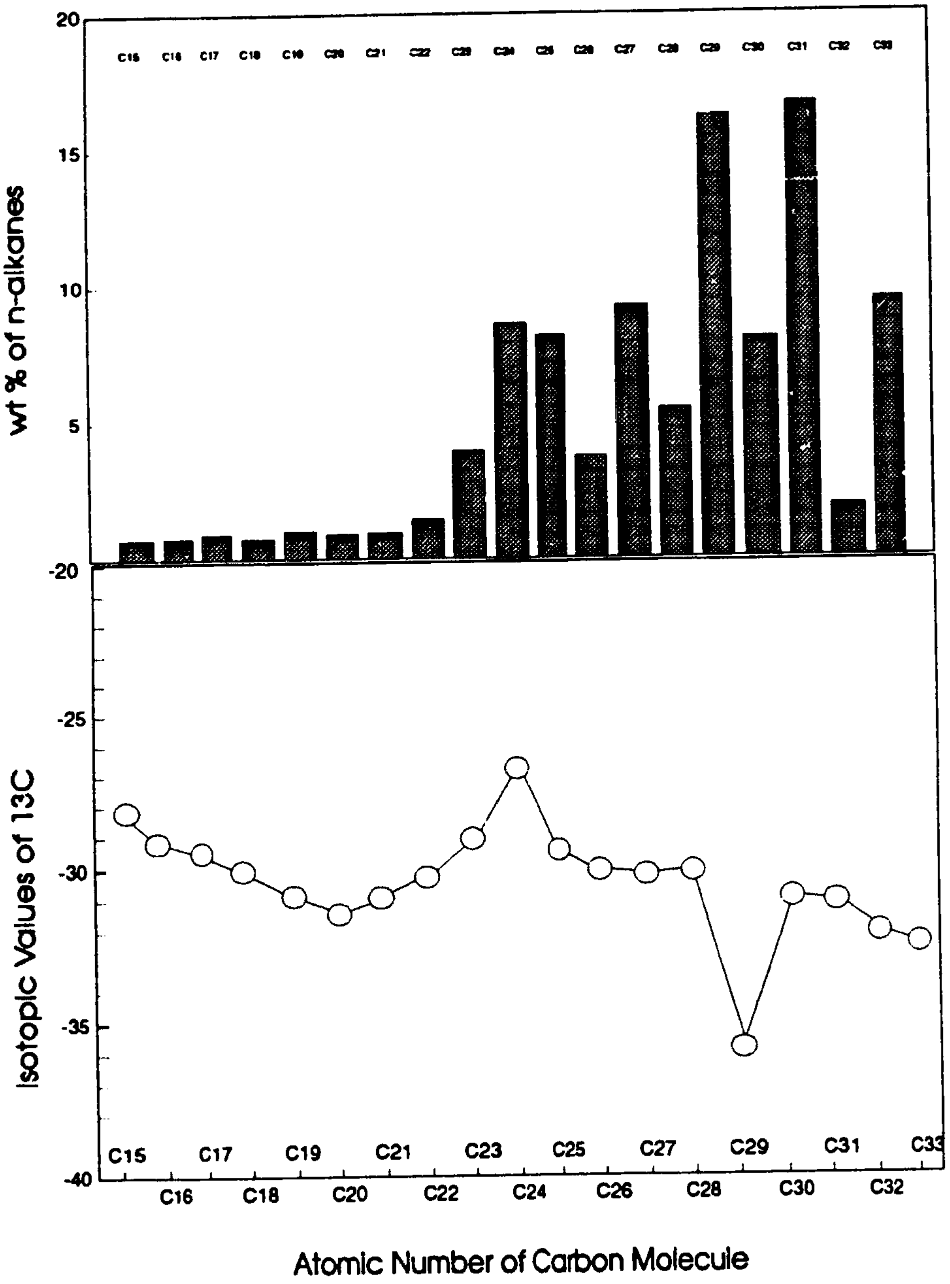
Two samples MM35 and MM40 whose FID chromatograms show big "hump" are not reported here.


MM45 (J1/1)
wt % of n-alkanes
20
15
10
5
C15
C16
C17
C18
C19
C20
C21
C22
C23
C24
C25
C26
C27
C28
C29
C30
C31
C32
C33
Isotopic Values of 13C
-20
-25
-30
-35
-40
C15
C17
C19
C21
C23
C25
C27
C29
C31
C33
C16
C18
C20
C22
C24
C26
C28
C30
C32
Atomic Number of Carbon Molecule

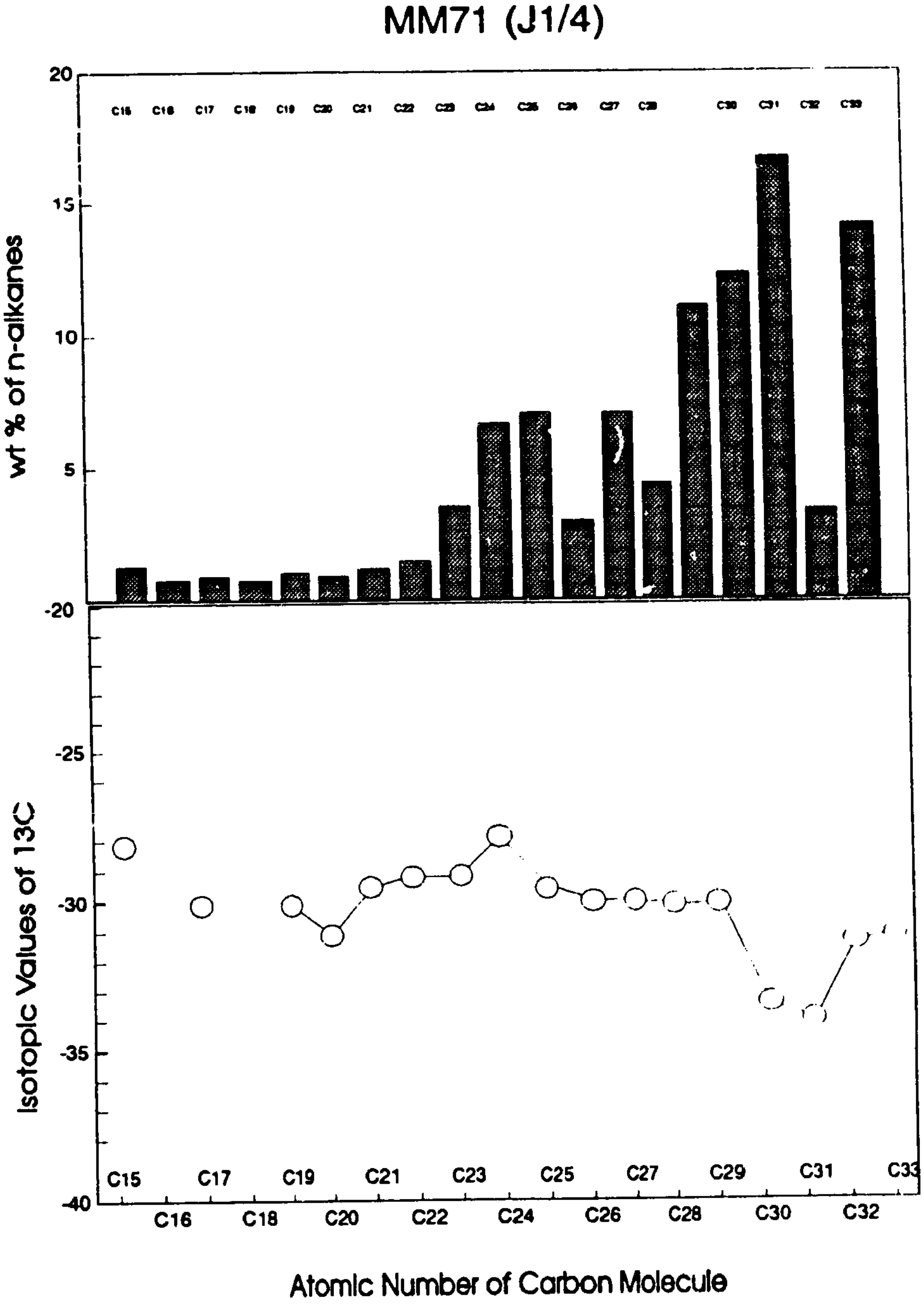

MM47 (J1/2)

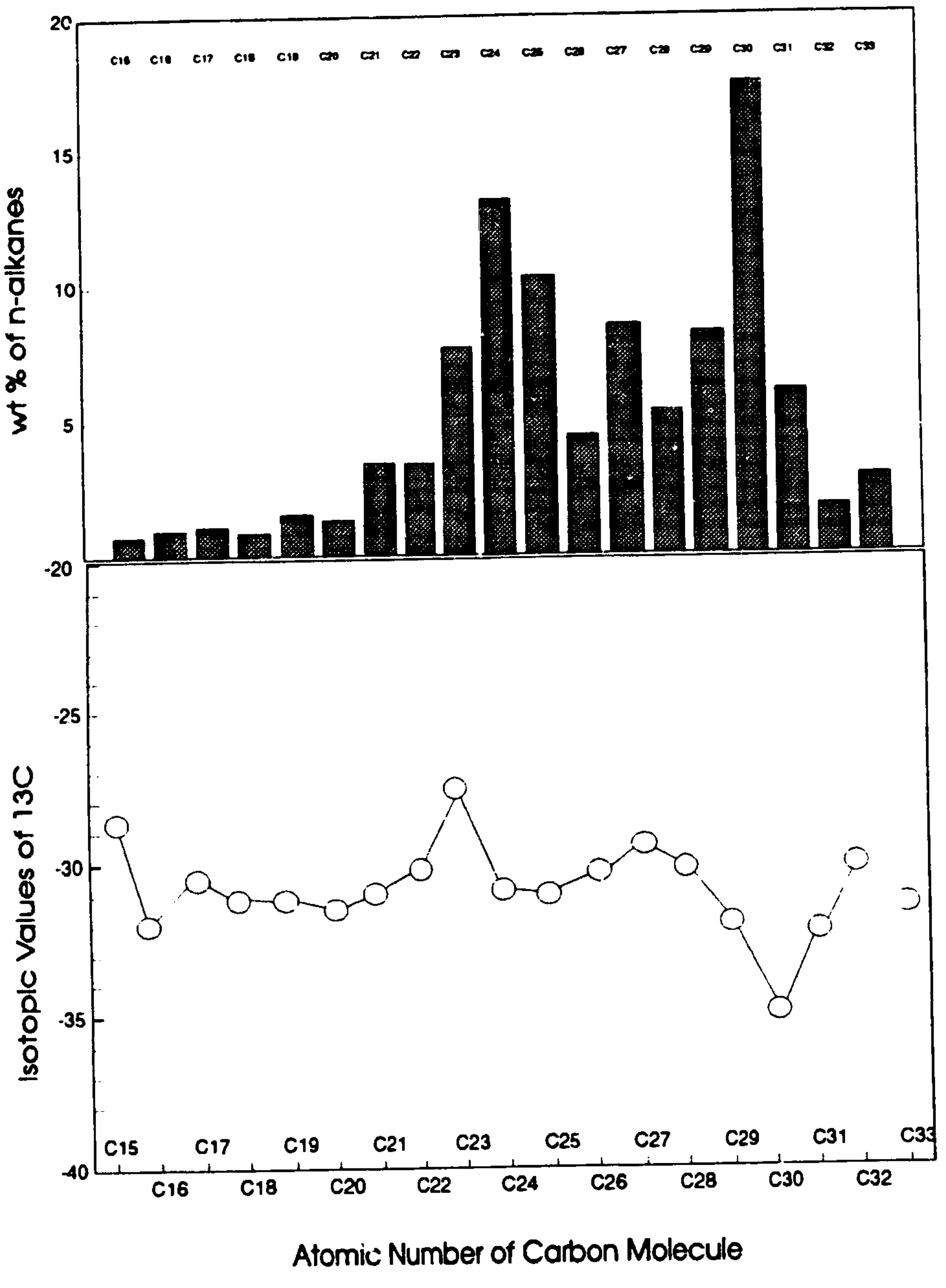
wt % of n-alkanes
20
15
10
5
C15
C16
C17
C18
C19
C20
C21
C22
C23
C24
C25
C26
C27
C28
C29
C30
C32
C33
Isotopic Values of 13C
-20
-25
-30
-35
-40
C15
C17
C19
C21
C23
C25
C27
C29
C31
C33
C16
C18
C20
C22
C24
C26
C28
C30
C32
Atomic Number of Carbon Molecule

MM68 (J1/3)



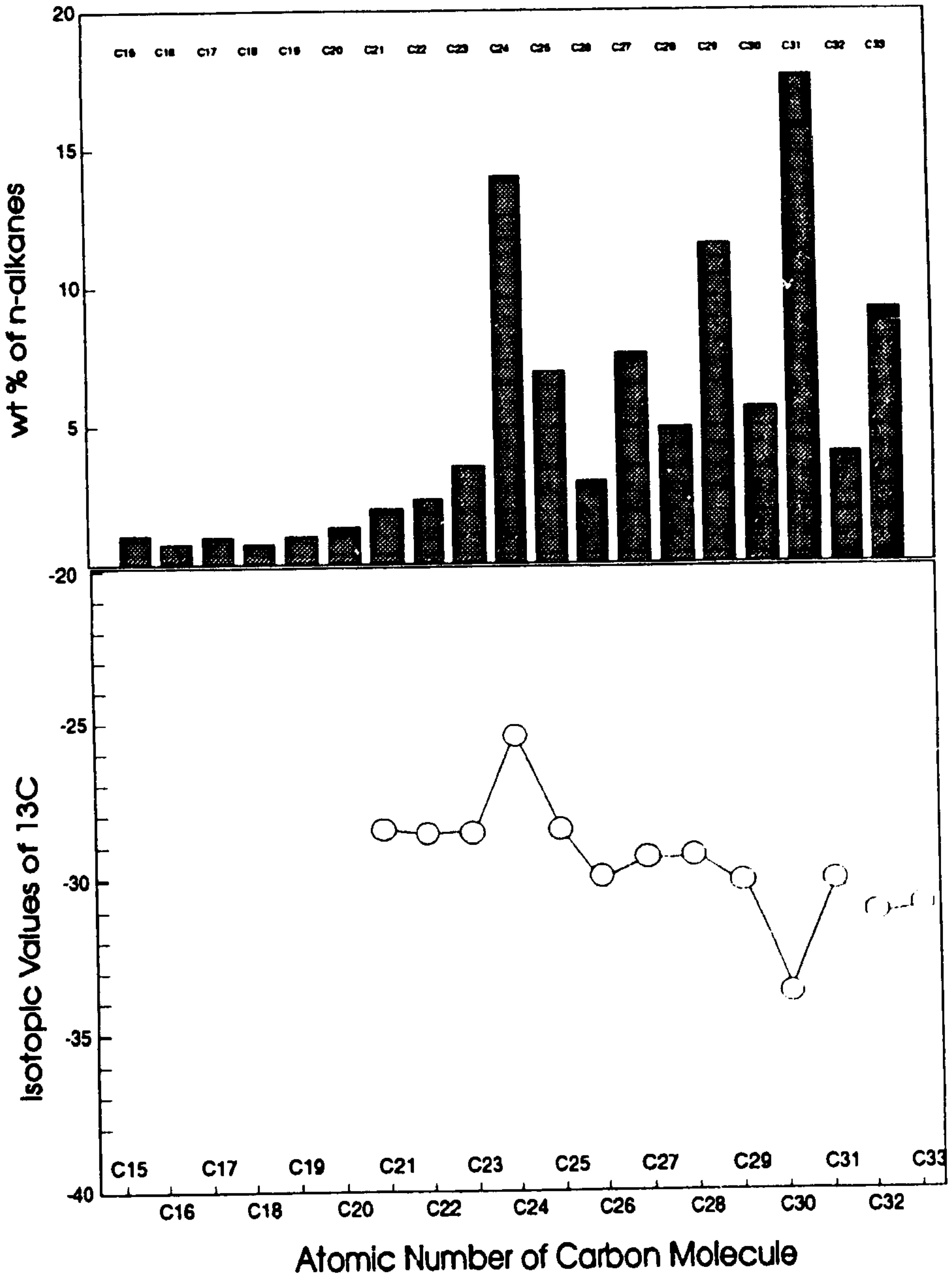
20
15
10
5
-20
-25
-30
-35
-40
wt % of n-alkanes
Isotopic Values of 13C
C15
C16
C17
C18
C19
C20
C21
C22
C23
C24
C25
C26
C27
C28
C29
C30
C31
C32
C33
Atomic Number of Carbon Molecule


MM71 (J1/4)
wt % of n-alkanes
20
15
10
5
C15 C16 C17 C18 C19 C20 C21 C22 C23 C24 C25 C26 C27 C28 C30 C31 C32 C33
Isotopic Values of 13C
-20
-25
-30
-35
-40
C15 C17 C19 C21 C23 C25 C27 C29 C31 C33
C16 C18 C20 C22 C24 C26 C28 C30 C32
Atomic Number of Carbon Molecule

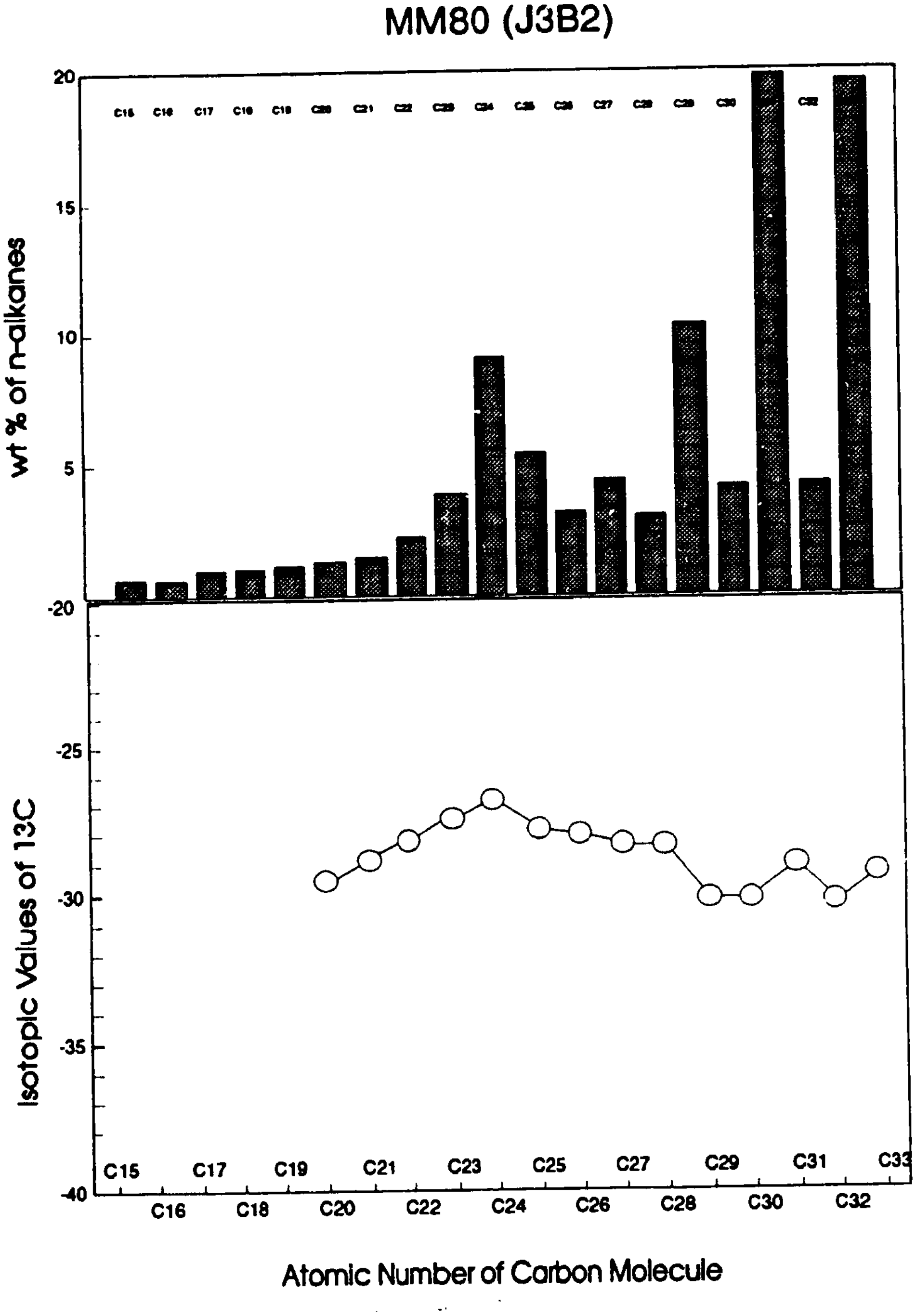


MM44 (J2)

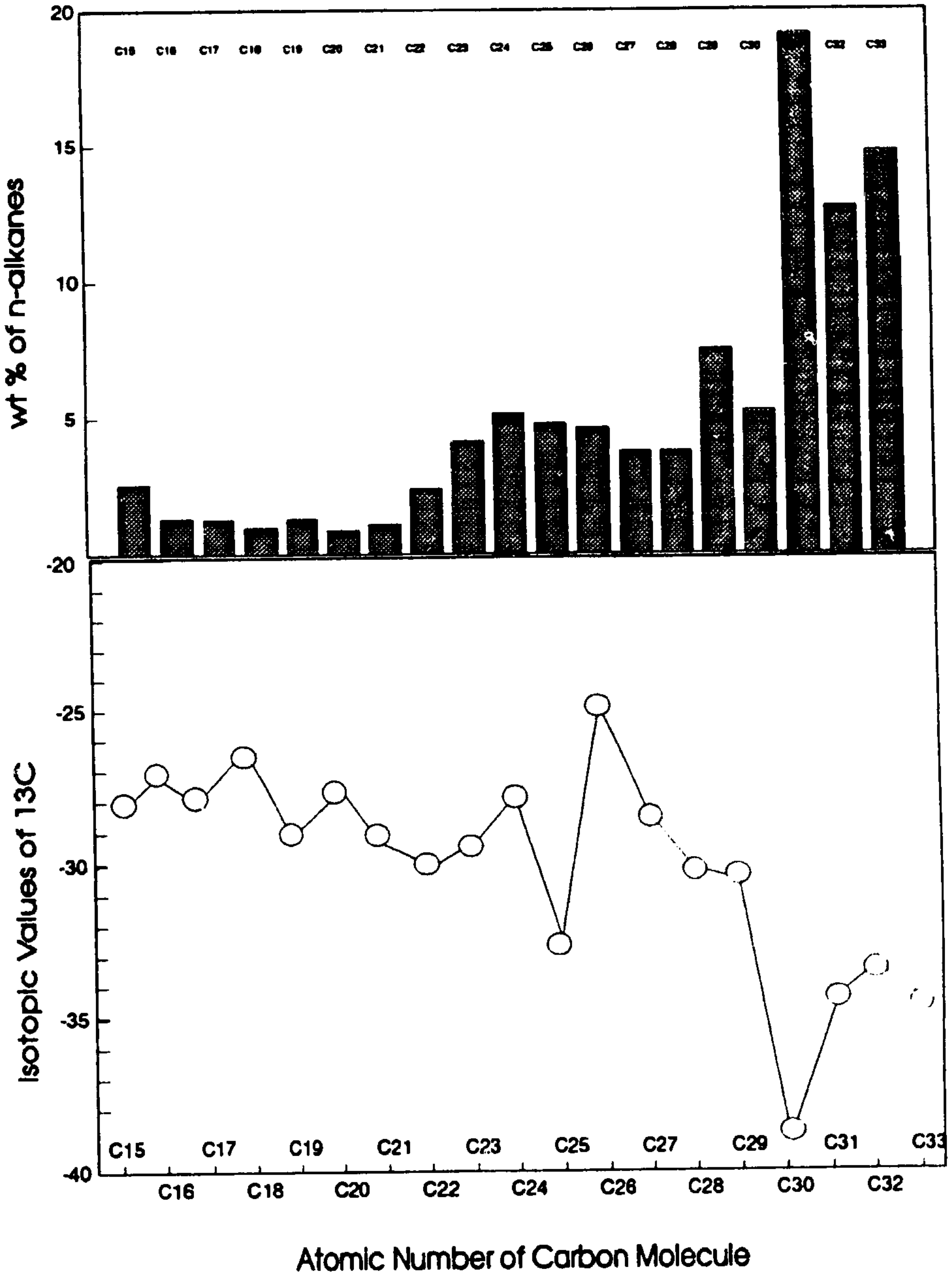
20
15
10
5
wt % of n-alkanes
C15 C16 C17 C18 C19 C20 C21 C22 C23 C24 C25 C26 C27 C28 C29 C30 C31 C32 C33
-20
-25
-30
-35
-40
Isotopic Values of 13C
C15
C17
C19
C21
C23
C25
C27
C29
C31
C33
C16
C18
C20
C22
C24
C26
C28
C30
C32
Atomic Number of Carbon Molecule


MM67 (J3B1)

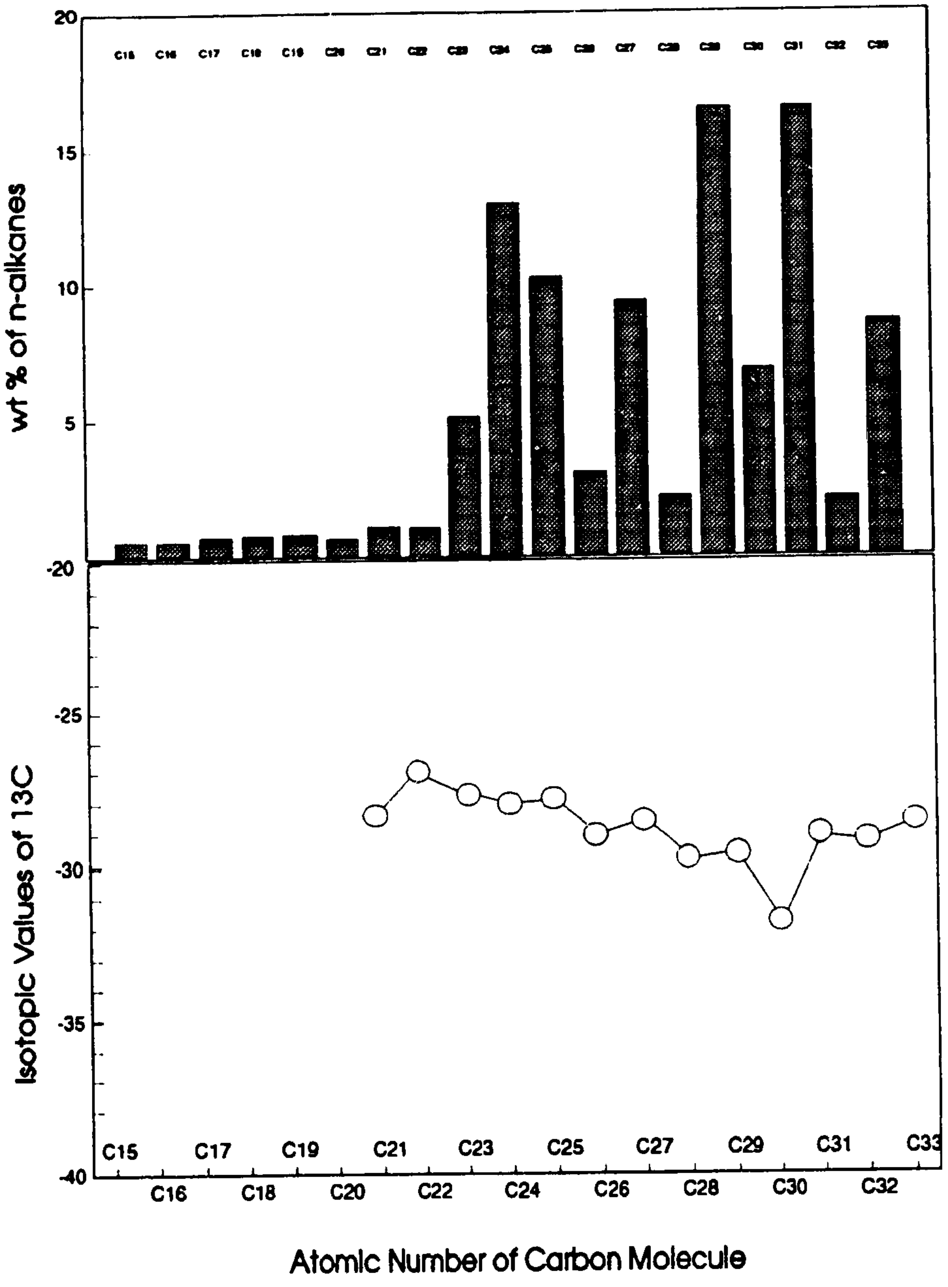
wt % of n-alkanes
20
15
10
5
C15 C16 C17 C18 C19 C20 C21 C22 C23 C24 C25 C26 C27 C28 C29 C30 C31 C32 C33
Isotopic Values of 13C
-20
-25
-30
-35
-40
C15 C17 C19 C21 C23 C25 C27 C29 C31 C33
C16 C18 C20 C22 C24 C26 C28 C30 C32
Atomic Number of Carbon Molecule


MM80 (J3B2)
wt % of n-alkanes
20
15
10
5
C15
C16
C17
C18
C19
C20
C21
C22
C23
C24
C25
C26
C27
C28
C29
C30
C32
Isotopic Values of 13C
-20
-25
-30
-35
-40
C15
C17
C19
C21
C23
C25
C27
C29
C31
C33
C16
C18
C20
C22
C24
C26
C28
C30
C32
Atomic Number of Carbon Molecule

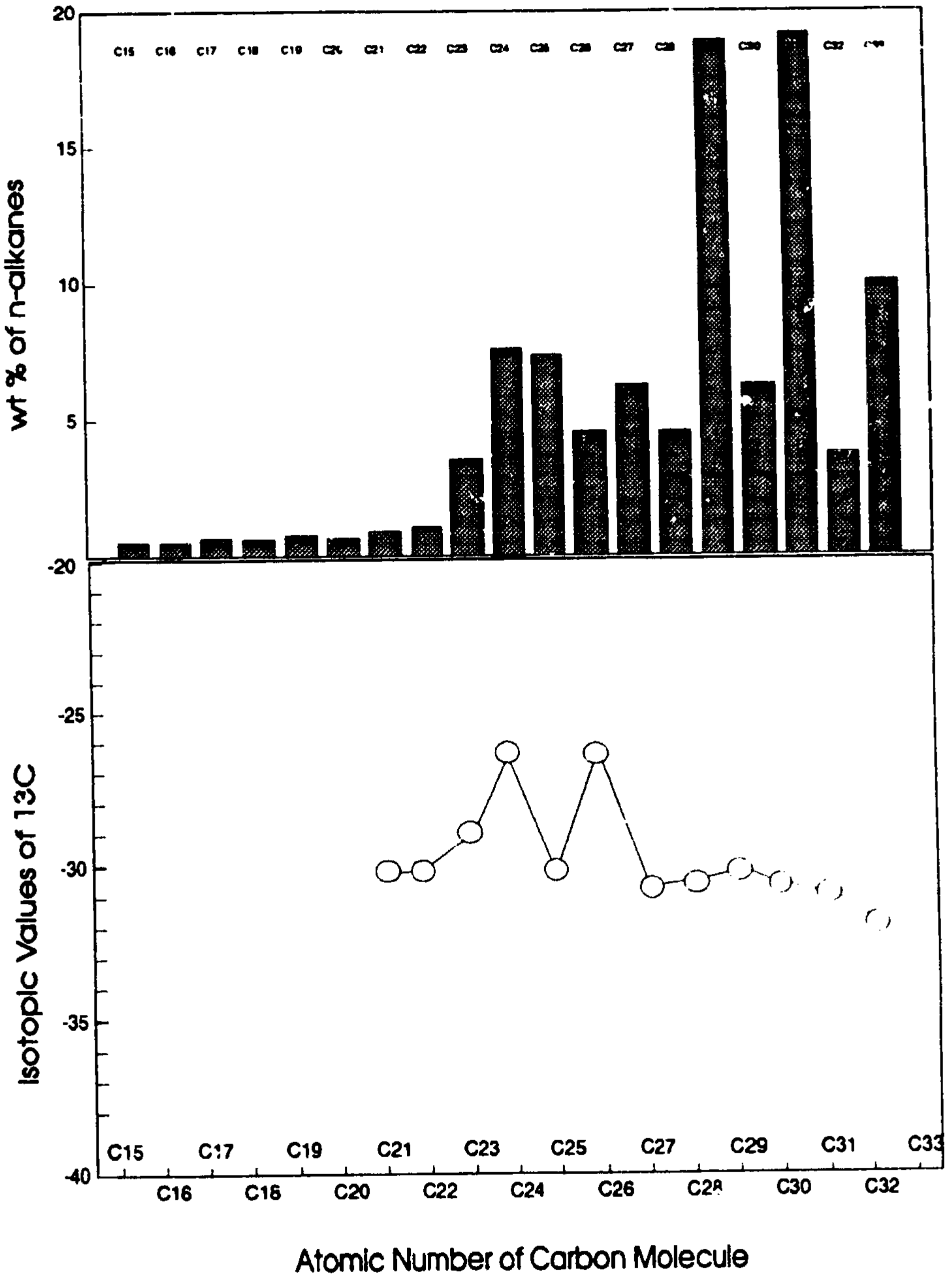
MM81 (J4)

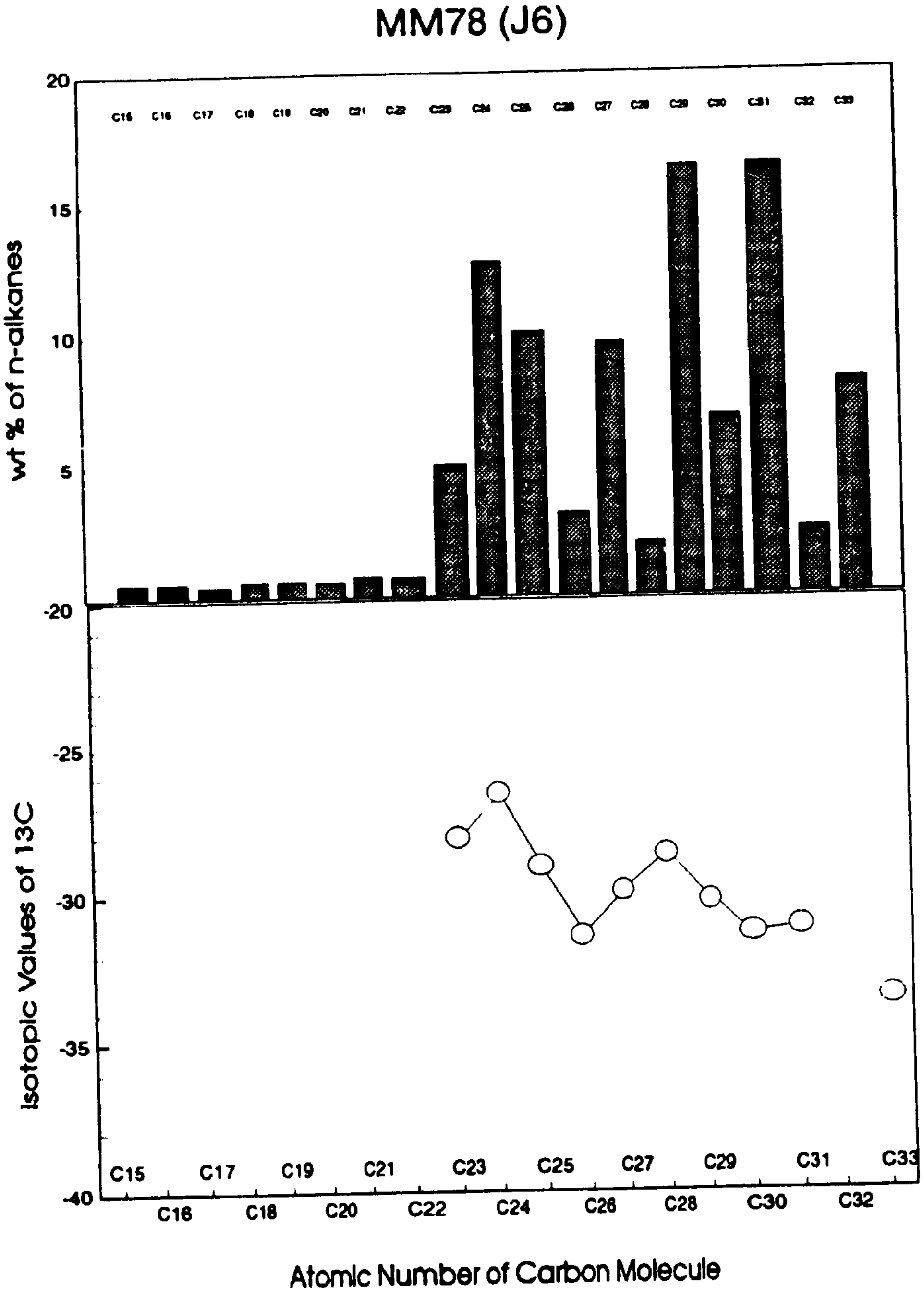

wt % of n-alkanes
20
15
10
5
C15
C16
C17
C18
C19
C20
C21
C22
C23
C24
C25
C26
C27
C28
C29
C30
C32
C33
Isotopic Values of 13C
-20
-25
-30
-35
-40
C15
C17
C19
C21
C23
C25
C27
C29
C31
C33
C16
C18
C20
C22
C24
C26
C28
C30
C32
Atomic Number of Carbon Molecule

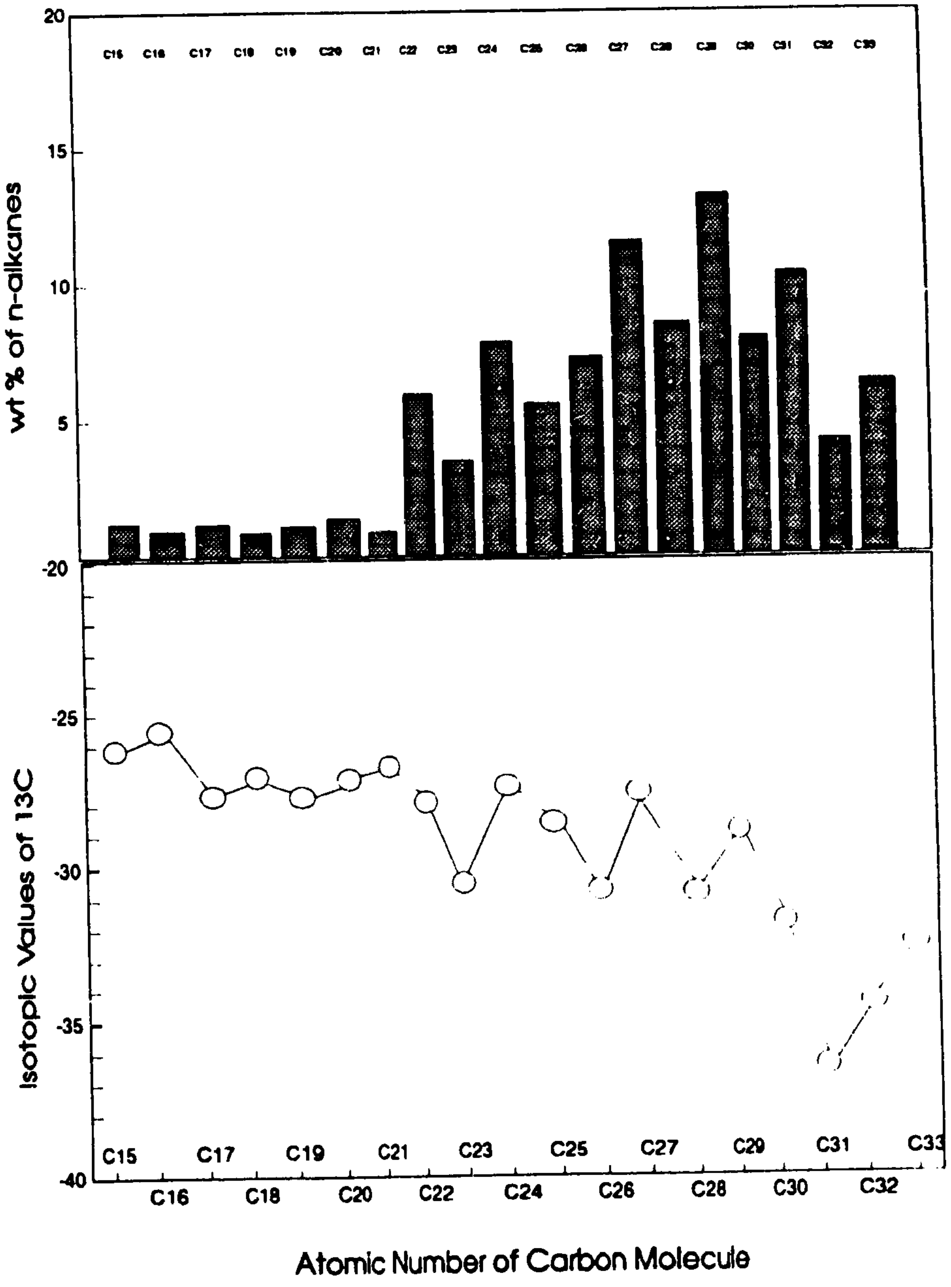
MM77 (J5B)


wt % of n-alkanes
20
15
10
5
C15 C16 C17 C18 C19 C20 C21 C22 C23 C24 C25 C26 C27 C28 C29 C30 C31 C32 C33
Isotopic Values of 13C
-20
-25
-30
-35
-40
C15
C16
C17
C18
C19
C20
C21
C22
C23
C24
C25
C26
C27
C28
C29
C30
C31
C32
C33
Atomic Number of Carbon Molecule

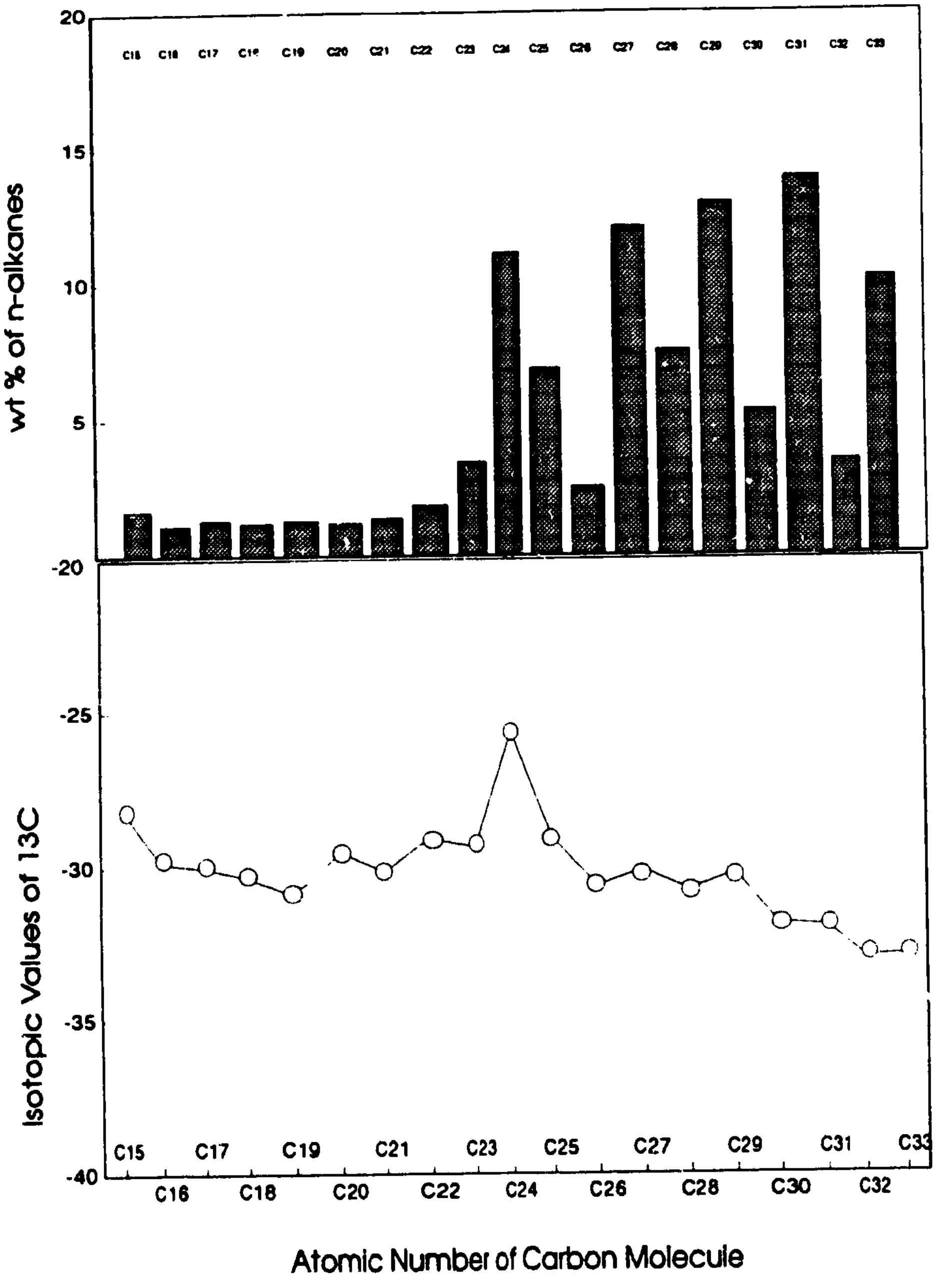
MM46 (J6)


wt % of n-alkanes
20
15
10
5
C15
C16
C17
C18
C19
C20
C21
C22
C23
C24
C25
C26
C27
C28
C29
C30
C31
C32
C33
Isotopic Values of 13C
-20
-25
-30
-35
-40
C15
C17
C19
C21
C23
C25
C27
C29
C31
C33
C16
C18
C20
C22
C24
C26
C28
C30
C32
Atomic Number of Carbon Molecule

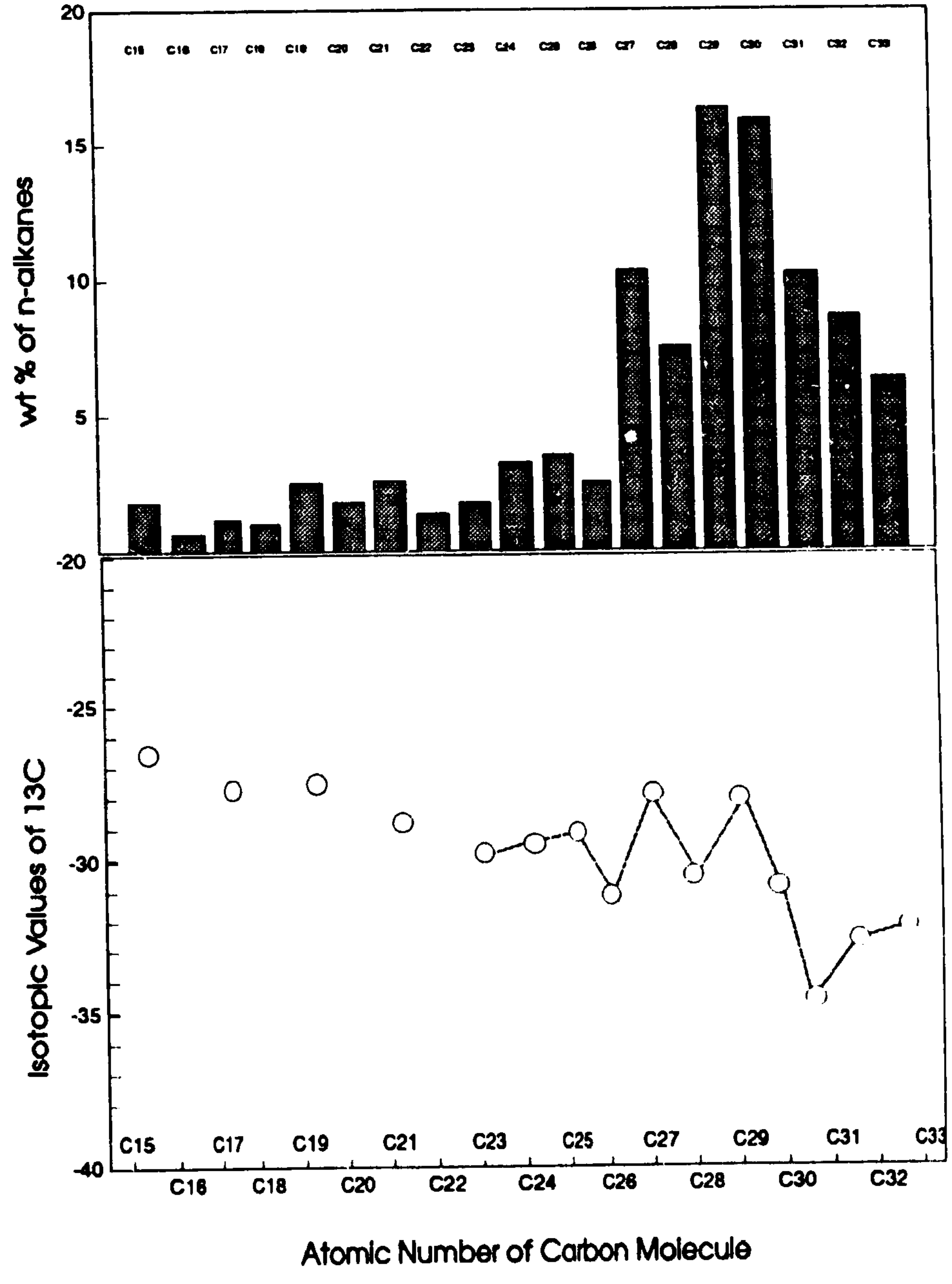
MM78 (J6)
wt % of n-alkanes
20
15
10
5
C15
C16
C17
C18
C19
C20
C21
C22
C23
C24
C25
C26
C27
C28
C29
C30
C31
C32
C33
Isotopic Values of 13C
-20
-25
-30
-35
-40
C15
C17
C19
C21
C23
C25
C27
C29
C31
C33
C16
C18
C20
C22
C24
C26
C28
C30
C32
Atomic Number of Carbon Molecule


MM85 (K1)
wt % of n-alkanes
20
15
10
5
C15 C16 C17 C18 C19 C20 C21 C22 C23 C24 C25 C26 C27 C28 C29 C30 C31 C32 C33
Isotopic Values of 13C
-20
-25
-30
-35
-40
C15 C17 C19 C21 C23 C25 C27 C29 C31 C33
C16 C18 C20 C22 C24 C26 C28 C30 C32
Atomic Number of Carbon Molecule

MM36 (K2)

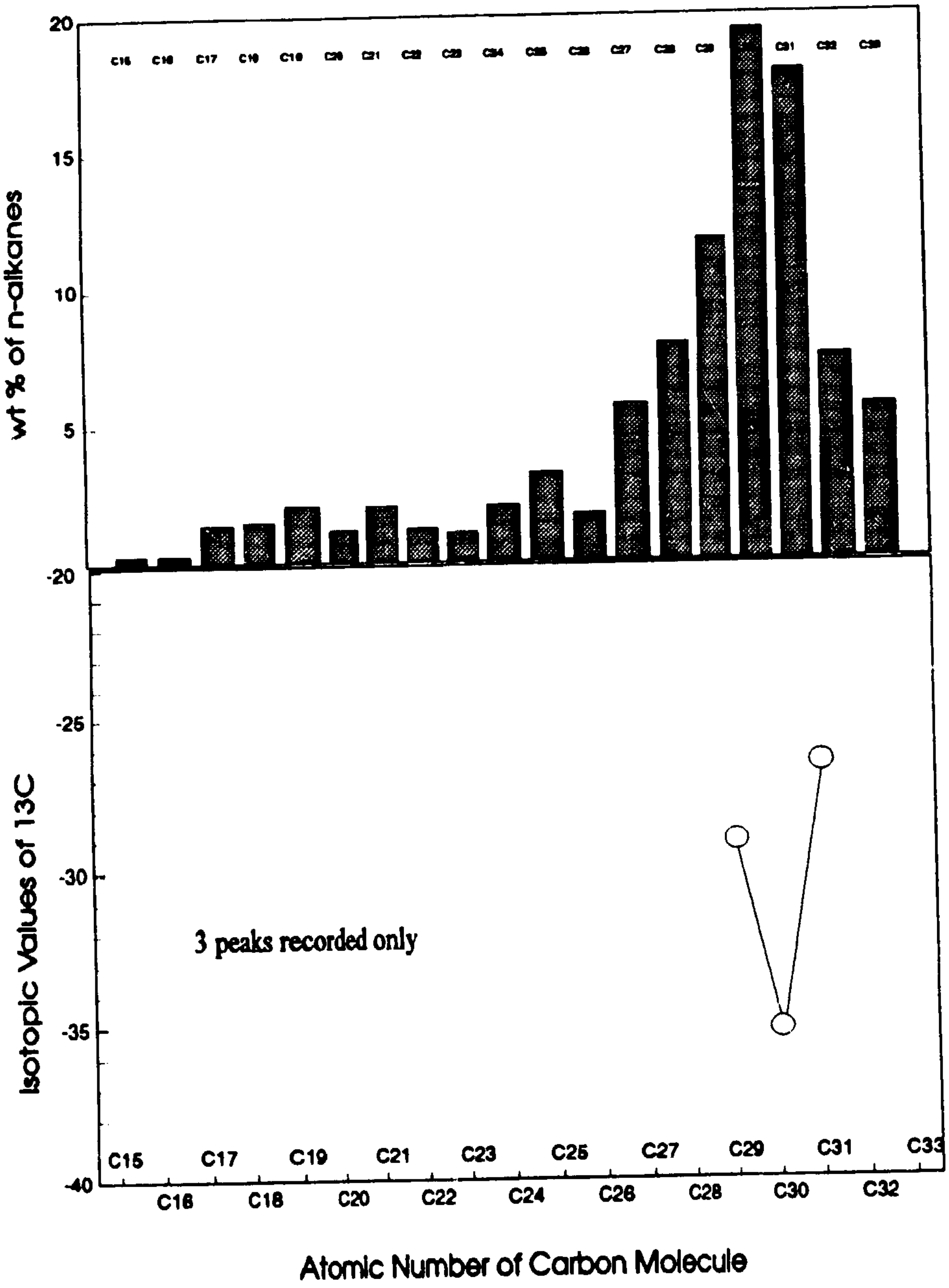

wt % of n-alkanes
20
15
10
5
C15 C16 C17 C18 C19 C20 C21 C22 C23 C24 C25 C26 C27 C28 C29 C30 C31 C32 C33
Isotopic Values of 13C
-20
-25
-30
-35
-40
C15
C17
C19
C21
C23
C25
C27
C29
C31
C33
C16
C18
C20
C22
C24
C26
C28
C30
C32
Atomic Number of Carbon Molecule

MM86 (R1)

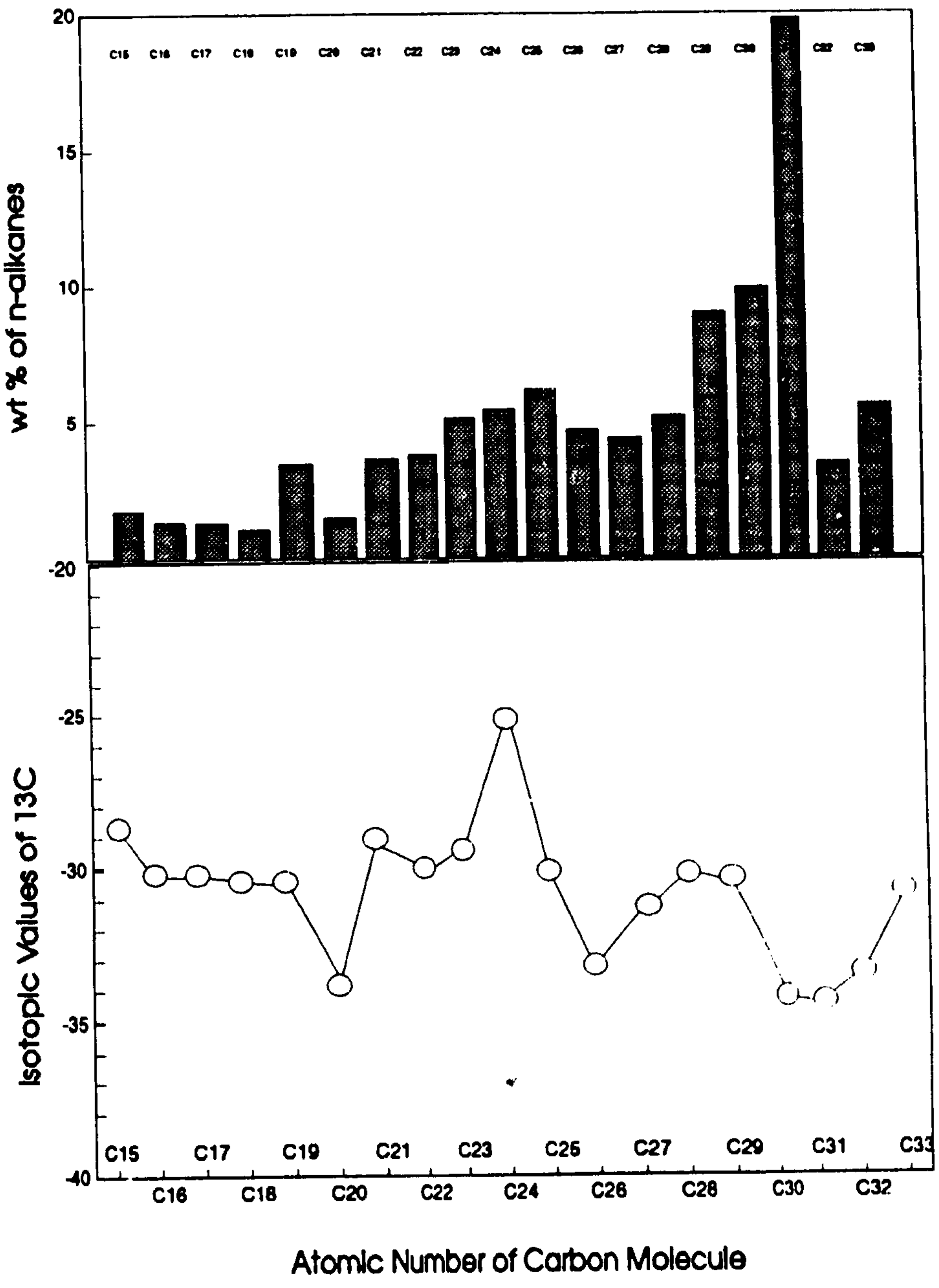


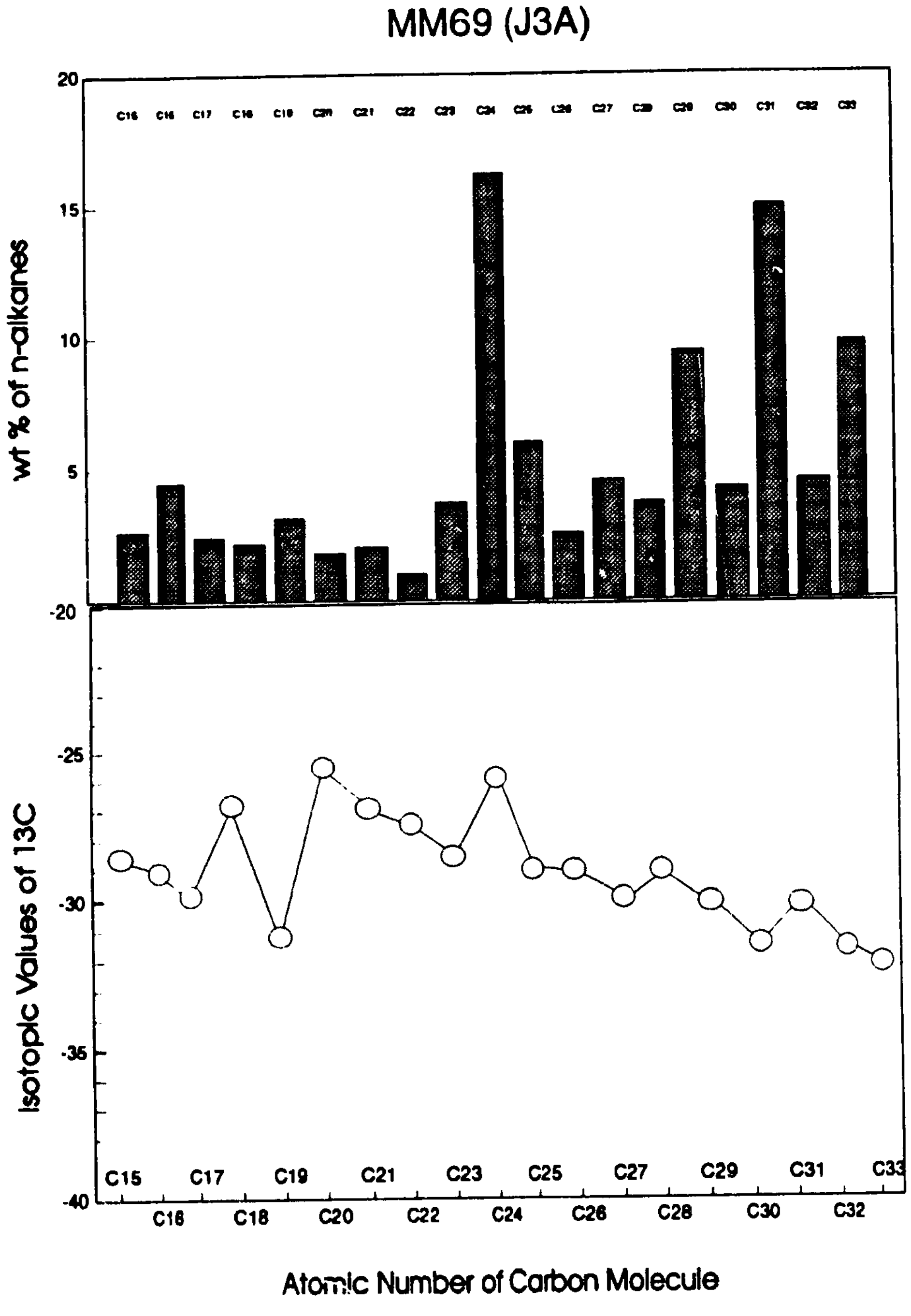
wt % of n-alkanes
20
15
10
5
C15
C16
C17
C18
C19
C20
C21
C22
C23
C24
C25
C26
C27
C28
C29
C30
C31
C32
C33
Isotopic Values of 13C
-20
-25
-30
-35
-40
C15
C17
C19
C21
C23
C25
C27
C29
C31
C33
C16
C18
C20
C22
C24
C26
C28
C30
C32
Atomic Number of Carbon Molecule

MM92 (R3)

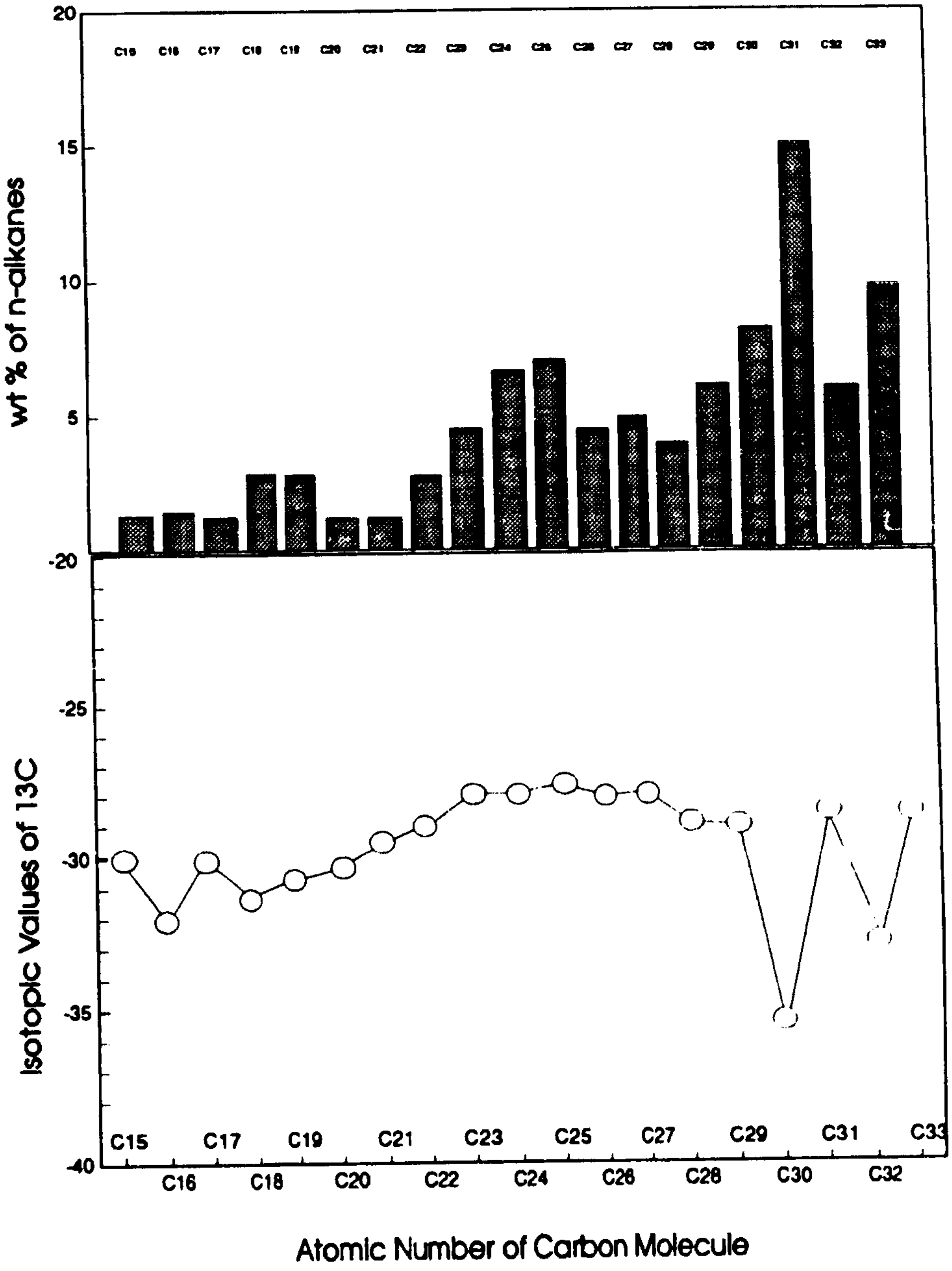

wt % of n-alkanes
20
15
10
5
C15 C16 C17 C18 C19 C20 C21 C22 C23 C24 C25 C26 C27 C28 C29 C31 C32 C33
-20
-25
-30
-35
-40
Isotopic Values of 13C
3 peaks recorded only
C15
C16
C17
C18
C19
C20
C21
C22
C23
C24
C25
C26
C27
C28
C29
C30
C31
C32
C33
Atomic Number of Carbon Molecule

MM70 (J2)

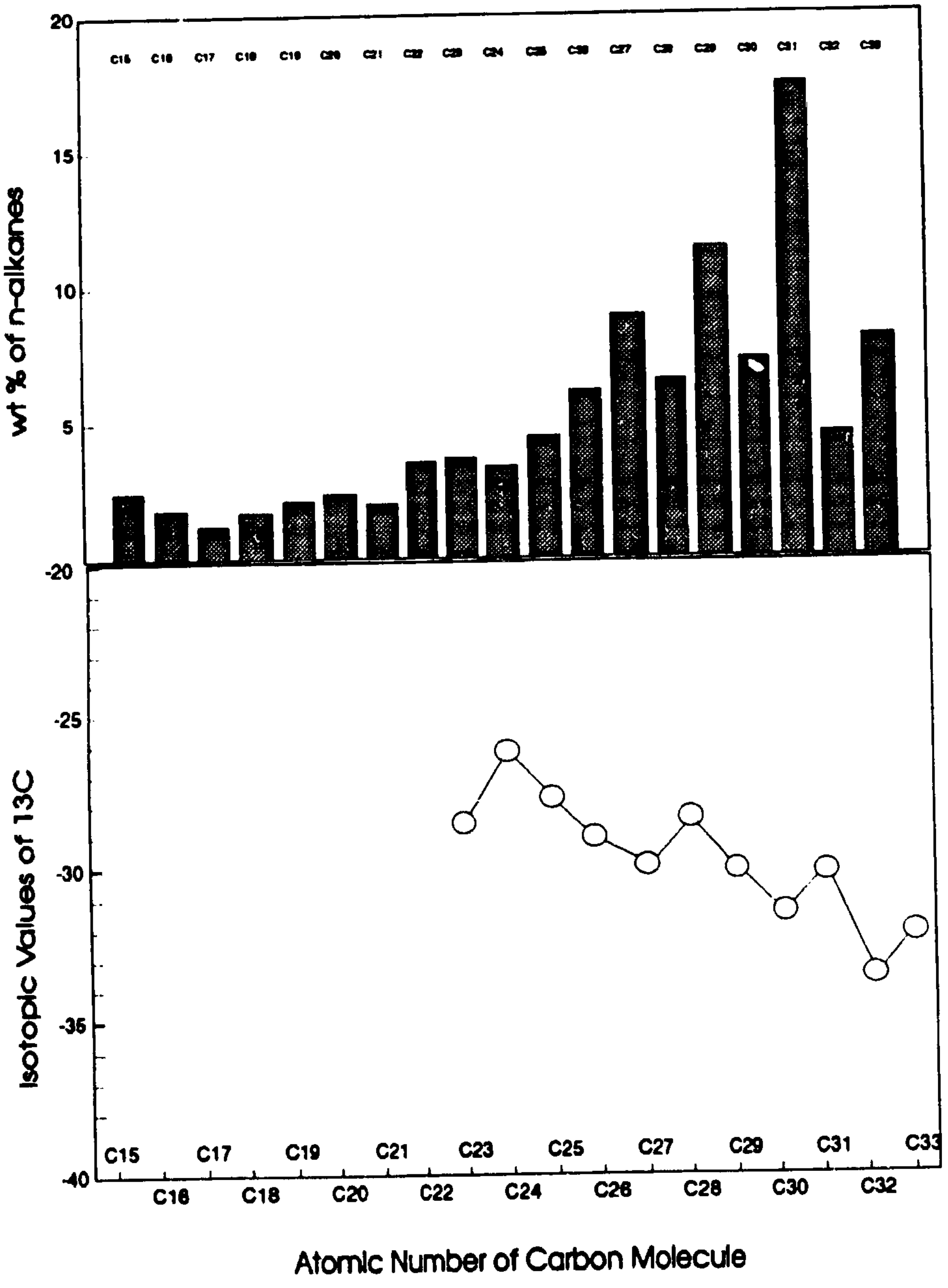

wt % of n-alkanes
20
15
10
5
-20
C15
C16
C17
C18
C19
C20
C21
C22
C23
C24
C25
C26
C27
C28
C29
C30
C32
C33
Isotopic Values of 13C
-25
-30
-35
-40
C15
C17
C19
C21
C23
C25
C27
C29
C31
C33
C16
C18
C20
C22
C24
C26
C28
C30
C32
Atomic Number of Carbon Molecule


MM69 (J3A)
wt % of n-alkanes
20
15
10
5
C15
C16
C17
C18
C19
C20
C21
C22
C23
C24
C25
C26
C27
C28
C29
C30
C31
C32
C33
Isotopic Values of 13C
-20
-25
-30
-35
-40
C15
C17
C19
C21
C23
C25
C27
C29
C31
C33
C16
C18
C20
C22
C24
C26
C28
C30
C32
Atomic Number of Carbon Molecule

MM72 (J5C)

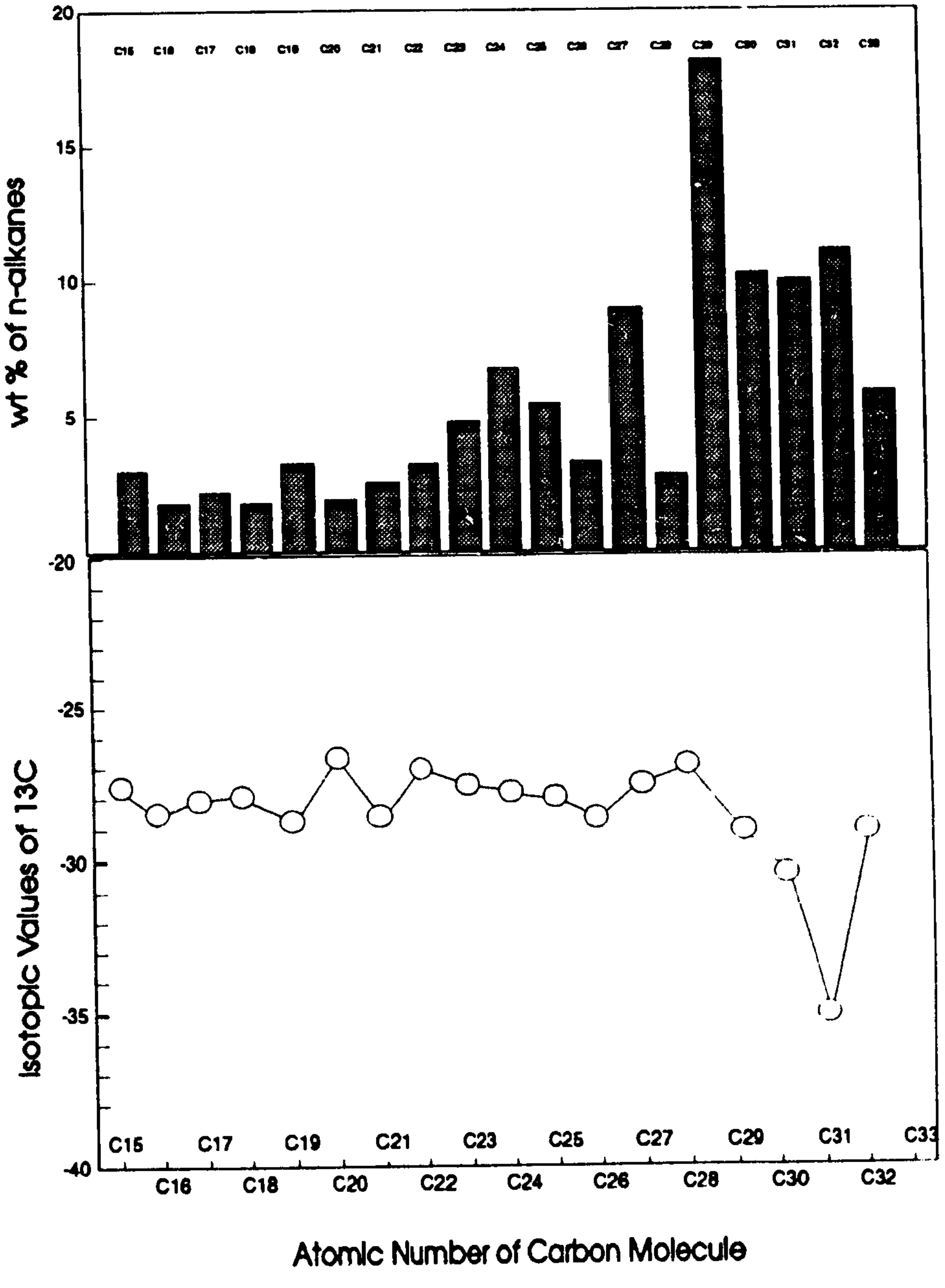

wt % of n-alkanes
20
15
10
5
-20
-25
-30
-35
-40
Isotopic Values of 13C
C15
C16
C17
C18
C19
C20
C21
C22
C23
C24
C25
C26
C27
C28
C29
C30
C31
C32
C33
Atomic Number of Carbon Molecule

MM84 (K2)



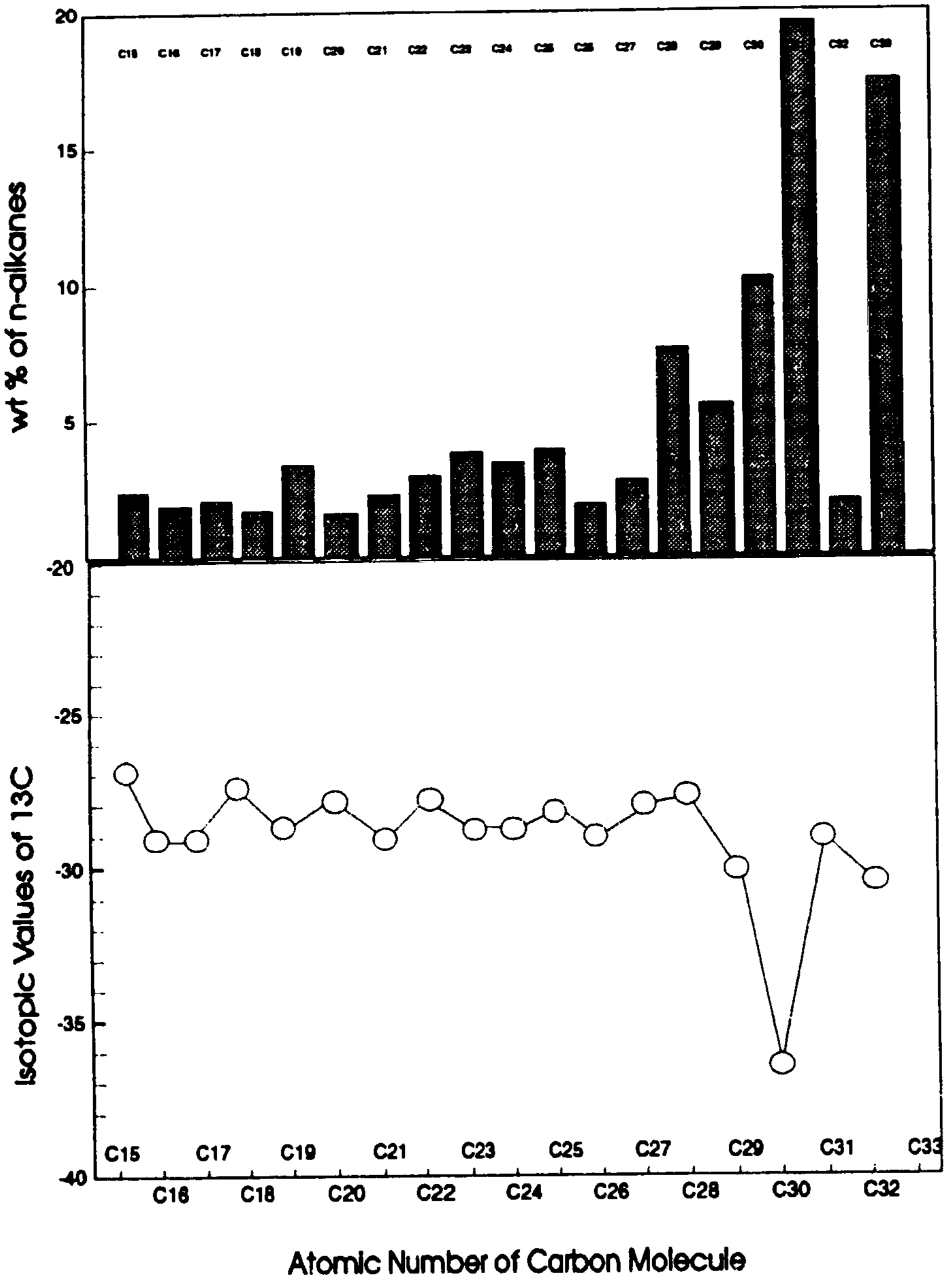
wt % of n-alkanes
20
15
10
5
C15
C16
C17
C18
C19
C20
C21
C22
C23
C24
C25
C26
C27
C28
C29
C30
C31
C32
C33
Isotopic Values of 13C
-20
-25
-30
-35
-40
C15
C17
C19
C21
C23
C25
C27
C29
C31
C33
C16
C18
C20
C22
C24
C26
C28
C30
C32
Atomic Number of Carbon Molecule

MM41 (Q1)

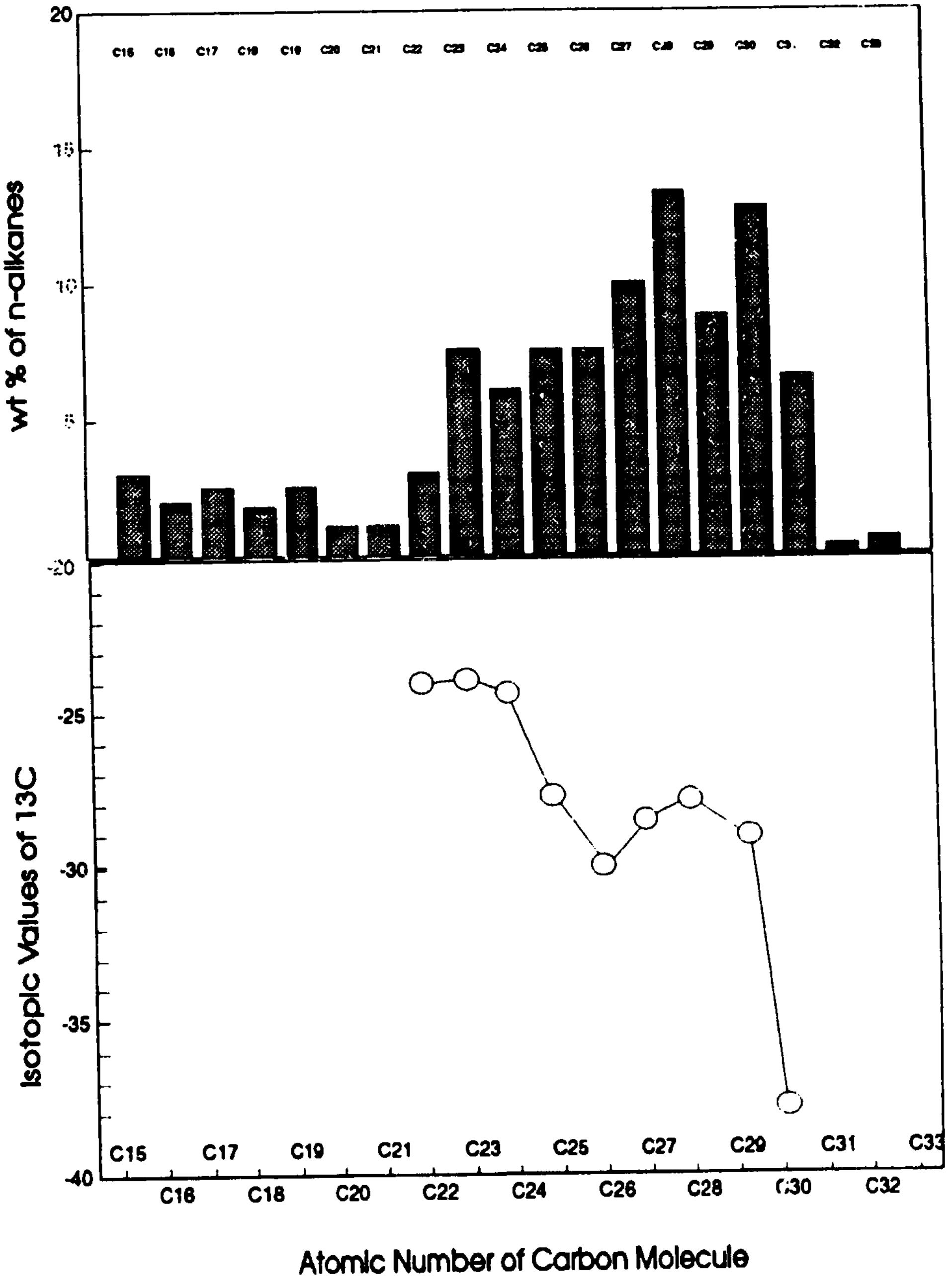


wt % of n-alkanes
20
15
10
5
C15
C16
C17
C18
C19
C20
C21
C22
C23
C24
C25
C26
C27
C28
C29
C30
C31
C32
C33
Isotopic Values of 13C
-20
-25
-30
-35
-40
C15
C17
C19
C21
C23
C25
C27
C29
C31
C33
C16
C18
C20
C22
C24
C26
C28
C30
C32
Atomic Number of Carbon Molecule

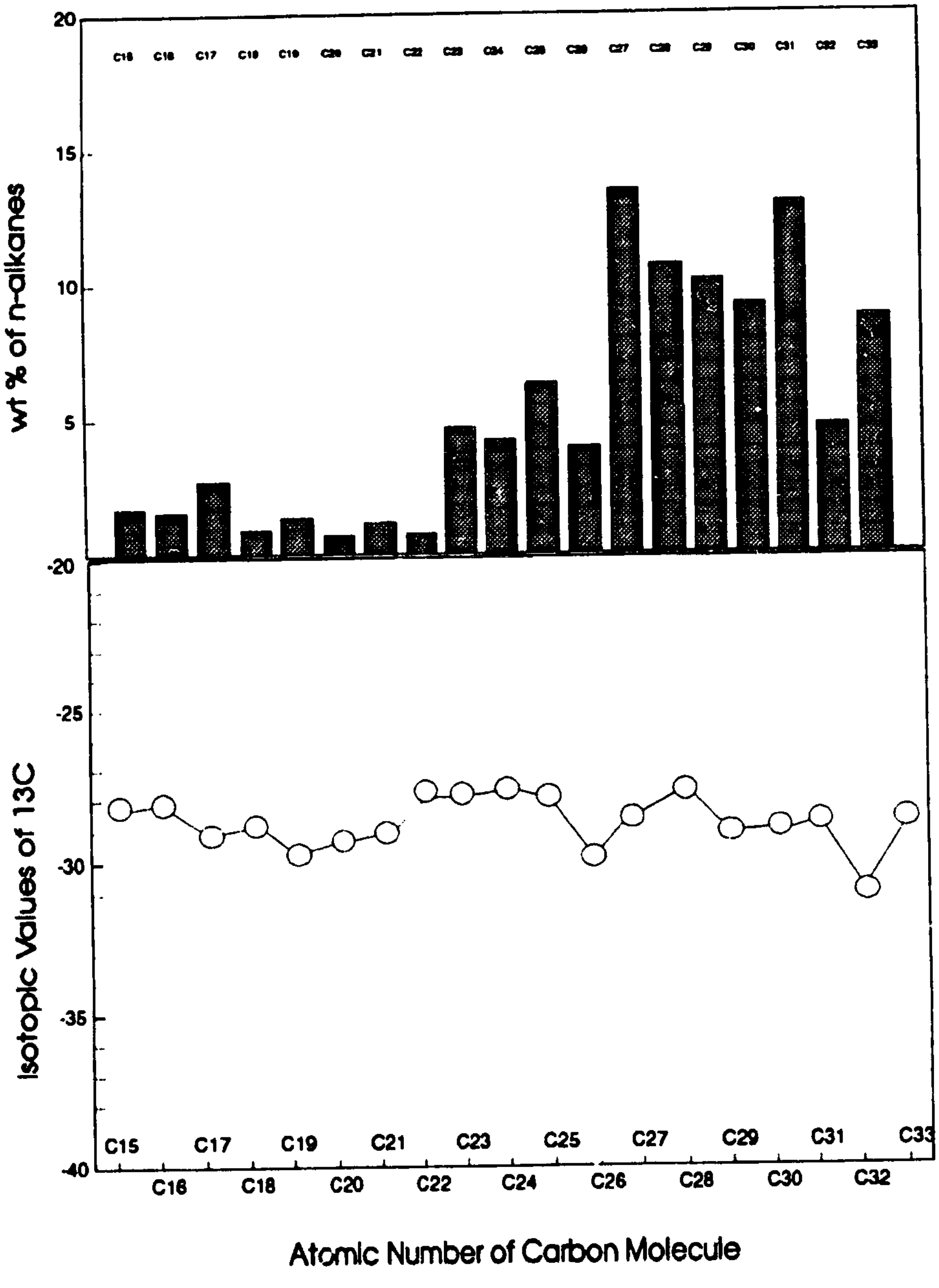
MM73 (Q1)


wt % of n-alkanes
20
15
10
5
C15
C16
C17
C18
C19
C20
C21
C22
C23
C24
C25
C26
C27
C28
C29
C30
C32
C33
Isotopic Values of 13C
-20
-25
-30
-35
-40
C15
C17
C19
C21
C23
C25
C27
C29
C31
C33
C16
C18
C20
C22
C24
C26
C28
C30
C32
Atomic Number of Carbon Molecule

MM49 (Q2)

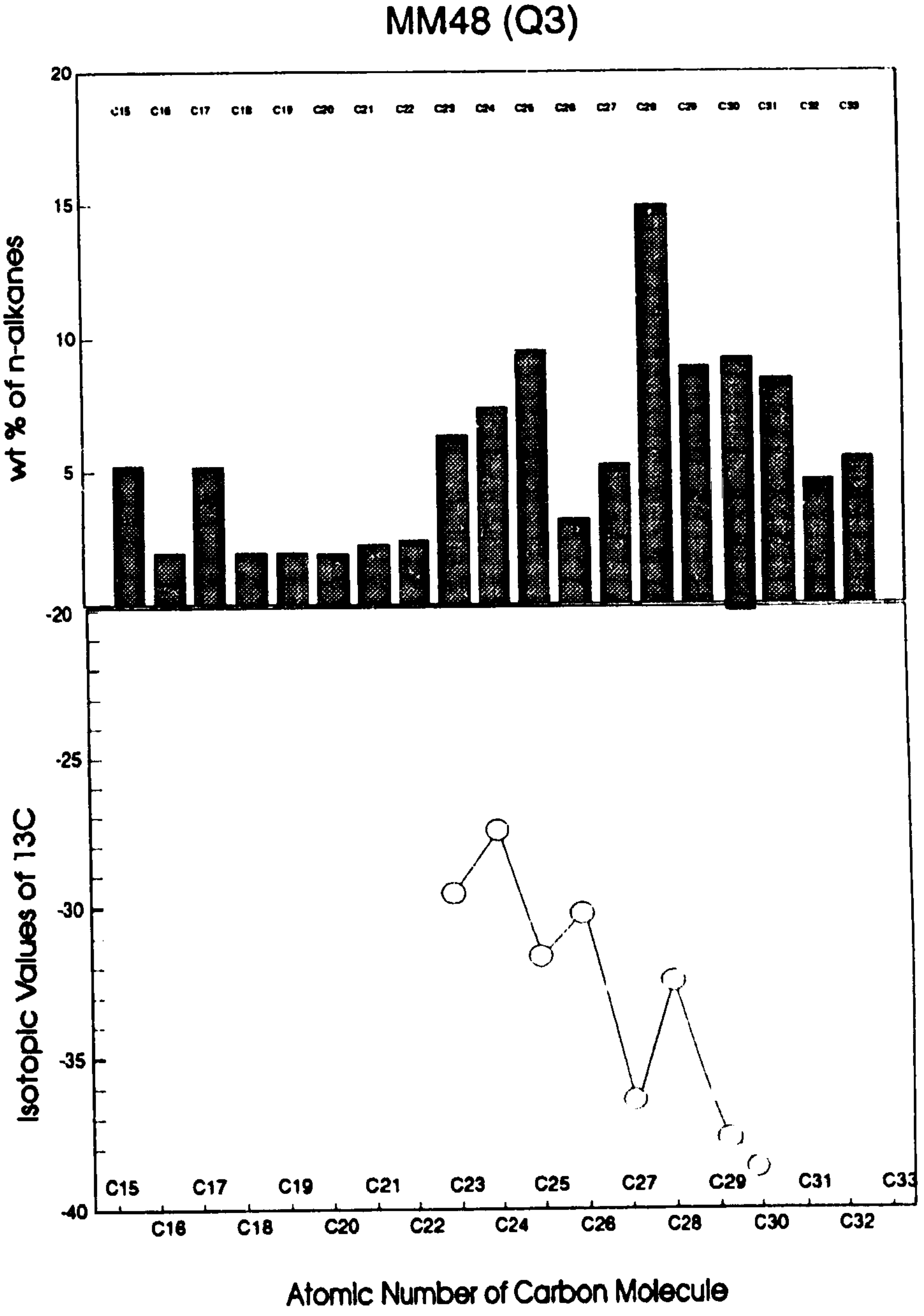


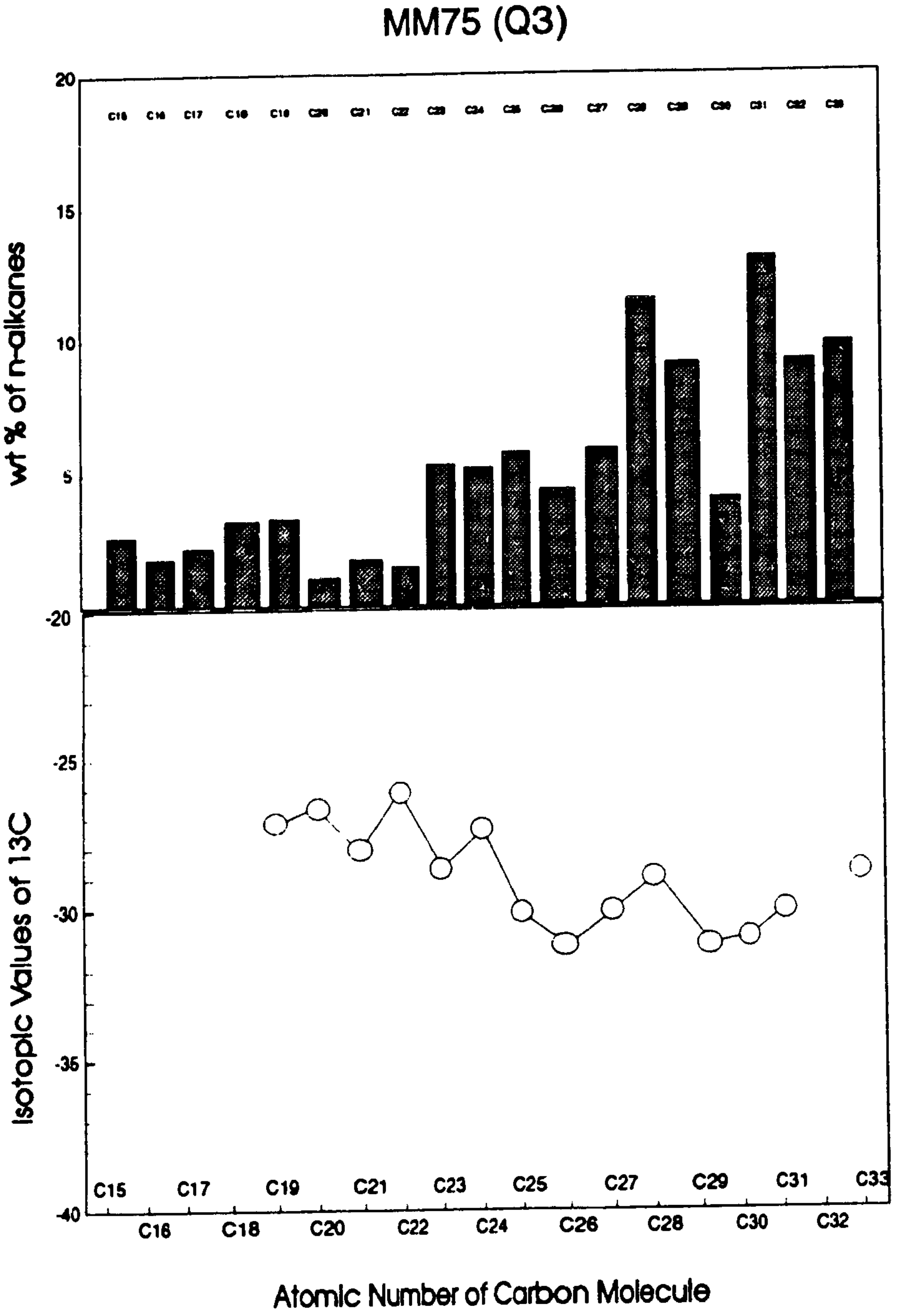
20
15
10
5
-20
-25
-30
-35
-40
wt % of n-alkanes
Isotopic Values of 13C
C15
C16
C17
C18
C19
C20
C21
C22
C23
C24
C25
C26
C27
C28
C29
C30
C31
C32
C33
Atomic Number of Carbon Molecule

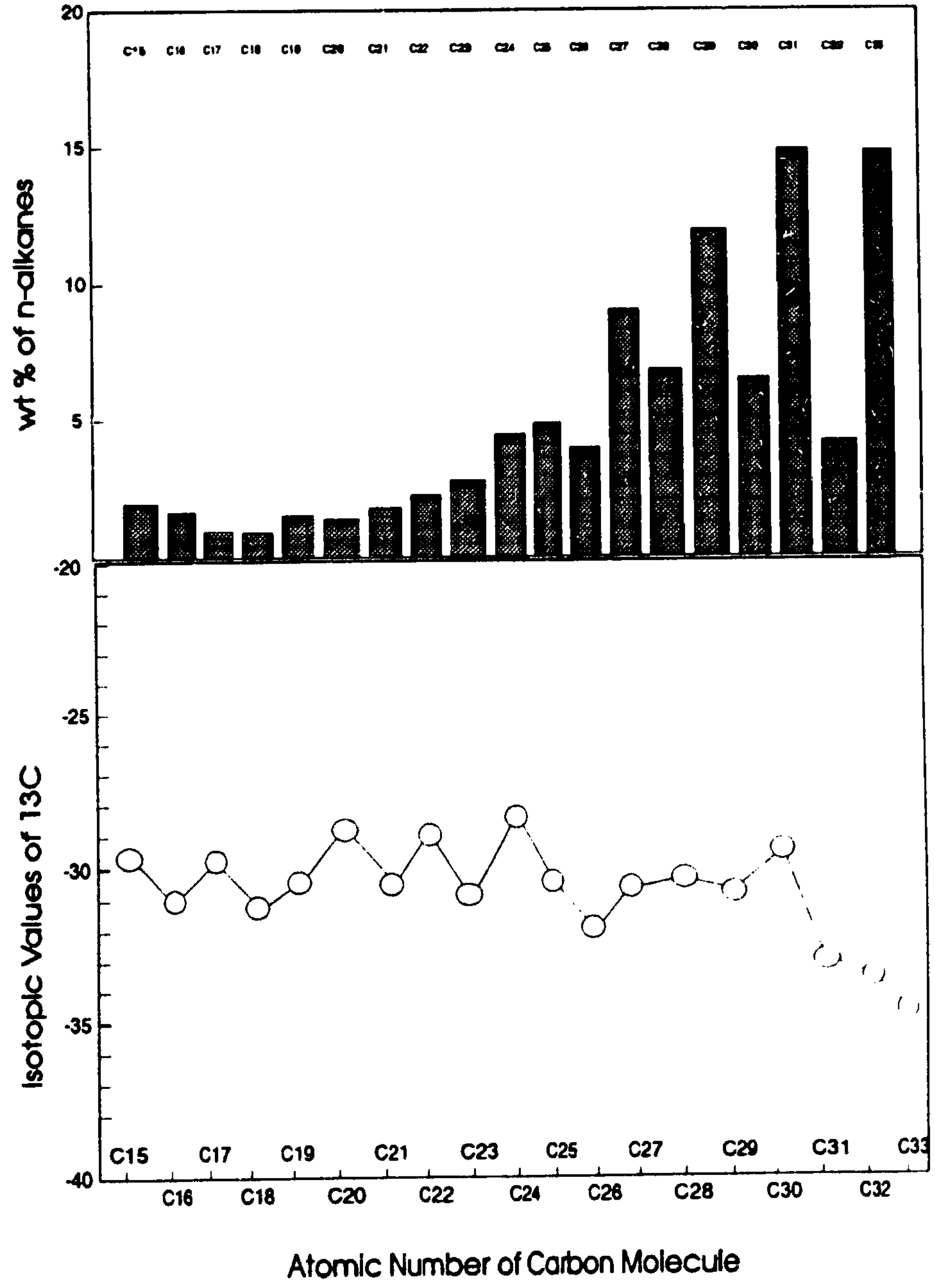


MM74 (Q2)

wt % of n-alkanes
20
15
10
5
C15
C16
C17
C18
C19
C20
C21
C22
C23
C24
C25
C26
C27
C28
C29
C30
C31
C32
C33
Isotopic Values of 13C
-20
-25
-30
-35
-40
C15
C17
C19
C21
C23
C25
C27
C29
C31
C33
C16
C18
C20
C22
C24
C26
C28
C30
C32
Atomic Number of Carbon Molecule


MM48 (Q3)
wt % of n-alkanes
20
15
10
5
C15
C16
C17
C18
C19
C20
C21
C22
C23
C24
C25
C26
C27
C28
C29
C30
C31
C32
C33
Isotopic Values of 13C
-20
-25
-30
-35
-40
C15
C17
C19
C21
C23
C25
C27
C29
C31
C33
C16
C18
C20
C22
C24
C26
C28
C30
C32
Atomic Number of Carbon Molecule

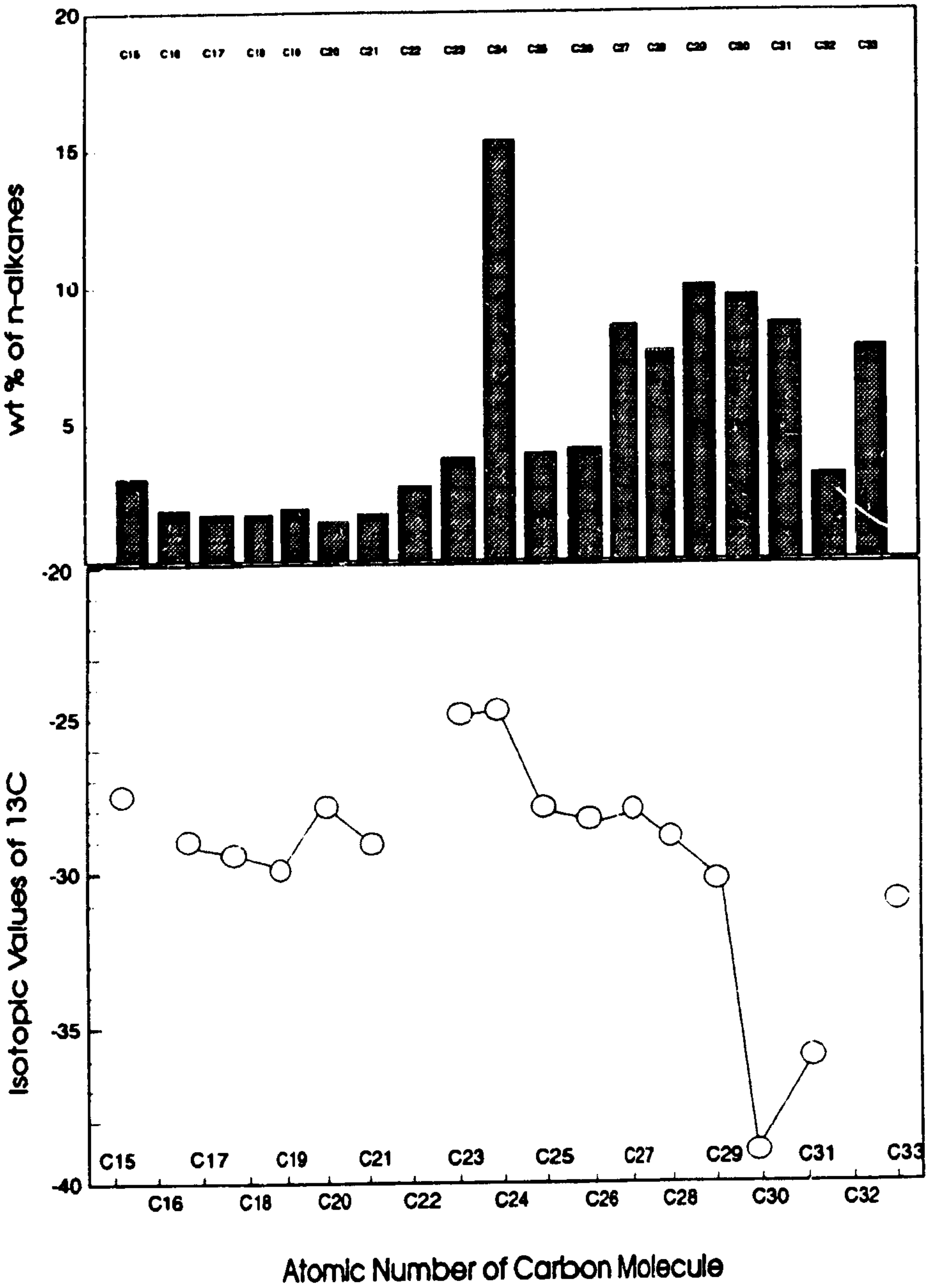

MM75 (Q3)
wt % of n-alkanes
20
15
10
5
-20
-25
-30
-35
-40
Isotopic Values of 13C
C15
C17
C19
C21
C23
C25
C27
C29
C31
C33
C16
C18
C20
C22
C24
C26
C28
C30
C32
Atomic Number of Carbon Molecule



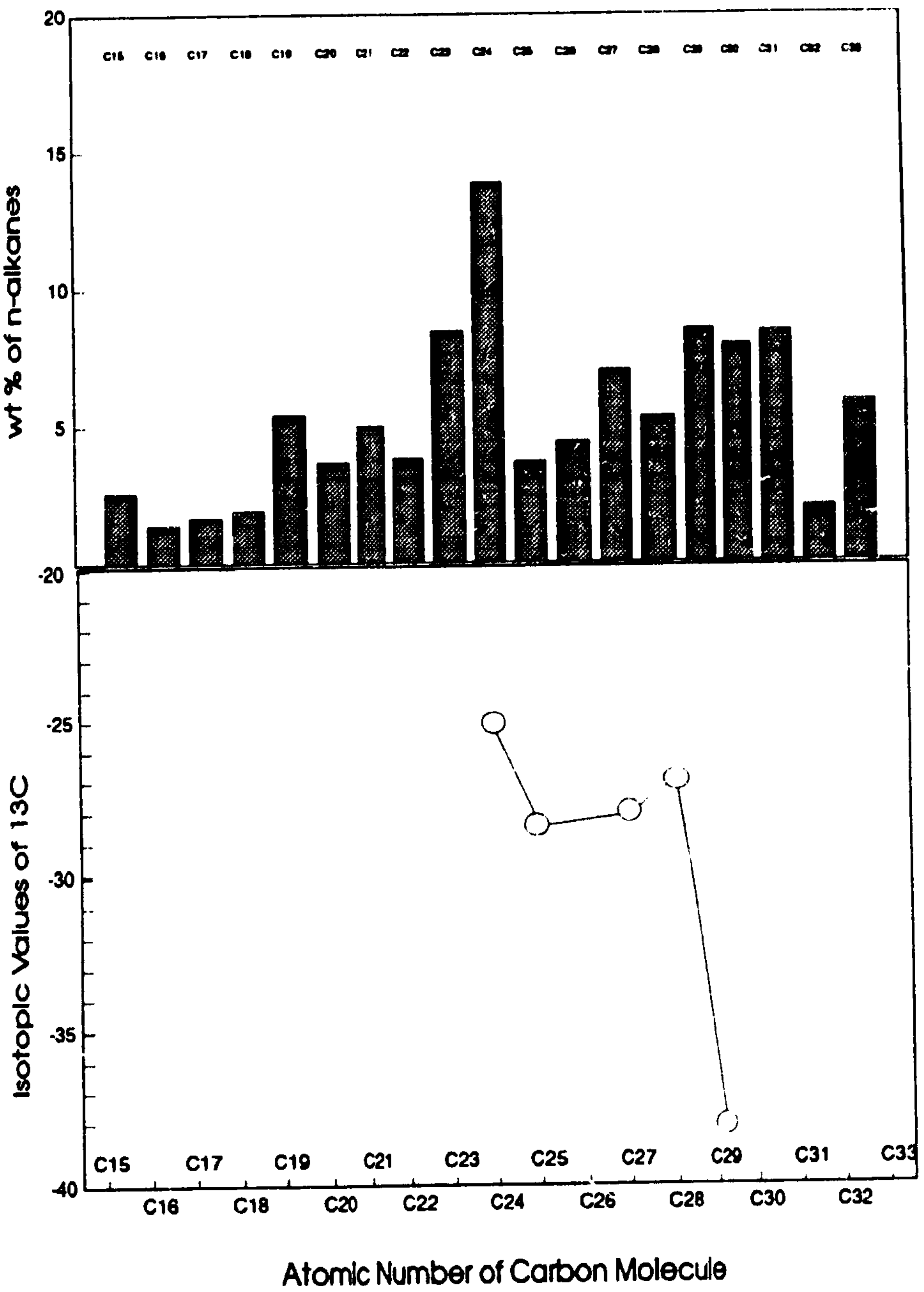
MM91 (R2)

wt % of n-alkanes
20
15
10
5
-20
-25
-30
-35
-40
Isotopic Values of 13C
C15
C16
C17
C18
C19
C20
C21
C22
C23
C24
C25
C26
C27
C28
C29
C30
C31
C32
C33
Atomic Number of Carbon Molecule

MM87 (S1)



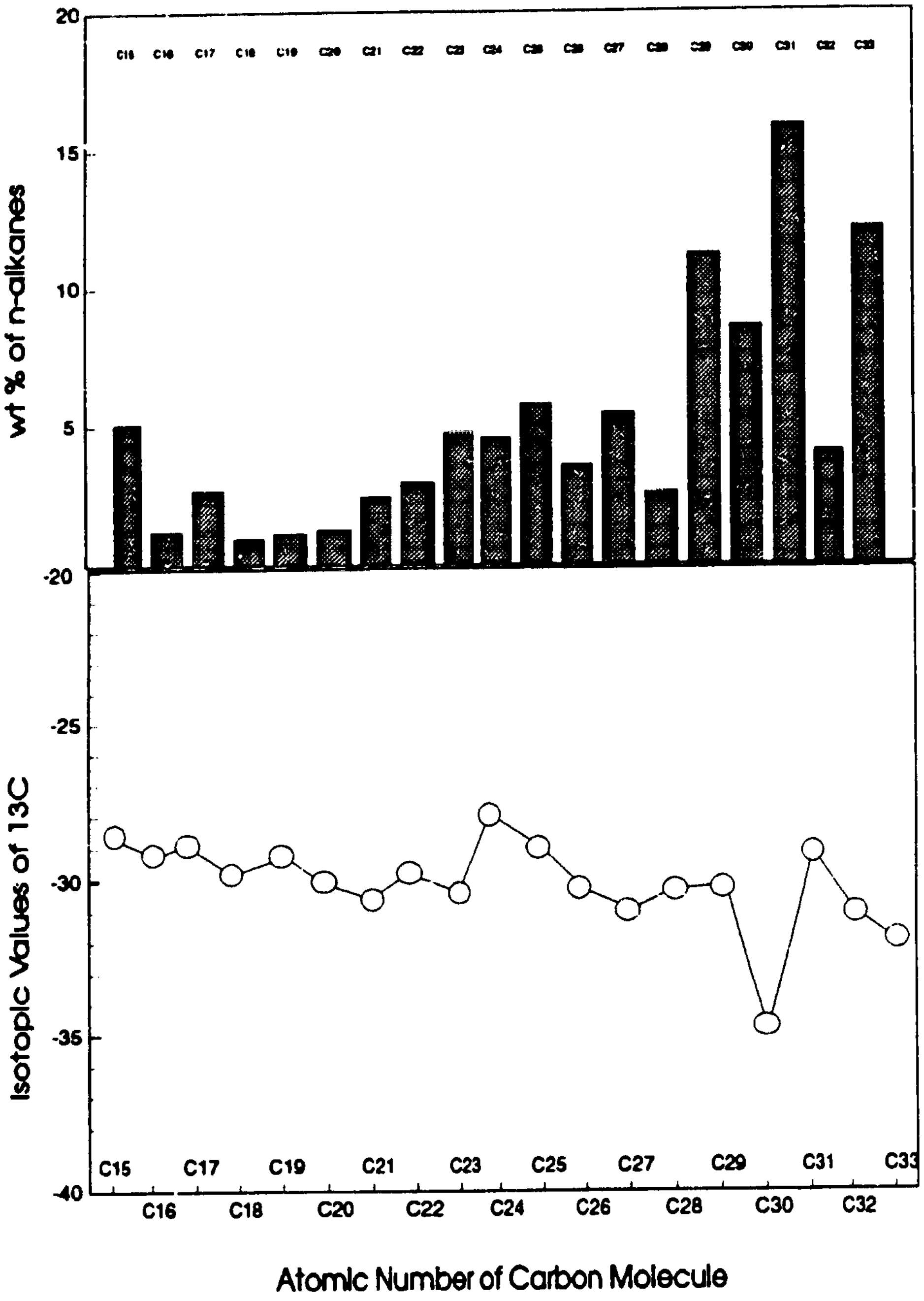
20
15
10
5
wt % of n-alkanes
C15
C16
C17
C18
C19
C20
C21
C22
C23
C24
C25
C26
C27
C28
C29
C30
C31
C32
C33
-20
-25
-30
-35
-40
Isotopic Values of 13C
C15
C17
C19
C21
C23
C25
C27
C29
C31
C33
C16
C18
C20
C22
C24
C26
C28
C30
C32
Atomic Number of Carbon Molecule

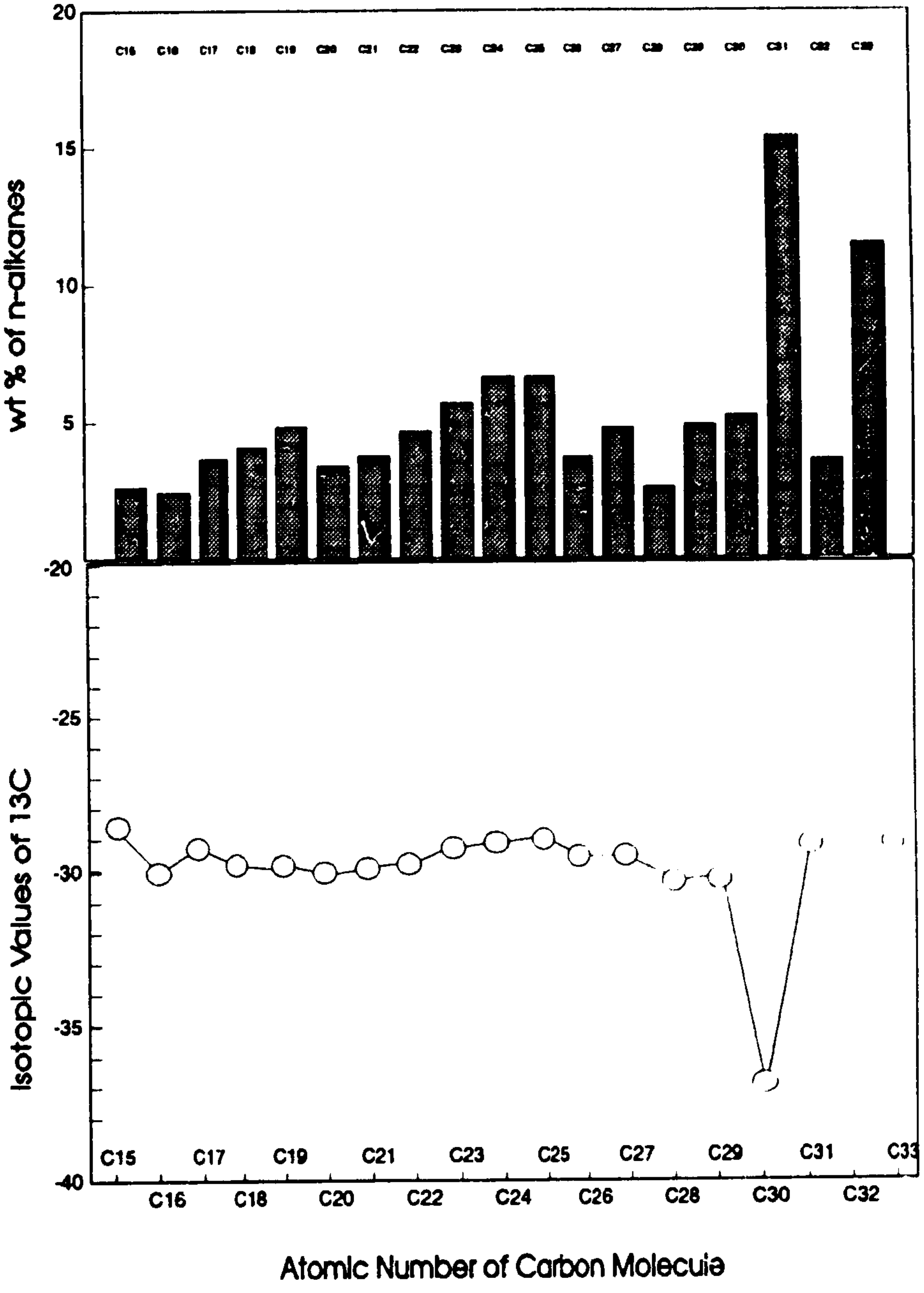


MM89 (S2)

wt % of n-alkanes
20
15
10
5
C15 C16 C17 C18 C19 C20 C21 C22 C23 C24 C25 C26 C27 C28 C29 C30 C31 C32 C33
Isotopic Values of 13C
-20
-25
-30
-35
-40
C15 C17 C19 C21 C23 C25 C27 C29 C31 C33
C16 C18 C20 C22 C24 C26 C28 C30 C32
Atomic Number of Carbon Molecule

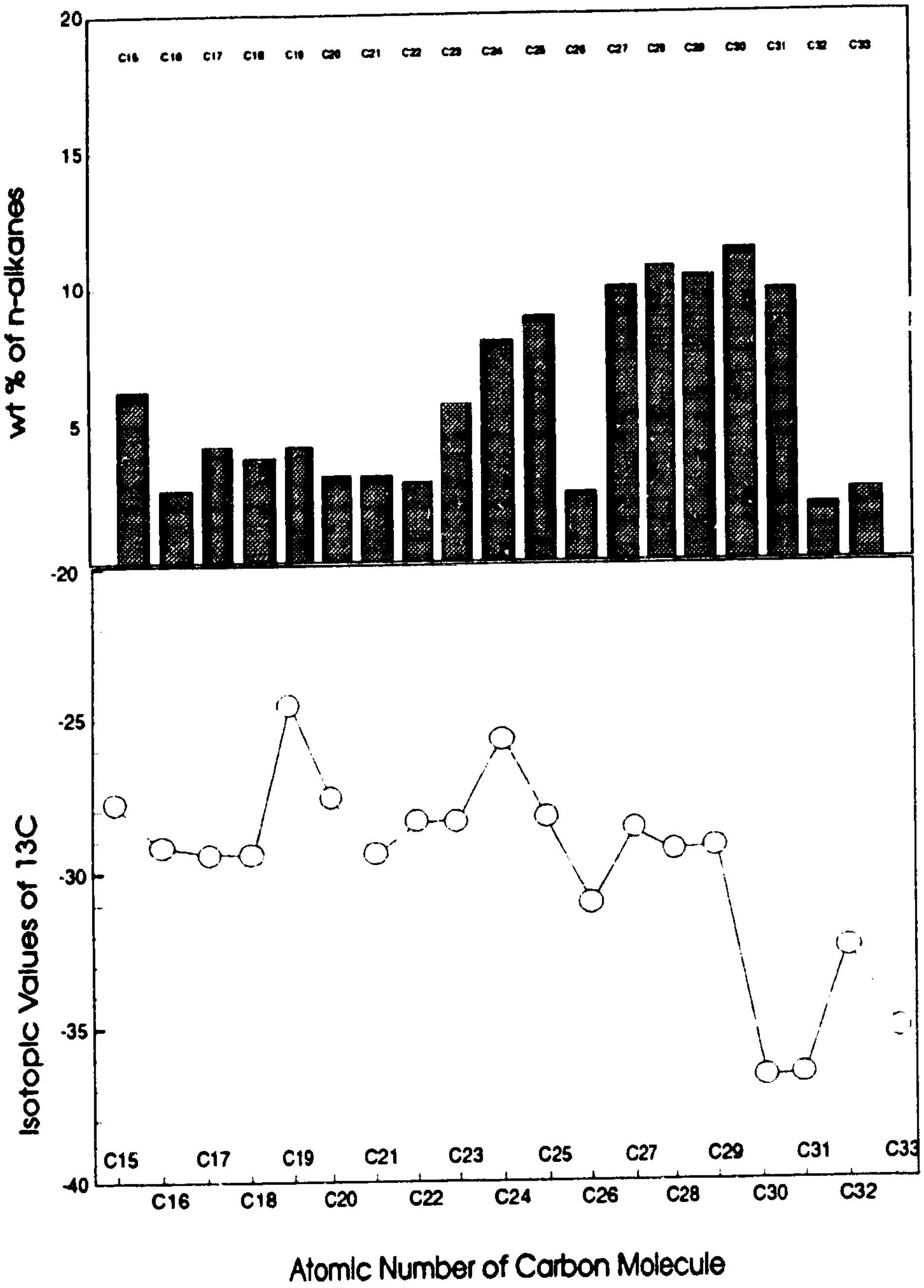
MM42 (J4)


wt % of n-alkanes
20
15
10
5
-20
-25
-30
-35
-40
Isotopic Values of 13C
C15
C16
C17
C18
C19
C20
C21
C22
C23
C24
C25
C26
C27
C28
C29
C30
C31
C32
C33
Atomic Number of Carbon Molecule


20
15
10
5
-20
-25
-30
-35
-40
wt % of n-alkanes
Isotopic Values of 13C
C15
C16
C17
C18
C19
C20
C21
C22
C23
C24
C25
C26
C27
C28
C29
C30
C31
C32
C33
Atomic Number of Carbon Moleculə

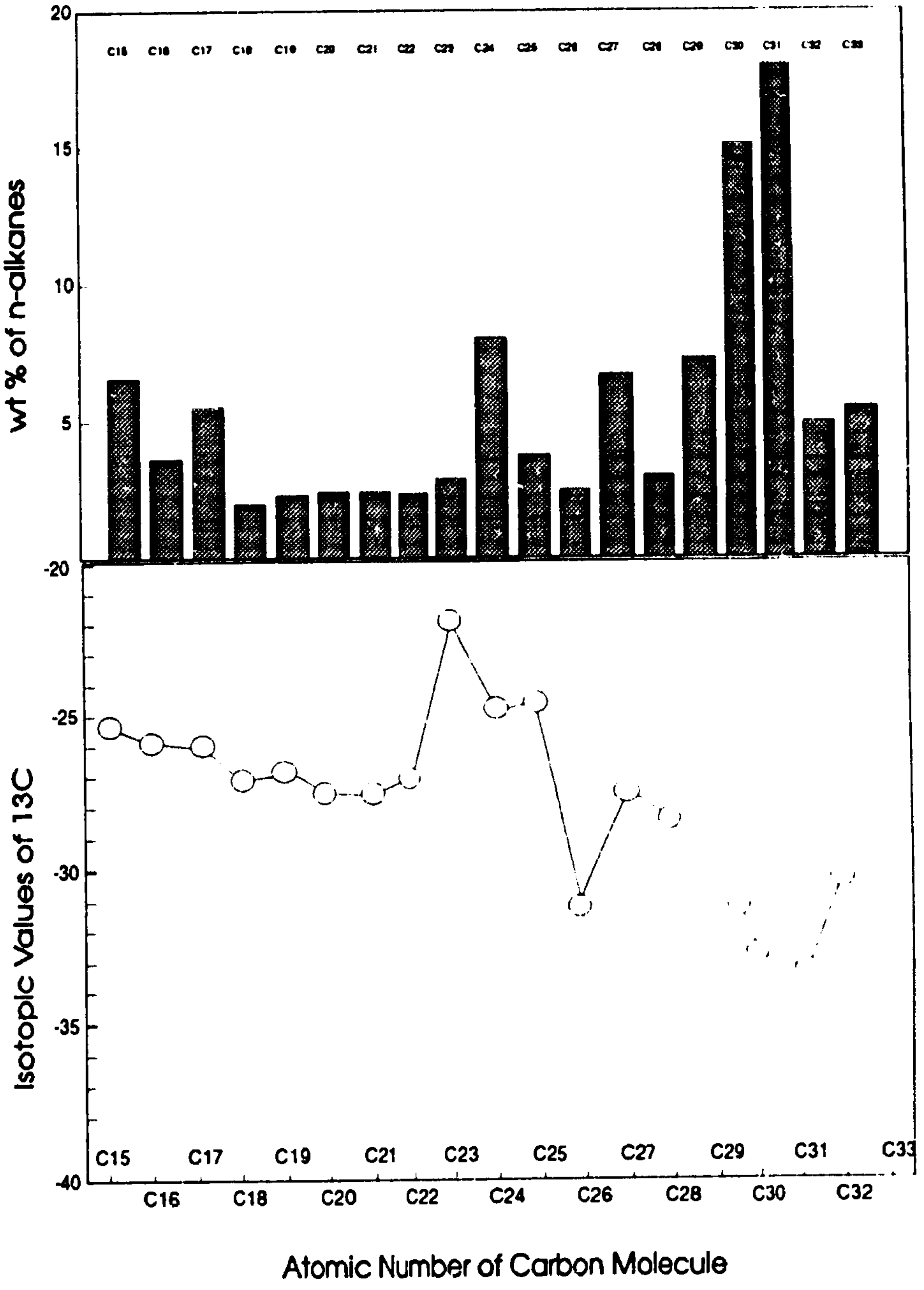
MM79 (J5A)

MM37 (K3)



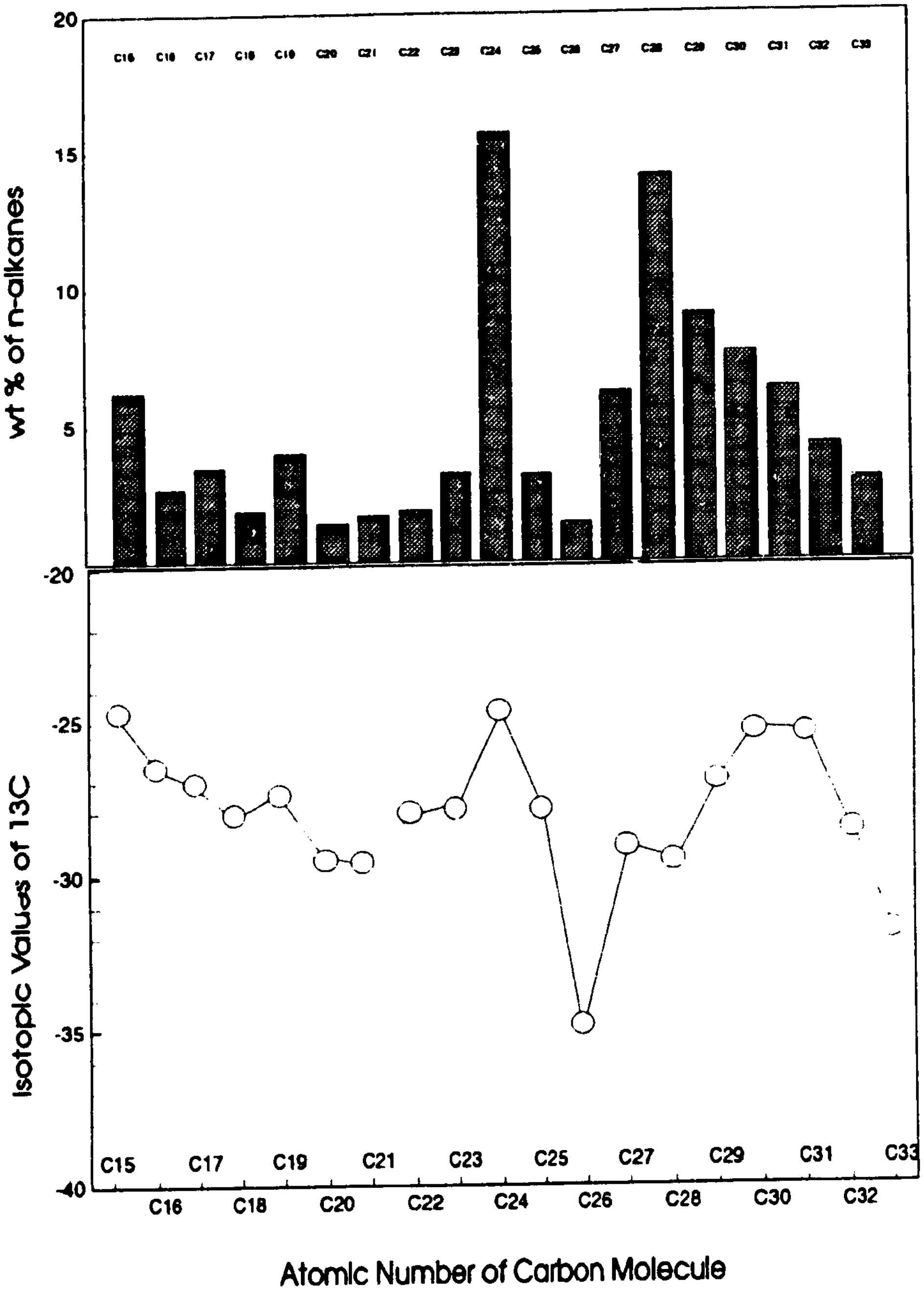
wt % of n-alkanes
20
15
10
5
C15 C16 C17 C18 C19 C20 C21 C22 C23 C24 C25 C26 C27 C28 C29 C30 C31 C32 C33
Isotopic Values of 13C
-20
-25
-30
-35
-40
C15 C17 C19 C21 C23 C25 C27 C29 C31 C33
C16 C18 C20 C22 C24 C26 C28 C30 C32
Atomic Number of Carbon Molecule

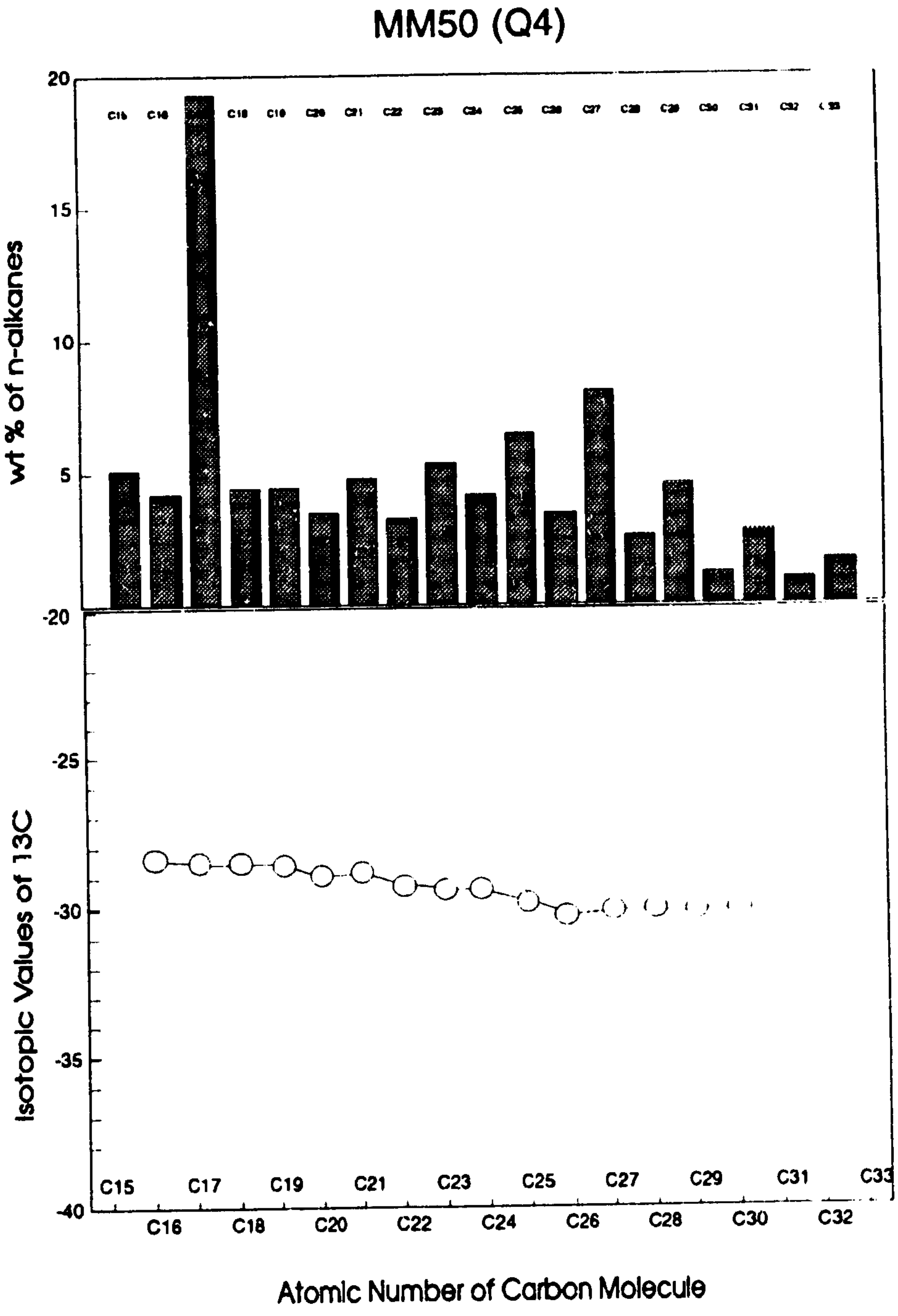
MM38 (K4)



wt % of n-alkanes
20
15
10
5
C15
C16
C17
C18
C19
C20
C21
C22
C23
C24
C25
C26
C27
C28
C29
C30
C31
C32
C33
Isotopic Values of 13C
-20
-25
-30
-35
-40
C15
C17
C19
C21
C23
C25
C27
C29
C31
C33
C16
C18
C20
C22
C24
C26
C28
C30
C32
Atomic Number of Carbon Molecule

MM82 (K4)


20
15
10
5
wt % of n-alkanes
C15
C16
C17
C18
C19
C20
C21
C22
C23
C24
C25
C26
C27
C28
C29
C30
C31
C32
C33
-20
-25
-30
-35
-40
Isotopic Values of 13C
C15
C17
C19
C21
C23
C25
C27
C29
C31
C33
C16
C18
C20
C22
C24
C26
C28
C30
C32
Atomic Number of Carbon Molecule


MM50 (Q4)
wt % of n-alkanes
20
15
10
5
C15
C16
C17
C18
C19
C20
C21
C22
C23
C24
C25
C26
C27
C28
C29
C30
C31
C32
C33
Isotopic Values of 13C
-20
-25
-30
-35
-40
C15
C17
C19
C21
C23
C25
C27
C29
C31
C33
C16
C18
C20
C22
C24
C26
C28
C30
C32
Atomic Number of Carbon Molecule

Appendix B

Identification of Spore and Pollen

Examination and microphotographs of individual spores/pollen were performed using Zeiss microscope.

Slides were prepared in the laboratory as discribed in Section 3.6.

Key references are studies of Gemeraad et.al (1968), Muller (1968, 1975), Morley (1981, 1982), Kemp and Harris (1977), Watanasak (1989, 1990), Ratanasthien (1989a), Anderson and Muller (1975), and Traverse (1988).

PLATE I

Figure 1. *Polypodiidites usmensis* Van Der Hammen (Slide #92-211, MM79, 126.8/52.5).
Description : Lateral view showing scattered prominent baculae sculpture; distal side concave and proximal side convex; ornament absent on the proximal surface.
Dimension : 40-45 μm
Remarks : This species has an affinity close to Verrucatosporites, The genus is common from middle Oligocene to lower Pleistocene in New Zealand (Couper, 1960).

Figure 2. *Dactylocladus* type (Slide #92-201, MM69, 90.5/14.6).
Description : Proximal view showing long, intruding colpi, thick exine, finely reticulate, and elliptical outline.
Dimension : 35 μm
Remarks : This genus is common throughout Tertiary up to present in the peat swamp deposits in northwest Borneo (Muller, 1975)

Figure 3. *Spinizonocolpites echinatus* (Slide #92-212, MM40, 17.5/106.5).
Description : Proximal view showing large colpi and scattered echinae on an oval and flattened grain.
Dimension : 30 μm
Remarks : This species is identical to the pollen of the palm genus *Nypa*, which is common in the Eocene strata of Sarawak (Muller, 1968)

Figure 4. *Verrucatosporites usmensis* Van Der Hammen (Slide #92-203, MM71, 123.7/38.5)
Description : a monolete spore, bilaterally symmetrical, anisopolar; lateral view showing a convex distal outline and a slightly straight proximal outline; gemmate, gemmae $1^{1}/_{2}$ to $2^{1}/_{2}$ μm; rather smooth on the proximal surface.
Dimension : 35 μm
Remarks : this species is a fern spore of varied taxonomic affinities. It is common throughout the Tertiary in northern South-America and in Borneo (Gemeraad et al., 1968).

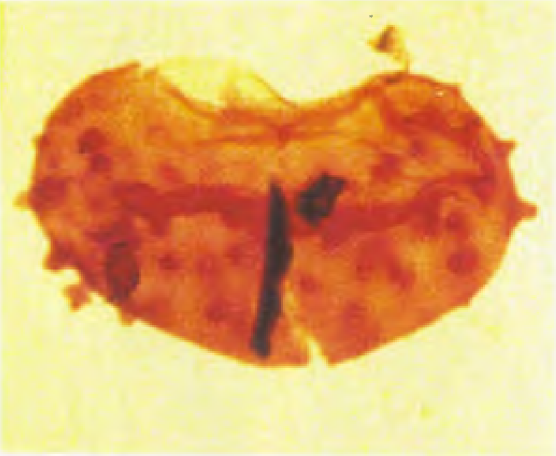


Figure 1

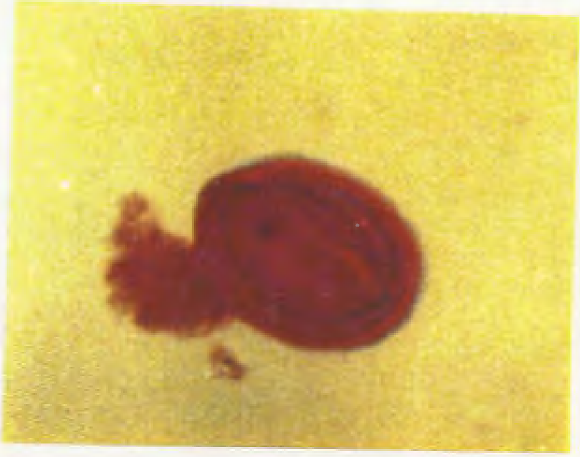


Figure 2

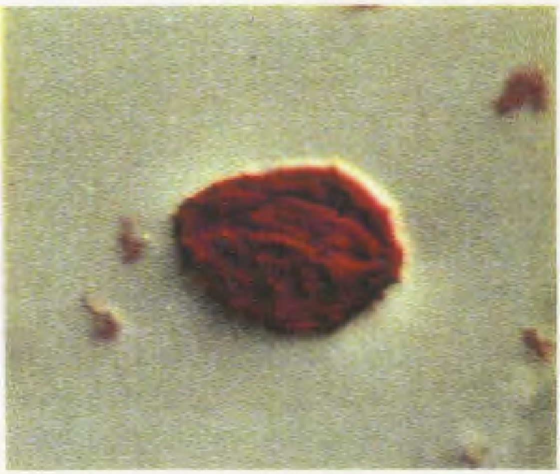


Figure 3

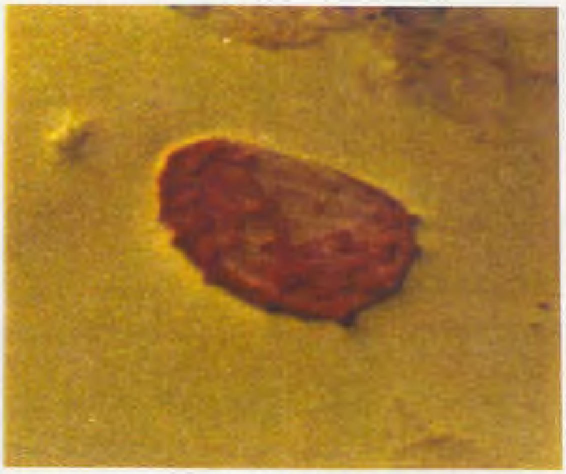


Figure 4

Plate I

Figure 1. *Polypodiidites usmensis* Van Der Hammen
Figure 2. *Dactylocladus* type
Figure 3. *Spinizonocolpites echinatus*
Figure 4. *Verrucatosporites usmensis* Van Der Hammen

PLATE II

Figure 1. Gramineae (Grass) (Slide #92-212, MM39, 107.6/22.7)
Lateral view showing the characteristic folded nature of most fossil grass pollen and thin sculpture surface. It is hardly distinguished the species of these genera (cf. Traverse, 1988).

Figure 2. *Biretisporites huonenesis* (Slide #92-176, MM84, 126.4/34.3).
Description : Proximal view showing trilete laesurae, subtriangular amb with apices rounded and sides convex to slightly straight.
Dimension : 40 μm
Remarks : the species is common in the Neogene in Papua New Guinea (Playford, 1982).

Figure 3. *Gleicheniidites* sp. (Slide #92-200, MM68, 125.7/63.4).
Description : Proximal view showing trilete laesurae with rather thick lips, triangular amb.
Dimension : 25-30 μm.
Remarks : This species is a distinctive fern spore, which is similar to the mordern fern *G. microphylla*. It is a common spore in Neogene formations (Playford, 1982; Traverse, 1988).

Figure 4. *Pinus* sp. (Slide #92-178, MM85, 121.3/43.3).
Description : Bissacate pollen; length of the corpus slightly exceeds width; thin proximal wall becomes finely reticulate on the distal side; coarser reticulate on the sacci; Sacci are smaller than the corpus and rather separated from it.
Dimension : corpus (45, 40, 40 μm for length, width, height).
sacci (27, 32, 25 μm for length, width, height).
Remarks : Coniferous pollen are common in Miocene-Pliocene sediments in northern hemisphere (Traverse, 1988).

PLATE II

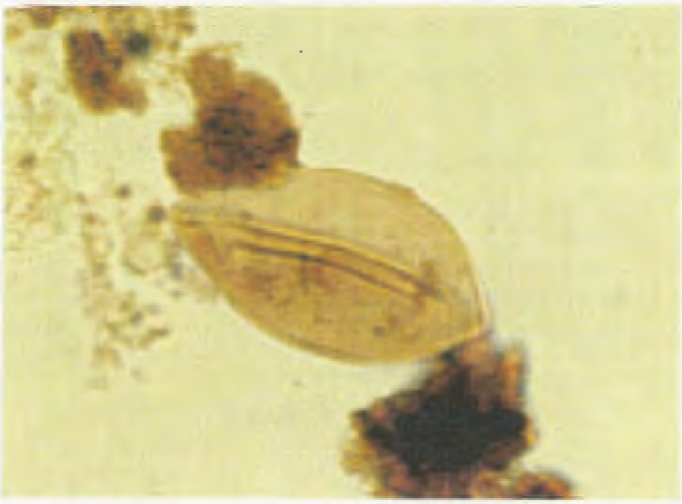


Figure 1

Figure 2

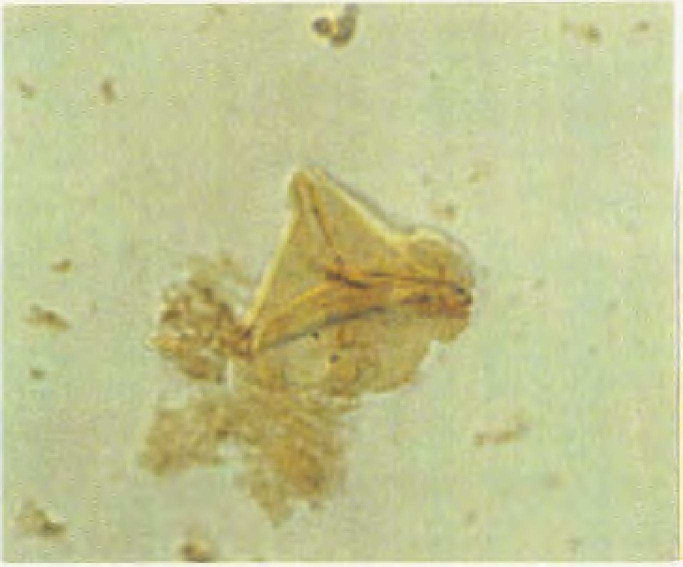


Figure 3

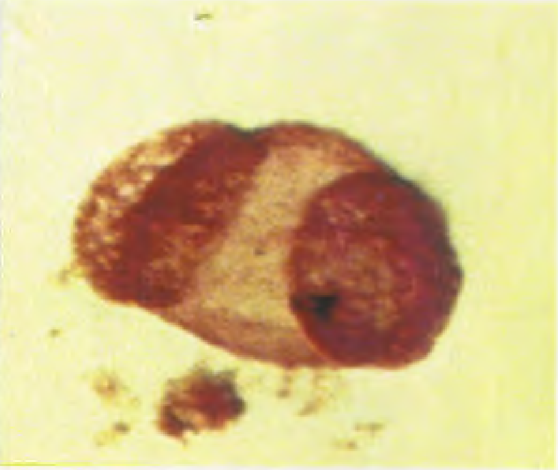


Figure 4

Plate II

Figure 1. Gramineae (Grass)
Figure 2. *Biretisporites huonenesis*
Figure 3. *Gleicheniidites* sp.
Figure 4. *Pinus* sp.

PLATE III

Figure 1. *Perisyncolporites* sp. (Slide #92-212, MM39, 129.7/42.5)
Description : A tetrahedral syncolpate arrangement; pores endexinous, circular to oval, 2-4 μm; thick wall; tectate unclear.
Dimension : 30-40 μm
Remarks : Hexahedral pattern is the most common form. The syncolpate arrangement, however, varies to higher orders (hepta- to dodecahedral) or lower orders (penta- to tetrahedral). The genus has an affinity related to Malpighiaceae and was found in the Caribbean area and Nigeria (Gemeraad et al., 1968).

Figure 2. *Crassoretitriletes* sp. (Slide #92-178, MM85, 122/54.1).
Description : High focus view showing rugulate-reticulate morphology. Laesurae trilete is covered by the sculpture.
Dimension : 60 μm.
Remarks : the genus has a close affinity to Lygodium microphyllum. It's found common in the tropial region (Germeraad et al., 1968).

Figure 3. *Dactylopollis magnificus* Muller (Slide #92-206, MM74, 117.4/38.5).
Description : High focus showing a large and long colpus-like; exine scabrate-echinate.
Dimension : 75-80 μm
Remarks : This species has a possible affinity to Anacardiaceae. It contributed to define botanical communities in Sarawak, Malaysia (Muller, 1968).

Figure 4. *Trichanthera* sp. (Slide #92-207, MM75, 118.9/26.2).
Description : Trilete leasurae are not clearly shown on the proximal side; exine thick with gemae and clavae sculpture.
Dimension : 95-105 μm
Remarks : similar genus was documented by Germeraad et al. (1968)

PLATE III

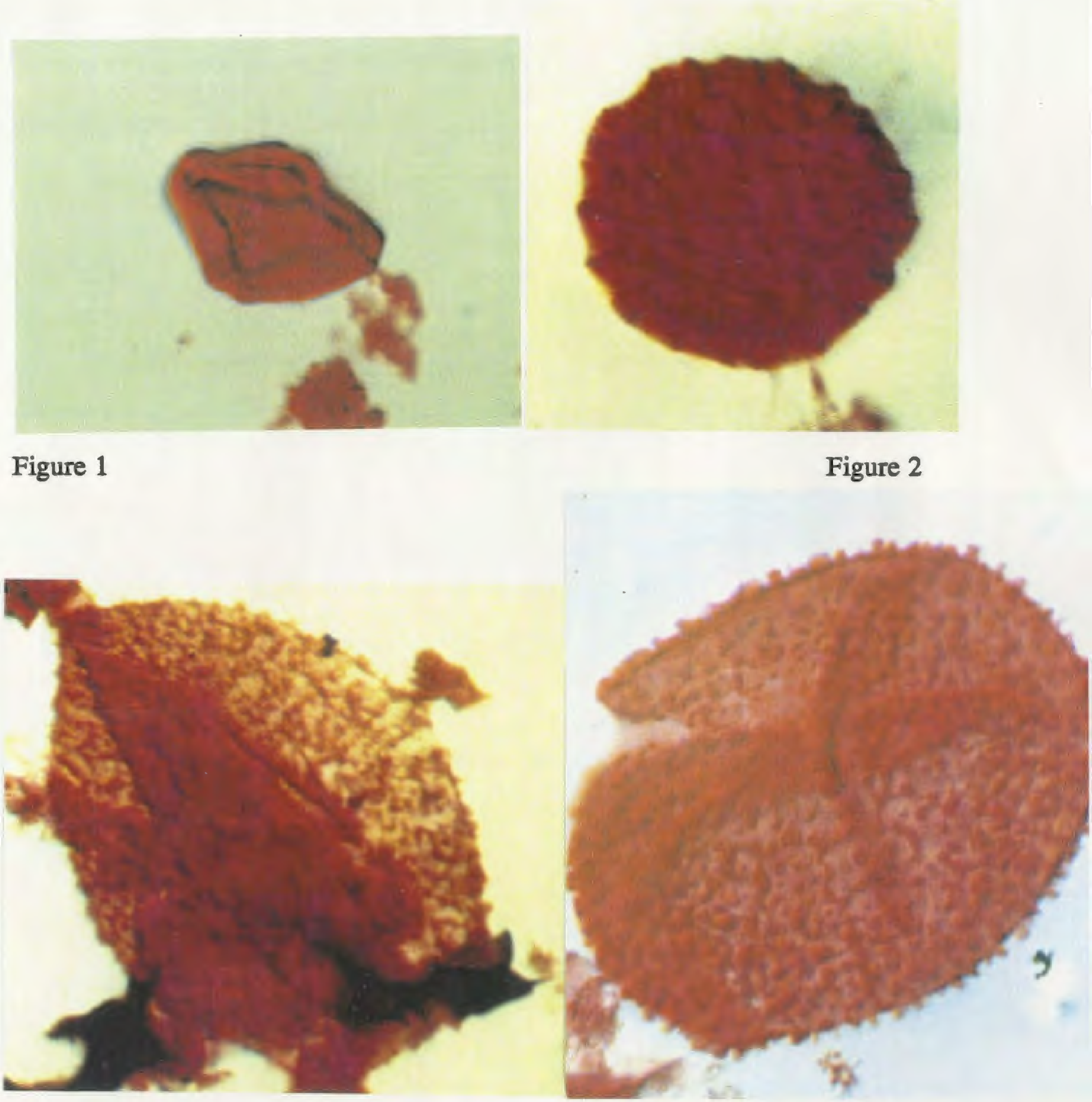


Figure 1

Figure 2

Figure 3

Figure 4

Plate III
Figure 1. *Perisyncolporites* sp.
Figure 2. *Crassoretitriletes* sp.
Figure 3. *Dactylopollis magnificus* Muller
Figure 4. *Trichanthera* sp.

PLATE IV

Figure 1. *Cyrtostachys* (Slide #92-222, MM50, 117.5/23.8).

Description : small grain, oval outline with fine reticulate sculpture; colpi extend along the long axis to the poles.

Dimension : 25-30 μm

Remarks : the genus was frequently occurred in Berakas and Marudi within the peat swamp deposits (Muller, 1975).

Figure 2. *Rhoipites microluminus* Kemp (Slide #92-177, MM84, 102.3/43.2)

Description : equatorial view showing tricoporate morphology; colpi distinct extending almost to the poles; exine finely reticulate.

Dimension : 20 μm (polar view)

Remarks : the pollen is botanically related to dicotyledonous families (Rutaceae, Umbelliferae, Euphorbiaceae, and Flacourtiaceae). *R. microluminus* was described by Kemp and Harris (1977) in the Tertiary sediments of the Ninetyeast Ridge.

Figure 3. *Monosulcites* sp. (Slide #92-208, MM76, 121.8/40.4)

Description : trilete mark is not seen clearly from lateral view; scattered thick echinae-baculae sculpture of 2-3 μm.

Dimension : 40 μm

Remarks : Monosulcites pollen has a rather long evolution since Jurassic. The genus has an affinity close to Androstobus (Cycadalean fructification) (Traverse, 1988).

Figure 4. *Trivestibulopollenites* sp.

Description : Polar view showing triporate-vestibulate morphology; thin wall exine.

Dimension : 30 μm

Remarks : the genus is referred to Porocolpopollenites and is characteristic of temperate forest in northern hemisphere (Traverse, 1988).

PLATE IV

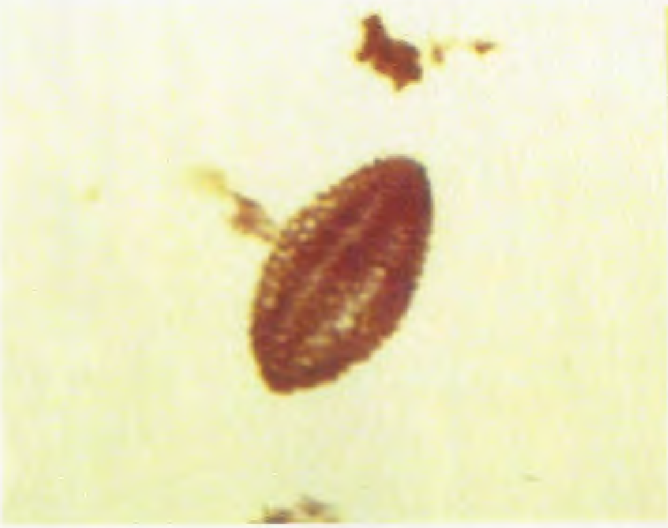


Figure 1

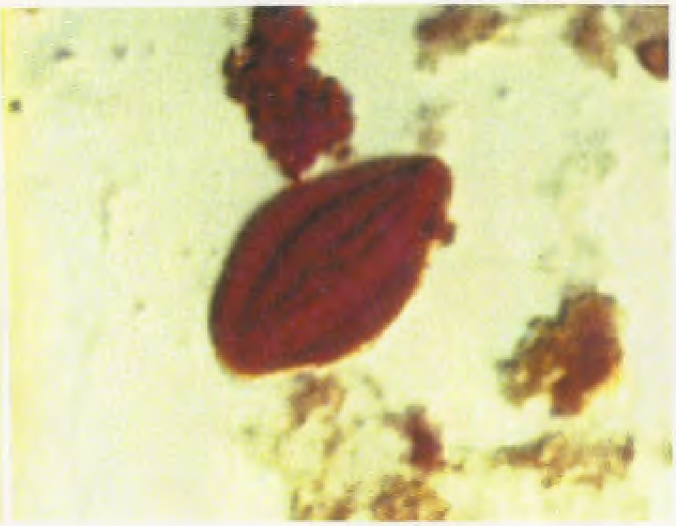


Figure 2

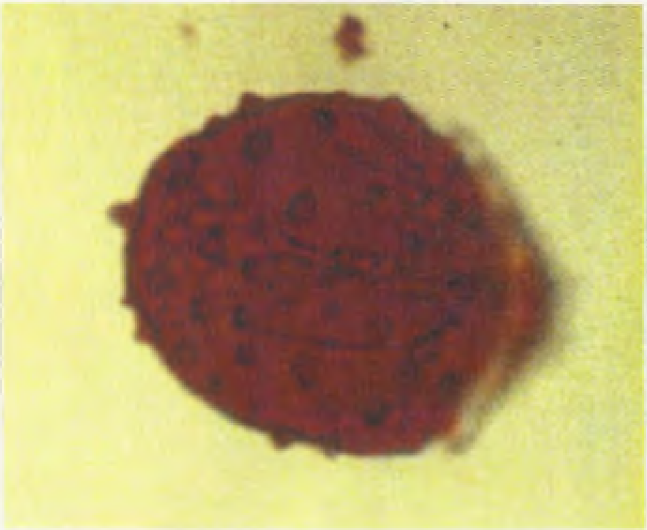


Figure 3

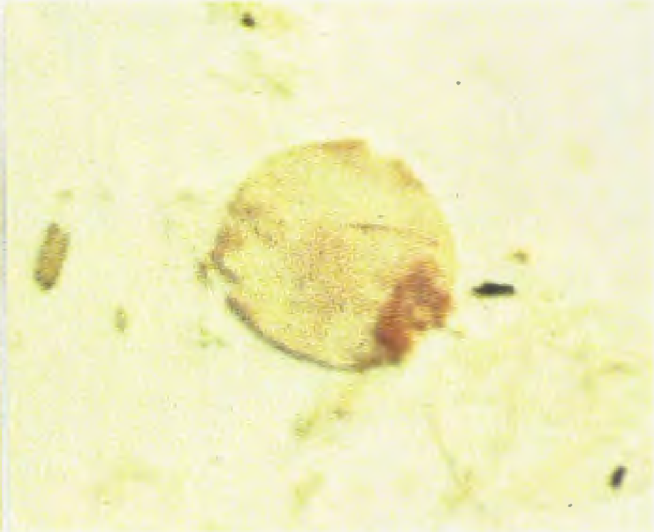


Figure 4

Plate IV

Figure 1. *Cyrtostachys*
Figure 2. *Rhoipites microluminus* Kemp
Figure 3. *Monosulcites* sp.
Figure 4. *Trivestibulopollenites* sp.

	J Layer						K Layer				Q Layer				R Layer			S Layer	
	J1	J2	J3	J4	J5	J6	K1	K2	K3	K4	Q1	Q2	Q3	Q4	R1	R2	R3	S1	S2
Oncosperma	0.7	1	0.5	0.4	0.4	0.9	1	0.2	0.6	0.5	1	1.3	0.4	0.4	0.3	0.5	0.4	0.4	0.4
Calamuspollenites	0.7	1	0.5	0.7	0.6	1	1.3	0.6	0.6	0.3	0.5	0.7	0.4	0.6	0.5	0.3	0.4	0.6	0.3
Spinizonocolpites	0.9	1.1	1.3	0.7	0.6	1	1.5	0.8	0.7	0.6	1.3	2.6	0.7	0.7	0.9	0.6	0.6	0.7	0.5
Proxapertites sp.	0.5	0.6	0.5	0.2	0.2	0.3	0.6	0.2	0.6	0.5	1	1.1	0.5	0.6	0.5	0.6	0.6	0.4	0.4
Trivestibulopollenites sp.	0.4	0.3	0.3	0.2	0.3	0.2	0.4	0.2	0.3	0.2	0.4	0.4	0.4	0.6	0.7	0.5	0.4	0.4	0.6
Alnipollenites sp.	0.4	0.3	0.3	0.4	0.2	0.2	0.4	0.4	0.4	0.2	0.4	0.4	0.2	0.4	0.9	0.8	1	0.8	0.8
Retitricolpites	1.8	0.3	0.3	0.2	0.2	0.3	0.6	0.2	0.3	0.2	0.4	0.4	0.2	0.3	0.3	0.5	0.6	0.7	0.4
Dactylocladus	1	1.6	1	0.4	0.4	0.9	1	0.7	0.7	0.4	0.5	0.2	0.2	0.3	0.2	0.2	0.2	0.3	0.4
Dactylopollis magnificus	0.7	1	0.5	0.3	0.2	0.3	0.4	0.2	0.3	0.1	0.2	0.2	0.2	0.3	0.3	0.2	0.2	0.3	0.2
Quercoidites sp.	1.8	0.8	0.5	0.4	0.3	0.3	0.4	0.5	0.4	0.3	0.4	0.7	0.5	0.4	0.5	0.3	0.4	0.3	0.4
Retibrevitricolpites sp.	0.7	1.6	1.3	0.7	0.5	0.7	1	0.6	0.7	0.3	0.4	0.4	0.2	0.3	0.2	0.2	0.4	0.3	0.2
Triorites sp.	0.7	0.8	0.8	0.4	0.4	0.7	1	0.6	0.7	0.4	0.4	0.7	0.4	0.4	0.3	0.3	0.4	0.3	0.2
Crassoretitriletes vanraadshovenii	0.7	0.5	0.3	0.2	0.2	0.3	0.4	0.4	0.4	0.4	0.5	1.1	0.5	0.6	0.3	0.5	0.6	0.7	0.6
Trichanthera sp.	0.9	0.6	0.5	0.4	0.3	0.5	0.4	0.2	0.3	0.3	0.4	0.4	0.2	0.3	0.2	0.2	0.2	0.2	0.2
Cyrtostachys	0.5	1	0.3	0.4	0.3	0.5	1	0.6	0.6	0.3	0.4	0.7	0.4	0.6	0.5	0.5	0.6	0.3	0.2
Roupites microluminus	1.4	0.3	0.3	0.2	0.2	0.3	0.4	0.4	0.3	0.3	0.4	0.4	0.4	0.4	0.5	0.5	0.6	0.7	0.6
Polypodiidites usmensis	1	1.6	1.3	1.5	1.1	1	1	0.4	0.3	0.4	0.5	0.7	0.4	0.4	0.3	0.3	0.4	0.3	0.4
Verrucatosporites usmensis	0.9	1.1	0.5	1.1	1	1.2	1.5	1.2	1.1	0.7	1	0.9	0.5	0.6	0.3	0.3	0.4	0.3	0.4
Caryapollenites	0.7	1	0.5	0.7	0.6	0.5	0.6	0.4	0.4	0.3	0.5	0.7	0.5	0.6	0.5	0.5	0.4	0.7	0.6
Monosulcites sp.	1		1				2												
Biretisporites huonensis	1										1					1			
Cupuliferoipollenites				1					1					1					1
Pinus sp.					1			2							2	1		1	

Table 1 - Infrequently enumerated spores and pollen counted. For numbers below unity, 0.7 means there are 2 palynomorphs encountered when examining 3 slides; 0.5 means one palynomorph for every 2 slides.